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Tunneling of methyl groups in toluquinone: Dependence on the electronic state of the molecule

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The torsional frequency and the tunneling splitting of the methyl group of crystalline toluquinone are reported for different electronic states of the molecule. Whereas in the ground state both values can be derived from a conventional cos 3ϕ potential with a barrier height of approximately 8 kJ/mol, the values in the lowest excited triplet state cannot be reconciled with such a simple potential. It is suggested that a chemical interaction between the methyl protons and the adjacent oxygen of the excited carbonyl group is responsible for the modification of the potential. Numerical calculations based on a simple modeling of this chemical interaction support this idea.

I. INTRODUCTION

Rotational tunneling of methyl groups in low temperature molecular solids has been investigated by electron spin resonance (ESR) techniques in the case of free radials in a matrix[1,2] and by inelastic neutron scattering (INS) on molecular crystals.[3,4] A more indirect method of evaluating tunneling splittings has been developed by Clough *et al.*[5,6] using proton nuclear magnetic resonance (NMR). This method relys on the observation of a strong correlation between the tunneling frequency and the temperature $\theta_{\min}$ at which the spin lattice relaxation time T_1 shows a minimum.

The rotational potential of a methyl group attached to a molecule has both intra- and intermolecular contributions. For molecules in the electronic ground state the dominant contributions stem from atom–atom repulsive forces. For a rigid methyl group the angular (ϕ) dependence of the hindering potential can be written in the form

$$V(\phi) = \frac{V_3}{2}(1 - \cos 3\phi) + \frac{V_6}{2}(1 - \cos 6\phi) + \cdots . \quad (1)$$

It has been demonstrated by Clough *et al.*[5] that mainly the first term with sometimes an additional smaller second term of this series is needed to describe the potential. The torsional frequency and the tunneling frequency of the rotor are thus correlated and a measure of both is a good probe of the shape of the potential. In view of the strong dependence of the tunneling frequency on barrier height, it is not surprising to find that the measured values of the former span a wide range from values less than 20 kHz to more than 100 GHz in different compounds.[6,7]

One case was reported by Clough *et al.*[6,8] where the hindering potential and consequently the tunneling splitting of a methyl group was modified considerably by the creation of free radicals by γ irradiation of the sample: Methylmalonic acid, CH_3–CH_2–$(COOH)_2$, has a tunneling frequency of 68 kHz.[6] The free radical CH_3–$\dot{C}H(COOH)_2$ in the same matrix exhibits a tunneling splitting of about 200 MHz, more than three orders of magnitude larger than that of the parent molecule. Apparently a large contribution to the hindering potential is of intramolecular origin in this case, produced by the environment and state of the carbon atom near to the methyl group.

It might be expected that the potential of a methyl rotor could also be modified when the molecule to which it is attached is electronically excited. The tunneling splitting would then be different for the same molecule in different electronic states. To our knowledge, no such measurements

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have been reported so far. It is the purpose of this paper to discuss the case of toluquinone (TQ) (methyl-*p*-benzoquinone) for which Lichtenbelt *et al.*[9] published a value of 2.96 GHz, or 12 μeV, for the tunneling splitting of the methyl group of molecules in the lowest excited electronic $n\pi^*$ triplet state T_1 measured by proton ENDOR techniques. We have performed experiments to determine the methyl tunneling splitting of the TQ molecules in the electronic ground state S_0 using INS and proton NMR, yielding a frequency on the order of 10 MHz, or 0.04 μeV. These two very different values for the tunneling splitting are discussed in this paper together with results about methyl torsional frequencies obtained from infrared, Raman, and optical absorption measurements.[10,12] The crystal structure of toluquinone is orthorhombic with the space group $Cmc2_1$; the two molecules in the unit cell are related by a twofold screw axis and lie on a crystallographic mirror plane; the molecular mirror plane is thus conserved in the crystal. This feature not only simplifies the orientation of the molecules in optical and ESR measurements on single crystals but also assures that the symmetry classification of the molecular orbitals with respect to the molecular plane is preserved in the crystal.

