Rotation of methyl groups in molecular solids and polymers at low temperatures: Recent developments

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The theory of Stejskal and Gutowsky, frequently used to explain the non-Arrhenius behaviour of log ν against $1/T$ for rotating methyl groups has been shown to be inconsistent with the published data. An alternative explanation of this phenomenon in terms of a potential which is not purely three-fold is offered. Recent experimental and theoretical developments in the studies of tunnelling frequencies of rotating methyl groups at low temperatures are presented.

(Keywords: methyl groups; tunnelling; low temperatures; polymers; molecular crystals; Stejskal and Gutowsky model)

INTRODUCTION

The reorientation of side-groups in polymer molecules has been subjected to detailed study by neutron scattering[1-4], nuclear magnetic resonance (n.m.r.)[5,6] and mechanical, viscoelastic and dielectric relaxation[7] with complementing data from Raman and infra-red spectroscopy[8] and ultrasonic measurements[9]. The choice of experimental technique for investigation of a particular motion is mainly dictated by the relevant selection rules and the frequency range over which such reorientation occurs. It is helpful to follow the investigated motion over as wide a temperature range as the technique permits.

Methyl groups are of special importance because motion has been recorded even below 77 K, though most investigations have been conducted above that temperature[10]. Although the temperature dependence of the methyl group reorientation rate is commonly assumed to follow the Arrhenius law, deviations from this law are observed with some polymers. These have been attributed to quantum-mechanical tunnelling of protons through the potential barrier which hinders free rotation[11-13], calling in aid the Stejskal and Gutowsky model (S & G)[14] originally established for the rotation of methyl groups in molecular crystals. Since 1958 extensive experimental and theoretical studies of the motion of methyl groups, including the effects of tunnelling, have been carried out. The theoretical predictions of the S & G model have not been confirmed. These developments have escaped the attention of polymer scientists. It is therefore useful to discuss briefly the current position in the experimental investigation of tunnelling by inelastic neutron scattering (INS), which provides a direct measurement, and by n.m.r., from which the S & G model stems. These two techniques are becoming increasingly important in investigations of side chain dynamics.

Although no penetrating theoretical analysis is attempted, an outline of the assumptions underlying the analysis of methyl group motion in molecular crystals is given in the subsequent section. A second objective of this paper is to suggest an alternative explanation for the occurrence of those phenomena in polymers, which have so far been attributed to quantum-mechanical tunnelling.

HINDERED MOTION OF METHYL GROUPS IN SOLID MOLECULAR CRYSTALS

The rotation of a rigid methyl group in a static environment about a fixed axis is a one-dimensional problem for which the theory is well established[15,16]. However, a recent reformulation of the approach to both free and hindered methyl rotators which introduces a different way of treating the potential energy function $V(\phi)$, where ϕ is an angle shown in *Figure 1a*, has led to new insights and predictions[17,18].

The conventional approach is to find the energy eigenvalues of the rotational Hamiltonian

$$\left\{-\frac{\hbar^2}{2I_0}\frac{\partial^2}{\partial\phi^2}+V(\phi)\right\} \tag{1}$$

where I_0 is the moment of inertia of the methyl group and ϕ is an angle measured in the plane perpendicular to the C_3-axis of the methyl group (*Figure 1b*). For a free rotor $V(\phi)=0$. For methyl groups rotating independently of each other, $V(\phi)$ is treated as a 'single particle' potential[15]. This assumption is equivalent to the adoption of a rigid methyl group whereby the strength of the CH bonds allows the internal degrees of freedom (vibrational excitations) to be neglected in comparison with both translational and rotational motions of the group as a whole. It follows from the C_3-symmetry and the indistinguishability of protons that the periodicity of the potential is the property of the methyl group itself and not of an underlying lattice, for even an environmentally imposed

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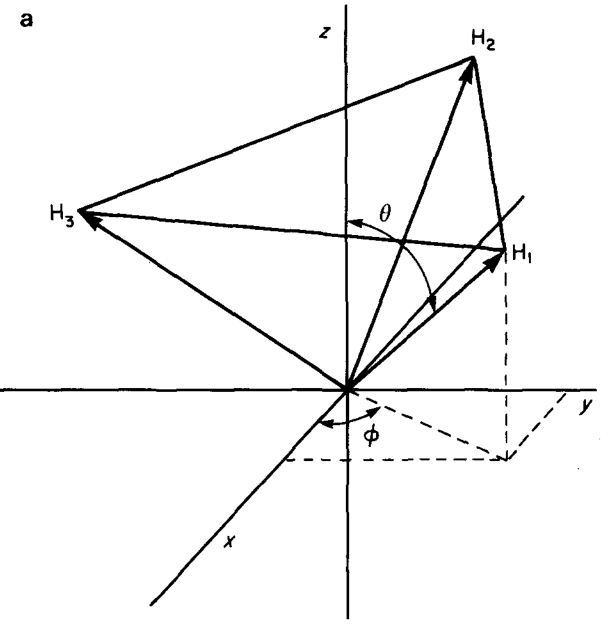

Figure 1a Schematic view of a methyl group in spherical polar coordinates. Each proton moves in the equatorial plane

