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Abstract

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THE INFLUENCE OF HINDERED ROTATION OF MOLECULES IN MOLECULAR CRYSTALS ON THE RATE OF MAGNETIC RELAXATION CAUSED BY INTRAMOLECULAR DIPOLE-DIPOLE INTERACTIONS

(Presented by Academician N. V. Belov on 28 I 1970)

Investigation of the influence of hindered rotation of molecules on nuclear magnetic resonance (NMR) spectra gives a fairly clear picture of the dynamics of molecular motion in a crystal lattice. Molecules in a crystal lattice can perform reorientational motions only through those angles that are permitted by the symmetry of the lattice. However, at the present time there is no theory that takes into account, in a general form, the symmetry of the lattice and the types of motions in which the nuclei studied by the NMR method participate.

The theory of magnetic relaxation in molecular crystals, caused by intramolecular magnetic interactions in the presence of hindered rotation, has been developed in a number of works ([1–7]). The narrowing of the resonance line caused by hindered rotation of the molecule has also been studied ([6,8,9]). Unfortunately, in ([1–9]) the theory is considered only for particular cases of molecular reorientations in a crystal lattice.

Recently, on the basis of the solution of the problem of random rotational walks of molecules in a crystal lattice, an expression was obtained for the distribution of molecular orientations in the lattice ([10]). In ([10]) it is assumed that reorientation of a molecule in a crystal lattice occurs only about one axis between the equilibrium positions of the molecules in the lattice, for an arbitrary symmetry of the crystal lattice.

In the present work we shall calculate the rate of magnetic relaxation caused by intramolecular dipole–dipole interactions in the presence of reorientational motions ([10]) and Brownian rotation about a fixed axis.

The energy $\mathcal{H}_{jk}$ of the dipole-dipole interaction of two nuclei j and k in one and the same molecule (the perturbation causing relaxation transitions between stationary Zeeman energy levels $E_{M_j} = -g_{I_j}\beta_{NH}0M_j$ of the spin of nucleus I_j of nucleus j) can be written in the form ([11–13])

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$$\mathcal{H}' = \mathcal{H}_{jk} = \sum_{n=-2}^{2} \mathcal{H}_{jk}^{n} = P_{jk} \sum_{n} A_{-n} \{jk\}_{-n} Y_{2n}(\theta_{jk}, \varphi_{jk}), \tag{1}$$

where

$$\begin{gathered} \{jk\}_2 = \{jk\}_{-2}^* = \hat{I}_j^+ \hat{I}_k^+, \qquad \{jk\}_1 = \{jk\}_{-1}^* = \hat{I}_j^+ \hat{I}_{kz} + \hat{I}_{jz} \hat{I}_k^+; \\ \{jk\}_0 = \hat{I}_{jz} \hat{I}_{kz} - \frac{1}{4} (\hat{I}_j^+ \hat{I}_k^- + \hat{I}_j^- \hat{I}_k^+); \qquad \hat{I}^{\pm} = \hat{I}_x \pm i \hat{I}_y; \\ A_2 = A_{-2} = A_1 = A_{-1} = \sqrt{6/5\pi}; \qquad A_0 = -\sqrt{16/5\pi}; \\ P_{jk} = g_{I_j} g_{I_k} \beta_N^2 r_{jk}^{-3}, \end{gathered} \tag{2}$$

I^2 and I_z are diagonal operators; $\mathbf{r}_{jk}(r_{jk}, \theta_{jk}, \varphi_{jk})$ is the radius vector connecting nuclei j and k in the molecule; in the molecular coordinate system $x'y'z'$, the coordinates $\mathbf{r}_{jk}(r_{jk}, \theta_{jk}, \varphi_{jk})$ will be considered constant.

