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Microwave Spectroscopic Study of Malonaldehyde (3-Hydroxy-2-propenal). 2. Structure, Dipole Moment, and Tunneling

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Abstract: The microwave rotational spectra of malonaldehyde and a number of its isotopic forms have been investigated. In the vapor phase the molecule is found to exist in a planar, intramolecularly hydrogen-bonded form with two equivalent, individually asymmetric equilibrium configurations between which tunneling occurs. The data indicate that the hydrogen bond may be described by a double-minimum potential function. The large amplitude tunneling motion complicates structure determination, but with use of symmetrically substituted isotopic species and asymmetrical species in which the tunneling is believed to be quenched, a modified r_s structure has been obtained. Dipole moment measurements of several isotopic species are also reported. The effect of tunneling and of various degrees of quenching of tunneling on the dipole moment is demonstrated and interpreted. From relative intensity measurements the tunneling energy separation of the normal isotopic species was calculated to be 26 ± 10 cm^{-1}. Far-infrared observations showed an absorbtion band near 21 cm^{-1}. Rotation–vibration interactions were observed which perturb the rotational spectra of a number of isotopic species.

A brief report[2] has appeared on a microwave spectroscopic study of the structure and nature of the hydrogen bond in the six-membered ring compound malonaldehyde (3-hydroxy-2-propenal). It was shown that in the vapor phase the molecule occurs in the internally hydrogen bonded form (see Figure 1) and that it is planar or essentially planar. A 3:1 intensity ratio was observed between states with different $K_{-1} + K_{+1}$ parity, where K_{-1} and K_{+1} are the limiting prolate and oblate rotational quantum numbers. A second set of rotational transitions, almost as strong as those of the ground vibrational state but with opposite nuclear spin weight, was also measured. From the observation of alternating intensities and the existence of two spectra of nearly the same average intensities but opposite nuclear spin weights, it was inferred that the molecule exists in two equivalent forms shown in Figure 1A, B, so that the proton (atom 6) is rapidly tunneling between the two equilibrium configurations shown. The symmetric configuration, C of Figure 1, represents a transition state of higher energy between the two energy minima. There are various ways to define an "effective" one-dimensional potential function for this large amplitude tunneling motion of the proton. This potential was found to have the double-minimum form shown in Figure 2. The variable x is approximately the displacement of the hydrogen atom 6 in the a direction shown in Figure 1.

Microwave spectra of 2-methylmalonaldehyde[3] and 2-nitromalonaldehyde[4] showed additional effects arising from hindered rotation about the C–X bond (where X is CH_3 or NO_2). With CH_3, the tunneling of the hydrogen was coupled with this rotation.

The main aim of this paper[5] (hereafter called paper 2) is to obtain a reasonably complete and fairly accurate quantitative molecular structure which can be compared with various ab initio quantum chemical calculations.[8-10] Evidence will be presented to support the conclusion that the proton tunneling is largely quenched in certain unsymmetrical isotopic species and partially quenched in others. Part of the evidence for this conclusion comes from an analysis of the dipole moment in tunneling and in nontunneling species. Finally, the nontunneling species will be used to determine most of the structural parameters without the complications introduced by tunneling. A more quantitative discussion of the rates of tunneling, the reaction path, and estimates of barrier height as well as consideration of excited vibrational states will be published later (paper 3). For a review of the earlier experimental and theoretical work on malonaldehyde see ref 6b.

To designate isotopic species, we will show the isotopic atoms which replace the normal ones at specified positions in parentheses, and a subscript will be used to indicate the atomic positions as shown in Figure 1. For example, (D_6) denotes monodeuterated malonaldehyde where deuterium is in the hydrogen bond. (D_{7-9}) denotes a tunneling mixture of (D_7) and (D_9).

Experimental Section

Most of the frequency measurements were made in the 8–40-GHz region, using a HP 8460A Stark modulated microwave spectrometer with phase-lock stabilized backward wave oscillators as frequency sources. Measurements were also made in the 7.5–8.0-GHz range by phase locking and sweeping a Polarad 3.8–8.2-GHz signal source. Rotational transitions of the normal isotopic species in the 55–113-GHz range were measured at the National Bureau of Standards by using a 80-kHz Stark modulated spectrometer with a 30-cm long parallel plate absorption cell. For these experiments, thermally stabilized klystrons[11] with a reported short-term stability of 1 part in 10^7 were used as microwave sources. Frequency measurements were usually made at a pressure of about 10 mtorr of malonaldehyde to minimize pressure broadening of the line.

Some of the assignments of rotational quantum numbers were confirmed by frequency-modulated microwave–microwave double resonance[12] and by amplitude-modulated radio frequency–microwave double resonance.[13] Revised relative intensity measurements were made[6b] on the normal isotopic species of malonaldehyde employing the method of Esbitt and Wilson.[14] Dipole moment measurements were made in the usual manner with the Stark effect.[15] The Stark septum was calibrated by using the dipole moment of OCS as a standard.[16]

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[2] W. F. Rowe, Jr., R. W. Duerst, and E. B. Wilson, *J. Am. Chem. Soc.*, **98**, 4021 (1976). Hereafter called paper 1.

[3] N. D. Sanders, *J. Mol. Spectrosc.*, **86**, 27 (1981).

[4] W. Caminati, private communication.

[5] The work presented here was taken partly from the Harvard Ph.D. theses of W. F. Rowe[6a] and S. L. Baughcum[6b] and is not presented in the same order as it was carried out. The study of malonaldehyde was suggested by Dr. H. M. Pickett, who earlier examined the more complicated hydrogen-bonded compound 6-hydroxy-2-formylfulvene in which he found the proton to be in a single-minimum symmetrical potential function.[7]

[6] (a) W. F. Rowe, Jr., Ph.D. Thesis, Harvard University, 1975. (b) S. L. Baughcum, Ph.D. Thesis, Harvard University, 1978.

[7] H. M. Pickett, *J. Am. Chem. Soc.*, **95**, 1770 (1973).

[8] J. E. Del Bene and W. L. Kochenour, *J. Am. Chem. Soc.*, 98, 2041 (1976).

[9] G. Karlstrom, B. Jonsson, B. Roos, and H. Wennerstrom, *J. Am. Chem. Soc.*, **98**, 6851 (1976).

[10] W. J. Bouma, M. A. Vincent, and L. Radom, *Int. J. Quantum Chem.*, **14**, 767 (1978).

[11] D. R. Johnson and R. Pearson, Jr., "Methods of Experimental Physics", Vol. 13, Part B, D. Williams, Ed., Academic Press, New York, 1976.

[12] R. C. Woods, A. M. Ronn, and E. B. Wilson, *Rev. Sci. Instrum.*, **37**, 927 (1966).

[13] F. J. Wodarczyk and E. B. Wilson, *J. Mol. Spectrosc.*, **37**, 445 (1971).

[14] A. S. Esbitt and E. B. Wilson, *Rev. Sci. Instrum.*, **34**, 901 (1963).

[15] J. E. Wollrab, "Rotational Spectra and Molecular Structure", Academic Press, New York, 1967, Chapter 8.

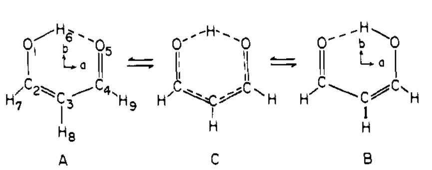

Figure 1. Hydrogen-bonded, tunneling structures of malonaldehyde: A and B, two equivalent equilibrium configurations of malonaldehyde; C, symmetric transition-state structure.

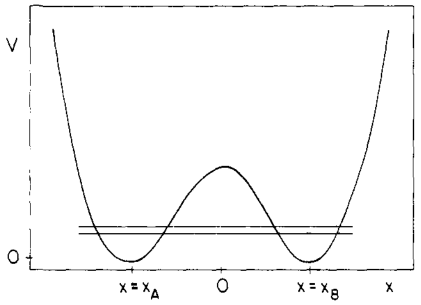

Figure 2. Double minimum potential, V, of malonaldehyde, showing two lowest tunneling states. x is approximately the displacement of H_6 in the a direction.

