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Temperature dependence of the librational tunneling and proton relaxation

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A coupling between the librations of the methyl groups or proton tetrahedra (e.g., CH_4 and NH_4^+) in a solid is shown to explain the experimentally observed decrease of the librational tunneling splitting without significant lifetime broadening when the temperature is raised at low temperatures. Due to the same coupling, the libration amplitude of a given group is influenced by neighboring groups. The amplitude can momentarily increase so much that the group undergoes random jumps to other equilibrium orientations even at liquid-helium temperatures. This model agrees with the nearly temperature-independent spin-lattice relaxation time T_1 of protons in some samples for $T \lesssim 4$ K and with the temperature-dependent T_1 described by the activation energy equal to the separation between the ground and first-excited-librational levels at somewhat higher temperatures.

I. INTRODUCTION

Nearly all the theories associated with the tunneling splitting of the librational levels of methyl groups or proton tetrahedra (for example CH_4, NH_4^+, SiH_4, etc.) in a solid employ the assumption of an isolated group, which feels the effect of its environment through a hindering potential. Such considerations generally lead to a good description of the experimental data for static properties like the magnitude of the tunneling splitting at $T = 0$ K (Refs. 1–3) and of the second moment M_2 of the proton-resonance absorption curve.[4–6]

On the other hand, the temperature-dependent properties are not so well understood. Although there are many experiments[7–13] supporting the somewhat loosely derived expression for the tunneling frequency $\nu(T)$ of a methyl group at temperature T,[14–16]

$$\nu(T) = \frac{\sum_n \nu_n \exp[-\epsilon_{0n}/(kT)]}{\sum_n \exp[-\epsilon_{0n}/(kT)]} , \qquad (1.1)$$

a firm theoretical explanation is still lacking. Here ν_n is the tunneling frequency of the methyl group for the nth excited librational state, and ϵ_{0n} is the difference between the nth excited and the ground librational level. The problem is that, although $\nu(T)$ decreases significantly when the temperature is raised, distribution of the tunneling frequency does not show any lifetime broadening until relatively high temperatures are attained.[11,12,16,17] Related to this problem are the motion responsible for the proton spin-lattice relaxation and its temperature dependence, which are not as yet completely understood despite many theoretical efforts.[13,18–20] In some samples containing methyl groups, the proton relaxation time T_1 seems to be determined by an activation energy equal to ϵ_{01} at low temperatures,[13] while in some other compounds the activation energy near $T = 10$ K is definitely smaller than ϵ_{01}.[19] A still larger deviation from ϵ_{01} is observed in some samples containing proton tetrahedra, for example solid CH_4,[21,22] $(NH_4)_2PbCl_6$,[23] and ND_4ClO_4.[24] In these compounds the apparent activation energy decreases with temperature until an almost temperature-independent T_1 is observed at liquid-helium temperatures.

A coupling between the librations of the neighboring proton groups is felt to provide the answer to the problems mentioned above. Although the coupling may not be large in comparison with the librational potential, its effect can nevertheless be important, because the libration frequencies of the single groups are equal in the absence of the coupling. There exists some experimental evidence of such an interaction between methyl-group librations in gaseous methyl ethers.[25] The coupling extends over all the groups, and the librational state of the sample is described by so-called normal modes. The amplitude of a normal mode is a linear combination of the librational amplitudes of the single groups. Therefore, an excited state of a normal mode is practically a linear combination of the ground and excited states of the single groups. The product of such combinations forms the librational wave function of the sample. The population of the excited states and, hence, the product function depend on temperature and therefore the result (1.1) is obtained (Sec. II).

