

## INFRARED SPECTRA OF $\text{H}_2\text{O}^+-\text{Ar}_n$ COMPLEXES (n=1-14)

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IR spectra of the open-shell ionic  $\text{H}_2\text{O}^+-\text{Ar}_n$  complexes (n=1-14) are recorded in the vicinity of the O-H stretch vibrations ( $\nu_1, \nu_3$ ) by means of photodissociation spectroscopy in a tandem mass spectrometer. Rotational and vibrational analysis of the dimer spectrum clearly shows that the first Ar ligand forms a linear ionic hydrogen bond to the  $\text{H}_2\text{O}^+$  cation. Complexation transforms the symmetric (antisymmetric) O-H stretch of  $\text{H}_2\text{O}^+$  into bound and free O-H oscillators in the  $\text{H}_2\text{O}^+-\text{Ar}$  dimer. Strong coupling between the bound O-H stretch ( $\nu_1$ ) and the intermolecular bond leads to a large red shift in the  $\nu_1$  frequency and a short lifetime. In contrast, the free O-H stretch ( $\nu_3$ ) is only little affected upon Ar complexation, and the resulting long lifetime allows for the resolution of the rotational structure (including spin-rotation). The second Ar ligand binds to the second proton of the water cation ( $\text{C}_{2v}$ ). Complexation with further Ar ligands cause smaller frequency shifts owing to weaker intermolecular bonds. Ab initio calculations show good agreement with the experimental data.