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Paramagnetic Resonance Intensity of Anisotropic Substances and Its Influence on Line Shapes

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Zusammenfassung. Für paramagnetische, anisotrope Substanzen wird eine einfache Formel für die Abhängigkeit der epr-Intensität von den Richtungen des statischen und des oszillierenden Magnetfeldes abgeleitet. Dabei wird das Fehlen von Hyperfeinstruktur-Termen vorausgesetzt. Als Anwendung werden Pulver-Linienformen berechnet und verglichen mit solchen, die unter Vernachlässigung der Intensitätsanisotropie bestimmt wurden. Der Einfluss des Feinstrukturterms wird für den axialsymmetrischen Fall studiert.

1. Introduction

Anisotropic paramagnetic centers with a random distribution of orientations are found in a great number of substances - polycrystalline material, powders, glasses[1]), biological samples[2]), matrices containing free radicals[3]), highly viscous solutions[5])[6]). Paramagnetic resonance applied to these substances can provide valuable information. However, the line shapes observed (powder line shapes) can be very complicated. Several papers have been published about this subject[1])[3])[5])[7]). For the calculation of the shape functions, the angular dependence of the absorption intensity arising from one individual paramagnetic center has usually been neglected and some objections concerning this procedure have been made. Recently, Bleaney[8]) determined for an axially symmetric g-tensor the variation of the transition probability with the orientations of the static and the oscillatory magnetic field. He has proved for this case, that the absorption intensity is largest if the two magnetic fields are orthogonal. In this paper, we wish to present a simpler and more general equation for the transition probability and its influence on powder line shapes. In addition, we shall demonstrate the effect of the fine structure term in the Hamiltonian on the intensity and the shapes. We shall neglect hyperfine interactions, spin-spin and spin-lattice broadening by referring to previous publications[1])[3])[6]).

2. Paramagnetic Resonance Intensity

Assuming a spin Hamiltonian

$$\begin{aligned}\mathfrak{H} &= \mathfrak{H}_D + \mathfrak{H}_{\text{st}} + e^{i\omega t}\,\mathfrak{H}_{\text{osc}} \\ &= \hbar^{-1}\,\beta\,\vec{S}\,\boldsymbol{D}\,\vec{S} + \beta\,\vec{H}_{\text{st}}\,\boldsymbol{G}\,\vec{S} + e^{i\omega t}\,\vec{H}_{\text{osc}}\,\boldsymbol{G}\,\vec{S}\end{aligned} \tag{1}$$

we shall neglect $\mathfrak{H}_D$ in a first approximation. $\mathfrak{H}_D$, $\mathfrak{H}_{\text{st}}$ and $\mathfrak{H}_{\text{osc}}$ represent components of the Hamiltonian arising from the fine structure, the static and the oscillatory magnetic field respectively. $\mathfrak{H}_{\text{st}}$ has the following eigenvalues and eigenfunctions:

$$\begin{aligned}&\mathfrak{H}_{\text{st}}\,\psi_M = E_M\,\psi_M\,, \\ &E_M = \hbar\,\beta\,|\boldsymbol{G}\,\vec{H}_{\text{st}}|\,M = \hbar\,\beta\,g\,H_{\text{st}}\,M\,, \\ &M = S,\,S-1,\,\ldots,\,-S+1,\,-S\,.\end{aligned} \tag{2}$$

The transition probability between two of these states, $P_{M,M'}$, is related to the matrix $\langle M\,|\,\mathfrak{H}_{\text{osc}}\,|\,M'\rangle$

$$P_{M,M'} \propto |\langle M\,|\,\mathfrak{H}_{\text{osc}}\,|M'\rangle\,|^2\,. \tag{3}$$

The calculation of $\langle M\,|\,\mathfrak{H}_{\text{osc}}|\,M'\rangle$, which we shall describe below, gives the following result:

$$\begin{aligned}\langle M\,|\,\mathfrak{H}_{\text{osc}}\,|\,M'\rangle &= \hbar\,\beta\,M\,\delta_{M,M'}\,\frac{(\boldsymbol{G}\,\vec{H}_{\text{osc}},\,\boldsymbol{G}\,\vec{H}_{\text{st}})}{|\boldsymbol{G}\,\vec{H}_{\text{st}}|} + \\ &+ \frac{1}{2}\,\hbar\,\beta\,(e^{-i\varphi}\sqrt{S\,(S+1) - M\,(M+1)}\,\delta_{M,M'-1} + \\ &+ e^{+i\varphi}\sqrt{S\,(S+1) - M'\,(M'+1)}\,\delta_{M-1,M'})\,\frac{|\boldsymbol{G}\,\vec{H}_{\text{osc}} \times \boldsymbol{G}\,\vec{H}_{\text{st}}|}{|\boldsymbol{G}\,\vec{H}_{\text{st}}|}\,.\end{aligned} \tag{4}$$

