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ON THE THEORY OF ELECTRON PARAMAGNETIC RESONANCE IN ELECTROLYTE SOLUTIONS

A. A. KOKIN

Ural' Polytechnical Institute

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The transverse and longitudinal relaxation times and the correction to the gyromagnetic ratio are calculated for electron paramagnetic resonance without taking hyperfine structure into account.

1. The theory developed for the case of nuclear resonance in liquids[1] is commonly used to describe the phenomenon of electron paramagnetic resonance in solutions. In doing this, however, the specific characteristic features of the phenomenon are not taken into account.

In nuclear resonance the principal role is played by the interaction of nuclear magnetic moments in the same molecule and between different molecules of the liquid. In the case of electron resonance in solutions, a significant role is played by the nature of the local electric field in the neighborhood of the ion which undergoes random variations both in magnitude and in its symmetry properties.

The mechanism by means of which the translational Brownian movement of the molecules of the liquid affects the line width of electron magnetic resonance is the same as in the case of nuclear magnetic resonance.

The effect of the asymmetry of the local electric field can be easily taken into account by assuming that only the orientation of the axes of symmetry of the local field has random variations, which may be represented by means of a Brownian rotation of a certain static asymmetric field.

Due to the interaction of this field with the electron cloud of the ion and due to the existence of spin-orbit and spin-spin interaction, the degeneracy of the levels in the system of coordinates associated with the local field is removed either partially or completely, depending on the symmetry of the local field and on whether the number of electrons is odd or even. In the laboratory system of coordinates the result of this splitting is an increase in the width of the absorption line.

2. In the majority of cases of the solid salts that have been studied, the local field may be represented by two components: a strong field of cubic symmetry and a weak field of lower, trigonal or tetragonal symmetry.[2]

At ordinary temperatures those levels are populated which are separated from the ground level by $\lesssim 10^2$ cm^{-1}. In many cases in order to describe the lower energy levels of the ion we may introduce the spin-Hamiltonian:[3]

$$\hat{\mathcal{H}}_s = g_{\parallel}\mu_0 \sum_j \hat{\mathbf{S}}_j \cdot \mathbf{H}_0 + \Delta g \mu_0 \sum_j (\hat{S}_{x'_j} H_{0x'_j} + \hat{S}_{y'_j} H_{0y'_j}) + \hbar D \sum_j \left(\hat{S}^2_{z'_j} - \frac{1}{3} S(S+1)\right), \tag{1}$$

where $\Delta g = g_{\perp} - g_{\parallel}$, while the z'_j axis is the axis of symmetry of the local field of the ion. We shall consider that a similar expression will also hold for an ion in solution.

By introducing the angles ϑ_j and φ_j which the z'_j axis makes with the stationary system of coordinates xyz, we obtain

$$\hat{\mathcal{H}}_s = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}'', \tag{2}$$

where

$$\hat{\mathcal{H}}_1 = \hbar\omega_0 \sum_j \hat{S}_{jz}, \tag{3}$$

$$\hbar\omega_0 = g'\mu_0 H_0, \tag{3'}$$

$$g' = g_{\parallel} + \frac{2}{3}\Delta g. \tag{3''}$$

The operator $\hat{\mathcal{H}}''$ may be regarded as a perturbation if $\Delta g/g \ll 1$, $D/\omega_0 \ll 1$.

3. In addition to $\hat{\mathcal{H}}_S$, the complete Hamiltonian of the system also includes $\hat{\mathcal{H}}_2$, which contains the kinetic energy and the interactions independent of the spins (we do not take exchange interactions into account), and $\hat{\mathcal{H}}'$ — the dipole-dipole magnetic interaction between ions, which is also treated as a perturbation.

