

VIBRATIONAL SPECTROSCOPY OF BENZONITRILE-(WATER)₁₋₂ CLUSTERS IN HELIUM DROPLETS

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Polycyclic aromatic hydrocarbons are considered as primary carriers of the unidentified interstellar bands. The recent discovery of the first interstellar aromatic molecule, benzonitrile (C_6H_5CN), suggests a repository of aromatic hydrocarbons in the outer earth environment. Herein, we report an infrared (IR) study of benzonitrile-(D_2O)_n clusters using mass-selective detection in helium nanodroplets. In this work, we use isotopically substituted water, D_2O , instead of (H_2O) because of our restricted IR frequency range ($2565-3100\text{ cm}^{-1}$). A comparison of 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 previous gas-phase molecular beam experiments. Here, 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 can be rationalized by the stepwise aggregation process of precooled monomers. 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 binds linearly 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.