Closed-Form Expressions for Level-Averaged Electron Spin Relaxation Times outside the Zeeman Limit: Application to Paramagnetic NMR Relaxation

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Paramagnetic enhancement of NMR relaxation (NMR-PRE) depends on thermal relaxation of the electron spin system. Most previous analyses of experimental NMR-PRE data have relied on Bloembergen–Morgan (B–M) theory to describe the magnetic field dependence of electron spin relaxation in liquid samples. However, B–M theory assumes a Zeeman-limit situation and is not physically appropriate to the common case of $S \geq 1$ transition metal ions which possess a permanent zero-field splitting (zfs) that is comparable to or larger than the Zeeman splitting. Theory has been needed which (1) includes the effects of the zfs interaction, thus providing a realistic description of the magnetic field dependence of the NMR-PRE outside the Zeeman limit, and (2) describes electron spin relaxation phenomena at a comparable level of complexity to that of B–M theory, i.e., with two magnetic field-dependent electron spin relaxation times, τ_{S1} and τ_{S2}, defined in the laboratory coordinate frame. Theory of this kind is developed. Expressions derived in a previous study (R. R. Sharp and L. L. Lohr, *J. Chem. Phys.* **115, 5005 (2001).) for level-specific relaxation rates have been averaged over spin eigenstates to give level-averaged quantities, $\tau_{S1,2}$. This kind of averaging leads to a great simplification in the mathematical form of the results. Simple zfs-limit molecular-frame and laboratory-frame expressions are given for electron spin $S = 1, 3/2, 2$, and $5/2$. General expressions, valid for $S \geq 1$ and for arbitrary magnitudes of the Zeeman and zfs energies, are derived for level-averaged electron spin relaxation times defined in both the laboratory- and the molecule-fixed coordinate frames. The new theory coincides with B–M theory in the Zeeman limit.** © 2002 Elsevier Science (USA)

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INTRODUCTION

NMR-paramagnetic relaxation enhancement or NMR-PRE refers to the enhancement of the NMR relaxation rate that is produced by addition of a paramagnetic solute to the sample. The traditional theory of the NMR-PRE is due to Solomon (*1*) and Bloembergen and Morgan (*2*) (SBM), who derived expressions for the NMR-PRE assuming the Zeeman limit situation, i.e., that the static Hamiltonians of both the electron and the nuclear spins are exclusively Zeeman Hamiltonians. For transition metal ions with spin $S \geq 1$, this assumption is frequently not appropriate physically due to the influence of zero-field splitting (zfs) interactions in the electron spin Hamiltonian. When the electronic Zeeman and permanent zfs Hamiltonians, H_Z and H_{zfs}^0, are comparable in magnitude and when the paramagnetic solute undergoes rapid Brownian reorientation, the physical description of the NMR-PRE experiment becomes complex, particularly with regard to the motion of the electron spin. The electron spin wavefunctions then depend on the orientation of the paramagnetic solute with respect to the Zeeman field. The spatial quantization of the spin motion is no longer aligned along the laboratory magnetic field but becomes complex; in the zfs limit, the spin motion is quantized (or more precisely, polarized) along molecule-fixed axes. Also, outside the Zeeman limit, the electron spin wavefunctions contain explicit time dependence due to molecular reorientation. In recent years, considerable progress has been made in this laboratory (*3–18*) (reviewed in Ref. (*3*)) and by groups in Sweden (*19–32*), Italy (*33–37*), and France (*38, 39*) in analyzing these complex situations.

An important aspect of theory that remains incompletely developed concerns the magnetic field dependence of electron spin relaxation outside the Zeeman limit. The Zeeman limit situation is described by the widely used theory of Bloembergen and Morgan (*2*) (B–M). Theory is needed (1) which incorporates the effects of the permanent zfs interaction, thereby providing a realistic description of the magnetic field dependence of the relaxation times; and (2) which describes electron spin relaxation at a similar level of complexity as B–M theory—namely, with two magnetic field-dependent relaxation times, τ_{S1} and τ_{S2}, defined in the laboratory frame. The present study provides theory of this kind. Expressions are derived for "level-averaged" (see below) electron spin relaxation times, which approximate the true relaxation behavior as an averaged decay over spin eigenstates. These expressions, defined both in the laboratory coordinate frame and in the molecule-fixed zfs principal axis system, are valid for $S \geq 1$ and for arbitrary magnitudes of the electronic Zeeman and zfs energies. Also,

simple closed-form expressions, valid in the zfs limit, are given for spins $S = 1$, 3/2, 2, and 5/2 (Appendix 3). The physical mechanism of relaxation is the same as that assumed by B–M, namely, collisional distortion of the permanent zfs tensor.

BACKGROUND

This section reviews related earlier work, particularly of Ref. (40), which provides the physical and mathematical framework of the current study. As described above, relaxation in the Zeeman limit is described by B–M theory. In the opposite physical limit ($H_{zfs}^0 \gg H_Z$), the electron spin motion is spatially quantized (or polarized) along the molecule-fixed principal axes of the permanent zfs tensor, and a description of the electron spin motion is most conveniently formulated in the molecule-fixed coordinate frame (4, 6). Electron spin relaxation for $S = 1$ in the zfs limit has recently been analyzed by Westlund (41) and by Bertini et al. (42), who used Redfield theory to derive closed-form zfs limit expressions for T_{S2} relaxation rates defined along molecule-fixed coordinate axes. These studies assumed, as in B–M theory, that relaxation results from collisionally induced distortion of the permanent zfs tensor.

Subsequently, Sharp and Lohr (40) derived expressions for molecular-frame (M-F) electron spin relaxation times for spins $S \geq 1$ subject to arbitrary magnitudes of the Zeeman and zfs interactions, likewise assuming slow Brownian reorientation. These authors employed a microcopic formulation of the problem which computes the electron spin time correlation functions by solving the equation of motion of the spin components in the thermal equilibrium sample (in contrast, Redfield theory computes the return of a perturbed density matrix to thermal equilibrium). Physically, "electron spin relaxation" times in NMR-PRE describe randomization of the microscopic electron-nuclear (S–I) hyperfine interaction in samples in which the electron spin density matrix remains at thermal equilibrium. The time correlation functions of the electron spin motion are

$$G_r(\tau) = \overline{\langle S_r(\tau) \cdot S_r(0) \rangle} \tag{1a}$$

$$= \text{Tr}\{\rho_S \overline{S_r(\tau) S_r(0)}\}, \tag{1b}$$

where r denotes Cartesian coordinates, which may be defined, as convenient for the physical situation, either in the laboratory frame (L-F: $r = x, y, z$, with $z || \mathbf{B}_0$) or in the molecule-fixed principal axis system of the permanent zfs tensor (M-F: $r = \hat{x}, \hat{y}, \hat{z}$). The density operator, ρ_S, of the electron spin remains at thermal equilibrium during the NMR-PRE experiment ($\rho_S = \rho^0$). The superscripting line in Eqs. [1] indicates an average over the nonspin molecular degrees of freedom. $G_r(\tau)$ describes both coherent and stochastic motions of the electron spin. The coherent motions are driven by the static electron spin Hamiltonian, H_S^0, which is assumed to consist of Zeeman plus permanent zfs

terms,

$$H_S^0 = H_Z + H_{zfs}^0, \tag{2a}$$

$$H_Z = g_e \beta_e B_o (\hat{S}_z \cos \beta + \sin \beta (\hat{S}_x \cos \varphi + \hat{S}_y \sin \varphi)) \tag{2b}$$

$$H_{zfs}^0 = (2/3)^{1/2} D \hat{S}_1^{(2)} + E \hat{S}_2^{(2)}. \tag{2c}$$

In Eqs. [2], g_e and β_e are the electron g value and the Bohr magneton, D and E are the cylindrical and orthorhombic principal values of the zfs tensor, and $\{\beta, \varphi\}$ are polar angles of the Zeeman field in the M-F. (Expressed in wavenumber units, $\tilde{D}$ and $\tilde{E}$ are the zfs parameters of ESR.) In Eq. [2c], additional terms proportional to fourth-rank tensor functions of the spin variables are present for $S \geq 2$ but are neglected.