II. THE OPTICAL SPECTRA

The Raman spectra of protonated and perdeuterated single crystals of TQ have been measured at 77 K; infrared solution spectra of these compounds and also of the ring deuterated methyl protonated compound were measured at room temperature. Together with normal mode calculations, these specta were used for a complete assignment of the ground state vibrations.[10] For the methyl torsional mode the frequency in a pure crystal at 77 K of the protonated compound was found to be 160 cm^{-1}. At 4 K we expect a slight, but not significant, increase of this value.

The first electronic transitions of TQ lie in the visible and are of $n\pi^*$ character. Two close-lying $n\pi^*$ states related to the presence of two C = O groups have been found in quinones in both the singlet and triplet manifolds and have been well characterized by extensive experimental and theoretical studies.[11–13] The S_1–T_1 gap in these compounds is 1400–1600 cm^{-1}, only, and the description of the electronic excitations is, to a first approximation, the same in both systems.

For *p*-benzoquinone, the unsubstituted parent compound, this similarity of the excited states is reflected in the vibrational structure of the vapor phase spectrum: the differences between ground and excited state frequencies of the most prominent progression forming modes are very similar in both the $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ transitions; the frequencies of these modes are therefore nearly the same in the singlet and triplet excited states.[14]

In the $S_1 \rightarrow S_0$ absorption spectrum at 2 K of single crystals of h_6-, d_3-h_3-, and d_6-TQ, the torsional mode of the methyl group could clearly be identified. Its frequency in the first excited singlet state of the h_6 compound is 157 cm^{-1}.[12] Analysis of the spectra shows that this mode is slightly perturbed by another mode of lower frequency and that the frequency of the unperturbed torsional mode is about 2–3 cm^{-1} lower. The spectra also show that the frequency of this mode is only slightly affected by ring deuteration of TQ.

In the singlet–triplet absorption or emission spectrum of TQ the methyl torsional mode could not be identified. This is not surprising as this transition is orbitally strongly allowed, whereas in the forbidden singlet–singlet system the mode appears due to Herzberg–Teller intensity borrowing from higher $\pi\pi^*$ transitions. There is no indication in the emission spectra of isotopically mixed crystals of any significant change of the potential for the torsional mode between the ground electronic state and the excited triplet state. The main difference between the singlet and triplet system in TQ is the presence of a $\pi\pi^*$ triplet state at an estimated energy of 1500–1300 cm^{-1} above T_1. This state does not seem to perturb significantly the lowest levels of the first excited triplet state and we do not expect that the methyl torsional mode is significantly affected. We conclude that the frequency of this mode in the first excited triplet state is, in all likelihood, similar to its value in the singlet state, and therefore only slightly lower than in the ground electronic state. We therefore propose the following values for the frequency of the methyl torsional mode: 160–165 cm^{-1} in the ground electronic state and 150–155 cm^{-1} in the lowest excited triplet state.

III. TUNNELING IN THE LOWEST $n\pi^*$ TRIPLET STATE OF TOLUQUINONE: AN ENDOR AND LAC STUDY

Lichtenbelt and Wiersma[13] recently reported results of a proton ENDOR and level anticrossing (LAC) study on the lowest excited $n\pi^*$ triplet state of TQ. In these experiments the intensity of the emission from the excited triplet state was monitored as a function of the frequency of the applied microwave and radio fields. While these studies were aimed at obtaining information on the spin-density distribution in the aromatic ring system, an ENDOR study of the methyl protons was also made. A triplet of lines around 23 MHz was assigned to the protons of the methyl group. On rotating the crystal with respect to the external magnetic field, the central frequency of this triplet of lines changed but the line separations remained virtually unchanged, indicating that the methyl group was undergoing "free" rotation. Using the effective spin Hamiltonian formalism for a tunneling methyl group, as derived by Clough and Poldy,[15] Lichtenbelt and Wiersma in a later paper[9] attempted to obtain the tunneling splitting ($3J$) and isotropic hyperfine constants of the methyl protons from the measured second order shifts in the ENDOR spectra. The best agreement with all the data available led to the conclusion that in the lowest triplet state of TQ, the tunneling splitting is 2.96 GHz. It was noticed, however, that with this tunneling splitting, the asymmetry in the proton ENDOR spectrum of the $|-1, A\rangle$ state was too large.

