The exit energy is then

$$[(1-h^2)^{1/2}(1+\eta^2)-2\eta^2](1-\eta^2-h^2)(1-\eta^2)^{-1/2}.$$

Finally, knowing the surface tension of a domain boundary,[3] we can write the expression for the period a:

$$a=\left\{\frac{(1-\eta^2)^{1/2}[(1-h^2)^{1/2}-(\pi/2-\theta_0)h]}{[(1-h^2)^{1/2}(1+\eta^2)-2\eta^2][1-\eta^2-h^2]}\right\}^{1/2}.$$

For $H_\parallel = 0$, the variation of the period with the field was obtained earlier.[5] For $H_\perp = 0$,

$$a=[(1-h^2)^{1/2}-(\pi/2-\theta_0)h]^{1/2}(1-h^2)^{-1/4},$$

this differs with respect to the exponent of the second expression in parentheses from the case $\beta \gg 4\pi$, where the exponent is $-\frac{1}{2}$. In particular, for $h \to 1$ (i.e. $H_\parallel \to \beta M$) the period approaches the finite value $3^{-1/2}$.

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Spin-lattice relaxation produced in identical nuclei by rotational tunneling

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Spin-lattice relaxation of symmetrical systems of identical nuclei is considered. The exclusion principle causes the relaxation coefficients to be expressed in terms of partial time correlation functions (TCF), in which the averaging is over states belonging to only one irreducible representation of the symmetry group of the system. The relaxation coefficients and the irreducible TCF are calculated for interacting groups of three nuclei with spin 1/2, which tunnel in a periodic potential in a solid. It is assumed that the rotation interaction with the phonon reservoir is weak and that the rotation is essentially a quantum effect—the distance between the torsion multiplets are large. An analysis of the temperature dependence of the spin-lattice relaxation time (true as well as effective) has demonstrated the possibility of appearance of several minima with different depths and different dependences on the Larmor frequency.

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1. INTRODUCTION

In gases and solids at low temperature, the rotational motion responsible for the spin relaxation has essentially a quantum character, so that the exclusion principle must be taken into account in the theory of spin relaxation of symmetrical nuclear systems. A relaxation theory for the region of fast motion, without account taken of the exclusion principle, has by now been well developed.[1, 2] In this theory the relaxation coefficients are expressed in terms of the time correlation functions (TCF) of the molecular motion. No such expressions have been obtained as yet in the theory of symmetrical identical nuclei. The existing analyses of relaxation in gaseous[3] and solid[4] methane and in solids containing methyl groups[5-7] dealt with the transition probabilities in the unified subsystem made up of the spin and rotational degrees of freedom under the influence of a nonsecular dipole dipole (DD) interaction and of the interaction V_{rp} of the rotation with the medium. In view of the complexity of this approach, it was necessary to introduce simplifying phenomenological assumptions. Another semi-phenomenological approach was used by Clough[8] for the relaxation of methyl groups in solids; he introduced in the equation of motion for the spin density matrix exchange operators that describe the classical hopping of the group and the quantum tunneling between equilibrium positions.

The analysis of the transitions in the unified subsystem can be faulted also for its insufficient rigor. In fact, the relaxation transitions are due to interaction with a reservoir that has a quasicontinuous spectrum, so that transitions induced by the intragroup DD interaction cannot be regarded as relaxation transitions. In a consistent approach the DD interaction would be included in the principal Hamiltonian and the analysis would be based on the total density matrix of the unified subsystem.

We propose in this paper a two-step approach. We

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assume first, just as in the theories that take no account of the exclusion principle, that all the non-spin degrees of freedom form a common reservoir—the lattice—and that the perturbation is taken to be the fluctuating part of the DD interaction. The basis for this approach is the slowness of the spin-lattice relaxation compared with the broadening transitions between the rotational levels. During this stage the interaction V_{rp} is bounded only from below. During the second stage, in the calculation of the TCF, the perturbation is now taken to be the Hamiltonian V_{rp}. The general relations are applied to a symmetrical system of three nuclei with $S = 1/2$, the rotation of which about a threefold symmetry axis is hindered by a triple potential (the methyl and ammonia groups in solids). The choice of this system is dictated both by its simplicity and by the fact that it has been relatively well studied (see, e.g.,[5-15]).

2. EFFECTS OF THE IDENTITY OF THE NUCLEI IN THE PROBABILITIES OF THE RELAXATION TRANSITIONS

We consider a system having a Hamiltonian

$$H=\hbar(E+G+F), \tag{2.1}$$

where $\hbar E$, $\hbar F$, and

$$\hbar G=\hbar\sum_{q}\mathscr{L}_q T_q \tag{2.2}$$

are respectively the Hamiltonians of the spin systems, of the lattice, and of the spin-lattice interaction ($\mathscr{L}_q$ and T_q are operators acting on the functions of the lattice and of the spin system).

For symmetrical systems of identical nuclei, in which the molecular motion effects a symmetry transformation, it is necessary to take the exclusion principle into account in the calculation of the relaxation-transition probabilities. When (anti)symmetrical complete wave functions are constructed, it is necessary to take into account the Longuet-Higgins rule,[16] according to which one should consider "realizable" symmetry transformations that do not call for surmounting impenetrable barriers. We do not therefore incur a great loss of generality greatly but abbreviate greatly the resultant relations if we consider cyclic subgroups of a point group. We introduce the index σ, which designates an irreducible representation of a symmetry group, and denote by $|\sigma m\rangle$ a spin wave function that is transformed under the symmetry transformation in accord with the representation σ. The corresponding coordinate function—the eigenfunction of the Hamiltonian F—will be designated $|\sigma f\rangle$. The known expression for the probability of the transition between the states of a spin system[1, 2] can be represented in the form

