

CONFORMATIONAL ISOMERIZATION OF *bis*-(4-HYDROXYPHENYL)METHANE IN A SUPERSONIC JET EXPANSION. PART II: INTERNAL MIXING AND LOW BARRIER POTENTIAL ENERGY SURFACE IN THE  $S_1$  STATE.

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The close proximity of two identical ultraviolet chromophores render *bis*-(4-hydroxyphenyl)methane (B4HPM) an interesting case for the study of the dependence of excitonic coupling on the distortion along low-frequency large-amplitude vibrational coordinates, in particular the phenol ring torsional coordinates present in B4HPM.

We have studied the fluorescence excitation spectrum, the UV-UV holeburning spectra and several single vibronic level fluorescence spectra of the  $\tilde{A}^1B(S_1) \leftarrow \tilde{X}^1A(S_0)$  and the  $\tilde{B}^1A(S_2) \leftarrow \tilde{X}^1A(S_0)$  transition of all three conformers of B4HPM in a supersonic jet. Excitonic splitting between the two chromophores shifts the second excited state  $S_2 \leftarrow S_0$  by merely  $132\text{ cm}^{-1}$  from the  $S_1 \leftarrow S_0$  origin in both symmetric conformers. The analysis of the dispersed fluorescence spectra of the  $S_2$  origins reveals that these levels are internally mixed with nearby  $S_1$  vibronic levels, providing a fingerprint of the levels involved in the mixing.

The dispersed fluorescence spectra of several low-energy  $S_1 \leftarrow S_0$  vibronic transitions of a specific conformer were taken under systematic variation of the collision frequency in the region where supersonic jet and laser pulse train intersect. These spectra reveal fluorescence contributions from the other two conformers, thus indicating the presence of low-energy conformational barriers ( $\sim 40\text{--}80\text{ cm}^{-1}$ ) in the  $S_1$  state of B4HPM.

