

the normal two-transition routes, even when the topology of the differential paths qualitatively suggests a three-transition route.

Appendix. Notation

A, B, C, D = $\partial x_i / \partial y_j$ values, defined by eq 13-14
 c = fluid-phase concentration of anionic or molecular species
 \bar{c} = same, for sum of complexed and uncomplexed forms
 F = feed
 K = stability constant
 M, N, O = counterion species
 P = presaturant
 Q = resin capacity, equivalents/mass
 q = resin-phase concentration of an ionic species, equivalents/mass
 u = composition velocity, dimensionless; see eq 4
 V = fluid volume
 v = packed volume of resin
 W = watershed
 X = coion, complex forming
 x = relative fluid-phase concentration, c/\bar{c}_x
 \bar{x} = same, for sum of complexed and uncomplexed forms

y = relative resin-phase concentration, q/Q
 α = selectivity coefficient
 ϵ = void fraction
 ρ = resin bulk density, mass/packed volume

References and Notes

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Analysis of Inertial Effects on Electron Spin Resonance Spectra in the Slow Tumbling Region¹

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An analysis is given of the inertial effects (which arise from the coupling of the molecular orientational degrees of freedom to the molecular angular momentum) on esr spectra of radicals in the model-sensitive slow tumbling region. The analysis is based on the stochastic-Liouville equation in combined spin, orientational, and angular momentum space, and it utilizes recently developed models of Langevin (or Brownian) diffusion and extended diffusion. The case of a simple line from an axial g tensor is studied in most detail. It is shown that the complete analysis for inertial effects in this case yields results similar to a very crude model of free diffusion found by Goldman, *et al.*, to be in good agreement with experimental results in their analysis of slow-tumbling nitroxide spectra. Results of Langevin and extended diffusion were virtually the same. However, results obtained for a familiar approximate inertial model, which neglects noncommutativity of the angular-velocity components, disagreed sharply with all other cases (including the even cruder free diffusion model derived from it) indicating that it is an unsatisfactory model. The less complete results obtained for the case of nitroxide spectra indicate similar conclusions.

I. Introduction

In a recent set of esr experiments in the slow tumbling region where the esr line shapes are no longer simple Lorentzians, it was found possible to distinguish between different models for the molecular reorientation.² The models considered were Brownian rotational diffusion, diffusion by molecular jumps of substantial angle, and a simplified model of free diffusion wherein the inertial effects were introduced in a crude fashion. Our results on small nitroxide molecules² were found to be consistent

with molecular jumps of moderate angle (the root-mean-square jump angle ~ 1 radian) but the simplified model of free diffusion utilized gave equally good agreement. The present study was undertaken to determine whether a more complete analysis of inertial effects which result from the coupling of the molecular orientational degrees of freedom to the angular momentum could alter the results previously obtained.

The basis of our theoretical analysis of the slow tumbling esr spectra has been the stochastic Liouville meth-

od³ as utilized by Freed, Bruno, and Polnaszek.⁴ In the past work, it has only been employed in combined spin and orientational space, the random behavior of the latter being described by a Markoff process.⁵ However, the stochastic-Liouville method is quite general, and for the problem of inertial effects one may introduce the combined orientational-angular momentum degrees of freedom in terms of which the Markoff process is defined. This generalization clearly renders the problem considerably more complex, but it has still been possible to obtain some useful results and insights.

Our analysis builds on some of the extensive recent work on inertial effects in rotational diffusion. In particular, we have found the work of Fixman and Rider⁶ lends itself quite naturally to adaptation to our stochastic-Liouville approach for slow tumbling esr spectra. Also, some of the earlier discussion by Sack on this subject has been useful.^{7a,b} Hubbard has also very recently discussed this subject.^{7c}

II. General Approach

We start with the stochastic-Liouville equation of motion for the spin-density matrix⁴

$$\frac{\partial}{\partial t} \rho(\Psi, t) = [-i\mathcal{K}(\Omega)^x - \Gamma_\Psi] \rho(\Psi, t) \quad (1)$$

and

$$\Gamma_\Psi P_0(\Psi) = 0 \quad (1a)$$

Here $\mathcal{K}(\Omega)^x$ is the superoperator of the orientation-dependent spin Hamiltonian and Γ_Ψ is a Markoffian operator for the collection of variables Ψ , which include the orientational angles Ω . In particular, for the consideration of inertial effects, Ψ includes the angular momentum (or velocity) variables as well. $P_0(\Psi)$ in eq 1a is the unique equilibrium distribution over all the variables in Ψ . We shall consider specifically (1) motion about a fixed axis, *i.e.*, one-dimensional free rotational diffusion and (2) three-dimensional free rotational diffusion of a spherical top.