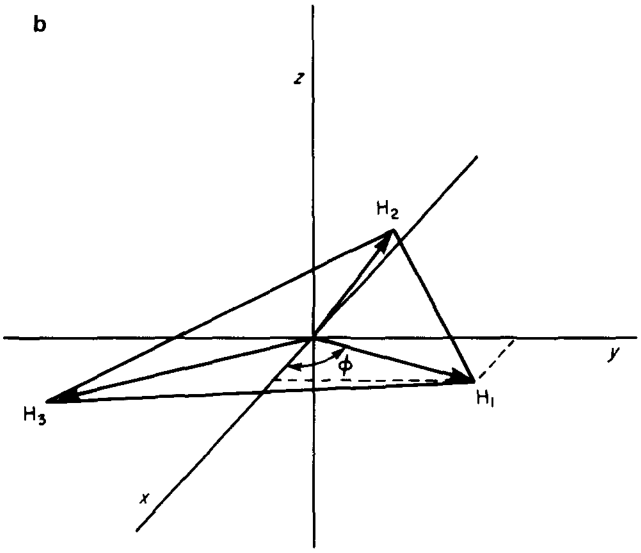

Figure 1b View from above of a methyl group rotating in the x–y plane. The origin coincides with the centre of the equilateral proton triangle (the carbon atom lying along the z-axis below the x–y plane is not shown here). The rotational angle is ϕ, the angle between the x-axis and the radius r

potential, which affects but one proton at a time, will restrict hindered rotation to unit steps of $(\pm 2\pi/3)$. Thus $V(\phi)=V(\phi+2\pi/3)=V(\phi+4\pi/3)$. Since $V(\phi)$ as experienced by the methyl groups can then be regarded as periodic in $2\pi/3$, it can formally be represented by a Fourier series expansion

$$V(\phi)=\sum_{k=0}^{\infty}(a_{3k}\cos 3k\phi+b_{3k}\sin 3k\phi) \qquad (2)$$

This series is usually truncated to the cosine terms by a convenient choice of the origin of $V(\phi)$[16] such that $\sin 3\phi=0$, neglecting higher order terms which are expected to be small. When the first and only term retained is $(1+\cos 6\phi)$, the potential is called a pure sixfold[19]. If $V(\phi)$ has to be described by more than one term, it is said to be of 'mixed' symmetry[20].

The hindering potential $V(\phi)$ is usually supposed to stem from electrostatic, van der Waals attractive and hard-core repulsive forces between the methyl group and its environment. Evaluation of the relative contributions is not easy, but in one attempt to calculate $V(\phi)$ from first principles which assumed the exchange (repulsive) interaction between nonbonded atoms in a molecule to be the primary source of the hindering potential, a good agreement between calculated and experimentally determined values of the barrier height was found[21].

An interesting complication arises when methyl groups no longer reorient independently of each other. Such a collective motion has been found in lithium acetate[22]. The interaction of methyl groups was also invoked to explain the observed far-infra-red spectra of molecular crystals containing methyl groups. Two such groups are treated as symmetric tops rotating in reference frames of various symmetry and the potential function is given in terms of the sums and differences of their respective Euler angles[23]. However, for most molecular crystals as well as polymers at higher temperatures[24], the experimental results are well described by the pure three-fold potential appropriate to independently rotating groups. It is evident that in experiments conducted over a wide temperature range or where the environment might undergo a phase transition, it is inadequate to treat the hindering potential as if it were independent of temperature, the energy of the rotator itself being the only temperature dependent feature. Accordingly, the potential is divided into a static part V_{stat} and a fluctuating (time-dependent) part V_{fluct}.

The magnitude of the fluctuations is at a maximum of order kT, the relative magnitude of the static and fluctuating parts determining the degree of hindrance of the rotor. At low temperatures only a few lattice phonons are present. They are generally of long wavelength whereby V_{fluct} becomes very small and a description of rotation in terms of V_{stat} is sufficient. At higher temperatures provided the magnitude of V_{stat} continues to be larger than V_{fluct}, the static part of the potential will determine the kind of rotation: rotational jumps $(2\pi/3)$ in the case of a very strong V_{stat} and free rotation for a weak V_{stat}, which will acquire the characteristics of rotational diffusion if V_{fluct} is large.

When a pure three-fold potential is assumed, the Schrödinger equation

$$\frac{d^2}{d\phi^2}\psi(\phi)+\frac{2I_0}{\hbar^2}\{E_r-\tfrac{1}{2}V_3(1-\cos 3\phi)\}\psi(\phi)=0 \qquad (3)$$

is first transformed into the Mathieu equation[16]

$$\frac{d^2}{dx^2}\psi(x)+(a_r+2\theta\cos 2x)\psi(x)=0 \qquad (4)$$

where

$$x=\frac{3}{2}\phi,\ \theta=\frac{2I_0}{\hbar^2}\frac{V_3}{9}\ \text{and}\ a_r=\frac{16I_0}{9\hbar^2}\left(E_r-\frac{V_3}{2}\right)$$

From the properties of the hindering potential described above, it immediately follows that the C_3 group symmetry operations leave the Hamiltonian in equation (1) invariant[26]. This implies that the particular solution of the Mathieu equation can be expanded in the form

$$\sum_{k=0}^{\infty} B_{3k}e^{i3k} \qquad A \text{ symmetry species}$$

$$\sum_{k=0}^{\infty} B_{3k+1}e^{i(3k+1)\phi} \qquad E_b \text{ symmetry species} \quad (5)$$

$$\sum_{k=0}^{\infty} B_{3k-1}e^{i(3k-1)\phi} \qquad E_a \text{ symmetry species}$$

The eigenvalues belonging to the non-degenerate fully symmetric representation are classified as A, whereas the doubly degenerate eigenfunctions are classified as E_a and E_b symmetry species[16]. Since there is no energy difference between the time-reversed E_a and E_b states, they are often referred to simply as E symmetry states.

The Mathieu equation is easy to solve analytically only in two limiting cases: for a strongly hindering potential, where the motion resembles that of an harmonic oscillator and the rotor librates around the equilibrium position or for a weak hindering potential, when the rotation is (nearly) free. However, solutions for moderate potential heights are easily obtained by numerical methods so that a smooth passage between these limiting cases is ensured. This is shown graphically in *Figure 2a*. A threefold potential and the corresponding energy states are illustrated in *Figure 2b*.

