2022 International Symposium on Molecular Spectroscopy

**Supported by the National Radio Astronomy Observatory**

_Monday, June 20_  
8:30 AM

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<th>Room 100</th>
<th>Noyes Laboratory</th>
<th>Room 116</th>
<th>Roger Adams Lab</th>
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<td><strong>MA</strong></td>
<td><strong>Plenary</strong></td>
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<td><strong>MS: Spectroscopy meets Chemical Dynamics</strong></td>
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**Lunch Break**

**Sessions Resume at 1:45 PM**

_Pleasant Panel Discussion_  
_University Union Ballroom_  
_Lunch Provided_

**Tuesday, June 21**  
8:30 AM

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**Lunch Break**

**Sessions Resume at 1:45 PM**

**Wednesday, June 22**  
8:30 AM

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<tbody>
<tr>
<td><strong>MA</strong></td>
<td><strong>Structure determination</strong></td>
<td><strong>TA</strong></td>
<td><strong>Comparing theory and experiment</strong></td>
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<tr>
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**Lunch Break**

**Sessions Resume at 1:30 PM**

**Thursday, June 23**  
8:30 AM

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<tr>
<td><strong>MA</strong></td>
<td><strong>MS: Benchmarking in Spectroscopy</strong></td>
<td><strong>TA</strong></td>
<td><strong>Trapping and Isolation</strong></td>
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**Lunch Break**

**Sessions Resume at 1:45 PM**

**Friday, June 24**  
8:30 AM

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<td><strong>TA</strong></td>
<td><strong>Spectroscopy as an analytical tool</strong></td>
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**Lunch Break**

**Sessions Resume at 1:45 PM**

**INFORMATION**

- **Venue:** University of Illinois at Urbana-Champaign
- **Dates:** June 20 - 24, 2022
- **Support:** National Radio Astronomy Observatory
Welcome to the 75th International Symposium on Molecular Spectroscopy  
June 20-24, 2022  
Urbana-Champaign, IL

On behalf of the Executive Committee, I extend a heartfelt welcome to all the attendees of the 75th 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 Vara-Weis  
Symposium Chair

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<th>ABSTRACTS</th>
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<td>Tuesday (T) ........... 9</td>
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<td>Wednesday (W) .......... 24</td>
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<td>Thursday (R) .......... 39</td>
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VENUE AND SPONSOR INFORMATION FOLLOWS AUTHOR INDEX
75th INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY

International Advisory Committee
Gang Feng, Chongqing University
Ashoka Fujii, Tohoku University
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Marsha Lester, University of Pennsylvania
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Amanda Ross, University Lyon 1
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Jacob Stewart, Connecticut College
Tim Zwier, Sandia National Laboratories

Executive Committee
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Gary Eden
Nick Gumac
Martin Gruebele
So Hirata
Leslie Louney
Ben McCall
Dave Woo

Please send correspondence to
Josh Vora-Wes
International Symposium on Molecular Spectroscopy
600 S. Mathews Avenue
Urbana IL 61801 USA
e-mail: chair@ism.illinois.edu
http://ism.illinois.edu

Mini-Symposia

BENCHMARKING IN SPECTROSCOPY
Organized by: Emilio Cocinero (Universidad del País Vasco), Gang Feng (Chongqing University), Daniel Obenchain (Georg-August-Universität Göttingen). This will be a forum to compare computational data sets to experimental results, and discuss the quality and methods employed. Invited Speakers: Taiga Fischer (University of Göttingen), Brian Esselman (University of Wisconsin, Madison), Qian Gu (Chongqing University), Lan Cheng (Johns Hopkins University)

MACHINE LEARNING
Organized by Kelvin Lee (MIT), Daniel Tabor (Texas A&M University). This mini-symposium will focus on the development and application of the rapidly advancing field of machine learning to spectroscopic problems, with a diverse set of practitioners (experimental and theoretical) and applications. Invited Speakers: Heather Kulik (MIT), Thomas Markland (Stanford), Andrés Montoya-Castillo (University of Colorado Boulder), Steven Shipman (New College of Florida), Andrew White (University of Rochester)

SPECTROSCOPY MEETS CHEMICAL DYNAMICS
Organized by David Osborn (Sandia National Lab), Krupa Ramasesha (Sandia National Lab), Timothy Zwier (Sandia National Lab). This mini-symposium brings together researchers in the fascinating area at the interface between spectroscopy and dynamics, in which frequency domain and time-domain experimental measurements can work in concert with advances in theory to uncover the unique signatures of dynamical events over a wide range of timescales. Invited Speakers: Randall Goldsmith (University of Wisconsin, Madison), Steve Leone (UC-Berkeley), Melanie Reber (University of Georgia), Dave Townsend (Heriot-Watt University)

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

Sponsorship
We are pleased to acknowledge the many organizations that support the 75th 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 Coblenz Society, Elsevier/JMS, Ideal Vacuum Products, Jasco, and Toptica. Please see the back of this book for their advertisements.

EL SEVIER

NRAO

COBLENZ

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Jasco

IDEAL VACUUM

We are also pleased to acknowledge IOS Press/Biomedical Spectroscopy and Imaging, ACS/The Journal of Physical Chemistry, Light Conversion USA, and Renishaw as Contributing Sponsors.

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

The four Rao Prizes for the most outstanding student talks at the 2021 meeting will be presented. The winners are Parker Crandall (Technische Universität Berlin), Nicholas Hölch (ETH Zuerich); Wey-Wey Su (Stanford University); and James Thorpe (University of Florida). 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 (University of Manitoba), and is composed of Dan Obenczine (Georg-August-Universität Göttingen); Brooks Pate (University of Virginia); 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 (vanwijngaarden@cc.umanitoba.ca).

Lewis E. Snyder Astrochemistry Award

The Snyder Award winner for the most innovative and unique astrochemical investigation in either observations, theory or laboratory work presented by a graduate student at the 2021 meeting is Divita Gupta (Institut de Physique de Rennes). 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 2021 meeting will be presented. The winner, Junjiang (Lawrence Livermore National Laboratory) 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 comprised Lan Cheng (Johns Hopkins University), Stephen Cooke (Purchase College, SUNY), Jinping Liu (University of Louisville), Edwin Sibert (University of Wisconsin), Cristina Puzzarini (University of Bologna), Susanna Widicus-Weaver (University of Wisconsin, Madison) and Lucy Ziurys (University of Arizona). 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. Hougén Memorial Award

The Hougén Award was created in honor of Jon Hougén, to support the travel expenses of an exceptional young international spectroscopist who would otherwise be unable to attend the ISMS. The 2022 winners are Lorrie Jacob (University of Cambridge) and Kenneth Kozioł (RWTH Aachen University) who will give talks in the WH and FB sessions, respectively. The Hougén award is administered by a Prize Committee consisting of Nasaaki Baba (Kyoto University), Malgorzata Biczynko (Shanghai University), Anthony Remijan (NRAO), and Maria Sanz (King’s College London).

Information

ACCOMMODATIONS

Check-In - 08 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 will be at Bousfield Hall, 1214 South First Street, from noon until ~10 PM.

Check-Out - 08 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.

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

PARKING

Parking permits are for lot E14 (map @ end of book). Purchase parking as part of your check-in at the dorm. You may purchase meter hang-tags for parking near the meeting rooms at the registration desk.

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.

VIDEO UPLOAD

You must upload your video presentation BEFORE MONDAY, JUNE 13th on our web site. All files will then be available on the website for our virtual attendees to view.

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
MH. Mini-symposium: Spectroscopy meets Chemical Dynamics
Monday, June 20, 2022 – 1:45 PM
Room: 100 Noyes Laboratory
Chair: Stephen R. Leone, University of California, Berkeley, Berkeley, CA, USA

MH01
Journal of Molecular Spectroscopy Review Lecture
1:45 – 2:15
MAPPING EXTENDED REACTION COORDINATES IN PISTROCHEMICAL DYNAMICS, Dave Townsend

MH02
FULLY ISOMER-RESOLVED SPECTROSCOPY AND ULTRAFAST DYNAMICS, Gite L. Abma, Daniel Horke

MH03
ABSOLUTE-PHASE-RESOLVED STRONG FIELD IONIZATION, Yasashri Ranganath Ranathunga, Duke A. Debrah, Gabriel A. Stewart, Sat Kyoung Lee, Wen Li

MH04
ALL-OPTICAL THREE-DIMENSIONAL ELECTRON MOMENTUM IMAGING, Emmanuel Ayorinde Orunesajo, Gabriel A. Stewart

Intermission

MH05
PROBING THE VIBRATIONAL WAVE PACKET DYNAMICS ON THE ELECTRONIC GROUND STATE OF NEUTRAL SILVER TETRAMER: VIBRATIONAL FREQUENCIES, ANHARMONICITIES AND ANISOTROPY, Jiaye Jin, Max Grellmann, Knut R. Asmis

MH06
PHOTOFRAGMENTATION PATHWAYS OF N-BUTYL BROMIDE, Lauren F Heald, Scott G Sayres

MH07
OBSERVATION OF RESONANCES IN THE F+NH3 REACTION VIA TRANSITION-STATE SPECTROSCOPY, Mark C Bansal, Martin DeWitt, Jascha Lau, Hongwei Song, Hua Guo, Daniel Neumark

MH08
TRACKING THE PHOTOIONIZATION OF ANILINE IN WATER: THE ROLE OF σ* STATES, Raul Montero, Iker León

MH09
PULSE INDUCED DARK STATE OF ACETYLENE, Antoine Aerts, Pascal Kockaert, Simon Pierre Gorza, Jean Vander Auwera, Nathalie Vanck

MH10
A PHASE DIAGRAM FOR ENERGY FLOW-LIMITED REACTIVITY, Chenghao Zhang, Edwin Sibert, Martin Gruebele

MI. Structure determination
Monday, June 20, 2022 – 1:45 PM
Room: 116 Roger Adams Lab
Chair: M. Eugenia Sanz, King’s College London, London, United Kingdom

MI01
Q. R. QUANTUM-BASED REFINEMENT OF BIOMACROMOLECULES, Malgorzata Biczysko, Yanting Xu, Nigel W Moriarty, Holger Kruse, Mark P Weller, Pavel V Afonine

MI02
THE NICOTINIC-AGONIST CYTISINE: THE ROLE OF THE NH···N INTERACTION, Raúl Aguado, Santiago Mata, Miguel Sanz-Novo, Elena R. Alonso, Iker León, José L. Alonso

MI03
WETTING FERROCENE AS A WAY TO INVESTIGATE ITS GAS PHASE STRUCTURE BY ROTATIONAL SPECTROSCOPY, Susana Blanco, Andres Verde, Juan Carlos Lopez, Manuel Yáñez, Ibon Alkorta

MI04
THE SHAPE OF PROGESTERONE, Elena R. Alonso, Aran Insamani, Lucie Kodrnová, Iker León, José L. Alonso

MI06
UNDERSTANDING THE SHAPE OF β-D-ALLOSE: A LASER ABLATION ROTATIONAL STUDY, Gabriela Juárez, Santiago Mata, José L. Alonso, Elena R. Alonso, Iker León

Intermission

MI07
THE PRECISE EQUILIBRIUM STRUCTURE DETERMINATION OF CHLOROBENZENE (C6H5Cl) BY ROTATIONAL SPECTROSCOPY, Natalie A. Schuler, P. Massimo Dorman, Brian J. Eschelman, Maria Zdanovskaia, Bryan Changhall, John F. Stanton, Michael C. McCarthly, R. Claude Woods, Robert J. McMahon

MI08
HIGH ACCURACY MOLECULAR STRUCTURES, Nitai Prasad Sahoo, John F. Stanton

MI09
MICROWAVE SPECTROSCOPY AND STRUCTURE DETERMINATION OF ORGANOSILICON COMPOUNDS: A CELEBRATION OF A DECADE OF COLLABORATION, Nathan A. Scheller, Thomas M. C. McFadden, Gamil A Guirgis, Nicole Moon, Amanda Darden, G. S. Grubbs II

MI10
CONFORMATIONAL ANALYSIS OF CYCLOBUTANECARBOXYLIC ACID, Karla V. Salazar, Joshua E. Isert, Nicole Moon, G. S. Grubbs II, Zunwu Zhou, Stephen G. Kukolich, Michael J. Carrillo, Shervin Fatehi, Wei Lin

MI11
A ROTATIONAL STUDY OF 6-APA, Sergio Mato, Santiago Mata, Elena R. Alonso, José L. Alonso, Iker León
**MJ. Comparing theory and experiment**

Monday, June 20, 2022 – 1:45 PM
Room: B102 Chemical and Life Sciences
Chair: Edwin Sibert, University of Wisconsin–Madison, Madison, WI, USA

**MJ01**
A FLEXIBLE APPROACH TO VIBRATIONAL PERTURBATION THEORY, Mark A. Boyer, Anne B McCoy
1:45 – 2:00

**MJ02**
UNDERSTANDING X−·HOCl (X=Cl, Br, I) THROUGH VIBRATIONAL PERTURBATION THEORY, Mark A. Boyer, Coire F Gavin-Hanner, Anne B McCoy
2:03 – 2:18

**MJ03**
VIBRONIC COUPLING MECHANISMS IN THE NITRATE RADICAL, John F. Stanton
2:21 – 2:36

**MJ04**
2:39 – 2:54

**MJ05**
ON THE USEFULNESS OF ELECTRON PROPAGATOR METHODS FOR A RELIABLE COMPUTATION OF EXPERIMENTAL OBSERVABLES, Lorenzo Paoloni
2:57 – 3:12

**MJ06**
3:15 – 3:30

**MK. Mini-symposium: Machine Learning**

Monday, June 20, 2022 – 1:45 PM
Room: 217 Noyes Laboratory
Chair: Daniel P. Tabor, Texas A&M University, College Station, TX, USA

**MK01**
INVITED TALK
ELUCIDATING, ANALYZING, AND DESIGNING SPECTROSCOPES: LEVERAGING THEORY AND CHEMICAL INTUITION TO GET THE MOST OUT OF MACHINE LEARNING, Thomas E Markland
1:45 – 2:15

**MK02**
LOW-FREQUENCY INFRARED SPECTRUM OF LIQUID WATER FROM MACHINE-LEARNING BASED PARTIAL ATOMIC CHARGES, Bowen Han, Christine M Isborn, Liang Shi
2:21 – 2:36

**MK03**
MULTI-FIDELITY DEEP LEARNING AND ACTIVE LEARNING FOR MOLECULAR OPTICAL PROPERTIES, Kevin P. Greenman, William H. Green, Rafael Gómez-Bombarelli
2:39 – 2:54

**MK04**
MULTIVARIATE ANALYSIS OF MOLECULAR SPECTROSCOPY DATA FOR COVID-19 DETECTION, Qizhong Liang, Ya-Chu Chan, Jutta Toscans, Kristen K. Bjorkman, Leslie A. Leinwand, Roy Parker, David J. Nesbit, Jin Ye
2:57 – 3:12

**Intermission**

**MK05**
INVITED TALK
CAPTURING, PREDICTING, AND UNDERSTANDING OPTICAL SIGNALS: HARNESSING MACHINE LEARNING TO TACKLE ENERGY DISSIPATION IN THE CONDENSED PHASE, Andres Montoya-Castillo
3:54 – 4:24

**MK06**
SYMMEY-CONSTRAINED MOLECULAR DYNAMICS, Andrew White, Sam Cox
4:30 – 4:45

**MK07**
ACCELERATING MANY-BODY EXPANSION THEORY THROUGH GRAPH CONVOLUTIONAL NETWORKS, Yi Shi, Chengwei Ju, Jun Yi, Zhou Lin, Hui Guan
4:48 – 5:03
**ML. Small molecules**

Monday, June 20, 2022 – 1:45 PM

Room: 1024 Chemistry Annex

Chair: Leah C O’Brien, Southern Illinois University, Edwardsville, IL, USA

**ML01 1:45 – 2:00**

CALCIUM MONOXIDE FORMATION IN LASER PLASMA STUDIED BY EMISSION AND FLUORESCENCE SPECTROSCOPY, Aleksandr Zakuskin, Babken Beglaryan, Andrey Popov, Timur A. Labutin

**ML02 2:03 – 2:18**

IN SEARCH OF EQUILIBRIUM IN LASER-PRODUCED CLOUD: ROLE OF PRESSURE, CHEMICAL QUENCHING, AND PLASMA EXPANSION, Timur A. Labutin, Aleksandr Zakuskin, Sergey Zaytsev, Andrey Popov, Vladislav E. Chernov, Alexey A. Berezhnoy, Ekaterina A. Boromtsova, Andrey Stoikaroy

**ML03 2:21 – 2:36**

TWO COLOR FORMALDEHYDE PLIF THERMOMETRY USING A BURST MODE LASER, Xunchen Liu

**ML04 2:39 – 2:54**

FLASH PYROLYSIS MECHANISM OF TRIMETHYLCHLOROSILANE BY FLASH PYROLYSIS VACUUM ULTRA-VIOLET PHOTOIONIZATION TIME-OF-FLIGHT MASS SPECTROMETRY, Kuanliang Shao, Jonah Brunson, Yi Tian, Jingsong Zhang

**ML05 2:57 – 3:12**

ULTRA VIOLET SPECTROSCOPY OF SUBCRITICAL AND SUPERCRITICAL ETHANOL, Timothy W Marin, Ireneusz Janik

**Intermission**

**ML06 3:54 – 4:09**

COLLISIONAL RELAXATION OF LOW-FREQUENCY VIBRATIONAL MODES OF SMALL MOLECULES IN A PULSED SEEDED SUPersonic JET, Piyush Mishra, Alexander W Hull, Timothy J Barnum, Stephen L Coy, Robert W Field

**ML07 4:12 – 4:27**

ROTATIONAL LEVEL INTERVALS IN HD FROM CRYO-COOLED SUB-DOPPLER ROVIBRATIONAL SPECTROSCOPY, Meissa Daud, Frank M.J. Czaja, Edejoh J Kumbah, Wim Ubachs

**ML08 4:30 – 4:45**

QUANTIFYING EMISSION OF NRI AND NRI-II DYES VIA FLUORESCENCE QUANTUM YIELD, David D. Ndaleh, Cameron L Smith, Mahesh Loku Yaddehige, Abdul Kalam Shaik, Nathan I Hammer, Jared Delcamp

**ML09 4:48 – 5:03**

FLUORESCENCE AND QUANTUM YIELD STUDIES OF NEW SWIR EMITTING RHODINDOLIZINE DYES, Abdul Kalam Shaik, Sadadar Chatterjee, Balaji Hirunika Wijesinghe, David D. Ndaleh, Amal Dass, Jared Delcamp, Nathan I Hammer

**ML10 5:06 – 5:21**

HIGHLY SELECTIVE GAS ANALYZER BASED ON MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY FOR SO₂ MONITORING IN AMBIENT AIR, Md Akbar Jamal, Sylvester Twagirayezu, Justin L. Neill

**ML11 5:24 – 5:39**

SENSITIVITY TO VARIATION OF FUNDAMENTAL CONSTANTS FROM FREQUENCY MEASUREMENTS OF ACETYLENE REFERENCE TRANSITIONS, Mosia Lucian Constantin

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**MM. Cold and ultracold molecules**

Monday, June 20, 2022 – 1:45 PM

Room: 124 Burrill Hall

Chair: Mitsunori Araki, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan

**MM01 1:45 – 2:00**

ELECTRONIC SPECTROSCOPY AND PROTOIONIZATION OF LiBe, Thomas D Persinger, Jiande Han, Michael Heaven

**MM02 2:03 – 2:18**

FLUORESCENCE SPECTROSCOPY DETECTION OF THE 4f⁻¹ STATES OF YbF, Thomas D Persinger, Jiande Han, Timothy Steimle, Michael Heaven

**MM03 2:21 – 2:36**

SINGLE-TRIPLET DOORWAY STATES OF ALUMINUM MONOFLUORIDE, Nicole Walter, Johannes Seiffert, Stefan Trupe, Christian Schewe, Boris Sartak, Gerard Meijer

**MM04 2:39 – 2:54**

FUNCTIONALIZED AROMATIC MOLECULES FOR LASER COOLING AND TRAPPING, Benjamin Augenbraun, Sean Burchesky, Guo-Zhu Zhu, Dehayan Mitra, Claire E Dickerson, Guanming Lao, Zach Lastue, Anastasia Alexandra, Wesley Campbell, Justin Caram, Eric Hudson, John M. Doyle

**MM05 2:57 – 3:12**

LASER SPECTROSCOPY OF BUFFER-GAS-COOLED POLYATOMIC MOLECULES, Yuki Takahashi, Masaki Baba, Katsunari Enomoto, Kana Iwakuni, Susumu Kuma, Ayami Hiramoto, Reo Tobaru, Yuki Miyamoto

**Intermission**

**MM06 3:54 – 4:09**

CRYOGENIC ION SPECTROSCOPY OF TRANSITION METAL-EDTA COMPLEXES: ION-DEPENDENT SPECTRAL AND STRUCTURAL SHIFTS, Madison M. Foreman, J Mathias Weber

**MM07 4:12 – 4:27**

DEVELOPMENT OF A SUPersonic EXPANSION SOURCE FOR HIGH-RESOLUTION INFRARED SPECTROSCOPY OF ISOPRENE, Katanna Reya, Binh Nguyen Vo, Sebastian Guerrero, Jacob Stewart

**MM08 4:30 – 4:45**

INTERSTELLAR PEPTIDE BOND FORMATION BY ACETALDEHYDE AND AMMONIA IN ANALOG ICE, Joshua H Marks, Jia Wang, Andre K. Eckhardt, N. Fabian Kleimeier, Andrew Martin Turner, Ralf Ingo Kaiser

**MM09 4:48 – 5:03**

THE COMPLEXES OF HYDROXYLAMINE VIA VIBRATIONAL AND ROTATIONAL SPECTROSCOPY, Xiaolong Li, Dingdong Li, Weixing Li, Mingfui Zhou

**MM10 5:06 – 5:21**

REACTION OF ELECTRONS TRAPPED IN CRYOGENIC MATRICES WITH BENZOPHENONE, Ankit Somani, Wolfram Sander
MN. Astronomy
Monday, June 20, 2022 – 1:45 PM
Room: 274 Medical Sciences Building
Chair: L. Margulès, Université de Lille, Villeneuve deAscq, France

MN01 1:45 – 2:00
NOEMA OBSERVATIONS OF COMPLEX ORGANIC CHEMISTRY IN THE W3 STAR-FORMING REGION,
Will E. Thompson, Tasamna L. Widicus Weaver, Dariusz Lis

MN02 2:03 – 2:18
A MACHINE LEARNING APPROACH TO CHARACTERIZING THE CHEMICAL INVENTORY OF ORION-KL,
Haley N. Scolati, Leslie Looney, Aasik Pathani, Zhe-Yun Li, Haifeng Yang, Ian Stephens, Richard Teague, Richard Churcher, Crystal C. Bregon, Erin Guilfoil Cox

MN03 2:21 – 2:36
USING HCO+ LINE (& ITS ISOMERS) AS AN ASTROCHEMICAL TOOL TO PROBE THE STRUCTURE OF CLASS 0/1 PROTOSTARS,
Mihika Rao, Anthony Remijan, Adele Plunkett

MN04 2:39 – 2:54
MAGNETIC FIELD STRENGTH LIMITS IN A PROTOPLANETARY DISK FROM MULTI-WAVELENGTH ZEIDMAN OBSERVATIONS,
Rachel E. Harrison, Leslie Looney, Aassik Pathani, Zhe-Yun Li, Haifeng Yang, Ian Stephens, Richard Teague, Richard Churcher, Crystal C. Bregon, Erin Guilfoil Cox

MN05 2:57 – 3:12
DETECTION OF c-C2H2, NO, AND CH3CN TOWARDS MOLECULAR CLOUDS AT THE EDGE OF THE GALAXY,
Lilia Koelmay, Lucy M. Ziurys

MN06 3:15 – 3:30
MOLECULAR LINE OBSERVATIONS IN TWO DUSTY STAR FORMING GALAXIES AT Z=6.9,
Sreevani Jarugula

Intermission

TA01 8:30 – 9:00
INVITED TALK
X-RAY MOLECULAR SPECTROSCOPIC DYNAMICS,
Stephen R. Leone

TA02 9:06 – 9:21
ULTRAFAST XUV MAGNETIC CIRCULAR DICHOISM: OBSERVING SPIN TRANSPORT AT INTERFACES,
Robert Baker, Martin Schultz, Harshad Gajapathy, Savini Sandunaka Bandaranayake, Emily B Hruska, Stephen Londo

TA03 9:24 – 9:39
ULTRAFAST ELECTRON TRANSFER AND SPIN FLIP IN A HETEROBIMETALLIC COMPLEX,
John H Buric, Josh Vans-Wes

TA04 9:42 – 9:57
MONITORING VALENCE-ELECTRON DYNAMICS IN MOLECULES WITH ULTRAFAST X-RAY DIFFRACTION,
Haiwang Yang, Stefano M. Caravalleto, Shaul Mukamel

TA05 10:00 – 10:15
ULTRAFAST DYNAMICS OF TWO- AND THREE-BODY DISSOCIATION CAPTURED BY CORE-TO-VALENCE TRANSIENT ABSORPTION SPECTROSCOPY,
Jan Tross, Neil C. Cole-Filipiak, Paul Schrader, Laura M McCalin, Kupya Ramasesha

TA06 10:18 – 10:33
MAPPING COMPLEX PHOTOCHEMICAL REACTIONS USING FEMTOSECOND UV-PUMP XUV-PROBE PHOTOELECTRON SPECTROSCOPY,
Daniel Hocke, Gino L. Alama

Intermission

TA07 11:15 – 11:30
ELECTRON LOCALIZATION IN MOLECULES INTERACTING WITH INTENSE LASER PULSES,
Agnieszka Jacob, Lauren Bauerle

TA08 11:33 – 11:48
PRONING SPATIAL EVOLUTION OF ULTRAFAST ELECTRONIC WAVEPACKETS WITH TWO-ELECTRON ANGULAR STREAMING,
Gabriel A. Stewart, Duke A. Debrah, Gihan Basnayake, Suk Kyoung Lee, Wen Li

TA09 11:51 – 12:06
IMAGING THE REACTIVE RADICAL-CATION COMPLEX IN THE IONIZED LIQUID WATER,
Ming-Fu Lin
**TB. Mini-symposium: Benchmarking in Spectroscopy**

*Tuesday, June 21, 2022 – 8:30 AM*

*Room: 116 Roger Adams Lab*

**Chair:** L. H. Coudert, Université Paris-Saclay, CNRS, Orsay, France

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<td>8:30–9:00</td>
<td>TB01</td>
<td>INVITED TALK: EXTENDING ACCURATE QUANTUM CHEMISTRY TO HEAVY ELEMENTS</td>
<td>Xuechen Zheng, Chaoqun Zhang, Lai Cheng</td>
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<td>9:06–9:21</td>
<td>TB02</td>
<td>ELECTRONIC STRUCTURE OF RuO₂</td>
<td>Yao Yu, Lei Zhang, Xiaowen Ma, Jie Yang</td>
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<td>9:42–9:57</td>
<td>TB04</td>
<td>ACCURATE PREDICTION OF EQUILIBRIUM STRUCTURE FOR HEAVY ELEMENT CONTAINING MOLECULES</td>
<td>Chaoqun Zhang, Lai Cheng</td>
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<td>TB05</td>
<td>Lab LINE LIST FOR THE B(3Σ⁺) - X(3Σ⁻) BAND SYSTEM</td>
<td>Peter F. Bernath, Randika Dodangodage, Jacques Liévin</td>
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<td>10:57–11:12</td>
<td>TB06</td>
<td>PREDICTION AND INTERPRETATION OF TRANSITION METAL X-RAY SPECTRA USING REAL-TIME TIME-DEPENDENT DENSITY FUNCTIONAL THEORY</td>
<td>Jun Yi, Zhou Lin, Ying Zhu</td>
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<td>11:15–11:30</td>
<td>TB07</td>
<td>SIMPLIFIED LR-TDDFT/ZORA APPROACH FOR GENERATING SPIN-ORBIT COUPLINGS FOR X-RAY ABSORPTION SPECTRA</td>
<td>Sarah Pak, Daniel R. Nascimento</td>
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<td>TB08</td>
<td>VIBRONIC ANALYSIS OF MOLECULES WITH QUASI-DEGENERATE ELECTRONIC STATES</td>
<td>Ketan Sharma, Terry A. Miller, Jinjun Liu</td>
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<td>12:09–12:24</td>
<td>TB10</td>
<td>ALKALI DIATOMICS: ASYMPTOTIC LONG RANGE BEHAVIOR OF ELECTRONIC MATRIX ELEMENTS BASED ON AB INTRIO CALCULATIONS</td>
<td>Haimerina A. Bormotova, Andrey Stolyarov</td>
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<td>8:30–8:45</td>
<td>TC01</td>
<td>HIGH-ACCURACY LINE LISTS OF METHANE AND FORMALDEHYDE BETWEEN 1240 AND 1380 cm⁻¹ FROM FOURIER-TRANSFORM OPTICAL FREQUENCY COMB SPECTROSCOPY</td>
<td>Matthias Germann, Adrian Hajibrahim, Iasik Silander, Aleksandra Poljnovicz, Vincent Boudon, Cyril Richard, Karel Křížek, Sławomir Hudeczkowiak, Aleksander Gniazdek, Grzegorz Sobol</td>
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<td>TC02</td>
<td>IMPROVED CO₂ IR LINE LIST FOR 1500K – 3000K</td>
<td>Xinchuan Huang, David Schwenke, Richard S Freedman, Timothy J. Lee</td>
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<td>TC03</td>
<td>AMES-1 296K IR LINE LISTS FOR CS₂ ISOTOPOLOGUES</td>
<td>Xinchuan Huang, David Schwenke, Timothy J. Lee</td>
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<td>9:24–9:39</td>
<td>TC04</td>
<td>AMES-1 296K IR LINE LISTS FOR OCS ISOTOPOLOGUES</td>
<td>Xinchuan Huang, David Schwenke, Timothy J. Lee</td>
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<td>TC05</td>
<td>AMES-1 296K IR LINE LISTS FOR N₂O ISOTOPOLOGUES</td>
<td>Xinchuan Huang, David Schwenke, Timothy J. Lee</td>
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<td>10:39–10:54</td>
<td>TC06</td>
<td>ROVIBRONIC INFRARED AND VISIBLE LINE LIST FOR O₂</td>
<td>Wilfried Somogyi, Sergei N. Yurchenko, Gap-Sue Kim</td>
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<td>TC07</td>
<td>EXOMOL ROVIBRONIC LINE LIST AND TEMPERATURE DEPENDENT PHOTODISSOCIATION CROSS SECTION CALCULATIONS FOR OH FROM AB INITIO ELECTRONIC STRUCTURE CALCULATIONS</td>
<td>Georgi B. Mitev, Jonathan Tennyson, Sergei N. Yurchenko</td>
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<td>11:15–11:30</td>
<td>TC08</td>
<td>HIGH LEVEL AB INITIO STUDY OF THE ROVIBRONIC SPECTRUM OF SULFUR MONOXIDE (SO): DIABATIC REPRESENTATION</td>
<td>Ryan Brady, Gap-Sue Kim, Wilfried Somogyi, Sergei N. Yurchenko, Jonathan Tennyson</td>
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<td>VISIBLE OPACITY OF M DWARFS AND HOT JUPITERS: THE TiO B(3Π) - X(3Δ) BAND SYSTEM</td>
<td>William D Cameron, Peter P. Bernath</td>
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<td>TC12</td>
<td>LINE LISTS FOR A(3Σ⁺) AND a(1Δ) VIBRATION-ROTATION BANDS OF SO</td>
<td>Peter P. Bernath, Ryan Johnson, Jacques Liévin</td>
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TD. Rotational structure/frequencies
Tuesday, June 21, 2022 – 8:30 AM
Room: 217 Noyes Laboratory
Chair: Kyle N. Crabtree, University of California, Davis, CA, USA

TD01  MICROWAVE SPECTROSCOPY OF ISOThIAZOLE, Hoga Furukawa, Karui Kobayashi, Maria Zdanovskaia, Brian J. Esselman, R. Claude Woods, Robert J. McMahon
8:30 – 8:45

TD02  EXTENDED LABORATORY INVESTIGATION OF THE PURE ROTATIONAL SPECTRUM OF THE CH2CN RADICAL IN THE (SUB-)MILLIMETER REGION (79-860 GHz), Olivia Chitarra, Thomas Sandow Hearne, Oliver Pirlai, Marie-Aline Martin-Drumel
8:48 – 9:03

TD03  ELECTRICAL DISCHARGE OF NITROGEN CONTAINING MOLECULES: A DETAILED STUDY OF THE DISCHARGE PRODUCTS OF PYRROLE AND PYRIDINE, Eva Giangrada, Donatella Loiu, Gayatri Bhat, Melanie Schnell
9:06 – 9:21

TD04  ACCURATE SPECTROSCOPIC CHARACTERIZATION OF UNSATURATED CARBON-CHAiNS OF ASTROCHEMICAL IMPORTANCE, Alessio Melli, Silvia Alessandrini, Vincenzo Barone, Mattia Melosso, Ningjing Jiang, Luca Dore, Cristina Puzzarini, Luca Bizzocchi, J.-C. Guillemin
9:24 – 9:39

TD05  SPECTROSCOPIC AND COMPUTATIONAL CHARACTERIZATION OF 2-AZA-1,3-BUTADIENE, A MOLECULE OF ASTROCHEMICAL SIGNIFICANCE, Ningjing Jiang, Mattia Melosso, Luca Bizzocchi, Silvia Alessandrini, J.-C. Guillemin, Luca Dore, Cristina Puzzarini
9:42 – 9:57

Intermission
10:39 – 10:54

TD06  THE MILLIMETER/SUBMILLIMETER SPECTRUM OF 3-HYDROXYPROPANAMIDE, Colton Moore, Hayley Bunn, Chase P Schultz, Susanna L. Widicus Weaver
10:57 – 11:12

TD07  ANALYSIS OF THE HIGH RESOLUTION ROTATIONAL SPECTRUM OF 2-CHLORETHANOL, Hayley Bunn, Brian J. Esselman, Andi Wright, Steven Shipman, Susanna L. Widicus Weaver
11:15 – 11:30

TD08  FOURIER TRANSFORM MICROWAVE SPECTRA OF cis-3-HEXENAL, trans-3-HEXENAL, cis-2,3-HEXENAL AND trans-2,3-HEXENAL: STRUCTURAL ISOMERS AND ISOMERIZATION, Kyoto Orawa, Nobuhiko Kaze, Yoshiyuki Kawashima
11:33 – 11:48

TD09  DECIPHERING THE COMPLETE NUCLEAR QUADRUPOLE COUPLING TENSOR OFIODINE WITH THE ROTATIONAL SPECTRUM OF 2-ETHOXYETHANOL. Michael J. Carrith, Lindsey Ann Speare, Dinesh Marasinghe, Michael Tu-bergen
11:51 – 12:06

TD10  CENTIMETER-WAVE SPECTROSCOPY OF SEVERAL NEW SILICON-BEARING CARBON CHAINS, Michael C. McCarthy, Bryan Changala, Brandon Carroll
12:09 – 12:24

Te. Chirality and stereochemistry
Tuesday, June 21, 2022 – 8:30 AM
Room: 1024 Chemistry Annex
Chair: Ha Vinh Lam Nguyen, Université Paris-Est Créteil, Créteil, France

TE01  HIGH RESOLUTION INFRARED SPECTROSCOPY OF AZIRIDINE-2-CARBOXYLATE (C3H4N2) , Karen Keplinger, Sieghard Albert, Carine Manca Tanner, Martin Quack, Jürgen Stobner
8:30 – 8:45

TE02  TRANSIENT CHIRALITY AND MICROSOlvation IN p-ETHYLPHENOL., Juan Carlos Lopez, Fernando Gonzalez, Alberto Macario, Susana Blanco
8:48 – 9:03

TE03  THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE CHIRAL AND ACHIRAL RO-TAMERS OF 2,3,3-TRIFLUOROPROPANE AND THEIR GAS PHASE HETERODIMERS WITH THE ARGON ATOM, Helen O. Leung, Mark D. Marshall, Taha Ahmad, David W. Borden, Caitlin Hoffman, Navee Kim
9:06 – 9:21

TE04  HIGH PRECISION SPECTROSCOPY AND CONTROLLED DIMER FORMATION IN A CRYOGENIC ENVIRONMENT, David Patterson, Greta Kourkarian, Lincoln Satterthwaite, Daniel Sorensen
9:24 – 9:39

TE05  BROADBAND MICROWAVE 3-WAVE MIXING ASSIGNMENT-FREE CHIRALITY DETECTION IN UNKNOWN SAMPLES, Greta Kourkarian, Irene Wang, Lincoln Satterthwaite, David Patterson
9:42 – 9:57

Intermission
10:39 – 10:54

TE06  THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE CHIRAL TAGGING CANDIDATE CIS-1,3,3,3-TETRAFLUORO-1,2-EPOXYPROPANE AND ITS GAS PHASE HETERODIMER WITH THE ARGON ATOM, Jonah H. Horowitz, Helen O. Leung, Mark D. Marshall
10:57 – 11:12

TE07  THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF CIS- and TRANS-1,1,1-TRIFLUORO-2,3-EPOXYBUTANE, Mark D. Marshall, Helen O. Leung, Caitlin Knight
11:15 – 11:30

TE08  ENHANCED ENANTIOmER-SELECTIVE POPULATION ENRICHMENT USING MICROWAVE SPECTROSCOPy WITH RAPID ADEIABATIC PASSAGE , Freya E. L. Bergg otz, Himanshi Singh, Weihao Sun, Cristobal Perez, Melanie Schnell
11:33 – 11:48

TE09  INSIGHT INTO CHIRAL RAMAN SIGNALS UNDER RESONANCE CONDITION., Guojie Li, Yunjie Xu
11:51 – 12:06

TE10  ANISOTROPIC CIRCULAR DICHRoISM SPECTROSCOPY OF JET-COOLED CHIRAL MOLECULES, Changseop Jeong, Nam Joon Kim
12:09 – 12:24
TF01 8:30 – 8:45
THE INTRIGUING $F_{\nu}({P_{l}P_{l} + P_{s}P_{s}})$ TERM IN THE INTERACTION HAMILTONIAN FOR TUNNELING BETWEEN EQUIVALENT GAUCHE CONFORMERS. Peter Goerz

TF02 8:45 – 9:00
A LOCAL MODE STUDY OF PSEUDOROTATIONAL EFFECTS IN THE INFRARED SPECTRA OF THE SCISSOR AND CH STRETCH VIBRATIONS OF CYCLOPENTANE. Edwin Shott, Peter F. Bernath

TF03 9:00 – 9:15
ROTATIONAL AND PHOTOELECTRON SPECTROSCOPIES MEET QUANTUM CHEMISTRY: N-DIETHYLHYDROXYLAMINE, Giovanna Salvati, Assimo Maris, Sonia Melandri, Luca Evangelisti, Fabrizia Negri, Marcello Coenzo, Alessandra Cavalotti, Haman Sr. adkh

TF04 9:15 – 9:30
CONFORMATIONAL EQUILIBRIUM OF THE CHALCOCEN-BRIDGED COMPOUNDS ALLYL, ETHYL ETHER AND ALLYL ETHYL SULFIDE REVEALED BY MICROWAVE SPECTROSCOPY AND COMPUTATIONAL CHEMISTRY. TAMANNA POONIA, Jennifer van Wijngaarden

TF05 9:30 – 9:45
MILLIMETER-WAVE SPECTRUM OF THE LOWEST ENERGY, VIBRATIONALLY EXCITED COUPLED DIAZ-3-TRANS-Z-1-CYANO-1,3-BUTADIENE. P. Masriha Dorman, Brian J. Eiselman, Robert J. McMahon, R. Claude Woods

TF06 9:45 – 10:00
THE ROTATIONAL SPECTRA OF 2-CYANO PYRIMIDINE ($\text{C}_{5}\text{H}_{4}\text{N}_{2}$) AND 2-CYANO PYRAZINE ($\text{C}_{5}\text{H}_{5}\text{N}_{2}$): VIBRATIONAL GROUND STATES AND DIAD OF LOWEST-ENERGY VIBRATIONALLY EXCITED STATES, Houston H. Smith, Brian J. Eiselman, Maria Zdanovskaia, R. Claude Woods, Robert J. McMahon

Intermission

TF07 10:00 – 10:15
HYDROXYL GROUPS TORSIONAL MOTION IN CATECHOL MOLECULE. Darya Kisyrina, Alex Malovich, Arinya Khrapunova, Udazimni Saperska, George Pitsevich

TF08 10:15 – 10:30
ORIGINS OF THE INTENSITY OF THE STRETCH-BEND COMBINATION TRANSITION IN WATER CLUSTERS AND IMPLICATIONS FOR CHARACTERIZING HYDROGEN BONDING. Rachel M. Huchmal, Anne B. McCoy

TF09 10:30 – 10:45
SPECTROSCOPY AND BRAIN CHEMISTRY OF SEROTONIN AND DOPAMINE CONFORMERS. Vipin Bahadur Singh

TF10 10:45 – 11:00
TORSIONAL POTENTIALS, BARRIER TO INTERNAL ROTATION, MOLECULAR STRUCTURE, VIBRATIONAL PROPERTIES, NBO BEHAVIOUR AND NBO CHARACTERISTICS OF 2-PHENYLISULFONYLVINYL BICYCLIZENE AND 2-TOSYLVINYL BICYCLIZENE EMPLOYING FTIR, FT RAMAN SPECTRAL TECHNIQUES AND DFT APPROACH. K. Shitalakshmi, Balakrishna Auguela, Byru Venkatram Reddy, G. Ramana Rao

TF11 11:00 – 11:15
THEORETICAL AND EXPERIMENTAL ROTATIONAL SPECTROSCOPIC STUDIES OF SUBSTITUTED BENZIC ACID HETERODIMERS. Mohammad H. Al-Ahmar, Mihael Erakovic, Aran Insausti, Marko Cvitaš, Wolfgang Jager

TG01 11:15 – 11:30
STRUCTURAL DEFORMATION OF 4-BENZYLZINOZANOATE UPON COMPLEXATION WITH METAL IONS AND SOLVENT UTILIZING MASS-SELECTED CRYOGENIC IR. Anna Gabriella del Rosario Rullán Buxó, Takeru Sato, R. Claude Woods, Fabian Peterß, Christopher J. Johnson

TG02 11:30 – 11:45

TG03 11:45 – 11:51
PHOSPHATE TERMINAL IN THE INTERACTION HAMILTONIAN FOR TUNNELING BETWEEN ALTERNATIVE GAUCHE CONFORMERS. Peter Goerz
TH. Mini-symposium: Spectroscopy meets Chemical Dynamics
Tuesday, June 21, 2022 – 1:30 PM
Room: 100 Noyes Laboratory

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

TH01
INVITED TALK
1:30 – 2:00
ULTRAFAST SPECTROSCOPY WITH FREQUENCY COMBS: ENABLING NEW MEASUREMENTS OF DILUTE SPECIES IN MOLECULAR BEAMS, Nicholas D. Cooper, Walker M. Jones, Todd Eliason, Melanie A.R. Reber

TH02
REAL-TIME TRACKING OF COHERENT VIBRATIONAL MOTION IN GROUND AND EXCITED ELECTRONIC STATES, Shaina Dhamija, Garimu Bhutani, Ajay Jayachandran, Arjit K De

TH03
PHOTOPHYSICS OF NiII PYRIDINOPHANE PHOTOCATALYSTS USED FOR C-O CROSS-COUPLING REACTIONS PROBED VIA FEMTOSECOND OPTICAL ABSORPTION SPECTROSCOPY, Rachel Wallack, Josh Vina-Weis, Reneke van der Veen

TH04
ULTRAFAST VIBRATIONAL DYNAMICS OF THE INTRAMOLECULAR H-BOND IN ACETYLACETONE INVESTIGATED WITH 2D IR SPECTROSCOPY, Jessika L.S. Dean, Joseph Fournier

TH05
RAPID FREQUENCY-COMB INFRARED SPECTROSCOPY WITH CROSS-DISPERSED SPECTROMETERS, D. Michelle Bailey, Joseph T. Hodges, Adam J. Fleisher

Intermission

TH06
SIMULATING FRANCK-CONDON SPECTRA WITH IMAGINARY-FREQUENCY VIBRATIONS, Bryan Changala, Navin Genossar, Joshua H Baraban

TH07
PROTON TRANSFER AND INTERSYSTEM CROSSING IN 2-NITROPHENOL PROBED BY GAS-PHASE TRANSIENT ABSORPTION SPECTROSCOPY, Mylka C Stiles, Arshad Mehmoon, Grzegorz Kowzan, Benjamin G Levine, Thomas K Alderson

TH08
SOLVENT DRIVEN COHERENT POPULATION TRANSFER IN TRYPTOPHAN, Vishal K. Jaiswal, Marzio Giuseppe Gentile, Irene Conti, Atat Nenov, Marco Garazzli, Piotr Kabacinski, Rocio Borrego-Varillas, Giulio Cerullo

TH09
TWO-DIMENSIONAL TRANSIENT UV INVESTIGATION OF REDUCED FLAVINS, Eric Yokie, Akagrabha Konur

TI. Mini-symposium: Benchmarking in Spectroscopy
Tuesday, June 21, 2022 – 1:30 PM
Room: 116 Roger Adams Lab

Chair: Eva Gougoula, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

TI01
THE “LEGO BRICK” APPROACH AT WORK: A COST-EFFECTIVE STRATEGY FOR PREDICTING ACCURATE ROTATIONAL CONSTANTS, Hexu Ye, Silvia Alessandrini, Mattia Meloso, Cristina Duzzanti

TI02
CONCENTRATION DETERMINATIONS FOR REACTIVE CHEMICAL INTERMEDIATES USING EMPIRICALLY DETERMINED AND THEORETICALLY CALCULATED TRANSITION PROBABILITIES, Lu Jones, Jonathan Swift Bresson, Junjun Lu, Ketan Sharma, Terry A. Miller, John F. Stanton

TI03
AMINO ACIDS AND PEPTIDES (AAP) STRUCTURES, ENERGETICS AND SPECTROSCOPY (SES) DATABASE, Malgorzata Biczysko

TI04
COMPUTATIONAL STUDIES OF MGC4H ISOMERS, Aland Sinjari, Tarun Roy, Subhas Ghosal, Venkatesan S. Thimmakondu

TI05
ULTRAHIGH FINESSE CAVITY-ENHANCED SPECTROSCOPY OF DEUTERIUM MOLECULE FOR QED TESTS, Mikolaj Zaborowski, Michal Slowinski, Kamal Stankiewicz, Frane Thibault, Agata Cygan, Hubert Jaywick, Grzegorz Kowzan, Piotr Mielowski, Akiko Nishiyama, Nikolaos Soldatou, Szymon Wojewicz, Roman Czylylo, Daniel Lisak, Piotr Wicido

Intermission

TI06
RESONANT INELASTIC X-RAY SCATTERING CALCULATIONS OF Ru COMPLEXES WITHIN A SIMPLIFIED TIME-DEPENDENT DENSITY FUNCTIONAL THEORY FRAMEWORK, Daniel R. Nascimento

TI07
DECONVOLVING VIBRATIONAL PROBE RESPONSES USING CRYOGENIC ION INFRARED SPECTROSCOPY, Ahmed Mohamed, Sean Coleman Edington, Mark Johnson

TI08
QUARANTINED CC-STRETCHED FORMIC ACID: MOLECULAR WORK-OUT IN (SELF) ISOLATION, Katharina A. E. Meyer, Arman Nejad

TI09
THE FORMIC ACID MONOMER: EXTENSION OF THE VIBRATIONAL DATABASE AND RIGOROUS ELECTRONIC AND NUCLEAR VIBRATIONAL STRUCTURE BENCHMARKS, Arman Nejad, Edwin Sibert, Martin A. Suhm
TJ. Photodissociation and photochemistry
Tuesday, June 21, 2022 – 1:30 PM
Room: B102 Chemical and Life Sciences

Chair: Fleming Crim, The University of Wisconsin, Madison, WI, USA

TJ01 1:30 – 1:45
RESONANCE ENHANCED PHOTODISSOCIATION SPECTROSCOPY OF AuAg+ REVEALS ISOTOPIC DEPENDANCE ON PHOTODISSOCIATION, Samuel Jack Palmer Marlton, Chang Liu, Patrick Watkins, Jack T Buntine, Evan Brooke

TJ02 1:48 – 2:03
PHOTODISSOCIATION SPECTRUM OF AuN2, Nima Nooh Nahvi, Marko Förstel, Kai Pollow, Taarna Studemund, Otto Dopfer

TJ03 2:06 – 2:21
GAS-PHASE ELECTRONIC SPECTROSCOPY OF C6+, Jason E. Colley, Dylan S. Orr, Michael A Duncan

TJ04 2:24 – 2:39
S2O2+ – PHOTODISSOCIATION AND OPTICAL ABSORPTION PROPERTIES, Taarna Studemund, Marko Förstel, Kai Pollow, Emil Miecke, Otto Dopfer

Intermission

TJ05 3:03 – 3:18
SPECTROSCOPIC STUDIES OF π-BACKDONATING EARLY TRANSITION METAL AND MONOVALENT LANTHANIDE DIBORIDES, Dakota M. Merriles, Kimberly H. Tomchuk, Christopher Nielsen, Michael D. Morse

TJ06 3:21 – 3:36
BOND DISSOCIATION ENERGIES AND IONIZATION ENERGIES OF RHENIUM CONTAINING SMALL MOLECULES, Kimberly H. Tomchuk, Erick Tien, Thomas T. Kawaijoe, Jordan Derbidge, Keith T. Clark, Michael D. Morse

TJ07 3:39 – 3:54
ULTRAFAST CARRIER DYNAMICS IN QUANTUM DOT SENSITIZED ZnO, Conner Dykstra, Thomas Rossi, Renske van der Veen, Josh Ira Weiss

TJ08 3:57 – 4:12
PHOTOCHEMISTRY OF CYANOMETHYLENE CYCLOPROPANE (C5H5N) IN A LOW TEMPERATURE RARE GAS MATRIX, Samuel A. Wood, Samuel M. Kougias, Brian J. Esselman, R. Claude Woods, Robert J. McMahon

TJ09 4:15 – 4:30
UV PHOTOLYSIS STUDY OF PARA-AMINOBENZOIC ACID USING PARAHYDROGEN MATRIX ISOLATED SPECTROSCOPY, Alexandre McKinnon, Brendan Moore, Pavle Djuricinac, Takamasa Momose

TJ10 4:33 – 4:48
UV PHOTOLYSIS OF AMINO ACIDS IN A SOLID PARAHYDROGEN MATRIX, Brendan Moore, Shin Yi Toh, Terneh Bashiri, Kyle Mahoney, Alexandra McKinnon, Mei Fei Zeng, Ying-Tung Angel Wong, Pavle Djuricinac, Takamasa Momose

TK. Mini-symposium: Machine Learning
Tuesday, June 21, 2022 – 1:30 PM
Room: 217 Noyes Laboratory

Chair: Andrew White, University of Rochester, Rochester, NY, USA

TK01 1:30 – 2:00
INVITED TALK
AN OVERVIEW OF MACHINE LEARNING IN ROTATIONAL SPECTROSCOPY, Steven Shipman

TK02 2:06 – 2:21
DEVELOPMENT OF HIGH-SPEED AB INITIO CCSD(T) LEVEL NEURAL NETWORK POTENTIAL ENERGY SURFACES FOR DIFFUSION MONTE CARLO, Fenris Lu, Anne B McCoy

TK03 2:24 – 2:39
DIFFUSION MONTE CARLO STUDY OF C2H+ USING AN AB INITIO POTENTIAL ENERGY SURFACE, Pattarapon Moosukarn, Fenris Lu, Anne B McCoy

Intermission

TK04 3:03 – 3:33
INVITED TALK
PUTTING DENSITY FUNCTIONAL THEORY TO THE TEST WITH MACHINE LEARNING, Heather J Kulik

TK05 3:39 – 3:54
PARTITION FUNCTION ESTIMATION FROM INCOMPLETE SPECTROSCOPIC GRAPHS, Kelvin Lee, Kyle N. Crabtree

TK06 3:57 – 4:12
ACCURATE PHOTO-PHYSICS OF ORGANIC RADICALS FROM MACHINE LEARNED RANGE-SEPARATED FUNCTIONALS, Chongwei Ju, Yili Shen, Aaron Tian, Ethan French, Hongshan Bi, Zhou Lin
**Theory and Computation**

*Tuesday, June 21, 2022 – 1:30 PM*

*Room: 1024 Chemistry Annex*

**Chair:** János Sarka, Texas Tech University, Lubbock, TX, USA

**TL01** 1:30 – 1:45

**Calculations of Actinide- and Lanthanide-Containing Small Molecules Using Spinor-Based Relativistic Coupled-Cluster Methods**, Tianxiang Chen, Chaoqun Zhang, Lan Cheng

**TL02** 1:48 – 2:03

**Theoretical Investigation of the X-Ray Stark Effect in Small Molecules**, Catherine Wright, Avdhoot Datar, Devin A. Matthews

**TL03** 2:06 – 2:21

**AB INTRO Investigation of Intramolecular Charge Transfer in DMABN by Calculation of Transient X-Ray Absorption Features**, Avdhoot Datar, Saisrinivas Gudivada, Devin A. Matthews

**TL04** 2:24 – 2:39

**Enhancing Thermally Activated Delayed Fluorescence Through Structural and Energetic Flexibility: Theoretical Studies**, Dieaa H Alhmoud, Zhou Lin

**TL05** 2:42 – 2:57


**Intermission**

**TL06** 3:21 – 3:36

**Vibrationally Unusual Behaviors Predicted for (AdxH)5+: Computational Molecular Spectroscopy Study**, Tatsuro Hiura, Umpei Nagashima, Masaki Baba

**TL07** 3:39 – 3:54

**Fine and Hyperfine: Resolved Empirical Energy Levels of Vanadium Oxide (VO)**, Charles A Bowesman, Scott Hopkins, Sergei N. Yurchenko, Jonathan Rebelsky

**TL08** 3:57 – 4:12


**TL09** 4:15 – 4:30

**The GPU Accelerated Absorption Simulation (GAAS) Platform**, Charlie Scott Callahan, Sean Coburn, Gregory B Rieker, Sean Coburn, Greg Rieker

**TL10** 4:33 – 4:48

**Quantum Scrambling in Molecules**, Chenghao Zhang, Martin Graebele, Peter Guy Wolynes

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**Clusters/Complexes**

*Tuesday, June 21, 2022 – 1:30 PM*

*Room: 124 Burrill Hall*

**Chair:** G. S. Grubbs II, Missouri University of Science and Technology, Rolla, MO, USA

**TM01** 1:30 – 1:45

**Pure Rotational Spectroscopy of Rare Gas Dimers Based on Rotational Wave Packet Imaging**, Kenta Mizuse, Yuya Tobata, Urara Sato, Yasuhiro Ohshima

**TM02** 1:48 – 2:03

**Partial Proton Transfer in the Trifluoroacetic Acid - Trimethylamine Complex**, Aaron J Reynolds, Nathan Love, Kenneth R. Leopold

**TM03** 2:06 – 2:21

**Alternating 1-Phenyl-2,2,2-Trifluoroethanol Conformational Landscape with the Addition of One Water: Tunneling and Large Amplitude Motions**, Colton Carlson, Daniel Mason, Qian Yang, Nathan A. Seifert, Yunjie Xu

**TM04** 2:24 – 2:39

**Conformational Behaviour of m-Anisaldehyde and its Microsolvates**, Andres Verde, Juan Carlos M. Lopez, Susana Blanco

**Intermission**

**TM06** 3:21 – 3:36

**Point Mutation Changes Vibrational Coupling in Lepidium Virginicum Water Soluble Chlorophyll Binding Protein**, Galina Grechishnikova, Amrit Srivastava, Shaif Alhab, Mike Earl Reppert, Lilai Huang

**TM07** 3:39 – 3:54

**Stability of Neutral Manganese Oxide Clusters**, Chase H Rotteger, Shaun Sutton, Scott G Sayres

**TM08** 3:57 – 4:12

**Excited State Photodynamics of Sub-Nanometer Metal Oxide Clusters**, Scott G Sayres

**TM09** 4:15 – 4:30

**The Millimeter-Wave Spectrum of the Weakly Bound Argon-Methanol Cluster**, Connor I Wright, Kevin Riehnitz, Jonathan Rebelsky, Anna Kay Gerossi, Morgan Giese, Steven Shipman, Susanna L. Widicus Weaver
### TN. Radicals

**Tuesday, June 21, 2022 – 1:30 PM**  
Room: 274 Medical Sciences Building  
Chair: Ugo Jacovella, CNRS, Université Paris-Saclay, Orsay, France

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<tr>
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<tr>
<td>TN01</td>
<td>HIGH-RESOLUTION INFRARED SPECTROSCOPY OF GAS-PHASE CYCLOBUTYL RADICAL IN THE $\alpha$-CH STRETCH REGION: STRUCTURAL AND DYNAMICAL INSIGHTS.</td>
<td>Ya-Chu Chan, David Nesbitt</td>
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<tr>
<td>TN02</td>
<td>EXTENDING PURE ROTATIONAL MEASUREMENTS OF THE CH$_3$O RADICAL TOWARD THE TERAHERTZ DOMAIN.</td>
<td>Marie-Aline Martin-Drumel, Olivia Chitarra, Jean-Thibaut Spaniol, Thomas Sandow Hearne, Olivier Pirali, J.-C. Loison</td>
</tr>
<tr>
<td>TN03</td>
<td>THE MICROWAVE SPECTRUM OF THE DIFLUOROCYANOMETHYL RADICAL, CF$_2$CN.</td>
<td>Lu Kang, Ha Vinh Lam Nguyen, Christopher Falls, Alexander Seys, Wallace C. Pringle, Thomas A. Blake, Stewart E. Novick, S. A. Cooke</td>
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<tr>
<td>TN04</td>
<td>IMPROVEMENTS TO NEW PROGRAM FOR SPIN-TORSION-ROTATION &amp; THE METHYL-PHENOXYL RADICALS.</td>
<td>J. H. Westerfield, Blair Welsh, Timothy S. Zwier, Kyle N. Crabtree</td>
</tr>
<tr>
<td>TN05</td>
<td>PRODUCT-SPECIFIC REACTION KINETICS OF CN WITH PROPENE PROBED BY CHIRPED-PULSE FOURIER TRANSFORM MILLIMETER WAVE SPECTROSCOPY.</td>
<td>Divita Gupta, Brian M Hays, Myriam Drissi, Theo Guillaume, Omar Abdellaker Khedaoui, Ilsa Rose Cooke, Ian R. Sims</td>
</tr>
<tr>
<td>TN06</td>
<td>EXAMINING METHYLAMINE DISSOCIATION PRODUCTS USING THEORY AND ROTATIONAL SPECTROSCOPY.</td>
<td>Connor J. Wright, Jonathan Rebelsky, Anna Kay Genovishna, John F. Stanton, Susanna L. Widicus Weaver</td>
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**Intermission**

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<tbody>
<tr>
<td>TN07</td>
<td>PRODUCTION OF CH$_3$N$_2$ AND CH$_3$NH IN THE REACTIONS OF METHYLAMINE (CH$_3$NH$_2$) WITH H$_2$ OR CH IN SOLID $\beta$-H$_2$ AND ITS IMPLICATION IN ASTROCHEMISTRY.</td>
<td>Prasad Ramesh Joshi, Yuan-Pern Lee</td>
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<tr>
<td>TN08</td>
<td>ORIENTATION DYNAMICS OF CH$_3$, CH$_4$, AND CD$_4$ QUANTUM ROTORS IN SOLID METHANES AT CRYOGENIC TEMPERATURES.</td>
<td>Yutin Dmitriev</td>
</tr>
<tr>
<td>TN09</td>
<td>FORMATION REACTION MECHANISM AND INFRARED SPECTRA OF CREIGEE INTERMEDIATE ANTI-TRANS-METHACROLEIN OXIDE (CH$_2$(CH)$_2$(CHO)$_2$) AND ITS ASSOCIATED PRECURSOR AND ADDUCT RADICALS.</td>
<td>Yuan-Pern Lee, Fu-Rong Cai, Jung-Hsuan Su, Chen-An Chung</td>
</tr>
<tr>
<td>TN10</td>
<td>STUDY OF THE KINETICS AND PRODUCT YIELDS FOR THE REACTION OF CREIGEE INTERMEDIATE: CH$_2$(CHO) WITH NO$_2$ USING MID-INFRARED TIME-RESOLVED DUAL-COMB SPECTROSCOPY.</td>
<td>Pei-Ling Luo</td>
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**TO. Plenary Special Session**

**Tuesday, June 21, 2022 – 5:15 PM**  
Room: 2025A/B/C Ikenberry Commons  
Chair: Helen O. Leung, Amherst College, Amherst, MA, USA

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<thead>
<tr>
<th>Block</th>
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<tr>
<td>TO01</td>
<td>SPECTROSCOPY TODAY: THE URGENT NEED FOR SCIENCE AND INNOVATION TO SAVE THIS WARMING PLANET.</td>
<td>Geraldine Richmond</td>
</tr>
<tr>
<td>TO02</td>
<td>ISMS AND NSF: SOME HISTORY AND A LOOK FORWARD.</td>
<td>Fleming Crim</td>
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</table>
WA. Mini-symposium: Spectroscopy meets Chemical Dynamics
Wednesday, June 22, 2022 – 8:30 AM
Room: 100 Noyes Laboratory
Chair: Melanie A.R. Reber, University of Georgia, Athens, GA, USA

WA01 INVITED TALK 8:30 – 9:00
MICROBUBBLE RESONATORS FOR FUN AND PROFIT, Randall Goldsmith

WA02 PHOTOELECTRON SPECTROSCOPIC STUDY ON DIPOLE-BOUND STATES: INTRAMOLECULAR ELECTRIC FIELD INDUCED ELECTRONIC CORRELATION, Daming Yuan, Yue-Ru Zhang, Lai-Sheng Wang

WA03 SINGLE-CONFORMATION SPECTROSCOPY AND DYNAMICS ON MULTIPLE POTENTIAL ENERGY SURFACES: FLEXIBLE NITROGEN-HETEROCYCLE CHROMOPHORES AND COMPLEXES IN AEROSOLS, Nathanael M. Kilbourn

WA04 DEVELOPMENT OF STRUCTURAL COMPLEXITY IN RARE AND HYDROGENATED CARBON CLUSTERS, Samuel Jack Palmer Martin, Jack T Runting, Chang Liu, Patrick Watkins, Evan Bierdz

WA05 POLYCYCLIC AROMATIC HYDROCARBON GROWTH IN A PLASMA REVEALED BY IR-UV ACTION SPECTROSCOPY, Alexander Karel Lemmero, Daniel Rap, Sandra Brinken, Wybren Jan Buma, Aneek Riji

Intermission

WA06 10:57 – 11:12
CONFORMATION-SPECIFIC INSIGHTS INTO THE CHEMICAL DYNAMICS OF NO-CH, MOLECULAR COMPLEXES, John Patrick Davenport, Nathanael M. Kilbourn

WA07 11:15 – 11:30
DFT INVESTIGATION ABOUT ELECTRONIC AND VIBRATIONAL PROPERTIES OF CHROMONE SCHIFF BASE LIGANDS WITH METAL COMPLEXES, SQM ANALYSIS, Berna Callakas

WA09 11:51 – 12:06
IR INDUCED ISOMERIZATION AND ITS BACKWARD REACTION OF COLD PHENOL-METHANOL CLUSTER CATIONS, Masayoshi Ozeki, Masataka Orito, Hikaru Sato, Kenta Mizuse, Hiduki Ishihara

Intermission

WA06 10:57 – 11:12
CONFORMATION-SPECIFIC INSIGHTS INTO THE CHEMICAL DYNAMICS OF NO-CH, MOLECULAR COMPLEXES, John Patrick Davenport, Nathanael M. Kilbourn

WB01 INVITED TALK 8:30 – 9:00
A NEW STANDARD OF AGREEMENT OF SEMI-EXPERIMENTAL EQUILIBRIUM (z, ε, χ) AND COMPUTED EQUILIBRIUM (z, ε) STRUCTURES, Brian J. Esselman

WB02 THE PREFERRED CONFORMATION AND NON-COVALENT INTERACTIONS OF THE METHYL ALLYL DISULFIDE-FORMALDEHYDE COMPLEX REVEALED BY ROTATIONAL SPECTROSCOPY, Zhen Wang, Yangbo Xu, Gang Feng

WB03 MILLIMETER/SUBMILLIMETER SPECTRUM AND PRECISE EQUILIBRIUM STRUCTURE OF 1H-1,2,4-TRIAZOLE, Hayley Bunn, Brian J. Esselman, Samuel M. Kougias, John F. Stanton, R. Claude Woods, Robert J. McMahon, Susanna L. Widicus Weaver

WB04 ON THE NATURE OF THE INTERACTION OF CO WITH PERFURINATED AROMATICS: NEW INSIGHTS FROM THE EXPERIMENTAL DATA AND THEORETICAL STUDY, Luca Evangelisti, Assimo Murti, Camilla Calabrese, Imanol Uzabaga, Weixing Li, Giovanni Bitonti, Sonia Melandri

WB05 10:00 – 10:15
ROTATIONAL SPECTROSCOPIC STUDY OF MICROSOLVATED CLUSTERS OF 1- AND 2-NITRONAPHTHALENE, Shefali Saxena, M. Eugenia Sanz

Intermission

WB06 10:57 – 11:12
SUB-PERMMILLE MEASUREMENTS AND CALCULATIONS OF 1D BAND CO LINE INTENSITIES, Zachary Bond, Katarzyna Bieska, Aleksandra A. Kyutbert, Gang Li, Ágiata Cypir, Roman Curylo, Daniel Lisak, Erin M. Adkins, Joseph Chang, Berna Callakas, John T. Hodges, Lorenzo Lodi, Nikolay F. Zobov, Volker Ebert, Jonathan Tennyson, Oleg L. Polyanovsky

WB07 11:15 – 11:30
QUANTUM CHEMICAL INVESTIGATION OF INTRAMOLECULAR HYDROGEN BONDS IN OXIDIZED AROMATIC MOLECULES: INFLUENCE OF RING SIZE, DONOR/ACCEPTOR GROUPS AND SUBSTITUENTS, Jonas Boukhoutian, Cecilia Gomez-Pech, Guillaume Dhost, Arnoud Causet, Malgorzata Olejniczak, Manuel Gobert, Valerie Vallet

WB08 11:33 – 11:48
INFRARED PREDISSOCIATION SPECTROSCOPY OF PROTONATED METHYL CYANIDE, Aravindh Nivas Marimuthu, Frank Huis in’t Veld, Sven Thorwirth, Britta Redlich, Sandra Brinken

WB09 11:51 – 12:06
AUTOMATED SEARCH ALGORITHMS FOR STRUCTURAL ISOMERISM: THE PROS AND CONS, Venkatesan S. Thimmakondu
WE. Coblentz Special Session

Wednesday, June 22, 2022 – 8:30 AM
Room: 1024 Chemistry Annex
Chair: Zachary Schultz, The Ohio State University, Columbus, OH, USA

WE01 UNDERSTANDING THE SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS) SIGNALS OF AMINO ACIDS, PEPTIDES, AND PROTEINS FOR BIOSENSING APPLICATIONS, Taylor Payne, Zachary Schultz

WE02 APTAMER BASED MICROPARTICLES IMMUNOASSAY METHOD FOR CA125 DETECTION USING RAMAN SPECTROSCOPY, Robinson Karamanithy, Terey E. Holland, P. Srikanth

WE03 CELL PHASE IDENTIFICATION IN A THREE-DIMENSIONAL TUMOR CELL CULTURE MODEL BY FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPIC IMAGING, Delain Blauk, Rohit Bhargava

WE04 LABEL-FREE AUTOFLUORESCENCE-DETECTED MID-IR PHOTOTHERMAL MICROSCOPY, Akshanto Ramanuj, Garth Simpson

WE05 A WIDE-FIELD IMAGING APPROACH FOR SIMULTANEOUS SUPER-RESOLUTION SURFACE-ENHANCED RAMAN SCATTERING IMAGING AND SPECTROSCOPY, Chen Sheng, Zachary Schultz

WE06 ISOLATING THE INTRINSIC SPECTRAL RESPONSES OF VIBRATIONAL PROBES: BENCHMARKS FOR REPORTERS OF CONDENSED PHASE AND BIOLOGICAL PROCESSES, Sean Coleman Edington, Ahmed Mohamed, Mark Johnson

Intermission

WE07 HIGH-THROUGHPUT MICROFLUIDIC MONITORING IN MICROFLUIDICS BY RAPID COHERENT RAMAN SCATTERING SPECTROSCOPY, Minjuan Lu, Yujia Zhang, Yan Li, Haoyun Wei

WE08 UNDERSTANDING POLARIZATION EFFECTS ON ABSORPTION SPECTRA MEASURED USING A QUANTUM CASCADE LASER-BASED SPECTROMETER, Ru-Jing Hu, Yamuna Dilip Phal, Rohit Bhargava

WE09 DETECTION OF MEDICAL INHALER USE VIA TERAHERTZ SPECTROSCOPY, Daniel J. Tyree

WE10 A PHOTONIC GAS SENSOR FOR THE MID-INFRARED, Travis A. Guzman, Nasser Moazzen-Ahmadi, A. J. Barclay

WE11 THE IMPACT OF PLASMONICALLY GENERATED HOT-CARRIERS ON SERS ANALYSIS, Chelsea M. Zoltowski, Zachary Schultz
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<th>Session</th>
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<th>Time</th>
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<tr>
<td>WG01</td>
<td>OPTICAL SPECTRUM OF Si₂⁺</td>
<td>8:30 – 8:45</td>
<td>Emil Miekie, Taarna Studemund, Kai Pollow, Sophie Verhoeven, Marko Förstel, Otto Dopfer</td>
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<tr>
<td>WG02</td>
<td>INTERESTING BEHAVIOR OF THE Si₃O₂⁺ SILICON OXIDE CLUSTER CATION</td>
<td>8:48 – 9:03</td>
<td>Kai Pollow, Taarna Studemund, Emil Miekie, Marko Förstel, Otto Dopfer</td>
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<tr>
<td>WG03</td>
<td>ON THE SPECTROSCOPY OF ACYLUM IONS: INFRARED ACTION SPECTROSCOPIC DETECTION OF NCO⁻</td>
<td>9:06 – 9:21</td>
<td>Oskar Asvany, Marcel Bast, Stephan Schlemmer, Sven Thorwirth</td>
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<tr>
<td>WG04</td>
<td>HIGH-RESOLUTION SPECTROSCOPY OF MgKr⁺ IN ITS GROUND AND LOW-LYING ELECTRONICALLY EXCITED STATES</td>
<td>9:24 – 9:39</td>
<td>Carla Krei, Matthieu Génévisse, Frédéric Merkt</td>
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<tr>
<td>WG05</td>
<td>RO-VIBRATIONAL SPECTROSCOPY OF LINEAR C₃H⁺</td>
<td>9:42 – 9:57</td>
<td>Philipp C Schmid, Thomas Salomon, Oskar Asvany, Stephan Schlemmer</td>
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<tr>
<td>WG06</td>
<td>GAS-PHASE CHARGE TRANSFER ELECTRONIC SPECTROSCOPY OF Ag⁺-BENZENE COMPLEX</td>
<td>10:00 – 10:15</td>
<td>Dylan S. Orr, Jason E. Colley, Michael A Duncan</td>
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<tr>
<td>Intermission</td>
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<tr>
<td>WG07</td>
<td>HIGH-RESOLUTION INFRARED SPECTRA OF THE OH-STRETCHING BANDS OF PROTONATED WATER DIMER, H₂O₂⁺</td>
<td>10:57 – 11:12</td>
<td>Thomas Salomon, Oskar Asvany, Charles R. Markus, Stephan Schlemmer</td>
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<tr>
<td>WG08</td>
<td>PROBING THE DEGREE OF NITROGEN ACTIVATION BY TRIDENTATE COPPER(I) COMPLEXES USING CIVP SPECTROSCOPY</td>
<td>11:15 – 11:30</td>
<td>Alexandru Tityuba, Vladimir Gorbachev, Peter Chen</td>
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<tr>
<td>WG10</td>
<td>CARBOXYLATE STRETCHING MODES ARE STRUCTURAL PROBES FOR ION-DEPENDENT BINDING PROPERTIES IN ALKALI EARTH METAL-EDTA COMPLEXES</td>
<td>11:51 – 12:06</td>
<td>Madison M. Foreman, J. Mathias Weber</td>
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<tr>
<td>Post-Deadline Abstract</td>
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<td>WG11</td>
<td>FIRST LABORATORY DETECTION OF N⁵⁺COCO⁻ AND SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURE OF THE NCO⁻ ANION</td>
<td>12:09 – 12:24</td>
<td>Luca Dore, Luca Bizzocchi, Valerio Lattanzi, Matia Melossi, Filippo Tamassia, Michael C McCarthy</td>
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**WLUN. Plenary Panel Discussion**

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<tr>
<td>WLUN01</td>
<td>A PERSONAL VIEW OF THE ISMS</td>
<td>12:35 – 1:30</td>
<td>Terry A. Miller, NRAO, Charlottesville, VA, USA</td>
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<tr>
<td>WLUN02</td>
<td>THANK YOU ISMS!</td>
<td>12:35 – 1:30</td>
<td>Takeshi Oka</td>
</tr>
<tr>
<td>WLUN03</td>
<td>MY ISMS</td>
<td>12:35 – 1:30</td>
<td>Yasuki Endo</td>
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WH. Mini-symposium: Spectroscopy meets Chemical Dynamics  
Wednesday, June 22, 2022 – 1:45 PM  
Room: 100 Noyes Laboratory

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

W1H01 1:45–2:00  
PHOTODISSOCIATION AND VELOCITY-MAP IMAGING OF CARBON CLUSTER CATIONS, Nathan John Dynak, Brandon M. Rittgers, Jason E. Colley, Douglas J. Kellar, Michael A Duncan

W1H02 2:03–2:18  
PHOTODISSOCIATION DYNAMICS OF CH$_2$OO ON MULTIPLE POTENTIAL ENERGY SURFACES: EXPERIMENT AND THEORY, Vincent J. Esposito, Tianlin Liu, Guanghan Wang, Adriana Caracciolo, Michael F. Vansco, Ernest Antivi, Olivia Werba, Sarah A. Bush, Rachel E. Bush, Barbara Marchetti, Tolga N. V. Karsili, Marsha Lester

W1H03 2:21–2:36  
OZONE PHOTODISSOCIATION IN THE SINGLET CHANNEL AT 226 NM, Megan Aardema, George McBane, Simon North

W1H04 2:39–2:54  
RAPID ALLYLIC H-ATOM TRANSFER IN A CRIEGEE INTERMEDIATE WITH UNSATURATED SUBSTUENTHS, Anne S Hansen, Yujie Qian, Stephen J. Klippenstein, Marsha Lester

W1H05 3:27–3:32  
THE VIBRATIONAL PREDISSOCIATION OF THE $\tilde{A}$ STATE OF THE C$_3$Ar VAN DER WAALS COMPLEX WITH VIBRATIONAL ENERGIES OF 1558–1660 cm$^{-1}$, Sheng-Chang Hsiao, Yen-Chu Hsu

W1H06 3:45–3:50  
THE VIBRATIONAL PREDISSOCIATION AND INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION OF THE $\tilde{A}$ STATE OF THE C$_3$Ar VAN DER WAALS COMPLEX, Sheng-Chang Hsiao, Yen-Chu Hsu

Intermission

W1H07 4:12–4:27  
DETECTION OF NASCENT PRODUCTS FROM THE PHOTOLYSIS OF ACRYLONITRILE VIA TIME-RESOLVED MILLIMETER WAVE SPECTROSCOPY, Nathan A. Seifert, Kirill Prozument

W1H08 4:30–4:45  
EXOMOL: RECENT PROGRESS ON PHOTODISSOCIATION OF SMALL MOLECULES, Marco Pettorino, Jonathan Tennyson, Sergei N. Yurchenko

W1H09 4:48–5:03  
CO FORMATION FROM ACETONE PHOTOLYSIS: THE ROAMING PATHWAY, Lorrie S. D. Jacob, Kelvin Lee, Timothy Schmidt, Kuan Nauta, Scott Kable

W1H10 5:06–5:21  
SPECTROSCOPY AND PREDISSOCIATION DYNAMICS OF SH RADICALS VIA THE A$^2\Sigma^+$ STATE, Yuan Qiu, Xianfeng Zheng, Yu Song, Ge Sun, Jingsong Zhang

