

Proton transfer in malonaldehyde: From reaction path to Schrödinger's Cat

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Abstract

Proton transfer in the chelated form of malonaldehyde is commonly supposed to occur between two tautomers, across a transition state involving changes of the chemical bonding. We show that this view is in conflict with rotational spectra. The molecule is better thought of as a superposition of indistinguishable and non-separable C_s tautomers and proton tunneling is totally decoupled from the other degrees of freedom. Double minimum potential functions are determined from experiments and ab initio calculations.

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In the gas phase, the chelated form of the malonaldehyde (3-hydroxy-2-propenal) molecule is a prototypical example of a symmetric double minimum potential for proton transfer through tunneling between two equivalent C_s structures (*L* and *R*, respectively, Fig. 1). This molecule has been thoroughly investigated experimentally [1–8], and theoretically [9–27].

The tunnel splitting for the hydrogenated derivative has been measured several times [1,2,5,7,8] with, finally, spectacular accuracy: $(21.58313829 \pm 0.00000063) \text{ cm}^{-1}$ [8]. The splitting decreases to 2.92 cm^{-1} for the deuterium bonded analogue, with a very small further decrease $\leq 0.2 \text{ cm}^{-1}$ upon ring deuteration, or $^{16}\text{O}/^{18}\text{O}$, or $^{12}\text{C}/^{13}\text{C}$ substitutions [5]. Rotational microwave spectra accord with the C_{2v} rigid rotor model and indistinguishable H7/H9 sites [1]. Proton transfer occurs essentially in one dimension, in the molecular plane and perpendicular to the twofold axis of the transition state. The $R_{\text{O}\dots\text{O}}$ distance is $\approx 2.57 \text{ \AA}$, and the estimated O–H bond is $r \approx 1.0 \text{ \AA}$, with substantial uncertainty [2]. On the other hand, infrared spectra accord with two equivalent C_s structures interconnected by tunneling

[3,4]. The OH stretching band, tentatively assigned at 2960 cm^{-1} , is partially hidden by the CH stretching.

Theoretical models are based on the interconversion scheme sketched in Fig. 1. Proton transfer is governed by a symmetric double minimum potential through an intermediate C_{2v} state. In the prevailing views, reorganization of the π -conjugation pattern along the reaction path decreases the barrier height, increases the distance between minima and, simultaneously, the effective oscillator mass [11]. Consequently, potential surfaces are calculated at a high level of accuracy in order to account for multidimensional quantum effects and heavy atom quantization [16,17,22,24]. Alternatively, parametrization of the full potential surface was realized with the ab initio path integral methodology [23]. A different view based on a topological analysis of the electron localization function suggests that interconversion does not involve any reorganization of the skeleton, although the scheme is still that of Fig. 1 [20]. Finally, potential barriers estimated with various methods, and various definitions of the reaction path, range from about 1000 to 5000 cm^{-1} [9–15,17,18,21–26].

This brief review emphasizes that proton transfer dynamics in malonaldehyde is well characterized experimentally, but still not yet precisely understood at the theoretical level. The purpose of this Letter is to propose a

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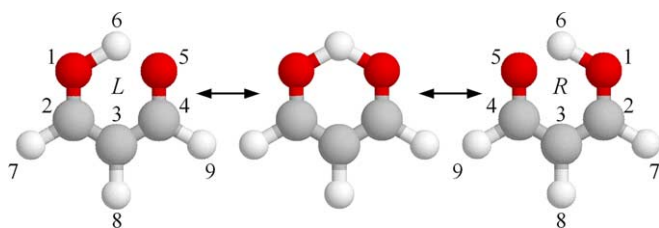


Fig. 1. Schematic representation of the most commonly accepted mechanism for interconversion of the chelated malonaldehyde molecule with C_s symmetry at equilibrium. The transition state symmetry is C_{2v} .

quantum model firmly based upon experimental data. To introduce this model, we feature the weakness of the interconversion scheme depicted in Fig. 1.

- (i) This scheme does not correspond to a minimum energy (or maximum probability) reaction path, because energy-free interconversion is readily realized through free rotation of the isolated rigid molecule.
- (ii) For an isotropic probability distribution of orientations in the gas phase, L and R are indistinguishable and non-separable. The ground state is a coherent superposition, like Schrödinger's Cat, with C_{2v} symmetry (Fig. 2).

