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Rotational motion of methyl groups in solids

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The symmetry properties of the $X\mathrm{H}_3$-type molecules are investigated. The possible wave functions of the molecule in the ground electronic state are calculated in the Born-Oppenheimer approximation and the question of the symmetry group of the molecular Hamiltonian (C_3 or C_{3v} or other) is considered. Further, the concept of quantum coherence is examined for the case of tunneling methyl groups. The results are extended to the high temperature region by introducing a suitable ''pointer basis'' which appears to be appropriate for the description of dynamics of the methyl groups interacting with lattice. Finally, the spin-lattice relaxation time is calculated within this model and is found to agree closely with the semiclassical result. [S0163-1829(96)09126-6]

I. INTRODUCTION

The rotational motion of hindered methyl groups in solids has been a subject of considerable interest and research activity in recent years. Its single particle aspects have been thoroughly described in Ref. 1. However, the most interesting aspect of the methyl dynamics and the one which, in our opinion, is still not yet completely understood, is the continuous transition from quantum mechanical tunneling at low temperatures to the apparently classical reorientation, or random hopping motion, at higher temperatures.[1]

The proper quantum mechanical description of this phenomenon valid at all temperatures involves, in general, a complicated many-body Hamiltonian for which no simple solution can be found. To make the problem tractable, a single methyl group is usually considered, interacting with the host lattice vibrations described as a heat bath at well defined temperature. At low temperatures, in the tunneling regime, the dynamics of methyl groups can be adequately described in terms of spin-rotational wave functions commonly chosen to belong to the A-type irreducible representation of the point group C_3.[1] Increasing the temperature, the question arises of the appropriate basis of the methyl group wave functions—let us call it ''pointer basis''[2,3]—that would lend themselves naturally, in the high temperature domain, to the interpretation of the associated methyl dynamics in terms of random rotational jumps as envisaged by Press.[1]

The correctness of the ''standard'' spin-rotational wave functions classified according to the irreducible representations of the C_3 point group[1] has been questioned in papers by Clough *et al.*,[4] and Stevens.[5] The authors argue that the methyl wave functions should be classified according to the irreducible representations of the symmetry group C_{3v} rather that C_3. Then, in order that the Pauli exclusion principle be satisfied also for single permutations, the total wave function is required to belong to the A_2 irreducible representation of C_{3v}. While it is undoubtedly true that the total wave function must transform under the C_{3v} symmetry operations in accordance with the Pauli exclusion principle, the introduction of the group C_{3v} instead of C_3 at the outset of the calculation brings, in our opinion, no novel features in the description of real methyl groups. We maintain that from a practical point of view, the ''standard arguments'' as presented in Ref. 1, and repeated very carefully in Refs. 4 and 5, are perfectly legitimate. Moreover, we would like to stress that the use of collective angular coordinates for the description of methyl rotational motion in no way restricts the rigorous implementation of the Pauli exclusion principle, contrary to what is sometimes erroneously suggested.

In Sec. II the problem of the appropriate symmetry point group, C_3 or C_{3v}, and the proper use of the Pauli exclusion principle in determining the wave functions and energy levels is discussed. In Sec. III, the question of the appropriate basis, the ''pointer basis,'' of the methyl group wave functions consistent with the Pauli exclusion principle is outlined, and its observational consequences regarding the high-temperature spin-lattice relaxation time are considered.

II. SYMMETRY CLASSIFICATION OF THE ENERGY LEVELS OF TUNNELING METHYL GROUPS

In discussing the symmetry properties of an $X\mathrm{H}_3$-type molecule of which the methyl group is an example, the Born-Oppenheimer approximation[6] enables one to write the complete molecular wave function as a product of the electronic and nuclear parts. We shall consider only the nuclear part of the wave function, as it is an experimental fact that the ground electronic state of almost all stable polyatomic molecules is completely symmetric under the operations of the underlying symmetry group.

In molecules possessing symmetrical equilibrium configurations, it is convenient to choose three Cartesian coordinates determining the position of the center of mass of the molecule, the three Euler angles (φ, ϑ, χ) describing the orientation in space of a set of rotating coordinate axes (ξ, η, ζ) whose origin coincides with the center of mass, and $3N-6$ (N being the number of the nuclei) normal coordinates which determine the positions of the nuclei relative to each other in the rotating coordinate system. Choosing the origin of the rotating coordinate system to coincide with the center of mass of the molecule does not suffice to define completely the rotating coordinate system. This problem, however, has a purely mechanical significance and arises whenever one attempts to separate the vibrational motion of a system of particles from its rotational motion. It turns out that a reasonable formulation of ''pure'' vibrations and ''pure'' rotations is obtained if the second Eckart-Sayvetz condition is imposed.[7,8]

Once a suitable system of coordinates has been chosen, one can write down the appropriate Lagrangian function and derive from it the corresponding quantum mechanical Hamiltonian. The details of the calculation are given, for example, in Refs. 9 and 10. In particular, the Hamiltonian separates naturally into translational, vibrational, and rotational parts together with a vibration-rotation coupling term. In many molecules, including most of the simple ones, the vibrational amplitudes, corresponding to a given equilibrium configuration of the nuclei, are small and the Coriolis interaction terms may be neglected. In addition, it is possible, in this case, to choose the rotating axes (ξ, η, ζ) to coincide with the principal axes of inertia of the molecule, resulting in a further simplification of the Hamiltonian.

