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LETTER TO THE EDITOR

Nuclear spin lattice relaxation and activation energies of tunnelling methyl groups

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Abstract. The coupling of lattice vibrations with the rotational motion of hindered methyl groups is considered. It is shown that the apparent activation energy for methyl group rotation is determined at relatively high temperatures by the methyl group torsional energy splittings, but at low temperatures it depends on the frequencies of short-wavelength lattice modes which couple relatively strongly with methyl-group rotation.

The temperature dependence of the proton spin lattice relaxation time from 6 to 50 K is reported for three samples containing methyl groups whose tunnelling frequencies have previously been measured very precisely. They are 4-methyl-2,6-ditertiarybutylphenol (MDBP) and two deuterated derivatives. The activation energy measured at temperatures between 18 and 50 K is in good agreement with the splitting between ground and first-excited methyl group torsional states, as computed from the known tunnelling frequencies assuming a three-fold hindering potential. At temperatures below 15 K the observed activation energy is only about half this value.

1. Introduction

An interesting property of the low-temperature proton spin lattice relaxation of compounds containing hindered methyl groups has been observed in several materials (Haupt and Müller-Warmuth 1968, 1969, Müller-Warmuth *et al* 1977). The activation energy for methyl-group rotation, determined from proton spin-lattice relaxation measurements, changes to a lower value as the temperature is reduced. This change often occurs near the maximum in the spin-lattice relaxation rate T_1^{-1} and so shows itself as a different slope on the two sides of the peak when $\ln(T_1^{-1})$ is plotted against θ^{-1} , the inverse temperature. The two activation energies have been identified in this earlier work with the height of the hindering potential barrier and with the energy difference between ground and first-excited torsional states of the methyl group. At low temperatures it is presumed that proton dipole-dipole matrix elements are modulated by processes which involve thermal excitation to the first excited torsional level, while the contribution of still higher torsional-rotational levels of the methyl group at higher temperatures is assumed to give rise approximately to an average activation energy of the order of the difference between the torsional ground state energy and the barrier height. There is, however, a problem with this model in that it is not easy to see how transitions to excited torsional states result in a

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sufficient modulation of the dipole-dipole matrix elements to account for the observed relaxation rates.

Proton spin-lattice relaxation of a methyl group containing compounds at low temperature is due to transitions which, besides involving flips of nuclear spins, also lead to conversion of a methyl group between two of its three possible nuclear spin-symmetry species (Haupt 1971). These are labelled A, E^a and E^b and two types of conversion may be distinguished, namely between A and E species and between the two E species. The former type of conversion involves an exchange of rotational energy $h\nu_t$ with the lattice, where ν_t is the methyl-group tunnelling frequency, a fact which is responsible for the different ways in which the two types of transition contribute to spin-lattice relaxation. Each type gives rise to a peak in the temperature dependence of T_1^{-1} . If the height of the potential barrier hindering rotation is not too great (less than about 1 kcal mol⁻¹) the peaks occur at sufficiently different values of θ^{-1} to be separately observable. In this case the E^a ↔ E^b peak occurs at the lower temperature and it is this peak which exhibits the asymmetric shape due to the changing activation energy. Another distinctive feature is that the E^a ↔ E^b peak is field dependent, reflecting the transfer of nuclear Zeeman energy, while the A ↔ E peak is independent of field because the Zeeman energy is only a small part of the total energy transferred in these transitions.

It is easy to see that excitation of the methyl group from the ground state to the first-excited torsional oscillator state results in frequency modulation of the dipole-dipole matrix elements between A and E states because the energy splitting between A and E levels is quite different in ground and excited states. Thus this provides a natural explanation of the A ↔ E peak in the temperature dependence of T_1^{-1} (Haupt 1971). However, the splitting between E^a and E^b states is usually considered to be the same in all torsional levels, and simply equal to the nuclear Zeeman splitting, so one concludes that there is no comparable frequency modulation of matrix elements between E^a and E^b states. There is a small amplitude modulation arising from the increase in the amplitude of torsional motion in the excited state compared with the ground state, but there is apparently no modulation which can be identified with the classical idea of rotation of the methyl group through 120° or 240°. The amplitude modulation of torsional oscillation is quite inadequate to account for the relatively rapid relaxation. It is possible to introduce classical rotational motion into the model (Clough 1976), but then it is not clear that its rate should be associated with a particular activation energy.