There are $3N$ librational normal modes in general (only N in the case of one-dimensional libration), where N equals the number of librating groups. Consequently, the libration amplitude ϕ_i of the group i is a time-varying combination of $3N$ normal modes. If these modes happen to be at such phases that they tend to increase ϕ_i, the group i may be able to jump to another equilibrium orientation or reorient. Since such reorientations do not necessarily involve any energy absorption, but rather require a momentary accumulation of the librational energy to a given point in the sample, they are believed to occur even at $T=0$ K. Their frequency is expected to increase with temperature in proportion to the mean librational amplitude. This model explains the behavior of the proton T_1 at low temperatures (Sec. III).

The relation between the reorientations and the broadening of the tunneling levels is discussed in Sec. IV. In addition some examples are given about the effect of the coupling strength on nuclear relaxation.

II. TEMPERATURE DEPENDENCE OF THE TUNNELING FREQUENCY

A. Librational wave function

For simplicity a sample containing equivalent methyl groups is considered. The CH_3 groups are assumed rigid, and the libration is restricted to take place in a fixed plane. Therefore, only one quantity, the librational amplitude ϕ_i, is needed to describe the motional state of the group i. The librational Hamiltonian for a single uncoupled group is

$$\mathcal{H}_i=-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_i^2}+V(\phi_i)\ , \tag{2.1}$$

where I is the moment of inertia of the methyl group, and $V(\phi_i)$ is the librational potential, which is the same for all the groups. If there were no coupling, one would obtain the same librational energy levels and frequencies for every group. But just because of the equality of the frequencies, even a small coupling is believed to have an important effect. In the case of only two coupled CH_3 groups, the librational Hamiltonian in the harmonic approximation is

$$\mathcal{H}_{12}=-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_1^2}+\frac{1}{2}k'\phi_1^2-\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi_2^2}+\frac{1}{2}k'\phi_2^2+k_{12}\phi_1\phi_2\ . \tag{2.2}$$

The corresponding eigenvalue equation $\mathcal{H}_{12}\psi=E\psi$ separates to two uncoupled equations by the substitution

$$\begin{pmatrix}Q_1\\Q_2\end{pmatrix}=2^{-1/2}\begin{pmatrix}1&1\\1&-1\end{pmatrix}\begin{pmatrix}\phi_1\\\phi_2\end{pmatrix}\ . \tag{2.3}$$

The librational frequencies are

$$\nu_{1,2}=\frac{1}{2\pi}[(k'\pm k_{12})/I]^{1/2}\ , \tag{2.4}$$

which do not differ much from the uncoupled frequency $(1/2\pi)(k'/I)^{1/2}$ when k_{12} is small.

In the case of N coupled librating CH_3 groups, the normal modes Q_j $(j=1,2,\ldots,N)$ are linear combinations of all the single-group amplitudes ϕ_i. In the harmonic approximation the wave function for the normal mode Q_j is

$$H_{m_j}(Q_j)\exp[-(k_jI)^{1/2}Q_j^2/(2\hbar)]\ . \tag{2.5}$$

Here $H_{m_j}(Q_j)$ is a Hermite polynomial of the order m_j corresponding to the m_jth excited state, and k_j is close to k'; actually the nearer k_j is to k', the smaller the coupling between the CH_3 librations. The total librational wave function is

$$\begin{aligned}F_1=F(1_1\cdots 1_i\cdots 1_N;\ m_1\cdots m_j\cdots m_N)&=\prod_j H_{m_j}(Q_j)\exp[-(k_jI)^{1/2}Q_j^2/(2\hbar)]\\&\cong\Big(\prod_j H_{m_j}(Q_j)\Big)\exp[-(k'I)^{1/2}(\phi_1^2+\phi_2^2+\cdots+\phi_N^2)/(2\hbar)]\ ,\end{aligned} \tag{2.6}$$

where the approximate equality holds for the coupling coefficients k_{ij} which are small in comparison with k'. The indices of F indicate that all the methyl groups librate about their equilibrium orientation labeled 1 and that the mode Q_j is at the m_jth excited state.