The TCFs $G_r(\tau)$ in Eqs. [1] can be expressed in either the M-F or the L-F, in which case the electron spin relaxation times are likewise defined in the M-F or L-F. In this section, as in Refs. (40–42), the M-F formulation is assumed, and hence H_S^0 in Eqs. [2b] and [2c] is expressed in the M-F. The L-F formulation is useful in some circumstances and is discussed in a subsequent section. The second-rank Cartesian spin tensor components, $S_q^{(2)}$, are defined in Appendix 1. In Eqs. [2], the spin operators are defined in the M-F and written with a circumflex ($\wedge$); spin operators without a circumflex are defined in the L-F. Thermal decay of the $G_r(\tau)$ results from a stochastic Hamiltonian, $H_S'(t)$, which defines the electron spin relaxation mechanism. As in Refs. (2, 40–44), $H_S'(t)$ is attributed to collisional distortion of the quadratic zfs tensor and can be written

$$H_{zfs}'(t) = \hbar \sum_q c_q(t) \hat{S}_q^{(2)}, \tag{3}$$

where the $c_q(t)$ are stochastic functions of time.

At thermal equilibrium, the density matrix of S is diagonal, and $G_r(\tau)$ consists of a sum of contributions, $G_r^{(\alpha)}(\tau)$, from individual eigenstates,

$$G_r(\tau) = \sum_\alpha (\rho^0)_{\alpha\alpha} \sum_{\alpha'} \overline{\langle \alpha | \hat{S}_r(\tau) | \alpha' \rangle \langle \alpha' | \hat{S}_r(0) | \alpha \rangle} \tag{4a}$$

$$= \sum_\alpha G_r^{(\alpha)}(\tau). \tag{4b}$$

The time dependence of the $G_r^{(\alpha)}(\tau)$ can be obtained (40) as the solution of the equation of motion using second-order time-dependent perturbation theory by procedure analogous to that of Redfield theory. Assuming the spin Hamiltonian to be separated into static and stochastic terms as in Eqs. [2] and [3], the $G_r^{(\alpha)}(\tau)$ can be written

$$G_r^{(\alpha)}(\tau) = (\rho^0)_{\alpha\alpha} \overline{\exp\left(-\tau/\tau_{S,r}^{(\alpha)}\right) \sum_\beta \left|\langle \alpha | \hat{S}_q^{(2)} | \beta \rangle\right|^2 \exp(-i\omega_{\alpha\beta}\tau)},$$

$$\tag{5}$$

where $\{|\alpha\rangle, |\beta\rangle\}$ are spin eigenfunctions, and $\omega_{\alpha\beta}$ are spin transition frequencies. Transforming $S_r(\tau)$ in Eqs. [1] to the interaction representation,

$$S_r(\tau) = e^{iH_s^0\hbar^{-1}\tau} \tilde{S}_r(\tau) e^{-iH_s^0\hbar^{-1}\tau}, \qquad [6]$$

leads (40) to the transformed quantities, $\tilde{G}_r^{(\alpha)}(\tau)$, the time dependence of which exhibit only thermal decay, not the coherent oscillations due to H_S^0:

$$\tilde{G}_r^{(\alpha)}(\tau) = (\rho^0)_{\alpha\alpha} \overline{\exp\left(-\tau/\tau_{S,r}^{(\alpha)}\right) \sum_{\beta} |\langle\alpha|\hat{S}_r|\beta\rangle|^2}. \qquad [7]$$

The spin TCFs, $\tilde{G}_r(\tau)$, are defined, as in Eq. [4b], by summing Eq. [7] over spin eigenstates.

According to Eq. [7], the decay of the $\tilde{G}_r^{(\alpha)}(\tau)$ is eigenstate-specific, in that decay in one eigenstate is uncoupled to decay in others. This is clearly unlike the decay of a perturbed density matrix, which involves coupled degrees of freedom of the density matrix. The reason that the $\tau_{S,r}^{(\alpha)}$ are eigenstate-specific quantities is as follows. Electron spin relaxation appears in the theory of the NMR-PRE as a description of randomization of the electron-nuclear hyperfine coupling, which results in part from stochastic motion of the electron spin (for dipolar relaxation, additional randomization results from Brownian reorientation of the interspin I–S vector). Thermal relaxation of $G_r(\tau)$ describes this randomization as a decay in the persistence of microscopic correlation in the spin motion. Over sufficiently short time intervals, the correlation is essentially perfect, $G_r(0) = \langle S_r^2 \rangle$, but over longer intervals, correlation is destroyed by thermal transitions. The decay of $G_r(\tau)$ within an eigenstate is uncoupled to that in different eigenstates: thermal transitions destroy the persistence of correlation in the spin motion and do not transfer an existing state of correlation from one eigenstate to another. In general, there are at most $3(2S+1)$ distinct relaxation times, $\tau_{S,r}^{(\alpha)}$ (3 spatial directions and $2S+1$ eigenstates). Outside the Zeeman and zfs limits, $\tau_{S,r}^{(\alpha)}$ depends on molecular orientation with respect to $\mathbf{B}_0$ so that in a powder, electron spin relaxation within a given eigenstate may involve a continuous distribution of decay constants.

The electron spin relaxation times of density matrix theory (41, 42) differ from those described by Eq. [7] and Ref. (40). The stochastic Liouville approach (19–32) developed in Sweden, on the other hand, appears to involve a comparable physical description of electron spin relaxation to that employed here. While the SL formalism has not been applied specifically to calculations of electron spin relaxation times (as opposed to calculations of the NMR-PRE), this approach appears to provide a suitable basis for including the effects of Brownian reorientation, thus generalizing the results of Ref. (40).

The following expression was derived (40) for the $\tau_{S,r}^{(\alpha)}$ in terms of the Redfield matrix elements, $R_{\alpha\alpha',\beta\beta'}$:

$$\left(\tau_{S,r}^{(\alpha)}\right)^{-1} = \langle\alpha|\hat{S}_r^2|\alpha\rangle^{-1} \sum_{\alpha',\beta,\beta'} R_{\alpha\alpha',\beta\beta'} \langle\beta|\hat{S}_r|\beta'\rangle \langle\alpha'|\hat{S}_r|\alpha\rangle. \qquad [8]$$

Equation [8] is valid for all $S \geq 1$ and for arbitrary magnitudes of the zfs and Zeeman energies, subject to the fundamental Redfield assumption that the fluctuations of $H'_{\text{zfs}}(t)$ are rapid compared to the time scale of relaxation; also, Eq. [2a] implies that reorientation is slower than electron spin relaxation. My object is to simplify the description of the relaxation process by averaging Eq. [8] over eigenstates, thus defining a single level-averaged relaxation time, $\tau_{S,r}$, along each spatial direction (r). This reduces the number of independent relaxation parameters to at most three (two for a cylindrical zfs tensor), providing a description of the electron spin relaxation process that has comparable complexity to B–M theory while accounting for effects of H_{zfs}^0. It is shown below that level averaging leads to great simplification in the mathematical form of the results.

