2 THEORY OF ESR SATURATION RECOVERY IN LIQUIDS AND RELATED MEDIA

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1 INTRODUCTION

This chapter is based on the original paper published in 1974, reference 1. It was motivated by the then growing interest in pulsed electron spin resonance (ESR) experiments on free radicals in liquids and related media, in particular saturation recovery-type experiments.[2] Since then the interest has greatly expanded, as is evidenced by this book. The basis of our theory of time-resolved ESR experiments is a natural outgrowth of our theory of steady-state saturation and multiple resonance behavior. This theory has now been summarized in a chapter in another book, and frequent reference is made to it (reference 3). In fact, it was most interesting to find that the steady-state saturation theory, which has been developed in great detail, could readily be extended, with all its sophistication, to the case of time-dependent, or time-resolved, spectroscopy.

We emphasize saturation recovery in this chapter, but we also include some comments on pulsed electron-electron double resonance (ELDOR),[2b] which, in principle, may be thought of as a saturation recovery, but with observation at a frequency displaced from the high-power pulse frequency. In later chapters we see how such methods may be extended to free-induction decay and echo-type experiments for the free-radical systems, where numerical techniques are useful.[4] We emphasize analytical techniques in the present chapter. This is possible because one finds that over a wide range of types of systems, the saturation recovery experiment is simply interpreted. We, however, give the general expressions that are amenable to computer methods already developed in connection with steady-state problems.[5]

Considerable theoretical and experimental work has focused on ESR spectra in the slow-tumbling region. Such work has (1) extended the range of motional reorientation times over which accurate analyses can be made of these motions and (2) demonstrated that more microscopic features of the motion (i.e., deviations from Brownian motion) could be studied.[2a,5] We also outline how the original steady-state theory may readily be extended to time-resolved experiments with emphasis again on slow-motional saturation recovery (and ELDOR-type) experiments. Again, because of a number of *formal* similarities between a motional narrowing theory and a slow motional theory, we are able to cast both in a single general framework. The analogies that are then established allow us to clarify the more complex slow-motional analysis.

2 GENERAL FORMULATION

We start with the usual density-matrix equation of motion for the

spin-density matrix[2a,3,6a], $\sigma(t)$:

$$\dot{\sigma} = -i(\mathcal{H}_0^x + \varepsilon(t)^x + iR)(\sigma - \sigma_{eq}), \tag{1}$$

where $\mathcal{H}_0$ is the zero-order Hamiltonian, $\varepsilon(t)$ is the interaction with the radiation field(s), R is the relaxation matrix, σ_{eq} is the time-independent equilibrium value of $\sigma(t)$, and the superscript x-implies that for two operators A and B, $A^x B \equiv [A, B]$. One speaks of A^x as the superoperator form of the operator A.

This is the usual expression one obtains for the motional narrowing region, where rotational modulation of the perturbing Hamiltonian $\mathcal{H}_1(\Omega)$ is sufficiently rapid that $|\mathcal{H}_1(\Omega)^2| \tau_R^2 \ll 1$, where τ_R is the rotational correlation time. The relaxation matrix R is made up from terms quadratic in matrix elements of $\mathcal{H}_1(\Omega)$, and it contains the linewidths, or in a time-resolved experiment the matrix of the T_2's, as well as the transition probabilities for relaxation from nonequilibrium population distributions. It should be clear, from the form of Eq. (1), that to have stable exponential relaxation, it must be true that the real part of the elements of R be negative (i.e., Re $R < 0$). The explicit appearance of σ_{eq} in Eq. (1) is part of a high-temperature approximation such that

$$\sigma_{eq} = e^{-\hbar \mathcal{H}_0/kT} / Tr\{e^{-\hbar \mathcal{H}_0/kT}\}$$
$$\approx \frac{1}{A}\left[1 - \frac{\hbar \mathcal{H}_0}{kT}\right], \tag{2}$$

where A is the total number of spin eigenstates and k is Boltzmann's constant. More generally, we may write a stochastic Liouville expression for $\sigma(\Omega, t)$ wherein the assumption of motional narrowing need not be made:[2a,5,7,8]

$$\dot{\sigma}(\Omega, t) = -i(\mathcal{H}_0^x + \varepsilon(t)^x + \mathcal{H}_1(\Omega)^x + iR' - i\Gamma_\Omega)[\sigma(\Omega, t) - \sigma_0(\Omega)]. \tag{3}$$

Here Γ_Ω is the Markov operator for the rotational tumbling that is modulating $\mathcal{H}_1(\Omega)^x$, R' is that part of the relaxation matrix that is orientation independent. Note that the expression is written for a $\sigma(\Omega, t)$, which is both a spin-density operator and a classical probability function in the values of the random variables Ω. One may recover the ordinary spin-density matrix by averaging over orientations

$$\sigma(t) = \int d\Omega \sigma(\Omega, t) P_{eq}(\Omega) \equiv \langle P_{eq}(\Omega)| \sigma(\Omega, t) |P_{eq}(\Omega)\rangle, \tag{4}$$

where $P_{eq}(\Omega)$ is the equilibrium distribution of orientations, and the convenient bra-ket notation is introduced. When $|\mathcal{H}_1(\Omega)|/|\Gamma_\Omega| \ll 1$ one may recover the motional narrowing limit from Eq. (3) [i.e., one obtains Eq. (1) for $\sigma(t)$].

We note that the Markov operator Γ_Ω has associated with it the expression

$$\frac{\partial}{\partial t} P(\Omega, t) = -\Gamma_\Omega P(\Omega, t), \tag{5a}$$

where $P(\Omega, t)$ is the probability density of finding Ω at a particular value at time t. The process is assumed to be stationary, so that Γ_Ω is time independent and we have

$$\Gamma_\Omega P_{eq}(\Omega) = 0. \tag{5b}$$

We first study the general approach to the time-dependent solution of Eq. (1); then we generalize to cover Eq. (3). We now introduce for the relevant off-diagonal elements of $\sigma(t)$:

$$\sigma_{\lambda_i}(t) = \sum_{n=-\infty}^{\infty} e^{in\omega t} Z(t)_{\lambda_i}^{(n)}, \tag{6a}$$

and

$$Z(t)_{\lambda_i}^{(n)} = Z(t)_{\lambda_i}^{(n)'} + iZ(t)_i^{(n)''}, \tag{6b}$$

for the λ_ith (ESR) transition. In our notation the matrix element $\sigma_{\alpha\alpha'}$, where α and α' differ by at least the value of electron spin quantum number $M_s = \pm\frac{1}{2}$, may be written as $\sigma_{\lambda_i^-\lambda_i^+} \equiv \sigma_{\lambda_i}$ corresponding to the λ_ith (ESR) transition. The states $\lambda^\pm$ are the $M_s = \pm\frac{1}{2}$ states; and λ_i^+ and λ_j^- have the same nuclear configuration, if one has an allowed ESR transition, or they have different nuclear configurations, if one has a forbidden ESR transition. The matrix elements $\sigma_{\lambda_i}(t)$ are then Fourier-analyzed in harmonics of the frequency ω of the applied radiation field. The $Z(t)_{\lambda_i}^{(n)}$ and $Z''(t)_{\lambda_i}^{(n)}$ are the real and imaginary parts, respectively, of $Z(t)_{\lambda_i}^{(n)}$ and correspond to the dispersive and absorptive modes of a resonant signal.

Similarly, for the diagonal elements, we can let

$$[\sigma(t) - \sigma_{eq}]_{\lambda_i^\pm} \equiv \chi(t)_{\lambda_i^\pm} \tag{7}$$

and Fourier-analyze the deviations of the diagonal elements of $\sigma(t)$ from their equilibrium values. In the present chapter we are only interested in the case of the $n = 0$ Fourier component of Eq. (7) representing the actual population deviations (i.e., recall that the diagonal elements σ_{aa} gives the population in state a). Also in Eq. (6a, b) we are only interested in the $n = 1$ case, corresponding to the Fourier component rotating with the radiation field.

One can now take matrix elements of Eq. (1) for a general multilevel spin system. The methods have been summarized in reference 3. The result is a set of coupled linear differential equations which may be neatly

arranged in matrix notation. That is, we have the matrix differential equation

$$
\begin{bmatrix} \dot{Z}(t) \\ \dot{Z}^*(t) \\ \dot{\chi}(t) \end{bmatrix} = \begin{bmatrix} R - iK & 0 & +id \\ 0 & R + iK & -id \\ +id^{tr} & -id^{tr} & -W \end{bmatrix} \begin{bmatrix} Z(t) \\ Z^*(t) \\ \chi^{(t)} \end{bmatrix} + \begin{bmatrix} iQ \\ -iQ \\ 0 \end{bmatrix}. \tag{8}
$$

The vector $Z(t)$ is a vector defined in the M-dimensional "space" of all the induced transitions with elements $Z(t)_{\lambda_i}$, whereas $\chi(t)$ is a vector defined in the A-dimensional "space" of all eigenstates with elements χ_{λ_i}. $Z^*(t)$ is the complex conjugate of $Z(t)$. The matrix W is the transition probability matrix, whose $\alpha\beta$th element for $\alpha \neq \beta$ is just minus the transition probability from state β to state α. It is defined in "eigenstate space" of dimension A. The width matrix R contains what in a steady-state experiment are the (coupled) widths of all the induced transitions; in a time-resolved experiment they represent the (coupled)-exponential decays of the off-diagonal density matrix elements. It is defined in "transition space." The coherence matrix K defined in "transition space" has as its λ_ith diagonal element the deviation of the Larmor frequency of the λ_ith transition from the applied (near)-resonant radiation field. The vector Q, defined in "transition space," results from the driving terms of the radiation field, and is nonzero only for allowed transitions. The transition-moment matrix d and its transpose d^{tr} are in general *not* square matrices. The rows of d are labeled according to transition space, whereas its columns are labeled according to eigenstate space. Thus it is an $M \times A$ rectangular matrix. Its elements represent the way pairs of eigenstates belonging to the λ_ith transition are coupled by the transitions induced by the radiation field(s). Detailed instructions for writing these matrices down are given in reference 3, and we illustrate with the following examples.

In the case of a simple two-level system between states $a \to (M_s = \frac{1}{2})$ and $b \to (M_s = -\frac{1}{2})$ one has $K \to \Delta\omega = \omega - \omega_0$, where ω is the frequency of the applied radiation field and ω_0 is the Larmor frequency for the transition. Also $-R \to T_2^{-1}$, W is the 2×2 matrix:

$$
\begin{bmatrix} +W_{ba} & -W_{ab} \\ -W_{ba} & +W_{ab} \end{bmatrix}
$$

involving the transition probability from state a to b, W_{ba}, and that from state b to a, W_{ab}. They are equal in the high-temperature approximation. Also d is the 1×2 matrix:

$$
(-d, +d),
$$

where $d = \frac{1}{2}\gamma_e B_1$. This arises from the radiation term

$$
\hbar\varepsilon(t) = \frac{1}{2}\hbar\gamma_e B_1 [S_+ e^{-i\omega t} + S_- e^{+i\omega t}], \tag{9a}
$$

which is the interaction of the spin $S = +\frac{1}{2}$ with a rotating field:

$$
B_1 = B_1(i \cos \omega t + j \sin \omega t). \tag{9b}
$$

Finally, $Q \to q\omega_0 d$ with $q = \hbar/2kT$ in this case.

If we now transform our expressions using the definitions

$$
\chi^+(t) \equiv \frac{1}{\sqrt{2}}(\chi_+ \pm \chi_-), \tag{10}
$$

for this two-level system, then we obtain

$$
\begin{bmatrix} \dot{Z}(t) \\ \dot{Z}^*(t) \\ \dot{\chi}^-(t) \\ \dot{\chi}^+(t) \end{bmatrix} = \begin{bmatrix} -T_2^{-1} - i\,\Delta\omega & 0 & -\sqrt{2}\,id & 0 \\ 0 & T_2^{-1} + i\,\Delta\omega & \sqrt{2}\,id & 0 \\ -\sqrt{2}\,id & \sqrt{2}\,id & -T_1^{-1} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}
$$

$$
\times \begin{bmatrix} Z(t) \\ Z^*(t) \\ \chi^-(t) \\ \chi^+(t) \end{bmatrix} + iq\omega_0 d \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix}, \tag{11}
$$

where $T_1^{-1} \equiv 2W_{ab}$.

