

VIBRATIONAL SPECTROSCOPY OF BENZENE-(WATER)_N CLUSTERS WITH $N = 6, 7$

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The investigation of benzene-water clusters (Bz-(H₂O)_n) provides insight into the relative importance π -hydrogen bond interactions in cluster formation. Taking advantage of the higher resolution of current IR sources, isomer-specific resonant ion-dip infrared (RIDIR) spectra were recorded in the OH stretch region (3000-3750 cm⁻¹). A local mode Hamiltonian for describing the OH stretch vibrations of water clusters is applied to Bz-(H₂O)₆ and Bz-(H₂O)₇ and compared with the RIDIR spectra. These clusters are the smallest water clusters in which three-dimensional H-bonded networks containing three-coordinate water molecules begin to be formed, and are therefore particularly susceptible to re-ordering or re-shaping in response to the presence of a benzene molecule. The spectrum of Bz-(H₂O)₆ is assigned to an inverted book structure while the major conformer of Bz-(H₂O)₇ is assigned to an S_4 -derived inserted cubic structure in which the benzene occupies one corner of the cube. The local mode model is used to extract monomer Hamiltonians for individual water molecules, including stretch-bend Fermi resonance and intra-monomer couplings. The monomer Hamiltonians divide into sub-groups based on their local H-bonding architecture (DA, DDA, DAA) and the nature of their interaction with benzene.