Welcome to the 76th International Symposium on Molecular Spectroscopy June 19-23, 2023 Urbana-Champaign, IL

On behalf of the Executive Committee, I extend a heartfelt welcome to all the attendees of the 76th Symposium and welcome you to the University of Illinois at Urbana-Champaign.

The Symposium presents research in fundamental molecular spectroscopy and a wide variety of related fields and applications. The continued vitality and significance of spectroscopy is annually re-affirmed by the number of talks, their variety, and the fact that many are given by students. These presentations are the heart of the meeting and are documented by this Abstract Book. Equally important is the information flowing from informal exchanges and discussions. As organizers, we strive to provide an environment that facilitates both kinds of interactions.

The essence of the meeting lies in the scientific discussions and your personal experiences this week independent of the number of times that you have attended this meeting. It is our sincere hope that you will find this meeting informative and enjoyable both scientifically and personally, whether it is your first or 50th meeting. If we can help to enhance your experience, please do not hesitate to ask the Symposium staff or the Executive Committee.

Josh Vura-Weis
Symposium Chair

SCHEDULE OF TALKS

ABSTRACTS

VENUE AND SPONSOR INFORMATION FOLLOWS AUTHOR INDEX

76th INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY

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Mini-Symposia

INFRARED SPECTROSCOPY IN THE JWST ERA

Organized by: **Sandra Brünken** (Radboud University), **Sergio Ioppolo** (Aarhus University), **Rens Waters** (Radboud University). JWST provides a wealth of infrared spectroscopic data of many astronomical objects like exoplanetary atmospheres, gas and (icy) solids in star-forming regions and planet-forming disks. This mini-symposium wants to bring together astronomers, spectroscopists and modelling / database scientists to discuss recent highlights and the demands for infrared spectroscopy in the era of JWST. Invited Speakers: **Klaus Pontoppidan** (Space Telescope Science Institute), **Ameek Sidhu** (University of Western Ontario), **Helen Fraser** (Open University)

SPECTROSCOPY AT LARGE-SCALE FACILITIES: FROM STEADY-STATE TO ULTRAFAST

Organized by **Renske van der Veen** (Helmholtz Zentrum Berlin), **Joost Bakker** (Radboud University), **Dugan Hayes** (University of Rhode Island). Large-scale facilities offer unique capabilities for spectroscopic investigations. With the recent advent of fourth-generation synchrotrons and free-electron lasers, yet a new era of molecular spectroscopy has begun. This symposium showcases techniques and applications of IR/XUV/X-ray spectroscopy at large-scale facilities. Time-resolved studies on ultrafast time scales receive particular attention. Invited Speakers: **Kelly Gaffney** (SLAC National Accelerator Laboratory), **Sandra Lang** (Ulm University), **Daniel Rolles** (Kansas State University), **Melanie Schnell** (Deutsches Elektronen-Synchrotron)

SPECTROSCOPY WITH CRYOGENIC ION TRAPS

Organized by **Joseph Fournier** (Washington University in St. Louis), **Chris Johnson** (Stony Brook University). Cryogenic ion traps have seen significant growth in molecular spectroscopy studies over the last decade. This mini-symposium will highlight the diverse applications and recent technical developments of cryogenic ion traps for spectroscopic studies. Invited Speakers: **Sandra Brünken** (Radboud University), **Masaaki Fujii** (Tokyo Institute of Technology), **Lai-Sheng Wang** (Brown University)

Picnic (Tuesday)

The Symposium picnic will be held on **Tuesday evening** at Ikenberry Commons. The cost of the picnic is included in your registration (at below cost to students), so that all may attend the event. The **Coblentz Society** is the host for refreshments for one hour.

Sponsorship

We are pleased to acknowledge the many organizations that support the 76th Symposium. Principal funding comes from the **National Radio Astronomy Observatory** (NRAO). We also acknowledge the many efforts and contributions of **The University of Illinois** in hosting the meeting, including financial contributions from the Departments of Chemistry, Electrical and Computer Engineering, and Astronomy.

Our Corporate Sponsors are **ACS/The Journal of Physical Chemistry, BrightSpec, The Coblentz Society, Elsevier/The Journal of Molecular Spectroscopy, Ideal Vacuum Products, Jasco, and Toptica Photonics**. Please see the back of this book for their advertisements.

We are also pleased to acknowledge **Light Conversion USA, and MonstrSense Technologies** as Contributing Sponsors. **IOS Press** is a special publishing partner.

Our sponsors will have exhibits at the Symposium and we encourage you to visit their displays.

Rao Prize

The three Rao Prizes for the most outstanding student talks at the 2022 meeting will be presented. The winners are **Madison Foreman** (JILA); **Thomas Salomon** (University of Cologne); **Yue-Rou Zhang** (Brown University). The Rao Prize was created by a group of spectroscopists who, as graduate students, benefited from the emphasis on graduate student participation, which has been a unique characteristic of the Symposium. This year three more Rao Prize winners will be selected. The award is administered by a Prize Committee chaired by Jennifer van Wijngaarden (York University), and is composed of Maria Sanz (King's College London); Jacob Stewart (Connecticut College); and Tim Zwier, (Sandia National Lab). Any questions or suggestions about the Prize should be addressed to the Committee. Anyone (especially post-docs) willing to serve on a panel of judges should contact Jennifer van Wijngaarden (vanwijng@yorku.ca).

Lewis E. Snyder Astrochemistry Award

The Snyder Award winners for the most innovative and unique astrochemical investigation in either observations, theory or laboratory work presented by a graduate student at the 2022 meeting are **Olivia Chitarra** (Université Paris-Saclay) and **Taarna Studemund** (Technical University of Berlin). This year one more Snyder Award winner will be selected. The award is administered by Anthony Remijan (NRAO). Anyone (especially post-docs) willing to serve on a panel of judges should email Anthony Remijan (aremijan@nrao.edu).

Miller Prize

The Miller Prize was created in honor of Professor Terry A. Miller, who served as chair of the International Symposium on Molecular Spectroscopy from 1992 to 2013. The Miller Prize for the best presentation given by a recent PhD at the 2022 meeting will be presented. The winner, **Ryan MacDonell** (University of Sydney) will give a lecture on Thursday. The Miller Prize winner and his or her co-authors will be invited to submit an article to the Journal of Molecular Spectroscopy based on the research in the prize-winning talk. After passing the normal review process, the article will appear in the Journal with a caption identifying the paper with the talk that received the Miller Prize. The award is administered by a Prize Committee chaired by Mike Heaven (Emory University) and composed of Lan Cheng (Johns Hopkins University),Michael Duncan (UGA), Chuan-Liang Li (Taiyuan University of Science and Technology), Leah O'Brien (SIUE), Cristina Puzzarini (University of Bologna), Edwin Sibert (University of Wisconsin), Amanda Ross (Université Lyon 1 & CNRS), Daniel Tabor (Texas A&M), Susanna Widucs-Weaver (University of Wisconsin, Madison). Any questions or suggestions about the Prize should be addressed to the Committee. Anyone willing to serve on a panel of judges should contact Mike Heaven (mheaven@emory.edu).

Jon T. Hougen Memorial Award

The Hougen Award was created in honor of Jon Hougen, to support the travel expenses of an exceptional young international spectroscopist who would otherwise be unable to attend the ISMS. The 2023 winners are **Nadav Genossar-Dan** (Ben-Gurion University of the Negev) and **Miguel Sanz-Novo** (Universidad de Valladolid) who will give talks in the MJ/WH and RI sessions, respectively. The Hougen award is administered by a Prize Committee chaired by Malgorzata Biczysko (Shanghai University) with members Masaaki Baba (Kyoto University), Anthony Remijan (NRAO), and Maria Sanz (King's College London).

Information

ACCOMMODATIONS

Check-In - Off hours check-in for dormitory accommodations is located in **Nugent Hall,** 207 E Gregory Drive and will be staffed 24/7. **On Sunday (only), check-in for Bousfield and Wassaja will be at Bousfield Hall, 1214 South First Street, from noon until ~10 PM.**

Check-Out - Off hours check-out for dormitory accommodations is located in **Nugent Hall,** 207 E Gregory Drive and will be staffed 24/7. **On Friday (only), check-out will be at Bousfield Hall, 1214 South First Street, from 7:00 AM – 1:30 PM. We will try to arrange a key dropbox at Wassaja, but if you don't see one, please check out at Bousfield or Nugent.**

Aside from check-in on Sunday and check-out on Friday, the desk at Bousfield will be unstaffed.

PARKING

Parking for dorm attendees is in lot E14 (map @ end of book) and is free for all attendees.

REGISTRATION

The registration desk is located in the Chemistry Library in Noyes Lab, and is open on Sunday from 4:00-6:00 PM, and Monday through Friday from 8:00 AM-4:30 PM. Refreshments will be available from 8:00 AM-4:30 PM. **It is possible that registration will be relocated nearby. Check for signs.**

CHEMISTRY LIBRARY

The Chemistry Library will be the home for our exhibitor space (plus coffee and donuts) again this year. The library has a few small conference rooms, and comfy chairs (and books!).

READY ROOM/STATION

We will have 2 desks in the Library with computers that you can use to test your powerpoint presentation. If you have any problems, the staff at the "Ready Station" (front counter in the library) can assist you.

INTERNET ACCESS/Wi-Fi

Each attendee will receive a login and password to access campus WiFi (SSID: IllinoisNet) as a guest. This access should work in most locations through campus. Please read the Internet Acceptable Use Policy below.

PRESENTATION UPLOAD INFORMATION & AUDIO/VIDEO

Each session room is equipped with a laptop computer, onto which presentation files will be pre-loaded by Symposium staff. To submit your presentation file, you must go to the **Manage Presentations** link on our web site and follow the instructions. All files must be submitted by **11:59 PM CDT THE DAY BEFORE** your presentation session. All submitted files will be loaded onto the presentation computer one half-hour prior to the beginning of the session.

ACKNOWLEDGMENTS

The Symposium Chair wishes to acknowledge the hard work of numerous people who made this meeting possible. First and foremost is the Symposium Coordinator Birgit McCall, who has smoothly and single-handedly taken care of almost all of the electronic and logistical aspects of the meeting. Second are our symposium assistants, Grant Barton, Lauren Boedicker, John Henry Burke, Conner Dykstra, Amanda Hungerford, Justin Malme, Erin Nicholas, Peisen Qian, Brandon Rasmussen, Juniper Shapiro, Laura Smith, and Rachel Wallick, who have handled innumerable important details to ensure the sessions and exhibitions go well. We thank Ben McCall for backend software support for the ISMS webpage. Finally, we wish to acknowledge the hospitality of the Chemistry Department and the School of Chemical Sciences (as well as the School of Molecular and Cell Biology) in tolerating our takeover of their buildings.

LIABILITY

The Symposium fees DO NOT include provisions for the insurance of participants against personal injuries, sickness, theft, or property damage. Participants and companions are advised to obtain whatever insurance they consider necessary. The Symposium organizing committee, its sponsors, and individual committee members DO NOT assume any responsibility for loss, injury, sickness, or damages to persons or belongings, however caused. The statements and opinions stated during oral presentations or in written abstracts are solely the author's responsibilities and do not necessarily reflect the opinions of the organizers.

INTERNET ACCEPTABLE USE POLICY

Each attendee will receive a login and password to access campus WiFi (SSID: IllinoisNet) as a guest. Guest accounts are intended to support a broad range of communications. Professional and appropriate etiquette is required. Anonymous access and posting through guest accounts is forbidden. All users must accept that their identity may be associated with any content they provide while using the service. By accessing the campus WiFi network, you expressly acknowledge and agree to the following:

Use of the guest account service is at your sole risk and the entire risk as to satisfactory quality and performance is with you. You agree not to use the guest account intentionally or unintentionally to violate any applicable local, state, national or international law, including, but not limited to, any regulations having the force of law. To the extent not prohibited by law, in no event shall the university be liable for personal injury, or any incidental, special, indirect or consequential damages whatsoever, including, without limitation, damages for loss of profits, loss of data, business interruption or any other commercial damages or losses, arising out of or related to your use or inability to use the guest account, however caused, regardless of the theory of liability (contract, tort or otherwise) and even if the university has been advised of the possibility of such damages. The use of the guest account is subject, but not limited to, all University policies and regulations detailed at the Campus Administrative Manual (http://www.cam.illinois.edu). See the University's Web Privacy Notice (http://www.vpaa.uillinois.edu/policies/web_privacy.cfm) for all applicable laws and policies.

MA. Plenary

Monday, June 19, 2023 – 8:30 AM

Room: Foellinger Auditorium

Chair: Jennifer van Wijngaarden, York University, Toronto, ON, Canada

Welcome **8:30**

Susan Martinis, Vice Chancellor for Research and Innovation
University of Illinois

MA01 **8:45 – 9:25**
WATCHING CHEMICAL REACTIONS HAPPEN ONE MOLECULE AT A TIME, Heather Lewandowski

MA02 **9:30 – 10:10**
HIGH RESOLUTION PHOTOELECTRON SPECTROSCOPY OF VIBRATIONALLY EXCITED ANIONS, Daniel Neumark

Intermission

MA03 **10:45 – 11:25**
VIBRATIONAL SPECTROSCOPY AT THE SERVICE OF QUANTUM CHEMISTRY, Martin A. Suhm

MA04 **11:30 – 12:10**
FOUR EXPERIMENTAL SYSTEMS THAT TEST DISPERSION INTERACTIONS IN LARGE MOLECULES, R. Pollice, M. Bot, Vladimir Gorbachev, Alexandra Tsybizova, L. Fritsche, Larisa Miloglyadova, Raphael Oeschger, Peter Chen

MG. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Monday, June 19, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Daniel Neumark, The University of California, Berkeley, CA, USA

MG01 *INVITED TALK* **1:45 – 2:15**
PROBING DIPOLE-BOUND STATES USING HIGH-RESOLUTION RESONANT PHOTOELECTRON IMAGING OF CRYOGENICALLY-COOLED ANIONS, Lai-Sheng Wang

MG02 **2:21 – 2:36**
VINYLIDENE-ACETYLENE ISOMERIZATION PROBED WITH HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY OF COLD ANIONS UPON SELECTIVE VIBRATIONAL EXCITATION, Martin DeWitt, Jascha Lau, Daniel Neumark

MG03 **2:39 – 2:54**
EXPLORING THE ELECTRONICALLY EXCITED STATES OF MELEM: AN ALL-ORGANIC HYDROGEN-EVOLVING PHOTOCATALYST, Kenneth Wilson, Etienne Garand

MG04 **2:57 – 3:12**
THRESHOLD PHOTODETACHMENT SPECTROSCOPY OF C_2^- IN A 16-POLE WIRE TRAP, Sruthi Purushu Melath, Christine Lochmann, Markus Nötzold, Robert Wild, Roland Wester

Intermission

MG05 **3:52 – 4:07**
RESOLVING ISOMERS OF COPPER TRIOXIDE ANION VIA TEMPERATURE DEPENDENT PHOTOELECTRON IMAGING, G. Stephen Kocheril, Han-Wen Gao, Lai-Sheng Wang

MG06 **4:10 – 4:25**
CRYOGENIC PHOTOELECTRON SPECTROSCOPY OF MICROSOLVATED ANIONS AND HYDROGEN BONDED CLUSTERS, Xue-Bin Wang

MG07 **4:28 – 4:43**
ELECTRONIC SPECTROSCOPY OF HYDROGENATED CARBON CLUSTER ISOMERS, Samuel Marlton, Chang Liu, Patrick Watkins, Evan Bieske

MG08 **4:46 – 5:01**
CHARACTERIZING THE ABSORPTION AND PHOTODISSOCIATION OF ATMOSPHERIC NITRATE VIA ACTION SPECTROSCOPY, Brianna Hopper, Etienne Garand

MG09 **5:04 – 5:19**
OPTICAL SPECTRA OF N-SUBSTITUTED ADAMANTANE CATIONS, Parker B. Crandall, Marko Förstel, Otto Dopfer

MG10 **5:22 – 5:37**
EXPLORING ATMOSPHERICALLY RELEVANT CLUSTERS OF GLYCINE, AMMONIA AND SULFURIC ACID VIA INFRARED SPECTROSCOPY AND MASS SPECTROMETRY, Annapoorani Hariharan, Conor J. Bready, Jack G Ajello, Samantha H. Black, George C. Shields, Christopher J. Johnson

MH. Mini-symposium: Spectroscopy at Large-scale Facilities

Monday, June 19, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Katharina Kubicek, University of Hamburg and European XFEL, Schenefeld, Germany

MH01 **1:45 – 2:00**
INVESTIGATING THE REACTIVITY OF CH_3NH WITH SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY AND COMPUTATIONAL CHEMISTRY, Sommer L. Johansen, Judit Zador, Carles Marti, Laura M McCaslin, Varun Rishi, Leonid Sheps, Arkke Eskola

MH02 **2:03 – 2:18**
PROBING QUANTUM COHERENCE IN MOLECULAR SYSTEMS, Suresh Yarlagadda, Temitayo A. Olowolafe, Suk Kyoung Lee, H. Bernhard Schlegel, Wen Li

MH03 **2:21 – 2:36**
CONICAL INTERSECTION DYNAMICS IN CYCLOPENTADIENE, Lisa Huang, Lingyu Ma, Nathan Goff, Asami Odate, Stuart W Crane, Thomas Northey, Joseph Geiser, Lauren Bertram, Andrés M Carrascosa, Mats Simmermacher, Zane Phelps, Michael Minitti, Mengning Liang, Xinxin Cheng, Ruaridh Forbes, Martin Centurion, Kenneth Lopata, Artem Rudenko, Daniel Rolles, Adam Kirrander, Peter M. Weber

MH04 ***INVITED TALK*** **2:39 – 3:09**
ULTRAFAST DIFFRACTION AND SPECTROSCOPY STUDIES OF GAS-PHASE PHOTOCHEMISTRY, Daniel Rolles

MH05 **3:15 – 3:30**
PROTON TRANSFER MECHANISMS OF o-NITROPHENOL OBSERVED BY MeV ULTRAFAST ELECTRON DIFFRACTION, Joao P.F. Nunez, Lauren F Heald, Monika Williams, Jie Yang, Thomas JA Wolf, Conor Rankine, Bryan Moore, Xiaozhe Shen, Ming-Fu Lin, Todd Martinez, Xijie Wang, Martin Centurion

Intermission

MH06 **4:10 – 4:25**
ULTRAFAST ENERGY TRANSFER AND STRUCTURAL DYNAMICS OF THE ORGANIC POLYMER ON AN MoS_2 MONOLAYER, Ming-Fu Lin, Andrew Attar, Hung-Tzu Chang, Aravind Krishnamoorthy, Alexander Britz, Xiang Zhang, Xiaozhe Shen, Ajayan Pulickel, Xijie Wang, Priya Vashishta, Uwe Bergmann

MH07 **4:28 – 4:43**
QUANTUM MOLECULAR DYNAMICS FOR X-RAY INDUCED STRUCTURAL DAMAGE, Adam E A Fouda, Stephen H Southworth, Gilles Doumy, Linda Young, Phay J Ho

MH08 **4:46 – 5:01**
REAL-TIME MONITORING OF CHIRALITY LOSS IN MOLECULAR PHOTODISSOCIATION BY TRANSIENT X-RAY CIRCULAR DICHROISM, Yeonsig Nam, Daeheum Cho, Shaul Mukamel

MH09 **5:04 – 5:19**
HIGH-RESOLUTION X-RAY STIMULATED RAMAN SPECTROSCOPY USING STOCHASTIC PULSES, Kai Li, Gilles Doumy, Christian Ott, Thomas Pfeifer, Alexander Magunia, Marc Rebholz, Marcus Agåker, Jan-Erik Rubensson, Marc Simon, Michael Meyer, Tommaso Mazza, Alberto De Fanis, Thomas Baumann, Sergey Usenko, Mette Gaarde, Linda Young

MH10 **5:22 – 5:37**
ADVANCED LASER-BASED TECHNIQUES FOR MATERIAL AND STRUCTURAL CHARACTERIZATION, Sneha Banerjee

MH11 **5:40 – 5:55**
TRANSIENT LABORATORY NEXAFS SPECTROSCOPY ON SOLID AND LIQUID SAMPLES, Richard Gnewkow, Adrian Jonas, Marc Dummin, Daniel Grötzsch, Silvana Schönfelder, Holger Stiel, Birgit Kanngießer, Ioanna Mantouvalou

MI. Fundamental physics

Monday, June 19, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Jun Jiang, Lawrence Livermore National Laboratory, Fremont, CA, USA

MI01 **1:45 – 2:00**
LASER SPECTROSCOPY OF AROMATIC MOLECULES WITH OPTICAL CYCLING CENTERS: STRONTIUM (I) PHENOXIDES, Guanming Lao, Guo-Zhu Zhu, Claire E Dickerson, Benjamin Augenbraun, Anastassia Alexandrova, Justin Caram, Eric Hudson, Wesley Campbell

MI02 **2:03 – 2:18**
STRUCTURAL AND ELECTRONIC TRENDS OF OPTICAL CYCLING CENTERS IN POLYATOMIC MOLCULES: MICROWAVE SPECTROSCOPY OF MgCCH, CaCCH, SrCCH, and YbCCH, Bryan Changala, Nadav Genossar-Dan, Ella Brudner, Tomer Gur, Joshua H. Baraban, Michael C McCarthy

MI03 **2:21 – 2:36**
LASER IONIZATION SPECTROSCOPY OF AcF AND KING-PLOT ANALYSIS OF MOLECULAR ISOTOPE SHIFTS, Michail Athanasakis-Kaklamanakis, Shane Wilkins, Mia Au, Alexander A. Breier, Gerda Neyens

MI04 **2:39 – 2:54**
PRECISION STUDIES OF RADIOACTIVE MOLECULES RELEVANT TO FUNDAMENTAL PHYSICS, Shane Wilkins, Michail Athanasakis-Kaklamanakis, Alexander A. Breier, Ronald Fernando Garcia Ruiz, Gerda Neyens, Silviu-Marian Udrescu

MI05 **2:57 – 3:12**
A SEARCH FOR TIME-REVERSAL SYMMETRY VIOLATION WITH THALLIUM FLUORIDE, Jianhui Li, Tanya Zelevinsky, Jakob Kastelic, Oskari Timgren, Steve Lamoreaux, Olivier Grasdijk, Yuanhang Yang, David Demille, Tristan Winick, David Kawall

Intermission

MI06 **3:52 – 4:07**
MODELING SPIN-SELECTIVE POSITRONIUM CHEMISTRY OF THE CLOSO-DODECABORATE DIANION, Larry W Burggraf, Xiaofeng F Duan

MI07 **4:10 – 4:25**
QUANTUM STATE CONTROL OF CHIRAL MOLECULES, Ju Hyeon Lee, Johannes Bischoff, A. O. Hernandez-Castillo, Boris Sartakov, Gerard Meijer, Sandra Eibenberger-Arias

MI08 **4:28 – 4:43**
ENANTIOMER-SELECTIVE POPULATION TRANSFER IN THE GAS PHASE USING PHASE-CONTROLLED RESONANT MICROWAVE FIELDS, Himanshi Singh, Freya E. L. Berggötz, Wenhao Sun, Melanie Schnell

MI09 **4:46 – 5:01**
HIGH ACCURACY SPECTROSCOPY OF H_2 ROVIBRATIONAL TRANSITIONS IN THE (2-0) BAND NEAR 1.2μm, Helene Fleurbaey, Aleksandra Koroleva, Samir Kassi, Alain Campargue

MJ. Comparing theory and experiment

Monday, June 19, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

Chair: Lan Cheng, The Johns Hopkins University, Lutherville Timonium, MD, USA

MJ01 **1:45 – 2:00**
THE LOCAL VIBRATIONAL MODE THEORY: AN EFFICIENT ANALYSIS TOOL FOR THE VIBRATIONAL SPECTROSCOPY COMMUNITY, Elfi Kraka

MJ02 **2:03 – 2:18**
ANHARMONICITY AT LARGER SCALES: VIBRATIONAL SPECTRA OF CHIRAL ORGANOMETALLIC COMPLEXES, Julien Bloino, Marco Fusè

MJ03 **2:21 – 2:36**
INTERPRETATION OF MOLECULAR SPECTRA USING VIBRATIONAL PERTURBATION THEORY , Anne B. McCoy, Mark A. Boyer

MJ04 **2:39 – 2:54**
STRUCTURAL INVESTIGATION OF HYDRATED ANIONIC PYRENE CLUSTERS WITH INFRARED SPECTROSCOPY, Heinrich Salzmann, Natalie LeMessurier, Anne P. Rasmussen, Joel D. Eaves, J. Mathias Weber

MJ05 **2:57 – 3:12**
VIBRATIONAL SPECTROSCOPY OF ANIONIC PAH-WATER CLUSTERS, Natalie LeMessurier, Heinrich Salzmann, J. Mathias Weber, Joel D. Eaves

MJ06 **3:15 – 3:30**
SYNTHESIS, MOLECULAR STRUCTURE, VIBRATIONAL CHARACTERISTICS, PROFILES OF OTHER MOLECULAR PROPERTIES AND ANTICANCER ACTIVITY OF 2-((2-AMINOPYRIDIN-3-YL)METHYLENE)-N-PHENYLHYDRAZINECARBOTHIOAMIDE AS PROVIDED BY SPECTROSCOPIC AND DFT INVESTIGATIONS, Ramaiah K, K Srishailam, Byru Venkatram Reddy, G. Ramana Rao

MJ07 **3:33 – 3:48**
TWO-PHOTON TRANSITIONS IN THE LASER INDUCED FLUORESCENCE OF NO_3 BY FUKUSHIMA, Takeshi Oka

Intermission

MJ08 **4:28 – 4:43**
THE THRESHOLD PHOTOELECTRON SPECTRUM OF SiH_2 AS MODELED WITH MCTDH, N. Chen, Bérenger Gans, Séverine Boyé-Peronne, L. H. Coudert, J.-C. Loison, G. A. Garcia, Sebastian Hartweg

MJ09 **4:46 – 5:01**
RING OPENING AND TUNNELING INVERSION IN THE CYCLOPROPYL RADICAL AND CATION, Nadav Genossar-Dan, Bryan Changala, Bérenger Gans, Marie-Aline Martin-Drumel, J.-C. Loison, Sebastian Hartweg, G. A. Garcia, John F. Stanton, Branko Ruscic, Joshua H. Baraban

MJ10 **5:04 – 5:19**
PROBING WEAK BONDING INTERACTIOINS THROUGH QUADRUPOLAR COUPLING OF CHLORINE, Robin Dohmen, Denis Fedosov, Daniel A. Obenchain

MJ11 **5:22 – 5:37**
IS THE HERZBERG-TELLER EFFECT SUFFICIENT TO SIMULATE ONE PHOTON ABSORPTION SPECTRA?, Qin Yang, Tao Wu, Li Li, Julien Bloino, Petr Bour

MK. Large amplitude motions, internal rotation

Monday, June 19, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: M. Eugenia Sanz, King's College London, London, United Kingdom

MK01 **1:45 – 2:00**
MILLIMETER-WAVE SPECTROSCOPY OF ACETYL CHLORIDE AND ACETYL BROMIDE, Prakash Gyawali, R. A. Motiyenko, L. Margulès

MK02 **2:03 – 2:18**
MICROWAVE SPECTROSCOPY AND LARGE AMPLITUDE MOTION OF CHLOROSULFONIC ACID ($ClSO_2OH$), Aaron J Reynolds, Diego Rodriguez, Wei Lin, Kenneth R. Leopold

MK03 **2:21 – 2:36**
APPROACHING THE FREE ROTOR LIMIT: EXTREMELY LOW METHYL TORSIONAL BARRIER OBSERVED IN THE MICROWAVE SPECTRUM OF 2,4-DIMETHYLFLUOROBENZENE, Safa Khemissi, Martin Schwell, Isabelle Kleiner, Ha Vinh Lam Nguyen

MK04 **2:39 – 2:54**
MICROWAVE SPECTRUM AND STRUCTURE OF PHENYLACETYLENE···METHANOL COMPLEX, Surabhi Gupta, Charlotte Cummings, Nick Walker, Elangannan Arunan

MK05 **2:57 – 3:12**
ANALYSIS OF A AND E COMPONENTS OF THE ν_{21} TORSIONAL FUNDAMENTAL OF PROPENE AT 188 cm^{-1}, Peter Groner, Stephen J. Daunt, Brant E. Billinghurst, Jianbao Zhao, Colin Western

MK06 **3:15 – 3:30**
BARRIERS TO INTERNAL ROTATION AND MOLECULAR GEOMETRIES OF COMPLEXES FORMED BETWEEN ISOMERS OF METHYLTHIAZOLE AND WATER STUDIED BY MICROWAVE SPECTROSCOPY, Charlotte Cummings, Wentao Song, Ha Vinh Lam Nguyen, Nick Walker

MK07 **3:33 – 3:48**
THEORETICAL SPECTROSCOPIC STUDY OF ISOPROPYL ALCOHOL ($CH_3-CHOH-CH_3$), Maria Luisa S Senent, Mohammed Salah

Intermission

MK08 **4:28 – 4:43**
MILLIMETER-WAVE SPECTROSCOPY OF AMMONIA-WATER WEAKLY BOUNDED COMPLEX, Prakash Gyawali, R. A. Motiyenko, L. Margulès, Luyao Zou, Isabelle Kleiner

MK09 **4:46 – 5:01**
INTERNAL ROTATION ANALYSIS AND STRUCTURE DETERMINATION OF R-CARVONE, Nicole Moon, G. S. Grubbs II

MK10 **5:04 – 5:19**
CONFORMATIONAL LANDSCAPE AND INTERNAL DYNAMIC OF LEVULINIC ACID FROM BROADBAND ROTATIONAL SPECTROSCOPY, Elias M. Neeman, Noureddin OSSEIRAN, Therese R. Huet

MK11 **5:22 – 5:37**
IMPROVED ANALYSIS OF THE ROTATION SPECTRUM OF META-CHLOROTOLUENE USING A FREE ROTOR BASIS AND NON-PERTURBATIVE HYPERFINE TREATMENT, J. H. Westerfield, S E Worthington-Kirsch, Kyle N. Crabtree

ML. Spectroscopy as an analytical tool

Monday, June 19, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: Rebecca A. Peebles, California State University, Sacramento, Sacramento, CA, USA

ML01 **1:45 – 2:00**
DEVELOPMENT OF QUANTITATIVE APPLICATIONS FOR MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY, Ann Adele Byars, Alex Mikhonin, Reilly E. Sonstrom, Voislav Blagojevic, Justin L. Neill, Brooks Pate

ML02 **2:03 – 2:18**
ON-SITE & REAL TIME THz MONITORING OF GASEOUS EMISSION FROM A WASTE RECOVERY CENTER, Jean Decker, Francis Hindle, Eirc Fertein, Nicolas Houzel, Fabrice Cazier, Gaël Mouret, Julien Dumont, Arnaud Cuisset

ML03 **2:21 – 2:36**
A SYNTHETIC METHODOLOGY TO PRODUCE TAILORED DEUTERATION PATTERNS IN BUILDING BLOCK MOLECULES WITH HIGH ISOTOPOMER SPECIFICITY VERIFIED BY MOLECULAR ROTATIONAL SPECTROSCOPY, Justin Weatherford-Pratt, W. Dean Harman, Sarah Brewster, Haley N. Scolati, Martin S. Holdren, Brooks Pate

ML04 **2:39 – 2:54**
LEAST SQUARES FIT OF LINE PROFILES IN TRANSMITTANCE AND ABSORBANCE SPECTRA WITH DETECTOR OR SOURCE NOISE II, Hiroyuki Sasada

Intermission

ML05 **3:34 – 3:49**
ULTRAVIOLET SPECTROSCOPY OF SUBCRITICAL AND SUPERCRITICAL METHANOL, Ireneusz Janik, Timothy W Marin

ML06 **3:52 – 4:07**
LASER EXCITATION SPECTROSCOPY: AN ANALYTICAL TOOL FOR STUDYING ENERGY TRANSFER MECHANISMS IN KXe AND OTHER GAS MIXTURES, Kavita V. Desai, Andrey E. Mironov, J. Gary Eden

ML07 **4:10– 4:25**
EMERGENCE OF INTRA/INTER MOLECULAR INTERACTIONS WITHIN BINARY MIXTURE OF DEEP EUTECTIC SOLVENTS AND AN ORGANIC CO-SOLVENT, Garima Bhutani, Tanvi, Anamika Mukhopadhyay, Arijit K De

ML08 **4:28– 4:43**
SPECTROSCOPIC SIGNATURES AND EXCITED STATE DYNAMICS OF ISOLATED AND HYDRATED METHYLATED XANTHINES, Vipin Bahadur Singh

TA. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Tuesday, June 20, 2023 – 8:30 AM

Room: 116 Roger Adams Lab

Chair: J. Mathias Weber, University of Colorado, Boulder, CO, USA

TA01 **8:30 – 8:45**
LEAK-OUT SPECTROSCOPY: A UNIVERSAL METHOD OF ACTION SPECTROSCOPY IN COLD ION TRAPS, Philipp C Schmid, Oskar Asvany, Sven Thorwirth, Thomas Salomon, Stephan Schlemmer

TA02 **8:48 – 9:03**
DETERMINATION OF THE ORTHO-TO-PARA RATIO OF H_3^+ IN A CRYOGENIC ION TRAP, Philipp C Schmid, Thomas Salomon, Oskar Asvany, Stephan Schlemmer

TA03 **9:06 – 9:21**
CAPTURE AND CHARACTERIZATION OF NASCENT UV PHOTODECOMPOSITION PRODUCTS WITH MASS-SELECTIVE CRYOGENIC TRAPPING TECHNIQUES, Olivia Moss, Payten Harville, Tim Schleif, Evan H Perez, Mark Johnson

TA04 **9:24 – 9:39**
ONLINE MONITORING OF ENANTIOMERIC RATIOS BY CHIRALITY RECOGNITION IN THE GAS PHASE, Sonja Schmahl, Jiaye Jin, Francine Horn, Hannes Westphal, Detlev Belder, Knut R. Asmis

TA05 **9:42 – 9:57**
NONLINEAR TIME-DOMAIN CRYOGENIC ION VIBRATIONAL SPECTROSCOPY WITH ULTRAFAST INFRARED PULSES, Zifan Ma, Liangyi Chen, Joseph Fournier

TA06 **10:00 – 10:15**
DEVELOPMENT OF AN ION-TRAP INSTRUMENT FOR ASTROCHEMICALLY RELEVANT REACTION KINETICS, Darya Kisuryna, Julianna Palotás, Jessica Palko, Leah G Dodson

Intermission

TA07 **10:55 – 11:10**
TANDEM CRYOGENIC MASS-SELECTIVE DIGITAL ION TRAPS TO PRODUCE MOLECULAR CLUSTERS WITH COMPLEX ENVIRONMENTS, Gina Roesch, Etienne Garand

TA08 **11:13 – 11:28**
AN EXPERIMENTAL SETUP TO STUDY THE INFLUENCE OF HYDRATION ON SMALL CHARGED MOLECULAR SYSTEMS BY ROTATIONALLY RESOLVED VIBRATIONAL SPECTROSCOPY, Eric S. Endres, Franziska Dahlmann, Christian Sprenger, Katharina Geistlinger, Roland Wester

TA09 **11:31 – 11:46**
EXPLORING THE CH STRETCH SPECTRAL REGION OF CRYPTAND/ION COMPLEXES WITH IR-UV DOUBLE RESONANCE SPECTROSCOPY AND LOCAL MODE HAMILTONIANS, Edwin Sibert, Casey Daniel Foley, Kendrew Au, Timothy S. Zwier

TA10 **11:49 – 12:04**
THAT'S JUST, LIKE, YOUR OPINION, MAN - HOW DO WE KNOW WHEN WE HAVE A GOOD MATCH BETWEEN EXPERIMENTAL AND COMPUTED SPECTRA?, Christopher J. Johnson

TB. Mini-symposium: Spectroscopy at Large-scale Facilities

Tuesday, June 20, 2023 – 8:30 AM

Room: 100 Noyes Laboratory

Chair: Anne Marie March, Argonne National Laboratory, Argonne, IL, USA

TB01 **8:30 – 8:45**
DIAGNOSTIC OF SMALL WEAK INTERACTIONS IN GASOLINE BLENDS BY ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY , Joshua G Smith , Sylvestre Twagirayezu, Brant E. Billinghurst, Jianbao Zhao

TB02 **8:48 – 9:03**
TOWARDS UNDERSTANDING FAR-IR INDUCED ISOMERISATION PROCESSES , Olga A. Duda, Joost M. Bakker, Daniel Horke

TB03 ***INVITED TALK*** **9:06 – 9:36**
MODELING THE ACTIVE CENTERS OF CATALYSTS: THE UNIQUE COMBINATION OF GAS-PHASE ION TRAP REACTIVITY AND INFRARED SPECTROSCOPY, Sandra Lang

TB04 **9:42 – 9:57**
COULOMB POTENTIAL EFFECT ON CARRIER ENVELOPE PHASE DEPENDENT (CEP) STRONG-FIELD IONIZATION, Emmanuel Ayorinde Orunesajo, Yasashri Ranganath Ranathunga, Temitayo A. Olowolafe, Suk Kyoung Lee, Wen Li

Intermission

TB05 **10:37 – 10:52**
IR CHARACTERIZATION OF METAL MEDIATED METHANE COUPLING, Frank J. Wensink, Peter B Armentrout, Joost M. Bakker

TB06 **10:55 – 11:10**
X-RAY SPECTROSCOPY STUDIES OF Ti-BASED METAL ORGANIC FRAMEWORKS, Conor L Long, Jenny V. Lockard

TB07 **11:13 – 11:28**
SPIN STATE CHARACTERIZATION OF METALLOEMZYMES VIA X-RAY EMISSION SPECTROSCOPY, Sahand Emamian, Kendra A Ireland, Vatsal Purohit, Kirklin L McWhorter, Olga Maximova, Yulia N Pushkar, Katherine M Davis

TB08 **11:31 – 11:46**
STRUCTURAL INVESTIGATION OF THE CU/W/CO-BASED MIXED METAL OXIDE ELECTROCATALYST USING X-RAY ABSORPTION SPECTROSCOPY, Nikita Gupta

TB09 **11:49 – 12:04**
PROBING HOST-GUEST INTERACTIONS IN CONDUCTIVE COPPER-BASED METAL ORGANIC FRAMEWORKS USING HIGH-RESOLUTION X-RAY ABSORPTION SPECTROSCOPY, Amy R. Turtz, Jenny V. Lockard

TC. Astronomy

Tuesday, June 20, 2023 – 8:30 AM

Room: 1024 Chemistry Annex

Chair: Harshal Gupta, National Science Foundation, Alexandria, VA, USA

TC01 **8:30 – 8:45**
MODELING OF SIMPLE AROMATIC SPECIES UNDER DARK CLOUD CONDITIONS, Ci Xue, Alex Byrne, Alec Paulive, Eric Herbst, Ilsa Rose Cooke, A B Kowsari, Brett A. McGuire

TC02 **8:48 – 9:03**
ASTROCHEMICAL MODELING OF THE PROPARGYL RADICAL IN COLD MOLECULAR CLOUDS, Alex Byrne, Ci Xue, Ilsa Rose Cooke, Michael C McCarthy, Brett A. McGuire

TC03 **9:06 – 9:21**
MACHINE LEARNING OF THE CHEMICAL INVENTORY AND RARE ISOTOPOLOGUES OF THE SOLAR-TYPE PROTOSTELLAR SOURCE IRAS 16293-2422 B, Zachary Taylor Philip Fried, Kelvin Lee, Alex Byrne, Brett A. McGuire

TC04 **9:24 – 9:39**
BEYOND THE MACHINE: AUTOMATING SPECTRA GENERATION AND ANALYSIS FROM MACHINE LEARNING RESULTS , Hannah Toru Shay, Gabi Wenzel, Ci Xue, Brett A. McGuire

TC05 **9:42 – 9:57**
RECENT UPDATES TO THE LILLE SPECTROSCOPIC DATABASE, R. A. Motiyenko, L. Margulès

Intermission

TC06 **10:37 – 10:52**
UPDATING THE SCIENTIFIC USEFULNESS OF THE SPLATALOGUE DATABASE, Daniel Joseph Lopez-Sanders, Anthony Remijan

TC07 **10:55 – 11:10**
ROTATIONAL SPECTROSCOPY OF REACTIVE SPECIES IN SUPPORT OF THE DETECTION OF INTERSTELLAR MOLECULES, Cristina Puzzarini, Silvia Alessandrini, Luca Bizzocchi, Mattia Melosso

TC08 **11:13 – 11:28**
A NOVEL APPROACH FOR AUTOMATED ANALYSIS OF HIGH-RESOLUTION MOLECULAR LINE SURVEYS, Samer El-Abd, Crystal L. Brogan, Todd R. Hunter, Kelvin Lee, Brett A. McGuire

TC09 **11:31 – 11:46**
H_2O AND HDO TEMPERATURE DEPENDENT LINESHAPES USING SUB-DOPPLER METHODS, Brian Drouin, Deacon J Nemchick, Timothy J. Crawford, Paul Von Allmen, D. C. Lis

TC10 **11:49 – 12:04**
ROTATIONAL SPECTRUM AND INTERSTELLAR DETECTION OF THE FIRST TORSIONALLY EXCITED STATE OF METHYLAMINE , Prakash Gyawali, R. A. Motiyenko, Arnaud Belloche, Isabelle Kleiner, V. Ilyushin, E. A. Alekseev, Iwona Gulaczyk, Marek Kreglewski

TD. Instrument/Technique Demonstration

Tuesday, June 20, 2023 – 8:30 AM

Room: 217 Noyes Laboratory

Chair: Liam Duffy, University of North Carolina at Greensboro, Greensboro, NC, USA

TD01 **8:30 – 8:45**
CAVITY-ENHANCED DUAL-COMB SPECTROSCOPY WITH QUANTUM CASCADE LASERS IN THE MOLECULAR FINGERPRINT REGION, Charles R. Markus, Jakob Hayden, Daniel I. Herman, Philip A. Kocheril, Douglas Ober, Termeh Bashiri, Markus Mangold, Mitchio Okumura

TD02 **8:48 – 9:03**
QUANTUM CASCADE LASER PUMPING FOR MOLECULAR LASING AND SPECTROSCOPY, Paul Chevalier, Arman Amirzhan, Federico Capasso, Henry O. Everitt

TD03 **9:06 – 9:21**
QUANTUM CASCADE LASER-BASED INFRARED PHOTODISSOCIATION ACTION SPECTROSCOPY OF HYDRATED AMINO ACIDS FOR PLANETARY SCIENCE IN SITU SENSING APPLICATIONS, Tyler M Nguyen, Douglas Ober, Robert Hodyss, Stojan Madzunkov, Frank Maiwald, Deacon J Nemchick, Mitchio Okumura

TD04 **9:24 – 9:39**
DEVELOPMENT OF A DUAL-COMB SPECTROMETER FOR ROTATIONALLY-RESOLVED MEASUREMENTS OF THE VIBRATIONAL OVERTONE OF BENZENE, Daniel L. Maser, Matthew D Carter

TD05 **9:42 – 9:57**
TWO-PHOTON ABSORPTION SPECTROSCOPY OF A $^{13}CO_2$ VIBRATIONAL TRANSITION, Yu-Zhong Liu, Cunfeng Cheng, Shui-Ming Hu

TD06 **10:00 – 10:15**
ION-DIP INFRARED SPECTROSCOPY OF CRIEGEE INTERMEDIATES, Meijun Zou, Tarun Kumar Roy, Marsha Lester

Intermission

TD07 **10:55 – 11:10**
HIGH RESOLUTION 2D INFRARED SPECTROSCOPY OF CHLOROMETHANE, Peter Chen, DeAunna A Daniels, Thresa Wells

TD08 **11:13 – 11:28**
ELECTRO-OPTIC FREQUENCY COMB GENERATION WITH PHASE-LOCKED LOOP STABILIZED RF MODULATION, Todd Eliason, Payton Avery Parker, Melanie A.R. Reber

TD09 **11:31 – 11:46**
LOCKING FREQUENCY COMBS TO OPTICAL CAVITIES FOR SIGNAL ENHANCEMENT OF TWO-DIMENSIONAL SPECTROSCOPY, Walker M. Jones, Parashu R Nyaupane, Melanie A.R. Reber

TD10 **11:49 – 12:04**
OPTICAL FREQUENCY COMB CAVITY ENHANCED VERNIER SPECTROSCOPY FOR THE DETECTION OF TRANSIENT SPECIES, Termeh Bashiri, Charles R. Markus, Tzu-Ling Chen, Douglas Ober, Lukasz A. Sterczewski, Chadwick L Canedy, Igor Vurgaftman, Clifford Frez, Jerry R Meyer, Mahmood Bagheri, Mitchio Okumura

TD11 **12:07 – 12:22**
STUDY OF XFEL PULSE PARAMETERS FOR GENERATION OF COHERENT FEMTOSECOND X-RAY PULSES, Zain Abhari

TE. Small molecules

Tuesday, June 20, 2023 – 8:30 AM

Room: B102 Chemical and Life Sciences

Chair: Samir Kassi, CNRS, Saint-Martin d'Hères, France

TE01 **8:30 – 8:45**
HARDWARE ACCELERATED SOLUTIONS FOR SPECTROSCOPY, Sean Michael Bresler, Charlie Scott Callahan, Thomas W LeBrun, Jason J Gorman, Gregory B Rieker, David A. Long

TE02 **8:48 – 9:03**
MOLECULAR BEAM DENSITY MEASUREMENT WITH CAVITY-ENHANCED ABSORPTION SPECTROSCOPY , Zhuang Liu, Cunfeng Cheng, Shui-Ming Hu

TE03 **9:06 – 9:21**
HIGH-RESOLUTION, JET-COOLED INFRARED SPECTROSCOPY OF *TRANS*-FORMIC ACID: ANALYSIS OF ν_1 OH STRETCHING FUNDAMENTAL, Ya-Chu Chan, David Nesbitt

TE04 **9:24 – 9:39**
HIGH-RESOLUTION DUAL-COMB SPECTROSCOPY IN THE 9.5 μm REGION TO STUDY PLASMA-ASSISTED AMMONIA FORMATION, Markus Mangold, Jakob Hayden, Andreas Hugi, Adam J. Fleisher, Ibrahim Sadiek, Norbert Lang, Jean-Pierre van Helden

Intermission

TE05 **10:19 – 10:34**
MEASUREMENT AND ASSIGNMENT OF METHANE HOT-BAND TRANSITIONS USING CAVITY-ENHANCED FREQUENCY COMB DOUBLE RESONANCE SPECTROSCOPY: EXTENDING TO HIGHER J STATES., Vinicius Silva de Oliveira, Isak Silander, Adrian Hjältén, Andrea Rosina, Aleksandra Foltynowicz, Lucile Rutkowski, Grzegorz Soboń, Kevin Lehmann

TE06 **10:37 – 10:52**
MODELING THE OPTICAL-OPTICAL DOUBLE RESONANCE LINESHAPES IN CH_4 , Vinicius Silva de Oliveira, Isak Silander, Adrian Hjältén, Andrea Rosina, Aleksandra Foltynowicz, Lucile Rutkowski, Kevin Lehmann

TE07 **10:55 – 11:10**
ARGON PRESSURE BROADENING IN THE OXYGEN A-BAND, Leah E. Stevenson, Erin M. Adkins, Mitchio Okumura, Joseph T. Hodges

TE08 **11:13 – 11:28**
CLOSING THE (SINGLET-TRIPLET) GAP: BeOBe AND ITS ANION STUDIED USING PHOTOELECTRON SPECTROSCOPY, Noah B Jaffe, Caitlyn M Dollar, Michael Heaven

TE09 **11:31 – 11:46**
NEW ELECTRONIC STATES OF MgCl: THE PURE ROTATIONAL SPECTRUM IN THE $(3)^2\Sigma^+$ AND $(4)^2\Sigma^+$ STATES, Tyler J Herman, Rajat Ravi, Lucy M. Ziurys, Robert W Field

TE10 **11:49 – 12:04**
A QUIRKY LITTLE FELLOW: Be_3 AND ITS ANION STUDIED BY PHOTOELECTRON SPECTROSCOPY, Noah B Jaffe, John F. Stanton, Michael Heaven

TE11 **12:07 – 12:22**
INVESTIGATION OF THE ZEEMAN EFFECT IN THE $e\ ^6\Pi - a\ ^6\Delta$ SYSTEM OF FeH: APPLICATION TO STELLAR SPECTROSCOPY, Amanda J. Ross, Patrick Crozet, Allan G. Adam, Timothy E Blackmore, Dennis W. Tokaryk

TF. Clusters/Complexes

Tuesday, June 20, 2023 – 8:30 AM

Room: 274 Medical Sciences Building

Chair: Mark D. Marshall, Amherst College, Amherst, MA, USA

TF01 **8:30 – 8:45**
MONOETHANOLAMINE-(H2O)N, N=1-7, AND -(CO2)M, M=1-4, CLUSTERS CHARACTERIZED BY ROTATIONAL SPECTROSCOPY, Fan Xie, Wenhao Sun, Pablo Pinacho, Melanie Schnell

TF02 **8:48 – 9:03**
FTIR DETECTION OF THE TERT-BUTYL HYDROPEROXIDE DIMER, Casper Vindahl Jensen, Henrik G. Kjaergaard

TF03 **9:06 – 9:21**
A COMPUTATIONAL AND EXPERIMENTAL VIEW OF HYDROGEN BONDING IN POLYOL WATER CLUSTERS, Anna C. Wannenmacher, Wenchao Lu, Chandika Amarasinghe, Ishan Gupta, Musahid Ahmed

TF04 **9:24 – 9:39**
TUNABLE EXCITED STATE DYNAMICS OF NEUTRAL COPPER OXIDE CLUSTERS WITH SIZE AND OXIDATION, Chase H Rotteger, Carter K Jarman, Shaun Sutton, Scott G Sayres

Intermission

TF05 **10:19 – 10:34**
THE HORMONE ANDROSTERONE VS. ITS ANALOG DECAHYDRO-2-NAPHTHOL: DIFFERENCES AND SIMILARITIES, Swantje V. M. Caliebe, Pablo Pinacho, Melanie Schnell

TF06 **10:37 – 10:52**
HIGH RESOLUTION LASER SPECTROSCOPY OF THE NITRIC OXIDE DIMER IN SUPERFLUID HELIUM NANODROPLETS, Daniel Mischenko, Paul Raston

TF07 **10:55 – 11:10**
IR SPECTRA OF BENZOIC ACID-WATER CLUSTERS IN A SUPERSONIC JET USING VUV IONIZATION DETECTION, Chia-I Huang, Jun-Ying Feng, Yuan-Pern Lee, Takayuki Ebata

TF08 **11:13 – 11:28**
ULTRAFAST EXCITED STATE DYNAMICS OF NEUTRAL ALUMINUM OXIDE CLUSTERS, Carter K Jarman, Chase H Rotteger, Shaun Sutton, Scott G Sayres

TF09 **11:31 – 11:46**
PROVING THE ROLE OF WATER MOLECULES IN SUGAR-PEPTIDE INTERACTIONS, Ander Camiruaga, Gildas Goldsztejn, Pierre Çarçabal

TF10 ***Post-Deadline Abstract*** **11:49 – 12:04**
THE CONFORMATIONAL LANDSCAPE OF TYROSOL AND ITS HYDRATES, Alberto Macario, Susana Blanco, Juan Carlos Lopez

TG. Spectroscopy as an analytical tool

Tuesday, June 20, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Christopher Thompson, BrightSpec, Inc., Charlottesville, VA, USA

TG01 **1:45 – 2:00**
THERMAL DECOMPOSITION OF 2-(CHLOROETHYL)BENZENE STUDIED VIA MATRIX-ISOLATION FTIR, Tess Courtney, Khaled Aley El-Shazly, Sophia Wylie, Laura R. McCunn

TG02 **2:03 – 2:18**
RAMAN LABELLED ANTIBODY/APTAMER BASED IMMUNOASSAY FOR THE DETECTION OF OVARIAN CANCER BIOMARKER CA125., Robinson Karunanithy, Noah Allen Ross, P Sivakumar, Torrey E. Holland

TG03 **2:21 – 2:36**
COMPOSITIONAL STUDY OF MULTIPLE AND SINGLE GALLBLADDER STONES USING PHOTOACOUSTIC SPECTROSCOPY, Zainab Gazali, Surya Narayan Thakur, A. K. Rai

TG04 **2:39 – 2:54**
DIRECT VISUALIZATION OF STRUCTURALLY SIMILAR POLYSACCHARIDES IN SINGLE YEAST CELLS IN VIVO BY MULTIVARIATE ANALYSIS ASSISTED RAMAN MICROSPECTROSCOPY, Imrul M Hossain, Hemanth Noothalapati, Tatsuyuki Yamamoto

TG05 **2:57 – 3:12**
SPECTROCHEMICAL ANALYSIS FOR NUTRIENTS AND TOXIC HEAVY METALS DETECTION IN ABUNDANTLY UTILIZED HERBAL MEDICINE (SCHILAJIT) BY EMPLOYING THREE ADVANCED ANALYTICAL TECHNIQUES, Mohammed A Gondal, R. K. Aldakheel, M A. Almessiere

TG06 **3:15 – 3:30**
ROOM TEMPERATURE OPTICAL DETECTION OF $^{14}CO_2$ AT PARTS-PER-QUADRILLION LEVEL ACCURACY WITH TWO-COLOR CAVITY RINGDOWN SPECTROSCOPY, Jun Jiang, A. Daniel McCartt

Intermission

TG07 **4:10 – 4:25**
DIRECT MEASUREMENT OF CATALYTIC OXIDATION OF SO_2 BY A K-BAND MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY, Sai Eswar Jasti, Sylvestre Twagirayezu, Justin L. Neill

TG08 **4:28 – 4:43**
THE SPECTROSCOPIC SOFTWARE UNIVERSE: A ”PICKETT 2.0” PROPOSAL, Nathan A. Seifert

TG09 **4:46 – 5:01**
WILL CHIRAL TAG ROTATIONAL SPECTROSCOPY ALWAYS GIVE ACCURATE ENANTIOMERIC EXCESS DETERMINATATIONS?, Luca Evangelisti, Josh Heman-Ackah, Taylor Chambers, Brooks Pate

TG10 **5:04 – 5:19**
MOLECULES IN LASER-INDUCED PLASMA: AN ANOMALY OR THE BEST WAY TO SOLVE INTRACTABLE PROBLEMS?, Timur A. Labutin, Sergey Zaytsev, Nikolai Sushkov, Aleksandr Zakuskin, Ekaterina A. Bormotova, Andrey Popov

TH. Mini-symposium: Spectroscopy at Large-scale Facilities

Tuesday, June 20, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Ming-Fu Lin, SLAC National Accelerator Laboratory, Menlo Park, CA, USA

TH01 **1:45 – 2:00**
PROBING THE FERROCYANIDE AQUATION REACTION WITH NONRESONANT X-RAY EMISSION SPECTROSCOPY, Anne Marie March, Christopher J Otolski, Gilles Doumy, Niranjan Govind, Amity Andersen, Gyorgy Vanko, Zoltán Németh, Wojciech Gawelda

TH02 **2:03 – 2:18**
DETERMINING THE CHARGE TRANSFER PROPERTIES OF METAL-COORDINATED COUMARIN DYES USING X-RAY AND OPTICAL TRANSIENT ABSORPTION SPECTROSCOPIES, Danielle J Jacoby, Cali Antolini, Abby E Civiello, Christopher J Otolski, Gilles Doumy, Anne Marie March, Dugan Hayes

TH03 **2:21 – 2:36**
PUMPING THE INTERVALENCE CHARGE TRANFSER AND PROBING ACROSS THE ELECTROMAGNETIC SPECTRUM: DIVERSE SPECTRAL PROBES REVEAL A UNIQUE RELAXATION MECHANISM, John H Burke, Renske van der Veen, Josh Vura-Weis

TH04 ***INVITED TALK*** **2:39 – 3:09**
CHEMICAL DYNAMICS CAPTURED WITH ATOMIC SPECIFICITY AND RESOLUTION USING ULTRAFAST X-RAY SPECTROSCOPY AND SCATTERING, Kelly Gaffney

TH05 **3:15 – 3:30**
MONITORING ELECTRON DELOCALIZATION IN A MIXED VALENCE RU DIMER USING TRANSIENT RU L-EDGE X-RAY AND INFRARED SPECTROSCOPIES, Benjamin I Poulter, Chelsea Liekhus-Schmaltz, Robert Weakly, Jason Sandwisch, Munira Khalil, Elisa Biasin, Soumen Ghosh, Niranjan Govind, Sven Augustin, Ivan Usov, Dmitry Ozerov, Christopher Arrell, Philip Johnson, Gregor Knopp, Claudio Cirelli, Christopher Milne, Amy Cordones-Hahn, Marco Reinhard, Dimosthenis Sokaras, Roberto Alonso Mori, Robert Schoenlein

TH06 **3:33 – 3:48**
MEASURING CHARGE DELOCALIZATION IN MIXED-VALANCE COMPLEXES USING ULTRAFAST X-RAY SPECTROSCOPY, Zhaoyuan Yang, Benjamin I Poulter, Michael Sachs, Soumen Ghosh, Robert Schoenlein, Roberto Alonso Mori, Leland Bruce Gee Jr., Tim van Driel, Ryan Ribson, Takahiro Sato, Yihan Xia, Elisa Biasin, Niranjan Govind, Munira Khalil

Intermission

TH07 **4:28 – 4:43**
GROUND- AND EXCITED-STATE CHARACTERIZATION OF A Ni-BIPYRIDINE PHOTOCATALYST USING X-RAY SPECTROSCOPY, Rachel Wallick, Sagnik Chakrabarti, Liviu M Mirica, Renske van der Veen, Josh Vura-Weis

TH08 **4:46 – 5:01**
TRACKING STRUCTURAL SOLVENT REORGANIZATION AND RECOMBINATION DYNAMICS FOLLOWING ELECTRON PHOTOABSTRACTION FROM AQUEOUS HALIDES WITH FEMTOSECOND X-RAY SPECTROSCOPY AND SCATTERING, Katharina Kubicek, Zhangatay Nurekeyev, Mohammed Sekkal, Michael Thorwart, Carmen Herrmann, Christian Bressler

TH09 **5:04 – 5:19**
USING POLARIZED ULTRAFAST SPECTROSCOPY AS A TOOL FOR DETERMINING SUBPICOSECOND STRUCTURAL DYNAMICS OF PHOTOEXCITED N-PROPYLCOBALAMIN, Ryan Lamb, R.J. Sension

TH10 **5:22 – 5:37**
ULTRAFAST PUMP-PROBE XANES ANALYZED WITH FDMNES SIMULATIONS REVEAL THE SEQUENTIAL STRUCTURAL EVOLUTION OF ADENOSYLCOBALAMIN AS A FUNCTION OF SOLVENT, Eilidh McClain

TH11 **5:40 – 5:55**
FIRST RESULTS FROM ATTOSECOND X-RAY PUMP-PROBE EXPERIMENTS IN LIQUIDS, Shuai Li, Kai Li, Gilles Doumy, Linda Young, Emily Nienhuis, Carolyn Pearce, Lixin Lu, Xiaosong Li, Stefan P. Moeller, Ming-Fu Lin, Georgi Dakovski, Ago Marineili, James Cryan, Dan DePonte, Robin Santra, Ludger Inhester

TI. Radicals

Tuesday, June 20, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Chuanliang Li, Taiyuan University of Science and Technology, Taiyuan, Shanxi, China

TI01 **1:45 – 2:00**
MILLIMETER/SUBMILLIMETER SPECTROSCOPY OF THE METHYLAMINE PHOTODISSOCIATION PRODUCT AMINOMETHYL RADICAL ($^{\cdot}CH_2NH_2$), Haocheng Liang, Jonathan Rebelsky, Connor J. Wright, John F. Stanton, Susanna L. Widicus Weaver

TI02 **2:03 – 2:18**
PURE ROTATIONAL SPECTRA OF ETHOXY RADICAL, Ching Hua Chang, Yasuki Endo

TI03 **2:21 – 2:36**
CRIEGEE INTERMEDIATE CH_2OO IN THE OXIDATION OF ETHANE, Nathan A. Seifert, RAGHU SIVARAMAKRISHNAN, Kirill Prozument

TI04 **2:39 – 2:54**
SPECTRAL STUDIES OF THE REACTION OF THE CRIEGEE INTERMEDIATE CH_3CHOO WITH HCL USING A STEP-SCAN FOURIER-TRANSFORM INFRARED ABSORPTION SPECTROMETER, Yuan-Pern Lee, Zih-Syuan Su

TI05 **2:57 – 3:12**
OBSERVATION OF THE OH-C_6H_6 RADICAL COMPLEX IN AN ARGON MATRIX USING MATRIX ISOLATION INFRARED SPECTROSCOPY WITH A VACUUM ULTRAVIOLET PHOTOLYSIS SOURCE, Jay C. Amicangelo, Catherine Kaiser, Tracy Jones, Dylan Johnson

TI06 **3:15 – 3:30**
PRODUCTION OF C_α-ALANYL RADICAL AND VINYLAMINE IN THE REACTION H + α-ALANINE IN SOLID p-H_2 AND ITS IMPLICATIONS IN ASTROCHEMISTRY , Prasad Ramesh Joshi, Yuan-Pern Lee

Intermission

TI07 **4:10 – 4:25**
ELECTRONIC STRUCTURE OF PROTOTYPICAL π- and σ-RADICALS: HYPERFINE-RESOLVED ROTATIONAL SPECTROSCOPY OF PROPARGYL AND PHENYL, Bryan Changala, Peter R. Franke, John F. Stanton, Barney Ellison, Michael C McCarthy

TI08 **4:28 – 4:43**
THE UV-VIS SPECTRUM OF ClSO RADICAL FROM THE PHOTOLYSIS of THIONYL CHLORIDE AT 248 nm, Wen Chao, Gregory H Jones, Mitchio Okumura, Carl J. Percival, Frank A. F. Winiberg

TI09 **4:46 – 5:01**
ANALYSIS OF THE OPEN-SHELL CH_3CO RADICAL: INTERNAL ROTATION, SPIN-ROTATION, AND HYPERFINE STRUCTURE, Olivier Pirali, Rosemonde Chahbazian, Marie-Aline Martin-Drumel, L. H. Coudert, Luyao Zou, R. A. Motiyenko, L. Margulès

TI10 **5:04 – 5:19**
RESONANCE RAMAN SPECTRA OF PROTOTYPE (HYDROXY)CYCLOHEXADIENYL RADICALS IN WATER, Ireneusz Janik, Susmita Bhattacharya

TI11 **5:22 – 5:37**
DIRECT TERAHERTZ ROTATIONAL MEASUREMENTS OF FeH AND FeD (X $^4\Delta_i$), Ambesh Pratik Singh, Tyler J Herman, Deacon J Nemchick, Brian Drouin, Lucy M. Ziurys

TJ. Electronic structure, potential energy surfaces

Tuesday, June 20, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

Chair: James H. Thorpe, Southern Methodist University, Dallas, TX, USA

TJ01 **1:45 – 2:00**
LIFE'S COSMIC HANDSHAKE: DFT AND TD-DFT PREDICTIONS FOR THE PROPERTIES OF ENSTATITE ($MgSiO_3$) MONOMERS AND DIMERS , Kamil B. Stelmach, Catherine A. Dukes, Robin T. Garrod

TJ02 **2:03 – 2:18**
PFI-ZEKE CHARACTERIZATION OF THE GROUND AND LOW-LYING EXITED STATES OF MgO^+, Joel R Schmitz, Carla Kreis, Frédéric Merkt

TJ03 **2:21 – 2:36**
COMPREHENSIVE ANALYSIS OF THE A $^4\Pi$ - X $^4\Sigma^-$ TRANSITION OF MOLYBDENUM NITRIDE, MoN: LIMITATIONS OF A HUND'S CASE(a) ANALYSIS, Nyla S Woods, Leah C O'Brien, Kristin N Bales, Gabriel A Hotz, Srisahithi Tadakamalla, James J O'Brien

TJ04 **2:39 – 2:54**
A FRESH LOOK AT THE B1 - $X0^+$ and A1 - $X0^+$ TRANSITIONS IN TUNGSTEN OXIDE, WO: EVIDENCE OF AN AVOIDED CROSSING?, Kristin N Bales, James J O'Brien, Leah C O'Brien

TJ05 **2:57 – 3:12**
ELECTRONIC STRUCTURE AND SPECTROSCOPY OF OThF, Arianna Rodriguez, Jiarui Yan, Jiande Han, Michael Heaven

TJ06 **3:15 – 3:30**
MULTIREFERENCE CALCULATIONS ON THE GROUND AND EXCITED STATES AND DISSOCIATION ENERGIES OF LANTHANIDE AND ACTINIDE OXIDES AND FLUORIDES , Nuno M. S. Almeida, Sasha C. North, Timothé R. L. Melin, Angela K. Wilson

TJ07 **3:33 – 3:48**
SOLVENT-TUNING OF A Fe^{II} EXCITED STATE TOWARD UNDERSTANDING LIGAND DESIGN, Justin Thomas Malme, Reese Clendening, Lauren Boedicker, Prakhar Gautam, Tong Ren, Josh Vura-Weis

Intermission

TJ08 **4:28 – 4:43**
ULTRAVIOLET INTRACAVITY LASER ABSORPTION SPECTROSCOPY, Uri Zamir, Maayan Cohen, Illya Rozenberg, Avi lerer, Yehoshua Kalisky, Amir Kaplan, Igor Rahinov, Joshua H. Baraban

TJ09 **4:46 – 5:01**
EXCITED STATE DOUBLE PROTON OR HYDROGEN TRANSFER ON INDIGO IN THE GAS PHASE: EFFECTS IN DEUTERATION., Trevor Cohen, Ana Delia Parejo Vidal, Nathan Nathan Svadlenak, Mattanjah DE VRIES

TJ10 **5:04 – 5:19**
DIABATIC VALENCE-HOLE STATES, Jun Jiang, Robert W Field

TK. Structure determination

Tuesday, June 20, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: Lai-Sheng Wang, Brown University, Providence, RI, USA

TK01 **1:45 – 2:00**
HIGH RESOLUTION INFRARED SPECTRA OF NEOPENTANE: ROVIBRATIONAL ANALYSIS OF BANDS AT 8.3-6.4 μm, Adam Pastorek, Peter F. Bernath, Vincent Boudon

TK02 **2:03 – 2:18**
THE STRUCTURAL DETERMINATION AND COMPARISON OF 1-ETHYLSILACYCLOPENTANE AND 1-ETHYL-1-FLUOROSILACYCLOPENTANE, J. E. Isert, Josie R. Glenn, Caitlyn Saiz, W. H. Rice IV, Gamil A Guirgis, G. S. Grubbs II

TK03 **2:21 – 2:36**
TWELVE CONFORMERS OF 4-FLUOROTHREONINE UNVEILED BY LASER ABLATION ROTATIONAL SPECTROSCOPY, Vincenzo Barone, Marco Fusè, Raúl Aguado, Simone Potenti, Iker León, Elena R. Alonso, Santiago Mata, Federico Lazzari, Lorenzo Spada, Giordano Mancini, Andrea Gualandi, Pier Giorgio Cozzi, Cristina Puzzarini, José L. Alonso

TK04 **2:39 – 2:54**
REINVESTIGATION OF THE ROTATIONAL SPECTRUM AND STRUCTURE OF CYCLOHEXYLAMINE, Michael J. Carrillo, Dinesh Marasinghe, Michael Tubergen

TK05 **2:57 – 3:12**
ROTATIONAL SPECTROSCOPY AND STRUCTURE OF CYCLOPROPYLCHLOROMETHYLDIFLUOROSILANE, A R Davies, Abanob George Hanna, Alma Lutas, Gamil A Guirgis, G. S. Grubbs II

Intermission

TK06 **3:52 – 4:07**
CHARACTERIZING THE STRUCTURE OF SUCCINIMIDE WITH BROADBAND ROTATIONAL SPECTROSCOPY, Sivanjali Elena Williams, Chisom Adaobi Dim, Caroline Sorrells, Kyle N. Crabtree, A. O. Hernandez-Castillo

TK07 **4:10 – 4:25**
K_A-BAND ROTATIONAL SPECTROSCOPY OF N-HALOSUCCINIMIDES, Chisom Adaobi Dim, Caroline Sorrells, S E Worthington-Kirsch, A. O. Hernandez-Castillo, Kyle N. Crabtree

TK08 **4:28 – 4:43**
THEORETICAL AND MICROWAVE SPECTROSCOPIC CHARACTERIZATION OF CYCLOBUTENONE , Michael J. Carrillo, Dinesh Marasinghe, Kristin Sobie, Rourke J. Zarzycki, Kevin Carter-Fenk, Christopher Fenk, Michael Tubergen

TK09 **4:46 – 5:01**
INVESTIGATING THREE CYCLIC DIKETONE MOLECULES USING ROTATIONAL SPECTROSCOPY, Laura Wu, Chisom Adaobi Dim, Caroline Sorrells, Kyle N. Crabtree, A. O. Hernandez-Castillo

TK10 **5:04 – 5:19**
SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE OF 1,3-OXAZOLE FROM MANY ISOTOPOLOGUES, Brian J. Esselman, Madeleine Atwood, Taylor K. Adkins, Maria Zdanovskaia, Manamu Kobayashi, Shozo Tsunekawa, Kaori Kobayashi, Nitai Prasad Sahoo, John F. Stanton, R. Claude Woods, Robert J. McMahon

TK11 **5:22 – 5:37**
THE STRUCTURE OF STRAINED MOLECULES: THE EXAMPLE OF PARACYCLOPHANES., Himanshi Singh, Pablo Pinacho, Melanie Schnell

TL. Mini-symposium: Infrared Spectroscopy in the JWST Era

Tuesday, June 20, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: Sandra Brünken, Radboud University, Nijmegen, The Netherlands

TL01 **1:45 – 2:00**
CHEMICAL DIVERSITY IN THE INNER REGIONS OF PLANET-FORMING DISKS AS REVEALED BY JWST-MIRI AND THE MINDS PROGRAM, Kamber Schwarz

TL02 **2:03 – 2:18**
HIGH-RESOLUTION MID-IR LINE SURVEY OF THE LATE-TYPE STAR VY CMa , Guido W. Fuchs, Eileen Döring, Daniel Witsch, Thomas Giesen, Thomas K Greathouse, Rohini S Giles, John H. Lacy, Edward J Montiel, Matthew J Richter

TL03 **2:21 – 2:36**
HIGH RESOLUTION 2D INFRARED SPECTROSCOPY: A NEW WAY TO ASSIGN NEAR INFRARED PEAKS, Peter Chen, DeAunna A Daniels, Thresa Wells

TL04 **2:39 – 2:54**
JWST OPENS A NEW ERA IN ASTROCHEMISTRY, Takeshi Oka

Intermission

TL05 **3:34 – 3:49**
THE BENDING OF C_3: EXPERIMENTALLY PROBING THE *l*-TYPE DOUBLING AND RESONANCE, Marie-Aline Martin-Drumel, Olivier Pirali, Michel Vervloet, Dennis W. Tokaryk, Colin Western, Kirstin D Doney, Harold Linnartz, Qiang Zhang, Yang Chen, Dongfeng Zhao

TL06 **3:52 – 4:07**
THE ELUSIVE METHYL CATION DISCOVERED BY JWST IN A PLANET FORMING DISK , Olivier Berné, Ilane Schroetter, Christine Joblin, Amelie Canin, Marie-Aline Martin-Drumel, Ugo Jacovella, Bérenger Gans, Emmanuel Dartois, L. H. Coudert, Javier Goicoechea, Jose Cernicharo, Edwin Bergin, Felipe Alarcon, Jan Cami, Els Peeters, Evelyne Roueff, Maryvonne Gerin, J. H. Black, Oskar Asvany, Sven Thorwirth, Stephan Schlemmer, Emilie Habart, Boris Trahin, Marion Zannese, Xander Tielens

TL07 **4:10 – 4:25**
LABORATORY INFRARED SPECTROSCOPY OF SMALL ASTROPHYSICALLY RELEVANT MOLECULES , Thomas Giesen, Eileen Döring, Alexander A. Breier, Fabian Peterß, Guido W. Fuchs

TL08 **4:28 – 4:43**
INVESTIGATING PREBIOTIC CHEMISTRY WITH CRYOGENIC ACTION SPECTROSCOPY - GAS-PHASE GLYCOLALDEHYDE FORMATION VIA A CATIONIC ”FORMOSE” REACTION, Hunarpreet Kaur, Weiqi Wang, Jesús Pérez-Ríos, Britta Redlich, Sandra Brünken

TL09 **4:46 – 5:01**
IRMPD SPECTROSCOPY OF $Fe(H_2)_{1,2}{}^+$ AND OVERTONE STUDY OF $Ar_{1,2}FeH^+$ AND THEIR DEUTERATED SPECIES: LOOKING FOR IRON HYDRADES IN THE INTERSTELLAR MEDIUM, Shan Jin, Marcos Juanes, Christian van der Linde, Milan Oncak, Martin K Beyer

WA. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Wednesday, June 21, 2023 – 8:30 AM

Room: 116 Roger Adams Lab

Chair: Christopher J. Johnson, Stony Brook University, Stony Brook, NY, USA

WA01 ***INVITED TALK*** **8:30 – 9:00**
CAN SILVER IONS PERMEATE THROUGH A POTASSIUM ION CHANNEL ? – DOUBLE ION TRAP LASER SPECTROSCOPY ON METAL COMPLEXES OF THE PARTIAL PEPTIDE OF A SELECTIVITY FILTER, Satoru Tanabe, Keisuke Hirata, Koichi Tsukiyama, James M. Lisy, Shun-ichi Ishiuchi, Masaaki Fujii

WA02 **9:06 – 9:21**
CARBONYL BANDS REPORT ON MOLECULAR STRUCTURE IN COMPLEX SPECTRA: CRYOGENIC ION SPECTROSCOPY OF METAL-CYCLAM COMPLEXES, Madison M. Foreman, Wyatt Zagorec-Marks, J. Mathias Weber

WA03 **9:24 – 9:39**
LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER I: RO-VIBRATIONAL SPECTRA, Thomas Salomon, Oskar Asvany, Stephan Schlemmer

WA04 **9:42 – 9:57**
LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER II: SPIN STATISTICAL WEIGHTS, Thomas Salomon, Charles R. Markus, Oskar Asvany, Stephan Schlemmer

WA05 **10:00 – 10:15**
AN ELECTRIC AFFAIR: THE IMPACT OF SOLVATION ON THE STRUCTURE OF METAL ION-PEPTIDE COMPLEXES, Katharina A. E. Meyer, Etienne Garand

Intermission

WA06 **10:55 – 11:10**
CRYOGENIC ION SPECTROSCOPY OF ION-RECEPTOR INTERACTIONS IN OCTAMETHYL CALIX[4]PYRROLE COMPLEXES WITH HALIDE IONS, Lane M. Terry, Madison M. Foreman, Anne P. Rasmussen, Anne B. McCoy, J. Mathias Weber

WA07 **11:13 – 11:28**
MISMATCHED HOST-GUEST PAIRINGS – CRYOGENIC ION SPECTROSCOPY OF OCTAMETHYL-CALIX[4]PYRROLES IN COMPLEXES WITH NITRATE AND FORMATE, Lane M. Terry, Madison M. Foreman, J. Mathias Weber

WA08 **11:31 – 11:46**
MICROHYDRATION OF $Mg^{2+}(CH_3COO^-)$ ION PAIRS FOLLOWED BY IR LASER SPECTROSCOPY: INSIGHTS INTO THE WATER-MEDIATED IONIC INTERACTIONS IN THE MAGNESIUM TRANSPORT CHANNEL , Jean-Xavier Bardaud, Eric Gloaguen, Valerie Brenner, Michel Mons, HIKARU TAKAYANAGI, Keisuke Hirata, Shun-ichi Ishiuchi, Masaaki Fujii

WA09 **11:49 – 12:04**
HIGH RESOLUTION SPECTROSCOPY IN A 5K CRYOGENIC ION TRAP: REVISITNG THE OH STRETCHING BANDS OF THE H_20 AND HDO ISOTOPOLOGUES OF THE BINARY COMPLEXES WITH IODIDE, Payten Harville, Sean Coleman Edington, Mark Johnson

WA10 **12:07 – 12:22**
A MOLECULAR CAGE REPORTS ON ITS CONTENTS: THE INFRARED AND ULTRAVIOLET SPECTRA OF [2.2.2]BENZOCRYPTAND COMPLEXED WITH K^+, Ba^{2+}, AND THE ION PAIR Ba^{2+}-ACETATE$^-$, Chin Lee, Casey Daniel Foley, Kendrew Au, Edwin Sibert, Timothy S. Zwier

WB. Linelists

Wednesday, June 21, 2023 – 8:30 AM

Room: 100 Noyes Laboratory

Chair: Amanda J. Ross, Universite de Lyon, Villeurbanne, France

WB01 **8:30 – 8:45**
ROTATIONAL SPECTROSCOPY OF UREA UP TO 500 GHZ: THE GROUND STATE AND EIGHT EXCITED VIBRATIONAL STATES, Daniel J Tyree, Thomas W Chapman, Ivan Medvedev, Zbigniew Kisiel

WB02 **8:48 – 9:03**
LaO LINE LIST FOR THE $A^2\Pi$-$X^2\Sigma^+$ BAND SYSTEM, Peter F. Bernath, Randika Dodangodage, Jacques Liévin

WB03 **9:06 – 9:21**
INTENSITY STUDIES OF OZONE IN THE 10 MICRON REGION BY SIMULTANEOUS SUB-MM/LASER-BASED INFRARED DIRECT ABSORPTION MEASUREMENTS , Deacon J Nemchick, Xu Zhang, Keeyoon Sung, Timothy J. Crawford, Brian Drouin

WB04 **9:24 – 9:39**
A NEW LINE LIST FOR THE O2 SCHUMANN-RUNGE SYSTEM, Elijah R Jans, Daniel Spencer Jensen, Laura M McCaslin

WB05 **9:42 – 9:57**
PRECISION MEASUREMENTS OF WATER VAPOR SPECTROSCOPY BROADENED BY O_2 FOR ACCURATE DETERMINATION OF POTENTIAL ENERGY SURFACE, Keeyoon Sung, Geoffrey C. Toon, Robert R. Gamache

Intermission

WB06 **10:37 – 10:52**
A NEW LINE LIST FOR THE N2 SECOND POSITIVE SYSTEM, Elijah R Jans

WB07 **10:55 – 11:10**
INVESTIGATING THE INTERSTELLAR SULFUR CHEMISTRY THROUGH ROTATIONALLY RESOLVED DISCHARGE EXPERIMENTS , Amanda Steber, Cristobal Perez, Wenqin Li, Alberto Lesarri

WB08 **11:13 – 11:28**
AN AB INITIO STUDY AND INITIAL REFINEMENT OF THE ROVIBRONIC SPECTRUM OF SULFUR MONOXIDE ($^{32}S^{16}O$): DIABATIC VS. ADIABATIC REPRESENTATION AND THEIR EQUIVALENCE IN NUCLEAR MOTION CALCULATIONS, Ryan Brady, Sergei N. Yurchenko, Gap-Sue Kim, Wilfrid Somogyi, Jonathan Tennyson, Charlie Drury

WB09 **11:31 – 11:46**
EXTENDED PRECISE SPECTROSCOPY OF THE ν_3 BAND OF METHANE, Hiroyuki Sasada, Sho Okubo, Hajime Inaba

WB10 **11:49 – 12:04**
FREQUENCY MEASUREMENTS WITH kHz-ACCURACY OF $^{12}CO_2$ TRANSITIONS IN THE 2.0 μm REGION, Helene Fleurbaey, Peter Čermák, Samir Kassi, Daniele Romanini, Ondřej Votava, Didier Mondelain

WC. Astronomy

Wednesday, June 21, 2023 – 8:30 AM

Room: 1024 Chemistry Annex

Chair: Anthony Remijan, NRAO, Charlottesville, VA, USA

WC01 **8:30 – 8:45**
LINKING CHEMISTRY AND KINEMATICS IN THE MOLECULAR GAS OF PROTOPLANETARY NEBULA M1-92 , Katherine R. Gold, Deborah Schmidt, Omar Khattab, Lucy M. Ziurys

WC02 **8:48 – 9:03**
POLYATOMIC MOLECULES IN PLANETARY NEBULAE: SEARCHES FOR C-C3H2, H2CO, CCH, AND HNC IN M1-59, NA2, HU1-1, AND M4-17, Katherine R. Gold, Deborah Schmidt, Lucy M. Ziurys

WC03 **9:06 – 9:21**
A 1 AND 2mm SURVEY OF THE CARBON-RICH STAR IRC+10216: A FOCUS ON ISOTOPES, Lilia Koelemay, Lucy M. Ziurys

WC04 **9:24 – 9:39**
ALMA PROBES REFRACTORY CHEMISTRY AND RELATED MASS-LOSS EVENTS IN VY CMa, Rajat Ravi, Ambesh Pratik Singh, Roberta M. Humphreys, Anita M Richards, Lucy M. Ziurys

WC05 **9:42 – 9:57**
ALMA REVEALS THE EXTENDED ENVELOPE OF THE HYPERGIANT STAR VY CMa, Ambesh Pratik Singh, Anita M Richards, Roberta M. Humphreys, Lucy M. Ziurys

Intermission

WC06 **10:37 – 10:52**
THE CENTRAL 300 pc OF THE GALAXY PROBED BY INFRARED SPECTRA OF H_3^+ AND CO, Takeshi Oka, Thomas R. Geballe

WC07 **10:55 – 11:10**
MILLIMETER/SUBMILLIMETER SPECTRUM AND INTERSTELLAR SEARCH FOR SINGLY DEUTERATED METHYL MERCAPTAN, CH_2DSH, Hayley A. Bunn, Silvia Spezzano, L. H. Coudert, Christian Endres, J.-C. Guillemin, Valerio Lattanzi, Paola Caselli

WC08 **11:13 – 11:28**
LABORATORY INVESTIGATION OF CARBON-SULFUR SPECIES FOR ASTROCHEMISTRY, Valerio Lattanzi, Christian Endres, Mitsunori Araki, Davide Alberton, Paola Caselli

WC09 **11:31 – 11:46**
EFFECTS OF STAR FORMATION ON BOUNDEDNESS IN LMC CLOUDS, Alex Green, Tony Wong, Rémy Indebetouw, Omnarayani Nayak, Alberto Bolatto, Elizabeth Tarantino, Mónica Rubio, Suzanne C Madden

WC10 **11:49 – 12:04**
PHOSPHORUS AT THE EDGE OF THE GALAXY: DETECTION OF PO AND PN BEYOND 16 kPC , Lilia Koelemay, Katherine R. Gold, Lucy M. Ziurys

WD. Instrument/Technique Demonstration

Wednesday, June 21, 2023 – 8:30 AM

Room: 217 Noyes Laboratory

Chair: Peter Chen, Spelman College, Atlanta, GA, USA

WD01 **8:30 – 8:45**
TOWARDS MULTIPLEXED SPECTROSCOPY IN AN ION TRAP: SELECTIVE MASS ELIMINATION USING SQUARE DIPOLAR RESONANT EXCITATION, Grace Capek, Etienne Garand

WD02 **8:48 – 9:03**
X-FAST: A NEW XUV FEMTOSECOND ABSORPTION SPECTROSCOPY TABLETOP INSTRUMENT AT UW-MADISON, Zain Abhari

WD03 **9:06 – 9:21**
TABLE-TOP TIME-RESOLVED X-RAY SPECTROSCOPY USING A LASER PLASMA X-RAY SOURCE AND TRANSITION-EDGE SENSORS, Nathan Nakamura, Luis Miaja-Avila, Galen C O'Neil, Daniel Swetz, Joel N Ullom

WD04 **9:24 – 9:39**
OBSERVING TRANSIENT MAGNETIC OXIDATION STATES WITH MAGNETIC CIRCULAR DICHROISM SPECTROSCOPY, Harshad Gajapathy, Savini Sandunika Bandaranayake, Emily B Hruska, Stephen Londo, Martin Schultze, Robert Baker

WD05 **9:42 – 9:57**
THE DESIGN AND CONSTRUCTION OF A MASS-SELECTED ION-MOLECULE CLUSTER BEAM APPARATUS FOR PHOTO-FRAGMENT SPECTROSCOPY., Xiaojun Wang, Mahmudul Hasan, Lin Fan, Yibo Wang, Hui Li, Daniel S. Slaughter, Martin Centurion

WD06 **10:00 – 10:15**
BENCHMARKING APPARATUS FOR PRODUCTION OF PROTONATED SPECIES, Jonathan Rebelsky, Haocheng Liang, Susanna L. Widicus Weaver

Intermission

WD07 **10:55 – 11:10**
DEVELOPMENT OF AN OPTICAL FEEDBACK-CAVITY RING DOWN SPECTROMETER AT 8.5 μm. APPLICATION TO THE SELF CONTINUUM OF WATER VAPOR., Quentin Fournier, Samir Kassi, Alain Campargue, Robert Georges

WD08 **11:13 – 11:28**
TOROIDAL ABSORPTON CELL WITH MULTI-LAYER PATTERNS BY A SINGLE RING SURFACE, Chuanliang Li

WD09 **11:31 – 11:46**
UTILIZING FPGA TECHNOLOGY FOR REAL-TIME SPECTROSCOPIC ANALYSIS IN CAVITY RING-DOWN COMB SPECTROSCOPY WITH MACHINE LEARNING-ASSISTED COMB LINE ALIGNMENT, Yi-Jan Huang, Charles R. Markus, Lukasz A. Sterczewski, Douglas Ober, Chadwick L Canedy, Igor Vurgaftman, Clifford Frez, Jerry R Meyer, Mahmood Bagheri, Mitchio Okumura, Tzu-Ling Chen

WD10 **11:49 – 12:04**
N_2O AS AN $O(^1D)$ SOURCE FOR GAS PHASE STUDY OF COMS, Colton Moore, Hayley A. Bunn, Chase P Schultz, Susanna L. Widicus Weaver

WD11 ***Post-Deadline Abstract*** **12:25 – 12:40**
MEASUREMENTS OF VIBRATIONALLY EXCITED OXYGEN MOLECULES IN PREHEATED O_2-Ar MIXTURES EXCITED BY A NANOSECOND PULSE DISCHAGE, Keegan Orr, Dirk van den Bekerom, Iole Armenise, Fabrizio Esposito, Igor V. Adamovich

WE. Rotational structure/frequencies

Wednesday, June 21, 2023 – 8:30 AM

Room: B102 Chemical and Life Sciences

Chair: Wei Lin, The University of Texas Rio Grande Valley, Brownsville, TX, USA

WE01 **8:30 – 8:45**
COMPUTATIONAL STUDIES OF NONADIABATIC ALIGNMENT OF ASYMMETRIC TOP MOLECULES, Haoran Zhao, Martin Centurion

WE02 **8:48 – 9:03**
NEW ANALYSIS OF THE ν_9 REGION OF 2,2-D_2-PROPANE FROM CLS HIGH RESOLUTION SPECTRA. FUNDAMENTAL AND HOT BAND SPECTRA. MORE ACCURATE CONSTANTS DETERMINED, Stephen J. Daunt, Robert Grzywacz, Colin Western, Daniel Gjuraj, Brant E. Billinghurst, Jianbao Zhao, Jean-Marie Flaud, Walter Lafferty

WE03 **9:06 – 9:21**
O(^{1}D) INSERTION REACTION FOR THE FORMATION AND SPECTRAL ANALYSIS OF CARBONIC ACID, Chase P Schultz, Colton Moore, Susanna L. Widicus Weaver

WE04 **9:24 – 9:39**
EXPLORING THE PROPERTIES AND REACTIVITY OF CARBONYL DIISOTHIOCYANATE WITH ROTATIONAL SPECTROSCOPY, Eva Gougoula, Frank Tambornino, Melanie Schnell

Intermission

WE05 **10:19 – 10:34**
ROTATIONAL SPECTROSCOPY OF FLUORONAPHTHALENES: THE MODEL STUDY OF HALOGENATED NAPHTHALENES, Sathapana Chawananon, Pierre Asselin, Marie-Aline Martin-Drumel, Olivier Pirali

WE06 **10:37 – 10:52**
ROTATIONAL SPECTROSCOPY OF 2- AND 4-CYANOBIPHENYL, Bettina Heyne, Mariyam Fatima, Lise von Rötel, Sven Thorwirth, Stephan Schlemmer

WE07 **10:55 – 11:10**
THE 235–500 GHZ ROTATIONAL SPECTRUM OF 1-CYANO-2-METHYLENECYCLOPROPANE (C_5H_5N), Dairen R Jean, Samuel A. Wood, Samuel M. Kougias, Brian J. Esselman, R. Claude Woods, Robert J. McMahon

WE08 **11:13 – 11:28**
THE ROTATIONAL SPECTROSCOPY OF 2-FORMYLTHIOPHENE UP TO 750 GHZ IN ITS GROUND AND TWO VIBRATIONALLY EXCITED STATES, Brian J. Esselman, Ha Vinh Lam Nguyen, R. Claude Woods, Robert J. McMahon

WE09 **11:31 – 11:46**
ROTATIONAL AND INFRARED SPECTRA OF PYRIMIDINE: VIBRATIONAL GROUND STATE AND NINE VIBRATIONALLY EXCITED STATES, William Styers, Brian J. Esselman, Zachary N. Heim, Brent K. Amberger, Brant E. Billinghurst, Jianbao Zhao, R. Claude Woods, Robert J. McMahon

WE10 **11:49 – 12:04**
ANALYSIS OF COMBINED MILLIMETER-WAVE AND HIGH-RESOLUTION INFRARED SPECTRA OF 2- AND 3-FURONITRILE, William Styers, Brian J. Esselman, Maria Zdanovskaia, Andrew N. Owen, Samuel M. Kougias, Brant E. Billinghurst, Jianbao Zhao, R. Claude Woods, Robert J. McMahon

WE11 ***Post-Deadline Abstract*** **12:07 – 12:22**
RICH CONFORMATIONAL LANDSCAPES OF MACROCYCLIC MUSKS BY BROADBAND ROTATIONAL SPECTROSCOPY: AN INSIGHT INTO THE MUSK SCENT MYSTERY , Ecaterina Burevschi, Donatella Loru, M. Eugenia Sanz

WF. Clusters/Complexes

Wednesday, June 21, 2023 – 8:30 AM

Room: 274 Medical Sciences Building

Chair: Cristina Puzzarini, University of Bologna, Bologna, Italy

WF01 **8:30 – 8:45**
BROADBAND ROTATIONAL SPECTROSCOPY OF CUMINOL AND ITS WATER COMPLEX, Elias M. Neeman, Noureddin OSSEIRAN, Therese R. Huet

WF02 **8:48 – 9:03**
SIX-DIMENSIONAL MODEL ANALYSIS AND INTERMOLECULAR VIBRATIONAL SPECTROSCOPY OF BENZENE-METHANE vdW COMPLEX, Toru Sasaki, Masaaki Nakamura, Yasuhiro Ohshima

WF03 **9:06 – 9:21**
PUSHING THE SIZE LIMITS OF BROADBAND ROTATIONAL SPECTROSCOPY: THE SEVOFLURANE TRIMER, Cristobal Perez, Amanda Steber, Wenqin Li, Alberto Lesarri, Brooks Pate

WF04 **9:24 – 9:39**
INVESTIGATION OF THE 2-6GHz REGION OF THE MICROWAVE SPECTRUM FOR THE O_2-H_2O VAN DER WAALS COMPLEX, W. H. Rice IV, Amanda Duerden, G. S. Grubbs II

Intermission

WF05 **10:19 – 10:34**
CHARACTERISATION OF THE MOLECULAR GEOMETRY OF 2-ETHYLFURAN$\cdots H_2O$ BY MICROWAVE SPECTROSCOPY, Charlotte Cummings, Nick Walker

WF06 **10:37 – 10:52**
CHIRAL RECOGNITION OF NEUTRAL ALANINE: A LASER ABLATION ROTATIONAL STUDY, Raúl Aguado, Santiago Mata, Elena R. Alonso, Iker León, José L. Alonso

WF07 **10:55 – 11:10**
ROTATIONAL SPECTROSCOPY OF THE PYRIMIDINE-CO_2 COMPLEX, Blair Welsh, Angie Zhang, Kendrew Au, Timothy S. Zwier

WF08 **11:13 – 11:28**
FIRST MONOSACCHARIDE-WATER COMPLEX CAUGHT BY MICROWAVE SPECTROSCOPY, Elena R. Alonso, Aran Insausti, Iker León, Emilio J. Cocinero

WF09 **11:31 – 11:46**
MICROWAVE SPECTROSCOPY OF FLUOROSULFONIC ACID (FSO_2OH) AND ITS MONO- AND DIHYDRATES, Aaron J Reynolds, Karla V. Salazar, Wei Lin, Kenneth R. Leopold

WF10 **11:49 – 12:04**
EXPLORING THE HYPERFINE STRUCTURE OF MOLECULAR HYDROGEN INTERACTING WITH SMALL AROMATIC SYSTEMS THROUGH ROTATIONAL SPECTROSCOPY, Robin Dohmen, Beate Kempken, Pablo Pinacho, Melanie Schnell, Daniel A. Obenchain

WG. Dynamics and kinetics

Wednesday, June 21, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Krupa Ramasesha, Sandia National Laboratories, Livermore, CA, USA

WG01 **1:45 – 2:00**
NUCLEAR SPIN CONVERSION OF CH_3D IN SOLID PARAHYDROGEN, Anh H. M. Nguyen, Ibrahim Muddasser, David T. Anderson

WG02 **2:03 – 2:18**
HYDROGEN ATOM QUANTUM DIFFUSION-LIMITED REACTION KINETICS OF $H + CO \rightarrow HCO$ IN SOLID PARAHYDROGEN: UNEXPECTED RESULTS, Ibrahim Muddasser, Anh H. M. Nguyen, Erin McDonald, David T. Anderson

WG03 **2:21 – 2:36**
PRODUCT BRANCHING RATIO MEASUREMENTS AT LOW TEMPERATURES FOR REACTIONS OF THE CN RADICALS WITH HYDROCARBONS, Myriam Drissi, Divita Gupta, Brian M Hays, Omar Abdelkader Khedaoui, Theo Guillaume, Ilsa Rose Cooke, Alberto Macario, Ian R. Sims

WG04 **2:39 – 2:54**
LOW TEMPERATURE REACTION KINETICS OF CN(v=1) WITH BUTADIENE ISOMERS., Shameemah Thawoos, Gregory Hall, Carlo Cavallotti, Arthur Suits

WG05 **2:57 – 3:12**
DETERMINATION OF FORMIC ACID YIELDS FROM THE REACTION OF THE SIMPLEST CRIEGEE INTERMEDIATE WITH FORMALDEHYDE, Pei-Ling Luo, I-Yun Chen

Intermission

WG06 **3:52 – 4:07**
INVESTIGATING THE ONSET OF NUCLEATION: LOW TEMPERATURE REACTION KINETICS OF HETERODIMER FORMATION, Alberto Macario, Myriam Drissi, Omar Abdelkader Khedaoui, Theo Guillaume, Brian M Hays, Ian R. Sims

WG07 **4:10 – 4:25**
PROBING REACTION CHANNELS OF CHLOROBENZENE-AMMONIA CLUSTERS: A TWO-COLOR STUDY. , Ronald Mutete, Damian L Kokkin, Scott Reid

WG08 **4:28 – 4:43**
ULTRAFAST MODE-SELECTIVE POPULATION CONTROL OF LARGE AMPLITUDE VIBRATION IN DIPHENYLMETHANE, Makoto Nikaido, Yasuhiro Ohshima

WG09 **4:46 – 5:01**
INTERROGATING STRONG INTRAMOLECULAR H-BONDS AND PROTON TRANSFER DYNAMICS WITH ULTRAFAST INFRARED SPECTROSCOPIES, Valerie S. Winkler, Jessika L.S. Dean, Joseph Fournier

WG10 **5:04 – 5:19**
SIMULATING VIBRATIONAL ENERGY TRANSFER THAT PROMOTES EXCITED STATE PROTON TRANSFER IN PYRANINE, Justin J Talbot, James Shee, Martin Head-Gordon, Claudius Hoberg, Martina Havenith

WG11 **5:22 – 5:37**
EXCITATION ENERGY TRANSFER AND PHOTOREGULATORY MECHANISMS IN INTACT PHYCOBILISOMES USING TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY , Sourav Sil, Ryan W. Tilluck, Nila Mohan T.M., Chase H. Leslie, Justin B. Rose, Cheryl A. Kerfeld, Warren F. Beck

WH. Mini-symposium: Spectroscopy at Large-scale Facilities

Wednesday, June 21, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Sylvestre Twagirayezu, Lamar University, Beaumont, TX, USA

WH01 **1:45 – 2:00**
EXPLORING THE FORMATION OF SILICON DERIVATIVES OF AROMATIC AND POLYCYCLIC AROMATIC HYDROCARBONS IN THE ELECTRICAL DISCHARGE OF PHENYL SILANE, Gayatri Batra, Donatella Loru, Alexander Karel Lemmens, Piero Ferrari, Britta Redlich, Melanie Schnell

WH02 **2:03 – 2:18**
EXPLORING THE FORMATION OF SILICON-CONTAINING PAH-LIKE MOLECULES IN THE ELECTRICAL DISCHARGE OF PHENYLSILANE AND NAPHTHALENE, Donatella Loru, Gayatri Batra, Alexander Karel Lemmens, Piero Ferrari, Britta Redlich, Melanie Schnell

WH03 **2:21 – 2:36**
PYRROLE + OH AS A MODEL SYSTEM: MECHANISM DETERMINATION WITH SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY AND COMPUTATIONAL CHEMISTRY, Sommer L. Johansen, Kendrew Au, Judit Zador, Leonid Sheps

WH04 **2:39 – 2:54**
DIRECT OBSERVATION OF ETHYL RADICAL IN THE PYROLYSIS OF ETHANE, Nadav Genossar-Dan, Sharona Atlas, Dana Bresker, Shani Har Lavan, Uri Zamir, Illya Rozenberg, Thanh Lam Nguyen, Patrick Hemberger, Joshua H. Baraban

Intermission

WH05 ***INVITED TALK*** **3:34 – 4:04**
A MULTI-SPECTROSCOPIC APPROACH TO REVEAL THE ASTROCHEMISTRY OF POLYCYLIC AROMATIC HYDROCARBONS, Melanie Schnell

WH06 **4:10 – 4:25**
NON-COVALENT DYNAMICS WITH A FEMTOSECOND LASER MOLECULAR BEAM MASS SPECTROMETER, Alexander Karel Lemmens, Nureshan Dias, Musahid Ahmed

WH07 **4:28 – 4:43**
DECIPHERING THE DYNAMICS AND VECTOR CORRELATIONS OF VACUUM ULTRAVIOLET (VUV) PHOTODISSOCIATION OF CO_2 AT 155 NM , Evangelia Sakkoula, Gautam Sharma, Xingan Wang, Simon North, David H. Parker, Wei Wei

WH08 **4:46 – 5:01**
3D MOMENT IMAGING WITH A USB3 OSCILLOSCOPE, Yasashri Ranganath Ranathunga, Temitayo A. Olowolafe, Suk Kyoung Lee, Wen Li

WH09 **5:04 – 5:19**
TIME-RESOLVED NUCLEAR FORWARD SCATTERING: BRINGING PUMP-PROBE SPECTROSCOPY INTO THE GAMMA-RAY REGIME, Dugan Hayes, Cali Antolini, Michael Y. Hu, Gilles Doumy, Anne Marie March, Benjamin T. Young

WH10 **5:22 – 5:37**
DEVELOPMENT OF A SOLID TARGET DELIVERY SYSTEM FOR APPLICATION IN X-RAY EXPERIMENTS, Noah Welke, Ryan T Ash, Alex Halavanau, Claudio Pellegrini, Uwe Bergmann

WI. Atmospheric science

Wednesday, June 21, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Laura R. McCunn, Marshall University, Huntington, WV, USA

WI01 **1:45 – 2:00**
IN SITU AND REMOTE SENSING OF SULFATE AEROSOLS, Dylan English, Peter F. Bernath, Chris Boone, Daniel Murphy

WI02 **2:03 – 2:18**
SATELLITE CHARACTERIZATION OF GLOBAL STRATOSPHERIC SULFATE AEROSOLS RELEASED BY TONGA VOLCANO, Peter F. Bernath, Chris Boone, Adam Pastorek, William D Cameron, Mike Lecours

WI03 **2:21 – 2:36**
VALIDATING LINE-OF-SIGHT WINDS CALCULATED FROM ACE-FTS SOLAR OCCULTATION MEASUREMENTS, Ryan Johnson, Chris Boone, Peter F. Bernath

WI04 **2:39 – 2:54**
X-MASS: A TOOL FOR SIMULTANEOUS CALCULATIONS OF CROSS-SECTIONS COVERING A LARGE PARAMETER SPACE FOR ATMOSPHERIC APPLICATIONS, Vladimir Yu Makhnev, Iouli E Gordon, Robert J. Hargreaves, Laurence S. Rothman

WI05 **2:57 – 3:12**
CO_2 MEASUREMENTS WITH DUAL-COMB SPECTROSCOPY AT MAUNA LOA OBSERVATORY, Nathan A Malarich, Kevin C Cossel, Fabrizio R. Giorgetta, Esther Baumann, Griffin J. Mead, Daniel I. Herman, Brian R Washburn, Nathan R. Newbury, Ian Coddington

Intermission

WI06 **3:52 – 4:07**
HIGH-RESOLUTION JET-COOLED INFRARED SPECTRUM OF THE ν_{26} BAND OF ISOPRENE, Jacob Stewart, Lauren Hino, Carter Pavlonnis, Katarina Reyna, Binh Nguyet Vo

WI07 **4:10 – 4:25**
JET-COOLED AND LONG PATH CELL HIGH RESOLUTION INFRARED SPECTROSCOPY OF FURFURAL CONFORMERS FROM FOURIER TRANSFORM AND QCL MEASUREMENTS, Pierre Asselin, Sathapana Chawananon, Manuel Goubet, Robert Georges, Arnaud Cuisset

WI08 **4:28 – 4:43**
THE CRIEGEE INTERMEDIATE-ACETIC ACID REACTION EXPLORED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY, Yi-Ting Liu, Yasuki Endo

WI09 **4:46 – 5:01**
COLLISION-INDUCED EFFECTS IN THE FINE-STRUCTURE RESOLVED SPECTRA OF ATMOSPHERIC OXYGEN FROM FIRST PRINCIPLES: THE EFFECT OF O_2-N_2 SCATTERING, Maciej Gancewski, Hubert Jóźwiak, Ernesto Quintas Sánchez, Richard Dawes, Piotr Wcislo

WI10 **5:04 – 5:19**
COLLISIONAL EFFECTS IN THE SPECTRA OF HYDROGEN HALIDES: TOWARDS RELIABLE *AB INITIO* MODELING OF THE TERRESTRIAL-ATMOSPHERIC MOLECULAR SPECTRA, Artur Olejnik, Maciej Gancewski, Hubert Jóźwiak, Ernesto Quintas Sánchez, Richard Dawes, Piotr Wcislo

WI11 **5:22 – 5:37**
ON THE NIR–VIS SPECTROSCOPY OF NO_2: POTENTIAL ENERGY CURVES OF THE X^2A_1, A^2B_2, B^2B_1, and C^2A_2 STATES AND THE $\widetilde{A}^2B_2$–$\widetilde{X}^2A_1$ CONICAL INTERSECTION, Gabriel J. Vázquez, Carolina Godoy Alcantar, José M. Amero, Hans-Peter Liebermann, Vassili N. Serov, OSMAN Atabek

WJ. Theory and Computation

Wednesday, June 21, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

Chair: Daniel P. Tabor, Texas A&M University, College Station, TX, USA

WJ01 **1:45 – 2:00**
SURFACE CROSSING AND ENERGY FLOW IN MANY-DIMENSIONAL QUANTUM SYSTEMS, Chenghao Zhang, Martin Gruebele, David E Logan, Peter Guy Wolynes

WJ02 **2:03 – 2:18**
A FULLY AB INITIO APPROACH TO THE EVALUATION OF VIBRATIONAL SPECTRA USING GAUSSIAN BASIS SETS, Mark A. Boyer, Edwin Sibert

WJ03 **2:21 – 2:36**
SUBPERCENT AND SUBPROMILLE INTENSITY CALCULATIONS OF ROVIBRATIONAL LINES OF MULTIPLE BANDS, Oleg L. Polyansky

WJ04 **2:39 – 2:54**
STEALING IDEAS FROM ELECTRONIC STRUCTURE THEORY TO IMPROVE VIBRATIONAL CALCULATIONS. PART I - THE HAMILTONIAN, James H. Thorpe

WJ05 **2:57 – 3:12**
STEALING IDEAS FROM ELECTRONIC STRUCTURE THEORY TO IMPROVE VIBRATIONAL CALCULATIONS. PART II - THE WAVEFUNCTION, James H. Thorpe

Intermission

WJ06 **3:52 – 4:07**
RELIABILITY AND RESONANCES IN VIBRATIONAL PERTURBATION THEORY, Julien Bloino, Marco Fusè, Qin Yang

WJ07 **4:10 – 4:25**
HIGHLY ACCURATE THERMOCHEMICAL PROPERTIES OF THE VINOXY RADICAL , Megan R Bentley, James H. Thorpe, Peter R. Franke, Bryan Changala, Branko Ruscic, John F. Stanton

WJ08 **4:28 – 4:43**
ACTINIDE M-EDGE X-RAY SPECTROSCOPY USING SPINOR-BASED COUPLED-CLUSTER TECHNIQUES, Xuechen Zheng, Chaoqun Zhang, Lan Cheng

WJ09 **4:46 – 5:01**
ARTIFICIAL INTELLIGENCE FOR AB INITIO ENERGIES: THE “AI ENERGIES” DATABASE, Nike Dattani

WJ10 **5:04 – 5:19**
SUPER-CORRELATION CONSISTENT COMPOSITE APPROACH (S-CCCA) FOR LATER 3D AND 4D TRANSITION METAL MOLECULES, Bradley Welch, Angela K. Wilson

WK. Structure determination

Wednesday, June 21, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: Martin A. Suhm, Georg-August-Universität Göttingen, Göttingen, Germany

WK01 **1:45 – 2:00**
INFLUENCE OF FOURTH-ORDER VIBRATIONAL CORRECTIONS ON SEMI-EXPERIMENTAL STRUCTURES ($r_e{}^{SE}$) OF LINEAR MOLECULES, Peter R. Franke, John F. Stanton

WK02 **2:03 – 2:18**
EQUILIBRIUM MOLECULAR STRUCTURES : HOW GOOD ARE COMPOSITE SCHEMES? , Nitai Prasad Sahoo, Peter R. Franke, John F. Stanton

WK03 **2:21 – 2:36**
MICROWAVE SPECTRUM AND STRUCTURE OF THIOBENZOIC ACID (C_6H_5COSH), Aaron J Reynolds, Kenneth R. Leopold

WK04 **2:39 – 2:54**
ROTATIONAL SPECTROSCOPIC STUDIES OF *PARA*-NITROBENZOIC ACID, *PARA*-AMINOBENZOIC ACID, *PARA*-CHLOROBENZOIC ACID, AND *PARA*-HYDROXYBENZOIC ACID , Mohamad H. Al-Jabiri, Arsh Singh Hazrah, Aran Insausti, Wolfgang Jäger

WK05 **2:57 – 3:12**
COMPARISON OF AN IMPROVED SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE ($r_e{}^{SE}$) OF KETENE TO A HIGH-LEVEL THEORETICAL EQUILIBRIUM STRUCTURE, Houston H. Smith, Brian J. Esselman, Samuel A. Wood, John F. Stanton, R. Claude Woods, Robert J. McMahon

WK06 **3:15 – 3:30**
THE PRECISE EQUILIBRIUM STRUCTURE DETERMINATION OF CHLOROBENZENE (C_6H_5Cl) BY MICROWAVE AND MILLIMETER-WAVE ROTATIONAL SPECTROSCOPY, Natalie A. Schuler, Nitai Prasad Sahoo, Maria Zdanovskaia, P. Matisha Dorman, Bryan Changala, Michael C McCarthy, John F. Stanton, Brian J. Esselman, R. Claude Woods, Robert J. McMahon

Intermission

WK07 **4:10 – 4:25**
SIZE-SELECTED SPECTRA OF WATER CLUSTERS USING ISOTOPE DILUTION, Cristobal Perez, Channing West, Brooks Pate

WK08 **4:28 – 4:43**
THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE GAS-PHASE HETERODIMERS, (*E*)-1,2,3,3,3-PENTAFLUOROPROPENE-ARGON AND (*E*)-1,2,3,3,3-PENTAFLUOROPROPENE-ACETYLENE, Kazuki M. Tayama, Helen O. Leung, Mark D. Marshall

WK09 **4:46 – 5:01**
THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE GAS-PHASE HETERODIMERS, (*Z*)-1,2,3,3,3-PENTAFLUOROPROPENE-ARGON AND (*Z*)-1,2,3,3,3-PENTAFLUOROPROPENE-ACETYLENE, Helen O. Leung, Mark D. Marshall, Max Hauschildt, Elizabeth A. Rose

WK10 **5:04 – 5:19**
DETERMINATION OF THE ABSOLUTE CONFIGURATION AND ENANTIOMERIC EXCESS OF MOLECULES THAT ARE CHIRAL BY VIRTUE OF DEUTERIUM SUBSTITUTION USING MOLECULAR ROTATIONAL SPECTROSCOPY, Zoua Pa Vang, Mitchell D Mills, Joseph R Clark, Justin L. Neill, Reilly E. Sonstrom, Kevin J Mayer, Channing West, Martin S. Holdren, Haley N. Scolati, Brooks Pate

WK11 **5:22 – 5:37**
CHARACTERIZING THE GAS-PHASE HETERODIMERS OF THE CHIRAL TAGGING CANDIDATES *TRANS*-1,3,3,3-TETRAFLUORO-1,2-EPOXYPROPANE AND 3,3,3-TRIFLUORO-1,2-EPOXYPROPANE BY QUANTUM CHEMISTRY AND MICROWAVE SPECTROSCOPY, Helen O. Leung, Mark D. Marshall, Jordan M. Aucoin

WL. Mini-symposium: Infrared Spectroscopy in the JWST Era

Wednesday, June 21, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: Sergio Ioppolo, Aarhus University, Aarhus, Denmark

WL01 ***INVITED TALK*** **1:45 – 2:15**
AN OBSERVATIONAL AND THEORETICAL VIEWPOINT ON PAHS IN THE JWST ERA, Ameek Sidhu

WL02 **2:21 – 2:36**
ANHARMONICITY AND DEUTERATION IN THE IR ABSORPTION AND EMISSION SPECTRA OF PHENYLACETYLENE, Vincent J. Esposito

WL03 **2:39 – 2:54**
NON-LTE SPECTRUM OF JET-COOLED NAPHTHALENE, Shubhadip Chakraborty, Giacomo Mulas, Olivier Pirali, Manuel Goubet, Pascale Soulard, Pierre Asselin, Samir Kassi, Ludovic Biennier, Robert Georges

WL04 **2:57 – 3:12**
NEAR-INFRARED SPECTROSCOPY OF DISSOCIATED NAPHTHALENE IN A RADIOFREQUENCY PLASMA, Julien Lecomte, Nicolas Suas-David, Christine Charles, Rod W Boswell, Eszter DUDÁS, Samir Kassi, Lucile Rutkowski, Robert Georges

WL05 **3:15 – 3:30**
INFRARED SPECTROSCOPY OF PYRENE FROM 14 TO 723K, Shubhadip Chakraborty, Giacomo Mulas, Mathias Rapacioli, Karine Demyk, Christine Joblin

Intermission

WL06 **4:10 – 4:25**
IR SPECTROSCOPY OF METALLO-FULLERENES: POTENTIAL ASTRONOMICAL PRESENCE?, Joost M. Bakker, Olga Lushchikova, Peter Lievens, Ewald Janssens, Leen Decin, Gao-Lei Hou

WL07 **4:28 – 4:43**
ON THE C-H STRETCHING MODE OF PROTONATED FULLERENES: AN IRMPD SPECTROSCOPY STUDY, Laura Finazzi, Julianna Palotás, Jonathan K Martens, Giel Berden, Jos Oomens

WL08 **4:46 – 5:01**
FORMATION OF THE ACENAPHTYLENE CATION AS A COMMON C_2H_2-LOSS FRAGMENT IN DISSOCIATIVE IONIZATION OF THE PAH ISOMERS ANTHRACENE AND PHENANTHRENE, Shreyak Banhatti, Stephan Schlemmer, Aude Simon, Heloise Leboucher, Christine Joblin, Gabi Wenzel, Daniel Rap, Britta Redlich, Sandra Brünken

WL09 **5:04 – 5:19**
EXTRATERRESTRIAL ISOMER OF PHENANTHRENE DICATION STUDIED BY TAGGING PHOTODISSOCIATION ION SPECTROSCOPY AND DFT CALCULATIONS, Aleksandr Y. Pereverzev, Corentin Rossi, Jana Roithová

WL10 **5:22 – 5:37**
INFRARED SPECTROSCOPY OF THE CATIONIC –H FRAGMENTS OF METHYL-PAHS, Gabi Wenzel, Aude Simon, Shreyak Banhatti, Pavol Jusko, Stephan Schlemmer, Sandra Brünken, Christine Joblin

RA. Plenary

Thursday, June 22, 2023 – 8:30 AM

Room: Foellinger Auditorium

Chair: Leslie Looney, University of Illinois at Urbana-Champaign, Urbana, IL, USA

RA01 **8:30 – 9:10**
A SELF-DRIVING LAB FOR THE ACCELERATED DISCOVERY OF ORGANIC SOLID-STATE LASERS, Alán Aspuru-Guzik

RA02 **9:15 – 9:55**
SPECTROSCOPY OF METAL AND PHOSPHORUS BEARING MOLECULES: A WINDOW ON THE UNIVERSE, Lucy M. Ziurys

Intermission

HOUGEN AWARD **10:30**
Presentation of Award by Isabelle Kleiner, CNRS, UPEC et Universite de Paris, Creteil, France

2023 Jon T. Hougen Memorial Award Winners
Nadav Genossar-Dann Ben-Gurion University of the Negev
Miguel Sanz-Novo, Universidad de Valladolid

SNYDER AWARDS **10:35**
Presentation of Award by Anthony Remijan, NRAO

2022 Snyder Award Winners
Olivia Chitarra, Université Paris-Saclay
Taarna Studemund, Technical University of Berlin

RAO AWARDS **10:40**
Presentation of Awards by Jennifer van Wijngaarden, York University

2022 Rao Award Winners
Madison Foreman, JILA
Thomas Salomon, University of Cologne
Yue-Rou Zhang, Brown University

MILLER PRIZE **10:50**
Introduction by Michael Heaven, Emory University

RA03 ***Miller Prize Lecture*** **10:55 – 11:10**
MODELLING MOLECULES WITH IONS AND LASERS: ANALOG QUANTUM SIMULATION OF TIME-DOMAIN SPECTROSCOPY AND BEYOND, Ryan J MacDonell

COBLENTZ AWARD **11:15**
Presentation of Award by Zac Schultz, Coblentz Society

RA04 ***Coblentz Society Award Lecture*** **11:20 – 12:00**
MEASURING ELECTRIC FIELDS AND INTERFACIAL SOLVATION AT ELECTROCHEMICAL INTERFACES USING SUM FREQUENCY GENERATION VIBRATIONAL SPECTROSCOPY, Robert Baker

RG. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Thursday, June 22, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Katharina A. E. Meyer, University of Wisconsin–Madison, Madison, WI, USA

RG01 ***INVITED TALK*** **1:45 – 2:15**
SPECTROSCOPIC PROBING OF LOW-TEMPERATURE ION-MOLECULE REACTIONS, Daniel Rap, Johanna G.M. Schrauwen, Aravindh Nivas Marimuthu, Britta Redlich, Sandra Brünken

RG02 **2:21 – 2:36**
N2 ACTIVATION ON SIZE SELECTED TRANSITION METAL CLUSTER IONS UNDER CRYO CONDITIONS, Maximilian Luczak

RG03 **2:39 – 2:54**
UNRAVELING THE VIBRATIONAL SPECTRAL SIGNATURES OF A DISLOCATED H ATOM IN MODEL PROTON COUPLED ELECTRON TRANSFER DYAD SYSTEMS, Liangyi Chen, Edwin Sibert, Joseph Fournier

RG04 **2:57 – 3:12**
THE INFLUENCE OF RARE-GAS TAGGING ON THE RENNER-TELLER PERTURBED $HCCH^+$ ION PROBED BY CRYOGENIC ACTION SPECTROSCOPY, Kim Steenbakkers, Tom van Boxtel, Britta Redlich, Gerrit Groenenboom, Philipp C Schmid, Oskar Asvany, Stephan Schlemmer, Sandra Brünken

Intermission

RG05 **3:52 – 4:07**
CIVP SPECTROSCOPY OF COBINAMIDES IN THE GAS PHASE: CLUES TO THE DESIGN OF VITAMIN B12, Alexandra Tsybizova, Vladimir Gorbachev, Peter Chen

RG06 **4:10 – 4:25**
VIBRATIONAL AND ROTATIONAL ACTION SPECTROSCOPY OF $H_2C_3H^+$, Weslley G. D. P. Silva, Divita Gupta, José Luis Doménech, Eline Plaar, Stephan Schlemmer, Oskar Asvany

RG07 **4:28 – 4:43**
LEAK-OUT SPECTROSCOPY OF THE C-C STRETCHING MODES OF C_3H^+, $NCCO^+$ AND HC_3O^+, Marcel Bast, Julian Böing, Thomas Salomon, Oskar Asvany, Igor Savic, Sandra Brünken, Mathias Schäfer, Sven Thorwirth, Stephan Schlemmer

RG08 **4:46 – 5:01**
CRYOGENIC ION SPECTROSCOPY OF VALINE AND CHEMICAL ANALOGS, Lane M. Terry, Deacon J Nemchick, J. Mathias Weber

RG09 **5:04 – 5:19**
INFRARED ACTION SPECTROSCOPY OF INDENYL AND FLUORENYL ANIONS, Miguel Jiménez-Redondo, Pavol Jusko, Gabi Wenzel, Daniel Rap, Paola Caselli, Sandra Brünken

RH. Photodissociation and photochemistry

Thursday, June 22, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Kelly Gaffney, Stanford University, Stanford, CA, USA

RH01 **1:45 – 2:00**
UV DYNAMICS OF CIS-STILBENE STUDIED BY ULTRAFAST ELECTRON DIFFRACTION, S. K. Saha, Pedro Nunes, Hayley Weir, Monika Williams, Andrew Attar, Bryan Moore, Duan Luo, Ming-Fu Lin, Matthias Hoffmann, Fuhao Ji, Matthew R Ware, Shashank Pathak, Thomas JA Wolf, Jie Yang, Keith Jobe, Todd Martinez, Martin Centurion

RH02 **2:03 – 2:18**
SIGNATURES OF PHOTODISSOCIATION MECHANISM OF *SYMMETRIC*-TIRAZINE ENCODED IN THE VIBRATIONAL POPULATION DISTRIBUTION OF HCN PHOTOFRAGMENTS USING 266 NM, Piyush Mishra, Alexander W Hull, Stephen L Coy, Robert W Field