The angle φ depends on the choice of the coordinate system and is not of importance. Equation (4) shows that the only allowed transitions are those with $\Delta M = \pm 1$. Their frequency and intensities are

$$\begin{aligned}&\omega = \beta\,|\boldsymbol{G}\,\vec{H}_{\text{st}}|\,, \\ &P_{M,M+1} \propto [S\,(S+1) - M\,(M+1)]\,\frac{(\boldsymbol{G}\,\vec{H}_{\text{osc}} \times \boldsymbol{G}\,\vec{H}_{\text{st}})^2}{(\boldsymbol{G}\,\vec{H}_{\text{st}})^2}\,.\end{aligned} \tag{5}$$

The absorption intensity $I_{M,M+1}$ is determined by the probability $P_{M,M+1}$ and the population of the levels E_M and E_{M+1}. Neglecting saturation effects, we can take the latter into account by introducting the Boltzmann factor[12])

$$I_{M,\,M+1} = P_{M,\,M+1}\, N_0\, \hbar\, \omega_0\, \omega / (2S+1)\, k\, T\,. \tag{6}$$

$I_{M,\,M+1}$ is a measurable quantity only if the spin S equals 1/2. Otherwise $I_{M,\,M+1}$ represents a first approximation to the Hamiltonian including fine structure or hyperfine interactions. The diagonal elements

$$\langle M \mid \mathfrak{H}_{\mathrm{osc}} \mid M \rangle$$

are important for the evaluation of forbidden transition intensities and distortions of the transition probability given by equation (5).

To consider the problem further, we introduce two orthonormal systems of coordinates, (x) and (x'), (Fig. 1). (x) represents a space-fixed system with the z-axis parallel to $\vec{H}_{\mathrm{st}}$ and $\vec{H}_{\mathrm{osc}}$ lying in the plane $y = 0$. (x') is a body-fixed system with the axes parallel to the principal axes of the g-tensor G. The two systems are related by a pure rotation $(x') = R(\alpha, \beta, \gamma)\,(x)$, where α, β, γ represent the Eulerian angles in the standard notation described by MARGENAU and MURPHY[9]). With our assumptions, we obtain instead of equation (5)

$$\omega = \beta\, g\, H_{\mathrm{st}}\,,$$

$$g^2 = g_1^2 \sin^2\beta \sin^2\gamma + g_2^2 \sin^2\beta \cos^2\gamma + g_3^2 \cos^2\beta\,,$$

$$P_{M,\,M+1} \propto \beta^2\, H_{\mathrm{osc}}^2\, [S\,(S+1) - M\,(M+1)]\, g_1^2\, g_2^2\, g_3^2\, g^{-2}\,.$$

$$\sin^2\vartheta \,.\, \begin{bmatrix} g_1^{-2}\,(\sin\alpha \cos\gamma + \cos\alpha \cos\beta \sin\gamma)^2 + \\ + g_2^{-2}\,(-\sin\alpha \sin\gamma + \cos\alpha \cos\beta \cos\gamma)^2 + \\ + g_3^{-2}\,(-\cos\alpha \sin\beta)^2 \end{bmatrix} . \tag{7a}$$

ϑ denotes the angle between $\vec{H}_{\mathrm{osc}}$ and $\vec{H}_{\mathrm{st}}$. Equation (7a) shows directly, that the intensity of the transition is greatest, if the static field is normal to the oscillatory field. If the two fields are parellel, there is no transition. The former has already been stated by BLEANEY[8]) for a substance with $g_1 = g_2 = g_\perp$, $g_3 = g_{||}$. For axial symmetry of the g-tensor, equations (7a) become

$$g^2 = g_\perp^2 \sin^2\beta + g_{||}^2 \cos^2\beta\,.$$

$$P_{M,\,M+1} \propto \beta^2\, H_{\mathrm{osc}}^2\, [S\,(S+1) - M\,(M+1)]\, g_\perp^2\, g^{-2} \sin^2\vartheta \times$$