W1H11 5:24–5:39  
VELOCITY MAP IMAGING OF GOLD ION - LIGAND COMPLEXES, Brandon M. Rittgers, Michael A Duncan

W1H01 4:45–2:00  
NON-ADIABATIC COUPLING IN NO@C$_60$: PREDICTION OF A BENNER-TELLER LIKE EFFECT FOR SPHERICALLY ENCAPSULATED DIATOMIC MOLECULES, Andreas W. Hauser, Johann V. Pototschnig

W1H02 2:03–2:18  
USING HIGH-RESOLUTION PHOTOELECTRON IMAGING TO PROBE THE SPECTROSCOPY OF CRYOGENICALLY COOLED AZOLIDE MOLECULES, Yue-Rou Zhang, Daofu Yuan, Lai-Sheng Wang

W1H03 2:21–2:36  
CAN LONDON DISPERSION OVERRIDE CATION-π INTERACTIONS?, Vladimir Gorbachev, Alexandra Tsybizova, Larisa Mikityukova, Peter Chen

W1H04 2:39–2:54  
ELECTRONIC SPECTROSCOPY OF THE PREVIOUSLY UNKNOWN PALLADIUM MONOSULFIDE (PdS) RADICAL, Lei Zhang, Yao Yu, Xinwen Ma, Ju Yang

W1H05 2:57–3:12  
NEW METHODS FOR CORE-HOLE SPECTROSCOPY BASED ON COUPLED CLUSTER, Megan Simons, Devin A. Matthews

W1H06 3:15–3:30  
GENERALIZED OSCILLATOR STRENGTH OF THE INNER SHELL EXCITATION OF NITROGEN STUDIED BY NONRESONANT INELASTIC X-RAY SCATTERING, Lilian Wang

Intermission

W1H07 4:12–4:27  
FESCHBACH RESONANCE IN TETRACENE RADICAL ANION: THE SECRET TO A LONG LIFETIME OF NEGATIVITY, Cole R. Sagan, Etienne Garand

W1H08 4:30–4:45  
FLUORESCENCE-DETECTED MID-INFRARED PHOTOTHERMAL MICROSCOPY, Minghe Li, Aleksandr Razumtcev, Garth Simpson

W1H09 4:48–5:03  
THE COUPLED-CHANNEL DEPERTURBATION ANALYSIS OF THE A$^2\Delta$–X STATES MANIFOLD OF CN WITH ALMOST SPECTROSCOPIC ACCURACY, Vera Tretiakhkina, Elena Aleksandrovna Pavlyuk, Andrei Stolyarov

W1H10 5:06–5:21  
CAVITY RING-DOWN SPECTROSCOPY OF WATER VAPOR IN THE NEAR-UV REGION, Q.-Y. Yang, Y. Tan, Shuming Hu, Eamon K Conway, Iouli E Gordon

W1H11 5:24–5:39  
IN SITU SPECTROSCOPIC DIAGNOSTIC OF SHOCK INDUCED DECOMPOSITION OF C$_6$I$_2$, Shubhadip Chakraborty, Sergei N. Yurchenko, Robert Georges, Vijayanand Chandrasekaran, V Jayaram, Elangannan Arunan, Ludovic Biennier
WJ. Instrument/Technique Demonstration
Wednesday, June 22, 2022 – 1:45 PM
Room: B102 Chemical and Life Sciences
Chair: Deacon J Nemchick, Jet Propulsion Laboratory, Pasadena, CA, USA

WJ01 1:45 – 2:00
INFRARED HIGH RESOLUTION COHERENT 2D SPECTROSCOPY, DeAunna A Daniels, Thresa Wells, Peter Chen

WJ02 2:03 – 2:18
A NEW FEMTOSECOND XVU SOURCE AT THE UNIVERSITY OF WISCONSIN, Ryan T Ash, Zain Abhari, Uwe Bergmann

WJ03 2:21 – 2:36
DEVELOPMENT OF A CRYOGENIC, MASS SELECTIVE, MULTI-REACTION TRAP ION SPECTROMETER, Gina Roesch, Etienne Garand

WJ04 2:39 – 2:54
DEMONSTRATION OF CRESU-REMPI FOR REACTION KINETIC MEASUREMENTS IN THE GAS-PHASE, Ranil Gurusinghe, Naresuan Dus, Jinxin Lang, Matthew L Edlin, Arthur Suits

WJ05 2:57 – 3:12
TOWARDS THE RESOLUTION LIMIT OF PFI-ZEKE PHOTOELECTRON SPECTROSCOPY, Holger Herburger, Vincent Wirth, Us Holleisstein, Frederic Merkt

Intermission

WJ06 3:54 – 4:09
MID-INFRARED CW OPTICAL PARAMETRIC OSCILLATOR PUMPED BY AN ELECTRO-OPTIC FREQUENCY COMB, Matthew J. Cich, Adam Heinsiger, David B. Poole, Walter Hurlbut, Chris Haimberger, David A. Long

WJ07 4:12 – 4:27
CAVITY RING-DOWN SPECTROSCOPY WITH INTERBAND CASCADE OPTICAL FREQUENCY COMBS, TsuLing Chen, Charles R. Matthias, Douglas Oster, Lukasz A. Stenczewski, Chadwick L Cady, Igor Vurgaftman, Clifford Frez, Jerry R Meyer, Mahmood Bagheri, Michio Okumura

WJ08 4:30 – 4:45
MID-INFRARED SPECTROSCOPY OF TRANSIENT SPECIES USING A CHIP-SCALE MID-INFRARED OPTICAL FREQUENCY COMB, Charles R. Matthias, TsuLing Chen, Douglas Oster, Lukasz A. Stenczewski, Chadwick L Cady, Igor Vurgaftman, Clifford Frez, Jerry R Meyer, Mahmood Bagheri, Michio Okumura

WJ09 4:48 – 5:03
HIGH-SPEED, HIGH-RESOLUTION, BROADBAND DUAL-COMB SPECTROMETER FROM 3-5 μm, Scott C Egbert, Peter Chang, Scott Diddams, Gregory B Rieker, Nazanin Hoghooghi

WJ10 5:06 – 5:21
RAPID DUAL-COMB COHERENT RAMAN SPECTROSCOPY IN THE HIGH-WAVENUMBER REGION, Yujie Zhang, Minjuan Lu, Yan Li, Haoyun Wei

WJ11 5:24 – 5:39
ABSOLUTE FREQUENCY SCALE FOR HIGH-RESOLUTION QUANTUM CASCADE LASER DUAL-COMB SPEC- TROMETER, Michele Gianella, Kenishi Komagata, Simon Vogel, Irène Faist, Thomas Südmeyer, Lukas Emmenegger

WK. Mini-symposium: Machine Learning
Wednesday, June 22, 2022 – 1:45 PM
Room: 217 Noyes Laboratory
Chair: Daniel R. Nascimento, The University of Memphis, Memphis, TN, USA

WK01 INVITED TALE 1:45 – 2:15
INTERPRETABLE DEEP LEARNING FOR MOLECULES AND MATERIALS, Andrew White

WK02 2:18 – 2:33
SUPERVISED LEARNING FOR SELECTIVE MULTI-SPECIES QUANTIFICATION FROM NOISY INFRARED SPECTROSCOPY DATA, Imad Al Ibraheem, Aamir Farooq

WK03 2:36 – 2:51
COMPUTATIONAL OPTIMAL TRANSPORT FOR MOLECULAR SPECTRA, Nathan A. Seifert, Kerri Proszmann, Michael J. Davis

Intermission

WK04 3:33 – 3:48
INVERSE INFRARED SPECTROSCOPY WITH BAYESIAN METHODS, Jezrielle R. Annis, Daniel P. Tabor

WK05 3:51 – 4:06
SEQUENCE-TO-SEQUENCE LEARNING FOR MOLECULAR STRUCTURE DERIV ATION FROM INFRARED SPECTRA, Ethan French, Zhou Lin

WK06 4:09 – 4:24
GAS-PHASE INFRARED SPECTRA ANALYSIS VIA DEEP NEURAL NETWORKS, Abigail A Enders, Nicole North, Heather C. Allen

WK07 4:27 – 4:42
COMPARISON OF EXPERIMENTAL AND SIMULATED RAMAN SPECTRA THROUGH REVERSE SELF MODEL-ING CURVE RESOLUTION FOR REGRESSION-BASED MACHINE LEARNING, Nicole North, Abigail A Enders, Heather C. Allen
WL. Conformers and isomers
Wednesday, June 22, 2022 – 1:45 PM
Room: 1024 Chemistry Annex
Chair: Isabelle Kleiner, CNRS, UPEC et Université de Paris, Créteil, France

WL01 FOURIER TRANSFORM MICROWAVE SPECTRA OF 1-PENTANETHIOL- α-Nobuhiko Kaze, Yoshiyuki Kawaiishi
1:45–2:00

WL02 MICROWAVE SPECTRUM OF ACETIC DIFLUORACETIC ANHYDRIDE, Kaitlyn Belmont, Nathan Love, Kenneth R. Leopold
2:03–2:18

WL03 FLUORINATION AND DEOXYGENATION AS CHEMICAL TOOLS TO STUDY THE CONFORMATIONAL PREFERENCES OF HEXOPYRANONES: A JOURNEY FROM GAS PHASE TO SOLUTION, Elena R. Alonso, Aran Insuasty, Camilla Calabrese, Francisco J. Basterretxea, Francisco Corzana, Omar Boutevrel, Emilio J. Coconero
2:21–2:36

WL04 UNVEILING THE EIGHT FORMS OF CAFFEIC ACID, Gabriela Juárez, Miguel Sanz-Navo, Elena R. Alonso, Iker León, Santiago Mata, José L. Alonso
2:39–2:54

WL05 THE MICROWAVE SPECTRUM OF FIFERONAL: DESIGNING AND TESTING A NEW HEATED NOZZLE ASSEMBLY, Brayden Carby, Galen Sedo
2:57–3:12

WL06 THE JET-COOLED ROTATIONAL SPECTRUM OF N,N'-BIS(HYDROXYMETHYL)UREA AND ITS PHOTO- BLY, Brayden Carty, Galen Sedo
3:15–3:30

Intermission

WL07 ROTAMERS OF METHANEDIOL: COMPOSITE AB INITIO PREDICTIONS OF FUNDAMENTAL FREQUENCIES AND ROTATIONAL CONSTANTS, Peter R. Franke, John F. Stanton
4:12–4:27

WL08 CONFORMATIONAL DIVERSITY OF NON-AROMATIC HETEROCYCLIC MOLECULAR COMPOUNDS AS STUDIED BY MEANS OF MATRIX ISOLATION INFRARED SPECTROSCOPY, Joanna Stöck, Reza Piatykhtey, Justinas Čepukas, Jolie MacIntyre, Daniel Vincent Hickman, Theodore Jacob Carrigan-Broda, Pawel Rodziewicz, Gamil A. Guirgis, Mohammad Ali Jafari, Wolfgang Jäger
4:30–4:45

WL09 STRUCTURAL ELUCIDATION OF IONS USING CHEMICAL REACTIONS, Ugo Jacovella, Corentin Rossi, Claire Romanzin, Christian Alcaraz, Roland Thissen
4:48–5:03

WL10 VISUALIZING ELECTRON DYNAMICS FOR A PHOTOSOMERIZATION REACTION, Lauren Baudel, Agnieszka Jaron
5:06–5:21

5:24–5:39
WN. Astronomy
Wednesday, June 22, 2022 – 1:45 PM
Room: 274 Medical Sciences Building
Chair: Brett A. McGuire, Massachusetts Institute of Technology, Cambridge, MA, USA

W101
1:45 – 2:00
SUBMILLIMETER WAVE STUDY OF NITROSOMETHANE (CH3NO).
L. Margulis, Layao Zou, R. A. Motiyenko, J.-C.
Guillemín

W102
2:03 – 2:18
MILLIMETER AND SUB-MILLIMETER SPECTROSCOPY OF DOUBLY DEUTERATED ACETALDEHYDE
(CD3HCHO), Judit Feser-Agenito, Silvia Spazzano, Christian Endres, Valerio Lattanzi, L. H. Cordt, Paula Caselli

W103
2:21 – 2:36
THE ROTATION-TUNNELING SPECTRUM OF DIMETHYLAMINE, (CH3)2NH. Holger S. P. Müller, Frank Lewin, Stephan Schlemmer

W104
2:39 – 2:54
RE-INVESTIGATION OF THE CYANOACETALDEHYDE (NCCH2CHO) ROTATIONAL SPECTRUM.
L. Margulis, Layao Zou, R. A. Motiyenko, J.-C. Guillemín

W105
2:57 – 3:12
ROTATIONAL STATES. V. Ilyushin, R. Poroshovoi, E. A. Alekseev, Olga Dorovskaya, Holger S. P. Müller, Frank Lewin, Stephan Schlemmer, Christof Mau, Ronald M. Lees

W106
3:15 – 3:30
LABORATORY MEASUREMENT OF MILLIMETER-WAVE TRANSITIONS OF 13CH3OH FOR ASTRONOMICAL
USE. Takahiro Oyama, Yuki Ohno, Akemi Tamanai, Shaosheng Zhan, Yoshimasa Watanabe, Riouhei Nakatani, Nami Takah, T. Takeda

Intermission

W107
3:42 – 3:57
MILLIMETER-WAVE SPECTRA OF 2-PROPANIMINE AND ITS SEARCH IN THE INTERSTELLAR MEDIUM.
L. Margulis, R. A. Motiyenko, J.-C. Guillemín, Amaud Belloche, Jes Jørgensen

W108
4:00 – 4:15
MILLIMETER AND SUB-MILLIMETER SPECTROSCOPY OF ISOBUTENE. Maryam Fatima, Oliver Zingsheim, Holger S. P. Müller, Dirk Hoppens, Stephan Schlemmer

W109
4:18 – 4:33
EXTENSION OF THE MILLIMETER AND SUBMILLIMETER SPECTRUM OF GLYCOLIC ACID: ROTATIONAL
SPECTROSCOPIC STUDY OF A POTENTIAL PREBIOTIC INTERSTELLAR MOLECULE. Chase P. Schulte, Hayley Bunn, Susanna L. Widicus Weaver

W110
4:36 – 4:51

W111
4:54 – 5:09

WN. Astronomy
Thursday, June 23, 2022 – 1:35 PM
Room: 274 Medical Sciences Building
Chair: Robin T. Garrod, Pilar Redondo, Carmen Barrientos, Juan Carlos
Valle, Lucie Kolesnikov´a, Holger S. P. M¨uller

W112
1:45 – 2:00
RE-INVESTIGATION OF THE CYANOACETALDEHYDE (NCCH2CHO) ROTATIONAL SPECTRUM.
L. Margulis, Layao Zou, R. A. Motiyenko, J.-C. Guillemín

W113
2:03 – 2:18
MILLIMETER AND SUB-MILLIMETER SPECTROSCOPY OF DOUBLY DEUTERATED ACETALDEHYDE
(CD3HCHO), Judit Feser-Agenito, Silvia Spazzano, Christian Endres, Valerio Lattanzi, L. H. Cordt, Paula Caselli

W114
2:21 – 2:36
THE ROTATION-TUNNELING SPECTRUM OF DIMETHYLAMINE, (CH3)2NH. Holger S. P. Müller, Frank Lewin, Stephan Schlemmer

W115
2:39 – 2:54
RE-INVESTIGATION OF THE CYANOACETALDEHYDE (NCCH2CHO) ROTATIONAL SPECTRUM.
L. Margulis, Layao Zou, R. A. Motiyenko, J.-C. Guillemín

W116
2:57 – 3:12
ROTATIONAL STATES. V. Ilyushin, R. Poroshovoi, E. A. Alekseev, Olga Dorovskaya, Holger S. P. Müller, Frank Lewin, Stephan Schlemmer, Christof Mau, Ronald M. Lees

W117
3:15 – 3:30
LABORATORY MEASUREMENT OF MILLIMETER-WAVE TRANSITIONS OF 13CH3OH FOR ASTRONOMICAL
USE. Takahiro Oyama, Yuki Ohno, Akemi Tamanai, Shaosheng Zhan, Yoshimasa Watanabe, Riouhei Nakatani, Nami Takah, T. Takeda

Intermission

W118
3:42 – 3:57
MILLIMETER-WAVE SPECTRA OF 2-PROPANIMINE AND ITS SEARCH IN THE INTERSTELLAR MEDIUM.
L. Margulis, R. A. Motiyenko, J.-C. Guillemín, Amaud Belloche, Jes Jørgensen

W119
4:00 – 4:15
MILLIMETER AND SUB-MILLIMETER SPECTROSCOPY OF ISOBUTENE. Maryam Fatima, Oliver Zingsheim, Holger S. P. Müller, Dirk Hoppens, Stephan Schlemmer

W120
4:18 – 4:33
EXTENSION OF THE MILLIMETER AND SUBMILLIMETER SPECTRUM OF GLYCOLIC ACID: ROTATIONAL
SPECTROSCOPIC STUDY OF A POTENTIAL PREBIOTIC INTERSTELLAR MOLECULE. Chase P. Schulte, Hayley Bunn, Susanna L. Widicus Weaver

W121
4:36 – 4:51

W122
4:54 – 5:09

WN. Astronomy
Thursday, June 23, 2022 – 8:30 AM
Room: Foellinger Auditorium
Chair: Anne B McCoy, University of Washington, Seattle, WA, USA

RA01
8:30 – 8:55
SPECTROSCOPY OF METAL AND PHOSPHORUS BEARING MOLECULES: A WINDOW ON THE UNIVERSE.
Lori T. Zurbas

RA02
8:55 – 9:05
THEORETICAL DESCRIPTIONS OF THE FUNDAMENTALS OF CH, NH, AND OH STRETCH VIBRATIONS WITH SIMPLE MODELS THAT INCLUDE ANHARMONIC EFFECTS. Edgar Shotten

Intermission

RA03
9:10 – 9:25
ADVANCING DYNAMIC METHODS FOR COMPUTATIONAL SPECTROSCOPY IN THE GAS AND CONDENSED PHASE. Sandra Luber

RA04
11:20 – 12:00
ADVANCING DYNAMIC METHODS FOR COMPUTATIONAL SPECTROSCOPY IN THE GAS AND CONDENSED PHASE. Sandra Luber
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<td>RH01</td>
<td>A DFT STUDY: SPECTROSCOPIC ANALYSIS OF SCHIFF-BASE LIGAND WITH FEIIJ COMPLEX</td>
<td>Berna Calikkan</td>
<td>1:45 – 2:00</td>
<td>100 Noyes Laboratory</td>
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<td>RH02</td>
<td>HIGH-RESOLUTION LASER SPECTROSCOPIC STUDIES OF UBOCANIC ACID AND DERIVATIVES: TOWARDS NOVEL, NATURE-INSPIRED SUNSCREENS</td>
<td>Sayun Fan, Laura Finazzi, Alexander Karel Lemmens, Wybren Jan Buma</td>
<td>2:03 – 2:18</td>
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<td>RH03</td>
<td>HIGH-RESOLUTION LASER SPECTROSCOPIC STUDIES OF CINNAMATE-BASED MOLECULAR HEATERS</td>
<td>I. Romanows, Y. Boeije, Wybren Jan Buma, Josene Maria Toldo, Mariana Telles do Casal, Matteo Barbatti</td>
<td>2:21 – 2:36</td>
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<td>RH04</td>
<td>HYPERFINE EXCITATION OF HC(17)O WITH p-H(3) COLLISIONS</td>
<td>Francesca Tonolo, Luca Bizzocchi, François Lique, Mattia Melioso, Vincenzo Barone, Cristina Puzzarini</td>
<td>2:39 – 2:54</td>
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<td>RH05</td>
<td>EXTENDED PRECISION OF CAF ELECTRONIC STATES: ENERGIES, MULTIPLE MOMENTS, AND A SHAPE RESONANCE STATE</td>
<td>Stephen L. Coy, Timothy J Bamum, Robert W Field, John F. Stanton</td>
<td>2:57 – 3:12</td>
<td>100 Noyes Laboratory</td>
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<td>RH06</td>
<td>STATE-RESOLVED MODELING FOR THE ENERGY-LASER-INDUCED FLUORESCENCE OF DIATOMIC MOLECULES</td>
<td>Shengkai Wang</td>
<td>3:54 – 4:09</td>
<td>100 Noyes Laboratory</td>
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<td>RH08</td>
<td>HITTING THE TRIFECTA: HOW TO SIMULTANEOUSLY PUSH THE LIMITS OF SCHRODINGER SOLUTION WITH RESPECT TO SYSTEM SIZE, CONVERGENCE ACCURACY, AND NUMBER OF COMPUTED STATES</td>
<td>János Sarka, Bill Porter</td>
<td>4:30 – 4:45</td>
<td>100 Noyes Laboratory</td>
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<td>RH09</td>
<td>ANALOG QUANTUM SIMULATION OF MOLECULAR DYNAMICS AND SPECTROSCOPIC OBSERVABLES</td>
<td>Ryan J. MacDonell, Ivan Kassal</td>
<td>4:48 – 5:03</td>
<td>100 Noyes Laboratory</td>
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<td>RH10</td>
<td>MEASUREMENTS OF HIGH-TEMPERATURE ABSORPTION SPECTRA OF DIMETHYL ETHER AND DIETHYL ETHER BETWEEN 950 AND 1190 cm(^{-1}) AND THEIR DIRECT PYROLYSIS STUDY IN A SHOCK TUBE</td>
<td>Mohammad Adil, Binod Giri, Aamir Farooq</td>
<td>5:06 – 5:21</td>
<td>100 Noyes Laboratory</td>
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**Intermission**

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<td>RI01</td>
<td>INVITED TALK: THE HYDRA BLIND CHALLENGE: INVITING THEORY TO PREDICT UNKNOWN VIBRATIONAL SPECTROSCOPY DATA</td>
<td>Taija L. Fischer, Maragrete Bodecker, Sophie M. Schweer, Anne Zehmacker-Rentien, Ricardo A Mata, Martin A. Suhm</td>
<td>1:45 – 2:15</td>
<td>116 Roger Adams Lab</td>
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<td>RI02</td>
<td>NEW JET-COOLED VIBRATIONAL SPECTROSCOPIC BENCHMARK DATA OF THE CYCLIC DIMER AND TRIMER OF FORMIC ACID</td>
<td>Arman Nejad, Katharina A. E. Meyen, Martin A. Suhm</td>
<td>2:21 – 2:36</td>
<td>116 Roger Adams Lab</td>
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<td>RI03</td>
<td>A VIBRATIONAL ACTION SPECTROSCOPIC STUDY OF THE RENNER-TELLER AND SPIN-ORBIT AFFECTED CYANOACETYLENE RADICAL CATION HC(=)N(^+) ((\Pi_1))</td>
<td>Kim Steenbakkers, Aravind Nivas Marimuthu, Gerrit Groenenboom, Brita Redlich, Sandra Brunken</td>
<td>2:39 – 2:54</td>
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<td>RI04</td>
<td>MOLECULAR CHEMISTRY RECOMMENDATIONS FOR HARMONIC FREQUENCY CALCULATIONS: A BENCHMARK STUDY</td>
<td>Juan C. Zapata Trujillo, Laura K. McKemmish</td>
<td>2:57 – 3:12</td>
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<td>RI05</td>
<td>NON-LTE INFRARED SPECTRUM OF JET-COOLED NAPHTHALENE</td>
<td>Shabbdip Chakraborty, Giacomo Mulas, Olivier Pirali, Pascale Soulard, Pierre Asselin, Manuel Good, Ludovic Binnemans, Robert Georges</td>
<td>3:15 – 3:30</td>
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<td>RI06</td>
<td>PROBING HALOGEN BONDING INTERACTIONS BETWEEN HEPTAFLUORO-2-IODOPROPAINE AND THREE AZABENZENES WITH RAMAN SPECTROSCOPY AND DENSITY FUNCTIONAL THEORY</td>
<td>Ethan Chase Lambert, Ashley E. Williams, Ryan C. Fortenberry, Nathan I Hammer</td>
<td>4:12 – 4:27</td>
<td>116 Roger Adams Lab</td>
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<td>RI07</td>
<td>VIBRATIONAL CHARACTERIZATION OF HEXA-BONDED HALIDE-THIOCYANATE DIMER RADICAL ANIONS (XSCN) – IN WATER</td>
<td>Ireneusz Janik, Susmita Bhattacharya</td>
<td>4:30 – 4:45</td>
<td>116 Roger Adams Lab</td>
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<td>RI08</td>
<td>THE HIGHER TORSIONAL STATES OF METHYLAMINE - PRELIMINARY ANALYSIS</td>
<td>Marek Krelewski, Justin E. Williams, Ryan C. Fortenberry, Nathan I. Hammer</td>
<td>4:48 – 5:03</td>
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<td>RI09</td>
<td>COMPLETION OF THE FIRST SOLVATION SHELL OF CARBON DIOXIDE IN ARGON, ROTATIONALLY RESOLVED INFRARED SPECTRA OF CO(2)-AR(_3) AND CO(2)-AR(_4), A. J. Baccay, A.R.W. McKellar, Nasir Mouazen-Abmad</td>
<td>5:06 – 5:21</td>
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<td>RI10</td>
<td>HIGH RESOLUTION INFRARED SPECTROSCOPY OF DIHORANE DISPERSED IN SOLID PARAHYDROGEN</td>
<td>Aaron I. Strom, Ibrahim Muddasser, David T. Anderson</td>
<td>5:24 – 5:39</td>
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<td>RI11</td>
<td>TRIHYBRID LINE LIST CONSTRUCTION FOR NH AND ZE0</td>
<td>Armando N. Perri, Laura K. McKemmish</td>
<td>5:42 – 5:57</td>
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**RJ. Instrument/Technique Demonstration**

**Thursday, June 23, 2022 – 1:45 PM**

**Room: B102 Chemical and Life Sciences**

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

**RJ01 1:45 – 2:00**

PROGRESS ON SHOCKGAS-IR: MEASUREMENTS OF METHYL FORMATE AT ELEVATED TEMPERATURES, Wey Wey Su, Yiming Ding, Christopher L Strand, Ronald K Hanson

**RJ02 2:03 – 2:18**

CO2 COLLISIONAL BROADENING OF THE 557 GHz WATER ABSORPTION FEATURE PROFILED WITH A DIFFERENTIAL ABSORPTION RADAR PLATFORM, Ken Cooper, Deacon J Nemchick, Omkar Pradhan, Robert Dengler, Raquel Rodgers Monte, Brian Drouin, Jose Silis, Leslie Tamppari

**RJ03 2:21 – 2:36**

ROOM-TEMPERATURE QUANTIFICATION OF $^{14}$CO$_2$ BELOW THE NATURAL ABUNDANCE WITH TWO-COLOR, CAVITY RINGDOWN SPECTROSCOPY, Jun Jiang, A. Daniel McCartt

**RJ04 2:39 – 2:54**

SELECTIVE PRODUCTION OF HCN MONOMER AND EVIDENCE FOR GAS-PHASE DIMERIZATION, Thomas Howard, Emily K Hockey, Darya Kisuryna, Jessica Palko, Leah G Dodson

**RJ05 2:57 – 3:12**

INSTRUMENT DESIGN AND PREPARATION OF PARA-HYDROGEN FOR MATRIX EXPERIMENTS, Korina Vlahos, Emily K Hockey, Leah G Dodson

**RJ06 3:15 – 3:30**

W BAND CHIRPED-PULSE: THE BEAUTY OF COHERENT SPECTROSCOPY, Bettina Heyne, Marius Herrmann, Nadin Wehres, Stephan Schlemmer

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**RK. Metal containing**

**Thursday, June 23, 2022 – 1:45 PM**

**Room: 217 Noyes Laboratory**

**Chair: Michael Heaven, Emory University, Atlanta, GA, USA**

**RK01 1:45 – 2:00**

SPECTROSCOPIC CHARACTERIZATION OF REACTIVE INTERMEDIATES IN VARIOUS METAL CATALYSTS, Kathleen Ann Nickson, Etienne Gruber

**RK02 2:03 – 2:18**

THE PURE ROTATIONAL SPECTRUM OF MgCl IN THE (2)$^2$I, EXCITED STATE, Tyler J Herman, Parker Crowther, Lucy M. Zaurys

**RK03 2:21 – 2:36**

METAL IDENTITY AND PRODUCT BINDING TUNE STRUCTURE AND CHARGE DISTRIBUTION: INFRARED SPECTRA OF CATALYTICALLY RELEVANT METAL BIPYRIDINE COMPLEXES, Madison M. Foreman, J. Gary Eden

**RK04 2:39 – 2:54**

OBSERVATIONS OF THE ZEEMAN/PASCHEN-BACK EFFECT IN THE A-X SYSTEM OF COH, Patrick Corzelt, Stéphane Mouville, Amanda J. Rose, Julien Morin

**RK05 2:57 – 3:12**

DEVELOPMENT OF A MM-WAVE ULTRA-SENSITIVE SPECTROMETER FOR THE DETECTION OF SEMI-VOLATILE ORGANIC VAPORS, Mhamad Chrayteh, Fabien Simon, Coralie Elmaleh, Francis Hindle, Gaël Mouret, Arnaud Cuisset

**RK06 3:15 – 3:30**


**RK07 3:54 – 4:09**

LOW- AND HIGH-RESOLUTION LASER-INDUCED FLUORESCENCE (LIF) OF JET-COOLED SmO, Joel R Schmitz, Arianna Rodriguez, Timothy Neimle, Michael Heaven

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**RJ01 4:12 – 4:27**

LLWP UPDATE – A NEW LOOMIS-WOOD SOFTWARE AT THE EXAMPLE OF ACETONE,$^{13}$C, Jian Ran, Oliver Zsingeim, Holger S. P. Muller, Sven Thowrth, J.-C. Guillemin, Frank Lewen, Stephan Schlemmer

**RJ02 4:30 – 4:45**

DUAL BAND MINIATURED SEMI-CONFOCAL FABRY-PEROT SPECTROMETERS FOR H2O AND HDO MILLIMETER-WAVE SENSING, Deacon J Nemchick, Brian Drouin, Ananda Q. Nole, Neda Khiabani, Chung-Tse Michael Wu, Maria Alonso, M.-C. Frank Chang

**RJ03 4:48 – 5:03**

DEVELOPMENT OF A MM-WAVE ULTRA-SENSITIVE SPECTROMETER FOR THE DETECTION OF SEMI-VOLATILE ORGANIC VAPORS, Muhammad Chrayteh, Fabien Simon, Coralie Elmaleh, Francis Hindle, Gail Mouret, Arnaud Cuisset

**RJ04 5:06 – 5:21**

INTERFERENCE BETWEEN THE 5r$_{1/2}$ – 5s$_{1/2}$ AND 5p$_{1/2}$ – 5s$_{1/2}$ COHERENCES (386.4 AND 384.1 THz) IN Rb OBSERVED BY ULTRAFAST FOUR-WAVE MIXING SPECTROSCOPY, Thomas Reboli, J. Gary Eden
RL. Structure determination
Thursday, June 23, 2022 – 1:45 PM
Room: 1024 Chemistry Annex
Chair: Nathan A. Seifert, University of New Haven, New Haven, CT, USA

RM. Fundamental physics
Thursday, June 23, 2022 – 1:45 PM
Room: 124 Burrill Hall
Chair: Terry A. Miller, The Ohio State University, Columbus, OH, USA
**RN. Astronomy**  
Thursday, June 23, 2022 – 1:45 PM  
Room: 274 Medical Sciences Building  
Chair: Gustavo A. Cruz-Diaz, University of Wisconsin-Madison, Madison, WI, USA

**RN01** 1:45 – 2:00  
LILLE SPECTROSCOPIC DATABASE FOR ASTROPHYSICALLY AND ATMOSPHERICALLY RELEVANT MOLECULES, R. A. Motiyenko, L. Margulës

**RN02** 2:03 – 2:18  
A NEW APPROACH FOR AUTOMATED ANALYSIS OF HIGH-RESOLUTION MOLECULAR LINE SURVEYS, Samer El-Ash, Crystal L. Bregan, Todd R. Hunter, Kelvon Lee, Brett A. McGuire

**RN03** 2:21 – 2:36  
REFERENCE DATA FOR AMMONIA SPECTRA IN THE 9000-6300 CM$^{-1}$ RANGE, Peter Čermák, Patrice Cacciani, Jean Cosleou, Alain Codina, Serge Béguier, Jean Vander Auwera, Ondřej Votava, Jozef Rakovsky

**RN04** 2:39 – 2:54  
FORBIDDEN ROTATIONAL TRANSITIONS AND ASTROPHYSICS, Takeshi Oka

**RN05** 2:57 – 3:12  
EXPERIMENTAL INSIGHTS INTO THE FORMATION OF INTERSTELLAR FULLERENES AND CARBON NANOTUBES, Jacob Bernal, Thomas J. Zega, Lucy M. Ziurys

**Intermission**

**RN06** 3:15 – 3:40  
PREBIOTIC MOLECULES IN INTERSTELLAR SPACE: THE ROLE OF ROTATIONAL SPECTROSCOPY AND QUANTUM-CHEMICAL CALCULATIONS, Cristina Puzzarini, Mattia Melosso, Luca Bizzocchi, Silvia Alessandrini

**RN07** 3:43 – 3:58  
MULTI-WAVELENGTH INVESTIGATION ON NEW MOLECULAR MASERS TOWARD THE GALACTIC CENTER, Cl Xue, Alexandre Faure, Emmanuel Momjian, Anthony Remijan, Todd R. Hunter, Brett A. McGuire

**RN08** 4:01 – 4:16  
ASSASINING 27 MOLECULES FOR SENSITIVITY TO PROTON-TO-ELECTRON MASS VARIATION: STRENGTHS AND LIMITATIONS OF A HIGH-THROUGHPUT APPROACH, Anna-Maree Syme, Laura K McKechnie

**RN09** 4:19 – 4:34  
THE OPTICAL SPECTRUM OF THE DIAMANTANE RADICAL CATION, Parker B. Grindall, Robert G. Radloff, Marko Förstel, Otto Dopfer

**RN10** 4:37 – 4:52  
CS ABSORPTION AT 140 NM IN SPECTRA ACQUIRED WITH THE HUBBLE SPACE TELESCOPE, Steven Federman, Adam Ritchey, Kyle N. Crabtree, Zhongxing Xu, William M. Jackson

**RN11** 4:55 – 5:10  
CATHEDRAL SPECTROSCOPY OF INTERSTELLAR PAHS AND PAH-RELATED ANALOGS - ASTRONOMICAL APPLICATIONS, Salma Bejaoui, Farid Salama

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**FA. Mini-symposium: Spectroscopy meets Chemical Dynamics**  
Friday, June 24, 2022 – 8:30 AM  
Room: 100 Noyes Laboratory  
Chair: Ryan T Ash, University of Wisconsin Madison, Madison, WI, USA

**FA01** 8:30 – 8:45  
MULTICHANNEL RADICAL-RADICAL REACTION DYNAMICS OF NO + PROPARGYL PROBED BY ROTATIONAL SPECTROSCOPY, Nareshan Dias, Ramil Gurusinghe, Arthur Suits

**FA02** 8:48 – 9:03  
DYNAMICS AND KINETICS STUDIED BY CHIRPED PULSE MICROWAVE SPECTROSCOPY IN COLD UNIFORM SUPERSONIC FLOWS, Alberto Macario, Myriam Drissi, Omar Abdelkader Khedaoui, Theo Guillaume, Brian M. Hays, Divita Gupta, Bia Rose Cooke, Ian R. Smit

**FA03** 9:06 – 9:21  
BRANCHING RATIO MEASUREMENTS FOR THE (3P) + PROPANE REACTION USING CHIRPED PULSE MICROWAVE SPECTROSCOPY AT LOW TEMPERATURE, Myriam Drissi, Alberto Macario, Omar Abdelkader Khedaoui, Brian M. Hays, Divita Gupta, Theo Guillaume, Bia Rose Cooke, Ian R. Smit

**FA04** 9:24 – 9:39  
CONFORMER SELECTED DIMER FORMATION IN A CRYOGENIC BUFFER GAS CELL, Lincoln Satterthwaite, Greta Kouramianou, David Patterson

**FA05** 9:42 – 9:57  
ROTATIONAL SPECTROSCOPY OF CHEMICAL REACTIONS IN A CRYOGENIC BUFFER GAS CELL, Brendan Carroll, Bryan Changala, Michael C McCarthy

**FA06** 10:00 – 10:15  
UV PHOTOFRAGMENT SPECTROSCOPY AND ELECTRONIC ENERGY TRANSFER ON A PEPTIDE SCAFFOLD: THE CASE OF NEAR-DEGENERATE UV CHROMOPHORES, Casey Daniel Foley, Etienne Chollet, Matthew A. Kubasik, Timothy S. Zwier

**Intermission**

**FA07** 10:57 – 11:12  
STRUCTURE AND DYNAMICS OF THE WEAKLY BOUND TRIMER (H$_2$)$_2$(H$_2$O) OBSERVED USING ROTATIONAL SPECTROSCOPY, Arjit Das, Ela Grogol, Nick Walker, Elangannan Arunan

**FA08** 11:15 – 11:30  
EVIDENCE OF NITROGEN AS ACCEPTOR IN NITROMETHANE-FORMALDEHYDE HETERODIMERS CHARACTERIZED USING MATRIX ISOLATION INFRARED SPECTROSCOPY AND COMPUTATIONAL METHODS, NANDALAL MAHAPATRA, S Chandra, Nagarajan Ramanathan, K Sundararajan

**FA09** 11:33 – 11:48  
OXYGEN ATOM DIFFUSION BY QUANTUM TUNNELING IN SOLID PARAHYDROGEN: A NEW TOOL TO STUDY LOW TEMPERATURE SOLID STATE REACTIONS, Ibrahim Maddakser, David T Anderson

**FA10** 11:51 – 12:06  
USING THE METROPOLIS MONTE CARLO METHOD TO EXTRACT REACTION KINETICS FROM EQUILIBRIUM DISTRIBUTIONS OF STATES, Sergei F. Chekmarev
FB. Mini-symposium: Benchmarking in Spectroscopy
Friday, June 24, 2022 – 8:30 AM
Room: 116 Roger Adams Lab
Chair: Brian J. Esselman, The University of Wisconsin, Madison, Madison, WI, USA

Chair: Steven Federman, University of Toledo, Toledo, OH, USA

FB01
8:30 – 8:45
ROTATIONAL STUDY OF ATMOSPHERIC VOCs USING THE NEW CF-FTMW SPECTROMETER OF LILLE, Elia M. Neeman, Noureddin OSSEIRAN, Manuel Goubet, Pascal Delun, Therese R. Huet

FB02
8:48 – 9:03
THE WATER VAPOUR SELF- AND FOREIGN CONTINUUM ABSORPTION AT ROOM TEMPERATURE IN THE 1.25 \textmu m window, Aleksandros Koroukas, Samir Kassi, Didier Mondelain, Alain Campagne

FB03
9:06 – 9:21
WILDFIRE SMOKE DESTROYS STRATOSPHERIC OZONE, Peter F. Bernath, Chris Boone, Jeff Crouse

FB04
9:24 – 9:39
STRATOSPHERIC AEROSOL COMPOSITION OBSERVED BY THE ATMOSPHERIC CHEMISTRY EXPERIMENT FOLLOWING THE 2019 RAIOKE Eruption, Chris Boone, Peter F. Bernath, Keith Labble, Jeff Crouse

FB05
9:42 – 9:57
ATLAS OF ACE SPECTRA OF CLOUDS AND AEROSOLS, Jason J Sorensen, Theo Jassaert, Maximilian Zibordi, Christiane Niemeyer, Bernd Schumann, Shane K. Johnson, Tobias Schneekloth

FB06
10:00 – 10:15
LOW-PRESSURE YIELDS OF STABILIZED CREIGEE INTERMEDIATES PRODUCED FROM OZONOLYSIS OF A SERIES OF ALKENES, Lei Yang, Micael Campos-Pineda, Jingzhe Zhang

FB07
10:18 – 10:33
REACTION MECHANISM AND KINETICS OF THE GAS PHASE REACTIONS OF METHANE SULFONAMIDE WITH CI RADICALS AND THE PATE OF CH$_3$(S(=O)$_2$)NH RADICAL- PANADANUM ARRHIL, Kab A. Musul

FB08
10:36 – 10:51
FIRST ANALYSIS OF THE $\nu_2$ BAND OF HNO$_2$, AT 351.766 cm$^{-1}$, Agnes Perrin, Laurent Manceron, raymond armante, P. Roy, F. Kribia Tchana, Geoffrey C. Toon

FB09
10:54 – 11:09
MILLIMETER-WAVE SPECTRA OF METHYLFURAN ISOMERS: LOCAL VS GLOBAL TREATMENT OF THE INTERNAL ROTATION, Jonas Bruckhuisen, SATHAPANA CHAWANANNON, Pierre Asselin, Isabelle Kleiner, Anthony Roucou, Guillaume Dhont, Colwyn Bracquart, Arnaud Cuisset

FB10
11:12 – 11:27
AN INITIO STUDY OF THE EXCITED STATES OF O$_3$, Gap-Sue Kim, Wilfrid Somogyi, Sergei N. Yurchenko, Rabi A. Musah

FB11
11:30 – 11:45
INFRARED SPECTROSCOPY AND QUANTUM CHEMICAL EXPLORATION OF AMMONIUM IODATE CLUSTERS, Nicola C. Frederiks, Danika Lee Heaney, John J. Kreinbihl, Christopher J. Johnson
FD. Clusters/Complexes
Friday, June 24, 2022 – 8:30 AM
Room: 217 Noyes Laboratory
Chair: Joseph Fournier, Washington University in St. Louis, St. Louis, MO, USA

FD01
CHARACTERIZATION OF ALCOHOL-WATER TETRAMERS AND PENTAMERS VIA CHIRPED PULSE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY, S. E. Dutton, Geoffrey Blake
8:30 – 8:45

FD02
INTERPLAY OF INTERMOLECULAR INTERACTIONS: COMPLEXES OF 2-DECALONE WITH WATER, BENZENE, AND PHENOL, Swanjy V. M. Calebe, Pablo Pinacho, Melanie Schnell
8:45 – 9:03

FD03
MOLECULAR STRUCTURES OF DIFLUOROBENZALDEHYDES AND THEIR HYDRATED COMPLEXES CHARACTERIZED BY CF-FTMW SPECTROSCOPY, Dingding Lu, Weixing Li, Xiaolong Li, Guanjun Wang, Mingfei Zhou
9:06 – 9:21

FD04
ANALYSIS OF THE MICROWAVE SPECTRUM, STRUCTURE AND INTERNAL ROTATION OF THE CH₃ GROUP IN N-METHYLIMIDAZOLE. (H₂O)₁ AND 2-METHYLIMIDAZOLE. (H₂O)₂ COMPLEXES, Charlotte Nicole Cummings, Eva Gougoula, Chris Medcraft, Juliane Heitkäper, Nick Walker
9:24 – 9:39

FD05
GEOMETRIES AND CONFORMATIONAL CONVERSION OF THE BINARY 3,3,3-TRIFLUOROPROPANOL CONTINUUM ABSORPTION WITHIN THE IR TRANSITION WAVE-LENGTH DEPENDENCE OF COLLISION-INDUCED ABSORPTION IN THE 0.76 μm AND 1.27 μm 01 BANDS, Kari Wissam Fakhardji, Alain Campargue, Didier Mondelain, Joseph T. Hodges
9:42 – 9:57

Intermission
10:39 – 10:54

FD06
MICROWAVE SPECTROSCOPY OF TERPENOIDS NON-COVALENTLY BONDED TO HYDROGEN SULFIDE, Nourreddin Osseiran, Elias M. Neeman, Manuel Gouber, Pascal Delan, Therese R. Hue
10:57 – 11:12

FD07
STRUCTURE AND NON-COVALENT INTERACTIONS OF THE BENZOFURAN-DIETHYL DISULFIDE COMPLEX CHARACTERIZED BY ROTATIONAL SPECTROSCOPY, Yuago Xu, Wenjun Li, Rizalina Tama Saragi, Alberto Lesarri, Gang Feng
11:15 – 11:30

FD08
MODELING CO₂ MICROSOVATION: MICROWAVE SPECTROSCOPIC STUDIES OF DIFLUOROBUTYLENE (DFE)(CO₂)₃, (DFE)₂(CO₂)₂, FOR A TRIMER, TETRAMER, AND PENTAMER, Hannah Fino, Tulana Ariyaratne, Pradhanthaa Kannangara, Rebecca A. Peebles, Sean A. Peebles, Channing West, Brooks Pad
11:33 – 11:48

FD09
REINVESTIGATION OF THE MICROWAVE SPECTRUM OF THE O₂-H₂O VAN DER WAALS COMPLEX, W. Ji, Hsu Li, Carolyn Saul, Amanda DuRend, Frank E. Marshall, G. S. Grubbs II
11:51 – 12:06

FD10
MICROSOVATION COMPLEXES OF α-METHOXY PHENYLACETIC ACID STUDIED BY MICROWAVE SPECTROSCOPY, Himamda Singh, Pablo Pinacho, Melanie Schnell
12:09 – 12:24

Intermission
12:57 – 1:12

FD11
EXECUTIVE SEMINAR ON ACADEMIC CAREER, TENGZHI TANG, YUANQING ZHANG, JUN JIA, ZHANQING MO, XIANGQIN ZHANG
1:15 – 1:30

FE01
A QUANTUM CASCADE LASER DUAL-COMB SPECTROMETER IN STEP-SWEEP MODE FOR HIGH-RESOLUTION MOLECULAR SPECTROSCOPY, Markus Mangold, Pitt Allmendinger, Jakob Hayden, Andreas Hugi, Olivier Brouet, Jean-Clement Bastien Vuipoel, Muriel Lipiere
8:30 – 8:45

FE02
A SPECTROSCOPIC PRESSURE SENSOR TARGETING ATOMIC POTASSIUM FOR HYPERSONIC FACILITIES, Tal Schwartz, Joshua A Vandervort, Sean Clees, Christopher L. Strand, Ronald K Hanson
8:45 – 9:03

FE03
LEAST SQUARES FIT OF LINE PROFILES IN TRANSMITTANCE AND ABSORBANCE SPECTRA WITH DETECTOR OR SOURCE NOISE, Haruyuki Sasa
9:06 – 9:21

FE04
MEASUREMENT OF COLLISIONAL SELF-BROADENING AT LOW-TEMPERATURES USING SUB-DOPPLER SPECTROCOPY, Brian Drouin, Deacon J Nemchick, Timothy J. Crawford, Paul Von Allmen, Dariusz Lis
9:24 – 9:39

FE05
APPLICATION OF THEORETICAL CONSTRAINTS TO MODEL THE MEASURED TEMPERATURE AND WAVELENGTH DEPENDENCE OF COLLISION-INDUCED ABSORPTION IN THE 0.76 μm AND 1.27 μm 01 BANDS, Jim M. Adkins, Helene Fleurbay, Tii Kamran, David A. Long, Alain Campargue, Didier Mondelain, Joseph T. Hodges
9:42 – 9:57

FE06
CHARACTERIZATION OF THE H₂O+CO₂ CONTINUUM ABSORPTION WITHIN THE INFRARED TRANSPARENCY WINDOWS FOR PLANETARY APPLICATIONS, Helene Fleurbay, Didier Mondelain, Jean-Michel Hartmann, Wissam Fakhardji, Alain Campargue
10:00 – 10:15

FE07
LINE MIXING STUDY OF CARBON MONOXIDE BROADENED BY NITROGEN, HELIUM, AND HYDROGEN, Wey-Wey Su, Yiming Ding, Christopher L. Strand, Ronald K Hanson
11:15 – 11:30

FE08
MAPPING O₃ MICROSOVATION: MICROWAVE SPECTROSCOPIC STUDIES OF DIFLUOROBUTYLENE (DFE)(O₃)₃, (DFE)₂(O₃)₂, FOR A TRIMER, TETRAMER, AND PENTAMER, Hannah Fino, Tulana Ariyaratne, Pradhanthaa Kannangara, Rebecca A. Peebles, Sean A. Peebles, Channing West, Brooks Pad
11:33 – 11:48

FE09
FTR MEASUREMENTS OF CROSSSECTIONS FOR TRANS-2-BUTENE IN THE 7.15 μm REGION AT 160-297 K FOR TITAN'S ATMOSPHERE, Brendan Steffens, Keywon Song, Michael Malaska, Rosaly M Lopes, Cora A Nixon
11:51 – 12:06

FE10
POTASSIUM LINESHAP STUDY WITH COLLISIONAL PARTNERS OF NITROGEN, HELIUM, AND HYDROGEN, Joshua A Vandervort, Yiming Ding, Richard S Freedman, Mark S Marley, Christopher L. Strand, Ronald K Hanson
12:09 – 12:24

FE11
FUZZY LOGIC IN THE PRESSURE-BROADENING DATA NEEDED FOR MODELING SUPER-EARTHS AND NEPTUNIAN ATMOSPHERES, Thuan Chau Nghi, Natasha E Batalha, Robert R. Gamache, Richard S Freedman
12:27 – 12:42
Chair: Cathy Murphy, University of Illinois at Urbana-Champaign, Urbana, IL, USA

Welcome
Timothy Killeen, President
University of Illinois

MA01
8:41 – 9:21
INTEGRATING CRYOGENIC ION CHEMISTRY AND OPTICAL SPECTROSCOPY: CAPTURING THE MOLECULAR LEVEL MECHANICS DRIVING BULK CHEMICAL BEHAVIORS FROM CATALYSIS TO THE SPECTRAL DYNAMICS OF WATER
MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA

The coupling between ambient ionization sources, developed for mass spectrometric analysis of biomolecules, and cryogenic ion processing, originally designed to study interstellar chemistry, creates a new and general way to capture transient chemical species and elucidate their structures with optical spectroscopies. Advances in non-linear optics over the past decade allow single-investigator, table-top laser systems to access excitation energies required to populate targeted chemical species providing spectroscopic windows. Together, these stages form our third-generation cryo-ambient ionization techniques which can be readily extended to analyze any reaction mixture. Pioneering applications include spectroscopic analysis of the interstellar media (ISM) and the laboratory studies of catalytic and chemical reactions. Together, these techniques offer access to reaction mechanisms of unprecedented detail.

Intermission

FLYGARE AWARDS
Introduction by Yunjie Xu, University of Alberta

10:36

MA02
9:26 – 10:06
CHEMISTRY IN THE ULTRACOLD REGIME: PRECISION MOLECULAR ASSEMBLY AND TEST OF Statistical REACTION DYNAMICS
KANG-KUEEN NI, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA

Advances in quantum manipulation of molecules bring unique opportunities, including the use of molecules to search for new physics, harnessing molecular resources for quantum engineering, and exploring chemical reactions in the ultra-low temperature regime. In this talk, I will focus on the latter two topics. First, I will introduce our effort on building single ultracold molecules with full internal and motional state control in optical tweezers for future quantum simulators and computers. This work allows us to go beyond the usual paradigm of chemical reactions that proceed via stochastic encounters. We create single reactions, a single control, and reaction of exactly two atoms. Second, we will present our work giving a detailed microscopic picture of molecules transforming from one species to another. We develop full quantum state mapping of chemical reaction product-pairs from single events, which we use to precisely benchmark statistical theory.

Intermission

FLYGARE AWARDS
Introduction by Yunjie Xu, University of Alberta

10:36

MA03
10:45 – 11:00
VIBRATIONAL SPECTRAL SIGNATURES AND DYNAMICS OF STRONG INTRAMOLECULAR H-BONDS INVESTIGATED WITH GAS-PHASE ION AND SOLUTION-PHASE ULTRAFAST INFRARED SPECTROSCOPES
JOSEPH FOURNIER, Department of Chemistry, Washington University, St. Louis, MO, USA

Strong H-bonding interactions often manifest in extremely broad-shared proton stretch vibrational transitions and exhibit ultrafast relaxation dynamics which have made the study of strongly H-bonded systems challenging both experimentally and computationally. Here, we report on the characterization of vibrational signatures and dynamics of strong, neutral intramolec- ular O-H H-bonds in several model systems by complementing frequency-resolved cryogenic ion vibrational spectroscopy on isolated gas-phase species with ultrafast solution-phase transient and 2D IR spectroscopies. The gas-phase experiments reveal the complex interplay between stretch-bend Fermi resonance interactions and coupling of the proton stretch to H-bond soft-mode vibrations. The nonlinear ultrafast experiments directly reveal the high degree of anharmonic mode mixing and coupling between the OH stretch, OH bend, fingerprint modes, and soft modes and show rapid intramolecular population relaxation dynamics. Significant isotopic dependence in polarization anisotropy dynamics suggest key differences in proton vs. deuteron transfer dynamics in the vibrationally excited systems. Time permitting, the initial steps towards combining ultrafast IR spectroscopies with cryogenic ion techniques for the acquisition of multidimensional and time-resolved spectra of isolated ion ensembles will be discussed.

MA04
11:05 – 11:20
NEW FRONTIERS IN COSMIC CARBON CHEMISTRY
BRETT A. MCGUIRE, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA

The last four years have seen a massive explosion in the spectroscopic detection and characterization of large carbon-containing molecules in the interstellar medium, including the first detections of individual polycyclic aromatic hydrocarbon (PAH) molecules. The detections of PAHs and other carbon rings in the cold, dark starless clouds TMC-1 by the GOTHAM and QUIJOTE projects has opened new frontiers for the exploration of this massive reservoir of as much as 25% of interstellar carbon. In this talk, I will highlight the GOTHAM collaboration’s pioneering work in laboratory (rotational) spectroscopy, radio-astronomical observational spectroscopy, astrochemical modeling, and machine learning all working together to unravel the chemistry and physics underlying these new discoveries.

MA05
11:25 – 11:40
PROBLEMS, PROBLEMS, PROBLEMS: THE LONG JOURNEY OF PHENYL ACETATE
LYNN FERRERES, WOLFGANG STAHL, Institute for Physical Chemistry, RWTH Aachen University, Aachen, Germany; LUCIA EVANGELISTI, ASSISI MARIS, SONIA MELANDRI, WALTHER CAMINATI, Departamento de Química, Universidade de São Paulo, São Paulo, Brazil

The rotational spectrum of phenyl acetate, CH$_3$COOC$_2$H$_5$, was measured using a free jet absorption millimeterwave spectrometer in the range from 60 to 78 GHz and two pulsed jet Fourier transform microwave spectrometers covering a total frequency range from 2 to 26.5 GHz. The features of two coupled large amplitude motions, the methyl group internal rotation and the skeletal torsion tunneling of the CH$_3$CO group with respect to the phenyl ring C$_6$H$_5$ (titled of about $70^\circ$), characterize the spectrum. The vibrational ground state splits into four widely spaced sublevels, labeled as A, E, A, and E, of them with inset of rotational transitions, and with additional intermediate states. A global fit of the line frequencies of the four sublevels leads to the determination of 40 spectroscopic parameters, including the $\Delta E_{\text{sub}}$ and $\Delta E_{\text{rot}}$ vibrational splittings of about 36.4 GHz and 34.0 GHz, respectively. These parameters were used to deduce the V$_5$ barrier to methyl internal rotation (about 136 cm$^{-1}$) and the skeletal torsion B$_2$ barrier to orthogonality of the two planes (about 64 cm$^{-1}$).
Chirality is pervasive in Nature and describes the property of an object not to be superimposable on its mirror image. To differentiate between the two mirror images of a chiral molecule, called enantiomers, one must probe them with a probe that is itself chiral. The probe can be of chemical nature, for example another chiral molecule, or of physical nature, for example a chiral light. I will give examples of these two approaches. I will describe how laser spectroscopy at low temperature sheds light on the structural differences between the homochiral and heterochiral complexes of chiral biomolecules, such as amino acids or sugars.

Then I will illustrate the sensitivity of chiroptical spectroscopy to conformational isomerism and molecular interactions on the example of 1-undanol studied by Vibrational Circular Dichroism (VCD) in the condensed phase and PhotoElectron Circular Dichroism (PECD) under jet-cooled conditions.
Many important physical processes such as non-linear optics and coherent control are highly sensitive to the absolute carrier-envelope-phase (CEP) of driving ultrashort laser pulses. A significant amount of previous theory work has been carried out to study the effect of the absolute CEP on strong-field ionization and related phenomena such as high harmonic generation (HHG) and nonsequential double ionization (NSDI). This makes the measurement of absolute CEP in the photoionization process immensely important in attosecond and strong-field physics. Even though relative CEPs can be measured with a few existing methods, the estimate of the absolute CEP has not been straightforward and has always required theoretical inputs. Recently, we have developed an in-situ method for measuring the absolute CEP of elliptical polarized few-cycle pulses. This has greatly enhanced the multi-hit capability of the 3D VMI technique in detecting two or more emissions from a single ion within a dead time (~ 0.48 ns). This has greatly enhanced the multi-hit capability of the 3D VMI technique in detecting two or more emissions from a single ion.

To achieve an efficient 3-D imaging detection of electrons/ions in coincidence, a conventional 2D imaging detector (MCP/phosphor screen) and a fast frame camera are used in the 3D velocity map imaging (VMI) technique[1, 2]. However, it is still difficult to obtain two separate TOF events for two electrons using a conventional MCP detector coupled with a multiphoton multiplier tube (PMT). This is because the phosphor screen is usually made of 4P7 phosphor which has longer decay time and thus not good to achieve high temporal resolution. Furthermore, due to the very short time separation interval between two electrons, it is imperative to use different phosphor/scintillator for improved 3D electron momentum imaging. Herein, we demonstrate that a scintillator screen coated with poly-para-phenylene laser dye (Exalite 404) can be used to achieve a greatly improved TOF resolution, which is sufficient for 3D electron imaging... A silicon photomultiplier tube (sPMT), utilizing strong field multi-electron dynamics, which are routinely carried out to understand the dynamics or calibrate CEP measurement. This failure could be due to the employed single active electron approximation and warrants further investigation. The results of this study will provide theoreticians with a clear understanding for studying strong-field ionization processes in atoms and molecules and will lead to independent experimental measurements of the absolute phase.

Small silver clusters possess remarkable luminescence and photoelectric properties, making them subject of current research. However, obtaining vibrations on small, neutral silver clusters remains challenging, due to difficulties in mass-selecting neutral clusters and a lack of easily accessible and widely wavelength-tunable far infrared light sources.

Here, we report our study on experimentally probing the vibrational wave packet dynamics on the ground state potential energy surface of the neutral silver tetramer Ag4+. A benchmark system for small neutral metal clusters, and unambiguously assign its structure. We combine femtosecond pump-probe spectroscopy employing the NeNePo (negative-neutral-positive) excitation scheme[2] with a cryogenic ion-trap tandem mass spectrometer. A linear polarized ultrashort pump pulse (~40 fs, tunable center wavelength from 700 nm - 820 nm) is used to selectively prepare a coherent wave packet by photodetachment from thermalized (20 - 300 K) Ag4+ ions. The wave packet dynamics on the electronic ground state are then probed using a second polarized ultrashort pulse (~50 fs, centered at 400 nm), which ionizes Ag4+ in a two-photon process. The mass-selected cation yield as a function of the delay time (0 - 60 ps) between the two laser pulses yields the fs-NeNePo spectrum. Frequency analysis with a resolution down to about 0.5 cm−1 by using Fourier transform of transient traces reveals one prime frequency band (195 ± 0.4 cm−1) in all conditions and four bands at 32 cm−1, 78 cm−1, 186 cm−1, and 295 cm−1 sensitive to the driving laser wavelengths and temperatures. These frequencies are consistent with predicted fundamental vibration frequencies ($\nu_1$, $\nu_2$, $\nu_4$, and $\nu_6$) and one combination (2$\nu_1 + \nu_4$) for the $D_4h$ geometry of Ag4+. The rephasing period of the wave packet allows determining vibrational anharmonicities. A strong dependence of the NeNePo cation signal on the polarization of ultrafast pulses is observed, revealing information on the anisotropy of the partial waves involved in the photodetachment process.

Dissociation of organic halides has been used for studying ultrafast processes over the last three decades given their relative simplicity and the significance in atmospheric chemistry. Specifically, photofragmentation of alkyl bromides with UV light has attracted substantial attention because of the ozone depletion potential of Br atoms. This presentation summarizes our recent results on the ultrafast photodissociation mechanisms of n-butyl bromide resolved using femtosecond time-resolved mass spectrometry. Multiple dissociative pathways occur upon photo excitation of n-butyl bromide including C-Br scission, C-C dissociation, and hydrogen elimination leading to unsaturated carbon bonds. The dissociative A state is accessed via two UV photon adsorption of two UV pump photons. This state undergoes direct dissociation of the C-Br bond within 160 fs. Three photon excitation reaches the n=5 Rydberg state, where several competing dissociation pathways are monitored. The fastest relaxations occur in states which are highly excited and have C-H dissociation leading to double and triple C-C bond formation with lifetimes of 500 fs. Dissociation on the ion-pair state occurs within 10 ps to produce the butyl radical. Additionally, 3 elimination of HBr from the parent molecule occurs within 4 ps. The population of the n=5 Rydberg state through internal conversion activates vibrations along the carbon backbone and produces an intermediate (bromopropyl radical) within 600 fs. The bromopropyl radical undergoes a concerted ring-closure and Br elimination into the Rydberg state through internal conversion activates vibrations along the carbon backbone and produces an intermediate (bromopropyl radical) within 600 fs. The bromopropyl radical undergoes a concerted ring-closure and Br elimination into the Rydberg state...
OBSERVATION OF RESONANCES IN THE F+NH3 REACTION VIA TRANSITION-STATE SPECTROSCOPY
MARK C BABIN, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA; MAARTEN DEwit, Chemistry, University of California, Berkeley, Berkeley, CA, USA; JASCHA LAG, Depart-ment of Chemistry, University of California, Berkeley, Berkeley, CA, USA; HONGWEI SONG, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan, China; RUI GUO, Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM, USA; DANIEL NEUMARK, Department of Chemistry, The University of California, Berkeley, CA, USA.

Transition state spectroscopy experiments, based on negative-ion photodechament, allow for the direct probing of the vibrational structure and metastable resonances that are characteristic of the neutral reactive surface. Here, we study the four-atom F + NH3 → HF + NH2 reaction using slow photoelectron velocity-map imaging spectroscopy of cryogenically cooled NH2F− ions. The resulting spectra reveal features associated with a manifold of vibrational Feshbach resonances in the post-transition state product well of this reactive surface. Beyond this, the spectra contain structure reporting on reactive resonances in the pre-transition state reaction complex well. Quantum dynamical calculations performed on a full-dimensional potential surface show excellent agreement with the experimental results, allowing for the assignment of spectral structure and demonstrating that key dynamics of this bimolecular reaction are well described by this theoretical framework.

TRACKING THE PHOTOIONIZATION OF ANILINE IN WATER: THE ROLE OF STATES
RAÚL MONTERO, Miller Laser Facility, Universidad del País Vasco (UPV/EHU), Bilbao, Spain; SGER LAMAS, ASIER LONGARTE, Physical Chemistry, Universidad del País Vasco (UPV/EHU), Bilbao, Spain.

The dynamics of aniline in water, after excitation along its lowest energy absorption (267 nm), has been investigated, from the femto (fs) to the nanoseconds (ns) scale, by pump-probe broadband transient absorption (TA) methods. The complex prompt TA spectrum, which evolves over the fs to ns scales, is analyzed by using a pump-repump-probe scheme that permits to interrogate the nature of the contributing species. The results permit us to identify, in addition to the long-living σ+ state responsible of the fluorescence, the formation of a charge transfer to solvent state (CTTS) that will autoionize to form the state characterized in the gas phase and the specific water-solute interactions established.

PULSE INDUCED DARK STATE OF ACETYLENE
ANTOINE AERTS, SQUARES, Université Libre de Bruxelles, Brussels, Belgium; PASCAL KOCKAERT, SI-MON PIERRE GORZA, OPERA Photonique, Université libre de Bruxelles, Brussels, Belgium; JEAN VANDER AUWERA, NATHALIE VAECK, SQUARES, Université Libre de Bruxelles, Brussels, Belgium.

We simulate laser-induced dynamics in acetylene (C2H2) using fully-experimental structural parameters. The rotation-vibration energy structure, including anharmonicities, is defined by the global spectroscopic Hamiltonian for the ground electronic state of C2H2 built from the extensive high resolution spectroscopy studies on the molecule, transition dipole moments from intensities, and effects of the (melodic) collisions are parameterized from line broadenings using the relaxation matrix [J. Chem. Phys. 184, 144508 (2021)]. The approach, based on an effective Hamiltonian outperforms today’s ab initio computations both in terms of accuracy and computational cost, however, is limited to a few small molecules. With such accuracy, the Hamiltonian permits to study the inside machinery of theoretical pulse shaping [J. Chem. Phys. 156, 084302 (2022)] for laser quantum control. With an adequate pulse shaping technique (in mid-IR) based on “super-Gaussian” pulses, we show a realistic and performant path to the population of a “dark” ro-vibrational state in C2H2.
These procedures allow at present quantum refinement of proteins based on both X-ray crystallography or Cryo-EM experiments. The NICOTINIC-AGONIST CYTISINE: THE ROLE OF THE NH···HO INTERACTION. This intramolecularity justifies the over-stabilization of the axial conformer over the equatorial one. In sight of the crucial role of the environment of the heteroatoms in cytisine molecule for docking the nicotinic receptor, we used the equatorial form and demonstrates the positive action of this alkaloid on the nicotinic receptor. The considerable molecular size of progesterone, one of the largest ever attempted solid, illustrates the potential of this technique in structural chemistry. The theoretical computations predict two possible low-energy structures of the complex. In one form, water lies in the πr plane of ferrocene. In the other form, water is close to the C5 axis of ferrocene on top of one of the cyclopentadienyl rings. Both forms have been observed. The most intense spectrum is that of a symmetric top with satellite patterns consistent with the effects of the free rotation of water. The rotational constant B determined for this spectrum is close to that predicted for the second axial form so that we can conclude that water is located along the C5 axis and freely rotating around it. This motion averages the ferrocene – H2O structure to that of a symmetric top. Different isotopic species have been detected, including 18O and 16O in their natural abundances, which have made it possible to determine the structure of the heavy atom skeleton of ferrocene and the axial location of water. A second weaker rotamer with an asymmetric top spectrum has rotational constants very close to those predicted for the other ferrocene-water conformer. Experimental and theoretical work is still in progress. The considerable molecular size of progesterone, one of the largest ever attempted solid, illustrates the potential of this technique in structural chemistry.
UNDERSTANDING THE SHAPE OF β-D-ALLOSE: A LASER ABLATION ROTATIONAL STUDY

GABRIELA JUÁREZ, SANTIAGO MATA, JOSÉ L. ALONSO, ELENA R. ALONSO, IKER LEÍN, Grupo de Espectroscopía Molecular, Lab. de Espectroscopía y Microscopía, Unidad Asociada CSIC: Universidad de Valladolid, Valladolid, Spain.

Allose, an aldohexose sugar, is a rare monosaccharide. It differs from the archetypal glucose in the hydroxyl group at the C3 position. However, this slight variation seems to be decisive in its natural abundance, as well as its biological role. Because of the structure-property relationship and to shed light on the effects of epimerization, we have brought β-D-allose into the gas phase using laser ablation techniques, and its conformational panorama has been characterized using chirped-pulse Fourier transform microwave (LA-CP-FTMW) spectroscopy. Three conformers have been unequivocally identified based on the spectroscopic rotational parameters. All the detected conformers exhibit a counter-clockwise arrangement (cc) network formed by an intramolecular hydrogen bond similar to what is observed in β-D-glucose. In opposition, we found that the intramolecular hydrogen bonds in β-D-allose are stronger than in β-D-glucose, which could have drastic biological implications.

INTERMISSION

THE PRECISE EQUILIBRIUM STRUCTURE DETERMINATION OF CHLOROBENZENE (C₆H₅Cl) BY ROTATIONAL SPECTROSCOPY

NATALIE A. SCHULER, P. MATISHA DORMAN, BRIAN J. ESSELMAN, MARIA ZDANOVSKAIA, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; BRYAN CHANGALA, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; JOHN F. STANTON, Quantum Theory Project, University of Florida, Gainesville, FL, USA; MICHAEL C. MCCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; R. CLAUDE WOODS, ROBERT J. McMAHON, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA.

The rotational spectra of over 30 isotopologues of chlorobenzene (C₆H₅Cl, C₅) have been collected over portions of the 2 – 360 GHz frequency region. The transitions of these isotopologues were least-squares fit to complete sextic Hamiltonians based on the spectroscopic rotational parameters. All the detected conformers exhibit a counter-clockwise arrangement (cc) network formed by an intramolecular hydrogen bond similar to what is observed in β-D-glucose. In opposition, we found that the intramolecular hydrogen bonds in β-D-allose are stronger than in β-D-glucose, which could have drastic biological implications.

MICROWAVE SPECTROSCOPY AND STRUCTURE DETERMINATION OF ORGANOSILICON COMPOUNDS: A CELEBRATION OF A DECADE OF COLLABORATION

NATHAN A. SEIFERT, Department of Chemistry, University of New Haven, West Haven, CT, USA; THOMAS R. F. MCCAFFREY, GAMAL A GUIRGIS, Department of Chemistry and Biochemistry, College of Charleston, Charleston, SC, USA; NICOLE MOON, AMANDA DUERDEN, G. S. GRUBBS II, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.

In this reflective presentation, we will discuss a fruitful, decade-long collaboration between the speaker and Prof. Gamal Guirgis at the College of Charleston and Gamal’s now distinct contributions to organosilicon chemistry. In particular, we will focus on Gamal’s facilitation of undergraduate and graduate students in their study of the chemical and spectroscopic properties of these molecules, as well as his use of microwave and infrared spectroscopy (and spectroscopists!) as essential methods for chemical analysis.

Our discussion will primarily focus on recent microwave studies, such as silylcyclohex-2-ene, 1,1-difluorosilylcyclohex-2-ene, and cyclopentylsilane, whose spectra were recently acquired in the Grubbs lab at Missouri S&T. However, given the timely nature of celebrating a decade of collaboration between Gamal and the speaker, we will highlight the history and past results of Gamal’s collaborations with microwave spectroscopists in the past decade, which stretches across multiple laboratories and research groups, many of which have been featured at ISMS in past years. Finally, we use this story as motivation to discuss the collaborative interface between the “spectroscopist” with the “chemist”. As microwave spectroscopy continues to climb up the formidable but traversable mountain towards mainstream chemical applicability, Gamal’s work with microwave spectroscopists offers a unique and compelling example of how microwave spectroscopy and spectroscopists can provide (and have provided) essential services for those interested in chemical synthesis.
There has been continued interest in the structure of substituted cyclobutanes. In this work, we measured the rotational spectrum of cyclobutanecarboxylic acid (CBCA) for the first time using a chip-pulse and a cavity-based Fourier transform microwave spectrometers. To aid in our analysis of the spectrum, we performed potential energy surface scans at B3LYP/aug-cc-pVTZ level in the ring-COOH dihedral angle of both equatorially- and axially-substituted CBCA. These scans revealed a unique local minimum and a shallow, symmetrical double-well at the global minimum, implying the existence of four distinct stable (yet faciety interconvertible) conformers. We re-optimized these conformers using both density functional theory and second-order Møller-Plesset perturbation theory with the aug-cc-pVTZ basis set and computed their relative energies, dipole moments, and rotational constants. We will present and discuss the corresponding assignments of features in the rotational spectrum.

A ROTATIONAL STUDY OF 6-APA

SERGIO MATO, SANTIAGO MATA, ELENA R. ALONSO, JOSÉ L. ALONSO, IKER LEÓN, Grupo de Espectroscopía Molecular, Lab. de Espectroscopía y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain

6-Aminopenicillanic acid (6-APA) is one of the essential intermediates in synthesizing semisynthetic and naturally occurring penicillins. We have transferred 6-APA into the gas phase using laser ablation techniques and characterized its conformational panorama using chirped-pulse Fourier transform microwave (LA-CP-FTMW) spectroscopy. The spectroscopic parameters derived from the spectrum analysis conclusively identify the existence of four conformers of 6-APA. The 14N quadrupole coupling constants have been analyzed, allowing an accurate structural determination. The observed structures correlate nicely with the biological function of 6-APA.

**Acknowledgments:** This research was funded by Ministerio de Ciencia e Innovación, Grant Number PID2019-111364GB-I00, and Junta de Castilla y León, Grant Number VAG014. We thank Consellería de Educación de la Universidad de Valladolid for an undergraduate fellowship.
VIBRONIC COUPLING MECHANISMS IN THE NITRATE RADICAL

JOHN F. STANTON, Quantum Theory Project, University of Florida, Gainesville, FL, USA.

An argument can be made that the nitrate radical (NO₃) is the most complicated tetrahedral molecule in nature, an assertion that becomes undoubtedly correct when its quantum mechanical complexity is convoluted with its environmental importance. The three lowest electronic states of this molecule (X′A**, A°B° and B°E°) are separated by less than 2 eV, and considerable vibronic mixing between these states leads to the complicated spectral patterns observed experimentally for NO₃. This talk reviews the various (qualitative) coupling mechanisms responsible for the abundance of various Frank-Condon forbidden features in electronic spectra of this species, with particular emphasis given to: photodetachment of the (well-behaved) nitrate anion; the A − X absorption spectrum; and the h − X absorption and dispersed fluorescence spectra. Apart from the A-X absorption spectrum, all of the above can be qualitatively reproduced by an extremely simple vibronic Hamiltonian, and semi-quantitative agreement is achieved with a more elaborate but conceptually identical form. As time permits, a progress report will be given on the interpretation of the A − X spectrum, some features of which remain poorly understood.

SUB TWENTY WAVENUMBER COMPUTATIONAL PREDICTION OF MOLECULAR BOND ENERGIES AND THE INTRIGUING BDE OF F₂

JAMES H. THORPE, Quantum Theory Project, University of Florida, Gainesville, FL, USA; JOSEIE L. KILHURN, Department of Chemistry, University of Florida, Gainesville, FL, USA; DAVID FELLER, Department of Chemistry, Washington State University, Pullman, WA, USA; BRYAN CHANGALGA, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; DAVID H. BROSS, 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 determination of molecular bond dissociation energies (BDE) is a fundamental pursuit of chemistry. This is an area where computational approaches have proved useful, especially when addressing molecules or environments that are difficult to study in the lab. High-accuracy composite methods can typically compute bond-energies to within one kJ mol⁻¹ via a series of additive energy increments, with corrections for relativistic effects, the vibrational zero-point energy, and the Born-Oppenheimer approximation.

Recently, the present authors explored an extension to the HEAT composite method, currently named KS-HEAT, which routinely reproduces the Active Thermochemical Tables (ATcT) total-atomization energies of small molecules to within 20 cm⁻¹. F₂, however, differs from the ATcT value by nearly 30 cm⁻¹. While fluoride-containing species are historically challenging to model, disagreement of this magnitude is surprising given the considerable level of theory and size of basis sets employed here.

To confound the issue, while the BDE predicted by KS-HEAT agrees closely with the combined ZEKE and IPP study of Yang et al. and the computational work of Conson et al., a recent CPP study by Mathiasson et al. and the PFP value calculated by Feller et al. agree with the current ATcT assignment. As the BDE of F₂ influences the ATcT enthalpies of formation of all fluorine containing molecules, this is an important quantity to get “right”. The details of these calculations are presented, and the BDE of F₂ is discussed.

ON THE USEFULNESS OF ELECTRON PROPAGATOR METHODS FOR A RELIABLE COMPUTATION OF EXPERIMENTAL OBSERVABLES

LORENZO FASOLINI, Dipartimento di Fisica e Astronomia, Università degli studi di Padova, Padova, Italy.

Electron propagator methods (EPMs) are well known in the physical-chemical community as a useful tool for the identification of signals observed in ultraviolet photoelectron spectroscopy (UPS) of isolated organic molecules. However, to completely reproduce an experimental UPS the vibrational signature associated to each electronic signal of interest should be computed.

In the first part of this contribution, the implementation of a simple protocol for the simulation of vibrationally resolved UPS is briefly described and its application to the calculation of the spectra of seven semi-rigid organic molecules is proposed. Chemical community is particularly interested in processes that occur in solutions, and therefore the energy which is needed to remove (or to add) an electron from a molecular system is often measured by means of electrochemical techniques. As a consequence, in this case the experimental observables of interest are oxidation and reduction potentials, which differ from the ionization potentials and the electron affinities computed through EPMs.

In the second part of this contribution, experimental redox potentials of 12 organic dyes are compared with ionization potentials and electron affinities computed through EPMs. Differences between computed and observed values are rationalized in terms of polarization and solvation effects, and the estimation of redox potentials through the employment of suitable corrections to the values calculated with EPMs is discussed.

