

EFFECT OF THE SHAPE OF MOLECULES ON THE MAGNETIC RELAXATION RATE IN LIQUIDS

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The rate of the magnetic relaxation due to Brownian rotation of nonspherical liquid molecules (of the symmetric and asymmetric top type) is calculated.

THE theory of magnetic relaxation under the action of rotation of the molecules in liquids has been studied repeatedly.^[1-4] However, all these researches have a common failing—the theory has been constructed for spherical molecules whose Brownian rotation is characterized by a single rotational diffusion constant $D = kT/8\pi\eta a^3$ (η is the viscosity of the liquid, a is the radius of the molecules). The aim of the present research was to develop a theory applicable to nonspherical molecules, characterizing their Brownian rotation by the diffusion tensor D_{jk} . Our calculations were carried out separately for quadrupole and dipole interactions of the nuclear spins, and also for the anisotropic g factor and hyperfine interaction constant in the case of the electron spins; in each case, molecules are considered that are of the type of symmetric or asymmetric tops (we define the symmetry of the top according to the properties of the rotational diffusion tensor of the molecule in the liquid and not by its moment of inertia tensor).

1. THE GREEN'S FUNCTION OF THE EQUATION OF ROTATIONAL DIFFUSION OF NONSPHERICAL MOLECULES

The equation describing the rotational diffusion of a particle of arbitrary shape was found by Favro;^[5] it has the form

$$\partial\omega/\partial t = -\hat{M}_j D_{jk} \hat{M}_k \omega, \quad j, k = x, y, z. \quad (1)$$

Here x, y, z are the laboratory coordinates; \hat{M}_j is the operator of rotation about the axis J ; D_{jk} are the components of the rotational diffusion tensor which is expressed in terms of the tensor of viscous friction β_{ij} by*

*Calculation of β_{jk} is carried out by hydrodynamic methods (see[6]).

$$D_{jk} = \frac{1}{2} \lim_{\Delta t \rightarrow 0} \frac{\overline{\alpha_j \alpha_k}}{\Delta t} = \frac{1}{2} kT (\beta_{jk}^{-1} + \beta_{kj}^{-1}) \quad (2)$$

(α_j, α_k are the rotations of the molecule about the axes j and k in the time Δt). In the case of a spherical particle of radius a , we have $\beta_{jk} = \delta_{jk} \cdot 8\pi\eta a^3$.

We fix the orientation of the molecule by specifying the Eulerian angles α, β, γ between the laboratory axes (x, y, z) and the axes of the molecular system (assuming the latter to be directed along the principal axes of the tensor D_{jk}).

We seek the Green's function of Eq. (1), which satisfies the condition

$$G(0) = \delta(\alpha - \alpha^0, \beta - \beta^0, \gamma - \gamma^0), \quad (3)$$

in the form of an expansion in the eigenfunctions $\psi_\nu(\alpha, \beta, \gamma)$ of the operator $\hat{M}_j \hat{D}_{jk} \hat{M}_k$, which is on the right side of (1):

$$\hat{M}_j D_{jk} \hat{M}_k \psi_\nu = D_\nu \psi_\nu. \quad (4)$$

In this way, it is easy to find

$$G(t) = \sum_\nu \psi_\nu^*(\alpha^0, \beta^0, \gamma^0) \psi_\nu(\alpha, \beta, \gamma) \exp(-D_\nu |t|). \quad (5)$$

$G(t)$ represents the probability density that at the moment t the molecule will have the orientation α, β, γ if it had the orientation $\alpha^0, \beta^0, \gamma^0$ at the moment $t = 0$.