B. Temperature dependence of $\nu(T)$

To calculate the tunneling frequency of the methyl group i one has to construct a function similar to Eq. (2.6), except that the group i is librating about its equilibrium orientation 2, which is obtained from the orientation 1 by a $\frac{1}{3}(2\pi)$ rotation. This function is denoted by

$$F_2=F(1_1\cdots 2_i\cdots 1_N;m_1\cdots m_j\cdots m_N)\ .$$

The third function representing the situation where the group i is librating about the equilibrium orientation 3, obtained from the orientation 1 by a $\frac{1}{3}(4\pi)$ rotation, is denoted by

$$F_3=F(1_1\cdots 3_i\cdots 1_N;m_1\cdots m_j\cdots m_N)\ .$$

In the following the equilibrium orientations of the other methyl groups and the states of the normal modes are assumed constant. Assuming this, it is then possible to construct librational functions ψ_s specified by the point-group symmetry C_3 of the methyl group i

$$\psi_s = \{3[1+(\lambda_s+\lambda_s^*)R]\}^{-1/2}\,(F_1+\lambda_s F_2+\lambda_s^* F_3) \ , \tag{2.7}$$

where s refers to the irreducible representation A, E^a, or E^b of the point group C_3, $\lambda_s=1$ for the identical representation A, $\lambda_s=\epsilon=e^{i2\pi/3}$ for E^a, $\lambda_s=\epsilon^*$ for E^b, and

$$R=\int\cdots\int F_1^* F_2\, dQ_1\cdots dQ_N$$

equals the overlap integral. Because the protons have the spin $\frac{1}{2}$, they must obey the Pauli exclusion principle. Thus the spin-librational wave functions must remain unaltered in the even permutations of the methyl protons, which means that the spin functions of the CH_3 group i associated with A, E^a- and E^b-species librational functions must transform as the A, E^b- and E^a-species functions, respectively. Because these spin functions are orthogonal, the tunneling frequency $\nu(T)$ of the group i is obtained from the expression

$$h\nu(T)=\langle\psi_{E^a}|\mathcal{H}_{\text{lib}}|\psi_{e^a}\rangle-\langle\psi_A|\mathcal{H}_{\text{lib}}|\psi_A\rangle \ , \tag{2.8}$$

where $\mathcal{H}_{\text{lib}}$ is the total librational Hamiltonian containing the coupling terms. The second matrix element in Eq. (2.8) is

$$\begin{aligned}\langle\psi_A|\mathcal{H}_{\text{lib}}|\psi_A\rangle &= [3(1+2R)]^{-1}(3\langle F_1|\mathcal{H}_{\text{lib}}|F_1\rangle\\ &\qquad +6\langle F_1|\mathcal{H}_{\text{lib}}|F_2\rangle)\\ &=(1+2R)^{-1}(\epsilon_{\text{lib}}+2\langle F_1|\mathcal{H}_{\text{lib}}|F_2\rangle) \ ,\end{aligned} \tag{2.9}$$

where ϵ_{lib} equals the librational energy of the sample for a vanishing overlap and with no tunneling. The overlap matrix element of $\mathcal{H}_{\text{lib}}$ is evaluated by resorting to the approximation of the uncoupled librations or $\mathcal{H}_{\text{lib}}=\sum_l \mathcal{H}_l$ [cf. Eq. (2.1)], which should not be so greatly in error since $k_{ij} << k$. Then

$$\begin{aligned}\langle F_1|\mathcal{H}_{\text{lib}}|F_2\rangle &= \langle F_1|\mathcal{H}_1+\cdots+\mathcal{H}_{i-1}+\mathcal{H}_{i+1}\\ &\qquad +\cdots+\mathcal{H}_N|F_2\rangle+\langle F_1|\mathcal{H}_i|F_2\rangle\\ &=(\epsilon_{\text{lib}}-\epsilon_i)R+\langle F_1|\mathcal{H}_i|F_2\rangle \ ,\end{aligned} \tag{2.10}$$

because F_1 and F_2 differ only in their dependence on ϕ_i. Replacing $\langle F_1|\mathcal{H}_{\text{lib}}|F_2\rangle$ in Eq. (2.9) by Eq. (2.10), one obtains

$$\langle\psi_A|\mathcal{H}_{\text{lib}}|\psi_A\rangle=\epsilon_{\text{lib}}+2\frac{\langle F_1|\mathcal{H}_i|F_2\rangle-\epsilon_i R}{1+2R} \ . \tag{2.11}$$