In order to model the dynamics of this superposition, the vibrational Hamiltonian for one of the tautomers (say L) can be decomposed as

$$\mathcal{H}_L = \mathcal{H}_{HL} + \mathcal{H}_{FL} + \mathcal{H}_{HFL}. \quad (1)$$

\mathcal{H}_{HL} accounts for the (O)H/D dynamics governed by a single minimum potential along the in-plane coordinate x , perpendicular to the twofold symmetry axis of the C_{2v} superposition

$$\mathcal{H}_{HL} = \frac{P_x^2}{2m} + V_L(x). \quad (2)$$

Here, x is not, strictly speaking, the stretching mode of L . Anticipating the superposition of tautomers, x is the symmetry coordinate for 'proton transfer'. The other symmetry coordinates for protons are in-plane and out-of-plane bending. The effective mass m depends on the exact representation of x in terms of internal coordinates. As a zero-order approximation $m = 1(2)$ for H(D).

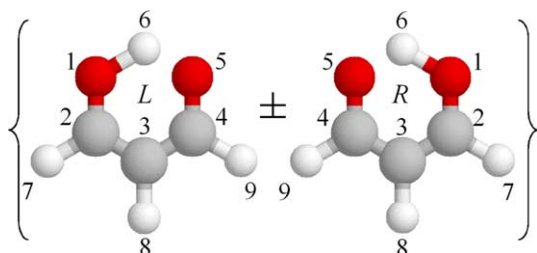


Fig. 2. Schematic representation of the superposition of C_s tautomers in the ground doublet state.

\mathcal{H}_{FL} accounts for the molecular frame dynamics including (C)H, C and O atoms, and the bending OH modes. For the sake of simplicity, spin statistics, or rotational and rovibrational dynamics are not included. Therefore, (1) does not address a detailed interpretation of high resolution rovibrational spectra. The purpose is limited to proton transfer dynamics.

Finally, \mathcal{H}_{HFL} accounts for non-linear coupling between the two subsystems. Owing to the great sensitivity of the ν OH frequency with respect to $R_{O \cdots O}$, non-linear coupling with the ν O \cdots O at ≈ 250 cm^{-1} is an important and well known band broadening mechanism [28].

For the superposition of L and R , the ground state is $|0 \pm\rangle = 2^{-1/2}[|L0\rangle \pm |R0\rangle]$. Only H6 occupies distinct sites, separated by $\Delta x_0 \approx 0.6$ Å, close enough to give tunnel splitting due to overlap of the wave functions $\langle x|HL0\rangle$ and $\langle x|HR0\rangle$. By contrast, C3 and H8 are degenerate and each other atom occupies distinct positions too far away from one another to give rise to tunneling. Hence, the ground state can be factored as

$$|0 \pm\rangle = 2^{-1}[|FL0\rangle + |FR0\rangle] \otimes [|HL0\rangle \pm |HR0\rangle] \quad (3)$$

and the tunneling coordinate is rigorously decoupled from the other internal coordinates, irrespective of the coupling terms \mathcal{H}_{HFL} and \mathcal{H}_{HFR} .

The C_{2v} state $2^{-1/2}[|FL0\rangle + |FR0\rangle]$ accounts for the orientational degeneracy of the frame. It accords with indistinguishability of H7/H9 [1], although, in contrast to the intermediate in Fig. 1, there is no rearrangement of the chemical bonds. Note that this state is different in nature from the hypothetical resonant superposition $2^{-1/2}[|FL0\rangle \pm |FR0\rangle]$ that would give rise to a tunnel splitting (say $h\nu_{F0\pm}$) of the molecular frame. Since there is no evidence of such splitting neither in the far infrared, up to 80 cm^{-1} , nor in rotational spectra [2,8], $h\nu_{F0\pm}$ should be, if real, less than 10^4 Hz, beyond microwave resolution. Then, the superposition would oscillate exceedingly slowly between L and R , and the instantaneous symmetry on the time scale of proton tunneling should be C_s , instead of C_{2v} . Rotational spectra discard this possibility. On the other hand, an incoherent density distribution $2^{-1}[\Psi_{FL0}^2 + \Psi_{FR0}^2]$ with statistical C_{2v} symmetry is incompatible with tunneling.