The potential energy of a molecule embedded in a solid lattice can be approximated by a sum of external field terms and the vibrational potential energy,

$$V=\sum_{i=1}^{N} U_i(\mathbf{R}+\mathbf{r}_i)+U(\{Q_k\}), \tag{1}$$

where $\mathbf{R}$ gives the position of the center of mass, $\mathbf{r}_i$, the position of the ith nucleus with respect to the center of mass, and $\{Q_k\}$ denotes the set of normal vibrational coordinates. The potential energy terms U_i are assumed to have the same form for identical nuclei. For small vibrations, (1) can be further simplified by taking $U_i(\mathbf{R}+\mathbf{r}_i)\cong U_i(\mathbf{R}+\mathbf{r}_{0i})$ for all i, where $\mathbf{r}_{0i}$ is the equilibrium position of the ith nucleus. For a given value of $\mathbf{R}$, the various $\mathbf{r}_{0i}$ referring to identical nuclei are related to each other by symmetry operations of the molecular point group. The sum $\Sigma_i U_i(\mathbf{R}+\mathbf{r}_{0i})$ is therefore invariant with respect to these symmetry operations and may be expressed in terms of the Euler angles (φ, ϑ, χ) which we define in accordance with Ref. 10.

Making use of the above simplifications together with the harmonic approximation, and omitting the motion of the center-of-mass of the molecule, the molecular Hamiltonian for an $X\mathrm{H}_3$-type molecule embedded in a solid lattice becomes[9,10]

$$H=(\mathbf{J}^2/2I_A)+(J_\zeta^2/2)(1/I_C-1/I_A)+V(\varphi,\vartheta,\chi) \\ +(1/2)\sum_{k=1}^{3N-6}(P_k^2+\lambda_k Q_k^2). \tag{2}$$

J_ξ, J_η, and J_ζ are the components of the total angular momentum $\mathbf{J}$ of the top, and $I_A=I_B$, I_C are the principal moments of inertia. The ζ axis is chosen to coincide with the symmetry axis of the molecule; P_k are vibrational momenta conjugate to normal coordinates Q_k. Three degrees of freedom—translational motion of the center of mass of the molecule—have been omitted in (2) since they have no effect on the rotational motion. Due to the form of the Hamiltonian (2), the complete wave function of the molecule (omitting the electronic part) can be written as a product

$$\psi_{\mathrm{total}}=\psi_v\psi_r\psi_\sigma, \tag{3}$$

where ψ_v, ψ_r, and ψ_σ represent the parts of the wave function dependent, respectively, on vibrational $\{Q_k\}$, rotational (φ, ϑ, χ), and spin coordinates σ ($\sigma_1,\sigma_2,\ldots,\sigma_N$ representing spin components of the nuclei along some chosen direction in space) which refer to identical particles of the molecule (protons). Since each of the component wave functions belongs to one of the irreducible representations (IR) of the symmetry group of the molecular Hamiltonian, the representation Γ(total) to which the total wave function belongs is given as a direct product

$$\Gamma(\mathrm{total})=\Gamma_v\otimes\Gamma_r\otimes\Gamma_\sigma, \tag{4}$$

and is, in general, reducible. If the symmetry group of the Hamiltonian is C_{3v}, which is not always the case, then Γ_v, Γ_r, and Γ_σ represent IR's A_1, A_2, or E. Although the general case presents no difficulties, let us assume the molecule to be in the ground vibrational state which is always completely symmetric under C_{3v}.[9–11] In this case the symmetry of the total wave function is determined by $\Gamma_r\otimes\Gamma_\sigma$. Not all of these direct products are allowed, however, because of the Pauli exclusion principle imposing specific requirements on the behavior of the complete wave function with respect to the permutations of positions and spins of identical nuclei. Because C_{3v} is isomorphic to the permutation group of three particles and since the protons are fermions this implies that Γ(total) must belong to the A_2 IR. The possible spin symmetry species Γ_σ based on spin functions $|\sigma_1\sigma_2\sigma_3\rangle$ (each σ_i can take on the values $\pm 1/2$) are either of type A_1 or E.[1] Consequently, the allowed symmetry species of the rotational wave functions are A_2 and E with nuclear statistical weights 4 and 2, respectively[11] (we are omitting the multiplicity due to the spin of the X nucleus). The products (4) which are compatible with the exclusion principle are thus $\Gamma_r^{(A_2)}\otimes\Gamma_\sigma^{(A_1)}$ and $\Gamma_r^{(E)}\otimes\Gamma_\sigma^{(E)}$ ($\Gamma_v\equiv A_1$). Moreover, the two wave functions belonging to the one-dimensional representations A_1 and A_2 contained in $\Gamma_r^{(E)}\otimes\Gamma_\sigma^{(E)}$ are given as[11]

$$\psi_{r,1}^{(E)}\psi_{\sigma,2}^{(E)}\pm\psi_{r,2}^{(E)}\psi_{\sigma,1}^{(E)}, \tag{5}$$

where $\psi_{r,1}^{(E)}$, $\psi_{r,2}^{(E)}$ and $\psi_{\sigma,1}^{(E)}$, $\psi_{\sigma,2}^{(E)}$ are partners of the two-dimensional IR's E.

