MODEL STUDIES OF PARTIAL HYDRATION OF PROTONATED PEPTIDE IONS: I. THE FORMAMIDE-WATER CLUSTERS

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Molecular structures of protonated formamide-water clusters are investigated by vibrational predissociation spectroscopy in combination with density functional theory calculations. We produce the cluster ions by a supersonic expansion and identify their structures from a comparison of the observed and calculated NH and OH stretch spectra at 3400 - 3800 cm^{-1}. The structural identification confirms theoretical predictions that O-protonation occurs in preference to N-protonation. The proton can be either localized at a site closer to formamide or at a site closer to water, depending sensitively on the structure and solvation number of cluster isomers. Further studies on the protonated N-methylformamide-water cluster ions reveal a characteristic free-NH stretch absorption at 3480 cm^{-1}. We demonstrate in this work that a combined investigation of cluster ions by infrared spectroscopy and *ab initio* calculations may allow for detailed structural interrogation of protonated peptide ions at early stages of hydration in the gas phase.