ESR spectrum can no longer be described as a simple superposition of Lorentzian lines, characteristic of the fast motional or motional narrowing region, for which the theory developed in the previous chapter applies. In this chapter we further take it to be the region for which the ESR spectrum still shows effects of the motion; i.e., the motion is not so slow as to yield a proper rigid-limit spectrum. For nitroxide free radicals, this usually means we are considering the range of rotational correlation times $10^{-9}$ sec $\leq \tau_R \leq 10^{-6}$ sec. This is an important range for nitroxide probes in viscous media or for nitroxide spin labels attached to large macromolecules.

In this region, the spectra are affected in a complicated way by both the motions and the magnetic spin interactions. As a result, a theory which can deal rigorously with describing this region must be both powerful and general. It is our objective to set forth this theory, which has been developed in the last few years, and to emphasize its general foundations. The general theory is presented in Section II.A. It is a characteristic of the slow motional region that it requires that we ask more intricate questions about the detailed nature of the molecular motions in order to properly analyze the spectra than is true for studies in the motional narrowing region. Thus in much of the remainder of Section II the dynamics of molecular motions is developed to an extent concomitant with the need to explain actual slow tumbling experiments.

It has also been our objective to demonstrate how the general theory can be applied to actual cases. Thus in Section III we give a detailed discussion of comparisons between the theoretical predictions and recent experimental studies. Wherever it appears reasonable, we have tried to indicate simplified approaches in the analysis of slow tumbling spectra short of running detailed computer simulations. Nevertheless, there are many cases where the researcher will need detailed simulations tailored to his specific needs. For that reason, we have, in Appendix B, supplied the computer program that is applicable to isotropic liquids.

The development of the theory and the specific examples given here draw most heavily on the recent work of the Cornell group, with which the author is most familiar. Detailed references to other work can be found in a recent review article (Freed, 1972b). Recently, Polnaszek (1975b) has reviewed our methods and compared them with the other approaches. It should be emphasized that the slow tumbling theory is in many ways based on a generalization of stochastic theories of jump models for magnetic resonance (Abragam, 1962; Kubo, 1962, 1969; Johnson, 1965) and we sometimes make use of the analogies when appropriate. A familiarity with motional narrowing theory, such as is discussed in Chapter 2, would be useful preparation for this chapter, and a familiarity with quantum mechanics and some statistical mechanics is assumed in Section II.

I. INTRODUCTION

In this chapter we develop the theory for slow tumbling in ESR spectroscopy, with specific application to nitroxide free radical spectra. The slow tumbling region is that range of rotational reorientation times for which the
II. THEORY

A. General Method

A quantum mechanical wave function $\Psi$ can be expanded in a complete set of orthonormal functions $U_n$ as

$$\Psi(t) = \sum_n c_n(t)U_n$$

(1)

The density matrix is defined to be

$$\rho_{mm}(t) = \overline{c_m(t)c_m^*(t)}$$

(2)

where the bar indicates an average over a statistical ensemble. A useful property of the density matrix is the calculation of the expectation value of an operator $O$ for a system described by the wave function $\Psi$. Thus

$$\langle \Psi | O | \Psi \rangle = \sum_{m,n} \langle \Psi | U_mU_m^*O | U_nU_n^* | \Psi \rangle = \sum_{m,n} c_n(t)c_n^*(t)O_{mn}$$

(3a)

and for an average expectation value of an ensemble of such systems we have

$$\langle \Psi | O | \Psi \rangle = \sum_{m,n} \rho_{mm}O_{mn} = \text{Tr} \rho O$$

(3b)

where $\text{Tr}$ is the trace. The trace is invariant to the choice of the complete orthonormal basis set. Thus all the information for calculating observable quantities is contained in the density matrix.

Since the wave function $\Psi$ will vary with time, the coefficients $c_n(t)$ will be functions of time, and this time dependence can be obtained from the time-dependent Schrödinger equation. Then the density matrix equation of motion, assuming the same Hamiltonian $\hat{H}(t)$ for all members of the ensemble, is given by the quantum mechanical Liouville equation

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

(4)

Now assume that the time dependence of the spin Hamiltonian $\hat{H}(t)$ for a free radical arises from interactions with its environment such that $\hat{H}(t)$ is fully determined by a complete set of random variables $\Omega$. Also assume that this time dependence of $\Omega$ is described by a stationary Markov process, so that the probability of being in a state $\Omega_1$ at time $t$, if in state $\Omega_2$ at time $t - \Delta t$, is (a) independent of the value of $\Omega$ at any time earlier than $t - \Delta t$ and (b) depends only on $\Delta t$ and not on $t$. A stationary Markov process can be described by a differential equation

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

(5)

where $P(\Omega, t)$ is the probability of the free radical being in a state $\Omega$ at time $t$. 
Since the process is assumed stationary, $\Gamma_\Omega$ is independent of time. The evolution operator $\Gamma_\Omega$ is an operator only on the random variables $\Omega$ and is independent of spin space. $\Gamma_\Omega$ includes such general Markov operators as the diffusion operators given by the Fokker–Planck equations and transition rate matrices among discrete states $\Omega_1, \Omega_2, \ldots, \Omega_n$. In this discussion, $\Omega \equiv \alpha, \beta, \gamma$ will represent Euler angles specifying orientation and $\Gamma_{\Omega}$ will be a rotational diffusion operator.

It is also assumed that the stochastic process has a unique equilibrium distribution $P_\Omega(\Omega)$ characterized by

$$\Gamma_\Omega P_\Omega(\Omega) = 0$$  \hspace{1cm} (6)

We can show (Kubo, 1969; Freed et al., 1971; Freed, 1972a) that Eqs. (4)–(6) lead to the stochastic Liouville equation of motion

$$\partial \rho(\Omega, t)/\partial t = -i[\hat{H}(\Omega), \rho(\Omega, t)] - \Gamma_\Omega \rho(\Omega, t)$$  \hspace{1cm} (7)

where $\rho(\Omega, t)$ is now understood to be the value of $\rho$ associated with a particular value of $\Omega$, hence of $\hat{H}(\Omega)$. Thus, instead of looking at the explicit time dependence of the spin Hamiltonian $\hat{H}(t)$ involving the interaction with its environment, the spin Hamiltonian is written in terms of random angle variables $\Omega$ and its modulation (due to rotational motions) is expressed by the time dependence of $\Omega$.

The steady-state spectrum in the presence of a single rotating microwave frequency field is determined by the power absorbed from this field. We find for the $l$th hyperfine line at an orientation specified by $\Omega$

$$P_l(\Omega) = 2N\hbar d_l Z_l^{1r}(\Omega)$$  \hspace{1cm} (8)

where $P_l$ is the power absorbed, $N$ is the concentration of electron spins, $d_l$ is a "transition moment" given by $d_l = \gamma_e H_\Omega \langle \lambda^\nu | \hat{S}_\nu | \lambda^* \rangle$ where $\hat{S}_\nu$ is the electron spin-lowering operator and $\lambda^\nu$ are the $M_\nu = \pm \frac{1}{2}$ states of the electron spin for the $l$th transition), and $Z_l^{1r}$ is defined by the series of equations

$$\rho - \rho_0 = \chi_l$$  \hspace{1cm} (9)

$$\chi_l = \sum_{n=\pm} \exp(in\omega t) Z_l^n$$  \hspace{1cm} (10)

and

$$Z_l^n = Z_l^{1r} + iZ_l^{2r}$$  \hspace{1cm} (11)

(Actually, the experimentally observed signal is proportional to $Z_l^{1r}$ and not to $d_l Z_l^{1r}$.)

3. Theory of Slow Tumbling ESR Spectra for Nitroxides

In Eq. (9), $\rho_0(\Omega)$ is the equilibrium spin density matrix. Equation (8) displays the fact that it is the $n = 1$ harmonic, i.e., the component rotating with the microwave field, that is directly observed. In the case of simple lines we can identify $Z_l^{1r}$ and $Z_l^{2r}$ with the magnetization components $M_x$ and $M_y$ for the $l$th line in the rotating frame.

The notation for a matrix element of an operator $O$ is

$$O_{ab} = \langle a | O | b \rangle$$  \hspace{1cm} (12a)

$$O_{\pm} = \langle \lambda^- | O | \lambda^+ \rangle$$  \hspace{1cm} (12b)

$$O_{\pm} = \langle \lambda^\mp | O | \lambda^\mp \rangle$$  \hspace{1cm} (12c)

where $a, b$ are eigenstates and $\lambda^\pm$ are, respectively, the upper and lower electron spin states between which the $l$th ESR transition occurs. For a nitroxide there are three allowed ESR transitions.

The total absorption is then obtained as the equilibrium average of Eq. (8) over all $\Omega$. Thus averages are introduced such as

$$\overline{Z_l^{1r}} = \int d\Omega Z_l^{1r}(\Omega) P_\Omega(\Omega)$$  \hspace{1cm} (13)

so that

$$P_l = 2N\hbar d_l \overline{Z_l^{1r}}$$  \hspace{1cm} (14)

where $d_l$ has been taken to be independent of orientation. The total spin Hamiltonian $\hat{H}(t)$, expressed in angular frequency units, is now separated into three components,

$$\hat{H}(\Omega) = \hat{H}_0 + \hat{H}_1(\Omega) + \hat{\theta}(t)$$  \hspace{1cm} (15)

In the high-field approximation

$$\hbar \hat{H}_0 = g_s \beta_e H_0 \hat{S}_z - \hbar \sum_i \gamma_i \hat{I}_i \hat{S}_z - H_0 \gamma_e \sum_i a_i \hat{S}_z \hat{I}_i$$  \hspace{1cm} (16)

yields the zeroth-order energy levels and transition frequencies (cf. Chapter 2). $\hat{H}_1(\Omega)$ is the perturbation depending on the orientation angles $\Omega$ and, being a scalar, can be expressed as the scalar product of two tensors. That is, in general, we write $\hat{H}_1(\Omega)$ as in [the notation of Freed and Fraenkel (1963)]

$$\hat{H}_1(\Omega) = \sum_{L, m, m', \mu, i} \mathcal{F}_{L, m, m'}^{\mu, i}(\Omega) A_{\mu, i}^{L, m', m}$$  \hspace{1cm} (17)

where the $F_{\mu, i}^{L, m, m'}$ and $A_{\mu, i}^{L, m', m}$ are irreducible tensor components of rank $L$ and component $m$, with the $F$ being spatial functions in molecule-fixed coordinates, while $A$ consists only of spin operators quantized in the laboratory axis system. The subscripts $\mu$ and $i$ refer to the type of perturbation and
to the different nuclei, respectively. The Wigner rotation matrix elements \( S_{m, m}(\Omega) \) include the transformation from the molecule-fixed axis system \((x', y', z')\) into the laboratory axis system \((x, y, z)\). We shall be concerned with the \( A \) and \( g \) tensors, for which \( L = 2 \). [It has been found that effects of the \(^{14}\text{N} \) quadrupole tensor is negligible (Goldman et al., 1972a; Goldman, 1973).] In addition,

\[
\hat{z}(t) = \frac{1}{2} g_s H_t [\hat{S}_+ \exp(-i\omega t) + \hat{S}_- \exp(i\omega t)]
\]  

is the interaction of the electron spin with the oscillating magnetic radiation field. When more than one oscillating field, e.g., ELDOR or ENDOR, is present and/or when field modulation effects are to be explicitly incorporated then Eq. (18) may be appropriately modified to include these effects.

When we take the \( \langle \lambda^- | \lambda^+ \rangle \) matrix elements of Eq. (7) and utilize Eqs. (9)–(11), we find the steady-state equation for \( \hat{Z}_1^{\(m\)} \) to be

\[
(n\omega - \omega_d)\hat{Z}_1^{(m)}(\Omega) + [\hat{S}_1^{(m)}(\Omega), \hat{Z}_1^{(m)}(\Omega)]_t = i[\Gamma_1^{(m)}(\Omega)]_t + d_4[\chi^{(m)}_{t+1} - \chi^{(m)}_{t-1}]
\]

\[
= q\omega_1 d_4
\]

[The superscripts to \( \chi_{t, \pm} \) refer to harmonics in the sense of Eq. (10). The harmonic components of any other oscillating fields present may be introduced in a similar manner.] For reasonable temperatures and typical ESR field strengths we may write \( \rho_0 = N^{-1} - q\hbar \omega_0 \), where \( N \) is the number of spin eigenstates of \( \Phi_0 \) and \( q = \hbar/NkT \). Also, \( \hbar\omega_1 = E_{t+} - E_{t-} \) and the \( Z_1^{(m)}(\Omega) \) are spin matrices defined by Eqs. (9)–(11), and the \( E_{t, \pm} \) are the eigenenergies of \( \Phi_0 \) for the \( \chi_t \) states.

It is convenient at this point to introduce a "symmetrizing" transformation for the evolution operator. It is not needed for isotropic liquids but becomes useful for anisotropic liquids.

Thus

\[
\Gamma_\Omega = P_0^{1/2}\Gamma_0 P_0^{1/2}
\]

and similarly

\[
\hat{Z}_1^{(m)}(\Omega) = P_0^{1/2}[\hat{Z}_1^{(m)}(\Omega)P_0]
\]

This transformation usually renders \( \Gamma_\Omega \) Hermitian. Now, Eqs. (6) and (20) combine to give

\[
\Gamma_\Omega P_0^{1/2} = 0
\]

Equations (21) and (13) yield

\[
\hat{Z}_1^{(m)} = \int d\Omega P_0^{1/2}\hat{Z}_1^{(m)}(\Omega)
\]
where $\theta$ is the angle between the magnetic field axis and the molecular $z$ axis.

The above equations yield coupled complex algebraic equations for the coefficients $[C_m^{(n)}]$, and we attempt to solve for these equations utilizing only a finite number of coefficients. (The complete orthonormal set includes an infinite number of such eigenfunctions.) The convergence depends essentially on the ratio $|\mathcal{F}_1(\Omega)|/\tau_\alpha^m$. The larger the value of this ratio of off-diagonal to diagonal terms, the more terms $[C_m^{(n)}]$, that are needed. The results obtained by relaxation theory valid in the fast motional limit (cf. Chapter 2) are recovered when only one order beyond $[C_0^{(1)}]_z$ is included.

### B. Rotational Modulation in Isotropic Liquids

When the general method of the previous section is applied to rotational modulation, $\Omega$ refers to the Euler angles for a tumbling molecular axis with respect to a fixed laboratory axis system. For a molecule undergoing many collisions, causing small random angular reorientations, the resulting isotropic Brownian rotational motion is a Markov process, which can be described by the rotational diffusion equation (Freed et al., 1971; Freed, 1972a,b)

$$\partial P(\Omega, t)/\partial t = R \nabla^2_P P(\Omega, t)$$

where $\nabla^2_P$ is the Laplacian operator on the surface of a unit sphere and $R$ is the rotational diffusion coefficient. If the molecule is approximated by a rigid sphere of radius $a$ rotating in a medium of viscosity $\eta$, then a rotational Stokes–Einstein relationship yields

$$R = kT/8\pi a^3\eta$$

In an isotropic liquid, the equilibrium probability $P_0(\Omega)$ of Eq. (6) will be equal for all orientations, so that $P_0(\Omega) = 1/8\pi^2$. Here the Markov operator $\Gamma_0$, Eq. (5), for isotropic Brownian rotation, Eq. (30), is $-R\nabla^2_P$, which is formally the Hamiltonian for a spherical top whose orthonormal eigenfunctions are the normalized Wigner rotation matrices or generalized spherical harmonics:

$$G_m \rightarrow \phi_{KM}(\Omega) = [(2L + 1)/8\pi^2]^{1/2} \mathcal{W}_M(\Omega)$$

with eigenvalues $RL(L + 1)$ (Freed, 1964, 1972a). Note that for $K = 0$, $\mathcal{W}_M(\alpha, \beta, \gamma) = [4\pi/(2L + 1)]^{1/2} Y_{LM}(\beta, \gamma)$, where $Y_{LM}$ is the well-known spherical harmonic (Rose, 1954; Edmonds, 1957).

