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, *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 $\mathrm{SO_2}$, $\mathrm{CHF_3}$, $\mathrm{CH_3CN}$ and a medium sized molecule $\mathrm{CH_2CHCN}$. 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-Lavie 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 $\mathrm{CH_3CN}$ (which has a degenerate bending mode, $2v_8{}^{0,2}$), efficient *l*-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.