

Effect of slow molecular motions on nuclear magnetic relaxation under "magic-angle conditions"

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The effect of slow molecular motions on the transverse and longitudinal nuclear magnetic relaxation in a condensed medium is analyzed. The relaxation is assumed to occur in effective fields which act in a rotating coordinate system and a doubly rotating coordinate system under conditions such that the NMR line is narrowed by the "magic-angle method" of Mefed and Atsarkin [Sov. Phys. JETP **47**, 378 (1978); **59**, 172 (1984)]. The Bloch-Redfield method is used. In addition to the ordinary nonsecular terms of the dipole Hamiltonian, an effective secular Hamiltonian, which arises in second-order perturbation theory, is taken into account. The validity of this approach is confirmed by calculations for a model of two isotropically reorienting spins 1/2 carried out by a random-trajectory method. In a certain interval of correlation times τ_c a slow molecular motion promotes an rf suppression of the dipole width of the NMR line in a rotating coordinate system. The width reaches a minimum at τ_c^{-1} on the order of the local field in a rigid lattice. The longitudinal relaxation time in a doubly rotating coordinate system is particularly sensitive to the details of "superslow" molecular motions ($\tau_c \sim 10^{-3}$ – 10^{-2} s), so that measurements of this time may prove to be an effective method for studying these motions.

1. INTRODUCTION

Studies of nuclear spin relaxation yield extensive information on the atomic and molecular motions in condensed matter (see Refs. 1 and 2, for example). The longitudinal relaxation time T_1 in a static magnetic field H_0 , for example, is particularly sensitive to motions with correlation times $\tau_c \sim (\gamma H_0)^{-1} \sim (10^{-8}$ – $10^{-6})$ s, where γ is the nuclear gyromagnetic ratio. To learn about slower motions one measures the longitudinal relaxation time $T_{1\rho}$ in an effective field H_e acting in a rotating coordinate system. The correlation times involved in this case are considerably longer,³ $\tau_c \sim (\gamma H_e)^{-1} \sim (10^{-5}$ – $10^{-4})$ s. Correlation times τ_c in approximately this range can also be studied by measuring the effective transverse relaxation time in narrowing multipulse NMR experiments^{4–6} and by several other methods.⁷ In many cases, on the other hand, we are interested in even slower motions, e.g., those characteristic of the vitrification region in amorphous substances, of the dynamics of macromolecules, and of low-temperature diffusion in solids. There is a difficulty in moving into this region, however: In measurements of $T_{1\rho}$ the effective field H_e cannot be weaker than the local field in a rigid lattice, which would typically be (in frequency units) $\omega_L \sim 10^4$ s⁻¹. Certain approaches to the solution of this problem have recently been suggested.^{8,9} In the present paper we discuss yet another approach, which involves the novel method proposed by Mefed and Atsarkin^{10,11} for observing NMR. The idea is to directly detect NMR signals and to measure the relaxation in effective fields H_e and H'_e which are acting in a rotating coordinate system¹⁰ and a doubly rotating coordinate system,¹¹ respectively. By imposing the field H_e in the "magic" orientation one can suppress the dipole width of the NMR line to values on

the order of 10^2 Hz. Mefed and Atsarkin^{10,11} believe that this suppression raises the possibility of using this method to study "superslow" motions with $\tau_c \sim (10^{-3}$ – $10^{-2})$ s. We offer a theoretical analysis of this problem here.

Two general approaches are taken in the theory of nuclear magnetic relaxation. The first is based on the Bloch-Redfield equation for the spin density matrix (see Refs. 1 and 12, for example). The spin interactions are treated in second-order perturbation theory, but this treatment is valid only for rather fast molecular motions, with $\tau_c \ll \omega_L^{-1}$. The second approach is the random-trajectory method, also known as the method of the stochastic Liouville equation.^{12–14} Although this approach is considerably more complicated, it is applicable to arbitrarily slow motions, provided that they can be modeled by a random Markov process.

The first of these approaches has been taken to describe the nuclear relaxation in a rotating coordinate system at the magic angle of Haeberlen and Waugh.⁴ We will expand their analysis here, moving partly up to the next order of perturbation theory and thereby obtaining a qualitatively new result, as we will see.

A similar approach will be taken to analyze the longitudinal relaxation in a doubly rotating coordinate system. The results will then be tested and generalized by the random trajectory method for two specific models of the reorientations of a molecule with two spins 1/2.