The unsaturated absorption of the λ_j th transition is obtained from $\text{Im } \bar{Z}_{\lambda_j}$ where⁴

$$\bar{Z}(\omega)_{\lambda_j} = \int d\Psi Z(\Psi, \omega)_{\lambda_j} P_0(\Psi) \quad (2)$$

and

$$\rho(\Psi, t)_{\lambda_j} = e^{i\omega t} Z(\Psi, \omega)_{\lambda_j} \quad (3)$$

That is $Z(\Psi, \omega)_{\lambda_j}$ is the steady-state solution of $\rho(\Psi, t)$ for the λ_j th transition and is time independent in the frame rotating with impressed frequency ω . Also, $\bar{Z}(\omega)_{\lambda_j}$ is the equilibrium average over all variables comprising Ψ .

Substituting of eq 3 into 1 leads for the case of no saturation to^{4,5}

$$\{[\omega - \mathcal{K}_0^x + \mathcal{K}_1(\Omega)^x - i\Gamma_\Psi] Z(\Psi, \omega)\}_{\lambda_j} = \frac{1}{2} \omega_1 [S_-^x \rho_0]_{\lambda_j} \quad (4)$$

where \mathcal{K}_0 is the zero-order orientation-independent and $\mathcal{K}_1(\Omega)$ the perturbing orientation-dependent parts of $\mathcal{K}(\Omega)$, $\omega_1 = \gamma_e B_1$ with B_1 the magnitude of the rf field, S_- is the electron spin lowering operator, and ρ_0 the equilibrium density matrix. The averaging of eq 4 to obtain an expression for $\bar{Z}(\omega)$ must follow the prescription of first postmultiplying eq 4 by $P_0(\Psi)$ and then integrating over all Ψ .^{3,5} One generally expands $Z(\Psi, \omega)_{\lambda_j}$ in a complete orthonormal set of eigenfunctions (when available) of Γ_Ψ to solve eq 4.⁴ However, when $P_0(\Psi) \neq \text{constant}$ it is usu-

ally more convenient to define⁸

$$\tilde{Z}(\Psi, \omega) = P_0^{-1/2}(\Psi) Z(\Psi, \omega) \quad (5)$$

and then expand the $\tilde{Z}(\Psi, \omega)$, and this is illustrated below.

(A) *One-Dimensional Free Rotational Diffusion.* By one-dimensional rotation, we mean rotation about a fixed axis. This model has been discussed in detail by Sack^{7a,b} and others.⁹ It is a simple generalization of the one-dimensional Fokker-Planck equation to cover rotational motion.¹⁰

Thus we may write

$$\Gamma_{\gamma, \dot{\gamma}} = \dot{\gamma} \frac{\partial}{\partial \gamma} - \beta \left(\frac{\partial}{\partial \dot{\gamma}} \dot{\gamma} + \beta R \frac{\partial^2}{\partial \dot{\gamma}^2} \right) \quad (6)$$

where γ is the angle of rotation about the fixed axis and $\dot{\gamma}$ its angular velocity. Also β is the damping coefficient and $R \equiv kT/I\beta$ is the diffusion coefficient for reorientation. This two dimensional Markovian operator will have the equilibrium probability distribution

$$P_0(\gamma, \dot{\gamma}) = P_0(\gamma) P_0(\dot{\gamma}) = (1/2\pi) ([2\pi\beta R]^{-1/2} \exp[-\dot{\gamma}^2/2\beta R]) \quad (7)$$

corresponding to a uniform distribution in orientation and a Boltzmann distribution in angular velocity. Because the latter is nonuniform, $\Gamma_{\gamma, \dot{\gamma}}$ given by eq 6 is a nonsymmetric operator. We may symmetrize by the transformation

$$\tilde{\Gamma} = P_0^{-1/2}(\gamma, \dot{\gamma}) \Gamma P_0^{1/2}(\gamma, \dot{\gamma}) = \dot{\gamma} \frac{\partial}{\partial \gamma} - \beta \left(\beta R \frac{\partial^2}{\partial \dot{\gamma}^2} - \frac{\dot{\gamma}^2}{4\beta R} + \frac{1}{2} \right) \quad (8)$$

One then immediately notes that the second term on the right-hand side of eq 8 is (within the constant term of $-\frac{1}{2}$) just the operator for the one-dimensional quantum-mechanical harmonic oscillator. Thus it has harmonic oscillator eigenfunctions as its eigenfunctions with the eigenvalues $n\beta$ ($n = 0, 1, 2, \dots$). Thus one first transforms eq 1 to be

$$\frac{\partial}{\partial t} \tilde{\rho}(\gamma, \dot{\gamma}, t) = [-i\mathcal{K}^x - \tilde{\Gamma}] \tilde{\rho}(\gamma, \dot{\gamma}, t) \quad (9)$$

where (*cf.* eq 5)

$$\tilde{\rho}(\gamma, \dot{\gamma}, t) = P_0^{-1/2}(\gamma, \dot{\gamma}) \rho(\gamma, \dot{\gamma}, t) \quad (9a)$$

