PROPYLBENZENE-$(H_2O)_n$ CLUSTERS: EFFECT OF THE ALKYL CHAIN ON THE π H-BOND

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This talk focuses on the mass resolved- resonant 2-photon ionization (R2PI), resonant ion-dip infrared spectroscopy (RIDIR) and IR-UV holeburning (IR-UV HB) spectroscopy of propylbenzene(pBz)-$(H_2O)_n$ clusters and the comparison with their Benzene(Bz)-$(H_2O)_n$ cluster counterparts, which are a well-studied prototype system for the π H-bond. Since the pBz monomer exists in *gauche* and *trans* conformers, one anticipates the presence of pBz-H_2O complexes with H_2O on the same or opposite sides of the ring as the *gauche* or *trans* propyl chain. Indeed, local minima associated with these four complexes were identified by dispersion-corrected DFT calculations. R2PI and IR-UV HB spectra of pBz-H_2O show long Franck-Condon progressions associated with the set of conformers of the complex. The OH stretch RIDIR spectra consist of a single transition in the symmetric stretch region, and a doublet with varying spacing in the antisymmetric stretch region, indicating coupling to a large-amplitude motion (LAM). The changes in the OH stretch region indicate that the water molecule bound to propylbenzene undergoes more restricted motion on the π cloud than its Bz-H_2O counterpart. The potential energy surface for H_2O tumbling on the pBz π cloud was mapped out, and used as the basis for calculating from first principles the OH stretch infrared spectrum. Comparison with the spectrum for Bz-H_2O further illustrates the source and restrictions of the LAM of H_2O in pBz compared to Bz. OH stretch IR spectra of the higher water clusters pBz-$(H_2O)_n$ with n=3, 4 are very similar to their Bz-$(H_2O)_n$ counterparts, existing as H-bonded cycles, with no evidence of LAM on the aromatic π cloud.