Similarly, the Markov operator for axially symmetric Brownian rotation about a molecule-fixed $z$ axis is formally the Hamiltonian for a symmetric top whose symmetry axis is the $z$ axis. The orthonormal eigenfunctions are again the normalized Wigner rotation matrices with eigenvalues given by

$$\Gamma_0 \phi_{KM} = [R_\perp L(L + 1) + (R_\parallel - R_\perp)K^2] \phi_{KM}$$

where $R_\perp$ and $R_\parallel$ are the rotational diffusion constants about the $x$, $y$ axes and $z$ axis, respectively (Freed, 1964; Favro, 1965). The “quantum numbers” $K$ and $M$ of the Wigner rotation matrices refer to projections along the body-fixed symmetry axis and along a space-fixed axis, respectively.

For completely asymmetric Brownian rotation (Freed, 1964, 1972a; Favro, 1965) $R_\perp \neq R_\parallel \neq R_z$, where $R_x$, $R_y$, and $R_z$ are the respective rotational diffusion constants about the $x$, $y$, and $z$ axes, the Markov operator $\Gamma_0$ has more complex solutions (see below). Also, for fast rotation about one axis (e.g., the $z$ axis, so that $R_\parallel \gg R_x, R_y$), the completely asymmetric rotation can be treated as axially symmetric with eigenvalues $R_\perp L(L + 1) + (R_z - R_\perp)K^2$, where $R_z = \frac{1}{2} (R_x + R_y)$.

In the fast rotational motion region, all rotational reorientation processes yield the same ESR line shapes, which, as predicted by earlier relaxation theories, yields Lorentzian lines (Abragam, 1961; Freed and Fraenkel, 1963). Naturally, in the very slow rotational motion region all models should tend to the rigid-limit powder line shape of the equilibrium distribution. However, in the intermediate slow rotational region $|\mathcal{F}_1(t)|/\tau_\alpha \gg 1$, the ESR line shapes are found to be sensitive to the details of the molecular reorientation process.

A number of different models for rotational reorientation can be proposed. Some useful ones are: (a) Brownian rotational diffusion; (b) free diffusion in which a molecule rotates freely for time $\tau$ (i.e., inertial motion with $\tau = I/B$, with $I$ the moment of inertia and $B$ the friction coefficient) and then reorients instantaneously; and (c) jump diffusion in which a molecule has a fixed orientation for time $\tau$ and then “jumps” instantaneously to a new orientation (Goldman et al., 1972; Egelstaff, 1970). For isotropic reorientation, we can summarize the results for these models as

(a) $\tau_L^{-1} = L(L + 1)\tau$

(b) $\tau_L^{-1} = L(L + 1)\tau [1 + L(L + 1)R_\perp]^{1/2}$

and

(c) $\tau_L^{-1} = \tau^{-1} \left[1 - (2L + 1)^{-1} \int_0^\infty d\theta W(\theta) \sin(L + \frac{1}{2})\theta/\sin(\frac{1}{2}\theta)\right]$}

where $W(\theta)$ is the distribution function for diffusive steps by angle $\theta$ and is normalized so that

$$\int_0^\infty W(\theta) \, d\theta = 1$$
3. THEORY OF SLOW TUMBLING ESR SPECTRA FOR NITROXIDES

For anisotropic rotational diffusion, there are no convenient solutions for the jump and free diffusion models. The most straightforward course then is to generalize the equations for spherically symmetric rotation. Thus we let

\[ \tau^{-1}_{L,k} = (B_{L}/R_{l})(R_{l} L(L+1) + (R_{l} - R_{v})K^{2}) \]  

where \( B_{L} \) is the same model parameter as in Eq. (42). In effect, it is assumed in Eq. (44) that although the \( L \) dependence of \( \tau^{-1}_{L,k} \) is model dependent, the “quantum number” \( K \) plays the same role in all models (Goldman et al., 1972a). Other interpretations of the model dependence in terms of more fundamental analyses of microscopic molecular dynamics have been discussed by Hwang et al. (1975).

C. Anisotropic Liquids

Suppose now that the liquid has a preferred axis of orientation, i.e., the director axis (cf. Chapter 8). We now write the perturbing Hamiltonian (17) as (Polnaszek et al., 1973) [with the \((-1)^{K}\) which was included into the \( F_{\mu}^{(L,K)} \) of Eq. (17) now explicitly displayed]:

\[ \mathcal{H}_{\mu}^{(L,M)}(\Omega, \Psi) = \sum_{L,M,K}(-1)^{K} \mathcal{D}_{L,KM}(\Omega) \mathcal{D}_{L,KM}^{*}(\Psi) F_{\mu}^{(L,K)} A_{\mu}^{(L,K)} \]  

Equation (45) is based on two sets of rotations of the coordinate systems: first from the molecular axis system \((x', y', z')\) into the director axis system \((x'', y'', z'')\) with Euler angles \(\Omega = (\alpha\beta\gamma)\); and then into the laboratory axis system \((x, y, z)\) with Euler angles \(\Psi\). The orientation of the director relative to the laboratory frame can be specified by the two polar angles \(\theta'\) and \(\phi'\) such that \(\Psi = (0, \theta', \phi')\). More precisely, one means by the molecular coordinate system \((x', y', z')\) the principal axis system for the orientation of the molecule in the mesophase. It may also be necessary to transform from the principal axis system of the magnetic interactions \(x'' \), \(y'' \), \(z'' \) to the \((x', y', z')\) system with Euler angles \(\Theta\), according to

\[ F_{\mu}^{(L,K)} = \sum_{K'} \mathcal{D}_{K,K'}(\Theta) F_{\mu}^{(L,K')} \]  

where \( \Theta = (\alpha',\beta',\gamma') \).

The diffusion equation for a particle undergoing Brownian rotational diffusion in the presence of a potential \( V \) is given by (Favro, 1965; Polnaszek and Freed, 1975; Polnaszek, 1975a)

\[ \frac{\partial P(\Omega, t)}{\partial t} = -\mathbf{R} \cdot \left[ \frac{1}{kT} \frac{\partial V(\Omega)}{\partial \mathbf{R}} + \mathbf{R} \cdot \frac{\partial \mathbf{R}}{\partial t} \right] P(\Omega, t) \equiv -\Gamma_{\Omega} P(\Omega, t) \]
where \( V(\Omega) \) can be taken to be the orienting pseudopotential for a liquid crystal. \( \mathcal{M} \) is the vector operator, which generates an infinitesimal rotation, and is identified with the quantum mechanical angular momentum operator for a rigid rotator, and \( \mathbf{R} \) is the diffusion tensor of the molecule. Both \( \mathcal{M} \) and \( \mathcal{M}^2 \) are defined in the \((x', y', z')\) molecular coordinate system. The angular momentum operator \( \mathcal{M} \) is defined by

\[
\mathcal{M}^2 \phi_{KM}(\Omega) = L(L + 1) \phi_{KM}(\Omega) \tag{48a}
\]

\[
\mathcal{M}_z \phi_{KM}(\Omega) = [(L \mp K)(L \pm K + 1)]^{1/2} \phi_{K \pm 1, M}(\Omega) \tag{48b}
\]

\[
\mathcal{M}_x \phi_{KM}(\Omega) = K \phi_{KM}(\Omega) \tag{48c}
\]

where the \( \phi_{KM}(\Omega) \) are the eigenfunctions of \( \mathcal{M}^2 \) and \( \mathcal{M}_z \), given by Eq. (32), and

\[
\mathcal{M}_z = \mathcal{M}_x \pm \mathcal{M}_y \tag{49}
\]

When \( V = 0 \), Eq. (47) is simply the equation for (asymmetric) Brownian rotational diffusion in isotropic liquids. [Simpler expressions have been given for special cases by Nordio and Busolin (1971), Nordio et al. (1972), and Polnaszek et al. (1973).] Equation (47) is based on the assumption that the external torque \( \mathbf{T} \) is derived from the potential \( V(\Omega) \):

\[
\mathbf{T} = -i. \mathcal{M} V(\Omega) \tag{50}
\]

[Cf. Eq. (30), where we have set \( V_0^2 = -\mathcal{M}^2 \).] The equilibrium solution to Eq. (47) is given by

\[
P_0(\Omega) = \frac{\exp[-V(\Omega)/kT]}{\int d\Omega \exp[-V(\Omega)/kT]} \tag{51}
\]

When the symmetrized forms of Eqs. (20)-(22) are used, we obtain the diffusion equation

\[
\partial \tilde{P}(\Omega, t)/\partial t = -\Gamma_\Omega \tilde{P}(\Omega, t) \tag{52}
\]

where

\[
\Gamma_\Omega = \mathcal{M} \cdot \mathbf{R} \cdot \mathcal{M} + \frac{\mathcal{M} \cdot \mathbf{R} \cdot V}{2kT} \tag{53}
\]

The restoring potential for liquid crystals can be written in its most general form as

\[
V(\Omega) = \sum_{L, K, M} \epsilon_{LKM}^2 \phi_{LKM}(\alpha, \beta, \gamma) \tag{54}
\]

The assumption of cylindrical symmetry about the director axis \( n \) implies that all averages taken over the angle \( \gamma \) vanish unless \( M = 0 \) (Glarum and

3. Theory of Slow Tumbling ESR Spectra for Nitroxides

Marshall, 1966, 1967). The uniaxial property of nematic liquid crystals (i.e., \( n \equiv -n \)) implies that \( L \) must be even. It is useful to use the linear combinations of the \( \phi_{KLM}^2 \) that are of definite parity, i.e., the real linear combinations

\[
V(\Omega) = \sum_{\text{even } L} \left( \epsilon_{L00}^2 \phi_{L00}(\Omega) + \sum_{K>0} \epsilon_{L,K}^2 \left[ \phi_{L0K}(\Omega) \pm \phi_{L2K}(\Omega) \right] \right) \tag{55}
\]

These have simpler properties for molecular symmetries less than cylindrical.

Usually we consider only the leading term \( \epsilon_{L00}^2 \phi_{L00}(\Omega) \), i.e., the Meier-Saupe (1958) potential. The cylindrically symmetric case when \( \epsilon_{L0}^2 \not= 0 \) has also been considered (Polnaszek et al., 1973) and it was shown that typical ESR spectral predictions are not very sensitive to having \( \epsilon_{L0}^2 \not= 0 \). In general, however, we expect the terms for \( L > 2 \) to be less important than those for \( L = 2 \), and we can approximate

\[
V(\Omega) \approx \epsilon_{L00}^2 \phi_{L00}(\Omega) + \sum_{K>0} \epsilon_{L,K}^2 \left[ \phi_{L0K}(\Omega) + \phi_{L2K}(\Omega) \right] \tag{56}
\]

The \( \epsilon_{L00}^2 \) and \( \epsilon_{L,K}^2 \) (with the upper sign for \( K > 0 \), and the lower sign for \( K < 0 \)) are themselves second-rank irreducible tensor components, so that in the principal axis of molecular orientation system \((x', y', z')\) their Cartesian components \( \epsilon_{L00}^2 \) are diagonalized, with \( \epsilon_{L00}^2 = 0 \), and complete specification is given by just \( \epsilon_{L0}^2 \) and \( \epsilon_{L,K}^2 \). [Equation (56) can be thought of as the scalar product of second-rank irreducible tensors.] The ordering tensor is defined by

\[
\langle \phi_{LKM}^2 \rangle = \int d\Omega P_0(\Omega) \phi_{LKM}^2(\Omega) \tag{57}
\]

where \( L = 2 \) and \( M = 0 \). It is also a second-rank irreducible tensor whose symmetry properties are related to those of the \( \epsilon_{L00}^2 \). Thus from Eqs. (51) and (56) and the orthogonality of the \( \phi_{LKM}(\Omega) \) terms it follows that in the \((x', y', z')\) system only \( \langle \phi_{L00}^2 \rangle \) and \( \langle \phi_{L20}^2 \rangle \) are nonzero, i.e., \( \langle \phi_{LKM}^2 \rangle \) is also diagonalized. Thus the "diagonalized" potential (retaining only \( L = 2 \) terms) becomes

\[
V(\Omega) = \epsilon_{L00}^2 \phi_{L00}(\Omega) + \epsilon_{L,K}^2 \left[ \phi_{L0K}(\Omega) + \phi_{L20}(\Omega) \right] \tag{58}
\]

or equivalently

\[
V(\alpha, \beta) = \gamma_2 \cos^2 \beta + \epsilon \sin^2 \beta \cos 2\alpha \tag{58'}
\]

where \( \epsilon_2 = 2\gamma_2/3 \) and \( \epsilon_4^2 = 2\epsilon(6)^{-1/2} \). For molecules in which the molecular \( x' \) and \( y' \) axes are aligned to different extents, \( \epsilon \) is nonzero. If we choose the orientation coordinate system such that the \( z' \) axis tends to align to a
greater degree either parallel or perpendicular to the director than does the \( x' \) axis or the \( y' \) axis, we have \( |\gamma_2| > |\epsilon| \). The case \( \epsilon < 0 \) corresponds to the \( y' \) axis being ordered preferential to the \( x' \) axis along the direction of \( n \) and/or to the \( x' \) axis being ordered to a greater degree perpendicular to the \( n \) than is the \( y' \) axis.

