

Electron Spin Resonance Line Shapes and Saturation in the Slow Motional Region^{1a}

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The stochastic Liouville method is developed and applied in a manner appropriate to analyze the problem of esr line shapes and saturation in the slow-motional region with particular emphasis on rotational diffusion. Detailed unsaturated line shape solutions are obtained for axial and asymmetric g tensors and axial dipolar tensors. These line shapes are compared to the predicted rigid-solid spectral shapes. In particular, it is shown that the pseudo-secular dipolar terms make significant contributions to the slow tumbling line shapes expected for ¹⁴N-containing radicals such as nitroxides and may not be neglected in such cases. Saturation effects are analyzed for a two-jump model, as well as for rotational diffusion of the g tensor. It is found that even in the slow-motional region, a fundamental role is played by the T_1 's that are obtained from the spin-relaxation theories. One finds that the significant line shape changes resulting from saturation are dependent on the rotational diffusion rates.

I. Introduction

There has recently been a growing interest in the character of esr line shapes in the region of slow tumbling where the earlier relaxation theories² are no longer adequate. The cause of the slow tumbling may be due to the use of a viscous solvent, a radical attached to a macromolecule, or a particularly large anisotropic term in the spin-Hamiltonian (*e.g.*, for triplets and other spins of higher multiplicity). In these cases, the condition $|\mathcal{H}_1(t)| \tau_R \ll 1$ required for the relaxation theories may no longer be fulfilled. Here $\mathcal{H}_1(t)$ is the rotationally dependent perturbation in the spin-Hamiltonian and τ_R is the rotational correlation time.

Kubo has called attention to the stochastic Liouville method, in recent work,^{3,4} as a general method for calculating spectral line shapes even when the conditions for motional narrowing are no longer fulfilled. The method is, in principle, applicable to any stochastic modulation of $\mathcal{H}_1(t)$ provided only that the stochastic process is assumed to be Markoffian. In Kubo's recent work it was also assumed that the processes were Gaussian, but this is not necessary for the method and not the case for rotational diffusion.

This method seems simpler and more general than the recent work on viscous media by Itzkowitz⁵ using a model of random jumps with Monte Carlo techniques as well as the work of Korst and Lazarev,⁶ which like the present work is based on the diffusion equation.

Of related interest is the straightforward manner in which we are able to include nonsecular effects in order to see to what extent they may be important for line shapes and saturation. Our rigorous analysis of nonsecular effects is based upon an approach utilizing fast motional spin states unlike the slow-motional "adia-

batic" approximation used by Itzkowitz⁵ and Korst and Lazarev.⁶ We note that recent work by Sillescu and Kivelson⁷ and Freed⁸ represent generalized solutions which can readily include nonsecular effects, but the detailed analyses given remained essentially perturbative in technique.⁹ Also, in related work on triplets by Norris and Weissman,¹⁰ only secular terms were needed.

Kubo's treatment of line shapes is based on linear response theory (the autocorrelation function) and is therefore not applicable for saturation phenomena. We have modified the approach, by starting from the density matrix equations of motion, so that the radiation field is included explicitly and saturation effects may be studied. The method is readily seen to be a generalization to a continuous range of the random

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(2) (a) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963); (b) D. Kivelson, *ibid.*, **33**, 1094 (1960).

(3) R. Kubo, "Stochastic Processes in Chemical Physics, Advances in Chemical Physics," Vol. XVI, K. E. Shuler, Ed., Wiley, New York, N. Y., 1969, p 101.

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(5) M. S. Itzkowitz, *J. Chem. Phys.*, **46**, 3048 (1967).

(6) (a) N. N. Korst and A. V. Lazarev, *Mol. Phys.*, **17**, 481 (1969); (b) I. V. Alexandrov, A. N. Ivanova, N. N. Korst, A. V. Lazarev, A. I. Prikhozhenko, and V. B. Stryukov, *ibid.*, **18**, 681 (1970).

(7) H. Sillescu and D. Kivelson, *J. Chem. Phys.*, **48**, 3493 (1968).

(8) J. H. Freed, *ibid.*, **49**, 376 (1968).

(9) R. G. Gordon (private communication) has developed a useful approach based on finite difference techniques.

(10) J. R. Norris and S. I. Weissman, *J. Phys. Chem.*, **73**, 3119 (1969).

variable of earlier and well-known techniques for handling relaxation resulting from jump phenomena occurring between a finite number of sites. The correspondence with a two-jump model (as well as the nature of the approximations for saturation) are shown in Appendix B.

II. General Method

The density-matrix equation of motion due to the random Hamiltonian $\mathcal{H}(t)$ is given by

$$\frac{\partial \rho}{\partial t} = -i[\mathcal{H}(t), \rho] \quad (1)$$

It is now assumed that there are a complete set of random variables Ω , which suffice to describe the random behavior of $\mathcal{H}(t)$ and which is described by a Markoff process. Thus

$$\frac{\partial}{\partial t} P(\Omega, t) = -\Gamma_{\Omega} P(\Omega, t) \quad (2)$$

where $P(\Omega, t)$ is the probability of finding Ω at the particular state at time t . The process is assumed to be stationary, so that Γ is a time-independent Markoff operator, and also that the process has a unique equilibrium distribution, $P_0(\Omega)$, characterized by

$$\Gamma P_0(\Omega) = 0 \quad (3)$$

Kubo⁴ shows that eq 1-3 lead to the equation of motion

$$\frac{\partial}{\partial t} \rho(\Omega, t) = -i[\mathcal{H}(\Omega), \rho(\Omega, t)] - \Gamma_{\Omega} \rho(\Omega, t) \quad (4)$$

where, however, $\rho(\Omega, t)$ is now understood to be an average ρ [defined by $\int \rho P(\Omega, \rho, t) d\rho$] associated with a particular value of Ω for the bath, hence a particular value of $\mathcal{H}(\Omega)$.

The steady-state spectrum in the presence of a single rotating radiofrequency field is determined by the power absorbed from this field. One finds for the λ th (multiple) hyperfine line at "orientation" specified by Ω ¹¹

$$\mathcal{P}_{\lambda}(\Omega) = 2\mathfrak{N}\hbar\omega \sum_j d_{\lambda_j} Z_{\lambda_j}^{(1)''}(\Omega) \quad (5)$$

where \mathcal{P}_{λ} is the power absorbed, \mathfrak{N} , the concentration of electron spins, and $Z_{\lambda_j}^{(1)''}$ is defined by the series of equations

$$(\rho - \rho_0)_{\lambda_j} \equiv \chi_{\lambda_j} \quad (6)$$

$$\chi_{\lambda_j} = \sum_{n=-\infty}^{\infty} e^{in\omega t} Z_{\lambda_j}^{(n)} \quad (7)$$

and

$$Z_{\lambda_j}^{(n)} = Z_{\lambda_j}^{(n)'} + iZ_{\lambda_j}^{(n)''} \quad (8)$$

In eq 6, $\rho_0(\Omega)$ is the equilibrium spin density matrix whose Ω dependence is such that $\Gamma_{\Omega} \rho_0 = 0$. In eq 7, the steady-state solution χ_{λ_j} has been expanded in a

Fourier series with time-independent coefficients $Z_{\lambda_j}^{(n)}$. Thus $\rho_0(\Omega) = \rho_0^{(0)}$. Equation 5 displays the fact that it is the $n = 1$ harmonic which is directly observed. (We will also use $\chi_a^{(0)}$ as the zeroth harmonic for the diagonal element corresponding to state a.)

In the above notation ρ_{λ_j} means the matrix element of ρ

$$\rho_{\lambda_j} \equiv \langle \lambda_{j-} | \rho | \lambda_{j+} \rangle \quad (9)$$

where λ_{j-} and λ_{j+} are the two levels between which the λ_j th transition occurs, and a "raising convention" is implied. This notation is discussed elsewhere.¹¹ Equivalent definitions apply to other operator matrix elements.

Also in eq 5 $d_{\lambda_j} = 1/2\gamma_e B_1$ for all allowed esr transitions induced by the radiofrequency field, and is otherwise zero.

The total absorption is then obtained as an equilibrium average of eq 5 over all Ω . Thus we introduce averages such as

$$\bar{Z}_{\lambda_j}^{(n)} = \int d\Omega P_0(\Omega) Z_{\lambda_j}^{(n)}(\Omega) \quad (10)$$

so that

$$\mathcal{P}_{\lambda} = 2\mathfrak{N}\hbar\omega \sum_j d_{\lambda_j} \bar{Z}_{\lambda_j}^{(1)''} \quad (11)$$

where we have taken d_{λ_j} essentially independent of orientation.¹² We now separate \mathcal{H} into three components

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(\Omega) + \epsilon(t) \quad (12)$$

where in the high-field approximation

$$\hbar\mathcal{H}_0 = \bar{g}_e \beta_e B_0 S_z - \hbar \sum_i \gamma_i I_{z_i} B_0 - \hbar \gamma_e \sum_i \bar{a}_i S_z I_{z_i} \quad (13)$$

yields the zero-order energy levels and transition frequencies

$$\mathcal{H}_1(\Omega) = \sum_{L, m, \mu, i} F'_{\mu, i}{}^{(L, m)}(\Omega) A'_{\mu, i}{}^{(L, -m)} \quad (14)$$

is the perturbation depending on orientation angles Ω expressed in the notation of Freed and Fraenkel,^{2a} and

$$\hbar\epsilon_1(t) = 1/2\hbar\gamma_e B_1 [S_+ \exp(-i\omega t) + S_- \exp(i\omega t)] \quad (15)$$

is the interaction with the radiation field.

When one takes the $\langle \lambda_{j-} | \lambda_{j+} \rangle$ matrix elements of eq 4 and utilizes eq 6-8, the steady-state equation for $Z_{\lambda_j}^{(1)}$ is found to be

$$\Delta\omega_{\lambda} Z_{\lambda_j}^{(1)} + [\mathcal{H}_1(\Omega), Z^{(1)}(\Omega)]_{\lambda_j} - i[\Gamma_{\Omega} Z^{(1)}(\Omega)]_{\lambda_j} + d_{\lambda_j} (\chi_{\lambda_{j+}^{(0)}} - \chi_{\lambda_{j-}^{(0)}}) = q\omega_{\lambda} d_{\lambda_j} \quad (16)$$

Here $\chi_{\lambda_{j+}^{(0)}}$ and $\chi_{\lambda_{j-}^{(0)}}$ represent the deviations from

(11) J. H. Freed, *J. Chem. Phys.*, **43**, 2312 (1965).

(12) This is reasonable for free radicals with small Δg values. For large Δg values the orientation dependence of γ_e must be considered (cf. B. Bleaney, *Proc. Phys. Soc. (London)*, **A75**, 621 (1960)).

spin equilibrium of the upper (+) and lower (-) electron spin states associated with the λ_j th transition, and $\Delta\omega_\lambda = \omega - \omega_\lambda$, where $\hbar\omega_\lambda = E_{\lambda_j+} - E_{\lambda_j-}$. The $Z^{(1)}(\Omega)$ are matrices defined by eq 6 and 8. Also $q = \hbar/kT(1/N)$ where $N =$ number of spin eigenstates and the high-temperature approximation has been assumed. The equation for $\bar{Z}_{\lambda_j}^{(1)}$ then becomes

$$\Delta\omega_\lambda \bar{Z}_{\lambda_j}^{(1)} + \int d\Omega P_0(\Omega) [\mathfrak{H}_1(\Omega), Z^{(1)}(\Omega)]_{\lambda_j} - i \int d\Omega P_0(\Omega) [\Gamma Z^{(1)}(\Omega)]_{\lambda_j} + d_{\lambda_j}(\bar{\chi}_{\lambda_j+}^{(0)} - \bar{\chi}_{\lambda_j-}^{(0)}) = q\omega_\lambda d_{\lambda_j} \quad (17)$$

To perform the integrations over Ω in eq 17 we expand the matrix element $Z(\Omega)_{\lambda_j}^{(n)}$ in a complete set of orthogonal eigenfunctions of Γ_Ω , call them $G_m(\Omega)$, with eigenvalues E_m

$$Z(\Omega, \omega)_{\lambda_j}^{(n)} = \sum_m [C_m^{(n)}(\omega)]_{\lambda_j} G_m(\Omega) \quad (18)$$

or in operator notation

$$Z(\Omega)^{(n)} = \sum_m C_m^{(n)}(\omega) G_m(\Omega) \quad (18a)$$

where $C_m^{(n)}$ is still an operator in spin space and is a function of ω , but is independent of Ω . Then eq 17 becomes

$$\Delta\omega_\lambda \bar{Z}_{\lambda_j}^{(1)} + \sum_m \int d\Omega P_0(\Omega) G_m(\Omega) \times [\mathfrak{H}_1(\Omega), C_m^{(1)}]_{\lambda_j} + d_{\lambda_j}(\bar{\chi}_{\lambda_j+}^{(0)} - \bar{\chi}_{\lambda_j-}^{(0)}) = q\omega_\lambda d_{\lambda_j} \quad (19)$$

In obtaining eq 19 we have assumed that $P_0(\Omega)$ gives an isotropic distribution of orientations. Thus $P_0 \propto G_0(\Omega)$ with eigenvalue $E_0 = 0$. Since $G_0(\Omega) \equiv 1$ is orthogonal to all $G_m(\Omega)$ with $m \neq 0$ in the Hilbert space of Ω , it then follows that the third term on the left-hand side of eq 17 vanishes upon averaging.

