THEORY OF ELECTRON PARAMAGNETIC RESONANCE IN SOLUTIONS

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Abstract

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THEORY OF ELECTRON PARAMAGNETIC RESONANCE IN SOLUTIONS

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In paramagnetic solutions the EPR lines are narrowed as a result of the combined averaging action of the thermal motion of the particles of the solution and the exchange interaction between paramagnetic particles. According to (1), the Hamiltonian $\hat{\mathcal{H}}$ of a system of N identical paramagnetic particles in solution can be represented in the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 + \hat{\mathcal{H}}' = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}'; \tag{1}$$

$$\hat{\mathcal{H}}_1 = \hat{\mathcal{H}}_z^u, \qquad \hat{\mathcal{H}}_2 = \hat{\mathcal{H}}_k + \hat{\mathcal{H}}_e, \qquad \hat{\mathcal{H}}' = \hat{\mathcal{H}}_{SS} + \hat{\mathcal{H}}_T + \hat{\mathcal{H}}_{\text{st}} + \hat{\mathcal{H}}_z^a, \tag{2}$$

i.e., the unperturbed Hamiltonian $\hat{\mathcal{H}}_0$ includes the isotropic part of the Zeeman interaction $\hat{\mathcal{H}}_z^u = g\beta\left(H_0 \sum_k \hat{S}^k\right)$ and the modulating term $\hat{\mathcal{H}}_2$, containing the kinetic energy $\hat{\mathcal{H}}_k$ and the exchange interaction $\hat{\mathcal{H}}_e = \frac{1}{2}\hbar \sum_{k\neq l} J(r_{kl})(\hat{S}^k \hat{S}^l)$; the perturbation $\hat{\mathcal{H}}'$, responsible for the broadening of the EPR line, includes the following interactions: magnetic dipole-dipole

$$\hat{\mathcal{H}}_{SS} = g^2\beta^2 \sum_{k>l} r_{kl}^{-3}\left[(\hat{S}^k \cdot \hat{S}^l) - 3r_{kl}^{-2}(\hat{S}^k \cdot r_{kl})(\hat{S}^l \cdot r_{kl})\right],$$

Stark

$$\hat{\mathcal{H}}_T = \hbar \sum_k \hat{S}^k D_k \hat{S}^k,$$

hyperfine

$$\hat{\mathcal{H}}_{\text{st}} = \hbar \sum_k \hat{I}^k A_k \hat{S}^k$$

and anisotropic Zeeman

$$\hat{\mathscr{H}}_z^a = \beta \sum_k H^0 G_k \hat{S}^k - \beta g \left(H_0 \cdot \sum_k \hat{S}^k \right) .$$

For simplicity, throughout what follows the symmetry of the local electric field at the site of the magnetic particle is assumed to be axial (2). The condition of strong exchange $\langle|\hat{\mathscr{H}}_e|^2\rangle \gg \langle|\hat{\mathscr{H}}'|^2\rangle$ is assumed to be satisfied, so that exchange narrowing occurs (1).

According to Kubo and Tomita (1), the longitudinal relaxation time T_1 and the transverse relaxation time T_2 can be expressed in the form

$$T_1^{-1} = \frac{1}{2} \sum_{\gamma \neq 0} \sigma^2_{z\gamma} \int_{-\infty}^{\infty} \exp(-i\gamma\omega_0\tau)\, f_{z\gamma}(\tau)\, d\tau; \tag{3}$$

$$T_2^{-1} = \frac{1}{2} \sum_{\gamma} \sigma^2_{+\gamma} \int_{-\infty}^{\infty} \exp(-i\gamma\omega_0\tau)\, f_{+\gamma}(\tau)\, d\tau, \tag{4}$$

where

$$\sigma^2_{\lambda\gamma} f_{\lambda\gamma}(\tau) = \frac{\langle [\hat{S}_\lambda, \hat{\mathscr{H}}'_\gamma(\tau)][\hat{\mathscr{H}}'_{-\gamma}(0), \hat{S}_{-\lambda}]\rangle}{\hbar^2 \langle |\hat{S}_\lambda|^2 \rangle} = \frac{\langle |[\hat{S}_\lambda, \hat{\mathscr{H}}'_\gamma(0)]|^2 \rangle}{\hbar^2 \langle |\hat{S}_\lambda|^2 \rangle} f_{\lambda\gamma}(\tau); \tag{5}$$