EXTENSIONS TO GUIDED DIFFUSION MONTE CARLO FOR EXCITED STATES

JACOB M. FINNEY, ANNE B. MCCONY, Department of Chemistry, University of Washington, Seattle, WA, USA.

Diffusion Monte Carlo (DMC) is a stochastic method that is used to obtain the ground state energy and ground state wave function of a system of interest. DMC requires a potential energy surface (PES) that describes all degrees of freedom of the system. We have found that the use of guiding functions, functions that describe some of the vibrational degrees of freedom of interest, in DMC also allows improved sampling of the ground state wave function. We have found that the use of guiding functions, functions that describe some of the vibrational degrees of freedom of interest, in DMC also allows improved sampling of the ground state wave function. Therefore, we have used the current ATcT assignment. As the BDE of F₂ differs from the ATcT value by nearly 30 cm⁻¹, we have used to obtain excited state wave functions from unguided DMC calculations. This approach has been applied to studies of OH stretching vibrations in H₂O and H₂O⁺, where comparisons to previous studies can be made. Various approaches for obtaining the intensities from the ground and excited state DMC wave functions are explored.

Intermission

TARO UDAGAWA, IKIKU TANAKA, Department of Chemistry and Biomolecular Science, Gifu University, Gifu, Japan; KAZUAKI KAWAHATA, Graduate school of Nanobiomsce, Yokohama City University, Yokohama, Japan; MAGAHI BABA, Molecular Photonics Research Center, Kobe University, Kobe, Japan; TSUNEIRO HIRANO, Department of Chemistry, Ochanomizu University, Tokyo, Japan; UMEJI NAGASHIMA, MASANORI TACHIKAWA, Graduate school of Nanobiomsce, Yokohama City University, Yokohama, Japan.

Recently, Baba found that ro-vibrationally averaged bond lengths of C–H and C–D are observed as being almost identical (\(r_{\text{av}}(\text{C–H}) \approx r_{\text{av}}(\text{C–D})\)) for planar aromatic hydrocarbons from high-resolution laser spectroscopy.\(^4\) Quite recently, the reason of the same \(r_{\text{av}}(\text{C–H})\) and \(r_{\text{av}}(\text{C–D})\) bond lengths has been brilliantly unveiled by Hirano et al. by high-level ab initio molecular orbital calculations.\(^3\) They revealed that the experimental bond lengths derived from effective rotational constants are "not" the ro-vibrationally averaged bond lengths but their projected lengths on the principal axis.

In this study, we have carried out the path integral molecular dynamics (PIMD) simulations for C6H6 and C6D6, to directly estimate the distribution of the C–H and C–D bond lengths projected onto the principle axis. Our PIMD simulation strongly supports the previous explanation by Hirano et al.\(^3\) for the experimentally observed fact \(r_{\text{av}}(\text{C–H}) \approx r_{\text{av}}(\text{C–D})\) in C6H6 and C6D6.

From the precise measurement of the ionization energy of H2, its dissociation energy can be determined,\(^2\) which serves as a benchmark quantity for QED calculations.\(^1\) The most precise determinations of the ionization energies of molecular hydrogen currently rely on the extrapolation of Rydberg series using multichannel quantum-defect theory (MQDT).\(^2\)

Nonpenetrating high-fl states offer significant advantages for these extrapolations: they have small quantum defects and are much less perturbed by channel interactions than low-fl states. Their high polarisabilities are a disadvantage in zero-field measurements, but can be exploited to our advantage in Stark measurements. We show that the combination of a 3-photon excitation scheme with application of relatively weak electric fields (10 - 250 nV/cm) provides easy access to the linear Stark manifolds associated with near-degenerate high-fl states. We perform spectroscopy of the high-Stark Rydberg manifold with both continuous-wave millimeter-wave and near-infrared (NIR) radiation.

The manifold states are desirable as spectroscopic targets because their positions are less sensitive to errors in the quantum defects, a limiting factor in the determination of ionization energies by Rydberg series extrapolation. Extrapolating the linear Stark manifold to zero field yields accurate values of the zero-quantum-defect positions, given by \(-R_D/\ell^2\) relative to the ionization thresholds. These positions constitute references for the respective \(\ell = 3\) states and provide an assessment of multichannel-quantum-defect-theory calculations at a precision on the order of 100 kHz.

We show that this method can contribute to a one-order-of-magnitude improvement in the determination of ionization energies in molecular hydrogen and that, by using narrow-band NIR laser light, it can be extended beyond the ground state of \(\text{H}_2\).

RELATIVISTIC COUPLED-CLUSTER CALCULATIONS OF CHLORINE L-EDGE SPECTRUM OF CHLICL

ZHENG YUCHEN, ZHENG CHAOQUN, CHENG LAN, DEPARTMENT OF CHEMISTRY, Johns Hopkins University, Baltimore, MD, USA.

We present a computational study of x-ray absorption spectra for CH2Cl and CHCl3 using relativistic equation-of-motion coupled-cluster methods with spin-orbit coupling. The 1:1 ratio of the peak intensities for the chlorine L2 edge and L3 edge in the experimental x-ray absorption spectrum of CH2Cl\(^6\) shows an interesting deviation from the ratio of 2:1 between \(2p_{\alpha}\) and \(2p_{\beta}\) electrons. Here we study the origin of this phenomenon using high-accuracy ab initio calculations. Our computational results explain the relation between this anomaly in intensities and "multiplet effects."\(^2\)

Reference:


HIGH-RESOLUTION LASER SPECTROSCOPY OF THE RYDBERG STARK MANIFOLD IN H2

NICOLAS HOLSCH, HOANA DORAN, FREDERIC MERKT, Laboratorium für Physikalische Chemie, ETH Zurich, Zurich, Switzerland.

From the precise measurement of the ionization energy of H2, its dissociation energy can be determined,\(^2\) which serves as a benchmark quantity for QED calculations.\(^1\) The most precise determinations of the ionization energies of molecular hydrogen currently rely on the extrapolation of Rydberg series using multichannel quantum-defect theory (MQDT).\(^2\)

Nonpenetrating high-fl states offer significant advantages for these extrapolations: they have small quantum defects and are much less perturbed by channel interactions than low-fl states. Their high polarisabilities are a disadvantage in zero-field measurements, but can be exploited to our advantage in Stark measurements. We show that the combination of a 3-photon excitation scheme with application of relatively weak electric fields (10 - 250 nV/cm) provides easy access to the linear Stark manifolds associated with near-degenerate high-fl states. We perform spectroscopy of the high-Stark Rydberg manifold with both continuous-wave millimeter-wave and near-infrared (NIR) radiation.

The manifold states are desirable as spectroscopic targets because their positions are less sensitive to errors in the quantum defects, a limiting factor in the determination of ionization energies by Rydberg series extrapolation. Extrapolating the linear Stark manifold to zero field yields accurate values of the zero-quantum-defect positions, given by \(-R_D/\ell^2\) relative to the ionization thresholds. These positions constitute references for the respective \(\ell = 3\) states and provide an assessment of multichannel-quantum-defect-theory calculations at a precision on the order of 100 kHz.

We show that this method can contribute to a one-order-of-magnitude improvement in the determination of ionization energies in molecular hydrogen and that, by using narrow-band NIR laser light, it can be extended beyond the ground state of \(\text{H}_2\).
INFRARED PHOTODISSOCIATION SPECTROSCOPY OF PLATINUM-CATION ACETYLENE COMPLEXES

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P\textsuperscript{+}(C\textsubscript{2}H\textsubscript{2})\textsubscript{n} (n = 1 – 9) complexes are studied with tunable infrared laser photodissociation spectroscopy. These complexes are produced with laser vaporization of a platinum rod in a pulsed supersonic expansion of argon seeded with acetylene. Argon-tagged and tag-free complexes are then mass-selected in a specially made reflectron time-of-flight mass spectrometer, and their spectra are measured in the C – H stretching region (2800 – 3400 cm\textsuperscript{-1}) with infrared laser photodissociation spectroscopy. A coordination number of three acetylenes is found for platinum-cation. The experimental spectra are assigned using B3LYP/DEF2TZVP with an effective core potential on platinum. Peaks for the asymmetric and normally forbidden symmetric stretch of acetylene are red shifted from free acetylene molecules. The presence of cation – pi complexes and reacted structures is investigated by comparing experiment to theory.

Modeling water in condensed phases is an indispensable part of modern water research and rigid non-polarizable water models, such as TIP3P\textsubscript{2005}, have been very popular in molecular simulations due to their high efficiency. Although these water models can reproduce many properties of water, they fail in predicting the dielectric properties of water, such as the dielectric constant and low-frequency infrared spectra. We propose to improve these models by re-assigning the partial atomic charges of water molecules according to their local environment using a machine-learning (ML) model that is trained on quantum chemical data. With the ML-based charges, the calculated low-frequency infrared spectrum of liquid water is in good agreement with experiment, showing a peak at about 200 cm\textsuperscript{-1}, which non-polarizable water models fail to reproduce. The effects of charge redistributions in liquid water and their dependence on the choice of the density functional are also discussed.
MULTIVARIATE ANALYSIS OF MOLECULAR SPECTROSCOPY DATA FOR COVID-19 DETECTION
QIZHONG LIANG, YA-CHU CHAN, JUTTA TOSCANO, JILA and NIST, University of Colorado, Boulder, CO, USA; KEESTEN K. BJORKMAN, LESLIE A. LEINWAND, ROY PARKER, BioFrontiers Institute, University of Colorado Boulder, Boulder, CO, USA; DAVID J. NESBITT, JUN YE, JILA and NIST, University of Colorado, Boulder, CO, USA.

In exhaled human breath, there exist hundreds of sparse molecular species and many contain rich information about various health conditions or diseases. When associated with a specific medical response, a co-variation in concentrations for multiple molecular species can occur, thereby facilitating diagnosis. A recent technological improvement to the cavity-enhanced frequency comb spectroscopy (CE-DFCS) has enabled broadband molecular spectra to be collected at the parts-per-trillion detection sensitivity, allowing unambiguous and objective detection of multiple molecular species in a simultaneous manner. Here, we show how the breath spectroscopy data collected by CE-DFCS can realize non-invasive medical diagnostics. The key to such realization comes from the use of supervised machine learning to process the comb spectroscopy data in parallel with extreme-dimensional data channel inputs. Using a total of 170 individual breath samples, we report cross-validated results with excellent discrimination capability for COVID-19. At the same time, significant differences are identified for several other personal attributes, including smoking, abdominal pain, and biological sex difference. Our demonstrated approach can be extended immediately to investigate the diagnostic potential for a number of other disease states, including breast cancer, asthma, and intestinal problems. We discuss how further development in machine learning and frequency comb-based breath analysis can benefit significantly from enriching the absorption database to include more molecular species.

INTERMISSION

CAPTURING, PREDICTING, AND UNDERSTANDING OPTICAL SIGNALS: HarnESsing MACHINE LEARNING TO Tackle ENERGY DIsPERSION IN THE CONDENSED PHASE
ANDRES MONTOYA-CASTILLO, Department of Chemistry, University of Colorado, Boulder, CO, USA.

While optical spectroscopies provide an essential and ever-expanding toolbox for probing and elucidating how materials absorb, transport, and dissipate energy, accurately predicting their signals remains a formidable challenge to theory. By drastically expanding our ability accurately and efficiently simulate complex systems and their dynamics, machine learning techniques are opening fascinating possibilities for the simulation and analysis of various spectroscopies. In this talk, I will focus on our latest advances showing how one can exploit chemical intuition to combine machine learning techniques with robust theoretical frameworks to faithfully capture and interpret energy transport pathways encoded in optical signals.
Calculated of the chemical composition of laser-produced clouds formed by laser heating of Fe and CaCO₃ targets were performed. Timescales of main reactions with participation of Fe- and Ca- containing species were calculated using rate constants of the reactions. Results of calculations of equilibrium composition of laser-produced and impact-produced clouds are presented. Quenching conditions of chemical reactions in laser-produced and impact-produced clouds are found.

This work was supported by the Russian Science Foundation (grant 18-13-00269-I1).
FLASH PYROLYSIS MECHANISM OF TRIMETHYLCHLOROSILANE BY FLASH PYROLYSIS VACUUM ULTRA-VIOLET PHOTONIZATION TIME-OF-FLIGHT MASS SPECTROMETRY

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The thermal decomposition mechanism of trimethylchlorosilane at temperatures up to 1400 K was investigated using flash pyrolysis microrocket coupled with vacuum ultraviolet (118.2 nm) photoionization time-of-flight mass spectrometry. The main initiation reaction of the parent molecule was identified to be molecular elimination producing HCl and Si(CH3)3. Other initiation pathways such as chlorine-atom loss, methyl radical loss, and methane elimination were also observed. Density function theory (DFT) calculations at UB3LYP/6-311+G(d,p) levels of theory, with Grimme’s empirical dispersion correction GD3, were performed to study the energetics of the possible initiation pathways. The theoretical calculations revealed that the HCl elimination channel via a van der Waals intermediate was the most energetically favored pathway among all initiation channels, in agreement with the experimental observations. Some secondary reactions of the initial products were identified, and their possible mechanisms were proposed.

ULTRAVIOLET SPECTROSCOPY OF SUBCRITICAL AND SUPERCRITICAL ETHANOL

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

Vacuum ultraviolet spectroscopy was used to investigate the lowest-lying electronic state band edge of subcritical ethanol as a function of temperature from 25-200 °C, and for supercritical ethanol as a function of density at 250 °C. For subcritical ethanol, the band edge is observed to red shift with increasing temperature. Supercritical spectra clearly demonstrate a gradual transition from gas-phase to liquid-phase behavior with increasing density, as evidenced by a gradual blue shift and loss of spectral detail. We discuss both effects regarding the extent of hydrogen bonding in the system and Rydbergization effects, similar to those observed for subcritical and supercritical water.

The spectroscopic investigation of the hydrogen molecule and its isotopologues has played a crucial role in the advancement of quantum mechanics in the molecular domain. Particularly, highly accurate measurements of rotational transitions allow for various tests of fundamental physics including searches for physics beyond the Standard Model. Recent Doppler-free measurements performed at room temperature in the (2,0) overtone band of the hydrogen deuteride molecule spurred a stimulating debate on the interpretation of the spectra which significantly differ from typical Lamb dips. New measurements were performed in a cryogenically cooled cavity with the hope of resolving the underlying hyperfine structure. However, the resulting spectra observed shared the same unusual lineshapes which still hindered the extraction of the absolute rotational positions. With the goal of extracting the rotational interval with a better accuracy, pairs of F and P transitions were considered. This leads to accurate values for rotational energy intervals and to a precise test of molecular QED theory.

COLLISIONAL RELAXATION OF LOW-FREQUENCY VIBRATIONAL MODES OF SMALL MOLECULES IN A PULSED SEEDED SUPERSONIC JET

PYUSH MISHRA, ALEXANDER W HULL, TIMOTHY J BARNUM, STEPHEN L COY, ROBERT W FIELD, Department of Chemistry, MIT, Cambridge, MA, USA.

Vibrational energy transfer is a fundamental process in molecules which is closely related to chemical reactivity. Supersonic jet expansions have been an important tool in spectroscopy and chemical physics. These expansions are used to produce cold molecules under collision-free conditions. Among the various degrees of freedom that are collisionally relaxed, our focus is on vibrationally inelastic collisions between the analyte molecule and the carrier gas. A chirped-pulse Fourier-transform millimeter wave spectrometer (CP-FTmmW) is employed to observe vibrational relaxation (VR) of low-frequency vibrational modes in small molecules H2, CH3F, CH3CN and a medium sized molecule CH3OH. Systematic study of several supersonic expansion parameters extracts empirical relationships between VR and collision conditions. This includes a study of VR in molecules seeded in helium considering different valve types (Even-Larve valve vs. General Valve), instrumental parameters (nozzle temperature, stagnation pressure, orifice dimensions), and variation of the seeded molecule concentration. The identity of the collision partner is explored using several carrier gases (neon, argon, nitrogen, and hydrogen) and comparing the observed VR with that of helium. A universal inverse-linear relationship between the extent of VR and the frequency of the vibrational mode has been revealed by the experiments using helium. This was strikingly different from what was observed for other choices of carrier gases, where mode-specific VR was observed. For CH3CN (which has a degenerate bending mode, 2b,3b), efficient relaxation was observed. Separate use of two complementary laser-based techniques, laser induced fluorescence and millimeter wave optical double resonance, led to characterization of the velocity slip effect, the onset of clustering, and effects of Van der Waals bonding, studied as analyte concentrations were increased. Apart from demonstrating the power of a multiplexed form of rotationally resolved spectroscopy (CP-FTmmW), a ‘roadmap’ is generated to aid the design of future experiments by tailoring the choices of supersonic conditions. Empirical and intuitive approximate models are assembled that will aid in understanding vibrationally inelastic scattering and VR across a wide range of expansion parameters.

Intermission
QUANTIFYING EMISSION OF NIR-I AND NIR-II DYES VIA FLUORESCENCE QUANTUM YIELD

DAVID D.N. NDALEH, CAMERON J. SMITH, MAHESH LOKU YADDEHGE, ABDUL KALAM SHAIK, DAVIDA WATKINS, NATHAN I. HAMMER, Chemistry and Biochemistry, University of Mississippi, Oxford, MS, USA; JARED DELCAMP, Chemistry, University of Mississippi, Oxford, MS, USA.

Fluorescence Quantum Yield allows scientists to both quantify spectroscopic properties of dyes and compare to literature references. With the growing interest in NIR-emissive dyes for biological imaging, it is of great importance to reliably measure the fluorescent quantum yield of these novel dyes. Using a broadband excitation source and liquid nitrogen cooled InGaAs detector, steady state emission of four novel pentamethine indoline cyanine dyes synthesized with N,N-dimethylaminine-based substituents on the indoline periphery at varied substituents sites is recorded.

Evaluation of the design and characterization of organic dyes emitting in the near infrared (NIR) and short-wave infrared (SWIR) regions are of a great interest to the research community for several applications including bio-imaging. These abstract reports the results of photo-physical studies of a set of four newly-designed and synthesized SWIR emissive Rhodindolizine dyes. All the dyes were found to absorb and emit well within the SWIR domain (reaching emission maximum up to 1256 nm) with an onset beyond 1400 nm and Stokes shifts varying between 140-170 nm. The quantum yields of these dyes were estimated relative to the emission standard of IR1061 with a quantum yield of 0.0059 or 0.59% in dichloromethane. Further, nanomolar concentration studies in a water-soluble surfactant demonstrate their efficiency towards biological imaging.

SENSITIVITY TO VARIATION OF FUNDAMENTAL CONSTANTS FROM FREQUENCY MEASUREMENTS OF ACETYLENE REFERENCE TRANSITIONS

FLORIN LUCIAN CONSTANTIN, Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, Villeneuve d'Ascq, France.

Space-time variations of fundamental constants that are assumed in theories beyond the Standard Model may be investigated by precision molecular spectroscopy. The molecular energy levels are intrinsically sensitive to a variation of the proton-to-electron mass ratio $\mu$ and the transitions between closely-spaced energy levels display an enhanced sensitivity. The lasers stabilized to isotopic acetylene lines probed by saturated absorption spectroscopy provided secondary frequency references in the 1.5 $\mu$m spectral region. The acetylene optical clock enables now access to fractional frequency stability of $3 \times 10^{-15}$ at one second in a compact and robust setup that ensures optical frequency referencing with drifts lower than 1 Hz/day. The potential contributions to constraining the time variation of $\mu$ from precision spectroscopy of $^{13}C_2H_2$ transitions pertaining to the $\nu_1+\nu_3$ and $\nu_3+\nu_4+\nu_5$ combination bands are calculated. The acetylene energy levels are modeled with a state-of-the-art Hamiltonian that takes into account different rovibrational interactions and the sensitivities of the reference acetylene transitions are calculated. The frequency splittings between near resonant transitions, that may arise from the cancellation of the rotational intervals with frequency shifts associated to the origins of the vibrational bands, the anharmonicity, and the rovibrational interactions, display sensitivity coefficients up to $10^{-13}$ level. The systematic frequency shifts are conservatively evaluated for intracavity spectroscopy setups. The constraint to the time variation of $\mu$ derived from absolute frequency measurements of acetylene optical clocks is estimated at the $10^{-15}$/yr level.

HIGHLY SELECTIVE GAS ANALYZER BASED ON MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY FOR SO$_2$ MONITORING IN AMBIENT AIR

MD-ASHAR JAMEL, SYLVESTRE TWAGIRAYEZU, Chemistry and Biochemistry, Lamar University, Beaumont, TX, USA; JUSTIN L. NEILL, BrighSpec Labs, BrighSpec, Inc., Charlotteville, VA, USA.

As part of the efforts to determine the applications of molecular rotational resonance (MRR) technique to SO$_2$ monitoring in ambient air, a K-band MRR analyzer has been employed to record the MRR signature of multiple synthetic air samples containing SO$_2$ pollutant as well as that of standard SO$_2$ samples. The observed MRR features reveal a rich rotational pattern due to MRR’s sensitivity. The interfering matrix (i.e., air moisture), which typically challenges other conventional techniques, showed no impact on MRR signatures of SO$_2$. The validity of MRR for SO$_2$ monitoring has been examined by measuring MRR signal response of a set of standard SO$_2$ samples over a range of sampling pressures (5-15). The obtained linear correlations allowed the determination of recovery percentage (97-100%) and low detection limit of better than 1mg/m$^3$. Work to improve this analytical procedure is underway and will be reported in this talk.
Heterodimers consisting of an alkaline and alkaline-earth metal, such as LiBe are plausibly candidate for laser cooling experiments. Once cooled, the unpaired electron on the lithium allows LiBe to be manipulated by both magnetic and electric fields. The electronic structure calculations of You et al. predicted that the 2Σ+ to 1Π− transition is very diagonal, with a 0-0 band Franck-Condon factor of 0.998. Prior to the present study, only the 2Σ+ − 1Π− bands (labeled as the C-X system in earlier literature) had been observed between 19,200 − 20,600 cm−1. We have subsequently extended the spectroscopic characterization of LiBe and recorded the first experimental data for LiBe+ (XΣ−). Included in this work are the first observations of the 1Σ+, 3Σ+, 3Π., and 4Π states of LiBe+ and the XΣ− ground state of LiBe−. Data for the 2Σ+ − 1Π− transition confirmed the theoretical prediction that LiBe is a promising candidate for laser cooling.


SINGLET-TRIPLET DOORWAY STATES OF ALUMINUM MONOFLUORIDE

ELECTRONIC SPECTROSCOPY AND PHOTIONIZATION OF LiBe

THOMAS D. PERSINGER, JIANDE HAN, MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA.

A measurement of the electron electric dipole moment (eEDM) might be achieved using ytterbium fluoride (YbF) under ultra-cold conditions. One-dimensional laser cooling using the AΣ1+ − BΠ2+ bands (labeled as the C−X system in earlier literature) had been observed between 19,200 − 20,600 cm−1. We have subsequently extended the spectroscopic characterization of LiBe and recorded the first experimental data for LiBe+. Included in this work are the first observations of the 1Σ+, 3Σ+, 3Π−, and 4Π states of LiBe+ and the XΣ− ground state of LiBe−. Data for the 2Σ+ − 1Π− transition confirmed the theoretical prediction that LiBe is a promising candidate for laser cooling.


FLUORESCENCE SPECTROSCOPY DETECTION OF THE 4Π1 levels of YbF have been demonstrated, but the relative intensities of the transitions have not been reported. In the present study, we have used dispersed laser induced fluorescence spectroscopy to observe the lowest energy 4Π1 states. These measurements were carried out using excitation of previously unobserved YbF transitions in the near UV spectral range. The 4Π1(1J = 1/2 and 3/2) states were found at energies of 8470 and 9070 cm−1 above the ground state. The results are in excellent agreement with the calculations, bolstering confidence in the predicted electronic transition dipole moments of Ref. 1.


FUNCTIONALIZED AROMATIC MOLECULES FOR LASER COOLING AND TRAPPING

BENJAMIN AUGENBRAUN, SEAN BURCHESKY, Department of Physics, Harvard University, Cambridge, MA, USA; GUD-ZHU ZHU, Department of Physics, University of California, Los Angeles, Los Angeles, CA, USA; DEBAYAN MITRA, Department of Chemistry, Emory University, Cambridge, MA, USA; CLAIRE E. DICKERSON, Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA, USA; GUANMING LAO, Department of Chemistry, Emory University, Atlanta, GA, USA; JOHN M. DOYLE, Department of Physics, Harvard University, Cambridge, MA, USA.

Rapid and repeated scattering of laser photons (“optical cycling”) underlies many uses of atoms and small molecules for quantum science and measurement. Larger polyatomic molecules are also appealing targets, partly because these species may be decorated with functional groups offering unique scientific opportunities. In this talk, we discuss a large class of aromatic molecules that can be functionalized with an alkaline-earth metal atom to enable optical cycling. We describe the gas-phase production of Ca- and Sr-bearing derivatives of phenyl (Ph) and naphthyl radicals and, using dispersed fluorescence spectroscopy, we show that these molecules contain multiple electronic transitions suitable for optical cycling and laser cooling. We present high-resolution laser excitation spectra for molecules such as fluorinated CaOPh and SrOPh and compare these to the well-known alkaline-earth monosilanes and monoxides. These data inform ongoing work to laser cool and magneto-optically trap a functionalized aromatic molecule.
LASER SPECTROSCOPY OF BUFFER-GAS-COOLED POLYATOMIC MOLECULES
YUIKI TAKAHASHI, Physics, Mathematics and Astronomy, Caltech, Pasadena, CA, USA; MASAAKI BABA, Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Japan; KATSUMI ENOMOTO, Department of Physics, University of Toyama, Toyama, Japan; KANA IWAKUNI, Institute for Laser Science, The University of Electro-Communications, Chofu-ku, Japan; SUSUMU KUMA, Atomic, Molecular and Optical Physics Laboratory, RIKEN, Saitama, Japan; YUKI MIYAMOTO, Research Institute for Interdisciplinary Science, Okayama University, Okayama, Japan.

Buffer gas cooling has emerged as a powerful tool in the study of cold and ultracold molecules. We have demonstrated buffer gas cooling and CW laser absorption spectroscopy on two species: Calcium monodiodoyl radical (CaO) and Phthalocyanine (C_{21}H_{8}N_{4}). CaO has gained increased attention from astrophysics community due to its expected presence in the atmospheres of cool stars and rocky exoplanets. 3D Magneto-Optical trapping and subsequent sub-Doppler cooling of buffer-gas-cooled CaO has also recently been reported [1]. Phthalocyanine, on the other hand, is much larger and more complex molecule than CaO, possessing extremely rich rotational and vibrational structure. For both species, significant rotational cooling has been observed inside the ~5 K Helium buffer gas cell with estimated rotational temperature of ~10 K. This is promising, especially for large molecules with spectral congestion, to move molecular population into fewer lines, enhance signals, and drastically simplify spectrum. In this talk, we will present these results and analyses, including the latest data.


CRYSOCRYIC ION SPECTROSCOPY OF TRANSITION METAL-EDTA COMPLEXES: ION-DEPENDENT SPECTRAL AND STRUCTURAL SHIFTS
MASSON M, FOREMAN, J, MATTHIAS WEBER, JILA and Department of Chemistry, University of Colorado, Boulder, CO, USA.

Ethyleneamidinetrifluoracetic acid (EDTA) is a useful model system for studying the ubiquitous divalent ion-carboxylate interactions in protein binding pockets. EDTA can chelate most metal cations by forming up to six bonds with its four carboxyl groups and two nitrogen atoms, resulting in water-soluble complexes that are biologically relevant. Here, we present cryogenic gas-phase infrared spectra of a series of transition metal-EDTA complexes of the form [M(II)EDTA]^{2-} and assign spectral features using density functional theory calculations. The vibrational spectra inform us of the structure of and intermolecular forces in each complex, revealing the binding geometry of the metal ion within the EDTA binding pocket and its response to changes in ionic radius and electron configuration. The positions of carboxylate vibrational bands depend on the identity of the bound metal, displaying a clear spectral response to changes in binding properties.

INTERSTELLAR PEPTIDE BOND FORMATION BY ACETALDEHYDE AND AMMONIA IN ANALOG ICE
JOSHUA H MARKS, JIA WANG, Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI, USA; ANDRE K. ECKHARDT, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA; N. FABIAN KLEIMEIER, ANDREW MARTIN TURNER, RAFI INGO KRAISER, Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI, USA.

Observation of complex organic molecules containing peptide bonds such as acetamide and propionamide in the interstellar medium raises the prospect of amino acid formation. Reactions of interstellar ice analog containing acetaldehyde and ammonia were investigated to better understand the reactivity of oxygen-containing organic molecules with ammonia. These ices were submitted to energetic electron irradiation to simulate the effects of secondary electrons generated by galactic cosmic rays. Photoionization mass spectrometry was used to detect reaction products, while four-wave mixing provided tunable vacuum UV light for single photon ionization. Isotopically labeled acetaldehyde was employed to verify the formula of the observed reaction products. Electronic structure calculations at the CCSD(T)/CBS level predicted the adiabatic ionization energy of all plausible isomers. The differences between the ionization energies of the C_2H_5NO reaction products were used to identify the isomers present. The amino radical, NH_2, was found to bind to the acetaldehyde radical at either carbon. This resulted in the formation of 1-aminocarboxylic acid (CH_3C(O)NH_2) better known as acetamide, and 2-aminocarboxylic acid (NH_2CH(CHO)). Furthermore, with sufficient irradiation, high energy tautomers of both 1- and 2-aminocarboxylic acid were found to form. Both 1-aminothiol (CH_3C(O)NH(H)_2) and 2-aminothiol (OHCH(NH)H) were identified by measurement of their photoionization efficiency spectra.

THE COMPLEXES OF HYDROXYLAMINE VIA VIBRATIONAL AND ROTATIONAL SPECTROSCOPY
XIAOLONG LI, DINGDING LV, Department of Chemistry, Fudan University, Shanghai, China; WEIXING LI, MINJIE ZHOU, Fudan University, Department of Chemistry, Shanghai, China.

Although hydroxyamine is detected in the interstellar medium, there is a fewer study about its complexes and photochemistry. Herein, we study the photodissociation of hydroxyamine using cryogenic matrix-isolation spectroscopy. Furthermore, the reactions of hydroxyamine in CO and CO_2 ice are investigated via cryogenic matrix-isolation. As a consequence, the organic molecules form in the matrix cage. The complexes between hydroxyamine and aromatics are also studied by rotational spectroscopy in 2.8 GHz. The structures of observed isomers are determined by their rotational constants.
REACTION OF ELECTRONS TRAPPED IN CRYOGENIC MATRICES WITH BENZOPHENONE

ANKIT SOMANI, WOLFRAM SANDER, Organische Chemie II, Ruhr-Universität Bochum, Bochum, Germany

Electron transfer reactions are among the most elementary chemical reactions, which play a fundamental role in organic synthesis, electrochemical processes, and biochemical reactions. In our study, we used sodium as a source of electrons and probed the formation of benzophenone radical anion 2 in an argon and low density amorphous (LDA) water ice matrices using matrix isolation technique.

In solid argon, mixture of sodium vapors and benzophenone 1 was co-deposited and after irradiating the matrix with the visible light, electron transfer takes place from sodium to 1 under the formation of radical anion 2. In LDA water ice, hydrated electrons are produced after co-deposition of water with sodium. The hydrated electrons react with benzophenone without photochemical activation and resulted in radical anion 2. However, the photoexcitation of radical anion 2 yielded back benzophenone 1 after losing an electron to the matrix.[1]

Reference:
USING HCO+ LINE (& ITS ISOMERS) AS AN ASTROCHEMICAL TOOL TO PROBE THE STRUCTURE OF CLASS 0/I PROTOSTARS

The chemistry of Class 0/I protostars have become increasingly important due to the mounting evidence of their impact on the chemical composition of future nascent planetary systems. Prior observations of molecular outflows, which are an energetic mass-ejection phenomenon associated with early stages of stellar evolution, have revealed that not only do these harsh environments contain a surprising array of complex molecules, but they also show highly-localized spatio-chemical differentiation. Because the velocities of these jets are relatively well-constrained based on mm-wave observations, it is possible to associate distance within the outflow with temporal evolution of chemistry. As well, the collimated nature of the outflows provides a relatively compact region in which comparisons can be made between outflow, shocked walls, and background ambient gas in a variety of density and temperature conditions as the chemistry evolves. We use Atacama Large Millimeter Array (ALMA) spectral line observations in the range of 300-360 GHz of HCO+ line and its isomers in five outflows in the southern hemisphere of widely-varying ages, velocities, and chemical conditions to elucidate the underlying links between physical conditions, outflow properties, and chemical evolution in these important pre-stellar environments.

MAGNETIC FIELD STRENGTH LIMITS IN A PROTOPLANETARY DISK FROM MULTI-WAVELENGTH ZEEMAN OBSERVATIONS

Magnetic fields likely play a critical role in the accretion of material from protoplanetary disks onto protostars by providing a mechanism of angular momentum transport, particularly through magnetic disk winds. Constraining magnetic field strengths in protoplanetary disks is therefore necessary to test theories of magnetically-driven accretion. Zeeman splitting observations offer a way to directly measure or set upper limits on magnetic field strengths. We present the results of Zeeman splitting observations of several hyperfine lines of the CN(2-1) and CN(1-0) transitions in the Class II protoplanetary disk V4046 Sgr. We also present observations of the linear continuum dust polarization in this source and discuss their implications for the disk’s dust population.

DETECTION OF C–C_H_2, NO, and C_2HCN TOWARDS MOLECULAR CLOUDS AT THE EDGE OF THE GALAXY

In previous studies, we detected methanol in molecular clouds towards the edge of the Milky Way galaxy using the Arizona Radio Observatory (ARO) 12m. These observations implied that the Galactic Habitable Zone (GHZ) may extend beyond 20 kpc from the Galactic Center. As a continuation of this study, we have searched for other organic molecules towards these same edge clouds. We have current detections of C–C_H_2, NO, and C_2HCN towards WB89-840, WB89-380, and 1942+2541, among other sources. These molecules appear to show no decrease in abundance with respect to galactic radius despite the decrease in metallicity. Clearly organic chemistry is active towards the edge of our galaxy. The detection of these organic molecules show that the universe is far more molecular in nature than previously thought.
EXAMINING ANOMALOUS PHOTOCHEMISTRY IN THE DENSE INNER WIND OF IRC+10216 THROUGH ALMA OBSERVATIONS OF HCN

MARK A. SIEBERT, Department of Astronomy, University of Virginia, Charlottesville, VA, USA; MARIE VAN DE SANDE, School of Physics and Astronomy, University of Leeds, Leeds, UK; THOMAS J. MILLAR, School of Mathematics and Physics, Queen’s University Belfast, Belfast, United Kingdom; ANTHONY REMJIAN, MASc, National Radio Astronomy Observatory, Charlottesville, VA, USA.

In recent years, many questions have arisen regarding the chemistry of CN-bearing molecules in the carbon-rich winds of evolved stars. To address them, it is imperative to constrain the distributions of such species through high angular resolution interferometric observations of multiple rotational transitions. To that end, we used several ALMA observations to observe high energy rotational transitions of cyanide-bearing molecules in the inner envelope (<8") of the carbon star IRC+10216. The observed lines include the J = 38 - 37 and J = 28 - 27 transitions of cyanoacetylene (HCN), and the J = 18 - 17 (K = 0 - 9) transition of methyl cyanide (HC3N). In contrast to previous observations of photosychemicals products in the same source, the maps of these molecular lines show spatially coincident, compact morphologies comprising various arcs and loops, with significant enhancement in dense clumps at an angular distance of ∼3") (350 AU) from the central AGB star. Considering the known gas phase formation mechanisms of these molecules, our results are consistent with photochemistry occurring in warm (∼200 K) knots present in the inner regions of this circumstellar envelope. Using visibility sampled LIME radiative transfer models accompanied by the results of a specialized photochemical model, we explore the possibility that the enhanced HCN abundances in the inner wind are due to a binary companion supplying UV photons to this region. In this talk, we will discuss the results of this analysis, and demonstrate how they may impact our understanding of circumstellar carbon chemistry at the final stages of stellar evolution.

ALMA REVEALS THE MOLECULAR OUTFLOWS IN THE ENVELOPE OF HYPERGIANT VY CANIS MAJORIS

AMBISSH PRATIK SINGH, Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA; ANITA M RICHARDS, Department of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA; MARIE V AN DE SANDE, School of Physics and Astronomy, University of Leeds, Leeds, UK; THOMAS J. MILLAR, School of Mathematics and Physics, Queen’s University Belfast, Belfast, United Kingdom; ANTHONY REMJIAN, MASc, National Radio Astronomy Observatory, Charlottesville, VA, USA; LUCY M. ZIURYS, Dept. of Astronomy, Dept. of Chemistry, Arizona Radio Observatory, The University of Arizona, Tucson, AZ, USA.

Extreme supergiants, or hypergiants, are thought to undergo extensive, chaotic mass loss events in their later stages, with complex envelope structures composed of arcs, clumps, and knots. The red hypergiant VY CMa is one of the best examples of these types of stars. Previous studies in the infrared of VY CMa’s dust emission have shown the presence of distinct arcs to the southwest (Arc 1, Arc 2), a NW arc, and another clumps and knots, many extending several arcseconds from the central star. Using ALMA, we imaged the envelope of VY CMa in multiple molecular lines at Band 6 (1 mm) with 0.25 arcsec resolution and with the sensitivity to structures as large as 3-4 arcseconds. While some observations are still in progress, preliminary maps of SO2, H3CN, and P30 have been produced. From SO2 emission, a map of the global molecular outflow structure of VY CMa has been obtained for the first time on scales of 6-8 arcseconds. These molecular data show the striking morphology seen in dust emission in VY CMa, including Arc 1, Arc 2, and the NW Arc, among other features. These new images will be presented, as well as other new data, and the implications for the evolution of massive stars will be discussed.

AN ABSORPTION SURVEY OF C2H+ AND C2H IN DIFFUSE CLOUDS TOWARDS GALACTIC CONTINUUM REGIONS


Observations of the diffuse interstellar gas over the past few decades have revealed a surprisingly rich molecular inventory comprising over 25% of all known interstellar molecules. While the molecules observed in diffuse clouds are small relative to ones found in dark clouds, considerable progress has been made in recent years towards detecting larger, more complex molecules. There is also clear evidence at optical wavelengths for a very large molecule—the fullerene C60—in the diffuse gas. Using the 100-m Green Bank Telescope, we undertook observations of 8 sightlines toward bright continuum regions in the Galaxy, and detected the C2H+ ion and the C2H radical in absorption from foreground diffuse clouds along 7 sightlines. Both molecules are thought to be key intermediates in the carbon chemistry of the interstellar medium, and our knowledge C2H+ is currently the largest carbon chain ion and C2H the largest carbon chain radical detected by radio astronomy in the diffuse gas. I will discuss our results within the context of understanding hydrocarbon chemistry, establishing the limits of molecular complexity, and bridging the gap between small molecules and very large molecules in the diffuse gas. I will also discuss the prospects of enlarging the molecular inventory of diffuse clouds, particularly large polyatomic ions and radicals by means of absorption surveys exploiting long pathlengths toward bright continuum sources.

REFERENCES

Chair: Nathanael M. Kidwell, The College of William and Mary, Williamsburg, VA, USA

TA01

INVITED TALK

8:30 – 9:00

X-RAY MOLECULAR SPECTROSCOPIC DYNAMICS

STEPHEN R. LEONE, Department of Chemistry, The University of California, Berkeley, CA, USA

Ultrafast X-ray spectroscopic investigations and molecular dynamics are now approachable with short pulses of laboratory, laser-produced, high-order harmonics. Those X-rays probe transitions from localized inner shells of specific atomic sites in the molecules to valence orbitals, conveying new information about photochemical transformations. The interpretations of these spectra involve a new regime of core-to-valence X-ray probing that depends on energy shifts due to the surrounding electronic densities, spin coupling effects, energy shifts due to bond elongation with vibrational excitation, and even zero-order distortions. Coherent vibrational superspositions reveal different slopes of inner shell potentials with bond extension and Fermi resonance coupling, for the first time, in the X-ray. Open shell radicals have characteristic features of singly occupied orbitals and energetic shifts upon bond cleavage, which can be viewed from the localized atomic perspective. Corresponding theory work by collaborators provides a powerful assessment of the X-ray spectroscopic dynamics. Progress for revealing the full potential of time-resolved X-ray spectroscopy for the investigation of numerous novel features in molecular photochemistry is discussed.

TA02

9:06 – 9:21

ULTRAFAST XUV MAGNETIC CIRCULAR DICHRIOISM: OBSERVING SPIN TRANSPORT AT INTERFACES

ROBERT BAKER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; MARTIN SCHULTZL, Institute of Experimental Physics, Graz University of Technology, Graz, Austria; HARSHAD GALAPATHY, Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; SANVINE SANDUNIKA BANDARANAYAKE, EMILY B HUSSKA, STEPHEN LONDO, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

In time resolved spectroscopy of molecular systems, spectral signatures are directly correlated with processes such as charge migration, intra- and intermolecular vibrational relaxation, internal conversion, and intersystem crossing. However, the challenge of probing these analogous processes in materials with surface sensitivity and ultrafast time resolution motivates the goal to extend a molecular-level understanding to dynamics at surfaces and interfaces. In this talk, we describe the recent ability to directly observe spin-polarized electron transport at semiconductor surfaces using XUV Magnetic Circular Dichroism (XUV-MCD) in a reflection geometry. The ability to produce spin polarized currents at interfaces underlies many promising applications ranging from spintronics to enantiomeric photocatalysis, but designing materials capable of these applications requires an improved understanding of spin-dependent electron dynamics at interfaces. Towards this goal, XUV-MCD reflection-absorption spectroscopy provides direct observation of spin dynamics in magnetic materials with ultrafast time resolution and surface sensitivity. Yttrium iron garnet ($Y_3Fe_5O_{12}$) is a ferromagnetic semiconductor, consisting of two sub-lattices based on octahedrally and tetrahedrally coordinated Fe(III) centers. A combination of linearly and circularly polarized XUV measurements at the Fe M$_{4,5}$-edge of YIG provides a detailed picture of these lattice-dependent electron dynamics, which give rise to spin polarized current at the YIG surface upon band gap excitation. These findings have important applications towards the development of spin selective photocatalysts as well as new platforms for ligand-induced control of ultrafast spin polarization at material interfaces.

TA03

ULTRAFAST ELECTRON TRANSFER AND SPIN FLIP IN A HETEROBIMETALLIC COMPLEX

JOHN H. BURKE, JOSH VURA-WEIS, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

A major channel of energy loss in solar energy conversion is nonradiative charge recombination, whereby photochemical or photovoltaic energy is lost to the surroundings as heat. Understanding the mechanism of charge recombination, particularly the timescale and coupling to nuclear and spin degrees of freedom, is critical for understanding how to promote long-lived charge separation. In this regard, binuclear molecules with metal-to-metal charge transfer (MMCT) transitions are valuable model systems where the charge recombination reaction can be initiated with light by directly promoting the charge transfer state.

We employed femtosecond optical transient absorption (OTA) spectroscopy to monitor charge recombination following MMCT excitation in a heterobimetallic Fe(II)/Co(III) complex. The measurements uncovered a long-lived excited state with a 500 ps lifetime. Time-dependent density functional theory (TDDFT) allowed for assignment of this state as a metal-centered high spin state. The combined experimental and theoretical approach pointed to an ultrafast inter-system crossing and charge recombination to a local, intermediate-spin, metal-centered excited state, followed by a slower inter-system crossing to the long-lived high-spin state. These results uncover the intimate mechanism of charge recombination in this molecule by elucidating the spectral signatures, lifetimes, assignments, energetics, and nuclear geometries of the states involved. The coupling of the electron transfer to vibrations and spin in this complex could account for the ultrafast timescales of the charge recombination and could be a target for promoting long-lived charge transfer states through synthetic tuning.

TA04

9:42 – 9:57

MONITORING VALENCE-ELECTRON DYNAMICS IN MOLECULES WITH ULTRAFAST X-RAY DIFFRACTION

HAIWANG YONG, STEFANO M. CAVALETTO, Department of Chemistry, UC Irvine, IRVINE, CA, USA; STEPHEN M. MUKAMEL, Department of Chemistry, Irvine, CA, USA.

Ultrafast x-ray diffraction has been used to directly observe excited state electron density distributions in molecule upon photoexcitation (1). Theoretical studies have shown that the signal contains mixed elastic-inelastic coherence term originating from electronic coherence (2,3). In this study, we present a simulation study of valence-electron dynamics of oxazole using time-resolved off-resonant x-ray diffraction (4). A valence-state electronic wavepacket is prepared with an attosecond soft x-ray pulse through a stimulated resonant x-ray Raman process (5), and then probed with off-resonant single-molecule x-ray diffraction. We find that the time dependent diffraction signal originates solely from the electronic coherences and can be detected by existing experimental techniques. The present study thus provides a practical way of imaging electron dynamics in free molecules. In addition, the created electronic coherences and subsequent electron dynamics can be manipulated by resonant x-ray Raman excitations tuned to different core-excited states.


TA05 10:00 – 10:15
ULTRAFAST DYNAMICS OF TWO- AND THREE-BODY DISSOCIATION CAPTURED BY CORE-TO-V ALENCE TRANSIENT ABSORPTION SPECTROSCOPY

JAN TROSS, NEIL C. COLE-FLIPPAK, PAUL SCHRADER, LAURA M. McCASLIN, KRUPA RAMASEH, Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA.

Molecular photodissociation is central to numerous photochemical processes relevant to atmospheric chemistry and photocatalysis. As platforms to understand the ultrafast excited state dynamics underlying complex molecular photodissociation mechanisms, we studied the ultra violet photodissociation of two gas-phase molecules: acetyl iodide, which is a photolytic precursor for the acetyl radical, and iron pentacarbonyl, which is a model photocatalyst system. Using ultrafast extreme ultraviolet transient absorption spectroscopy, we followed the photodissociation dynamics of these molecules via core-to-valence transitions of their respective heavy atom constituents I and Fe5, giving access to atom-specific signatures of excited electronic states.

In acetyl iodide, we observe transient features with sub-100 fs lifetimes associated with the excited state wavepacket evolution prior to dissociation. These features then evolve to yield spectral signatures corresponding to the dissociation of the C-I bond. In iron pentacarbonyl, we observe transient features evolving on 100 fs to few-picosecond timescales due to excited state loss of carbonyl groups. We combine experimental findings with quantum chemical calculations to gain insight into the photodissociation dynamics.

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SAND No. SAND2022-2283- A

TA06 10:18 – 10:33
MAPPING COMPLEX PHOTOCHEMICAL REACTIONS USING FEMTOSECOND UV-PUMP XUV-PROBE PHO TOELECTRON SPECTROSCOPY

DANIEL HORKE, GRITE L. AIBA, Institute for Molecules and Materials (I2M), Radboud University Nijmegen, Nijmegen, Netherlands.

Time-resolved photoelectron spectroscopy has emerged as one of the premier tools to study the complex coupled motion of electrons and nuclei that underlies ultrafast photochemical processes. To study the entire reaction pathway from reactants through intermediates to products, however, requires sufficient energetic photons to ionize all species involved. The advent of high-flux high-harmonic generation sources now puts this within reach, and we present here femtosecond photoelectron spectroscopy studies using UV-pump XUV-probe pulses. We used this approach to probe the dynamics of dissociating CS2 molecules across the entire reaction pathway upon excitation. Figure 1. Dissociation occurs either in the initially excited singlet manifold or, via intersystem crossing, in the triplet manifold. Both product channels are monitored and we show that, despite being more rapid, the singlet dissociation is the minor product and that the triplet state products dominate the final yield. We will also show first results of our recent UV-pump XUV-probe studies of acetaldehyde photodissociation and aim to unravel the complex competing direct and roaming dissociation channels.

Figure 2: Time-resolved photoelectron spectroscopy of CS2 dissociation. XUV probe pulses allows us to map all intermediate and final states.

Intermission

TA07 11:15 – 11:30
ELECTRON LOCALIZATION IN MOLECULES INTERACTING WITH INTENSE LASER PULSES

AGNIESZKA JARON, JILA and Department of Physics, University of Colorado, Boulder, CO, USA; LAUREN BAURLE, JILA and the Department of Chemistry, University of Colorado, Boulder, CO, USA.

We theoretically study dynamic localization in molecules interacting with intense laser pulses. Mechanism is responsible for the effect of Charge Resonance Enhanced Ionization (CREI) studied for H2+ and I2+ for over 2 decades within the field of ultrafast intense laser AMO. Here we focus on the multi-electron aspects and the attosecond electronic dynamics.

Calculations are performed for di- and polyatomic molecules at equilibrium internuclear distances and we discuss multi-electron, or more precisely multi-orbital character of the process. CREI has been connected to the dynamic electron localization as well as to the multiple ionization bursts over one laser field cycle. We discuss the similarities and differences between CREI and results for multi-electron molecules at equilibrium distances. Results obtained within TDDFT show that as expected if we use laser wavelength tuned to the resonance one could observe resonance enhancement of multiphoton ionization of valence orbitals, analogous to CREI. But calculations also reveal that in contrast to CREI studied for H2+ and I2+, the resonance one photon transition acts as a trigger for other excitations and leads to enhancement of ionization from multiple inner valence orbitals and the dynamical properties exhibit more complicated behavior than expected from simple ‘2-level’ - H2+ picture of CREI.

SAND No. SAND2022-2283- A

TA08 11:33 – 11:48
PROBING SPATIAL EVOLUTION OF ULTRAFAST ELECTRONIC WAVEPACKETS WITH TWO-ELECTRON ANGULAR STREAINING

GABRIEL A. STEWART, Chemistry, Wayne State University, Detroit, MI, USA; DURKL A. DEBRAH, Chemistry, Wayne State University, Detroit, MI, USA; GHIAN BASNAYAKE, Chemistry, Wayne State University, Detroit, MI, USA; SIK KYOUNG LEE, Chemistry Department, Wayne State University, Detroit, MI, USA; WEN LI, Department of Chemistry, Wayne State University, Detroit, MI, USA.

Coherence among several electronic states can produce electronic wavepackets. Due to the delocalized nature of electronic orbitals, electronic wavepackets initiated by strong field ionization have significant spatial evolution. However, the spatial evolution was not previously accessible to experimental investigations at the attosecond time scale. Using the two-electron-angular-streainig (2eAS) method, we carried out measurements on xenon and krypton, in which the yields of double ionization were measured with a time range between 0 and 2.4 fs. A clear difference in the time-resolved double ionization yield between xenon and krypton was observed: at around 1.3 fs, xenon shows a higher double ionization yield than that of krypton. At this time, the ionization site by the laser field is roughly about 180 degrees from that of the first ionization.

This suggests that the second ionization is modulated by a dynamical process evolving at one femtosecond time scale. We attribute this to a spin-orbit electronic wave packet produced by the first ionization. A simulation using the time dependent conformational interaction with single excitation (TDCIS-IP-CAP) method was carried to model the ionization yield of a coherent superposition between two spin-orbit (SO) states. The calculation shows that due to the energy difference in SO splitting, the wavepackets evolve different temporally and spatially and the measured ionization yields have captured these detailed dynamics.
The advent of ultrashort laser pulses in the femtosecond to attosecond regime allows the study of ultrafast molecular dynamics with unprecedented time resolution [1,2]. These powerful modern light sources can result in the ionization of matter and thereby trigger electronic and nuclear dynamics [3,4]. In my talk, I will give an overview of the ongoing research efforts in the Worth group at UCLA addressing the following fundamental questions: (i) Can we control photochemical processes by creating/manipulating a quantum superposition state with a laser pulse? (ii) Can we understand the coupled electronic-nuclear motion and the associated ultrafast decoherence? (iii) Can we design laser pulses in a simple way to make use of the quantum interference pathways? (iv) Can we simulate an experimental photoelectron spectrum by developing simple theoretical models?

These elementary aspects of laser-matter interactions are governed by quantum mechanics and therefore we solve the time-dependent Schrödinger equation using state-of-the-art quantum dynamics method, MCTDH [5], in combination with vibronic coupling Hamiltonian [6]. This further allows us to deal with the non-adiabatic coupling between the electrons and the nuclei [6]. The ionized electron is modeled explicitly by incorporating the continuum of free-electron states [7]. The QUANTS suite of programs are used to run the dynamical simulations [8].

References

Chair: L. H. Coudert, Université Paris-Saclay, CNRS, Orsay, France

ThB01
EXTENDING ACCURATE QUANTUM CHEMISTRY TO HEAVY ELEMENTS

XUICHEN ZHENG, CHAOQUN ZHANG, LAN CHENG, Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA.

The presentation will be focused on development and applications of relativistic wave-function based approaches aiming to extend the accuracy and applicability of quantum chemistry to heavy elements. An atomic mean-field spin-orbit approach within exact two-component theory, the X2CAMF scheme, is shown to enhance the computational efficiency while retaining the accuracy of the parent four-component Dirac-Coulomb-Breit approach. An efficient implementation of the X2CAMF scheme together with analytic energy gradients for spin-orbit coupled-cluster methods enables accurate calculations of geometries and properties for molecules containing heavy atoms. The applicability of these relativistic quantum-chemical methods is demonstrated with applications in heavy-element chemistry and spectroscopy.

ThB02
ELECTRONIC STRUCTURE OF RuO

YAO YU, LEI ZHANG, XIONGWEI MA, JIE YANG, Atomic Physics Center, Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou, CHINA.

The laser-induced fluorescence (LIF) excitation spectra of jet-cooled ruthenium monoxide (RuO) molecule in the gas phase have been investigated in the range of 13,800 to 19,250 cm\(^{-1}\). As shown in the figure, a total of sixteen vibronic bands were experimentally observed and grouped into the transition systems from the ground \(X^3\Delta\) and \(X^5\Delta\) states to six excited electronic states, labeled as \([15.075] - X^3\Delta\), \([16.055] - X^3\Delta\), \([16.433] - X^3\Delta\), \([16.198] - X^5\Delta\), \([18.089] - X^3\Delta\), \([18.465] - X^3\Delta\). The spin-orbit splitting and the rotational constants in the lower and upper states were obtained accurately by the rotationally and isotopically resolved LIF spectra. In addition, the single-vibronic-level (SVL) emission spectra from the excited states were recorded, and the vibrational constants in the ground \(X^3\Delta\) and \(X^5\Delta\) states were obtained. Our results are sufficiently reliable and accurate to guide spectroscopists on further studies of RuO molecule.

ThB04
ACCURATE PREDICTION OF EQUILIBRIUM STRUCTURE FOR HEAVY ELEMENT CONTAINING MOLECULES

CHAOQUN ZHANG, LAN CHENG, Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA.

Accurate prediction of molecular geometries is a central subject in electronic structure theory. For accurate calculations of vibronic branching ratios in laser coolable molecules, it requires accurate calculations of molecular geometries for both electronic ground states and excited states. Using exact two-component theory with atomic-mean-field (X2CAMF) framework and analytical gradient techniques for spin-orbit coupled-cluster (5D-CC) method, we can obtain molecular equilibrium structures with accurate treatment of electron correlation and relativistic effects. By comparing with the experimental measurements of period-four-element containing diatomic molecules, the calculated bond lengths are accurate to 0.001 Å and the calculated harmonic frequencies are accurate to a few cm\(^{-1}\).
LaO LINE LIST FOR THE B*Σ+-X 2Σ+ BAND SYSTEM

PETER F. BERNATH, Department of Chemistry and Biology, Old Dominion University, Norfolk, VA, USA; ANANDA DASGUPTA, Physical, Old Dominion University, Norfolk, VA, USA; JACQUES LEVY, Service de Chimie Quantique et Photophysique, Université Libre de Bruxelles, Brussels, Belgium.

LaO bands appear in the optical spectra of S-type stars. The formation of the elements can be studied by measuring the stellar abundances of heavy metals such as La. For cooler stars, the visible and near-infrared electronic transitions of LaO are more useful than La atomic lines.

We have analyzed the LaO B*Σ+-X 2Σ+ band system up to v=5 in both ground and excited states. The rotational analysis of the B*Σ+-X 2Σ+ transition was carried out using the PGOPHER program. Most of the ground state spectroscopic parameters and hyperfine parameters of the excited B*Σ+ state were taken from literature and kept fixed. The equilibrium constants for X 2Σ+ and B*Σ+ states were determined. The line strengths were calculated based on the ab initio transition dipole moment and RKR potential curves. We also provide radiative lifetimes of the B*Σ+ state for v=0 to v=4. With this work, we provide a moderate line list for the LaO B*Σ+-X 2Σ+ transition that can be used to simulate LaO spectra of cool S-type stars to determine La abundances.

A similar analysis is in progress for the LaO A 3Π-H 3Σ+ transition.

Intermission

TB06 10:57–11:12
PREDICTION AND INTERPRETATION OF TRANSITION METAL X-RAY SPECTRA USING REAL-TIME TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

JUN XI, ZHOU LIN, Department of Chemistry, University of Massachusetts, Amherst, MA, USA; YING ZHU, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

Many transition metal complexes are popular catalysts for homogeneous organic synthesis. Their instantaneous geometric and electronic configurations and roles in the reaction mechanisms can be directly probed by in-situ K-edge X-ray absorption near-edge structure (XANES) spectroscopy. First-principles modeling is indispensable to translate the frequencies and lineshapes of K-edge absorptions into orbital and structural configurations. In the present study, we performed real-time time-dependent density functional theory (RT-TDDFT) calculations for (2,6-dimethylphenylcyclovinyl)trichloride and its methyl-substituted derivatives, and obtained time-dependent electronic densities and transition dipole moments by solving the time-dependent Kohn-Sham equations under applied electromagnetic field. Compared to traditional linear-response TDDFT (LR-TDDFT), RT-TDDFT allows a significant rearrangement of electronic densities after photoexcitations and provides a broad-band spectrum in the frequency domain after the Fourier transform. Based on our RT-TDDFT calculations, we managed to reproduce the pre-edge peaks for these species and assigned them to the dipole-allowed transitions of electrons from 1s orbital to the 3d4p hybridized orbitals of vanadium. Both characters align with the results from LR-TDDFT. In addition, RT-TDDFT leads to important features from the shoulder peaks, which correspond to the dipole-allowed, density-rearranging transitions of electrons from 1s orbital of vanadium to the 3d4p orbitals or the 3p orbitals of chlorine. These shoulder peak features have never been provided by LR-TDDFT. From the present study, we provided a proof-of-concept that the next-generation RT-TDDFT approach is a versatile and powerful computational tool for the prediction and interpretation of X-ray spectroscopy of transition metal complexes.

TB07 11:15–11:30
SIMPLIFIED LR-TDDFT/ZORA APPROACH FOR GENERATING SPIN-ORBIT COUPLINGS FOR X-RAY ABSORPTION SPECTRA

SARAH PAK, DANIEL R. NASCIMENTO, Chemistry, University of Memphis, Memphis, TN, USA.

Transition metals represent a space of continual interest due to their complex electronic structure and the diverse range of possible ligands and oxidation states. Studies of transition metal complexes often rely on X-ray spectroscopies (usually at the L or M edges) and computational methods to explain spectral features and help design new experiments. Most computational approaches either account for relativistic effects at the scalar level, by omitting spin-orbit coupling terms, or completely neglect them sacrificing accuracy in favor of a lower computational cost. On the other hand, explicit ab-initio treatments of spin-orbit couplings are costly and labor intensive, restricting their applications to smaller atomic systems. In the present work, we propose a simplified approach based on linear-response time-dependent density functional theory (LR-TDDFT) and the relativistic two-component zeroth order regular approximation (ZORA) to generate spin-orbit couplings of closed-shell molecular systems. The proposed approach was validated by computing the L-edge absorption spectra of several first and second row transition metal complexes. The method reproduces experimental data with satisfactory accuracy at a fraction of the cost of exact two-component or fully relativistic methods.

TB08 11:33–11:48
VIBRATIONAL ANALYSIS OF MOLECULES WITH QUASI-DEGENERATE ELECTRONIC STATES

KETAN SHAHMA, TERRY A. MILLER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; JIYUN LIU, Department of Chemistry, University of Louisville, Louisville, KY, USA.

Progress in laser cooling and trapping molecules has lead to a renewed interest in alkaline earth monoalkoxide (MOR) free radicals as promising candidates for direct laser-cooling of polyatomic molecules. Theoretical understanding of these molecules is challenging due to the presence of quasi-degenerate electronic states in these molecules. In addition to that, pseudo-Jahn Teller interactions and spin-orbit coupling also play a very important role. Understanding these couplings and their effects on the molecular spectra will provide critical information for future direct laser cooling of MORs and similar radicals. In this talk we discuss the theoretical intricacies involved in calculating the spin-vibronic spectra of such molecules from first principles. A Hamiltonian has been developed in a spin-vibronic representation for molecules with quasi-degenerate electronic states. We will describe calculating the parameters in this Hamiltonian using ab-initio methods and the software developed for solving such Hamiltonians (XOCFT). Our discourse includes both frequency calculations and relative transition intensities from first principles for both excitation and emission spectra which can be compared to experimentally observed using LIF and DF spectra of CaOCaH4, CaOCaH3, and iso-CaOCaH3 to be reported in succeeding talk. Typical Franck-Condon factor calculations done under the Born-Oppenheimer approximation reproduce the dominant features of these spectra, but the inclusion of Jahn-Teller and pseudo-Jahn-Teller couplings and spin-orbit interactions in the calculations not only improves the accuracy of simulation but also leads to additional vibronic transitions that help to explain the finer structure observed in the spectra. A major limitation of these methods is the amount of computational resources required as the molecules become larger. Efforts to minimize the amount of resources required as well as approximations involved in simulating the spin-vibronic spectra for larger molecules like iso-CaOCaH4 have also been discussed.
ELECTRONIC SPECTROSCOPY OF THE $\tilde{A} - \tilde{X}$ TRANSITIONS OF JET-COOLED CALCIUM MONOALKOXIDE RADICALS: SPIN-VIBRONIC STRUCTURE OF NONLINEAR MOLECULES AS CANDIDATES FOR DIRECT LASER COOLING

ANAM C. PAUL, HAMZEH TELFAH, Department of Chemistry, University of Louisville, Louisville, KY, USA;
KETAN SHARMA, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; S M SHAH RIYADE, Department of Physics and Astronomy, University Of Louisville, Louisville, KY, USA; TERRY A. MILLER, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA; JINJUN LI, Department of Chemistry, University of Louisville, Louisville, KY, USA.

We report a combined experimental and computational study of spin-vibronic structure and transition intensities of the lowest electronic states of nonlinear alkaline earth monoalkoxide (MRO) radicals, including calcium methoxide (CaOCH$_3$), calcium ethoxide (CaOC$_2$H$_5$), and calcium isopropoxide (CaOCH(CH$_3$)$_2$). Experimentally, laser-induced fluorescence and cavity ring-down (CRRD) spectra of the $\tilde{A}^2E - \tilde{X}^2A_1$ electronic transition of CaOCH$_3$ (C$_1$), the $\tilde{A}^2E - \tilde{X}^2A_2$ transition of CaOC$_2$H$_5$ (C$_2$), and the $\tilde{A}^2E - \tilde{X}^2A_2$ transition of CaOCH(CH$_3$)$_2$ were recorded under jet-cooled conditions. An essentially constant $\tilde{A} - \tilde{A}_n$ energy separation for different vibronic levels is observed in the LIF spectrum of each radical, attributed to spin-orbit (SO) interaction and, in the case of the two C$_2$ molecules, the zero-point-energy-corrected "difference potential". The complete active space self-consistent field (CASSCF) and the coupled-cluster (CC) methods are used to calculate electronic transition energies and vibrational frequencies and to predict parameters governing the spin-vibronic energy level structure and simulate the recorded LIF/DIF spectra. The Jahn-Teller (JT), pseudo-Jahn-Teller (pJT), and SO interactions, especially those between the $\tilde{A}_1$ and the neighboring $\tilde{B}_2$ states, induce a number of off-diagonal Franck-Condon (FC) matrix elements leading to additional vibronic transitions. The spin-vibronic Hamiltonian presented in the preceding talk has been employed for the spectral simulation. Computational and experimental results on all three free radicals will be compared, and the implications for future laser cooling experiments will be discussed.

ALKALI DIATOMICS: ASYMPTOMATIC LONG RANGE BEHAVIOR OF ELECTRONIC MATRIX ELEMENTS BASED ON AB INITIO CALCULATIONS

EKATERINA A. BORMITSOVA, ANDREY STOLYAROV, Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia.

Ultracold molecules have been widely utilized in various fields of study from the search for new physics in the ultracold regime to ultracold chemistry. Systems at such (< 1 mK) temperatures are usually made with laser cooling techniques, i.e. photoassociation and stimulated Raman adiabatic passage, which utilize closed optical schemes with non-adiabatic levels of electron-excited states serving as intermediate steps to create ultracold molecules from pre-cooled atoms. This process requires full and detailed data for the ground and excited states in a wide range of internuclear distances, $R$. Sufficiently accurate data requires going beyond the adiabatic approximation, calculating non-adiabatic interaction matrix elements (IMEs), i.e. the spin-orbit (SO) and L-coupling (LC) IMEs, with special attention paid to correct long-range behavior.

Here, the asymptotic behavior near the dissociation limit (DL) of IMEs is studied focusing on the transition-dipole moment (TDM), SO and LC IMEs. These were calculated for LiNa, LiK, LiRb, LiCs using spin-averaged wavefunctions corresponding to Hund’s case (a) and effective core pseudopotentials. The electronic correlation is accounted for using a 2 valence electron multi-reference configuration interaction calculation. Core-polarization potentials take the core-valence effect into account. Where possible, theoretical curves were compared to ones derived from experiment. The leading asymptotic trends for the TDMs, SO and LC IMEs, have been determined for three groups of state pairs: (a) dipole allowed transitions between an excited state and one converging to the first DL; (b) forbidden transitions between two states converging to the same DL<1; (b) forbidden transitions between two states converging to different DL>1. Thus, for the TDMs type (a) pairs converge as $R^{-3}$ to the atomic dipole moment, while type (b,c) pairs converge to zero as $R^{-1}$. The SO IMEs converge: as $R^{-7}$ to zero for (a); as $R^{-7}$ to the atomic SO splitting for (b), as $R^{-3}$ to zero for (c). Finally, the LC functions: approach infinity linearly for (a); converge as $R^{6}$ to a constant for (b); converge as $R^{-3}$ to zero for (c).

RELATIVISTIC DELTA-COUPLED-CLUSTER CALCULATIONS OF K-EDGE CORE-IONIZATION ENERGIES FOR THIRD-ROW ELEMENTS

XUECHEN ZHENG, CHAOQUN ZHANG, LAN CHENG, Department of Chemistry, Johns Hopkins University, Baltimore, MD, USA.

Core-valence separated delta-coupled-cluster (CVS-ΔCC) with spin-free exact two-component theory in its one-electron variant (SFΔCC–1e) has been shown to provide quantitative description of core-ionization energies for second-row elements [1]. Here we extend the applicability of CVS–ΔCC calculations to K-edge core-ionization energies for third-row elements. We develop a revised CVS scheme to make it applicable in larger basis sets. Basis-sets effects have been demonstrated to be important. The use of uncontracted cc-pVTZ basis sets for target atom and cc-pVTZ sets for the other atoms appears to be an efficient and accurate approach (cc-pVTZ-unc*). High-level relativistic (HLR) corrections beyond the SFΔCC–1e, including two-electron picture change, spin-orbit coupling, Breit interaction and QED effects have been taken into account and shown to play an important role. SFΔCC–1e CVS–ΔCCSD(T)/cc-pVTZ-unc* calculations augmented with high-level relativistic corrections can provide highly accurate K-edge core-ionization energies of third-row elements with deviation of less than 0.5 eV from experimental values.

Reference

FOURIER-TRANSFORM OPTICAL FREQUENCY COMB SPECTROSCOPY

Aim: To improve the high-accuracy line lists for several important molecules,

Method: Using FT-IR spectroscopy and SIM-FIT line-fitting software,

Results: Improved line lists for CO, CH$_4$, C$_2$H$_2$, with reduced uncertainties,

Conclusions: Better detection of trace gases in Earth's atmosphere and space missions.
AMES-1 296K IR LINE LISTS FOR OCS ISOTOPOLOGUES

XINCHUAN HUANG, Carl Sagan Center, SETI Institute, Mountain View, CA, USA; DAVID SCHWENKE, MS 258-2, NASA Facility, NASA Ames Research Center, Moffett Field, CA, USA; TIMOTHY J. LEE, Space Science and Astrobiology Division, NASA Ames Research Center, Moffett Field, CA, USA.

To fill in the OCS data gaps in IR databases, Ames-1 296K IR line lists are reported for OCS isotopologues in the range of 0 - 16,000 cm\(^{-1}\), with line intensity cut off at 16-30 cm/molecule. Seven isotopologues (622,624,632,623,822,634, and 722) are included in a "natural" OCS line list with their terrestrial abundances. The Ames-1 potential energy surface (PES) for OCS was refined using selected HITRAN data and band origins up to 13,952 cm\(^{-1}\) (with reduced weight). It can reproduce most HITRAN levels with \(\sigma_{a} < 0.01\) cm\(^{-1}\), except a few bands of the main isotopologue: 5002, 4112 and 9110. The Ames-1 dipole moment surface (DMS) was fit from extrapolated CCSD(T)/aug-cc-pV(T,Q,5)Z dipoles, with fitting \(\sigma_{p} = 3.8\) cm\(^{-1}\).

\[\text{rms}\] for 1862 points in 0 - 20,000 cm\(^{-1}\). In general, the Ames-1 296K intensity finds good agreement with experiment and HITRAN. Agreements for bands >10,000 cm\(^{-1}\) are also reasonable. In future, we need to identify the source of discrepancies observed in the Ames-1 vs Experiment/HITRAN comparisons, and focus on higher energy and higher temperature line lists. See http://huang.seti.org for latest update.

\[\text{Funded by NASA Grant 18-APRA18-0013 and through NASA/SETI Co-operative Agreement 80NSSC20K1358.}\]
We present a high level ab initio study of the rovibronic spectrum of sulfur monoxide (SO) using internally contracted multireference configuration interaction (IC-MRCI) method using aug-cc-pv5z basis sets and a fully diabatised model for the molecule. The diabatic model covers the lowest 13 singlet and triplet electronic states of SO $X^3\Pi$, $a^3\Sigma^+$, $e^3\Sigma^+$, $A^3\Delta$, $A^1\Sigma^+$, $A^1\Pi$, $B^3\Sigma^-$, $C^1\Pi$, $C^1\Sigma^+$, $d^1\Pi$, $C^3\Pi$, $d^3\Pi$, $b^1\Pi$, and $f^1\Pi$ states through a unitary transformation who’s rotation angle is determined by the Ry on enforcing smoothness properties of the diabatic potential energy curves. A rovibronic line list of SO is computed covering the wavelength range up to 167 nm.

The HITEMP database [1] provides line-by-line spectroscopic parameters for use at high temperatures. HITEMP line lists are used for numerous applications that include spectral modeling of exoplanets, brown dwarfs, and stellar atmospheres, as well as the high-resolution remote sensing of combustion environments. It is therefore necessary that these spectroscopic line lists are sufficiently complete in order to reproduce high-temperature spectra, but it is also essential that the line positions, intensities, and broadening parameters are accurate for high-resolution studies.

Over recent years, HITEMP has been undergoing a significant upgrade that has improved the quality and extent of the available spectroscopic data and the number of line lists available: $H_2O$, $CO_2$, $N_2O$, $CH_3$, $N_3$, $NO_2$, $OH$ [1–4]. HITEMP line lists are typically built upon a state-of-the-art ab initio (or semi-empirical) line list that is cross-evaluated against other works. The line list is then combined with HITRAN (when possible), and broadening parameters are applied for each line. The resultant line list is validated against available high-resolution experimental studies at elevated temperatures, and improvements are incorporated where necessary. This methodology will be presented for the recent additions to HITEMP [3,4], along with an “effective line” technique that was used for $CH_4$. The presentation will also discuss the forthcoming planned updates for the $H_2O$ and $CO_2$ line lists.

Sulfur monoxide (SO) is found in several astronomical sources including the atmospheres of Io and Venus. Continuing our previous work to make a more complete line list for SO, we used our previous fits of rotational constants for v=0-6 for the X 3Σ− state and v=0-5 for the a 1Δ state along with high-level ab initio calculations to produce line strengths and positions for all of the vibration-rotation transitions. All possible vibrational bands were calculated and line strengths included the Herman-Wallis effect caused by vibration-rotation interaction.

Recently, cyclic molecules such as benzonoritile 3 and 2-cyanocyclopentadene 4 have been discovered in the interstellar medium. Cyclic molecules with large dipole moments are considered good candidates for further search. Isothiazole (CH(N(S))S) is a five-membered ring molecule with two adjacent hetero atoms, nitrogen and sulfur. Previous studies of millimeter-wave spectroscopy have been conducted below 35 GHz 1-4, and at data higher frequencies are desired. Therefore, we performed a new measurement in the region of 40-560 GHz at room temperature.

The ground state, and the vibrational excited states (v1 = 1, v2 = 1, v3 = 1, v4 = 1, v5 = 1, v6 = 1, v7 = 1, v8 = 1, v9 = 1, and v10 = 1) were analyzed by using AAB, SPFIT/SPCAT 4 packages. More than 10000 lines were assigned and analyzed using Watson’s A-reduced Hamiltonian.
ELECTRICAL DISCHARGE OF NITROGEN CONTAINING MOLECULES: A DETAILED STUDY OF THE DIS-
CHARGE PRODUCTS OF PYRROLE AND PYRIDINE

EVA GOGUGOŁA, DONATELLA LORU, GAVATRI BATRA, MELANIE SCHNELL, FS-SMP, Deutsches
Elektronen-Synchrotron (DESY), Hamburg, Germany.

Five- and six-membered aromatic rings have received significant attention in the exploration of interstellar space. Not
only have recent detections expanded our understanding of interstellar chemistry but also highlight the timeliness and impor-
tance of investigation of the laboratory rotational spectra of such molecules. Following the detections of cyclopentadiene and
benzene via rotational and infrared spectroscopies, respectively, their respective nitrogen containing analogues, pyrrole
(C5H4N) and pyridine (C5H5N), call for extensive investigation of their rotational spectra as well as their chemistry under
harsh energetic conditions.

Here, we present a detailed study of the products of pyrrole (C5H4N) and pyridine (C5H5N) generated through electrical
discharge of the precursors and supersonic expansion. The spectra of the resulting species are simultaneously recorded with
a Chirped Pulse Fourier Transform Microwave (CP/FTMW) Spectrometer operating in the 18-26 GHz frequency region. The
observed species, varying from cyclopentene to linear cyanopyrroles, contain both fewer and more, or the same number of
aromatics as their respective precursors suggesting that both fragmentation and recombination processes take place during
electrical discharge. Our results support the detection of related molecules in the interstellar medium which may also provide
an insight into potential pathways around their formation.


SPECTROSCOPIC AND COMPUTATIONAL CHARACTERIZATION OF 2-AZA-1,3-BUTADIENE, A MOLECULE
OF ASTROCHEMICAL SIGNIFICANCE

NINGJING JIANG, MATTIA MELOSSO, Dept. Chemistry “Giacomo Ciamician”, University of Bologna,
Bologna, ITALY; LUCA BIZZOCCHI, Dipartimento di Chimica G. Ciamician, University of Bologna,
Bologna, Italy; SILVIA ALESSANDRINI, Scuola Normale Superiore, Pisa, Italy; J-C. GUILLEMIN, Ecole

In this work, we relied on a solid computational study to complete the experimental data available in literature. The ac-
curate spectroscopic characterization of 2-azabutadiene (C3H3N2) family which has not been observed in the
ISM, while unsaturated carbon chains like C5V and C5N-2 can play important roles in reactivity, e.g., the
pathways leading to the formation of aromatic molecules. In this work, we relied on a solid computational study to complete the experimental data available in literature. The ac-
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ISM, while unsaturated carbon chains like C5V-2 can play important roles in reactivity, e.g., the
pathways leading to the formation of aromatic molecules.
ANALYSIS OF THE HIGH RESOLUTION ROTATIONAL SPECTRUM OF 2-CHLOROETHANOL

HAYLEY BUNN, BRIAN J. ESSELMAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; ANDREW WRIGHT, STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA; SUSANNA L. WIDICUS WEAVER, Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA.