Note also that

$$\bar{Z}_{\lambda_j}^{(n)} = [C_0^{(n)}]_{\lambda_j} \quad (20)$$

from the definitions of eq 10 and 18. Thus the absorption (eq 11) depends only on the $[C_0^{(1)}]_{\lambda_j}$ for all allowed transitions λ_j .

When we premultiply eq 16 by $G_m^*(\Omega)$ and integrate over Ω , we obtain for $[C_m^{(1)}]$

$$N_{m'}(\Delta\omega_\lambda - iE_{m'}) [C_m^{(1)}]_{\lambda_j} + \sum_m \int d\Omega G_m^*(\Omega) G_m(\Omega) [\mathfrak{H}_1(\Omega), C_m^{(1)}]_{\lambda_j} + N_{m'} d_{\lambda_j} ([C_m^{(0)}]_{\lambda_j+} - [C_m^{(0)}]_{\lambda_j-}) = q\omega_\lambda d_{\lambda_j} \delta(m', 0) N_{m'} \quad (21)$$

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

$$N_m = \int d\Omega G_m^*(\Omega) G_m(\Omega) \quad (22)$$

Thus the coupling to the Markovian relaxation process of Γ_Ω comes about only if the perturbation $\mathfrak{H}_1(\Omega)$ can couple $[C_0^{(1)}]_{\lambda_j}$ to some coefficient $C_m^{(1)}$ where $m \neq 0$.

A form of eq 21, but written for the diagonal elements $[C_m^{(n)}]_{\lambda_j}$, is needed in problems involving a nonsecular \mathfrak{H}_1 which induces electron spin flips. It is given in section IIIB on saturation.

The above approach, hence eq 21, is valid for any Markovian or diffusive process. Equation 21 will yield coupled algebraic equations for the coefficients $[C_m^{(n)}]_{\lambda_j}$, and one attempts to solve for the $[C_0^{(1)}]_{\lambda_j}$, utilizing only a finite number of such coefficients. The convergence depends essentially on the ratio $|\mathfrak{H}_1(\Omega)|/E_{m'}$. 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 are recovered when only one order beyond $[C_0^{(1)}]_{\lambda_j}$ 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

$$\Gamma_\Omega \longrightarrow R\nabla_\Omega^2 \quad (23)$$

where ∇_Ω^2 is the rotational diffusion operator and R is the diffusion coefficient. Although the method is fully applicable to problems involving anisotropic rotational diffusion, we have assumed isotropic diffusion for simplicity in obtaining and illustrating typical results. A complete set of eigenfunctions of Γ_Ω for eq 23 are then the Wigner rotation matrices $\mathfrak{D}_{L, KM}^L(\Omega)$ with eigenvalues $E_m = E_{L, K, M} = RL(L+1)$.¹³ We now express eq 14 as

$$\mathfrak{H}_1(t) = \sum_{L, m, m', \mu, i} \mathfrak{D}_{-m, m'}^{L, L}(\Omega) F'_{\mu, i}{}^{(L, m)} A_{\mu, i}{}^{(L, m')} \quad (24)$$

where both the $F'_{\mu, i}{}^{(L, m)}$ and the $A_{\mu, i}{}^{(L, m')}$ are irreducible tensor components of rank L and component m and m' . The F' in eq 24 are expressed in molecule-fixed coordinates, while A is a spin operator quantized in space-fixed axes. The $\mathfrak{D}_{-m, m'}^{L, L}(\Omega)$ terms include the transformation from space-fixed to molecule-fixed axes. It follows from the orthogonality relation¹⁴ of the \mathfrak{D}_{KM}^L 's that

$$N_{KM}^L = \frac{8\pi^2}{2L+1} \quad (25)$$

and

$$P_0(\Omega) = \frac{1}{8\pi^2} = \frac{1}{8\pi^2} \mathfrak{D}_{0, 0}^0(\Omega) \quad (26)$$

The evaluation of the integral on the left-hand side of eq 21 is obtained utilizing¹⁴

$$\int d\Omega \mathfrak{D}_{m_1 m_1'}^{L_1}(\Omega) \mathfrak{D}_{m_2 m_2'}^{L_2}(\Omega) \mathfrak{D}_{m_3 m_3'}^{L_3}(\Omega) = 8\pi^2 \begin{pmatrix} L_1 & L_2 & L_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L_3 \\ m_1' & m_2' & m_3' \end{pmatrix} \quad (27)$$

(13) J. H. Freed, *J. Chem. Phys.*, **41**, 2077 (1964).

(14) A. R. Edmonds, "Angular Momentum in Quantum Mechanics," Princeton University Press, Princeton, N. J., 1957.

Table I: Line Shape Deviations from Lorentzian as $|\mathcal{F}|/R$ Increases, for Single Line Broadened by Axial g Tensor

$ \mathcal{F} /R$	Relative $1/2^{-1/2}$ width ^d	Relative abs heights	I_{abs}^a	Relative deriv width	Relative deriv height	I_{deriv}^b	Derivative asymmetry ^c
0.2	1.00	1.000	1.00	1.00	1.000	1.00	1.000
1.0	2.57	0.393	1.01	2.59	0.154	1.03	1.000
2.5	5.50	0.188	1.034	5.62	0.034	1.074	1.008
5.0	10.4	0.107	1.11	10.75	0.0103	1.20	1.11
8.0	14.55	0.0815	1.185	13.9	0.0059	1.14	1.52

^a $I_{\text{abs}} \equiv$ relative $1/2^{-1/2}$ width \times relative absorption height; $I_{\text{abs}} = 1$ for a Lorentzian. ^b $I_{\text{deriv}} \equiv$ (relative derivative width)² \times relative derivative height; $I_{\text{deriv}} = 1$ for a Lorentzian. ^c Derivative asymmetry is the ratio of the height of the low-field derivative extremum to the height of the high-field derivative extremum. Note $(g_{\parallel} - g_{\perp})$ is taken as negative. ^d Rotationally invariant width component of 0.61 is included.

where the terms in parentheses in eq 27 are the $3j$ symbols; also

$$\mathcal{D}_{m,m'}^{L*} = (-)^{m-m'} \mathcal{D}_{-m,-m'}^L \quad (28)$$

III. Applications

A. No Saturation. The case of no saturation is achieved by setting $\chi_{\lambda,+} = \chi_{\lambda,-} = 0$, so the last term on the left-hand side of eq 21 is zero.

1. 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 $g_z = g_{\parallel}$. When $\omega_0^2 \tau_R^2 \gg 1$, the nonsecular term will make a negligible contribution compared to the secular term.

For this case eq 24 is

$$\mathcal{H}_1(t) = \mathcal{D}_{0,0}(\Omega)^2 / \delta \hbar^{-1} \beta_e B_0 (g_{\parallel} - g_{\perp}) S_z \equiv \mathcal{D}_{0,c}^{(2)}(\Omega) \mathcal{F} S_z \quad (29)$$

We have

$$- [S_z, C_m^{(1)}]_{\lambda_i} = [C_m^{(1)}]_{\lambda_i} \quad (30)$$

for a doublet state. When eq 29 and 30 are substituted into eq 21 (for no saturation), and eq 25–28 are utilized, then one obtains

$$[(\omega - \omega_0) - iRL(L+1)] [C_{0,0}^{L'}(\omega)]_{\lambda_i} - (2L+1) \mathcal{F} \sum_{L'} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 [C_{0,0}^{L'}(\omega)]_{\lambda_i} = q\omega_{\lambda} d_{\lambda} \delta(L,0) \quad (31)$$

Now from eq 11 the absorption is proportional to

$$\pi \cdot \bar{Z}_{\lambda_i}^{(1)''} = \text{Im} [C_{0,0}^{(1)}]_{\lambda_i} \quad (32)$$

Equation 31 defines an infinite set of coupled algebraic equations for the complex coefficients $C_{0,0}^{L'}(\omega)$ (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 $L \pm 2$ th equations, so only even L values appear. Approximations to the complete solution may be ob-

tained by terminating the coupled equations at some finite limit by letting $C_{0,0}^{L'} = 0$ for $L' > n$ where $r = (n/2) + 1$ gives the order of the equations. The order r needed to obtain a satisfactory solution depends on the ratio $|\mathcal{F}/R|$; the larger this ratio, the greater the value of n needed. A crude discussion of the convergence problem for this case appears in Appendix A, and it utilizes the fact that the present simple case has a continued fraction representation. We have found the convergence to be very rapid. Thus for $|\mathcal{F}/R| \leq 10$, $r \leq 4$ is sufficient, for $|\mathcal{F}/R| \sim 100$, $r \approx 7$, while for $|\mathcal{F}/R| \leq 1000$, $r \approx 10$ is needed (when $T_2 |\mathcal{F}| \approx 75$). (Note that the validity of relaxation theory² requires $|\mathcal{F}/6R| \ll 1$ since the rotational correlation time in this case is $[L(L+1)R]^{-1}$ with $L = 2$.)

The results, given as both absorptions and first derivatives, in Table I and Figure 1, show the expected trends. As $|\mathcal{F}/R|$ increases to unity (the region where relaxation theory applies), the main effect of the line shape is a broadening (cf. Table I). 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 1000 the solidlike spectrum is sharpening up (one is observing a decrease of "motional broadening") as it clearly is approaching the powder spectrum given in Figures 1C and D. The powder spectrum was computed from the expressions given by Lefebvre and Maruani.¹⁵

The effect of including a rotationally invariant Lorentzian line width, T_2^{-1} , by letting $\omega_0 \rightarrow \omega_0 + iT_2^{-1}$ in eq 31 is shown in Figure 2. The effect of increasing T_2^{-1} is to smooth out the appearance of a solidlike spectrum.

2. Asymmetric Secular g Tensor. If now we let $g_x \neq g_y$, then

$$\mathcal{H}_1(\Omega) = \mathcal{F}_0 \mathcal{D}_{0,0}^2 S_z + \mathcal{F}_2 S_z [\mathcal{D}_{-2,0}^2 + \mathcal{D}_{2,0}^2] \quad (33)$$

where

(15) R. Lefebvre and J. Maruani, *J. Chem. Phys.*, **42**, 1480 (1965). Their formulas were first converted into units of gauss from reciprocal seconds.

$$\mathfrak{F}_0 = \frac{2}{3}[g_z - \frac{1}{2}(g_x + g_y)]\hbar^{-1}\beta_e B_0 \quad (34a)$$

and

$$\mathfrak{F}_2 = \frac{1}{\sqrt{6}}(g_x - g_y)\hbar^{-1}\beta_e B_0 \quad (34b)$$