The energy difference Λ between A and E symmetry states within the same torsional level is called the *tunnel splitting* (*Figure 2a*). Such a splitting occurs in each torsional state and its sign alternates as the harmonic oscillator quantum number v increases: (+) in the ground state, (−) in the first excited state, etc. The splitting also increases with the number of the torsional state; thus in the first excited state Λ is 20–30 times greater than in the ground state. Since Λ can be written as $\Lambda = h\nu_t$ it has often been termed 'the tunnelling frequency' which in turn has generated a misleading classical interpretation of ν_t as a 'frequency of the passage under the barrier' from one potential well to another based on a distant analogy with the problem of a free particle encountering a repulsive potential barrier of a finite width. In this paper, we understand ν_t only as defined from $\nu_t = \Lambda/h$.

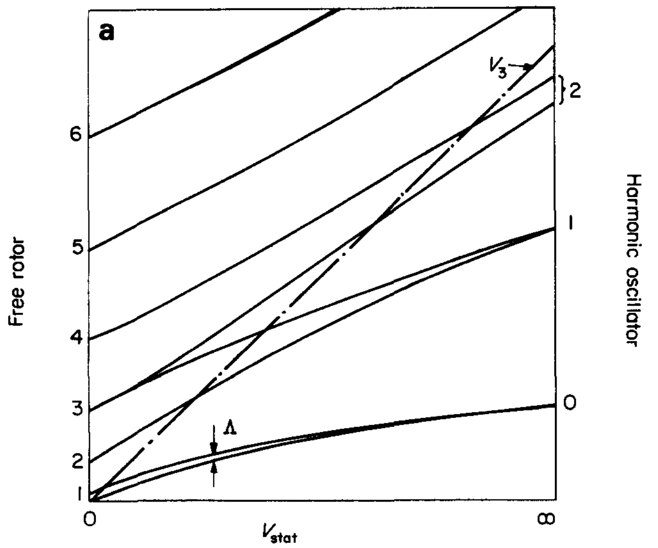

Figure 2a Hindered rotational energy levels as a function of the barrier height V_{stat}. The free rotation quantum numbers m are shown at a zero barrier and the torsional quantum numbers v are at a very high barrier. The diagonal line V_3 shows the height of the barrier in relation to the energy levels. Λ denotes the ground state tunnel splitting. The alternating A and E symmetry levels are marked in *Figure 2b*

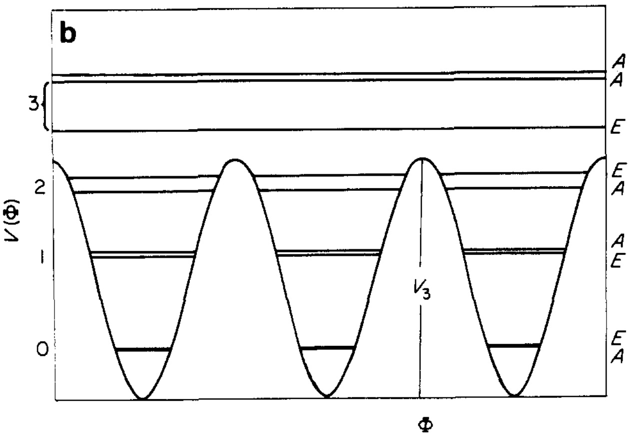

Figure 2b Cosine potential barrier V_3 as a function of ϕ and its associated energy levels. The torsional quantun numbers v are shown on the left ordinate. The sublevels are listed by symmetry

In a recent re-examination of the one-dimensional rotor problem[17,18] the rigidity of the group has been discarded and emphasis placed on its internal permutation symmetry. Each proton is then held close to one corner of an equilateral triangle by a two-particle repulsive potential, which depends on the difference of the respective (spherical polar coordinates) angles ϕ_i with origin on the C_3-axis in the plane of the H-atoms. Each proton then moves in a combination of two potential fields with deep wells. One field has a minimum at $r = r_0$ the equilibrium distance of a proton from the C_3-axis while the other field reaches a minimum at $\theta = \pi/2$ and thus serves to confine the H-atoms to a plane. Equi-energy contours of the combined fields are represented by a torus. However, in practice still deeper minima separated by $2\pi/3$ are imposed on this field by the pairwise interactions between H-atoms.

Retracing the steps of the simple argument given earlier one can recommence with the Hamiltonian for a free, non-rigid rotor[18]

$$H = \frac{-\bar{h}^2}{2m_0r_0^2}\left\{\frac{\partial^2}{\partial\phi_1^2} + \frac{\partial^2}{\partial\phi_2^2} + \frac{\partial^2}{\partial\phi_3^2}\right\}$$

$$+U(\phi_1 - \phi_2) + U(\phi_2 - \phi_3) + U(\phi_3 - \phi_1)$$

where it should be clearly understood that the potential field described by a threefold modulated torus rotates with the methyl group. It is a Hamiltonian for internal degrees of freedom.

This Hamiltonian fulfils the requirement of indistinguishability of protons, since it is symmetric under interchange of particles. It is also invariant to a simultaneous change in each ϕ_i by an arbitrary angle (Bloch's Theorem). This latter symmetry is then exploited in a change to new variables x,y,z expressed as linear combinations of the ϕ_i whereby the Hamiltonian H can be written as a sum of two Hamiltonians H_z and $H_{x,y}$[18]

$$H = H_z + H_{x,y}$$

where the distinctive property of H_z is that it is independent of potential energy. This transformation recalls an early solution for the motion of an electron in a magnetic field in the Landau gauge. The eigenvalues of H_z are then related to the eigenvalues of the free rigid rotor Hamiltonian through the relation $I_0=3m_0r_0^2$, I_0 being a moment of inertia of the rigid triangle. The eigenfunctions are $\exp(i\lambda Z)$ where $Z=(\phi_1+\phi_2+\phi_3)/\sqrt{3}$.

