

SPECTROSCOPIC INTERROGATION OF PHOTOINDUCED, SITE-TO-SITE MIGRATION OF SOLVENT MOLECULES IN WATER CLUSTER ANIONS

TIMOTHY L. GUASCO, BEN M. ELLIOTT, MICHAEL Z. KAMRATH, and MARK A. JOHNSON, *Sterling Chemistry Laboratory, Yale University, PO Box 208107, New Haven, CT 06520.*

We present results of a new trace isotope variation of our recently developed experimental approach in which we use IR-IR pump-probe methods to measure the transition states and relative energies of isomers associated with the negatively charged water clusters. This modification, in which clusters of the form $[(\text{D}_2\text{O})_6 \cdot \text{H}_2\text{O}]^- \cdot \text{Ar}_n$ are produced, allows us the powerful ability to monitor discrete, site-to-site migration of a lone water molecule as cluster melting and refreezing occurs. This technique works by first systematically disentangling the vibrational spectra of various isotopomers using hole-burning Ar predissociation spectroscopy in a triple-stage time-of-flight mass spectrometer and then monitoring the spectra of fragment ions that are created by photoevaporation of Ar atoms through the various vibrational levels identified in the spectroscopic step.