$$\hat{\mathscr{H}}'_\gamma(\tau) = \exp(it\hat{\mathscr{H}}_2/\hbar)\, \hat{\mathscr{H}}'_\gamma\, \exp(-it\hat{\mathscr{H}}_2/\hbar), \tag{6}$$

where $\hat{S}_z = \sum_k \hat{S}_z^k$, $\hat{S}_\pm = \sum_k (\hat{S}_x^k \pm i\hat{S}_y^k)$. $f_{\lambda\gamma}(\tau)$ has the meaning of a correlation function and describes the rate of change in time of the perturbation under the action of the modulating term $\hat{\mathscr{H}}_2$. At low concentrations of magnetic particles (exchange may be neglected), $\hat{\mathscr{H}}_2 = \hat{\mathscr{H}}_k$, and one usually takes $f_{\lambda\gamma}(\tau) = \exp(-|\tau|/\tau_c)$ (3,1). Conversely, in the absence of motion (solids, supercooled liquids) $\hat{\mathscr{H}}_2 = \hat{\mathscr{H}}_e$, and one may take $f_{\lambda\gamma}(\tau) = \exp(-\omega_e^2\tau^2/2)$ (1). In the general case $\hat{\mathscr{H}}_2 = \hat{\mathscr{H}}_k + \hat{\mathscr{H}}_e$; direct calculation of $f_{\lambda\gamma}(\tau)$ from (5) is difficult because, in a liquid, the exchange-interaction energy $\hat{\mathscr{H}}_e$ is itself modulated by the thermal motion $\hat{\mathscr{H}}_k$ with a certain characteristic time τ_1, so that, approximately, one may put (4)

$$\left\langle \exp(i\tau\hat{\mathscr{H}}_k/\hbar)\hat{\mathscr{H}}_e \exp(-i\tau\hat{\mathscr{H}}_k/\hbar)\hat{\mathscr{H}}_e^* \right\rangle = \left\langle \hat{\mathscr{H}}(\tau)\hat{\mathscr{H}}^* \right\rangle = \left\langle |\hat{\mathscr{H}}_e|^2 \right\rangle \exp(-|\tau|/\tau_1). \tag{7}$$

One may expect that $\tau_1 \lesssim \tau_c$, since the exchange interaction is very sensitive to changes in the mutual positions of the particles. Taking into account that in solutions the exchange energy is much smaller than the kinetic energy, i.e. $\langle|\hat{\mathcal{H}}_e|^2\rangle \ll \langle|\hat{\mathcal{H}}_k|^2\rangle$, (6) can be expanded in a series in powers of $\hat{\mathcal{H}}_e$. Retaining only the first three terms in this series and substituting them into (5), we obtain for $f_{\lambda\gamma}(\tau)$ the approximate expression

$$f_{\lambda\gamma}(\tau) = \exp(-|\tau|/\tau_c)\exp(-\omega_e^2 F(\tau)); \tag{8}$$

where

$$F(\tau) = \int_0^\tau (\tau - \tau')\exp(-|\tau'|/\tau_1)\,d\tau'; \tag{9}$$

$$\omega_e^2 = \left\langle |[\hat{\mathcal{H}}_e, [\hat{S}_\lambda, \hat{\mathcal{H}}'_\gamma]]|^2 \right\rangle / \hbar \left\langle |[\hat{S}_\lambda, \hat{\mathcal{H}}'_\gamma]|^2 \right\rangle . \tag{10}$$

It is easy to verify that

$$F(\tau) \approx \begin{cases} |\tau|\tau_1, & \text{for } \tau_1^{-1}, \tau_c^{-1} \gg \sigma \ (8.1); \\ \tau^2/2, & \text{for } \tau_1^{-1}, \tau_c^{-1} \ll \sigma \ (8.2). \end{cases} \tag{1}$$

Thus, for rapid thermal motion in the system, $\tau_c^{-1} \gg \sigma$, one should use a correlation function of the form

$$f_{\lambda\gamma}(\tau) = \exp[-|\tau|(\tau_c^{-1} + \tau_1\omega_e^2)] = \exp(-|\tau|/K),$$

$$K = \tau_c/(1 + \tau_1\tau_c\omega_e^2), \tag{11}$$

whose characteristic time K takes into account the simultaneous action of exchange and motion. For slow thermal motion, $\tau_c^{-1} \ll \sigma$ (very viscous liquids), one must use the function

$$f_{\lambda\gamma}(\tau) = \exp(-\tau^2\omega_e^2/2). \tag{12}$$

It follows from (12) that in viscous liquids only exchange narrowing is effective (the quantity ω_e coincides with the definition of the exchange frequency (1)). We note that the study of the temperature dependence of T_1 and T_2 makes it possible to choose between (11) and (12). In particular, a weak or even complete independence of T_1 and T_2 from temperature in solutions often indicates the predominant role of exchange narrowing (provided, of course, that the concentration of magnetic particles is sufficient for its occurrence), the theory and applications of which have been developed in (1,4,5).