The eigenvalues of the other part of the Hamiltonian, which does depend on the potential energy, are obtained for the six deep minima in the potential which are generated in the x,y plane and correspond to distinct arrangements of protons after allowing for proton spin. They are classified under the permutation group on those variables and denoted as $^4A_2$ (the total nuclear spin $I=\frac{3}{2}$) and ^2E (the total nuclear spin $I=\frac{1}{2}$). For wells with a *finite* width and depth there will be an energy difference between A and E states, the so-called tunnel splitting. Hindrance to the free rotation of this non-rigid methyl group imposed by the molecular environment is introduced by adding a term to H, namely $V(\phi_1)+V(\phi_2)+V(\phi_3)$ which has no particular symmetry at least when the lowest energy states are considered. If higher-lying energy states are used for which the H-atom wave functions are increasingly delocalized the added (hindering) potential may cause a change in the symmetry of the effective hindering potential[18].

If the protons are treated as indistinguishable, then the product wavefunctions are invariant under cyclic permutation involving two pairwise interchanges of protons. This cyclic permutation group is isomorphous with the point group C_3 and leads to A and E-states, where the E-state can be regarded as a pair E_a, E_b of distinct, time-reversed states which can be differently populated, leading to rotational polarization. If, however, it is further borne in mind that the product wave function $\psi(\text{spatial})\times\psi(\text{spin})$ must be antisymmetric under a single pair exchange, the full permutation group ($N=3$), which is isomorphous with the point group C_{3v}, applies. In these circumstances, Clough and McDonald argue that the E-state while remaining doubly degenerate can no longer be separated into distinct E_a and E_b species because antisymmetrized products of functions are involved. Such an argument has important implications for spin-diffusion experiments believed to involve differential populations of E_a, E_b[27] but does not affect the principal investigations of tunnelling described in the present paper.

THE TEMPERATURE DEPENDENCE OF TUNNELLING FREQUENCY, ν_t

The model of Stejskal and Gutowsky

In order to compare the model of methyl group reorientation with the n.m.r. experiment which essentially yielded the spin-lattice relaxation rate T_1^{-1} as a function of temperature, Stejskal and Gutowsky[14] introduced the tunnel energy as a 'correcting parameter' into the classical (BPP) spectral density functions of reorientational motion[28]. $1/T_1$ is a function of temperature through the correlation time τ_c, given by the Arrhenius law

$$\tau_c=\tau_0\exp(E_A/kT) \tag{7}$$

where E_A is a constant activation energy of the motion and τ_0 is related to a partition function of the activated energy state $E=V_3$.[24] The introduction of the tunnelling phenomenon expressed in frequency units causes the appearance of a maximum in the $(1/T_1,T)$ curve which is additional to that predicted by BPP theory, as can be seen in the work of Haupt[31].

In the S & G model the independently reorienting methyl groups are treated in a conventional way (cf. previous section), using numerical solutions of the Mathieu equation with the potential $V(\phi)=\frac{1}{2}V_3(1+\cos 3\phi)$. An *averaged tunnelling frequency* $\langle\nu_t\rangle$ for a given set of levels is introduced, weighted in proportion to its relative population over a Boltzmann distribution as follows:

$$\langle\nu_t\rangle=\frac{1}{Q}\sum_{i=0}^{\infty}\nu_i\exp(-\bar{E}_i/kT) \tag{8}$$

In this expression ν_i is the tunnelling frequency of the ith torsional pair of levels, E_i is the average energy of the pair and $Q=\sum\limits_{i=0}^{\infty}\exp(-\bar{E}_i/kT)$ is the partition function. Using equation (8), Stejskal and Gutowsky calculated $\langle\nu_t\rangle$ as a function of temperature for a family of barriers to rotation ranging from about 33 kJ mol^{-1} to 9.9 kJ mol^{-1}. The alternating signs of tunnel splittings in consecutive energy states were *not* taken into account in this calculation.

Another important feature of the model is the levelling-off of the averaged tunnelling frequency $\langle\nu_t\rangle$ as the temperature is reduced to about 100 K and the concomitant temperature-independence of $\langle\nu_t\rangle$ below 70 K. That means that at some stage the value of $\langle\nu_t\rangle$ should become equal to the ground state torsional tunnel splitting Λ/h as can be seen from Boltzmann statistics.* It then follows from equation (8) that the averaged tunnelling frequency $\langle\nu_t\rangle$ is at its lowest at very low temperatures, *increases* with increasing temperature and is approximately 10^{13} Hz well above room temperature. Such a model is unconvincing and potentially confusing for it predicts that with increasing temperature the probability of tunnelling as a dominant relaxation process will decrease sharply above 100 K whereby classical rotational jumps over the barrier will become relatively favoured energetically. If, on the other hand, one treats $\langle\nu_t\rangle$ as the reorientational rate, the S & G model is seen to describe classical hopping motion between equilibrated states and leads to an unphysical picture of a temperature independent reorientation *rate* below 70 K. It then follows that the S & G model does not give a correct quantum-mechanical description of the tunnelling motion. Also, recent n.m.r. and INS experiments (next section) have not confirmed the conclusions following from the S & G model.

Recent theories of temperature dependence of ν_t

The temperature dependence of the tunnelling frequency is intimately connected with a change of rotation mechanism from the quantum-mechanical region (low temperatures) to the classical region (high temperature), but the simple view implied by this statement does not yield a $(\langle\nu_t\rangle,T)$ dependence in agreement with experiment. A new approach was suggested by some n.m.r. results[3]. Since the transitions between the rotational levels are

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* In the case of 2,4-hexadiyne, we have $E_0=7.06$ meV, $E_1=21.09$ meV and $E_2=34.62$ meV (as calculated from the observed (1–0) and (2–0) torsional transitions[29]), which gives for $T=10$ K, $Q\simeq 7.540\times 10^{-5}$, where Q is taken as $Q\simeq\exp(-E/kT)+\exp(-E_1/kT)+\exp(-E_2/kT)$.