A similar calculation for the first matrix element of Eq. (2.8) produces

$$\langle\psi_{E^a}|\mathcal{H}_{\text{lib}}|\psi_{E^a}\rangle=\epsilon_{\text{lib}}-\frac{\langle F_1|\mathcal{H}_i|F_2\rangle-\epsilon_i R}{1-R} \ . \tag{2.12}$$

By ignoring the R-dependent terms in Eq. (2.11) as nearly vanishing, the tunneling frequency becomes

$$h\nu(T)=-3\langle F_1|\mathcal{H}(i)|F_2\rangle \ . \tag{2.13}$$

In principle one should determine the linear combinations of ϕ_i's for each normal mode Q_j and calculate the overlap matrix element (2.13). This is nearly an impossible problem, but one can get a fairly good idea concerning the magnitude of the matrix element by resorting to approximations. The Hermite polynomial $H_{m_j}(Q_j)$ contains powers $Q_j^{m_j}$, $Q_j^{m_j-2}$, $Q_j^{m_j-4}$, etc., but, in the following, $H_{m_j}(Q_j)$ is replaced by $Q_j^{m_j}$. In addition, Q_j is assumed to be a symmetric linear combination

$$Q_j=\frac{1}{\sqrt{N}}(\phi_1+\phi_2+\cdots+\phi_N) \ . \tag{2.14}$$

For a moment let the mode Q_j assume the first excited state corresponding to $Q_j\exp[(k_jI)^{1/2}Q_j^2/(2\hbar)]$ and all the other modes be in the ground state. Then the probability of finding the methyl group i in the ground state equals $P_0=(N-1)/N$ and the probability of finding it in the first excited state equals $P_1=1/N$. Here the probability means the fraction of time that the group i stays in a given state when the librational phonon of the normal mode Q_j travels coherently through the crystal. If the mode Q_j is in the m_jth excited state, the various probabilities are obtained from the expansion

$$\begin{aligned}\left[\frac{N-1}{N}+\frac{1}{N}\phi_i\right]^{m_j} &= \left[\frac{N-1}{N}\right]^{m_j}+m_j\left[\frac{N-1}{N}\right]^{m_j-1}\frac{1}{N}\phi_i\\ &\quad+\binom{m_j}{2}\left[\frac{N-1}{N}\right]^{m_j-2}\frac{1}{N^2}\phi_i^2+\cdots\end{aligned} \tag{2.15}$$

For example the multiplier of ϕ_i^2 equals the probability of finding the group i in the second excited state, in agreement with the approximate representation of $H_{m_j}(Q_j)$ by $Q_j^{m_j}$. If the other normal modes besides Q_j are also in excited states, the probabilities of finding the group i in various librational states are obtained from

$$\sum_l P_l\phi_i^l=\left[\frac{N-1}{N}+\frac{1}{N}\phi_i\right]^{m_1+m_2+\cdots+m_N} \ , \tag{2.16}$$

because the methyl group i can be at an excited state in any normal mode.