The relevant coupled equations are given by

$$(2L + 1)^{-1}[(\omega - \omega_0) - iT_2^{-1} - iRL(L + 1)]\bar{C}_{K,0}^{L'} - \mathfrak{F}_0 \sum_{L'} \begin{pmatrix} L & 2 & L' \\ K & 0 & -K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} \bar{C}_{K,0}^{L'} - \mathfrak{F}_2 \sum_{L'} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} \left[\begin{pmatrix} L & 2 & L' \\ K & -2 & -(K - 2) \end{pmatrix} \bar{C}_{K-2,0}^{L'} + \begin{pmatrix} L & 2 & L' \\ K & 2 & -(K + 2) \end{pmatrix} \bar{C}_{K+2,0}^{L'} \right] = q\omega_\lambda d_{\lambda,0} \delta_{L,0} \delta_{K,0} \quad (35)$$

where K is positive, and eq 32 as well as the triangle rule requiring $L' = L \pm 2$ or L still holds. Also one must have $K \leq L$, etc. The superbars in eq 35 imply the following symmetrization

$$\bar{C}_{K,0}^{L'} = \frac{1}{2}(C_{K,0}^{L'} + C_{-K,0}^{L'}) \quad (36a)$$

and

$$\bar{C}_{0,0}^{L'} = C_{0,0}^{L'} \quad (36b)$$

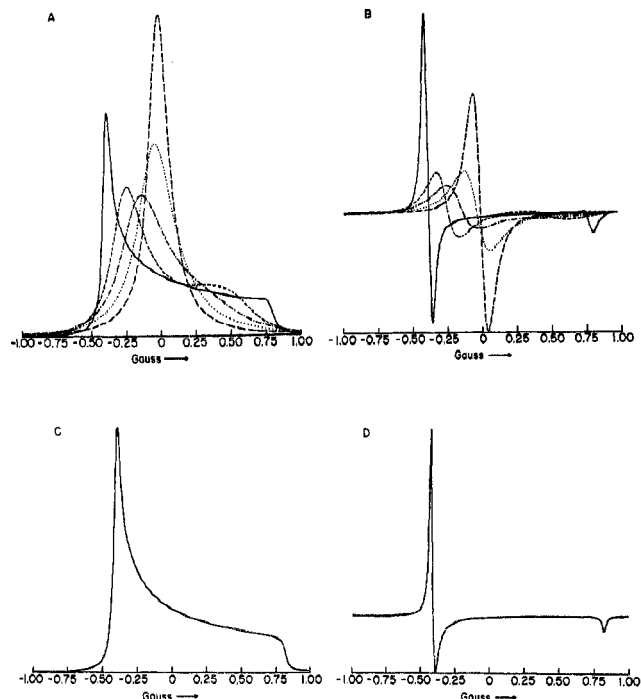


Figure 1. Line shapes for an axially symmetric g tensor as a function of $|\mathfrak{F}|/R$: A, absorption line shapes; B, first derivative. The different $|\mathfrak{F}|/R$ values are —, 2.5; ···, 5; - - -, 10; - · - ·, 25; — — —, 1000; C and D, rigid limit absorption and derivative line shapes. All correspond to $(g_{||} - g_{\perp}) = -7.50 \times 10^{-4}$, $\bar{g} = 2.00285$ and are centered about $\hbar\omega_0/\bar{g}\beta_e \equiv B_0 = 3300$ G and a rotationally invariant $(2/\sqrt{3})T_2^{-1}/|\gamma_e| = 0.02$ G.

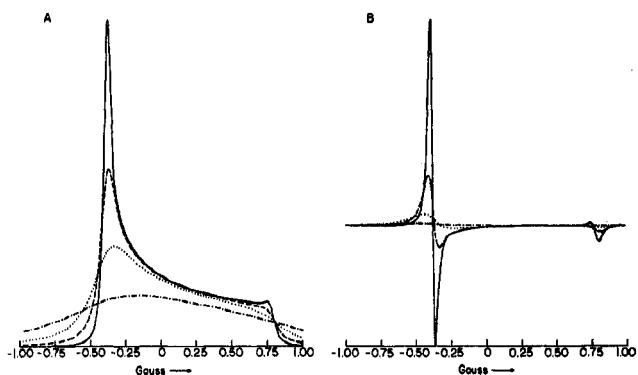


Figure 2. Line shapes for an axially symmetric g tensor as a function of the rotationally invariant component T_2^{-1} : A, absorption; B, derivative. The different values of $(2/\sqrt{3})T_2^{-1}/|\gamma_e|$ are —, 0.01 G; ···, 0.05 G; - - -, 0.150 G; - · - ·, 0.500 G. In all cases $|\mathfrak{F}|/R = 1000$.

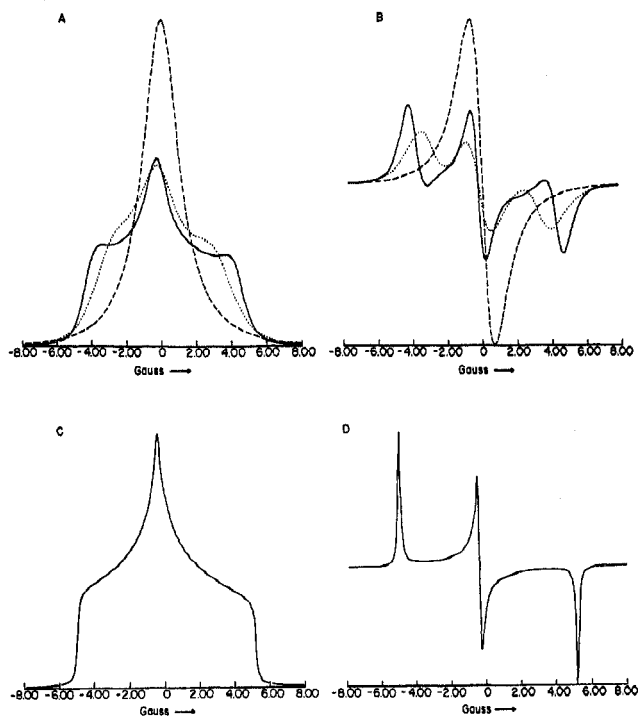


Figure 3. Line shapes for an asymmetric g tensor as a function of $|\mathfrak{F}_0|/R$: A, absorption; B, derivative. The different $|\mathfrak{F}_0|/R$ values are ···, 5; - - -, 25; —, 100. C and D, rigid limit absorption and derivative line shapes. All correspond to $g(x) = 2.00890$, $g(y) = 2.00610$, $g(z) = 2.00270$ and are centered about $B_0 = 3300$ G, with a rotationally invariant $(2/\sqrt{3})T_2^{-1}/|\gamma_e| = 0.1$ G.

The order of the equations, when one terminates for $L > n$ is now $1 + n(n + 6/8)$. However the proper value of n , again depends on $|\mathfrak{F}_0|/R$ for $|\mathfrak{F}_0| > |\mathfrak{F}_2|$, and values of n equivalent to those of case 1 are again applicable.

The progress of the line shapes, as $|\mathfrak{F}_0|/R$ increases, is seen from Figure 3 to be similar to case 1, but in the region of 10 to 100 three peaks now appear. The limiting powder spectrum appears in Figure 3c, and

although there still is appreciable motion for $|\mathfrak{F}_0/R| = 100$, this case is seen to be beginning to approach the powder spectrum (note that intensities of separately computed viscous liquid and powder spectra are arbitrary).

3. g Tensor plus END Tensor Including Pseudo-Secular Terms. The power of the method is exemplified in this case, where the pseudo-secular ($S_z I_{\pm}$) terms, which can cause nuclear spin flips, can be comparable in importance to the secular terms when ω_n , the nuclear spin Larmor frequency is small.² The retention of the pseudo-secular terms results in $[\mathfrak{H}_1, \mathfrak{H}_0] \neq 0$, unlike the previous cases.

a. One Nuclear Spin of $I = 1/2$. This is the simplest case for illustrating the method. The labeling of the energy levels and relevant transitions is given in Figure 4a. The resonance frequencies for the two allowed transitions (1 and 2) and the two forbidden transitions (3 and 4) are

$$\begin{aligned}\omega_1 &= \omega_{aa'} = \omega_e - 1/2\gamma_e \bar{a} \longrightarrow -a' \\ \omega_2 &= \omega_{bb'} = \omega_e + 1/2\gamma_e \bar{a} \longrightarrow a' \\ \omega_3 &= \omega_{ba'} = \omega_e + \omega_n \longrightarrow \omega_n \\ \omega_4 &= \omega_{ab'} = \omega_e - \omega_n \longrightarrow -\omega_n\end{aligned}\quad (37)$$

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

$$\mathfrak{H}_1(\Omega) = \mathfrak{D}_{0,0}^2 S_z [\mathfrak{F} + D' I_z] + (\mathfrak{D}_{0,1}^2 I_+ S_z - \mathfrak{D}_{0,-1}^2 I_- S_z) D \quad (38)$$

where

$$D = -2\pi \xi_i D_i^0 \quad (39a)$$

with $\xi_i = 1/2\pi |\gamma_e| |\gamma_i|^{\hbar}$ and D_i^0 is discussed elsewhere.¹⁶ Also

$$D' = -(\frac{8}{3})^{1/2} D \quad (39b)$$

If we write $[\mathfrak{H}, \rho] \equiv \mathfrak{H}^x \rho$,⁸ then one has

$$[\mathfrak{H}_1^x]_{\alpha\alpha'\beta\beta'} = [\mathfrak{H}_{1,\alpha\beta} \delta_{\alpha'\beta'} - \mathfrak{H}_{1,\beta'\alpha'} \delta_{\alpha\beta}] \quad (40)$$

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

$$\mathfrak{H}_1^x(\Omega) = \begin{pmatrix} 1 & & & \\ \mathfrak{D}_{0,0}^2(\mathfrak{F} + 1/2 D') & & & \\ 0 & & & \\ s^* & & & \\ s & & & \end{pmatrix}$$

where $s = 1/2 \mathfrak{D}_{0,1}^2 D$. One must now develop eq 21 for nondegenerate transitions $\lambda = 1, 2, 3,$ and 4 . We shall represent the appropriate coefficients as $C_{K,M}^L(\lambda)$. Then we obtain

$$\begin{aligned}(2L+1)^{-1}[(\omega+a') - i\{T_2^{-1} + \\ RL(L+1)\}] C_{0,0}^{L'}(1) - \\ (\mathfrak{F} + 1/2 D') \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} C_{0,0}^{L'}(1) + \\ 1/2 D \sum_{L' \neq 0} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{0 \ 1 \ -1} [C_{0,1}^{L'}(3) - \\ C_{0,-1}^{L'}(4)] = q\omega_1 d_1 \delta_{L,0}\end{aligned}\quad (42a)$$

$$\begin{aligned}(2L+1)^{-1}[(\omega-a') - i\{T_2^{-1} + RL(L+1)\}] \times \\ C_{0,0}^{L'}(2) - (\mathfrak{F} - 1/2 D') \sum_{L'} \binom{L' \ 2 \ L'}{0 \ 0 \ 0} C_{0,0}^{L'}(2) + \\ 1/2 D \sum_{L' \neq 0} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{0 \ 1 \ -1} [C_{0,1}^{L'}(3) - \\ C_{0,-1}^{L'}(4)] = q\omega_2 d_2 \delta_{L,0}\end{aligned}\quad (42b)$$

$$\begin{aligned}\frac{D}{2} \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{1 \ -1 \ 0} [C_{0,0}^{L'}(1) + \\ C_{0,0}^{L'}(2)] + (2L+1)^{-1}[(\omega - \omega_n) - \\ i\{T_2^{-1} + RL(L+1)\}] C_{0,1}^{L'}(3) + \\ \mathfrak{F} \sum_{L' \neq 0} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{1 \ 0 \ -1} C_{0,1}^{L'}(3) = 0\end{aligned}\quad (42c)$$

$$\begin{aligned}-\frac{D}{2} \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{-1 \ 1 \ 0} [C_{0,0}^{L'}(1) + \\ C_{0,0}^{L'}(2)] + (2L+1)^{-1}[(\omega + \omega_n) - \\ i\{T_2^{-1} + RL(L+1)\}] C_{0,-1}^{L'}(4) + \\ \mathfrak{F} \sum_{L' \neq 0} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{-1 \ 0 \ 1} C_{0,-1}^{L'}(4) = 0\end{aligned}\quad (42d)$$

While eq 42a and b are applicable for $L = 0$, eq 42c and d require $L, L' > 0$, and in all cases L and L' must be even and $L' = L \pm 2$ or L . Equations 42 represent four infinite sets of coupled equations (*i.e.*, expansions in L) which are then coupled among each other due to the pseudo-secular contribution from the END term.

The absorption is proportional to

$$Z_1'' + Z_2'' = \text{Im}[C_{0,0}^0(1) + C_{0,0}^0(2)] \pi^{-1} \quad (43)$$

When the series of eq 42 are terminated for $L > n$, the coupled algebraic equations are of order $r = 2(n+1)$ (the coefficients $C_{0,0}^0(3)$ and $C_{0,0}^0(4)$ are not needed to

$$\begin{array}{ccc} & 2 & 3 & 4 \\ & 0 & s & s^* \\ \mathfrak{D}_{0,0}^2(\mathfrak{F} - 1/2 D') & & s & s^* \\ s^* & & \mathfrak{D}_{0,0}^2 \mathfrak{F} & 0 \\ s & & 0 & \mathfrak{D}_{0,0}^2 \mathfrak{F} \end{array} \quad (41)$$

(16) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967). Specifically for an axially symmetric hyperfine tensor we have $A_{||} = \bar{a} + \frac{2\sqrt{6}}{3} \xi_i D_i^{(0)}$ and $A_{\perp} = \bar{a} - \frac{\sqrt{6}}{3} \xi_i D_i^{(0)}$ where the A 's are in sec^{-1} and $D_i^{(0)}$ is in cm^{-3} .