2-Chloroethanol (HOCH2CH2Cl) is the smallest terrestrially stable chlorohydrin and is predicted to exist in the interstellar medium, forming from HCl with either oxirane or ethylene glycol, each of which are known interstellar constituents. Rotational and ro-vibrational spectra of 2-chloroethanol have been previously reported from 9-40 GHz and 100-500 cm⁻¹, respectively. However, attempts at the detection of 2-chloroethanol towards Sgr B2(N) have been unsuccessful. It is uncertain if the detection arises from its lack of presence in this sightline, or whether the extrapolated spectral information for 2-chloroethanol is not of sufficient accuracy to guide astronomical searches. Therefore, we have measured the spectrum of 2-chloroethanol from 140 to 700 GHz to further improve the molecular constants and provide spectral frequencies directly comparable to radio telescope data. Analysis of this spectrum has resulted in the determination of refined rotational constants and centrifugal distortion constants up to the octic level for both naturally occurring Cl isotopologues. Partially resolved nuclear quadrupole coupling arising from the presence of the chlorine atom is observed throughout the spectral range. New spectra from 8 to 26 GHz have been obtained to refine the quadrupole coupling constants with well resolved microwave transitions. We also have tentative least-squares fits of transitions for all vibrationally excited states below 500 cm⁻¹ for each isotopologue, where the majority appear to be perturbed by Coriolis interactions. Analysis of the vibrationally excited states will be facilitated by the previously published high resolution far-IR data and may provide new insights into the vibrational energies and coupling interactions of these states. Here we will report the in-depth spectral analysis of the rotational spectrum of 2-chloroethanol.

We have previously reported the development of a high speed algorithm for the calculation of asymmetric rotor spectra. Probabilistic matches that can be readily evaluated by hand. Since its original release, we have added several new features, including support, and new calculation types. We will discuss the program, improvements, and implementation of its new features.
TE. Chirality and stereochemistry
Tuesday, June 21, 2022 – 8:30 AM
Room: 1024 Chemistry Annex
Chair: Ha Vinh Lam

Molecular parity violation has been critically discussed in relation to biomolecular homochirality in the early evolution of life. In this context molecules of potential importance for prebiotic chemistry like the small, chiral three-membered carbocycle molecule aziridine-2-carbonitrile (C₃H₅N) are of interest. Indeed, this molecule has been previously examined and the parity violating energy difference between the enantiomers in their ground state has also been calculated. Molecular parameters for the ground state of this molecule are available from earlier microwave studies, and its conformations have been examined by ab initio theory. Here we report initial results of a high resolution spectroscopic study of aziridine-2-carbonitrile, carried out at room temperature with an instrumental resolution of 0.0011 mm⁻¹ in the 800-1000 cm⁻¹ region using the Bruker BIFS15 Zurich Prototype (2001) Fourier transform spectrometer. Transitions in the ν₁ and ν₁̅̅̅ bands have been assigned, and molecular parameters have been determined using the Watson Hamiltonian. Simulations performed using these parameters reproduce the observed spectra well. The results are discussed in relation to astrophysical spectroscopy and recent efforts on parity violation in chiral molecules.

KAREN KEPPFER, SIEGHAARD ALBERT, CARINE MANCA TANNER, MARTIN QUACC, Laboratorium für Physikalische Chemie, ETH Zürich, Zurich, Switzerland; JÜRGEN STOHNER, ICTR Institut für Chemie und Biotechnologie, ZHAW, Winterthur, Switzerland.


TE02 8:48 – 9:03
TRANSIENT CHIRALITY AND MICROSOLVATION IN p-ETHYLPHENOL
JUAN CARLOS LOPEZ, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid; FERNANDO MACARIE, Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain; SUSANA BLANCO, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid, Valladolid, Spain,

p-Ethylphenol (PEP) and other volatile phenols appear in wines contaminated with Brettanomyces yeast giving undesirable off-aromas (“Brett” or phenolic character) which spoil wines even at very low concentrations. These phenols are produced by an enzymatic transformation of the hydroxycinnamic acids present in wines. In this work, we have analyzed the rotational spectrum of PEP and its microsolvated complexes using FTMW spectroscopy in the 2-0 GHz region. The equilibrium configuration of PEP has the ethyl group carbon plane perpendicular to the phenyl ring while the OH group lies in the ring plane. The two possible orientations of the OH group originate two non-superposable enantiomeric forms, energetically equivalent, but with opposite signs for the μ₀ electric dipole component. The interconversion of both enantiomers by the OH internal rotation leads to a situation of transient chirality. This motion is expected to have a two-fold periodic potential energy function with the torsional states appearing as doublets as happen in phenol. The rotational spectrum reflects this behavior. The μ₀ spectrum consists of single lines resulting from the collapse of the individual torsional 0° and 180° spectra. The μ₀ transitions, forbidden within each torsional state, are allowed as chiral 0° → 0° transitions. Therefore, the μ₀-type spectrum consists of doublets spaced twice the energy difference between the 0° and 180° torsional states. We have observed the 1H, 13C and OD isotopologues and have determined the molecular structure of PEP alone with the internal rotational potential energy profile. In addition, we have measured the spectra of the PEP-H₂O, PEP-Ne-H₂O and PEP-H₂O₂ complexes. The PEP-H₂O and PEP-Ne-H₂O spectra show doublets with 1:1 intensities revealing the water rotation dynamics exchanging the H atoms. For these species the spectra of different isotopologues 1H₂, 13C, D, 14O, and 2H₂ have also been measured to determine their structures.

JUAN CARLOS LOPEZ, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid; FERNANDO MACARIE, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid; SUSANA BLANCO, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid, Valladolid, Spain.

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TE03 9:06 – 9:21
THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE CHIRAL AND ACHIRAL ROTAMERS OF 2,3,3-TRIFLUOROPROPENE AND THEIR GAS PHASE HETERODIMERS WITH THE ARGON ATOM
HELG N. LEUNG, MARK D. MARSHALL, TAH A. AHMAD, DAVID W. BORDEN, CAITLIN HOFFMAN, NAVIE KIM, Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA; GRETA KOUMARIANOU, Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA; LINCOLN SATTERTHWAITE, DAVID SORENSEN, Physics, University of California, Santa Barbara, CA, USA,

The three minima obtained upon rotation of the difluoromethyl group in 2,3,3-trifluoropropylene correspond to a higher energy, achiral rotamer that contains a plane of symmetry while the two minima that share a lower energy value characterize a chiral, enantiomeric pair. Four isotopologues of each form are observed in the microwave rotational spectrum obtained using a pulsed-jet, chirped pulse Fourier transform spectrometer and the spectra of all eight have been assigned and analyzed. Additionally, spectra for four isotopologues of the gas phase heterodimer formed between the chiral rotamer and an argon atom have been obtained and analyzed using a narrowband, Balle-Flygare cavity Fourier transform instrument. For the heterodimer of the achiral rotamer with argon, only the spectrum of the most abundant isotopologue has been observed.

JUAN CARLOS LOPEZ, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid; FERNANDO MACARIE, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid; SUSANA BLANCO, Departamento de Química Física y Química Inorgánica - U. CINQUIMA, Universidad de Valladolid, Valladolid, Spain.

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TE01 8:30 – 8:45
HIGH RESOLUTION INFRARED SPECTROSCOPY OF AZIRIDINE-2-CARBONITRILE (C₃H₅N)
KAREN KEPPFER, SIEGHAARD ALBERT, CARINE MANCA TANNER, MARTIN QUACC, Laboratorium für Physikalische Chemie, ETH Zürich, Zurich, Switzerland; JÜRGEN STOHNER, ICTR Institut für Chemie und Biotechnologie, ZHAW, Winterthur, Switzerland.


TE04 9:24 – 9:39
HIGH PRECISION SPECTROSCOPY AND CONTROLLED DIMER FORMATION IN A CRYOGENIC ENVIRONMENT
DAVID PATTERSON, Physics, University of California, Santa Barbara, CA, USA; GRETA KOUMARIANOU, Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA; LINCOLN SATTERTHWAITE, DAVID SORENSEN, Physics, University of California, Santa Barbara, CA, USA,

A cryogenic buffer gas cell at a few degrees Kelvin provides a bright source of internally cold and slow moving molecules. I will be presenting recent results from our buffer gas spectrometers, including direct observation of dimer formation with conformationally selected reagents and high-resolution spectroscopy in slow, bright buffer-gas cooled molecular beams.
TE05  9:42 – 9:57
BROADBAND MICROWAVE 3-WAVE MIXING: ASSIGNMENT-FREE CHIRALITY DETECTION IN UNKNOWN SAMPLES
G RETA KOU MARIANOU, Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA, I RENE WANG, Physics, University of California, Santa Barbara, CA, USA, LINCOLN SAT TERTHWAITE, Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA, DAVID PATTERSON, Physics, University of California, Santa Barbara, CA, USA.

Straightforward identification of chiral molecules in multi-component mixtures of unknown composition is extremely challenging. Current spectrometric and chromatographic methods cannot unambiguously identify components while the state of the art spectroscopic methods are limited by the difficult and time-consuming task of spectral assignment. Here, we introduce a highly sensitive generalized version of microwave three-wave mixing that uses broad-spectrum fields to detect chiral molecules in enantiomeric excess without any prior chemical knowledge of the sample. This method does not require spectral assignment as a necessary step to extract information out of a spectrum. We demonstrate our method by recording three-wave mixing spectra of multi-component samples that provide direct evidence of enantiomeric excess. Our method opens up new capabilities in ultrasensitive phase-coherent spectroscopic detection that can be applied for chiral detection in real-life mixtures, raw products of chemical reactions and difficult to assign novel exotic species.

Intermission

TE06  10:39 – 10:54
THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF THE CHIRAL TAGGING CANDIDATE CS-1,3,3,3-TETRAFLUORO-1,2-EPoxypropane AND ITS GAS PHASE HETERODIMER WITH THE ARGON ATOM
J OnA H. H o r o w itz, HELE N O. L e u n g, M ARK D. M ARSHALL, Chemistry Department, Amherst College, Amherst, MA, USA.

We are exploring how argon binding to substituted oxiranes, which have potential applications as chiral tags, is modulated by varying the identity of the substituents on the epoxy ring. Previously studied systems generally showed close contacts primarily to atoms contained in the ring. However, for complexes with CS-1,3,3,3-tetrafluoro-1,2-epoxypropane (cPTO) multiple minima with similar energies are predicted by quantum chemistry calculations including some with significant interactions between the argon atom and substituents on the oxirane. Analysis of the rotational spectra obtained using chirped pulse Fourier transform microwave spectroscopy for four isopropyls of Ar-cPTO reveals that the argon atom binds to the back of the ring, very different from Ar-3,3,3-trifluoro-1,2-epoxypropane (Ar-PTO) and Ar-3,3,3-difluoro-1,2-epoxypropane, but similar to Ar-trans-1,3,3,3-tetrafluoro-1,2-epoxypropane. The utility of cPTO in chiral analysis is explored via quantum chemistry calculations on the TFO-cPTO heterodimer and progress on the observation and analysis of the two diastereomeric forms of this species will be reported.

TE07  10:57 – 11:12
THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF CIS- and TRANS-1,1,1-TRIFLUORO-2,3-EPoxybutane
M ARK D. M ARSHALL, HELE N O. L EUNG, CAIT LIN N IGHT, Chemistry Department, Amherst College, Amherst, MA, USA.

Connected to our efforts in characterizing substituted oxiranes for use as potential chiral tags for the conversion of enantiomeric molecules into spectroscopically distinct diastereomeric complexes for chiral analysis, we have obtained and analyzed the spectra of both the cis and trans isomers of 1,1,1-trifluoro-2,3-epoxybutane. Although the spectrum of the trans isomer and all four of its singly-substituted C13 isotopologues, obtained in natural abundance, could be satisfactorily analyzed as a centrifugally-distorting rigid rotor asymmetric top, the spectrum of the cis isomer showed the effects of methyl group internal rotation. Progress on assigning and analyzing the spectrum of this isomer will be reported.
ANISOTROPIC CIRCULAR DICHROISM SPECTROSCOPY OF JET-COOLED CHIRAL MOLECULES

CHANGSEOP JEONG, NAM JOON KIM, Chemistry/Lab of ion and laser chemistry, Chungbuk National University, Chungmuh, Chungbuk, Republic of Korea.

Circular dichroism (CD) spectroscopy is one of the most powerful methods to investigate the structures and reactions of chiral molecules. The CD of molecules with fixed spatial distribution is called anisotropic CD (ACD). ACD spectroscopy has been extensively used to probe the orientation of macromolecules in anisotropic medium. Here, we have obtained the resonant two photon ionization CD (R2PICD) spectra of c-PED using a dual laser beam method. It is found that the CD values of the P-, Q-, and R-branch transitions of the origin bands are different from each other. Furthermore, the CD values of the rotational transitions of conformers A and C do not exhibit mirror images between (+) and (-)PED. These results are explained by ACD phenomena of jet-cooled molecules undergoing the P-, Q-, and R-branch transitions.

We report and interpret recently recorded high resolution infrared spectra for the fundamentals of the CH stretches and SC-OH internal rotation, the interaction Hamiltonians for TA and TA-S required the term $F_{bc} = \{ P_{bc} + P'_{bc} \}$. In contrast, the Coriolis term $\mu$-tensors, of both the right- and left-handed forms of the gauche conformers need to be expressed in the same molecule-fixed axis system; 2) The Cartesian coordinates of some or all atoms and the components of 1 depend on the internal rotation coordinate $\tau$. If we define a Cartesian axis system with two of the axes in the symmetry plane of the transition state between the two conformers, the third axis is perpendicular to it. When $\tau$ changes, the moving atoms will eventually cross the symmetry plane and their 3rd Cartesian coordinate will change its sign and with it also the signs of two off-diagonal components of $I$ and the $\mu$-tensors.

Detailed explanations and a demonstration that this particular interaction may be especially important for $K_C = 1$ energy levels will be presented.

This study was triggered by the results of the microwave investigation of triflic acid (TA), CF$_3$SO$_2$OH, and its deuterated (TA-d) and $^{13}$C(TA-S) isotopologues by Huff et al.$^a$ To fit the observed transitions split by gauche-gauche tunneling due to the CS-OH internal rotation, the interaction Hamiltonians for TA and TA-S required the term $F_{bc} = \{ P_{bc} + P'_{bc} \}$. In contrast, the Coriolis term $\mu$-tensors had to be used for TA-d.

The $F_{bc}$ terms result from two facts: 1) The moment of inertia tensor $I$ and its inverse, the $\mu$-tensors, of both the right- and left-handed forms of the gauche conformers need to be expressed in the same molecule-fixed axis system; 2) The Cartesian coordinates of some or all atoms and the components of $I$ depend on the internal rotation coordinate $\tau$. If we define a Cartesian axis system with two of the axes in the symmetry plane of the transition state between the two conformers, the third axis is perpendicular to it. When $\tau$ changes, the moving atoms will eventually cross the symmetry plane and their 3rd Cartesian coordinate will change its sign and with it also the signs of two off-diagonal components of $I$ and the $\mu$-tensors.

The rotational Hamiltonian in a 2-by-2 block format contains the contributions of the right and left gauche conformers ($H_{KL}$ and $H_{KL}$, respectively) on the diagonal and the Coriolis interactions in the off-diagonal blocks. If the internal rotation wave functions $\phi_a$ and $\phi_b$ are symmetrized to $H_{bc}$ and $H_{bc}$ to conform with $C_s$ symmetry, the diagonal blocks of the Hamiltonian become $H_{bc}$ and $H_{bc}$. The off-diagonal blocks contain now the Coriolis terms and the contributions from the sign-changing $\mu$-tensor components.

Detailed explanations and a demonstration that this particular interaction may be especially important for $K_C = 1$ energy levels will be presented.

We report a combination of quantum mechanical calculations and different spectroscopic techniques used to investigate in the gas phase N,N-dethyldihydroxylamine (DEHA), an important scavenger compound. The molecule has been first studied by rotational spectroscopy using Pulsed Jet Fourier Transform Microwave (PJ-FTMW) spectrometer in the 6.5-18.5 GHz frequency range and Stark modulated Free Jet Absorption Millimeter-Wave (FJ-AMM-W) spectrometer in the 59.6-74.4 GHz range. Three conformers have been overall observed. They are all characterized by the hydroxyl hydrogen atom being in trans isomerism with respect to the bisector of the NNC angle. For the global minimum, also the 13C and 15N isotopologues have been observed in natural abundance, allowing for the core structure determination. Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron spectroscopy (XPS) measurements have been performed at the Gas Phase Photoemission beamline (GapPhase) of the Eletra Synchrotron light laboratory (Trieste, Italy). The core (C(1s), N(1s) and O(1s)) photoemission spectra have been assigned with the support of SAC-CI/Cc-pVTZ calculations. Density Functional Theory (DFT) approaches, including Time-Dependent DFT, have been exploited to reproduce the outer valence electron binding energies and peaks profiles, through the calculation of the Huang-Rhys factors. Interestingly, the resulting spectroscopic database is quite precious for detecting in the interstellar medium. Many hundreds of transitions were collected in the 130 – 575 GHz range for each isomer, but s-trans-Z-1-cyano-1,3-butadiene is the only isomer with an isolated ground state. s-trans-Z-1,Cyano-1,3-butadiene ($\mu_0 = 3.6$ D, $\mu_1 = 2.3$ D, MP2/6-311+G(2d,2p) is a probe ($\omega = -0.9$ cm$^{-1}$), asymmetric top with C$_3$ symmetry, and its ground state was fit to a partial octic, distorted rotor Hamiltonian model with over 5500 distinct transitions. The lowest-energy vibrationally excited state ($v_0, 2_0^-$) is predicted to be 129 cm$^{-1}$ higher in energy than the ground state and is close in energy to the second-lowest energy vibrationally excited state ($v_0, 2_1^-$). These states form a Coriolis coupled dyad with intense coupling along the $\mu_0$- and $\mu_1$-principal axes causing the formation of sharp local resonance hundreds of MHz away from their unperturbed predicted frequencies. This presentation will detail the effects of strong Coriolis coupling in a dyad of vibrational states < 6 cm$^{-1}$ apart and the strategies used to assign and least-squares fit these transitions.


**Intermediate**
HYDROXYL GROUPS TORSIONAL MOTION IN CATECHOL MOLECULE

DARYA A KISURYNA, Physics, University of Maryland, College Park, MD, USA; ALEX MALEVICH, ARYNA KHIRAPUNOVA, Physics, Belarusian State University, Minsk, Belarus; ULADZIMIR SAPESHKA, Department of Physics, University of Illinois at Chicago, Chicago, IL, USA; GEORGE PITSIVECH, Physics, Belarusian State University, Minsk, Belarus.

Catechol molecule $C_6H_4(OH)_2$ is the representative of a separate class of aromatic hydrocarbons. It is an important component of biochemical, industrial and commercial products. In a recently published article [1] rotationally resolved Fourier Transform far-infrared spectrum of the free and bonded O $\rightarrow$ H groups forming the intramolecular hydrogen bond was recorded. The authors were also able to measure pure rotational spectrum in the 70–230 GHz frequency range using a millimeter-wave spectrometer. Splitting due to tunneling was resolved for free O $\rightarrow$ H torsional state. Having this solid experimental background, we have performed extensive calculations of the kinetic parameters and 2D potential energy surfaces formed by variation of the O $\rightarrow$ H torsional coordinates of the catechol molecule at few levels of theory. It was found that almost all used levels of theory very well predict the frequency value of the fundamental torsional vibration of the free hydroxyl group: $224 \pm 227$ cm$^{-1}$, while experimental value is $221.9$ cm$^{-1}$. At the same time calculated frequencies of the $H$ $\rightarrow$ bonded hydroxyl group torsional fundamental vibration is higher $(422 \pm 425$ cm$^{-1})$ than experimental one $(415$ cm$^{-1})$. We associate this difference with overestimating intramolecular $H$ $\rightarrow$ bond energy in the frame of used levels of theory. It is also worth noting that there was a good agreement between calculated and experimental tunneling splitting of the first excited torsional state of free $O$ $\rightarrow$ $H$ group $(8 \times 10^{-4}$ and $1 \times 10^{-3}$ respectively). Besides, complete information about the second conformer of the catechol molecule with $C_2$ symmetry has been obtained.


ORIGINS OF THE INTENSITY OF THE STRETCH-BEND COMBINATION TRANSITION IN WATER CLUSTERS AND IMPLICATIONS FOR CHARACTERIZING HYDROGEN BONDING

RACHEL M. HECIMALA, ANNE B. McCLOY, Department of Chemistry, University of Washington, Seattle, WA, USA.

Water and hydrogen bonding have been actively studied for many years. The unique features of hydrogen bonding lead to processes such as proton transport which is essential to a variety of chemical, biochemical, and electrochemical processes. Despite the longstanding interest, many questions still remain surrounding the intricacies of hydrogen bonding. One goal of this study is to understand how the strength and other properties of hydrogen bonding can be extracted from the spectral signatures near 5000 cm$^{-1}$, which corresponds to combinations involving the HOH bend and the OH stretch. This region is of interest because, like the bend region, the intensities are relatively insensitive to the hydrogen bonding environment. At the same time, unlike the bend fundamental region, the frequencies of the transitions reflect the hydrogen bond strength as they follow the trends for the $\nu=1$ levels of the OH stretches. This makes interpretation easier and introduces an interesting question, what are the origins of the intensities of the bend and the combination transitions? In order to investigate this question, we use various structures of water clusters, and dissect the intensity of the combination transition into mechanical and electrical contributions. Through this process, we are able to gain insights into the origin of the intensities. Further for the electrical contributions, we explore how the bending vibration is tuning the transition moment for the OH stretch.

SPECTROSCOPY AND BRAIN CHEMISTRY OF SEROTONIN AND DOPAMINE CONFORMERS

VIPIN BAHADUR SINGH, Department of Physics, Udaipur Pratap Autonomous College, Udaipur, India.

The neurotransmitters Serotonin and Dopamine are thought to play a distinct role in brain chemistry and human behavior. In the present work we will discuss the Conformer specific spectroscopic signatures of protonated Serotonin and Dopamine in the gas phase and aqueous media. A comparison of the computed frequencies of protonated Dopamine with the observed Raman spectrum indicates that gauche and trans conformers coexist in the liquid dopamine and exhibit population redistribution upon a change in pH during stress. Since the trans-conformers have more affinity for the receptor site than the gauche conformers, the higher population distribution of trans conformers is hypothesized to be associated with efficient neurotransmission and normal human behavior. The strong cation-pi interaction in the isolated gauche conformers of serotonin in the gas phase is predicted to be a possible cause of human aggression. 1. VIPin Bahadur Singh, ACS Chem Neurosci. 12, 613-625 (2021)

TORSIONAL POTENTIALS, BARRIER TO INTERNAL ROTATION, MOLECULAR STRUCTURE, VIBRATIONAL PROPERTIES, NLO BEHAVIOUR AND NBO CHARACTERISTICS OF 2-(PHENYL-SULFONYL)-VINYL-BENZENE AND 2-(TOSYL)-VINYL-BENZENE EMPPLOYING FT-IR, FT RAMAN SPECTRAL TECHNIQUES AND DFT APPROACH

K SHISHA LAHMAM, PHYSICS, SR UNIVERSITY, HANAMKONDHA, TELANGANA, INDIA; BALAKRISHNA AE, G. RAMANA RAO, Department of Physics, KAKATIYA UNIVERSITY, WARANGAL, India.

2-(Phenyl-sulfonyl)vinylbenzene (2PVB) and 2-(Tosyl)vinylbenzene (2TVB) molecules were characterized, by recording their FT-IR(4000-400 cm$^{-1}$) and FT Raman(4000-50 cm$^{-1}$) spectra. Torsional potentials, barrier to internal rotation around phenyl-sulfonyl C=S bond, sulfonyl-vinyl S-C bond, vinyl-benzene C=C bond, and phenyl-methyl C-C bond (this bond is relevant for 2TVB only). Optimized structure parameters, general valence force field, harmonic vibrational fundamentals, potential energy distribution, infrared and Raman intensities, frontier molecular orbital parameters, NLO behaviour and NBO characteristics were determined using density functional theory, employing B3LYP exchange-correlation in conjunction with functional 6-311+G(d,p) basis set. Time dependent DFT was made use of to compute absorption maxima ($\lambda_{\text{max}}$) and oscillator strengths, for both molecules, in their electronic transitions, in DMs0-d6 solution. Good agreement was found, between measured and computed parameters involving structure parameters, IR and Raman spectra and UV-Vis transitions. The rms error between experimental and theoretical vibrational frequencies was 6.4 and 4.35 cm$^{-1}$, for 2PVB and 2TVB, respectively. With the help of PED and eigenvectors, all vibrational fundamentals of both the molecules were assigned for the first time. The computations demonstrated that both the molecules were good for NLO applications, that was substantiated by NBO analysis for both 2PVB and 2TVB.
Theoretical and experimental rotational spectroscopic studies of substituted benzoic acid heterodimers

Mohamad H. Al-Jabri, Department of Chemistry, University of Alberta, Edmonton, AB, Canada; Mile Hael Erakovic, Department of Physical Chemistry, Ruder Bošković, Zagreb, Croatia; Aran Insassut, Departamento de Química Física, Universidade do País Vasco (UPV-EHU), Bilbao, Spain; Marko Cytas, Department of Physical Chemistry, Ruder Bošković, Zagreb, Croatia; Wolfgang Jager, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.

The complex tunnelling dynamics of double proton transfer in carboxylic acid dimers has been the focus of many theoretical and experimental studies. The combination of spectroscopic and computational approaches to model and understand how functional groups in substituted benzoic acid heterodimers can influence these dynamics. Dimers of benzoic acid with its 4-chloro-, 4-nitro-, and 4-amino-analogues were studied using a 2 to 6 GHz chirped-pulse Fourier transform microwave spectrometer, which is based on the design by Pates et al. to obtain experimental tunneling line splittings. Jacobs field instanton theory (JFI) was used to compute tunneling splittings in the ground vibrational state. The use of the JFI method, which necessitates a smaller number of potential energy and gradient calculations compared to other methods, enabled us to use ab initio on-the-fly potentials and compute the splitting in full dimensionality, in spite of the large system sizes. Furthermore, final expressions for the tunneling splittings provided a way to examine the influence of substituents on both the potential initio on-the-fly potentials and compute the splitting in full dimensionality, in spite of the large system sizes. Furthermore, final expressions for the tunneling splittings provided a way to examine the influence of substituents on both the potential energy barrier height and shape, and on the vibrational modes, which can either promote or inhibit tunnelling.


TG. Vibrational structure/frequencies Tuesday, June 21, 2022 – 8:30 AM Room: 274 Medical Sciences Building Chair: Stephen J. Daunt, University of Tennessee, Knoxville, TN, USA

TG01 8:30 – 8:45

Is it possible to improve theoretical prediction of the frequencies of the torsional vibrations by accounting ZPVE? Testing most simple molecules

George Pitsevich, Alex Malevich, Aryna Kirapunova, Physics, Belarusian State University, Minsk, Belarus; Uladzimir Sapelnka, Department of Physics, University of Illinois at Chicago, Chicago, IL, USA; Dar’ya Kuryukova, Physics, University of Maryland, College Park, MD, USA.

Torsional vibrations and internal rotation are the one kind of large amplitude motion in polyatomic molecules and clusters. It is well known that the standard approach within the frame of harmonic approximation to calculating the frequencies of torsional vibrations is unworkable. In this case, one must calculate full potential energy surface (PES) while varying torsional coordinates throughout all intervals of their determination. Recently, when calculating PES, one must take into account zero-point vibrational energy (ZPVE). Sometimes it leads to an improvement in the agreement between calculated and experimental data, and sometimes it rather worsens the agreement between them [1,2]. To obtain more complete information on the efficiency of taking into account ZPVE, we have made a calculation of energy of stationary torsional states for hydrogen peroxide and methyl alcohol molecules with and without taking into account ZPVE. It is well known that there is much more experimental data about the energy of excited torsional states for these molecules than for any others. The calculations were performed on several levels of theory.


TG02 8:45 – 9:03

First high-resolution study of vibrationally excited states \( \nu_1 \) and \( \nu_2 \) of propylene oxide

Karel Vavra, Eileen Doring, Jan Jakob, Guido W. Fuchs, Pascal Stahl, Arne Vereiden, Marcel Schlesag, Thomas Giessen, Institute of Physics, University of Kassel, Kassel, Germany.

Propylene oxide, \( \text{CH}_2\text{CH} \equiv \text{CH}_2 \), is a stable chiral molecule that gained new attention through its recent radio astronomical discovery in the interstellar medium toward the galactic center. Subsequently, extensive laboratory data on rotational transitions in the ground state and in the lowest vibrationally excited \( \nu_2 \) torsion state were published. Previously, only the 3 cm spectral range of the four C-H stretching vibration modes was measured with high spectral resolution at mid-infrared wavelengths.

In the present study we used two quantum cascade laser spectrometers at 8 and 10 µm to record ro-vibrational spectra of the \( \nu_2 \) fundamental mode (\( \text{CH}_2 \text{rock} \)) at 1023 cm\(^{-1}\) and the \( \nu_1 \) ring breathing mode at 1266 cm\(^{-1}\). The spectra were measured in a static cell at room temperature and in a supersonic jet expansion at low temperatures. The room temperature measurement allowed a quick assignment via graphical techniques (Loomis-Wood diagram) and determination of the molecular parameters using the SPT/SPCAT program package. In the supersonic jet spectrum line splittings could be observed for certain transitions. The combination of measurements at low temperature (30 K) and at room temperature conditions led to an assignment of hundreds of transitions of the very dense infrared spectrum and covers quantum numbers from lowest J and K up to \( J = 55 \) and \( K_a = 56 \).
CHARACTERIZATION OF 4-PYRONE PYROLYSIS PRODUCTS VIA MATRIX-ISOLATION FT-IR

KHALED ALEY EL-SHAZLY, LAURA R. MCCUNN, Department of Chemistry, Marshall University, Huntington, WV, USA

The characterization of the byproducts of biomass pyrolysis is an integral part in the development of viable biofuels and renewable energy sources. 4-Pyrones, (IUPAC name: 4-pyran-1-one) are one of the by-products observed in the pyrolysis of many forms of biomass, such as wood chips, straw, and cotton husks. Using the technique of argon matrix-isolation FT-IR spectroscopy, the pyrolysis products of 4-pyrones were characterized by performing a diluted sample of 4-pyrones through a heated silicon carbide tube onto a cold window that captures the products and allows for their analysis via FT-IR spectroscopy. Computational analysis using Gaussian 09 was also utilized to model the unimolecular decomposition pathways, and these results were compared to the experimental spectra for product identification. Current data collected at pyrolysis temperatures ranging between 900 K and 1400 K indicate the formation of acetylene, vinylacetylene, propyne, and carbon monoxide. The formation of formylketene is also likely, as some peaks have been observed that match computational predictions.

WEAKLY-BOUND COMPLEX FORMATION BETWEEN HCN AND CH

EMILY K HOCKETT, 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; THOMAS HOWARD, JESSICA PALKO, LEAH G DODDSON, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA.

Matrix-isolation spectroscopy is used to characterize the weakly-bound complex(es) of hydrogen cyanide with methyl boronic acid, two astrophysically relevant molecules. HCN and its polymers capture interstellar discussions of protobiotic monomers and other life-bearing polymers, while CH2 leads as the first organohalogen detected in space. This highlights the importance of studying their reactivity. In this talk, we will describe our new matrix-isolation instrument, constructed at the University of Maryland, and how we identify the structure of the weakly-bound complexes [(HCN), (CH2)] that form upon co-condensation of HCN and CH2 in an argon matrix. Infrared spectroscopy is used in tandem with quantum chemistry calculations to characterize the vibrational spectrum of the resulting complexes. Our work reveals preferential formation of matrix-isolated HCN-trimer species in the presence of CH2, which qualitatively characterizes the results of our computational calculations. Finally, we will discuss the astrochemical implications of the resulting complexes and CH2 inner formation.

SUPERSONIC JET CAVITY RING DOWN SPECTROSCOPY OF MOLECULES IN THE MID INFRARED

FABIAN PETERS, GUIDO W. FUCHS, Institute of Physics, University of Kassel, Kassel, Germany.

Many molecular compounds of spectroscopic interest are difficult to produce or can only be produced in situ with low production rates, e.g., transient species. One way to produce such species is to use a discharge source in combination with a supersonic jet expansion. The hereby rotationally cooled spectra increase the line intensity at low rotational quantum numbers and ease the detection of absorption features. Nevertheless, the detection of rare species remains difficult and requires an extremely sensitive detection scheme. The Cavity Ringdown (CRD) technique with its high sensitivity is ideally suited to address this kind of problem. In addition, CRD spectroscopy can also be used to detect very weak molecular rovibrational transitions of otherwise well-known stable molecules.

While CRD spectroscopy of supersonic jets is a new idea, the application to wavelengths in the mid-IR (2.5-µm - 4.5-µm), where CH3, N2H, and CH stretching vibrations can be investigated, only got possible in recent times with the availability of suitable laser sources and highly reflective dielectric mirrors for this wavelength range. Here, we report about our progress in building up a CRD spectrometer operating in the mid infrared range utilizing a tunable cw-OPO laser system with high-quality cavity mirrors (R>99.99%) between 3µm - 3.4µm. First spectroscopic results will be presented.

INTERMIXION

JESSE CROMER, ROBERT FONARES, Department of Physics, University of Maryland, College Park, MD, USA.

Proton-coupled electron transfer (PCET) has been of great interest in chemical and biochemical catalysis. The electron transfer process in numerous biomimetic systems has been investigated in solution, but direct interrogation of the proton transfer coordinate remains largely unexplored. We have measured cryogenic iron biomimetic spectral series of phenol-benzimidazolyl proton-coupled electron transfer model complexes with cryogenic iron biomimetic spectral series. Highly redshifted and broadened H-bonded OH stretch transitions were observed throughout the model series. Isotopic substitution and anharmonic vibrational calculations suggest that the broadness arises from an interplay between strong OH stretch- and Fermi resonance interactions and coupling of the OH stretch to low frequency H-bond soft-mode motions accessible at the zero-point level. The effects of steric hindrance, resonance stabilization and charge distribution are also investigated through systematic structural variation of the model compounds.
CRYOGENIC IR SPECTROSCOPY OF CARBANION INTERMEDIATES: CIRCUMAMBULATORY REARRANGEMENT FOLLOWING DECARBOXYLATION OF BENZOIC ACID DERIVATIVES

OLIVIA MOSS, JOSEPH P. MESSINGER, EVAN H. HEPREV, ANNA GABRIELLA DEL ROSARIO RULLÁN BUJO, TIM SCHLEIF, Department of Chemistry, Yale University, New Haven, CT, USA; KIM GREIS, Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany; MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

Collusion induced dissociation (CID) of benzoates, the conjugate bases of benzoic acids, tend to form highly reactive carbaniomers. This study specifically investigates a series of formylbenzoic acid (FBA) isomers and their respective decarboxylated phenides. Cryogenic ion vibrational predissociation spectroscopy (1000 cm−1 – 4200 cm−1) reveals the spectroscopic signatures of the 2, 3, and 4-FBA anions as well as those of the decarbonylates resulting from heterolytic C–C bond cleavage. Comparison of quantum chemical calculations with the isomer selective two color IR–IR photobleaching experiments confirms that the phenides isomerize after decarboxylation such that the anionic charge center migrates around the phenyl ring. The propensity for anti-to-site interconversions are observed to strongly depend on the starting location of the anionic charge center. These trends are considered in the context of the calculated barriers for charge migration by N–atom transfers and the initial energy content of the nascent species created by CID.

PROTON, HYDRIDE, OR NEITHER? THE IDENTITY OF H IN THE AUN Cluster

HANNA MORALES HERNANDEZ, JONATHAN WOOD FAGAN, CHRISTOPHER J. JOHNSON, Chemistry, Brown University, Providence, RI, USA

The diverse tunability of gold nanocontours via size, geometry, and ligand chemistry allows them to be optimized for greater catalytic activity, selectivity, and optoelectronic properties. The binding of a hydride to AunH4+ has raised the question of whether the hydride behaves as a metal dopant which donates its two electrons to the Au core or whether it behaves as an electron-withdrawing ligand such as CT- and Br-. We previously showed significant similarities between its electronic absorption spectrum to that of AunH4+Cl4− and AunH4+Br4−, but follow-up theoretical work suggested that this was a coincidence. Here we analyze the infrared absorption spectra of AunH4+H2O+ with a single N2 or H2O molecular physisorbed onto the cluster to further elucidate the role of the hydride in AunH4+H2O+.

INFRARED SPECTROSCOPY OF CARBONIUM SPECIES IN MOLECULAR BEAMS

SWETHA ERUKALA, ALEXANDRA J. FEINBERG, AMANDEEP SINGH, ANDREY VILEsov,*, Department of Chemistry, University of Southern California, Los Angeles, CA, USA

The electron impact ionization of helium droplets doped with ethylene molecules and clusters yields diverse C2H4+ cations embedded in the droplets. The ionization primarily produces C2H4+, C2H3−, C2H5+ and CH3++, whereas larger carbonopents are produced upon the reactions of the primary ions with ethylene molecules. The vibrational excitation of the cations leads to the release of rare cations and cations with a few helium atoms attached. The laser excitation spectra of the embedded cations show well resolved vibrational bands with a few wavenumber widths—an order of magnitude less than those previously obtained in solid matrices or molecular beams by tagging techniques. Comparison with the previous studies of free and tagged CH3+ , C2H4+ , C2H3−, C2H5+ , and C3H7+ cations shows that the helium matrix typically introduces a shift in the vibrational frequencies of less than about 20 cm−1, enabling direct comparisons with the results of quantum chemical calculations with the same level of theory.

In this work we describe a facile technique for the production and spectroscopic study of diverse carbonopents, which act as important intermediates in gas and condensed phases.

References:
PHOTOPHYICS OF NiII PYRIDINOPHANE PHOTOCATALYSTS USED FOR C-O CROSS-COUPLING REACTIONS

RACHEL WALLICK, JOSHI VURA-WEIS, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA; RENKIE VAN DER VEEEN, Photochemistry, Helmholtz Zentrum Berlin, Berlin, Germany.

Ni catalysis has garnered much attention over the past decades as a low-cost, abundant alternative to Pd catalysis. NiII cycles are thought to be critically important to the cross-coupling step in the catalytic cycle, but typical Ni catalysts contain bipyridine ligands which are generally unable to stabilize high-valent NiII. Tridentate pyridinophane ligands, on the other hand, are able to stabilize both high- and low-valent Ni, making them optimal ligands to use in Ni catalysis. Tridentate pyridinophane NiII dichloride complexes form a highly reactive NiII catalyst upon photoexcitation of the metal-ligand charge transfer (MLCT) band. This process is thought to occur from the 3d charge transfer state, though there is no experimental evidence for this and little is known about the photophysics following the photoexcitation of the MLCT transition. Optical transient absorption gives insight into the photophysics of the catalyst formation. We report highly-efficient back electron transfer (BET) following MLCT excitation. We will vary the excitation energy to investigate if the BET is suppressed or enhanced. We will perform transient XUV spectroscopy to probe the dynamics at the Ni M-edge and determine the states that are involved in the NiII catalyst formation.

ULTRASTRUCTURAL DYNAMICS OF THE INTRAMOLECULAR H-BOND IN ACETYLACETONE INVESTIGATED WITH 2D IR SPECTROSCOPY

JESSICA S. DEAN, Chemistry, Washington University in St. Louis, St. Louis, MO, USA; JOSEPH FOUNIER, Department of Chemistry, Washington University, St. Louis, MO, USA.

We report ultrafast transient absorption and 2D IR spectra of the light and deuterated isotopologues of acetylacetone to study the vibrational coupling and dynamics of the strong intramolecular hydrogen bond. Strong 2D IR cross-peaks in the fingerprint region reveal a high level of OH bend character throughout this region. This mode mixing gives rise to a large manifold of OH bend overtone and combination bands in the OH stretch region as evidenced by a highly elongated OH bend excited state absorption transition. As a consequence, strong OH stretch/bend Fermi resonance interactions contribute to a broad OH stretch absorption band that exhibits ultrafast population dynamics on a time scale less than 100 fs. The deuterated species displays similarly strong anharmonic coupling and relaxation dynamics, in addition to coherent oscillations corresponding to the O-H hydrogen bond stretch motion which are absent in the light isotope. Polarization anisotropy measurements shows a fast 200 fs reorientation relaxation of OH stretch while the OH stretch displays a slow 1 ps component. The large isotopic dependence of the anisotropy dynamics is attributed to a combination of differences in anharmonic couplings and proton/deuteron transfer dynamics in the vibrationally hot molecules.

RAPID FREQUENCY-COMB INFRARED SPECTROSCOPY WITH CROSS-DISPERSED SPECTROMETERS

D. MICHELLE BAILEY, JOSEPH P. HODGES, ADAM J. FLEISHER, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA.

Time-resolved spectroscopy with optical frequency combs combines rapid acquisition with high sensitivity, broad bandwidth, and high resolution.1 This presents an opportunity to study chemistry on a microsecond timescale with molecular specificity and multiplexing. Here we introduce two cross-dispersed comb spectrometers operating in two wavelength ranges of the infrared: one from 1.5 μm to 3.7 μm and another from 4.4 μm to 4.7 μm. In the latter mid-infrared region, we resolve the ro-vibrational lines of several isotopocules of nitrous oxide (N2O). Vibronic spectra simulated under the harmonic Franck-Condon approximation are ubiquitous tool for interpreting the structure of optical, photoelectron, and photoionization spectra. For transitions to bound final states located in a well on their potential energy surface, it is straightforward to calculate overlap integrals between discrete vibrational eigenstates, but this approach breaks down when the surface has locally negative curvature, such as near transition states. Time-dependent methods based on the vibrational autocorrelation function alleviate many of these difficulties, but suffer from certain analytical and technical deficiencies, including branch-cut discontinuities (associated with bound, periodic vibrations) and unstable finite-precision arithmetic (associated with unbound, imaginary-frequency modes). In this talk, we present a new derivation of the multidimensional, harmonic autocorrelation function that resolves these issues. An application is illustrated with the cyclopentyl radical, c-C5H5, which undergoes prompt ring-opening to allyl upon photoionization. We will also discuss progress towards perturbative anharmonic corrections within the time-dependent approach.

PROTON TRANSFER AND INTERSYSTEM CROSSING IN 2-NITROPHENOL PROBED BY GAS-PHASE TRANSIENT ABSORPTION SPECTROSCOPY

MYLES C. SILFIES, ARSHAD MERHOOD, GREGZIEG KOWZAN2, BENJAMIN G. LEVINE, THOMAS K. ALLISON, Departments of Physics and Chemistry, Stony Brook University, Stony Brook, NY, USA.

Recent work in both experimental and ab-initio theory indicates that intersystem crossing (ISC) can occur on ultrafast timescales in certain organic compounds, offering a relaxation channel competing with internal conversion. In particular, many nitroaromatic compounds are being investigated for this behavior. 2-nitrophenol (2NP) is one such system, after UV excitation the S1 state has both strong spin-orbit coupling to neighboring triplet states allowing for fast ISC and a low barrier to excited-state intramolecular proton transfer. Recent trajectory surface hopping calculations indicate that both of these relaxation channels occur on similar sub-picosecond timescales. Both transient absorption spectroscopy (TAS) in solution and time-resolved photoelectron spectroscopy (TRPES) were used to probe the dynamics but the measured time constants were not consistent between methods which makes interpretation more difficult. To further elucidate the dynamics in 2NP, we perform gas-phase TAS measurements using a newly-developed broadband cavity-enhanced ultrafast transient absorption spectrometer. The spectrometer has a pump wavelength of 350 nm and a tunable probe from 450 to 700 nm with a demonstrated detection limit of LOD < 3 x 10^-15/√B. This technique serves as a complement to both solution-phase TAS and TRPES and provides additional information for comparison with theory. Using molecular beam techniques we are able to vary the sample vibrational/rotational temperature or change the solvent environment with clustering to observe the effects of this relaxation dynamics. In this talk, we will discuss results from 2NP under various conditions and compare to previous experiments and theory.

SOLVENT-DRIVEN COHERENT POPULATION TRANSFER IN TRYPTOPHAN

VISHAL K. JAISWAL, MARZIO GIUSEPPE KABACINSKI, ROCCO BORREGO-VARILLAS, GIULIO CERULLO, Dipartimento di Fisica, Politecnico di Milano, Milano, Italy.

The environment has a profound effect on the ultrafast photophysics of tryptophan due to radically different electronic nature of the lowest two singlet electronic states which make up the first absorption band. In aqueous environment the polar La state becomes fluorescent. Therefore previous works have attributed the ultrafast dynamics to a sub-50 fs La → Lb internal conversion followed by picosecond relaxation of solvent around the La state.

We have investigated the primary photoinduced processes in solvated tryptophan by combining UV transient absorption spectroscopy with sub-30 fs temporal resolution and CASPT2/MM calculations and unveiled a richer mechanism comprising two population transfer events involving the La and Lb electronic state.

Our results reveal two consecutive coherent solvent population transfer events involving the lowest two singlet states: a sub-50 fs nonadiabatic La → Lb through a coexistence of the two states followed by a picosecond sub-30 fs adiabatic stabilization of La state. Vibrational fingerprints present in the transient spectra show compelling evidence of the vibronic coherence established between the two states from the earliest times after excitation and lasting till the back-transfer to La is complete.

I will present how the delayed response of solvent causes a dynamic inversion of the energetical order of the vibronically coupled states, which determines the direction of the population transfer.

TWO-DIMENSIONAL TRANSIENT UV INVESTIGATION OF REDUCED FLAVINS


UV radiation in sunlight is responsible for DNA damage. It leads to the formation of photoproducts. Photocytosis, a class of flavoproteins that photogenerate reactive oxygen species (ROS) have been suggested to be involved in the repair mechanism. Understanding the role and nature of excited states is required to properly interpret kinetics due to electron transfer, solvation etc. Controversy surrounding the nature of excited states was put to rest recently by Stanley et. al. who used Stark spectroscopy to determine the lowest two singlet states: a sub-50 fs nonadiabatic La → Lb internal conversion followed by picosecond relaxation of solvent around the La state. Vibrational fingerprints present in the transient spectra show compelling evidence of the vibronic coherence established between the two states from the earliest times after excitation and lasting till the back-transfer to La is complete.

I will present how the delayed response of solvent causes a dynamic inversion of the energetical order of the vibronically coupled states, which determines the direction of the population transfer.
In this work, we present works towards the set-up of database, which will extend over purely computational databases available so far. Both semi-empirical and accurate theoretical methods will make a reliable reference and their combination allows an extensive benchmark exploration of DFT methodologies. In fact, the application of DFT for specific problems usually requires careful benchmarking, but the databases available in literature usually tend to focus on the DFT performance for the computation of atomic and molecular energies rather than on structural and spectroscopic parameters. In this work we focus on the structural and spectroscopic properties as well as conformational energies suggesting that desired accuracy can be obtained by means of dispersion-corrected double hybrid functionals (DHF).

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We present the most accurate measurement of the position of the weak quadrupole S(2) 2–0 line in molecular deuterium. We have collected the spectra with a frequency-stabilized cavity ring-down spectrometer (FN-CRDS) with an ultrahigh finesse optical cavity (F = 637,000), optical frequency comb and operating in the frequency-agile, rapid scanning spectroscopy (FARS) mode. To reduce the systematic errors in line position determination, we analyzed our spectra with one of the most physically justified line-shape model describing the collisional effects, the second-order broadband profile (SBBP), parameters of which are derived from ab initio quantum-scattering calculations.

Despite working in the Doppler-limited regime, we reached 40 kHz of statistical uncertainty and 161 kHz of absolute accuracy. The accuracy of our measurement corresponds to the fifth significant digit of the leading term in QED correction. We were also able to test two other higher-order QED terms. We observed 2.3% discrepancy with the recent theoretical value.
QUARANTINED CC-STRETCHED FORMIC ACID: MOLECULAR WORK-OUT IN (SELF) ISOLATION

Ahmed Mohamed, Armansh Arman Nejad, Edwin Sibert, Department of Chemistry, Yale University, New Haven, CT 06520, USA

The vibrational spectroscopy of formic acid, \( F \), has seen new and important experimental and theoretical impulses in the past six years. Particularly, using a performance test of different symmetry which are shown to be a particularly useful benchmarking target, but also the focus of the CC-stretched form of formic acid, \( F \), and prove to be an excellent reference system for benchmarking. Potentially, this is due to the fact that \( F \) is almost isoenergetic with the formic acid monomer with its cis-benchmarking study is the formic acid monomer with its cis-isomerisation threshold, this resonance polyad is indicated to play an important role in the perturbations of the OH stretching fundamental. New insights into this contribution. Of particular theoretical interest are two almost isoenergetic \( \text{trans} \) and \( \text{cis} \) benchmarking target, but also the dimers of the CC-stretched formic acid prove to be an insightful reference system for benchmarking by the form and manner in which vibrational information is extracted from vibronic calculations, vibrational characters in the form of CC-stretched formic acid and CC-stretched formic acid can be combined with accurate ab initio calculations. Particularly, using for a performance test of different symmetry which are shown to be a particularly useful benchmarking target, but also the focus of the CC-stretched form of formic acid, \( F \), and prove to be an excellent reference system for benchmarking.

A new key insight is that the impact of the OH bend-torsion resonance between \( \text{cis} \) and \( \text{trans} \)-rotamers will be discussed in this contribution. Of particular theoretical interest are two almost isoenergetic \( \text{trans} \) and \( \text{cis} \) benchmarking target, but also the dimers of the CC-stretched formic acid prove to be an insightful reference system for benchmarking by the form and manner in which vibrational information is extracted from vibronic calculations, vibrational characters in the form of CC-stretched formic acid and CC-stretched formic acid can be combined with accurate ab initio calculations. Particularly, using for a performance test of different symmetry which are shown to be a particularly useful benchmarking target, but also the focus of the CC-stretched form of formic acid, \( F \), and prove to be an excellent reference system for benchmarking.

Essentially, the vibrational characterisation of its skeletal modes, below 3000 \( \text{cm}^{-1} \), can be regarded as complete. \( \text{cis} \) essentially, the vibrational characterisation of its skeletal modes, below 3000 \( \text{cm}^{-1} \), can be regarded as complete. Particularly suited for a performance test of different symmetry which are shown to be a particularly useful benchmarking target, but also the focus of the CC-stretched form of formic acid, \( F \), and prove to be an excellent reference system for benchmarking.

2021

Criteria, non-vibrational quantum chemical transition (CTP) is a powerful tool to obtain the detailed information needed to unambiguously measure the intrinsic response of vibrational electric field probes. In particular, this approach has proven successful, there are shortcomings which have not been addressed. In the condensed phase, the intrinsic molecular level response (polarization, isomerization, etc.) is reviewed and extended to 189 band centres. Recent key insights are collected and凝聚ates are made with the assistance of electronic structure calculations. The technique provides a new window to the intrinsic response of vibrational probes that are widely used in biological applications.

Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA


TJ01
RESONANCE ENHANCED PHOTODISSOCIATION SPECTROSCOPY OF AuAg+ REVEALS ISOTOPIC DEPENDENCE ON PHOTODISSOCIATION
SAMUEL JACK PALMER MARLTON, CHANG LIU, PATRICK WATKINS, JACK T BUNTINE, EVAN BIESKE, School of Chemistry, The University of Melbourne, Melbourne, Victoria, Australia.

Bimetallic materials comprised of gold and silver have useful optical and electronic properties, which are complicated by quantum mechanical, relativistic, and isotopic effects. To provide a bottom-up perspective on these larger systems, the smallest monocation comprised of gold and silver—diatomic AuAg+—is spectroscopically probed using resonance enhanced photodissociation (REPD). The 197Au109Ag+ and 197Au107Ag+ isotopologues are confined in a cryogenically cooled (ca. 5 K) quadrupole ion trap and are exposed to tunable light while detecting AuAg photofragments ions using a time-of-flight mass spectrometer. Electronic spectra in the UV exhibit a transition from the XΣ+ ground state to an excited state that is yet to be assigned. Vibronic progressions for this transition extend over more than 30 quanta for both isotopologues, but with striking differences in band intensities (see Figure). This difference in photodissociation yield between the two isotopologues arises because the vibronic energies and associated wavefunctions depend on the reduced mass, leading to a difference in the coupling of the excited state levels and the repulsive electronic state that leads to dissociation. The observed photodissociation intensities for 197Au109Ag+ and 197Au107Ag+ are successfully modelled by calculating respective vibronic energies and wavefunctions of their bound and dissociative electronic states.

TJ02
PHOTODISSOCIATION SPECTRUM OF Au2N2
NIMA-NOAH NAHVI, MARKO FORSTEL, KAI POLLOW, TAARNA STUDEMUND, OTTO DOPFER, Institut für Optik und Atomspeich Physik, Technische Universität Berlin, Berlin, Germany.

The binding motif of nitrogen on transition metals is an interesting issue. Here we present the electronic spectrum of the A2Σ+ → X2Σ+ transition of Au2N2, which was measured via photodissociation spectroscopy. The spectrum contains a long progression, caused by symmetric and asymmetric stretch vibrations. We extract harmonic frequencies, anharmonicities and cross-anharmonicities of the excited state via a Dunham expansion and harmonic frequencies of the ground state via Franck-Condon simulations. In comparison to density functional theory calculations, the observed frequencies agree well with the theory. We also discuss the binding motif of Au2N2 in the ground and excited state.


Figure 3: Electronic spectrum of Au2N2

TJ03
GAS-PHASE ELECTRONIC SPECTROSCOPY OF C6+∗
JASON E. COLLEY, DYLAN S. ORR, MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA, USA.

Electronic spectrum measurements are reported for mass selected C6+∗ in the gas phase using photodissociation spectroscopy. Carbon cluster cations are produced by laser vaporization and mass selected using a time-of-flight mass spectrometer. Photodissociation of C6+∗ measured a strong absorption at 417.1 nm. Experimental results are accompanied with calculations of B3LYP/6-31G(∗∗) level that explores predicted isomeric structures, their energetics, and vibrational and electronic spectra. Electronic excitations and vibrational hot bands in the spectrum agree more with frequencies predicted for the linear structure than those of the cyclic structure.

TJ04
SiO2+∗ - PHOTODISSOCIATION AND OPTICAL ABSORPTION PROPERTIES
TAARNA STUDEMUND, MARKO FORSTEL, KAI POLLOW, EMIL MICKEIN, OTTO DOPFER, Institut für Optik und Atomspeich Physik, Technische Universität Berlin, Berlin, Germany.

Interstellar dust consists mainly of micrometer-sized silicate particles. Their origin and evolutionary development processes are still poorly understood. So far, only molecular SO2 as a possible precursor has been observed and identified in a circumstellar disk [1]. We present experimental data and quantum chemical calculations of absorption and dissociation properties of SiO2+ clusters. These cations represent possible intermediates between the circumstellar diatomic SiO molecule and the silicate grains observed in the interstellar medium. These optical spectra provide the first spectroscopic information for any SiO2+ cation larger than SO3+. These spectra are the first optical absorption spectra of SiO2+ cations. We were able to obtain those by photodissociation spectroscopy of mass-selected ions a tandem mass spectrometer coupled to a laser vaporization source [2]. Here, the experimental results will be compared with TD-DFT calculations and discussed in an astrophysical context.

Literature:
BOND DISSOCIATION ENERGIES AND IONIZATION ENERGIES OF RHENIUM CONTAINING SMALL MOLECULES

KIMBERLY H. TOMCHAK, ERICK TIEU, THOMAS T. KAWAOGE, JORDAN DERRIDGE, KEITH T. CLARK, MICHAEL D. MORSE, Department of Chemistry, University of Utah, Salt Lake City, UT, USA.

Resonant two-photon ionization spectroscopy has been used to determine the bond dissociation energies (BDEs) and ionization energies (IEs) of rhenium containing small molecules. The ultraviolet spectra of these molecules display a highly congested collection of indeterminate vibronic states. Couplings among these states allow the molecule to find a path to dissociation as soon as the ground separated atom limit is exceeded in energy, allowing a precise measurement of the bond energy from the observation of a sharp predissociation threshold. Measurements provide BDE values of 5.73(3) eV (ReC), 5.35(9) eV (ReCN), 5.85(6) eV (ReN=C≡N), 5.51(3) eV (ReO), and 3.94(7) eV (ReS). The ionization energy of ReC 8.42(5) eV was determined from the observed onset of one-color two-photon ionization. By combining our ReC results with the ionization energy of ReC (7.8392(11) eV) in a thermochemical cycle, the BDE of cationic ReC+ was determined as 5.14(0) eV. This is in excellent agreement with that measured using guided ion beam mass spectrometry, 5.13(12) eV.

PHOTOCHEMISTRY OF CYANOMETHYLENE CYCLOPROPANE (C3H2N)

CONNIE DYEESTRA, Chemistry, University of Illinois Champaign - Urbana, Champaign, IL, USA; THOMAS ROSSI, RENSKE VAN DER Veen, Photovoltaics, Helmholtz-Zentrum Berlin, Berlin, Germany; JOSHI VURA, WEISS, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA.

Quantum dot sensitized solar cells have been a rising star in the field of photovoltaics and materials science. Here, UV probe transient spectroscopy is employed to directly investigate the metal oxide dynamics in CdSe sensitized ZnO. The excitonic transition in ZnO lays at 365 nm, and charge injection results in a bleaching of this transition due to phase space filling. Combining UV and visible probe transient spectroscopy allows direct comparison between the spectrally separated CdSe and ZnO signals. The two regions show a different in kinetics, with the ZnO showing a delayed signal from charge injection contrary to the CdS dots which has a faster transient decay.

Matrix isolation has recently proven successful for the spectroscopic characterization of amino acids in their neutral form. Here, we utilize solid parahydrogen, a cage-free matrix host, to study the photochemistry of a number of amino acids. The photochemistry of alanine, glycine, leucine, proline, and serine will be presented. Irradiation by 213 nm light results in c-carbon bond cleavage and hydroxycarboxyl (HOCO) radical production from all five amino acids. The temporal behavior of the Fourier-transform infrared spectra revealed that HOCO radicals rapidly reach a steady state, which occurs predominantly due to photodissociation of HOCO into CO + OH or CO2 + H. In alanine, glycine, and leucine, the amine radicals generated by the c-carbon bond cleavage rapidly undergo hydrogen elimination to yield ethyamine, methanimine and 3-methylbutane-1-imine, respectively. As an analogue to gas phase photochemistry, the photodissociation pathways identified here provide new insights into the behavior of amino acids in interstellar space.

PHOTOCHROMISTRY OF CYANOMETHYLENE CYCLOPROPANE (C₃H₂N) IN A LOW TEMPERATURE RARE GAS MATRIX

SAMUEL A. WOOD, SAMUEL M. KOUGIAS, BRIAN J. ESSLERMAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; R. CLAUDE WOODS, Department of Chemistry, University of Wisconsin, Madison, WI, USA; ROBERT J. MCMAHON, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA.

We are interested in the photochemistry and spectroscopy of interstellar molecules, and recently focused on isomers of pyridine. We examined the photochemistry of cyanomethylenecyclopropane in low temperature conditions relevant to the interstellar medium. Cyanomethylenecyclopropane was mixed with argon prior to deposition onto a CsI window at temperatures below 30 K. We collected IR spectra in the range of 400-4000 cm⁻¹. We irradiated the molecule at λ > 295 nm using a XeEr laser, and observed IR bands indicative of a new organic nitrite develop over time; no change to the IR spectrum of cyanomethylenecyclopropane was observed when a λ < 295 nm UV cut-off filter was used. The new IR bands produced from this process were compared to other experimental and predicted IR spectra of C₃H₂N isomers to investigate the C₃H₂N potential energy surface.
TK. Mini-symposium: Machine Learning
Tuesday, June 21, 2022 – 1:30 PM
Room: 217 Noyes Laboratory
Chair: Andrew White, University of Rochester, Rochester, NY, USA

AN OVERVIEW OF MACHINE LEARNING IN ROTATIONAL SPECTROSCOPY
STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA

Over the last several years, particularly with the advent of well-documented open source libraries, it has become increasingly easy to apply machine learning techniques to a wide range of problems. Spectroscopy has not been immune to this, and literature searches for "machine learning" and "spectroscopy" return thousands of hits. However, these techniques have not yet found widespread use in the area of high-resolution rotational spectroscopy. In this talk, I will give an overview of the current work in the field and highlight some of the challenges that make this a difficult problem. Along the way, I hope to also provide a kind of "baseline", showing what can be done without the use of machine learning techniques and where they may be particularly applicable.

PUTTING DENSITY FUNCTIONAL THEORY TO THE TEST WITH MACHINE LEARNING
HEATHER J KULIK, Chemical Engineering, MIT, Cambridge, MA, USA

Accelerated simulation with machine learning (ML) has begun to provide the advances in efficiency to make property prediction tractable at an unprecedented scale. Nevertheless, ML-accelerated workflows both inherit the biases of training data derived from density functional theory (DFT) and leads to many attempted calculations that are doomed to fail. Many compelling molecular systems involve strained chemical bonds, open shell radicals and diradicals, or metal–organic bonds to open-shell transition-metal centers. Although promising targets, these materials present unique challenges for electronic structure calculations and particularly the possibility of accessing the classical carbocation structure through vibrational excitation.

DIFFUSION MONTE CARLO STUDY OF C$_2$H$^+_5$ USING AN AB INITIO POTENTIAL ENERGY SURFACE
PATTARAPONG MOONKAEN, FENRIS LU, 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 (C$_2$H$_2^+$) is one such carbocation, which is formed from the smallest alkene family. 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 C$_2$H$_2^+$ obtained by the Dopfer and Duncan groups.

In this work, the ground state wavefunction and structure of C$_2$H$_2^+$ is obtained from Diffusion Monte Carlo (DMC) based on a potential with CCSD(T)-level accuracy, evaluated using several machine learning approaches. The effect of the shared proton motion on the IR spectrum as well as the coupling between the vibration of the shared proton and other higher frequency motion will be discussed. The impact of deuteration on these couplings also will be described. Lastly, the excited state for the shared proton motion can be obtained by fixed-node DMC, allowing us to explore the excited state wave functions, and particularly the possibility of accessing the classical carbocation structure through vibrational excitation.

Intermission
PARTITION FUNCTION ESTIMATION FROM INCOMPLETE SPECTROSCOPIC GRAPHS

KELVIN LEE, Accelerated Computing Systems and Graphics, Intel Corporation, Hillsboro, OR, USA; KYLE N. CRAFTSHEE, Department of Chemistry, University of California, Davis, CA, USA.

Statistical mechanical treatment of molecules is a crucial part of the analysis workflow for many fields, ranging from reaction dynamics, spectral intensity simulation, to abundance characterization in the interstellar medium, to materials research and simulation. At the heart of this is computation of the partition function—the statistical equivalent to the quantum mechanical wavefunction—which involves summation over thermally relevant energy levels. Despite being conceptually straightforward, calculation of the partition function can be a challenging task: at high temperatures, the number of contributing states grows exponentially, and often the list of states is truncated for computational and portability reasons.

Here, we propose the use of physics informed graph neural networks to parameterize the partition function calculation based off incomplete spectroscopic graphs, and as a proof-of-concept, demonstrate its applicability and weaknesses through the study of pure rotational energy levels. In contrast to approximate analytical expressions based on the principal rotational components, graph structures natively capture effects such as centrifugal distortion of varying degrees, which otherwise significantly undermine the accuracy of calculated partition functions at elevated temperatures. As part of our study, we discuss implications on computational performance, data requirements, and applicability in typical workflows.

ACCURATE PHOTOELECTRONICS OF ORGANIC RADICALS FROM MACHINE LEARNED RANGE-SEPARATED FUNCTIONALS

CHENWEII LI, Pitzer School of Molecular Engineering, The University of Chicago, Chicago, IL, USA; WEN SHEN, College of Software Engineering, Tongji University, Shanghai, China; AARON TIAN, NCH, Massachusetts Academy of Math and Science, Worcester, MA, USA; ETHAN FRENCH, HONGSHAN BI, ZHOU LIN, Department of Chemistry, University of Massachusetts, Amherst, MA, USA.

Luminescent doublet-spin organic semiconducting radicals are emerging as promising candidates for organic light-emitting diodes because their internal quantum efficiency is not limited by intersystem crossing into any non-emissive high-spin state. The multi-configurational nature of their electronic structures challenges the usage of single-reference density functional theory (DFT), but the problem can be mitigated by designing more powerful exchange-correlation (XC) functionals. In an earlier study, we developed a molecule-dependent range-separated functional, referred to as ML-PBE, using a stacked ensemble machine learning framework. In the present study, we assessed the performance ML-PBE for 64 organic semiconducting radicals from four categories, where similar radicals are absent from the training set. Compared to the first-principles GTF-PBE functional, ML-PBE reproduced the molecule-dependent range-separation parameter, ω, with a small mean absolute error (MAE) of 0.0214 a.u. Using single-reference time-dependent DFT (TD-DFT), ML-PBE exhibited outstanding behaviors in absorption and fluorescence energies for most radicals in question, with small MAE’s of 0.22 and 0.12 eV compared to experimental sources, and approached the accuracy of GTF-PBE (0.22 and 0.11 eV). Our results demonstrated excellent generalizability and transferability of our ML-PBE functional from closed-shell organic semiconducting molecules to open-shell doublet-spin organic semiconducting radicals.
TH04 2:24–2:39

DEEPA H ALIMOHID, ZHOU LIN, Department of Chemistry, University of Massachusetts, Amherst, MA, USA.

Thermally activated delayed fluorescence (TADF) is one of the most promising routes to enhance the luminescent efficiency of an organic light-emitting diode (OLED) device by converting a non-emissive triplet exciton (T1) back to an emissive singlet configuration (S1) through reverse intersystem crossing (RISC) before it fluorescence back to the ground state (S0). However, the TADF rate is generally restricted if only the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are involved. This is due to the conflict between a fast RISC rate between S1 and T1 (which requires a small HOMO-LUMO overlap), and a large transition dipole moment (μ) between S1 and S0 (which requires a large HOMO-LUMO overlap). In the present study, we proposed two solutions to enhance the overall fluorescent rate: an inclusion of higher-lying singlet and triplet states (S2, S3, T2, T3) in ISC-RISC routes to avoid the trade-off, and a fluxional molecular conformation to sample a broad range of HOMO-LUMO overlap. We provided a proof-of-concept for our solutions based on computational modeling of sample di-tert-butyl carbazole derivatives with the pyrazine or dipyrazine substituents (DTCCz-Pz), using a combination of density functional theory (DFT) and molecular dynamics (MD). Our study will provide a computational and quantitative strategy for the design of new TADF emitters with maximum luminescent efficiency.

TL05 2:42–2:57

AB INITIO MODELING OF ULTRAPFAST NONLINEAR OPTICAL SIGNALS IN MOLECULAR SYSTEMS INVOLVING ELECTRONIC TRANSITIONS

RICHARD THURSTON, THORSTEN WEBER, Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA; LIANG Z. TAN, Molecular Foundry Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA; DANIEL S. SLAUGHTER, Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

The observation of ultrafast time-resolved molecular dynamics after electronic excitation often relies on the measurement and interpretation of nonlinear optical signals. These signals can be very challenging to interpret without the aid of a theoretical model. A common approach to understand these signals is by using parameterized semi-empirical models that describe the specific process under study. These methods can be very useful and are very flexible but finding appropriate parameter values can be challenging, and the physical interpretation of these parameters can be ambiguous. Ab initio calculations can reduce the number of free parameters. However, available quantum chemistry packages like Dalton, QChem, and others, typically report frequency domain information, and tracking the evolution of the target usually requires the mapping of time onto a nuclear reaction coordinate which may not be observable. Here we present an ab initio approach to modeling time domain ultrafast nonlinear optical signals that addresses these issues by using the Dalton quantum chemistry package to parameterize a general N-level model which is then evaluated using a Liouville space representation. We compare these results to recent Ultrafast Transient Polarization Spectroscopy measurements of nitrobenzene.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract no. DE-AC02-05CH11231.
USING ASIMUT-ALVL TO MODEL THE VIS-NIR SPECTRUM OF JUPITER’S ATMOSPHERE

MIRIAM E. CISNEROS-GONZÁLEZ, Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium, MANUEL LOPEZ-PUERTAS, Terrestrial Planetary Atmospheres, Astrophysics Institute of Andalusia (IAA), Granada, Spain, JUSTIN ERWIN, ANN CARINE VAN-DAELE, Planetary Astronomy, Royal Belgian Institute for Space Astronomy (BIRA-IASB), Brussels, Belgium, CLEMENT LAUZIN, Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium, SEVERINE ROBIERT, Planetary Astronomy, Royal Belgian Institute for Space Astronomy (BIRA-IASB), Brussels, Belgium.

MAJIS (Moons And Jupiter Imaging Spectrometer) is one of the key scientific instruments on board the Jupiter ICy Moons Explorer (JUICE), the next mission to the Jovian system. A reliable determination of H₂O and CH₄ densities in the vertical structure and distribution of Jupiter’s atmosphere is one of its main goals. In order to achieve this, we implemented the current knowledge of physical and chemical properties of Jupiter in ASIMUT-ALVL to perform simulations with different viewing geometries of the MAJIS instrument from 0.5µm to 2.5µm. ASIMUT-ALVL is a Radiative Transfer (RT) code developed at BIRA-IASB that has been extensively used to characterize Mars and Venus atmospheres.\(^a\) Our simulations are benchmarked to those from KOPRA, another RT software previously used for the study of Titan, Mars and Jupiter.\(^b\) The next step is to validate our model against Jupiter observational data to finally assess the performances of the MAJIS VIS-NIR channel\(^c\) to characterize the vertical structure of the Jovian atmosphere.\(^d\)

\(^a\) Also part of the Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium.


\(^d\) This project acknowledges the funding provided by the Belgian National Scientific Research Fund (FNRS) by its acronym in French through the Avenue 更新 Grant 16420172, MAJIS detectors and Impact on Science.

THE GPU ACCELERATED ABSORPTION SIMULATION (GAAS) PLATFORM

CHARLIE SCOTT CALLAHAN, Mechanical Engineering, University of Colorado Boulder, Boulder, CO, USA; SEAN COBURN, GREGORY B RIEKER, Department of Mechanical Engineering, University of Colorado Boulder, Boulder, CO, USA.

We present the GPU Accelerated Absorption Simulation (GAAS). GAAS is an open-source software package for simulating broadband absorption spectra rapidly using Nvidia graphics processing units (GPUs). GAAS is intended to provide a fast alternative to HAPI\(^1\), capable of simulating absorbance spectra given a pressure, temperature, and concentration. GAAS is written in C++ and C and comes with a python interface so that it can be easily integrated into existing codebases. GAAS supports Voigt lineshape profiles and primarily contains a python function to replace HAPI’s absorptionCoefficientVoigt. GAAS uses spectroscopic data in HITRAN’s “par” format in order to be compatible with existing codebases that use HAPI. The software realizes up to a 100x reduction in computation time by simulating each Voigt lineshape in the spectrum on its own GPU thread, achieving enough parallelization for full utilization of GPU resources for spectra containing a few thousand absorption lines.

TM. Clusters/Complexes
Tuesday, June 21, 2022 – 1:30 PM
Room: 124 Burrill Hall
Chair: G. S. Grubbs II, Missouri University of Science and Technology, Rolla, MO, USA

**TM01**
1:30 – 1:45
PURE ROTATIONAL SPECTROSCOPY OF RARE GAS DIMERS BASED ON ROTATIONAL WAVE PACKET IMAGING

**KENTA MIZUSE**, Department of Chemistry, School of Science, Kitasato University, Sagamihara, Japan; **YUYA TOBATA**, Department of Chemistry, Tokyo Institute of Technology, Tokyo, Japan; **UKURA SATO**, Department of Chemistry, Kitasato University, Sagamihara, Japan; **YASUHIRO OISHIMA**, Department of Chemistry, Tokyo Institute of Technology, Tokyo, Japan.

We report time-domain rotational spectroscopy of argon dimers and krypton dimer by implementing time-resolved Coulomb explosion imaging of rotational wave packets. The rotational wave packets are created in the dimers by a ultra-short laser pulse, and their spatiotemporal evolution is fully characterized by measuring angular distribution of the fragment ions. The pump-probe measurements have been carried out up to a delay time of 16 ns. The alignment parameters, derived from the observed images, exhibit periodic oscillation lasting for more than 15 ns. Pure rotational spectrum of Ar2 is obtained by Fourier transformation of the time traces of the alignment parameters. The frequency resolution in the spectrum is about 90 MHz, the highest ever achieved for Ar2. The rotational constant and the centrifugal distortion constant are determined with much improved precision than the previous experimental results: \( B_0 = 1.72713(9) \text{ GHz} \) and \( D_0 = 0.0108(5) \text{ MHz} \). The present \( B_0 \) value does not match within the quoted experimental uncertainty with that from the VUV spectroscopy, so far accepted as an experimental reference to assess theories. Spectrum of the krypton dimer will be also reported.

**TM02**
1:48 – 2:03
PARTIAL PROTON TRANSFER IN THE TRIFLUOROACETIC ACID - TRIMETHYLAMINE COMPLEX

**AARON J. REYNOLDS**, NATHAN LOVE, KENNETH R. LEIPOLD, Chemistry Department, University of Minnesota, Minneapolis, MN, USA.

Chirped-pulse and cavity microwave spectra are presented for the complex formed from trifluoroacetic acid (TFA) and trimethylamine (TMA). Both the parent complex and that formed from deuterated TFA have been observed. Based on measured \(^1\text{N}\) nuclear quadrupole coupling constants and supplemental computations at the MP2/6-311++G(d,p) level of theory, the complex is shown to involve partial transfer of the TFA proton to the amine. Structural indicators of the degree of proton transfer are used to support this conclusion and comparisons with other related hydrogen bonded systems are presented. The relatively strong acidity of TFA as compared with other carboxylic acids, together with the relatively strong Brønsted basicity of TMA, likely underlie the ability of this system to undergo partial proton transfer in the gas phase without the aid of microsolvation.

**TM03**
2:06 – 2:21
ALTERNATING 1-PHENYL-2,2,2-TRIFLUOROETHANOL CONFORMATIONAL LANDSCAPE WITH THE ADDITION OF ONE WATER: TUNNELLING AND LARGE AMPLITUDE MOTIONS

**COLTON CARLSON, DANIEL MASON, QIAN YANG**, Department of Chemistry, University of Alberta, Edmonton, AB, Canada; **NATHAN A. SEIFERT**, Department of Chemistry, University of New Haven, West Haven, CT, USA; **YUNJIE XU**, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.

The 1:1 adduct of 1-phenyl-2,2,2-trifluoroethanol (PhTFE) with water was investigated using chirped pulse Fourier transform microwave spectroscopy and computational methods. PhTFE itself was previously reported to have two stable conformations, I (gauche) and II (trans), however, only the most stable conformer, PhTFE I, was experimentally observed.\(^3\) Rotational spectra of the two most stable PhTFE-H₂O conformers along with several deuterium and oxygen-18 isotopologues were assigned and their structures analyzed. The most stable complex exhibits PhTFE in the gauche configuration with water inserted into the existing intramolecular O-H-F hydrogen bond. This conformer is stabilized by two intermolecular hydrogen bonds in addition to the intramolecular interactions present in the PhTFE monomer. These bring a strong interaction between the alcohol hydrogen on PhTFE and the oxygen on water O-H₂O and a weaker interaction between a thione on PhTFE and a water hydrogen F-H-OH. Water tunnelling splitting was identified in the rotational spectrum showing the characteristic ortho versus para intensity ratio, which was attributed to the interchange of bonded and nonbonded hydrogen atoms of the water subunit. The second observed complex exhibits PhTFE in the trans configuration, indicating that complexation with water sufficiently stabilized PhTFE II such that it can survive the supersonic expansion. Stabilization is achieved by water interacting with both the alcohol hydrogen and the phenyl ring of PhTFE. The nonbonded hydrogen of the water subunit was shown to exhibit a large amplitude motion in both conformers.


**TM04**
2:24 – 2:39
CONFORMATIONAL BEHAVIOUR OF m-ANISALDEHYDE AND ITS MICROSOLVATES

**ANDRES VERDE**, JUAN CARLOS LOPEZ, SUSANA BLANCO, Departamento de Química Física y Química Inorgánica - IU CINQUIMA, Universidad de Valladolid, Valladolid, Spain.