The next problem is to calculate the quantum numbers m_j. According to Bose-Einstein statistics, m_j or the number of phonons of a harmonic oscillator librating at the frequency $\nu=\epsilon_{01}/h$, at thermal equilibrium, equals

$$m_j=\{\exp[\epsilon_{01}/(kT)]-1\}^{-1}=r \ . \tag{2.17}$$

Because all the normal-mode frequencies are nearly equal when $k_{ij} << k$, then $m_1 + m_2 + \cdots + m_N = Nr$. Therefore Eq. (2.16) becomes

$$\sum_l P_l \phi_i^l = \left(\frac{N-1}{N} + \frac{1}{N}\phi_i\right)^{Nr} = \left(\frac{N}{N-1}\right)^{-Nr}\left(1 + \frac{1}{N-1}\phi_i\right)^{Nr}$$

$$= e^{-r}\left(1 + \frac{Nr}{N-1}\phi_i + \frac{Nr(Nr-1)}{2(N-1)^2}\phi_i^2 + \cdots\right) \cong e^{-r}\left(1 + r\phi_i + \tfrac{1}{2}r^2\phi_i^2 + \cdots\right) . \quad (2.18)$$

The effective tunneling frequency is then

$$\nu(T) = \sum_l P_l \nu_l = e^{-r}(\nu_0 + r\nu_1 + \tfrac{1}{2}r^2\nu_2 + \cdots) \ . \quad (2.19)$$

At low temperatures $r \simeq \exp[-\epsilon_{01}/(kT)] << 1$, and Eq. (2.19) becomes

$$\nu(T) \cong \nu_0\{1 - \exp[-\epsilon_{01}/(kT)]\} + \nu_1 \exp[-\epsilon_{01}/(kT)] + O(r^2) \ . \quad (2.20)$$

This agrees with the zero- and first-order terms of Eq. (1.1), although the higher-order terms are different. Actually Eq. (2.19) approaches the value $\nu(T) = 0$ more quickly than Eq. (1.1) with increasing temperature.

The above derivation suffers from weak assumptions concerning Q_j's and the Hermite polynomials, and Eq. (2.19) cannot therefore be claimed to be exact. The fact that its leading terms are the same as in the experiment-supported Eq. (1.1) proves nevertheless that the model of coupled librations of the methyl groups can explain the temperature dependence of the tunneling frequency. A good point of the present model is its simple description of the librational state of a single CH_3 group as a linear combination of the ground and excited states without resorting to rapid jumps between librational states. Actually the above theory interprets the fluctuating lattice potential[16] in terms of the coupling between the CH_3 librations.

III. TEMPERATURE DEPENDENCE OF T_1

The libration amplitude ϕ_i of the methyl group i is a time- and site-dependent linear combination of the normal-mode amplitudes Q_j. If Q_j's are sufficiently large and have proper phases, then ϕ_i may grow so large that the CH_3 group jumps to another equilibrium orientation. The critical librational energy, which is proportional to the critical amplitude, is not many times larger than the zero-point energy of a CH_3 libration, since the zero-point energy is often a substantial fraction of the potential barrier hindering the librational motion. Therefore, such reorientations are believed to occur even at $T = 0$ K, at least in some compounds with a small hindering barrier and a large coupling between the CH_3 librations. A coupling-induced jump is not in contradiction with the principle that the zero-point motion cannot give energy away. The reorientation requires only an accumulation of the librational energy to one methyl group, which, after jumping, continues librating at the same modes with the same energies. If the temperature somewhat deviates from $T = 0$ K, energy changes may occur between the modes, but they involve low-energy ($\leq kT$) lattice vibrations so as to conserve the total energy.

The relaxation rate depends on how frequent reorientations are. It would seem natural to claim that the reorientation rate $1/\tau$ is proportional to the libration amplitude of the CH_3 groups. Because of the coupling, the libration amplitude of a single group increases continuously with temperature and is assumed to obey the Bose-Einstein statistics

$$\langle \phi_i^2 \rangle = a + b\{\exp[\epsilon_{01}/(kT)] - 1\}^{-1} \ . \quad (3.1)$$