It is not difficult to note that upon the substitution $D_{jk} \rightarrow \frac{1}{2} \hbar^2 J_j J_k$ the operator $\hat{M}_j \hat{D}_{jk} \hat{M}_k$ is identical with the Hamiltonian of a top with inertia tensor J_{jk} . Therefore, the ψ_ν in (4) and (5) are orthonormalized wave functions of the quantum mechanical top, and the D_ν are obtained from the energy eigenvalues of the top by the substitution

*For the solution of Eq. (1) Favro chose the Cayley-Klein parameters as the variables fixing the orientation of the molecule; however, the Eulerian angles are much more convenient in specific problems.

shown. In the case of a symmetric top we have (see [7,8]):

$$D_\nu = D_{mn}^{(l)s} = D_1 l(l+1) + (D_3 - D_1) n^2, \quad (6)$$

$$\psi_\nu = \psi_{mn}^{(l)} = \left(\frac{2l+1}{8\pi^2} \right)^{1/2} T_{mn}^{(l)}(\alpha, \beta, \gamma), \quad -l \leq m, n \leq l, \quad (7)$$

$$G^s(t) = \sum_{l,m,n} \frac{2l+1}{8\pi^2} \bar{T}_{mn}^{(l)}(\alpha^0, \beta^0, \gamma^0) T_{mn}^{(l)}(\alpha, \beta, \gamma) \times \exp(-D_{mn}^{(l)s} |t|). \quad (8)$$

Here $T_{mn}^{(l)}$ are the generalized spherical functions satisfying the relation (see [8])

$$\frac{1}{8\pi^2} \int \bar{T}_{m_1 n_1}^{(l_1)}(\alpha, \beta, \gamma) T_{m_2 n_2}^{(l_2)}(\alpha, \beta, \gamma) \sin \beta \, d\beta d\alpha d\gamma = \frac{1}{2l_1+1} \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{n_1 n_2}. \quad (9)$$

In the case of an asymmetric top, we use perturbation theory to find ψ_ν and D_ν . [7] We write down the quantities found in such a way with $l=2$, $-2 \leq m, n \leq 2$ (we shall not need the explicit form of the remaining functions):

$$D_{m,-2}^{(2)a} = 3(D+D_3), \quad \psi_{m,-2}^{(2)} = \frac{\sqrt{5}}{4\pi} (T_{m,2}^{(2)} - T_{m,-2}^{(2)}),$$

$$D_{m,-1}^{(2)a} = 3(D+D_2), \quad \psi_{m,-1}^{(2)} = \frac{\sqrt{5}}{4\pi} (T_{m,1}^{(2)} - T_{m,-1}^{(2)}),$$

$$D_{m,0}^{(2)a} = 3(D+D_1), \quad \psi_{m,0}^{(2)} = \frac{\sqrt{5}}{4\pi} (T_{m,1}^{(2)} + T_{m,-1}^{(2)}),$$

$$D_{m,1}^{(2)a} = 6D + 2g_D,$$

$$\psi_{m,1}^{(2)} = \frac{\sqrt{5}}{4\pi} \left[\sqrt{\frac{c_+}{4g_D}} (T_{m,2}^{(2)} + T_{m,-2}^{(2)}) - \sqrt{\frac{c_-}{2g_D}} T_{m,0}^{(2)} \right],$$

$$D_{m,2}^{(2)a} = 6D - 2g_D,$$

$$\psi_{m,2}^{(2)} = \frac{\sqrt{5}}{4\pi} \left[\sqrt{\frac{c_-}{4g_D}} (T_{m,2}^{(2)} + T_{m,-2}^{(2)}) + \sqrt{\frac{c_+}{2g_D}} T_{m,0}^{(2)} \right];$$

$$D = \frac{1}{3} D_{ij}, \quad g_D = (D_1^2 + D_2^2 + D_3^2 - D_1 D_2 - D_2 D_3 - D_3 D_1)^{1/2}, \quad c_\pm = 2g_D \pm 3(D_3 - D). \quad (10)$$

Here D_1, D_2, D_3 are the principal values of the tensor D_{jk} . The indices s and a refer to molecules of the type of symmetric (s) and asymmetric (a) tops.

2. RELAXATION OF NUCLEAR SPINS BY QUADRUPOLE INTERACTIONS

The quadrupole relaxation of nuclear spins in molecular liquids (spherical molecules) was first studied by Masuda. [3] We consider the more complicated case of nonspherical molecules.