LEVEL-AVERAGED RELAXATION TIMES

The ensemble average of Eq. [1] involves two independent sets of spatial variables, one involving the stochastic motions of $H'_{\text{zfs}}(t)$ (Eq. [3]), the other comprising the angular variables $\{\beta, \gamma\}$ which specify molecular orientation in Eq. [2] (i.e., H_S^0 in Eq. [2] is a function of the orientation of the permanent zfs tensor relative to $\mathbf{B}_0$). The molecular orientation is assumed, for the purpose of the calculation, to be time-independent as in a powder. The calculation assumes a single specified molecular orientation, and thus the resulting level-averaged relaxation times, $\tau_{S,r}$, are functions of the Euler angles, $\{\beta, \gamma\}$ (like the $\tau_{S,r}^{(\alpha)}$ in Eq. [8]). The orientational average is deferred to a later stage of the calculation.

The time derivative of $\tilde{G}_r(\tau)$ at $\tau = 0$ is, from Eq. [7],

$$\left[\frac{d\tilde{G}_r(\tau)}{d\tau}\right]_0 = \sum_{\alpha}(\rho^0)_{\alpha\alpha}\left(-\tau_{S,r}^{(\alpha)}\right)^{-1}\langle\alpha|\hat{S}_r^2|\alpha\rangle. \qquad [9]$$

We wish to approximate $\tilde{G}_r(\tau)$ by a single exponential,

$$\tilde{G}_r(\tau) \cong \tilde{G}_r(0)\exp(-\tau/\tau_{S,r}), \qquad [10]$$

for which the time derivative at $\tau = 0$ is

$$\left[\frac{d\tilde{G}_r(\tau)}{d\tau}\right]_0 = \tilde{G}_r(0)(-\tau_{S,r})^{-1}, \qquad [11a]$$

$$= \langle\hat{S}_r^2\rangle(-\tau_{S,r})^{-1}. \qquad [11b]$$

Using Eqs. [8], [9], and [11b] with

$$\langle\hat{S}_r^2\rangle = S(S+1)/3 \qquad [12]$$

gives

$$(\tau_{S,r})^{-1} = \sum_{\alpha} (\rho^0)_{\alpha\alpha} \frac{\langle \alpha | \hat{S}_r^2 | \alpha \rangle}{\langle \hat{S}_r^2 \rangle} (\tau_{S,r}^{(\alpha)})^{-1}, \qquad [13]$$

$$= [S(S+1)/3]^{-1} \sum_{\alpha,\alpha',\beta,\beta'} (\rho^0)_{\alpha\alpha} R_{\alpha\alpha',\beta\beta'}$$

$$\times \langle \beta | \hat{S}_r | \beta' \rangle \langle \alpha' | \hat{S}_r | \alpha \rangle. \qquad [14]$$

To evaluate the sums in Eq. [14], the Redfield matrix elements need to be written explicitly in terms of spin matrix elements. The coefficients, $c_q(t)$, of $H'_{\text{zfs}}(t)$ are stochastic in time and are assumed to be uncorrelated for different Cartesian modes (q), so that

$$\overline{c_q(t)c_{q'}(t+\tau)} = \overline{|c_q(0)|^2} e^{-\tau/\tau_q} \delta_{q,q'}, \qquad [15]$$

where τ_q is the correlation time for the qth mode of zfs distortion. From the assumed form of $H'_{\text{zfs}}(t)$ in Eq. [2], the Redfield matrix elements can be written

$$R_{\alpha\alpha',\beta\beta'} = \sum_q \left[\langle \alpha | \hat{S}_q^{(2)} | \beta \rangle \langle \beta' | \hat{S}_q^{(2)} | \alpha' \rangle (k_q(\alpha'-\beta') + k_q(\alpha-\beta)) \right.$$

$$- \delta_{\alpha'\beta'} \sum_{\gamma} \langle \gamma | \hat{S}_q^{(2)} | \beta \rangle \langle \alpha | \hat{S}_q^{(2)} | \gamma \rangle k_q(\gamma - \beta)$$

$$\left. - \delta_{\alpha\beta} \sum_{\gamma} \langle \gamma | \hat{S}_q^{(2)} | \alpha' \rangle \langle \beta' | \hat{S}_q^{(2)} | \gamma \rangle k_q(\gamma - \beta') \right], \qquad [16]$$

where

$$k_q(\omega) = 2^{-1} \int_{-\infty}^{\infty} \overline{c_q(t)c_q(t+\tau)} \cos(\omega\tau) \, d\tau \qquad [17a]$$

$$= C_q \frac{\tau_q}{1 + \omega^2 \tau_q^2}, \qquad [17b]$$

with

$$C_q = \overline{|c_q(0)|^2}. \qquad [18]$$

Inserting Eqs. [3], [15], [16], and [17] into Eq. [14] gives, on the rhs, a sum of terms, each composed of a product of five matrix elements (two elements each of $\langle \hat{S}_q^{(2)} \rangle$ and $\langle \hat{S}_r \rangle$ and one of $\langle \rho^0 \rangle$), times a spectral density function, $k_q(\omega_{\alpha\beta})$. In each term, all but two of the spin indices (those which appear in $k_q(\omega_{\alpha\beta})$) can be contracted by invoking closure. After renaming dummy indices, Eq. [14] can be written

$$(\tau_{S,r})^{-1} = [S(S+1)/3]^{-1}$$

$$\times \sum_{\alpha,\beta} \sum_q k_q(\omega_{\alpha\beta}) \langle \alpha | \hat{S}_q^{(2)} | \beta \rangle \langle \beta | (\hat{S}_r \rho^0 \hat{S}_q^{(2)} \hat{S}_r$$

$$+ \hat{S}_r \hat{S}_q^{(2)} \hat{S}_r \rho^0 - \hat{S}_r \hat{S}_r \rho^0 \hat{S}_q^{(2)} - \hat{S}_q^{(2)} \tilde{S}_r \rho^0 \hat{S}_r) | \alpha \rangle. \qquad [19]$$

Relaxation within the Scalar Part of the Density Matrix

In a thermal equilibrium sample, the density operator, ρ^0, is diagonal in the spin eigenbasis and has the form

$$\rho^0 = Q_S^{-1} \exp(-H_S^0/kT) \qquad [20a]$$

$$\cong Q_S^{-1} (\mathbf{1} - (H_Z + H_{\text{zfs}}^0)/kT). \qquad [20b]$$

Q_S is the partition function of S, equal to $(2S+1)$ in the high temperature limit. The Zeeman and permanent zfs Hamiltonians, H_Z and H_{zfs}^0, give rise to components of macroscopic spin order with, respectively, dipolar and quadrupolar tensor character, the former corresponding to the macroscopic spin magnetization vector observed in ESR. The scalar part of $\langle \rho^0 \rangle$ is not observed in ESR. However, the NMR-PRE involves randomization of the microscopic electron-nuclear hyperfine interaction and is influenced by all parts of the electron spin density matrix including the scalar term, which is normally the largest. We retain only the scalar term in Eq. [20b]. In this approximation, the density operator, $\rho^0 \cong Q_S^{-1} \underline{\mathbf{1}}$ commutes with the spin operators, and the terms of Eq. [19] can be collected, giving

$$(\tau_{S,r})^{-1} = [S(S+1)/3]^{-1} Q_S^{-1} \sum_{\alpha,\beta} \sum_q k_q(\omega_{\alpha\beta})$$

$$\times \langle \alpha | \hat{S}_q^{(2)} | \beta \rangle \langle \beta | [[\hat{S}_r, \hat{S}_q^{(2)}], \hat{S}_r] | \alpha \rangle. \qquad [21]$$

