ESR LINESHAPES AND SATURATION IN THE SLOW MOTIONAL REGION—THE STOCHASTIC LIOUVILLE APPROACH

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XIV.1. GENERAL APPROACH[1]

Let us define an orientation-dependent spin-density matrix, $\sigma(\Omega, t)$ by:

$$\sigma(\Omega, t) = e^{-(i\mathcal{H}^{\times}+\Gamma_{\Omega})t}\,\sigma(0) \tag{1}$$

such that $\langle P_0|\sigma(\Omega, t)|G_0\rangle = \sigma(t)$ as given by eq. VIII-119. Then it obeys the stochastic Liouville equation of motion:[1,2,3]

$$\frac{\partial}{\partial t}\sigma(\Omega, t) = -[i\mathcal{H}(\Omega)^{\times}+\Gamma_{\Omega}]\sigma(\Omega, t). \tag{2}$$

We again consider the steady-state spectrum in the presence of a single rotating rf-field. One has for the λth (multiple) hyperfine line at "orientation" specified by Ω (cf. eq. XVIII-16):

$$P_{\lambda}(\Omega) = 2\mathfrak{N}\hbar\omega\sum_{j} d_{\lambda_j} Z^{(1)''}_{\lambda_j}(\Omega) \tag{3}$$

where P_{λ} is the power absorbed, $\mathfrak{N}$ is the concentration of electron spins, d_{λ_j} is the "transition moment" for the λ_jth component line and is usually given by $d_{\lambda_j} = \frac{1}{2}|\gamma_e|B_1$ (see below), and $Z^{(1)''}_{\lambda_j}$ is defined by the series of equations:

$$(\sigma - \sigma_0)_{\lambda_j} \equiv \chi_{\lambda_j} \tag{4}$$

L. T. Muus et al. (eds.), *Electron Spin Relaxation in Liquids*
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$$\chi_{\lambda_j} = \sum_{n=-\infty}^{\infty} e^{in\omega t} Z_{\lambda_j}^{(n)} \tag{5}$$

and

$$Z_{\lambda_j}^{(n)} = Z_{\lambda_j}^{(n)\prime} + iZ_{\lambda_j}^{(n)\prime\prime} \tag{6}$$

In eq. 4, $\sigma_o(\Omega)$ is the equilibrium spin-density matrix whose Ω dependence is such that $\Gamma_\Omega \sigma_o = 0$. In eq. 5 the steady-state solution, χ_{λ_j} has been expanded in a Fourier series with time independent coefficients $Z_{\lambda_j}^{(n)}$. Thus $\sigma_o(\Omega) = \sigma_o^{(0)}$. Eq. 3 displays the fact that it is the $n = 1$ harmonic which is directly observed. (We will also use $\chi_a^{(0)}$ as the 0th harmonic for the diagonal element corresponding to state a.)

In the above notation σ_{λ_j} means the matrix element of σ:

$$\sigma_{\lambda_j} \equiv \langle \lambda_j - | \sigma | \lambda_j + \rangle \tag{7}$$

where λ_j- and λ_j+ are the two levels between which the λ_jth transition occurs, and a "raising convention" is implied. Some aspects of this notation are discussed in Ch. XVIII.

The total absorption is then obtained as an equilibrium average of eq. 3 over all Ω. Thus we introduce averages such as:

$$\bar{Z}_{\lambda_j}^{(n)} \equiv \langle P_o(\Omega) | Z_{\lambda_j}^{(n)}(\Omega) | P_o(\Omega) \rangle \equiv \int d\Omega \, Z_{\lambda_j}^{(n)}(\Omega) P_o(\Omega) \tag{8}$$

so that

$$P_\lambda = 2\mathfrak{N}\hbar\omega \sum_j d_{\lambda_j} \bar{Z}_{\lambda_j}^{(1)\prime\prime}, \tag{9}$$

where we have taken d_{λ_j} essentially independent of orientation. We now separate $\mathcal{H}$ into three components:

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_1(\Omega) + \mathcal{E}(t) \tag{10}$$

where in the high-field approximation:

$$\hbar\mathcal{H}_o = \bar{g}_s B_e B_o S_z - \hbar \sum_i \gamma_i I_{z_i} B_o - \hbar\gamma_e \sum_i \bar{a}_i S_z I_{z_i} \tag{11}$$

yields the zero-order energy levels and transition frequencies,

$$\mathcal{H}_1(\Omega) = \sum_{L,m,\mu,i} F'^{(L,m)}_{\mu,i}(\Omega) A'^{(L,-m)}_{\mu,i} \tag{12}$$

is the perturbation depending on orientation angles Ω, and $\epsilon(t)$ is given by:

$$\hbar\epsilon_1(t) = \tfrac{1}{2}\hbar\gamma_e B_1 [S_+ \exp(-i\omega t) + S_- \exp(i\omega t)] \tag{13}$$

and is the interaction with the radiation field.

When one takes the $\langle\lambda_{j-}|\ |\lambda_{j+}\rangle$ matrix elements of eq. 2, and utilizes eqs. 4-6, the steady-state equation for $Z^{(1)}_{\lambda_j}$ is found to be in the high temperature approximation (cf. Ch. XVIII):

$$\Delta\omega_\lambda Z^{(1)}_{\lambda_j} + [H_1(\Omega)^\times Z^{(1)}(\Omega)]_{\lambda_j} - i[\Gamma_\Omega Z^{(1)}(\Omega)]_{\lambda_j} + d_{\lambda_j}\left(\chi^{(0)}_{\lambda_{j+}} - \chi^{(0)}_{\lambda_{j-}}\right) = q\omega_\lambda d_{\lambda_j} \tag{14}$$

The equation for $\bar{Z}^{(1)}_{\lambda_j}$ then becomes:

$$\Delta\omega_\lambda \bar{Z}^{(1)}_{\lambda_j} + \int d\Omega [\mathcal{H}_1(\Omega)^\times Z^{(1)}(\Omega)]_{\lambda_j} P_0(\Omega) - i\int d\Omega [\Gamma_\Omega Z^{(1)}(\Omega) P_0(\Omega)]_{\lambda_j} + d\left(\bar{\chi}^{(0)}_{\lambda_{j+}} - \bar{\chi}^{(0)}_{\lambda_{j-}}\right) = q\omega_\lambda d_{\lambda_j} \tag{15}$$

In order to perform the integrations over Ω in eq. 15, we expand the matrix element $Z(\Omega)^{(n)}_{\lambda_j}$ in a complete set of orthogonal eigenfunctions of Γ_Ω, call them $G_m(\Omega)$, with eigenvalues E_m:

$$Z(\Omega,\omega)^{(n)}_{\lambda_j} = \sum_m [C^{(n)}_m(\omega)]_{\lambda_j} G_m(\Omega), \tag{16}$$

or in operator notation:

$$Z(\Omega)^{(n)} = \sum_m C^{(n)}_m(\omega) G_m(\Omega) \tag{16a}$$

where $C_m^{(n)}$ is still an operator in spin space, and is a function of ω, but is independent of Ω. Then eq. 15 becomes:

$$\Delta\omega_\lambda \bar{Z}^{(1)}_{\lambda_j} + \sum_m \int d\Omega P_0(\Omega) G_m(\Omega) [\mathcal{H}_1(\Omega)^\times C^{(1)}_m]_{\lambda_j} + d_\lambda\left(\bar{\chi}^{(0)}_{\lambda_{j+}} - \bar{\chi}^{(0)}_{\lambda_{j-}}\right) = q\omega_\lambda d_\lambda \tag{17}$$

In obtaining eq. 17 we have assumed that $P_0(\Omega)$ gives an isotropic distribution of orientations.

Note also that:

$$\bar{Z}^{(n)}_{\lambda_j} = [C^{(n)}_0]_{\lambda_j} \tag{18}$$

from the definitions of eqs. 8 and 16. Thus the absorption (eq. 9)

depends only on the $[C_o^{(1)}]_{\lambda_j}$ for all allowed transitions λ_j.