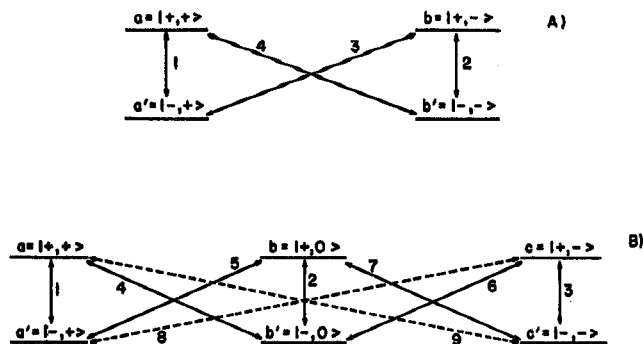


Figure 4. Energy levels and transitions for A, $S = 1/2$, $I = 1/2$ case; B, $S = 1/2$, $I = 1$ case. The notation is $|M_S, M_I\rangle$.

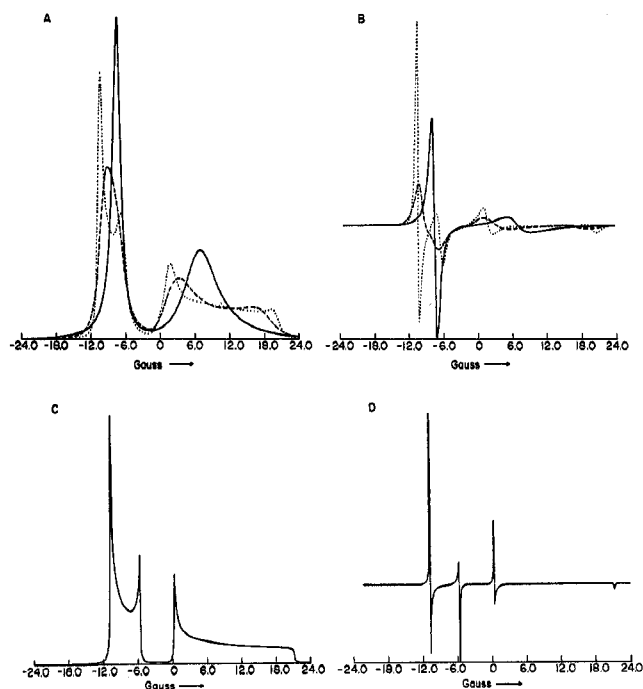


Figure 5. Line shapes for $S = 1/2$, $I = 1/2$ with axially symmetric g tensor and hyperfine tensor and small ω_n : A, absorption; B, derivative. The different $|\mathcal{F}|/R$ values are —, 2; ---, 15; ···, 100. C and D, rigid limit absorption and derivative line shapes. All correspond to $g_{||} = 2.00270$, $g_{\perp} = 2.00750$, $A_{||} = 32$ G, $A_{\perp} = 6$ G, $|\omega_n/\gamma_e| = 0.36$ G, $(2/\sqrt{3})T_2^{-1}/|\gamma_e| = 0.1$ G, and are centered about $B_0 = 3300$ G.

obtain the spectrum from eq 43). When $|D| \ll |a \pm \omega_n|$, then it is possible to use a perturbation technique to uncouple the coefficients for $\lambda = 1$ and 2 from those for $\lambda = 3$ and 4. (This technique is discussed in some detail in section B2.)

The solutions to eq 42 and 43 for the case of a small ω_n are given in Figure 5. This is a situation wherein a perturbation approach is not applicable. The parameters utilized for Figure 5 are appropriate for a nitroxide,¹⁷ except that here $I = 1/2$. (An ^{15}N nucleus is thus moderately well represented.) One again sees the gradual transition from liquidlike to solidlike line shapes as $|\mathcal{F}|/R$ is increased, and even at $|\mathcal{F}|/R = 100$ the correspondence to the rigid limit (Figure 5C) is clear.

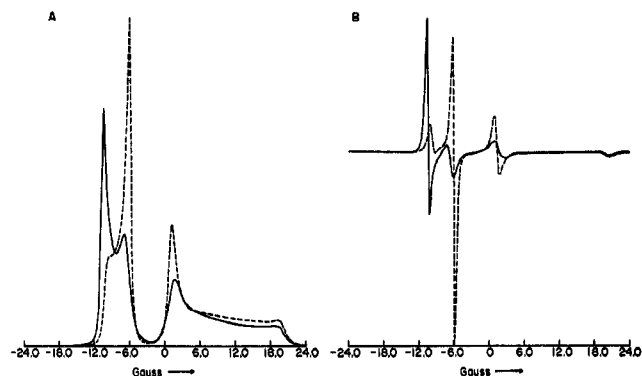


Figure 6. Comparison for $S = 1/2$, $I = 1/2$ of line shapes which include pseudo-secular contributions to line shapes for which they are omitted, when ω_n is small; $|\mathcal{F}|/R = 100$. All other parameters as in Figure 5: A, absorption; B, derivative. — corresponds to inclusion of pseudo-secular terms; --- corresponds to their omission.

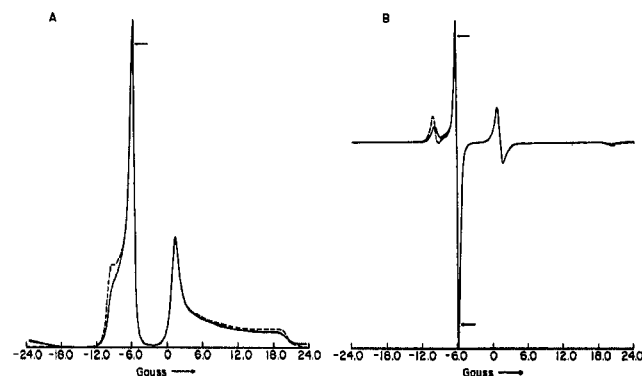


Figure 7. Comparison for $S = 1/2$, $I = 1/2$ of line shapes which include pseudo-secular contributions to line shapes for which they are omitted, when ω_n is large; $|\mathcal{F}|/R = 100$. $|\omega_n/\gamma_e| = 23.0$ G. All other parameters as in Figure 5: A, absorption; B, derivative. — corresponds 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.]

Figures 6 and 7 show the results of a study to determine the importance of the pseudo-secular contributions. Figure 6 corresponds to the same parameters as Figure 5 with $|\mathcal{F}|/R = 100$, but the complete solution is compared to the simplified solution obtained by the neglect of the pseudo-secular terms (*i.e.*, the terms in eq 42a and b which couple in forbidden transitions 3 and 4). There is no question but that the absorption and derivative line shapes are significantly altered by the presence of pseudo-secular terms. In Figure 7, a similar comparison was made, but here ω_n was increased by a factor of 65 while all other parameters were kept constant. With this choice of ω_n , the relevant spin parameters scale reasonably well to those for a typical aromatic

(17) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965); T. J. Stone, T. Buckman, P. L. Nordio, and H. M. McConnell, *Proc. Nat. Acad. Sci. U. S. A.*, **54**, 1010 (1965).

ring proton when one divides them by 4.6. In this case it is seen that the pseudo-secular terms make only a minor contribution to the line shapes, as expected, since $|D| \ll |a' \pm \omega_n|$. Such small effects can be accounted for by perturbation techniques. Similar results are obtained at lower values of $|\mathcal{F}|/R$, although for $|\mathcal{F}|/R = 10$ the primary effect of the pseudo-secular terms is to further broaden and shift the peaks rather than to change the spectral shapes markedly.

b. One Nuclear Spin of $I = 1$ (^{14}N). The energy levels and three allowed and six forbidden transitions are shown in Figure 4B for this case. We again assume axially symmetric tensors, and following a procedure similar to that used in part a for $I = 1/2$, we obtain sets of equations which couple all nine transitions and are of order $r = (9/2)n + 3$. They can be summarized as follows.

$$(2L + 1)^{-1} \{ [\omega + (2 - \lambda)2a'] - i[T_2^{-1} + RL(L + 1)] \} C_{0,0}^{L'}(\lambda) - [\mathcal{F} + (2 - \lambda)D'] \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \times C_{0,0}^{L'}(\lambda) + \frac{\sqrt{2}}{2} D \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{0 \ 1 \ -1} f(L', \lambda) = q\omega_\lambda d_\lambda \delta_{L,0} \quad (\text{for } \lambda = 1, 2, \text{ or } 3) \quad (44)$$

where

$$f(L', 1) = C_{0,1}^{L'}(4) - C_{0,-1}^{L'}(5) \quad (44a)$$

$$f(L', 3) = C_{0,1}^{L'}(6) - C_{0,-1}^{L'}(7) \quad (44b)$$

$$f(L', 2) = f(L', 1) + f(L', 3) \quad (44c)$$

$$(2L + 1)^{-1} \{ [\omega - (-1)^\lambda \omega_n + \nu a'] - i[T_2^{-1} + RL(L + 1)] \} C_{0,-1}^{L'}(\lambda) + (\mathcal{F} + \nu^{1/2} D') \times \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{1 \ 0 \ -1} C_{0,-1}^{L'}(\lambda) + (-1)^\lambda \frac{\sqrt{2}}{2} D \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{1 \ -1 \ 0} \times [C_{0,0}^{L'}(\epsilon) + C_{0,0}^{L'}(2)] - (-1)^\lambda \frac{\sqrt{2}}{2} D \times \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{1 \ 1 \ -2} C_{0,2(-1)}^{L'}(\nu') = 0 \quad (\text{for } \lambda = 4, 5, 6, \text{ or } 7) \quad (45)$$

where $\nu = +1$ and $\epsilon = 1$ when $\lambda = 4$ or 5 and $\nu = -1$ and $\epsilon = 3$ when $\lambda = 6$ or 7 ; also $\nu' = 8$ for $\lambda = 4$ or 6 and $\nu' = 9$ for $\lambda = 5$ or 7 . Also

$$(2L + 1)^{-1} \{ [\omega - (-1)^\lambda 2\omega_n] - i[T_2^{-1} + RL(L + 1)] \} C_{0,2(-)}^{L'}(\lambda) - \mathcal{F} \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L \ 2 \ L'}{2 \ 0 \ -2} C_{0,2(-)}^{L'}(\lambda) - (-1)^\lambda \frac{\sqrt{2}}{2} D \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} \binom{L' \ 2 \ L}{2 \ -1 \ -1} f(L', \lambda) = 0 \quad (\text{for } \lambda = 8 \text{ or } 9) \quad (46)$$

where

$$f(L', 8) = C_{0,1}^{L'}(4) + C_{0,1}^{L'}(6) \quad (46a)$$

$$f(L', 9) = C_{0,-1}^{L'}(5) + C_{0,-1}^{L'}(7) \quad (46b)$$

The above equations are valid for even L and L' . Finally

$$I(\omega) = \frac{1}{\pi} \text{Im} [C_{0,0}^0(1) + C_{0,0}^0(2) + C_{0,0}^0(3)] \quad (47)$$

Computer simulations of these equations for the nitroxide-like values employed in part a are given in Figures 8 and 9. In Figure 8 results for a range of $|\mathcal{F}|/R$ values are given, and they show the progress from liquidlike to solidlike spectra. In Figure 9 a comparison is made between line shapes obtained (for $|\mathcal{F}|/R = 100$) when pseudo-secular terms are both included and omitted. Again it is clear that these terms make important contributions. Also shown in Figure 9 is a comparison of the rigid limit spectra predicted for the two cases when pseudo-secular terms are either included or omitted, and the difference is significant.

B. Saturation. 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 4 and performing a derivation like that which leads to eq 21. We obtain

$$N_m (i n \omega + E_m) [C_m^{(n)}]_{\lambda_j^\pm} = \mp i d_{\lambda_j} N_m ([C_m^{(n+1)}]_{\lambda_j^\pm} - [C_m^{(n-1)}]_{\lambda_j^\pm}) - i \sum_m \int d\Omega G_m^*(\Omega) G_m(\Omega) [\mathcal{H}_1^{(\text{nonsec})}, C_m^{(n)}]_{\lambda_j^\pm, \lambda_j^\pm} \quad (48)$$

(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 (nonsec) refers to the fact that only the nonsecular part of \mathcal{H}_1 need be retained. Equation 48 is also needed for problems involving no saturation, but a nonsecular \mathcal{H}_1 which induces electron spin flips.

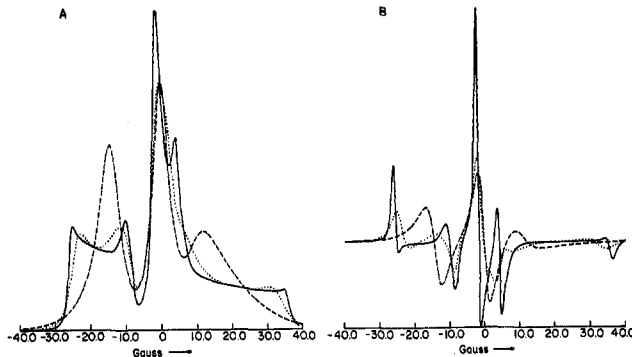


Figure 8. Line shapes for $S = 1/2$, $I = 1$ (^{14}N nucleus) with axially symmetric g tensor, hyperfine tensor, and small ω_n : A, absorption; B, derivative. Parameters same as in Figure 5 except $(2/\sqrt{3})T_2^{-1}/|\gamma_e| = 0.3$ G. The $|\mathcal{F}|/R$ values are ---, 2; ..., 15; —, 100.