The double commutators in Eq. [21] can be evaluated by straightforward operator algebra, from which it can be shown that

$$[S_r, [S_q^{(2)}, S_r]] = n_q^{(r)} S_q^{(2)} + m_{q,q'}^{(r)} S_{q'}^{(2)}, \qquad [22]$$

with the numerical coefficients $n_q^{(r)}$ and $m_{q,q'}^{(r)}$ given in Table 1. From the table, the double commutator of $\hat{S}_q^{(2)}$ regenerates $\hat{S}_q^{(2)}$ times an integer factor, $n_q^{(r)}$, plus a cross-term ($q \neq q'$) which vanishes except for $r = \{x, y\}$ and $\{q, q'\} = \{z^2, x^2 - y^2\}$. (That the cross-term vanishes in all but these cases can be shown from the transformation properties of the functions, $\hat{S}_q^{(2)}$, under the D_{2h} point group, of which they form a representation; see Appendix 2).

TABLE 1
Coefficients $n_q^{(r)}$ and $m_{q,q'}^{(r)}$ in Eq. [22]

$S_q^{(2)}$	$n_q^{(z)}$	$n_q^{(x)}$	$n_q^{(y)}$	$m_{q,q'}^{(r)} S_{q'}^{(2)}$
S_{z^2}	0	3	3	$\sqrt{3} S_{x^2-y^2}$
$S_{x^2-y^2}$	4	1	1	$\sqrt{3} S_{z^2}$
S_{xz}	1	1	4	0
S_{yz}	1	4	1	0
S_{xy}	4	1	1	0

Inserting Eq. [22] into Eq. [21] gives

$$(\tau_{S,r})^{-1} = [S(S+1)/3]^{-1} Q_S^{-1}$$
$$\times \left(\sum_q n_q^{(r)} \sum_{\alpha,\beta} \left| \langle \alpha | \hat{S}_q^{(2)} | \beta \rangle \right|^2 k_q(\omega_{\alpha\beta}) + \text{c.t.} \right). \quad [23a]$$

The cross-term (c.t.) results from the nonvanishing coefficients, $m_{q,q'}^{(r)}$, and has the form

$$\text{c.t.} = 3^{1/2} c_r \sum_{\alpha,\beta} \langle \alpha | \hat{S}_1^{(2)} | \beta \rangle \langle \beta | \hat{S}_2^{(2)} | \alpha \rangle [k_1(\omega_{\alpha\beta}) + k_2(\omega_{\alpha\beta})], \quad [23b]$$

where the subscripts {1, 2} correspond to $\{\hat{z}^2, \hat{x}^2 - \hat{y}^2\}$ (see Appendix 1). The numerical factor, c_r, is defined such that $3^{1/2} c_r$ equals the cross-coefficient, $m_{q,q'}^{(r)}$. From Table 1, $c_r = (+1, -1, 0)$ according to $r = \hat{x}, \hat{y}, \hat{z}$, and hence,

$$c_r = (\delta_{r,\hat{x}} - \delta_{r,\hat{y}})(1 - \delta_{r,\hat{z}}). \quad [24]$$

In the above calculation, the Cartesian spin operators, $\hat{S}_r$ and $\hat{S}_q^{(2)}$, and the relaxation times, $\tau_{S,r}$, are defined in the zfs-PAS. Practical computation of $\tau_{S,r}$ is most conveniently carried out in the eigenbasis of H_{zfs}^0, rather than in the Zeeman basis (i.e., $\langle \hat{S}_z \rangle$, *not* $\langle S_z \rangle$, is diagonal).

Comments on the Calculation

The above calculation describes relaxation times defined with respect to the zfs principal axes (the M-F). It was derived from Eq. [8] using two approximations. First, the level-specific relaxation behavior of Eq. [5] is approximated in Eq. [10] as a single exponential. Second, only spin relaxation within the scalar part of the density matrix is considered. These approximations lead to the relatively simple expressions of Eqs. [23], which are valid for all $S \geq 1$ and for arbitrary magnitudes of the Zeeman and permanent zfs Hamiltonians. In the zfs limit, Eqs. [23] reduce to simple closed-form expressions, which are given in Appendix 3.

Outside the zfs limit, the relaxation times of Eqs. [23] depend on the molecular orientation relative to the Zeeman field. In this situation, spin relaxation in an isotropic sample is multiphasic, involving a distribution of decay modes and decay constants. A simple example of the multiphasic nature of M-F relaxation outside the zfs limit is provided by a Zeeman limit physical situation ($H_{\text{zfs}}^0 = 0$) in which the L-F relaxation times differ, $\tau_{S1}^0 > \tau_{S2}^0$. When this relaxation process is defined in the M-F, the relaxation times (i.e., $\tau_{S,r}$ in Eqs. [23]) depend on the orientation of the zfs tensor with respect to $\mathbf{B}_0$. For the parallel orientation ($\hat{z} \| \mathbf{B}_0$), $\tau_{S,\hat{z}} = \tau_{S1}^0$; in the perpendicular orientation ($\hat{z} \perp \mathbf{B}_0$), $\tau_{S,\hat{z}} = \tau_{S2}^0$; in other orientations, relaxation along the M-F coordinate axes is biphasic. In an isotropic powder, M-F relaxation in the intermediate regime ($H_Z \approx H_{\text{zfs}}^0$) is described by a distribution of rate constants. A very simple approximate representation of this multiphasic behavior is as a monophasic

decay, the decay constant, $(\bar{\tau}_{S,r})^{-1}$, of which is computed as the orientational average of Eqs. [23]. The utility of this kind of approximation is discussed further below.

It is easily seen that the M-F relaxation rate constants, $(\bar{\tau}_{S,r})^{-1}$, averaged over orientations, coincide with each other in the Zeeman limit,

$$(\bar{\tau}_{S,\hat{x}})^{-1} = (\bar{\tau}_{S,\hat{y}})^{-1} = (\bar{\tau}_{S,\hat{z}})^{-1} \quad \text{(Zeeman limit).} \quad [25a]$$

In this situation the $(\bar{\tau}_{S,r})^{-1}$ equal the mean of the B-M values:

$$(\bar{\tau}_{S,\hat{z}})^{-1} = 3^{-1} \left(\tau_{S1}^{0^{-1}} + 2\tau_{S2}^{0^{-1}} \right) \quad \text{(Zeeman limit).} \quad [25b]$$

That the orientationally averaged M-F relaxation times coincide in the Zeeman limit (Eq. [25a]) even if the B–M relaxation times differ ($\tau_{S1}^0 > \tau_{S2}^0$) results from the fact that the M-F coordinate frame is randomly oriented with respect to the Zeeman field, and in the Zeeman limit, the M-F axes are physically equivalent with respect to the spin motion after orientational averaging.