RH03 **2:21 – 2:36**
PHOTODISSOCIATION OF DIBORANE ISOLATED IN SOLID PARAHYDROGEN: EVIDENCE OF SLOW DIFFUSION-CONTROLLED RECOMBINATION, Aaron I. Strom, Anh H. M. Nguyen, Ibrahim Muddasser, David T. Anderson

RH04 **2:39 – 2:54**
PHOTOISOMERIZATION OF (CYANOMETHYLENE)CYCLOPROPANE (C_5H_5N) IN A LOW TEMPERATURE RARE GAS MATRIX, Samuel A. Wood, Samuel M. Kougias, Brian J. Esselman, R. Claude Woods, Robert J. McMahon

RH05 **2:57 – 3:12**
ULTRAFAST ELECTRON DIFFRACTION OF THE PHOTODISSOCIATION OF BROMOCYCLOPROPANE, Jackson Lederer, Pedro Nunes, Conor Rankine, SLAC MeV-UED Collaboration, Martin Centurion

Intermission

RH06 **3:52 – 4:07**
IMAGING THE PHOTOELECTRON CIRCULAR DICHROISM EFFECT IN THE PHOTODETACHMENT OF MASS SELECTED CHIRAL ANIONS, Jenny Triptow, Andre Fielicke, Gerard Meijer, Mallory Green

RH07 **4:10 – 4:25**
THE INFLUENCE OF METHANOL IN WATER ICE ON THE DISTRIBUTION OF VOLATILE CARBON-CONTAINING PHOTOPRODUCTS, Catherine E Walker, Gustavo A. Cruz-Diaz, Will E. Thompson, Collette C Sarver, Katarina Yocum, Olivia H. Wilkins, Perry A. Gerakines, Stefanie N Milam, Susanna L. Widicus Weaver

RH08 **4:28 – 4:43**
SUBLIME RESULTS: THE EFFECTS OF UV PHOTOLYSIS ON METHANOL WATER ICES AND THE PRODUCTION OF COMPLEX ORGANIC MOLECULES, Collette C Sarver, Gustavo A. Cruz-Diaz, Will E. Thompson, Catherine E Walker, Katarina Yocum, Olivia H. Wilkins, Perry A. Gerakines, Stefanie N Milam, Susanna L. Widicus Weaver

RH09 **4:46 – 5:01**
$Si_3O_2{}^+$ - OPTICAL ABSORPTION AND PHOTODISSOCIATION PROPERTIES , Taarna Studemund, Kai Pollow, Marko Förstel, Otto Dopfer

RH10 **5:04 – 5:19**
EXPLORING THE MECHANISM OF THE ELECTRONIC QUENCHING OF NO ($A^2\Sigma^+$) WITH CO_2 , Aerial Bridgers, Andrew S. Petit

RH11 **5:22 – 5:37**
PHOTOCATALYTIC DEGRADATION OF INDUSTRIAL WASTEWATER AND ANTIBACTERIAL ACTIVITY, Emmanuel Rosas, Mahesh B. Dawadi

RI. Astronomy

Thursday, June 22, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: R. A. Motiyenko, Université de Lille, Villeneuve d'Ascq, France

RI01 **1:45 – 2:00**
CONNECTING PREBIOTIC CHEMISTRY IN THE LABORATORY TO PROTOSTELLAR OBSERVATIONS, Will E. Thompson, Morgan M. Giese, Gustavo A. Cruz-Diaz, Catherine E Walker, Collette C Sarver, Katarina Yocum, Olivia H. Wilkins, D. C. Lis, Perry A. Gerakines, Stefanie N Milam, Susanna L. Widicus Weaver

RI02 **2:03 – 2:18**
CHEMICAL INVENTORIES OF MOLECULAR CLOUDS REVEALED BY HERSCHEL HIFI SPECTRAL LINE SURVEYS, Catherine E Walker, Luyao Zou, Shiya Wang, D. C. Lis, Susanna L. Widicus Weaver

RI03 **2:21 – 2:36**
NEW METAL DICARBIDES IN THE LABORATORY AND IN SPACE, Bryan Changala, Harshal Gupta, Michael C McCarthy

RI04 **2:39 – 2:54**
THE EXCITATION, ABUNDANCE, AND DISTRIBUTION OF MgC_2 AND CaC_2 IN IRC+10216, Harshal Gupta, Bryan Changala, Michael C McCarthy, Jose Cernicharo, Juan R. Pardo, Marcelino Agúndez, Carlos Cabezas, Belén Tercero, Michel Guélin

Intermission

RI05 **3:34 – 3:49**
LABORATORY DETECTION AND ASTRONOMICAL SEARCH FOR AN UNCHARTED GLYCINE ISOMER, Miguel Sanz-Novo, José L. Alonso, Iker León, Santiago Mata, Victor Manuel Rivilla, Izaskun Jiménez-Serra, Jesús Martín-Pintado, Brett A. McGuire

RI06 **3:52 – 4:07**
INVESTIGATING THE PRECURSORS OF ETHANOLAMINE, THE SIMPLEST PHOSPHOLIPID IN THE CELLULAR MEMBRANES DISCOVERED IN THE ISM, Davide Alberton, Valerio Lattanzi, Christian Endres, Natalia Inostroza, Ryan C. Fortenberry, Paola Caselli

RI07 **4:10 – 4:25**
UNLOCKING THE POTENTIAL OF THE MOST DEFINITIVE MOLECULAR TRACER OF UV-ENHANCEMENT: l-C_3H^+ , Andy Lipnicky, Ryan A Loomis, Crystal L. Brogan, Brett A. McGuire

RI08 **4:28 – 4:43**
CARBON CLUSTER CATIONS AND THE "BUMP" OF THE INTERSTELLAR UV EXTINCTION CURVE, Jason E. Colley, Dylan S. Orr, Michael A Duncan

RI09 **4:46 – 5:01**
ASTRONOMICAL DETECTION OF THE INTERSTELLAR ANION $C_{10}H^-$ TOWARDS TMC-1 FROM THE GOTHAM LARGE PROGRAM ON THE GBT, Anthony Remijan

RI10 **5:04 – 5:19**
A NEW MULTIBAND RECEIVER FOR THE 12 M TELESCOPE AT THE ARIZONA RADIO OBSERVATORY (ARO) , Lucy M. Ziurys, Eugene F. Lauria, George P. Reiland, Arthur W. Lichtenberger, Anthony R. Kerr

RJ. Conformers and isomers

Thursday, June 22, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

Chair: Maria Luisa S Senent, IEM-CSIC, Madrid, Spain

RJ01 **1:45 – 2:00**
CONFORMATIONAL COOLING AND ISOMERIZATION OF METHYL NITRITE ISOLATED IN LOW-TEMPERATURE MATRICES, Emily K Hockey, Korina Vlahos, Laura M McCaslin, Leah G Dodson

RJ02 **2:03 – 2:18**
ISOMERIZATION AMONG THE ISOMERS OF 2-HEXENAL and 3-HEXENAL BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY, Nobuhiko Kuze, Ryoto Ozawa, Yoshiyuki Kawashima

RJ03 **2:21 – 2:36**
BROADBAND ROTATIONAL SPECTROSCOPIC DETECTION OF BUFFER GAS COOLED MOLECULES DESORBED FROM AN ICE: ISOMER AND CONFORMER-SPECIFIC BRANCHING RATIOS OF N- AND I-PROPANOL, Quentin D Borengasser, Travis Hager, Anudha Kanaherarachchi, Bernadette M. Broderick

RJ04 **2:39 – 2:54**
DETERMINATION OF ISOMER AND CONFORMER-SPECIFIC BRANCHING RATIOS OF BUFFER GAS COOLED MOLECULES DESORBED FROM AN ICE SURFACE WITH BROADBAND MM-WAVE ROTATIONAL SPECTROSCOPY, Anudha Kanaherarachchi, Travis Hager, Quentin D Borengasser, Bernadette M. Broderick

RJ05 **2:57 – 3:12**
REVEALING INTRINSIC PROPERTIES OF SMALL BIOMOLECULES BY IONIZATION-LOSS STIMULATED RAMAN SPECTROSCOPY , Rami Rahimi, Noga Saban, Ilana Bar

RJ06 **3:15 – 3:30**
EXPLORING THE CONFORMATIONAL LANDSCAPE OF BIOACTIVE MOLECULES BY CHIRPED PULSE MICROWAVE SPECTROSCOPY AND LASER VAPORIZATION , Otger Crehuet i Viladelbosch, Pablo Pinacho, Emilio J. Cocinero, Maider Parra-Santamaria

Intermission

RJ07 **4:10 – 4:25**
A BROADBAND ROTATIONAL SPECTROSCOPIC STUDY OF TETRAHYDRO-2H-PYRAN-2-OL, Aran Insausti, Jiarui Ma, Arsh Singh Hazrah, Wolfgang Jäger, Yunjie Xu

RJ08 **4:28 – 4:43**
MICROHYDRATION ON MULTICONFORMATIONAL LARGE MOLECULES: INTRA- AND INTERMOLECULAR INTERACTIONS OF MACROLACTONES WITH WATER, Maider Parra-Santamaria, Pablo Pinacho, Emilio J. Cocinero, Camilla Calabrese, Himanshi Singh, Melanie Schnell

RJ09 **4:46 – 5:01**
INTERMOLECULAR INTERACTIONS OF TOLUNITRILES ($CH_3C_6H_4CN$), Celina Bermúdez, Elias M. Neeman, Wenqin Li, Alberto Lesarri

RJ10 **5:04 – 5:19**
URONIC ACIDS IN GAS PHASE, Aran Insausti, Elena R. Alonso, Ander Camiruaga, Pierre Çarçabal, Emilio J. Cocinero

RJ11 **5:22 – 5:37**
COMPARATIVE AB-INITIO STUDIES OF HELICAL STRUCTURE OF PERFLUOROOCTANOIC ACID (PFOA) AND PERFLUOROOCTANE (PFO), Heena S. Karani, Sylvestre Twagirayezu

RK. Vibrational structure/frequencies

Thursday, June 22, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: Jacob Stewart, Connecticut College, New London, CT, USA

RK01 **1:45 – 2:00**
ANALYSIS OF COMBINED MILLIMETER-WAVE AND FOURIER TRANSFORM INFRARED SPECTRA OF DN_3: EXTENSION OF THE ANALYSIS TO EIGHT NEW VIBRATIONAL STATES, R. Claude Woods, Brent K. Amberger, Brant E. Billinghurst, Brian J. Esselman, Patrik Kania, Zbigniew Kisiel, Robert J. McMahon, Vanessa L. Orr, Andrew N. Owen, Houston H. Smith, Stepan Urban, Karel Vávra, Samuel A. Wood

RK02 **2:03 – 2:18**
LEVERAGING DOUBLE-RESONANCE SPECTROSCOPY TO UNDERSTAND TRANS-GLYCIALDEHYDE AND 17 OF ITS VIBRATIONALLY EXCITED STATES, Luis Bonah, Sven Thorwirth, Holger S. P. Müller, J.-C. Guillemin, Stephan Schlemmer

RK03 **2:21 – 2:36**
CAVITY RING DOWN MEASUREMENTS ON PROPYLENE OXIDE IN THE 3μm REGION , Fabian Peterß, Karel Vávra, Thomas Giesen, Guido W. Fuchs

RK04 **2:39 – 2:54**
INFRARED PHOTODISSOCIATION SPECTROSCOPY OF COBALT CATION ACETYLENE COMPLEXES, Anna G Batchelor, Ian Webster, Timothy B Ward, Michael A Duncan

RK05 **2:57 – 3:12**
MEASUREMENT OF PERFLUORO-N-HEXANE AND PERFLUORO-2-METHYLPENTANE ABSORPTION CROSS-SECTIONS FROM 298 TO 350 K, Muhammad Osama Ishtiak, Orfeo Colebatch, Karine Le Bris, Paul Godin, Kimberly Strong

RK06 **3:15 – 3:30**
INSIGHTS INTO HYDROGEN BONDING FROM VIBRATIONAL SPECTRA, Rachel M. Huchmala, Anne B. McCoy

Intermission

RK07 **4:10 – 4:25**
INVESTIGATING THE NUCLEAR QUANTUM EFFECT ON $H^+(H_2O)_6$, Jacob M. Finney, Rachel M. Huchmala, Anne B. McCoy

RK08 **4:28 – 4:43**
DIFFUSION MONTE CARLO STUDY OF VIBRATIONAL EXCITED STATES OF PROTONATED ETHYLENE ($H^+(C_2H_4)$), Pattarapon Moonkaen, Jacob M. Finney, Anne B. McCoy

RK09 **4:46 – 5:01**
THE TUNNELLING SPLITTINGS OF THE SOME STATIONARY VIBRATIONAL STATES OF THE HYDRONIUM ANION AND RADICAL DUE TO INVERSION MOTION, Uladzimir Sapeshka, Alex Malevich, Aryna Khrapunova, George Pitsevich

RK10 **5:04 – 5:19**
TUNNELING SPLITTINGS OF THE GROUND AND EXITED TORSIOMAL STATES OF THE TRISULFANE MOLECULE., Uladzimir Sapeshka, George Pitsevich, Alex Malevich

RK11 **5:22 – 5:37**
IMPORTANCE OF THE VIBRONIC EFFECTS IN CHIROPTICAL SPECTRA, Qin Yang, Julien Bloino, Petr Bour

RL. Mini-symposium: Infrared Spectroscopy in the JWST Era

Thursday, June 22, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: David E. Woon, University of Illinois at Urbana-Champaign, Urbana, IL, USA

RL01 ***INVITED TALK*** **1:45 – 2:15**
THE FIRST YEAR OF ASTROCHEMISTRY WITH THE JAMES WEBB SPACE TELESCOPE , Klaus Pontoppidan

RL02 **2:21 – 2:36**
HITRAN AND HITEMP DATABASES IN THE ERA OF JWST (JUST WHEN SPECTROSCOPY THRIVES), Iouli E Gordon, Robert J. Hargreaves, Vladimir Yu Makhnev, Laurence S. Rothman

RL03 **2:39 – 2:54**
THE IMPENDING OPACITY CHALLENGE IN EXOPLANET ATMOSPHERIC CHARACTERIZATION, Prajwal Niraula, Julien de Wit, Iouli E Gordon, Robert J. Hargreaves, Clara Sousa-Silva, Roman Kochanov

RL04 **2:57 – 3:12**
PROVIDING THE PRESSURE AND TEMPERATURE BROADENING PARAMETERS OF N_2O FOR OBSERVATION OF EXOPLANET ATMOSPHERES. , Hayley A. Bunn, Silvia Spezzano, Paola Caselli

RL05 **3:15 – 3:30**
ACCURATE IR INTENSITY PREDICTION FOR N_2O ANALYSIS AS A POTENTIAL BIOSIGNATURE MOLECULE IN PLANETARY AND EXOPLANETARY ATMOSPHERES: UNCERTAINTY AND UPGRADES, Xinchuan Huang, David Schwenke

RL06 **3:33 – 3:48**
PSEUDOLINE GENERATION FOR TRANS-2-BUTENE IN THE 7-15 μM REGION IN SUPPORT OF TITAN ATMOSPHERE STUDY, Brendan Steffens, Keeyoon Sung, Michael Malaska, Rosaly M Lopes, Geoffrey C. Toon, Conor A Nixon

Intermission

RL07 **4:28 – 4:43**
SPECTROSCOPY OF HYDROCARBONS RELEVANT TO THE ATMOSPHERES OF HOT JUPITER EXOPLANETS IN THE 1.6-1.7 μm RANGE: UNAMBIGUOUS ASSIGNMENT OF ETHYLENE TRANSITIONS, Solène Perot, Michael Rey, Vladimir Tyuterev, Nicolas Suas-David, Julien Lecomte, Samir Kassi, Lucile Rutkowski, Robert Georges

RL08 **4:46 – 5:01**
INSIGHTS INTO THE INFRARED SPECTRUM OF A PREBIOTIC SPECIES: THE CASE OF AMINOACETONITRILE, Mattia Melosso, Silvia Alessandrini, Luca Bizzocchi, Cristina Puzzarini, Marie-Aline Martin-Drumel, Olivier Pirali

RL09 **5:04 – 5:19**
ANALYSIS OF EXPERIMENTAL SPECTRA OF PHOSPHINE IN THE TETRADECAD NEAR 2.2 μM USING *AB INITIO CALCULATIONS, Andrei V. Nikitin, Alain Campargue, Michael Rey, Keeyoon Sung, Vladimir Tyuterev*

RL10 **5:22 – 5:37**
MID-INFRARED DOPPLER-FREE SATURATION ABSORPTION SPECTROSCOPY OF THE Q BRANCH OF CH_4 ν_3=1 BAND USING A RAPID-SCANNING CONTINUOUS-WAVE OPTICAL PARAMETRIC OSCILLATOR, S M Shah Riyadh, Hamzeh Telfah, Ian Jones, Jonathan Swift Bersson, David B. Foote, Cunfeng Cheng, Shui-Ming Hu, Jinjun Liu

RL11 **5:40 – 5:55**
EMPIRICAL ENERGY LEVELS OF METHANE UP TO POLYAD 6, Kyriaki Kefala, Vincent Boudon, Sergei N. Yurchenko, Jonathan Tennyson

FA. Non-covalent interactions

Friday, June 23, 2023 – 8:30 AM

Room: 116 Roger Adams Lab

Chair: Elias M. Neeman, University of Lille , Villeneuve d'Ascq, France

FA01 **8:30 – 8:45**
THE MICROWAVE SPECTRA AND ROTAMER-DEPENDENT STRUCTURES OF THE GAS-PHASE HETERODIMERS FORMED BETWEEN 2,3,3-TRIFLUOROPROPENE AND ACETYLENE, Helen O. Leung, Mark D. Marshall

FA02 **8:48 – 9:03**
WEAKLY-BOUND COMPLEXES OF γ-BUTYROLACTONE AND WATER: A MATRIX ISOLATION FTIR AND COMPUTATIONAL ANALYSIS., Annabelle N Carney, Josh Newby

FA03 **9:06 – 9:21**
WATER BINDING TO KETONES: CYCLOOCTANONE$\cdots(H_2O)_{3-7}$ COMPLEXES, Valerie W. Y. Tsoi, Ecaterina Burevschi, M. Eugenia Sanz

FA04 **9:24 – 9:39**
A ROTATIONAL STUDY OF THE INTERACTIONS OF WATER WITH THE MONOTERPENOID CARVONE, S. Indira Murugachandran, M. Eugenia Sanz

Intermission

FA05 **10:19 – 10:34**
AB INITIO INVESTIGATIONS ON HYDROGEN BOND INTERACTIONS OF 1:1 THEOBROMINE-WATER COMPLEXES, Tanvi, G.S.S. Saini, Anamika Mukhopadhyay

FA06 **10:37 – 10:52**
SMALL NON-COVALENT DIMERS WITH COMPETING HYDROGEN BONDED & HALOGEN BONDED MOTIFS, Gregory S. Tschumper

FA07 **10:55 – 11:10**
DYNAMICS OF $(HCN)_n$ DEPOSITION IN MATRIX-ISOLATION EXPERIMENTS, Thomas Howard, Emily K Hockey, Shannon E Ganley, Leah G Dodson

FA08 **11:13 – 11:28**
PROBING THE CONFORMATIONAL SPACE OF COPPER(I)-BOX COMPLEXES USING IRMPD SPECTROSCOPY , Alexandra Tsybizova, Vladimir Gorbachev, Peter Chen

FA09 **11:31 – 11:46**
CONTROLLING INTRAMOLECULAR H-BOND IN ONIUM IONS BY TUNING LONDON DISPERSION - PAULI REPULSION BALANCE , Vladimir Gorbachev, Alexandra Tsybizova, Peter Chen

FB. Theory and Computation

Friday, June 23, 2023 – 8:30 AM

Room: 100 Noyes Laboratory

Chair: Mark A. Boyer, University of Wisconsin, Madison, WI, USA

FB01 **8:30 – 8:45**
PUSHING THE BOUNDARIES OF SPECTROSCOPIC SIMULATIONS WITH REAL TIME PROPAGATION, Johann Mattiat, Sandra Luber

FB02 **8:48 – 9:03**
SPIN-VIBRONIC CALCULATIONS FOR JAHN-TELLER ACTIVE MOLECULES IN QUASI-DIABATIC BASIS WITH SOCJT3, Ketan Sharma, Oleg A. Vasilyev, Terry A. Miller, John F. Stanton

FB03 **9:06 – 9:21**
TRANSFORMATION OF QUANTUM MECHANICAL OPERATOR MATRIX FROM CARTESIAN TO CYLINDRICAL NORMAL COORDINATES IN QUASI-DIABATIC BASIS, Oleg A. Vasilyev, Ketan Sharma, Terry A. Miller, John F. Stanton

FB04 **9:24 – 9:39**
CALCULATED AND EMPIRICAL VALUES OF VIBRONIC TRANSITION DIPOLE MOMENTS OF REACTIVE CHEMICAL INTERMEDIATES FOR DETERMINATION OF CONCENTRATIONS, Ian Jones, Jonathan Swift Bersson, Jinjun Liu, Ketan Sharma, Oleg A. Vasilyev, Terry A. Miller, John F. Stanton

FB05 **9:42 – 9:57**
LEARNING MOLECULAR HAMILTONIANS DIRECTLY FROM SPECTRA, Daniel P. Tabor

Intermission

FB06 **10:37 – 10:52**
OPTICAL PROPERTIES FOR ALL SYNTHESIZABLE MOLECULES FROM QUANTUM CHEMISTRY-BASED MACHINE LEARNING, Chenxi Sun, Yili Shen, Chengwei Ju, Zhou Lin

FB07 **10:55 – 11:10**
THEORETICAL MODELLING OF LIGHT-MATTER INTERACTIONS AT THE NANOSCALE, Diptesh Dey, George C. Schatz

FB08 **11:13 – 11:28**
CHEMFLUOR-VAE: REVERSE DESIGN OF ORGANIC FLUOROPHORES BASED ON EXPERIMENTAL OPTICAL PROPERTIES AND VARIATIONAL AUTOENCODER, Chengwei Ju, Yongrui Luo, Bo Li, yuzhi xu, Hanzhi Bai, Ruiming Lin, Zehan Mi, Haozhe Zhang

FB09 **11:31 – 11:46**
MOLECULAR DOCKING AND DYNAMICS SIMULATIONS OF AMMI VISNAGA L. CONSTITUENTS AS ANTI-MELANOGENIC AGENTS, Berna Catikkas, Nurcan Karacan

FC. Astronomy

Friday, June 23, 2023 – 8:30 AM

Room: 1024 Chemistry Annex

Chair: Bryan Changala, Ctr for Astrophysics/Harvard & Smithsonian, Cambridge, MA, USA

FC01 **8:30 – 8:45**
THE LOW LYING SINGLET STATES OF ZIRCONIUM OXIDE., Manish Bhusal, Peter F. Bernath, Jason J Sorensen, Jacques Liévin

FC02 **8:48 – 9:03**
ELECTRONIC SPECTRA OF *PERI*-HEXABENZOCORONENE AND OVALENE ISOLATED IN SOLID *PARA*-HYDROGEN, Isabelle Weber, Johanna Langner, Henryk A. Witek, Yuan-Pern Lee

FC03 **9:06 – 9:21**
THE SUBMILLIMETER WAVE SPECTRUM OF METHYL HYPOCHLORITE UP TO 500 GHz, Brian M Hays, L. Margulès, R. A. Motiyenko, J.-C. Guillemin

FC04 **9:24 – 9:39**
THE ROTATION-TUNNELING SPECTRUM OF 3-HYDROXYPROPENAL, HOCHCHCHO, Holger S. P. Müller, R. A. Motiyenko, L. Margulès, J.-C. Guillemin, A. Coutens, Jes Jorgensen

FC05 **9:42 – 9:57**
ROTATIONAL SPECTRA AND INTERSTELLAR SEARCH OF MALEONITRILE (CNCHCHCN), Celina Bermúdez, Carlos Cabezas, Jose Cernicharo, J.-C. Guillemin

FC06 **10:00 – 10:15**
QUANTIFICATION OF METHANOL PHOTOLYSIS BRANCHING RATIOS USING MULTIPLEXED PHOTOIONIZATION MASS SPECTROMETRY, Emily K Hockey, Thomas Howard, Julianna Palotás, David L. Osborn, Leah G Dodson

Intermission

FC07 **10:55 – 11:10**
SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF INTERSTELLAR CANDIDATE ALKYNYL THIOCYANATE: HCCSCN., Elena R. Alonso, Aran Insausti, Lucie Kolesniková, Iker León, J.-C. Guillemin

FC08 **11:13 – 11:28**
COMMENTS ON THE IMPACT OF WING CUT-OFF ON COMPUTING ABSORPTION CROSS SECTIONS: BEST PRACTICE WITH APPLICATION TO MAESTRO OPACITY DATABASE, Ehsan Gharib-Nezhad, Natasha E Batalha, Katy Chubb, Richard S Freedman, Iouli E Gordon, Robert R. Gamache, Robert J. Hargreaves, Nikole K Lewis, Jonathan Tennyson, Sergei N. Yurchenko

FC09 **11:31 – 11:46**
OBSERVATION OF VIBRATIONALLY EXCITED STATES OF SiC_2 BY STIMULATED EMISSION PUMPING (SEP) SPECTROSCOPY, Sederra D. Ross, Kelvin Lee, Jonathan Flores, Michael C McCarthy, Neil J. Reilly

FD. Instrument/Technique Demonstration

Friday, June 23, 2023 – 8:30 AM

Room: 217 Noyes Laboratory

Chair: Charles R. Markus, California Institute of Technology, Pasadena, CA, USA

FD01 **8:30 – 8:45**
FOURTH GENERATION BUFFER GAS CELL FOR MICROWAVE SPECTROSCOPY, Lincoln Satterthwaite, Greta Koumarianou, Daniel Sorensen, David Patterson

FD02 **8:48 – 9:03**
CRESU-REMPI- A TOOL TO CHARACTERIZE EXTENDED QUASI-UNIFORM FLOW, Shameemah Thawoos, Nicolas Suas-David, Matthew L Edlin, Arthur Suits

FD03 **9:06 – 9:21**
DEVELOPMENT OF A NEW CAVITY RINGDOWN SPECTROSCOPY SYSTEM FOR ASTROCHEMICAL STUDIES , Shannon E Ganley, Thomas Howard, Leah G Dodson

FD04 **9:24 – 9:39**
CONSTRUCTION OF A CRYO-COOLED BUFFER GAS CELL FOR PERFORMING BROADBAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTROSCOPY, Blair Welsh, Angie Zhang, Kendrew Au, Timothy S. Zwier

FD05 **9:42 – 9:57**
IMPACT PRESSURE MEASUREMENTS OF MODIFIED LAVAL NOZZLE GEOMETRIES, Adam Culick, S E Worthington-Kirsch, Kyle N. Crabtree

FD06 **10:00 – 10:15**
THE DEVELOPMENT OF A NEW L-SHAPED FTMW SPECTROMETER WITH CAVITY AND CHIRPED PULSE SETUPS FOR SPECTROSCOPIC AND REACTION DYNAMICS/KINETICS INVESTIGATIONS , Rusiru PH Rajapaksha, Vas Zhukova, Jared Michael Starnes, Mitchell W Swann, Ranil Gurusinghe

Intermission

FD07 **10:55 – 11:10**
ASSESSING THE PERFORMANCE OF A 6-18GHz BROADBAND MICROWAVE SPECTROMETER, Ezra Bacon-Gershman, Laura Wu, Sivanjali Elena Williams, Ethan T York, Caroline Sorrells, Drew Price, A. O. Hernandez-Castillo

FD08 **11:13 – 11:28**
HIGH RESOLUTION SPECTROSCOPY OF EXPLOSIVE TAGGANTS USING INTRACAVITY MILLIMETER-WAVE SPECTROMETER, Mhamad Chrayteh, Fabien Simon, Francis Hindle, Gaël Mouret, Anthony Roucou, Alexandre Deguine, Manuel Goubet, Arnaud Cuisset

FD09 **11:31 – 11:46**
FINALLY – A CONVENTIONAL CONFOCAL FABRY-PÉROT AT SUB-THz FREQUENCIES, Liam Duffy

FD10 ***Post-Deadline Abstract*** **11:49 – 12:04**
KINETICS OF HO_2 RADICAL IN NS PULSE O_2-He PLASMAS OVER A LIQUID WATER SURFACE AND UNDER ATMOSPHERIC PLASMA JET USING CAVITY RING DOWN SPECTROSCOPY, Hamzeh Telfah, Sai Raskar, Elijah R Jans, Igor V. Adamovich

FE. Photodissociation and photochemistry

Friday, June 23, 2023 – 8:30 AM

Room: B102 Chemical and Life Sciences

Chair: Wei Wei, Franklin College, Franklin, IN, USA

FE01 **8:30 – 8:45**
INTERROGATING INTERFACIAL EFFECTS IN QUANTUM DOT SENSITIZED ZNO WITH DUAL PROBE TRANSIENT ABSORPTION SPECTROSCOPY , Conner Dykstra, Michael J Enright, Thomas Rossi, Josh Vura-Weis, Renske van der Veen

FE02 **8:48 – 9:03**
OBSERVATION OF ELECTRONIC AND STRUCTURAL INTERACTION BETWEEN SMALL POLARONS AND HOST MATERIALS USING FEMTOSECOND XUV REFLECTION SPECTROSCOPY, Hanzhe Liu, Scott Kevin Cushing

FE03 **9:06 – 9:21**
FORMAMIDE 193 NM PHOTODISSOCIATION DYNAMICS INVESTIGATED WITH TIME-RESOLVED CHIRPED-PULSE MILLIMETER-WAVE SPECTROSCOPY AND AB INITIO THEORY, Kacee L. Caster, Nathan A. Seifert, Ahren W Jasper, Kirill Prozument

FE04 **9:24 – 9:39**
PHOTODISSOCIATION SPECTROSCOPY AND PHOTOFRAGMENT IMAGING OF THE Fe^+(acetylene) AND $Fe^+(benzene)_{1,2}$ COMPLEXES TO PROBE DISSOCIATION ENERGIES, John R. C. Blais, Jason E. Colley, Nathan John Dynak, Michael A Duncan

Intermission

FE05 **10:19 – 10:34**
INVESTIGATION OF ULTRAFAST ELECTRON AND PROTON TRANSFER PROCESSES IN COPPER-ANTHRAQUINONE DONOR-ACCEPTOR MOLECULES, Tyler N Haddock, Wade C Henke, Karen Mulfort, Lin X Chen

FE06 **10:37 – 10:52**
EXCITED STATE DEACTIVATION VIA SOLVENT TO CHROMOPHORE PROTON TRANSFER IN ISOLATED 1:1 MOLECULAR COMPLEX: EXPERIMENTAL VALIDATION BY MEASURING THE ENERGY BARRIER AND KINETIC ISOTOPE EFFECT, Ramesh Jarupula, Saurabh Khodia, Md Shabeeb, Baweja Simran, Bhavika Kalal, Surajit Maity

FE07 **10:55 – 11:10**
REMPI AND IMAGING STUDIES OF SINGLET O_2 FOLLOWING SPIN-FORBIDDEN PHOTODISSOCIATION OF OZONE, Megan Aardema, Megan Fast, Benjamen Meas, Simon North

FE08 **11:13 – 11:28**
UNRAVELING THE MECHANISM OF THE ELECTRONIC QUENCHING OF NO ($A^2\Sigma^+$) WITH C_2H_2 , Ken Jones, Andrew S. Petit

FE09 **11:31 – 11:46**
A FIVE-CARBON UNSATURATED CRIEGEE INTERMEDIATE: SYNTHESIS, SPECTROSCOPIC IDENTIFICATION, AND THEORETICAL STUDY OF 3-PENTEN-2-ONE OXIDE, Tarun Kumar Roy, Tianlin Liu, Christopher Sojdak, Marisa Kozlowski, Marsha Lester

FF. Mini-symposium: Infrared Spectroscopy in the JWST Era

Friday, June 23, 2023 – 8:30 AM

Room: 274 Medical Sciences Building

Chair: Xinchuan Huang, NASA Ames Research Center, Moffett Field, CA, USA

FF01 ***Journal of Molecular Spectroscopy Review Lecture*** **8:30 – 9:00**
THE JWST ICEAGE: UNRAVELLING SOLID STATE CHEMISTRY THROUGH EPOCHS OF STAR AND PLANET FORMATION, Helen Fraser

FF02 **9:06 – 9:21**
IR SPECTRA OF PHOSPHINE ICES., José Luis Doménech, Victor Jose Herrero, Isabel Tanarro, Vicente Timón, Belén Maté

FF03 **9:24 – 9:39**
FAR-IR SPECTROSCOPY AS DIRECT PROBE OF INTERMOLECULAR DYNAMICS IN PAH-WATER COMPLEXES, Alexander Karel Lemmens, Piero Ferrari, Bruno Martinez-Haya, Donatella Loru, Gayatri Batra, Amanda Steber, Melanie Schnell, Britta Redlich

FF04 **9:42 – 9:57**
VIBRATIONAL SPECTROSCOPY AND REACTIVITY OF ULTRA-SMALL SILICA and SILICATE FRAGMENTS IN THE GAS-PHASE, Sandra Lang

Intermission

FF05 **10:37 – 10:52**
SOLID INDENE PURE AND IN WATER ICE: INFRARED SPECTRA AND DESTRUCTION CROSS SECTIONS, Belén Maté, Victor Jose Herrero, Vicente Timón, Jose Cernicharo, Isabel Tanarro

FF06 **10:55 – 11:10**
LABORATORY ICE ASTROCHEMISTRY IN THE ERA OF JWST, Sergio Ioppolo

FF07 **11:13 – 11:28**
QUANTUM CHEMICAL MODELING OF ASTROCHEMICAL REACTIONS OF C ATOM AND C^+ CATION WITH NH_3 BOUND TO AMORPHOUS WATER ICE, David E. Woon

FF08 **11:31 – 11:46**
QUANTUM TUNNELING IN INTERSTELLAR ICE BY AMMONIA (NH_3) AND ACETALDEHYDE (CH_3CHO): CHELATION AGENTS TO ASSIST RNA REPLICATION, Joshua H Marks, Jia Wang, Andrew Martin Turner, N. Fabian Kleimeier, Mikhail M. Evseev, Oleg V. Kuznetsov, Mason McAnally, Ivan Antonov, Alexander M Mebel, Ralf Ingo Kaiser

FF09 **11:49 – 12:04**
REACTIVITY OF KETENE UNDER INTERSTELLAR CONDITIONS: FROM THE DILUTE PHASE TO THE CONDENSED PHASE, Lahouari Krim, Mohamad Ibrahim, J.-C. Guillemin

MA. Plenary

Monday, June 19, 2023 – 8:30 AM

Room: Foellinger Auditorium

Chair: Jennifer van Wijngaarden, York University, Toronto, ON, Canada

Welcome **8:30**
Susan Martinis, Vice Chancellor for Research and Innovation
University of Illinois

MA01 **8:45 – 9:25**

WATCHING CHEMICAL REACTIONS HAPPEN ONE MOLECULE AT A TIME

HEATHER LEWANDOWSKI, *JILA and Department of Physics, University of Colorado, Boulder, CO, USA*.

Control over the quantum states of atoms and molecules can lead to a fundamentally new understanding of how these particles interact and react. This knowledge has the potential to impact our ability to probe processes in planetary atmospheres and in the interstellar medium.

Experimental techniques developed for control and measurement of atoms are now being used to study more and more complex molecules. We study these rich systems at low temperatures, where we can trap and examine their properties for many minutes, as compared to small fractions of a second in standard experiments. Using these cold, trapped molecular ions, we investigate mechanisms of ion-molecule reactions to gain insights into the mechanisms driving these processes.

MA02 **9:30 – 10:10**

HIGH RESOLUTION PHOTOELECTRON SPECTROSCOPY OF VIBRATIONALLY EXCITED ANIONS

DANIEL NEUMARK, *Department of Chemistry, The University of California, Berkeley, CA, USA*.

The method of slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) is a variant of anion photoelectron spectroscopy with a resolution as high as 1-2 cm^{-1}. It has proved invaluable in obtaining well-resolved photoelectron spectra of molecular anions, bare and complexed metal oxide clusters, and anionic precursors to transition states for bimolecular and unimolecular reactions. However, cryo-SEVI is subject to the same selection rules that govern photoelectron spectroscopy, and thus yields frequencies for only a small set of vibrational modes of the neutral species created by photodetachment. We have recently incorporated a tunable infrared laser into our experiment with the goal of vibrationally pre-exciting the anions prior to photodetachment. Results on diatomic and polyatomic anions will be presented that illustrate the capabilities and complexities of this new type of spectrscopy, IR cryo-SEVI.

Intermission

MA03 **10:45 – 11:25**

VIBRATIONAL SPECTROSCOPY AT THE SERVICE OF QUANTUM CHEMISTRY

MARTIN A. SUHM, *Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany*.

Vibrational spectroscopists profit enormously from the advances in quantum chemistry codes for spectral assignment and interpretation. This is certainly true for the study of weakly bound complexes, often generated in supersonic jet expansions with limited equilibration. It is time to pay back for this valuable support by generating dedicated new experimental data which can help theory to assess the quality of their approximate methods. This is complementary and in the end perhaps superior to important theory-internal benchmarking activities, which rely on a hierarchy of methods and may be limited in molecular complexity [1]. Experimental benchmarking only works if every effort has been made to secure the results. It comes in two variants, which can alternate with each other, to systematically approach the right answers for the right reasons. Blind challenges hide the experimental result and invite theory groups to predict it [2], followed by full disclosure and a discussion of the theory performance. Databases provide carefully curated compilations of spectroscopic observables [3], to save the interested theoreticians from tedious searches and misinterpretation. The talk will address a few examples from the Göttingen research training group BENCh [4], to convey the general idea. Close competition between conformational energies or for spectral properties are particularly valuable, because they invite binary decisions [5]. If you got a nice spectroscopy experiment running in your lab, choose and publish your systems and observable quantities in a way which is useful and challenging for the benchmarking of computational methods! If your experiment is reasonably unique but still well tested against others, consider to organize a blind challenge! If you are a theoretician, try to put your models to the (blind) test by experiment, although it seems so much easier to compare them to a reference theory!

[1] R. A. Mata, M. A. Suhm: Angew. Chem. Int. Ed. 56 (2017) 11011–11018 [2] T. L. Fischer, M. Bödecker, A. Zehnacker-Rentien, R. A. Mata, M. A. Suhm: Phys. Chem. Chem. Phys. 24 (2022) 11442–11454 [3] Challenges for Numerical Quantum Chemistry: https://qmbench.net/ [4] Benchmark Experiments for Numerical Quantum Chemistry: https://uni-goettingen.de/en/587836.html [5] R. Medel, J. R. Springborn, D. L. Crittenden, M. A. Suhm: Molecules 27 (2022) 101

MA04 **11:30 – 12:10**

FOUR EXPERIMENTAL SYSTEMS THAT TEST DISPERSION INTERACTIONS IN LARGE MOLECULES

R. POLLICE, M. BOT, VLADIMIR GORBACHEV, ALEXANDRA TSYBIZOVA, L. FRITSCHE, LARISA MILOGLYADOVA, RAPHAEL OESCHGER, PETER CHEN, *Laboratorium für Organische Chemie, ETH Zürich, Zürich, Switzerland*.

Non-covalent interactions have been proposed to play a large role in organic and organometallic chemistry, with the magnitude of the interactions increasing rapidly with the number of atoms. Detailed experimental tests of the proposition in the gas phase focus on small molecules, for a variety of technical reasons. For small molecules, though, the magnitude of the interactions is small, which introduces its own suite of technical constraints. We report four different experimental systems, examined with a range of gas-phase, physical techniques ranging from energy-resolved collision-induced dissociation cross-sections to ion spectroscopy by cryogenic ion vibrational predissociation spectroscopy or IRMPD, of electrosprayed molecular ions, in which the non-covalent interactions become large enough that the experiments can provide hard benchmarks against which theory can be tested. We find that the present generation of dispersion-corrected DFT methods appear to overestimate the attractive component of the interaction, at least for certain interaction geometries.

MG. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Monday, June 19, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Daniel Neumark, The University of California, Berkeley, CA, USA

MG01 ***INVITED TALK*** **1:45 – 2:15**

PROBING DIPOLE-BOUND STATES USING HIGH-RESOLUTION RESONANT PHOTOELECTRON IMAGING OF CRYOGENICALLY-COOLED ANIONS

LAI-SHENG WANG, *Department of Chemistry, Brown University, Providence, RI, USA*.

Negative ions do not possess Rydberg states, but polar anions may have diffuse dipole-bound states just below the detachment threshold, analogous to Rydberg states of neutral molecules. Excitation to vibrational levels of the dipole-bound state can induce autodetachment via vibronic coupling. The resulting resonant photoelectron spectrum is highly non-Franck-Condon and yields much richer vibrational information than conventional photoelectron spectroscopy. We developed an experimental apparatus integrating an electrospray ionization source with photoelectron spectroscopy [1], which allowed negative ions from solution samples to be studied in the gas phase. Subsequent development of a cryogenically-cooled Paul trap to create cold anions from electrospray [2] has allowed high-resolution photoelectron imaging to be conducted for complex molecular anions [3], opening opportunities to probe dipole-bound excited states using photodetachment spectroscopy and resonant photoelectron imaging [4]. I will present recent advances in our investigation of dipole-bound excited states, including the observation of pi-type dipole-bound states [5], electron correlation induced by the electric field of the diffuse dipole-bound electron [6], the observation of polarization-assisted dipole-bound states.

References: [1] L. S. Wang, C. F. Ding, X. B. Wang, and S. E. Barlow, Rev. Sci. Instrum. 70, 1957-1966 (1999). [2] X. B. Wang and L. S. Wang, Rev. Sci. Instrum. 79, 073108 (2008). [3] L. S. Wang, J. Chem. Phys. 143, 040901 (2015). [4] G. Z. Zhu and L. S. Wang, Chem. Sci. 10, 9409-9423 (2019). [5] D. F. Yuan, Y. Liu, C. H. Qian, Y. R. Zhang, B. M. Rubenstein, and L. S. Wang, Phys. Rev. Lett. 125, 073003 (2020). [6] D. F. Yuan, Y. Liu, C. H. Qian, G. S. Kocheril, Y. R. Zhang, B. M. Rubenstein, and L. S. Wang, J. Phys. Chem. Lett. 11, 7914-7919 (2020).

MG02 **2:21 – 2:36**

VINYLIDENE-ACETYLENE ISOMERIZATION PROBED WITH HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY OF COLD ANIONS UPON SELECTIVE VIBRATIONAL EXCITATION

MARTIN DeWITT, *Chemistry, University of California, Berkeley, Berkeley, CA, USA*; JASCHA LAU, *Department of Chemistry, University of California, Berkeley, Berkeley, CA, USA*; DANIEL NEUMARK, *Department of Chemistry, The University of California, Berkeley, CA, USA*.

Vinylidene (H_2CC) has been shown to have a complex vibronic structure, with strong coupling between the ground and excited electronic states as well as vibrational wavefunction mixing between vinylidene and its isomeric counterpart, acetylene (HCCH). Our group has previously used slow photoelectron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) to probe such dynamics. However, the vibrational states of neutral vinylidene that exhibit the strongest coupling between electronic states are nominally inaccessible from the vibrational ground state of the anion, making them difficult or even impossible to observe with the cryo-SEVI technique. Here, we use the recently developed technique of infrared-pump, cryo-SEVI-probe (IR-cryo-SEVI) to further uncover vinylidene's complexities by vibrationally exciting the anion along the antisymmetric CH2 stretch (ν_5) and CH2 in-plane rocking (ν_6) modes prior to photodetachment. Vibrational pre-excitation along these antisymmetric modes gives access to vibrational states in the neutral that are otherwise inaccessible to cryo-SEVI. Additionally, IR-cryo-SEVI is used as an action technique, able to measure the infrared absorption spectrum of the bare anion without perturbations from tagged atoms or matrices, giving the true vibrational frequencies of these modes.

MG03 **2:39 – 2:54**

EXPLORING THE ELECTRONICALLY EXCITED STATES OF MELEM: AN ALL-ORGANIC HYDROGEN-EVOLVING PHOTOCATALYST

KENNETH WILSON, ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

Herein we present the investigation of the electronic structure of melem, the carbon nitride (CN) monomer, by means of photoelectron spectroscopy of the corresponding melem radical anion. Melem belongs to a class of molecules called aza-phenalenes, many of which are computationally predicted and experimentally shown to violate Hund's rule: namely, their S_1 singlet excited state lies energetically below their T_1 triplet excited state. This inversion could play an important role in the significant photocatalytic activity of CN towards the production of hydrogen from water. Despite widespread computational evidence of S_1-T_1 inversion, quantification of the S_1-T_1 splitting using absorption-based spectroscopic techniques is precluded by the spin selection rule. Photoelectron spectroscopy is an ideal technique for quantifying excited state term energies because it is not beholden to this spin selection rule. Following electron photodetachment from the melem radical anion, we have used slow electron velocity-map imaging (SEVI) to identify a spectral region at 20,000 - 24,000 cm^{-1}above the melem radical anion ground state that is expected to contain three electronically excited states of neutral melem. The presence of optically allowed anion resonances in the same spectral region complicates the analysis of the photoelectron spectra. Assignment of the spectra is also hindered by the poor agreement between the Franck-Condon simulations and experimental results. Early interpretations suggest possible spectral distortion from vibronic coupling, or unexpected deviations from the planar geometry of the S_0 state in the S_1 and T_1 excited states.

MG04 **2:57 – 3:12**

THRESHOLD PHOTODETACHMENT SPECTROSCOPY OF C_2^- IN A 16-POLE WIRE TRAP

SRUTHI PURUSHU MELATH, CHRISTINE LOCHMANN, MARKUS NÖTZOLD, ROBERT WILD, ROLAND WESTER, *Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria*.

Photodetachment spectroscopy is a powerful spectroscopic technique for determining the internal state distribution of a molecular anion. Previously, our group studied the threshold photodetachment spectroscopy of CN^- at both 16 Kelvin and 295 Kelvin in a 22-pole ion trap and measured the electron affinity of CN with great precision (EA: 3.864(2) eV)[1]. The dicarbon anion, our current molecule of interest, is a well-studied system due to its stable electronic level structure and potential laser cooling transition[2].

Here we present the threshold photodetachment spectroscopy study of C_2^- in a radiofrequency 16-pole ion trap at 8 Kelvin. We investigated the behaviour of the cross section near the threshold for the ground state transition, $C_2X^1\Sigma_g^+ \leftarrow C_2^-X^2\Sigma_g^+$. We see a *p*-wave behavior for this ground state detachment. And we measured the electron affinity, which is consistent with the previously measured values[3][4].

[1]. M. Simpson et al., J. Chem. Phys. 153, 184309 (2020).
[2]. M. Nötzold et al., Phys. Rev. A 106, 023111 (2022).
[3]. K. M. Ervin, et al., J. Phys. Chem. 95, 2244 (1991).
[4]. B. A. Laws et al., Nat. Commun. 10, 1(2019).

Intermission

MG05 **3:52 – 4:07**

RESOLVING ISOMERS OF COPPER TRIOXIDE ANION VIA TEMPERATURE DEPENDENT PHOTOELECTRON IMAGING

G. STEPHEN KOCHERIL, *Department of Chemistry, Brown University, Providence, RI, USA*; HAN-WEN GAO, *Chemistry, Brown University, Providence, RI, USA*; LAI-SHENG WANG, *Department of Chemistry, Brown University, Providence, RI, USA*.

Although the photoelectron spectrum of copper trioxide was first reported in the late 1990's, it has remained unassigned to date. Several calculations have predicted the presence of multiple isomers, but the complexity of the system has prevented any assignment of the experimental spectrum. We have revisited the photoelectron spectrum of copper trioxide, now with high-resolution photoelectron imaging and a cryogenically-cooled ion trap. The new temperature dependent photoelectron spectra have resolved the presence of two distinct isomers, allowing for the full assignment of the photoelectron spectrum of copper trioxide for the first time.

MG06 **4:10 – 4:25**

CRYOGENIC PHOTOELECTRON SPECTROSCOPY OF MICROSOLVATED ANIONS AND HYDROGEN BONDED CLUSTERS

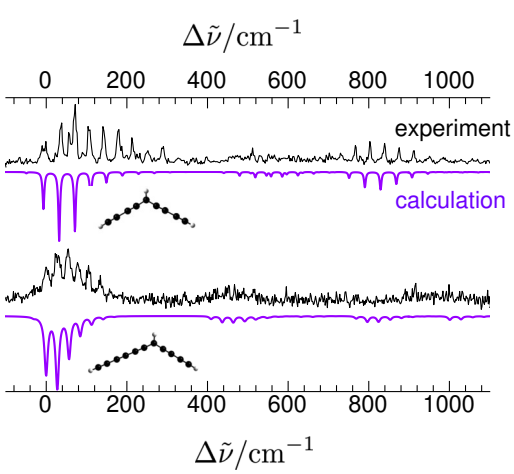
XUE-BIN WANG, *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA*.

Employing size-selective cryogenic photoelectron spectroscopy (cryo-PES) coupled with electrospray ionization (ESI), we have been studying the physical and chemical properties of a wide variety of complex molecular clusters ranging from microsolvated anions, hydrogen bonded complexes to atmospherically relevant pre-nucleation clusters. Our studies on a series of B12X122-(H2O)n (X = H, F, I) clusters established the formation of hydridic-to-protonic dihydrogen bonds (DHBs) and unraveled the predominance of DHB strength by comparing to those conventional B-X···H-O (X = F, I) HBs. The primary gas phase hydration shell of hydroxide has recently been investigated as well.

MG07 **4:28 – 4:43**

ELECTRONIC SPECTROSCOPY OF HYDROGENATED CARBON CLUSTER ISOMERS

SAMUEL MARLTON, CHANG LIU, PATRICK WATKINS, EVAN BIESKE, *School of Chemistry, The University of Melbourne, Melbourne, Victoria, Australia*.



Highly unsaturated $C_xH_y^+$ clusters are important in combustion and the chemistry of interstellar space. However, interrogating carbonaceous molecules containing more than 10 carbon atoms is complicated by the coexistence of different isomers possessing unique spectroscopic properties. To disentangle this complexity, we have developed an apparatus that allows formation and selection of a particular $C_xH_y^+$ isomer population by ion mobility and mass to charge ratio. The selected ions are then incarcerated in a cryogenically cooled ion trap and subjected to tunable radiation. Resonant excitation of an electronic transition leads to cluster fragmentation, which when monitored as a function of wavelength yields an action spectrum. We have also measured electronic spectra for a variety of $C_xH_y^+$ ions, which are formed by photoionizing and photodissociating PAHs in the ion source. The $C_xH_y^+$ clusters can be linear or cyclic, but can be selected by their ion mobility arrival time and mass to charge ratio. Pyrene photoproducts include $C_{2n+1}H_3^+$ and $C_{2n+1}H^+$ clusters. The $C_{2n+1}H_3^+$ clusters are mostly linear isomers with characteristic vibronic progressions of low frequency modes (see Figure). $C_{2n+1}H^+$ clusters are shown to exist as linear and cyclic isomers that have distinct electronic spectra. These results provide clues on how different $C_xH_y^+$ cluster isomers form, dissociate, and isomerise in interstellar space, and provide spectroscopic fingerprints to aid their astronomical detection.

MG08 **4:46 – 5:01**

CHARACTERIZING THE ABSORPTION AND PHOTODISSOCIATION OF ATMOSPHERIC NITRATE VIA ACTION SPECTROSCOPY

BRIANNA HOPPER, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

The nitrate anion is the final sink for NOx species and plays a crucial role in the chemical processes of Earth's atmosphere, hydrosphere, and cryosphere. In particular, the photodissociation of nitrate from Antarctic snow forms radical oxygen which, when reacted with ambient water, forms radical OH, arguably the most important oxidative species in the atmosphere. While it is well-known that actinic radiation (>290 nm) can be absorbed by the nitrate ion and photodissociate it, the exact mechanism is unclear. In particular, the absorption mechanism is unclear since the only singlet state in that range is a symmetry forbidden transition. Theoretical studies have shown that the absorption could be allowed via vibronic coupling or by spin-orbit coupling to the nearby triplet state. It has also been shown that the intensity of the forbidden transition is highly sensitive to the presence of water. Here, we perform photodissociation action spectroscopy over the 300 nm range to experimentally determine a gas phase NO_3^- and $NO_3^-(H_2O)$ UV absorption spectrum. Our setup also enables the investigation of the photodissociation products branching ratios as a function of wavelength. This will allow for a more comprehensive understanding of the nitrate photodissociation mechanism.

MG09 **5:04 – 5:19**

OPTICAL SPECTRA OF N-SUBSTITUTED ADAMANTANE CATIONS

PARKER B. CRANDALL, MARKO FÖRSTEL, OTTO DOPFER, *Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany*.

Diamondoids are a class of aliphatic molecules arranged in cage-like structures and serve as a link between small, cyclic hydrocarbons and bulk nanodiamonds. They are well-known for their interesting optical properties, as they typically exhibit large optical band gaps of around 6 eV or higher.[1] Their radical cations, however, are predicted to display transitions in the visible and, due to their favorable structural and optical properties, may be viable candidates as carriers of the diffuse interstellar bands.[2] So far, only the optical spectra of adamantane and diamantane cations have been measured, which exhibit broad and mostly vibronically unresolved features.[3,4] To explore the effects of functionalization, we report the first optical spectra of N-substituted adamantane cations, namely 1-cyanoadamantane ($C_{11}H_{15}N^+$) and urotropine ($(CH)_6N_4{}^+$) between 260 and 1200 nm in the gas phase. Measurements were taken in a tandem mass spectrometer by photodissociation of mass-selected ions cooled in a cryogenic 22-pole ion trap held at 5 K. The experimental results are compared to photoelectron spectra and time-dependent DFT calculations for interpretation.

Literature:
[1] L. Landt et al., PRL, 103, 047402 (2009).
[2] M. Steglich et al., ApJ, 729, 91 (2011).
[3] P. Crandall et al., ApJL, 900, L20 (2020).
[4] P. Crandall et al., ApJ, 940, 104 (2022).

MG10 **5:22 – 5:37**

EXPLORING ATMOSPHERICALLY RELEVANT CLUSTERS OF GLYCINE, AMMONIA AND SULFURIC ACID VIA INFRARED SPECTROSCOPY AND MASS SPECTROMETRY

ANNAPOORANI HARIHARAN, *Department of Chemistry, Stony Brook University, Stony Brook, NY, USA*; CONOR J. BREADY, *Department of Chemistry, Furman University, Greenville, SC, USA*; JACK G AJELLO, *Department of Chemistry, Stony Brook University, Stony Brook, NY, USA*; SAMANTHA H. BLACK, *Chemistry, Washington University in St. Louis, St. Louis, MO, USA*; GEORGE C. SHIELDS, *Department of Chemistry, Furman University, Greenville, SC, USA*; CHRISTOPHER J. JOHNSON, *Chemistry, Stony Brook University, Stony Brook, NY, USA*.

The impact of atmospheric aerosols on climate is one of the largest uncertainties in global climate models so far. New particle formation (NPF) is an all-important initial step that brings together trace gases in the atmosphere to form aerosols. Identifying the structural motifs and intermolecular interactions stabilizing newly-formed clusters is key to establishing their growth mechanisms and developing quantitative models for their growth. Sulfuric acid and bases such as ammonia have been heavily studied as prototypical new particles, but recent evidence suggests that organic vapors (such as dicarboxylic acids, amino acids, etc.) are likely to play a significant role in NPF. In this work we explore the structural motifs in cationic clusters composed of glycine, ammonia, and sulfuric acid. We find that glycine stabilizes these clusters, with collision induced dissociation (CID) mass spectra showing that ammonia is preferentially lost from these clusters. Gas phase vibrational spectra and quantum chemical calculations show that the largest of these clusters have strong hydrogen bonds between bisulfate groups, hinting at potential phase separation in pre-nucleation clusters containing both organic and inorganic compounds. Lastly, variable temperature mass spectrometry (VTMS) experiments show that the glycine-containing clusters uptake water at atmospherically relevant temperatures. Combined, these results imply that in the atmosphere, glycine will likely replace ammonia in ammonium bisulfate clusters, forming stable clusters that can potentially increase NPF efficiency.

MH. Mini-symposium: Spectroscopy at Large-scale Facilities

Monday, June 19, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Katharina Kubicek, University of Hamburg and European XFEL, Schenefeld, Germany

MH01 **1:45 – 2:00**

INVESTIGATING THE REACTIVITY OF CH_3NH WITH SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY AND COMPUTATIONAL CHEMISTRY

SOMMER L. JOHANSEN, JUDIT ZADOR, CARLES MARTI, LAURA M McCASLIN, VARUN RISHI, LEONID SHEPS, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*; ARKKE ESKOLA, *Department of Chemistry, University of Helsinki, Helsinki, Finland*.

Reactivity of nitrogen-centered radicals is known to differ significantly from that of carbon-centered radicals due in large part to the presence of the N-lone pair. This reactivity difference is particularly important for the gas-phase chemistry of amines, which are released to Earth's atmosphere through various industrial and natural processes and play a role in the combustion of biomass and mixtures of ammonia and natural gas. Methylamine (CH_3NH_2), the simplest amine, has been shown to form either a N-centered (CH_3NH) or a C-centered radical (CH_2NH_2) upon H-abstraction by OH. In environments where O_2 is present, CH_2NH_2 will react rapidly with O_2 to form methanimine (CH_2NH). CH_3NH, however, reacts very slowly with O_2, so that other reactions may become competitive. Here, we present evidence for fast, barrierless reactions of CH_3NH with both HO_2 and OH, leading to CH_3NO and CH_3NHOH, respectively, that have not been previously reported. These products were identified with multiplexed photoionization mass spectrometry experiments at 4 Torr and 298 K using VUV radiation from the Advanced Light Source at LBNL and confirmed by isotopic substitution and comparison to integrated photoelectron spectra within the literature. Potential energy surfaces were calculated with KinBot, an automated chemical kinetics workflow code, at the ωB97X-D/6-311++G(d,p) level of theory with energies refined at CCSD(T)-F12/cc-pVDZ-F12, followed by master equation calculations and the development of a chemical kinetics model. Additionally, we resolved a long-standing discrepancy within the literature regarding the potential existence of a barrier along the $CH_3NH + O_2$ entrance channel; a coordinate scan at the CASPT2 level of theory revealed no evidence of a transition state. Implications of these results to both atmospheric and combustion chemistry will be discussed, as well as potential extensions to chemistry of N-centered radicals in the interstellar medium and planetary atmospheres, such as that of Titan, where radical-neutral reactions are operative and N-containing species are known to be abundant.

MH02 **2:03 – 2:18**

PROBING QUANTUM COHERENCE IN MOLECULAR SYSTEMS

SURESH YARLAGADDA, *Department of Chemistry, Wayne State University, Detroit, MI, USA*; TEMITAYO A. OLOWOLAFE, *Chemistry, Wayne State University, Detroit, MI, USA*; SUK KYOUNG LEE, *Chemistry Department, Wayne State University, Detroit, MI, USA*; H. BERNHARD SCHLEGEL, WEN LI, *Department of Chemistry, Wayne State University, Detroit, MI, USA*.

Ultrafast spectroscopy can initiate and probe electronic dynamics in molecules within femtoseconds to attoseconds timescale. Here, we report the use of strong field ionization pump-probe technique to detect multimode vibrational motions and electronic coherence in methyl iodide cation (CH3I+). For the first time, the coherence between the spin-orbit components of methyl iodide cation ground states and all symmetric vibrational modes were captured. The periodicities of the detected quantum beats vary between 6.0 fs and 117.0 fs. A few vibrational beatings from the first excited state (A state) were also detected. Furthermore, our approach reveals the time evolution of the quantum coherence in methyl iodide cation. The electronic coherence decays in the first picosecond while vibrational quantum beats persist. Our study further showed that rotational revival does not revive electronic coherence, suggesting both vibrational and rotational dephasings play a role in the decay of electronic quantum beatings. Theoretical analysis using a quantum model reveals intimate interaction between electronic and vibrational coherence in polyatomic systems.

MH03 **2:21 – 2:36**

CONICAL INTERSECTION DYNAMICS IN CYCLOPENTADIENE[a]

LISA HUANG, LINGYU MA, NATHAN GOFF, ASAMI ODATE, STUART W CRANE, THOMAS NORTHEY, JOSEPH GEISER, *Department of Chemistry, Brown University, Providence, RI, USA*; LAUREN BERTRAM, ANDRÉS M CARRASCOSA, MATS SIMMERMACHER, *Department of Chemistry, Oxford University, Oxford, United Kingdom*; ZANE PHELPS, *J.R. Macdonald Laboratory, Kansas State University, Manhattan, KS, USA*; MICHAEL MINITTI, MENGNING LIANG, XINXIN CHENG, RUARIDH FORBES, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; MARTIN CENTURION, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; KENNETH LOPATA, *Department of Chemistry, Louisiana State University, Baton Rouge, LA, USA*; ARTEM RUDENKO, DANIEL ROLLES, *J.R. Macdonald Laboratory, Kansas State University, Manhattan, KS, USA*; ADAM KIRRANDER, *Department of Chemistry, Oxford University, Oxford, United Kingdom*; PETER M. WEBER, *Department of Chemistry, Brown University, Providence, RI, USA*.

Photochemical reactions of cyclic organic molecules are commonly used in many biological systems, solar energy resources, synthetic materials, and pharmaceuticals. Though energetically unfavored, highly strained ring structures produced from photolysis are of particular interest because their reaction mechanisms, once fully understood, could be leveraged for synthetic methods. In particular, we are interested in studying cyclopentadiene (CP), a small organic molecule whose photochemical pathway involves an electrocyclic process to form highly strained ring products upon UV excitation. We performed ultrafast time-resolved, gas-phase X-ray scattering experiments on cyclopentadiene at the CXI endstation of LCLS to explore the structural dynamics as the reaction evolves through a set of conical intersections.

[a]This work is supported by U.S Department of Energy (DE-SC0017995).

MH04 ***INVITED TALK*** **2:39 – 3:09**

ULTRAFAST DIFFRACTION AND SPECTROSCOPY STUDIES OF GAS-PHASE PHOTOCHEMISTRY

DANIEL ROLLES, *J.R. Macdonald Laboratory, Kansas State University, Manhattan, KS, USA*.

The continuing progress of ultrafast sources such as X-ray free-electron lasers, high-repetition-rate near-infrared lasers, and Mega-electronvolt ultrafast electron diffraction facilities enable studies of electronic and structural dynamics in gas-phase molecules with unprecedented spatial and temporal resolution. I will present a series of experiments utilizing a variety of different spectroscopic techniques such as time-resolved photoelectron spectroscopy and Coulomb explosion imaging to study ring-opening and other isomerization reactions of molecules such a furan, toluene, thiophenone, and quadricyclane. The results are compared to experiments performed with other ultrafast techniques such as ultrafast electron and X-ray diffraction in order to highlight strengths and limitations of each technique.[a]

[a]This work is supported by the Chemical Science, Geosciences, and Bioscience Division, Office of Basic Energy Science, Office of Science, U.S. Department of Energy, grants no. DE-FG02-86ER13491 and DE-SC0020276, and by the National Science Foundation grant no. PHYS-1753324.

MH05 **3:15 – 3:30**

PROTON TRANSFER MECHANISMS OF o-NITROPHENOL OBSERVED BY MeV ULTRAFAST ELECTRON DIFFRACTION

JOAO P.F. NUNEZ, LAUREN F HEALD, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; MONIKA WILLIAMS, *Department of Chemistry, Stanford University, Stanford, CA, USA*; JIE YANG, *ARD FEL and Beam Physics , SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; THOMAS JA WOLF, *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; CONOR RANKINE, *Department of Chemistry, University of York, York, United Kingdom*; BRYAN MOORE, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; XIAOZHE SHEN, MING-FU LIN, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; TODD MARTINEZ, *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; XIJIE WANG, *Acceleratory Directory, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; MARTIN CENTURION, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*.

Excited state intramolecular proton transfer (ESIPT) is key to many important biological mechanisms. However, direct observation of the structural dynamics of ESIPT has been limited given both the required spatial and temporal resolution. The combination of femtosecond temporal resolution and sub-Angstrom spatial resolution possible from mega-electronvolt ultrafast electron diffraction (MeV-UED) make it an ideal method for observing ESIPT. Furthermore, the neighboring -OH and -NO_2 groups on o-nitrophenol are known to undergo proton transfer upon excitation to the lowest singlet state (S_1). Using MeV-UED, the structural dynamics of proton transfer in o-nitrophenol have been resolved following excitation to the S_1 state. In contrast to the S_1 state, higher lying excited states are suspected to follow different relaxation pathways and their structural evolution could provide further insight into the dynamics of ESIPT in o-nitrophenol. This presentation will discuss previous findings of ESIPT following excitation of o-nitrophenol to the S_1 state and will present new findings related to the relaxation dynamics of the S_4 state.

Intermission

MH06 **4:10 – 4:25**

ULTRAFAST ENERGY TRANSFER AND STRUCTURAL DYNAMICS OF THE ORGANIC POLYMER ON AN MoS_2 MONOLAYER

MING-FU LIN[a], *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; ANDREW ATTAR, *Photonics, Vescent Photonics, LLC, Golden, CO, USA*; HUNG-TZU CHANG, *Ultrafast Dynamics, Max Planck Institute, Göttingen, Germany*; ARAVIND KRISHNAMOORTHY, *Mechanical Engineering, Texas A&M, College Station, TX, USA*; ALEXANDER BRITZ, *Facilitating Science, Facilitating Science, Berlin, Germany*; XIANG ZHANG, *Materials Science and Nano Engineering, Rice University, Houston, TX, USA*; XIAOZHE SHEN, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; AJAYAN PULICKEL, *Materials Science and Nano Engineering, Rice University, Houston, TX, USA*; XIJIE WANG, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; PRIYA VASHISHTA, *Viterbi School of Engineering, University of Southern California, Los Angeles, CA, USA*; UWE BERGMANN[b], *Physics, University of Wisconsin-Madison, Madison, WI, USA*.

Energy transfer across a heterogeneous interface is an important topic to understand detailed functioning mechanisms of solar cells. Here, we used mega-electronvolt ultrafast electron diffraction (MeV UED) as a sensitive time-resolved "thermometer" to simultaneously measure structural dynamics and energy transfer between a polymer (PTB7) and an atomic thin MoS_2 monolayer. Optical excitation of the polymer at 700 nm induces a short-lived temperature jump that relaxes quickly through the heterojunction interface to the monolayer MoS_2. The thermal energy transfers from the polymer to the atomic layer is described by the thermal transport model. The time-resolved structural dynamics of polymer suggests a bond dissociation located specifically at the C-O sidechain during the flattening motion of the two aromatic conjugated rings in the excited state, providing the fundamental mechanism of the photo-instability of a polymer in the applications of solar cell materials.

[a]corresponding author
[b]corresponding author

MH07 **4:28 – 4:43**

QUANTUM MOLECULAR DYNAMICS FOR X-RAY INDUCED STRUCTURAL DAMAGE

ADAM E A FOUDA, STEPHEN H SOUTHWORTH, GILLES DOUMY, LINDA YOUNG, PHAY J HO, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*.

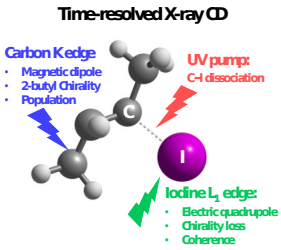
We will present a quantum dynamics theory for modelling the structural damage of molecules following the autoionization decay of molecular core-hole states generated by X-rays. Our theory will model the fundamental processes underlying the distortion of metalloprotein geometries characterized by X-ray crystallography, as well as the decay of radionucleotides used in highly targeted cancer-therapies. Both the absorption of X-rays and radionucleotide decay creates unstable core-hole states which can decay via autoionization involving the ejection of an electron and the collapse of another to the core-hole. The structural damage occurs via the Coulomb explosion of highly charged molecular cations created by the autoionization. Hence, simulations coupling the autoionization to structural dynamics will provide fundamental insight into this complex phenomenon. However, the required theoretical treatment is challenging, due to the complexity of autoionization and exponential scaling of possible decay channels with respect to the system size. Here we propose a quantum molecular dynamics method, which uses a time-dependent set of trajectory functions for modelling autoionization decay across multiple potential energy surfaces. The initial implementation of our method uses autoionization rates from atomic simulations, and our results are benchmarked against experimental x-ray/ion coincidence data of IBr molecule.

This work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

MH08 **4:46 – 5:01**

REAL-TIME MONITORING OF CHIRALITY LOSS IN MOLECULAR PHOTODISSOCIATION BY TRANSIENT X-RAY CIRCULAR DICHROISM

YEONSIG NAM[a], *Departments of Chemistry, University of California, Irvine, Irvine, CA, USA*; DAEHEUM CHO, *Department of Chemistry, Kyungpook National University, Daegu, South Korea*; SHAUL MUKAMEL[b], *Department of Chemistry, University of California, Irvine, Irvine, CA, USA*.



Newly developed X-ray sources offer valuable insight on molecular dynamics with unprecedented spatiotemporal resolutions and element sensitivity. Significant advances made in the control of the polarization of X-ray beams enables real-time monitoring of molecular chirality, which is an indispensable subject for understanding and controlling biological process. We theoretically apply time- and frequency-resolved X-ray Circular dichroism (TRXCD) spectroscopy to discern the time evolution of molecular chirality at different element windows during the photodissociation of 2-iodobutane. Following an optical excitation, the iodine atom dissociates from the chiral center, which we capture by quantum nuclear dynamics simulations. A resonant X-ray pulse then probes the iodine or carbon atom through an element-specific core-to-valence transition. The TRXCD signal at the iodine L_1-edge captures the timing of chirality loss, c.a 70 fs. The strong electric dipole–electric quadrupole (ED−EQ) response at this high X-ray regime makes this signal sensitive to vibronic coherences. At the carbon K-edges, the signals re-capture the chirality of 2-butyl radical and the spin state of the iodine atom. The stronger electric-magnetic dipole response make the signals more intuitive for the electronic population than coherence. Overall, the element-specific TRXCD signal offers a unique window into the time-dependent chirality of molecules.

Reference: Nam Y. et al., *J. Am. Chem. Soc.* 2022, 144, 20400-20410

[a]Email: yeonsign@uci.edu. Special thanks to coauthors, Bing Gu and Daniel Keefer (Department of Chemistry, University of California, Irvine, Irvine, CA, USA), Jérémy R. Rouxel (Graduate School Optics Institute, Laboratoire Hubert Curien, Saint-Etienne, France), and Niranjan Govind (Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA)

[b]Email: smukamel@uci.edu

MH09 **5:04 – 5:19**

HIGH-RESOLUTION X-RAY STIMULATED RAMAN SPECTROSCOPY USING STOCHASTIC PULSES

KAI LI, *Department of Physics, The university of chicago, Chicago, IL, USA*; GILLES DOUMY, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; CHRISTIAN OTT, THOMAS PFEIFER, ALEXANDER MAGUNIA, MARC REBHOLZ, *Quantum Dynamics and Control, Max-Planck-Inst Kernphys, Heidelberg, Germany*; MARCUS AGÅKER, JAN-ERIK RUBENSSON, *Department of Physics and Astronomy, Uppsala Universitet, Uppsala, Sweden*; MARC SIMON, *LCPMR, Sorbonne Université, Paris, France*; MICHAEL MEYER, TOMMASO MAZZA, ALBERTO DE FANIS, THOMAS BAUMANN, SERGEY USENKO, *SQS, European XFEL, Schenefeld, Germany*; METTE GAARDE, *Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA, USA*; LINDA YOUNG, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*.

X-ray free-electron lasers (XFELs) generate high-intensity x-ray pulses which enable x-ray nonlinear spectro-scopies. The extension of nonlinear spectroscopies to the x-ray domain promises the observation of electronic dynamics on their natural timescales with atomic spatial resolution. Stimulated x-ray Raman spectroscopy is an especially powerful tool, which in a propagation geometry combines large signal enhancement through stimulated emission with ultrahigh energy resolution that overcomes core-hole lifetime broadening. We present high-resolution stimulated Raman spectroscopy realized using stochastic XFEL pulses and correlation techniques. A covariance map between the transmitted SASE pulse and the stimulated Raman scattering produces a high-resolution x-ray Raman spectrum. This promising tool could be applied to study ultrafast electronic and molecular dynamics such as charge transfer in complex systems.

MH10 **5:22 – 5:37**

ADVANCED LASER-BASED TECHNIQUES FOR MATERIAL AND STRUCTURAL CHARACTERIZATION

SNEHA BANERJEE, *Central Laser Facility, STFC - CLF -RAL, Didcot, Oxfordshire, United Kingdom*.

The Central Laser Facility (CLF), based at the Harwell Science & Innovation Campus in Oxfordshire, UK, is one of the leading international laser facilities. Providing cutting-edge laser-based technologies to academics and industry from all over the UK, Europe, and the world. The facility offers various technological solutions ranging from high-energy lasers, to ultrafast pulses and super-resolution microscopic techniques.

The use of molecular spectroscopy and advanced imaging techniques has always been predominant in fundamental academic research. At the CLF, we are trying to push the boundaries of applications of advanced spectroscopy and microscopy to solve problems in industry. We apply these techniques to answer important questions related to green chemistry, drug delivery, alternative fuel sources, health and therapeutic science, and various other fields.

CLF can broadly be classified into five departments: Ultra – for ultrafast spectroscopy, Octopus – for super-resolution microscopy, Artemis – for femtosecond and attosecond spectroscopy, and Vulcan and Gemini, which are our intense high-power lasers for understanding science at extreme conditions. CLF is also building another facility called EPAC – the Extreme Photonics Application Centre, which will deliver a new generation of laser-based accelerators, providing multi-modal capabilities for the automotive, aerospace, and medical industries.

I am the joint CLF and Johnson Matthey Research Fellow. I will be working at the forefront of applying these advanced ultrafast spectroscopic techniques, especially time-resolved spectroscopy, to solve interesting questions related to real-world scenarios and explore the wide range of capabilities the CLF can provide to both academia and industry.

MH11 **5:40 – 5:55**

TRANSIENT LABORATORY NEXAFS SPECTROSCOPY ON SOLID AND LIQUID SAMPLES

RICHARD GNEWKOW, *SyncLab, Helmholtz-Zentrum Berlin für Material und Energie, Berlin, Germany*; ADRIAN JONAS, MARC DUMMIN, DANIEL GRÖTZSCH, SILVANA SCHÖNFELDER, *Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany*; HOLGER STIEL, *Department B2, Max-Born-Institute, Berlin, Germany*; BIRGIT KANNGIESSER, *Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany*; IOANNA MANTOUVALOU, *SyncLab, Helmholtz-Zentrum Berlin für Material und Energie, Berlin, Germany*.

Molecular systems can be used for a wide range of applications but for a complete description knowledge about their transient electronic properties is often required. Optical-pump soft X-ray-probe NEXAFS spectroscopy is an ideal technique to investigate these systems due to its elemental and orbital selectivity which allows probing the time evolution of the electronic structure. Our laboratory transient NEXAFS spectrometer [a] is based on a laser-produced plasma source covering an energy range between 200 – 1500 eV with an energy resolving power of $\geq$1000 and 500 ps time resolution. Due to the high efficiency of the setup, the investigation of absorption changes as small as 10^{-4} is possible [b]. These parameters allow obtaining high-quality time-resolved NEXAFS spectra formerly only attainable at synchrotron radiation sources.

Static and transient NEXAFS measurements in transmission of solid samples and measurements in the liquid phase with a flatjet system at the Carbon and Nitrogen K-edge as well as 3d metal L-edges will be presented. Possible synergies of these laboratory-based measurements in combination with synchrotron instrumentation will be discussed.

[a] A. Jonas et al., Opt. Express 27, 2019, 36524-36537
[b] A. Jonas et at., Anal. Chem. 92, 2020, 15611-15615

MI. Fundamental physics

Monday, June 19, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Jun Jiang, Lawrence Livermore National Laboratory, Fremont, CA, USA

MI01 **1:45 – 2:00**

LASER SPECTROSCOPY OF AROMATIC MOLECULES WITH OPTICAL CYCLING CENTERS: STRONTIUM (I) PHENOXIDES

GUANMING LAO, *Department of Physics, University of California, Los Angeles, Los Angeles, CA, USA*; GUO-ZHU ZHU, *Physics & Astronomy Department, University of California, Los Angeles, Los Angeles, CA, USA*; CLAIRE E DICKERSON, *Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA, USA*; BENJAMIN AUGENBRAUN, *Department of Physics, Harvard University, Cambridge, MA, USA*; ANASTASSIA ALEXANDROVA, JUSTIN CARAM, *Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA, USA*; ERIC HUDSON, WESLEY CAMPBELL, *Department of Physics, University of California, Los Angeles, Los Angeles, CA, USA*.

Optical cycling, a phenomenon in which atoms or molecules rapidly emit photons after optical excitation in a repeated cycle, is important in laser cooling and trapping, as well as state preparation and measurement. Theoretical and experimental works [1, 2, 3] show that aromatic compounds functionalized with an M-O unit for optical cycling (M = Ca or Sr) can be made suitable for repeated photon scattering. Here, we report the production and spectroscopic characterization of strontium (I) phenoxide (SrOC6H5, or SrOPh) and variants featuring electron-withdrawing groups designed to suppress vibrational excitation during spontaneous emission from the electronically excited state. By using dispersed laser-induced fluorescence spectroscopy, we discovered that the cycling closure of these species, which is the decoupling of vibrational state changes from spontaneous optical decay, is high, which is consistent with theoretical predictions. A high-resolution, rotationally resolved laser excitation spectrum is also recorded for SrOPh, allowing the estimation of spectroscopic constants and identification of candidate optical cycling transitions for future work. The results show the promise of strontium phenoxides for laser cooling and quantum state detection at the single-molecule level. This work also suggests that a larger class of molecules than previously realized may be amenable to laser cooling.

(1) Dickerson, C. E.; et al. Phys. Rev. Lett. 2021, 126, 123002. (2) Dickerson, C. E.; et al. J. Phys. Chem. Lett. 2021, 12, 3989–3995. (3) Zhu, G. Z.; et al. Nat. Chem. 2022, 14, 995–999.

MI02 **2:03 – 2:18**

STRUCTURAL AND ELECTRONIC TRENDS OF OPTICAL CYCLING CENTERS IN POLYATOMIC MOLCULES: MICROWAVE SPECTROSCOPY OF MgCCH, CaCCH, SrCCH, and YbCCH

BRYAN CHANGALA, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; NADAV GENOSSAR-DAN, ELLA BRUDNER, TOMER GUR, JOSHUA H. BARABAN, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

The unique optical cycling properties of metal-ligand molecules containing alkaline earth(-like) elements are essential to laser cooling and trapping of molecules. As the chemical complexity of target systems increases, so does the necessity of understanding the relationships between their chemical bonding, electronic structure, and critical spectroscopic properties. We present a comprehensive isotopic study of the microwave rotational spectra of the metal-bearing acetylides MgCCH, CaCCH, SrCCH, and YbCCH in their ground $^2\Sigma^+$ electronic states. Their precise semi-experimental equilibrium geometries have been derived using high-accuracy theoretical corrections for electronic and zero-point motion effects. The well resolved hyperfine structure of the ^{1,2}H, ^{13}C, and metal nuclear spins provides complementary information on the distribution and hybridization of the optically active metal-centered unpaired electron. Our measurements of this reference family of molecules reveal trends in chemical bonding and structure that are correlated with the electronic properties that promote efficient optical cycling. The development of such chemical design principles supports next-generation experiments in precision measurement and quantum control of complex polyatomic molecules.

MI03 **2:21 – 2:36**

LASER IONIZATION SPECTROSCOPY OF AcF AND KING-PLOT ANALYSIS OF MOLECULAR ISOTOPE SHIFTS

MICHAIL ATHANASAKIS-KAKLAMANAKIS, *Physics, CERN, Geneva, Switzerland*; SHANE WILKINS, *Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, USA*; MIA AU, *Physics, CERN, Geneva, Switzerland*; ALEXANDER A. BREIER, *Physics, University Kassel, Kassel, Germany*; GERDA NEYENS, *Physics, KU Leuven, Leuven, Belgium*.

The research potential of radioactive molecules for both fundamental and applied science has recently been recognized [1,2] and significant progress has been marked at ISOLDE on both the production and the spectroscopy [3,4] of radioactive molecules. In addition to the first laser spectroscopy of RaF at the collinear resonance ionization spectroscopy (CRIS) experiment [3,4], which was triggered by theoretical predictions in Ref. [5], and its subsequent high-resolution study, the CRIS collaboration recently performed the first laser spectroscopy of AcF [6]. AcF has been proposed as a promising system for the first measurement of a nuclear Schiff moment across the nuclear chart. Simultaneously, experimental and theoretical progress in the excited electronic states of RaF and the manifestation of nuclear observables in molecular spectra [7] carried out by members of the CRIS collaboration has highlighted the potential of laser spectroscopy of radioactive molecules at radioactive ion beam facilities to probe nuclear and molecular observables that are not easily accessible by other methods and systems.

In this talk, recent results by the CRIS collaboration on the laser spectroscopy of AcF will be presented, along with theoretical work on the spectroscopy of lighter radioactive molecules that can provide access to nuclear and molecular observables that cannot be studied via other methods. The future directions of laser-spectroscopic studies of radioactive molecules at CRIS will also be discussed.

[1] arXiv:2302.02165 (2023) [2] CERN-INTC-2021-017 (2021) [3] Nature **581**, 396 (2020) [4] Physical Review Letters **127**, 033001 (2021) [5] Phys. Rev. A **82**, 052521 (2010) [6] CERN-INTC-2021-053 (2021) [7] Physical Review X **13** (1), 011015 (2023)

The complete author list is omitted from this abstract due to length constraints but will appear in the talk.

MI04 **2:39 – 2:54**

PRECISION STUDIES OF RADIOACTIVE MOLECULES RELEVANT TO FUNDAMENTAL PHYSICS

SHANE WILKINS, *Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, USA*; MICHAIL ATHANASAKIS-KAKLAMANAKIS, *Physics, CERN, Geneva, Switzerland*; ALEXANDER A. BREIER, *Physics, University Kassel, Kassel, Germany*; RONALD FERNANDO GARCIA RUIZ, *Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, USA*; GERDA NEYENS, *Physics, KU Leuven, Leuven, Belgium*; SILVIU-MARIAN UDRESCU, *Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, USA*.

Certain molecules that contain heavy, deformed radioactive nuclei are predicted to be exceptionally sensitive laboratories to examine the fundamental symmetries of nature [1-4]. Despite their recognized potential, technical challenges prevented experimental studies of these systems until very recently. The first landmark study of a short-lived molecule was able to determine the rovibronic structure of different isotopologues of radium monofluoride [5,6], a promising system in which to search for signatures of symmetry violations.

This contribution presents results from subsequent experimental campaigns in which a massive improvement in resolution enabled an unprecedented glimpse into the structure of the radioactive ^{223,225,226}RaF. This allowed the laser cooling scheme of ^{226}RaF to be established which will be critical for realizing future high-precision studies. Furthermore, the hyperfine structure in ^{225}RaF is shown to be highly sensitive to the Bohr-Weisskopf effect, laying the foundation for the first studies of the distribution of nuclear magnetization in a molecule. Additional results characterizing a plethora of newly observed excited electronic states as well as an accurate determination of the molecule's ionization potential will also be presented.

[1] Altuntaş, E. et al., Phys. Rev. Lett. 120, 142501 (2018)
[2] ACME Collaboration, Nature 562, 355–360 (2018)
[3] Flambaum, V. V. et al., Phys. Rev. Lett. 113, 103003 (2014)
[4] Berger, R. et al., WIREs Comput. Mol. Sci. 9, e1396 (2019)
[5] Garcia Ruiz, R. F. et al., Nature 581 396–400 (2020)
[6] Udrescu, S. M. et al. Phys. Rev. Lett. 127 03301 (2021)

MI05 **2:57 – 3:12**

A SEARCH FOR TIME-REVERSAL SYMMETRY VIOLATION WITH THALLIUM FLUORIDE

JIANHUI LI, TANYA ZELEVINSKY, *Physics, Columbia University, New York, NY, USA*; JAKOB KASTELIC, OSKARI TIMGREN, STEVE LAMOREAUX, *Department of Physics, Yale University, New Haven, CT, USA*; OLIVIER GRASDIJK, *Physics, Argonne National Laboratory, Lemont, IL, USA*; YUANHANG YANG, DAVID DEMILLE, *Physics, University of Chicago, Chicago, IL, USA*; TRISTAN WINICK, DAVID KAWALL, *Physics, University of Massachusetts Amherst, Amherst, MA, USA*.

The Cold molecule Nuclear Time-Reversal EXperiment (CeNTREX) aims to look for the fundamental time-reversal (T) symmetry violations in the hadronic sector. Violation of T symmetry is a necessary condition to dynamically generate the asymmetry in matter and anti-matter we observe in the universe. Many extensions of the standard model imply additional sources of T-violation larger than the standard model prediction. CeNTREX utilizes Ramsey interferometry on cryogenic beam of thallium fluoride (TlF) molecules to look for shifts in nuclear magnetic resonance frequencies in ^{205}Tl nucleus when it is electrically polarized. To increase sensitivity, CeNTREX employs lasers, microwaves and electric fields to prepare and manipulate molecular quantum states. Laser-induced fluorescence readout of TlF then provides information on T-violating phase acquired during the Ramsey interferometry. We project significant improvements in the experimental upper bounds of various T-violating parameters. Here, we present on the motivation and progress of the experiment as well as the techniques involved.

Intermission

MI06 **3:52 – 4:07**

MODELING SPIN-SELECTIVE POSITRONIUM CHEMISTRY OF THE CLOSO-DODECABORATE DIANION

LARRY W BURGGRAF, *Department of Engineering Physics, Air Force Institute of Technology, WPAFB, OH, USA*; XIAOFENG F DUAN, *DoD Supercomputer Resource Center, Air Force Research Laboratory, Wright-Patterson AFB, OH, USA*.

The measured lifetime of the positron with closo-dedecaborate dianion in water is 250 ps and in solid state 265 ps. This lifetime is consistent with modeled annihilation rate estimates. Lifetime spectroscopy measurements of positronium (Ps) annihilation have shown that the singlet p-Ps is quenched by the closo-dodecaborate dianion in water, while the triplet o-Ps is not efficiently quenched. This spin-selective behavior we attribute to electron exchange between the Ps atom and the anion in the excited addition complex. In order to gain insight into e+ binding and Ps elimination reactions we have performed ab initio and DFT calculations to describe the vibrational spectroscopy and photoelectron spectroscopy of the closo-dodecaborate dianion including VDE and ADE. We have calculated the positron wavefunction for the positronic closo-dodecaborate dianion using the NEO-positron code to understand the nature and energy of the complex of positron with the closo-dodecaborate dianion.

MI07 **4:10 – 4:25**

QUANTUM STATE CONTROL OF CHIRAL MOLECULES

JU HYEON LEE, JOHANNES BISCHOFF, *Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*; A. O. HERNANDEZ-CASTILLO, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; BORIS SARTAKOV, GERARD MEIJER, SANDRA EIBENBERGER-ARIAS, *Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*.

Recently, enantiomer-specific state transfer (ESST) was demonstrated using frequency-, phase-, and polarization-controlled microwaves [1]. This method allows to populate or depopulate a rotational state of a chosen enantiomer, providing a way of quantum-controlled chiral separation. In the past, the transfer efficiency of ESST was limited by the initial thermal population of the energy levels participating in ESST [1,2] and by spatial degeneracy [3].

To address these prior limitations, we developed a new experimental scheme by combining optical methods [4] with microwave spectroscopy. This increased the efficiency of ESST by over a factor of ten compared to previously reported values [5]. Our scheme enables a quantitative comparison between experiment and theory involving the absolute ground state level. I will discuss recent experimental results and our ongoing work aiming at perfect ESST in my presentation.

[1] S. Eibenberger, J. Doyle, D. Patterson, Phys. Rev. Lett. 118, 123002 (2017)

[2] C. Pérez, A. L. Steber, S. R. Domingos, A. Krin, M. Schnell, Angew. Chem. Int. Ed. 56, 12512 (2017)

[3] K. K. Lehmann, J. Chem. Phys. 149, 094201 (2018)

[4] A. O. Hernandez-Castillo, J. Bischoff, J. H. Lee, J. Langenhan, M. Karra, G. Meijer, and S. Eibenberger-Arias, Phys. Chem. Chem. Phys. 23, 7048-7056 (2021)

[5] J. H. Lee, J. Bischoff, A. O. Hernandez-Castillo, B. Sartakov, G. Meijer, and S. Eibenberger-Arias, Phys. Rev. Lett. 128, 173001 (2022)

MI08 **4:28 – 4:43**

ENANTIOMER-SELECTIVE POPULATION TRANSFER IN THE GAS PHASE USING PHASE-CONTROLLED RESONANT MICROWAVE FIELDS

HIMANSHI SINGH, FREYA E. L. BERGGÖTZ, WENHAO SUN, MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Chiral molecules are present ubiquitously in nature. They have two enantiomeric forms, which are mirror images of each other and cannot be superimposed onto one another through rotation. Due to the mirror-imaged mass distribution, the two enantiomers have the same moments of inertia (I_A, I_B, and I_C) in the principal axis system and thus have almost identical rotational signatures and cannot be distinguished with conventional microwave spectroscopy. In order to achieve chiral analysis for the chiral molecules in the gas phase, microwave three-wave mixing (M3WM) technique has been developed,[a] which exploits three-dimensional light-matter interactions in the dipole approximation. Beyond chiral analysis, this technique is further extended to achieve enantiomer-selective chiral control in the rotational state of interest, which is capable of inducing a state-specific enantiomeric excess "on the fly" when starting from a racemic mixture.

Previously, it has been reported that enantiomeric excess of about 0.5% and 6% were successfully generated using this approach with 1,2-propanediol[b] and carvone,[c] respectively. The enantiomer in excess can be induced selectively by tuning the phase of the microwave pulses. Here we present our recent investigation aimed at further improving the efficiency of this technique with solely microwave fields. We performed the population transfer experiment with a racemic sample of 2-trifluoromethyl oxirane and show that an enantiomeric excess of about 13% was induced by employing a population transfer scheme starting from the ground rotational state $|0_{00}\rangle$, which diminishes the spatial degeneracy of the rotational states. Furthermore, by depleting the initial thermal population with a resonant π-pulse or a microwave chirp in the rapid adiabatic passage regime, the obtained enantiomeric excess can be significantly improved to over 40%. These effects will be discussed in detail along with the theoretical simulations.

[a] D. Patterson, M. Schnell, J. M. Doyle, *Nature* **497**, 475–477 (2013).

[b] S. Eibenberger, J. Doyle, D. Patterson, *Phys. Rev. Lett.* **118**, 123002 (2017).

[c] C. Pérez, A. L. Steber, S. R. Domingos, A. Krin, D. Schmitz, M. Schnell, *Angew. Chem. Int. Ed.* **56**, 12512–12517 (2019).

MI09 **4:46 – 5:01**

HIGH ACCURACY SPECTROSCOPY OF H_2 ROVIBRATIONAL TRANSITIONS IN THE (2-0) BAND NEAR 1.2μm

HELENE FLEURBAEY, ALEKSANDRA KOROLEVA, SAMIR KASSI, ALAIN CAMPARGUE, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*.

Metrological measurements of rovibrational frequencies in molecular hydrogen provide stringent tests for the most advanced theoretical calculations and for searching for physics beyond the standard model. We will present the accurate transition frequencies of a series of lines belonging to the (2-0) vibrational band of H_2 near 1.2 μm. These weak electric-quadrupole transitions were measured at room temperature by comb referenced cavity ring-down spectroscopy and are the first H_2 (2-0) transition frequencies referenced to an absolute frequency standard. Accurate transition frequencies determination - up to three orders of magnitude better than previous measurements - will be presented. The impact of the line profile on zero-pressure line centers will be evaluated. These transition frequencies are used to infer the separation of lower energy levels in the vibrational ground state. All these experimental results will be compared to the most recent calculated frequencies.

MJ. Comparing theory and experiment

Monday, June 19, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

Chair: Lan Cheng, The Johns Hopkins University, Lutherville Timonium, MD, USA

MJ01 **1:45 – 2:00**

THE LOCAL VIBRATIONAL MODE THEORY: AN EFFICIENT ANALYSIS TOOL FOR THE VIBRATIONAL SPECTROSCOPY COMMUNITY

ELFI KRAKA, *Chemistry, Southern Methodist University, Dallas, TX, USA*.

The local vibrational mode theory originally introduced by Konkoli and Cremer has become over the past years a versatile tool for extracting important chemical information, hidden in vibrational spectroscopy data caused by the delocalized nature of normal vibrational modes in polyatomic molecules.[1,2]

After a short introduction of the theoretical background and description how local vibrational modes are derived from fundamental vibrational normal modes, we will present three recent examples, elucidating how our tool can help finding answers to open vibrational spectroscopy questions: (i) metal-ligand bonding in heme proteins, such as myoglobin and neuroglobin; (ii) disentanglement of DNA normal modes; and (iii) hydrogen bonding in water clusters and ice.

Finally, we will present the open-source local mode program LModeA which can easily be applied after a routine quantum chemical calculation of vibrational frequencies but also to measured vibrational frequencies, with moderate computational costs.

References:
1. Feature Article: The Local Vibrational Mode Theory and Its Place in the Vibrational Spectroscopy Arena, E. Kraka, M. Quintano, H. W. La Force, J. J. Antonio and M. Freindorf, J. Phys. Chem. A, 126, 8781 (2022)
2. Decoding chemical information from vibrational spectroscopy data: Local vibrational mode theory. E. Kraka, W. Zou, and Y. Tao, WIREs: Comput. Mol. Sci., e1480 (2020)

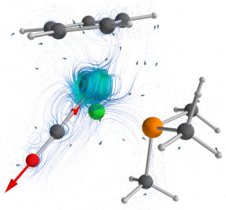
MJ02 **2:03 – 2:18**

ANHARMONICITY AT LARGER SCALES: VIBRATIONAL SPECTRA OF CHIRAL ORGANOMETALLIC COMPLEXES

JULIEN BLOINO, *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; MARCO FUSÈ, *Department of Molecular and Translational Medicine, University of Brescia, Brescia, Italy*.

Beyond their central roles in some enzymes and proteins, chiral organometallic complexes have potential applications in synthetic drugs, as biomarkers or in catalysis for instance. Their structural characterization can help rationalize their activity, including their bioactivity and toxicology. Experimentally, a key role is played by vibrational spectroscopies like IR and Raman scattering, with a more comprehensive picture achieved by the use of their chiroptical counterparts, respectively vibrational circular dichroism (VCD) and Raman optical activity (ROA).[1] Because of the complexity of the signal, the interpretation of chiral spectra needs to be assisted by computations.

However, chiral spectroscopies are characterized by a higher sensitivity and low-intensity spectra (typically 4-5 orders of magnitude lower than the non-chiral ones), so standard protocols rooted into the density functional theory within the harmonic-oscillator approximation can be insufficient. A straightforward path of improvement is the inclusion of anharmonicity, but the typical size of organometallic compounds is generally too large even for relatively cheap methods such as the second-order vibrational perturbation theory (VPT2). On the other hand, a full anharmonic treatment may be unnecessary to investigate probe vibrations or specific spectral regions. Indeed, a model system can be built by considering the anharmonic contributions only for a subset of relevant modes without loss of accuracy. In this contribution, we will discuss how this can be done and analyze the potential pitfalls. Finally, we will show how computations can be used to provide new visual insights on the local origin of the observed bands.[2]



[1] T. Wu, X.-Z. You, P. Bouř, *Coord. Chem. Rev.* 2015, **284**, 1-18
[2] a) L. A. Nafie, *J. Phys. Chem. A* 1997, **101**, 7826; b) M. Fusè, F. Egidi, J. Bloino, *Phys. Chem. Chem. Phys.* 2019, **21**, 4224-4239

MJ03 **2:21 – 2:36**

INTERPRETATION OF MOLECULAR SPECTRA USING VIBRATIONAL PERTURBATION THEORY

ANNE B. McCOY, MARK A. BOYER, *Department of Chemistry, University of Washington, Seattle, WA, USA*.

We recently developed an implementation of vibrational perturbation theory (VPT) based on the approach described by Sakurai in which the perturbation theory calculations are performed numerically using linear algebra approaches. This has been incorporated in the PyVibPTn codes. Advantages that are realized by this approach include flexibility with respect to the coordinates used to expand the Hamiltonian and in the identification of possible resonance interactions. Specifically, in PyVibPTn resonances are identified based on the size of corrections to the wave function from higher-order terms in the Hamiltonian. This approach has the advantage over the Martin test, which focuses on corrections to the energies from the first order corrections to the Hamiltonian, in that our approach treats the first and second order corrections to the Hamiltonian in a more balanced manner. It also allows us to identify resonance interactions that have large effects on the intensities or other properties, while having only small impacts on the energies.

This implementation of VPT has been used in several studies of vibrational spectra. These include an analysis of the IR-cryo-SEVI spectra of vyonxide in collaboration with the Neumark group. In this study, the vynoxide ion is excited to states with one quantum of excitation in the CO or CH stretching vibration prior to electron photodetachment. We also describe how VPT was used to reassess the assignment of the vibrational spectrum of $H^+(C_2H_4)$. Additionally, we use VPT to obtain insights into the origins of IR intensity for transitions by decomposing the transition moment into contributions from higher order terms in the expansions of the potential and dipole moment surfaces.

MJ04 **2:39 – 2:54**

STRUCTURAL INVESTIGATION OF HYDRATED ANIONIC PYRENE CLUSTERS WITH INFRARED SPECTROSCOPY[a]

HEINRICH SALZMANN, *JILA and Department of Chemistry, University of Coloroado, Boulder, CO, USA*; NATALIE LEMESSURIER, *Department of Chemistry, University of Colorado, Boulder, CO, USA*; ANNE P. RASMUSSEN, *Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark*; JOEL D. EAVES, *Department of Chemistry, University of Colorado, Boulder, CO, USA*; J. MATHIAS WEBER, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*.

Hydrated pyrene anions are model systems for microsolvation and hydrogen bonded (H-bonded) networks on charged graphene like materials. Tandem mass spectrometry was employed to collect mass selected messenger-tag and photodissociation infrared (IR) spectra. Photodissociation spectra of cold cluster anions of the form $C_{16}H_{10}{}^{-}\cdot(H_2O)_n\cdot Ar_2$ (n=1-4) losing Argon upon irradiation are compared to spectra of warmer $C_{16}H_{10}{}^{-}\cdot(H_2O)_n$ (n=1-4) cluster anions. Structural and dynamic information about the H-bond network is encoded in OH stretching frequencies. Experimental IR spectra are compared to density functional theory calculations, and various cluster geometries are predicted. Generally, water molecules form H-bonds with other water molecules and with the excess charge in pyrene's π-system. These binding motifs are compared to the ones found on anionic hydrated naphthalene clusters.[b]

[a] We gratefully acknowledge funding from the Department of Energy (Award No. DE-SC0021387)

[b] 1. B.J. Knurr, C.L. Adams, and J.M. Weber, Infrared Spectroscopy of Hydrated Naphthalene Cluster Anions. J. Chem. Phys. 137 (2012) 104303.

MJ05 **2:57 – 3:12**

VIBRATIONAL SPECTROSCOPY OF ANIONIC PAH-WATER CLUSTERS

NATALIE LEMESSURIER[a], *Department of Chemistry, University of Colorado, Boulder, CO, USA*; HEINRICH SALZMANN, J. MATHIAS WEBER, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*; JOEL D. EAVES, *Department of Chemistry, University of Colorado, Boulder, CO, USA*.

The intermolecular forces that govern water-hydrocarbon interactions have profound effects in interfacial phenomena, like wetting, and large-scale applications to issues like water security through water desalination with two-dimensional membranes[b]. I will discuss our work on building dynamical methods and water models to describe and interpret the vibrational spectroscopy of anionic water-polycyclic aromatic hydrocarbon (PAH) clusters which act as a minimal model for aqueous-carbon interfaces. Even in a small system of one water with a charged PAH, there is significant complexity, including non-Gaussian fluctuations and ergodicity-breaking at low temperatures. Systematically accounting for these effects leads to semi-quantitative agreement between theoretical predictions and experimental measurements for the IR spectrum in the OH stretching region.

[a]We gratefully acknowledge the Department of Energy for their funding of this work (Award No. DE-SC0021387)

[b]S. Strong; J.D. Eaves. The dynamics of water in porous two-dimensional crystals. *J. Phys. Chem. B* 2017, 121, 189-207

MJ06 **3:15 – 3:30**

SYNTHESIS, MOLECULAR STRUCTURE, VIBRATIONAL CHARACTERISTICS, PROFILES OF OTHER MOLECULAR PROPERTIES AND ANTICANCER ACTIVITY OF 2-((2-AMINOPYRIDIN-3-YL)METHYLENE)-N-PHENYLHYDRAZINECARBOTHIOAMIDE AS PROVIDED BY SPECTROSCOPIC AND DFT INVESTIGATIONS

RAMAIAH K, *Chemistry Division,H&S Department, CVR College of Engineering, HYDERABAD, TELANGANA, India*; K SRISHAILAM, *PHYSICS, SR UNIVERSITY, HANAMKONDA, TELANGANA, INDIA*; BYRU VENKATRAM REDDY, G. RAMANA RAO, *Department of Physics, KAKATIYA UNIVERSITY, WARANGAL, India*.

Synthesis of 2-((2-aminopyridin-3-yl)methylene)-N-phenylhydrazinecarbothioamide (APHB) was attempted. Elemental analysis and NMR spectra were used to ascertain its formation. Torsional potential energy scans, for all the rotating bonds were made to get approximate initial values of dihedral angles. FT-IR, FT Raman, and UV-Vis spectra were measured for APHB. Their anticancer activity was determined experimentally, for human carcinoma cell lines pertaining to liver, colorectal, and lung. Barrier heights, around six rotating bonds in APHB were computed. Optimized structure parameters, general valence force field, harmonic vibrational fundamentals, potential energy distribution, infrared and Raman intensities, frontier molecular orbital (FMO) parameters, NLO behaviour, and NBO characteristics were determined using DFT/B3LYP/6-311++G(d,p) level of theory. TD-DFT was used to compute absorption maxima (λ_{max}) of electronic transitions for the molecule in DMSO-d_6 solvent. Frontier molecular orbitals were used to understand origin of UV-Vis spectrum and chemical reactivity of the molecule. Good agreement was found between measured and computed structure parameters, IR, Raman and UV-Vis spectra. The rms error between experimental and theoretical vibrational frequencies was 9.5 cm^{-1}, for APHB. All vibrational fundamentals were assigned unambiguously. The computations demonstrated that the molecule was good for NLO applications, which was substantiated by NBO analysis. Existence of bifurcated intramolecular hydrogen bond was predicted for APHB.

MJ07 **3:33 – 3:48**

TWO-PHOTON TRANSITIONS IN THE LASER INDUCED FLUORESCENCE OF NO_3 BY FUKUSHIMA

TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, The Enrico Fermi Institute, University of Chicago, Chicago, IL, USA*.

Recently, Fukushima reported laser-induced fluorescence of the $\tilde{B}^2E'$ - $\tilde{X}^2A'_2$ transition from the vibrationless $\tilde{B}^2E'$ excited state of jet cooled $^{14}NO_3$ and $^{15}NO_3$ in which two beautiful series of ν_4 progressions in the ground $X^2A'_2$ state have been identified.[a] One of the progressions corresponds to transitions with vibrational symmetry a_1' - a_1' while the other with a_1' - e'. The former is the ordinary single-photon spontaneous emission given in Eq.(II,11) of Herzberg Vol.III, while the latter is not discussed in ordinary textbook of spectroscopy. Here I propose that the latter is due to Raman-type laser stimulated two-photon processes that were commonly observed around 1970.[bc]

Contrary to the previous assignments which invoke vibronic mixing between the $\tilde{B}^2E'$ and $\tilde{X}^2A'_2$ states, the 2-photon assignment leaves the vibrational angular momentum l_4 in the ground $\tilde{X}^2A'_2$ state a good quantum number except for the $\Delta l = 3$ mixing. Therefore the l_4 assignment and the vibrational structure are extremely simple as reported in the Fukushima paper. The calculation using the Kramers-Heisenberg formula indicates that the laser power density indicates sufficiently high to cause the two-photon process.

The perfectly normal ν_4 progression suggests strongly that the ν_3 progression is also normal. This suggests that the so-called "Assignment I" in which the intensity of the ν_3 fundamental band is higher than that of the $\nu_3 + \nu_4$ combination band is more reasonable than the "Assignment II" in which a theoretical calculation gives the ν_3 band weaker than the $\nu_3 + \nu_4$ band by a factor of 60[d] and an experimental observation by $\sim$ 2000.[e]

[a] Fukushima, M. 2022, J. Mol. Spectrosc. 387, 111646

[b] Freund, S.M., Oka, T. 1976, Phys. Rev. A. 13, 2178

[c] Oka, T. 1977, Frontiers in Laser Spectroscopy, II (Proceedings, Summer School of Theoretical Physics, Les Houches), R. Balian, S. Haroche and S. Lieberman, eds., North-Holland, Amsterdam, pp. 531–569

[d] Stanton, J.F. 2009, Mol. Phys. 107, 1059

[e] Kawaguchi, K., Tang, J., Akikusa, N. 2021, Chem. Phys. Lett. 765, 138365

Intermission

MJ08 **4:28 – 4:43**

THE THRESHOLD PHOTOELECTRON SPECTRUM OF SiH_2 AS MODELED WITH MCTDH

N. CHEN, BÉRENGER GANS, SÉVERINE BOYÉ-PERONNE, L. H. COUDERT, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, Orsay, France*; J.-C. LOISON, *Institut des Sciences Moléculaires, Université de Bordeaux, Bordeaux, France*; G. A. GARCIA, SEBASTIAN HARTWEG, *DESIRS beamline, Synchrotron SOLEIL, Gif-sur-Yvette, France*.

Although the ground $\widetilde{X}\,^1A_1$ electronic state of silylene SiH_2 is fairly well characterized,[a] fewer results are available about its first excited triplet $\tilde{a}\,^3B_1$ electronic state and about its cationic species $SiH{-}2^+$. The ground electronic state of the latter is split into bent $\widetilde{X}^+\,^2A_1$ and linear $\widetilde{A}^+\,^2B_1$ doublet electronic states by the Renner-Teller coupling.[b]

Threshold photoelectron (TPE) spectroscopy has been used to obtain spectroscopic information about the cationic species SiH_2^+ of silylene and about the first excited triplet electronic state of neutral SiH_2. The TPE spectrum, recorded at Synchrotron SOLEIL from 7.5 to 11.5 eV using VUV synchrotron radiation, displays several sharp features and was modeled using wavepacket propagation.[c] ωB97XD *ab initio* calculations were carried out using cc-PVTZ correlation-consistent basis set functions to retrieve 3-D potential energy surfaces for the four electronic states involved in the TPE spectrum. The MCTDH method[d] was first used to obtain the 3-D vibrational wavefunctions of the neutral species $\widetilde{X}\,^1A_1$ and $\tilde{a}\,^3B_1$ electronic states using propagation in negative imaginary time. The wavefunctions thus obtained were then time-propagated in the potential energy surfaces of the coupled electronic states of the cationic species using also MCTDH.[c,d] The photoionisation cross-section was at last computed as the Fourier transform of the auto-correlation function.

In the talk, the results of the rovibronic energies calculation will be reported and the experimental TPE spectrum will be compared to the theoretical one. The importance of the Renner-Teller coupling will be assessed and the vibrational temperature which best reproduces the experimental spectrum will be evaluated.

[a] Clark, Ownes, Tennyson, and Yurchenko, *J. Quant. Spec. Rad. Transf.* **246** (2020) 106929
[b] Gu, Huang, Kong, and Liu, *J. Mol. Struct. (Theochm)* **253** (1992) 217
[c] Viel, Eisfeld, Evenhuis, and Manthe, *Chem. Phys.* **347** (2008) 331; and Eroms, Jungen, and Meyer, *J. Phys. Chem. A* **114** (2010) 9893
[d] Beck, Jäckle, Worth, and Meyer, *Phys. Rep.* **324** (2000) 1; and Meyer, Graham, and Worth, *Theor. Chem. Acc.* **109** (2003) 251

MJ09 **4:46 – 5:01**

RING OPENING AND TUNNELING INVERSION IN THE CYCLOPROPYL RADICAL AND CATION

NADAV GENOSSAR-DAN, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*; BRYAN CHANGALA, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; BÉRENGER GANS, MARIE-ALINE MARTIN-DRUMEL, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*; J.-C. LOISON, *Institut des Sciences Moléculaires, Universté de Bordeaux, Bordaux, Hauts-de-Seine, France*; SEBASTIAN HARTWEG, *Institute of Physics, University of Freiburg, Freiburg, Germany*; G. A. GARCIA, *DESIRS beamline, Synchrotron SOLEIL, Gif-sur-Yvette, France*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; BRANKO RUSCIC, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; JOSHUA H. BARABAN, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*.

We report spectroscopic and theoretical studies of the cyclopropyl radical and cation (c-C_3H_5)[1]. Through synchrotron VUV photoionization spectroscopy and novel spectral simulations, we establish the transition state nature of the cation, which is unstable towards ring-opening to the allyl cation. Additionally, we report preliminary results of the rotational spectroscopy of the radical, which exhibits inversion tunneling of the α-H atom through the C-C-C ring plane.

The large energy difference between the allylic equilibrium geometry and the unstable cyclic configuration on the cation potential energy surface (PES) required the development of propagator-based methods that avoid the construction of cationic vibronic eigenstates to simulate the ionization spectrum[2]. The results of our simulations, combined with high accuracy single-point *ab initio* calculations, compare well with new mass-selected threshold photoelectron measurements performed at the SOLEIL synchrotron, and attest to the transition state nature of the cation. Our results shed light on the most basic properties of the fundamental pericyclic reactions between allyl and cyclopropyl radicals and cations, which were among the very first systems to be studied from the perspectives of Woodward-Hoffmann rules and correlation diagrams. Additionally, we provide a qualitative explanation for the quantum mechanical effects that make the ionization transition favorable to a portion of a PES with negative curvature.

[1] Genossar *et al.*, J. Am. Chem. Soc., 144 (40), 18518-18525, 2022. [2] Changala *et al.*, J. Chem. Phys., 157, 124102, 2022.

MJ10 **5:04 – 5:19**

PROBING WEAK BONDING INTERACTIOINS THROUGH QUADRUPOLAR COUPLING OF CHLORINE

ROBIN DOHMEN, DENIS FEDOSOV, DANIEL A. OBENCHAIN, *Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany*.

Among the most challenging aspects of spectral assignment in rotational spectroscopy are complex hyperfine coupling patterns and a flat potential energy surface with many stable conformers. Electronic structure calculations are an essential tool for predicting geometries and spectroscopic constants such as nuclear quadrupole splitting. Reliable predictions are therefore essential for a fast assignment process.

Computational data for 22 weakly bound chlorine containing complexes is compared to experimental spectroscopic data from literature. The chosen methods are commonly used among rotational spectroscopists for initial theoretical screening of a target system. Ab initio methods with a large basis set are found to perform best overall in prediction both the geometry of the complex and the quadrupolar coupling with moderate computational costs. As inexpensive calculations determining equilibirum structures disregard large amplitude motions, which are often observed in weakly-bound complexes. Inacccurate geometries result in an incorrect projection of the nuclear quadrupole coupling tensor into the principle axis system. The quality of nuclear quadrupole predictions overall decreases compared to monomer studies from William Bailey's quadrupolar coupling data set,[a] which was focused on monomers. This study aims to expand upon Bailey's benchmarking dataset and cautions for critical evaluation of secondary parameters obtained from electronic structure calculations.

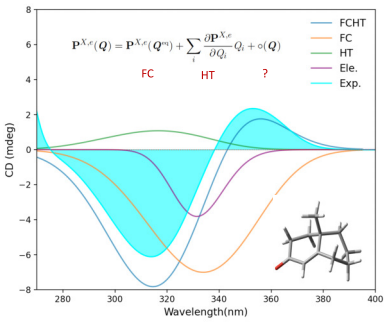
[a] W. C. Bailey, Calculation of Nuclear Quadrupole Coupling Constants in Gaseous State Molecule, 2019, https://nqcc.wcbailey.net/

MJ11 **5:22 – 5:37**

IS THE HERZBERG-TELLER EFFECT SUFFICIENT TO SIMULATE ONE PHOTON ABSORPTION SPECTRA?

QIN YANG, *Institute of Organic Chemistry and Biochemistry, Czech Academy of Science, Prague, Czechia*; TAO WU, *Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Prague, Czechia*; LI LI, *Department of Synthetic Medicinal Chemistry, Institute of Materia Medica , Beijing, China*; JULIEN BLOINO, *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; PETR BOUR, *Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Prague, Czechia*.

UV-vis absorption and circular dichroism spectra play a significant role in probing excited-state molecular properties. They developed to become routine tools used in a variety of fields, such as pharmacology, chemical analysis, and environmental monitoring. With the advances of instrumentation and broader applications, spectral simulations face increasing challenges. Theoretical methods including vibrational effects have replaced cruder models based purely on electronic transitions. With a better balance of computational cost and accuracy, such simulations are becoming routine.



An important aspect of vibronic simulations is the treatment of the transition dipole moments. The usual Franck-Condon approximation may not be adequate for weak or forbidden electronic transitions and the first order expansion (Herzberg-Teller, HT) term must be considered. For several organic molecules we show the importance of the HT effects for understanding the spectra. A family of porphyrin molecules not only exhibits the HT effects, but also hints at the need for higher-order terms to be included.

MK. Large amplitude motions, internal rotation

Monday, June 19, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: M. Eugenia Sanz, King's College London, London, United Kingdom

MK01 **1:45 – 2:00**

MILLIMETER-WAVE SPECTROSCOPY OF ACETYL CHLORIDE AND ACETYL BROMIDE[a]

PRAKASH GYAWALI, R. A. MOTIYENKO, L. MARGULÈS, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, Univ. Lille, CNRS, F-59000 Lille, France*.

Millimeter-wave spectra of acetyl chloride (CH_3COCl) and acetyl bromide (CH_3COBr) were measured in the frequency range 50–330 GHz. From a spectroscopic point of view, these molecules are interesting cases for studying methyl top internal rotation with relatively strong nuclear quadrupole coupling. Due to nonzero quadrupole moment of Cl and Br, the quadrupole hyperfine splittings in CH_3COCl and CH_3COBr molecules are comparable with splittings due to internal rotation. To fit the observed rotational transitions we used the so-called Rho-Axis-Method and RAM36hf code[b] that take nuclear quadrupole hyperfine structure into account. The analysis, which is in progress, includes the ground vibrational state as well as lowest excited torsional states. The latest results will be presented.

[a]This work has been supported by the ANR Labex CaPPA through the PIA under Contract No. ANR-11-LABX-0005-01
[b]V.V. Ilyushin, *J. Mol. Spec.* **345**, 64-69 (2018)

MK02 **2:03 – 2:18**

MICROWAVE SPECTROSCOPY AND LARGE AMPLITUDE MOTION OF CHLOROSULFONIC ACID ($ClSO_2OH$)

AARON J REYNOLDS, *Chemistry Department, University of Minnesota, Minneapolis, MN, USA*; DIEGO RODRIGUEZ, WEI LIN, *Department of Chemistry, University of Texas Rio Grande Valley, Brownsville, TX, USA*; KENNETH R. LEOPOLD, *Chemistry Department, University of Minnesota, Minneapolis, MN, USA*.

The high-resolution rotational spectrum of chlorosulfonic acid ($ClSO_2OH$) was studied using both broadband chirped pulse and cavity-based Fourier transform microwave spectrometers over the frequency range of 5–18 GHz for the first time. The observation of *a*-, *b*-, and *c*-type transitions for both ^{35}Cl and ^{37}Cl isotopomers suggests that the molecule exhibits large amplitude motion of the hydroxyl hydrogen flipping between two equivalent structures. The rotational constants, the centrifugal distortion constants, and the nuclear quadrupole coupling constants for the chlorine nucleus have been determined. The quantum chemical calculations were carried out using MP2 and B3LYP density functional theory (DFT) with aug-cc-pVTZ basis set. The rotational constants from the optimized geometric structures were in good agreement with the experimental values. The energy barrier of the large amplitude motion was calculated to be 12 kJ/mol. The effect of the large amplitude motion will be compared to the recent rotational spectroscopic study on triflic acid.[a]

[a]Anna K.Huff, Nathan Love, C. J. Smith Kenneth R. Leopold; Parent, 34S, and deuterated triflic acid: Microwave spectra and tunneling splittings due to hydroxyl torsion, J. Mol. Spectrosc., 2022, 385, 111623.

MK03 **2:21 – 2:36**

APPROACHING THE FREE ROTOR LIMIT: EXTREMELY LOW METHYL TORSIONAL BARRIER OBSERVED IN THE MICROWAVE SPECTRUM OF 2,4-DIMETHYLFLUOROBENZENE

SAFA KHEMISSI, MARTIN SCHWELL, *Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, 94010, Créteil, France*; ISABELLE KLEINER, *Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, 75013, Paris, France*; HA VINH LAM NGUYEN, *Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, 94010 Créteil, France, Institut Universitaire de France (IUF), 75231, Paris, France*.

Dimethylfluorobenzene isomers (DMFB) are aromatic heterocyclic volatile organic compounds (VOCs). These VOCs are methylated toluene derivatives, one of the most prevalent aromatic hydrocarbons in the troposphere and considered as atmospheric pollutants. The spectrum of 2,4-dimethylfluorobenzene (24DMFB) has been recorded between 2.0 and 26.5 GHz using the LISA molecular jet Fourier transform microwave spectrometer with an estimated measurement accuracy of 4 kHz. Due to the internal rotation of two inequivalent methyl groups, all rotational transitions split into quintets. The spectral analysis was challenging due to the fact that one of the two methyl groups in 24DMFB have a torsional barrier of about 1 cm^{-1}, leading to large splittings between the torsional species. Using the *SFLAMS*[a] program, the assignments were checked by fitting separately each of the five torsional species. A global fit of 813 torsional lines was performed using the programs *XIAM*[b], *ntop*[c] and *BELGI-Cs-2Tops*[d] giving standard deviations of 578.4 kHz, 13.3 and 4.7 kHz, respectively. The torsional barriers of the methyl groups in the *ortho* and *para* positions were determined to be 226.2087(16) and 1.4387(58) cm^{-1}, respectively.[e]

[a] S. Herbers, S.M. Fritz, P. Mishra, H.V.L. Nguyen, T.S. Zwier, J. Chem. Phys. 152, 074301, 2020.
[b] H. Hartwig, H. Dreizler, Z. Naturforsch. 51a, 923, 1996.
[c] L. Ferres, W. Stahl, H. V. L. Nguyen, J. Chem. Phys. 151, 104310, 2019.
[d] M. Tudorie, I. Kleiner, J. T. Hougen, S. Melandri, L. W. Sutikdja, W. Stahl, J. Mol. Spectrosc. 269, 211, 2011.
[e] This work has been funded by the Programme National de Physique Chimie du Milieu Interstellaire (PCMI).