$$\times\, (g_{||}^2 \sin^2\alpha + g^2 \cos^2\alpha)\,. \tag{7b}$$

To prove equation (4), we diagonalize $\mathfrak{H}_{st}$ by introducing a coordinate system with the z-axis parallel to $\boldsymbol{G}\,\vec{H}_{st}$. Because this system is connected to the space-fixed system of equation (1) by a pure rotation, the Pauli spin matrices retain their initial form. We split now $\boldsymbol{G}\,\vec{H}_{osc}$ into two components parallel and perpendicular to $\boldsymbol{G}\,\vec{H}_{st}$. This transforms $\mathfrak{H}_{osc}$ into equation (4), its first (second) term corresponding to the component parallel (perpendicular) to $\boldsymbol{G}\,\vec{H}_{st}$.

A different proof can be given by application of the following equation:

$$\langle M \,|\, \mathfrak{H}_{osc}(\boldsymbol{G}\,\vec{H}) \,|\, M' \rangle = \frac{i}{M - M'} \langle M \,|\, \mathfrak{H}(\boldsymbol{G}\,\vec{H}') \,|\, M' \rangle \tag{8}$$

where

$$\boldsymbol{G}\,\vec{H}' = \frac{\boldsymbol{G}\,\vec{H}_{st} \times \boldsymbol{G}\,\vec{H}}{|\boldsymbol{G}\,\vec{H}_{st}|} \,.$$

This relation can be found by the evaluation of

$$\langle M \,|\, \mathfrak{H}_{osc} \cdot \mathfrak{H}_{st} \,|\, M' \rangle - \langle M \,|\, \mathfrak{H}_{st} \cdot \mathfrak{H}_{osc} \,|\, M' \rangle$$

taking into account that for Pauli spin matrices

$$S_i\, S_k - S_k\, S_i = i\,\hbar\,\varepsilon_{ikl}\, S_l \,.$$

3. Powder Line Shapes

We can describe the shape function $S(H)$ by

$$S(H) = N(g_1, g_2, g_3)\, \frac{d(g^2)}{dH}\, \frac{d}{d(g^2)} \int_{g^2_{min}}^{g^2} d\alpha\, \sin\beta\, d\beta\, d\gamma\, I(\alpha, \beta, \gamma)\,, \tag{9}$$

if we assume, that our spectrometer works with a constant frequency ω and a variable magnetic field H_{st}. We have evaluated $S(H)$ before[5]) considering $I(\alpha, \beta, \gamma)$ to be constant. We wish to study the influence of the angular dependance of $I(\alpha, \beta, \gamma)$ on that approximation. Because ω is fixed, the Boltzmann factor of equation (6) remains constant and $I(\alpha, \beta, \gamma)$ can be replaced by $P(\alpha, \beta, \gamma)$ of the equations (7a, b). The integration of equation (9) is carried out in two steps. Because g^2 is independent of the Eulerian angle α, (7a), we start by averaging $P(\alpha, \beta, \gamma)$ over α. By the aid of the transformation

$$t = \sin^2\gamma\,, \qquad s = (g^2 - g_2^2)\,(g_1^2 - g_2^2)^{-1}$$

we reduce the remaining integral into a combination of standard elliptic integrals[10]). The result is

If $H_2 < H_{st} < H_3$,

$$S_{M,M+1}(H, S, M) = N(H_1, H_2, H_3, S) \frac{H^{-2}(S(S+1) - M(M+1))}{\sqrt{(H_3^2 - H_2^2)(H^2 - H_1^2)}} \times$$

$$\times \left[(H^2 H_3^2 + H_1^2 H_2^2) \left(F\left(\frac{\pi}{2}, k\right) - E\left(\frac{\pi}{2}, k\right) \right) + \right.$$

$$\left. + (H^2 H_2^2 + H_1^2 H_3^2)\, E\left(\frac{\pi}{2}, k\right) \right].$$

If $H_1 < H_{st} < H_2$,

$$S_{M,M+1}(H, S, M) = N(H_1, H_2, H_3, S) \frac{H^{-2}(S(S+1) - M(M+1))}{\sqrt{(H_3^2 - H^2)(H_2^2 - H_1^2)}} \times$$