In what follows, we consider an $X\mathrm{H}_3$-type molecule in a three fold hindering potential. The corresponding results pertaining to free $X\mathrm{H}_3$-type molecules can be found in Refs. 11–14.

In case of nonzero threefold hindering potential $V(\varphi,\vartheta,\chi)\equiv V(\chi)=(V_3/2)(1-\cos 3\chi)$, $\varphi,\vartheta=\mathrm{const}$, the rotational eigenvalue equation is the Mathieu equation.[15] According to Floquet's theorem, the rotational wave functions can be written in the form

$$\psi_s^{(l)}(\chi)=e^{is\chi}\sum_{n=-\infty}^{\infty}A_{n,s}^{(l)}e^{i3n\chi}, \tag{6}$$

where $s=0,\pm1$, and $l=0,1,2,\ldots$ is recognized, in the limit of infinite hindering potential, as the librational or torsional quantum number. Wave functions with $s=\pm1$ represent E symmetry species while those with $s=0$ generate one-dimensional representations. In the limit of strong hindering potential and for not too large values of l, the functions $\psi_s^{(l)}(\chi)$ may be approximated by Bloch sums of the form[16]

$$\psi_s^{(l)}(\chi)\cong(1/\sqrt{3})\sum_j \varepsilon^{sj}H^{(l)}(\chi-j2\pi/3),\quad j=0,\pm1. \tag{7}$$

$H^{(l)}(\chi-j2\pi/3)$ are the harmonic oscillator functions centered at the minima of the hindering potential and obeying the relation $H^{(l)}(\chi)=(-1)^l H^{(l)}(-\chi)$. Note that they refer to the state of the molecule as a whole not to that of single protons.

The spin-rotational functions which obey the Pauli exclusion principle are

$$(\psi_0^{(l)}(\chi)\pm\psi_0^{(l)}(-\chi))\begin{cases}|\alpha\alpha\alpha\rangle\\ [|\beta\alpha\alpha\rangle+|\alpha\beta\alpha\rangle+|\alpha\alpha\beta\rangle]\\ [|\alpha\beta\beta\rangle+|\beta\alpha\beta\rangle+|\beta\beta\alpha\rangle]\\ |\beta\beta\beta\rangle\end{cases} \tag{8a}$$

$$\begin{aligned}&\psi_s^{(l)}(\chi)\left\{\begin{matrix}[|\beta\alpha\alpha\rangle+\varepsilon^s|\alpha\beta\alpha\rangle+(\varepsilon^*)^s|\alpha\alpha\beta\rangle]\\ [|\alpha\beta\beta\rangle+\varepsilon^s|\beta\alpha\beta\rangle+(\varepsilon^*)^s|\beta\beta\alpha\rangle]\end{matrix}\right\}\\ &\quad\pm\psi_s^{(l)}(-\chi)\left\{\begin{matrix}[|\beta\alpha\alpha\rangle+(\varepsilon^*)^s|\alpha\beta\alpha\rangle+\varepsilon^s|\alpha\alpha\beta\rangle]\\ [|\alpha\beta\beta\rangle+(\varepsilon^*)^s|\alpha\beta\alpha\rangle\varepsilon^s|\beta\beta\alpha\rangle]\end{matrix}\right\},\\ &\qquad s\neq0,\end{aligned} \tag{8b}$$

and they are either of A_1 or A_2 symmetry ($\varepsilon=e^{2i\pi/3}$, α denotes the spin projection value $+1/2$, and β the value $-1/2$). However, if the vibrational component has A_1 symmetry, only the A_2 type spin-rotational functions are permissible. For example, if we take $\psi_s^{(0)}(\chi)$ as given by (7) then the ± sign in (8b) gives the A_1 and A_2 type functions, respectively, (8a), on the other hand, yields only one nonzero function in this case (for + sign) which is of A_1 symmetry.

Next, let us recall that the effective vibrational potential energy can often have such a form that vibrational wave functions have appreciable magnitude only in certain small and fairly delocalized regions of the configuration space $\{\mathbf{r}_i\}$. For each of these regions or vibrational domains the molecular Hamiltonian can be approximated by the expression (2). The domains are symmetrically equivalent and consequently give rise to the same set of vibrational levels. The resulting degeneracy is split, however, in higher-order approximation.[17,18] It turns out that in the case of $X\mathrm{H}_3$-type molecules, one only needs to consider two distinct domains or, as they are sometimes referred to, *frameworks*,[17] which are not related to each other by rigid rotations of the molecule. Since the rotational properties of each framework, denoted by the superscripts a and b, are the same, the complete wave function with the correct A_2 symmetry is obtained by taking the appropriate linear combinations of the lowest vibrational wave functions associated with each framework. By analogy with a ''double-well'' problem, we can write for the two lowest vibrational states