When we premultiply eq. 14 by $G_m^*(\Omega)$ and integrate over Ω, we obtain for $[C_m^{(1)}]$ and isotropic orientations:

$$N_{m'}(\Delta\omega_\lambda - iE_{m'})[C_{m'}^{(1)}]_{\lambda_j} + \sum_m \int d\Omega G_{m'}^*(\Omega) G_m(\Omega) [\mathcal{K}_1(\Omega)^\times C_m^{(1)}]_{\lambda_j} +$$

$$N_{m'} d_{\lambda_j} ([C_{m'}^{(0)}]_{\lambda_j +} - [C_{m'}^{(0)}]_{\lambda_j -}) = q\omega_\lambda d_\lambda \delta(m', 0) N_{m'}. \tag{19}$$

Here $N_{m'}$ is a normalizing factor:

$$N_m = \int d\Omega G_m^*(\Omega) G_m(\Omega). \tag{20}$$

Thus the coupling to the Markovian relaxation process of Γ_Ω comes about only if the perturbation $\mathcal{K}_1(\Omega)$ can couple $[C_o^{(1)}]_{\lambda_j}$ to some coefficient $C_m^{(1)}$ where $m \neq 0$.

The above approach, hence eq. 19, is valid for any Markovian or diffusive process. Eq. 19 will yield coupled algebraic equations for the coefficients $[C_m^{(n)}]_{\lambda_j}$, and one attempts to solve for the $[C_o^{(1)}]_{\lambda_j}$ utilizing only a finite number of such coefficients. The convergence depends partially on the ratio $|\mathcal{K}_1(\Omega)|/E_{m'}$. The larger the value of this ratio the more terms $[C_m^{(1)}]_{\lambda_j}$ are needed. The results obtained by second order relaxation theory (cf. Ch. VIII) are recovered when only one order beyond $[C_o^{(1)}]_{\lambda_j}$ is included.

When we apply the method to rotational modulation, then Ω refers to the values of the Euler angles for a tumbling molecular axis with respect to a fixed laboratory axis system. Thus we have for isotropic rotational diffusion (cf. eq. VIII.86):

$$-\Gamma_\Omega \rightarrow R\nabla_\Omega^2 \tag{21}$$

where ∇_Ω^2 is the rotational diffusion operator and R is the diffusion coefficient. Although the method is fully applicable to problems involving completely anisotropic rotational diffusion, we shall assume axially symmetric diffusion for simplicity. Then the complete set of eigenfunctions of Γ_Ω for eq. 21 are the Wigner rotation matrices:

$$E_m = E_{L,K,M} = R_1 L(L+1) + (R_3 - R_1)K^2 \tag{21a}$$

(cf. Sect. VIII.5.B). We now express eq. 12 as (cf. eq. VIII.101):

$$\mathcal{K}_1(t) = \sum_{L,m,m',\mu} \mathfrak{D}^{L}_{-m,m'}(\Omega) F'^{(L,m)}_{\mu} A^{(L,m')}_{\mu} \tag{22}$$

where both the $F'^{(L,m)}_{\mu}$ and the $A^{(L,m')}_{\mu}$ are irreducible tensor components of rank L and component m and m′. The F′ in eq. 22 are expressed in molecule-fixed co-ordinates, while A is a spin operator quantized in space-fixed axes. The $\mathfrak{D}^{L}_{-m,m'}(\Omega)$ terms include the transformation from space-fixed to molecule-fixed axes. It follows from the orthogonality relation[4] of the $\mathfrak{D}^{L}_{KM}$'s that:

$$N^{L}_{KM} = \frac{8\pi^2}{2L+1} \tag{23}$$

and

$$P_o(\Omega) = \frac{1}{8\pi^2} = \frac{1}{8\pi^2}\mathfrak{D}^{0}_{0,0}(\Omega). \tag{24}$$

The evaluation of the integral on the lhs of eq. 19 is obtained utilizing:

$$\int d\Omega \mathfrak{D}_{m_1 m_1'}^{L_1}(\Omega)\mathfrak{D}_{m_2 m_2'}^{L_2}(\Omega)\mathfrak{D}_{m_3 m_3'}^{L_3}(\Omega) = 8\pi^2 \begin{pmatrix} L_1 & L_2 & L_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} L_1 & L_2 & L_3 \\ m_1' & m_2' & m_3' \end{pmatrix} \tag{25}$$

where the terms in parenthesis in eq. 25 are the 3j symbols;[4] also

$$\mathfrak{D}^{L*}_{m,m'} = (-)^{m-m'}\mathfrak{D}^{L}_{-m,-m'}. \tag{26}$$

XIV.2. FREE RADICALS OF S = ½—NO SATURATION[1]

The case of no saturation is achieved by setting $\chi_{\lambda_j+} = \chi_{\lambda_j-} = 0$, so the last term on the lhs of eq. 19 is zero.

A. Axially Symmetric Secular G-Tensor

A particularly simple example of the above formulation is for a one-line ESR spectrum broadened mainly by the secular anisotropic g-tensor term, for which $g_x = g_y = g_\perp$ and $g_z = g_\parallel$. (We assume the z axis of the diffusion tensor is coincident.) When $\omega_o^2\tau_R^2 \gg 1$ the non-secular term will make a negligible contribution compared to the secular term.

For this case eq. 22 is:

$$\mathcal{K}_1(t) = \mathfrak{D}^{2}_{0,0}(\Omega)\tfrac{2}{3}\hbar^{-1}\beta_e B_0(g_\parallel - g_\perp)S_z \equiv \mathfrak{D}^{2}_{0,0}(\Omega)\mathcal{F}S_z. \tag{27}$$

We have

$$-[S_z^{\times} C_m^{(1)}]_{\lambda_j} = [C_m^{(1)}]_{\lambda_j} \tag{28}$$

for a doublet state. When eqs. 27 and 28 are substituted into eq. 19 (for no saturation), and eqs. 23-26 are utilized, then one obtains:

$$[(\omega-\omega_o)-iR_1 L(L+1)][C^L_{o,o}(\omega)]_{\lambda_j} - (2L+1)\mathcal{F}\sum_{L'}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 [C^{L'}_{o,o}(\omega)]_{\lambda_j}$$

$$= q\omega_\lambda d_{\lambda_j}\delta(L,0). \tag{29}$$

Now from eq. 9 the absorption is proportional to:

$$\bar{Z}^{(1)''}_{\lambda_j} = \frac{1}{\pi}\mathrm{Im}[C^0_{0,0}{}^{(1)}]_{\lambda_j}. \tag{30}$$

Equation 29 defines an infinite set of coupled algebraic equations for the complex coefficients $C^L_{0,0}(\omega)$ (where we have dropped the superscript (1) for simplicity). The triangle property of the 3j symbols means, however, that the L^{th} equation is coupled only to the $L\pm2^{th}$ equations, so only even L values appear. Approximations to the complete solution may be obtained by terminating the coupled equations at some finite limit by letting $C^L_{0,0} = 0$ for $L>n$ where, $r = \frac{n}{2}+1$ gives the order of the equations.

One finds that as $|\mathcal{F}/R|$ increases to unity (the region where relaxation theory applies) the main effect on the line shape is a broadening. In the region $|\mathcal{F}/R|$ of 1 to 10 the resonance peak shifts downfield and the shape becomes markedly asymmetric. Between 10 and 100 a new high field peak appears, and at 1,000 the solid-like spectrum is sharpening up (one is observing a decrease of "motional broadening") as it is approaching the powder spectrum. (Jensen in Ch. III Fig. 2 obtains similar results.)

B. Asymmetric Secular G-Tensor

If now we let $g_x \neq g_y$, then

$$\mathcal{H}_1(\Omega) = \mathcal{F}_o \mathfrak{D}^2_{o,o} S_z + \mathcal{F}_2 S_z[\mathfrak{D}^2_{-2,o} + \mathfrak{D}^2_{2,o}] \tag{31}$$

where

$$\mathcal{F}_o = \tfrac{2}{3}[g_z - \tfrac{1}{2}(g_x+g_y)]\hbar^{-1}\beta_e B_o \tag{32a}$$

and

$$\mathcal{F}_2 = \frac{1}{\sqrt{6}} (g_x - g_y)\hbar^{-1}\beta_e B_0 \qquad (32b)$$

The relevant coupled eqs. are given by:

$$(2L+1)^{-1}[(\omega-\omega_0)-iT_2^{-1}-iE_{L,K}]\bar{C}^L_{K,0} - \mathcal{F}_0 \sum_{L'} \begin{pmatrix} L & 2 & L' \\ K & 0 & -K \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\bar{C}^{L'}_{K,0}$$

$$-\mathcal{F}_2 \sum_{L'} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\left[\begin{pmatrix} L & 2 & L' \\ K & -2 & -(K-2) \end{pmatrix}\bar{C}^{L'}_{K-2,0} + \begin{pmatrix} L & 2 & L' \\ K & 2 & -(K+2) \end{pmatrix}\bar{C}^{L'}_{K+2,0}\right] = q\omega_\lambda d_{\lambda j}\delta_{L,0}\delta_{K,0} \qquad (33)$$

where K is positive, $E_{L,K}$ is given by eq. 21a, and eq. 30 as well as the triangle rule requiring $L' = L\pm 2$ or L still holds. Also one must have $K \leq L$, etc. The order of the equations, when one terminates for $L>n$ is now $1+n(\frac{n}{4}+1)$.

