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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 $\cos 3\phi$ 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 radicals in a matrix and by inelastic neutron scattering (INS) on molecular crystals. A more indirect method of evaluating tunneling splittings has been developed by Clough et al. using proton nuclear magnetic resonance (NMR). This method relies on the observation of a strong correlation between the tunneling frequency and the temperature $\theta_{\text{min}}$ 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 ($\phi$) dependence of the hindering potential can be written in the form

$$V(\phi) = \frac{V_2}{2}(1 - \cos 3\phi) + \frac{V_4}{2}(1 - \cos 6\phi) + \cdots . \quad (1)$$

It has been demonstrated by Clough et al. 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.

One case was reported by Clough et al. where the hindering potential and consequently the tunneling splitting of a methyl group was modified considerably by the creation of free radicals by $\gamma$ irradiation of the sample: Methylmalonic acid, CH$_3$-CH$_2$-(COOH)$_2$, has a tunneling frequency of 68 kHz. The free radical CH$_3$-CH(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...
have been reported so far. It is the purpose of this paper to
discuss the case of toluquinone (TQ) (methyl-p-benzoquin­
one) for which Lichtenbelt et al.\textsuperscript{9} published a value of 2.96
GHz, or 12 \(\mu\text{eV}\), 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 tun­
eling 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 \(\mu\text{eV}\). These two very different
values for the tunneling splitting are discussed in this paper
together with results about methyl torsional frequencies ob­
tained from infrared, Raman, and optical absorption mea­
surements.\textsuperscript{10,12} The crystal structure of toluquinone is ortho­
 rhromic 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 mea­
surements 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 spectra were used for a complete assignment of the
ground state vibrations.\textsuperscript{10} For the methyl torsional mode
the frequency in a pure crystal at 77 K of the protonated
compound was found to be 160 \(\text{cm}^{-1}\). 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 theo­
retical studies.\textsuperscript{11-13} The \(S_T-T_1\) gap in these compounds is
1400–1600 \(\text{cm}^{-1}\), only, and the description of the electronic
excitations is, to a first approximation, the same in both sys­
tems.

For \(p\text{-benzoquinone, the unsubstituted parent compound},\non one similarity of the excited states is reflected in the
vibrational structure of the vapor phase spectrum: the dif­
fferences between ground and excited state frequencies of
the most prominent progression forming modes are very similar
in both the \(S_T\rightleftharpoons S_0\) and \(T_1\rightleftharpoons S_0\) transitions; the frequencies of
these modes are therefore nearly the same in the singlet and
triplet excited states.\textsuperscript{14}

In the \(S_T\rightleftharpoons S_0\) absorption spectrum at 2 K of single
crystals of \(h_T\), \(d_T\), and \(d_T^-\text{-TQ}, the torsional mode of the methyl

group could clearly be identified. Its frequency in the first
excited singlet state of the \(h_T\) compound is 157 \(\text{cm}^{-1}\).\textsuperscript{12} Anal­
ysis 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 \(\text{cm}^{-1}\) 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 signif­
icant 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 \(\text{cm}^{-1}\) above \(T_1\). This state does not seem to per­
turb 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 there­
fore propose the following values for the frequency of the
methyl torsional mode: 160–165 \(\text{cm}^{-1}\) in the ground elec­
tronic state and 150–155 \(\text{cm}^{-1}\) in the lowest excited triplet
state.

III. TUNNELING IN THE LOWEST \(n\pi^*\) TRIPLET STATE

Lichtenbelt and Wiersma\textsuperscript{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 mi­
crowave 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 pro­
ton 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 cen­
tral 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,\textsuperscript{15} Lichtenbelt and
Wiersma in a later paper\textsuperscript{7} attempted to obtain the tunneling
splitting (\(J_T\)) and isotropic hyperfine constants of the methyl
protons from the measured second order shifts in the EN­
DOR 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 pro­
ton ENDOR spectrum of the \(| - 1, A \rangle\) state was too large.

Level anticrossing spectra of triplet TQ were also ob­
tained, 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 methyl 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. The sample, polycrystalline $h_2$-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. 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 $\theta_{\text{min}}$ of 78 K. With the help of the correlation between the tunneling splitting and $\theta_{\text{min}}$ mentioned in the introduction, we estimate a tunneling splitting of $(12 \pm 12)$ 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.

**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

$$V^0 = \frac{1}{2} V_2 (1 - \cos 3\phi).$$

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>
<thead>
<tr>
<th>$h_2$-toluquinone</th>
<th>Frequency of the methyl group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic state and energy with respect to $S_0$ (single crystal at 1.5 K)</td>
<td>Torsional mode $v_{\text{tort}}$</td>
</tr>
<tr>
<td>$S_0$</td>
<td>160 cm$^{-1}$ Raman at 77 K single crystal</td>
</tr>
<tr>
<td>$T_1$</td>
<td>18 691 cm$^{-1}$</td>
</tr>
<tr>
<td>$S_1$</td>
<td>150-155 cm$^{-1}$ estimation</td>
</tr>
<tr>
<td></td>
<td>155 cm$^{-1}$ Absorption at 2 K single crystal</td>
</tr>
</tbody>
</table>

*J. Chem. Phys., Vol. 81, No. 7, 1 October 1984*
$T_1$, 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 $V_6 = V_1 = 280$ K in Eq. (1), the estimated torsional frequency of 150 ± 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.

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 a $A$- and an $E$-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.

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 $V_3 \cos 3n\phi$ 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 $\pi^*$ orbital and a highly localized $p$ orbital in the plane of the molecule centered at the oxygen atoms. 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:

$$V = V^0 - V_{chem} \left[ \exp - \gamma(\phi - \pi/3)^2 \right.$$

$$+ \exp - \gamma(\phi + \pi/3)^2 + \exp - \gamma(\phi - \pi)^2 \right],$$

where $\gamma$ 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

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

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

<table>
<thead>
<tr>
<th>$V_3$ (K)</th>
<th>$V_{chem}$ (K)</th>
<th>$\Delta E_{tot}$ (MHz)</th>
<th>$\nu_{tot}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>857 K</td>
<td>0</td>
<td>20</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>428</td>
<td>340</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>571</td>
<td>1 146</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>643</td>
<td>2 326</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>714</td>
<td>5 294</td>
<td>91</td>
</tr>
<tr>
<td>928 K</td>
<td>0</td>
<td>12</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>428</td>
<td>171</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>571</td>
<td>525</td>
<td>134</td>
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<td></td>
<td>643</td>
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<td>12 510</td>
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<tr>
<td>1000 K</td>
<td>0</td>
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<td>847</td>
<td>133</td>
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<tr>
<td></td>
<td>857</td>
<td>3 630</td>
<td>96</td>
</tr>
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</table>

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 $V_{\text{chem}}$ and $\gamma$ 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 $\mu$eV (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 $V_{\text{chem}} = 570$ K and $\gamma = 20$, the frequency is unchanged while the splitting is now 0.30 $\mu$eV. 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 $\mu$eV (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 $V_{\text{chem}} = 714$ K, the vibrational frequency is 152 cm$^{-1}$ and the tunneling splitting is 1.9 $\mu$eV (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 ~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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