MK04 **2:39 – 2:54**

MICROWAVE SPECTRUM AND STRUCTURE OF PHENYLACETYLENE···METHANOL COMPLEX

SURABHI GUPTA, *Department of Inorganic and Physical Chemistry, Indian Institute of Science Bangalore , Bangalore, Karnataka, India*; CHARLOTTE CUMMINGS, *School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom*; NICK WALKER, *School of Natural and Environmental Sciences, Newcastle University, Newcastle-upon-Tyne, United Kingdom*; ELANGANNAN ARUNAN, *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India*.

Phenylacetylene (PhAc) is a multifunctional molecule and has been termed a "Hydrogen Bonding Chameleon"[a]. In 2008, Patwari and co-workers studied complexes of PhAc with various molecules, including H_2O and CH_3OH, by the IR-UV double resonance spectroscopic technique[b]. This study found that H_2O donates the H-bond to the acetylenic π-system, whereas CH_3OH donates the H-bond to the phenyl π-system. Recently, Suhm's group used FTIR spectroscopy of supersonic jet expansions to study PhAc with H_2O and CH_3OH and observed that both H_2O and CH_3OH donate H-bond to the acetylenic π-system[c]. The acetylenic preference in the PhAc···H_2O complex has already been confirmed by rotational spectroscopy[d]. In this work, the rotational spectrum of PhAc···CH_3OH complex has been studied. The rotational spectrum of the parent and isotopologues of PhAc···CH_3OH complex was recorded over the 2-8 GHz frequency range using the Chirped Pulse Fourier Transform Microwave (CP-FTMW) Spectrometer at Newcastle University, UK, and from 8-14 GHz using the Pulsed Nozzle Fourier Transform Microwave Spectrometer (PN-FTMW) at IISc Bangalore, India. The structure where CH_3OH donates the H-bond to the acetylenic π-system and CH_3OH accepts a weak H-bond through the ortho hydrogen of the PhAc was observed. The rotational transitions were split, indicating the internal motion of the CH_3 group in CH_3OH. The observed global minimum structure has been compared with several CH_3OH-containing complexes to understand the internal rotation of the CH_3 group and its effect on V_3 barrier height.

[a] Maity, S., Guin, M., Singh, P. C., & Patwari, G. N. (2011). *ChemPhysChem*, 12(1), 26-46.
[b] Singh, P. C., & Patwari, G. N. (2008). *The Journal of Physical Chemistry A*, 112(23), 5121-5125
[c] Karir, G., Lüttschwager, N. O., & Suhm, M. A. (2019). *Physical Chemistry Chemical Physics*, 21(15), 7831-7840
[d] dGoswami, M., & Arunan, E. (2011). *Physical Chemistry Chemical Physics*, 13(31), 14153-14162

MK05 **2:57 – 3:12**

ANALYSIS OF A AND E COMPONENTS OF THE ν_{21} TORSIONAL FUNDAMENTAL OF PROPENE AT 188 cm^{-1}

PETER GRONER, *Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO, USA*; STEPHEN J. DAUNT, *Department of Physics & Astronomy, The University of Tennessee-Knoxville, Knoxville, TN, USA*; BRANT E. BILLINGHURST, JIANBAO ZHAO, *Materials and Chemical Sciences Division, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada*; COLIN WESTERN[a], *School of Chemistry, University of Bristol, Bristol, United Kingdom.*

The far infrared spectrum of propene, $\mathrm{CH_3-CH=CH_2}$, has been measured at 193.65 K with a resolution of 0.00096 cm^{-1}on the FIR beamline at the Canadian Light Source (CLS) synchrotron. The torsional fundamental band ν_{21} at 188 $\mathrm{cm}^{-1}$is quite complex because the coupling of the angular momenta of the overall rotation with the internal rotation of the $\mathrm{CH_3}$ group splits every rovibrational energy level (without internal rotation) into an A- and an E-component. As a result, every rovibrational transition splits into two or three components. To predict and assign the spectrum and to determine spectroscopic constants by the LS method, the ERHAM program [b] has been modified to use it for rovibrational spectra.

Initially, the spectroscopic constants for the ground state (GS) were fixed at the values determined by Craig et al.[c] from almost 900 microwave and millimeter-wave frequencies. This was good enough to begin the assignment of transitions of ν_{21} involving low K_a levels. However, for $K_a > 3$, the ratio of the standard deviation over the estimated experimental uncertainty increased with increasing K_a despite the introduction of additional tunneling parameters.

Only the inclusion of the internal rotation parameters ρ and β (which had been held constant with the GS constants) among the variable parameters brought the standard deviation down to an acceptable level. From then on, the transitions of ν_{21} were used simultaneously with all GS transitions (footnote b) to fit the parameters of two different effective internal rotation Hamiltonians (one each for the GS and ν_{21} levels) but with shared ρ and β. More than 6000 individual transitions (J up to 50, K_a up to 8) have been assigned so far for the ν_{21} band and preliminary constants have been obtained, among them an improved internal rotation barrier.

[a] Deceased Sept. 21, 2021
[b] P. Groner, J. Chem Phys. (1997) 107, 4483; J. Mol. Spectrosc. (2012) 278, 52
[c] N. C. Craig et al., J. Mol. Spectrosc. (2016) 328, 1

MK06 **3:15 – 3:30**

BARRIERS TO INTERNAL ROTATION AND MOLECULAR GEOMETRIES OF COMPLEXES FORMED BETWEEN ISOMERS OF METHYLTHIAZOLE AND WATER STUDIED BY MICROWAVE SPECTROSCOPY

CHARLOTTE CUMMINGS, *School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom*; WENTAO SONG, *Dipartimento di Chimica "Giacomo Ciamician", University of Bologna, BOLOGNA, BOLOGNA, Italia*; HA VINH LAM NGUYEN, *Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, 94010 Créteil, France, Institut Universitaire de France (IUF), 75231, Paris, France*; NICK WALKER, *School of Natural and Environmental Sciences, Newcastle University, Newcastle-upon-Tyne, United Kingdom.*

The (V_3) barriers to internal rotation of many five-membered heteroaromatic rings have been investigated using microwave spectroscopy. The rotational spectra of 2-methylthiazole$\cdots\mathrm{H_2O}$, 4-methylthiazole$\cdots\mathrm{H_2O}$ and 5-methylthiazole$\cdots\mathrm{H_2O}$ were recorded over the frequency range 7.0-18.5 GHz using Chirped Pulse Fourier Transform Microwave (CP-FTMW) spectroscopy. The complexes were generated in a supersonic expansion containing low concentrations of a methylthiazole isomer and water in an argon buffer gas. In total spectra of five isotopologues of each complex have been assigned and analysed. The fitting of observed *A*-species transition frequencies to Watson's S-reduced Hamiltonian within PGOPHER gave "effective" fits of each complex. Global fits (simultaneous fitting of both *A*- and *E*- species transitions) have been performed using XIAM allowing the determination of rotational constants (A_0, B_0, C_0), centrifugal distortion constants (D_J, D_{JK}, d_1, d_2) and nuclear quadrupole coupling constants (χ_{aa}(N) and χ_{bb}(N) - χ_{cc}(N)) as well as the V_3 barrier to internal rotation. The monohydrate complexes are formed by a non-linear hydrogen bond between $\mathrm{H_2O}$ acting as the hydrogen bond donor and the nitrogen atom of the methylthiazole ring which is the hydrogen bond acceptor. The influence formation of the monohydrate complex on the V_3 barrier will be discussed.

MK07 **3:33 – 3:48**

THEORETICAL SPECTROSCOPIC STUDY OF ISOPROPYL ALCOHOL ($CH_3 - CHOH - CH_3$)

MARIA LUISA S SENENT, *Inst. Estructura de la Materia, IEM-CSIC, Madrid, Spain*; MOHAMMED SALAH, *LS3MN2E/CERNE2D, Faculté des Sciences Rabat, Mohammed V Rabat, Rabat, Morocco*.

Isopropyl alcohol ($CH_3 - CHOH - CH_3$) is a non-rigid species of atmospheric and astrophysical interest. We present highly correlated ab initio calculations (CCSD(T)-F12/CVTZ-F12) performed for the study of the FIR region of the spectrum. The molecule can be classified in the MSG G_{18}. It shows three interacting internal rotations corresponding to the two methyl groups and the OH alcoholic group. Torsional energy levels and subcomponents are determined variationally from a three-dimensional potential energy surface. For the classification of the computed levels, we apply symmetry considerations. Final torsional wave-functions denote the relevance of the interactions on the results. Perturbation theory is also used to determine the vibrational corrections of rotational constants. This project has received funding from the European Unionś Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 872081.

Intermission

MK08 **4:28 – 4:43**

MILLIMETER-WAVE SPECTROSCOPY OF AMMONIA-WATER WEAKLY BOUNDED COMPLEX[a]

PRAKASH GYAWALI, R. A. MOTIYENKO, L. MARGULÈS, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, Univ. Lille, CNRS, F-59000 Lille, France*; LUYAO ZOU, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*; ISABELLE KLEINER, *Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, 75013, Paris, France*.

The broadband rotational spectra of ammonia-water (NH_3-H_2O) complex were measured in the frequency range from 50 to 250 GHz using a supersonic-jet emission spectrometer. The NH_3-H_2O complex exhibits two large amplitude motions (LAMs): almost free internal rotation of ammonia owing to very low torsional barrier ($\approx 10\ \mathrm{cm}^{-1}$), and the inversion of water characterized by relatively high barrier ($\approx 700\ \mathrm{cm}^{-1}$). Because of the latter and taking Doppler-limited resolution of spectrometer into account, we could not observe inversion tunneling splittings of a-type rotational transitions. In total, about 150 rotational transitions of NH_3-H_2O were assigned in this study. They were fitted together with the data from previous studies[b] using the "hybrid" Hamiltonian approach[c]. The analysis is in progress as we are currently trying to modify the characteristics of supersonic expansion in order to achieve higher rotational temperatures and consequently to measure higher K_a transitions. The latest results will be presented.

[a]This work has been supported by the French PN LEFE and ANR Labex CaPPA through the PIA under Contract No. ANR-11-LABX-0005-01
[b]P. A. Stockman, R. E. Bumgarner, S. Suzuki, & G. A. Blake, *J. Chem. Phys.* **96**, 2496 (1992); G. T. Fraser & R.D. Suenram, *J. Chem. Phys.* **96**, 7287 (1992)
[c]I. Kleiner & J. T. Hougen, *J. Mol. Spectrosc.* **368**, 111255 (2020)

MK09 **4:46 – 5:01**

INTERNAL ROTATION ANALYSIS AND STRUCTURE DETERMINATION OF R-CARVONE

NICOLE MOON, G. S. GRUBBS II, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.

When the spectrum of R-carvone was collected at Missouri S&T in preparation for a three-wave mixing experiment, splittings within the rotational transitions were observed that were unassigned in both the original study of S-carvone by Moreno et al.[a] and the monoterpenoid study by Loru et al.[b] As reported at the 75th annual ISMS, it was discovered that these splittings were due to internal rotations caused by two non-equivalent methyl rotors. This prompted a reinvestigation into the pure rotational spectrum of R-carvone using chirped-pulse, Fourier transform microwave (CP-FTMW) spectroscopy within the 5-18 GHz region of the electromagnetic spectrum. Since initially reporting this finding, all parent species and singly substituted isotopologues for the six conformers of carvone have been analyzed using XIAM[c]. Within this presentation, the results of the reinvestigation will be reported, including the experimentally derived molecular structures for the six conformers as well as the experimentally determined barrier heights to internal rotation.

[a]Moreno, J. R. A.; Huet, T. R.; González, J. J. L. Struct Chem. 2013, 24, 1163.
[b]Loru, D.; Vigorito, A.; Santos, A. F. M.; Tang, J.; Sanz, M. E. Phys. Chem. Chem. Phys. 2019, 21, 26111-26116.
[c]Hartwig, H.; Dreizler, H. Z. Naturforsch. 1996, 51a, 923-932.

MK10 **5:04 – 5:19**

CONFORMATIONAL LANDSCAPE AND INTERNAL DYNAMIC OF LEVULINIC ACID FROM BROADBAND ROTATIONAL SPECTROSCOPY

ELIAS M. NEEMAN, NOUREDDIN OSSEIRAN, THERESE R. HUET, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*.

Lignocellulose is the most abundantly available raw material on the Earth for the production of biofuels.[a] The main challenge is to produce useful chemicals from it. A variety of chemicals and biomolecules are produced via the hydrothermal conversion of waste biomass. Among the produced products is levulinic acid (LA). This biomolecule is considered to be of the top 10 chemical compounds[b] as it has an important potential to be considered as a platform chemical.[c] It is used in the production of diverse chemical compounds in different area such as pharmaceuticals, herbicides, polymers, fuels etc.. Gas phase rotational studies permit a better understanding of intermolecular interactions that control the conformation landscape of molecules and their internal dynamics. We present herein, a broadband rotational study in jet-cooled conditions, of the relevant levulinic acid in the 6-18 GHz range. One conformer has been identified in the gas phase. The spectrum showed clearly that the lines were split. This splitting is due to the internal rotation of the methyl group. The *A* and *E* states lines were assigned and fitted, and the experimental barrier of the methyl torsion was determined.

[a] C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong and J. Beltramini, Chem. Soc. Rev., 2011, 40, 5588–5617

[b] T. Werpy, and G. Petersen, Top Value Added Chemicals from Biomass: Volume I, Results of Screening for Potential Candidates from Sugars and Synthesis Gas. United States: N. p., 2004.

[c] G.C. Hayes, and C.R. Becer, 2020. Polymer Chemistry, 11, 4068-4077.

MK11 **5:22 – 5:37**

IMPROVED ANALYSIS OF THE ROTATION SPECTRUM OF META-CHLOROTOLUENE USING A FREE ROTOR BASIS AND NON-PERTURBATIVE HYPERFINE TREATMENT

J. H. WESTERFIELD, S E WORTHINGTON-KIRSCH, KYLE N. CRABTREE, *Department of Chemistry, University of California, Davis, Davis, CA, USA*.

Using the soon to be publicly available westerfit package, the rotational spectrum of meta-chloro-toluene has been re-examined. This program allows for treatment of a C_s molecule with an arbitrary-fold internal rotor and a single strong spin source which makes meta-chloro-toluene a promising test case for the code. Unlike other programs designed for internal rotation with spin effects, westerfit includes matrix elements off-diagonal in N rather than the perturbative treatment of the spin-rotation and quadrupole interactions. This allows fitting of all symmetrically allowed terms in both the spin-rotation and the quadrupole tensors as well as inclusion of any higher order terms coupling the large amplitude motion to the spin angular momentum. Meta-chloro-tolune is a particularly challenging case for internal rotor packages due to the low V_3 term coupled to a large V_6 term as well as the spin 3/2 nucleus. Previous attempts to fit this molecule[a] were complicated by XIAM's limitations at very low barrier heights and perturbative quadrupole treatment. This work presents a more complete treatment of the meta-chloro-toluene spectrum and demonstrates comparisons between westerfit and other programs.

[a] Nair et al, J. Mol. Spec. 361 (2019), p1-7

ML. Spectroscopy as an analytical tool

Monday, June 19, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: Rebecca A. Peebles, California State University, Sacramento, Sacramento, CA, USA

ML01 **1:45 – 2:00**

DEVELOPMENT OF QUANTITATIVE APPLICATIONS FOR MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY

ANN ADELE BYARS, ALEX MIKHONIN, REILLY E. SONSTROM, VOISLAV BLAGOJEVIC, JUSTIN L. NEILL, *BrightSpec Labs, BrightSpec, Inc., Charlottesville, VA, USA*; BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

The greatest strength of molecular rotational resonance spectroscopy as an analytical technique is its ability to unambiguously resolve the spectral signatures of multiple compounds, including isomers, within a mixture without requiring separation or purification. When a mixture of compounds is present, it is extremely desirable to accurately quantify each of these components. For applications in the chemical and pharmaceutical industry, a majority of the challenges in quantitative analysis are related to how the sample is handled and measured. In this talk, I will discuss our ongoing efforts to address these challenges. Some of these topics include absolute quantitation of analytes within an unknown matrix; relative quantification of a set of compounds with a difference in vapor pressure; and calibration of molecular response factors without pure reference standards.

ML02 **2:03 – 2:18**

ON-SITE & REAL TIME THz MONITORING OF GASEOUS EMISSION FROM A WASTE RECOVERY CENTER

JEAN DECKER, FRANCIS HINDLE, EIRC FERTEIN, NICOLAS HOUZEL, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*; FABRICE CAZIER, *Centre Commun de Mesures, Université du Littoral Côte d'Opale, Dunkerque, France*; GAËL MOURET, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*; JULIEN DUMONT, *Paprec Energies 59, Paprec, Dunkerque, France*; ARNAUD CUISSET, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*.

The Dunkirk waste recovery center continuously treats all of the urban community's household waste by converting it into electrical and thermal energy through incineration. These activities are carried out with a controlled environmental impact, based on continuous improvement. The TeraWaste project explores the potential of high-resolution TeraHertz spectroscopy for continuous monitoring of gaseous emissions by developing an on-site diagnostic unit. The selectivity and the ability to detect in scattering media make it a relevant alternative to current multi-compounds monitoring solutions[abc]. A new sub-millimeter wave source, acquired for this project and allowing the detection of trace gases, was characterized, the spectrometer developed and the detection limits of regulated compounds determined. Rotational spectroscopy measurements on real process and emission gases, sampled and analyzed off-line as well as in real time on-site, were performed and compared with standard reference methods and the certified continuous measurement system. Using preconcentration[de], a quantified multi-species mapping, extended to the various polar compounds absorbing the sub-mm waves of the plant's gaseous emissions, in particular VOCs by discriminating them, will enable the operator to better meet current standards and anticipate potential evolution in the regulations.

[a] G. Mouret et al., IEEE Sensors J., vol. 13, no. 1, pp. 133–138, Jan. 2013, doi: 10.1109/JSEN.2012.2227055.
[b] T. Uno et al., Jpn. J. Appl. Phys., vol. 49, no. 4S, p. 04DL17, Apr. 2010, doi: 10.1143/JJAP.49.04DL17.
[c] H. Bidgoli et al., IEEE Trans. THz Sci. Technol., vol. 4, no. 6, pp. 722–733, Nov. 2014, doi: 10.1109/TTHZ.2014.2357344.
[d] C. F. Neese et al., IEEE Sensors J., vol. 12, no. 8, pp. 2565–2574, Aug. 2012, doi: 10.1109/JSEN.2012.2195487.
[e] N. Rothbart et al., Sensors, vol. 19, no. 12, p. 2719, Jun. 2019, doi: 10.3390/s19122719.

ML03 **2:21 – 2:36**

A SYNTHETIC METHODOLOGY TO PRODUCE TAILORED DEUTERATION PATTERNS IN BUILDING BLOCK MOLECULES WITH HIGH ISOTOPOMER SPECIFICITY VERIFIED BY MOLECULAR ROTATIONAL SPECTROSCOPY

JUSTIN WEATHERFORD-PRATT, *Department of Chemistry, University of Virginia, Charlottesville, VA, USA*; W. DEAN HARMAN, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*; SARAH BREWSTER, *Department of Chemistry, University of Virginia, Charlottesville, VA, USA*; HALEY N. SCOLATI, MARTIN S. HOLDREN, BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

Building block molecules with precisely controlled deuteration patterns are needed for several applications in chemistry including mechanistic studies and the production of deuterated active pharmaceutical ingredients with improved efficacy and safety. The Harman group recently reported an organometallic chemistry methodology to add deuterium to benzene with high stereoselectivity providing access to a wide range of deuteration patterns in the cyclohexene reaction product. This methodology provides access to 52 unique isotopic variants of cyclohexene covering 10 isotopologues. Establishing the stereoselectivity of the synthesis is a challenge, especially for highly deuterated substrates, and requires a technique that can quantitatively analyze both the isotopologue and isotopomer distribution in a potentially complex mixture of deuterated reaction products. Molecular rotational resonance (MRR) spectroscopy is well-suited for this analysis challenge. The application of MRR analysis to understand the stereoselectivity in the different reaction steps of the conversion of benzene to target deuterated cyclohexene reaction products is the focus of the current work. In one example, the availability of a routine, rapid isotopologue/isotopomer analysis technique is used to gain insight on the mechanistic chemistry and, subsequently, to improve the selectivity for the synthesis of cis-3,4-cyclohexene-d2. Optimization of the reaction conditions leads to the production of the target species with less than 0.1% over-deuteration and low levels of underdeuteration (mainly from the 3-cyclohexene-d1 isotopomer). The stereoselectivity of the synthesis is demonstrated by the low levels of the anti-3,4-cyclohexene-d2 isotopomer that is present at below 0.3%.

ML04 **2:39 – 2:54**

LEAST SQUARES FIT OF LINE PROFILES IN TRANSMITTANCE AND ABSORBANCE SPECTRA WITH DETECTOR OR SOURCE NOISE II

HIROYUKI SASADA, *National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan*.

In line profile analyses of an observed spectrum using an equally weighted least squares method, statistic mathematics states that we have to use transmittance spectrum (TS) / absorbance spectrum (AS), a negative logarithm of the TS, when the detector noise (DN) / the source noise (SN) is dominant in the observed spectrum. To evaluate quantitative differences between the correct analyses, TS with DN and AS with SN, and the incorrect analyses, TS with SN and AS with DN, we calculate TS of a Lorentz profile with three profile parameters of absorption strength, center frequency, and width and simulate the observed spectrum by adding a certain magnitude of either DN or SN to the calculated TS. The simulated TS and AS with DN or SN are fitted to the Lorentz profile using the least squares methods. The correct analyses reproduce the noise magnitude and the profile parameters and properly give expected uncertainties of the parameters regardless of the absorption strength and the noise magnitude. The incorrect analyses reproduce the profile parameters but not the noise magnitude even for rather small absorption strength and do not give the proper expected uncertainties of the parameters for the large absorption strength. Properly weighted least squares fits of TS with SN and AS with DN properly provide the noise magnitude and the expected uncertainties of the parameters but the determined absorption strengths and widths are considerably biased in some cases. We also show how to determine the noise magnitudes of DN and SN in the observed spectrum, which must be reported in a paper on experimental spectroscopy because the noise property is essential for the least squares methods.

Intermission

ML05 **3:34 – 3:49**

ULTRAVIOLET SPECTROSCOPY OF SUBCRITICAL AND SUPERCRITICAL METHANOL

IRENEUSZ JANIK, *Radiation Laboratory, University of Notre Dame, Notre Dame, IN, USA*; TIMOTHY W MARIN, *Physical Science, Benedictine University, Lisle, IL, USA*.

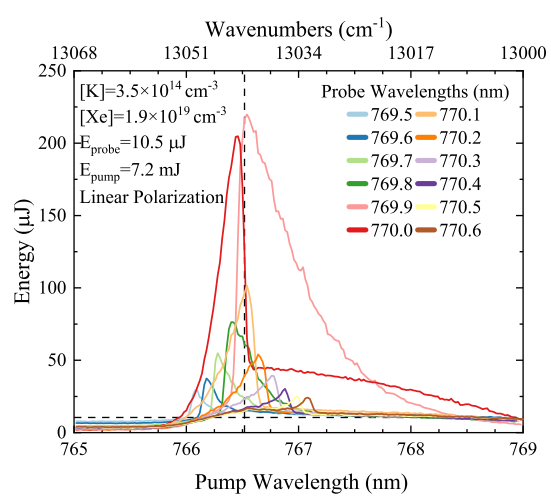
Measuring far UV light transmission through thin fluid films, methanol's absorption spectra were recorded between 150 and 220 nm (8.27-5.63 eV). Spectral changes were monitored in the function of temperature (from ambient to supercritical conditions) and pressure (at 250°C i.e., above the supercritical point). The room temperature spectrum peak is shifted red by 4.5 nm from the previously reported position obtained by the same technique, yet agrees well with the position recorded by the attenuated total reflection (ATR) method. Unlike in water, the neat methanol spectrum shows no apparent red tail, which contradicts previous findings based on ATR studies. Upon an increase in temperature, the edge of the spectrum progressively shifts red. Still, unlike in water, this is not a symmetrical shift of the band as the lower part of the band shifts almost twice as much as the upper one, and the apparent peak position progressively shifts blue by an overall 0.13 eV upon reaching 250°C. At this temperature, a gradual decrease of pressure from 150 to 85 bar results in continuous narrowing and red shifting of the apparent band to 7.8eV, accompanied by a steady growth of an additional broad continuum band at 6.7eV. Further decrease of pressure to 14.5 bar leads to the full emergence of the low-density spectrum of supercritical MeOH. This spectrum resembles the methanol monomer, with characteristic 1st weak absorption band at 6.7eV due to the promotion on oxygen from $2p_z$ (HOMO) to 3s Rydberg orbital (acquiring antibonding character along the OH vibrational coordinate) and 2nd structured band at 7.84eV due to transition between a" and the 3p Rydberg orbitals. An increase in density depresses the intensity of the first band. It has a dramatic effect on the second absorption band, in which the sharp vibrational structure gradually diminishes in magnitude and disappears above 0.1 g cm^{-3}. This loss of detail cannot be explained solely by collisional broadening and/or dimerization. Still, it may suggest a gradual shift of the character of a transition from Rydberg to exciton.

ML06 **3:52 – 4:07**

LASER EXCITATION SPECTROSCOPY: AN ANALYTICAL TOOL FOR STUDYING ENERGY TRANSFER MECHANISMS IN KXe AND OTHER GAS MIXTURES

KAVITA V. DESAI, ANDREY E. MIRONOV, J. GARY EDEN, *Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Laser excitation experiments were conducted to study the energy transfer mechanisms in K-Xe mixtures with narrowband dye lasers. Specifically, the K-Xe gas mixture was excited by a tunable dye laser in the vicinity of the K D_2 line such that a population inversion on the K D_1 line was achieved. The second dye laser served as the probe and scanned around the K D_1 transition. Through these experiments, the amplified probe energy is measured and the pump gain profile is obtained as shown in the spectra. The obtained data suggests than an electronic and molecular stimulated Raman scattering (SRS) process occur and compete in KXe in addition to a broad pump absorbance for emission on the K D_1 line. The Raman shift associated with the molecular SRS process of $\sim$59 cm^{-1} is associated with the KXe $B^2\Sigma^+_{1/2}$ and the dissociative $X^2\Sigma^+_{1/2}$ interatomic potentials. Consequently, the $B^2\Sigma^+_{1/2}$ and $X^2\Sigma^+_{1/2}$ interatomic potentials of KXe at large R can be determined by comparing experiment with calculations of the Franck-Condon integrals and quasistatistic line-broadening theory.



ML07 **4:10 – 4:25**

EMERGENCE OF INTRA/INTER MOLECULAR INTERACTIONS WITHIN BINARY MIXTURE OF DEEP EUTECTIC SOLVENTS AND AN ORGANIC CO-SOLVENT

GARIMA BHUTANI, *Department of Chemical Sciences, Indian Institute of Science Education & Research, Mohali, Punjab, India*; TANVI, *Department of Physics, Punjab University, Chandigarh, Chandigarh, India*; ANAMIKA MUKHOPADHYAY, *Department of Physics, Sri Guru Gobind Singh College, Chandigarh, Chandigarh, India*; ARIJIT K DE, *Department of Chemical Sciences, Indian Institute of Science Education & Research, Mohali, Punjab, India*.

Deep eutectic solvents (DESs), a 'green' (i.e., environment-friendly) alternative to ionic liquids (ILs), have become a subject of intense research because of their widespread applications and advantages over organic volatile solvents. The physicochemical properties of DESs, particularly their polarities, can be easily tailored by choosing a vast range of combination of hydrogen bond donors and acceptors (HBDs-HBAs) and organic co-solvents in a binary mixture. Here, intra/inter molecular interactions play an important role in tuning these bulk physicochemical properties. Thus, it is essential to comprehend its solvent-solvent and solute-solvent interactions at the molecular level. In the present study, the synergistic effect or the HBD-HBA interactions in binary mixture of DESs with organic co-solvent such as dimethyl sulfoxide (DMSO) is investigated [1]. Additionally, we mapped the emergence of new vibrational interactions in binary mixture at a particular composition of DMSO [2]. To track these vibrational interactions, we implemented impulsive stimulated Raman spectroscopy (ISRS) [3-4]. These experimental findings are further supported by theoretical studies.

References: [1] G. Bhutani, V. Yadav, A. Yadav, and A. K. De, Frontiers in Optics + Laser Science 2022 (FIO, LS), Technical Digest Series (Optica Publishing Group, 2022), paper LW6F.4, 2022. [2] G. Bhutani, V. Yadav, A. Yadav, and A. K. De, Asian Journal of Physics, 905-912, 31 (9-10), 2022. [3] S. Dhamija, G. Bhutani, A. Jayachandran, and A. K. De, The Journal of Physical Chemistry A, 1019-1032, 126(7), 2022. [4] S. Dhamija, G. Bhutani, and A. K. De, ChemPhysChem, 2023 (under review, Manuscript ID: 202300087).

ML08 **4:28 – 4:43**

SPECTROSCOPIC SIGNATURES AND EXCITED STATE DYNAMICS OF ISOLATED AND HYDRATED METHYLATED XANTHINES

VIPIN BAHADUR SINGH, *Department of Physics, Udai Pratap Autonomous College, Varanasi, India*.

We present a detailed analysis of vibrational spectroscopic signatures and hydration effects on the properties of low-lying excited electronic states of caffeine and theophylline. The reported experimental spectra and structural motifs of methylated xanthines are compared and analyzed with our computed quantum chemical values to make an incredible interpretation more systematic. The binding energy of the newly characterized theophylline dimer Form IV linked by a double hydrogen bond was found to be 88 KJ/mole at the MP2 level, more significant than that of a similar xanthine dimer. Computed IR spectra of theophylline dimer are in remarkable agreement with the experiment, and the out-of-phase (C=O)2 stretching mode shows a tripling of intensity upon dimerization. One striking feature found is the coexistence of the blue and red shift of the vertical excitation energy of the optically bright state S1 (1 ΠΠ*) of caffeine, theophylline, and xanthine upon forming a complex with water at C2=O and C6=O carbonyl sites, respectively, probably arisen due to variation in pi-electron delocalization. We would also discuss recently reported Coherent energy transfer between the symmetric and asymmetric carbonyl stretching modes of caffeine and theophylline that gives rise to a Quantum Beat in our results framework. The missing of the most stable O6-bonded monohydrated complexes of caffeine in the R2PI spectra illuminated the assumption that water at conjugated carbonyl sites can alter the relaxation profile by opening an additional channel for the ultrafast radiationless decay from the lowest photo-excited state S1 to the electronic ground state. The high photostability of nucleic acid bases, adenine, and guanine is consistent with the efficient nonradiative deactivation of O-bonded monohydrates of caffeine and theophylline, suggesting that these stimulants could have been photostable building blocks in prebiotic environments.

1. A T Hanes et al J. Chem. Phys. 158, 044302 (2023) 2. S. Gomez et al Phys. Chem. Chem. Phys 22 5929 (2020) 3. Vipin Bahadur Singh, RSC Adv 5, 11433 _11444(2015) 4. Vipin Bahadur Singh, RSC Adv 4, 58116 _58126(2014)

TA. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Tuesday, June 20, 2023 – 8:30 AM

Room: 116 Roger Adams Lab

Chair: J. Mathias Weber, University of Colorado, Boulder, CO, USA

TA01 **8:30 – 8:45**

LEAK-OUT SPECTROSCOPY: A UNIVERSAL METHOD OF ACTION SPECTROSCOPY IN COLD ION TRAPS

PHILIPP C SCHMID, OSKAR ASVANY, SVEN THORWIRTH, THOMAS SALOMON, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

So far, action spectroscopy in cold ion traps has been relying on a change of the ion mass by fragmentation upon photon absorption, pre-dissociation of tagged ions or via laser induced chemical reactions. Despite the advances of these techniques they could not be applied to many important ions. Here, a new method of action spectroscopy in cold ion traps, termed leak-out spectroscopy (LOS [a]) is presented. LOS is based on transfer of internal energy to translational energy upon collision of the excited ion with a neutral collision partner. By detecting these accelerated ions leaving the ion trap, their spectrum is recorded. [b] This method is background free and may be applied to any ion (cation/anion). Ro-vibrational spectra are recorded in high-resolution. IR-MMW double resonance is used to record rotational spectra. The method also works using pulsed lasers. Recent examples will be highlighted. Moreover, due to the trapping of a finite ensemble, all ions addressed by the excitation can be kicked out. Therefore, the content of the trap can be analyzed for isomers or other isobaric but spectroscopically distinct species. This analysis can also be used for an isomer specific preparation prior to subsequent experiments.

[a] Patent pending: DE 10 2021 127 556.3 (Universität zu Köln), 22.10.2021

[b] P. C. Schmid, O. Asvany, T. Salomon, S. Thorwirth, and S. Schlemmer, "Leak-Out Spectroscopy, A Universal Method of Action Spectroscopy in Cold Ion Traps", J. Phys. Chem. A, 126, 8111-8117 (2022)

TA02 **8:48 – 9:03**

DETERMINATION OF THE ORTHO-TO-PARA RATIO OF H_3^+ IN A CRYOGENIC ION TRAP

PHILIPP C SCHMID, THOMAS SALOMON, OSKAR ASVANY, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

A clean sample of ortho (o) and para (p) H_3^+ is prepared in a cryogenic 22-pole ion trap by removing one of the two nuclear spin species. This isolation is reached on time scales below one second by a selective excitation of the ν_2 vibrational mode of H_3^+ addressing a rotational state associated with one of the two species. In subsequent collisions of the excited H_3^+ with Helium buffer gas the vibration-to-translation (V-T) energy transfer produces fast H_3^+ of the addressed spin configuration which then leaves the trap via a small electrostatic barrier. Rotationally inelastic collisions ensure that all species belonging to one nuclear spin state are visiting the state which is subject to laser excitation. Following this protocol the o/p-ratio of H_3^+ coming from the ion source is determined to be 1:1, as expected. In the presence of normal hydrogen, n-H_2, as an additional collision gas in the cryogenic ion trap the o/p-ratio of H_3^+ reaches a stationary value close to 1:3. This ratio can be rationalized by the ordering of the lowest energy states of o-H_3^+ and p-H_3^+ as will be discussed. This work shows that nuclear spin specific but also structural isomer specific preparation and analysis is now possible in cryogenic ion traps thanks to LOS. With this aid, action spectra of isomer mixtures can be disentangled and it will become possible to determine isomer branching ratios of chemical reactions, as well as to study state-specific reactions like for the fundamental H_3^+ + H_2 collision system considered in this work. Using a clean sample of p-H_2 as a collision gas will allow us to even determine state-to-state rate coefficients for this reaction. These rate coefficients are most important for the o/p-ratio of H_3^+ in space.

TA03 **9:06 – 9:21**

CAPTURE AND CHARACTERIZATION OF NASCENT UV PHOTODECOMPOSITION PRODUCTS WITH MASS-SELECTIVE CRYOGENIC TRAPPING TECHNIQUES

OLIVIA MOSS, PAYTEN HARVILLE, TIM SCHLEIF, EVAN H PEREZ, MARK JOHNSON, *Department of Chemistry, Yale University, New Haven, CT, USA*.

The photodecomposition pathways of polyatomic molecules are important processes ranging from UV photodamage of biopolymers to the transformations undergone by aerosols in the troposphere. This typically occurs in complex environments in which chromophores are embedded in electrolyte solvents. In this poster, we will present an experimental scheme in which target molecular ions are complexes with ions and solvent molecules and exposed to UV light in a temperature controlled ion trap. The nascent photoproducts are then cooled and tagged with H_2 molecules so that their structures can be established by comparison of their vibrational band patterns with those calculated for candidate structures. We demonstrate this approach on the photodecarboxylation of the conjugate base of benzoylbenzoic acid, a proxy molecule widely used to simulate radical photoinitiation by UV excitation at the air-water interface. We cool and trap the phenide carbanion photoproduct as well as a radical anion generated by loss of HCO_2 from the deprotonated scaffold. We will discuss the dependence of the branching ratios for CO_2 loss vs solvent loss in the BBA-M^{2+}-(solvent)$_n$ complexes with M=Mg and Ca and solvent = CH_3CN and H_2O. Analysis of the frequency dependence of the product branching ratios supports a model in which some of the UV photon energy remains trapped in an electronically excited state, potentially revealing formation of triplet states long invoked to rationalize their propensity to act as radical photosensitizers.

TA04 **9:24 – 9:39**

ONLINE MONITORING OF ENANTIOMERIC RATIOS BY CHIRALITY RECOGNITION IN THE GAS PHASE

SONJA SCHMAHL, JIAYE JIN, FRANCINE HORN, *Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie , Universität Leipzig, Leipzig, Germany*; HANNES WESTPHAL, DETLEV BELDER, *Institut für Analytische Chemie, Universität Leipzig, Leipzig, Germany*; KNUT R. ASMIS, *Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie , Universität Leipzig, Leipzig, Germany*.

Asymmetric synthesis with high stereoselectivity and yield remains a fundamental challenge in organic chemistry. Optimization of reaction parameters requires universal methods for fast and accurate characterization of chiral reaction products and intermediates with low sample consumption. In the present work, a gas-phase method for online monitoring of enantiomeric ratios is developed. The asymmetric synthesis is performed on a microfluidic chip reactor coupled to a cryogenic ion trap triple mass spectrometer. The chiral analyte is transferred from solution to the gas phase By electrospray ionization, where it is thermalized to room temperature and then interacts with a chiral selector molecule. Diastereomeric complexes are formed, and the gas phase vibrational spectra of the mass-selected complexes are recorded in the O-H and N-H stretching region. Differences in the position and intensity of the modes allow differentiation and quantification of the enantiomers.

The method is first demonstrated for mixtures of L- and D-alanine. Diastereomeric complexes are formed with one to three 2-butanol molecules. For a fast determination of the diastereomeric ratio, a smaller spectral region (60 cm^{-1}) of the vibrational spectrum of the complex with two 2-butanol molecules is recorded. Evaluation of the data with cosine similarity matching shows that the ratio of the diastereomeric complexes determined using this method is directly transferable to the enantiomeric ratio in solution. The method is then used to optimize the parameters of an on-chip transfer hydrogenation. The influence of reaction parameters, such as the nature of the solvent and acid, on the selectivity of the reaction is optimized using this method. The influence of varying the chiral selector is also studied.

TA05 **9:42 – 9:57**

NONLINEAR TIME-DOMAIN CRYOGENIC ION VIBRATIONAL SPECTROSCOPY WITH ULTRAFAST INFRARED PULSES

ZIFAN MA, LIANGYI CHEN, JOSEPH FOURNIER, *Department of Chemistry, Washington University, St. Louis, MO, USA*.

Nonlinear infrared spectroscopy in condensed phases offers valuable structural and dynamical information, but can be challenging to interpret due to factors like spectral congestion, solvent background, and low sensitivity. Cryogenic Ion Vibrational Spectroscopy (CIVS) overcomes some of these challenges by measuring infrared spectra of isolated ions quenched into their lowest-energy configurations. Spectra must be recorded indirectly using an action response, typically the photodissociation of weakly bound "tag" molecules like N_2. Traditionally, CIVS employs tunable single-color laser sources with few-cm^{-1}bandwidth and ns pulse durations. The combination of ultrafast laser sources with the sensitivity of CIVS presents an exciting new platform to directly probe vibrational dynamics in complex molecular ion systems. Here, the instrumentation and methodology for time-resolved CIVS will be discussed, and preliminary nonlinear (pump-probe) spectra of N_2-tagged tris(acetonitrile)tricarbonyl rhenium(I) ($Re(CO)_3(CH_3CN)_3{}^+{\cdot}N_2$) will be presented. The pump-probe experiments capture the bleaching signals of the asymmetric and symmetric carbonyl stretching modes. Excited-state absorption features are not observed, consistent with the expected Feynman pathways and previous action-based nonlinear measurements. The intensities of the two carbonyl stretch transitions oscillate with pump-probe delay time with a period equal to the energy difference between the transitions, demonstrating coherent coupling between the modes. These studies show the potential of combining CIVS with ultrafast sources into a single platform. This technique is expected to be extended to two-dimensional nonlinear spectroscopy and other systems of chemical and biological interest.

TA06 **10:00 – 10:15**

DEVELOPMENT OF AN ION-TRAP INSTRUMENT FOR ASTROCHEMICALLY RELEVANT REACTION KINETICS

DARYA KISURYNA, JULIANNA PALOTÁS, JESSICA PALKO, LEAH G DODSON, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*.

Metal-bearing cyanide species (MgCN, MgNC, MgC_3N, etc) have been detected in the outer circumstellar envelope of IRC+10216. However, data on the formation of these species, as well as the kinetic rates of such reactions is lacking. In our laboratory, we are developing a versatile custom-built ion instrument, which unites a glow-discharge ion source and ion trapping. This combination leverages the advantages of both techniques in reaction kinetics study. In this work, we describe not only our unique ion instrument, but also share preliminary results, details of the upcoming experiments, and future directions of implementing cavity ringdown spectroscopy to the system and making the ion trap cryogenic for astrochemically relevant research.

Intermission

TA07 **10:55 – 11:10**

TANDEM CRYOGENIC MASS-SELECTIVE DIGITAL ION TRAPS TO PRODUCE MOLECULAR CLUSTERS WITH COMPLEX ENVIRONMENTS

GINA ROESCH, ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

Cryogenic Ion Vibrational Spectroscopy (CIVS) is a tandem mass spectrometry and infrared spectroscopy technique used to gather structural information about ionic species. When coupled with a "reaction trap", the technique is especially powerful because ion manipulations can be performed prior to spectroscopic investigation. Species which are difficult to obtain directly the solution phase (i.e. solvated species, catalytic intermediates, etc.) can be accessed in the gas phase via ion-molecules reactions. Despite the robustness of the technique, there are still limitations in the complexity of the clusters that are achievable because only one synthetic step can be performed. Additionally, the inability to perform mass selection creates heavily cluttered spectra which can hinder the subsequent spectroscopic characterization step.

Here, we present a next-generation prototype instrument with a pair of cryogenic mass-selective digital ion traps. The advantages of the new design include a smaller footprint, less expensive circuitry and modular ion trap design to create a larger number of ion manipulation and mass filtering steps. The digital ion traps run on square wave RF potentials whose frequency and duty cycle can be manipulated to create high- and low-mass pass filters, respectively. Together, frequency and duty cycle filtering allow for mass selection within each cryogenic ion trap. These RF manipulations are compatible with the high pressure and low temperature necessary for solvent clustering. We show preliminary studies highlighting the performance in creating microsolvated clusters followed by in-situ mass selection of a specific cluster size. We also show that that the preferential formation of a particular cluster size can be achieved with duty cycle manipulation during the clustering process. Finally, we show that a mass-selected cluster can be transferred to a second ion trap and undergo a second clustering step, resulting in a multi-solvent cluster. Future plans for the multi-reaction trap instrument include characterizing water networks around small peptides by inserting a D_2O as a position sensitive spectroscopic molecular probe.

TA08 **11:13 – 11:28**

AN EXPERIMENTAL SETUP TO STUDY THE INFLUENCE OF HYDRATION ON SMALL CHARGED MOLECULAR SYSTEMS BY ROTATIONALLY RESOLVED VIBRATIONAL SPECTROSCOPY

ERIC S. ENDRES, FRANZISKA DAHLMANN, CHRISTIAN SPRENGER, KATHARINA GEISTLINGER, ROLAND WESTER, *Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria*.

Many biomolecules exhibit several structural isomers, which govern their functionality. The structure and thus the function of biomolecules are strongly influenced due to hydration with single water molecules and further by hydration shells.[a] This influence can be observed in different molecular systems e.g. in the change of the selective binding in host-guest complexes involving crown ethers [b], in the influence on the delocalized proton in charged water complexes [c] or in intramolecular vibrational energy redistribution after excitation by photons or collisions. Spectroscopy plays an increasingly important role in the study of structural details and thereby the function in molecular systems. [d] In this contribution an experimental setup to study the structure of small biomolecular ions and the influence of hydration by means of rotationally resolved pre-dissociation spectroscopy will be presented.

The setup consists of a nano-ESI, followed by two skimmers, enabling a gentle transfer into vacuum and avoiding breaking apart of the loosely bound water molecules. Further, the ions are confined in a cryogenic 16-pole wire ion trap, reaching temperatures below 3 K [e], leading to the binding of up to four helium atoms on protonated glycine ions.[f]

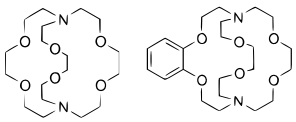
[a] Laage, Chem. Rev. 2017
[b] Glendening, JACS 1999
[c] Tuckerman, Science 1997
[d] Wolk, Acc. Chem. Res. 2014
[e] Geistlinger, Rev. Sci. Instrum. 2021
[f] Geistlinger, J. Mol. Spectrosc. 2021

TA09 **11:31 – 11:46**

EXPLORING THE CH STRETCH SPECTRAL REGION OF CRYPTAND/ION COMPLEXES WITH IR-UV DOUBLE RESONANCE SPECTROSCOPY AND LOCAL MODE HAMILTONIANS

EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*; CASEY DANIEL FOLEY, KENDREW AU, TIMOTHY S. ZWIER, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*.

The infrared spectroscopy of cryptands containing Na^+, K^+, Rb^+, Sr^{+2}, and Ba^{+2} ions are studied both theoretically and experimentally. Specifically, $[2, 2, 2]$ cryptand complexes are modified to contain a phenyl group as shown below.



The complexes are formed in solution and brought into the gas phase by electrospray methods. After mass selection, the complexes are introduced into a cryo-cooled octupole ion trap and cooled to 5 K. The aromatic chromophore in the crypt provides a UV absorption that is used to record a UV photofragment spectrum that shifts to unique wavelengths depending on size and charge of the embedded ion. Infrared spectra in the alkyl CH stretch region are recorded using IR-UV double resonance. The UV wavelength is fixed on the S_0-S_1 origin of the complex, while a tunable IR laser records the IR spectrum in the ground electronic state by depleting the photofragment ion signal. The resulting spectra are investigated theoretically by first searching for low-lying conformers and subsequently modeling the CH stretch fundamentals of these conformers with local mode Hamiltonians which include anharmonic coupling between CH stretches and nearby background states. In contrast to our previous work on alkanes, the ethoxy bridges enhance both CH_2 scissor and wag vibrational frequencies, with the result that scissor overtones and combination bands are detuned from the CH stretch vibrations. The increase in the wag frequencies leads to these modes playing a significant role in the spectral patterns of the CH stretch spectral region. These spectra are used to identify those conformers that are observed experimentally and to explore the role of the central ion's size in altering the structure of the crypt and, consequently, the peak patterns in the CH stretch spectral region.

TA10 **11:49 – 12:04**

THAT'S JUST, LIKE, YOUR OPINION, MAN - HOW DO WE KNOW WHEN WE HAVE A GOOD MATCH BETWEEN EXPERIMENTAL AND COMPUTED SPECTRA?

CHRISTOPHER J. JOHNSON, *Chemistry, Stony Brook University, Stony Brook, NY, USA*.

The use of quantum chemistry to compute spectra, vibrational or electronic, for use in assigning gas phase spectra and structures, is common. However, there is no accepted standard for appropriate criteria for what constitutes an acceptable match, in particular for the purposes of structure determination. This is due to challenges associated with anharmonic effects, systematic deficiencies of electronic structure methods, and a host of other idiosyncratic effects. I will discuss examples of these challenges from my own lab and propose some best practices and figures of merit. I hope this will provide a judgement-free starting point for the development of more rigorous methods for comparing experimental and computed spectra.

TB. Mini-symposium: Spectroscopy at Large-scale Facilities

Tuesday, June 20, 2023 – 8:30 AM

Room: 100 Noyes Laboratory

Chair: Anne Marie March, Argonne National Laboratory, Argonne, IL, USA

TB01 **8:30 – 8:45**

DIAGNOSTIC OF SMALL WEAK INTERACTIONS IN GASOLINE BLENDS BY ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY

JOSHUA G SMITH , SYLVESTRE TWAGIRAYEZU, *Chemistry and Biochemistry, Lamar University, Beaumont, TX, USA*; BRANT E. BILLINGHURST, JIANBAO ZHAO, *Materials and Chemical Sciences Division, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada*.

Attenuated Total Reflection Infrared Spectra of artificially-prepared gasoline blends have been recorded using the Far-Infrared Beamline at Canadian Light Source in the 600-1200 cm^{-1}region. The CLS Far-infrared Beamline is a synchrotron facility equipped with a high-resolution FT-IR spectrometer and an attenuated total reflection instrument capable of offering a very stable bright light sources and spectral high resolution. The present vibrational spectra display multiple, but distinct, vibrational signatures of ethanol,isopropanol,and hydrocarbon. The analysis of OH bend, C-C and CO stretches by fitting the observed vibrational spectra to a Voigt profile allowed the determination of vibrational centers. For both gasoline blends, we noted significant vibrational shifts and attribute these to changes in force constants as a result of small weak interactions between hydrocarbons and polar component of gasoline blend.

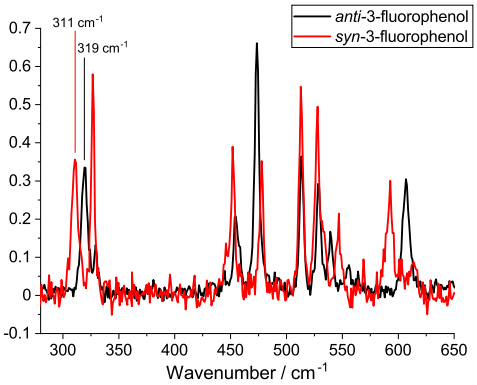
TB02 **8:48 – 9:03**

TOWARDS UNDERSTANDING FAR-IR INDUCED ISOMERISATION PROCESSES

OLGA A. DUDA, JOOST M. BAKKER, *HFML-FELIX, Radboud University, Nijmegen, The Netherlands*; DANIEL HORKE, *Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands*.

Conformational interconversion is a key aspect of such processes as protein folding, enzyme action via the induced fit mechanism, or the action of molecular motors. Although studies of the dynamics of interconversion exist, they are mostly limited to pump-probe spectroscopy involving electronic excitations, whereas the simplest of these interconversions take place on the ground state potential energy surface. *Ortho*- and *meta*-substituted phenols are simple model systems exhibiting *syn-anti* isomerism, with the two isomers differing by the orientation of the hydroxyl group either towards or away from the heteroatom substituent. The isomerisation reactions between *syn*- and *anti*- conformers are characterized by relatively low energy barriers and could potentially be driven using resonant IR vibrational excitation provided by a free electron laser, opening the potential to study interconversion dynamics on the ground state PES.

As a first step we have obtained isomer-specific IR spectra of 3-fluorophenol and 3-chlorophenol by means of IR-UV depletion spectroscopy. Each of these exhibit torsional –OH vibrational bands in the 250-350 cm^{-1}region, with isomer-specific frequencies observed for 3-fluorophenol (as shown in the figure). We subsequently probe the UV spectral response of these molecules following IR excitation of selected bands, employing an IR-UV double resonance scheme. We will present the results of these experiments aimed at understanding vibrational energy coupling in small aromatic systems, as well as discuss the potential for observing direct population transfer between *syn*- and *anti*-isomers.



TB03 ***INVITED TALK*** **9:06 – 9:36**

MODELING THE ACTIVE CENTERS OF CATALYSTS: THE UNIQUE COMBINATION OF GAS-PHASE ION TRAP REACTIVITY AND INFRARED SPECTROSCOPY

SANDRA LANG, *Department of Chemistry, Universität Ulm, Ulm, Germany*.

Catalysis represents the key of our modern chemical industry, is essential to reduce waste and air pollution, and plays an important role for solar energy storage as well as electrochemical energy conversion. To direct the optimization of heterogeneous and homogeneous catalysts and to develop new tailor-made catalytic materials a fundamental understanding of the catalytic reactions is indispensable. However, industrial catalysts are typically very complex systems often comprising multiple (nano)materials which render a detailed investigation of the catalytic processes on an atomic and molecular level difficult. To nevertheless gain an essential understanding of catalytic processes, we utilize small (sub)nanometer sized metal, metal-oxide, and metal-sulfur clusters as gas phase model systems. An important aspect that supports the feasibility of such very small isolated systems as catalytic model systems is the fact that catalysis is a local effect and thus generally very restricted to an Ångstrom size atomic area, the so called catalytically active center. These catalytically active centers are typically characterized by unsaturated bonds, like kinks, steps, defects, or very small particles in the sub-nanometer size range and can, thus, be very well modeled by isolated gas phase particles of appropriate size, charge, and material composition. In this talk I will demonstrate the power of gas-phase ion trap reactivity studies in combination with infrared multiple-photon dissociation (IR-MPD) spectroscopy and first-principles calculations to provide a molecular level understanding of fundamental catalytic processes. Particular focus will be on recent spectroscopic studies performed at the free-electron laser facility FELIX (Radboud University Nijmegen, The Netherlands) which are essential for understanding the catalytically active centers of heterogeneous catalysts, biocatalysts, as well as materials of astrochemical relevance.

TB04 **9:42 – 9:57**

COULOMB POTENTIAL EFFECT ON CARRIER ENVELOPE PHASE DEPENDENT (CEP) STRONG-FIELD IONIZATION

EMMANUEL AYORINDE ORUNESAJO, YASASHRI RANGANATH RANATHUNGA, *Chemistry Department, Wayne State University, Detroit, MI, USA*; TEMITAYO A. OLOWOLAFE, *Chemistry, Wayne State University, Detroit, MI, USA*; SUK KYOUNG LEE, *Chemistry Department, Wayne State University, Detroit, MI, USA*; WEN LI, *Department of Chemistry, Wayne State University, Detroit, MI, USA*.

To achieve a better understanding of strong-field dynamics, the role of Coulomb-potential of the parent ion must be taken into consideration. Several theoretical studies have investigated the effect of coulomb on CEP dependence strong field ionization. However, there are still limited experimental studies on the impact of coulomb potential on the CEP dependent momentum distributions of the photoelectrons. In this work, we experimentally investigated the effect of the long-range and short-range Coulomb potential effect on the phase dependent momentum distributions of photoelectrons by subjecting different gases to the same laser conditions using phase-resolved coincidence imaging technique. The study was performed using both linear and circular polarized light. Our experimental results show that the CEPs at which the low energy electrons have the highest asymmetry is strongly influenced by the ionization potentials but not the electronic structures. This suggests that the long-range potentials are at play. On the contrary, in the case of high-energy electrons, the CEP dependent measurement is mainly governed by the short-range coulomb potential and thus sensitive to the electronic structure of the gas being ionized. These results show that the CEP dependent momentum distributions can be a sensitive probe of the Coulomb potentials.

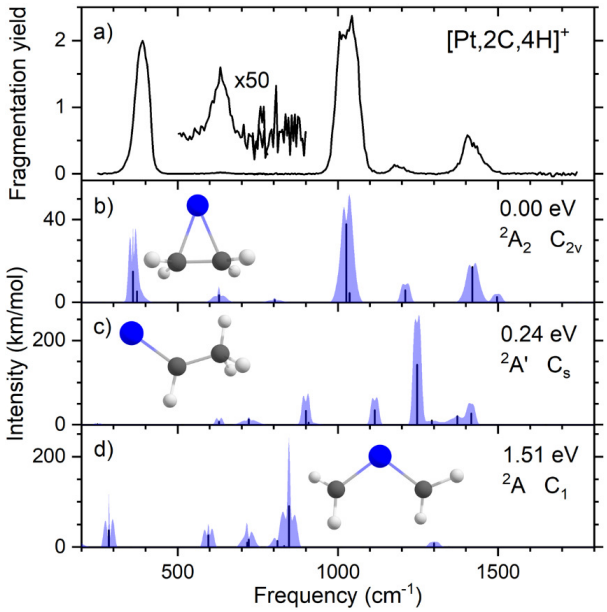
Intermission

TB05 **10:37 – 10:52**

IR CHARACTERIZATION OF METAL MEDIATED METHANE COUPLING

FRANK J. WENSINK, *HFML-FELIX, Radboud University, Nijmegen, The Netherlands*; PETER B ARMENTROUT, *Department of Chemistry, University of Utah, Salt Lake City, UT, USA*; JOOST M. BAKKER, *HFML-FELIX, Radboud University, Nijmegen, The Netherlands*.

Large amounts of methane are present in natural gas, but its great stability hinders wide-spread utilization. Conversion of methane requires a suitable, often transition metal-based catalyst. However, the reaction mechanism is often only poorly understood. To get insight in fundamental chemical interactions at the highest level of detail, we study the interaction between isolated metal ions and methane. For this, we generate metal ions using laser vaporization and react them with methane in a radio-frequency ion trap. After the reaction we analyze the formed products via a combination of mass spectrometry and IR spectroscopy using the Free Electron Laser for IntraCavity Experiments FELICE. We elucidate product structures and reconstruct the reaction pathway by comparison with Density Functional Theory calculations. In this contribution we focus on methane activation by Pt^+ and Ru^+ ions. Previously, it was shown that Pt^+ ions can activate methane to form $PtCH_2^+$. Here, we show how the subsequent reaction with more methane molecules leads to dehydrogenation and C–C coupling to form ethene on both Pt^+ and Ru^+ ions.

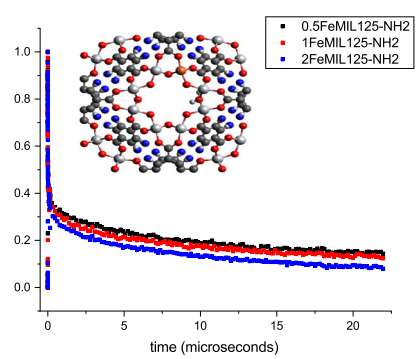


TB06 **10:55 – 11:10**

X-RAY SPECTROSCOPY STUDIES OF Ti-BASED METAL ORGANIC FRAMEWORKS

CONOR L LONG, *Chemistry, Rutgers University Newark, Newark, New Jersey, United States*; JENNY V. LOCKARD, *Chemistry, Rutgers Unitersity-Newark, Newark, NJ, United States*.

Some Ti-based metal organic frameworks (MOFs) have demonstrated photocatalytic properties. MIL125-NH_2 is a well-studied Ti-based MOF consisting of titanium-oxo clusters connected via amino terephthalic acid linkers. This structure possesses a stable, long-lived charge separated excited state in which, upon photoexcitation, an electron migrates from a linker to the metal cluster. The band structure of this framework can be modified through the replacement of Ti metal sites with d block transition metals via a direct synthesis pathway. However, further research is required on the underlying electronic structure and excited state behavior of the modified framework. Fundamental steady state and time resolved X-ray spectroscopy experiments have been carried out in order to determine the effects of heterometal doping concentration on the charge separation lifetime and the electronic environment of MIL125-NH_2. Fe K-edge X-ray transient absorption (XTA) measurements have been conducted, which show that doped MIL125-NH2 has a long-lived excited state lifetime component of over 20 microseconds, due to iron trap sites on the metal ring. The long-lived charge separation excited state is seen even in higher doping levels, as the framework inhibits charge recombination. Ti K-β resonant x-ray emission spectroscopy (RXES) measurements show a shift in pre-edge resonant features towards lower emission energy, with the inclusion of iron heterometals. Localized d transitions on the Ti seem to be less intense with the addition of Fe into the MOF structure.



TB07 **11:13 – 11:28**

SPIN STATE CHARACTERIZATION OF METALLOEMZYMES VIA X-RAY EMISSION SPECTROSCOPY

SAHAND EMAMIAN, *Department of Physics, Emory University, Atlanta, Georgia, USA*; KENDRA A IRELAND, VATSAL PUROHIT, KIRKLIN L McWHORTER, *Department of Chemistry, Emory University, Atlanta, GA, USA*; OLGA MAXIMOVA, YULIA N PUSHKAR, *Department of Physics, Purdue University, West Lafayette, IN, USA*; KATHERINE M DAVIS, *Department of Chemistry, Emory University, Atlanta, GA, USA*.

Enzyme reactivity is often enhanced by changes in oxidation state, spin state, and metal-ligand covalency of associated metallocofactors. The development of spectroscopic methods for studying these processes coincidentally with structural rearrangements is essential for elucidating metalloenzyme mechanisms. Herein, we demonstrate the feasibility of collecting X-ray emission spectra of metalloenzyme crystals at a third-generation synchrotron source.

In particular, we report the development of a von Hamos spectrometer for the collection of Fe Kβ emission optimized for analysis of dilute biological samples. We further showcase the application of this high-resolution, ”DIY” mini-spectrometer in crystals of the immunosuppressive heme-dependent enzyme indoleamine 2,3-dioxygenase (IDO).

Spectra obtained from reference compounds were compared to catalytically-relevant states of IDO via integrated absolute difference analysis to determine their spin numbers. Complementary density functional calculations assessing covalency support our spectroscopic analysis and identify active site conformations that correlate to high- and low-spin systems. These experiments validate the suitability of an X-ray emission approach for determining spin states of previously uncharacterized metalloenzyme reaction intermediates.

TB08 **11:31 – 11:46**

STRUCTURAL INVESTIGATION OF THE CU/W/CO-BASED MIXED METAL OXIDE ELECTROCATALYST USING X-RAY ABSORPTION SPECTROSCOPY

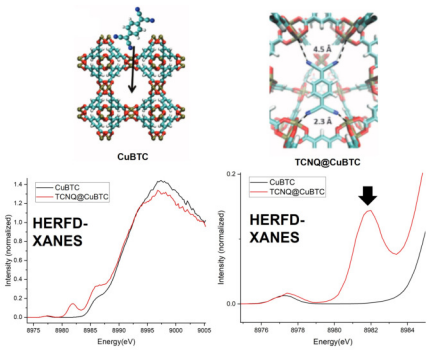
NIKITA GUPTA, *Chemistry , University of Illinois at chicago , Chicago, Illinois , United states*.

Transition-metal oxides, especially nickel, copper and cobalt oxides, are potential candidates for robust water splitting electrocatalysts as they are valence-tunable, earth-abundant, cost-efficient and stock-available. Bifunctional polyoxometalate electrocatalysts are becoming more common because of their low production cost and enhanced. water splitting activity as compared to noble metals. The water electrolysis can be divided into two half reactions: hydrogen evolution reaction (HER) occurring at the cathode, while the anodic process involves the oxygen evolution reaction (OER). Both half-reactions involve proton-coupled multi-electron transfers, varied by the pH and other reaction conditions. The general mechanism of HER involves an electrochemical hydrogen adsorption step followed by an electrochemical desorption or recombination reaction. In the case of OERs, it involves the formation of adsorbed OH* on the catalyst surface with the subsequent transformation to OOH* and the eventual release of O2. We (Streb group) recently reported cobalt tungstate bifunctional catalyst deposited on copper foam, showing high water electrolysis activity. The composite catalyst showed sustained OER and HER activity in 0.1 M aqueous KOH over prolonged periods (t more than 10 h) at low overpotentials (OER: 300 mV; HER: 100 mV). But studies evaluating the mechanistic understanding of each step in water splitting electrolysis, structural changes and true active sites during HERs and OERs at high pH values still remain ambiguous. XAS was used to study the catalytic intermediates represents a novel approach to probe the catalytic intermediates and to understand the mechanism of a catalytic process which is of outmost importance for designing new and more efficient systems.

TB09 **11:49 – 12:04**

PROBING HOST-GUEST INTERACTIONS IN CONDUCTIVE COPPER-BASED METAL ORGANIC FRAMEWORKS USING HIGH-RESOLUTION X-RAY ABSORPTION SPECTROSCOPY

AMY R. TURTZ, *Chemistry, Rutgers University, Newark, NJ, United States*; JENNY V. LOCKARD, *Chemistry, Rutgers Unitersity-Newark, Newark, NJ, United States*.



Metal-organic framework (MOF) materials are porous coordination polymers that have gained interest due to the tunability of the guest and host structures. This tunability can be particularly useful in electroconductivity applications yet has been challenging to implement due to their intrinsic insulating nature. Exploring ways to tune the electronic structure to promote electron migration is a key component in furthering research for applications that rely on conductivity such as electrocatalysis and sensing. Introduction of redox active guest species into effectively insulating MOF structures is one strategy being explored to impart electrical conductivity. This talk will focus on one particular host-guest system: a Cu3(BTC)2 MOF (; BTC=benzene 1,3,5-triboxylic acid) infiltrated with redox active 7,7,8,8-tetracyanoquinododimethane (TCNQ) guest molecules. It has been reported previously that the introduction of TCNQ into the pores Cu3(BTC)2 leads to an increase in conductivity. A key component of understanding this system is the interaction occurring between the copper sites of the framework and TCNQ guest molecules. A fundamental study using vibrational and X-ray spectroscopy were used to further understand this interaction. Copper K-alpha, resonant X-ray emission spectroscopy (RXES) was used to specifically probe the Cu interaction with this redox active guest. HERFD XANES spectra extracted from the 2D RXES planes reveal subtle changes of the pre-edge features and additional edge features corresponding the pi-backbonding of the TCNQ cyano groups to the Cu sites in the framework. Cu K-edge data are supplemented by TD-DFT calculations to determine the orbital contributions to different edge features and therefore the nature of this host-guest interaction on a molecular level.

TC. Astronomy

Tuesday, June 20, 2023 – 8:30 AM

Room: 1024 Chemistry Annex

Chair: Harshal Gupta, National Science Foundation, Alexandria, VA, USA

TC01 **8:30 – 8:45**

MODELING OF SIMPLE AROMATIC SPECIES UNDER DARK CLOUD CONDITIONS

CI XUE, ALEX BYRNE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*; ALEC PAULIVE, *Department of Chemistry, University of Virginia, Charlottesville, VA, USA*; ERIC HERBST, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*; ILSA ROSE COOKE, *Department of Chemistry, University of British Columbia, Vancouver, BC, Canada*; A B KOWSARI, *Physikalische Chemie II, Ruhr University Bochum, Bochum, Germany*; BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

The very recent discoveries of monocyclic and bicyclic aromatic molecules in rotational emission suggest that small aromatic molecules may actively form in prestellar dark clouds (McGuire et al. 2018, 2021). Although the high densities ($\sim 10^4$ cm^{-3}) allow molecules in dark clouds to collide and stick to grains and the low temperature ($\leq$10 K) further precludes thermal evaporation (Bergen 2003), benzonitrile, a monocyclic aromatic molecule, is still observed toward multiple prestellar environments (Burkhardt et al. 2021). In this talk, we will present our efforts to numerically model these simple aromatic molecules with the rate-equation-based kinetic code, Nautilus, in dark cloud environments. To produce a more comprehensive chemical network for aromatics, we systematically added new species that may serve as precursors to the aromatic species and pathways leading to the formation of the most fundamental aromatic species, benzene (C_6H_6), under low temperature and high density conditions. In particular, we examined possible formation pathways, including the ion-molecule reaction of ethynyl radical (CCH) and 1,3-butadiene ($CH_2CHCHCH_2$), the neutral-neutral reaction of acetylene (HCCH) and vinyl acetylene (CH_2CHC_2H), and the dissociative recombination reaction of benzenium ions ($C_6H_7^+$). Although the current model under-predicts the observed abundance of both monocyclic and bicyclic aromatic molecule, the updates we have made to the reaction network of related species have shown substantial progress in bringing the models into alignment with observations. Our results suggest that viable reactions forming and releasing small aromatic molecules on grains may be necessary to bridge the gap between models and observations in prestellar dark clouds.

TC02 **8:48 – 9:03**

ASTROCHEMICAL MODELING OF THE PROPARGYL RADICAL IN COLD MOLECULAR CLOUDS

ALEX BYRNE, CI XUE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*; ILSA ROSE COOKE, *Department of Chemistry, University of British Columbia, Vancouver, BC, Canada*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

Recent detections of aromatic species in dark molecular clouds suggest formation pathways may be efficient at very low temperatures and pressures, yet current astrochemical models are unable to account for their derived abundances, which can often deviate from model predictions by several orders of magnitude. The propargyl radical, a highly abundant species in the dark molecular cloud TMC-1, is an important aromatic precursor in combustion flames and possibly interstellar environments. In this talk, we present the results of astrochemical modeling of TMC-1 using the NAUTILUS code and an updated chemical network, with a focus on the propargyl radical and chemically related species. Predicted abundances for the connected C_4H_3N isomers within an order of magnitude of observed values corroborate the high efficiency of CN addition to closed-shell hydrocarbons under dark molecular cloud conditions. In addition to other resonance-stabilized radicals, the propargyl radical remains an important potential precursor to aromatic formation.

TC03 **9:06 – 9:21**

MACHINE LEARNING OF THE CHEMICAL INVENTORY AND RARE ISOTOPOLOGUES OF THE SOLAR-TYPE PROTOSTELLAR SOURCE IRAS 16293-2422 B

ZACHARY TAYLOR PHILIP FRIED, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*; KELVIN LEE, *Accelerated Computing Systems and Graphics, Intel Corporation, Hillsboro, OR, USA*; ALEX BYRNE, BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

Machine learning techniques have been previously used to model and predict column densities in the TMC-1 dark molecular cloud. However, in interstellar sources further along the path of star-formation, such as those where a protostar itself has been formed, the chemistry is known to be drastically different from that of largely quiescent dark clouds. In this talk, I will describe the ability of various machine learning models to fit the column densities of the molecules detected in source B of the Class 0 protostellar binary IRAS 16293-2422. By including a simple encoding of isotopic composition in the molecular feature vectors, I also examine for the first time how well these models can replicate the isotopic ratios. Finally, these trained models provide a list of predicted high-abundance molecules that may be excellent targets for laboratory spectroscopy and subsequent radioastronomical detection in IRAS 16293-2422 B.

TC04 **9:24 – 9:39**

BEYOND THE MACHINE: AUTOMATING SPECTRA GENERATION AND ANALYSIS FROM MACHINE LEARNING RESULTS

HANNAH TORU SHAY, GABI WENZEL, CI XUE, BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

Almost 300 molecules have been detected in the interstellar medium, with an exponential explosion in recent years thanks to rapid innovation in technology and technique. However, detections alone only offer tantalizing hints to future chemistry; we generally have been unable to make reliable predictions of the chemical species that will be subsequently detected. Prior work in the McGuire group was able to use Machine Learning approaches to accurately reproduce the inventories of 87 known species in TMC-1. The model went on to make over 1500 predictions of potential targets. Not only is this more than can efficiently be pursued, but these predictions provided only column densities and did not account for other key factors of detectability such as how many spectral lines fall within the range of our astronomical observations and the intensities of those lines. My work takes the results of this machine learning model, and others like it, and further narrows the list of candidates for detection by applying detectability metrics. Through automation, this workflow leads to extended usability of ML inventory predictions.

TC05 **9:42 – 9:57**

RECENT UPDATES TO THE LILLE SPECTROSCOPIC DATABASE

R. A. MOTIYENKO, L. MARGULÈS, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, Univ. Lille, CNRS, F-59000 Lille, France*.

Lille Spectroscopic Database (https://lsd.univ-lille.fr)[a] hosts the predicted rotational spectra studied by our group in Lille during last 15 years. We will present recent data updates to the database as well as to the application programming interface (API) that allows the integration of the database into third party software. The question of degeneracy factors in case of molecules exhibiting large amplitude motions will be also discussed.

[a] We thank the Mésocentre de Calcul Scientifique Intensif de l'Université de Lille for hosting the database.

Intermission

TC06 **10:37 – 10:52**

UPDATING THE SCIENTIFIC USEFULNESS OF THE SPLATALOGUE DATABASE

DANIEL JOSEPH LOPEZ-SANDERS, *Department of Physics & Astronomy, Benedictine College, Atchison, KS, USA*; ANTHONY REMIJAN, *NAASC, National Radio Astronomy Observatory, Charlottesville, VA, USA*.

Splatalogue is an online database for astronomical spectroscopy created and maintained by the National Radio Astronomy Observatory (NRAO) that contains over 11 million spectral lines of over 1300 different species; these lines are from over 15 different linelists. The Splatalogue user interface (splatalogue.online) was built on an old interface and while it has worked very well for the community over the course of the past 15 years, it does lack basic functionality that will allow for more scientific analysis done with the data contained in the database. This project involved working to complete four goals to facilitate both future development of this website and the work of astronomers who use it; the first, second, and fourth goals were fully completed within the time of this Research Experience for Undergraduates (REU) project at the NRAO in the summer of 2022. The third was partially completed in that the switch was made from PHP to Python as the base of the web server technology, but the feature integration was not fully completed.

1. **Security:** Ensuring the site was safe from attacks so it can be consistently available as a secure resource for the astronomical community.
2. **Documentation:** Documenting the project code to facilitate future development of the site.
3. **Modern Technology Base:** Switching the base of the web server technology from PHP to Python for security and feature integration reasons.
4. **User Interface (UI) Improvements:** Facilitating the use of the website through user interface style improvements.

Overall, this project represents a valuable advance in astronomical software that will facilitate both future modifications to the website and astronomical research going forward.

TC07 **10:55 – 11:10**

ROTATIONAL SPECTROSCOPY OF REACTIVE SPECIES IN SUPPORT OF THE DETECTION OF INTERSTELLAR MOLECULES

CRISTINA PUZZARINI, SILVIA ALESSANDRINI, LUCA BIZZOCCHI, MATTIA MELOSSO, *Dep. Chemistry 'Giacomo Ciamician', University of Bologna, Bologna, Italy*.

Interstellar molecules are often highly reactive species, which are unstable under terrestrial conditions, such as radicals, ions and unsaturated carbon chains. Their detection in space is usually based on the astronomical observation of their rotational fingerprints. However, laboratory investigations have to face the issue of efficiently producing these molecules and preserving them during rotational spectroscopy measurements. A general approach for producing and investigating unstable/reactive species is presented by means of selected case-study molecules. The overall strategy starts from quantum-chemical calculations that aim at obtaining accurate predictions of the missing spectroscopic information required to guide spectral analysis and assignment. Rotational spectra of these species are then recorded by exploiting the approach mentioned above, and their subsequent analysis leads to accurate spectroscopic parameters. These are then used for setting up accurate line catalogs for astronomical searches.

TC08 **11:13 – 11:28**

A NOVEL APPROACH FOR AUTOMATED ANALYSIS OF HIGH-RESOLUTION MOLECULAR LINE SURVEYS

SAMER EL-ABD, *Department of Astronomy, The University of Virginia, Charlottesville, VA, USA*; CRYSTAL L. BROGAN, TODD R. HUNTER, *NAASC, National Radio Astronomy Observatory, Charlottesville, VA, USA*; KELVIN LEE, *Accelerated Computing Systems and Graphics, Intel Corporation, Hillsboro, OR, USA*; BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

Massive star-forming regions are hotbeds of interstellar chemistry where unique physical conditions allow for the formation of a wide variety of molecular species. Accurately characterizing the morphology of these molecules allows us to glean information from the energetic physical processes taking place during massive star formation as well as achieve a better understanding of how such relatively large molecules are formed in the interstellar medium. In order to more efficiently process the vast amounts of data that modern interferometers such as ALMA are producing, we have developed a least-squares fitting routine capable of fitting the combined spectra of a given list of molecules across a broadband line survey for thousands of pixels in a data cube. Results of the application of this routine to high mass star-forming regions will be presented in the form of spatial maps for the derived parameters incuding excitation temperature, kinematics, and column densities. Most previous approaches to analyzing the spatial morphology rely on spectra extracted from a handful of pixels and extrapolating across the field of view with a moment map, using the intensity of a single transition as a proxy for the abundance of a molecule. In contrast, the maps generated by our fitting routine utilize the full suite of available lines and will showcase the physical parameters of the region in an unbiased manner. Maps showcasing the physical column density ratios will be presented as well; these unique products of our approach will give insight into how the protostellar environment influences the relative abundance of interstellar molecules.

TC09 **11:31 – 11:46**

H_2O AND HDO TEMPERATURE DEPENDENT LINESHAPES USING SUB-DOPPLER METHODS

BRIAN DROUIN, DEACON J NEMCHICK, TIMOTHY J. CRAWFORD, PAUL VON ALLMEN, D. C. LIS, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*.

Collisional energy transfer in volatized exospheric materials dominates the uncertainty of comet models that trace comae composition back to surface composition. Methods for ab initio and semi-empirical calculation of quantum-state dependent collisional efficiencies are typically benchmarked to pressure broadening experiments when available. Last year we detailed experimental efforts to determine collisional efficiencies for selected transitions of water at temperatures demonstrative of the comet environment and well below the water condensation temperature. This year we add two HDO transitions to the data set. The method utilizes a collisional cooling cell with water and/or deuterated water injected into a bath gas at the target temperature or held at temperatures that produce relevant vapor pressures for measurement. THz radiation is passed twice through the cooled gas to record a transmission spectrum exhibiting the Lamb dip effect. The sub-Doppler feature is subject to collisional broadening at pressures commensurate with the partial pressure of water and deuterated water in the system. Data analysis involves extraction of intensity and pressure broadening information. The method, results and comparisons to calculated values will be discussed.

TC10 **11:49 – 12:04**

ROTATIONAL SPECTRUM AND INTERSTELLAR DETECTION OF THE FIRST TORSIONALLY EXCITED STATE OF METHYLAMINE

PRAKASH GYAWALI, R. A. MOTIYENKO, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*; ARNAUD BELLOCHE, *Millimeter- und Submillimeter-Astronomie, Max-Planck-Institut für Radioastronomie, Bonn, NRW, Germany*; ISABELLE KLEINER, *Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, 75013, Paris, France*; V. ILYUSHIN, E. A. ALEKSEEV, *Radiospectrometry Department, Institute of Radio Astronomy of NASU, Kharkov, Ukraine*; IWONA GULACZYK, MAREK KREGLEWSKI, *Faculty of Chemistry, Adam Mickiewicz University, Poznan, Poland*.

Methylamine (CH_3NH_2) was first detected in the interstellar medium (ISM) toward Sgr B2 almost 50 years ago by observation of its v_t = 0 rotational transitions[a]. Methylamine exhibits two large amplitude motions, methyl torsion and amine wagging, that complicate the spectral analysis especially in excited vibration states. This work aims to study experimentally and theoretically the terahertz rotational spectrum of methylamine to provide a reliable basis for the ISM detection of rotational transitions in v_t = 1 state. The terahertz spectrum of methylamine was measured from 150 to 1520 GHz with the Lille fast scan spectrometer. Using a new "hybrid" Hamiltonian model, we were able to fit accurately the rotational spectrum of the v_t= 1 state of methylamine including the analysis of the nuclear quadrupole hyperfine structure. The results of this spectroscopic analysis allowed us to search for rotational transitions of methylamine in its first torsionally excited state toward the high-mass star forming region Sgr B2(N) that was the target of the imaging spectral line survey ReMoCA performed with the Atacama Large Millimeter/submillimeter Array (ALMA). We report the first interstellar detection of methylamine in its v_t = 1 state on the basis of this interferometric data set.

[a]Kaifu, et al. 1974, ApJ, 191, L135; Fourikis et al. 1974, ApJ, 191, L139

TD. Instrument/Technique Demonstration

Tuesday, June 20, 2023 – 8:30 AM

Room: 217 Noyes Laboratory

Chair: Liam Duffy, University of North Carolina at Greensboro, Greensboro, NC, USA

TD01 **8:30 – 8:45**

CAVITY-ENHANCED DUAL-COMB SPECTROSCOPY WITH QUANTUM CASCADE LASERS IN THE MOLECULAR FINGERPRINT REGION

CHARLES R. MARKUS, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; JAKOB HAYDEN, DANIEL I. HERMAN, *IRsweep AG, IRsweep AG, Stäfa, Switzerland*; PHILIP A. KOCHERIL, DOUGLAS OBER, TERMEH BASHIRI, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; MARKUS MANGOLD, *IRsweep AG, IRsweep AG, Stäfa, Switzerland*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*.

Optical frequency combs pose a promising approach to molecular spectroscopy and trace gas detection, offering the benefits of both broadband and high-resolution sources. When combined with enhancement cavities, extremely long effective pathlengths can be achieved in a benchtop system. Combining the benefits of enhancement cavities and combs can be technically challenging, and often requires multiple feed-back loops which preclude measurements in the field. There is also desire to push direct frequency comb spectroscopy into the mid-infrared where strong fundamental vibrational bands exist, which adds additional difficulty.

Here, we demonstrate cavity-enhanced dual-comb spectroscopy in the mid-infrared for the first time, covering 60 cm^{-1} centered at 9.4 μm using quantum cascade lasers (QCLs). The cavity length was set such that the repetition rate of the probing comb matched an integer multiple of the cavity's free spectral range. In order to avoid feedback from reflections off the cavity, a bow-tie geometry was used. The frequency comb that was transmitted from the cavity was heterodyned with a second QCL frequency comb and the signals were processed using a commercial dual-comb spectrometer. The high power-per-mode and heterodyne detection provided high signal-to-noise on the transmitted light, while the large difference in repetition rate between the combs allowed for high temporal resolution. The system was completely free running, allowing for robust and sensitivity measurements. A demonstration using trace methanol was performed to characterize the sensitivity of the system. The effective pathlength was increased to 285 m (cavity Finesse of 800), and the system reached a sensitivity of 2.7×10^{-8} cm^{-1} per spectral element.

TD02 **8:48 – 9:03**

QUANTUM CASCADE LASER PUMPING FOR MOLECULAR LASING AND SPECTROSCOPY

PAUL CHEVALIER, ARMAN AMIRZHAN, FEDERICO CAPASSO, *Harvard John A Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA*; HENRY O. EVERITT, *Physics, Duke University, Durham, NC, USA*.

The lack of powerful and tunable sources in the terahertz frequency (100 GHz to 10 THz) can limit the accuracy and resolution of rotational molecular spectroscopy. While the ground state rotational spectrum of molecules is easily measured, thanks to the large thermal population of lower rotational levels at room temperature, measuring the rotational spectra in sparsely populated excited vibrational states can be much harder. Unlike molecular infrared lasers, quantum cascade lasers offer continuous tunabilty across the ro-vibrational transitions of most molecules. Here, we exploit this tunability to demonstrate a new type of laser and a new type of spectroscopy. Pumping molecules using a quantum cascade laser dramatically enhances the population of sparsely populated vibrational states, and the resulting enhancement of their rotational absorption or emission lines enables the direct measurement of their otherwise weak spectra. In some molecules, this pumping even exceeds the lasing threshold, and every line in the rotational spectrum may be made to lase.

TD03 **9:06 – 9:21**

QUANTUM CASCADE LASER-BASED INFRARED PHOTODISSOCIATION ACTION SPECTROSCOPY OF HYDRATED AMINO ACIDS FOR PLANETARY SCIENCE IN SITU SENSING APPLICATIONS

TYLER M NGUYEN, DOUGLAS OBER, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; ROBERT HODYSS, STOJAN MADZUNKOV, FRANK MAIWALD, DEACON J NEMCHICK, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*.

In the search for life on other worlds in our solar system, overlooked approaches to in situ sensing instrumentation can increase science return relating to the detection of prebiotic molecules such as amino acids, lipids, and nucleic acids at low size, weight, and power cost. Ongoing work at Caltech and the Jet Propulsion Laboratory (JPL) aims to explore how moderate power, continuous wave (CW) laser sources can be leveraged to execute single- and multi-photon photodissociation schemes adaptable to mass spectrometer (MS)-based in situ sensing platforms. These techniques could serve as potent analysis tools that provide unambiguous molecular identification through combined initial *m/z*, the IR or UV/Vis spectrum, as well as the photofragment mass spectrum. This talk will present an initial study of a low-power CW variant of messenger-assisted infrared photodissociation (IRPD) spectroscopy of singly hydrated, protonated phospho-tyrosine ($pTyrH^+(H_2O)$) generated from an electrospray source with both complexation and analysis performed in a single stage linear ion trap MS. The room temperature IRPD spectrum of $pTyrH^+(H_2O)$ was recorded by monitoring the loss of water tag when irradiated with a moderate power (<100 mW) quantum cascade laser (QCL) source in the fingerprint region (865-950 cm^{-1} and 1000-1670 cm^{-1}). Findings are compared against literature analog spectra collected using a free electron laser radiation source with presented results constituting a dramatic reduction in experimental complexity. Discussions will be aided with the support of quantum chemical calculations (DLPNO-CCSD(T)-F12/cc-pVTZ-F12//ωB97X-V/def2-QZVPP). Additionally, this presentation will briefly describe efforts to adapt flight heritage MS hardware at JPL to execute similar analysis schemes. Overall, the current study is the first demonstration of using low-power, CW QCL-based action spectroscopy for the goal of analyzing a broad range of prebiotic molecules on future search for life missions.

TD04 **9:24 – 9:39**

DEVELOPMENT OF A DUAL-COMB SPECTROMETER FOR ROTATIONALLY-RESOLVED MEASUREMENTS OF THE VIBRATIONAL OVERTONE OF BENZENE

DANIEL L. MASER, MATTHEW D CARTER, *Department of Physics, Astronomy and Geophysics, Connecticut College, New London, CT, USA*.

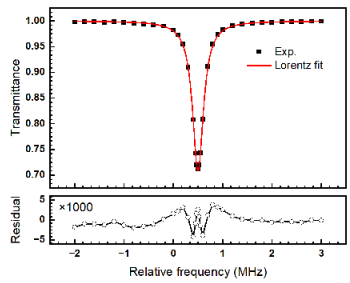
Optical frequency combs have proven to be a powerful tool in precision molecular spectroscopy due to their unique blend of a coherent, low-noise spectral source and the broad bandwidth they offer. One particularly useful technique to take full advantage of the high-resolution potential of these devices is dual-comb spectroscopy, in which two frequency combs with slightly different repetition rates are heterodyned together to generate an interferogram, akin to the signal an FTIR produces, through which the optical spectrum can be retrieved.

We have constructed a pair of fiber-based optical frequency combs in-house at Connecticut College, one of which has an adjustable repetition rate, for use in a dual-comb spectrometer. We will present details on the two frequency combs, report our progress toward this dual-comb spectrometer, and discuss its future implementation in conducting rotationally-resolved measurements of the 1.65 μm vibrational overtone of benzene in a supersonic beam apparatus.

TD05 **9:42 – 9:57**

TWO-PHOTON ABSORPTION SPECTROSCOPY OF A $^{13}CO_2$ VIBRATIONAL TRANSITION

YU-ZHONG LIU, *School of Physical Sciences, University of Science and Technology of China, Hefei, China*; CUNFENG CHENG, SHUI-MING HU, *Department of Chemical Physics, University of Science and Technology of China, Hefei, China*.



Two-photon absorption spectroscopy is an ideal method for precision measurements of molecular energy levels and trace gas concentration. We report a two-photon absorption of the Q(36) rovibrational transition of $^{13}CO_2$, measured by cavity-enhanced absorption spectroscopy (CEAS) at λ = 2.8 μm. The high signal-to-noise ratio of two-photon absorption spectra was obtained by optical locking of a narrow-linewidth mid-infrared laser to a high finesse cavity. One longitudinal mode of the cavity was shifted to scan the frequency, calibrated by an optical frequency comb. We studied the properties of the two-photon absorption spectrum. It is expected that this method can be applied in the field of molecular frequency reference and high-sensitivity detection.

TD06 **10:00 – 10:15**

ION-DIP INFRARED SPECTROSCOPY OF CRIEGEE INTERMEDIATES

MEIJUN ZOU, TARUN KUMAR ROY, MARSHA LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA*.

In the troposphere, alkene ozonolysis produces carbonyl oxide intermediates, known as Criegee intermediates, which can undergo unimolecular decay to generate hydroxyl (OH) radicals, an important atmospheric oxidant. This study focuses on the *syn* conformer of the methyl-substituted Criegee intermediate (*syn*-CH_3CHOO) that decays via 1,4 hydrogen transfer from the methyl group to the terminal oxygen, followed by O-O bond fission to yield OH radical products. IR excitation of jet-cooled *syn*-CH_3CHOO in the overtone CH stretch ($2\nu_{CH}$) region facilitates this process, leading to rapid dissociation to OH + vinoxy radicals within 10 ns.[a] Here, we demonstrate ion-dip infrared spectroscopy of *syn*-CH_3CHOO by combining IR activation in the $2\nu_{CH}$ region with VUV photoionization (10.5 eV, preferentially probing the *syn* conformer)[b] and time-of-flight mass spectrometry detection (m/z 60). The resultant ground state depletion spectrum is recorded and compared with that previously obtained by IR action spectroscopy with detection of OH products using laser-induced fluorescence.[c] The ion-dip infrared spectrum reproduces the two main features at 5987 and 6081 cm^{-1}, but with notable changes that are being explored. In addition, the experimental results are compared with anharmonic frequency calculations at various levels of theory, which predict a single strong absorption in the $2\nu_{CH}$ region. Further calculations of vibrational couplings are needed to interpret the experimental observations.

[a] Y. Fang, F. Liu, V. P. Barber, S. J. Klippenstein, A. B. McCoy and M. I. Lester, *J. Chem. Phys.* **145**, 234308 (2016).
[b] C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke, D. K. W. Mok, D. L. Osborn and C. J. Percival, *Science* **340**, 177-180 (2013).
[c] F. Liu, J. M. Beames, A. S. Petit, A. B. McCoy and M. I. Lester, *Science* **345**, 1596-1598 (2014).

Intermission

TD07 **10:55 – 11:10**

HIGH RESOLUTION 2D INFRARED SPECTROSCOPY OF CHLOROMETHANE

PETER CHEN, *Department of Chemistry, Spelman College, Atlanta, GA, USA*; DeAUNNA A DANIELS, *Chemistry, Spelman College, Atlanta, GA, USA*; THRESA WELLS, *Department of Chemistry, Spelman College, Atlanta, GA, USA*.

HR-2DIR spectroscopy is a new technique that can be used to resolve congested spectra, create 2D patterns, and assign rovibrational peaks in the near infrared region of the spectrum. This talk describes the use HR-2DIR to assign peaks in the CH overtone region of chloromethane.

TD08 **11:13 – 11:28**

ELECTRO-OPTIC FREQUENCY COMB GENERATION WITH PHASE-LOCKED LOOP STABILIZED RF MODULATION

TODD ELIASON, PAYTON AVERY PARKER, MELANIE A.R. REBER, *Department of Chemistry, University of Georgia, Athens, GA, USA*.

Electro-optic frequency combs are attractive light sources for dual comb spectroscopy because they are turn-key, robust lasers. The EOM comb presented in this work has a novel architecture, utilizing multiple modulators, to optimize spectral bandwidth with MHz comb tooth spacing. The repetition rate is dictated by the final EOM operating at 70-150 MHz, which matches many commercial mode-locked ultrafast laser systems. Each frequency source is phase and frequency locked using a phase locked loop, which offers long term stability without optics. The frequencies can be tuned without any change to the optics or electrical hardware. The comb tooth linewidth is controlled by the seed laser, a commercial Nd:YAG with a kHz linewidth. Integration of this laser into a dual comb spectroscopy experiment will also be discussed.

TD09 **11:31 – 11:46**

LOCKING FREQUENCY COMBS TO OPTICAL CAVITIES FOR SIGNAL ENHANCEMENT OF TWO-DIMENSIONAL SPECTROSCOPY

WALKER M. JONES, PARASHU R NYAUPANE, MELANIE A.R. REBER, *Department of Chemistry, University of Georgia, Athens, GA, USA*.

Ultrafast Two-Dimensional (2D) Spectroscopy is a powerful technique that has provided valuable insight into diverse systems from protein folding to isomerization of metal complexes. We aim to bring this technique to the realm of small molecules in molecular beams. 2D spectroscopy is unique because it allows for the direct measurement of coupled excitations, represented by off diagonal peaks within the spectra. However, because 2D spectroscopy is a third-order process, the signals are necessarily weak, requiring a combination of higher laser power and concentrated sample to obtain detectable signals. To increase the sensitivity of this technique, our lab built a frequency comb laser and coupled it to an external enhancement cavity. This combination of a frequency comb and optical cavity allows for Cavity Enhanced 2D Spectroscopy to be performed with broadband ultrafast pulses. Even with a modest cavity finesse, the resonant cavity pulses see a 2-3 order increase in their electric fields, greatly increasing the sensitivity of the 2D experiment. We explore the use of enhancement cavities on 2D spectroscopy signal levels, as well as trade-offs inherent to the technique.

TD10 **11:49 – 12:04**

OPTICAL FREQUENCY COMB CAVITY ENHANCED VERNIER SPECTROSCOPY FOR THE DETECTION OF TRANSIENT SPECIES

TERMEH BASHIRI, CHARLES R. MARKUS, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; TZU-LING CHEN, *Department of Photonics, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; DOUGLAS OBER, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; LUKASZ A. STERCZEWSKI, *Instruments Division, Jet Propulsion Laboratory/Caltech, Pasadena, CA, USA*; CHADWICK L CANEDY, IGOR VURGAFTMAN, *Optical Sciences, U.S. Naval Research Laboratory, Washington, DC, USA*; CLIFFORD FREZ, *Instruments Division, Jet Propulsion Laboratory/Caltech, Pasadena, CA, USA*; JERRY R MEYER, *Optical Sciences, U.S. Naval Research Laboratory, Washington, DC, USA*; MAHMOOD BAGHERI, *Instruments Division, Jet Propulsion Laboratory/Caltech, Pasadena, CA, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*.

When paired with cavity enhancement, interband cascade optical frequency combs offer a highly sensitive method for broadband spectroscopy. We present a new method for the detection of UV photolysis-generated transient species using cavity enhanced Vernier spectroscopy with a mid-IR interband cascade frequency comb. The cavity is used to generate an enhanced spectrum by extending the pathlength. This technique allows for the real-time high-resolution detection of short-lived species. We will discuss the benchmark reaction between hydroxymethyl radicals and oxygen to form formaldehyde, as well as the application of this new technique for the detection of resonance-stabilized radicals.

TD11 **12:07 – 12:22**

STUDY OF XFEL PULSE PARAMETERS FOR GENERATION OF COHERENT FEMTOSECOND X-RAY PULSES

ZAIN ABHARI, *Physics, University of Wisconsin-Madison, Madison, WI, USA*.

The extension of nonlinear coherent spectroscopies to the hard X-ray regime could be achieved through the creation of intense, phase stable, femtosecond X-ray pulse pairs, thus potentially further revolutionizing studies of chemistry. XFEL pulses are inherently stochastic, structurally and temporally, which is a limiting factor in advancing nonlinear spectroscopy, but stimulated emission generated by XFEL pulses can result in the pulse pairs necessary for this progress. One potential approach to creating these pairs is highlighted in previous work describing the generation of intense, coherent, X-ray pulse pairs on the femtosecond timescale. These pulse pairs were realized based on the observation of spectral fringes that appeared in the X-ray superfluorescence and seed stimulated emission.

The aim of this work is to establish the optimal pump and seed pulse conditions that lend to repeatable generation of femtosecond X-ray pulse pairs. The first step in doing so is to determine the correlation between the parameters of the incoming SASE pulses and the generated pulse pairs. Here we present an overview of the correlation of measured pump pulses and stimulated emission generated from Cu foils, and $MnCl_2$, and $NaMnO_4$ jets.

TE. Small molecules

Tuesday, June 20, 2023 – 8:30 AM

Room: B102 Chemical and Life Sciences

Chair: Samir Kassi, CNRS, Saint-Martin d'Hères, France

TE01 **8:30 – 8:45**

HARDWARE ACCELERATED SOLUTIONS FOR SPECTROSCOPY

SEAN MICHAEL BRESLER, *Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA*; CHARLIE SCOTT CALLAHAN, *Mechanical Engineering, University of Colorado Boulder, Boulder, CO, USA*; THOMAS W LEBRUN, JASON J GORMAN, *Physical Measurement Lab, National Institute of Standards and Technology, Gaithersburg, MD, USA*; GREGORY B RIEKER, *Department of Mechanical Engineering, University of Colorado Boulder, Boulder, CO, USA*; DAVID A. LONG, *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA*.

The graphical processing unit (GPU) offers massive speed advantages in a variety of spectroscopic applications. Single and dual optical frequency comb experiments generally require massive amounts of repetitive signal transformations. We demonstrate continuous, effectively indefinite readout for a comb-based optomechanical accelerometer by performing millions of Fourier transforms and lineshape fit iterations per second with a scheme that is applicable to many comb and chirp-based experiments. Within the realm of molecular absorption and emission spectroscopy, Hartmann-Tran lineshape generation speed is also heavily accelerated with the GPU, with lineshape improvements of 3-4 orders of magnitude compared to standard Python packages. These two examples lead to the possibility of real-time broadband sensing applications for molecular targets using inexpensive, mass-produced hardware.

TE02 **8:48 – 9:03**

MOLECULAR BEAM DENSITY MEASUREMENT WITH CAVITY-ENHANCED ABSORPTION SPECTROSCOPY

ZHUANG LIU, CUNFENG CHENG, SHUI-MING HU, *Department of Chemical Physics, University of Science and Technology of China, Hefei, China*.

Molecular beams have played an important role in chemical physics research, and beam density is crucial in determining beam properties, reaction rate, and differential cross-section in chemical dynamic experiments. However, few results present the absolute molecular beam density at the moment. We set up an experimental setup that combines the supersonic molecule beam and cavity-enhanced method. The absorption spectrum of carbon monoxide in the beam is continuously recorded when the beam is passing the cavity and we have demonstrated that the absolute molecular beam density can be measured. The absorption spectrum of the CO $R_3(0)$ transition in the beam is shown in figure 1, the beam density can be obtained by measuring the absorption spectrum at different pressures and correcting the effective absorption length. It is expected that with the laser-locked cavity-enhanced method beam density of other molecules, such as C_2H_2, H_2O, CH_4, etc., can be measured quantitatively, which is significant in the crossed molecular beam experiments. This also provides a new method for measuring reaction products in chemical dynamic experiments.

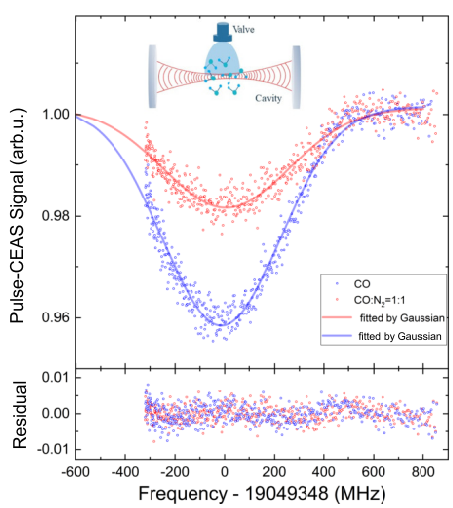


Figure 1: CEAS of carbon monoxide $R_3(0)$ transition in the beam.

TE03 **9:06 – 9:21**

HIGH-RESOLUTION, JET-COOLED INFRARED SPECTROSCOPY OF *TRANS*-FORMIC ACID: ANALYSIS OF ν_1 OH STRETCHING FUNDAMENTAL

YA-CHU CHAN, *JILA and the Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA*; DAVID NESBITT, *JILA, Department of Chemistry, and Department of Physics, University of Colorado Boulder, Boulder, CO, USA*.

High-resolution infrared reduced-Doppler absorption spectra of jet-cooled gas phase *trans*-formic acid at $T_{rot} \approx 10.9(5)$ K are reported for the first time in the ν_1 OH stretching fundamental region, obtained by supersonically expanding *trans*-formic acid/Ar mixtures through a slit jet nozzle source. Four rovibrational bands are observed, with origins at 3570.493(5) (*a*/*b*-type), 3566.793(5) (*a*/*b*-type), 3560.032(9) (*b*-type), and 3534.6869(2) (*a*-type) cm^{-1}, respectively. Based on previous Raman jet spectroscopic work by Nejad and Sibert[a], these four bands have been assigned to ν_1, $\nu_2 + \nu_7$, $\nu_6 + 2\nu_7 + 2\nu_9$ (tentatively by our work), and $2\nu_3$, respectively. Specifically, two of the three upper dark states $2^1 7^1$ (a′) and $6^1 7^2 9^2$ (a′) are close enough to the "bright" 1^1 (a′) state to facilitate strong anharmonic resonance interactions, resulting in intensity mixing into the two zero-order bands that would otherwise be "dark". Furthermore, our high-resolution spectral analysis reveals that there are local rotational crossings between zero-order 1^1 and $2^1 7^1$ states. This motivates the development of a 3 coupled state (1^1, $2^1 7^1$, and $6^1 7^2 9^2$) picture to aid in the spectral analysis, which is able to match all 3 observed band origins and relative band intensities, as well as indicate the necessity of multistate coupling. Though limited by the range of J and K_a levels ($J' \leq 9$ and $K'_a \leq 3$) populated at supersonic jet temperatures, this work offers the first precision spectroscopic analysis of *trans*-formic acid in the ν_1 OH stretching region, which should aid in the assignment of the more complete yet highly congested room temperature FTIR spectra[b].

[a] A. Nejad, E.L. Sibert III, The Raman jet spectrum of trans-formic acid and its deuterated isotopologs: Combining theory and experiment to extend the vibrational database, J. Chem. Phys. 154(6) (2021) 064301.

[b] D. Hurtmans, F. Herregodts, M. Herman, J. Liévin, A. Campargue, A. Garnache, A. Kachanov, Spectroscopic and ab initio investigation of the ν_{OH} overtone excitation in trans-formic acid, J. Chem. Phys. 113(4) (2000) 1535.

TE04 **9:24 – 9:39**

HIGH-RESOLUTION DUAL-COMB SPECTROSCOPY IN THE 9.5 μm REGION TO STUDY PLASMA-ASSISTED AMMONIA FORMATION

MARKUS MANGOLD, JAKOB HAYDEN, ANDREAS HUGI, *IRsweep AG, IRsweep AG, Stäfa, Switzerland*; ADAM J. FLEISHER, *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA*; IBRAHIM SADIEK, NORBERT LANG, JEAN-PIERRE VAN HELDEN, *INP, Leibniz Institute for Plasma Science and Technology, Greifswald, Germany*.

To improve plasma-assisted processes, optical methods such as tunable continuous-wave (CW) laser absorption spectroscopy provide in-situ measurements of plasma parameters including chemical composition, number density, and temperature (e.g., [1]). However, the narrow spectral coverage of many CW lasers reduces the number of transitions and thereby different parameters that can be interrogated at once.

To measure many quantities simultaneously, we employ quantum cascade laser dual-comb spectroscopy (QCL-DCS) in the long-wave infrared to measure plasma-generated NH_3 within a research-grade industrial plasma reactor. Simulations using the HITRAN2020 database [2] reveal absorptionS from both the ν_2 fundamental and $2\nu_2$ hot-band of NH_3 in our targeted spectral region, which together can enable a precise determination of rotational and vibrational temperatures.

The experimental setup comprises a commercial dual-comb spectrometer (IRis-core, IRsweep AG) coupled to a multipass cell on a plasma reactor. Spectra covering the range from 1035 cm^{-1} to 1085 cm^{-1} with 5×10^{-4} cm^{-1} resolution were recorded in seven minutes employing a spectral interleaving technique [3]. With a 3.16 m effective optical pathlength, the limit of detection for NH_3 from a single scan was $\sim 2 \times 10^{11}$ cm^{-3} (10 ppm at 1 mbar and 400 K).

We will present measurements in an H_2/N_2 plasma at different mixing ratios and plasma conditions. The combination of high spectral resolution and parallel detection of many absorption lines in the long-wave infrared makes QCL-DCS a powerful tool for plasma diagnostics.

[1] J. Röpcke, P.B. Davies, S. Hamann, M. Hannemann, N. Lang, and J.-P. H. Van Helden, Photonics 3, 45 (2016).
[2] I. E. Gordon, L. S. Rothman, R. J. Hargreaves, et al. J. Quant. Spectrosc. Radiat. Transfer 277, 107949 (2022).
[3] M. Lepère, O. Browet, J. Clément, et al., J. Quant. Spectrosc. Radiat. Transfer 287, 108239 (2022).

Intermission

TE05 **10:19 – 10:34**

MEASUREMENT AND ASSIGNMENT OF METHANE HOT-BAND TRANSITIONS USING CAVITY-ENHANCED FREQUENCY COMB DOUBLE RESONANCE SPECTROSCOPY: EXTENDING TO HIGHER J STATES.

VINICIUS SILVA DE OLIVEIRA, ISAK SILANDER, ADRIAN HJÄLTÉN, ANDREA ROSINA, ALEKSANDRA FOLTYNOWICZ, *Department of Physics, Umea University, Umea, Sweden*; LUCILE RUTKOWSKI, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*; GRZEGORZ SOBOŃ, *Faculty of Electronics, Photonics and Microsystems, Wrocław University of Science and Technology, Wrocław, Poland*; KEVIN LEHMANN, *Department of Chemistry and Physics, The University of Virginia, Charlottesville, VA, USA*.

Accurate assignments of highly-excited molecular vibrational states are needed for the verification of theoretical predictions of high-temperature spectra observed in astrophysics and combustion environments. We previously demonstrated optical-optical double resonance spectroscopy with a continuous wave 3.3 μm pump and a 1.67 μm centered frequency comb probe, which allows simultaneous measurement of multiple hot-band transitions from a selectively populated state of CH_4 with sub-Doppler resolution[1]. The probe spectrum is dispersed using a Fourier transform spectrometer with comb-mode-limited resolution, and interleaving of spectra measured with different f_{rep} produces a final spectrum with 2 MHz point spacing. More recently, we implemented an enhancement cavity for the comb probe that improved the absorption sensitivity by more than two orders of magnitude. In addition, the use of both co- and counter-propagating probe light eliminated errors in the final state term value due to errors in the Lamb-dip locking point of the pump, which limited the accuracy of the earlier single-pass measurements. Here we use this cavity-enhanced system to measure $3\nu_3 \leftarrow \nu_3$ methane transitions from higher J states with much-improved frequency and relative intensity accuracy, which allows unambiguous assignments of the final states using two independent methods. The first method relies on combination differences in probe spectra observed when the pump is sequentially Lamb-dip locked to P, Q, and R ν_3 band transitions from a fixed rotational level of the ground state. We also observe spectra with probe polarization both parallel and perpendicular to that of the pump light and compare the intensity ratio with predictions for the case of a strongly saturated pump. The two experimental methods of final state assignment agree, and are largely confirmed by theoretical predictions from the TheoReTS database.

1. A. Foltynowicz, et al., Phys. Rev. Lett. 126, 063001 (2021); Phys. Rev. A 103, 022810 (2021).

TE06 **10:37 – 10:52**

MODELING THE OPTICAL-OPTICAL DOUBLE RESONANCE LINESHAPES IN CH_4

VINICIUS SILVA DE OLIVEIRA, ISAK SILANDER, ADRIAN HJÄLTÉN, ANDREA ROSINA, ALEKSANDRA FOLTYNOWICZ, *Department of Physics, Umea University, Umea, Sweden*; LUCILE RUTKOWSKI, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*; KEVIN LEHMANN, *Department of Chemistry and Physics, The University of Virginia, Charlottesville, VA, USA*.

Optical-optical double resonance spectroscopy is a powerful tool to unravel and assign complex molecular spectra, such as found when exciting the overtone transitions of methane. When essentially monochromatic radiation is used for both pump and probe waves, such spectra are often described as “Doppler-free”, but it is more accurate to describe them as having much reduced Doppler broadening. Common treatments describe the lineshape of individual transitions as homogeneously broadened, however, they have widths multiple times the power-broadened homogeneous broadening of the levels involved, even when treated using simplified Bloch equations of three coupled levels. The spatial variation of pump field intensity, both transverse to the propagation vector and due to pump absorption, as well as the M_J dependence or transition dipole moments, further complicate the lineshape but are easily accounted for. More difficult to account for is the presence of inelastic scattering, which changes the Doppler shifts in the probe spectrum, and requires a full collision Kernel to properly model. This talk will present the results of an ongoing attempt to quantitatively model the double resonance spectra we observe using a 3.3 μ continuous wave pump and a 1.67 μm comb probe, in particular their dependence on pump power and sample pressure.

TE07 **10:55 – 11:10**

ARGON PRESSURE BROADENING IN THE OXYGEN A-BAND

LEAH E. STEVENSON, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; ERIN M. ADKINS, *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; JOSEPH T. HODGES, *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA*.

The oxygen A-band, centered at 760 nm, is commonly used in space- and ground-based remote sensing to determine air mass because of the constant mixing ratio of oxygen in Earth's atmosphere. Since the retrieved air mass has a direct impact on measured concentrations of target species like carbon dioxide, increasingly precise greenhouse gas measurements require high-accuracy spectroscopy of the A-band. Pressure broadening, which results from collisions between the absorbing species and other atoms or molecules, dominates line widths in the A-band and is dependent on the identity of the collision partner. Pressure broadening by argon, which comprises 0.934% of Earth's atmosphere by volume, is typically neglected in atmospheric and laboratory measurements of the A-band. To investigate the magnitude of pressure broadening by argon, we used cavity ring-down spectroscopy to measure lineshapes of high J'' lines in the P-branch of the oxygen A-band over a range of pressures and argon concentrations. Argon foreign-broadening parameters for these lines were determined in combination with other lineshape parameters using a multi-spectrum fitting algorithm. In addition to comparing the results to literature values, we will discuss the implications of including argon pressure broadening in atmospheric and laboratory measurements of the A-band.

TE08 **11:13 – 11:28**

CLOSING THE (SINGLET-TRIPLET) GAP: BeOBe AND ITS ANION STUDIED USING PHOTOELECTRON SPECTROSCOPY

NOAH B JAFFE, *Department of Chemistry, Emory University, Atlanta, GA, USA*; CAITLYN M DOLLAR, *Chemistry, Emory University, Atlanta, GA, USA*; MICHAEL HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA, USA*.

Beryllium containing molecules often exhibit intense multi-reference character that can lead to large discrepancies in computational results depending on the treatment of electron correlation. Exemplary of this multi-reference character is the BeOBe molecule, which has long been a source of frustration for computational methods due to is very small singlet-triplet energy splitting. While the molecule has been studied experimentally before by laser induced florescence, this singlet-triplet gap had yet to be rigorously determined. Here we present the first experimental values for the BeOBe singlet triplet gap, obtained via Slow Electron Velocity Map Imaging (SEVI) spectroscopy on the BeOBe anion, as well as comparison to previous experiment and theoretical calculations. This new data links the singlet and triplet manifolds obtained in previous studies, providing new insight into this strange molecule.

TE09 **11:31 – 11:46**

NEW ELECTRONIC STATES OF MgCl: THE PURE ROTATIONAL SPECTRUM IN THE $(3)^2\Sigma^+$ AND $(4)^2\Sigma^+$ STATES

TYLER J HERMAN, RAJAT RAVI, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*; ROBERT W FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

The millimeter/submillimeter spectrum of magnesium chloride (MgCl) has been recorded in electronic excited sates not previously measured, using direct absorption spectroscopy in the range of 210-450 GHz. The molecule was synthesized by reacting chlorine gas (Cl_2) with magnesium vapor, produced using a Broida-type oven, in the presence of argon carrier gas. Two distinct rotational patterns were observed, with significantly different rotational constants (B=5504 and 6349 MHz). The first vanishes at N=30←29, while the latter only appears at and above N=26←25, with this effect being observed across all vibrational states. There is no evidence of perturbations in either pattern prior to their disappearance. In the first pattern, at least seven rotational transitions in each of six isotopologues ($^{24}Mg^{35}Cl$, $^{24}Mg^{37}Cl$, $^{25}Mg^{35}Cl$, $^{25}Mg^{37}Cl$, $^{26}Mg^{35}Cl$, $^{26}Mg^{37}Cl$) were measured in the ground vibrational state, with numerous vibrationally excited satellite lines (v=1-13) also being observed for each species. For the second pattern, measurements were taken for v=0-2. From both sets of data, rotational and fine structure parameters were determined for $^{24}Mg^{35}Cl$, as well as equilibrium constants and the equilibrium bond lengths, r_e = 2.54 Å and 2.36 Å. From the first pattern, constants for the other five isotopologues were also established, including ^{25}Mg hyperfine parameters. Based on comparison with theoretical calculations, one excited state has been identified as the $(3)^2\Sigma^+$ state, and the other may arise from the $(4)^2\Sigma^+$ state. The excited state manifold of MgCl has already been the subject of several computational studies, and the unexpected formation of these states emphasizes the need to further investigate both this molecule, as well as other alkaline earth metal halides.

TE10 **11:49 – 12:04**

A QUIRKY LITTLE FELLOW: Be_3 AND ITS ANION STUDIED BY PHOTOELECTRON SPECTROSCOPY

NOAH B JAFFE, *Department of Chemistry, Emory University, Atlanta, GA, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; MICHAEL HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA, USA*.

Pure beryllium clusters have been the subject of a number of theoretical studies, but experimental validation for these studies has been lacking due to experimental hazards. The beryllium trimer has been predicted to be a closed shell D_3h neutral molecule, but limited computational studies have been carried out on the anion. In this study we present the first experimental data for the beryllium trimer and its anion. These data provide information on two transitions from the anion to the neutral, namely the $Be_3^- X^2A_2^{''} \rightarrow Be_3X^1A_1^{'}$ and $Be_3^- 1^2A_1^{'} \rightarrow Be_3X^1A_1^{'}$ transitions. Ab inito electronic structure calculations have been validated against the experimental data, confirming the D_{3h} geometry of the neutral and anion ground states. Electronic transition energies computed at the EOM-CCSDT level of theory agree well with experimental measurements, but the spectra show little excited vibrational activity, in contrast to Franck-Condon simulations.

TE11 **12:07 – 12:22**

INVESTIGATION OF THE ZEEMAN EFFECT IN THE $e\ ^6\Pi - a\ ^6\Delta$ SYSTEM OF FeH: APPLICATION TO STELLAR SPECTROSCOPY

AMANDA J. ROSS, PATRICK CROZET, *Inst. Lumière Matière, Univ Lyon 1 & CNRS, Université de Lyon, Villeurbanne, France*; ALLAN G. ADAM, *Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada*; TIMOTHY E BLACKMORE, DENNIS W. TOKARYK, *Department of Physics, University of New Brunswick, Fredericton, NB, Canada*.

We investigate the Zeeman effect in the $e\ ^6\Pi - a\ ^6\Delta$ system of FeH. The molecule has been produced by reaction of $Fe(CO)_5$ with H atoms, and examined by laser excitation with selective detection and by Fourier transform resolved fluorescence. The field-free spectrum of the $e\ ^6\Pi - a\ ^6\Delta$ system was extensively studied by the J.M. Brown group and collaborators in the 1990's [a]. Their analysis located the low-lying excited $a\ ^6\Delta$ state 1890 cm^{-1} above the $X\ ^4\Delta$ electronic ground state.

One of the infrared systems of FeH already recognised[b] in the spectra of cool stars around 1.6 μm, $E\ ^4\Pi - A\ ^4\Pi$, originates in an excited state lying only 920 cm^{-1} lower in energy in energy than $a\ ^6\Delta$, so it seemed not unreasonable to expect signatures from the known sextet systems $e-a$ and $g-a$ to appear in the spectra of cool stars as well. We found that the $e-a$ system can indeed be used as a diagnostic for FeH. Cross-correlation functions between a mask of laboratory-measured $e-a$ transitions and spectra from four M- dwarf stars taken on spectropolarimetric instruments ESPaDOnS (on Maunakea) and Narval (in the French Pyrenees), show that reliable radial-velocity information can be extracted for these objects. Our new Zeeman measurements are intended to improve reference data for cross-correlation calculations for M-type stars, whose magnetic fields are typically $0 - 5000$ Gauss.

[a] Goodridge *et al* J . Chem. Phys. 106 (12), 4823 (1997); Wilson *et al* J. Chem. Phys. 115 (13), 5943 (2001)
[b] Wallace & Hinkle, ApJ, 559, 424 (2001)

TF. Clusters/Complexes

Tuesday, June 20, 2023 – 8:30 AM

Room: 274 Medical Sciences Building

Chair: Mark D. Marshall, Amherst College, Amherst, MA, USA

TF01 **8:30 – 8:45**

MONOETHANOLAMINE-(H2O)N, N=1-7, AND -(CO2)M, M=1-4, CLUSTERS CHARACTERIZED BY ROTATIONAL SPECTROSCOPY

FAN XIE, WENHAO SUN, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; PABLO PINACHO, *Physical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

In this study, we present the structures of MEA-H2O and MEA-CO2 complexes identified in pulsed jet expansion using the broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy COMPACT that operated in the 2-18 GHz range[1]. We reveal the microhydration processes of MEA from these observed MEA-H2O clusters and show that the structures of MEA-(H2O)n are closely analogous to the pure water clusters (H2O)n+2. For example, the MEA monohydrate, dihydrate, and trihydrate adopt cyclic topologies similar to water trimer, tetramer, and pentamer, respectively. With four water molecules participating, we identified two isomers of MEA-(H2O)4, named Cage and Prism. In the observed MEA-H2O clusters, the intramolecular OH-NH2 H-bond of MEA is broken to form an energetically favorable intermolecular H-bond with water. In contrast, without the presence of water, CO2 is unable to break the intramolecular H-bond based on the observed MEA-CO2 complexes[2]. Interestingly, we discovered that the OH lone pair-CO2 interaction has higher energetic priority than the NH2 lone pair-CO2 interaction, which is in sharp contrast to the results from aqueous solutions. How would the CO2 bind to MEA with the presence of a few water molecules? A short discussion on the topic will be made based on what we learned from the observed structures of MEA-H2O and MEA-CO2.

[1] D. Schmitz, V. A. Shubert, T. Betz, M. Schnell, J. Mol. Spectrosc. 2012, 280, 77–84. [2] F. Xie, W. Sun, P. Pinacho, M. Schnell, Angew. Chem. Int. Ed. 2023, e202218539; Angew. Chem. 2023, e202218539.

TF02 **8:48 – 9:03**

FTIR DETECTION OF THE TERT-BUTYL HYDROPEROXIDE DIMER

CASPER VINDAHL JENSEN, HENRIK G. KJAERGAARD, *Department of Chemistry, University of Copenhagen, Copenhagen, Denmark*.

We have detected the *tert*-butyl hydroperoxide dimer (t-BuOOH)$_2$ in gas phase at room temperature using conventional FTIR techniques. The dimer is identified by an asymmetric absorbance band assigned to the hydrogen-bound OH$_b$-stretch. The gas-phase dimer assignment is supported by Ar matrix isolation FTIR experiments at 12 K. The dimer OH$_b$-stretching band is located at $\sim$3452 cm^{-1} redshifted by $\sim$145 cm^{-1} from the monomer OH-stretching band. Theoretically, we find the lowest energy structure of (t-BuOOH)$_2$ to be a doubly hydrogen bound 6-membered ring. The ring strain in this structure leads to non-optimal H-bond angles and a smaller than expected redshift. We calculate the transition frequency and oscillator strength of the OH$_b$-stretching transition with a 1D local mode model and DFT electronic structure methods. The constant of dimer formation K is estimated from the experimental integrated absorbance and the theoretically calculated oscillator strength of the OH$_b$-stretching band. The unitless K is estimated to be $\sim$0.41 for (t-BuOOH)$_2$.

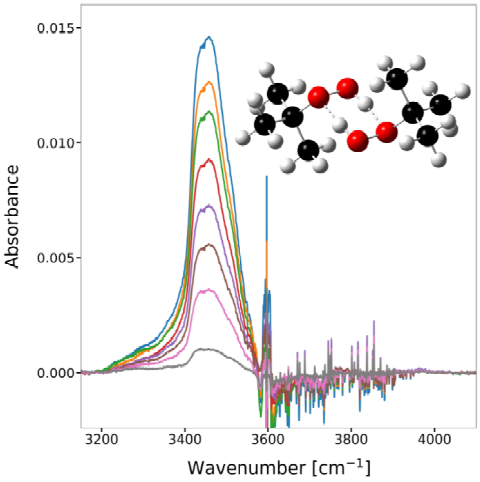


Figure 2: (t-BuOOH)$_2$ spectra at increased pressure.

