

## INFRARED SPECTRA OF $\text{NH}_3^+ \text{-Ar}_n$ (n=1-6) COMPLEXES (n=1-6)

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Intermolecular forces and microsolvation processes in  $\text{NH}_3^+ \text{-Ar}_n$  complexes (n=1-6) are studied by infrared photodissociation spectroscopy in a tandem mass spectrometer. Analysis of the rovibrational structure yields a proton bound dimer equilibrium structure with  $\text{C}_{2v}$  symmetry. Observed tunnelling splittings are attributed to hindered internal rotation of the planar  $\text{NH}_3^+$  cation within the dimer. Systematic frequency shifts observed in the spectra of larger clusters provide a detailed picture of the cluster growth. The first three Ar ligands form equivalent linear proton bonds, leading to highly symmetric cluster structures with  $\text{C}_{2v}$  or  $\text{D}_{3h}$  symmetry. The next two Ar atoms bind to the  $2p_z$  orbital of the central N atom on opposite sites of the  $\text{C}_3$  axis, leading to structures with  $\text{C}_{3v}$  and  $\text{D}_{3h}$  symmetry. Ab initio calculations support the interpretation of the experimental data.