$$\begin{aligned}W_{\sigma m\to\sigma' m'}&=\int_{-\infty}^{\infty}dt\exp\{-i\omega_{\sigma m\sigma' m'}t\}\\&\times\sum_{ff'}\rho^{\sigma}_{fcq}\langle\sigma m|\langle\sigma f|G|\sigma' f'\rangle|\sigma' m')\\&\times\langle\sigma' m'|\langle\sigma' f'|e^{iFt}Ge^{-iFt}|\sigma f\rangle|\sigma m\rangle\\&=\int_{-\infty}^{\infty}dt\exp\{-i\omega_{\sigma m\sigma' m'}t\}\sum_{qq'}\langle\sigma m|T_q|\sigma' m'\rangle\\&\times\langle\sigma' m'|T_{q'}|\sigma m\rangle\langle\mathscr{L}_q(0)\mathscr{L}_{q'}(t)\rangle^{\sigma\sigma'},\end{aligned}\tag{2.3}$$

where

$$\rho^{\sigma}_{feq}=\exp(-\beta E_{f\sigma})\Big/\sum_{f}\exp(-\beta E_{f\sigma})$$

is the matrix element of the conditional equilibrium statistical operator ρ^{σ}_{eq} with specified σ,

$$\begin{aligned}\langle\mathscr{L}_q(0)\mathscr{L}_{q'}(t)\rangle^{\sigma\sigma'}&=\sum_{ff'}\rho^{\sigma}_{feq}\\&\times\langle\sigma f|\mathscr{L}_q(0)|\sigma' j'\rangle\langle\sigma' f'|\mathscr{L}_{q'}(t)|\sigma f\rangle\end{aligned}\tag{2.4}$$

is the "irreducible" time correlation function, in which the summation extends only to states belonging to specified irreducible representations. Thus, the effect of the exclusion principle on the probability of the relaxation transitions reduces to a dependence of the irreducible TCF on the indices σ and and σ'. For the sake of brevity, we assume the temperature to be high enough to make

$$\sum_{f}\exp(-\beta E_{f\sigma})$$

independent of σ. The definition (2.4) leads to symmetry properties of the irreducible ICF analogous to the properties of the complete ICF:

$$\langle\mathscr{L}_q(0)\mathscr{L}_{q'}(t)\rangle^{\sigma\sigma'}=\langle\mathscr{L}_q(-t)\mathscr{L}_{q'}(0)\rangle^{\sigma\sigma'}, \tag{2.5}$$

$$\langle\mathscr{L}_q(0)\mathscr{L}_{q'}(t)\rangle^{\sigma\sigma'}=\langle\mathscr{L}_{q'}(0)\mathscr{L}_q(-t+i\hbar\beta)\rangle^{\sigma'\sigma}. \tag{2.6}$$

To calculate the irreducible TCF it is convenient to use the chain of equations

$$\begin{aligned}\langle\mathscr{L}_q(0)\mathscr{L}_{q'}(t)\rangle^{\sigma\sigma'}&=\sum_{ff'}\langle\sigma f|\rho_{eq}{}^{\sigma}\mathscr{L}_q|\sigma' f'\rangle\\&\times\langle\sigma' f'|e^{iFt}\mathscr{L}_{q'}e^{-iFt}|\sigma f\rangle\\&=\sum_{ff'}\langle\sigma f|e^{-iFt}\rho_{eq}{}^{\sigma}\mathscr{L}_q e^{iFt}|\sigma' f'\rangle\\&\times\langle\sigma' f'|\mathscr{L}_{q'}|\sigma f\rangle=\langle\rho(t)\mathscr{L}_{q'}\rangle^{\sigma\sigma'}.\end{aligned}\tag{2.7}$$

It follows therefore that the irreducible TCF can be expressed in terms of the solution of the equation for the lattice density matrix with the initial condition

$$\rho(0)=\rho_{eq}{}^{\sigma}\mathscr{L}_q. \tag{2.8}$$

It is particularly convenient to use relations (2.7) and (2.8) in the case of weak interaction of the rotational degrees of freedom with the medium, for in this case we know the kinetic equation for the rotational density matrix, which is obtained from the lattice density matrix by averaging over the variables of the medium. If we start, in the very same approximation, from the kinetic equation for the density matrix of the unified spin-rotational subsystem and, as noted in the introduction, do not regard from the very outset the interaction G as a perturbation, then if the rotational relaxation is fact compared with the spin-lattice relaxation we again obtain the relations given above.

3. RELAXATION EQUATIONS FOR INTERACTING SYMMETRICAL THREE- SPIN SYSTEMS

Consider a solid containing N groups in which three nuclei with spin 1/2 are located at the vertices of an equilateral triangle. The nuclei are coupled by DD interaction both within the group and between the groups. We neglect other types of interaction. The groups rotate about a threefold symmetry axis. An example of such a system is a molecular crystal in which all the protons belong to the methyl groups.

The spin Hamiltonian E [see (2.1)] consists of the Zeeman Hamiltonian

$$E_z=-\omega_0 I_z, \tag{3.1}$$

where ω_0 is the Larmor frequency and I_z is the component of the summary spin directed along the strong constant magnetic field, while $E_{dd}=E_{dd}^{(i)}+E_{dd}^{(e)}$ is that part of the secular DD interaction which is invariant to rotation and which can be written in the form (cf., e.g.,[5])

$$E_{dd}^{(i)}=-\sqrt{\frac{3}{2}}k\sum_{a=1}^{N}P_2(\cos\beta_a)T_{20}(0,a), \tag{3.2}$$

$$E_{dd}^{(e)}=\sqrt{\frac{3}{2}}k\sum_{a}\sum_{b\neq a}\frac{r^3}{R_{ab}^3}P_2(\cos\theta_{ab})T_{20}(0,a;0,b). \tag{3.3}$$

