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

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The magnetic-resonance line widths and longitudinal relaxation times for nonspherical liquid particles are calculated by the Kubo and Tomita method. The Brownian rotation of the particles is characterized by the diffusion tensor D_{ij}. The calculations are performed for quadrupole and dipole interactions between nuclear spins, as well as for anisotropic g factors and hyperfine and Stark interaction constants in the case of electron spins.

THE Brownian rotation of molecules in liquids determines the character of a wide range of phenomena: the width of vibrational lines of combination scattering and infrared absorption, the spectrum of Rayleigh scattering, depolarization of fluorescence radiation, magnetic relaxation, and so forth. In the theories of these phenomena one generally uses the hydrodynamic Stokes formula to determine the rate of Brownian rotation of the molecules: $D = kT/8\pi\eta a^3$ (D is the rotational diffusion constant, a the "radius" of the molecule, and η the viscosity of the liquid). Since this formula applies to spherical particles, the discrepancies observed between experimental and calculated values of D are often attributed to a failure to take the shape of the molecule (almost always nonspherical) into account. Thus, so long as these theories do not take molecular shape into account, it will be difficult to solve the fundamental question of the applicability of hydrodynamics to the analysis of the Brownian rotation of molecules.

A number of calculations taking molecular shape into account have been performed by one of the present authors.[1,2] In these the Brownian rotation was characterized by a rotational diffusion tensor D_{ij} with principal values D_1, D_2, D_3. In particular, the probabilities of relaxation transitions between magnetic sublevels of nonspherical liquid particles were calculated.[1]

Such probability calculations are necessary in the treatment of dynamic processes such as nuclear polarization and saturation; with their aid one can also find the relaxation time T_1, solving the system of kinetic equations for the populations of the spin sublevels of energy. However, such a method for calculating T_1 (and T_2) is not always convenient. Therefore it is expedient to generalize the theory of [1] in the framework of the Kubo and Tomita method [3] of calculation; thereby one obtains at once expressions for the experimentally measured parameters T_1 and T_2. As a result the dependence of T_1 and T_2 on D_1, D_2, D_3 is found. In addition, certain other types of interaction which were not considered in [1] are treated in the present paper.

1. According to Kubo and Tomita,[3] the half-width $\Delta\omega_{1/2} = 1/T_2$ of a magnetic resonance line and the spin lattice relaxation time T_1 are determined by the formulas

$$1/T_2 = \sum_\beta \sigma_{1\beta}^2 \tau'_{1\beta}, \quad 1/T_1 = \sum_\beta \sigma_{0\beta}^2 \tau'_{0\beta}; \tag{1}$$

$$\tau'_{\alpha\beta} = \operatorname{Re} \int_0^\infty e^{i\omega_\beta \tau} f_{\alpha\beta}(\tau)\, d\tau, \tag{2}$$

$$\hbar^2 \sigma_{\alpha\beta}^2 f_{\alpha\beta}(\tau) = \langle \{ [\hat{I}_\alpha, \hat{\mathscr{H}}'_\beta(\tau)] [\hat{\mathscr{H}}'_{-\beta}, \hat{I}_{-\alpha}] \} / \langle |\hat{I}_\alpha|^2 \rangle, \tag{3}$$

$$f_{\alpha\beta}(0) = 1; \quad \{AB\} = {}^1\!/_2 (AB + BA);$$

$$\hat{I}_0 = \hat{I}_z, \; \hat{I}_{\pm 1} = \hat{I}_{x \pm} i\hat{I}_y. \tag{4}$$

Formulas (1) through (4) are valid for $E_l - E_k \ll kT$ and $\sigma\tau_c < 1$ (E_l and E_k are the energies of the magnetic sublevels of the particles; τ_c is a parameter having the meaning of a correlation time of the perturbation $\mathscr{H}'(\tau)$; in our case $\tau_c \approx (1/6D)$. The indicated inequalities are almost always fulfilled for liquids. The angular brackets in Eq. (3) signify averages over the spin and lattice variables with the density matrix of the system; we have $\rho_{spin} = 1/(2I + 1)^{NI}(2S + 1)^{NS}$, since $E_l - E_k \ll kT$.