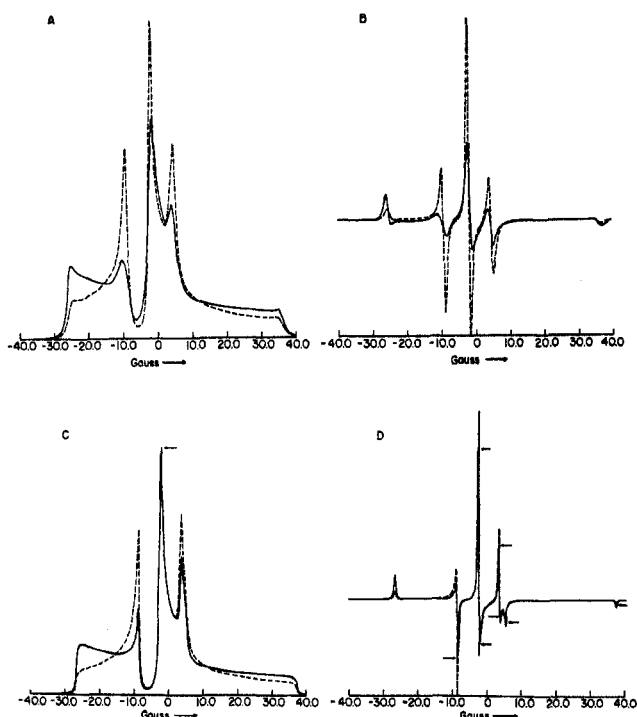


Figure 9. Comparison for $S = 1/2$, $I = 1$ (^{14}N nucleus) of line shapes which include pseudo-secular contributions to line shapes for which they are omitted, when ω_n is small; $|\mathfrak{F}|/R = 100$. All other parameters as in Figure 5: A, absorption; B, derivative; C and D, rigid limit. — corresponds to inclusion of pseudo-secular terms; --- corresponds to their omission. Arrows are used to locate derivative extrema in D when otherwise unclear. Note that in A and B the shapes are normalized to a common integrated intensity, while in C and D they are normalized to the same total height.

It is often convenient to look at the difference

$$[b_{m'}^{(n)}]_{\lambda_i} \equiv [C_{m'}^{(n)}]_{\lambda_i^+} - [C_{m'}^{(n)}]_{\lambda_i^-} \quad (49)$$

which is found, from eq 48, to obey the equation

$$\begin{aligned} N_{m'}(i\omega + E_{m'})[b_{m'}^{(n)}]_{\lambda_i} = & \\ & -i2d_{\lambda_i}N_{m'}([C_{m'}^{(n+1)}]_{\lambda_i \rightarrow} - C_{m'}^{(n-1)}]_{\lambda_i \leftarrow}) - \\ & i\sum_m \int d\Omega G_{m'}^*(\Omega)G_m(\Omega) (\mathfrak{F}\mathcal{C}_1^{(\text{nonsec})}, C_m^{(n)}]_{\lambda_i^+, \lambda_i^+} - \\ & \mathfrak{F}\mathcal{C}_1^{(\text{nonsec})}, C_m^{(n)}]_{\lambda_i^-, \lambda_i^-}) \quad (50) \end{aligned}$$

It follows from the Hermitian properties of ρ and ρ_0 as well as eq 6, 7, and 18 that

$$N_{m'}[C_{m'}^{(n)}]_{ab} = \sum_m [C_m^{(-n)}]_{ba}^* \int G_{m'}^*(\Omega)G_m^*(\Omega)d\Omega \quad (51)$$

Equation 51 also applies for $b = a$. Thus in eq 48

$$\begin{aligned} [C_{m'}^{(n-1)}]_{\lambda_i \leftarrow} = & N_{m'}^{-1} \sum_m [C_m^{(-n+1)}]_{\lambda_i \rightarrow}^* \times \\ & \int G_{m'}^*(\Omega)G_m^*(\Omega)d\Omega \quad (52) \end{aligned}$$

A form of eq 21 generalized to any n (not just $n = 1$) is sometimes needed. It is

$$\begin{aligned} N_{m'}[(n\omega - \omega_{\lambda}) - iE_{m'}] \times \\ [C_{m'}^{(n)}]_{\lambda_i} + \sum_m \int d\Omega G_{m'}^*(\Omega)G_m(\Omega) \times \\ [\mathfrak{F}\mathcal{C}_1(\Omega), C_m^{(n)}]_{\lambda_i} + d_{\lambda_i}N_{m'}[b_{m'}^{(n-1)}]_{\lambda_i} = \\ q\omega_{\lambda}d_{\lambda_i}\delta(m',0)\delta(n,1) \quad (53) \end{aligned}$$

In eq 48 (or 50) and 53, one sees that it is only through effects of the radiation field, where the strength of interaction with the spins is given by $d_{\lambda_i} \equiv 1/2\omega_1$, that the n th harmonics $[C_{m'}^{(n)}]$ are coupled to harmonics $[C_{m'}^{(n\pm 1)}]$. An analysis of these equations (which is given in more detail for the simple two-jump case in Appendix B) leads to the result that the extent of coupling depends essentially on the ratio ω_1/ω_0 , 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 $[C_0^{(1)}]_{\lambda_i}$, the observed signal) and the $n = 0$ terms (which include $[b_0^{(0)}]_{\lambda_i}$, the dc population differences). Higher harmonics become important in a variety of multiple resonance schemes or experiments done at lower dc fields.

1. *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 just as in section IIIA1, while there is a rotationally invariant $T_1 = (2W_e)^{-1}$, where W_e is the lattice-induced electron spin flip process. This is introduced by replacing in eq 50 $E_{m'} \rightarrow E_{m'} + 2W_e$. We also include a rotationally invariant $T_2 \leq T_1$ by letting $iE_{m'} \rightarrow i(E_{m'} + T_2^{-1})$ in eq 53.

For the secular perturbation of eq 29, it is only necessary to consider $[C_{0,0}^{L(1)}]_{\lambda_i}$ and $[b_{0,0}^{L(0)}]_{\lambda_i}$, and one obtains from eq 50 and 53

$$\begin{aligned} [(\omega - \omega_0) - iRL(L+1)] - \\ iT_2^{-1}[C_{0,0}^{L(1)}]_{\lambda_i} - (2L+1)\mathfrak{F}\sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0}^2 \times \\ [C_{0,0}^{L'(1)}]_{\lambda_i} + \frac{4|d_{\lambda_i}|^2}{RL(L+1) + 2W_e} \times \\ \text{Im}[C_{0,0}^{L(1)}]_{\lambda_i} = q\omega_{\lambda}d_{\lambda_i}\delta(L,0) \quad (54) \end{aligned}$$

Equation 54 with eq 32 then determines the saturated spectrum. Note that the saturation term (*viz.* the last term on the left-hand side of eq 54) for $L = 0$ is unaffected by the rotational motion; while for $L > 0$ we find $W_e \rightarrow W_e + 1/2RL(L+1)$, *i.e.*, the rotational motion aids the spin relaxation by spreading the spins over all orientations, which, due to $\mathfrak{F}\mathcal{C}_1(\Omega)$ have different "static" resonant frequencies.

The computer solution to eq 54 is conveniently developed after the real and imaginary parts have been separated. The results for $|\mathfrak{F}|/R = 10$ and 100 are given, respectively, in Figures 10 and 11. Each figure shows curves corresponding to values of B_1 covering a

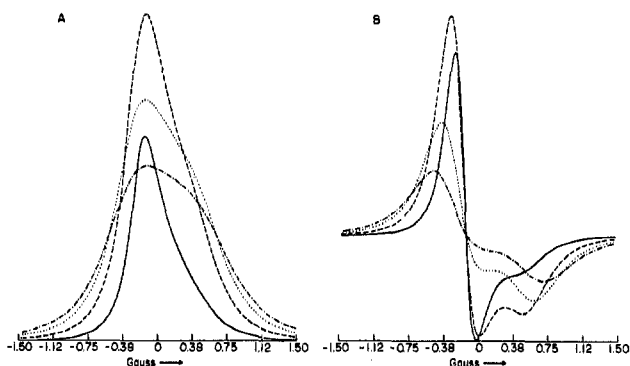


Figure 10. Saturation of single line with rotationally invariant T_1 , as a function of B_1 for $|\mathfrak{F}|/R = 10$: $g_{\parallel} = 2.00235$, $g_{\perp} = 2.00310$, $T_2 = T_1 = (2W_0)^{-1}$ and $(2/\sqrt{3})T_2^{-1}/|\gamma_0| = 0.02$ G. The different values of $(1/2)B_1$ are —, 0.01 G; ---, 0.0333 G; ···, 0.0667 G; -·-·-, 0.100 G. These correspond to intensity factors of 1418, 913, 481, and 280, respectively. A, absorption; B, derivative.

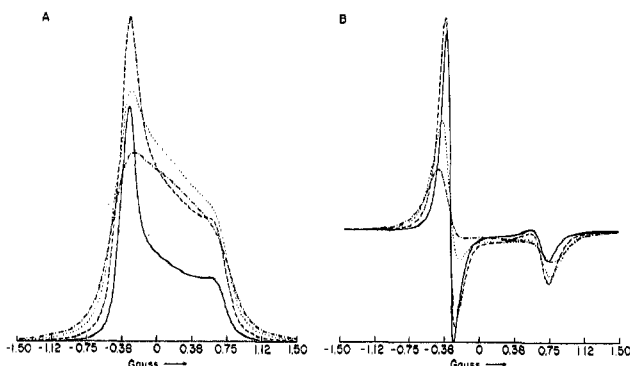


Figure 11. Saturation of single line with rotationally invariant T_1 , as a function of B_1 for $|\mathfrak{F}|/R = 100$. The different values of $(1/2)B_1$ are —, 0.01 G; ---, 0.025 G; ···, 0.050 G; -·-·-, 0.075 G. These correspond to intensity factors of 1414, 1052, 580, and 352, respectively. All other parameters as in Figure 10: A, absorption; B, derivative.

range in which saturation is important. A measure of the extent of saturation of a particular line shape is given by the integrated area under the absorption curve. These are given as intensity factors in relative units in the figure captions. They aid cross-comparisons between the different figures. Thus we note that roughly the same degree of saturation is achieved for a given B_1 in both figures. 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 (cf. Figure 2) (except for the reduction of intensity in the case of saturation).

2. g Tensor (Axially Symmetric). We now include the nonsecular portion of the g tensor to give

$$\mathcal{H}_1 = \mathfrak{F}[\mathcal{D}_{0,0}^2 S_z - (3/8)^{1/2}(\mathcal{D}_{0,1}^2 S_+ - \mathcal{D}_{0,-1}^2 S_-)] \quad (55)$$

Equation 55 substituted into eq 53 and 50, respectively, leads to

$$\begin{aligned} & (-)^{K-M} [n\omega - \omega_0 - iT_2^{-1} - iRL(L+1)] \times \\ & [C_{-K,-M}^{L(n)}]_{\lambda_i} - (2L+1)\mathfrak{F} \sum_{L',K',M'} \binom{L \ 2 \ L'}{K \ 0 \ K'} \times \\ & \binom{L \ 2 \ L'}{M \ 0 \ M'} [C_{K',M'}^{L'(n)}]_{\lambda_i} + (-)^{K-M} d_{\lambda_i} \times \\ & [b_{-K,-M}^{L(n-1)}] + (2L+1)(3/8)^{1/2}\mathfrak{F} \times \\ & \sum_{L',K',M'} \binom{L \ 2 \ L'}{K \ 0 \ K'} \binom{L \ 2 \ L'}{M \ -1 \ M'} [b_{K',M'}^{L'(n)}]_{\lambda_i} - \\ & q\omega_0\delta(n,0)\delta_{K,0}\delta_{M,1}(3/8)^{1/2}\mathfrak{F} = q\omega_\lambda d_{\lambda_i}\delta_{L',0}\delta_{n,1} \quad (56) \end{aligned}$$

and

$$\begin{aligned} & (-)^{K-M} [(1/2)i n\omega + (1/2)RL(L+1) + W_0] \times \\ & [b_{-K,-M}^{L(n)}]_{\lambda_i} = -id_{\lambda_i}(-)^{K-M} \times \\ & ([C_{-K,-M}^{L(n+1)}]_{\lambda_i} - [C_{-K,-M}^{L(n-1)}]_{\lambda_i}) + \\ & i(2L+1)(3/8)^{1/2}\mathfrak{F} \sum_{L',K',M'} \binom{L \ 2 \ L'}{K \ 0 \ K'} \left\{ \binom{L \ 2 \ L'}{M \ 1 \ M'} \times \right. \\ & \left. [C_{K',M'}^{L'(n)}]_{\lambda_i} + \binom{L \ 2 \ L'}{M \ -1 \ M'} [C_{K',M'}^{L'(n)}]_{\lambda_i} \right\} \quad (57) \end{aligned}$$

We find from eq 25, 28, and 51 that

$$[C_{-K,-M}^{L(n)}]_{\lambda_i} = (-)^{K-M} [C_{K,M}^{L(-n)*}]_{\lambda_i} \quad (58a)$$

and

$$[b_{-K,-M}^{L(n)}]_{\lambda_i} = (-)^{K-M} [b_{K,M}^{L(-n)*}]_{\lambda_i} \quad (58b)$$

so $[b_{0,0}^{L(0)}]_{\lambda_i}$ is real, and eq 57 can be more conveniently rewritten.

