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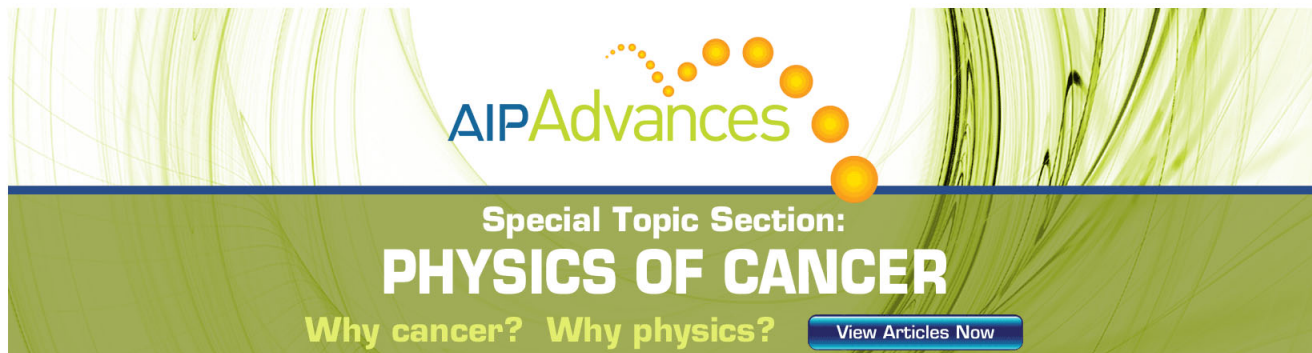
Nuclear spin–lattice relaxation of methyl groups via multiphonon processes

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The empirical correlation between the logarithm of tunneling splittings and the temperature at which the spin–lattice relaxation time is minimum for methyl groups in different molecular crystals is explained successfully by taking multiphonon processes into account. We show that one-phonon transitions dominate in the low barrier limit. However, in the intemediate barrier range and high barrier limit, it is necessary to include multiphonon processes. We also show that the empirical correlation depends only logarithmically on the details of the phonon bath.

I. INTRODUCTION

The hindered motion of methyl groups in molecules embedded in a crystal has been the subject of many recent investigations by high resolution inelastic neutron scattering (INS), nuclear magnetic resonance (NMR),[1-3] and recently by optical measurements[4] since it is one of the few examples where the indistinguishability of the three protons in a methyl group has an observable quantum effect. This dynamics also exhibits a continuous transition from coherent tunneling motion at low temperature to incoherent thermally activated motion (classical "hopping") at high temperature for many different compounds. Rotational tunneling frequencies in the range 0.1–100 GHz are accessible to INS, while small tunneling splitting (below 50 MHz) can be studied by an NMR field cycling cross relaxation technique.[5,6] In addition, the activation energy for methyl group rotation at higher temperatures can be determined from proton spin–lattice relaxation time (T_1) measurements. This is quite different from translational tunneling in which the tunneling splittings of only a few systems have been reported.[7,8] The reason that we can observe tunneling splitting for methyl groups even at high temperature is that rotational tunneling is a many body problem in which the exact threefold symmetry of the potential is produced by the indistinguishability of three protons in methyl group.

Several years ago, Clough[9-14] observed that an empirical correlation exists between the logarithm of the tunneling splitting ($\ln \omega_t$) and the temperature at which spin–lattice relaxation time is a minimum ($T_{\min}$) for all the compounds which have been measured up to now. This correlation curve is shown in the Fig. 1. This correlation strongly suggests that the only relevant parameters are the temperature and the potential height, and more importantly, that the details of the phonon bath do not play a major role in this empirical correlation. This correlation curve also provides a way to estimate the order of the magnitude for the tunneling splitting, a property usually measured at low temperature, by measuring the spin–lattice relaxation time at high temperature where the thermal fluctuations are large. Note that the slope of the $\ln \omega_t$ vs $T_{\min}$ curve decreases as $T_{\min}$ increases, suggesting a change in the basic physics for small ω_t (high barriers). In the following, we will explain this trend quantitatively. In Fig. 2, we plot the barrier height determined from the tunnel splitting vs the observed activation energy (in T_1).

We approach the problem in this paper by the standard quantum statistical method. Starting from the Hamiltonian for the whole system including phonons[15] we derive the transition rates for the spin states which determine spin–lattice relaxation time under the assumption of the existence of a single spin temperature. Comparing with the tunneling splitting from exactly diagonalizing the spatial part of the system Hamiltonian, we find that this empirical correlation can be explained successfully by taking into account multiphonon processes. It is also shown that the relationship between tunneling splitting and $T_{\min}$ is insensitive to the parameters of the phonon bath, since these enter only logarithmically.