The rotational spectra of m-anisaldehyde and its microsolvated complexes generated in a supersonic jet have been studied by chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW) in the 2-8 GHz region. Four conformers have been detected for the monomer. The three most intense rotamers have line intensities high enough to allow the observation of the monosubstituted \(^1\text{C}\) isotopologues in natural abundance allowing the determination of their \( \tau_{\text{AM}}, \tau_{\text{AH}}, \) and \( \tau_{\text{CH}_2} \) structures. When allowing water vapor to expand in the supersonic jet, the spectra of ten new species assigned to microsolvated complexes appear. Seven monohydrated species have been identified reflecting the two possible interactions of water and the aldehyde group. The two dihydrated species observed are related to the most stable m-anisaldehyde conformer. The most abundant dihydrated complex presents a structure with water dimer closing a cycle with the aldehyde and methoxy groups which confers high stability. In the less abundant dihydrate, water dimer closes a cycle with the aldehyde group, a structure of great interest to better understand the solvation of aldehydes. Additionally, one complex of m-anisaldehyde with four molecules of water has been detected. In this species, the most stable conformer of m-anisaldehyde captures the tertramer of water adopting a stacked configuration. Work is in progress.

Intermission
Low temperature photoluminescence spectroscopy (PL) revealed a change in vibrational coupling of mutated Water soluble chlorophyll binding protein complexes (WSCP) with Chlorophyll a. Pigment-protein systems can adjust the range of absorbed wavelengths according to living conditions. However, the mechanism of spectral tuning is unclear. A study of point mutations in the Q57 site of the Lepidium virginicum (Lv) WSCP is expected to shed light on how hydrogen bonds and electrostatic interactions influence the emission spectrum of Chlorophyll a (Chl a) bound to WSCP. Steady state PL revealed the change of the electron-photon coupling strength within the mutants at 7 K. Time-resolved (TR) PL detected the difference in the lifetimes of the WSCP mutants at 7 K. Both PL and TRPL results cannot be ascribed to the charge difference in the Q57 site of Lv: WSCP alone. The influence of hydrogen bonding together with electrostatic interactions and geometry changes should be considered to correctly describe the mechanism of vibrational coupling in WSCP bound with Chl a complex.

Manganese oxides are among the most widely explored transition metal oxides for diverse biomedical applications and are also employed in a wide number of industrial processes. Its wide range of oxidation states provide manganese with extreme flexibility in electron occupancy that has also attracted increasing attention for use in photocatalytic processes. Neutral clusters are excellent mimics of the active sites of bulk materials, and can be employed to understand the local geometric and electronic structure properties, and oxidation states that provide the best charge carrier lifetimes and by extension optimal photochemical efficiency. Here, we present our ongoing work on the ultrafast relaxation dynamics of neutral manganese oxide clusters, which are prepared through the laser ablation of a pure metal rod with a 532 nm Nd:YAG laser. A synchronized pulse of femtosecond (fs) laser system (400 nm = 3.1eV) and subsequently ionized through strong field ionization with the fundamental through by combining two-color femtosecond spectroscopy with time-of-flight mass spectrometry. Our cluster distribution in the Q57 site of Lv: WSCP alone. The influence of hydrogen bonding together with electrostatic interactions and geometry changes should be considered to correctly describe the mechanism of vibrational coupling in WSCP bound with Chl a complex.

The structure of the study and internal motion of weakly bound gas-phase clusters is of considerable interest in understanding the nature of intermolecular bonding. Van der Waals clusters with rare gas atoms such as argon are particularly interesting due to their ability to freely internally rotate about the host molecule. Additionally, many experiments that utilize argon as the buffer gas for supersonic expansions suffer from subsequent clustering of the argon to the sample of interest. In high-resolution spectroscopy, this can cause difficulties with line identification and assignment. Therefore, it is useful to have a complete and accurate characterization of the rotational transitions for such complexes. In our research, nearly all of our supersonic expansions involve the use of argon gas, and methanol is often a molecular starting material for the chemistry we wish to study making the target of this study the Ar-CH$_3$OH cluster. The spectrum from 140-335 GHz was collected via direct absorption spectroscopy using a supersonic expansion of argon seeded with vapor from a pure methanol sample. Numerous spectral lines were detected across this frequency range. Spectral analysis was conducted using the Effective Rotational Hamiltonian program (ERHAM) due to the presence of a low barrier methyl rotor, which ERHAM is well-suited to address. The spectral results and associated analysis for Ar-CH$_3$OH will be presented here.
The pure rotational spectrum of the open shell difluorocyanomethyl radical, CF₂-CN, has been measured using two Bolts-Pygmy-type cavity Fourier-Transform-Microwave (FTMW) spectrometers both equipped with pulsed discharge nozzles. A total of 156 transitions (from $N = 1$ to $0$ to $6$, $5$, and $K_{a} = 0$, $1$, $2$, $3$) in the electronic ground state were observed between 6.5 GHz and 38.4 GHz with a typical linewidth of approximately 5 kHz full-width-half-maximum. A Hamiltonian that included a semi-rigid rotor, spin-rotation, and nuclear hyperfine parameters was fit to the observed data set and these parameters have been interpreted and compared to similar radicals. Excellent agreement between experimental and ab initio calculated rotational constants, the experimental inertial defect, $-0.6858(2)$ $\text{au}^2$, and the failure of a coupling scheme in which the fluorine nuclei are treated as aligned and related by a $C_2$ symmetry axis combine to indicate a nonplanar structure for the CF₂-CN radical.
PRODUCT-SPECIFIC REACTION KINETICS OF CN WITH PROPENE PROBED BY CHIRPED-PULSE FOURIER TRANSFORM MILLIMETER WAVE SPECTROSCOPY

DIVITA GUPTA, BRIAN M. HAYS, MYRIAM DRESSL, THEO GUILLAUME, OMAR ABDELKADER KHEIRADIN, ILSA ROSE COOKE, JAN R. SIMS, CNRS, IFR (Institut de Physique de Rennes) - UMR 6251, Univ Rennes, F-35000 Rennes, France.

Studying the different possible reactions and their dynamics under the low-temperature conditions of the interstellar medium and various planetary atmospheres is essential to understand the chemical evolution of various species detected in these environments. I will discuss the CPUF (Chirped Pulse in Uniform supersonic Flow) technique, which is a combination of the CRESU (Cinetique de Reaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Supersonic Uniform Flow) method to provide a low temperature environment and chirped-pulse Fourier transform millimeter spectroscopic detection. This technique has been further modified with an additional expansion chamber to enhance the detection of a wider variety of species and to overcome pressure effects in a CRESU flow. I will show our measurements for the reaction of CN radical with propene down at 35 K. I will discuss the impact of these experimental measurements, their application to astrochemical studies, and the future outlook for this technique at Rennes.

M ethylamine (CH$_3$NH$_2$) is considered to be a potential precursor for the formation of interstellar glycolaldehyde through the reaction between ammonium radical (•CH$_2$NH$_2$) and HOCO, but direct evidence of the formation and spectral identification of •CH$_2$NH$_2$ remains unreported. Taking advantage of unique properties associated with the para-hydrogen (p-H$_2$) matrix, we performed the reaction H + CH$_3$NH$_2$ in solid p-H$_2$ at 3.2 K. To generate H atoms, photoysis at 365 nm of a co-deposited mixture of CH$_3$NH$_2$/p-H$_2$ and Cl$_2$ to produce Cl atoms and subsequent IR irradiation for promoting the Cl + H$_2$ → H + Cl + H reaction were carried out. IR spectra of •CH$_2$NH$_2$ and CH$_3$NH$_2$ were observed upon UV/IR irradiation and when the matrix was maintained in darkness. The new IR spectrum of •CH$_2$NH$_2$ clearly indicates that •CH$_2$NH$_2$ can be formed from the reaction H + CH$_3$NH$_2$ in dark interstellar clouds. Experiments on CdH$_2$ produced CdH$_2$CHO in addition to •CD$_2$CHO and CdH$_2$NH$_2$, confirming the occurrence of H addition to •CD$_2$CHO. The potential-energy scheme of H + CH$_3$NH$_2$ reactions reveals the feasibility of sequential H-abstraction and H-addition reactions for the formation of products observed in this study. The observed dual-cycle mechanism containing two consecutive H-abstraction and two H-addition steps chemically connects CH$_3$NH$_2$ and CH$_3$NH and might imply their quasi-equilibrium. In another experimental method, photoysis of 250 nm of a H$_2$O$_2$-doped CH$_3$NH$_2$/p-H$_2$ matrix was performed to generate •OH to facilitate the •OH + CH$_3$NH$_2$ reaction; further reaction of •OH + H$_2$ → H$_2$O + H might also trigger the H + CH$_3$NH$_2$ reaction. Significantly more •CH$_2$NH$_2$ was produced than in CH$_3$NH$_2$/Cl$_2$/p-H$_2$ experiments, consistent with a barrier predicted for •OH + CH$_3$NH$_2$ much smaller than that for H + CH$_3$NH$_2$. All species observed herein are plausible starting materials for interstellar glycolaldehyde in molecular clouds.

EXAMINING METHYLAMINE DISSOCIATION PRODUCTS USING THEORY AND ROTATIONAL SPECTROSCOPY: THE CH$_3$NH$_2$ RADICAL

CONNOR J. WRIGHT, JONATHAN REBELSKY, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; ANNA KAY GEORGIOLA, Chemistry and Astronomy, 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.

Studying the chemical inventory of the interstellar medium (ISM) is critical to developing new theories of molecular formation and evolution. Furthermore, the search for biologically-relevant species and their precursors has been at the forefront of astrobiology and astrochemistry in recent years. As such, this work focuses on the dissociation products of methylamine (CH$_3$NH$_2$), a known precursor to the simplest amino acid, glycine (C$_2$H$_5$NO$_2$). It is likely that the radical products of cosmic-ray induced photodissociation of methylamine are important in protobiotic interstellar pathways as well as astrophysical models of planetary bodies such as Titan. Therefore, we are studying the radical species produced in a methylamine discharge as a guide for future studies of methylamine photodissociation. Our initial molecular target is the CH$_3$NH$_2$ radical, for which no rotational spectroscopic information is available. We examined the structure of this radical using high-level computational methods and then predicted the rotational spectrum based off of this information. We then compared these predictions to the rotational spectra of species obtained using a high voltage discharge of methylamine in argon at the throat of a supersonic expansion. Here we will present the spectroscopic predictions and the initial experimental results for CH$_3$NH$_2$, and discuss the implications of this work for astrochemistry and astrobiology.
FORMATION REACTION MECHANISM AND INFRARED SPECTRA OF CRIEGEE INTERMEDIATE ANTI-TRANS-METHACROLEIN OXIDE [CH$_2$C(=O)CH$_2$I] AND ITS ASSOCIATED PRECURSOR AND ADDUCT RADICALS

YUAN-PERN LEE, JIA-RONG CAL JUNG-HSUAN SU, CHEN-AN CHUNG, Department of Applied Chemistry, National Taiwan University, Taipei, Taiwan.

Methacrolein oxide (MACRO, CH$_2$C(=O)CH$_2$I) is an important Criegee intermediate produced in ozonolysis of isoprene, the most abundantly-emitted non-methane hydrocarbon in the atmosphere. We employed a step-scan Fourier-transform infrared spectrometer to investigate the source reaction of MACRO in laboratories. Upon UV irradiation of precursor 1,3-diodo-2-methyl-prop-1-ene CH$_2$C(=O)CH$_2$I (1), the 3-iodo-2-methyl-prop-1-en-3-yl CH$_2$C(=O)CH$_2$I radical (2) was detected, confirming the fission of the allylic C-I bond rather than the vinyl C-I bond. Upon UV irradiation of (1) and O$_2$ near 21 Torr, anti-trans-MACRO (3a) was observed to have an intense O=O-stretching band near 917 cm$^{-1}$, much greater than those of syn-CH$_2$C(=O)CH$_2$I and (CH$_3$)$_2$CO, supporting a stronger O-O bond in MACRO because of resonance stabilization. At increased pressure (86-346 Torr), both reaction adducts CH$_2$C(=O)CH$_2$I (4a) and CH$_2$I(=O)(CH$_2$I)CH$_2$I (5a) radicals were observed, indicating that O$_2$ can add to either carbon of the delocalized propenyl radical moiety of (2,3). We also employed a quantum-cascade laser and an UV laser to investigate the yield and kinetics of MACRO. The yield of MACRO is only 5% from the source reaction, significantly smaller than other carbonyl oxides. The rate coefficients of the formation reaction and the self-reaction of MACRO will also be discussed.

STUDY OF THE KINETICS AND PRODUCT YIELDS FOR THE REACTION OF CRIEGEE INTERMEDIATE CH$_2$OO WITH HNO$_2$ USING MID-INFRARED TIME-RESOLVED DUAL-COMB SPECTROSCOPY

PEI-LING LUO, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

The reaction of Criegee intermediates with HNO$_2$ have been thought to be important in the oxidation of atmospheric HNO$_2$ because of the fast reaction rates, over 3 orders of magnitude larger than that of the OH + HNO$_2$ reaction. In particular, a new catalytic conversion of the simplest Criegee intermediate CH$_2$OO to OH and HCO radicals by HNO$_2$ was proposed in recent theoretical study. Herein, the mid-infrared dual-comb spectrometers with the capability of widely wavelength tunability and switchable dual-comb and continuous-wave operation modes were employed to investigate the reaction kinetics and determine the branching ratios of the primary product channels in the reaction CH$_2$OO + HNO$_2$.

At quantitative determinations of pressure-dependent yields of the OH and HO$_2$ was observed, indicating that O$_2$ can add to either carbon of the delocalized propenyl radical moiety of (2). We also employed a quantum-cascade laser and an UV laser to investigate the yield and kinetics of MACRO. The yield of MACRO is only 5% from the source reaction, significantly smaller than other carbonyl oxides. The rate coefficients of the formation reaction and the self-reaction of MACRO will also be discussed.

SPECTROSCOPY TODAY: THE URGENT NEED FOR SCIENCE AND INNOVATION TO SAVE THIS WARMING PLANET

GERALDINE RICHMOND, Under Secretary of Science and Innovation, U.S. Department of Energy, Washington, DC, USA.

In this year that we celebrate the 75th anniversary of the International Symposium on Molecular Spectroscopy we find ourselves on a very different planet. Carbon dioxide, a favorite of many molecular spectroscopy studies over these years, is a major contributor to the rising global temperature and climate change as its concentration in the atmosphere continues to rise. We all, and especially scientists like ourselves, can play a role in slowing and hopefully reversing these rising temperature trends. In this session I will talk about what we are doing at the Department of Energy to support all who want to contribute to helping in this critical task at hand, and how my career in molecular spectroscopy helps me every day in this new role.

ISMS AND NSF: SOME HISTORY AND A LOOK FORWARD

PLEMING CRIM, Department of Chemistry, The University of Wisconsin, Madison, WI, USA.

The International Symposium on Molecular Spectroscopy is celebrating its 75th anniversary, and the National Science Foundation recently celebrated its 70th. The two organizations have many confluences, and support from the NSF has enabled the research of many ISMS contributors. Both the Foundation and the Symposium have evolved over the years while adhering to a set of organizing principles. From the perspective of a former leader of the Mathematical and Physical Sciences Directorate of NSF (2013-2017) and a former Chief Operating Officer of NSF (2018-2021), I will discuss some of that history, the current state, and speculate on the future.
In recent years, optical microresonators with exquisite sensitivity have grown into powerful platforms for label-free sensing and imaging, including reaching the single-molecule detection limit. Combining optical microresonators with spectroscopic measurements on nanoscale objects adds chemical identification to label-free detection schemes, offering deeper insights into their fundamental chemical, biological, material, and photonic properties. Particularly, single-molecule measurements allow distinct observations of unclassified chemical dynamics properties, otherwise obscured in bulk measurements. Simultaneously, optical microresonators are also flexible playgrounds for exploring nanophasonic phenomena and quantum optics. I will tell two stories focusing on microbubble resonators. In the first, I will describe how microbubble resonators can be used to watch chemical dynamics of single nanoparticles. In the second, I will describe how microbubble resonators allow solvent control of photonic-plasmonic hybridization.

**Photon-electronic spectroscopic study on dipole-bound states: Intramolecular electric field induced electronic correlation**

**DAIYU YANG**
Department of Chemistry, Brown University, Providence, RI, USA; YUE-ROU ZHANG, Chemistry department, Brown university, Providence, RI, USA; LALI-SHENG WANG, Department of Chemistry, Brown University, Providence, RI, USA.

Polar molecules with sufficiently large dipole moments can form highly diffuse dipole-bound anions. Dipole-bound anions possess noncovalent dipole-bound states (DBSs) just below the detachment threshold by the long-range electron-dipole interaction. The diffuse electron in a DBS is spatially well separated from the valence electrons and is known to have negligible effects on the DBS’s molecular structure. Electron correlation effects between the distant dipole-bound electron and the valence electrons of the neutral cores are known to be important for the accurate calculation of the binding energies of the dipole-bound electron. However, how the oriented intramolecular electric field of the dipole-bound electron influences the valence electrons has not been examined. We present the observation of a DBS in deprotonated 4-(2-phenylethynyl)phenolate anions. The photodetachment of the dipole-bound electron is observed to accompany a simultaneous shakeup process in valence orbitals by the intramolecular electric field of the dipole-bound electron. This shakeup process is due to configuration mixing as a result of valence orbital polarization by the intramolecular electric field of the dipole-bound electron.

**Single-conformation spectroscopy and dynamics on multiple potential energy surfaces: Flexible nitrogen-heterocycle chromophores and complexes in aerosols**

**NATHANIEL M. KITWELL**
Department of Chemistry, William & Mary, Williamsburg, VA, USA.

The interplay between chemical functionality and structure is a key factor in the photophysics and photochemistry of complex, flexible molecules, often giving rise to multiple potential energy surfaces. Adequate description of this relationship is necessary to understand the outcomes and properties of polyatomic molecules is made even more difficult as the number of isomers and conformations increase substantially with the size of the system. The inclusion of water-mediated interactions is often needed due to dramatic effects on the conformational preferences and photophysics. Therefore, the synergy between spectroscopy and chemical dynamics methods is required to obtain a molecular-level view of such complex chemical systems. To address these opportunities, we will illustrate our efforts to investigate the intermolecular interactions of molecular complexes using single-conformation spectroscopy and dynamics techniques to probe the photo-initiated outcomes on multiple potential energy surfaces. Thus, the photophysical, photochemical and structural details of the target conformational and complexes enable multifaceted comparisons to several theoretical predictions.

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CONFORMATION-SPECIFIC INSIGHTS INTO THE CHEMICAL DYNAMICS OF NO:CH MOLECULAR COMPLEXES

JOHN PATRICK DAVIS, NATHANIEL M. KIDWELL, Department of Chemistry, William & Mary, Williamsburg, VA, USA.

The photochemistry of flexible molecular complexes, such as a nitric oxide methane (NO:CH₄), are defined by potential energy surfaces that depend on the chemical functionality and the relative orientation of conformational isomers. Experimental results are required to test and improve modern theoretical methods for accurate prediction of photoinitiated processes and chemical mechanisms. A thorough understanding of the intermolecular interactions and reaction mechanism outcomes can be obtained by elucidating the conformations adopted by NO:CH₄ molecular complexes. Moreover, by investigating the specific vibrational modes inherent to NO:CH₄ conformational isomers, we can assess their impact on energy transfer following fragmentation of the molecular complex isomers. We will leverage a synergy of laser-induced spectroscopy and chemical dynamics techniques, in particular conformation-specific infrared spectroscopy and velocity map imaging, to understand these fundamental mechanisms and dynamics at play within NO:CH₄ and NO:alkane complexes more broadly. Ultimately, we will gain insights into the mode-specific energy transfer pathways following fragmentation of NO:CH₄ molecular complex isomers. Furthermore, our experimental results will be compared to several theoretical approaches in order to reveal the multifaceted signatures of dynamical events using spectroscopy probes.

DFT INVESTIGATION ABOUT ELECTRONIC AND VIBRATIONAL PROPERTIES OF CHROMONE SCHIFF BASE LIGANDS WITH METAL COMPLEXES, SQM ANALYSIS

BERNA CATIKKAS, Department of Physics, Mustafa Kemal University, Hatay, Turkey.

This research attempts to electronic and vibrational properties of metal complexes of chromone Schiff base ligands were calculated using the gauge independent atomic orbital (GIAO) method. Using time-dependent density functional theory, the theoretical electronic absorption spectra were determined. To obtain information about the ability of the molecule to react with chemicals, Frontier Molecular Orbital properties, energies, descriptors, and total/partial state density diagram were obtained. The charge distribution and chemical reactivity sites were visualized monitored by mapping electron density isosurface with electrostatic potential surfaces (ESP). To learn nonlinear optical properties (NLO), the polarizability and hyper polarizability tensors of the complexes were computed using density functional (DFT) theory at mPW1PW91 6-311+G(d,p) and LanL2DZ level. The study’s second section focused on vibrational spectroscopic analysis. To fit the calculated harmonic wavenumbers with the observed Fourier Transform Infrared (FTIR) and Raman spectra in the solid phase of the complexes, the calculated harmonic force constants were refined using the Scaled Quantum Mechanical Force Field (SQM-FF) procedure. When combined with the results of the SQM approach, it is possible to create a comprehensive assignment of the observed spectra.
A NEW STANDARD OF AGREEMENT OF SEMI-EXPERIMENTAL EQUILIBRIUM ($r_{e}$, $\theta_{e}$) AND COMPUTED EQUILIBRIUM ($r_{e}^\text{SE}$, $\theta_{e}^\text{SE}$) STRUCTURES

BRIAN J. ESSELMAN, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA.

Recently, the CCSD(T) equilibrium ($r_{e}$) structures and the Semi-Experimental Equilibrium ($r_{e}^\text{SE}$, $\theta_{e}^\text{SE}$) structures of several small molecules (hydrazonic acid, benzoic, pyridine, pyrimidine, thiophene, thiazole, etc.) demonstrated a new standard of agreement between theory and experiment (typically 0.001 Å for bond distances and 0.01° for bond angles). In each of these examples, all or nearly all of the computed parameters fell within the 2σ statistical uncertainties of their corresponding experimental values. This agreement is typically possible by obtaining an $r_{e}^\text{SE}$ structure calculated upon many isotopologues beyond single-isotopic substitution from many hundreds or thousands of transitions for each isotopologue. The resulting rotational constants are corrected using CCSD(T) calculations for the impact of the vibration-rotation interaction and for the electron-mass distribution. Additionally, we have found that such close agreement requires an $r_{e}^\text{SE}$ structure calculated at the CCSD(T)/cc-pCV5Z level further corrected to account for an incomplete basis set, untreated correlation, and relativistic effects. This talk will feature examples to demonstrate the agreement possible, current best practices, and the tools used to analyze these structures. Outstanding questions and future investigations will be discussed.

THE PREFERRED CONFORMATION AND NON-COVALENT INTERACTIONS OF THE METHYL ALLYL DISULFIDE-FORMALDEHYDE COMPLEX REVEALED BY ROTATIONAL SPECTROSCOPY

ZHENG WANG, YUAGUO XU, GANG FENG, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China.

The methyl allyl disulfide-formaldehyde adduct were probed using Fourier transform microwave spectroscopy and quantum chemical computations. The low energy isomers of the adduct were sampled using the conformer-isomer ensemble sampling tool (CREST) and geometrically optimized at the B3LYP-D3BJ/def2-TZVP level of theory. Although many isomers of the adduct were theoretically predicted to have close stability, only one isomer of the methyl allyl disulfide-formaldehyde adduct have been detected in the helium supersonic jet. Each observed transition exhibited multiple splitting arising from internal rotation of formaldehyde and methyl internal rotations. In the observed isomer, the non-covalent bonding distance between the carbon atom of formaldehyde and the nearest sulfur atom of methyl allyl disulfide has been found to be well within the corresponding sum of van der Waals radii, indicating the existence of a $\pi^\perp \cdots \pi$ interaction. Also, formaldehyde acts as a lone pair donor forming a weak CH···O hydrogen bond with methyl allyl disulfide. Detailed spectral analysis, spectroscopic and computational results will be presented.

ON THE NATURE OF THE INTERACTION OF CO WITH PERFURINATED AROMATICS: NEW INSIGHTS FROM THE EXPERIMENTAL DATA AND THEORETICAL STUDY

LUCA EVANGELISTI, ASSIMO MARIS, Department of Chemistry, University of Bologna, Bologna, Italy; CAMILLA CALABRESE, IMANOL USABAGA, Departamento de Química Física, Universidad del País Vasco (UPV/EHU), Bilbao, Spain; WIEJING LI, Fudan University, Department of Chemistry, Shanghai, China; GIOVANNI BISTONI, Department of chemistry, biology and biotechnology, Università degli Studi di Perugia, Perugia, Italy; SONIA MILANDRI, Departamento de Química C. G. Cianciar, Universidad de Bologna, Bologna, Italy.

The rotational spectra of pentafluoropyridine-CO and hexafluorobenzene-CO have shown unambiguously that substituents only modify the electronic properties and do not change the nature of the interaction which is by definition a hydrogen bond. In contrast, substituents can have a significant effect on the nature of the interaction between CO and fluoroaromatics: the binding ability of CO with fluorinated aromatics has been shown to be non-covalent over the range of symmetry of the CO group. This non-covalent interaction is shown to be dominant in the high-energy region of the CO molecule. The results of these studies suggest that the nature of the interaction between CO and fluorinated aromatics is non-covalent and that the nature of the interaction is determined by the electronic properties of the fluorinated aromatics. The results of these studies have implications for the design of new CO sensors and for the understanding of the role of CO in biological systems.
Intermission

WB06 10:57 – 11:12
SUB-PERMISS MEASUREMENTS AND CALCULATIONS OF 3-0 BAND CO LINE INTENSITIES

ZACHARY REED, Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA; KATARZYNA BIELSKA, Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland; ALKESANDRA A. KYBERIS, Van Swinderen Institute, Universiteit Groningen, Groningen, Netherlands; GANG LI, PTB, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany; AGATA CYGAN, ROMAN CREYROL, DANIEL LISAK, Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland; ERIN M. ADRINS, JOSÉP T. HODGES, Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA; LORENZO LODI, Department of Physics and Astronomy, University College London, London, UK; NIKOLAY F. ZOBOV, Microwave Spectroscopy, Institute of Applied Physics, Nizhny Novgorod, Russia; VELKER EBERT, PTB, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany; JONATHAN TEN-NYSON, OLEG L. POLYANSKY, Department of Physics and Astronomy, University College London, London, UK.

Here we present new measurements and calculations of line intensities in the 3-0 band of CO. These experimental results exhibit unprecedented consistency and low uncertainty. Calibration-free agreement at the 1 permille level relative standard deviation level has been demonstrated between theoretical ab initio calculations and three sets of independent experiment techniques, corresponding to a nearly twenty-fold reduction in uncertainty by comparison to literature values. The experimental techniques cover a broad range of rotational quantum numbers from J = 3 to 50, including three separate laser-based measurements of high-J lines performed at two institutions, along with independent Fourier transform spectroscopy measurements for J = 5 to 18. The most accurately determined intensity is that of the R23 transition determined within 0.4 permille. The intensity of this transition is a possible intrinsic reference for evaluating and reducing biases in future spectroscopic determinations of molecular line intensities.

WB07 11:15 – 11:30
QUANTUM CHEMICAL INVESTIGATION OF INTRAMOLECULAR HYDROGEN BONDS IN OXYGENATED AROMATIC MOLECULES: INFLUENCE OF RING SIZE, DONOR/ACCEPtOR GROUPS AND SUBSTITuNTS

JONAS BRUCKHUISEn, CECILIA GOMEZ-PRECh, GUILLAUME BOUR, ARNAUD CUsSET, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, Dunkerque, France; MALCORZATA GOLENIEZAK, Centre of New Technologies, University of Warsaw, Warsaw, Poland; MANUEL GOBBIET, VALERIE VALLET, Laboratoire PILAM, UMR 8523 CNRS - Université Lille 1, Villeneuve d’Ascq, France.

Hydrogen bonds (HBs) are important for a broad range of applications and play a fundamental role in structural chemistry and biology. HB interactions, dynamics and their directionality are discussed for almost one century and there is still a need for further experiments and theoretical investigations to fully encompass this complex interaction. Especially the experimental investigation of weak intramolecular HBs of isolated molecules in the gas phase remains challenging. Quantum chemical tools are needed to support high resolution HBs and IR spectroscopies which can reveal the influence of intramolecular HBs on the vibrational dynamics.

In this work we focus on intramolecular HBs of oxygenated aromatic molecules. They are investigated through a combination of quantum theory of atoms in molecules QTA(3M), non-covalent interactions NCI, natural bond orbitals NBO(3), and topological data analysis TDA. We studied the influence of the substituents, of the donor or acceptor groups and of the number of hydrogen bonds included in the ring formed by the HB. We relate our findings with recent rovibrational measurements in catechol (1,2-dihydroxybenzene) and quinol. We provide an overview of the problems arising when studying weak intramolecular HBs stabilizing oxygenated aromatic compounds and we discuss the performance of the different quantum chemical tools.


Methyl cyanide (CNH3) was among the first polyatomic molecules detected by radio-astronomical observations of the interstellar medium (ISM) (1). As methyl cyanide has a proton affinity much larger than that of H2, its protonated version (CNH3+) is postulated to form efficiently via exothermic proton transfer from CH3CN to CH3CN (2). In this talk, we present a comprehensive experimental and quantum-chemical study of the gas phase vibrational spectrum of CNH3/CH3CN (3). We employed the widely tunable free electron lasers for infrared experiments (FELIX) coupled to a cryogenic ion trap instrument (3) for our measurements. The spectrum was recorded in the 300-1700 and 2000-3300 cm⁻¹ spectral regions using infrared predissociation (RPDP) action spectroscopy with neon as a weakly bound messenger atom. The assignments of the vibrational modes is based on anharmonic frequency calculations performed at the CCSD(T)/ANO2 level of theory. We demonstrate that the comparatively low-cost ANDO basis-set provides accurate estimates on the influence of the weakly-bound neon atom as a tag in the RPDP experiments. The data presented here will support astronomical searches for the CH3CN+ ion in space.

Although automated search algorithms are highly powerful tools to find out various structural isomers for a given elemental composition, human chemical intuition still delivers more geometries than automated searches once we know the initial geometries. This indirectly emphasizes the fact that creating an unbiased algorithm for structural isomerism is simply difficult. Moreover, it also illustrates that an integrated approach is necessary between search algorithms and chemical intuition to further our knowledge of chemical space for any given elemental composition.

Magnesium Sulfide (MgS) is an astrophysically interesting molecule. Its solid form is the main component of the mineral niningerite (found in enstatite chondrite meteorites) and the MgS component of solid dust grains has generally been agreed upon as the carrier of the 30 μm feature seen in the emission spectra of some carbon-rich stars. However, investigations of the visible spectrum of gas phase MgS remain relatively sparse in the literature.

The first analysis of a rotationally-resolved spectrum of MgS in the gas phase was undertaken by Marcano and Barrow in 1970, who investigated the $B^3\Sigma^+ \rightarrow X^1\Sigma^+$ system in absorption. Their group at UNB previously reported the first experimental observation and rotational analysis of the low-lying $A^3\Pi$ state of MgS at 4531.94 cm$^{-1}$ from a series of laser-induced dispersed fluorescence spectra taken using a grazing spectrometer. Since then we have extended this work by recording a series of dispersed fluorescence spectra of the $B^3\Sigma^+ \rightarrow A^3\Pi$ and $B^3\Sigma^+ \rightarrow X^1\Sigma^+$ systems at higher resolution using a BOMEM DA3 Fourier transform interferometer. The weak $B^3\Sigma^+ \rightarrow a^3\Pi$ transition was also observed. We present here our extended analyses of the $B^3\Sigma^+ \rightarrow A^3\Pi$ and $B^3\Sigma^+ \rightarrow X^1\Sigma^+$ systems, as well as the first analysis of the $B^3\Sigma^+ \rightarrow a^3\Pi$ system in MgS.


ELECTRONIC STRUCTURE OF THE GROUND AND EXCITED STATES OF EUROPIUM OXIDE (EuO)

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Despite being subject to numerous single reference computations, Europium Oxide (EuO) to date has not had its electronic structure studied with multireference methods. High-level ab initio approaches were performed detailing its numerous excited states, and spin multiplicities. Complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) were utilized to compute the ground and excited state properties of EuO. The potential energy curves for the ground; excited states; and different dissociation channels are explored. Spin-orbit corrections were performed with the Breit-Pauli hamiltonian. When available comparisons to experiment are made.

MULTIREFERENCE CALCULATIONS ON THE GROUND AND EXCITED STATES AND DISSOCIATION ENERGIES OF LrF AND LrO

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High-level ab initio approaches were performed on LrF and LrO detailing their numerous excited states, and spin multiplicities. Herein, multi reference methodologies such as the complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) were utilized to calculate ground and excited state properties of LrF and LrO. The potential energy curves for the ground, several excited states, and different dissociation channels are explored at CASSCF and MRCI-Q. Spin-orbit corrections were performed by diagonalizing the MRCI wavefunction on the basis of the ground state. For the second part of this work the bond dissociation energies (BDEs) of LrF and LrO were performed at different levels of theory using a range of basis sets. Core-valence, relativistic effects and spin-orbit contributions to the ground state are discussed. In addition, density functional theory (DFT) is also compared against wavefunction methods. Detailed spectra for intricate diatomic complexes such as actinide oxides and fluorides are essential for future experimental studies on heavy metal containing species.


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Phosphorus and sulfur are integral to life on Earth, and their role in the chemistry of the interstellar medium is highly debated and unknown. Only a handful of phosphorus-bearing species have been detected thus far, with the most recent confirmed detection taking place in 2014. The simultaneous detection of molecules such as PO, SH, and OH indicate the possibility of reactive intermediate species existing in the interstellar medium and circumstellar envelopes of evolved stars. To explore this possibility, we have characterized the [H, P, S, O] tetrameric isomer family using high level ab initio methods. We provide rotational, vibrational, and electronic spectroscopic data to help drive experimental and observational detection of new phosphorus and sulfur-bearing molecules and explore chemical and photochemical pathways to explain possible reservoirs and sources for the as of yet undetected PH and PS diatomic molecules.

Intermission

COMPUTATIONAL AND SPECTROSCOPIC STUDIES OF NITROGEN-CONTAINING DIPOLE BOUND ANIONS

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Nitrogen is an essential ingredient in molecules that support life. Its presence also typically leads to the delocalization of electrons, causing large dipole and quadrupole moments. Such molecules are sometimes able to form negative ions through the electrostatic binding of an excess electron via a process known as Rydberg Charge Exchange. These so-called multipole-bound (dipole-bound, quadrupole-bound, etc.) anions have been shown to be important in radiation damage in biology as well as electron transport processes. Here, we present our recent computational and experimental results studying the creation of new multipole-bound anions.

LOW AND HIGH-RESOLUTION LASER-INDUCED FLUORESCENCE (LIF) OF JET-COOLED NAO

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The chemi-ionization reactions of atomic lanthanides M + O → MO + e− are currently being investigated as a method to artificially increase the ion density in the ionosphere for uniform radio wave propagation. Recent experiments involving the release of atomic neodymium (Nd) into the upper atmosphere have resulted in the production of a cloud with green emission[1]. Based on the cloud emission, it is believed that NdO was the primary product, but spectroscopic characterization of NdO is needed to properly identify the emitting species. While NdO is well characterized above 590 nm, little spectroscopic data exists at emission wavelengths below 590 nm[2,3]. In this work, jet-cooled NdO was produced and low- and high-resolution laser-induced fluorescence (LIF) and dispersed laser-induced fluorescence (DLIF) techniques were used to characterize the electronic structure of NdO from 15,500-21,000 cm−1. Congested DLIF spectra allowed vibrational characterization of the ground X4 state as well as five low-lying states for the first time. By employing high-resolution LIF, the hyperfine structure of the ground X4 state was obtained. Data and analysis of the ground and low-lying states of NdO will be presented.

PHOTOPHYSICS OF A RIGID MACROCYCLE: FeII(CO)2 COMPLEX WITH A NANOSECOND LIFETIME MLCT EXCITED STATE

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Replication of the long lifetimes of 4d transition metal complexes in their 3d counterparts is desirable for both cost reduction and environmental concerns. FeII(μ-HMTI)CN2 is an FeII complex with a remarkable nanosecond lifetime metal-to-ligand charge transfer (MLCT) state in low polarity solvents. Architecturally, the FeII center is ligated to axially-oriented strong field cyanide ligands, and equatorially to a rigid [14]-methylene-N4 macrocycle. This rigidity enforces poor vibrational overlap of excited states, significantly raising the barrier of vibrational relaxation and extending their lifetimes. FeII(CN)2 is studied by optical transient absorption, and spectroelectrochemical studies reproduce the features of the OTA at potentials consistent with metal oxidation and ligand reduction, confirming the attribution of MLCT character to the transition. DFT, TD-DFT and CASSCF computational methods are also used to create a theoretical potential energy manifold, to better describe the deactivation mechanism of the excited state. Further understanding of this molecule’s photophysics will allow for more targeted development of longer-lived FeII complexes.
MECHANISM AND KINETICS OF THE REACTION OF CRIEGEE INTERMEDIATE CH$_2$OO WITH ACETIC ACID STUDIED WITH A STEP-SCAN FOURIER-TRANSFORM IR SPECTROMETER

Rebecca Behera, Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Taiwan; Kaiko Takahashi, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; Yuan-Fern Lee, Department of Applied Chemistry, Institute of Molecular Science, and Centre for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan.

Acetic acid CH$_3$COOH plays an important role in the acidity in the troposphere. The reaction of Criegee intermediate with CH$_3$COOH was proposed to be a potential source of secondary organic aerosol in the atmosphere. We investigated the detailed mechanism and kinetics of the reaction of Criegee intermediate CH$_2$OO with CH$_3$COOH. The time-resolved infrared absorption spectra of transient species produced upon irradiation at 308 nm of a flowing mixture of CH$_3$I/CH$_3$OH/CH$_2$OO at 298 K were recorded with a step-scan Fourier-transform infrared spectrometer. Bands of CH$_3$OO were observed initially upon irradiation; their decrease in intensity was accompanied with the appearance of bands near 886, 971, 1021, 1078, 1160, 1225, 1337, 1402, 1434, and 1777 cm$^{-1}$, assigned to the absorption of hydroperoxymethyl acetic acid (CH$_3$COOHCH$_2$OOH, HPMA), the hydrogen-transfer adduct of CH$_3$OO and CH$_3$COOH. Two conformers of HPMA, an open form and an intramolecularly hydrogen-bonded form, were identified. At a later reaction period, bands of the open-form HPMA became diminished and new bands appeared at 930, 1045, 1200, 1378, 1792, and 1810 cm$^{-1}$, assigned to the formic acetic anhydride (CH$_3$COOHCH$_2$OOH, FAH), a dehydrolysis product of HPMA. The intramolecularly hydrogen-bonded HPMA is stable. From the temporal profiles of HPMA and FAH, we derived a rate constant $k$ = (1.3 ± 0.3) × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the reaction CH$_3$OO + CH$_3$COOH to form HPMA and a rate coefficient $k$ = 980 ± 40 s$^{-1}$ for the dehydrolysis of the open-form HPMA to form FAH. Theoretical calculations were performed to elucidate the CH$_3$OO + CH$_3$COOH reaction pathway and to understand the different reactivity of the two forms of HPMA.

A MICROWAVE AND COMPUTATIONAL STUDY OF PIVALIC SULFURIC ACID MONOMER: MECHANISTIC INSIGHTS INTO THE RCOOH + SO$_2$ REACTION

Nathan Love, Kenneth R. Leopold, Chemistry Department, University of Minnesota, Minneapolis, MN, USA.

Recent microwave studies in our laboratory have explored a series of carboxylic sulfuric anhydrides (RCOOSO$_2$OH, CSA)s that are formed from a cyclic reaction between carboxylic acids and SO$_2$. These studies have shown that the reaction occurs readily with a wide range of carboxylic acids. Moreover, the zero-point corrected activation energies are typically small and, in some cases even negative, but there remains uncertainty as to the factors which control the size and sign of the barrier. In this talk we present chirped-pulse and cavity microwave spectra of pivalic sulfuric anhydride, (CH$_3$)$_2$COOSO$_2$OH (PivSA), and explore the reaction pathway for its formation using computational chemistry. The reaction is found to be best described as a pericyclic heteroene reaction coupled with a 60 degree rotation of the t-butyl group. The process can occur through either a sequential (two-step) or a concerted (one-step) pathway. Based on zero-point corrected single-point CASSI(T) calculations, the sequential pathway has the lowest energy transition state, with a value of -0.52 kcal/mol relative to that of a pivalic acid - SO$_2$ precursor complex. This value represents the lowest barrier for SO$_2$ + carboxylic acid reactions studied to date. When compared with CF$_3$COOSO$_2$OH, which has the highest barrier among the systems studied, the PivSA results provide insight into the relative influence of the electronic and mass effects on the reaction energetics. Additional computational studies further explore the effects of the R group of the RCOOH reactants. Finally, as a precursor to the experimental work on PivSA, the microwave spectrum of the pivalic acid monomer was also recorded and is reported here as well.

INVESTIGATING STRUCTURE AND REACTIVITY RELATIONSHIPS OF NITROGEN-CONTAINING RADICALS WITH COMPUTATIONAL CHEMISTRY AND PHOTOIONIZATION MASS SPECTROMETRY

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Nitrogen-containing organic molecules play significant roles within atmospheric and combustion chemistry due to their presence as volatiles emitted during wildfires, significant components of crude biofuels, and their use in carbon capture technology. The historical focus of gas-phase nitrogen chemistry was on small molecules formed during high-temperature combustion, where the molecular structure of fuel-N has a limited effect on the chemistry due to significant fragmentation. At lower temperatures relevant to Earth’s atmosphere and modern combustion technology, oxidation out-competes thermal decomposition and fuel-N structure can have a substantial effect on reactivity. However, the degree to which chemical pathways differ between N-containing compounds is unclear due to the lack of detailed kinetic studies and potential energy surfaces, resulting in poor representation of these pathways within chemical kinetics models. Here, we present the first set of results in a research program designed to build a comprehensive understanding of the structure and reactivity relationships for model nitrogen-containing compounds, with a focus on differences between radical isomers. Five-membered rings pyrrole (− C$_5$H$_4$N) and pyrrolidine (− C$_5$H$_6$N) serve as model compounds due to their broad chemical importance and ability to form three different radicals. Using KinBot, a computational tool that automatically locates kinetically important stationary points, we have developed potential energy surfaces for reactions of the pyrrolyl and pyrrolidinyl radicals with O$_2$ at the B3LYP/6-31G level of theory for reaction searches, conformational analyses, and IRC calculations, followed by reoptimization of the most relevant stationary points at a B97X-D//M06-2X level of theory and energies refined at CCSD(T)/F12//cc-pVQZ-F12. These results indicate stark differences in reactivity between radical isomers and support our ongoing experimental kinetics studies using a high-pressure laser photolysis reactor coupled to a photoionization mass spectrometer. Characterization of pyrrole and pyrrolidine oxidation will not only provide a detailed knowledge base for future studies of N-containing compounds, but also will allow for comparison to well-studied oxidation pathways of isoelectronic species, such as furan and tetrahydrofuran. Such comparisons will give us a better understanding of the key differences in reactivity between nitrogenuous, oxygenated, and pure hydrocarbon volatiles.
In this talk we will present our work to date on Be$_5$, with comparisons to theory and the Beryllium tetramer from molecular to metallic electron dynamics. MPCs are well-described by three structural motifs that include (i) an all-metal cluster, (ii) an organic ligand, and (iii) an inorganic ligand. The structure and composition of these domains influence the nanocluster optical and electronic properties, providing a well-defined platform to elucidate structure-dependent energy relaxation mechanisms in quantum confined metals. In this presentation, ultrafast electronic and charge carrier relaxation will be discussed. Coherent two-dimensional electronic spectroscopy (2DES) provides an excitation-detection frequency-frequency correlation by spreading the transient signal over two axes that spectrally and temporally resolves state-to-state electronic dynamics on the femtosecond timescale. Here, 2DES was used to distinguish several electronic fine-structure peaks that comprise a charge transfer resonance in molecular-like Au$_{16}$(SC$_2$H$_{11})_3$S nanoclusters. By manipulating the polarization vector of the femtosecond pulses, additional insights on the coupling of transition dipole moments were obtained from cross-peak specific spectra. These results revealed a low-amplitude excited state absorption signal that uniquely relaxed through a charge transfer resonance within 150 femtoseconds. Evidence of population changes of excited vibrational states within the electronic manifold, which undergo intramolecular vibrational relaxation (IVR), were quantified by fitting time-dependent amplitudes of 2DES-detected cross-peaks spanning a frequency range of 1000 cm$^{-1}$. Anisotropy and orientation parameters obtained from polarization-selective 2DES were applied to better understand state-specific relaxation through coupled electronic states. Solvent dependences on charge carrier relaxation will be discussed. These results demonstrate the ability of polarization-selective 2DES to map state-resolved electron dynamics in molecular-like metal nanoclusters.

ZINC OXIDE ELECTRONIC STRUCTURE STUDY USING PES

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As the global energy landscape currently dominated by the fossil fuels is causing environmental and energy issues, there is an urgent need to shift to renewable energy sources. Production of Hydrogen gas a source of energy from water is by far the cleanest renewable energy source. Transition metal oxides are effective catalysts for the hydrogen evolution reaction. Small metal oxide clusters are used as a model to understand the catalytically active sites in bulk. In this study we use photoluminescence and remnant neutral clusters are observed.

SPECTROSCOPIC STUDY OF THE N$_2$H$_2$O COMPLEX IN THE 2 OH STRETCHING REGIONS

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Rovibrational spectra of N$_2$H$_2$O van der Waals complexes were measured in the overtone range, around the 2 OH stretching regions. The rotationally resolved $\nu_1$ and $\nu_2$←$\nu_0$ transitions were observed, where $\nu_1, \nu_2, \nu_3$ are the vibrational quantum numbers of the isolated water molecule. As well, a combination band involving the (0,0,1) state and the intermolecular in-plane N$_2$ bending vibration will be presented. The spectra were measured using continuous wave cavity ringdown spectroscopy in a supersonic expansion, as implemented in the PANTASIO setup [1]. These spectra were analyzed by considering the feasible tunneling motions of this complex, fitted as separate asymmetric rotors for the four observed tunneling states. The tunneling splittings are discussed as a function of the vibrational state and compared with other isotope labels. The assignment of a rovibrational state will be discussed.

WEAKLY BOUND CLUSTERS OF ATMOSPHERIC MOLECULES: INFRARED SPECTRA AND STRUCTURAL CALCULATIONS OF (CO)23-, (CO)2(CO)N2, and (N2)3-

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Structural calculations and high-resolution infrared spectra are reported for trimers and tetramers containing CO2 together with CO and/or N2. Among the 9 clusters studied here, only (CO)32- was previously observed by high-resolution spectroscopy. The spectra, which occur in the region of the ν1 fundamental of CO2 (2350 cm^-1), were recorded using a tunable optical parametric oscillator source to probe a pulsed supersonic slit jet expansion. The trimers (CO)22- and (CO)32- have structures in which the CO or N2 is aligned along the symmetry axis of a staggered side-by-side CO2 dimer unit. The observation of two fundamental bands for (CO)22- and (CO)32- shows that this CO2 dimer unit is non-planar, unlike (CO2)2 itself. For the trimers CO2-CO2 and CO2-N2, the CO or N2 monomers occupy equivalent positions in the “equatorial plane” of the CO2, pointing toward its C atom. To form the tetramers CO2-CO2 and CO2-N2, a third CO or N2 monomer is then added off to the “side” of the first two. In the mixed tetramers CO2-CO2-N2 and CO2-CO2-N2, this “side” position is taken by N2 and not CO. In addition to the fundamental bands, combination bands are also observed for (CO)22-, (CO)32-, and (CO)2-N2, yielding some information about their low-frequency intermolecular vibrations.

Interruption

MATRIX ISOLATION FTIR ANALYSIS OF WEAKLY-BOUND COMPLEXES OF WATER WITH γ-LACTONES
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The interaction preferences of water with small molecules has been an area of interest for many years as we endeavor to better understand solution at the molecular scale. Here, a study of weakly-bound complexes of γ-lactones with water is presented. In this study, matrix isolation FTIR and computational methods were used to examine stable 1:1 complexes of γ-butyrolactone, γ-valerolactone, and Angelica lactone complexes with water. These five-membered heterocycles contain multiple regions that could serve as binding sites for a single water molecule including two chemically distinct oxygen atoms and a lone pair. Matrix isolation FTIR experiments identified several peaks that were not associated with isolated water or lactone, implying the bands are due to weakly-bound complexes of the two. In addition to normal water, D2O and HD2O complexes with the lactones were also observed. The spectra can be interpreted with the aid of computational chemistry. In this work, multiple density functional theories along with MP2 calculations were used to find minimum energy configurations and vibrational structure of the complexes that can be directly compared to our spectra. Possible interpretations of the experimental and computational results are presented.

VIBRATIONAL SPECTROSCOPY OF BENZONITRILE–(W ATER)1–2 CLUSTERS IN HELIUM DROPLETS
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Formic acid is the simplest carboxylic acid and plays a pivotal role in atmospheric chemistry. It is an intermediate in the Water-Gas-Shift reaction, decomposing into either CO2 and H2O or into H2O and CO under ionizing radiation. Furthermore, it is important in acid rain and seeding the nucleation of water molecules in cloud formation. Here, we present our recent work, where femtosecond lasers are applied to study the microsolvation and photodynamics of molecular gas-phase formic acid-water clusters using time-of-flight mass spectrometry. Our cluster distribution confirms the enhanced stability of (FA)n(H2O)n+, where the formic acid cluster forms a cage-like structure surrounding the water molecule. Upon exposure to high laser intensities (400 nm, 200 fs, laser intensities of 1.9x1015 W/cm2), the clusters undergo an enhanced ionization which produces multiply charged ions of CO, CN, and CO2. Coulomb explosion of these ions leads to a large kinetic energy release that is shown to increase with the size of clusters. The measured values are in agreement with a Molecular Dynamics simulation of the Coulomb explosion for the mean size of the clusters within the cluster distribution, suggesting that no movement occurs during ionization. Of particular relevance, we record a large amount of signal for the carbon monoxide trication. KER values were recorded as high as 44 eV for (FA)6+, but increases to 75.3 eV when the cluster distribution is shifted toward (FA)5+, the largest signal. Potential energy curves for CO2+ are calculated using the multireference configuration interaction (MRCl+Q) method to confirm the existence of metastable states with a large potential barrier with respect to dissociation. This combined experimental and theoretical effort confirms the existence of metastable CO2+. Microsolvation and photodynamics in formic acid-water clusters
**THE 2OH OVERTONE SPECTRUM OF H2O-CO2 VAN DER WAALS COMPLEX: SEARCH FOR INTERMOLECULAR MODES EXCITATION AND LARGER COMPLEXES**

BRIAN M HAYS, ROBIN GLORIEUX, Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium; MICHEL HERMAN, Laboratoire de Chimie Quantique et Photophysique, Université Libre de Bruxelles, Brussels, Belgium; CLÉMENT LAUZIN, Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve, Belgium.

The H2O-CO2 van der Waals complex is a rich chemical system composed of two major constituents of the atmosphere. To further expand the knowledge surrounding the structure of this system, the vibrational spectrum of the H2O-CO2 complex was explored around the 2OH stretching region using the FANTASIO+ set-up [1]. The complex was formed in a pulsed slit supersonic expansion and was probed using continuous-wave cavity ringdown spectroscopy in the near infrared range. Combination bands that include intermolecular modes will be reported and compared to recent high-level ab initio calculations [2]. The frequency of such modes is very sensitive to the potential energy surface morphology. Improvements of the FANTASIO+ experimental set-up allowing such observation and the search for larger clusters will be presented.


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**UNDERSTANDING THE SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS) SIGNALS OF AMINO ACIDS, PEPTIDES, AND PROTEINS FOR BIOSENSING APPLICATIONS**

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One promising diagnostic tool for viral infection is surface enhanced Raman spectroscopy (SERS), which is a quick, sensitive light scattering technique that uses the energy of the bonds as a fingerprint to identify molecules. SERS yields enhanced Raman signals by positioning analytes near the surface of metal nanostructures and creating localized, electric fields around the metal with a resonant laser. Fundamentally, the vibrational signatures of peptides and proteins rely on their amino acid composition, secondary structure, and local environment. The SERS signals of these species are further complicated by interactions with the metal nanostructures. For instance, the SERS signals of a peptide can differ if the peptide is adsorbed to a gold nanostructured substrate versus a gold nanoparticle. As another example, tryptophan is an important aromatic residue within the binding domain of many proteins, but its SERS signal shows distinct differences from its Raman signal. These changes in tryptophan’s signal can impact the overall signal from the peptides or proteins it comprises. Using SERS for biosensing requires determining the vibrational signature of the target molecule, which then allows for identification. In SERS sensing of viruses, a common concern is signal variability based on the orientation of these large species on the nanostructure surface. Fortunately, capture molecules can improve signal reproducibility by forcing the analyte into a consistent surface orientation, as well as by selectively targeting the analyte to avoid interference. Peptides can be used to bind the surface proteins of viruses and capture them on SERS surfaces to identify their SERS signatures. In this work, we investigate the SERS signals of a SARS-CoV-2 spike-binding peptide both before and after spike protein binding, along with those of tryptophan and tryptophan-containing peptides, on gold SERS surfaces. Understanding the origins of these signals will provide a basis for the design of a peptide-surface protein-based SERS assay for SARS-CoV-2, along with other potential viruses in the future.

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**APTAMER BASED MICROPARTICLES IMMUNOASSAY METHOD FOR CA125 DETECTION USING RAMAN SPECTROSCOPY**

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Epithelial ovarian cancer (EOC) is considered to have higher mortality, with no or few symptoms at an early stage and a poor prognosis. The treatments and survival solely depend on the stage of cancer at diagnosis. Developing a non-invasive technique that can detect biomarkers (antigens) with sufficient sensitivity, selectivity, and reproducibility is a promising approach to overcome the challenges in the early diagnosis of EOC. The bispecific aptamer is a promising approach to detecting cancer antigens such as CA125 and HE4 at low concentrations. Typically, antibodies are used to recognize the specific type of cancer antigens. However, aptamers have been recently shown to work similarly to antibodies for recognizing antigens, with some advantages over antibodies, including relatively smaller size compared to antibodies that make them recognize the target molecules relatively accurately and chemically synthesized and modified easily according to the target. In this work, we evaluate the affinity and specificity of aptamer towards CA125 using an aptamer-based affinity purification with gold nanoparticles (AuNps) Raman-label. For this purpose, Ni-NTA (Nickel-nitriotic acid) microparticles, used for the magnetic separation process, were conjugated to CA 125-His6 (CA 125 His Tag). It was then allowed to bind biotinylated aptamer. Later, this conjugate was incubated with gold nanoparticles pre-modified with streptavidin and a Raman label. The final conjugate was investigated with surface enhanced Raman spectroscopy following the magnetic separation process. The Raman signatures from the label verified the sandwich-type conjugation of the CA 125-aptamer complex in between Ni-NTA and AuNps.
CELL PHASE IDENTIFICATION IN A THREE-DIMENSIONAL TUMOR CELL CULTURE MODEL BY FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPIC IMAGING

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Cell cycle progression plays a vital role in regulating proliferation, metabolism and apoptosis. Specifically, assessing cell phase is of significant importance since the development of cancer is tightly linked with the dysregulation of cell cycle. However, investigating the cellular status in three-dimensional in vitro models and tissue is often limited to the complexity of sample preparation and the loss of structural integrity. The most common technique nowadays is flow cytometry, which requires a full disintegration of cellular organization and additional fluorescence staining. To overcome these challenges, Fourier transform infrared (FT-IR) spectroscopic imaging is introduced in this study. It is a powerful approach for analyzing biological samples by detecting the vibrational modes of indigenous molecules, thereby eliminating the need for stains and greatly expanding the information beyond phase or intensity contrast of optical imaging. Drawing upon these advantages, we apply FT-IR imaging integrated with unsupervised learning technique to distinguish subtle biochemical compositions between cell phases while retaining a spatial distribution of the innate constituents. The spectral variation in DNA quantity from 2D cell culture is used as an indicator to understand the relative cell cycle stages in a 3D MCF10A acini model. We further evaluate the temporal dependence of these spectral changes throughout the acini formation and validate that cells present to be more proliferative in the early stages of acini formation compared to fully developed acini. Taken altogether, our study presents a computational approach to provide a comprehensive cell phase in tissue-like structure without any requisite for specific biomarker staining, which has the potential to accelerate pharmaceutical agents design with more defined targeted effects. Moreover, the integration of FT-IR spectroscopy and computational methodologies could also expand to the field of pathology and lead to an improvement for clinical diagnostics.

LAFAYETTE, IN, USA

The instrument and methodology to perform autofluorescence-detected photothermal mid-IR (AF-PTIR) microscopy are demonstrated experimentally and applied for chemically-selective label-free imaging of an active pharmaceutical ingredient (API) within a mixture with common pharmaceutical excipients. In AF-PTIR, the heat released from mid-IR absorption induces changes in two-photon excited UV-fluorescence (TPE-UVF) intensity. The spectral dependence of the fluorescence modulation locally informs on chemical composition with a spatial resolution dictated by the diffraction limit of visible light. AF-PTIR provides high selectivity and sensitivity in image contrast for aromatic APIs, complementing broadly applicable commercial methods such as optical photothermal mid-IR (O-PTIR) microscopy.

Figure 1. (a), (c – f) – Bright field, second harmonic generation (SHG), TPE-UVF, AF-PTIR and O-PTIR images of the field of view respectively. (b) – Segmentation results showing the spatial distribution of individual components (lactose particles are shown in blue, indomethacin in green, TiO$_2$ in yellow and Mg stearate is shown in red).

Ft.1.png

A WIDE-FIELD IMAGING APPROACH FOR SIMULTANEOUS SUPER-RESOLUTION SURFACE-ENHANCED RAMAN SCATTERING IMAGING AND SPECTROSCOPY

DEBEN SHOUP, ZACHARY SCHULTZ, Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.

The ability to simultaneously obtain high spatial resolution images and chemical specific information is of interest in a variety of biological and physical processes. Surface-enhanced Raman scattering (SERS) is particularly suited for this purpose due to its ability to enhance signal from Raman vibrational modes by probing molecules near the surface of plasmonic metal nanostructures. The spatial resolution in SERS imaging is limited by the diffraction limit of light, limiting the resolution to hundreds of nanometers. However, Raman reporter molecules absorbed to single nanoparticles experience temporal intensity fluctuations that enable the SERS signal to be fit with localization algorithms, such as stochastic optical reconstruction microscopy (STORM). STORM fittings can be applied to generate images with sub-diffraction limited localization of the emitting centers from the nanoparticles. In this work, we demonstrate a wide-field spectrally resolved SERS imaging approach where a transmission diffraction grating placed before the imaging array detector captures the image and first-order diffraction on the same detector. The first-order diffraction corresponds to the SERS spectrum and can be directly correlated to the location and features of a nanoparticle. STORM fitting both the spatial and spectral response results in improved localization in the spatial response and improved peak identification compared to the measured spectra in the spectral response. We show that spatially correlated Raman spectra from multiple nanoparticles in a wide-field of view are readily obtained on a 10-100 ms time scale, which enables spatially resolved monitoring of chemical processes.

WE06 ISOLATING THE INTRINSIC SPECTRAL RESPONSES OF VIBRATIONAL PROBES: BENCHMARKS FOR REPORTERS OF CONDENSED PHASE AND BIOLOGICAL PROCESSES

SEAN COLEMAN EDINGTON, AHMED MOHAMED, MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

We use cryogenic infrared vibrational predissociation spectroscopy of isolated, nitrite-containing vibrational probe molecules to provide benchmarks for the probe molecule spectral response. Popular probes, such as paracynanophenylalanine, and other nitrite-containing molecules are manipulated in solution to modify conformation and charge state prior to extraction and isolation using electrospray ionization and He buffer gas cooling to 10 K. The vibrational spectra of the cold, He- or H$_2$-tagged molecules are collected in a linear predissociation regime and interpreted with the aid of electronic structure calculations. The results provide insight into the intrinsic spectral response of isolated nitrite vibrational reporters decoupled from solvent effects.

Vibrational probe molecules are popularly employed to provide spectroscopic readouts of local electrostatic environments in phenomena including bulk solvation dynamics, interfacial proton transfer, and enzyme catalysis. A range of these molecules has been developed, allowing investigators to exploit absorption-free “windows” in the infrared spectrum to ease measurement. However, in the condensed phase it is often a challenge to separate the components of the reporter’s response arising from external factors, such as local electric fields or hydrogen bonding, from these due to intrinsic factors such as molecular electrostatic potential or reporter isomerization.

Intermission
Despite the inherent polarization source allows direct probing of other parameters, for instance, the dichroic properties of the samples. In particular, polarimetric detection can enhance structural and chemical contrasts and has been applied for imaging, chemical sensing, and biological tissue classification. While specific optical configurations are known to introduce polarization deviations and reduce sensitivity in anisotropy detection, the influence on absorption measurements has been downplayed as a systematic error. In this work, we characterize the polarization effects introduced by optical components. Using full-Stokes’ measurements, we investigate the polarization scrambling and other effects introduced by various factors such as focusing optics, optical coatings, and incident source polarization. With this thorough analysis, we account for most of the polarization deviation factors introduced in typical experimental systems. Lastly, we optimize spectrometer design based on the characterization and demonstrate infrared absorbance spectra of polymer films with higher precision and anisotropy sensitivity.
Plasmonic nanostructures have paved the way for the development of surface enhanced Raman spectroscopy (SERS), a technique that takes advantage of the Raman signal specific to the molecular vibrational modes. SERS enhances the Raman signal up to 10^9-fold allowing for lower limits of detection. Through the illumination of the nanostructure with a laser, a localized surface plasmon resonance (LSPR) is excited and further the enhances the electric field at the surface of the nanostructure. While the excitation of the LSPR enhances the Raman signal, it can also generate hot carriers that cause the formation of photoproducts that can change the Raman signal. Photoproducts have been reported for various nanostructures in different SERS experiments and can include cross-linking/dimerization, fragmentation, and radical formation. Understanding the parameters and occurrences of these photoproducts will allow for the ability to prevent them when not desired and generate them for further applications. Previously, our group has reported on radical formation with the amino acid tryptophan as well as 4-mercaptobenzoic acid, a common Raman reporter molecule. This work will use changes in the SERS signal to elaborate on the conditions and dynamics of these radical formation reactions associated with the plasmonic activity of nanostructures.

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WF03 9:06 – 9:21
ANDREW W. C. DEWYER, ANGIE ZHANG, KENDREW AU, NILS HANSEN, TIMOTHY S. ZWIEBEL, Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA

Perfluorophenol (C₆F₅OH) is analogous to hexafluorobenzene (C₆F₆), with one fluorine atom replaced by a hydroxyl group. This substitution has a threefold effect: it provides a permanent dipole moment, the molecule remains very close to the oblate symmetric top limit, and intramolecular hydrogen bonds between the H and adjacent fluorine atoms are formed. Hydrogen can tunnel through the barrier to internal rotation of the OH group, lifting the degeneracy of the torsional states. These factors result in the unusual case of a polar, tunneling, near-symmetric top.

To probe these effects, the 1 K rotational spectrum of perfluorophenol between 7.5 and 17.5 GHz has been measured using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. The asymmetry parameter (ς) was experimentally determined to be 0.944, in agreement with the near-oblate geometries predicted by MP2/aug-cc-pVTZ calculations. Tunneling splittings were observed for both a-type and b-type transitions due to the C-O bond axis lying between the a and b inertial axes, a consequence of the near-symmetry of perfluorophenol. The energy difference between the split 0⁻⁻ and 0⁻⁺ tunneling levels was established to be 24 850 MHz. Preliminary wB97XD/aug-cc-pVTZ calculations estimate a barrier to internal rotation of $\chi = 137$ MHz, which allows its spectrum to be easily observed. The microwave spectrum of acetoin has been collected by Gou and coworkers and multiple methyl rotors, the study of diacetyl is challenging. Acetoin, conversely, has a strong dipole moment of 2.55 D, which allows its spectrum to be easily observed. The microwave spectrum of acetoin has been collected by Gou and coworkers.

A curious rotational spectrum of perfluorophenol, AN OH IN FLUORINE’S CLOTHING - THE CURIOUS ROTATIONAL SPECTROSCOPY OF PERFLUOROPHENOL

WF05 9:42 – 9:57
CONFORMATIONAL ANALYSIS OF VALINE METHYL ESTER BY MICROWAVE SPECTROSCOPY

DINESH MARASINGHE, Michael Tuberger, Department of Chemistry and Biochemistry, Kent State University, Kent, OH, USA

The rotational spectra of two conformers of valine methyl ester (ValOMe) have been measured and assigned using a cavity based Fourier-transform microwave spectrometer in the range of 9–18 GHz as a part of a project investigating the structures of a series of amino acid methyl esters. We modelled 15 possible conformers of ValOMe using the b97XD/aug-cc-pVTZ level of theory. 59 rotational transitions assigned to conformer I were fit to Watson’s A-reduced Hamiltonian: A = 2552.011(1) MHz, B = 1041.812(2) MHz, and C = 938.549(2) MHz. 2-H nuclear quadrupole hyperfine splittings were resolved, and the 137 hyperfine components were fit to $\chi = 4.28(2)$ MHz and $\chi = 1.28(1)$ MHz. The spectrum of conformer II also reveals tunneling splittings from the ester methyl rotor. The XIAm program was used to fit the barrier to the internal rotation of the methyl rotor. The best fit $\chi_b$ barrier was found to be 387(8) cm⁻¹. 20 rotational transitions were assigned for conformer II and the fitted rotational constants are A = 2544.049(9) MHz, B = 1092.337(2) MHz, and C = 896.301(1) MHz. The transitions were split by nuclear quadrupole coupling and tunneling, and complete assignment of these components is ongoing.

WF06 10:39 – 10:54
ROTATIONAL SPECTRUM OF ACETIN (CH₃COCH(OH)CH₃)

JONATHAN REBELSKY, Department of Chemistry, University of Wisconsin Madison, Madison, WI, USA; CHASE FISCHLZT, Department of Chemistry, University of Wisconsin Madison, Madison, WI, USA; STEVEN SHIPMAN, Department of Chemistry, New College of Florida, Sarasota, FL, USA; SUSANNA L. WEAVER, Chemistry and Astronomy, University of Wisconsin Madison, Madison, WI, USA

Acetin (CH₃COCH(OH)CH₃) is a common additive to e-cigarette fluids. Though not toxic itself, it decomposes into diacetyl (CH₃COCCH₃), which is known to cause lung damage. Diacetyl may be important in interstellar chemistry because it has been observed as a VUV desorption product from an interstellar ice analog experiment studying acetaldehyde-based ices. We reported on an attempt to study this molecule at this conference in 2021. Given its extremely small dipole moment and multiple methyl rotors, the study of diacetyl is challenging. Acetin, conversely, has a strong dipole moment of 2.55 D, which allows its spectrum to be easily observed. The microwave spectrum of acetin has been collected by Gou and coworkers as reported in the Microwave Newsletter. We extended measurements of rotational lines from 70 to 115 GHz and from 140 to 800 GHz. These data were collected using a long-path length direct absorption flow cell spectrometer. The spectral analysis is underway. The results of this spectrum will enable astronomical observations for both acetoin and, by proxy, diacetyl. Here we will report on the millimeter/submillimeter spectrum of acetin and our progress towards its analysis and comparison to observations.
WF07
10:57–11:12
ON THE CHOICE OF HAMILTONIAN REDUCTION AND REPRESENTATION FOR THE ROTATIONAL SPECTRUM
OF 1,1-DIFLUOROACETONE RECORDED UP TO 640 GHz

S. A. COOKE, Natural and Social Science, Purchase College SUNY, Purchase, NY, USA; PETER R. FRANKE, Department of Chemistry, University of Florida, Gainesville, FL, USA; PETER GRONER, Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO, USA; L. MARQUÉS, R. A. MOITIENKO, UMR 8523 - PIKAM - Physique des Lasers Atomes et Molécules, University of Lille, CNRS, F-59000 Lille, France.

While recording the cm-wave spectrum of the title compound, we discovered that the Watson A reduction in the $^1$ representation resulted in a poorly fitting Hamiltonian to the observed ground state transition. However, the Watson S reduction in the $^2$ representation gave satisfactory results as did both reductions in the $^3$ representation. The prior work used only measurements between 6 GHz and 16 GHz and only quartic centrifugal distortion (CD) constants were needed in the fits. In order to further explore the reduction/representation-dependence of the spectroscopic fits quartic and sextic CD constants have been obtained from quantum chemical calculations. Furthermore higher frequency measurements have been recorded which provide greater certainty in the experimental CD constants, and ii) now require up to 26 CD constants in the Hamiltonian. Further insights into the failure of the $^3$-representation will be presented. In the course of performing this work the methyl group barrier to internal rotation has been improved and will also be discussed.


WF09
11:33–11:48
LINE POSITION AND LINE INTENSITY ANALYSES OF H$_2^18$O UP TO THE FIRST TRIAD AND $J = 20^a$

L. H. COUDERT, Institut des Sciences Moléculaires d’Orsay, Université Paris-Saclay, CNRS, Orsay, France; GEORGI CH. BALEV, Ryhodinichemisches Institut, Jana weisz Universität Gießen, Giessen, Germany; SEMEN MIKHAILENKO, Atmospheric Spectroscopy Div., Institute of Atmospheric Optics, Tomsk, Russia; ALAIN CAMPAURRE, UMR5588-CPMP, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France.

We present a line position analysis of a large body of data pertaining to H$_2^18$O and involving all 5 vibrational states up to the First Triad, namely, the lowest lying states (000), (010), (020), (100), and (001). The data set contains infrared lines retrieved in this work, from WFS and from high-temperature emission spectra, and already published high-resolution measurements including microwave and THz transitions, and kHz accuracy transitions. The analysis, carried out with the Binding-Rotation fitting Hamiltonian, allows us to reproduce more than 11700 data with a unitless standard deviation of 1.6 up to $J = 20$ and $K_a = 16$. The highly accurate THz transitions are reproduced with an RMS of 0.2 MHz and the kHz accuracy transitions with an RMS better than 0.3 MHz. A line intensity analysis of absorption transitions involving the same vibrational states will also be presented. FIR line intensities measured in this work using FTS were fitted in addition to previously measured line intensities. 3890 line intensities are accounted for with a unitless standard deviation of 1.4.

The absorption line list calculated using these results will be compared to that recently obtained from theoretical calculations. With the present set of spectroscopic parameters, discrepancies up to 0.09 cm$^{-1}$ are noted for the line positions.

1. Research support from the French Programme National de Physique et Chimie des Molecules Interazoniales is acknowledged

WF08
11:15–11:30
THE FAR-INFRARED SPECTRA OF CYCLOPROPYLAMINE

YUE LIANG, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, China; BRANT E. BILLINGHURST, EFD, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada; BOWEN LIU, JIQIU CHEN, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, China.

The infrared spectra of cyclopropylamine (c-C$_3$H$_7$NH$_2$) in the region of 35-600 cm$^{-1}$ have been measured at 298K with a resolution of 0.0006 cm$^{-1}$ using the far-infrared beamline at the Canadian Light Source synchrotron. We report here the results of the rotational analysis of transitions associated with the ground state and the first excited state of the -N$_2$H$_2$ torsional mode between 35 and 60 cm$^{-1}$. The ongoing assignment and analysis of hot bands and overtones involving higher torsional states will also be discussed.


WF10
11:51–12:06
HIGH-RESOLUTION LASER SPECTROSCOPY OF THE S$_1 ← S_0$ TRANSITION OF ACETALDEHYDE

KOSUKE NAKADOMA, Graduate School of Science, Kobe University, Kobe, Japan; SHUNJI KASAHARA, Molecular Photonics Research Center, Kobe University, Kobe, Japan; AKIRA SHIMIZU, BIN TANGMUG, Graduate School of Science, Kobe University, Kobe, Japan; MASAKA BABIA, Graduate School of Science, Kyoto University, Kyoto, Japan.

Acetaldehyde is one of a prototype molecule to study large amplitude motion. In the ground state, the energy level structure were well understood by considering the methyl torsional motion (rotation of the C$_3$-H$_2$ axis)$^{10}$, $^{20}$ On the other hand, in the $S_1$ state, it is necessary to consider the aldehyde-hydron inversion motion (rotation of the C$_3$-H$_2$ axis)$^{10}$ in addition to the methyl torsion. Rotationally resolved spectrum of the $S_1 ← S_0$ transition were observed by using a pulsed amplified CW laser, and obtained effective rotational constants $^{b, c}$.

In this work, rotationally-resolved high-resolution fluorescence excitation spectra of the $S_1 ← S_0$ transition of acetaldehyde have been observed: Sub-Doppler excitation spectra were measured by crossing a single-mode UV laser beam perpendicular to a collimated molecular beam. The typical linewidth of observed spectra was about 40 MHz. The absolute wavenumber was calibrated with accuracy 0.0002 cm$^{-1}$ by measurement of the Doppler-free saturation spectrum of iodine molecule and fringe pattern of the stabilized etalon. The observed spectra around 30118 cm$^{-1}$ and 30375 cm$^{-1}$ correspond to $^3$1$^2$ and $^1$1$^2$ band respectively. We are trying to analyze the rotational structure including the interaction with the large amplitude motions and then determine the parameters of the $S_1$ state.

ROTATIONAL SPECTROSCOPY OF n-PROPANOL: Aa AND Ag CONFORMERS

OLIVER ZINGSHEIM, HOLGER S. P. MÜLLER, BETTINA HEYNE, MARIYAM FATIMA, LUIS BONAH, STEPHAN SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; ARNAUD BELLOCHE, Millimeter- and Submillimeter-Astronomie, Max-Planck-Institut für Radioastronomie, Bonn, NRW, Germany; FRANK LEWEN, I. Physikalisches Institut, Universität zu Köln, Köln, Germany.

PROPANOL occurs in two isomers, as a primary alcohol normal-propanol (CH₃CH₂CH₂OH) and as a secondary alcohol iso-propanol (CH₂CH(OH)CH₃). Moreover, normal-Propanol occurs in five different conformers: Gg, Gp, Gg’, Aa, and Ag. Rotational spectra of all three conformers of the G family are well described [1], hence, an astronomical search of their rotational fingerprints is possible, in contrast to Aa and Ag.

Rotational spectra of normal-propanol were recorded in the frequency region of 18 to 50 GHz. Double-modulation double-resonance (DM-DR) measurements were performed additionally, in particular to unambiguously assign weak transitions of the Aa and to verify assignments of the Ag conformer. An extended quantum mechanical model for Aa was derived, based on Ref. [2]. Furthermore, the existence of two tunneling states, Ag’ and Ag”, has been proven by unambiguously assigned transitions, but a quantum mechanical model description for Ag could not be given yet. The astronomical detection of all five conformers is now possible, but the quantum mechanical description of the A family should still be improved in the future.

ON THE SPECTROSCOPY OF ACYLIUM IONS: INFRARED ACTION SPECTROSCOPIC DETECTION OF NCCO+

OSKAR ASVANY, MARCEL BAST, STEPHAN SCHLEMMER, SVEN THORWIRTH, J. Physikalisch-Institut, Universität zu Köln, Köln, Germany.

The linear N≡C−C≡O ion has been studied spectroscopically for the first time using the Free Electron Laser for Infrared Experiments, FELIX, at Radboud University (Nijmegen, The Netherlands) in combination with the 4K 22-pole ion trap facility FELEX. The vibrational spectrum of NCCO was observed in the range from 500 to 1500 and 2000 to 2500 cm⁻¹ using resonant photodissociation of the corresponding Ne-complex while monitoring the depletion of the ion-Ne cluster signal as a function of wavenumber. Spectroscopic assignment of vibrational bands relies on comparison against results from high-level quantum-chemical calculations performed at the CCSD(T)/level of theory and very good agreement is found.

INTERMISSION

HIGH-RESOLUTION SPECTROSCOPY OF MgKr²⁺ IN ITS GROUND AND LOW-LYING ELECTRONICALLY EXCITED STATES

CARLA KREIS, Laboratory of Physical Chemistry, ETH Zurich, Zurich, Switzerland.