2. RELAXATION IN A ROTATING COORDINATE SYSTEM

A spin system is in a strong static magnetic field $H_0 \parallel z$ and an rf field $2H_1 \cos \omega t$, where $\omega = \gamma H_0 + \Delta$; the rf field is perpendicular to the static field. For molecular motions satisfying the condition $\gamma H_0 \tau_c \gg 1$, we should consider only the

secular part of the dipole-dipole interaction. If we transform to an oblique rotating coordinate system in which the Z axis makes an angle $\theta = \text{arctg}(\gamma H_1/\Delta)$ with the field \mathbf{H}_0 , i.e., in which this axis is directed along the effective field \mathbf{H}_e , then we can write the Hamiltonian of the spin system as (see Refs. 1 and 12, for example)

$$\hat{\mathcal{H}}_p = \omega_e \hat{I}_z + \hat{\mathcal{H}}_{dp}, \quad (1)$$

where $\omega_e = \gamma H_e = [\Delta^2 + (\gamma H_1)^2]^{1/2}$ is the Larmor frequency of the nuclei in the effective field, the operator \hat{I}_z represents the Z component of the total spin of the system, and the dipole-interaction Hamiltonian $\hat{\mathcal{H}}_{dp}$ can be written (see Ref. 6, for example)

$$\hat{\mathcal{H}}_{dp} = - \sum_{i \neq k} b_{ik} \sum_{m=-2}^2 d_{0m}^2(\theta) \hat{T}_{2m}(i, k). \quad (2)$$

Here

$$b_{ik} = \frac{\gamma^2 \hbar}{r_{ik}^3} P_2(\cos \beta_{ik}) = \frac{\gamma^2 \hbar}{2r_{ik}^3} (3 \cos^2 \beta_{ik} - 1);$$

r_{ik} is the length of the vector \mathbf{r}_{ik} , which connects spins i and k ; β_{ik} is the angle between \mathbf{r}_{ik} and the Z axis; $d_{mn}^2(\theta)$ is the Wigner function of the Euler angles $0, \theta, 0$;

$$\hat{T}_{2m}(i, k) = \left(\frac{3}{2}\right)^{1/2} \sum_{\mu, \nu} C_{1\mu 1\nu}^{2m} \hat{I}_{i\mu} \hat{I}_{k\nu}$$

is an irreducible spherical tensor constructed from the operators of the spherical components of the spins i and k ; and $C_{Jm J'm'}^{Ln}$ is a Clebsch-Gordan coefficient.

Everywhere below we assume $\omega_e \gg \omega_L$. The problem of relaxation in a system of two spins under this condition was solved by Haeberlen and Waugh⁴ for correlation times $\tau_c \ll \omega_L^{-1}$. We know that the longitudinal relaxation time in a rotating coordinate system is determined exclusively by the terms of Hamiltonian (2) which are nonsecular with respect to the effective field, while the transverse relaxation time $T_{2\rho}$ is also determined by a secular term (with $m = 0$). When the angle θ takes on the magic value

$$\theta_M = \arccos(1/\sqrt{3}),$$

however, the coefficient $d_{00}^2(\theta_M)$ vanishes; i.e., the secular part of Hamiltonian (2) vanishes. As a result, the expressions for $T_{1\rho}^{-1}$ and $T_{2\rho}^{-1}$ turn out to be similar: Each reaches a maximum near $\tau_c = \omega_e^{-1}$ and falls off monotonically on each side of this maximum along the τ_c scale.

For $T_{2\rho}^{-1}$, however, this result is actually nothing more than a consequence of the assumption adopted in the calculations. We know that in a rigid lattice (i.e., in the limit $\tau_c \rightarrow \infty$) the width of an NMR line in a rotating coordinate system with $\theta = \theta_M$ does not vanish and is determined by the "secular" dipole interactions, which can be separated from the nonsecular part of Hamiltonian (2) in second-order perturbation theory.¹⁵⁻¹⁷ The corresponding effective secular Hamiltonian was calculated in Refs. 16 and 17. For a system of spins 1/2 this Hamiltonian can be written

$$\begin{aligned} \hat{\mathcal{H}}_{dp}^{(0)} &= \frac{3}{16\omega_e} \sum_{i \neq k} b_{ik}^2 (\hat{I}_{i0} + \hat{I}_{k0}) \\ &+ \frac{1}{\omega_e} \sum_{i \neq k \neq l} b_{ik} b_{il} [\hat{U}_{10}(ikl) + \hat{U}_{30}(ikl)], \end{aligned} \quad (3)$$