2. In the case of quadrupole relaxation the perturbation is the energy of the quadrupole moment of the nucleus being considered in the charge cloud of the molecule. The operator for this energy has the form [1]

$$\hat{\mathscr{H}}' = \sum_{\beta=-2}^{2} (-1)^{\beta} \hat{\mathscr{H}}'_{\beta}, \quad \hat{\mathscr{H}}'_{\beta} = \tfrac{1}{6} q_{\beta}\varphi_{-\beta}; \tag{5}$$

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

$$\varphi_0 = \tfrac{1}{2}\sqrt{6}\,\varphi_{zz}; \qquad q_2 = q^*_{-2} = \tfrac{3}{2} P\hat{I}^2_{+},$$

$$-q_1 = q^*_{-1} = \tfrac{3}{2} P(\hat{I}_z\hat{I}_+ + \hat{I}_+\hat{I}_z), \tag{6}$$

$$q_0 = 3\cdot 6^{-1/2} P(3\hat{I}^2_z - I(I+1)), \tag{7}$$

$$\varphi_{ij} = \partial^2\varphi/\partial x_i\,\partial x_j, \quad P = eQ/I(2I-1). \tag{8}$$

Here Q and $\hat{I}$ are the quadrupole moment and the spin of the nucleus, and φ_{ij} is a component of the tensor of the gradient of the moleculer electric field intensity at the nucleus.

The quantities φ_β in (6) vary randomly during Brownian rotations of the molecule

$$\varphi_s = \sum_{p=-2}^{2} T^{(2)}_{sp}(\alpha(t), \beta(t), \gamma(t))\,\varphi'_p, \tag{9}$$

where $T^{(l)}_{sp}(\alpha, \beta, \gamma)$ is an element of the matrix of order l corresponding to a rotation α, β, γ. [4] Equation (9) is valid for the components of any tensor that transforms according to the $l = 2$ representation. Throughout the paper $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ are the Eulerian angles between the axes of laboratory (x, y, z; $z \parallel h_0$) and molecular (ξ, η, ζ) systems, such that the ξ, η, ζ axes are chosen along the principal axes of the diffusion tensor D_{ij}. The ξ, η, ζ axes do not necessarily coincide with the principal axes of φ_{ij} and other tensors to be considered in the following sections.

Using Eq. (5), Eq. (3) can be written in the form

$$\sigma^2_{\alpha\beta} f_{\alpha\beta}(\tau) = \frac{\langle |\{[I_\alpha, q_\beta]\}|^2\rangle \langle |\varphi_\beta(0)|^2\rangle}{36\hbar^2 \langle |I_\alpha|^2\rangle} \frac{\langle \varphi_{-\beta}(\tau)\varphi_\beta(0)\rangle}{\langle|\varphi_\beta(0)|^2\rangle}. \tag{10}$$

In calculating $\sigma^2_{\alpha\beta}$ in Eq. (10) we use the commutation relation [5]

$$[I_{\pm 1}, q_\beta] = \sqrt{(2 \mp \beta)(2 \pm \beta + 1)}\, q_{\beta\pm 1}, \quad [I_z, q_\beta] = \beta q_\beta. \tag{11}$$

It is easy to find the mean values

$$\langle |q_\beta|^2\rangle = \tfrac{8}{15} I(I+1)[I(I+1) - \tfrac{3}{4}](3P/2)^2,$$

$$\langle |\varphi_\beta|^2\rangle = \tfrac{2}{15} g^2_\varphi, \tag{12}$$

$$g^2_\varphi = \tfrac{3}{2} \sum_{n=-2}^{2} |\varphi'_n|^2 = \tfrac{1}{2}[(\varphi_{\xi\xi} - \varphi_{\eta\eta})^2 + (\varphi_{\eta\eta} - \varphi_{\zeta\zeta})^2$$

$$+ (\varphi_{\zeta\zeta} - \varphi_{\xi\xi})^2 + 6(\varphi^2_{\xi\eta} + \varphi^2_{\eta\zeta} + \varphi^2_{\zeta\xi})]. \tag{13}$$