Diatomic molecules R₂M consisting of a rare-gas atom R and an alkaline-earth-metal atom M and their singly and doubly-charged cations RM⁺ and RM²⁺ have unusual chemical properties that are related to the low first and second ionization energies of R and the high ionization energy of M. In MgAr the second ionization energy of Mg is lower than the first ionization energy of Ar. Consequently, MgAr²⁺ is thermodynamically stable and Rydberg series of MgAr⁺ can be observed that converge on the X₁Σ⁺, 5₂⁺ ground state of MgAr⁺. In this contribution, we present the results of spectroscopic investigations of MgKr²⁺ in its ground and low-lying electronically excited states that complement earlier studies of this cation. Pulsed-field ionization-zero-kinetic-energy (PF-EZEK) photoelectron spectra of the X₁Σ⁺ ground state of MgKr⁺ were recorded following single-photon excitation from the a₁Π₉, metastable state of MgKr. Vibrational channel interactions enabled the observation of the lowest vibrational levels of MgKr²⁺ and the determination of an accurate value of the adiabatic ionization energy of metastable MgKr (38183 ± 2 cm⁻¹). Using isolated-core multiphoton Rydberg dissociation (ICMRD) spectroscopy, spectra of several low-lying electronically excited states of MgKr²⁺ were observed that are associated with the Kr + Mg (n) dissociation limits with n = 3, 4 and 1 ≤ s, p and d. These states may be regarded as the lowest members of Rydberg series converging on the ground state of MgKr²⁺. These studies represent first steps towards studying the doubly charged cation MgKr²⁺.

INTERMISSION

RO-VIBRATIONAL SPECTROSCOPY OF LINEAR C₃H⁺

PHILIPP SCHMID, THOMAS SALOMON, SVEN THORWIRTH, OSKAR ASVANY, STEPHAN SCHLEMMER, J. Physikalisch-Institut, Universität zu Köln, Köln, Germany.

The C₃H⁺ ion has been identified as an important reaction intermediate in the carbon chemistry network in the interstellar medium and was recently detected via its rotational lines. Laboratory measurements on the rotational spectrum of linear C₃H⁺ provided accurate spectroscopic parameters for the vibrational ground state. In addition, vibrational predissociation spectroscopy of the linear C₃H⁺-Ne complex offered first insights on the vibrational band positions of this molecule. Here, we report on the first infrared study of C₃H⁺ at high spectral resolution that was targeted at the C−H stretching mode ν₁, located around 3170 cm⁻¹. The experiment was performed in our cryogenic multipole 22-pole ion trap instrument LIRtrap. In addition to the vibrational fundamental, the associated ν₂ + ν₂ → ν₂ hot band originating from the energetically lowest bending mode could be detected. Both spectra are in good agreement with estimates based on previous quantum-chemical calculations and low-resolution measurements.

GAS-PHASE CHARGE TRANSFER ELECTRONIC SPECTROSCOPY OF AG⁺-BENZENE COMPLEX

DYLAN S. ORR, JASON E. COLLEY, MICHAEL A DUNCAN, Department of Chemistry, University of Georgia, Athens, GA, USA.

Charge transfer electronic spectroscopic results were reported for the Ag⁺-benzene complex in the gas phase using photodissociation. The Ag⁺-benzene complex was generated by laser vaporization of a silver rod in combination with pulsing an inert gas seeded with benzene then mass selected and probed using a time-of-flight mass spectrometer. The mass-selected ions were then fragmented and scanned using a solid-state OPO capable of scanning through the UV-Visible range. A high-resolution electronic spectrum of Ag⁺-benzene was reported in the UV-Visible range to determine the upper threshold for the dissociation energy of the Ag⁺-benzene complex which were compared with previous velocity map imaging results. An unexpected feature was observed in the lower UV region which was attributed to the HOMO-LUMO absorption on an excited benzene ligand.
HIGH-RESOLUTION INFRARED SPECTRA OF THE OH-STRETCHING BANDS OF PROTONATED WATER DIMER, H$_2$O$^+$. THOMAS SALOMON, OSKAR ASVANY, I. Physikalisches Institut, University of Cologne, Cologne, Germany; CHARLES R. MARKUS, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA; STEPHAN SCHLEMMER, I. Physikalisches Institut, University of Cologne, Cologne, Germany.

We present high-resolution infrared action spectra of cold H$_2$O$^+$. For this purpose the mass selected parent ions are stored in a cryogenically cooled 22-pole ion-trap (CO2-trap). There we employ a two-color photodissociation scheme where first the symmetric or the anti-symmetric O-H-stretching band is excited by a narrow linewidth cw-OPO. Then, Light from a CO2 laser is used to efficiently dissociate the parent molecule. The infrared-absorption of the parent ion is recorded by the appearance of H$_2$O photoproducts. This procedure follows the seminal approach first invented in the group of Y.T. Lee. The rotationally resolved and basically background-free spectrum exhibits a complex structure, making the assignment of individual rotational tunnelling features challenging. Nonetheless, recurring spectral spacings are used to start to unfold the rotational tunnelling structure. Moreover, spectral indicators are found that support the assumption of hydratine-like tunnelling dynamics being present in this peculiar molecule of fundamental interest.

a) L. J. Yeh, M. Okamura, J. D. Myers, J. M. Price, and Y. T. Lee, Vibrational spectroscopy of the hydrated dinitrogen cluster ions H$_2$O$^+$(H$_2$O)$_n$ (n ≥ 1, J. Chem. Phys. 91, 7,110-7,130 (1989)).

ANIONIC REARRANGEMENTS FOLLOWING DECARBOXYLATION OF BENZOPHENONE DERIVATIVES WITH CRYOGENIC IR SPECTROSCOPY

JOSEPH P. MESSINGER, EVAN H. PEREZ, ANNA GABRIELLA DEL ROSARIO RULLÁN BUXÓ, TIM SCHLEIF, OLIVIA MOSS, Department of Chemistry, Yale University, New Haven, CT, USA; KIM GREIS, Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany; MARK JOHNSON, Department of Chemistry, Yale University, New Haven, CT, USA.

Carbanions are highly reactive intermediates that are commonly used in organic synthesis. Here, we investigate the fundamental gas phase spectroscopy and isomerization of substituted aromatic phenides (deprotonated benzene derivatives) using isomer-selective cryogenic ion vibrational predissociation spectroscopy (1000 cm$^{-1}$ - 4200 cm$^{-1}$). The phenide is formed by the decarboxylation of the 4-benzoyl benzene anion (4BBA, C$_{14}$H$_9$O$_3$), a substituted benzophenone, in a commercial Orbitrap mass spectrometer before being transferred to the triple focusing time-of-flight photofragmentation mass spectrometer. The resulting spectra are congested, suggesting the presence of multiple isomers. They are revealed by quantum chemical calculations in conjunction with two color IR-IR photobleaching spectroscopy to be the expected phenide, and a new molecule formed by multiple steps of isomerization that end in ring-closed product. The identities of these compounds and the proposed mechanism are confirmed by additional experiments using 4BBA and 2BBA.

CARBOXYLATE STRETCHING MODES ARE STRUCTURAL PROBES FOR ION-DEPENDENT BINDING PROPERTIES IN ALKALINE EARTH METAL-EDTA COMPLEXES

ALEXANDRA TSYBISOVA, VLADIMIR GORBACHYOV, PETER CHEN, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland.

The activation and utilization of N$_2$ have become attractive areas of research, with the ultimate goals of dinitrogen fixation and reduction. A deep understanding of the interaction and electronic influences between transition metal atoms and the inert N$_2$ molecule would allow facilitating the transformation of inert molecular nitrogen to useful nitrogen-containing chemicals. In this work, we used cryogenic ion vibrational predissociation (CIVP) spectroscopy to experimentally probe the activation of the molecular nitrogen by copper complexes bearing terpyridine and pyridine-2,6-bis(oxazoline) ligands. We used the N$_2$ stretching vibration as a reporter chromophore to estimate how electronic and steric effects affect the activation of the molecular nitrogen by these copper complexes. In contrast to the previous studies on nitrogen activation that probe “late activation” of the nitrogen molecule, our cryogenic studies give access to the “early activation” states that otherwise difficult to study, due to the tunneling barriers and the proposed mechanism that is confirmed by additional experiments using 4BBA – d$_6$ and 2BBA – d$_6$.

For this purpose the mass selected ions are photoexcited with a narrow linewidth cw-OPO, then, light from a CO$_2$ laser is used to dissociate the parent molecule. The infrared-absorption of the parent ion is recorded as the appearance of H$_2$O photoproducts. This procedure follows the seminal approach first invented in the group of Y.T. Lee. The rotationally resolved and basically background-free spectrum exhibits a complex structure, making the assignment of individual rotational tunnelling features challenging. Nonetheless, recurring spectral spacings are used to unfold the rotational tunnelling structure. Moreover, spectral indicators are found that support the assumption of hydratine-like tunnelling dynamics being present in this peculiar molecule of fundamental interest.

b) L. J. Yeh, M. Okamura, J. D. Myers, J. M. Price, and Y. T. Lee, Vibrational spectroscopy of the hydrated dinitrogen cluster ions H$_2$O$^+$(H$_2$O)$_n$ (n ≥ 1, J. Chem. Phys. 91, 7,110-7,130 (1989)).

We present high-resolution infrared action spectra of cold H$_2$O$^+$. For this purpose the mass selected parent ions are stored in a cryogenically cooled 22-pole ion-trap (CO$_2$-trap). There we employ a two-color photodissociation scheme where first the symmetric or the anti-symmetric O-H-stretching band is excited by a narrow linewidth cw-OPO. Then, Light from a CO$_2$ laser is used to efficiently dissociate the parent molecule. The infrared-absorption of the parent ion is recorded by the appearance of H$_2$O photoproducts. This procedure follows the seminal approach first invented in the group of Y.T. Lee. The rotationally resolved and basically background-free spectrum exhibits a complex structure, making the assignment of individual rotational tunnelling features challenging. Nonetheless, recurring spectral spacings are used to unfold the rotational tunnelling structure. Moreover, spectral indicators are found that support the assumption of hydratine-like tunnelling dynamics being present in this peculiar molecule of fundamental interest.

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FIRST LABORATORY DETECTION OF N\(^{13}\)CO\(^{-}\) AND SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURE OF THE NCO\(^{-}\) ANION

LUCA DORE, Dept. Chemistry “Giacomo Cianiian”, University of Bologna, Bologna, ITALY; LUCA BIZ-ZOCCHI, Dipartimento di Chimica G. Cianiian, Università di Bologna, Bologna, Italy; VALERIO LAT-TANGLI, The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany; MATTIA MELOSSO, Dept. Chemistry “Giacomo Cianiian”, University of Bologna, Bologna, ITALY; FILIPPO TAMASSIA, Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Bologna, Italy; MICHAEL C. CARL, Center for Astrophysics, Harvard & Smithsonian, Cambridge, MA, USA.

The cyanate anion NCO\(^{-}\) is a species of considerable astrophysical relevance. It is widely believed to be embedded in interstellar ices present in young stellar objects but has not yet been detected in the dense gas of the interstellar medium. Here, very accurate laboratory measurements of the rotational spectrum of the N\(^{13}\)CO\(^{-}\) isotopologue at millimeter wavelengths and three additional lines of the parent isotopologue up to 437.4 GHz are reported. With this new data, the rotational spectrum of both isotopologues can be predicted to better 0.25 km s\(^{-1}\) in equivalent radial velocity up to 1 THz. Moreover, a semi-experimental equilibrium structure of the anion is derived by combining the experimental ground-state rotational constants of the two isotopologues with theoretical vibrational corrections, obtained by using the coupled-cluster method with inclusion of single and double excitations and perturbative inclusion of triple excitations (CCSD(T)). The estimated accuracy of the two bond distances is on the order of 5 \(\times\) 10\(^{-4}\) Å.

Molecular spectroscopists are blessed because they can attend the annual international symposium throughout their lives. I am grateful to David Dennison, Harald Nielsen, Gerhard Herzberg, Bright Wilson and Charlie Townes who initiated the ISMS in 1947, and chairmen Harald Nielsen, Narahari Rao, Terry Miller, Ben McCall, and Josh Vura-Weis who maintained the high standard. Although the basic organization and the spirit of the symposium remained the same there were a few major changes. The biggest change was of course the change of venue from the Ohio State University to the University of Illinois Urbana Champaign in 2014. Thus Columbus meeting changed to the UIUC meeting. We are grateful to Ben McCall for undertaking this big task. Other big change I remember was change of dinner and after dinner speech to picnic. My first ISMS was the 17th in 1964 when I was a postdoc in Ottawa. When I started my search for the laboratory spectrum of H\(^{3}\)CN I stopped attending conferences so I missed ISMS for 6 years from 1976 to 1981 but otherwise attended all meetings till this year. John Johns and Jon Hougen also from Ottawa started attending the ISMS several years before me. Hougen never missed the meeting till he passed away in 2019. Hougen was the champion attendee of the ISMS. I have given 6 plenary talks: in 1969 (collision selection rules), 1975 (forbidden rotational transitions), 1984 (H\(^{3}\)CN in the laboratory plasmas), 1986 (IR spectra of molecular ions), 1999 (H\(^{3}\)CN in interstellar plasmas), and 2008 (H\(^{3}\)CN in the Galactic center). I also gave an after dinner speech with the title Astronomy and Spectroscopy. One scientific change of ISMS has been introduction of astronomy. This gradually happened but was accelerated around 2014. This was convenient for me because my research moves from spectroscopy to astronomy. Recently my papers have been exclusively presented in astronomy session. I shall be 90 years old at the symposium this year. Perhaps I am the oldest participant of this symposium.
MY ISMS

Y ASUKI ENDO, Department of Applied Chemistry, National Yang Ming Chiao Tung University, Hsinchu, Tai-
wan.

My first ISMS was 35th meeting in 1980. At that time I was working at Institute for Molecular Science as a research
associate of prof. Hirotu’s group, mainly doing mm-wave spectroscopy of short lived species. In that meeting Terry A. Miller
gave a plenary talk, where the word Jahn-Teller interaction attracted me.

A few years later I was able to observe a Jahn-Teller molecule, CH₂O. Results were presented at my second attendance
in 1984. In the meeting, spectroscopy of molecular ions is hot topics, and impressive plenary talks were given by T. Oka
and R. J. Seykally.

My next attendance was 1990, six years later. In the meantime, I moved to the University of Tokyo and started a new
laboratory, where I constructed an FTMW spectrometer. At the 1990 meeting, there was a presentation by T. A. Miller and V.
E. Bondybey’s group showing a pulsed discharge nozzle (PND) to produce short lived species in the supersonic jet. Since I
was looking for an effective method to produce short lived species for my FTMW spectrometer, the PND seemed to be quite
attractive. When I came back to Japan, we started to combine the PND with our FTMW spectrometer. Soon we were able
to observe a number of short lived species. The PND-FTMW system gave me a chance to give my first plenary talk at 1993
ISMS meeting. Since the 1990 meeting, I or my colleagues, students attended the meeting almost every year.

Another important meeting for me was the 2012 ISMS, where M. I. Lester gave a plenary talk mentioning the importance
of so called Criegee intermediates. Inspired by her talk, we started FTMW study of the Criegee intermediates. Until now I
were able to write more than 20 papers for the Criegee intermediates. Furthermore, the results led me to give my third
plenary talk in 2014. After my retirement from the University of Tokyo in 2015, I moved to National Yang Ming Chiao Tung
University with my FTMW spectrometer, and I am still working in the microwave region.

PHOTODISSOCIATION AND VELOCITY-MAP IMAGING OF CARBON CLUSTER CATIONS

NATHAN JOHN DYNAK, BRANDON M. RITTGERS, JASON E. COLLEY, DOUGLAS J. KELLAR,
MICHAEL A DUNCAN, Department of Chemistry, University of Georgia, Athens, GA, USA.

Carbon cluster cations are generated in the gas phase by laser vaporization of a carbon rod in a pulsed supersonic
expansion. Cn+ clusters (n = 6, 10, 11, 12, 15, 20) are mass selected using a reflection time-of-flight mass spectrometer
and photodissociated at 355 nm. The main channel for this multiphoton dissociation process is the loss of neutral Cn, resulting in Cn−1 cystions. The cationic fragments are reaccelerated into an imaging flight tube with velocity-map imaging grids and detected with an imaging detector. Significant kinetic energy release (KER) is observed for all of the cationic fragments, but with much greater KER values detected for the larger species. Specifically, the n = 10, 11, 12, 15 and 20 species known to have monocylic ring structures produce much greater KER than the n = 6 and 7 species known to have linear structures. Consideration of photon energies for two- or three-photon processes, together with the KER values and estimates for ring strain energies allow investigation of the energetics of the bonding and dissociation in these systems.

PHOTODISSOCIATION DYNAMICS OF CH₃OO ON MULTIPLE POTENTIAL ENERGY SURFACES: EXPERIMENT
AND THEORY

VINCENT J. ESPOSTIO, TANLIN LIU, GUANGHAN WANG, ADRIANA CARACCIOLO, Department
of Chemistry, University of Pennsylvania, Philadelphia, PA, USA; MICHAEL F. VANSCO, Chemical Dynamics
Group, Argonne National Laboratory, Lemont, IL, USA; ERNEST ANTWI, Department of Chemistry, Univer-
sity of Louisiana at Lafayette, Lafayette, LA, USA; OLIVIA WERBA, Department of Chemistry, University of
Pennsylvania, Philadelphia, PA, USA; SARAH A. BUSH, RACHEL E. BUSH, BARBARA MARCHETTI,
TOLGA N. KARSHI, Department of Chemistry, University of Louisiana at Lafayette, Lafayette, LA, USA;
MARSHA LESTER, Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA.

Criegee intermediates are zwitserionic carbonyl oxide species that result from alke ne ozonolysis in the Earth’s tropo-
sphere. UV excitation of the simplest Criegee intermediate, CH₃OO, across most of the broad span of the (B' - X') spectrum results in prompt dissociation to two energetically accessible asymptotes: O (O) + H₂CO (X''A') and O (O') + H₂CO (X''A''). Dissociation proceeds on multiple singlet potential energy surfaces that are coupled by two regions of conical intersection (CI). Velocity map imaging studies reveal a bimodal total kinetic energy (TKER) distribution for the O (O') + H₂CO (X''A') products. The unexpected low TKER component corresponds to highly internally excited H₂CO (X''A') products. Full dimensional trajectory calculations suggest that the bimodal TKER distribution of the O (O') + H₂CO (X''A') products originates from two different dynamical pathways: a primary pathway involving a CI located mid-way through one Cn region to products, and a smaller component sampling both Cn regions during the dissociation process. Those that access both Cn regions likely give rise to the more highly internally excited H₂CO (X''A') products. The remaining trajectories dissociate to O (O') + H₂CO (X''A') products after traversing through both Cn regions. No trajectories follow the more thermodynamically favorable spin-forbidden pathway to O (O') + H₂CO (X''A') products. This complementary experimental and theoretical investigation provides insight into the photodissociation of CH₃OO via multiple dissociation pathways through two regions of Cn that control the branching and energy distributions of products.
OZONE PHOTODISSOCIATION IN THE SINGLET CHANNEL AT 226 NM
MEGAN AARDEMA, Department of Chemistry, Texas A & M University, College Station, TX, USA; GEORGE MIBANE, Department of Chemistry, Grand Valley State University, Allendale, MI, USA; SIMON NORTH, Department of Chemistry, Texas A & M University, College Station, TX, USA.

Ozone photodissociation plays an important role in atmospheric chemistry and has been the focus of many experimental and theoretical studies. In the Hartley band (200-300 nm) there are two spin-allowed dissociation channels, one forming excited state, singlet products (O2(a 1Σg) + O(1D)), and one forming ground state, triplet products (O2(X 3Σg) + O(3P)). The singlet channel is the primary dissociation channel in the Hartley band, and numerous studies have characterized the dissociation at longer wavelengths within the Hartley band. There has been considerable interest in the triplet channel dissociation at 226 nm following the observation of low velocity O(3P) fragments, but the singlet channel dissociation dynamics at 226 nm has not been previously reported. We report the rotational state distribution and vector correlations of the O2(a 1Σg) + O(3P) fragments arising from the 226 nm photodissociation of jet-cooled O3. Consistent with previously reported trends, the rotational distribution is shifted to higher rotational states with decreasing wavelength. We observe highly suppressed odd rotational state populations due to a strong A-doubt propensity. The measured rotational distribution is in agreement with classical trajectory calculations for the v=0 products, although the distribution is narrower than predicted. The spatial anisotropy follows the previously observed trend of decreasing β with increasing photon energy with β = 0.72 ± 0.14 for ν=0, ν=38. As expected for a triatomic molecule, the v-j correlation is consistent with v perpendicular to j, but the measured correlation is non-limiting due to rotational and translational depolarization. The j-dependent linewidth of the O2(a 1Σg) REMPI spectrum is also discussed in connection with the lifetime of the resonant O2(a 1Σg) state and predissociation via the II 11g valence state.

RAPID ALLYLIC 1,6 H-ATOM TRANSFER IN A CRIEGEE INTERMEDIATE WITH UNSATURATED SUBSTITUENTS
ANNE S HANSEN, Chemistry, University of Pennsylvania, Philadelphia, PA, USA; YUH-JIN CHAN, Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA; STEPHEN J. KLIPPENSTEIN, Chemical Science and Engineering Division, Argonne National Laboratory, Lemont, IL, USA; MARSHA LESTER, Chemistry, University of Pennsylvania, Philadelphia, PA, USA.

A new allylic 1,6-H-atom transfer mechanism is established through infrared (IR) excitation of the 2-butenyl-oxirane intermediate [CH2=CH-CH=CHO]. Rapid 1,6-H-atom transfer is facilitated for certain conformers of 2-butenyl oxide by extended conjugation across the vinyl and carbonyl oxide groups. A low-energy conformer (ζZZ) of 2-butene oxide is identified by IR action spectroscopy in the fundamental CH region with ultraviolet (UV) detection of OH products by laser-induced fluorescence (LIF). The strongest observed IR transition at 2996 cm⁻¹ is consistent with the anharmonic frequency computed for the ζ(zz) conformer. A low energy reaction pathway involving isomerization of 2-butene oxide from a lower energy conformer (ζ(zz) to a higher energy conformer ζZZ) followed by 1,6-H-atom transfer via a 7-membered ring transition state with relatively low ring strain, is theoretically predicted and shown experimentally to yield the OH products. The rapid appearance of OH products (ca. 2.3 ± 1.0 × 10⁻⁷ s⁻¹) agrees with a statistical RRKM calculation for an effective reaction rate (k_eff) on the order of 10⁻⁷ s⁻¹ at ca. 3000 cm⁻¹ including tunneling. Unimolecular decay involves a combination of conformational isomerization and unimolecular dissociation via 1,6-H-atom transfer. The excellent agreement between experiment and theory confirms the allylic 1,6-H-atom transfer mechanism in 2-butene-oxide Criegee intermediate and provides a novel pathway for non-photolytic OH generation upon alkene ozonolysis in the troposphere.

THE VIBRATIONAL PREDISSOCIATION OF THE Α STATE OF THE C3Ar VAN DER WAALS COMPLEX WITH VIBRATIONAL ENERGIES OF 1558-1660 cm⁻¹
SHENG-CHANG HSIAO, Department of Physics, National Central University, Taoyuan, Taiwan; YEN-CHU HSU, Department of Physics, National Central University, Jhongli, Taiwan.

The laser-induced fluorescence (LIF) and wavelength-resolved emission spectroscopic techniques have been used to study the rotational levels and VP processes of the product state branching ratios of the Α state of the C3Ar van der Waals complex. The excited states were prepared by exciting the complex bands associated with 0.8 0-0, 0.4 0-0 and 0 2-0 bands of the A 1Π, X 1Σᵣ, Α 1Π, system of C3A. The superscripts “g” and “a” denote the lower and upper Renner components, respectively. The type A and C bands of the complex bands are in pairs and they are separated by 2νs (h, van der Waals bending vibration) of 11 bands, only two associated with the 002-000 band of C3A, are rotationally resolved with a laser of 0.04 cm⁻¹ resolution. The lifetimes of these complex bands are in the order of a few to a few tens of picoseconds estimated from the rotational linewidths of the LIF spectra. The VP processes are quite complex; more than one vibrational state of the C3Ar fragments is identified from each upper complex level. The fragment states were the pure bending levels (0 νz 0) and the combination levels (1 νz 0) of the Α state.

THE VIBRATIONAL PREDISSOCIATION AND INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION OF THE Α STATE OF THE C3Ar VAN DER WAALS COMPLEX
SHENG-CHANG HSIAO, Department of Physics, National Central University, Taoyuan, Taiwan; YEN-CHU HSU, Department of Physics, National Central University, Jhongli, Taiwan.

The vibrational predissociation (VP) products of eighteen rovibrational levels of the Α state of the C3Ar complex have been studied. The complex levels are associated with the 0.2 0-0, 0.2 0-0, 0.2 0-0, 0.2 0-0, 0.2 0-0, 0.2 0-0 and 0.2 0-0 vibrational levels of C3A. The distributions of the fragment branching ratios versus the square root of the excess energies (the sum of the translational and rotational energy of the VP product) obtained from these complex levels do not necessarily follow the momentum gap law or energy gap law. Effects such as spectroscopic perturbation, energy gap, angular momentum, threshold predissociation and intramolecular vibrational redistribution on the VP processes have been previously reported. In this study, these effects will be examined and the VP mechanism of the Α state of the C3Ar complex will be proposed.

Intermission
DETECTION OF NASCENT PRODUCTS FROM THE PHOTOLYSIS OF ACRYLONITRILE VIA TIME-RESOLVED MILLIMETER WAVE SPECTROSCOPY

NATHAN A. SEIFERT, Department of Chemistry, University of New Haven, West Haven, CT, USA; KRILL PROZUMENT, Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, USA.

In 2017, we presented at ISMS a new Time-Resolved Kinetic Chirped-Pulse (TReK-CP) spectrometer. By coupling a UV photolysis source to a chirped pulse millimeter-wave (mm-wave) spectrometer, we demonstrated the ability to measure kinetic and thermodynamic properties of the photolysis of acrylonitrile (CH$_2$CHCN), including product branching ratios and rotational and vibrational thermalization rates at reasonable time resolution (ca. 10 μs). However, sensitivity to vibrationally excited states and pre-collisional dynamics was limited, so the observation of truly nascent molecules was still out of reach.

Here, we present improvements to the TReK-CP design that enables detection of nascent product molecules from the photolysis of acrylonitrile, with particular focus on the formation of cyanocetylene (HC$_2$N). Moving to the 260-295 GHz mm-wave band significantly improves sensitivity to small polyatomics, enabling detection of HC$_2$N within 1 μs after photolysis in a variety of vibrational states. We have also devised a new detection scheme that enables a time resolution of 1 μs, amongst other improvements.

Revisiting the photolysis of acrylonitrile with these improvements has led to surprising observations. We will present evidence that HC$_2$N has different dynamics than the primary photoproduct, HCN, which clearly forms rotationally hot and is undetectable until the first collisional event takes place. Meanwhile, cyanocetylene forms slower, exhibiting low temperature state distributions, a large kinetic isotopic effect, and strong kinetic dependence on the initial temperature of the precursor. This consistent with the theoretical prediction that the final step, CH$_2$(CCN) + HCN → HC$_2$N + H, occurs with little excess energy.

We will also show that we are, in fact, detecting truly nascent cyanocetylene, in that the kinetics show a distinct change from first to second order on the collisional timescale of the reaction.

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EXOMOLHD: RECENT PROGRESS ON PHOTODISSOCIATION OF SMALL MOLECULES

MARCO PEZZELLA, JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, London, London, UK; SERGEI N. YURCHENKO, Physics and Astronomy, University College London, London, United Kingdom.

The destruction of hot molecules by photodissociation influences the composition and dynamics of exoplanets, particularly in the presence of a UV-rich stellar environment. We compute temperature-dependent photodissociation cross sections and rates for molecules found in these atmospheres, for a more realistic model of the planetary chemistry. The cross sections are calculated by solving the nuclear-motion Schrödinger equation as part of the ExoMol project using codes Dvo, DVR3D and Excovox, using the methodology previously described. Photodissociation rates are computed integrating the cross section with different stellar field models representing different star types.

New tools and results for H$_2$, HCl and HCN. Cross sections and rates for the diatomics are compared with previously available data, finding a good agreement for the interstellar medium for low temperatures. Both cross sections and rates have a dramatic temperature dependence for temperatures above 1000 K. Our results for HCN are compared with the results obtained by previous works employing the time dependent Schrödinger equation.

CO FORMATION FROM ACETONE PHOTOLYSIS: THE ROAMING PATHWAY


Acetone is one of the most abundant ketones in the atmosphere, with 73 million tonnes emitted or formed in the atmosphere annually. Additionally, as the simplest ketone, understanding the photodynamics of acetone can improve our understanding of the photolysis pathways of other ketones.

CO formation from acetone photolysis was studied over the whole S$_1$ ← S$_2$ absorption spectrum, however, this talk focuses on the longer wavelengths (305-320 nm). Resonance enhanced photodissociation (REPD) and photofragment excitation (PHOFEX) of the CO photofragment at photolysis wavelengths longer than 300 nm, combined with laser-induced fluorescence (LIF) of acetone, found CO was forming from a unimolecular pathway, attributed to roaming. Although roaming is often associated with cold rotational distributions, this does not seem to be the case for CO formed from roaming in acetone. The CO product had significant rotational excitation up to J ∼ 80,

Fourier transform infrared spectroscopy was used to obtain quantum yields of the photolysis products of acetone from 285 – 325 nm at various pressures of synthetic air and nitrogen bath gas (3-760 Torr total pressure). Carbon monoxide was found to have a quantum yield of up to 10% in non-oxidative conditions at 3 Torr and 760 Torr. In an atmosphere of synthetic air at actinic wavelengths, this pathway was reduced to a maximum of 3%.

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CO FORMATION FROM ACETONE PHOTOLYSIS: THE ROAMING PATHWAY

YUAN QIN, XIAOFENG ZHENG, YU SONG, GE SUN, Department of Chemistry, University of California, Riverside, CA, USA; JINGSONG ZHANG, Department of Chemistry and Air Pollution Research Center, University of California, Riverside, CA, USA.

The spectroscopy and predissociation dynamics of several vibronic levels (ν’ = 0-6) of the SH A$^3Π_{1/2}$ state have been studied using the high-o Rydberg atom time-of-flight (HITRAP) technique. By measuring the product translational energy distributions as a function of excitation wavelength, the H + S$^1P$ photofragmentation yield (PFY) spectra are obtained across the various A$^3Π_{1/2}$ ← X$^1Σ^+$ bands. The PFY spectra of the A$^3Π_{1/2}$ ← X$^1Σ^+$ bands exhibit broad linewidths (<4 cm$^{-1}$), indicating that these levels undergo rapid predissociation with lifetimes on the order of picosecond. The measured spin-orbit branching fractions of the H + S$^1P$(ν$^1P_{1/2,3}$) product channels provide insights to the predissociation dynamics of the A$^3Π_{1/2}$ state, which change dramatically as the vibrational level ν’ increases. The A$^3Π_{1/2}$ ← X$^1Σ^+$ state of SH predissociates mainly through adiabatic coupling to the A$^3Σ^+$ repulsive state, while all three repulsive states (A$^3Π_{1/2}$, A$^3Π_{3/2}$, and A$^3Σ^+$) are involved in the dissociation pathways for higher vibrational levels.

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SPECTROSCOPY AND PREDISSOCIATION DYNAMICS OF SH RADICALS VIA THE A$^3Σ^+$ STATE

YUAN QIN, XIAOFENG ZHENG, YU SONG, GE SUN, Department of Chemistry, University of California, Riverside, CA, USA; JINGSONG ZHANG, Department of Chemistry and Air Pollution Research Center, University of California, Riverside, CA, USA.

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VELOCITY MAP IMAGING OF GOLD ION - LIGAND COMPLEXES

BRANDON M. RITTGERS, MICHAEL A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA, USA

Au⁺(L) (L = H₂O, NH₃, O₂, formaldehyde, or acetone) complexes are generated in the gas phase by laser vaporization off of a gold rod during a supersonic expansion of rare gases seeded with the ligand of interest and detected using time-of-flight mass spectrometry. Metal ionization potentials are typically lower than that of many molecules, leading to the charge being localized on the metal in a cation-molecule complex. Gold has a relatively high ionization potential that is closer to that of molecules, and laser excitation of a gold ion – molecule complex can lead to a charge transfer dissociation channel that produces the molecular ion fragment. If the excitation wavelength is sufficiently high, excess kinetic energy release above the dissociation threshold can be detected using velocity map imaging. This energy release is then be used to determine an upper bound on the gold ion – molecule binding energy.

NON-ADIABATIC COUPLING IN NO@C₆₀: PREDICTION OF A RENNER-TELLER LIKE EFFECT FOR SPHERICALLY ENCAPSULATED DIATOMIC MOLECULES

ANDREAS W. HAUSER, JOHANN V. POTOTSCHNIG, Institute of Experimental Physics, Graz University of Technology, Graz, Austria.

The Renner-Teller effect describes the coupling of a symmetry-reducing molecular vibration with a two-fold degenerate electronic state. Its discovery goes back to work of Herzberg and Teller, who realized in 1933 that the potential energy surface of a triatomic, linear molecule splits into two as soon as the molecule is bent. In this work, we show that a very similar, yet unknown type of non-adiabatic coupling can even occur for diatomic (!) molecules. This seems absurd at first sight, but becomes possible as soon as the diatomic molecule is embedded in a spherically symmetric confinement. In this case, its translational degrees of freedom become quantized and can couple to electronically degenerate states in a very similar fashion as predicted by Renner-Teller effect theory. To our knowledge, it is the first time that this novel type of non-adiabatic coupling has been investigated either in theory or experiment.[1]

We demonstrate this effect for the experimentally accessible case of NO embedding in a C₆₀. Endofullerenes, in particular those carrying a radical molecule, are highly topical objects of ongoing research in molecular spectroscopy, reaction chemistry and carbon-based nanomaterial design. Also, suitable confinements in molecular traps for quantum information and quantum computing will produce a similar effect of nonadiabatic coupling as predicted by our study.


USING HIGH-RESOLUTION PHOTOELECTRON IMAGING TO PROBE THE SPECTROSCOPY OF CRYOGENICALLY COOLED AZOLIDE MOLECULES

YUE-ROU ZHANG, Chemistry department, Brown university, Providence, RI, USA; DAOFU YUAN, LAISHENG WANG, Department of Chemistry, Brown University, Providence, RI, USA.

Photoelectron spectroscopy is a powerful technique to investigate the electronic structure and chemical bonding of anions and the corresponding neutrals upon electron detachment. Here, we use our electrospray ionization photoelectron spectroscopy apparatus, which couples a cryogenically-cooled 3D Paul trap and a high resolution imaging system to get the vibrational and electronic information about three azolide: pyrazolide, pyrrolide and imidazolide. Besides the expected conventional dipole bound state, a core-excited dipole bound state is observed in pyrazolide with the neutral core in its first excited electronic state. And a completely different threshold behavior is observed for pyrrolide and imidazolide with a similar pi type HOMO: a d-wave-dominated spectrum is found for pyrrolide and an s-wave-dominated spectrum is found for imidazolide.
Can London Dispersion Override Cation-π Interactions?

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We report an evaluation of the importance of London dispersion in moderately large (up to 32 heavy atoms) organic molecules by means of a molecular torsion balance whose conformations “weigh” London forces against cation-π in the absence of solvent. The experimental gas-phase study is performed using cryogenic ion vibrational predissociation (CIVP) spectroscopy covering both the N-H and the effectively “deperturbed” N-D stretching modes, taking into account possible perturbation due to the tag molecule. The gas-phase data is supported by solid-state FT-IR spectroscopy, single-crystal X-ray crystallography, and is accompanied by DFT calculations, including an extensive analysis and search of the accessible conformations. We begin with the unsubstituted molecular torsion balance, and then step up the complexity systematically by adding alkyl groups incrementally as dispersion energy donors (DEDs) to achieve a degree of chemical complexity comparable to what is typically found in transition states for many regio- and stereoselective reaction in organic and organometallic chemistry. We find clear evidence for the small attractive contribution by DEDs, as had been reported in other studies, but we also find that small individual contributions by London dispersion, when they operate in opposition to other weak non-covalent interactions, produce composite effects on the structure that are difficult to predict intuitively, or by modern quantum chemical calculations. The experimentally observed structures, together with a reasonable value for a reference cation-π interaction, indicate that the pairwise interaction between two tert-butyl groups, in the best case, is modest. Moreover, the visualization of the conformational space, and comparison to spectroscopic indicators of structure, as one steps up the complexity of the manifold of non-covalent interactions, makes clear that in silico predictive ability for the structure of moderately large, flexible, organic molecules falters sooner than one might have expected.

Equation-of-Motion Coupled cluster (EOM-CC) is a preferred method for high-precision electronic spectroscopy due to its size-extensivity and implicit inclusion of higher-order excitation effects in the electronic wavefunction. The accuracy of the EOM-CC wave function can be tuned by truncating the cluster operator, T, and/or excitation operator, R, at increasing levels of excitation. Within core-hole calculations (XPS, XAS/NEXAFS, XES, and RIXS), the inclusion of triple excitations, in concert with the core-valence separation (CVS), is critical in accurately treat orbital relaxation effects; however, including triple excitations unavoidably leads to high computational cost. Instead, we propose two alternative approaches: first, as Transition-Potential Coupled Cluster (TP-CCSD), orbital relaxation is explicitly included in the reference orbitals through the use of a fractional-occupation SCF calculation followed by CVS-EOM-CCSD. Second, the CVS-STO-MC-CI model extends the similarity-transformed EOM-CC approach of Noojin with triple excitations, but for the inexpensive core ionization potentials. We benchmark both methods for first-row K-edge vertical ionization and excitation energies of 14 small molecules, compared to the accurate but extremely expensive CVS-EOM-CCSDT method, as well as select comparisons to experimental gas-phase XAS. We find that both methods are effective in treating the orbital relaxation of core-hole states, with absolute energy errors below 0.5 eV and relative errors for peak positions typically below 0.3 eV. Both methods are also computationally efficient: TP-CCSD has the same computational cost as the less-accurate CVS-EOM-CCSD method, while CVS-STO-MC-CI is only marginally more expensive for a small number of excitations. For large numbers of excited states, the STO-MC-based approach may be significantly faster.
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) have been surmised as carriers of the diffuse interstellar bands (DIBs), hundreds of unidentified spectral lines in the infrared through ultraviolet regions. These DIBs are often thought to be in their cationic or neutral forms in the interstellar medium, although there have been models that feature these molecules as the primary carriers of negative charge in dense interstellar clouds, rather than just free electrons. We monitored the photodetachment cross section as a function of wavelength for tetracene radical anion (C42H6−) to explore the resonances of the tetracene radical anion above the detachment threshold. The observed electronic states closely align with a previously reported absorption spectrum of the molecule, with one major exception. Sharp features (less than 10 cm−1) corresponding to a long-lived Feshbach resonance of the molecule were found in the near-IR. This corresponds to a lifetime of no faster than 160 fs, a much longer lifetime than typically observed for such detachment resonances. These features can potentially be used to detect the presence of anionic aromatic species in the interstellar medium. However, we were not able to make any assignments based on our spectra for tetracene and available DIB data. Still, by acquiring photoelectron spectra at these anion excited electronic states, we identify specific photodetachment channels by which these resonances relax to the ground state. These features will be compared to the anthracene radical anion (C24H−) and the tetracene anion to explore the effect of PAH size and deuteration on these resonances. In addition, we will report on possible fragmentation in the UV spectral region mediated by these resonances. Finally, photoelectron spectra are collected using slow electron velocity-map imaging (SEVI), yielding high precision electron affinity values and Td term energies for tetracene, as well as identifying active vibrations in these transitions. Interestingly, the Td state in the tetracene radical anion photoelectron spectrum features highly non-Franck Condon activity, most likely due to vibronic coupling. The anion resonances shown here along with the photoelectron spectra acquired have interesting implications for the possibility of tetracene as a negative charge carrier in the interstellar medium.
IN SITU SPECTROSCOPIC DIAGNOSTIC OF SHOCK INDUCED DECOMPOSITION OF C\textsubscript{60}

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The applications of the shock wave research are multi-modal. The potential of the shock wave is a large amount of energy is transferred to the material within a very short timescale, leading to the formation of new chemical species and the kinetics of product formation can be studied.

Far from the laboratory, shock waves play an important role in controlling the physical and chemical evolution of the interstellar medium (ISM). In the ISM, shock waves are generated due to supernova explosions, bipolar outflows and stellar winds. However, the application of shock waves to study the chemistry of the ISM is a relatively new area of research. One of the objectives of our research is to identify new possible shock tracers in the low velocity shocked regions of the ISM.

Shock induced decomposition of C\textsubscript{60} (one of the interstellar building blocks of dusts) was explored in situ with the help of a UV-Vis spectrometer and a monochromator. The integrated emission spectrum reveals the presence of C\textsubscript{2} features with a broad continuum and was affected by self-absorption. The broad continuum is likely due to the combined effect of the black-body emission from small carbon particles and the recurrent fluorescence of various carbon clusters produced via the dissociation of C\textsubscript{60}. The emission spectrum of C\textsubscript{2} was computed using Exocross module and the column density of the C\textsubscript{2} units were determined.
DEMONSTRATION OF CRESU-REMPI FOR REACTION KINETIC MEASUREMENTS IN THE GAS-PHASE
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The CRESU technique (French acronym for “reaction kinetics in uniform supersonic flows”) provides a wall-less gas-phase reactor to measure low-temperature reaction kinetics. In the past, probing methods such as laser-induced fluorescence (LIF), mass spectrometry, and chirped-pulse uniform flow (CPUF) microwave spectroscopy have been successfully used to measure reaction kinetics in CRESU flows, but the latter two call for sampling of the flow prior to detection. Here we show a selective, low-cost, and highly sensitive probing tool to measure the kinetics of reactions that involve both molecular and atomic species. This new detection method uses resonance-enhance multi-photon ionization (REMPI) and an electron capture probe, adapted from approaches successfully used in flames, to selectively identify atomic and molecular species. A negative-biased high voltage applied to two electrodes, that are placed on either side of a grounded probe, enables rapid capture of electrons from the REMPI ionization from the selective ionization from the REMPI spectroscopy. The performance of this setup was verified by recording the (1s−1s) REMPI spectra of nitric oxide in 20 K and 50 K uniform supersonic flows. The REMPI probe response is proportional to the number of electrons produced by ionization, and therefore to the concentration of ionized species. Thus, the time-dependent REMPI signal can be used to measure the rate of decay or growth of a reactant or product in fast chemical reactions in CRESU flows.

TOWARDS THE RESOLUTION LIMIT OF PFI-ZEKE PHOTOLETTRON SPECTROSCOPY
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The spectral resolution in Pulsed-Field Ionization Zero-Kinetic Energy (PFI-ZEKE) photoelectron spectroscopy is related to the state selectivity in the ionization process of the Rydberg states. The selectivity is determined by the applied electric field pulse sequence. Hollestein et al. used discrete electric field pulses with increasing field strength in combination with a preceding field pulse of opposite polarity. By using such field pulse sequences with the smallest possible field step size (i.e., approximately 9 mV/cm), a spectral resolution of 0.06 cm$^{-1}$ could be achieved. To improve the resolution further Harper et al. recently suggested replacing the sequence of field steps by a linearly increasing field, as used earlier by Reiser et al., in combination with a pulse of opposite polarity and obtained promising results on the PFI-ZEKE photoelectron spectrum of NO and CO$_2$. Using a home-built narrow-bandwidth long-pulse laser system (pulse lengths up to 50 ns) in combination with a field pulse ramp, we explore the resolution limit of this approach. To avoid overlap of spectral lines, we chose an atomic system, Ar, as test system and recorded PFI-ZEKE photoelectron spectra of transitions from the metastable states (3p$^3$P$^0$) to the (3p$^3$P$^0$, 3p$^3$D$^0$, 3p$^1$D$^0$, 3p$^3$F$^0$) states of Ar$^+$. This system also offers the advantage of a precisely known ionization energy with which the ionization energy determined with the new method can be compared.

MID-INFRARED CW OPTICAL PARAMETRIC OSCILLATOR PUMPED BY AN ELECTRO-OPTIC FREQUENCY COMB
MATTHEW J. CICH, ADAM HEINIGER, DAVID B. FOOTE, WALTER HURLBUT, CHRIS HAIMBERGER, TOPTICA Photonics Inc., Farmington, NY, USA; DAVID A. LONG, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA.

Optical frequency comb (OFC) spectroscopy in the mid-infrared (MIR) promises faster, more precise, and more sensitive molecular spectroscopy. To date, demonstrations of MIR OFCs have suffered from low power, poor wavelength coverage, or low sensitivity. Systems that do excel in these areas have high cost and complexity. The technique and measurements reported here demonstrate that singly resonant, single frequency optical parametric oscillators (OPO’s) are a powerful platform for generating MIR OFCs with properties not shown by other MIR light sources. As an example, we demonstrate the effectiveness of this technique for trace gas detection and discuss the overall performance.

CAVITY RING-DOWN SPECTROSCOPY WITH INTERBAND CASCADE OPTICAL FREQUENCY COMBS
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The spectrum of an optical frequency comb is composed of many equidistant lines, which is a natural match for enhancement cavities. Cavity ring-down spectroscopy is known to be a robust and highly sensitive technique, although it is challenging to implement with optical frequency combs. Here we demonstrate a new approach to performing direct frequency comb cavity-ring-down spectroscopy in the CH stretching region using an interband cascade optical frequency comb. These chip-scale devices generate combs with large repetition rates (10 GHz), wide bandwidth, and wavelength-detuning detection using Vernier spectroscopy. The decay of each comb mode can be obtained as the comb is being scanned, providing sensitive and broadband detection. Here we demonstrate the effectiveness of this technique for trace gas detection and discuss the overall performance.

Intermission
HIGH-SPEED, HIGH-RESOLUTION, BROADBAND DUAL-COMB SPECTROMETER FROM 3.5 µm

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Dual Comb Spectroscopy (DCS) is an emerging technique for measuring infrared molecular absorption at higher speeds and spectral resolution than historically possible using Michelson interferometer-based Fourier Transform Spectroscopy. While Quantum Cascade Laser (QCL) DCS is capable of fast acquisition speeds and the ability to probe between 4-10 µm, these benefits also come at the cost of a low instantaneous bandwidth, spectral resolution, and coherence time over which measurements can be averaged.

Here we present the development of a GHz repetition rate intra-pulse DFG mid-IR DCS system. This system is based on mode-locked lasers simultaneously spanning 3.5 µm with 0.03 cm⁻¹ comb tooth spacing, µs acquisition speeds, and single-cycle residual noise below 10⁻⁵. Spectra and noise characteristics from a static spectroscopy cell containing various hydrocarbons are reported and discussed. The system shows promise for sensing in rapid transient systems given the high single shot signal to noise ratio and rapid interferogram acquisition time afforded by the GHz pulse repetition rates.

RAPID DUAL-COMB COHERENT RAMAN SPECTROSCOPY IN THE HIGH-WAVENUMBER REGION

YUE JIANG, MINHAN LUI, YAN LI, HAOYUN WEI. Department of Precision Instrument, Tsinghua University, Beijing, China.

Delay-spectral focusing dual-comb coherent anti-Stokes Raman spectroscopy is proposed and performed, realizing a 40000 spectra/s acquisition rate, which is the fastest Raman spectral detection in the high-wavenumber region up to the present. The spectral resolution (∼10 cm⁻¹) and the signal-to-noise ratio (>260) keep stable along the detection process. This novel spectroscopic technique avoids the invalid scanning time wasted in waiting for the superposition in time of the dual-comb pulses by actively modulating the repetition frequency difference and thus the relative echo delay. An intra-cavity electro-optic modulator (EOM), with high modulation amplitude and response frequency, is applied for fast repetition frequency modulation. Delay-spectral focusing method also helps to obtain the high-wavenumber region spectrum, which is difficult to realize for previously-used Fourier transform CARs (FT-CARS) due to the intrinsic coherence of ultra-broadband pulses. This technique shows huge potentials in which both high speed and high-wavenumber region detection are required, such as fast microspectroscopic imaging and flow cytometry.
The use of computational optimal transport for the comparison of molecular spectra is presented. Computational optimal transport provides a comparator, the transport distance, which can be used in machine learning applications and for the comparison of theoretical and experimental spectra. Unlike many other comparators, the transport distance encodes line positions and intensities. It can be used to compare two discrete spectra, a discrete spectrum and a continuous spectrum, as well as two continuous spectra. Because the transport distance reflects the movement of density from one spectrum to another, the two spectra being compared do not have to have the same number of lines or features and need not closely match up in frequency space.

Several well-chosen examples will be shown to demonstrate how computational optimal transport is used and its overall utility. In addition, it is used to make quantitative comparisons between theoretical and experimental spectra including a rotational spectrum of 1-hexanal and an electronic absorption spectrum of SO32−.

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 REFERENCES


INTERPRETABLE DEEP LEARNING FOR MOLECULES AND MATERIALS

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Deep learning has begun a renaissance in chemistry and materials. We can devise and fit models to predict molecular properties in a few hours and deploy them in a web browser. We can create novel generative models that were previously PhD theses in an afternoon. In my group, we’re exploring deep learning in soft materials and molecules. We are focused on two major problems: interpretability and data scarcity. Now that we can make deep learning models to predict any molecular property at nascent, what can we learn? I will discuss our recent efforts on interpreting deep learning models through symbolic regression and counterfactuals. Data scarcity is a common problem in chemistry: how can we learn new properties without significant expense of experiments? One method is in judicious choice of experiments, which can be done with active learning. Another approach is self-supervised learning and constraining symmetries, which both try to exploit structure in data. I will cover recent progress in these areas. Finally, one consequence of the state of deep learning is that you can just make cool things in chemistry with minimal effort. I’ll review a few fun projects, including making molecules by hanging on the keyboard, doing math with emojis, and doing molecular dynamics with ImageNet derived potentials.

SUPERVISED LEARNING FOR SELECTIVE MULTI-SPECIES QUANTIFICATION FROM NOISY INFRARED SPECTROSCOPY DATA

EMAD AL IBAHIM, AAMIR PAROOQ, Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.

A supervised learning approach is implemented to extract information from noisy vibrational spectroscopy data. Our method tackles two of the main problems in any commercial sensing application: sensitivity and selectivity. First, an encoder takes in noisy spectra of complex mixtures and learns reduced representations referred to as embeddings. The learned embeddings are then used in the decoder to filter out noise and unwanted species. Embeddings are also simultaneously used as input to a regression network for the prediction of concentrations and baseline shift. The model was applied for gas sensing using Fourier-Transform infrared spectroscopy (FTIR) data. We focus on identifying common volatile organic compounds (VOCs) in a realistic scenario. The multitask nature of the model gives better results compared to single task denoising followed by regression and classical techniques like non-negative linear regression. The denoising capability was also compared to other denoising methods like Savizky-Golay filters (SVG) and wavelet transformations (WT).

COMPUTATIONAL OPTIMAL TRANSPORT FOR MOLECULAR SPECTRA

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The use of computational optimal transport for the comparison of molecular spectra is presented. Computational optimal transport provides a comparator, the transport distance, which can be used in machine learning applications and for the comparison of theoretical and experimental spectra. Unlike many other comparators, the transport distance encodes line positions and intensities. It can be used to compare two discrete spectra, a discrete spectrum and a continuous spectrum, as well as two continuous spectra. Because the transport distance reflects the movement of density from one spectrum to another, the two spectra being compared do not have to have the same number of lines or features and need not closely match up in frequency space.

Several well-chosen examples will be shown to demonstrate how computational optimal transport is used and its overall utility. In addition, it is used to make quantitative comparisons between theoretical and experimental spectra including a rotational spectrum of 1-hexanal and an electronic absorption spectrum of SO32−.
GAS-PHASE INFRARED SPECTRA ANALYSIS VIA DEEP NEURAL NETWORKS

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Infrared spectroscopy provides unique molecular vibrational information that is molecule and environment specific. Spectral responses, as images rather than array-based data, were used to train a deep neural network to develop analytical methods capable of large-scale information processing. We label spectra based on the present and absent functional groups, but the model must determine the frequencies, peak shape, and variability of each molecular response to identify functional groups. The resultant machine learning models significantly reduce the time required for traditional infrared spectral analysis and the functional group assignments is found to be more accurate than expert chemists. Application of machine learning methods to spectroscopic data is made approachable by a straightforward model system that is generalizable, broad, and well-performing on thousands of gas-phase infrared spectra from the NIST spectral database. Future improvement will involve more specific and applied models, such as the investigation of field samples for environmental contaminants or component identification, with increased solvent complexity to continue developing a broad range of models. To the best of our knowledge, this is the first presentation of a generalizable machine learning model for infrared analysis because it is capable of analyzing a diverse spectral database.

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FLUORINATION AND DEOXYGENATION AS CHEMICAL TOOLS TO STUDY THE CONFORMATIONAL PREFERENCES OF HEXOPYRANOSES: A JOURNEY FROM GAS PHASE TO SOLUTION

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The 3D-arrangement of carbohydrates and, particularly, the orientation of their hydroxymethyl groups are structural features crucial for their biological activities. In this work, we investigate the influence of water on the conformational preferences of model hexopyranoses by performing a comparative analysis in the gas phase via microwave spectroscopy \cite{1} of different fluorinated and deoxygenated carbohydrate analogues and comparing the results with those obtained in solution using a combination of NMR data and molecular dynamics simulations. The gg conformation is stabilized in the gas phase by intra molecular HBs that lock this conformation when oriented clockwise. However, and contrary to previously reported data, the conformation of the hydroxymethyl group in D-gluco and D-mannopyranose series follows a similar tendency in the gas phase and in solution, indicating the importance of stereo electronic and minimizing the importance of competing water molecules against stabilizing intra molecular HBs.

THE JET-COOLED ROTATIONAL SPECTRUM OF N,N'-BIS(HYDROXYMETHYL)UREA AND ITS PHOTO-FRAGMENTED SPECIES

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A novel approach based on laser ablation of solid organic precursors has been recently proposed for the laboratory in situ generations of new chemical species.\textsuperscript{4} The chemical compounds generated in the laser ablation process are cooled in a supersonic expansion and probed by eyes of high-resolution microwave spectroscopy. This "micro-laboratory" enhances the scope of in situ experiments using precursors not typically accessible to traditional techniques such as electric discharge and pyrolysis. In this contribution, N,N'-Bis(hydroxymethyl)urea is chosen as a precursor. It contains a C=O functional group and two pairs of NH and OH groups, very appealing from the astrochemical point of view. Guided by the theoretical predictions, we assigned the precursor's rotational spectrum (four conformers), and then we focused on tuning up our experiments to achieve the experimental conditions that maximize the photo-fragmentation. A detailed analysis of the spectrum revealed the generation of hydroxymethylurea and the simultaneous formation of other species in the jet, showing that the laser ablation of solid organic precursors constitutes an innovative tool in generating new chemical species.

 Acknowledgements: The authors thank the financial fundings from the Czech Science Foundation (GAČR, grant 19-25111Y), Ministerio de Ciencia e Innovación (grant PID2019-111396GB-I00), Junta de Castilla y León (grants VA244P20), and European Research Council under the European Union’s Seventh Framework Programme ERC-2013-Syg, Grant Agreement n. 610256 NANO COSMOS.

WV04
UNVEILING THE EIGHT FORMS OF CAFFEIC ACID

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Herein we report a complete conformational analysis of caffeic acid, a relevant polyphenol\textsuperscript{2}, and the main hydroxyacetic acid found in humans’ diet using laser ablation chirped-pulse Fourier transform microwave (LA-CP-FTMW) spectroscopy. The entire conformational space consisting of eight distinct rotameric species has been fully deciphered based on a thorough inquiry of the trend of the rotational constants supported by high-level theoretical computations.\textsuperscript{2,3}

THE MICROWAVE SPECTRUM OF PIPERONAL: DESIGNING AND TESTING A NEW HEATED NOZZLE ASSEMBLY

BRAIDEN CARTY, Department of Natural Sciences, University of Virginia’s College at Wise, Wise, VA, USA; GALLEN SEGDO, Department of Natural Sciences, University of Virginia’s College at Wise, Wise, VA, USA; AMANDA DUERDEN, JOSHUA E. ISERT, NICOLE MOON, G. S. GRUBBS II, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.

A modular heated nozzle assembly with an open source external temperature control unit was designed for use in a new broadband microwave spectrometer under construction at Missouri University of Science and Technology. The first version of the heated source was tested using MS&T’s existing cp-FTMW. As an initial proof of concept, the microwave spectrum of molecular piperonal was collected in the 5.5 to 18.75 GHz region. The parent isotopeologues of two conformers, s-cis- and s-trans-piperonal, were observed and an analysis of the 13C substituted species are ongoing.

WV06
THE RET-COOLED ROTATIONAL SPECTRUM OF N,N'-BIS(HYDROXYMETHYL)UREA AND ITS PHOTO-FRAGMENTED SPECIES

PETER R. FRANKE, Department of Chemistry, University of Florida, Gainesville, FL, USA; JOHN F. STANTON, Quantum Theory Project, University of Florida, Gainesville, FL, USA.

The class of geminal diols comprises molecules known to be intermediates in atmospheric ozonolysis and the aerosol cycle. Owing to their thermodynamic propensity to decompose into water and an aldehyde/ketone, geminal diols have proved difficult to isolate and characterize. Recently, experimental evidence was published for the existence of methanediol, the simplest member of this class, in seas of methanol and oxygen following electron bombardment.\textsuperscript{4} To aid in future spectroscopic investigations of methanediol in the gas phase, we report fundamental frequencies and rovibrational constants for the two rotamers of methanediol using ab initio composite methods along with vibrational perturbation theory. Sensitivity of the predictions to the level of theory and the treatment of anharmonic resonances are carefully assessed. The OH stretching and C-H stretches of the two rotamers are sensitive to the treatment of anharmonic resonances with VPT2-based effective Hamiltonian models. Equilibrium bond distances and harmonic frequencies are converged to within $0.0001 \text{ Å}$ and $1 \text{ cm}^{-1}$, respectively. The effect of tunneling on the rotational constants is investigated with a 2D variational calculation, based on a relaxed hydroxyl torsional potential energy surface. Tunneling is found to be negligible in the lower energy C$_2$ rotamer but should modify the rotational constants of the C$_4$ rotamer on the order of MHz, giving rise to rotational line splittings of the same order. The rovibrational constants of the C$_2$ rotamer are dominated by torsional effects, and here we see evidence for the breakdown of vibrational perturbation theory.

WV07
ROTAMERS OF METHANEDIOL: COMPOSITE AB INITIO PREDICTIONS OF FUNDAMENTAL FREQUENCIES AND ROVIBRATIONAL CONSTANTS

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The class of geminal diols comprises molecules known to be intermediates in atmospheric ozonolysis and the aerosol cycle. Owing to their thermodynamic propensity to decompose into water and an aldehyde/ketone, geminal diols have proved difficult to isolate and characterize. Recently, experimental evidence was published for the existence of methanediol, the simplest member of this class, in seas of methanol and oxygen following electron bombardment.\textsuperscript{4} To aid in future spectroscopic investigations of methanediol in the gas phase, we report fundamental frequencies and rovibrational constants for the two rotamers of methanediol using ab initio composite methods along with vibrational perturbation theory. Sensitivity of the predictions to the level of theory and the treatment of anharmonic resonances are carefully assessed. The OH stretching and C-H stretches of the two rotamers are sensitive to the treatment of anharmonic resonances with VPT2-based effective Hamiltonian models. Equilibrium bond distances and harmonic frequencies are converged to within $0.0001 \text{ Å}$ and $1 \text{ cm}^{-1}$, respectively. The effect of tunneling on the rotational constants is investigated with a 2D variational calculation, based on a relaxed hydroxyl torsional potential energy surface. Tunneling is found to be negligible in the lower energy C$_2$ rotamer but should modify the rotational constants of the C$_4$ rotamer on the order of MHz, giving rise to rotational line splittings of the same order. The rovibrational constants of the C$_2$ rotamer are dominated by torsional effects, and here we see evidence for the breakdown of vibrational perturbation theory.
Non-aromatic heterocyclic molecular compounds due to their π electron orbitals have potential to be used in the surface science as coatings with good surface adhesion properties. Such properties are even more pronounced when silicon atom is present in the ring. It is due to formation of stable covalent bonding between the coating and an inorganic substrate. The objective of this study is to elucidate conformational diversity of newly synthesized five and six membered non-aromatic cyclic compounds, namely 1-chloromethyl-1-fluorosilacyclohexane, 1-chloro-1-chloromethylsilacyclohexane, 1-chloromethyl-1-fluorosilacyclohexane, 1-chloromethyl-1-fluorosilacyclohexane, 1-chloromethyl-1-fluorosilacyclohexane, and 1-chloromethyl-1-fluorosilacyclohexane. In order to obtain structural parameters and to perform conformational analysis of such yet unknown molecules detailed computational and experimental studies were performed. The samples were investigated by means conventional IR and Raman spectroscopy as well as matrix isolation FTIR spectroscopy, solid nitrogen acting as matrix medium. Calculations were performed using ORCA 4.1.1 software package.

We used a general method is proposed to disentangle isomeric structures by combining mass spectrometry, tunable synchrotron light source, and quantum-chemistry calculations. Reactive chemical monitoring technique is used and consists in tracking reactivity changes as a function of photoionization energy i.e., internal energy related to isomerization barriers. The capability of this technique will be illustrated with charge transfer reactions of C6H4+ isomers with allene and propyne. The methodology can be generalized using neutral reaction partners with ionization energies forming a chemical ruler to elucidate the ionic structure. It can also serve as a structural probe as a function of photonization energy, unveiling isomerization routes.

Using time-dependent density functional theory, we probe the electron dynamics involved in the photo-chemical isomerization of 1,3-cyclohexadiene to 1,3,5-hexatriene by analyzing changes to the harmonic spectra. The reaction is often used as an analog for the photo-induced reaction of provitamin D3 to vitamin D3 in the skin, as that reaction proceeds through a similar scheme. Calculations are performed for 1,3-cyclohexadiene and 1,3,5-hexatriene as well as two intermediate conformers. There are distinct changes in the harmonic spectra that could be used to mark reaction progress. As expected, the breaking of the molecular symmetry leads to peaks outside of the expected odd harmonics. In addition to the harmonic spectra, we discuss the dynamical changes to the electron density and electron localization function (ELF). From these measures of electron probability, we can see ionization and recombination occur throughout the pulse, from each of the isomers.
Recent years. In 2020, Li et al. reported the geometry of the monohydrate complex of thiazole. The microsolvation of aromatic and heteroaromatic rings has been the subject of many microwave spectroscopy studies in the environment. The mid-infrared spectra of helium solvated methanol and methanol-water clusters have been investigated in the symmetric methyl stretching band.

The mid-infrared spectra of helium solvated methanol and methanol-water clusters have been investigated in the symmetric methyl stretching band.

CHARACTERISATION OF THE STRUCTURE OF THE HYDROGEN-BONDED COMPLEX, THIAZOLE... (H2O)n, BY FOURIER-TRANSFORM MICROFARAD ELECTROSCOPY


AN INTERNAL AFFAIR: THE INFLUENCE OF INTRAMOLECULAR HYDROGEN BONDING ON THE STRUCTURE OF METAL-ION-PEPTIDE COMPLEXES

KATHARINA A. E. MEYER, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; KATHERINE ANN NICKSON, ETIENNE GARAND, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA

Interpreting the interplay of the various non-covalent interactions present in biomolecular systems is important as these are the driving forces of the structure of these systems. In the condensed phase, however, it is difficult to disentangle the individual contributions of these interactions due to the plethora of structures present, which ultimately limits any systematic studies. One popular way of bypassing this is to study relevant model complexes in the gas phase where these can be mass-isolated and spectroscopically interrogated. In this way, one can obtain an in-depth understanding of the competing non-covalent interactions on a molecular level and correlate structural changes systematically, for example by increasing the system size or changing interaction partners. Due to their structural flexibility, popular model systems for such studies are small amino acids or peptides and their complexes with water or metal ions. In this contribution, we will study the complexes of three alkali metal ions (Li+, Na+, K+) with di- and tripeptides with cysine and cys-glycine ion vibrational spectroscopy illustrating how the interaction strength changes with the size of the cation and peptide chain length by analyzing their OH, NH, and C=O stretching as well as NH bonding vibrations. Of particular interest is the interplay of metal ion peptide interaction with internal NH, NH2 hydrogen bonding of the neutral peptide itself, whose strength is modulated by the metal cation interaction.

MOLECULAR RECOGNITION IN SOLUTION: INTERACTIONS OF THE ODORANT CARVONE WITH ETHANOL AND WATER

S. INDIRA MURUGAICHANDAN, DONATELLA LORU, ISABEL PIÑA, M. EUGENIA SANZ, Depart- ment of Chemistry, King’s College London, London, United Kingdom

Non-covalent interactions are vitally important for molecular recognition in many biological and chemical processes. Understanding the interplay between intra- and intermolecular forces is crucial for advancing our knowledge on these events and how they influence by slight changes. Here we report the influence of the common odorant carvone with ethanol, a mimic to the amino acid side chain serine. It has been studied through combination of chirped-pulse Fourier transform microsecond rotational spectroscopy and computational calculations, including density functional theory and ab initio methods. Seven carvone-ethanol complexes have been observed showing an O=H-O primary bond between the carbonyl group of carvone, acting as a hydrogen bond acceptor, and the hydroxyl group of ethanol as the hydrogen bond donor. Secondary C=O stretching interactions anchoring ethanol to carvone are also established. Changes in the conformational preferences of the monomers upon complexation will be discussed.

EXAMINING INTERMOLECULAR INTERACTIONS BETWEEN HYDROCARBONS AND WATER: A BROADBAND ROTATIONAL SPECTROSCOPIC STUDY OF THE α-OXOANION – WATER COMPLEX

ARSH SINGH HAZRAH, MOHAMAD H. AL-JABIRI, WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.

Released into the atmosphere by vegetation, biogenic volatile organic compounds (VOCs) contribute substantially to yearly carbon emission, amounting to approximately 1150 Tg of carbon per year1. α-Oxiane, a bicyclic monoterpen, is not only one of the most abundant biogenic VOCs released, but also plays a critical role in the generation of secondary organic aerosol. Once released, α-oxiane can be photo-oxidized by atmospheric species such as ozone or various radical species. Water is relatively abundant in the atmosphere and has therefore a high probability of a close contact with α-oxiane. Complexation with water may affect the reactivity of species such as ozone, thus altering product yield, and ultimately the rate of aerosol formation. It is difficult to predict a preferred structure for the α-oxiane-water cluster using chemical intuition alone, and a study of its structure and energetics can provide insights into intermolecular interactions between weakly-polar hydrocarbons and water. The α-oxiane clustering is expected to provide a wealth of information regarding intermolecular forces and hydrogen bonding capable species, as well as data relevant to atmospheric processes. To experimentally identify α-oxiane-water clusters we used a chirped pulse Fourier transform microwave spectrometer in the 2-6 GHz range1 and the experiments were supplemented with electronic structure calculations. Two potential conformers were theoretically identified, both of which involve formation of the OH radical bond between water and α-oxiane. However, only the higher energy conformer could be assigned experimentally. From various one-dimensional energy scans along internal coordinates, the ab initio lower energy conformer is most likely due to a large amplitude OH wagging motion, which leads to a partial dipole moment cancellation. The OH···e interaction in both complexes was then visualized and quantified using non-covalent interactions2 and natural bond orbital analyses3, respectively.


THE 3-METHYL CATECHOL-(H2O)N=1–4 COMPLEXES: STUDYING MSISOLUTION USING BROADBAND ROTATIONAL SPECTROSCOPY

ARSH SINGH HAZRAH, MOHAMAD H. AL-JABIRI, HAMAD H. AL-JABIRI, JIARUI MA, YUNJIE XU, WOLFGANG JÄGER, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.

Biomass burning greatly influences the Earth–cloud–climate system by releasing complex mixtures of organic and inorganic species into the atmosphere.1 During biomass burning, lignin, an organic polymer and a major component of wood,2 undergoes pyrolysis resulting in the direct release of substituted catechols.3 3-methylcatechol (3MC), a common substituted catechol, may be photo-oxidized or aggregated with other atmospherically relevant molecules, such as water, forming small molecular clusters or hydrates. These hydrates play an important role in the early phases of aerosol and cloud processes and can provide valuable thermodynamic data for modelling. To elucidate the conformationally complex hydrate structures we analyzed rotational spectra measured with a chirped-pulse Fourier transform microwave spectrometer in the 2–6 GHz range.1 To aid in spectral assignment, we used the Conformer-Rotamer Ensemble Sampling Tool (CREST) to generate an ensemble of conformers. Two monomer conformations with their respective1C isotopologues were assigned, followed by the determination of substitution structures and semi-experimental effective structures. With the aid of the CREST results, transitions of several hydrates, (3-Methylcatechol-(H2O))N=1–4, were also assigned in the experimental spectrum. For the monohydrate and dihydrate, splittings of rotational transitions into quartets were observed. These splittings are a consequence of methyl rotational (MR) and the proton exchange motion of water. Only MR splittings are present for the trihydrate, while no MR or proton exchange splitting is present for the tetrahydrate. Non-covalent interactions2 and natural bond orbital analyses3 were used to visualize and quantify the intermolecular interactions within each cluster. 1. M. Fromm et al., J. Geophys. Res. Atmospheres, 2019, 124, 13254–13272; 2. A. V. Bridgeswater, Th. Graff, R. Schuch, K. L. Halter, B. J. A. Glendening, J. Chem. Phys., 2011, 129, 214701; 3. A. Hashimi et al., J. Anal. Appl. Pyrolysis, 2011, 92, 88–98; 4. N. A. Seifert et al., Phys. Chem. Chem. Phys., 2018, 20, 27630–27637; 5. P. Pracht et al., Phys. Chem. Chem. Phys., 2020, 22, 7169–7173; 6. J. Contreras-Garcia et al., J. Chem. Theory Comput., 2017, 13, 625–632; 7. E. D. Glendening et al., J. Comput. Chem., 2013, 34, 1429–1437.
WM10
5:06–5:21
INTERMOLECULAR FREQUENCIES OF N₂O-Kr AND SYMMETRY BREAKING OF THE N₂O BENDING MODE IN THE PRESENCE OF A RARE GAS

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Rotationally-resolved infrared spectra of N₂O-Kr and N₂O-Kr van der Waals clusters are studied in the region of the N₂O ν₁ vibration (~2224 cm⁻¹) using a tunable Quantum Cascade laser source to probe a pulsed supersonic jet. The N₂O-Kr ν₁ fundamental band is re-analyzed, together with previous ν₂ band data, using a unified scheme to fit the small observed Kr isotope splittings. This scheme is then transferred to analyze the bending combination band of N₂O-Kr near 2257 cm⁻¹ where isotope effects are much larger due to stretch-bend Coriolis interactions. As a result, N₂O-Kr intermolecular bend (33.29 cm⁻¹) and stretch (34.48 cm⁻¹) frequencies are directly determined for the first time. We also report observation of weak spectra for both N₂O-Ar and -Kr corresponding to the (ν₂, ν₂, ν₂) = (1,1,0) hot band of N₂O located near 2257 cm⁻¹. In the presence of Argon/Krypton atom, the doubly-degenerate ν₂ bending mode of the N₂O monomer splits into an in-plane and an out-of-plane mode. These two infrared bands are heavily linked by Coriolis interactions and their analysis yields the magnitude of the splitting of the bending modes which are significantly smaller than those observed in the analogous CO₂-containing dimers. The experimental results obtained here are valuable for testing the accuracy of theoretical calculation towards a better understanding of intermolecular interactions.

WM11
5:24–5:39
AB INITIO INVESTIGATIONS ON THE TRIMERS CONTAINING HC₃N IN COMBINATION WITH H₂C=CH₂ AND/OR HCN

ANDREA PIETROPOLLI CHARMET*, Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari, Venezia, Italy.

The present contribution focuses on the main results coming from ab initio investigations carried out on the mixed trimers containing (at least one molecule of) cyanacetylene in combination with acetylene and/or hydrogen cyanide units. The several optimized structures corresponding to true minima on the PES of these complexes have been characterized at different levels of theory, and a set of their spectroscopic parameters relevant to rotational and vibrational spectroscopies have been determined. Besides, by employing different approaches, also the kinds and the topologies of the interactions present in each of these minima have been investigated.

WN01
1:45–2:00
SUBMILLIMETER WAVE STUDY OF NITROSOMETHANE (CH₃NO)

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The knowledge of synthetic routes of complex organic molecules is still far to be fully understood. The creation of reliable models is particularly challenging. Hollis et al.² pointed out that the observations of molecular isomers provides an excellent tool to evaluate the hypothesis of the synthetic pathways. Formamide (HCONH₂) is an abundant molecule in ISM detected in 1971 in SgrB². We decided to investigate two isomers of formamide some years ago: formaldoxime and nitrosomethane, like they are interesting ISM targets. Formaldoxime is a classic asymmetrical spinning top, its spectrum does not present any identification difficulties, it has been published recently. Concering nitrosomethane, the methyl top internal rotation should be taken into account, therefore the analysis is not obvious. We have been working on the project for several years. Analysis is performed using the version of RAMiS coded which includes the treatment of the nuclear quadrupole hyperfine structure.² Up to now the spectroscopic studies are only available up to 40 GHz. We recently recorded the spectra in L from 225 to 660 GHz using the bolometric detector in order to improve the signal to noise ratio. The new spectroscopic results will be presented. Its presence in ISM will also be discussed. This work was supported by the CNES and the Action sur Projets de l’INSU - PCM1.

WN02
2:03–2:18
MILLIMETER AND SUB-MILLIMETER SPECTROSCOPY OF DOUBLY DEUTERATED ACETALDEHYDE (CD₂CHO)

JUDY FERRER-ASENSIO, SILVIA SPEZZANO, CHRISTIAN ENDRES, VALERIO LATTANZI, The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany; L. H. COUDDERT, Institut des Sciences Moléculaires d’Orsay, Université Paris-Saclay, CNRS, Orsay, France; PAOLA CASELLI, The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany.

In the last years the number of multi-deutered molecules detected in the Interstellar Medium (ISM) increased substantially. These molecules are found to be more abundant than expected when taking into account the ISM deuterium abundance (D/H ≈ 2.0 ± 0.1 × 10⁻⁵; Doudoukaoka et al.² and references therein). In order to better understand the nature of deuterium fractionation, and the interplay of the chemistry in the gas phase and on the surface of dust grains, chemical models need to be constrained by observations of singly- and multi-deuterated molecules. Doubly deuterated acetaldehyde (CD₂CHO) has not been detected in ISM yet as it has been studied in the laboratory only up to 40 GHz (Turner & Comelli,² Turner et al.² and hence lacks an extensive spectroscopic study, in contrast with the singly-deuterated forms CH₃CHO and CH₂OD that were detected towards the protostellar core IRS16293-31228 (Coudert et al.²). In order to allow the first detection of CD₂CHO in the ISM, and to understand its deuterium fractionation, we are studying the rotational band of CD₂CHO in the millimetre and sub-millimeter frequency range. This work allows us to obtain an accurate spectral catalogue for CD₂CHO, which will be used to search for this molecule in star-forming regions.

THE ROTATION-TUNNELING SPECTRUM OF DIMETHYLAMINE, (CH$_3$)$_2$NH

HOLGER S. P. MÜLLER, FRANK LEWEN, STEPHAN SCHLEMMER, J. Physikalisches Institut, Universität zu Köln, Köln, Germany

Methylamine (CH$_3$NH$_2$) was among the molecules detected early by means of radio astronomy. Detected initially only by the giant star-forming region Sagittarius B2 close to the Galactic center. Recently, vinylamine (C$_2$H$_3$NH) and ethyl-

amine (C$_2$H$_5$NH) were detected securely and tentative, respectively, toward the cold Galactic center source G0.003−0.013, making (CH$_3$)$_2$NH a prime target for searches in space.

The microwave spectrum of dimethylamine was studied more than 50 years ago up to 45 GHz and J = 8. The spectrum displays an inversion splitting of the amino H atom of 2466 MHz, and the $^{13}$N hyperfine splitting was well resolved for transitions with J ≤ 1. The internal rotation splitting of the two equivalent methyl rotors was not resolved. Very recently, a Fourier transform microwave spectroscopic (FTMW) study (2 – 40 GHz) of secondary amines revealed a small internal rotation splitting of order of ~200 MHz in dimethylamine.

We have studied the rotation-inversion spectrum of dimethylamine between 76 and 1091 GHz covering quantum numbers up to $J = 60$ and $K_a = 21$. Hyperfine splitting was resolved at least partly for many transitions and was treated in the analysis. The small internal rotation splitting was resolved in particular for transitions at lower frequencies or with lower quantum numbers, but was not considered thus far. The analysis was carried out with Pickett's spfit program. As the program is capable of treating internal rotation, we want to combine our data with the FTMW data.