According to the conditions of the problem, the energy of the individual nucleus is composed of the Zeeman energy in the external field h_0 (this part \mathcal{H}_0 of the Hamiltonian determines the stationary energy levels of the nuclear spin J) and the

energy of the quadrupole moment of the nucleus in the charge cloud of the molecule (the perturbation \mathcal{H}' , which produces transitions between the stationary levels):

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}' = -g\beta_N h_0 \hat{J}_z + \frac{1}{6} \sum_{i,j} q_{ij} \Phi_{ij};$$

$$q_{ij} = P \left[\frac{3}{2} \{J_i J_j\} - \delta_{ij} J(J+1) \right], \quad P = eQ/J(2J-1);$$

$$\Phi_{ij} = \partial^2 \varphi / \partial x_i \partial x_j, \quad \{J_i J_j\} = J_i J_j + J_j J_i; \quad (11)$$

the z axis of the laboratory system is parallel to the field h_0 ; φ is the potential of the field at the nucleus, produced by the electron cloud of the molecule.

We introduce five independent components φ_m and q_m ($m = -2, -1, 0, 1, 2$) of the symmetric tensors φ_{ij} and q_{ij} (with zero trace) by means of the relations

$$\varphi_{\pm 2} = \frac{1}{2} (\varphi_{xx} - \varphi_{yy}) \pm i\varphi_{xy}, \quad \varphi_{\pm 1} = \mp \varphi_{xz} - i\varphi_{yz};$$

$$\varphi_0 = \frac{\sqrt{6}}{2} \varphi_{zz}; \quad (12)$$

$$q_2 = q_{-2}^* = \frac{3P}{2} J_+^2, \quad q_1 = -q_{-1}^* = \frac{3P}{2} \{J_z J_+\};$$

$$q_0 = \frac{\sqrt{6}}{2} P [3J_z^2 - J(J+1)]; \quad J_\pm = J_x \pm iJ_y. \quad (13)$$

It is easy to establish the fact that

$$\sum_{i,j} q_{ij} \Phi_{ij} = \sum_m q_{-m} \varphi_m.$$

Making use of the transformation rule

$$\varphi_m = \sum_n T_{mn}^{(2)}(\alpha, \beta, \gamma) \varphi'_n, \quad (14)$$

we find the matrix element of the perturbation \mathcal{H}' , which corresponds to the transition $M \rightarrow M-m$:

$$\mathcal{H}'_{M, M-m} = \frac{1}{6} (q_{-m})_{M, M-m} \sum_n T_{m,n}^{(2)}(\alpha, \beta, \gamma) \varphi'_n, \quad (15)$$

$$|\overline{\mathcal{H}'_{M, M-m}}|^2 = \frac{1}{36} |(q_{-m})_{M, M-m}|^2 \cdot \frac{2}{15} g_\varphi^2, \quad (16)$$

$$g_\varphi^2 = \frac{3}{2} \sum_n |\varphi'_n|^2 = \frac{1}{2} [(\varphi_{zz} - \varphi_{\eta\eta})^2 + (\varphi_{\eta\eta} - \varphi_{\zeta\zeta})^2 + (\varphi_{\zeta\zeta} - \varphi_{\xi\xi})^2 + 6(\varphi_{\xi\eta}^2 + \varphi_{\eta\zeta}^2 + \varphi_{\zeta\xi}^2)]. \quad (17)$$

φ'_n are constant parameters which depend on the charge distribution in the molecule and consequently characterize the molecular structure; their determination is one of the purposes of magnetic-resonance investigations; g_φ is an invariant of the tensor φ_{ij} (coefficient of anisotropy).