With the aid of Eqs. (11) and (12) we obtain

$$\sigma^2_{1,-2} = \sigma^2_{1,1} = \tfrac{2}{3}\sigma^2_{1,-1} = \tfrac{2}{3}\sigma^2_{1,0} = 2\sigma^2_{0,\pm 1} = \tfrac{1}{2}\sigma^2_{0,\pm 2}$$

$$= \tfrac{2}{75}\hbar^{-2} g^2_\varphi (eQ/I(2I-1))^2 [I(I+1) - \tfrac{3}{4}]. \tag{14}$$

We calculate the correlation function $f_{\alpha\beta}(\tau)$ of the random quantities $\varphi_\beta(\tau)$ by using the probability of a transition $G(\alpha, \beta, \gamma; \tau | \alpha^0, \beta^0, \gamma^0; 0)$ of the molecule from orientation $\alpha^0, \beta^0, \gamma^0$ at time $t = 0$ to the orientation α, β, γ at time τ:

$$f_{\alpha\beta}(\tau) = \langle \varphi_{-\beta}(\tau)\varphi_\beta(0)\rangle / \langle |\varphi_\beta|^2\rangle = f(\tau)$$

$$= \tfrac{1}{8\pi^2}\int \varphi_\beta(\alpha^0, \beta^0, \gamma^0)\varphi_{-\beta}(\alpha, \beta, \gamma)\, G(\alpha, \beta, \gamma; \tau | \alpha^0, \beta^0, \gamma^0; 0)$$

$$\times \sin\alpha^0\, d\alpha^0\, d\beta^0\, d\gamma^0 \sin\alpha\, d\alpha\, d\beta\, d\gamma / \tfrac{2}{15} g^2_\varphi. \tag{15}$$

The probability of the transition $G(\tau)$ is a solution of the equation for the rotational diffusion of a particle [see Eqs. (5) to (10) in [1]].

Performing the integration in Eq. (15), and then in Eq. (2), we obtain

$$f(\tau) = \sum_{l=-2}^{2} \Omega_l \exp(-D_{kl}|\tau|), \tag{16}$$

$$\tau'_{\alpha\beta} = \tau'_\beta = \sum_l \Omega_l \rho(D_{kl}, \beta) = \sum_l \Omega_l D_{kl}(D^2_{kl} + \beta^2\omega^2_z)^{-1}. \tag{17}$$

Here

$$\Omega^{(s)}_{\pm 2} = \tfrac{3}{2} g^{-2}_\varphi [\varphi^2_{\xi\eta} + \tfrac{1}{4}(\varphi_{\xi\xi} - \varphi_{\eta\eta})^2], \quad \Omega^{(s)}_{\pm 1} = \tfrac{3}{2} g^{-2}_\varphi [\varphi^2_{\xi\zeta} + \varphi^2_{\eta\zeta}],$$

$$\Omega^{(s)}_0 = \tfrac{9}{4} g^{-2}_\varphi \varphi^2_{\zeta\zeta}; \quad D^{(s)}_{k,\pm 2} = 2D_1 + 4D_3,$$

$$D^{(s)}_{k,\pm 1} = 5D_1 + D_3, \; D^{(s)}_{k,0} = 6D_1; \tag{18}$$

$$\Omega^{(a)}_{-2} = 3g^{-2}_\varphi \varphi^2_{\xi\eta}, \quad \Omega^{(a)}_{-1} = 3g^{-2}_\varphi \varphi^2_{\xi\zeta}, \quad \Omega^{(a)}_0 = 3g^{-2}_\varphi \varphi^2_{\eta\zeta},$$

$$\Omega^{(a)}_{1,5\mp 0,5} = \tfrac{3}{4} g^{-2}_\varphi \left| \sqrt{C_\pm / 4g_D}\,(\varphi_{\xi\xi} - \varphi_{\eta\eta}) \mp \sqrt{3C_\mp / 4g_D}\,\varphi_{\zeta\zeta} \right|^2; \tag{19}$$

$$D^{(a)}_{k,-2} = 3(D + D_3), \quad D^{(a)}_{k,-1} = 3(D + D_2),$$

$$D^{(a)}_{k,0} = 3(D + D_1), \quad D^{(a)}_{k,1} = 6D + 2g_D, \quad D^{(a)}_{k,2} = 6D - 2g_D;$$

$$D = \tfrac{1}{3} D_{ii}; \quad C_\pm = 2g_D \pm 3(D_3 - D)$$

$$g_D = (D^2_1 + D^2_2 + D^2_3 - D_1D_2 - D_2D_3 - D_3D_1)^{1/2}. \tag{20}$$

The indices s and a differentiate quantities pertaining to molecules of the symmetrical ($D_1 = D_2 \neq D_3$) and asymmetrical type.