We present the results of our new study of the torsion-rotation spectrum of the fully deuteriated isotopologue of methanol (CD$_3$OH). The new measurements were carried out from the millimeter wave range (starting at 54.5 GHz) to the terahertz range (up to 1.1 THz) using spectrometers in Kurikawa and Köln. We extend the rotational quantum number coverage up to $J_{max} = 50$ in this work. The analysis is done using the rho axis method and the RAM36 program code, as in our earlier studies on CD$_3$OH and CH$_3$OD. One preliminary fit shows that the $v_1 = 2$ torsional state is affected by intermode interferences with non-torsional vibrational modes which propagate down through intermodial interferences, similar to the cases of CD$_3$OH and CH$_3$OD.

Taking into account the astrophysical significance of methanol and its isotopologs, we decided at this stage of the analysis to concentrate our fitting attempts on the ground and first excited torsional states of CD$_3$OD. We will present the status of our investigations.

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LABORATORY MEASUREMENT OF MILLIMETER-WAVE TRANSITIONS OF $^{13}$CH$_3$DOH FOR ASTRONOMICAL USE

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Methanol (CH$_3$OH) is known to be an important precursor of various interstellar complex organic molecules. As a monodeuterated methanol, CD$_3$OD is one of the most abundant isotopologues of CH$_3$OH which is often used to study the deuterium fractionation of CH$_3$OH in interstellar medium. One of the problems regarding CH$_3$DOH is that its emission lines are sometimes optically thick, and thus the derivation of its abundance is very difficult and frequently unreliable. Observations of its presumably optically thin $^{13}$C substituted species, $^{13}$CD$_3$OH, would give us an opportunity to overcome this issue.

In this study, the rotational transitions of $^{13}$CD$_3$OH have been measured in the millimeter wave region between 216 GHz and 264 GHz with an emission type millimeter and submillimeter-wave spectrometer, SUMIRE, by using a deuterated and $^{13}$C enriched samples. The absolute intensities for the α-type transitions are within 10% from their theoretical values except for perturbed lines, whereas large differences are seen in the τ-type transitions. Our experimental results will contribute to identify $^{13}$CD$_3$OH in observational spectra from respective astronomical environments, and thereby allow us to study the deuterium fractionation of CH$_3$OH in various sources with accurate determination of the CD$_3$OH abundance.

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Intermission
MILLIMETER-WAVE SPECTRUM OF 2-PROPANIMINE AND ITS SEARCH IN THE INTERSTELLAR MEDIUM


Methylpropene, (CH\textsubscript{3}CH=CH\textsubscript{2}), also known as 2-butene, is a promising candidate for interstellar detection because it is the next step in molecular complexity from known interstellar species such as formic acid and methyl formate. Glycolic acid has also been confirmed as a product of the UV photolysis of simple (H\textsubscript{2}O\textsubscript{2}CO-NH\textsubscript{3}) interstellar ice analogues. Glycolic acid has two conformers: The SSC, or syn-syn-cis, conformer is the most stable species, followed by the trans conformer ATT, anti-trans-trans. Previous rotational spectroscopic studies of glycolic acid reported lines in the range of 113 – 318 GHz. We have extended the spectra of both the SSC and ATT conformers from 318 GHz to 1 THz using long-pathlength direct absorption flow cell spectroscopy. Here we will report on the spectroscopic results and the associated analysis for glycolic acid.

Acknowledgments: L.K., J.K., K.V., K.L., and P.K. acknowledge the financial fundings from the Czech Science Foundation (GAČR, grant No. 19-25111Y) and the Ministry of Education, Youth and Sports of the Czech Republic (MSMT, grant No. 18-13130S). J.C.G. thanks the Barrande project No. 46662VH and the Centre National d’Etudes Spatiales (CNES) for a grant I2C 132/4500065585.

References:

The millimeter wave vacuum of vinyl isocyanate and vinyl ketene, candidates for astro-nomical observations

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Interstellar detections of isocyanic acid (H\textsubscript{2}C=NH) and methyl isocyanate (CH\textsubscript{3}C=NH) provide the possibility of detecting the related molecule vinyl isocyanate in the interstellar medium. Similarly, astronomical observations of ketene (CH\textsubscript{2}=CH\textsubscript{2}) place vinyl ketene among the species of potential interstellar relevance. In the present work, both vinyl isocyanate and vinyl ketene were detected and their rotational spectra were recorded between 218 and 330 GHz using the Prague millimeter wave spectrometer. The spectroscopic measurements and analyses presented here will allow for the search for both molecules in the millimeter wave surveys of interstellar sources such as those recorded by Atacama Large Millimeter/submillimeter Array.

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References:
Large organic molecules of extraordinary complexity have recently been found in diverse regions of the interstellar medium (ISM). In this context, we aim to provide accurate frequencies of the ground vibrational state of two key aliphatic aldehydes, n-butyraldehyde, and its branched-chain isomer i-butyraldehyde. We employed a frequency modulated millimeter-wave absorption spectrometer to measure the rotational features of n- and i-butyraldehyde; several thousands of transitions belonging to the lower-energy conformers have been assigned up to 325 GHz. A precise set of the relevant rotational spectroscopic constants have been determined for each structure as a first step to identifying both molecules in the ISM. We then used the spectral line survey named Re-Exploring Molecular Complexity with ALMA, performed toward the star-forming region Sgr B2(N) with ALMA to search for n- and i-butyraldehyde. We also searched for both aldehydes toward the molecular cloud G+0.693-0.027 with IRAM 30m and Yebes 40m observations. We report the nondetection of the aldehyde’s abundance while increasing the level of complexity.

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DIABATIC VALENCE-HOLE STATES IN THE C2 MOLECULE: “PUTTING HUMPTY DUMPTY TOGETHER AGAIN”

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Each of the six C,N,O diatomic molecules has a unique role in shaping our intuitive understanding of electronic structure theory. In this work, the pathologically pervasive configuration interactions that occur in four electronic symmetry manifolds (\(\Pi_u\), \(\Pi_g\), \(\Sigma_u^+\), \(\Sigma_u^\prime\)) of the C2 molecule are disentangled by a global multi-state diabatization scheme. The key concept of our model is the existence of two “valence-hole” configurations, \(2s^22p^2\bar{2}e\bar{2}e\) (\(\Pi_u^1\)) and \(2s^22p^2\bar{2}e\bar{2}e\) (\(\Sigma_u^\prime\)) that derive from a \(3s\rightarrow 2e\) electron promotion. The lowest energy state from each of the four C2 symmetry species is dominated by this type of valence-hole configuration at its equilibrium internuclear separation. These valence-hole configurations have a nominal bond order of 3 and correlate with the \(2\bar{2}e\bar{2}e\) separated-atom configurations. Facilitated by chemical intuition, the diabatic picture uncovers the disruptive impact of the valence-hole configurations on the global electronic structure and unimolecular dynamics of C2. In each of the four symmetry manifolds studied in this work, the strongly bound diabatic valence-hole state, the energy of which starts low and ends high, crosses multiple weakly-bound and repulsive states that are composed of electron configurations with a \(2\bar{2}e\bar{2}e\) valence-core. These diabatic crossings result in an extensive, interconnected network of avoided-crossings among the low-lying electronic states of C2. The C2 molecule behaves “badly,” yet its secrets are revealed by diabatic modeling of their lumpy adiabatic potentials and broken spectroscopic patterns. Based on our demonstration of the importance of valence-hole configurations in C2, we propose a diabatic model re-analysis of similar interactions in the other second-row diatomic molecules, for which the valence-hole states are expected to have a similar impact on their global electronic structure.
A DFT STUDY: SPECTROSCOPIC ANALYSIS OF SCHIFF BASE LIGAND WITH Fe(II) COMPLEX

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Department of Physics, Mustafa Kemal University, Hatay, Turkey.

In this study, the molecular geometry, electronic, magnetic, and vibrational spectra of Schiff base ligand with Fe(II) Complexes were simulated by using density functional theory hybrid methods. NMR, UV-Vis, Raman, Infrared Spectroscopic investigations were carried out. The calculated values have been compared with the corresponding experimental results. Molecular orbital properties, descriptors, the mapping molecular electrostatic potential surface (MEP), and nonlinear optical (NLO) properties have been reported for better understanding at the molecular level. Normal modes analysis and their vibrational assignments were searched by using the Scaled Quantum Mechanical Force Field (SQM-FF) method based on total energy distribution (TED).

NOVEL NATURE-INSPIRED SUNSCREENS

JAYUN FAN, Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands.

Trans-urocanic acid (UA) is found in the outer layer of human skin, where –due to its favorable UV absorption properties- it is thought to act as a natural sunscreen protecting DNA from photodamage. In recent decades it has become clear, however, that the cis-isomer produced upon irradiation has immunosuppressive properties, which is the main reason why UA is no longer employed in commercial sunscreens formulations. As a basic chromophore UA is nevertheless an excellent starting point for the search for novel, nature-inspired sunscreens.

HIGH-RESOLUTION LASER SPECTROSCOPIC STUDIES OF UROCANIC ACID AND DERIVATIVES: TOWARDS NOVEL, NATURE-INSPIRED SUNSCREENS

HAYUN FAN, Van’t Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, Netherlands.

Together with UV/Vis and FT-IR studies of these compounds in various solvents they provide a comprehensive view on the photoactive properties of these compounds, as well as the influence of the presence of different conformers and tautomers.

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The formyl ion (HCO \(^+\)) is one of the most abundant ions in molecular clouds and represents an excellent candidate to trace dense molecular gas through the evolutionary stages of the interstellar medium (ISM). For this reason, the accurate rotational rate coefficients of HCO \(^+\) and its isotopes with the most abundant perturbing species in the ISM are crucial in non-local thermal equilibrium (LTE) models and deserve special attention. To this end, many efforts have been made in order to retrieve accurate collisional parameters of HCO \(^+\) interacting with the H\(_2\) and H\(_2\)\(^+\) colliders as well as for some of its isotopologues \(^{11}\)\(^1\)O and \(^{12}\)\(^1\)O. However, in spite of laboratory and observational studies on HCO \(^+\)/\(^{12}\)\(^1\)O \(^+\)/\(^{13}\)\(^1\)O, to the best of our knowledge, no accurate characterization of its collisional parameters has not been carried out yet. Although rare, the \(^{13}\)\(^1\)O isotope assumes a prominent role to avoid problems due to the optical thickness of the parent species emissions. With the aim of filling this lack, this work reports the first calculations of hyperfine resolved rate coefficients for the excitation of HCO \(^+\)/\(^{13}\)\(^1\)O by \(^{p-}\)H\(_2\) (J \(=\) 1–3).

We characterized the potential energy surface of the HCO \(^+\)/\(^{13}\)\(^1\)O collisional system by means of the CCSD(T)/F12/aug-cc-pVQZ level of theory. The interaction energy has been averaged over five H\(_2\) orientations and then fitted as an expansion in terms of Legendre polynomials. The rate coefficients are given as a function of the impact parameter and the scattering angle. The rate coefficients are found to decay exponentially with the impact parameter as a result of the van der Waals interaction between the approaching species. The rate coefficients for the formation of H\(_2\)CO \(^+\) show a pronounced enhancement for the H\(_2\)\(^+\) collider due to a repulsive interaction.

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**R105**

**EXTENDED PREDICTION OF CAF ELECTRONIC STATES: ENERGY, MULTIPOLE MOMENTS, AND A SHAPE RESONANCE STATE**

**STEPHEN L COY, TIMOTHY J BARNUM, ROBERT W FIELD. Department of Chemistry, MIT, Cambridge, MA, USA; JOHN P STANTON, Physical Chemistry, University of Florida, Gainesville, FL, USA.**

The alkaline earth monohalides have a number of applications. They are a continuing focus of ultracold experiments; they provide insight into the calcium ionic bonding of biological relevance; and they are molecular prototypes for Rydberg spectroscopy. In Rydberg spectroscopy, a MQDT model is extremely effective, but not all states are of purely Rydberg type since a lifetime matrix calculated in Serhan Altunata’s work describes a shape resonance that couples Σ states to dissociation.

To explore this, a wide range of CAF properties have been obtained in a series of UHF-CCSD(T) calculations extending to nearly 40,000 cm⁻¹ above the ground state. Excited states were converged from QRHF initial guesses and extended to include CCSD(T) first-order properties, computed analytically. Remarkably accurate results are obtained for dipole moments known from molecular beam experiments, as well as very good results found for known values of bond length, vibrational frequency, and anharmonicity. Several new states are predicted. In general, it is not possible for states of two of the same symmetry to be quite close in energy and yet cross unless electronic configurations are very different. The calculation finds that to be the case for two higher Σ states that differ dramatically in electron density and bond length, one with a short bond length and electron density along the axis far away from the center of mass, and a second with a long bond length with density in a ring close to the center of mass. The states have large quadrupole moments of opposite signs. The long bond length state may be related to the predicted shape resonance.

**Intermission**

**R106**

**STATE-RESOLVED MODELING FOR THE ENERGY TRANSFER PROCESSES IN LASER-INDUCED FLUORESCENCE OF DIATOMIC MOLECULES**

**SHENGKAI WANG**. State Key Laboratory for Turbulence and Complex Systems, College of Engineering, Peking University, Beijing, China.

This work presents a generic framework for modeling the energy transfer processes between rovibronic quantum states in diatomic molecules upon laser excitation. A comprehensive set of rate equations (denoted here as the master equation) was developed to describe the interactions between radiation processes (i.e., absorption, stimulated emission and fluorescence), collision processes (including rotational energy transfer, vibrational energy transfer, and electronic quenching), and losses such as inter-system crossing across chemical reactions (including predissociation and ionization). The rate coefficients were fully parameterized using physical quantities such as the transnational temperature of the excited molecule, the energy gap and the transition quanta across the process, and the numerical expressions of parameterization were guided by a critical review of the existing literature. A stiff ODE solver with adjustable step-size was implemented to accommodate the wide range of physical timescales involved in the master equation. To demonstrate the utility of the current modeling approach, simulations were performed for OH and NO molecules excited by selected transitions in the A-X (0,0) and (1,0) bands, and the spectro-temporal features of the predicted fluorescence signals were analyzed and validated against previous experimental results. Additional simulations were also conducted at extreme conditions of ultra-short laser pulses and very high laser energy densities, exploring new spectroscopic phenomena and spectral trends resulting from complications of strong non-linear interactions, and the impact of such conditions, indicating the existence of an optimal pulse length or laser energy (not necessarily the shorter or higher the better) for typical LIF applications. This modeling framework will be released online soon and should prove useful in aiding the design and analysis of modern quantitative LIF measurements.

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**R107**

**PRESSURE AND TEMPERATURE DEPENDENCE OF ABSORPTION CROSS-SECTION OF HCN IN THE LONG-WAVE MID-INFRARED REGION**

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Hydrogen cyanide (HCN) is extensively studied in combustion and exoplanetary research for its important role in both fields. Laser-based detection of HCN in both fields, among other applications, necessitates quantifying the pressure and temperature dependence of its absorption cross-section. Here, we introduce a method to access HCN’s strongest IR band, ν2 near 712 cm⁻¹ via a high-resolution custom-designed laser source. Difference-frequency generation (DFG) between a cw EC-QCL and a pulsed CO2 gas laser in an orientation-patterned GaAs crystal is employed to generate laser light in the long-wavelength mid-IR region. The DFG laser can be wavelength-tuned over 667 - 855 cm⁻¹. We employed our DFG laser to quantify the pressure dependence of absorption cross-section of the Q-branch of the ν2 band of HCN over the range 100 - 800 Torr. Furthermore, we exploited the developed laser source in conjunction with a shock tube to measure the temperature dependence of absorption cross-section of the peak of the Q-branch behind reflected shock waves over the temperature range 850 - 3000 K. We compared our results with HITRAN simulations. Ultimately, we utilized these results in measuring HCN formation time-sequences in a reactive environment beyond reflected shock waves.

**R108**

**HITTING THE TRIFECTA: HOW TO SIMULTANEOUSLY PUSH THE LIMITS OF SCHRÖDINGER SOLUTION WITH RESPECT TO SYSTEM SIZE, CONVERGENCE ACCURACY, AND NUMBER OF COMPUTED STATES**

**JÁNOS SÁRKA, BILL PORRIER. Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA.**

Methods for solving the Schrödinger equation have seen an explorative growth in recent years, as the importance of incorporating quantum effects in numerical simulations in order to obtain experimentally accurate data becomes increasingly recognized. In practical terms, there are just three primary factors that currently limit what can be achieved. These are: (a) SYSTEM SIZE, i.e., the number of degrees of freedom that can be treated explicitly quantum mechanically; (b) NUMERICAL ACCURACY, measured in terms of convergence with respect to ALL POSSIBLE computational parameters such as basis sizes; (c) ENERGY EXCITATION or the total number of accurately computed states. Broadly speaking, current methods can deliver on any two of these goals, but achieving all three at once remains an enormous challenge.

In this presentation, we shall describe just such a method, and demonstrate how it can be used to “hit the trifecta” in the context of molecular vibrational spectroscopy calculations. In particular, we compute thousands of vibrational states for the 12D acetonitrile molecule (CH₃CN), to a target numerical convergence of a few 10⁻³ cm⁻¹ or better. In other words, we compute ALL vibrational states for this six-atom system in full quantum dimensionality, and throughout the entire dynamically relevant spectral range, to near spectroscopic accuracy. To our knowledge, no such vibrational spectroscopy calculation has ever previously been performed—although given the current availability of the method, we anticipate there will be many more such calculations to follow.


**SHENGKAI W ANG**

**Peking University, Beijing, China**

**STEPHEN L COY**

**Texas, USA**

**IANOS SÁRKA**

**Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, USA**

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ANALOG QUANTUM SIMULATION OF MOLECULAR DYNAMICS AND SPECTROSCOPIC OBSERVABLES
RYAN J MacDONELL, IVAN KASSAL, School of Chemistry, University of Sydney, Sydney, NSW, Australia.

Modern computational techniques used to simulate quantum chemistry are on the boundary of tractability due to the exponential growth of the molecular wavefunction, requiring a careful balance between molecule size and simulation accuracy. In recent years, quantum computing has risen in popularity as a potential alternative to conventional (classical) techniques; however, most methods rely on access to "digital" quantum computers composed of qubits and quantum gates, which at present are severely limited by noise. We have developed a real-time, analog approach to simulate vibronic, chemical dynamics with existing quantum technology. Our approach uses an intuitive mapping of molecular electronic and vibrational degrees of freedom onto quantum resonators and qudit (d-level system) states, with controllable couplings between degrees of freedom. The measurement output can be mapped onto different time-dependent observables, including the time-domain simulation of vibronic spectra. Our approach can also incorporate controlled sources of noise to simulate system-bath interactions and dissipative dynamics at a minimal cost. We present experimental results using a trapped-ion device, thus showing the potential for near-term simulation of chemical dynamics in complex environments beyond the abilities of classical computers.

MEASUREMENTS OF HIGH-TEMPERATURE ABSORPTION SPECTRA OF DIMETHYL ETHER AND DIETHYL ETHER BETWEEN 950 AND 1190 cm\(^{-1}\) AND THEIR DIRECT PYROLYSIS STUDY IN A SHOCK TUBE
MOHAMMAD ABDEH, BINOD GIRI, AAMIR FAROOQ, Clean Combustion Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia.

Laser absorption spectroscopy has been proved to be a powerful diagnostic tool for high enthalpic systems like exoplanets, combustion applications and hypersonic flows. But there is a scarcity of high-temperature absorption data, especially for large molecules due to technical challenges like limited availability of optical materials necessary to withstand high temperatures. Furthermore, generating a chemically stable, homogeneous and steady gas state for a sufficient duration to carry out such high-temperature measurements is rather complicated and most experimental approaches satisfy only a few of these requirements. In this work, we present measurements of temperature-dependent absorption cross-section between 950-1190 cm\(^{-1}\) of dimethyl ether (DME) and diethyl ether (DEE) and their direct pyrolysis study. The methodology employed here consists of rapid tuning, wide range/tuned wavelength MIRcat-QT laser in conjugation with shock tube. The spectral measurements are performed between 600-900 K, at around 1.2 bar. The measured IR absorption spectra are the first experimental measurements of high-temperature spectra of these species and show strong temperature dependence. For the first time absorption cross-section correlation has been provided for a wide range of spectra over a wide range of temperatures. These measured spectra have provided a significant idea about the trend in spectra at elevated temperatures and helped in the selection of promising wavelengths for sensitive detection. DME and DEE pyrolysis studies are performed at 1121.7 cm\(^{-1}\) and 1115 cm\(^{-1}\) respectively by providing the marginal temperature dependence absorption cross-section correlations.
The linear radical cation of cyanoacetylene, $\text{HCN}^+$ (1H), is of fundamental spectroscopic interest due to its strong spin-orbit and Renner-Teller interactions, which have been investigated previously in several high-resolution photoelectron spectroscopic (PES) studies \(^{1,2-7}\). Here, we present the first broadband vibrational action spectroscopic investigation of this ion through the infrared pre-dissociation (IRPD) method using a Ne tag. Experiments have been performed using the FELion cryogenic ion-trap instrument in combination with the Free Electron Lasers for Infrared Experiments (FELIX) Laboratory at the Radboud University (Nijmegen, The Netherlands). \(^{8}\) The vibronic splitting patterns of the 3 interacting bending modes ($\nu_5$, $\nu_{15}$, $\nu_{28}$), ranging from 180-1600 cm\(^{-1}\), could be fully resolved revealing several bands that were previously unobserved.

The associated Renner-Teller and cross-coupling constants were determined by fitting an effective Hamiltonian to the experimental data, and the obtained spectroscopic constants were in reasonable agreement with previous studies of the $\text{HCN}^+$ ion. The influence of the attached Ne atom on the infrared spectrum was investigated by ab initio calculations at the CASSIDY level of theory, showing that the discrepancies between the IRPD and FES data can be explained by the effect of the Ne binding.

The intermolecular charge flow mechanism of halogen bonding in methylamine has been experimentally identified. The spectra were recorded with a resolution of 0.00125 cm⁻¹ using Bruker IFS-120HR spectrometer at the University of Oulu. The accurate energy levels of the first excited torsional state, \( v = \frac{15}{2} \), have been apparent. Quantum chemical calculations using a range-separated hybrid density functional (\( \omega B97X-D \)) with flexible augmented correlation-consistent basis sets support the spectroscopic assignments of the strongest fundamental vibrations to a predominantly S-X (X = Br, I) stretching mode and (SCN)⁻ and (SCN)⁻⁻ vibrations at 415 nm in order to collect and then subtract their contributions from the composite spectrum.
COMPLETION OF THE FIRST SOLUTION SHELL OF CARBON DIOXIDE IN ARGON: ROTATIONALLY RESOLVED INFRARED SPECTRA OF CO$_2$-Ar$_2^*$ AND CO$_2$-Ar$_3^*$

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There have been a number of theoretical papers on the structures and energetics of CO$_2$-Ar$_n$ clusters. But in terms of experiment, the only previous spectroscopic results are for $n = 1$ (extensive work on the CO$_2$-Ar dimer) and $n = 2$ (microwave and infrared spectra of CO$_2$-Ar$_2^*$). We have now obtained and analyzed infrared spectra in the CO$_2$ $v_2$ region for a number of clusters in the range $n = 3$ to 17. Notable among these are CO$_2$-Ar$_3^*$ and CO$_2$-Ar$_{17}^*$, which mark completion of the first solution shell for CO$_2$ in argon. These clusters have highly symmetric structures with D$_5$ and D$_{6h}$ symmetry, respectively, in good agreement with theory. For $n = 15$, CO$_2$ is surrounded by five argon rings, each containing three Ar atoms. For $n = 17$, there are three rings of five atoms each, plus two additional Ar atoms located on the symmetry axis at each end. The observed spectra are symmetric top parallel bands, and both exhibit distinct intensity alteration which helps to confirm their assignment. Observed B-values are 69.93 MHz for CO$_2$-Ar$_{17}^*$ and 54.52 MHz for CO$_2$-Ar$_{15}^*$. As usual for symmetric rotors, the spectra are not sensitive to the A constant, but we do obtain precise values for the band origins, and hence the vibrational shifts (relative to free CO$_2$) as induced by the argon cages.

HIGH RESOLUTION INFRARED SPECTROSCOPY OF DIBORANE DISPERSED IN SOLID PARAHYDROGEN

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Few polyatomic molecules have been the subject of more ab initio studies than B$_2$H$_6$, diborane. The earliest studies were focused on elucidating the structure of its prototypical three-center, two-electron “banana” bonds. Information about the force field and motion of atoms in B$_2$H$_6$ can be most directly derived from its vibrational frequencies. However, with eight atoms, high symmetry, and significant vibrational anharmonicities, an exclusively spectroscopic determination of its anharmonic force field is nearly an intractable problem. However, with advances in ab initio methods and the development of methods to treat vibrational frequencies and intensities beyond the harmonic approximation, this challenging system is now amenable to deeper understanding. We decided to use parahydrogen (pH$_2$) matrix isolation infrared spectroscopy to measure the vibrational wavenumbers and intensities of as many infrared absorptions of B$_2$H$_6$ as possible in the 800 to 5000 cm$^{-1}$ “region to compare with more recent ab initio studies by Zagler and Rudut that go beyond the double harmonic approximation.” Our studies show nearly quantitative agreement between theory and experiment for the allowed infrared vibrational modes in the surveyed region. We devised a scheme to assign peaks in our spectra that then can be compared directly with computational predictions. Indeed, earlier spectroscopic assignments were hampered by not knowing the anharmonic contributions to the measured vibrational frequencies. We are currently investigating the analogous spectra of the B$_2$D$_6$ isonopolog and will present our latest findings and comparisons with available theory at the meeting.
PROGRESS ON SHOCKGAS-IR: MEASUREMENTS OF METHYL FORMATE AT ELEVATED TEMPERATURES

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Methyl formate plays an important role in multiple combustion mechanisms, such as the oxidation of dimethoxymethane, warranting further study of its absorbance spectra at elevated temperatures. However, pyrolysis reactions make broadband measurements at elevated temperatures difficult, and currently available spectra are mostly limited to lower temperatures around 296 K. In this study, we have shock heated methyl formate, dilute in argon, at temperatures up to 1000 K and measured the cross sections from 1655 to 1875 cm⁻¹. Measurements within the short ms-scale test times were achieved through a rapid-tuning, broad-band external-cavity quantum-cascade laser. We have also supplemented these elevated temperature measurements with elevated pressure cross sections at room temperature in a static cell, at pressures up to 35 atm. Our measurements were validated through excellent 206 K agreement with that in the literature. The elevated temperature cross sections reveal an additional absorbance structure near 1800 cm⁻¹, possibly the emergence of a combination band. Interestingly, the cross sections at elevated pressure conditions display a dependence on pressure, contrary to its common use and implementation in previous literature. These cross sections expand our ShockGas-IR database (https://searchworks.stanford.edu/view/wsl021dc3029), containing elevated temperature cross sections of many other molecules important for combustion mechanisms.

CO₂ COLLISIONAL BROADENING OF THE 557 GHZ WATER ABSORPTION FEATURE PROFILLED WITH A DIFFERENTIAL ABSORPTION RADAR PLATFORM

KEN COOPER, DEACON J. NEMCHICK, OKMAR PRADHAN, ROBERT DENGLER, RAQUEL RO-DRIGUEZ MONÉ, BRADY DRUNIN, ROSE SILES, LESLIE TAMPARIL, Jet Propulsion Laboratory, Cali-
fornia Institute of Technology, Pasadena, CA, USA.

Millimeter and sub-millimeter differential absorption radar (DAR) systems, which measure the attenuation of a transmitted beam as a function of both frequency and range, are currently in development for a variety of Earth and planetary science applications. This talk will summarize efforts to realize a portable DAR system optimized to profile the 557 GHz ν₁+ν₅带 rotational transition of water that is suited for humidity measurements between scatter targets in low-pressure Martian-like en-
vironments. This emerging class of active remote sensing instrumentation, if deployed on future Mars lander/rover missions, could provide local near-surface humidity profiles that are unresolvable to the current generation of passive orbiting sensors. This presentation will include an overview of DAR operational principles, system architecture, and deployment scenarios. Room temperature laboratory measurements recorded with the DAR prototype system of the 557 GHz pure rotational water transition broadened by carbon dioxide in a sample mixture that is reasonably analogous to that found on Mars (~200 ppm H₂O in 5 Torr CO₂) will be presented. Observed results will be discussed in the context of previously measured line shape parameters with extrapolation made to the lower surface temperatures (200 - 250 K) found on Mars.

SELECTIVE PRODUCTION OF HCN MONOMER AND EVIDENCE FOR GAS-PHASE DIMERIZATION

THOMAS HOWARD, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA; EMILY K. HOCKEY, Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, MD, USA; DARYA KISURYNA, Physics, University of Maryland, College Park, MD, USA; JES- SICA PALKO, LEAH G. DODSON, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA.

Hydrogen cyanide (HCN) is an important molecule in astrochemistry. To prepare for experiments to study its reactivity, we selectively produced a molecular beam of monomeric HCN using a cryogenic buffer-gas source. The HCN beam was first interrogated by condensing it on a 10K substrate using argon as a bath gas to create an inert matrix. Based on a comparison of the resulting infrared spectrum with experiments that use conventional effusive sources, HCN polymers can be nearly eliminated from the matrix using a cryogenic buffer-gas beam source. Our experiments suggest that HCN undergoes polymerization in the gas phase and may exist, to some extent, as a dimer under ambient conditions. We will discuss further investigations using continuous-wave cavity ringdown spectroscopy to examine the first vibrational overtone of the alkynyl C=H stretch of HCN monomer and dimer in the near infrared.
INSTRUMENT DESIGN AND PREPARATION OF PARA-HYDROGEN FOR MATRIX EXPERIMENTS

KORINA VLAHOS, Chemistry and Biochemistry, University of Maryland, College Park, MD, USA; EMILY K. HOCKEY, 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.

Para-hydrogen (p-H$_2$) is used as a host matrix in matrix-isolation experiments because of its unique properties to act as a quantum solid. However, p-H$_2$ is not commercially available and needs to be produced in house with a custom-built p-H$_2$ converter. Throughout this presentation, we will describe the design and building phases of the custom-built p-H$_2$ converter at the University of Maryland. Instrument drawings, schematics, and preliminary results will be presented. This talk will also explore the spectroscopic techniques that are used to both prove the enrichment of p-H$_2$ and determine the purity of p-H$_2$. The p-H$_2$ will be used in future experiments to study novel astrochemistry interactions and reactions in the interstellar medium (ISM). The production of p-H$_2$ is critical for future astrochemistry relevant experiments such as its properties as a quantum solid allow us to further understand molecular properties and interactions that would be otherwise unattainable with rare-gas host matrices.

Intermission
Cavity-Enhanced Absorption Spectroscopy (CEAS) and Cavity Ring-Down Spectroscopy (CRDS) are well established for sensitive infrared measurements of gas phase compounds at trace level using their rovibrational signatures. The recent successful development of a THz Fabry-Pérot spectrometer shows that the adaptation of such techniques to the THz and millimeter wave regions is possible by probing rotational transitions of light polar compounds. Here we report on the development of a new millimeter resonator based on a low-loss corrugated waveguide with highly reflective photonic mirrors obtaining a finesse above 3500 around 150 GHz. With an effective path length of one kilometer, a significant sensitivity has been evaluated by the measurement of line intensities as low as 10^{-18}cm^{-1}(molecule/cm^3). This spectrometer will be used to detect semi-volatile organic compounds at trace level which could not be envisaged with a conventional detection technique.1,2


Acknowledgment: This work received financial support from the French Agence Nationale de la Recherche via funding of the project Millimeter-wave Explosive Taggant vapors Investigations using Spectral taxonomy (METIS) under contract number ANR-20-ASTR-0016-03.

INTEREST BETWEEN THE 5d_{3/2} – 5p_{1/2} AND 5p_{1/2} – 5s_{1/2} COHERENCES (386.4 AND 384.1 THz) IN Rb OBSERVED BY ULTRAFAST FOUR-WAVE MIXING SPECTROSCOPY

THOMAS REBEUL
Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA

Coherences at 386.2 THz and 384.1 THz, corresponding to the 5d_{3/2} – 5p_{1/2} and 5p_{1/2} – 5s_{1/2} difference frequencies, respectively, have been established in the Rb atom during pump-probe experiments involving pairs of identical 150 fs pulses produced by a Ti:Al_2O_3 laser and a Michelson interferometer. The interference between the two coherences within the atom is observed through a parametric four-wave mixing process in Rb and detected via second harmonic generation. A Fano interference window is observed through a parametric four-wave mixing process in Rb and detected via second harmonic generation. A Fano interference window is observed through a parametric four-wave mixing process in Rb and detected via second harmonic generation.

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THE PURE ROTATIONAL SPECTRUM OF MgCl IN THE (2)^3Π \rightarrow (1)^1Π EXCITED STATE

TYLER HERMAN
Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ, USA

The millimeter/submillimeter spectrum of magnesium chloride (MgCl) has been measured in an electronic excited state, using direct absorption spectroscopy in the range of 240-310 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. Seven rotational transitions in each of six isotopologues (5^{24}Mg\textsuperscript{35}Cl, 5^{24}Mg\textsuperscript{37}Cl, 5^{26}Mg\textsuperscript{35}Cl, 5^{26}Mg\textsuperscript{37}Cl, 5^{27}Mg\textsuperscript{35}Cl, 5^{27}Mg\textsuperscript{37}Cl) were measured in the ground vibrational state, with a number of vibrational excited states (v=1-4) also being observed for each species. From the data, rotational, fine structure, and hyperfine (2^{15}Mg\textsuperscript{35}Cl only) parameters were determined for the six isotopologues in this state, as well as equilibrium constants and the equilibrium bond length, r = 2.54 Å. Based on theoretical calculations, this excited state manifold of MgCl has been identified as (2)^3Π, which has never before been observed experimentally. The excited state manifold of MgCl has been a subject of a number of computational studies, and is of interest for laser cooling experiments.
Electrocatalytic reduction of CO$_2$ into feedstock for chemical fuels is a promising approach to achieving a carbon neutral fuel cycle. While this has been an active field of study for decades, relatively little is known about the key reaction intermediates and molecular-level processes of proposed catalytic mechanisms, necessitating a deeper understanding to inform the design of future catalysts.

We present cryogenic gas-phase infrared spectra of catalytically relevant model systems consisting of a transition metal center (Co, Ni, or Cu) coordinated to two bipyridine-based ligands, either bare or with a formate adduct. Bipyridine derivatives are frequently ligands for molecular catalysts where a transition metal ion is coordinated to four N atoms. This family of metal-4N catalysts has been studied extensively due to their exceptional performance and ease of synthesis. Formate is one of many possible CO$_2$ reduction products. Density functional theory was used to assign spectral features and calculate charge distributions.

The vibrational spectra inform us of the structure of and intermolecular forces in each complex, revealing the binding motif of the formate adduct to the metal center and the dependence of this arrangement on the identity of the metal. The calculated charge distributions demonstrate the role of the organic ligands to act as charge reservoirs, where they show remarkable electronic flexibility in response to the addition of a formate adduct and the nature of the coordinated metal center. This work showcases the influence of transition metal identity on the formate-metal binding motif and the significant role of the organic ligand framework in adjusting the redox properties of these complexes.

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ANALYSIS OF THE A 4Πr – X 4Σ− ELECTRONIC TRANSITION OF MOLYBDENUM NITRIDE (MoN)

LEAH C O'BRIEN, Department of Chemistry, Southern Illinois University, Edwardsville, IL, USA; GABRIEL A HOTZ, KRISTIN N BALES, JACK C HARMs, JAMES J O'BRIEN, Chemistry and Biochemistry, University of Missouri, St. Louis, MO, USA; NYLA S WOODS, Department of Chemistry, Southern Illinois University, Edwardsville, IL, USA; WENLI ZOU, Institute of Modern Physics, Northwest University, Xi'an, China.

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 4Πr – X 4Σ− 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% N2, 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=0), 92MoN(14.6%), 93MoN(9.2%), 95MoN(16.7%), 97MoN(24.3%), and 99MoN(9.7%). The progress, preliminary results of this analysis, and comparison to a recent high-level computational study will be provided.

LOW- AND HIGH-RESOLUTION LASER-INDUCED FLUORESCENCE (LIF) OF JET-COOLED SmO

JOEL R SCHMITZ, ARIANNA RODRIGUEZ, Department of Chemistry, Emory University, Atlanta, GA, USA; TIMOTHY STEIMLE, School of Molecular Sciences, Arizona State University, Tempe, AZ, USA; MICHAEL HEAVEN, Department of Chemistry, Emory University, Atlanta, GA, USA.

The chemi-ionization reactions of atomic lanthanides M+O → MO+ + e− are currently being investigated as a method to artificially increase the localized electron density in the ionosphere for uniform radio wave propagation. Recent experiments involving the release of atomic samarium (Sm) into the upper atmosphere have resulted in the production of a cloud with blue and red emission[1]. Spectroscopic characterization of SmO is required to accurately determine the fraction of SmO present in the release cloud. While the low-lying states of SmO have been previously spectroscopically characterized, the analysis was hindered due to the production of SmO under high temperature conditions[2,3]. In this work, jet-cooled SmO was produced and low- and high-resolution laser-induced fluorescence (LIF) as well as dispersed laser-induced fluorescence (DLIF) techniques were employed for electronic structure characterization. For the first time, vibrational constants for several low-lying states have been determined. Using high-resolution LIF, the hyperfine structure of the (1) v = 0 and [15.35] 1 + states was recorded. Data and analysis of ground and low-lying excited states of SmO will be presented.

Sulfanilamide (SA, 5-amino-benzenesulffonamide) is an antibacterial drug that interferes with the conversion of para-aminobenzoic acid (PABA) to folic acid, preventing the synthesis of folic acid (vitamin B9), essential in multiple carbon transfer reactions. Due to its importance, in this work, we characterize sulfanilamide in the isolation conditions of a supersonic expansion using Fourier transform microwave assisted by laser ablation. A single conformer of the bare molecule, stabilized by an H-N=O intramolecular interaction of the sulfonyl group, has been detected. Because the docking process is controlled by the difference in Gibbs free energy between the ligands solvated by the extracellular medium and the ligand interacting with the receptor’s active site, we have also studied the sulfanilamide’s microsolvation process. Interestingly, a single water molecule is enough to trigger a conformational switch.

In a collaborative effort with the University of Texas Rio Grande Valley, a chirped pulse microwave (CP-FTMW) spectroscopy experiment was carried out on nonafluoro-tert-butyl alcohol (NFTBA) monomer from 5.5 to 18.75 GHz. Calculations were run in order to identify the lowest energy conformation and these will be compared to the experimentally determined structure. In addition to the structure, the spectrum, the spectrum of NFTBA exhibits a large amplitude motion and these complexes will be examined and discussed. NFTBA exhibits high acidity comparable to carboxylic acids, and this presentation will draw comparisons between these two classes of molecules.

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 unreported in the original study of S-carvone by Moreno et al. It was discovered that these splittings were due to internal rotations caused by two non-equivalent methyl rotors. This prompted a re-investigation 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. Spectral analyses were performed using a combination of the SPIIT and XNAM software packages. Current work on the parent and singly substituted isotopologues species for the E\(\text{X}\) and E\(\text{X}\) conformers will be reported. In addition, the potential energy barrier heights to internal rotation for both rotors have been analyzed and will be discussed.

**RL01** 1:45 – 2:00

**THE ROTATIONAL SPECTRUM OF SULFANILAMIDE AND ITS HYDRATED CLUSTER**

**SERGIO MATA, RAÚL AGUADO, JOSÉ L. ALONSO, IKER LEÓN, Grupo de Espectroscopia Molecular, Lab. de Espectroscopía y Bioespectroscopía, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain.**

Sulfanilamide (SA, 5-amino-benzenesulffonamide) is an antibacterial drug that interferes with the conversion of para-aminobenzoic acid (PABA) to folic acid, preventing the synthesis of folic acid (vitamin B9), essential in multiple carbon transfer reactions. Due to its importance, in this work, we characterize sulfanilamide in the isolation conditions of a supersonic expansion using Fourier transform microwave assisted by laser ablation. A single conformer of the bare molecule, stabilized by an H-N=O intramolecular interaction of the sulfonyl group, has been detected. Because the docking process is controlled by the difference in Gibbs free energy between the ligands solvated by the extracellular medium and the ligand interacting with the receptor’s active site, we have also studied the sulfanilamide’s microsolvation process. Interestingly, a single water molecule is enough to trigger a conformational switch.

**RL02** 2:03 – 2:18

**THE ROTATIONAL SPECTRUM OF NONAFLUORO-TERT-BUTYL ALCOHOL**

**JOSHUA E. ISSERT, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA; ZAYRA LÉTICA GONZALEZ, KARLA V. SALAZAR, DIEGO RODRIGUEZ, Department of Chemistry, University of Texas Rio Grande Valley, Brownsville, TX, USA; NICOLE MOON, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA; WELLIN, Department of Chemistry, University of Texas Rio Grande Valley, Brownsville, TX, USA; G. S. GRUBBS II, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.**

In a collaborative effort with the University of Texas Rio Grande Valley, a chirped pulse microwave (CP-FTMW) spectroscopy experiment was carried out on nonafluoro-tert-butyl alcohol (NFTBA) monomer from 5.5 to 18.75 GHz. Calculations were run in order to identify the lowest energy conformation and these will be compared to the experimentally determined structure. In addition to the structure, the spectrum of NFTBA exhibits a large amplitude motion and these complexes will be examined and discussed. NFTBA exhibits high acidity comparable to carboxylic acids, and this presentation will draw comparisons between these two classes of molecules.

**RL03** 2:21 – 2:36

**INTERNAL ROTATION ANALYSIS AND STRUCTURAL 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 unreported in the original study of S-carvone by Moreno et al. It was discovered that these splittings were due to internal rotations caused by two non-equivalent methyl rotors. This prompted a re-investigation 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. Spectral analyses were performed using a combination of the SPIIT and XNAM software packages. Current work on the parent and singly substituted isotopologues species for the E\(\text{X}\) and E\(\text{X}\) conformers will be reported. In addition, the potential energy barrier heights to internal rotation for both rotors have been analyzed and will be discussed.
Semi-Experimental Equilibrium Structure of Methacrylonitrile (C5H5N)

Housten H. Smith, Samuel M. Kougas, Danny J. Lee, Brian J. Esselman, 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; R. Claude Woods, Robert J. McMahon, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA.

The detection of acrylonitrile (C2H3N) in Titan’s atmosphere and the interstellar medium suggests methacrylonitrile may also have astronomical relevance. To aid in the astronomical observation, we synthesized methacrylonitrile via the hydrocyanation and subsequent dehydration of acetonitrile and obtained its rotational spectrum from 6 – 40 GHz and 130 – 500 GHz. The ground vibrational state of the main isotopologue has been least-squares fit to a sextic Hamiltonian accounting for internal rotation. The synthesis of methacrylonitrile was modified by using partially deuterated or fully deuterated acetonitrile to yield samples of varying deuterium incorporation. We will present our analysis of 23 isotopologues, including the main isotopologue, and the resulting (r* SE) structure.

Intermission

Spectroscopic Constants and Potential Functions for the A3Π1 and X1Σ+ States of IBr by Using Merged Data of Stark Spectroscopy

Nobuo Nishimya, Tokio Yuriya, Katsuki Nomura, Masao Suzuki, Faculty of Engineering, Tokyo Polytechnic University, Atsugi, Japan.

The A ← X electronic transition spectra of halogen diatomic molecules have been measured to determine the molecular constants and the parameters of potential energy by various researchers. In 2002, the Dunham coefficients of the X state and rotation-vibration parameters of the A state of IBr were determined by using the assigned line position of spectroscopic data in the range from ν1 = 3 – 20 to ν6 = 1 – 6 and nuclear quadrupole coupling constants were also reported. An anomalous fluctuations in the ν5 – dependence of the first differences of the inertial rotational constant, ΔI5′′ = I3′′ − I′ + I′′, in the A1Π1 was found more than ν5 ≈ 19 region. In 2015, we reported a new nonlinear direct potential fitting (DPF) analysis that uses “vobas” nonlinear least-squares fits to average properly over the effect of such fluctuations in order to provide an optimum delineation of the underlying potential energy curves for it.

In the near dissociation limit, it would be difficult to assign the spectra, because in that area, too dense spectra would be observed. By adopting Stark spectroscopy, the relatively low J spectra are emphasized and the high J spectra become smaller as shown in the figure. This makes it easier to assign the low J spectra even in dense regions. This work reports the spectroscopic constants refined and the parameters of potential energy curve recalculated.

The Conformational Panorama of D-Penicillamine: A Laser Ablation Rotational Study

Diego Herreras, Eileen R. Alonso, Iker Leon, Jose L. Alonso, Grupo de Espectroscopia Molecular, Lab. de Espectroscopia y Bioespectroscopia, Unidad Asociada CSIC, Universidad de Valladolid, Valladolid, Spain.

D-Penicillamine, a drug widely used to treat Wilson’s disease, removes copper excess from the human body by acting as a chelating agent. In the present work, we address unraveling this molecule’s three-dimensional structure as a first approach to shed light on its mechanism of action. Using a laser ablation source, we have transferred solid D-Penicillamine to the gas phase by laser ablation LA and probed it employing CP-FTWM spectroscopy in the isolated conditions of a supersonic jet.

Two dominant conformers of the D-Penicillamine have been identified so far.
STRUCTURE AND DYNAMICS OF HHe+: THE EMERGENCE OF LARGE-SCALE NUCLEAR DELOCALIZATION

IRÉN SIMKÓ, CSABA FÁBRI, ATTILA CSÁSZÁR, MTA-ELTE Complex Chemical Systems Research Group, ELTE Department of Macromolecular Structure and Dynamics, ELTE Eötvös Loránd University, Budapest, Hungary, FA- BÉN BRIEU, CHRISTOPH SCHRAN, DOMINIK MAXX, Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany, OSKAR ASVANY, STEPHAN SCHLEMESER, I. Physikalisches Institut, University of Cologne, Cologne, Germany.

The HHe\(^+\) cation is a model system for solvated triatomic molecules, which consists of a quasilinear HHe\(^+\) core (chromophore) and a weakly-bound solvating He.\(^6\) The equilibrium structure is T-shapd, but the “quantum” structure is very different, showing large-scale nuclear delocalization. In order to investigate the structure and dynamics of HHe\(^+\) we performed path-integral molecular dynamics and variational nuclear-motion computations,\(^5\) based on a new, highly accurate, network potential-energy surface.\(^4\) We tested the new potential on the HHe\(^+\) cation. The computed rovibrational transitions have excellent agreement with experimental data, showing the high quality of the potential.\(^5\) As we determined the vibrational states below and above the dissociation limit, corresponding to the solvating He and the chromophore, respectively. The computed chromophore vibrational frequencies have good agreement with the experimental results. Note that, the frequencies of the chromophore vibrations are significantly shifted compared to that of the HHe\(^+\) because the intermolecular bond is relatively strong. In order to investigate the “quantum” structure, we computed and plotted the nuclear density, which plots reveal that the true shape of the complex is completely different from the equilibrium structure: the solvating He is fully delocalized, forming a torus around the central proton even in the vibrational ground state. Delocalization is observed for each state, and its exact pattern reflects the type of vibrational excitation.

\(^4\) Central address: Virgil Humblet Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge, CB2 1EW, UK.


For planar aromatic hydrocarbons, intersystem crossing to the triplet state is expected to be very slow according to El Sayed’s rule.\(^8\) The fluorescence lifetime in the S\(^1\) state of dibenzothiophene is remarkably shorter compared with the analogous molecules such as dibenzofuran. Pratt et al. suggested that the main fast process was intersystem crossing on the basis of the result of high-resolution laser spectroscopy.\(^9\) We observed the high-resolution spectrum in the external magnetic field in order to confirm the contribution of the triplet state. However, no change has been found in the spectrum up to 1.0 Tesla, indicating that the intersystem crossing is slow and is not the main process for the fluorescence decay in the S\(^1\) state of dibenzothiophene. It should be noted that the spectral feature of the S\(^1\) → S\(^0\) band of dibenzothiophene is \(\lambda\)-type, whereas that of dibenzofuran is \(\iota\)-type. The relatively faster decay is considered to be the result of different character in the S\(^1\) electronic state. Several electronic excited states are expected to be located in the lower energy region.\(^7\) Ab initio theoretical calculations of BLYP/6-311+G(d,p) accurately reproduced the experimental values of rotational constants and excitation energy. The S\(^1\) state has been assigned to \(\Lambda\)-type, which is consistent with the fact that the S\(^1\) → S\(^0\) transition is \(\lambda\)-type.


HIGH-RESOLUTION LASER SPECTROSCOPY AND THE ZEEMAN EFFECT: DIBENZOTHIOPHENE

NAOFUMI NAKAYAMA, Computational Chemistry, Conflex Corporation, Tokyo, Japan; MASAAKI BABA, Molecular Photons Research Center Keio University, Koh, Japan.

Post-Deduction Absorption Spectrum

MID-INFRARED DOPPLER-FREE SATURATION ABSORPTION SPECTROSCOPY OF METHANE FOR FUTURE CAVITY-ENHANCED DOUBLE-RESONANCE SPECTROSCOPY INVESTIGATING ITS HIGH POLYADYS.

S. M. SHAHRIYARI, Department of Physics and Astronomy, University Of Louisville, Louisville, KY, USA; RAMZEH TELFAH, MD TOCHDUL ISLAM, JINJIN LUI, Department of Chemistry, University of Louisville, Louisville, KY, USA.

Understanding the rotational structure of molecular spectra requires high resolution and high-frequency accuracy. Furthermore, a capability of high-speed, wide-range spectral scan is strongly desired. We have developed a mid-infrared Doppler-free saturation absorption spectroscopy apparatus using a continuous-wave optical parametric oscillator (CW-OPO).\(^8\) Here we report a comprehensive spectral scan of the \(\nu_3\) = 1 band of methane (CH\(_4\)). The absolute frequency calibration was achieved using previously reported transition frequencies determined using optical frequency combs,\(^7\) while a home-build Fabry-Perot etalon was used for relative frequency calibration. A linewidth of less than 5 MHz has been reached, and the frequency accuracy is estimated to be better than 1 MHz, both of which can be further improved. We have successfully locked the frequency of the OPO to a Doppler-free line of CH\(_4\) using a top-of-fringe locking method. A cavity-enhanced double-resonance spectroscopy apparatus is under construction. It combines the Doppler-free saturation absorption setup and an existing continuous-wave cavity ring-down (CW-CRDS) spectroscopy apparatus. The first mid-infrared photon from the frequency-locked OPO pumps the CH\(_4\) molecule to the \(\nu_3\) = 1 vibrational levels, followed by a further excitation to high polyadys using a Ti:Saphire ring laser.

Chair: Terry A. Miller, The Ohio State University, Columbus, OH, USA

Thursday, June 23, 2022 – 1:45 PM
Room: 124 Burrill Hall

Chair: Terry A. Miller, The Ohio State University, Columbus, OH, USA

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RM. Fundamental physics

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Chair: Terry A. Miller, The Ohio State University, Columbus, OH, USA

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RM01 1:45–2:00

ROTATIONAL CLOSURE IN LASER-COOLING NONLINEAR MOLECULES


Toward a global eight-state fit of the rotational and vibrational spectra of HN3
R. Claude Woods, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; Bhrent R. Amberger, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; E. Billinghurst, EFD, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada; Brian J. Eisenman, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; Patrik Kania, Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Czech Republic; Zbyněk Kiselí, CN2, Institute of Physics, Polish Academy of Sciences, Warsaw, 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 Vavra, Institute of Physics, University of Kassel, Kassel, Germany; Samuel A. Wood, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA.

Our longstanding goal has been achieving a global fit of the ground state and seven lowest excited states of HN3 (ν5, ν3, ν2, ν1, ν5+ν2+ν3, 2ν3, and ν1+ν3+ν5) of all of which are strongly connected by Coriolis, anharmonic, and Darling-Dennison resonance perturbations. From the combined effort of the Wisconsin and Prague groups, we observed and assigned most of the millimeter-wave spectrum from low-frequency microwave lines up to 720 GHz. Recently, we have acquired an extensive set of infrared (IR) spectral data at the Canadian Light Source (CLS), 30-5000 cm⁻¹ at 0.0009 cm⁻¹ resolution and pressures between 1 and 100 mTorr. This data supersedes all previous IR data, in that it provides higher sensitivity (providing transitions with higher J and K) and higher frequency accuracy for all the ground and fundamental states. More importantly, it has permitted assignment of thousands of lines in about 30 subbands involving the combination and overtone states. Using linear least-squares treatment of individual subbands (Fortrat or Q branch plots), we have so far determined absolute energies of Kc = 0.7 of 2ν3, Kc = 2.6 of ν5+ν2+ν3, and Kc = 0.6 of 2ν5, using redundant measurements from multiple subbands confirmed by combination differences with known a-type lines in the mm-wave spectrum. Several additional mm-wave series were assigned using improved predictions from the BR spectra, and several others have been reassigned. We present our current spectral analysis and progress on the implementation of an eight-state global fit.
PUSHING MULTIPHOTON RESONANT IONIZATION OF ARGON TO LOW-INTENSITY REGIME

XUAN YU, Atomic Physics Center, Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou, CHINA; NA WANG, College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou, China; JIANTING LEI, School of Nuclear Science and Technology, Lanzhou University, Lanzhou, CHINA; KENNACEUR NASABRI, SHAOFENG ZHANG, Atomic and molecular physics, Institute of Modern Physics, Lanzhou, CHINA; XINWEI MA, Atomic Physics Center, Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou, CHINA.

Resonance-enhanced multiphoton ionization process of argon atom by 800 nm, 30 fs linearly polarized laser filed is investigated at an intensity range from 1.1 to $1.5\times10^{13}$ W/cm$^2$. At $4.5\times10^{12}$ W/cm$^2$ intensity the experimental photoelectron energy spectrum is in a good agreement with the time-dependent Schrödinger equation (TDSE) calculation where the double structure originating from dressed 4p-4d coupled transition are clearly identified. From the spectrum, it is shown that the pulse duration can obviously influence the resonant ionization yield. At lower intensity of $1.1\times10^{12}$ W/cm$^2$, the resonant ionization process via 4f state is observed, however, by comparing our results with those given in other papers, the significant differences in the PADs suggest that in the corresponding regime the orbital angular momentum of the intermediate state cannot simply be assigned to the number of jets in the PAD.

Intermission

PRECISION MEASUREMENT WITH CAVITY-ENHANCED BUFFER-GAS COOLED 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.

We report for the first time highly precise differential microwave spectroscopy, carried out in a cavity-buffer gas cell. We report a statistically limited differential measurement of 0.08 ± 0.72 Hz between (R)- and (S)-1,2-propanediol at frequencies around 15 GHz.6 This highly repeatable measurement opens new avenues in studying molecular structure at the 10$^{-12}$ level. We also report the coupling of a neon buffer gas beam to this cavity, reaching linewidths of 3 kHz in methyltrioxorhenium, and future modifications to reach 1.5 Hz linewidth.

4kHz linewidth at the pulse duration can obviously influence the resonant ionization yield. At lower intensity of $1.1\times10^{12}$ W/cm$^2$, the resonant ionization process via 4f state is observed, however, by comparing our results with those given in other papers, the significant differences in the PADs suggest that in the corresponding regime the orbital angular momentum of the intermediate state cannot simply be assigned to the number of jets in the PAD.

Molecular ringdown times place a fundamental upper limit on the precision of measurements in microwave spectroscopy. A Fabry-Pérot cavity has been designed and implemented in an existing buffer-gas cell to enhance molecular ringdown signals, allowing for measurements of greatly enhanced precision. This includes a differential measurement of 1.2 -Photopumped sub-Hz precision. Design elements include: a coupler designed to transmit light out of the cavity proportionally to the intensity of Gaussian-Hermite modes; optimization of Q-Factor related to diffusive, reflected, and coupling losses; and a tuning mechanism that allows for full and precise adjustment of resonant frequency in its cryogenic environment. Additionally, work will be presented in ongoing research that implements a columnated molecular beam in a newly-designed cavitewith greatly increased mode waist sizes for measurements of groundbreaking precision in a low collision environment.
A COMBINED mm-WAVE AND FAR-INFRARED STUDY OF PYRAZOLE
DENNIS W. TOKARYK, Department of Physics, University of New Brunswick, Fredericton, NB, Canada; BRIAN J. ESSELMAN, R. CLAUDE WOODS, ROBERT J. MAHON, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; JEFF CROUSE, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada; DOYEN KIM, Department of Physics, University of New Brunswick, Fredericton, NB, Canada.

Pyrazole (C\textsubscript{4}H\textsubscript{4}N\textsubscript{2}, C\textsubscript{4}N\textsubscript{2}) is an aromatic heterocycle consisting of a 5-membered ring molecule doubly substituted with adjacent nitrogen atoms. Search for similar heterocyclic compounds (imidazole, furan, etc.) have been recently conducted in the interstellar medium. This study provides the necessary transition frequencies for a search for pyrazole across the frequency range of available radio-telescopes. We have collected the mm-wave spectrum of pyrazole from 130-750 MHz, which extends the previously published microwave studies from 13 to 35 MHz. The new data greatly expand the range of rotational quantum numbers observed in the ground vibrational state rotational transitions and provide transitions for over a dozen excited vibrational states. These rotational data are simultaneously analyzed with high-resolution rotation-vibration spectra of pyrazole between 500-1300 cm\textsuperscript{-1} that we have obtained at the Canadian Light Source synchrontron’s far-infrared beam line. The considerable benefits of simultaneously analyzing mm-wave and high-resolution IR transitions that cover the same approximate ranges of J and K will be discussed. The results provide a thorough characterization of all eight vibrationally excited states below 950 cm\textsuperscript{-1}, of which the highest energy states (\textit{J}=9, \textit{K}=8) form a Coriolis-coupled triad.

We have recently observed the infrared spectrum of DN\textsubscript{3} at a resolution of 0.0009 cm\textsuperscript{-1} using the synchrotron at the Canadian Light Source between 30 and 5000 cm\textsuperscript{-1} at several pressures between 1 and 100 mTorr. A special heavy walled stainless steel apparatus was constructed to perform the synthesis of the highly toxic and explosive substance on site in the rigorous safety standards of the facility. We have also measured the millimeter wave spectrum of DN\textsubscript{3} at Wisconsin and at Prague covering altogether the range from 130-750 GHz. We are working toward combining all this spectral data to achieve a global eight state fit with SPFIT. While the many perturbing interactions between these lowest eight vibrational states cause somewhat less dramatic shifts than the same ones do in HN\textsubscript{3}, it remains a very challenging problem in spectroscopy. A substantial additional complication in this isotopologue though is the fact that it has proved to be impractical to obtain an isotopically pure sample of DN\textsubscript{3} because of facile H/D exchange on the walls of the absorption cells employed. This makes it desirable at least to assign the DN\textsubscript{3} spectrum first, so that the corresponding features can be eliminated from consideration in the DN\textsubscript{3} work.
REFERENCE DATA FOR AMMONIA SPECTRA IN THE 3900–6300 CM\(^{-1}\) RANGE

PETER ČERMÁK, Department of Experimental Physics, Comenius University, Bratislava, Slovakia, PATRICE CACCIANI, JEAN COUILLON, UMR CNRS 8253 - Université de Lille I, Laboratoire PHILAM, F-59005 LILLE, FRANCE, ALAIN CAMPAGNIE, SERGE BÉGUÉRIER, UMR5588 LIP, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France; JEAN VANDER AUWERA, SQUAIRES, Université Libre de Bruxelles, Brussels, Belgium, ONDREJ VITAVA, JOZEF KAROBOVSKY, Heyrovsky Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic.

Accurate reference laboratory data represents a key element for understanding any remote observations in particular astrophysical surveys. The subject has grown in importance with the recent discovery of the capability to observe spectra of exoplanets or the ability to closely probe space objects like in the case of the Rosetta mission. This need is even timelier with the James Webb telescope being deployed for operation and the new space missions dedicated to the exoplanetary spectroscopic studies like Twinkle, and the Atmospheric Remote-sensing Infrared Exoplanet Large-Survey (ARIEL) destined to be launched in 2024 and 2029, respectively.

The current contribution is an overview of our work concerning the acquisition of such accurate reference data in the case of ammonia molecule based on the combination of room temperature Fourier transform spectra (both old and new), tunable laser spectroscopy in cooled Herriott cell, and in a supersonic expansion. In addition, multiple new techniques to improve the whole process of spectra analysis were used, mainly: the enhanced multi-temperature treatment for determination of laser spectroscopy in cooled Herriott cell, and in a supersonic expansion. In addition, multiple new techniques to improve the accuracy of the referenced frequency calibration to verify the absolute line positions with a sub 0.001 cm\(^{-1}\) accuracy.

FORBIDDEN ROTATIONAL TRANSITIONS AND ASTROPHYSICS

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

When I read Townes and Schawlow’s textbook as a beginning student, I was puzzled by the symmetric top selection rule \(\Delta K = 0\), because this rule corresponds to cylindrical symmetry \(C\_2\_v\), applying it to \(\text{NH}_3\) with \(C\_3\) symmetry cannot be right. At that time, however, I did not pursue how this wrong rule affect the actual spectrum. 10 years later interstellar \(\text{NH}_3\) was discovered by ‘Townes’ group. When I read the discoverers’ claim that lifetimes of \((J, K) = (2,2)\) and \((3,3)\) metastable levels are ‘longer than the lifetime of the Universe’, it was obvious that this wrong statement resulted from the wrong \(\Delta K = 0\) selection rule. Accurate theory gave the life times of the \((2,2)\) and \((3,3)\) metastable levels to be 230 years and 44 years, respectively, 10\(^\text{th}\) times shorter than the lifetime of the Universe. The theory also predicted \(\Delta J = \pm 1\) pure rotational transitions which were observed for \(\text{PH}_3\), \(\text{PD}_3\), and \(\text{AH}_3\).

In this paper I calculate spontaneous emission via forbidden transitions for astrophysically important symmetric tops, oblate tops \(\text{NH}_3\), \(\text{H}_2\text{O}\), \(\text{H}_2\), and prolate tops \(\text{CH}_3\text{CN}\). These calculations are preparations for future analyses of their thermalization.

EXPERIMENTAL INSIGHTS INTO THE FORMATION OF INTERSTELLAR FULLERENES AND CARBON NANOTUBES

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The detection of the fullerenes \(C_{60}\) and \(C_{70}\) in the interstellar medium (ISM) has transformed our understanding of chemical complexity in space, and have also raised the possibility for the presence of even larger molecules in astrophysical environments. Here we report in situ heating of analog silicon carbide (SiC) presolar grains using transmission electron microscopy (TEM). These heating experiments are designed to simulate shocks occurring in post-AGB stellar envelopes. Our experimental findings reveal that heating the analog SiC grains yields hemispherical \(C_{60}\)-sized nanostuctures, which later transform into multi-walled carbon nanotubes (MWCNTs). These MWCNTs are larger than any of the currently observed interstellar fullerene species, both in overall size and number of C atoms. These experimental results suggest that such MWCNTs are likely to form in post-AGB shocks, where the structures, along with the smaller fullerenes, are subsequently injected into the ISM.

PREBIOTIC MOLECULES IN INTERSTELLAR SPACE: THE ROLE OF ROTATIONAL SPECTROSCOPY AND QUANTUM-CHEMICAL CALCULATIONS

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While it is now well established that the interstellar medium (ISM) is characterized by a rich and complex chemistry, we are far from a complete census of the interstellar molecules and the understanding about how they form and evolve is at a primitive stage. Concerning the former issue, a significant number of features in radioastronomical spectra are still unassigned. To fill this gap, a huge laboratory effort is required, which is increasingly based on integrated experimental and computational strategies. This contribution aims to present examples of an integrated rotational spectroscopy - quantum chemistry approach for supporting radioastronomical observations. In this respect, a significant example is provided by the recent characterization of \((Z=1,2)\) ethenediol, a key prebiotic intermediate in the formose reaction*.
MULTI-WAVELENGTH INVESTIGATION ON NEW MOLECULAR MASERS TOWARD THE GALACTIC CENTER

CIXUE, ANNA-MAREE SYME, LAURA K McKEMMISH, School of Chemistry, University of New South Wales, Sydney, NSW, Australia

At the centimeter wavelength, the single-dish observation has suggested that the Sgr B2 molecular cloud at the Galactic center hosts weak maser emission from complex molecules, including CH$_2$NH, HNCNH, and HCOOCH$_3$ (McGure et al., 2012; Fauré et al., 2014, 2016). Because molecular masers often trace specific conditions within the massive star-forming regions, finding new maser transitions and species provides critical insights into the physical structures hidden behind the thick dust. However, the lack of distribution information of these new maser species had prevented us from not only quantitatively assessing the observed spectral profiles but also constraining their pumping mechanisms. In this talk, we present a rigorous mapping study toward the galactic center to resolve the region where the complex maser emission originates. By comparing the distribution of several maser emissions, it is revealed that the new maser species have a close spatial relationship with the CH$_3$OH Class I masers. This relationship serves as observational evidence to suggest a similar collisional pumping mechanism for these maser transitions.

THE OPTICAL SPECTRUM OF THE DIAMANTANE RADICAL CATION

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Atmospheric molecular spectroscopy is an important method of searching for new physics through probing the variation of the proton-to-electron mass ratio, $\mu$, with existing constraints limiting variation to a fractional change of less than 10$^{-17}$/year. To improve on this constraint and therefore provide better guidance to theories of new physics, new molecular probes will be useful. These molecular probes must have spectral transitions that are observable astrophysically and have different sensitivities to variation in the proton-to-electron mass ratio. This talk will focus on the development of a high-throughput methodology to calculate the sensitivities of transitions in diatomic and polyatomic molecules with established spectroscopic models. The calculations required are straightforward; reproducing the line list with a slight increase in nuclear masses and comparing the original and mass-shifted energies and transition frequencies. The major challenge was in matching the quantum states in the original and mass-shifted data as the quantum number descriptions were not always preserved when the state was heavily mixed — unfortunately precisely those states likely to have high sensitivities to $\mu$ variation. These challenges were far more severe in polyatomics than diatomics.

Our results found that even a conservative intensity cut-off of 10$^{-16}$ cm/molecule at 100 K (astrophysically relevant interstellar conditions) removed almost all transitions with high sensitivity to $\mu$ variation. There were no new clear transitions of interest were identified in the 22 diatomic and 5 polyatomic molecules investigated, with the low-frequency diatomic parity changing and polyatomic inversion transitions having the strongest sensitivities. In the diatomics we investigated, high sensitivity was observed in low-frequency rovibrionic transitions arising from accidental near-degeneracy between electronic states were observed, but these have very low intensity (as the states involved were high in energy) and thus not likely to be observable astrophysically. This insight allows screening of diatomics without spectroscopic models for sensitivity to $\mu$ variation; we conclude that no diatomic known extragalactically is likely to have transitions with high sensitivity to $\mu$ variation.

CS ABSORPTION AT 140 NM IN SPECTRA ACQUIRED WITH THE HUBBLE SPACE TELESCOPE

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We reexamine the abundance of CS in diffuse molecular clouds from lines in the C−X (0, 0) band by including additional sight lines not available in previous work and by extracting information on molecular structure. The analysis incorporates results from our recent large-scale calculations on CS photodissociation and adopts the approach taken in our study of the F−X (0, 0) and (1, 0) bands in C$_2$. Syntheses of the high-resolution spectra with the best signal to noise yielded wavelengths for the R(0), R(1), and P(1) lines and their widths. Significant line broadening is seen, yielding a predissociation width of 7.5 km/s, which this value is within a factor of 2 of the predictions from the calculations. The computations also revealed similar rotational constants for the C and X states. The differences in transition frequencies among the three lines then suggest that the P(1) line is shifted by 2.7 cm$^{-1}$. We also found evidence that the strengths for the R(1) and P(1) lines were affected by the perturbation. The fits to the data for the other directions in the sample adopted these refined line parameters to determine column densities. A comparison of the CS column densities with results for CH, CN, CO, and H$_2$ helped inform us of the chemical pathways leading to CS in diffuse molecular gas.
Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous in space and most astronomical spectra, from the interstellar medium (ISM) to distant galaxies, including regions of massive star formation, the general ISM, and star forming spiral galaxies out to red-shifts of z ≈ 4. They are dominated by their ubiquitous infrared emission features. Whether the PAH bands are intimately associated with the object, or foreground/background confounding features, they will have to be understood, separated from other features in the spectra, and analyzed for the information they contain on the physical and chemical properties of their surrounding environments. High-resolution laboratory spectra of PAHs measured in an astrophysically-relevant environment are critical to answer these questions. The most challenging task is to reproduce, as closely as technically possible, the physical and chemical conditions that are present in space (i.e., cold gas phase molecules and ions, isolated in a collision-free environment). Comparable conditions can be achieved using the cosmic simulation chamber (COSmIC) developed at NASA Ames. COSmIC allows to measure gas phase spectra of neutral and ionized interstellar PAH analogs by associating a free supersonic jet with a soft ionizing discharge that generates a cold plasma expansion (100 K). Using the Cavity Ring Down Spectroscopy (CRDS) technique, rovibronic absorption spectra of PAHs and PAH derivatives seeded in Ar supersonic jet expansions are measured in the NUV-Vis-NIR region. The resulting spectra provide a critical tool to characterize specific molecules and ions in astrophysical environments. We intend to expand the capabilities of our current CRDS system to the NIR and MIR up to 3.5 μm in order to provide accurate high-resolution laboratory spectra that will help validate the extensive NASA Ames’ PAH database and will greatly benefit the interpretation of future James Webb Space Telescope NIRSpec observational data.

SALMA BEJAOUI, FARID SALAMA, Space Science and Astrobiology Division, NASA Ames Research Center, Moffett Field, CA, USA
BRANCHING RATIO MEASUREMENTS FOR THE O( 3P) + PROPENE REACTION USING CHIRPED PULSE MICRO-MICROWAVE SPECTROSCOPY AT LOW TEMPERATURE

MYRIAM DRESS
CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, Univ Rennes, Rennes, France;
ALBERTO MACARIO, OMAAR ABDELKADER KHEDAOUI, BRIAN M HAYS, DIVITA GUPTA, THEO OUILLAUME, ILSA ROSE COOKE, IAN R. SIMS, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, Univ Rennes, F-35000 Rennes, France.

Atomic oxygen can be found in many places in space from interstellar molecular clouds, to planetary systems such as ours. This atom represents an important building block as it is part of many chemical groups and therefore acts as a vector of a rich chemistry in the interstellar medium. Propene (C\textsubscript{3}H\textsubscript{5}) has been detected in molecular clouds and in Titan’s atmosphere. The rate constant of the chemical reaction between these two species has been shown to have a negative temperature dependence at low temperatures, but questions remain on the product branching ratios at low temperature. In this work, we coupled the CRESU (French acronym for Cible En Rotation d’Ecoulement Supersonique Uniforme) technique for reactant state selection to chirped pulse microwave spectroscopy to detect reaction products, in an adaptation of the CPUF (Chirped Pulse in Uniform supersonic Flow) technique. The nature of the reaction products detected at low temperatures will be presented along with their branching ratios. The limitation and impact of vibrational relaxation will be discussed in relation to these values along with future directions of this project.

CONFORMER SELECTED DIMER FORMATION IN A CRYOCENIC BUFFER GAS CELL

LINCOLN SATTERThWAITE, GRETA KOUmARIANou, Chemistry and Biochemistry, UCSB, Santa Barbara, CA, USA;
DAVID PATTERSON, Physics, University of California, Santa Barbara, CA, USA.

Non-covalently bound clusters have long been a target of study in microwave spectroscopy, however, the typical method of forming these small clusters precludes observation of that formation. Here, we present observation of the conformer-selected formation of ethanol-2methanol dimers in a cryogenic buffer gas cell via microwave spectroscopy. Use of a buffer gas cell allows for observation of a complete time-domain picture of the reaction of two monomers to form a dimer, as the dimers are formed in the interaction region of the experiment as opposed to just after a pulsed valve. Relaxation cross sections and collisional cross sections are also presented for ethanol.

ROTATIONAL SPECTROSCOPY OF CHEMICAL REACTIONS IN A CRYOCENIC BUFFER GAS CELL

BRANDON CARRILL, BRYAN CHANGALA, MICHAEL C McCARTHY, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA.

Low temperature reactions play a critical role in the chemistry of the interstellar medium (ISM). Measuring the kinetics of these reactions is key to constraining models of ISM chemistry, and to understanding ISM chemistry at large. However, measuring chemical kinetics at temperatures relevant to the ISM presents numerous experimental challenges, including creating homogeneous and cooled reactants. Buffer gas cooling offers a near universal method of achieving uniform, electronic, vibrational, rotational, and translational cooling, while consuming minimal sample. When combined with microwave spectroscopy, buffer gas cooling offers a unique method for probing reactions occurring at very low temperatures. We will report our progress in building and characterizing a buffer gas cell configuration capable of measuring biomolecular reactions of thermalized species occurring within the cell, and discuss its applications for studying ISM chemistry.

Intermission

UV PHOTOFRAGMENT SPECTROSCOPY AND ELECTRONIC ENERGY TRANSFER ON A PEPTIDE SCAFFOLD: THE CASE OF NEAR-DEGENERATE UV CHROMOPHORES

CASEY DANIEL FOLEY, Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA;
ETIENNE CHOLLET, MATTHEW A. KUBASK, Department of Chemistry and Biochemistry, Fairfield University, Fairfield, CT, USA;
TIMOTHY S. ZWER, Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA.

Some of the most important molecular architectures in nature, such as light harvesting antennae, feature the presence of several nearly identical electronic chromophores in close proximity, in which directed electronic energy transfer plays a key part in the initial events following absorption of a visible photon. This is an area in which spectroscopy and dynamics are intractably linked, and for which gas phase spectroscopy can play a role in testing model systems in a way not possible in their natural environments. We have studied the UV photofragment spectroscopy of a series of cyo-covalently bonded in the gas phase that are close analogues of protonated Leu-tryptophan, the porphopptide Tyr-Gly-Gly-Phe-Leu-OH (in short-hand notation, YGGFL-OH). This protonated ion has been studied previously, and folds into a single peptide backbone conformation that incorporates a beta-turn. We replace the Tyr and Phe UV chromophores with other chromophores chosen to bring their electronic absorptions into near degeneracy. UV photofragmentation reports on the location of the electronic excitation via a unique fragmentation pathway involving loss of the resonance-stabilized aromatic, CH2-Phe-X. We identify the chromophore responsible for the UV absorption and map out the efficiency of electronic energy transfer as a function of vibronic state via the fragmation behavior, a fragmentation based version of fluorescence resonance energy transfer (FRET).

STRUCTURE AND DYNAMICS OF THE WEAKLY BOUND TRIMER (H\textsubscript{2}S\textsubscript{2})(O\textsubscript{2}) OBSERVED USING ROTATIONAL SPECTROSCOPY

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KAYLA GODDALLA, Photon Science - Spectroscopy of Molecular Processes, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany;
NICK WALKER, School of Natural and Environmental Sciences, Newcastle University, Newcastle-upon-Tyne, UK;
ELANGAN ANNARAN, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India.

The weakly bound complex between two hydrogen sulfide molecules and one water molecule, (H\textsubscript{2}S\textsubscript{2})(O\textsubscript{2}), was identified from its rotational spectrum observed at conditions of superionic expansion. The spectra of parent species were obtained using a chirped-pulse Fourier transform microwave spectrometer (Newark, UK). The isotopeologues were identified with Balle-Blythe Fourier transform microwave spectrometer (Bangalore, India). Distinct physical properties of H\textsubscript{2}O and H\textsubscript{2}S under ambient settings have long been recognized as a result of their significantly different hydrogen-bonding capabilities. It has conclusively shown (H\textsubscript{2}S\textsubscript{2})(O\textsubscript{2}) is hydrogen-bonded similar to (H\textsubscript{2}O\textsubscript{2})(O\textsubscript{2}) at very low temperature\textsuperscript{a} the break with axial molecular symmetry and the simplified internal dynamics allowed us to investigate (H\textsubscript{2}S\textsubscript{2})(O\textsubscript{2}) at a level of structural detail that has not yet been possible for (H\textsubscript{2}O\textsubscript{2})(O\textsubscript{2}) and (H\textsubscript{2}S\textsubscript{2})\textsubscript{2} with rotational spectroscopy due to their zero-dipole moment. The rotational spectrum of (H\textsubscript{2}S\textsubscript{2})(O\textsubscript{2}) shows a doubling of the lines, close to 1:3 relative intensity for the parent species, caused by the internal rotation of the H\textsubscript{2}O moiety about its C\textsubscript{2h} axis. Analysis of experimental results reveals that the three monomers are arranged in a triangular arrangement in the S-H ·· O-H ·· S-H of hydrogen bonds. The r\textsubscript{SH} and r\textsubscript{SH} structural parameters have been evaluated, and the three heavy atom distances (r\textsubscript{SH} = 3.451(11) Å and r\textsubscript{SH} = 3.451(11) Å) are appreciably shorter than the respective distances in (H\textsubscript{2}S\textsubscript{2}), H\textsubscript{2}O - H\textsubscript{2}O and H\textsubscript{2}O - H\textsubscript{2}O. The geometry contains numerous characteristics that indicate the cooperative nature of the intermolecular interaction. The experimental results for all observables determinable from the rotational spectrum are found to be in excellent agreement with ab initio predictions.