Malonaldehyde was prepared by hydrolysis of the acetal followed by reaction with sodium hydroxide to form the sodium salt, which was treated with anhydrous hydrogen chloride in ether to yield malonaldehyde.[17,18] The malonaldehyde was then purified by vacuum sublimation. The (D_6D_8) isotopic form of malonaldehyde was prepared by chemical exchange with D_2O previously absorbed onto the walls of the absorption cell. The (D_6) and (D_8) monodeuterated forms of malonaldehyde were prepared similarly by using a mixture of 50% H_2O and 50% D_2O. Isotopic substitution of the oxygen atoms was accomplished by acid hydrolysis of 1,1,3,3-tetramethoxypropane by using ^{18}O-labeled water (80.75% ^{18}O by weight) or ^{17}O-enriched water (20% ^{17}O and 36.8% ^{18}O) followed by gas chromatographic purification at 85 °C on a 60-cm copper column packed with Porapak Q. This purification procedure furnishes an average yield of greater than 20% of the compound by weight. (D_7) malonaldehyde was prepared as follows: First, deuteriotrimethylorthoformate was synthesized by a modification of an existing synthesis for triethylorthoformate.[19] Then the 1-deuterio-1-ethoxy-1,3,3-trimethoxypropane was prepared by the method of Skoldinov,[20] using the previously prepared deuteriotrimethylorthoformate and ethyl vinyl ether. The resulting 1-deuterio-1-ethoxy-1,3,3-trimethoxypropane was purified by gas chromatography at 175 °C on the previously described column and then acid hydrolyzed and purified by gas chromatography as described above.

For the ^{13}C species, the general scheme was to heat, with a torch, a closed tube containing a mixture of amorphous carbon (enriched with ^{13}C) and calcium to form calcium carbide. The calcium carbide was then reacted with either water or deuterium oxide to yield acetylene.[21] The acetylene was reacted with methanol under high pressure to furnish methyl vinyl ether. At this stage of the synthesis, the reactions were similar to those utilizing ethyl vinyl ether. ($^{13}C_2$) was prepared from ^{13}C chloroform utilizing the orthoformate as an intermediate.

The far-infrared spectrum of gaseous malonaldehyde was measured on the Nicolet 7000 Fourier Transform infrared spectrometer using a 20-m cell and 25-μm beam splitter.

Analysis of Data

1. Assignment of Microwave Spectra. Malonaldehyde is a very asymmetric prolate top ($\kappa = -0.44$) which complicates the analysis, particularly when rotation–vibration interactions perturb the spectrum. The molecule has a large μ_b dipole moment and exhibits a strong b-type rotational spectrum. Microwave spectra for a large number of isotopic species of malonaldehyde were observed, and each spectrum was assigned to a particular isotopic isomer. Further, ground and several excited states were identified. Standard methods were used for making these assignments including predictions from a plausible structure based on both prior calculations[8,9] and on an electron diffraction structure of acetylacetone.[22] Alternating intensities, Stark patterns, microwave–microwave, and radio frequency–microwave double resonance were also employed. These techniques were needed because often very small amounts of the samples were available, and these samples frequently were mixtures of several (up to 10) isotopic species.

The low J transitions fit quite well to a simple rigid rotor model for a number of isotopic species. Where enough transitions were measured and perturbations were not severe, centrifugal distortion terms were included in the analysis by using Watson's form.[23,24] In certain cases large perturbations were observed due to Coriolis coupling between the near degenerate rotational levels of the two low lying tunneling states. These will be discussed in paper 3 and used to determine the tunneling splitting accurately. See also ref 6b.

The observed frequencies and their quantum number assignments are available as supplementary material. The rotational constants A, B, and C, which were determined from least-square analyses of the spectra, are given in Table I for the species studied. The inertial defect $\Delta I = (I_C - I_A - I_B)$ of malonaldehyde was found to be nearly zero, indicating that the molecule is essentially planar (see Table II).

2. Approximate Wave Function, Spin Weights, and Tunneling. We can approximate the wave function for the molecule by a product of a vibrational function ψ_V, a rotational factor ψ_R, and a nuclear spin factor ψ_S.

$$\psi = \psi_V\psi_R\psi_S \tag{2.1}$$

By the Pauli principle the overall wave function ψ for the normal isotopic species must be converted to $-\psi$ by the simultaneous exchange of the two oxygens 1 and 5, the two carbons 2 and 4, and the two hydrogens 7 and 9, i.e. by the application of the permutation $C'_2 = (15)(24)(79)$. The four nuclear spin functions (due to the two hydrogens 7 and 9) give spin weights of 3 for the symmetric case and a spin weight of 1 for the antisymmetric case, as with ortho–para hydrogen. The permutation only changes the labels on otherwise indistinguishable nuclei; hence it has no effect on the directions of the principal axes of inertia of the molecule, which will be used here to define the molecular axes. However, if we choose to define the positive direction of the a axis (axis of least inertia) as being toward atoms 4 and 5, the permutation will reverse the direction of a and hence has the same effect on the Eulerian angles defining the orientation of these principal axes as rotating the molecule-fixed axes by π about the intermediate axis b (c flips by π also to maintain a right-handed system). This rotation is known to change the sign of ψ_R if $K_{-1} + K_{+1}$ is odd, and it sends ψ_R into itself if $K_{-1} + K_{+1}$ is even.[25]

The vibrational factor ψ_V can also be affected by C'_2. Perhaps the simplest approximation for ψ_V is constructed by first obtaining the ordinary product of harmonic oscillator functions of the normal coordinates appropriate for small displacements about the equilibrium configuration A of Figure 1. Next the equivalent set for the other equilibrium configuration B of Figure 1 is similarly constructed. Finally, plus and minus linear combinations are formed.

$$\psi_{V\pm} \approx \psi_V(\mathrm{A}) \pm \psi_V(\mathrm{B}) \tag{2.2}$$

The permutation C'_2 will interchange the equilibrium configurations A and B, and hence the vibrational energy levels should occur in pairs, one symmetric and the other antisymmetric. For the lower levels these pairs should have a quite small energy separation, called the tunneling splitting.

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[16] J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

[17] R. Huttel, *Chem. Ber.*, **74**, 1825 (1941).

[18] E. J. J. Grabowski and R. L. Autrey, *Tetrahedron*, **25**, 4315 (1969).

[19] W. E. Kaufman and E. E. Dreger, "Organic Syntheses", Collect. Vol. **1**, Wiley, New York, 1941, p 258.

[20] A. P. Skoldinov, *Zh. Obshch. Khim.*, **27**, 57 (1957).

[21] M. D. Freeberg, D. K. Hsu and R. W. Duerst, *J. Labelled Compds Radiopharm.*, in press.

[22] A. L. Andreassen and S. H. Bauer, *J. Mol. Struct.*, **12**, 381 (1972).

[23] J. K. G. Watson, *J. Chem. Phys.*, **45**, 1360 (1966).

[24] J. K. G. Watson, *J. Chem. Phys.*, **46**, 1935 (1967).

[25] (a) G. W. King, R. M. Hainer, and P. C. Cross, *J. Chem. Phys.*, **11**, 27 (1943). (b) P. R. Bunker, "Molecular Symmetry and Spectrosc.", Academic Press, New York, 1979.