Substituting the known values of $\sigma^2_{\alpha\beta}$ (14) and $\tau'_{\alpha\beta}$ (17) into Eq. (1), we have

$$\frac{1}{T_2} = \frac{1}{25}\left(\frac{eQg_\varphi}{\hbar}\right)^2 \frac{I(I+1) - 3/4}{I^2(2I-1)^2} \sum_l \Omega_l [\rho(D_{kl}, 0)$$

$$+ \tfrac{5}{3}\rho(D_{kl}, 1) + \tfrac{2}{3}\rho(D_{kl}, 2)] \tag{21}$$

$$\frac{1}{T_1} = \frac{1}{25}\left(\frac{eQg_{\varphi}}{\hbar}\right)^2 \frac{I(I+1)-{}^3/_4}{I^2(2I-1)^2} \sum_l \Omega_l \left[\frac{2}{3}\rho(D_{kl},\ 1) + \frac{8}{3}\rho(D_{kl},\ 2)\right]. \tag{22}$$

The tensor components φ_{ij} ($i, j = \xi, \eta, \zeta$) have been determined for a large number of molecules from quadrupole resonance spectra in crystals; these data have been collected in [6]. It can be assumed that these quantities do not undergo substantial changes in the transition from the solid to the liquid state. As a result, the unknown parameters in Eqs. (21) and (22) turn out to be the constants of the rotational diffusion of the molecule D_1, D_2, D_3; the latter can be determined from a comparison of the theoretical and experimental values of T_1 and T_2. It can also be noted that in molecular liquids having a quadrupole mechanism for relaxation, the contribution of the dipole mechanism (whether intra- or inter-molecular) becomes insignificant. (We have in mind dipole interaction between nuclear spins.)

The number of measurements on nuclei possessing quadrupole moments is not large (see, e.g., [7]), even though existing spectrometers are capable of readily providing accurate information about molecular motion.

3. We consider magnetic relaxation caused by intra-molecular spin-spin interactions. We begin with the general case, in which the nuclei in the molecule have different spins I and S with gyromagnetic ratios γ_I and γ_S. We shall be interested in the relaxation of spin I. We assume that the interaction between spins I and S is accomplished via dipole and contact forces; the contributions of these interactions to the relaxations can easily be shown to be additive.

The operator for the energy of the dipole interaction has the form

$$\mathcal{H}' = \mathcal{H}'^{ij}_{dip} = P_{ij} \sum_{m,\,n=-1}^{1} (-1)^{n+m}\, Y_2^{-(n+m)}(\theta_{ij},\ \varphi_{ij})\, V_{nm}(I_i,\ S_j), \tag{23}$$

$$Y_2^{k*} = (-1)^k Y_2^{-k}, \quad P_{ij} = (6\pi/5)^{1/2}\gamma_i\gamma_j r_{ij}^{-3}, \tag{24}$$

$$V_{00} = -({}^8/_3)^{1/2} I_z S_z, \quad V_{01} = I_z S_+,$$

$$V_{10} = I_+ S_z \quad V_{11} = -I_+ S_+,$$

$$V_{1,\,-1} = {}^1/_4\,({}^8/_3)^{1/2} I_+ S_-, \quad V_{-n,\,-m} = (-1)^{n+m} V^*_{nm}. \tag{25}$$

where $Y_2^k(\theta_{ij},\ \varphi_{ij})$ are spherical harmonics, and $\mathbf{r}_{ij}(r_{ij},\ \theta_{ij},\ \varphi_{ij})$ is the vector joining nuclei i and j in the molecule. During molecular rotations the functions Y_2^k vary analogously to Eq. (9)

$$Y_2^k(\theta_{ij}(t), \varphi_{ij}(t)) = \sum_l T^{(2)}_{kl}(\alpha(t),\ \beta(t),\ \gamma(t))\, Y_2^l(\theta'_{ij}, \varphi'_{ij}), \tag{26}$$

where θ'_{ij}, φ'_{ij} are the angles of the vector $\mathbf{r}_{ij}$ in the molecular coordinate system.