In the zfs limit, orientational averaging of Eqs. [23] is not required (since $H_S^0 = H_{\text{zfs}}^0$ does not depend on molecular orientation), and the $\tau_{S,r}$ are given by the simple closed-form zfs limit expressions of Appendix 3. There are at most three distinct level-averaged M-F relaxation times, $\tau_{S,r}$ ($r = \hat{x}, \hat{y}, \hat{z}$) (or two ($r = \hat{z}, \hat{x}$) for a cylindrical zfs tensor). As described above, M-F relaxation in the intermediate regime is described by a continuum of rate constants, of which the orientational average, $(\bar{\tau}_{S,r})^{-1}$, provides a simple approximate description.

Laboratory-Frame Relaxation

The choice of the zfs-PAS as coordinate frame is not obligatory, and a parallel calculation of level-averaged laboratory-frame (L-F) relaxation times, $\tau_{S1,2}$, is described below. In the Zeeman limit, these quantities coincide with the relaxation times of B–M theory, $\tau_{S1,2} = \tau_{S1,2}^0$; however, the L-F relaxation times, $\tau_{S1,2}$, are also well defined in non-Zeeman limit situations, including the zfs limit. In the zfs limit, all laboratory-frame directions are physically equivalent with respect to the spin motion after orientational averaging, and thus there is only one orientationally averaged L-F relaxation rate, which equals the average of the three M-F relaxation rates (this inverts Eqs. [25]):

$$(\bar{\tau}_{S1})^{-1} = (\bar{\tau}_{S2})^{-1}$$
$$= 3^{-1}[(\tau_{S,\hat{x}})^{-1} + (\tau_{S,\hat{y}})^{-1} + (\tau_{S,\hat{z}})^{-1}] \quad \text{(zfs limit)}$$
$$= 3^{-1}[2(\tau_{S,\hat{x}})^{-1} + (\tau_{S,\hat{z}})^{-1}] \quad \text{(cylindrical zfs limit).}$$
$$[26]$$

In the intermediate regime, the L-F relaxation times, $\tau_{S1,2}$, are functions of molecular orientation (like the M-F relaxation times, $\tau_{S,r}$), and spin relaxation in an isotropic sample is described by a distribution of rate constants. An orientationally

averaged rate constant, $(\bar\tau_{S1,2})^{-1}$, with an approximate significance analogous to $(\bar\tau_{S,r})^{-1}$, can be defined.

Expressions for the L-F relaxation rates, $(\tau_{S1,2})^{-1}$, can be derived from a calculation parallel to that above in which the $G_r(t)$ are defined in the Zeeman frame. The static spin Hamiltonian, H_S^0, of Eq. [2] can be expressed in the L-F as

$$H_S^0 = g_e\beta_e B_o S_z + (2/3)^{1/2} D \sum_{q'} S_{q'}^{(2)} R_{q',1}^{(2)}(\alpha, \beta, \gamma)$$

$$+ E \sum_{q'} S_{q'}^{(2)} R_{q',2}^{(2)}(\alpha, \beta, \gamma). \qquad [27]$$

The quantities, $R_{q',q}^{(2)}(\alpha, \beta, \gamma)$, are rotation matrix elements which transform the second-rank Cartesian tensor functions from the M-F to the L-F; they are functions of the Euler angles $\{\alpha, \beta, \gamma\}$, which take the L-F into the M-F. The stochastic Hamiltonian of Eq. [3] can likewise be transformed to the L-F,

$$H_{zfs}'(t) = \hbar \sum_q c_q(t) \sum_{q'} S_{q'}^{(2)} R_{q',q}^{(2)}(\alpha, \beta, \gamma)$$

$$= \hbar \sum_{q'} S_{q'}^{(2)} \sum_q c_q(t) R_{q,q'}^{(2)}(\alpha, \beta, \gamma)$$

$$= \hbar \sum_{q'} c_q'(\alpha, \beta, \gamma; t) S_{q'}^{(2)}, \qquad [28]$$

where

$$c_q'(\alpha, \beta, \gamma; t) = \sum_q c_{q'}(t) R_{q,q'}^{(2)}(\alpha, \beta, \gamma).$$

Thus the coefficients in the L-F expression for $H_{zfs}'(t)$ are functions of molecular orientation as well as of time. After averaging Eq. [28] over spatial orientations, the coefficients, $c_{q'}(t)$, are functions only of time. However, it is not meaningful to assign distinct dynamical properties to the L-F Cartesian modes of zfs distortion, and so we treat zfs distortion as isotropic, with all $c_{q'}(t) = c'(t)$, and describe the decay by a single correlation time, τ_v:

$$\overline{c'(t)c'(t+\tau)} = C' \exp(-\tau/\tau_v). \qquad [29]$$

As is true for the M-F C_q parameters, the sum of the parameters $(\hbar^2 C')$ equals the trace, $(\hbar\Delta_t)^2$, of $\overline{[H_S'(t)]^2}$. Taking the principal values of $H_S'(t)$ to be D' and E', the relationships among these quantities are

$$\Delta_t^2 = (2/3)\overline{(D'/\hbar)^2} + 2\overline{(E'/\hbar)^2} \qquad [30a]$$

$$= \sum_q C_q \quad \text{(M-F)} \qquad [30b]$$

$$= 5C' \quad \text{(L-F)}. \qquad [30c]$$

In Eqs. [30], $H_S'(t)$, D', and E' have units of J; C', C_q, and Δ_t^2 have units of $(rad/s)^2$.

The laboratory-frame formulation yields a mathematical expression similar to Eq. [23] but in which the Cartesian spin operators, S_q, are defined in the laboratory frame. The numerical coefficients, $n_q^{(r)}$, are defined by Eq. [22] and retain the values in Table 1. From Eq. [30c], there is only a single mean-square coefficient, C', and correlation time, τ_v, describing the stochastic motions. In the high temperature limit, the expression equivalent to Eq. [23] for L-F relaxation is

$$(\tau_{S1,2})^{-1} = 3(S(S+1))^{-1}(2S+1)^{-1}\left(\Delta_t^2/5\right)$$

$$\times \sum_q n_q^{(z)}\left(\sum_{\alpha,\beta} |\langle\alpha|S_q^{(2)}|\beta\rangle|^2 j(\omega_{\alpha\beta}) + \text{c.t.}\right) \qquad [31a]$$

$$\text{c.t.} = 3^{1/2} c_r \sum_{\alpha,\beta} \langle\alpha|S_1^{(2)}|\beta\rangle\langle\beta|S_2^{(2)}|\alpha\rangle[2j(\omega_{\alpha\beta})] \qquad [31b]$$

$$j(\omega) = \tau_v/\left(1 + \omega^2\tau_v^2\right).$$

The quantities τ_{S1} and τ_{S2} describe spin relaxation parallel and perpendicular to the Zeeman field direction. The expression for τ_{S2} is the same as Eqs. [31] except that $n_q^{(x)}$ replaces $n_q^{(z)}$. These expressions are valid for $S \geq 1$ and for arbitrary magnitudes of the Zeeman and static zfs Hamiltonians, subject to the same approximations as for Eqs. [23]. In the Zeeman limit, it can be shown that Eq. [31] reduces to the Bloembergen–Morgan result,