We now employ the high-field, moderate saturation approximations (*i.e.*, $|\omega_1/\omega_0| \ll 1$, where $\omega_1 = 2d_{\lambda_i}$ and $|\mathfrak{F}/\omega_0| \ll 1$), as well as the *ad hoc* relaxation to thermal equilibrium assumption, which are discussed in Appendix B. This leads to simplified coupled equations between the coefficients $C_{0,0}^{L(1)}$ and $b_{0,0}^{L(1)}$ and between $C_{0,0}^{L(0)}$ and $b_{0,0}^{L(0)}$ as a result of the nonsecular part of eq 55, while $C_{0,0}^{L(1)}$ and $b_{0,0}^{L(0)}$ are coupled *via* the saturating microwave field. However, the assumption that $|\mathfrak{F}/\omega_0| \ll 1$ further allows one to employ second-order perturbation theory and decouple $C_{0,0}^{L(1)}$ from $b_{0,0}^{L(1)}$ and $b_{0,0}^{L(0)}$ from $C_{0,0}^{L(0)}$. The resulting equations are

$$\begin{aligned} & \{(\omega - \omega_0) - i[T_2^{-1} + RL(L+1)]\} C_{0,0}^{L(1)} - \\ & (2L+1)\mathfrak{F} \sum_{L'} \binom{L \ 2 \ L'}{0 \ 0 \ 0} C_{0,0}^{L'(1)} + d_{\lambda_i} b_{0,0}^{L(0)} + \\ & \left[\text{terms in } C_{0,0}^{L''(1)} \text{ of order } \frac{\mathfrak{F}^2}{-\omega_0 + iRL(L+1)} \right] = \\ & q\omega_\lambda d_{\lambda_i} \delta_{(L,0)} \quad (59) \end{aligned}$$

and

$$\begin{aligned}
 & \left[\frac{RL(L+1)}{2} + W_e \right] b_{0,0}^{L(0)} - 2d_{\lambda} \text{Im} C_{0,0}^{L(1)} - \\
 & \quad \left(\frac{3}{8} \right) (2L+1) \mathfrak{F}^2 \sum_{L',L''} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix} \times \\
 & \quad \begin{pmatrix} L' & 2 & L'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & 2 & L'' \\ 1 & -1 & 0 \end{pmatrix} \left[\frac{(2L+1)V(L,L')}{V(L,L')^2 + \left(\frac{2L+1}{2L'+1} \omega_0 \right)^2} + \right. \\
 & \quad \left. \frac{(2L''+1)V(L'',L')}{V(L'',L')^2 + \left(\frac{2L''+1}{2L'+1} \omega_0 \right)^2} \right] b_{0,0}^{L''(0)} = 0 \quad (60)
 \end{aligned}$$

where

$$\begin{aligned}
 V(L,L') &= \frac{1}{2} RL(L+1) + W_e - \\
 & \quad \left(\frac{2L+1}{2L'+1} \right) [RL'(L'+1) + T_2^{-1}] \quad (60a)
 \end{aligned}$$

In eq 59 we are neglecting terms of order $\mathfrak{F}^2 C_{0,0}^{L''(1)} / [-\omega_0 + iRL(L+1)]$ since when $RL(L+1) \ll |\omega_0|$, as is the case for slow tumbling, then these nonsecular terms are of order $|\mathfrak{F}/\omega_0|$ smaller than the secular terms in \mathfrak{F} ; *i.e.*, we are neglecting the nonsecular contributions to the unsaturated line widths as compared to the secular contributions for slow tumbling (*cf.* section A1). These nonsecular terms must, however, be included in eq 60 since this equation predicts the T_1 -type behavior and is not explicitly affected by the secular terms in \mathfrak{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 left-hand side of eq 60 may be omitted. Furthermore, in this limit a perturbation analysis of the coupling of $b_{0,0}^{L(0)}$ to $b_{0,0}^{L''(0)}$ in equation 60 shows that it is sufficient to restrict the summation over L'' in this equation to just $L'' = L$. This, then, just leaves the terms diagonal in $b_{0,0}^{L(0)}$ in eq 60. However, these diagonal corrections are of order of magnitude $|\mathfrak{F}/\omega_0|^2 R$ and are thus negligibly small compared to $\frac{1}{2} RL(L+1)$. Thus, the contribution of the nonsecular terms in eq 60 is negligible in our approximation except for the diagonal term for $L = 0$! This contribution to $L = 0$ is readily calculated, and is

$$W_e^{(G)} = \left(\frac{9}{10} \right) (\mathfrak{F}/\omega_0)^2 R \quad (61)$$

which is just the result obtained from relaxation theory for $|R/\omega_0| \ll 1$,^{2a,11} even though we are now allowing for slow tumbling: $|\mathfrak{F}/R| > 1$ (*cf.* Appendix B). The net conclusion is that for $|\mathfrak{F}|, R \ll |\omega_0|$, the solution to the present case is just given by eq 54 for the rotationally invariant T_1 , but with $W_e \rightarrow W_e + W_e^{(G)} \delta_{L,0}$ in that equation, where $W_e^{(G)}$ is given by eq 61.

The solutions for different $\omega_1 = \gamma_e B_1$ in the region of saturation are given in Figures 12 and 13 for values of $|\mathfrak{F}|/R = 10$ and 100, respectively. One notes, from the intensity factors given in these figures, that roughly the

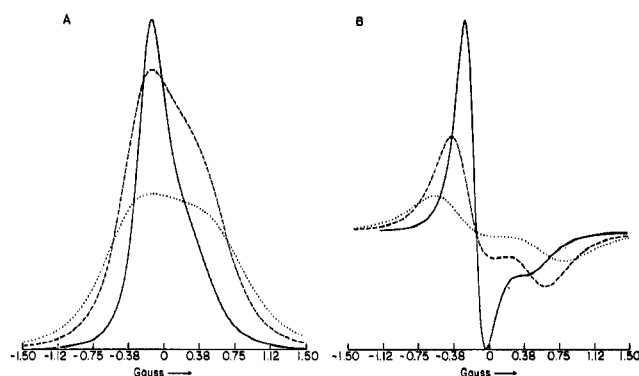


Figure 12. Saturation of single line with g -tensor relaxation as a function of B_1 for $|\mathfrak{F}|/R = 10$; $g_{||} = 2.00235$, $g_{\perp} = 2.00310$; $W_e = T_2^{-1} = 0$. The different values of $(1/2)B_1$ are —, 1×10^{-5} G; ---, 5×10^{-1} G; ···, 1×10^{-4} G. Corresponding to intensity factors of 1053, 342, 139, respectively. A, absorption; B, derivative.

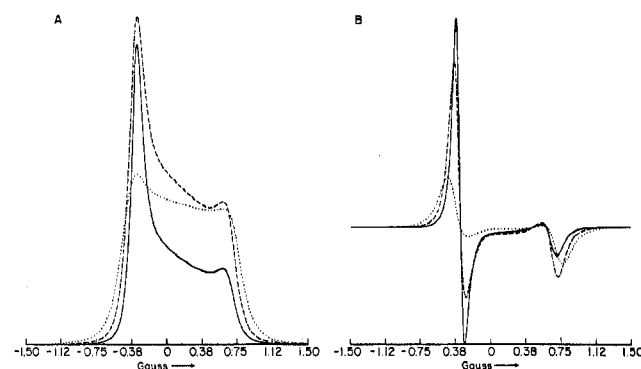


Figure 13. Saturation of single line with g tensor relaxation as a function of B_1 for $|\mathfrak{F}|/R = 100$. The different values of $(1/2) \times B_1$ are —, 3×10^{-6} G; ---, 7.5×10^{-6} G; ···, 2×10^{-5} G. These correspond to intensity factors of 1382, 914, 308, respectively. All other parameters as in Figure 12.

same degree of saturation is achieved for cases $|\mathfrak{F}|/R = 10$ and 100 when B_1 is only about three times weaker for the latter case. One again finds that the effect of saturation is to broaden out and to tend to reduce the asymmetry of the spectrum.

The rather surprisingly weak dependence of the intensity factors as a function of B_1 for the different $|\mathfrak{F}|/R$ values in the slow tumbling region is most likely due to the fact that different portions of the spectrum are found to saturate to a different extent. This is most clearly seen in Figures 11 and 13 for the cases of $|\mathfrak{F}|/R = 100$. What should be an equivalent point of view is suggested by the nature of the coupled eq 54 (also as modified by inclusion of eq 61). We note that as $|\mathfrak{F}|/R$ becomes larger, coefficients $C_{0,0}^{L(1)}$ for the larger L values play a greater role in the coupled equations. But these terms have "effective" T_1 's of $[2W_e + RL(L+1)]^{-1}$ in eq 54, so that while R may become smaller, $L(L+1)R$ for the contributing terms is not decreasing as fast. Similar comments apply to the width com-

ponents where T_2^{-1} replaced by $RL(L+1) + T_2^{-1}$ (although here their relative value compared to \mathfrak{F} becomes important). The components of higher L value are therefore not as easily saturated as the components of lower L value, and the latter are expected to make the major contribution to an unsaturated spectrum. This, one would expect, is the reason for the significant line shape changes obtained as a result of saturation.

A comparison of Figures 10 and 11 for a rotationally invariant T_1 and Figures 12 and 13 for the g -tensor contribution suggests that appropriate experimental studies might distinguish between such cases. The differences are clearer from the absorption plots. Thus in Figure 13A the line shape appears to be "squaring-up" more than in Figure 11A, for comparable intensity factors.

IV. Conclusions

It has been shown that the stochastic Liouville method may be successfully applied to obtain rapidly convergent solutions for a wide variety of esr line shape problems in the slow tumbling region. These included esr line shapes in the presence of g tensor and dipolar perturbations as well as the effects of saturation on the slow tumbling line shapes. The method may also be readily applied to include other relaxation effects (*e.g.*, nuclear quadrupolar terms), to spins of higher multiplicity, and to multiple resonance effects. Further, Markovian processes other than isotropic rotational diffusion could be incorporated.

Our results on unsaturated line shapes have clearly demonstrated the importance of the pseudo-secular dipolar terms in determining the line shapes in the slow tumbling region. The criterion for when they have major effects is $D \gtrsim |a' \pm \omega_n|$; *i.e.*, the anisotropic dipolar terms are comparable to or larger than the pure nuclear-spin transition frequencies. This is the usual case for ^{14}N nuclei in nitroxide compounds but not for typical ring protons. No recourse had to be made in our work to the "adiabatic" approximation used by earlier workers^{5,6} which is valid in the near rigid limit, but begins to break down as the tumbling becomes faster due to "pseudo-secular" contributions.⁷

Our results on the effects of saturation have shown that rather significant line shape changes are predicted to be induced as a function of the saturating fields (Figures 10-13). This suggests that experimental saturation studies, in which the line shape changes are monitored, could be useful in extracting out spin relaxation information in the slow tumbling region. Also, our analysis of both a simple two-jump case (Appendix B) and a rotational diffusion case show that, even in the slow motional region, a fundamental role is played by the T_1 's that are obtained from the spin relaxation theories (where $|\mathfrak{C}_1\tau_c| \ll 1$ is assumed).

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and for calling the stochastic Liouville method to his attention.