Besides the temporal dependence of $\mathcal{H}'$ caused by molecular rotations [see Eq. (26)], the spin variable S in $\mathcal{H}'(\tau)$ can also be considered time dependent: $S = S(\tau)$, because the relaxation of spin S is independent of I. For example, nucleus j with spin S can have an electric quadrupole moment, and spin S will relax by the mechanism described in the preceding section.

To calculate relaxation times from Eqs. (1) to (3) we first calculate the statistical moments $\sigma^2_{\alpha\beta}$, keeping in mind that β signifies n, m in the expansion (23):

$$\sigma^2_{100} = \frac{4}{3}\sigma^2_{101} = \frac{4}{3}\sigma^2_{10-1} = \frac{4}{3}\sigma^2_{1-10} = 4\sigma^2_{1-11} = \frac{2}{3}\sigma^2_{1-1-1}$$
$$= \frac{4}{3}\sigma^2_{0-10} = 4\sigma^2_{01-1} = \frac{2}{3}\sigma^2_{0-1-1} = \frac{4}{15}\gamma_i^2\gamma_j^2\hbar^2 S_j(S_j+1) r_{ij}^{-6}. \tag{27}$$

For the correlation function $f^{ij}_{\alpha nm}(\tau)$ we have, instead of Eq. (3),

$$f^{ij}_{\alpha nm}(\tau) = f^{j\,(1)}_m(\tau)\, f^{ij\,(2)}(\tau) = \frac{\langle\{S^j_m(\tau)\, S^j_{-m}(0)\}\rangle}{\langle|S^j_m|^2\rangle}\,\frac{\langle Y_2^{-k}(\tau)\, Y_2^k(0)\rangle}{\langle|Y_2^k|^2\rangle}. \tag{28}$$

The components S^j_m vary with characteristic times (of relaxation) T_{mj} such that we can take

$$f^{j\,(1)}_m = \langle S^j_m(\tau)\, S^j_{-m}(0)\rangle / \langle|S^j_m|^2\rangle = \exp(-|\tau|\, T^{-1}_{mj}). \tag{29}$$

The calculation of $f^{ij(2)}(\tau)$ is carried out as in Sec. 2, since the dependence on molecular rotations is completely determined by Eq. (26), which is analogous to Eq. (9). Thus

$$f^{ij\,(2)}(\tau) = \sum_{l=-2}^{2} \Omega^{(ij)}_l \exp(-D_{kl}|\tau|). \tag{30}$$

where the quantities Ω_l are determined by the equalities

$$\Omega^{(s)}_l(ij) = (4\pi/5)\,|Y'^l_2(\theta'_{ij},\ \varphi'_{ij})|^2, \tag{31}$$

$$\Omega^{(a)}_{-2}(ij) = (4\pi/10)\,|Y'^2_2 - Y'^{-2}_2|^2,$$

$$\Omega^{(a)}_{-0,5\mp0,5} = (4\pi/10)\,|Y'^1_2 \mp Y'^{-1}_2|^2,$$

$$\Omega^{(a)}_{1,5\mp0,5} = (4\pi/10)\,|\sqrt{C_\pm/4g_D}\,(Y'^2_2 + Y'^{-2}_2) \mp \sqrt{C_\mp/2g_D}\,Y'^0_2|^2, \tag{32}$$

and the D_{kl} are given in Eqs. (18) and (20).