$$\left(\tau_{S2}^0\right)^{-1} = c_Z\Delta_t^2[(3/2)j(0) + (5/2)j(\omega_S) + j(2\omega_S)] \qquad [32a]$$

$$\left(\tau_{S1}^0\right)^{-1} = c_Z\Delta_t^2[j(\omega_S) + 4j(2\omega_S)], \qquad [32b]$$

where

$$c_Z = [4S(S+1) - 3]/5. \qquad [32c]$$

Short τ_v Limit

It is interesting to compare Eqs. [31] with a result of McLachlan (45) that in the fast motion limit where all $(\omega_{\alpha\beta}\tau_v) \ll 1$, the relaxation rate defined in any coordinate frame, e.g., $(\tau_{S1,2})^{-1}$ or $(\tau_{S,\hat{r}})^{-1}$, approaches the limiting value,

$$(\tau_{S,r})_0^{-1} = [4S(S+1) - 3]\left(\Delta_t^2/5\right)\tau_v, \qquad [33]$$

as $\tau_v \to 0$. In this limit, Eq. [31] reduces to

$$(\tau_{S,r})_0^{-1} = 3[(2S+1)S(S+1)]^{-1}\left(\Delta_t^2/5\right)\tau_v \sum_q n_q^{(r)}\text{Tr}\{S_q^{(2)} S_{q'}^{(2)}\}.$$

$$[34]$$

The cross-term, c.t., in Eqs. [31] vanishes:

$$\text{c.t.} = 3^{1/2} c_r(2\tau_v)\sum_{\alpha,\beta}\langle\alpha|S_1^{(2)}|\beta\rangle\langle\beta|S_2^{(2)}|\alpha\rangle$$

$$= 3^{1/2} c_r(2\tau_v)\text{Tr}\{S_1^{(2)} S_2^{(2)}\}$$

$$= 0.$$

The spin trace in Eq. [34] equals

$$\mathrm{Tr}\{S_q^{(2)} S_{q'}^{(2)}\} = 2^{-1} 3^{-1} 5^{-1} S(S+1)(2S+1)[4S(S+1) - 3]\delta_{q,q'}$$

[35]

(this result is tedious to derive but is readily confirmed by calculation). Inserting Eq. [35] into Eq. [34], and using the fact that $\Sigma n_q^{(r)} = 10$ for any r, gives

$$(\tau_{S,r})_0^{-1} = [4S(S+1) - 3]\tau_{\mathrm{v}}(\Delta_{\mathrm{t}}^2 / 5),$$

which is McLachlan's result. The zfs-limit expressions in Appendix 3 likewise approach McLachlan's limit when $\tau_{\mathrm{v}} \to 0$.

IMPLEMENTATION

The Zfs and Zeeman Limits

The expressions given in Appendix 3 for M-F electron spin relaxation times can be incorporated directly into the zfs-limit theory of the NMR-PRE. The appropriate zfs-limit expressions for the NMR-PRE, valid for $S = 1$ to $S = 5/2$ assuming slow reorientation and a cylindrical zfs tensor, are summarized in Appendix 4. Equations [A4.1]–[A4.8] are similar to expressions derived previously (3) but have been modified as needed to incorporate the level-averaged electron spin relaxation times of Appendix 3. The corresponding Zeeman-limit expressions for the NMR-PRE are those of SBM Theory.

Calculations outside the Zfs- and Zeeman-Limit Regimes

Equations [23] and [31] are more general expressions for level-averaged electron spin relaxation that are valid for arbitrary magnitudes of the Zeeman and zfs interactions and for any value of the spin, again subject to slow Brownian reorientation. Equation [23] can be incorporated into formulations of NMR-PRE theory which describe the electron spin motion in the M-F, and Eq. [27] can be used when the electron spin motion is described in the L-F. A computer program which implements these calculations is described below.

While Eqs. [23] and [31] describe electron spin relaxation due to the zfs distortion mechanism in the intermediate regime, it should be appreciated that zfs interactions affect the NMR-PRE in other ways as well. In particular, reorientational modulation of the static zfs coupling provides an electron spin relaxation mechanism in addition to the collisional mechanism described above. The reorientational relaxation contribution, $(\tau_{S,r}^{(\mathrm{R})})^{-1}$, which is often significant when $H_{\mathrm{zfs}}^0 > H_Z$, can be computed using either of two different approaches: we use spin dynamics simulation methods (3, 13, 18) (see below); alternatively, Swedish workers have used the stochastic Liouville equation (SLE) approach of Benetis, Westlund, Kowalewski et al. (19, 20, 23, 25, 26).

In addition, a static zfs interaction affects the NMR-PRE in other ways than simply through its effect on electron spin relax-

ation. The zfs interaction exerts an important influence on electron spin precession, on the spin wavefunctions, and on the axes of spatial quantization, all of which have an important influence on the NMR-PRE. While we have simple analytical expressions for the Zeeman and slow-reorientation zfs limits, this is not true of the intermediate regime, or when Brownian reorientation is rapid. A realistic description of these more complicated situation is provided by spin dynamics simulation (as well as by the SLE approach). When Brownian reorientation is slow (i.e., slower than electron spin relaxation), the intermediate regime can also be described by slow-reorientation (S-R) NMR-PRE theory (6, 11, 35).

Computer Implementation

To implement the various levels of theory both of the NMR-PRE and of electron spin relaxation in a coherent and (we hope) user-friendly manner, we have over a period of years developed a Fortran program, ParRelax.2. This program, which is available on request, extends and refines our earlier programs, PARELAX (6), SpinDyn.f (12), and RotJmpDyn.f (16–18). ParRelax.2 implements the theory of the NMR-PRE at four levels: (1) SBM theory; (2) the orthorhombic zfs limit theory of Ref. (11); (3) slow-reorientation theory of the NMR-PRE, which is valid for arbitrary magnitudes of the Zeeman and zfs interactions; and (4) spin dynamics simulation. In the initial analysis of NMR-PRE data, we always use the S-R theory of levels (2) and (3), because S-R theory is amenable to a highly intuitive physical interpretation (3, 11), especially in the zfs limit. The analysis is subsequently refined and the effects of Brownian reorientation introduced using SD simulation.

Within each of the four levels of theory, electron spin relaxation can be described by the following methods as selected by the user: (i) by a set of constant (magnetic field-independent) user-defined relaxation parameters; (ii) by B-M theory; (iii) by the level-averaged relaxation times defined above; or (iv) by the level-specific relaxation times of Ref. (40). All of these methods are useful in practice. It is, for example, frequently useful to begin an analysis with the crude assumption of method (i) and subsequently to refine it to level (iii)/(iv), thereby displaying phenomena associated with the magnetic field dependence of the electron spin relaxation times. ParRelax.2 will, with an appropriate setting of flags, calculate the NMR $R_{1,2p}$ relaxation rates (dipolar and scalar) for each of the four levels (1)–(4) of theory, and, for the same set of physical assumptions, calculate the electron spin relaxation times by methods (i)–(iv).

Orientational averaging is carried out in the algorithms of ParRelax.2 as follows. The Zeeman field is positioned in the molecular frame at a series of polar angles defined by the vertices and face centers of the truncated icosahedron (buckeyball). There are 92 sampled orientations, at each of which H_S^0 is diagonalized. The Cartesian spin matrices, $\langle S_q \rangle$ and $\langle S_r \rangle$, and transition frequencies, $\omega_{\alpha\beta}$, needed in Eqs. [23] and [31] are computed in the spin eigenbasis at each orientation. This sampling

procedure provides unbiased and highly effective spatial averaging.