The changes in the matrix element (15) with time are random; therefore, the probability $A_{MM'}$ of the relaxation transition $M \rightarrow M'$ can be computed from the formula [1]

$$A_{MM'} = \hbar^{-2} \int_{-\infty}^{+\infty} K_{MM'}(t) \exp(-i\omega_{MM'} t) dt, \quad (18)$$

where $K_{MM'}(t)$ is the time correlation function of the random quantity $\mathcal{H}'_{MM'}(t)$, and is determined by the formula

$$K_{MM'}(t) = \frac{1}{8\pi^2} \int \mathcal{H}'_{MM'}(\alpha^0, \beta^0, \gamma^0) \mathcal{H}'_{MM'}^*(\alpha, \beta, \gamma) G \\ \times (0, \alpha^0, \beta^0, \gamma^0; t, \alpha, \beta, \gamma) \\ \times \sin\alpha^0 d\alpha^0 d\beta^0 d\gamma^0 \sin\beta d\beta d\alpha d\gamma. \quad (19)$$

Carrying out the successive integrations in (19) and (18) with the functions $G(t)$ from (8) and (10), we find the general formula for the correlation function and the probability of the relaxation transition

$$K_{M, M-m}(t) = |\overline{\mathcal{H}'_{M, M-m}}|^2 \sum_{n=-2}^2 \Omega_n \exp(-D_{mn}^{(2)} |t|), \quad (20)$$

$$A_{M, M-m} = \frac{2\pi}{\hbar^2} |\overline{\mathcal{H}'_{M, M-m}}|^2 \sum_n \Omega_n \rho(D_{mn}^{(2)}), \quad (21)$$

where

$$\Omega_{\pm 2}^s = \frac{3}{2} g_\varphi^{-2} |\varphi'_{\pm 2}|^2 = \frac{3}{2} g_\varphi^{-2} [\varphi_{\xi\xi}^2 + \frac{1}{4} (\varphi_{\xi\xi} - \varphi_{\eta\eta})^2],$$

$$\Omega_{\pm 1}^s = \frac{3}{2} g_\varphi^{-2} |\varphi'_{\pm 1}|^2 = \frac{3}{2} g_\varphi^{-2} [\varphi_{\xi\xi}^2 + \varphi_{\eta\xi}^2],$$

$$\Omega_0^s = \frac{3}{2} g_\varphi^{-2} \varphi_0^2 = \frac{9}{4} g_\varphi^{-2} \varphi_{\xi\xi}^2, \quad (22)$$

$$D_{m, \pm 2}^{(2)s} = 2D_1 + 4D_3, \quad D_{m, \pm 1}^{(2)s} = 5D_1 + D_3, \quad D_{m, 0}^{(2)s} = 6D_1,$$

$$\Omega_{-2}^a = \frac{3}{4} g_\varphi^{-2} |\varphi'_2 - \varphi'_{-2}|^2 = 3g_\varphi^{-2} \varphi_{\xi\xi}^2,$$

$$\Omega_{-1}^a = \frac{3}{4} g_\varphi^{-2} |\varphi'_1 - \varphi'_{-1}|^2 = 3g_\varphi^{-2} \varphi_{\xi\xi}^2,$$

$$\Omega_{1,2}^a = \frac{3}{4} g_\varphi^{-2} \left| \sqrt{\frac{c_\pm}{4g_D}} (\varphi'_2 + \varphi'_{-2}) \mp \sqrt{\frac{c_\mp}{2g_D}} \varphi'_0 \right|^2 \\ = \frac{3}{4} g_\varphi^{-2} \left| \sqrt{\frac{c_\pm}{4g_D}} (\varphi_{\xi\xi} - \varphi_{\eta\eta}) \mp \sqrt{\frac{3c_\mp}{4g_D}} \varphi_{\xi\xi} \right|^2,$$

$$\Omega_0^a = \frac{3}{4} g_\varphi^{-2} |\varphi'_1 + \varphi'_{-1}|^2 = 3g_\varphi^{-2} \varphi_{\xi\xi}^2;$$

$$\rho(x) = (x/\pi)/(x^2 + \omega_{MM'}^2). \quad (23)$$

The values of $D_{mn}^{(2)a}$ are given by the formulas (10). It is not difficult to establish the fact that $\sum \Omega_n = 1$. It is also easy to show that the formula (21) for the case of a symmetric top, under the assumptions made in the work of Masuda (spherical molecules), transforms to the well known formula (see [3])

$$A_{M, M-m} = 2\hbar^{-2} |\overline{\mathcal{H}'_{M, M-m}}|^2 \tau_c / (1 + \omega_{MM'}^2 \tau_c^2), \\ \tau_c^{-1} = 6D = 3kT/4\pi\eta a^3. \quad (24)$$