Recently, Clough[14] has adopted an unusual approach to explain the transition from low temperature quantum motion to incoherent classical motion at high temperature, in which the C_3 symmetry is broken by including a vector potential in the Hamiltonian of the methyl group in analogy with electromagnetism and the discussion of Berry[16] on the geometrical phase. This approach has not yet led to quantitative results for the present problem. We will comment on a possible connection with our work in the conclusions.
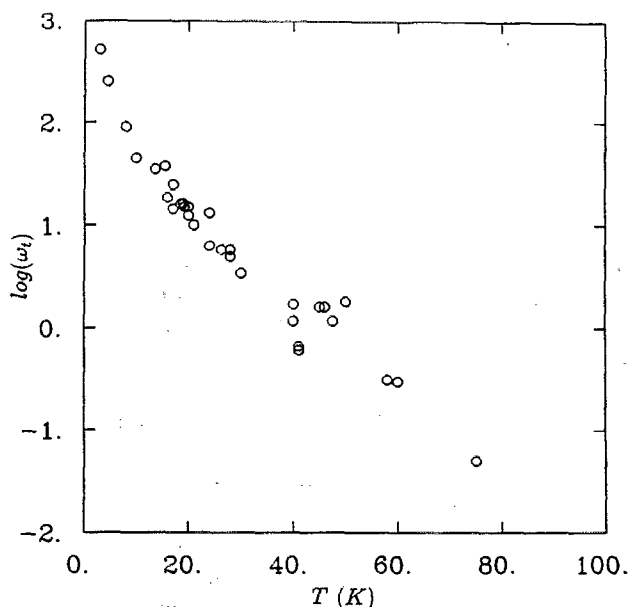

FIG. 1. The empirical correlation between $\ln \omega_t$ and minimum temperature of the spin lattice relaxation $T_{\min}$. Based on Ref. 9.
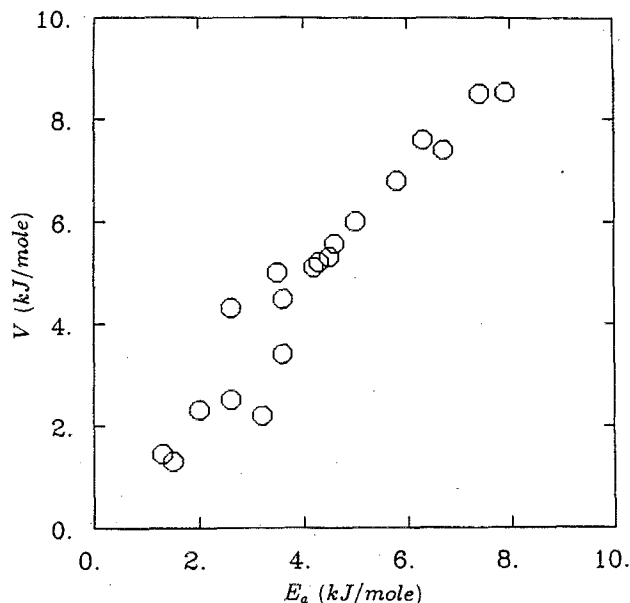
FIG. 2. The empirical correlation between the potential barrier and the activation energy. Estimated from Refs. 2, 3, 5, and 9.

II. MODEL

A. Hamiltonian

The Hamiltonian for the combined system of methyl group and phonon bath is described by

$$H = H_z + H_r + H_p + H_D + H_{rp}, \tag{1}$$

where

$$H_z = \sum_{i=1}^{3} \omega_L I_{zi}, \tag{2}$$

$$H_r = \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2} + \frac{V_3}{2} \cos(3\theta), \tag{3}$$

$$H_p = \sum_j \left(\frac{p_j^2}{2m} + \tfrac{1}{2} m\omega_j^2 x_j^2 \right), \tag{4}$$

$$H_D = \sum_{i<j} \sum_{q=-2}^{2} F_{ij}^{(q)} A_{ij}^{(q)}, \tag{5}$$

$$H_{rp} = \sum_j g_j x_j \cos(3\theta + \phi). \tag{6}$$

Here H_z, H_r, H_p are Zeeman interaction for the nuclear spins, rotor Hamiltonian, phonon bath, respectively, while H_D, H_{rp} are dipolar interaction and rotor–phonon interaction, respectively. ω_L is the Larmor frequency, I_{zi} are the z components of the nuclear spins, and $F_{ij}^{(q)}$, $A_{ij}^{(q)}$ are the spatial and the spin parts of the dipolar interaction in spherical coordinates. We assume that methyl groups couple independently to the phonon bath and nuclear spins of three protons can interact only indirectly to the phonon bath via spatial part of the rotors. The potential of the methyl group is threefold symmetric with respect to the C_3 rotation since the three protons in the methyl group are indistinguishable. The rotor–phonon interaction is assumed for simplicity to be linear in phonon coordinate, but threefold symmetric with respect to the rotational degrees of freedom.

The rotor wave functions can be obtained by diagonalizing the Hamiltonian in the eigenbasis set of the free rotor (i.e., $|k\rangle = e^{ik\theta}$). Since $\cos 3\theta$ can only connect free rotor $|k\rangle$ by $|k+3\rangle$ and $|k-3\rangle$, the spatial wave functions are then represented by the Fourier series $\psi_A = \Sigma_k a_{3k} e^{i3k\theta}$, $\psi_{E_a} = \Sigma_k a_{3k+1} e^{i(3k+1)\theta}$, and $\psi_{E_b} = \Sigma_k a_{3k-1} e^{i(3k-1)\theta}$. In this basis set, the rotor Hamiltonian can be expanded in terms of operator basis $X'_{nm} = |ns\rangle\langle ms|$, and the phonon bath can be written in the second quantized operators b and b^+, the Hamiltonian for the combined rotor and phonon system is given by[18]

$$H_0 = \sum_{ns} \epsilon_{ns} X_{nn}^s + \sum_j \omega_j (b_j^+ b_j + \tfrac{1}{2})$$

$$+ \sum_{mn} \sum_j g_j^{nm} (b_j + b_j^+) X_{nm}^s,$$

where ϵ_n is the eigenvalue of the nth level, and $s = A, E_a, E_b$. Since the rotor–phonon interaction is spin independent, we will neglect the symbol s whenever only the rotor–phonon system is considered.