non-magnetic, an operator H_{RP} which induces such transitions through the influence of phonon modes on rotor states has been introduced[31]. H_{RP} modulates the hindering barrier under the influence of a phonon propagating through the crystal[31,32]. It can then be related to the elasticity tensor, ε, when $H_{RP}=V'-V=\varepsilon f(\phi)$, where V is the potential barrier in thermal equilibrium, V' the potential barrier during passage of the phonon, $f(\phi)$ is a function proportional to $V'-V$, and ε the elasticity tensor can be written as $\varepsilon_{xx}=\partial u/\partial x$, u being the displacement vector of the atom under the influence of the phonon wave from its equilibrium position. The influence of H_{RP} on the magnetic levels is assumed to be small. In this model, the lattice vibrations are treated as a system of harmonic oscillators, where every oscillator has an averaged energy

$$E=(\bar{N}_0+\tfrac{1}{2})\cdot E_{10}$$

where E_{10} = the energy difference between the two lowest levels, and $\bar{N}_0$ is the mean phonon number in equilibrium given by

$$\bar{N}_0=(\exp(E_{10}/kT)-1)^{-1}$$

Thus with increasing temperature the torsional transition lines will broaden ($\sim\exp(-E_{10}/kT)$ as the fluctuations in barrier height become larger. Note that this approach still does not give the correct $(\langle v_t\rangle, T)$ dependence.

However, the dependence of v_t on temperature can be obtained by assuming that as well as affecting the barrier height the phonons cause random 'jumps' between the ground and first excited state of the hindered rotator (the Allen model[33]). Such a mixing of the ground and the first excited state causes a sharp decrease in the value of v_t because of the large, negative value of v_t in the first excited state and brings about some broadening of $A\leftrightarrow E$ transitions, but it does not account for the broadening of $E\leftrightarrow E$ at all. An alternative view[34] is that the influence of phonon modes on rotor states results in shifting the minimum in the potential function $V(\phi)$ in proportion to the local strain produced by the two nearest neighbour molecules and the last molecule in the linear chain. This induces the required mixing of the ground and the first excited harmonic oscillator states of the rotor. Thus, the operator H_{RP} can either distort the shape of the potential or 'shake' it[35], that is displace the origin of the potential without changing its shape. The distortion is an anharmonic correction and the shaking is a harmonic (bilinear) contribution in the librations of the methyl groups and small translational displacements of the environment. In calculations only the shaking term, bilinear in vibrations and displacements, is retained; it couples the rotational and the translational motion. However, in the absence of the anharmonic distortion there is almost no broadening of the transition lines.

The operator H_{RP} can be also constructed in such a way that it couples the vibrations of one methyl group with the vibrations of the neighbouring proton groups[36]. Since the groups are assumed to be equivalent and to have the same vibrational frequencies in the absence of coupling, the effect of the coupling (which is a small parameter) may become important.

Yet another theory of temperature dependence of tunnel splitting is based on the description of a methyl group as being in a mixture of states belonging to the three symmetry species A and E[37]. The most recent published theory[38] is closely connected with the quantities measured in the INS experiment. It is based on the assumption that the weak interaction of the rotating methyl group with the lattice modes can be written in the form of a Fourier series (similar to equation (2)). The cosine term of this series modulates the height of the potential, the sine term causes the distortion of the potential, when the expansion coefficients become the normal coordinates associated with the lattice mode. This model accounts for both broadening and shifting of the tunnel splitting observed in the INS experiment and well reproduces the observed temperature dependence of v_t in MDBP[39] (4-methyl 2,6 ditertiarybutylphenol) (*Figures 3a* and *3b*, respectively). The shift below 25 K is governed by a relation $\exp(-E_p/kT)$, where $E_p<E_{10}$.

Generally, two basic approaches to this problem can be

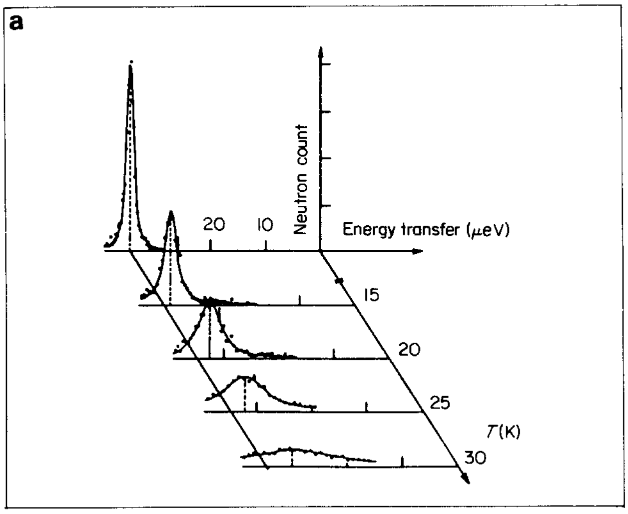

Figure 3a Inelastic peak in the INS spectrum of MDBP (D_{21}) illustrating the shift and broadening with increasing temperature. Data taken from ref. 39

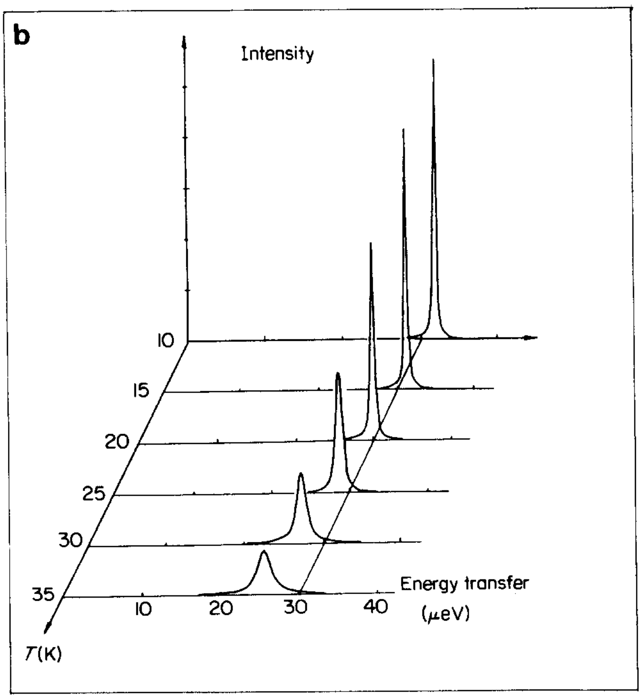

Figure 3b Calculated temperature dependence of the inelastic peak in the INS spectrum of MDBP D_{21}. Data taken from ref. 38a