We first of all see that $\chi^+(t)$ is uncoupled to the other density-matrix elements and is time independent. This is because it represents the conservation of probability condition, which more generally is

$$
\text{Tr}\,\sigma = \text{Tr}\,\sigma_{eq} = 1, \tag{12a}
$$

or equivalently,

$$
\text{Tr}\,\chi = \text{Tr}\,[\sigma - \sigma_{eq}] = 0. \tag{12b}
$$

The remaining portion of Eq. (11) involves a 3×3 symmetric matrix, which, in fact, is nothing more than the well-known Bloch equations[6] describing a single-line spectrum. We need only make the further identifications

$$
2d = \omega_1 \equiv \gamma_e B_1, \qquad Z' = \text{Re}\,Z \to \bar{M}_x, \qquad Z'' = \text{Im}\,Z \to \bar{M}_y,
$$

where $\bar{M}_x$ and $\bar{M}_y$ are the x and y components of magnetization in the rotating frame, whereas $(1/\sqrt{2})\chi^- \to (M_{eq} - M_z)$, where M_{eq} is the equilibrium value of the magnetization and M_z is its z-component. These Bloch

equations may be solved by standard methods (e.g., Laplace transforms).[6b]

We now return to the general Eq. (8). We wish to transform them in a manner analogous to the type of transformation that led to the simplified form of Eq. (11) for the simple two-level system. We can do that by generalizing the definition Eq. (10) for each eigenstate pair χ_{λ_i} and χ_{λ_i}, and defining new vectors

$$\chi^{\pm} = \frac{1}{\sqrt{2}}(\chi_+ \pm \chi_-), \tag{13}$$

where χ_+ is the subvector of dimension $A/2$ including all the χ_{λ_i}. Thus the vectors χ' are also of dimension $A/2$. This transformation leads to the matrix equations

$$\begin{bmatrix} \dot{\mathbf{Z}}(t) \\ \dot{\mathbf{Z}}^*(t) \\ \dot{\chi}^-(t) \\ \dot{\chi}^+(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R}-i\mathbf{K} & 0 & \sqrt{2}\,i\hat{\mathbf{d}} & \sqrt{2}\,i\hat{\mathbf{d}} \\ 0 & \mathbf{R}+i\mathbf{K} & -\sqrt{2}i\hat{\mathbf{d}} & -\sqrt{2}\,i\hat{\mathbf{d}} \\ \sqrt{2}\,i\hat{\mathbf{d}}'' & -\sqrt{2}\,i\hat{\mathbf{d}}'' & -\hat{\mathscr{W}} & -\mathscr{W} \\ \sqrt{2}\,i\hat{\mathbf{d}}'' & -\sqrt{2}\,i\hat{\mathbf{d}}'' & -\mathscr{W}'' & -\tilde{\mathbf{W}} \end{bmatrix} \begin{bmatrix} \mathbf{Z}(t) \\ \mathbf{Z}^*(t) \\ \chi^-(t) \\ \chi^+(t) \end{bmatrix} + \begin{bmatrix} i\mathbf{Q} \\ -i\mathbf{Q} \\ 0 \\ 0 \end{bmatrix}, \tag{14}$$

where we have introduced the definitions

$$2\hat{\mathbf{d}} \equiv \mathbf{d}_+ - \mathbf{d}_- \tag{15a}$$

$$2\bar{\mathbf{d}} \equiv \mathbf{d}_+ + \mathbf{d}_-, \tag{15b}$$

and the $\mathbf{d}_{\pm}$ are defined by analogy to $\chi_{\pm}$. That is, we may write $\mathbf{d} = (\mathbf{d}_+, \mathbf{d}_-)$ (i.e., a partitioned matrix where $\mathbf{d}_{\pm}$ represents the couplings to the $M_s = \pm$ eigenstates and is of dimension $M \times A/2$. Also we have

$$2\hat{\mathbf{W}} \equiv (\mathbf{W}_{+,+} + \mathbf{W}_{-,-}) - (\mathbf{W}_{+,-} + \mathbf{W}_{-,+}) \tag{16a}$$

$$2\tilde{\mathbf{W}} \equiv (\mathbf{W}_{+,+} + \mathbf{W}_{-,-} + \mathbf{W}_{+,-} + \mathbf{W}_{-,+}) \tag{16b}$$

$$2\mathscr{W} \equiv (\mathbf{W}_{+,+} - \mathbf{W}_{-,-}) + (\mathbf{W}_{+,-} - \mathbf{W}_{-,+}), \tag{16c}$$

where we have partitioned $\mathbf{W}$ according to the $M_s = \pm$ states as

$$\mathbf{W} = \begin{pmatrix} \mathbf{W}_{+,+} & \mathbf{W}_{+,-} \\ \mathbf{W}_{-,+} & \mathbf{W}_{-,-} \end{pmatrix}. \tag{16d}$$

[Note that in reference 1 we used $\hat{\mathbf{X}}(t) \equiv \sqrt{2}\chi^-(t)$ and $\tilde{\chi}(t) \equiv \sqrt{2}\chi^+(t)$, which led to a slightly more complex form of Eq. (11), but we use both forms below]. The form of Eq. (14) and (16a–d) does indeed appear to be more complex than Eq. (8). However, it is often the case that $\mathscr{W} = 0$. This will be exactly the case [cf. Eq. (16c) and below] when the matrix

elements of $\mathbf{W}$ obey

$$W_{\alpha\pm,\beta\mp} = W_{\alpha\mp,\beta\pm}, \tag{17a}$$

$$W_{\alpha\pm,\beta\pm} = W_{\alpha\mp,\beta\mp}, \tag{17b}$$

(where α and β represent any nuclear configurations and the $\pm$ signs refer to M_s), which is a common situation.[3] We further assume that only electron spin resonance (ESR) transitions are excited, in which case one finds that $\bar{\mathbf{d}} = 0$ [but for electron-nuclear double resonance (ENDOR) $\bar{\mathbf{d}} \neq 0$] and the $\chi(t)^+$ may now be decoupled from the relevant part of the solution, that is Eq. (14) becomes

$$\begin{bmatrix} \dot{\mathbf{Z}}(t) \\ \dot{\mathbf{Z}}^*(t) \\ \dot{\chi}^-(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R}-i\mathbf{K} & 0 & \sqrt{2}\,i\hat{\mathbf{d}} \\ 0 & \mathbf{R}+i\mathbf{K} & -\sqrt{2}\,i\hat{\mathbf{d}} \\ \sqrt{2}\,i\hat{\mathbf{d}}'' & -\sqrt{2}i\hat{\mathbf{d}}'' & -\hat{\mathbf{W}} \end{bmatrix} \begin{bmatrix} \mathbf{Z}(t) \\ \mathbf{Z}^*(t) \\ \chi^-(t) \end{bmatrix} + \begin{bmatrix} i\mathbf{Q} \\ -i\mathbf{Q} \\ 0 \end{bmatrix}. \tag{18}$$

Also we have from Eq. (16a) that

$$\hat{\mathbf{W}} = \mathbf{W}_{+,+} - \mathbf{W}_{+,-}, \tag{19}$$

since from Eq. (15a, b) and the fact that $\mathbf{W}$ is symmetric one has $\mathbf{W}_{+,-} = \mathbf{W}_{-,+}$ and $\mathbf{W}_{-,-} = \mathbf{W}_{+,+}$. Equation (18) is the natural generalization for a multilevel spin system to the Bloch equations for a simple line. It is, however, only valid provided that Eq. (17a) and (17b) are at least approximately correct and that no nuclear magnetic resonance (NMR) transitions are excited. If either or both of these conditions are not valid, then one should use Eq. (18), which is of larger dimension (by the amount of $A/2$). In either case one has a complex symmetric matrix, and one may solve the general case on a computer by diagonalizing this matrix.[8] In Eq. (8) there are one or more eigenvalues of zero corresponding to Eq. (12b) for conservation of total probability, but this does not appear in Eq. (14).

Note that since the $\mathbf{Z}''$ elements are typically detected, we need the unitary transformation

$$\sqrt{2} \begin{bmatrix} \mathbf{Z}' \\ i\mathbf{Z}'' \\ \frac{1}{\sqrt{2}}\chi \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}}\mathbf{1} & \frac{1}{\sqrt{2}}\mathbf{1} & 0 \\ \frac{1}{\sqrt{2}}\mathbf{1} & -\frac{1}{\sqrt{2}}\mathbf{1} & 0 \\ 0 & 0 & \mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{Z} \\ \mathbf{Z}^* \\ \chi^- \end{bmatrix} \equiv \mathbf{u} \begin{bmatrix} \mathbf{Z} \\ \mathbf{Z}^* \\ \chi^- \end{bmatrix}, \tag{20}$$

which transforms Eq. (18) into

$$\begin{bmatrix} \dot{\mathbf{Z}}'(t) \\ i\dot{\mathbf{Z}}''(t) \\ (2)^{-1/2}\dot{\boldsymbol{\chi}}^-(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} & -i\mathbf{K} & 0 \\ -i\mathbf{K} & \mathbf{R} & 2i\hat{\mathbf{d}} \\ 0 & 2i\hat{\mathbf{d}}^{tr} & -\hat{\mathbf{W}} \end{bmatrix} \begin{bmatrix} \mathbf{Z}'(t) \\ i\mathbf{Z}''(t) \\ (2)^{-1/2}\boldsymbol{\chi}^-(t) \end{bmatrix} + \begin{bmatrix} 0 \\ i\mathbf{Q} \\ 0 \end{bmatrix}, \qquad (21)$$

with the new symmetric matrix on the right-hand side of Eq. (21).

We note that the steady-state solutions to Eq. (8) or (18) may be calculated by the methods reviewed in reference 5. In particular, the form of Eq. (8) or (18) is

$$\Delta \dot{\mathbf{m}}(t) = \mathbf{L}\mathbf{m} + \mathbf{Q}'. \qquad (22)$$

Then the steady-state solution $\mathbf{m}^{ss}$ is formally given as

$$\mathbf{m}^{ss} = -\mathbf{L}^{-1}\mathbf{Q}' \qquad (23)$$

(ignoring for the moment the singularity of the $\mathbf{W}$ matrix of Eq (8), cf. reference 3). If we define

$$\Delta\mathbf{Z}(t) \equiv \mathbf{Z}(t) - \mathbf{Z}^{ss}, \text{ and so on,} \qquad (24)$$

or

$$\Delta\mathbf{m}(t) \equiv \mathbf{m}(t) - \mathbf{m}^{ss}, \qquad (25)$$

then Eq. (22) may be written in terms of these deviations from steady-state value as

$$\Delta\dot{\mathbf{m}}(t) = \mathbf{L}\Delta\mathbf{m}(t) \qquad (26a)$$

$$\Delta\mathbf{m}(t) = e^{\mathbf{L}t}\Delta\mathbf{m}(0), \qquad (26b)$$

so as $t \to \infty$, $\Delta\mathbf{m}(t) \to 0$.

It is shown in reference 3 that the solution of Eq. (23) may be simplified in terms of smaller submatrices as

$$\mathbf{Z}'' = \mathbf{M}^{-1}(-\mathbf{R}^{-1})\mathbf{Q} \qquad (27a)$$

$$\mathbf{Z}' = (-\mathbf{R}^{-1})\mathbf{K}\mathbf{Z}'' \qquad (27b)$$

$$\hat{\mathbf{d}}\tilde{\boldsymbol{\chi}} + \hat{\mathbf{d}}\hat{\boldsymbol{\chi}} = -\mathbf{S}\mathbf{Z}'', \qquad (27c)$$

where

$$\mathbf{M} = 1 + (\mathbf{R}^{-1}\mathbf{K})^2 + (-\mathbf{R}^{-1})\mathbf{S}. \qquad (27d)$$

Since we are assuming that $\bar{\mathbf{d}} = 0$ (see above), this means that Eq. (27d) simplifies to

$$\hat{\mathbf{d}}\hat{\boldsymbol{\chi}} = -\mathbf{S}\mathbf{Z}'', \qquad (27c')$$

and the saturation matrix $\mathbf{S}$ simplifies to

$$\mathbf{S} = 4\hat{\mathbf{d}}(\hat{\mathbf{W}})^{-1}\hat{\mathbf{d}}^{tr} \qquad (28)$$

(and recall that $\hat{\mathbf{W}}$ is nonsingular). It is then only necessary to invert the real symmetric matrices $\mathbf{S}$, $\mathbf{R}$, and then $\mathbf{M}$ to obtain the steady-state solutions. We must proceed differently for convenient solutions to the time-dependent case.

