

NEAR-INFRARED SPECTROSCOPY OF SMALL PROTONATED WATER CLUSTERS

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Small protonated water clusters and their argon tagged analogues of the general formula $\text{H}^+(\text{H}_2\text{O})_n\text{Ar}_m$ have been generated in a pulsed electric discharge source. Clusters containing $n = 1-8$ water molecules were mass-selected and their absorptions in the near-infrared were probed with a tunable Nd: YAG pumped OPA/OPA laser system in the region from $4850-7350\text{ cm}^{-1}$. A doublet corresponding to overtones of the free O—H stretches of the external waters was observed around 7200 cm^{-1} that was continuously decreasing in intensity with increasing cluster size. Broad, mostly featureless absorptions were found around 5300 cm^{-1} associated with stretch/bend combinations and with the hydrogen bonded waters in the core of the clusters. Vibrational assignments were substantiated by comparison to anharmonic frequency computations via second-order vibrational perturbation theory (VPT2) at the MP2/aug-cc-pVTZ level of theory.