distinguished. The first one starts from the assumption that the temperature dependence of tunnelling in all systems containing methyl groups can be described by a universal theory in which phonon modes (the lattice) are treated as a thermal bath and the quantities of interest can be expressed in terms of thermal averages. The S & G model, the models proposed by Clough and Clough *et al.*[34,37,45] and Allen's model[33] belong to this group. The second class of theories emphasizes the role of phonons and relates the temperature dependence of the tunnelling frequency to the detailed shape of the phonon density functions. These in principle can be related to the measurable physical properties of the investigated substances. The theories of Haupt[31], Hüller[35], Hewson[38] and Punkkinen[36] fall in this class. The interested reader can find a detailed theoretical analysis and extension of the Hewson and Punkkinen models in ref. 40.

METHYL GROUP TUNNEL SPLITTING: THE DIRECT DETECTION AND THE OBSERVED TEMPERATURE DEPENDENCE

Inelastic neutron scattering

Since the tunnel splitting is defined as the energy difference between the A and E symmetry rotational states which can certainly be defined at the low temperatures used (see second section), it can be measured using either absorption or emission of energy. INS measures the energy transfer directly and so is well suited for this purpose. The energies of interest for methyl groups range from 0.3 μ eV (the instrumental resolution of the backscattering spectrometer IN10, ILL Grenoble) to about 0.65 meV, as calculated for a 0–1 torsional transition of a free quantum rotor. The first INS measurement of a methyl group tunnel splitting in 4-methylpyridine yielded the value of 0.52 ± 0.01 meV, close to the free rotor limit[41]. Such a measurement is performed at low temperatures, usually below 10 K, in order to avoid the complicating effects of populating the higher energy states. From this measurement using a specified model one can calculate the hindering barrier height, the distribution of the energy levels and details of the potential shape appropriate to the parameterized model. 'Tunnel peaks' appear in the INS spectrum as two symmetric features around the elastic peak. The typical spectrum shown in *Figure 4a*[42] was taken on pentamethylbenzene (PMB). This substance has one methyl group *para* to H, two *meta* to H and two *ortho* to H. There should therefore be three distinct tunnel splittings. Two are observed, at 6.3 μeV and 0.6 μeV; the high energy peaks coming from the *para*–CH_3–; the low energy shoulders on the edges of the elastic peak corresponding probably to the *meta*-CH_3-group, the tunnel splitting of the *ortho*-CH_3 group being too small for inclusion. An example of tunnel splittings ranging from 0.3 μeV to 45 μeV investigated by INS is provided by the acetate series[43].

In INS of this type there are serious problems of sensitivity: one must first ensure a sufficient number of similarly located methyl groups and the experimental resolution must be compatible with the measured tunnel splitting.

Many more examples of investigation of tunnel splittings and of other than CH_3-group systems can be found in the quoted references and in the recent literature.

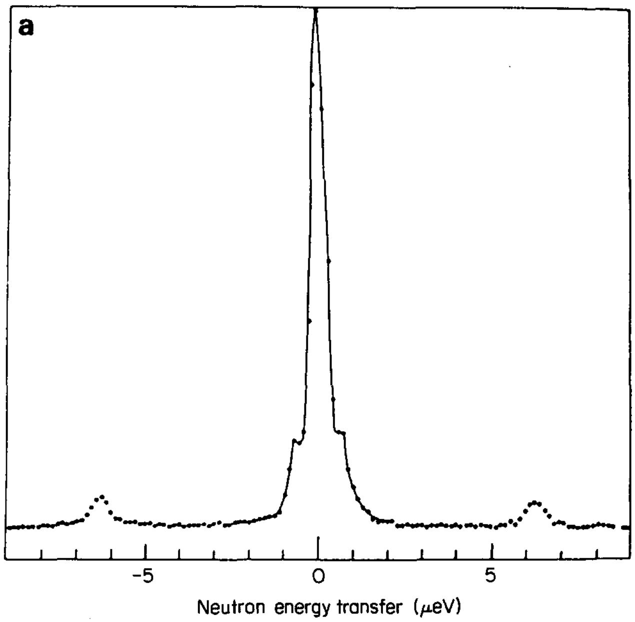

Figure 4a High-resolution inelastic neutron scattering spectrum of pentamethylbenzene showing tunnel peaks at $\pm 6.3\,\mu$eV (± 1.5 GHz) and $\pm 0.6\,\mu$eV (± 150 MHz). Data taken from ref. 42

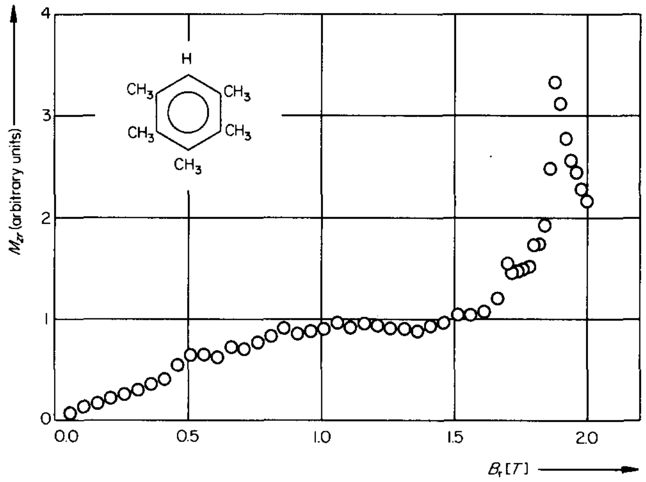

Figure 4b Partially relaxed proton magnetization M_{zr} as a function of the relaxation field B_r in pentamethylbenzene. A lower tunnel peak is visible at $B_r = 1.88T$ ($\nu_t/2 = 80$ MHz). Data taken from ref. 49

N.m.r.