We can utilize Eqs. (50), (48b) and (48c) to obtain \( \mathcal{F} \) from the potential in Eq. (58) in terms of its components in the \( (x', y', z') \) coordinate system:

\[
\mathcal{F}_x = \pm i \mathcal{F}_y = \pm 2e i \sin(2\beta)(ee^{\pm i\alpha} - \gamma_2 e^{\pm i\alpha})
\]

(59a)

\[
\mathcal{F}_y = 2e \sin^2 \beta \sin 2\alpha
\]

(59b)

We assume axially symmetric rotation about \( z' \) such that \( R_{x'x'} = R_{y'y'} = R_\perp \) and \( R_{z'z'} = R_\parallel \). Further, we introduce the definitions

\[
\lambda \equiv -\gamma_2/kT
\]

(60a)

and

\[
\rho \equiv -\epsilon/kT
\]

(60b)

Then the symmetrized Markov operator defined in Eq. (52) becomes (Polnaszek and Freed, 1975; Polnaszek, 1975a)

\[
\mathcal{F} = \mathcal{H} \cdot \mathbf{R} \cdot \mathcal{H} - \mathcal{F}(R_\perp, R_\parallel, \lambda, \rho, \Omega)
\]

(61a)

where

\[
f(R_\perp, R_\parallel, \lambda, \rho, \Omega) = \sum_{L=0,1,4} \sum_{0 < k_0 < L} \left[ X_{00}^L \mathcal{D}_{00}(\Omega) + \sum_{0 < k_0 < L} X_{k_00}^L \mathcal{D}_{k_00}(\Omega) \right]
\]

(61b)

with

\[
X_{00}^0 = -(2/15)[R_\perp(\lambda^2 + \rho^2) + 4R_\parallel \rho^2]
\]

(62a)

\[
X_{00}^2 = 2[R_\perp \lambda - [R_\perp(\lambda^2 + \rho^2) - 4R_\parallel \rho^2]/21]
\]

(62b)

\[
X_{00}^4 = 4R_\perp(\lambda^2 + \rho^2) - 4R_\parallel \rho^2/35
\]

(62c)

\[
X_{20}^2 = 6^{1/2}\rho[3(R_\perp + 2R_\parallel) + 3R_\perp \lambda]
\]

(62d)

\[
X_{20}^4 = 4(10)^{1/2}R_\perp \rho \lambda/35
\]

(62e)

\[
X_{40}^2 = (8/35)^{1/2}R_\parallel \rho^2
\]

(62f)

and \( \mathcal{H} \cdot \mathbf{R} \cdot \mathcal{H} \) is just the \( \mathcal{G}_0 \) of Eq. (33) with its associated eigenvalues.

We can also write the diffusion equation in terms of the general angular momentum operator \( \mathcal{N} \) referred to the director frame (Favro, 1965). This is appropriate when \( \mathbf{R} \) is diagonal in this frame, i.e., one has anisotropic viscosity. We then generate an analogous set of expressions (Polnaszek, 1975a; Polnaszek and Freed, 1975). It is now assumed that \( R_{xx} = R_{yy} = 1 \) and \( R_{zz} = \tilde{R}_\parallel \). The result is

\[
\mathcal{G}_0 = \mathcal{N} \cdot \mathbf{R} \cdot \mathcal{N} - \tilde{R}_\parallel \tilde{f}(\lambda, \rho, \Omega)
\]

(63)

where

\[
\tilde{f}(\lambda, \rho, \Omega) = \sum_{L=0,2,4} \left[ X_{00}^L \mathcal{D}_{00}(\Omega) + \sum_{0 < k_0 < L} X_{k_00}^L \mathcal{D}_{k_00}(\Omega) \right]
\]

(64)

with

\[
\tilde{X}_{00}^0 = -2(\lambda^2 + \rho^2)/15
\]

(65)

\[
\tilde{X}_{20}^2 = 2[\lambda - (\lambda^2 - \rho^2)/21]
\]

(66)

\[
\tilde{X}_{00}^4 = 4(\lambda^2 + \rho^2)/35
\]

(67)

\[
\tilde{X}_{20}^4 = 6^{1/2}\rho[1 + (2\lambda/7)]
\]

(68)

\[
\tilde{X}_{40}^4 = 4(10)^{1/2}\rho/35
\]

(69)

\[
\tilde{X}_{40}^4 = (8/35)^{1/2}\rho^2
\]

(70)

and

\[
\mathcal{N} \cdot \mathbf{R} \cdot \mathcal{N} \cdot \Phi_{KM}^0 = [\tilde{R}_\parallel L(L + 1) + (\tilde{R}_\parallel - \tilde{R}_\perp)M^2] \Phi_{KM}^0
\]

(71)

It is shown in Appendix A how the slow tumbling equations for isotropic liquids can be simply modified to deal with anisotropic liquids in the same case of a Meier–Saue potential and with \( \Psi = (0, 0, 0) \) and \( \Theta = (0, 0) \), except that permutation of the labeling of the molecular axis is permitted. The more complex expressions for the general cases are given Polnaszek (1975a).

Finally, note that when \( |\lambda| \gg 1 \), and the eigenfunction expansion \( \Phi_{KM}^0(\Omega) \) is only slowly convergent for solutions of the diffusion equations then there are other types of eigenfunction expansions, specifically tailored to these limiting cases, which become very useful (Polnaszek et al., 1975).

D. Exchange and Slow Tumbling

In cases where the concentration of nitrooxide spin probes is high, we have to consider the effects of Heisenberg spin exchange. This phenomenon involves bimolecular collisions of radicals during which time an exchange integral \( J' \) is turned on, and, because of the Pauli principle, can be written an added term in the spin Hamiltonian:

\[
\mathcal{H}_{SS} = J(t)S_1 \cdot S_2
\]

(72)
where \( J = 2J' \) and is time dependent due to the relative motion of the radical pairs. Its effect (viewed from an ESR point of view) is to cause the electron spins to exchange their nuclear environments.

A rigorous analysis of exchange (cf. Freed, 1967; Eastman et al., 1969) shows that we can add to the left side of Eq. (19) for the allowed transitions \( \lambda \), the terms:

\[
- \omega_{ss} \left( 1 - \frac{2D_2}{N'} \right) Z_4 + \omega_{ss} \sum_{\eta \neq \lambda} \frac{2D_2}{N'} Z_\eta
\]

(68)

where \( D_4 \) and \( D_\eta \) are the degeneracies of the \( \lambda \)th and \( \eta \)th allowed ESR transitions, respectively. That is, for nitroxides \( D_4 = D_\eta = 1 \) and \( N' = 6 \). The sum in Eq. (68) is over all allowed transitions \( \eta \) not equal to \( \lambda \). Also, the effective exchange frequency \( \omega_{ss} \) obeys

\[
\omega_{ss} = \tau^{-1}_1 \left[ J^2 \tau^{-1}_1 (1 + J^2 \tau^{-1}_1) \right]
\]

(69)

where \( \tau_1 \) is the mean time between successive new bimolecular encounters of radicals, and \( \tau_1 \) is the lifetime of the interacting pair. In the case of simple Brownian diffusion of uncharged radicals in solution we can write (Eastman et al., 1969; Pedersen and Freed, 1973a, b):

\[
\tau^{-1}_1 = 4\pi d DN
\]

(70)

\[
\tau^{-1}_1 = D/d\Delta r_j
\]

(71)

where \( N \) is the density of radicals, \( d \) is the “interaction distance” for \( J(r) \) which is nonzero (and equal to \( J \)) only in the range of \( d < r < d + \Delta r_j \), and the diffusion coefficient in a Stokes–Einstein model is

\[
D = kT/6\pi a n \eta
\]

(72)

Expression (68) is only appropriate for the allowed transitions, which then couple together by this mechanism. For each forbidden ESR transition (see below), we have instead of (68) to add the term to the left side of Eq. (19)

\[
- \omega_{ss} Z_\varepsilon
\]

(73)

If we make the simplifying assumption that \( \omega_{ss} \) is independent of any orientational effects [i.e., \( J(r) \) is taken as a function only of the relative internuclear separation of the radical pair], then (68) and (73) can be added to the LHS of Eq. (27), where we let \( Z_\varepsilon (\Omega) \rightarrow \{ C_m \}_{\varepsilon} \), etc.

Expressions (69) and (70) are based on a simple contact-exchange model (Eastman et al., 1969). More complex models of the motional modulation of \( J(r_1, r_2) \) can also be dealt with (Pedersen and Freed, 1973a,b). Effects of radical charge and/or electrolyte concentration on Eqs. (70) and (71) must also be considered (Eastman et al., 1970). Expressions (68) and (73) are also useful for two-dimensional motions, but Eqs. (69)–(72) would have to be modified. Also, in general, effects of intermolecular electron-spin dipole–dipole interactions become important at higher concentrations as the motions slow down (Eastman et al., 1969).

E. Nitroxides

For nitroxides, there are three allowed ESR transitions and six forbidden transitions which must be considered in a rigorous solution of Eq. (27). These are illustrated in Fig. 1a. The asymmetric \( g \) tensor \( g \) and the hyperfine tensor \( A \) yield an \( \mathcal{H}_1 (\Omega) \) given by

\[
\mathcal{H}_1 (\Omega) = \mathcal{D}_0 \left[ F_0 + D^{(+)} \right] \hat{S}_z + \left[ \mathcal{D}_2 \left( 0(\Omega) + \mathcal{D}_2 \left( 0(\Omega) \right) - \mathcal{D}_0 \left( 0(\Omega) \right) \right) \right] D \hat{S}_y
\]

(7)

where

\[
F_0 = \sqrt{3} g(0) h^{-1} B_0 H_0
\]

(75)

\[
\mathcal{D}_0 = 6^{-1/2} [2g_x - (g_x + g_y)]
\]

(76)

\[
\mathcal{D}_2 = 4[g_y - g_x]
\]

(77)

\[
D = (1/2) \gamma_e [2(\hat{S}_x - \hat{A}_x - 2\hat{A}_y)]
\]

(78)

\[
D^{(2)} = \frac{1}{4} \gamma_x \left( \hat{A}_x - \hat{A}_y \right)
\]

(79)

with \( D' = -(8/3)^{1/2} D \) and \( D^{(2)} = -(8/3)^{1/2} D^{(2)} \). The forbidden transitions 4–9 of Fig. 1a are coupled into the expressions for the allowed transitions because of the pseudoequatorial terms in Eq. (74), i.e., the terms involving \( \hat{I}_z \), where \( \hat{I}_z \) are the nuclear spin raising and lowering operators. The Euler angles \( \Omega = a, \beta, \gamma \) define the rotation between the laboratory coordinate system \( (x, y, z) \) and the principal axis system in the molecular frame in which the \( g \) and hyperfine tensors are diagonal. We assume they are diagonal in the same axis system [which is rigorously the \( x''', y''', z''' \) system, b)}
Eqs. (75a)-(75c) and (76a) and (76b) are written as though they correspond to the \( x', y', z' \) system.

It can be shown that the nuclear Zeeman term (which appears in the resonance frequencies of the forbidden transitions) makes a negligible contribution, so one can neglect it. Then it is only necessary to consider forbidden transitions 4 and 5, 6 and 7, and 8 and 9 in pairs, and this simplifies the expressions (see Appendix A).

We can now evaluate Eq. (27) (for \( n = 1 \)) and the resulting expressions, neglecting saturation [i.e., set \( d_\perp = 0 \) on the LHS of Eq. (27)], are given in Appendix A. They define an infinite set of coupled algebraic equations coupling the allowed and forbidden transitions. Only even values of the "quantum number" \( L \) appear for the allowed transitions for which \( M = 0 \). Also, one has the general restriction

\[
0 \leq K \leq L \quad \text{with } K \text{ even} \tag{77}
\]

while \( M = 1 \) for the coefficients \( C_{KM} \) representing the "single forbidden" transition pairs (4, 5) and (6, 7) and \( M = 2 \) for the "doubly forbidden" pair (8, 9).

Approximations to the complete solution can be obtained by terminating the coupled equations at some finite limit by letting \( C_{KM}^{(l)} = 0 \) for all \( L > n_L \). While the number of equations needed to obtain a satisfactory convergent solution depends on the value of \( \tau_\parallel \) (the larger the \( \tau_\parallel \), the greater is the value of \( n_L \) needed) the convergence also depends on the rotational reorientation model. The model that yields eigenvalues with the greatest dependence on \( L \) value in Eqs. (34)-(40) will have the fastest convergence. Therefore, in general, the convergence becomes poorer as one progresses from Brownian to simple free and intermediate jump, to strong collisional jump diffusion. For Brownian rotational diffusion with \( \tau_\parallel \sim 2 \times 10^{-8} \text{ sec} \), \( n_L = 6 \) is sufficient; with \( \tau_\parallel \sim 2 \times 10^{-7} \text{ sec} \), \( n_L = 12 \) is sufficient; and with \( \tau_\parallel \sim 2 \times 10^{-6} \text{ sec} \), \( n_L = 24 \) is sufficient. However, for simple free diffusion and \( \tau_\parallel \sim 2 \times 10^{-8} \text{ sec} \), \( n_L = 10 \) is needed and for a strong jump model \( n_L = 16 \) is needed. It is also often useful to terminate \( K \) at some value considerably less than \( n_L \) (i.e., for \( n_K < n_L \)). This would be especially applicable for isotropic or for axially symmetric reorientation about an axis parallel to the \( 2p_\pi \) orbital of nitrogen, because in such a principal axis system, the \( A \) tensor is almost axially symmetric. Typical values for the nitroxide radical in this coordinate frame (cf. Table I) are \( |F_0| \simeq 4.8 \text{ G} \) and \( |D| \simeq 10.4 \text{ G} \), while the asymmetric values are \( |F_2| \simeq 1.6 \text{ G} \) and \( |D^{(2)}| \simeq 0.4 \text{ G} \). These smaller terms are the coefficients for coupling the variable \( C_{KM}^{(l)} \) with \( K \neq 0 \) into the problem, so their smallness guarantees faster convergence (cf. Appendix A). Also, if \( R_\parallel \gg R_\perp \) or \( R_\perp \), then this will greatly improve the convergence in \( K \) relative to that in \( L \).

3. Theory of Slow Tumbling ESR Spectra for Nitroxides

The computer program in Appendix B has provision for separate terminating values for \( K \) and \( L \). The number of coupled equations is then found to be

\[
r = 3 + \frac{3}{2}(n_L - \frac{1}{2}n_K + 1)n_K + \frac{3}{2}n_L, \quad n_L \geq n_K, \quad n_K \geq 2 \tag{78}
\]

or

\[
r = 9 + 3(n_L - 2) \quad \text{if } n_K = 0 \quad \text{and } n_L \geq 2 \tag{78}
\]

A further reduction in the number of equations can be made by distinguishing between the allowed and forbidden transition coefficients. That is, the coefficients for the allowed transitions \( C_k^{(l)} \) are terminated at \( L = r \) then the coefficients for the singly forbidden transitions \( C_k^{(l)}(j, k) \) are terminated at \( L = n' \) and the doubly forbidden \( C_k^{(l)}(8, 9) \) at \( L = n'' \), where \( n', n'' \leq n_L \). We have found that for convergence usually \( n' \approx n_L \) or \( n_L \) but \( n'' \) may be truncated at values significantly below \( n_L \) (e.g., when \( n_L = n' = 16 \) was needed, \( n'' = 8 \) was sufficient). Also the terms of odd which exist only for the forbidden transitions, may be truncated at value of \( L \approx n_L \). The computer program in Appendix B also provides for the truncations.

III. Applications

A. Isotropic Liquids: Experiments

The validity of the slow tumbling theory has now been carefully confirmed in studies on model systems of PADS (peroxynitrate disulfonate and PD-TEMPONE (perdeuterated 2,2,6,6-tetramethyl-4-piperidone oxyl) (cf. Fig. 1b) in viscous media (Goldman et al., 1972a; Goldman, 19; Hwang et al., 1975).

