INFRARED AND ULTRAVIOLET SPECTROSCOPY OF JET-COOLED 2-BENZYLPHENOL: I. STRUCTURE AND LARGE-AMPLITUDE TORSIONAL MOTION

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The ultraviolet and infrared spectroscopy of jet-cooled 2-benzylphenol (2bp) was studied using fluorescence excitation (FE), single vibronic level fluorescence (SVLF), UV-UV holeburning (UVHB), and fluorescence-dip infrared (FDIR) methods. The presence of an OH group in the 2-position on one ring asymmetrizes this bichromophore, localizing the electronic excitation in the S_1 state to the OH-substituted ring. Nevertheless, the two rings, which are separated only by a methylene group, interact strongly with one another. UVHB spectroscopy proves that there is only one conformation of 2bp. The monomer 2bp S_0–S_1 origin is at 36142 cm^{-1}, with long progressions and combination bands involving low-frequency phenyl ring torsions of frequency 29 and 41 cm^{-1}. FDIR spectroscopy was used to determine the frequency of the OH stretch fundamental in both S_0 (3585 cm^{-1}) and S_1 states (3452 cm^{-1}). These wavenumber positions indicate the formation of an OH$\cdots\pi$ H-bond in which the OH group on one ring binds to the π cloud of the other ring. The strength of this H–bond is increased by electronic excitation of the OH-containing phenyl ring. SVLF spectra of the origin band and several members of the torsional progressions have been recorded. Evidence will be presented for strong Duschinsky mixing involving these torsional modes, serving as the starting point for the analysis outlined in part II.