Here a represents the zero-point amplitude and $b = 2a$ if the energy is proportional to $\langle \phi_i^2 \rangle$, as it is in classical mechanics. It is not clear to which power of $\langle \phi_i^2 \rangle$ the rate is proportional, but for simplicity it is assumed to be $1/\tau \simeq \langle \phi_i^2 \rangle$. Besides, one has to take into account that a methyl group in an excited librational state is more likely to reorient than a group in the ground state. Therefore, $\langle \phi_i^2 \rangle$ has to be multiplied by a factor

$$\frac{\sum_n c_n \exp[-\epsilon_{0n}/(kT)]}{\sum_n \exp[-\epsilon_{0n}/(kT)]} \ , \quad (3.2)$$

where $\exp[-\epsilon_{0n}/(kT)]$ equals the fraction of time that the CH_3 group stays in the nth librational state. The factor c_n increases with n, and it takes into account that reorientations from a higher initial librational level require less energy and are more frequent for larger couplings. For descriptive purposes it might be approximated by a Guassian function

$$c_n = \frac{K}{w}\exp[-(\epsilon_b - \epsilon_{0n})^2/w^2] \ , \quad (3.3)$$

where ϵ_b is the energy difference between the top of the barrier and the ground state, K is a constant, and w represents the width of the distribution of the CH_3 librational energy, which should be proportional to the width of $\phi_i^2 - \langle \phi_i^2 \rangle$. The width w probably increases with the strength of the coupling. If $w << (\epsilon_b - \epsilon_{01})$, then $c_0 << c_1 << c_2 \cdots$. The reorientation rate now becomes

$$\frac{1}{\tau}=\left(a+\frac{b}{\exp[\epsilon_{01}/(kT)]}\right)\frac{\sum_n c_n\exp[-\epsilon_{0n}/(kT)]}{\sum_n \exp[-\epsilon_{0n}/(kT)]} \quad . \tag{3.4}$$

For $\exp[-\epsilon_{01}/(kT)] << 1$, one obtains

$$\frac{1}{\tau}\cong c_0 a\left(1+\frac{c_1}{c_0}\exp\frac{-\epsilon_{01}}{(kT)}\right)$$

$$=\alpha+\beta\exp\frac{-\epsilon_{01}}{(kT)} \quad , \tag{3.5}$$

with $\beta/\alpha=c_1/c_0>>1$. Below the temperature of the T_1 minimum corresponding to $\omega_0\tau\cong 1$, where ω_0 is the angular Larmor frequency, T_1 is generally believed to vary proportionally to τ, provided that ω_0 and the tunneling frequency $\omega(T)$ are far away from the level-crossing conditions $\omega(T)=\omega_0$ or $\omega(T)=2\omega_0$. Therefore

$$T_1\simeq\{\alpha+\beta\exp[-\epsilon_{01}/(kT)]\}^{-1} \quad . \tag{3.6}$$

If there exists a temperature range with $\beta\exp[-\epsilon_{01}/(kT)]>>\alpha$, then $T_1\simeq\exp[\epsilon_{01}/(kT)]/\beta$ and

$$\ln T_1=\epsilon_{01}/kT+\text{const} \quad . \tag{3.7}$$

This agrees well with recent experimental data for some methylpyridines, showing that the activation energy equals ϵ_{01} within a certain temperature range below the temperature of the T_1 minimum.[13] When the temperature is lowered further, the present model predicts $\alpha>>\beta\exp(-\epsilon_{01}/kT)$, and T_1 should become independent of temperature. The results for methylpyridines do not extend to sufficiently low temperatures for verification of this prediction, but the apparent activation energy shows some tendency to decrease with temperature. Additional evidence about T_1 becoming nearly constant is provided by experiments on proton tetrahedra. The activation energy describing the proton T_1 in $(NH_4)_2PbCl_6$ decreases steadily from the high-temperature value 5.9 kJ/mol to 0.06 kJ/mol between 5 and 10 K,[23] and there is no reason to believe that the latter value should be the lower limit. The deuteron T_1 in ND_4ClO_4 is nearly constant below 4 K.[24] And the proton T_1 in solid CH_4 is known to become constant below 4 K except for a small variation due to the spin-isomer conversion.[21,22] Actually the τ data for $T<15$ K by Nijman and Trappeniers[22] can be represented quite accurately by the expression (Fig. 1)

$$\frac{1}{\tau}=[0.22+1870\exp(-100/T)]10^{10}\ \text{s}^{-1} \quad . \tag{3.8}$$