One of the most important requirements in analyzing a slow tumbling spectrum is to have accurate values for the magnetic tensors \( A \) and \( g \). The best are obtained from viscous solutions in the same solvent as is the slow tumbling spectrum. This is because, in general, nitroxides will exhibit magnetic parameters which are rather solvent dependent. Figure 2 shows o

---

Fig. 1b. (I) Peroxynitrate disulfonate anion (PADS). (II) Perdeuterated 2,2,6,6-tetramethyl-4-piperidone-1-oxyl (PD-TEMPONE).
such rigid-limit spectrum from PD-TEMPO in toluene-$d_6$ (Hwang et al., 1975). This is a convenient case, where the solution can be cooled sufficiently without any changes in phase until a rigid-limit spectrum is achieved. This is a particularly well-resolved spectrum because the effects of magnetic interactions of intra- and intermolecular protons in the ESR have been replaced with much weaker deuteron interactions. Note that while $A_z$ and $g_z$ can be read from the spectrum, accurate determination of the other principal values of the hyperfine tensor requires careful computer simulation. The rigid-limit computer simulations were performed according to standard methods; a program listing for nitroxides appears in Polanszcz’s thesis (1975a). Note that a Lorentzian line shape gives an overall better fit in this case. (Other cases show line shapes ranging from near Lorentzian to intermediate between Lorentzian and Gaussian.)

Table I gives accurate sets of magnetic parameters determined for PD-TEMPO and PADS in a variety of solvents, as well as other nitroxide magnetic parameters.† In Table I the x axis is taken as being along the N-O bond, the z axis along the 2p π orbital of the nitrogen, and the y

† Editor’s note: See also Appendix II (page 564) and Chapter 6, Table II (p. 247) for additional g and A data.
### 3. Theory of Slow Tumbling ESR Spectra for Nitroxides

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<th>TABLE 1 (cont.)</th>
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axis perpendicular to the other two. [These axes should more rigorously be written as \(x', y', z'\), cf. Eq. (46), but the primes have been dropped for convenience, since there should be no confusion with the laboratory axes.] The \(x', y', z'\) axes are the principal axes of the diffusion tensor \(\mathbf{R}\) and they are assumed in Table I to be either the same as the \(x, y, z\) axes or else to be a cyclic permutation of them. It should be clear from this tabulation that (1) nitroxides do exhibit significant solvent dependences in their magnetic parameters and (2) the different nitroxides will exhibit some difference in their magnetic parameters. One interesting observation in this context is the result for PD-TEMPONE (cf. Fig. 1b) in ethanol-\(d_6\). It exhibits two distinct values of \(A_z\), the larger one characteristic of the values in hydrogen-bonding solvents, while the smaller one is characteristic of the values in non-hydrogen-bonding solvents. In general, one must expect some variation in the magnetic parameters from site to site in a given solvent, and this will be an important source of the [orientation-dependent, cf. Eq. (29)] rigid-limit intrinsic width. These matters are discussed elsewhere (Hwang et al., 1975).

Another source of valuable information for the analysis of the slow tumbling spectrum is the relaxation results from the fast motional spectrum in less viscous media, if it is at all available.

Figure 3 shows the results for PADS (cf. Fig. 1b) in \(D_2O\) (Goldman et al., 1972a) where the derivative width \(\delta(\bar{M})\) is plotted as

\[
\delta(\bar{M}) = A + B\bar{M} + C\bar{M}^2
\]  

(79)

The analysis of motional narrowing spectra is discussed by Nordio in Chapter 2. Suffice it to say here, that the motional narrowing theory, coupled with experimental values of \(B\) and \(C\) and accurate values of the magnetic parameters, is sufficient to determine \(R_{||}\) and \(R_\perp\) at each temperature. It is important to note that in Fig. 3 the curves for \(B\) and \(C\) are very nearly parallel. This fact and the temperature insensitivity of \(a_n\) and \(g_s\) provide strong evidence against competing relaxation mechanisms affecting the interpretation. Figures 4a and 4b are plots of \(C\) versus \(B\) for PADS in glycerol-H\(_2\)O and for PD-TEMPONE in toluene-\(d_6\), respectively. These results can be analyzed to yield

\[
\tau_\xi \equiv (6R)^{-1}
\]

(80)

\[
R \equiv (R_\perp R_z)^{1/2}
\]

(80')

and

\[
N \equiv R_z/R_\perp
\]

(81)

It is found that the PADS system exhibits anisotropic rotational diffusi \((N = 4.7\) in aqueous glycerol solvents) where the \(z\) axis for the rotation diffusion tensor is parallel to the line through the two sulfur atoms, while t PD-TEMPONE system rotates isotropically (within experimental error).

An interesting sidelight to this result is that, if we were to interpret t PD-TEMPONE motional narrowing results in glycerol solvent in terms the magnetic parameters from toluene solvent, we would obtain \(N \approx 3\) with fastest rotation about the molecular \(y\) axis, but when we use the corre magnetic parameters for glycerol, we again obtain \(N = 1\).

The value of these motional narrowing results for the slow tumbling studies is that one can extrapolate the information obtained on \(\tau_\xi\) and into the slow motional region. That is, \(\log \tau_\xi\) is found to have a nearly linear

dependence on \(1/T\), as expected for an activation process. More precise for PD-TEMPONE in toluene, it is linear in \(\eta/T\), as shown in Fig. 5. This expected from Eq. (31) for Stokes–Einstein-type behavior. Also, \(N\) is four to be temperature independent. Figure 6 shows one such comparison of experimental spectrum with computer simulated results utilizing the value of \(\tau_\xi\) and \(N\) extrapolated from the motional narrowing region. This is the case of PADS in \(D_2O\), where \(N = 3\), and is one of incipient slow tumbling
3. THEORY OF SLOW TUMBLING ESR SPECTRA FOR NITROXIDES

Fig. 5. $\tau_R$ versus $1/T$ for PD-TEMPONE in toluene-$d_4$. Motional narrowing results designated by $\Delta$ ($\tau_R$ from $B$ values) and $\bigcirc$ ($\tau_R$ from $C$ values). They are extrapolated to the slow tumbling region ($\cdots$) and are compared to best fits for the different models: (1) free diffusion, (2) Brownian diffusion, (3) strong jump diffusion. ($\cdots$) $N = 1$, $\varepsilon = 5.4$. ($\cdots$) $N = 1$, $\varepsilon = 5.4$. [Reprinted with permission from Hwang et al., J. Phys. Chem. 79, 489-511 (1975). Copyright by the American Chemical Society.]

($\tau_R = 4 \times 10^{-9}$ sec). A comparison is given for different values of $N$, and clearly shows that the best fit is for $N = 3$. These simulations were performed for a Brownian diffusion model, with the model parameter $B_t = \text{When slower motional spectra were obtained (}$\tau_R \gtrsim 10^{-5}$ sec), it was found that a Brownian motion model was not yielding good simulations for small spin probes PADS and PD-TEMPONE. Therefore other models were tried, i.e., the strong jump diffusion of Eq. (39) with $R_t = 1$ and the f diffusion of Eq. (35) also with $R_t = 1$. A typical comparison for the two models is shown in Fig. 7, from which it is clear that the best result is obtained with the free diffusion model. In this context, it is important to recognize that the values of $B_t$ for this free diffusion model are not unique. For $\tau_R \lesssim 10^{-5}$ sec the simulated spectrum is determined mainly by the coefficients of $L = 2, 4, 6, 8$. Over this range of values of $L$, it is possible to reproduce the values of $B_t$ of the free diffusion case reasonably well by jump diffusion models given by Eq. (36) (and the special case of Eq. (36) with $R_t \approx 0.13$ corresponding to an rms jump angle of 50°). In fact, co
computer simulations of such jump models do yield virtually identical results. Figure 8 shows the results for PADS in D$_2$O in the model-sensitive region of $\tau_N$ for free diffusion and a range of values of $N$. This is also a case where free diffusion fits best.

Another way of testing the model dependence of the results is to extrapolate the $\tau_N$ values obtained in the motional narrowing region and to compare them with the “best” $\tau_N$ values obtained for each model. (This is associated with the $S$ parameter discussed in Section III.B.) It is seen in Fig. 5 that the free diffusion model gives good agreement, but the others do not, especially for the slower values of $\tau_N > 10^{-8}$ sec.

The parameters $\tau_N$ and $N$ are not the only ones that can be extrapolated from the motional narrowing region. Another is the parameter $A'$ in G (c Fig. 7), which is that part of $\tilde{A}$ in Eq. (79) that is not attributable to $g$-tensor sources. (It is given as $T_{2g}^{-1} = \frac{1}{2\gamma_e A'}$ in sec$^{-1}$ in the computer programs.) The best $A'$ for free diffusion again falls closest to the values extrapolated from the motional narrowing region, although the distinction here is not so clear (cf. Mason et al., 1974).

An important point to emphasize at this stage is that the mode dependent studies summarized above were greatly aided by the very well resolved spectra obtained from PADS and PD-TEMPONE in deuterate solvents. In general, the added intrinsic widths of typical spin labels due to the unresolved proton superhyperfine splitting will tend to obscure many of the spectral details in the slow motional and rigid-limit spectra. The analysis of the motional narrowing spectra would be particularly seriously affected...
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B. Simplified Methods of Estimating $\tau_R$

An important characteristic of a typical nitroxide slow motional spectrum is that it has two well-separated outer hyperfine extrema with an overlapped central region. It has been found that a useful parameter for describing these spectra is $S = A'_z/A_z$, where $A_z$ has already been defined in Fig. 2 as one-half the separation of the outer hyperfine extrema, and $A'_z$ is the slow tumbling value for the same spectral feature (Goldman et al., 1972b). McCalley et al. (1972) have discussed the separate deviations of high-field and low-field positions from their rigid-limit values. Figure 9 compares the

![Graphical representation with labels]

Fig. 9. Superposition of computed rigid-limit nitroxide spectrum with a computed slow tumbling spectrum at $\tau_R = 5.0 \times 10^{-8}$ sec, demonstrating the measurements required for the parameters $S = A'_z/A_z$, $W_z = \Delta'_z/\Delta_z$, and $W_r = \Delta_r/\Delta_z$. In an actual experiment, it is often necessary to estimate the $\Delta'_r$ in place of the $\Delta'_z$ as described in the text. The magnetic parameter utilized are $\delta = 3.0$ G, $g_x = g_y = 2.0075$, $g_z = 2.0027$, $A_z = A'_z = 6.0$ G, $A_r = 32.0$ G, and $B_0 = 3.300$ G. [Reprinted with permission from Mason and Freed, J. Phys. Chem. 78, 1321–132 (1974). Copyright by the American Chemical Society.]

It is interesting to note, however, that the ESR spectra obtained by McCalley et al. (1972b) from spin-labeled oxyhemoglobin in H$_2$O at $\tau_R \approx 2.6 \times 10^{-8}$ sec show many of the features that are characteristic of Brownian diffusion (cf. Fig. 7). This is an important confirmation of the theory, because one would expect that a macromolecule (unlike the small spin probes) would obey simple Brownian motion.

† Editor's note: Appendix 1 (p. 362) contains simulated spectra calculated by this model for a broad range of $\tau_R$ values.

quantities $A_z$ and $A'_z$. Note that $A'_z$ decreases monotonically from its rigid limit value of $A_z$ as the motion becomes more rapid. Thus $S$ is a sensitive monotonically increasing function of $\tau_R$. Furthermore, simulations performed for axial and asymmetric $A$ and $g$ tensors show that for a given value of $A_z$, the value of $S$ is insensitive to changes in $A_x$, $A_y$, and the $g$-tensor components. Changes in the magnitude of $A_z$, however, do affect the value of $S$. This is expected, of course, since, as can be seen from Fig. 2, $A_z$, $A_x$, and $g$ only contribute to the central regions of the rigid limit spectrum. The
dependence can be approximately expressed in the functional form
\( S = S(\tau_R A_i) \), where \( S \) is simply dependent on the product \( \tau_R A_i \). This functional dependence permits the scaling of results for one value of \( A_i \) to the range of values of \( A_i \) typical for nitroxides (27-40 G) with an error of less than 3%. Thus, if we know how \( S \) is affected by changes in the linewidth and rotational diffusion model, then it is possible to estimate \( \tau_R \) without the necessity of making detailed line-shape calculations and comparisons. This is particularly useful for nitroxides that are broadened by inhomogeneous intramolecular or intermolecular (solvent) hyperfine and dipolar interactions. As already noted, this line broadening decreases the spectral resolution and obscures other \( \tau_R \)-dependent line-shape changes.

The variation of \( S \) with \( \tau_R \) is shown in Fig. 10 for Brownian, free, and strong jump diffusion models and isotropic diffusion, with \( A_i = 32 \) G and peak-to-peak derivative Lorentzian linewidths \( \delta = (2/\sqrt{3})|\tau_R|^{-1} T_{2\text{sp}}^{-1} \) of 0.3 and 3.0 G. It can be seen that \( S \) is model sensitive, and for an equivalent value of \( \tau_R \), \( S \) increases from a Brownian to a free to a jump reorientational model. (This is consistent with the analysis we have already given for the best \( \tau_R \) fit as a function of model; cf. Fig. 7.) These curves can be fit to the expression

\[
\tau_R = a(1 - S)^b
\]

(82)
to within 2, 3, or 5% in the value of \( \tau_R \) for a given \( S \) for jump, Brownian, or free diffusion, respectively, with the values of \( a \) and \( b \) given in Table II.

---

**TABLE II**

<table>
<thead>
<tr>
<th>Diffusion model</th>
<th>Linewidth(^c) (G)</th>
<th>( a )</th>
<th>( b )</th>
<th>( \tau_R(S = 0.99)) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brownian diffusion</td>
<td>0.3</td>
<td>2.57 ( \times 10^{-10} )</td>
<td>-1.78</td>
<td>9 ( \times 10^{-7} )</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>5.4 ( \times 10^{-10} )</td>
<td>-1.36</td>
<td>3 ( \times 10^{-7} )</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>8.52 ( \times 10^{-10} )</td>
<td>-1.16</td>
<td>2 ( \times 10^{-7} )</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>1.09 ( \times 10^{-9} )</td>
<td>-1.05</td>
<td>2 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>Free diffusion</td>
<td>0.3</td>
<td>6.99 ( \times 10^{-10} )</td>
<td>-1.20</td>
<td>3 ( \times 10^{-7} )</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.10 ( \times 10^{-9} )</td>
<td>-1.01</td>
<td>1 ( \times 10^{-7} )</td>
</tr>
<tr>
<td>Strong diffusion</td>
<td>0.3</td>
<td>2.46 ( \times 10^{-9} )</td>
<td>-0.589</td>
<td>4 ( \times 10^{-8} )</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>2.55 ( \times 10^{-9} )</td>
<td>-0.615</td>
<td>5 ( \times 10^{-8} )</td>
</tr>
</tbody>
</table>

* These values are calculated for an axial nitroxide with \( A_i = 32 \) G, \( A_z = 6 \) G, \( \theta_z - \theta_i = 0.0041 \), and isotropic reorientation. (From Goldman et al., 1972b.)

* These models are discussed in detail in the text.

* Peak-to-peak derivative Lorentzian width: \( \delta \).

* For this \( \tau_R \) value, \( 1 - S = 0.01 \).

---

(Goldman et al., 1972b; Goldman, 1973). The parameters for Brownian diffusion with linewidths of 5 and 8 G are also given. It should be noted that for \( \tau_R < 7 \times 10^{-9} \) sec, \( S \) is undefined since the outer lines begin to converge to the motionally narrowed spectrum. For longer \( \tau_R \)'s than shown in Fig. 10, the spectrum approaches the rigid limit, and the value of \( 1 - S \) becomes comparable to experimental uncertainties. The value of \( \tau_R \) for which \( 1 - S = 0.01 \) is given in Table II. The least squares fit to Eq. (82) was calculated for \( 7 \times 10^{-9} \) sec \( \leq \tau_R \leq \tau_R(S = 0.99) \).