where

$$\hat{U}_{1m}(ikl) = \frac{1}{2} \left[\hat{I}_{im}(\hat{\mathbf{I}}_k \hat{\mathbf{I}}_l) + \sqrt{\frac{2}{5}} \sum_{\mu\nu} C_{2\mu 1\nu}^{1m} \hat{I}_{i\nu} \hat{T}_{2\mu}(kl) \right]$$

and

$$\hat{U}_{3m}(ikl) = \frac{7}{2\sqrt{15}} \sum_{\mu\nu} C_{2\mu 1\nu}^{3m} \hat{I}_{i\nu} \hat{T}_{2\mu}(kl)$$

are irreducible tensors of ranks 1 and 3, respectively.

For the rest of this section of the paper we adopt the same simple model as was analyzed by Haeberlen and Waugh⁴: an isotropically reorienting system of two spins 1/2 separated by a fixed distance r . In this case we are left with only the first term, proportional to \hat{I}_z , in Hamiltonian (3). In a rigid lattice this term leads to only a slight shift of the resonant frequency ω_e (Ref. 17), but under conditions of molecular motion it also contributes to the relaxation, since b_{ik}^2 becomes time-dependent by virtue of the fluctuations in the angle β_{ik} . This term, however, is not averaged to zero by the thermal motion:

$$\langle \hat{\mathcal{H}}_{dp}^{(0)} \rangle = (\omega_L^2 / 2\omega_e) \hat{I}_z,$$

where the angle brackets denote a statistical average over the lattice variables, and where we have used $\omega_L^2 = 3\gamma^4 \hbar^2 / 20r^6$. We write

$$\hat{\mathcal{H}}_{dp}^{(0)} = \langle \hat{\mathcal{H}}_{dp}^{(0)} \rangle + \hat{G}_{dp}^{(0)}, \quad (4)$$

where

$$\hat{G}_{dp}^{(0)} = (3B/8\omega_e) \hat{I}_z \quad (5)$$

$$B = b^2 - \langle b^2 \rangle = b^2 - 4\omega_L^2 / 3 \quad (6)$$

(here we are omitting the subscripts from b_{ik}). The first term in Hamiltonian (4) thus leads to a small constant shift of the frequency ω_e , while the second term causes relaxation.

We now introduce the local field in the rotating coordinate system, averaged over the angle, $\omega_{L\rho}$:

$$\omega_{L\rho}^2 = \text{Sp} \langle (\hat{\mathcal{H}}_{dp}^{(0)})^2 \rangle / \text{Sp} \hat{I}_z^2 = 2\omega_L^4 / 7\omega_e^2. \quad (7)$$

We assume that the correlation time of the molecular motion lies in the range $\omega_e^{-1} \ll \tau_c \ll \omega_L^{-1}$. The first of these inequalities allows us to ignore the nonsecular terms of Hamiltonian (2), and the second allows us to treat $\hat{G}_{dp}^{(0)}$ as a slight perturbation. Using the familiar method^{1,4} for deriving the Bloch equation, we find that the contribution to the transverse relaxation rate from secular Hamiltonian (5) is

$$1/T_{2\rho}^{(0)} = (\omega_L^4 / 49\omega_e^2) [5J_2(0) + 9J_4(0)], \quad (8)$$

where we have introduced the spectral densities

$$J_L(\omega) = 4\pi \int_0^\infty dt \langle Y_{Lm}(t) Y_{Lm}^*(0) \rangle \cos \omega t, \quad (9)$$

and Y_{Lm} is a spherical harmonic of the polar angles of the vector \mathbf{r}_{12} .

The quantity $1/T_{2\rho}^{(0)}$ is proportional to the correlation time, and at $\tau_c \leq \omega_e^{-1}$ it is negligibly small in comparison with the relaxation rate

$$1/T_{2\rho}^{(1)} = 1/3 \omega_L^2 [5J_2(\omega_e) + J_2(2\omega_e)], \quad (10)$$

due to the nonsecular terms of Hamiltonian (2). We can therefore join the regions $\omega_e^{-1} \ll \tau_c \ll \omega_L^{-1}$ and $\tau_c \lesssim \omega_e^{-1}$, setting

$$T_{2p}^{-1} = (T_{2p}^{(0)})^{-1} + (T_{2p}^{(4)})^{-1}. \quad (11)$$

Relation (11) means that we are adopting the expression

$$\hat{\mathcal{H}}_{d_p} = \hat{G}_{d_p}^{00} + b \sum_{m \neq 0} \bar{d}_{0m}^2(\theta_M) \hat{T}_{2m} \quad (12)$$

as the effective Hamiltonian at $\theta = \theta_M$. Strictly speaking, Hamiltonian (12) is "illegitimate," since its first term was derived from its second term. However, when Hamiltonian (12) is analyzed in second-order perturbation theory in a relaxation problem, $\hat{G}_{d_p}^{00}$ gives the fourth-order terms approximately.