If we neglect the correlation between the translational and the rotational motion then the inverse relaxation times and the correction to the gyromagnetic ratio can be separated into two parts, which correspond to the translational and the rotational Brownian motion of the ions. In this procedure the part that corresponds to the translational Brownian motion determined by $\hat{\mathcal{H}}'$ and by the thermal motion of the ions will in the case of electron resonance be the same as in the case of nuclear resonance. The other part of the inverse relaxation times and of the correction to the gyromagnetic ratio due to the rotational Brownian motion must be calculated differently.

The perturbation which depends on the orientation of the local field with respect to the external field is given by $\hat{\mathcal{H}}''$ which can be written in the form

$$\hat{\mathcal{H}}'' = \sum_{\lambda} \hat{\mathcal{H}}''_{\lambda} \quad (\lambda = 0, \pm 1, \pm 2), \tag{4}$$

where

$$\hat{\mathcal{H}}_0 = -\sqrt{16\pi/45}\,\hbar \times \sum_j \left(C\hat{S}_{0j} - D\frac{3\hat{S}_{0j}^2 - S(S+1)}{2}\right) Y_{20}(\vartheta_j \varphi_j); \tag{5}$$

$$\hat{\mathcal{H}}_{\pm 1} = \pm i\sqrt{4\pi/15}\,\hbar \sum_j (C\hat{S}_{\pm 1j} - D(\check{S}_{\pm 1j}\hat{S}_{0j} + \hat{S}_{0j}\hat{S}_{\pm 1j}))\, Y_{2\mp 1}(\vartheta_j \varphi_j); \tag{6}$$

$$\hat{\mathcal{H}}_{\pm 2} = -\sqrt{8\pi/15}\,\hbar D \sum_j \hat{S}^2_{\pm 1j} Y_{2\mp 2}(\vartheta_j \varphi_j); \tag{7}$$

$$\hat{S}_{\pm 1} = \mp (1/\sqrt{2})(\hat{S}_x \pm i\hat{S}_y), \quad S_0 = S_z,$$
$$C = (\Delta g / g')\,\omega_0.$$

Now, by making use of expressions (7) of reference 4 and by assuming the distribution of z'_j to be isotropic, we obtain for $\Omega^2_{\alpha\lambda}$ and $f_\lambda(\tau)$ the following expressions:

$$\begin{gathered} \Omega^2_{00} = \Omega^2_{\pm 1 \mp 2} = 0, \\ \Omega^2_{0\pm 1} = {}^1/_{15}\,[C^2 + D^2(4S(S+1) - 3)/5], \\ \Omega^2_{0\pm 2} = {}^4/_{75} D^2(4S(S+1) - 3), \\ \Omega^2_{10} = {}^4/_{45}\,[C^2 + {}^9/_4 D^2(4S(S+1) - 3)/5], \\ \Omega^2_{1-1} = \Omega^2_{12} = {}^2/_{75} D^2(4S(S+1) - 3), \\ \Omega^2_{11} = {}^1/_{15}[C^2 + {}^3/_5\, D^2(4S(S+1) - 3)], \end{gathered} \tag{8}$$

$$f_\lambda(\tau) = \frac{4\pi}{N}\left\langle \sum_j Y_{2\lambda}(\vartheta_j(\tau)\,\varphi_j(\tau))\, Y^*_{2\lambda}(\vartheta_j \varphi_j)\right\rangle. \tag{9}$$

In the above the angle brackets denote averaging over the angle coordinates.

We choose the correlation function $f_\lambda(\tau)$ to be of the same form as in the case of rotational Brownian motion in nuclear resonance:[4]

$$f_\lambda(t) = f(t) = \exp(-t/\tau'_c). \tag{10}$$

By utilizing the results of reference 4, we can easily obtain expressions for the inverse relaxation times and for the correction to the gyromagnetic ratio in arbitrary fields.

We shall write them down for the case of weak fields when $\omega_0\tau_c \ll 1$, and for the case of strong fields when $\omega_0\tau_c \gg 1$.