The effect of linewidth on the value of \( S \) is also shown in Fig. 10. For Brownian and free diffusion models, \( S \) increases with increasing linewidth while for jump diffusion a decrease in \( S \) is observed. The uncertainty in estimating \( \tau_R \) due to an uncertainty in intrinsic linewidth, for a given value of \( S \), increases for longer \( \tau_R \). Thus for a Brownian diffusion model and a 1.5 C uncertainty in the intrinsic width, the uncertainty in calculating \( \tau_R \) for a given value of \( S \) increases from about 5% for \( \tau_R \approx 1 \times 10^{-8} \) sec to about 50% for \( \tau_R \approx 1 \times 10^{-7} \) sec to an order of magnitude for \( \tau_R \geq 1 \times 10^{-6} \) sec. Linear interpolations along the vertical line between the curves A and B of
which very simple equations exist (Johnson, 1965), we find that the separation of the lines decreases by the factor \(1 - 2(\tau_S)^{-1} \approx 1 - \tau_S^{-1}\) when the line shifts are small, where \(\tau_S/2\) and \(2\zeta\) are the lifetime in one state and separation between peaks, respectively. If we now draw the analogy between the rotational motion (carrying the nitroxide radical between different orientations corresponding to substantially different ESR frequencies) at a rate the order of \(\tau_S^{-1}\) and the \(r^{-1}\) of the two jump model, and we use the furti analogy between \(A_z\) and \(S\), then we predict the form of Eq. (82) w a \(= 1.78 \times 10^{-9}\) sec for \(A_z = 32\) G and \(b \approx -\frac{1}{3}\). We see from Table that these results are of the correct order for strong jump diffusion, where the analogy is probably the best, but are substantially different than the Brownian diffusion results.

However, the analogy between \(\tau_S^{-1}\) and \(r^{-1}\) suggests that we examine incipient line broadening of the outer hyperfine extrema, which should roughly correspond to \(\tau_S^{-1}\) and (2) be a more sensitive function of motion than the shifts in position. Indeed, accurate computer simulations have confirmed these suggestions as being theoretically correct (Mason and Freed, 1974). In fact, the residual width is found to be given by \(\tau_S^{-1}\) to a factor of \(\sim 2\) (or \(\frac{1}{3}\)) over most of the range of interest. This is about as good an agreement as we might hope for, when we recognize that the analogy incomplete, because in the slow tumbling case, the rotational motion modulates the ESR frequency over a continuous range, (and not between discrete values) and (b) induces nuclear spin flips as well because the quantization axis of the nuclear spins is orientation dependent; this is known to nonadiabatic effect (Freed, 1972a). However, a recent approximate treatment, for small pseudosecular terms in Eq. (74), has shown that this latter effect is roughly proportional to \(\tau_S^{-1}\) (Freed, 1974).

We give now a more quantitative discussion of this width effect (Mason and Freed, 1974). The average of the measured half-widths at half-heights for the two outer extrema of a rigid-limit spectrum is found from simulation to be equal, to a very good approximation, to \(\frac{1}{2} \sqrt{3} \delta = |y_e|^{-1} T_{2,2}^{-1}\). Heights of the hyperfine extrema are measured from the true baseline Fig. 9). More precisely, we have

\[
2\Delta_l = 1.59\delta
\]

\[
2\Delta_h = 1.81\delta
\]

where the subscripts \(l\) and \(h\) refer to the low- and high-field lines, respectively, and the superscript \(r\) refers to the rigid-limit value. This result is for to be independent of \(\delta\) over the range \(1.0 \leq \delta \leq 4.0\) G and virtu.
independent of $A_x$ over the range $27 \leq A_x \leq 40$ G. It is, of course, essentially independent of variations in the other nitroxide rigid-limit parameters. Equations (83a) and (83b) are valid for the assumption of Lorentzian inhomogeneous broadening. (No calculations for non-Lorentzian broadening have yet been performed for the method discussed.)

In the slow motional region, near the rigid limit, the linewidth $\Delta$ for Lorentzian line shapes can be decomposed into two contributions (cf. Abraham, 1961): (1) the Lorentzian inhomogeneous component given by Eqs. (83a) and (83b) and (2) the excess motional width (of order of magnitude $\tau^{-1}$). (It is convenient to think in terms of this decomposition even though it is not necessary for the method.) A useful dimensionless parameter for describing these spectra is then

$$W_i = \frac{\Delta_i}{\Delta_i}, \quad W_i - 1 = \frac{(\Delta_i - \Delta_i)}{\Delta_i}$$  \hspace{1cm} (84)

where $i = l, h$. In general, $W_i - 1$ is about an order of magnitude larger than $1 - S$ for a particular value of $\tau_R$ (cf. Fig. 11), and furthermore, it can be measured to at least comparable accuracy ($\sim 1\%$; cf. Fig. 9). The results in Fig. 11 were calculated utilizing the computer program in Appendix B. A study of how $W_i$ is affected by changes in (1) the spin parameters, (2) linewidth, and (3) rotational diffusion model has been made. It was found that $W_i$, like $S$, is insensitive to deviations from axial $A$ and $g$ tensors, as well as to variations in $A_x$ and $g$ typical of a nitroxide. However, in contrast to $S$, which is dependent on the product $\tau_R A_x$, $W_i$ is virtually independent of $A_x$ over the range $27 \leq A_x \leq 40$ G; (we have used $A_x = 32$ G in obtaining the results in Fig. 11), as expected from our simple analogy. However, $W_i$ is found to depend on $\delta$. Generally, a smaller $\delta$ implies a larger $\Delta_i - \Delta_i$ for a given $\tau_R$. In particular, $\delta = 1$ G yields values of $\Delta_i - \Delta_i$ ranging from 1.3 to 2.5 times greater than those for $\delta = 3$ G. We can try to explain this observation qualitatively. The rigid-limit extrema of finite width $\Delta_i$ arise from those nitroxide radicals whose $2p_\pi N$-atom orbitals lie within a cone of angle $\Omega$ about the applied field direction, and the size of the cone increases rapidly with an increase in the rigid-limit $\delta$ (McConnell and McFarland, 1970). If we roughly identify the excess width $\Delta_i - \Delta_i$ with the rate at which radicals reorient out of the cone, then extrema from the larger cones (which result from greater values of $\delta$) will be less broadened, since it takes longer for the radicals to leave the cone. The observation that $\Delta_i - \Delta_i$ is always significantly larger than $\Delta_i - \Delta_i$ at a given $\tau_R$ could be explained in a similar manner. It is known that the high-field resonance for a single-crystal spectrum changes with angle more rapidly than the low-field resonance; thus the range of $\Omega$ contained in the observed cone (from a polycrystalline sample) must be smaller for the high-field line. Reorientations out of the high-field cone thus occur at a more rapid rate, and, in general, $W_i$ is a more sensitive function of $\tau_R$ than is $W_i$, as can be seen from Fig. 11.

![Fig. 11. Graph of $W_i - 1$ (curves A-H); and $1 - S$ (curves a-d) vs. $\tau_R$ for nitroxide isotropic rotational reorientation. Curves a and b are for free diffusion and $\delta = 3.0$ and 1.0 G respectively; curves c and d are for Brownian diffusion and $\delta = 3.0$ and 1.0 G, respectively. Curves A and B are for free diffusion, $\delta = 3.0$ G, and the low- and high-field extrema, respectively, and curves C and D are the same as A and B, respectively, except $\delta = 1.0$ G. Curves E, F, G, and H correspond respectively to curves A, B, C, and D except that they are for Brownian diffusion. See also Table III. (Reprinted with permission from Mason and Freed, J. Phys. Chem. 78, 1321-1323 (1974). Copyright by the American Chemical Society.)](image_url)

The choice of a proper $\delta$ is clearly at the heart of the method. Near the rigid limit, an appropriate estimate of $\delta$ can be deduced from the $\Delta_i$. The narrowest rigid-limit $\delta$ found in our laboratory is 1.5 G, which corresponds to $2\Delta_i = 2.4$ G. Hubbell and McConnell (1971) reported values of 4.6 an 5.5 G for $2\Delta_i$ for pseudooxial "rigid-limit" spectra, corresponding to $\delta$ of 2 and 3.5 G, respectively. The rigid limit spectrum of the N-oxyl-4',4'-dimethylazolidine derivative of 5a-androstan-3-one appears to have $2\Delta_i \approx 5.0$ G, which corresponds to a $\delta$ of 3.1 G (McConnell and McFarland, 1970). The motional broadening can easily double the widths of the outer extrema when the separation of the hyperfine extrema is not much different from the rigid-limit value (i.e., $S > 0.95$). Thus, very near the rigid limit, where $\delta$ can be determined from the rigid-limit extrema widths, two independent determinations of $\tau_R$ can be made using Fig. 11.
As has been noted, the major contributions to the $\Delta_i^\ast$ are electron nuclear hyperfine interactions between the electron and the protons of the spin label and host, while heterogeneity of the environment also contributes to $\Delta_i^\ast$. These interactions will be quickly averaged with the onset of molecular motion, resulting in a decrease in the appropriate $\delta$. When this is the case, it becomes necessary to estimate a single $\delta$ such that the rotational correlation times obtained from Fig. 11 for both the low- and high-field extrema are equal within experimental error. For this process we can define “effective inhomogeneous widths” $\Delta_i^{\ast\ast}$, which obey Eqs. (83a) and (83b) and which generally obey the relation $\Delta_i^{\ast\ast} \leq \Delta_i^\ast$. Then we should rewrite Eq. (84) as

$$W_i = \Delta_i^\ast / \Delta_i^{\ast\ast}$$  \hspace{1cm} (84')

with the $W_i$ given by Fig. 11. This procedure should then yield both $\tau_R$ and $\delta$.

As noted, the uncertainty in $\delta$ can result in serious errors when $\tau_R$'s of $> 3 \times 10^{-8}$ sec are determined from $S$. Once $\delta$ has been determined from the $W_i$, another estimate of $\tau_R$ may (when feasible) be obtained from a measurement of $S$. In other words, $\tau_R$ and $\delta$ could be obtained as a function of three experimental parameters, $S$ and the $W_i$.

The model-dependent results shown in Fig. 11 were obtained for Brownian diffusion and free diffusion, as before. The free diffusion model results in a more nearly linear dependence (in a log–log plot) of $W_i - 1$ versus $\tau_R$ in Fig. 11 than the Brownian motion model. The plots in Fig. 11 have been fitted to the form

$$\tau_R = a' (W_i - 1)^{-b'}$$  \hspace{1cm} (85)

for the region $W_i - 1 > 0.01$, and the coefficients are given in Table III. The maximum variation between the curves and the results predicted from Eq. (85) is also given. It is clear that the use of Eq. (85) is a less accurate means of estimating $\tau_R$ than the curves. However, the fact that $b' \approx 1$ (except for the anomalous curve F, which is presumably affected by overlap) is consistent with the interpretation of $\Delta_i^\ast - \Delta_i^{\ast\ast}$ as a lifetime broadening.

When there is axially symmetric rotational diffusion about the molecular $z$ axis with $R_{||} > R_{\perp}$, it should mean that $\tau_R$ is again obtained. Also, the introduction of an angle-dependent rigid-limit width given by Eq. (29) should have no effect on the outer hyperfine extrema, except that now

$$\delta = (2/\sqrt{3}) |\gamma_e|^{-1} (T_{2,1}^{-1} + T_{2,1}^{-1}) = (2/\sqrt{3}) |\gamma_e|^{-1} (\alpha + \beta)$$  \hspace{1cm} (86)

It is very important in the experimental application of this method to avoid distortion of the true linewidth by overmodulation of the magnetic field and/or power saturation. Experimental applications of this method have not yet been reported.

### Table III

<table>
<thead>
<tr>
<th>Curve</th>
<th>$a' \times 10^4$ sec</th>
<th>$b'$</th>
<th>Maximum deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.29</td>
<td>1.033</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>1.96</td>
<td>1.062</td>
<td>6</td>
</tr>
<tr>
<td>C</td>
<td>5.32</td>
<td>1.076</td>
<td>18</td>
</tr>
<tr>
<td>D</td>
<td>7.97</td>
<td>1.125</td>
<td>18</td>
</tr>
<tr>
<td>E</td>
<td>1.15</td>
<td>0.943</td>
<td>5</td>
</tr>
<tr>
<td>F</td>
<td>2.12</td>
<td>0.778</td>
<td>18</td>
</tr>
<tr>
<td>G</td>
<td>5.45</td>
<td>0.999</td>
<td>30</td>
</tr>
<tr>
<td>H</td>
<td>9.95</td>
<td>1.014</td>
<td>55</td>
</tr>
</tbody>
</table>

*Table is based on approximate fit of Fig. 11 data to Eq. (85) for $W_i - 1 > 0.01$. See Fig. 11 for explanation of the different curves.

*Based on comparing values in Fig. 11 with Eq. (85).

The simplified methods discussed above are based on the relatively simple to analyze behavior of the outer extrema. While it is true that the central region of the nitroxide spectrum is very sensitive to motional effects it is also very sensitive to the deviations of the nitroxide magnetic parameters from cylindrical symmetry and this can vary considerably (cf Table I). Thus it would be difficult to develop general methods based on the central region; computer simulation with accurate magnetic parameters is probably required.

### C. Very Anisotropic Rotational Reorientation

The simplified methods discussed in the previous section have an important failing in that they are not really applicable to spectra arising from highly anisotropic motion, especially when the molecular $z$ axis is not itself a principal axis. The phenomenon of spin labels undergoing very rapid anisotropic rotational reorientation is a common one. In fact, the Stanford group (Hubbell and McConnell, 1969a,b, 1971; McConnell and McFarland, 1970 McFarland and McConnell, 1971) have developed a simple analysis in terms of an effective time-independent spin Hamiltonian $\tilde{H}_{\text{eff}}$ to account for rapid anisotropic motion.

Suppose that there is very rapid motion about some molecular axis $\alpha$ while motion perpendicular to that axis $\beta$. This is the case, for example, if the nitroxide spin label rotates about a single bond while the overall motion is that of the macromolecule to which it is attached. Then we...
can introduce effective $g'$ and $A'$ tensors that are axially symmetric about $v$, and this yields an effective rigid-limit Hamiltonian to predict the spectrum. The use of such an effective Hamiltonian implies (1) a large enough $R_\perp$ (representing rotational reorientation about $v$) that residual time-dependent effects of the averaging process, which could lead to line broadening, are negligible; and (2) motion about axes perpendicular to $v$, described by an effective $R_\perp$, is so slow that its effects on the spectrum are negligible.

Suppose that either of these conditions is not fulfilled, and that motional effects assert themselves in the spectrum. If condition 1 is fulfilled, but $R_\perp$ becomes fast enough to affect the spectrum, then one can simulate spectra using the program in Appendix B with the effective axial tensors $A'$ and $g'$. The tensor $A'$ is given in terms of the true $A$ and the direction cosines $\alpha_i$ ($i = x'', y'', z''$, but we drop the triple primes for convenience in this section) of $v$, in the molecular principal axis system as

$$A'' = \sum_i \alpha_i^2 A_i$$

$$A'_\perp = \frac{1}{2} \sum_i (1 - \alpha_i^2) A_i$$

(87) 

The simplified methods of the previous section would only apply in modified form if $A''$ and $A'_\perp$ are not much different from typical nitrooxide values (see below).