Apart from these conceptual difficulties, it appears that the lowest observed activation energy can not always be identified with a torsional splitting. In this paper we report measurements of T_1^{-1} between 6 and 50 K for three samples whose methyl group tunnelling frequencies are known very precisely (Clough and Nugent 1976). They are 4-methyl-2,6-ditertiarybutylphenol and two deuterated derivatives, one having the phenolic hydrogen atom replaced by deuterium, and one having all hydrogen atoms except those of the 4-methyl group replaced by deuterium atoms. We refer to these samples as MDBP, MDBP(D₁) and MDBP(D₂₁) respectively. The energy difference between ground and first-excited torsional states calculated from the tunnelling frequencies using a three-fold hindering potential, accords quite well with the larger of the two activation energies observed, but the smaller one does not fit into this level scheme. It may be possible, by choosing a more complicated hindering potential, to obtain both activation energies as torsional splittings, consistent with the known tunnelling frequencies, but this would still leave unsolved the question of the modulation of the matrix elements discussed above. In §3 we describe a modification to the theory of spin-lattice relaxation which accounts for the modulation of the matrix elements between

E^a and E^b states, and leads to the expectation of an activation energy at low temperature which is not dependent on the torsional levels of the methyl group, providing a straightforward interpretation of our data.

2. Experimental Results

Figure 1 shows the temperature dependence of T_1^{-1} measured at a nuclear resonance frequency $\omega_0/2\pi$ of 21 MHz. The results fit the following expressions with the parameters given in table 1.

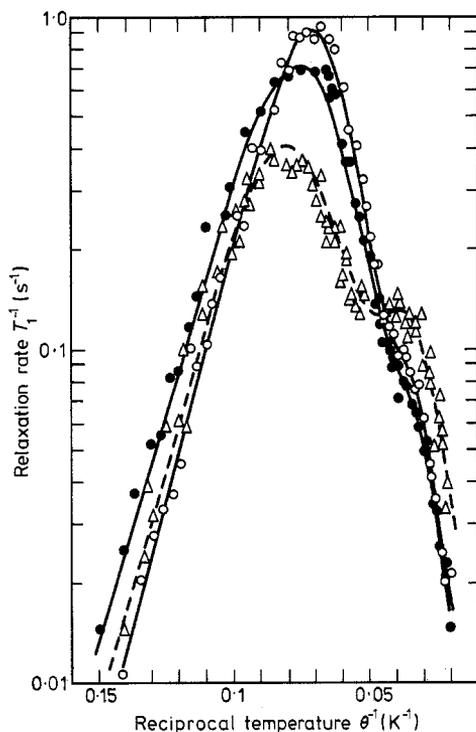


Figure 1. The dependence of the proton spin-lattice relaxation rate T_1^{-1} on the reciprocal temperature for MDBP (open circles), MDBP(D_1) (full circles) and MDBP(D_{21}) triangles. The curves are obtained from equations (1)–(5) with the parameters of table 1. The activation energy at low temperatures is about half the computed torsional splitting.

Table 1. Relaxation parameters for MDBP and deuterated derivatives

		MDBP	MDBP(D_1)	MDBP(D_{21})
ν_i	GHz	9.4	9.24	8.47
$C_{AE} \times 10^{-9}$	s^{-2}	6.0	4.5	11.5
$C_{EE} \times 10^{-7}$	s^{-2}	8.4	6.6	3.7
$\lambda_{AE} \times 10^{-12}$	s^{-1}	7.1	5.6	5.9
$\lambda_1 \times 10^{-12}$	s^{-1}	1.7	1.0	1.0
$\lambda_2 \times 10^{-10}$	s^{-1}	1.3	2.9	3.7

$$T_1^{-1} = (T_1^{-1})_{AE} + (T_1^{-1})_{EE} \quad (1)$$

$$(T_1^{-1})_{AE} = C_{AE}\tau_{AE}(1 + 4\pi^2\nu_i^2\tau_{AE}^2)^{-1} \quad (2)$$

$$(T_1^{-1})_{EE} = C_{EE}[\tau_{EE}(1 + \omega_0^2\tau_{EE}^2)^{-1} + 4\tau_{EE}(1 + 4\omega_0^2\tau_{EE}^2)^{-1}] \quad (3)$$

$$\tau_{AE}^{-1} = \lambda_{AE} \exp(-W_1/k\theta) \quad (4)$$

$$\tau_{EE}^{-1} = \lambda_1 \exp(-W_1/k\theta) + \lambda_2 \exp(-W_2/k\theta). \quad (5)$$