The progress of the line shapes as $|\mathcal{F}_0/R|$ increases, is similar to case 1, but in the region of >10 three peaks now appear. Typical results are shown in Fig. 1.

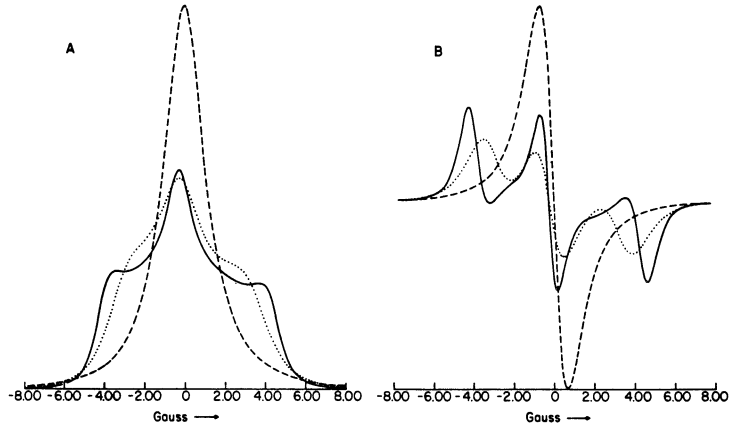

Fig. 1. Lineshapes for an asymmetric g-tensor as a function of $|\mathcal{F}|/R$. A) Absorption Lineshapes; B) First derivative. The different $\mathcal{F}/R$ values are _ _ _5, ...25, _____100. [By permission from Ref. 1.]

C. G-Tensor plus END Tensor Including Pseudosecular Terms

The retention of the pseudo-secular terms (i.e. terms in $I_\pm S_z$) results in $[\mathcal{H}_1, \mathcal{H}_0] \neq 0$, unlike the previous cases.

i) <u>One Nuclear Spin of $I = \frac{1}{2}$</u>. This is the simplest case for illustrating the method. The labelling of the energy levels and

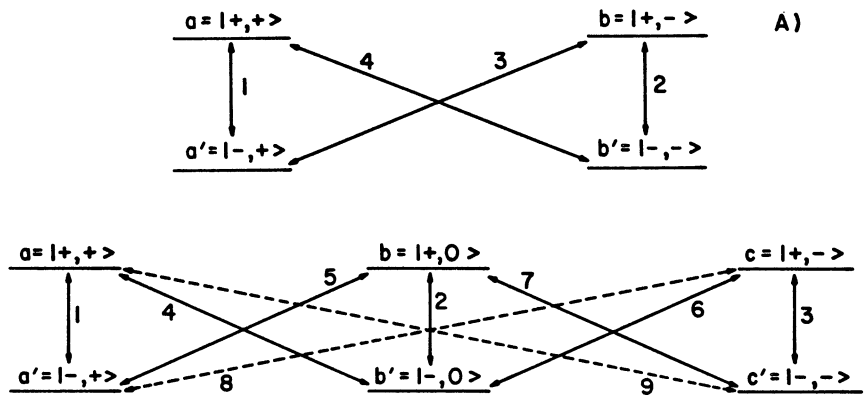

Fig. 2. Energy levels and transitions for A) $S = \frac{1}{2}$, $I = \frac{1}{2}$; B) $S = \frac{1}{2}$, $I = 1$. The notation is $|M_S, M_I\rangle$.

relevant transitions are given in Fig. 2a. The resonance frequencies for the two allowed transitions (1 and 2) and the two forbidden transitions (3 and 4) are:

$$\begin{aligned} \omega_1 &= \omega_{aa'} = \omega_e - \tfrac{1}{2}\gamma_e \bar{a} \rightarrow -a' \\ \omega_2 &= \omega_{bb'} = \omega_e + \tfrac{1}{2}\gamma_e \bar{a} \rightarrow a' \\ \omega_3 &= \omega_{ba'} = \omega_e + \omega_n \rightarrow \omega_n \\ \omega_4 &= \omega_{ab'} = \omega_e - \omega_n \rightarrow -\omega_n \end{aligned} \tag{34}$$

The resonant frequencies become $\pm a' = \pm\gamma_e \bar{a}/2$ and $\pm\omega_n$ when ω_e is taken as the origin of the spectrum for convenience.

For simplicity we again assume axial symmetry for the g-tensor and the dipolar tensor. Then:

$$\mathcal{H}_1(\Omega) = \mathcal{D}^2_{0,0} S_z [\mathcal{F} + D' I_z] + (\mathcal{D}^2_{0,1} I_+ S_z - \mathcal{D}^2_{0,-1} I_- S_z) D \tag{35}$$

where

$$D = -2\pi \xi_i D_i^0 \tag{36a}$$

where $\xi_i = \frac{1}{2\pi}|\gamma_e|\gamma_i \hbar$ and D_i^0 is given in XVIII.85. Also

$$D' = -(8/3)^{\frac{1}{2}} D \tag{36b}$$

Note that one has

$$[\mathcal{H}_1^{\times}]_{\alpha\alpha'\beta\beta'} = [\mathcal{H}_{1\alpha\beta}\delta_{\alpha'\beta'} - \mathcal{H}_{1\beta'\alpha'}\delta_{\alpha\beta}] \tag{37}$$

where α, α', β and β' are eigenstates of $\mathcal{H}_0$. $\mathcal{H}_1^{\times}$ may be represented as a simple Hermitian matrix in the space of transitions 1-4:

$$\mathcal{K}_1^{\times}(\Omega) = \begin{array}{c} \begin{array}{cccc} 1 & 2 & 3 & 4 \end{array} \\ \begin{pmatrix} \mathcal{J}^2_{0,0}(\mathcal{F}+\frac{1}{2}D') & 0 & s & s^* \\ 0 & \mathcal{J}^2_{0,0}(\mathcal{F}-\frac{1}{2}D') & s & s^* \\ s^* & s^* & \mathcal{J}^2_{0,0}\mathcal{F} & 0 \\ s & s & 0 & \mathcal{J}^2_{0,0}\mathcal{F} \end{pmatrix} \end{array} \qquad (38)$$

where $s = \frac{1}{2}\mathcal{J}^2_{0,1}D$. One must now develop eq. 19 for non-degenerate transitions $\lambda = 1$, 2, 3, and 4. We shall represent the appropriate coefficients as $C^L_{K,M}(\lambda)$. Then we obtain:

$$(2L+1)^{-1}[(\omega+a')-i\{T_2^{-1}+RL(L+1)\}]C^L_{0,0}(1)-(\mathcal{F}+\tfrac{1}{2}D')\sum_{L'}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C^{L'}_{0,0}(1)$$
$$+\tfrac{1}{2}D\sum_{L'\neq 0}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix}[C^{L'}_{0,1}(3)-C^{L'}_{0,-1}(4)] = q\omega_1 d\delta_{L,0} \qquad (39a)$$

$$(2L+1)^{-1}[(\omega-a')-i\{T_2^{-1}+RL(L+1)\}]C^L_{0,0}(2)-(\mathcal{F}-\tfrac{1}{2}D')\sum_{L'}\begin{pmatrix} L' & 2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 C^{L'}_{0,0}(2)$$
$$+\tfrac{1}{2}D\sum_{L'\neq 0}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix}[C^{L'}_{0,1}(3)-C^{L'}_{0,-1}(4)] = q\omega_2 d\delta_{L,0} \qquad (39b)$$

$$\frac{D}{2}\sum_{L'}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 1 & -1 & 0 \end{pmatrix}[C^{L'}_{0,0}(1)+C^{L'}_{0,0}(2)] + (2L+1)^{-1}[(\omega-\omega_n)$$
$$-i\{T_2^{-1}+RL(L+1)\}]\,C^L_{0,1}(3)+\mathcal{F}\sum_{L'\neq 0}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 1 & 0 & -1 \end{pmatrix}C^{L'}_{0,1}(3)=0 \qquad (39c)$$

$$-\frac{D}{2}\sum_{L'}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -1 & 1 & 0 \end{pmatrix}[C^L_{0,0}(1)+C^L_{0,0}(2)] + (2L+1)^{-1}[(\omega+\omega_n)$$
$$-i\{T_2^{-1}+RL(L+1)\}C^L_{0,-1}(4) + \mathcal{F}\sum_{L'\neq 0}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -1 & 0 & 1 \end{pmatrix}C^{L'}_{0,-1}(4) = 0 \qquad (39d)$$

While eqs. 39a and b are applicable for $L = 0$, eqs. 39c and d require $L, L' > 0$, and in all cases L and L' must be even and $L' = L \pm 2$ or L. Equations 39 represent four infinite sets of coupled equations (i.e. expansions in L) which are then coupled amongst each other due to the pseudo-secular contribution from the dipolar term.

