

STEPPING ACROSS THE DISSOCIATION THRESHOLD OF THE $I^{-}\cdot(H_2O)$ COMPLEX: RESONANCE ENHANCED TWO-COLOR IR-IR PHOTODISSOCIATION (R2PD)

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The $X^{-}\cdot(H_2O)$ ($X=I, Cl, F$) clusters ion provide a microscopic window into the intracluster energy relaxation dynamics that ultimately lead to dissociation when excited above threshold (D_0). Here we explore the spectra of simple binary complexes of one water molecule with an iodide ion when the system is excited to vibrational levels that span the energy range through D_0 . This is accomplished by recording the vibrational photodissociation spectra of different vibrational excited states of $X^{-}\cdot(H_2O)$ using a two-color, IR-IR photodissociation technique. We first quantify the ground state spectra by recording the single photon absorption spectra of cryogenically cooled cluster ions with messenger tag technique. Then we fix the pump laser frequency on a transition known to the ground state cluster ion and scan the probe laser to obtain the excited state photodissociation spectra. Owing to the long lifetime of the vibration excitations in this class of clusters, each pump laser excitation frequency yields a different spectrum (the traces on the right in the figure). This provides an opportunity to obtain a kind of 2DIR spectroscopy (left bottom figure) of cryogenically cooled gas phase ions. The result is a cluster variation of the vibrationally-mediated photodissociation experiments pioneered in the 1990s by Crim and Rizzo on polyatomic molecules. In the cluster regime, we find remarkably long lived (greater than 50 μs !) vibrational levels 300 cm^{-1} above the dissociation threshold and surprisingly localized excitations for the bound OH stretches. This feature allows us to follow many pathways up the vibrational landscape far beyond the dissociation limit.