The contribution $(T_1^{-1})_{AE}$ peaks near $\theta^{-1} = 0.03$ and is more prominent for MDBP(D₂₁) than for the other samples because there are no non-methyl protons to dilute the relaxation due to the modulation of the intra-methyl group interactions. On the other hand the contribution $(T_1^{-1})_{EE}$ is relatively less strong for the heavily deuterated sample because the dipolar interactions of the methyl group with other magnetic nuclei are diminished by deuteration. The three samples have similar activation energies in the high- and low-temperature regions which we find to be $W_1/k = 130 \pm 20$ K and $W_2/k = 65 \pm 10$ K. We compute values between 120 and 125 K for W/k where W is the energy splitting between ground and first-excited torsional level, using the measured tunnel frequencies and assuming a three-fold hindering potential.

3. Methyl group rotation and the dynamic splitting of the E levels

For a time independent hindering potential, the energies of E^a and E^b species are the same in each torsional state of the methyl group. When the dynamic coupling between methyl-group motion and the lattice vibrations is taken into account, the E^a and E^b levels may be regarded as split by an amount which fluctuates in response to the local lattice strain. It has been shown (Clough 1976) for a simple model system consisting of a linear chain of molecules with a methyl group attached to one molecule, that a coupling of the form $A\phi x(t)$ exists between the local lattice strain $x(t)$ and the methyl-group rotational coordinate ϕ . The parameter A depends on inter-molecular forces and on the moments of inertia of molecule and methyl group. The angle ϕ measures the orientation of the group relative to the hindering atoms. Since these atoms move in response to lattice vibrations, the orientation of the group relative to the crystal as a whole is ϕ' , the difference $(\phi' - \phi)$ being a lattice displacement. In the reference frame in which the hindering atoms are stationary, the methyl group experiences a time-independent three-fold hindering potential plus a fluctuating inertial torque which is responsible for the coupling term $A\phi x(t)$.

In order to calculate the magnitude of the resulting fluctuating splitting, we need the matrix elements of ϕ . The spatial part of the state function $|E^a\rangle$ is periodic in ϕ , reflecting the indistinguishability of the protons and it can be written in terms of harmonic oscillator functions ψ centred at different values of ϕ as follows:

$$|E^a\rangle = N^{-1/2} \sum_{n=-\infty}^{n=\infty} [\psi(\phi - 2\pi n) + \epsilon\psi(\phi - 2\pi n - 2\pi/3) + \epsilon^*\psi(\phi - 2\pi n + 2\pi/3)]. \quad (6)$$

N is a normalizing constant and $\epsilon = \exp(2\pi i/3)$. Note that (6) is defined for all ϕ rather than for an interval of 2π as has previously been the case. This is necessary because we deal with a potential which is not periodic in ϕ . $|E^b\rangle$ is the complex conjugate of (6).

In evaluating $\langle E^a | \phi | E^a \rangle$, we ignore contributions involving pairs of harmonic oscillator states displaced by more than $2\pi/3$. Terms like

$$\int \psi^*(\phi - z)\phi\psi(\phi - z)d\phi$$

where $z = 2\pi(n + y/3)$ with $y = 1, 0$ or -1 , contribute nothing to the matrix element. This can be seen by changing the variable to $u = \phi - z$ to make the integral

$$\int \psi^*(u)u\psi(u)du + z \int \psi^*(u)\psi(u)du.$$

The first term is zero because $\psi^*(u)\psi(u)$ is an even function and u is odd. The second term sums to zero because the average value of z is zero. Treating the terms connecting adjacent harmonic oscillator states in the same way, one finds

$$\langle E^a | \phi | E^a \rangle = (\epsilon - \epsilon^*) \int_{-\infty}^{\infty} \psi^*(u)u\psi(u - 2\pi/3)du. \quad (7)$$

$\langle E^b | \phi | E^b \rangle$ is the negative of this. Like (7) it is imaginary, indicating a $\pi/2$ phase shift of the splitting relative to the strain $x(t)$.

