and 0.33) fluorescent quantum yields of the longest chain pair, **3** and **6**.

The somewhat longer intrinsic lifetimes of the sulfur compounds are almost compensated by their lower fluorescent quantum yields so that the oxygen and sulfur compounds of comparable chain length have nearly the same predicted lifetimes.

Since these predicted observable lifetimes were determined in dilute solutions without the presence of obvious quenchers or energy receptors and since the composite rate of all decay processes from the excited state is the inverse of the observable lifetime, a minimum may be placed on the rate of energy transfer from the first excited singlet state of these dyes to quenchers or acceptor molecules. Investigation of the energy transfer rates to acceptors in dilute solutions is a logical step which we plan to investigate.

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Theory of Saturation and Double Resonance in Electron Spin Resonance Spectra. VI. Saturation Recovery[1]

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The general theory of Freed for steady-state saturation and double resonance in esr spectra of free radicals is extended to cover time-dependent experiments. The solution is again found to depend on the same matrix representations developed in the earlier work. Particular attention is paid to saturation recovery in the light of recent such experiments. It is shown that while the general solutions yield sums of many exponential decays, the dominant observation may, to a first approximation in many cases, be described in terms of single $T_1 = \frac{1}{2}W_e$, where W_e is the electron-spin flip rate, in agreement with recent observations. This T_1 is characteristically the slowest decay constant, and is either well separated from the much faster decays (due to nuclear spin flip, exchange, and/or reorientational effects), or may be difficult to distinguish from decay constants of comparable magnitude (due to the same type of effects). Both conventional saturation recovery and eldor-type recoveries are discussed from this point of view. The general approach given is equally adaptable to cases of esr spectra in the motional narrowing region as well as esr spectra characteristic of slow tumbling. Both cases are discussed in detail with several examples given. In particular, in the slow tumbling region for the case of a radical with hyperfine structure (*e.g.*, a nitroxide), it is shown that, in general, both direct reorientational effects as well as nuclear spin flip processes contribute directly to the relaxation modes. The analysis given emphasizes analytic aspects although the general expressions, appropriate for accurate computer simulation, are given.

I. Introduction

Recently, there has been growing interest in pulsed esr experiments on free radicals in liquids, in particular, saturation recovery-type experiments.[2] The relaxation behavior of such systems is, in general, rather complex, and has been the subject of a series of papers (I–V) analyzing steady-state saturation and double resonance behavior.[3-9] A review of some of these aspects has recently been given.[10] In the future, one may expect to see an increase in importance of pulsed techniques, so it was deemed ap-

propriate to adapt the steady-state saturation theory to such techniques, and this is the main objective of the present paper. Our main emphasis is on saturation recovery, but we also include some comments on pulsed eldor,[9] which, in principle, may be thought of as a saturation recovery, but with observation at a frequency displaced from the high-power pulse frequency. Our methods, however, could be extended to free-induction decay and echo-type experiments for the free-radical systems.

In developing our analysis, we are struck by the close similarity between the values of W_e obtained by steady-state saturation techniques involving an analysis of the complex relaxation paths[6,11-14] and $(2T_1)^{-1}$ obtained (but not analyzed) from the saturation recovery experiments for similar systems also involving complex relaxation.[2] Thus, another objective of the present work is to demonstrate that over a wide range of types of systems, the saturation recovery experiment is simply interpreted. In this context we emphasize analytic results, but we also give the general expressions which are amenable to computer methods already developed.

Also, recent theoretical and experimental work, which has focused on esr spectra in the slow-tumbling region, has (1) extended the range of motional reorientation times over which accurate analyses could be made of these motions and (2) demonstrated that interesting features of the motion (*i.e.*, deviations from Brownian motion) could be obtained.[15] There have been some studies of saturation effects in such cases[12,15-17] and a theoretical framework has been developed.[12,18-21] It is another objective of the present work to show how slow-motional saturation-recovery (and eldor-type) experiments may be analyzed by an extension of the theories already developed. We are able to take advantage of a number of *formal* similarities between a motional-narrowing theory and a slow motional theory to cast both in a single general framework. We are then able to establish analogies to clarify the more complex slow motional analysis.

We give in section II the extensions of the general formalism to time-dependent experiments. Our discussion here borrows heavily from the previous notation and methods[3-8,12,18-21] and the reader is referred to these sources for more complete discussion. Motional narrowing examples are discussed in section III, while slow tumbling is discussed in section IV. A summary is given in section V.

II. General Formulation

We start with the usual density-matrix equation of motion for $\sigma(t)$[3-8,10,22]

$$\dot{\sigma} = -(\mathcal{H}_0^{\times} + \epsilon(t)^{\times} + iR)(\sigma - \sigma_0) \tag{2.1}$$

where $\mathcal{H}_0$ is the zero-order Hamiltonian, $\epsilon(t)$ the interaction with the radiation field, R the relaxation matrix, σ_0 the equilibrium value, and the superscript times sign implies that for two operators A and B, $A^{\times}B \equiv [A,B]$.

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 $|\mathcal{H}_1(\Omega)^2|\tau_R^2 \ll 1$. More generally, we may write a stochastic Liouville expression for $\sigma(\Omega,t)$ wherein the assumption of motional narrowing need not be made[10,18,21]

$$\dot{\sigma}(\Omega,t) = -i(\mathcal{H}_0^{\times} + \epsilon(t)^{\times} + \mathcal{H}_1(\Omega)^{\times} + iR' - i\Gamma_\Omega)(\sigma(\Omega,t) - \sigma_0(\Omega)) \tag{2.2}$$

Here Γ_Ω is the Markov operator for the rotational tumbling, R' is that part of the relaxation matrix which is orientation independent, while

$$\sigma(t) = \int d\Omega \sigma(\Omega,t) P_0(\Omega) \equiv \langle P_0(\Omega)|\sigma(\Omega,t)|P_0(\Omega)\rangle \tag{2.3}$$

where the convenient bra-ket notation is introduced. When $|\mathcal{H}_1(\Omega)|/|\Gamma_\Omega| \ll 1$ eq 2.2 again becomes eq 2.1.

We first study the general approach to the time-dependent solution of eq 2.1, and then we generalize to cover eq 2.2. Thus we introduce the definitions

$$(\sigma(t) - \sigma_0)_{\lambda_j} \equiv \chi(t)_{\lambda_j} \tag{2.4a}$$

$$\chi(t)_{\lambda_j} = \sum_{n=-\infty}^{\infty} e^{in\omega t} Z(t)_{\lambda_j}^{(n)} \tag{2.4b}$$

and

$$Z(t)_{\lambda_j}^{(n)} = Z(t)_{\lambda_j}^{(n)'} + iZ(t)_{\lambda_j}^{(n)''} \tag{2.4c}$$

for the λ_jth transition. Then by analogy with the steady-state solutions,[3-8,10] we obtain the coupled partitioned-matrix equations

$$\begin{bmatrix} \frac{1}{\sqrt{2}}\dot{\mathbf{Z}}(t) \\ \frac{1}{\sqrt{2}}\dot{\mathbf{Z}}^*(t) \\ \frac{1}{2}\dot{\hat{\mathbf{X}}}(t) \\ \frac{1}{2}\dot{\tilde{\mathbf{X}}}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} - i\mathbf{K} & 0 & \sqrt{2}i\hat{\mathbf{d}} & \sqrt{2}i\tilde{\mathbf{d}} \\ 0 & \mathbf{R} + i\mathbf{K} & -\sqrt{2}i\hat{\mathbf{d}} & -\sqrt{2}i\tilde{\mathbf{d}} \\ \sqrt{2}i\hat{\mathbf{d}}^{\mathrm{tr}} & -\sqrt{2}i\hat{\mathbf{d}}^{\mathrm{tr}} & -\hat{\mathbf{W}} & -\mathbb{W} \\ \sqrt{2}i\tilde{\mathbf{d}}^{\mathrm{tr}} & -\sqrt{2}i\tilde{\mathbf{d}}^{\mathrm{tr}} & -\mathbb{W}^{\mathrm{tr}} & -\mathbf{W} \end{bmatrix} \times \begin{bmatrix} \frac{1}{\sqrt{2}}\mathbf{Z}(t) \\ \frac{1}{\sqrt{2}}\mathbf{Z}^*(t) \\ \frac{1}{2}\hat{\mathbf{X}}(t) \\ \frac{1}{2}\tilde{\mathbf{X}}(t) \end{bmatrix} + \begin{bmatrix} i\mathbf{Q}/\sqrt{2} \\ -i\mathbf{Q}/\sqrt{2} \\ 0 \\ 0 \end{bmatrix} \tag{2.5}$$

where we have introduced the definitions

$$\hat{X}_{\lambda_j} \equiv X_{\lambda_j^+} - X_{\lambda_j^-} \tag{2.6a}$$

and

$$\tilde{X}_{\lambda_j} \equiv X_{\lambda_j^+} + X_{\lambda_j^-} \tag{2.6b}$$

(where $\lambda_j^{\pm}$ are the $m_s = \pm$ states corresponding to the λ_jth transition) with the matrices $\hat{\mathbf{d}}, \tilde{\mathbf{d}}$, the transition probability matrices, $\hat{\mathbf{W}}$, $\tilde{\mathbf{W}}$, and $\mathbb{W}$, the width matrix $\mathbf{R}$, the coherence matrix $\mathbf{K}$, and the $\mathbf{Q}$ vector defined elsewhere.[6,7] Equation 2.5 is of the form of a complex symmetric matrix, which may therefore be solved by first diagonalizing the matrix of matrices (*i.e.*, partitioned matrix) on the right-hand side.

The steady-state solutions to eq 2.5 may be calculated by the methods already developed in I–V. In particular, the form of eq 2.5 is

$$\dot{\mathbf{M}}(t) = \mathbf{L}\mathbf{M} + \mathbf{Q}' \tag{2.7}$$

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

$$\mathbf{M}^{ss} = -\mathbf{L}^{-1}\mathbf{Q}' \tag{2.8}$$

If we define

$$\Delta\mathbf{Z}(t) \equiv \mathbf{Z}(t) - \mathbf{Z}^{ss} \tag{2.9a}$$

etc. or

$$\Delta\mathbf{M}(t) \equiv \mathbf{M}(t) - \mathbf{M}^{ss} \tag{2.9b}$$

then eq 2.7 may be written in terms of these deviations from steady-state value as

$$\Delta\dot{\mathbf{M}}(t) = \mathbf{L}\Delta\mathbf{M}(t) \tag{2.7a}$$

or

$$\Delta\mathbf{M}(t) = e^{\mathbf{L}t}\Delta\mathbf{M}(o) \tag{2.10}$$

so as $t \rightarrow \infty$, $\Delta\mathbf{M}(t) \rightarrow 0$.