Comparing (21) and (24), we see that account of the effect of the shape of the molecules on the rate of magnetic relaxation is taken by replacement of the factor $\rho(6D)$ in (24) by a factor of the form $\sum \Omega_n \rho(D_{mn}^{(2)})$, in which the quantities Ω_n and $D_{mn}^{(2)}$ are determined by Eqs. (22) (in the case of a molecule of the type of a symmetric top) and (10) and (23) (in the case of a molecule of the type of an asymmetric top). Correspondingly, the nor-

malized correlation functions of the matrix elements change the form $\exp(-|\tau| \tau_c^{-1})$ to $\sum_n \Omega_n \exp(-|\tau| D_{mn}^{(2)})$. * These results remain valid also in consideration of relaxation in terms of the dipole-dipole interaction of nuclei which enter into the combination of the same molecule. We shall find expressions for the quantities Ω_n in this case.

3. MAGNETIC RELAXATION DUE TO INTRA-MOLECULAR DIPOLE-DIPOLE INTERACTIONS

The energy \mathcal{H}_{jk} of the dipole-dipole interaction of two nuclei j and k in a single molecule (the perturbation which produces relaxation transitions between stationary Zeeman energy levels E_{M_j} = $-g_j \beta_N \hbar_0 M_j$ of spin J_j of the nucleus j) can be represented in the form (see [1,2])

$$\mathcal{H}' = \mathcal{H}'_{jk} = \sum_{m=-2}^2 \mathcal{H}'_{jk}^m = P_{jk} \sum_m A_{-m} \{jk\}_{-m} Y_{2m}(\theta_{jk}, \varphi_{jk}), \quad (25)$$

where

$$\{jk\}_2 = \{jk\}_{-2}^* = \hat{J}_j^+ \hat{J}_k^+, \quad \{jk\}_1 = \{jk\}_{-1}^* = \hat{J}_j^+ \hat{J}_{kz} + \hat{J}_{jz} \hat{J}_k^+,$$

$$\{jk\}_0 = \hat{J}_{jz} \hat{J}_{kz} - \frac{1}{4} (\hat{J}_j^+ \hat{J}_k^- + \hat{J}_j^- \hat{J}_k^+), \quad \hat{J}^\pm = \hat{J}_x \pm i\hat{J}_y;$$

$$A_2 = A_{-2} = A_1 = -A_{-1} = \sqrt{6\pi/5}, \quad A_0 = -\sqrt{16\pi/5}, \\ P_{jk} = g_j g_k \beta_N^2 r_{jk}^{-3}. \quad (26)$$

Here J^2 and J_z are diagonal operators;

\mathbf{r}_{jk} (r_{jk} , θ_{jk} , φ_{jk}) is the radius vector connecting the nuclei j and k in the molecule; in the molecular system of coordinates ξ , η , ζ , the \mathbf{r}_{jk} (r_{jk} , θ'_{jk} , φ'_{jk}) are obviously constants.

The dependence of (25) on the rotations of the molecule is expressed by the presence of the functions $Y_{2m}(\theta_{jk}, \varphi_{jk})$. This dependence can be expressed by the Eulerian angles α , β , γ which fix the orientation of the system ξ , η , ζ (of the molecule) in the system x , y , z , if use is made of the conversion formula [8]

$$Y_{2m}(\theta_{jk}, \varphi_{jk}) = \sum_n T_{mn}^{(2)}(\alpha, \beta, \gamma) Y'_{2n}(\theta'_{jk}, \varphi'_{jk}), \quad (27)$$

where Y'_{2n} are constant numbers which are easy to find if we know the orientation of the axes ξ , η , ζ and the location of the atoms j and k in the molecule. The matrix element of the transition $M_j \rightarrow M_j - m$ [with account of (27)] and its mean square value are equal to

