EXCITONIC COUPLING AND PHENYL RING TORSION IN DIPHENYLMETHANE

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Diphenylmethane is a simple bichromophore in which two phenyl rings are connected only by a methylene group, giving considerable flexibility in the ring torsion coordinates as well as substantial electronic coupling between the rings. According to DFT calculations, the minimum energy structure has C_2 symmetry with a ring torsion angle near 60°. There are two such minima connected by a C_{2v} structure 176 cm^{-1} higher in energy. The rotationally-resolved fluorescence excitation spectrum of the S_0-S_1 origin indicated a 70% a-type, 30% c-type transition moment, suggestive of an excitonic state in which the zero-order transition moment is rotated significantly from that of toluene. CIS underestimates the a-type character of the band, while time-dependent DFT overestimates it. The ground state experimental rotational constants are consistent with those predicted by DFT. A Franck-Condon progession in the torsional coordinate was observed in the experimental jet-cooled resonant two-photon ionization and dispersed fluorescence spectra. This progression was well-fit using a harmonic Franck-Condon analysis indicating a 3° change in the ring torsion angle upon excitation to S_1. The S_0-S_2 origin was assigned to a vibration 123 cm^{-1} above the S_0-S_1 origin. The dispersed fluorescence spectrum from this transition showed a great deal of activity in low frequency vibrations which were not present in the excitation spectrum, indicating that a vibronic band of the S_1 state may be resonant with the S_0-S_2 origin. To test the effect of asymmetry on the excitonic coupling, the spectroscopy of 4-methyldiphenylmethane has also been studied. Addition of a methyl group to one chromophore completely localizes the electronic excitation, demonstrated by the fact that the two electronic origins are very near those of toluene and *para*-xylene. Dispersed fluorescence from the S_0-S_2 origin showed only S_0-S_1 origin-like emission broadened by IVR, indicative of extremely rapid electronic energy transfer.