We now assume that we may let $\mathcal{W} = 0$. This is so when the matrix elements of $\mathbf{W}$ obey

$$W_{\alpha\pm,\beta\mp} = W_{\alpha\mp,\beta\pm} \tag{2.11a}$$

$$W_{\alpha\pm,\beta\pm} = W_{\alpha\mp,\beta\mp} \tag{2.11b}$$

(where α and β represent any nuclear spin configurations and the $\pm$ signs refer to m_s) which is a common situation.[6,7] We further assume that only esr tranitions are excited, so that $\hat{\mathbf{d}} = 0$ (For endor $\hat{d} \neq 0$) and the $\tilde{\chi}(t)$ may now be decoupled from the relevant part of the solution, *i.e.*, eq 2.5 becomes

$$\begin{bmatrix} \frac{1}{\sqrt{2}}\dot{\mathbf{Z}}(t) \\ \frac{1}{\sqrt{2}}\dot{\mathbf{Z}}(t) \\ \frac{1}{2}\dot{\hat{\mathbf{X}}}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R}-i\mathbf{K} & 0 & \sqrt{2}i\hat{\mathbf{d}} \\ 0 & \mathbf{R}+i\mathbf{K} & -\sqrt{2}i\hat{\mathbf{d}} \\ \sqrt{2}i\hat{\mathbf{d}}^{tr} & -\sqrt{2}i\hat{\mathbf{d}}^{tr} & -\hat{\mathbf{W}} \end{bmatrix} \times \begin{bmatrix} \frac{1}{\sqrt{2}}\mathbf{Z}(t) \\ \frac{1}{\sqrt{2}}\mathbf{Z}^*(t) \\ \frac{1}{2}\hat{\mathbf{X}}(t) \end{bmatrix} + \begin{bmatrix} i\mathbf{Q}/\sqrt{2} \\ -i\mathbf{Q}/\sqrt{2} \\ 0 \end{bmatrix} \tag{2.12}$$

In the simple two-level, one-line case, the substitutions $\mathbf{K} \rightarrow \Delta\omega_\lambda$, $-\mathbf{R} \rightarrow T_2^{-1}$, $2\hat{\mathbf{d}} \rightarrow -\omega_1$, $\hat{\mathbf{W}} \rightarrow T_1^{-1}$, $\mathbf{Z} \rightarrow M_x$, $\mathbf{Z}'' \rightarrow M_y$, $\frac{1}{2}\hat{X} \rightarrow (M_0 - M_z)$ yield the familiar Bloch equations, which may be solved by standard methods (*e.g.*, Laplace transforms).[23] However the more general eq 2.12 in operator form are more conveniently handled by diagonalization methods. (The $\mathbf{R}$ and $\mathbf{K}$ matrices are $M \times M$ square matrices in the "space" of induced transitions while $\mathbf{W}$ is an $\frac{1}{2}M \times \frac{1}{2}N$ square matrix in the "eigenstate-pair" space; thus $\mathbf{d}$ is an $M \times \frac{1}{2}N$ rectangular matrix.) Note that since the $\mathbf{Z}''$ elements are typically detected, we shall need the unitary transformation

$$\begin{bmatrix} \mathbf{Z}' \\ i\mathbf{Z}'' \\ \frac{1}{2}\hat{\mathbf{X}} \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}}\mathbf{1} & \frac{1}{\sqrt{2}}\mathbf{1} & 0 \\ \frac{1}{\sqrt{2}}\mathbf{1} & -\frac{1}{\sqrt{2}}\mathbf{1} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}}\mathbf{Z} \\ \frac{1}{\sqrt{2}}\mathbf{Z}^* \\ \frac{1}{2}\hat{\mathbf{X}} \end{bmatrix} = \mathbf{u} \begin{bmatrix} \frac{1}{\sqrt{2}}\mathbf{Z} \\ \frac{1}{\sqrt{2}}\mathbf{Z}^* \\ \frac{1}{2}\hat{\mathbf{X}} \end{bmatrix} \tag{2.13}$$

which transforms eq 2.12 into

$$\begin{bmatrix} \mathbf{Z}'(t) \\ i\mathbf{Z}''(t) \\ \frac{1}{2}\dot{\hat{\mathbf{X}}}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} & -i\mathbf{K} & 0 \\ -i\mathbf{K} & \mathbf{R} & 2i\hat{\mathbf{d}} \\ 0 & 2i\hat{\mathbf{d}}^{tr} & -\hat{\mathbf{W}} \end{bmatrix} \begin{bmatrix} \mathbf{Z}'(t) \\ i\mathbf{Z}''(t) \\ \frac{1}{2}\mathbf{X}(t) \end{bmatrix} + \begin{bmatrix} 0 \\ i\mathbf{Q} \\ 0 \end{bmatrix} \tag{2.14}$$

with the new symmetric matrix on the right-hand side of eq 2.14.

We now particularize the solutions to saturation recovery-type experiments, such that observations are made only for small d. We thus wish to develop a perturbation scheme to lowest order in $\mathbf{d}$. For this purpose, the matrix of eq 2.12 is more satisfactory than that of eq 2.14, since it lacks the two degenerate submatrices ($\mathbf{R}$) along the partitioned-diagonal which appear in eq 2.14. Note, however, that for $K_\lambda = 0$, *i.e.*, λth line is on resonance, that if $-R_\lambda \equiv T_{2,\lambda}^{-1} = T_{1,\lambda}^{-1}$ then a triple degeneracy occurs with respect to the λth transition which 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.[24] We first introduce the partitioned matrices

$$\mathbf{A} = \begin{bmatrix} \mathbf{R}-i\mathbf{K} & 0 & 0 \\ 0 & \mathbf{R}+i\mathbf{K} & 0 \\ 0 & 0 & -\hat{\mathbf{W}} \end{bmatrix}$$

$$\mathbf{B} = i\sqrt{2} \begin{bmatrix} 0 & 0 & \hat{\mathbf{d}} \\ 0 & 0 & -\hat{\mathbf{d}} \\ \hat{\mathbf{d}}^{tr} & -\hat{\mathbf{d}}^{tr} & 0 \end{bmatrix} \tag{2.15b}$$

where $\mathbf{L} = \mathbf{A} + \mathbf{B}$ and consider a vector $\mathbf{M}$ (*cf.* eq 2.7) and solve for

$$\mathbf{OAO}^{-1}(\mathbf{OM}) + \mathbf{OBO}^{-1}(\mathbf{OM}) \cong (\mathbf{A}+\mathbf{b})\mathbf{M}' \tag{2.16}$$

where the partitioned matrix $\mathbf{B}$ is transformed approximately to the form of $\mathbf{A}$, (*i.e.*, partitioned matrices along the diagonal) by the (complex) orthogonal transformation $\mathbf{O}$ to lowest order in d. That is we let

$$\mathbf{M}' = e^{i\mathbf{S}}\mathbf{M} \cong (1 + i\mathbf{S})\mathbf{M} \tag{2.17}$$

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

$$\mathbf{S} = +i(\mathbf{A}^{\times})^{-1}\mathbf{B} \tag{2.18}$$

and

$$\mathbf{b} = \tfrac{1}{2}\mathbf{B}^{\times}\mathbf{S} = -\tfrac{1}{2}\mathbf{B}^{\times}[(\mathbf{A}^{\times})^{-1}\mathbf{B}] \tag{2.19}$$

That is

$$\mathbf{S} = \begin{bmatrix} 0 & 0 & -(\mathbf{A}^{0,d\times})^{-1}\sqrt{2}\hat{\mathbf{d}} \\ 0 & 0 & (\mathbf{A}^{c,d\times})^{-1}\sqrt{2}\hat{\mathbf{d}} \\ -(\mathbf{A}^{d,o\times})^{-1}\sqrt{2}\hat{\mathbf{d}}^{tr} & (\mathbf{A}^{d,c\times})^{-1}\sqrt{2}\hat{\mathbf{d}}^{tr} & 0 \end{bmatrix} \tag{2.20}$$

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

$$(\mathbf{A}^{j,d\times})^{-1}\hat{\mathbf{d}} = \lim_{\epsilon\to 0_+} -\int_0^\infty d\tau \exp[-\epsilon\tau]\exp[\mathbf{A}^j\tau]\hat{\mathbf{d}}\exp[-\mathbf{A}^d\tau] \qquad j = o \text{ or } c \quad (2.21a)$$

and

$$(\mathbf{A}^{d,j\times})^{-1}\mathbf{d}^{tr} = \lim_{\epsilon\to 0_+} -\int_0^\infty \hat{d}\tau \exp[-\epsilon\tau]\exp[\mathbf{A}^d\tau]\hat{\mathbf{d}}^{tr}\exp[-\mathbf{A}^j\tau] \qquad j = o \text{ or } c \quad (2.21b)$$

where

$$\mathbf{A}^o = \mathbf{R} - i\mathbf{K},\ \mathbf{A}^c = \mathbf{R} + i\mathbf{K} = \mathbf{A}^{o*},\ \mathbf{A}^d = -\hat{W} \quad (2.22)$$

(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 performing the integration.) Thus in an M dimensional basis set $a, b \ldots$ in which $\mathbf{A}^o$ (or $\mathbf{A}^c$) is diagonal and an $N/2$ dimensional basis set $\alpha,\beta \ldots$ in which $\mathbf{A}^d$ is diagonal, one has, for example

$$[(\mathbf{A}^{o,d\times})^{-1}]_{a\alpha b\beta} = \frac{\delta_{ab}\delta_{\alpha\beta}}{A_{aa}{}^o - A_{\alpha\alpha}{}^d} = \frac{\delta_{ab}\delta_{\alpha\beta}}{(-R_{aa}) - \hat{W}_{\alpha\alpha} + iK_{aa}} \quad (2.23)$$

Thus the expansion is in terms of

$$|\sqrt{2}\hat{d}_{aa}|/|(-R_{aa}) - \hat{W}_{\alpha\alpha} + iK_{aa})| \ll 1 \quad (2.24)$$

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

$$|\frac{\sqrt{2}}{2}\omega_1|/|T_2^{-1} - T_1^{-1} + i\Delta\omega| \ll 1 \quad (2.24a)$$

One finds, utilizing the fact that the $\mathbf{A}^j$ are symmetric matrices, that

$$[(\mathbf{A}^{j,d\times})^{-1}\hat{\mathbf{d}}]^{tr} = -[(\mathbf{A}^{d,j\times})^{-1}\hat{\mathbf{d}}^{tr}] \qquad j = o,c \quad (2.25)$$

from which it follows that $\mathbf{S}$ is antisymmetric, as required. Also we have

$$\mathbf{b} = \begin{bmatrix} \mathbf{C}+\mathbf{C}^{tr} & -(\mathbf{C}^{tr}+\mathbf{C}^*) & 0 \\ -(\mathbf{C}+\mathbf{C}^{tr*}) & \mathbf{C}^*+\mathbf{C}^{tr*} & 0 \\ 0 & 0 & \mathbf{E}+\mathbf{E}^{tr} \end{bmatrix} \quad (2.26)$$

where

$$\mathbf{C} = \hat{\mathbf{d}}(\mathbf{A}^{d,o\times})^{-1}\hat{\mathbf{d}}^{tr} \quad (2.27a)$$

$$\mathbf{E} = 2\hat{\mathbf{d}}^{tr}\,\mathrm{Re}[(\mathbf{A}^{o,d\times})^{-1}]\hat{\mathbf{d}} \quad (2.27b)$$