We have introduced here the notation: $k=\hbar\gamma^2/r^3$ (γ is the gyromagnetic ratio of the nuclei and r is the distance between them in the group), β_a is the angle between the rotation axis of the a-th group and the constant magnetic field, θ_{ab} is the angle that the line joining the centers of the a-th and b-th groups makes with the magnetic field; R_{ab} is the distance between the centers of the groups; $P_L(x)$ is a Legendre polynomial of rank L;

$$\begin{gathered}T_{Lm}(\lambda,a)=T_{Lm}(12)+\varepsilon^{\lambda}T_{Lm}(31)+\varepsilon^{-\lambda}T_{Lm}(23),\\ \varepsilon=\exp\left(\frac{2\pi i}{3}\right),\quad T_{Lm}(jk)=\sum_{\mu\nu}C_{1\mu1\nu}^{Lm}I_{j\mu}I_{k\nu},\end{gathered} \tag{3.4}$$

$T_{Lm}(jk)$ is an irreducible spherical tensor operator constructed on cyclic components of the spins j and k belonging to the a-th group ($C_{j\mu j'\nu}^{Lm}$ is a Clebsch-Gordan coefficient):

$$\begin{gathered}T_{Lm}(\lambda,a;\delta,b)=\sum_{\mu\nu}C_{1\mu1\nu}^{Lm}I_{\mu}(\lambda,a)I_{\nu}(\delta,b),\\ I_{\mu}(\lambda,a)=I_{1\mu}+\varepsilon^{-\lambda}I_{2\mu}+\varepsilon^{\lambda}I_{3\mu}.\end{gathered} \tag{3.5}$$

We note that the operators (3.4) and (3.5) transform in accord with the $A(\lambda=0)$ and $E(\lambda=\pm 1)$ representations of the C_3 group upon cyclic permutation of the nuclei.

The spin-lattice interaction Hamiltonian is that part of the DD interaction which fluctuates because of the rotation, and consists of intragroup ($G^{(i)}$) and intergroup ($G^{(e)}$) contributions. The first contribution is given by

$$G^{(i)}=\frac{3}{4}k\sum_{d}\sum_{m}\sum_{\lambda=1,-1}(-1)^m d_{m,2\lambda}^{2}(\beta_a)e^{2i\lambda\varphi_a}T_{2-m}(\lambda,a), \tag{3.6}$$

where $d_{mn}^{j}(\beta_a)$ is a factor in the finite-rotation matrix and depends on the second Euler angle (see, e.g.,[17]), and φ_a is the angle of rotation of the group, for example the azimuthal angle of nucleus 1 in the coordinate frame in which the rotation axis coincides with the polar axis. We expand the fluctuating part of the intergroup DD interaction in powers of r/R_{ab} and confine ourselves to the first nonvanishing term. In the series expansion of the spherical harmonics we can use the results of[18] and obtain

$$G^{(e)}=2k\sum_{a}\sum_{b\neq a}\sum_{m}\sum_{\lambda=1,-1}(-1)^m\mathscr{L}_{\lambda}^{(m)}(a,b)e^{-i\lambda\varphi_a}T_{2-m}(\lambda,a;0,b), \tag{3.7}$$

where

$$\mathscr{L}_{\lambda}^{(m)}(a,b)=\lambda\sqrt{3\pi}\left(\frac{r}{R_{ab}}\right)^4\sum_{\mu}C_{3m-\mu1\mu}^{2m}Y_{3m-\mu}(\theta_{ab},\varphi_{ab})d_{\mu-\lambda}^{1}(\beta_a); \tag{3.8}$$

$Y_{Lm}(\theta,\varphi)$ is a spherical function. We assume that the Hamiltonian of the lattice is of the form

$$F=\sum_{a}[H_r(a)+V_{rp}(a)]+H_p, \tag{3.9}$$

where H_r, H_p, and V_{rp} are respectively the Hamiltonians of the a-th uniaxial rotator, phonon reservoir, and their interaction.

When the rotation is considered, it suffices to classify the wave functions in accord with the representations of the group C_3. The index σ (see the preceding section then takes on the values 0 (A representation) and ±1 (E representation). The eight spin states of the a-th group will be designated $|\sigma_a m_a\rangle$, where m_a is the magnetic quantum number. In a cyclic (123) permutation this function is multipled by ϵ^{σ_a}. Since the cyclic permutation is the product of two pairwise permutations, the coordinate wave functions should be multiplied by ϵ^{σ_a} upon the cyclic permutation (132). To describe the wave functions of the entire system we introduce the vector $\sigma=\{\sigma_1,\dots,\sigma_a,\dots,\sigma_N\}$. The eigenfunctions of the Hamiltonians will be designated $|\sigma\{m\}\rangle$, where $\{m\}$ is the aggregate of the remaining quantum numbers of the spin system. In particular, for noninteracting groups we have $\{m\}=m_1,\dots,m_2,\dots,m_N\equiv\mathrm{m}$.

The spin-lattice relaxation in a solid is much slower than the processes of establishment of equilibrium within a spin system, such as spin-spin relaxation and spin diffusion, and reduces therefore to transitions between spin states. The same slowness of relaxation makes it possible to describe it by a system in which the number of equations is much less than the 8^N states. To find the equations for the spin-lattice relaxation it is convenient to expand the diagonal part of the spin statistical operator in the total set of operators Q_k, which are diagonal in the basis of the eigenfunctions E[19]:

$$\rho_s=\sum_{k}u_kQ_k, \tag{3.10}$$

where the expansion coefficients u_k are macroscopic observables—the modes of the spin polarization. From the Pauli control equation follows a system of relaxation equations

$$\frac{du_j}{dt}=-\sum_{k}R_{jk}u_k. \tag{3.11}$$

We normalize the operators Q_k by the conditions

$$\sum_{\sigma,\mathrm{m}}\langle\sigma\mathrm{m}|Q_jQ_k|\sigma\mathrm{m}\rangle=8^N\delta_{jk}. \tag{3.12}$$