*These conclusions evidently also apply to the relaxation rate T_2^{-1} of the transverse components $\langle M_x \rangle$, $\langle M_y \rangle$ of the nuclear magnetization, which is determined by the value of the diagonal (in the J_z representation) matrix elements of the perturbation.

$$(\mathcal{H}_{jk})_{M_j, M_j-m} = P_{jk} A_{-m} (\{jk\}_{-m})_{M_j, M_j-m} \sum_n T_{mn}^{(2)} Y'_{2n},$$

$$|(\mathcal{H}_{jk})_{M_j, M_j-m}|^2 = P_{jk}^2 A_{-m}^2 |(\{jk\}_{-m})_{M_j, M_j-m}|^2. \quad (28)$$

The calculation, which is similar to that given in Sec. 2, yields the following result for the transition probability of $M_j \rightarrow M_j - m$:

$$A_{M_j, M_j-m}^k = 2\pi\hbar^{-2} |(\mathcal{H}_{jk})_{M_j, M_j-m}|^2 \sum_n \Omega_n \rho(D_{mn}^{(2)}), \quad (29)$$

where the quantities $D_{mn}^{(2)}$ are given by Eq. (10) [or (22)] in the case of an asymmetric [or symmetric] top, and Ω_n by the respective formulas

$$\Omega_n^s = (4\pi/5) |Y'_{2, n}|^2 \quad (30)$$

or

$$\Omega_{-2}^a = (4\pi/10) |Y'_{2,2} - Y'_{2,-2}|^2, \quad \Omega_{-1,0}^a = (4\pi/10) |Y'_{2,1} \mp Y'_{2,-1}|^2,$$

$$\Omega_{1,2}^a = (4\pi/10) |V_{c\pm}/4g_D (Y'_{2,2} + Y'_{2,-2}) \mp V_{c\mp}/2g_D Y'_{2,0}|^2. \quad (31)$$

It is easy to prove* that $\sum_n \Omega_n = 1$. We note that

$$A_{M_j, M_j-m} = \sum_k A_{M_j, M_j-m}^k.$$

The calculation† which establishes the connection of the relaxation time T_1 of the longitudinal component $\langle M_z \rangle$ of the nuclear magnetization with the probabilities $A_{MM'}$ is well known, and we shall not dwell on it (see, for example, [3,9]).

4. RELAXATIONS DUE TO THE ANISOTROPIES OF THE g FACTOR AND THE HYPERFINE STRUCTURE CONSTANT

The relaxation of a paramagnetic particle due to the anisotropies of the g factor and the hyperfine structure constant a_{ij} were first considered (applicable to spherical particles) by McConnell. [4] We generalize his results to the case of particles of the type of symmetric and asymmetric tops.

We divide the Hamiltonian of the paramagnetic ion (complex, molecule) into parts that are independent (\mathcal{H}_0) and dependent (\mathcal{H}') on rotations:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \quad \mathcal{H}_0 = g^1 \beta S_z h_0 + a^1 S_z J_z,$$

$$g^1 = \frac{1}{3} g_{ii}, \quad a^1 = \frac{1}{3} a_{ii},$$

$$\mathcal{H}' = g_{ij}^{11} \beta h_i S_j + a_{ij}^{11} J_i S_j, \quad g_{ij}^{11} = g_{ij} - \delta_{ij} g^1,$$

$$a_{ij}^{11} = a_{ij} - \delta_{ij} a^1, \quad i, j = x, y, z. \quad (32)$$

With the help of the equality $\sum_n |Y'_{2n}|^2 = 5/4\pi$, which follows from the identities $\sum_n |T_{m,n}^{(l)}|^2 = 1$ (the matrix $T_{m,n}^{(l)}$ is unitary) and $T_{0n}^{(l)}(\alpha, \beta, \gamma) = \sqrt{4\pi/(2l+1)} Y_{ln}^(\beta, \gamma)$ ([8], p. 318).

† T_1, T_2 are parameters which are measured by the spin echo method.

