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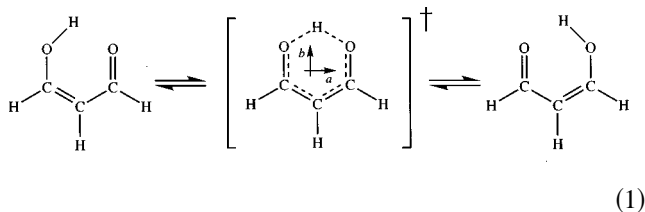
Angela A. Arias, Thierry A. W. Wasserman, and Patrick H. Vaccaro^{a)}

Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520-8107

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The dynamics of proton transfer in the first excited singlet state of malonaldehyde [$\tilde{A}^1B_1(\pi^*n)$] have been investigated through the use of high-resolution degenerate four-wave mixing spectroscopy. Observed $\tilde{A}^1B_1-\tilde{X}^1A_1(\pi^*\leftarrow n)$ rovibronic features are at odds with previous absorption measurements and cannot be explained readily through the accepted description of tunneling behavior within the $\tilde{A}^1B_1(\pi^*n)$ potential surface. © 1997 American Institute of Physics. [S0021-9606(97)02338-6]

The interrelated phenomena of hydrogen bonding and proton transfer represent two important aspects of molecular behavior which play crucial roles in a wide variety of chemical and biological processes.¹ The model system for the investigation of these concepts has been malonaldehyde, the most stable isomer of 3-hydroxy-2-propenal, which contains an intramolecular hydrogen bond that adjoins hydroxylic (i.e., proton donor) and ketonic (i.e., proton acceptor) oxygen atoms. As demonstrated conclusively by the pioneering studies of Wilson and co-workers,^{2,3} the isolated gas-phase molecule exists almost completely as the chelated (planar) enol tautomer²⁻⁵ with a finite barrier, having an estimated height⁵ of 2000 cm⁻¹, separating two stable conformers of C_s symmetry.^{6,7}



Although hindered, rapid interconversion between these equivalent structures can occur through quantum mechanical proton tunneling. This leads to a characteristic doubling of all rovibrational features,^{2,7} with the recent far-infrared work of Firth *et al.*⁵ providing the most refined estimate for the tunneling-induced splitting between the $0^+(a_1)$ and $0^-(b_2)$ components of the vibrationless (zero-point) level in the \tilde{X}^1A_1 ground electronic state: $\Delta E_{01} = 21.584\,76(17)$ cm⁻¹. Rather than depending solely on the motion of the “shuttling” proton along the O–H···O coordinate, the magnitude of such spectral splittings contains information regarding the concomitant displacement of all other nuclei in the molecular framework⁸ as well as the redistribution of charge density among the various atoms.^{9,10} Consequently, vibrational and/or electronic excitation can be expected to have a pronounced effect upon the overall efficiency and detailed pathway of proton migration. This communication describes the use of nonlinear degenerate four-

wave mixing (DFWM) spectroscopy as a probe of proton-transfer dynamics exhibited by the first excited singlet state [$\tilde{A}^1B_1(\pi^*n)$] of malonaldehyde.

In contrast to the wealth of experimental and theoretical information that exists for the \tilde{X}^1A_1 potential surface, very little work has been reported on electronically excited malonaldehyde. In the near-ultraviolet region of the spectrum, Seliskar and Hoffmann^{11,12} have identified a weak, highly structured absorption system which stems from a $\pi^*\leftarrow n$ electron promotion. These authors proposed the pertinent excited state to be of 1B_1 symmetry, with the corresponding $\tilde{A}^1B_1-\tilde{X}^1A_1$ transition moment directed orthogonal to the molecular plane [i.e., a type-*c* transition as per Eq. (1)]. The origin band, assigned to a prominent feature at $\sim 28\,273$ cm⁻¹ (~ 354 nm), was found to exhibit a splitting of roughly 7 cm⁻¹ magnitude. Isotopic substitution studies led Seliskar and Hoffmann to conclude that this spectral bifurcation arises from a decrease in the separation of tunneling doublets (i.e., heightening of effective proton-transfer barrier) upon electronic excitation. Two strong vibronic progressions built on excited state frequencies of 185 and 1300 cm⁻¹ were attributed to in-plane skeletal bending and carbonyl stretching modes, respectively. Each member of these progressions, as well as those ascribed to other $\tilde{A}^1B_1(\pi^*n)$ vibrations, displayed a similar doubling of vibronic structure. Absorption measurements¹³ performed on cyclohexane/malonaldehyde mixed crystals at 30 K corroborate many of these findings but provide no evidence of proton tunneling, an effect attributed to the quenching of hydrogen migration by host/guest interactions. More recently, *ab initio* investigations of malonaldehyde by Luth and Scheiner¹⁴ have cast doubts on the interpretation of previous spectroscopic studies by predicting a *negative* barrier height for the $^1\pi^*\leftarrow n$ excited state. The existence of such a “single-minimum” potential well along the O–H···O coordinate would require the equilibrium geometry of the $\tilde{A}^1B_1(\pi^*n)$ surface to display symmetric displacement of the “shuttling” proton between the two oxygen atom centers.