For the same reason as for the ground state, the tunnel splitting in the ν OH excited state is decoupled from the molecular frame. Simultaneously, the coupling of the stretching dynamics for each tautomer with the frame, through \mathcal{H}_{HFL} and \mathcal{H}_{HFR} , accounts for the bandwidth of ≈ 100 cm^{-1} . The tunneling is unaffected by this broadening and it is relevant to accord the splitting with the mean frequencies of the ν OH bands.

The tunneling dynamics can be modelled with a symmetric double minimum potential in one dimension

$$V(x) = a_2 x^2 + a_4 x^4 \cdots + b \exp(-cx^2). \quad (4)$$

Parameters can be determined to fit the tunneling splitting $h\nu_{\text{H}0-}$ and the estimated ν OH mean frequency of 2960 cm^{-1} , we attribute to the $|0+\rangle \leftrightarrow |1-\rangle$ transition. In addition, we tentatively re-assign to $|0-\rangle \leftrightarrow |1+\rangle$ the weak and broad infrared band at $\approx 2450\text{ cm}^{-1}$ (half-width at half-height of $\approx 100\text{ cm}^{-1}$), previously assigned to combinations [4]. Then, Δx_0 and m are correlated free parameters.

Some of the best fits are presented in Table 1. Case A is the best fit to OH frequencies for $m = 1\text{ amu}$. The potential barrier $H = 4420\text{ cm}^{-1}$ is much higher than recent ab initio estimates ranging from ≈ 1000 to 3500 cm^{-1} [14,15,22]. $\Delta x_0 = 0.61\text{ \AA}$ confirms that the potential coordinate x is along a straight line. Alternative distorted paths (minimum energy, maximum probability, instanton, etc.) are, therefore, much less probable.

The analytical formula (4) is not unique, but any alternative model based upon the same assignment scheme should give about the same barrier height. Δx_0 is largely determined by $h\nu_{0-}$ and m . Clearly, $\Delta x_0 = 0.61\text{ \AA}$ is consistent with $R_{\text{O}\dots\text{O}} \approx 2.57\text{ \AA}$. Note that a detailed comparison with x_{min} values derived from rotational spectra of C_s isotope derivatives $\text{D}_6\text{D}_7(\text{D}_9)\text{D}_8$ (0.39 and 0.375 \AA) [2,5] is hampered by the significant change of the structure.

If, while keeping the same assignment scheme, we multiply m by a factor ρ , Δx_0 is divided by a factor $\approx \rho^{1/2}$. For example, an increase of 1% for the effective mass would decrease Δx_0 by $\approx 10\%$, close to any reasonable limit. Therefore, the effective mass is certainly very close to 1 amu and the tunneling coordinate represents linear displacements of a bare proton.

For the D_6 analogue, the calculated tunneling splitting of $\approx 1.2\text{ cm}^{-1}$ in Table 1 is quite at variance with the observed value of $\approx 2.9\text{ cm}^{-1}$. One could argue that $m_{\text{D}}/m_{\text{H}} < 2$, but this is actually impossible if the (O)H dynamics is that of a bare proton. The most likely explanation is a change of the effective potential function upon deuteration. The best fit to OD frequencies (Table 1B) gives $\Delta x_0 = 0.572\text{ \AA}$, and $H = 4110\text{ cm}^{-1}$. The decreasing of H is consistent with the shorter Δx_0 .

It should be remarked that vibrational states are related to effective potentials averaged over zero-point motions along all degrees of freedom. This may account for mar-

ginal effects observed upon isotope substitutions (C)H/D, $^{16}\text{O}/^{18}\text{O}$, and $^{12}\text{C}/^{13}\text{C}$ [2]. For (O)H/D substitution, we anticipate the effective potential be also affected by the different mean-square amplitudes for the bending modes. Therefore, a change of the effective potential is not in conflict with the decoupling of the tunneling coordinate.