EVIDENCE OF NITROGEN AS ACCEPTOR IN NITROMETHANE-FORMALDEHYDE HETERODIMERS CHARACTERIZED USING MATRIX ISOLATION INFRARED SPECTROSCOPY AND COMPUTATIONAL METHODS

NANDALAL MAHAPATRA, S CHANDRA, NAGARAJAN RANAMATHAN, K SUNDARARAJAN, Materials Chemistry and Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Homi Bhabha National Institute, Kalpakkam, Tamil Nadu, India.

Formaldehyde (FA) is a fascinating molecule for astrochemists due to the complex mechanistic pathways leading to its formation. Being a very important prebiotic precursor, understanding its participation in various weak interactions is crucial. FA is well established to form hydrogen bonds. In the present work, the interaction of FA with Nitromethane (NM) was studied at low temperature and supported by ab initio theoretical calculations. The heterodimers of NM and FA, NM-FA, were generated within Ar and N₂ matrices and characterized using infrared spectroscopy. Perturbation in the ν₂ mode of NM and ν₁ mode of FA due to the formation of heterodimers has been investigated, as these infrared spectral signatures were shifted from the monomer absorption of NM and FA. The variation of the intensity of these features, in response to the variation in concentration of FA and NM, additionally supported with computations, affirm the formation NM-FA. The red shifts observed, agree well with the predictions by harmonic frequency calculations on the pnicogen-hydrogen-tetrel bound geometry. Computations indicated three minima on the potential energy surface at MP2/CBS and B3LYP/D3/CBS levels of theory. The most stable heterodimer, observed experimentally, was stabilized by cooperative pnicogen (O...N), hydrogen (O...H) and tetrel (O...C) bonds as confirmed by QTAIM and NBO analyses. Dominance of electrodynamics over other effects in forming the bonds has been established by energy decomposition analysis (EDA). The ability of FA, as a potential electron donor to pnicogen bonding while being a weak tetrel donor too, in addition to its expected participation in hydrogen bonding, stands established experimentally and computationally.

OXYGEN ATOM DIFFUSION BY QUANTUM TUNNELING IN SOLID PARAHYDROGEN: A NEW TOOL TO STUDY LOW TEMPERATURE SOLID-STATE REACTIONS

Ibrahim Mudaqser, David T. Anderson, Department of Chemistry, University of Wyoming, Laramie, WY, USA.

In quantum crystals such as solid parahydrogen (pH₂), there is considerable overlap between the wavefunctions of molecules in neighboring lattice sites, such that added chemical impurities can exchange positions with nearest-neighbor PH₂ molecules and thereby quantum diffuse through the solid. Our group and others have taken advantage of the quantum diffusion of hydrogen atoms in solid pH₂ to study various low temperature hydrogenation reactions. In this talk, we report the first experimental evidence of atomic oxygen diffusion in solid pH₂. O₂ doped pH₂ samples are irradiated at 193 nm to produce O(3P) atoms, and repeated FTIR spectra are collected to map out the temporal behavior during and after photolysis. The experimental proof of mobile O-atoms is provided by the formation of ozone (O₃), which forms via the barrierless O + O₂ → M + O₂ + M reaction. After photolysis, while the system is kept in the dark, continued growth in the O₃ concentration with time is detected, indicating that O-atoms are mobile and reacting with O₂ present in the solid. The O₂ growth after photolysis is fit to first-order kinetics equations to extract the rate constant. Kinetics measurements show that the O-atom reaction rate more than doubles in annealed crystals compared to as-deposited crystals. This finding is consistent with the expectations that quantum diffusion is more facile in homogeneous samples with minimum defects. In fact, some proportion of the photo-produced O-atoms get trapped in as-deposited samples and can only be made mobile by annealing the sample. Currently, we are studying the effects of the photolysis conditions, temperature, and doped O₂ concentration on the reaction rate constant. This study shows that O-atoms can be isolated in solid pH₂ and that they are delocalized. Through double doping experiments, we hope to develop this method to study O-atom reactions with other species under controlled low temperature conditions.
INVITED TALK 8:30 – 9:00

ROTATIONAL SPECTROSCOPIC BENCHMARK FOR τ INTERACTION

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A great deal of attention has been given to noncovalent interactions involving τ systems because of their widespread presence in biology as well as materials, where they are pivotal in determining the three-dimensional structures of, e.g., proteins and polymers or the selectivity of molecular affinity. Despite dramatic advances in our understanding over past decades, many aspects of τ interactions have only recently been recognized. Many remaining questions about rotational spectroscopy is arguably the most accurate high resolution molecular spectroscopic technique due to its high sensitivity to mass distributions of molecules and molecular complexes. Since the interaction sites and the relative arrangement of moieties can be determined without environmental bias, rotational spectroscopy allows describing the intermolecular forces at play and enables testing of quantum chemical methods. In this talk, with the recent rotational spectroscopic results we have obtained on τ interactions, the comparisons between experimental and computational data will be discussed.

FIRST OBSERVATIONS OF THE HONO - H2O COMPLEX WITH MICROWAVE SPECTROSCOPY

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The impact of gaseous nitrous acid (HONO) in atmospheric chemistry is well described, being a major source of OH radicals acting as a strong oxidant1. In standard conditions, HONO is in equilibrium with various nitrous oxides under rapid decomposition at daytime. However, results by Lammet and Cape describe a steady production of OH radicals by HONO in the atmosphere whose source might be the complex of HONO with water2. Recent experiments have revealed that HONO remains stable in an aqueous environment as the HONO·H2O complex, supporting its greater stability in environments with higher humidity3. In the present work, gaseous HONO - H2O was generated in a laboratory scale and investigated with two molecular jet Fourier transform microwave spectrometers operating from 2 to 40 GHz. To guide the experimental observation, geometry optimizations were performed to obtain rotational constants using the standard coupled-cluster theory with single and double excitations. The HONO - H2O spectrum has been assigned with the 2NJ quadrupole coupling taken into account. Further splittings by the ortho-hydrogens, resulting from spin-spin coupling interactions, could be fully resolved. Comparing the results to those of the dimethylamine-water complex4 confirmed an absence of the water tunneling motion.


MULTIDIMENSIONAL TUNNELING IN 2-NITROTOLUENE∗

ANTHONY BOUCOU, ARNAUD CUSSIEZ, Laboratoire de Physico-Chimie de l’Atmosphère, Université du Littoral Côte d’Opale, Dunkerque, France; MANUEL GOURBET, Laboratoire PILAM, UMR 8225 CNRS - Université Lille 1, Villeneuve d’Ascq, France; L. H. COUPERT, Institut des Sciences Moléculaires d’Orsay, Université Paris-Saclay, CNRS, Orsay, France.

Although many non-rigid molecules displaying a single LAM have been spectroscopically characterized, less results are available about non-rigid molecules displaying several LAMs, as they are theoretically more challenging. This is confirmed by a recent spectroscopic investigation of nitrotoluene5 which revealed that 2-nitrotoluene isospecific species displays two LAMs corresponding to internal rotations of the CH3 and NO2 groups. In this investigation, because no approach accounting for two LAMs was available, the microwave spectrum of 2-nitrotoluene was analyzed using a simplified approach accounting only for the torsional motion of the CH3 group. In this talk, the IAM water dimer formalism6 will be applied to 2-nitrotoluene. As this theoretical approach is designed for multidimensional tunneling in the high-barrier limit, it is well suited for this species. Once the equilibrium configurations and the tunneling paths are chosen, the IAM approach7 allows us to derive a fitting Hamiltonian accounting for the rotational dependence of the tunneling splittings, but not for their magnitude, which should be obtained fitting the spectroscopic data. In 2-nitrotoluene, there are six C2 symmetry equilibrium configurations and two tunneling paths. The first and most feasible one corresponds to a 2π/3 rotation of the methyl group. The second one is the complicated geared internal rotation of both the CH3 and NO2 groups identified using quantum chemistry calculations8.

The results of the line position analysis of the available microwave data9 with the new IAM approach will be presented. It is hoped that the analysis results will be more satisfactory than with the simplified approach and this will provide us with a better understanding of the 2-nitrotoluene multidimensional potential energy surface.

∗The work received financial support from the French NSF, Project MEPS under contract number ANR-20-CE01-0015-07

1 Boucou, Gruber, Klemm, Bechel and Cuisset, ChemPhysChem 21 (2020) 1
DOUBLE-PROTON TRANSFER OVER A PHENYL RING REVEALED BY CP-FTMW SPECTROSCOPY

WEIHENG LI, Department of Chemistry, Fudan University, Shanghai, China; DENIS TIKHONOV, MELANIE SCHINELL, FS-SMF Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; WALTHER CAMINATI, Dpto Chimica G. Cianci, Università di Bologna, Bologna, Italy; DINGDING LV, Department of Chemistry, Fudan University, Shanghai, China; GUANYUN WANG, MINGFEI ZHOU, Fudan University, Department of Chemistry, Shanghai, China.

Our previous work demonstrated that the measurement of pure rotational spectroscopy of “non-polar” dimers of formic acid can be achieved by means of asymmetric-H-D substitution. [1] The concerted double proton transfer of the two hydroxyl hydrogen ions takes place between equivalent minima and generates a tunneling splitting of 331.65 MHz. In this talk, we will discuss the double proton transfer over a phenyl ring in the complex of formic acid dimer (FAD) with phenyl compounds. For example, in the FAD-fluorene complex, the presence of fluorene as a neighboring molecule does not quench the double proton transfer in the FAD but decreases its tunneling splitting to 267.608(1) MHz. [2] In the FAD-fluorene benzaldehyde complex, the proton transfer does not occur via tunneling, but produces two non-equivalent isomers.

The experiments were carried out by using the CP-FTMW spectrometer in Hamburg and the new-build one in Shanghai.


Interruption

BRIDGING THE GAP: ROTATIONAL STUDY OF H2 IN COMPLEXES WITH SMALL AROMATIC MOLECULES

ROBIN DÖHLE, Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany; MELANIE SCHINELL, PABLO PINACHO, FS-SMF Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; DANIEL A. ORENBENCH, Institute of Physical Chemistry, Georg-August-Universität Göttingen, Göttingen, Germany.

Molecular hydrogen plays a key role in our efforts to shift our energy production to renewable resources. Hydrogen is an important energy storage molecule which in the future may replace our fossilized fuels as a transportable energy source. To appropriately model hydrogen storage materials, an understanding of the fundamental binding to organic systems is required. In previous works only a few inorganic and metallic complexes with hydrogen have been investigated by rotational spectroscopy. [1] This work aims to bridge the gap to large covalent organic frameworks (COF) by focusing on the microwave structure of hydrogen heterodimers with small aromatic ring systems. [2]

In this work, the binding sites of hydrogen to halogen benzaldehydes which serve as mimics COF monomers, specifically boron based ester COFs, are studied. These volatile systems possess a large dipole moment and provide a method of increasing the complexity of the system by the introduction of quadrupolar nuclei to finally look at small boronic esters in hydrogen complexes. 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 significant differences between these two species demonstrate there are significant differences in binding strength of ortho-H2 and para-H2 which are experimentally observable. Broadband rotational spectra are presented, are supplemented with cavity Fourier transform microwave spectroscopy data to resolve the additional hyperfine splitting of ortho-H2 (j = 1). These experimental results can be directly compared to a number of quantum chemical predictions to provide a foundation for the simulation of large scale covalent organic frameworks.


ACCURATE EXPERIMENTAL VALIDATION OF AB INITIO QUANTUM SCATTERING CALCULATIONS USING THE SPECTRA OF H2-PERTURBED H2

MICHAŁ SŁOWIŃSKI, HUBERT JÓZWIĄK, MACIEJ GRZEGORZ GANCZEWSKI, KAMIL STANKIEWIECZ, NIKODEM STOLARZCYK, PIOTR ZUCHOWSKI, ROMAN CURYLO, PIOTR WUSTL, Institute of Physics, Faculty of Astronomy and Informatics, Nicolaus Copernicus University, Toruń, Poland; YAN TAN, JIN WANG, AN-WEN LU, SHU-MING HU, Hebei National Laboratory for Physical Science at Microscale, University of Science and Technology of China, Hefei, China; SAMIR KASSI, ALAIN CAMPAGNUE, UMR5588 LPAJ, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France; KONRAD PATKOWSKI, Chemistry and Biochemistry, Auburn University, Auburn, AL, USA; FRANK THIBAULT, Institute of Physics, Univ. Rennes, CNRS, Rennes, France.

Due to its simplicity, molecular hydrogen perturbed by helium atom constitutes a great benchmark system for tests of ab initio quantum scattering calculations as a method of precise description of collisional effects in ultra-accurate experimental spectra. Here we present our recent cavity-enhanced measurements of H2 lines perturbed by He. Our results exhibit an unprecedented subpercent agreement with fully quantum ab initio calculations. We investigate collisional line-shape effects that are present in highly accurate experimental spectra of the 3-0 S(1) and 2-0 Q(1) lines. We clearly distinguish the influence of six different collisional effects (i.e. collisional broadening and shift, their speed dependences and the complex Dicke effect) on the shapes of H2 lines. We demonstrate that if any of the six contributions is neglected, then the experiment-theory comparison deteriorates at least several times. We also analyze the influence of the centrifugal distortion on our ab initio calculations and we demonstrate that the inclusion of this effect slightly improves the agreement with the experimental spectra.

In addition, we describe the theoretical calculations that were performed to obtain the subpercent agreement with experiment. In the analysis described here, we employed the state-of-the-art statistical model of the collision-perturbed shape of molecular lines. We obtained all the parameters of this model from quantum scattering calculations, and the dynamical calculations were performed on the most accurate potential energy surface (PES) to date.
In the context of collisional effects in molecular spectra, a comprehensive dataset of line-shape parameters from ab initio calculations for He-perturbed HD is presented. The abundance of molecular hydrogen and atomic helium in the universe makes them an important system to study in various fields. A mixture of molecular hydrogen and helium is the main component of the atmospheres of gas giants in the Solar System and is predicted to be a dominant constituent of the atmospheres of some types of exoplanets. The hydrogen molecule is also the simplest molecule, the structure of which can be calculated from first principles, which makes it well suited for accurate tests of ab initio calculations. In particular, HD molecule, despite its lower abundance than H2, is isotopologue in noticeable in spectroscopic studies due to the presence of its dipole moment. Studies show that in some cases the uncertainty of astronomical observations (e.g., measuring the HD ratio) of hydrogen molecule spectra is dominated by the uncertainties of collisional parameters, including pressure broadening and pressure shift coefficients.

We utilize the methodology of populating line-by-line spectroscopic databases with beyond-Voigt line-shape parameters, which is based on ab initio quantum scattering calculations and was first applied to the He-perturbed HD. We report a comprehensive dataset of beyond-Voigt line-shape parameters (pressure broadening and shift coefficients, their speed-dependences, and the complex Dicke parameters) for all electric dipole and quadrupole transitions within the ground electronic state in He-perturbed HD that are present in HITRAN (11 575 lines) at temperatures spanning from 20 to 1000 K. We parametrize the temperature dependence of the line-shape parameters with double-power-law representation (DPL), recommended for the He-perturbed HD that are present in HITRAN. In addition to the presentation of the calculations, we will discuss our latest experimental determination of collisional line-shape parameters for He-perturbed HD and its comparison with theoretical results.

**Methodology**

1. **Calculation of line-shape parameters**
   - Ab initio quantum scattering calculations were performed for HD molecule, despite its lower abundance than H2, as an isotopologue in noticeable in spectroscopic studies due to the presence of its dipole moment.
   - The methodology involves populating line-by-line spectroscopic databases with beyond-Voigt line-shape parameters, which are based on ab initio calculations.

2. **Data presentation**
   - The comprehensive dataset of beyond-Voigt line-shape parameters, including pressure broadening and pressure shift coefficients, is reported for HD molecule in the ground electronic state.
   - The dataset includes all electric dipole and quadrupole transitions at temperatures ranging from 20 to 1000 K.

3. **Parametrization**
   - The temperature dependence of the line-shape parameters is parametrized using double-power-law representation (DPL), which is recommended for He-perturbed HD.

4. **Experimental determination**
   - Latest experimental determinations of collisional line-shape parameters for He-perturbed HD will be discussed, along with their comparison with theoretical results.

**Conclusion**

The presented calculations and experimental determinations provide a comprehensive dataset for HD molecule, which is essential for accurate interpretation of spectroscopic observations, especially in the context of exoplanet atmospheres and astrophysical studies.
WILDFIRE SMOKE DESTROYS STRATOSPHERIC OZONE

PETER F. BERNATH, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA, USA; CHRISTINE BOIGNE, JEFF CROUSE, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Large wildfires inject smoke and biomass burning products into the midlatitude stratosphere where they destroy ozone, which protects us from ultraviolet radiation. The infrared spectrometer on the Atmospheric Chemistry Experiment (ACE) satellite has measured the spectra of smoke particles from the Black Summer Australian fires in late 2019 nearly 2020, demonstrating that they contain oxygenated organic functional groups and water adsorption on the surfaces. The injected smoke particles produce unexpected and extreme perturbations in stratospheric gases beyond any seen in the previous 15 years of measurements: increases in formaldehyde, chlorine nitrate, chlorine monoxide and hypochlorous acid, and decreases in ozone, nitrogen dioxide and hydrochloric acid. These perturbations in stratospheric chemistry may have the potential to affect ozone chemistry in unexpected ways.

STRATOSPHERIC AEROSOL COMPOSITION OBSERVED BY THE ATMOSPHERIC CHEMISTRY EXPERIMENT FOLLOWING THE 2019 RAIKOKE Eruption

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; KEITH LABELLE, Department of Physics, Old Dominion University, Norfolk, VA, USA; JEFF CROUSE, Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

Following the eruption of the Raikoke volcano in 2019, infrared spectra from the Atmospheric Chemistry Experiment Satellite 
were used to evaluate the composition of stratospheric aerosols in the Northern Hemisphere. The layer of aerosols observed after the eruption ranged from 9 to 20 km in altitude and persisted in the stratosphere for several months. This layer was composed nearly entirely of sulfate aerosols, droplets of a mixture of sulfonic acid and water. To determine the aerosol composition, the spectra were modeled using extinction values calculated with Mie scattering code and sulfuric acid optical constants. Contrary to previous reports, there is no evidence of stratospheric smoke being present in the Arctic region.

REACTION MECHANISM AND KINETICS OF THE GAS PHASE REACTIONS OF METHANE SULFONAMIDE WITH CI RADICALS AND THE FATE OF CH(S=O)2NH2 RADICAL∗

PARANDAMAN ARATHALA, RARI A. MUSAH, Department of Chemistry, University at Albany—State University of New York, Albany, NY, USA.

Methane sulfonamide (CH3SO2NH2, MSAM) is an important trace compound detected for the first time in ambient air over the Red Sea and the Gulf of Aden. The average mixing ratios of this compound were found to be in the range of 20–50 ppt with a maximum value of 60 ppt. The energetics and rate coefficients for its reactions with Cl radical and in presence of atmospheric oxygen (O3) to form various products have not been reported. In the present work, we investigated the atmospheric oxidation mechanism and energetics of the reaction of MSAM with Cl radicals using high level quantum chemistry calculations. The MSAM + Cl radical reaction mainly proceeds by H-abstraction paths. Abstraction of H-atom from the methyl group of MSAM by Cl radical to form CH3Cl(=O)NH2 radical + HCl products was found to be dominant compared to other possible paths. The barrier height for this reaction was found to be 4.8 kcal mol−1 above the energy of the starting reactants at the CCSD(T) level. The rate coefficients were calculated for all possible H-atom abstraction paths associated with the MSAM + Cl radical using canonical variational transition state theory (CVT) with a small curvature tunneling (SCT) approximation in the temperatures between 200 and 300 K. The rate coefficient data, atmospheric lifetime of MSAM, branching ratios and thermodynamic parameters associated with the MSAM + Cl radical reaction are discussed. In addition, the atmospheric fate of the major product (i.e., CH3SO2(O)NH2 radical) with respect to its interaction with O3 to form the RO2 radical adduct (R = CH3S(O)2NH2) using the same level of theory was also investigated. The formed RO2 radical adduct proceeds through various multichannel pathways in the presence of HO2 radical to form several greenhouse gases and environmental pollutants including SO2, CO2, CO, HC(O)OH and HNO3 as final products.

The authors are grateful to NSF (grant numbers 1310350 and 1710221) for support of this work.


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FIRST ANALYSIS OF THE $\nu_1$ BAND OF HNO$_3$ AT 3551.766 CM$^{-1}$

AGNES PERRIN, Laboratoire de Météorologie Dynamique, École Polytechnique, University Paris Saclay and CNRS, Paris, France; LAURENT MANCERON, Synthétroïne SOLEIL, CNRS-MONASIR UMR 8235 and Beamline AILES, Saint Aubin, France; RAYMOND ARMANTE, École Polytechnique, CNRS / Laboratoire de Météorologie Dynamique, 91128 Palaiseau, France; P. ROY, AILES beamline, Synchrotron Soleil, Gif-sur-Yvette, France; P. KWABIA TCHANA, CNRS - Université de Paris - Université Paris Est Créteil, LISA, Créteil, France; GEOFFREY C. TOON, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

We present the first (preliminary) investigation of the $\nu_1$ band (OH stretching mode) of Nitric acid (HNO$_3$) centered at 3551.766 cm$^{-1}$ using high resolution Fourier transform spectra. These spectra were recorded in the 2.5 um to 3.25 um spectral regions on the spectrometer located on the AILES beamline of the SOLEIL synchrotron. Because of the large value of the Doppler linewidth (about 0.003 cm$^{-1}$) in the 2.8 um region at 220 K or 296 K, the analysis was very complex and often uncertain and dubious. Furthermore, the $\nu_1$ band is severely affected by numerous perturbations. Among these ones, unexpected line splittings were observed during all the analyses. Finally we have generated a preliminary list of “reasonable” line positions and intensities for the $\nu_1$ band and of the $\nu_{2+3+4-5}$ hot bands and $\nu_{4+5-7}$ hot bands.

FIRST ANALYSIS OF THE EXCITED STATES OF O$_2$

GAP-SUE KIM, Dharma College, Dongguk University, Seoul, Korea; WILFRID SOMOGYI, SERGEI N. YURCHENKO, Department of Physics and Astronomy, University College London, London, UK.

O$_2$ is important for spectroscopic applications in the IR, Visible and UV regions. In this work eight lowest electronic states were studied using the CASSCF and MRCI methods and the 4$\Sigma^+_u$/2$\Pi$ basis sets with the D$_2$h point group symmetry, namely $X^2\Sigma^+_g$, $A^2\Pi_g$, $A^2\Sigma^+_u$, $a^2\Sigma^+_u$, $a^2\Sigma^+_g$, $e^2\Sigma^+_u$ (bound), $3\Pi_u^-$, $1\Pi_g^-$ (bound). Potential energy curves (PECs) for 8 electronic states and spin-orbit coupling, electronic angular moment and transition quadrupole moment curves for the five states $X^2\Sigma^+_g$, $a^2\Sigma^+_u$, $b^2\Pi_g$, $d^2\Pi_u$, and $C^2\Pi_u$ were computed and used to predict rovibronic spectra and lifetimes of O$_2$. Our aim is to construct an accurate ro-vibrational molecular line list for O$_2$. This will require an empirical refinement of the ab initio curves and will be considered in our future work.

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NEW PARTICLE FORMATION (NPF) COMPRIS A SUBSTANTIAL PART OF SECONDARY AEROSOL PARTICLE FORMATION IN THE ATMOSPHERE, AND THESE PARTICLES PLAY AN IMPORTANT ROLE IN THE RADIATIVE FORCING BALANCE GOVERNING CLIMATE CHANGE. SIGNIFICANT UNCERTAINTIES IN CURRENT GLOBAL CLIMATE MODELS Persist IN PART DUE TO THE UNCERTAINTY SURROUNDING NPF GROWTH MECHANISMS. ESTABLISHING THE SURFACE STRUCTURE AND GROWTH MECHANISMS OF EARLY-STAGE NPF CLUSTERS IS NECESSARY TO DEVELOP ACCURATE DESCRIPTIONS OF PARTICLE FORMATION AND GROWTH RATES THAT CAN BE INCLUDED IN CLIMATE MODELS. CLUSTERS CONTAINING AMMONIUM, BISULFATE, AND WATER HAVE PREVIOUSLY BEEN STUDIED VIA MASS SPECTROMETRY COUPLED WITH INFRARED SPECTROSCOPY AS WELL AS VIA QUANTUM CHEMICAL CALCULATIONS WHICH PROVIDED STRUCTURAL AND BONDING INFORMATION AS WELL AS POTENTIAL ISOMER STABILITY. HERE WE FOCUS ON AN EMERGING CLASS OF CLUSTERS MADE OF AMMONIUM AND SODIUM, WHICH MAY BE IMPORTANT FOR PARTICLE FORMATION IN COASTAL AND POLAR REGIONS. CATIONIC CLUSTERS CONTAINING AMMONIUM, SODIUM, AND DIODIDE PENTOXIDE MOLECULES ARE THE FOCUS OF THIS STUDY.

AMMONIUM IS IMPORTANT FOR STABILIZING THE CLUSTERS AND PROMOTE THE FORMATION OF LARGER IODIDE OXIDES WITH PRESUMABLY LOWER VAPOR PRESSURE, WHICH WOULD BE EXPECTED TO LEAD TO HIGHER STABILITY AND FASTER GROWTH. HALOGEN BINDING COMPETES WITH HYDROGEN BINDING IN DETERMINING THE MINIMUM ENERGY STRUCTURES OF THESE CLUSTERS. THESE STUDIES ARE KEY BENCHMARKS FOR COMPUTATIONAL EFFORTS TO MODEL THESE CLUSTERS FOR THEIR INCLUSION IN LARGER-SCALE MODELING EFFORTS.
In this presentation, the identification and characterization of alcohol and water tetramers and pentamers using Chirped Pulse Fourier-transform Microwave (CP-FTMW) spectroscopy is described. This talk will address calculating candidate cluster structures using ab initio techniques, fitting the observed lines to obtain experimentally derived rotational constants, and analyzing the splitting of these rotational states due to the internal rotation of methyl groups present in the clusters of interest. Continued work on the characterization of alcohol-water mixing will be discussed, as will other future targets of interest for this instrument.

Pulse Fourier transform microwave (CP-FTMW) spectroscopy is described. This talk will address calculating candidate structures for complexes between 2-decalone and water, benzene, and phenol. The broadband rotational spectra of 10 deuterated isotopologues. These results can benchmark theoretical methods for the structural optimization of weakly bound complexes. The effect of deuterium substitutions on intermolecular interactions is also discussed.

Here we report the study on complexes between 2-decalone (C10H14O) and water, benzene, and phenol, respectively. The goal was to compare the interactions between the complex partners and the contributions of electrostatic and dispersion forces and which of them dominates when both forces are present. For that, a small hydrogen bond donor, water, was selected. Benzene is a good example for forming dispersion interactions, while in phenol both a phenyl ring and a hydrogen bond donor group are present and there could be competition between both forces. The complexes 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 sample consists of cis and trans 2-decalone, and complexes with both isomers were detected. In total five water complexes were identified with benzene. The broadband rotational spectra of 10 deuterated isotopologues. These results can benchmark theoretical methods for the structural optimization of weakly bound complexes. The effect of deuterium substitutions on intermolecular interactions is also discussed.

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FD05
10:04 – 10:57
GEOMETRIES AND CONFORMATIONAL CONVERSION OF THE BINARY 3,3,3-TRIFLUOROPROPANOL CONFORMERS: ROTATIONAL SPECTRA AND DFT CALCULATIONS
ALEX NEILSON MORT, FAN XIE, YUNJIE XU, Department of Chemistry, University of Alberta, Edmonton, AB, Canada.
Fluorinated alcohols have been widely used as co-solvents to study folding and unfolding behaviors of proteins and peptides. The detailed mechanism by which this happens is yet to be established. Recent molecular dynamics simulations suggested that clusters of the fluorocohol play an important role in the mechanism. In the current study, we applied jet-cooled chirped pulse Fourier transform microwave spectroscopy to probe structure and dynamics of 3,3,3-trifluoropropanol (TFP) and its dimer. In comparison to 2,2,2-trifluoroethanol, TFP is the smallest trifluorocohol molecule which exhibits folded conformations in its monomer form, thus serving as a prototype system for structural diversity associated with folding. The possible structural candidates of the TFP dimer were explored by using CREST, a recently developed computational searching tool and nearly 70 stable binary conformers were identified. Rotational spectra of these low energy binary TFP conformers were assigned and their carriers identified. To help explain the observation of the binary conformers, a combined kinetic and thermodynamic conformational distribution model was developed to explain the non-observation of some lower energy conformations and to provide quantitatively explanation for the experimental conformational abundances. The study of the conformations of TFP and its dimer is a first and important step in understanding how TFP aggregates in bulk.


FD06
10:57 – 11:02
INTERMEDIARY OF THE TBP SPECTRUM OF THE BENZOFURAN-DIETHYL DISULFIDE COMPLEX CHARACTERIZED BY ROTATIONAL SPECTROSCOPY
YUANGO XU, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China; WEN-QIN LI, RIZALINA TAMA SARAGI, ALBERTO LESARI, Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain; GANG FENG, School of Chemistry and Chemical Engineering, Chongqing, China.
The complex of benzofuran and diethyl disulfide has been investigated using Fourier transform microwave spectroscopy complemented by theoretical calculations. Two isomers have been observed, in which diethyl disulfide configures as gauche-gauche-conformation sitting on the face of the benzofuran ring. The lone pair electrons of the sulfur atom points to the 5-electron cloud of the benzofuran with a distance of about 3.6 Å, thus indicating a direct interaction between S and aromatic ring. NCPolit analysis suggests both observed isomers are stabilized by cooperative S···S interaction and S···C weak intermolecular interactions with total interaction energies of about 26 KJmol⁻¹ and is dominated by dispersion. Detailed spectroscopic and computational results will be presented.

FD07
10:57 – 11:12
STRUCTURE AND NON-COMPONENT INTERACTIONS OF THE BENZOFURAN-DIETHYL DISULFIDE COMPLEX CHARACTERIZED BY ROTATIONAL SPECTROSCOPY
YUANGO XU, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing, China; WEN-QIN LI, RIZALINA TAMA SARAGI, ALBERTO LESARI, Departamento de Química Física y Química Inorgánica, Universidad de Valladolid, Valladolid, Spain; GANG FENG, School of Chemistry and Chemical Engineering, Chongqing, China.
The complex of benzofuran and diethyl disulfide has been investigated using Fourier transform microwave spectroscopy complemented by theoretical calculations. Two isomers have been observed, in which diethyl disulfide configures as gauche-gauche-conformation sitting on the face of the benzofuran ring. The lone pair electrons of the sulfur atom points to the 5-electron cloud of the benzofuran with a distance of about 3.6 Å, thus indicating a direct interaction between S and aromatic ring. NCPolit analysis suggests both observed isomers are stabilized by cooperative S···S interaction and S···C weak intermolecular interactions with total interaction energies of about 26 KJmol⁻¹ and is dominated by dispersion. Detailed spectroscopic and computational results will be presented.

FD08
11:15 – 11:30
MODELING CO₂ MICROSOVATATION MICROWAVE SPECTROSCOPIC STUDIES OF DIFLUOROETHYLETHANE (DFE)/CO₂ CLUSTERS, (DFE)₂/CO₂, FOR A TRIMMER, TETRAMER, AND PENTAMER
HANNAH FINK, TULANAARIYATRATE, PRASHANSA KANNAGARIA, REBECCA A. PEEBLES, SEAN A. PEEBLES, Department of Chemistry, Eastern Illinois University, Charleston, IL, USA; CHANNING WEST, BROOKS PATE, Department of Chemistry, The University of Virginia, Charlottesville, VA, USA.
Microwave spectroscopy allows for analysis of weakly-bound clusters in a mixture of difluoroethane (DFE) and CO₂. The present study probes variations in interactions and orientations of DFE and CO₂ within weakly-bound clusters as cluster size increases. Four chirped-pulse FTMW spectra of DFE/CO₂ mixtures were obtained from 2-8 GHz, where the concentration of CO₂ was varied from 1% to 4%, with a constant DFE concentration of 1%. This experimental design allowed variation in intensity to be observed based on the variation of CO₂ concentration, where the pattern of intensity variation was used to identify transitions belonging to a particular cluster. In addition, patterns of intensity variation provided information about the size and DFE:CO₂ ratio of the cluster. Using these methods based on intensity variation analysis, three separate sets of transitions, each with unique intensity variation patterns, were extracted from the original raw spectra. Cluster composition was hypothesized based on further evidence from the intensity variation analyses, leading to compositions of (DFE/CO₂)₁, (DFE/CO₂)₂, and (DFE/CO₂)₃. Fitted rotational constants for the spectra were compared to the results of ab initio calculations, which further supported hypothesized cluster compositions for the trimer, tetramer and pentamer. These results indicate that instead of forming a solvation shell around DFE, CO₂ molecules appear preferable to interact with other CO₂ molecules to form arrangements more closely resembling pure CO₂ clusters, with DFE on the outside of the cluster.

FD09
11:33 – 11:48
REINVESTIGATION OF THE MICROWAVE SPECTRUM OF THE O₂-H₂O VAN DER WAALS COMPLEX
W. R. REESE, Chemistry, Missouri University of Science and Technology, Rolla, MO, USA; CAITLIN SAZ, AMANDA DIERDEN, FRANK E. MARSHALL, G. S. GRUBBS II, Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA.
Further spectral data of the O₂-H₂O van der Waals complex was obtained, expanding the range of transition lines for structural determination. Previous work was done in the 14-29 GHz range a Transitions have been measured as low as 11 GHz using a chirp pulse FTMW spectrometer. Working fits inclusive of these newfound transitions will be presented. Furthermore, current work with higher resolution cavity FTMW data utilizing Helmholtz coils on the complex will be discussed.

MICROSOLVATION COMPLEXES OF α-METHOXY PHENYLACETIC ACID STUDIED BY MICROWAVE SPECTROSCOPY

HIMANSHI SINGH, PARRO PINACHO, MELANIE SCHNELL, FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany.

Mandelic acid and its derivatives are useful as chiral synths in the chemical and pharmaceutical industry because of their versatility. Their wide use in organic reactions makes them an important case to study their solute-solvent interactions. α-methoxy phenylacetic acid (AMPA), a methoxy-derived mandelic acid, can serve as a model to characterize the non-covalent interactions of such chiral solutes with different solvents. The different functional groups in this chiral acid provide flexibility to the molecule, that conformational flexibility has been presented previously. Furthermore, the presence of a carboxylic acid and a methoxy group in AMPA provides good binding sites for solute-solvent interactions and thus serves as a good model system.

In this work, we investigate the microsolvation of AMPA in three different solvents using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. This technique coupled with the supersonic expansion reveals accurate structures of weakly bound complexes isolated in the gas phase. We chose three solvents that offer different functional groups and thus model more types of solute-solvent interactions. The three solvents were water, a small hydrogen bond donor partner, DMSO with a sulfoxide group, and phenol with a phenyl ring and a hydroxyl group. The preferred intermolecular interactions and the structural changes in complexes with three different solvents will be discussed.

A QUANTUM CASCADE LASER DUAL-COMB SPECTROMETER IN STEP-SWEEP MODE FOR HIGH-RESOLUTION MOLECULAR SPECTROSCOPY

MARKUS MAGGIOLI, PIT ALLENDINGER, JAKOB HAYDEN, ANDREAS HUGLI, IRsweep AG, IR-sweep AG, Stäfa, Switzerland, OLIVIER BROWET, JEAN CLÉMENT, BASTIEN VISPOEL, MURIEL LEPÈRE, Institute of Life, Earth and Environment (ILEE), Université de Namur, Namur, Belgium.

To meet the challenges of high-resolution molecular spectroscopy, increasingly sophisticated spectroscopic techniques were developed. For a long time FTIR and laser-based spectroscopies were used for these studies. The recent development of dual-comb spectroscopy at high-resolution makes this technique a powerful tool for gas phase studies. We report on the use and characterization of the IRs-F1, a tabletop mid-infrared dual-comb spectrometer, in the newly developed step-sweep mode. The resolution of the wavenumber axis is increased by step-wise tuning (interleaving) and accurate measurement of the laser center wavelength and repetition frequency. Doppler limited measurements of N₂O and CH₄ reveal a wavenumber accuracy of 10⁻⁴ cm⁻¹ on the complete covered range of 50 cm⁻¹. Measured half-widths of absorption lines show no systematic broadening, indicating a negligible instrument response function. Finally, measurements of nitrogen pressure broadening coefficients in the e₁ band of methane show that the dual-comb spectrometer in step-sweep mode is well adapted for measurements of precision spectroscopic data, in particular line shape parameters.

A SPECTROSCOPIC PRESSURE SENSOR TARGETING ATOMIC POTASSIUM FOR HYPERSONIC FACILITIES

TAI SCHWARTZ, JOSHUA A VANDERVORT, SEAN CLEES, CHRISTOPHER L STRAND, RONALD K HANSON, Mechanical Engineering, Stanford University, Stanford, CA, USA.

We apply laser absorption spectroscopy to design a diagnostic measuring bulk gas pressure from collisionally-broadened absorption lineshapes. This diagnostic targets atomic potassium with a measurement rate of 200 kHz. The diagnostic is intended to operate in hypersonic ground-based facilities, where atomic potassium is nascent in the freestream flow and where microsecond temporal resolution is often crucial.

Recent studies have found atomic potassium in trace amounts in the freestream of hypersonic ground-based facilities, making it an attractive spectroscopic target. Potassium also has convenient spectroscopic transitions in the near-infrared – the D-line transitions ⁴S¹/₂ → ⁴P⁰/₂ at 770.1 nm and ⁴S¹/₂ → ⁴P₂/₂ at 766.7 nm, which absorb strongly and are easily accessible with low-cost commercial lasers and optics.

This line-of-sight laser-based diagnostic infers bulk gas pressure from the spectroscopic lineshape of the potassium D₂ transition, specifically the collisional linewidth parameter Δν<sub>coll</sub>. We apply empirical correlations to extract pressures from a Voigt fit of these lineshapes. These correlations depend on gas composition and temperature, which must be known. Lineshape parameters must also be corrected to account for power broadening effects, and hyperfine splitting is considered at low pressures.

For verification, the diagnostic is deployed in a shock tube to generate the temperatures, pressures, and timescales relevant to freestream flows in hypersonic ground-based facilities. Since atomic potassium is not present in sufficient quantity for measurement in our shock tube, we implement a novel technique to uniformly seed potassium into the shock-heated gas. We achieve excellent signal-to-noise ratios and measure pressures in good agreement with expected values between 0.25-2 atmospheres.
MEASUREMENT OF COLLISIONAL SELF-BROADENING AT LOW-TEMPERATURES USING SUB-DOPPLER SPECTROSCOPY

BRIAN DROUIN, DEACON J NEAMCHICK, TIMOTHY J. CRAWFORD, PAUL VIN ALLMEN, DARIUSZ LIT, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA

Collisional energy transfer in volatilized exospheric materials dominates the uncertainty of comet models that trace coma 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. Here we detail 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. The method utilizes a collisional cooling cell with water injected into a bath gas at the target temperature. THz radiation is passed twice through the cooled gas to record a trans-

APPLICATION OF THEORETICAL CONSTRAINTS TO MODEL THE MEASURED TEMPERATURE AND WAVE-LENGTH DEPENDENCE OF COLLISION-INDUCED ABSORPTION IN THE 0.76 μm AND 1.27 μm O2 BANDS

ERIN M. ADKINS, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA; HELENE FLEURBAEY, UMR5588 LPJh, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France; TIJS KARMAN, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands; DAVID A. LONG, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA; ALAIN CAMPARGUE, DIDIER MONDELAIN, UMR5588 LPJh, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France; JOSEPH T. HODGES, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA.

Understanding collision-induced absorption (CIA) is a critical component to improving the O2 spectroscopy for remote sensing applications. Traditionally in experimental spectra, CIA is defined as the remaining absorption after accounting for the baseline, Rayleigh scattering, and resonant absorption. This approach can present difficulties in systems like the O2 A-Band at 0.76 μm, where the CIA is relatively weak and is highly correlated with the line-mixing model. Theoretical constraints on the magnitude and shape of the CIA could aid in decoupling the resonant and broadband features ultimately leading to an improved spectroscopic model. The CIA model reported by Karman et al. [1] provides a theoretical basis for the CIA in the 1.27 μm and 0.76 μm O2 bands [1]. In this work, we evaluate the theoretical model using cavity ring-down spectroscopy measurements collected at multiple temperatures in both the 1.27 μm [2-4] and 0.76 μm O2 bands. In addition to a qualitative comparison between experiment and theory, this work explores parameterization of the CIA model reported by Karman et al. [1] for future inclusion in integrated multi-spectrum analyses incorporating advanced line shape models, line-mixing, and CIA.


CHARACTERIZATION OF THE H2O+CO2 CONTINUUM ABSORPTION WITHIN THE INFRARED TRANSPARENCY WINDOWS FOR PLANETARY APPLICATIONS

HELENE FLEURBAEY, DIDIER MONDELAIN, UMR5588 LPJh, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France; JEAN-MICHEL HARTMANN, WISSAM FAKHARIDJ, Ecole Polytechnique, CNRS / Laboratoire de Mécanique et Modélisation, 91128 Palaiseau, France; ALAIN CAMPARGUE, DIDIER MONDELAIN, UMR5588 LPJh, Université Grenoble Alpes/CNRS, Saint Martin d’Hères, France.

Accurate knowledge of the absorption by a gas mixture of CO2 and water is crucial for planetary sciences, as it allows for better modeling the atmospheres of rocky planets, e.g. improving our understanding of the early climate of Mars or why Venus and the Earth have evolved so differently. In addition to local monomer lines proportional to the density of each species, the absorbance spectrum of such a gas mixture includes binary absorption features varying smoothly with frequency: self-continuum absorption proportional to the squared density, and “crossed” absorption involving both species and scaling as the product density2ρ1ρ2ν1ν2. We used highly sensitive spectroscopy techniques (CRDS and OPFES) to measure the absorbance by H2O+CO2 gas mixtures in several spectral regions situated in transparency windows where the monomer absorption of both species is weak (1.5 – 1.5 μm, 1.68 – 1.75 μm, 2.06 μm, 2.22 – 2.35 μm, 3.5 μm). For both water and CO2, the monomer lines, modeled using HITRAN parameters, and the self-continuum absorption, calculated from literature values or measured in dedicated experiments, were subtracted from the measured absorption. The obtained “crossed absorption” coefficients are compared to the only available empirical model based on far wings of line shapes profiles scaled by χ factors. An additional absorption peak centered at about 6000 ν2 cm−1 was attributed to a collision induced simultaneous transition of H2O and CO2 through the ν1 and ν2 modes, respectively. The assignment was confirmed using humidified CO2, where a similar band was observed about 68 cm−1 away corresponding to the isopinocial spectral shift of the ν2 band of CO2. Classical molecular dynamics simulations (CMDs) of the considered collision-induced absorption were conducted and are found in good agreement with the experiment.6


Intermission
Upcoming exoplanet infrared imaging will likely include carbon monoxide (CO) absorption from deeper, higher-pressure regions of larger Jupiter-like exoplanets, with compositions of majority hydrogen (H₂) and helium (He). However, there have been limited experimental CO spectroscopy studies in H₂ and He at elevated pressure conditions. We present quantitative, broadband absorbance measurements of the fundamental ro-vibrational band of CO between 2050 and 2200 cm⁻¹, in both gas mixtures. The room-temperature static cell measurements were taken using a narrow linewidth, broadband scan external cavity quantum cascade laser at pressures of 15–35 atm. For CO in H₂ and He, minor adjustments to the MEG line mixing model were made to reproduce the weaker F-dependence of the broadening coefficients relative to that of CO in N₂. The resulting MEG line mixing model shows improved agreement with the measured spectra across different pressures and broadening partners. Further reduction of the residuals to within approximately 1% (CO/H₂, 35 atm) is shown through the fitting of MEG coefficients directly to measured spectra, resulting in relatively small adjustments to each of the coefficients.

Potassium can be used as a convenient tracer species in combustion and hypersonic test facilities and is naturally present in trace amounts in the atmospheres of brown dwarfs, where the resonance doublet is highly detectable. Currently, there are no experimental data of potassium line shape parameters at temperatures over 500 K and model predictions vary widely above 1000 K. We present measurements of collisional broadening and pressure shift parameters for the potassium D-lines, near 770 nm, with collisional partners of N₂, H₂, and He. Atomic potassium is generated in a shock tube by shock heating KCl salts at temperatures between 1100–1900 K, and line parameters are measured using rapid-scanning tunable diode laser absorption spectroscopy. The line shape measurements were modeled as Voigt profiles and a fitting algorithm determined pressure shift and collisional full-width at half-maximum. The collisional broadening and pressure shift coefficients are given as temperature-dependent partial collision cross sections for the potassium of interest. The potassium results agree well with lower temperature experimental data, within 15–20%, and high-temperature theoretical predictions, within 10–30%. The nitrogen results, however, have larger discrepancies with existing data and simplified impact theory predictions. This may suggest the need for a more detailed model for the nitrogen collisional broadening of potassium. The presented correlations may be useful for the development of potassium-based sensing methods with application to combustion, hypersonics, and astrophysics.

One of the key findings regarding exoplanet science is that majority of the detected close-in planets from Kepler fall into the super-Earth to sub-Neptune regime 1–3.5 Earth Radii. Planet formation models of these systems suggest broad compositional diversity in this radius regime, with a high likelihood for large atmospheric metal content 100–1000 Solar. Our ability to unlock the mysteries of this new class of planet hinges on our ability to link the spectral observations to theoretical models, and then our ability to link those models to fundamental molecular and atomic opacities. However, there is a critical lack of data that is required to compute opacities and the subsequent theoretical atmosphere for high-metallicity atmospheres. This is because high-metallicity atmospheres are expected to contain larger fractional quantities of H₂O, CO, CO₂, and CH₄, relative to H₂-dominated systems that have been the focus of the majority of previous observing campaigns. Therefore, they require fundamentally different pressure-broadening parameters that are currently lacking. Nevertheless, ignoring the impact of these parameters will lead to errors in the calculation of the planet’s energy budget, as well as errors in the ultimate atmospheric spectra. We will present an overview of our team’s efforts to fill this gap by computing the theoretical broadening coefficients relevant to the super-Earth to sub-Neptune temperature range. The importance of these results will be discussed and their impact on exoplanet radiative transfer modeling of objects from space-based telescopes will be discussed.
**FF. Spectroscopy as an analytical tool**
Friday, June 24, 2022 – 8:30 AM
Room: 124 Burrill Hall
Chair: R. A. Motyjenko, Université de Lille, Villeneuve d’Ascq, France

**FF01**
8:30–8:45
**FLUORESCENCE EXCITATION, EMISSION, AND SYNCHRONOUS SPECTRA AT LOW TEMPERATURES**
CARLOS MANZANARES, SURESH SUNUWAR, Department of Chemistry and Biochemistry, Baylor University, Waco, TX, USA

Computer deconvolution of experimental excitation and emission fluorescence spectra is presented and used to generate synchronous spectra. The computer simulation successfully predicts the number of synchronous fluorescence (SF) bands, band shapes, and band maximum wavelengths for any constant wavelength difference ($\Delta \lambda$). To test the simulation, emission, excitation, and synchronous spectra were obtained for anthracene in n-hexane. Excellent agreement is obtained reproducing and finding the origin of the experimental SF bands for values of $\Delta \lambda$ between 2 and 100. The excitation, emission, and synchronous ($\Delta \lambda=10$) spectra of toluene, aniline, naphthalene, acenaphthene, pyrene, and anthracene are obtained. The synchronous spectrum ($\Delta \lambda=50$) of the same mixture is presented and assigned based on the synchronous bands of the individual compounds. The synchronous fluorescence technique and the computer simulation method are proposed to complement other techniques in the analysis of fluorescent samples from comets, as well as in missions to planets and satellites of the solar system. With our experimental setup we will be able to obtain spectra for temperatures between 77 K and 298 K. Our laboratory is currently obtaining excitation, emission, and synchronous spectra of PAHs at temperatures that could be found on the surface of Titan and Mars.

**FF02**
8:45–9:03
**NEAR INFRARED SPECTROSCOPY AS EFFICIENT ANALYTICAL TOOL IN PLASTIC ADDITIVES INDUSTRY**
EMANUELE PEZZANO, ASSIMO MARI, Dipartimento di Chimica G. Ciamician, Università di Bologna, Bologna, Italy, MARZIA MAZZACURATI, Analytical service, BASF Italia S.p.A., Pontecchio Marconi, Italy

Near Infrared spectroscopy (NIRS) is a potent tool for the analysis of several materials. It finds vast applications due to its versatility and finds applications in many fields such as pharmaceutical industry, food science, environmental, biochemistry. In this work we report several applications in plastic additives industry. The determination of specific analytes in this kind of products is challenging without expensive and difficult sample preparation. The NIR technique instead, with the application of chemometric approach, permits the quantitative analysis in complex matrices with simple, fast, and cheap procedures. To clarify the structure of the dataset spectra employed in the calibration curve, and so the nature of the bands involved, the calculated NIR spectrum of model compound is also reported and compared to its experimental gas phase counterpart.

**FF03**
9:06–9:21
**ANALYSIS OF TINNEVELLY SENNA LEAVES HERBAL MEDICINE USING LASER-INDUCED BREAKDOWN SPECTROSCOPY AND ITS ANTI-CANCEROUS & ANTIBACTERIAL EFFICACY STUDIES**
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.

Tinnevelly Senna is a herbal plant whose leaves are being applied to cure many diseases in developing countries due to containing many bioactive compounds such as sennosides, phenols, and flavonoids. The conventional methods to determine the main contents of such Senna leaves are lengthy, cost-effective, require hazardous chemical solvents and reagents. In this work an elegant technique like LIBS was applied as a qualitative and quantitative method for Senna leaves sample’s elemental analysis and their biological activities were measured by evaluating anti-cancer and anti-bacterial analysis. The quantitative analysis of Senna leaves was conducted using calibration-free LIBS algorithm indicating the concentration of many nutrient elements, and the LIBS results were counter verified by using the standard analytical ICP-OES technique. The bactericidal efficacy of the Senna leaves was also studied against Staphylococcus aureus (S. aureus) by AWD assays and morphological scanning electron microscopy (SEM) and the anticancer activity was also investigated where different concentrations of Senna leaves extract were tested on cancer cells (HCT-116 and HeLa) and normal cells (HEK-293) using the cell metabolic activity MTT assay and Propidium iodide (PI) staining. We also estimated the inhibitory concentration (IC50) value for the various extracts’ concentrations. The bactericidal efficacy of the Senna leaves extract showed significant inhibition against Gram positive bacterium. Both MTT and PI analysis showed that Senna leaves extract induced profound inhibition on HCT-116 growth and proliferation. Additionally, Senna leaves extract did not exert an inhibitory influence on normal (HEK-293), which is non-cancerous cells. The extract specifically targets the cancerous cells is highly beneficial for the development of future safe anticancer and antibacterial drugs using these extracts.

**FF04**
9:24–9:39
**IDENTIFICATION OF CHLOROBENZENE IN MIXTURES WITH THE SUGGESTED PRECURSORS BENZENE, BENZOIC ACID, PHTHALIC ACID, AND MELLITIC ACID IN MARS SAMPLES**
SURESH SUNUWAR, CARLOS MANZANARES, Department of Chemistry and Biochemistry, Baylor University, Waco, TX, USA

The discovery of chlorobenzene detected in a soil sample obtained in Mars has been controversial. The original sample was subjected to pyrolysis before the analysis with the gas chromatography-mass spectrometry (GC-MS) of the Sample Analysis at Mars (SAM) instrument on the Curiosity rover. It is believed that chlorobenzene was a product of other organic molecules reacting with chlorates of the Martian soil. In this paper, synchronous fluorescence spectroscopy is suggested for analysis of Mars samples in future missions. Synchronous fluorescence spectroscopy is a variation of the fluorescence technique where the excitation and emission scans are detected simultaneously with a predetermined wavelength difference ($\Delta \lambda$) between the two and multiplied. Depending on the $\Delta \lambda$ chosen, the resulting signal could produce a narrow single fluorescence band with a peak wavelength that is characteristic of the compound. To demonstrate the utility of this technique for Mars samples and in general for planetary and astrochemical applications, we present laboratory results with the characteristic synchronous peaks of chlorobenzene, benzene, benzoic acid, phenol, phthalic acid, and mellitic acid in solutions of n-hexane or water. Finally, we demonstrate a successful application of the technique using a mixture of chlorobenzene in the presence of the likely organic precursors that have been suggested for the Cumberland drill sample on Mars. The application of SFS for solid samples of Mars analog soils is also discussed for future experiments.
SYNCHRONIZED-BASED ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY OF ARTIFICIAL GASOLINE BLEND

JOSHUA G SMITH, SYLVESTRE TWAGIRAYEZU, Chemistry and Biochemistry, Lamar University, Beaumont, TX, USA; BRANT E BILLINGHURST, RANBO ZHAO, EFD, Canadian Light Source Inc., Saskatoon, Saskatchewan, Canada.

Attenuated Total Reflection (ATR) Infrared spectra of artificially-prepared gasoline blends have been recorded in the 600-4000 cm\(^{-1}\) region, using the Far-Infrared Beamline at Canadian Light Source. The observed spectra reveal rich but distinct vibrational signatures of the gasoline and ethanol. The analysis of C=C and CO stretch bands indicates significant vibrational shifts due to the changes of force constants as the hydrocarbon content increases. The present data provide vibrational centers useful for the characterization of ethanol in the presence of hydrocarbons. The sensitivity of ATR-IR for ethanol determination in gasoline mixture has been examined by measuring the ATR-IR signal response of artificial gasoline blend over a wide range of ethanol contents (95-100%). The obtained linear correlation allows the determination of recovery percentage (95-100%) and thus confirming the accuracy of ATR-IR method.

INTERMEDIATION OF THE METHANE CH STRETCH OVERTONE USING INFRARED HIGH RESOLUTION COHERENT TWO DIMENSIONAL SPECTROSCOPY

DAUNNA A DANIELS, Chemistry, Spelman College, Atlanta, GA, USA; THRESA WELLS, PETER CHEN, Department of Chemistry, Spelman College, Atlanta, GA, USA.

Methane is an important and heavily studied molecule because of its significance in astronomy, energy, and climate change. Studies of methane as a model are also important because it is the simplest hydrocarbon. For many molecules, the vibrational, rotational, and electronic modes are well understood, but overtones and combination bands are often difficult to accurately identify. At higher frequencies there is significant congestion due to combination bands and overtones overlapping, making it difficult to determine which modes are responsible for each line. We have used a newly developed technique called IR HRCDS to investigate the overtones region of CH stretches in methane. This technique uses a broadband source with wavelengths spanning the CH overtone region (5950-7000 cm\(^{-1}\)) and a tunable source scanning the CH fundamental (2900-3100 cm\(^{-1}\)). Coupling these two modes gives doubly resonant features which could allow us to confirm several frequencies from the CH overtones of methane, and to calculate the Coriolis constants for these overtones.

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DAUNNA A DANIELS, Chemistry, Spelman College, Atlanta, GA, USA; THRESA WELLS, PETER CHEN, Department of Chemistry, Spelman College, Atlanta, GA, USA.

Methane is an important and heavily studied molecule because of its significance in astronomy, energy, and climate change. Studies of methane as a model are also important because it is the simplest hydrocarbon. For many molecules, the vibrational, rotational, and electronic modes are well understood, but overtones and combination bands are often difficult to accurately identify. At higher frequencies there is significant congestion due to combination bands and overtones overlapping, making it difficult to determine which modes are responsible for each line. We have used a newly developed technique called IR HRCDS to investigate the overtones region of CH stretches in methane. This technique uses a broadband source with wavelengths spanning the CH overtone region (5950-7000 cm\(^{-1}\)) and a tunable source scanning the CH fundamental (2900-3100 cm\(^{-1}\)). Coupling these two modes gives doubly resonant features which could allow us to confirm several frequencies from the CH overtones of methane, and to calculate the Coriolis constants for these overtones.

Like Carbon Dioxide (CO\(_2\)), Nitrous Oxide (N\(_2\)O) behaves as a long-lived greenhouse gas. Increases in atmospheric concentrations of N\(_2\)O due to anthropogenic sources have contributed to stratospheric ozone depletion and climate change. For these reasons it is imperative to formulate effective techniques for trace N\(_2\)O detection. Spectral line resolution and detection sensitivity are crucial for efficient trace gas quantification. One technique which enables the precise determination of the transition frequency between the ground and excited states of an analyte is saturated absorption spectroscopy (SAS). In SAS, counter-propagating beams of the same frequency produce Doppler-free peaks in absorption spectra. Each beam produces opposite Doppler shifts, therefore only atoms/molecules traveling with nearly zero-velocity along the axis of beam propagation couple with both beams, leading to Doppler-free spectral-hole burning. Additionally, cavity enhanced spectroscopic methods, such as the revolutionary cavity ring-down spectroscopy (CRDS), employ the use of a high finesse optical cavity, wherein light is trapped and the concentration of the analyte is determined by the rate of decay of the cavity light. Due to the high intensity of the light inside the optical cavity, this technique is remarkably sensitive, even for the detection of weakly absorbing transitions. However, the high density of one-photon transitions can often lead to spectral overlap and resolution loss. On the other hand, near-resonance two-level transitions, like those found in N\(_2\)O, result in low density spectra. Here we present a novel approach of gaseous N\(_2\)O detection by SAS and two-photon CRDS of the P(18) and Q(18) ro-vibrational transitions.
GERRIT CHRISTENSON, ZIWEI YU, RENEÉ R. FRONTIERA, Department of Chemistry, University of Minnesota - Twin Cities, Minneapolis, Minnesota, United States.

Plasmonic materials have increasingly grown in interest in chemical sensing, optoelectronics, and photocatalysis. Plasmonic media interact strongly with light, focusing and enhancing electromagnetic radiation to nanoscale volumes, not seen with typical propagation of electromagnetic radiation. Although plasmonic materials have countless desirable properties, we still struggle to form a fundamental understanding of energy and charge transfer at plasmonic interfaces.

We specifically desire to quantify energy transfer in plasmonic-molecular systems in this work. We utilize continuous wave, surface-enhanced anti-Stokes and Stokes Raman spectroscopy to probe the vibrational energy transfer. Further, we employ a Boltzmann distribution analysis to quantify our results, to correlate the anti-Stokes to Stokes scattering ratio in Raman-active vibrational modes to their corresponding temperatures. Specifically, we examine the temperatures of plasmonic-fluorophore systems, where molecules can undergo electronic transitions, which specifically follow an unforeseen mechanism. In comparison to room temperature population densities, we observe a 100K decrease in the temperature of various fluorophore molecules under resonant steady-state excitation. In contrast, under non-resonant excitation, we see an increase in temperature up to 200K. This resonant plasmonic cooling effect occurs regardless of vibrational mode selection and solvating environment. Our work provides new insight into plasmonic-molecular interactions and an initial investigation of this occurrence.

DOUGLAS BORCHMAN, Ophthalmology and Visual Sciences, University of Louisville, Louisville, KY, USA.

NMR and Infrared spectroscopies were instrumental in determining the relationships between lens and tear lipid composition, conformation and function. The major lipid of the human lens is dihydrosphingomyelin, discovered by NMR spectroscopy and found in quantity only in the lens. The lens contains a cholesterol to phospholipid molar ratio as high as 10:1. Lens lipids contribute to maintaining lens clarity, and alterations in lens lipid composition due to age are likely to contribute to cataract. Lens lipid composition reflects adaptations to the unique characteristics of the lens: no turnover of lens lipids or proteins and contains almost no intracellular organelles. Long-lived species such as humans and the bowhead whale exhibit lens lipid adaptations that confer resistance to oxidation, and thereby allowing the lens to stay clear for a relatively longer time than is the case in many other species. With cataract, light scattering increases due to the increase in the lipid order of lens membranes measured using infrared spectroscopy. It is plausible that the increase in lipid-lipid interactions may contribute to myopia by causing greater compaction and overall stiffness of the lens. The TFLL is a thin, 100 nm layer of lipid on the surface of tears covering the cornea that contributes to tear film stability. NMR spectroscopy found that the major lipids of the TFLL are wax esters and cholesterol esters. The hydrocarbon chains associated with the esters are longer than those found anywhere in the body, as long as 32 carbons, and many are branched. More ordered lipid with dry eye, measured using FTIR, could inhibit the flow of mibemid from the meibomian glands and contribute to the formation of a discontinuous patchy TFLL, which in turn results in deteriorated spreading, and decreased surface elasticity. One may also speculate that more ordered lipid results in the attenuated capability to restore tear film lipid layer structure between blinks.

OLIVIA H. WILKINS, KATARINA YOCUM, NASA Postdoctoral Program Fellow, NASA Goddard Space Flight Center, Greenbelt, MD, USA; STEFANIE N MILAM, PERRY A. GERAKINES, Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA; WILL E. THOMPSON, GUSTAVO A. CRUZ-DIAZ, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; SUSANNA L. WIDICUS WEAVER, Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA.

Cosmic ice analogue experiments are an important aspect of astrochemistry because they help researchers construct the chemical pathways leading to molecules found in young stellar objects, comets, and meteors. Decades of cosmic ice experiments have demonstrated the formation of various organics and how ice composition is affected by UV photons and temperature. The ice chemistry can be challenging to elucidate, and structure-specific techniques are required to uniquely identify products. We present the Sublimation Laboratory Ice Millimeter/submillimeter Experiment (SubLIME), which uses rotational spectroscopy to complement previous laboratory ice studies. Using this technique, we can detect a wide range of products, including structural and conformational isomers, of UV-photolyzed ice samples from a single spectrum. Furthermore, this technique can be used to model the observational spectra of protostellar and cometary comae. We will present the SubLIME setup and new spectroscopic results of sublimated UV-photolyzed ice samples containing water (H2O) and carbon monoxide (CO).
THE SEARCH FOR COMPLEX ORGANIC MOLECULES DESORBING FROM INTERSTELLAR ICE ANALOGS:
PRESENTING SubLIME2

GUSTAVO A. CRUZ-DIAZ, WILL E. THOMPSON, Department of Chemistry, University of Wisconsin-Madison, Madison, WI, USA; COLLETTE C SAVER, CATHERINE E WALKER, Chemistry, UW-Madison, Madison, WI, USA; PERRY A. GERAKINES, STEFANIE N MILAM, Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA; SUSANNA L. WIDECUS WEAVER, Chemistry and Astronomy, University of Wisconsin-Madison, Madison, WI, USA.

Dark and cold regions in space, including regions like prestellar cores and protoplanetary disks, have been shown to harbor high densities of complex organic molecules. Many organic molecules can form in interstellar ices and be deposited into the gas phase via heating, shocks, or other desorption mechanisms. Nonetheless, the expectation is that the density of large organic in cold, dark regions should be low because the molecules readily freeze out onto ices during collisions. Therefore, there is a debate about how molecules like methanol can be detected in the gas phase in regions where they should be depleted on the surface of dust particles. We have developed a new experimental technique, Sublimation Laboratory Ice Millimeter/submillimeter Experiment (SubLIME), to study these processes. We will present the latest experimental findings using SubLIME, the newest ultra-high vacuum setup focused on detecting complex organics from interstellar ice analogs studied at cryogenic temperatures. With these experiments, we perform FTIR spectroscopy in the mid-IR to monitor solid-phase molecules, mass spectrometry to detect the molecules in the gas phase, and millimeter/submillimeter rotational spectroscopy from 100 to 1000 GHz to look for complex molecules desorbing from the solid phase. Here we will report on our recent experiments to study photolysis and photodesorption of simple ices containing water, methanol, and carbon monoxide.

SPECTROSCOPY AND ASTROCHEMISTRY OF THE CN-TAGGED CYCLIC HYDROCARBONS CYANOCYCLOPENTADIENE AND CYANOINDENE

BRYAN CHANGALA, Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA; KELVIN LEE, Accelerated Computing Systems and Graphics, Intel Corporation, Hillsboro, OR, USA; RYAN A. LOOMIS, NASA; National Radio Astronomy Observatory, Charlottesville, VA, USA; ANDREW M. BURKHARDT, Department of Physics, Wellesley College, Wellesley, MA, USA; CI XUE, Department of Chemistry, MIT, Cambridge, MA, USA; ILSA ROSE CROCKE, Department of Chemistry, University of British Columbia, Vancouver, BC, Canada; MARTIN CORDENIER, STEVEN B CHARNLEY, Astrochemistry, NASA Goddard Space Flight Center, Greenbelt, MD, USA; 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.

The weak, often vanishing, dipole moments of polycyclic aromatic hydrocarbons pose a challenge to exploring their interstellar chemistry through radio astronomy. Fundamentalization of a pure hydrocarbon with a highly polar nitrile (-CN) group yields a useful proxy, so long as the spectroscopy and chemistry of such CN-tagged molecules are well understood. In this talk, we present recent laboratory measurements of the CN-substituted cyclic hydrocarbons cyanocyclopentadiene, C₆H₅CN, and cyanooindene, C₆H₅HCN, produced in a discharge expansion source and probed by cavity-enhanced Fourier transform microwave spectroscopy. We discuss the role that resonantly stabilized radical intermediates play in the likely formation chemistry of these species and the astrochemical implications of their abundances in the cold, dense molecular cloud TMC-1.

BROADBAND ROTATIONAL SPECTROSCOPY OF 2,4,6-CYCLOHEPTATRIENE-1-CARBONITRILE: A POTENTIAL INTERSTELLAR MOLECULE

LAURA PILLE, GAYATRI BATERA, FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; BENJAMIN E. ARENAS, Department of Chemistry, Durham University, Durham, United Kingdom; DONATELLA LORU, MELANIE SCHNELL, FS-SMP, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany.

The recent astronomical observations of the simplest aromatic nitrile benzocarbonitrile, c-C₆H₅CN, followed by a five-membered [1], [2] and a bicyclic [3] CN functionalized ring in TMC-1 have opened up a new field of complex organic molecules (COMs) in space. These new findings provided an impetus for the laboratory rotational spectroscopy studies of larger-CN functionalized rings. One such example is 2,4,6-cycloheptatriene-1-carbonitrile (2,4,6-C₇H₇-CN), a seven-membered ring with a-CN group attached to the sp³-hybridized carbon atom. With a permanent electric dipole moment of 4.3 D and a low boiling point, the molecule is an excellent candidate for laboratory rotational spectroscopy. Experiments were performed in the 18-26 GHz and 75-110 GHz frequency range in a supersonic expansion setup and a room temperature flow cell setup, respectively. The measurements across the 18-110 GHz region enabled the identification and assignment of the vibrionic ground state, singly substituted rare-atom isotoopes, and vibrationally excited states. In this work, we report the precise determination of the rotational constants, quartic centrifugal distortion constants, as well as nitrogen nuclear quadrupole coupling constants for the vibrionic ground state. The rotational spectroscopy study of 2,4,6-C₇H₇-CN presented here forms the basis for future astronomical detection. Two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering.


THE SOLEIL VIEW ON PROTOTYPE ORGANIC NITRILES: THE $^{13}$C SPECIES OF ETHYL CYANIDE

CHRISTIAN ENDRES, The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany; MARIE-ALINE MARTIN-DRUMEL, OLIVIER PIRALI, Institut des Sciences Moléculaires d’Orsay, Université Paris Sud, CNRS, Orsay, France; J.-C. GUILLAUME, UMR 6225 CNRS - ESSCR, Institut des Sciences Chimiques de Rennes, Rennes, France; OLIVIER ZENGHEIM, LUIS BONAH, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; MICHAEL C. MCDERMOTT, Center for Astrophysics, Harvard & Smithsonian, Cambridge, MA, USA; PAOLA CASELLI, The Center for Astrochemical Studies, Max-Planck-Institut für extraterrestrische Physik, Garching, Germany; STEPHAN SCHLEMMER, SVEN THORKWIRTH, I. Physikalisches Institut, Universität zu Köln, Köln, Germany.

Vibrational spectra of the three singly substituted $^{13}$C isotopic species of ethyl cyanide, ake propionitrile (CH$\equiv$CH-CN), have been studied at high spectral resolution at the synchrotron facility SOLEIL, using Fourier-transform far-infrared spectroscopy. The measurements, recorded up to 700 cm$^{-1}$, cover the fundamental modes of the CCN in-plane bending $\nu_2$, the methyl torsion $\nu_3$, the CCN out-of-plane bending $\nu_30$, and as well as the CCC in-plane bending $\nu_{52}$. A first vibrational analysis has been performed using the Automated Spectral Assignment Procedure (ASAP) to derive accurate excited-state rotational level energies with a focus on the $\nu_2$ and $\nu_{52}$ vibrational modes.

FG08

PROTONATED ETHYL CYANIDE: QUANTUM CHEMISTRY AND ROTATIONAL SPECTROSCOPY

HARSHAL GUPTA, Division of Astronomical Sciences, National Science Foundation, Alexandria, VA, USA; KELVIN LEE, Accurated Computing Systems and Graphics, Intel Corporation, Hillsboro, OR, USA; SVEN THORKWIRTH, OSKAR ASVANY, STEPHAN SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; MICHAEL C. MCDERMOTT, Center for Astrophysics, Harvard & Smithsonian, Cambridge, MA, USA.

Protonated ethyl cyanide, CH$_3$CN$^+$, a likely intermediate in interstellar clouds and in the planetary atmosphere of Titan, has been detected at high spectral resolution by means of Fourier transform microwave spectroscopy at centimeter wavelengths. From 13 $a^3$-type rotational transitions between 8 and 44 GHz, the three rotational constants have been determined to better than 0.05% and two of the leading centrifugal distortion terms to a few percent. Since nitrogen hyperfine structure in the lower rotational transitions is highly compact, only the quadrupole coupling tensor element along the $\alpha$-inertial axis $\lambda_{\alpha}$ could be determined. The agreement between the experimental rotational constants and those calculated theoretically is very good, of order 0.2%, a clear indication that the CCSD(T) level of theory provides an accurate treatment of the electronic structure. By scaling to isoelectronic butyne, even better agreement between the two is achieved (≈ 0.15%). The similarity of the $\Omega JNT$ values derived along the C-N bond axis for both protonated vinyl cyanide and protonated ethyl cyanide along with the very small magnitudes of these constants implies a quadruply-bound nitrogen atom and an H–N$^+$–C–C type structure that is affected little by protonation. Closely spaced torsional doubles in one $K_a = 0$ line and three $K_a = 1$ lines allow an estimate of the threefold barrier to internal rotation of $V_2 \approx 2.50 \pm 0.09$ kcal mol$^{-1}$, which is within 6% of that calculated theoretically. Ethyl cyanide has a high proton affinity and is abundant in rich astronomical molecular sources, implying its protonated variant is a good candidate for astronomical detection, particularly since this species is calculated to possess a sizable dipole moment along the $\alpha$-inertial axis (2.91 D).

FG10

LABORATORY SPECTROSCOPY OF A$^2\Sigma^+$–X$^2\Pi_{3/2}$ ELECTRONIC TRANSITION OF ICN$^+$ TO ESTIMATE PROFILES OF INTERSTELLAR ABSORPTION LINES BY HALOGEN CYANIDE CATIONS

TAKUMI ITO, MITSUNOSHI ARAKI, SHOMA HOSHINO, KOICHI TSUKIYAMA, Faculty of Science Division I, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan.

Diffuse interstellar bands (DIBs) are optical absorption lines by electronic transitions of interstellar molecules in diffuse clouds. Almost all bands are not identified yet, except for C$_2$H$_2$. As a hint of DIB carriers, the presence of C$_2$H$_2$ infers that molecules in diffuse clouds are ionized. Additionally, the molecules will frequently contain a cyanogroup and more or less include a halogen atom. Hence, halogen cyanide cations are good carrier candidates. To identify origin molecules of DIBs, laboratory data of band profiles of electronic transitions are essential as well as those of their wavelengths. Generally, a band profile is determined by a structural change of an electronic transition. In this work, the high-resolution spectrum of the A$^2\Sigma^+$–X$^2\Pi_{3/2}$ electronic transition for ICN$^+$, which is one of the halogen cyanide cations, was observed for the first time by cavity ringdown spectroscopy. The rotational constants were determined to be 0.10700(12) and 0.11002(12) cm$^{-1}$ for the A$^2\Sigma^+$ and X$^2\Pi_{3/2}$ states, respectively. Therefore, the rotational constant ratio $J_{21} = (0^2 - 1^2) W = 2010(12) cm$ was derived to be 2.7%.

This small J ratio suggests that the profiles of the absorption bands of the halogen cyanide cations have symmetric structures irrespective of diffuse-cloud temperature. This information allows us to search the halogen cyanide cations in space.

JET-COOLED MID-INFRARED LASER SPECTROSCOPY OF CENTROSYMMETRIC TWO-RING PAHS

PIERRE ASSELIN, SATHAPANA CHAWANANON, CNRS, De la Molécule aux Nano-Objets: Réactivité, In- 

FRONTIÈRES, MONASIER, Sorbonne Université, PARIS, France; M. G. GOBET, UMR 5237 - PIALAM - Physique des Lasers Atomes et Molécules, Université de Lille, F-59000 Lille, France; OLIVIER PIRALI, Institut des Sciences Moléculaires d’Orsay, Université Paris Sud, CNRS, Orsay, France.

The recent detection of cyanogen naphthalenes within TMC-1 using radioastronomy provided the first unambiguous confirmation of the interstellar PAHs hypothesis. In the mid-infrared (IR) domain, the launch of the James Webb Space Telescope opens exciting perspectives to collect information about polycyclic aromatic compounds. In this context, high resolution (HR) IR studies enabling to resolve the rotational structure of vibrational bands of large aromatic species mainly used synchrotron-based Fourier Transform (FT) spectroscopy coupled to room temperature long path cells but the spectral analysis of such recordings remains very challenging. Nowadays, very few set-ups combining HR IR spectroscopy to the supersonic jet technique were developed to target low volatile PAH compounds. A tunable mid-IR quadratic cascade laser spectrometer coupled to a pulsed supersonic jet (SPIRALES set-up) recently implemented allows to record the rotationally resolved spectra of large molecules at low temperatures. We report the jet-cooled vibrational IR study of three centrosymmetric two-ring PAH molecules: naphthalene, 1,5-naphthyridine and biphenyl in both regions of in-plane ring C-H bending and C=C ring stretching vibrations, enabling to extract reliable spectroscopic parameters both in ground and excited vibration states. Comparison between experiment and quantum chemistry calculations give confidence in the predictive power of corrected calculated rotational parameters. Last, experimental inertial defects of naphthalene and 1,5-naphthyridine complemented by similar two-ring and larger species agree well with an extended Oka’s empirical formula developed for estimating the inertial defects of aromatic ring compounds.

Because of similar formation conditions, the diatomic molecule vanadium oxide (VO) is thought to occur in similar locations around stars as TiO. VO has already been detected in the near-infrared region in the envelope of the red hypergiant VY CMa, which was subsequently expanded into a carbonaceous cloud. The rotationally cooled spectrum was measured using the geoprobe software and the molecular constants were determined. The experimental data as well as line predictions will enable a dedicated search for this molecule in space at mid-IR wavelengths.
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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 also a member organization of the Federation of Analytical and Spectroscopic Societies (FACSS).

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Please register online with your name, email, and department using this link: https://go.illinois.edu/ISMS_JASCO_LnL.

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All contributed talks will be held in the Chemistry complex (and immediately adjoining buildings). The plenary talks will be held across the quad (about 600') in Foellinger Auditorium.
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Noyes Laboratory houses our Registration and Exhibitor/Refreshment Rooms (Chemistry Library), the Computer Lab (151), and two lecture halls (NL 100 and 217).
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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).
Burrill Hall is due north of Medical Sciences. It has one lecture hall (124).

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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.
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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 Kenberry Commons, drops off at the Krannert Center (across the street from CSL-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.

PLEASE NOTE NEW DROP-OFF LOCATION AT KRANNERT CENTER DUE TO WRIGHT STREET CLOSURE!
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 CSLI-B). Return locations are across the street. Runs every ~10 minutes during the day (offset from the Yellow Line by 5 minutes).
NOTES
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