UNIVERSITY OF RHODE ISLAND
Department of Chemistry
SEMINAR

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"Infrared Action Spectroscopy of Ions Trapped in Helium Nanodroplets: From Ion Chemistry to Biomolecular Conformers"

HOST

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Infrared Action Spectroscopy of Ions Trapped in Helium Nanodroplets: From Ion Chemistry to Biomolecular Conformers

Helium nanodroplets serve as ideal "nanocryostats" in which to perform infrared (IR) spectroscopy experiments. Analytes trapped in these nanodroplets are rapidly cooled to 0.4 K and experience minimal matrix-induced spectral perturbation, allowing the acquisition of highly resolved IR spectra. Although this method has long been applied to the interrogation of neutral species, the coupling of electrospray ionization mass spectrometry and helium nanodroplet isolation spectroscopy has been realized only recently, enabling the facile preparation and interrogation of an incredible diversity of intriguing molecular ions and clusters.

This talk will highlight our recent results obtained utilizing this methodology. First, we explore the complex reaction pathways encountered in the reaction of fluoride anions with gas-phase carbon dioxide in the presence of water, which involve the intricate interplay of fluoride nucleophilic attack, strong hydrogen bonding, and proton transfer reactions. Characterization of two particularly fascinating molecules produced under these conditions, fluoroformate and a carbonic acid-fluoride complex, will be discussed. Second, we examine the properties of the carboxylate proton-bound dimer, a ubiquitous chemical motif found for example in ionic liquids and in proteins. A particular focus is the location of the shared proton and the importance of nuclear quantum effects in these systems. Finally, we detail recent efforts to take advantage of the rapid cooling properties of the helium nanodroplet to kinetically trap temperature-dependent conformer populations in model dinucleotide systems, thereby enabling the measurement of the relative enthalpy and entropy of conformers through a van 't Hoff analysis.