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CALCULATION OF THE SPIN-LATTICE RELAXATION TIME FOR RADICALS IN MOLECULAR CRYSTALS

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It is shown that anisotropy of the g factor (i.e., anisotropy of the hyperfine structure) can lead to a spin-lattice relaxation time for radicals in molecular crystals that is of the order of 10^{-3} sec or less in the presence of orientational oscillations.

THE spin-lattice relaxation mechanism of radicals in liquids is well understood at the present time.[1] We have already shown[2] that in most cases relaxation in liquids results from Brownian rotation of the radicals, as was suggested by McConnell.[1] It is obvious, however, that McConnell's mechanism is ineffective in solids, where all internal rotations are usually frozen. It can therefore be assumed that the spin-lattice relaxation time T_1 in a solid will be considerably longer than in a liquid, and the literature contains indications[3] that we can expect T_1 to be of the order of one second.

We shall consider spin-lattice relaxation of a radical in a magnetically dilute molecular crystal, which is the most characteristic case. It is evident at once that the method of calculating the relaxation transition probability in [2] cannot be applied to a solid, where the spectrum of thermal motions differs essentially from that given in Eqs. (5) and (8) of [2]. In complete analogy with liquids, the interaction between electron spin and the oscillations of individual atoms of a radical in molecular crystals appears to be considerably weaker than that between spin and orientational motions of the radical as a whole.[4]

Let the spin Hamiltonian be

$$\mathcal{H} = \beta g_{\alpha\gamma} S_\alpha H_\gamma + A_{\alpha\gamma} S_\alpha I_\gamma, \tag{1}$$

where $g_{\alpha\gamma}$ and $A_{\alpha\gamma}$ are the tensors of the spin-orbit and hyperfine interaction, respectively, with summation over Greek subscripts. H_α is the external magnetic field component in the α direction; S_α and I_α are the projections of the electron and nuclear spin operators on the α axis (assuming that the electron spin interacts with the spin of only one nucleus); β is the Bohr magneton. We shall assume for the sake of simplicity that the spin-orbit and hyperfine interactions are axially symmetric, i.e., in some system of coordinates $x''y''z''$ fixed rigidly in the radical the tensors $g_{\alpha\gamma}$ and $A_{\alpha\gamma}$ are diagonal, with

$$\begin{aligned} g_{x''x''} &= g_{y''y''} = g_\perp, & g_{z''z''} &= g_\parallel, \\ A_{x''x''} &= A_{y''y''} = A_\perp, & A_{z''z''} &= A_\parallel. \end{aligned} \tag{2}$$

We shall use the linear model of orientational waves in a molecular crystal that was investigated in [4], assuming that in the equilibrium position the principal (z'') axis of g and A is parallel to the direction of propagation κ of orientational waves. Assuming that the angular deviation χ from equilibrium is small and denoting the angle between κ and the magnetic field H by φ, we find that when χ lies in a plane passing through κ and H (the $z'y'$ plane in Fig. 1), the spin Hamiltonian (1) becomes

$$\begin{aligned} \mathcal{H} = {} & \beta H g_{zz}(\varphi) S_z + A(\varphi) S_z I_z + \beta H g_{xz}(\varphi, \chi) S_x \\ & + A_{xx}(\varphi, \chi) S_x I_x + A_{xz}(\varphi\chi) S_x I_z, \end{aligned} \tag{3}$$

$$\begin{aligned} g_{zz}(\varphi) &= g_\perp \sin^2\varphi + g_\parallel \cos^2\varphi, \\ A_{zz}(\varphi) &= A_\perp \sin^2\varphi + A_\parallel \cos^2\varphi, \\ g_{xz}(\varphi, \chi) &= \Delta g\, [\chi \cos 2\varphi + \chi^2 \sin 2\varphi], \\ A_{xx}(\varphi, \chi) &= \Delta A\, [-\chi \sin 2\varphi + \chi^2 \cos 2\varphi], \\ A_{xz}(\varphi, \chi) &= \Delta A\, [\chi \cos 2\varphi + \chi^2 \sin 2\varphi], \end{aligned}$$

$$\Delta g = g_\parallel - g_\perp, \quad \Delta A = A_\parallel - A_\perp. \tag{4}$$

In (3) we have neglected terms of the form $(A_\perp \cos^2\varphi + A_\parallel \sin^2\varphi) S_x I_x$, which cause small level shifts in higher approximations, as well as $\chi \Delta A \cos^2 2\varphi\, S_z I_x$ terms, which do not induce electron spin flip.