TF03 **9:06 – 9:21**

A COMPUTATIONAL AND EXPERIMENTAL VIEW OF HYDROGEN BONDING IN POLYOL WATER CLUSTERS

ANNA C. WANNENMACHER, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; WENCHAO LU, CHANDIKA AMARASINGHE, *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*; ISHAN GUPTA, *Department of Chemistry, University of California, Berkeley, Berkeley, CA, USA*; MUSAHID AHMED, *UXSL, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*.

Polyol water clusters can act as a proxy for alcohol water ices in the interstellar medium. By studying these clusters, conclusions can be drawn about ionization and solvation processes of atmospheric and interstellar chemical interest, as was done with the polyols ethylene glycol, 1,2 propylene glycol, and 1,3 propylene glycol. These polyol water clusters are generated in a continuous supersonic jet expansion, then photionized with synchrotron based tunable vacuum ultraviolet light, and detected by a reflectron time-of-flight mass spectrometer. Polyol water cluster fragments are observed and the appearance energies for these clusters as well as water clusters are determined. To explain the experimentally obtained mass spectra, theoretical calculations are performed on neutral and ionized polyol water clusters as well as the detected fragments and fragment clusters. From these calculations, interaction and ionization energies are determined and hydrogen bond networks may be visualized.

TF04 **9:24 – 9:39**

TUNABLE EXCITED STATE DYNAMICS OF NEUTRAL COPPER OXIDE CLUSTERS WITH SIZE AND OXIDATION

CHASE H ROTTEGER, CARTER K JARMAN, SHAUN SUTTON, SCOTT G SAYRES, *School of Molecular Sciences and Biodesign Center for Applied Structural Discovery, Arizona State University, Tempe, AZ, USA*.

Copper oxides exhibit several useful electronic attributes such as electron correlation effects, spin dynamics, magnon behavior, and high temperature superconductivity. The atomic precision and tunability of gas phase neutral clusters provides insights into the charge carrier excitation dynamics of strongly correlated bulk materials by revealing how their excited state dynamics change with subtle changes in stoichiometry, local geometry, and electronic density. I will present our recent measurements of the ultrafast relaxation dynamics of sub-nanometer neutral copper oxide clusters investigated with femtosecond pump-probe spectroscopy coupled with time-of-flight mass spectrometry and supported by theoretical calculations. The carrier dynamics of neutral copper oxides clusters can be tuned upon the addition/subtraction of each atom and is attributed to the ligand-to-metal charge-transfer (LMCT) character of the photoexcitation. The sub-picosecond excited state lifetimes decrease almost linearly upon sequential oxidation, for Cu_nO_x (n $\leq$ 7), of $\sim$30-100 fs per oxygen atom. Stoichiometric clusters show an increase in excited state lifetimes as cluster size increases and is supported by DFT calculations attributing the trend to the localization of electrons in the excited state. Understanding the electronic properties and dynamics of copper oxide clusters promises to shape a new era of semiconductor and superconductor physics through development of new materials containing tunable properties.

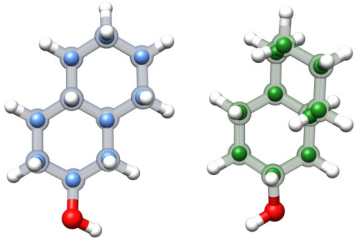
Intermission

TF05 **10:19 – 10:34**

THE HORMONE ANDROSTERONE VS. ITS ANALOG DECAHYDRO-2-NAPHTHOL: DIFFERENCES AND SIMILARITIES

SWANTJE V. M. CALIEBE, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; PABLO PINACHO, *Physical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Here we report the study on the *cis* and *trans* isomers of decahydro-2-naphthol and various complexes with it. Decahydro-2-naphthol is structurally analogous to a section of the steroid hormone androsterone, which has been recently studied by rotational spectroscopy.[a] For the large (from a rotational spectroscopy point of view) molecule androsterone, no experimental gas-phase structure was observed. In addition, intermolecular interactions in complexes with androsterone and smaller molecules cannot be experimentally studied due to the size of the steroid hormone. Because of that, decahydro-2-naphthol is an excellent system to indicate intermolecular interactions with other molecules and gain knowledge of the experimental gas-phase structure and thus, the conformational flexibility and arrangement in order to start to understand reaction mechanisms and functions of steroid hormones. Further, the orientations of the OH-groups in the decahydro-2-naphthol molecules were determined and also compared with the results from androsterone. The molecules were studied in the gas phase in a cold and isolated environment generated by a supersonic expansion. The spectra were recorded using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 2-8 GHz frequency region. The assignment was supported by quantum-chemical calculations.



[a] Caliebe, S. V. M.; Pinacho, P., Schnell, M. J. *Phys. Chem. Lett.* **2022**, *13*, 11913-11917.

TF06 **10:37 – 10:52**

HIGH RESOLUTION LASER SPECTROSCOPY OF THE NITRIC OXIDE DIMER IN SUPERFLUID HELIUM NANODROPLETS

DANIEL MISCHENKO, PAUL RASTON, *Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA, USA*.

Previously, the ν_1 and ν_5 bands of helium solvated nitric oxide clusters were investigated with a pulsed OPO system having a resolution of 0.25 cm^{-1} [1]. Here, we investigated the ν_1 band with a continuous-wave quantum cascade laser at high resolution (10 MHz), and uncover substructure that provides additional insight. In particular, in the vicinity of the fundamental band of the nitric oxide dimer, we observed baseline-resolved rotational substructure with relative intensities that are consistent with the *cis*-(ON-NO) isomer, along with a weaker band with similar substructure shifted slightly to lower frequencies. We tentatively attribute this weaker band to an anharmonic resonance between the fundamental and a combination band (which could be, e.g., $4\nu_6 + \nu_3$), although we cannot rule out that it is due to the higher energy triplet nitric oxide dimer.

[1] Hoshina et al., *J Phys. Chem. A.* **2016**, 120, 527.

TF07 **10:55 – 11:10**

IR SPECTRA OF BENZOIC ACID-WATER CLUSTERS IN A SUPERSONIC JET USING VUV IONIZATION DETECTION

CHIA-I HUANG, JUN-YING FENG, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; YUAN-PERN LEE, *Department of Applied Chemistry, Institute of Molecular Science, and Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; TAKAYUKI EBATA, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.

Hydrogen bonding (H-bonding) of aromatic clusters in dilute aqueous solutions has been a subject of great interest in recent years. In the present work, we investigated the hydrogen-bonded structures of jet-cooled benzoic acid-water clusters, $(BA)_m$-$(H_2O)_n$ (m, n = 1 or 2), with IR spectroscopy and quantum-chemical calculations. We measured the IR spectra of mass selected $(BA)_m$-$(H_2O)_n$ in the C-H and O-H stretching regions by IR excitation -VUV ionization with a reflectron time-of-flight mass spectrometer (RF-TOF-MS). The IR spectrum of BA monomer was obtained by 1+1 IR-VUV photoionization technique, and those of the clusters were obtained by the depletion of the VUV-induced ion signal upon IR predissociation. The observed IR spectra were analyzed by comparison with spectra of possible structures predicted with anharmonic calculations at the B3LYP/6-311++G(d,p) level of theory. We discuss the structures of $(BA)_m$-$(H_2O)_n$ and how the H-bonding network developed in these clusters.

TF08 **11:13 – 11:28**

ULTRAFAST EXCITED STATE DYNAMICS OF NEUTRAL ALUMINUM OXIDE CLUSTERS

CARTER K JARMAN, CHASE H ROTTEGER, SHAUN SUTTON, SCOTT G SAYRES, *School of Molecular Sciences and Biodesign Center for Applied Structural Discovery, Arizona State University, Tempe, AZ, USA*.

Aluminum oxides are an affordable, abundant, and commonly utilized material for many applications such as magnetic devices, gas sensing, and catalysis. To maximize catalytic activity, a modern frontier of material science is aimed at creating ever-decreasing sizes of materials which drives new demands to understand the electronic properties and geometric structures down to the molecular (cluster) scale. I will present recent measurements investigating the excited state dynamics of neutral aluminum clusters collected with femtosecond pump-probe spectroscopy coupled with time-of-flight mass spectrometry. Neutral clusters are excellent mimics of bulk material properties and show tunable ultrafast dynamics and excited state lifetimes with the addition and subtraction of each atom in their composition. Our preliminary results on the ultrafast dynamics of aluminum oxide clusters reveals a trend where sequential addition of oxygen atoms decreases the measured excited state lifetimes. For example, in the Al_4O_y series (y = 0-2), the measured excited state lifetimes decrease by 37% with the addition of 2 oxygen atoms, which is consistent across our measurements for other aluminum oxide series. By understanding the electron dynamics and charge carrier separation in aluminum oxide clusters, bulk material defects and vacancies can be capitalized upon to increase the efficiency of aluminum containing species.

TF09 **11:31 – 11:46**

PROVING THE ROLE OF WATER MOLECULES IN SUGAR-PEPTIDE INTERACTIONS

ANDER CAMIRUAGA, GILDAS GOLDSZTEJN, PIERRE ÇARÇABAL, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, Orsay, France*.

Sugars are one of the most important families of biomolecules. They act as mediators of molecular recognition processes. Among the possible biomedical applications, one example is the addition of mannosides to photosensitizers used in PhotoDynamic Therapy, targeting Mannose Receptor (MR) proteins on pathogenic cells. A precise description of the structural basis of Mannose-MR local and direct interplay, which can be provided by gas phase spectroscopy, critically lacks to design PSs with improved selectivity.

In the gas phase, combining experimental mass resolved and conformer selective double resonance vibrational spectroscopy and theoretical chemistry studies,[a] we have already been able to observe several complexes between sugars and peptide models.[bc] We can now also observe such complexes with a controlled number of water molecules. Our most recent results on complexes of mannose with different peptide models, either hydrated or not, allow resolving the nature of the interactions between the molecules, for each donor and acceptor molecular group involved in the non-covalent bonds governing the complexes. These results evidence the adaptability of the sugar moiety to its peptide receptor. In particular, the study of the complexes formed with few water molecules may highlight the role of water in molecular recognition processes in an unprecedented manner.

[a] Cocinero E.J.; Çarçabal P., Top. Curr. Chem., 2015, 364, pp. 299-333.
[b] Cocinero E.J.; Çarçabal P.; Vaden T.D.; Simons J.P.; Davis B.G., Nature, 2011, 469, 76-79.
[c] Cocinero E.J.; Çarçabal P.; Vaden T.D.; Davis B.G.; Simons J.P., J. Amer. Chem. Soc., 2011, 133, 4548-4557.

TF10 ***Post-Deadline Abstract*** **11:49 – 12:04**

THE CONFORMATIONAL LANDSCAPE OF TYROSOL AND ITS HYDRATES

ALBERTO MACARIO, SUSANA BLANCO, JUAN CARLOS LOPEZ, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*.

2-(4-Hydroxyphenyl)ethanol, commonly known as Tyrosol, is a powerful antioxidant in the human diet, mainly found in olive oil. It also presents other biological properties such as cardiovascular drug or geroprotector agent, among others. As it widely known, these biological properties are related with its molecular structure and its conformational landscape. Here we presented the study of the molecular structure and conformational panorama of tyrosol and its mono- and dihydrated complexes, by means of gas-phase high-resolution rotational spectroscopy. From a vast number of predicted conformers, three of them have been experimentally identified for the monomer. The large amplitude motions interconverting the predicted and observed forms have been studied by means of computational methods. Five different conformers were observed for the monohydrated complex, all of them preserving the monomer structures with the water being able to interact as a proton acceptor with both hydroxy groups. In this competition between these two groups the interaction with the hydroxy group attached to the phenyl ring seems to present a higher stability. This is corroborated with the observation of two conformers of the dihydrated complex, which also preserves the structures of the two most stable monomer forms with water dimer forming a cycle only with the hydroxy group attached to the phenyl ring.

TG. Spectroscopy as an analytical tool

Tuesday, June 20, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Christopher Thompson, BrightSpec, Inc., Charlottesville, VA, USA

TG01 **1:45 – 2:00**

THERMAL DECOMPOSITION OF 2-(CHLOROETHYL)BENZENE STUDIED VIA MATRIX-ISOLATION FTIR

TESS COURTNEY, *Chemistry, Marshall University, Huntington, WV, USA*; KHALED ALEY EL-SHAZLY, *Department of Chemistry, Marshall University, Huntington, WV, USA*; SOPHIA WYLIE, *Chemistry, Marshall University, Huntington, WV, USA*; LAURA R. McCUNN, *Department of Chemistry, Marshall University, Huntington, WV, USA*.

Chemical recycling of plastics is an important strategy to improve both the effectiveness and financial sustainability of plastics recycling. Pyrolysis of plastic to decompose polymers, followed by the refining of the pyrolysate into valuable chemicals, is advantageous but there is an incomplete understanding of the chemical mechanisms governing plastics pyrolysis. Pyrolysis of the plastic polyvinyl chloride produces a variety of chlorinated hydrocarbons, such as 2-(chloroethyl)benzene. The purpose of these experiments is to probe the pyrolysis pathways of 2-(chloroethyl)benzene via matrix-isolation FTIR. A dilute mixture of the sample in argon was subject to pyrolysis in a resistively heated SiC tubular reactor at temperatures up to 1400 K. Matrix-isolation FTIR spectroscopy was used to identify pyrolysis products. The products observed include HCl, acetylene, ethylene, propyne, isobutene, vinylacetylene, propargyl radical, styrene, and phenylacetylene. Matrix-isolation FTIR spectra were recorded for commercial samples of styrene and phenylacetylene in order to verify the assignment of these species in the spectra collected following pyrolysis of 2-(chloroethyl)benzene.

TG02 **2:03 – 2:18**

RAMAN LABELLED ANTIBODY/APTAMER BASED IMMUNOASSAY FOR THE DETECTION OF OVARIAN CANCER BIOMARKER CA125.

ROBINSON KARUNANITHY, NOAH ALLEN ROSS, P SIVAKUMAR, TORREY E. HOLLAND, *Department of Physics, Southern Illinois University Carbondale, Carbondale, IL, USA*.

Epithelial ovarian cancer (EOC) is one of deadliest cancers among women, ranking as the 5th leading cause for cancer related deaths in women in the United States. The higher mortality can be linked to the poor ability to diagnose this type of cancer at an early, treatable stage due to the lack of sensitivity and specificity in the methods that have been clinically used. Therefore, developing new techniques that can identify individuals who are at the treatable or early stage is important to increase the survival rate. Spectroscopic aided bio-conjugation technique is one such technique that could potentially alleviate some of the problems associated with the current clinical methods. In this immunoassay method, we conducted two separate investigations into the individual affinities of an antibody and an aptamer towards the ovarian cancer biomarker CA125 aided by gold nanoparticles (AuNPs) pre-modified with a Raman marker and evaluate the sensitivity of each aptamer or antibody based assay. For this goal, we used Ni-NTA (Nickel-nitrilotriacetic acid) micro particles (magnetic beads) to sandwich and purify the CA125-antibody or aptamer complex labelled with Raman markers. Firstly, Ni-NTA magnetic beads were conjugated to CA125 through histidine (CA125 His-tag). It was then incubated with a biotinylated antibody or aptamer. Finally, the conjugate was labelled by streptavidin coated AuNPs, which are pre-modified with a Raman marker. Following the magnetic separation, the final conjugates were investigated with surface enhanced Raman spectroscopy. The Raman signatures from the label verified the purification of the CA125-antibody or CA125-aptamer complex sandwiched by magnetic beads and AuNPs.

TG03 **2:21 – 2:36**

COMPOSITIONAL STUDY OF MULTIPLE AND SINGLE GALLBLADDER STONES USING PHOTOACOUSTIC SPECTROSCOPY

ZAINAB GAZALI[a], *Department of Physics, Allahabad University, Allahabad, India*; SURYA NARAYAN THAKUR, *Department of Physics, Banaras Hindu University, Varanasi, Uttar Pradesh, India*; A. K. RAI, *Department of Physics, Allahabad University, Allahabad, India*.

The presence of long-standing gallbladder stones, one of the most painful diseases worldwide, has been recognized as one of the highest risk factors for gallbladder cancer. However, the complex composition of gallbladder stones is still not well known as well as some people have a single gallstone while some have multiple (aggregate of a large number of small stones) gallstones at the same time. Using sensitive techniques, the compositional analysis of gallbladder stones has been a challenge and of great concern for scientists and medical practitioners. The literature reviews show that photo-acoustic spectroscopy (PAS) is a promising candidate for the compositional analysis of gallbladder stones. The presence of organic compounds such as cholesterol, calcium carbonate, bilirubin, fatty acid, protein, and bile acid is confirmed by the PAS technique. We have also recorded the Fourier transform infrared (FTIR) spectra of gallbladder stones, which show vibrational bands of CH, CO, C-C, and CN molecules. This is in good agreement with the result obtained by PAS and these studies are likely to reveal the compositions of gallbladder stones.

[a]The author is thankful to University Grant Commission (Maulana Azad National Fellowship) for providing financial assistance.

TG04 **2:39 – 2:54**

DIRECT VISUALIZATION OF STRUCTURALLY SIMILAR POLYSACCHARIDES IN SINGLE YEAST CELLS IN VIVO BY MULTIVARIATE ANALYSIS ASSISTED RAMAN MICROSPECTROSCOPY

IMRUL M HOSSAIN, *The United Graduation School of Agricultural Sciences, Tottori University, Tottori, Tottori, Japan*; HEMANTH NOOTHALAPATI, TATSUYUKI YAMAMOTO, *Life and Environmental Sciences, Shimane University, Matsue, Shimane, Japan*.

Raman spectrophotometry is a molecular vibrational and rotational spectroscopy. Raman spectrum, otherwise called molecular fingerprint, provides molecular information with high specificity in living organisms in a label-free manner. A confocal Raman micro-spectrophotometer with 632.8 nm He-Ne laser excitation was used in this study. Multivariate analysis such as multivariate curve resolution and alternative least squire (MCR-ALS) is a non-negative matrix factorization analytical method that can constrain physically meaningful components among the large data set. Fission yeast is a model organism that is used for various purposes such as biological and medical research, industrial, food and beverage, etc. Recently the demand for functional food like β-glucan has increased enormously owing to human and animal health. among the many natural sources of glucans such as oats, barley, mushrooms, and seaweeds, yeast has a special advantage for the industrial production of glucans. However, it is not easy to characterize glucans since there are numerous structural variations such as α- or β-glucans with various configurations which vary in their physical and chemical properties. Currently, microscopy, chemical, or genetic approaches are followed to study glucan synthesis and accumulation in single yeast cells, however, they are either time-consuming, lack molecular specificity, or are practically not feasible for real applications. Therefore, we developed a Raman microspectroscopy-based method to identify, distinguish and visualize structurally similar glucan polysaccharides. We successfully separated Raman spectra of α- and β-glucans from mixtures with high specificity and visualized heterogeneous molecular distributions during yeast sporulation at the single-cell level in a label-free manner using multivariate curve resolution analysis. We believe such an approach, when combined with a flow cell, can achieve the sorting of yeast cells based on the accumulation of glucans for various applications. Further, by implementing this approach, commercial β-glucan can be produced from yeast in the future and can also be extended to various other biological systems to investigate structurally similar carbohydrate polymers in a fast and reliable manner.

TG05 **2:57 – 3:12**

SPECTROCHEMICAL ANALYSIS FOR NUTRIENTS AND TOXIC HEAVY METALS DETECTION IN ABUNDANTLY UTILIZED HERBAL MEDICINE (SCHILAJIT) BY EMPLOYING THREE ADVANCED ANALYTICAL TECHNIQUES

MOHAMMED A GONDAL, *Department of Physics, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia*; R. K. ALDAKHEEL, M A. ALMESSIERE, *Physics, Imam Abdulrahman Bin Faisal University, Dammam, Saudi Arabia*.

Shilajit, a Rasayana herbo-mineral substance, is a popular Ayurvedic treatment throughout the world to restore the body's energetic balance and fend off diseases like Alzheimer's and cognitive disorders. In Saudi Arabia, patients with bone fractures are treated locally with Shilajit. Due to its multiple usage elemental analysis of Shilajit to determine its nutritional value and heavy metal contamination for the patients' safety is highly significant. Using three cutting-edge analytical methods (LIBS, ICP, and EDX), the elemental composition of Shilajit was determined. The two varieties of Shilajits that are most frequently used are made in Pakistan and India were gathered for comparative studies. To hinge on Shilajit's therapeutic potential, our main focus is to draw attention to nutritional excellence and heavy metal contamination. In this study, Shilajit was analyzed both qualitatively and quantitatively using Laser-Induced Breakdown Spectroscopy (LIBS). Our LIBS analysis revealed that Shilajit samples contains several elements like Ca, S, K, Mg, Al, Na, Sr, Fe, P, Si, Mn, Ba, Zn, Ni, B, Cr, Co, Pb, Cu, As, Hg, Se and Ti. Shilajits from Pakistan and India had levels of Al, Sr, Mn, Ba, Zn, Ni, B, Cr, Pb, As, and Hg toxins that were higher than the standard permissible limit while also being highly enriched in beneficial nutrients like Ca, S, and K for human body. Even though the amounts of the majority of elements were comparable between the two Shilajits, the Indian Shilajit had higher concentrations of nutrients and toxins overall, with the exception of Hg and Ti. The self-developed calibration-free laser-induced breakdown spectroscopy (CF-LIBS) method was applied for the elemental quantification, and the LIBS results are in good agreement with the concentrations revealed using the conventional ICP OES/MS method. The presence of the aforementioned elements was confirmed by EDX spectroscopy, which was also used to validate our results from LIBS and ICP OES/MS techniques. This work is vital for raising awareness among those who are suffering from overdoses of this product and thus saving many lives worldwide.

TG06 **3:15 – 3:30**

ROOM TEMPERATURE OPTICAL DETECTION OF $^{14}CO_2$ AT PARTS-PER-QUADRILLION LEVEL ACCURACY WITH TWO-COLOR CAVITY RINGDOWN SPECTROSCOPY

JUN JIANG, A. DANIEL McCARTT, *Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA, USA*.

In this talk, we report room-temperature optical detection of radiocarbon dioxide ($^{14}CO_2$) with better than 10 parts-per-quadrillion (10^{15}, ppq) (^{14}C/C) measurement accuracy with the two-color cavity ringdown (2C-CRD) technique. The current sub-10-ppq measurement accuracy of $^{14}CO_2$ is 10X better than our previous work [McCartt, A. D., & Jiang, J. (2022). *ACS Sensors*, 7(11), 3258-3264], which demonstrated the first-ever room temperature detection of $^{14}CO_2$ at concentrations below the natural abundance ($\sim$1200 ppq ^{14}C/C). This significantly enhanced measurement capability of our 2C-CRD technique, achieved with under 2 minutes of averaging, is made possible by a combination of 30X improvement in the signal-to-noise ratio in our detection system and nearly 10X reduction in the magnitude of the collisionally-induced background 2C signal. As in our previous work, cavity-enhanced pump and probe laser beams are used to excite a pair of ν_3=1-0 and ν_3=2-1 rovibrational transition of $^{14}CO_2$. With the pump radiation switched off during every other probe ringdown events, the net 2C signals from the difference between the pump-on and pump-off decay rates is immune to drifts of the CRD rates and spectral overlaps from one-photon molecular transitions. The 10-ppq level detection capability of our 2C-CRD technique has been reproducibly demonstrated with several rounds of measurements of combusted ^{14}C standard samples (with close to contemporary ^{14}C concentrations) and low ^{14}C content biofuel samples (10-80 ppq ^{14}C/C). Room temperature optical detection of $^{14}CO_2$ at our demonstrated sensitivity and accuracy is not possible with other existing one-photon detection methods, because of severe spectral overlap between the very weak $^{14}CO_2$ ν_3-band transitions ($\sim$4/s RD rate at natural abundance) and the strong hot-band transitions of other CO_2 isotopologues ($\sim$10000/s). In addition to its use for ultra-trace analysis, our cavity-enhanced 2C technique is well-suited for rovibrational-state-resolved measurements in chemical dynamics and high-resolution spectroscopic studies, which we will discuss at the end of the talk.

Intermission

TG07 **4:10 – 4:25**

DIRECT MEASUREMENT OF CATALYTIC OXIDATION OF SO_2 BY A K-BAND MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY

SAI ESWAR JASTI, SYLVESTRE TWAGIRAYEZU, *Chemistry and Biochemistry, Lamar University, Beaumont, TX, USA*; JUSTIN L. NEILL, *BrightSpec Labs, BrightSpec, Inc., Charlottesville, VA, USA*.

A Molecular rotational resonance (MRR) spectrometer, which operates in the 18-26GHz, has been evaluated for monitoring the oxidation process of SO_2 and O_2 in the presence of NH_4VO_3. This work is performed as a part of effort to determine the utility of rotational spectroscopy as a tool for monitoring the conversion of SO_2 to H_2SO_4. The initial MRR measurements revealed the reduction of $SO_2$and the presence of small polar impurities (i.e., water vapor and ammonia). The current data have been further employed to validate K-Band MRR for SO_2 removal. The MRR maintains its linearity confirming its strength to monitor the removal of SO_2 in presence of other polar impurities. Work to improve this analytical procedure is underway and will be reported in this talk.

TG08 **4:28 – 4:43**

THE SPECTROSCOPIC SOFTWARE UNIVERSE: A ”PICKETT 2.0” PROPOSAL

NATHAN A. SEIFERT, *Department of Chemistry, University of New Haven, West Haven, CT, USA*.

An important yet often unappreciated aspect of the spectroscopist's workflow is the use of key software packages for data analysis. Spectroscopists young and old alike recall their first experiences with a multitude of packages, such as Herb Pickett's CALPGM for rovibrational spectra, Colin Western's powerful PGOPHER graphical user interface, David Plusquellic's JB95 and its magical B+C/B-C rotational constant sliders, or Kisiel's AABS for speedrunning assignment for large broadband microwave or millimeter wave datasets. There are, of course, many other examples of spectroscopic software, whose existences evoke a wide range of emotions, including passion, apathy, and sometimes even mortal fear.

However, the 21st century has provided a difficult inflection point in the interplay between experiment and software for microwave spectroscopy. Chirped-pulse microwave spectroscopy has ushered in routine acquisition of species- and transition-dense spectroscopic data sets, and the typical workflow for such data is generally split between a series of software packages that each provide only a partial solution to efficient workflow. With the growing promise of high-throughput, library-free spectroscopic analysis using machine learning techniques, there is an increased need for performant and “black box” solutions to interpreting and evaluating spectra. Even worse, with the recent passings of Herb Pickett and Colin Western, the community is left with an issue of sustainability and transparency for continuing use and training in these legacy packages.

In this talk, I propose a new, unified software package for spectroscopic prediction and assignment, the so-called “Pickett 2.0” package, which was introduced as an idea that was informally discussed between a set of concerned microwavers last year at this conference. I will outline the features that modern broadband microwave spectroscopists require from a software package for efficient analysis, as well as those required by an emergent community of chemists who use rotational techniques as merely an analytical tool. I will also present new ideas for features that are more applicable for machine learning and high-throughput applications, as well as a brief discussion about the necessity for long-term software sustainability and methodological transparency.

TG09 **4:46 – 5:01**

WILL CHIRAL TAG ROTATIONAL SPECTROSCOPY ALWAYS GIVE ACCURATE ENANTIOMERIC EXCESS DETERMINATATIONS?

LUCA EVANGELISTI, *Dipartimento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy*; JOSH HEMAN-ACKAH, TAYLOR CHAMBERS, *Department of Chemistry, University of Virginia, Charlottesville, VA, USA*; BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

Chiral tag rotational spectroscopy is a general method for determining the absolute configuration and enantiomeric excess (EE) of a chiral analyte. It is a chiral derivatization method where noncovalent interactions are used to attach a small, chiral molecule to the analyte via cluster formation in a pulsed jet expansion. The addition of a new, known chiral center converts the analyte enantiomers into spectroscopically distinguishable diastereomers. The high spectral resolution in rotational spectroscopy spectrometers makes it possible to fully resolve the diastereomeric chiral tag complex spectra – a favorable situation for quantitative EE measurements. The formula used to determine the analyte EE, when the tag EE is known, is derived under the assumption that transition intensities in the homochiral and heterochiral tag complex spectra are linear in the number densities of the tag and monomer. Using a simple kinetics model, it can be shown that this assumption breaks down in the case where complex formation has reversibility. In this model, chiral recognition, which results from binding energy differences in the homochiral and heterochiral complexes, leads to different dissociation rates of the initial complexes. This kinetics model has been used to explain the enhancement of ^{22}Ne complexes (relative to ^{20}Ne complexes) where the binding energy difference is caused by zero-point vibrational energy differences. If the dissociation rate of the initial collision complex is on the order of the stabilization rate of the complex, then deviations from the derived EE formula are expected in chiral tag rotational spectroscopy. A study of the accuracy of EE determinations using chiral tag rotational spectroscopy in the autotag analysis of trifluoroisopropanol is presented. Quantum chemistry calculations of the binding energy in the homochiral and heterochiral dimers gives an energy difference of about 2 kJ/mol suggesting that deviations from the EE formula could be observed. However, the formula is quantitative across the full EE range. This observation suggests that collision stabilization is rapid compared to the dissociation rate of the initial collision complex for a cluster formed from strong noncovalent interactions.

TG10 **5:04 – 5:19**

MOLECULES IN LASER-INDUCED PLASMA: AN ANOMALY OR THE BEST WAY TO SOLVE INTRACTABLE PROBLEMS?

TIMUR A. LABUTIN, SERGEY ZAYTSEV, NIKOLAI SUSHKOV, ALEKSANDR ZAKUSKIN, EKATERINA A. BORMOTOVA, ANDREY POPOV, *Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia*.

Laser-induced breakdown spectrometry (LIBS) uses a laser ablation process when a pulsed laser vaporizes a small amount of a solid or liquid sample and generates a plasma. In general, the atomic emission originated from the laser-induced plasma serves for elemental analysis of the sample. Molecular emission appear at later observation times due to plasma cooling and recombination. Since atomic concentration is reduced due to the formation of molecules and their broadband emission overlaps with numerous atomic lines, molecules are usually "unwelcome guests" for analytical measurements. However, in some cases, molecules are the only way to solve the problem. In this paper, we consider three such cases: (i) direct chlorine determination in concrete, (ii) plasma thermometry, and (iii) laboratory modeling to study meteor wake emission. The advantages of the molecular bands are related to a sufficiently lower excitation potential of CaCl compared to Cl, as well as a low degree of its atomization in plume. A simple multivariate technique (PCR) solved the problem of mutual interference between the molecular band and atomic lines and provided reliable chlorine determinationin concrete by means of CaCl emission at the threshold level even with the use of a portable LIBS setup. The second case is related to the plasma diagnostics of plasmas with a small number of atomic lines (organic target, relatively low temperature). Molecules such as CN, AlO, and CaO are ideally suited for rapid temperature estimation in this case. We have shown the possibility of using vibrational or rotational temperature for plasmas induced on various organic matrices. We discuss the benefits as well as some problematic aspects of their use. Finally, we study the Fe and FeO emission in laser-induced plasma under reduced pressure to develop an approach for finding the conditions under which the laboratory plasma state matches the state of the meteor wake. Several combinations of pressure (75-150 Torr) and delay lead to the highest degree of similarity between the laser-induced plasma and the Benešov bolide spectra at an altitude of 39 km. Thus we assume that the pressure in the bolide wake is higher than the ambient pressure by a factor of 20-30. Undoubtedly, the developed approach would be beneficial to support the modeling of a meteoroid entry.

TH. Mini-symposium: Spectroscopy at Large-scale Facilities

Tuesday, June 20, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Ming-Fu Lin, SLAC National Accelerator Laboratory, Menlo Park, CA, USA

TH01 **1:45 – 2:00**

PROBING THE FERROCYANIDE AQUATION REACTION WITH NONRESONANT X-RAY EMISSION SPECTROSCOPY

ANNE MARIE MARCH, CHRISTOPHER J OTOLSKI, GILLES DOUMY, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; NIRANJAN GOVIND, *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA*; AMITY ANDERSEN, *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, USA*; GYORGY VANKO, ZOLTÁN NÉMETH, *Wigner Research Centre for Physics, Hungarian Academy of Sciences, Budapest, Hungary*; WOJCIECH GAWELDA, *Departamento de Quimica, Universidad Autonoma de Madrid, Madrid, Spain*.

Observing light-induced reactions in liquids, where much of chemistry happens, and on the timescales during which these reactions occur, has been a long-standing objective. Knowledge of the mechanistic details at the molecular scale can inform rational design of new molecules for applications such as light harvesting and energy conversion and illuminate new means of controlling reactions. We have been exploring how time-resolved x-ray spectroscopy can be used to understand fundamental mechanisms underlying ligand exchange, a reaction common to coordination complexes in solution. Our recent focus has been on the aquation reaction of ferrous hexacyanide in water, where absorption of UV light initiates an exchange of a CN- ligand with a water molecule from the solvent. Using the MHz repetition-rate laser-pump/x-ray-probe capabilities our group has built at the Advanced Photon Source we have investigated the reaction using both absorption spectroscopy at the Fe K-edge and nonresonant Fe 1s emission spectroscopy. Pre-edge resonances sensitive to geometry revealed a 20-ps lived pentacoordinated intermediate species. QM/MM molecular dynamics simulations explain the rather long time for aquation as being due to fluctuations in the geometry of the pentacoordinated complex that leave very short time intervals when there is room for a water molecule to bond. The K alpha, K beta, and valence-to-core emission spectra yield complementary information beyond geometry for the species involved. The measured K beta line confirms the triplet spin state of the pentacoordinated intermediate, and also reveals a subtle spectral difference for the low-spin aquated product compared to the ground state complex. This work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

TH02 **2:03 – 2:18**

DETERMINING THE CHARGE TRANSFER PROPERTIES OF METAL-COORDINATED COUMARIN DYES USING X-RAY AND OPTICAL TRANSIENT ABSORPTION SPECTROSCOPIES

DANIELLE J JACOBY, CALI ANTOLINI, ABBY E CIVIELLO, *Department of Chemistry, University of Rhode Island, Kingston, RI, USA*; CHRISTOPHER J OTOLSKI, GILLES DOUMY, ANNE MARIE MARCH, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; DUGAN HAYES, *Department of Chemistry, University of Rhode Island, Kingston, RI, USA*.

Organic dyes present a promising alternative to the more expensive ruthenium and iridium complexes commonly used in photoredox reactions. Ideally, such a framework should offer facile tunability of the excited state redox potential while maintaining sufficiently long excited state lifetimes for intermolecular charge transfer. Here we have augmented the coumarin derivative 4-methylesculetin with dipicolylamine to form a tetrahedral binding pocket that can then coordinate different divalent first-row transition metals, allowing us to tune the excited state redox potential by simply adding a salt. Using X-ray transient absorption spectroscopy, we have observed photoinduced reductive shifts in the K-edge spectra of the corresponding complexes of Mn^{2+} through Zn^{2+} that are consistent with the varying degrees of intramolecular charge transfer to the metals predicted by density functional theory calculations. We have also combined these X-ray measurements with optical transient absorption spectroscopy to characterize the relaxation dynamics of these complexes on timescales ranging from 100s of femtoseconds to 10s of microseconds. As expected, the Zn^{2+} complex exhibits little to no charge transfer character, and any electronic or nuclear rearrangement at the metal site fully relax within the temporal resolution of our measurement. On the other hand, all other metal complexes exhibit long-lived charge transfer states that persist for 100s of nanoseconds. Notably, the relaxation dynamics of the Co^{2+} complex include an additional time component of approximately 10 nanoseconds that is entirely absent in the other metal complexes.

TH03 **2:21 – 2:36**

PUMPING THE INTERVALENCE CHARGE TRANFSER AND PROBING ACROSS THE ELECTROMAGNETIC SPECTRUM: DIVERSE SPECTRAL PROBES REVEAL A UNIQUE RELAXATION MECHANISM

JOHN H BURKE, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; RENSKE VAN DER VEEN, *Photovoltaics, Helmholtz Zentrum Berlin, Berlin, Germany*; JOSH VURA-WEIS, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Using transient absorption (TA) spectroscopy with a barrage of spectral probes, we investigate the charge recombination dynamics following intervalence charge transfer (IVCT) excitation of a heterobimetallic Fe(II)Co(III) molecule. Femtosecond optical probes in the near-infrared and visible regions reveal long-lived excited states following IVCT excitation. In order to determine the electronic structure at each metal center in these excited states, we turn to element-specific extreme ultraviolet (XUV) and X-ray techniques. Femtosecond XUV TA at the Fe and Co M2,3 edges demonstrates that a local, Fe-centered, triplet (d-d) state is formed within 1 picosecond of IVCT excitation. This observation uncovers a unique IVCT relaxation mechanism whereby ultrafast intersystem crossing and back electron transfer populates a local, triplet excited state instead of the singlet ground state. The triplet state then evolves to a long-lived excited state, which we examined with hard and soft X-ray probes from synchrotron sources. Picosecond soft X-ray TA at the Fe and Co L3 edges shows that this state is also an Fe-centered (d-d) state. Hard X-ray TA at the Fe and Co K-edges reveal large bond length elongations of the Fe coordination sphere that are consistent with a high-spin quintet state. Altogether, these experiments highlight the importance of local, Fe-centered triplet and quintet (d-d) states on the IVCT relaxation dynamics of this heterobimetallic complex. By employing a diverse range of spectral probes, we were able to track charge and spin at each metal center over a broad range of timescales, which enabled the elucidation of this unique IVCT relaxation mechanism.

TH04 ***INVITED TALK*** **2:39 – 3:09**

CHEMICAL DYNAMICS CAPTURED WITH ATOMIC SPECIFICITY AND RESOLUTION USING ULTRAFAST X-RAY SPECTROSCOPY AND SCATTERING

KELLY GAFFNEY, *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*.

Electronic excited states enables novel non-equilibrium pathways to chemical transformations. The complexity of potential outcomes for light-driven reactions has made harnessing electronic excited states for chemistry challenging. One approach to addressing this challenge is advancing the tools we have for capturing the complex dynamics of electronic excited states. I will discuss how advances in ultrafast x-ray sources and experimental methods provide a pathway to capturing the non-equilibrium trajectories of electronic excited states with precision, particularly for transition metal complexes.

Of particular importance for 3d metal compounds is characterizing the population dynamics of charge-transfer (CT) and metal-centered (MC) electronic excited states and understanding how the inner coordination sphere structural dynamics mediate the interaction between these states. I will focus on the value of using simultaneous X-ray emission spectroscopy (XES) and X-ray solution scattering (XSS) studies to disentangle the electronic and structural dynamics.

TH05 **3:15 – 3:30**

MONITORING ELECTRON DELOCALIZATION IN A MIXED VALENCE RU DIMER USING TRANSIENT RU L-EDGE X-RAY AND INFRARED SPECTROSCOPIES

BENJAMIN I POULTER, CHELSEA LIEKHUS-SCHMALTZ, ROBERT WEAKLY, JASON SANDWISCH, MUNIRA KHALIL, *Department of Chemistry, University of Washington, Seattle, WA, USA*; ELISA BIASIN, SOUMEN GHOSH, NIRANJAN GOVIND, *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA*; SVEN AUGUSTIN, IVAN USOV, DMITRY OZEROV, CHRISTOPHER ARRELL, PHILIP JOHNSON, GREGOR KNOPP, CLAUDIO CIRELLI, *Photonics, Paul Scherrer Institute, Villigen, Switzerland*; CHRISTOPHER MILNE, *FXE, European XFEL, Schenefeld, Germany*; AMY CORDONES-HAHN, *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; MARCO REINHARD, *Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; DIMOSTHENIS SOKARAS, ROBERTO ALONSO MORI, ROBERT SCHOENLEIN, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*.

Recent spectro-electrochemical studies have shown that the Ru-Ru dimer, [Ru(tpy)(bpy)(μ-CN)Ru(bpy)$_2$(CH$_3$CN)]$^{3+}$(tpy = terpyridine, bpy = bipyridine), exhibits Class III mixed valency (complete delocalization between metal centers) upon one electron oxidation. Photochemically, this could be achieved by metal-to-ligand-charge transfer (MLCT) excitation where one Ru center is oxidized while one of the polypyridine ligands is reduced. Characterizing the extent of electron delocalization on the excited states of donor-bridge-acceptor complexes remains an important target in the field of mixed-valence chemistry. Transient X-ray spectroscopies are well suited to investigate electron delocalization processes as they offer element and orbital specific probes of local electronic and atomic structure. Here, we utilized solution phase, femtosecond, Ru L$_3$-edge resonant inelastic X-ray scattering, performed at the Alvra Prime end station of the Swiss X-ray Free Electron Laser, to probe valence electron and hole motions during the ultrafast delocalization process following MLCT excitation. A complementary study using transient Infrared spectroscopy was done to determine role of the CN bridge in the delocalization process. Additionally, TD-DFT calculations of spectroscopic observables were performed to help interpret and describe the X-ray and infrared experiments.

TH06 **3:33 – 3:48**

MEASURING CHARGE DELOCALIZATION IN MIXED-VALANCE COMPLEXES USING ULTRAFAST X-RAY SPECTROSCOPY

ZHAOYUAN YANG, BENJAMIN I POULTER, *Department of Chemistry, University of Washington, Seattle, WA, USA*; MICHAEL SACHS, *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; SOUMEN GHOSH, *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA*; ROBERT SCHOENLEIN, ROBERTO ALONSO MORI, LELAND BRUCE GEE JR., TIM VAN DRIEL, RYAN RIBSON, TAKAHIRO SATO, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; YIHAN XIA, *Department of Chemistry, University of Washington, Seattle, WA, USA*; ELISA BIASIN, NIRANJAN GOVIND, *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA*; MUNIRA KHALIL, *Department of Chemistry, University of Washington, Seattle, WA, USA*.

One of the challenging problems in the field of mixed valence complexes is determining the extent of electronic delocalization between metal centers in the ground and excited states. In this study, we applied femtosecond transient Fe K-edge X-ray absorption spectroscopy measurement on a tri-metallic, mixed valence complex, [L$_4$Ru^{II}(NC-Fe^{III}(CN)$_5$)$_2$]$^{4-}$ (L=pyridine and 4-methoxypyridine) , in methanol. The experiment was performed at X-ray Pump Probe end station of Linac Coherent Light Source. We observed 0.3 eV and 1.5 eV red shifts for the Fe 1s to 3d e$_g$ and ligand π* transition, confirming the delocalized nature of the excited metal-to-metal charge transfer state. The appearance of a spectral feature at 7107.5 eV in the excited state was first reported, suggesting that a short-lived transition was enabled unique to the trimer system. Complementary TD-DFT calculations were performed to visualize the transition orbitals and interpret experimental results.

Intermission

TH07 **4:28 – 4:43**

GROUND- AND EXCITED-STATE CHARACTERIZATION OF A Ni-BIPYRIDINE PHOTOCATALYST USING X-RAY SPECTROSCOPY

RACHEL WALLICK, SAGNIK CHAKRABARTI, LIVIU M MIRICA, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; RENSKE VAN DER VEEN, *Photovoltaics, Helmholtz Zentrum Berlin, Berlin, Germany*; JOSH VURA-WEIS, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Photo-assisted catalysis using Ni complexes is an emerging field for cross-coupling reactions in organic synthesis. however, the mechanism by which light enables and enhances reactivity is poorly understood. Optical techniques can lend insight into the ground- and excited-states of the photocatalysts but lack the specificity to interrogate electronic and geometric structural changes at specific atoms. Through static and transient L- and K-edge X-ray absorption spectroscopy of a prototypical bipyridine-based Ni(II) photocatalyst, we are able to determine that the ground-state of complex features an unexpected mixed-spin character. We are also able to unambiguously determine that the long-lived (5 ns) excited state is a tetrahedral metal-centered triplet state. The mixed-spin character of the ground state can have profound impact on the excited-state properties and reactivity that are not well understood. In addition, these findings can drive future synthetic design of improved photocatalysts via judicious tuning of the electronic and geometric properties of the ligands.

TH08 **4:46 – 5:01**

TRACKING STRUCTURAL SOLVENT REORGANIZATION AND RECOMBINATION DYNAMICS FOLLOWING ELECTRON PHOTOABSTRACTION FROM AQUEOUS HALIDES WITH FEMTOSECOND X-RAY SPECTROSCOPY AND SCATTERING

KATHARINA KUBICEK, ZHANGATAY NUREKEYEV, MOHAMMED SEKKAL, *Institute of Experimental Physics, University of Hamburg, Hamburg, Germany*; MICHAEL THORWART, *I. Institute of Theoretical Physics, University of Hamburg, Hamburg, Germany*; CARMEN HERRMANN, *Department of Chemistry, University of Hamburg, Hamburg, Germany*; CHRISTIAN BRESSLER, *ALO, European XFEL, Schenefeld, Germany*.

We present a sub-picosecond resolved investigation of the structural solvent reorganization and geminate recombination dynamics of photogenerated halogen atoms in aqueous solutions. Nascent iodine radicals were generated via 400 nm 2-photon ionization of the parent iodide, while nascent bromine and chlorine atoms were generated via 1-photon ionization with 200 nm light. Time-resolved X-ray Absorption Near Edge Structure Spectroscopy around the L_1-edge of the photogenerated nascent iodine atoms (I^0) delivered kinetic traces in agreement with a purely diffusion-driven geminate iodine-electron recombination model without the need of a long-lived (I^0:e^-) contact pair [1]. Nonequilibrium classical MD simulations indicate a delayed (ca. 100 fs) response of the caging H_2O solvent shell supported by the structural analysis of the X-ray Solution Scattering data. In-house QM/MM simulations [2] indicate a decreasing cage orientation time in the homologue series from Cl to I, which may be due to a more rigid H bond network around the smaller halogen atom. We will compare the femtosecond photodetachment results on iodide, measured at the LCLS X-ray Free Electron Laser (XFEL), with those on aqueous bromide ions, measured at SACLA XFEL, together with laser-only spectroscopy measurements on the nascent solvated electrons.

[1] P. Vester, K. Kubicek et al., J. Chem. Phys. 157, 224201 (2022); [2] M. Reidelbach et al., J. Phys. Chem. B 127, 1399–1413 (2023)

TH09 **5:04 – 5:19**

USING POLARIZED ULTRAFAST SPECTROSCOPY AS A TOOL FOR DETERMINING SUBPICOSECOND STRUCTURAL DYNAMICS OF PHOTOEXCITED N-PROPYLCOBALAMIN

RYAN LAMB, *Chemistry, University of Michigan, Ann Arbor, MI, USA*; R.J. SENSION, *Department of Chemistry, University of Michigan, Ann Arbor, MI, USA*.

Pump-probe spectroscopy has been utilized for decades to take ultrafast "snapshots" of molecular systems as they traverse their excited state surfaces. Recently, linearly polarized pump and probe pulses have been manipulated to separate "magic angle" X-ray spectra from isotropic solutions into two components: signal from the transition dipole moment direction and signal from the two orthogonal directions. This polarized ultrafast spectroscopy provides more electronic and/or structural information compared to using magic angle. In the study presented here, polarized X-ray absorption near-edge structure (XANES) at the Cobalt K-edge and UV-visible transient absorption (TA) spectroscopy were used to monitor the evolution of the excited-state structure of n-propylcobalamin following visible excitation. Finite difference method near edge structure (FDMNES) is used in conjunction with polarized XANES experimental data to correlate changes in spectral features to changes in the structure of n-propylcobalamin on a subpicosecond timescale. These measurements provide a cobalt-centered movie of the excited molecule as it evolves to the local excited-state minimum.

TH10 **5:22 – 5:37**

ULTRAFAST PUMP-PROBE XANES ANALYZED WITH FDMNES SIMULATIONS REVEAL THE SEQUENTIAL STRUCTURAL EVOLUTION OF ADENOSYLCOBALAMIN AS A FUNCTION OF SOLVENT

EILIDH McCLAIN, *Department of Biophysics, University of Michigan, Ann Arbor, MI, USA*.

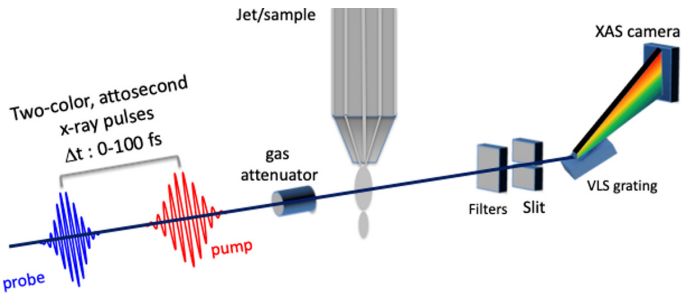
Adenosylcobalamin (AdoCbl) is a highly light-sensitive member of the cobalamin family. It features a central cobalt coordinated to a corrin ring, a 5'-deoxyadenosyl upper ligand, and a dimethylbenzimidazole lower ligand. The photochemistry of AdoCbl is important due to its central role as the chromophore in the CarH gene regulatory photoreceptor found in various bacterial species. Time-resolved X-ray absorption near-edge structure (XANES) examines the excited states of AdoCbl through the lens of atomic structural change from the central cobalt's perspective. The use of polarization selection deconvolves the changes into orthogonal molecule-defined directions, yielding more specific structural information instrumental in a thorough analysis with higher confidence. Extensive time-resolved XANES data have been collected on AdoCbl in both water and ethylene glycol solvent. To assign specific spectral features to structural changes in the AdoCbl, the XANES spectra are simulated and compared with the experimental difference spectra using the finite difference method near-edge structure (FDMNES) method. FDMNES allows for systematic investigation of the structural manipulations required to reproduce the experimental difference spectra. These simulations help to quantitatively uncover the sequential structural evolution of AdoCbl on an ultrafast timescale as a function of solvent, allowing for a better understanding of the fundamental relationship between this cofactor and its environment as well as the relationship between XANES spectral features and molecular structure in general.

TH11 **5:40 – 5:55**

FIRST RESULTS FROM ATTOSECOND X-RAY PUMP-PROBE EXPERIMENTS IN LIQUIDS

SHUAI LI, KAI LI, GILLES DOUMY, LINDA YOUNG, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; EMILY NIENHUIS, CAROLYN PEARCE, *EED, Pacific Northwest National Laboratory, Richland, WA, USA*; LIXIN LU, XIAOSONG LI, *Chemistry, University of Washington, Seattle, WA, USA*; STEFAN P. MOELLER, MING-FU LIN, GEORGI DAKOVSKI, AGO MARINEILI, JAMES CRYAN, DAN DePONTE, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; ROBIN SANTRA, LUDGER INHESTER, *Center for Free-Electron Laser Science (CFEL), Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Understanding the elementary steps following ionization in aqueous systems provides a framework for radiation-matter interactions in chemistry and biology. However, a microscopic understanding of the reaction mechanisms in the relevant physico-chemical time regime is missing as typical techniques, EPR, and UV spectroscopies, lack either time resolution or spectral clarity. A powerful two-color sub-femtosecond time-resolved X-ray pump/X-ray probe scheme developed at LCLS provides a qualitatively new window to systematically understand the electronic and nuclear dynamics following outer-, inner-valence, and core ionization in aqueous systems.



Recently we investigated radiation-induced reactions in liquid water by X-ray transient absorption in a sheet jet using sub-fs XLEAP pulses on the ChemRIXS beamline at LCLS. The x-ray pump (255 eV to 275 eV) produces outer- and inner-valence holes, and the probe (510-550 eV) covers the valence hole through oxygen K-edge absorption. Starting from 0.6 fs delay absorption spectra were measured to capture ultrafast processes, e.g. Auger decay, intermolecular Coulombic decay (ICD), electron transfer mediated decay (ETMD), and proton transfer.

TI. Radicals

Tuesday, June 20, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Chuanliang Li, Taiyuan University of Science and Technology, Taiyuan, Shanxi, China

TI01 **1:45 – 2:00**

MILLIMETER/SUBMILLIMETER SPECTROSCOPY OF THE METHYLAMINE PHOTODISSOCIATION PRODUCT AMINOMETHYL RADICAL ($^{\cdot}CH_2NH_2$)

HAOCHENG LIANG, JONATHAN REBELSKY, CONNOR J. WRIGHT, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; JOHN F. STANTON, *Physical Chemistry, University of Florida, Gainesville, FL, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

Methylamine (CH_3NH_2) is the simplest primary amine and a precursor of the simplest amino acid, glycine. Therefore, methylamine is a molecule of particular interest in astrochemistry and prebiotic chemistry. Previous astronomical observations have detected methylamine in multiple star-forming regions, molecular clouds, meteorites, and the atmosphere of Titan. Studying the formation and dissociation mechanisms of methylamine is thus important for the modeling of chemistry in these environments and for laying the groundwork for future astronomical observations. This work focuses on the aminomethyl radical ($^{\cdot}CH_2NH_2$), which is one of the expected products arising from the cosmic-ray induced photodissociation of methylamine. A pulsed supersonic expansion of methylamine in argon was coupled with a high-voltage needle discharge source to produce $^{\cdot}CH_2NH_2$ in a vacuum chamber. The rotational spectrum of $^{\cdot}CH_2NH_2$ was collected in the millimeter/submillimeter regime, and the results were compared to theoretical predictions based on the molecular structure of $^{\cdot}CH_2NH_2$. Here we will present the laboratory measurements and the results of the spectral analysis, as well as initial searches for $^{\cdot}CH_2NH_2$ in the interstellar medium.

TI02 **2:03 – 2:18**

PURE ROTATIONAL SPECTRA OF ETHOXY RADICAL

CHING HUA CHANG, *Department of Applied Chemistry, Institute of Molecular Science, and Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; YASUKI ENDO, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.

The ethoxy radical (C_2H_5O) is a reactive intermediate exciting in many important combustion and atmospheric reactions. The near-UV electronic transitions of ethoxy radical were studied by Tan at el. in 1993, where the rotational and spin-rotation splittings were resolved.[a] In the present study, the rotational spectra of C_2H_5O are measured by Fourier-transform Microwave (FTMW) and FTMW-microwave double-resonance spectroscopy in the frequency region of 4-40 GHz. The electric discharge of diluted ethanol is used to generate the ethoxy radical. Four a-type transitions and two b-type transitions including K_a = 0 and K_a = 1 are observed. The 2_{02}-1_{01} and 1_{10}-1_{01} transitions are reproduced with the double resonance technique. The rotational and spin-rotation coupling constants agree with Tan et al's results. However, the hyperfine splittings due to the five protons in the C_2H_5O radical are so complicated that definite assignment has not been obtained yet. We are trying to assign them with the help of the double resonance spectra.

[a] X. Q. Tan, J. M. Williamson, S. C. Foster and T. A. Miller, J. Phys. Chem. 1993, 97, 9311-9316

TI03 **2:21 – 2:36**

CRIEGEE INTERMEDIATE CH_2OO IN THE OXIDATION OF ETHANE

NATHAN A. SEIFERT, *Department of Chemistry, University of New Haven, West Haven, CT, USA*; RAGHU SIVARAMAKRISHNAN, KIRILL PROZUMENT, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*.

The family of Criegee intermediates, commonly designated as QOO, where Q is CH_2, CH_3CH, and so on, has been predicted by Rudolf Criegee in 1949 and discovered recently in laboratory studies. These highly unstable and reactive species are important in the atmosphere where they are formed by ozonolysis of alkenes. To investigate its chemistry, CH_2OO has been produced in various laboratory settings by either ozonolysis of CH_2CH_2, photodissociation of CH_2I_2 followed by oxidation, or oxidation of CH_4 under the discharge conditions. At Argonne, we observe CH_2OO resulting from the oxidation of CH_3CH_3 in a continuous-flow SiC microreactor heated to 1700 K. Cold ($T_{\mathrm{rot}} = 7$ K) Criegee intermediate is detected in the supersonic molecular beam emerging from the hot microreactor and using the chirped-pulse Fourier transform millimeter-wave spectrometer, which operates in the 60–90 GHz region and is equipped with a fast narrowband digitizer for averaging 10^7 free induction decay traces in 5 minutes. The branching ratios of CH_2OO to the main oxidation products HO_2 and CH_2O are measured as a function of reactor temperature. We discuss the possible chemical pathways and the thermodynamic conditions within the reactor and outside of it that may lead to the formation and retention of the "fragile" CH_2OO intermediate in this experiment.

TI04 **2:39 – 2:54**

SPECTRAL STUDIES OF THE REACTION OF THE CRIEGEE INTERMEDIATE CH_3CHOO WITH HCL USING A STEP-SCAN FOURIER-TRANSFORM INFRARED ABSORPTION SPECTROMETER

YUAN-PERN LEE, *Department of Applied Chemistry, Institute of Molecular Science, and Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; ZIH-SYUAN SU, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.

Reactions between Criegee intermediates and hydrogen halides are important in atmospheric chemistry, because of their large rate coefficients. Employing a Fourier-transform absorption spectrometer in a step-scan mode or a continuous-scan mode, we recorded infrared spectra of transient species and end products in a flowing mixture of $CH_3CHI_2/HCl/N_2/O_2$ irradiated at 308 nm. Eight bands near 1383.7, 1357.9, 1323.8, 1271.8, 1146.2, 1098.2, 1017.5 and 931.5 cm^{-1}were experimentally observed and assigned to bands ν_8 to ν_{15} of the *anti*-conformer of chloroethyl hydroperoxide (CEHP, $CH_3CHClOOH$), according to comparison of vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. We derived a rate coefficient of *anti*-CH_3CHOO + HCl to be k_{HCl} = (3.1 $\pm$ 0.2)x10^{-10} cm^3 $molecule^{-1}$ s^{-1} from the formation of *anti*-CEHP. At a later reaction period, absorption bands of H_2O and acetyl chloride, $CH_3C(O)Cl$, at 1819.1 cm^{-1}were observed; these species were produced from the decomposition of *anti*-CEHP or the secondary reactions of $CH_3CHClO + O_2 \rightarrow CH_3C(O)Cl + HO_2$ and $OH + HCl \rightarrow H_2O + Cl$ according to temporal profiles of CEHP, H_2O, and $CH_3C(O)Cl$; both O_2 and HCl are major species in the system to participate in the secondary reactions. By adding methanol to deplete *anti*-CH_3CHOO, we observed only *anti*-CEHP, indicating that the interconversion from *syn*-CEHP to *anti*-CEHP is rapid. The branching ratio of the formation of $CH_3C(O)Cl + H_2O$ to that of $CH_3CHClO + OH$ was estimated to be 0.5 : 0.5. This observation serves as an excellent example that secondary reactions might interfere with the observation of the original products.

TI05 **2:57 – 3:12**

OBSERVATION OF THE OH-C_6H_6 RADICAL COMPLEX IN AN ARGON MATRIX USING MATRIX ISOLATION INFRARED SPECTROSCOPY WITH A VACUUM ULTRAVIOLET PHOTOLYSIS SOURCE

JAY C. AMICANGELO, CATHERINE KAISER, TRACY JONES, DYLAN JOHNSON, *School of Science (Chemistry), Penn State Erie, Erie, PA, USA*.

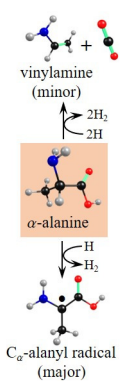
Utilizing matrix isolation infrared spectroscopy with a vacuum ultraviolet (VUV) photolysis source (121 nm), a 1:1 complex of the hydroxyl radical (OH) with benzene (C_6H_6) was observed in low temperature argon matrices. Co-deposition experiments with simultaneous VUV photolysis of H_2O and C_6H_6 mixtures were conducted in an argon matrix at 15 K. The OH stretching peak for the OH-C_6H_6 complex was observed at 3502.3 cm^{-1}. Identification of the observed peak of the OH-C_6H_6 complex was established by performing experiments with varying concentrations of the H_2O and C_6H_6 relative to the argon matrix, comparing the co-deposition spectra to the individual monomer spectra of H_2O and C_6H_6 in argon matrices both with and without VUV photolysis, as well as matrix annealing experiments (30 - 35 K). Experiments were also performed using the D_2O isotopomer and the OD stretching peak for the OD-C_6H_6 complex was observed at 2584.1 cm^{-1}. Quantum chemical calculations were performed at the MP2, M06-2X, and ωB97X-D levels of theory with the aug-cc-pVDZ basis set to obtain the optimized geometry and simulated infrared spectrum for the OH-C_6H_6 complex. The observed OH and OD stretching peaks of the OH(D)-C_6H_6 radical complexes observed in argon matrices in the current experiments are in good agreement with the values previously reported in argon matrices using a different production method.[a,b]

[a] A. Mardyukov, E. Sanchez-Garcia, R. Crespo-Otero, and W. Sander, Angew. Chem. Int. Ed. 48, 4804 (2009)
[b] A. Mardyukov, R. Crespo-Otero, E. Sanchez-Garcia, and W. Sander, Chem. Eur. J. 16, 8679 (2010)

TI06 **3:15 – 3:30**

PRODUCTION OF C_α-ALANYL RADICAL AND VINYLAMINE IN THE REACTION H + α-ALANINE IN SOLID *p*-H_2 AND ITS IMPLICATIONS IN ASTROCHEMISTRY

PRASAD RAMESH JOSHI, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; YUAN-PERN LEE, *Department of Applied Chemistry, Institute of Molecular Science, and Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.



Amino acids, key building blocks of protein, gained enormous attention in interstellar chemistry because they were detected in comets and meteorites; these observations provided strong evidence for the cosmic origin of amino acids on Earth. However, detailed investigations regarding their formation and reactivities with interstellar relevant species under cosmic-like conditions are scarce. We utilized the characteristics of *para*-hydrogen (*p*-H_2), which served as a quantum-solid matrix host and a medium for efficient hydrogen-atom reaction, to investigate the reaction between α-alanine [$H_2NCH(CH_3)C(O)OH$] and H atoms at 3.2 K. To produce H atoms, we performed UV photolysis at 365 nm on a matrix co-deposited with a mixture of $H_2NCH(CH_3)C(O)OH$/*p*-H_2 and Cl_2 to produce Cl atoms, followed by infrared irradiation to promote the Cl + H_2 (ν = 1) $\rightarrow$ H + HCl reaction. Among four different hydrogen-containing moieties of $H_2NCH(CH_3)C(O)OH$, H abstraction on the -CH moiety to produce C_α-alanyl radical [$H_2N \bullet C(CH_3)C(O)OH$] from the conformer with the least energy is the most favorable. This radical plays a vital role in the asymmetric synthesis of complex organic molecules. In parallel, possibly H abstraction on both -C(O)OH and CH_3 moieties led to the fragmentation to produce vinylamine ($NH_2CH = CH_2$) and CO_2 through the second-most favorable channel. Recently, vinylamine has been detected in the interstellar medium.[a] These assignments were supported by isotopic substitution experiments and a comparison of experimental results with vibrational wavenumbers of possible products predicted with the B3LYP/aug-cc-pVTZ method.

[a] S. Zeng et al. Astrophys. J. Lett. 2021, 921, L27.

Intermission

TI07 **4:10 – 4:25**

ELECTRONIC STRUCTURE OF PROTOTYPICAL π- and σ-RADICALS: HYPERFINE-RESOLVED ROTATIONAL SPECTROSCOPY OF PROPARGYL AND PHENYL

BRYAN CHANGALA, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; PETER R. FRANKE, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; BARNEY ELLISON, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

The reactivity of hydrocarbon radicals is strongly influenced by the orbital character and distribution of the unpaired electron. Hyperfine-resolved microwave spectroscopy is an ideal tool for measuring this structure in isolated, gas-phase molecules, providing fundamental insights into their open-shell electronic properties and chemical structure. We present examples of this approach applied to two prototypical reactive species: propargyl ($HCCCH_2$), the smallest resonance-stabilized π-radical, and phenyl (c-C_6H_5), the simplest aryl σ-radical. Using cavity Fourier transform microwave measurements of isotopically substituted propargyl, combined with highly accurate *ab initio* rovibrational corrections, we have derived its complete semi-experimental equilibrium structure and unpaired spin distribution, which provide vivid, complementary illustrations of π-electron delocalization. Our parallel work on phenyl has focused on the complete assignment of the complex hyperfine structure associated with its five ^{1}H nuclear spins. In addition to characterizing the singly occupied, carbon-centered σ-orbital, the precisely determined hyperfine parameters enable us to generate a kHz-accuracy cm-wave catalog. These laboratory data are an essential prerequisite for a sensitive astronomical search for phenyl in radio surveys of narrow-linewidth interstellar objects such as cold, dark molecular clouds, where phenyl is thought to be a critical intermediate in the formation of the first aromatic ring. Our work suggests that other large, weakly polar, open-shell hydrocarbons, including benzyl and indenyl, may be amenable to high-resolution microwave characterization.

TI08 **4:28 – 4:43**

THE UV-VIS SPECTRUM OF ClSO RADICAL FROM THE PHOTOLYSIS of THIONYL CHLORIDE AT 248 nm

WEN CHAO, GREGORY H JONES, MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; CARL J. PERCIVAL, FRANK A. F. WINIBERG, *Science Diviion, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*.

Sulfinyl radicals (R-SO) play a critical role in various fields, from biology to atmospheric chemistry, such as aerosol formation in which chlorine atoms was proposed to potentially catalyze the oxidation of sulfur species in Venus' atmosphere. In this study, we performed a Pulsed Laser Photolysis experiment to detect ClSO from Cl_2SO photolysis at 248 nm in a gas flow reactor using time-resolved UV-Vis transient absorption spectroscopy. A strong absorption near 303 nm and a weak one around 385 nm, with a vibrational progression of about 658 $\mathrm{cm}^{-1}$and 227 cm^{-1}, was recorded. Ab initio calculations at the EOMEE-CCSD/ano-pVQZ level revealed that the strong and weak band corresponds to the 1^2A" $\leftarrow$ X^{2}A" and the 2^2A' $\leftarrow$ X^{2}A" transitions. Further analysis showed that there might be a conical intersection between the 1^2A' and 2^2A' state near the ground-state geometry, which poses a challenge for further theoretical work. Furthermore, we constructed a molecular orbital diagram analysis to understand the electronic structure of the sulfinyl functional group. The analysis suggested that sulfinyl radicals tend to form chemical bonds with other radicals. As an example, a fast recombination rate coefficient of Cl + ClSO $\rightarrow$ Cl_2SO reaction was investigated to be $k_{Cl+ClSO}$ = (1.48 $\pm$ 0.42)$\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 292 K and 90 Torr utilizing the strong absorption band. These results suggest that the Cl-containing SO_x species might act as radical reservoirs in sulfur oxide-rich environments such as Venus' atmosphere.

Refernce:

1.Wen Chao, Gregory H. Jones, Mitchio Okumura, Carl J. Percival, and Frank A. F. Winiberg*, Spectroscopic and Kinetic Studies of the ClSO Radical from Cl_2SO Photolysis, J. Am. Chem. Soc, 2022, 144, 44, 20323-20331. DOI: 10.1021/jacs.2c07912

TI09 **4:46 – 5:01**

ANALYSIS OF THE OPEN-SHELL CH_3CO RADICAL: INTERNAL ROTATION, SPIN-ROTATION, AND HYPERFINE STRUCTURE[a]

OLIVIER PIRALI, ROSEMONDE CHAHBAZIAN, MARIE-ALINE MARTIN-DRUMEL, L. H. COUDERT, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*; LUYAO ZOU, R. A. MOTIYENKO, L. MARGULÈS, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*.

Although many non-rigid open-shell molecules can be spectroscopically accounted for without a dedicated approach, a subclass of these requires specific theoretical treatments. Such is the case of the CH_2 and CH_2OH radicals and of the Na_3 trimer for which new approaches were setup to model a large amplitude motion together with the electron spin-rotation coupling.[b] The acetyl radical CH_3CO is a benchmark molecule for this subclass of molecules as it presents a low barrier torsional motion and fine interaction. This radical was first studied some time ago[c] and a new theoretical model was developed to analyze its spectroscopic data. Unfortunately, only a few low-J transitions could be measured then.

An analysis of the new submillimeter wave transitions recorded at the ISMO and PhLAM laboratories for the CH_3CO radical will be presented. The theoretical approach developed parallels that of Hirota *et al.*[c] It relies on an effective torsion-rotation Hamiltonian[d] to which the spin-rotation and hyperfine couplings[e] are added.

The results of preliminary line frequency analyses will be presented. Values for the torsion-rotation Hamiltonian parameters A, B, C, D_{ab}, and ρ were obtained from a data set consisting of 143 rotation-torsion transitions split by spin-rotation and hyperfine couplings. The electron spin-rotation coupling tensor components were also determined.

[a]Supported by the Programme National PCMI of CNRS/INSU with INC/INP co-funded by CEA and CNES

[b]Ohashi, Tsuura, Hougen, Ernst, and Rakowsky, *J. Mol. Spec.* **184** (1997) 22; Coudert, *J. Chem. Phys.* **153** (2020) 144115; and Coudert, Chitarra, Spaniol, Loison, Martin-Drumel, and Pirali, *J. Chem. Phys.* **156** (2022) 244301

[c]Hirota, Mizoguchi, Ohsima, Katoh, Sumiyoshi, and Endo, *Mol. Phys.* **105** (2007) 455

[d]Nakagawa, Tsunekawa, and Hojima, *J. Mol. Spec.* **126** (1987) 329

[e]Brown and Sears, *J. Mol. Spec.* **75** (1979) 111; and Coudert, Gutlé, Huet, Grabow, and Levshakov, *J. Chem. Phys.* **143** (2015) 044304

TI10 **5:04 – 5:19**

RESONANCE RAMAN SPECTRA OF PROTOTYPE (HYDROXY)CYCLOHEXADIENYL RADICALS IN WATER

IRENEUSZ JANIK, SUSMITA BHATTACHARYA, *Radiation Laboratory, University of Notre Dame, Notre Dame, IN, USA*.

The simplest symmetric cyclohexadienyl radical produced upon H atom addition to benzene was generated pulse radiolytically and characterized vibrationally using Raman scattering in resonance with its first optical absorption band located at 312 nm. After the initial assignment of Raman bands of the intermediate, we performed corresponding studies on its lower symmetry hydroxyl analog, which we also produced by pulsed irradiation using the addition of OH radical to benzene. To assist in band assignments, parallel experiments were performed with benzene-d6 analogs and theoretical calculations of all intermediates' molecular geometries and vibrational frequencies using DFT methodology. Resonance Raman spectrum of cyclohexadienyl radical recorded in 500-4800 cm^{-1}consists of 8 bands which can be assigned in terms of strongly enhanced fundamental ν_3 at 1560 cm^{-1}accompanied by two weakly enhanced fundamentals ν_1 and ν_2 at 556 and 1174 cm^{-1}, respectively, and additional weaker overtones and combinations at 1738, 2131, 2744, 3152 and 4715 cm^{-1}. In deuterated analog radical, all of these bands shift to lower wavenumbers. The first three fundamentals shift by 23, 279, and 40 cm^{-1}. Based on these shifts along with DFT computations ν_1- ν_3 fundamental vibrations of cyclohexadienyl radical were assigned to CCC bending, CH bending, and C=C stretching ring modes, or 6a, 9a, and 8a in Wilson notation, respectively. Due to the lower symmetry of the hydroxy-cyclohexadienyl radical, its resonance Raman spectrum exhibits a higher number of bands in the same spectral region. The first eight fundamental bands lay below 1700 cm^{-1}, and the remaining combinations and overtones (6 bands) are above. The strongest fundamental ν_7 at 1560 $\mathrm{cm}^{-1}$was assigned to 8a mode (C=C stretching). Weaker fundamentals located at 554, 961, 1176, and 1420 cm^{-1}were assigned to ring modes 6a, 18a, 9a, and 19a, respectively. Moving the laser excitation wavelength around the absorption peak position allowed us to record the excitation profile of recorded vibrations and observe the change of relative intensity pattern in the observed fundamental bands. Based on this observation, we could discuss the nature of the overlapping excited states contributing to the absorption envelope in these types of intermediates.

TI11 **5:22 – 5:37**

DIRECT TERAHERTZ ROTATIONAL MEASUREMENTS OF FeH AND FeD (X $^4\Delta_i$)

AMBESH PRATIK SINGH, TYLER J HERMAN, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; DEACON J NEMCHICK, BRIAN DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

Iron-bearing molecules have eluded radio astronomers for decades, in part due to the dearth of laboratory spectroscopic data. To this day, there has been only one definitive detection of an iron-bearing molecule, FeCN. One molecule of much interest is FeH. The rotational spectrum of this radical thus far has only been measured with Laser Magnetic Resonance (LMR), which utilizes the Zeeman effect. Therefore, LMR requires extrapolation to zero field frequencies, which can introduce uncertainties. Here we present the first measurements of the rotational spectrum of FeH and its deuterated analog FeD in their ground electronic state using direct absorption methods in the THz region. The molecule was created in an AC discharge in a mixture of H_2, argon, and $Fe(CO)_5$, with pressures of 30 milli-torr and 3 milli-torr, respectively. Thus far, five transitions of FeH in the Ω = 1/2, 3/2, and 7/2 ladders (0.7 - 1 THz) and eight transitions of FeD in the Ω = 3/2, 5/2, and 7/2 ladders (0.5 - 1 THz) were recorded. Additional measurements are underway.

TJ. Electronic structure, potential energy surfaces

Tuesday, June 20, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

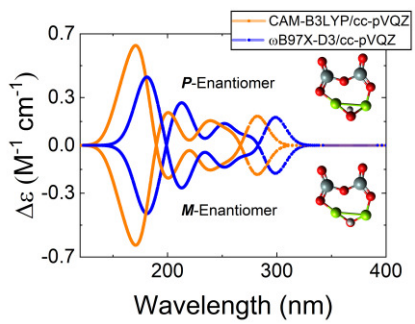
Chair: James H. Thorpe, Southern Methodist University, Dallas, TX, USA

TJ01 **1:45 – 2:00**

LIFE'S COSMIC HANDSHAKE: DFT AND TD-DFT PREDICTIONS FOR THE PROPERTIES OF ENSTATITE ($MgSiO_3$) MONOMERS AND DIMERS

KAMIL B. STELMACH, *Department of Chemistry, University of Virginia, Charlottesville, VA, USA*; CATHERINE A. DUKES, *Laboratory for Astrophysics and Surface Physics, University of Virginia, Charlottesville, VA, USA*; ROBIN T. GARROD, *Departments of Chemistry and Astronomy, The University of Virginia, Charlottesville, VA, USA*.

Silicates represent an understudied class of molecules in astrochemistry despite surfaces having been shown to have important chemical and physical effects. Clinoenstatite has been detected in interstellar space[a] and is a major component of meteorites.[b] Clinoenstatite is also interesting because it has chiral faces.[c] Structural and spectral studies utilizing density functional theory (DFT) and time-dependent (TD-) DFT were conducted on the monomer and a nanosilicate dimer of enstatite first described in Valencia et al.[d]; in addition, a 2D chiral conformer of the dimer was also studied. The HSE06/aug-cc-pVQZ level of theory was chosen for optimization, frequency, and energy calculations. CAM-B3LYP and ωB97X-D3 functionals were used with the cc-pVQZ basis set in the TD-DFT calculations to obtain the UV-Vis and ECD spectra. We modeled each structure in its bare silicate form but also with H, H^+, and H_2. Placing the neutral H on the 2D chiral enstatite conformer produces a 3D structure that makes it optically active. This provides a symmetry breaking mechanism for chiral silicates in the ISM.



[a] Jones, A. P. (2007). *EJM*, 19(6), 771-782.
[b] Mason, B. (1968). *Lithos*, 1(1), 1-11.
[c] Hazen, R.M. (2006). *Am Min*, 91(11/12), 1715.
[d] Valencia, E. M., et al. (2020). *MNRAS*, 492(1), 276-282.

TJ02 **2:03 – 2:18**

PFI-ZEKE CHARACTERIZATION OF THE GROUND AND LOW-LYING EXITED STATES OF MgO^+

JOEL R SCHMITZ, CARLA KREIS, FRÉDÉRIC MERKT, *Laboratorium für Physikalische Chemie, ETH Zurich, Zurich, Switzerland*.

We report on the characterization of the rovibrational structure of the ground and first excited electronic states of MgO^+ by high-resolution pulsed-field ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy. Rotationally cold (T_{rot}=5 K) MgO molecules in the $X^1\Sigma^+$ (v = 0-2) levels are generated in a supersonic expansion of a 0.1% N_2O/He carrier gas following laser ablation off an magnesium (Mg) rod[1].The rovibrational ionization thresholds corresponding to both spin-orbit components ($\Omega = \frac{1}{2}, \frac{3}{2}$) of the $X^+\ ^2\Pi_\Omega$ (v^+ = 0-10) states and to the lowest vibrational levels of the $A^+\ ^2\Sigma_{\frac{1}{2}}{}^+$ state are reached in a resonant 1+1′ two-photon excitation sequence via the $F^1\Pi$, $E^1\Sigma^+$, and $G^1\Pi$ rovibrational intermediate levels of MgO studied previously by Breckenridge and coworkers [2]. Our new results include accurate values for the adiabatic ionization energy of MgO and for the dissociation energies of the MgO $X\ ^1\Sigma^+$ and MgO^+ $X^+\ ^2\Pi_{\frac{1}{2}}$ states. This work is carried out in the context of our studies of the rovibrational structure of doubly charge dications by high-resolution PFI-ZEKE spectroscopy of singly charged cations following a similar approach as recently taken to characterize the ground state of the thermodynamically stable dication $MgAr^{2+}$ [3]. The talk will present a roadmap towards characterizing the ground state of MgO^{2+} by resonant multiphoton excitation via electronically excited states of MgO^+. The experiments will reveal whether MgO^{2+} is thermodynamically stable as predicted in Ref. [4] or metastable as predicted in Ref. [5].

[1] T.D. Persinger, D.J. Frohman, W.M. Fawzy and M.C. Heaven, J. Phys. Chem. **153** (5), 054308 (2020).
[2] J. Wang and W.H. Breckenridge, J. Chem. Phys. **124** (12), 124309 (2006).
[3] D. Wehrli, M. Génévriez and F. Merkt, Phys. Chem. Chem. Phys. **23** (18), 10978-10987 (2021).
[4] R. Linguerri, M. Hochlaf, M.C. Bacchus-Montabonel and M. Desouter-Lecomte, Phys. Chem. Chem. Phys. **15**, 824-831 (2013).
[5] M. Kolbuszewski and J.S. Wright, Chemical Physics Letters **218** (4), 338-342 (1994).

TJ03 **2:21 – 2:36**

COMPREHENSIVE ANALYSIS OF THE A $^4\Pi$ - X $^4\Sigma^-$ TRANSITION OF MOLYBDENUM NITRIDE, MoN: LIMITATIONS OF A HUND'S CASE(a) ANALYSIS

NYLA S WOODS, LEAH C O'BRIEN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL, USA*; KRISTIN N BALES, GABRIEL A HOTZ, *Chemistry and Biochemistry, University of Missouri, St. Louis, MO, USA*; SRISAHITHI TADAKAMALLA, *Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, MO, USA*; JAMES J O'BRIEN, *Chemistry and Biochemistry, University of Missouri, St. Louis, MO, USA*.

Transition metal nitrides are of growing interest due to their catalytic, energy storage, sensing, superconducting, and mechanical properties. The (0,0) band of the A $^4\Pi$ - X $^4\Sigma^-$ transition of MoN was recorded at Doppler-limited resolution using intracavity laser spectroscopy (ILS) integrated with a Fourier-transform spectrometer used for detection (ILS-FTS). The target MoN molecules were produced in the plasma discharge of a molybdenum-lined copper hollow cathode, using a gas mixture of Ar with about 1% N_2 in a reaction chamber with about 1 Torr total pressure. Isotopologue structure in the spectrum is clearly visible and analysis is underway for the five abundant isotopologues with no nuclear spin (I_{Mo}=0): ^{92}MoN (14.6%), ^{94}MoN (9.2%), ^{96}MoN (16.7%), ^{98}MoN (24.3%), and ^{100}MoN (9.7%). Hyperfine structure in the spectrum is not resolved, but clearly adds to the profile of each feature. To perform a comprehensive fit, the line positions ^{95}MoN (15.9%) and ^{97}MoN (9.6%) from Cheung et al. [JMS 202, (2000)] were included in the fit. PGOPHER was used with mass-constrained parameters based on ^{98}MoN, using a Hund's case(a) approach for both states. Although the constrained approach worked well for spectral analysis, several parameters needed to be fit individually for each isotopologue.

TJ04 **2:39 – 2:54**

A FRESH LOOK AT THE B1 - X0$^+$ and A1 - X0$^+$ TRANSITIONS IN TUNGSTEN OXIDE, WO: EVIDENCE OF AN AVOIDED CROSSING?

KRISTIN N BALES, JAMES J O'BRIEN, *Chemistry and Biochemistry, University of Missouri, St. Louis, MO, USA*; LEAH C O'BRIEN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL, USA*.

The complex electronic structure of transition metal diatomic molecules, such as tungsten monoxide (WO), makes them intriguing targets for high level spectroscopic analysis. A plethora of electrons and accessible valence orbitals make WO a difficult molecule to model computationally due to the large number of possible electronic interactions. The (0,0) and (0,1) vibrational bands of the A1 - X0$^+$ and B1 - X0$^+$ transitions of WO were recorded in absorption at Doppler-limited resolution using intracavity laser spectroscopy integrated with a Fourier-transform spectrometer [for the (0,1) band] and a 1-m monochromator with CCD detector [for the (0,0) band]. The target WO molecules were produced in the plasma discharge of a tungsten-lined copper hollow cathode, using a gas mixture of approximately 70% Ar and 30% H_2 giving a reaction chamber pressure of about 1 torr total. All 4 stable WO isotopologues were observed and analyzed. Initial fits using mass-constained parameters based on the most abundant isotope were not successful, and hint at strong interactions between the two excited electronic states.

TJ05 **2:57 – 3:12**

ELECTRONIC STRUCTURE AND SPECTROSCOPY OF OThF

ARIANNA RODRIGUEZ, JIARUI YAN, JIANDE HAN, MICHAEL HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA, USA*.

Electronic spectra of gas-phase polyatomic actinide species such as UO_2[a] and UF_2 have yielded electronic spectra where the rotational structure cannot be resolved at a resolution of 0.06 cm^{-1}. The molecules are predicted to be linear, so the lack of resolvable rotational structure appears to be a consequence of high electronic state densities. To probe this notion we have examined OThF, where the electronic complexity is reduced as there is only one unpaired electron in the metal-centered orbitals. Gas phase OThF has been generated by laser ablating Th metal in the presence of trace amounts of SF_6 and O_2. Six prominent vibronic bands were observed in the range 27700-28900 cm^{-1}. These bands were detected using both REMPI and LIF techniques. An additional intense band was observed at 22430 cm^{-1}. TD-DFT calculations indicate that OThF is a bent molecule in the ground and low-lying electronically excited states. Attempts to obtain rotationally resolved data and computational studies of OThF are in progress.

[a] Han, J.; Goncharov, V.; Kaledin, L. A.; Komissarov, A. V.; Heaven, M. C., Electronic spectroscopy and ionization potential of UO_2 in the gas phase. *Journal of Chemical Physics* **2004**, *120*, 5155-5163.

TJ06 **3:15 – 3:30**

MULTIREFERENCE CALCULATIONS ON THE GROUND AND EXCITED STATES AND DISSOCIATION ENERGIES OF LANTHANIDE AND ACTINIDE OXIDES AND FLUORIDES

NUNO M. S. ALMEIDA, SASHA C. NORTH, TIMOTHÉ R. L. MELIN, ANGELA K. WILSON, *Department of Chemistry, Michigan State University, East Lansing, MI, USA*.

High-level ab initio approaches are often necessary in detailing the many excited states and spin multiplicities of lanthanide and actinide species, while offering reliable routes towards calculating accurate spectroscopic properties. In this work, multi-reference methodologies including the complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) methods were utilized to calculate the ground and excited state properties of lanthanide and actinide oxides and fluorides. Potential energy curves for the ground state, several excited states, and different dissociation channels were determined. Spin-orbit corrections were performed by diagonalizing the MRCI wavefunction on the basis of the Breit-Pauli Hamiltonian. Bond dissociation energies (BDEs) of the lanthanide and actinide oxides and fluorides species were also determined, and the impact of core-valence, relativistic, and spin-orbit contributions to the ground state were considered. Density functional theory (DFT) and wavefunction method predictions were compared.

TJ07 **3:33 – 3:48**

SOLVENT-TUNING OF A Fe^{II} EXCITED STATE TOWARD UNDERSTANDING LIGAND DESIGN

JUSTIN THOMAS MALME, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; REESE CLENDENING, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*; LAUREN BOEDICKER, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; PRAKHAR GAUTAM, TONG REN, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*; JOSH VURA-WEIS, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Cyanide-containing d^6 transition metal complexes are known to exhibit strong solvatochromism of their MLCT band, but also a solvent-lifetime dependence. These effects are understood to be modulated by second-shell donor-acceptor interactions at the cyanide nitrogen, the strength of which are dictated by solvent acceptor number, a measure of relative Lewis acidity. These modulations can be understood as altering the σ-donor π-acceptor character of the cyanide ligands. A recently reported long-lived Fe^{II} complex, $Fe(HMTI)(CN)_2$, exhibits a biphasic solvent-lifetime relationship, with a rising and falling edge as acceptor number increases, making it difficult to pin down the nature of the relationship. In this work, a variant of the $Fe(HMTI)(CN)_2$, $Fe(TIM)(CN)_2$ (TIM=2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and its bound lewis acid counterpart, $Fe(TIM)(CNBPh_3)_2$, are investigated. $Fe(TIM)(CN)_2$ exhibits a largely monophasic solvent-lifetime relationship, with lifetime falling nearly exponentially as solvent acceptor number rises. This relationship is probed more closely by UV-Vis transient absorption experiments, and DFT calculations, to elucidate the effects of modulating σ-donor π-acceptor character of ligands bound to Fe^{II} chromophores.

Intermission

TJ08 **4:28 – 4:43**

ULTRAVIOLET INTRACAVITY LASER ABSORPTION SPECTROSCOPY

URI ZAMIR, MAAYAN COHEN, ILLYA ROZENBERG, AVI LERER, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*; YEHOSHUA KALISKY, AMIR KAPLAN, *Chemistry, IAEC, Beer-Sheva, Israel*; IGOR RAHINOV, *Chemistry, Open University of Israel, Ra'anana, Israel*; JOSHUA H. BARABAN, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*.

Intracavity Laser Absorption Spectroscopy (ICAS) provides an excellent solution for ultrasensitive, multiplexed, quantitative detection of reactive species, but has traditionally been limited to the visible and infrared spectral regions by the requirement for direct broadband lasing media. We report the first realization of this technique in the ultraviolet (UV-ICAS), based on a home-built Ce:LiCAF laser that operates in the 280-316 nm range. Three key species were investigated using our prototype UV-ICAS spectrometer: formaldehyde, sulfur dioxide, and hydroxyl radical. Successful initial measurements of static gases (the formaldehyde $\tilde{A}\,^1A_2 - \tilde{X}\,^1A_1$ electronic transition and the sulfur dioxide $\tilde{X}\,^1B_2 - \tilde{B}\,^1A_1$ electronic transition) led us to record in situ the $A\,^2\Sigma^+ - X\,^2\Pi$ spectrum of hydroxyl radical in a butane flame. Comparison of the latter to a LIFBASE simulation allowed single shot extraction of the temperature of hydroxyl radicals in the flame, demonstrating the data acquisition efficiency of UV-ICAS. We will also discuss the technique's potential for novel ultrasensitive, high resolution, broadband spectroscopy.

TJ09 **4:46 – 5:01**

EXCITED STATE DOUBLE PROTON OR HYDROGEN TRANSFER ON INDIGO IN THE GAS PHASE: EFFECTS IN DEUTERATION.

TREVOR COHEN, ANA DELIA PAREJO VIDAL, NATHAN NATHAN SVADLENAK, MATTANJAH DE VRIES, *Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA*.

Indigo is a highly photostable molecule used in many ancient civilizations such as the Roman and Mayan empires. This brilliant and deep color survived for centuries in many pieces of art. Its photostability is explained by its excited state dynamics. In a previous study, we measured two decay channels upon excitation of the S1 and we concluded that this peculiar molecule undergoes an excited state hydrogen transfer (ESHT) and an excited state proton transfer (ESPT). In our recent work, we studied this de-excitation through selective deuteration of the two target transfer sites on indigo. We monitored the photo-reaction pathways of this molecule using Resonance Enhanced Multi-Photon Ionization (REMPI) coupled with a time-of-flight mass spectrometer and measured the lifetimes of the excited states using pump-probe spectroscopy with mass spectrometric isotopomer selection. We revealed that the slower decay was unaffected by deuteration. The calculated excited state potential energy surfaces show trajectories with a different pathway to the ground state: a sequential double proton or hydrogen transfer.

TJ10 **5:04 – 5:19**

DIABATIC VALENCE-HOLE STATES

JUN JIANG, *Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA, USA*; ROBERT W FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

Diatomic molecules are fundamental in shaping our intuitive understanding of electronic structure theory. Despite their structural simplicity, chemical binding mechanisms (i.e., from R_e to dissociation) are well understood only for a few lowest energy electronic states, even for the C/N/O diatomic species. Pervasive configuration interactions and lumpy adiabatic potentials are prominent features of most electronically excited states. Interpretation of energy level structure and spectroscopic patterns becomes increasingly challenging for these higher energy states, because of the reduced utility of simple concepts such as bond order and correlation diagrams.

In this work, a global diabatization scheme, based on the valence-hole concept, is used to model the extensive web of avoided-crossing patterns in the electronically excited states of the CN ($^2\Sigma$), N_2 ($^1\Pi_u$, $^3\Pi_u$), Si_2 ($^3\Pi_g$), and SiC ($^3\Pi$) molecules. The validity of this diabatization scheme will be further demonstrated by its ability to reproduce the unusual energy level structure and predissociation dynamics of the extensively studied CN $^2\Sigma$ and N_2 $^3\Pi_u$ electronic states. As we have previously demonstrated with C_2 ($^1\Pi_g$, $^3\Pi_g$, $^1\Sigma_u^+$, $^3\Sigma_u^+$), the key concept of the model is the existence of valence-hole configurations that derive from an electron promotion from the nominally anti-bonding $2\sigma_u$ molecular orbital, i.e., $3\sigma_g(5\sigma) \leftarrow 2\sigma_u(4\sigma)$ for C_2, Si_2, CN, and SiC, and $1\pi_g \leftarrow 2\sigma_u$ for N_2. These valence-hole configurations have a nominal bond order of 3 or higher and correlate with separated-atom configurations with a 2p←2s promotion in one of the atomic constituents. The strongly-bound diabatic valence-hole state crosses multiple weakly-bound or repulsive states that are composed of electron configurations with a $2\sigma_g^2 2\sigma_u^2$ valence-core. These curve-crossings of diabatic potential curves result in an interconnected network of many avoided-crossings among multiple electronic states. Considering their systematic, disruptive impact on the global electronic structure and unimolecular dynamics, the valence-hole states should be treated as an integral part of our intuitive electronic structure model, along with familiar concepts such as Rydberg and ionic states.

TK. Structure determination

Tuesday, June 20, 2023 – 1:45 PM

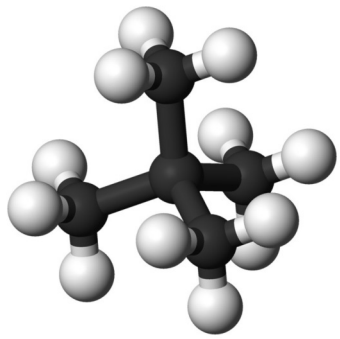
Room: B102 Chemical and Life Sciences

Chair: Lai-Sheng Wang, Brown University, Providence, RI, USA

TK01 **1:45 – 2:00**

HIGH RESOLUTION INFRARED SPECTRA OF NEOPENTANE: ROVIBRATIONAL ANALYSIS OF BANDS AT 8.3-6.4 μm

ADAM PASTOREK, PETER F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*; VINCENT BOUDON, *Laboratoire ICB, CNRS/Université de Bourgogne, DIJON, France*.



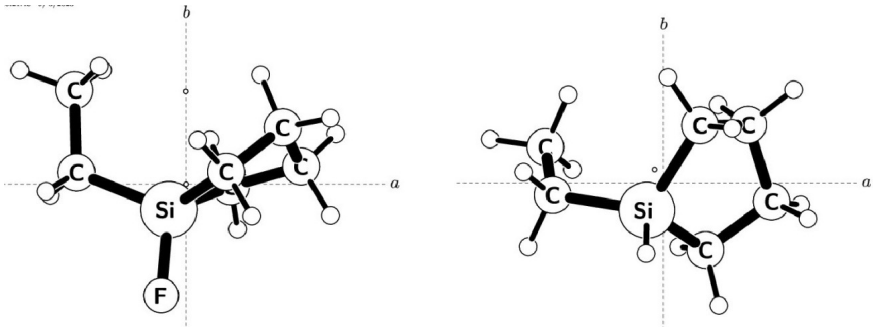
New high resolution (0.0014 cm^{-1}) infrared spectra of neopentane (2,2-dimethylpropane) have been recorded at 203 K by use of synchrotron radiation (Canadian Light Source). Spectra were recorded in the IR (8.3-6.4 μm) with 8 m of optical path. Neopentane is a spherical top molecule with T_d (tetrahedral) symmetry. A low temperature is favorable for a detailed rotational analysis of its fundamental bands. This study focuses on the analysis of 3 band systems of neopentane. The first system is a dyad consisting of a ν_{15} fundamental band and a $\nu_7 + \nu_{19}$ combination band located at 1472.5 and 1489 cm^{-1}, respectively. The second system is a ν_{16} fundamental band located at 1369.4 $\mathrm{cm}^{-1}$with uncertain band origin. The third band system is a dyad of a ν_{17} fundamental and a $\nu_8 + \nu_{18}$ combination band. Only the ν_{17} fundamental band was analyzed in this last system due to the weaker structure of the combination band. For all spectral simulations and calculations the 'XTDS' program based on the tensorial formalism by V. Boudon was used. A subprogram 'SPVIEW', paired with XTDS, was used for spectral assignment.

A special emphasis will be given to the first dyad located at 1472.5 and 1489 cm^{-1}.

TK02 **2:03 – 2:18**

THE STRUCTURAL DETERMINATION AND COMPARISON OF 1-ETHYLSILACYCLOPENTANE AND 1-ETHYL-1-FLUOROSILACYCLOPENTANE

J. E. ISERT, JOSIE R. GLENN, CAITLYN SAIZ, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; W. H. RICE IV, *Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; GAMIL A GUIRGIS, *Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC, USA*; G. S. GRUBBS II, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.



The rotational spectrum of 1-ethylsilacyclopentane (1ESCP) and 1-ethyl-1-fluorosilacyclopentane (1E1FSCP) were collected and assigned in the 5.0 - 19.0 GHz region of the electromagnetic spectrum. In collaboration with Dr. Gamil Guirgis of the College of Charleston, the title molecules were synthesized in Charleston, SC and rotational spectra were recorded on a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer at the Missouri University of Science and Technology in Rolla, MO. The substitution of a fluorine atom in place of the hydrogen on the silicon atom inside the five member ring has an influence on the types of transitions being observed. Differences in the two structures and their comparisons to theoretical calculations will be discussed.

TK03 **2:21 – 2:36**

TWELVE CONFORMERS OF 4-FLUOROTHREONINE UNVEILED BY LASER ABLATION ROTATIONAL SPECTROSCOPY

VINCENZO BARONE, MARCO FUSÈ, *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; RAÚL AGUADO, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; SIMONE POTENTI, *Dept. Chemistry "Giacomo Ciamician", University of Bologna, Bologna, ITALY*; IKER LEÓN, ELENA R. ALONSO, SANTIAGO MATA, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; FEDERICO LAZZARI, LORENZO SPADA, *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; GIORDANO MANCINI, *High Performance Computer Centre, Scuola Normale Superiore, Pisa, Italy, Italy*; ANDREA GUALANDI, PIER GIORGIO COZZI, *Dept. Chemistry "Giacomo Ciamician", University of Bologna, Bologna, ITALY*; CRISTINA PUZZARINI, *Dep. Chemistry 'Giacomo Ciamician', University of Bologna, Bologna, Italy*; JOSÉ L. ALONSO, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*.

Fluorinated amino acids are rare bio-organic compounds gaining great relevance in the pharmaceutical field. 4-fluorothreonine (4FT) is the only natural fluoro amino acid discovered so far. The fluorination of the methyl group significantly increases the complexity of the already intricate conformational panorama of threonine[a], making any conformational study even more challenging. Guided by state-of-the-art machine-learning methodologies[b] and using a tandem of laser ablation rotational spectroscopies, up to twelve rotameric species have been discovered in the supersonic expansion of our experiments. These species have been ascribed to twelve of the thirteen low-energy predicted conformers based on rotational constants, nuclear quadrupole coupling constants, and dipole moment selection rules. These results again proved the potential of the laser ablation rotational spectroscopy techniques in structural studies of non-volatile solid biomolecules.

[a] Alonso J. L, Pérez C, Sanz M. E, López J. C, Blanco S. Phys Chem Chem Phys. 2009 Jan 6;11(4):617–27
[b] León I, Fusè M, Alonso ER, Mata S, Mancini G, Puzzarini C, et al. J Chem Phys. 2022;157(7).

TK04 **2:39 – 2:54**

REINVESTIGATION OF THE ROTATIONAL SPECTRUM AND STRUCTURE OF CYCLOHEXYLAMINE

MICHAEL J. CARRILLO, DINESH MARASINGHE, MICHAEL TUBERGEN, *Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA*.

Cyclohexylamine was re-investigated by high-resolution Fourier transform microwave spectroscopy. In order to interpret the microwave spectrum, high-level first-principle quantum chemical calculations were carried out at the B3LYP and MP2 methods using the aug-cc-pVTZ basis set. Two potential energy surface scans (one for the axial and another for equatorial conformer) were performed along the H-N-C-C dihedral angle at the B3LYP/6-311++G level of theory. The scan identified four conformers which correlates with previously reported vibrational spectra and theoretical calculations. Eighteen rotational transitions were assigned to the gauche-equatorial conformer and fit to A= 4264.343(57) MHz, B=2222.446 (39) MHz, and C=1604.877(31) MHz. Ring strain and spectral assignment for additional conformers will be discussed.

TK05 **2:57 – 3:12**

ROTATIONAL SPECTROSCOPY AND STRUCTURE OF CYCLOPROPYLCHLOROMETHYLDIFLUOROSILANE

A R DAVIES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; ABANOB GEORGE HANNA, ALMA LUTAS, GAMIL A GUIRGIS, *Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC, USA*; G. S. GRUBBS II, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.

The rotational spectrum of cyclopropylchloromethyldifluorosilane has been investigated in the 5 — 19 GHz region of the electromagnetic spectrum using a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer. The molecule was synthesised by collaborators in the Guirgis group at the College of Charleston. Owing to sample limitations, it was only possible to acquire ∼80,000 free induction decays (FIDs), although this was sufficient to yield a spectrum with appreciable signal to noise. As a result, both ^{35}Cl and ^{37}Cl isotopologues have been observed, primarily arising from the high relative natural abundances of the Cl isotopes, and their spectra have been assigned. The presence of the Cl nuclei, both with I = 3/2, leads to transitions splitting into multiple hyperfine components, and thus a good estimation of the nuclear electric quadrupole coupling constants is essential for an accurate assignment. The observation of the Cl isotopologues allows some conclusions to be made pertaining to the electronic and geometric structure of the molecule, and shall be compared to the equilibrium structures obtained from both DFT and *ab inito* methods. Additionally, a conformer arising from a rotation of the chloromethyl group has also been observed.

Intermission

TK06 **3:52 – 4:07**

CHARACTERIZING THE STRUCTURE OF SUCCINIMIDE WITH BROADBAND ROTATIONAL SPECTROSCOPY

SIVANJALI ELENA WILLIAMS, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; CHISOM ADAOBI DIM, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; CAROLINE SORRELLS, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; KYLE N. CRABTREE, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; A. O. HERNANDEZ-CASTILLO, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*.

Succinimide is a heterocyclic organic compound whose derivatives have anticonvulsant applications. We measured its molecular parameters using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy in the 26-40 GHz frequency range, which is highly sensitive to the molecular structure. The spectrometer is equipped with a heated reservoir to increase the vapor pressure of solid samples, and is coupled to a supersonic expansion which results in rotational temperatures on the order of 1-5 K. The rotational spectra were analyzed with the help of state-of-the-art ab initio calculations. We have determined the rotational constants, inertial defect, and centrifugal distortion constants of succinimide. In this talk we will discuss our findings on the molecular structure and comparisons to structurally similar molecules.

TK07 **4:10 – 4:25**

K_A-BAND ROTATIONAL SPECTROSCOPY OF N-HALOSUCCINIMIDES

CHISOM ADAOBI DIM, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; CAROLINE SORRELLS, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; S E WORTHINGTON-KIRSCH, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; A. O. HERNANDEZ-CASTILLO, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; KYLE N. CRABTREE, *Department of Chemistry, University of California, Davis, Davis, CA, USA*.

N-halosuccinimides are important reagents in organic synthesis and in the chemistry of natural products, they can mediate or catalyze many reactions including halocyclizations and formation of heterocyclic systems. Surprisingly, these molecules have not been previously investigated by rotational spectroscopy. In organic chemistry, halogen substituents are known to be inductively electron withdrawing and resonance donating. To explore the effect of the halogen substituents on the structure and electronics of succinimide, N-chlorosuccinimide, N-bromosuccinimide, and N-iodosuccinimide have been studied in the 26.5-–40 GHz range using the chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy technique. The samples were heated and coupled to a pulsed supersonic expansion to achieve rotational cooling. Experimental details and the determined molecular parameters will be discussed, along with structural comparisons among the halogenated series.

TK08 **4:28 – 4:43**

THEORETICAL AND MICROWAVE SPECTROSCOPIC CHARACTERIZATION OF CYCLOBUTENONE

MICHAEL J. CARRILLO, DINESH MARASINGHE, KRISTIN SOBIE, ROURKE J. ZARZYCKI, *Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA*; KEVIN CARTER-FENK, *Department of Chemistry, University of California, Berkeley, Berkeley, CA, USA*; CHRISTOPHER FENK, MICHAEL TUBERGEN, *Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA*.

Cyclobutenone has been characterized by high-resolution Fourier transform microwave spectroscopy for the first time. High level first-principles quantum chemical calculations at the B3LYP, MP2, and CCSD levels of theory were employed to better understand the molecular structure and obtain model rotational and centrifugal distortion constants to aid spectral assignment. Results from the different levels of theory are compared. Nine rotational transitions were measured and fit to a Watson A-reduced Hamiltonian (3 kHz error) and S-reduced Hamiltonian (4.2 kHz error). Cyclobutane and its derivatives are known to undergo ring-puckering inversion and were observed to have tunneling splittings of their rotational transitions. No tunneling splittings were observed for cyclobutenone indicating no significant ring-puckering tunneling in this four-membered ring system.

TK09 **4:46 – 5:01**

INVESTIGATING THREE CYCLIC DIKETONE MOLECULES USING ROTATIONAL SPECTROSCOPY

LAURA WU, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; CHISOM ADAOBI DIM, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; CAROLINE SORRELLS, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; KYLE N. CRABTREE, *Department of Chemistry, University of California, Davis, Davis, CA, USA*; A. O. HERNANDEZ-CASTILLO, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*.

Diketones are a family of compounds extensively investigated in chemistry, mainly due to their keto-enol tautomerism. Rotational spectroscopy is a uniquely powerful tool to probe tautomerization processes owing to its direct sensitivity to molecular structure. The broadband microwave spectra of three cyclic diketone molecules, 4-cyclopentene-1,3-dione, 1,3-cyclopentanedione, and 2-methyl-1,3-cyclopentanedione, have been investigated in the 26-40 GHz frequency range region using a chirped pulse Fourier transform microwave spectrometer coupled to a supersonic expansion. The spectroscopic data were analyzed with the aid of ab-initio calculations to yield complete sets of molecular parameters, including rotational constants and centrifugal distortion constants for all the observed molecules. Details on the molecular structure and the equilibrium between keto- and enol- forms will be discussed.

TK10 **5:04 – 5:19**

SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE OF 1,3-OXAZOLE FROM MANY ISOTOPOLOGUES

BRIAN J. ESSELMAN, MADELEINE ATWOOD, TAYLOR K. ADKINS, MARIA ZDANOVSKAIA, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; MANAMU KOBAYASHI, SHOZO TSUNEKAWA, KAORI KOBAYASHI, *Department of Physics, University of Toyama, Toyama, Japan*; NITAI PRASAD SAHOO, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

The rotational spectrum of 1,3-oxazole (c-C_3H_3NO, C_s) has been studied from 40 GHz to 750 GHz. Transitions of the main isotopologue and five heavy-atom isotopologues (^{15}N, ^{18}O, and three ^{13}C) were fit to S- and A-reduced, sextic distorted-rotor Hamiltonians. Rotational spectra have been obtained for several deuterium-enriched samples from 235 to 360 GHz, and rotational constants for more than a dozen deuterium-containing isotopologues have been determined. A highly accurate and precise semi-experimental (r_e^{SE}) equilibrium structure of oxazole has been determined using spectroscopic constants for all available isotopologues and CCSD(T) corrections to the rotational constants. Comparison will be made to a CCSD(T)/cc-pCV5Z equilibrium (r_e) structure and the r_e^{SE} structures of other heteroaromatic compounds.

TK11 **5:22 – 5:37**

THE STRUCTURE OF STRAINED MOLECULES: THE EXAMPLE OF PARACYCLOPHANES.

HIMANSHI SINGH, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; PABLO PINACHO, *Physical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Cyclophanes are an interesting family of strained organic molecules that contain aromatic rings and aliphatic units that bridge the aromatic rings.[a] [2,2]-Paracyclophanes are an example of cyclophanes with two co-facially stacked benzene rings linked through ethylene chains.[b] The rigid connectivity and close positioning of the aromatic units in paracyclophane scaffolds makes them fundamentally important in supramolecular chemistry, while they find applications in material sciences due to their chiroptical and optoelectronic properties.[b,c] Structural homologues of [2,2]-paracyclophanes and different substitutions have features of chemical and industrial importance as they alter the photophysical and electrochemical properties of molecular scaffolds. Gas-phase studies of such molecular systems can provide the necessary isolated conditions to elucidate their structures and dynamics. One of the most powerful techniques to provide accurate gas-phase structures is high-resolution rotational spectroscopy.

We report an in-depth study of [2,2]-paracyclophanes using our broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer COMPACT in the 2-8 GHz frequency range.[d] We have explored the conformations and the intramolecular interactions of an alcohol-, an aldehyde- and, a ketone-substituted [2,2]-paracyclophane. The most stable conformations of all three derivatives obtained from quantum-chemical calculations and observed in experiments will be discussed along with the singly-substituted ^{13}C-isotopologues that facilitated the determination of the experimental structure of these molecules from the paracyclophane family.

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[a] S. Kotha, M. E. Shirbhate, and G. T. Waghule, *Beilstein journal of organic chemistry*, **2015**, *11*, 1274-1331.
[b] Z. Hassan, E. Spuling, D. M. Knoll, J. Lahann, and S. Bräse, *Chemical Society Reviews*, **2018**, *47(18)*, 6947-6963.
[c] Y. Morisaki and Y. Chujo, *Bulletin of the Chemical Society of Japan*, **2019**, *92(2)*, 265–274.
[d] D. Schmitz, V. A. Shubert, T. Betz, and M. Schnell, *Journal of Molecular Spectroscopy*, **2012**, *280*, 77–84.

TL. Mini-symposium: Infrared Spectroscopy in the JWST Era

Tuesday, June 20, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: Sandra Brünken, Radboud University, Nijmegen, The Netherlands

TL01 **1:45 – 2:00**

CHEMICAL DIVERSITY IN THE INNER REGIONS OF PLANET-FORMING DISKS AS REVEALED BY JWST-MIRI AND THE MINDS PROGRAM

KAMBER SCHWARZ, *MPIA, Max Planck Institute for Astronomy, Heidelberg, Germany*.

JWST allows us to characterise the properties of gas and dust in the inner regions of protoplanetary disks with unprecedented sensitivity and spectral resolution. These planet-forming disks are dynamic objects. Solids grow in size and drift inward, potentially enriching the gas of the inner disk in volatile molecules transported from the outer disk as ices. Concurrently, the formation of substructures such as rings and vortices may prevent this material from being delivered to the inner disk, changing the chemical composition of the material available to forming planets. JWST spectra show emission from H_2O, CO_2, hydrocarbons, and multiple as yet unidentified species. Here, I present the first results from the MINDS (MIRI mid-IR Disk Survey, PI: Th. Henning) program, which has observed multiple disks around brown dwarf and T-Tauri stars. Observations include the first detections of benzene and $^{13}CO_2$ in protoplanetary disks and a range of derived gas-phase carbon to oxygen ratios. These data allow us to make preliminary connections between the composition of the inner disk and that of the outer disk.

TL02 **2:03 – 2:18**

HIGH-RESOLUTION MID-IR LINE SURVEY OF THE LATE-TYPE STAR VY CMa

GUIDO W. FUCHS, EILEEN DÖRING, DANIEL WITSCH, *Institute of Physics, University of Kassel, Kassel, Germany*; THOMAS GIESEN, *Institute of Physics, University Kassel, Kassel, Germany*; THOMAS K GREATHOUSE, ROHINI S GILES, *Space Science Department, Southwest Research Institute, San Antonio, TX, USA*; JOHN H. LACY, *Department of Astronomy, The University of Texas at Austin, Austin, TX, USA*; EDWARD J MONTIEL, *USRA, NASA Ames Research Center , Moffett Field, CA, USA*; MATTHEW J RICHTER, *Department of Physics , University of California, Davis , Davis, CA, USA*.

VY CMa is a supermassive, late-type, oxygen-rich star surrounded by a dense envelope of dust and molecules. Radio observations have identified about 25 different molecular species (plus many isotopologues) in the vicinity of this star, but little is known about molecular features in the mid-IR wavelength range. In a recent (and ongoing) line survey, we investigated the region around 7 to 8 and 10 μm with the TEXES instrument at IRTF (Mauna Kea, Hawai'i) and the EXES spectrograph aboard the SOFIA airborne telescope. Both instruments are high-resolution instruments with R=100,000. Preliminary results on the observed NH_3 and SiO spectra will be presented. Other observed spectral features will be discussed. With the decommissioning of SOFIA in September 2022, a high-resolution mid-IR telescope will no longer be available for frequency ranges blocked by the Earth's atmosphere. However, for some applications, the space telescope JWST can be a very valuable tool for studying the envelope of VY CMa, even though it has only a resolution of R=3000. Possible synergies with the current mid-IR line survey and JWST will be discussed.

TL03 **2:21 – 2:36**

HIGH RESOLUTION 2D INFRARED SPECTROSCOPY: A NEW WAY TO ASSIGN NEAR INFRARED PEAKS

PETER CHEN, *Department of Chemistry, Spelman College, Atlanta, GA, USA*; DeAUNNA A DANIELS, *Chemistry, Spelman College, Atlanta, GA, USA*; THRESA WELLS, *Department of Chemistry, Spelman College, Atlanta, GA, USA*.

The near infrared region of the spectrum is useful for applications such as the JWST Near Infrared Spectrograph, but assigning peaks in that region can be challenging and could benefit from additional experimental validation. HD-2DIR is a new technique that is being developed to decongest rovibrational spectra and to experimentally assign peaks in the near infrared region using previously assigned peaks in the mid-infrared region.

TL04 **2:39 – 2:54**

JWST OPENS A NEW ERA IN ASTROCHEMISTRY

TAKESHI OKA, *Department of Astronomy and Astrophysics and Department of Chemistry, The Enrico Fermi Institute, University of Chicago, Chicago, IL, USA*.

Historical sketch: Charlie Townes and I are the only two astronomical spectroscopists who switched to infrared after few years of radio astronomy. Townes did atomic spectroscopy and discovered the black hole at the center of the Galaxy.[a] I switched because H_3^+, central in astrochemistry, has spectrum only in the infrared region.

Dense and diffuse clouds: It took us 16 years to observe the spectrum of H_3^+ in dense clouds[b] as theoretically predicted by Herbst and Klemperer and Watson, but had we tried diffuse clouds in the Galactic center we would have had found it withing a few years. Radio (ALMA) astronomy is for emission spectroscopy in dense clouds while infrared (JWST) spectroscopy is for absorption spectroscopy in diffuse clouds.

Molecules of interest: So far astrochemistry has been mostly the science of dense clouds, but JWST will bring in rich chemistry in diffuse clouds. Dense clouds are localized. Diffuse clouds give a bigger picture. Patrick Thaddeus said, "One should not look at an elephant with a magnifying glass". Spectra of the following molecules will be observed: HD, CH, NH, OH, HD^+, CH^+, NH^+, OH^+, H_3^+, H_2D^+, CH_2, NH_2, H_2O, CH_2^+, NH_2^+, H_2O^+. These are kind of molecules observed by Herschel Observatory. Many of them were analyzed as in dense clouds, but they are all in diffuse clouds. Apart from H_3^+ they are all polar molecules with high rotational constants therefore the spectrum is composed of 1 line apart from fine and hyperfine structure. For H_3^+ three rotational levels (J,K) = (1,1), (1,0), and (3,3) levels are populated.

Stars of interest: Absorption spectroscopy needs bright and young stars with a smooth continuum for the radiation source. Ben McCall found 27 stars that are usable to conduct absorption spectroscopy toward the Galactic disk.[c] We found 18 stars toward the Galactic center[d] These stars will be useful for the JWST observation.

[a] Wollman, E.R., Geballe, T.R., Lacy, J.H., Townes, C.H. 1976, ApJ 205, L5; 1977, ApJ 218, L103
[b] Geballe, T.R., Oka, T. 1996 Nature, 384, 334
[c] Indriolo, N., McCall, B.J. 2012, ApJ 745, 91
[d] Oka, T., Geballe, T., Goto, M., Usuda, T., McCall, B.J., Indriolo, N. 2019, ApJ 883, 54(31pp)

Intermission

TL05 **3:34 – 3:49**

THE BENDING OF C_3: EXPERIMENTALLY PROBING THE l-TYPE DOUBLING AND RESONANCE

MARIE-ALINE MARTIN-DRUMEL, OLIVIER PIRALI, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*; MICHEL VERVLOET, *AILES Beamline, Synchrotron SOLEIL, Saint-Aubin, France*; DENNIS W. TOKARYK, *Department of Physics, University of New Brunswick, Fredericton, NB, Canada*; COLIN WESTERN, *School of Chemistry, University of Bristol, Bristol, United Kingdom*; KIRSTIN D DONEY, HAROLD LINNARTZ, *Leiden Observatory, Laboratory for Astrophysics, Universiteit Leiden, Leiden, Netherlands*; QIANG ZHANG, YANG CHEN, DONGFENG ZHAO, *Hefei National Laboratory for Physical Science at Microscale, University of Science and Technology of China, Hefei, China*.

C_3, a pure carbon chain molecule that has been identified in different astronomical environments, is considered a good probe of kinetic temperatures through observation of transitions involving its low-lying bending mode (ν_2) in its ground electronic state. With the aim to investigate this bending mode with multiple quanta of excitation, we have undertaken high resolution optical and mid-infrared investigations on the species produced in discharge experiments.

We report here the most complete analysis of the $\tilde{X}$ and $\tilde{A}$ states of C_3 (literature and present study) using a single PGOPHER file. New experimental measurements, reported in the past years at ISMS, result in 36 rovibronic $\tilde{A}\ ^1\Pi_u - \tilde{X}\ ^1\Sigma_g^+$ bands (originating from $\tilde{X}(0v_20)$, $v_2 = 0 - 5$, levels) recorded by laser induced fluorescence spectroscopy at the University of Science and Technology of China and the rovibrational ν_3 band (revealing hot bands involving up to 5 quanta of excitation in ν_2) recorded by Fourier-transform infrared spectroscopy using a globar source on the AILES beamline of the SOLEIL synchrotron facility.

The combined fit allows for the accurate determination of the rotational parameters and absolute energy levels of C_3, in particular for states involving the bending mode. The spectroscopic information derived from this work enables new interstellar searches for C_3, not only in the infrared and optical regions investigated here but also notably in the ν_2 band region (around 63 cm^{-1}) where vibrational satellites can now be accurately predicted. This makes C_3 a universal diagnostic tool to study very different astronomical environments, from dark and dense to translucent clouds.

TL06 **3:52 – 4:07**

THE ELUSIVE METHYL CATION DISCOVERED BY JWST IN A PLANET FORMING DISK [a]

OLIVIER BERNÉ, ILANE SCHROETTER, CHRISTINE JOBLIN, AMELIE CANIN, *IRAP, Université de Toulouse 3 - CNRS, CNES, Toulouse, France*; MARIE-ALINE MARTIN-DRUMEL, UGO JACOVELLA, BÉRENGER GANS, EMMANUEL DARTOIS, L. H. COUDERT, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*; JAVIER GOICOECHEA, JOSE CERNICHARO, *Instituto de Fisica Fundamental, CSIC, Madrid, Spain*; EDWIN BERGIN, FELIPE ALARCON, *Department of Astronomy, University of Michigan, Ann Arbor, MI, USA*; JAN CAMI, ELS PEETERS, *Department of Physics and Astronomy, University of Western Ontario, London, Ontario, Canada*; EVELYNE ROUEFF, MARYVONNE GERIN, *LERMA, Observatoire de Paris, Paris, France*; J. H. BLACK, *Onsala Space Observatory, Chalmers University of Technology, Onsala, Sweden*; OSKAR ASVANY, SVEN THORWIRTH, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*; EMILIE HABART, BORIS TRAHIN, MARION ZANNESE, *Institut d'Astrophysique Spatiale, Université Paris Saclay, CNRS, Orsay, France*; XANDER TIELENS, *Leiden Observatory, University of Leiden, Leiden, Netherlands*.

The methyl cation (CH_3^+), one of the simplest cations, is postulated to play a pivotal role in the chemistry of interstellar and circumstellar environments, but remains so far elusive outside the Solar System. We report the detection of a series of infrared lines in a protoplanetary disk in Orion using the JWST, which we attribute to CH_3^+. The presence of CH_3^+ results from the hot UV-driven chemistry, initiated at the surface of the disk by the nearby massive stars of the Trapezium cluster. The detection of this species, which is at the root of carbon chemistry in space, opens the possibility to study yet unexplored pathways of hot gas-phase organic chemistry at play in planet forming disks and beyond.

[a] The authors would like to recognize the PDRS4ALL extended core team, pdrs4all.org

TL07 **4:10 – 4:25**

LABORATORY INFRARED SPECTROSCOPY OF SMALL ASTROPHYSICALLY RELEVANT MOLECULES

THOMAS GIESEN, *Institute of Physics, University Kassel, Kassel, Germany*; EILEEN DÖRING, *Institute of Physics, University of Kassel, Kassel, Germany*; ALEXANDER A. BREIER, *Institute of Physics, University Kassel, Kassel, Germany*; FABIAN PETERSS, GUIDO W. FUCHS, *Institute of Physics, University of Kassel, Kassel, Germany*.