For several simple models of rotational motion, the spectral densities (9) have a Lorentzian shape,¹⁸

$$J_L(\omega) = \tau_L / (1 + \omega^2 \tau_L^2). \quad (13)$$

In particular, for a model of arbitrary jumps all the τ_L are equal to τ_c , and in the other limit—of diffusive motion—we define τ_L by

$$\tau_L = [6/L(L+1)] \tau_c.$$

The first model leads to a simple expression for the transverse relaxation rate:

$$T_{2p}^{-1} = \omega_L^2 \tau_c + \frac{\omega_L^2 \tau_c}{3} \left(\frac{5}{1 + \omega_e^2 \tau_c^2} + \frac{1}{1 + 4\omega_e^2 \tau_c^2} \right). \quad (14)$$

It is clear from this discussion that expression (14) holds as long as the inequalities $\omega_L \ll \omega_e$ do. Under typical experimental conditions,^{10,11} these inequalities hold by a wide margin.

Figure 1 shows T_{2p}^{-1} as a function of τ_c^{-1} according to (14) for the typical ratio $\omega_e/\omega_L = 30$. We see that the incorporation of the new secular Hamiltonian (5) gives rise to an ascending branch on the $T_{2p}^{-1}(\tau_c^{-1})$ curve in the region of slow motions. This result means that in addition to the ordinary maximum in the width of the NMR line at $\tau_c \approx \omega_e^{-1}$ we have also acquired a fairly deep minimum at $\tau_c \sim \omega_L^{-1}$. We wish to emphasize that the maximum broadening due to the

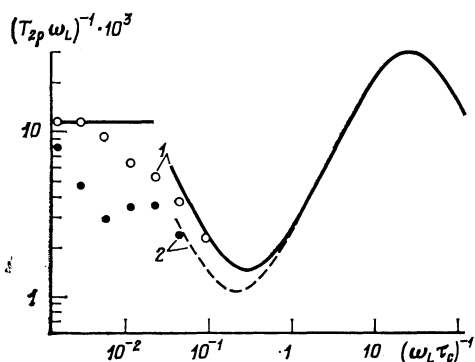


FIG. 1. The transverse relaxation rate in the rotating coordinate system versus the reciprocal of the correlation time for a two-spin system with $\theta = \theta_M$ and $\omega_e/\omega_L = 30$. 1—Model of random rotational jumps; 2—model of a rotational diffusion; curves—calculated from Eqs. (8), (10), and (11); points—results of a numerical solution of Eq. (17); horizontal line—the limit of a rigid lattice.

motion here (under the condition $\tau_c \omega_e = 1$) agrees in order of magnitude with ω_L , i.e., with the width of the line in a rigid lattice. It follows that for correlation times in the interval $\omega_L^{-1} > \tau_c > \omega_e^{-1}$ the molecular motion promotes an rf suppression of the dipole interactions, improving the resolution of this method.

This conclusion agrees with some recent results¹⁹ on multipulse narrowing, but it contradicts the widely held opinion that a natural (thermal) motion of spins could only hinder an artificial "mixing" of these spins by means of rf fields (see Refs. 4 and 6, for example).

We turn now to the solution of this relaxation problem by the random trajectory method. For the system under consideration here Hamiltonian (2) depends on the parameter $x = \cos \beta$, so that we need to introduce a spin density matrix $\hat{\rho}(x, t)$ in the random trajectory method to represent those spin pairs for which this parameter has a given value. The stochastic Liouville equation is

$$\frac{\partial \hat{\rho}}{\partial t} = i[\hat{\rho}(x, t), \hat{\mathcal{H}}_p(x, t)] - \hat{\Gamma} \hat{\rho}(x, t), \quad (15)$$

where the operator $\hat{\Gamma}$ characterizes the Markov process of the motion [the probability that the molecule will have the orientation x satisfies the equation $\partial P(x, t)/\partial t = -\hat{\Gamma} P(x, t)$]. The standard way to analyze Eq. (15) is to reduce it to an infinite system of ordinary differential equations through an expansion of the density matrix in the eigenfunctions of the operator $\hat{\Gamma}$:

$$\hat{\rho}(x, t) = \sum_{k=0}^{\infty} \hat{\rho}_k(t) g_k(x).$$

For simple models of isotropic rotation, in which the spectral densities are of the form in (13), a convenient system of functions $g_k(x)$ is the system of normalized Legendre polynomials of even index:

$$g_k(x) = (2k+1/2)^{1/2} P_{2k}(x).$$

In this case we have

$$\hat{\Gamma} g_k(x) = \tau_{2k}^{-1} g_k(x) \quad (k > 0) \quad (16)$$

(we have $\hat{\Gamma} g_0 = 0$ by virtue of the conservation of the normalization of the probability P). The single-sided Fourier transformation

$$\hat{\varphi}_k(s) = \int_0^{\infty} \hat{\rho}_k(t) \exp(-ist) dt$$

converts the differential equations into algebraic equations. If we assume $s = \mu \omega_e + \sigma$ ($\mu = 0, \pm 1$) and $\sigma \ll \omega_e$, we can show that by ignoring terms of order ω_L/ω_e , which are small in comparison with unity, we can obtain three uncoupled systems of equations which are satisfied by the coefficients

$$f_{\mu k}(\sigma) = \int_0^{\infty} dt e^{-i\sigma t} \int_{-1}^1 S_{\mu}(x, t) g_k(x) dx.$$

Here $S_0(x, t) = S_z(x, t)$ is the spin polarization along the effective field of the pairs of spins which have the orientation x at the time t , and $S_{\pm 1}(x, t) = \mp (S_x \pm iS_y)/\sqrt{2}$ are the trans-

verse polarization components, which rotate at a frequency ω_e around the effective field. It follows that the $\sqrt{2}f_{\mu 0}$ are the Fourier transforms of the total spin polarization, while $\text{Re} f_{\pm 1,0}(\sigma)$ describes the shape of the line which can be observed at $\theta = \theta_M$. The equations for $f_{\mu k}$ are

$$(i\sigma + \tau_{2k}^{-1}) f_{\mu k} - i \sum_j \Omega_{kj}^{(\mu)} f_{\mu j} = \sqrt{2} S_\mu(x, 0) \delta_{k0}, \quad (17)$$

where

$$\Omega_{kj}^{(\mu)} = \frac{1}{4} \sum_i \Psi_{i\mu} \int_{-1}^1 b(x) g_k(x) g_i(x) dx \int_{-1}^1 g_i(x') g_j(x') b(x') dx', \quad (18)$$

$$\Psi_{i,\pm 1} = \pm \tau_{2i} \left(\frac{\xi_i \pm 5i}{1 + \xi_i^2} + \frac{2\xi_i \pm i}{1 + 4\xi_i^2} \right), \quad (19)$$

$$\Psi_{i0} = 2i\tau_{2i} \left(\frac{1}{1 + \xi_i^2} + \frac{2}{1 + 4\xi_i^2} \right),$$

and $\xi_i = \omega_e \tau_{2i}$. If the molecular motion is slow enough to satisfy $\tau_c \gg \omega_e^{-1}$, and if we can ignore terms of order τ_c^{-1} in comparison with ω_e in (19), then we can write

$$\Omega_{kj}^{(\mu)} \approx \frac{3\mu}{8\omega_e} \int_{-1}^1 b^2(x) g_k(x) g_j(x) dx. \quad (20)$$

It follows from (15) that expression (20) corresponds to Hamiltonian (3).

We turn now to Eq. (17), and we assume that the thermal motions are so fast that the following condition holds:

$$\tau_c \ll \omega_e / \omega_L^2. \quad (21)$$

As follows from (17)–(19), under this condition we have $f_{\mu k} \ll f_{\mu 0}$ for $k > 0$. If we also assume that the condition $\sigma \tau_c \ll 1$ holds along with (21), we can write

$$\left[i\sigma - i\Omega_{00}^{(\mu)} + \sum_{k>0} (\Omega_{0k}^{(\mu)})^2 \tau_{2k} \right] f_{\mu 0} = \sqrt{2} S_\mu(x, 0). \quad (22)$$