It corresponds to $\epsilon_{01}/k=100$ K, which is near the prediction $\epsilon_{01}/k\simeq 70$ K stated by Kataoka *et al.*[26]

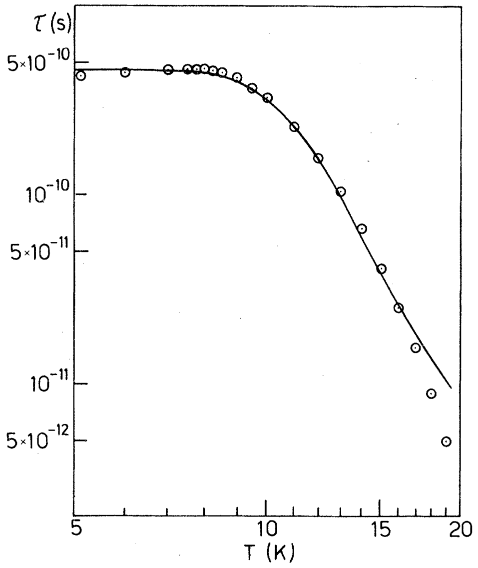

FIG. 1. Temperature dependence of the correlation time of the CH_4 reorientations in solid methane. The solid curve represents Eq. (3.8) and the experimental points are from Ref. 22.

Probably a part of the discrepancy arises from the weakening of the hindering potential for CH_4 reorientations between 10 and 20 K.

The expression (3.5) is expected to be valid as far as the librations are nearly harmonic, which is probably true for $T\lesssim\epsilon_{01}/k$. At temperatures $T>\epsilon_{01}/k$ the effect of the higher excited librational states with $n\geqq 2$ in Eqs. (3.3) and (3.4) becomes dominant, and the activation energy increases towards the height of the rotation barrier. An alternative explanation would be that the internal and lattice vibrations mask the coupling between the CH_3 librations more effectively at higher temperatures, so that finally a CH_3 group becomes an uncoupled hindered rotator with the activation energy comparable to the height of the potential barrier. Although the transition between the two regions is determined by ϵ_{01} and not by τ, it often seems to occur near the minimum of T_1, corresponding to $\omega_0\tau\approx 1$.

IV. DISCUSSION

The models presented above depend in two different ways on the coupling between the librations of the methyl groups. First, the coupling causes a mixing of the librational states of a methyl group, and consequently the tunneling frequency of this group is a weighted average of the tunneling frequencies of the ground and excited librational states. The model introduces no broadening of the tunneling distribution in so far as the frequency of the reorientations remains low in comparison with the tunneling frequency. Such a constant width has been noted, for example, in $(NH_4)_2PbCl_6$,[9] NH_4ClO_4,[10,11] and $(NH_4)_2SnCl_6$.[12]

Second, the coupling between the CH_3 librations leads to a momentary local accumulation of the libration energy and to a consequent reorientation. The reorientations induce relaxation transitions and broaden the tunneling levels. The broadening of the T-species levels of the NH_4^+ ions becomes observable by NMR about 10 to 20 K below the temperature of the T_1 minimum with $\omega_0\tau \simeq 1$. It is important to note that the beginning of the broadening corresponds roughly to $\langle\Delta\omega_t^2\rangle\tau^2 \cong 1$, where $\Delta\omega_t$ is the low-temperature width of the tunneling levels. This result can also be obtained from the proton-relaxation theory, based on the assumption of a common spin temperature, predicting that[22,27]

