THEORETICAL STUDY OF THE IR SPECTROSCOPY OF BENZENE-(WATER)$_N$ CLUSTERS

DANIEL P. TABOR, EDWIN SIBERT, Department of Chemistry, The University of Wisconsin, Madison, WI, USA; RYOJI KUSAKA, Chemistry, Hiroshima University, Higashi-Hiroshima, Japan; PATRICK S. WALSH, TIMOTHY S. ZWIER, Department of Chemistry, Purdue University, West Lafayette, IN, USA.

The local mode Hamiltonian that assigns RIR spectra for Bz-(H$_2$O)$_6$ and Bz-(H$_2$O)$_7$ is explored in detail for Bz-(H$_2$O)$_n$ with $n=3-7$. In addition to contributions from OH stretches, the Hamiltonian includes the anharmonic coupling of each water monomer’s bend overtone and its OH stretch fundamentals, which is necessary for accurately modeling 3150-3300 cm$^{-1}$ region of the spectra. The parameters of the Hamiltonian can be calculated using either MP2 or density functional theory. The relative strengths and weaknesses of these two electronic structure approaches are examined to gain further physical understanding. Initial assignments of Bz-(H$_2$O)$_6$ and Bz-(H$_2$O)$_7$ were based on a linear scaling of M06-2X harmonic frequencies. In most cases, counterpoise-corrected MP2 calculations obtain similar frequencies (across all cluster sizes) if stretch anharmonicity is taken into account. Individual “monomer Hamiltonians” are constructed via the application of fourth order Van Vleck perturbation theory to MP2 potential energy surfaces. These calculations elucidate the sensitivity of intra-monomer couplings to chemical environment. The presence of benzene has particularly important consequences for the spectra of the Bz-(H$_2$O)$_3$–5 clusters, in which the symmetry of the water cycles is broken by $\pi$-H-bonding to benzene. The nature of these perturbations is discussed.