\mathcal{H}_0 determines the stationary magnetic energy levels of the ion

$$E_{M_s M_J} = g^1 \beta h_0 M_s + a^1 M_s M_J;$$

\mathcal{H}' is a perturbation which produces transitions between stationary levels. Introducing five independent components g_n and a_n ($n = -2, \dots, 2$) of the tensors g_{ij}^{II} and a_{ij}^{II} by the relations (12), and also identical relations in three independent components V_+, V_0, V_- for the vectors $\mathbf{h}, \mathbf{S}, \mathbf{J}$ ([10], pp. 38):

$$V_{\pm} = (\mp V_x + iV_y)/\sqrt{2}, \quad V_0 = V_z, \quad (33)$$

we transform \mathcal{H}' to the form

$$\mathcal{H}' = \frac{2}{\sqrt{6}} \beta g_0 S_0 h_0 + \frac{1}{\sqrt{2}} \beta h_0 (g_1 S_+ + g_{-1} S_-) + \frac{2}{\sqrt{6}} a_0 S_0 J_0$$

$$+ a_{-2} S_- J_- + a_{-2} J_+ S_+ + \frac{a_1}{\sqrt{2}} (S_0 J_+ + J_0 S_+)$$

$$+ \frac{a_{-1}}{\sqrt{2}} (S_0 J_- + J_0 S_-) + \frac{a_0}{\sqrt{6}} (J_+ S_- + J_- S_+). \quad (34)$$

In (34), it is taken into consideration that $h_+ = h_- = 0$ in the laboratory system (the magnetic field is directed along the z axis). It is easy to see also that

$$(S_+)_{M_s, M_s-1} = -\frac{1}{\sqrt{2}} \sqrt{(S+M_s)(S-M_s+1)},$$

$$(S_-)_{M_s-1, M_s} = \frac{1}{\sqrt{2}} \sqrt{(S+M_s)(S-M_s+1)},$$

$$(S_0)_{M_s, M_s} = M_s \quad (35)$$

(and similarly for J_+, J_-, J_0). It is not difficult now to describe the matrix elements which produce the relaxing transitions $M_s, M_J \rightarrow M'_s, M'_J$ between the energy sublevels of the paramagnetic particle, for example,

$$\mathcal{H}'_{M_s M_J, M_s-1, M_J} = (g_1 \beta h_0 + a_1 M_J) (S_+)_{M_s, M_s-1} / \sqrt{2}.$$

Similarly, one can find the matrix elements of \mathcal{H}' , which correspond to a change in the orientation of the nuclear spin or to a simultaneous change in the orientations of the electronic and nuclear spins.

Making use of the transformation formula (14) of the components g_n and a_n , we can give explicit expressions for the dependence of the matrix elements on the rotations of the paramagnetic particles:

$$\mathcal{H}'_{M_s, M_J; M_s-1, M_J} = \frac{1}{2} \sqrt{(S+M_s)(S-M_s+1)}$$

$$\times \sum_n T_{1,n}^{(2)}(\alpha, \beta, \gamma) (g'_n \beta h_0 + M_J a'_n). \quad (36)$$

In the following, we introduce [similarly to (17)] the coefficients of anisotropy g_a and g_p of the tensors a_{ij} and $p_{ij} = \beta h_0 g_{ij}^{\text{II}} + M_J a_{ij}^{\text{II}}$:

$$g_a^2 = \frac{3}{2} \sum_n |a'_n|^2, \quad g_p^2 = \frac{3}{2} \sum_n |\beta h_0 g'_n + M_J a'_n|^2. \quad (37)$$

Then, in accord with (36), we have

$$|\mathcal{H}_{M_S, M_J; M_S-1, M_J}|^2 = \frac{1}{30} (S + M_S) (S - M_S + 1) g_p^2. \quad (38)$$