Then the matrix elements of $\tilde{Z}(\gamma, \dot{\gamma}, \omega)$ for the relevant transitions may be expanded in complete sets of eigenfunctions for γ and $\dot{\gamma}$ as

$$\tilde{Z}(\gamma, \dot{\gamma}, \omega)_{\lambda_j} = \sum_{r,n} [C_{r,n}(\omega)]_{\lambda_j} f_r(\gamma) h_n(\dot{\gamma}) \quad (10)$$

with

$$f_r(\gamma) = \frac{1}{\sqrt{2\pi}} e^{ir\gamma} \quad (10a)$$

$$h_n(\dot{\gamma}) = [(2\pi\beta R)^{1/2} 2^n n!]^{-1/2} \exp\left(\frac{-\dot{\gamma}^2}{4\beta R}\right) H_n\left(\frac{\dot{\gamma}}{\sqrt{2\beta R}}\right) \quad (10b)$$

and

$$P_0^{1/2}(\gamma, \dot{\gamma}) = f_0(\gamma) h_0(\dot{\gamma}) \quad (10c)$$

where $H_n(x)$ are the Hermite polynomials. Thus

$$\tilde{\Gamma} f_r(\gamma) h_n(\dot{\gamma}) = E_{r,n} f_r(\gamma) h_n(\dot{\gamma}) = (n\beta + ir\dot{\gamma}) f_r(\gamma) h_n(\dot{\gamma}) \quad (11)$$

and the "matrix elements" of $\tilde{\Gamma}$ may be obtained from the known properties of the Hermite functions $h_n(\dot{\gamma})$. Then in

a manner analogous to eq 16-21 of I we have for the λ_j th transition (from eq 4 and 10)

$$(\Delta\omega_\lambda - in\beta)[C_{r,n}]_{\lambda_j} + \sum_{r'} \int_0^{2\pi} d\gamma f_{r'}^* [\mathcal{H}_1^* C_{r',n}]_{\lambda_j} f_{r'} + r\{\sqrt{\beta R(n+1)}[C_{r,n+1}]_{\lambda_j} + \sqrt{\beta Rn}[C_{r,n-1}]_{\lambda_j}\} = q\omega_\lambda \delta_{r,0} \delta_{n,0} d_{\lambda_j} \quad (12)$$

[Note $\Delta\omega_\lambda = \omega - \omega_\lambda$, $d_{\lambda_j} = \frac{1}{2}\omega_1(S_-)_{\lambda_j}$, $q = \hbar/NkT$, with N the number of spin eigenstates.] We have, in obtaining eq 12, utilized the fact that \mathcal{H}_1^* does not depend explicitly on angular velocity, but it does depend on orientation. The absorption for the λ_j th transition is given by

$$\begin{aligned} \text{Im } \bar{Z}(\omega)_{\lambda_j} &= \text{Im} \int_0^{2\pi} d\gamma \int_{-\infty}^{\infty} d\dot{\gamma} Z(\gamma, \dot{\gamma}, \omega)_{\lambda_j} P_0(\gamma, \dot{\gamma}) \\ &= \text{Im} \int_0^{2\pi} d\gamma \int_{-\infty}^{\infty} d\dot{\gamma} \tilde{Z}(\gamma, \dot{\gamma}, \omega)_{\lambda_j} f_0(\gamma) h_0(\dot{\gamma}) \\ &= \text{Im} [C_{o,o}]_{\lambda_j} \end{aligned} \quad (13)$$

It is possible to replace the Brownian diffusion case by a "strong-collision-in-angular-velocity-space" model which has been referred to as an extended diffusion or J-diffusion model.¹¹ This possibility, as well as related ones, are discussed by Sack.^{7a,b} For our purposes, it is easy to show from Sack's expressions (cf. eq 2.11 of 7a) that for the case where each collision results in $\dot{\gamma}$ being restored to its equilibrium distribution given by $P_0(\dot{\gamma})$ (but with γ unchanged by the collision), one merely may replace

$$n\beta \rightarrow \beta(1 - \delta_{n,o}) \quad (14)$$

in eq 12. (Such simple changes with model have an analogy in the methods of treating orientational-jump models.)^{2a}

Equations 12 and 13 may then be solved in the usual manner for different values of R and β by truncating the eigenfunction expansion in n and r after a sufficient number of terms are taken. We are, however, primarily interested in the three-dimensional case which may be handled analogously, although it is considerably more complex. This one-dimensional model is, however, useful in illustrating how the general format of the theory may be applied. Also we shall use it later to attempt a simplified treatment of the three-dimensional case.