Substituting the values found above for $\sigma^2_{\alpha nm}$ (27) and $f_{\alpha nm}(\tau)$ [Eqs. (28) to (3)] into the general formula (1), we obtain the final expression for the relaxation time of the i-th nucleus subjected to intramolecular dipole interaction with the j-th nucleus:

$$T_\alpha^{-1}(ij) = \sum_{l=-2}^{2} \Omega_l(ij) \sum_{n,m=-1}^{1} \sigma^2_{\alpha,\,nm}(ij)(T_{mj}^{-1} + D_{kl})(T_{mj}^{-1} + D_{kl})^2$$

$$+ [n\omega_i + m\omega_j)^2]^{-1},$$

$$T_\alpha^{-1}(i) = \sum_j T_\alpha^{-1}(ij). \qquad (33)$$

It remains to consider the possibility, in the case of inequivalent nuclei, of relaxation of spin I_i via an interaction with the spin S_j of nucleus j of the type $\hbar A_{ij}(I_iS_j)$, where A_{ij} are coupling constants and the time variations of S_j are characterized by the correlation functions (29), as before. The contributions of this mechanism to $T_2^{-1}(ij)$ and $T_1^{-1}(ij)$ are easily obtained (see, e.g., [8]):

$$T_2^{-1}(ij) = {}^1/_3\, S_j(S_j+1)\, A_{ij}^2\, [T_{1j}$$

$$+ T_{2j}(1 + (\omega_i - \omega_j)^2\, T_{2j}^2)^{-1}], \qquad (34)$$

$$T_1^{-1}(ij) = {}^2/_3\, S_j(S_j+1)\, A_{ij}^2 T_{2j}(1 + (\omega_i - \omega_j)^2\, T_{2j}^{-1})^{-1}. \qquad (35)$$

Equations (34) and (35) are for $A_{ij} < T_{\alpha j}^{-1}$; in the opposite case the interaction $\hbar A_{ij}(I_iS_j)$ causes structure in the spectrum of nucleus i. Although the constants A_{ij} are not large ($A_{ij} \lesssim 100$ cps), the contributions (34) and (35) can be commensurate with (33), since it is frequently the case that $T_{\alpha j}^{-1} \ll D_{kl}$.

In the case of equivalent nuclei, when $I_i = I_j$, $\gamma_i = \gamma_j$, it is necessary to set $T_{mj}^{-1} = 0$; then T_2 and T_1 are easily obtained:

$$\frac{1}{T_\alpha(ij)} = \sum_{l=-2}^{2} \Omega_l(ij) \sum_{\beta=-2}^{2} \sigma^2_{\alpha\beta}(ij)\, D_{kl}(D_{kl}^2 + \beta^2\omega_z^2)^{-1}, \qquad (36)$$

where (see [9])

$$\sigma^2_{12} = \sigma^2_{1-1} = \frac{2}{3}\sigma^2_{11} = \frac{2}{3}\sigma^2_{10} = \frac{1}{2}\sigma^2_{0\pm2} = 2\sigma^2_{0\pm1} = \frac{2}{3}\sigma^2,$$

$$\sigma^2_{1-2} = \sigma^2_{00} = 0; \quad \sigma^2 = \frac{3}{5} I(I+1)\gamma_I^4\hbar^2 r_{ij}^{-6}, \qquad (37)$$

and the Ω_l^{ij} are given in (31) and (32).

Nuclei of a single isotope, having the same gyromagnetic ratio, but screened to different degrees from the electron cloud of the molecule and therefore giving distinct, but close lines, can be considered in our treatment as being equivalent, since the measurements of T_1 and T_2 are usually made by the spin-echo method, in which the sample is irradiated by a wide-band impulse.

The successful application of the equations given in Sec. 3 to the analysis of measured values of T_1 for protons on the nonspherical molecules of benzene, naphthalene, and anthracene has been made by Agishev, [10] who also presents formulas for D_1, D_2, D_3 obtained by hydrodynamic methods for viscous liquids and that pertain to molecules whose shape can be approximated by ellipsoids.

