NON-LINEAR OPTICAL SPECTROSCOPY AS A PROBE OF PROTON-TRANSFER DYNAMICS IN THE $\tilde{A}^1$ B_1 STATE OF MALONALDEHYDE

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Intramolecular proton transfer and hydrogen bonding are ubiquitous processes, occurring in nearly all realms of biology and chemistry. The model compound for the investigation of such phenomena is malonaldehyde, a molecule whose gas-phase species exists predominately as a chelated enol tautomer with a finite barrier of 2000 cm^{-1}height separating two equivalent planar geometries. Numerous theoretical and experimental studies have shown that rapid interconversion between these equilibrium conformers can occur by means of quantum mechanical proton tunneling, thereby leading to a characteristic doubling of all rovibrational features within the $\tilde{X}^1\mathrm{A}_1$ ground potential surface. In contrast, very little information is available on the electronically excited states of malonaldehyde. Linear absorption measurements have revealed a weak, highly structured $\pi^* \leftarrow n$ absorption system in the vicinity of 354 nm which has been assigned to an $\tilde{A}^1\mathrm{B}_1(\mathrm{n}\pi^*)$ excited state. A prominent vibronic progression built upon an excited state in-plane skeletal vibration of 185 $\mathrm{cm}^{-1}$was identified; moreover, all members of this progression exhibited a splitting of $\sim 7\ \mathrm{cm}^{-1}$. Sub-Doppler Degenerate Four-Wave Mixing (DFWM) spectroscopy has been used to interrogate malonaldehyde and its symmetrically deuterated isotopomer under ambient bulk-gas conditions. Gross features are in reasonable agreement with the prior medium resolution linear absorption measurements. The same 185 cm^{-1}progression is observed; however, all members exhibit a pronounced splitting of $\sim 19\ \mathrm{cm}^{-1}$with isotopic substitution affirming the tunneling-induced nature of these doublets. This splitting has been interpreted previously as overlapping type-*c* transitions indicative of a decrease in tunneling efficiency upon electronic excitation. Assuming the same interpretation to hold, the four-wave mixing data sets would suggest an enormous increase in the height and/or width of the proton transfer barrier supported by the $\tilde{A}^1\mathrm{B}_1$ manifold. DFWM spectra acquired for the two malonaldehyde isotopomers, as well as their corresponding weak-field spectral simulations, will be discussed in conjunction with results obtained from high level *ab initio* calculations.