(B) *Three-Dimensional Free Rotational Diffusion.* Here we make considerable use of the treatment of Fixman and Rider.⁶ They treat the cases of both Brownian (or Langevin) diffusion and extended diffusion from a stochastic Liouville-type approach. In particular one has for a spherical-top in these cases

$$-\Gamma = i\nu S + \mathcal{L} \quad (15)$$

where \mathcal{L} is the relaxation or diffusion operator for the angular velocity \mathbf{v} , which for a Brownian model is^{6,7b}

$$\mathcal{L} = \beta[\nabla_v \cdot \mathbf{v} + R\beta\nabla_v^2] \quad (16)$$

The inertial or streaming term νS (where $\nu = |\mathbf{v}|$), describes the dynamical coupling of angular momentum ($\mathbf{L} = I\mathbf{v}$) and orientation.^{6,7b} One has

$$S = \mathbf{l} \cdot \mathbf{j}_u$$

where

$$\mathbf{l} = \mathbf{v}/\nu \text{ and } \mathbf{j}_u \equiv -i\mathbf{u} \times \nabla_u \quad (17)$$

where \mathbf{u} is a unit orientational vector, the components of which give the projections of the laboratory unit z axis vector (\mathbf{k}) in a molecular coordinate frame.⁶ (This repre-

sentation is adequate for an axially symmetric $\mathcal{H}_1(\Omega)$, and we are only considering spherical top motion.) Thus S depends on the orientation of \mathbf{u} : θ_u , φ_u as well as the orientation of \mathbf{l} in the molecular coordinate frame or θ_v , φ_v . The products of spherical harmonics $Y_{nm}(\theta_u, \varphi_u)$ and $Y_{jp}(\theta_v, \varphi_v)$ form a basis set in which to evaluate S . Fixman and Rider find for their purposes that the coupled linear combinations which are eigenfunctions of the "angular momentum-type" operators $\mathbf{J} = \mathbf{j}_u + \mathbf{j}_v$ and $M = m + m'$ (the components of \mathbf{j}_u and \mathbf{j}_v on the molecular z axis) are more desirable for evaluating S simply. However, in the slow tumbling problem, where the perturbation $\mathcal{H}_1(\Omega)$ enters in a more complex fashion, it appears a little more convenient to choose the natural basis set for $\mathcal{H}_1(\Omega)$ ($\propto Y_{no}(\theta_u, \varphi_u)$ in the simple axially symmetric secular g tensor case, see below), which is the simple product representation.¹²

Now eq 16 leads to the equilibrium distribution in ν

$$P_0(\nu) = \left(\frac{I}{2\pi kT}\right)^{3/2} \exp(-I\nu^2/2kT) \quad (18)$$

and one may symmetrize \mathcal{L} (and Γ) by the analogous transformation to that used in eq 8. The eigenfunctions of $\tilde{\mathcal{L}}$ (the symmetrized form) are

$$|kjp\rangle = Y_{jp}(\theta_v, \varphi_v) R_k(j\nu) \quad (19)$$

where

$$R_k(j\nu) = \left[\frac{2\pi^{3/2} k!}{(j+1/2+k)!}\right]^{1/2} P_o(\nu)^{1/2} v^j L_k^{j+1/2}(v^2) \quad (19a)$$

and $L_k^{j+1/2}$ is the associated Laguerre polynomial. The eigenvalues of \mathcal{L} are for Brownian (or Langevin) diffusion⁶

$$\tau_{jk}^{-1} \equiv \langle kjp | \tilde{\mathcal{L}} | k'j'p' \rangle = +\delta_{kk'} \delta_{jj'} \delta_{pp'} (j+2k)\beta \quad (20)$$

In the case of extended diffusion (i.e., each collision thermalizes \mathbf{L}) one obtains^{6,7a,b}

$$\tau_{jk}^{-1} \equiv \langle kjp | \tilde{\mathcal{L}} | k'j'p' \rangle = +\delta_{kk'} \delta_{jj'} \delta_{pp'} \beta(1 - \delta_{j,o} \delta_{k,o}) \quad (21)$$

The "matrix elements" of νS are found to be

$$\begin{aligned} \langle Lm; kjp | \nu S | L'm'; k'j'p' \rangle &= \langle kjp | \nu | k'j'p' \rangle \times \\ &\langle Lm; jp | S | L'm'; j'p' \rangle = \\ &\delta_{L,L'} \delta_{j',j-1} S_{j-1}(L, m, m', p, p') [\delta_{k,k'} (j+1/2+k)^{1/2} - \\ &\delta_{k',k+1} (k+1)^{1/2}] + \delta_{j',j+1} S_{j+1}(L, m, m', p, p') [\delta_{k,k'} (j+3/2 + \\ &k)^{1/2} - \delta_{k',k-1} (k)^{1/2}] \sqrt{R\beta/2} \end{aligned} \quad (22)$$