When the transformation of eq 2.13 is utilized, then in the basis of $\mathbf{Z}'$, $i\mathbf{Z}''$, $\frac{1}{2}\hat{\mathbf{X}}$ one has

$$\mathbf{S} = 2\begin{bmatrix} 0 & 0 & -i[\mathrm{Im}\,(\mathbf{A}^{d,o\times})^{-1}]\hat{\mathbf{d}}^{tr} & -[\mathrm{Re}\,(\mathbf{A}^{d,o\times})^{-1}]\hat{\mathbf{d}}^{tr} \\ 0 & 0 & -i[\mathrm{Im}\,(\mathbf{A}^{o,d\times})^{-1}]\hat{\mathbf{d}} & -[\mathrm{Re}(\mathbf{A}^{o,d\times})^{-1}]\hat{\mathbf{d}} \\ -i[\mathrm{Im}\,(\mathbf{A}^{d,o\times})^{-1}]\hat{\mathbf{d}}^{tr} & -i[\mathrm{Im}\,(\mathbf{A}^{o,d\times})^{-1}]\hat{\mathbf{d}} & 0 & 0 \\ -[\mathrm{Re}\,(\mathbf{A}^{d,o\times})^{-1}]\hat{\mathbf{d}}^{tr} & -[\mathrm{Re}(\mathbf{A}^{o,d\times})^{-1}]\hat{\mathbf{d}} & 0 & 0 \end{bmatrix} \quad (2.28)$$

while

$$\mathbf{b} = 2\begin{bmatrix} 0 & 2i\,\mathrm{Im}\,\mathbf{C}^{tr} & 0 \\ 2i\,\mathrm{Im}\,\mathbf{C} & 2\mathrm{Re}\,(\mathbf{C}+\mathbf{C}^{tr}) & 0 \\ 0 & 0 & \mathbf{E}+\mathbf{E}^{tr} \end{bmatrix} \quad (2.29)$$

Thus one may solve either eq 2.12 or 2.14 in the approximations used as

$$\Delta\dot{\mathbf{M}}'(t) \cong (\mathbf{A}+\mathbf{b})\Delta\mathbf{M}'(t) \quad (2.30a)$$

so

$$\Delta\mathbf{M}'(t) \cong \exp[-(\mathbf{A}+\mathbf{b})t]\Delta\mathbf{M}'(0) \quad (2.30b)$$

and

$$\Delta\mathbf{M}(t) \cong (1-i\mathbf{S})\exp[-(\mathbf{A}+\mathbf{b})t](1+i\mathbf{S})\Delta\mathbf{M}(0) \quad (2.30c)$$

Note that $\mathbf{A} + \mathbf{b}$ given either by eq 2.15a plus eq 2.26 (in the representation of eq 2.12) or by $\mathbf{uAu}^{tr}$ plus eq 2.29 (in the representation of eq 2.14) have the eigenstate-pair space (represented by superscript d) (approximately) uncoupled from the transition space (o and c superscripts) so $-\hat{\mathbf{W}}' + (\mathbf{E} + \mathbf{E}^{tr})$ may be diagonalized separately. However

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

will in general couple $\mathbf{Z}'$ to $\mathbf{Z}''$ (or alternatively the coupling can be written for $\mathbf{Z}$ and $\mathbf{Z}''$ from eq 2.15a and eq 2.26).

We note here that it is always possible to choose basis sets $a,b \ldots$ for transition space and $\alpha,\beta \ldots$ for eigenstate-pair space such that $\hat{\mathbf{d}}$ has a simple structure with $\hat{d}_{i,\hat{j}} = \hat{d}_{i,i}\delta_{\hat{i},j}$ where $\hat{j}$ refers to the eigenstate-pair corresponding to the jth esr transition. Several examples appear below.[24b] However, this choice will not, in general, simultaneously diagonalize $\mathbf{A}^o$ and $\mathbf{A}^d$. In those cases where it does, and if $\hat{d}_{i,\hat{i}} = d$ independent of i, it then follows from the above definitions that $\mathbf{U}^d = \mathbf{U}^o$ (see below), $\mathbf{C}^{tr} = \mathbf{C}$, and $\mathbf{E}^{tr} = \mathbf{E}$. 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 elements $K_{i,i} \to 0$ representing resonances.

(A) Simple One Line Case. We illustrate the above 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 $\mathbf{C} = \mathbf{C}^{tr}$, $\mathbf{E} = \mathbf{E}^{tr}$ and

$$\mathbf{S} = \frac{+\omega_1}{(T_2^{-1} - T_1^{-1})^2 + \Delta\omega^2} \times \begin{bmatrix} 0 & 0 & -i\Delta\omega \\ 0 & 0 & (T_2^{-1} - T_1^{-1}) \\ i\Delta\omega & -(T_2^{-1} - T_1^{-1}) & 0 \end{bmatrix} \quad (2.31a)$$

and

$$\mathbf{b} = \frac{\omega_1^2}{(T_2^{-1} - T_1^{-1})^2 + \Delta\omega^2} \times \begin{bmatrix} 0 & -i\Delta\omega & 0 \\ -i\Delta\omega & (T_2^{-1} - T_1^{-1}) & 0 \\ 0 & 0 & -(T_2^{-1} - T_1^{-1}) \end{bmatrix} \quad (2.31b)$$

in the Z', iZ'', $\frac{1}{2}\hat{X}$, 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

$$\mathbf{A}+\mathbf{b} \cong \begin{bmatrix} -T_2^{-1} & -i\Delta\omega & 0 \\ -i\Delta\omega & -T_2^{-1}+\delta & 0 \\ 0 & 0 & -T_1^{-1}-\delta \end{bmatrix} \tag{2.32}$$

where

$$\delta = \omega_1^2(T_2^{-1}-T_1^{-1})/[(T_2^{-1}-T_1^{-1})^2+\Delta\omega^2] \tag{2.32a}$$

The 2 × 2 submatrix may be diagonalized by the orthogonal transformation U

$$\mathbf{U} = \begin{bmatrix} [1-a_+]^{-1/2} & [1-a_+^{-1}]^{-1/2} \\ [1-a_-]^{-1/2} & -[1-a_-^{-1}]^{-1/2} \end{bmatrix} \tag{2.33a}$$

such that

$$\mathbf{U}[\mathbf{A}+\mathbf{b}]\mathbf{U}^{-1} = \begin{bmatrix} E_+ & O \\ O & E_- \end{bmatrix} \tag{2.33b}$$

where

$$a_\pm = (\delta \pm \sqrt{\delta^2-4\Delta\omega^2})^2/4\Delta\omega^2 \tag{2.33c}$$

and

$$E_\pm = -T_2^{-1}+\delta/2 \pm \tfrac{1}{2}\sqrt{\delta^2-4\Delta\omega^2} \tag{2.33d}$$

For $|\delta^2/\Delta\omega^2| \ll 1$, *i.e.*, a line off-resonance, one has complex eigenvalues of eq 2.33 of $\lambda \cong -T_2^{-1} + (\delta/2) \mp i\Delta\omega$ corresponding to the eigen solutions $(1/\sqrt{2})Z$ and $(1/\sqrt{2})Z^*$ (*cf.* eq 2.15a); while for $|\delta^2/\Delta\omega^2| \gg 1$, *i.e.*, a line close to resonance, one has simple decaying solutions $\lambda \cong -T_2^{-1}$ and $-T_2^{-1} + \delta$ for eigen solutions $\mathbf{Z}'$ and $i\mathbf{Z}''$, respectively (*cf.* eq 2.32). It then follows from the above equations that the complete solution is

$$\begin{bmatrix} \Delta Z' \\ \Delta Z'' \\ \frac{1}{2}\Delta\hat{X}(t) \end{bmatrix} = (1-i\mathbf{S})\mathbf{U}^{tr} \begin{bmatrix} e^{-E_+t} & & \\ & e^{-E_-t} & \\ & & e^{-(T_1^{-1}+\delta)t} \end{bmatrix} \times \mathbf{U}(1+i\mathbf{S}) \begin{bmatrix} \Delta Z'(0) \\ \Delta Z''(0) \\ \frac{1}{2}\Delta\hat{X}(0) \end{bmatrix} \tag{2.34}$$

where only terms linear in **S** are kept. Some simple and well-known limiting cases are[25]

(1) $\Delta\omega = 0$. Then

$$\Delta Z''(t) = e^{-t(T_2^{-1}-\delta)}\Delta Z''(0) + \frac{\omega_1}{(T_2^{-1}-T_1^{-1})}(e^{-t[T_2^{-1}-\delta]}-e^{-t[T_1^{-1}+\delta]})\Delta\tfrac{1}{2}\hat{X}(0) \tag{2.35}$$

(2) $T_2^{-1} \gg T_1^{-1}$, then for $t > T_2^{-1}$

$$\Delta Z''(t) \cong \frac{-\omega_1 T_2^{-1}}{T_2^{-2}+\Delta\omega^2} e^{-t[(T_1^{-1}+\delta]} \left[\tfrac{1}{2}\Delta\hat{X}(0)\right] \tag{2.36}$$

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

$$M_x(0) = \alpha\Delta\omega\omega_1 T_2^2 M_0$$
$$M_y(0) = \alpha\omega_1 T_2 M_0 \tag{2.37}$$
$$M_z(0) = \alpha M_0$$

and

$$\Delta Z'(0) = \Delta M_x(0) = \Delta\omega T_2 \Delta M_y(0) = \Delta\omega T_2^2\omega_1(\alpha-1)M_0$$
$$\Delta Z''(0) = \Delta M_y(0) = (\alpha-1)\omega_1 T_2 M_0$$
$$-\Delta\tfrac{1}{2}\hat{X} = \Delta M_z(0) = (\alpha-1)M_0 \tag{2.38}$$

Then for case 1 we have

$$\Delta Z''(t) \cong \frac{-(1-\alpha)\omega_1 T_2 M_0}{(T_2^{-1}-T_1^{-1})}[T_2^{-1}e^{-t(T_1^{-1}+\delta)} - T_1^{-1}e^{-t(T_1^{-1}-\delta)}] \tag{2.39}$$

while for case 2 we have

$$\Delta Z''(t) \cong \frac{-(1-\alpha)\omega_1 T_2^{-1} M_0}{T_2^{-2}+\Delta\omega^2} e^{-t[T_1^{-1}+\delta]} \tag{2.40}$$

B. General Case for $T_2 \ll T_1$. The formalism given above permits the solution of a variety of situations involving saturation recovery for which eq 2.34 is immediately generalized, and the general expression of eq 2.5 may be used for more general cases. We will 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 which otherwise appear complex to describe. In this case we have from eq 2.14, 2.15, 2.28, and 2.29 that for

$$|\mathbf{R}|t > 1 \tag{2.41}$$

$$\Delta\mathbf{Z}''(t) \cong [\mathrm{Re}(\mathbf{A}^{o,d^\times})^{-1}2\mathbf{d}]e^{-\hat{\mathbf{W}}t}\Delta\tfrac{1}{2}\hat{X}(0) \tag{2.42}$$