If, however, condition 1 is relaxed somewhat, then a motional narrowing theory can be applied to consider how the motion represented by $R_\perp$ yields line broadening, etc., from the deviations between $\tilde{H}$ and the true $\tilde{H}$. However, using our example above, the relaxation effects are a function of the orientation of the macromolecule, and we would have to compute such effects from $R_\perp$ for each orientation.

However, the general theory given here can be rigorously applied to this example, including effects from both types of motion simultaneously. A series of simulations in which $R_\perp$ is just large enough to show incipient slow motional effects, namely $\tau_{R_\perp} = 5 \times 10^{-8}$ sec, were performed where $\tau_{R_\perp} = \frac{5 \times 10^{-8}}{6 \times 10^{-11}}$ sec (Mason et al., 1974). This series of simulations, shown in Fig. 12b, was motivated by experimental results (cf. Fig. 12a) of Wee and Miller (1973) on a spin-labeled polybenzyl glutamate in DMF solution (cf. Fig. 13). These simulations required that the principal axes of $R$ (i.e., $x'$, $y'$, and $z'$) be tilted relative to the principal axes of the magnetic tensors ($x''$, $y''$, $z''$). In this modified computer program, $A$ and $g$ are expressed in the $x'$, $y'$, $z'$ coordinate system (cf. Polnaszek, 1975a). The spectra were calculated for a spatially isotropic distribution of spin labels with a tilt angle between respective $z$ axes of $41.7^\circ$. The simulated spectra of

3. THEORY OF SLOW TUMBLING ESR SPECTRA FOR NITROXIDES

![Fig. 12](image)

Fig. 12. (a) ESR spectra of polybenzyl glutamate labeled with 2,2,6,6-tetramethyl aminopiperidine-1-oxyl (TEMP-NH$_2$) in DMF solutions of varying concentrations at room temperature. The polymer concentration (volume fraction) was A, 0.008; B, 0.0917; C, 0.128; 0.148; E, 0.200; F, 0.420 (0.5 weight fraction); and G, 1.0 (solid polymer). [Reprinted with permission from Wee and Miller, J. Phys. Chem. 77, 182-189 (1973). Copyright by the American Chemical Society.] (b) Simulations computed with the magnetic parameters of the TEMP-NH$_2$ spin label: $A_s = 30.8$ G, $A_e = A_s = 5.8$ G, $g_s = 2.0089$, $g_e = 2.0058$, $g_s = 2.0021$. The symmetry axis of the rotational diffusion tensor is defined in the molecular axis system by the angle $\cos^{-1}(x''_{11}) = 48.3^\circ$, $\cos^{-1}(x''_{22}) = 90^\circ$, $\cos^{-1}(x''_{33}) = 41.7^\circ$. $\tau_{R_\perp}$ is $5.0 \times 10^{-8}$ sec and $\tau_p$ is varied in this series, except for the rigid-limit simulation J. See Table IV for values of $\tau_{R_\perp}$ and $\delta$. [Reprinted with permission from Mason et al., J. Phys. Chem., 78, 1324-13 (1974). Copyright by the American Chemical Society.]
McConnell (1969a, b, 1971) is based on analogy with liquid crystalline spectra, on a so-called order parameter $S_0$ given by

$$S_0 = \frac{1}{2}(3A_0^2 - 1) \approx (A''_0 - A'_0)/(A_0 - A_a)$$  \hspace{1cm} (89)

where the bar implies a time average and the second equality is based on letting $A_x = A_y$ as is the case in many nitroxides. $S_0$ is a measure of the extent of the motion leading to $H_{\text{eff}}$. We then have

$$A''_0 = A_0 + \frac{3}{4}(A_0 - A_a)S_0$$  \hspace{1cm} (90a)

$$A'_0 = \frac{1}{2}(3A_0 - A''_0)$$  \hspace{1cm} (90b)

and

$$A_0 = \frac{1}{2} \text{Tr } A = \frac{1}{2} \text{ Tr } A' = A'_0$$  \hspace{1cm} (91)
A check on the validity of using $\mathcal{K}_{\text{eff}}$ for interpreting a spectrum in terms of the "pseudoaxial" rigid limit is that one must have $\text{Tr} \ A = \text{Tr} \ A'$, which follows directly from the rotational invariance of the trace of a tensor. The simulated spectra of Fig. 12b have been analyzed just as though they were experimental results from anisotropically immobilized spin labels, and the results are summarized in Table IV (Mason et al., 1974). These results are in fact very similar to those obtained by Wee and Miller (1973) and in spin label studies in membrane models and membranes (Hubbell and McConnell, 1969a,b, 1971; McConnell and McFarland, 1970; McFarland and McConnell, 1971). Note that (1) $A'$ does vary slightly from $A_n = 14.13$ G but (2) the apparent $S_n$ varies considerably even though the calculated spectra were from a tilt angle of 41.7°, corresponding to a constant true value of $S_n = 0.336$. The results for A and B in Fig. 12b, where $\tau_{R_{11}}$ is very fast, are reasonable; the only discrepancy with the true results probably arises from the residual motional effects on the spectrum of having $\tau_{R_{11}} = 5 \times 10^{-8}$ sec. However, for spectra such as E and F, where $\tau_{R_{11}} \sim 5 \times 10^{-9}$ sec, the motional effects for the fast motion about a single bond are already slow enough for us to utilize the simple time-independent $\mathcal{K}_{\text{eff}}$. Thus the invariance of $S_n$ is a necessary but not really sufficient condition for the simple approach.

Thus we note that a change in $S_n$ can arise from a real change in the angle between $v$ and $z$ or a change in the rotational rate about $v$, as is the predominant phenomenon in the spectra of Fig. 12a (the spectrum A, however, has a shorter $\tau_{R}$ than the other spectra) (Mason et al., 1974). In general, these two phenomena cannot be distinguished unless the rotational rate about $v$ slows to where $A'$ is clearly anomalous and/or the slowed motion manifests itself in the other spectral characteristics shown in Fig. 12a.

Note that the analysis in terms of a single $R_1$ and $R_{11}$ represents a considerable simplification of the complex dynamics of polymer motion including localized bond motions and internal rotations. However, (1) as long as the internal rotation is much faster than the overall motion, it can be treated as uncoupled from the latter, and (2) if the overall motion is only showing marginal spectral effects, it would be difficult to obtain anything more precise than an effective $\tau_{R_{11}}$.

D. Anisotropic Liquids: Simulations

Some examples will now be given for nitroxides oriented in nematic liquid crystals (Polnaszek et al., 1973; Polnaszek, 1975a). For convenience, the Meier–Saupe potential, coincidence of the magnetic and orientation principal axes, and axial magnetic parameters were used, unless otherwise noted. In all cases the director was assumed parallel to the static magnetic field.

3. THEORY OF SLOW TUMBLING ESR SPECTRA FOR NITROXIDES

First, the effect of keeping the rotational correlation time $\tau_R \equiv (6R)^{-1}$ constant but varying the ordering by changing the potential parameter $\lambda$ is considered. Figure 14 shows such a case for an oblate nitroxide, i.e., one that tends to orient with its $z$ axis perpendicular to the magnetic field. The rotational correlation time was held constant at a value of $1.84 \times 10^{-9}$ sec which is in the incipient slow motional region for nitroxides. One sees that the effect of increasing the absolute magnitude of the orienting potential is (1) to decrease line widths considerably, and (2) to introduce larger shifts in the positions of the lines. The first effect is due to the fact that the effective $[\mathcal{K}_1(t) - \langle \mathcal{K}_1 \rangle]$ is reduced as the sample is being ordered, while $\langle \mathcal{K}_1 \rangle$, the average part of the perturbation, which causes the line shifts, departs more from its isotropic value of zero. It appears that the slow tumbling spectra begin to resemble motional narrowing results as $|\lambda|$ is increased at a constant $\tau_R$, although the shift of line positions is characteristic of liquid crystals in the nematic range. However, the observed line shifts are not predicted correctly by expressions appropriate for the motional narrowing region.
Chapter 10. We can use these shifts as an indication of slow motion in the mesophase. For \( \lambda > 0 \) a prolate top (a nitroxide that tends to orient with its \( z \) axis parallel to the field) similar linewidth behavior is observed, except that the spectrum spreads out and shifts to higher fields. In Fig. 15, \( \lambda \) is held constant at a value of \(-0.975\), corresponding to a low degree of ordering typical of small nitroxides. Comparison with figures for isotropic liquids (cf. Figs. 6–8) shows that the trends are quite similar in both cases, but that there are distinct quantitative differences in the details of the line shapes at comparable \( \tau_R \)’s.

In Figs. 16a and b, \( \lambda \) is held constant (at \(-7.5 \) and 8.5, respectively) for large ordering parameters, with the correlation time varying over several orders of magnitude. They correspond respectively to large dislikelike and rodlike nitroxide molecules, which tend to be very well ordered. They show that spectra with correlation times \( < 3 \times 10^{-8} \) sec will be fairly insensitive to changes in \( \tau_R \). In fact the observed ordering parameter for the oblate top nitroxide is nearly equal to the theoretical value for \( \tau_R \lesssim 10^{-8} \) sec, and it is found that the rigid limit is not approached until \( \tau_R \approx 10^{-6} \) (cf. Fig. 16c), compared to \( \tau_R \approx 3 \times 10^{-7} \) for the low ordering case in Fig. 15. Thus if a very highly ordered nitroxide, we can extend the upper limit of rotation correlation times obtainable from the unsaturated slow motional line shape.

For values of the potential parameter \( \lambda \) that lead to intermediate ordering (e.g., \( \lambda = -3.5 \), corresponding to \( \langle \Delta \theta \rangle = -0.30 \)), it has been found that the deviations from symmetric lines and from the theoretical order parameter begin to occur at somewhat longer values of \( \tau_R \) in the incipient slow tumbling region than for isotropic liquids, but that the linewidth asymmetry starts to be appreciable at somewhat shorter \( \tau_R \)’s than those for which the apparent ordering parameter deviates significantly from the corre value. Therefore the linewidth asymmetry can be used as an indication of slow tumbling in nematics. This can also be seen from Fig. 16 for high ordered nitroxides.

The effect of using different models of rotational reorientation has also been studied. For weakly ordered systems, one again sees the same qualitative behavior of spectral changes as the rotational model is changed, but there are qualitative differences between the spectral changes for the isotropic and nematic phases. As has been usually done for isotropic liquids, the correlation times for the non-Brownian models were determined to be those that gave the same values for the separation of the outer hyperfine extremum (i.e., \( S \)) as observed in the Brownian diffusion case. For liquid crystals \( S \) is expected to be a function of \( \lambda \) as well as of \( \tau_R \) and \( A_z \), thus complicating attempts to use it as a quantitative measure of \( \tau_R \)’s in nematic phases. If it was found to be true for weakly ordered systems. For the strongly ordered cases, the parameter \( S \) is meaningless since no outer extremum are observe

Figure 17 gives an example in which the principal axis of orientation permutated among the three principal axes of the nitroxide magnetic tensor. The hyperfine tensor is taken as axially symmetric, but the \( g \) tensor is asymmetric, as is typical for nitroxides. The rotational correlation time \( 10^{-8} \) sec and \( \lambda \) was adjusted to make the \( S \) values nearly equal. The \( x \)- and \( y \)-axis spectra are cases where the molecule tends to align parallel to the axes, respectively, while the \( z \) axis tends to be perpendicular to the field. One sees significant changes in the line shapes as the principal axis of orientation is changed, even for this weakly ordered system. There are also apparent shifts in \( \Delta g \). The \( g \) shifts persist in the motional narrowing region for this case of three different orientations. Thus, especially when using any cylindrically symmetric potential, one must be careful to choose the principal axis of orientation correctly. However, when an asymmetric potential such that given in Eq. (58) is used, the potential is invariant to permutation of the principal axes (i.e., the relabeling of \( x''', y''', z''' \) to obtain \( x', y', z' \)). Since \( g \) coefficients of the potential transform as the components of an irreducible tensor, we can transform the potential parameters for a principal axis syste
in the molecule into those for another molecular axis system. For the potential given by Eq. (58), one has for a permutation of axes such that the axis → \( z' \) axis
\[
\lambda_y = -(\lambda_z - 3\rho_y)/2
\]
and
\[
\rho_y = -(\lambda_z + \rho_z)/2
\]
where the subscripts refer to the principal axis of orientation of the molecule.

We can also determine \( \lambda_x \) and \( \rho_x \) from the relation
\[
\sum_i \lambda_i = \sum_i \rho_i = 0
\]
which follows from the fact that the ordering tensor is traceless.
It is well known that liquid crystals exhibit an anisotropic viscosity when oriented in a magnetic field (Miesowicz, 1946). The effects of anisotropic viscosity on nitrooxide slow tumbling spectra are shown in Fig. 18. In this figure \( \tau_{\perp} = (6R_\perp)^{-1} \) is kept constant at \( 1 \times 10^{-8} \) sec, the potential parameter \( \lambda \) is \(-0.975\), and \( \tau_{||} \) is varied. The effect of keeping \( R_\perp \) constant is to keep the value of \( S \) virtually constant. However, there are gross changes in the central region of the spectrum as \( R_\perp \) is increased relative to \( R_\perp \). Note from Eq. (66) that the terms that contain the effect of anisotropic viscosity have \( M \neq 0 \). It is seen from Eq. (74) that such terms are the pseudosecular terms in \( \mathcal{H}_1(\Omega) \). Thus we must include them in the Hamiltonian in order to see the effects of anisotropic viscosity. The effects of anisotropic viscosity on the slow motion line shapes are negligible when the ordering parameter is large or if the molecule tends to be aligned with its \( z \) axis, the axis of cylindrical symmetry of the hyperfine tensor, parallel to the field. Note that

the effects of anisotropic molecular reorientation on slow tumbling spectra from nitroxides are not as dramatic as the effects of anisotropic reorientation with respect to the director axis. Birrell et al. (1973) observed a system that can be thought of in terms of a highly anisotropic viscosity. Nitroxide free radicals were oriented in tubular cavities in inclusion crystals in which the molecule is free to rotate about the long axis but with its rotation hindered about the other two axes because of the cavity geometry. The system behaves as a highly ordered liquid crystal, which, as has already been noted, is fairly insensitive to the dynamics of the motion.

In all the preceding discussion, it has been assumed that \( n \) is fixed along the laboratory \( z \) axis, so that \( \Psi = (0, 0, 0) \). When \( n \) is tilted relative to the axis, then Eq. (45) must be used to expand \( \mathcal{H}_1(\Omega, \Psi) \), but otherwise the same diffusion equations in terms of \( \Omega \) are applicable. If there are random static distributions of directors, then, in principle, one must solve the problem for each value of \( \Psi \) and then integrate over the correct static distribution to predict the spectrum. When there is residual motion of the director, the
the stochastic Liouville equation can be augmented to deal effectively with the simultaneous motions of \( \Psi \) and \( \Omega \) (Polnaszek, 1975a; Polnaszek and Freed, 1975).†

E. Anisotropic Liquids: Experiments

Experiments have now been carried out to test the applicability of the slow tumbling theory to anisotropic liquids using the same general approach as has already been described for studies in isotropic liquids (Polnaszek, 1975a; Polnaszek and Freed, 1975). In particular, the PD-TEMPO probe has been studied in several viscous nematic solvents. The study was limited by the fact that before very large viscosities could be reached, the nematics would freeze. However, in the case of phase V solvent, it was possible to reach the slow motional region (cf. Fig. 19). Note in Fig. 20 how the apparent \( \langle \omega'^2 \rangle \) changes markedly when the slow motional region is approached.