Table I. Observed Rotational Constants A, B, and C of Malonaldehyde (MHz)

species	A	B	C	model[a]
parent, $\upsilon = 0$[b]	9833.857 (2)	5212.535 (2)	3404.362 (2)	RR + CD
parent, $\upsilon = 1$	9846.052 (3)	5158.738 (3)	3383.236 (2)	RR + CD
(D_6), $\upsilon = 0$	9579.83 (3)	5154.05 (2)	3348.62 (2)	RR + Cor
(D_6), $\upsilon = 1$	9581.16 (3)	5144.50 (2)	3344.85 (2)	RR + Cor
(D_{7-9}), $\upsilon = 0$	9675.30 (2)	4961.55 (2)	3277.83 (1)	RR
(D_{7-9}), $\upsilon = 1$	9682.34 (2)	4931.92 (2)	3265.96 (1)	RR
(D_8), $\upsilon = 0$	8980.74 (4)	5210.88 (3)	3295.39 (3)	RR
(D_8), $\upsilon = 1$	8992.88 (4)	5157.41 (2)	3275.95 (2)	RR
$(^{18}O_{1-5})$, $\upsilon = 0$	9590.59 (1)	5042.13 (1)	3202.46 (1)	RR + CD
$(^{18}O_{1-5})$, $\upsilon = 1$	9603.09 (5)	4990.36 (40)	3282.02 (4)	RR + CD
$(^{17}O_{1-5})$, $\upsilon = 0$	9704.46 (9)	5125.77 (8)	3351.82 (2)	RR
$(^{17}O_{1-5})$, $\upsilon = 1$	9716.88 (2)	5072.79 (2)	3330.98 (1)	RR
$(^{13}C_{2-4})$, $\upsilon = 0$	9800.15 (3)	5135.52 (7)	3367.38 (2)	RR
$(^{13}C_{2-4})$, $\upsilon = 1$	9812.02 (1)	5083.47 (4)	3346.73 (1)	RR
(D_6D_8), $\upsilon = 0$	8758.98 (1)	5152.68 (1)	3241.92 (1)	RR + Cor
(D_6D_8), $\upsilon = 1$	8760.41 (1)	5143.21 (1)	3238.45 (1)	RR + Cor
(D_7D_9), $\upsilon = 0$	9492.27 (4)	4753.73 (4)	3165.79 (3)	RR
(D_7D_9), $\upsilon = 1$	9500.37 (2)	4708.68 (2)	3146.98 (2)	RR
$(^{13}C_{2-4}{}^{13}C_3)$, $\upsilon = 0$	9563.78 (1)	5135.55 (1)	3339.00 (1)	RR + CD[c]
$(^{13}C_{2-4}{}^{13}C_3)$, $\upsilon = 1$	9576.12 (1)	5083.63 (1)	3318.91 (1)	RR + CD[c]
$(^{13}C_2{}^{13}C_4)$, $\upsilon = 0$	9765.57 (2)	5059.39 (2)	3330.47 (2)	RR + CD[c]
$(^{13}C_2{}^{13}C_4)$, $\upsilon = 1$	9777.11 (1)	5008.88 (2)	3310.26 (1)	RR + CD[c]
$(^{18}O_1{}^{18}O_5)$, $\upsilon = 0$	9340.02 (2)	4883.68 (2)	3204.70 (2)	RR
$(^{18}O_1{}^{18}O_5)$, $\upsilon = 1$	9351.70 (14)	4832.37 (13)	3184.26 (12)	RR
$(D_6D_7D_9)$, $\upsilon = 0$	9241.62 (2)	4705.06 (2)	3115.85 (1)	RR
$(D_6D_7D_9)$, $\upsilon = 1$	9242.26 (2)	4697.07 (2)	3112.49 (1)	RR
$(D_6D_7D_8)$	8630.732 (1)	4914.726 (2)	3130.010 (1)	RR + CD
$(D_6D_8D_9)$	8645.182 (1)	4906.101 (2)	3128.514 (2)	RR + CD
$(D_6D_8{}^{13}C_{2-4})$, $\upsilon = 0$	8733.80 (3)	5077.36 (2)	3208.57 (1)	RR + Cor
$(D_6D_8{}^{13}C_{2-4})$, $\upsilon = 1$	8735.41 (3)	5068.04 (2)	3205.16 (1)	RR + Cor
$(D_6D_8{}^{18}O_{1-5})$, $\upsilon = 0$	8567.17 (2)	4977.51 (2)	3146.40 (2)	RR + CD
$(D_6D_8{}^{18}O_{1-5})$, $\upsilon = 1$	8560.86 (5)	4976.75 (5)	3145.49 (4)	RR + CD
$(^{13}C_2{}^{13}C_3{}^{13}C_4)$, $\upsilon = 0$	9533.102 (3)	5059.399 (3)	3302.982 (3)	RR + CD
$(^{13}C_2{}^{13}C_3{}^{13}C_4)$, $\upsilon = 1$	9545.173 (6)	5009.032 (6)	3283.306 (6)	RR + CD
$(D_6D_7D_8D_9)$, $\upsilon = 0$	8491.53 (2)	4703.86 (2)	3025.32 (1)	RR + Cor
$(D_6D_7D_8D_9)$, $\upsilon = 1$	8492.41 (2)	4695.93 (2)	3022.22 (1)	RR + Cor
$(D_6D_8{}^{13}C_{2-4}{}^{13}C_3)$, $\upsilon = 0$	8550.73 (2)	5077.53 (2)	3180.60 (1)	RR + Cor
$(D_6D_8{}^{13}C_{2-4}{}^{13}C_3)$, $\upsilon = 1$	8552.66 (2)	5068.16 (2)	3180.27 (1)	RR + Cor
$(D_6D_8{}^{13}C_2{}^{13}C_4)$, $\upsilon = 0$	8707.81 (2)	5002.77 (2)	3175.18 (2)	RR + Cor
$(D_6D_8{}^{13}C_2{}^{13}C_4)$, $\upsilon = 1$	8709.05 (2)	4993.48 (2)	3172.54 (2)	RR + Cor
$(D_6D_8{}^{18}O_1{}^{18}O_5)$, $\upsilon = 0$	8353.10 (5)	4826.32 (6)	3056.70 (4)	RR + CD
$(D_6D_8{}^{18}O_1{}^{18}O_5)$, $\upsilon = 1$	8354.38 (5)	4817.40 (6)	3053.48 (4)	RR + CD
$(D_6D_7D_8{}^{18}O_1)$	8407.743 (4)	4773.292 (4)	3043.252 (4)	RR + CD
$(D_6D_8D_9{}^{18}O_5)$	8414.625 (6)	4769.812 (5)	3042.840 (5)	RR + CD
$(D_6D_7D_8{}^{18}O_5)$	8456.581 (10)	4747.028 (9)	3038.884 (9)	RR + CD
$(D_6D_8D_9{}^{18}O_1)$	8477.341 (7)	4734.716 (7)	3036.603 (6)	RR + CD
$(D_6D_7D_9{}^{13}O_4)$	8606.823 (3)	4841.483 (3)	3097.043 (3)	RR + CD
$(D_6D_8D_9{}^{13}C_2)$	8609.011 (3)	4840.393 (3)	3096.980 (3)	RR + CD
$(D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4)$, $\upsilon = 0$	8527.750 (10)	5002.816 (8)	3150.963 (7)	RR + Cor
$(D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4)$, $\upsilon = 1$	8529.162 (10)	4993.944 (8)	3147.732 (7)	RR + Cor

[a] RR represents rigid rotor, CD centrifugal distortion, and Cor Coriolis perturbation terms.[4] [b] $\upsilon = 0$ and $\upsilon = 1$ label two lowest tunneling states. [c] Only some CD constants are determined independently and others assumed at parent values.

Table II. Centrifugal Distortion Constants and Inertial Defect for Some Isotopic Species of Malonaldehyde (kHz)

species	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_k	ΔI
$(D_6D_7D_8)$	2.64 (2)	−3.53 (2)	4.09 (6)	0.986 (4)	2.96 (2)	0.077
$(D_6D_8D_9)$	2.73 (4)	−4.13 (2)	4.66 (7)	0.922 (3)	2.68 (2)	0.071
$(D_6D_7D_8{}^{18}O_1)$	2.59 (6)	−3.58 (7)	3.74 (14)	0.98 (1)	2.66 (7)	0.080
$(D_6D_8D_9{}^{18}O_5)$	2.81 (8)	−3.87 (9)	4.19 (16)	0.97 (1)	2.61 (9)	0.075
$(D_6D_7D_8{}^{18}O_5)$	2.78 (14)	−2.80 (13)	2.69 (25)	0.96 (1)	2.41 (10)	0.080
$(D_6D_8D_9{}^{18}O_1)$	2.41 (10)	−4.10 (21)	4.49 (10)	0.96 (1)	2.47 (9)	0.075
$(D_6D_7D_8{}^{13}C_4)$	2.55 (7)	−3.53 (5)	4.22 (13)	0.94 (1)	3.01 (4)	0.078
$(D_6D_8D_9{}^{13}C_2)$	2.53 (6)	−3.88 (6)	4.52 (13)	0.94 (1)	2.72 (5)	0.072
tunneling						
parent, $\upsilon = 0$	3.83 (4)	−0.30 (4)	1.32 (11)	1.42 (1)	7.84 (5)	0.103
parent, $\upsilon = 1$	3.11 (5)	−10.96 (6)	12.17 (15)	1.10 (1)	0.30 (7)	0.084
$(^{13}C_2{}^{13}C_3{}^{13}C_4)$, $\upsilon = 0$	3.46 (7)	−1.2 (2)	2.0 (2)	1.25 (3)	6.2 (2)	0.105
$(^{13}C_2{}^{13}C_3{}^{13}C_4)$, $\upsilon = 1$	2.6 (1)	−8.5 (4)	10.8 (5)	1.03 (4)	0.3 (5)	0.084
$(D_6D_8{}^{18}O_{1-5})$, $\upsilon = 0$[a]	3.4 (5)	19.4 (4)	−16.0 (7)	1.59 (5)	16.1 (5)	0.099
$(D_6D_8{}^{18}O_{1-5})$, $\upsilon = 1$[a]	3.4 (1)	−42.3 (1)	41.37 (6)	0.53 (1)	−3.4 (1)	0.086
(D_6D_8), $\upsilon = 0$[a]	13.93	117.24	−97.14	4.48	147.14	0.110
(D_6D_8), $\upsilon = 1$[a]	8.33	−233.17	283.80	30.14	−59.17	0.105