When waves are polarized in the perpendicular direction (i.e., the deviation from equilibrium occurs in the $z'x'$ plane, as shown in Fig. 2), Eq. (1) becomes

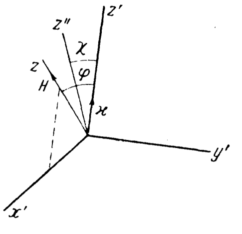

FIG. 1

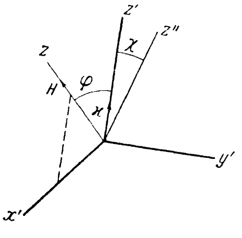

FIG. 2

$$\mathcal{H} = \beta H g_{zz}(\varphi) S_z + A_{zz}(\varphi) S_z I_z + \beta H g_{xz} S_x + \beta H g_{yz} S_y + A_{xx} S_x I_x + A_{xy} S_x I_y + A_{xz} S_x I_z + A_{yx} S_y I_x + A_{yy} S_y I_y + A_{yz} S_y I_z, \quad (5)$$

where

$$g_{xz} = \tfrac{1}{2}\Delta g \chi^2 \sin 2\varphi,\ g_{yz} = \Delta g \chi \cos\varphi,\ A_{xx} = -\Delta A \chi^2 \sin^2\varphi,$$
$$A_{xy} = A_{yx} = -\Delta A\, \chi \sin\varphi, \quad A_{xz} = \tfrac{1}{2}\Delta A \chi^2 \sin 2\varphi,$$
$$A_{yy} = \Delta A \chi^2, \quad A_{yz} = \Delta A \chi \cos\varphi. \quad (6)$$

In (5), as in (3), we have omitted all terms that are unimportant for our purposes.

We thus find that in the cases of both (3) and (5), when calculating the probability of a relaxation transition between any two levels of the spin system, the spin Hamiltonian can be put into the form

$$\mathcal{H} = \beta H g(\varphi) S_z + A(\varphi) S_z I_z + \chi R_1(\varphi) + \chi^2 R_2(\varphi), \quad (7)$$

where $R_1(\varphi)$ and $R_2(\varphi)$ are linear combinations of the spin operators with nonvanishing matrix elements for the transition of interest. The coefficients in these linear combinations are functions of the angle φ.

In (7) we shall first consider the term linear in χ that is responsible for transitions involving absorption of a single orientational phonon. The probability per unit time of a relaxation transition between spin levels (with spin flip) is given by[5]

$$w_{12} = \frac{2\pi}{\hbar^2} |(1|R_1|2)|^2 \langle |\chi_{n,n+1}(\omega_L)|^2 \rangle g(\omega_L), \quad (8)$$

where $(1|R_1|2)$ is the matrix element between spin states 1 and 2, $\chi_{n,n+1}(\omega) = (n\hbar/2J\omega)^{1/2}$ is the matrix element between states n and n+1 of the rotational oscillator, where J is the moment of inertia of the rotational oscillator, i.e., of the radical with respect to the appropriate axis; $g(\omega)d\omega$ is the number of normal orientational oscillations with frequencies from ω to $\omega + d\omega$; the sign $\langle\ \rangle$ denotes averaging over the quantum numbers n; and $\hbar\omega_L$ is the separation between the magnetic levels 1 and 2.

It follows from [4] that for the linear model of orientational waves, when the centers of rotational oscillations of individual molecules are fixed (i.e., there are no interactions between orientational and translational oscillations) the frequencies ω are determined from

$$\omega = \Omega_2 \sqrt{1 + q\cos\eta}\ , \quad (9)$$

where Ω_2 is the frequency of rotational oscillations of an individual molecule if all other molecules are at their equilibrium positions, q is determined by the interaction constants of the individual molecules and can assume values from −1 to +1, and η varies from 0 to π. It is easily seen that $g(\omega)$, normalized to 1, is then represented by

$$g(\omega) = \begin{cases} 2\omega(\pi q \Omega_2^2)^{-1}\left[1 - \dfrac{1}{q^2}\left(\dfrac{\omega^2}{\Omega_2^2} - 1\right)^2\right]^{-1/2} & \text{for } \Omega_2\sqrt{1-|q|} < \omega < \Omega_2\sqrt{1+|q|} \\ 0 & \text{for } \omega < \Omega_2\sqrt{1-|q|} \text{ and for } \omega > \Omega_2\sqrt{1+|q|}. \end{cases} \quad (10)$$

In other words, unlike the spectrum of translational vibrations, the frequency spectrum of orientational waves generally starts at some lower limit $\Omega_{min} = \Omega_2\sqrt{1-|q|}$ instead of zero frequency.

From the Raman scattering spectra in molecular crystals it follows that the frequency threshold Ω_{min} lies in the optical infrared region ($\Omega_{min} \gg \omega_L$). We then obviously have $g(\omega_L) = 0$ in (8). This corresponds to the fact that the minimum energy of an orientational phonon is considerably greater than the Zeeman quantum. Consequently, one form of energy cannot be converted directly into the other, and spin energy transfer to the lattice requires at least two orientational phonons (a Raman transition).