The total wave functions are antisymmetric with respect to the permutation of any two protons because the three protons in methyl group are indistinguishable. The strong chemical bonds between protons and carbon prohibit just one permutation at the temperatures we consider. Thus the total wave functions for the methyl group need only to be symmetrized with respect to C_3 rotation which is equivalent to two permutations. However, if we apply the exclusion principle rigorously, the wave functions for the methyl group are the linear combination of the direct product:[10] $|\Psi_A\rangle|\Phi_A\rangle$, $|\Psi_{E_a}\rangle|\Phi_{E_b}\rangle - |\Psi'_{E_b}\rangle|\Phi_{E_a}\rangle$, and $|\Psi_{E_b}\rangle|\Phi_{E_a}\rangle - |\Psi'_{E_a}\rangle|\Phi_{E_b}\rangle$, where Ψ and Φ are the spatial and spin parts of the wave function, respectively, and Ψ'_{E_b} is Ψ_{E_a} with one exchange of protons. The spatial and spin parts of the methyl group are therefore strongly correlated in the sense that they cannot reduce to a simple product form.

After defining the Hamiltonian, the matrix elements for H_D and H_{rp} can be calculated directly. There are only a few nonvanishing elements between different states due to the symmetry of methyl group and dipolar interaction. For instance, no transition between A states and E states can be induced by rotor–phonon interaction, since the coupling is spin independent, which implies that rotor–phonon interaction can only scatter methyl group from one state to another state without changing its spin state. The dipolar interacion can mix different spin states due to the weak magnetic interaction among protons. However, intramethyl and intermethyl interactions behave quite differently: intramethyl dipolar interaction can only connect A and E species, but there is no symmetry restriction for the intermethyl dipolar interaction.

B. Transition rates

Transition rates can be calculated by the Fermi Golden Rule, which gives

$$W_{\alpha r p, \beta' r' p'} = \frac{2\pi}{\hbar} |\langle \beta n p' | H_{\text{dipolar}} | \alpha m p \rangle|^2 \delta(E_{\alpha m p} - E_{\beta n p'}),$$

$$\tag{7}$$

where we have used Greek letters to represent spin states, mn torsional states, and pp' phonon states. $E_{\alpha mp}$ and $E_{\beta np'}$ are the total energies of the whole system. Employing the identity

$$\delta(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} dx,$$

Eq. (7) becomes

$$W_{\alpha rp, \beta r'p'} = \sum_q \frac{|\langle \alpha | A^{(q)} | \beta \rangle|^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{i\omega_{\alpha\beta} t}$$
$$\times \langle mp | F^{(q)}(t) | np' \rangle \langle np' | F^{(q)} | mp \rangle. \quad (8)$$

The thermal average of the transition rates from $|\alpha\rangle$ to $|\beta\rangle$ is given by

$$W_{\alpha\beta} = \sum_{rp'p'} P_r(m) P_p(p) W_{\alpha mp, \beta np'}$$
$$= \sum_q \frac{|\langle \alpha | A^{(q)} | \beta \rangle|^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{i\omega_{\alpha\beta} t} \langle F^{(q)}(t) F^{(q)} \rangle, \quad (9)$$

where $P_r(m), P_p(p)$ are the Boltzmann factors for the initial rotational and phonon states. $F^{(q)}(t) = e^{-i(H_r^x + H_p^x + H_{rp}^x)t} F^{(q)}$. The transition rate therefore becomes a Fourier transform of time correlation function $\langle F^{(q)}(t) F^{(q)} \rangle$. Taking the partial trace over the phonon bath and making the cumulant expansion to the second order, we get an effective Liouvillian $H_r^x - i\Gamma$ for the rotational degrees of freedom, where Γ is the relaxation matrix for the rotational states. The rotational correlation function in Eq. (9) becomes

$$\langle F^{(q)}(t) F^{(q)} \rangle = \mathrm{Tr}_r \left[P_r (e^{-iH_r^x t - \Gamma t} F^{(q)}) F^{(q)} \right].$$

In the basis of rotor eigenfunctions, the thermal transition rate between different states can be written as

$$W_{\alpha\beta} = \sum_q \frac{|\langle \alpha | A^{(q)} | \beta \rangle|^2}{\hbar^2} \sum_{mn} P_r(m) |F_{mn}^{(q)}|^2$$
$$\times \frac{\Gamma_{mn}}{(\omega_{\alpha\beta} + \omega_{mn})^2 + \Gamma_{mn}^2}. \quad (10)$$

