

RAPID EVAPORATIVE COOLING SUPPRESSES FRAGMENTATION IN MASS SPECTROMETRY: SYNTHESIS OF “UNPROTONATED” WATER CLUSTER IONS

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Hydrogen bonded water clusters were formed with inert gasses adsorbed to them in a strong molecular beam expansion. Upon photoionization of such mixed clusters, fragmentation of the substrate water cluster ion is markedly suppressed. Experimental evidence is presented, showing that the rapid evaporation of the inert gas from the newly formed water cluster ion efficiently removes internal energy on a time scale much faster than the usual fragmentation reactions present in pure water cluster, i.e., rates of fragmentation that are normally $>10^9 \text{ s}^{-1}$. This phenomenon is exploited to produce “unprotonated” water clusters, formally $(\text{H}_2\text{O})_n^+$. Using post source decay reflectron time-of-flight mass spectrometry, the structure of the “unprotonated” water cluster ions is experimentally determined for the first time. The structure determined, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k \cdot \text{OH}$ where the hydroxyl radical is found outside the first solvation shell of the charge, is consistent with recent *ab initio* calculations. This simple approach to the control of fragmentation in mass spectrometry appears to have promise in applications to other interesting polymeric samples, for example biopolymers.