where

$$\begin{aligned} S_{j\pm 1}(L, m, m', p, p') &= [(2[j\pm 1] + 1)(2j+1)3]^{1/2} \times \\ &\begin{pmatrix} j\pm 1 & 1 & j \\ 0 & 0 & 0 \end{pmatrix} \times \{m\delta_{m,m'} \begin{pmatrix} j\pm 1 & 1 & j \\ -p & 0 & p \end{pmatrix} \delta_{p,p'} (-)^p + \\ &\frac{1}{\sqrt{2}} \delta_{m',m-1} \delta_{p',p+1} [L(L+1) - m(m-1)]^{1/2} \times \\ &\begin{pmatrix} j\pm 1 & 1 & j \\ -(p+1) & 1 & p \end{pmatrix} (-)^p - \frac{1}{\sqrt{2}} \delta_{m',m+1} \delta_{p',p-1} \times \\ &[L(L+1) - m(m+1)]^{1/2} \begin{pmatrix} j\pm 1 & 1 & j \\ -(p-1) & -1 & p \end{pmatrix} (-)^p\} \end{aligned} \quad (23)$$

For an (axially symmetric) secular perturbation, one only needs terms for which $M = m + p = 0$ and $M' = m' + p' = 0$. In view of the complexity of the problem, we only consider here this simplest of esr cases, i.e., a single line

broadened by an axially symmetric g tensor. (A detailed discussion of the expressions for the case of an axially symmetric nitroxide is given by Bruno.¹³) We may then write⁴

$$\mathfrak{H}_1(\Omega) = \left(\frac{4\pi}{5}\right)^{1/2} Y_{2,0}(\theta_u, 0) \mathfrak{F} S_z \quad (24)$$

$$\mathfrak{F} \equiv 2/3\hbar^{-1}\beta_e B_0 (g_{\parallel} - g_{\perp}) \quad (24a)$$

where B_0 is the magnitude of the dc magnetic field, and g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the g tensor. The matrix elements of $\mathfrak{H}_1(\Omega)$ are simply

$$\langle Lm; k_j p | \mathfrak{H}_1(\Omega) | L'm'; k' j' p' \rangle = (-)^m \mathfrak{F} (2L'+1)^{1/2} (2L+1)^{1/2} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ -m & 0 & m \end{pmatrix} \times \delta_{m,m'} \delta_{k,k'} \delta_{j,j'} \delta_{p,p'} \quad (25)$$

We may then expand the spin-density "matrix elements" as

$$\tilde{Z}(\theta_u, \varphi_u, \theta_v, \varphi_v, L, \omega)_{\lambda} = \sum_{L,m,k,j} [C_{L,m,k,j}(\omega)]_{\lambda} \times Y_{L,m}(\theta_u, \varphi_u) Y_{j-m}(\theta_v, \varphi_v) R_{kj}(v) \quad (26)$$

and in an analogous manner to eq 13 one obtains

$$\text{Im } \bar{Z}(\omega) = \text{Im} [C_{o,o,o}(\omega)]_{\lambda} \quad (27)$$

for the single (λ th) transition with matrix elements equivalent to eq 12

$$[(\omega - \omega_0) - i\tau_{jk}^{-1}] C_{L,m,k,j} + \sum_{L'} \langle L, m; k_j - m | \mathfrak{H}_1(\Omega) | L', m; k_j - m \rangle C_{L',m,k,j} - \sum_{k',j',m'} \langle L, m; k_j - m | vS | L', m'; k', j' - m' \rangle C_{L,m',k',j'} = q\omega_{\lambda} d_{\lambda} \delta_{L,o} \delta_{m,o} \delta_{k,o} \delta_{j,o} \quad (28)$$

The solution may be simplified by noting that only the following linear combinations are needed

$$\bar{C}_{L,m,k,j} = \frac{1}{\sqrt{2}} (C_{L,m,k,j} \pm C_{L,-m,k,j}) \quad m \neq 0 \quad (29)$$

where the + sign is for even j and the - sign for odd j .

(C) *An Approximate Approach.* As may be seen, the coupled equations defining even the simplest esr problem are themselves very complex. It is thus not very practical to attempt to solve a free diffusion model for more complex slow-tumbling esr cases such as a nitroxide. We therefore have examined a highly simplified description of inertial effects. Essentially what we have done is to employ the one dimensional model in modified form. That is, we replace eq 15-17 simply by

$$\Gamma = i v |j_u^2|^{1/2} - \beta \left(\frac{\partial}{\partial v} v + \beta R \frac{\partial^2}{\partial v^2} \right) \quad (30)$$

where $|j_u^2|^{1/2}$ is defined by

$$|j_u^2|^{1/2} Y_{Lm} \equiv [L(L+1)]^{1/2} Y_{Lm} \quad (30a)$$

In this fashion the angular velocity diffusion of the spherical top is treated simply in terms of its magnitude, while the effects of the orientation of v on the description of the orientational motion of the molecule are neglected. We show below that this assumption results in a description

of inertial effects on molecular reorientation which is equivalent to an earlier approximate treatment by Steele.¹⁴ In Steele's analysis the approximation amounted to defining a rotational-diffusion tensor as

$$R_{ij}(t) = \int_0^t \langle v_i(0) v_j(t) \rangle dt$$

This assumption neglects the noncommutativity of the angular momentum operators.