It is easy to see that a splitting of the E levels is equivalent to the assumption that the methyl group rotates. To illustrate this we suppose that there is no splitting between the E and A levels since this gives rise not to rotation, but to the flip-flop motion (Clough and Hill 1976). We suppose that the E levels are split by $2\hbar\omega(t)$ and that at $t = 0$ the group is in the localized harmonic oscillator state $\sum_n \psi(\phi - 2\pi n)$. As a combination of $|A\rangle$, $|E^a\rangle$ and $|E^b\rangle$ this is $(1/3)^{1/2}(|A\rangle + |E^a\rangle + |E^b\rangle)$ or, introducing the time dependence

$$(1/3)^{1/2}[|A\rangle + |E^a\rangle \exp(i\eta) + |E^b\rangle \exp(-i\eta)]$$

where

$$\eta = \int_0^t \omega(t')dt'.$$

In terms of the harmonic oscillator functions this is (unnormalized)

$$(1/3) \sum_n [(1 + 2 \cos \eta)\psi(\phi - 2\pi n) + (1 - \cos \eta + 3^{1/2} \sin \eta)\psi(\phi - 2\pi n - 2\pi/3) \\ + (1 - \cos \eta - 3^{1/2} \sin \eta)\psi(\phi - 2\pi n + 2\pi/3)]$$

which is just $\sum_n \psi(\phi - 2\pi n)$ or $\sum_n \psi(\phi - 2\pi n - 2\pi/3)$ or $\sum_n \psi(\phi - 2\pi n + 2\pi/3)$ as η takes the values $0, 2\pi/3$ or $-2\pi/3$. Thus η may be identified with the angle through which the group has rotated. It is not restricted to three values though, as classical ideas imply. This is an interesting reversal of the usual distinction between classical and quantum models, since it is the classical picture which exhibits a kind of quantization while the quantum description allows a continuum of values of η .

4. Relaxation due to methyl group rotation

Using standard time-dependent perturbation theory, one finds transition probabilities for conversion between E^a and E^b species with the flip of p proton spins ($p = 1$ or 2) proportional to the spectral density functions ($F(p\omega_0)$).

$$F(p\omega_0) = \int_0^{\infty} \langle \exp(2i\eta) \rangle \exp(ip\omega_0 t) dt \quad (8)$$

where the angular brackets indicate an average over time. If we further assume that $2\omega(t)$ is a random function of time with a mean-square value Ω^2 , a Gaussian probability distri-

bution and an exponential correlation function so that

$$4\langle\omega(t')\omega(t+t')\rangle_{\text{average over } t'} = \Omega^2 \exp(-\omega_e t) \quad (9)$$

and if also $\omega_e^2 \gg \Omega^2$, then we may use a known result (Anderson 1954) for the rotational correlation function.

$$\langle\exp(2i\eta)\rangle = \exp(-\Omega^2 t/\omega_e). \quad (10)$$

When (10) is inserted into (8), the Lorentzian spectral density functions of (3) are obtained with new light on the parameter τ_{EE} .

The splitting $2\hbar\omega(t)$ of the E levels is proportional to the local strain $x(t)$, so that it follows from (9) that τ_{EE}^{-1} is proportional to X^2/ω_e where X^2 is the mean square value of $x(t)$. Now $x(t)$ is a linear combination of all the lattice normal coordinates, but the short-wavelength modes predominate since only the displacements of atoms close to the methyl group are coupled to its rotational motion. We suppose therefore that the coupled modes have roughly the same frequency ω_e corresponding to the short wavelength end of the lattice spectrum. X^2 is proportional to the number of these lattice oscillators which are excited, and this is proportional to $\exp(-\hbar\omega_e/k\theta)$. Thus if the methyl group were limited to its ground state we should expect to observe behaviour corresponding to the second term on the right-hand side of (5) with $W_2 = \hbar\omega_e$.

When the methyl group is excited to the first torsional excited state, the constant of proportionality between $\omega(t)$ and $x(t)$ as obtained from (7) changes sign and has a larger magnitude. This sudden switch in $\omega(t)$ affects the correlation function (10). We suppose that the lifetime of the excited state is sufficiently short and rotation in the excited state sufficiently fast, that an excursion to the excited state can be regarded as an event which destroys the memory of the previous value of $\eta(t)$. Then the correlation function (10) becomes

$$\langle\exp(2i\eta)\rangle = \exp(-\Omega^2 t/\omega_e) \exp(-t/T_g) = \exp(-t/\tau_{EE}) \quad (11)$$

where T_g is the lifetime of the ground torsional state. If this is limited only by transitions to the first excited torsional state, then (5) follows directly from (11) with λ_1^{-1} being the lifetime of the first excited state. Higher levels contribute additional terms to (5) at higher temperatures.

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