[a] These values were obtained by fitting only low J transitions ($J \leqslant 8$). They cannot be used to predict higher J transitions.

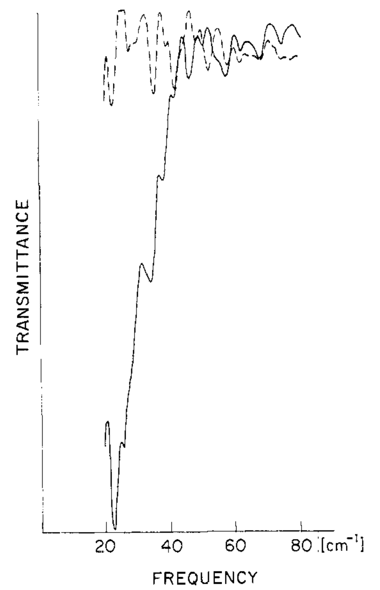

Figure 3. Portion of far-IR spectrum of malonaldehyde vapor, showing the absorption attributed to tunneling. The solid line denotes the sample and the broken line the background.

From the above discussion it is clear that, depending upon the symmetry of the particular vibrational state ψ_V and the parity of $K_{-1} + K_{+1}$ of ψ_R, the overall antisymmetry requirement will result in spin weights 3 and 1 for the two kinds of levels and hence alternating intensities of rotational transitions. These alternations will be reversed on going from a ψ_V to its partner of opposite symmetry but nearby energy.

If the energy barrier separating the configurations A and B is sufficiently increased, the spacing of the two lowest tunneling levels will become unresolvable and their opposite spin weights will combine to give a total spin weight of 4 for each rotational level. The observation of alternating intensities thus proves that the barrier is not sufficiently high to prevent resolution.

As the barrier is lowered, the energy splitting of the two lowest levels with opposite alternating intensities in their associated rotational spectra will continue to increase until there is no barrier. Then the two states become the ordinary ground state and first excited vibrational state of the appropriate normal coordinate for the hydrogen motion. These levels should be then so widely separated that few molecules would occupy the excited level at room temperature, so only the pure rotational spectrum of the ground state, with alternating intensities, would be observable. Thus in both high and low barrier limits, only one spectrum of intensity appropriate to a really low-lying level will be seen, in the former limit without, and in the latter with, alternating intensities. Since two low-lying states are observed, malonaldehyde must have a double-minimum energy surface with an intermediate barrier.

3. **Estimation of Tunneling Separation.** Relative intensity measurements[6b] on corresponding lines of the two lowest tunneling levels indicate a revised energy separation of 26 ± 10 cm^{-1} for the normal species and a considerably smaller separation for species with deuterium in position 6.

A 20–80-cm^{-1} far-infrared spectrum of malonaldehyde at a pressure of 570 mtorr is shown in Figure 3. It appears that an absorption band occurs at ~21 cm^{-1}. Actually, microwave perturbations to be discussed in paper 3 show that the tunneling splitting is ~3 cm^{-1} for the (D_6D_8) species[6b] (confirmed by direct microwave transitions) and ~21 cm^{-1} for the normal species.[26] These results will be used in paper 3.

4. **Quenching of Tunneling.** The tunneling motion of the hydrogen is almost exclusively parallel to the a inertial axis of the molecule. If the tunneling is one dimensional, the moments of inertia about the a axis (I_a) should be nearly the same for the ground vibrational state (here designated as $v = 0$) and the low-lying excited tunneling state ("$v = 1$"), while the moments about the other axes should reflect the difference in vibrational averaging due to the tunneling. For the normal isotopic species, the differences in moments of inertia between the two states were $\Delta I_a = -0.064$, $\Delta I_b = 1.011$, and $\Delta I_c = 0.927$ amu Å^2. Thus, since $\Delta I_a << \Delta I_b$, the tunneling can be treated here as one dimensional.

Table III. Differences in Rotational Constants between the Two Lowest Observed States for Some Isotopic Forms of Malonaldehyde (MHz)

group[a]	species	ΔA	ΔB	ΔC
I	parent	12.19	−53.80	−21.12
	($^{18}O_1{}^{18}O_5$)	11.68	−51.31	−20.44
	(D_8)	12.14	−53.47	−19.44
	[($^{18}O_{1-5}$)	12.50	−51.83	−20.44]
II	(D_{7-9})	7.04	−29.63	−11.87
III	(D_6)	1.33	−9.55	−3.77
	(D_6D_8)	1.43	−9.47	−3.47
	($D_6D_8{}^{13}C_2{}^{13}C_4$)	1.26	−9.28	−2.66
IV	($D_6D_8{}^{18}O_{1-5}$)	−6.05	−0.23	−1.02
V	($D_6D_7D_8$)-($D_6D_8D_9$)	14.45	−8.63	−1.50
	($D_6D_7D_8{}^{18}O_1$)-($D_6D_8D_9{}^{18}O_5$)	6.88	−3.48	−0.41
	($D_6D_7D_8{}^{18}O_5$)-($D_6D_8D_9{}^{18}O_1$)	20.76	−12.31	−2.28
	($D_6D_7D_8{}^{13}C_4$)-($D_6D_8D_9{}^{13}C_2$)	2.19	−1.09	−0.06

[a] I: symmetrical species with H in the O–H bond. II: tunneling mixture of D_7 and D_9. III: symmetrical species with D in H bond. IV: tunneling mixture of ($D_6D_8{}^{18}O_1$) with ($D_6D_8{}^{18}O_5$). V: nontunneling isomers.

In symmetric isotopic species (i.e., those symmetrical to the interchange (1,5), (2,4), and (7,9)), the value of the rotational constant B is expected to diminish on going from $v = 0$ to $v = 1$ because the $v = 1$ wave function has a node at $a_6 = 0$ and $v = 0$ does not. Table III contains values for the differences $\Delta A = A_{v=1} - A_{v=0}$ etc. for a number of species. Note that all symmetrical species with an H in position 6 (group I) have roughly the same ΔB value, while all D_6 symmetrical species (group III) have their own small range of ΔB values. However, the D_6 unsymmetrical isotopic species, especially those with $D_6D_7D_8$ (group V), show quite different changes in the rotational constants. It is reasonable to interpret this as evidence for at least partial quenching of the tunneling in the unsymmetrical species.