Since the dominant contribution comes from the nearest tunneling pairs, Eq. (10) can be simplified to

$$W_{\alpha\beta} = \sum_q \frac{|\langle \alpha | A^{(q)} | \beta \rangle|^2}{\hbar^2} \sum_m P_r(m) |F_m^{(q)}|^2$$
$$\times \frac{\Gamma_m}{(\omega_{\alpha\beta} + \omega_t^m)^2 + \Gamma_m^2}, \quad (11)$$

where we have approximated Γ_{mm+1} by Γ_m. ω_t^m is the tunneling splitting of the nth torsional state. Furthermore, since the correlation time for the spin degrees of freedom is usually much longer than that of rotational motion, we can apply a short time expansion to the rotational degrees of freedom. Therefore, $W_{\alpha\beta}$ becomes

$$W_{\alpha\beta} = \sum_q \frac{|\langle \alpha | A^{(q)} | \beta \rangle|^2}{\hbar^2} \frac{\Gamma}{(\omega_{\alpha\beta} + \omega_t)^2 + \Gamma^2}, \quad (12)$$

where

$$\Gamma = \tau^{-1} = \sum_n P_n \tau_n^{-1}, \quad (13)$$

$$\omega_t = \sum_n P_n \omega_t^n. \quad (14)$$

In Eq. (12), τ is the correlation time for the rotational degrees of freedom and τ_n^{-1} is the width of the nth level, given by the sum of the transition rates from n to all the other states, $\tau_n^{-1} = \Sigma'_{mn} W_{nm}$, where Σ'_{mn} means sum over all m and n except $m = n$. In other words, the correlation time for the rotational motion is the thermal average of the broadening for each torsional state. Essentially, this result was observed by Haupt 20 years ago.[15] The interpretation given here is similar to that of Haupt, but quite different from the work of Clough and Stejskal and Gutowsky,[9,17] who associate the inverse of correlation time with the thermal average of angular momentum and tunneling splittings for rotation states, respectively. Note that the tunneling splitting appearing in the equation for the spin conversion rate is also reduced to the thermal average of all tunneling splittings in each torsional manifold. Since the sign of the tunneling splittings alternates, ω_t reduces to zero as temperature increases.

C. Multiphonon processes

As mentioned in the Introduction, since in the high barrier limit Debye frequencies are smaller than the energy difference between ground and first torsional state, we cannot neglect multiphonon processes in this system, a fact which has been ignored in previous work. Neglecting multiphonon processes causes the activation energies calculated from $\tau = \tau_0 \exp(\beta E_a)$ to be smaller than the experimental results. The latter are usually slightly smaller than the potential barrier height for most compounds, in the temperature range that experiments have been performed. Furthermore, only a small fraction of acoustic phonons are populated in that temperature range. More importantly, we should note that methyl group is a pure quantum mechanical system since the energy spacings for the rotor states go like m^2. Hence, we should not assume that classical behavior holds for methyl group dynamics. In order to explain the high activation energy, multiphonon processes have to be taken into account.

Multiphonon processes are included by making a polaron transformation which eliminates the diagonal coupling completely. Effecting the transformation $\widetilde{H} = e^{-S} H e^S$, where

$$S = \sum_n \sum_j g_j^{nn} (b_j - b_j^+) X_{nn},$$

we find

$$\widetilde{H} = \sum_n \tilde{\epsilon}_n X_{nn} + \sum_j \omega_j (b_j^+ b_j + \tfrac{1}{2})$$
$$+ \sum_{mnj}' g_j^{nm} (b_j + b_j^+) X_{nm} \Theta_{nm}$$
$$- 2 \sum_{mnj}' \frac{g_j^{nm} g_j^{nn}}{\omega_j} X_{nm} \Theta_{nm}, \quad (15)$$

and $\tilde{\epsilon}_n$ is renormalized energy for the nth rotor eigenfunction given by

$$\tilde{\epsilon}_n = \epsilon_n - \sum_j \frac{|g_j^{nn}|^2}{\omega_j}, \tag{16}$$

$$\Theta_{nm} = \exp\left[-\sum_j \frac{g_j^{nn} - g_j^{mm}}{\omega_j} (b_j - b_j^+) \right]. \tag{17}$$

This same transformation had also been employed by Hewson,[18] but he assumed that the only effect of removing diagonal coupling is the renormalization of the rotor eigenvalues. The effect on the off-diagonal coupling has been completely neglected. Due to the difference of g_j^{nn} and g_j^{mm} in Θ_{nm}, the transformed perturbation can produce multiphonon processes. Substituting the new coupling term into Fermi Golden Rule, we get the general form for the multiphonon transition rates:

$$W_{mn} = \exp\left[-\sum_q \kappa_q^2 \phi_q(0) \right] \int_{-\infty}^{\infty} dt\, e^{i\omega_{mn}t}$$

$$\times \sum_\alpha |g_\alpha^{mn}|^2 \{ \phi_\alpha(t) - \kappa_\alpha^2 [1 - \phi_\alpha'(t)^2] \}$$

$$\times \exp\left[\sum_q \kappa_q^2 \phi_q(t) \right], \tag{18}$$

where

$$\kappa_q = \frac{g_q^{nm} - g_q^{mm}}{\omega_q}, \tag{19}$$

$$\phi_q(t) = (n_q + 1)e^{-i\omega_q t} + n_q e^{i\omega_q t}, \tag{20}$$

$$\phi_q'(t) = (n_q + 1)e^{-i\omega_q t} - n_q e^{i\omega_q t}. \tag{21}$$

In the weak coupling limit, Eq. (18) can be simplified by expanding the exponential term to the first few terms, i.e.,

$$\exp\left[\sum_q \kappa_q^2 \phi_q(t) \right] = 1 + \sum_q \kappa_q^2 \phi_q(t)$$

$$+ \frac{1}{2} \left[\sum_q \kappa_q^2 \phi_q(t) \right]^2 + \cdots.$$

Collecting the contribution according to the number of phonons involved, multiphonon processes appear automatically. The lowest order term is simply one-phonon processes or $\kappa_q = 0$, i.e., $g_\alpha^{nn} = g_\alpha^{mm}$). The result is