The absorption is proportional to:

$$Z''_1 + Z''_2 = \frac{1}{\pi}\mathrm{Im}\,[C^0_{0,0}(1)+C^{(0)}_{0,0}(2)] \qquad (40)$$

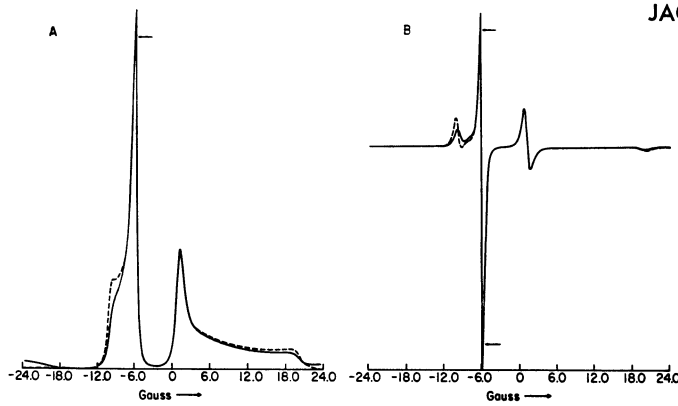

Fig. 3. Comparison for S = $\frac{1}{2}$, I = $\frac{1}{2}$ of lineshapes which include pseudo-secular contributions to lineshapes for which they are omitted $|\mathcal{F}|/R = 100$. $|\omega_n/\gamma_e| = 23.0$ G. All other parameters as in Fig. 4. A) Absorption; B) Derivative. _____corresponds to inclusion of pseudo-secular terms, _ _ _ _corresponds to their omission. [Spin parameters $(g_{||}-g_{\perp})$, $|\omega_n/\gamma_e|$, $A_{||}, A_{\perp}$ and the abscissas of graph scale to a typical ring proton case when divided by 4.6]. [By permission from Ref. 1.]

When the series of eqs. 39 are terminated for L>n, the coupled algebraic equations are of order r=2(n+1).

We show in Fig. 3 a case where $|\mathcal{F}|/R = 100$ and $|D| << |a' \pm \omega_n|$. This result scales reasonably well to that for a typical aromatic ring proton (one need only divide the spin parameters by 4.6). The dotted lines are for neglect of pseudo-secular terms (i.e. let $c^L_{0,1}(3) = c^L_{0,-1}(4) = 0$ for all L). The minor pseudo-secular contributions can be accounted for by perturbation techniques (cf. Section 3).

ii) One Nuclear Spin of I = 1; (^{14}N). The energy levels, and the 3 allowed and 6 forbidden transitions are shown in Fig. 2b for this case, and the details for axially symmetric tensors and for the true asymmetric nitroxide tensors are given elsewhere.[1,5] It is important to note that because D~a, pseudo-secular contributions must be explicitly included as they may not be handled by perturbation techniques. Typical simulations are shown in Figs. 4, 5 and 6 (see also Gordon, Ch. XIII). Fig. 4 gives the progress from liquid-like to solid-like spectra for axially symmetric tensors; Fig. 5 compares axially symmetric results for different models (a) Brownian dif-

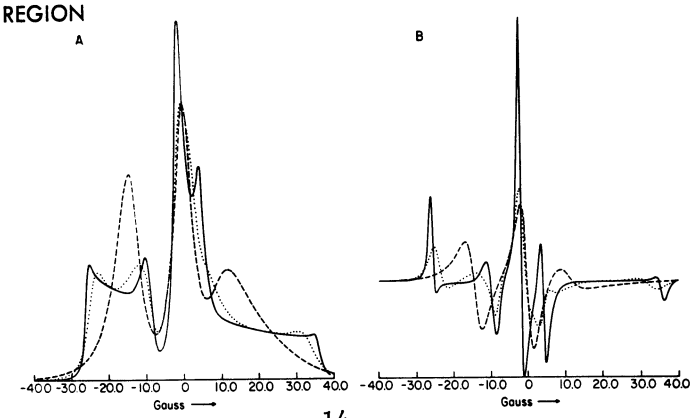

Fig. 4. Lineshapes for $S=\frac{1}{2}$, I=1 (^{14}N nucleus) with axially symmetric g-tensor and hyperfine tensor. A) Absorption; B) Derivative. All correspond to $g_{||} = 2.00270$, $g_{\perp} = 2.00750$, $A_{||} = 32$ G., $A_{\perp} = 6$ G., $|\omega_n/\gamma_e| = 0.36$ G. $(2/\sqrt{3})T_2^{-1}/|\gamma_e| = 0.3$ G. The $|\mathcal{F}|/R$ values are _ _ _ _2, ...15, _____100. [By permission from Ref. 1.]

fusion; (b) Free diffusion (i.e. approximate inclusion of reorientational effects, cf. Ch.VIII.5); (c) Jump diffusion. There are clearly significant differences. These models may be approximated by multiplying the rhs of eq. 21a by a "model parameter" B_L which has different L dependence for the different models.[5] Figure 6 gives a comparison between an experimental result and the best theoretical fit, which is obtained with model (b), for several values of $R_3/R_1 \equiv N$ (cf. eq. 21a). The complete anisotropic magnetic parameters are used in the simulations.

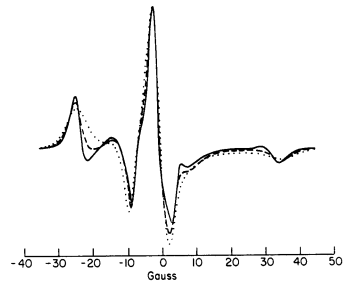

Fig. 5. Comparison of lineshapes for different reorientational models for $S = \frac{1}{2}$, I = 1 (nitroxide) with axially symmetric tensors given in Fig. 4. Solid line-Brownian Diffusion ($|\mathcal{F}(0)\tau_R| = 2.5$); Dashed line-free diffusion ($|\mathcal{F}(0)\tau_R| = 5/3$); Dotted line-jump diffusion ($|\mathcal{F}(0)\tau_R| = 7/6$). [By permission from Ref. 5.]

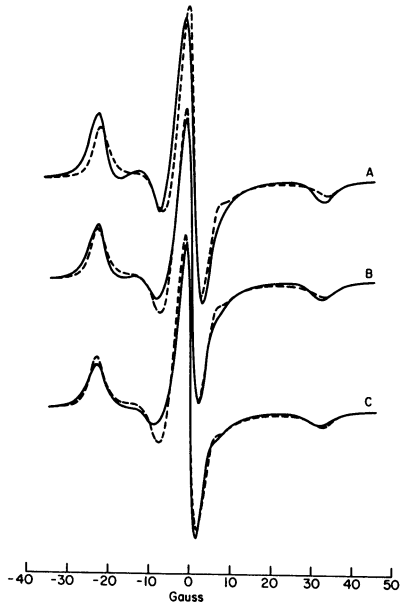

Fig. 6. Comparison of experimental (peroxylamine disulfonate in frozen D_2O at -60°C) lineshape— dashed line, with simulated lineshapes— solid line, for free diffusion model with $\mathcal{J}(0)\tau_R = 5/3$ and for $R_3/R_1 = N = 1$, 3 and 6 (from top to bottom). The complete anisotropic parameters are utilized in the simulations. [By permission from Ref. 5.]