In the isotropic studies, the motional narrowing line shapes were carefully corrected for the residual inhomogenous broadening effects of the deuteron splittings given in Table I. In the nematic phase, the splittings were found to vary with temperature as a result of the increase of \( \langle \omega'^2 \rangle \) with decreasing temperature. This added factor had to be corrected for in order to adequately deal with the line shapes.

Furthermore, careful measurements of the \( a_n \) and \( g \) shifts clearly demonstrated that the radical ordering required the use of the two-parameter potential of Eq. (58). For most cases (including phase V solvent), if the choice \( x'' = x', y'' = y', \) and \( z'' = z' \) is made, then \( |\lambda| > |\rho| \), with typical values for phase V being \( \lambda = -0.8 \) and \( \rho = 0.3 \). The higher temperature spectra from the isotropic phase again showed \( N = 1 \) for the anisotropic diffusion parameter, corresponding to isotropic rotation. However, in the nematic phase, only if the correct ordering potential involving both \( \lambda \) and \( \rho \) were used could the linewidth results be fit to isotropic rotational diffusion.

The appropriate values of \( \tau_R, N = 1, \lambda, \) and \( \rho \) were then extrapolated to the slow motional region to obtain parameters to predict the slow motional spectrum. A typical comparison is shown in Fig. 21a, where \( \tau_R = 3.6 \times 10^{-9} \) sec at \(-25^\circ\). There are serious discrepancies between experiment and prediction, unlike the good agreement (cf. Fig. 16) for isotropic liquids. This incipient slow tumbling region has been found to be rather model insensitive. However, careful analysis of the motional narrowing region for \( \tau > 2 \times 10^{-10} \) sec showed that the discrepancy was developing

† Editor's note: Further and more expanded discussions of order parameters and the anisotropic motion of spin labels in liquid crystals and bilayer model membrane systems are found in Appendix IV and Chapters 10-12, respectively.
there as well [i.e., the $\tau_R$ obtained from the B and C terms in Eq. (79) were no longer the same]. It was found possible to largely remove this discrepancy by the physically unreasonable model that anisotropic viscosity was developing such that while $\tau_R$ increased with $\eta/T$ as is normal for a liquid, $\tau_{R^*}$ remained virtually constant at $\sim 2 \times 10^{-10}$ sec. However, some alternative explanations have been proposed. To appreciate them, one must first examine Figs. 3 and 4 for isotropic liquids. There it is found that the nonsecular spectral densities for the rotational motion, which are expected to obey a Debye-type expression (cf. Chapter 2)

$$j(\omega_z) = \tau_R/(1 + \omega_z^2 \tau_R^*)$$  \hspace{1cm} (94)

were better fitted instead by the expression

$$j(\omega_z) = \tau_R/(1 + \omega_z^2 \tau_R^*)$$  \hspace{1cm} (94')

with $\varepsilon \approx 5$. A similar correction was found to be the case in the work with nematic solvents both above and below the isotropic-nematic transition with a smaller one below the transition. Deviations from the simple Debye

formula would be expected to arise if the rotational reorientation is significantly coupled to other degrees of freedom of the molecule or its surroundings (e.g., the angular momentum of the molecule or internal rotational degrees of freedom). A detailed statistical mechanical theory in terms of fluctuating torques experienced by the spin probe in its liquid environment has been proposed by Hwang et al. (1975).

The pseudosecular terms reflect the nuclear spin-flip transitions $\omega_+ \approx a_n/2$ for isotropic liquids and $\langle a_n \rangle/2$ for nematics. Thus one might try

$$j(\omega_z) = \tau_R/(1 + \varepsilon^2 \omega_z^2 \tau_R^*)$$  \hspace{1cm} (95)

It was found that a large value of $\varepsilon$ could account reasonably for the motional narrowing and slow tumbling spectra in the nematic (cf. Fig. 21b).

Actually, the analysis of this effect is fairly complex, involving incipient slow tumbling corrections from which it transpires that the secular spectral densities are now also characterized by nonzero frequencies and the pseudosecular spectral densities are modified. The proper analysis, which is complex, is discussed by Polnashke and Freed (1975). It is found that the pseudosecular spectral densities require a correction of $\varepsilon^2 \omega^2 \sim 15 - 20$ while for the secular spectral densities $\varepsilon \omega^2 \sim 1 - 2$. This yields satisfactory agreement with experiment (cf. Fig. 21b). Another approach to this problem, in terms of slowly fluctuating torques, has been introduced by Polnashke and Freed (1975). It is based upon the concept of a local structure or ordering which is relaxing more slowly than the probe molecule. This structure is expected to result from the surrounding rodlike nematic solvent molecules, which reorient more slowly than the smaller spin probe. [Such effects are not included in the Meier-Saupe (1958) mean field analysis that leads to the effective pseudopotential.] A simple analysis of the spin relaxation effects of such a mechanism shows that it has many of the proper trends. We may let $\Psi$ be the slowly relaxing set of Euler angles between the local structure and the lab frame, then for an axially symmetric potential of the spin probe relative to the local structure, rough estimates of $S_2^2 = \langle \mathcal{D}_{20}(\Omega) \rangle^2 \sim 0.1$ and $\tau_z/\tau_R \sim 10$ are obtained from the simple model, where $\tau_z$ is the local structure relaxation time. If such a hypothesis were correct, further careful studies including larger spin probes of different shapes could shed further light on this phenomenon.

Some preliminary experimental spectra of the rodlike cholesteric spin label 3-doxyl-5a-cholesterol in the viscous nematic phase of phase V are shown in Fig. 22 (Polnashke, 1975a). The system is highly ordered and the apparent splitting constants do not change appreciably with temperature. The observed $\langle \mathcal{D}_{20} \rangle$ values calculated from a motional narrowing theory analysis (cf. Chapter 8) are $-0.35$, $-0.39$, and $-0.46$ for $T = 26$, 3, and $-26^\circ$C, respectively. The two splittings are not equal at the lowest tempera-
3. Theory of Slow Tumbling ESR Spectra for Nitroxides

F. Saturation and Nonlinear Effects

The general slow tumbling theory presented in Section I can also be applied to saturation phenomena (Freed et al., 1971; Goldman et al., 1974; Goldman, 1973; Bruno, 1973). A careful study of saturation and slow tumbling for PADS in viscous media has shown that the stochastic Liouville approach can be effectively employed to predict slow tumbling spectra (Goldman et al., 1973). This is illustrated in Fig. 23. Note that the simulations were performed for axial nitroxide parameters, so the agreement should not be expected to be perfect.

In the discussion of Section II.B on simplified methods of estimating from features of the outer hyperfine extrema, it was found that in the region where $\tau_R > 10^{-8}$ sec they are quite insensitive to all parameters other than $\tau_{R_i}$, $A_2$, and $A$ (the intrinsic width), while the central region is affected by other magnetic tensor components. It is therefore reasonable to expect that simulations based on axial parameters should agree quite well with the saturation behavior of the outer extrema but not necessarily with the central extrema. Such a comparison is shown in Fig. 24, which shows the ratios $d_{\text{max}}(M) = \frac{1}{2} |\gamma| H(M)$ (where $H_{\text{max}}(M)$ is the microwave field strength at which the $M = -1, 0, +1$ regions of the spectra maximize where these regions correspond, respectively, to the low field, central, a high-field extrema). In particular, for $\tau_R > 10^{-8}$ sec, there is rather good agreement between experiment and prediction for $d_{\text{max}}(+1)/d_{\text{max}}(-1)$. It is possible to use such a ratio (which depends only on relative values of $B_1$ and not on its absolute magnitude) as a means of estimating $\tau_R$, but this has not yet been studied in detail. In particular, we are adding the new param $W_c$, the electron-spin relaxation rate, into the analysis. Also note the small changes in the ratio for large changes in $\tau_R$.

At the heart of all saturation and nonlinear phenomena is the fact that the eigenfunction expansion coefficients for the density matrix elements representing population differences (cf. Eq. (27), the terms $[C_m^{(i)}]_{\lambda} - [C_m^{(i)}]$ where $n = 0$) are relaxed at rates that depend on $2W_c + B_L RL(L + 1)$

when (1) an orientation-independent $W_c$ is used and (2) isotropic reorientation is assumed. There is, of course, coupling among the different ES transitions due to the nuclear spin-flip transitions induced by the peridoecular terms in $\mathcal{H}_t(Q)$. Thus while the expansion coefficients for $t$ representing the population difference for the proper isotropic average orientations, is relaxed by $T_{L_\perp} = (2W_c)^{-1}$, the coefficients for $L > 0$ are relaxed by the rotational motion as well. Furthermore, when $R \gg W_c$ (typical values of $W_c$ are $\sim 10^{-5}$ sec), then (1) the rotational motion is ve
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Fig. 24. Variation of $d_{\text{max}}(+1)/d_{\text{max}}(0)$ and $d_{\text{max}}(+1)/d_{\text{max}}(-1)$ with $\tau_R$. Solid lines are drawn through the experimental points for the system PADS in 85% glycerol-H$_2$O. [From Goldman et al. (1973).]

Fig. 23. (a) Experimental saturation spectra for PADS in 85% glycerol-H$_2$O at $T = -41^\circ$C and A, $d_e = 0.025$ G; B, $d_e = 0.079$ G; and C, $d_e = 0.45$ G. (b) Spectra simulated for free diffusion with $\tau_R = 2 \times 10^{-8}$ sec, $\delta = 1.2$ G, $W_e = 6.2 \times 10^4$ sec$^{-1}$, and A, $d_e = 0.03$ G; B, $d_e = 0.08$ G; and C, $d_e = 0.47$ G. Axial magnetic parameters were used in the simulations. $d_e = \frac{1}{2} \gamma H_1$. [From Goldman (1973).]

Effective in spreading the saturation throughout the spectrum, and (2) only the $L = 0$ component is effectively saturated. These ideas and the implications they have for pulsed saturation recovery studies are explored elsewhere (Freed, 1974). It is found in that work that the saturation recovery times (or at least the slowest relaxing mode) are often well approximated by $T_1, e \simeq (2W_e)^{-1}$ over a wide range of conditions, including the slow tumbling region.

Such considerations suggest that slow tumbling ELDOR experiments could be very interesting (Bruno, 1973; Bruno and Freed, 1974a; Smigel et al., 1974). In such experiments, we saturate with a pump microwave field at a particular resonant frequency corresponding to a particular orientation (and nuclear spin) of the nitroxide and then observe at another position corresponding to a different orientation. Then the indirect saturation at the observing position will depend on the rotational motion of the molecule. We therefore expect that the ratio $R/W_e$ will determine the relative importance of transmission of saturation to different environments (a form of "spin diffusion") versus simple ESR spin relaxation. The application of the stochastic Liouville theory to such experiments is discussed in detail elsewhere (Bruno, 1973; Bruno and Freed, 1974a; Smigel et al., 1974).

Finally, we note the existence of a great variety of nonlinear phenomena, such as the modulation-frequency dependence of adiabatic rapid-passage effects explored by Hyde and Dalton (1972). This latter, more complex phenomenon can also be dealt with by stochastic Liouville methods and is
discussed elsewhere (Dalton, 1973; Leniart, 1972; Thomas and McConnell, 1974). The rather striking spectral effects observed have been calibrated with typical samples by the use of the S parameter and extrapolation of τₖ with known values of η/τ to yield estimates of τᵣ ≈ 10⁻⁶ sec (Hyde and Dalton, 1972).

In the discussion of saturation and nonlinear effects there is an important distinction to be made with respect to intrinsic widths, which was not important in the theory for unsaturated spectra. Note that in Eqs. (28) and (29) intrinsic widths were introduced by replacing ωₙ by ωₙ + iT₂⁻¹ with no distinction made as to whether these widths are due to homogeneous or inhomogeneous broadening. It is possible to show, from the general form of the solutions in terms of superpositions of "complex Lorentzians" (cf. Appendix A), that this is entirely adequate for the case of a Lorentzian distribution of inhomogeneous broadening and no saturation (Abragam, 1961; Goldman et al., 1973). If the inhomogeneous widths may not be approximated as Lorentzian, then we must convolute the line shapes obtained from the slow tumbling theory given here with a more appropriate inhomogeneous line-shape function (e.g., a Gaussian). This can become a real problem when unresolved proton extra hyperfine structure is a dominant source of broadening (in which case rigorous line-shape simulations require adequate knowledge of the proton splittings and their orientation dependence). It is well known, however, that in the case of saturation, homogeneous and Lorentzian inhomogeneous lines are no longer formally equivalent (Abragam, 1961). Then Eqs. (28) and (29) are only appropriate for the homogeneous broadening. Again, inhomogeneous broadening could be accounted for by convolution methods, but for Lorentzian inhomogeneous broadening there is a simpler method. The solutions for saturated cases require both the coefficients Cₖₙ(t) of Eq. (27) and their complex conjugates Cₖₙ(t)*, to which they are coupled by the saturating terms. For homogenous broadening we replace ωₙ → ωₙ + iT₂⁻¹ for the former, as already noted, but ωₙ → ωₙ - iT₂⁻¹ for the latter. But for Lorentzian inhomogeneous broadening, we can merely let ωₙ → ωₙ + iT₂⁻¹ for both types of terms (Goldman et al., 1973). The computer simulations of Fig. 23b were made for the case of homogeneous broadening.