The wave functions for $|0+\rangle$ and $|0-\rangle$ (Fig. 3) accord with the C_{2v} symmetry probed with microwaves [1,2]. By contrast, infrared spectra at room temperature probe a superposition of almost equally probable tunneling states ($h\nu_{0-} \ll kT$) giving rise to quantum beats, very slow on the time scale for vibrational dynamics of the molecular frame. The time dependent wave function,

$$\Psi(x, t) \approx 2^{-1/2}[\Psi_{0+}(x) \exp(i\omega_{0+}t) + \Psi_{0-}(x) \exp(i\omega_{0-}t)], \quad (5)$$

gives the probability density [29]

$$|\Psi(x, t)|^2 \approx 2^{-1}|\Psi_{0+}(x)|^2 + 2^{-1}|\Psi_{0-}(x)|^2 + \Psi_{0+}(x)\Psi_{0-}(x) \cos \omega_{0\pm}t. \quad (6)$$

The system oscillates at the tunneling frequency $\omega_{0\pm}/(2\pi)$ between L and R (Fig. 4). The probability for the proton to be in the vicinity of the midpoint is always negligible and reorganization of the chemical bonding is irrelevant. Note that quantum beating is observed because, according to (3), the tunneling dynamics is decoherence-free with respect to the molecular frame and, in the gas phase at a low pressure, collision induced decoherence is negligible. This is witnessed by the very long life-time of the tunneling states.

According to quantum laws, measurements in the infrared probe the instantaneous C_s symmetry and automatically destroy quantum beating (measurement induced decoherence). Subsequent measurements of the same ensemble would give the same outcome as an incoherent population density $2^{-1}[\Psi_{0+}^2 + \Psi_{0-}^2]$ with stationary C_{2v} symmetry. In the gas phase, however, the probability to measure twice the same ensemble before coherence recovery is negligible and the paradox of quantum measurement is pointless.

The dynamical model accords with ab initio calculations carried out with the GAUSSIAN98 software at the appropriate B3LYP level of theory [17]. We utilized the extended

Table 1
Tentative double minimum potential functions for proton transfer dynamics

	a_2 ($\text{cm}^{-1} \text{ \AA}^{-2}$)	a_4 ($\text{cm}^{-1} \text{ \AA}^{-4}$)	b (cm^{-1})	c ($\text{cm}^{-1} \text{ \AA}^{-2}$)	Δx_0 (\AA)	H (cm^{-1})	m (amu)	$h\nu_{0-}$ (cm^{-1})	$h\nu_{1+}$ (cm^{-1})	$h\nu_{1-}$ (cm^{-1})
A	247210	0	94968	3.662	0.610	4420	{ 1 2	21.6 1.19	2450 2020	2960 2080
B	292120	0	105250	3.782	0.562	4110	{ 2 1	2.90 39.8	2013 2400	2140 3114
C	-62999	414910	4118	6.52	0.610	4140	{ 1 2	27.0 1.60	2360 1985	2970 2075

A: Best fit to the ν OH frequencies. B: Best fit to the ν OD frequencies. C: Best fit to ab initio calculations. Wave functions were projected on a basis set of 40 harmonic wave functions. Eigen values and eigen functions were computed with the variational method.