In the case of weak fields:

$$\frac{1}{T_\perp} = \frac{6\pi}{5} S(S+1)\, g^4\mu_0^4\hbar^{-2}\frac{N}{V} a^{-3}\tau_c + \left\{\frac{7}{45}C^2 + \frac{2}{15}D^2(4S(S+1) - 3)\right\}\tau'_c; \tag{11}$$

$$\frac{1}{T_\parallel} = \frac{6\pi}{5} S(S+1)\, g^4\mu_0^4\hbar^{-2}\frac{N}{V} a^{-3}\tau_c + \left\{\frac{2}{15}C^2 + \frac{2}{15}D^2(4S(S+1) - 3)\right\}\tau'_c; \tag{12}$$

$$\gamma^* = \gamma\left\{1 + \frac{6\sqrt{2} + 3}{\sqrt{2}}\frac{\pi}{10} S(S+1) \times g^4\mu_0^4\hbar^{-2}\frac{N}{V} a^{-3}\tau_c\sqrt{\tau_c/\omega_0}\right\}. \tag{13}$$

In strong fields:

$$\frac{1}{T_\perp} = \frac{9\pi}{25} S(S+1)\, g^4\mu_0^4\hbar^{-2}\frac{N}{V} a^{-3}\tau_c + \left\{\frac{4}{45}C^2 + \frac{1}{25}D^2(4S(S+1) - 3)\right\}\tau'_c; \tag{14}$$

$$\frac{1}{T_\parallel} = \frac{\sqrt{2} + 1}{30\sqrt{2}}\pi S(S+1)\, g^4\mu_0^4\hbar^{-2}\frac{N}{V} a^{-3}\tau_c(\tau_c\omega_0)^{-3/2}; \tag{15}$$

$$\gamma^* = \gamma\left(1 + \frac{1}{15}(\Delta g / g')^2\right). \tag{16}$$

Here, just as in the case of nuclear resonance, $T_\parallel$ has a minimum in the neighborhood of $\omega_0\tau_c \sim 1$.

4. It is known from experiment that the line width in solution decreases with increasing degree of dilution down to a certain concentration.[2] Thus, in the case of aqueous solutions of salts of Cr^{+++}, VO^{++}, Cu^{++} and Mn^{++} the decrease in line width ceases at a concentration of ~0.1 mole/*l*, with the limiting line width being of the order of 30 Oe in the case of Mn^{++} and 200 Oe in the case of Cr^{+++} at room temperature and for $\omega_0 \sim 7.8 \times 10^7\ \mathrm{sec}^{-1}$.

The particularly small line width in the case of a solution of Mn^{++} is associated with the high symmetry of the local field of the ion. Since in this case the Mn^{++} ion is in an S state, we have $\Delta g = 0$.

Assuming in the case of Mn^{++} $a = 2.4 \times 10^{-8}$ cm[5], $g = 2$, $S = 5/2$, we shall obtain, in accordance with (11)

$$1/T_\perp = 0.25\tau_c N/V + (64/15)\, D^2\tau'_c. \tag{17}$$

By utilizing experimental values[6] for the variation of the half width of the line with concentration ~80 for 1 mole/*l* at 20°C we obtain $\tau_c = 1 \times 10^{-11}$ sec and $D = 0.08\ \mathrm{cm}^{-1}$. If we take in the case of water $\eta = 0.01$ poise, then in the case of the Mn^{++} ion the correlation time corresponding to the rotational motion of the ion is given by $\tau_c = 1.4 \times 10^{-11}$ sec ($\tau_c \approx \tau'_c$).

The value of the constant indicates a stronger asymmetry of the local field in the neighborhood of the ion than in the case of the solid salts of Mn^{++} ($D = 0.01\ cm^{-1}$).

To determine the constants D and Δg for other salts it is necessary to have also the frequency dependence of that part of the half-width of the absorption line which does not depend on the concentration.

In conclusion, it is my duty to express my gratitude to G. V. Skrotskiĭ for discussing this work.

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