$$W_{mn} = \sum_\alpha |g_\alpha^{mn}|^2 [(n_\alpha + 1)\delta(\omega_{mn} - \omega_\alpha)$$

$$+ n_\alpha \delta(\omega_{mn} + \omega_\alpha)]. \tag{22}$$

Applying the deformation potential approximation to the rotor–phonon coupling and assuming the density of the states $\rho(\omega_\alpha)$ is proportional to ω_α^2, the transition rates can be simplified as

$$W_{mn} = \begin{cases} |g_{mn}|^2 \omega_{mn}^3 [n(\omega_{mn}) + 1] & \text{for one phonon emission} \\ |g_{mn}|^2 \omega_{nm}^3 n(\omega_{mn}) & \text{for one phonon absorption,} \end{cases} \tag{23}$$

where $n(\omega_{mn})$ is the phonon occupation number at the frequency ω_{mn} given by $(e^{\beta\omega_{mn}} - 1)^{-1}$. Keeping terms to the second order, we have two-phonon transition rates given by

$$W_{mn} = \begin{cases} |g_{mn}|^2 |g_{nn} - g_{mm}|^2 \int_0^{\omega_D} d\omega\, \omega^3(\omega_{mn} - \omega)n(\omega)n(\omega_{mn} - \omega) \\ \qquad \text{for the two phonon absorption,} \\ |g_{mn}|^2 |g_{nn} - g_{mm}|^2 \int_0^{\omega_D} d\omega\, \omega^3(\omega_{mn} + \omega)[n(\omega) + 1][n(\omega_{mn} + \omega) + 1] \\ \qquad \text{for the two phonon emission} \end{cases} \tag{24}$$

where ω_D is the Debye frequency, and the Debye–Waller factor $\exp[-\sum_q \kappa_q^2 \phi_q(0)]$ is close to 1 for weak coupling (κ_q small).

From these expressions, we shall show later that two-phonon emission and absorption become the dominant processes when the energy spacings between rotational states are larger than Debye frequency and thus one-phonon processes become zero. Raman processes can be neglected completely since energy cannot be conserved. In the next section, we shall apply these two processes to the calculation of the spin–lattice relaxation time.

III. SPIN–LATTICE RELAXATION

Under the assumption of the existence of a single spin temperature, the spin–lattice relaxation rate can be written in a closed form[19]

$$T_1^{-1} = \frac{1}{2} \frac{\sum_{\alpha\beta} W_{\alpha\beta}(E_\alpha - E_\beta)^2}{\sum_\alpha E_\alpha^2}. \tag{25}$$

Substituting the thermal transition rate $W_{\alpha\beta}$ into Eq. (25), we get a general expression for the spin–lattice time:[3]

$$T_1^{-1} = C_1 \left(\frac{\tau}{1 + (\omega_L - \omega_t)^2\tau^2} + \frac{4\tau}{1 + 4(\omega_L - \omega_t)^2\tau^2} \right.$$

$$\left. + \frac{\tau}{1 + (\omega_L + \omega_t)^2\tau^2} + \frac{4\tau}{1 + 4(\omega_L + \omega_t)^2\tau^2} \right)$$

$$+ C_2 \left(\frac{\tau}{1 + \omega_L^2\tau^2} + \frac{4\tau}{1 + 4\omega_L^2\tau^2} \right), \tag{26}$$

where T_1^{-1} contains two contributions, intramethyl (C_1) and intermethyl (C_2) relaxation. Due to the symmetry, in-

tramethyl dipolar interactions only induce relaxation be-
tween A states and E states, therefore it only contributes to
the first term, but intermethyl dipolar can cause relaxation
between E_a and E_b and makes a contribution to the second
term. The qualitative behavior of the empirical correlation
between $\ln \omega_t$ and $T_{\min}$ can be easily inferred from Eq. (26)
and the activation energy defined through the Arrhenius law
$\tau = \tau_0 \exp(\beta E_a)$, or more explicitly through $E_a(T)$
$= \partial \ln \tau / \partial \beta$, which is a function of temperature generally.
In the low barrier limit ω_L is much larger than ω_L, and Eq.
(26) is reduced to

$$T_1^{-1} = C_1 \tau / (1 + \omega_t^2 \tau^2) + C_2 \tau / (1 + \omega_L^2 \tau^2), \qquad (27)$$

which implies $(T_1^{-1})_{\min}^{\text{intra}} = C_1 \tau_{\min} = C_1 \omega_t^{-1} \approx 10^{-2} \text{ s}^{-1}$,
while $(T_1^{-1})_{\min}^{\text{inter}} = C_2 \omega_L^{-1} \approx 10^2 \text{ s}^{-1}$. Hence, intermethyl
contributions to $(T_1^{-1})_{\min}$ are much more important in this
limit. In the high barrier limit two contributions merge to-
gether; however, the position of the temperature for the max-
imum relaxation rate is still determined by the intermethyl
dipolar interaction. Therefore $\beta_{\min} = -\ln(\omega_L \tau_0)/E_a$
$= -\gamma \ln(\omega_L \tau_0)/V$ at the maximum relaxation rate, with
$\gamma = V/E_a$. When we employ the property that $\ln \omega_t$ is pro-
portional to V, then a linear correlation $\ln \omega_t = \alpha T_{\min}$
$+ \text{const}$ exists, where $\alpha = \gamma \ln \omega_L \tau_0$ and τ_0 is proportional
to λ^2. This accounts for the approximate linearity in the em-
pirical correlation. The phonon spectrum appears in the
preexponential factor τ_0 only and therefore affects the slope
logarithmically. This is the reason why this correlation is
insensitive to the parameters of phonon bath as noted by
Clough. However, note that the slope depends on the activa-
tion energy linearly which is important for the understand-
ing of the decreasing of the slope as barrier height increases.