$$\psi_v^{(0)}\sim\psi_v^{(a)}\pm\psi_v^{(b)}. \tag{9}$$

The energy difference between these two vibrational states depends on the height of the potential barrier separating the two configurations a and b. In most $X\mathrm{H}_3$-type molecules the barrier is so high that the states (9) are nearly degenerate which implies that for a given torsional state both signs are possible in (8b). Therefore we now have a choice of using either [for the sake of simplicity we choose $l=0$ in (8b)]

$$\begin{aligned}&(\psi_v^{(a)}\pm\psi_v^{(b)})\{\psi_1^{(0)}(\chi)[|\beta\alpha\alpha\rangle+\varepsilon|\alpha\beta\alpha\rangle+\varepsilon^*|\alpha\alpha\beta\rangle]\\ &\quad\mp\psi_{-1}^{(0)}(\chi)[|\beta\alpha\alpha\rangle+\varepsilon^*|\alpha\beta\alpha\rangle+\varepsilon|\alpha\alpha\beta\rangle]\}\end{aligned} \tag{10}$$

or

$$\begin{aligned}&\psi_v^{(a)}\psi_1^{(0)}(\chi)[|\beta\alpha\alpha\rangle+\varepsilon|\alpha\beta\alpha\rangle+\varepsilon^*|\alpha\alpha\beta\rangle]\\ &\quad-\psi_v^{(b)}\psi_{-1}^{(0)}(\chi)[|\beta\alpha\alpha\rangle+\varepsilon^*|\alpha\beta\alpha\rangle+\varepsilon|\alpha\alpha\beta\rangle],\end{aligned} \tag{11}$$

together with another similar expression with the labels a and b interchanged. We can simplify the description of molecular energy levels still further by using the near orthogonality of the states $\psi_v^{(a)}$ and $\psi_v^{(b)}$ and taking into account the fact that all the relevant matrix elements describing the time evolution of the system, which are off-diagonal with respect to the framework superscript, are vanishingly small. In other words, no spectroscopic information gets lost if the classification of the molecular energy levels is carried out with respect to the subgroup C_3 instead of C_{3v}.

III. QUANTUM COHERENCE AT LOW TEMPERATURES AND THE ONSET OF CLASSICAL REORIENTATION AT HIGH TEMPERATURES

Let us consider an ensemble of isolated methyl groups in thermal equilibrium with a heat bath characterized by a temperature T_L. As shown in the preceding section, the methyl group wave functions may be written as

$$\psi_{lIM}^{(\nu)}(\chi,\{\sigma_i\})=\psi_l^{(\nu)}(\chi)\psi_\sigma^{(\nu)*}(\{\sigma_i\}), \tag{12}$$

where $\nu=A$, E_a, and E_b, denoting IR's of the symmetry group C_3, has replaced the subscript $s=0$, ±1 introduced in (6). The spin functions $\psi_\sigma^{(\nu)}$ are identical, up to a normalization factor, to the spin functions appearing in (8), and are also given, for example, in Ref. 1. I is the total proton spin and M its z component. I takes on the values 1/2 and 3/2 and there is a bijection between I and the symmetry species ν, viz. $A\leftrightarrow3/2$, E_a and $E_b\leftrightarrow1/2$.

At low enough temperatures, only the lowest-lying torsional states with $l=0$ are populated. With increasing temperature, however, it soon becomes more convenient to choose, instead of the basis (12), a set of states $\{|\psi_i\rangle\}$ defined as

$$\langle\chi|\psi_1\rangle=(1/\sqrt{3})[H^{(0)}(\chi-2\pi/3)+H^{(0)}(\chi)+H^{(0)}(\chi+2\pi/3)]|\alpha\alpha\alpha\rangle, \tag{13a}$$

$$\langle\chi|\psi_2\rangle=(1/\sqrt{3})[H^{(0)}(\chi-2\pi/3)|\alpha\beta\alpha\rangle+H^{(0)}(\chi)|\alpha\alpha\beta\rangle+H^{(0)}(\chi+2\pi/3)|\beta\alpha\alpha\rangle]; \tag{13b}$$

the states $\langle\chi|\psi_3\rangle$ and $\langle\chi|\psi_4\rangle$ are obtained from (13b) by cyclic permutations of α's and β's, while $\langle\chi|\psi_i\rangle$, $i=5$–8, are obtained from (13) by replacing α's with β's and vice versa. The new basis is approximately orthonormal as long as the overlap between the harmonic oscillator functions $H^{(0)}(\chi-j2\pi/3)$, centered at different minima of the hindering potential, may be neglected. It is characteristic of the states $|\psi_i\rangle$ that they are orientationally localized to the extent as this is consistent with Pauli exclusion principle and the temperature range considered.

