

Vibrational Spectroscopy of Benzonitrile – (Water)₁₋₂ Clusters in Helium Droplets

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Polycyclic aromatic hydrocarbons (PAH) are considered as primary carriers of the unidentified interstellar bands. The recent discovery of the first interstellar aromatic molecule, benzonitrile (C₆H₅CN), suggests a large repository of aromatic hydrocarbons in the outer earth environment. Herein, we report the microhydration framework of benzonitrile using mass-selective infrared spectroscopy inside the helium nanodroplets. The comparison between the experimental and predicted spectra computed at the MP2/6-311++G(d,p) level of benzonitrile-(water)₁₋₂ clusters reveals the formation of a unique local minimum structure, which was not detected in the previous gas-phase experiment. In this newly observed benzonitrile-water dimer structure, the solvent water forms a nearly linear hydrogen bond (H-bond) with the nitrile nitrogen of benzonitrile, while the previously reported most stable cyclic H-bonded isomer is not observed. This is rationalized by the unique cluster growth condition that exists in helium droplets. In this work, we use isotopically substituted water, D₂O, instead of normal H₂O because of our IR frequency limitation (2565-3100 cm⁻¹). The addition of a second water molecule results in the formation of two different isomers. In one of the observed isomers, a H-bonded water chain linearly binds to the nitrile nitrogen similar to the monohydrated benzonitrile-water complex. In the other observed isomer, the water dimer forms a ring-type structure, where a H-bonded water dimer simultaneously interacts with the nitrile nitrogen and the adjacent *ortho* CH group. Finally, we compare the water-binding motif in the neutral benzonitrile-water complex with the corresponding positively and negatively charged benzonitrile-water monohydrates to comprehend the charge-induced alteration of the solvent binding motif.