4. We now consider the line width and relaxation time of electron resonance in liquids. We begin with relaxation for a nonspherical paramagnetic particle in the case when the isotropic part of the Zeeman and hyperfine interactions of the particle bring about a resolved hyperfine structure (hfs) of the line. The perturbation that widens the hfs lines is contributed by the anisotropic parts $\mathcal{H}'$ of the Zeeman and hyperfine energies and the energy $\mathcal{H}''$ of the Stark interaction [1]:

$$\mathcal{H}'(t) = \sum_{\beta=-1}^{1} S_\beta \Phi_{-\beta}(t), \; S_0 = S_z, \; S_{\pm1} = \mp(S_x \pm iS_y)/\sqrt{2},$$

$$\Phi_0 = 2\cdot6^{-1/2}(\beta g_0 h_0 + a_0 I_0) + 2^{-1/2} a_{-1} I_1 + 2^{-1/2} a_1 I_{-1},$$

$$\Phi_1 = -\overset{*}{\Phi}_{-1} = 2^{-1/2}(\beta g_1 h_0 + a_1 I_0) + a_2 I_{-1} + a_0 I_1/\sqrt{6}, \qquad (38)$$

$$\hat{\mathcal{H}}''(t) = \sum_{\beta=-2}^{2} (-1)^\beta \hat{\mathcal{H}}''_\beta, \quad \mathcal{H}''_\beta = q_\beta(s)\, d_{-\beta}(t),$$

$$q_2 = \overset{*}{q}_{-2} = 2S_1^2, \quad q_1 = \overset{*}{q}_{-1} = \sqrt{2}(S_0S_1 + S_1S_0),$$

$$q_0 = 2\cdot6^{-2}(3S_0^2 - S(S+1)). \qquad (39)$$

The components of the zero-trace symmetrical tensors g_n, a_n, and d_n are determined in the same way as in (6), replacing the φ_{ij} respectively by g_{ij}, a_{ij}, and $1/2d_{ij}$. Because of the Brownian rotation of the molecules the tensor components in (38) and (39), written in the laboratory system of coordinates, depend on time, and this dependence can be expressed in a manner analogous to (9).

By a direct application of (3), it can be shown that the contributions $\hat{\mathcal{H}}'$ and $\mathcal{H}''$ to the line width and relaxation are additive; hence they can be treated separately in the calculation. The statistical moments are easily found:

$$\sigma'^2_{1,\,-1;\,m} = \sigma'^2_{0,\,\pm1;\,m} = \frac{2}{15}\hbar^{-2}\left\{\frac{1}{2} g_p^2(m) + \frac{7}{12} f_m g_a^2\right\}, \qquad (40)$$

$$\sigma'^2_{1,\,0;\,m} = \frac{2}{15}\hbar^{-2}\left\{\frac{2}{3} g_p^2(m) + \frac{1}{2} f_m g_a^2\right\}, \qquad f_m = I(I+1) - m^2,$$

$$\sigma''^2_{1,0} = \sigma''^2_{1,\,-1} = \frac{3}{2}\sigma''^2_{1,\,-2} = \frac{3}{2}\sigma''^2_{1,1} = \frac{3}{2}\sigma''^2_{0,\,\pm1} = \frac{3}{8}\sigma''^2_{0,\pm2}$$

$$= \frac{4}{25}[S(S+1) - \frac{3}{4}]\, g_d^2. \qquad (41)$$

The moments (40) correspond to the transition

$M - 1, m \longleftrightarrow M, m$, whereas the moments (41) are the same for all hfs components in the spectrum. The g_p, g_a, g_d are determined as in (13) via the tensor components $p_{ij}(m) = \beta h_0 g_{ij} + m a_{ij}$, a_{ij}, and d_{ij}, respectively.

For the correlation functions of the quantities $\hat{\mathcal{H}}'$ and $\hat{\mathcal{H}}''$ we obtain from Eq. (3)

$$f'_{\alpha\beta;\,m}(\tau) = f'_{\beta;\,m}(\tau) = \sum_{l=-2}^{2} \Omega_l^{(\beta,\,m)} \exp\left(-D_{kl}\,|\tau|\right), \quad (42)$$

$$\Omega_l^{(0,\,m)} = \left(\tfrac{2}{3} g_p^2(m)\,\Omega_l^p + \tfrac{1}{2} f_m g_a^2 \Omega_l^a\right) \Big/ \left(\tfrac{2}{3} g_p^2(m) + \tfrac{1}{2} f_m g_a^2\right),$$