XIV.3. SATURATION[1] (cf. Ch. XVIII).

In order to describe a saturated spectrum, one needs, according to eq. 21, expressions for the $[C_m^{(0)}]_{\lambda_j\pm}$. These may be obtained by taking the $\langle\lambda_{j\pm}|-|\lambda_{j\pm}\rangle$ matrix elements of eq. 2, and performing a derivation like that which leads to eq. 19. We obtain:

$$N_{m'}(in\omega + E_{m'})[C_{m'}^{(n)}]_{\lambda_j\pm} = \mp id_{\lambda_j} N_{m'}([C_{m'}^{(n+1)}]_{\lambda_j^{\rightarrow}} - [C_{m'}^{(n-1)}]_{\lambda_j^{\leftarrow}})$$
$$-i\sum_m \int d\Omega G_{m'}^{*}(\Omega)[\mathcal{H}_1^{\times}(\text{non-sec})C_m^{(n)}]_{\lambda_j\pm,\lambda_j\pm} \qquad (41)$$

(Here the subscript $\lambda_j^{\rightarrow} \equiv \lambda_j$ refers to the $\langle\lambda_{j-}|-|\lambda_{j+}\rangle$ matrix element, while $\lambda_j^{\leftarrow}$ refers to the $\langle\lambda_j+|-|\lambda_j-\rangle$ matrix element). The superscript (non-sec) refers to the fact that only the non-secular part of $\mathcal{H}_1$ (including pseudo-secular terms) need be retained.

Equation 41 is also needed for problems involving no saturation, but a non-secular $\mathcal{H}_1$ which induces electron spin-flips.

It is often convenient to look at the difference:

$$[b_{m'}^{(n)}]_{\lambda_j} \equiv [C_{m'}^{(n)}]_{\lambda_j +} - [C_{m'}^{(n)}]_{\lambda_j -} \tag{42}$$

It follows that the Hermitian properties of σ and σ_o as well as eqs. 4, 5, and 16 that:

$$N_{m'}[C_{m'}^{(n)}]_{ab} = \sum_m [C_m^{(-n)}]_{ba}^* \int G_m^*(\Omega) d\Omega . \tag{43}$$

A form of eq. 19 generalized to any n (not just n = 1) is sometimes needed. It is:

$$N_{m'}[(n\omega - \omega_\lambda) - iE_{m'}][C_{m'}^{(n)}]_{\lambda_j} + \sum_m \int d\Omega G_{m'}^*(\Omega) G_m(\Omega) [\mathcal{H}_1(\Omega) \times C_m^{(n)}]_{\lambda_j} +$$
$$d_{\lambda_j} N_{m'}[b_m^{(n-1)}]_{\lambda_j} = q\omega_\lambda d_{\lambda_j} \delta_{m',0} \delta_{n,1} \tag{44}$$

In eqs. 41 and 44, one sees that it is only though the effects of the radiation field, where the strength of interaction with the spins is given by $d_{\lambda_j} \equiv \frac{1}{2}\omega_1$, that the n^{th} harmonics $[C_{m'}^{(n)}]$ are coupled to harmonics $[C_m^{(n\pm1)}]$. An analysis of these equations leads to the result that the extent of coupling depends essentially on the ratio ω_1/ω_o, which is very small in the presence of large applied DC fields. Hence, it is sufficient for high-field saturation cases to retain only the n=1 terms (which include $[C_0^{(1)}]_{\lambda_j}$, the observed signal) and the n=0 terms (which include $[b_0^{(0)}]_{\lambda_j}$, the dc population differences). Higher harmonics become important in a variety of multiple resonance schemes, or experiments done at lower DC fields.

A. Rotationally Invariant T_1.

We consider a simple case of saturation. The unsaturated line shape is assumed to be due mainly to the secular part of an axially-symmetric g-tensor, while there is a rotationally invariant $T_1 = (2W_e)^{-1}$ where W_e is the lattice-induced electron spin-flip process (e.g. the spherically symmetric part of the spin-rotational interaction). This is introduced by replacing in the equation obtained

from eq. 41 and 42, $E_m' \rightarrow E_m' + 2W_e$. We also include a rotationally invariant $T_2 \leqq T_1$ by letting $iE_m' \rightarrow i(E_m' + T_2^{-1})$ in eq. 44.

For the secular perturbation of eq. 27, it is only necessary to consider $[C^L_{0,0}{}^{(1)}]_{\lambda_j}$ and its coupling to $[b^L_{0,0}{}^{(0)}]_{\lambda_j}$, and one obtains from eqs. 41-43:

$$[(\omega-\omega_0)-iRL(L+1)-iT_2^{-1}][C^L_{0,0}{}^{(1)}]_{\lambda_j} - (2L+1)\mathcal{F}\sum_{L'}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 \times$$
$$\times [C^{L'}_{0,0}{}^{(1)}]_{\lambda_j} + \frac{4|d_{\lambda_j}|^2}{RL(L+1)+2W_e}\,\mathrm{Im}[C^L_{0,0}{}^{(1)}]_{\lambda_j} = q\omega_\lambda d_{\lambda_j}\delta_{L,0} \quad (45)$$

Equation 45 with eq. 30 then determines the saturated spectrum. Note that the saturation term (viz. the last term on the lhs of eq. 45) for L = 0 is unaffected by the rotational motion, while for $L>0$ we find $W_e \rightarrow W_e + \frac{1}{2}RL(L+1)$, i.e. the rotational motion aids the spin relaxation by spreading the spins over all orientations, which, due to $\mathcal{H}_1(\Omega)$ have different "static" resonant frequencies.

In general, one sees that the effect of the saturation on the line shape is to broaden out the spectrum while acting to "wash out" the asymmetric appearance. This is similar to the effect of increasing T_2^{-1} for the unsaturated spectrum, (except for the reduction of intensity in the case of saturation). The results for $|\mathcal{F}|/R=100$ are shown in Fig. 7.

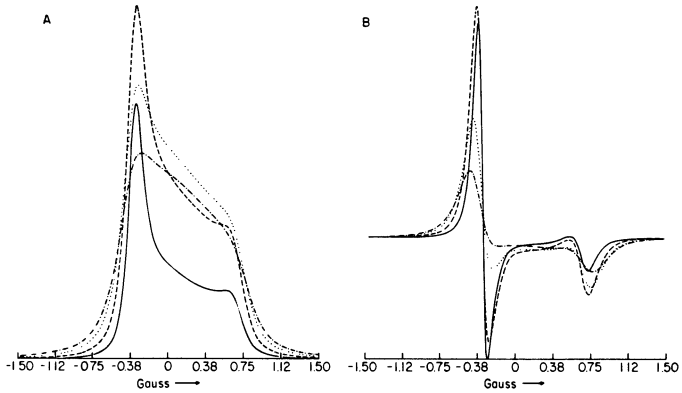

Fig. 7. Saturation of Single Line with rotationally invariant T_1, as a function of B_1 for $\mathcal{F}/R=100$. $g_{\|} = 2.00235$, $g_{\perp} = 2.00310$, $T_2 = T_1 = (2W_e)^{-1}$ and $(2/\sqrt{3})\,T_2^{-1}|\gamma_e| = 0.02G$. The different values of $(1/2)B_1$ are _____0.01 G, _ _ _0.025 G, ...0.050 G, _ . _ . 0.075 G. A) Absorption, B) Derivative. [By permission from ref. 1.]