A thorough understanding of proton-transfer dynamics in $\tilde{A}^1B_1(\pi^*n)$ malonaldehyde requires that rovibronic structure of the $\pi^*\leftarrow n$ transition be examined under high-resolution conditions. Unfortunately, this molecular system

^{a)} Author to whom all correspondence should be addressed.

has not proven amenable to interrogation by conventional laser spectroscopy, with no laser-induced fluorescence signal detected upon excitation of the 354 nm origin band. While traditional (linear) absorption methods provide a viable means for accomplishing such measurements,^{11–13} the overall utility of this approach is limited by the small $\tilde{A}-\tilde{X}$ oscillator strength and the requirement for high spectral resolution. As demonstrated by studies conducted in our laboratory^{15–17} and at other facilities,^{18–20} nonlinear optical techniques built upon the concepts of four-wave mixing^{21,22} can provide an absorption-based probe of molecular structure and dynamics which combines trace sensitivity and laser-limited resolution with general species applicability.

DFWM spectroscopy makes use of three intersecting optical fields which have identical (or degenerate) frequency ω but are otherwise distinguishable owing to their unique spatial and polarization characteristics.^{16,18,21} Coupled by strong nonlinear interactions within a target medium, these input waves give rise to a fourth output (or signal) beam which energy conservation requires also to be of frequency ω . The polarization properties and direction of propagation for the signal field follow from similar conservation criteria,²² with judicious selection of experimental geometry enabling the emerging signal photons to be isolated spatially and detected sensitively through various polarization-selective schemes. Since resonant excitation of allowed molecular transitions leads to an enormous enhancement in signal production efficiency, DFWM provides an essentially background-free means for recording “absorptionlike” spectra.

Tunable ultraviolet light was generated by frequency doubling the ~ 700 nm output of a Nd:YAG-pumped dye laser which could be operated both with and without an intracavity etalon so as to produce measured (fundamental) bandwidths of ≤ 0.03 and ≤ 0.13 cm^{-1} , respectively. The ~ 350 nm radiation was spatially filtered and recollimated before being separated into three beams of roughly equal intensities destined to become the input waves for a backwards-box implementation of the DFWM process.^{17,23} This scheme requires that the incident electromagnetic waves be directed through the target medium along three distinct diagonals of a rectangular parallelepiped (or box) with the signal constrained to emerge along the “dark” axis of detection defined by the remaining diagonal. The use of small crossing angles yields a nearly coaxial arrangement of counterpropagating beams that maximizes the DFWM interaction volume and imparts sub-Doppler spectral resolution.^{18,21} Following traversal of polarization, spectral, and spatial filters, the collected signal photons impinged upon an uncooled photomultiplier tube. The resulting photocurrent was amplified and sent to a gated integrator system that enabled the DFWM spectrum to be recorded as a function of laser frequency. Observed rovibronic features were shown to be unsaturated^{21,24} for all optical powers utilized in the present work (≤ 150 $\mu\text{J}/\text{pulse}$ in each 0.3 cm diameter beam) and active normalization of the DFWM response by the cube of incident pulse energy^{16,21} served to minimize signal fluctuations. Malonaldehyde was synthesized²⁵ by acid-catalyzed hydrolysis of tetramethoxypropane and stored as a sodium