We now particularize the solutions to saturation recovery-type experiments, such that observations are made only for small d. [If we were to consider free-induction decay and spin-echo experiments, then we would be looking for solutions for $d = 0$ after the spins have been prepared by a pulse (90° and/or 180°) of short enough duration that spin relaxation is not yet operative.] We thus wish to develop for present purposes a perturbation scheme to lowest order in d. For this purpose the matrix of Eq. (18) is more satisfactory than that of Eq. (21), since it lacks the two degenerate submatrices ($\mathbf{R}$) along the partitioned diagonal that appear in Eq. (21). Note, however, that for $K_\lambda = 0$ (i.e., λth line is on resonance), if $-R_\lambda \equiv T_{2,\lambda}^{-1} = T_{1,\lambda}^{-1}$, then a triple degeneracy occurs in Eq. (21) with respect to the λth transition that is lifted by $d_\lambda \neq 0$. We must consider the case of $T_{2,\lambda} \neq T_{1,\lambda}$ separately from that for $T_{2,\lambda} = T_{1,\lambda}$. We develop the perturbation scheme by a generalization of the Van Vleck transformation procedure.[9] We first introduce the partitioned matrices

$$\mathbf{A} = \begin{bmatrix} \mathbf{R}-i\mathbf{K} & 0 & 0 \\ 0 & \mathbf{R}+i\mathbf{K} & 0 \\ 0 & 0 & -\hat{\mathbf{W}} \end{bmatrix}, \quad (29a) \qquad \mathbf{B} = i\sqrt{2}\begin{bmatrix} 0 & 0 & \hat{\mathbf{d}} \\ 0 & 0 & -\hat{\mathbf{d}} \\ \hat{\mathbf{d}}^{tr} & -\hat{\mathbf{d}}^{tr} & 0 \end{bmatrix}. \qquad (29b)$$

where $\mathbf{L} = \mathbf{A} + \mathbf{B}$ and consider a vector $\mathbf{m}$ [cf. Eq. (22)] and solve for

$$\mathbf{O}\mathbf{A}\mathbf{O}^{-1}(\mathbf{O}\mathbf{m}) + \mathbf{O}\mathbf{B}\mathbf{0}^{-1}(\mathbf{O}\mathbf{m}) = (\mathbf{A}+\mathbf{b})\mathbf{m}', \qquad (30)$$

where the partitioned matrix $\mathbf{B}$ is transformed approximately to be block diagonal [i.e., partitioned matrices along the diagonal as is $\mathbf{A}$ in eq. (29a)] by the (complex) orthogonal transformation $\mathbf{O}$ to lowest order in d. That is, we let

$$\mathbf{m}' = e^{i\mathbf{s}}\mathbf{m} \cong (1 + i\mathbf{s})\mathbf{m}, \qquad (31)$$

where $\mathbf{s}$ is found to be the (complex) antisymmetric operator

$$\mathbf{s} = +i(\mathbf{A}^-)^{-1}\mathbf{B}. \qquad (32)$$

and

$$\mathbf{b} = i\tfrac{1}{2}\mathbf{B}'\mathbf{s} = -\tfrac{1}{2}\mathbf{B}'[(\mathbf{A}^-)^{-1}\mathbf{B}]. \qquad (33)$$

That is

$$
s = \begin{bmatrix}
0 & 0 & -(A^{o,d^-})^{-1}\sqrt{2}\hat{d} \\
0 & 0 & (A^{c,d^-})^{-1}\sqrt{2}\hat{d} \\
-(A^{d,o^-})^{-1}\sqrt{2}\hat{d}^{tr} & (A^{d,c^-})^{-1}\sqrt{2}\hat{d}^{tr} & 0
\end{bmatrix} . \tag{34}
$$

[Our present use of the symbols s and m replaces S and M in reference 1 in order not to have these symbols confused with the saturation and M matrices; cf. Eq. (27).]

Here the inverse operator $(A^{j,k^-})^{-1}$ for $j, k = o, c, d$ may be conveniently defined by the prescription

$$
(A^{j,d^-})^{-1}\hat{d} = \lim_{\epsilon \to 0} - \int_0^\infty d\tau \exp[-\epsilon\tau] \exp[A^j\tau]\hat{d}\exp[-A^d\tau],
$$

$$
j = o \text{ or } c \tag{35a}
$$

and

$$
(A^{d,j^-})^{-1}\hat{d}^{tr} = \lim_{\epsilon \to 0} - \int_0^\tau d\tau \exp[-\epsilon\tau] \exp[A^d\tau]\hat{d}^{tr}\exp[-A^j\tau],
$$

$$
j = o \text{ or } c \tag{35b}
$$

where

$$
A^o = R - iK; \quad A^c = R + iK = A^{o*}; \quad A^d = -\hat{W}. \tag{36}
$$

(The convergence factor $\epsilon > 0$ is always taken as large enough to guarantee vanishing of the integrand as $\tau \to \infty$, and the limit is taken only after preforming the integration.) Thus in a M-dimensional basis set $a, b, \ldots$ in which A^o (or A^c) is diagonal and an $A/2$ dimensional basis set $\alpha, \beta \ldots$ in which A^d is diagonal, one has, for example

$$
[(A^{o,d^-})^{-1}]_{a\alpha b\beta} = \frac{\delta_{ab}\delta_{\alpha\beta}}{A^o_{aa} - A^d_{\alpha\alpha}} = \frac{\delta_{ab}\delta_{\alpha\beta}}{(-R_{aa}) - \hat{W}_{\alpha\alpha} + iK_{aa}} . \tag{37}
$$

Thus the expansion is in terms of

$$
\frac{|\sqrt{2}\hat{d}_{a\alpha}|}{|(-R_{aa}) - \hat{W}_{\alpha\alpha} + iK_{aa}|} \ll 1, \tag{37b}
$$

for any nonvanishing $\hat{d}_{a\alpha}$, or more simply for a simple line:

$$
\frac{|(\sqrt{2}/2)\omega_1|}{|T_2^{-1} - T_1^{-1} + i\,\Delta\omega|} \ll 1. \tag{37c}
$$

One finds, utilizing the fact that A^j are symmetric matrices, that

$$
[(A^{j,d^-})^{-1}\hat{d}]^{tr} = -[(A^{d,j^-})^{-1}\hat{d}^{tr}], \quad j = o, c \tag{37d}
$$

from which it follows that s is antisymmetric, as required. Also we have

$$
b = \begin{bmatrix}
C + C^{tr} & -(C^{tr} + C^*) & 0 \\
-(C + C^{tr*}) & C^* + C^{tr*} & 0 \\
0 & 0 & E + E^{tr}
\end{bmatrix} , \tag{38}
$$

where

$$
C = \hat{d}(A^{d,o^-})^{-1}\hat{d}^{tr}, \tag{39a}
$$

and

$$
E = 2\hat{d}^{tr} \, \text{Re}\,[(A^{o,d^-})^{-1}]\hat{d}. \tag{39b}
$$

When the transformation of Eq. (18) is utilized, then in the basis of Z', iZ'', $(1/\sqrt{2})X^-$ one has

$$
s = 2\begin{bmatrix}
0 & 0 & -i[\text{Im}(A^{o,d^-})^{-1}]\hat{d} \\
0 & 0 & -[\text{Re}(A^{o,d^-})^{-1}]\hat{d} \\
-i[\text{Im}(A^{d,o^-})^{-1}]\hat{d}^{tr} & -[\text{Re}(A^{d,o^-})^{-1}]\hat{d}^{tr} & 0
\end{bmatrix} . \tag{40}
$$

whereas

$$
b = 2\begin{bmatrix}
0 & 2i\,\text{Im}\,C^{tr} & 0 \\
2i\,\text{Im}\,C & 2\,\text{Re}\,(C + C^{tr}) & 0 \\
0 & 0 & E + E^{tr}
\end{bmatrix} . \tag{41}
$$

Thus one may solve either Eq. (18) or (21) in the approximations used as

$$
\Delta\dot{m}'(t) \cong (A + b)\,\Delta m'(t) \tag{42a}
$$

so

$$
\Delta m'(t) \cong \exp[+(A + b)t]\,\Delta m'(0), \tag{42b}
$$

and

$$
\Delta m'(t) \cong (1 - is)\exp[+(A + b)t](1 + is)\Delta m(0). \tag{42c}
$$

Note that $A + b$ given either by Eq. (29a) plus Eq. (38) [in the representation of Eq. (18)] or by uAu^{tr} plus Eq. (41) [in the representation of Eq. (21)] have the eigenstate-pair space (represented by superscript d) approximately uncoupled from the transition space (o and c superscripts) so $-\hat{W} + (E + E^{tr})$ may be diagonalized separately. However,

$$
\begin{bmatrix}
R & -i(K - 4\,\text{Im}\,C^{tr}) \\
-i(K - 4\,\text{Im}\,C) & R + 4\,\text{Re}\,(C + C^{tr})
\end{bmatrix}
$$

will in general couple Z' to Z''. [Alternatively, the coupling can be written for Z and Z'' from Eq. (29a) and Eq. (38).]

We note here that it is always possible to choose basis sets $a, b \cdots$ for transition space and $\alpha, \beta \cdots$ for eigenstate-pair space such that $\hat{\mathbf{d}}$ has a simple structure with $\hat{d}_{i,j} = d_{i,i}\delta_{i,j}$ where j refers to the eigenstate pair corresponding to the jth ESR transition. Several examples appear below.[24a] However, this choice does not, in general, simultaneously diagonalize $\mathbf{A}''$ and $\mathbf{A}^d$. In those cases where it does, and if $\hat{d}_{i,i} = d$ independent of i, it then follows from the preceding definitions that $\mathbf{U}^d = \mathbf{U}''$ (see below), $\mathbf{C}'^r = \mathbf{C}$ and $\mathbf{E}'' = \mathbf{E}$. Also the mixing of the $\mathbf{Z}$ and $\mathbf{Z}^*$ components by the terms in $\mathbf{b}$ is in general not easily simplified. This mixing becomes important as the elements $K_{i,j} \to 0$ representing exact resonances.

2.1 Simple One-Line Case

We illustrate the preceding formalism for the simple one-line case, which is otherwise well known, in preparation for the more complex cases given below. In this case we have $\mathbf{C} = \mathbf{C}''$, $\mathbf{E} = \mathbf{E}''$ and

$$
\mathbf{s} = \frac{+\omega_1}{(T_2^{-1} - T_1^{-1})^2 + \Delta\omega^2}
\begin{bmatrix}
0 & 0 & -i\,\Delta\omega \\
0 & 0 & (T_2^{-1} - T_1^{-1}) \\
i\,\Delta\omega & -(T_2^{-1} - T_1^{-1}) & 0
\end{bmatrix}
\tag{43a}
$$

and

$$
\mathbf{b} = \frac{\omega_1^2}{(T_2^{-1} - T_1^{-1})^2 + \Delta\omega^2}
\begin{bmatrix}
0 & -i\,\Delta\omega & 0 \\
-i\,\Delta\omega & (T_2^{-1} - T_1^{-1}) & 0 \\
0 & 0 & -(T_2^{-1} - T_1^{-1})
\end{bmatrix}
\tag{43b}
$$

in the Z', iZ'', $(1/\sqrt{2})X^-$ representation. When we neglect terms of order $\omega_1^2/[(T_2^{-1} - T_1^{-1})^2 + \Delta\omega^2]$ compared to unity, one has

$$
\mathbf{A} + \mathbf{b} \cong
\begin{bmatrix}
-T_2^{-1} & -i\,\Delta\omega & 0 \\
-i\,\Delta\omega & -T_2^{-1} + \delta & 0 \\
0 & 0 & -T_1^{-1} - \delta
\end{bmatrix},
\tag{44}
$$

where

$$
\delta = \frac{\omega_1^2(T_2^{-1} - T_1^{-1})}{[(T_2^{-1} - T_1^{-1})^2 + \Delta\omega^2]}.
\tag{44a}
$$

The 2×2 submatrix may be diagonalized by the orthogonal transformation $\mathbf{U}$

$$
\mathbf{U} =
\begin{bmatrix}
[1 - a_+]^{-1/2} & [1 - a_+^{-1}]^{-1/2} \\
[1 - a_-]^{-1/2} & -[1 - a_-^{-1}]^{-1/2}
\end{bmatrix},
\tag{45a}
$$

such that

$$
\mathbf{U}[\mathbf{A} + \mathbf{b}]\mathbf{U}^{-1} =
\begin{bmatrix}
E_+ & 0 \\
0 & E_-
\end{bmatrix},
\tag{45b}
$$

where

$$
a_\pm = \frac{(\delta \pm \sqrt{\delta^2 - 4\,\Delta\omega^2})^2}{4\,\Delta\omega^2},
\tag{45c}
$$

and

$$
E_\pm = -T_2^{-1} + \delta\sqrt{2} \pm \tfrac{1}{2}\sqrt{\delta^2 - 4\,\Delta\omega^2}.
\tag{45d}
$$

For $|\delta^2/\Delta\omega^2| \ll 1$, that is, a line off resonance, one has complex eigenvalues of eq. (44) of $\lambda = -T_2^{-1} + \delta/2 \mp i\,\Delta\omega$ corresponding to the eigensolutions $(1/\sqrt{2})Z$ and $(1/\sqrt{2})Z^*$ [cf. Eq. (29a)]; whereas for $|\delta^2/\Delta\omega^2| \gg 1$, that is, a line close to resonance, one has simple decaying solutions $\lambda = -T_2^{-1}$ and $-T_2^{-1} + \delta$ for eigensolutions Z' and iZ'', respectively [cf. Eq. (44)]. It then follows from the preceding equations that the complete solution is

$$
\begin{bmatrix}
\Delta Z'(t) \\
\Delta Z''(t) \\
\frac{1}{\sqrt{2}}\Delta\chi^-(t)
\end{bmatrix}
= (1 - i\mathbf{s})\mathbf{U}''
\begin{bmatrix}
e^{-E_+ t} & & \\
& e^{-E_- t} & \\
& & e^{-(T_1^{-1} + \delta)t}
\end{bmatrix}
\mathbf{U}(1 + i\mathbf{s})
\begin{bmatrix}
\Delta Z'(0) \\
\Delta Z''(0) \\
\frac{1}{\sqrt{2}}\Delta\chi^-(0)
\end{bmatrix},
\tag{46}
$$

where only terms linear in $\mathbf{s}$ are kept. Some simple and well-known limiting cases are[10]

CASE 1 $\Delta\omega = 0$.