If we use for the transition probabilities the relations (2.3) in which $|\sigma m\rangle$ is replaced by $|\sigma,\{m\}\rangle$ and assume that the integrand has no poles on the imaginary axis in the interval $\pm i\hbar\beta$, then we obtain for the relaxation coefficients

$$R_{jk}=\frac{1}{2}\int_{-\infty}^{\infty}dt\sum_{qq'}\sum_{\sigma\sigma'}\frac{1}{8^N}\sum_{\{m\}\{m'\}}\langle\sigma,\{m\}|[T_q,Q_j]|\sigma',\{m'\}\rangle$$
$$\times\langle\sigma',\{m'\}|[Q_k,e^{iEt}T_{q'}e^{-iEt}]|\sigma,\{m\}\rangle\langle\mathscr{L}_q(0)\mathscr{L}_{q'}(t)\rangle^{\sigma\sigma'}. \qquad (3.13)$$

Of course, Eqs. (3.11) and (3.13) can be obtained in more rigorous fashion directly from first principles, by the known methods of statistical thermodynamics (see, e.g.,[20-22]).

Emid and Wind,[15] by analyzing the symmetry-limited spin diffusion[12] between methyl groups, reached the conclusion that the operator set should consist of four operator groups. Under the normalization (3.12), these operators are [cf. (3.1)]

$$Q_1=\frac{2}{(3N)^{1/2}}I_z,\qquad Q_2=c_2E_{dd}, \qquad (3.14)$$

where the normalization factor is

$$c_2=\frac{4}{3k}\left\{\frac{1}{2}\sum_a[P_2(\cos\beta_a)]^2+3\sum_a\sum_{b\neq a}\left(\frac{r}{R_{ab}}\right)^6[P_2(\cos\theta_{ab})]^2\right\}^{-1/2}, \qquad (3.15)$$

N operators

$$Q_{3a}=\frac{3}{2}-\frac{2}{3}[I_0(0,a)]^2=\frac{4}{3^{1/2}}T_{00}(0,a), \qquad (3.16)$$

and N operators

$$Q_{4a}=\frac{8i}{3^{1/2}}\sum_\mu(-1)^\mu[T_{1\mu}(32)I_{1-\mu}+T_{1\mu}(21)I_{3-\mu}+T_{1\mu}(13)I_{2-\mu}] \qquad (3.17)$$

[see the definitions (3.3)–(3.15)].

Thus, the system (3.11) has formally a microscopically large dimensionality. In fact, for a single crystal the number of equations will be small, because groups having identical angles and identically arranged neighboring groups will have identical relaxation coefficients, and Eqs. (3.11) will contain their sums. It is this circumstance that produces the ensemble needed for the application of statistical methods. For polycrystalline and amorphous bodies, the dimensionality of the system of equations is much larger, but in experiment one always measures a certain initial section of the relaxation curve, and this makes it possible to limit the set of relaxation coefficients. Consider, for example, the spin-lattice relaxation in a strong static field following an inverting 180-degree pulse. The detailed-balancing conditions allow us to write the system (3.11) in the form

$$\frac{d\Delta u_j}{dt}=-\sum_k R_{jk}\Delta u_k, \qquad (3.18)$$

where Δu_k is the difference between u_k and its equilibrium value $u_k^{(0)}$. Since $u_2^{(0)}\ll u_1^{(0)}$ and the remaining u_k are not sensitive to the momentum, only $\Delta u_1^{(0)}=-2u_1^{(0)}$ differs from zero. From this and from (3.18) we have for nonequilibrium magnetization the expansion

$$\ln\frac{\Delta M_z(t)}{\Delta M_z(0)}=-R_{11}t+\frac{t^2}{2}\sum_{k\neq1}R_{1k}^2+\ldots, \qquad (3.19)$$

where the symmetry of the relaxation coefficients is taken into account. The expansion (3.19) converges rapidly enough if all the R_{ik} are of the same order. If, however, some diagonal coefficient is much larger than the others, this means rapid relaxation of the corresponding spin-polarization mode, which should therefore be excluded from the system (3.18). In accord with (3.19), we shall define as the true relaxation time $T_1=R_{11}^{-1}$, and the effective relaxation time can be defined, for example, as $t_0/\ln 2$ (see, e.g.,(9)), where t_0 is the time of passage of the magnetization zero after a 180° pulse. It follows from (3.19) that

$$T_{1\mathrm{eff}}=T_1\left[1+\frac{\ln 2}{2}T_1^2\sum_{k\neq1}R_{1k}^2\right]. \qquad (3.20)$$

It is well known that formulas such as (2.3) for the transition probabilities can be used to calculate the spin-lattice relaxation under the condition $T_1\gg\tau_c$, where τ_c is the characteristic damping time of the TCF that determine T_1 (see, e.g.,[2]). We supplement this fast-motion condition by the inequality $(\langle E_{dd}^{(e)2}\rangle)^{1/2}\tau_c\ll1$. We can then replace the evolution operator $\exp(iEt)$ in (3.13) by $\exp(iE_z t)$ and then calculate the sums over $\{m\}$ and $\{m'\}$ in the basis $|\sigma m\rangle$.