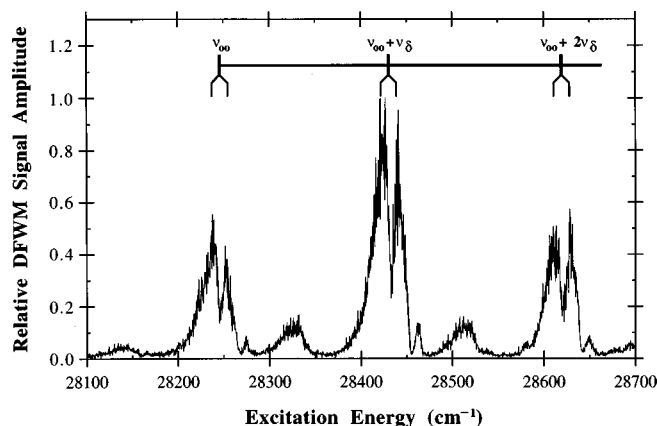


FIG. 1. DFWM spectroscopy of the nonfluorescing malonaldehyde molecule. A backwards-box DFWM configuration incorporating a polarization-selective detection scheme was used to probe the lowest-lying features in the malonaldehyde $\tilde{A}^1B_1-\tilde{X}^1A_1(\pi^* \leftarrow n)$ absorption spectrum. These data were acquired under ambient bulk-gas conditions with an excitation source having an estimated bandwidth of 0.2 cm^{-1} . The highlighted $\nu_\delta \approx 185$ cm^{-1} vibronic progression builds upon the ν_{00} origin band and has been attributed (Ref. 12) to an in-plane skeletal vibration of a_1 symmetry in the $\tilde{A}^1B_1(\pi^*n)$ excited state.

salt that could be protonated to yield the desired monomeric material. The sample vessel consisted of a ~ 1 m glass tube having fused silica windows mounted upon O-ring seals at both ends. Malonaldehyde pressures were maintained in the 300–600 mTorr range as measured by a capacitance manometer.

The DFWM spectrum in Fig. 1 depicts the lowest-lying features in the malonaldehyde $\tilde{A}^1B_1-\tilde{X}^1A_1$ system and was obtained under ambient bulk-gas conditions with an excitation source having an ultraviolet bandwidth of ~ 0.2 cm^{-1} . The gross structure revealed by this measurement is found to be in reasonable accord with that reported in the long-path-length (50–100 m), medium-resolution (~ 5 cm^{-1}) absorption studies of Seliskar and Hoffmann.¹² The vibronic assignments postulated by these authors would attribute the most pronounced peaks to a $\nu_\delta \approx 185$ cm^{-1} progression which starts from the ν_{00} origin band at roughly 28 250 cm^{-1} (vacuum corrected) and builds upon monotonically increasing quanta of an a_1 in-plane skeletal vibration. As demonstrated by the high-resolution trace in Fig. 2, much of the “noise” observed on the four-wave mixing signal stems from spectral congestion caused by overlapping rovibronic transitions. Assuming the narrowest linewidths to reflect pure homogeneous broadening processes, a lower limit of ≥ 10 ps can be placed on the lifetime of the excited state.²⁶

All members of the ~ 185 cm^{-1} progression in Figs. 1 and 2 exhibit a pronounced bifurcation of their vibronic band contours. The measured energy separations have a near-constant value of roughly 19 cm^{-1} which is to be contrasted with the ~ 7 cm^{-1} splittings observed in previous linear absorption studies.¹² In particular, by attributing such spectral patterns to the pair of type-*c* transitions expected to occur between the vibrationless tunneling doublet of the \tilde{X}^1A_1