The dependence (2) on random reorientations of the molecule is expressed by the presence of the functions $Y_{2n}(\theta_{jk}, \varphi_{jk})$. This dependence can also be expressed in terms of the Euler angles α, β, γ, which fix the orientation of the system $x'y'z'$ (of the molecule) in the system xyz, if one uses the transformation formula ([14])

$$Y_{2n}(\theta_{jk}, \varphi_{jk}) = \sum_{m} T_{mn}^{(2)}(\alpha, \beta, \gamma)\, Y'_{2m}(\theta'_{jk}, \varphi'_{jk}); \tag{3}$$

Y'_{2m} are constant numbers that are easily found if the orientation of the axes x', y', z' and the positions of the atoms j and k in the molecule are known. Then the matrix element of the transition $M \to M - n$ can be written as

$$(\mathcal{H}_{jk})_{M,M-n} = P_{jk} A_{-n} (\{jk\}_{-n}) \sum_{m} T_{mn}^{(2)}(\alpha, \beta, \gamma)\, Y'_{2m}(\theta'_{jk}, \varphi'_{jk}). \tag{4}$$

The changes of the matrix element (4) with time are random; therefore the probability $w_{M,M-n}$ of the relaxation transition $M, M-n$ can be calculated by the formula ([11])

$$w_{M,M-n} = \hbar^{-2} \int_{-\infty}^{\infty} K_{M,M-n}(t) \exp(-i\omega_{M,M-n} t)\, dt. \tag{5}$$

$K_{M,M-n}$ is the time correlation function of the random quantity $\mathcal{H}'_{M,M-n}(t)$, which by definition is equal to

$$K_{M,M-n} = \frac{1}{2\pi} \int [(\mathcal{H}_{jk})_{M,M-n}(\alpha_0)] \left[(\mathcal{H}_{jk})_{M,M-n}(\alpha)\right]^* W(\alpha, t/\alpha_0, 0)\, d\alpha\, d\alpha_0. \tag{6}$$

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In (6), $W(\alpha, t/\alpha_0, 0)$ is the probability density that at time t the molecule will have orientation α, if at time $t = 0$ it had orientation α_0, which, according to ([10]), has the form

$$W(\alpha, t/\alpha_0, 0) = \frac{1}{2\pi} \sum_l \exp\left[-\frac{t}{\tau_c}(1 - A_l) - il(\alpha - \alpha_0)\right]; \tag{7}$$

here τ_c is the mean time between two successive rotations; $A_l = \cos l\chi$; χ is the minimum angle of rotation allowed by the symmetry of the crystal lattice. Obviously, $\chi = 2\pi/n_\chi$ (n_χ is an integer equal to the order of the one-dimensional point group of rotations). Calculating $K_{M,M-n}(t)$ from (6) by direct integration with the distribution function (7), we obtain

$$K_{M,M-n}(t) = \overline{|(\mathcal{H}^0_{jk})_{M,M-n}|^2} \sum_m \left|P_{mn}(\cos\beta_0) \exp(-im\gamma_0) Y'_{2m}(\theta'_{jk}, \varphi'_{jk})\right|^2 \times$$

$$\times \exp[\tau_c^{-1}(1 - \cos n\chi)t]\,, \tag{8}$$

$$\overline{|(\mathcal{H}^0_{jk})_{M,M-n}|^2} = P^2_{jk} A^2_{-n}\, \overline{|\{jk\}_{-n}|^2}.$$

Using expression (8) in calculating $w_{M,M-n}$ from (5), we find

$$w_{M,M-n} = 2\hbar^{-2} \overline{|(\mathcal{H}_{jk})_{M,M-n}|^2} \sum_m \left|P_{mn}(\cos\beta_0) \exp(-im\gamma_0) Y'_{2m}(\theta'_{jk}, \varphi'_{jk})\right|^2 \times$$

$$\times \frac{\tau_c^{-1}(-\cos n\chi)}{[\tau_c^{-1}(1 - \cos n\chi)^2 + \omega^2_{M,M-n}]}. \tag{9}$$

Expression (9) for the magnetic-relaxation rate differs from those known previously ([1–7]) in that in (9) the parameter χ, characterizing the symmetry of the crystal lattice, enters explicitly.