It follows from this discussion that Eqs. (22) are Fourier transforms of the Bloch equations with the relaxation times

$$T_{1\rho}^{-1} = -i\Omega_{00}^{(0)} + \sum_{k>0} (\Omega_{0k}^{(0)})^2 \tau_{2k}, \quad (23)$$

$$T_{2\rho}^{-1} = \text{Re} \left[-i\Omega_{00}^{(1)} + \sum_{k>0} (\Omega_{0k}^{(1)})^2 \tau_{2k} \right].$$

Substituting (18) and (19) into (23), we find, in particular,

$$T_{2\rho}^{-1} = \frac{\omega_L^2 \tau_2}{3} \left(\frac{5}{1 + \omega_e^2 \tau_2^2} + \frac{1}{1 + 4\omega_e^2 \tau_2^2} \right) + \left(\frac{2\omega_L^2}{21} \right)^2 (5\bar{\tau}_2 + 9\tau_4) \text{Re} \Psi_{11}^2. \quad (24)$$

In this expression the first term is the same as $1/T_{2\rho}^{(1)}$ [see (10)]. It can be shown that if (13) holds then expression (24) will be essentially the same as (11). This means that the simplified analysis which we began with is actually based on the "eclectic" Hamiltonian (12), which has proved to be a rather good approximation.

Expression (23) for $T_{1\rho}$ is essentially the same as the relation derived by Haeberlen and Waugh.⁴ It is not difficult to show that this result also applies to slower motions which would violate condition (21). Specifically, we note that (18) and (19) tells us that all the $\Omega_{kj}^{(0)}$ are on the order of $\omega_L^2 \tau_c / \omega_e^2$, i.e., much smaller than the diagonal coefficients with $k > 0$. It follows that for arbitrary τ_c we can assume

$$T_{1\rho}^{-1} = -i\Omega_{00}^{(0)},$$

which again agrees with Hamiltonian (12), since the secular terms do not contribute to the longitudinal relaxation. The fact that Hamiltonian (12) is successful in describing the relaxation in the region of slow motions raises the hope that it may also be possible to describe the relaxation in multipulse experiments in the region of slow motions if the fluctuating part of the average Hamiltonian^{6,20} is treated in second-order perturbation theory.

To go beyond restrictions (21) in the description of the transverse relaxation and to obtain a gradual transition to a rigid lattice we must solve Eq. (17) directly; this solution requires numerical methods, but the calculations are simplified substantially by the fact that we can use approximation (20) in the region of superslow motions.

The points in Fig. 1 are line half-widths calculated from Eq. (17) under approximation (20). The calculations were carried out by the Lanczos algorithm.^{21,22} As the limit of a rigid body is approached, the line becomes non-Lorentzian, acquiring two peaks which become singularities in the limit $\tau_c \rightarrow \infty$. In this region, the distance between those points on the outer slopes of the peaks which are at half the height of the highest peak is adopted as the line width. Shown for comparison by the horizontal line in Fig. 1 is $5\omega_L^2 / 16\omega_e \approx 0.58\omega_{L\rho}$, half the distance between the singularities in the limit of a rigid lattice.

We see from Fig. 1 that there is a completely definite region of motions with $\tau_c \gg \omega_L^{-1}$ in which the results of the numerical solution of Eq. (17) are essentially the same as the curves plotted from (8), (10), and (11).

The reason for the somewhat nonmonotonic behavior of $T_{2\rho}^{-1}$ as a function of τ_c^{-1} at $(\omega_L \tau_c)^{-1} < 10^{-2}$ is somewhat arbitrary method we have used to determine the line width; this nonmonotonic behavior has no real significance.

3. LONGITUDINAL RELAXATION IN A DOUBLY ROTATING COORDINATE SYSTEM

We turn now to the experiment of Ref. 11, in which the condition $\theta = \theta_M$ was maintained, and in addition another alternating field $2H_2 \cos \Omega t$ was imposed in the direction perpendicular to the effective field, with a frequency and a strength satisfying $\Omega = \omega_e + \Delta'$ and $\gamma H_2 \gg \omega_{L\rho}$. In the doubly rotating coordinate system (the second rotation is around \mathbf{H}_e at the frequency Ω) a new effective field $H'_e = [(\Delta'/\gamma)^2 + H_2^2]^{1/2}$, is acting. This field makes an angle $\theta' = \text{arctg}(\gamma H_2 / \Delta')$ with the "old" field. In an oblique doubly rotating coordinate system whose Z' axis is directed along H'_e , the Hamiltonian of the system becomes

$$\hat{\mathcal{H}}_{\rho\rho} = \omega_e' I_{Z'} + \hat{\mathcal{H}}_{\rho\rho},$$

where $\omega'_e = \gamma H'_e$, and the operator $\hat{\mathcal{H}}_{dpp}$ represents the dipole interaction in the double rotating coordinate system.