A large number of astrophysically relevant molecules can be clearly identified by characteristic spectra in the mid-infrared range. Among them are important species such as CO_2 or C_3, which cannot be detected in the microwave range due to the lack of a permanent dipole moment. The broad spectral coverage of the MIRI spectrometer aboard JWST allows detection of a large number of molecules in the envelopes of aging stars. Together with observations in the microwave and optical spectral regions, the infrared region provides valuable information about the physical and chemical processes in the gas surrounding these stars. While infrared observations with Earth-based telescopes such as the IRTF on Mauna Kea / Hawaii are limited due to infrared absorption in the Earth's atmosphere, JWST will provide an unrestricted view over the entire spectral range from 5 - 28 μm. The spectral resolution of JWST (R = 2000 - 3000) is sufficient to detect rotational vibrational transitions of small diatomic to triatomic molecules as well as characteristic vibrational bands of larger molecules. A large number of new molecules are expected to be discovered in the infrared spectra of late-type stars, provided their spectral signatures are known from precise laboratory studies.

The laboratory astrophysics group in Kassel is conducting experiments in the 3-12 μm range with quantum cascade lasers and OPO lasers. In combination with electric discharge sources and laser ablation, a variety of molecules such as Si_2C [1], C_3, TiO [2], Al_2O and VO can be produced in cold supersonic jets, which are studied with high resolution infrared spectroscopy. The talk will give a brief insight into the ongoing work.

[1] D. Witsch, V. Lutter, A.A. Breier, K.M.T. Yamada, G.W. Fuchs, J. Gauss, T.F. Giesen, JPC A, 123, 4168 (2019).
[2] D. Witsch, A.A. Breier, E. Döring, K.M.T. Yamada, T.F. Giesen, G.W. Fuchs JMS, 377, 111439 (2021).

TL08 **4:28 – 4:43**

INVESTIGATING PREBIOTIC CHEMISTRY WITH CRYOGENIC ACTION SPECTROSCOPY - GAS-PHASE GLYCOLALDEHYDE FORMATION VIA A CATIONIC "FORMOSE" REACTION

HUNARPREET KAUR, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; WEIQI WANG, *Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*; JESÚS PÉREZ-RÍOS, *Department of Physics and Astronomy, Stony Brook University, New York, NY, USA*; BRITTA REDLICH, SANDRA BRÜNKEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*.

Many complex organic molecules (iCOMs) ranging from diatoms to molecules containing up to 70 atoms, including formaldehyde, protonated formaldehyde, and glycolaldehyde[a] have been detected in space using astronomical observations. To understand the synthetic pathways of such potential prebiotic species in space, it is crucial to investigate their formation in the laboratory. In this work, we present results relevant to the synthesis of the simplest "sugar", glycolaldehyde, using a cryogenic 22-pole ion trap stationed at the infrared free-electron laser laboratory FELIX.[b] We investigate the ion-neutral gas-phase formation of (protonated) glycolaldehyde starting from neutral formaldehyde and its cationic forms, $[H_2CO]^+$ and $[H_3CO]^+$. Gas-phase vibrational spectra of the reactant $[H_3CO]^+$ and the mass-spectroscopically identified products $[H_5C_2O]^+$ and $[H_5C_2O_2]^+$ were recorded using cryogenic IR action spectroscopy in the frequency range 650-1900 cm^{-1}, and are compared to results of quantum chemical calculations for structural characterization between different isomers. First insights into potential reaction pathways will be presented based on this combined approach, and they will be complemented with a Markov state model of the reaction mechanisms based on molecular dynamics simulations[c,d] to identify efficient pathways for forming glycolaldehyde and other iCOMs under low-temperature astrophysical conditions.

[a] L.E. Snyder, D. Buhl, B. Zuckerman, P. Palmer, Phys. Rev. Lett. 22 (1969) 679–681.; M. Ohishi, S.I. Ishikawa, T. Amano, H. Oka, W.M. Irvine, J.E. Dickens, L.M. Ziurys, A.J. Apponi, Astrophys. J. 471 (1996) L61–L64.; J.M. Hollis, F.J. Lovas, P.R. Jewell, Astrophys. J. 540 (2000) L107–L110.

[b] D.B. Rap, J.G.M. Schrauwen, A.N. Marimuthu, B. Redlich, S. Brünken, Nat. Astron. 6 (2022) 1059–1067.

[c] W. Wang, X. Liu, J. Pérez-Ríos, J. Phys. Chem. A. 125 (2021) 5670–5680.

[d] X. Liu, W. Wang, S.C. Wright, M. Doppelbauer, G. Meijer, S. Truppe, J. Pérez-Ríos, J. Chem. Phys. 157 (2022) 074305.

TL09 **4:46 – 5:01**

IRMPD SPECTROSCOPY OF $Fe(H_2)_{1,2}{}^+$ AND OVERTONE STUDY OF $Ar_{1,2}FeH^+$ AND THEIR DEUTERATED SPECIES: LOOKING FOR IRON HYDRADES IN THE INTERSTELLAR MEDIUM

SHAN JIN, MARCOS JUANES, CHRISTIAN VAN DER LINDE, MILAN ONCAK, MARTIN K BEYER,
Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria.

Apart of being the most abundant metal in earth and the well-known leading role in the field of organic prosthetic group of proteins, iron potentially represents a crucial element for understanding interstellar processes, the evolution of interstellar dust and interstellar medium (ISM) composition. Despite the presumable gas-phase presence of iron in the ISM due to its very high abundance in the galaxy, its difficult detection in the interstellar gas-phase to date may be due to depletion of iron hidden in interstellar dust. Nevertheless, although ISM observations show iron to be severely depleted, it is highly expected to find iron-containing gas-phase molecular species in the ISM. This idea is reinforced by detection of FeCN in the ISM[a] or observed evidence of FeO presence in interstellar molecular clouds.[b] Gas-phase iron dihydrogen clusters and their deuterium substitutes were formed and stored in a cooled cell (ca. 80K) of a 4.7 T Fourier-Transform Ion Cyclotron Resonance instrument. Infrared photodissociation spectra were recorded in the H–H and D–D stretch region of 2230–4000 cm–1, supported by quantum chemical calculations. The spectral signature of the infrared photon absorption was reflected in the dissociation of intact H_2 or D_2 molecule. Additionally, to provide spectroscopic data on FeH^+ and complete previous analysis of Ar_2FeH^+,[c] we investigated overtone bands of Ar_2FeH^+ and $ArFeH^+$ in the 2300–4000 cm–1 region. We observed that while $ArFeH^+$ exhibits only a Fe–H overtone vibration in this region other plausible electronic transitions appear for Ar_2FeH^+, correlated with the ^5D state of the iron atom. Ion FT-IR spectroscopy combined with mass spectrometry represent a proven high-resolution tool to determine the molecular composition and structural behavior. Furthermore, overtone bands recognition may be used as a valuable strategy to obtain unambiguous identification of polyatomic aggregates fingerprints and further understanding of ISM composition and reactivity.

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[a] L.N. Zack, D.T. Halfen and L.M. Ziurys, Astrophys. J. Lett., 2011, 733(2), L36
[b] C.M. Walmsley, R. Bachiller, G.P. Des Forêts and P. Schilke, Astrophys. J., 2002, 566(2), L109-L112
[c] S. Jin, J. Heller, C. van der Linde, M. Ončák and M.K. Beyer, J Phys Chem Lett, 2022, 13(25), 5867

WA. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Wednesday, June 21, 2023 – 8:30 AM

Room: 116 Roger Adams Lab

Chair: Christopher J. Johnson, Stony Brook University, Stony Brook, NY, USA

WA01 ***INVITED TALK*** **8:30 – 9:00**

CAN SILVER IONS PERMEATE THROUGH A POTASSIUM ION CHANNEL ? – DOUBLE ION TRAP LASER SPECTROSCOPY ON METAL COMPLEXES OF THE PARTIAL PEPTIDE OF A SELECTIVITY FILTER

SATORU TANABE, *IR Free Electron Laser Research Center, Tokyo University of Science, Tokyo, Japan*; KEISUKE HIRATA, *Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan*; KOICHI TSUKIYAMA, *Faculty of Science Division I, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan*; JAMES M. LISY, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; SHUNICHI ISHIUCHI, MASAAKI FUJII, *Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan*.

We would like to present a challenge of the gas phase ion spectroscopy to ion recognition mechanism in potassium ion channels. Our systematic studies have been reported (see references) and the relation between the ion permeability and conformation of Ac-Tyr-NHMe (a model for GYG peptide) which is a portion of the selectivity filter in the K+ channel have been revealed. In tis presentation, the permeability of silver ion for the potassium channel is discussed. Silver and silver ions have a long history antimicrobial activity and medical applications. Nevertheless, the activity of Ag+ against bacteria, how it enters a cell, has not yet been established. The K+ channel, a membrane protein, is a possible route. The addition of a channel inhibitor (4-aminopyridine) to modulate the Ag+ uptake could support this view. However, the inhibitor enhances the uptake of Ag+, the opposite result. We have applied cold ion trap infrared laser spectroscopy to complexes of Ag+ and Ac-Tyr-NHMe (a model for GYG peptide) which is a portion of the selectivity filter in the K+ channel to consider the question of permeation. With support from quantum chemical calculations, we have determined the stable conformations of the complex. The conformations strongly suggest that Ag+ would not readily permeate the K+ channel. The mechanism of the unexpected enhancement by the inhibitor is discussed. References 1) S. Tanabe et al., JPCL in press. 2) Y. Suzuki et al., Bull. Chem. Soc. Jpn. in press. 3) Y. Suzuki et al., PCCP, 24, 20803 (2022). 4) Y. Suzuki et al., JPCA, 125, 9609 (2021) (Front Cover). 5) T. Negoro et al., PCCP, 23, 12045 (2021) (Inside Back Cover) 6) R. Otsuka et al., ChemPhysChem, 21, 712 (2020) (Front Cover) 7) S. Ishiuch et al., PCCP, 21, 561 (2019) (Cover)

WA02 **9:06 – 9:21**

CARBONYL BANDS REPORT ON MOLECULAR STRUCTURE IN COMPLEX SPECTRA: CRYOGENIC ION SPECTROSCOPY OF METAL-CYCLAM COMPLEXES[a]

MADISON M. FOREMAN, WYATT ZAGOREC-MARKS, J. MATHIAS WEBER, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*.

The feasibility of industrial scale electrocatalytic CO_2 reduction requires the development of catalysts that are both selective and efficient, making it imperative to understand the catalytic structure-function relationship to inform the design of improved catalysts. Nickel cyclam is a high-performing CO_2 reduction catalyst, and its derivatives have demonstrated differing catalytic abilities. Here, we present cryogenic gas-phase infrared spectra of a series of transition metal-cyclam derivative complexes of the form $[M(II)\cdot TEC]^{2+}$ (TEC = cyclam with four ethyl acetate substituents) and interpret spectral features using density functional theory calculations. The size and conformational flexibility of these complexes cause spectral congestion that complicates peak assignment. We address this challenge by utilizing the carbonyl stretching bands as spectroscopic reporters of molecular structure.

[a]The authors gratefully acknowledge funding from the National Science Foundation (CHE-2154271, CHE-1764191, and PHY-1734006)

WA03 **9:24 – 9:39**

LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER I: RO-VIBRATIONAL SPECTRA

THOMAS SALOMON, OSKAR ASVANY, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

The symmetric O-H stretching band of the protonated water dimer is re-investigated at high spectral resolution applying the novel action spectroscopic technique leak-out spectroscopy (LOS) in the 22-pole ion trap experiment COLtrap operated at 4 K. Ro-vibrational transitions of Helium buffer gas cooled $H_5O_2^+$ are excited using a narrow linewidth optical parametric oscillator prior to collisions with Neon as a second buffer gas. In doing so, part of the internal energy of the previously excited cation is transferred into kinetic energy (V-T-transfer) allowing it to surpass the electrostatic potential at the exit electrode of the 22-pole trap. The amount of cations exiting the trap time during the total trap time is monitored using a quadrupole mass-filter and a Daly-type ion detector. The resulting rotationally resolved spectrum is intrinsically background-free because the parent ground state ions are trapped without loss. The line intensities measured by LOS turn out to be closely related to the line intensities of conventional absorption spectroscopy. The new and extensive spectra are compared to previously presented high-resolution data obtained using a two-color-photodissociation scheme. Basically, the previously observed spectral complexity is confirmed by the novel action spectroscopic technique. The single-color leak-out spectra are more reliable in their actual line intensities as any impact on the dissociation efficiency originating from a variation of the optical overlap between two lasers experiments or power fluctuations are avoided. This improvement further simplifies the identification of Q-branches which can be nicely spotted in the high S/N spectra. Based on the multiplicity of these Q-branches and their separation, the tunneling motions at play for this molecular complex can be deciphered. Our findings challenge the current view on the struture and dynamics of the protonated water dimer.

WA04 **9:42 – 9:57**

LEAK-OUT SPECTROSCOPY OF PROTONATED WATER DIMER II: SPIN STATISTICAL WEIGHTS

THOMAS SALOMON, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*; CHARLES R. MARKUS, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; OSKAR ASVANY, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

It is widely believed that in the protonated water dimer the central proton is equally shared between the two water molecules (Zundel structure). This complex is subject to large amplitude motions and tunneling. It is an interesting question which motions are feasible and the answer to this question is tightly related to the underlying molecular symmetry group. For a semi-rigid complex the symmetry group is $G_{16}^{(2)}$. But when all five protons can swap places the underlying group is G_{240}. For these two situations the nuclear spin statistical weights are different. In a trap experiment where a finite ensemble of cold and mass selected ions is stored, it is now possible to determine the fractions of nuclear spin species by kicking out all ions belonging to one nuclear spin configuration using leak-out spectoscopy (LOS). Results from these measurements are much more reliable than comparing line intensities, which is a traditional approach to determine those fractions. This is because the fractions are directly determined from the temporal evolution of the number of ions in the trap. In this contribution we will present results for such LOS depletion experiments for the protonated water dimer. From a detailed analysis of our findings we infer information on the mobility of the central proton of this fundamental complex.

WA05 **10:00 – 10:15**

AN ELECTRIC AFFAIR: THE IMPACT OF SOLVATION ON THE STRUCTURE OF METAL ION-PEPTIDE COMPLEXES

KATHARINA A. E. MEYER, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

The impact of electric fields on the structure and function of biomolecules is a well-known, yet not well understood phenomenon. One prominent example are enzymes, where electrostatic preorganization around the active site is thought to be vital for their catalytic function. [1] To shed light on the unique catalytic ability of enzymes, we need a better understanding of the impact of such (local) electric fields. This requires a systematic study of the interplay of the various non-covalent interactions present in biomolecular systems such as electrostatic interactions as well as inter- and intramolecular hydrogen bonding. Due to the structural complexity, however, this is difficult to obtain from studies of the condensed phase. A popular approach is therefore to prepare model complexes in the gas phase, where the individual contributions of different types of interactions can be studied in much greater detail.

In this contribution, we will study the solvation of diglycine complexes with three alkali metal ions (Li^+, Na^+, K^+) with cryogenic ion vibrational spectroscopy scrutinising the interplay of the electrostatic metal ion-peptide and metal ion-water interaction with intra- and intermolecular hydrogen bonding. We observe interesting structural differences in the singly hydrated complexes, which can be related to the potassium selectivity of potassium ion channels. [2] In larger solvated clusters, the competition between intramolecular hydrogen bonding in the peptide backbone and intermolecular hydrogen bonding between water and the peptide increases in favour of the latter, leading to a change in peptide structure as the number of water molecules increases, whereas switching point occurs earlier for the Li^+ compared to the Na^+ and K^+ complexes. Differences in internal hydrogen bond strength between the complexes of the three metal ions decrease in the larger solvated clusters, which is important to consider for comparisons between environments where partial solvation dominates versus the bulk phase.

References: [1] N. G. Léonard, R. Dhaoui, T. Chantarojsiri, J. Y. Yang, *ACS Catal.* 2021, *11*, 10923–10932. [2] Y. Suzuki, K. Hirata, J. M. Lisy, S. Ishiuchi, M. Fujii, *Phys. Chem. Chem. Phys.* 2022, *24*, 20803–20812.

Intermission

WA06 **10:55 – 11:10**

CRYOGENIC ION SPECTROSCOPY OF ION-RECEPTOR INTERACTIONS IN OCTAMETHYL CALIX[4]PYRROLE COMPLEXES WITH HALIDE IONS[a]

LANE M. TERRY, *JILA and Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA*; MADISON M. FOREMAN, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*; ANNE P. RASMUSSEN, *Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark*; ANNE B. McCOY, *Department of Chemistry, University of Washington, Seattle, WA, USA*; J. MATHIAS WEBER, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*.

Molecular recognition of ions is important in both the natural world within proteins and the synthetic world of supramolecular chemistry. Therefore, a deeper understanding of ion receptors and binding competitiveness in solution is desirable for the advancement of synthetic hosts for ionic guests. Octamethyl calix[4]pyrrole (omC4P), is a prototypical receptor for halide anions in aqueous solution chemistry.

We present cryogenic gas-phase infrared spectra of a series of anion-omC4P complexes of the form [X^-·omC4P] (X^- = fluoride, chloride, bromide), and assign spectral features using density functional theory calculations. The vibrational spectra encode the structures of and intermolecular forces in each complex, revealing the geometry of each complex and the binding motif of halide anions within the omC4P binding pocket. The position of the NH stretching modes depend on the identity of the anion, portraying a clear spectral response to changes in binding properties.

[a]The authors gratefully acknowledge funding from the National Science Foundation (CHE-2154271)

WA07 **11:13 – 11:28**

MISMATCHED HOST-GUEST PAIRINGS – CRYOGENIC ION SPECTROSCOPY OF OCTAMETHYL-CALIX[4]PYRROLES IN COMPLEXES WITH NITRATE AND FORMATE[a]

LANE M. TERRY, *JILA and Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA*; MADISON M. FOREMAN, J. MATHIAS WEBER, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*.

Octamethyl-calix[4]pyrrole (OMC4P) is a prototypical anion receptor, and it has been mainly used to bind halide ions, particularly fluoride and chloride. It is not a good receptor for polyatomic anions without chemical modifications. In the present work, we study the structures of complexes of OMC4P with nitrate and formate, using cryogenic ion vibrational spectroscopy with N_2 messenger tagging. We present the vibrational spectra of these species and obtain structural information by comparison of the experimental spectra with calculated spectra based on density functional theory.

[a]The authors gratefully acknowledge funding from the National Science Foundation (CHE-2154271)

WA08 **11:31 – 11:46**

MICROHYDRATION OF $Mg^{2+}(CH_3COO^-)$ ION PAIRS FOLLOWED BY IR LASER SPECTROSCOPY: INSIGHTS INTO THE WATER-MEDIATED IONIC INTERACTIONS IN THE MAGNESIUM TRANSPORT CHANNEL

JEAN-XAVIER BARDAUD, ERIC GLOAGUEN, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, Orsay, France*; VALERIE BRENNER, MICHEL MONS, *CEA Saclay, LIDYL, Gif-sur-Yvette, France*; HIKARU TAKAYANAGI, KEISUKE HIRATA, SHUN-ICHI ISHIUCHI, MASAAKI FUJII, *Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan*.

Ionic interactions play a crucial role in ion transport and selectivity to maintain cellular ion homeostasis. For example, the Mg^{2+} channel is a membrane protein that regulates Mg^{2+} cation concentration on both sides of the cell membrane. Crystal structure of the Magnesium Transport E channel suggests a transport mechanism for Mg^{2+} ions involving the motion of hexa-hydrated Mg^{2+} cations recognized through water-mediated ionic interactions between the Mg^{2+} cation and the carboxylate groups of the channel interior.[a]

In order to characterize these water-mediated ionic interactions, we investigated $Mg^{2+}(CH_3COO^-)(H_2O)_n$ clusters. We probed their structures from $n = 4$ to 17 by measuring cryogenic gas phase infrared spectra, further interpreted by high level quantum chemistry DFT-D calculations of vibrational frequencies. This comparison allowed us to investigate size-selected microhydrated Mg^{2+} ion pairs.

In accordance with previous findings obtained on hydrated calcium[b] and barium[c] acetate clusters, hydration by 6 water molecules is insufficient to induce the ion separation. Nonetheless, partially-separated or separated ion pairs are formed from at least 10 water molecules, and more significantly with 14 water molecules. These results highlight the necessity of a second water-mediated ionic interaction for the transport of Mg^{2+} within the channel and possibly in cooperation with weaker secondary interactions, such as involving carbonyl groups, as suggested by the crystal structure.

[a]Takeda, H.; Hattori, M.; Nishizawa, T.; Yamashita, K.; Shah, S. ; Caffrey, M.; Maturana, A. D.; Ishitani, R.; Nureki, O. Nat. Commun. 2014, 5374.

[b]Denton, J. K.; Kelleher, P. J.; Johnson, M. A.; Baer, M. D.; Kathmann, S. M.; Mundy, C. J.; Wellen, R. B. A.; Allen, H. C.; Choi, T. H.; Jordan, K. D. Proc. Natl. Acad. Sci. U.S.A. 2019, 116, 14874-14880.

[c]Donon, J.; Bardaud, J.-X.; Brenner, V.; Ishiuchi, S.; Fujii, M.; Gloaguen, E. Phys. Chem. Chem. Phys. 2022, 24, 12121-12125.

WA09 **11:49 – 12:04**

HIGH RESOLUTION SPECTROSCOPY IN A 5K CRYOGENIC ION TRAP: REVISITNG THE OH STRETCHING BANDS OF THE H_20 AND HDO ISOTOPOLOGUES OF THE BINARY COMPLEXES WITH IODIDE

PAYTEN HARVILLE, SEAN COLEMAN EDINGTON, MARK JOHNSON, *Department of Chemistry, Yale University, New Haven, CT, USA*.

We report fully rotationally resolved spectra of the $I^-(H_2O)$ and I^-(HDO) ion-molecule complexes measured by predissociation spectroscopy in a 3D cryogenic ion trap. The spectra were obtained by excitation with a single-frequency, cw infrared laser (TOPAS by Toptica Corp.) directly into the trap. The formation of bare iodide photoproducts was observed by first ejecting the bare ion from the trap by excitation at the secular frequency, followed by formation of I^- photoproducts on the timescale of 40 ms. The product ions were then detected by injecting the contents of the trap into a time-of-flight mass spectrometer. The spectra reveal a plethora of very sharp transitions associated with overlapping rotational band structures arising from at least three vibrational transitions. Despite the fact that this excitation occurs about 300 cm^{-1}above the dissociation threshold, the lines are very narrow, revealing very long lived (ca. 2 ns) rovibrational levels. Analysis of these patterns quantifies the anharmonic behavior of this system arising from tunneling as well as intramolecular mode coupling involving soft modes and the bending overtone.

WA10 **12:07 – 12:22**

A MOLECULAR CAGE REPORTS ON ITS CONTENTS: THE INFRARED AND ULTRAVIOLET SPECTRA OF [2.2.2]BENZOCRYPTAND COMPLEXED WITH K^+, Ba^{2+}, AND THE ION PAIR Ba^{2+}-ACETATE$^-$

CHIN LEE, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*; CASEY DANIEL FOLEY, *Department of Chemistry, University of Missouri, Columbia, MO, USA*; KENDREW AU, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*; EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*; TIMOTHY S. ZWIER, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*.

Cryptands are 3D molecular cages that initiated the field of supramolecular chemistry. They feature three ether bridges capped on either end by a tertiary amine, leading to a structure in which six oxygens and two nitrogens can bind to cations that fit inside the cage. We incorporate a phenyl ring in one of the ether bridges, forming [2.2.2]benzocryptand, in order to have an ultraviolet chromophore for our studies. Investigated complexes include benzocryptand with metal cations of potassium, barium and ion pair of barium-acetate. We will describe our results on the UV photofragment spectroscopy and IR-UV double resonance spectra that provide single-conformation IR spectra of the complexes under cryo-cooled conditions. In each case, there is a single dominant conformation of the complex. IR spectra in the alkyl CH stretch region are surprisingly sensitive to the ion in the cage, and to an anion binding to this caged cation.

WB. Linelists

Wednesday, June 21, 2023 – 8:30 AM

Room: 100 Noyes Laboratory

Chair: Amanda J. Ross, Universite de Lyon, Villeurbanne, France

WB01 **8:30 – 8:45**

ROTATIONAL SPECTROSCOPY OF UREA UP TO 500 GHZ: THE GROUND STATE AND EIGHT EXCITED VIBRATIONAL STATES

DANIEL J TYREE, THOMAS W CHAPMAN, IVAN MEDVEDEV, *Department of Physics, Wright State University, Dayton, OH, USA*; ZBIGNIEW KISIEL, *ON2, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland*.

Urea has an important role in the nitrogen cycle of organisms and is produced at large scales industrially for food production among other uses. Its significance in the formation of complex prebiotic molecules has made it an appealing target for astronomers searching for precursors to life in space [1]. Some of the data presented here has enabled definitive detection of urea in the interstellar medium with modern submillimeter telescopes [2]. Assignment of the ground and eight lowest vibrational states of urea, $(\mathrm{NH_2})_2\mathrm{CO}$, was performed over a spectral range between 210-500 GHz [3]. Intensities of the excited state lines were calibrated by means of a global fit of the ground state and excited state intensities to determine relative vibrational energies. The lowest of these states was found to be $61\ \mathrm{cm}^{-1}$above the ground state which is consistent with previously determined values and could potentially aid in the determination of the temperature urea spectra. The next two lowest vibrational states we found to be significantly coupled and were treated with a Coriolis coupling model. Other higher vibrational states also demonstrated significant coupling. Combined, the vibrational symmetries along with the relative energies provide insight into the structure of urea vibrational energies.

[1] A. J. Remijan et al., "OBSERVATIONAL RESULTS OF A MULTI-TELESCOPE CAMPAIGN IN SEARCH OF INTERSTELLAR UREA [(NH2)2CO]," *Astrophys J*, vol. 783, no. 2, p. 77, 2014, doi: 10.1088/0004-637X/783/2/77.

[2] A. Belloche et al., "Re-exploring Molecular Complexity with ALMA (ReMoCA): interstellar detection of urea," *Astron & Astrophys*, vol. 628, 2019, . Available: https://doi.org/10.1051/0004-6361/201935428

[3] D. J. Tyree, T. W. Chapman, I. R. Medvedev, and Z. Kisiel, "Rotational spectroscopy of urea up to 500 GHz: The ground and eight excited vibrational states," *J Mol Spectrosc*, vol. 390, p. 111706, 2022, doi: https://doi.org/10.1016/j.jms.2022.111706.

WB02 **8:48 – 9:03**

LaO LINE LIST FOR THE $A^2\Pi$-$X^2\Sigma^+$ BAND SYSTEM

PETER F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*; RANDIKA DODANGODAGE, *Department of Physics, Old Dominion University, Norfolk, VA, USA*; JACQUES LIÉVIN, *Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, Brussels, Belgium*.

The bands of LaO appear prominently in the spectra of cool S-type stars and can be used to determine La abundances. We have rotationally analyzed the LaO $A^2\Pi$-$X^2\Sigma^+$ band system up to v=3 in the excited state using PGOPHER. The spectroscopic constants for the ground state were taken from our previous analysis of $B^2\Sigma^+$-$X^2\Sigma^+$ band system [1]. The band and equilibrium constants for the $A^2\Pi$ state were determined. RKR potentials were calculated and band strengths were obtained using LeRoy's LEVEL program with an *ab initio* transition dipole moment. This work also provides calculated radiative lifetimes for v=0 to v=3 of the A state. A line list for the LaO $A^2\Pi$-$X^2\Sigma^+$ transition is provided which can be used to simulate LaO spectra in S-type stars.

1. P. F. Bernath, R. Dodangodage and J. Liévin, S-type stars: LaO line list for the $B^2\Sigma^+$ - $X^2\Sigma^+$ band system, Astrophys. J. 933, 99 (2022).

WB03 **9:06 – 9:21**

INTENSITY STUDIES OF OZONE IN THE 10 MICRON REGION BY SIMULTANEOUS SUB-MM/LASER-BASED INFRARED DIRECT ABSORPTION MEASUREMENTS

DEACON J NEMCHICK, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; XU ZHANG, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; KEEYOON SUNG, TIMOTHY J. CRAWFORD, BRIAN DROUIN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*.

Ozone is a common retrieval target from a variety of remote sensing platforms owing to both its importance in tropospheric and stratospheric chemical processes and readily accessible observation grade absorption/emission bands in the THz, infrared, visible, and ultraviolet. Refinement of the ν_3 band line intensities in the 10 micron region has been the target of many spectroscopic studies in the past decades with uncertainty claims now approaching the 1% level. These studies typically constrain experimental ozone number density using UV cross section measurements while simultaneously performing Fourier transform or laser-based measurements in the infrared. This talk will summarize ongoing efforts to perform dual band measurements using a mode-hop-free quantum cascade laser in the infrared that instead derives ozone partial pressures from simultaneously collected direct absorption spectra in the sub-millimeter (500-600 GHz) region. This alternative approach, which serves as the first sub-millimeter/laser-based infrared attempt to determine ozone intensities, is unique in that infrared intensities are ultimately anchored to dipole measurements accurate to the 0.1% level. A brief overview of previous ozone studies will be provided along with a detailed description of the experiment configuration and preliminary results.

WB04 **9:24 – 9:39**

A NEW LINE LIST FOR THE O2 SCHUMANN-RUNGE SYSTEM

ELIJAH R JANS, *Diagnostics for Hypersonics and Extreme Environments, Sandia National Laboratories , Albuquerque, NM, USA*; DANIEL SPENCER JENSEN, *Computational Multiscale, Sandia National Laboratories, Albuquerque, NM, USA*; LAURA M McCASLIN, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*.

In this work, a spectrally accurate linelist has been generated for the O_2 Schumann-Runge band system, $X^3\Sigma_g^-$ - $B^3\Sigma_u^-$, including both the bound-bound and bound-unbound transitions. *Ab initio* potential energy curves (PECs) for both states and the transition dipole moment (TDM) have been computed using the multi-reference configuration interaction (MRCI) method. Empirical refinement of the potential energy curves along with spin coupling constants have been performed using the DUO software utilizing the O_2 MARVEL database from Furtenbacher et al (J. Phys. Chem. Ref. Data 48, 023101 (2019)). Comparison with room and high temperature cross-sections have also been performed.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

WB05 **9:42 – 9:57**

PRECISION MEASUREMENTS OF WATER VAPOR SPECTROSCOPY BROADENED BY O_2 FOR ACCURATE DETERMINATION OF POTENTIAL ENERGY SURFACE

KEEYOON SUNG, GEOFFREY C. TOON, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; ROBERT R. GAMACHE, *Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts, Lowell, MA, USA*.

We have investigated collisional broadening and pressure-induced frequency shift for H_2O transitions broadened by O_2. For this, we have obtained one pure and four O_2-mixture spectra of H_2O in the ν_2 region at room temperature using a high-resolution Fourier transform spectrometer (Bruker IFS-125HR) at the Jet Propulsion Laboratory. Using a high-precision spectrum fitting package, Labfit, which adopted non-linear least squares curve fitting algorithm based on a Voigt line shape profile, we have retrieved the two line shape parameters as well as the line positions by fitting all the five spectra simultaneously. It should be noted, however, that their line intensities have been held to the HITRAN values, which improved the precision of the widths and shifts retrieval to a sub% level for most of the transitions. Results from this work have been used to improve the intermolecular potential of the collisional pair, H_2O-O_2, as part of the theoretical model calculations for O_2-broadened H_2O transitions. We will present and discuss the retrieval methodology and the impact of the measurement results on the theoretical model calculations, which are expected to produce more accurate line shape parameters for the entire rovibrational transitions of H_2O in the infrared.[a]

[a]Government support acknowledged.

Intermission

WB06 **10:37 – 10:52**

A NEW LINE LIST FOR THE N2 SECOND POSITIVE SYSTEM

ELIJAH R JANS, *Diagnostics for Hypersonics and Extreme Environments, Sandia National Laboratories , Albuquerque, NM, USA*.

The second positive system ($C^3\Pi_u$ - $B^3\Pi_g$) for N_2 has been widely used for optical diagnostics in plasma systems, hypersonic environments, and astrophysics. To this end, a spectrally accurate linelist has been generated for the second positive band system. Ab initio potential energy curves (PECs) and the transition dipole moment (TDM) from Ni and Cheng [1] have been used to calculate new electronic-vibrational transition moments, extending up to v = 29 for the $B^3\Pi_g$, using the DUO program. Spectral constants from Western et al. [2] and Roux et al. [3] have been compiled along with the new electronic-vibrational transition moments in PGOPHER software to generate the new linelist. Comparisons to experimental data and the SpecAir software have been used to validate the new linelist.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

1. Ni, C., and Cheng, X. "Ab initio study of the second positive system of N_2 at high temperature," Computational and Theoretical Chemistry Vol. 1197, 2021, p. 113158.
2. Western, C. M., Carter-Blatchford, L., Crozet, P., Ross, A. J., Morville, J., and Tokaryk, D. W. "The spectrum of N_2 from 4,500 to 15,700 cm^{-1} revisited with PGOPHER," Journal of Quantitative Spectroscopy and Radiative Transfer Vol. 219, 2018, pp. 127-141.
3. Roux, F., Michaud, F., and Vervloet, M. "High-resolution Fourier spectrometry of $^{14}N_2$ violet emission spectrum: extensive analysis of the $C^3\Pi_u \rightarrow B^3\Pi_g$ system," Journal of molecular spectroscopy Vol. 158, No. 2, 1993, pp. 270-277.

WB07 **10:55 – 11:10**

INVESTIGATING THE INTERSTELLAR SULFUR CHEMISTRY THROUGH ROTATIONALLY RESOLVED DISCHARGE EXPERIMENTS

AMANDA STEBER, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*; CRISTOBAL PEREZ, *Faculty of Science - Department of Physical Chemistry, University of Valladolid, Valladolid, Spain*; WENQIN LI, ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*.

While the number of sulfur containing species detected in the interstellar medium has grown in recent years, the detected species still cannot account for the interstellar abundance of sulfur. Thus, in a effort to identify new species that might be of astrochemical interest, an electrical discharge nozzle has been used to generate terrestrially unstable sulfur-bearing species. In our experiment we have paired an electrical DC-discharge nozzle with a broadband microwave spectrometer to measure the resulting products of the discharge of small organic compounds previously identified in the molecular inventory. The rotational spectra from new species are then used for astronomical searches with radio telescopes. Furthermore, we investigate probable reaction pathways that these species could participate in through quantum chemical calculations, providing a global view of the matter cycle in the interstellar medium. In this talk we will present the optimization and benchmarking of our newly-built source as well as some preliminary results on sulfur chemistry and their interpretation.

WB08 **11:13 – 11:28**

AN AB INITIO STUDY AND INITIAL REFINEMENT OF THE ROVIBRONIC SPECTRUM OF SULFUR MONOXIDE (^{32}S^{16}O): DIABATIC VS. ADIABATIC REPRESENTATION AND THEIR EQUIVALENCE IN NUCLEAR MOTION CALCULATIONS

RYAN BRADY, SERGEI N. YURCHENKO, *Department of Physics and Astronomy, University College London, London, United Kingdom*; GAP-SUE KIM, *Dharma College, Dongguk University, Seoul, Korea*; WILFRID SOMOGYI, JONATHAN TENNYSON, *Department of Physics and Astronomy, University College London, London, United Kingdom*; CHARLIE DRURY, *Physics and Astronomy , University College London, London, United Kingdom*.

An ab initio study of the rovibronic spectra of sulphur monoxide (^{32}S^{16}O) using internally contracted multireference configuration interaction (ic-MRCI) method using aug-cc-pV5Z basis sets is presented. It covers 13 electronic states $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^-$, $c^1\Sigma^-$, $A''^3\Sigma^+$, $A'^3\Delta$, $A^3\Pi$, $B^3\Sigma^-$, $C^3\Pi$, $d^1\Pi$, $e^1\Pi$, $C'^3\Pi$, and $(3)^1\Pi$ ranging up to 66800 cm^{-1}. The ab initio spectroscopic model includes 13 potential energy curves, 29 dipole and transition dipole moment curves, 25 spin-orbit curves, and 18 electronic angular momentum curves. A diabatic representation is built by removing the avoided crossings between the spatially degenerate pairs $C^3\Pi$-$C'^3\Pi$ and $e^1\Pi$-$(3)^1\Pi$ through a property-based diabatisation method. Non-adiabatic couplings and diabatic couplings for these avoided crossing systems are also presented. Finally, a rovibronic spectrum of SO is computed, where an initial refinement of the model to experimental data is shown - producing an initial semi-empirical line list for SO. All phases for our coupling curves are defined, and consistent, providing the first fully reproducible spectroscopic model of SO covering the wavelength range up to 147 nm.

We present a diabatisation procedure where the numerical equivalences between the diabatic and adiabatic representations are tested. We show that the commonly ignored first and second order non-adiabatic coupling terms are essential to the equivalence of the two representations, where we provide an analysis on the energy level convergences with basis size for Yitrium Oxide (YO) and a physical set of synthetic potential energy curves in the diabatic and adiabatic representations. The effect of this diabatisation on the accuracy of the final semi-empirical line list of SO is then discussed.

WB09 **11:31 – 11:46**

EXTENDED PRECISE SPECTROSCOPY OF THE ν_3 BAND OF METHANE

HIROYUKI SASADA, SHO OKUBO, HAJIME INABA, *National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan*.

We measured transition frequencies of the ν_3 fundamental band of methane from P(1) to P(12), from Q(1) to Q(14), and from R(0) to R(8) with an uncertainty from a few to seventeen kilohertz using a difference-frequency-generation source, an enhanced-cavity absorption cell, and an optical frequency comb. [a] [b] This paper presents that the tunable range of the spectrometer has extended to the higher frequency and that 37 allowed and 20 forbidden transition frequencies of R(8) to R(12) have been precisely measured using similar apparatus as Refs *a* and *b*. The forbidden transitions have allowed us to determine precise combination differences of the ground state. We have improved molecular constants of the ground state from the combination differences of the present work and Refs *a* and *b* together with the previous microwave measurements.

[a] S. Okubo, H. Nakayama. K. Iwakuni, H. Inaba, and H. Sasada, Opt. Express, vol. 19, p. 23878 (2011).
[b] M. Abe, K. Iwakuni, S. Okubo, and H. Sasada, J. Opt. Soc. B vol. 30, p. 1027 (2013).

WB10 **11:49 – 12:04**

FREQUENCY MEASUREMENTS WITH kHz-ACCURACY OF $^{12}CO_2$ TRANSITIONS IN THE 2.0 μm REGION

HELENE FLEURBAEY, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*; PETER ČERMÁK, *Department of Experimental Physics, Comenius University, Bratislava, Slovakia*; SAMIR KASSI, DANIELE ROMANINI, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*; ONDŘEJ VOTAVA, *Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic*; DIDIER MONDELAIN, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*.

Absolute frequencies of 106 ro-vibrational transitions belonging to the 20012-00001 and 20013-00001 bands of $^{12}CO_2$ have been measured by saturation spectroscopy. Lamb dips were observed using a cavity ring-down spectrometer linked to an optical frequency comb referenced to a GPS-disciplined Rb oscillator. The feed-forward technique[a] was applied to transfer the coherence of very stable comb emission lines to the laser source of the spectrometer (an external cavity diode laser) via an electro-optic modulator. This setup allows achieving transition frequencies measurements with kHz-level accuracy. The transition frequencies of the two bands are reproduced with a (1σ)-rms of about 1 kHz using the standard expression of the ground and upper energy levels, the ground state constants being constrained to the values reported in Wu et al.[b] The 20012 and 20013 vibrational states appear thus to be highly isolated except for a local perturbation of the 20012 state leading to an energy shift of 15 kHz at J'=43. Finally, comparison to transition frequencies reported in the HITRAN2020 database and the literature will be presented and discussed.

[a] Gotti et al., J Chem Phys 2018, 148, 054202
[b] Wu et al., Phys Chem Chem Phys, 2020, 22, 2841-2848

WC. Astronomy

Wednesday, June 21, 2023 – 8:30 AM

Room: 1024 Chemistry Annex

Chair: Anthony Remijan, NRAO, Charlottesville, VA, USA

WC01 **8:30 – 8:45**

LINKING CHEMISTRY AND KINEMATICS IN THE MOLECULAR GAS OF PROTOPLANETARY NEBULA M1-92

KATHERINE R. GOLD, *Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ, USA*; DEBORAH SCHMIDT, OMAR KHATTAB, *Department of Physics and Astronomy, Franklin and Marshall College, Lancaster, PA, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

Protoplanetary nebulae (PPNe) play a significant role in the evolution of low and intermediate mass stars, serving as the link between the asymptotic giant branch (AGB) and planetary nebulae phases. Previous observations have revealed that planetary nebulae are rich in molecular content that varies considerably from the AGB phase, suggesting that significant chemical transformations take place during the brief intermediate PPN stage. To further investigate this problem, we have conducted new molecular observations towards M1-92, an oxygen-rich, bipolar PPN. These measurements have been conducted using the using the Kitt Peak 12 m antenna and the Sub-Millimeter Telescope (SMT) of the Arizona Radio Observatory, as well as the IRAM 30 m telescope. These observations have extended the molecular identifications to include CN, HCO^+, $H^{13}CO^+$, HCN, HNC, H_2CO, H_2S, SO_2, SiO, $Si^{17}O$, and other isotopologues of these species. Further, some spectra, for example, CS, contain at least five velocity components, tracing the equatorial disk of the nebula, the bipolar lobes and the bipolar tips. The "tips" may track a high velocity wind that has punctured through the slower-moving material in the lobes, sweeping up the lobe gas. These observations will be discussed, with implications for the chemical evolution in this O-rich PPN and its relationship to the kinematic structure.

WC02 **8:48 – 9:03**

POLYATOMIC MOLECULES IN PLANETARY NEBULAE: SEARCHES FOR C-C3H2, H2CO, CCH, AND HNC IN M1-59, NA2, HU1-1, AND M4-17

KATHERINE R. GOLD, *Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ, USA*; DEBORAH SCHMIDT, *Department of Physics and Astronomy, Franklin and Marshall College, Lancaster, PA, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

Observations from the past decade show that a variety of polyatomic species such as HCN and HCO^+ are present in over 30 planetary nebulae. Contrary to chemical models, which predict rapid photodissociation, molecular abundances appear to remain relatively constant with evolutionary age. To further explore molecular content of PNe, four planetary nebula containing HCO^+ and/or HCN have been further investigated: Hu 1-1, M4-17, M1-59, and Na2. These nebulae were chosen on the basis of their varied morphologies (e.g., Hu 1-1 is elliptical, M1-59 is multipolar) or age (Na2 is 28,000 years old). Observations of these PNe were conducted using the ARO Submillimeter Telescope (1mm) and the IRAM 30m telescope (2mm). Current results include the detection of CS, c-C_3H_2, H_2CO, CCH, HNC and CN towards at least one of Hu1-1, M1-59, and M4-17, as well as various isotopologues of these species. These new identifications expand the known molecular species contained in these PNe. Molecular abundances and isotope ratios will be presented and compared with other PNe that foster similar chemistries.

WC03 **9:06 – 9:21**

A 1 AND 2mm SURVEY OF THE CARBON-RICH STAR IRC+10216: A FOCUS ON ISOTOPES

LILIA KOELEMAY, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

A 2 mm survey has been conducted of IRC+10216 (135-175 GHz) using the new 2 mm receiver of the Arizona Radio Observatory (ARO) 12 m, coupled with the ARO Wideband Spectrometer (AROWS) 4 GHz backend. The mixers were developed at ARO and have exceptional noise temperatures. Due to the unparalleled sensitivity of this new receiver, a peak-to-peak noise of 3 mK was achieved over the whole frequency range. Over 900 lines were measured in this survey, many of which were previously undetected in prior surveys. Many of these lines display intensities of 1 or 2 mK and have yet to be identified. Combined with an ongoing survey of the 1mm (215-285 GHz) with the ARO SMT and previous data from a 3 mm (67-115 GHz) survey conducted by the Ziurys group, several molecules, including CCH, C_4H, CN, and their ^{13}C isotopologues are being analyzed across a large frequency range, using the ESCAPADE code. From these data, a comprehensive study of the $^{12}C/^{13}C$ ratio for IRC+10216 is being carried out. Preliminary results indicate a $^{12}C/^{13}C$ ratio of $\sim$38, but this value will be further refined. Other isotope ratios will also be examined.

WC04 **9:24 – 9:39**

ALMA PROBES REFRACTORY CHEMISTRY AND RELATED MASS-LOSS EVENTS IN VY CMa

RAJAT RAVI, AMBESH PRATIK SINGH, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; ROBERTA M. HUMPHREYS, *Minnesota Institute for Astrophysics, University of Minnesota, Minneapolis, MN, USA*; ANITA M RICHARDS, *Physics, University of Manchester , Manchester , United Kingdom*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

The hypergiant star VY Canis Majoris, or VY CMa provides an excellent opportunity to study the evolution of massive stars, which undergo significant mass-loss and are characterized by asymmetric outflows. The arcs, knots, and clumps formed in these processes contain dust and molecules. Using the ALMA, images of PO, PN, NaCl, and $Na^{37}Cl$ have been obtained in Band 6 at 0.25 and 1 arcsec resolution and combined with single-dish data from the ARO Submillimeter Telescope (SMT). While PO emission is confined to the spherical outflow directly on the star, that of PN is more extended, forming a bridge between the star and the SW Clump seen in HST data. NaCl and $Na^{37}Cl$, on the other hand, trace two distinct sources: the spherical outflow and the SW Clump. NaCl is known to condense out of the gas-phase rapidly in circumstellar material. The survival of NaCl in the SW Clump supports the idea that this material was ejected directly from the photosphere. PN and PO are not observed in the more extended structures seen in SO_2 and HCN, indicating likely grain condensation as well.

WC05 **9:42 – 9:57**

ALMA REVEALS THE EXTENDED ENVELOPE OF THE HYPERGIANT STAR VY CMa

AMBESH PRATIK SINGH, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; ANITA M RICHARDS, *Physics, University of Manchester , Manchester , United Kingdom*; ROBERTA M. HUMPHREYS, *Minnesota Institute for Astrophysics, University of Minnesota, Minneapolis, MN, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

VY CMa is one of the best examples to study the stellar evolution of massive stars. Such stars are characterized by complex envelope dynamics resulting from highly directional ejecta of molecular gas and dust. Previous studies of VY CMa using HST show two SE arcs (Arc I, Arc II), an NW arc, SW clumps, and multiple knots. Using ALMA at Band 6 with 1 and 0.25-arcsecond resolution, combined with previous single-dish observations, VY CMa has been imaged in various molecules at 1 mm. From the combined data sets, all the flux from the molecular envelope has been recovered, resulting in the first complete image of the ejecta on a 15-arcsecond scale. In addition to the well-known features such as Arcs 1 and 2, new, more extended structures have been found in CO and HCN, reaching as far as 8 arcseconds from the star, including a NE plume and an E arc. Additionally, images of ^{13}CO and $H^{13}CN$ have been created to compare isotopic ratio variations of known features. These data will complement previous studies conducted on smaller spatial scales star and provide a more complete picture of the mass loss history of VY CMa.

Intermission

WC06 **10:37 – 10:52**

THE CENTRAL 300 pc OF THE GALAXY PROBED BY INFRARED SPECTRA OF H_3^+ AND CO

TAKESHI OKA, *Department of Astronomy and Astrophysics, Chemistry, The University of Chicago, Chicago, IL, USA*; THOMAS R. GEBALLE, , *Gemini Observatory/NSF's NOIRLAB, Hilo, HI, USA*.

Our 15 years' observations of the infrared spectra of H_3^+ and CO toward 30 young and bright stars with smooth continuum and their analyses have led to the following conclusions.

I. Predominance of Warm and Diffuse Gas and High H_2 Ionization Rate[a]: The CMZ is filled with warm (T $\sim$ 200 K) and diffuse (n $\sim$ 50 cm^{-3}) hydrogen gas with a volume-filling factor f $\sim$ 2/3 and atomic and molecular hydrogen number densities are comparable. The cosmic ray H_2 ionization rate, $\zeta \sim 2 \times 10^{-14}$ s^{-1}, is 1000 times higher than in the solar vicinity suggesting stray magnetic field of $\sim$ 100 μG in the CMZ if equipartition between cosmic rays and magnetic field is assumed. The X-ray-emitting ultra-hot (10^8 K) plasma, which some thought to dominate the CMZ, does not exist.

II. Expansion and Morphology of the Warm Diffuse Gas[b]: The wide velocity profiles of H_3^+ lines have allowed us to draw longitude-velocity diagrams toward 18 stars. They indicated that the diffuse molecular gas is expanding with a front speed of $\sim$ 150 km s^{-1}. This revives the Expanding Molecular Ring proposed by Kaifu et al. and Scoville in 1972 but there are three differences: (1) the expanding gas is diffuse, (2) the expansion is radial, and (3) the gas fills the CMZ. This revives the circular geometry of the CMZ, as viewed face-on. The elliptic structure with high eccentricity is negated.

III. Locations of Sgr B2 and Star Iota[c]: The radial motion of the diffuse gas allows us to determine radial location of a star from velocity profiles of H_3^+ or other molecules. Star ι, which has a strong H_3^+ absorption spectrum and is at galactic longitude 0°.5476 , is close to Sgr B2 (at 0°.6667). Using velocity profiles of H_3^+ lines toward Star ι and of H_2O^+, OH^+, and $^{13}CH^+$ spectra toward Sgr B2 observed by HIFI on the Herschel Space Observatory, we find that both Star ι and Sgr B2 are $\sim$ 90 pc behind the GC's central black hole, Sgr A*. This contradicts the previous conclusion based on trigonometric parallax, which placed Sgr B2 130 $\pm$ 60 pc in front of Sgr A*, as well as most models of the CMZ.

[a] Oka, T., Geballe, T.R., Goto, M., Usuda, T., McCall, B.J., Indriolo, N. 2019, ApJ. 883, 54 (31pp)
[b] Oka, T., Geballe, T.R. 2020, ApJ. 902, 9 (17pp)
[c] Oka, T., Geballe, T.R. 2022, ApJ. 927, 97 (8pp)

WC07 **10:55 – 11:10**

MILLIMETER/SUBMILLIMETER SPECTRUM AND INTERSTELLAR SEARCH FOR SINGLY DEUTERATED METHYL MERCAPTAN, CH_2DSH

HAYLEY A. BUNN, SILVIA SPEZZANO, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*; L. H. COUDERT, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, Orsay, France*; CHRISTIAN ENDRES, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*; J.-C. GUILLEMIN, *UMR 6226 CNRS - ENSCR, Institut des Sciences Chimiques de Rennes, Rennes, France*; VALERIO LATTANZI, PAOLA CASELLI, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*.

Methyl mercaptan, CH_3SH, has been detected in the interstellar medium (ISM) with abundances that make detection of minor isotopic species, like the deuterated isotopologues, plausible (e.g.[a]). Isotopologue abundance ratios are pivotal for tracing the origin and evolution of the molecular material in the process of star and planet formation. The search for deuterated isotopologues of CH_3SH, however, is limited by the lack of spectroscopy on these molecules. The microwave spectra of CH_2DSH and CHD_2SH have been reported, but provides insufficient rotational information for extension up to higher frequencies needed for astronomical observation[b,c]. Therefore, additional spectral information is required for their interstellar identification. We have recently collected the millimetre spectrum of CH_2DSH from 70 and 500 GHz to provide the necessary spectral information for its detection in the ISM. The analysis of this spectrum, however, is complicated by the hindered torsional rotation of the CH_2D group. The torsional potential resulting from this internal motion has three minima corresponding to three different substates, two *gauche* (e_0 and o_1) and one *anti* (e_1). We have, so far, identified and assigned about 800 transitions including the dominant *a*-type R branch band structure of all three substates, the weaker *b*-type Q branch transitions as well as transitions between the torsional substates. We will present on the spectral analysis of CH_2DSH as well as the results of our first search towards low-mass star-forming regions.

[a] Drozdovskaya, M. N., *et al.*, MNRAS, 476, 4 (2018)
[b] Su, C. F., and Quade, C. R., JCP, 79, 5828, (1983)
[c] Su, C. F., Liu, M. J., and Quade, C. R., JMS, 158, 21 (1993)

WC08 **11:13 – 11:28**

LABORATORY INVESTIGATION OF CARBON-SULFUR SPECIES FOR ASTROCHEMISTRY

VALERIO LATTANZI, CHRISTIAN ENDRES, MITSUNORI ARAKI, DAVIDE ALBERTON, PAOLA CASELLI, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*.

Carbon-Sulfur species represent a good fraction of the chemical content of interstellar gas and dust. The electronic properties of these compounds generate peculiar molecular structure and chemical reactivity. Detected C-S molecules in space span from the simplest diatomic carbon monosulfide to long carbon chain (e.g. C_5S[a]) and complex organic (e.g. CH_3CH_2SH[b]). Sulfur chemistry is also particularly interesting due to the still puzzling "missing sulfur" behaviour away from diffuse interstellar regions[c].
In this talk we review some of the current projects undergoing in our laboratories, involving the characterisation of rotational spectra of carbon-sulfur species. Techniques adopted for our study, and here briefly reviewed, comprise absorption spectroscopy in cells and in microwave/millimeter supersonic jet, chirped-pulse broadband and frequency modulation spectroscopy.

[a] Cernicharo, J. et al. A&A 648, L3 (2021)
[b] Kolesniková L. et al. ApJ 784, L7,(2014)
[c] Laas J.C. and Caselli P. A&A 624, A108 (2019)

WC09 **11:31 – 11:46**

EFFECTS OF STAR FORMATION ON BOUNDEDNESS IN LMC CLOUDS

ALEX GREEN, *Department of Astronomy, University of Illinois Urbana-Champaign, Urbana, IL, USA*; TONY WONG, *Department of Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; RÉMY INDEBETOUW, *Department of Astronomy, University of Virginia, Charlottesville, VA, USA*; OMNARAYANI NAYAK, *Space Telescope Science Institute, Baltimore, MD, USA*; ALBERTO BOLATTO, ELIZABETH TARANTINO, *Department of Astronomy, University of Maryland, College Park, MD, USA*; MÓNICA RUBIO, *Departamento de Astronomía, Universidad de Chile, Santiago, Chile*; SUZANNE C MADDEN, *Département d'Astrophysique, Université Paris-Saclay, Gif-sur-Yvette, France*.

To investigate the effects of stellar feedback on the gravitational state of giant molecular clouds, we study ALMA maps of nine molecular clouds distributed throughout the Large Magellanic Cloud (LMC), the nearest star-forming galaxy to our own. Each cloud has been observed in both CO and ^{13}CO, enabling analysis based on assuming LTE conditions. We trace molecular hydrogen mass using the J=1-0 transitions for five of the clouds and J=2-1 for the other four. We perform noise and resolution matching on the sample, with a common resolution of 3.5 arcseconds (0.9 pc at the LMC distance of 50 kpc), and use the *SCIMES* clustering algorithm to identify discrete substructure, or "clumps." We supplement these data with tracers of recent star formation, such as resolution-matched Spitzer IRAC 8μm maps. The CO (^{13}CO) clumps identified cover a range of 4.4 (2.6) dex in luminosity-based mass and 2.3 dex in average 8μm surface brightness. The excess linewidth relative to the best-fit size-linewidth relation is well-correlated to the average 8μm flux in a clump, suggesting that the combined effects of radiative feedback and turbulence driven on large scales can explain the local energy injection observed at the clump scales. The magnitude of the excess linewidths we measure does not appear to result from opacity broadening. Further multi-line analysis may better constrain the assumptions made in these calculations.

WC10 **11:49 – 12:04**

PHOSPHORUS AT THE EDGE OF THE GALAXY: DETECTION OF PO AND PN BEYOND 16 kPC

LILIA KOELEMAY, *Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA*; KATHERINE R. GOLD, *Department of Chemistry and Biochemistry, The University of Arizona, Tucson, AZ, USA*; LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

The Galactic Habitable Zone (GHZ) is characterized by orbital kinematics, star formation rates, lack of SN explosions, time, metallicity, and, specifically, the NCHOPS elements – those required for life. Recently, molecules containing all the NCHOPS elements have been identified in dense clouds located in the Outer Galaxy (>16 kpc from the Galactic Center), with the exception of phosphorus. Because this element is integral for biological chemistry, a search was conducted for P-bearing molecules in dense clouds in the Outer Galaxy using the 12 m telescope of the Arizona Radio Observatory (ARO) at 2 mm in wavelength and the 30 m telescope of the Institut de radioastronomie millimétrique (IRAM) at 3mm. The J=2→1 and J=3→2 rotational transitions of PN were detected in WB89-621, located 22.6 kpc from the Galactic Center, as well as four hyperfine components of the J=2.5→1.5 of PO. The fractional abundance, relative to H_2, of PN was determined to be 3.0($\pm$1.6) $\times 10^{-12}$, and that of PO to be 2.0($\pm$1.1)$\times 10^{-11}$. The identification of PN and PO at the edge of the Galaxy represents the furthest detection of phosphorus from the Galactic Center. All the NCHOPS elements have now been confirmed in out to $\sim$ 20 kpc, possibly extending the GHZ to the outer regions of the Galaxy.

WD. Instrument/Technique Demonstration

Wednesday, June 21, 2023 – 8:30 AM

Room: 217 Noyes Laboratory

Chair: Peter Chen, Spelman College, Atlanta, GA, USA

WD01 **8:30 – 8:45**

TOWARDS MULTIPLEXED SPECTROSCOPY IN AN ION TRAP: SELECTIVE MASS ELIMINATION USING SQUARE DIPOLAR RESONANT EXCITATION

GRACE CAPEK, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

Traditional instrumentation for cryogenic ion vibrational spectroscopy (CIVS) employs reflectron-time-of-flight (Re-TOF) mass analyzers which can only monitor the photodissociation of one m/z species at a time. The use of a linear quadrupole ion trap (LQIT) as a mass analyzer would allow for multiplexed spectroscopy experiments, however, it would also require selective mass filtration of multiple parent ions of "tagged" species in a mass range before spectroscopic analysis. Here we present a method for performing this selective m/z elimination using a novel digitally produced square auxiliary waveform with a home-built digital ion trap mass spectrometer being developed for CIVS experiments.

Digital Ion Technology (DIT) is an alternate method for quadrupolar mass filtering and ion trapping in which the variable amplitude, fixed frequency sine waves are replaced with variable frequency, fixed amplitude rectangular waveforms. Facile production of square waveforms is possible with modern Direct Digital Synthesis circuitry and MOSFET based high-voltage switches. Mass analysis is performed in a digital LQIT by mass-selective radial ejection of ions by scanning the applied frequency or duty cycle. The addition of the digital auxiliary waveform described here as a dipolar signal enables us to resonantly excite an ion by its m/z-dependent secular frequency of motion. This allows for selective elimination of untagged or unwanted species before mass analysis, and excitation of ions during ejection for improved mass resolution and instrument performance.

WD02 **8:48 – 9:03**

X-FAST: A NEW XUV FEMTOSECOND ABSORPTION SPECTROSCOPY TABLETOP INSTRUMENT AT UW-MADISON

ZAIN ABHARI, *Physics, University of Wisconsin-Madison, Madison, WI, USA*.

Core-level spectroscopies enable element specific measurements of electronic and vibrational dynamics on the femtosecond timescale. Advancements in the generation of XUV light through high harmonic generation (HHG) has opened the door to doing such measurements in-house; we are currently in the commissioning phase of the X-FAST instrument at the University of Wisconsin - Madison. Here, we describe the instrument and show the initial capabilities and studies carried out using the X-FAST instrument.

The instrument is comprised of two paths, an optical pump in air and an XUV probe in vacuum. We used this system to carry out two preliminary experiments: a study of the kinetics and dynamics of transition-metal perovskite oxides, and a collection of static transient absorption spectra of a metallic shape-memory alloy, Ni_2MnGa.

WD03 **9:06 – 9:21**

TABLE-TOP TIME-RESOLVED X-RAY SPECTROSCOPY USING A LASER PLASMA X-RAY SOURCE AND TRANSITION-EDGE SENSORS

NATHAN NAKAMURA, LUIS MIAJA-AVILA, GALEN C O'NEIL, DANIEL SWETZ, JOEL N ULLOM, *Physical Measurement Laboratory, National Institute of Standards and Technology, Boulder, CO, USA*.

We present a table-top instrument capable of ultrafast time-resolved x-ray absorption spectroscopy (TR-XAS) and emission spectroscopy (TR-XES). A laser plasma source provides better than 6 ps time resolution, while superconducting transition-edge sensor (TES) microcalorimeters are used for efficient, broadband, high-energy resolution x-ray detection. With TR-XAS, we have studied the photoreduction of ferrioxalate, supporting a framework in which the reduction of the central ion is complete within 100 ps and contradicting a theory in which the photoreduction occurs on much longer timescales. With TR-XES, we have studied spin cross-over in photoexcited iron tris-bipyridine and accurately measured the lifetime of the quintet state from simultaneous observation of Kα and Kβ features. The x-ray source and detector are currently being upgrading to enable new capabilities and probe chemical dynamics with increased time and energy resolution. Upgrades to the laser plasma source will result in a 10-40x improvement in the x-ray flux and time resolution on the order of 100s of fs. The energy resolving TES microcalorimeter will also be upgraded to achieve a 2x improvement in the energy resolution. The end result will be a laboratory tool capable of ultrafast time-resolved x-ray spectroscopy, with time resolution previously achievable only at free electron lasers.

WD04 **9:24 – 9:39**

OBSERVING TRANSIENT MAGNETIC OXIDATION STATES WITH MAGNETIC CIRCULAR DICHROISM SPECTROSCOPY

HARSHAD GAJAPATHY, *Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; SAVINI SANDUNIKA BANDARANAYAKE, EMILY B HRUSKA, STEPHEN LONDO, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; MARTIN SCHULTZE, *Institute of Experimental Physics, Graz University of Technology, Graz, Austria*; ROBERT BAKER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*.

Electron transfer induced by the optical pumping of systems leads to the formation of transient species that can be observed by time-resolved optical spectroscopy. However traditional linear spectroscopy cannot detect the formation of transient magnetic species formed by spin-polarized pump excitation of electrons. These transient magnetic species can be long-lived and have a wide variety of applications in spintronics and photocatalysis.

In this talk, we utilize time-resolved XUV magnetic circular dichroism spectroscopy to detect transient magnetic states in Yttrium Iron Garnet ($Y_3Fe_5O_{12}$, YIG). This method provides direct observation of electron dynamics at the surfaces with element and spin state resolution. YIG is a ferrimagnetic semiconductor with two different lattices of tetrahedral and octahedral Fe(III) atoms with opposite spins. The measurements on YIG show lattice-dependent electron dynamics upon photoexcitation. When excited above the bandgap, a charge transfer occurs from oxygen to iron atoms. Depending on the lattice of iron where the electron is excited, the dynamics of these charge transfer electron varies. The electrons in the octahedral iron form a small polaron at the surface. The tetrahedral electrons are more mobile and diffuse from surface to bulk forming a natural spin filter. This filtering of spin depending on the lattice causes the surface to be spin-polarized. This spin-polarized electron localizes in the oxygen and octahedral iron atoms on the surface due to exchange interaction and can be observed with XUV-MCD Spectroscopy.

WD05 **9:42 – 9:57**

THE DESIGN AND CONSTRUCTION OF A MASS-SELECTED ION-MOLECULE CLUSTER BEAM APPARATUS FOR PHOTO-FRAGMENT SPECTROSCOPY.

XIAOJUN WANG, MAHMUDUL HASAN, LIN FAN, YIBO WANG, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; HUI LI, *Department of Chemistry, University of Nebraska - Lincoln, Lincoln, NE, USA*; DANIEL S. SLAUGHTER, *Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*; MARTIN CENTURION, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*.

Cluster research offers doorways to establish connections between the macroscopic features of solutions- and condensed phase materials and the properties of their microscopic constituents. Apart from studying the solvation of diverse molecules and the properties of solvated electrons, clusters have also been employed to explore the mechanisms of intra-cluster charge transfer processes. In electron attachment processes, upon photoexcitation of the cluster or ion-molecule complex, the excess electron in ion can be transferred to the molecule. Numerous previous studies have shown that I^- is a proficient intra-cluster donor.

Here, a new apparatus for ultrafast photofragmentation studies is described for investigating the charge transfer process and subsequently detecting the fragments from the photoexcitation of iodide-molecule clusters. Ions and ion-clusters are produced by perpendicularly oriented pulsed gas jet and continuous electron beam, accelerated and separated by a time-of-flight mass spectrometer, and then size-selected (iodide-molecule clusters) by a mass filter. The iodide molecule clusters are focused into the interaction region and are excited by UV laser pulse propagating perpendicularly. A linear-plus-quadratic (LPQ) reflectron capable of operating over a large voltage range is used to reverse the trajectories of the anions and mass-resolve the anion fragments and parent anion. The instrument can detect both charged and neutral fragments simultaneously.

To test the performance of the instrument, $CF_3I.I^-$ is photoexcited by 266 nm UV laser pulse. Anion fragments I^- and CF_3I^- are detected and identified with neutral fragments. Detection of CF_3I^- provides evidence of the charge transfer inside the $CF_3I.I^-$ cluster when it is excited by 4.66 eV photons and implies the existence of charge-transfer excited state of $CF_3I.I^-$.

WD06 **10:00 – 10:15**

BENCHMARKING APPARATUS FOR PRODUCTION OF PROTONATED SPECIES

JONATHAN REBELSKY, HAOCHENG LIANG, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

Molecular ions and radicals are important in astrochemical processes, but difficult to study in the lab. This talk will present benchmarking experiments on the production of protonated species of astrochemical relevance in the interstellar medium. We will be presenting on two apparatus. The first of these is a hollow cathode based on the designs of Amano and coworkers. Here, the precursor species and hydrogen are flowed through a plasma discharge to produce protonated species. In the other, hydrogen is converted to H_3^+ and then combined with the precursor gas. In both of these experiments, we use a long path length to increase absorbance, increasing the signal-to-noise ratio of the spectra.

Intermission

WD07 **10:55 – 11:10**

DEVELOPMENT OF AN OPTICAL FEEDBACK-CAVITY RING DOWN SPECTROMETER AT 8.5 μm. APPLICATION TO THE SELF CONTINUUM OF WATER VAPOR.

QUENTIN FOURNIER, SAMIR KASSI, ALAIN CAMPARGUE, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*; ROBERT GEORGES, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*.

The effective atmospheric absorption of the earth atmosphere within its 10 μm transparency window is crucial for radiative transfer calculations. The contribution of the water continuum in this region is still under discussion. The proposal of an updated value at 1184 cm^{-1}should increase the accuracy of the semi-empirical MTCKD model, which is incorporated in radiative transfer codes. For this purpose, we used a newly developed spectrometer combining a quantum cascade laser (QCL) with a high finesse linear cavity, working around 8.45 μm. This setup takes benefit of optical feedback from an optical cavity and constitutes a Optical-Feedback-Cavity Ring Down Spectrometer (OF-CRDS). We will present the behavior of the laser in such a configuration and demonstrate the sharpening of the QCL emission profile under optical feedback from a TEM_{00} resonant mode of a linear cavity. Absorption spectra are measured using the CRDS method, and reach a sensitivity of 10^{-8} cm^{-1}per ring down event. Long-term performance will be presented. The spectral resolution, governed by the free spectral range of the optical resonator, is about 300 MHz. The spectra are obtained by adjusting the temperature of the QCL. Some already known water absorption lines were identified in the spectra, from 1183 $\mathrm{cm}^{-1}$and 1186 cm^{-1}, and used for calibration. The broadband absorption of the water self-continuum is evaluated and will be compared to the literature.
Acknowledgements: ANR FULLDIBS for financial support

WD08 **11:13 – 11:28**

TOROIDAL ABSORPTON CELL WITH MULTI-LAYER PATTERNS BY A SINGLE RING SURFACE

CHUANLIANG LI, *Department of Physics, School of Applied Science, Taiyuan University of Science and Technology, Taiyuan, Shanxi, China*.

We developed a type of toroidal multi-pass cell with multilayer patterns based on the off-axis model. The effective path length of the original toroidal multi-pass cell is extended several roundtrips in comparison with the single-layer pattern, since the inner surface of the toroidal multi-pass cell is more efficiently utilized. The light pattern has been achieved by using the simple ring surface, which is easy to fabricate. The exact analytical equations for the design of the toroidal multi-pass cell were derived based on analytical vector calculations. A homemade electronic system was designed for implementing a DFB diode laser controller, an analog lock-in amplifier, data acquisition, and communication. Calibration-free scanned wavelength modulation spectroscopy was employed to determine the concentration of the gas and reduce the random fluctuations from electronical noise and mechanical vibration. The measurement of CH4 in ambient air was demonstrated using a DFB laser at 1.653 μm. The rise time and fall time for renewing the gas mixture are approximately 16 and 14 s, respectively. Vibration and temperature tests have been carried out for verifying the performance of the spectrometer, and standard deviations of 0.38 ppm and 0.11 ppm for 20 ppm CH4 at different vibration frequencies and temperatures, respectively, have been determined. According to the Allan deviation analysis, the minimum detection limit for CH4 can reach 22 ppb at an integration time of 57.8 s.

WD09 **11:31 – 11:46**

UTILIZING FPGA TECHNOLOGY FOR REAL-TIME SPECTROSCOPIC ANALYSIS IN CAVITY RING-DOWN COMB SPECTROSCOPY WITH MACHINE LEARNING-ASSISTED COMB LINE ALIGNMENT

YI-JAN HUANG, *Department of Photonics, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; CHARLES R. MARKUS, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; LUKASZ A. STERCZEWSKI, *Instruments Division, Jet Propulsion Laboratory/Caltech, Pasadena, CA, USA*; DOUGLAS OBER, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; CHADWICK L CANEDY, IGOR VURGAFTMAN, *Optical Sciences, U.S. Naval Research Laboratory, Washington, DC, USA*; CLIFFORD FREZ, *Instruments Division, Jet Propulsion Laboratory/Caltech, Pasadena, CA, USA*; JERRY R MEYER, *Optical Sciences, U.S. Naval Research Laboratory, Washington, DC, USA*; MAHMOOD BAGHERI, *Instruments Division, Jet Propulsion Laboratory/Caltech, Pasadena, CA, USA*; MITCHIO OKUMURA, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; TZU-LING CHEN, *Department of Photonics, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.

In this work, we propose a novel approach for spectroscopic analysis in Cavity Ring-Down Comb Vernier Spectroscopy (CRDCVS) by exploiting FPGA architecture and an Arm-based embedded Linux system. This approach takes advantage of the high-speed data processing and acquisition capabilities of FPGA. In the Vernier configuration, a mode-resolved comb spectrum should align non-equidistant comb peaks in different scans and fitting the ring down time for each comb line. Especially a significant challenge in spectroscopic analysis is presented when the sample accumulation is required for improved sensitivity or temporal resolution. To address this challenge, we developed a machine-learning framework to predict comb line appearance in the operating platform. This enables ring-down-time accumulation for different comb peaks in CRDCVS. We demonstrated the proof-of-principle performance of the developed system with CRDCS measurements of toluene using a 3.3um chip-scale Interband Cascade Laser (ICL) comb. We will discuss the overall performance and the potential to advance the field of CRDCVS by improving measurement accuracy and reliability.

WD10 **11:49 – 12:04**

N_2O AS AN O(^{1}D) SOURCE FOR GAS PHASE STUDY OF COMS

COLTON MOORE, HAYLEY A. BUNN, CHASE P SCHULTZ, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

Gas phase O(^{1}D) insertion reactions are a useful laboratory tool for the spectroscopic study of transient species that are believed to exist in extreme environments, such as star-forming regions of the interstellar medium. One of the most common and efficient methods of O(^{1}D) production is the photolysis of ozone (O_3) at 248 nm. However, previous studies in our group have revealed that numerous side products are generated because of the high reactivity of O_3 and $O_2(^1\Delta)$. Here we present modelling that demonstrates the feasibility of N_2O as an alternative to O_3 as an O(^{1}D) precursor. Using the Framework for 0-Dimensional Atmospheric Modelling (F0AM), we show that the number of unwanted side products should be reduced owing to the absence of O_3 and $O_2(^1\Delta)$. Additionally, we present initial laboratory experiments utilizing N_2O as an O(^{1}D) precursor to produce CH_3OH from CH_4 via O(^{1}D) insertion.

WD11 ***Post-Deadline Abstract*** **12:25 – 12:40**

MEASUREMENTS OF VIBRATIONALLY EXCITED OXYGEN MOLECULES IN PREHEATED O_2-Ar MIXTURES EXCITED BY A NANOSECOND PULSE DISCHAGE

KEEGAN ORR, DIRK VAN DEN BEKEROM, *Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA*; IOLE ARMENISE, FABRIZIO ESPOSITO, *Istituto per la Scienza e Tecnologia dei Plasmi, Consiglio Nazionale delle Ricerche, Bari, Italy*; IGOR V. ADAMOVICH, *Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA*.

Kinetics of O_2 vibrational excitation is studied during the O atom recombination in an O_2-Ar mixture partially dissociated by a burst of ns discharge pulses in a heated flow reactor at T=400-800 K and P=200-600 Torr. Time-resolved vibrational level populations of molecular oxygen in the ground electronic state, O_2(v=8-13,17-20), are measured by ps Laser Induced Fluorescence on the O_2 Schumann Runge bands, with absolute calibration by NO LIF in a NO-N_2 mixture with a known composition, at quenching-free conditions. O atom number density in the same mixture is measured by ps Two-Photon absorption LIF (TALIF). The discharge generates a diffuse volumetric plasma, without well-pronounced filaments. The results indicate a rapid initial decay of the O_2(X,v=8-20) molecules generated by electron impact in the discharge, on 20 μs time scale, due to the V-V exchange and V-T relaxation. This decay is followed by a much slower decay, on the time scale much longer compared to the characteristic time for V-V relaxation, 1 ms. This indicates an additional process of O_2(v) generation by chemical reactions initiated by the O atom recombination and possibly ozone chemistry. Comparison of the experimental data with the master equation kinetic modeling predictions is used to infer the state-specific rates of chemical reactions generating vibrationally excited O_2.

WE. Rotational structure/frequencies

Wednesday, June 21, 2023 – 8:30 AM

Room: B102 Chemical and Life Sciences

Chair: Wei Lin, The University of Texas Rio Grande Valley, Brownsville, TX, USA

WE01 **8:30 – 8:45**

COMPUTATIONAL STUDIES OF NONADIABATIC ALIGNMENT OF ASYMMETRIC TOP MOLECULES

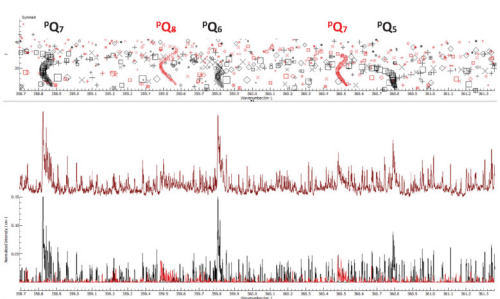
HAORAN ZHAO, MARTIN CENTURION, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*.

We numerically simulated rotational wavepacket dynamics in asymmetric top molecules. The molecules are aligned impulsively using a short, intense linearly-polarized laser pulse. The alignment of molecules is important for capturing dynamics in the molecular frame and for molecular imaging. The alignment process is challenging to simulate because of the large number of initial rotational states involved. The alignment is simulated under the rigid-rotor assumption and field-free conditions. The evolution of the degree of alignment and angular distributions of 4-fluorobenzotrifluoride (FC6H4CF3) are calculated and the numerical results show good agreement with the experimental results.

WE02 **8:48 – 9:03**

NEW ANALYSIS OF THE ν_9 REGION OF 2,2-D_2-PROPANE FROM CLS HIGH RESOLUTION SPECTRA. FUNDAMENTAL AND HOT BAND SPECTRA. MORE ACCURATE CONSTANTS DETERMINED

STEPHEN J. DAUNT, ROBERT GRZYWACZ, *Department of Physics & Astronomy, The University of Tennessee-Knoxville, Knoxville, TN, USA*; COLIN WESTERN[a], *School of Chemistry, University of Bristol, Bristol, United Kingdom*; DANIEL GJURAJ, *Department of Physics, Iona College, New Rochelle, NY, USA*; BRANT E. BILLINGHURST, JIANBAO ZHAO, *Materials and Chemical Sciences Division, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada*; JEAN-MARIE FLAUD, *LISA, CNRS, Universités Paris Est Créteil et Paris Diderot, Créteil, France*; WALTER LAFFERTY[b], *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*.



We have now extended line assignments to higher J and K_a values in both low and higher pressure scans for 2,2-D_2-Propane spectra recorded on the CLS FT-IR beamline. We reported abbreviated results for only the fundamental ν_9 band at the 2018 ISMS meeting[c]. Now we have assigned many more transitions for both lower and higher pressure spectra to obtain higher J and K_a values. This has been done for both the fundamental ν_9 band as well as the intertwined $2\nu_9$-ν_9 hot band. Much more accurate ro-vibrational constants have been determined for the GS, v_9=1 and v_9=2 states. A very good reproduction of the spectra have been produced using the PGOPHER program[d]. Average error of 0.00012 $\mathrm{cm}^{-1}$for ν_9 and 0.00022 $\mathrm{cm}^{-1}$for the hot band transition. In the PGOPHER Figure at left ν_9 lines are in black and hot band lines are in red.

[a]Deceased Sept. 21, 2021
[b]Deceased Dec. 21, 2018
[c]2018 ISMS Paper WH11
[d]C.M.Western and B.E. Billinghurst, PCCP 21 (2019) 13986

WE03 **9:06 – 9:21**

O(^{1}D) INSERTION REACTION FOR THE FORMATION AND SPECTRAL ANALYSIS OF CARBONIC ACID

CHASE P SCHULTZ, COLTON MOORE, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

The first excited singlet state of atomic oxygen (O(^{1}D)) has relevance in numerous disciplines of chemistry including combustion chemistry, astrochemistry, and atmospheric chemistry. O(^{1}D) is known to react via highly exothermic insertion mechanisms with X-H bonds, where X is H, C, N, or O. Our lab uses these reactions to generate unstable prebiotic molecules and study them in the gas phase using a supersonic expansion and rotational spectroscopy. This technique has been benchmarked by producing and detecting methanol from O(^{1}D) insertion into methane, and vinyl alcohol from O(^{1}D) insertion into ethylene. We now wish to apply this approach to the production of prebiotic molecules of astrochemical interest. We present here our efforts to investigate the reaction between formic acid (HCOOH) and O(^{1}D) to produce carbonic acid (H_2CO_3).

WE04 **9:24 – 9:39**

EXPLORING THE PROPERTIES AND REACTIVITY OF CARBONYL DIISOTHIOCYANATE WITH ROTATIONAL SPECTROSCOPY

EVA GOUGOULA, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; FRANK TAMBORNINO, *Fachbereich Chemie, Philipps-Universitaet Marburg, Marburg, Germany*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Accessing simple molecules is crucial to our understanding of chemical reactivity. Particularly, characterization of heavier homologues of molecules essential to life, *e.g.*, carbonic acid and urea, can lead to new insights. Synthetic routes to such compounds, followed by exploration of their reactivity, could not only deepen our knowledge of synthetic chemistry, but also create the basis for novel applications and new research fields. It is known that the reactivity and properties of a compound are a function of its structure. Subsequently, exploring molecular structure in an isolated environment in the absence of lattice and solvent effects is key to our understanding of the structure *vs* properties relationship.

Carbonyl diisothiocyanate (CDIT), $C_3N_2O_2S_2$, a highly unstable and reactive compound, was first synthesized in 1902.[1] It recently has been characterized in the condensed phase,[2] however, to the best of our knowledge, this is the first study addressing its properties in the gas phase. The rotational spectra of two isomers of CDIT, *syn-syn* and *syn-anti*, were recorded with Chirped Pulse Fourier Transform Microwave (CP-FTMW). Presence of two quadrupolar nuclei (N, I=1) results in hyperfine splitting of rotational transitions, which is analyzed and provides a direct insight into the electronic environment of the molecule. Detection of ^{13}C, ^{34}S, ^{15}N and ^{18}O isotopologues in their natural isotopic abundances allowed for structure determination of the most abundant *syn-syn* isomer in the gas phase. The gas phase structure is compared to the previously determined crystal structure and demonstrates a high level of consistency. Spectral analysis is guided by quantum chemical calculations and CDIT, owing to the isothiocyanate substituents, makes an interesting case for theoretical benchmarking.

[1] Dixon, A. E., *Proc. Chem. Soc., London*, 1902, 18 (257), 235

[2] Pfeiffer, J.; Trost, C.; Pachkovska, A.; and Tambornino, F.; *Inorg. Chem*, 2021, 60 (14) 10722–10728

Intermission

WE05 **10:19 – 10:34**

ROTATIONAL SPECTROSCOPY OF FLUORONAPHTHALENES: THE MODEL STUDY OF HALOGENATED NAPHTHALENES

SATHAPANA CHAWANANON, PIERRE ASSELIN, *CNRS, De la Molécule aux Nano-Objets: Réactivité, Interactions, Spectroscopies, MONARIS, Sorbonne Université , PARIS, France*; MARIE-ALINE MARTIN-DRUMEL, OLIVIER PIRALI, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*.

The presence of a fluorine atom in fluoronaphthalenes ($C_{10}H_7F$) induces both mesomeric and inductive effects. The mesomeric effect results in electron redistribution, making particular carbon atoms susceptible to undergo nucleophilic attack at meta-position and electrophilic attack around ortho- and para- positions, while the inductive effect creates a polar bond that affects the polarity and the stability of the molecule and makes the para-position pre-dominant for the electrophilic attack. By studying the rotational structure in both the ground and excited vibrationally states, the higher order terms of rotational constants inform on molecular distorsion relatively to the equilibrium structure from a reference frame in the molecular rotation model. Furthermore, the Coriolis or rotation-vibration terms which involve both the time variation of molecular displacement and the angular velocity of the frame can be characterized to demonstrate the influence of fluorine group on the variation of molecular flexibility in vibrational states.

Our present study reports the rotational spectroscopic measurements of 1- and 2-fluoronaphthalene in the millimeter-wave spectral region using both a chirped-pulse instrument (75-110 GHz) and a frequency multiplication chain-based spectrometer (140-220 GHz). By combining newly recorded transitions of fluoronaphthalenes with existing literature data[a], a refined set of spectroscopic parameters is derived for each species both in the ground and excited vibrational states up to 300 cm^{-1}. This study could serve as a valuable database for future investigations about the role of halogen groups in aromaticity.

[a] Carey, S. J., Sun, M., & Kukolich, S. G. (2014). Microwave spectra of 1-fluoronaphthalene and 2-fluoronaphthalene. Journal of Molecular Spectroscopy, 304, 25-27.

WE06 **10:37 – 10:52**

ROTATIONAL SPECTROSCOPY OF 2- AND 4-CYANOBIPHENYL

BETTINA HEYNE, MARIYAM FATIMA, LISE VON RÖTEL, SVEN THORWIRTH, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

The class of polycylic aromatic hydrocarbons (PAHs) presents an important motif in building the chemical environment of the interstellar medium. Around 10 to 25% of all interstellar carbon is thought to be locked up as PAHs. Recently benzonitrile[a] as well as 1- and 2- cyanonapthalene ($C_{10}H_7CN$), have been identified in radio observations of TMC-1[b] based on their laboratory rotational spectra. The detection of these molecules raises possibilities for the presence/formation of other cyano-aromatic molecules in the interstellar medium.

In this work, we present chirped-pulse Fourier transform microwave (CP-FTMW) spectra of 2- and 4-cyanobiphenyl (CBP) [$C_{12}H_9CN$], that are cyano-aromatic molecules. They are measured in the frequency range from 11.5 to 27 GHz. The Cologne CP-FTMW instrument has been designed to achieve high stability and sensitivity, which made it possible to measure the ^{13}C isotopologs in natural abundance. In a recent modification to the instrument, we are using state-of-the-art RF modulation and detection technology to directly generate and receive signals in this frequency range, thus abandoning the up- and down-mixing processes of our previous chirped-pulse microwave spectrometer setup[c]. As a result, the tedious side-band separation is no longer needed. Moreover, the number of elements influencing the intensities is reduced to a minimum. The setup and the results of the CBP measurements will be presented.

[a] B. A. McGuire et al., *Science* **359** (2018) 202–205.
[b] B. A. McGuire et al., *Science* **371** (2021) 1265–1269.
[c] M. Hermanns et al., *Journal of Molecular Spectroscopy* **358** (2019) 25-36.

WE07 **10:55 – 11:10**

THE 235–500 GHZ ROTATIONAL SPECTRUM OF 1-CYANO-2-METHYLENECYCLOPROPANE (C_5H_5N)

DAIREN R JEAN, SAMUEL A. WOOD, SAMUEL M. KOUGIAS, BRIAN J. ESSELMAN, R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

The gas-phase rotational spectrum of 1-cyano-2-methylencyclopropane (C_1, C_5H_5N), an isomer of pyridine first generated by the photoisomerization of (cyanomethylene)cyclopropane, has been synthesized by dehydration of its corresponding amide. Its rotational spectrum has been obtained from 235 GHz to 500 GHz and over 3600 a-, b-, and c-type transitions for the ground vibrational-state have been least-squares fit to partial octic, A- and S-reduced Hamiltonians with low statistical uncertainty (σ_{fit} = 42 kHz). Transitions for the two lowest-energy fundamentals (ν_{27} and ν_{26}) and the lowest energy overtone ($2\nu_{27}$) have been similarly least-squares fit to single state Hamiltonians. Many additional vibrationally excited states have been observed, which form a complex polyad of interacting states. The spectroscopic constants presented here form the foundation of future searches for 1-cyano-2-methylencyclopropane in the interstellar medium.

WE08 **11:13 – 11:28**

THE ROTATIONAL SPECTROSCOPY OF 2-FORMYLTHIOPHENE UP TO 750 GHZ IN ITS GROUND AND TWO VIBRATIONALLY EXCITED STATES

BRIAN J. ESSELMAN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; HA VINH LAM NGUYEN, *Université Paris-Est Créteil et Université de Paris, Laboratoire Interuniversitaire des systèmes atmosphériques (LISA), CNRS UMR7583, Créteil, France*; R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

The rotational spectrum of 2-formylthiophene (C_s, μ_a = 3.9 D, μ_b = 2.4 D) has been observed from 2 to 750 GHz and over 8500 transitions have been observed, measured, and least-squares fit for the ground vibrational state. The extensive frequency coverage allowed measurement of transitions up to J = 180 and K_a = 72. Spectroscopic constants have been obtained for a complete sextic distorted-rotor A- and S-reduced Hamiltonians, in the I^r representation. The first two vibrationally excited states of 2-formylthiophene are the torsional mode (ν_{27}, A$''$, 122 cm^{-1}) and the in-plane C-C-O bend (ν_{19}, A$'$, 173 cm^{-1}) of the formyl group. These two vibrationally excited states exhibit rotational transitions with frequencies perturbed by a- and b-axis Coriolis coupling despite an energy gap of nearly 50 cm^{-1}. Rotational transitions for the first two vibrationally excited states have been assigned, measured, and least-squares fit to a two-state Hamiltonian, which will provide an accurate and precise energy gap and Coriolis-coupling constants for these two modes.

WE09 **11:31 – 11:46**

ROTATIONAL AND INFRARED SPECTRA OF PYRIMIDINE: VIBRATIONAL GROUND STATE AND NINE VIBRATIONALLY EXCITED STATES

WILLIAM STYERS, BRIAN J. ESSELMAN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; ZACHARY N. HEIM, *Department of Chemistry, The University of California, Berkeley, CA, USA*; BRENT K. AMBERGER, *Department of Chemistry, University of Wisconsin, Madison, WI, USA*; BRANT E. BILLINGHURST, JIANBAO ZHAO, *Materials and Chemical Sciences Division, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada*; R. CLAUDE WOODS, *Department of Chemistry, The Univeristy of Wisconsin, Madison, WI, USA*; ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

Pyrimidine is an aromatic heterocycle in which meta C-H units of benzene are replaced by nitrogen atoms. Its detection in the ISM has been sought for decades as it is not only a building block of many biologically relevant molecules, but it could serve as a valuable tracer molecule for other aromatic and polycyclic aromatic compounds. In this work, we collected the millimeter-wave spectrum of pyrimidine from 130-750 GHz. This extended range greatly increases the range of rotational transitions we can observe in the ground and its nine lowest-energy vibrationally excited states. Over 10,000 transitions for the vibrational ground state have been least-squares fit to a A- and S-reduced sextic distorted-rotor Hamiltonians. To supplement the millimeter-wave spectrum, high-resolution infrared spectra were obtained from the Canadian Light Source and provide highly accurate and precise band origins for the vibrationally excited states. The three lowest energy fundamentals (ν_{16}, ν_{11}, and ν_{24}) have been fit to single-state Hamiltonians. The remaining vibrationally excited states presented in this work have perturbed frequencies due to Coriolis, Darling-Dennison, and Fermi coupling. The current progress toward a satisfactory treatment of these interactions will be presented.

WE10 **11:49 – 12:04**

ANALYSIS OF COMBINED MILLIMETER-WAVE AND HIGH-RESOLUTION INFRARED SPECTRA OF 2- AND 3-FURONITRILE

WILLIAM STYERS, BRIAN J. ESSELMAN, MARIA ZDANOVSKAIA, ANDREW N. OWEN, SAMUEL M. KOUGIAS, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; BRANT E. BILLINGHURST, JIANBAO ZHAO, *Materials and Chemical Sciences Division, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada*; R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

2-Furonitrile and 3-furonitrile are highly polar CN-substituted derivatives of furan. These molecules are attractive targets for interstellar search due to their strong dipole moments (μ_a = 4.3 D, μ_b = 0.7 D and μ_a = 4.0 D, μ_b = 0.4 D, respectively) and their ability to serve as tracer molecules for furan. In our recent work, we analyzed and assigned the millimeter-wave and high-resolution infrared (IR) spectra of 2- and 3-furonitrile for the first time. From 140-750 GHz and 140-500 GHz, respectively, the vibrational ground-state transitions of each molecule have been least-squares fit to partial octic, distorted-rotor Hamiltonians with each data set containing several thousand independent transitions. The two lowest-energy fundamental modes of both furonitriles are the Coriolis-coupled bending modes of the nitrile (ν_{17} and ν_{24}). High-resolution infrared spectra were obtained from the Canadian Light Source and provided the precise band origins of these modes for both furonitriles, as well as of ν_{23} for 2-furonitrile. We recently reported our work on 2-furonitrile [1] and will discuss our progress in the analysis of the ground state and first two fundamental modes of 3-furonitrile.

[1] Millimeter-Wave and High-Resolution Infrared Spectroscopy of 2-Furonitrile - A Highly Polar Substituted Furan. *J. Phys. Chem. A*, ASAP (2023)

WE11 ***Post-Deadline Abstract*** **12:07 – 12:22**

RICH CONFORMATIONAL LANDSCAPES OF MACROCYCLIC MUSKS BY BROADBAND ROTATIONAL SPECTROSCOPY: AN INSIGHT INTO THE MUSK SCENT MYSTERY

ECATERINA BUREVSCHI, DONATELLA LORU, M. EUGENIA SANZ, *Department of Chemistry, King's College London, London, United Kingdom.*

Musk odorants are key compounds in perfumery due to their warm, sensual and animalistic scent, and their fixative properties. Natural musks are macrocycles typically containing ketone or lactone functional groups. However, despite their widespread use, the molecular features conductive to musk smell are not clear. No experimental information is available on the conformations of macrocyclic musks and the structural elements determining their binding to odorant receptors. Here we present the study of several prototypical macrocyclic musks using broadband microwave spectroscopy in combination with quantum chemistry calculations. Their conformations have been identified and compared to start understanding the molecular determinants that lead to musk odour.

WF. Clusters/Complexes

Wednesday, June 21, 2023 – 8:30 AM

Room: 274 Medical Sciences Building

Chair: Cristina Puzzarini, University of Bologna, Bologna, Italy

WF01 **8:30 – 8:45**

BROADBAND ROTATIONAL SPECTROSCOPY OF CUMINOL AND ITS WATER COMPLEX

ELIAS M. NEEMAN, NOUREDDIN OSSEIRAN, THERESE R. HUET, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*.

Monoterpenoids are chemical compounds derivatives of isoprene. They are naturally produced mainly by plants and vegetations. Many of them are involved in atmospheric chemistry since they represent about 11% of the global biogenic emission, while some of them have important biological activity. Cuminol (4-isopropylbenzyl alcohol, CA), a monocyclic monoterpenoid, was found to be the main compound in Rhodiola essential oil, having a specific spicy fragrance, which emphasizes the flower scent of rose root rhizomes. It may play a role in atmospheric chemistry since it is related to the abundant atmospheric monoterpene *p*-cymene. CA is an important biological compound since it has an analgesic effect,[a] and it has been found in different medicinal plants. It is also a potent insulinotropic molecule that can enhance insulin secretion.[b] As biological activity is linked to the structure, it is important to characterize the conformational landscape in the gas phase. Using a combination of broadband rotational spectroscopy and theoretical calculations, one rotamer has been observed. Its identity has been confirmed by studying deuterated species enabling the determination of OH position and consequently been assigned to the lowest energy conformer. The interaction between CA and one water molecule has been also studied. Its spectrum showed tunneling effect. The splitting is associated with an internal dynamic of water inside the complex.

[a] M.A. Sheikholeslami, S. Ghafghazi, S. Parvardeh, S. Koohsari, S.H. Aghajani, R. Pouriran, L.A. and Vaezi, 2021. European Journal of Pharmacology, 900, p.174075.
[b] S.B. Patil, S.S. Takalikar, M.M. Joglekar, V. S. Haldavnekar, and A.U. Arvindekar, British journal of nutrition, 2013, 110, 1434-1443.

WF02 **8:48 – 9:03**

SIX-DIMENSIONAL MODEL ANALYSIS AND INTERMOLECULAR VIBRATIONAL SPECTROSCOPY OF BENZENE-METHANE vdW COMPLEX

TORU SASAKI, MASAAKI NAKAMURA, YASUHIRO OHSHIMA, *Department of Chemistry, Tokyo Institute of Technology, Tokyo, Japan*.

The benzene-methane complex is a prototypical model for CH/π interaction. The binding energy[a] and UV spectra[b] of this system have been reported and *ab initio* calculations were performed[c]. However, full dimensional (6D) intermolecular potential energy surface (IPS) has not been evaluated because of difficulties caused by high dimensionality.

In order to reconstruct a full dimensional IPS in the benzene-methane system, stimulated emission pumping and wave-packet observation pertinent to the S_0 state were carried out. The latter was performed as a pump-probe experiment combining impulsive stimulated Raman excitation by femtosecond pulses with state-selective ionization by resonant two-photon ionization. A new 6D model potential analysis was also performed. Single-point energy calculations were performed at CCSD(T)/aug-cc-pVTZ level of theory for 525 different complex configurations, and calculated results were fitted by the new model potential. Observed intermolecular bands were assigned by comparing the theoretical prediction. Deviations of the prediction from the observation are well within 3 cm^{-1}, which verifies the utility of the present IPS for benzene-methane.

[a] K. Shibasaki, A. Fujii, N. Mikami, and S. Tsuzuki, *J. Phys. Chem. A* **110**, 4397-4404 (2006).
[b] J. A. Menapace and E. R. Bernstein, *J. Phys. Chem.* **91**, 2533-2544 (1987).
[c] S. Tsuzuki, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, **108**, 69-95 (2012).

WF03 **9:06 – 9:21**

PUSHING THE SIZE LIMITS OF BROADBAND ROTATIONAL SPECTROSCOPY: THE SEVOFLURANE TRIMER

CRISTOBAL PEREZ, *Faculty of Science - Department of Physical Chemistry, University of Valladolid, Valladolid, Spain*; AMANDA STEBER, WENQIN LI, ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*; BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

The size of the attainable target systems for broadband rotational spectroscopy has been steadily increasing since its introduction in 2006. In 2013, we presented at this conference the characterization of the sevoflurane dimer. This complex represented, at that time, one of the larger systems observed through rotational spectroscopy. The collected spectrum exhibited a large dynamic range and many transitions remained unassigned. With the advent of newer, faster and more reliable conformation sampling tools like CREST and automated fitting routines such autofit and its implementation in Pgopher, we reassessed the ability of rotational spectroscopy to probe increasingly larger, heavier systems. In this talk we will present the observation of the sevoflurane trimer by chirped-pulse Fourier transform microwave spectroscopy, identified through the interplay of experimental and computational methods. The trimer (>600 Da), one of the largest molecular aggregates observed through rotational spectroscopy, showcases the potential of rotational spectroscopy to study larger biochemical systems but also uncovers the challenges ahead as the mass of the system increases. These will be presented and discussed.

WF04 **9:24 – 9:39**

INVESTIGATION OF THE 2-6GHz REGION OF THE MICROWAVE SPECTRUM FOR THE O_2-H_2O VAN DER WAALS COMPLEX

W. H. RICE IV, *Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; AMANDA DUERDEN, G. S. GRUBBS II, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.

Based on a preliminary investigation into the rotational transitions of the van der Waals complex O_2-H_2O using a chirp pulse FTMW spectrometer, the 2-6GHz region of the electromagnetic spectrum was explored for rotational transitions using a cavity FTMW instrument. Focus of the study was around the 5 GHz region as the preliminary chirp pulse FTMW spectra, theoretical calculations, and previous work[a] imply transitions are present in this region but have yet been reported. The collected spectra will be presented and discussed along with new working fits taking these rotational transition assignments into account.

[a] Kasai, Y., Dupuy, E., Saito, R., Hashimoto, K., Sabu, A., Kondo, S., Sumiyosihi, Y., & Endo, Y. (2011). The H_2O-O_2 water vapour complex in the Earth's atmosphere. Atmospheric Chemistry and Physics, 11(16), 8607-8612. https://doi.org/10.5194/acp-11-8607-2011

Intermission

WF05 **10:19 – 10:34**

CHARACTERISATION OF THE MOLECULAR GEOMETRY OF 2-ETHYLFURAN$\cdots$$H_2O$ BY MICROWAVE SPECTROSCOPY

CHARLOTTE CUMMINGS, *School of Chemistry, Newcastle University, Newcastle-upon-Tyne, United Kingdom*; NICK WALKER, *School of Natural and Environmental Sciences, Newcastle University, Newcastle-upon-Tyne, United Kingdom*.

Microwave spectroscopy is a powerful technique for the study of weakly bound complexes formed between aromatic/heteroaromatic rings and other small molecules. However, there has been limited studies of binary complexes formed between alkyl-substituted heteroaromatic rings and water. The rotational spectrum of 2-ethylfuran$\cdots$$H_2O$ was recorded while probing a gaseous mixture of 2-ethylfuran, water and an inert carrier gas (argon or neon) using Chirped Pulse Fourier Transform Microwave (CP-FTMW) spectroscopy. Microwave spectra of five isotopologues of this complex have been assigned and analysed to determine rotational constants (A_0, B_0, C_0) and centrifugal distortion constants (D_J, D_{JK}, d_1). A previous microwave spectroscopy study[a] identified two conformations (C_s and C_1) of 2-ethylfuran in a helium supersonic expansion. The C_s conformation is planar, with the ethyl group lying coplanar with the ring, while the ethyl group in the C_1 conformation is tilted out of the plane of the ring. The analysis of the molecular geometry of the monohydrate complex has revealed that the binary complex is formed with the C_1 conformation of 2-ethylfuran only and is stabilised by a primary O_W-H$\cdots$O hydrogen bond. Additionally, non-covalent interaction (NCI) and natural bond orbital (NBO) analysis have revealed the presence of additional weak interactions between the oxygen atom of the water molecule and the ethyl group. Preliminary results of 2-ethylimidazole$\cdots$$H_2O$ and 2-ethylthiazole$\cdots$$H_2O$ will also be discussed.

[a] H. V. L. Nguyen, *Journal of Molecular Structure*, 2020, **1208**, 127909.

WF06 **10:37 – 10:52**

CHIRAL RECOGNITION OF NEUTRAL ALANINE: A LASER ABLATION ROTATIONAL STUDY

RAÚL AGUADO, SANTIAGO MATA, ELENA R. ALONSO, IKER LEÓN, JOSÉ L. ALONSO, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*.

The chiral-tagging method based on rotational spectroscopy is gaining relevance for investigating chirality in the gas phase [a,b] Enantiomers of chiral molecules of interest can be complexed with a well-characterized chiral molecule of known handedness, the chiral tag. This results in the formation of diastereomeric complexes, which can be differentiated by their rotational spectra and establishes the absolute configuration of the molecule of interest. However, up to date, this methodology has been limited to molecular specimens having an appreciable vapor pressure. Thus, the study of the whole series of relevant chiral biomolecules, like amino acids, escapes from chiral-tagging studies due to its intrinsically high melting points and associated low vapor pressures.

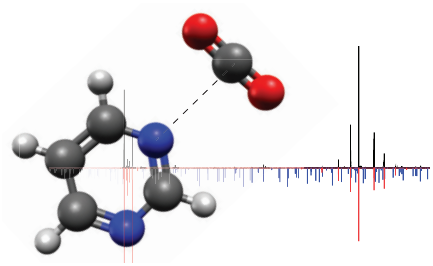
Laser ablation rotational spectroscopic techniques made the transfer of bare neutral amino acids into the gas phase possible to probe their most stable conformers in a supersonic expansion. However, severe experimental difficulties arise when they are applied to the formation of complexes due to the hot plasma created by the laser ablation process. In the last years, we have made some technical and experimental advances allowing a precise control of the experimental conditions and, therefore, of the complexation process. We report the first chiral determination of the simplest chiral proteogenic amino acid alanine. A broadband, chirped-pulse LA-CP-FTMW spectrometer has been used to perform structural characterization of the complexes formed between racemic alanine (R/S alanine) and S-propylene oxide (S-PO) as a chiral tag. The observation of two different complexes for each alanine enantiomer, characterized by their values of rotational and quadrupole coupling constants, allows the conclusive determination of the absolute configurations of R- and S- enantiomeric forms.

[a] B. H. Pate, L. Evangelisti, W. Caminati, Y. Xu, J. Thomas, D. Patterson, C. Pérez and M. Schnell, Chiral Analysis, Elsevier, 2nd edn, 2018, pp. 679–729.
[b] Sergio R. Domingos, Cristóbal Pérez, Mark D. Marshall Helen O. Leung b and Melanie Schnell, Chem. Sci., 2020, 11, 10863

WF07 **10:55 – 11:10**

ROTATIONAL SPECTROSCOPY OF THE PYRIMIDINE-CO_2 COMPLEX

BLAIR WELSH, ANGIE ZHANG, KENDREW AU, TIMOTHY S. ZWIER, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*.



The looming threat of anthropogenic climate change has driven a significant amount of research into efficient methods of capturing and storing[1] CO_2. Reversible capture mechanisms, such as those governed by weakly bound intermolecular interactions, have been a mainstay of such research.

To this end, the rotational spectrum of the pyrimidine ($C_4H_4N_2$)-CO_2 van der Waal's complex has been measured using broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy across a frequency range of 7.5 to 17.5 GHz, in an effort to investigate the viability of pyrimidine as an active site in CO_2 capture media.

A preliminary fit of the spectrum indicates a structure whereby the lone pair of one of the nitrogen atoms is directed towards the CO_2 carbon atom, with the O=C=O axis lying in the plane of the pyrimidine moiety and approximately perpendicular to a line drawn through the corresponding nitrogen atom and the pyrimidine centre-of-mass. This is analogous to the structure of the pyridine-CO_2 complex[2], and in agreement with the structures predicted by DFT calculations performed at a wB97XD/6-311++G** level of theory, as well as previously published computational studies[3]. The principal rotational constants produced by this fit are: A = 4070.9905(46) MHz, B = 859.4088(12) MHz and C = 710.01942(85) MHz.

[1] C. Yu, *et. al.*, *Aerosol Air Qual. Res.* **2012**, *12*, 745-769
[2] J. L. Doran., *et. al.*, *J. Mol. Struct.* **2012**, *1019*, 191-195
[3] K. D. Vogiatzis, *et. al.*, *ChemPhysChem* **2009**, *10*, 374-383

WF08 **11:13 – 11:28**

FIRST MONOSACCHARIDE-WATER COMPLEX CAUGHT BY MICROWAVE SPECTROSCOPY

ELENA R. ALONSO, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; ARAN INSAUSTI, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*; IKER LEÓN, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; EMILIO J. COCINERO, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*.

Carbohydrates are the main source of energy and make up the main backbone of DNA and RNA, which make them, among many biological systems, of particular interest. Furthermore, they take part in the recognition process, where has been demonstrated that water is actively involved. The role that water molecules play in glycobiology is crucial and is not yet well understood, in part, for the lack of experimental information about how water comes into play in the monosaccharide conformations. Here we present xylopyranose-water complex, first microhydrated monosaccharide studied in gas phase using the combination of laser ablation and broadband microwave spectroscopy. The revealed way in which water binds to the xylopyranose molecule, among the many possibilities due to the high capacity to form hydrogen bonds, can be considered the first step in understanding the mutarotation processes that monosaccharides undergo in biological environments.

WF09 **11:31 – 11:46**

MICROWAVE SPECTROSCOPY OF FLUOROSULFONIC ACID (FSO_2OH) AND ITS MONO- AND DIHYDRATES

AARON J REYNOLDS, *Chemistry Department, University of Minnesota, Minneapolis, MN, USA*; KARLA V. SALAZAR, WEI LIN, *Department of Chemistry, University of Texas Rio Grande Valley, Brownsville, TX, USA*; KENNETH R. LEOPOLD, *Chemistry Department, University of Minnesota, Minneapolis, MN, USA*.

We report on the hydration of the superacid fluorosulfonic acid (FSO_2OH) as characterized by chirped-pulse and cavity microwave spectroscopy. Rotational transitions of the monomer in the 3-18 GHz region were readily observed. Each has a weaker partner arising from OH wagging, as previously observed in the spectra of triflic and methanesulfonic acids. Spectra for the monohydrate and dihydrate were collected using a chirped-pulse method, and rapidly assigned using the DAPPERS software. Cavity spectroscopy revealed two states for the monohydrate, presumably arising from an internal motion associated with the water moiety. Deuterium isotopologues of these complexes were collected by on-the-fly mixing using D_2O in place of H_2O. The computed structures (benchmarked against the observed rotational constants), involve hydrogen bonded rings analogous to those observed for many other hydrated oxyacids. Consistent with previously published theoretical work[a], acid dissociation is not predicted or observed for the mono- or dihydrates, although a correlation between degree of partial proton transfer and hydration is noted. The trihydrate is predicted to exist as a hydrated ion pair, but no such species has yet been identified in the observed spectrum.

[a] Li, S.; Weber, K.H.; Tao, F.-M.; Gu, R. Theoretical Investigation of Ionic Dissociations of Fluorosulfonic Acid in Microsolvated Clusters, Chem. Phys. 2006, 323, 397-406.

WF10 **11:49 – 12:04**

EXPLORING THE HYPERFINE STRUCTURE OF MOLECULAR HYDROGEN INTERACTING WITH SMALL AROMATIC SYSTEMS THROUGH ROTATIONAL SPECTROSCOPY

ROBIN DOHMEN, BEATE KEMPKEN, *Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany*; PABLO PINACHO, MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; DANIEL A. OBENCHAIN, *Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany*.

Non-covalent interactions play a key role in the formation of molecular complexes and reactivity. In previous works only interactions of small molecules with hydrogen have been investigated by rotational spectroscopy while interactions of molecular hydrogen with aromatic systems are unexplored.

In this work, the bond of hydrogen to the π-system of halogenated benzaldehydes is investigated. These volatile systems possess a large dipole moment and have multiple non-covalent binding sites to investigate selectivity. By introducing quadrupolar nuclei the complexity of the system is increased, the quadrupolar nucleus acts as a spectroscopic probe for the electronic field gradient and provides insights into the long-range dispersive interactions. Of particular interest are the differences observed for the rotational spectrum of $ortho$- and $para$-hydrogen and its structural impact investigated by isotopic substitution. The two spin isotopes show significant differences in rotational constants which demonstrate that there are significant differences in binding strength of o-H_2 and p-H_2 to the π-system, which are experimentally observable. Broadband rotational spectra are presented which are supplemented with cavity data to resolve the additional hyperfine splitting caused by the spin-spin coupling of o-H_2. We present elements of the spin-spin coupling tensor and draw experimental conclusions about hydrogen bond distance and the orientation of the o-H_2 with respect to the benzaldehyde plane.

WG. Dynamics and kinetics

Wednesday, June 21, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Krupa Ramasesha, Sandia National Laboratories, Livermore, CA, USA

WG01 **1:45 – 2:00**

NUCLEAR SPIN CONVERSION OF CH_3D IN SOLID PARAHYDROGEN

ANH H. M. NGUYEN, IBRAHIM MUDDASSER, DAVID T. ANDERSON, *Department of Chemistry, University of Wyoming, Laramie, WY, USA*.

Nuclear spin symmetry conservation provides strong selection rules in radiative transitions, inelastic collisions, and chemical reactions[a] and yet when a molecule is trapped in a cryocrystal at low temperatures, nuclear spin symmetry conversion is observed. In this study we report observations of the nuclear spin conversion (NSC) of monodeuterated methane (CH_3D) trapped in solid parahydrogen (pH_2) samples at approximately 1.7 K via high-resolution Fourier transform infrared spectroscopy. CH_3D doped pH_2 crystals are prepared using a rapid vapor deposition technique to co-deposit room temperature CH_3D and precooled pH_2 gases onto a cold substrate. This project focuses on the ν_2 (CD stretch) and ν_6 (CH_3 rock) modes corresponding to parallel and perpendicular rovibrational bands, respectively. The temporal changes in peak intensities extracted from the IR spectra are characteristic of NSC and can be used to assign peaks originating from the ortho (J,K = 0,0, I = 3/2) and para (J,K = 1,1, I = 1/2) nuclear spin states. Measurements performed on as-deposited and annealed samples show comparable first-order NSC dynamics with an average time constant τ = 311(33) min. The measured NSC time constants for a variety of methyl containing molecules, CH_3F, CH_3OH, and CH_3CCH isolated in pH_2 display a range of time constants.[bcd] By systematically studying the NSC of methyl containing molecules trapped in solid pH_2 we hope to better understand how solvation/confinement of the molecule results in a breakdown of the nuclear spin symmetry conservation rules.

[a] V. Horka-Zelenkova, G. Seyfang, P. Dietiker and M. Quack, *J. Phys. Chem. A*, 2019, 123, 6160-6174.
[b] Y.-P. Lee, Y.-J. Wu and J. T. Hougen, *J. Chem. Phys.*, 2008, 129.
[c] Y.-P. Lee, Y.-J. Wu, R. M. Lees, L.-H. Xu and J. T. Hougen, *Science*, 2006, 311, 365-368.
[d] A. I. Strom, A. Gutiérrez-Quintanilla, M. Chevalier, J. Ceponkus, C. Crépin and D. T. Anderson, *J. Phys. Chem. A*, 2020, 124, 4471-4483.

WG02 **2:03 – 2:18**

HYDROGEN ATOM QUANTUM DIFFUSION-LIMITED REACTION KINETICS OF $H + CO \rightarrow HCO$ IN SOLID PARAHYDROGEN: UNEXPECTED RESULTS

IBRAHIM MUDDASSER, ANH H. M. NGUYEN, ERIN McDONALD, DAVID T. ANDERSON, *Department of Chemistry, University of Wyoming, Laramie, WY, USA*.

Our group recently showed that the rate constant for the diffusion-limited $H + N_2O$ reaction in solid parahydrogen (pH_2) is inversely related to the N_2O concentration.[a] This finding was rationalized by the idea that chemical impurities disrupt the long-range order of the crystal and slow the H-atom quantum diffusion rate. We investigated this finding further by studying the $H + CO \rightarrow HCO$ reaction in solid pH_2. To explore how the reaction rate constant depends on the CO concentration, we prepared solid pH_2 matrix samples co-doped with CO and Cl_2 using the Rapid Vapor Deposition technique,[b] H-atoms are produced *in situ* using a UV-IR method described previously.[c] We performed kinetic studies at $1.56(3)$ and $4.00(2)$ K with a range of CO concentrations ($10 - 250$ ppm). We observe a similar inverse relationship between the rate constant and the CO concentration. Furthermore, it looks like the rate constant decreases from $1.56(3)$ to $4.00(2)$ K. This work is ongoing, and the latest results and analysis will be presented at the meeting.

[a] F. M. Mutunga *et al.*, J. Chem. Phys **154** (2021) 014302.
[b] M. E. Fajardo and Simon Tam, J. Chem. Phys. **108.10** (1998) 4237.
[c] S. C. Kettwich, P. L. Raston, and D. T. Anderson, J. Phys. Chem. A **113** (2009) 7621.

WG03 **2:21 – 2:36**

PRODUCT BRANCHING RATIO MEASUREMENTS AT LOW TEMPERATURES FOR REACTIONS OF THE CN RADICALS WITH HYDROCARBONS

MYRIAM DRISSI, DIVITA GUPTA, BRIAN M HAYS, OMAR ABDELKADER KHEDAOUI, THEO GUILLAUME, ILSA ROSE COOKE, ALBERTO MACARIO, IAN R. SIMS, *Univ. Rennes, Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes , Rennes, France*.

Molecular clouds are known to host a rich chemistry despite seemingly unfavorable conditions. In particular, a wide variety of cyano-polyynes and cyano-aromatic species have been detected in the past years. These nitrile compounds are also present in the atmospheres of various moons such as Titan. This suggests that the CN radical may be a vector of a rich chemistry in astrophysical media. To further understand the abundances of these molecules, astrochemical models are needed. These require accurate kinetic parameters, including rate coefficients and branching ratios measured at low temperature. Here, we present a new implementation of the Chirped Pulse in Uniform Flow (CPUF) technique, designed for branching ratio measurements. It combines the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique to reach low temperatures, with molecular beam sampling into an E-band chirped pulse Fourier transform millimeter wave spectrometer to detect reaction products. For the reaction between CN and propene we have measured the branching fraction of the vinyl cyanide channel at 35 and 50 K. Upper limits for all the different cyanopropene isomer channels were also determined. Theoretical calculations of the reaction potential energy surface and product branching fractions will be also be presented along with our latest results on other CN + hydrocarbon reactive systems.

WG04 **2:39 – 2:54**

LOW TEMPERATURE REACTION KINETICS OF CN(v=1) WITH BUTADIENE ISOMERS.

SHAMEEMAH THAWOOS, *Department of Chemistry, University of Missouri, Columbia, MO, USA*; GREGORY HALL, *Division of Chemistry, Department of Energy and Photon Sciences, Brookhaven National Laboratory, Upton, NY, USA*; CARLO CAVALLOTTI, *Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Politecnico di Milano, Milano 20133, Italy*; ARTHUR SUITS, *Department of Chemistry, University of Missouri, Columbia, MO, USA*.

Formation pathways and mechanisms of unsaturated nitrogen-containing compounds at very low temperatures are of great interest in the field of astrochemistry. The reaction of butadiene isomers with CN is one such reaction class that can be a key elementary step in the formation of large nitrogen rich molecules of potential biological importance in astrochemical environments. We present a joint experimental and theoretical investigation of reaction kinetics of vibrationally excited CN with 1,3 and 1,2-butadiene isomers at 70 K. The experimental method involves a newly built apparatus that couples a pulsed uniform supersonic flow with a continuous wave cavity ringdown spectrometer (UF-CRDS). The well-matched hydrodynamic time of the uniform flow with the long ringdown time decay allows the measurement of the complete kinetics over observation times up to 200 μs on each ringdown decay, an approach termed SKaR (Simultaneous kinetics and ringdown). The vibrationally excited CN is produced by photolyzing BrCN with a 248 nm excimer laser. The adjustable butadiene density greatly exceeds that of the photolytic CN radicals, ensuring pseudo first order conditions for the loss of CN. The time-dependent density of CN(v=1, j=5.5) is probed by tuning the DFB diode laser at 7070.24 cm^{-1}, the R_1(5.5), line of the (0-1) band of $A^2\Pi$–$X^2\Sigma^+$ electronic transition.The measured bimolecular rates are (3.96 $\pm$ 0.28) x 10^{-10} and (3.06 $\pm$ 0.35) x 10^{-10} cm^3 $\mathrm{molecule}^{-1}$ s^{-1} for 1,3 and 1,2-butadiene, respectively. The experimental rates were modeled by VRC-TST (Variable Reaction Coordinate Transition State Theory) calculations on a high-level multireference potential energy surface. For the 1,2-butadiene case the entrance channel branching was combined with earlier predictions of branching following the decays of the initial adducts to predict the overall branching.

WG05 **2:57 – 3:12**

DETERMINATION OF FORMIC ACID YIELDS FROM THE REACTION OF THE SIMPLEST CRIEGEE INTERMEDIATE WITH FORMALDEHYDE

PEI-LING LUO, I-YUN CHEN, *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan*.

Formic acid, one of the most abundant acids in the Earth's atmosphere, plays an important role in atmospheric acidity. Here, we report the direct observation of formic acid generated by the reaction of the simplest Criegee intermediate (CH_2OO) with formaldehyde (HCHO). By employing mid-infrared comb lasers and synchronized two-color time-resolved dual-comb spectroscopy, we investigated the kinetics of the reaction CH_2OO + HCHO as well as the yields of the reaction products HCOOH + HCHO and CO + H_2O + HCHO. The potential implications of the reaction CH_2OO + HCHO in the atmospheric chemistry are also discussed in this work.

Intermission

WG06 **3:52 – 4:07**

INVESTIGATING THE ONSET OF NUCLEATION: LOW TEMPERATURE REACTION KINETICS OF HETERODIMER FORMATION

ALBERTO MACARIO, MYRIAM DRISSI, OMAR ABDELKADER KHEDAOUI, THEO GUILLAUME, BRIAN M HAYS, IAN R. SIMS, *Univ. Rennes, Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes , Rennes, France*.

Nucleation is a key process in cloud and dust particle formation in different systems including planetary atmospheres and circumstellar shells. It consists of a succession of unions of small gas-phase molecules leading to the formation and growth of droplets and particles. Under the appropriate conditions, low temperatures and/or high degrees of supersaturation, nucleation can become a barrierless process, and dimerization, the complexation of the two smallest molecular species involved, becomes its rate-limiting step. The kinetics of formation of homodimers have been investigated in a few previous studies, using the CRESU (reaction kinetics in uniform supersonic flow) technique mainly coupled with mass spectrometric detection. Here we have employed a completely new detection scheme, chirped-pulse Fourier transform mm-wave spectroscopy, to study for the first time the kinetics of formation of heterodimers. This innovative technique combines the ability to generate continuous cold uniform supersonic flows with the high selectivity and general applicability of rotational spectroscopy, allowing us to follow both reactant and product concentrations simultaneously. Furthermore, the high sensitivity achieved has allowed us to employ pseudo-first-order conditions to obtain absolute rate constants. We will report the first measurements of rate constants for the formation of a set of heterodimers, including formic acid, CO2 and water among others, at temperatures between 35 and 150 K.

WG07 **4:10 – 4:25**

PROBING REACTION CHANNELS OF CHLOROBENZENE-AMMONIA CLUSTERS: A TWO-COLOR STUDY.