Level anticrossing spectra of triplet TQ were also obtained, with the magnetic field parallel to the x and z axes of the fine-structure tensor. Such spectra might also reveal the tunneling of the methyl group as new crossings, not available in the case of a fixed methly group, become available. In Figs. 3 and 4 of Ref. 9 the obtained LAC spectra for the indicated field directions are given. The central line in each case is interpreted as "the normal" LAC crossing and the

satellites as being due to cross relaxation between translationally equivalent triplet-excited molecules, one in an A, the other in an E rotational state. The field positions of these lines were found to be in agreement with the calculated ones, using the measured magnetic constants and the derived value of the tunneling splitting (2.96 GHz) from the proton ENDOR spectra.

IV. INS AND NMR MEASUREMENTS

The INS experiments have been performed with the backscattering spectrometer IN10 at the HFR in Grenoble.[16] The sample, polycrystalline h_6-TQ, was mounted in a variable temperature helium cryostat and cooled to 5 K. A search for inelastic features within an energy window of $\pm$ 3.6 GHz with an energy resolution of 80 MHz (FWHM) was unsuccessful. From this result one can conclude that the methyl tunneling splitting is either larger than 3.6 GHz; i.e., the tunneling peaks are outside the energy window of the spectrometer, or smaller than about 30 MHz; i.e., the inelastic peaks are so near to the elastic line that it becomes impossible to detect them. In order to be able to discriminate between the two possibilities two additional experiments were performed.

A so-called fixed window experiment was carried out on IN10, where the intensity at energy transfer $\hbar\omega = 0$ was recorded as a function of the sample temperature. For a tunneling splitting between 3.5 and 40 GHz a significant intensity drop is expected when the temperature is raised from 10 to 30 K.[17] The experiment showed, however, that the intensity began to decrease only at temperatures about 100 K, consistent with a tunneling splitting of less than 30 MHz.

In order to be able to make a more quantitative statement, an NMR experiment was performed with protonated TQ. The spin-lattice relaxation time T_1 was measured as a function of the sample temperature. A Larmor frequency of 21 MHz was used. T_1 exhibited a well defined minimum at a temperature $\theta_{\min}$ of 78 K. With the help of the correlation between the tunneling splitting and $\theta_{\min}$ mentioned in the introduction, we estimate a tunneling splitting of (12^{+12}_{-5}) MHz. With this value we can calculate the temperature at which in the INS experiment the steepest intensity change would have occurred. This gives a value of 140 K which is consistent with the observation that the intensity of the $\hbar\omega = 0$ peak begins to decrease at about 100 K.

Combining the INS and NMR results, we conclude that the tunneling splitting of protonated TQ in the electronic ground state is on the order of 10 MHz. Tunneling splittings of this size can be studied using nuclear Zeeman level crossing experiments. A search for a peak using this technique was performed but so far it has not been located. The value of 10 MHz sharply contrasts with the value of 2.96 GHz for TQ in its lowest triplet state reported by Lichtenbelt and Wiersma.[9]

V. DISCUSSION

In Table I, the values of the tunneling splittings and the torsional frequencies of the methyl group are given as far as known for three electronic states of TQ. The model potential normally used to describe the methyl group rotation is in first approximation given by

$$V^0 = \frac{V_3}{2}(1 - \cos 3\phi). \tag{2}$$

Here, V^0 is the first term in a Fourier series representing the true potential which is more complex. But in most methyl systems studied to date, it has been possible to fit the data quite well with the above potential with, in some cases, the addition of a small sixfold term. However, in all these systems only the methyl tunneling splitting of the molecule in the ground electronic state is known. In the present case we have more data; for the ground electronic state S_0, both the tunneling splitting and the vibrational frequency are known and are within the stated experimental error bars consistent with a potential of the form of V^0 with a barrier height of 1000 K. In the excited singlet state S_1, only the vibrational frequency is known, its value of 155 cm^{-1} is only slightly smaller than that of the S_0 state; for the excited triplet state

TABLE I. Summary of experimental data concerning the methyl group torsional motion in toluquinone.