APPENDIX A. GENERAL SOLUTIONS AND DISCUSSION OF THE COMPUTER PROGRAM FOR NITROXIDES

The equations upon which the computer program given in Appendix B for the ESR spectrum of a nitrooxide in an isotropic fluid are based are (Bruno, 1973)
\[
\begin{align*}
[(\omega - \omega_e - 2b) - i(T_{zh} + \tau_{zh})]C_{kz, 0}^{L'}(3)
&\quad - \left( F_0 - D' + iT_{zh} \right) \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz, 0}^{L'}(3) \\
&\quad - \left( F_2 - D^{(2)} \right) \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz-2, 0}^{L'}(3) \\
&\quad \times \left[ \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \right] C_{kz+2, 0}^{L'}(3) \\
&\quad + \left( \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \right] C_{kz-2, 0}^{L'}(3) \\
&\quad + D \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz, 1}^{L'}(6, 7) \\
&\quad \times C_{kz+1, 1}^{L'}(6, 7) + D^{(2)} \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz-1, 1}^{L'}(6, 7) \\
&\quad = 2^{1/2} \omega_3 a_3 \delta(L, 0) \delta(K, 0) \tag{A.3}
\end{align*}
\]

\[
[(\omega - \omega_e + b) - i(T_{zh} + \tau_{zh})]C_{kz, 1}^{L}(4, 5)
\]

\[
+ (F_0 + \frac{1}{2}D' + iT_{zh}) \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz, 1}^{L}(4, 5) \\
\times \left( \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \right) C_{kz+1, 1}^{L}(4, 5) \\
+ (F_2 + \frac{1}{2}D^{(2)}) \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz-1, 1}^{L}(4, 5) \\
\times \left( \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \right) C_{kz-1, 1}^{L}(4, 5) \\
+ D^{(2)} \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -1 & 0 & 1 \end{pmatrix} C_{kz, 0}(2) + C_{kz+1, 0}(3) \\
+ D^{(2)} \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz, 0}(4, 5) \\
\times \left( \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \right) C_{kz-1, 1}^{L}(4, 5) \\
+ D \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -1 & 0 & 1 \end{pmatrix} [C_{kz, 0}^{L}(1) + C_{kz+1, 0}^{L}(2)] \\
- 2^{1/2} D \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} C_{kz+2, 1}^{L}(8, 9) \\
\times \left( \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \right) C_{kz-2, 1}^{L}(8, 9)
\end{align*}
\]
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where the plus sign is used for even $L$ and the minus sign for odd $L$. For even $L$, $i$ refers to all transitions; for odd $L$, $i$ refers only to transitions 4, 5, 6, 7, 8, and 9;

$$C_{k,1}(i, j) = 2^{-1/2}[C_{k,1}'(i) + C_{k,1}''(j)]$$

(A.9)

where $(i, j)$ are either $(4, 5)$ or $(6, 7)$, and the minus (plus) sign is for even (odd) $L$; and

$$C_{k,2}'(8, 9) = 2^{-1/2}[C_{k,2}'(8) \pm C_{k,2}''(9)]$$

(A.10)

where the plus (minus) sign is for even (odd) $L$. Also,

$$N(L, L') = [(2L + 1)(2L' + 1)]^{1/2}$$

(A.11)

and

$$T_{2,1}^{-1} = \alpha + \frac{1}{2} \beta$$

(A.12a)

$$T_{2,1}^{-\frac{1}{2}} = \frac{3}{2} \beta$$

(A.12b)

The quantity $\langle \gamma, \gamma, \gamma \rangle$ is a $3j$ symbol, whose values are tabulated or given by formulas (Rotenberg et al., 1959; Edmonds, 1957). These are used to evaluate the integrals on the LHS of Eq. (27), utilizing

$$\int d\Omega \Omega_{m_1, m_2}^{L_1}(\Omega) \Omega_{m_1, m_2}^{L_2}(\Omega) \Omega_{m_1, m_2}^{L_3}(\Omega) = \frac{8\pi^2}{m_1 m_2 m_3} \begin{vmatrix} L_1 & L_2 & L_3 \\ m_1 & m_2 & m_3 \end{vmatrix}$$

(A.13)

with the relationship

$$\Omega_{m_1, m_2}^{L}(\Omega) = (-)^{m-m'} \Omega_{m, -m}^{L}(\Omega)$$

(A.14)

There are many symmetry relations (Edmonds, 1957) in a $3j$ symbol $(L_1, L_2, L_3)$. Among the more useful ones are: (1) The sum of the $m$ values must be zero. (2) Naturally, $L$ must be positive and the absolute value of $m$ must not be greater than the corresponding $L$ in a given column. (3) The columns can be permuted without changing the value of the $3j$ symbol if the sum of $L$ values is even. If the sum of $L$ values is odd, then a permutation of the columns results in a change in sign for the value of the $3j$ symbol. (4) If the sum of $L$ values is even, then all the $m$ values can change sign without changing the value of the $3j$ symbol. If the sum of $L$ values is odd, then a change in sign for all $m$ values results in a change in sign for the value of the $3j$ symbol. (5) The triangular property holds whereby the sum of any two $L$ values must be equal to or greater than the third $L$ value. Properties (4) and (5) result in the equations in $L$ being coupled only to the equations in $L$ and $L \pm 2$, for the three allowed transitions; but the forbidden transitions (only
when there are asymmetric magnetic parameters) result in a coupling to equations in \( L \pm 1 \) as well. The coupling of odd \( L \) values is important only for slow motions when \( \tau_R \geq 5 \times 10^{-8} \) sec. The required \( 3j \) symbols are automatically calculated in the computer program in Appendix B.

The solutions in Eqs. (A.1)-(A.6) can be expressed by the matrix equation

\[
\mathbf{C} = \mathbf{U} \quad (A.15)
\]

where \( \mathbf{C} \) is an \( r \)-dimensional column vector consisting of the independent variables [i.e., the expansion coefficients \( C_{k, \mathbf{M}}(l) \)], which are to be solved for, \( \mathbf{U} \) is an \( r \)-dimensional column vector of constants given by the RHS of Eqs. (A.1)-(A.6), and \( \mathbf{C} \) is an \( r \times r \) square matrix formed by the coefficients of the \( C_{k, \mathbf{M}}(l) \) variables in Eqs. (A.1)-(A.6). For purposes of computer programming efficiency, it is best that the coefficient matrix \( \mathbf{C} \) be complex symmetric.

The above equations, except for saturation, are “naturally” symmetric because orthonormal expansions as well as a properly “normalized” linear combination of terms were used. [Actually, one must first replace the \( C_{k, \mathbf{M}}(l) \) in Eqs. (A.1)-(A.6) by \( C_{k, \mathbf{M}}(l) \) to be able to render \( \mathbf{C} \) symmetric.]

The diagonalization method for obtaining a spectrum is especially applicable, since Eq. (A.15) can be written in the form

\[
(\mathbf{C} + k\mathbf{1}) \mathbf{C} = \mathbf{U} \quad (A.15')
\]

where \( \mathbf{C} \) does not contain the “sweep variable” (e.g., \( \omega_s \) for a field-swept spectrum), \( \mathbf{1} \) is the unit matrix, and \( k \) is a constant containing the sweep variable [i.e., \( k = (\omega - \omega_s) - i T_{z1}^{-1} \)].

For a nondegenerate complex symmetric matrix \( \mathbf{C} \), a complex orthogonal matrix \( \mathbf{O} \) exists such that

\[
\mathbf{O}^{\dagger} \mathbf{C} \mathbf{O} = \mathbf{C}
\]

where \( \mathbf{O} \) is a diagonal matrix and \( \mathbf{O}^{\dagger} \) is the transpose of \( \mathbf{O} \). Premultiplication of Eq. (A.15') by \( \mathbf{O}^{\dagger} \), use of Eq. (A.16), and noting that \( \mathbf{O}^{\dagger} = \mathbf{O}^{-1} \) leads to

\[
(\mathbf{C} + k\mathbf{1}) \mathbf{C} = \mathbf{O}^{\dagger} \mathbf{U} \quad (A.17)
\]

or

\[
\mathbf{C} = \mathbf{O}(\mathbf{C} + k\mathbf{1})^{-1} \mathbf{O}^{\dagger} \mathbf{U} \quad (A.17')
\]

Note that the absorption \( Z' \) is given by

\[
Z' = \text{Im}[\mathbf{D} \mathbf{C} \mathbf{C}^{\dagger}] \quad (A.18)
\]

where

\[
\mathbf{D} = \mathbf{Y} \mathbf{U} \quad (A.19a)
\]

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with

\[
Y = [2^{-1/2} \omega_s d_1]^{-1} \quad (A.19b)
\]

where we use the fact that \( \omega_1 \equiv \omega_2 \equiv \omega_3 \equiv \omega_s \) in high fields and \( d_1 = d_2 = d_3 = d_s \). It follows from Eqs. (A.17) and (A.18) that

\[
\mathbf{Z} = \text{Im}[\mathbf{D} \mathbf{U} (\mathbf{C} + k\mathbf{1})^{-1} (\mathbf{O}^{\dagger} \mathbf{U})]
\]

which can be written for the \( r \) dimensions as

\[
\mathbf{Z} = Y \text{Im} \left[ \sum_{l=1}^{r} \frac{(\mathbf{O}^{\dagger} \mathbf{U})^2}{(\omega - \omega_l - i T_{z1})^2} \right]
\]

and for the first derivative of an absorption field-swept spectrum

\[
\frac{d\mathbf{Z}}{d\omega_s} = Y \text{Im} \left[ \sum_{l=1}^{r} \frac{(\mathbf{O}^{\dagger} \mathbf{U})^2}{(\omega - \omega_l - i T_{z1})^2} \right]
\]

Thus only a single diagonalization is required to calculate an absorption line shape or the \( n \)h derivative of the absorption. Another advantage is that \( \mathbf{C} \) and \( \mathbf{O} \) are not functions of \( T_{z1}^{-1} \), so that spectral line shapes can be calculated for different values of \( T_{z1}^{-1} \) without performing additional diagonalizations.

The diagonalization subroutine used for the slow tumbling computer program in Appendix B is due to Gordon and Messenger (1972). Th subroutine had the fastest execution time of all diagonalization subroutines tried. Besides its speed in diagonalizing a matrix, it has characteristics that make it especially useful in solving the slow motion equations. First, the subroutine takes advantage of the symmetry of \( \mathbf{C} \), so that only the elements to one side of the diagonal are stored. Second, the subroutine retains fully banded nature of the equations, so that only the subdiagonals contain nonzero elements are stored. Third, the subroutine performs the operation \( \mathbf{O}^{\dagger} \mathbf{U} \) “instantaneously” for each step of the diagonalization, so that only single column vector \( \mathbf{O}^{\dagger} \mathbf{U} \) need be stored rather than the construction and storage of the entire \( r \times r \) matrix. A modified version of this subroutine which can be used to obtain all the eigenvectors, is given by Bruno (1972).

Anisotropic Liquids

Because \( \Gamma_0 \) for anisotropic liquids is composed of a simple sum of terms in \( \mathbf{D}_{k, \mathbf{M}}(\Omega) \) plus the isotropic liquid \( \Gamma_0 \), there is much similarity between the equations for anisotropic liquids and those for isotropic liquids. In fact, the resulting equations for anisotropic liquids can be obtained by simply modifications of the isotropic liquid equations (A.1)-(A.6). The modifications can be specified by the following definitions for the simp
case of a Meier–Saupe potential, in which \( n \) is completely aligned by the magnetic field (Polnaszek et al. (1973)):

\[
C_A(j) = -\frac{2}{15} R^2 C_k, \mu(j) + i 2 R \lambda \left( 1 - \frac{\lambda}{21} \right) (-)^{k-M} \times \sum_{L'} N(L, L') \begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ -M & 0 & M \end{pmatrix} C_{k, \mu}(j) + \frac{8}{35} R^2 
\times (-)^{k-M} \sum_{L'} N(L, L') \begin{pmatrix} L & 4 & L' \\ -K & 0 & K \end{pmatrix} \begin{pmatrix} L & 4 & L' \\ -M & 0 & M \end{pmatrix} C_{k, \mu}(j)
\]  

(A.23)

and

\[
U^k_{\lambda} = q \omega d_e \delta(K, 0) \delta(M, 0) \frac{(2L + 1)^{1/2}}{I^0} \int_{-1}^{1} \phi_{0, 0}(0, \beta, 0) \exp \left( \frac{i}{2} x^2 \lambda \right) dx
\]

(A.24)

with \( I^0_0 = \int_{-1}^{1} \exp \left( \frac{i}{2} x^2 \lambda \right) dx \) and \( \lambda \) given by Eq. (60a). The addition of the term \( C_A(j) \) to the left-hand side and the replacement of the right-hand side by the term \( U^k_{\lambda} \) for each of the respective isotropic equations (A.1)–(A.6) gives the desired set of equations for the anisotropic liquid.

The equations for Brownian axially symmetric rotational diffusion and for anisotropic (axially symmetric) viscosity are obtained by using Eqs. (61a), (61b), and (62a)–(62f) and Eqs. (63), (64), and (65a)–(65f), respectively.

The absorption is, from Eq. (23) or Eq. (13), proportional to

\[
\overline{Z}^\prime = \Im \sum_{j=1}^{3} \sum_{L} \left( \frac{(2L + 1)^{1/2}}{I^0_0} \int_{-1}^{1} dx \phi_{0, 0}(0, \beta, 0) \exp \left( \frac{i}{2} x^2 \lambda \right) \right) C_{0,0}(j)
\]

(A.25)

If the anisotropic liquid equations are written in the matrix notation of Eq. (A.15), then from Eqs. (A.24) and (A.25) the absorption can again be written as proportional to

\[
\overline{Z}^\prime = \Im [U \cdot C]
\]

(A.26)

In the numerical evaluation of the terms in \( U^k_{\lambda} \) the following recursion formulas are useful:

\[
\phi_{0, 0}(x) = \left( (2L - 1)x \phi_{0, 0}^{-1}(x) - (L - 1) \phi_{0, 0}^{-1}(x) \right) / L
\]

(A.27a)

and

\[
I_n = \int_{-1}^{1} x^n \exp(x^2 \lambda_2) dx = \lambda_2^{-1} \left[ \exp(\lambda_2) - \frac{1}{2} (n - 1) I_{n-2} \right]
\]

(A.27b)

for \( n \) even. Appropriate expressions for the more complicated cases are given by Polnaszek (1975a).

Convergence for isotropic spectra has been discussed in Section II.E in terms of an \( n_L \). The effect of having \( \lambda \neq 0 \) means that the ordering affects the convergence of the solutions. For example, in the motionally narrowed region where \( n_L = 2 \) is sufficient for isotropic liquids, then for \( \lambda = -0.1 \) (weak ordering) one needs \( n_L = 4 \) and for \( \lambda = -3.5 \) (moderately strong ordering) \( n_L = 6 \). It appears safe, for the slow motional region, to use as \( n \) the sum of the value required for isotropic liquids and \( n_L = 2 \), where \( n_L \) is required for convergence for that value of \( \lambda \) in the motional narrowing region, although usually smaller values of \( n_L \) may be used.

Computer programs are given by Polnaszek (1975a) for calculating nitroxide line shapes when (1) the asymmetric potential defined by Eq. (58) describes the orientation of a nitroxide radical for which the principal magnetic \((x', y', z')\) and orientation \((x, y, z)\) axes are coincident, and (a) Eq. (61a), (61b), and (62a)–(62f) apply or (b) Eqs. (64) and (65a)–(65f) apply; (2) a Meier–Saupe potential is used; but the \( x' \) and \( z' \) axes are tilted by angle \( \beta \) (3) different reorientational models are used for a Meier–Saupe potential. All these programs contain the correction terms for nonsecular contributions of the resonant frequency shifts.

All the programs, including that given in Appendix B, have been written in FORTRAN IV language for an IBM 360/65 computer.

APPENDIX B. COMPUTER PROGRAM FOR SLOW TUMBLING NITROXIDES IN ISOTROPIC LIQUIDS

The following program was written in FORTRAN IV and is listed with 72 print positions per line. One of the subroutines in this program has been taken from Gordon and Messenger (1972), pp. 376–381, and has been reproduced with 60 print positions per line. The Gordon and Messenger subroutine is used with permission of Plenum Press.
3. Theory of Slow Tumbling ESR Spectra for Nitroxides

The structure of the program has an inner and outer loop. The outer loop is executed three times for each cycle of the outer loop.

The values of T and T,’ the outer loop values, are determined by the dimensions of the problem.

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ACKNOWLEDGMENTS

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