Then

$$
\Delta Z''(t) = e^{-t(T_1^{-1} - \delta)}\Delta Z''(0) + \frac{\omega_1}{(T_2^{-1} - T_1^{-1})}(e^{-t[T_2^{-1} - \delta]} - e^{-t(T_1^{-1} + \delta)})\frac{1}{\sqrt{2}}\Delta\chi^-(0),
\tag{47}
$$

CASE 2 $T_2^{-1} \gg T_1^{-1}$.

Then for $t > T_2^{-1}$

$$
\Delta Z''(t) = \frac{-\omega_1 T_2^{-1}}{T_2^{-2} + \Delta\omega^2}e^{-t(T_1^{-1} + \delta)}\left[\frac{1}{\sqrt{2}}\Delta\chi^-(0)\right].
\tag{48}
$$

If we use conditions of partial saturation such that $M_z(0) = \alpha M_0$, $0 \le \alpha \le 1$, with M_0 the equilibrium magnetization, then

$$\tilde{M}_x(0) = \alpha\,\Delta\omega\,\omega_1 T_2^2 M_0$$
$$\tilde{M}_y(0) = \alpha\omega_1 T_2 M_0$$
$$M_z(0) = \alpha M_0, \tag{49}$$

and

$$\Delta Z'(0) = \Delta \tilde{M}_x(0) = \Delta\omega T_2 \Delta \tilde{M}_y(0) = \Delta\omega T_2^2 \omega_1(\alpha - 1) M_0$$
$$\Delta Z''(0) = \Delta \tilde{M}_y(0) = (\alpha - 1)\omega_1 T_2 M_0$$
$$-\frac{1}{\sqrt{2}}\Delta\chi = \Delta M_z(0) = (\alpha - 1) M_0. \tag{50}$$

Then for Case 1 we have

$$\Delta Z''(t) = \frac{-(1-\alpha)\omega_1 T_2 M_0}{(T_2^{-1} - T_1^{-1})}[T_2^{-1}e^{-t(T_1^{-1}+\delta)} - T_1^{-1}e^{-t(T_1^{-1}-\delta)}]. \tag{51}$$

whereas for Case 2 we have

$$\Delta Z''(t) \cong \frac{-(1-\alpha)\omega_1 T_2^{-1} M_0}{T_2^{-2} + \Delta\omega^2} e^{-t(T_1^{-1}+\delta)}. \tag{52}$$

[Note that to achieve a (partial) saturation condition it is necessary to apply a strong microwave field over a time $t > T_1$, so the spins can properly respond to the saturating field. This is of course different from the use of 90° and 180° pulses in free-induction decay and spin-echo experiments.[6]]

2.2 General Case for $T_2 \ll T_1$

The preceding formalism permits the solution of a variety of situations involving saturation recovery for which Eq. (46) is immediately generalized, and the general expression of Eq. (8) or (18) may be used for more general cases. We now, however, particularize our solutions to the case for $T_2 \ll T_1$ or, more generally, $|\mathbf{R}| \gg |\mathbf{W}|$. This is a useful case, especially in the slow-tumbling region, and also one for which some relatively simple analytic solutions may be obtained even for spectra that otherwise appear complex. In this case we have from Eq. (18), (21), (29), (40), and (41) that for

$$|\mathbf{R}|t > 1, \tag{53}$$

$$\Delta Z''(t) \cong [\mathrm{Re}(\mathbf{A}^{-d})^{-1}2\mathbf{d}]e^{-\hat{W}t}\frac{1}{\sqrt{2}}\Delta\chi^-(0). \tag{54}$$

In Eq. (54) we have dropped the small correction $\mathbf{E} + \mathbf{E}^{tr}$ of Eq. (44) to $\hat{\mathbf{W}}$. In the simple line case, this is just the neglect of δ of Eq. (44a) compared to T_1^{-1}, which is valid since for $T_2^{-1} > T_1^{-1}$:

$$\delta T_1 \cong \frac{\omega_1^2 T_1 T_2^*}{1 + T_2^{*2}\Delta\omega^2} \le \omega_1^2 T_1 T_2^* \ll 1 \tag{55}$$

(where $T_2^{*-1} = T_2^{-1} - T_1^{-1}$). The last inequality is a consequence of the no-saturation condition during the recovery. Now if $\mathbf{U}_o$, $\mathbf{U}_c$, and $\mathbf{U}_d$ are the orthogonal transformations that diagonalize $\mathbf{A}^o$, $\mathbf{A}^c$, and $\mathbf{A}^d$, respectively, we may rewrite Eq. (54) as

$$\Delta Z''(t) \cong -\int_0^\infty d\tau\{\mathbf{U}_o^{tr}\exp[\tau\mathbf{U}_o(\mathbf{R}-i\mathbf{K})\mathbf{U}_o^{tr}]\mathbf{U}_o$$
$$+ \mathbf{U}_c^{tr}\exp[\tau\mathbf{U}_c(\mathbf{R}+i\mathbf{K})\mathbf{U}_c^{tr}]\mathbf{U}_c\}\hat{\mathbf{d}}\mathbf{U}_d^{tr}$$
$$\times \exp[\tau\mathbf{U}_d(+\hat{\mathbf{W}})\mathbf{U}_d^{tr}]\exp[\mathbf{U}_d(-\hat{\mathbf{W}}t)\mathbf{U}_d^{tr}]\mathbf{U}_d\frac{1}{\sqrt{2}}\Delta\chi^-(0). \tag{56}$$

[The convergence factor has been dropped in Eq. (56) since $|\mathbf{R}| > |\mathbf{W}|$ implies satisfactory behavior of the integrals.] Note, however, by the functional properties $\mathbf{U}_o = \mathbf{U}_o\{\mathbf{R}, -i\mathbf{K}\}$ and $\mathbf{U}_c = \mathbf{U}_c\{\mathbf{R}, +i\mathbf{K}\}$ it follows that $\mathbf{U}_c = \mathbf{U}_o^*$. Then if we let

$$\mathbf{r} - i\mathbf{k} \equiv \mathbf{U}_o(\mathbf{R} - i\mathbf{K})\mathbf{U}_o^{tr}, \tag{57a}$$

and

$$\mathbf{w} \equiv \mathbf{U}_d(\hat{\mathbf{W}})\mathbf{U}_d^{tr}, \tag{57b}$$

Eq. (56) may be written more simply as

$$\Delta Z''(t) \cong -\int_0^\infty d\tau\,\mathrm{Re}\{\mathbf{U}_o^{tr}\exp[\tau(\mathbf{r}-i\mathbf{k}]\mathbf{U}_o\}(2\hat{\mathbf{d}})\mathbf{U}_d^{tr}$$
$$\times \exp[(\tau - t)\mathbf{w}]\mathbf{U}_d\frac{1}{\sqrt{2}}\Delta\chi^-(0). \tag{58}$$

We consider specific examples in the next section.

3 MOTIONAL NARROWING EXAMPLES

3.1 Well-Separated Hyperfine Lines (Nitroxide)

We first illustrate the application of our expression to a nitroxide (^{14}N) in the motional narrowing region when the three Lorentzian hyperfine lines
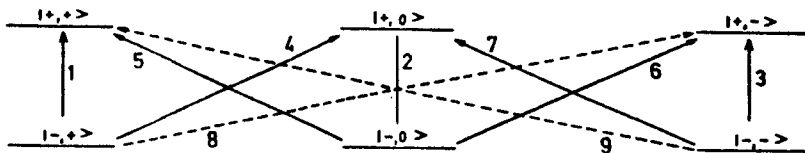
Figure 1 Energy levels and transitions for a nitroxide in high fields. Here $S = \frac{1}{2}$ and $I = 1$ and the notation is $|M_S, M_I\rangle$. The forbidden transitions are 4–9, and the allowed transitions are 1–3.

are well separated. If we consider just pure electron spin-flip transitions with rate W_e; pure nuclear spin-flip transition rates, which arise from the pseudosecular contributions of the electron-nuclear dipolar (END) interactions, and are, for a spin $I = 1$, given by $2W_n$ (where detailed expressions for W_n are given in reference 3), and spin exchange with rate ω_{HE}, we have

$$\mathbf{W}_{-,-} = \mathbf{W}_{-,-} = W_n \begin{bmatrix} 1+4b''+2b & -2b''-2b & -2b'' \\ -2b''-2b & 1+4b''+4b & -2b''-2b \\ -2b'' & -2b'' & 1+4b''+2b \end{bmatrix}. \quad (59a)$$

and

$$\mathbf{W}_{+,-} = \mathbf{W}_{-,+} = W_e \mathbf{1}, \quad (59b)$$

where we have introduced the dimensionless parameters $b \equiv W_n/W_e$ and $b'' = \omega_{HE}/AW_e$. Then from Eq. (19) we have

$$\hat{\mathbf{W}} = 2W_e \begin{bmatrix} 1+2b''+b & -b''-b & -b'' \\ -b''-b & 1+2b''+2b & -b''-b \\ -b'' & -b''-b & 1+2b''+b \end{bmatrix}. \quad (60)$$

Now we may write (by symmetry considerations, see below)

$$\mathbf{U}_d = \begin{bmatrix} \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} \\ \dfrac{1}{\sqrt{2}} & 0 & \dfrac{-1}{\sqrt{2}} \\ \dfrac{1}{\sqrt{6}} & \dfrac{-2}{\sqrt{6}} & \dfrac{1}{\sqrt{6}} \end{bmatrix}, \quad (61a)$$

so that

$$\mathbf{w} = 2W_e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1+3b''+b & 0 \\ 0 & 0 & 1+3b''+3b \end{bmatrix}. \quad (61b)$$

We also have

$$-R_{i,i} = T_{2,i}'^{-1} \delta_{i,i} + (\hat{W}_{i,i} - W_e \delta_{i,i}), \quad (62)$$

where the $T_{2,i}'^{-1}$ give the purely secular contributions to the ith hyperfine line and the terms involving transition probabilities add up to the Heisenberg uncertainty in lifetime contributions to the linewidths (cf. reference 3). Also

$$K_{i,i} = \Delta\omega_i \, \delta_{i,i}, \quad (63)$$

and

$$-\hat{d}_{i,i} = \tfrac{1}{2}\omega_1 \, \delta_{i,i} = \tfrac{1}{2}\gamma_e B_1, \quad (63a)$$

where j refers to the eigenstate pair associated with the jth transition.

For the general spectrum of well-separated lines we have for $i \neq j$ (cf. 3):

$$|-R_{i,j}| = |\hat{W}_{i,j}| \ll |\omega_i - \omega_j|, \qquad i \neq j. \quad (64)$$

Thus $\mathbf{R} \pm i\mathbf{K} = \mathbf{r} \pm i\mathbf{k}$ is diagonal in the basis of the separate transitions, and $\mathbf{U}_o = \mathbf{1}$ [except for higher-order terms in $2W_e b''$ and $2W_e b$ vs. $(\omega_i - \omega_j)$]. Then elements of Eq. (58) are just

$$\Delta Z''(t) = -\sum_{j,\beta} \int_0^\tau d\tau \, \mathrm{Re} \exp\left[\tau(r_{i,i} - ik_{i,i})\right] \omega_1 (U_d^{tr})_{i,\beta}$$

$$\times \exp\left[(\tau - t)w_{\beta\beta}\right] (U_d)_{\beta j} \frac{1}{\sqrt{2}} \Delta\chi_j^-(0)$$

$$= +\omega_1 \, \mathrm{Re} \sum_{j,\beta} \frac{e^{-w_{\beta\beta}t}}{r_{i,i} + w_{\beta\beta} - i\,\Delta\omega_i} (U_d^{tr})_{i\beta}(U_d)_{\beta j} \frac{1}{\sqrt{2}} \Delta\chi_j^-(0). \quad (65)$$

To complete the solution we must specify the initial condition

or

$$\frac{1}{\sqrt{2}} \chi_i^-(0) = -(M_{z,i}(0) - M_{0,i}) = (1 - \alpha_i)M_{0,i}, \quad (66)$$

$$\alpha_i = \frac{M_{z,i}(0)}{M_{0,i}}. \quad (66a)$$

It is now convenient to consider two limiting cases depending on whether $b, b'' \ll 1$ or $\gg 1$.

