Glenn T. Seaborg Center Seminar

IRMPD Spectroscopy of Discrete, Gas-phase Complexes Containing Uranyl Ion

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4:00 - 5:00 pm
Perseverance Hall - Bldg. 54 Room 130

The chemical behavior of uranium is controlled by the structure and reactivity of an array of ligated complexes and clusters that is derived from competitive influences of 5f, 6d, and 7s orbitals on the metal center. In solution, $[UO_2]^{2+}$ (uranyl ion) is the dominant species, but for this cation there is a multiplicity of interconverting species that complicates study in the condensed phases. This has motivated extensive modeling efforts using computational chemistry at a variety of levels of theory and computing power. However, it is frequently difficult to experimentally validate computational methods/approaches and calculated values, especially for actinide species. The combination of ion-trapping mass spectrometry and photodissociation using infrared-wavelength free electron lasers has provided unprecedented access to the vibrational spectra of discrete, gas-phase metal ion complexes. In this action spectroscopy approach, photon absorption is monitored by measuring the fragmentation yields from wavelength-selected infrared multiple-photon photodissociation (IRMPD). We have used IRMPD to provide the first glimpses of the vibrational features of gas-phase ions that contain lanthanide or actinide metal cations. The IRMPD studies provide unprecedented benchmarks for validation of theory, and key insight into intrinsic interactions between uranyl or lanthanide ions and coordinating ligands. Here, the IRMPD approach will be discussed, focusing on studies of intrinsic structure and bonding characteristics of cationic and anionic complexes featuring uranyl ion and wide variety of coordinating ligands. In addition, the correlation between spectral features and predictions made using density function theory calculations will be presented. For example, The asymmetric O=U=O stretching frequency systematically red shifts with addition of multiple donor ligands, consistent with increased donation of electron density to the uranium center in complexes with higher coordination number. Values generated computationally using LDA, B3LYP, and ZORA-PW91 are in good agreement with experimental measurements.

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