A comparison of eq 30 with 6 immediately shows that the treatment given in section A for one-dimensional free-rotational diffusion applies. One need only make the replacements in eq 12 of $f_r(\gamma) \rightarrow Y_{Lm}(\theta_u, \varphi_u)$, $r^2 \rightarrow L(L+1)$, and $\int_0^{2\pi} d\gamma \rightarrow \int_0^{\pi} d\theta_u \int_0^{2\pi} d\varphi_u$. In particular, we have for the axially symmetric g tensor mechanism

$$[(\omega - \omega_0) - i(T_2^{-1} + n\beta)] C_{L,n} - \mathfrak{F} \sum_{L'} (2L'+1)^{1/2} (2L+1)^{1/2} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C_{L',n} + \sqrt{\beta R} \sqrt{L(L+1)} \left[\sqrt{(n+1)} C_{L,n-1} + \sqrt{n} C_{L,n+1} \right] = q\omega_{\lambda} d_{\lambda} \delta_{L,o} \delta_{n,o} \quad (31)$$

and again

$$Z''(\omega) = \text{Im } C_{o,o} \quad (32)$$

For the case $R/\beta \ll 1$, one expects that eq 31 should be equivalent to the spectrum for simple Brownian reorientation. One may readily show this to be so by considering the third term on the left-hand side of eq 31 as a perturbation compared to diagonal elements $n\beta$. Then, to second order in this third term, we obtain for the coefficients $C_{L,o}$

$$[(\omega - \omega_0) - i(T_2^{-1} + RL[L+1])] C_{L,o} - \mathfrak{F} \sum_{L'} (2L'+1)^{1/2} (2L+1)^{1/2} \times \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C_{L',o} = q\omega_{\lambda} d_{\lambda} \delta_{L,o} \quad (33)$$

which is identical with the equation obtained in I for simple rotational diffusion.

Suppose, on the other hand, $R/\beta \geq 1$. Then coefficients $C_{L,n}$ for $n > 0$ become significantly coupled into the $C_{L,o}$ coefficients that ordinarily determine the spectrum. Suppose one may initially neglect the term in \mathfrak{F} in eq 31, i.e., $\mathfrak{F} \ll \beta, R$. Then, for this case we need consider the coupling of $C_{L,n}$ to the other $C_{L,n'}$. Let us first consider the simplified coupled set of equations

$$[(\omega - \omega_0) - in\beta] a_{L,n} + (\sqrt{n+1} a_{L,n+1} + \sqrt{n} a_{L,n-1}) \gamma_L = \delta_{n,o} \quad (34)$$

where $\gamma_L = [R\beta L(L+1)]^{1/2}$. Equation 34 may be solved for $a_{L,o}$, and it generates a continued fraction, the solution of which is known.³ It yields

$$a_{L,o}(\omega) = i \int_0^{\infty} \exp\{-L(L+1) \frac{R}{\beta} (e^{-\beta t} - 1 + \beta t)\} - i(\omega - \omega_0)t \{ dt \equiv i j_L(\omega - \omega_0) \quad (35)$$

which is the Fourier-Laplace transform of a type of correlation function well known in Brownian motion theory and obtained by Steele in his approximate treatment of inertial effects in rotational diffusion (for a spherical rotor).¹⁴ If we now introduce the effects of \mathfrak{F} to lowest