To analyze the longitudinal relaxation in the region of superslow motions we follow the recipe formulated in the preceding section: We form $\hat{\mathcal{H}}_{dpp}$ from the sum of Hamiltonians (2) and (3), transformed into the doubly rotating coordinate system. From Hamiltonian (3) we must single out the expectation value $\langle \hat{\mathcal{H}}_{dpp}^{00} \rangle$, since it may in general be nonzero. We thus have

$$\hat{\mathcal{H}}_{dpp} = \hat{G}_{dpp}^{00} + \hat{\mathcal{H}}_{dpp}^{(1)}, \quad \hat{G}_{dpp}^{00} = \hat{\mathcal{H}}_{dpp}^{00} - \langle \hat{\mathcal{H}}_{dpp}^{00} \rangle, \quad (25)$$

and for N spins $1/2$ we find

$$\begin{aligned} \hat{G}_{dpp}^{00} = & \frac{3}{16\omega_e} \sum_{i \neq k} B_{ik} \sum_n d_{0n^1}(\theta') (\hat{I}_{in'} + \hat{I}_{kn'}) \\ & + \frac{1}{\omega_e} \sum_{i \neq k \neq l} D_{ikl} \left[\sum_n d_{0n^1}(\theta') \hat{U}_{1n'}(ikl) \right. \\ & \left. + \sum_n d_{0n^3}(\theta') \hat{U}_{3n'}(ikl) \right], \quad (26) \end{aligned}$$

$$\hat{\mathcal{H}}_{dpp}^{(1)} = - \sum_{m \neq 0} d_{0m^2}(\theta_M) \sum_n d_{mn^2}(\theta') \sum_{i \neq k} b_{ik} \hat{T}_{2n'}(ik), \quad (27)$$

where $B_{ik} = b_{ik}^2 - \langle b_{ik}^2 \rangle$ [cf. (7)] and $D_{ikl} = b_{ik} b_{il} - \langle b_{ik} b_{il} \rangle$. The primes on the operators mean that they are acting in the oblique double rotating coordinate system.

The Bloch equations are strictly applicable only to a two-spin system.¹ The relaxation of a multispin system may be nonexponential, but even in this case the standard expressions for the relaxation times (see Ref. 12, for example) give us the initial slope of the relaxation curve. It is in this sense that we should understand T_{1pp} , the longitudinal relaxation time in the doubly rotating coordinate system, which will be calculated from Hamiltonian (25). By analogy with partition (8), we introduce the times $T_{1pp}^{(0)}$ and $T_{1pp}^{(1)}$, defined by Hamiltonians (26) and (27), respectively. The terms in these Hamiltonians which are secular in the effective field \mathbf{H}'_e are proportional to $d_{00}^1(\theta')$ or $d_{00}^3(\theta')$, vanishing at $\theta' = \pi/2$; i.e., this angle is a magic angle in the doubly rotating coordinate system.¹⁷ For $\theta' = \pi/2$ we find

$$\begin{aligned} \frac{1}{T_{1pp}^{(0)}} = & \frac{9}{64\omega_e^2 N} \left\{ \sum_{i \neq k} J_{ik,ik}(\omega_e') + \sum_{i \neq k \neq l} J_{ik,il}(\omega_e') \right. \\ & \left. + \sum_{i \neq k \neq l} \left[\frac{29}{24} J_{ikl,ikl}(\omega_e') \right] \right\}, \quad (28) \end{aligned}$$

$$\begin{aligned} & + \frac{5}{12} J_{ikl,kil}(\omega_e') + \frac{49}{8} J_{ikl,ikl}(3\omega_e') + \frac{49}{4} J_{ikl,kil}(3\omega_e') \left. \right\}, \\ \frac{1}{T_{1pp}^{(1)}} = & \frac{1}{8N} \sum_{i \neq k} [5j_{ik,ik}(\omega_e) + j_{ik,ik}(2\omega_e)], \quad (29) \end{aligned}$$

where we have introduced the spectral densities

$$J_{ik,i'k'}(\omega) = \int_0^\infty dt \cos \omega t \langle B_{ik}(t) B_{i'k'}(0) \rangle,$$

$$J_{ikl,i'k'l'}(\omega) = \int_0^\infty dt \cos \omega t \langle D_{ikl}(t) D_{i'k'l'}(0) \rangle,$$

$$j_{ik,i'k'}(\omega) = \int_0^\infty dt \cos \omega t \langle b_{ik}(t) b_{i'k'}(0) \rangle.$$

