THE SPECTROSCOPIC CONSEQUENCES OF LOCALIZED ELECTRONIC EXCITATION IN ANTHRANILIC ACID DIMER

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The electronic and infrared spectroscopy of the anthranilic acid (*o*-aminobenzoic acid) dimer has been studied in a supersonic jet. Fluorescence-dip infrared (FDIR) spectra have been obtained in both the ground and first excited electronic states. The ground state FDIR spectrum shows a broad, highly shifted OH stretch absorption commensurate with a cyclic, doubly-hydrogen-bonded structure, as has been observed for other carboxylic acid dimers. The excited state FDIR spectrum shows NH stretch fundamentals that are the sum of the S_0 and S_1 FDIR spectra of the anthranilic acid monomer, indicating that the electronic excitation is localized in one of the monomer subunits in the excited electronic state. The ultraviolet spectrum of the dimer shows a strong Franck-Condon progression involving a 58 cm^{-1} vibration and many combination bands with this mode. Comparison with density functional theory calculations indicates that the 58 cm^{-1} mode involves the in-plane gearing motion of the two monomer units, which has b_u symmetry in the C_{2h} ground state. While this non-totally symmetric fundamental appears in the excitation spectrum, the dispersed fluorescence spectra from the S_1 origin, +58, and +118 cm^{-1} bands produce intensity only in even members of the 58 cm^{-1} progression. This Franck-Condon activity is quantitatively fit by a model in which the excited state vibrations are simple sums and differences of localized, shifted harmonic oscillator vibrational wave functions, producing unresolved a_g/b_u tunneling doublets associated with the large barrier that separates the two minima on the excited state surface.