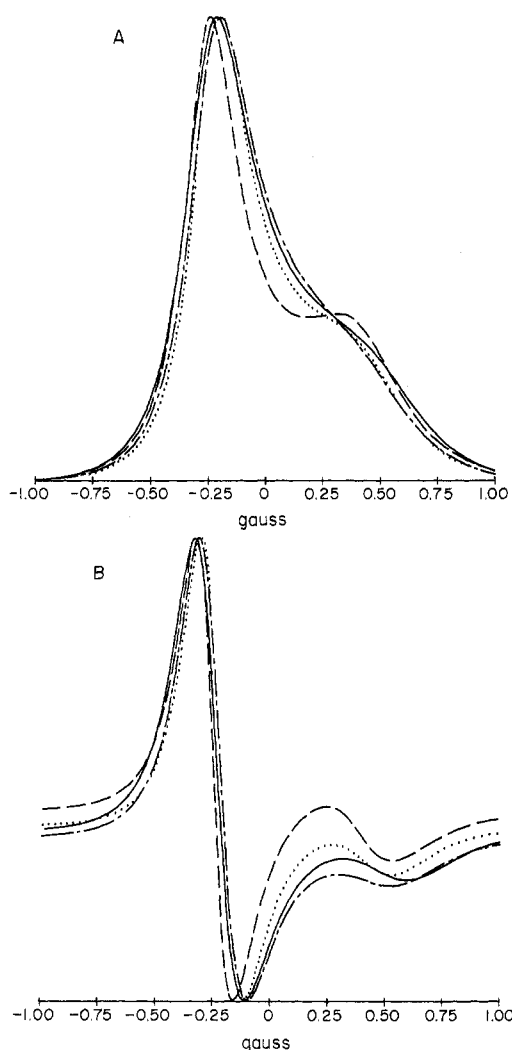


Figure 1. Comparison of line shapes for axially symmetric g tensor for different free rotational diffusion models: A, absorption line shapes; B, first derivative line shapes. The different rotational diffusion models are , simple Brownian; ———, motion described in full three-dimensional angular momentum space for Brownian particle with $\beta = 4R$ and $R = 0.13|\mathcal{F}|$; - - -, motion described in one-dimensional angular momentum space for Brownian particle with $\beta = 4R$ and $R = 0.13|\mathcal{F}|$; - · - · -, simple free diffusion with $\beta/R = (R\tau)^{-1} = 4$ and $R = 0.105|\mathcal{F}|$. All have $\tau_R = 1.72 \times 10^{-7}$ sec, $g_{\parallel} = 2.00235$, $g_{\perp} = 2.00310$, $B_0 = 3300$ G, $(2/3^{1/2})T_2^{-1}/|\gamma_e| = 0.02$ G.

order, so that $C_{0,0} \approx 1$, we then obtain from eq 31

$$\left[\left(\omega - \omega_0 - \frac{2}{7} \mathcal{F} \right) - i(5)^{-1} \mathcal{F}^2 j_2 \left(\omega - \omega_0 - \frac{2}{7} \mathcal{F} \right) \right] C_{0,0} \approx 1 \quad (36)$$

And since $R, \beta \gg \mathcal{F}$, one may let $j_2(\omega - \omega_0 - (2/7)\mathcal{F}) \approx j_2(0)$ for values of ω for which the resonance signal is not negligible.

The approximation suggested by Egelstaff in another connection¹⁵ and which served as the basis of our earlier simplified model of free diffusion^{2a} is to estimate the half-width for the (approximate) form of the $j_L(\omega)$ given by eq 35 and then use it to replace the inverse eigenvalues $[RL(L+1)]^{-1}$ appropriate for the rotational diffusion operator. (For $R/\beta \ll 1$, the result is of course just $[RL(L+1)]^{-1}$ cf. eq 33.) This is equivalent to approximating the $j_L(\omega)$ of eq 35 to a Lorentzian. In actual fact, it is highly

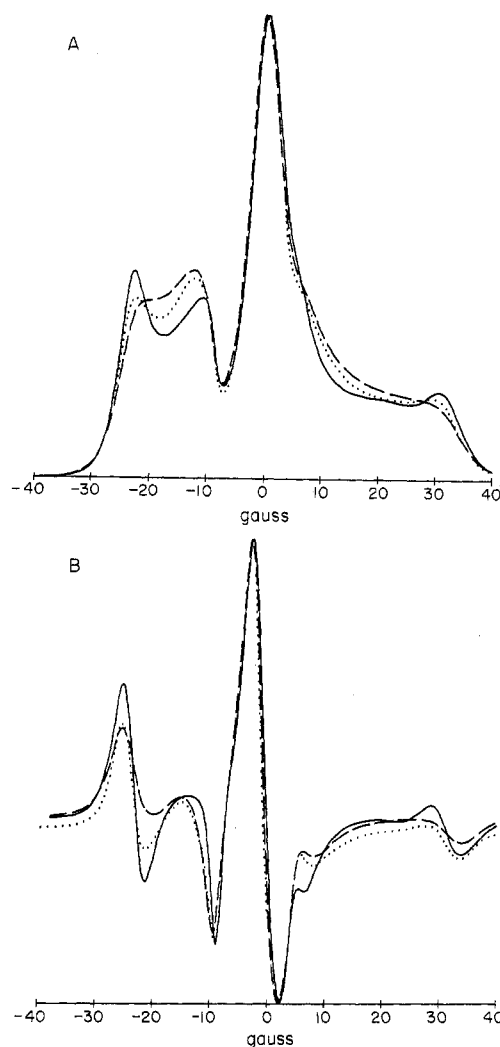


Figure 2. Comparison of line shapes for axial nitroxide for different free rotational diffusion models: A, absorption line shapes; B, first derivative line shapes. The different rotational diffusion models are , simple Brownian diffusion with $R = 0.0856|\mathcal{F}|$ ($\tau_R = 2.10 \times 10^{-8}$ sec); ———, motion described in one-dimensional angular momentum space with $\beta = 4R$ and $R = 0.164|\mathcal{F}|$ ($\tau_R = 2.16 \times 10^{-8}$ sec); - - -, simple free diffusion with $\beta/R = (R\tau)^{-1} = 4$ and $R = 0.182|\mathcal{F}|$ ($\tau_R = 1.58 \times 10^{-8}$ sec). All have $g_{\parallel} = 2.00270$, $g_{\perp} = 2.00750$, $A_{\parallel} = 32$ G, $A_{\perp} = 6$ G, $B_0 = 3300$ G, and $(2/3^{1/2})T_2^{-1}/|\gamma| = 0.3$ G.