B. G-Tensor-(Axially Symmetric).

We now include the non-secular portion of the g-tensor to give:

$$\mathcal{H}_1 = \mathcal{F}[\mathcal{D}^2_{0,0}S_z - (\tfrac{3}{8})^{\frac{1}{2}}(\mathcal{D}^2_{0,1}S_+ - \mathcal{D}^2_{0,-1}S_-)] \tag{46}$$

Equation 46 is substituted into eqs. 44, 41 and 42 respectively and leads to:

$$(-)^{K-M}[n\omega-\omega_0 - iT_2^{-1} - iRL(L+1)][C^{L(n)}_{-K,-M}]_{\lambda_j} - (2L+1)\mathcal{F}\sum_{L',K',M'}\begin{pmatrix}L & 2 & L'\\ K & 0 & K'\end{pmatrix}\begin{pmatrix}L & 2 & L'\\ M & 0 & M'\end{pmatrix}[C^{L'(n)}_{K',M'}]_{\lambda_j} + (-)^{K-M}d_{\lambda_j}[b^{L(n-1)}_{-K,-M}] + (2L+1)(\tfrac{3}{8})^{\frac{1}{2}}\mathcal{F}\sum_{L',K',M'}\begin{pmatrix}L & 2 & L'\\ K & 0 & K'\end{pmatrix}\begin{pmatrix}L & 2 & L'\\ M & -1 & M'\end{pmatrix}[b^{L'(n)}_{K',M'}]_{\lambda_j} - q\omega_0\delta_{n,0}\delta_{K,0}\delta_{M,1}(\tfrac{3}{8})^{\frac{1}{2}}\mathcal{F} = q\omega_\lambda d_{\lambda_j}\delta_{L',0}\delta_{n,1} \tag{47}$$

and

$$(-)^{K-M}[\tfrac{1}{2}in\omega + \tfrac{1}{2}RL(L+1)+W_e][b^{L(n)}_{-K,-M}]_{\lambda_j} = -id_{\lambda_j}(-)^{K-M}([C^{L(n+1)}_{-K,-M}]_{\lambda_j^{\rightarrow}} - [C^{L(n-1)}_{-K,-M}]_{\lambda_j^{\leftarrow}}) + i(2L+1)(\tfrac{3}{8})^{\frac{1}{2}}\mathcal{F}\sum_{L',K',M'}\begin{pmatrix}L & 2 & L'\\ K & 0 & K'\end{pmatrix}\begin{pmatrix}L & 2 & L'\\ M & 1 & M'\end{pmatrix}[C^{L'(n)}_{K'M'}]_{\lambda_j^{\rightarrow}} + \begin{pmatrix}L & 2 & L'\\ M & -1 & M'\end{pmatrix}[C^{L'(n)}_{K'M'}]_{\lambda_j^{\leftarrow}} \tag{48}$$

We now employ the high field, moderate saturation approximations, (i.e. $|\omega_1/\omega_0| << 1$, and $|\mathcal{F}/\omega_0| << 1$), as well as the ad hoc relaxation to thermal equilibrium assumption.[1] This leads to simplified coupled eqs. between the coefficients $C^{L(1)}_{0,0}$ and $b^{L(1)}_{0,0}$ and between $C^{L(0)}_{0,0}$ and $b^{L(0)}_{0,0}$ as a result of the non-secular part of eq. 46, while $C^{L(1)}_{0,0}$ and $b^{L(0)}_{0,0}$ are coupled via the saturating microwave field. However, the assumption that $|\mathcal{F}/\omega_0| << 1$, further allows one to employ second order perturbation theory and decouple $C^{L(1)}_{0,0}$ from $b^{L(1)}_{0,0}$ and $b^{L(0)}_{0,0}$ from $C^{L(0)}_{0,0}$. The resulting eqs. are:

$$\{(\omega-\omega_0)-i[T_2^{-1}+RL(L+1)]\}C^{L(1)}_{0,0} - (2L+1)\mathcal{F}\sum_{L}\begin{pmatrix}L & 2 & L'\\ 0 & 0 & 0\end{pmatrix}^2 C^{L'(1)}_{0,0} + d_{\lambda_j}b^{L(0)}_{0,0} + [\text{terms in } C^{L''(1)}_{0,0} \text{ of order } \frac{\mathcal{F}^2}{-\omega_0+iRL(L+1)}] = q\omega_\lambda d_\lambda \delta_{L,0} \tag{49}$$

$$\left[\frac{RL(L+1)}{2}+W_e\right]b^{L(0)}_{0,0} - 2d_{\lambda_j}\mathrm{Im}C^{L(1)}_{0,0} - (\tfrac{3}{8})(2L+1)\mathcal{F}^2\sum_{L',L''}\begin{pmatrix}L & 2 & L'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L & 2 & L'\\ 0 & 1 & -1\end{pmatrix}\times\begin{pmatrix}L' & 2 & L''\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L' & 2 & L''\\ 1 & -1 & 0\end{pmatrix}\times\left[\frac{(2L+1)V(L,L')}{V(L,L')^2+\left(\frac{2L+1}{2L'+1}\omega_0\right)^2}+\frac{(2L''+1)V(L'',L')}{V(L'',L')^2+\left(\frac{2L''+1}{2L'+1}\omega_0\right)^2}\right]\times b^{L''(0)}_{0,0} = 0 \tag{50}$$

where

$$V(L,L') = \tfrac{1}{2}RL(L+1) + W_e - \left(\frac{2L+1}{2L'+1}\right)[RL'(L'+1)+T_2^{-1}]. \qquad (50a)$$

In eq. 49 we are neglecting terms of order $\frac{\mathcal{F}^2 C^{L''}_{0,0}(1)}{-\omega_0+iRL(L+1)}$ since when $RL(L+1)\ll|\omega_0|$, as is the case for slow tumbling, then these non-secular terms are of order $|\mathcal{F}/\omega_0|$ smaller than the secular terms in $\mathcal{F}$, i.e. we are neglecting the non-secular contributions to the unsaturated linewidths as compared to the secular contributions for slow tumbling. These non-secular terms must, however, be included in eq. 50 since this eq. predicts the T_1-type behavior and is not explicitly affected by the secular terms in $\mathcal{F}$. Note that for $RL(L+1)\ll|\omega_0|$, then $|V(L,L')|$, $|V(L'',L')|\ll \omega_0^2$ and the terms in V^2 in the denominators of the last terms on the lhs of eq. 50 may be omitted. Furthermore, in this limit a perturbation analysis of the coupling of $b^{L(0)}_{0,0}$ to $b^{L''(0)}_{0,0}$ in eq. 50 shows that it is sufficient to restrict the summation over L'' in this eq. to just $L'' = L$. This, then, just leaves the terms diagonal in $b^{L(0)}_{0,0}$ in eq. 50. However, these diagonal corrections are of order of magnitude $|\mathcal{F}/\omega_0|^2R$ and are thus negligibly small compared to $(\frac{1}{2})RL(L+1)$. Thus, the contribution of the nonsecular terms in eq. 50 is negligible in our approximation except for the diagonal term for $L = 0$. This contribution to $L=0$ is readily calculated, and is

$$W_e^{(G)} = (9/10)(\mathcal{F}/\omega_0)^2R \qquad (51)$$

which is just the result obtained from relaxation theory for $|R/\omega_0|\ll 1$, even though we are now allowing for slow tumbling: $|\mathcal{F}/R|>1$. The net conclusion is $|\mathcal{F}|, R, \ll|\omega_0|$, the solution to the present case is just given by eq. 45 for the rotationally invariant T_1, but with $W_e \rightarrow W_e + W_e^{(G)}\delta_{L,0}$ in that eq., where W_e^G is given by eq. 51.

One again finds that the effect of saturation is to broaden out and to tend to reduce the asymmetry of the spectrum. The results for $|\mathcal{F}|/R=100$ are shown in Fig. 8.

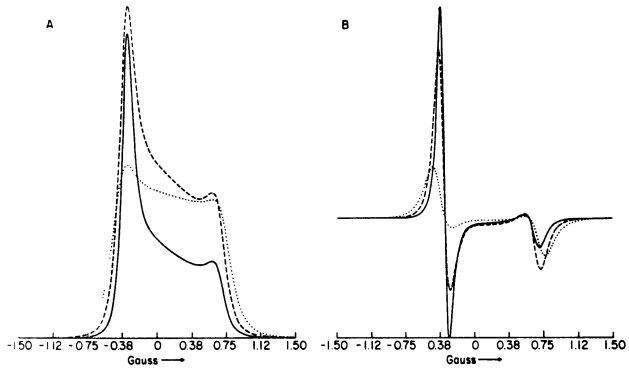

Fig. 8. Saturation of Single Line with g-tensor relaxation as a function of B_1 for $|\mathcal{F}|/R=100$. The different values of $(\frac{1}{2})B_1$, are _____ 3×10^{-6}G, _ _ _ 7.5×10^{-6}G, ... 2×10^{-5}G. All other parameters as in Fig. 5, except $W_e=T_2^{-1}=0$. [By permission from Ref. 1.]

XIV.4. TRIPLETS[6]

A. General Solutions

For triplets, we cannot necessarily utilize high-field approximations if the zero field splitting is large. It is thus better to employ linear response theory.