Appendix A

On the Convergence of the Solutions. We examine some aspects of the convergence of the simplest case: section IIIA1, the axially symmetric g tensor. This solution is of the form (in matrix notation)

$$(\mathbf{A} + k\mathbf{1})(\mathbf{C}) = (\mathbf{U}) \quad (\text{A1})$$

where \mathbf{A} is a complex continuant matrix with diagonal elements $A_{LL} = -iRL(L+1) - (2L+1)\mathfrak{F} \begin{pmatrix} L & 2 & L \\ 0 & 0 & 0 \end{pmatrix}^2$ and the only off-diagonal elements, $A_{L,L\pm 2} = -(2L+1)\mathfrak{F} \begin{pmatrix} L & 2 & L\pm 2 \\ 0 & 0 & 0 \end{pmatrix}^2$, $A_{L\pm 2,L} = -[2(L+2) + 1]\mathfrak{F} \begin{pmatrix} L & 2 & L\pm 2 \\ 0 & 0 & 0 \end{pmatrix}^2$. The unit matrix of eq A1 is multiplied by $k = (\omega - \omega_0) - iT_2^{-1}$; \mathbf{C} is a column vector of the coefficients $C_{0,0^L}$, and \mathbf{U} is a column vector where $U_L = \delta(L,0)$. Let us partition \mathbf{A} as

$$\mathbf{A} = \begin{pmatrix} A_{0,0} & \mathbf{A}^{0,P} \\ \mathbf{A}^{P,0} & \mathbf{A}^P \end{pmatrix} \quad (\text{A2})$$

where $A_{0,0}$ is the first diagonal element of \mathbf{A} . Then let \mathbf{t} define the transformation which diagonalizes \mathbf{A}^P ; $\mathbf{t}^{-1}\mathbf{A}^P\mathbf{t} = a$. Note that \mathbf{A}^P is symmetrized by the similarity transformation

$$\mathbf{S}^{-1}\mathbf{A}^P\mathbf{S} = \hat{\mathbf{A}}^P \quad (\text{A3})$$

where \mathbf{S} is a diagonal matrix with elements $S_{L,L} = [2L+1]^{1/2}$. Specifically $\hat{A}_{L,L\pm 2} = [(2L+1)^{-1} \times (2[L\pm 2] + 1)]^{1/2} A_{L,L\pm 2}$ while $\hat{A}_{L,L} = A_{L,L}$. Then we may write $\mathbf{t} = \mathbf{S}\mathbf{O}$ where \mathbf{O} is the complex orthogonal transformation (*i.e.*, $\mathbf{O}^{-1} = \mathbf{O}^*$) which diagonalizes $\hat{\mathbf{A}}^P$. If we define \mathbf{T} as partitioned according to eq A2 by

$$\mathbf{T} \equiv \begin{pmatrix} 1 & 0 \\ 0 & \mathbf{t} \end{pmatrix} \quad (\text{A4})$$

then by transforming eq A1 by \mathbf{T} and solving for $C_{0,0^0}$ we obtain

$$C_{0,0^0} = [(A_{0,0} + k) - A_{0,2}A_{2,0} \sum_{L>0}^n O_{2,L}(a_L + k)^{-1}O_{-1,L,2}^{-1}]^{-1} \quad (\text{A5})$$

Note that if $|A_{n,n} - A_{n-2,n-2}| \gg |\hat{A}_{n,n-2}|$, then in the diagonalization by \mathbf{O} , the n th coefficient $C_{0,0^n}$ will mix in very weakly with $C_{0,0^2}$, so that $O_{2,n}$ and $O_{n,2}^{-1}$ are very small. Thus unless $(a_n + k)^{-1}$ is unusually large (*e.g.*, a resonance) we can neglect its contribution to $C_{0,0^0}$ compared to the other terms in eq A6. Since, $A_{L,L} > A_{L-2,L-2}$ for both the real and imaginary parts, we expect that $a_n > a_{n-2}$. We can then terminate the expansion with reasonable confidence when the above inequality is fulfilled. This is undoubtedly too strong

a condition, because we have not considered the chain whereby $C_{0,0}^n$ couples *via* $C_{0,0}^{n-2}$, $C_{0,0}^{n-4}$, ... to $C_{0,0}^2$, which further reduces the magnitude of $O_{2,n}$.

Now

$$A_L - A_{L+2} = +iR(4L + 6) + \mathfrak{F}(2L + 3)^{-1} \left[\frac{(L + 2)(L + 3)}{(2L + 7)} - \frac{L(L + 1)}{(2L - 1)} \right]$$

$$\text{while } \hat{A}_{L,L+2} = \mathfrak{F}[(2L + 1)(2L + 5)]^{1/2} \begin{pmatrix} L+2 & L & 2 \\ 0 & 0 & 0 \end{pmatrix}^2.$$

It is sufficient to consider just $+Im(A_L - A_{L+2})$ in place of $|A_L - A_{L+2}|$. Thus we want

$$\frac{|\mathfrak{F}|}{R} < \frac{4n + 6}{[(2n + 1)(2n + 5)]^{1/2}} \begin{pmatrix} n+2 & n & 2 \\ 0 & 0 & 0 \end{pmatrix}^{-2} \xrightarrow{n \text{ large}} \frac{8}{3}(4n + 6) \quad (\text{A6})$$

(e.g., for $n = 12$ we have $|\mathfrak{F}|/R < 143$) as a reasonable guide to convergence. We have found from the computer simulations that for $|\mathfrak{F}|/R = 100$ a value of $n = 12$ is sufficient. Also, these criteria are found to carry over into the more complex cases studied.

When a rotationally invariant T_2^{-1} is introduced, it both increases the value of $(A_{0,0} + k)$ in eq A6 while reducing *all* values of $(a_L + k)^{-1}$ in the summation term of this equation. It thus reduces the importance of each term in the summation by the factor $A_{0,0}a_L / (A_{0,0} + k) \cdot (a_L + k)$. Finally as ω (or ω_0 in a field sweep) is swept away from resonance, thus increasing k , one again gets a suppression of the summation terms, *except for resonances* that appear for $Im(a_L + k) = 0$ (as well as coupled resonances of these terms with the $(A_{0,0} + k)$ term). The effect of these resonances is found to yield spurious "local peaks" when the cut-off value, n is too small for a good approximation.

We note that if the above diagonalization scheme is applied to the *full* \mathbf{A} matrix, one then obtains solutions of $C_{0,0}^0$ in the form of a superposition of Lorentzians

$$Im(C_{0,0}^0) = Im \sum_{L=0}^n (O_{0,L})^2 (a_{LL} + k)^{-1} \quad (\text{A7})$$

where the terms in eq A7 are defined as before but now as applied to \mathbf{O} diagonalizing the full \mathbf{A} . This procedure (for the case of only secular terms) is similar to the approach of Korst and Lazarev.⁶ Similar diagonalizations should be appropriate for the more complex cases. (Note that to the extent $O_{0,L}$ is complex, there will be "dispersion-shaped" components in the absorption.)

Appendix B

The Two-Jump Case and Saturation. A two-jump modulation of \mathfrak{C}_1 is assumed, such that

$$\mathfrak{C}_1(i) = \mathfrak{F}(i) [S_z + 1/2(S_+ + S_-)] \quad (\text{B1})$$

where $\mathfrak{F}(1) = -\mathfrak{F}(2) = \mathfrak{F}$ a real quantity. A simple two-level esr transition is considered.

In the space of the two jumps

$$\Gamma = \begin{pmatrix} +\omega_J & -\omega_J \\ -\omega_J & +\omega_J \end{pmatrix} \quad (\text{B2})$$

where ω_J is the mean jump rate between the two sites, and clearly $P_0(1) = P_0(2) = 1/2$. We now write eq 53 and 50 for this case, but in the form appropriate *before* the substitution of eq 18 is made (cf. eq 16)

$$\begin{aligned} (n\omega - \omega_0 + (-)^i \mathfrak{F} - i\omega_J) Z^{(n)}(i) + \\ i\omega_e Z^{(n)}(j) + dY^{(n-1)}(i) - (-)^{i+1} \mathfrak{F} [Y^{(n)}(i) - \\ q\omega_0 \delta(n,0)] = 1/2 q\omega_0 d\delta(n,1) \quad (i \neq j) \quad (\text{B3}) \end{aligned}$$

and

$$\begin{aligned} (1/2 n\omega - 1/2 i\omega_J - iW_e) Y^{(n)}(i) + \\ 1/2 i\omega_J Y^{(n)}(j) = d(Z^{(n+1)}(i) - Z^{(1-n)*}(i)) + \\ (-)^{i+1} \mathfrak{F} (Z^{(n)}(i) - Z^{(-n)*}(i)) \quad (i \neq j) \quad (\text{B4}) \end{aligned}$$

Note that we have let $Y^{(n)}(i) \equiv \chi_{\lambda^+}^{(n)} - \chi_{\lambda^-}^{(n)}$, and we have dropped the λ_j and $\lambda_{j\pm}$ subscripts for this single transition. A rotationally invariant electron spin flip rate, W_e has been introduced.

The eigenfunctions of eq B2 are just the sum and difference of the two-jump sites with eigenvalues of zero and $-2\omega_J$, respectively. Thus we introduce the sum and difference modes

$$Z^{(n)}(\pm) = Z^{(n)}(1) \pm Z^{(n)}(2) \quad (\text{B5a})$$

$$Y^{(n)}(\pm) = Y^{(n)}(1) \pm Y^{(n)}(2) \quad (\text{B5b})$$

and rewrite eq B3 and B4 as

$$\begin{aligned} (n\omega - \omega_0) Z^{(n)}(+)-\mathfrak{F} Z^{(n)}(-)+dY^{(n-1)}(+)+ \\ 1/2 \mathfrak{F} Y^{(n)}(-)=q\omega_0 d\delta(n,1) \end{aligned}$$

$$\begin{aligned} (n\omega - \omega_0 - 2i\omega_J) Z^{(n)}(-)-\mathfrak{F} Z^{(n)}(+)+ \\ dY^{(n-1)}(-)+1/2 \mathfrak{F} Y^{(n)}(+)= -\mathfrak{F} q\omega_0 \delta(n,0) \end{aligned}$$

and

$$\begin{aligned} (1/2 n\omega - iW_e) Y^{(n)}(+)= \\ -d(Z^{(n+1)}(+)-Z^{(-n+1)*}(+)) - \\ 1/2 \mathfrak{F} (Z^{(n)}(-)-Z^{(-n)*}(-)) \quad (\text{B6a}) \end{aligned}$$

$$\begin{aligned} (1/2 n\omega - i\omega - iW_e) Y^{(n)}(-)= \\ -d(Z^{(n+1)}(-)-Z^{(-n+1)*}(-)) - \\ 1/2 \mathfrak{F} (Z^{(n)}(+)-Z^{(-n)*}(+)) \quad (\text{B6b}) \end{aligned}$$

The spectrum is given by $ImZ^{(1)}(+)$. In the absence of saturation, the secular term in \mathfrak{C}_1 (proportional to \mathfrak{F} in eq B5) couple $Z^{(n)}(+)$ with $Z^{(n)}(-)$, and the extent of coupling depends on the ratio $|\mathfrak{F}/2\omega_J|$. (This is seen by comparing the off-diagonal elements with the differences in diagonal elements for the matrix of the coupled equations of B5 and B6.) The non-secular terms (proportional to $\mathfrak{F}/2$ in eq B5 and B6)

couple the $Z^{(n)}(\pm)$ with the $Y^{(n)}(\pm)$ by eq B5, while the $Y^{(n)}(\mp)$ are coupled to both $Z^{(n)}(\pm)$ and $Z^{(-n)*}(\pm)$ by eq A6b. The extent of these latter couplings depends essentially on the ratios $\mathfrak{F}/|n\omega + 2ik\omega_J|$ and $\mathfrak{F}/|3n\omega + 2ik\omega_J|$, respectively (with $k = 1$ or 2 depending on whether one has $Z^{(n)}(+)$ or $Z^{(n)}(-)$), where we want $\omega \sim \omega_0$. For small values of $\mathfrak{F}/2\omega_J$, relaxation theory suffices.

In the presence of saturation, the interaction with the radiation term leads to a coupling of $Z^{(n)}(\pm)$ to $Y^{(n-1)}(\pm)$ (via eq B5), and the $Y^{(n-1)}(\pm)$ are coupled to $Z^{(n)}(\pm)$ and $Z^{(-n+2)*}(\pm)$ via eq B6. Here the extent of coupling depends on the ratios $|\omega_1|/|(n+1)\omega - 2\omega_0 + 2iW_e|$ and $|\omega_1|/|(-n+3)\omega - 2\omega_0 - 2iW_e|$, respectively, for the plus signs (with $W_e \rightarrow W_e - \omega_J$ for the minus signs), and we have taken W_e to be small. Thus in the high-field saturation case where $|\omega_1/\omega_0| \ll 1$, the $Z^{(1)}(\pm)$ and $Y^{(0)}(\pm)$ terms are dominant. The $Z^{(0)}(\pm)$ and $Y^{(1)}(\pm)$ terms coupled in by \mathfrak{C}_1 must also be considered. Also we are neglecting $Z^{(-1)*}(\pm)$, since $|\mathfrak{F}/3\omega_0|$ is assumed small.