IV. RESULTS AND DISCUSSIONS

Employing Eqs. (23) and (24) for one- and two-
phonon processes, respectively, we numerically calculate the
temperature dependence of the rotational correlation time,
the activation energy, and the spin–lattice relaxation for dif-
ferent potential barriers. Figure 3 shows the temperature
dependence of activation energies for one-phonon processes
which are just the energy spacing between ground state and
second excited state. It is easy to see the increase of the acti-
vation energy is quite linear as a function of barrier height.
The same behavior is also found in the Fig. 4, which shows
the evolution of the spin–lattice relaxation time for several
barrier heights. Therefore in Fig. 5, we find a linear correla-
tion for $T_{\min}$ and ω_t under the assumption that only one-
phonon processes are involved.

Hence, this remarkable correlation can be obtained
qualitatively by just considering one-phonon process. How-
ever one-phonon processes still fail to account for the small
change of the slope of this correlation at high barrier limit.
As we discussed in the previous paragraph, the reason for
this is that the activation energies calculated from the one-
phonon calculation are smaller than the potential barrier
height in the experimental temperature range. The change of
the slope at higher potential barrier for the experimental
data can be shown to be as a result of the multiphonon pro-
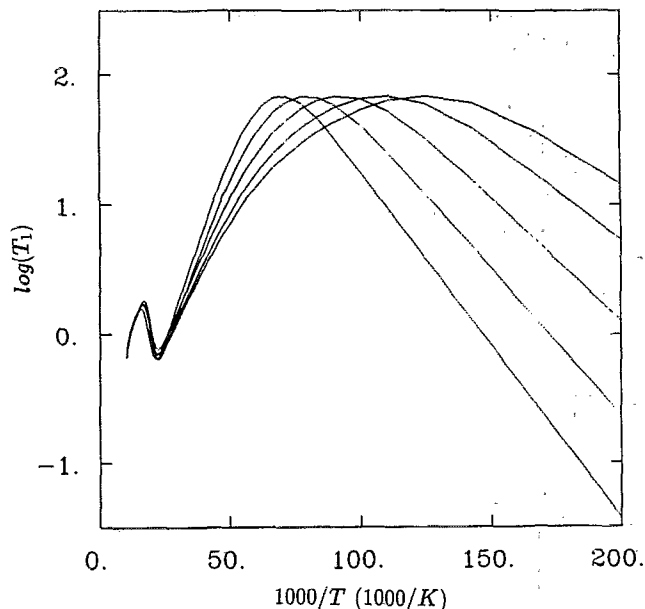cesses. In Fig. 6, the activation energies due to the multi-

FIG. 4. One-phonon induced spin–lattice relaxation time T_1 vs temperature
for various potential barrier heights. The small bumps in the diagram are the
contribution from the intramethyl dipolar interaction.

phonon processes show much higher values than that from
one-phonon processes. Further calculations on the spin–lat-
tice relaxation for the two-phonon processes are shown in
Fig. 7. Considering only one-phonon processes, the activa-
tion energy is simply the energy spacing between the ground
and the first excited states. Due to the restriction of the con-
servation of energy, the states with higher energy do not
contribute to the activation energy. However, when the mul-
tiphonon processes are included, more eigenstates can inter-
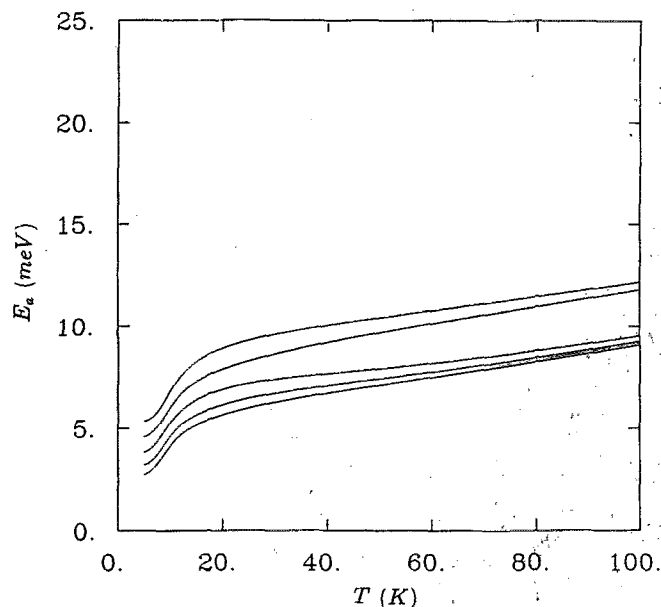act with the phonon bath. Hence, the activation energy in-