$$\times \left[(H^2 H_1^2 + H_2^2 H_3^2) \left(F\left(\frac{\pi}{2}, k^{-1}\right) - E\left(\frac{\pi}{2}, k^{-1}\right) \right) + \right.$$

$$\left. + (H^2 H_2^2 + H_1^2 H_3^2)\, E\left(\frac{\pi}{2}, k^{-1}\right) \right]$$

where

$$k^2 = \frac{(H_3^2 - H^2)(H_2^2 - H_1^2)}{(H_3^2 - H_2^2)(H^2 - H_1^2)},$$

$$H_k = \frac{\hbar\,\omega}{\beta\, g_k},$$

$$M = -S, -S+1, \ldots, S-1. \tag{10a}$$

$F(\pi/2, k)$ and $E(\pi/2, k)$ are the complete elliptic integrals of the first and the second kind respectively. For an axially symmetric g-tensor, $S(H, S, M)$ is

$$S_{M,M+1}(H, S, M) = N(H_\perp, H_\parallel, S) \frac{(1 + H_\parallel^2 H^{-2})(S(S+1) - M(M+1))}{\sqrt{(H^2 - H_\perp^2)(H_\parallel^2 - H_\perp^2)}}. \tag{10b}$$

Comparison of $S(H, S, M)$ according to (10a, b) with the equations (4) and (7) and figure 2 of the publication already mentioned[5]) shows a comparatively small difference arising from the different $I(\alpha, \beta, \gamma)$. The difference can be of importance if we determine g-values by the method of SEARL *et al.*[4]), taking spin-spin and spin-lattice interactions into account.

4. The Influence of the Fine Structure Term $\mathfrak{H}_D$

The question arises whether the powder line shape of a system with $S > 1/2$ and $D \neq 0$ consists of a superposition of $2\,S$ shapes each roughly corresponding to equations (10a, b). For simplicity, we assume axial symmetry and a tensor $\boldsymbol{D}$

$$D'_{ij} = D\,\delta_{ij} = D\,\delta_{ij}\left(-\frac{1}{3} + \delta_{i3}\right), \tag{11}$$

expressed in the body-fixed system. Diagonalization of $\mathfrak{H}_{\mathrm{st}}$ is achieved by a rotation

$$\begin{aligned} (x'') &= R'(\alpha', \beta', \gamma')\,(x')\,, \\ \alpha' &= \pi - \gamma\,, \\ \beta' &= \tan^{-1}(g_\perp\, g_{||}^{-1} \tan\beta)\,, \\ \gamma' &= \frac{\pi}{2} \end{aligned} \tag{12}$$

where α, β, γ represent the Eulerian angles of Figure 1. In the new coordinates (x'') the total Hamiltonian has the form

$$\begin{aligned} \mathfrak{H} = \beta\, g\, H_{\mathrm{st}} S_z - \frac{1}{3}\hbar^{-1}\beta\, D\, S^2 + \hbar^{-1}\beta\, D\, g^{-2}\,[g_\perp^2 \sin^2\beta\, S_x^2 + g_{||}^2 \cos^2\beta\, S_z^2 + \\ + g_\perp\, g_{||} \sin\beta \cos\beta\,(S_x\, S_z + S_z\, S_x] + \\ + e^{i\omega t} H_{\mathrm{osc}}\, g^{-1}\,[g_\perp\, g_{||} \sin\alpha\, S_x + g_\perp\, g \cos\alpha\, S_y + \\ + (g_{||}^2 - g_\perp^2) \sin\alpha \sin\beta \cos\beta\, S_z]\,. \end{aligned} \tag{13}$$

This equation allows the calculation of forbidden transitions induced by $\mathfrak{H}_D$ (they will not be calculated, because in most cases they do not influence our line shapes). The static components $\mathfrak{H}_{\mathrm{st}}$ and $\mathfrak{H}_D$ are in agreement with those determined by BLEANEY and LOW[11]). We have evaluated, to the first approximation, the energy level E_M, the transition frequency $\omega_{M,\,M+1}$ and the transition probability $P_{M,\,M+1}(D)$ corresponding to the Hamiltonian of equation (13):

$$\begin{aligned} E_M &= \hbar\,\beta\, H_{\mathrm{st}}\, g\, M + \\ &+ \frac{1}{2}\hbar\,\beta\, D\left[M^2 - \frac{1}{3}\, S\,(S+1)\right](3\, g_{||}^2\, g^{-2} \cos^2\beta - 1)\,, \\ \beta^{-1}\,\omega_{M,\,M+1} &= H_{\mathrm{st}}\, g + D\left(M + \frac{1}{2}\right)(3\, g_{||}^2\, g^{-2} \cos^2\beta - 1)\,. \end{aligned} \tag{14a}$$

