

ADDING THE TEMPERATURE DIMENSION TO SIZE-SELECTED ION VIBRATIONAL PREDISSOCIATION SPECTROSCOPY: OBSERVATION OF "MELTING" IN THE PRIMARY SOLVATION SHELL OF MICROHYDRATED IODIDE CLUSTERS

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Over the past decade, an intensive integrated effort involving theory and experiment have revealed the structures at play in the first hydration shell of simple ions. The water molecules generally adopt configurations in which one OH group is directed toward the ion while the other is integrated into a water network. One of the reasons this endeavor was difficult is that the three-body repulsion in this regime acts to significantly lower the effective inter-water binding energies, making the equilibrium structures much more fragile than their neutral counterparts. Here we exploit very recent advances in the temperature control of size-selected ionic clusters using cryogenic ion traps to monitor how the spectroscopic signatures of the water networks evolve as the temperature of the  $\text{I}^-(\text{H}_2\text{O})_n$  clusters is varied over the range 10 to 200 K. The breaking of the hydrogen bond interactions is observed around 150 K in the dimer. Qualitative assignments of the free, bound and ring hydrogens in the OH stretching region clarify the evolution from closed to linear hydrogen bond networks as the temperature changes. The success of this temperature programmed ion vibration predissociation (TPIVP) spectroscopy opens the way to sample large amplitude exploration of potential energy landscapes of such systems.