To discuss the phenomenon of quantum coherence as it applies, in our opinion, to the problem of methyl groups embedded in solid lattices, let us imagine that a methyl group undergoes a ''collision'' with the lattice after which it is found in one of the states $|\psi_i\rangle$. The density matrix immediately after the ''collision'' is thus given by the statistical mixture with respect to the states $|\psi_i\rangle$ as

$$\rho=\sum_{j=1}^{8} P_i(0)|\psi_i\rangle\langle\psi_i|, \tag{14}$$

where $P_i(0)=\delta_{ij}$, and $j=1,2,\ldots,8$. At some later time $t>0$, but before the next ''collision'' occurs, the time evolution of the density matrix $\rho(t)$ is given by

$$\rho(t)=\exp(-iHt/\hbar)\rho(0)\exp(iHt/\hbar), \tag{15}$$

with H representing the rotational Hamiltonian (including, in general, also the Zeeman term). The populations $P_i(t)\equiv\mathrm{Tr}\{\rho(t)|\psi_i|\rangle\langle\psi_i|\}$ of the states $|\psi_i\rangle$ at time t are

$$P_i(t)=\sum_j A_{ij}(t)P_j(0), \quad i=1,2,\ldots,8, \tag{16}$$

where the matrix A is symmetric and can be written as a direct sum $1\oplus A'\oplus A'\oplus 1$ with $A'_{11}=A'_{22}=A'_{33}\equiv a(t)$, and $A'_{12}=A'_{13}=A'_{23}\equiv b(t)$. Here,

$$a(t)=(1/9)(5+4\cos\omega_T^{(0)}t), \tag{17a}$$

$$b(t)=(2/9)(1-\cos\omega_T^{(0)}t), \tag{17b}$$

and $\omega_T^{(0)}\equiv[E(0EM)-E(0AM)]/\hbar$, is the tunneling frequency. Equations (16) and (17) represent the phenomenon of quantum coherence in the case of tunneling methyl groups which is analogous to the well known problem of a particle in the double-well potential.[19] While in the double-well problem one is dealing with coherent oscillations of the particle back and forth between the two potential minima, in the present case the corresponding motion takes place with respect to the states $|\psi_i\rangle$ as defined by (13). The label by which the states (13) can be distinguished is thus not the orientation of the methyl group but the location, with respect to the minima of the hindering potential, of the spin down state. This is a consequence of the Pauli exclusion principle which insures that there is no discrimination between the three oscillator states $H^{(0)}(\chi-j2\pi/3)$.

It is well known,[19] and it also follows directly from the uncertainty principle,[11] that the coherent oscillations discussed above are observable, in principle, only if the evolution of the system as described by (15) is left undisturbed over times of the order at least $1/\omega_T^{(0)}$. For barrier heights 10 meV$\leqslant V_3\leqslant$70 meV this time covers the range 4×10^{-9} sec$\leqslant 1/\omega_T^{(0)}\leqslant 3\times10^{-2}$ sec. Therefore, with increasing temperature the increased methyl-lattice interaction will tend to destroy quantum coherence. We can illustrate this by using a rapid sequence of ''collisionlike'' processes discussed above, analogous to the model considered previously, in a different context, by Simonius[20] and Harris *et al.*[21] We therefore assume that the methyl group is perturbed periodically at time intervals $\tau\ll 1/\omega_T^{(0)}$. During each time interval, the density matrix evolves according to (15), while each ''collision'' changes $\rho(N\tau)$, the density matrix immediately after the Nth collision, into a statistical mixture,

$$\rho(N\tau)=\sum_{j=1}^{8} P_i(N\tau)|\psi_i\rangle\langle\psi_i|. \tag{18}$$

Here

$$P_i(N\tau)=\sum_{j=1}^{8} (A^N(\tau))_{ij}P_j(0), \tag{19}$$

with the matrix A given by (16) and (17). Choosing the initial condition $P_i(0)=\delta_{ij}$ such that $P_3(0)=1$, taking into account $\omega_T^{(0)}\tau\ll1$ and writing $t=N\tau$, we obtain

$$\begin{pmatrix} P_2(t)\\ P_3(t)\\ P_4(t)\end{pmatrix}=\begin{pmatrix} 1/3-(1/3)\exp(-\tau\omega_T^{(0)2}t/3)\\ 1/3+(2/3)\exp(-\tau\omega_T^{(0)2}t/3)\\ 1/3-(1/3)\exp(-\tau\omega_T^{(0)2}t/3)\end{pmatrix}, \tag{20}$$

with the remaining $P_i(t)$'s equal to zero. This result for the probabilities $P_i(t)$ is formally identical to the classical hopping result[1] provided the hopping rate ν_3 around the symmetry axis of the methyl group is identified as $\nu_3=(2/9)\omega_T^{(0)2}\tau$. However, let us stress again that ''hopping'' is taking place among the states $|\psi_i\rangle$, while the classical hopping as visualized in Ref. 1 represents random jumps among the methyl orientations corresponding to the minima of the hindering potential.

To extend the above analysis to higher temperatures, we assume that the set (13), with the oscillator functions $H^{(0)}(\chi-j2\pi/3)$ replaced by some arbitrary functions $\Phi(\chi-j2\pi/3)$ peaked sharply at the minima of the hindering potential, continues to play the role of a suitable pointer basis.[2,3] We could imagine this behavior to be a consequence of continuous ''monitoring'' of the methyl motion by the lattice. To check whether this has any observational consequences distinct from the standard random jumps model we shall analyze the spin-lattice relaxation as caused by the intragroup dipole-dipole interaction H_D.