This method of orientational averaging can be applied both to the NMR-PRE and to the electron spin relaxation times. In the slow-reorientation NMR-PRE calculations of levels (2) and (3), the electron spin relaxation times are computed at each of the 92 sampled orientations using either an L-F formulation or an M-F formulation as required in the calculation of the NMR-PRE. Then the NMR-PRE is computed at the same set of orientations, using these spatially unaveraged electron spin relaxation times. Alternatively, the electron spin relaxation times can be calculated and employed as the orientationally averaged quantities, $(\bar{\tau}_{S,r})^{-1}$ or $(\bar{\tau}_{S1,2})^{-1}$. The former procedure is more accurate but involves greater complexity in the physical description.

Spin dynamics simulations of the NMR-PRE require the use of orientationally and level-averaged L-F relaxation times, $(\bar{\tau}_{S1,2})^{-1}$. While SD simulation generalizes the description of the NMR-PRE in accounting for effects of Brownian reorientation, it uses a less detailed description of electron spin relaxation than is possible within S-R theory (levels (2) and (3)). This kind of trade-off needs to be considered in practical analyses.

SUMMARY AND ILLUSTRATIVE CALCULATIONS

In the preceding discussion, electron spin relaxation times have been defined in six ways, which I summarize. There are three sets of L-F relaxation times: (1) $\tau_{S1,2}^0$ from B–M theory (Eqs. [32]); (2) the level-averaged relaxation times, $\tau_{S1,2}$, of Eq. [31]; these quantities are functions of molecular orientation; and (3) the level- and orientationally averaged quantities, $(\bar{\tau}_{S1,2})^{-1}$. There are likewise three sets of relaxation times defined in the M-F: (4) $\tau_{S,r}^{(\alpha)}$ are eigenstate-specific relaxation times of Eq. [8]; outside the zfs limit, these quantities are functions of molecular orientation; (5) the level-averaged relaxation times, $\tau_{S,r}$, of Eq. [23], which are also functions of molecular orientation; and (6) the level- and orientationally averaged quantities, $(\bar{\tau}_{S,r})^{-1}$. In the Zeeman limit, the L-F relaxation times, $\tau_{S1,2}$, reduce to the relaxation times of B–M theory, $\tau_{S1,2}^0$. In the zfs limit, the M-F relaxation times do not depend on molecular orientation and can be written as in Appendix 3.

Illustrative Calculations

Figures 1–4 compare M-F relaxation rates calculated from Eqs. [23] with L-F relaxation rates calculated from Eqs. [31] for values of the spin quantum number, $S = 1$, 3/2, 2, and 5/2. Bloembergen–Morgan (B–M) relaxation rates computed from Eqs. [32] are shown for comparison. In these plots, the variable along the abscissa is the zfs $\tilde{D}$ parameter. However, the calculations assumed that $(\tilde{\omega}_S + \tilde{D}) = 2$ cm^{-1}, where $\tilde{\omega}_S$ is the Larmor frequency in wavenumbers. Thus the plots range from the Zeeman limit on the left to the zfs limit on the right. The plotted quantities are $\bar{\tau}_{S1,2}$ and $\bar{\tau}_{S,r}$; i.e., Eqs. [23] and [31] are averaged over molecular orientations.
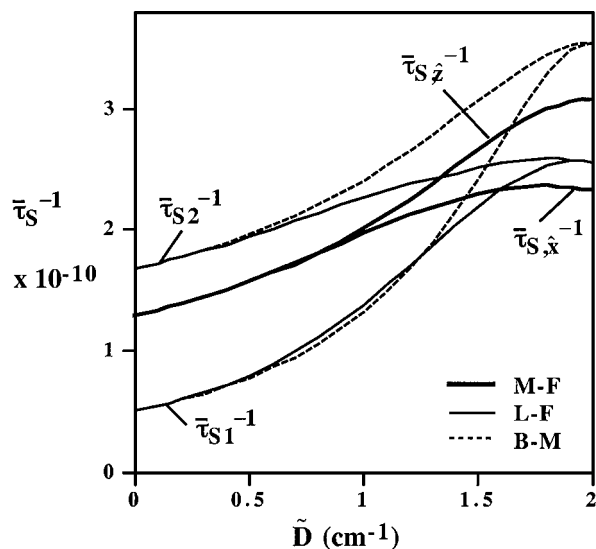

FIG. 1. Variation of laboratory-frame (L-F) and molecular-frame (M-F) relaxation rates from the zfs limit to the Zeeman limit for $S = 1$. The calculations assumed $\tilde{\omega}_S + \tilde{D} = 2$ cm^{-1}, where $\tilde{\omega}_S$ ($\equiv \omega_S/2\pi c$) is the Larmor frequency in wavenumbers; the left-hand side of the graph is the zfs limit and the right-hand side is the Zeeman limit. L-F relaxation rates were calculated from Eq. [31] and M-F relaxation rates from Eq. [23], and both quantites were averaged over molecular orientations as described in the text. Bloembergen–morgan (B–M) relaxation rates, calculated from Eqs. [32], are shown for comparison. Other parameters of the calculation were $E = 0$, $\tau_q = \tau_v = 4$ ps, $\Delta_t = 0.5$ cm^{-1}.

Consistent with the above discussion, the L-F relaxation times coincide in the Zeeman limit with B–M values (dashed). Also, consistent with Eqs. [26], the computed L-F relaxation rates, $(\bar{\tau}_{S1})^{-1}$ and $(\bar{\tau}_{S2})^{-1}$, differ in the Zeeman limit but coincide in
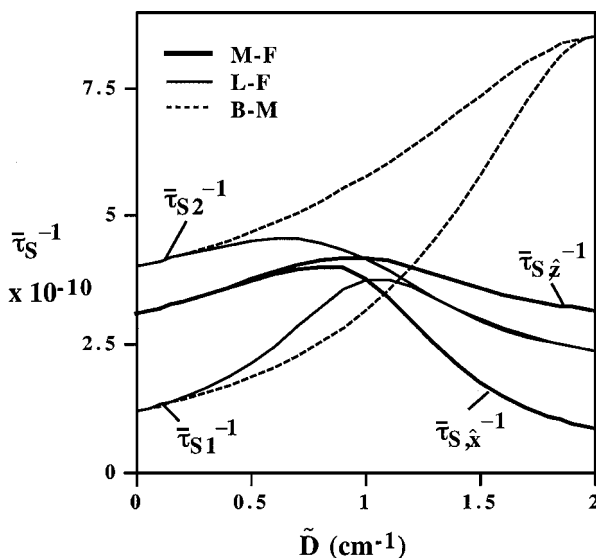

FIG. 2. Variation of laboratory-frame (L-F) and molecular-frame (M-F) relaxation rates from the zfs limit to the Zeeman limit for $S = 3/2$. Except for the spin quantum number, the calculations were carried out as described in the legend to Fig. 1.