RONALD MUTETE, DAMIAN L KOKKIN, SCOTT REID, *Department of Chemistry, Marquette University, Milwaukee, WI, USA*.

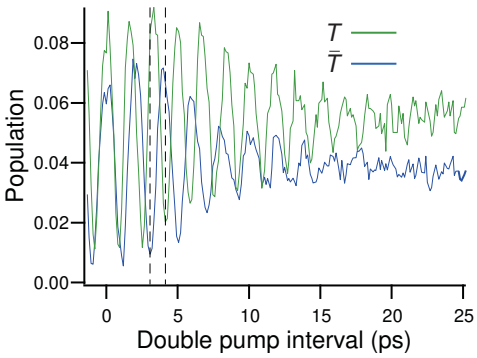
Noncovalent interactions including π-π stacking, CH/π interactions and halogen bonding play a significant role in many chemical and biological processes. Understanding their nature and behavior gives insight into how they influence processes such as protein folding, molecular self-assembly, and drug-substrate interactions. Using a combination of velocity mapped ion imaging, two-color photoionization, and theoretical calculations we probe the chlorobenzene-ammonia cluster system. From our previous studies, we have insight into the reactive pathways as well as the possible geometries of the σ-type reaction intermediate (Reid, et al. 2013 [a]). This study is focusing on probing the reaction pathways around the activation energy. The first photon is for excitation and a time delayed second photon is for ionization to initiate the radical reaction. The dimer cation radical reacts via Cl- atom or HCl loss pathways forming protonated aniline and aniline cation respectively or H-atom loss forming ortho-chloro protonated aniline. The energy of the photons can be controlled enabling the experiment to determine threshold energy of the reaction as well as confirm the primary reaction channel.

[a] S.A Reid, S. Nyambo, A. Kalume, B. Uhler, C. Karshenas, L. Muzangwa, J.Phys. Chem. A 2013, 117, 12429-12437

WG08 **4:28 – 4:43**

ULTRAFAST MODE-SELECTIVE POPULATION CONTROL OF LARGE AMPLITUDE VIBRATION IN DIPHENYLMETHANE

MAKOTO NIKAIDO, YASUHIRO OHSHIMA, *Department of Chemistry, Tokyo Institute of Technology, Tokyo, Japan*.



Large-amplitude motion (LAM) may induce a substantial conformational change in molecules, which is deeply relevant to molecular functionality e.g., in biomolecules. However, the creation and manipulation of vibrational wave packets pertinent to LAM in isolated molecular systems have been rarely realized, and most studies on molecules in the electronic ground states deal with one-dimensional LAM[ab]. Here we study diphenylmethane (DPM), which has two degrees of freedom for LAM, i.e., symmetric and anti-symmetric torsional vibration, T (20 cm^{-1}) and $\bar{T}$ (16 cm^{-1}). Adiabatically cooled DPM was irradiated by a pair of femtosecond laser pulses (pumps) to excite modes T and $\bar{T}$ through impulsive stimulated Raman scattering. Then, resonance two-photon ionization (R2PI) spectra were obtained by nanosecond UV pulses (∼268 nm, probe). Populations in $v = 1$ of both vibrational modes were evaluated from the integrated intensities of hot bands appearing in the R2PI spectra. The experimental results show that the populations in $v = 1$ of mode T and $\bar{T}$ oscillate against the double pump interval as a result of the wave-packet interference (Figure). By utilizing the difference in these oscillation periods, mode selective excitation was realized (dashed lines). We also conducted semiclassical calculations, where molecular vibration is treated quantum mechanically while molecular rotation is simulated by classical trajectory calculation, to show a good match-up with the observed time-evolution of populations.

[a] C. B. Madsen, et al., J. Chem. Phys. 130, 234310 (2009).
[b] M. Nikaido, et al., 2021 International Symposium on Molecular Spectroscopy, RH06 (2021).

WG09 **4:46 – 5:01**

INTERROGATING STRONG INTRAMOLECULAR H-BONDS AND PROTON TRANSFER DYNAMICS WITH ULTRAFAST INFRARED SPECTROSCOPIES

VALERIE S. WINKLER, *Chemistry, Washington University in Saint Louis, St. Louis, MO, USA*; JESSIKA L.S. DEAN, *Chemistry, Washington University in St. Louis, St. Louis, MO, USA*; JOSEPH FOURNIER, *Department of Chemistry, Washington University, St. Louis, MO, USA*.

Proton transfer reactions are essential in many biological and chemical processes, but are notoriously difficult to study directly due to strong anharmonic effects and ultrafast vibrational relaxation dynamics. Here, we present ultrafast transient absorption (TA) and two-dimensional infrared (2DIR) spectroscopies to characterize the intramolecular H-bonding interactions and proton transfer dynamics in a series of acetylacetone derivatives and their deuterated isotopologues. Strong 2DIR cross peaks are observed in the OH/OD bend region, indicating significant coupling between the OH/OD bends and other fingerprint modes. The OH/OD stretch regions display broad, homogeneous ground-state bleach signals that decay within 100 fs to intramolecular modes, resulting in long-lived hot-ground state signatures. Interestingly, polarization-dependent measurements reveal anisotropic signals that persist beyond the vibrational lifetimes with large isotopic differences. In general, the OH stretch anisotropies decay within about 200 fs, equivalent to one period of the intramolecular O-O stretch H-bond soft mode. The OD stretch anisotropies decay within 1-2 ps and correlate with the H-bond strength. The observed anisotropy timescales are interpreted in terms of the delocalization and transfer timescales of the proton/deuteron upon vibrational excitation.

WG10 **5:04 – 5:19**

SIMULATING VIBRATIONAL ENERGY TRANSFER THAT PROMOTES EXCITED STATE PROTON TRANSFER IN PYRANINE

JUSTIN J TALBOT, JAMES SHEE, MARTIN HEAD-GORDON, *Chemistry, University of California, Berkeley, Berkeley, CA, USA*; CLAUDIUS HOBERG, MARTINA HAVENITH, *Physikalische Chemie II, Ruhr University Bochum, Bochum, Germany*.

Identifying molecular-level details of the solvent reorganizations that facilitate photo-induced excited-state proton transfer is challenging for current experimental and theoretical approaches. One distinct challenge for computations is accessing the long time scales required to get frequency-resolved data. In this talk, I will discuss our recent work modelling optical pump THz probe experiments using molecular dynamics simulations to elucidate the ultrafast changes in the solvation environment for three derivatives of pyranine: the photoacid HPTS, the methoxy derivative MPTS, and the photobase OPTS. The experiments show damped oscillations in the THz signal at short times for all three derivatives and our simulations enable their assignment to vibrational energy transfer beatings between the photoexcited chromophore and nearby solvent molecules. Additionally, the simulations of HPTS reveal strikingly efficient sub-ps energy transfer into a particular solvent mode, that is active near 4 THz, and which can provide the requisite energy required for solvent reorganization promoting proton transfer.

WG11 **5:22 – 5:37**

EXCITATION ENERGY TRANSFER AND PHOTOREGULATORY MECHANISMS IN INTACT PHYCOBILISOMES USING TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

SOURAV SIL, RYAN W. TILLUCK, NILA MOHAN T.M., CHASE H. LESLIE, JUSTIN B. ROSE, *Department of Chemistry, Michigan State University, East Lansing, MI, USA*; CHERYL A. KERFELD, *MSU-DOE Plant Research Laboratory, Michigan State University, East Lansing, MI, USA*; WARREN F. BECK, *Department of Chemistry, Michigan State University, East Lansing, MI, USA*.

The phycobilisome is the principal light-harvesting chromoprotein complex in cyanobacteria and red algae. We have employed broadband multidimensional electronic spectroscopy with 6.7-fs laser pulses for the first time to study the excitation energy transfer mechanisms in intact phycobilisomes isolated from *Fremyella diplosiphon*. The results show that excitation energy transfer pathways include delocalized optical excitations of bilin (linear tetrapyrrole) chromophores, which transfer excitation energy along the rods in $<$600 fs. Excitation energy moves more slowly from the rods to the core on the $>$10 ps time scale, indicating that excitation energy is localized on individual bilin chromophores in the allophycocyanin-containing segments of the phycobilisome. The intramolecular charge-transfer character of the β84 chromophore in allophycocyanin would strongly favor dynamic exciton localization upon transfer of excitation energy from the rod segments. This phenomenon contributes to a kinetic bottleneck, which allows photoregulatory mechanisms, including that involving binding of the orange carotenoid protein, to operate efficiently in the core. In phycobilisomes isolated from *Fremyella diplosiphon* grown under red light, in contrast to those grown under white light, the terminal emitting APC680 segments exhibit significantly shorter excited-state lifetimes. These findings further show that trapping bilin sites are accumulated in the core of the phycobilisome during growth as part of a chromatic adaptation response.

(Work supported by grant awards DE-SC0010847 (W.F.B. laboratory) and DE-SC0020606 (C.A.K. laboratory) from the Photosynthetic Systems program of the Office of Basic Energy Sciences, U.S. Department of Energy.)

WH. Mini-symposium: Spectroscopy at Large-scale Facilities

Wednesday, June 21, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Sylvestre Twagirayezu, Lamar University, Beaumont, TX, USA

WH01 **1:45 – 2:00**

EXPLORING THE FORMATION OF SILICON DERIVATIVES OF AROMATIC AND POLYCYCLIC AROMATIC HYDROCARBONS IN THE ELECTRICAL DISCHARGE OF PHENYL SILANE

GAYATRI BATRA, DONATELLA LORU, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; ALEXANDER KAREL LEMMENS, *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*; PIERO FERRARI, BRITTA REDLICH, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Silicon is one of the most abundant elements in the Earth's crust and is also prevalent in space in the form of gaseous molecules, interstellar dust, and ice grains. The recent radio astronomy detection of cyano-substituted benzene, e.g., benzonitrile [1] in TMC-1 has accelerated the search for substituted aromatic molecules in the interstellar medium. Considering the presence of silicon in the interstellar medium, silicon-containing aromatic molecules are likely targets of future astronomical searches. To aid these searches and understanding the silicon chemistry in space, laboratory data are crucial.

In the laboratory, exotic neutral silicon-containing molecules can be produced and spectroscopically characterized by combining spectroscopic techniques with electrical discharge sources. In this work, using mass-selective IR-UV ion dip spectroscopy coupled with a molecular beam and the free electron laser FELIX (Nijmegen, The Netherlands), we have investigated the electrical discharge chemistry of phenyl silane in selected IR regions (500 – 3200 cm^{-1}) [2]. Such broad coverage provides significant information about the structure and chemical composition of the discharge products formed in the experiment. The aim is to investigate the variety of discharge products generated by the electrical discharge experiment of pure phenyl silane. Numerous fragments, products, and reaction intermediates are identified by mass-selective IR-UV spectroscopy combined with quantum-chemical calculations.

[1] B.A. McGuire, A.M. Burkhardt, S. Kalenskii, C.N. Shingledecker, A.J. Remijan, E. Herbst, M.C. McCarthy, Detection of the aromatic molecule benzonitrile (c-$\mathrm{C_6H_5CN}$) in the interstellar medium, Science. 359 (2018) 202–205.

[2] A.K. Lemmens, D.B. Rap, J.M.M. Thunnissen, B. Willemsen, A.M. Rijs, Polycyclic aromatic hydrocarbon formation chemistry in a plasma jet revealed by IR-UV action spectroscopy, Nat. Commun. 11 (2020) 269.

WH02 **2:03 – 2:18**

EXPLORING THE FORMATION OF SILICON-CONTAINING PAH-LIKE MOLECULES IN THE ELECTRICAL DISCHARGE OF PHENYLSILANE AND NAPHTHALENE

DONATELLA LORU, GAYATRI BATRA, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; ALEXANDER KAREL LEMMENS, *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*; PIERO FERRARI, BRITTA REDLICH, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Silicon is among the most abundant elements in interstellar environments, being only one order of magnitude less than C, N, and O. More than 15 gas-phase silicon bearing molecules have been already detected and a large fraction of silicon is considered to be locked up in interstellar dust grains, where also polycyclic aromatic hydrocarbons (PAHs) are a major constituent. Due to its abundance, silicon can represent an important player in the chemical evolution of the interstellar medium and, in particular, in many interstellar PAHs formation zone. Because of its chemical analogy with carbon, both are tetravalent atoms that form primarily covalent bonds, silicon could substitute either within or on the carbon skeleton of a PAH under the energetic conditions of the ISM, and silicon-substituted PAHs could represent promising candidates for future astronomical searches. In the laboratory, one way to study the make-up of silicon containing PAH-like molecules is by combining cutting-edge spectroscopic techniques with plasma sources. In this work, we used molecular beam mass-selective IR spectroscopy with the free-electron laser FELIX and quantum-chemical calculations to analyze the electrical discharge of phenylsilane and naphthalene. A variety of molecular species resulting from the combination of the precursors were identified via their mass and their IR spectra. The analysis of the latter could help elucidate the influence of Si on the IR spectra of PAHs.

WH03 **2:21 – 2:36**

PYRROLE + OH AS A MODEL SYSTEM: MECHANISM DETERMINATION WITH SYNCHROTRON VUV PHOTOIONIZATION MASS SPECTROMETRY AND COMPUTATIONAL CHEMISTRY

SOMMER L. JOHANSEN, KENDREW AU, JUDIT ZADOR, LEONID SHEPS, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*.

Gas-phase reaction pathways of aromatics in atmospheric chemistry and combustion are initiated largely by reactions with OH. Addition to the aromatic ring, rather than H-abstraction, dominates at temperatures relevant for Earth's atmosphere and low-temperature ($\leq$ 900 K) combustion. There has been an extensive amount of experimental and computational work done to elucidate the mechanisms of OH-addition to hydrocarbon and oxygenated aromatics. In contrast, OH reactions with N-containing aromatics (NCAs) have been rather poorly studied, despite the known emissions of NCAs from biomass burning and industrial processes. OH addition to pyrrole (c-C_4H_5N), one of the simplest NCAs, has been determined to be a fast, and likely barrierless route to a hydroxypyrrolyl adduct, but additional experiments are needed to understand the full mechanism, particularly in the presence of O_2. Here, we present results of atmospheric pressure photoionization mass spectrometry experiments on pyrrole + OH, with and without O_2, from 298 – 500 K, taken at the Advanced Light Source on the Chemical Dynamics Beamline. Using this highly-sensitive, time-resolved technique, we identified a number of products and short-lived intermediates, including what we believe to be the hydroxypyrrolyl adduct. To assist in mechanism determination, we calculated potential energy surfaces of both pyrrole + OH and hydroxypyrrolyl + O_2 using KinBot, an automated chemical kinetics workflow code, at the ωB97X-D/6-311++G(d,p) level of theory with energies refined at CCSD(T)-F12/cc-pVDZ-F12. We will discuss our efforts to model these reactions, as well as planned future experiments to provide better insight into the branching ratios and reactivity of different isomers on the hydroxypyrrolyl + O_2 potential energy surface. Additionally, experimental validation of our calculations opens the door to calculations of more complex NCAs that are difficult to study experimentally, such as imidazole derivatives that are potential brown carbon aerosol precursors.

WH04 **2:39 – 2:54**

DIRECT OBSERVATION OF ETHYL RADICAL IN THE PYROLYSIS OF ETHANE

NADAV GENOSSAR-DAN, SHARONA ATLAS, DANA BRESKER, SHANI HAR LAVAN, URI ZAMIR, ILLYA ROZENBERG, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*; THANH LAM NGUYEN, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; PATRICK HEMBERGER, *General Energy, Paul Scherrer Institute, Villigen, Switzerland*; JOSHUA H. BARABAN, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*.

The observation and quantification of reactive intermediates is crucial for the validation and development of kinetic models. However, very often the same reactivity that makes the role of such species important in reaction networks hinders our ability to detect them, due to their low concentrations and short lifetimes. As a result, many kinetic models rely on the formation of various intermediates which were never quantified, and sometimes not even established.

One particularly important case is the pyrolysis of ethane (C_2H_6). As this reaction plays a central role in industrial processes such as production of ethylene (C_2H_4) and combustion of ethane, the understanding of its underlying mechanism is crucial for process optimization, in order to reduce economic and environmental costs. Although ethyl (C_2H_5) is a key intermediate towards the formation of ethylene, it has never been directly observed in this reaction.

We report a double imaging photoelectron photoion coincidence (i^2-PEPICO) spectroscopy study of the flash pyrolysis of ethane and its isotopologue CH_3CD_3 using VUV radiation generated by the Swiss Light Source (SLS) and a resistively heated SiC microreactor reaching temperatures of up to 1700 K. This apparatus is especially appropriate for the observation of reactive radicals in thermal reactions – the short residence times before quenching of the intermediates, and the low ionization energies of radicals favor their observation. These properties allowed the observation of ethyl and its isotopologues, which were identified through their threshold photoelectron spectrum (TPES), by comparison to reported spectra and simulated ones. Together with observation of isotopic selectivity and comparison to fully coupled computational fluid dynamics and kinetics simulations, these results provide valuable mechanistic insights into the initiation steps of this reaction.

Intermission

WH05 ***INVITED TALK*** **3:34 – 4:04**

A MULTI-SPECTROSCOPIC APPROACH TO REVEAL THE ASTROCHEMISTRY OF POLYCYLIC AROMATIC HYDROCARBONS

MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.

Polycyclic aromatic hydrocarbons (PAHs) are of great interest for its potential central role in astrochemistry. They are assumed to connect the chemistry between fullerenes and smaller carbon species, and it is assumed that they contain up to 20 % of the galactic carbon. To unravel the various aspects of their impact in astrochemistry, we perform a multi-spectroscopic approach covering large areas of the electromagnetic spectrum.

The structures and intermolecular interactions of PAH-water complexes are investigated using high-resolution chirped-pulse rotational spectroscopy in our lab and infrared spectroscopy using the Free-Electron Laser (FEL) FELIX in Nijmegen in the gas phase. With this work, we aim at understanding interactions between PAHs themselves and water. Another motivation is to learn how an ice layer begins to form on an extended carbon surface.

In another series of experiments, we perform plasma studies with PAHs and other astrochemically relevant molecules as precursors using an electric discharge. We observe a rich chemistry that we can then characterize spectroscopically using IR and rotational spectroscopy, which is highly complementary.

To study PAH photophysics, we use the Hamburg XUV to soft-X-ray Free-Electron Laser FLASH and perform ultrafast XUV-UV/IR pump-probe experiments, with ionization and dissociation as competing pathways. We can extract life times of electronically excited neutral and cationic states and investigate characteristic fragmentation patterns depending on the nature of the PAH under investigation.

In my presentation, I will provide an overview of our research activities on PAHs and discuss some of the latest results.

WH06 **4:10 – 4:25**

NON-COVALENT DYNAMICS WITH A FEMTOSECOND LASER MOLECULAR BEAM MASS SPECTROMETER

ALEXANDER KAREL LEMMENS, NURESHAN DIAS, MUSAHID AHMED, *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*.

At Berkeley lab we are developing a versatile mass spectrometer to probe spectroscopic and time-resolved chemical dynamics involving non-covalent interactions. We are interested in the dynamic interactions of water weakly bound to hydrophobic molecular substrates (water in confinement).[1] Despite the cold conditions used to produce such complexes, they still retain large amounts of flexibility. Related are solvent-molecule rearrangements. Solvation can have a strong influence on chemical properties, and of particular interest is solvent dynamics as response to a stimulus, such as photoexcitation.[2]

Within the framework of astrochemistry, dynamics in larger molecules or their van der Waals clusters are largely unexplored. Processes that occur upon (V)UV radiation such as dehydrogenation, fragmentation, and ionization will be explored with the new laser system. Moreover, the tunability and high repetition rate of the UV/VIS pulses allows for fast electronic spectroscopy of reaction products for identification but also to spectroscopically characterize possible candidates for the diffuse interstellar bands.

The system will use 35% of the output from a 300 fs Yb fiber laser for generating the 115 nm ninth harmonic by a phase matched process of the third harmonic in a Xenon gas cell, running at up to 750 kHz.[3] The remaining 65% is used to pump an OPA that covers a tuning range of 210 nm to 16 μm. The resulting wide spectral range allows for direct ionization as well as electronic and vibrational spectroscopy of gas phase systems. The combination with short laser pulses allows for the characterization of fast structural and/or electronic changes upon excitation, ideal for tracking the dynamics of non-covalent systems.

1. Molina, E. R., et al. (2022), PCCP, 24(38), 23106-23118.
2. Miyazaki, M., et al. (2018), PCCP, 20(5), 3079-3091.
3. Peli, S., et al. (2019), arXiv preprint arXiv:1911.05590.

WH07 **4:28 – 4:43**

DECIPHERING THE DYNAMICS AND VECTOR CORRELATIONS OF VACUUM ULTRAVIOLET (VUV) PHOTODISSOCIATION OF CO_2 AT 155 NM

EVANGELIA SAKKOULA, *Molecular and Laser Physics, Radboud University, Nijmegen, Netherlands*; GAUTAM SHARMA, *Molecular and Laser Physics, Radboud University Nijmegen, Nijmegen, Netherlands*; XINGAN WANG, *Department of Chemical Physics, University of Science and Technology of China, Hefei, China*; SIMON NORTH, *Department of Chemistry, Texas A & M University, College Station, TX, USA*; DAVID H. PARKER, *Molecular and Laser Physics, Radboud University Nijmegen, Nijmegen, Netherlands*; WEI WEI, *Department of Chemistry and Physics, Franklin College, Franklin, IN, USA*.

The Vacuum Ultraviolet (VUV) photodissociation of CO_2 via the dominant $O(^1D)$ channel near 155 nm were studied using Velocity Map Imaging (VMI) technique. Speed dependent vector correlations (the correlations among the transition dipole moment μ of the parent molecule, the recoil velocity vector **v** and rotational angular momentum vector **j** of the photofragments) were extracted. This was made possible via the application of a set of equations first developed by Grubb *et al*. And in combination with a Monte Carlo style simulation program and necessary approximations, full vector correlation information were extracted from the anisotropic angular distributions of the images. Our results indicated a picture of photodissociation dynamics mainly via the excited 2^1A' (A) state. The transition dipole moment lies in the bent molecular plane. It was not parallel, but pointing away from the dissociating C-O bond. In addition, speed dependent μ -**v** correlation showed a clear trend, with higher rotationally excited CO correlating to larger angle between μ and the recoil direction. Such clear trend was successfully explained with a mathematical model (first developed by Reisler and coworkers) considering non-axial recoil effect. Although 1^1A" (B) state was also energetically available, we do not believe it was involved in this case.

WH08 **4:46 – 5:01**

3D MOMENT IMAGING WITH A USB3 OSCILLOSCOPE

YASASHRI RANGANATH RANATHUNGA, *Chemistry Department, Wayne State University, Detroit, MI, USA*; TEMITAYO A. OLOWOLAFE, *Chemistry, Wayne State University, Detroit, MI, USA*; SUK KYOUNG LEE, *Chemistry Department, Wayne State University, Detroit, MI, USA*; WEN LI, *Department of Chemistry, Wayne State University, Detroit, MI, USA*.

In 1997 Eppink and Parker introduced velocity map imaging (VMI) based on the ion imaging technique developed by Chandler and Houston. This method has been as a high-resolution tool to study the detailed dynamics of chemical or physical processes. This approach can measure the momenta and angular distributions of charged particles (ions/electrons) released in these processes and provide detailed information about the potential energy surfaces. Over the years, this technique has been evolving; now it can do direct three-dimenssional measurements with multi-hit capability. In this work, we report further improvement to the 3D-VMI setup. With the conventional digitizers employed previously replaced by a low-cost USB oscilloscope, VMI has become more cost-effective, simpler and even portable. The performance of this new VMI apparatus was characterized in a study of laser desorption ionization of 2,5-dihydroxybenzoic acid.

WH09 **5:04 – 5:19**

TIME-RESOLVED NUCLEAR FORWARD SCATTERING: BRINGING PUMP-PROBE SPECTROSCOPY INTO THE GAMMA-RAY REGIME

DUGAN HAYES, CALI ANTOLINI, *Department of Chemistry, University of Rhode Island, Kingston, RI, USA*; MICHAEL Y. HU, *X-ray Science Division, Argonne National Laboratory, Lemont, IL, USA*; GILLES DOUMY, ANNE MARIE MARCH, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; BENJAMIN T. YOUNG, *Department of Physical Sciences, Rhode Island College, Providence, RI, USA*.

Over the last several decades, the development of time- and frequency-domain nuclear resonance spectroscopies that take advantage of the tunability and pulsed nature of synchrotron radiation at storage ring facilities has greatly expanded both the portfolio of routinely accessible nuclei and the range of material properties that may be probed via the Mössbauer effect. Continuing in this tradition, we recently developed a method to probe the photophysical dynamics of solid-state materials using a pump-probe implementation of time-domain Mössbauer spectroscopy that we refer to as time-resolved nuclear forward scattering (TRNFS). After introducing this novel technique and discussing its challenges, I will present our measurements of tin(II) oxide to showcase the power and unique opportunities of TRNFS. In particular, I will demonstrate how variable repetition rate TRNFS may be used to distinguish between electronic and thermal contributions to laser-induced difference spectra and how small contributions to the quantum beating signal originating from the photoexcited material may be clearly identified using reference scatterers.

WH10 **5:22 – 5:37**

DEVELOPMENT OF A SOLID TARGET DELIVERY SYSTEM FOR APPLICATION IN X-RAY EXPERIMENTS

NOAH WELKE, RYAN T ASH, *Physics, University of Wisconsin-Madison, Madison, WI, USA*; ALEX HALAVANAU, CLAUDIO PELLEGRINI, *Acceleratory Directory, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; UWE BERGMANN, *Physics, University of Wisconsin-Madison, Madison, WI, USA*.

Synchrotron insertion devices and x-ray free electron lasers deliver pulse trains of x-rays with up-to MHz to sub-GHz repetition rate. These x-rays can ablate samples in a single shot, necessitating material replacement in a short time before the next pulse arrives. Typically, this is done with a dilute solution in a high-speed jet or with a sputtering source, yet many applications make these solutions unworkable. We present the development of a fast, solid-target sample delivery system for high repetition rate x-ray sources, to alleviate these issues. Tests of the system at the LCLS nano-focusing beamline and future applications in various user experiments are outlined.

WI. Atmospheric science

Wednesday, June 21, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Laura R. McCunn, Marshall University, Huntington, WV, USA

WI01 **1:45 – 2:00**

IN SITU AND REMOTE SENSING OF SULFATE AEROSOLS

DYLAN ENGLISH, *Department of Physics, Old Dominion University, Norfolk, VA, USA*; PETER F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*; CHRIS BOONE, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada*; DANIEL MURPHY, *Chemical Sciences Division, NOAA Earth System Research Lab, Boulder, CO, USA*.

Stratospheric sulfate aerosols play a crucial role in the physical and chemical processes in the Earth's atmosphere. They have a strong impact on climate by absorbing and scattering both incoming and outgoing radiation. The Atmospheric Chemistry Experiment Fourier Transform Spectrometer is recording infrared transmittance spectra of the Earth's limb from low Earth orbit (solar occultation). These infrared spectra provide accurate measurements of sulfate aerosol composition[1], but have difficulty providing information on physical properties such as the particle size distribution. In contrast, optical extinction measurements, such as from the SAGE III/ISS instrument on the International Space Station, provide information on physical properties, but little data on composition. *In situ* measurements, made from aircraft, with a mass spectrometer and laser light scattering provide some information on composition and reliable information on physical properties[2]. By combining the information from satellite observations and *in situ* measurements, a more complete characterization of stratospheric sulfate aerosols has been obtained.

References

[1] P. Bernath, C. Boone, A. Pastorek, D. Cameron, M. Lecours (2023). Satellite characterization of global stratospheric sulfate aerosols released by Tonga volcano. Journal of Quantitative Spectroscopy and Radiative Transfer 299, 108520 DOI:10.1016/j.jqsrt.2023.108520

[2] D. Murphy, K. Froyd, I. Bourgeois, C. Brock, A. Kupc, J. Peischl, G. Schill, C. Thompson, C. Williamson, P. Yu (2021). Radiative and chemical implications of the size and composition of aerosol particles in the existing or modified global stratosphere. Atmos. Chem. Phys. 21, 8915 DOI:10.5194/acp-21-8915-2021.

WI02 **2:03 – 2:18**

SATELLITE CHARACTERIZATION OF GLOBAL STRATOSPHERIC SULFATE AEROSOLS RELEASED BY TONGA VOLCANO

PETER F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*; CHRIS BOONE, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada*; ADAM PASTOREK, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*; WILLIAM D CAMERON, *Department of Physics, Old Dominion University, Norfolk, VA, USA*; MIKE LECOURS, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada*.

Large volcanic eruptions create an enhanced layer of sulfate aerosols in the stratosphere. These sulfuric acid droplets persist for many months, altering the climate and stratospheric chemistry. Sulfate aerosols scatter sunlight back to space, cooling the surface of the Earth and absorb outgoing thermal radiation, heating the stratosphere. The calculation of the climate impact of sulfate aerosols depends on their physical properties such as droplet size and chemical composition. These properties are not well known, and this uncertainty contributes to the errors in climate model predictions. Here we derive the first empirical formula that predicts the composition of stratospheric sulfate aerosols from volcanic eruptions from the air temperature and water vapor pressure. Measurements of atmospheric infrared transmittance of the Hunga Tonga-Hunga Ha'apai sulfate aerosol plume by the Atmospheric Chemistry Experiment (ACE) satellite were analyzed to determine composition (weight percent of sulfuric acid) and median particle radius. These data are supplemented by measurements of the Raikoke and Nabro eruptions. Our analysis allows the properties of volcanic aerosols in the stratosphere to be predicted reliably in atmospheric models.

Reference to publication: Bernath, P.; Boone, C.; Pastorek, A.; Cameron, D.; Lecours, M. Satellite characterization of global stratospheric sulfate aerosols released by Tonga volcano. JQSRT, 299, 108520 (2023)

WI03 **2:21 – 2:36**

VALIDATING LINE-OF-SIGHT WINDS CALCULATED FROM ACE-FTS SOLAR OCCULTATION MEASUREMENTS

RYAN JOHNSON, *Department of Physics, Old Dominion University, Norfolk, VA, USA*; CHRIS BOONE, *Department of Chemistry, University of Waterloo, Waterloo, ON, Canada*; PETER F. BERNATH, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*.

The Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) measures infrared transmittance spectra of the atmosphere from low Earth orbit using the Sun as a light source (solar occultation)[a]. These spectra are used to derive altitude abundance profiles of more than 40 molecules, and properties of clouds and aerosols[b]. The Doppler shifts on atmospheric lines can be used to determine line-of-sight winds[c]. Line-of-sight winds are a new data product for version 5.0 of ACE-FTS processing. These winds are being validated through comparison with independent winds observations from meteor radars and from the ICON-MIGHTI satellite instrument.

[a] Bernath, P.F. The Atmospheric Chemistry Experiment (ACE). J. Quant. Spectrosc. Radiat. Transf. 2017, 186, 3–16.

[b] Lecours, M.J.; Bernath, P.F.; Sorensen, J.J.; Boone, C.D.; Johnson, R.M.; LaBelle, K. Atlas of ACE spectra of clouds and aerosols, Journal of Quantitative Spectroscopy and Radiative Transfer, Volume 292, 2022, 108361

[c] Boone, C.D.; Steffen, J.; Crouse, J.; Bernath, P.F. Line-of-Sight Winds and Doppler Effect Smearing in ACE-FTS Solar Occultation Measurements. Atmosphere 2021, 12, 680.

WI04 **2:39 – 2:54**

X-MASS: A TOOL FOR SIMULTANEOUS CALCULATIONS OF CROSS-SECTIONS COVERING A LARGE PARAMETER SPACE FOR ATMOSPHERIC APPLICATIONS

VLADIMIR YU MAKHNEV, IOULI E GORDON, ROBERT J. HARGREAVES, LAURENCE S. ROTHMAN, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

Reliable spectroscopic information, including that provided in the HITRAN database[a], is essential when interpreting data from high-resolution remote sensing spectrometers that monitor the concentrations of gases in the terrestrial atmosphere. High spectral resolution molecular absorption calculations over a wide spectral range and diverse parameter space using line-by-line models are often considered too slow to be used in operational retrieval algorithms. This is further slowed when using advanced line-shapes and line-mixing parametrizations that are available in HITRAN for many molecules (e.g. Hashemi et al.[b]), which are necessary for accuracy. As an alternative, retrieval codes often rely on massive sets of pre-calculated tables of absorption cross-sections for target molecules that cover a representative set of environmental conditions. For some missions, such as the NASA Orbiting Carbon Observatory (OCO-2/3)[c], molecular absorption coefficients are calculated off-line for a range of pressures, temperatures, and H_2O volume mixing ratios and stored in "ABSCO" lookup tables[d]. We present a Python tool (X-MASS) that allows the massive set of ABSCO tables to be calculated using the HAPI software package[e] with complete utilization of the parameters' accuracy in HITRAN, including sophisticated line shapes. The outputs will be made available in the convenient HDF5 or NetCDF formats given user-defined wavenumber step, set of pressures, temperatures, and diluent gas contents. X-MASS will be an open-source library where users can specify parameters for their applications. In addition, a set of pre-calculated ABSCO tables covering spectral range of molecules at a finer grid and resolution will be provided on the HITRAN website. This work will facilitate the timely integration of state-of-the-art spectroscopic data into atmospheric radiative transfer codes.

[a] Gordon, I. E., *et al.* JQSRT 277 (2022): 107949.

[b] Hashemi, R., *et al.* JQSRT 271 (2021): 107735.

[c] Crisp, D., *et al.* Atmospheric Measurement Techniques 10.1 (2017): 59-81.

[d] Payne, V.H., *et al.* JQSRT 255 (2020): 107217.

[e] Kochanov, R.V., *et al.* JQSRT 177 (2016): 15-30.

WI05 **2:57 – 3:12**

CO_2 MEASUREMENTS WITH DUAL-COMB SPECTROSCOPY AT MAUNA LOA OBSERVATORY

NATHAN A MALARICH, KEVIN C COSSEL, FABRIZIO R. GIORGETTA, ESTHER BAUMANN, GRIFFIN J. MEAD, DANIEL I. HERMAN, BRIAN R WASHBURN, NATHAN R. NEWBURY, IAN CODDINGTON, *Spectrum Technology and Research Division, NIST, Boulder, CO, USA*.

Global measurements of greenhouse gas sources and sinks require accurate molecular absorption models. These absorption models are frequently developed using laboratory gas cells in known concentrated conditions, and applied to satellite measurements over different unknown non-uniform gas conditions. Dual-comb spectroscopy (DCS) can bridge these measurements by measuring the same absorption features in relatively known, uniform atmospheric conditions. To this end, we present open-path DCS measurements at the Mauna Loa Observatory in Hawaii, co-located with the longstanding calibrated point measurements of CO_2, CH_4, and meteorology at the Mauna Loa site. Nocturnal measurements at this alpine site are typically unaffected by local sources and sinks, providing the most controlled conditions for comparison of open-path measurements and molecular absorption models with reference-gas-calibrated point sensors.

We compare laboratory- and ab initio-derived CO_2 absorption models near 1600 nm in the 30012 and 30013 bands. Our fits using HITRAN2020 match the point sensors to 0.4%, although we also observe wavelength-dependence in the retrieved mole fraction.

Intermission

WI06 **3:52 – 4:07**

HIGH-RESOLUTION JET-COOLED INFRARED SPECTRUM OF THE ν_{26} BAND OF ISOPRENE

JACOB STEWART, LAUREN HINO, CARTER PAVLONNIS, KATARINA REYNA, BINH NGUYET VO, *Department of Chemistry, Connecticut College, New London, CT, USA*.

Isoprene (C_5H_8) is an important hydrocarbon that is naturally produced by plants and is the most abundant nonmethane hydrocarbon in the atmosphere. Isoprene plays an important role in the formation of secondary organic aerosol particles and the production of ozone in the troposphere. Isoprene is also one of the simplest conjugated organic molecules, exhibiting interesting confromational properties with respect to rotation about the central C-C single bond. To better understand the spectral and structural properties of isoprene, we have measured the high-resolution rovibrational spectrum of the ν_{26} band of isoprene near 992 cm^{-1}. The isoprene was cooled in a supersonic expansion to better resolve and analyze the rotational structure of this band and measured with a quantum cascade laser (QCL)-based spectrometer. This work complements previous spectra our group has obtained of room-temperature isoprene. We will present our analysis of the rovibrational spectrum and the insights the cold spectrum provides in the context of the room-temperature spectrum, as well as a comparison to anharmonic quantum calculations previously done in our group.

WI07 **4:10 – 4:25**

JET-COOLED AND LONG PATH CELL HIGH RESOLUTION INFRARED SPECTROSCOPY OF FURFURAL CONFORMERS FROM FOURIER TRANSFORM AND QCL MEASUREMENTS

PIERRE ASSELIN, SATHAPANA CHAWANANON, *CNRS, De la Molécule aux Nano-Objets: Réactivité, Interactions, Spectroscopies, MONARIS, Sorbonne Université , PARIS, France*; MANUEL GOUBET, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*; ROBERT GEORGES, *IPR UMR6251, CNRS - Université Rennes 1, Rennes, France*; ARNAUD CUISSET, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*.

Furfural, C_4H_3OCHO, is a volatile organic compound produced from biomass burning. Its oxidation may lead to secondary organic aerosol formation, making necessary to provide accurate spectroscopic data to evaluate its impact. Two conformations exist in the gas phase, with the oxygen atoms oriented in a more stable *trans* configuration than the *cis* one. Durig et al.[a] exploited far-infrared (IR) data to determine relative stabilities and the conformational barrier height. Motiyenko et al.[b] realized extensive microwave spectroscopic studies providing molecular parameters in the ground state (GS) and low-lying vibrational states up to 400 cm^{-1}. No splitting due to the internal rotation of the CHO top has been observed in these states. We report here a high resolution study of furfural on a wide infrared range combining the Jet-AILES set-up, a continuous supersonic jet on the IR AILES beamline at SOLEIL, and a long path cell, both coupled to a Fourier Transform Spectrometer and the SPIRALES set-up at MONARIS, a pulsed supersonic jet coupled to mid-IR quantum cascade lasers[c]. In the fingerprint region, 7 bands of *trans*- and 2 bands of *cis*-furfural were recorded at low temperature. About 15000 lines from GS and 7(2) excited states (ES) of *trans*(*cis*-)furfural, respectively, were fitted within experimental accuracy. In the far-IR range, global fits including GS and ES rotational and ES rovibrational transitions enable to refine molecular parameters derived from the microwave study and to determine precise vibrational band centers.

[a] T. S. Little, J. Qiu, J. R. Durig, Spectrochimica Acta, 45A, 789-794 (1989)

[b] R. A. Motiyenko, E. A. Alekseev, S. F. Dyubko, F. J. Lovas, J. Mol. Spectr., 240, 93-101 (2006), R. A. Motiyenko, E. A. Alekseev, S. F. Dyubko, J. Mol. Spectr., 244, 9-12 (2007)

[c] P. Asselin, J. Bruckhuisen, A. Roucou, M. Goubet, M-A. Martin-Drumel, A. Jabri, Y. Belkhodja, P. Soulard, R. Georges, A. Cuisset, J. Chem. Phys. 151, 194302 (2019), S. Chawananon, O. Pirali, M. Goubet, P. Asselin, J. Chem. Phys. 157, 064301 (2022)

WI08 **4:28 – 4:43**

THE CRIEGEE INTERMEDIATE-ACETIC ACID REACTION EXPLORED BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

YI-TING LIU, YASUKI ENDO, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.

Rapid reactions of organic acids with Criegee intermediates provide efficient gas phase removal process and are proposed to trigger the formation of atmospheric aerosols. The gas phase reaction between the simplest Criegee intermediate, CH_2OO, and acetic acid has been investigated by pulsed discharge nozzle Fourier transform microwave spectroscopy (PDN-FTMW). Two low lying conformers of hydroperoxymethyl acetate ($HOOCH_2OCOCH_3$, HPMA),which serves as the dominate nascent product from this reaction, was observed in the discharged plasma of a CH_2I_2/O_2/acetic acid gas mixture. Due to the three-fold methyl internal rotation and the low barrier height of the hindered methyl rotation, most of the observed pure rotational transitions in 13-21 GHz show large splitting corresponding to the A/E components. The relative abundance of the two observed hydroperoxymethyl acetate isomers is in agreement with the calculated relative energy. Also, the dehydrated product of HPMA, formic acid anhydride ($OHCOCOCH_3$), was observed in this work.

WI09 **4:46 – 5:01**

COLLISION-INDUCED EFFECTS IN THE FINE-STRUCTURE RESOLVED SPECTRA OF ATMOSPHERIC OXYGEN FROM FIRST PRINCIPLES: THE EFFECT OF O_2-N_2 SCATTERING

MACIEJ GANCEWSKI, HUBERT JÓŹWIAK, *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Toruń, Poland*; ERNESTO QUINTAS SÁNCHEZ, RICHARD DAWES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; PIOTR WCISLO, *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Toruń, Poland*.

The properties of our planet's atmosphere are derived from models which are mostly based on remote-sensing data. A detailed knowledge of spectra of various chemical compounds making up the terrestrial atmosphere is therefore crucial for understanding the various ongoing kinetic and dynamic processes. As these compounds are not isolated, intermolecular interactions involving most abundant atmospheric constituents – N_2 ($\sim 78\%$) and O_2 ($\sim 21\%$) – may affect the shapes of the spectra under consideration. In this context, oxygen spectra are of particular interest. O_2 is a prominent example of a diatomic molecule with a $^3\Sigma$ ground-electronic term, and fine-structure resolved transitions involving this term have a wide range of applicability – from monitoring the plant vegetation status on the Earth's surface, to the quantification of the pollutant concentration in the atmosphere [*J. Quant. Spectrosc. Radiat. Transf.* **186**, 118 (2017)].

Here, we consider the effect of O_2-N_2 collisions on the shape of the oxygen spectral lines from the theoretical point of view. Utilizing the exact close-coupling approach, we calculate the relevant scattering amplitudes based on the *ab initio* intermolecular potential energy surfaces (PESs). We account for the non-zero spin of the $X^3\Sigma_g^-$ term of O_2 by performing a unitary transformation on the spin-free S-matrix, which allows us to compute the line shape parameters for the fine-structure resolved transitions in O_2 immersed in the bath of N_2. Having successfully tested our methodology against the experimental data in our previous study of the 118 GHz fine-structure transition in $O_2(X^3\Sigma_g^-)$ [*J. Chem. Phys.* **155**, 124307 (2021)], we apply it to the problem of N_2-perturbed lines in the oxygen A-band (i.e., electronic transition $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$). This problem is more challenging as it requires the use of two PESs in the scattering calculations. The PESs used in this study were constructed automatically using the `AUTOSURF` code [*J. Chem. Inf. Model.* **59**, 262 (2018)].

WI10 **5:04 – 5:19**

COLLISIONAL EFFECTS IN THE SPECTRA OF HYDROGEN HALIDES: TOWARDS RELIABLE *AB INITIO* MODELING OF THE TERRESTRIAL-ATMOSPHERIC MOLECULAR SPECTRA

ARTUR OLEJNIK, MACIEJ GANCEWSKI, HUBERT JÓŹWIAK, *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Toruń, Poland*; ERNESTO QUINTAS SÁNCHEZ, RICHARD DAWES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; PIOTR WCISLO, *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Toruń, Poland*.

It has been long recognized that the spectroscopy of hydrogen halides (such as HF, HCl, HBr, and HI) provides a valuable tool, with atmospheric and astrophysical, as well as industrial applications [*J. Quant. Spectrosc. Radiat. Transf.* **130**, 284 (2013)]. As far as the terrestrial-atmospheric studies are concerned, two halide species – HF and HCl – may be considered the most important of the bunch. Being the main reservoirs of fluorine and chlorine, HF and HCl are used as pollutant trace gases in the determination of the anthropogenic chlorofluorocarbons' concentration in the Earth's atmosphere. Since these molecular species are of the pollutant-type, their atmospheric spectra must neccesseriliy be considered as perturbed by intermolecular interactions involving the main constituents of our planet's atmosphere – N_2 and O_2. Indeed, the process of ozone depletion is mainly induced by Cl and ClO, which result from the photodissociation of HCl. Therefore, to be applicable in atmospheric science, the spectra of the terrestrial hydrogen halides must be considered in the presence of the surrounding molecular bath of N_2 and O_2.

Here, we take a fully *ab initio* approach to the theoretical determination of atmospheric spectra of hydrogen halides, starting from the O_2-induced line shape perturbations. Taking the state-of-the-art potential energy surfaces (PESs) as our starting point, we perform close-coupling calculations of HF-O_2 and HCl-O_2 quantum scattering. We take a novel approach to the construction of the energy-level basis used in the close-coupling computations, and we study the convergence of the calculated cross sections against the size of the employed basis in full detail. Further, we calculate the temperature-dependent line shape parameters of the O_2-perturbed rotational R(0) line in HCl. The PESs used in this study were constructed automatically using the `AUTOSURF` code [*J. Chem. Inf. Model.* **59**, 262 (2018)].

WI11 **5:22 – 5:37**

ON THE NIR–VIS SPECTROSCOPY OF NO_2: POTENTIAL ENERGY CURVES OF THE X^2A_1, A^2B_2, B^2B_1, and C^2A_2 STATES AND THE $\widetilde{A}^2B_2$–$\widetilde{X}^2A_1$ CONICAL INTERSECTION

GABRIEL J. VÁZQUEZ[a], *Instituto de Ciencias Fisicas, Universidad Nacional Autonoma de Mexico (UNAM), Cuernavaca, Morelos, Mexico*; CAROLINA GODOY ALCANTAR, *Centro de Investigaciones Químicas-IICBA, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos, MX*; JOSÉ M. AMERO, *(without affiliation), , Cuernavaca, Mexico*; HANS-PETER LIEBERMANN, *Fachbereich C-Mathematik und Naturwissenschaften, Universität Wuppertal, Wuppertal, Germany*; VASSILI N. SEROV, OSMAN ATABEK, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, Orsay, France*.

Ab initio SCF MRD–CI electronic structure calculations are carried out in C_s symmetry for the three lowest $^2A'$ and $^2A''$ states of NO_2. The four lowest-lying species correspond, respectively, to $X^2A_1(1^2A')$, $A^2B_2(2^2A')$, $B^2B_1(1^2A'')$ and $C^2A_2(2^2A'')$ in C_{2v} symmetry. A cc–pVQZ basis set augmented with s, p, and d Rydberg functions is employed together with an extensive treatment of electron correlation. One–dimensional (1D) potential energy curves (PECs), associated to the equilibrium geometrical parameters of the X^2A_1 ground state (GS), were computed for the four aforementioned doublet states located in the near-IR and visible regions. These 1D cuts are related loosely to the bending, symmetric stretch and asymmetric stretch vibrational modes of the GS. The PECs are then employed to discuss the NIR-Vis absorption/emission spectroscopy of NO_2 and the strong conical intersection (CI) between the ground and first excited A^2B_2 states. In spite of being a small triatomic made up of 2nd-row atoms only, NO_2, a relatively "simple" molecule turns out to be an important testing ground for the study of a number of fundamental molecular processes such as the dynamics of intramolecular energy redistribution which involves the coupling of electronic and nuclear motions and entails the breakdown of the adiabatic BO approximation (e.g., the $\widetilde{A}$–$\widetilde{X}$ conical intersection, Renner-Teller interactions, electronic-to-vibrational (E-V) energy transfer, relaxation of vibrational energy), and for studies of the dynamics of photodissociation/predissociation and photoionization/autoionization. The NO_2 PECs reported in this work may be instrumental to visualize some of the above processes.

[a]While this manuscript was underway Dr. Osman Atabek passed away suddenly; in this posthumous contribution the authors would like to pay homage to the scientist, colleague and friend.

WJ. Theory and Computation

Wednesday, June 21, 2023 – 1:45 PM

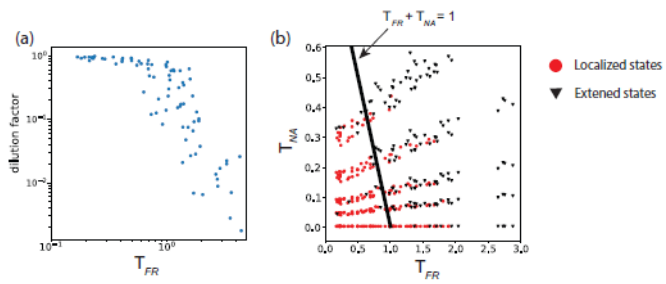
Room: 217 Noyes Laboratory

Chair: Daniel P. Tabor, Texas A&M University, College Station, TX, USA

WJ01 **1:45 – 2:00**

SURFACE CROSSING AND ENERGY FLOW IN MANY-DIMENSIONAL QUANTUM SYSTEMS

CHENGHAO ZHANG, *Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; MARTIN GRUEBELE, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; DAVID E LOGAN, *Department of Chemistry, Oxford University, Oxford, United Kingdom*; PETER GUY WOLYNES, *Department of Chemistry, Rice University, Houston, TX, USA*.



Vibrational energy flow in molecules, like the dynamics of other many dimensional finite systems, involves quantum transport across a dense network of near resonant states. For molecules in their electronic ground state, the network is ordinarily provided by anharmonic vibrational Fermi resonances. Surface crossing between different electronic states provides another route to chaotic motion and energy redistribution. We show that nonadiabatic coupling between electronic energy surfaces facilitates vibrational energy flow, and conversely, anharmonic vibrational couplings facilitate nonadiabatic electronic state mixing. A generalization of the Logan-Wolynes theory of quantum energy flow in many-dimensional Fermi resonance systems to the two-surface case gives a phase diagram describing the boundary between localized quantum dynamics and global energy flow. We explore these predictions and test them using a model inspired by the problem of electronic excitation energy transfer in the photosynthetic reaction center. Using an explicit numerical solution of the time dependent Schrödinger equation for this ten-dimensional model, we find quite good agreement with the expectations from the approximate analytical theory.

WJ02 **2:03 – 2:18**

A FULLY AB INITIO APPROACH TO THE EVALUATION OF VIBRATIONAL SPECTRA USING GAUSSIAN BASIS SETS

MARK A. BOYER, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*.

We have developed a black-box method to evaluate vibrational spectra using only the information provided by semi-classical *ab initio* molecular dynamics simulations. Using a distributed Gaussian basis set centered at the points sampled by an AIMD trajectories and a local harmonic approximation to the potential at each point, it is possible to obtain accurate vibrational spectra. By exploiting the locality of molecular vibrations, this method is applicable to the evaluation of spectra systems of moderate size. The judicious choice of Gaussian width parameters as well as selection augmentation of the basis with appropriate harmonic basis functions can lead to high-fidelity spectra even for relatively short trajectories.

This method provides a complement to perturbative approaches, as it treats low-frequency vibrations accurately and is amenable to systems with multiple low-lying energetic minima. Furthermore, by running more AIMD trajectories, it is possible to refine the vibrational spectrum obtained.

WJ03 **2:21 – 2:36**

SUBPERCENT AND SUBPROMILLE INTENSITY CALCULATIONS OF ROVIBRATIONAL LINES OF MULTIPLE BANDS

OLEG L. POLYANSKY, *Department of Physics and Astronomy, University College London, London, United Kingdom.*

I will review our recent (up to one or two years) and very recent (months and days) results on the line intensity calculations and comparison with high accuracy and extra high accuracy experimental observations. High accuracy is about 1 % and extra high accuracy is better than 0.1 % (pro-mille). I will focus mostly on CO and CO_2 line intensities. Time permitting the results on water, ozone, HCN and N_2O will be mentioned.

WJ04 **2:39 – 2:54**

STEALING IDEAS FROM ELECTRONIC STRUCTURE THEORY TO IMPROVE VIBRATIONAL CALCULATIONS. PART I - THE HAMILTONIAN

JAMES H. THORPE, *Department of Chemistry, Southern Methodist University, Dallas, TX, USA.*

The fields of electronic and vibrational structure theory have largely evolved independently over the years. Demonstrative of this is the fact that the electronic structure community has generally embraced coupled-cluster wavefunctions as the gold standard for small, well-behaved systems, while vibrational structure practitioners tend to prefer treatments based on vibrational perturbation theory or vibrational configuration interaction. While this is not surprising — the two fields face dramatically different challenges and goals — one does wonder if ideas from one can be used to improve or inform the other.

To this point, Part I of this presentation borrows the concept of normal-ordered strings of creation/annihilation operators from electronic coupled-cluster to develop a new form of the vibrational Hamiltonian which is amenable to vibrational many-body (VMP,VCI,VCC) calculations. This "GEN" Hamiltonian generates greatly simplified equations to be implemented in black-box software, and folds-in higher-order many-body effects into lower-order treatments. The goal is to present these (somewhat complicated) concepts in a way accessible to theorists from both communities, as well as to the broader field of spectroscopists as a whole.

WJ05 **2:57 – 3:12**

STEALING IDEAS FROM ELECTRONIC STRUCTURE THEORY TO IMPROVE VIBRATIONAL CALCULATIONS. PART II - THE WAVEFUNCTION

JAMES H. THORPE, *Department of Chemistry, Southern Methodist University, Dallas, TX, USA.*

The fields of electronic and vibrational structure theory have largely evolved independently over the years. Demonstrative of this is the fact that the electronic-structure community has generally embraced coupled-cluster wavefunctions as the gold standard for small, well-behaved systems, while vibrational structure practitioners tend to prefer treatments based on vibrational perturbation theory or configuration interactions. While this is not surprising — the two fields face dramatically difference challenges and goals — one does wonder if ideas from one can be used to improve or inform the other.

To this point, Part II of this presentation borrows the diagrammatic techniques of electronic coupled-cluster to develop a set of Davidson-like corrections to the vibrational CI wavefunction, which help resolve some of the size-consistency problems that can arise in VCI calculations. The goal is to present these (somewhat complicated) concepts in a way accessible to theorists from both fields, as well as to the broader field of spectroscopists as a whole.

Intermission

WJ06 **3:52 – 4:07**

RELIABILITY AND RESONANCES IN VIBRATIONAL PERTURBATION THEORY

JULIEN BLOINO[a], *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; MARCO FUSÈ, *Department of Molecular and Translational Medicine, University of Brescia, Brescia, Italy*; QIN YANG, *Institute of Organic Chemistry and Biochemistry, Czech Academy of Science, Prague, Czechia*.

The availability of integrated solutions in user-friendly computational packages coupled with capabilities of modern hardware have facilitated the inclusion of anharmonicity in the simulation of vibrational spectra over the recent years. Cost-effective methods such as the second-order vibrational perturbation theory (VPT2) can even be applied to molecular systems comprising dozens of atoms. However, the well-documented problem of resonances, their identification and correction remain a critical pitfall of perturbative methods. Recent works have highlighted the sensitivity of band intensities to even subtle resonance effects, underlying the importance of a correct treatment to predict accurate spectral band-shapes.[1] This aspect is even more critical with chiroptical spectroscopies whose signal is weak.

In this contribution, we analyze the impact of resonances and explore strategies to identify and correct them, not only in energy calculations, but also on the transition moments.[2] A selection of representative molecules of different sizes was used for the study. We show how resonances can affect the overall spectral band-shapes, especially on chiroptical spectroscopies, and the accuracy achievable once they are properly treated, even beyond the fingerprint region.[3,4]

[1] Q. Yang, M. Mendolicchio, V. Barone, J. Bloino, *Front. Astron. Space Sci.* 2021, **8**, 665232

[2] Q. Yang, J. Bloino, *J. Phys. Chem. A* 2022, **126**, 9276-9302

[3] M. Fusè, G. Longhi, G. Mazzeo, S. Stranges, F. Leonelli, G. Aquila, E. Bodo, B. Brunetti, C. Bicchi, C. Cagliero, J. Bloino, S. Abbate, *J. Phys. Chem. A* 2022, **126**, 6719-6733

[4] Q. Yang, J. Kapitán, P. Bouř, J. Bloino, *J. Phys. Chem. Lett.* 2022, **13**, 8888-8892.

[a]Financial support from the Italian Ministry of University and Research for the financial support (PRIN Grant num. 2020HTSXMA) is acknowledged.

WJ07 **4:10 – 4:25**

HIGHLY ACCURATE THERMOCHEMICAL PROPERTIES OF THE VINOXY RADICAL

MEGAN R BENTLEY, *Chemistry, University of Florida, Gainesville, FL, USA*; JAMES H. THORPE, *Department of Chemistry, Southern Methodist University, Dallas, TX, USA*; PETER R. FRANKE, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; BRYAN CHANGALA, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; BRANKO RUSCIC, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*.

The vinoxy radical is an important intermediate in the combustion of hydrocarbon fuels, however, experimental investigations have faced considerable challenges in obtaining estimates of desired thermochemical quantities to within 10 kJ/mol. Computational studies thus account for the bulk of the Active Thermochemical Tables (ATcT) provenance for vinoxy, with the uncertainty of the ATcT enthalpy of formation lingering near 0.6 kJ/mol. In an attempt to reduce the uncertainty of these quantities, we apply an extended version of the HEAT model chemistry currently under development to the vinoxy radical and its associated cations. These treatments elucidate bond energies of small molecules containing first- and second-row atoms to within 20 cm^{-1}. Composite techniques provide very accurate zero-point energies for use in the thermochemical protocol and fundamental vibrational frequencies that are in excellent agreement with experiment. Anharmonic resonances are reanalyzed, suggesting an uncharacteristically complex CH stretching region. To compound matters, very little information is available concerning the photoionization spectrum of vinoxy, which is thought to undergo a large geometry change upon ionization. We report the adiabatic ionization energy for the vinoxy radical and a simulated photoionization spectrum generated from a harmonic autocorrelation function approach.

WJ08 **4:28 – 4:43**

ACTINIDE M-EDGE X-RAY SPECTROSCOPY USING SPINOR-BASED COUPLED-CLUSTER TECHNIQUES

XUECHEN ZHENG, CHAOQUN ZHANG, LAN CHENG, *Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA*.

We present spinor-based relativistic equation-of-motion coupled-cluster (EOM-CC) calculations for the actinide M-edge x-ray absorption spectra for uranyl, neptunyl, and plutonyl-containing molecules. An efficient implementation of core-valence separation for the spinor-based EOM-CC methods have enabled the calculations of the x-ray absorption spectra with rigorous treatments of relativistic and correlation effects. The benchmark calculations demonstrate the importance of the spin-orbit coupling and solvation effects on the computed spectra. The computed spectra are then compared with high-resolution x-ray absorption spectra extracted from the resonant inelastic x-ray spectroscopy (RIXS) map. The covalency of actinide 5f electrons is discussed.

WJ09 **4:46 – 5:01**

ARTIFICIAL INTELLIGENCE FOR AB INITIO ENERGIES: THE "AI ENERGIES" DATABASE

NIKE DATTANI[a], *Computer Spectroscopy Group, HPQC Labs, Waterloo, Canada*.

The AI ENERGIES database was first made available on GitHub in January 2018, and by February 2023 has had more than 600 commits involving *ab initio* ground and excited state energies for various atoms and molecules with various charges, spin multiplicities and geometries. It attempts to make available all *ab initio* calculations ever done by participants, and to use artificial intelligence to predict energies for systems that are too difficult for running full *ab initio* calculations.

What began as a repository to preserve output files and summaries of various calculated energies for the Li_2 molecule, and to make them available for artificial intelligence training, has grown now to include molecules as big as $C_{12}H_{10}B_2N_2$, and state-of-the-art benchmark calculations on systems as small as the H atom but with basis sets as large as aug-cc-pV10Z.

The repository also contains an FCI database which attempts to curate and make available all full configuration interaction energies known, and it contains a coupled cluster (CC) database which attempts to include an unusually thorough level of detail about all coupled cluster calculations ever done by participants. By including the maximum RAM and CPU time used, along with as many details about the system for which an FCI or CC calculation is performed, and details about the hardware used, estimations can be made in advance for the cost (or feasibility) of doing for example a CCSDTQ(P) calculation on a singlet C_{2v} system with 8 correlated electrons in 200 spatial orbitals with three CPU threads: the estimation in this case would be approximately two weeks with 147GB of RAM. In this way, scientists can refer to the database and the predictions that it is able to provide, which can help with the planning of projects and the evaluation of a project's feasibility.

The repository additionally contains a `GENBAS` file which contains 70,000+ lines of Gaussian basis set exponents and contraction coefficients with an unusually large amount of care towards reproducibility and inclusion of some of the most coveted and specialized basis sets that are not available in the ordinary basis set repositories available online.

Anyone is able to contribute data to the AI ENERGIES database on GitHub (https://github.com/HPQC-LABS/AI_ENERGIES), and this can help them preserve and organize data that might otherwise get accidentally deleted or lost. The database also has a Digital Object Identifier (DOI): https://doi.org/10.5281/zenodo.5529103

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WJ10 **5:04 – 5:19**

SUPER-CORRELATION CONSISTENT COMPOSITE APPROACH (S-CCCA) FOR LATER 3D AND 4D TRANSITION METAL MOLECULES

BRADLEY WELCH, ANGELA K. WILSON, *Department of Chemistry, Michigan State University, East Lansing, MI, USA*.

The super-correlation consistent composite approach (s-ccCA) has been successful in the prediction of accurate dissociation energies for early 3d and 4d transition metal-containing species[a]. As one moves across the periodic table the computational cost requirements also increase. Thus, this increase in computational cost is an important consideration in the development of composite methodologies. Here we present s-ccCA for the late 3d and 4d transition metal molecules with an important modification, employing a simple Continued Fraction approximant. This approach was evaluated against s-ccCA results on the early 3d and 4d species. This reduced cost s-ccCA was then applied to the late 3d and 4d species, and the resulting dissociation energies were compared with state-of-the-art Resonant Two-Photon Ionization bond dissociation energies [bcd].

[a] Mol. Phys. 119, (2021)
[b] J. Chem. Phys. 153, 074303, (2020)
[c] J. Chem. Phys. 146, 144310, (2017)
[d] J. Chem. Phys. 151, 044302, (2019)

WK. Structure determination

Wednesday, June 21, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: Martin A. Suhm, Georg-August-Universität Göttingen, Göttingen, Germany

WK01 **1:45 – 2:00**

INFLUENCE OF FOURTH-ORDER VIBRATIONAL CORRECTIONS ON SEMI-EXPERIMENTAL STRUCTURES ($r_e{}^{SE}$) OF LINEAR MOLECULES

PETER R. FRANKE, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*.

Semi-experimental structures ($r_e{}^{SE}$) are derived from experimental ground-state rotational constants combined with theoretical vibrational corrections. They permit a meaningful comparison with equilibrium structures based on high-level *ab initio* computations. Typically, the vibrational corrections are evaluated by second-order vibrational perturbation theory (VPT2). The amount of error introduced by this approximation is generally thought to be small; however, it has not been thoroughly quantified. Herein, we assess the accuracy of the theoretical vibrational corrections by extending the treatment to fourth-order (VPT4) for a series of small, linear molecules. When possible, comparisons to exact variational results are also made. Typical corrections to bond distances are on the order of 10^{-5} Å. Treatment of vibrational effects beyond VPT2 will thus be important when one wishes to know bond distances confidently to four decimal places. More substantial corrections (10^{-4} Å) are seen for HNC, CNCN, and NCCN. Certain molecules with shallow bending potentials, e.g., HOC^+, are not amenable to a VPT2 description and are not improved by VPT4.

WK02 **2:03 – 2:18**

EQUILIBRIUM MOLECULAR STRUCTURES : HOW GOOD ARE COMPOSITE SCHEMES?

NITAI PRASAD SAHOO, PETER R. FRANKE, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; JOHN F. STANTON, *Physical Chemistry, University of Florida, Gainesville, FL, USA*.

Molecular structures help determine spectroscopic parameters that allow molecular identification and reveal qualitative information about bonding, energetics and other things. Today, the most satisfactory method for determining very high-accuracy structures is a mixed experimental-theoretical approach that uses ground state rotational constant data from microwave and/or high-res vibrational spectroscopy and vibrational corrections obtained from quantum-chemical calculations (r_e^{SE}). Here we consider two different ab initio composite schemes for obtaining equilibrium structures (energy scheme vs geometry scheme) and compare them to the semi-experimental equilibrium structure. The comparison is performed for a test set of ten molecules which includes ome diatomics, linear triatomics and a few polyatomics. The ab initio calculations were performed using three levels of composite chemical recipes. The results showed that as the overall rigor of calculation is increased, the semi-experimental and the ab initio numbers agree with each other within the desirable level of accuracy (< 0.0003 $\AA$) for all molecules in the test set. The composite recipe based on correcting the PES (energy scheme) and the one dependent on correcting the geometry directly (geometry scheme) also show excellent agreement with each other.

WK03 **2:21 – 2:36**

MICROWAVE SPECTRUM AND STRUCTURE OF THIOBENZOIC ACID (C_6H_5COSH)

AARON J REYNOLDS, KENNETH R. LEOPOLD, *Chemistry Department, University of Minnesota, Minneapolis, MN, USA*.

We report the characterization of thiobenzoic acid (C_6H_5COSH) by broadband and cavity microwave spectroscopy. Assignment of the chirped-pulse spectrum was carried out with the DAPPERS software. Using cavity spectroscopy, isotopologue spectra were observed for all carbons (^{13}C), the oxygen (^{18}O), and the sulfur (^{34}S and ^{33}S). Hyperfine structure for ^{33}S was observed and quadrupole coupling constants were determined. Spectra of the deuterated species were obtained via H/D exchange in a mixture of thiobenzoic acid and D_2O. A Kraitchman analysis was performed using all heavy-atom isotopic data, and yielded excellent agreement with M06-2X 6-311++G(d,p) calculations. No conformers or tautomers were observed.

WK04 **2:39 – 2:54**

ROTATIONAL SPECTROSCOPIC STUDIES OF *PARA*-NITROBENZOIC ACID, *PARA*-AMINOBENZOIC ACID, *PARA*-CHLOROBENZOIC ACID, AND *PARA*-HYDROXYBENZOIC ACID

MOHAMAD H. AL-JABIRI, ARSH SINGH HAZRAH, *Department of Chemistry, University of Alberta, Edmonton, AB, Canada*; ARAN INSAUSTI, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*; WOLFGANG JÄGER, *Department of Chemistry, University of Alberta, Edmonton, AB, Canada*.

*p*ara-substituted benzoic acids, such as *p*ara-nitrobenzoic acid, *p*ara-aminobenzoic acid, *p*ara-chlorobenzoic acid, and *p*ara-hydroxybenzoic acid, play important roles in atmospheric chemistry and are used as precursors for a wide range industrial products. Surprisingly, there are no high-resolution spectroscopic studies of these compounds, and we describe here their rotational spectroscopic investigations combined with electronic structure calculations. The rotational spectra were recorded using a 2 to 6 GHz chirped-pulse Fourier transform microwave spectrometer, which is based on the design by Pate et al.[1] Experimentally, all four substituted benzoic acids were found to exist in the cis-configuration, the global minimum energy configuration, of the carboxylic acid group. In all instances, except *para*-aminobenzoic acid, the global minimum structure is planar. Nudged elastic band calculations[2] for the wagging motion of the amino group in *para*-aminobenzoic acid suggest that it is a barrierless large amplitude motion and indeed, no tunnelling splittings were observed in the spectra. For *para*-chlorobenzoic acid, the nuclear quadrupole hyperfine structures of the ^{35}Cl and ^{37}Cl isotopologues were measured and analyzed. In the case of *para*-hydroxybenzoic acid two conformers were experimentally and theoretically identified. We noticed in the theoretical structures of the trans-conformers that the carboxylic acid group is pushed slightly out of plane, depending on the nature of the *para*-substituent. We were able to correlate the out-of-plane angle with the corresponding Hammett constant[3] via the molecular electrostatic potential.[4] [1]Pérez, C., et al., Chem. Phys. Lett. 2013, 571, 1–15. [2]Ásgeirsson, V., et al., J. Chem. Theory Comput. 2021, 17 (8), 4929–4945. [3]Hansch, C., et al., Chem. Rev. 1991, 91 (2), 165–195. [4]Sayyed, F. B., et al., New J. Chem. 2009, 33 (12), 2465–2471.

WK05 **2:57 – 3:12**

COMPARISON OF AN IMPROVED SEMI-EXPERIMENTAL EQUILIBRIUM STRUCTURE ($r_e{}^{SE}$) OF KETENE TO A HIGH-LEVEL THEORETICAL EQUILIBRIUM STRUCTURE

HOUSTON H. SMITH, BRIAN J. ESSELMAN, SAMUEL A. WOOD, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

The millimeter-wave spectrum of ketene has been collected and analyzed from 130 GHz to 750 GHz and provided highly precise spectroscopic constants from a sextic S-reduced Hamiltonian. The synthesis of deuteriated samples enabled the spectroscopic measurements of five previously unreported ketene isotopologues. Combined with previous work, this resulted in a new highly precise and accurate semi-experimental ($r_e{}^{SE}$) structure for ketene from 32 independent moments of inertia. This $r_e{}^{SE}$ structure was determined with the experimental rotational constants from all available isotopologues, together with computed vibration-rotation interaction and electron-mass distribution corrections from coupled-cluster singles, doubles, and perturbative triple calculations [CCSD(T)/cc-pCVTZ]. The 2σ uncertainties of the parameters of the $r_e{}^{SE}$ are ≤ 0.007 Å and $0.014°$ for the bond distances and independent angle, respectively. Only S-reduced spectroscopic constants were used in the structure determination, due to a breakdown in the A reduction of the Hamiltonian for the most prolate ketene species. All four structural parameters are in agreement with the "best theoretical estimate" (BTE) calculated from the CCSD(T)/cc-pCV6Z r_e structure with corrections for extrapolation to the complete basis set, the incomplete treatment of electron correlation, the diagonal Born-Oppenheimer breakdown, and relativistic effects. The discrepancies between the current $r_e{}^{SE}$ and previously reported $r_e{}^{SE}$ structures will be discussed.

WK06 **3:15 – 3:30**

THE PRECISE EQUILIBRIUM STRUCTURE DETERMINATION OF CHLOROBENZENE (C_6H_5Cl) BY MICROWAVE AND MILLIMETER-WAVE ROTATIONAL SPECTROSCOPY

NATALIE A. SCHULER, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; NITAI PRASAD SAHOO, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; MARIA ZDANOVSKAIA, P. MATISHA DORMAN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; BRYAN CHANGALA, MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*; BRIAN J. ESSELMAN, R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

The rotational spectra of many isotopologues of chlorobenzene (C_6H_5Cl) have been collected over portions of the 2 to 360 GHz frequency region. Several deuterium-enriched samples were generated via Grignard reaction of bromochlorobenzenes with a D_2O quench. The measured transitions of 22 isotopologues were least-squares fit to A- and S-reduced, sextic distorted-rotor Hamiltonians. The resultant rotational constants of all available isotopologues, with CCSD(T)/cc-pCVTZ corrections for vibration-rotation interaction and electron-mass distribution, were used to determine a highly precise semi-experimental equilibrium (${r_e}^{SE}$) structure of chlorobenzene. The preliminary ${r_e}^{SE}$ structure proved critical for finding ^{13}C-atom isotopologues of the deuterium-substituted species in the available rotational spectra by enabling more accurate predictions of the rotational constants for these very low-abundance species. Transitions for several more isotopologues are expected to be available in the collected data. The highly accurate and precise ${r_e}^{SE}$ structure will be compared to a CCSD(T)/cc-pCV5Z equilibrium (r_e) and ${r_e}^{SE}$ structures of other molecules determined with the same methodology.

Intermission

WK07 **4:10 – 4:25**

SIZE-SELECTED SPECTRA OF WATER CLUSTERS USING ISOTOPE DILUTION

CRISTOBAL PEREZ, *Faculty of Science - Department of Physical Chemistry, University of Valladolid, Valladolid, Spain*; CHANNING WEST, BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

Molecular rotational spectroscopy is a powerful for determining the structures of molecular clusters. A key feature of the technique is the high spectral resolution that makes it possible to record the spectra of the large number of isomers generated in the pulsed jet expansion without significant spectral overlap. However, when many clusters are produced the spectral line density can make it difficult to identify individual spectra. This work explores the potential to assign a cluster size for each transition in the spectrum of water clusters using isotopic dilution. Previous work on the structures of water clusters used ^{18}O water "spiking" to obtain the oxygen atom framework geometry from the analysis of the set of isotopomers coming from single $H_2{}^{18}O$ incorporation into the water cluster. That work showed that, to a good approximation, the $H_2{}^{18}O$ substitutes into the geometry according to simple statistics. This observation suggests that the water cluster size for each transition in the spectrum can be determined by the reduction in the signal intensity when a known percentage of $H_2{}^{18}O$ is spiked into the water sample. The success of this isotope dilution approach to generating seize-selected cluster spectra is illustrated using the known assignments of water cluster spectra. The analysis method is then used to identify a weak spectrum for the water heptamer that was previously unassigned. On the large water cluster size limit, the method led to the successful identification of four hydrogen bond network isomers of $(H_2O)_{14}$ and a polar isomer of $(H_2O)_{16}$. Many transitions are left unassigned including many in the N=8-10 size range based on their isotope dilution behavior.

WK08 **4:28 – 4:43**

THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE GAS-PHASE HETERODIMERS, (*E*)-1,2,3,3,3-PENTAFLUOROPROPENE-ARGON AND (*E*)-1,2,3,3,3-PENTAFLUOROPROPENE-ACETYLENE

KAZUKI M. TAYAMA, HELEN O. LEUNG, MARK D. MARSHALL, *Chemistry Department, Amherst College, Amherst, MA, USA*.

(*E*)-1,2,3,3,3-pentafluoropene results from the formal replacement of one of the two geminal fluorine atoms in 1,1,2-trifluoroethylene (the one located *cis* to the fluorine on the singly halogenated carbon) with a trifluoromethyl group. As determined from the analysis of the rotational spectra of the respective species, the structure of (*E*)-1,2,3,3,3-pentafluoropene-argon is consistent with the often-observed preference for maximizing the number of argon-heavy atom interactions, with argon locating away from the olefinic place and in the FC=CCF cavity, which is in many ways similar to the structure of 1,1,2-trifluoroethylene. However, the replacement of the fluorine atom with the trifluoromethyl group has a significant effect on the structure of the heterodimer with acetylene. Whereas the acetylene interacts with the geminal fluorine-carbon pair in the ethylene, when binding to the propene it does so via the cis fluorine-carbon pair.

WK09 **4:46 – 5:01**

THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE GAS-PHASE HETERODIMERS, (*Z*)-1,2,3,3,3-PENTAFLUOROPROPENE-ARGON AND (*Z*)-1,2,3,3,3-PENTAFLUOROPROPENE-ACETYLENE

HELEN O. LEUNG, MARK D. MARSHALL, MAX HAUSCHILDT, ELIZABETH A. ROSE, *Chemistry Department, Amherst College, Amherst, MA, USA*.

(*Z*)-1,2,3,3,3-pentafluoropene results from the formal replacement of one of the two geminal fluorine atoms in 1,1,2-trifluoroethylene (the one located *trans* to the fluorine on the singly halogenated carbon) with a trifluoromethyl group. Structures for the gas-phase heterodimers of (*Z*)-1,2,3,3,3-pentafluoropene with argon and with acetylene are obtained from the analysis of the microwave spectra of each complex. While the binding of argon to the two olefins is similar in both cases, with argon locating in the FC=CF cavity, but away from the olefinic plane, the predicted structures of the corresponding heterodimers with acetylene show the possibility of distinct differences.

WK10 **5:04 – 5:19**

DETERMINATION OF THE ABSOLUTE CONFIGURATION AND ENANTIOMERIC EXCESS OF MOLECULES THAT ARE CHIRAL BY VIRTUE OF DEUTERIUM SUBSTITUTION USING MOLECULAR ROTATIONAL SPECTROSCOPY

ZOUA PA VANG, MITCHELL D MILLS, JOSEPH R CLARK, *Department of Chemistry, Marquette University, Milwaukee, WI, USA*; JUSTIN L. NEILL, REILLY E. SONSTROM, *BrightSpec Labs, BrightSpec, Inc., Charlottesville, VA, USA*; KEVIN J MAYER, CHANNING WEST, MARTIN S. HOLDREN, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*; HALEY N. SCOLATI, *Department of Chemistry, University of Virginia, Charlottesville, VA, USA*; BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

New techniques for chiral analysis have recently emerged from the field of rotational spectroscopy. Traditional approaches to chiroptical spectroscopy, like circular dichroism, produce chiral signatures that are too weak for practical applications in rotational spectroscopy. The introduction of microwave three-wave mixing spectroscopy by Patterson, Schnell, and Doyle in 2013 renewed interest in chiral analysis by rotational spectroscopy. Work in the field has included the development of a chiral derivatization method that uses noncovalent interactions to generate complexes between the analyte and a small, chiral "tag" molecule in the pulsed jet expansion used in many Fourier transform microwave spectroscopy instruments. Recently, there has been increasing interest in using deuterium incorporation to improve the safety and efficacy of active pharmaceutical ingredients (APIs). The most chemically specific modification of the API needed to achieve improved drug performance can potentially involve the incorporation of a single deuterium atom at a prochiral R_1-CH_2-R_2 position. Applications of rotational spectroscopy approaches to chiral analysis will be discussed in the context of aiding the development of catalytic methods to add a single deuterium at the enzyme targeted benzylic CH_2 position. The relative strengths and weaknesses of three-wave mixing and chiral tag rotational spectroscopy in meeting the needs of rapid analysis of the enantioisotopomers produced using this new chemistry will be discussed.

WK11 **5:22 – 5:37**

CHARACTERIZING THE GAS-PHASE HETERODIMERS OF THE CHIRAL TAGGING CANDIDATES *TRANS*-1,3,3,3-TETRAFLUORO-1,2-EPOXYPROPANE AND 3,3,3-TRIFLUORO-1,2-EPOXYPROPANE BY QUANTUM CHEMISTRY AND MICROWAVE SPECTROSCOPY

HELEN O. LEUNG, MARK D. MARSHALL, JORDAN M. AUCOIN, *Chemistry Department, Amherst College, Amherst, MA, USA*.

As part of our efforts in evaluating substituted oxiranes for use as potential chiral tags for the conversion of enantiomeric molecules into spectroscopically distinct diastereomeric complexes for chiral analysis, we examine the gas-phase heterodimers formed between two such species using quantum chemistry and microwave spectroscopy. The lowest energy isomers of the various diastereomers of 3,3,3-trifluoro-1,2-epoxypropane–trans-1,3,3,3-tetrafluoro-1,2-epoxypropane are predicted to share structural features with the previously characterized 3,3,3-trifluoro-1,2-epoxypropane homodimers. Like the homodimers, the diastereomeric heterodimers have significantly different rotational constants, and thus, easily distinguishable microwave spectra. The spectrum of (*S*)-3,3,3-trifluoro-1,2-epoxypropane–(1*R*, 2*S*)-trans-1,3,3,3-tetrafluoro-1,2-epoxypropane and its enantiomer has been obtained and analyzed to be consistent with the quantum chemistry predictions. Despite being predicted at a lower energy, the search for the spectrum of (*S*)-3,3,3-trifluoro-1,2-epoxypropane–(1*S*, 2*R*)-trans-1,3,3,3-tetrafluoro-1,2-epoxypropane and its enantiomer is on-going.

WL. Mini-symposium: Infrared Spectroscopy in the JWST Era

Wednesday, June 21, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: Sergio Ioppolo, Aarhus University, Aarhus, Denmark

WL01 ***INVITED TALK*** **1:45 – 2:15**

AN OBSERVATIONAL AND THEORETICAL VIEWPOINT ON PAHS IN THE JWST ERA

AMEEK SIDHU, *Department of Physics and Astronomy, University of Western Ontario, London, Ontario, Canada*.

Polycyclic Aromatic Hydrocarbons (PAHs) are known to dominate the infrared spectra of a wide range of objects in the Universe. The earlier space missions, the Infrared Space Observatory and the Spitzer Space Observatory have revealed the spectral richness of the mid-infrared spectrum and have been critical in revealing the ubiquitous nature of PAHs in the Universe. Now, the James Webb Space Telescope (JWST), with its unprecedented spectral resolution and wavelength coverage for PAHs, is set to revolutionize the field of PAH astrochemistry. In this talk, I will give an overview of the richness of PAH emission as seen in high-resolution spectra of the Orion Bar obtained through the ERS program PDRS4All ID:1288. This new JWST data emphasizes the importance of sophisticated theoretical models in fully understanding the molecular physics underlying PAH emission. One of the limitations of developing a theoretical model of PAHs is the lack of experimental data on PAH characteristics. In this talk, I will also discuss the relevant molecular data required to develop the photochemical evolution model of PAHs.

WL02 **2:21 – 2:36**

ANHARMONICITY AND DEUTERATION IN THE IR ABSORPTION AND EMISSION SPECTRA OF PHENYLACETYLENE

VINCENT J. ESPOSITO, *Planetary Systems Branch, NASA Ames Research Center, Moffett Field, CA, USA*.

Emission from polycyclic aromatic hydrocarbons (PAHs) is believed to dominate the infrared (IR) spectra of a wide variety of astronomical objects and environments. Quantum chemically computed PAH spectra, combined with experimental studies, are indispencible to analyze and interpret astronomical observations. To provide a foundation for the analysis of the high-fidelity JWST data, new computational tools have been developed at NASA Ames to produce fully anharmonic IR absorption and cascade emission spectra of various PAHs, including deuterated species. The substituted, aromatic molecule, phenylacetylene, is used as a test case for validation of the newly developed theoretical methods via comparison with IR absorption and emission experiments. This work sets the stage for future implementation of the code as a tool for populating the NASA Ames PAH IR Spectroscopic Database (PAHdb) with anharmonic spectra of vast numbers of PAHs for use in the analysis of astronomical PAH data.

WL03 **2:39 – 2:54**

NON-LTE SPECTRUM OF JET-COOLED NAPHTHALENE

SHUBHADIP CHAKRABORTY, *Department of Chemistry, GITAM School of Science, GITAM Deemed-to-be-University, Bengaluru, Karnataka, India*; GIACOMO MULAS, *Osservatorio Astronomico di Cagliari, Istituto Nazionale di Astrofisica (INAF), Selargius, Italy*; OLIVIER PIRALI, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*; MANUEL GOUBET, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*; PASCALE SOULARD, PIERRE ASSELIN, *CNRS, De la Molécule aux Nano-Objets: Réactivité, Interactions, Spectroscopies, MONARIS, Sorbonne Université , PARIS, France*; SAMIR KASSI, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*; LUDOVIC BIENNIER, ROBERT GEORGES, *IPR UMR6251, CNRS - Université Rennes 1, Rennes, France*.

IR spectrum of naphthalene was recorded under jet-cooled conditions around 12.7 μm using the jet-AILES setup, coupled to a Fourier transform spectrometer (Bruker IFS 125 HR) equipping the AILES beamline of the synchrotron SOLEIL, and between 1.65 and 1.7 μm using cavity ringdown spectroscopy and a set of distributed-feedback laser diodes. In the slit nozzle supersonic expansion, an efficient rotational relaxation of naphthalene occurs resulting in a rotational temperature of about 25 K, while the vibrational cooling is limited due to an insufficient number of two-body collisions. This causes an interesting non-LTE situation, favorable for the detection of hot bands: the low rotational temperature drastically simplifies the rotational structure and magnifies the Q-branches, while the higher vibrational excitation allows the presence of many transitions from moderately excited vibrational states. The observed hot bands at 12.7 μm were assigned with the aid of the AnharmoniCaOs software developed by some of us. Non-thermal populations of individual vibrational states from which transitions originate were derived further, allowing us to simulate the non-LTE CRD spectrum recorded around 1.67 μm region.

WL04 **2:57 – 3:12**

NEAR-INFRARED SPECTROSCOPY OF DISSOCIATED NAPHTHALENE IN A RADIOFREQUENCY PLASMA

JULIEN LECOMTE, NICOLAS SUAS-DAVID, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*; CHRISTINE CHARLES, ROD W BOSWELL, *Research School of Physics, Australian National University, Canberra, ACT, Australia*; ESZTER DUDÁS, *Département "Physique Moléculaire", Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, Rennes, France*; SAMIR KASSI, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*; LUCILE RUTKOWSKI, ROBERT GEORGES, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*.

Polycyclic aromatic hydrocarbons (PAHs) are abundant organic molecules detected in several objects in the universe, such as molecular clouds in the interstellar medium (ISM) [a]. Their structure can be modified through plasma-driven processes occurring in the ISM. The present study focuses on the dissociation of naphthalene ($C_{10}H_8$) in a radiofrequency (RF) plasma, probed using cavity ringdown spectroscopy (CRDS) in the near-infrared. Namely, the low-power RF plasma source, called Platypus, is adapted from a small plasma thruster ("Pocket Rocket") designed by the Space Plasma Power and Propulsion laboratory of the ANU [b]. A stable supersonic jet plasma is generated by expanding a mixture of argon and dissociated $C_{10}H_8$ into a vacuum chamber through a 20 mm long, 4 mm wide slit nozzle [c]. The jet-cooled fragmented $C_{10}H_8$ is finally probed with the ultra-sensitive CRDS technique. We recorded a spectrum from 5950 to 6120 cm^{-1} composed of several hundred transitions originating from many different molecules, radicals, and probably ions [d].

[a] L.J. Allamandola et al., The Astrophysical Journal 290, L25-L28 (1985).
[b] C. Charles and R. W. Boswell. Plasma Sources Science and Technology, 21.2, 022002 (2012).
[c] E. Dudás, Ph.D Thesis, 149-162 (2021).
[d] M. Alliati et al., The Journal of Physical Chemistry A 123.10, 2107-2113 (2019).

WL05 **3:15 – 3:30**

INFRARED SPECTROSCOPY OF PYRENE FROM 14 TO 723K

SHUBHADIP CHAKRABORTY, *Department of Chemistry, GITAM School of Science, GITAM Deemed-to-be-University, Bengaluru, Karnataka, India*; GIACOMO MULAS, *Osservatorio Astronomico di Cagliari, Istituto Nazionale di Astrofisica (INAF), Selargius, Italy*; MATHIAS RAPACIOLI, *LCPQ, Université de Toulouse 3 - CNRS, Toulouse, France*; KARINE DEMYK, CHRISTINE JOBLIN, *IRAP, Université de Toulouse 3 - CNRS, CNES, Toulouse, France*.

The mid-infrared emission features at 3.3, 6.2, 7.7, 8.6, 11.2 and 12.7 μm, observed in various astronomical objects are due the infrared fluorescence of thermally excited polycyclic aromatic hydrocarbons (PAHs) pumped by UV photons[a]. The observed bands are very broad and strongly affected by anharmonic effect. For the appropriate modelling of these bands, it is important to quantify anharmonicity parameters.

We have recorded the MIR spectrum of solid pyrene embedded in KBr from 14 to 723 K. From the evolution of the band positions and width with temperature we derived empirical anharmonicity parameters. In parallel we also simulated the spectrum of pyrene using *ab initio* and molecular dynamics simulations and compared with our experimental data[b],[c].

[a] Allamadolla et. al. Astrophys. J. 1985, 290, L25-L28
[b] Chakraborty et. al. J. Phys. Chem. A 2019, 123, 4139-4148
[c] Chakraborty et. al. J. Mol. Spectrosc. 2021, 378, 111466

Intermission

WL06 **4:10 – 4:25**

IR SPECTROSCOPY OF METALLO-FULLERENES: POTENTIAL ASTRONOMICAL PRESENCE?

JOOST M. BAKKER, *HFML-FELIX, Radboud University, Nijmegen, The Netherlands*; OLGA LUSHCHIKOVA, *Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria*; PETER LIEVENS, EWALD JANSSENS, *Laboratory of Solid State Physics and Magnestism, Katholieke Universiteit Leuven, Leuven, Belgium*; LEEN DECIN, *Institute of Astronomy, KU Leuven, Leuven, Belgium*; GAO-LEI HOU, *MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an, China*.

Efforts over 40 years still leave the source of astronomical infrared emission bands largely unidentified. We report the first laboratory infrared (6–25 μm) spectra of gas-phase fullerene-metal complexes, $[C_{60}\text{-Metal}]^+$ (Metal = Fe, V), and show with density functional theory calculations that complexes of C_{60} with cosmically abundant metals, including Li, Na, K, Mg, Ca, Al, V, Fe, all have similar spectral patterns. Comparison with observational infrared spectra from several fullerene-rich planetary nebulae demonstrates a strong positive linear cross-correlation. The infrared features of $[C_{60}\text{-Metal}]^+$ coincide with four bands attributed earlier to neutral C_{60} bands, and in addition also with several to date unexplained bands.

WL07 **4:28 – 4:43**

ON THE C-H STRETCHING MODE OF PROTONATED FULLERENES: AN IRMPD SPECTROSCOPY STUDY

LAURA FINAZZI, *FELIX Laboratory, Radboud University, Nijmegen, The Netherlands*; JULIANNA PALOTÁS, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*; JONATHAN K MARTENS, *Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands*; GIEL BERDEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; JOS OOMENS, *FELIX Laboratory, Radboud University, Nijmegen, The Netherlands*.

Fullerenes (C_{60}, C_{70} and C_{60}^+) have been found to be the largest molecular species identified to date in the interstellar medium (ISM), and it has already been suggested that protonated C_{60} and its complex analogues are among the most abundant C_{60} analogues present in space.

In a recent paper [a], we presented the first experimental IR spectrum of $C_{60}H^+$, although we were at the time unable to record the spectrum in the 3 μm range. In this work, the vibrational spectra of gaseous protonated and deuterated C_{60} are recorded via infrared multiple-photon dissociation (IRMPD) for the first time in the CH and CD stretching region using the free electron laser FELIX interfaced with a quadrupole ion trap. In addition to the CH stretch band, the spectrum of $C_{60}H^+$ shows in the 1600-3000 cm^{-1} range the presence of other bands, which could be tentatively assigned as combination bands and overtones. The bands observed in this region are obviously weak but well-resolved, entailing that they may be excellent diagnostic features for protonated C_{60}. In fact, the single CH stretching band of $C_{60}H^+$ falls at a frequency that is significantly lower than the CH stretching mode of aliphatic C-H bonds.

Comparison of the IR spectra of several ionized fullerene analogues to IR emission spectra from planetary nebulae suggests that these species may exist in significant amounts in the ISM and be responsible for the unidentified interstellar features.

[a] Nat. Astron. 4, 240–245 (2020)

WL08 **4:46 – 5:01**

FORMATION OF THE ACENAPHTYLENE CATION AS A COMMON C_2H_2-LOSS FRAGMENT IN DISSOCIATIVE IONIZATION OF THE PAH ISOMERS ANTHRACENE AND PHENANTHRENE

SHREYAK BANHATTI, STEPHAN SCHLEMMER, *I. Physikalisches Institut, University of Cologne, Cologne, Germany*; AUDE SIMON, HELOISE LEBOUCHER, *LCPQ, Université de Toulouse 3 - CNRS, Toulouse, France*; CHRISTINE JOBLIN, *IRAP, Université de Toulouse 3 - CNRS, Toulouse, France*; GABI WENZEL, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*; DANIEL RAP, BRITTA REDLICH, SANDRA BRÜNKEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*.

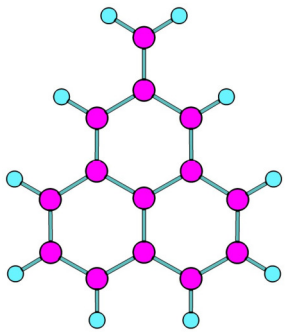
Polycyclic aromatic hydrocarbons (PAHs) are thought to be a major constituent of astrophysical environments, being the carriers of the ubiquitous aromatic infrared bands (AIBs) observed in the spectra of galactic and extra-galactic sources that are irradiated by ultraviolet (UV) photons. Small (2-cycles) PAHs were unambiguously detected in the TMC-1 dark cloud, showing that PAH growth pathways exist even at low temperatures. The processing of PAHs by UV photons also leads to their fragmentation, which has been recognized in recent years as an alternative route to the generally accepted bottom-up chemical pathways for the formation of complex hydrocarbons in UV-rich interstellar regions. Here we consider the $C_{12}H_8^+$ ion that is formed in our experiments from the dissociative ionization of anthracene and phenanthrene ($C_{14}H_{10}$) molecules. By employing infrared pre-dissociation (IRPD) spectroscopy in a cryogenic ion trap instrument coupled to the free-electron lasers at the FELIX Laboratory, we have recorded broadband and narrow line-width gas-phase IR spectra of the parent ($C_{14}H_{10}^+$) and fragment ($C_{12}H_8^+$) ions and also reference spectra of three low energy isomers of the latter. By comparing the experimental spectra to those obtained from quantum chemical calculations we have identified the dominant structure of the fragment ion to be the acenaphthylene cation for both isomeric precursors[a]. Ab initio molecular dynamics simulations are presented to elucidate the fragmentation process. This result reinforces the dominant role of species containing a pentagonal ring in the photochemistry of small PAHs.

[a] Banhatti et al., Phys. Chem. Chem. Phys. 24 (2022) 27343

WL09 **5:04 – 5:19**

EXTRATERRESTRIAL ISOMER OF PHENANTHRENE DICATION STUDIED BY TAGGING PHOTODISSOCIATION ION SPECTROSCOPY AND DFT CALCULATIONS

ALEKSANDR Y. PEREVERZEV, *Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands*; CORENTIN ROSSI, *Institut de Chimie Physique, Université Paris Saclay, CNRS, Orsay, France*; JANA ROITHOVÁ, *Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands*.



The search for the chemical structures that account for diffuse interstellar bands (DIBs) remains the main challenge in astrochemistry. It relies on experimental verification of structures obtained from stable isomers in laboratory conditions. The actual interstellar medium (ISM), however, is exposed to much harsher conditions. Herein we demonstrate the isomerization of small, doubly charged polyaromatic hydrocarbon phenanthrene obtained by electron ionization at relatively high electron energies. We performed electronic and vibrational tagging photodissociation spectroscopy measurements. Our results show that phenanthrene dication has a minor $C_{14}H_{10}{}^{2+}$ isomer, originating from the isomerization of phenanthrene dication during the harsh ionization process. Hole-burning spectroscopy experiments provided the IR spectrum of an isomer which could be assigned based on DFT calculations as a fully conjugated system representing the global minimum on the $C_{14}H_{10}{}^{2+}$ potential energy surface. The found isomer has no neutral closed-shell form and can only exist as a radical or as an ion. Finally, the IR spectrum of this isomer reveals features characteristic for the ISM, suggesting that it can potentially be a candidate for the DIB search. These results open new directions in searching for potential DIB candidates.

WL10 **5:22 – 5:37**

INFRARED SPECTROSCOPY OF THE CATIONIC –H FRAGMENTS OF METHYL-PAHS

GABI WENZEL, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*; AUDE SIMON, *LCPQ, Université de Toulouse 3 - CNRS, Toulouse, France*; SHREYAK BANHATTI, *I. Physikalisches Institut, University of Cologne, Cologne, Germany*; PAVOL JUSKO, , *Max Planck Institute for Extraterrestrial Physics, Munich, Germany*; STEPHAN SCHLEMMER, *I. Physikalisches Institut, University of Cologne, Cologne, Germany*; SANDRA BRÜNKEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; CHRISTINE JOBLIN, *IRAP, Université de Toulouse 3 - CNRS, CNES, Toulouse, France*.

Cationic benzylium and tropylium are two competitive isomers formed by dissociative ionization of methylbenzene (toluene). Infrared predissociation (IRPD) spectroscopy of ions tagged with Ne has been established as a powerful tool in disentangling these cationic species[a]. Methylated polycyclic aromatic hydrocarbons (PAHs) are expected to be abundant in space and their dissociative ionization could lead to the formation of both the benzylium- (XCH_2^+) and tropylium-like (XC_7^+) cations, which are expected to be the two lowest-energy isomers and whose isomerization process might impact their chemical evolution in photodissociation regions (PDRs). Here, we consider three methyl-PAHs as precursors, namely 1-methylpyrene, 2-methylnaphthalene, and 2-methylanthracene. Their cationic –H fragments, $C_{17}H_{11}^+$, $C_{11}H_9^+$, and $C_{15}H_{11}^+$, were probed at the Free Electron Laser for Infrared eXperiments (FELIX) Laboratory using IRPD spectroscopy at the FELion cryogenic ion trap beamline. Their strongest vibrational band is located at about 6.2 μm revealing the predominance of the XCH_2^+ isomers[b]. Isomer abundance measurements and spectral comparison to computed anharmonic IR spectra show that only this isomer is present for $C_{17}H_{11}^+$, whereas at least two isomers are present with a large abundance for the acene-derived species. Clear spectral evidence for the XC_7^+ isomer is found in the $C_{11}H_9^+$ case consistent with a relative abundance of 30 %. These results demonstrate the important role of steric hindrance in the formation of XC_7^+ and reveal the potential of XCH_2^+ to account for the aromatic IR emission band (AIB) observed at 6.2 μm in astrophysical environments, e.g. the planetary nebula NGC 7027 and the PDR at the Orion Bar.

[a] Jusko et al., ChemPhysChem 19 (2018) 3182
[b] Wenzel et al., J. Mol. Spectros. 385 (2022) 111620

RA. Plenary

Thursday, June 22, 2023 – 8:30 AM

Room: Foellinger Auditorium

Chair: Leslie Looney, University of Illinois at Urbana-Champaign, Urbana, IL, USA

RA01 **8:30 – 9:10**

A SELF-DRIVING LAB FOR THE ACCELERATED DISCOVERY OF ORGANIC SOLID-STATE LASERS

ALÁN ASPURU-GUZIK, *Department of Chemistry, University of Toronto, Toronto, Canada*.

In this talk, I will discuss our group's efforts toward the development of solid-state organic laser candidate emitting compounds. We employ automated systems to synthesize and characterize them, as well as make devices out of them. This is part of a large international collaboration that can be thought of as a delocalized laboratory.

RA02 **9:15 – 9:55**

SPECTROSCOPY OF METAL AND PHOSPHORUS BEARING MOLECULES: A WINDOW ON THE UNIVERSE

LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*.

Small molecules containing refractory elements such as metals and phosphorus hold important clues to understanding astrochemistry and the connection between gas-phase matter and solid-state constituents of the interstellar medium. They also are extremely relevant for the origin of life and the delivery of the biogenic elements to planet surfaces. Studies of these types of molecules in interstellar space have clearly been driven by laboratory spectroscopy. For almost three decades, the Ziurys lab has been conducting measurements of rotational spectra of highly reactive metal and phosphorus-bearing species, and subsequently searching for these molecules in the interstellar medium with radio telescopes. These studies have led to the interstellar detection of exotic metal-bearing radicals such as FeCN and VO, as well as new phosphorus compounds such as CCP and SiP. Critical to this endeavor has been the development of unusual synthetic methods to create these unstable molecules, and the challenge of unraveling spectra of states with high spin and orbital angular momenta. Molecules of recent interest include metal dicarbide species, for example, TiC_2. An overview of the laboratory spectroscopy work will be presented, and their implications in unraveling the chemistry between the stars.

Intermission

HOUGEN AWARD **10:30**

Presentation of Award by Isabelle Kleiner, CNRS, UPEC et Universite de Paris, Creteil, France

2023 Jon T. Hougen Memorial Award Winners

Nadav Genossar-Dann Ben-Gurion University of the Negev

Miguel Sanz-Novo, Universidad de Valladolid

SNYDER AWARDS **10:35**

Presentation of Award by Anthony Remijan, NRAO

2022 Snyder Award Winners

Olivia Chitarra, Université Paris-Saclay

Taarna Studemund, Technical University of Berlin

RAO AWARDS **10:40**

Presentation of Awards by Jennifer van Wijngaarden, York University

2022 Rao Award Winners

Madison Foreman, JILA

Thomas Salomon, University of Cologne

Yue-Rou Zhang, Brown University

MILLER PRIZE **10:50**
Introduction by Michael Heaven, Emory University

RA03 ***Miller Prize Lecture*** **10:55 – 11:10**

MODELLING MOLECULES WITH IONS AND LASERS: ANALOG QUANTUM SIMULATION OF TIME-DOMAIN SPECTROSCOPY AND BEYOND

RYAN J MacDONELL, *Department of Chemistry, Dalhousie University, Halifax, NS, Canada*.

For roughly a century, spectroscopy has been our window into the molecular domain. It has served as a benchmark for the development of new theoretical methods in quantum chemistry, which in turn have aided the assignment and characterization of molecular spectra. The advent of quantum computing is no exception. Quantum computers have the potential to greatly increase the scale and accuracy of simulated molecular systems. However, current ”digital” quantum computers will remain limited in size and number of operations in the near future due to environmental noise. Conversely, analog quantum computers may be used to simulate realistic molecular systems with current technology. They consist of controllable quantum devices with a system-specific mapping onto a quantum system of interest, such as a molecule. I will present our recent work on the development of an analog quantum toolkit for the simulation of vibronic coupling Hamiltonians, including the prediction of vibronic spectra. I will show the theoretical capabilities and limits of our approach, and show proof-of-principle experimental results from collaborators. Finally, I will discuss what is next in the exciting world of analog quantum simulation.

COBLENTZ AWARD **11:15**
Presentation of Award by Zac Schultz, Coblentz Society

RA04 ***Coblentz Society Award Lecture*** **11:20 – 12:00**

MEASURING ELECTRIC FIELDS AND INTERFACIAL SOLVATION AT ELECTROCHEMICAL INTERFACES USING SUM FREQUENCY GENERATION VIBRATIONAL SPECTROSCOPY

ROBERT BAKER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*.

This talk will describe the application of sum frequency generation (SFG) vibrational spectroscopy to understand the relationship between interfacial charge transfer, solvation structure, and surface reactivity at electrode/electrolyte interfaces. Observing interfacial solvation structure under conditions relevant for electrocatalysis represents a major challenge for bridging surface science and electrochemistry. Employing plasmon-enhanced SFG, it is possible to detect the very low steady state surface coverage of CO produced on gold during electrochemical reduction of CO_2 and to use this as a Stark reporter of interfacial solvation structure. Because CO_2 reduction is extremely sensitive to catalyst surface structure, it is necessary to differentiate between CO adsorbed to inactive (i.e., spectator) sites compared to CO produced directly at active surface sites. Separating signals from these species, we show that electrolyte cations retain their entire solvation shell upon adsorption to inactive sites, while active sites retain only a single water layer between the gold surface and the adsorbed cation. We also measure the total interfacial electric field as a function of electrolyte cation and show that this field can be separated into two independent contributions from the electrochemical double layer (Stern field) and from the polar solvation environment (Onsager field). Although both contributions to the electric field depend strongly on the identity of the alkali cation, correlating SFG spectra with reaction kinetics reveals that it is actually the solvation-mediated Onsager field that governs the cation-specific chemical reactivity at the electrode/electrolyte interface. These findings highlight the importance of understanding and controlling interfacial solvation in electrochemical systems, a challenge that will require ongoing collaboration between experiment and theory.

RG. Mini-symposium: Spectroscopy with Cryogenic Ion Traps

Thursday, June 22, 2023 – 1:45 PM

Room: 116 Roger Adams Lab

Chair: Katharina A. E. Meyer, University of Wisconsin–Madison, Madison, WI, USA

RG01 ***INVITED TALK*** **1:45 – 2:15**

SPECTROSCOPIC PROBING OF LOW-TEMPERATURE ION-MOLECULE REACTIONS

DANIEL RAP, JOHANNA G.M. SCHRAUWEN, ARAVINDH NIVAS MARIMUTHU, BRITTA REDLICH, SANDRA BRÜNKEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*.

Polycyclic aromatic hydrocarbons (PAHs) are abundant in many regions of the Universe, representing a major reservoir for cosmic carbon. However, their formation pathways in cold regions of space, such as dense molecular clouds and Titan's atmosphere, remain elusive despite the recent advances in the detection of aromatic molecules there[a]. Astronomical observations show that astrochemical models significantly underestimate the abundance of these aromatic molecules, indicating that efficient formation pathways, such as ion-molecule reactions involving aromatic ions and hydrocarbon neutrals, are likely missing in the existing models.
In our work, we use a cryogenic 22-pole ion trap apparatus[b] to study ion-molecule reactions at low temperature, and to structurally identify ionic reactants, reaction intermediates and products in-situ employing infrared-predissociation (IRPD) and infrared multiple-photon dissociation (IRMPD) spectroscopy using the infrared free-electron lasers at the FELIX Laboratory. We reveal efficient low-temperature formation pathways towards PAHs and related species via exothermic ion-molecule reactions. The experimental approach combines kinetic and spectroscopic studies, and unambiguously identifies key reaction intermediates, and, in the case of the reaction of pyridine$^+$ with acetylene, the final nitrogen-containing PAH product ion quinolizinium$^+$.[c] These studies not only reveal competing formation pathways relevant in cold astronomical environments, but also deliver a variety of information to verify in-silico potential energy surfaces, astronomical models, and to guide infrared observations.

[a] B.A. McGuire et al., Science 359, 202 (2018); B.A. McGuire et al., Science 371, 1265 (2021); J. Cernicharo et al., A&A 649, L15 (2021)
[b] P. Jusko, S. Brünken, O. Asvany, S. Thorwirth, A. Stoffels, L. van der Meer, G. Berden, B. Redlich, J. Oomens, and S. Schlemmer, Faraday Discuss. 217, 172 (2019)
[c] D.B. Rap, J.G.M. Schrauwen, A.N. Marimthu, B. Redlich, and S. Brünken, Nat. Astron. 6, 1059 (2022)

RG02 **2:21 – 2:36**

N2 ACTIVATION ON SIZE SELECTED TRANSITION METAL CLUSTER IONS UNDER CRYO CONDITIONS

MAXIMILIAN LUCZAK, *Chemistry Department, RPTU Kaiserslautern-Landau, Kaiserslautern, Rheinland-Pfalz, Deutschland*.

The tandem cryo ion trap FRITZ allows the investigation of organometallic complexes as well as transition metal cluster ions in the gas phase with adsorbed reaction gases. The setup enables studies on uptake kinetics as well as IR-PD action spectroscopy under cryo conditions. In this talk we present studies of dinitrogen adsorbed to transition metal cluster anions and cations with regard to the elementary steps of N2 activation. Supported by DFT modeling we aim to explain the influence of geometric and electronic features of the transition metal cluster ions to the N2 activation process.

RG03 **2:39 – 2:54**

UNRAVELING THE VIBRATIONAL SPECTRAL SIGNATURES OF A DISLOCATED H ATOM IN MODEL PROTON COUPLED ELECTRON TRANSFER DYAD SYSTEMS

LIANGYI CHEN, *Department of Chemistry, Washington University, St. Louis, MO, USA*; EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*; JOSEPH FOURNIER, *Department of Chemistry, Washington University, St. Louis, MO, USA*.

Proton-coupled electron transfer (PCET) processes are vitally important throughout chemical and biochemical catalysis. While electron transfer kinetics have been well studied, direct interrogation of the proton transfer coordinate has remained largely unexplored. We present cryogenic ion vibrational spectra of a series of phenol-benzimidazole and phenol-pyridine PCET model dyads to explore the nature of the strong OH—N H-bond in the ground electronic state. Highly red shifted and asymmetrically broadened H-bonded OH stretch transitions are observed throughout the model series, while the deuterated isotopologues yield much weaker OD stretch transitions that are more symmetrically broadened. To explain the origins of the spectral broadening, we employ a computational model that couples the two-dimensional potentials describing the stretching and in-plane bending degrees of freedom of the shared H atom to the remaining vibrational degrees of freedom. These two-dimensional potentials are predicted to be very shallow along the H atom transfer coordinate, enabling significant dislocation of the H atom between the donor and acceptor groups upon excitation of the OH vibrational modes. These soft H atom potentials result in strong coupling between the OH modes, which exhibit extensive bend-stretch mixing, and a large number of normal mode coordinates. Vibrational spectra are calculated using a Hamiltonian that linearly and quadratically couples the H atom potentials to over thirty of the most strongly coupled normal modes treated at the harmonic level. The calculated vibrational spectra qualitatively reproduce the shape and breadth of the experimentally observed bands in both isotopologues. The results highlight a unique broadening mechanism and complicated anharmonic effects present within these biologically relevant PCET model systems.

RG04 **2:57 – 3:12**

THE INFLUENCE OF RARE-GAS TAGGING ON THE RENNER-TELLER PERTURBED $HCCH^+$ ION PROBED BY CRYOGENIC ACTION SPECTROSCOPY

KIM STEENBAKKERS, TOM VAN BOXTEL, BRITTA REDLICH, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; GERRIT GROENENBOOM, *Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands*; PHILIPP C SCHMID, OSKAR ASVANY, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*; SANDRA BRÜNKEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*.

Infrared predissociation action spectroscopy in its form as messenger spectroscopy, is a well-established technique to record vibrational spectra of reactive molecular ions. One of its major drawbacks is that the spectrum of the messenger-ion complex is taken as a proxy of that of the bare ion. In particular for small open-shell species, such as the Renner-Teller (RT) affected $HCCH^+$, the attachment of the tag may have a significant impact on the spectral features. In order to investigate this effect, we have recorded the vibrational spectra of Ne- and Ar-tagged $HCCH^+$ using a cryogenic ion trap end user station at the FELIX laboratory[a], and compared them to previous data of the bare ion obtained with laser induced reactions (LIR) spectroscopy[b]. The Ne-attachment led to a shift in band positions and change in relative intensities, while the Ar-attachment even led to a complete quenching of the RT splitting. Whereas for $HCCH^+$ LIR offers a tag-free spectroscopic method[b], this is not the case for most other reactive open-shell species. The newly developed leak-out spectroscopy (LOS)[c], seems to provide a much more universal tag-free method. Here we present the application of this method to record the cis-bending of the $HCCH^+$ cation (700 cm^{-1}), and demonstrate that the obtained LOS spectrum is equivalent to the previously recorded LIR spectrum. Not only presents this the energetically lowest-lying vibrational mode targeted with LOS so far, but it also shows its potential to overcome the tag problem in other Renner-Teller affected species.

[a] Jusko, P.; Brünken, S.; Asvany, O.; Thorwirth, S., Stoffels, A. *et al.*. Faraday Discuss., **2019**, 217, 172-202.
[b] Schlemmer, S.; Asvany, O.; Giesen, T. Phys. Chem. Chem. Phys., **2005**, 7(7), 1592-1600.
[c] Schmid, P. C.; Asvany, O.; Salomon, T.; Thorwirth, S.; Schlemmer, S. J. Phys. Chem. A, **2022**, 126(43), 8111-8117

Intermission

RG05 **3:52 – 4:07**

CIVP SPECTROSCOPY OF COBINAMIDES IN THE GAS PHASE: CLUES TO THE DESIGN OF VITAMIN B12

ALEXANDRA TSYBIZOVA, VLADIMIR GORBACHEV, PETER CHEN, *Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland*.

Alkyl and aryl cobinamides are close relatives to adenosylcobalamine, vitamin B12, which is an essential cofactor for a large number of enzymatic transformations. We report gas-phase investigations of the Co-C bond strength by means of energy-resolved collision-induced dissociation experiments, which found unexpected discrepancies to predictions made by dispersion-corrected DFT. Attempted resolution of the discrepancies led us to further cobinamide derivatives, whose ion spectroscopy provide key information on the gas-phase structure of these large molecules (ca. 150 atoms). The structural considerations lead to a hypothesis for the mechanism of control and regulation of vitamin B12 in the enzymatic reactions.

RG06 **4:10 – 4:25**

VIBRATIONAL AND ROTATIONAL ACTION SPECTROSCOPY OF $H_2C_3H^+$

WESLLEY G. D. P. SILVA, DIVITA GUPTA, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*; JOSÉ LUIS DOMÉNECH, *Instituto de Estructura de la Materia, (IEM-CSIC), Madrid, Spain*; ELINE PLAAR, STEPHAN SCHLEMMER, OSKAR ASVANY, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

The high-resolution rovibrational and pure rotational spectra of $H_2C_3H^+$ are reported here for the first time. The spectra were collected in a 4K 22-pole cryogenic ion trap (COLTRAP) instrument using the novel leak-out spectroscopy (LOS) method.[a] Rovibrational signatures within the fundamental ν_1 (C-H stretch) and the combination ν_3+ν_5 (C-C stretches) bands were detected in the 3 μm spectral region using a continuous wave optical parametric oscillator and were successfully assigned, aided by previous theoretical calculations.[b] These observations allowed accurate spectroscopic constants for the ground and vibrationally excited states to be determined. Significant differences were observed in the values of the rotational constant *A*, which decreases by about 2.7% and 5.0% in the ν_1 and ν_3+ν_5 bands, respectively, in comparison to ν_0. By analyzing the changes in *A*, information about the molecular structure of $H_2C_3H^+$ upon excitation of the C-H and C-C stretches was obtained, which indicates that the HCH angle may have an increase of approximately 3° in ν_1 and 6° in ν_3+ν_5. Guided by the ground state constants obtained from the infrared (IR) measurements, 14 pure rotational lines were observed in the 90-200 GHz frequency range using a double resonance scheme, in which the ions are excited simultaneously by the IR and a mm-wave radiation. These rotational measurements allowed even more accurate ground state spectroscopic parameters to be determined and open up the possibility for the first (radio)astronomical search of $H_2C_3H^+$ in the interstellar medium. Finally, the capability of the novel LOS method in isolating isomers in the ion trap will be discussed with a focus on the abundances of $H_2C_3H^+$ and its cyclic sibling, c-$C_3H_3{}^+$.

[a] Schmid, P. C., Asvany, O., Salomon, T., Thorwirth, S., and Schlemmer, S. 2022, J. Phys. Chem. A, 126, 8111.
[b] Huang, X., Taylor, P. R., and Lee, T. J. 2011, The Journal of Physical Chemistry A, 115, 5005.

RG07 **4:28 – 4:43**

LEAK-OUT SPECTROSCOPY OF THE C-C STRETCHING MODES OF C_3H^+, $NCCO^+$ AND HC_3O^+

MARCEL BAST, JULIAN BÖING, THOMAS SALOMON, OSKAR ASVANY, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*; IGOR SAVIC, *Department of Physics, University of Novi Sad, Novi Sad, Serbia*; SANDRA BRÜNKEN, *FELIX Laboratory, Radboud University, Nijmegen, The Netherlands*; MATHIAS SCHÄFER, *Institute of Organic Chemistry, Department of Chemistry, University of Cologne, Köln, Germany*; SVEN THORWIRTH, STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

High-resolution ro-vibrational spectra of the C-C stretching fundamentals of C_3H^+, $NCCO^+$, and HC_3O^+ are recorded using the leak-out action spectroscopy method in the 22-pole ion trap apparatus COLtrap II. In this experiment parent ions are mass selected prior to storing them in the cryogenic ion trap. Here they are cooled to the ambient temperature by collisions with a pulse of Helium buffer gas. A mode-hop-free quantum cascade laser emitting at around 5μm is used to excite the desired molecular vibrations. N_2 is used as second collision partner which is provided continuously to the cold trap. The trap is kept at a nominal temperature of 40 K in order to avoid freezing of the gas. The vibration to translation (V-T) energy transfer of the excited ions leads to a loss of those ions via an electrostatic barrier at the exit electrode. A spectrum is recorded with high S/N ratio by measuring the number of lost ions as a function of the excitation frequency. Nicely resolved P- and R- branches for the three linear molecular ions are observed with rotational, i.e. collisional temperatures slightly larger than the trap temperature and with line widths slightly exceeding the corresponding Doppler-widths. Accurate molecular parameters are determined from these measurements. Thanks to the high sensitivity of our experimental approach also hot-band transitions as well as combination bands can be identified in favorable cases. Results from these experiments will be presented.

RG08 **4:46 – 5:01**

CRYOGENIC ION SPECTROSCOPY OF VALINE AND CHEMICAL ANALOGS

LANE M. TERRY, *JILA and Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA*; DEACON J NEMCHICK, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; J. MATHIAS WEBER, *JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA*.

The success of future missions to search for life on ocean/icy worlds or investigate organic molecule rich planetary atmospheres depends on the ability to accurately identify and quantify biomarkers in the presence of a mixture of molecules.[a] Mass spectrometry alone is insufficient to unambiguously identify biomarkers due to the existence of isomers, but combined with infrared spectroscopy additional information can be extracted.

Amino acids are a prime target in the search for biomarkers due to their importance in terrestrial biology. Here, we present cryogenic gas-phase infrared spectra of protonated valine and some chemical analogs. We assign spectral features using density functional theory calculations, and we discuss prospects for chemical identification.

[a]The authors gratefully acknowledge support from a JPL/NASA Strategic University Research Partnership Grant, as well as helpful discussions with Madison Foreman (JILA), Dr. Frank Maiwald (JPL), Dr. Robert Hodyss (JPL), and Dr. Deacon Nemchick (JPL).

RG09 **5:04 – 5:19**

INFRARED ACTION SPECTROSCOPY OF INDENYL AND FLUORENYL ANIONS

MIGUEL JIMÉNEZ-REDONDO, PAVOL JUSKO, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*; GABI WENZEL, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*; DANIEL RAP, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; PAOLA CASELLI, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*; SANDRA BRÜNKEN, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*.

Polycyclic aromatic hydrocarbons (PAHs) play an important role in the chemistry of the interstellar medium. The recent unambiguous detection of several comparably small PAHs in the cold interstellar medium through radioastronomical observations[a] has rekindled the interest in spectroscopic studies of PAHs consisting of only two or three aromatic rings and their derivatives.

In this work, the vibrational spectra of indenyl and fluorenyl anions has been studied by infrared predissociation (IRPD) action spectroscopy using the Free Electron Laser for Infrared eXperiments, FELIX, at Radboud University, in combination with the cryogenic 22 pole ion trap setup FELion[b]. The range of 650 – 1650 cm^{-1} was sampled by measuring the depletion of the signal of the H_2-tagged ion as a function of the laser wavelength. High-level quantum-chemical calculations at the CCSD(T) level of theory have also been performed for the spectroscopic assignment of the detected vibrational bands.

[a] McGuire *et al.* Science 2021 **371** 1265, Cernicharo *et al.* A&A 2021 **649** L15
[b] Jusko *et al.* Faraday Discuss. 2019 **217** 172

RH. Photodissociation and photochemistry

Thursday, June 22, 2023 – 1:45 PM

Room: 100 Noyes Laboratory

Chair: Kelly Gaffney, Stanford University, Stanford, CA, USA

RH01 **1:45 – 2:00**

UV DYNAMICS OF CIS-STILBENE STUDIED BY ULTRAFAST ELECTRON DIFFRACTION

S. K. SAHA, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; PEDRO NUNES, *HeXI, Diamond Light Source, Didcot, United Kingdom*; HAYLEY WEIR, MONIKA WILLIAMS, *Department of Chemistry, Stanford University, Stanford, CA, USA*; ANDREW ATTAR, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; BRYAN MOORE, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; DUAN LUO, MING-FU LIN, MATTHIAS HOFFMANN, FUHAO JI, MATTHEW R WARE, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; SHASHANK PATHAK, *J.R. Macdonald Laboratory, Kansas State University, Manhattan, KS, USA*; THOMAS JA WOLF, *Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; JIE YANG, *Department of Chemistry, Tsinghua University, Beijing, China*; KEITH JOBE, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; TODD MARTINEZ, *Department of Chemistry, Stanford University, Stanford, CA, USA*; MARTIN CENTURION, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*.