A rough treatment of the quenching can be carried out as follows. Let ψ_0 and ψ_1 be the accurate (or approximate) vibrational wave functions for $v = 0$ and $v = 1$, at nearly the same energies E_0 and E_1 with tunneling splitting $\delta = E_1 - E_0$. Localized wave functions ψ_A and ψ_B with an overlap integral $S = \langle\psi_A\psi_B\rangle$ can be defined via

$$\psi_0 = (2 + 2S)^{-1/2}(\psi_A + \psi_B) \tag{4.1}$$

$$\psi_1 = (2 - 2S)^{-1/2}(\psi_A - \psi_B) \tag{4.2}$$

or

$$\psi_A = (1/2)[(2 + 2S)^{1/2}\psi_0 + (2 - 2S)^{1/2}\psi_1] \tag{4.3}$$

$$\psi_B = (1/2)[(2 + 2S)^{1/2}\psi_0 - (2 - 2S)^{1/2}\psi_1] \tag{4.4}$$

Evidently ψ_A and ψ_B are not defined until a choice of S is made. S can be small but if $S = 0$ is chosen, ψ_A and ψ_B cannot both be nodeless. For symmetric isotopic species, ψ_A and ψ_B are symmetrically equivalent, one peaked near the equilibrium configuration A and the other near B. The Hamiltonian, $\mathcal{H}$, for unsymmetrical species will be slightly unsymmetrical and will give different local energies $E_A = \langle\psi_A|\mathcal{H}|\psi_A\rangle$ and $E_B = \langle\psi_B|\mathcal{H}|\psi_B\rangle$. Use as a variation function

$$\phi = \alpha\psi_A + \beta\psi_B \tag{4.5}$$

with undetermined coefficients α and β. This yields the usual secular equation ($\mathcal{H}_{AB} = \langle\psi_A|\mathcal{H}|\psi_B\rangle$)

$$\begin{vmatrix} E_A - E & H_{AB} - SE \\ \mathcal{H}_{AB} - SE & E_B - E \end{vmatrix} = 0 \tag{4.6}$$

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(26) P. Turner, private communication.

Table IV. Dipole Moment Components of Several Isotopic Forms of Malonaldehyde (D)

species	μ_a	μ_b
parent, $v = 0$		2.59 (2)
parent, $v = 1$		2.58 (1)
(D_6D_8), $v = 0$		2.58 (2)
(D_6D_8), $v = 1$		2.57 (3)
(D_8), $v = 0$		2.58 (1)
$(^{18}O_{1-5})$, $v = 0$	0.076 (1)	2.570 (3)
$(D_6D_8{}^{18}O_{1-5})$, $v = 1$	0.23 (6)	2.59 (1)
(D_{7-9}), $v = 0$	0.371 (1)	2.561 (4)
(D_{7-9}), $v = 1$	0.140 (7)	2.586 (13)
$(D_6D_8D_9)$	0.443 (2)	2.565 (3)
$(D_6D_8D_9)$	0.192 (1)	2.584 (2)

For the symmetrical cases, E_A equals E_B and the tunneling separation can be written as

$$E_1 - E_0 = \delta = -2(\mathcal{H}_{AB} - SE_A)/(1 - S^2) \qquad (4.7)$$

For the unsymmetrical case with $\Delta = E_B - E_A \neq 0$ (with E_A chosen to be zero and with S equal to zero), the coefficient ratio reduces to

$$\alpha/\beta = (\mathcal{H}_{AB}/E) \qquad (4.8)$$

with

$$E = \tfrac{1}{2}[\Delta \pm (\Delta^2 + \delta^2)^{1/2}] \qquad (4.9)$$

$$\beta/\alpha = -(\Delta/\delta) - [(\Delta/\delta)^2 + 1]^{1/2} \qquad (4.10)$$

An appreciable deviation from 50–50 mixing ($\alpha = \beta$) results even when Δ is no larger than half of δ, and almost complete quenching of the tunneling is obtained for $\Delta \geq 5\delta$ (i.e., $\alpha^2 \geq 0.99$; $\beta^2 \leq 0.01$). In the D_6 symmetric compounds δ is ~ 3 cm^{-1} so Δ would be 15 cm^{-1} if Δ is arbitrarily taken to be 5δ. This same value of Δ applied to the normal species where $\delta \approx 21$ cm^{-1} would predict only partial quenching ($\alpha^2 \approx 0.79$; $\beta^2 \approx 0.21$).

This rough treatment illustrates that a small asymmetry in the double-well potential function itself or in the values of the two local energies could have an appreciable quenching effect on the D_6 species and only a partial effect on the H_6 species.

Another indicator of strong quenching of tunneling comes from the centrifugal distortion (CD) coefficients. A good fit can be obtained, at least for low J transitions, with rigid rotor plus centrifugal distortion without any special Coriolis terms.[6] However, where the Coriolis coupling term is actually large, it is necessary to use different values of the CD constants for the $v = 0$ and $v = 1$ transitions. Where the two spectra belong to separate isomers (i.e., the tunneling is quenched), the coefficients should have nearly the same values for the two states, since true CD coefficients in normal molecules are not usually much changed by isotopic substitution.

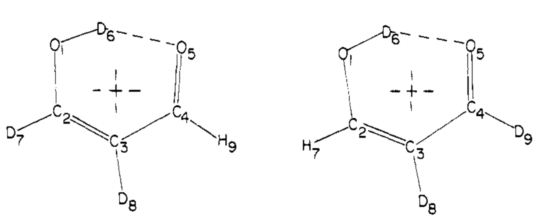
Table II shows the CD coefficients for a number of species. The examples in the upper part show agreement between the two sets of coefficients and are considered to be nontunneling pairs of isomers. The lower part contains tunneling species for which different coefficients are required to fit $v = 0$ and $v = 1$ spectra.

A third type of evidence supporting this classification of isotopic species into fully tunneling (symmetric) species, partially quenched species, and largely quenched species is discussed below under dipole moments.

Finally, a quantitative result can be obtained by fitting the rotational spectrum of a partially quenched unsymmetrical species with a rigid rotor plus CD plus Coriolis terms and an unsymmetrical double-minimum potential. This treatment can give the actual mixing coefficients α and β discussed above and will be published elsewhere.[26]

5. Dipole Moment Components. The observed dipole moment components are given in Table IV. It is seen that only μ_b is nonvanishing for the symmetric species, whereas small values of μ_a are found for unsymmetric species. The absence of a μ_c component is in accord with the other evidence for planarity.

In discussing these results it is convenient to consider separately three cases: nontunneling unsymmetrical species, symmetrically substituted, fully tunneling species, and unsymmetrical species in which the tunneling is partially quenched.



(D_6 D_7 D_8) (D_6 D_8 D_9)

Figure 4. Nontunneling isomers of trideuterated malonaldehyde.

5.1. Nontunneling Species. The criteria previously discussed suggest that the unsymmetrical trideuterio species such as ($D_6D_7D_8$), with or without a fourth substituent (^{18}O or ^{13}C), are essentially not tunneling; i.e., they consist of two isomers in thermal equilibrium, as shown in Figure 4. The correct wave functions are approximately ψ_A and ψ_B, respectively, unmixed. The dipole moment should have very nearly the same magnitude and the same direction relative to the chemical bond framework for each of these species, since isotope effects on dipole moments are normally small (<1%). From one isotopic form to another the directions of the principal axes of inertia relative to the bond framework do change; therefore the components μ_a and μ_b also change as shown in Table IV for ($D_6D_7D_8$) and ($D_6D_8D_9$). The total dipole moments are 2.603 and 2.591 D for these two species, respectively, with average value 2.597 D. The angles between μ and the principal axis b are 9.80° for ($D_6D_7D_8$) and 4.25° for ($D_6D_8D_9$). From the structure (see next section) the angle between b and the C=O bond is 4.38° and −1.00°, respectively, which yields a result for the angle between μ and the C=O bond of 5.42° for ($D_6D_7D_8$) and 5.25° for ($D_6D_8D_9$). This agreement supports the assumption of quenched tunneling.