Carrying out the integrations (19) and (18), we find for the probabilities of the relaxation transitions

$$A_{M_S, M_J; M_S-1, M_J} = \frac{\pi}{15\hbar^2} (S + M_S) (S - M_S + 1) g_p^2 \sum_n \Omega_n \rho (D_{m, n}^{(2)}), \quad (39.1)$$

$$A_{M_S, M_J; M_S, M_J-1} = \frac{\pi}{15\hbar^2} (J + M_J) (J - M_J + 1) M_S^2 g_a^2 \sum_n \Omega_n \rho (D_{m, n}^{(2)}), \quad (39.2)$$

$$A_{M_S, M_J; M_S-1, M_J-1} = \frac{\pi}{15\hbar^2} (S + M_S) (S - M_S + 1) (J + M_J) (J - M_J + 1) \times g_a^2 \sum_n \Omega_n \rho (D_{m, n}^{(2)}). \quad (39.3)$$

Here the quantities Ω_n are determined by the components of the tensors p_{ij} [in (39)] and a_{ij} [in (39.2) and (39.3)], similar to (22) in the case of a symmetric top, or (23) in the case of an asymmetric top; the quantities $D_{mn}^{(2)}$ are given by (22) and (10), respectively.

From (39.1) it is easy to obtain the result of McConnell:^[4]

$$A_{M_S, M_S-1} = \frac{1}{15\hbar^2} (S + M_S) (S - M_S + 1) \times (\beta h_0 \Delta g + M_J b)^2 \tau_c / (1 + \omega_0^2 \tau_c^2), \quad (40)$$

inasmuch as for the spherical top,

$$D_{mn}^{(2)} = 6D = \tau_c^{-1} = 3kT/4\pi\eta a^2,$$

while in the case of the axially symmetric tensors a_{ij}^{II} and g_{ij}^{II} we have

$$\begin{aligned} a'_1 &= a'_{-1} = a'_2 = a'_{-2} = g'_1 = g'_{-1} = g'_2 = g'_{-2} = 0, \\ a'_0 &= \frac{\sqrt{6}}{2} a_{33}^{\text{II}} = \frac{\sqrt{6}}{2} (a_{33} - a^1) \\ &= \frac{\sqrt{6}}{2} \left(A - \frac{1}{3} (A + 2B) \right) = \sqrt{\frac{2}{3}} b, \\ g'_0 &= \sqrt{\frac{2}{3}} \Delta g, \\ g_p^2 &= \frac{3}{2} \sum_n |\beta h_0 g'_n + M_J a'_n|^2 = (\beta h_0 \Delta g + M_J b)^2. \end{aligned} \quad (41)$$

The notation of McConnell has been used in (41).

The contribution of the spin-lattice relaxation to the width of the electron resonance lines, corresponding to the transition $M_S - 1, M_J \rightarrow M_S, M_J$ is equal to the sum of the widths of the levels $(M_S - 1, M_J)$ and (M_S, M_J) ; the width $\Delta\nu_{M_S M_J}$

of the level (M_S, M_J) is equal to the sum of all the relaxation transitions from it to all the remaining levels:

$$\Delta\nu_{M_S M_J} = \sum_{M'_S M'_J} A_{M_S, M_J; M'_S M'_J}.$$

In such a method of calculation, contributions to the width of the electron resonance line that are purely electronic will be taken into account, as well as the electron-nuclear and purely nuclear relaxation transitions.

The so-called secular broadening ($1/T'_2$) of the resonance line $M_S - 1, M_J \rightarrow M_S, M_J$ corresponds to the diagonal matrix element of the perturbation \mathcal{H}' (34); according to McConnell, $1/T'_2$ can be found from the equation ($S = 1/2$)

$$(T'_2)^{-2} = (32\pi/45) (\Delta g \beta h_0 + b M_J)^2 h^{-2} \tan^{-1}(2\tau_c/T'_2). \quad (42)$$

The generalizations of this equation to the case of nonspherical molecules will be

$$(T'_2)^{-2} = (32\pi/45) g_p^2 h^{-2} \sum_n \Omega_n \tan^{-1}(2/D_{m, n}^{(2)} T'_2). \quad (43)$$

Application of the formulas obtained for the analysis of magneto-resonance experiments allows us to obtain more detailed information on the structure, Brownian rotation, and interactions of molecules in liquids.

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