We start with the general expression for the imaginary part of the magnetic susceptibility resulting from a very weak linearly polarized rf field of frequency $\omega/2\pi$ being applied to the system:[7]

$$\chi''_{\alpha\alpha}(\omega) = \frac{\omega}{2NkT}\int_0^\infty (e^{i\omega t} + e^{-i\omega t})\mathrm{Tr}[M_\alpha(t)M_\alpha]dt. \tag{52}$$

The perturbation of the spins by the rf field is given by

$$\epsilon(t) = M_\alpha B_1 \cos\omega t, \tag{53}$$

i.e. an oscillating field along the α = x, y, or z direction. We shall assume an essentially isotropic g-value and an ensemble of non-interacting triplets so:

$$\mathrm{Tr}[M_\alpha(t)M_\alpha] = \mathfrak{N}\gamma_e^2\mathrm{Tr}[S_\alpha(t)S_\alpha] \tag{52a}$$

We now separate $\mathcal{H}$ into

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_1(\Omega)$$

where $\mathcal{H}_z$ is the Zeeman part of the Hamiltonian and $\mathcal{H}_1(\Omega)$ contains the orientation dependent zero-field splitting terms. Here $\mathcal{H}_1(\Omega)$ need not be small compared to $\mathcal{H}_z$. We again assume that the motional

process modulating $\mathcal{H}_1(\Omega)$ can be described as a stationary Markoff Process. It then follows that the operator $S_\alpha(\Omega,t)$ obeys the stochastic Liouville equation of motion (cf. eq. 2):

$$\frac{\partial}{\partial t} S_\alpha(\Omega,t) = i\mathcal{H}^\times S_\alpha(\Omega,t) - \Gamma_\Omega S_\alpha(\Omega,t) \tag{54}$$

with initial condition:

$$S_\alpha(\Omega,0) = S_\alpha(0). \tag{55}$$

Let:

$$S_\alpha(s) \equiv \int_0^\infty e^{-st} S_\alpha(t)dt \tag{56}$$

be the Laplace Transform of $S_\alpha(t)$. Then equations 54 and 55 yield:

$$(s-i\mathcal{H}^\times + \Gamma_\Omega)S_\alpha(s,\Omega) = S_\alpha(0) \tag{57}$$

Now in equation 52a, the trace over orientational degrees of freedom is replaced by a classical average:

$$\overline{S_\alpha(t)S_\alpha} \equiv \int d\Omega\, S_\alpha(t,\Omega) P_0(\Omega) S_\alpha = \overline{S_\alpha(t)S_\alpha}. \tag{58}$$

It follows from eqs. 56 and 58 that the susceptibility, eq. 52 may be rewritten as:

$$\chi''(\omega) = \frac{\pi\gamma_e^2\omega}{2NkT} \mathrm{Tr}[(\overline{S_\alpha(i\omega)} + \overline{S_\alpha(-i\omega)})S_\alpha] \tag{59}$$

where $S_\alpha(\pm i\omega)$ are the Laplace transforms of the spin operator with $s = \pm i\omega$, and the trace is now only over spin degrees of freedom. The plus and minus signs are found to correspond to the two counter rotating components of the rf field. Note that it follows from eq. 53, the Hermiticity of $S_\alpha(t)$, and the fact that Γ_Ω is a real operator independent of spin that:

$$S_\alpha(i\omega)^\dagger = S_\alpha(-i\omega) \tag{59a}$$

where the dagger indicates Hermitian conjugate. Thus we require $\overline{S_\alpha(s)}$ given by:

$$\overline{S_\alpha(\Omega,s)} = \overline{[s-i\mathcal{H}^\times + \Gamma_\Omega]^{-1}S_\alpha(0)}$$

$$\equiv \int d\Omega\, [s-i\mathcal{H}^\times + \Gamma_\Omega]^{-1} P_0(\Omega) S_\alpha(0) \tag{60}$$

We expand $S_\alpha(\Omega,s)$ in a complete set of orthogonal eigenfunctions of Γ_Ω, i.e. $G_m(\Omega)$, with eigenvalues E_m(cf. eq. 16 and isotropic liquids):

$$S_\alpha(\Omega,\pm i\omega) = \sum_m a_{\alpha,m}(\pm\omega) G_m(\Omega) \tag{61}$$

where $a_{m,\alpha}(\omega)$ are still operators in spin space. Clearly from eqs. 56, 58, and 61

$$\overline{S_\alpha(\Omega,\pm i\omega)} = a_{\alpha,0}(\pm\omega) \tag{62}$$

when we take $P_0 \propto G_0 \equiv 1$.

When $B_1 \perp B_0$ we are interested in S_x. Now the non-zero matrix elements of S_x are $\langle \pm|S_x|0\rangle = \langle 0|S_x|\pm\rangle = \frac{\sqrt{2}}{2}$. It thus follows from eqs. 59 and 62 that

$$\chi''(\omega) = \frac{\sqrt{2}\,\omega}{2NkT}\hbar\gamma_e^2 R_e[\langle -|a_{x,0}(\pm\omega)|0\rangle + \langle 0|a_{x,0}(\pm\omega)|+\rangle] \tag{63}$$

where the $a_{x,0}(\pm\omega)$ terms imply that the effects of both the rotating and counter-rotating components are to be added. Also, we have for the zero-field terms:

$$\mathcal{H}_1 = \sum_{m'}[\frac{1}{\sqrt{6}}D\mathcal{D}^2_{0,m'}(\Omega) + \frac{E}{2}(\mathcal{D}^2_{2,m'}(\Omega) + \mathcal{D}^2_{-2,m'}(\Omega))]A^{2,m'} \tag{64}$$

where

$$A^{2,0} = \sqrt{6}\,(S_z^2 - \tfrac{1}{3}S^2)$$

$$A^{2,\pm1} = \mp(S_\pm S_z + S_z S_\pm)$$

$$A^{2,\pm2} = S_\pm^2 \tag{65}$$

As before, eqs. 57 and 61 yield sets of coupled differential equations for matrix elements of the coefficients: $a^L_{K,M}(\pm\omega)$. We note the following relation.*

---

*The modified coefficients $C^L_{KM}(\pm\omega)$ are introduced in this way to correspond with the coefficients as used in eq. 16 for the expansion of the density matrix rather than the magnetization. The change of sign in defining $C^L_{KM}(-\omega)$ as compared to $C^L_{KM}(\omega)$ does <u>not</u> correspond to the usage in eq. 16 unless eq. 14 and all those which follow have $q\omega_\lambda d_\lambda$ replaced by $q\omega d_\lambda$, i.e. the modified form required for a Bloch-Redfield type approach to yield the correct dependence of $\chi''(\omega)$ on ω as obtained naturally from linear response theory. A redefined $C'_m(-\omega) = -C_m(-\omega)$ would correspond to the exact usage in the previous sections.

$$C^{L}_{KM}(\pm\omega) = \pm i(-)^{K-M} a^{L*}_{-K-M}(\mp\omega) \tag{66}$$

and abbreviate the matrix elements of the $C^{L}_{K,M}(\pm\omega)$ as:

$$\begin{aligned} &\langle -|C|0\rangle = C(1),\ \langle 0|C|-\rangle = C(-1),\ \langle 0|C|1\rangle = C(2) \\ &\langle 1|C|0\rangle = C(-2),\ \langle -1|C|1\rangle = C(3),\ \langle 1|C|-1\rangle = C(-3) \\ &\langle -1|C|-1\rangle = C(a),\ \langle 0|C|0\rangle = C(b),\ \langle 1|C|1\rangle = C(c). \end{aligned} \tag{67}$$

This generates a set of coupled eqs. of order $(9/2)n+2$ for the solution of the triplet problem ($E = 0$).[6] Typical simulations are shown in Figs 9 and 10. One can repeat this for $B_1 \| B_0$ where the