5.2. Tunneling, Symmetrical Species. The dipole moment of the tunneling, symmetrical species has $\mu_a = 0$ because the vibrational wave function gives equal probabilities for finding the molecule in each of the equilibrium conformations A and B. In these conformations the signs for μ_a are different so the expectation value of μ_a vanishes if averaged over a tunneling state. The quantity extracted from the microwave second-order Stark data is given by the following formula

$$\sum_{J'}{}' |\langle \psi_{vJ} | \mu_Z | \psi_{vJ'} \rangle|^2 / \Delta E_{vJ,vJ'}$$

in which ψ_{vJ} is the rotational, vibrational wave function with vibrational quantum numbers v, rotational quantum numbers J or J', μ_Z is the space fixed Z component of the instantaneous dipole moment, and $\Delta E_{vJ,vJ'}$ is a rotational energy interval. The sum is given over J' ($\neq J$) only. Actually, this sum should also include terms involving $\langle \psi_{vJ} | \mu_Z | \psi_{v'J} \rangle$ where $v' \neq v$. Particularly, if $v = 0$ and $v' = 1$ (the lowest tunneling pair), contributions from μ_a will appear. Because of the fact that, in each equilibrium configuration $|\mu_a| << |\mu_b|$, these terms are unimportant here, unless $\Delta E_{vJv'J'}$ is exceptionally small, which rarely occurs for low J values. Further

$$\mu_Z = \mu_a \cos(aZ) + \mu_b \cos(bZ) \qquad (5.1)$$

with μ_a and μ_b the components along the instantaneous principal axes a and b and (aZ) the angle between a and Z. Next, let

$$\psi_{vJ} = (1/2)^{1/2} \psi_R{}^J (\psi_V(A) + \psi_V(B)) \qquad (5.2)$$

in which the tunneling vibrational wave function is represented as a sum of two localized wave functions (as in eq 4.1) with the overlap S chosen to be negligible. $\psi_R{}^J$ is the rotational factor. From this

$$\begin{aligned}\langle \psi_{vJ} | \mu_Z | \psi_{vJ'} \rangle = {} & \tfrac{1}{2} \langle \psi_R{}^J | \cos aZ | \psi_R{}^{J'} \rangle [\langle \psi_V(A) | \mu_a | \psi_V(A) \rangle + \\ & \langle \psi_V(B) | \mu_a | \psi_V(B) \rangle] + \tfrac{1}{2} \langle \psi_R{}^J | \cos bZ | \psi_R{}^{J'} \rangle \times \\ & [\langle \psi_V(A) | \mu_b | \psi_V(A) \rangle + \langle \psi_V(B) | \mu_b | \psi_V(B) \rangle] \end{aligned} \qquad (5.3)$$

where $\langle \psi_V(A) | \mu_a | \psi_V(B) \rangle = 0$ by symmetry[25b] and $\langle \psi_V(A) | \mu_b | \psi_v(B) \rangle$ has been neglected as small because of the choice of S near zero.

Table V. Internuclear Distances (Å) and Angles (Deg) in Malonaldehyde ($D_6D_7D_8$)

parameter	this work	Del Bene[a]	Karlstrom[b]	acrolein[c] r_s	butadiene[d] r_{av}
O=C	1.234	1.23 (1)	1.243	1.219 (5)	
O–C	1.320	1.36 (1)	1.332		
C=C	1.348	1.33 (1)	1.350	1.345 (3)	1.341 (2)
C–C	1.454	1.48 (1)	1.451	1.470 (3)	1.463 (3)
C_2–H_7	1.089	1.09 (1)		1.086 (5)	1.090 (4)
C_3–H_8	1.091	1.08 (1)		1.084 (3)	
C_4–H_9	1.094	1.10 (1)		1.108 (3)	
O–H[e]	(0.969)	1.00 (1)	0.975		
O···O[f]	2.553	2.561	2.609		
O···O	2.574				
O···H[f]	1.68	1.65	1.78		
O–C=C	124.5	125 (1)	124.4		
C=C–C	119.4	119 (1)	120.4	119.8 (2)	123.3 (3)
C–C=O	123.0	122 (1)	123.1	123.3 (3)	
C–O–H	106.3	104 (1)	110.5		
O–H···O[f]	147.6	148.7	140.3		
O–H···O	146.9				
C=C–H_7	122.3	122 (1)		121.5 (2)	
C=C–H_8	128.1[g]	121.5 (5)		122.8 (2)	
C–C–H_9	117.6	117 (1)		115.1 (2)	

[a] Reference 8. [b] Reference 9. [c] r_s structure of *trans*-acrolein.[39] [d] Reference 40. [e] Value 0.969 Å assumed from ref 37. [f] In H_6 species ($v = 0$). [g] Due to the positions of C_3 and H_8 close to the axis, this number is probably not accurate.

Note that the directions in space for the *a* and *b* axes are the same for both the A and B equilibrium configurations (see Figure 1), but

$$\langle \psi_V(A)|\mu_a|\psi_V(A)\rangle = -\langle \psi_V(B)|\mu_a|\psi_V(B)\rangle \tag{5.4}$$

$$\langle \psi_V(A)|\mu_b|\psi_V(A)\rangle = \langle \psi_V(B)|\mu_b|\psi_V(B)\rangle \tag{5.5}$$

so that *a* contributions cancel out leaving only the localized expectation value of μ_b to contribute to the Stark effect for the symmetrical, tunneling species.

5.3. Tunneling, Unsymmetrical Species. Finally, some isotopically unsymmetrical tunneling species show μ_a values different from zero. Except for ($^{18}O_{1-5}$), which is a tunneling mixture of ($^{18}O_1$) and ($^{18}O_5$), these have moderately abnormal values of ΔA, ΔB, and ΔC and, in measured cases, considerable differences between the centrifugal distortion constants for the low-lying pair of states. These observations can be explained by assuming that the isotopic asymmetry has partially quenched the tunneling, that is, the observed states are to be expressed as

$$\psi = \alpha\psi_A + \beta\psi_B \tag{5.6}$$

where the mixing coefficients α and β ($\alpha^2 + \beta^2 = 1$) are not equal (as in the symmetric species) nor is either α or β negligible as in the fully quenched species. As a consequence μ_a does not average to zero. This is the case even for ($^{18}O_{1-5}$) where the μ_a cannot be explained just by axes rotation.

Only for species (D_{7-9}) is sufficient data available to test these ideas. The dipole moment for ($D_6D_7D_8$) can be rotated to give μ_a for each of the two equilibrium configurations of (D_{7-9}) by using the structure in Table V. Comparison with the experimental average (0.371 D) yields $\alpha = 0.94$ and $\beta = 0.35$. These in turn predict $\mu_a = 0.155$ for the other state for which $\mu_a = 0.140$ D experimentally.

6. Structure. As was discussed above, the molecule appears to be planar[27] and thus has C_s symmetry. Large amplitude inplane tunneling motion complicates structure determination, as will be discussed below. This can be partially avoided by using species with quenched tunneling such as the trideuterio species ($D_6D_7D_8$) of Figure 4 in combination with quadruply substituted forms such as ($D_6D_7D_8{}^{18}O_1$) or ($D_6D_7D_8{}^{18}O_5$). The ordinary Costain[29]–Kraitchman[30] r_s method is directly applicable and yields the coordinates of the fourth substituted atom (here ^{18}O in position 1 or position 5) in the principal axes of ($D_6D_7D_8$). Likewise the coordinates of both oxygens can be located in the axes of ($D_6D_8D_9$) in combination with ($D_6D_8D_9{}^{18}O_1$) and ($D_6D_8D_9{}^{18}O_5$) (for numbering of the atoms see Figure 4). From these results two values of the interatomic distance $O_1 \cdots O_5$ can be obtained, namely, 2.5748 and 2.5731 Å.

This same distance can be also calculated by applying the formulas of Chutjian[31] and Nygaard[32] to the changes in moments of inertia from (D_6D_8) to ($D_6D_8{}^{18}O_1{}^{18}O_5$), both of which are symmetrically substituted tunneling species. The formulas used are extensions of Kraitchman's equations to the case in which two equivalent atoms (here O_1 and O_5) are substituted. Since the two oxygen atoms are not in truly equivalent positions, this cannot give the separate coordinates of O_1 and O_5 but should give a good $O_1 \cdots O_5$ distance because the first-order errors cancel in this distance. The O···O distance calculated from average rotational constants between $v = 0$ and $v = 1$ states of these species is 2.5746 Å (distance obtained from rotational constants of $v = 0$ and $v = 1$ is 2.5736 and 2.5756 Å, respectively).

If the Nygaard formula is applied to the normal species combined with ($^{18}O_1{}^{18}O_5$), a slightly different O···O distance is obtained, namely, 2.5528 for $v = 0$ and 2.5700 Å for $v = 1$. This is an illustration of the well-known Ubbelohde effect[7,33] in which replacement of H by D in an O–H···O hydrogen bond causes a small change in the O···O distance.

