INTERNAL MIXING, PHENYL RING TORSION AND EXCITONIC INTERACTION IN DIPHENYLMETHANE

NATHAN R. PILLSBURY, JAIME A. STEARNS, CHRISTIAN W. MÜLLER, ALOKE DAS, TALITHA M. SELBY and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084*.

The close proximity of two identical ultraviolet chromophores render diphenylmethane (DPM) 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 phenyl ring torsional coordinates present in DPM.
We have studied the fluorescence excitation spectrum and several single vibronic level fluorescence (SVLF) spectra of the $\tilde{A}^1B(\mathrm{S}_1) \leftarrow \tilde{X}^1A(\mathrm{S}_0)$ and the $\tilde{B}^1A(\mathrm{S}_2) \leftarrow \tilde{X}^1A(\mathrm{S}_0)$ transition of DPM cooled in a supersonic jet.
The band in the excitation spectrum blue-shifted by $123\,\mathrm{cm}^{-1}$ from the $\mathrm{S}_1 \leftarrow \mathrm{S}_0$ origin was assigned to the $\mathrm{S}_2 \leftarrow \mathrm{S}_0$ origin. Its SVLF spectrum shows two-region fluorescence reminiscent of that previously observed in the gas-phase and supersonic jet spectra of naphthalene[1] and ovalene[2]. The high-energy region of this S_2 0^0 SVLF spectrum was tentatively assigned to transitions originating in vibrationally excited levels of the S_1 state. This finding indicates the presence of efficient internal mixing of the S_2 0^0 level with the sparse manifold of S_1 vibronic background levels. The quantum number changes in the non-totally symmetric torsional mode (see figure) upon internal mixing suggest that additional to the internal conversion transitions accounted for by the Jortner-Berry $\Delta v = \pm 1$ rule higher order vibronic mechanisms[3] have to be considered as well.

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