Stilbene is a prototype molecule for studying photoisomerization and photocyclization mechanisms which are pivotal to converting light into chemical and mechanical energy in nature. Despite multiple decades of research, the exact details of the photoisomerization of cis-stilbene into trans-stilbene and/or its cyclization into 4a,4b-dihydrophenanthrene (DHP) have remained a topic of debate. We have used mega-electronvolt ultrafast electron diffraction (UED) to capture and spatially resolve the photoexcitation dynamics with sub-angstrom resolution. At the SLAC MeV-UED beamline, cis-stilbene was optically pumped with 267 nm ultraviolet light with different pulse energy and probed with 3.7 MeV electrons. We compare our experimental difference-diffraction signals with Ab initio multiple spawning simulations (AIMS) for single-photon excitation dynamics and molecular dynamics simulation for two-photon excitation leading to ionization. We found that with 80uJ pulse energy, the single and two-photon excitation channels are comparable, while with 130uJ pulse energy the two-photon channel dominates. Our data and simulations revealed very different dynamics and end products in the one-photon and two-photon channels.

RH02 **2:03 – 2:18**

SIGNATURES OF PHOTODISSOCIATION MECHANISM OF *SYMMETRIC*-TIRAZINE ENCODED IN THE VIBRATIONAL POPULATION DISTRIBUTION OF HCN PHOTOFRAGMENTS USING 266 NM

PIYUSH MISHRA, ALEXANDER W HULL, STEPHEN L COY, ROBERT W FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

We present photodissociation reaction dynamics utilizing *rotationally-resolved* Chirped-Pulse Fourier Transform Millimeter-Wave (CP-FTmmW) spectroscopy. The *state-specific vibrational population distribution* (VPD) of the photofragments contains mechanistic details of the reaction. VPD obtained from our experiments is complementary to dynamics experiments that measure the kinetic energy distributions of the photofragments. This complementarity to previous classic experiments yields tantalizing insights.

We study photodissociation dynamics of 1,3,5-Triazine (*symmetric*-Triazine) to form 3 HCN molecules in a seeded supersonic jet using 266 nm radiation. The vibrational cooling *inefficiency* in the jet preserves the VPD of the photofragments, while rotational cooling enhances the signal of low-J pure-rotational transitions. The multiplexed nature of the spectrometer enables *simultaneous sampling* of several 'vibrational satellite transitions' that belong to different vibrational states but the same (J+1)-J rotational transition, in this case the J:1-0 transition of HCN. With at least 3.2% vibrational excitation among the photofragments, we observe a higher excitation in the bending vibrational mode of HCN (up to ν_2=6) than in the CN stretching mode (up to ν_3=2); no C-H stretching (ν_1) excitation was observed, nor was any HNC isomer population detected. The observed VPD along the even-v states of ν_2 vibrational progression is at least bimodal, implying an *asymmetric* partitioning of vibrational energy among the HCN photofragments. This signature in the HCN VPD indicates a *sequential* dissociation mechanism of *symmetric*-Triazine initiated by 266 nm radiation.

Since VPDs are mode-specific, the *adiabatic* Franck-Condon projection onto the vibrational modes is capable of providing *local structural* information regarding the photolysis transition state geometry. The reaction mechanism, encoded in the VPD recorded as vibrational satellites by CP-FTmmW spectroscopy, could be deduced for any chemical reaction in which the products (i) are produced in the *gas-phase*, (ii) have a permanent dipole moment, and (iii) are *small-sized* and undergo *inefficient* vibrational cooling in the time period between the initiation of the reaction and the spectroscopic detection.

RH03 **2:21 – 2:36**

PHOTODISSOCIATION OF DIBORANE ISOLATED IN SOLID PARAHYDROGEN: EVIDENCE OF SLOW DIFFUSION-CONTROLLED RECOMBINATION

AARON I. STROM, ANH H. M. NGUYEN, IBRAHIM MUDDASSER, DAVID T. ANDERSON, *Department of Chemistry, University of Wyoming, Laramie, WY, USA*.

Our group is interested in characterizing the diffusion of chemical impurities in quantum solids such as solid parahydrogen (pH_2). In this work we report FTIR studies of the 193 nm photodissociation of diborane (B_2H_6) isolated in solid pH_2 in the 1.5 K to 4.3 K temperature range. In the gas phase, diborane photodissociation at 193 nm has been shown to produce BH_3 with a quantum yield of 2.00(25).[a] In our studies, we deposit B_2H_6 in solid pH_2 and fully resolve vibrational peaks for the $^{11}B_2H_6$, $^{11}B^{10}BH_6$, and $^{10}B_2H_6$ isotopologs of diborane in natural abundance. We then photolyze the B_2H_6/pH_2 sample for a short period of time (30 min, 100 mW/cm^2) and observe the B_2H_6 peaks decrease in intensity as new peaks grow in. We suspect that we are producing BH_3 upon photolysis which forms a complex with the pH_2 host to form BH_3-pH_2. What we found surprising is that after we stop the 193 nm laser, we observe regrowth of the diborane peaks indicating that the photoproducts can readily diffuse through solid pH_2 even at the lowest temperatures studied (T = 1.52 K). We can track the regrowth in the concentration of each diborane isotopolog separately, which means we can extract rate constants for the kinetics of recombination for each isotopolog. Assuming the recombination process is diffusion-controlled, we can use the fitted rate constants to look for kinetic isotope effects in the recombination reaction. We use these measurements to distinguish between two potential diffusion mechanisms, activated thermal hopping and quantum tunneling. This project is still ongoing, and the most recent results and analysis will be presented.

[a] M. P. Irion and K.-L. Kompa, *J. Photochem.* **32**, 139 (1986).

RH04 **2:39 – 2:54**

PHOTOISOMERIZATION OF (CYANOMETHYLENE)CYCLOPROPANE (C_5H_5N) IN A LOW TEMPERATURE RARE GAS MATRIX

SAMUEL A. WOOD, SAMUEL M. KOUGIAS, BRIAN J. ESSELMAN, R. CLAUDE WOODS, ROBERT J. McMAHON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

The C_5H_5N potential energy surface is experimentally and computationally investigated through matrix isolation photolysis of 1-cyano-2-methylenecyclopropane, a pyridine isomer containing nitrile and methylenecyclopropane functional groups. Synthesis of the novel isomer 1-cyano-2-methylenecyclopropane, presented here for the first time, involves dehydration of the corresponding amide. 1-Cyano-2-methylenecyclopropane is also generated upon photoisomerization (λ>200 nm) of (cyanomethylene)cyclopropane in argon at 19 K. Under these irradiation conditions, the photoisomerization favors the formation of 1-cyano-2-methylenecyclopropane, for which the UV absorption is blue-shifted, relative to (cyanomethylene)cyclopropane. The solution-phase UV-vis spectra and matrix-isolation IR spectra of both pure species are presented and compared to predicted spectra obtained using TD-DFT and anharmonic vibrational frequency calculations, respectively. Photoisomerization to pyridine was not observed.

RH05 **2:57 – 3:12**

ULTRAFAST ELECTRON DIFFRACTION OF THE PHOTODISSOCIATION OF BROMOCYCLOPROPANE

JACKSON LEDERER, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*; PEDRO NUNES, *HeXI, Diamond Light Source, Didcot, United Kingdom*; CONOR RANKINE, *Department of Chemistry, University of York, York, United Kingdom*; SLAC MEV-UED COLLABORATION, *Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA, USA*; MARTIN CENTURION, *Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, NE, USA*.

In this work, the photodissociation of bromocyclopropane (BCP) was captured using gas phase ultrafast electron diffraction at the SLAC MeV-UED facility. BCP is a prototypical molecule for the study of organobromides, a class of molecules that have a significant impact on the Earth's atmospheric ozone through their photochemistry. Thus, studying the dynamics of BCP offers a deeper understanding of organobromide photoreactivity. Previous studies[a] have revealed two possible reaction pathways for the dissociation of BCP; either the bromine dissociates from the BCP molecule leaving behind a cyclopropyl ring, or there is a concerted opening of the cyclopropyl ring along with the dissociation of the bromine. Experimental results are compared to simulation for the first few picoseconds of the reaction, showing good agreement for the first picosecond. The results of this study indicate that the majority of BCP molecules follow the first reaction pathway in which the cyclopropyl ring remains closed during the bromine dissociation.

[a] Orr-Ewing et al., J. Chem. Phys. 144, 244312 (2016).

Intermission

RH06 **3:52 – 4:07**

IMAGING THE PHOTOELECTRON CIRCULAR DICHROISM EFFECT IN THE PHOTODETACHMENT OF MASS SELECTED CHIRAL ANIONS

JENNY TRIPTOW, ANDRE FIELICKE, GERARD MEIJER, MALLORY GREEN, *Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*.

PhotoElectron Circular Dichroism (PECD) is a forward/backward asymmetry in the angular photoemission of an electron from a non-racemic sample, upon irradiation by circularly polarized light. In comparison to other chiroptical effects (e.g. absorptive circular dichroism), this effect is not reliant on weak interactions with the molecule's magnetic moment, which leads to a significant increase in the sensitivity to the molecule's chirality. This characteristic holds promise for analytical techniques, which target the study of dilute chiral samples. Additionally, the use of anions for this technique would allow for mass-selectivity and enable simple experimental schemes that employ table-top light sources, leading to a potentially robust analytical tool for chiral discrimination of multicomponent gas-phase samples. Support for PECD in anion photodetachment is limited, and knowledge of the forces that govern PECD electron dynamics in this photoemission process is missing. By coupling pre-photodetachment mass selection, tunable detachment, and velocity-map imaging-anion photoelectron spectroscopy, we provide an energy-resolved PECD signal for mass-selected anions, for the first time: In the study of the deprotonated 1-indanol anion we observed a PECD effect for many detachment channels, and a maximum PECD effect of 11%, which is similar to what has been measured for neutral species.[1] This work marks the first steps to understanding this chiral effect in this new photoemission regime.

[1]Triptow, J., Fielicke, A., Meijer, G., Green, M. (2023). Imaging Photoelectron Circular Dichroism in the Detachment of Mass Selected Chiral Anions. Angew. Chem. 62, e2022120.

RH07 **4:10 – 4:25**

THE INFLUENCE OF METHANOL IN WATER ICE ON THE DISTRIBUTION OF VOLATILE CARBON-CONTAINING PHOTOPRODUCTS

CATHERINE E WALKER, GUSTAVO A. CRUZ-DIAZ, WILL E. THOMPSON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; COLLETTE C SARVER, *Chemistry, UW-Madison, Madison, WI, USA*; KATARINA YOCUM, OLIVIA H. WILKINS, *NASA Postdoctoral Program Fellow, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; PERRY A. GERAKINES, STEFANIE N MILAM, *Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

Recent JWST observations of icy grains in molecular clouds have highlighted the complexity of organic chemistry developing in water ice at the early stages of star formation. Following the chemical evolution of icy grain mantles as stars form can provide clues about the observed compositions of comets and icy planetary bodies. We deposited ice mixtures of water and methanol in varying ratios under cryogenic, ultrahigh vacuum conditions. We monitored the chemical composition of the ice mixtures during UV photolysis and their sublimated products during subsequent controlled warmup using infrared spectroscopy in transmission, quadrupole mass spectrometry, and rotational spectroscopy in the mm/submm-wave regime. Here we highlight the impact of the water:methanol ratio on the production of various carbon-containing volatiles (carbon dioxide, carbon monoxide, methane, formaldehyde, and the formyl radical). We find that higher proportions of water favor the production of more highly oxidized carbon-containing volatiles over their reduced counterparts.

RH08 **4:28 – 4:43**

SUBLIME RESULTS: THE EFFECTS OF UV PHOTOLYSIS ON METHANOL WATER ICES AND THE PRODUCTION OF COMPLEX ORGANIC MOLECULES

COLLETTE C SARVER, *Chemistry, UW-Madison, Madison, WI, USA*; GUSTAVO A. CRUZ-DIAZ, WILL E. THOMPSON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; CATHERINE E WALKER, *Chemistry, UW-Madison, Madison, WI, USA*; KATARINA YOCUM, *NASA Postdoctoral Program Fellow, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; OLIVIA H. WILKINS, *Astrochemistry Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; PERRY A. GERAKINES, STEFANIE N MILAM, *Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

Ultraviolet radiation facilitates chemical reactions in interstellar ice mantle during star and planet formation. These chemical reactions produce complex organic molecules (COMs) that may be essential in the production of prebiotic molecules. We are studying UV-driven chemistry in ices with the SubLIME technique, a laboratory set up that works at cryogenic conditions and ultra-high vacuum. Experiments were conducted to study the abundance ratios of organics sublimated from UV-photolyzed methanol/water ice mixtures with varying methanol concentrations. Submillimeter rotational spectroscopy, quadrupole mass spectrometry, and Fourier-transform infrared transmission spectroscopy were used to monitor the products in both the solid and gas phases. COMs were seen to form at all concentrations of methanol. However, at higher concentrations of methanol, COMs containing oxygen atoms formed quickly. In contrast, we detected COMs with higher hydrogen content at higher concentrations of water. This talk will present the experimental design and results for the ice chemistry. A second talk will discuss the impact of the water:methanol ratio on the formation of carbon-containing gas phase volatiles under the same experimental conditions.

RH09 **4:46 – 5:01**

$Si_3O_2{}^+$ - OPTICAL ABSORPTION AND PHOTODISSOCIATION PROPERTIES

TAARNA STUDEMUND, KAI POLLOW, MARKO FÖRSTEL, OTTO DOPFER, *Institut für Optik und Atomare Physik, Technische Universität Berlin, Berlin, Germany*.

Interstellar dust is an essential constituent in the evolution of solar systems, stars, and planets - like our Earth - but its origin and processes are still insufficiently understood. Key components of such interstellar dust are μm-sized silicates, which are mainly silicon-containing compounds, with oxygen, among others.[1] Furthermore, silicon and oxygen are the two most abundant elements in our Earth's crust. However, only molecular SiO has been identified as a possible precursor in space and circumstellar disks yet.[2] Experimental data and quantum chemical calculations on larger $Si_nO_m{}^+$ cations are expected to provide information on further intermediate steps of the dust grain formation. Therefore, we focus on these and present the first results on the $Si_3O_2{}^+$ molecular ion. The optical spectra are among the first spectroscopic information for $Si_nO_m{}^+$ cations larger than SiO^+ and $Si_2{}^+$.[2–5] The electronic photodissociation spectra are obtained by photodissociation spectroscopy of mass-selected ions in a tandem mass spectrometer coupled to a laser vaporization source.[6] The data generated by action spectroscopy are compared and interpreted with TD-DFT calculations.

Literature:

[1] K. Nagashima et al., Nat. 428, 6986 (2004)
[2] R. W. Wilson et al., Astrophys. J. 167 (1971)
[3] R. R. Reddy et al., Astrophys. Space Sci. 281, 4 (2002)
[4] S. D. Rosner et al., J. Mol. Spectrosc. 189, 1 (1998)
[5] T. Studemund et al., J. Phys. Chem. Lett. 13, 33 (2022)
[6] M. Förstel et al., Rev. Sci. Instrum. 88, 12 (2017)

RH10 **5:04 – 5:19**

EXPLORING THE MECHANISM OF THE ELECTRONIC QUENCHING OF NO ($A^2\Sigma^+$) WITH CO_2

AERIAL BRIDGERS, ANDREW S. PETIT, *Department of Chemistry, California State University, Fullerton, Fullerton, CA, USA*.

As a reactive radical species, NO has the potential to interact with other atmospheric molecules in unique ways. The method of experimental quantification, laser-induced fluorescence (LIF), measures NO along its $A^2\Sigma^+ \leftarrow X^2\Pi$ transition band. The electronic quenching of NO ($A^2\Sigma^+$) through interactions with other molecules provides alternate photochemical pathways that compete with fluorescence. Previous experimental studies demonstrated that the room temperature electronic quenching cross section of the NO ($A^2\Sigma^+$)+CO_2 system is quite large at 64 $Å^2$. Recent experimental work by Paci et al. demonstrated that NO ($A^2\Sigma^+$)+CO_2 electronic quenching is accompanied by the formation of vibrationally excited CO_2 in its asymmetric stretching mode. However, the specific photochemical pathways responsible for this have not been identified.

In this work, we develop potential energy surfaces (PESs) to identify the photochemical pathways for the electronic quenching of NO ($A^2\Sigma^+$) by CO_2. The PESs are calculated at the EOM-EA-CCSD/d-aug-cc-pVTZ//EOM-EA-CCSD/aug-cc-pVDZ level of theory. This method is well-suited for open-shell systems and provides a balanced treatment of valence and Rydberg states. Long-range interactions between the N of NO ($A^2\Sigma^+$) and the O of CO_2 are attractive, causing the two molecules to move closer together. As the intermolecular distance decreases, electronic density shifts from the 3sσ orbital of NO ($A^2\Sigma^+$) to a 2pπ^* orbital of CO_2. This phenomenon, known as the harpoon mechanism, causes increased intermolecular attractions, distortion of CO_2 into a bent conformation, and a downhill pathway to a conical intersection. Overall, our work gives new insights into the chemical physics of an atmospherically relevant system that will inform future velocity map imaging experiments.

RH11 **5:22 – 5:37**

PHOTOCATALYTIC DEGRADATION OF INDUSTRIAL WASTEWATER AND ANTIBACTERIAL ACTIVITY

EMMANUEL ROSAS, MAHESH B. DAWADI, *Natural Sciences and Engineering, Black Hawk College, Moline, IL, USA*.

Photocatalysts have been paid great attention owing to their excellent performance in the degradation of dangerous organic pollutants. A facile green route has been employed for the synthesis of un-doped ZnO, Ag-doped, Cu-doped, and Co-doped ZnO using curcuma (turmeric) root and moringa oleifera (drumstick) leaf extract as the reducing and stabilizing agent. These nanoparticles have been employed as photocatalytic agents to degrade the organic dyes present in the industrial wastewater under visible and ultraviolet irradiation. Herein, we compared the photocatalytic degradation activity of these nanoparticles using three industrial wastewater samples. We found that Ag-doped ZnO nanoparticles under UV-irradiation performed the best in comparison to the un-doped ZnO, Co-doped and Cu-doped ZnO nanoparticles for these samples. In addition, the antibacterial activities of the nanoparticles with moringa oleifera leaf extract were analyzed against different human pathogenic bacterial strains, *E. coli C* and *E. coli K-12* by the optical density method.

RI. Astronomy

Thursday, June 22, 2023 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: R. A. Motiyenko, Université de Lille, Villeneuve d'Ascq, France

RI01 **1:45 – 2:00**

CONNECTING PREBIOTIC CHEMISTRY IN THE LABORATORY TO PROTOSTELLAR OBSERVATIONS

WILL E. THOMPSON, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; MORGAN M. GIESE, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*; GUSTAVO A. CRUZ-DIAZ, CATHERINE E WALKER, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; COLLETTE C SARVER, *Chemistry, UW-Madison, Madison, WI, USA*; KATARINA YOCUM, OLIVIA H. WILKINS, *NASA Postdoctoral Program Fellow, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; D. C. LIS, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; PERRY A. GERAKINES, STEFANIE N MILAM, *Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

During the process of star formation, radiative and thermal processing of icy grain mantles leads to the formation of complex organic molecules (COMs). This protostellar processing produces the bulk chemical inventory which is subsequently delivered to forming planetary systems. To investigate this process, we have used the Sublimation Laboratory Ice Millimeter/submillimeter Experiment (SubLIME) on water:methanol interstellar ice analogs at a variety of ratios to study the dependence of organic molecule formation on the concentration of methanol to water. The results of these experiments will be compared to the λ = 2 mm astronomical observations of the W3 star-forming region using the NOrthern Extended Millimeter Array (NOEMA). From these observations, we have imaged and analyzed molecular distributions in the neighboring star-forming cores W3(H_2O) and W3(OH). By comparing the ratios of COMs produced in the laboratory ice experiments to those observed in W3, we will discuss astrochemical implications for the ice and gas composition in these active star-forming regions.

RI02 **2:03 – 2:18**

CHEMICAL INVENTORIES OF MOLECULAR CLOUDS REVEALED BY HERSCHEL HIFI SPECTRAL LINE SURVEYS

CATHERINE E WALKER, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; LUYAO ZOU, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*; SHIYA WANG, *Hazardous Materials and Waste Management Division, Colorado Department of Public Health and Environment, Denver, CO, USA*; D. C. LIS, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; SUSANNA L. WIDICUS WEAVER, *Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA*.

Accurate models of interstellar chemistry enable predictions of the chemical inventory of molecular clouds. Observations probing the effects of physical conditions of interstellar clouds on their chemical complexity allow the refinement of astrochemical models. To this end, we observed ten sources including hot cores, hot corinos, Class 0 protostars, HII regions, and shocked regions using Herschel HIFI Bands 2 and 5 in 12 GHz windows centered at 670 GHz and 1.16 THz. We constrained the temperatures and column densities of detected complex organic molecules using GOBASIC, a global fitting algorithm which performs Boltzmann analyses under the assumption of local thermodynamic equilibrium. Here we present the observations and comparisons of the molecular abundances to the physical properties of their environments for benchmarking of astrochemical models.

RI03 **2:21 – 2:36**

NEW METAL DICARBIDES IN THE LABORATORY AND IN SPACE

BRYAN CHANGALA, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; HARSHAL GUPTA, *Division of Astronomical Sciences, National Science Foundation, Alexandria, VA, USA*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

We present a joint laboratory, theoretical, and astronomical study of several new metal-carbon clusters including the alkaline earth metal-bearing molecules MgC_2, CaC_2, and SrC_2, as well as the closely related rare earth molecule YbC_2. We have synthesized these species in the laboratory with a laser-ablation supersonic expansion source and detected their rotational spectra at high resolution with cavity Fourier transform microwave spectroscopy. Combining extensive isotopic measurements with highly accurate *ab initio* rovibrational calculations, we have derived their precise semi-experimental equilibrium geometries, which are all T-shaped with highly ionic metal-carbon bonds. Our measured laboratory rest frequencies have enabled the identification of MgC_2 and CaC_2 as the carriers of several strong, previously unassigned radio emission lines in the circumstellar envelope of the well known evolved carbon-rich star IRC+10216. These laboratory and astronomical discoveries yield fundamental insights into the chemical structure and bonding of s- and f-block metal compounds, and place critical new constraints on the postulated astrochemical pathways that incorporate metal atoms into complex polyatomic molecules. Our work suggests that larger metal-carbon clusters may now be detectable in the laboratory and in circumstellar environments, providing a new probe of the formation of refractory metal-carbon particles.

RI04 **2:39 – 2:54**

THE EXCITATION, ABUNDANCE, AND DISTRIBUTION OF MgC_2 AND CaC_2 IN IRC+10216

HARSHAL GUPTA, *Division of Astronomical Sciences, National Science Foundation, Alexandria, VA, USA*; BRYAN CHANGALA, MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; JOSE CERNICHARO, JUAN R. PARDO, MARCELINO AGÚNDEZ, CARLOS CABEZAS, *Instituto de Fisica Fundamental, CSIC, Madrid, Spain*; BELÉN TERCERO, *OAN-IGN, Observatorio Astronómico Nacional, Madrid, Spain*; MICHEL GUÉLIN, *Astronomy and Science Group, IRAM, Saint Martin D'heres, France*.

The laboratory and astronomical discovery of the metal dicarbides, MgC_2 and CaC_2, discussed in the preceding talk represents a key advance in the study of metal carbides and fills a longstanding gap in the molecular inventory of evolved carbon stars. In this talk we will discuss how characterizing the distribution of the two species in IRC+10216, together with a careful analysis of their excitation and abundance might help elucidate the role of metals in the chemistry of IRC+10216, and the state of refractory elements in carbon-rich circumstellar environments more generally. We will also discuss the utility of dicarbides as physico-chemical probes[a] of circumstellar regions, as well as the prospects of detecting larger metal-carbon compounds there.

[a]Possessing dipole moments of nearly 8 D and 11 D, MgC_2 and CaC_2 are among the most polar molecules detected in IRC+10216, and consequently strong discriminators between radiative and collisional excitation processes.

Intermission

RI05 **3:34 – 3:49**

LABORATORY DETECTION AND ASTRONOMICAL SEARCH FOR AN UNCHARTED GLYCINE ISOMER

MIGUEL SANZ-NOVO[a], JOSÉ L. ALONSO, IKER LEÓN, SANTIAGO MATA, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; VICTOR MANUEL RIVILLA, IZASKUN JIMÉNEZ-SERRA, JESÚS MARTÍN-PINTADO, *Departamento de Astrofísica, Centro de Astrobiología CAB, CSIC-INTA, Madrid, Spain*; BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

In recent years, astrochemistry has shown that interstellar chemistry is able to generate several building blocks of key biomolecules. These investigations aim the detection of new interstellar systems, especially those that have a relevant prebiotic role, such as peptide-like molecules. Herein, we present the laboratory detection and astronomical search for acetohydroxamic acid ($CH_3CONHOH$), an uncharted glycine isomer. We provide frequencies of its ground state (up to 40 GHz), measured by broadband and narrowband rotational spectroscopies combined with a laser ablation device. The ^{14}N nuclear quadrupole hyperfine structure and the A-E splittings due to the internal rotation were resolved and interpreted. Hence, we determined a precise set of the rotational spectroscopic parameters for the two distinct Z- and E-conformers. [b] Our laboratory data were subsequently employed to search for the lowest-energy Z-conformer toward two prominent astronomical sources. Firstly, we used the spectral GOTHAM survey performed with the Green Bank Telescope to search for the molecule toward the cold molecular cloud TMC-1. We also employed a sensitive spectral survey of the Galactic Center molecular cloud G+0.693-0.027, based on IRAM 30 m and Yebes 40 m observations. We report the nondetection of acetohydroxamic acid toward both astronomical sources but, interestingly, the derived upper limit to its column density lies close to that obtained glycine. Its corresponding molecular abundance with respect to molecular hydrogen is found to be $\leq 1 \times 10^{-9}$ and 2×10^{-10} in TMC-1 and G+0.693-0.027, respectively, which further constrain the abundance of this glycine isomer in the ISM and provide additional insights into the chemistry of amino acid-related species in space.

[a] M. Sanz-Novo (currently at CAB, CSIC-INTA) thanks the Hougen committee and the ISMS organizers for the Jon Hougen Memorial Award.
[b] M. Sanz-Novo, J. L. Alonso, V. M. Rivilla, B. A. McGuire et al. 2022, A&A, 666, A134.

RI06 **3:52 – 4:07**

INVESTIGATING THE PRECURSORS OF ETHANOLAMINE, THE SIMPLEST PHOSPHOLIPID IN THE CELLULAR MEMBRANES DISCOVERED IN THE ISM

DAVIDE ALBERTON, VALERIO LATTANZI, CHRISTIAN ENDRES, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*; NATALIA INOSTROZA, *Department of Electrical Engineering, University of Chile, Santiago, Chile*; RYAN C. FORTENBERRY, *Chemistry and Biochemistry, University of Mississippi, Oxford, MS, USA*; PAOLA CASELLI, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*.

Ethanolamine ($NH_2CH_2CH_2OH$, EtA), a key molecular component of phospholipids in cell membranes, has been recently detected in the G+0.693 molecular cloud[1]. This same molecule was detected in the Almahata Sitta meteorite as well. In this case, its formation has been suggested to be due to the unusual thermal conditions that might have caused the decomposition of amino acids[2]. On the other hand, its formation route in the interstellar medium (ISM) is suggested in a work led by Charnley et al. 2002[3]. Due to the addition of a carbon atom to CO, through subsequent hydrogenation and nitrogenation steps of the already detected HCCO radical intermediate, it might be possible to produce EtA. Additionally, a recent study showed the NH_3+CO+C reaction to be a barrier-less process, paving the way to an alternative route to the formation of EtA precursors in the ISM[4]. We herein perform a comprehensive quantum chemical analysis of the isomers involved in the EtA formation pathway. We extend the ensemble of isomers that can take part in this route, and we compute the energy of those that might be acting as crucial actors in the chemical steps. We optimise their molecular geometry and obtained a set of rotational and distortion constants at a high level of theory to assist their spectroscopic characterization for their future interstellar search.

[1] Rivilla, V. M. et al. PNAS, 118, 22 (2021)
[2] Glavin, D.P. et al. 45, 10-11 (2010)
[3] Charnley, S.B., et al. Earth, Moon, and Planets, v. 90, Issue 1, p. 349-360 (2002)
[4] Krasnokutski, S.A. et al. Nat Astron 6, 381–386 (2022)

RI07 **4:10 – 4:25**

UNLOCKING THE POTENTIAL OF THE MOST DEFINITIVE MOLECULAR TRACER OF UV-ENHANCEMENT: l-C_3H^+

ANDY LIPNICKY, *North American ALMA Science Center, National Radio Astronomy Observatory, Charlottesville, VA, USA*; RYAN A LOOMIS, CRYSTAL L. BROGAN, *NAASC, National Radio Astronomy Observatory, Charlottesville, VA, USA*; BRETT A. McGUIRE, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA*.

The interstellar molecule l-C_3H^+ appears to be the most sensitive and definitive molecular tracer of enhanced UV-flux ever observed in the ISM. Extensive, deep searches for this species in dozens of sources show its presence nearly exclusively in UV-enhanced regions. Yet, our understanding of the spatial distribution of the molecule within these sources, and the excitation conditions (and abundances) in previously-observed regions, is sorely lacking. I will discuss recent ALMA observations of l-C_3H^+ in the Horsehead PDR region that have revealed an unexpected large-scale distribution of l-C_3H^+. With these data we wish to better understand the spatial distribution, abundance, and excitation of this potentially transformational molecule in our ability to probe the extent of UV-enhanced flux in these and other key regions. The results will be used to refine state-of-the-art PDR chemical modeling codes.

RI08 **4:28 – 4:43**

CARBON CLUSTER CATIONS AND THE ”BUMP” OF THE INTERSTELLAR UV EXTINCTION CURVE

JASON E. COLLEY, DYLAN S. ORR, MICHAEL A DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA, USA*.

Light travelling from far-off stars interacts with interstellar molecules, ice grains, and dust particles, which can show up in astronomical observations. These observations reveal the results of scattering, absorption, and emission across the spectrum. In the ultraviolet region, the wavelength of light is of comparable size to the dimensions of dust particles. This enhances scattering, giving rise to the ultraviolet extinction curve. In photoionizing regions of space, there exists an additional feature of an intense absorption “bump” on this curve at 217.5 nm. The massive intensity of this feature requires that the carrier be made from very abundant interstellar element(s), so many studies have focused on the spectra of polyaromatic hydrocarbons or graphite-containing particles to identify the carrier, but no match has been found. Here, we measure the ultraviolet spectra of ionized carbon monocyclic rings ($C_n{}^+$, n = 13 – 19) which are produced by laser vaporization using mass selection and tunable laser photodissociation spectroscopy. The resulting spectra show that ionized carbon rings have the ultraviolet spectra and relevant astrochemistry to explain the bump.

RI09 **4:46 – 5:01**

ASTRONOMICAL DETECTION OF THE INTERSTELLAR ANION $C_{10}H^-$ TOWARDS TMC-1 FROM THE GOTHAM LARGE PROGRAM ON THE GBT

ANTHONY REMIJAN[a], *Science Support and Research, National Radio Astronomy Observatory, Charlottesville, VA, USA*.

Using data from the GOTHAM (GBT Observations of TMC-1: Hunting for Aromatic Molecules) survey, we report the first astronomical detection of the $C_{10}H^-$ anion. The astronomical observations also provided the necessary data to refine the spectroscopic parameters of $C_{10}H^-$. From the velocity stacked data and the matched filter response, $C_{10}H^-$ is detected at $>9\sigma$ confidence level at a column density of $4.04^{+10.67}_{-2.23} \times 10^{11}$ cm^{-2}. A dedicated search for the $C_{10}H$ radical was also conducted towards TMC-1. In this case, the stacked molecular emission of $C_{10}H$ was detected at a $\sim 3.2\sigma$ confidence interval at a column density of $2.02^{+2.68}_{-0.82} \times 10^{11}$ cm^{-2}. However, since the determined confidence level is currently $<5\sigma$, we consider the identification of $C_{10}H$ as tentative. The full GOTHAM dataset was also used to better characterize the physical parameters including column density, excitation temperature, linewidth, and source size for the C_4H, C_6H and C_8H radicals and their respective anions, and the measured column densities were compared to the predictions from a gas/grain chemical formation model and from a machine learning analysis. Given the measured values, the $C_{10}H^-/C_{10}H$ column density ratio is $\sim 2.0^{+5.9}_{-1.6}$ - the highest value measured between an anion and neutral species to date. Such a high ratio is at odds with current theories for interstellar anion chemistry. For the radical species, both models can reproduce the measured abundances found from the survey; however, the machine learning analysis matches the detected anion abundances much better than the gas/grain chemical model, suggesting that the current understanding of the formation chemistry of molecular anions is still highly uncertain.

[a]Presenting on behalf of the entire GOTHAM collaboration

RI10 **5:04 – 5:19**

A NEW MULTIBAND RECEIVER FOR THE 12 M TELESCOPE AT THE ARIZONA RADIO OBSERVATORY (ARO)

LUCY M. ZIURYS, *Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA*; EUGENE F. LAURIA, GEORGE P. REILAND, *Arizona Radio Observatory, University of Arizona, Tucson, AZ, USA*; ARTHUR W. LICHTENBERGER, *Innovations in Fabrication Laboratory, University of Virginia, Charlottesville, VA, USA*; ANTHONY R. KERR, *Central Development Lab, National Radio Astronomy Observatory, Charlottesville, VA, USA*.

A new receiver has been constructed for the 12 m telescope of the Arizona Radio Observatory (ARO). The receiver package consists of four separate, dual polarization, frequency bands in a modular cryostat. The four bands cover the astronomically important atmospheric windows at 1.2, 2, 3, and 4 mm wavelengths. In the 3 mm and 1.2 mm wavelength regions, the receiver employs ALMA Band 3 (84 - 116 GHz) and ALMA Band 6 (211 - 275 GHz) sideband-separating (SBS) SIS mixers, while at 4 mm (67 - 90 GHz), cryogenic HFET amplifiers are used. Sideband separation for the 4 mm band is achieved through a room temperature E band downconverter developed at ARO. The 2 mm band (125 - 180 GHz) consists of SBS mixers developed from the device level by ARO in collaboration with the Central Development Laboratory (CDL) at the National Radio Astronomy Observatory (NRAO) and the University of Virginia Innovations in Fabrication Laboratory. The 2 mm window is accessible by a single broadband mixer, which covers all of ALMA Band 4 and 40% of ALMA Band 5. The mixer chip has a series array of four SIS junctions, similar to ALMA Bands 3 and 6. The new 2 mm mixers have typical noise temperatures less than 45 K with image rejection greater than 15 dB at most frequencies. The 2 mm mixers have proven to be exceptionally robust, with system temperatures around 100 K on the sky and with excellent baseline stability. The backend used for the receiver is the ARO Wideband Spectrometer (AROWS). AROWS is a digital Fourier transform spectrometer with a sampling rate of 10 Gs per sec, and can be configured to produce 2 x 4 GHz of continuous and usable instantaneous bandwidth. The digitizer card was developed by Curtiss-Wright. Two such cards can be used to generate 16 GHz of instantaneous bandwidth (4 x 4 GHz), allowing all four IF channels of any receiver band to be processed simultaneously for observations.

RJ. Conformers and isomers

Thursday, June 22, 2023 – 1:45 PM

Room: 217 Noyes Laboratory

Chair: Maria Luisa S Senent, IEM-CSIC, Madrid, Spain

RJ01 **1:45 – 2:00**

CONFORMATIONAL COOLING AND ISOMERIZATION OF METHYL NITRITE ISOLATED IN LOW-TEMPERATURE MATRICES

EMILY K HOCKEY, *Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA*; KORINA VLAHOS, *Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA*; LAURA M McCASLIN, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*; LEAH G DODSON, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*.

Conformational cooling is a phenomenon that can occur in matrix-isolation experiments when the gas phase ratio of conformers is not represented in the freshly deposited matrix-isolated sample. Gaseous methyl nitrite exists in two stable conformations: cis-CH_3ONO and trans-CH_3ONO, with cis being the more stable conformer. Previous literature does not show evidence of a change in cis to trans ratio of gas phase methyl nitrite in a supersonic beam, but there is no experimental data studying the effects of conformational cooling using an effusive source combined with matrix isolation. Our experimental results show evidence of conformational cooling, where the relative population of the cis conformer is increased compared to the ratio observed in the gas phase. We also observe an increased degree of conformational cooling when different bath gases are employed (Ar, N_2, and Xe). In addition to demonstrating this phenomenon, we investigated the photoinduced isomerization mechanism in each low-temperature matrix using 355 nm light. In this talk, we will describe the isomerization of matrix isolated CH_3ONO within the framework of caging effects and excited state dynamics, and discuss the role of conformational cooling during matrix deposition.

RJ02 **2:03 – 2:18**

ISOMERIZATION AMONG THE ISOMERS OF 2-HEXENAL and 3-HEXENAL BY FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

NOBUHIKO KUZE, RYOTO OZAWA, YOSHIYUKI KAWASHIMA, *Department of Materials and Life Sciences, Sophia University, Tokyo, Japan*.

cis-3-Hexenal (*c*3H; $O = CH - CH_2 - CH = CH - CH_2 - CH_3$) is known as a grass odorant molecule, and this compound readily isomerizes to *trans*-2-hexenal (*t*2H). We have previously identified two conformers of *c*3H by Fourier transform microwave (FTMW) spectroscopy [1]. We also found the isomers of *c*3H, *trans*-3-hexenal (*t*3H) and *cis*-2-hexenal (*c*2H), from rotational spectra observed on liquid sample of *c*3H. In this study, the intensities of the rotational spectral lines of these conformers of 3- and 2-hexenal were measured repeatedly to obtain reliable temperature-dependent intensity ratio profiles of the isomerization reactions. The rotational spectra of *c*3H and *t*3H were observed at 30:1 in the first step in room temperature. The *t*3H isomer was found to be contained in the liquid *c*3H sample as an impurity. As the nozzle temperature was increased, the line intensities of the *t*2H and *c*2H became stronger, and finally, the ratio of *t*2H and *c*2H was 6:1. This indicates that *c*3H may isomerize to both *t*2H and *c*2H. We also discuss the identification of the second conformer for *c*3H; the structural model in which all dihedral angles of the C-C single bond are in the skew configuration, *SScS*, is better than the previously identified conformer [1], *CScS*, in which the OCCC dihedral angle is in the *cis* configuration.

[1] R.Ozawa, N. Kuze and Y. Kawashima, *ISMS*, P6243 (2022).

RJ03 **2:21 – 2:36**

BROADBAND ROTATIONAL SPECTROSCOPIC DETECTION OF BUFFER GAS COOLED MOLECULES DESORBED FROM AN ICE: ISOMER AND CONFORMER-SPECIFIC BRANCHING RATIOS OF N- AND I-PROPANOL

QUENTIN D BORENGASSER, TRAVIS HAGER, ANUDHA KANAHERARACHCHI, BERNADETTE M. BRODERICK, *Department of Chemistry, University of Missouri, Columbia, MO, USA*.

A new instrument which combines buffer gas cooling with broadband rotational spectroscopy to detect molecules desorbed from an ice surface is described. Here, we report isomer and conformer-specific branching ratios of n- and i-propanol, the former of which contains 5 symmetry-unique conformations (Ga, Aa, Ag, Gg, and Gg'). Following deposition of these species at 4 K, temperature-programmed desorption is performed where the sublimed molecules are injected into a 25 K buffer gas cell (BGC) and detected with broadband rotational spectroscopy in the 60 – 90 GHz regime. We compare these results with direct room temperature gas-phase injection and report differences in the conformer branching ratios for species that are first deposited onto an ice at 4 K and sublimed, versus those observed following direct gas-phase injection and cooled within a BGC.

RJ04 **2:39 – 2:54**

DETERMINATION OF ISOMER AND CONFORMER-SPECIFIC BRANCHING RATIOS OF BUFFER GAS COOLED MOLECULES DESORBED FROM AN ICE SURFACE WITH BROADBAND MM-WAVE ROTATIONAL SPECTROSCOPY

ANUDHA KANAHERARACHCHI, TRAVIS HAGER, QUENTIN D BORENGASSER, BERNADETTE M. BRODERICK, *Department of Chemistry, University of Missouri, Columbia, MO, USA*.

A new instrument is described which combines buffer gas cooling with broadband rotational spectroscopy to probe molecules desorbed from an ice surface (CP-ICE). Here we report isomer and conformer-specific branching ratios of *n*- and *i*-propyl cyanide, the former of which may be in either the *gauche* or *anti* configuration. Following deposition of these species onto a 4 K surface, temperature programmed desorption (TPD) experiments are performed where the sublimed gas-phase molecules are injected into a buffer gas cell (BGC) at 25 K, cooled, and detected by broadband rotational spectroscopy in the 60 – 90 GHz regime. We compare these results with room-temperature gas-phase injection of these species into the 25 K BGC and report differences observed in the conformer branching ratios.

RJ05 **2:57 – 3:12**

REVEALING INTRINSIC PROPERTIES OF SMALL BIOMOLECULES BY IONIZATION-LOSS STIMULATED RAMAN SPECTROSCOPY

RAMI RAHIMI, NOGA SABAN, ILANA BAR, *Physics, Ben-Gurion University of the Negev, Beer-Sheva, Israel*.

The spectral study of isolated molecules and clusters, assisted by quantum chemical calculations, allows for predicting their three-dimensional electronic structures and gaining insight into their relative energies, non-covalent interactions, and contributions to structure stabilization. Here we will show double resonance measurements, with ionization-loss stimulated Raman spectroscopy probing single-conformation hydrates of neurotransmitters and providing their vibrational signatures in a broad frequency range for obtaining new information on the structural details and uncovering the approach potential.

RJ06 **3:15 – 3:30**

EXPLORING THE CONFORMATIONAL LANDSCAPE OF BIOACTIVE MOLECULES BY CHIRPED PULSE MICROWAVE SPECTROSCOPY AND LASER VAPORIZATION

OTGER CREHUET I VILADELBOSCH, *Physical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain*; PABLO PINACHO, *Physical Chemistry, University of the Basque Country, Leioa Bilbao, Spain*; EMILIO J. COCINERO, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*; MAIDER PARRA-SANTAMARIA, *Physical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain*.

The study of bioactive molecules is an important field if we want to understand how living organisms work, in this contribution we present three molecules: indole-3-carbinol (I3C), picaridin and DEET.

By a combination of quantum-chemical calculations and microwave spectroscopy all molecules were interrogated. I3C was vaporized by ultrafast UV laser radiation and 1 conformers were detected. In addition, the structure could be determined by minor isotopologues species[1]. Picaridin and DEET were examined in the pulse-chirped spectrometer [2][3] and 2 and 4 species were observed respectively. Studies are in progress and higher energy conformers will be investigated and hydrated species will be analysed.

References

[1] E. J. Cocinero, A. Lesarri, P. Écija, J. Grabow, J. A. Fernández, F. Castaño. Angew. Chem. Int. Ed. 2012, 51, 3119 –3124 [2] E. J. Cocinero, A. Lesarri, P. Écija, J. Grabow, J. A. Fernández, F. Castaño. Phys. Chem. Chem. Phys., 2010,12, 12486-12493. [3] I. Uriarte, C. Pérez, E. Cballero-Mancebo, F. J. Basterretxea, A. Lesarri, J. A. Fernández, E. J. Cocinero, Chem. Eur. J. 2017, 23, 7238–7244.

Intermission

RJ07 **4:10 – 4:25**

A BROADBAND ROTATIONAL SPECTROSCOPIC STUDY OF TETRAHYDRO-2H-PYRAN-2-OL

ARAN INSAUSTI, JIARUI MA, ARSH SINGH HAZRAH, WOLFGANG JÄGER, YUNJIE XU, *Department of Chemistry, University of Alberta, Edmonton, AB, Canada*.

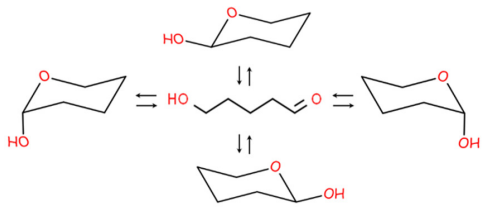


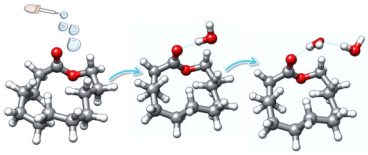
Figure 1: Tetrahydro-2H-pyran-2-ol molecule.

Tetrahydro-2H-pyran-2-ol (THP) is an alcohol containing pyranose ring. The lack of substituents in THP minimizes the conformational flexibility and the non-covalent interactions within the structure, drastically simplifying the system in relation to physiologically relevant carbohydrates, such as glucose. This makes THP a prototypical system to study various phenomena and dynamics of carbohydrate chemistry. Such phenomena include the anomeric effect, which describes the preference for the axial conformation over the less hindered and more energetically favoured equatorial conformation. When in solution, THP is in equilibrium with its linear counterpart, 5-hydroxypentanal, and readily interconverts between its two chiral forms. A high resolution gas phase study of THP may not only confirm phenomena such as the anomeric affect, but also allow for the study of chiral interconversion in the gas phase. An in-depth study of THP will also lay a foundation for future gas phase carbohydrate systems with more physiological relevance. However, before we can study the various phenomena and dynamics, it is first beneficial to study the structure of THP in great detail. To elucidate the THP structure we analyzed rotational spectra measured with a chirped-pulse Fourier transform microwave spectrometer, operating in the 2-6 GHz range. In addition to the monomers, some dimer conformations were assigned to the rotational spectrum. The intermolecular interactions within the dimers were then visualized using a non-covalent interactions (NCI) analysis.

RJ08 **4:28 – 4:43**

MICROHYDRATION ON MULTICONFORMATIONAL LARGE MOLECULES: INTRA- AND INTERMOLECULAR INTERACTIONS OF MACROLACTONES WITH WATER

MAIDER PARRA-SANTAMARIA, PABLO PINACHO, EMILIO J. COCINERO, *Physical Chemistry, University of the Basque Country (UPV/EHU), Bilbao, Spain*; CAMILLA CALABRESE, *Departamento de Química Física y Química Inorgánica - I.U. CINQUIMA, Universidad de Valladolid, Valladolid, Spain*; HIMANSHI SINGH, MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*.



Exploring the conformational landscape of multi-conformational systems, such as macrolactones, can be challenging, as their great flexibility leads to small structural changes that result in a large number of energy minima. High-resolution gas-phase microwave spectroscopy has proven to be unique technique, being able to isolate and discern conformers or clusters unambiguously without masking effects. Macrolactones are considered "privileged scaffolds" within the medicinal chemistry community, because their study led to the discovery of bioactive compounds. However, gas-phase studies on the changes in structure and intra/intermolecular interactions after solvation of these biomolecules are very scarce. Based on the previous rotational study of oxacyclotridecan-2-one (C12) and 16-hexadecanolide (C15),[a] in this work we have studied the structural behaviour of these molecular systems after the addition of individual water (W) molecules.

Using broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy, five conformers have been observed so far for the C12$^{\cdots}$W complex and the global minimum for C15$^{\cdots}$W. This study has once again challenged the limits of rotational spectroscopy and quantum chemical calculation due to the structural complexity of these complexes. These results are the initial steps for future microsolvation studies with different solvents.

[a] M. Parra-Santamaria, I. Usabiaga, A. Insausti, E. R. Alonso, F. J. Basterretxea, C. Calabrese, E.J. Cocinero, HRMS2022, Prague (Czech Republic), 2022.

RJ09 **4:46 – 5:01**

INTERMOLECULAR INTERACTIONS OF TOLUNITRILES ($CH_3C_6H_4CN$)

CELINA BERMÚDEZ, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*; ELIAS M. NEEMAN, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*; WENQIN LI, ALBERTO LESARRI, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*.

Aromatic rings have taken a lot of attention of the scientific community during the last years due, in part, to their detection in the interstellar medium (ISM). Benzonitrile, cyanonaphtalene, and cyanoindene are examples of the first and the few individual aromatic species detected, all of them in TMC-1 molecular cloud.[a] Their presence is certain but their formation under the ISM conditions remains unclear. In the present work, we have analyzed the intermolecular interactions in small gas-phase clusters of a family of aromatic species: tolunitriles, also known as methylbenzonitriles ($CH_3C_6H_4CN$). Our aim is to understand the very first steps of the reactivity of small aromatic molecules by unveiling the principal binding sites for polar molecules, where the reactions might be initiated. Likewise, we have analyzed the influence of the relative position of the ring substituents (methyl and cyano groups). The rotational spectra of the complexes of *ortho*, *meta* and *para* tolunitriles were studied using a broadband chirped pulsed Fourier transform microwave spectrometer with an operating frequency range of 2-8GHz. We have employed water as polar probing molecule. A comparative analysis of the hydration sites of the three tolunitriles together with that of benzonitrile[b] has unveiled the influence of the methyl group in the water anchoring site.

[a] McGuire B. *et al., Science*, 359, 202-205, **2018**; McGuire B. *et al., Science*, 371, 1265-1269, **2021**; Sita M.L. *et al., ApJL*, 938, L12, **2022**
[b] Melandri, S. *et al., J.Chem.Phys.* 111, 3874 **1999**

RJ10 **5:04 – 5:19**

URONIC ACIDS IN GAS PHASE

ARAN INSAUSTI, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*; ELENA R. ALONSO, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; ANDER CAMIRUAGA, PIERRE ÇARÇABAL, *Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, CNRS, Orsay, France*; EMILIO J. COCINERO, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*.

Sugars are versatile molecules that play a variety of roles in the organism. For example, they are important in energy storage processes, cellular recognition or as structural scaffolds. Here, we focus on uronic acids derivatives of the most abundant monosaccharides in the nature, concretely in glucuronic acid (GlcA) and galacturonic acid (GalA). By the combination of high resolution spectroscopy, supersonic expansions and laser ablation as vaporization technique with quantum chemistry calculations we are able to obtain valuable information in gas phase about the bare structures of both anomers of GlcA and GalA (with rotational spectroscopy) and water clusters of the 1-O-phenylated derivative of GlcA (using ion-dip spectroscopy (IR-UV)). Previous studies in the gas phase had been performed on α/β-Glucose1,2 and β-Galactose2,3 where the importance of –CH2OH backbone in H-bond orientation and hydration was reported. In this work, we focus on how the characteristic –COOH group of uronic acids and their anomeric hydroxyl group configuration have effect in the H-bond network cooperativity/orientation and microsolvation process.

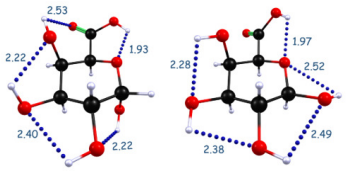


Figure 1: Observed conformers of both anomers of GalA

RJ11 **5:22 – 5:37**

COMPARATIVE AB-INITIO STUDIES OF HELICAL STRUCTURE OF PERFLUOROOCTANOIC ACID (PFOA) AND PERFLUOROOCTANE (PFO)

HEENA S. KARANI, SYLVESTRE TWAGIRAYEZU, *Chemistry and Biochemistry, Lamar University, Beaumont, TX, USA*.

As flexible molecules with long fluoroalkyl chain and multiple internal rotations, PFOA and PFO are excellent candidates for studies of molecular helicity and resulting conformational dynamics. Additionally, the exact structure of PFOA, as man-made environmental pollutant, is highly desired for the development of new spectroscopic tools for its detection in environmental samples. We present potential energy landscapes and helical structures of PFOA and PFO that are computed at Density Functional Theory levels with B3LYP-D3BJ/6-311G basis set by scanning dihedral angles and bending angles in steps of 10 degree each. The resulting potential energy surfaces show three equivalent minima for PFO (at 70^0, 190^0, and 310^0) while only two minima(at 120 ^{0} and 320^0) are seen for PFOA. These minima correspond to stable helical conformers as results of maximizing the separation between F-atoms and rotating the carboxylic end terminal (PFOA only). The nature of helical coiling has been further explored by displacing the fluoroalkyl chain away from trans configurations back to the stable helical coiling structures. We notice that a helical angle of 14 degrees is necessary for the helical coiling to be realized and is insensitive to the end terminal. The work to evaluate the exact impact of fluoroalkyl chain on the helical coiling is underway and will be presented this talk.

RK. Vibrational structure/frequencies

Thursday, June 22, 2023 – 1:45 PM

Room: B102 Chemical and Life Sciences

Chair: Jacob Stewart, Connecticut College, New London, CT, USA

RK01 **1:45 – 2:00**

ANALYSIS OF COMBINED MILLIMETER-WAVE AND FOURIER TRANSFORM INFRARED SPECTRA OF DN_3: EXTENSION OF THE ANALYSIS TO EIGHT NEW VIBRATIONAL STATES

R. CLAUDE WOODS, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; BRENT K. AMBERGER, *Department of Chemistry, University of Wisconsin, Madison, WI, USA*; BRANT E. BILLINGHURST, *Materials and Chemical Sciences Division, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada*; BRIAN J. ESSELMAN, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; PATRIK KANIA, *Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Czech Republic*; ZBIGNIEW KISIEL, *ON2, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland*; ROBERT J. McMAHON, VANESSA L. ORR, ANDREW N. OWEN, HOUSTON H. SMITH, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*; STEPAN URBAN, *Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Czech Republic*; KAREL VÁVRA, *Institute of Physics, University of Kassel, Kassel, Germany*; SAMUEL A. WOOD, *Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA*.

We present a combined millimeter-wave and high-resolution infrared (FTIR) analysis of the the spectra of DN_3. We have observed the infrared spectrum of DN_3 at a resolution of 0.0009 cm^{-1}using the synchrotron at the Canadian Light Source between 30 and 5000 cm^{-1}at several pressures between 1 and 100 mTorr. We have also measured the millimeter-wave spectrum of DN_3 at Wisconsin and at Prague, covering a frequency range from 130 to 730 GHz. Using classical linear least-squares fitting and combination differences, we have assigned the spectra for the ground state and 15 lowest-energy vibrationally excited states (including 8 not previously studied). The latter include the four combination states of either ν_3 or ν_4 with either ν_5 or ν_6 and the tetrad of states involving three quanta of ν_5 and ν_6. In fact, all sixteen of these vibrational states are a complex polyad coupled by Coriolis, Darling-Dennison, and Fermi interactions that strongly perturb the observed transition frequencies. We are working toward combining all of this spectral data to achieve a global sixteen-state fit using SPFIT.

RK02 **2:03 – 2:18**

LEVERAGING DOUBLE-RESONANCE SPECTROSCOPY TO UNDERSTAND TRANS-GLYCIALDEHYDE AND 17 OF ITS VIBRATIONALLY EXCITED STATES

LUIS BONAH, SVEN THORWIRTH, HOLGER S. P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*; J.-C. GUILLEMIN, *UMR 6226 CNRS - ENSCR, Institut des Sciences Chimiques de Rennes, Rennes, France*; STEPHAN SCHLEMMER, *I. Physikalisches Institut, Universität zu Köln, Köln, Germany*.

Rotational spectra of vibrationally excited species are important tracers for the temperature structure of astronomical objects such as high-mass star-forming regions and are also assumed to be the reason for many yet unassigned spectroscopic features observed in line-rich sources. Thus, they bear high astronomical interest but are so far largely unexplored.

Here, the ground state and 17 vibrationally excited states of the trans conformer of glycialdehyde ($C_3H_4O_2$) are examined. The low-lying torsional motion of the aldehyde group trans to the oxirane ring at about 140 ± 10 cm^{-1} and the three non-zero dipole moment components lead to a dense and complicated mm-wave spectrum.

High-resolution broadband spectra were recorded in the frequency ranges of 75−170 GHz and 500−750 GHz with an in-house synthesized sample. The broadband spectra alone were not sufficient for identifying the weak rotational transitions of vibrationally excited states high in energy and therefore were supported by double-resonance double-modulation (DM-DR) measurements for which an updated experimental implementation was used.[a] DM-DR measurements are a convenient method to derive the relationships of transitions by identifying transitions that share a common energy level. This greatly simplified the assignment of series of perturbed or weak vibrational satellites. Candidates were identified either by visual inspection in Loomis-Wood plots in our LLWP software[b] or automated with peaklists.

The preliminary results of the analysis including the interaction analysis of selected states will be presented.

[a] O. Zingsheim et al., J. Mol. Spectrosc. **381** (2021) 111519

[b] L. Bonah et al., J. Mol. Spectrosc. **388** (2022) 111674; https://llwp.astro.uni-koeln.de/

RK03 **2:21 – 2:36**

CAVITY RING DOWN MEASUREMENTS ON PROPYLENE OXIDE IN THE 3μm REGION

FABIAN PETERSS, KAREL VÁVRA, THOMAS GIESEN, GUIDO W. FUCHS, *Institute of Physics, University of Kassel, Kassel, Germany*.

Propylene oxide (also known as methyloxirane) is one of the simplest chiral molecules and also shows effects of internal rotation of its methyl group. It is a much studied molecule and has received much scientific attention in the past.
Propylene oxide has 24 fundamental vibrational modes, with each vibrational mode consisting out of thousands of ro-vibrational transitions.
So far, ro-vibrationally resolved experimental data for the vibrational spectrum however, have been quite sparse. To address this problem, there has recently been a strong effort in our research group to obtain jet-cooled ro-vibrationally resolved spectra of propylene oxide. In this way the CH_3 torsion, CH_2, CH_3 rocking and ring breathing fundamental vibrational modes have been investigated with different experimental techniques.
In this work we will present our efforts in obtaining a continuous jet-cooled spectrum of propylene oxide in the 3μm region with a cw-OPO cavity ringdown spectrometer and report about our latest progress in analysing the C-H stretching group in the 3μm region. In the measured spectrum, various combination bands have also been observed, whose impact on neighbouring vibration bands will also be discussed.

RK04 **2:39 – 2:54**

INFRARED PHOTODISSOCIATION SPECTROSCOPY OF COBALT CATION ACETYLENE COMPLEXES

ANNA G BATCHELOR, IAN WEBSTER, TIMOTHY B WARD, MICHAEL A DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA, USA*.

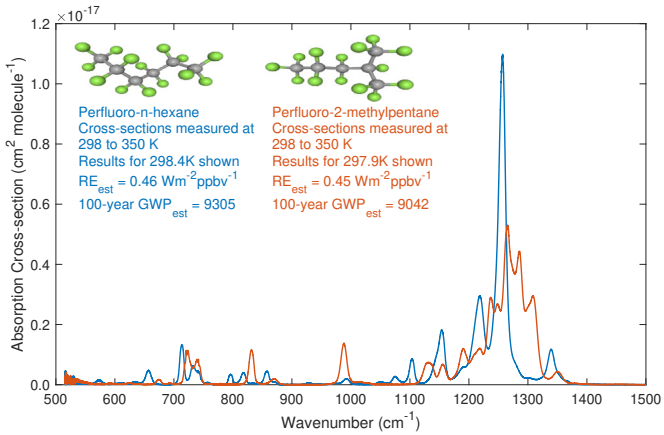
Cobalt cation-acetylene complexes are size-selected and studied with infrared laser photodissociation spectroscopy. $Co^+(C_2H_2)_n$ complexes are produced via laser vaporization in a pulsed supersonic expansion of argon seeded with acetylene. These complexes are mass-selected in a reflectron time-of-flight mass spectrometer, and their infrared spectra are measured in the C–H stretching region (2800 - 3400 cm^{-1}) with photodissociation spectroscopy. A coordination number of three is found for cobalt cation. Density functional theory calculations are performed with the B3LYP functional with the Def2TZVP basis set to support experimental spectra. Bands are observed for both the asymmetric and symmetric stretch of acetylene and are red-shifted from those of free acetylene. The presence of reacted and cation-π structures is investigated by comparing experiment to theory.

RK05 **2:57 – 3:12**

MEASUREMENT OF PERFLUORO-N-HEXANE AND PERFLUORO-2-METHYLPENTANE ABSORPTION CROSS-SECTIONS FROM 298 TO 350 K

MUHAMMAD OSAMA ISHTIAK, ORFEO COLEBATCH, *Department of Physics, University of Toronto, Toronto, ON, Canada*; KARINE LE BRIS, *Department of Physics and Astronomy, California State University, Los Angeles, CA, USA*; PAUL GODIN, *Institute for Quantum Computing, University of Waterloo, Waterloo, Ontario, Canada*; KIMBERLY STRONG, *Department of Physics, University of Toronto, Toronto, ON, Canada*.

Perfluoroalkanes are used as industrial solvents, coolants, and cleaning agents. They are potent greenhouse gases due to their infrared properties and long atmospheric lifetimes. Although regulated under the Kyoto Protocol, their atmospheric concentrations continue to rise. To quantify the potential climate impact of n$-C_6F_{14}$ and i$-C_6F_{14}$, we recorded their infrared absorption cross-sections between 515 and 1500 cm^{-1} from 298 to 350 K. To our knowledge, the i$-C_6F_{14}$ infrared absorption cross-section has been measured for the first time in this work. Using these cross-sections, we calculated the radiative efficiency (RE) and global warming potential (GWP) for each compound. The RE is 0.46±0.06 Wm^{-2}ppbv^{-1} for n$-C_6F_{14}$ and 0.45±0.06 Wm^{-2}ppbv^{-1} for i$-C_6F_{14}$. The 100-year GWP is 9305±1224 n$-C_6F_{14}$ and 9042±1189 for i$-C_6F_{14}$. These results confirm that both compounds are potent greenhouse gases.



RK06 **3:15 – 3:30**

INSIGHTS INTO HYDROGEN BONDING FROM VIBRATIONAL SPECTRA

RACHEL M. HUCHMALA, ANNE B. McCOY, *Department of Chemistry, University of Washington, Seattle, WA, USA*.

The vibrational frequencies of water molecules that are incorporated into water clusters encode an abundance of information about the strength of inter- and intramolecular interactions, and how these interactions are affected by the hydrogen-bonding environment. The addition of intensity information provides insights on how the electronic structure changes with molecular vibrations. In this talk, we will focus on the spectra of water and water clusters, and will explore how the strength and types of hydrogen bonds are encoded in these spectra. We start by considering the 1-0 transitions of the OH oscillators in the 3000 – 3500 cm^{-1} region. A challenge with this spectral region comes from the fact that with increased hydrogen bond strength, the OH stretch frequency becomes more red-shifted, the intensity increases, and the transitions become more spread out. This makes it difficult to use the shape of spectral envelope in this region to enumerate the number of water molecules that sample a specific hydrogen bonding environment. In contrast, the sensitivity of the intensity to the hydrogen bonding environment is much weaker for transitions to states with one quantum of excitation in both the OH stretching and the HOH bending vibrations in the same water molecule. We will explore the origins of the differences in the sensitivity of the intensities of these two types of transitions to the hydrogen bonding environment, and how we can use the shape of thee spectral envelope in the 5200 cm^{-1} region to enumerate of the hydrogen bonding environments sampled by individual water molecules.

Intermission

RK07 **4:10 – 4:25**

INVESTIGATING THE NUCLEAR QUANTUM EFFECT ON $H^+(H_2O)_6$

JACOB M. FINNEY, RACHEL M. HUCHMALA, ANNE B. McCOY, *Department of Chemistry, University of Washington, Seattle, WA, USA*.

Water clusters provide a set of systems where the influence of nuclear quantum effects on the stability of the hydrogen-bonding network can be studied both experimentally and theoretically. While electronic structures calculations indicate that the lowest energy isomer of $(H_2O)_6$ is the prism structure, analysis of the spectra of $(H_2O)_6$ by Johnson and Pate and their co-workers showed that the cage isomer is the lowest energy structure for $(H_2O)_6$. However, when deuterated, the prism isomer becomes the lowest energy structure again. This was further explored by our group using diffusion Monte Carlo, where we found the introduction of zero-point energy to $(D_2O)_6$ leads to the cage and prism isomers being nearly degenerate as opposed to $(H_2O)_6$ where the cage isomer is significantly lower in energy than the prism isomer. Similar effects are seen in protonated water clusters. While smaller protonated water clusters, $H^+(H_2O)_{2-5}$, show no observable change in the populations of the isomers observed in the spectra upon deuteration, the spectra of $H^+(H_2O)_6$ and $D^+(D_2O)_6$ have significant differences due to changes in the populations of isomers that are present.

Through a combination of high-level electronic structure calculations performed by the Jordan and Xantheas groups, vibrational perturbation theory, and diffusion Monte Carlo studies we investigated the effect that deuteration has on the spectrum of $H^+(H_2O)_6$. Vibrational perturbation theory provides some insights into how the spectral signatures of each of the isomers of $H^+(H_2O)_6$ changes. The challenge of vibrational perturbation theory is that it does not handle large amplitude motions well. Using diffusion Monte Carlo, we obtained an exact anharmonic ground state wave function and relative zero-point energies of several isomers of $H^+(H_2O)_6$. The ground state wave functions were found to be localized near the stationary point that each simulation started from. This allows us to use mappings between the structural information, such as OO and OH distances, to the frequencies of hydrogen-bonded OH stretches to explore the contributions of various isomers to the observed spectrum.

RK08 **4:28 – 4:43**

DIFFUSION MONTE CARLO STUDY OF VIBRATIONAL EXCITED STATES OF PROTONATED ETHYLENE ($H^+(C_2H_4)$)

PATTARAPON MOONKAEN, JACOB M. FINNEY, ANNE B. McCOY, *Department of Chemistry, University of Washington, Seattle, WA, USA*.

Carbocations are a class of important organic intermediates, which exist in hydrocarbon plasmas and are believed to play a role in the chemistry in the interstellar medium. Protonated ethylene ($H^+(C_2H_4)$) is one such carbocation, which is formed from the smallest alkene. It is also important in mass spectrometry as it appears in the mass spectra of many organic molecules and it is used as the protonating agent in chemical-ionization mass spectrometry. High-level electronic structure calculations predict that the minimum energy structure is the non-classical one in which the excess proton is equidistant from the two carbon atoms. This was confirmed by the IR spectrum of $H^+(C_2H_4)$ obtained by the Dopfer and Duncan groups.

In this work, we use fixed-node Diffusion Monte Carlo (DMC), based on a potential with CCSD(T)-level accuracy to obtain excited state wave functions and vibration frequencies. The analysis of excited state wave functions confirms that the ion is localized in the non-classical minimum on the potential. It also allows us to explore the couplings among the motions of the hydrogen atoms. The frequencies obtained from the DMC calculations are compared to the experimental frequencies in the IR spectrum. Based on this, one of the weak features between 2500 and 3000 cm^{-1} in the spectrum is assigned to the combination band of the proton transfer and breathing mode. Lastly, extensions of DMC to calculations of intensity will be discussed

RK09 **4:46 – 5:01**

THE TUNNELLING SPLITTINGS OF THE SOME STATIONARY VIBRATIONAL STATES OF THE HYDRONIUM ANION AND RADICAL DUE TO INVERSION MOTION

ULADZIMIR SAPESHKA, *Department of Physics, University of Illinois at Chicago, Chicago, IL, USA*; ALEX MALEVICH, *Mechanics and Mathematics, Belarusian State University, Minsk, Belarus*; ARYNA KHRAPUNOVA, GEORGE PITSEVICH, *Physics, Belarusian State University, Minsk, Belarus*.

Two closely related compounds, the $H_3O\cdot$ radical (HR) and H_3O^- anion (HA), are of significant interest in astrophysics. Both species exist as pyramidal isomers, but are not stable at room temperature. However, they can be stable at low temperatures and have been observed in interstellar space and comets. Similar to the ammonia molecule, HR and HA exist in two equivalent configurations, which makes tunneling between them possible. However, to our knowledge, no attempts have been made to calculate tunneling splittings even for the ground vibrational states of these species.

In this work, a non-standard set of vibrational coordinates was utilized to describe the inversion motion. The first coordinate used was the distance (h) between the oxygen atom and the plane formed by three hydrogen atoms. The second coordinate was a fully symmetrical coordinate q_{123}, which was composed of three coordinates (q_1, q_2, q_3) describing the distances between valence-free hydrogen atoms. These coordinates were tested on NH_3 and H_3O^+ species, and tunneling splittings of the ground states were obtained for both at the CCSD(T)/Aug-cc-pVQZ level of theory, yielding values of 0.78 and 53.5 cm^{-1}, respectively.

For the HR and HA species, calculations of the two-dimensional potential energy surface (2D PES) were performed at the UHF CCSD(T)/d-aug-cc-pVQZ, UHF CCSD(T)/aug-cc-pVQZ, and CCSD(T)/aug-cc-pVQZ, CCSD(T)/d-aug-cc-pVQZ levels of theory. The calculated tunneling splittings in the ground states of the hydronium anion (4.1 cm^{-1}) and radical (3.4 cm^{-1}) were found to be significantly lower than the tunneling splitting in the ground state of the hydronium cation (53.5 cm^{-1}).

RK10 **5:04 – 5:19**

TUNNELING SPLITTINGS OF THE GROUND AND EXITED TORSIOMAL STATES OF THE TRISULFANE MOLECULE.

ULADZIMIR SAPESHKA, GEORGE PITSEVICH, *Physics, Belarusian State University, Minsk, Belarus*; ALEX MALEVICH, *Mechanics and Mathematics, Belarusian State University, Minsk, Belarus*.

In 1989, M. Quack's group began searching for a suitable chiral molecule in which one could observe very small splittings of energy levels due to the parity breaking effect [1]. They performed 2D PES calculations for the trisulfane molecule in [2,3]. According to their estimations, the splitting of the ground level due to parity violation in the analyzed molecule should be on the order of 10^{-12} cm^{-1}, while the ground level splitting due to tunneling should be on the order of 10^{-23} cm^{-1}. However, the latter splitting value was obtained using extrapolation approaches. The authors in [2] noted that direct variational computation of tunneling splittings was challenging due to numerical limitations.

Despite these challenges, we aimed to test the possibilities of variational approaches and calculated the 2D PES of the HSSSH molecule at the MP2/CBS(T,Q) level of theory. By taking into account the symmetry properties of (a) the PES, (b) kinetic coefficients, and (c) Fourier series used for fittings of calculated parameters, we obtained values of tunneling splittings of the ground vibrational state for the HSSSH and DSSSD molecules of 10^{-22} and 10^{-26} cm^{-1}, respectively. Additionally, we calculated structural parameters and torsional vibration frequencies of the trisulfane molecule.

References: [1] M. Quack, Angew.Chem.Int.Engl., 28 (1989) 571-586. [2] C. Fábri, . Horný, M. Quack, ChemPhysChem, 16 (2015) 3584 - 3589 [3] S. Albert, and etc, Phys.Chem.Chem.Phys., 19 (2017) 11738

RK11 **5:22 – 5:37**

IMPORTANCE OF THE VIBRONIC EFFECTS IN CHIROPTICAL SPECTRA

QIN YANG, *Institute of Organic Chemistry and Biochemistry, Czech Academy of Science, Prague, Czechia*; JULIEN BLOINO, *Scuola Normale Superiore, Scuola Normale Superiore, Pisa, Italy*; PETR BOUR, *Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Prague, Czechia*.

Chirality is an important property of biosystems and can be found also in technologies such as 3D displays or energy storage. The chirality is reflected in the chiroptical signal. For a full understanding, it is important to know the link between the observed optical spectra and the structure. To this aim, computational spectroscopy plays a crucial role. However, common protocols, which rely on pure electronic transitions, have limited accuracy, and are generally insufficient to predict chiroptical properties, such as electronic circular dichroism or circularly polarized luminescence. Our previous studies have shown the importance of considering the vibrational contributions in simulations of UV-visible spectra of chiral molecules as well. However, the inclusion of vibronic contributions significantly increases the computational cost, and the underlying harmonic approximation is particularly problematic for flexible compounds.

We present a systematic approach to account for the vibronic effects in large chiral molecules. Starting from a prototypical molecule to highlight the importance of vibronic effects in chiroptical spectra, a general protocol is tested on Ir-complex molecules[1]. The procedure is then applied to a chiral boron dipyrromethene dye (BODIPY), which exhibits a variety of conformations and crossing of excited electronic states[2].

To analyze the results, graphical tools were developed and used. The data generated by the simulations and potential sources of inaccuracy can be overviewed more easily. These visualization techniques can provide new insights into the origin of the chiroptical signal and help design more efficient chiral molecules of technological interest.

[1] Yang, Q.; Fusé, M.; Bloino, J. et. al. *Spectrochim. Acta A* 2021, **254**, 119631.

[2] Yang, Q.; Fusé, M.; Bloino, J. *Front. Chem.* 2020, **801**.

RL. Mini-symposium: Infrared Spectroscopy in the JWST Era

Thursday, June 22, 2023 – 1:45 PM

Room: 274 Medical Sciences Building

Chair: David E. Woon, University of Illinois at Urbana-Champaign, Urbana, IL, USA

RL01 ***INVITED TALK*** **1:45 – 2:15**

THE FIRST YEAR OF ASTROCHEMISTRY WITH THE JAMES WEBB SPACE TELESCOPE

KLAUS PONTOPPIDAN, *Space Telescope Science Institute, Baltimore, MD, USA*.

About 75% of observing time with JWST is used for spectroscopy. With its versatile infrared spectroscopic instrumentation, JWST is powerful tool for enabling new understanding of the universe. From the Solar System and exoplanets, over star- and planet formation, and to the distant Universe, JWST is already revealing new aspects of our molecular universe, and at the same time posing intriguing new questions. We are seeing new detections of molecules in exoplanetary atmospheres from sensitive transit spectroscopy, revealing complex organic molecules in prestellar ices, and opening a new window on bulk volatile chemistry in protoplanetary disks. I will provide an overview of the status of the JWST mission, and in particular discuss how JWST spectroscopy is becoming a driving force in astrochemistry and beyond. I will present highlights from key JWST observing programs, including new observations of protostellar and protoplanetary chemistry, and look ahead to the next year of infrared spectroscopy from space.

RL02 **2:21 – 2:36**

HITRAN AND HITEMP DATABASES IN THE ERA OF JWST (JUST WHEN SPECTROSCOPY THRIVES)

IOULI E GORDON, ROBERT J. HARGREAVES, VLADIMIR YU MAKHNEV, LAURENCE S. ROTHMAN, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

The HITRAN and HITEMP molecular spectroscopic databases are critical for interpreting and modeling planetary spectra, including those of moons and exoplanets. With the launch of JWST, we have a unique opportunity to observe exoplanetary atmospheres that are very diverse in temperature, pressure, and composition. However, to fully utilize this opportunity, we need to ensure that the spectroscopic databases are up for the challenge.

To this end, the HITRAN2020 edition has made significant improvements to enhance the scientific output of the JWST mission. For example, broadening parameters due to the ambient pressure of He-, H_2-, CO_2, and H_2O gases have been added for many HITRAN molecules. This addition is crucial since hydrogen and helium are the primary constituents in the atmospheres of gas giants, while carbon dioxide and water vapor dominate the atmospheres of many rocky planets. Furthermore, spectral and dynamic ranges for many relevant molecules have been extended, and new isotopologues have been added. Additionally, six new molecules have been included bringing the total to 55. There are also experimental cross-sections for over 300 molecules for which no reliable quantum mechanical models exist yet. Another significant improvement is the substantial update that has been made to the database of collision-induced absorption.

This presentation will highlight the state-of-the-art data available in HITRAN, as well as the significant updates that HITEMP is currently undergoing. We will also discuss the next steps and data demands required to continue advancing our understanding of planetary atmospheres.

RL03 **2:39 – 2:54**

THE IMPENDING OPACITY CHALLENGE IN EXOPLANET ATMOSPHERIC CHARACTERIZATION

PRAJWAL NIRAULA, JULIEN DE WIT, *EAPS, MIT, Boston, MA, USA*; IOULI E GORDON, , *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; ROBERT J. HARGREAVES, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; CLARA SOUSA-SILVA, , *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; ROMAN KOCHANOV, *Laboratory of Quantum Molecular Mechanics and Radiation Processes, Tomsk State University, Tomsk, Russia*.

With a new generation of observatories coming online this decade, the process of characterizing exoplanet atmospheres will need to be reinvented. Currently mostly on the instrumental side, characterization bottlenecks will soon stand by the models used to translate spectra into atmospheric properties. Limitations stemming from our stellar and atmospheric models have already been highlighted. Here, we show that the current limitations of the opacity models used to decode exoplanet spectra propagate into an accuracy wall at $\sim$0.5-1.0 dex (i.e., 3 to 10$\times$) on the atmospheric properties, which is an order of magnitude above the precision targeted by some *JWST* Cycle 1 programs and needed for, e.g., meaningful C/O-ratio constraints and biosignatures identification. We perform a sensitivity analysis using nine different opacity models and find that most of the retrievals produce harmonious fits owing to compensations in the form of $>5\sigma$ biases on the derived atmospheric parameters translating in the aforementioned accuracy wall. We suggest a two-tier approach to alleviate this problem involving a new retrieval procedure and guided improvements in opacity data, their standardization and optimal dissemination.

RL04 **2:57 – 3:12**

PROVIDING THE PRESSURE AND TEMPERATURE BROADENING PARAMETERS OF N_2O FOR OBSERVATION OF EXOPLANET ATMOSPHERES.

HAYLEY A. BUNN, SILVIA SPEZZANO, PAOLA CASELLI, *The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany*.

In preparation for the upcoming observing facilities that will observe exoplanets, such as the ELT, ARIEL, and VLTI/GRAVITY+ and the recently launched JWST, laboratory work is necessary. These facilities will provide an unprecedented sample of spectra of exoplanetary atmospheres and will, therefore, build a 'standard model' of how a planet's chemistry depends on its star and the condition of its birth. Laboratory data on stable molecules that compose exoplanetary atmospheres, however, are far from complete, especially at high temperatures. The impact of dominant gases on the trace species is also rather unknown, thereby making the determination of molecular abundances difficult. Infrared laboratory spectra will therefore be critical to interpret the upcoming data on exoplanetary atmospheres. We use high resolution laboratory infrared spectroscopy to determine the effect of broadening and frequency shifts induced on N_2O from H_2 and He, and from temperature. This work will contribute to the growing database of spectral catalogues available to astronomers for the accurate characterisation of exoplanetary atmospheres.

RL05 **3:15 – 3:30**

ACCURATE IR INTENSITY PREDICTION FOR N_2O ANALYSIS AS A POTENTIAL BIOSIGNATURE MOLECULE IN PLANETARY AND EXOPLANETARY ATMOSPHERES: UNCERTAINTY AND UPGRADES

XINCHUAN HUANG[a], *Carl Sagan Center, SETI Institute, Moutain View, CA, USA*; DAVID SCHWENKE, *MS 258-2, NAS Facility, NASA Ames Research Center, Moffett Field, CA, USA*.

Accurate IR line lists of astronomically important molecules can help their quantitative analysis and modeling in planetary and exoplanetary atmosphere studies. To minimize the uncertainty of analysis resulting from IR line list or opacity data, the intensity prediction accuracy of semi-empirically computed IR line lists may be improved by using more accurately refined potential energy surface (PES) and more accurate ab initio dipole moment surface (DMS). Recently we reported Ames-1 296K IR line list for N_2O and its isotopologues, based on a PES refinement with σ_{rms} = 0.02 $cm^{-1}$for selected HITRAN2020 levels and band origins, and a DMS fitted from extrapolated CCSD(T)/aug-cc-pV(T,Q,5)Z dipoles in the range of 0 - 20,000 cm^{-1}, with fitting σ_{rms} = 2.7×10^{-5} a.u.. It has overall good agreement with published experimental data and effective dipole models, plus more reliable predictions for minor isotopologues. However, relatively larger discrepancies and extra sensitivities have been noticed on several bands, calling for further studies to verify and improve the accuracy of Ames intensity predictions. This investigation focuses on the dipole surface. A new CCSD(T) DMS series are fitted from various dipole sets computed on 8000 - 13,000 geometries with E_{max} = 10,000 - 17,000 cm^{-1}. With fitting σ_{rms} in the range of 10^{-5} - 10^{-7} a.u., we are able to track the DMS impact on IR intensities for each individual band or transition. Results and findings will be presented, e.g., the DMS sensitive predictions for bands like $1113\leftarrow0000$, and the stable predictions for other bands like $\nu_1\leftarrow\nu_2$. The differences among the best performing DMS candidates increases beyond 10,000 cm^{-1}. It probably requires new experimental studies to consolidate a choice of "Ames-2" DMS and line lists. Other potential factors behind the intensity accuracy and uncertainties will also be discussed.

[a]Funded by NASA Grant 18-APRA18-0013 and through NASA/SETI Co-operative Agreement 80NSSC20K1358.

RL06 **3:33 – 3:48**

PSEUDOLINE GENERATION FOR TRANS-2-BUTENE IN THE 7-15 μM REGION IN SUPPORT OF TITAN ATMOSPHERE STUDY

BRENDAN STEFFENS, *NASA Postdoctoral Program Fellow, NASA Goddard Space Flight Center, Greenbelt, MD, USA*; KEEYOON SUNG, MICHAEL MALASKA, ROSALY M LOPES, GEOFFREY C. TOON, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA*; CONOR A NIXON, *Planetary Systems Laboratory, NASA Goddard Space Flight Center, Baltimore, MD, USA*.

Butene (C_4H_8) is one of many C_4-hydrocarbons predicted to be up to 10 ppb in Titan's atmosphere by photochemical models, but yet to be detected most likely due to lack of reliable high-resolution spectroscopy, particularly at cold temperatures. As a continued work on high-resolution spectroscopy of trans-2-Butene (trans-2-C_4H_8: CH_3-CH=CH-CH_3), we present the pseudoline generation made from the same spectrum data sets in the 7 - 15 μm region (See F09 in the ISMS 2022). In total, 28 pure and N_2-mixture spectra were obtained at temperatures between 180 – 297 K using a Fourier transform spectrometer (Bruker IFS-125HR). All the spectra were fit together to derive a single set of pseudoline parameters, which includes line intensity and lower-state energy value at individual frequency bins that are considered as pseudoline positions. The pseudolines are found to reproduce the observed spectra via line-by-line radiative transfer calculations to within a few % across the spectral region. We have the pseudoline list compiled in a HITRAN database format to facilitate their implementation into existing radiative transfer codes, which use the HITRAN database for other molecules. We will present and discuss the results and performance of the pseudolines. It is anticipated that the results from this work will provide critical laboratory input toward a search for trans-2-Butene in Titan stratosphere that may be captured in the Cassini/CIRS spectra, or in future space-based (MIRI/JWST) and ground-based observations (e.g., TEXES/IRTF).[a]

[a]Government support acknowledged.

Intermission

RL07 **4:28 – 4:43**

SPECTROSCOPY OF HYDROCARBONS RELEVANT TO THE ATMOSPHERES OF HOT JUPITER EXOPLANETS IN THE 1.6-1.7 μm RANGE: UNAMBIGUOUS ASSIGNMENT OF ETHYLENE TRANSITIONS

SOLÈNE PEROT, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*; MICHAEL REY, VLADIMIR TYUTEREV, *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, Reims Cedex 2, France*; NICOLAS SUAS-DAVID, JULIEN LECOMTE, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*; SAMIR KASSI, *UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France*; LUCILE RUTKOWSKI, ROBERT GEORGES, *Institut de Physique de Rennes, UMR 6251 - CNRS, Université de Rennes, Rennes, France*.

Accurate knowledge of the absorption fingerprint of the species expected in the atmospheres of the hot Jupiter exoplanets is required to allow their detection. Methane[a] and acetylene[b] were already detected in such environments, and the presence of other small hydrocarbons such as ethylene (C_2H_4) is expected. However, spectral assignment of C_2H_4 transitions is not available at wavenumbers higher than 3500 cm^{-1}, partly due to its highly congested absorption spectrum at room temperature. To provide accurate assignments of the cold transitions, we perform cavity ring-down spectroscopy of a jet-cooled ethylene gas sample in the 1.6-1.7 μm spectral range. The gas contained in a high pressure reservoir is expanded into a low-pressure chamber through an 8.5cm-long slit with a tunable opening width ranging from 0 to 350 μm. This process induces a simplification of the absorption spectrum by reducing drastically the rotational temperature and by narrowing the absorption line widths. Three spectra were recorded with a vibrational temperature of about 220K but different rotational temperatures: 5K, 35K and 75K. Unambiguous assignment of the observed lines is performed using the TheoReTS *ab initio* line list[c] and the temperature dependence of the transition intensities.

[a] M. R. Swain, G. Vasisht, G. Tinetti, Nature, 463 (7281), 637-639 (2008)
[b] P. Giacobbe, et al., Nature, 592 (7853), 205-208 (2021)
[c] M. Rey, A. V. Nikitin, Y. L. Babikov, and V. G. Tyuterev, J. Mol. Spectrosc., 327, 138–158 (2016)

RL08 **4:46 – 5:01**

INSIGHTS INTO THE INFRARED SPECTRUM OF A PREBIOTIC SPECIES: THE CASE OF AMINOACETONITRILE

MATTIA MELOSSO, SILVIA ALESSANDRINI, LUCA BIZZOCCHI, CRISTINA PUZZARINI, *Dep. Chemistry 'Giacomo Ciamician', University of Bologna, Bologna, Italy*; MARIE-ALINE MARTIN-DRUMEL, OLIVIER PIRALI, *Institut des Sciences Moléculaires d'Orsay, Université Paris Saclay, CNRS, Orsay, France*.

Aminoacetonitrile is an interstellar molecule with a prominent prebiotic role, already detected in the chemically-rich molecular cloud Sagittarius B2(N) and postulated to be present in the atmosphere of the largest Saturn's moon, Titan. To further support its observation in such remote environments and laboratory experiments aimed at improving our understanding of interstellar chemistry, we report a thorough spectroscopic characterization of aminoacetonitrile. Fundamental bands as well as spectroscopic and molecular parameters have been accurately computed by exploiting a composite scheme rooted in the coupled-cluster theory that accounts for the extrapolation to the complete basis set limit and core-correlation effects. From the experimental side, we report the analysis of the three strongest fundamental bands of aminoacetonitrile observed between 500 and 1000 cm^{-1} in high-resolution infrared spectra. More generally, all computed band positions are in excellent agreement with the present and previous experiments. The only exception is the ν_{15} band, for which we provide a revision of the experimental assignment, now in good agreement with theory.

RL09 **5:04 – 5:19**

ANALYSIS OF EXPERIMENTAL SPECTRA OF PHOSPHINE IN THE TETRADECAD NEAR 2.2 μM USING *AB INITIO CALCULATIONS*

ANDREI V. NIKITIN, Atmospheric Spectroscopy Div., Institute of Atmospheric Optics, Tomsk, Russia; ALAIN CAMPARGUE, UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France; MICHAEL REY, Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, Reims Cedex 2, France; KEEYOON SUNG, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA; VLADIMIR TYUTEREV, Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, Reims Cedex 2, France.

In support of planetary atmosphere remote sensing and exobiology, we studied spectroscopy of phosphine (PH_3) in the full Tetradecad range, involving 26 rotationally resolved bands, for the first time. For this, we analyzed high-resolution FT-IR spectra in the 3769 - 4763 cm^{-1}region recorded at temperatures 200 K and 296 K. Overall 3242 line positions were assigned and modeled by using a combined theoretical model based on $ab\ initio$ calculations. The total nuclear motion Hamiltonian, including $ab\ initio$ Potential Energy Surface (PES), was reduced to an effective Hamiltonian using the high-order contact transformation method adapted to vibrational polyads of the AB_3 symmetric top molecules, followed by empirical optimization of the parameters. At this step, the measured line positions could be reproduced with a standard deviation of 0.0026 cm^{-1}, providing unambiguous identification for the observed features. We also obtained the effective dipole transition moments of the bands by fitting to the intensities from variational calculations using the $ab\ initio$ Dipole Moment Surface (DMS). The assigned lines were used to additionally determine 1609 vibration-rotational levels up to Jmax = 18 with their energy in the range of 3896-6037 cm^{-1}. Transitions for all 26 sublevels of the Tetradecad were identified but with noticeably a fewer number of transitions for fourfold excited bands due to their weaker intensity. We present the latest results and comparison with existing experimental spectra in the discussion of their validation and applications toward planetary atmosphere characterization.

RL10 **5:22 – 5:37**

MID-INFRARED DOPPLER-FREE SATURATION ABSORPTION SPECTROSCOPY OF THE Q BRANCH OF CH_4 ν_3=1 BAND USING A RAPID-SCANNING CONTINUOUS-WAVE OPTICAL PARAMETRIC OSCILLATOR

S M SHAH RIYADH, *Department of Physics and Astronomy, University Of Louisville, Louisville, KY, USA*; HAMZEH TELFAH, IAN JONES, JONATHAN SWIFT BERSSON, *Department of Chemistry, University of Louisville, Louisville, KY, USA*; DAVID B. FOOTE, *TOPTICA Photonics, Inc, Farmington, NY, USA*; CUNFENG CHENG, SHUI-MING HU, *Department of Chemical Physics, University of Science and Technology of China, Hefei, China*; JINJUN LIU, *Department of Chemistry, University of Louisville, Louisville, KY, USA*.

We have developed a mid-infrared Doppler-free saturation absorption spectroscopy apparatus using a continuous-wave optical parametric oscillator (CW-OPO). Here we report a comprehensive spectral scan of the Q branch transitions of the ν_3=1 band of methane (CH_4) with an average linewidth (FWHM) of 4.5 MHz. The absolute frequency calibration was achieved using previously reported transition frequencies determined using optical frequency combs, while an etalon was used for relative frequency calibration. We report 12 transitions with improved accuracies of 3 MHz. These measurements are then used to lock to a single transition, which then can be used to access the higher polyads with a second photon via a transition that is measured through CW-CRDS.

RL11 **5:40 – 5:55**

EMPIRICAL ENERGY LEVELS OF METHANE UP TO POLYAD 6

KYRIAKI KEFALA, *Physics and Astronomy , University College London, London, United Kingdom*; VINCENT BOUDON, *Laboratoire ICB, CNRS/Université de Bourgogne, DIJON, France*; SERGEI N. YURCHENKO, JONATHAN TENNYSON, *Physics and Astronomy , University College London, London, United Kingdom*.

An extensive analysis of the available spectroscopic data on methane is being performed. The MARVEL (Measured Active Rotational-Vibrational Energy Levels) algorithm by Furtenbacher et al is used to provide accurate empirical rovibrational energy levels for methane.

Experimental data are collected from 159 sources; these are evaluated and then added to a database of measured transitions with their experimental uncertainties. Each transition must have assigned quantum numbers for their upper and lower states and an uncertainty. The database is being built starting from lower and moving towards higher polyads and used as an input for MARVEL. The self-consistency of the input transitions is evaluated during the MARVEL procedure, and the uncertainties are adjusted accordingly until a self-consistent network of energy levels is achieved. As part of this process, a constant cleansing of the database of incorrect and wrongly assigned transitions is performed.

The output of the procedure is a set of empirical energy levels with their respective uncertainties, derived from the inversion of the input measured lines which will be used to update our calculated line lists. At the same time, the resulting energy levels will be used for the attribution of quantum numbers to unassigned experimental transitions.

FA. Non-covalent interactions

Friday, June 23, 2023 – 8:30 AM

Room: 116 Roger Adams Lab

Chair: Elias M. Neeman, University of Lille , Villeneuve d'Ascq, France

FA01 **8:30 – 8:45**

THE MICROWAVE SPECTRA AND ROTAMER-DEPENDENT STRUCTURES OF THE GAS-PHASE HETERODIMERS FORMED BETWEEN 2,3,3-TRIFLUOROPROPENE AND ACETYLENE

HELEN O. LEUNG, MARK D. MARSHALL, *Chemistry Department, Amherst College, Amherst, MA, USA*.

Rotation of the difluoromethyl group in 2,3,3-trifluoropropene results in three minima: a higher energy, achiral rotamer that contains a plane of symmetry and two equivalent, chiral lower-energy rotamers that form an enantiomeric pair. As revealed though the analysis of the microwave spectra of the gas-phase heterodimers formed between each rotamer and acetylene, the acetylene adopts a different bonding motif in each case. Furthermore, both modes of bonding are distinct from that observed in 1,2-difluoroethylene-acetylene where the acetylene interacts with an ethylenic fluorine-hydrogen pair located cis to each other, despite the existence of a similar pair in 2,3,3-trifluoropropene.

FA02 **8:48 – 9:03**

WEAKLY-BOUND COMPLEXES OF γ-BUTYROLACTONE AND WATER: A MATRIX ISOLATION FTIR AND COMPUTATIONAL ANALYSIS.

ANNABELLE N CARNEY, JOSH NEWBY, *Chemistry, Nazareth College, Rochester, NY, USA*.

The interaction preferences of water with small molecules has been an area of interest for many years as we endeavor to better understand solvation at the molecular scale. Here, a study of the 1:1 weakly-bound complexes of γ-butyrolactone (GBL) with water is presented. GBL is a five-membered heterocycle that contains two distinct regions that could serve as binding sites for a single water. Matrix isolation FTIR experiments identified several peaks that were not associated with isolated water or GBL, implying the bands are due to weakly-bound complexes of the two. In addition to normal water, the spectra of D_2O and HDO complexes with GBL were also recorded. These spectra were interpreted with the aid of computational chemistry. In this work, multiple density functional theories and MP2 calculations were used to find minimum energy configurations and vibrational structure of the complexes. Possible interpretations of the experimental and computational results will be presented here.

FA03 **9:06 – 9:21**

WATER BINDING TO KETONES: CYCLOOCTANONE$\cdots(H_2O)_{3-7}$ COMPLEXES

VALERIE W. Y. TSOI, ECATERINA BUREVSCHI, M. EUGENIA SANZ, *Department of Chemistry, King's College London, London, United Kingdom*.

Understanding the first interaction stages of water with organic molecules is of great interest given the ubiquity of water in nature. Here we explore the microsolvation of the eight-membered cyclic ketone cyclooctanone (CYO) using chirped pulse Fourier transform microwave spectroscopy. We previously assigned three conformers of CYO monomer and complexes of CYO$\cdots(H_2O)_{1,2}$[1,2]. Cyclooctanone hydrates with higher number of water molecules, CYO$\cdots(H_2O)_{3-7}$, have now been observed and identified with the aid of ab initio and DFT methods. Most of the complexes show several arrangements, highlighting the versatility of water molecules in their interactions with an organic solute. Binding preferences and relevant interactions will be discussed.

[1] E. Burevschi, I. Peña, M. E. Sanz, *Phys. Chem. Chem. Phys.* **2019**, *21*, 4331-4338.

[2] E. Burevschi, I. Peña, M. E. Sanz, *J. Phys. Chem. Lett.* **2021**, *12*, 12419-12425.

FA04 **9:24 – 9:39**

A ROTATIONAL STUDY OF THE INTERACTIONS OF WATER WITH THE MONOTERPENOID CARVONE

S. INDIRA MURUGACHANDRAN, M. EUGENIA SANZ, *Department of Chemistry, King's College London, London, United Kingdom.*

Carvone ($C_{10}H_{14}O$, 5-isopropenyl-2-methyl-2-cyclohexenone) is one of the most abundant monoterpenoids. It is present in many essential oils and released by plants to the atmosphere. Moreover, it is widely used as an odorant in household products, perfumes and cosmetics. Water is abundant in the atmosphere and in the mucus layer, and thus carvone interactions with water are of atmospheric and biological interest. We have studied the complexes of carvone with water using chirped pulse Fourier transform microwave spectroscopy in the 2-8 GHz frequency range. Supporting calculations have been carried out using MP2 and B3LYP-D3BJ methods. Eight different isomers of carvone-(H_2O) have been observed and identified based on the comparison between their experimental and theoretical rotational constants and the observation of the ^{18}O water isotopologues. Water forms complexes with all observed conformations of carvone in the gas phase [1,2]. Binding preferences are dictated by the formation of O–H···O and C–H···O hydrogen bonds. To visualise these interactions and gain further insight on their relative strength, non-covalent interaction and natural bond orbital analyses were performed. We will discuss our results in the context of other complexes formed by carvone.

[1] J. R. A. Moreno, T. R. Huet and J. J. L. González, *Struct. Chem.*, **2013,** *24*, 1163–1170.

[2] D. Loru, A. Vigorito, A. F. M. Santos, J. Tang and M. E. Sanz, *PCCP*, **2019**, *21*, 26111-26116.

Intermission

FA05 **10:19 – 10:34**

AB INITIO INVESTIGATIONS ON HYDROGEN BOND INTERACTIONS OF 1:1 THEOBROMINE-WATER COMPLEXES

TANVI G.S.S. SAINI, *Department of Physics, Panjab University, Chandigarh, Chandigarh, India*; ANAMIKA MUKHOPADHYAY, *Department of Physics, Sri Guru Gobind Singh College, Chandigarh, Chandigarh, India.*

Theobromine, a derivative of caffeine, which is commonly found in chocolates, leaves of tea plant, cola nut, cocoa, guarana berry etc., has been investigated since many years because of its clinical and scientific importance along with its applications in biological and pharmacological activities for living organisms. Being a heterocyclic molecule, theobromine has various potential sites which can act as either hydrogen bond (H-bond) donor or acceptor while interacting with any other biological molecule. To develop the fundamental understanding about the nature of interaction of these active sites, we have studied here the 1:1 interaction of theobromine molecule with water molecule. The electrostatic potential energy surface of 1:1 interaction between theobromine and water molecule has been explored using MP2 and wB97XD level of calculations with 6-311++ G(d,p) basis set. With an extensive search, eight different structures of the 1:1 complex of theobromine and water molecule have been obtained involving O-H—O, N-H—O, O-H—N and C-H—O H-bond interactions. Dual H-bond interactions play a key role in stabilizing all the structures. The structure having O-H—O and N-H—O interactions shows global minimum, whereas the structure with the C-H—O is the least stable one. NBO analysis has also been performed to reveal the role of hyperconjugation interaction in the stability of the complexes. Charge density topology for each complex has been analyzed using AIM calculation.

FA06 **10:37 – 10:52**

SMALL NON-COVALENT DIMERS WITH COMPETING HYDROGEN BONDED & HALOGEN BONDED MOTIFS

GREGORY S. TSCHUMPER, *Department of Chemistry & Biochemistry, University of Mississippi, University, MS, USA*.

The MP2 and CCSD(T) methods have been used in conjunction with large correlation consistent basis sets to characterize simple dimers in which halogen-bonded configurations can be energetically competitive with the hydrogen-bonded structures [1,2]. In the case of dimers formed between HCN and a diatomic hydrogen halide molecule (HX where X = Cl, Br or I), the linear halogen-bonded arrangement (HCN$\cdots$XH) is a local minimum with an electronic energy that gets closer to that of the corresponding linear hydrogen-bonded global minimum (HCN$\cdots$HX) as the size of the halogen atom increases. These relative electronic energies decrease from around 4 kcal mol^{-1} for X = Cl and roughly 3 kcal mol^{-1} for X = Br to as little as 0.5 kcal mol^{-1} for X = I near the CCSD(T) complete basis set (CBS) limit. The MP2 and CCSD(T) harmonic vibrational frequencies suggest that it may be feasible to differentiate between these structures spectroscopically. We have also conducted a similar analysis of the dimer formed between HI and acetonitrile (CH_3CN) to investigate the tentative assignment of a second feature in the HI stretching region of the infrared spectrum from matrix isolation experiments to the halogen-bonded configuration. In this system, both the hydrogen-bonded global minimum and the halogen-bonded local minimum have C_{3v} point group symmetry. The latter lies within 1 kcal mol^{-1} of the former at the CCSD(T) CBS limit, and our harmonic vibrational frequencies corroborate the tentative assignment of that spectral feature in the HI stretching region to the halogen-bonded configuration ($CH_3CN\cdots IH$). This work on small non-covalent dimers is being extended to azabenzene systems capable of interacting with multiple hydrogen halide molecules (e.g., $C_4H_4N_2(HX)_2$ and $C_3H_3N_3(HX)_3$).

[1] Perkins, M.A.; Tschumper, G.S.; Characterization of Competing Halogen- and Hydrogen-Bonding Motifs in Simple Mixed Dimers of HCN and HX (X = F, Cl, Br, and I), *J. Phys. Chem. A*, 2022, **126**, 3688–3695. DOI: 10.1021/acs.jpca.2c02041
[2] Perkins, M.A.; Tschumper, G.S.; Characterization of Competing Halogen-Bonding and Hydrogen-Bonding Motifs in the Acetonitrile/Hydrogen Iodide Dimer, *Chem. Phys.*, 2023, **568**, 111843. DOI: 10.1016/j.chemphys.2023.111843

FA07 **10:55 – 11:10**

DYNAMICS OF $(HCN)_n$ DEPOSITION IN MATRIX-ISOLATION EXPERIMENTS

THOMAS HOWARD, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*; EMILY K HOCKEY, SHANNON E GANLEY, *Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA*; LEAH G DODSON, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*.

Hydrogen cyanide (HCN) is a molecule of particular note in astrochemistry due to its usefulness as a molecular thermometer in star forming regions, its presence in the atmospheres of celestial bodies, such as Titan, and its ability to form Van der Waals complexes and polymerize with itself. The formation of weakly bound HCN dimer complexes has been controversially suggested as a first coordinating step to more complex polymerization reactions in astrophysical environments, motivating further study of this complex.

Weakly bound complexes are observed using matrix-isolation spectroscopy, leading to the assumption that complex formation occurs in the condensed-phase matrix environment. However, our previous experiments showed that the amount of HCN dimer in the condensed phase can be tuned by altering the physical conditions of gas-phase samples before deposition. We further investigate this behavior by examining how the deposition temperature from an effusive beam source affects HCN complexation.

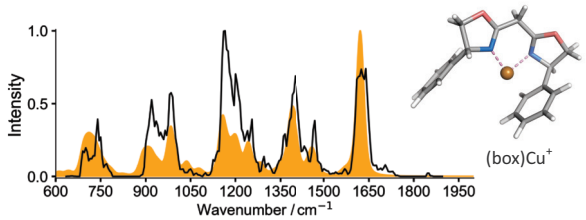
FA08 **11:13 – 11:28**

PROBING THE CONFORMATIONAL SPACE OF COPPER(I)-BOX COMPLEXES USING IRMPD SPECTROSCOPY

ALEXANDRA TSYBIZOVA, VLADIMIR GORBACHEV, PETER CHEN, *Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland*.

Chiral oxazolines are attractive ligands for enantioselective catalysis as they are easily accessible from amino alcohols and exhibit high stereocontrol. In 2007 Zocher et al. obtained experimental bond dissociation energies (BDEs) for different bisoxazoline (box) and azacorrin copper complexes.[a] Later, these reactions were investigated computationally.[b] The calculations revealed an enormous spread in calculated values for BDEs, depending on the method used. The addition of dispersion corrections did not afford an improved performance but, on the contrary, gave even worse results, compared to the non-dispersion-corrected reference values obtained with BP86.

Overall, no computational method agreed well with the experimentally obtained results. Recent computational investigations have revealed that these discrepancies might also be caused by the difficulties in locating the correct structure of the parent $(box)_2Cu^+$ ion and the corresponding $(box)Cu^+$ ion formed after the ligand dissociation. Conformational analysis showed the presence of many local minima on the conformational PES. As a result, the predicted BDEs depend significantly on the structures of the parent and the daughter ions. Therefore, it is important to obtain experimental information on their structure-a feat that may be achieved with IR ion spectroscopy. To this end, we performed IRMPD spectroscopic measurements on the $(box)_2Cu^+$, $(box)Cu^+$ and L^+ ions, which we used as a guiding tool to choose an appropriate computational method, determine the structure of the ions, and calculate more accurate BDEs.



[a] Zocher, E.; Sigrist, R.; Chen, P. Threshold CID Investigation of Isomeric Cu(I) Azabox Complexes. Inorg. Chem. 2007, 46 (26), 11366–11370.
[b] Weymuth, T.; Couzijn, E. P. A.; Chen, P.; Reiher, M. New Benchmark Set of Transition-Metal Coordination Reactions for the Assessment of Density Functionals. J. Chem. Theory Comput. 2014, 10 (8), 3092–3103.

FA09 **11:31 – 11:46**

CONTROLLING INTRAMOLECULAR H-BOND IN ONIUM IONS BY TUNING LONDON DISPERSION - PAULI REPULSION BALANCE

VLADIMIR GORBACHEV, ALEXANDRA TSYBIZOVA, PETER CHEN, *Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland*.

London Dispersion is an essential element of structural stability and thus affects chemical reactivity and selectivity. However, estimating London forces is challenging due to the omnipresent solvent or crystal lattice effects that attenuate attractive interactions. Here, we report a spectroscopic study of the intramolecular H-bond in five series of onium ions with a systematic increase in Dispersion energy donors (DEDs). Remarkably, the intramolecular H-bond might be localized/delocalized, and therefore its spectroscopic signature is used as a readout reflecting overall steric effects in the system. Therefore, we can probe a delicate London Dispersion - Pauli Repulsion balance by analyzing 2D PESs, applying different energy decomposition schemes, and performing a comparative analysis of experimental data obtained in the gas phase without any external encumbrances, including messenger tags. [1,2] Finally, considering these findings, we can tune the barrier's height to achieve the desired reactivity for the intramolecular H-transfer reaction or, in other words, turn the hydrogen bond ON/OFF upon request.

[1] V. Gorbachev, A. Tsybizova, L. Miloglyadova, P. Chen, *J. Am. Chem. Soc.* **2022**, *144*, 20, 9007–9022
[2] A. Tsybizova, E. Paenurk, V. Gorbachev, P. Chen, *J. Phys. Chem. A* **2020**, *124*, 41, 8519–8528

FB. Theory and Computation

Friday, June 23, 2023 – 8:30 AM

Room: 100 Noyes Laboratory

Chair: Mark A. Boyer, University of Wisconsin, Madison, WI, USA

FB01 **8:30 – 8:45**

PUSHING THE BOUNDARIES OF SPECTROSCOPIC SIMULATIONS WITH REAL TIME PROPAGATION

JOHANN MATTIAT, SANDRA LUBER, *Department of Chemistry, University of Zurich, Zurich, Switzerland.*

Real-time time-dependent density functional theory (RT-TDDFT) has become a widely used tool for the simulation of optical response. Apart from its favorable scaling and its capacity to resolve the whole frequency dependent linear response functions in one go, RT-TDDFT provides a non-perturbative framework to apply finite electro-magnetic fields, mimicking actual experiments.

In this contribution the versatility of RT-TDDFT is illustrated by showcasing its ability to simulate UV-VIS absorption, electric circular dichroism (ECD), (resonance) Raman and (resonance) Raman optical activity (ROA) spectra [1], the latter two within the short time approximation. For the formulation of the spectroscopic response tensors a unified formalism in terms of linear response propagators is applied, allowing insights into how the perturbation and response operators are distinguishable in the practical real-time linear response protocol. Special emphasis is on the choices of gauge, specifically length-, velocity- and symmetric gauges, and the coupling of the electro-magnetic fields to the non-local part of pseudo potentials, a proper handling of which proves to be vital for an adequate description of the chiral spectroscopic responses, ECD and ROA [2]. For UV-VIS absorption and Raman spectroscopy results for non-periodic and periodic simulation cells are presented, drawing on the velocity gauge and the modern theory of polarization. The results were obtained with a modified development version of the CP2K package.

These developments allow applications beyond single molecules, e. g. the study of liquids and interfaces [3].

[1] J. Mattiat, S. Luber, *J. Chem. Phys.* **151**, 234110, (2019)
[2] J. Mattiat, S. Luber, *J. Chem. Theory Comput.* **18**, 9, 5513–5526, (2022)
[3] J. Mattiat, S. Luber, *J. Chem. Theory Comput.* **17**, 1, 344–356 (2021)

FB02 **8:48 – 9:03**

SPIN-VIBRONIC CALCULATIONS FOR JAHN-TELLER ACTIVE MOLECULES IN QUASI-DIABATIC BASIS WITH SOCJT3

KETAN SHARMA, OLEG A. VASILYEV, TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*.

Jahn-Teller active molecules demonstrate significant vibronic and spin-orbit couplings which has always posed a computational challenge in quantum chemistry. The presence of a conical intersection in the adiabatic potential energy surfaces makes getting a reliable quantum chemistry calculation of these terms challenging due to breakdown of Born-Oppenheimer (BO) approximation. Calculating experimentally observable parameters for rotationally resolved spectra of such molecules involves three basic steps, a) generating a potential energy surface in quasi-diabatic basis, b) transformation of the potential energy surface from Cartesian to cylindrical coordinates c) diagonalizing the spin-vibronic Hamiltonian. One of the major obstacles in these calculations is solving the eigenvalue problem in quasi-diabatic basis due to the size of matrices that need to be diagonalized. In this talk we talk about pushing the boundaries for such calculations with our program package (SOCJT3). We have implemented new algorithms that diagonalize huge matrices and include coupling terms up to quartic order. This is further utilized to calculate experimentally observable rotational parameters. The primary objective of our work is to generate a simulation to understand and characterize the previously unanalyzed rotationally resolved spectra of open-shell radicals.

FB03 **9:06 – 9:21**

TRANSFORMATION OF QUANTUM MECHANICAL OPERATOR MATRIX FROM CARTESIAN TO CYLINDRICAL NORMAL COORDINATES IN QUASI-DIABATIC BASIS

OLEG A. VASILYEV, KETAN SHARMA, TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; JOHN F. STANTON, *Quantum Theory Project, University of Florida, Gainesville, FL, USA*.

As described in the previous talk, if one is analyzing a spectrum involving rotational and fine structure, the cylindrical representation of the potential energy matrix in the quasi-diabatic basis, $\mathbf{V_{cyl}}$, is more convenient due to the simple form of rovibronic Hamiltonian. It also facilitates the identification of the symmetry of the vibronic basis functions.[a] On the other hand, *ab initio* parameterization of the vibronic Hamiltonian is typically performed in the Cartesian representation, $\mathbf{V_{cart}}$. The two matrix representations for a molecule with a simple, linear Jahn–Teller $E \times e$ effect can be written as

$$\mathbf{V_{cyl}} = \begin{bmatrix} \frac{1}{2}\omega Q_+ Q_- & kQ_+ \\ kQ_- & \frac{1}{2}\omega Q_+ Q_- \end{bmatrix} \qquad \mathbf{V_{cart}} = \begin{bmatrix} \frac{1}{2}\omega(Q_a^2 + Q_b^2) + kQ_a & -kQ_b \\ -kQ_b & \frac{1}{2}\omega(Q_a^2 + Q_b^2) - kQ_a \end{bmatrix}$$

where $Q_\pm = Q_a \pm iQ_b$ are the normal modes. Here the corresponding electronic basis sets are related as $\Phi_\pm = \frac{1}{\sqrt{2}}(\Phi_a \pm i\Phi_b)$. Transforming $\mathbf{V_{cart}}$ into $\mathbf{V_{cyl}}$ through coordinate substitution together with the basis set transformation becomes tedious for higher-order expansions, especially considering multimode and multistate problems. It is therefore desirable to develop a general procedure that can be used for the transformation of operators from the Cartesian form to the cylindrical one.

In this talk, we will show that the potential energy operator represented in a tensor form can be naturally transformed from Cartesian to cylindrical representation through a series of tensor-matrix multiplications, provided that the two matrices transforming the vibrational normal coordinates and the electronic basis set are known. In general, this method can be used to transform any quantum mechanical operator matrix.

We demonstrate the effectiveness of this method with calculations for NO_3 and CH_3O.

[a] Bunker, P.R., and Jensen, P. 2006. Molecular symmetry and spectroscopy. 2nd ed. NRC Research Press, Ottawa, Canada, p. 290 ff.

FB04 **9:24 – 9:39**

CALCULATED AND EMPIRICAL VALUES OF VIBRONIC TRANSITION DIPOLE MOMENTS OF REACTIVE CHEMICAL INTERMEDIATES FOR DETERMINATION OF CONCENTRATIONS

IAN JONES, JONATHAN SWIFT BERSSON, JINJUN LIU, *Department of Chemistry, University of Louisville, Louisville, KY, USA*; KETAN SHARMA, OLEG A. VASILYEV, TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; JOHN F. STANTON, *Physical Chemistry, University of Florida, Gainesville, FL, USA*.

Absorption spectroscopy has long been known as a technique for making molecular concentration measurements and has received enhanced visibility in recent years with the advent of new techniques, like cavity ring-down spectroscopy, that have increased its sensitivity. To apply the method, it is necessary to have a known molecular absorption cross-section for the species of interest, which typically is obtained by measurements of a standard sample of known concentration. However, this method fails if the species is highly reactive, and indirect means for attaining the cross section must be employed. The HO_2 and alkyl peroxy radicals are examples of reactive species for which absorption cross-sections have been reported. This work explores and describes for these peroxy radicals the details of an alternative approach for obtaining these cross sections using quantum chemistry methods for the calculation of the transition dipole moment upon whose square the cross section depends. Likewise, details are given for obtaining the transition moment from the experimentally measured cross sections of individual rovibronic lines in the near-IR, $\tilde{A}$-$\tilde{X}$ electronic spectrum of HO_2 and the peaks of the rotational contours in the corresponding electronic transitions for the alkyl (methyl, ethyl, and acetyl) peroxy radicals. In the case of the alkyl peroxy radicals, good agreement for the transition moments, approximately 20%, is found between the two methods. However, rather surprisingly, the agreement is significantly poorer, approximately 40%, for the HO_2 radical. Possible reasons for this disagreement are discussed.

FB05 **9:42 – 9:57**

LEARNING MOLECULAR HAMILTONIANS DIRECTLY FROM SPECTRA

DANIEL P. TABOR, *Department of Chemistry, Texas A & M University, College Station, TX, USA*.

Assigning and interpreting the spectroscopy of large molecules and clusters often requires a manual trial-and-error approach. Here, we present our efforts to automate spectroscopic assignments through a data-driven approach. We will consider two cases: vibrational spectra of cold clusters and simulated electronic spectra of conjugated molecules. Our method first assumes a local mode form of the Hamiltonian and then performs an active search through the space of physically reasonable couplings that could be present in the system (e.g., anharmonicities for vibrations and electronic couplings for conjugated molecules). By finding the Hamiltonian(s) that can best fit the spectra, the assignment can be automatically performed. This approach employs a Bayesian-optimization-derived algorithm as its driver and does not require a large volume of initial training data. In this talk, we focus on applying the method to model problems, higher-level calculations of benchmark systems, and real experimental spectra found in the literature. Finally, we will present our efforts on modeling the framework's robustness to noisy input data.

Intermission

FB06 **10:37 – 10:52**

OPTICAL PROPERTIES FOR ALL SYNTHESIZABLE MOLECULES FROM QUANTUM CHEMISTRY-BASED MACHINE LEARNING

CHENXI SUN, *Department of Chemistry, University of Massachusetts- Amherst, Amherst , MA, USA*; YILI SHEN, CHENGWEI JU, ZHOU LIN, *Department of Chemistry, University of Massachusetts, Amherst, MA, USA*.

Luminescent organic molecules have been widely applied in optoelectronics and biological research. First-principles time-dependent density functional theory (TDDFT) and machine learning methods have demonstrated great success in the predictions of optical properties of large organic molecules. However, the systematic error, large time cost, and narrow range of predictable properties of TDDFT hinder its applications in high-throughput screening of real-life systems. On the other side, statistics-based methodologies have the advantages of high accuracy and low costs. While the generalizability of the models and synthesizability of the molecules still pose challenges.

Herein, we developed a ML model that implemented semi-empirical quantum chemical properties to accurately predict the absorption frequencies, emission frequencies, and photoluminescence quantum yield (PLQY) of organic molecules. Based on the evaluation on chromophore families and chromophore-solvent pairs, we illustrated that our extension of the semi-empirical quantum chemical properties remarkably improved the accuracy and generalizability of the model with only a margin increase of computational costs. Meanwhile, tree-based algorithms outperformed neural networks and managed to reach mean absolute errors (MAEs) as low as 0.061 eV for absorption frequencies, 0.065 eV for emission frequencies, and 0.10 for PLQY. Tested on another database containing 96 million compounds with semi-empirical calculations, our model exhibited great success in the predictions of optical properties for all synthesizable molecules at very low computational costs, and thus substantially promote the discovery of potential optical materials at a large scale.

FB07 **10:55 – 11:10**

THEORETICAL MODELLING OF LIGHT-MATTER INTERACTIONS AT THE NANOSCALE

DIPTESH DEY[a], GEORGE C. SCHATZ, *Department of Chemistry, Northwestern University, Evanston, IL, USA*.

In the past few decades, metal nanoparticles have attracted a lot of interest due to their ability to confine light in nanometric volumes [1] resulting in interesting applications of plasmonic nanoparticles such as optical sensors [2]. Nanometer-sized metallic particles or structures can strongly absorb and scatter light due to their ability to support surface plasmon resonances - coherent oscillations of surface conduction electrons in response to the electric field of light [3].

In my talk, I will briefly present the theory from a classical electrodynamics perspective [4] and discuss my ongoing research on (a) plasmonic enhancement and circular dichroism response of 2D metamaterials (nanoslits arrays) with circularly-polarized light, and (b) optical response of 1D and 2D arrays of gold, silver and aluminium particles with linearly polarized light. Numerical modelling will be based on finite-difference time-domain [5] and coupled-dipole methods [6].

References:

[1] E. Ozbay, Science 311, 189 (2006).

[2] K. A. Willets and R. P. Van Duyne, Annu. Rev. Phys. Chem. 58, 267 (2007).

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[4] J. Zhao, A. O. Pinchuk, J. M. Mcmahon, S. Li, L. K. Ausman, A. L. Atkinson and G. C. Schatz, Acc. Chem. Res. 41, 1710 (2008).

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FB08 **11:13 – 11:28**

CHEMFLUOR-VAE: REVERSE DESIGN OF ORGANIC FLUOROPHORES BASED ON EXPERIMENTAL OPTICAL PROPERTIES AND VARIATIONAL AUTOENCODER

CHENGWEI JU, *Pritzker School of Molecular Engineering, The University of Chicago, Chicago, IL, USA*; YONGRUI LUO, *Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China*; BO LI, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*; YUZHI XU, *Department of Chemistry, New York University, New York, NY, USA*; HANZHI BAI, *Department of Electronic Engineering, Shanghai Jiao Tong University, Shanghai, China*; RUIMING LIN, ZEHAN MI, HAOZHE ZHANG, *Pritzker School of Molecular Engineering, The University of Chicago, Chicago, IL, USA*.

Organic fluorescent molecules with desired optical properties attracted great attention, while the rational design was hindered by unclear structure properties relationship and the lack of rapid/affordable prediction methods. With the introduction of statistics-based methods in the prediction of photophysical properties for organic dyes, reverse design of fluorophores without traversing chemical space is still challenged by the features used for current methodologies.

In this work, we construct a self-referencing embedded strings (SELFIES)-based variational autoencoder (VAE) and a prediction model, which uses the latent space as the input, for the organic fluorophores, in the absence of joint training. The VAE can reproduce the structure of midsize organic dyes with acceptable accuracy. A tree-based prediction model based on Gradient Boosted Regression Trees (GBRT) can estimate the optical properties of organic dyes with a MAE 0.134 eV for emission energy and an accuracy of 0.81 for photoluminescence quantum yield (PLQY), which is comparable with the state-of-the-art quantum-mechanical based approach, time-dependent density-functional theory (TD-DFT). The feasibility of our approach in reverse design is proved by preliminary attempts at skeleton optimization and validated by first-principles calculations. New experimental synthesized molecules demonstrated the accuracy of our prediction model. Meanwhile, due to the continuous values in the latent space, this VAE-based methodology makes gradient optimization become possible for large organic materials. Combined, our statistical learning methodology opens a new venue for the design of organic fluorophore, can also be extended to the field of organic solar cell (photo conversion efficiency, PCE) and organic field-effect transistor (conductivity).