h_6-toluquinone		
Electronic state and energy with respect to S_0 (single crystal at 1.5 K)	Frequency of the methyl group	
	Torsional mode ν_{tor}	Tunnel splitting ΔE_{tun}
S_0	160 cm^{-1} Raman at 77 K single crystal	< 30 MHz, INS at 4 K, powder
		$(12 \pm {}^{12}_{5})$ MHz, T_1, NMR, powder
T_1 18 691 cm^{-1}	150–155 cm^{-1} estimation	2960 MHz ENDOR at 1.6 K *per proto* in ring-deutero host single crystal
S_1 20 230 cm^{-1}	155 cm^{-1} Absorption at 2 K single crystal	unknown

T_1, only an estimate of 2.96 GHz for the tunneling splitting exists. Since the electronic structure of the T_1 state is similar to the S_1 state, and different from that of the S_0 state, we expect nearly the *same* form of the potential for the molecule in the S_1 and T_1 state.

With a potential of the form of V^0 the tunneling splitting of 2.96 GHz in T_1 correlates with a barrier height of about 320 K and a torsional frequency of only 90 cm^{-1}. The addition of even a large sixfold term does not eliminate this discrepancy; with $V_6 = V_3 = 280$ K in Eq. (1), the estimated torsional frequency of 150 cm^{-1} is reproduced but the tunneling splitting is still nearly one order of magnitude smaller than the experimental value.

One way out of this contradiction is to assume that the estimate of the tunneling frequency of the CH_3 group of TQ in its T_1 state is not correct and to try an alternative interpretation of the LAC spectra. If the satellites observed in the LAC experiment were due to an intramolecular level anticrossing between an *A*- and and *E*-rotational state, then a tunneling frequency of only 65 ± 10 MHz would result. It is, however, very difficult to reconcile this value with the second-order ENDOR shifts in the $m_s = 0$ state measured by Lichtenbelt *et al.*[9]

Another way to try to eliminate the contradiction which results partly from the barrier height calculation on the basis of a purely threefold cosine potential and the experimental values of the tunneling splittings and torsional frequencies would be to add more terms of the type $V_{3n} \cos 3n\phi$ to V^0. This changes the tunneling splitting and the vibrational frequency in different ways. Without an *ab initio* calculation of the true potential, there is no way of knowing how many terms to add. This will, in addition, lead to a multiparameter fit with little physical insight. Another procedure is to appeal to the known chemical properties of the excited ketone group. In the first excited $n\pi^*$ state the two unpaired electrons occupy respectively an antibonding π^* orbital and a highly localized *p* orbital in the plane of the molecule centered at the oxygen atoms.[11] Both of these electrons will be attractive to the methyl protons, but it will be the unpaired *n*-electron density in the *p* orbital which is symmetric with respect to the molecular plane which will have the largest effect on the potential of the methyl proton. It will give rise to an additive attractive term in the immediate vicinity of the angles at which the methyl protons lie in the molecular plane and point in the direction of the nearest oxygen atom; that is at precisely the configuration at which V^0 has maxima. This added potential will not be simply representable by one $\cos 3n\phi$ term, but will be a localized threefold symmetric one, and so it represents a sum of many such terms.

Thus in order to fit the vibrational frequency and the tunneling splitting, we propose the following potential:

$$V = V^0 - V_{\text{chem}} [\exp - \gamma(\phi - \pi/3)^2 + \exp - \gamma(\phi + \pi/3)^2 + \exp - \gamma(\phi - \pi)^2], \quad (3)$$

where γ is related to the angular width of the interaction between the oxygen and the methyl protons and V_{chem} represents the strength of this interaction.

This potential can be derived by expanding an exponentially decreasing attractive potential between the oxygen and the methyl protons about the angles of closest contact between the two centers. Clearly, the real potential due to the unpaired electrons will be more complex, but the purpose here is to demonstrate that the addition of such a chemical term to the classical (ground state) hindering potential of the methyl rotor dramatically increases the tunneling splitting while leaving the torsional frequency nearly unaffected.

Inserting this potential in the Schrödinger equation for the hindered rotation of the methyl group, we have

$$\left[- \frac{d^2}{d\phi^2} + \hat{V} \right] \psi_n(\phi) = \hat{E}_n \psi_n(\phi), \quad (4)$$

where $\hat{V}$ and $\hat{E}_n$ are V and E_n in units of $\hbar^2/2I$. We use the

TABLE II. Tunneling splittings (ΔE_{tun}) and torsional frequencies ν_{tor} for various values of potential parameters.