$$\frac{1}{T_1} = \sum_{s=T,E}\sum_{k=-2}^{2} C_{sk}\int_{-\infty}^{\infty} \frac{\tau_s}{1+(\omega_s-k\omega_0)^2\tau_s^2} f(\omega_s)\,d\omega_s \;, \tag{4.1}$$

where $f(\omega_s)$ is the distribution of the tunneling frequency $\omega_s = (\epsilon_s - \epsilon_A)/\hbar$. The correlation times τ_s are represented here by the common symbol τ. As far as $(\omega_s - k\omega_0)^2\tau^2 >> 1$ for most of the tunneling groups, the shape of the T_1 minimum, observed as a function of the resonance frequency, should stay constant. But when a substantial fraction of the groups obeys $(\omega_s - k\omega_0)^2\tau^2 \leq 1$, one should observe changes in the shape of the minimum. This condition corresponds to the equation $\langle\Delta\omega_t^2\rangle\tau^2 \simeq 1$ mentioned above.

Although the model of Sec. III predicts an activation energy ϵ_{01} for a certain temperature range in agreement with a recent derivation,[13] the two models are different in principle. The accumulation of the libration energy to one methyl group or proton tetrahedron and the consequent coupling-induced jump to another equilibrium orientation do not require transitions between librational states of the same symmetry. Such a jump does not necessarily involve any change in librational energy either, because all the modes can retain their original states after the jump. The nuclear spin-lattice relaxation always means an energy transfer from the spin system to the lattice. Therefore, because the lattice modes can absorb energy even at $T = 0$ K, a low temperature does not reduce the effectiveness of the coupling-induced reorientations in the relaxation.

One should also realize that the motion just described is probably not the main reason for a lifetime broadening of the librational levels. Thus the jump rate at low temperatures is not related to the width of the first librational level, nor need such a relation be valid at higher temperatures, since a change of the librational energy is not automatically followed by a reorientation. The transitions between different librational states may have some effect on τ at higher temperatures, but not necessarily a dominant effect.[12] Such transitions broaden the librational levels, but their effect on tunneling levels is nearly vanishing. This can be seen by repeating the calculation of $\nu(T)$ for a librational state defined by the normal mode quantum numbers $m_1, m_2, \cdots, m_j' = m_j + 1, \cdots, m_N$ [cf. Eq. (2.16)]. In the present model it is only the jumps over the barrier which determine τ, and such jumps require a coupling between the CH_3 librations at low temperatures.

The experimental results for samples containing methyl groups do not always show temperature ranges of a decreasing tunneling frequency with a constant distribution width and of a temperature-independent T_1.[13] This fact may arise from the rather large distance between the neighboring methyl groups, which makes the coupling weak. The width of the distribution of the CH_3 librational energy or w should decrease with the coupling, and thus the ratio c_1/c_0 is large, according to Eq. (3.3). Therefore α in Eq. (3.5) is believed to be many orders of magnitude smaller than β, and a very low temperature in comparison with ϵ_{01}/k is required before the region $1/\tau = \alpha$ is reached. However, in samples containing NH_4^+ ions and in solid methane, the distance between the neighboring proton tetrahedra is small and consequently the libration coupling large. Hence α is quite large, and the plateau in T_1 can already be observed at temperatures of some kelvin. On the other hand a high potential barrier makes the energy ϵ_b large, and the factors c_n small in Eq. (3.3), and therefore the spin-lattice relaxation due to libration coupling may be very slow indeed. The proton relaxation in NH_4Cl is believed to be an example of such a case.[28]

The present models for the temperature dependence of the tunneling frequency and the proton relaxation time T_1 are based on a many-body consideration and therefore can not yet be solved quantum mechanically in detail. The semiquantitative and qualitive considerations presented here explain many experimentally observed results and open a totally new way of approaching the low-temperature data of librational tunneling and nuclear relaxation.

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