In eq 2.42, we have dropped the small correction $\mathbf{E}+\mathbf{E}^{tr}$ of eq 2.29 to $\hat{\mathbf{W}}$. In the simple line case, this is just the neglect of δ of eq 2.32a compared to T_1^{-1}, which is valid since for $T_2^{-1} > T_1^{-1}$

$$\delta T_1 \cong \frac{\omega_1^2 T_1 T_2^*}{1+T_2^{*2}\Delta\omega^2} \le \omega_1^2 T_1 T_2^* \ll 1 \tag{2.43}$$

(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 which diagonalize $\mathbf{A}^o$, $\mathbf{A}^c$, and $\mathbf{A}^d$, respectively, we may rewrite eq 2.42 as

$$\Delta\mathbf{Z}''(t) \cong -\int_0^\infty d\tau\{\mathbf{U}_0^{tr}\exp[\tau\mathbf{U}_0(\mathbf{R}-i\mathbf{K})\mathbf{U}_0^{tr}]\mathbf{U}_0 + \mathbf{U}_c^{tr}\exp[\tau\mathbf{U}_c(\mathbf{R}+i\mathbf{K})\mathbf{U}_c^{tr}]\mathbf{U}_c\}\hat{\mathbf{d}}\mathbf{U}_d^{tr} \times \exp[\tau\mathbf{U}_d(+\hat{\mathbf{W}})\mathbf{U}_d^{tr}]\exp[\mathbf{U}_d^{tr}(-\hat{\mathbf{W}}t)\mathbf{U}_d^{tr}]\mathbf{U}_d\Delta\tfrac{1}{2}\hat{\mathbf{X}}(0) \tag{2.44}$$

(The convergence factor has been dropped in eq 2.44 since $|\mathbf{R}| > |\mathbf{W}|$ implies satisfactory behavior of the integrals.) Note, however, by the functional properties $\mathbf{U}_o = \mathbf{U}_o\{\mathbf{R}, -\mathbf{ik}\}$ and $\mathbf{U}_c = \mathbf{U}_c\{\mathbf{R}, +\mathbf{iK}\}$ it follows that $\mathbf{U}_c = \mathbf{U}_o^*$. Then if we let

$$\mathbf{r}-i\mathbf{k} \equiv \mathbf{U}_0(\mathbf{R}-i\mathbf{K})\mathbf{U}_0^{tr} \tag{2.45a}$$

and

$$\mathbf{w} \equiv \mathbf{U}_d(\hat{\mathbf{W}})\mathbf{U}_d^{tr} \tag{2.45b}$$

eq 2.44 may be written more simply as

$$\Delta\mathbf{Z}''(t) \cong -\int_0^\infty d\tau\,\mathrm{Re}\{\mathbf{U}_0^{tr}\exp[\tau(\mathbf{r}-i\mathbf{k})]\mathbf{U}_0\}(2\hat{\mathbf{d}})\mathbf{U}_d^{tr} \times \exp[(\tau-t)\mathbf{w}]\mathbf{U}_d\Delta\tfrac{1}{2}\hat{\mathbf{X}}(0) \tag{2.46}$$

We now consider specific examples.

III. Motional Narrowing Examples

(A) *Well-Separated Hyperfine Lines (Nitroxide).* We first illustrate the application of our expression to a nitroxide in the motional narrowing region when the three Lorentzian hyperfine lines are well separated. If we consider just pure electron spin flip transitions or W_e, pseudo-secular END terms (bW_e), and spin exchange ($b''W_e$), we have[3-8]

$$\hat{\mathbf{W}} = 2W_e \begin{bmatrix} 1+2b''+b & -b''-b & -b'' \\ -b''-b & 1+2b''+2b & -b''-b \\ -b'' & -b''-b & 1+2b''+b \end{bmatrix} \tag{3.1}$$

Then

$$\mathbf{U}_d = \begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 1/\sqrt{6} & -2/\sqrt{6} & 1/\sqrt{6} \end{bmatrix} \tag{3.2}$$

and

$$\mathbf{w} = 2W_e \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1+3b''+b & 0 \\ 0 & 0 & 1+3b''+3b \end{bmatrix} \tag{3.3}$$

We also have

$$-R_{i,j} = T'_{2,i}{}^{-1}\delta_{i,j} + (\hat{W}_{i,j} - W_e\delta_{i,j}) \tag{3.4}$$

where the $T''_{2,i}{}^{-1}$ give the purely secular contributions to the ith hyperfine line. Also

$$K_{i,j} = \Delta\omega_i\delta_{i,j} \tag{3.5}$$

and

$$-\hat{d}_{i,j} = \tfrac{1}{2}\omega_1\delta_{i,j} = \tfrac{1}{2}\gamma_e B_1 \tag{3.5a}$$

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

For the general spectrum of well-separated lines we have for $i \neq j$[7]

$$|-R_{i,j}| = |\hat{W}_{i,j}| \ll |\omega_i - \omega_j| \qquad i \neq j \tag{3.6}$$

Thus $\mathbf{R} \pm i\mathbf{K} = \mathbf{r} \pm i\mathbf{k}$ is diagonal in the basis of the separate transitions, and $\mathbf{U}_0 = \mathbf{1}$ (except for higher-order terms in $2W_e b''$ and $2W_e b$ *vs.* $(\omega_i - \omega_j)$). Then elements of eq 2.46 are

$$\Delta Z''_i(t) = -\sum_{j,\beta}\int_0^\infty d\tau\, \mathrm{Re}\exp[\tau(r_{i,i} - ik_{i,i})]\omega_1(U_d{}^{tr})_{i,\beta} \times \exp[(\tau - t)w_{\beta\beta}](U_d)_{\beta j}\Delta\tfrac{1}{2}\hat{X}_j(0) =$$

$$+\omega_1 \mathrm{Re}\sum_{j,\beta}\frac{e^{-w_{\beta\beta}t}}{r_{i,i} + w_{\beta\beta} - i\Delta\omega_i}(U_d{}^{tr})_{i\beta}(U_d)_{\beta\hat{j}}\Delta\tfrac{1}{2}X_{\hat{j}}(0) \tag{3.7}$$

It is necessary, in order to complete the solution, to specify the initial condition

$$\tfrac{1}{2}\hat{X}_{\hat{j}}(0) = -(M_{z,\hat{j}}(0) - M_{0,\hat{j}}) = (1-\alpha_j)M_{0,\hat{j}} \tag{3.8}$$

or

$$\alpha_{\hat{j}} = M_{z,\hat{j}}(0)/M_{0,\hat{j}} \tag{3.8a}$$

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

(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

$$w_{\beta\beta} \cong 2W_e = T_1{}^{-1} \quad \text{all } \beta \tag{3.9}$$

Then, since $\Sigma_\beta(U_d{}^{tr})_{\hat{i}\beta}(U_d)_{\beta\hat{j}} = \delta_{i,j}$, eq 3.7 becomes

$$\cong -\mathrm{Re}\,\frac{\omega_1(1-\alpha_{\hat{i}})M_{0,\hat{j}}}{T'_{2\hat{i},j}{}^{-1} + i\Delta\omega_i}e^{-t/T_1}\delta_{i,j} \tag{3.10}$$

which is just eq 2.40 for each line.

(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 $\alpha_{\hat{i}} = \alpha_{\hat{j}} = \alpha = \frac{1}{3}\alpha_{\text{total}}) \neq 0$. Then since $\Sigma_j(U_d)_{\beta\hat{j}} = \delta_{\beta,1}\sqrt{3}$ eq 3.7 becomes

$$\Delta Z''_i(t) = -\mathrm{Re}\,\omega_1(1-\alpha)M_{0,\hat{i}}\frac{e^{-t/T_1}}{(-R_{i,i})^{-1} - T_1{}^{-1} + i\Delta\omega_i} \tag{3.11}$$

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 2.12 of the values of $\hat{\mathbf{X}}$ resulting from a pulse of finite duration, $\Delta t'$. However if $\Delta t' \geq w_{\beta\beta}{}^{-1} \leq T_1 = (2W_e)^{-1}$, then one may use as the ratios $\alpha_{\hat{j}}/\alpha_{\hat{i}} \cong \hat{\mathbf{X}}_{\hat{j}}{}^{ss}/\hat{\mathbf{X}}_{\hat{i}}{}^{ss}$, *i.e.*, the steady-state values obtained in the presence of the saturating field. Thus for case 3, the steady-state approximation on the pulse duration, one has

$$\hat{\mathbf{X}}^{satd} = -2\hat{\mathbf{W}}^{-1}\mathbf{d}_{satd}{}^{tr}\mathbf{Z}''^{satd} \tag{3.12}$$

with $\mathbf{Z}''^{satd}$ calculated by standard means.[3-8] Then we can use the relation (appropriate when only pure esr transitions are generated) for the saturation parameters $\Omega_{i,j}$[7]

$$4(\hat{W}^{-1})_{\hat{i},\hat{j}} = \Omega_{i,j} \tag{3.12a}$$

to rewrite eq 3.7 as (with $\hat{d}_{i,\hat{j}}{}^{satd} \equiv \frac{1}{2}\omega_1{}^s$).

$$\Delta Z''_i(t) = \omega_1 \mathrm{Re}\sum_{j,\beta,k}\frac{e^{-w_{\beta\beta}t}}{r_{i,i} + w_{\beta\beta} - i\Delta\omega_i}(U_d)_{\hat{i}\beta}{}^{tr}(U_d)_{\beta\hat{j}} \times \frac{\Omega_{j,k}}{4}\frac{Z''_k{}^{satd}}{2}\omega_1{}^s = \omega_1 \mathrm{Re}\sum_{k,\beta}\frac{e^{-w_{\beta\beta}t}}{r_{i,i} + w_{\beta\beta} - i\Delta\omega_i}\frac{1}{w_{\beta\beta}} \times (U_d)_{\hat{i}\beta}{}^{tr}(U_d)_{\beta\hat{k}}\frac{Z''_k{}^{satd}}{2}\omega_1{}^s \tag{3.13}$$

where the second equality follows because

$$\mathbf{w}^{-1} = \mathbf{U}_d\hat{\mathbf{W}}^{-1}\mathbf{U}_d{}^{tr} \tag{3.14}$$

Case 1 is obtained from the second form of eq 3.13 by setting only one $Z''_k{}^{satd}$ unequal to zero and then using eq 3.9. Case 2 is obtained from the first form of eq 3.13 by recognizing that for b and/or $b'' \gg 1$, $\Omega_{j,k}$ becomes independent of j and k, *i.e.*, $\Omega_{j,k} \to 2/(N/2)W_e$.[6] (These $\Omega_{j,k}$ are given explicitly for the nitroxide case in Table V of ref 8.) Then one may use $\Sigma_j(U_d)_{\beta\hat{j}} = \delta_{\beta,1}\sqrt{N/2}$. (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 3.13. (Note that eq 3.13 also covers eldor-type situations.) It follows from eq 3.13 that the exponential decays of larger $w_{\beta\beta}$ have the weaker amplitudes.[26]

In particular, let us assume that the $w_{\beta\beta}$ are nearly equal so $b, b'' \ll 1$. Then if the line observed is $i = 1$, while $k = 1$ has been saturated (simple saturation recovery), one obtains from eq 3.13

$$\Delta Z''_1(t) \cong T_1\omega_1 \mathrm{Re}\,(r_{1,1} + T_1^{-1} - i\Delta\omega_1)^{-1} e^{-t/T_1} \times [1-(2b''+b)(1+t/T_1)] Z''_1{}^{\mathrm{satd}}\omega_1{}^{\mathrm{s}} \quad (3.15)$$

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

$$\Delta Z''_1(t) \cong \frac{b+b''}{1+b+b''} e^{-t/T_1} T_1\omega_1 \mathrm{Re}\,(r_{1,1} + T_1^{-1} - i\Delta\omega_1)^{-1} \times (1+t/T_1) Z''_2{}^{\mathrm{satd}}\omega_1{}^{\mathrm{s}} \quad (3.16)$$

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.