1. *Neglect of Nonsecular Terms, but $W_e \neq 0$.* Equations B5 and B6 need only be written for $Z^{(1)}(\pm)$ and $Y^0(\pm)$ for this case. The solution for $Z^{(1)}(+)$ is given by

$$\left[(\omega - \omega_0) \left(1 - \frac{\mathfrak{F}^2}{S} \right) - i2\omega_J \mathfrak{F}^2/S \right] Z^{(1)}(+) + 2d^2 \left[\frac{1}{W_e} + \frac{\mathfrak{F}^2}{S} \frac{1}{\omega_J + W_e} \right] Z^{(1)}(+)'' = q\omega_0 d \quad (\text{B7})$$

where

$$S = (\omega - \omega_0)^2 + 4\omega_J^2 [1 + d^2/\omega_J(\omega_J + W_e)] \quad (\text{B7a})$$

The resonance frequency(ies) and width(s) are obtained from the coefficient of $Z^{(1)}(+)$ in eq B7, while the saturation parameter or T_1 appears in the coefficient of $Z^{(1)}(+)''$. In the motional narrowing region, where $\mathfrak{F}^2/\omega_J^2 \ll 1$, we have $\mathfrak{F}^2/S \ll 1$, and we may set $(\omega - \omega_0)^2 \approx 0$ in eq B7a for S for the region of resonance. We then get a single line at $\omega = \omega_0$; with

$$T_2^{-1} = \mathfrak{F}^2 / \{ 2\omega_J [1 + d^2/\omega_J(\omega_J + W_e)] \} \quad (\text{B8a})$$

and

$$T_1^{-1} = (2W_e) \quad (\text{B8b})$$

Thus T_2 can be affected by the strength of the radio-frequency field. The slow motional region ($\mathfrak{F}^2/\omega_J^2 \gg 1$) is recovered by first letting $\omega_J = 0$, and solving for the zeroes in the coefficient of $Z^{(1)}(+)$ which are, of course, $\omega - \omega_0 = \pm \mathfrak{F}$. Then we let $(\omega - \omega_0)^2 = \mathfrak{F}^2$ in eq B7a. This yields, for each of the two distinct resonance lines

$$T_2^{-1} = 2\omega_J [1 + 4d^2\omega_J/\mathfrak{F}^2(\omega_J + W_e)]^{-1} \quad (\text{B9a})$$

$$T_1 = (2W_e)^{-1} \left[1 + \left(\frac{W_e}{\omega_J + W_e} \right) \times \left(1 + \frac{4d^2\omega_J}{\mathfrak{F}^2(\omega_J + W_e)} \right)^{-1} \right] \quad (\text{B9b})$$

Again it is possible for a large d^2 to affect the relaxation times. Note that for $W_e \gg \omega_J$ (and small enough d^2), $T_1 = W_e^{-1}$ and is thus twice as long as the motional narrowing result of eq B8b.

2. *Nonsecular Terms Included and $W_e = 0$.* We now must include contributions from $Z^{(1)}(\pm)$, $Y^{(0)}(\pm)$, $Z^{(0)}(\pm)$, and $Y^{(1)}(\pm)$, and we neglect all other harmonics. It is useful to employ the other high-field condition: $\mathfrak{F}^2/\omega_0^2 \ll 1$, to facilitate the solution, which after some algebra (and an important assumption; see below) is

$$\left[\Delta\omega_0'' - \frac{\mathfrak{F}^2}{S} \Delta\omega_0' - ia_\omega - 2i\omega_J \frac{\mathfrak{F}^2}{S} \right] Z^{(1)}(+) + 2d^2 \left[\frac{\mathfrak{F}^2}{\omega_J S} + a(\omega_0)^{-1} \right] Z^{(1)}(+)'' = q\omega_0 d \quad (\text{B10})$$

where

$$a(\omega_0) = \frac{\mathfrak{F}^2\omega_J}{\omega_0^2 + 4\omega_J^2} \quad (\text{B10a})$$

$$S = \Delta\omega_0'^2 + 4\omega_J^2(1 + d^2/\omega_J^2) \quad (\text{B10b})$$

$\Delta\omega_0' = \omega - \omega_0 - \mathfrak{F}^2/2\omega$, and $\Delta\omega_0'' = \omega_0 - \omega_0 - (\omega/2\omega_J) \cdot a(\omega)$. The imaginary term $ia(\omega)$ in the coefficient of $Z^{(1)}(+)$ in eq B10 gives the nonsecular contribution to the width according to eq B10a (for $\omega \sim \omega_0$). This is a well-known result from relaxation theory, but it is obtained in the present case *without any assumptions regarding the magnitude* of $\mathfrak{F}^2/\omega_J^2$. This is also true for the T_1 contribution of $1/2a(\omega_0)^{-1}$ in the coefficient of $Z^{(1)}(+)''$ (but see below). The associated dynamic frequency shift is $(\omega/2\omega_J)a(\omega)$. The terms in eq B10 shown explicitly with \mathfrak{F}^2 all arise from the secular contribution (compare eq B7). The motional narrowing result, wherein we have $\mathfrak{F}^2/\omega_J^2 \ll 1$, and $\mathfrak{F}^2/S \ll 1$ is obtained as in case 1, and we neglect the small dynamic frequency shifts. Then we have for the single line at $\omega \cong \omega_0$

$$T_2^{-1} = \mathfrak{F}^2 / \{ 2\omega_J [1 + d^2/\omega_J^2] \} + a(\omega_0) \quad (\text{B11a})$$

and

$$T_1^{-1} = 2a(\omega_0) \quad (\text{B11b})$$

The dependence of T_2 on the strength of the saturating field is equivalent to the result discussed by Abragam¹⁸ and Bloch¹⁹ for the case of a "viscous liquid" where $\mathfrak{F}^2/4\omega_J^2 \ll 1$, but $d^2/\omega_J^2 \gtrsim 1$. The methods of this paper (including rotational diffusion) allow for solu-

(18) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, Chapter XII.

(19) F. Bloch, *Phys. Rev.*, **105**, 1206 (1957).

tions even when $\mathfrak{F}^2/4\omega_J^2$ is not small. When $\mathfrak{F}^2/4\omega_J^2 \gg 1$, *i.e.*, slow motion (and we let $d^2/\mathfrak{F}^2 \ll 1$), then one has two lines at $\Delta\omega_0' = \pm\mathfrak{F}$ each having $T_2^{-1} = 2\omega_J$ and $T_1^{-1} = 2a(\omega_0)$ with $T_1 \gg T_2$. Thus T_1 is given by the second-order relaxation theory result even though the condition for validity of the theory no longer applies.

An important assumption was made in the above in order to guarantee relaxation to equilibrium. The nature of this assumption can more clearly be seen by writing the solution for the case where the secular terms have been omitted with $W_e \neq 0$, but small. Then one has

$$[\Delta\omega_0'' - ia(\omega)]Z^{(1)}(+) + dY^{(0)}(+) = q\omega_0 d \quad (\text{B12a})$$

and

$$dZ^{(1)}(+)'' = \frac{1}{2}a(\omega_0)[Y^{(0)}(+) - q\omega_0] + \frac{1}{2}W_e Y^{(0)}(+) \quad (\text{B12b})$$

In eq B12b we see that $a(\omega_0)$ plays a role identical with W_e in causing spin relaxation except for the term in $q\omega_0 = (P_b)_0 - (P_a)_0$ (the difference in spin populations at equilibrium). That is, $Y^{(0)}(+) - q\omega_0 = \rho_{aa} - \rho_{bb}$ and the effect of $a(\omega_0)$ in eq B12b is to tend to relax the spins to infinite temperature (where $(P_b)_0 = (P_a)_0$) rather than to the proper thermal distribution. This is the well-known fundamental difficulty in semiclassical relaxation theories, which in the present method may be overcome in a manner analogous to those theories by letting $Y^{(0)}(+) + q\omega_0 \rightarrow Y^{(0)}(+) + q\omega_0$ for such terms (where we are assuming a high temperature approximation) and the equivalent has also been done in section IIIB. The question remains of a rigorous justification for such an *ad hoc* assumption for small ω_J (hence small $a(\omega_0)$) when a rigorous spin relaxation theory approach is no longer applicable.²⁰ We note, however, that should the extra term in $q\omega_0$ be included, it would affect an unsaturated as well as a saturated line shape equally and merely in their *absolute* intensities. That is from eq B12 one has

$$[\Delta\omega_0'' - ia(\omega)]Z^{(1)}(+) + \frac{2d^2}{a(\omega_0) + W_e}Z^{(1)}(+)'' = q\omega_0 d \left[1 - \frac{a(\omega_0)}{a(\omega_0) + W_e} \right]$$

so the *relative* intensity changes due to the onset of saturation are unaffected by the assumption, and for small enough $a(\omega_0) \ll W_e$, even the absolute effects become negligible.

Discussion

J. HARRIMAN. Can you handle anisotropic rotation? What will the effect be?

J. FREED. Yes. Let me illustrate with the case of axially symmetric rotational diffusion. For this case the eigenfunctions for eq 23 are still the Wigner rotation matrices: $D_{KM}^L(\Omega)$ but now with eigenvalues

$$E_m = E_{L,K,M} = R_z L(L+1) + (R_z - R_x)K^2$$

with $R_x = R_y$ and R_z the principal values of the diffusion tensor and the molecular z axis as the axis of symmetry. If the z axis also corresponds to a principal axis of the g and dipolar tensors, then it is an almost trivial matter to correct the equations in our paper for effects of such diffusion. One then sees that the K -dependent term in $E_{L,K,M}$ will only affect the spectrum if $g_x \neq g_y$ and/or the dipolar terms $D_i^{(\pm 2)} \neq 0$.

When the rotational diffusion is asymmetric, the proper eigenfunctions for eq 23 become linear combinations of spherical harmonics (see J. H. Freed, *J. Chem. Phys.*, **41**, 2077 (1964), for further details), and while the method applies, the equations constituting a solution to the spectrum become more complex though tractable.

We might note that a situation like $R_z \gg R_x$, or the reverse inequality, allows for the interesting possibility that there is fast tumbling about one axis, while there is slow tumbling about another.

O. H. GRIFFITH. In your calculations of rotational correlation times, are there any other parameters in addition to the intrinsic line width and the principal values of the hyperfine and g tensors?

J. FREED. No. A particular calculated spectrum is determined solely by the rotational diffusion coefficient R , an intrinsic line width, and the principal values and axes of the hyperfine and g tensors.

In our experimental studies (S. Goldman, G. Bruno, C. Polnaszek, and J. H. Freed, *J. Chem. Phys.*, in press) we find that the intrinsic line widths needed to get good agreement between the computed and experimental spectra are temperature dependent, *e.g.*, essentially zero in the faster tumbling regions to a few gauss in the near-rigid and rigid regions.

D. LENIART. Since the esr line shape depends critically upon the pseudo-secular contribution of the dipolar interaction, do you feel that it would be advantageous to study these slow tumbling systems by multiple resonance techniques such as Electron-Electron Double Resonance (Eldor) to extract more *explicit experimental data*?

J. FREED. I think our predicted spectra showing effects of saturation on slow tumbling line shapes encourages one to think that useful information may be obtained by saturation studies. J. S. Hyde has independently come to similar conclusions from his experimental work. Eldor would certainly be a means of extending such studies, and we plan to develop appropriate solutions utilizing the approach given in our paper.

D. E. WOOD. How much computer time is required to fit a series of spectra from slow to fast limit, for say a nitroxide radical?

J. FREED. The following are typical computer times for the nitroxidelike spectra, $I = 1$, $S = 1/2$, given in our paper: 575, 350, and 200 sec for F/R values of 100, 15, and 3, respectively. The computer is an IBM 360/65 and the Gaussian elimination method was used. We anticipate order of magnitude reductions in computer time when we have converted our method of solution to diagonalization by the QR transform method, since only one diagonalization per F/R value is required to obtain the whole spectrum. Further reductions in time may be possible by utilizing more modern iterative computer methods.

(20) That $a(\omega_0)$ still represents a relaxation mechanism resulting from modulation of the nonsecular terms even by a small ω_J , can be illustrated in a manner analogous to that discussed by Abragam for scalar relaxation of the second kind (ref 18, p 312). For the present case one may formally let $\mathfrak{F} = 2AI_z(t)$ where $I = 1/2$ and assume $I_z(t)$ is rapidly equilibrated. The process modulating $I_z(t)$ must have a white spectrum up through frequencies of the order of ω_0 in order to recover eq B10a.