The general theory of n.m.r. measurements can be found in ref. 44, while refs. 5 and 6 deal with applications to polymers.

When tunnelling dominates the relaxation of methyl groups, it will influence the n.m.r. line shape[3], the behaviour of the proton spin-lattice relaxation rate T_1^{-1} as a function of temperature[32,45] and the proton spin-lattice relaxation time $T_{1\rho}$ measured in the rotating frame[45,52]. The existence and the order of magnitude of the tunnel splitting of the ground state is inferred from the magnitude and the temperature at which a (T_1^{-1}) maximum appears. This is not a direct method, since at the temperature of $(T_1^{-1})_{\max}$ states higher than the ground state will normally be populated to a significant extent. However, measurement of T_1^{-1} as a function of magnetic field[47] at a constant, low temperature provides a direct way of determining the tunnel splitting by matching it with the Zeeman splitting of protons[48]. Resonant transfer between the tunnel energy, $h\nu_t$, and the Zeeman energy, $h\nu_Z$, occurs when either of the conditions (*level-crossing conditions*)

$$\nu_t = n\nu_Z, \qquad n = 1,2$$

is met.

The measuring procedure comprises three phases reminiscent of the standard $\pi/2 - \tau - \pi/2$ pulse technique. In the first, preparation phase, a saturation pulse train is applied in the measuring field $B_m (B_m = B_0 = 2\pi\nu_Z/\gamma$, γ being the proton gyromagnetic ratio). In the second, relaxation phase immediately following the preparation phase, the magnetic field is switched to the relaxation (off-resonance) field B_r. In the third, measuring phase the measuring pulse is applied in B_m. The magnetic field is switched between, and stabilized, at each value of the magnetic field by Hall stabilization. The duration of the relaxation phase, the value of measuring field and of temperature are kept constant during one sequence of the experiment. Upon completion of one measuring sequence covering a range of relaxation field B_r the values of the partially relaxed proton magnetization M_{zr} are plotted as a function of the relaxation field B_r. The presence of the tunnelling process is directly monitored as an anomalous relaxation feature, namely a peak, in the (M_{zr}, B_r) curve[48].

An example of such a measurement on pentamethylbenzene is shown in *Figure 4b*[49]. Here only the lower peak fulfilling the condition $\nu_t = 2\nu_Z$ is visible. The measured value of ν_t, (0.66 ± 0.03) μeV agrees very well with the value of the shoulder on the elastic peak, (0.62 ± 0.08) μeV measured by INS[42]. The principles underlying the Zeeman-tunnel spectroscopy and conditions necessary for carrying out a successful experiment are discussed in ref. 50.

Evidence for the temperature dependence of ν_t

The experimental data provided by INS and n.m.r. have given support to the theories outlined in the previous section and have stimulated new developments. There are few published results of investigations of the temperature dependence of ν_t by Zeeman-tunnel spectroscopy, because the proton spin-lattice relaxation time T_1 can become too short to contribute significantly to the (M_{zr}, B_r) curve. However, in two reported cases, hexamethylbenzene[51] and SiH_4[48], the tunnel peaks broaden and shift towards lower frequencies with increasing temperature. The standard n.m.r. data analysis is less straightforward. As mentioned above, in the (T_1, T) measurements the existence of tunnelling is deduced from the appearance of the low-temperature minimum and the deviation from the classical law $T_1 \sim \nu_Z^2$, where $h\nu_Z$ is the Zeeman splitting. For the latter condition to be obvious one has to carry out the measurements at several fixed common frequencies. In such a case, the minimum in T_1 which is attributable to tunnelling shifts towards *lower* temperatures with decreasing field[52].

Inelastic peaks in the INS spectrum, due to tunnelling of methyl groups, shift towards the elastic peak with increasing temperature. This shift is often accompanied by broadening of the inelastic peak in most cases investigated. An example of such behaviour is shown in *Figure 3a* (data taken from ref. 39). Owing to the central position of the elastic peak this means that the measured value of the tunnel splitting decreases with increasing temperature. All but a very few substances which have so far been investigated do show a decrease of the tunnelling frequency with increasing temperature. A particular example is 2,4-hexadiyne[29], for which the experimental values of ν_t are plotted in *Figure 5*, where for comparison the temperature dependence calculated for this substance from the S & G model is shown. Despite special exceptions such as solid methane[15] the experimental evidence does not support the conclusions of the S & G model. Its continued use is no longer justified.

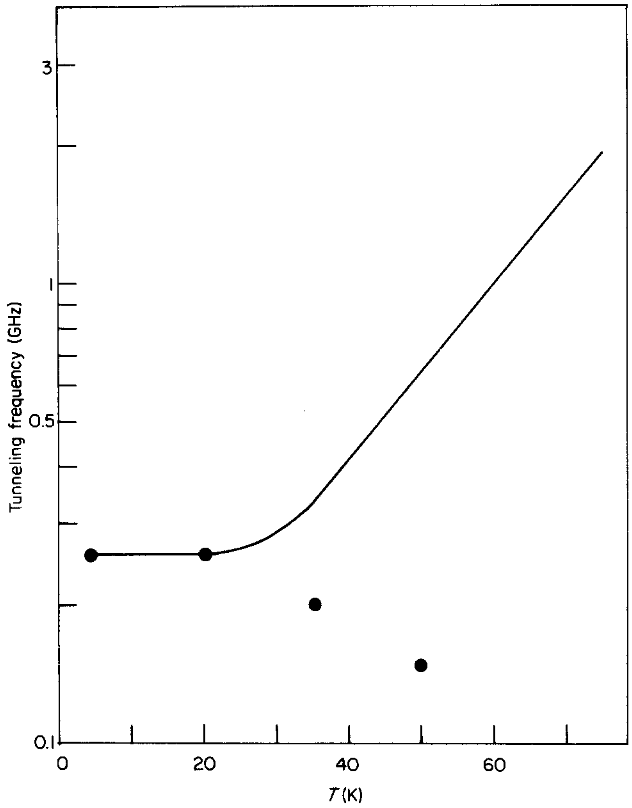

Figure 5 Temperature dependence of tunnelling frequency in 2,4-hexadiyne. Solid circles denote the values measured by INS[29]. Solid line shows the theoretical dependence calculated from the S&G formula[7]