Relaxational transitions of this kind involving two phonons are induced by the last term in (7). The transition probability per unit time is then

$$w_{12} = (2\pi/\hbar^2)\, |(1|R_2|2)|^2 \int_{\Omega_{min}}^{\Omega_{max}} \langle |\chi_{n,n+1}(\omega)|^2 \rangle \langle |\chi_{n,n+1}(\omega + \omega_L)|^2 \rangle g(\omega)\, g(\omega + \omega_L)\, d\omega,$$
$$\Omega_{max} = \Omega_2\sqrt{1 + |q|}. \quad (11)$$

Averaging over n and using (10), we obtain

$$w_{12} = (2/\pi)\left(|(1|R_2|2)|/qJ\Omega_2^2\right)^2 \times \int_{\Omega_{min}}^{\Omega_{max}-\omega_L} F(\omega)\left[\left(1 - \frac{1}{q^2}\left(\frac{\omega^2}{\Omega^2} - 1\right)^2\right) \times \left(1 - \frac{1}{q^2}\left(\frac{(\omega + \omega_L)^2}{\Omega^2} - 1\right)\right)\right]^{-1/2} d\omega,$$
$$F(\omega) = \exp\{\hbar(\omega + \omega_L)/kT\} / [(\exp\{\hbar\omega/kT\} - 1) \times (\exp\{\hbar(\omega + \omega_L)/kT\} - 1)]. \quad (12)$$

It is easily shown that although the integrand in (12) has singularities at the ends of the integration range, the integral always converges when $|q| \neq 1$. The divergence when $|q| = 1$ is associated with the use of a linear model for the orientational waves, and can be eliminated by employing a two-dimensional model.

The evaluation of (12) given below leads to the result

$$w_{12} \geqslant \frac{2}{\pi}\left(\frac{|(1\,|\,R_2\,|\,2)|}{qJ\Omega_2^2}\right)^2 \frac{\exp\{\hbar\Omega_{max}/kT\}}{(1-\exp\{\hbar\Omega_{max}/kT\})^2}\,(\Omega_{max}-\Omega_{min}). \tag{13}$$

It can be shown that in the most interesting case, $\hbar\Omega_2/kT \ll 1$, we have

$$w_{12} = \frac{2}{\pi}\,\xi(q)\left(\frac{|(1\,|\,R_2\,|\,2)|}{q\Omega_2^2 J}\right)^2 \frac{1}{\Omega_2}\left(\frac{kT}{\hbar}\right)^2, \tag{14}$$

where

$$\xi(q) = \frac{27\,q^2\,(\sqrt{1+|q|}-\sqrt{1-|q|})}{4\,[1+{}^1\!/_2\sqrt{1+3q^2}]\,[3q^2-1+\sqrt{1+3q^2}]}\,.$$

By calculating the matrix elements $(1\,|\,R_2\,|\,2)$ we can obtain from Eqs. (12) – (14) the probability of a relaxational transition between any spin levels.

We shall now consider as a specific example the transition $\frac{1}{2}, \frac{1}{2} \rightarrow -\frac{1}{2}, -\frac{1}{2}$ in which the electron spin and nuclear spin are flipped simultaneously. For an orientational wave polarized in the z′x′ plane Eqs. (3) and (4) give

$$|(1\,|\,R_2\,|\,2)|^2 = \tfrac{1}{16}\,\Delta A^2\cos^2 2\varphi.$$

With polarization in the z′y′ plane, Eqs. (5) and (6) give

$$|(1\,|\,R_2\,|\,2)|^2 = \tfrac{1}{16}\,\Delta A^2\,(1+\sin^2\varphi)^2.$$

Finally, adding the probabilities of transitions induced by each of the waves, we obtain

$$w_{12} = \frac{1}{8\pi}\,\xi(q)\left(\frac{\Delta A}{qJ\Omega_2^2}\right)^2 [\cos^2 2\varphi + (1+\sin^2\varphi)^2]\left(\frac{kT}{\hbar\Omega_{max}}\right)^2\Omega_2. \tag{15}$$

Averaging this expression over all angles, we obtain a mean value of T_1 that is characteristic of a polycrystalline sample. The final evaluation of w_{12}, with $\Delta A = 10$ gauss and $q = \frac{1}{2}$,[6] gives

$$1/T_1 = w_{12} \approx 5\cdot 10^7\,T^2/\nu^5 J^2. \tag{16}$$

Here T is the absolute temperature, $\nu = \Omega_2/2\pi$ in cm^{-1}, and J is the corresponding moment of inertia of the radical in the unit 10^{-40} g-cm². Since the Raman scattering spectra in molecular crystals[7] show that the minimum frequencies of orientational oscillations lie in a region below 10 – 100 cm⁻¹ for J = 100 and T = 200°, we obtain $1/T_1 = w_{12} \gtrsim 2 \times 10^3\ \mathrm{sec}^{-1}$.