If $\omega_{M, M+1} = \text{constant} = \omega$,

$$H_{M, M+1} = g^{-1} \left[\beta^{-1} \omega - D \left(M + \frac{1}{2}\right) (2\, g_{\|}^2 + g_{\perp}^2)\, (g_{\|}^2 - g_{\perp}^2)^{-1}\right] + + g^{-3} \left[D \left(M + \frac{1}{2}\right) 3\, g_{\perp}^2\, g_{\|}^2\, (g_{\|}^2 - g_{\perp}^2)^{-1}\right] . \tag{14b}$$

$$\overline{P_{M, M+1}}^{\alpha} (D) / \overline{P_{M, M+1}}^{\alpha} (D = 0) = = 1 + \left(\frac{D}{H_{st}}\right) \left(M + \frac{1}{2}\right) \sin^2\beta \cdot g^{-3} \left(\frac{4\, g^2\, g_{\|}^2 + g^2\, g_{\perp}^2 - 5\, g_{\|}^2\, g_{\perp}^2}{g^2 + g_{\|}^2}\right) \tag{14c}$$

(averaged over α).

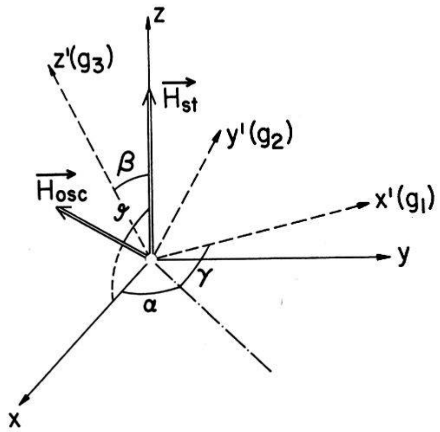

Fig. 1
Experimental arrangement assumed for our calculations

The distortion caused by $\mathfrak{H}_D$ of the simple shape function $S(H, M, S)$ of (10b) can occur in two ways: by the change of $P_{M, M+1}$ and by the influence of the g^{-3} term of $H_{M, M+1}$ in (14b). The former introduces the factor $\overline{P_{M, M+1}}^{\alpha}(D) / \overline{P_{M, M+1}}^{\alpha} (D = 0)$ into equation (10b) and has no serious effects on the line shape. The latter, however, can lead to $dH/d(g^2) = 0$ for a real g-value. In this case, the correspondance between H and g^2 ceases to be one-to-one, thus introducing an additional peak in the shape function. Figure 2 demonstrates an example of this effect, which is absent if ω und D fulfil the condition

$$\frac{\omega}{\beta\, |D|} > 8 \left(S - \frac{1}{2}\right) g_{max}^2\, |g_{\perp}^2 - g_{\|}^2|^{-1} \tag{15}$$

derived from equation (14b). Because of the factor $| g_{\perp}^2 - g_{\|}^2 |^{-1}$, this condition is very restrictive. Therefore, we shall quite often encounter complicated powder line shapes if $S > 1/2$.

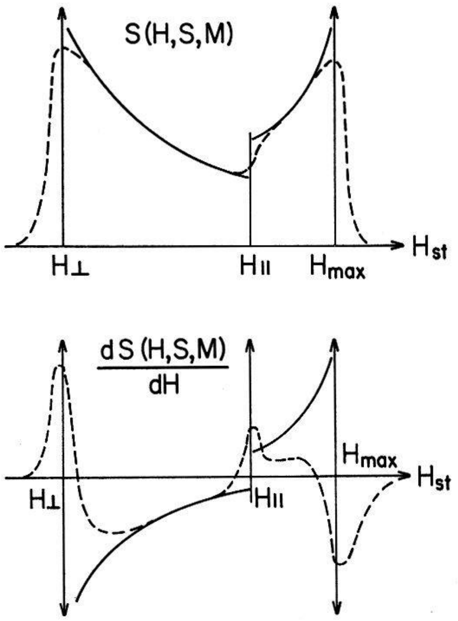

Fig. 2
Single line shape $S(H, S, M)$ and its derivative, which can occur if condition (15) is not fulfilled

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