The Costain–Kraitchman method, applied also to the species ($D_6D_8D_9$) combined with ($D_6D_8D_9{}^{13}C_2$), should locate carbon 2. Here there was a difficulty. The sample was a mixture of ($D_6D_8D_9{}^{13}C_2$) and ($D_6D_7D_8{}^{13}C_4$). The ^{13}C was always ^{13}C–H, not ^{13}C–D, from the method of preparation. Two low-lying rotational spectra were found, and it was necessary to decide which spectrum belonged to which isotopic species. The two alternative assignments could not be distinguished from the two structures they led to. However a decision was made by internal comparison of three pairs of nontunneling species in which the two species differed by the transfer of D_6 from one oxygen to the other, namely, ($D_6D_7D_8$)–($D_6D_8D_9$), ($D_6D_7D_8{}^{18}O_1$)–($D_6D_8D_9{}^{18}O_5$), and ($D_6D_7D_8{}^{18}O_5$)–($D_6D_8D_9{}^{18}O_1$). It was noted in all three pairs that the first member had the smaller rotational constant *A*, the larger rotational constant *B* (see Table III, group V), the larger inertial defect $I_c - I_a - I_b$ (see Table II), and the greater intensity (by 8–19%). Therefore the spectrum which shared all these characteristics was assigned to the species ($D_6D_7D_8{}^{13}C_4$) and the other one to ($D_6D_8D_9{}^{13}C_2$). Although the above considerations are empirical, they are rationally supported as follows: a rough, simple valence force field normal-coordinate treatment (with force constants transferred from related molecules where possible[34]) gave inertial defect values in the same order. Also, the same calculation gave total zero-point vibrational energies which would yield the same order of relative intensities as observed. The force field used is available in the supplementary material.

The coordinates of C_2 in the basis ($D_6D_8D_9$) and C_4 in basis ($D_6D_7D_8$), plus the oxygen coordinates in both bases, give C_2–O_1, $C_2 \cdots O_5$ and C_4=O_5, $C_4 \cdots O_1$. It is then a simple geometric problem to obtain the coordinates of both carbons in both bases, and a value for $C_2 \cdots C_4$ (2.4196 Å). $C_2 \cdots C_4$ can also be obtained from the doubly substituted symmetric tunneling species ($D_6D_8{}^{13}C_2{}^{13}C_4$) and ($D_6D_8$). The value thus obtained from average rotational constants was 2.4219 Å. (The parent plus ($^{13}C_2{}^{13}C_4$) gives 2.4179 Å.)

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[27] Kato et al.[28] report that one out of plane vibrational mode has a negative force constant, from their calculations. It would be necessary to examine vibrational excited states carefully to be able to decide whether a small nonplanarity exists or not.

(28) S. Kato, H. Kato, and K. Fukui, *J. Am. Chem. Soc.*, **99**, 684 (1977).

(29) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(30) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

(31) A. Chutjian, *J. Mol. Spectrosc.*, **14**, 361 (1964).

(32) L. Nygaard, *J. Mol. Spectrosc.*, **62**, 292 (1976).

(33) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, 1968, Chapter 3.

(34) (a) C. Di Lauro, S. Califano, and G. Adembri, *J. Mol. Struct.*, **2**, 173 (1968); (b) A. Borg, Z. Smith, G. Gundersen, and P. Klaeboe, *Spectrochim. Acta*, **36**, 119 (1980); (c) H. E. Breed, G. Gundersen, and R. Seip, *Acta Chem. Scand.*, **33**, 225 (1979).

In order to locate the atoms H_7, H_9, C_3, H_8, and H_6, we applied the so-called "rotation method".[35] This is an extension of the Costain–Kraitchman method, to which it reduces when the mass of only one atom is changed. It permits the coordinates of one atom in a multiply substituted species to be determined when the coordinates of the other substituted atoms are known.

In order to determine the coordinates of atoms H_7 and H_9, one must combine nontunneling species like $(D_6D_7D_8)$, $(D_6D_8D_9)$ and a symmetrical tunneling species, e.g., (D_6D_8), which introduces some uncertainty. This uncertainty is reduced but not eliminated by using the average of B over $v = 0$ and $v = 1$ for the tunneling species. The $H_7 \cdots H_9$ distance thus found was 4.3298 Å. One can also calculate this distance from the symmetrically substituted species like (D_6D_8) and $(D_6D_7D_8D_9)$, or (D_6) and $(D_6D_7D_9)$, or parent malonaldehyde and (D_7D_9) by using the Nygaard formula[32] for doubly substituted species. The $H_7 \cdots H_9$ distance calculated from average rotational constants of these species was 4.3129, 4.3126, and 4.3133 Å, respectively. The error caused by assuming that these symmetrically substituted tunneling species have C_2 symmetry was estimated to be less than 0.005 Å; thus the discrepancy between the values obtained by the two different routes is too large and is believed to be due to different vibrational averaging in the tunneling and the nontunneling species. Since the rotational constants A are less influenced by this (see below the determination of coordinates of H_6), the values of coordinates b_7 and b_9 calculated from the rotational constants A should be quite well determined. Also the $H_7 \cdots H_9$ distance obtained from the tunneling species should be well determined since the vibrational effects in these similar species mostly cancel out when r_s coordinates are calculated. The final a coordinates of H_7 and H_9 were therefore determined by using the $H_7 \cdots H_9$ distance calculated from deuterated tunneling species, b_7 and b_9 determined from (D_6D_8), $(D_6D_7D_8)$, and $(D_6D_8D_9)$, and the difference $a_7^2 - a_9^2$ obtained by the "rotation method" using the species $(D_6D_7D_8)$ and $(D_6D_8D_9)$.

Atom C_3 is very close to the b axis so that direct Kraichman calculations fail, giving imaginary a_3 values. The use of the "rotation method" with $(D_6D_7D_8)$ and $(D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4)$ gave a satisfactory value of $b_3 = 1.1094$ Å and a real value of $a_3 = 0.0202$ Å, but it is clearly not very accurate for a. Finally, the result from a first moment calculation

$$a_3 = -\sum_{i \neq 3} m_i a_i / m_c = 0.0245 \text{ Å}$$

where $m_c = 12$, the carbon mass, is within the error bound of the "rotation method" value.

Coordinates of atom H_8 were first determined with only tunneling species (D_6D_8) and (D_6). These were rotated into the $(D_6D_7D_8)$ frame by using the "rotation method" for finding the angle of rotation of the principal axes between the $(D_6D_7D_8)$ and (D_6D_8) species. This process required a knowledge of the coordinates of D_7.

A simple Kraitchman calculation of the H_6 position (using parent malonaldehyde and (D_6)) and correcting for the expansion of the $O \cdots O$ distance upon deuteration yields an O–H distance of 0.86 Å. Since this model does not correct for the different vibrational averaging of the H or D within the hydrogen bond (which will be important for a double minimum potential), this anomalously low value for the O–H distance can probably be rejected. A summary of neutron diffraction results for hydrogen-bonded systems shows that the O–H distance for most hydrogen-bonded systems is between 0.95 and 1.05 Å.[36,37] All known gas-phase O–H bonds also fall in this range.[38]

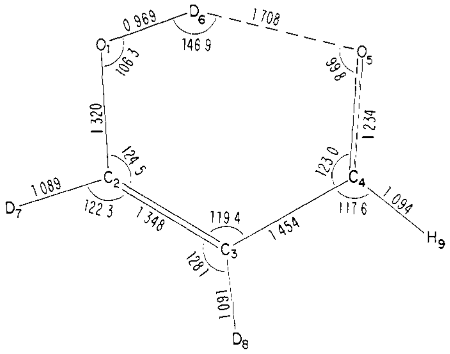

Figure 5. Final structure of malonaldehyde (D_6 species).

With the one-dimensional model of the tunneling motion of the hydrogen, the coordinate of the hydrogen atom along the b axis can be calculated by using Kraitchman's equations with the normal species plus (D_6). The a coordinate cannot be reliably determined because of the large amplitude of vibration. The b coordinate and the $O \cdots O$ distance, together with an assumed O–H distance of 0.95–1.05 Å, lead to an $O–H \cdots O$ angle between 147 and 149°.