CASE 1   Uncoupled relaxation: $b, b'' \ll 1$. For this case a saturating pulse on the jth transition leading to $\alpha_j \neq 0$ will not appreciably affect the $i \neq j$ lines (except for terms higher order in b, b'', see below). Furthermore,

$$w_{\beta\beta} \cong 2W_e = T_1^{-1}, \quad \text{all } \beta. \quad (67)$$

Then, since $\sum_\beta (U_d^{tr})_{i\beta}(U_d)_{\beta i} = \delta_{i,i}$, Eq. (65) becomes

$$\Delta Z_i''(t) \cong -\mathrm{Re} \, \frac{\omega_1(1 - \alpha_i)M_{0,i}}{T_{2,i}'^{-1} + i\,\Delta\omega_i} e^{-t/T_1} \, \delta_{i,i}. \quad (68)$$

which is just Eq. (41) for each line.

CASE 2   Coupled relaxation $b', b'' \gg 1$. For this case a saturating pulse on the jth transition will have its effects transmitted equally to all the eigenstate pairs so that $\alpha_f = \alpha_i = \alpha = \frac{1}{3}\alpha_{Total} \neq 0$. Then since $\sum_i (U_d)_{\beta f} = \sqrt{3}\,\delta_{\beta,1}$, Eq. (65) becomes

$$\Delta Z_i''(t) = -\operatorname{Re} \omega_1 (1-\alpha) M_{0,i} \frac{e^{-t/T_1}}{(-R_{i,i})^{-1} - T_1^{-1} + i\,\Delta\omega_i}, \qquad (69)$$

for $i = 1, 2,$ or 3 (corresponding to transitions with nuclear spin of $-1, 0,$ and $+1$). Thus only one of the eigenvalues of $\mathbf{w}$ (i.e., $2W_e = T_1^{-1}$) is seen.

If it were possible to saturate one of the lines relative to the other two, then one could obtain a superposition of three decay terms each decaying by one of the eigenvalues of $\mathbf{w}$. Such would be the case if b and/or b'' is of order of magnitude unity. But then the three eigenvalues of $\mathbf{w}$ would not be much different, so that the superposition of three decay terms would not differ much from a single average exponential decay. A rigorous solution of this intermediate region would require a calculation from Eq. (18) of the values of χ^- resulting from a pulse of finite duration $\Delta t'$. However, if $\Delta t' > w_{\beta\beta}^{-1} \leq T_1 = (2W_e)^{-1}$, then one may use as the ratios $\alpha_f/\alpha_i = \chi_f^{-ss}/\chi_i^{-ss}$ (i.e., the steady-state values obtained in the presence of the saturating field). Thus

CASE 3   The steady-state approximation on the pulse duration is

$$\hat{\chi}^{sat'd} = -2\hat{\mathbf{W}}^{-1}\hat{d}_{sat'd}^{tr} Z^{sat'd}, \qquad (70)$$

with $Z^{sat'd}$ calculated by standard means (cf. reference 3). Then we can use Eq. (28) for the saturation matrix elements $S_{i,j}$ or the saturation parameters $\Omega_{i,f}$ defined by

$$S_{i,j} = \hat{d}_i \Omega_{f,f} \hat{d}_{i,j}^{tr}, \qquad (71a)$$

that is,

$$4(\hat{\mathbf{W}}^{-1})_{i,j} = \Omega_{i,j},$$

to rewrite Eq. (65) as (with $\hat{d}_{i,isat'd} \equiv \frac{1}{2}\omega_1^s$). Thus

$$\Delta Z_i''(t) = \omega_1 \operatorname{Re} \sum_{\substack{i,\beta \\ k}} \frac{e^{-w_{\beta\beta}t}}{r_{i,i} + w_{\beta\beta} - i\,\Delta\omega_i} (U_d)_{i\beta}^{tr} (U_d)_{\beta f} \frac{\Omega_{f,k}}{4} \frac{Z_k^{sat'd}}{2} \omega_1^s$$

$$= \omega_1 \operatorname{Re} \sum_{k,\beta} \frac{e^{-w_{\beta\beta}t}}{r_{i,i} + w_{\beta\beta} - i\,\Delta\omega_i} \frac{1}{w_{\beta\beta}} (U_d)_{i\beta}^{tr} (U_d)_{\beta k}^{tr} \frac{Z^{sat'd}}{2} \omega_1^s, \qquad (72)$$

where the second equality follows because

$$\mathbf{w}^{-1} = U_d \hat{\mathbf{W}}^{-1} U_d^{tr}. \qquad (73)$$

Case 1 is obtained from the second form of Eq. (72) by setting only one $Z_k^{nsat'd}$ unequal to zero and then using Eq. (67). Case 2 is obtained from the first form of Eq. (72) by recognizing that for b and/or $b'' \gg 1$, $\Omega_{i,k}$ becomes independent of j and k, that is $\Omega_{i,k} \to 2/(A/2)W_e$. (See reference 3.) (These $\Omega_{i,k}$ are given explicitly for the nitroxide case in Table V of reference 11.) Then one may use $\sum_i (U_d)_{\beta f} = \delta_{\beta,1}\sqrt{A/2}$. (Recall, however, that our original derivations of Cases 1 and 2 did not require the "steady-state pulse" approximation.) Cases intermediate between 1 and 2 exhibiting effects of all three decay constants are also obtained from Eq. (72). [Note that eq. (72) also covers ELDOR-type situations.] It follows from Eq. (72) that the exponential decays of larger $w_{\beta\beta}$ have the weaker amplitudes.

Now let us assume that the $w_{\beta\beta}$ are nearly equal, because $b, b'' \ll 1$. Then if the line observed is $i = 1$, while $k = 1$ has been saturated (simple saturation recovery), one obtains the following from Eq. (72):

$$\Delta Z_1''(t) \cong T_1 \omega_1 \operatorname{Re} (r_{1,1} + T_1^{-1} - i\,\Delta\omega_1)^{-1} e^{-t/T_1}\left[1 - (2b'' + b)\left(\frac{1+t}{T_1}\right)\right] Z^{nsat'd}\omega_1^s. \qquad (74)$$

However, if we let $k = 2$ (an ELDOR case),

$$\Delta Z_1''(t) = \frac{b+b''}{1+b+b''} e^{-t/T_1} T_1 \omega_1 \operatorname{Re} (r_{1,1} + T_1^{-1} - i\,\Delta\omega_1)^{-1}\left(\frac{1+t}{T_1}\right) z_2^{nsat'd}\omega_1^s. \qquad (75)$$

This emphasizes how the relaxation is dominated by T_1 and how an ELDOR effect would be weak (but potentially noticeable) compared to the direct saturation recovery effect for this case. When the $w_{\beta\beta}$ are very different (e.g., b and/or $b'' \gg 1$, such that $w_{22}, w_{33} > w_{11}$), other steady-state approximations appropriate to pulses of duration Δt fulfilling $w_{22}^{-1}, w_{33}^{-1} \ll \Delta t \ll w_{11}^{-1} = 2T_1$ may be used by solving for the steady-state solutions appropriate for $W_e \approx 0$ but W_n and/or $\omega_{HE} \neq 0$. This steady-state solution yields equal degrees of saturation of all the eigenstate pairs, and thus gives comparable results to that for Case 2. [Note, however, that for a steady-state approximation to apply here, $\Delta t \geq 2(T_1^{-1} + T_2^{-1})^{-1}$ and $(\omega_1^s)^2 \geq \frac{1}{4}(T_1^{-1} - T_2^{-1})^{2}$.[6]]

3.2   Single Average Hyperfine Line (Nitroxide)

Here we assume the opposite of Eq. (64), that is,

$$|-R_{i,i}| = |\hat{W}_{i,i}| \gg |\omega_i - \omega_j|, \qquad i \neq j. \qquad (76)$$

or

$$2W_eb \text{ and/or } 2W_eb'' \gg |\omega_i - \omega_j| \sim a_N, \qquad (76a)$$

so the original three-line spectrum has collapsed into a single average Lorentzian. If we also assume $|T_{2,i}^{-1} - T_{2,j}^{-1}| \ll 2W_eb$ and/or $2W_eb''$ then $U_o \cong U_d$ of Eq. (60) and Eq. (58) becomes

$$\sum_{i=1}^{3} \Delta Z_i''(t) = - \sum_{i,a,k,m,\beta} \int_0^\infty d\tau \, \text{Re} \, \{ U_{oi,a}^{tr} \exp [\tau(r_{a,a} - k_{a,a})] U_{oak}(2\hat{d})_{k,\ell} U_{k,\beta}^{tr}$$

$$\times \exp [(\tau - t)w_{\beta\beta}] (U_d)_{\beta m} \frac{1}{\sqrt{2}} \Delta \chi_m^-(0). \qquad (77)$$

But since $\hat{d}_{k,\ell}$ is independent of k and $\sum_k U_{oa,k} U_{dk,\beta}^{tr} \cong \delta_{a,\beta}$, whereas $\sum_i U_{oi,a}^{tr} = \sum_i U_{im,i} = \sqrt{3} \, \delta_{a,1}$ and $\chi_m^-(0) = \alpha$ independent of m, one has

$$\sum_i \Delta Z_i''(t) \cong 3\omega_1 \, \text{Re} \, \frac{e^{-w_{11}t}}{r_{11} + w_{11} - i \, \Delta\omega_{11}} \alpha, \qquad (78)$$

where $w_{11} = 2W_e$,

$$r_{11} = T_{2,av}^{-1} + 2W_e, \quad \text{with} \quad T_{2,av}^{-1} = \frac{1}{3} \sum_{i=1}^{3} T_{2,(i)}^{-1},$$

and

$$\Delta\omega_{11} = \frac{1}{3} \sum_{i=1}^{3} \Delta\omega_i. \qquad (79)$$

Corrections due to the incomplete averaging of effects of the b and b'' terms can be obtained by perturbations methods in the usual fashion. Again the relaxation is dominated by $T_1 = 1/2W_e$. [Note that Eq. (72) does not violate the validity of the perturbation approach as long as $T_2^{-1} > 2W_e$.]

3.3 General Case

The preceding discussion, given for the example of a nitroxide in the motional narrowing region, is seen to apply quite generally to the case of any hyperfine spectrum in the motional narrowing region. That is, Eq. (65) is still applicable in the well-resolved spectral region, as are the discussions and conclusions of cases (1), (2), and (3); Eq. (77) also applies in the limit of a single average hyperfine line. When there are degenerate hyperfine lines, it is only necessary to replace the vectors (e.g., Z, X$^-$) and matrices (e.g., R, $\hat{W}$) by their appropriate symmetrized forms as discussed

in reference 3, which then properly include the degeneracy factors. [Care must be exercised in describing the (coupled) relaxation of the components of the degenerate line, but the methods previously described are applicable.]

