

MULTI-FACETED SPECTROSCOPIC STUDY OF THE STRUCTURAL CHANGES ASSOCIATED WITH ELECTRONIC EXCITATION OF METHYL ANTHRANILATE

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Methyl anthranilate (MA) is the methyl ester of anthranilic acid. We present the jet-cooled Laser Induced Fluorescence (LIF) UV excitation spectrum, ground (S_0) and excited state (S_1) Fluorescence Dip Infrared (FDIR) spectra, IR-UV Holeburning (IR-UV HB) spectra, and Dispersed Fluorescence (DFL) spectra of the MA monomer and MA- H_2O complex. MA is a close analog of salicylic acid, a well-studied molecule thought to undergo keto-enol tautomerism involving excited state H-atom transfer. In the MA monomer, the C6 ring formed by the $H_aNH_b \cdots O=C$ hydrogen bond in the ground state undergoes an unusual increase in hydrogen bond strength following electronic excitation to the S_1 state. This is evident in the spectroscopy in several ways. The LIF excitation and DFL spectra both show long progressions in several modes involving motion of the NH_2 and COOMe groups relative to one another. Furthermore, the coupled NH_2 symmetric and asymmetric stretch fundamentals appear to uncouple upon UV excitation, giving rise to a broadened (8 cm^{-1} FWHM), nominally “free” $N-H_a$ stretch at 3458 cm^{-1} and an $N-H_b$ stretch shifted all the way down to $\sim 2900\text{ cm}^{-1}$. FDIR spectra collected in the mid-IR frequency range show the change in hydrogen bond strength from the perspective of the C=O acceptor group, where the stretch fundamental is shifted down from its S_0 position at 1721 cm^{-1} to 1637 cm^{-1} in S_1 . Calculations at the B3LYP-D3/def2TZVP level of theory in large measure capture these frequency shifts and give insight into likely explanations for such drastic changes. Similar behavior is observed in the MA- H_2O complex, although the extent of the hydrogen bond strengthening in the S_1 state is modulated by the HOH interactions with both the NH_2 and C=O groups.