It can be shown that the contributions to T_1 and T_2 from the various interactions assigned by us to the perturbation $\hat{\mathcal{H}}'$ are additive, and they can be calculated bydifferent. In calculating the contribution to T_1 and T_2 from $\hat{\mathcal{H}}_z^a$, the correlation function (11) simplifies to $f_{\lambda\gamma}(\tau) = \exp(-|\tau|/\tau_c)$, since exchange does not affect the Zeeman energy, $[\hat{\mathcal{H}}_e, \hat{\mathcal{H}}_z^a]$. On the other hand, for the isotropic part of the hyperfine interaction $\hat{\mathcal{H}}_{\text{ct}}^u = \frac{1}{3}(A+2B)\sum_k(\hat{I}^k \cdot \hat{S}^k)$, which does not interact with thermal motion, $[\hat{\mathcal{H}}_k, \hat{\mathcal{H}}_{\text{ct}}^u] = 0$, the correlation function (11) becomes $f_{\lambda\gamma}(\tau) = \exp(-|\tau|\tau_1\omega_e^2)$, which agrees with the result of Ref. (^{4}). Taking these simplifications into account for $\hat{\mathcal{H}}_z^a$ and $\hat{\mathcal{H}}_{\text{ct}}^u$, and using the correlation function (11) for the remaining terms in the perturbation $\hat{\mathcal{H}}'$ (2), after straightforward but rather lengthy calculations we obtain

$$\begin{aligned} T_1^{-1} &= \sigma^2 K\left(\frac{2}{5}\frac{1}{1+\omega_0^2K^2} + \frac{8}{5}\frac{1}{1+4\omega_0^2K^2}\right) \\ T_2^{-1} &= \sigma^2 K\left(\frac{3}{5} + \frac{1}{1+\omega_0^2K^2} + \frac{2}{5}\frac{1}{1+4\omega_0^2K^2}\right) \end{aligned} \quad \text{for } \hat{\mathcal{H}}_{SS} \text{ and } \hat{\mathcal{H}}_T; \tag{12.1}$$

$$\begin{aligned} T_1^{-1} &= \sigma^2 K\,\frac{2}{1+\omega_0^2K^2} \\ T_2^{-1} &= \sigma^2 K\left(1 + \frac{1}{1+\omega_0^2K^2}\right) \end{aligned} \quad \text{for } \hat{\mathcal{H}}_{\text{ct}}^u \text{ and } \hat{\mathcal{H}}_{\text{ct}}^a = \hat{\mathcal{H}}_{\text{ct}} - \hat{\mathcal{H}}_{\text{ct}}^u; \tag{13.1}$$

$$\begin{aligned} T_1^{-1} &= \sigma^2 K\,\frac{2}{1+\omega_0^2K^2} \\ T_2^{-1} &= \sigma^2 K\left(\frac{4}{3} + \frac{1}{1+\omega_0^2K^2}\right) \end{aligned} \quad \text{for } \hat{\mathcal{H}}_z^a, \tag{14.1}$$

where

$$\text{for } \hat{\mathcal{H}}_{SS} \qquad K = \tau_c/(1+\tau_c\tau_1\omega_e^2), \qquad \sigma^2 = g^4\beta^4\hbar^{-2}S(S+1)\sum_l \langle r_{kl}^{-6}\rangle; \tag{15}$$

$$\text{for } \hat{\mathcal{H}}_T \qquad K = \tau_c/(1+\tau_c\tau_1\omega_e^2), \qquad \omega_e^2 = 2J^2S(S+1), \tag{2}$$

$$\sigma^2 = \frac{4}{15}D^2\left[S(S+1) - \frac{3}{4}\right]; \tag{16}$$

$$\text{for } \hat{\mathcal{H}}_{\text{ct}}^u \qquad K = 1/\tau_1\omega_e^2, \qquad \omega_e^2 = \frac{2}{3}J^2S(S+1), \tag{3}$$