non-Lorentzian for $L(L+1)R/\beta \geq 1$, becoming a Gaussian for $L(L+1)R/\beta \gg 1$. Also, the deviations from Lorentzian character of $j_L(\omega)$ are greater for greater values of ω , i.e., the short-time effects are more important.⁹ Thus as the tumbling slows down and $\mathcal{F} > R, \beta$, then, e.g., $j_2(\omega - \omega_0 - (2/7)\mathcal{F})$ is no longer well approximated by a Lorentzian over the region of ω for which there is a nonnegligible ESR signal.

There is still another and more serious way in which an Egelstaff-type approximation breaks down for $\mathcal{F} \geq R, \beta$. In eq 31 $C_{0,0}$ is coupled to the $C_{L,0}$ ($L > 0$) by \mathcal{K}_1 and these $C_{L,0}$ then couple to the $C_{L,n}$ ($n > 0$) (by the inertial terms) which then bring in the effects of the angular velocity diffusion. As \mathcal{F} becomes larger, the coupling of the $C_{L,n}$ to the $C_{L',n}$ ($n \geq 0$) becomes important, leading, for example, to indirect coupling of the $C_{0,0}$ to the $C_{0,n}$ ($n > 0$) indicating that the mixing of effects of angular velocity diffusion into the spectrum is becoming more complex than even that predicted only by the frequency dependent

$j_L(\omega)$ given by eq 35.¹⁵ This represents the kind of complication which sets in when several time scales (*i.e.*, spin-relaxation, orientational relaxation, and angular velocity diffusion) all become comparable.

While we have discussed the complicating effects of inertial motion on slow tumbling spectra in terms of the approximate model, similar problems apply to the more complex situations for the more rigorous descriptions of inertial effects. However, as we shall find, they appear to have a *cancelling* effect.

III. Results

(A) *Single-Line Axially Symmetric g Tensor.* One finds that for $\beta \gg R$ the proper Brownian rotational diffusion results are obtained for all inertial models of section II in both the fast and slow motional region. However, for $\beta \leq R$ they exhibit significant differences. This is illustrated in Figure 1 for $\beta = 4R$ for line shapes calculated from eq 27–28 and 31–32. Also included for comparison are the line shapes for Brownian rotational diffusion and for the simple free diffusion model. All models were calculated to have the same rotational correlation time τ_R , such that, if the spectrum were in the fast motional region, all models would give the same Lorentzian width.^{2a} While all the inertial-effect models yield spectra which deviate somewhat from that for Brownian rotational diffusion, one is struck by the fact that the approximate one-dimensional angular momentum model of eq 31 yields results qualitatively different from any other case. It shows the inertial effects for this model lead to a sharpening of the features of the Brownian rotational diffusion spectrum, while the line shapes from the complete model of eq 28 as well as the simple free diffusion case show the inertial effects to cause a smoothing out of the features. The results for the latter two cases are quite similar. We have also found that line shapes calculated for extended diffusion (eq 21 for eq 28 and eq 14 for eq 31) give results which deviate only very slightly from the line shapes for the Langevin diffusion model (eq 20 for eq 28 and eq 31).

(B) *Axial Nitroxide.* The detailed equations for all the inertial models considered above are given by Bruno.¹³ We show in Figure 2 a comparison of the line shapes calculated for $\beta = 4R$ for all models except the complete three-dimensional angular momentum case,¹³ since this case is extremely complex. The value of R was slightly adjusted in each of the models so that the distance between the outer first derivative extrema would be the same. As was seen for the axially symmetric g tensor, the inertial

effects from the approximate one-dimensional momentum produce line shapes with sharper features than the Brownian rotational diffusion. This is again in direct contrast to the simple free rotational diffusion model line shape (as well as any of the comparable appearing line shapes for the moderate jump models discussed in ref 2a).

It is anticipated, from the results for the g tensor case and the similar structure of the equations in that case and that for the axial nitroxide,¹³ that the complete three-dimensional angular-momentum treatment will yield line shapes similar to those for the simple free-diffusion results. In that case it would still be difficult to distinguish an inertial model from that of moderate jump models on the basis of line shape alone, and other considerations would be required.^{2b}

References and Notes

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