(*B*) *Single Average Hyperfine Line (Nitroxide).* Here we assume the opposite of eq 3.6, *i.e.*

$$|-R_{i,j}| = |\hat{W}_{i,j}| \gg |\omega_i - \omega_j| \qquad i \neq j \quad (3.17)$$

or

$$2W_e b \text{ and/or } 2W_e b'' \gg |\omega_i - \omega_j| \sim a_N \quad (3.17a)$$

so the original three-line spectrum has collapsed into a single average Lorentzian. If we also assume $|T_{2,i}{}^{-1} - T_{2,j}{}^{-1}| \ll 2W_e b$ and/or $2W_e b''$ then $\mathbf{U}_o \cong \mathbf{U}_d$ of eq 3.2 and eq 2.46 becomes

$$\sum_{i=1}^{3} \Delta Z''_i(t) \cong -\sum_{i,\alpha,k,m,\beta} \int_0^\infty d\tau\, \mathrm{Re}\{U_{0i,\alpha}{}^{\mathrm{tr}} \times \exp[\tau(r_{\alpha,\alpha} - k_{\alpha,\alpha})] U_{0\alpha k} (2\hat{d})_{k,\hat{k}} U_{\hat{k},\beta}{}^{\mathrm{tr}}\} \times \exp[(\tau - t) w_{\beta\beta}] (U_d)_{\beta\hat{m}} \Delta \frac{1}{2} \hat{X}_{\hat{m}}(0) \quad (3.18)$$

But since $d_{k,\hat{k}}$ is independent of k and $\Sigma_k U_{o\alpha\hat{k}} U_{dk,\beta}{}^{\mathrm{tr}} \cong \delta_{\alpha\beta}$, while $\Sigma_i U_{oi,\alpha}{}^{\mathrm{tr}} = \Sigma_i U_{o\alpha,i} = \sqrt{3}\delta_{\alpha,1}$ and $X_{\hat{m}}(0) = \alpha$ independent of m, one has

$$\sum_{i=1}^{3} \Delta Z''_i(t) \cong 3\omega_1 \mathrm{Re} \frac{e^{-w_{11}t}}{r_{11} + w_{11} - i\Delta\omega_{11}} \alpha \quad (3.19)$$

where $w_{11} = 2W_e$

$$r_{11} = T'_{2\,\mathrm{av}}{}^{-1} + 2W_e \quad \text{with } T'_{2\,\mathrm{av}}{}^{-1} = \frac{1}{3}\sum_{i=1}^{3} T'_{2,(i)}{}^{-1}$$

and

$$\Delta\omega_{11} = \frac{1}{3}\sum_{i=1}^{3} \Delta\omega_i \quad (3.20)$$

Corrections due to the incomplete averaging of effects of the b and b'' terms can be obtained by perturbation methods in the usual fashion. Again the relaxation is dominated by $T_1 = 1/2W_e$. (Note that eq 3.17 does not violate the validity of the perturbation approach as long as $T_2'^{-1} > 2W_e$.)

(*C*) *General Case.* The discussion given above in terms of 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 3.7 is still applicable in the well-resolved spectral region as are the discussions and conclusions of cases 1, 2, and 3; also eq 3.18 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.*, $\mathbf{Z}$, $\hat{\mathbf{X}}$) and matrices (*e.g.*, $\mathbf{R}$, $\hat{\boldsymbol{W}}$) by their appropriate symmetrized forms as given in V, 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 of I–V are applicable.)

Note that in the diagonalization of $\hat{\boldsymbol{W}}$ (and $\mathbf{R}$), 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.*, $-\hat{W}_{i,j}{}^{\mathrm{ex}} = 2W_e b''$, $i \neq j$),[4] means that $\hat{\boldsymbol{W}}$ in the presence of exchange (but absence of END terms) is invariant to all permutations of the $N/2$ nondegenerate eigenstate pairs, *i.e.*, it commutes with the permutation group $P_{N/2}$. It is then a simple matter to show from the properties of this group that there is one eigenvalue.

$$w_{11} = T_1{}^{-1} = 2W_e \quad (3.20)$$

corresponding to $U_{i1} = 1/\sqrt{N/2}$ (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 $(N/2 - 1$ dimensional representation of $P_{N/2}$) and equal to

$$w_{ii} = 2W_e\left(1 + \frac{N}{2}b''\right) \qquad i \neq 1 \quad (3.21)$$

The END interaction shows less symmetry. However, for the eigenstate pairs of a single nucleus of I (or for the $J^{(\kappa)\mathrm{th}}$ set of eigenstate pairs corresponding to n completely equivalent nuclei with $J = \Sigma_{i=r} I_i$ and κ refers to a particular partner[3]) the $W_{i,j}{}^{\mathrm{END}}$ are symmetric in the quantum number M. Thus the only symmetry operation involves $W_{M,M\pm1} \rightarrow W_{-M,-M\pm1}$, and $\hat{X}_M \rightarrow \hat{X}_{-M}$. However, one may also take advantage of the structure of $\hat{\boldsymbol{W}}$[7]

$$\hat{W}_{\hat{i},\hat{j}} = 2W_e\delta_{i,j} + \hat{W}(\mathrm{END})_{\hat{i},\hat{j}} \quad (3.22)$$

so only $\hat{W}(\mathrm{END})_{\hat{i},\hat{j}}$ the END contribution, needs to be diagonalized. Then since[7]

$$\hat{W}(\mathrm{END})_{\hat{i}\hat{i}} = -\sum_{j\neq i} \hat{W}(\mathrm{END})_{\hat{i}\hat{j}} = -\sum_{j\neq 1} \hat{W}(\mathrm{END})_{\hat{j}\hat{i}} \quad (3.23)$$

the matrix $\hat{\mathbf{W}}(\mathrm{END})$ must have a single eigenvalue of zero corresponding to the eigenvector $\Sigma_i \hat{X}_i$ (by analogy with the equivalent property of symmetric $\mathbf{W}$ matrices corresponding to the conservation of probability). Thus one again has

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

corresponding to $U_{i1} = 1/\sqrt{N/2}$ 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 3.3. (The above symmetry considerations are sufficient to determine the w_{ii} for the nitroxide.)

When both END and exchange are present, then 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 $\hat{\mathbf{W}}^{\mathrm{s}}$ matrix (the symmetrized form, *cf.* V), in the presence of exchange only, one no longer has $P_{N/2}$ symmetry but usually symmetry such as $\hat{\mathbf{W}}(\mathrm{END})$, 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 $\hat{\boldsymbol{W}}$ which depends upon M (*i.e.*, effects of the cross term between g and dipolar tensors). This will, however, destroy

the symmetries discussed above. When cross transitions are not negligible, then the $\mathcal{W}$ matrix is nonzero and one must return to eq 2.5, but perturbation methods comparable to those of section II may still be employed.

On Contributions of T_2-Type Decays. We now wish to discuss the validity of the neglect of the terms appropriate when $|\mathbf{R}| \gg |\hat{\mathbf{W}}|$ *cf.* eq 2.41–2.42. 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 $T_1 \approx T_2$.[14] In the latter case, each hyperfine line is uncoupled from the others, and one treats each such line separately.[12] 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 3.4, so $T_{2,i}^{-1}$ is only somewhat larger than W_n. However, $b \equiv W_n/W_e$ is then usually substantially greater than unity. Thus, while $w_{11} = 2W_e \ll T_{2,i}^{-1}$ in this case, the w_{22} and w_{33} of eq 3.3 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 $\omega_{EX} \equiv Nb''W_e$) 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 2.30 might become important to consider. 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 above, since $\mathbf{U}_o = \mathbf{1}$ (even though $\mathbf{U}_d$ is not so simple).

IV. Slow Tumbling Examples

(*A*) *Simple Line.* By means of the eigenfunction expansion method of FBP,[18] one obtains from eq 2.2

$$\frac{1}{\sqrt{2}}\dot{C}_m(t) = \sum_n (R_{m,n} - iK_{m,n})\frac{1}{\sqrt{2}}C_n(t) - i\sqrt{2}d_{m,\hat{m}} \times \left(\frac{1}{2}b_{\hat{m}}(t)\right) + i\frac{1}{\sqrt{2}}Q_m \quad (4.1)$$

as well as the complex-conjugate form of eq 4.1, and

$$\frac{1}{2}\dot{b}_{\hat{m}}(t) = i\sqrt{2}\hat{d}^{\mathrm{tr}}_{\hat{n},m}\left(\frac{1}{\sqrt{2}}C_m(t) - \frac{1}{\sqrt{2}}C_m^*(t)\right) - \sum_n \hat{W}_{\hat{m},\hat{n}}\left(\frac{1}{2}b_{\hat{n}}(t)\right) \quad (4.2)$$

where the absorption is proportional to Im $C_o \equiv C_o''$. Equations 4.1 and 4.2 have been obtained by expanding the orientation-dependent terms

$$Z(\Omega,t)_{\lambda_j} = \sum_m C_m(t)|G_m(\Omega)\rangle \quad (4.3a)$$

and

$$X(\Omega,t)_{\lambda_j} = \Sigma b_{\hat{m}}(t)|G_{\hat{m}}(\Omega)\rangle \quad (4.3b)$$

in eigenfunctions $G_m(\Omega)$ of the Markov operator Γ_Ω

$$\Gamma_\Omega G_m(\Omega) = E_m G_m(\Omega) \quad (4.4)$$

and in this section we drop the λ_j subscript, since only a simple line is being considered. (We also let $\hat{m} \rightarrow m$.) These eigenfunctions $G_n(\Omega)$ may be written for Brownian rotation in isotropic liquids as the normalized Wigner rotation matrices

$$G_n(\Omega) \longrightarrow \sqrt{\frac{(2L+1)}{8\pi^2}}\,\mathfrak{D}_{KM}^{L}(\Omega) \quad (4.5)$$

with eigenvalues E_n for isotropic motion

$$E_n \longrightarrow E_{L,K,M} = L(L+1)\mathcal{R} \quad (4.6)$$

where $\mathcal{R}$ is the rotational diffusion coefficient.[10,18] For models involving reorientation by appreciable jumps, it is found that the functions of eq 4.5 are still good eigenfunctions, and eq 4.6 becomes

$$E_n \longrightarrow E_{K,M}{}^{L} = B_L L(L+1)\mathcal{R} \quad (4.6')$$

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.[19,21,23] (We note that there is a simple analog 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" while the latter have none.)