$$\sigma^2 = \frac{1}{3}\left[\frac{1}{3}(A+2B)\right]^2 I(I+1); \tag{17}$$

$$\text{for } \hat{\mathscr{H}}^a_{\text{ct}} \qquad K = \tau_c/(1+\tau_c\tau_1\omega_e^2), \qquad \omega_e^2 = \frac{2}{3}J^2S(S+1), \tag{4}$$

$$\sigma^2 = \frac{1}{6}\left[\frac{2}{3}(A-B)\right]^2 I(I+1); \tag{18}$$

$$\text{for } \hat{\mathscr{H}}^a_z \qquad K = \tau_c, \qquad \sigma^2 = \frac{1}{15}\left[(g_\parallel - g_\perp)\beta H_0\hbar^{-1}\right]^2. \tag{19}$$

Here $\omega_0 = g\beta H_0\hbar^{-1}$; $g = \frac{1}{3}(g_\parallel + 2g_\perp)$; D and A, B are the constants of the fine and hyperfine interactions; $g_\parallel$ and $g_\perp$ are components of the G-tensor; $J^2 = N^{-1}\sum_{k\neq l} J_{kl}^2$ is the mean square of the exchange integral. The contribution to T_1 and T_2 from the anisotropy of the g-factor (14.1), has been studied in sufficient detail in (^{4,6}). Here we shall consider in greater detail expressions (12.1)–(13.1), from which it is evident that the dependence of T_1 and T_2 on the temperature and viscosity of the solution is completely determined by the characteristic time K. In particular, for sufficiently strong exchange $\tau_c\tau_1\omega_e^2 \gg 1$, one may put $K = 1/\tau_1\omega_e^2$. Therefore, for

low frequencies, when

$$T_1^{-1} = T_2^{-1} = 2\sigma^2 K \quad \text{for } \omega_0^2 K^2 \ll 1, \tag{20}$$

we obtain

$$T_1^{-1} = T_2^{-1} = 2\sigma^2/\tau_1\omega_e^2. \tag{21}$$

An increase in temperature (or a decrease in viscosity) under such conditions will lead to a broadening of the absorption line and a shortening of T_1, since the effectiveness of exchange decreases because of the shortening of the time τ_1 during which the exchange interaction between two magnetic particles in the solution is realized.

In strong fields $\omega_0^2 K^2 \gg 1$

$$T_1^{-1} \sim \sigma^2/\omega_0^2 K, \qquad T_2^{-1} \sim \sigma^2 K, \tag{22}$$

whence it follows that: 1) $T_1 \gg T_2$ and 2) the type of dependence of T_1 on temperature changes to the opposite as compared with (21).

The dependence of T_1 and T_2 on concentration is contained in K (through $\omega_e^2, \tau_c, \tau_1$), and for the contribution from $\hat{\mathscr{H}}_{SS}$ also in σ (15). For the very lowest concentrations of the paramagnetic substance, when the exchange term in K may be neglected ($K = \tau_c$), expressions (12.1) for the contribution to T_1 and T_2 from $\hat{\mathscr{H}}_{SS}$ and $\hat{\mathscr{H}}_T$ remain valid; while for calculating the contributions from $\hat{\mathcal{H}}_z^a$ and $\hat{\mathcal{H}}_{\mathrm{st}}^a$ one must use the formulas of Ref. (4). The latter is connected with the fact that, in the absence of exchange, $\hat{\mathcal{H}}_{\mathrm{st}}^u$ should be assigned to the unperturbed Hamiltonian $\hat{\mathcal{H}}_0$. In experiment this circumstance appears in the form of hyperfine structure of the EPR spectra.

Let us consider aqueous solutions of Cr^{3+} ions. According to (7), the width of the Cr^{3+} absorption line decreases upon dilution (at room temperature) to $\Delta H = 200$ Oe and is independent of further dilution as well as of the frequency ω_0. This indicates that the contribution of dipole-dipole interactions and of the anisotropy of the g-factor may be neglected. Therefore, using (20) and (16) and taking $S = 3/2$, $\tau_c \simeq 2 \cdot 10^{-11}$ sec, we obtain $D = 0.12\ \mathrm{cm}^{-1}$.

It should be noted that detailed measurements of T_1 and T_2 in paramagnetic solutions can provide information on the structure of paramagnetic centers (fine- and hyperfine-structure constants), on the magnitude of exchange interactions (ω_e), and on the character of motions in the liquid (τ_c, τ_1).

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Note: Figure translations are in progress. See original paper for figures.