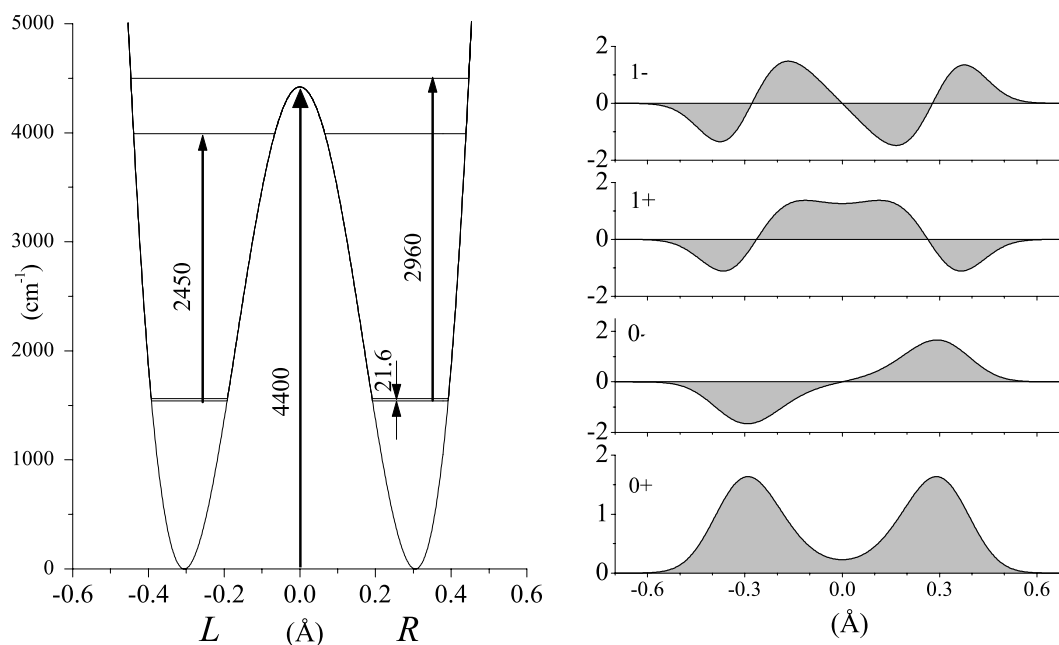


Fig. 3. Effective potential, energy levels and wave functions for proton dynamics (see Table 1A).

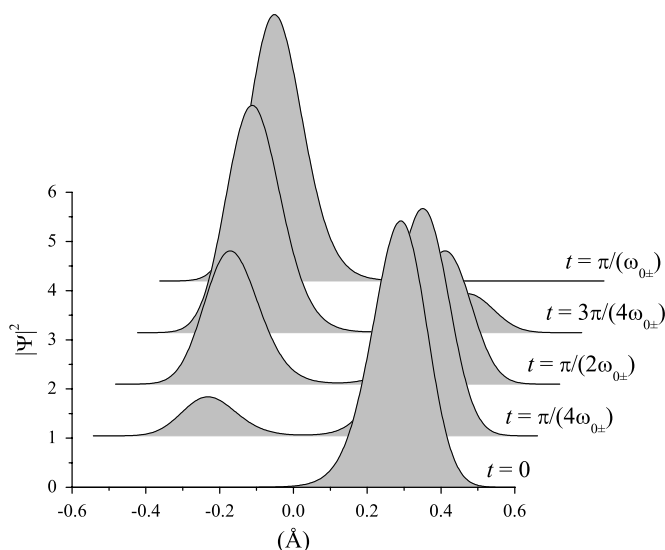


Fig. 4. Time evolution of the proton probability density arising from quantum beats for a superposition of tunneling states $|0+\rangle$ and $|0-\rangle$.

6–311⁺⁺G** basis set including polarization functions on all atoms. The purpose was not to reach the best level of accuracy, but to envisage how to model a superposition state with a desk-top computer. The optimized geometry of a tautomer is planar with bond lengths and angles very close to those derived from rotational spectra and similar calculations. Then, the hydrogen bonding proton was moved while keeping frozen the other degrees of freedom. The O–H length was varied from 0.798 to 1.798 Å, by 0.1 Å steps, and the COH angle from 90.5 to 115.5°, by steps of 2.5°. The minimum-energy path over this grid of 21×11 points is very closely parallel to the straight line between the two oxygens. A cut of the potential surface along this

line gives an asymmetric potential and symmetrization is realized by adding such potentials for the *L* and *R* tautomers. This is supposed to model the superposition $|FL0\rangle + |FR0\rangle$.

The best fit to the calculated cut is given in Table 1C. The agreement with potentials derived from spectroscopic data is quite conclusive. Presumably, it should be confirmed this is not fortuitous.

In conclusion, the isolated malonaldehyde molecule in the C_{2v} ground state is a superposition of indistinguishable and non-separable C_s tautomers. The hydrogen bonding proton (deuteron) is delocalized over two sites, while the molecular frame is a superposition state of the two configurations. Proton tunneling is totally decoupled from other internal dynamics and, therefore, decoherence-free. The proton oscillates harmonically between the two C_s tautomers. The transition state is irrelevant for all practical purposes.

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