Note that in the diagonalization of $\hat{W}$ (and R), one can take advantage of the symmetries of these matrices. Thus the feature of spin exchange for *nondegenerate* transitions—viz., that it leads to equal transition probabilities among *all* the eigenstate pairs (i.e., $-W_{i,j}^{ex} = 2W_eb''$, $i \neq j$)[3]—means that $\hat{W}$ in the presence of exchange [but absence of electron-nuclear dipolar (END) terms] is invariant to all permutations of the $A/2$ nondegenerate eigenstate pairs (i.e., it commutes with the permutation group $P_{A/2}$). It is then a simple matter to show from the properties of this group that there is one eigenvalue

$$w_{11} = T_1^{-1} = 2W_e, \qquad (80)$$

corresponding to $U_{i1} = 1/(\sqrt{A/2}$ (for all i) or the totally symmetric linear combination of eigenstate pairs. Furthermore, all the other eigenvalues are found to be degenerate [belonging to an $(A/2)-1$ dimensional representation of $P_{A/2}$] and equal to

$$w_{ii} = 2W_e \left(1 + \frac{A}{2} b''\right), \qquad i \neq 1. \qquad (81)$$

The END interaction shows less symmetry. However, for the eigenstate pairs of a single nucleus of I (or for the $J^{(\kappa)}$'th set of eigenstate pairs corresponding to n completely equivalent nuclei with $J = \sum_{i=r} I_i$ and κ referring to a particular partner[3]) the $W_{i,j}^{END}$ are symmetric in the quantum number M. Thus the only symmetry operation involves $W_{M,M\pm1} \to W_{-M,-M\mp1}$ and $\chi_M^- \to \chi_{-M}^-$. However, one may also take advantage of the structure of W (see reference 3):

$$\hat{W}_{i,j} = 2W_e \, \delta_{i,j} + \hat{w}(END)_{i,j} \qquad (82)$$

so only $\hat{W}(END)_{i,j}$ the END contribution, needs to be diagonalized. Then since[3]

$$\hat{W}(END)_{ii} = -\sum_{j \neq i} \hat{W}(END)_{ij} = -\sum_{j \neq i} \hat{W}(END)_{ji}, \qquad (83)$$

the matrix $\hat{W}(END)$ must have a single eigenvalue of zero corresponding to the eigenvector $\sum_i \chi_i^-$ (by analogy with the equivalent property of symmetric W matrices corresponding to the conservation of probability). Thus one again has

$$w_{11} = T_1^{-1} + 2W_e.$$

corresponding to $U_{i1} = 1/\sqrt{A/2}$ with $w_{ii} = 2W_e[1 + f_i(b)] > 2W_e$ for $i \neq 1$ where the function $f_i(b)$ is of form seen in Eq. (61). (The preceding symmetry considerations are sufficient to determine the w_{ii} for the nitroxide.)

When both END and exchange are present, the lower symmetry of the END interaction is to be used. Also, if the hyperfine pattern is degenerate with different degeneracies for the different lines, then the $\hat{W}'$ matrix (the symmetrized form; see reference 3), in the presence of exchange only, one no longer has $P_{A/2}$ symmetry but usually symmetry like $\hat{W}(END)$, since, $D(\lambda)$ the degeneracy of the λth transition is symmetric about the center of the spectrum.

One can further generalize the problem to include a $\hat{W}$ that depends on M (i.e., effects of the cross term between g- and dipolar tensors). This will, however, destroy the symmetries discussed. When cross transitions are not negligible, the W matrix is nonzero and one must return to Eq. (8) but perturbation methods comparable to those of Section 2 may still be employed.

3.4 On Contributions of T_2-Type Decays

We now wish to discuss the validity of the neglect of the terms appropriate when $|\mathbf{R}| \gg |\hat{\mathbf{W}}|$. [See Eq. (53) and (54).] Such an approximation is valid, for example, for dilute solutions of semiquinones where the secular g-tensor broadening dominates the widths, except at higher temperatures when spin rotation is most important and $T_1 \approx T_2$.[12] In the latter case, each hyperfine line is uncoupled from the others, and one treats each such line separately. This latter case is also the case for the nitroxides at low viscosity; at higher viscosity the secular g-tensor broadening is, however, not dominant, and $T_{2,i}^{-1} \sim W_n$ in Eq. (62), so $T_{2,i}^{-1}$ is only somewhat larger than W_n. However, $b = W_n/W_e$ is then usually substantially greater than unity. Thus, although $w_{11} = 2W_e \ll T_{2,i}^{-1}$ in this case, the w_{22} and w_{33} of Eq. (61) are of comparable order of magnitude to $T_{2,i}^{-1}$. We have already seen that for $b \gg 1$ we can neglect the effects of w_{22} and w_{33} in the saturation recovery, and for the same reason of rapid decay we can neglect terms decaying with time constant of order T_2. A similar argument applies when exchange makes a major contribution to the widths. However, in that region where W_e and W_n (or $\omega_{EX} \equiv Ab''W_e$) are of the same order, and $T_{2,i}^{-1}$ is not large, then the complicating effects of the decay of T_2-type terms from the complete solution of Eq. (42) might become important. Note further that in the well-resolved region, where only a single hyperfine line is observed, this solution may be achieved fairly simply utilizing the techniques given earlier, since $U_n = 1$ (even though U_d is not so simple).

4 SLOW-TUMBLING EXAMPLES

4.1 Simple Line

By means of the eigenfunction expansion method of Freed, Bruno, and Polnaszek (FBP),[7] one obtains the following from Eq. (3):

$$\frac{1}{\sqrt{2}}\dot{C}_m(t) = \sum_n (R_{m,n} - iK_{m,n})\frac{1}{\sqrt{2}}C_n(t) + i\sqrt{2}d_{m,\hat{m}}(\tfrac{1}{2}b_{\hat{m}}(t)) + i\frac{1}{\sqrt{2}}Q_m,$$

(84)

as well as the complex-conjugate form of Eq. (84), and

$$\tfrac{1}{2}\dot{b}_{\hat{m}}(t) = i\sqrt{2}d_{m,n}^{tr}\left(\frac{1}{\sqrt{2}}C_m(t) - \frac{1}{\sqrt{2}}C_m^*(t)\right) - \sum_n \hat{W}_{\hat{m},\hat{n}}(\tfrac{1}{2}b_{\hat{n}}(t)).$$

(85)

Equations (84) and (85) are obtained by expanding the orientation-dependent matrix elements of $\sigma(\Omega, t)$ of Eq. (3) as

$$Z(\Omega, t)_{\lambda_i} = \sum_m C_m(t) |G_m(\Omega)),$$

(86a)

and

$$\hat{\chi}(\Omega, t)_{\lambda_i} = \sum_{\hat{m}} b_{\hat{m}}(t) |G_{\hat{m}}(\Omega)),$$

(86b)

where $Z(\Omega, t)$ and $\chi(\Omega, t)$ are defined by analogy with Eq. (6) and (7) and the $G_m(\Omega)$ are eigenfunctions of the Markov operator Γ_Ω,

$$\Gamma_\Omega G_m(\Omega) = E_m G_m(\Omega).$$

(87)

After the expansions of Eq. (86a) are performed in Eq. (5) one multiplies through by $\langle G_{m'}(\Omega) |$ and uses the orthonormality property of the $G_m(\Omega)$ to obtain Eq. (84) and (85). (In this section we drop the λ_i subscript, since only a simple line is being considered. We also let $\hat{m} \to m$.) These eigenfunctions $G_n(\Omega)$ may be written for Brownian rotation in isotropic liquids as the normalized Wigner rotation matrices

$$G_n(\Omega) \to G_{KM}^L(\Omega) = \sqrt{\frac{(2L+1)}{8\pi^2}}\mathscr{D}_{KM}^L(\Omega),$$

(87a)

with eigenvalues E_n for isotropic motion

$$E_n \to E_{L,K,M} = L(L+1)\mathscr{R},$$

(87b)

where $\mathscr{R}$ is the rotational diffusion coefficient.[2a,5,7] For models involving reorientation by appreciable jumps, it is found that the functions of Eq. (87a) are still good eigenfunctions, and Eq. (87b) becomes

$$E_n \to E_{K,M}^L = B_L(L+1)\mathscr{R},$$

(87c)

where the model parameter B_L ranges from unity for Brownian motion to $B_L = [L(L+1)]^{-1}$, $L \neq 0$ (and $B_L = 1$ for $L = 0$) for a strong collision model. It is discussed in detail elsewhere.[5,8,13-15] (We note that there is a simple analogue between Brownian rotational diffusion with an END mechanism, on the one hand, and strong jump diffusion with a Heisenberg exchange mechanism, on the other hand. The former pair have significant "selection rules", the latter have none.)

Note that the probability function of Eq. (5a) is itself representable by the eigenfunction expansion[5,9]

$$P(\Omega, t) = \sum_{L,K,M} a_{KM}^L(t) G_{KM}^L(\Omega). \tag{88a}$$

In particular, the conditional probability distribution $P(\Omega_0; \Omega, t)$ defined as the probability density of finding Ω at a particular value at time t provided it had the value Ω_0 *at time* $t = 0$, obeys

$$P(\Omega_0; \Omega, t) = \sum_{L,K,M} |G_{KM}^L(\Omega)\rangle e^{-E_{KM}^L t} \langle G_{KM}^L(\Omega_0)|, \tag{88b}$$

where we again use bracket notation. In addition, for an isotropic liquid we have [cf. Eq. (5b)]

$$P_{eq}(\Omega) = \frac{1}{8\pi^2} \mathscr{D}_{0,0}^0(\Omega) = \frac{1}{8\pi^2}. \tag{88c}$$

Now one observes an average over the orientations according to the prescription of Eq. (4). It then follows that the absorption is given by

$$Z''(t) = \langle P_{eq}(\Omega)| Z(\Omega, t) |P_{eq}(\Omega)\rangle \propto C_{0,0}^0(t), \tag{89}$$

and the other coefficients $C_{KM}^L(t)$ and $b_{KM}^L(t)$ are coupled into the problem by Eq. (84) and (85).

In particular, if we assume the orientation-dependent perturbation in Eq. (3) is an axially symmetric g-tensor, one finds only the $C_{o,o}^L(t)$ and the $b_{0,0}^L(t)$ for L even affect the observed signals [cf. Eq. (91b)]. For this case the terms in Eq. (84) and (85) are[7]

$$R_{L,L'} = r_{L,L} \delta_{L,L'} = -(T_2^{-1} + E_L) \delta_{L,L'} \tag{90}$$

$$K_{L,L'} = \Delta\omega + \kappa_{L,L'}, \tag{91a}$$

with

$$\kappa_{L,L'} = [(2L+1)(2L'+1)]^{1/2} \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 \mathscr{F}, \tag{91b}$$

and

$$\mathscr{F} = \tfrac{2}{3}\hbar^{-1}\beta_e B_0(g_\parallel - g_\perp). \tag{91c}$$

These expressions include only the secular contribution of the axially symmetric g-tensor with parallel and perpendicular components $g_\parallel$ and $g_\perp$, respectively. Also β_e is the Bohr magneton and B_0 is the dc magnetic-field strength, and $\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}$ is a 3-j symbol for which $L' = L$ or $L \pm 2$.[16] [The nonsecular contributions have been omitted in Eq. (84) and (85) (see FBP, Section IIIB1).] Also

$$\hat{W}_{L,L'} = w_{l,L} \delta_{L,L'} = (2W_e + E_L) \delta_{L,L'}, \tag{92}$$

and

$$O_l = q\omega_\lambda d_\lambda \delta_{l,0}. \tag{93}$$

We have introduced an orientation-independent width T_2' and $T_1^{-1} = 2W_e$ into Eq. (90) and (92), respectively. Equation (84), its complex conjugate, and Eq. (85) are seen to be of the same matrix form as Eq. (18) (with the matrices $\hat{\mathbf{d}}$ and $\hat{\mathbf{d}}''$ which by Eq. (84) and (85) only couple $C_{0,0}^L$ with $b_{0,0}^L$). So provided the inequality of Eq. (36) for the present case applies; then the same perturbation treatment in d_λ utilized for solving Eq. (18) may be utilized for the present case.

We wish to point out at this stage that the eigenfunction expansion method immediately yields $R_{m,n}$ and $W_{m,n}$ in *diagonal* form. Thus when $E_m/\mathscr{F} \gg 1$ corresponding to motional narrowing the $\mathbf{R} \pm i\mathbf{K}$ is approximately diagonal in this representation. However, κ, which arises from $\mathscr{H}_1(\Omega)$, is diagonal in the space of orientational unit vectors $|\delta(\Omega - \Omega_0)\rangle$.[2a] We note that from the representation of the δ-function:

$$|\delta(\Omega - \Omega_0)\rangle = \sum_n G_n^*(\Omega_0) |G_n(\Omega)\rangle, \tag{94a}$$

where, here, $|G_n(\Omega)\rangle$ are any complete orthonormal set of functions, one has

$$|G_n(\Omega)\rangle = \int d\Omega_0 G_n(\Omega_0) |\delta(\Omega - \Omega_0)\rangle, \tag{94b}$$

and if they are also eigenfunctions of Γ_Ω, then

$$\langle \delta(\Omega - \Omega_1)| \Gamma_\Omega |\delta(\Omega - \Omega_0)\rangle = \sum_n G_n^*(\Omega_0) G_n(\Omega_1) E_n. \tag{95}$$

[Equation (95) also follows from evaluating $\partial P(\Omega_0, \Omega, t)/\partial t$ at $t = 0$, since this is the same as Eq. (94a).]

Equations (94a) and (94b) define the unitary transformation

$$U_{n,\Omega_0} = G_n(\Omega_0) \tag{96a}$$

$$(U^{-1})_{\Omega_0,n} = U_{n,\Omega_0}^* = G_n^*(\Omega_0), \tag{96b}$$

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between the two sets of basis vectors. It is often the case, however, that the real linear combinations of the $G_n(\Omega)$ can be used so $\mathbf{U}$ becomes an orthogonal transformation.

