

INTERNAL MIXING, PHENYL RING TORSION AND EXCITONIC INTERACTION IN DIPHENYLMETHANE

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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 $\tilde{A}^1B(S_1) \leftarrow \tilde{X}^1A(S_0)$ and the $\tilde{B}^1A(S_2) \leftarrow \tilde{X}^1A(S_0)$ transition of DPM cooled in a supersonic jet.

The band in the excitation spectrum blue-shifted by 123 cm^{-1} from the $S_1 \leftarrow S_0$ origin was assigned to the $S_2 \leftarrow S_0$ origin. Its SVLF spectrum shows two-region fluorescence reminiscent of that previously observed in the gas-phase and supersonic jet spectra of naphthalene¹ and ovalene². 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 mechanisms³ have to be considered as well.

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