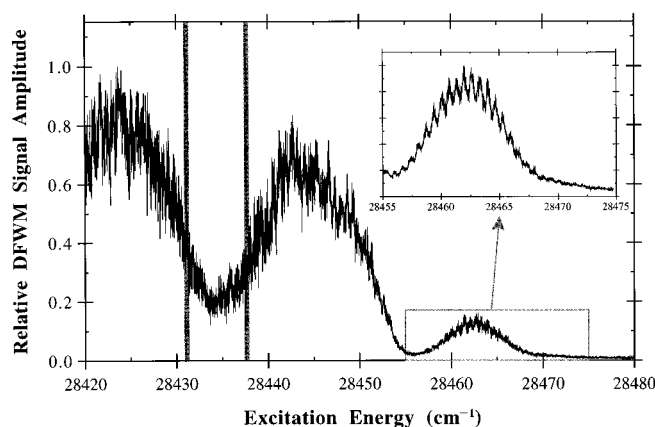


FIG. 2. High-resolution DFWM spectroscopy of malonaldehyde. An excitation source of ~ 0.045 cm^{-1} bandwidth was used to examine the second member (viz., $\nu_{00} + \nu_s$) of the 185 cm^{-1} vibronic progression depicted in Fig. 1 under higher spectral resolution. The pair of gray bars at $28\,430.9$ and $28\,437.4$ cm^{-1} denotes the (vacuum corrected) position of tunneling-doublet features reported in previous linear absorption measurements (Ref. 12). The inset shows unmistakable evidence of rotational fine structure with observed widths for the narrowest spectral features placing a lower limit of ≥ 10 ps on the lifetime of the $\tilde{A}^1B_1(\pi^*n)$ state (Ref. 26).

ground state and the tunneling-split levels of an a_1 vibration in the $\tilde{A}^1B_1(\pi^*n)$ excited state:

$$\begin{aligned} 0^+(\tilde{A}^1B_1; a_1) &\xleftarrow{c} 0^+(\tilde{X}^1A_1; a_1), \\ 0^-(\tilde{A}^1B_1; b_2) &\xleftarrow{c} 0^-(\tilde{X}^1A_1; b_2), \end{aligned} \quad (2)$$

Seliskar and Hoffmann¹² concluded that a ~ 7 cm^{-1} decrease in the separation of tunneling doublets (from ~ 21.6 to ~ 14.6 cm^{-1}) accompanies the $\pi^* \leftarrow n$ electron promotion. Assuming the same interpretation to hold, the four-wave mixing data sets would indicate that tunneling-induced splitting of the $\tilde{A}^1B_1(\pi^*n)$ state is reduced to barely 2.5 cm^{-1} , thereby suggesting a substantial increase in the height and/or width of the proton-transfer barrier supported by the electronically excited potential surface. As a point of comparison, \tilde{X}^1A_1 energy gaps on the order of 3 cm^{-1} have been reported³ for the vibrationless tunneling doublets of malonaldehyde isotopomers in which the migrating hydrogen is replaced by a deuterium atom.

Aside from the substantially higher resolution employed in the present work, a partial explanation for the apparent discrepancies noted between DFWM and absorption spectra of malonaldehyde might reside in the nonlinear nature of the resonant four-wave mixing process. In contrast to the $N|\mu|^2$ scaling exhibited by the vast majority of (linear) spectroscopic probes, the weak-field DFWM response has a characteristic $N^2|\mu|^8$ dependence on state-specific number density (N) and transition dipole moment (μ).^{16,21,27} This behavior, in conjunction with the additional spectral discrimination afforded by a sub-Doppler, polarization-based detection scheme,^{17,23} might lead to intensity patterns that depart significantly from those obtained through linear techniques.

However, such effects can be interpreted fully and under appropriate circumstances can be exploited for the assignment of observed rovibronic features.

Assuming that both electronic potentials in the $\tilde{A}-\tilde{X}$ system support double minimum wells along the $\text{O}-\text{H}\cdots\text{O}$ coordinate, the 19 cm^{-1} energy gaps highlighted Figs. 1 and 2 should represent the *difference* in tunneling-induced splitting between the pertinent vibrational levels of the ground and excited states. The spectral interpretations of Seliskar and Hoffmann¹² stem from the chemically intuitive consequences of an isolated $\pi^* \leftarrow n$ resonance where promotion of an electron from the nonbonding “lone-pair” orbital of the carbonyl moiety leads to a net removal of negative charge density from the ketonic oxygen atom which, in turn, diminishes its ability to act as a proton acceptor. Based upon this localized first-order description of electronic structure, a decrease in hydrogen bond strength would be anticipated subsequent to the $\tilde{A}^1B_1-\tilde{X}^1A_1$ transition, with the energy barrier separating chelated asymmetric forms of malonaldehyde increasing in overall magnitude. However, given the *ab initio* predictions of Luth and Scheiner,¹⁴ it is interesting to speculate that the $\tilde{A}^1B_1(\pi^*n)$ proton-transfer barrier is negligibly small. Under such circumstances, analysis of our DFWM measurements in terms of c -polarized bands would require an *increase* in tunneling-doublet separation from the vibrationless \tilde{X}^1A_1 value⁵ of $\Delta E_{01} \approx 21.6$ cm^{-1} to approximately 40 cm^{-1} in the excited state. Further corroboration for this assertion follows from the recorded pattern of intensities in the room-temperature malonaldehyde spectrum. Provided that the two type- c transitions connecting tunneling-split vibronic states [cf. Eq. (2)] have near-identical rotational contours and Franck-Condon factors, the quadratic number density dependence of DFWM requires features originating from the $0^-(b_2)$ level to exhibit roughly 80% of the amplitude carried by the corresponding $0^+(a_1)$ resonances. The high-resolution four-wave mixing data of Fig. 2 display this expected ratio of peak intensities, thereby permitting the structures at $\sim 28\,424$ and $\sim 28\,443$ cm^{-1} to be identified as the $1^+ \leftarrow 0^+$ and $1^- \leftarrow 0^-$ transitions, respectively, where the \tilde{A}^1B_1 terminal levels nominally possess one quantum of excitation in an a_1 vibrational mode. The relative location of such vibronic bands indicates that an increase in tunneling-doublet separation (or decrease in proton-transfer barrier) must accompany the $\pi^* \leftarrow n$ process.