FIG. 3. The activation energies for potential barrier 2, 4, 6, 8, and 10 meV as
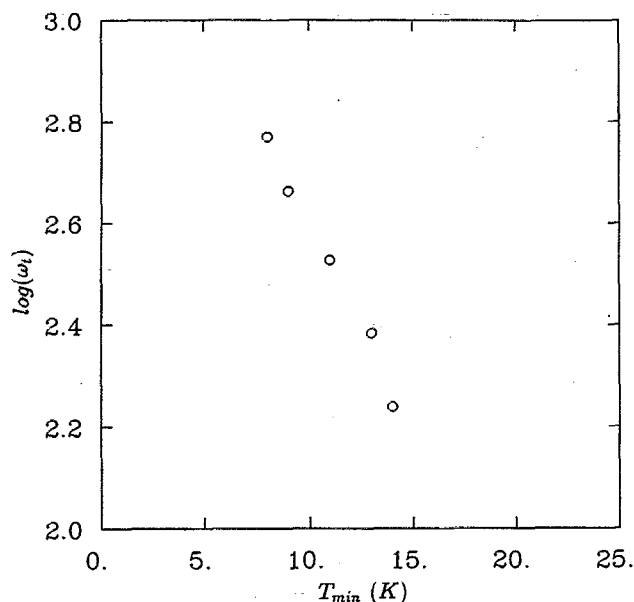a function of temperature calculated from one-phonon processes.

FIG. 5. The correlation curve between $\ln \omega_t$ and minimum temperature of T_1 calculated from one-phonon processes.

FIG. 7. Two-phonon induced spin–lattice relaxation time T_1 vs temperature for various potential barrier height.

creases since more higher quantum states join the processes. As we have shown in the previous section, the slope of the empirical correlation is dependent on the activation energy linearly, therefore the change of the slope to lower value when we include multiphonon processes is expected. The results of calculation for the two-phonon processes are shown in Fig. 8. The result is very similar to the one-phonon processes at the low barrier limit (10–40 meV) except that the slope of the two-phonon processes is still smaller than that of one-phonon processes. But at the intermediate potential range, a new channel for the transition between different
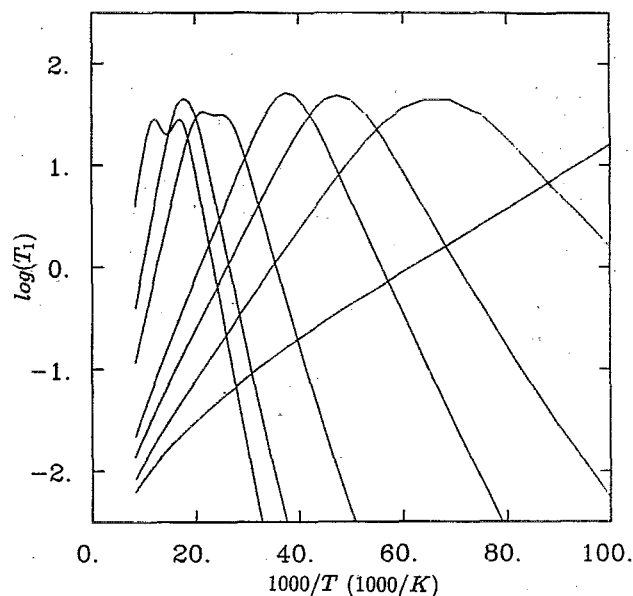
rotational states is opened up, and the activation energy becomes the difference between the ground and the third excited states ($\sim$50 meV). As we increase the potential further, the original channel becomes less important, and a new channel dominates. We therefore get a even higher activation energy which corresponds to the ground and fourth excited states (60~70 meV). The results in Fig. 9 show that the matrix element between different rotor states have some interesting trends. For instance, g^{02}, g^{13}, and g^{24} are much larger than those elements connected closest torsional states. Multiplying with the Boltzmann factor, the activation ener-
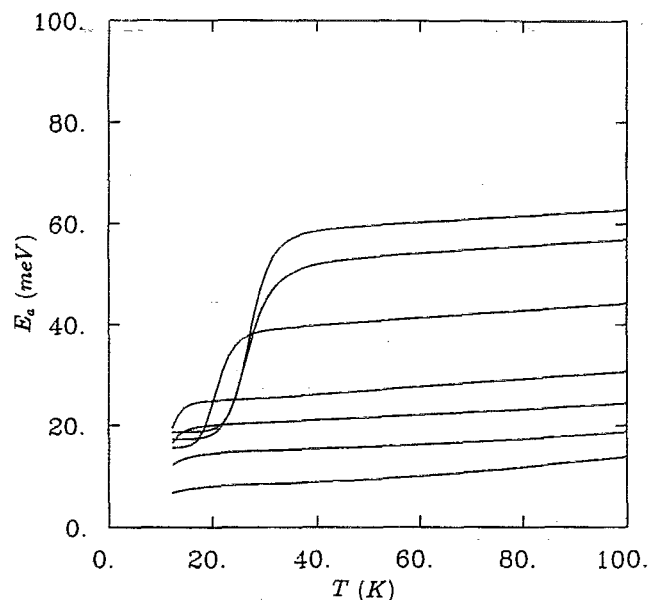