Comparison with (10) shows that we have $T_{1pp}^{(1)} = T_{2p}^{(1)}$. In particular, for a two-spin system which undergoes reorientations in arbitrary jumps (see the preceding section) we have

$$T_{1pp}^{-1} = \frac{\omega_L^2 \tau_c}{1 + (\omega_e' \tau_c)^2} + (T_{2p}^{(1)})^{-1}. \quad (30)$$

The first term, $1/T_{1pp}^{(0)}$, can be comparable to the second only in that interval of slow motions in which the condition $\tau_c \gtrsim (\omega_e')^{-1}$ holds; for faster motions, the first term is negligibly small. If $\gamma H_2 \ll \omega_L$, on the other hand, then in the region $\tau_c \gtrsim (\omega_e')^{-1}$ the first term will be predominant, and the curve of T_{1pp}^{-1} versus τ_c^{-1} will have a maximum at $\tau_c^{-1} = \omega_e'$.

The longitudinal relaxation of this model two-spin system in a doubly rotating coordinate system has also been analyzed by the random trajectory method, by analogy with the preceding section. We again found that if we ignore the terms of order ω_L/ω_e and $\omega_L^2/\omega_e \omega_e'$ in comparison with unity we find a result for T_{1pp}^{-1} which is essentially the same as (30). As in the case of T_{1p}^{-1} , we find that relation (30) holds for arbitrary τ_c within the specified accuracy. We may thus expect that result (28) and (29) for a multispin system will also be valid at arbitrary τ_c —more precisely, as long as T_{1pp} is smaller than the corresponding relaxation time in a rigid lattice.

Figure 2 shows curves of T_{1pp}^{-1} versus τ_c^{-1} calculated from (28) and (29) for two spins separated by a fixed distance and for three spins at the vertices of an equilateral triangle under the assumption that the isotropic rotation occurs either in a diffusive manner or in arbitrary jumps. We see that there are extrema or inflection points on the curves at $\tau_c^{-1} \approx \omega_e'$, i.e., at $\tau_c \sim 10^{-3}$ – 10^{-2} s. Consequently, measurements of T_{1pp} by the method of Ref. 11 can indeed furnish information on some extremely slow molecular motions.

We wish to emphasize that, as can be seen from Fig. 2, we have the freedom of choosing between different models for the molecular motion; there is essentially no such flexibility in the measurements of T_{1p} . To illustrate the situation

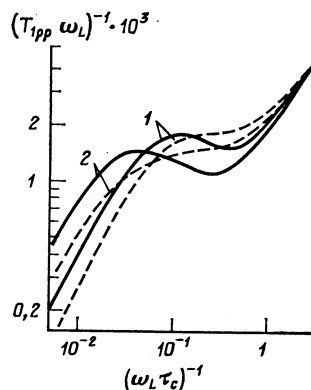


FIG. 2. Longitudinal relaxation rate in a doubly rotating coordinate system versus the reciprocal of the correlation time for $\theta = \theta_M$, $\theta' = \pi/2$, $\omega_e/\omega_L = 30$, and $\omega_e'/\omega_L = 0.1$. 1—Model of random rotational jumps; 2—Model of a rotational diffusion; solid lines—two-spin system; dashed lines—three-spin system.

we could plot, instead of $(T_{1\rho\rho}\omega_L)^{-1}$ in Fig. 2, the corresponding curves for the quantity $(T_{1\rho}\omega_L)^{-1}$; we would find that all four curves merge to form a common curve. The reason why the measurements of $T_{1\rho\rho}$ are more informative is that, according to (28), the values of $T_{1\rho\rho}$ are expressed in terms of both two-particle and three-particle autocorrelation and cross-correlation functions, not simply in terms of two-particle autocorrelation functions, as T_1 and $T_{1\rho}$ are. It would be particularly promising to use measurements of $T_{1\rho\rho}$ to study diffusion in crystals, since in diffusion by a vacancy mechanism there would be a correlation in the motions of the atoms which would have a slightly effect on the values of T_1 and $T_{1\rho}$ (Ref. 23). Measurements of $T_{1\rho\rho}$ thus not only extend the range of motions which can be studied but also furnish substantially more information about these motions.

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