In particular, if we assume the orientation-dependent perturbation in eq 2.2 is an axially symmetric g tensor, one finds only the $C_{0,0}{}^{L}(t)$ and the $b_{0,0}{}^{L}(t)$ for L even affect the observed signals (*cf.* eq 4.8b below). For this case the terms in eq 4.1 and 4.2 are[18]

$$R_{L,L'} = r_{L,L}\delta_{L,L'} = -(T_2^{-1} + E_L)\delta_{L,L'} \quad (4.7a)$$

$$K_{L,L'} = \Delta\omega + \kappa_{L,L'} \quad (4.8a)$$

with

$$\kappa_{L,L'} = [(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 \mathfrak{F} \quad (4.8b)$$

$$\mathfrak{F} = \frac{2}{3}\hbar^{-1}\beta_e B_0(g_\parallel - g_\perp) \quad (4.8c)$$

These expressions include only the secular contribution of the axially symmetric g tensor. (The nonsecular contributions have been omitted in eq 4.1 and 4.2 (*cf.* FBP section IIIB1).) Also

$$\hat{W}_{L,L'} = w_{L,L}\delta_{L,L'} = (2W_e + E_L)\delta_{L,L'} \quad (4.9)$$

and

$$Q_L = q\omega_\lambda d_\lambda \delta_{L,0} \quad (4.10)$$

We have introduced an orientation-independent width T_2^{-1} and $T_1^{-1} = 2W_e$ into eq 4.7a and 4.9, respectively. Equations 4.1 and 4.2 are seen to be of the same matrix form as eq 2.12 (with the matrices $\hat{\mathbf{d}}$ and $\mathbf{d}^{\mathrm{tr}}$ defined by eq 4.1 and 4.7. So, provided the inequality of eq 2.24 for the present case applies, then the same perturbation treatment in d_λ utilized for solving eq 2.12 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 $\hat{W}_{m,n}$ in *diagonal* form. Thus, when $E_m/\mathfrak{F} \gg 1$ corresponding to motional narrowing, the $\mathbf{R} \pm i\mathbf{K}$ is approximately diagonal in this representation. However, κ, which arises from $\mathcal{H}_1(\Omega)$, is diagonal in the space of orientational unit vectors $|\delta(\Omega - \Omega_0)\rangle$.[15] We note that from the representation of the δ function

$$|\delta(\Omega - \Omega_0)\rangle = \sum_n G_n^*(\Omega_0)|G_n(\Omega)\rangle \quad (4.11a)$$

where, here, $|G_n(\Omega)\rangle$ are any complete *O.N.* set of functions, one has

$$|G_n(\Omega)\rangle = \int d\Omega_0 G_n(\Omega_0)|\delta(\Omega-\Omega_0)\rangle \quad (4.11b)$$

and, if they are also eigenfunctions of Γ_Ω, then

$$\langle\delta(\Omega-\Omega_1)|\Gamma_\Omega|\delta(\Omega-\Omega_0)\rangle = |\sum_n G_n^*(\Omega_0)G_n(\Omega_1)E_n \quad (4.12)$$

Equations 4.11 define the unitary transformation

$$U_{n,\Omega_0} = G_n(\Omega_0) \quad (4.13a)$$

$$(U^{-1})_{\Omega_0,n} = U_{n,\Omega_0}^* = G_n^*(\Omega_0) \quad (4.13b)$$

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 $E_L/\mathfrak{F} \ll 1$, 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

$$K_{\Omega_j,\Omega_j} \equiv k(\Omega_j) = \Delta\omega_\lambda - \omega'(\Omega_j) \quad (4.14a)$$

where

$$\omega'(\Omega_j) = \mathfrak{F}\,\mathfrak{D}_{00}^2(\Omega_j) = \mathfrak{F}\,P_2(\beta_j) \quad (4.14b)$$

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 2.46, with an equation such as eq 3.7 appropriate when $E_L/\mathfrak{F} \ll\ll 1$, except that $\mathbf{U}_0 \cong (\mathbf{U}^{-1})$ are defined by eq 4.13b while $\mathbf{U}_d = \mathbf{1}$ (since the initial basis sets are the eigenfunctions of Γ and not the individual orientational component; whereas in the motional-narrowing case of section III the individual hyperfine components are utilized). When $E_L/\mathfrak{F} \lesssim 1$, 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[12,15,18,19] while $\mathbf{U}_d = \mathbf{1}$. Thus we may write from eq 2.46

$$\Delta C_0''(t,\omega) = \omega_1 \mathrm{Re}\sum_{L,j}\frac{e^{-w_{LL}t}}{(R-ik)_{jj}+w_{LL}}(U_o^{\mathrm{tr}})_{0,j}\times (U_o)_{j,L}\tfrac{1}{2}\Delta b_L(0) \quad (4.15')$$

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

$$\Delta C_0''(t,\omega) \cong \frac{\omega_1 \mathrm{Re}}{\sqrt{8\pi^2}}\sum_L \int d\Omega_j \frac{e^{-w_{LL}t}}{r(\Omega_j)-ik(\Omega_j)+w_{LL}} G_L(\Omega_j)\Delta\tfrac{1}{2}b_L(0) \quad (4.15)$$

In both cases, it follows from eq 4.8b that only even values of L are required. Note that in eq 4.15, 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. 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 4.15 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 $r(\Omega_i)$ being $-T_2^{-1}$ (with any small residual motional broadening calculated using the correct representation which diagonalizes $\mathbf{R} - i\mathbf{K}$ which, for practical purposes involves finite difference methods.) We can also rewrite eq 4.15 in a form more closely resembling eq 3.7

$$\Delta Z''(\Omega_i,t,\omega) = \omega_1 \mathrm{Re}\sum_{L\,\mathrm{even}}\frac{e^{-w_{LL}t}}{r_{ii}-ik_{i,i}+w_{LL}}\int d\Omega_j G_L(\Omega_i)G_L^*(\Omega_j)\Delta\tfrac{1}{2}\hat{X}(\Omega_{j,0}) \quad (4.16)$$

First suppose that $E_L \ll W_e$, so that $w_{LL} \cong 2W_e$ for all values of L which 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 4.16 becomes

$$\Delta Z''(\Omega_i,t) \approx \omega_1 e^{-t/T_1}\frac{1}{r_{i,i}-ik_{i,i}+2W_e}\Delta\tfrac{1}{2}\hat{X}(\Omega_i,0) \quad (4.17)$$

representing the fact that the spin packet at Ω_i is uncoupled to the other orientations (compare with eq 3.10) and

$$\Delta C_0''(t,\omega) = \frac{1}{\sqrt{8\pi^2}}\int d\Omega_i \Delta Z''(\Omega_i,t,\omega) \quad (4.17a)$$

(Note that it is $\Delta C_0''(t,\omega)$ 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, *i.e.*, only $b_0(0)$ is normally saturated, so only $\Delta\frac{1}{2}b_0(0) \neq 0$, and eq 4.15 becomes (with an equivalent form for the more general eq 4.15')

$$\Delta C_0''(t,\omega) = \frac{\omega_1}{8\pi^2}e^{-t/T_1}\times \mathrm{Re}\left[\int d\Omega_i \frac{1}{r(\Omega_i)-ik(\Omega_i\omega)+2W_e}\right]\tfrac{1}{2}\Delta b_0(0) \quad (4.18)$$

again giving relaxation with a simple $T_1 = 1/2W_e$ (compare with eq 3.11).

We can, again, introduce the "steady-state approximation on the pulse duration" and the analog of eq 3.12 becomes

$$\tfrac{1}{2}\hat{X}(\Omega_i)^{\mathrm{satd}} = -\int d\Omega_j \hat{W}_{\Omega_j\Omega_j}{}^{-1}\hat{d}_{\Omega_j,\Omega_j}{}^{\mathrm{trsatd}}Z''(\Omega_j)^{\mathrm{satd}} \quad (4.19)$$

where

$$\hat{W}_{\Omega_j\Omega_j}{}^{-1} = \sum_m G_m(\Omega_i)w_{mm}{}^{-1}G_m^*(\Omega_j) = \sum_{L,K,M}\left(\frac{2L+1}{8\pi^2}\right)\mathfrak{D}_{KM}{}^L(\Omega_i)w_{KM}{}^{L-1}\mathfrak{D}_{KM}{}^{L*}(\Omega_j) \quad (4.19a)$$

and for an orientation-independent transition moment we may write $d(\Omega_i,\Omega_j)^{\mathrm{tr\,satd}} = -\frac{1}{2}\omega_1{}^s\delta_{i,j}$. While, in principle, the sum in eq 4.19a includes a complete sum over the *O.N.* set, the nature of $Z''(\Omega_j)$ for the present case, as determined by eq 4.8, again means that only the restricted sum of L even and $K = M = 0$ need be used in eq 4.19. An alternative form of eq 4.19 is

$$b_L{}^{\mathrm{satd}} = \omega_1{}^s w_{LL}{}^{-1}C_L{}'^{(\mathrm{satd})} \quad (4.19b)$$

In general, the $b_L{}^{\mathrm{satd}}$ will be nonnegligible only for those L such that the $C_L{}'^{\mathrm{satd}}$ are strongly coupled into the problem by the term in $\mathfrak{F}$ of eq 4.14b *and* for which $4d^{\mathrm{satd}\,2}w_{LL}{}^{-1} \gtrsim (-R_{L,L})$, *i.e.*, the $C_L{}'^{\mathrm{satd}}$ are indeed being saturated. It is usually the latter condition which is limiting, since one has

$$T_2{}^{-1}/E_L,\ W_e/E_L \ll |\mathfrak{F}|/E_L$$

and usually

$$(\omega_1{}^s)^2 \gtrsim (2W_e)^{-1}T_2$$

(but not very much greater). Note also that the C^{satd} are obtained from eq 4.1 to 4.8 once $\dot{C}_L(t)$ and $\dot{b}_L(t)$ are set equal to zero. We now obtain from eq 4.15'

$$\Delta C_0''(t) = +\omega_1 \mathrm{Re} \sum_{L,j} \frac{e^{-w_{LL}t}}{(R-iK)_{j,j}+w_{LL}} \left(\frac{1}{w_{LL}}\right) (U_o^{\mathrm{tr}})_{0,j}(U_o)_{j,m} C_L''^{(\mathrm{satd})} \frac{1}{2}\omega_1^{\mathrm{s}} \quad (4.20)$$

with the obvious modification when eq 4.15 is appropriate. Equation 4.16 may be rewritten as

$$\Delta Z''(\Omega_i,\omega,t) = \omega_1 \mathrm{Re} \sum_L \frac{e^{-w_{LL}t}}{r(\Omega_i)-ik(\Omega_i)+w_{L,L}} \times \int \frac{G_L(\Omega_i)G_L^*(\Omega_j)}{w_{L,L}} Z''^{\mathrm{satd}}(\Omega_j)\frac{\omega_1^{\mathrm{s}}}{2}\mathrm{d}\Omega_j \quad (4.21)$$

where it is again clear that only w_{00} and those $w_{L,L}$ comparable to w_{00} would contribute substantially. And the saturation recovery spectrum given by $\Delta C''(\omega,t)$ is obtained by integrating eq 4.21 over Ω_i, and utilizing $\langle G_L(\Omega_j)|Z''(\Omega_j)\rangle = C_L$. The case of $w_{L,L}$ comparable to $w_{0,0}$ for all L contributing appreciably to eq 4.21 may be dealt with in the manner of eq 3.13 to yield

$$\Delta Z''(\Omega_i,\omega,t) \cong \omega_1 \mathrm{Re} \frac{e^{-w_{00}t}}{r(\Omega_i)-ik(\Omega_j)+w_{0,0}} \int \mathrm{d}\Omega_j \times [\delta(\Omega_i-\Omega_j)-\overline{\gamma(\Omega_i,\Omega_j)}(1+w_{00}t)]w_{00}^{-1}Z''(\Omega_j)^{\mathrm{satd}}\frac{1}{2}\omega_1^{\mathrm{s}} \quad (4.22)$$

where

$$\overline{\gamma(\Omega_i,\Omega_j)} = \sum_{L\neq 0}{}' \gamma_L G_L^*(\Omega_i)G_L(\Omega_j) \quad (4.22a)$$