When $E_L/\mathcal{F} \ll 1$, corresponding to the very slowly tumbling region, then $\mathbf{R} \pm i\mathbf{K}$ is approximately diagonal in the $|\delta(\Omega - \Omega_0)\rangle$ representation, with

$$K_{\Omega_i,\Omega_i} \cong k(\Omega_i) = \Delta\omega_\lambda - \omega'(\Omega_i), \quad (97a)$$

where

$$\omega'(\Omega_i) = \mathcal{F}\mathscr{D}_{0,0}^2(\Omega_i) = \mathcal{F}P_2(\beta_i), \quad (97b)$$

with $P_2(\beta)$ the second-rank Legendre polynomial. (Of course, actual calculations are performed using finite grid points on the unit sphere.)

Again the solution may be written in the form of Eq. (58), with an equation like Eq. (65) appropriate when $E_L/\mathcal{F} \ll 1$, except that $\mathbf{U}_o \cong (\mathbf{U}^{-1})$ are defined by Eq. (96b), whereas $\mathbf{U}_d = 1$, (since the initial basis sets are the eigenfunctions of Γ and not the individual orientational component; whereas in the motional-narrowing case of Section 3 the individual hyperfine components are utilized). When $E_L/\mathcal{F} < 1$, defining the slow-tumbling region where the spectrum is intermediate between the motional narrowing and rigid limit ones, the matrix $\mathbf{U}_o$ may be obtained by diagonalizing $(\mathbf{R} - i\mathbf{K})$ following methods already well described[5] while $\mathbf{U}_d = 1$. Thus we may write from Eq. (58)

$$\Delta C_0''(t, \omega) = \omega_1 \operatorname{Re} \sum_{L,i} \frac{e^{-w_{Li}t}}{(R - iK)_{ii} + w_{LL}} (U_0^{\text{tr}})_{0,i}(U_0)_{i,L} \tfrac{1}{2}\Delta b_L(0), \quad (98)$$

and when $E_L \ll \mathcal{F}$, this may be rewritten as

$$\Omega C_0''(t, \omega) \cong \frac{\omega_1 \operatorname{Re}}{\sqrt{8\pi^2}} \sum_L \int d\Omega_i \frac{e^{-w_{LL}t}}{r(\Omega_i) - ik(\Omega_i) + w_{LL}} G_L(\Omega_i) \tfrac{1}{2}\Delta b_L(0). \quad (99)$$

In both cases it follows from Eq. (91b) that only even values of L are required.

Note that in Eq. (99) it is never really necessary to take an infinite sum over L. This is because in the integration over Ω_i, the $G_L(\Omega_i)$ for large L have rapid oscillations compared to the rest of the integrand, so that they average to zero, and for large enough L one usually has $W_{LL} \gg W_{00}$. That is, we do not need values of L so large that $G_L(\Omega_i)$ varies much faster in Ω_i than $[r(\Omega_i) - ik(\Omega_i) + w_{LL}]^{-1}$. The effect of a large T_2^{-1} in $r(\Omega_i)$ is to broaden out the features of the near-rigid spectrum, thus decreasing the maximum value of L required. The approximate equality of Eq. (99) reflects the fact that we have taken $\mathbf{R} - i\mathbf{K}$ as diagonal in the $|\delta(\Omega - \Omega_0)\rangle$ representation, with the dominant part of $f(\Omega_i)$ being $-T_2^{-1}$ (with any

small residual motional broadening calculated using the correct representation that diagonalizes $\mathbf{R} - i\mathbf{K}$, which for practical purposes, involves difference methods).

We can also rewrite Eq. (99) in a form more closely resembling Eq. (65):

$$\Delta Z''(\Omega_i, t, \omega) = \omega_1 \operatorname{Re} \sum_{L \text{ even}} \frac{e^{-w_{LL}t}}{r_{ii} - ik_{i,i} + w_{LL}} \int d\Omega_j G_L(\Omega_i) G_L^*(\Omega_j) \tfrac{1}{2}\Delta\chi(\Omega_j, 0). \quad (100)$$

First suppose that $E_L \ll W_e$, so that $w_{LL} \cong 2W_e$ for all values of L that contribute appreciably to the sum [since as already noted the sum may be truncated, but also the $b_L(0)$ may be negligible for large L], then Eq. (100) becomes

$$\Delta Z''(\Omega_i, t) \approx \omega_1 e^{-t/T_1} \frac{1}{r_{i,i} - ik_{i,i} + 2W_e} \tfrac{1}{2}\Delta\hat\chi(\Omega_i, 0), \quad (101)$$

representing the fact that the spin packet at Ω_i is uncoupled to the other orientations [cf. Eq. (60). Then one may use the general relation

$$\Delta C_0''(t, \omega) = \frac{1}{\sqrt{8\pi^2}} \int d\Omega_i \, \Delta Z''(\Omega_i, t, \omega) \quad (102)$$

to calculate $\Delta C_0''(t, \omega)$, which is observed in an experiment. Now suppose that $E_L \gg W_e$ for $L > 0$ such that $w_{LL} \gg 2W_e$ for $L > 0$. Then a saturating pulse will have its effects transmitted by the rotational diffusion equally to all parts of the line; that is, only $b_0(0)$ is normally saturated, so only $\tfrac{1}{2}\Delta b_0 \neq 0$, and Eq. (99) becomes [with an equivalent form for the more general equation (98)]

$$\Delta C_0''(t, \omega) = \frac{\omega_1}{8\pi^2} e^{-t/T_1} \operatorname{Re} \left[\int d\Omega_i \frac{1}{r(\Omega_i) - ik(\Omega_i, \omega) + 2W_e} \right] \tfrac{1}{2}\Delta b_0(0), \quad (103)$$

again giving relaxation with a simple $T_1 = \tfrac{1}{2}W_e$ [cf. Eq. (69)].

We can, again, introduce the "steady-state approximation on the pulse duration" and the analogue of Eq. (70) becomes

$$\tfrac{1}{2}\hat\chi(\Omega_i)^{\text{sat'd}} = -\int d\Omega_i \hat{W}_{\Omega_i\Omega_i}^{-1} d_{\Omega_i,\Omega_i}^{\text{tr sat'd}} Z''(\Omega_i)^{\text{sat'd}} \quad (104)$$

where

$$\hat{W}_{\Omega_i\Omega_i}^{-1} = \sum_m G_m(\Omega_i) w_{mm}^{-1} G_m^*(\Omega_i) = \sum_{L,K,M} \left(\frac{2L+1}{8\pi^2}\right) \mathscr{D}_{KM}^L(\Omega_i) w_{KM}^L \mathscr{D}_{KM}^{L*}(\Omega_i). \quad (104a)$$

and for an orientation-independent transition moment we may write $d_{\Omega,\Omega}^{tr\,sat'd} = -\frac{1}{2}\omega_1^*\,\delta_{i,j}$. Although, in principle, the sum in Eq. (104a) includes a complete sum over the orthonormal set, the nature of $Z''(\Omega_i)$ for the present case, as determined by Eq. (91), again means that only the restricted sum of L even and $K = M = 0$ need be used in Eq. (104). An alternative form of Eq. (104) is

$$b_L^{sat'd} = \omega_1^* w_{LL}^{-1} C_L^{''(sat'd)}. \tag{104b}$$

In general, the $b_L^{sat'd}$ will be nonnegligible only for those L such that the $C^{''(sat'd)}$ are strongly coupled into the problem by the term in $\mathcal{F}$ of Eq. (97b) and for which $4(d^{(sat'd)})^2 w_{LL}^{-1} \geq (-R_{LL})$, that is, the $C^{''(sat'd)}$ are indeed being saturated. It is usually the latter condition that is limiting, since one has

$$\frac{T_2^{-1}}{E_l} \cdot \frac{W_e}{E_l} \ll \frac{|\mathcal{F}|}{E_l},$$

and usually

$$(\omega_1^*)^2 \geq (2W_e)^{-1} T_2$$

(but not very much greater). Note also that the $C^{sat'd}$ are obtained from Eq. (84)–(91) once $\dot{C}_L(t)$ and $\dot{b}_L(t)$ are set equal to zero.

We now obtain from Eq. (98):

$$\Delta C_0''(t) = +\omega_1 \,\mathrm{Re} \sum_{L,j} \frac{e^{-w_{Lj}t}}{(R - iK)_{Lj} + w_{LL}} \left(\frac{1}{w_{LL}}\right)(U_o^{tr})_{0,l}(U_o)_{l,m} C_L^{''(sat'd)}\tfrac{1}{2}\omega_1^*, \tag{105}$$

with the obvious modification when Eq. (99) is appropriate. Equation (100) may be rewritten as

$$\Delta Z''(\Omega_i, \omega, t) = \omega_1 \,\mathrm{Re} \sum_{even\,L} \frac{e^{-w_{Lj}t}}{r(\Omega_i) - ik(\Omega_i) + w_{LL}}$$
$$\times \int \frac{G_L(\Omega_i) G_L^*(\Omega_j)}{w_{LL}} Z^{sat'd}(\Omega_j)\frac{\omega_1^*}{2}\,d\Omega_j. \tag{106}$$

where it is again clear that only $w_{0,0}$ and those w_{LL} comparable to $w_{0,0}$ would contribute substantially. And the saturation recovery spectrum given by $\Delta C''(\omega, t)$ is obtained by integrating Eq. (106) over Ω_i and utilizing $\langle G_l(\Omega_i) | Z''(\Omega_i)\rangle = C_L$. The case of w_{LL} comparable to $w_{0,0}$ for all L contributing appreciably to Eq. (106) may be dealt with in the manner of Eq. (72) to yield

$$\Delta Z''(\Omega_i, \omega, t) = \omega_1 \,\mathrm{Re}\, \frac{e^{-w_{0,0}t}}{r(\Omega_i) - ik(\Omega_i) + w_{0,0}}$$
$$\times \int d\Omega_j[\delta(\Omega_i - \Omega_j) - \overline{\gamma(\Omega_i, \Omega_j)}(1 + w_{0,0}t)]w_{0,0}^{-1} Z''(\Omega_j)^{sat'd}(\tfrac{1}{2}\omega_1^*), \tag{107}$$

where

$$\overline{\gamma(\Omega_i, \Omega_j)} = \sum_{L \neq 0}{}' \gamma_L G_L^*(\Omega_i) G_L(\Omega_j), \tag{107a}$$

and γ_L is defined by $w_{LL} = w_{00}\gamma_L$ with $\gamma_L \ll 1$ for all values of L contributing appreciably to Eq. (106). [The prime on Eq. (107a) indicates it may be calculated over this restricted set of L values. Note also that $\sum_L' G_L(\Omega_i)G_L^*(\Omega_j) \approx \delta(\Omega_i - \Omega_j)$ compared to the much slower variation of $Z''(\Omega_j)$ with Ω_j. For Brownian diffusion $\gamma_L = L(L+1)\mathcal{R}/2W_e$; whereas for the limit of strong jumps

$$\overline{\gamma(\Omega_i, \Omega_j)} = \frac{[\delta(\Omega_i - \Omega_j) - 1/8\pi^2]\mathcal{R}}{2W_e}. \tag{108}$$

Equation (107) again emphasizes how the dominant relaxation is via $T_1 = 1/2W_e$ and it shows how one may calculate the magnitude of the weak recovery signal for an ELDOR experiment in this case when Ω_i and Ω_j are quite different. Equation (108) substituted into Eq. (107) gives the simple orientation-independent result expected for a strong-collision model (for $\Omega_i \neq \Omega_j$). For this model, the more general expression, Eq. (106) takes on the simpler form

$$\Delta Z''(\Omega_i, \omega, t) = \omega_1 \,\mathrm{Re}\, \frac{e^{-w_{0,0}t}}{r(\Omega_i) - ik(\Omega_i) + w_{0,0}} \left(\frac{C^{''(sat'd)}}{w_{0,0}\sqrt{8\pi^2}}\right)$$
$$+ \frac{e^{-w't}}{r(\Omega_i) - ik(\Omega_i) + w'}\left(\frac{1}{w'}\right)\left[Z''(\Omega_i)^{sat'd} - \frac{C_0^{''(sat'd)}}{\sqrt{8\pi^2}}\right]\tfrac{1}{2}\omega_1^*, \tag{109}$$

where $w' = w_{0,0} + \mathcal{R}$.

