

Plenary Talk PV VIII Thu 9:00 E 415
Capturing Reaction Intermediates with Cryogenic Ion Spectroscopy — ●MARK JOHNSON — Yale University

We will describe the characterization of catalytic reaction intermediates by combining electrospray ionization with cryogenic mass spectrometry. This technique uses a cold (10-30K) RF ion trap to rapidly cool reaction partners and freeze the intermediates into well-defined structures. After mass-selection, these species occur as isomers at a particular mass, and we isolate the spectra of each using a photochemical hole burning scheme involving three stages of mass selection and two independently tunable pulsed infrared lasers. The table-top lasers yield highly resolved vibrational fingerprints of the cold chemical

species in a linear action regime, which can be directly compared with theory to recover the structures at play. We will focus on a biomimetic synthetic peptide catalyst (developed at Yale) to carry out stereoselective bromination of a biaryl compound. In this case, the catalyst is first isolated and sharp features associated with particular C=O groups are identified using site-specific isotopic substitution. The catalyst is then docked to the substrate, and the geometry of the host-guest complex is unravelled, again using isotope-dependent vibrational spectroscopy to follow how specific functional groups are attached in the non-covalent interaction. Applications of this methodology to a variety of systems, including larger peptides and organometallic homogeneous catalytic intermediates, will also be presented.