		$\gamma = 5$ rad^{-2}		$\gamma = 10$ rad^{-2}		$\gamma = 20$ rad^{-2}	
V_3 (K)	V_{chem} (K)	ΔE_{tun} (MHz)	ν_{tor} (cm^{-1})	ΔE_{tun} (MHz)	ν_{tor} (cm^{-1})	ΔE_{tun} (MHz)	ν_{tor} (cm^{-1})
	0	20	155	20	155	20	155
	428	340	134	148	150	77	155
857 K	571	1 146	121	347	147	137	154
	643	2 326	114	569	145	188	154
	714	5 294	91	996	128	269	153
	0	12	162	12	162	12	162
	428	171	143	78	158	42	162
	571	525	134	170	156	71	161
928 K	643	985	128	263	155	95	161
	714	1 989	119	428	152	130	161
	785	4 500	94	742	133	184	160
	857	12 510	57	1440	94	274	151
	0	7	170	7	170	7	170
	428	90	151	41	165	24	168
1000 K	571	266	143	87	164	39	168
	714	847	133	201	161	68	168
	857	3 630	96	557	137	128	167

well-known eigenfunctions of the free rotor as basis states and diagonalize the resulting matrix in order to find both the tunneling splitting and the vibrational frequency. The results are listed for various values of V_{chem} and γ in Table II.

As an example of the effect of the chemical interaction, consider the entries in Table II referring to $V_3 = 928$ K. For no chemical interaction, the tunneling splitting is 0.05 μeV (12 MHz) and the vibrational frequency is 162 cm^{-1}. As we increase the strength of the chemical interaction, the frequency decreases slowly while the tunneling splitting increases rapidly. Thus, at a chemical interaction of $V_{chem} = 570$ K and $\gamma = 20$, the frequency is unchanged while the splitting is now 0.30 μeV. When the chemical interaction is increased to 785 K, the vibrational frequency is 160 cm^{-1}, essentially unchanged, while the tunneling splitting is 0.76 μeV (0.2 GHz). For less localized chemical interaction, i.e., $\gamma < 20$, the effect is even more pronounced, as seen in Table II. For example, for $\gamma = 10$ and $V_{chem} = 714$ K, the vibrational frequency is 152 cm^{-1} and the tunneling splitting is 1.9 μeV (0.43 GHz). These results suggest very strongly that a local chemical interaction can have a substantial effect on the tunneling splitting without at the same time changing significantly the vibrational frequency, especially if the chemical interactions are quite localized and strong. Molecules with carbonyl groups are particularly good candidates for this effect, since they interact strongly with nearby hydrogens.

Experimentally, there is a 300-fold increase in the tunneling splitting in TQ on excitation; our model calculations indicate that the chemical effect can produce a $\sim$40-fold increase in the tunneling splitting while the vibrational frequency changes from 162 to 152 cm^{-1}.

Thus, the localized chemical effect as modeled here is not able to account for the entire change. This is not surprising in view of the crudeness of the model. It is likely that even in the ground electronic state the potential is not represented by a V_3 term only. The addition of a small V_6 term in Eq. (1) would be required in order to fit both the torsional frequency and the tunneling splitting, but as the latter is only approximately known (7–24 MHz), we cannot estimate the relative magnitude of this V_6 term. Upon excitation the values of both the V_3 and V_6 terms are likely to change as the difference between double and single bond character of the two adjacent carbon–carbon bonds is decreased in the excited state. It is of course possible to obtain complete agreement with the experimental values by an adjustment of all parameters, but no new insight will be gained from such multiparameter fittings as we do not dispose of an independent control that the potential thus produced is closer to reality.

In addition to intramolecular effects, there can be a modification in the intermolecular interactions upon electronic excitation. Since an excited molecule has, in general, a different molecular geometry from a ground state molecule, the interactions between it and neighboring molecules change upon excitation. This means that the intermolecular contribution to V_3 may also change upon excitation.

Finally, it should be remembered that the proximity of other excited triplet states, which may have strong vibronic coupling, will not only modify the excited state potentials but will also make the Born–Oppenheimer approximation less accurate as matrix elements of the nuclear kinetic moments between different electronic states may no longer be negligible. The effect of these couplings on tunneling remains to be explored.

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