CONFORMATIONAL SPECIFIC IVR IN FLEXIBLE BIOMOLECULES

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Dispersed fluorescence spectroscopy has been used to obtain conformation-specific emission spectra of the three observed trans-amide conformers of melatonin (5-methoxy-N-acetyl tryptamine). These three conformers (labeled A-C) differ in the amount of low-frequency vibronic structure observed, with conformer A exhibiting the most (torsional modes at 32, 50, and 62 cm^{-1}), conformer B next (a single mode at 37 cm^{-1}), and conformer C the least (no low frequency modes observed). A Franck-Condon Factor analysis will be presented to establish the geometry changes in the chain accompanying electronic excitation. Melatonin conformer A exhibited complete IVR when a vibronic band 502 cm^{-1} above the S_1 origin was pumped. In this case all observed emission appears in a broadened origin-like emission characteristic of IVR from the ring mode into the low-frequency modes of the chain. Interestingly, when the identical band is pumped in conformer B, sharp bands from the initial level carrying the oscillator strength are observed, and the broadened origin-like emission is much narrower. Both effects indicate that IVR in conformer B is much less efficient than in A, by a factor of ten or more. Analogous conformation-specific IVR data will be presented using tryptamine and 3-indole-propionic acid as model systems. An analysis of the reasons for such dramatic conformation-specific effects on IVR will be discussed.