$$\Omega_l^{(\pm 1,\,m)} = \left(\tfrac{1}{2} g_p^2(m)\,\Omega_l^p + \tfrac{7}{12} f_m g_a^2 \Omega_l^a\right) \Big/ \left(\tfrac{1}{2} g_p^2(m) + \tfrac{7}{12} f_m g_a^2\right), \quad (42')$$

$$f''_{\alpha,\,\beta;\,m}(\tau) = f''(\tau) = \sum_{l=-2}^{2} \Omega_l^d \exp\left(-D_{kl}\,|\tau|\right), \quad (43)$$

where the quantities Ω_l^p, Ω_l^a, Ω_l^d appearing in (42) and (43) are determined analogously to (18) or (19) via the tensor components p_{ij}, a_{ij}, and d_{ij}, respectively.

With the known $\sigma^2_{\alpha\beta;m}$ and $f_{\alpha\beta;m}(\tau)$ of (40) to (43) the half-width of the line $\Delta\omega_{1/2}$ and relaxation rate T_{1m}^{-1} are readily obtained according to Eq. (1):

$$\begin{aligned}\Delta\omega_{1/2,\,m} = \tfrac{2}{15}\hbar^{-2} \sum_{l=-2}^{2} \Big\{ &\left[\tfrac{2}{3} g_p^2 + \tfrac{1}{2} g_a^2 f_m\right] \Omega_l^{(0,\,m)} \rho\left(D_{kl}, \omega_{0,\,m}\right) \\ &+ \left[\tfrac{1}{2} g_p^2 + \tfrac{7}{12} g_a f_m\right] \Omega_l^{(-1,\,m)} \rho\left(D_{kl}, \omega_{-1,\,m}\right) \\ &+ \tfrac{6}{5}\left(S(S+1) - \tfrac{3}{4}\right) g_d^2\,\Omega_l^d \\ &\times \left[\rho\left(D_{kl}, \omega_{0,0}\right) + \tfrac{5}{3}\rho\left(D_{kl}, \omega_{10}\right) + \tfrac{2}{3}\rho\left(D_{kl}, \omega_{-2,0}\right)\right]\Big\}, \end{aligned} \quad (44)$$

$$\begin{aligned}T_{1m}^{-1} = \tfrac{4}{15}\hbar^{-2} \sum_{l=-2}^{2} \Big\{ &\left[\tfrac{1}{2} g_p^2 + \tfrac{7}{12} g_a^2 f_m\right] \Omega_l^{(-1,\,m)} \rho\left(D_{kl}, \omega_{-1,\,m}\right) \\ &+ \tfrac{4}{5}\left(S(S+1) - \tfrac{3}{4}\right) \Omega_l^d g_d^2 \left[\rho\left(D_{kl}, \omega_{1,0}\right) \right. \\ &\left. + 4\rho\left(D_{kl}, \omega_{2,0}\right)\right]\Big\}. \end{aligned} \quad (45)$$

In the functions $\rho(d_{kl}, \omega_{\beta m})$ in (44) and (45) it is sufficient to retain only the electronic precession frequencies ω_S, since usually $\omega_S \gg a^I/\hbar$, so that $\omega_{\beta m} \approx \beta\omega_S$.

Hyperfine structure lines of particles with spin $S = 1/2$ are not broadened by the Stark interaction ($d_{ij} \equiv 0$) and hence remain relatively narrow. As a result, the dependence of the hfs line width on the nuclear quantum number m [11] described by the initial terms of Eqs. (44) and (45) is clearly distinguished in the spectra of spin 1/2 particles. For particles with spin greater than 1/2 the principal contribution to the width is caused, as a rule, by the Stark interaction of the spin of the particle; hence the distinguishment just referred to may not be possible.

Besides broadening caused by Brownian rotation of the particles, that caused by the interaction of the spin with internal vibrations of the particle (ionic complex, molecule) can be important. [12] This broadening, like the Stark broadening, is the same for all hfs components, and can produce the same width for the hfs lines also for spin 1/2 particles. Which of the two indicated widening mechanisms dominates in the case of particles with $S > 1/2$ can be decided on the basis of temperature measurements of electron resonance linewidths.

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