When orientational oscillations exist in a molecular crystal the spin-lattice relaxation time can thus be smaller than 1 sec by a few orders of magnitude. This result agrees well with data obtained in the laboratory of V. V. Voevodskii at the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences. According to these data the absence of saturation in the electron paramagnetic resonance spectrum of some molecular crystal radicals shows that $T_1 < 10^{-4}$ sec. (We have confined ourselves to estimating the order of magnitude of T_1 from the simplest model of orientational waves, making no comparison with specific experimental results, since the literature contains no direct measurement of T_1 in molecular crystals, and whenever indirect data for T_1 are obtained in the absence of saturation we lack optical data for the frequency thresholds of orientational oscillations.)

We have pointed out above that a direct transformation of a Zeeman quantum into an orientational phonon is impossible, since the spectrum of orientational waves begins at a minimum frequency $\Omega_{\min} \gg \omega_L$; this result does not depend on whether a linear or a spatial model is being considered. However, the situation changes if orientational and translational oscillations interact. In this case (in the linear model) the frequency spectrum consists of two branches, one of which, as previously, begins at $\Omega_{\min}$, while the other branch begins at zero frequency. In the absence of coupling between orientational and translational oscillations the second branch represents pure translational waves. However, the presence of coupling results in the mixing of orientational and translational motions.[4] The amplitude of orientational oscillations will, of course, approach zero as $\omega \rightarrow 0$, but remain finite for any $\omega \neq 0$. Direct (single-phonon) relaxational transitions thus become possible.

If the indicated interaction is represented in the potential energy of the system by terms of the form

$$U_l = g(\chi_{l-1}x_l + \chi_l x_{l-1} + 2\chi_l x_l), \tag{17}$$

where χ_l is the angle of deviation from the equilibrium position and x_l is the shift of the center of gravity of a molecule with index l, then at low frequencies the amplitudes of rotational and translational oscillations are related by

$$\frac{\chi}{x} = -\frac{2g_0\,\omega}{(1+q)\Omega_2^2}\left[\frac{1}{2}\,\Omega_1^2 - \frac{4g_0^2}{(1+q)\Omega_2^2}\right]^{-1/2}\sqrt{\frac{M}{J}}\,. \tag{18}$$

where M is the molecular mass, $g = g_0(MJ)^{-1/2}$, and Ω_1 is the frequency of translational oscillations of an individual molecule if all other molecules are at their equilibrium positions.

From (18), assuming in first approximation that at low frequencies translational oscillations are independent of orientational oscillations, the probability of a single-phonon relaxational transition is easily calculated:

$$w_{12} = \frac{4\sqrt{2}}{\pi(1+q)^2} \frac{|(1|R_1|2)|^2}{\hbar} \frac{\omega_L}{e^{\hbar\omega/kT}-1} \frac{g_0^2}{J\Omega_1^3 \Omega_2^4} . \tag{19}$$

This result obviously is subject to the condition of weak interactions between orientational and translational oscillations. Using (17) of [4], we can show that this condition has the form

$$\Omega_1^2\Omega_2^2 \gg 8g_0^2/(1+q).$$

When $\hbar\Omega_L/kT \ll 1$, Eq. (19) becomes

$$w'_{12} = \frac{4\sqrt{2}}{\pi(1+q)^2} \frac{|(1|R_1|2)|^2}{\hbar^2} \frac{g_0^2}{J\Omega_1^3 \Omega_2^4} kT . \tag{20}$$

In order to determine the order of magnitude represented by (19) and (20) it is necessary to know the value of g_0, which can be determined experimentally only with great difficulty.

It is easily seen that in determining the temperature dependence of relaxational transition probabilities when $\hbar\Omega_2/kT \ll 1$ it is not important to distinguish between a linear and a spatial model. In this case we always have $W_{12} \sim T^2$ for Raman transitions, and $W_{12} \sim T$ for direct transitions; this follows directly from (8) and (12). Thus the experimental temperature dependence of the spin-lattice relaxation time in conjuction with a specific model as described above would yield the characteristic parameters of a molecular crystal.

We note, finally, that since the matrix elements $(1|R_{1,2}|2)$ differ for transitions between different spin levels, the values of T_1 must differ for different hyperfine lines. Moreover, (14) and (20) show that for a single crystal T_1 depends, as a general rule, on crystal orientation in an external magnetic field. Experimental confirmation of the indicated regularities would constitute direct evidence for the proposed relaxation mechanism.

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