Assuming that the energy values corresponding to the states (13) may be approximated by the respective expectation values, i.e., $E_i \cong \langle \psi_i | H_R | \psi_i \rangle - M_i \hbar \omega_0$, where H_R is the rotational Hamiltonian, ω_0 the Zeeman frequency, and M_i the magnetic quantum number, we make use of the model of Punkkinen and Clough[22] in order to calculate the high-temperature spin-lattice relaxation time T_1. As shown in more detail in the Appendix, the result is

$$\begin{aligned} 1/T_1 = {} & (5/2)(9/16)(1-\cos^4\vartheta)[\omega_D^2 \tau_c/(1+\omega_0^2\tau_c^2)] \\ & + (9/16)(1+6\cos^2\vartheta + \cos^4\vartheta) \\ & \times [\omega_D^2 \tau_c/(1+4\omega_0^2\tau_c^2)], \end{aligned} \tag{21}$$

where ϑ is the angle between the direction of the external magnetic field and the symmetry axis of the methyl group, τ_c is the correlation time, and ω_D is defined in the Appendix. It is essential to note that in deriving this result one has to retain, in the dipolar matrix elements $\langle \psi_i | H_D | \psi_j \rangle$, only those terms which depend explicitly on the methyl rotation angle χ. This is required in order to be consistent with the interpretation of H_D as a random function of time.

Comparing (21) with the corresponding semiclassical result as given, for example, in Ref. 23, we see that the results are identical apart from an additional factor of 5/2 multiplying the first term of (21). This extra factor is a consequence of the constraint imposed on the rate equations (A4) by (20), requiring that the $M = \pm 1/2$ states are characterized by a single population number. This is correct as long as $\tau_c \ll T_1$. The implications of (21) for the analysis of experimental results will be discussed in the next section.

IV. CONCLUSIONS

It has been suggested[4,5] that methyl wave functions of correct permutational symmetry cannot be obtained unless the corresponding eigenvalue problem is formulated explicitly in terms of individual coordinates of the methyl protons. To illustrate this point the case was considered where three protons are constrained to move on a circle and the problem was analyzed in terms of Jacobi coordinates.[24] It is clear that physics does not depend on parametrization of the configuration space and, moreover, the use of Jacobi coordinates is not even a very judicious choice because the permutations of particle coordinates do not correspond, in general, to any simple transformations of Jacobi coordinates. What is crucial, in our opinion, is the question of the separability of the Hamiltonian. If the methyl Hamiltonian can be written as a sum of electronic, vibrational, and rotational parts, then the use of a rotating coordinate system (ξ, η, ζ) seems to be a natural choice. As we have shown, symmetrization of the resulting wave functions as required by Pauli principle can be carried out consistently also when single permutations are included.

In Sec. III the concept of quantum coherence, for the case of tunneling methyl groups, was formulated in a manner to resemble as closely as possible to the analogous problem of a particle tunneling in a double well potential. The results were then extended to the high temperature region by introducing a suitable ''pointer'' basis which appears to be appropriate for the description of the dynamics of the methyl groups interacting with the lattice. When this basis is incorporated into a modified Punkkinen-Clough model of spin-lattice relaxation, the result (21) for T_1, the spin-lattice relaxation time, is obtained. The powder averaged rate $\langle 1/T_1 \rangle$ as given by (A8) has a maximum at $\omega_0 \tau_c = 0.74$ and its value, expressed in units of ω_D^2/ω_0, is 0.96. This is to be compared with the corresponding semiclassical results[23] of 0.62 and 0.64, respectively. Assuming that the temperature dependence of the correlation time τ_c is given by the Arrhenius law, $\tau_c = \tau_0 \exp(E_a/kT)$, the maxima of $\langle 1/T_1 \rangle$ and the semiclassical expression occur at approximately the same temperature. For $\tau_0 \cong 10^{-12}$ sec and $E_a \cong 2$ kcal/mol the corresponding temperature difference is $\Delta T \cong 3$ K. Furthermore, the two models agree fairly well on the high-temperature side of the $\langle 1/T_1 \rangle$ maximum, i.e., for $\omega_0 \tau_c \ll 1$. In this range of temperatures (A8) yields $\langle 1/T_1 \rangle = 2.92 \omega_0 \tau_c$, while the semiclassical result[23] gives $2.25 \omega_0 \tau_c$. The discrepancy is somewhat larger on the low-temperature side ($\omega_0 \tau_c \gg 1$) where the corresponding results, expressed again in units of ω_D^2/ω_0, are $1.57/\omega_0 \tau_c$ and $0.90/\omega_0 \tau_c$, respectively. If, for example, $1/\langle 1/T_1 \rangle$ is plotted against the inverse temperature, we observe that, on the average, (A8) predicts slightly smaller values than those obtained from the result quoted in Ref. 23. This is illustrated in Fig. 1 for $\tau_0 = 10^{-12}$ sec and $E_a \cong 2$ kcal/mol.