In accord with the Hamiltonian (3.9) we postulate independence of the rotations of the different groups. Under this assumption the calculation of the relaxation coefficients from relations (3.6), (3.7), and (3.13) for the operators (3.14)–(3.17) that enter in the expansion (3.19) has shown that they are expressed in terms of the Fourier transforms of the irreducible ICF

$$K_M^{\sigma\sigma'}(t)=\langle\exp[-iM\varphi(0)]\exp[iM\varphi(t)]\rangle^{\sigma\sigma'}\ \mathrm{c}\ M=\pm1,\ \pm2. \qquad (3.21)$$

Since the E states are complex conjugate, $|\sigma f\rangle^*=|-\sigma f\rangle$, we have in addition to the symmetry properties (2.5) and (2.6) the relations

$$K_M^{\sigma\sigma'}(t)=K_{-M}^{-\sigma,-\sigma'}(t), \qquad (3.22)$$
$$K_M^{\sigma\sigma'*}(t)=K_M^{\sigma\sigma'}(-t). \qquad (3.23)$$

From the symmetry properties (2.5), (2.6), (3.22), and (3.23) it follows that

$$\int_{-\infty}^{\infty}dt\exp(im\omega_0t)K_M^{\sigma\sigma'}(t)$$
$$=\exp(-\hbar\beta m\omega_0)\int_{-\infty}^{\infty}dt\exp(im\omega_0t)K_{-M}^{\sigma'\sigma*}(t). \qquad (3.24)$$

Eliminating the region of extremely low temperatures, where the conditions of fast motions are apparently no longer satisfied, we can put in (3.24) $\exp(-\hbar\beta m\omega_0)=1$. Relations (3.22)–(3.24) have made it possible to express all the considered relaxation coefficients in terms of the spectral densities

$$J_\pm^{(M)}(\omega)=\mp\mathrm{Re}[\Phi_M^{01}(\pm\omega)\pm\Phi_M^{01}(\mp\omega)], \qquad (3.25)$$
$$J^{(M)}(\omega)=\mathrm{Re}[\Phi_M^{1,-1}(\omega)+\Phi_M^{1,-1}(-\omega)], \qquad (3.26)$$

where

$$\Phi_M^{\sigma\sigma'}(\omega)=\int_0^{\infty}dt\,e^{i\omega t}K_M^{\sigma\sigma'}(t), \qquad (3.27)$$

in the following manner:

$$R_{11}^{(1)}=\frac{9k^2}{32N}\sum_a[X_aJ_+^{(2)}(\omega_0)+Y_aJ_+^{(2)}(2\omega_0)], \qquad (3.28)$$

$$R_{12}^{(1)}=\frac{3^4k^3}{2^9(3N)^{1/2}}c_2\sum_a d_{00}{}^2(\beta_a)[-X_aJ_-^{(2)}(\omega_0)+Y_aJ_-^{(2)}(2\omega_0)], \tag{3.29}$$

$$R_{13a}^{(1)}=\frac{3^{5/2}k^2}{64N^{1/2}}[2X_aJ_-^{(2)}(\omega_0)+Y_aJ_-^{(2)}(2\omega_0)], \tag{3.30}$$

$$R_{14a}^{(1)}=\frac{3^{5/2}k^2}{16(2N)^{1/2}}\cos\beta_a[\sin^2\beta_aJ_+^{(2)}(\omega_0)+(1+\cos^2\beta_a)J_+^{(2)}(2\omega_0)]; \tag{3.31}$$

we have introduced here the notation $X_\alpha=1-\cos^4\beta_\alpha$, $Y_\alpha=1+6\cos^2\beta_\alpha+\cos^4\beta_\alpha$. If we assume that $N=1$ and

$$K_2^{01}(t)=d_t^2\exp(i\omega_tt-|t|/\tau_c), \tag{3.32}$$

where d_t^2 is the "relaxation effectiveness factor" and ω_t is the "observed tunneling frequency",[15] then relations (3.8)–(3.31) coincide with the corresponding results of Emid and Wind[15] apart from a difference in the renormalization.

The intergroup contribution to the spin-lattice relaxation

$$R_{11}^{(e)}=k^2\Big\{\frac{1}{N}\sum_a\sum_{b\neq a}[|\mathscr{L}_{-1}^{(1)}(a,b)|^2+|\mathscr{L}_1^{(1)}(a,b)|^2][2J_+^{(1)}(\omega_0)+J^{(1)}(\omega_0)]$$
$$+\frac{4}{N}\sum_a\sum_{b\neq a}[|\mathscr{L}_{-1}^{(2)}(a,b)|^2+|\mathscr{L}_1^{(2)}(a,b)|^2][2J_+^{(1)}(2\omega_0)+J^{(1)}(2\omega_0)]\Big\} \tag{3.33}$$

is according to (3.8) of the order of $(r/R_{ab})^8$. Calculations have shown that the intergroup contribution to R_{12}, R_{13a}, and R_{14a} is of the same order.

Within the framework of his semiphenomenological apporach, Clough[8] considered intergroup interactions, but did not carry out his calculations to conclusion, so that it is difficult to compare his result with (3.33).

For reasons that will be made clear in the next section, we shall not consider the influence of the intergroup interactions on the parameter of the non-exponential character of the relaxation

$$n=\frac{\ln 2}{2}T^2\sum_{k\neq 1}R^2 \tag{3.34}$$

[see (3.20)].

Emid and Wind[15] did not take into account the intergroup interaction in their analysis, yet this interaction can give rise to correlation between spin states of neighboring groups. We should therefore have to add to the operators (3.15)–(3.17) the products $Q_{3a}Q_{3b}$, $Q_{4a}Q_{4b}$, etc., which commute, just as the operators (3.15)–(3.17), with the spin Hamiltonian E.

Most experiments were performed on polycrystals, for which all the rotation-axis directions are equally probable. In this case summation over the groups is equivalent to averaging over β_a. The averaging results will be marked with a superior bar:

$$\bar{R}_{11}=\frac{1}{T_1}=\frac{9k^2}{40}[J_+^{(2)}(\omega_0)+4J_+^{(2)}(2\omega_0)]$$
$$+\frac{k^2}{2}\sum_{b\neq a}\Big(\frac{r}{R_{ab}}\Big)^8\Big\{\Big[1-\frac{2}{35}P_2(\cos\psi_{ab})\Big][2J_+^{(1)}(\omega_0)+J^{(1)}(\omega_0)]$$
$$+\Big[4-\frac{667}{1470}P_2(\cos\psi_{ab})\Big][2J_+^{(1)}(2\omega_0)+J^{(1)}(2\omega_0)]\Big\}, \tag{3.35}$$

where ψ_{ab} is the angle between the rotation axis of the a-th group and the direction joining the centers of the groups a and b.