METHYL GROUP TUNNELLING IN POLYMERS

Quantum-mechanical tunnelling of methyl groups as a viscoelastic relaxation mechanism in polymers was proposed in the early stages of development of the 'tunnelling concept'[53,54]. The appearance below 60 K of the mechanical loss $\tan\delta$ peaks and their temperature dependence in materials containing methyl groups (cf. references in ref. 53) was explained on the basis of the S & G model. This model was also later used to explain the non-linearity of the classical Arrhenius plot of $\log \nu$ against $1/T$ for the γ_1 relaxation in poly(methyl methacrylate) (PMMA)[12,13] and in poly(α-methyl styrene)[55], which would suppose that the classical rotational frequency is governed by

$$\nu = \nu_0 \exp(-E_A/kT)$$

However, only a qualitative agreement with the S & G model was achieved, cf. Figure 6 of ref. 13 for PMMA-h_8. The third argument used to support the hypothesis of tunnelling as a macroscopic (viscoelastic) relaxation mechanism is the appearance of the isotope effect: the $(\log \nu, T^{-1})$ plots are different for protonated and deuterated samples[13,55].

However, experimental evidence not only contradicts the predictions of the S & G model but the temperatures in the range ~125 K where the non-linearity of the $(\log \nu, T)$ plots occurs are much too high for tunnelling to govern the relaxation process effectively. It has also been pointed out that the appearance of peaks around 40–50 K in the plot of mechanical loss tan δ as a function of T may be due to the presence of other compounds[56]. Similarly the reported large change of the supposed tunnel splittings upon isotopic substitution reported at ~125 K in refs. 13 and 55 cannot be unambiguously ascribed to tunnelling since the temperature is much too high.

A brief comment on the effects of deuteration is in order. The potential V_3 is determined by the attractive and repulsive interaction between non-bonded species and so will not be affected by deuteration of the methyl groups. Moreover, the effective potential V_{stat}, written as $I_0 V_3/\hbar^2$ and used in that form in the Mathieu equation will be increased in amplitude by a factor of 2 because I_0 the moment of inertia depends directly on the proton/-deuteron mass. This is not the only effect, for the zero-point energy of the methyl groups is also reduced on deuteration whereby both the A and E levels of the ground state are lowered by approximately a factor of $1/\sqrt{2}$. This will not only reduce the tunnel splitting in first order, but also affect the tunnel splitting in second order because the overlap of the wave functions between adjacent deuterium atoms will be smaller than for hydrogen atoms in the same situation. Such effects cannot be estimated reliably, as the discrepancies between the theoretical[50] and experimental[30] values for methane clearly demonstrate[15]. At the present stage of development of the subject it is necessary to measure deuterium tunnel splittings directly.

The hypothesis of quantum tunnelling of methyl groups based on the S & G models was also put forward in order to explain the value of the hindering barrier to methyl group rotation in PMMA[11]. However, the recent theoretical developments and the experimental evidence discussed in previous sections have motivated us to look for another explanation. To this end, we have carried out INS experiments on two stereospecific forms of PMMA, syndio (PMMAS) and isotactic (PMMAI), in a temperature range 35–391 K[58,59]. We have observed non-Arrhenius behaviour of the widths of quasi-elastic scattering peaks (FWHM) as a function of $1/T$ and a difference in the values of the reorientational rates of PMMAS and PMMAI[58]. This effect can be explained by inclusion of higher than V_3 terms in the Fourier series expansion of the potential function hindering the methyl group motion. This will reduce the symmetry of the effective potential and thus provide an efficient relaxation mechanism at low temperatures, by permitting jumps over a barrier lower than V_3.[58] Also, the motion of protons belonging to the ester methyl group will be a superposition of two sorts of motion, convergent on the limiting case of classical jumps over the V_3 barrier at high temperatures. This hypothesis has been confirmed by our measurements on PMMAI where we had succeeded in partially resolving two sorts of motion within an effective measured width of the quasi-elastic peak in a temperature range 45–140 K[59].

The idea of a not purely threefold potential is frequently encountered in the literature (cf. e.g. refs. 6 and 61), although it has not been presented in great detail. It also explains the observed differences in the absolute magnitude of the rotational rates of PMMAI and PMMAS below room temperature: the different steric hindrance will cause a different shape of the potential in the two stereoregular forms[58]. This approach also explains the non-linearity of the Arrhenius plot in the visco-elastic measurements[13] by virtue of two different sorts of motion. Additional support in favour of our approach can be provided by the fact that no tan δ peaks appear in the mechanical measurements if the potential is purely threefold[7], yet tan δ peaks are observed. Although a number of n.m.r. measurements (both line shape and the standard T_1 vs. T) has been published[10,61–64] and references therein, there is no unambigious evidence that tunnelling provides an efficient relaxation mechanism at low temperatures. The T_1 minima are usually very broad and shallow and the possible values of the tunnelling frequencies obtained on the basis of phenomenological relaxation from ref. 45 do not agree with those obtained on the basis of other experiments. The understanding of this disagreement is a challenging problem and a number of INS and n.m.r. experiments are in progress.

Finally, we re-emphasise that current theoretical understanding and experimental observation of tunnelling phenomena as manifested in the temperature dependence invalidate the Stejskal and Gutowsky model. In polymers the evidence is that barriers which hinder rotation are more complicated than simple threefold. Explanations of the temperature dependence of relaxation phenomena should be sought in terms of the factors influencing these barriers.

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