However, studies of the width of the NMR resonance line $\delta\nu$ show that, in the presence of hindered rotation in solids about a fixed axis, $\delta\nu$ has the form ([8,9,15])

$$(\delta\nu)^2 = A^2(2/\pi)\,\mathrm{arctg}[a\delta\nu/\lambda_c],$$

where A is the width of the resonance absorption line for a rigid lattice, $\lambda_c = 1/2\pi\tau_c$ is the rate of rotation of the molecule. At values $\tau_c^{-1} \gg A$, the width of the resonance line is narrowed by the motion ([9]). Narrowing of the resonance-line width obviously means that the local magnetic field created by neighboring

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magnetic nuclei at the nucleus under study is averaged to some value, and in this case the nucleus under study no longer "feels" the symmetry of the crystal lattice. Thus equation (9) is applicable only for "slow" reorientational motions of molecules ($\tau_c^{-1} < A$). Then, taking into account that the condition $\omega_{M,M-n} \gg A$ is usually easily satisfied, expression (9) is simplified and written as

$$w_{M,M-n} = 2\hbar^{-2} \left|(\mathcal{H}_{jk})_{M,M-n}\right|^2 \sum_m \left|P_{mn}(\cos\beta_0) \exp(-im\gamma_0) Y'_{2m}(\theta'_{jk}, \varphi'_{jk})\right|^2 \times \frac{1 - \cos n\chi}{\omega^2_{M,M-n}\tau_c}. \tag{10}$$

For "fast" motions of molecules ($\tau_c^{-1} \gg A$), in calculating the rate of magnetic relaxation due to hindered rotation about a fixed axis it is more reasonable to apply a Brownian-type rotation model, as in a liquid. For this case, the use of equation (4) with time-dependent perturbation theory ([11]) leads to the following expression for the transition probability:

$$w^{(r)}_{M,M-n} = 2\hbar^{-2} \overline{\left|(\mathcal{H}_{jk})_{M,M-n}\right|^2} \sum_m \left|P_{mn}(\cos\beta_0) \exp(-im\gamma_0) Y'_{2m}(\theta'_{jk}, \varphi'_{jk})\right|^2 \times \frac{\tau_c}{1 + \omega^2_{M,M-n}\tau_c}. \tag{11}$$

Usually, for "fast" hindered rotations the condition $\omega_{M,M-n}\tau_c \ll 1$ is easily satisfied.

The temperature dependence of the rate of spin–lattice relaxation in (9) and (11) is determined by the parameter τ_c, whose dependence on the temperature T and on the magnitude of the potential barrier U is determined in the form ([16])

$$\tau_c = \tau_0 \exp(U/RT), \tag{12}$$

where τ_0 is the period of torsional oscillations of the molecule in the potential well, which in molecular crystals has a value $\sim 10^{-13}$ sec.

In formulas (9) and (11), the angle β_0 explicitly takes into account the anisotropy of the relaxation rate in a single crystal relative to the external magnetic field H_0. Let us note that expression (9), for particular values of χ, leads to definite values of $(T_1)_{\min}$. For example, for $\chi = 2/3\pi$ the value $(T_1)_{\min}$ occurs at $\omega\tau_c \sim 1.2$. Similar behavior of the temperature dependence of T_1 was observed (see § 6, Ch. X ([17]); ([18])). However, in most cases the temperature behavior of T_1 in molecular crystals is described by a formula analogous to (11) ([15,17–20]), and $(T_1)_{\min}$ from (11) occurs at $\omega\tau_c \sim 0.6$.

The application of formulas (9) and (11) for "slow" and "fast" hindered rotations is not sharply limited by the motion, since even when the condition $\tau_c^{-1} \gg$

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A is fulfilled, the width of the line $\delta\nu$ in NMR may not narrow, whereas in NQR spectra manifestations of motions of this kind are clearly separated by the disappearance of the signal and its appearance after a phase transition ([21–24]).

A detailed study of the temperature dependence over a wide temperature range in single crystals would make it possible to judge the validity of our approach to questions concerning the mechanism of relaxation and the dynamics of molecular motion in anisotropic hindered rotations.

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