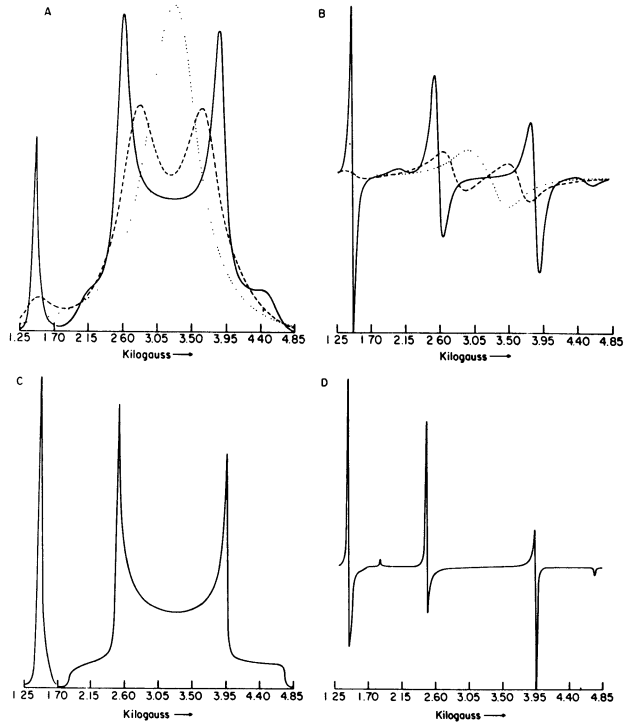

Fig. 9. Lineshapes as a function of D/R for a triplet with B_1 perpendicular to B_0. A) Absorption lineshapes. B) First derivative lineshapes. The different lines correspond to .....D/R=5, n = 6; _ _ _ _D/R = 20, n = 8; _____D/R = 200, n = 12; C and D) Rigid limit absorption and first derivative lineshapes. All plots are for D = 1,435 G., $\frac{\omega}{|\gamma_e|}$ = 3,300 G., a rotationally invariant $(\sqrt{3}\, T_2^{-1}/2)$ $|\gamma_e|$ = 15 G and E = 0. The field B_0 is swept. [By permission from Ref. 6.]

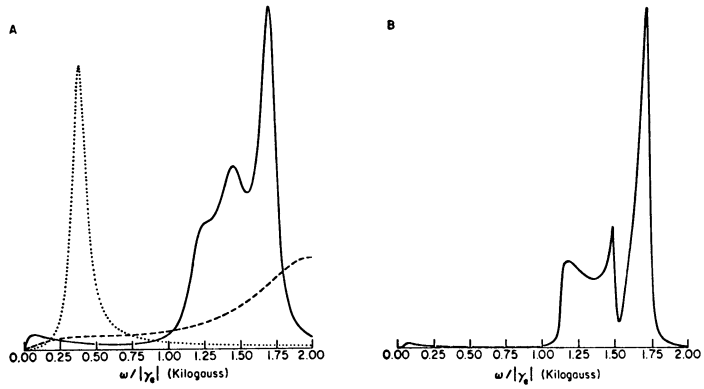

Fig. 10. Low field absorption lineshapes as a function of D/R for a triplet with B_1 perpendicular to B_0. A) The different lines correspond to .....D/R = 0.2, n = 2; _ _ _D/R = 20, n = 8; _____D/R = 200, n = 12. B) Rigid limit. All plots are for D = 1,435 G., B_0 = 300 G. and $T_2^{-1}/|\gamma_e| = \sqrt{\frac{2}{3}}$ 15 G. The frequency, $\omega = |\gamma_e|B$ is swept. [By permission from Ref. 6.]

spectrum is given by:

$$\chi''(\omega) = \frac{\pi\gamma_e^2\omega}{NkT}\left[\langle +|a_{z,o}(-\omega)|+\rangle - \langle -|a_{z,o}(-\omega)|-\rangle\right] \tag{68}$$

with a somewhat different set of coupled equations.

B. Perturbation Theory

There are two limiting cases in which the coupled equations may be solved more simply.

i. High Field Case. Here D, $6R \ll \omega_0$. One can show that for this case the $\Delta m = 2$ transition is a simple Lorentzian of width $6R \equiv \tau_R^{-1}$ provided $D^2/\omega_0 R \ll 330$ both for $B_1 \perp B_0$ and $B_1 \| B_0$. Note that the observed derivative linewidth of the half-field line in a field swept experiment is given by:

$$\delta = (2\gamma_e)^{-1}\left[\sqrt{\frac{2}{3}}\{T_2^{-1} + 6R\}\right] \tag{69}$$

where $2\gamma_e$ is the "effective" gyromagnetic factor and T_2^{-1} is the rotationally invariant width term.

ii. Fast Motional Case. Here $D \ll 6R$. This is the condition for conventional relaxation theory to apply. One obtains a single

Lorentzian line at $\omega = \omega_0$ with:

$$T_2^{-1} = \frac{\Delta^2}{20}[3J(0)+5J(\omega_0)+2J(2\omega_0)] \tag{70}$$

where $\Delta^2 = 2(D^2/3+E)$ and $J(\omega) = 12R/[(6R)^2+\omega^2]$. This result can also be obtained from a perturbation analysis of our coupled equations using only terms up through L = 2. Cases 1 and 2 are clearly not mutually exclusive.

C. Summary of Spectra

i. High-Frequency and Field Sweep ($\omega/|\gamma_e| \equiv B = 3,300$ G.)

Figure 9 shows typical results when $B_1 \perp B_0$. As the rotational motion increases from the rigid limit, both the $\Delta m = 1$ and 2 lines initially broaden. However, fast motion leads to a narrowing of the $\Delta m = 1$ transition until it becomes Lorentzian with its absorption maximum at B = 3,300 G. and width given by eq. 70.

The $\Delta m = 2$ transition for $B_1 \| B_0$ gives results that are very similar to what is obtained for the $B_1 \perp B_0$ case.

ii. Low Field and Frequency Sweep ($B_0 = \omega_0/|\gamma_e| = 300$ G.).

Typical results for this case are given in Fig. 10 which shows the $B_1 \perp B_0$ rf orientation. As the motion starts, the rigid limit spectra occurring in the region of $\omega \sim D = 1,435$ G. $|\gamma_e|$ are seen to broaden out. However, as the motion becomes rapid, one finds that for $B_1 \perp B_0$ a Zeeman line appears at $\omega \sim \omega_0 = 300$ G$|\gamma_e|$, while there is a negligible contribution in the region of $\omega \sim D$. In fact, in the motional narrowing region the width of the Zeeman line is found to be given by eq. 70, as it should. This, then, is a simple example of a more general phenomenon; that if, in the rigid limit the spins are quantized essentially in a molecular frame (the Zeeman field is only a perturbation), they will nevertheless appear to be quantized in the laboratory frame yielding the usual Zeeman line, when the tumbling rate of the molecule is fast compared to zero field splittings.

In the case of $B_1 \| B_0$, a Zeeman line cannot appear. Instead a line appears at $\omega = 0$ with width predicted by eq. 70. This line

is apparent if $\chi''(\omega)/\omega$ is plotted instead of $\chi''(\omega)$. It is seen from eq. 52 that the latter must go to zero at $\omega = 0$. It is also found that for very slow motion $\chi''(\omega)/\omega$ shows a resonance at $\omega \sim 0$, which broadens out as does the regular line which occurs around $\omega \sim D$.

iii. Zero Field and Frequency Sweep. The results for this case are qualitatively similar to $B_1 \| B_0$ and low fields.

An analysis of $\chi''(\omega)/\omega$ shows two lines of equal intensity at $\omega = D$ and $\omega = 0$, for the rigid limit and for slow motion. These lines are found to be Lorentzian in shape with T_2^{-1} very well approximated by $T_2^{-1} = 4R$ for $|D/6R| \gg 1$. They correspond to the doubly degenerate $T_x \leftrightarrow T_z$ and $T_y \leftrightarrow T_z$ transitions occurring at $\omega = \pm D$ and to the $T_x \leftrightarrow T_y$ transition at $\omega = 0$. Here T_x, T_y, and T_z are the standard zero-field triplet wave functions with zero-field energies of D, D and 0 respectively. For fast motion a line narrows up at $\omega = 0$, with width as predicted by eq. 70. Of course, the $\omega = 0$ lines are suppressed since $\chi''(\omega)$ is studied in a real experiment rather than $\chi''(\omega)/\omega$.

Initial high field results, where $|D| \ll \omega_0$ (thus simplifying the analysis) have been discussed by Norris and Weissman[8] who found a Brownian diffusion-type model best fit their experiments.

We note in conclusion, that an important possibility for slow-tumbling experiments is that they may well prove useful in distinguishing between different models for molecular reorientation.[5]

XIV.5. ACKNOWLEDGEMENT

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