The quadratic term in the expansion (3.19) for a polycrystal can be approximately written in the form

$$\sum_{k\neq 1}R_{1k}{}^2=k^4\{0.036[J_+^{(2)}(\omega_0)]^2+0.181J_+^{(2)}(\omega_0)J_+^{(2)}(2\omega_0)+0.416[J_+^{(2)}(2\omega_0)]^2$$
$$+0.172[J_-^{(2)}(\omega_0)]^2+0.514J_-{}^2(\omega_0)J_-^{(2)}(2\omega_0)+0.981[J_-^{(2)}(2\omega_0)]\}. \tag{3.36}$$

4. IRREDUCIBLE TIME CORRELATION FUNCTION OF ONE-DIMENSIONAL ROTATION IN A PERIODIC POTENTIAL

To calculate the irreducible TCF (3.21) we assume that the Hamiltonian of the operator [see (3.9)] is given by

$$\hbar H_r=\frac{\hbar^2p^2}{2I}+V(\varphi),\quad p=-i\frac{\partial}{\partial\varphi},\quad V(\varphi)=V\Big(\varphi+\frac{2\pi}{3}\Big), \tag{4.1}$$

where I is the moment of inertia. We assume that the retarding potential is close to sinusoidal in the sense that it has minima only at $\varphi=2k\pi/3$ and maxima only at $\varphi=(2k+1)\pi3$. The eigenfunctions of the Hamiltonians will be designated $|\sigma v\rangle$, where v is the torsion quantum number. The nondegenerate level $|0v\rangle$ and the doubly degenerate level $|\pm 1v\rangle$ form a tunnel multiplet with a splitting

$$\Delta_v=E_{1v}-E_{0v}=(-1)^v|\Delta_v|. \tag{4.2}$$

Assume that the barrier $V_0=V(\pi/3)-V(0)$ is high enough, so that the oscillator approximation is valid for the lower subbarrier levels

$$|\Delta_v|\ll E_{0\,v+1}-E_{0v}\approx E_{1\,v+1}-E_{1v}=\hbar\Omega\sim\hbar(V_0/I)^{1/2}. \tag{4.3}$$

We assume that the rotator interacts weakly with the phonon reservoir (PR), so that the inequality $\mu\tau_p\ll 1$ is satisfied, where μ is the characteristic interaction frequency and τ_p is the PR correlation time. In accord with the statements made in Sec. 2, when the TCF (3.21) are calculated the density matrix in relations (2.7) and (2.8) must be determined in the basis of the eigenfunctions $|\sigma v\rangle$ of the Hamiltonian (4.1). The kinetic equation for the density matrix (see, e.g.,[22,23]) for the unilateral Fourier transform

$$\tilde\rho(\omega)=\int_0^\infty dt\exp(i\omega t)\rho(t)$$

yields

$$(-i\omega+i\omega_{v_1v_2}^{\sigma_1\sigma_2})\tilde\rho_{v_1v_2}^{\sigma_1\sigma_2}(\omega)=\rho_{v_1v_2}^{\sigma_1\sigma_2}(0)-\sum_{v_3v_4}\Gamma_{v_1v_2v_3v_4}^{\sigma_1\sigma_2}\tilde\rho_{v_3v_4}^{\sigma_1\sigma_2}(\omega),$$
$$\omega_{v_1v_2}^{\sigma_1\sigma_2}=\omega_{v_1}^{\sigma_1}-\omega_{v_2}^{\sigma_2},\qquad\rho_{v_1v_2}^{\sigma_1\sigma_2}=\langle\sigma_1v_1|\rho|\sigma_2v_2\rangle, \tag{4.4}$$

$$\Gamma_{v_1v_2v_3v_4}^{\sigma_1\sigma_2}=i\int\frac{d\omega'}{2\pi}J_{v_4v_2v_1v_3}^{\sigma_2\sigma_1}(\omega')\Big[\frac{1}{\omega'+\omega_{v_1v_4}^{\sigma_1\sigma_2}-i\varepsilon}-\frac{1}{\omega'+\omega_{v_2v_3}^{\sigma_2\sigma_1}+i\varepsilon}\Big]$$
$$-i\sum_v\int\frac{d\omega'}{2\pi}\frac{J_{v_1vvv_3}^{\sigma_1\sigma_1}(\omega')}{\omega'-\omega_{v_2v}^{\sigma_2\sigma_1}-i\varepsilon}\delta_{v_2v_4}+i\sum_v\int\frac{d\omega'}{2\pi}\frac{J_{v_2vvv_4}^{\sigma_2\sigma_2}(\omega')}{\omega'-\omega_{v_1v}^{\sigma_1\sigma_2}+i\varepsilon}\delta_{v_1v_3},\quad\varepsilon\to+0, \tag{4.5}$$

$$J_{v_1v_2v_3v_4}^{\sigma_1\sigma_2}(\omega)=\int_{-\infty}^{+\infty}dt\exp(i\omega t)\langle Q_{v_1v_2}^{\sigma_1}(t)Q_{v_3v_4}^{\sigma_2}(0)\rangle, \tag{4.6}$$

where $Q_{v_1v_2}^{\sigma}=\langle\sigma v_1|H_{rp}|\sigma v_2\rangle$ is an operator in the PR space.