FB09 **11:31 – 11:46**

MOLECULAR DOCKING AND DYNAMICS SIMULATIONS OF AMMI VISNAGA L. CONSTITUENTS AS ANTI-MELANOGENIC AGENTS

BERNA CATIKKAS, *Department of Physics, Mustafa Kemal University, Hatay, Turkey*; NURCAN KARACAN, *Department of Chemistry, Gazi University, Ankara, Turkey*.

Ammi Visnaga has been reported to possess various biological activities such as anti-inflammatory, antioxidant, antifungal, antidiabetic, cytotoxic, antibacterial effects etc. In the present study, nineteen selected constituents of Ammi Visnaga such as osthenol, visnadin, dihydrosamidin, samidin, apiumetin, celereoin, visnagin, khellin, visamminol, cimifugin, acacetin, quercetin, isoformonometin, visnaginone, khellinone etc. were docked to agaricus bisporus tyrosinase (PDB ID:2Y9X), priestia megaterium tyrosinase (PDB ID: 3NQ1) and homo sapiens tyrosinase (PDB ID: 5M8M) to investigate the potential anti-melanogenic activity. All compounds showed higher docking scores and binding free energy than cognate ligand tropolone for 2Y9X. However, A. visnaga constituents such as coumarin (osthenol), pyranocoumarins (visnadin, dihydrosamidin, samidin), furanocoumarins (apiumetin, celeroin), visamminol (furanochromones), flavonoids (cimifugin, quercetin) have higher binding energy than kojic acid. Kojic acid is a cognate ligand of human tyrosinase (PDB ID: 5M8M) and bacillus megaterium tyrosinase (PDB ID: 3NQ1). Apiumetin (L5) has the highest binding energy of all compounds in three tyrosinase enzymes than cognate ligands. Molecular dynamic analysis shows that Apiumetin (L5) is more stable than the cognate ligand in the binding pocket. ADME analyses calculated by the QikProp program show that all compounds obey Lipinski's rule of five without violations. Schrödinger module was used for molecular docking (IFD) and molecular dynamic (Desmond) analyses. The binding free energies of the compounds were calculated by MM/GBSA approach.

FC. Astronomy

Friday, June 23, 2023 – 8:30 AM

Room: 1024 Chemistry Annex

Chair: Bryan Changala, Ctr for Astrophysics/Harvard & Smithsonian, Cambridge, MA, USA

FC01 **8:30 – 8:45**

THE LOW LYING SINGLET STATES OF ZIRCONIUM OXIDE.

MANISH BHUSAL, *Department of Physics, Old Dominion University, Norfolk, VA, USA*; PETER F. BERNATH, JASON J SORENSEN, *Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA*; JACQUES LIÉVIN, *Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, Brussels, Belgium*.

The spectra of ZrO molecules are prominent in the near infrared and optical spectra of S-type stars. S-type stars have approximately equal carbon and oxygen abundances. We have analyzed the $B^1\Pi - X^1\Sigma^+$, $C^1\Sigma^+ - X^1\Sigma^+$, and $B^1\Pi - A^1\Delta$ electronic transitions of ZrO. The emission spectrum was collected from a high temperature (2405 K) carbon furnace at the National Solar Observatory (Kitt Peak). The rotational analysis was performed using the PGOPHER program to provide spectroscopic constants. These constants were used to calculate line lists with intensities obtained from *ab initio* transition dipole moments.

FC02 **8:48 – 9:03**

ELECTRONIC SPECTRA OF *PERI*-HEXABENZOCORONENE AND OVALENE ISOLATED IN SOLID *PARA*-HYDROGEN

ISABELLE WEBER, JOHANNA LANGNER, HENRYK A. WITEK, *Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*; YUAN-PERN LEE, *Department of Applied Chemistry, Institute of Molecular Science, and Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan*.

Diffuse interstellar bands (DIB), narrow absorption features observed from the near IR to the UV, have drawn a lot of interest since their first discovery in 1922. Polycyclic aromatic hydrocarbons (PAH) and their cationic, protonated and hydrogenated derivatives are considered particularly promising candidates for the DIB carriers, but laboratory spectra of these unstable species suitable for comparison to astronomical observations are scarce.

para-Hydrogen (*para*-H_2) matrix isolation spectroscopy has frequently been employed to record the IR spectra of PAH derivatives. The obtained spectra exhibit only small shifts in line positions due to small interactions with the matrix host, in line with the 'softness' of the quantum solid *para*-H_2. However, electronic spectra of PAH isolated in solid *para*-H_2 have rarely been reported.

Ovalene ($C_{32}H_{14}$) and *peri*-hexabenzocoronene (HBC, $C_{42}H_{18}$) have both been discussed as potential DIB carriers and, therefore, their electronic absorption spectra have been studied in the gas-phase and in rare gas matrices. To assess the properties of *para*-H_2 as a matrix host for electronic spectroscopy, we present the fluorescence excitation and dispersed fluorescence spectra of these two large PAH isolated in solid *para*-H_2. We located the 0_0^0 bands of the S_1–S_0 transitions at 21049 $\mathrm{cm}^{-1}$and about 22075 $\mathrm{cm}^{-1}$for ovalene and HBC, respectively. The recorded excitation spectra in general show a good agreement with previously reported absorption spectra indicating a matrix shift below 100 cm^{-1}due to the *para*-H_2 matrix host, consistent with our earlier experiments on several smaller PAH. We complemented our experimental work with Franck-Condon Herzberg-Teller simulations on the basis of optimized geometries and vibrational frequencies obtained from (TD-)DFT calculations to derive a first assignment of individual vibrational modes to the observed absorption and emission bands associated with the electronic S_1–S_0 transition. For ovalene, we find that a consideration of the closely lying S_2 state is required to reproduce the complexity of the experimental excitation spectrum by the simulation.

FC03 **9:06 – 9:21**

THE SUBMILLIMETER WAVE SPECTRUM OF METHYL HYPOCHLORITE UP TO 500 GHz

BRIAN M HAYS, L. MARGULÈS, R. A. MOTIYENKO, *UMR 8523 - PhLAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France*; J.-C. GUILLEMIN, *Ecole Nationale Supèrieure de Chimie de Rennes, Univ. Rennes, Rennes, France*.

Organohalogen molecules are important reactants in Earth's atmosphere contributing to ozone layer loss. The simplest oxygen bearing organochloride, methyl hypochlorite CH_3OCl, is expected as a product in ozone hole chemistry. Interstellar chemistry of organohalogens has received recent interest through the detection of the methylchloride, while searches for more complex organochlorides is limited due to lack of available spectra. We synthesized and recorded the submillimeter wave spectrum of methyl hypochlorite between 150-500 GHz using absorption spectroscopy. The fitted spectra are extended for both chlorine isotopologues, with hyperfine structure present to high frequencies. The details of the spectroscopic analysis and prospects for detection in space will be discussed.

FC04 **9:24 – 9:39**

THE ROTATION-TUNNELING SPECTRUM OF 3-HYDROXYPROPENAL, HOCHCHCHO

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3-Hydroxypropenal is the lower energy tautomeric form of propanedial, also known as malonaldehyde. It has two equivalent minima separated by a modest barrier which leads to two tunneling states separated by 647 GHz. Its rotational spectrum was analyzed in several studies, most recently through its a-type rotation-tunneling spectrum near 650 GHz.[a] 3-Hydroxypropenal was identified tentatively within the framework of the Protostellar Interferometric Line survey (PILS) toward the prototypical solar-type Class 0 young stellar system IRAS 16293−2422 carried out with the Atacama Large Millimeter/submillimeter Array (ALMA).[b] The conclusions drawn from this study were severely limited by the fact that the rest frequencies of many potentially observable transitions were so uncertain that they could not be identified unambiguously. We have analyzed spectral recordings of 3-hydroxypropenal taken in Lille[c] that cover large parts of the 150−660 GHz region to overcome these limitations. We will present our results and the astronomical implications.

[a] T. Baba et al., J. Chem. Phys. **110** 1999, 4131.
[b] A. Coutens et al., Astron. Astrophys. **660** 2022, L6.
[c] This work was supported by the Programme National "Physique et Chimie du Milieu Interstellaire" (PCMI) of CNRS/INSU with INC/INP co-funded by CEA and CNES

FC05 **9:42 – 9:57**

ROTATIONAL SPECTRA AND INTERSTELLAR SEARCH OF MALEONITRILE (CNCHCHCN)

CELINA BERMÚDEZ, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*; CARLOS CABEZAS, JOSE CERNICHARO, *Instituto de Fisica Fundamental, CSIC, Madrid, Spain*; J.-C. GUILLEMIN, *Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - ENSCR, Rennes, France*.

Maleonitrile (N≡C-CH=CH-C≡N) is a complex organic molecule (COM) isoelectronic to the *trans*-cyanovinylacetylene (H-C≡C-CH=CH-C≡N), which has been recently detected in the interstellar medium (ISM) towards the dark molecular cloud TMC-1.[a] Both structures only differ from the ubiquitous vinyl cyanide (H-CH=CH-C≡N) by replacing one of the terminal hydrogens by a nitrile or acetyl group. The generation of maleonitrile and *trans*-cyanovinylacetylene in the space might follow similar synthetic routes. However, the lack of precise rotational constants for maleonitrile, only studied up to 15GHz,[b] hamper its detection in the space. In the present work, our goal is, firstly, to provide a complete and precise set of rotational parameters for maleonitrile and, finally, to search for in the interstellar medium. For its rotational analysis we have employed the broadband millimeterwave spectrometer based on radioastronomical receivers GACELA (GAs CEll for Laboratory Astrophysics) working in the W band (72-116.5 GHz).[c] The rotational spectra of maleonitrile have been analyzed for the ground state, and the first vibrational excited states: ν_7, $2\nu_7$, ν_{10} and ν_{18}. All of them with energy bellow 300cm^{-1}. A total of 537, 318, 55, 64 and 63, respectively, pure rotational transitions have been included in the fit. Maleonitrile was search in the space towards the TMC-1 molecular cloud.

[a] Lee K.L.K. *et al., ApJL*, 908, L11, **2021**
[b] Halter, R.J., *et al., J. Am. Chem. Soc.*, 123, 49, 12353–12363, **2019**
[c] Cernicharo, J. *et al. A&A*, 626, A34 **2019**

FC06 **10:00 – 10:15**

QUANTIFICATION OF METHANOL PHOTOLYSIS BRANCHING RATIOS USING MULTIPLEXED PHOTOIONIZATION MASS SPECTROMETRY

EMILY K HOCKEY, *Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA*; THOMAS HOWARD, JULIANNA PALOTÁS, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*; DAVID L. OSBORN, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*; LEAH G DODSON, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*.

Over 250 distinct chemical species have been detected in the interstellar regions of space. The harsh conditions of astrophysical objects mean that the molecules that form and evolve there are not subject to the same reaction conditions as on Earth. The products formed upon UV excitation of methanol, an extremely prevalent molecule in space, have not been well constrained. In a collaborative project between UMD and two government research labs—Sandia National Laboratories and Lawrence Berkeley National Laboratory—we carried out UV photodissociation studies on gas-phase methanol using 193 nm light at the Advanced Light Source synchrotron. We have identified and quantified the photodissociation products and their associated branching ratios via Multiplexed Photoionization Mass Spectrometry. Empowered by the tunability of the synchrotron source, isomeric products such as CH_3O/CH_2OH and $HCOH/H_2CO$ were able to be differentiated at different ionization energies, providing a more complete understanding of each species independently. The results of this work will inform astronomers of the destruction processes possible for this important astrochemical in regions of space with high ultraviolet radiation fields.

Intermission

FC07 **10:55 – 11:10**

SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF INTERSTELLAR CANDIDATE ALKYNYL THIOCYANATE: HCCSCN.

ELENA R. ALONSO, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; ARAN INSAUSTI, *Departamento de Química Física, Universidad del País Vasco (UPV-EHU), Bilbao, Spain*; LUCIE KOLESNIKOVÁ, *Department of Analytical Chemistry, University of Chemistry and Technology, Prague, Prague, Czech Republic*; IKER LEÓN, *Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain*; J.-C. GUILLEMIN, *UMR 6226 CNRS - ENSCR, Institut des Sciences Chimiques de Rennes, Rennes, France*.

Thiocyanates (RSCN) are not only important for their implication in functional materials and pharmaceutical chemistry, but also as potential candidates to be present in the interstellar medium (ISM). In fact, thiocyanic acid (HSCN)[a] [b] and its isomer isothiocyanic acid (HNCS)[c] have already been detected. It is a logical step to keep studying more complex molecules of the same family, also to shed light on the sulphur chemistry in the ISM. Microwave and millimetre-wave spectroscopy are the ultimate tools that enable the detection of molecular systems in the ISM. Here we present a challenging laboratory characterization of the simplest alkynyl thiocyanate HCCSCN in the microwave and millimetre-wave ranges. Results of this work will allow to search for HCCSCN in different regions of the ISM.

[a] Brunken, S. et al. (2009) 'LABORATORY DETECTION OF THIOCYANIC ACID HSCN', The Astrophysical Journal. IOP Publishing, 706(2), p. 1588. doi: 10.1088/0004-637X/706/2/1588.

[b] Halfen, D. T. et al. (2009) 'DETECTION OF A NEW INTERSTELLAR MOLECULE: THIOCYANIC ACID HSCN', The Astrophysical Journal. IOP Publishing, 702(2), p. L124. doi: 10.1088/0004-637X/702/2/L124.

[c] Frerking, M. A., Linke, R. A. and Thaddeus, P. (1979) 'Interstellar isothiocyanic acid'. United States, 234:2. doi: 10.1086/183126.

FC08 **11:13 – 11:28**

COMMENTS ON THE IMPACT OF WING CUT-OFF ON COMPUTING ABSORPTION CROSS SECTIONS: BEST PRACTICE WITH APPLICATION TO MAESTRO OPACITY DATABASE

EHSAN GHARIB-NEZHAD, *Space Science Division, NASA Ames Research Center, Moffett Field, CA, USA*; NATASHA E BATALHA, *Space Science and Astrobiology Division, NASA Ames Research Center, Moffett Field, CA, USA*; KATY CHUBB, *School of Physics and Astronomy, University of St Andrews, St Andrews, United Kingdom*; RICHARD S FREEDMAN, *Carl Sagan Center, SETI Institute, Moutain View, CA, USA*; IOULI E GORDON, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; ROBERT R. GAMACHE, *Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts, Lowell, MA, USA*; ROBERT J. HARGREAVES, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; NIKOLE K LEWIS, *Department of Astronomy, Cornell University, Ithaca, NY, USA*; JONATHAN TENNYSON, SERGEI N. YURCHENKO, *Department of Physics and Astronomy, University College London, London, United Kingdom*.

Wing cut-off dictates the frequency extent to which the Lorentzian line wings are computed from the line core. Establishing a consistent policy for determining the limit of the extent of the line profile is a difficult and complex problem. For any given species a knowledge of the true shape of the line wing usually defined as the region beyond a certain multiple of the line width of the central core may not be well established either by theory, experiment, or a combination of the two. Inaccuracy in the wing cut-off results in up to a few magnitudes of error in the opacity continuum and biases the modeled transmission and emission spectra, and ultimately impacts/biases the interpretation of observational spectra and the derived composition and thermal structure. Uncertainties in the calculation of absorption cross-section data in far wings and the line shape spectroscopic parameters for high pressures ($>$100 atm) are among those challenges that should be considered for generating accurate data for atmospheric radiative transfer modeling studies. In this talk, our community efforts to address these issues will be presented.

FC09 **11:31 – 11:46**

OBSERVATION OF VIBRATIONALLY EXCITED STATES OF SiC_2 BY STIMULATED EMISSION PUMPING (SEP) SPECTROSCOPY

SEDERRA D. ROSS, *Department of Chemistry, University of Massachusetts Boston, Boston, MA, USA*; KELVIN LEE, *Center for Astrophysics , Harvard & Smithsonian, Cambridge, MA, USA*; JONATHAN FLORES, *Department of Chemistry, University of Massachusetts Boston, Boston, MA, USA*; MICHAEL C McCARTHY, *Center for Astrophysics , Harvard & Smithsonian, Cambridge, MA, USA*; NEIL J. REILLY, *Department of Chemistry, University of Massachusetts Boston, Boston, MA, USA*.

Recent observations of the evolved carbon star IRC+10216 with unprecedented high angular resolution have revealed a plethora of unassigned (U) rovibrational lines associated with the dust formation zone. Because SiC_2 is a known, abundant molecular constituent of this region, it is a reasonable supposition that some fraction of the observed U lines arise from vibrationally excited levels of SiC_2 populated at elevated temperatures. At present, the laboratory rotational data that would permit testing of this hypothesis are largely absent: *ab initio* prediction of relevant spectroscopic constants has proved particularly challenging for SiC_2, and its excited vibrational levels are not efficiently populated in supersonic jet sources. However, the electronic transition responsible for the well-known blue-green Merrill-Sanford bands of SiC_2 admits Franck-Condon access to vibrational levels at least 4000 K above ground, inviting the application of SEP spectroscopy for the observation of vibrationally excited states. SiC_2 has been generated in our laboratory in a jet-cooled discharge of silane and acetylene, optically pumped via the M-S bands, and fluorescence depletion SEP spectra observed for dump transitions terminating in a variety of excited rovibrational levels for all three modes in the $\tilde{X}$-state. For known rotational levels of $1\nu_3$ and $2\nu_3$ (the pinwheel mode), the rotational energies derived from SEP spectra are in generally excellent agreement (a factor of at least 5 smaller than the dump laser linewidth) with previous observations, giving us good faith in our experimental procedure. The $1\nu_2$ level is notably perturbed, which likely accounts for its as-yet non-observation in the laboratory by rotational spectroscopy. A Fermi resonance with $6\nu_3$ depresses the $1\nu_2$ B and C constants significantly below the predictions of high-level theory. Vibrationally averaged rotational constants calculated using Fermi resonance mixing coefficients obtained from $\tilde{A}$-state zero-point dispersed fluorescence are broadly consistent with this interpretation.

FD. Instrument/Technique Demonstration

Friday, June 23, 2023 – 8:30 AM

Room: 217 Noyes Laboratory

Chair: Charles R. Markus, California Institute of Technology, Pasadena, CA, USA

FD01 **8:30 – 8:45**

FOURTH GENERATION BUFFER GAS CELL FOR MICROWAVE SPECTROSCOPY

LINCOLN SATTERTHWAITE, GRETA KOUMARIANOU, *Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA*; DANIEL SORENSEN, DAVID PATTERSON, *Physics, University of California, Santa Barbara, CA, USA*.

Cryogenic buffer gas cells have been widely used in experimental chemistry and physics, and have seen recent success and adoption for use for microwave spectroscopy of reactive species as well as precision measurement. Here, I present the latest in buffer gas-cooled microwave spectroscopy, including the highest resolution microwave spectroscopy ever performed, in a cryogenic, cavity enhanced buffer gas beam. The high averaging rate and low noise temperature lends extreme sensitivity to the this instrument, and measures of sensitivity will also be presented on isotopologues of carbonyl sulfide (OCS). Limitations of this technique will also be discussed.

FD02 **8:48 – 9:03**

CRESU-REMPI- A TOOL TO CHARACTERIZE EXTENDED QUASI-UNIFORM FLOW

SHAMEEMAH THAWOOS, *Department of Chemistry, University of Missouri, Columbia, MO, USA*; NICOLAS SUAS-DAVID, *IPR UMR6251, CNRS - Université Rennes 1, Rennes, France*; MATTHEW L EDLIN, *Chemistry, University of Missouri, Columbia, MO, USA*; ARTHUR SUITS, *Department of Chemistry, University of Missouri, Columbia, MO, USA*.

CRESU is a French acronym for *reaction kinetics in uniform supersonic flow*. Since the inception of this method the overwhelming studies have been carried out using laser induced fluorescence detection. In our group we have taken up diversifying the method of detections used to probe uniform supersonic flows to study reaction kinetics at very low temperatures. One such method involves coupling Chirped-Pulse Fourier-Transform mmWave spectroscopy with the flow, "CPUF" (chirped-pulse uniform flow). However, sampling and detection using the CPUF method has its own limitations as the high-density flow and the collisional environment can interfere with the free induction decay and attenuate the signal. To prevent this and maximize the capabilities of CPUF method we have developed an extended quasi-uniform flow design. The approach involves using an extended nozzle such that the reaction of interest takes place *within the nozzle itself* where the flow is considered to be uniform. Then, at the nozzle exit, the flow undergoes a second expansion to lower density and temperature which is ideal for the CPUF detection. To implement this, we need to monitor the conditions within the nozzle, and commonly used impact pressure measurements are not feasible inside the nozzle. We have instead implemented a REMPI (resonance-enhanced multiphoton ionization) detection scheme which allows characterization of the conditions of the flow inside the extended nozzle. We have built and characterized an extended nozzle with a series of electrodes to capture the electron signals produced in the REMPI detection step. We have characterized this 22 K He uniform flow using (1+1) REMPI of NO. Ongoing studies with this extended flow setup involve investigation of low temperature reaction kinetics of HCO with NO and O_2.

FD03 **9:06 – 9:21**

DEVELOPMENT OF A NEW CAVITY RINGDOWN SPECTROSCOPY SYSTEM FOR ASTROCHEMICAL STUDIES

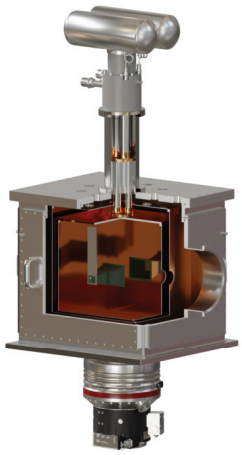
SHANNON E GANLEY, *Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA*; THOMAS HOWARD, LEAH G DODSON, *Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA*.

Cavity ringdown spectroscopy (CRDS) is a valuable tool for observing the rovibrational spectra of extremely dilute molecules. By adopting laboratory techniques like CRDS and quantifying the near-IR spectra of molecules of interstellar interest, we can increase our understanding of the properties and reactions of molecules in space. I present the design and construction of a new continuous-wave CRDS system at the University of Maryland for astrochemical studies. Further, I present the rotationally resolved vibrational spectrum of the first overtone of the C-H stretch in HCN measured with this system in the near-IR (1.5 μm). In future studies, this CRDS system will be used in tandem with a cryogenic buffer-gas cell to perform low-temperature experiments.

FD04 **9:24 – 9:39**

CONSTRUCTION OF A CRYO-COOLED BUFFER GAS CELL FOR PERFORMING BROADBAND CHIRPED-PULSE FOURIER TRANSFORM MICROWAVE (CP-FTMW) SPECTROSCOPY

BLAIR WELSH, ANGIE ZHANG, KENDREW AU, TIMOTHY S. ZWIER, *Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*.



The preparation of rotationally cold molecules through the use of supersonic expansions has long been a mainstay of high-resolution gas-phase microwave spectroscopy[1]. An increasingly popular alternative to this method is to cool molecules of interest through continuous collisions with a large reservoir of cryogenic, inert buffer gas, typically helium[2]. This offers several advantages over pulsed supersonic jet methods, namely higher data acquisition rates, higher sample throughput and lower electronics noise.

We report the construction of such a cryo-cooled buffer gas cell at the Combustion Research Facility at Sandia National Laboratories in California. The instrument has been designed to perform broadband chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy across a frequency range of 6 to 18 GHz. A cooling capacity of 2.7 W at 4 K has been leveraged in order to accommodate a broad range of source assemblies and their associated heat loads, including flash pyrolysis reactors heated up to $\sim$ 1600 °C. Interleaved, perforated radiation shielding has been employed in concert with a hybrid cryopump/turbopump regime in an effort to reduce the frequency of degenerative thermal "crashes" that often plague such instruments. The performance of the instrument with respect to benchmark species will be discussed, as well as the future of the instrument and its experimental endeavours.

[1] M. McCarthy, *et. al.*, *Astrophys. J. Supp. Ser.* **2000**, *129*, 611
[2] J. P. Porterfield, *et. al.*, *Rev. Sci. Instrum.* **2019**, *90*, 053104

FD05 **9:42 – 9:57**

IMPACT PRESSURE MEASUREMENTS OF MODIFIED LAVAL NOZZLE GEOMETRIES

ADAM CULICK, S E WORTHINGTON-KIRSCH, KYLE N. CRABTREE, *Department of Chemistry, University of California, Davis, Davis, CA, USA*.

Over 270 distinct molecules have been detected in the interstellar medium (ISM). Chemical kinetics models are used to elucidate the formation mechanisms of these species under astrophysical conditions, and these models require accurate temperature-dependent rate coefficients for gas-phase reactions. The combination of laser-induced fluorescence (LIF) with uniform supersonic molecular beams (i.e., CRESU) has proven to be a powerful method for measuring total rate constants. In recent years, there has been considerable interest in coupling chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy with the CRESU method, but the high density environment of the uniform flow causes rapid rotational dephasing, dramatically limiting its sensitivity. The Suits group at the University of Missouri-Columbia has proposed the design of an extended nozzle which contains the uniform flow, followed by a free-jet expansion where CP-FTMW spectroscopy may be employed. However the use of a nozzle extension prevents optical access to the uniform flow, complicating LIF measurements. Here, we discuss the incorporation of a fiber optic access port within the nozzle extension to provide in situ LIF measurements. Pitot tube impact pressure measurements were recorded to assess flow uniformity for solid extended nozzles, an extended nozzle with a hole, and a nozzle outfitted with a fiber optic collimator, for He and Ar nozzles spanning a range of temperatures. The effects of flow perturbation and the prospects for in situ fluorescence measurements will be discussed.

FD06 **10:00 – 10:15**

THE DEVELOPMENT OF A NEW L-SHAPED FTMW SPECTROMETER WITH CAVITY AND CHIRPED PULSE SETUPS FOR SPECTROSCOPIC AND REACTION DYNAMICS/KINETICS INVESTIGATIONS

RUSIRU PH RAJAPAKSHA, VAS ZHUKOVA, JARED MICHAEL STARNES, *Chemistry, Tennesse Tech University, Cookeville, TN, USA*; MITCHELL W SWANN, RANIL GURUSINGHE, *Chemistry, Tennessee Tech University , Cookeville, TN, USA*.

We are reporting the progress in developing a new molecular beam Fourier transform microwave (FTMW) spectrometer at Tennessee Tech University. The spectrometer uses an L-shaped vacuum chamber to house Cavity and Chirped pulse FTMW setups. This configuration allows faster switching between narrowband and broadband modes without interference from one to the other. The Fabry-Perot cavity is established using two 7.5 in. diameter and 30 cm radius of curvature Aluminum mirrors. The chamber for the chirped pulse setup is built using a polycarbonate tube, following the design of the CPUF Spectrometer from the Suits Group[a]. This microwave transparent polycarbonate chamber enables mounting the horn antennas outside of the vacuum chamber for easier adjustment of their positions with respect to the supersonic expansion, which is a particularly useful feature for using FTMW spectroscopic detection with uniform supersonic flows. The initial setup will be used for recording high-resolution and broadband rotational spectra of supersonically cooled molecular systems in the 8 - 18 GHz frequency range.

[a]Oldham, James M., Chamara Abeysekera, Baptiste Joalland, Lindsay N. Zack, Kirill Prozument, Ian R. Sims, G. Barratt Park, Robert W. Field, and Arthur G. Suits. 2014. 'A Chirped-Pulse Fourier-Transform Microwave/Pulsed Uniform Flow Spectrometer. I. the Low-Temperature Flow System'. Journal of Chemical Physics 141(15).

Intermission

FD07 **10:55 – 11:10**

ASSESSING THE PERFORMANCE OF A 6-18GHz BROADBAND MICROWAVE SPECTROMETER

EZRA BACON-GERSHMAN, LAURA WU, SIVANJALI ELENA WILLIAMS, ETHAN T YORK, CAROLINE SORRELLS, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*; DREW PRICE, *Department of Engineering, Harvey Mudd College, Claremont, CA, USA*; A. O. HERNANDEZ-CASTILLO, *Department of Chemistry, Harvey Mudd College, Claremont, CA, USA*.

Rotational spectroscopy is an incredible tool for determining molecular structures, with capabilities that include experimentally establishing bond lengths and angles with incomparable precision and investigating transient, weakly bonded, chemical species. We have designed, built, and characterized a broadband microwave spectrometer based on chirped pulse excitation, built to measure rotational spectra in the 6-18 GHz range. We introduce our molecules using a supersonic expansion, thereby achieving a rotational temperature of 1-2 K for our molecules. This brings the maximum in the rotational Boltzmann distribution into the frequency range of the instrument. The spectrometer performance has been benchmarked by measuring the pure rotational spectrum of carbonyl sulfide (OCS). We are in the process of performing spectroscopic measurements of halothane. Details of how the spectrometer works and analysis of the acquired data will be presented.

FD08 **11:13 – 11:28**

HIGH RESOLUTION SPECTROSCOPY OF EXPLOSIVE TAGGANTS USING INTRACAVITY MILLIMETER-WAVE SPECTROMETER

MHAMAD CHRAYTEH, FABIEN SIMON, FRANCIS HINDLE, GAËL MOURET, ANTHONY ROUCOU, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*; ALEXANDRE DEGUINE, MANUEL GOUBET, *Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, Villeneuve d'Ascq, France*; ARNAUD CUISSET, *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*.

Cavity measurements are well established for sensitive infrared measurements of gas-phase compounds. A recent development of a Fabry-Perot cavity by Hindle et al. [Optica, 2019, 6, 1449-1454] has allowed to adapt this technique in the sub millimeter-wave range for rotational spectral measurements using cavity enhanced absorption spectroscopy (CEAS) and cavity ring-down spectroscopy (CRDS) around 620 GHz.

Recently, we have developed a similar cavity for larger wavelengths in the 150-215 GHz range in order to measure at trace levels semi-volatile organic compounds. The capability of the spectrometer to measure semi-volatiles explosive taggants such as dinitrotoluenes or 2,3-dimethyl-2,3-dinitrobutane (DMNB) and to measure at ppm level nitromethane in this spectral range will be presented. In particular, the recent measurement in cavity and the spectral analysis of DMNB based on quantum chemistry calculations and microwave spectral analysis performed at the PhLAM laboratory will be presented.

FD09 **11:31 – 11:46**

FINALLY – A CONVENTIONAL CONFOCAL FABRY-PÉROT AT SUB-THz FREQUENCIES

LIAM DUFFY, *Department of Chemistry and Biochemistry, University of North Carolina at Greensboro, Greensboro, NC, USA*.

Confocal Fabry-Pérot resonators are ubiquitous in spectroscopy throughout the optical region of the electromagnetic spectrum and are often used for cavity ring down or Cavity Enhanced Absorption Spectroscopy (CEAS). Their use in the sub-THz region, however, is uncommon due to the lack of spherical dichroic mirrors at these wavelengths. To get around this, sub-THz spectroscopists often employ multi-pass or unconventional cavity geometries. Some of these, use planar free-standing wire-grid polarizers to couple radiation into and/or out of the cavity. A few years ago, we demonstrated that it is simple to fabricate a concave wire-grid polarizer by lithographically patterning and etching copper that is adhered to the concave surface of a spherical plastic blank. By placing a matching pair of these spherical mirror/polarizers in a confocal geometry, we demonstrate cavity Qs on the order of 100,000. This simple open-resonator geometry favors the TEM_{00} mode of the field and allows us to pass a molecular beam directly through the cavity beam waste. Underscoring the increased sensitivity of this molecular beam setup, we readily observe the weak fine-structure band near 60 GHz from the magnetic dipole allowed transitions of molecular oxygen and their splitting in the earth's magnetic field. While the setup is simple, the resulting saturated absorption/dispersion signals are surprisingly complex. At molecular beam temperatures and densities, sub-THz CEAS signals display comparable Doppler, pressure, and transit-time broadening effects. This is complicated further by the dramatic dispersion effects the molecular beam has on the cavity mode resonance. This talk will give a brief overview of the cavity and then focus on the theory for modelling and fitting the sub-THz CEAS signals.

FD10 ***Post-Deadline Abstract*** **11:49 – 12:04**

KINETICS OF HO_2 RADICAL IN NS PULSE O_2-He PLASMAS OVER A LIQUID WATER SURFACE AND UNDER ATMOSPHERIC PLASMA JET USING CAVITY RING DOWN SPECTROSCOPY

HAMZEH TELFAH, *Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, United States*; SAI RASKAR, *Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA*; ELIJAH R JANS, *Diagnostics for Hypersonics and Extreme Environments, Sandia National Laboratories , Albuquerque, NM, USA*; IGOR V. ADAMOVICH, *Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH, USA*.

Time-resolved, absolute HO_2 number density in O_2-He mixtures excited by a repetitive ns pulse discharge over a pool of distilled water and in atmospheric pressure plasma jets is measured in situ by Cavity Ringdown Spectroscopy (CRDS). The discharge cell with external electrodes to generate the plasma and a water reservoir are integrated into the CRDS cavity. The experimental results are obtained at near room temperature, both during the discharge pulse burst and in the afterglow. The HO_2 number density is inferred from the CRDS data using a spectral model exhibiting good agreement with previous measurements of absolute HO_2 absorption cross sections. HO_2 is generated during the discharge burst and decays in the afterglow between the bursts, on a ms time scale. Comparison with the kinetic modeling predictions demonstrates good agreement with the data and identifies the dominant HO_2 generation and decay processes. HO_2 in the plasma is formed predominantly by the recombination of H atoms, generated by the electron impact of water vapor, with O_2 molecules. Reactions with O atoms and OH radicals are among the main HO_2 decay processes in the afterglow. CRDS was also be used for HO_2 measurements in atmospheric pressure plasma jets, where the jet is integrated in the Open-air Cavity, the mirrors were protected with purge. The HO_2 number density is inferred from the CRDS data using a spectral model exhibiting good agreement with previous measurements of absolute HO_2 absorption cross sections.

FE. Photodissociation and photochemistry

Friday, June 23, 2023 – 8:30 AM

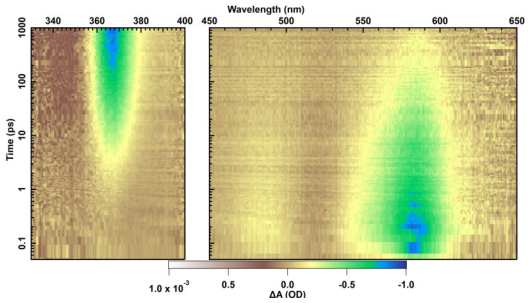
Room: B102 Chemical and Life Sciences

Chair: Wei Wei, Franklin College, Franklin, IN, USA

FE01 **8:30 – 8:45**

INTERROGATING INTERFACIAL EFFECTS IN QUANTUM DOT SENSITIZED ZNO WITH DUAL PROBE TRANSIENT ABSORPTION SPECTROSCOPY

CONNER DYKSTRA, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; MICHAEL J ENRIGHT, *Chemistry, San Francisco State University, San Francisco, CA, USA*; THOMAS ROSSI, *Photovoltaics, Helmholtz Zentrum Berlin, Berlin, Germany*; JOSH VURA-WEIS, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; RENSKE VAN DER VEEN, *Photovoltaics, Helmholtz Zentrum Berlin, Berlin, Germany*.



Quantum dot - metal oxide heterostructures (QDHs) have been heavily studied in the past 15 years for their use in harvesting solar energy. Great strides have been made in understanding their limitations, what is still unclear however is how much the two materials interact after charge injection. So far it's been presumed that QDHs share behavior with dye sensitized solar cells after charge injection, but this is not necessarily true. This work applies UV probe transient absorption spectroscopy to measure spectrally distinct signals of ZnO and CdSe, and uses global target analysis to distinguish models of interfacial dynamics. Four samples are measured and analyzed in this way to distinguish effects that can be attributed to quantum dots from effects that can be attributed to ZnO surface chemistry, three with different sizes of CdSe and one with a post-synthesis annealed ZnO sample. All samples showed evidence of split population dynamics that indicates two energetic regimes at play. It's found that an interfacial excitonic state, which is currently a favored explanation, is likely not formed due to the environmental screening of the coulombic interaction. Instead, carriers may localize near the surface due to band bending induced by adsorbed species. This explanation is consistent with a holistic view of the involved materials and previous terahertz conductivity results. Annealing the ZnO increases the overall yield and shifts charge injection towards longer timescales, which can only be explained in the context of band bending.

FE02 **8:48 – 9:03**

OBSERVATION OF ELECTRONIC AND STRUCTURAL INTERACTION BETWEEN SMALL POLARONS AND HOST MATERIALS USING FEMTOSECOND XUV REFLECTION SPECTROSCOPY

HANZHE LIU, *Department of Chemistry, Purdue University, West Lafayette, IN, USA*; SCOTT KEVIN CUSHING, *Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA*.

Small polaron formation in transition metal oxides is believed to be a reaction bottleneck in many solar energy conversion applications. While polaron formation has been previously confirmed, the microscopic interaction between a small polaron and its host material is largely unexplored. Here, using femtosecond XUV reflection spectroscopy, we report the evidence of electronic and structural interaction between the small polaron and its host material in $CuFeO_2$, a photoelectrode material for CO_2 reduction. Initial small polaron formation is observed as a spectral blue shift occurring within the first 100 fs. After polaron formation, we observe an increased coherent oscillation signal around the polaron sites, which is attributed to polaron-induced optical phonons. This observation suggests that the polaron-associated local lattice distortion can launch optical phonons in neighboring unit cells. In addition to structural coupling, the electronic states in the host materials can also be modified during polaron formation. As an example, we report an increase of Fe oxidation states after photoexcitation. The population of these highly oxidized Fe atoms strongly correlates with polaron dynamics, suggesting that a polaron can alter its surrounding electronic states in host materials.

FE03 **9:06 – 9:21**

FORMAMIDE 193 NM PHOTODISSOCIATION DYNAMICS INVESTIGATED WITH TIME-RESOLVED CHIRPED-PULSE MILLIMETER-WAVE SPECTROSCOPY AND AB INITIO THEORY

KACEE L. CASTER, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*; NATHAN A. SEIFERT, *Department of Chemistry, University of New Haven, West Haven, CT, USA*; AHREN W JASPER, KIRILL PROZUMENT, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*.

Formamide, NH_2CHO, is invoked in the prebiotic chemistry on Earth and outside of our planet because it is the simplest molecule containing a peptide linkage $[-NH-C(=O)-]$ that has a relatively high boiling point of 210 °C. There are few laboratory studies on its photodissociation possibly because the formamide vapor pressure is too low for supersonic jet experiments. In this work, we use a low-pressure (1 μbar) flow-tube reactor and *in situ* chirped-pulse Fourier transform millimeter-wave (CP-FTmmW) spectroscopy in the 260–290 GHz region to study the post-photolysis kinetics of the HCN, HNC, $HNCO$, and HCO products of the 193 nm photodissociation of formamide. The time evolution of the HCN and HNC CP-FTmmW signals is analyzed alongside complementary ab initio quasiclassical trajectory and transition state theory calculations to understand the dynamics on the NH_2CHO potential energy surface following absorption of a UV photon. The HCN/HNC branching is deduced, with good agreement demonstrated for the experimental and theoretical results.

FE04 **9:24 – 9:39**

PHOTODISSOCIATION SPECTROSCOPY AND PHOTOFRAGMENT IMAGING OF THE Fe^+(acetylene) AND $Fe^+(benzene)_{1,2}$ COMPLEXES TO PROBE DISSOCIATION ENERGIES

JOHN R. C. BLAIS, JASON E. COLLEY, NATHAN JOHN DYNAK, MICHAEL A DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA, USA*.

Tunable laser photodissociation spectroscopy and photofragment imaging experiments are employed to investigate the dissociation energies of the Fe^+(acetylene), Fe^+(benzene), and $Fe^+(benzene)_2$ ion-molecule complexes. In the spectroscopy experiment, continuous dissociation is observed above a certain energy threshold throughout the visible wavelength region for all three complexes. Photofragment imaging of the Fe^+ photoproduct in the cases of Fe^+(acetylene) and Fe^+(benzene), and imaging of the benzene$^+$ charge transfer photoproduct of Fe^+(benzene), provide upper limits on the dissociation energies of these two complexes. The dissociation energies measured from this two-pronged approach agree nicely with values determined previously by collision-induced dissociation. However, these values are inconsistent with those produced from computational chemistry at the DFT level, despite the implementation of functionals recommended for transition metal chemistry.

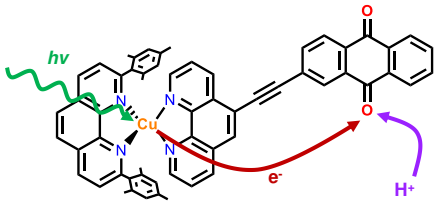
Intermission

FE05 **10:19 – 10:34**

INVESTIGATION OF ULTRAFAST ELECTRON AND PROTON TRANSFER PROCESSES IN COPPER-ANTHRAQUINONE DONOR-ACCEPTOR MOLECULES

TYLER N HADDOCK, WADE C HENKE, KAREN MULFORT, LIN X CHEN, *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA*.

We have investigated the photochemistry of molecular dyads composed of a light absorbing Cu(I) diimine species covalently linked to an anthraquinone moiety (CuAnQ). These donor-acceptor molecules serve as Earth-abundant prototypes for studying charge accumulation mechanisms in donor-acceptor-donor triads. We have utilized ultrafast optical and NIR spectroscopy to study the kinetics of the electron transfer, taking advantage of the optical and NIR signatures of the AnQ^- radical anion.



After excitation into a ^{1}MLCT band, we observe electron transfer from Cu to AnQ in 10's of picoseconds, forming a charge-separated state (CSS). The assignment of the CSS to $Cu^{2+}AnQ^-$ was confirmed by spectroelectrochemical study of the Cu^+AnQ^- species. The CSS relaxes back to the ground state in 3 nanoseconds.

In the presence of a protic solvent, the charge-separated state further transforms into a new species. The spectral changes suggest this product results from protonation of the AnQ^- into the semiquinone radical ($HAnQ^\bullet$). Accompanying this protonation is an extension of the charge-separated state lifetime from 3 ns to 15 ns.

These results provide promise for future studies on the CuAnQCu triad, which can potentially form the double reduced $Cu^{2+}AnQ^{2-}Cu^{2+}$ and $Cu^{2+}H_2AnQCu^{2+}$ CSSs. Preliminary experiments which indicate CO_2 binding to the $Cu^{2+}AnQ^-$ and $Cu^{2+}HAnQ^\bullet$ CSSs are still underway.

FE06 **10:37 – 10:52**

EXCITED STATE DEACTIVATION VIA SOLVENT TO CHROMOPHORE PROTON TRANSFER IN ISOLATED 1:1 MOLECULAR COMPLEX: EXPERIMENTAL VALIDATION BY MEASURING THE ENERGY BARRIER AND KINETIC ISOTOPE EFFECT

RAMESH JARUPULA, SAURABH KHODIA, MD SHABEEB, BAWEJA SIMRAN, BHAVIKA KALAL, SURAJIT MAITY, *Chemistry, Indian institute of technology Hyderabad, Hyderabad, Telanagana, India*.

We have experimentally demonstrated conclusive evidence of solvent-to-chromophore excited state proton transfer (ESPT) as a deactivation mechanism in a binary complex isolated in the gas phase. The above was achieved by quantitatively determining the energy barrier of the ESPT processes, qualitatively analyzing the quantum tunneling rates, and evaluating the kinetic isotope effect. The 1:1 complexes of 2,2'-pyridylbenzimidazole (PBI) with H_2O, D_2O, and NH_3, produced in a supersonic jet-cooled molecular beam, were characterized spectroscopically. The vibrational frequencies of the complexes in the S_1 electronic state were recorded using a resonant two-color two-photon ionization method coupled to a Time-of-Flight mass spectrometer set-up. In the PBI-H_2O, the ESPT energy barrier of 431 ± 10 cm^{-1} was measured using UV-UV hole-burning spectroscopy. The exact reaction pathway was experimentally determined by isotopic substitution of the tunneling-proton (in PBI-D_2O) and increasing the width of the proton transfer barrier (in PBI-NH_3). In both cases, the energy barrier was significantly increased to > 1030 cm^{-1} in the PBI-D_2O and to > 868 cm^{-1} in PBI-NH_3. The heavy atom in PBI-D_2O decreased the zero-point energy in the S_1 state significantly, resulting in the elevation of the energy barrier. Secondly, the solvent-to-chromophore proton tunneling was found to decrease drastically upon deuterium substitution. In the PBI-NH_3 complex, the solvent molecule formed a preferential hydrogen bonding with the acidic (PBI)N-H group. This led to the formation of a weak hydrogen bonding between the ammonia and the pyridyl-N atom, thus, increasing the proton transfer barrier width (H_2N-H...$N_{pyridyl}$(PBI)). The above resulted in both an increase in barrier height and a decrease in the quantum tunneling rate in the excited state. The experiment, aided by computational investigations, demonstrated the variation observed for both the energy barrier and the quantum tunneling rate by substituting NH_3 in place of H_2O can be directly correlated to the drastically different photochemical and photo-physical reactions of biomolecules under various microenvironments. To validate the above methods in different chemical environments, such as PBI-CH_3OH and PBI-CH_3OD complexes show a similar mechanism.

FE07 **10:55 – 11:10**

REMPI AND IMAGING STUDIES OF SINGLET O_2 FOLLOWING SPIN-FORBIDDEN PHOTODISSOCIATION OF OZONE

MEGAN AARDEMA, MEGAN FAST, BENJAMEN MEAS, SIMON NORTH, *Department of Chemistry, Texas A & M University, College Station, TX, USA*.

Ozone photodissociation in the Hartley (200-300 nm) and Huggins (310-370 nm) bands has been the focus of numerous studies due to its critical role in atmospheric chemistry. While Hartley band dissociation occurs primarily through two spin-allowed dissociation channels, three additional spin-forbidden channels have previously been observed following dissociation in the Huggins band. We report 1-D and 2-D REMPI spectra and velocity-mapped ion images of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ fragments following spin-forbidden dissociation in the Huggins band. We have previously observed a preference for the formation of even rotational states of $O_2(a^1\Delta_g)$ arising from Hartley band dissociation due to a Λ-doublet propensity. In the Huggins band, however, odd rotational states are enhanced in the REMPI spectrum, which we attribute to greater coupling between the initial excited state of O_3 and $^3A''$ states producing odd rotational states of $O_2(a^1\Delta_g)$, than between the initial excited state and $^3A'$ states producing even rotational states. Ion image angular distributions of the $O_2(a^1\Delta_g)$ fragment in odd and even rotational states showed significant differences following Hartley band dissociation, supporting the Λ-doublet propensity model, but are indistinguishable following Huggins band dissociations. This supports a preference for the A$'$ Λ-doublet and even rotational states following O_3 transitions from the B state to $^3A'$ states and a preference for the A'' Λ-doublet and odd rotational states following O_3 transitions from the B state to the $^3A''$ states, but indicates that in the Huggins band, the A$''$ Λ-doublet does not originate from a warmer distribution of parent molecules as seen in the Hartley band. 2D-REMPI allows simultaneous measurements of the rotational distributions for v=0-2 of the $b^1\Sigma_g^+$ state as well as v=0 of the $a^1\Delta_g$ state. The relative signal in v=0-2 of the $b^1\Sigma_g^+$ can provide information about the vibrational distribution, and rotational state distributions of each vibrational state can be fit individually. Spectra indicate a broad rotational distribution of the $O_2(a^1\Delta_g)$ fragment and a narrow distribution of the $O_2(b^1\Sigma_g^+)$ fragment. While determination of the $O_2(a^1\Delta_g)$ rotational distribution is limited due to the highly perturbed resonant state accessed in the REMPI scheme, a broad distribution is additionally supported by the multimodality of the radial distributions in the ion images.

FE08 **11:13 – 11:28**

UNRAVELING THE MECHANISM OF THE ELECTRONIC QUENCHING OF NO ($A^2\Sigma^+$) WITH C_2H_2

KEN JONES, ANDREW S. PETIT, *Department of Chemistry, California State University, Fullerton, Fullerton, CA, USA*.

NO is an important reactive intermediate in combustion and atmospheric chemistry. The experimental detection of NO commonly utilizes laser-induced fluorescence (LIF) on the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition band. However, the electronic quenching of NO ($A^2\Sigma^+$) with other molecular species provides alternative photochemical pathways that compete with fluorescence. Prior experimental studies have demonstrated that collisions with C_2H_2 are effective at driving the non-radiative relaxation of NO ($A^2\Sigma^+$). Moreover, H-atom production has been observed in this electronic quenching. However, no detailed experimental or theoretical studies have been performed on this system, and the specific photochemical pathways of NO ($A^2\Sigma^+$)+C_2H_2 remain unexplored.

Here, we describe the development of high-quality potential energy surfaces (PESs) that provide new physical insights into the long-range interactions and conical intersections that facilitate the electronic quenching of NO ($A^2\Sigma^+$) by C_2H_2. The PESs are calculated at the EOM-EA-CCSD/d-aug-cc-pVTZ//EOM-EA-CCSD/aug-cc-pVDZ level of theory, an approach that ensures a balanced treatment of the valence and Rydberg electronic states as well as an accurate description of the open-shell character of NO. We demonstrate that intermolecular interactions between NO ($A^2\Sigma^+$) and C_2H_2 cause C_2H_2 to isomerize into its *trans*-bent confirmation. We further identify a downhill pathway for internal conversion. Finally, we are beginning to explore the role that low-lying electronic excited states of C_2H_2 play in the electronic quenching of NO ($A^2\Sigma^+$) by C_2H_2. Our work informs future velocity-map imaging experiments and non-adiabatic dynamics simulations on this system.

FE09 **11:31 – 11:46**

A FIVE-CARBON UNSATURATED CRIEGEE INTERMEDIATE: SYNTHESIS, SPECTROSCOPIC IDENTIFICATION, AND THEORETICAL STUDY OF 3-PENTEN-2-ONE OXIDE

TARUN KUMAR ROY[a], TIANLIN LIU[b], CHRISTOPHER SOJDAK, MARISA KOZLOWSKI, MARSHA LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA*.

Biogenic alkenes, such as isoprene and α-pinene are the prominent source of volatile organic compounds (VOCs) emitted into the atmosphere. Atmospheric processing of alkene molecules via reaction with ozone leads to formation of zwitterionic reactive intermediates with a carbonyl oxide functional group, known as Criegee intermediates (CIs).[c] CIs exhibit strong absorption $\pi^* \leftarrow \pi$ in the near ultraviolet and visible (UV-vis) region due to the carbonyl oxide moiety. Previously, this laboratory reported the electronic spectra of the four-carbon CIs with unsaturated substituents derived from isoprene ozonolysis, methyl vinyl ketone oxide (MVK-oxide) and methacrolein oxide (MACR-oxide), on the first $\pi^* \leftarrow \pi$ to transition under jet-cooled conditions.[d,e] In the present study, we focus on the laboratory identification of a five-carbon, unsaturated Criegee intermediate 3-penten-2-one oxide, which can be produced upon atmospheric ozonolysis of substituted isoprenes. The UV–vis induced depletion spectrum of 3-penten-2-one oxide was recorded via depletion of the VUV photoionization signal (at 10.5 eV) on the m/z 100 mass channel using a time-of-flight mass spectrometer (TOF-MS). The effects of an additional methyl group in the stability of the CI and its associated electronic properties are revealed by comparing the experimentally observed UV–vis spectrum of the 3-penten-2-one oxide with isoprene-derived CI, MVK-oxide.

[a] equal contribution
[b] equal contribution
[c] D. Johnson; G. Marston, *Chem. Soc. Rev* **37**, 699(2008).
[d] M. F. Vansco; B. Marchetti, M.I. Lester, *J. Chem. Phys.* **149**, 244309(2018).
[e] M. F. Vansco; B. Marchetti; N. Trongsiriwat; T. Bhagde, G. Wang, P. J. Walsh; S.J. Klippenstein; M: I. Lester, *J. Am. Chem. Soc.* **141**, 15058(2019).

FF. Mini-symposium: Infrared Spectroscopy in the JWST Era

Friday, June 23, 2023 – 8:30 AM

Room: 274 Medical Sciences Building

Chair: Xinchuan Huang, NASA Ames Research Center, Moffett Field, CA, USA

FF01 ***Journal of Molecular Spectroscopy Review Lecture*** **8:30 – 9:00**

THE JWST ICEAGE: UNRAVELLING SOLID STATE CHEMISTRY THROUGH EPOCHS OF STAR AND PLANET FORMATION[a]

HELEN FRASER, *School of Physical Sciences, The Open University, London, United Kingdom.*

Solid state condensed molecular materials, or ices, are ubiquitous in our galaxy, particularly in regions where star and planet formation dominates. After H_2, molecular ices like H_2O, CO, CO_2 and CH_3OH are the most abundant molecules in star-forming regions. These ices are also the key reservoir of volatile elements (C, H , N, O, S), and the potential origins of so-called complex organic molecules 9COMs), the organic chemicals with more than 6 atoms that represent the increasing chemical complexity that emerges as star-formation progresses.

With the launch of JWST, a space IR telescope, in 2022, astronomers have a new ”eye” on the cold icy star-forming regions of our galaxy, particularly the pre-stellar clouds, protostars and protoplanetary discs where ices dominate the IR spectra. In this talk I’ll present the first results from the JWST ICEAGE Early Release Science Programme (http://jwst-iceage.org/). The first results show the showcase the exquisite data quality from JWST and reveal the diversity of icy chemistry found in dark regions of molecular clouds. We present a new budget for the C, O, N, and S budgets of ices in the cloud and our understanding of the chemical pathways by which ices form, including evidence for early formation of methanol, the simplest COM, in water rich ice mixtures and a potential detection of ethanol in this cloud.

All of this is only possible by combining observational spectroscopy with modelling and experiments from the laboratory. I’ll highlight the work ongoing across the ICEAGE team, in gas-phase sub-mm observations, astrochemical modelling and laboratory spectroscopy, to enable us to extract the maximum understanding and analysis of the ICEAGE spectra. One aspect of this is the potential to map the distribution of ices in space, utilising slit-less spectroscopy techniques. Our ability to exploit JWST to extract and compare 100’s of ice spectra concurrently will be briefly shown - with the first ”look” ice map data from the ERS ICEAGE programme.

[a] on behalf of the JWST ERS ICEAGE Team

FF02 **9:06 – 9:21**

IR SPECTRA OF PHOSPHINE ICES.

JOSÉ LUIS DOMÉNECH, VICTOR JOSE HERRERO, ISABEL TANARRO, VICENTE TIMÓN, BELÉN MATÉ, *Molecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain.*

Phosphorus is an element of particular interest from the astronomical point of view, since it is an essential element for life. However, not many P-containing molecules have been found in space, both because a low cosmic abundance of P (P/H$\sim 3 \times 10^{-7}$) and because P is thought to be considerably depleted on dust grains. In particular, phosphine (PH_3), has only been observed in the atmospheres of Jupiter and Saturn, and, outside of the solar system, in the circumstellar envelope of IRC +10216.[a]

Phosphine ice is thought to be a constituent of comets, and, in the ISM, a source for gas phase P upon sublimation from icy grains. In this work the infrared spectra of PH_3 ices and PH_3:H_2O ice mixtures have been studied both experimentally and theoretically. PH_3 ices were generated by vapour deposition at 10 K.[b] It was found that the amorphous to crystalline transition takes place between 35 and 40 K. A theoretical modelling of crystalline PH_3 and of a tentative amorphous PH_3 solid phase, as well as of amorphous PH_3:H_2O ice mixtures, has been performed. The infrared spectroscopic information given in this work is expected to be useful for the detection and quantification of PH_3 in astrophysical ices.[c]

[a] M. Agúndez et al. 2014 ApJL 790 L27

[b] B. Maté et al. 2021 ApJ 909 123

[c] Work supported by the spanish Ministry of Science and Innovation (MCINN) through grant PID2020-113084GB-I00.

FF03 **9:24 – 9:39**

FAR-IR SPECTROSCOPY AS DIRECT PROBE OF INTERMOLECULAR DYNAMICS IN PAH-WATER COMPLEXES

ALEXANDER KAREL LEMMENS, *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*; PIERO FERRARI, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*; BRUNO MARTINEZ-HAYA, *Department of Physical, Chemical and Natural Systems, Universidad Pablo de Olavide, Seville, Spain*; DONATELLA LORU, GAYATRI BATRA, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; AMANDA STEBER, *Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain*; MELANIE SCHNELL, *FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany*; BRITTA REDLICH, *FELIX Laboratory, Institute for Molecules and Materials (IMM), Radboud University, Nijmegen, Netherlands*.

Even though the interaction between polar water and hydrophobic molecules such as PAHs is very subtle, soot or dust particles do play a key role in the water nucleation in atmospheres and in interstellar space. To understand this process and predict their structures and properties, an accurate understanding of the shallow potential energy surface between PAH-water clusters is essential. Infrared spectroscopy is a particularly well-suited technique to study the PES of such ground-state systems. Previous IR studies, as well as complementary microwave work, established that the hydrogen bonding within the water network is more important than the interactions between water substrate. However, most infrared studies focused on the XH stretch region, which only indirectly reveals information on weaker, non-covalent interactions.

This study, focusing on neutral naphthalene interacting with up to three water molecules, shows that far-IR radiation can probe the intermolecular potential directly and reveals notable effects of the substrate on the water clusters. Despite the clusters being produced in a cold environment, the weak interactions necessitate their spectra to be interpreted within a dynamic, rather than a static framework. Purely intermolecular vibrational modes are identified and changes of the far-IR water libration modes upon complexation are investigated. Both show the perturbative effect of the substrate on water and the dynamics between PAH and water.

FF04 **9:42 – 9:57**

VIBRATIONAL SPECTROSCOPY AND REACTIVITY OF ULTRA-SMALL SILICA and SILICATE FRAGMENTS IN THE GAS-PHASE

SANDRA LANG, *Department of Chemistry, Universität Ulm, Ulm, Germany*.

Silicates are ubiquitously found as small dust grains throughout the universe. These particles are frequently subject to high-energy processes and subsequent condensation in the interstellar medium (ISM), where they are broken up into many ultra-small silicate fragments. Such fragments can be astrochemically relevant for the formation and dissociation of small molecules, such as H_2, H_2O, O_2, or CO_2. In our work, we use methods that are well established in the field of cluster chemistry and physics and are now transferred to addressing astrochemically relevant materials: infrared multiple-photon dissociation (IR-MPD) spectroscopy combined with ion trap and flow tubes reaction studies. With this approach we aim to gain insight into the geometric structure of ultra-small silica and silicate fragments as well as their reactive and catalytic properties. In particular, I will present first results on the infrared spectrum of the pyroxene monomer $MgSiO_3$, its surprisingly strong interaction with molecular oxygen, and potential initial steps of particle nucleation. Furthermore, I will address the interaction of ultra-small silica clusters with water leading to the hydroxylation of the clusters and a characteristic band in the IR-MPD spectrum, which was not detected for bulk silica.

Intermission

FF05 **10:37 – 10:52**

SOLID INDENE PURE AND IN WATER ICE: INFRARED SPECTRA AND DESTRUCTION CROSS SECTIONS

BELÉN MATÉ, VICTOR JOSE HERRERO, VICENTE TIMÓN, *Molecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain*; JOSE CERNICHARO, *Instituto de Fisica Fundamental, CSIC, Madrid, Spain*; ISABEL TANARRO, *Molecular Physics, Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain*.

In 2021, the first pure PAH molecule, indene, was finally detected in the cold pre-stellar core TMC-1[a], with an estimated gas-phase abundance of 1 - 1.6 10^{-9} with respect to H_2. The observed high relative abundance of indene in cold molecular clouds raises the question about the cycling of this molecule between the gas and the ice mantles of dust grains, and further modeling and laboratory data are required to understand these processes.

The present work is focused on the IR spectroscopy of solid phases of indene at low temperatures that, to our knowledge, have not been reported previously. Using the same experimental setup described in our previous works on urea[b], IR spectra of vapor deposited amorphous and crystalline indene and of indene mixtures with water ice have been recorded. Solid structures and vibrational spectra have been calculated using density functional theory and the results of the calculations have been used for the assignment of the measured IR spectra. Experimental and theoretical band strengths have also been determined. The IR spectra provided are expected to guide the possible detection of this species in the solid phase with the JWST. Our results suggest that some weak absorptions tentatively attributed to mixtures of large PAHs in the IR spectra of interstellar ices[c]) should have a large contribution of indene and other small aromatic hydrocarbons.

Additionally, experiments on energetic processing of indene ices with 5 keV and VUV photons have been performed, to mimic the effect that Cosmic Rays and the secondary UV field, respectively, will have on this species if present on the surface of dust grains in dense clouds. Indene radiolysis and VUV photolysis destruction cross sections have been derived.[d]

[a] Cernicharo et al. 2021, A&A 649, L15; Bukhardt et al. 2021, ApJL, 913:L18
[b] Maté et al. 2021, PCCP, 23, 22344; Herrero et al.2022, MNRAS 517, 1058–1070
[c] E. Chiar et al. 2021, ApJ, 908, 239
[d] Authors acknowledge support from the Ministerio de Ciencia e Innovacion (MICINN) of Spain under grant PID2020-113084GB-100

FF06 **10:55 – 11:10**

LABORATORY ICE ASTROCHEMISTRY IN THE ERA OF JWST

SERGIO IOPPOLO, *Department of Physics and Astronomy, University of Aarhus, Aarhus, Denmark*.

Complex organic species are expected to be formed in a variety of interstellar environments at the surface of ice grains by means of a combination of energetic and nonenergetic processing, e.g., photons, electrons, ions, and atoms. However, to date, many fundamental questions on the physicochemical origin of the observed molecular complexity in space and its link to life on Earth remain unanswered. The recent successful launch, deployment, and commissioning of James Webb Space Telescope (JWST) is a remarkable milestone, marking the onset of a new era for space science, astrophysics, astrochemistry, and astrobiology. The unprecedented combination of JWST and ground-based Atacama Large Millimeter/submillimeter Array (ALMA) observations will map and trace the ice and gas content of the interstellar medium toward a variety of space environments and physicochemical conditions, revolutionizing our understanding of the star formation process. A coordinated effort from the laboratory ice community is now needed to provide state-of-the-art ice spectral analogs that will allow for a correct interpretation of observational ice data. In my talk, I will review the current status of laboratory ice databases and a few emerging techniques that can potentially help address some of the “Grand Challenges” in astrochemistry of the next decade.

FF07 **11:13 – 11:28**

QUANTUM CHEMICAL MODELING OF ASTROCHEMICAL REACTIONS OF C ATOM AND C^+ CATION WITH NH_3 BOUND TO AMORPHOUS WATER ICE

DAVID E. WOON, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Reactions of C atoms and C^+ cations with NH_3 on water ice were characterized with density function theory using modestly sized water clusters. Both reactions are expected to occur in dense interstellar clouds and in protostellar sources. The neutral C(^{3}P) + NH_3 reaction on ice begins with the formation of triplet CNH_3 via dative bonding involving the $2s^2$ lone pair on nitrogen. Assuming it is not ejected into the gas phase, CNH_3 can subsequently react with one or two H atoms to yield CH_2NH_2 and then CH_3NH_2. The ion-molecule C^+(^{2}P) + NH_3 reaction on ice begins with charge transfer so that C(^{3}P) reacts with NH_3^+. The short-lived CNH_3^+ intermediate, which has a covalent C-N bond, deprotonates to yield the H_2NC radical, which was detected in 2021 toward the dark cloud L483 and other sources. Doublet H_2NC can react with H atoms to yield several different products. The vibrational spectrum of NH_3 on amorphous ice will also be presented.

FF08 **11:31 – 11:46**

QUANTUM TUNNELING IN INTERSTELLAR ICE BY AMMONIA (NH_3) AND ACETALDEHYDE (CH_3CHO): CHELATION AGENTS TO ASSIST RNA REPLICATION

JOSHUA H MARKS, JIA WANG, ANDREW MARTIN TURNER, N. FABIAN KLEIMEIER, *Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI, USA*; MIKHAIL M. EVSEEV, OLEG V. KUZNETSOV, *Center for Laboratory Astrophysics, Lebedev Physical Institute of the Russian Academy of Sciences (LPIRAS), Samara, Russia*; MASON McANALLY, *Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI, USA*; IVAN ANTONOV, *Center for Laboratory Astrophysics, Lebedev Physical Institute of the Russian Academy of Sciences (LPIRAS), Samara, Russia*; ALEXANDER M MEBEL, *Department of Chemistry and Biochemistry, Florida International University, Miami, FL, USA*; RALF INGO KAISER, *Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI, USA*.

Ion transport represents a vital process in all modern lifeforms, but how early cells could have accomplished this without the complex proteins used by modern cells has remained a mystery. Here, we investigate thermal reactions in interstellar analog ices of ammonia (NH_3) and acetaldehyde (CH_3CHO) with high-sensitivity and isomer-specific tunable vacuum-ultraviolet photoionization techniques. Nucleophilic addition allows access to 1-aminoethanol ($CH_3CH(OH)NH_2$) at temperatures as low as 65 K. Isotopic substitution experiments in concert with computational analysis provide mechanistic information on addition and dehydration reactions in the unique environment of interstellar ices. The high sensitivity of photoionization mass spectrometry reveals the formation of additional products such as ethanimine (CH_3CHNH) and the first observations of 1-(1-hydroxyethylamino)ethanol ($NH(CH(OH)CH_3)_2$) and 1-ethylideneaminoethanol ($CH_3CH(OH)NCHCH_3$). Low-temperature formation of these molecules indicates that sequential addition and dehydration reactions are feasible in cold interstellar environments and represent an unconventional starting point from which large chelating agents of biorelevant metal ions may have been produced abiotically and with delivery to planets like early earth could enable ion transport in primitive cells.

FF09 **11:49 – 12:04**

REACTIVITY OF KETENE UNDER INTERSTELLAR CONDITIONS: FROM THE DILUTE PHASE TO THE CONDENSED PHASE

LAHOUARI KRIM, *Chemistry/ MONARIS, CNRS, UMR 8233, Sorbonne Universités, UPMC Univ Paris 06, Paris, France*; MOHAMAD IBRAHIM, *MONARIS, Sorbonne Université, CNRS, Paris, France*; J.-C. GUILLEMIN, *ISCR - UMR6226, Univ. Rennes. Ecole Nationale Supérieure de Chimie de Rennes, Rennes, France*.

The photodecomposition of ketene under interstellar conditions and how the resulting photofragments may recombine in the 3-300 K temperature range could play an important role in investigations related to astrochemistry and astrobiology. Using a combination of bulk ice and rare-gas matrix isolation studies coupled to FTIR spectroscopy, the present work aims to understand the VUV photochemistry of CH_2CO in solid phase to mimic the photochemistry of organic species trapped in the icy interstellar grains. We show that the photolysis of CH_2CO depends strongly on the environments where it is trapped. The VUV photolysis of CH_2CO/Ne in dilute phase leads to kinetically stable and instable species such as CO, C_2H_2, CH_4, C_2H_4, C_2H_6, H_2CO, CH_3CHO, HCCO, C_2O, C_3O and C_4O. However, the same experiment carried out in condensed phase shows that the photolysis of CH_2CO ice produces mainly an organic residue which is directly observed at 10 K and remains stable in solid phase at 300 K. The IR spectroscopy analysis suggests that the resulting organic residue could be a polyketone formed at 10 K through the VUV photo-polymerization of ketene.

AUTHOR INDEX

D

E

F

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K

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Q

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V

W

X

Y

Z

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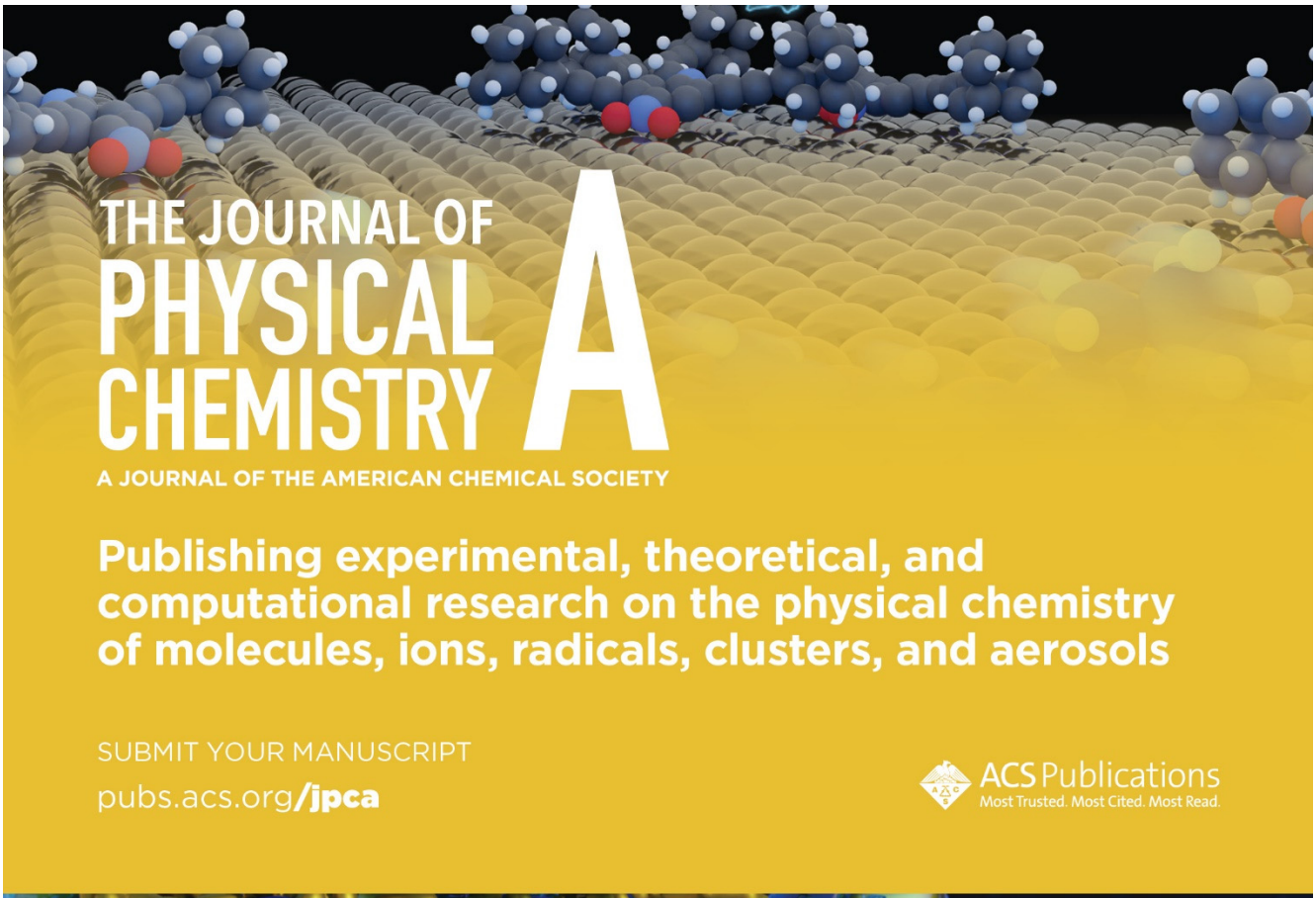

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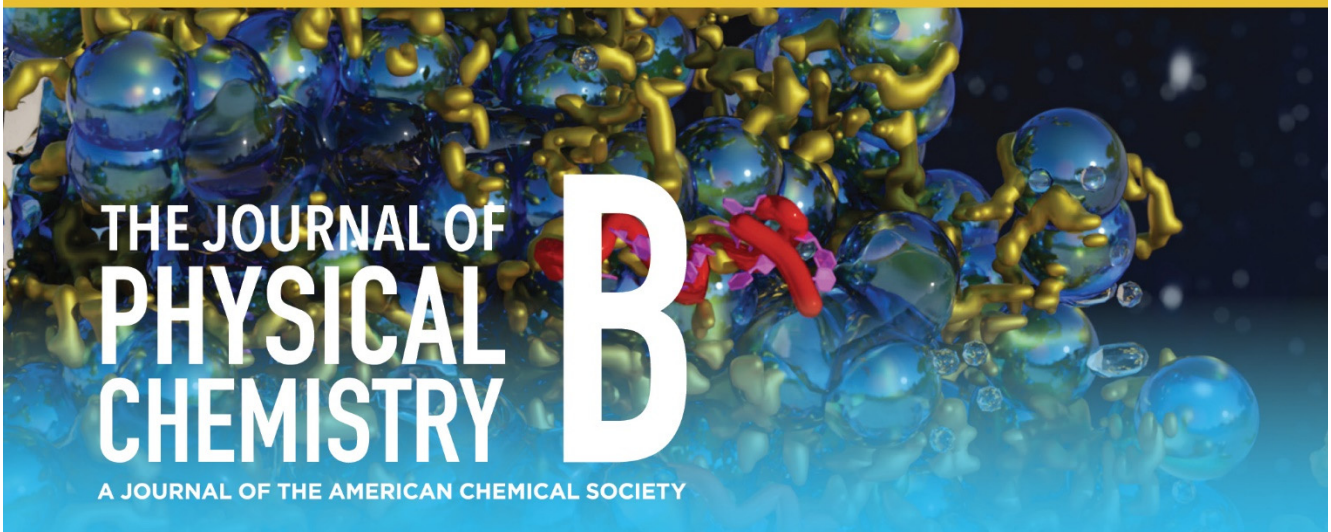

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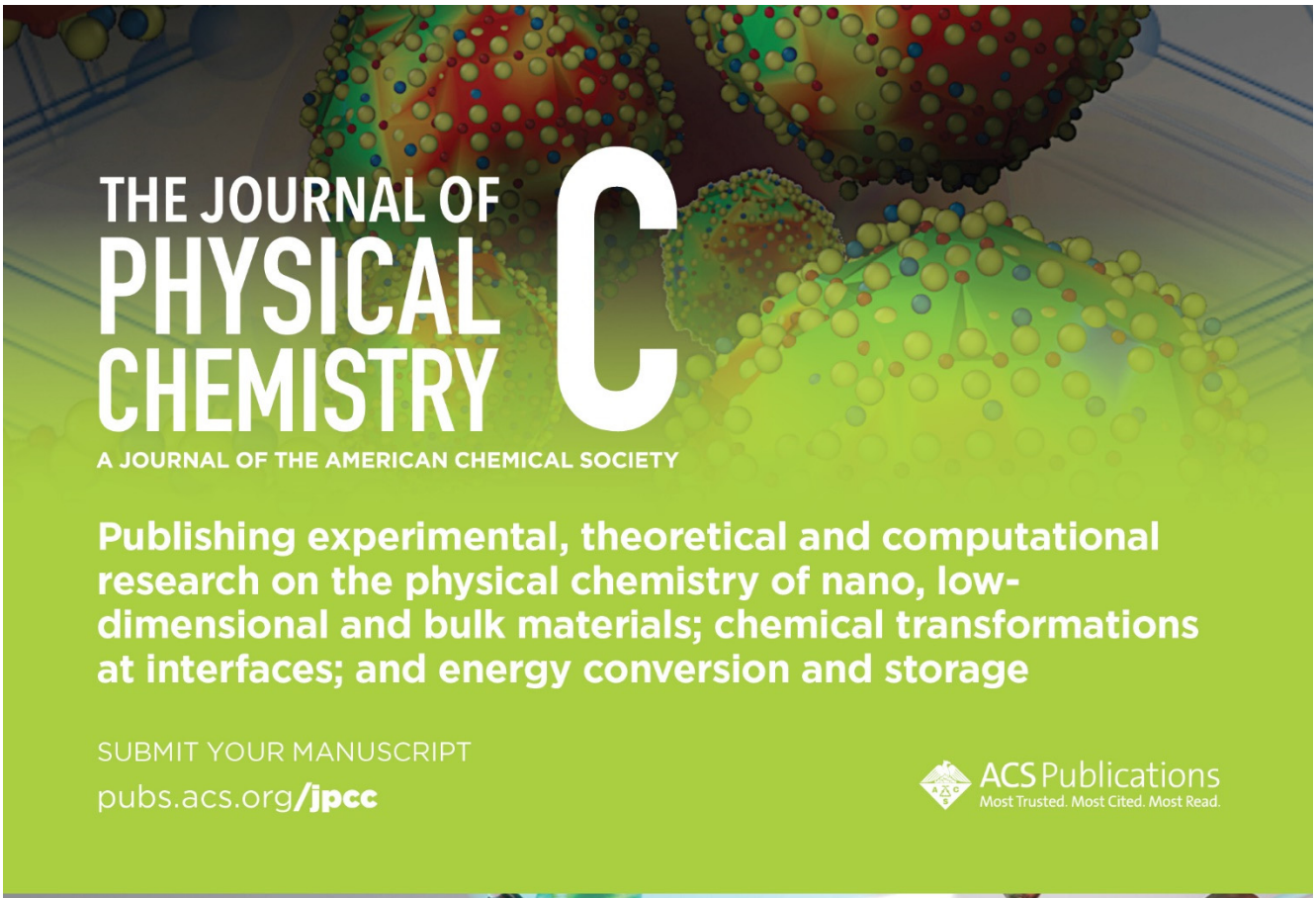

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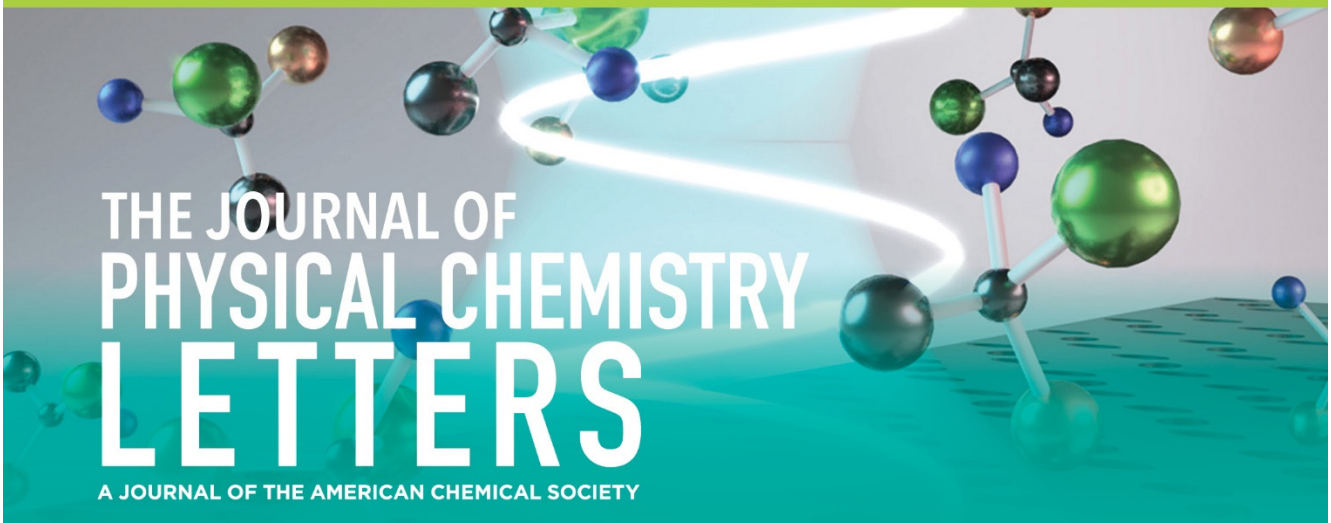

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The Coblentz Society, founded in 1954, is a non-profit organization of scientists interested in fostering the understanding and application of vibrational spectroscopy within the fields of Chemistry, Physics, and Biology. Vibrational spectroscopy includes infrared (IR), near-infrared (NIR), and Raman spectroscopies along with their associated sampling techniques, instrumentation, and data processing. The Coblentz Society is a technical affiliate of the Society for Applied Spectroscopy (SAS).

As part of fulfilling our mission, the Society presents several awards to recognize the efforts of professional spectroscopists who have made significant contributions in vibrational spectroscopy. These Awards are presented at conferences where The Coblentz Society is an active participant - Pittcon, ISMS, SciX, and EAS. The Society is a member organization of the Federation of Analytical and Spectroscopy Societies (FACSS).

By encouraging the visibility and recognition of quality science, the Society hopes to highlight solutions and chart new opportunities in vibrational spectroscopy.

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Everyone needs mentors – people who guide us by advising, questioning, doubting, or supporting us as we progress through life. Mentoring is for everyone at all stages of their career; we are happy to advise anyone whose interest is in the interaction of light with matter. One way in which the Society promotes mentoring is through our speed mentoring program. Speed Mentoring is a fun, fast-paced session that enables a structured interaction between young spectroscopists and chemists and a dozen or more spectroscopists and chemists from various industries, academia, and government labs.

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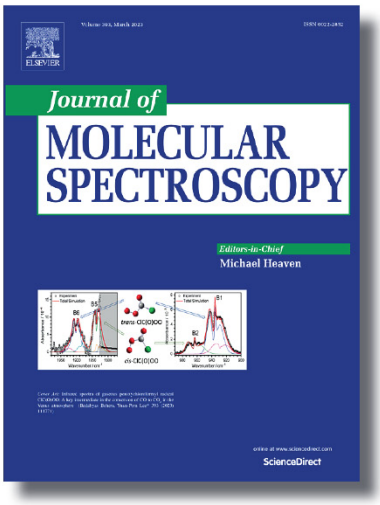

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It is planned to have several peer reviewed Feature articles in the *Journal of Molecular Spectroscopy* each year. These articles will overview areas of particular significance in molecular spectroscopy. They may review and consolidate an area of theoretical development or a collection of experimental data, in each case offering some new insights. The articles may also summarize the present status of a rapidly developing and/or evolving field. All the articles should serve as introductions to areas of **spectroscopy** other than one's specialty and should be particularly valuable to students entering the field.
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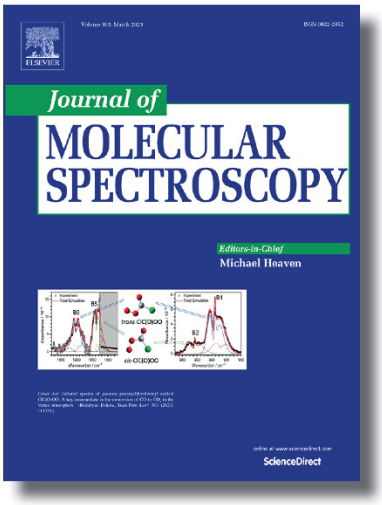

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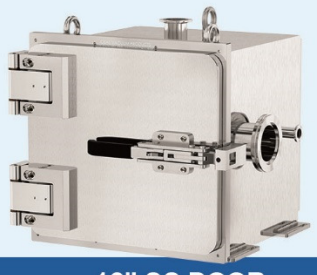

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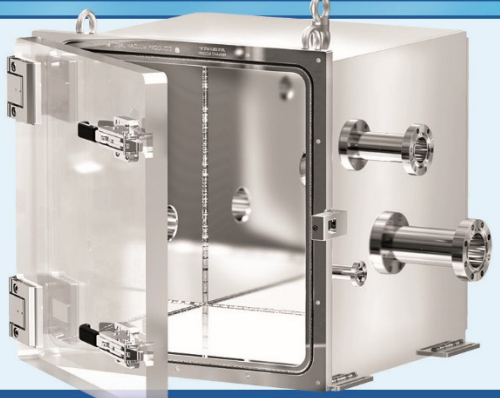

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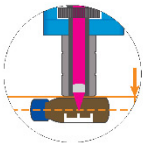

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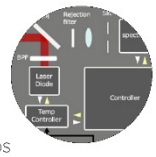

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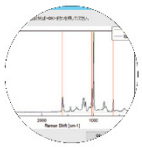

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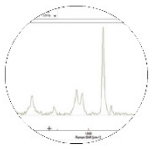

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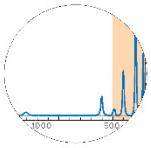

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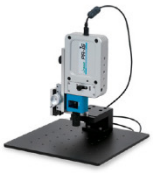

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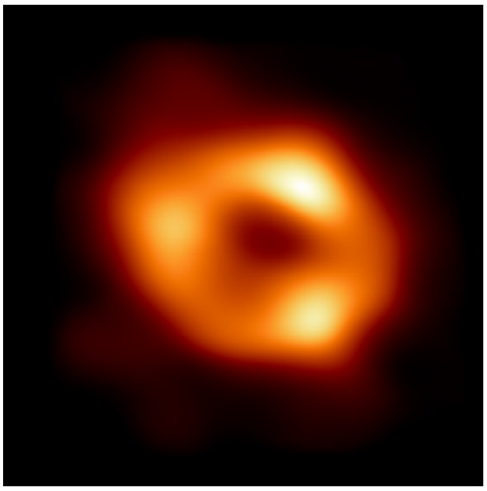

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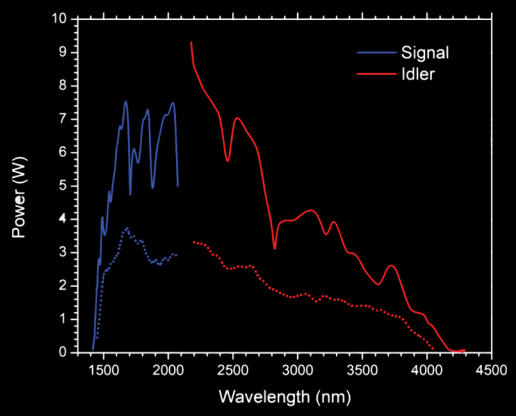

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157 Noyes Lab
12:30 PM

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Monday, June 19, 2023
12:30 – 1:30 pm, 157 Noyes Lab

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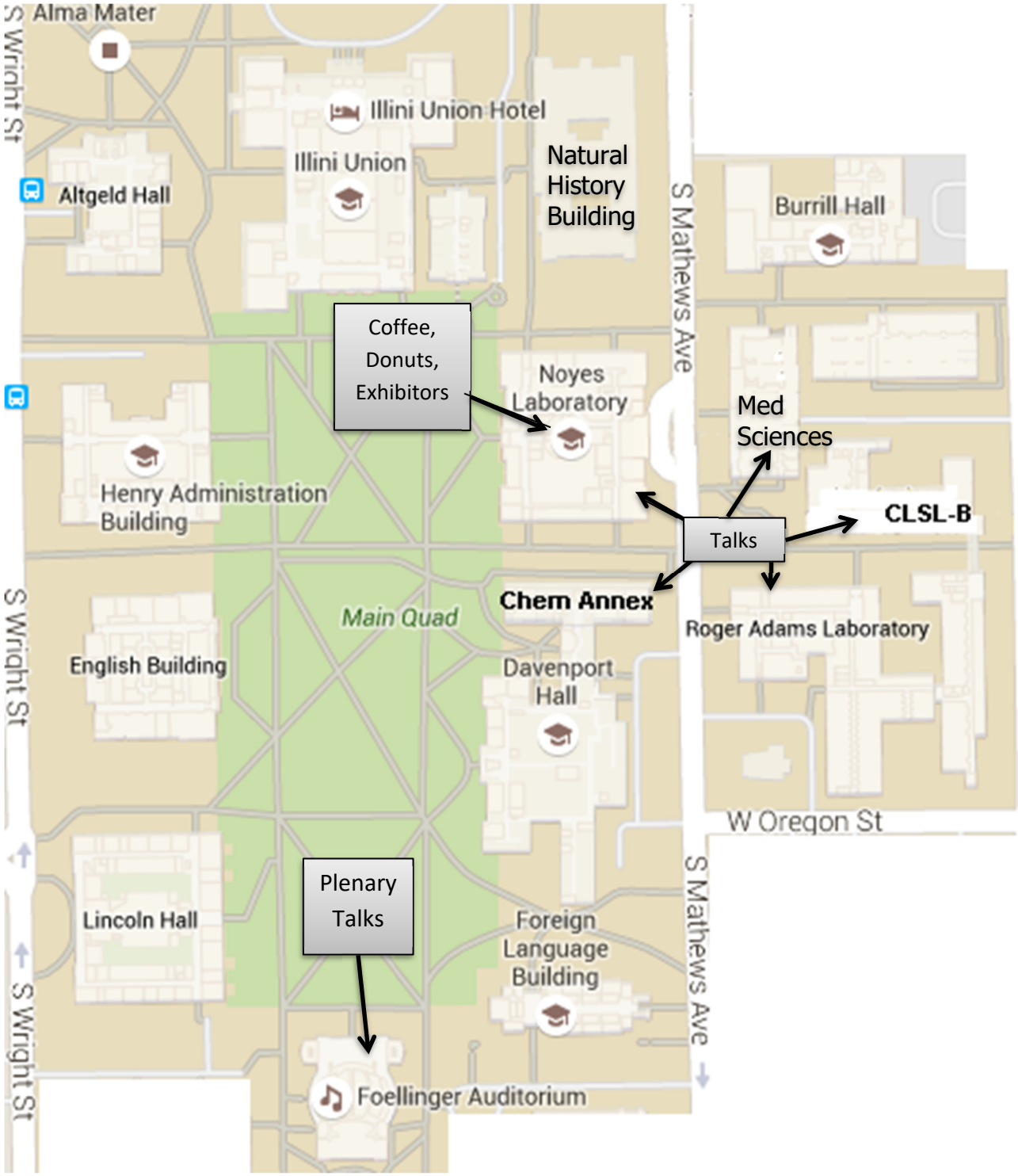
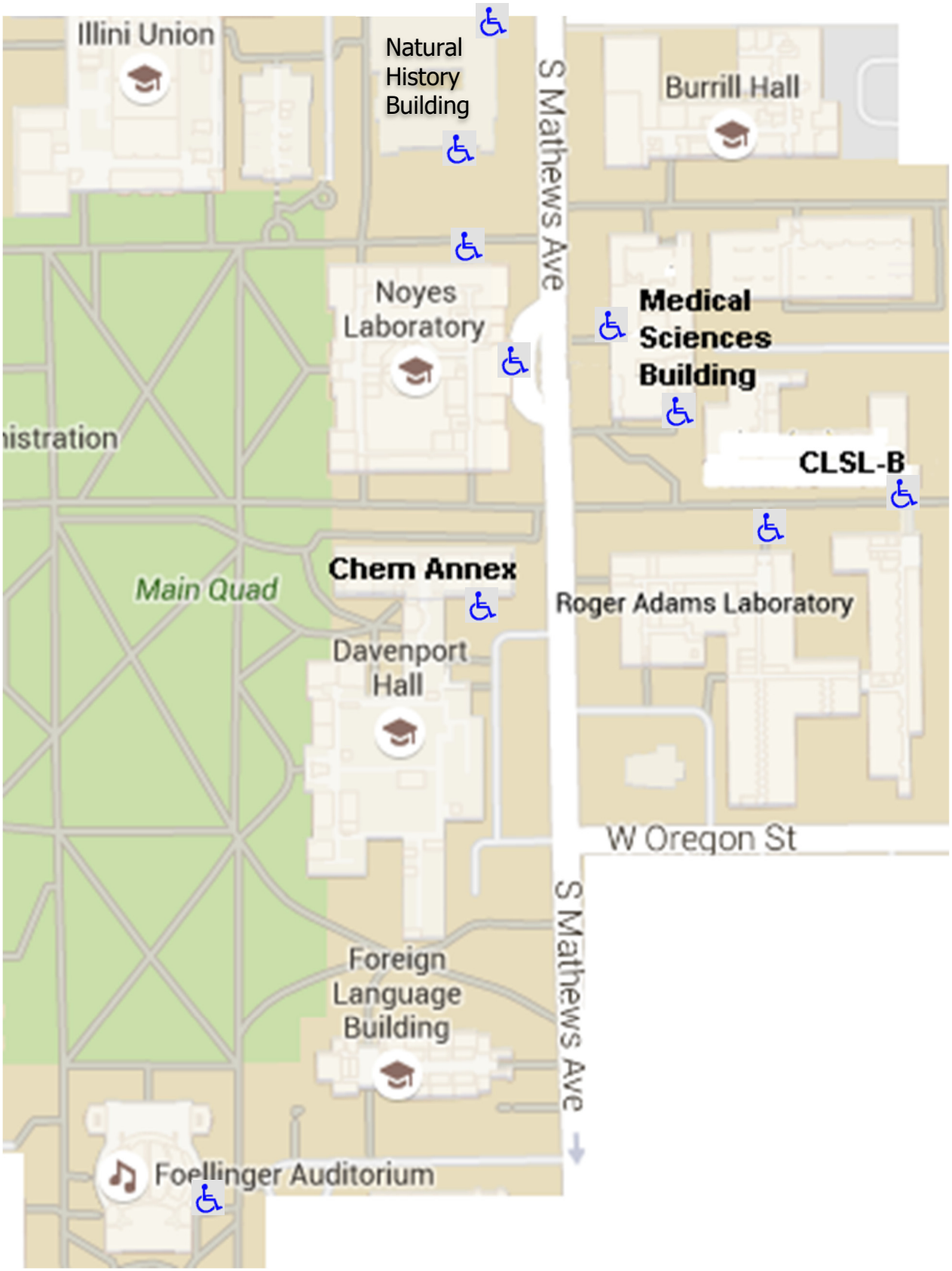
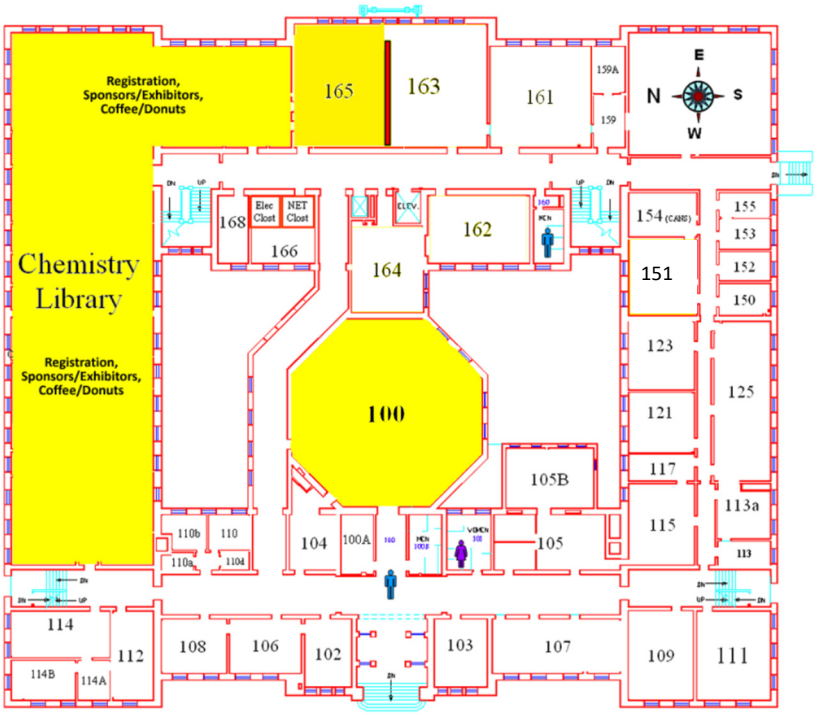


ACCESSIBLE ENTRANCES

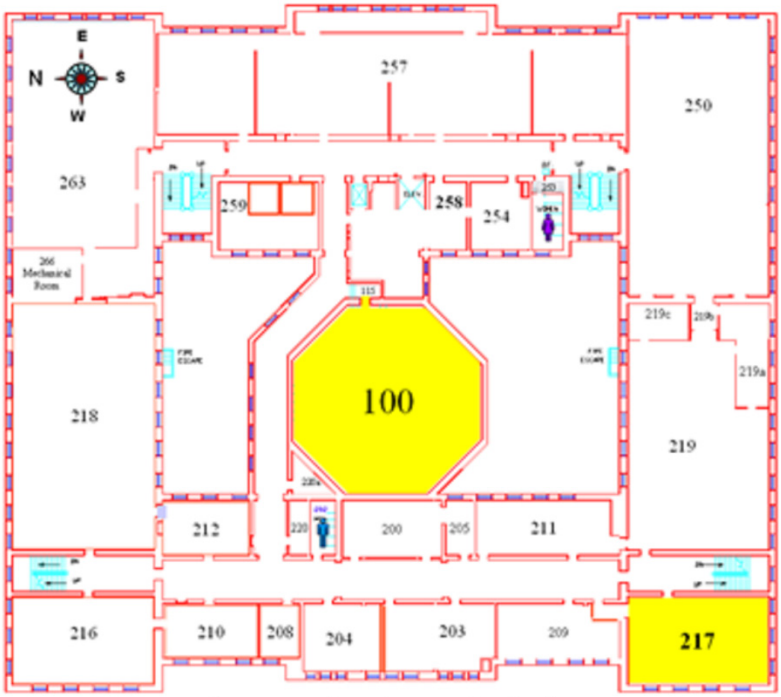


NOYES LABORATORY (NL)

Noyes Laboratory houses our Registration and Exhibitor/Refreshment Rooms (Chemistry Library), and two lecture halls (NL 100 and 217).



Noyes Laboratory - 1st Floor



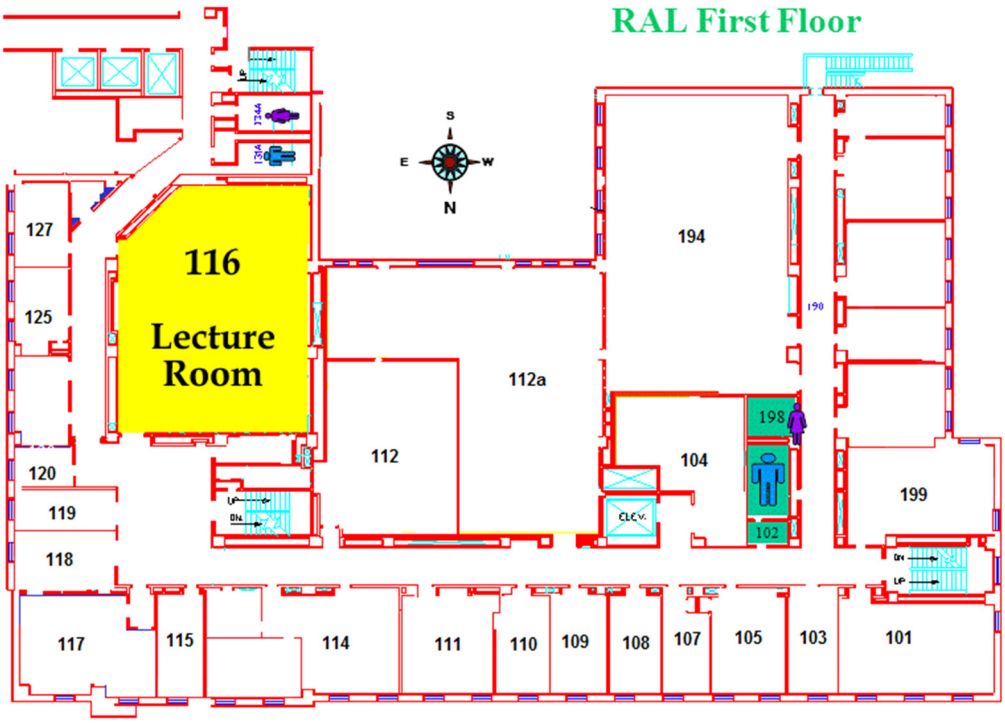
Noyes Laboratory - 2nd Floor

CHEMISTRY ANNEX (CA)

Chemistry Annex is immediately to the south of Noyes Laboratory across a pedestrian walkway. It has one lecture hall (CA 1024)

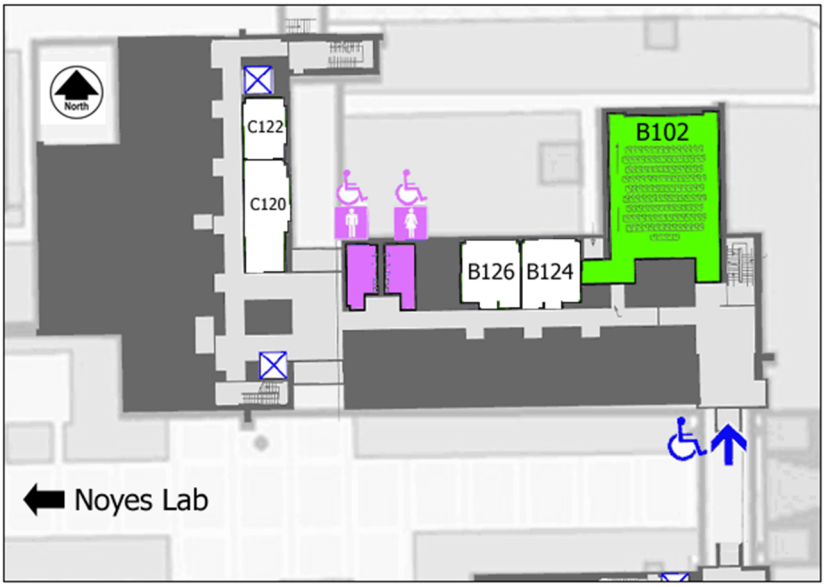
ROGER ADAMS LABORATORY (RAL)

Roger Adams Laboratory is across the street to the east of Chemistry Annex. It has one lecture hall (RAL 116). Please note that in Roger Adams Lab, the ground level is called "Ground" and the First Floor is equivalent to the Second Floor in the other buildings.



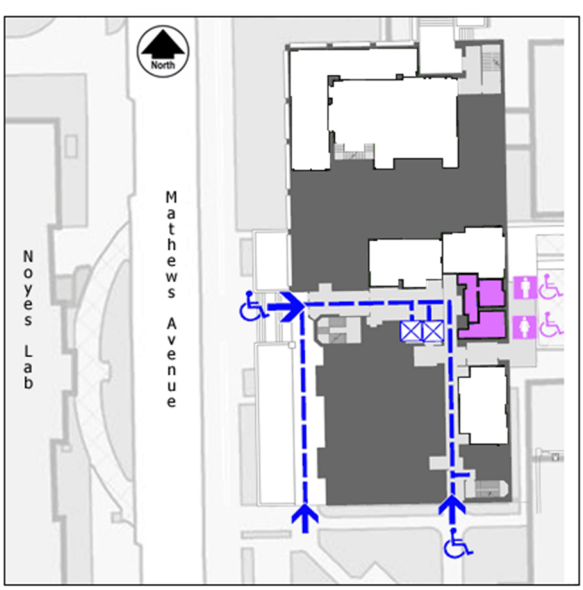
CHEMICAL AND LIFE SCIENCES (CLSL)

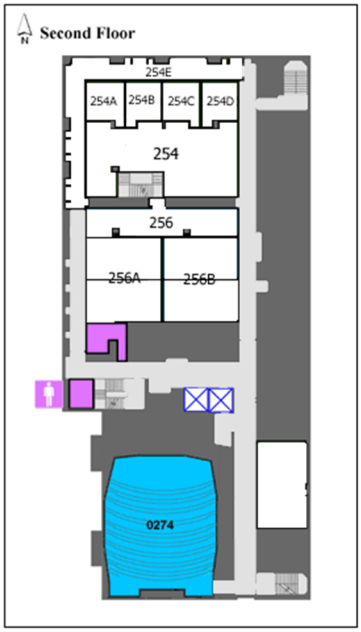
CLSL is a multi-wing building located across the street to the east of Noyes Laboratory. The lecture hall (CLSL B102) is in the B wing across the pedestrian walkway to the northeast of Roger Adams.



MEDICAL SCIENCES BUILDING (MSB)

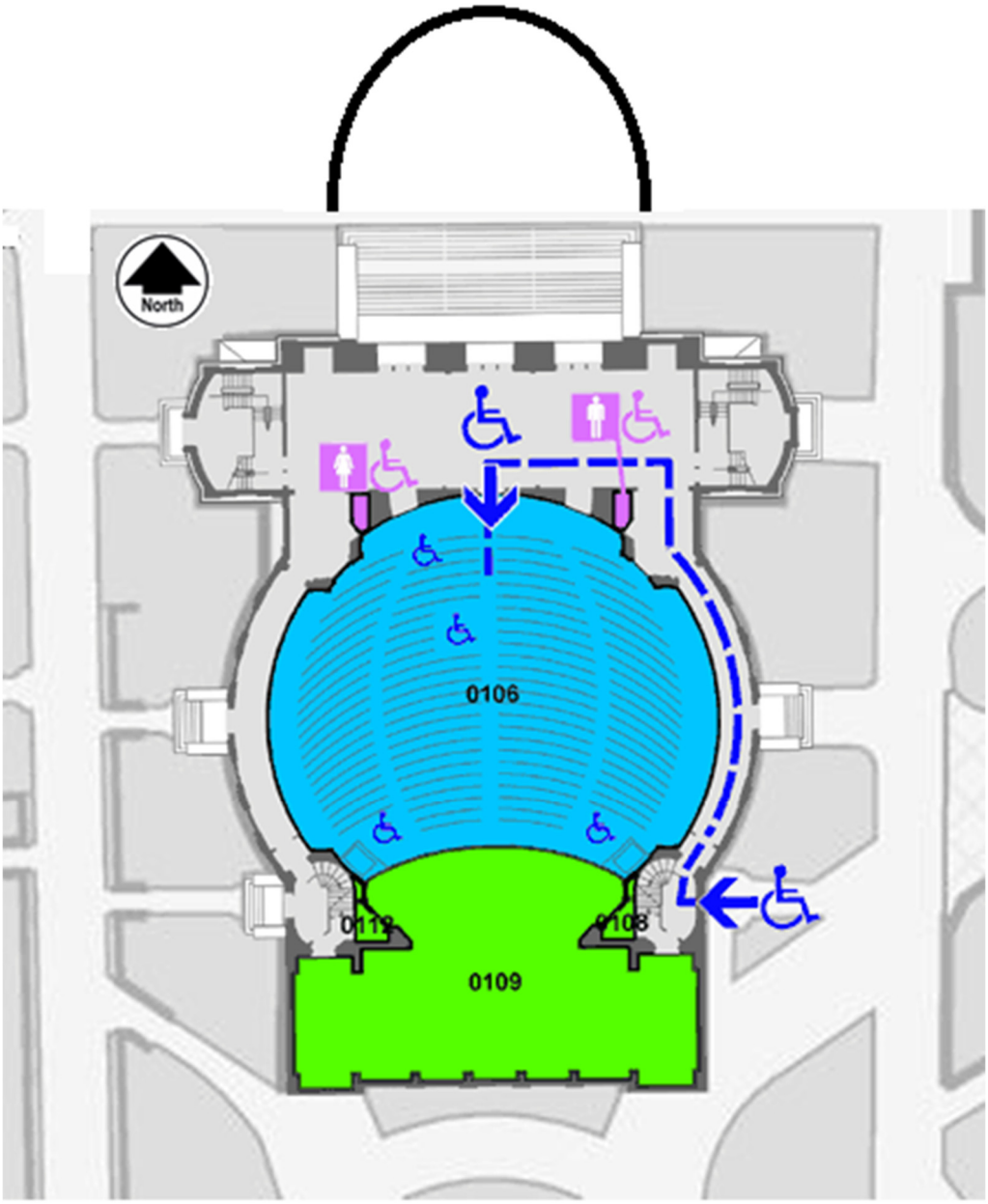
Medical Sciences is across the pedestrian walkway to the north of RAL. It has one lecture hall (274).





Foellinger Auditorium (Plenary and Intermission)

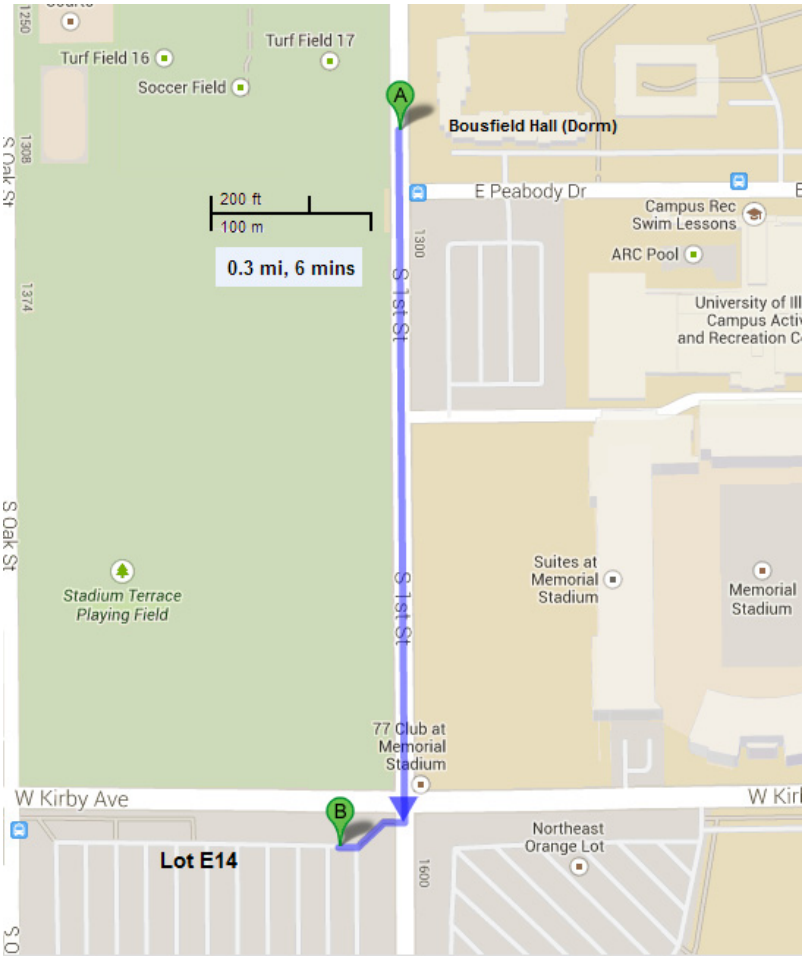
Foellinger Auditorium is located at the south end of the Quad. The main doors on the north (quad) side will open at 8:10 AM (the side ADA/wheelchair door will be open around 8:00 AM). There is seating on the main level and the upper balcony. There is no elevator in the building.



PARKING (E14) TO BOUSFIELD DORM

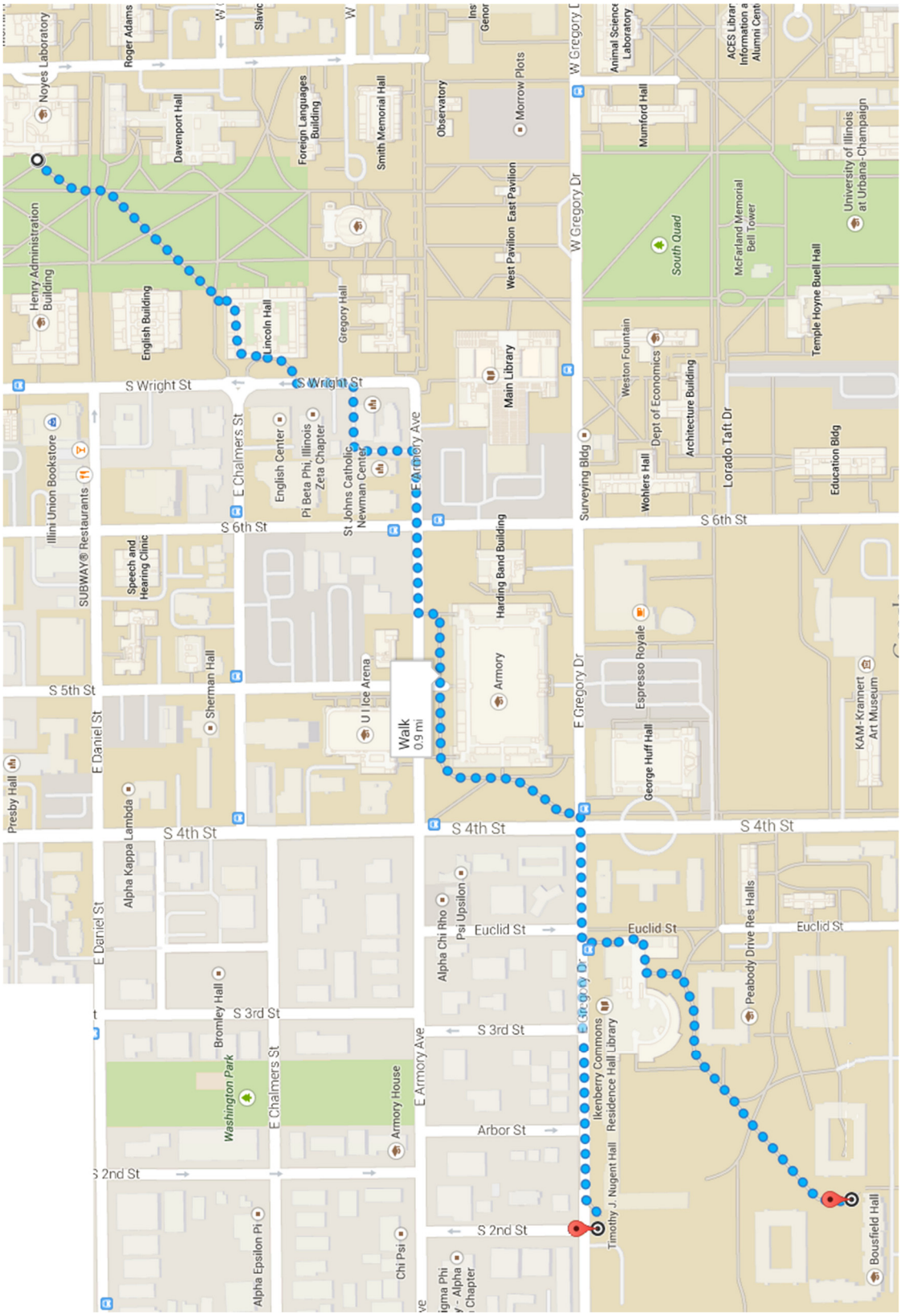
If you are staying at the dorm, you will park in lot E14 (any spot). E14 is nearly due south of Bousfield Hall Dorm. Parking in this lot is free for all ISMS attendees.

Parking enforcement begins at 6:00 AM on Monday, so you will need to have your car in lot E14 before then. There are many parking meters on E. Peabody Drive (and in the lot across from Bousfield) if you wish to park closer for short periods (25 cents/15 minutes – generally between 6 AM and 6 PM, but check the meter because some go until 9 PM).



BOUSFIELD/WASSAJA DORM to MEETING VENUE (walking)

Bousfield & Wassaja Halls are just under a mile (15-20 minute walk) from the main symposium buildings



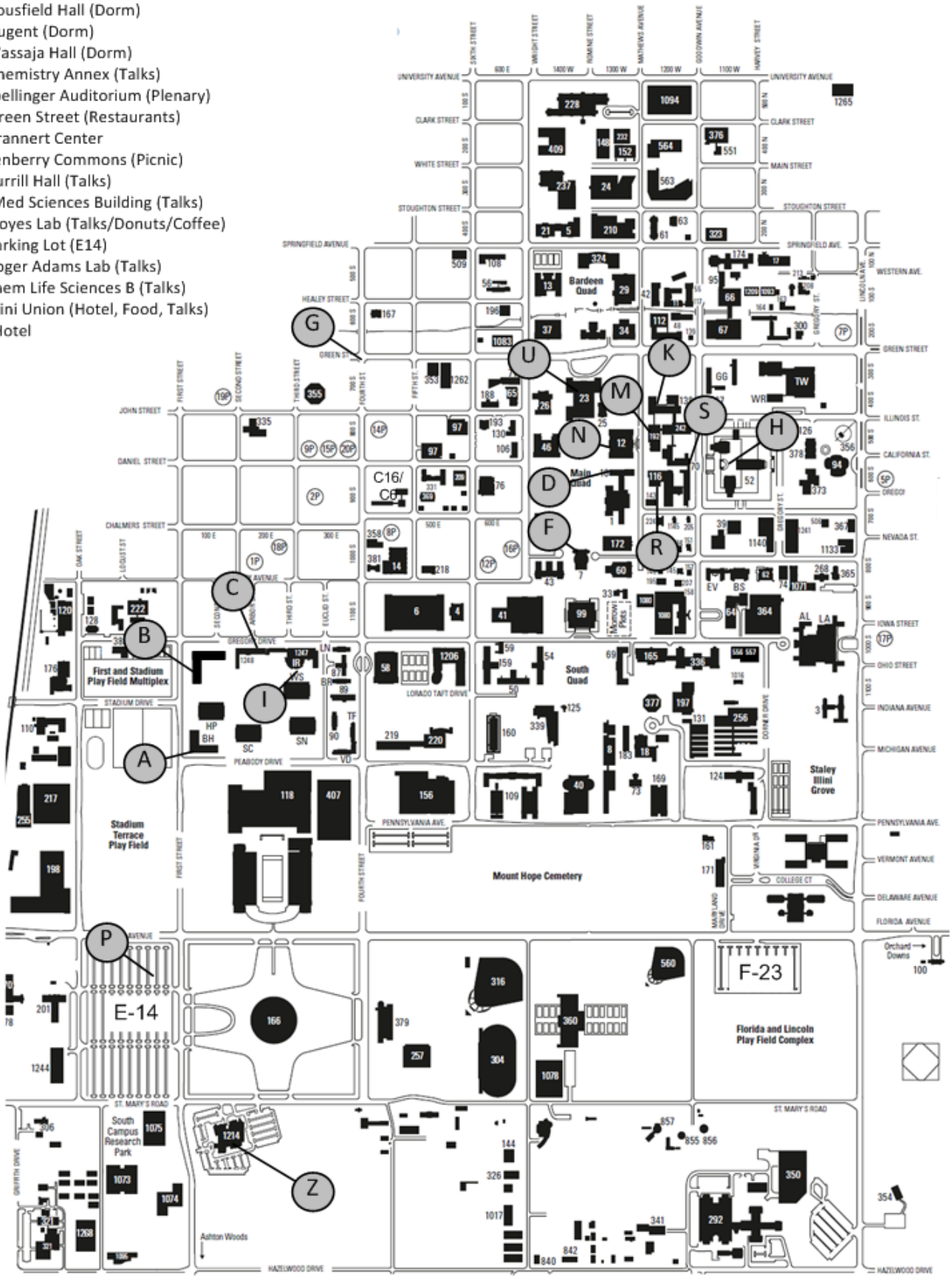
BOUSFIELD/WASSAJA DORM to MEETING VENUE (bus)

There is convenient and free bus service between Bousfield/Wassaja Dorms and 1 block from the meeting venue. The Yellow Line picks up on the corner of First and Peabody (Bousfield), and also on Gregory Drive (Wassaja) in front of Ikenberry Commons, drops off at the Krannert Center (across the street from CLSL-B). Return locations are the same but across the street. The Yellow Line will also take you to downtown Champaign, but you will need to pay for your return (only iStops are free). Approximately every 10 minutes during the day.

The Gold Line picks up on the corner of First and Peabody, and also on Gregory Drive in front of Ikenberry Commons and drops off at the Krannert Center (across the street from CLSL-B). Return locations are across the street. Runs every ~10 minutes during the day (offset from the Yellow Line by 5 minutes).

Visit https://mtd.org/maps-and-schedules/apps/ for more information and app downloads.

A: Bousfield Hall (Dorm)
B. Nugent (Dorm)
C: Wassaja Hall (Dorm)
D: Chemistry Annex (Talks)
F: Foellinger Auditorium (Plenary)
G: Green Street (Restaurants)
H. Krannert Center
I: Ikenberry Commons (Picnic)
K: Burrill Hall (Talks)
M: Med Sciences Building (Talks)
N: Noyes Lab (Talks/Donuts/Coffee)
P: Parking Lot (E14)
R: Roger Adams Lab (Talks)
S: Chem Life Sciences B (Talks)
U: Illini Union (Hotel, Food, Talks)
Z: iHotel



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