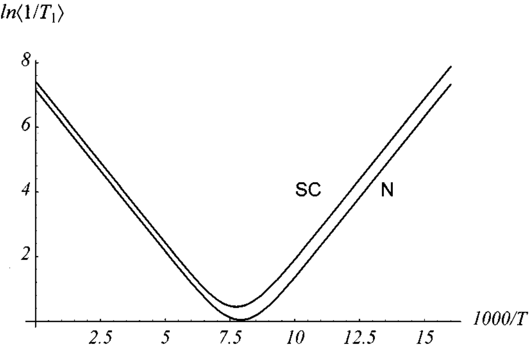

FIG. 1. Plot of $-\ln(1/\langle T_1 \rangle)$, where $1/\langle T_1 \rangle$ is expressed in units of ω_D^2/ω_0, versus inverse temperature. The parameters used in the graph are $\tau_0 = 10^{-12}$ sec and $E_a = 2$ kcal/mol. SC and N denote the semiclassical result and the result (A8), respectively.

To summarize, we propose the following scheme of methyl dynamics as it emerges from the above calculation. At the lowest temperatures, where the methyl spin-rotational states are well defined, the spin-lattice relaxation time can be calculated using the Punkkinen-Clough model[22] with the low-temperature tunneling frequency $\omega_T^{(0)}$. When the temperature is increased, and $\omega_T^{(0)} \tau_c \ll 1$, the symmetry adapted spin-rotational states (12) loose their validity as the proper stationary states, and should be replaced by a ''pointer basis'' set, such as (13) with $H^{(0)}(\chi - j2\pi/3)$ replaced by some reasonably localized pocket states $\Phi(\chi - j2\pi/3)$. The modified Punkkinen-Clough model, as described in the Appendix, could then be applied to calculate T_1. At still higher temperature when $\omega_c \tau_c \approx 1$, ω_c being the classical librational frequency, the ''collisions'' of the methyl group with the lattice are very frequent and it is usually assumed that the semiclassical model of Hilt *et al.*[23] is valid. In terms of the present work this is equivalent to saying that the density matrix (18) becomes effectively indistinguishable from the statistical mixture

$$\rho(t)=\Sigma_j\Sigma_{\{\sigma\}}P_{j,\{\sigma\}}(t)(|\Phi_j\rangle\langle\Phi_j|)(|\sigma_1\sigma_2\sigma_3\rangle\langle\sigma_3\sigma_2\sigma_1|), \tag{22}$$

where $\langle\chi|\Phi_j\rangle\equiv\Phi(\chi-j2\pi/3)$. The weight factors $P_{j,\{\sigma\}}(t)$ are taken to be of the form (20) with a rate of jumping ν_3 replacing $2\omega_T^{(0)2}\pi/9$.

In conclusion, we suggest that the experimental data on T_1 could possibly be explained using only the two versions of the Punkkinen-Clough model. Consequently, the assumption of classical hopping motion as embodied in (22) may not even be necessary.

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APPENDIX

We calculate the rate of nuclear Zeeman spin-lattice relaxation assuming that in the temperature range where $\omega_T^{(0)}\tau\ll 1$ holds, the appropriate basis to describe methyl dynamics is given by (13) modified to the extent that the functions $H^{(0)}(\chi-j2\pi/3)$ are replaced by some arbitrary pocket states $\Phi(\chi-j2\pi/3)$ peaked sharply at the minima of the hindering potential. To this end, we make use of the model, appropriately modified, used previously by Punkkinen and Clough[22] for the calculation of the relaxation rate in the tunneling regime. Denoting by ΔN_i the deviation of the population of the state $|\psi_i\rangle$ from the thermal equilibrium value, we can write the corresponding deviation of the magnetization, $\Delta M_z=M_z-M_0$, from its equilibrium value as

$$\Delta M_z=\gamma\hbar\{(3/2)(\Delta N_1-\Delta N_8)+1/2[(\Delta N_2+\Delta N_3+\Delta N_4) -(\Delta N_5+\Delta N_6+\Delta N_7)]\}, \tag{A1}$$

where γ is the proton gyromagnetic ratio. The assumption of spin temperature and ''particle'' number conservation yield, respectively, $\Delta N_1-\Delta N_8=\Delta N(+1/2)-\Delta N(-1/2)$, and $\Delta N_1+\Delta N_8=-[\Delta N(+1/2)+\Delta N(-1/2)]$, where

$$\Delta N(+1/2)\equiv\Delta N_2+\Delta N_3+\Delta N_4, \tag{A2}$$

$$\Delta N(-1/2)\equiv\Delta N_5+\Delta N_6+\Delta N_7. \tag{A3}$$

Equation (20) further suggests that $\Delta N_2=\Delta N_3=\Delta N_4$ and $\Delta N_5=\Delta N_6=\Delta N_7$. Using the above relations we can write

$$(d/dt)\begin{pmatrix}\Delta M_z/\gamma\hbar\\ \Delta N\end{pmatrix}=-\begin{pmatrix}k_{11} & k_{12}\\ k_{21} & k_{22}\end{pmatrix}\begin{pmatrix}\Delta M_z/\gamma\hbar\\ \Delta N\end{pmatrix}, \tag{A4}$$