We consider sufficiently high barriers, for which

$$\beta V_0 = V_0/k_B T \gg 1. \tag{4.7}$$

This inequality means that the rotation proceeds mainly by tunneling. We assume also that the barrier is so high and (or) the moment of inertia so small that all the coefficients Γ satisfy the condition

$$|\Gamma| \ll \Omega, \tag{4.8}$$

which can apparently be regarded as satisfied for the proton groups, since the torsion transitions $v \to v+1$ in condensed media are observed in experiment by IR-spectroscopy methods.[19, 24] For the methyl groups, for example, $\hbar\Omega \sim 100-200$ cm^{-1}.[24] Since we need the values of the low-frequency (of the order of the Larmor frequency) Fourier components of the TCF, we assume the following inequality to be satisfied:

$$|\omega| \ll \Omega. \tag{4.9}$$

By virtue of (4.8) and (4.9) we need retain in (4.4) only the density-matrix elements $\tilde{\rho}_{v\,v}^{\sigma\sigma'}(\omega) = \tilde{\rho}_{v}^{\sigma\sigma'}(\omega)$ that are diagonal in v:

$$(-i\omega + i\omega_v^{\sigma\sigma'})\tilde{\rho}_v^{\sigma\sigma'}(\omega) = \rho_v^{\sigma\sigma'}(0) - \sum_{v'} \gamma_{vv'}^{\sigma\sigma'} \tilde{\rho}_{v'}^{\sigma\sigma'}(\omega),$$

$$\omega_v^{\sigma\sigma'} = \omega_{vv}^{\sigma\sigma'}, \qquad \gamma_{vv'}^{\sigma\sigma'} = \Gamma_{vvv'v'}^{\sigma\sigma'}. \tag{4.10}$$

The initial condition (2.8) in the calculation of the TCF (3.21) takes the form

$$\rho_v^{\sigma\sigma'}(0) = A_{vM}^{\sigma} P_{v\sigma} \delta_{\sigma'\varepsilon(\sigma-M)}, \tag{4.11}$$

$$P_{v\sigma} = \exp(-\beta E_{v\sigma}) \Big/ \sum_v \exp(-\beta E_{v\sigma}), \tag{4.12}$$

where the function

$$\varepsilon(x) = \begin{cases} x & |x| \leqslant 1 \\ x-3, & x > 1, \\ x+3, & x < -1 \end{cases}$$

and the coefficients $A_{vM}^{\sigma} = \langle \sigma v | \exp(-iM\varphi) | \varepsilon(\sigma - M) v \rangle$ are given in the oscillator approximation by[25]

$$A_{vM}^{\sigma} = 1 - a_{vM} = 1 - \frac{(2v+1)M^2\hbar}{4I\Omega}. \tag{4.13}$$

For the lowest below-the-barrier levels we have $a_{vM} \ll 1$. We introduce the matrix $H^{\sigma\sigma'}$ with elements

$$H_{vv'}^{\sigma\sigma'}(\omega) = [-i\omega + i\omega_v^{\sigma\sigma'}]\delta_{vv'} + \gamma_{vv'}^{\sigma\sigma'}. \tag{4.14}$$

With the aid of this matrix, the Fourier transform (3.27) is rewritten as

$$\Phi_M^{\sigma\sigma'}(\omega) = \sum_{vv'} A_{vM}^{\sigma *} [H^{\sigma\sigma'}(\omega)^{-1}]_{vv'} P_{v'\sigma} A_{v'M}^{\sigma}. \tag{4.15}$$

To analyze the matrix $H^{\sigma\sigma'}$, we introduce the tunnel approximation for the rotator wave functions[26]:

$$|\sigma v\rangle = 3^{-1/2}[\psi_v^{(1)} + \varepsilon^{\sigma}\psi_v^{(2)} + \varepsilon^{-\sigma}\psi_v^{(3)}], \tag{4.16}$$

where $\psi_v^{(k)}$ is the wave function of the torsion motion in the k-th well. The parameters $\gamma_{v\,v'}^{\sigma\sigma}$ with $v \neq v'$ are determined mainly by the overlap of the functions $\psi_v^{(k)}$ and $\psi_v^{(k')}$, and are therefore weakly dependent on the number v. The spacings $|\Delta_v|$ increase steeply with increasing number v. The dimensionality of the matrix $[H^{01}(\omega)]^{-1}$, which determines the intragroup contribution to the spin-lattice relaxation, is limited by the level starting with which $|\gamma_{v\,v'}^{01}|/|i\Delta_v + \gamma_{v\,v}^{01}| \ll 1$, $v \neq v'$. By way of illustration, we consider a case when we can confine ourselves to the two lowest levels. The main contribution to $\Phi_M^{01}(\omega)$ is of the form

$$\Phi_M^{01}(\omega) = \frac{|A_{0M}^{0}|^2 P_{00}}{-i(\omega + \Delta_t) + \nu}, \tag{4.17}$$

where terms of order $\exp(-\hbar\beta\Omega)$ have been discarded and the following parameters introduced:

$$i\Delta_t - \nu = \frac{(i\Delta_0 - \gamma_{00}^{01})(i\Delta_1 - \gamma_{11}^{01}) - \gamma_{01}^{01}\gamma_{10}^{01}}{i(\Delta_0 + \Delta_1) - \gamma_{00}^{01} - \gamma_{11}^{01}}. \tag{4.18}$$

The results (4.17) coincides in form with the Fourier transform of the TCF (3.32) postulated by Emid and Wind,[15] but the definition of the frequency Δ_t differs from the definition of the "observable tunneling frequency" given in [15].

The diagonal elements of the matrix $H^{1,-1}$ depend little on v (they do not contain the spacings Δ_v), and some of the off-diagonal elements are comparable in magnitude with the diagonal ones. In the calculation of the function $\Phi_M^{1,-1}(\omega)$ it is therefore necessary to take into account a larger number of levels than in the calculation of $\Phi_M^{0,-1}(\omega)$. For this calculation it is necessary to specify the form of the potential $V(\varphi)$ and the Hamiltonian of the interaction with the PR, and to use numerical methods, a procedure beyond the scope of the present paper. At sufficiently low temperatures, however, a situation is possible wherein an analytic solution can be obtained.