Similarly, to locate D_6 in the trideuterated coordinate system, the coordinate b was determined by the "rotation method" using $(D_6D_7D_8)$ and (D_8). Then in order to calculate the a coordinate, we assumed the O–H distance to be 0.969 Å.[37]

It should be noted that this is essentially an r_s structure; i.e., only differences in moments of inertia were used, not their absolute values. Furthermore, most of the differences involved either a pair of tunneling or a pair of nontunneling species. For these either rigid-rotor plus CD or rigid-rotor plus Coriolis values were used for both members of a pair. In a few cases (b_6, b_7, and b_9) it was necessary to use the difference of a tunneling and a nontunneling species. In the case of b_6 rigid-rotor values were combined, and in the case of b_7 and b_9 rigid-rotor plus CD was combined with rigid-rotor plus CD plus Coriolis model.[26] Whenever the moments of inertia of tunneling species were utilized, the average value between $v = 0$ and $v = 1$ were used.

The final structure is given in Figure 5 and the parameters in Table V. For the Cartesian coordinates see supplementary material.

Discussion

The structure determination for $(D_6D_7D_8)$ shows clearly the unsymmetrical nature of each of the two equivalent equilibrium configurations between which tunneling occurs (in the isotopically if not geometrically symmetrical species). There are distinct double and single C–O and C–C bonds. Note also that the single-bond–double-bond angles are near to or larger than 120° and single-bond–single-bond angles are distinctly less than 120°.

The $O \cdots O$ nonbonded distance is well determined for D_6 species and is slightly larger ($\sim$0.021 Å) than in the H_6 species, another example of the well-known Ubbelohde effect. This increase in the $O \cdots O$ distance is a consequence of the higher effective barrier to tunneling for D_6 than H_6. Since the hydrogen spends more time near the midpoint of the two oxygens, a shortening of the $O \cdots O$ distance will occur because of attractive interactions.[33] This difference should vanish for true Born–Oppenheimer equilibrium distances. A similar effect (expansion of about 0.017 Å from $v = 0$ to $v = 1$) seems to be observed between the two tunneling states for the H_6 species. The wave function for the $v = 1$ state has a node at the middle of the potential so the hydrogen spends more time near the midpoint of the oxygens in the ground state. This explanation is supported by the fact that the D_6 species show this effect only slightly.

Three a priori calculations of structure have been published.[8-10] Two of these[8,10] seem to be identical in basis set etc. and in structural results. The deviations between the two different a priori

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(35) E. B. Wilson and Z. Smith, *J. Mol. Spectrosc.*, **87**, 569 (1981).

(36) I. Olovsson and P. G. Jonsson, "The Hydrogen Bond", P. Schuster, G. Zundel, and C. Sandorfy, Eds., North-Holland Publishing Co., New York, 1976, Chapter 8.

(37) C. Ceccarelli, G. A. Jeffrey, and R. Taylor, *J. Mol. Struct.*, **70**, 255 (1981).

(38) M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data*, **8**, 619 (1979).

(39) E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, **45**, 104 (1966).

(40) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1967).

calculated structures themselves and between each and the experimental structure are comparable, and one is led to believe that all three have similar uncertainties, perhaps with a root-mean-square value of 0.01 or 0.02 of 1 Å. All three yield planar, unsymmetrical structures with markedly bent H bonds. The Karlstrom[9] structure disagrees somewhat seriously in the $O\cdots O$ distance and H bond local structure.

It should be noted that the analysis of the experimental data has yielded, not the structure averaged over the two equivalent oppositely unsymmetrical equilibrium configurations, but the unsymmetrical structures themselves.

The theoretical results can be viewed as a considerable success in the prediction of a rather complicated situation, even as one wishes that both theory and experiment were perhaps 5 times more accurate. On the other hand, there still remain two difficulties with the theory. The first is the present uncertainty in deciding which calculation to believe, even when one calculation uses a more flexible basis set. The second is the fact that an equally good prediction of structure can often be made by transferring bond lengths and angles from similar molecules.

A geometrical optimization by the CNDO/2 semiempirical method[28] gives an unsymmetrical structure with a bent H bond which is somewhat further from the experimental structure than are the a priori calculations referred to above.

A good deal of data on rates of tunneling will be discussed in paper 3.

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Supplementary Material Available: Part 1, the Cartesian coordinates and the valence force field, and part 2, microwave transitions (24 pages). Ordering information is given on any current masthead page.

Spectroscopy and Decay Dynamics of Several Methyl- and Fluorine-Substituted Benzene Radical Cations

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Abstract: Spectra of several fluorobenzene cation radicals containing 1-3 methyl substituents were observed in solid Ne matrix and analyzed. Comparisons between these compounds and other fluorobenzenes studied previously as well as comparisons between the $\tilde{B}$ state lifetimes in the gas phase and in the matrix are used to gain a deeper insight into the $\tilde{B}$ state decay dynamics.

Substantial progress has occurred in the last several years in the field of electronic spectroscopy of molecular cations. While several years ago the spectra of only a handful of diatomics were known, a variety of new techniques have been recently developed[1-15] which permitted observation and characterization of a large number of polyatomic cations. In these experiments the ions were produced by electron impact,[1,2] Penning ionization,[3-5] in electric discharge,[6-8] or by photoionization[9,10] in media as diverse as molecular beams,[11,12] ion traps,[13-15] and low temperature matrices.

While the information obtainable from gas-phase studies is frequently limited due to the complexity and congestion of the high temperature spectra and by the weakness of the available signals, these problems are often overcome in low temperature condensed phase studies. We have recently developed techniques for obtaining absorption,[16] fluorescence excitation,[10] and laser-induced resolved emission spectra[16-19] of molecular cations, usually in solid Ne matrix, and demonstrated that such spectra show in general insignificant perturbatin by the solid Ne medium.[18]

These techniques are particularly valuable for large, polyatomic ions whose ambient temperature spectra frequently appear like featureless continua with only hints of vibrational structure but whose matrix spectra provide a wealth of detailed vibrational information. Thus matrix spectra were instrumental in providing

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(1) M. Allan and J. P. Maier, *Chem. Phys. Lett.*, **34**, 442 (1975).
(2) M. Allan, J. P. Maier, and O. Marthaler, *Chem. Phys.*, **26**, 131 (1977).
(3) J. A. Coxon, P. J. Marcoux, and D. W. Setser, *Chem. Phys.*, **17**, 403 (1976).
(4) P. C. Engelking and A. L. Smith, *Chem. Phys. Lett.*, **36**, 21 (1975).
(5) K. T. Wu and A. T. Yencha, *Can. J. Phys.*, **55**, 767 (1977).
(6) C. Cossart-Magos, D. Cossart, and S. Leach, *Mol. Phys.*, **37**, 793 (1979).
(7) J. H. Callomon, *Proc. R. Soc. London, Ser. A*, **A244**, 220 (1958).
(8) T. Oka, *Phys. Rev. Lett.*, **45**, 531 (1980).
(9) J. Daintith, R. Dinsdale, J. P. Maier, D. A. Sweigart, and D. W. Turner, "Molecular Spectroscopy 1971", Institute of Petroleum, pp 16-23.
(10) V. E. Bondybey, J. H. English, and T. A. Miller. *J. Am. Chem. Soc.*, **100**, 5251 (1978).
(11) A. Carrington, *Proc. R. Soc.* **367**, 433 (1979).
(12) J. T. Shy, J. W. Farley, W. E. Lamb, and W. H. Wing, *Phys. Rev. Lett.*, **45**, 535 (1980).
(13) R. C. Dunbar and M. Teng, *J. Am. Chem. Soc.*, **100**, 2279 (1978).
(14) M. S. King and R. C. Dunbar, *Chem. Phys. Lett.*, **60**, 247 (1979).
(15) F. J. Grieman, B. H. Mahan, and A. O'Keefe, *J. Chem. Phys.*, **72**, 4246 (1980).
(16) V. E. Bondybey, T. A. Miller, and J. H. English, *J. Chem. Phys.*, **72**, 2193 (1980).
(17) V. E. Bondybey, T. A. Miller, and J. H. English, *J. Chem. Phys.*, **71**, 1088 (1979).
(18) V. E. Bondybey and J. H. English, *J. Chem. Phys.*, **71**, 777 (1979).
(19) V. E. Bondybey, T. A. Miller, and J. H. English, *J. Chim. Phys.*, **77**, 667 (1980).

0002-7863/81/1503-6303$01.25/0