and we have introduced

$$\Delta N\equiv\Delta N(+1/2)+\Delta N(-1/2). \tag{A5}$$

The rate coefficients k_{11}, k_{22}, k_{12}, and k_{21} are given in terms of the transition probabilities per unit time, $W_{i\leftrightarrow j}$, induced between the states $|\psi_i\rangle$ and $|\psi_j\rangle$ by the dipolar interaction H_D, as

$$k_{11}=(2/3)\sum_{i=2}^{4}\sum_{j=5}^{7}W_{i\leftrightarrow j}+(1/3)\sum_{i=2}^{4}(2W_{i\leftrightarrow 8}-W_{i\leftrightarrow 1}) +(1/3)\sum_{j=5}^{7}(2W_{1\leftrightarrow j}-W_{8\leftrightarrow j}), \tag{A6a}$$

$$k_{12}=(4/3)\left[\sum_{i=2}^{4}(W_{i\leftrightarrow 1}+W_{i\leftrightarrow g})-\sum_{j=5}^{7}(W_{1\leftrightarrow j}+W_{8\leftrightarrow j})\right], \tag{A6b}$$

$$k_{21}=(1/6)\left[\sum_{i=2}^{4}(2W_{i\leftrightarrow g}-W_{i\leftrightarrow 1})-\sum_{j=5}^{7}(2W_{1\leftrightarrow j}-W_{8\leftrightarrow j})\right], \tag{A6c}$$

$$k_{22}=(2/3)\left[\sum_{i=2}^{4}(W_{i\leftrightarrow 1}+W_{i\leftrightarrow 8})+\sum_{j=5}^{7}(W_{1\leftrightarrow j}+W_{8\leftrightarrow j})\right]. \tag{A6d}$$

Considering the intragroup dipolar interaction H_D as a random function of time, the transition probabilities $W_{i\leftrightarrow j}=W_{j\leftrightarrow i}$ are

$$W_{i\leftrightarrow j}=(1/\hbar^2)|\langle\psi_i|H_D|\psi_j\rangle|^2\{2\tau_c/(1+(M_i-M_j)^2\omega_0^2\tau_c^2)\}, \tag{A7}$$

ω_0 being the Zeeman frequency and τ_c the correlation time. Using the expression for H_D as given in Ref. 25, the following nonvanishing results for $W_{i\leftrightarrow j}$ are obtained:

$$\begin{aligned}W_{1\leftrightarrow 5}=W_{1\leftrightarrow 6}=W_{8\leftrightarrow 3}=W_{8\leftrightarrow 2}&\\ =(9/256)[(1+\cos^2\vartheta)^2+12\cos^2\vartheta]&\\ \times\{2\omega_D^2\tau_c/(1+4\omega_0^2\tau_c^2)\},&\end{aligned}$$

$$W_{1\leftrightarrow 7}=W_{8\leftrightarrow 4}=(9/64)(1+\cos^2\vartheta)^2\{2\omega_D^2\tau_c/(1+4\omega_0^2\tau_c^2)\},$$

$$\begin{aligned}W_{1\leftrightarrow 2}=W_{1\leftrightarrow 3}=W_{8\leftrightarrow 5}=W_{8\leftrightarrow 6}&\\ =(9/252)\sin^2\vartheta(3+\cos^2\vartheta)\{2\omega_D^2\tau_c/(1+\omega_0^2\tau_c^2)\},&\end{aligned}$$

$$W_{1\leftrightarrow 4}=W_{8\leftrightarrow 7}=(9/64)\sin^2\vartheta\cos^2\vartheta\{2\omega_D^2\tau_c/(1+\omega_0^2\tau_c^2)\},$$

$$W_{2\leftrightarrow 6}=W_{3\leftrightarrow 5}=(27/64)\sin^2\vartheta\{2\omega_D^2\tau_c/(1+\omega_0^2\tau_c^2)\},$$

$$\begin{aligned}W_{2\leftrightarrow 7}=W_{3\leftrightarrow 7}=W_{4\leftrightarrow 5}=W_{4\leftrightarrow 6}&\\ =(27/256)(3\sin^2\vartheta\cos^2\vartheta+\sin^2\vartheta)&\\ \times\{2\omega_D^2\tau_c/(1+\omega_0^2\tau_c^2)\}.&\end{aligned}$$

$\omega_D=\gamma^2\hbar/R_0^3$, where $R_0\approx 1.78$ Å is the proton-proton distance and ϑ is the angle between the direction of external magnetic field and the symmetry axis of the methyl group.

Inserting the above results for $W_{i\leftrightarrow j}$ in (A6) yields $k_{12}=k_{21}=0$, and the spin-lattice relaxation time T_1 is foundto be equal to $1/k_{11}$, and is given by (21). The corresponding powder average $\langle 1/T_1\rangle$ is

$$\langle 1/T_1\rangle=(9/8)\{\omega_D^2\tau_c/(1+\omega_0^2\tau_c^2)\} +(9/5)[\omega_D^2\tau_c/(1+4\omega_0^2\tau_c^2)]. \tag{A8}$$

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