UNIVERSITY OF RHODE ISLAND
Department of Chemistry
SEMINAR

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"Ultrafast 2DIR Spectroscopy in Dense Gas and Near-Critical Fluids: J-scrambling, Rovibrational Dynamics and the Onset of Liquid Character"

HOST

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Ultrafast 2DIR Spectroscopy in Dense Gas and Near-Critical Fluids: J-scrambling, Rovibrational Dynamics and the Onset of Liquid Character

Abstract

Rates of chemical reactions are often controlled by how quickly excited or highly energetic species lose internal energy and return to rotational and vibrational thermal equilibrium. Much of what we know about gas phase reaction dynamics has come from spectroscopic measurements necessarily in low density systems where discrete rovibrational spectroscopic features are resolvable. However, many important chemical environments, such as in internal combustion engines for example, operate under high pressures, and often in the supercritical fluid (SCF) regime. Furthermore, the unique solvation properties of SCFs offer the potential for controlling chemical processes. Given the lack of spectral resolution in such high density/pressure fluids, echo-like spectroscopic techniques are uniquely suited to uncover dynamical information on how excited molecules in these dense environments return to equilibrium with both J and v specificity. Over the last two decades, ultrafast 2DIR spectroscopy has emerged as one of the leading techniques for investigations of molecular structure and dynamics in condensed phases. We have observed and analyzed the first 2DIR spectra of molecules in high density fluids. The unique, complex 2DIR lineshapes of samples with free rotor character contrast with condensed phase 2DIR spectra, and demonstrate a new capability for measuring rotational relaxation dynamics in dense environments. Timescales for re-establishing rotational equilibrium, independent of the longer vibrational relaxation timescale, evidence for the co-existence of both free rotors and liquid-like inhomogeneities in high density fluids and a real time dynamical description of the special solvation properties of SCFs are achievable from these observations.