If *ab initio* predictions¹⁴ of a negative proton-transfer barrier in the $\tilde{A}^1B_1(\pi^*n)$ surface are correct, a well-spaced manifold of vibrational levels will exist along the $\text{O}-\text{H}\cdots\text{O}$ coordinate and a mechanism that does not invoke tunneling-induced doubling of rovibronic structure within the excited electronic state would be required to account for the observed splitting of vibronic features. In this case, a plausible explanation for our DFWM measurements might reside in the guise of rotational band contours incurred through a conspiracy of insufficient spectral resolution and extreme rovibronic congestion. While type- c transitions are dominated by a single pronounced feature that stems primarily from overlapping Q -branch lines, DFWM simulations suggest that

type-*a/b* band contours will exhibit two distinct clumps of unresolved rovibronic structure separated fortuitously by gaps of 18–20 cm⁻¹. Since the weak $\tilde{A}^1B_1-\tilde{X}^1A_1$ system is electric dipole allowed only under type-*c* selection rules, the presence of *a*-polarized and *b*-polarized bands would implicate a Herzberg–Teller vibronic coupling mechanism²⁸ which, as well documented for the analogous $\tilde{A}^1A_2-\tilde{X}^1A_1(\pi^*\leftarrow n)$ spectrum of formaldehyde,²⁹ causes mixing of electronic parentage among neighboring states. For malonaldehyde, intense $\pi^*\leftarrow\pi$ absorption features assigned to the $\tilde{B}^1B_2-\tilde{X}^1A_1$ and $\tilde{C}^1A_1-\tilde{X}^1A_1$ resonances have been reported¹¹ in the vicinity of 4.5 and 5.9 eV. Admixture of $\tilde{B}^1B_2(\pi^*\pi)$ and $\tilde{C}^1A_1(\pi^*\pi)$ character into the $\tilde{A}^1B_1(\pi^*n)$ manifold will be mediated by vibrations of *a*₂ and *b*₁ symmetry, thereby resulting in the appearance of *a*-polarized and *b*-polarized features. The bifurcated vibronic profiles of Fig. 1 could thus signify involvement of a transition moment component residing in the molecular plane, however, this interpretation would require the highlighted progression to be attributed to odd quanta of excitation in an antisymmetric \tilde{A}^1B_1 mode that has an unusually low frequency of <100 cm⁻¹.

In summary, high-resolution DFWM spectroscopy has been used to probe the first excited singlet state [$\tilde{A}^1B_1(\pi^*n)$] of malonaldehyde under bulk-gas conditions. Recorded $\tilde{A}^1B_1-\tilde{X}^1A_1$ vibronic features exhibit the same general patterns revealed by previous medium-resolution (linear) absorption measurements,¹² however, tunneling-related structures documented in these prior investigations are not reproduced. At this juncture, the pronounced ~19 cm⁻¹ splittings uncovered by our studies can most directly be attributed to a substantial increase in tunneling doublet separation or decrease in effective proton transfer barrier upon $\pi^*\leftarrow n$ excitation, a conclusion in accord with the trends suggested by recent *ab initio* predictions.¹⁴ Extension of this effort to a molecular beam environment is currently underway, as is a parallel investigation designed to examine the effects of malonaldehyde deuteration on the four-wave mixing spectrum. This work, as well as the results of ongoing electronic structure calculations and polarization-selective DFWM spectral simulations, will be reported in a forthcoming publication.

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