From the symmetry properties of the spectral densities (4.6) and from the degeneracy of the levels of E it follows that $\gamma_{v\,0}^{1,-1} = \gamma_{0v}^{1,-1}\exp(-\hbar\,\beta\,\omega_{v\,0}^{11})$. Since the diagonal coefficients $\gamma_{v\,v}^{1,-1}$ contain a term with the spectral density of the PR at zero frequency [see (4.6)], there exists a region with temperatures low enough to have

$$\gamma_{00}^{1,-1} \gg \gamma_{v0}^{1,-1}. \tag{4.19}$$

Neglecting the terms of order $\exp(-\hbar\beta\Omega)$ we obtain here

$$\Phi_M^{1,-1}(\omega) = \frac{|A_{0M}^{1}|^2}{-i\omega + \gamma_{00}^{1,-1}}. \tag{4.20}$$

If we have in analogy with (4.19)

$$\gamma_{00}^{01} \gg \gamma_{v0}^{01}, \tag{4.21}$$

then according to (4.18) we have $\Delta_t = \Delta_0$ and $\nu = \gamma_{00}^{01}$.

An analysis of the relations (4.17), (4.18), and (4.20) shows that the temperature dependence of T_1 can have several minima. We consider the case when the splitting of the ground level Δ_0 is much larger than the Larmor frequency ω_0. If we assume that when the condition (4.19) is satisfied $\gamma_{00}^{1,-1}$ can be of the order of ω_0, then T_1 has a minimum that stems from the intergroup contribution (the spectral densities $J^{(1)}(m\omega_0)$ in (3.35)), with a classical dependence on the Larmor frequency,[11] $T_{1\,\min} \propto \omega_0$.

For two-spin groups (e.g., CH_2D), we have in place of (3.35), taking into account only the intragroup contribution

$$\bar{R}_{11}(\mathrm{CH_2D})=\frac{1}{T_1(\mathrm{CH_2D})}$$

$$=\frac{3k^2}{80}[2J_+^{(2)}(\omega_0)+8J_+^{(2)}(2\omega_0)+J^{(2)}(\omega_0)+4J^{(2)}(2\omega_0)]. \qquad (4.22)$$

Comparison of (3.35), (4.22), and (4.20) explains the large depth of the low-temperature minimum(approximately three times lower than classical) compared with the CH_3 group[14] (see also[27]).

If the condition (4.21) were satisfied, the intragroup contribution would lead to a minimum of T_1 at $\gamma_{00}^{01} \sim \Delta_0$, with a depth Δ_0/ω_0 lower than classical.

We note that Δ_t determined by (4.18) can strongly depend on temperature. If we neglect the matrix elements between the wave functions $\psi_v^{(k)}$ [see (4.16)] in different wells then, as follows from (4.5), $\gamma_{vv}^{\sigma\sigma}$ does not depend on the indices σ and the relation $\gamma_{00}^{01}/\gamma_{11}^{01} \approx \exp(-\hbar\beta\Omega)$ is valid. Of course, the inequality (4.21) is not satisfied here. We assume also that $\gamma_{11}^{01} \gg |\Delta_1|$, and then

$$\Delta_t=\Delta_0-|\Delta_1|\exp(-\hbar\beta\Omega). \qquad (4.23)$$

It follows therefore that in a certain temperature region $\sim T_m$, when Δ_t goes through the interval $(+2\omega_0, -2\omega_0)$, minima should be observed on the temperature dependence of T_1 in the narrow interval $\Delta T \sim 4(\omega_0 k_B T_m/\Delta_0\hbar\Omega)T_m$. If $\nu \gtrsim \omega_0$, then all these minima merge into one. At $\nu \sim \omega_0$ the depth of the minimum is close to classical and depends strongly on ω_0. At $\nu \gg \omega_0$ the depth of the minimum is ν/ω_0 times lower than classical and does not depend on ω_0. It is natural to assume that we are dealing here with a high-temperature minimum. Of course, a minimum of T_1 can occur also at $\Delta_t \gg \omega_0$, when ν becomes of the order of Δ_t, but its depth is of the order of ω_0/Δ_t compared with classical.

The situations described above were observed in experiment.[6,10,11,12,14]

We proceed to estimate the deivation (3.34) of the relaxation from exponential. Within the framework of the interpretation proposed, here, the low-temperature minimum is due to the intergroup contribution, i.e., in the region of this minimum the spectral density $J^{(1)}(m\omega_0) \gg |J_\pm^{(M)}(m\omega_0)|$. The intermolecular contributions to η contains, in the first non-vanishing approximation in r/A_b, the products $J^{(1)}(m\omega_0)J^{(M)}(m'\omega_0)$, and consequently η is of the order of $J_\pm^{(M)}(m'\omega_0)/J^{(1)}(m\omega_0) \sim \omega_0^2/\Delta_0^2$, i.e., the relaxation should be exponential in the region of the low-temperature minimum. The region of the high-temperature almost-classical minimum will be analyzed on the basis of relation (4.17). In this region, the situation $\Delta_t \lesssim \omega_0 \lesssim \nu$ should be realized. Estimates based on (3.25), (3.34)–(3.36), and (4.17) yields $\eta \approx 0.2$.

An analysis within the framework of the approximation (4.17) has shown that a strong deviation from exponentiality ($\eta \sim 1$) can be observed at low temperatures when $\nu \ll \omega_0 \approx \Delta_t$, $\Delta_t/2$.

Thus, a great variety of experimental situations can be observed, depending on the singularities of the rotor-phonon interaction, which determines the coefficients $\gamma_{vv}^{\sigma\sigma'}$. Consequently, a relaxing three-spin system can serve as a probe for the study of the dynamics of a molecular crystal.

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