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 4.21. (The prime on eq 4.22a indicates it may be calculated over this restricted set of L values.) Note also that $\Sigma_L' G^L(\Omega_i)G^L{}^*(\Omega_j) \approx \delta(\Omega_i - \Omega_j)$ compared to the much slower variation of $Z''(\Omega_j)$ with Ω_j. For Brownian diffusion $\gamma_L = L(L+1)\Re/2W_e$; while for the limit of strong jumps

$$\overline{\gamma(\Omega_i,\Omega_j)} = \left[\delta(\Omega_i-\Omega_j)-\frac{1}{8\pi^2}\right]\Re/2W_e \quad (4.23)$$

Equation 4.22 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 4.23 substituted into eq 4.22 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 4.21, takes on the simpler form

$$\Delta Z''(\Omega_i,\omega,t) = \omega_1 \mathrm{Re}\left[\frac{e^{-w_{00}t}}{r(\Omega_i)-ik(\Omega_i)+w_{0,0}} \frac{C_0''^{\mathrm{satd}}}{w_{00}\sqrt{8\pi^2}} + \frac{e^{-w't}}{r(\Omega_i)-ik(\Omega_i)+w'}\left(\frac{1}{w'}\right)\left(Z''(\Omega_i)^{\mathrm{satd}}-\frac{C_0''^{\mathrm{satd}}}{\sqrt{8\pi^2}}\right)\right]\frac{1}{2}\omega_1^{\mathrm{s}} \quad (4.24)$$

where $w' = w_{00} + \Re$.

Other Aspects of a Simple Line. (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 $T_{1,\Omega}^{-1}\ {}_{00}{}^2(\Omega)$ and $T_{2,}{}^{-1}\mathfrak{D}_{00}{}^2(\Omega)$. Then

$$R_{L,L'} = -(T_2^{-1}+E_L)\delta_{L,L'} - T_{2,\Omega}{}^{-1}[(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (4.25)$$

and

$$\hat{W}_{L,L'} = (T_1^{-1}+E_L)\delta_{L,L'} + T_{1,\Omega}{}^{-1}[(2L+1)(2L'+1)]^{1/2}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (4.26)$$

When eq 4.25 is compared with eq 4.7 and 4.8, it is seen that its only effect on the previous results is to change $\mathfrak{F} \rightarrow \mathfrak{F} - iT_{2,\Omega}{}^{-1}$, but eq 4.26 renders $\hat{W}_{L,L}$ nondiagonal. When $T_{1,\Omega}E_L \gg 1$ (or more precisely $T_{1,\Omega}E_2 \gg 1$) 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).

(2) Asymmetric g Tensor. The correct expressions may be obtained for this case by direct comparison of the above expressions with the steady-state case given by FBP. The main feature to note is that the $\mathfrak{D}_{K0}^L(\Omega)$ for even L and nonzero K appear in the problem, so effects of anisotropic rotational diffusion can appear.[12] Otherwise the discussion is analagous to that given for symmetric g tensors.

(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 $E_L = \Re L(L+1)$ to play a dominant role for large L in eq 4.7a and 4.9, *i.e.*, $\Re L(L+1) \gg T_1^{-1}$ and T_2^{-1}. But this is the case where these terms of large L decay too rapidly in $e^{-\hat{W}t}$ 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 2.30 for a detailed examination of such effects. We note that in the slow tumbling region, the $K_{L,L}$ of eq 4.8 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 2.32–2.33. Our analysis given above 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.[12,22,23]

(B) Complex Spectra. E.g., 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 in FBP[18] and Goldman, *et al.*,[12,19] and in Bruno's thesis.[21] However, the partitioned-matrix concept of eq 2.12 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 $C_{KM}^L(t)$ and $b_{KM}^L(t)$ as vectors in spin space,[18] such that $C_{KM}^L(t,i)$ 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 (mixed) forbidden transitions.[12,19,21]

These forbidden transitions are coupled into the (high-field motional narrowing) allowed transitions by the pseudo-secular terms in $\mathfrak{IC}_1(\Omega)$ which 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: *i.e.*, three for the allowed transitions (i = 1, 2, or 3) and three which are really (mixed) nmr transitions. These latter arise from the pseudo-secular terms in $\mathfrak{IC}_1(\Omega)$, and thus play a role closely analogous to the three forbidden

transitions for the $C_{KM}{}^{L}(i)$. As the rigid limit is approached (in particular for $|\mathcal{K}_1(\Omega)|/\mathcal{R} \gg 1$) they become equivalent to representing the diagonalized eigenstates characteristic of the rigid limit.

One may thus generalize all our above procedures to such cases wherein the vector spaces of eq 2.12 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

$$|\mathcal{K}_1(\Omega)|\,\mathcal{R} \gtrsim 1$$

i.e., the unsaturated slow tumbling spectra still show important motional effects, the detailed diagonalizations required for eq 2.46 for example are complex although tractable.[12,18,19,21] However, this is typically the region where

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

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 $w_{00} = (2W_e)$ and $w_{LL} \gg w_{00}$ 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 (*cf.* section III). For $|\mathcal{K}_1(\Omega)|/\mathcal{R} \lesssim 1$ (*i.e.*, $\tau_R \lesssim 10^{-9}$ sec) one gets values of $b \sim 20$–40 representing strong coupling of the hyperfine lines.[12,13] But when $|\mathcal{K}_1(\Omega)|/\mathcal{R} \gg 1$, and only residual motional effects are important, one must examine their effects more carefully.

In order to obtain some insight into the nuclear spin flip aspect of the problem, we consider a "quasi-nitroxide" case, such that for an axial hyperfine tensor one has $\sqrt{3/10}(A_\parallel - a_N)$ being considerably smaller than a_N (see eq below) where a_N is the isotropic hyperfine splitting and $A_\parallel$ is the rigid limit value of $A_{z'z'}$, (in reality $a_N \approx 15$ G and $\sqrt{3/10}(A_\parallel - a_N) \approx 11$ G).[13,19] For this "quasi-nitroxide" case, one may effectively decouple the $C_{KM}{}^{L}(t,i)$ for the three allowed transitions from the three (mixed) forbidden transitions and the $b_{KM}{}^{L}(t,i)$ representing the three eigenstate pairs from the three (mixed) nmr transition terms, by means of a perturbation theory approach which is closely equivalent to that discussed in Appendix A of ref 23 for the $C_{KM}{}^{L}(t,i)$ and to that plus the general perturbational approach given here in section II for the $b_{KM}{}^{L}(t,i)$.[27] In the limit of fast motion, *i.e.*, $|\mathcal{K}_1(\Omega)|\tau_R \ll 1$, the results are indeed quite general (independent of the smallness of $|A_\parallel - a_N|$) and are just the familiar END terms discussed in section III. For slow motions, however, the nuclear spin flips persist and our axial "quasi-nitroxide" calculation gives an idea of their effects. In particular, one obtains a nuclear spin flip rate coupling $b_{00}{}^{L}(t,i)$ with $b_{0,0}{}^{L}(t,i \pm 1)$ where $i = 1, 2$, or 3 given by

$$W_n'(i,L,0,0 \leftrightarrow i \pm 1, L'', 0, 0) \equiv W_n'(i,L;i \pm 1, L'') = \frac{D^2}{2} \sum_{\text{even } L', L''} (2L'+1)[(2L+1)(2L''+1)]^{1/2} \times \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & 2 & L'' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix}\begin{pmatrix} L' & 2 & L'' \\ 1 & -1 & 0 \end{pmatrix} \times [V(L,L') + V(L''+L')] \quad (4.27)$$

where

$$V(L,L') = \frac{E_{L'} - E_L - 2W_e + T_{2,n}{}^{-1}}{\tilde{b}_{L'}{}^2 + (E_{L'} - E_L - 2W_e + T_{2,n}{}^{-1})^2} \quad (4.28)$$

with

$$D = -|\gamma_e|\left(\frac{3}{2}\right)6^{-1/2}(A_\parallel - a_N) \quad (4.29a)$$

and

$$\tilde{b}_L = -\frac{|\gamma_e|}{2}\left[a_N + D'(2L+1)\begin{pmatrix} L & 2 & L \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -1 & 0 & 1 \end{pmatrix}\right] \quad (4.30)$$

with

$$D' = -(8/3)^{1/2}D \quad (4.29b)$$

and E_L is given by eq 4.6 (or 4.6′) with $T_{2,n}{}^{-1}$ being the orientation-independent width component for the nmr transition.[3,5,7] This result for the nuclear spin flip rate is to be compared with the relaxation term for $b_{KM}{}^{L}(i)$ itself of $2W_e + E_L$. In particular, the diagonal contribution to the $L = 0$ term is just (when we drop $2W_e{}^{-1} - T_{2,n}{}^{-1}$)

$$W_n'(i,o;i \pm 1, 0)\frac{D^2}{5}\frac{E_2}{\tilde{b}_2{}^2 + E_2{}^2} = \frac{D^2}{5}\frac{\tau_R}{\tilde{b}_2{}^2\tau_R{}^2 + 1} \quad (4.31)$$

with

$$\tilde{b}_2 = -\frac{1}{2}|\gamma_e|\left[a_N + \frac{1}{7}(A_\parallel - a_N)\right] \quad (4.30a)$$

or essentially the fast-motional result, but it is correct for slow motion (for the quasi-nitroxide) where its asymptotic behavior goes as $(D^2/5)\tilde{b}_2{}^{-2}\tau_R{}^{-1}$. Note that we can define a term in this limit

$$b = \frac{1}{2}\frac{D^2}{5}\tilde{b}_2{}^{-2}\tau_R{}^{-1}/W_e$$

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 $\mathcal{R}/W_e \lesssim 1$, then the contribution of nuclear spin flips decreases relative to effects of W_e.