One may speculate, for slow tumbling, whether other initial conditions may be created before observing the recovery. In particular, one could try initially to saturate a single orientation. In the case of $E_L \ll W_e$ (i.e., $w_{LL} \cong 2W_e$ for all L) this is essentially the same as Eq. (109). The opposite limit of $w_{LL} \gg w_{0,0}$ for $L > 0$, a normal saturating pulse is transmitted to all parts of the line. However, it may be possible by such techniques as the use of a relatively weak 180° pulse (i.e., $\omega_1\tau = \pi$ where τ is the pulse duration, such that $\tau \ll r_{LL}^{-1}, w_{LL}^{-1}$ for values of L contribute to the spectrum, and $r_{LL}, w_{LL} \ll \omega_1 = \pi/\tau < \kappa_{LL}$) initially to saturate a small range of orientations, and still allow for $w_{LL} > 2W_e$ for $L > 0$ (but not $w_{LL} \gg 2W_e$). This situation could then show interesting effects from several decay constants: w_{LL}.

4.2 Other Aspects of a Simple Line

4.2.1 ORIENTATION-DEPENDENT T_1 AND T_2

Near the rigid limit it is possible that orientation-dependent effects of T_1 and T_2 begin to show up. We can examine such effects by introducing terms: $T_{1,0}^{-1}\mathscr{D}_{0,0}^2(\Omega)$ and $T_{2,0}^{-1}\mathscr{D}_{0,0}^2(\Omega)$. Then

$$R_{L,L'} = -(T_2^{-1} + E_L)\,\delta_{L,L'} - T_{2,0}^{-1}[(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2,$$

(110)

and

$$W_{L,L'} = (T_1^{-1} + E_L)\,\delta_{L,L'} + T_{1,0}^{-1}[(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2.$$

(111)

When Eq. (110) is compared with Eq. (90) and (91), it is seen that its only effect on the previous results is to change $\mathscr{F} \rightarrow \mathscr{F} - iT_{2,0}^{-1}$, but Eq. (111) renders $\hat{W}_{L,L'}$ nondiagonal. When $T_{1,0}E_L \gg 1$ (or more precisely $T_{1,0}E_2 \gg 1$) then these orientation-dependent effects may be neglected, but for very slow motions it would be necessary to diagonalize $\hat{W}_{L,L}$ [where, in the limit $E_L \rightarrow 0$, one would obtain the $|\delta(\Omega - \Omega_i)\rangle$ representation].

4.2.2 ASYMMETRIC g-TENSOR

The correct expressions may be obtained for this case by direct comparison of the preceding expressions with the steady-state case given by FBP. The main feature to note is that the $\mathscr{D}_{K,0}^L(\Omega)$ for even L and nonzero K appear in the problem, so effects of anisotropic rotational diffusion can appear.[5] Otherwise the discussion is analogous to that given for symmetric g-tensors.

4.2.3 CONTRIBUTION FROM T_2-TYPE DECAYING TERMS

In general, one finds that T_2^{-1} is significantly larger than $2W_e$ in the slow-motional region, so the T_2-type decaying terms should decay much faster. However, it is possible for $E_L = \mathscr{R}L(L+1)$ to play a dominant role for large L in Eq. (90) and Eq. (92), that is, $\mathscr{R}L(L+1) \gg T_1^{-1}$ and T_2^{-2}. But this is the case where these terms of large L decay too rapidly in e^{-Wt} to be important compared to the $w_{0,0}$ case, and similar comments would apply to the T_2-type decaying terms. Again one can return to the complete Eq. (42) for a detailed examination of such effects. We note that

in the slow-tumbling region, the $K_{L,L'}$ of Eq. (91a) will result in contributions from slightly off-resonant components of the line, and their T_2-type decay (but not T_1-type decays) will have some oscillatory character [cf. Eq. (44) and (45)]. Our preceding analysis can be further refined by distinguishing between that portion of the line broadening which is homogeneous, and that which is inhomogeneous (assumed Lorentzian). This is unimportant for unsaturated effects but is important when considering saturation.[5,6,14]

4.3 Complex Spectra: Nitroxides

Very often a slow-tumbling spectrum is not just describable as a simple line but is, rather, a complex one involving the coupling of the different transitions. Methods for solving the steady-state spectra in such cases are given in detail elsewhere.[5,7-9,13,14] However, the partitioned-matrix concept of Eq. (18) may again be applied in a manner analogous to the simple line case treated in the previous section. The important generalizations are just to regard each of the coefficients $C_{K,M}^L(t)$ and $b_{K,M}^L(t)$ as vectors in spin space,[17] such that $C_{K,M}^L(t, i)$ refers to the component representing the ith ESR transition. For the particular case of nitroxides, one need only consider the three allowed transitions ($i = 1, 2,$ or 3) and three linear combinations of the six forbidden transitions (cf. Fig. 1).

These forbidden transitions are coupled into the (high-field motional narrowing) allowed transitions by the pseudosecular terms in $\mathscr{H}_1(\Omega)$ that induce nuclear spin flips, and as the motion slows, they also affect the actual resonance frequencies. For very slow motions, one achieves the rigid-limit resonance frequencies, which may, to a good approximation, be described by three allowed transitions for each orientation.

Similarly, there are six components $b_{KM}^L(t, i)$ representing population differences between pairs of eigenstates, that is, three for the allowed transitions ($i = 1, 2,$ or 3) and three that are really (mixed) nuclear magnetic resonance (NMR) transitions. These latter arise from the pseudosecular terms in $\mathscr{H}_1(\Omega)$, and thus play a role closely analogous to the three (mixed) forbidden transitions for the $C_{KM}^L(i)$. As the rigid limit is approached (in particular, for $|\mathscr{H}_1(\Omega)|/\mathscr{R} \gg 1$) their inclusion becomes equivalent to representing the diagonalized eigenstates characteristic of the rigid limit.

One may thus generalize all our preceding procedures to such cases wherein the vector spaces of Eq. (18) include the product space of the $C_{KM}^L(t)$ for the different L, K, M (or alternatively, the $|\delta(\Omega - \Omega_i)\rangle$ representation) with the appropriate spin space as just described. In the slow-tumbling region where

$$|\mathscr{H}_1(\Omega)|\,\mathscr{R} > 1,$$

that is, the unsaturated slow-tumbling spectra still show important motional effects, the detailed diagonalizations required for Eq. (58), for example, are complex although tractable.[5,8,21] However, one usually (but not always) has the condition

$$2W_e \ll \mathcal{R},$$

and any saturation effects are transmitted throughout the spectrum. In this event we again have a case where the $\hat{\mathbf{W}}$ matrix is characterized by a $w_{0,0} = (2W_e)$ and $w_{L,L} \gg w_{0,0}$ for $L \neq 0$, and the dominant (slow) decay will again give just $T_1^{-1} = 2W_e$.

A more careful analysis of the slow-tumbling region shows that two types of saturation transmission effects are operative: (1) the motional effect, which contributes terms of type $B_L L(L+1)\mathcal{R}$ to the $w_{L,L}$, and (2) nuclear spin-flip processes, which in the fast-motional case depend on b. (See Section 3.) For $|\mathcal{H}_1(\Omega)|/\mathcal{R} \lesssim 1$ (i.e., $\tau_R \lesssim 10^{-9}$ sec) one gets values of $b \sim 10$–40 representing strong coupling of the hyperfine lines.[14] But when $|\mathcal{H}_1(\Omega)|/\mathcal{R} \gg 1$, and only residual motional effects are important, one must examine their effects more carefully.

In Section 1 a hypothetical case called the *quasi-nitroxide* case, such that $\sqrt{\frac{3}{10}}|A_\parallel - a_N| \ll |a_N|$ (where a_N is the isotropic hyperfine splitting and $A_\parallel$ is the parallel component of an axially symmetric hyperfine tensor), was considered. [In reality, $a_N \approx 15$ G and $\sqrt{\frac{3}{10}}(A_\parallel - a_N) \approx 11$ G.] The quasi-nitroxide case allows one to use (van Vleck) perturbation theory on the pseudosecular terms to decouple the $C_{K,M}^L(t, i)$ and the $b_{K,M}^L(t, i)$ for the three allowed transitions and the three eigenstate pairs from the forbidden ESR transitions and the three NMR-type transitions. In particular, one obtains a simplified approximate nuclear spin-flip-induced transition probability (i.e., a W_n for $L = 0$) given by $2W'_n = (D^2/5)[\tau_R/(1 + \bar{b}_2^2\tau_R^2)]$, where $\tau_R = 1/6\mathcal{R}$, $D = -\frac{3}{2}(1/\sqrt{6})|\gamma_e|(A_\parallel - a_N)$ and $\bar{b}_2 = -\frac{1}{2}|\gamma_e|[a_N + \frac{1}{7}(A_\parallel - a_N)]$, which is essentially the fast-motional result, but is correct for slow motion (for the quasi-nitroxide) where its asymptotic behavior goes as $(D^2/5)\bar{b}_2^{-2}\tau_R^{-1}$. This W_n term couples the relaxation of all three allowed transitions (or more precisely eigenstate pairs) for $i = 1$, 2, and 3. [More generally, for $L \neq 0$, these W_n-type terms will couple the three allowed eigenstate pairs and will also couple coefficients $b_{K,M}^L(i)$ of different L values.]

In the limit of slow motion we can then write $b = W'_n/W_e$ as

$$b = \frac{\frac{1}{2}(D^2/5)\bar{b}_2^{-2}\tau_R^{-1}}{W_e},$$

which for $\mathcal{R}/W_e \gg 1$ will still allow $b \gtrsim 1$, and nuclear spin flips are an important part of the problem. For $\mathcal{R}/W_e \lesssim 1$, the contribution of nuclear spin flips is less important relative to effects of W_e.

The quasi-nitroxide model immediately leads to

$$\frac{W'_n}{6\mathcal{R}} = \frac{1}{5}\left(\frac{D}{\bar{b}_2}\right)^2 \ll 1,$$

indicating that motional effects spread the saturation within a hyperfine line much faster than nuclear spinflips occur. But for a true nitroxide, where D^2/b_2^2 is *not* much smaller than unity, this is no longer true, and one may expect the nuclear spin flips to play an almost comparable role. Thus we would not expect $b \ll 1$ until $\mathcal{R}/W_e \ll 1$, so that the importance of nuclear spin-flip terms should persist to almost as slow motions as does the direct motional effects.

5 SUMMARY

One may conclude that the general methods developed for steady-state saturation experiments in both the motional narrowing and slow-tumbling region may be applied to time-dependent experiments such as saturation recovery. The solution is again dependent on the same matrix representations. The complex coupled differential equations are most effectively solved in terms of separate diagonalizations in transition space (in which the relaxation and coherence matrices are defined) and in eigenstate (or eigenstate-pair) space (in which the transition probability matrix is defined). The saturation recovery-type experiment (which also includes pulsed-ELDOR) may be readily handled by a general procedure, based on having a weak nonsaturating observing mode.

One finds from the analysis of spectra with hyperfine lines exhibiting coupled relaxation (with a nitroxide being a particular example) that, quite generally, the saturation recovery signal is dominated by a single exponential decay of time constant $T_1 = (2W_e)^{-1}$ despite the complexities of coupled relaxation that may exist. Simply stated, this is because when W_n or ω_{HE} are much greater than W_e, so as strongly to couple the relaxation of the eigenstate pairs, then the whole spectrum first rapidly adjusts to a common level of saturation with time constants $\sim W_n^{-1}$ or ω_{HE}^{-1} and then proceeds to relax to equilibrium more slowly with T_1, which is the slow decay observed experimentally. When a steady-state pulse approximation (i.e., the saturating pulse is on for times > the T_1's) is applicable, then one finds the fast decays all have much weaker amplitudes (proportional to their decay time constants). For W_n, $\omega_{HE} \ll W_e$, the lines are essentially uncoupled and all decays are $\sim T_1$. However, when W_n, $\omega_{HE} \sim W_e$, then more complex behavior may be seen with several (not very different) decay constants, which are weighted

differently for ELDOR versus direct observation. Thus ELDOR would be helpful in deciphering the different decays. When W_n, $\omega_{HE} \ll W_e$, it is still possible to observe ELDOR-recovery effects with time constant $\approx T_1$, but with a signal attenuated by factors of the order of $b = W_n/W_e$ or $Ab'' = \omega_{HE}/W_e$.

In the slow-motional case, for a simple line, the important comparison is between $\mathcal{R}$ versus W_e, where $\mathcal{R}$ is the rotational diffusion constant. For $\mathcal{R} \gg W_e$ (a frequent situation even in the slow-motional region), the rotational reorientation spreads the saturation over the whole spectrum, and the observed slow decay is again given by $T_1 = (2W_e)^{-1}$. For $\mathcal{R} \ll W_e$ each orientational component of the spectrum is separately saturated and it relaxes with $T_1 = (2W_e)^{-1}$. The region of $6\mathcal{R} \sim W_e$ allows for the superposition of several decays of comparable order of magnitude that might be effectively explored by a combination of direct and ELDOR-observational techniques. The multiple-line (e.g., the nitroxide) case involves a combination of reorientational and nuclear spin-flip effects.

ACKNOWLEDGMENTS

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