FIG. 6. The activation energies for $V = 10$–70 as a function of temperature calculated from two-phonon processes. A substantial increase of activation energy for $V = 50$, 60, and 70 meV can easily be seen.
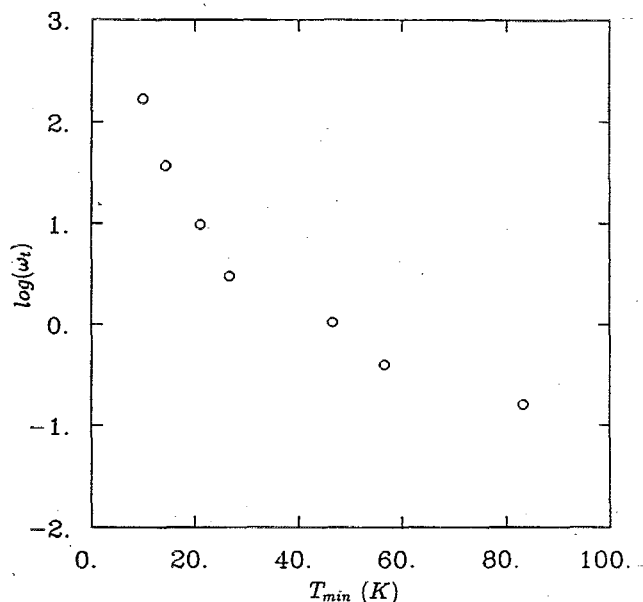

FIG. 8. The correlation curve between $\ln \omega_t$ and minimum temperature of T_1 calculated from two-phonon processes.
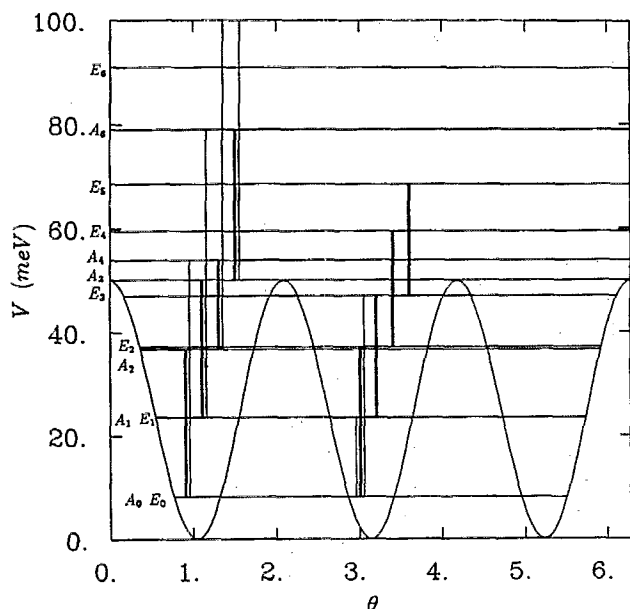
FIG. 9. The eigenvalues and the matrix elements ($g_{mn} = \langle m|\cos 3\theta |n\rangle$) for $V = 50$ meV where the horizontal lines represent nonvanishing matrix transition elements between different rotational levels. The matrix elements between some lowest eigenstates are given by: $g_{02}^A = 0.218$, $g_{13}^A = 0.357$, $g_{24}^A = 0.475$, $g_{35}^A = 0.485$, $g_{01}^E = 0.001$, $g_{02}^E = -0.22$, $g_{03}^E = 0.022$, $g_{13}^E = 0.336$, $g_{24}^E = 0.389$, $g_{35}^E = 0.433$, and $g_{mn,n+1}^A = 0$. The matrix elements between next nearest neighbor are much larger than all other elements.

gy is usually determined by the competition between E_{01} at the low temperature and E_{02}, E_{03}, or E_{04} at the high temperature. Due to this multichannel effect in the multiphonon processes, the activation energies tend to be close to the potential barrier which explains the experimental results on the relationship between activation energy and the potential barrier shown in Fig. 2. From the previous discussion, we know that the gradual changing of the slope to lower value as the potential barrier is increased is due to the activation energy and the potential barrier being close to each other, which has been explained quite successfully using multiphonon processes.

V. CONCLUSION

In this study, we have been able to clarify the underlying physics of the tunneling motion of methyl groups from low to high temperature. The correlation between T_{min} and $\ln \omega_t$ has been explained and we have pointed out that the slope of the T_{min} vs $\ln \omega_t$ curve decreases as T_{min} increases due to a change in the basic physics for small ω_t. One phonon transitions have been shown to dominate in the low barrier limit; however, in the intermediate barrier range and high barrier limit the Debye frequency is always less than the energy spacing between the torsional levels, and two-phonon (and multiphonon) processes have to be considered. The unusual high activation energy is identified as the key to understand-

ing the change of the slope for this empirical correlation. The insensitivity of the correlation to the parameters of the phonon bath is justified in the sense that the unknown coupling constant between the rotor and phonon bath appears only in a logarithmic term.

The suggestion of Clough[14] that a vector potential be introduced into the Hamiltonian for the methyl rotation in order to explain the quantum dynamics and spin relaxation is an interesting and potentially important one. Our approach, on the other hand, has been very traditional, and it is therefore difficult to see the connection to the suggestion of Clough. However, one possibility does exist: it has long been shown[20,21] that when considering the internal torsional motion of a methyl group and the overall rotation of the molecule *in the gas phase*, the solution for the internal torsion is nonperiodic. In other words, there is an extra phase in the wave function for the torsional motion; this is now known as the Berry or geometric phase.[16] In the solid, the role of the total rotation of the molecule may be played by the torsional motion of the molecule as a whole, in other words by a lattice optical phonon. This provides a connection between our work and Clough's. If the dominant phonon interaction with the methyl rotation is a torsional mode, then a slight rewriting of our analysis may be able to provide a quantitative model verifying Clough's hypothesis. We are presently undertaking such a study.

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