The analysis of this case would thus appear to be a generalization and combination of our previous discussions of a simple line in slow tumbling, *e.g.*, eq 4.9 and the fast motional nitroxide case, *e.g.*, eq 3.3 for an END mechanism. We must thus consider a $\hat{\mathbf{W}}$ matrix of type

$$\hat{W}(i,L;j,L'') = \left(2W_e + E_L + \sum_k W_n(i,k)\right)\delta_{i,j}\delta_{L,L''} + \sum_k W_n'(i,L;k,L'')\delta_{i,j} - [W_n(i,j)\delta_{L,L''} + W_n'(i,L;j,L'')]\delta_{j,i\pm1} \quad (4.32)$$

Note that this introduces off-diagonal terms between different L values of the type similar to eq 4.26 (*e.g.*, $W_n'(i,o;i \pm 1,2) = W_n'(i,o;i \pm 1, 0)$ ($\sqrt{5/14}$)). Thus the diagonalization of the $\mathbf{W}$ matrix of form of eq 4.32 is not, in general, trivial. When W_n type terms are neglected, each of the three allowed transitions behave independently as simple lines, while the W_n type terms couple the relaxation of all three lines, and mix L values. Our general arguments apply for $R \gg W_e$, such that the whole spectrum relaxes together. In our quasi-nitroxide model $W_n'/\mathcal{R}$ is of order of $D_2/\tilde{b}_2{}^2 \ll 1$, so W_n' becomes small sooner than E_L, but for a true nitroxide where $D_2/b_2{}^2$ is *not* much smaller than unity, our perturbation analysis is not quantitative but suggests that the importance of nuclear spin flip terms persists roughly almost as long as the terms in E_L.

Some other comments about the application of eq 2.46

to nitroxides are appropriate. First we note that $\hat{\mathbf{d}}$ just couples $C_{KM}{}^{L}(i)$ with $b_{KM}{}^{L}(i)$. The diagonalization of the $\mathbf{R}$-$i\mathbf{K}$ matrix in the vector space of the $C_{KM}{}^{L}(i)$ may be performed as discussed elsewhere, but for the "quasi-nitroxide" model, the perturbational decoupling of the forbidden transitions renders the three allowed transitions separable, with the pseudosecular contribution between $C_{KM}{}^{L}(j)$ and $C_{KM}{}^{L''}(j)$ for $\mathbf{R}$-$i\mathbf{K}$ given by

$$D^2 \sum_{\substack{\text{even} \\ L,L''}} (2L'+1)[2L+1)(2L''+1)]^{1/2} \times \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & 2 & L'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} L' & 2 & L'' \\ 0 & -1 & 0 \end{pmatrix} \times \frac{1}{2}[\pm i\tilde{b}_{L'} - (E_{L'} - E_L)]^{-1} + [\pm i b_{L'} - (E_{L'} - E_{L''})]^{-1} \quad (4.33)$$

where the plus and minus signs are for $j = 1$ and 3 respectively, and for $j = 2$ one uses the sum of the two expressions for $j = 1$ and 3. Equation 4.33 is of closely similar form to eq 4.27, but it includes the frequency shifts due to the pseudo-secular terms as well as the line-broadening effects due to the nuclear spin flips. Secular g tensor contributions have been neglected for simplicity, but they can readily be added in. (One also takes the terms in eq 4.33 as small compared to δ_0 in decoupling the transitions for the "quasi-nitroxide" and we have neglected the small effects of weakly mixing in allowed character into the forbidden transitions).

We note that in a pulsed eldor experiment, if the observing and pulsed pumping modes are set at different frequencies corresponding to the same hyperfine transition, one may approximate the analysis in terms similar to those discussed for eq 4.22, etc. However, when they are set to different hyperfine transitions, the combined effects of reorientation and spin flip will, in general, be seen.

V. Summary

We have shown how our general methods applicable to steady-state saturation experiments in both the motional narrowing and slow tumbling region may also be generally applied to time-dependent experiments such as saturation recovery. The solution is again dependent upon the same matrix representations including the relaxation matrix $\mathbf{R}$, the coherence matrix $\mathbf{K}$, the transition-probability matrix $\mathbf{W}$ (or $\hat{\mathbf{W}}$), and the transition moment matrix $\mathbf{d}$ which have already been extensively discussed. The complex coupled differential equations are most effectively solved in terms of separate diagonalizations in transition space (in which $\mathbf{R}$ and $\mathbf{K}$ are defined) and in eigenstate (or eigenstate-pair) space (in which $\mathbf{W}$ (or $\hat{\mathbf{W}}$) is defined). This is because of a general feature of these problems, such that usually the different eigenstates (pairs) exhibit coupled relaxation even while their associated transitions are uncoupled.

Particular attention has been given to the saturation-recovery-type experiment, which also includes pulsed eldor with a weak observing mode. A general procedure, based on having a weak nonsaturating observing mode, has been developed, which permits convenient solutions. The procedure is illustrated with examples of the well-known case of a single line.

The analysis of spectra with hyperfine lines exhibiting coupled relaxation (with a nitroxide being a particular example) has shown 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 which may exist. Simply stated, this is because when W_n or ω_{EX} are much greater than W_e, so as to strongly 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 $\omega_{EX}{}^{-1}$, 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 $\geq$ the T_1's) is applicable, then one finds the fast decays also have much weaker amplitudes (proportional to their decay time constants). For W_n, $\omega_{EX} \ll W_e$, the lines are essentially uncoupled and all decays are $\sim T_1$. However, when W_n, $\omega_{EX} \sim W_e$, then more complex behavior may be seen with several (not very different) decay constants, which are weighted differently for eldor *vs.* direct observation. Thus eldor would be helpful in deciphering the different decays. When W_n, $\omega_{EX} \ll W_e$, 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 $Nb'' = \omega_{HE}/W_e$. T_2-type decays (including oscillatory effects) were not considered in detail in the examples, but, in those special cases where they could be important, the general methods given may be satisfactorily employed.

The slow motional case has been discussed from the point of view of examples of (1) a simple line and (2) a nitroxide (also a "quasi-nitroxide" in which the pseudo-secular terms are taken as small but not negligible). Here the important comparison is between $\mathcal{R}$ *vs.* 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 $T_1 \cong 2W_e$. For $\mathcal{R} \ll W_e$ each component of the spectrum is separately saturated and it relaxes with $T_1 \cong 2W_e$. The region of $6\mathcal{R} \sim W_e$ allows for the superposition of several decays of comparable order of magnitude which might be effectively explored by a combination of direct and eldor-observational techniques. Effects of model dependence on the reorientational motion are also given. The nitroxide case involves a combination of reorientational, and nuclear-spin-flip effects. Advantage is taken of the simplicity of the quasi-nitroxide model to analyze effects of the latter, showing their importance even when the pseudo-secular terms are small, thus implying their importance for real nitroxides. (The comments given for effects of W_n in the motional narrowing case apply here in a qualitative sense.) Computational techniques already well developed for computer simulation are fully applicable to a more thorough analysis of this case.

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(24) (a) C. F. Polnaszek, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.*, **58**, 3185 (1973). (b) This is based on a rigorous definition of **d** as a transition moment. However, in previous usage we have set $d_{i,j} = 0$ for any transition which is not excited even though it is allowed.[3-8] Such a usage is a convenience for well-separated lines, but it breaks down for overlapping lines or in the slow tumbling region, so we return here to the rigorous definition of **d** for general discussions.
(25) The special case of $\Delta\omega = 0$ and $T_1 = T_2 \equiv T$, which, as noted, represents a breakdown of the expansion eq 2.24a, results in $\Delta Z'(t)$ decaying as $e^{-t/T}$, while the coupled modes $[\Delta Z''(t) \pm \frac{1}{2}\Delta X(t)]$ decay as $e^{-t}(T^{-1} \pm i\omega_1)$. Since we are assuming $\omega_1^2 T_1 T_2 = (\omega_1 T)^2 \ll 1$, it follows that $e^{-t}(T^{-1} \pm i\omega_1) \cong e^{-t/T}(1 \pm i\omega_1 t)$, essentially an exponential decay in T_1.
(26) When the $w_{\beta\beta}$ are very different, *e.g.*, b and/or $b'' \gg 1$, such that $w_{22}, w_{33} \gg w_{11}$, then other steady-state approximations appropriate to pulses of duration Δt fulfilling $w_{22}^{-1}, w_{33}^{-1} \ll w_{11}^{-1} = 2T_1$ may be used by solving for the steady-state solutions appropriate for $W_e \approx 0$ but W_n and/or $\omega_{EX} \neq 0$. This steady-state solution yields equal degrees of saturation of all the eigenstate pairs, and thus gives comparable results to that for case (2) above. [Note, however, that for a steady-state approximation to apply here, $\Delta t \gtrsim 2(T_1^{-1} + T_2^{-1})^{-1}$ and $\omega_1^2 \geq (T_1^{-1} - T_2^{-1})$.[22,23]
(27) This perturbation approach was first used by FBP in ref 18 to discuss effects of nonsecular g tensor contributions to saturation behavior. There are some minor errors in eq 60 of that reference, due to a use of nonsymmetric matrices (*i.e.*, the unnormalized $\mathfrak{D}_{KML}$ were used as the basis), but this has no effect on the discussion which follows, nor on the final result of eq 61.

A Molecular Orbital Study of the Addition of Singlet Methylene to Butadiene

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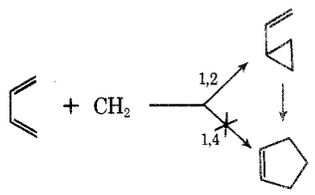
A simple molecular orbital method is proposed to deal with chemically reacting systems in terms of the molecular orbitals of two isolated reactants. The electron population of a reacting system is partitioned into several orbital interaction terms, allowing a tracing of the origin of intermolecular bond formation and of the intramolecular reorganization of the electron distribution. The method is applied to the interaction between singlet methylene and butadiene. Both 1,2- and 1,4 addition are electronically allowed, but the 1,4 addition is discriminated against by excessive closed-shell repulsive interactions.

Introduction

The interpretation of chemical interactions between two systems in terms of the electronic structures of isolated reactants is a problem of crucial importance to chemistry. Some useful reactivity indices and generalized stereoselection rules have been derived by rather simplified molecular orbital (MO) methods.[1-8] There perturbation theory and orbital correlation diagrams have been found to be quite powerful. Several more detailed MO theoretical methods have been proposed in order to calculate the interaction energy and the electron distribution of chemically interacting systems from the wave functions of two isolated reactants.[9-17] Although the application of the "isolated-molecule-approximation"[18] is limited to the case of relatively weak interactions, *e.g.*, the early stage of chemical reactions, it can often be very informative in disclosing the governing factors of complicated chemical reactions.

The typical reactions of methylenes, namely, addition to a double bond, insertion into a single bond, and dimerization, have proven a useful testing ground for approximate calculations of bimolecular potential energy surfaces and reaction coordinates.[19,20] In the present work we continue our study of methylene reactions, returning to the addition reaction. We seek to understand a negative result; experiments on the reaction of singlet methylene with dienes have given no direct evidence of 1,4 concerted addition.[21] Normal 1,2 addition apparently prevails as the initial step.[22] This is so despite the least-motion cheletropic reaction of 1,4 addition clearly being a symmetry allowed process.[7]



In this paper we first present a simple way of discussing the reorganization of the electronic distributions of two interacting molecules, and then apply our formalism to the reaction of singlet methylene and butadiene.

Population Analysis of Chemically Reacting Systems

Let us consider an interaction between two molecular systems, A and B. The MO's of A and B in their isolated states are given by linear combinations of atomic orbitals (AO's) as