FIG. 3. Variation of laboratory-frame (L-F) and molecular-frame (M-F) relaxation rates from the zfs limit to the Zeeman limit for $S = 2$. Except for the spin quantum number, the calculations were carried out as described in the legend to Fig. 1.
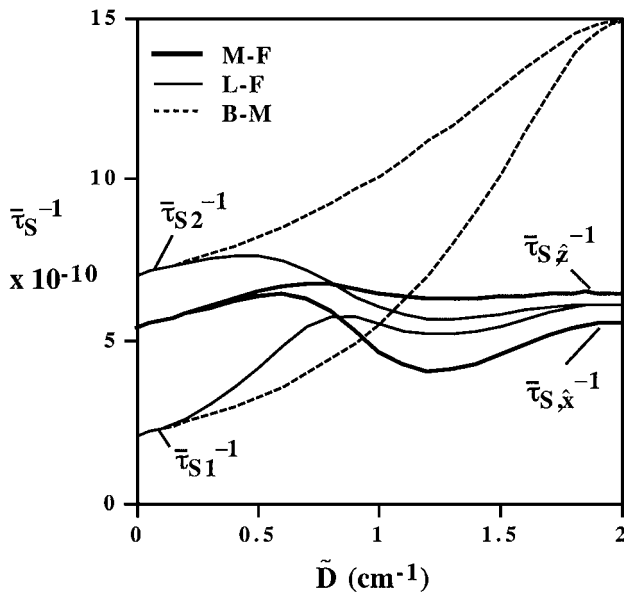
the zfs limit at a value equal to the mean of the M-F relaxation rates, $\bar{\tau}_{S,r}^{-1}$ ($r = \hat{x}, \hat{y}, \hat{z}$). Conversely, the M-F relaxation rates differ from each other in the zfs limit but coincide in the Zeeman limit at a value equal to the mean of the L-F relaxation rates. (The calculations assumed a cylindrical zfs tensor
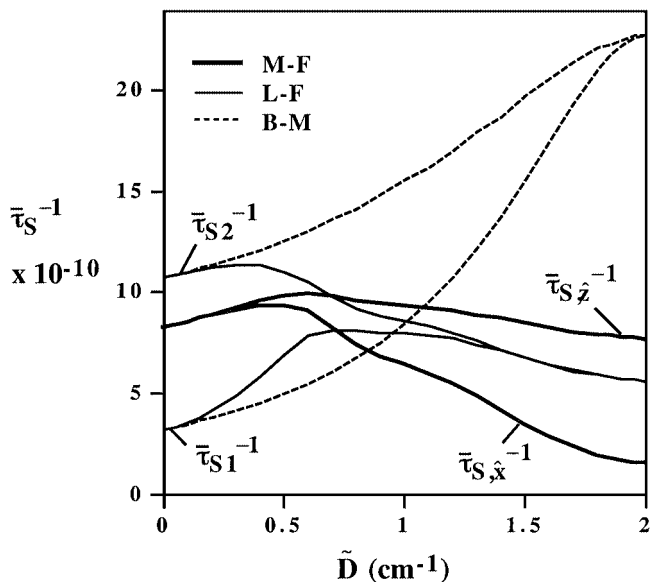

FIG. 4. Variation of laboratory-frame (L-F) and molecular-frame (M-F) relaxation rates from the zfs limit to the Zeeman limit for $S = 5/2$. Except for the spin quantum number, the calculations were carried out as described in the legend to Fig. 1.

so that there are two, rather than three, distinct M-F relaxation times.) A comparison of Figs. 1–4 shows that the deviation of B–M theory from the results of the generalized expressions (i.e., $\bar{\tau}_{S1,2}$ computed from Eq. [31]) becomes more pronounced as the spin quantum number increases. The relaxation rates also become increasingly complex functions of the parameters, $\tilde{D}$ and $\tilde{\omega}_S$, that determine the level structure. The plots in Figs. 3 and 4 exhibit bi-sigmoidal character, reflecting the relatively complex level structures of $S = 2$ and $S = 5/2$.

Zfs-limit values for the M-F relaxation times are given by the closed-form expressions of Appendix 3. These expressions describe the cylindrical zfs limit, except fot $S = 1$, for which expressions for the orthorhombic zfs limit are given as well (Eqs. [A3.9]–[A3.11]). For $S \geq 3/2$, the spin wavefunctions depend on the rhombicity ratio (E/D), and simple expressions analogous to Eqs. [A3.3]–[A3.8] cannot be given.

APPENDIX 1

Second-Rank Cartesian Tensor Operators

The second-rank Cartesian tensor operators in Eq. [3] are defined as follows:

$$S_1^{(2)} \equiv S_{z^2} = (3/2)^{1/2}\left(S_z^2 - S(S+1)/3\right) \qquad [A1.1]$$

$$S_2^{(2)} \equiv S_{x^2-y^2} = 2^{-1/2}\left(S_x^2 - S_y^2\right) \qquad [A1.2]$$

$$S_3^{(2)} \equiv S_{xz} = 2^{-1/2}(S_x S_z + S_z S_x) \qquad [A1.3]$$

$$S_4^{(2)} \equiv S_{yz} = 2^{-1/2}(S_y S_z + S_z S_y) \qquad [A1.4]$$

$$S_5^{(2)} \equiv S_{xy} = 2^{-1/2}(S_x S_y + S_y S_x). \qquad [A1.5]$$

APPENDIX 2

Double Commutators of the Cartesian Spin Tensors

The quadratic spin functions, $S_q^{(2)}$, of Appendix 1 form a representation of the D_{2h} point group in which $\{S_{z^2}^{(2)}, S_{x^2-y^2}^{(2)}, S_{xy}^{(2)}, S_{xz}^{(2)}, S_{yz}^{(2)}\}$ transform as $\{A_g, A_g, B_{1g}, B_{2g}, B_{3g}\}$. The symmetry of the commutator, $[S_r, [S_q^{(2)}, S_r]]$, can be evaluated from the direct product of the irreducible representations of the factors which form it. The double commutator, $[S_x, [S_{z^2}^{(2)}, S_x]]$, for example, transforms as $B_{2g} \otimes A_g \otimes B_{2g} = A_g$ and thus equals a linear combination of $S_{z^2}^{(2)}$ and $S_{x^2-y^2}^{(2)}$. In the same way, each double commutator $[S_r, [S_q^{(2)}, S_r]]$ belongs to the same irreducible representation as $S_q^{(2)}$. The double commutators contain cross-terms only for $\{q, q'\} = \{z^2, x^2 - y^2\}$, and for these, only for $r = x, y$, since $[S_z, S_{z^2}^{(2)}] = 0$, and $[S_z, [S_{x^2-y^2}^{(2)}, S_z]] = -4S_{x^2-y^2}^{(2)}$.

APPENDIX 3

Zfs Limit Electron Spin Relaxation Formulae

Formulae [A3.1]–[A3.11] are for level-averaged zfs limit relaxation times, $\tau_{S,r}$ $(r = \hat{x}, \hat{z})$, defined in the M-F. A cylindrical zfs limit Hamiltonian, $H_S^0 = H_{\text{zfs}}^0$, is assumed except where stated for $S = 1$. It is also assumed that all Cartesian modes (q) are described by a single value of τ_q and C_q in Eq. [17b]. In the zfs limit, there is a single spatially averaged L-F relaxation time, $\bar{\tau}_{S1} = \bar{\tau}_{S2}$, which can be computed from Eq. [26] using the M-F relaxation times below:

$S = 1$:

$$(\tau_{S,\hat{x}})^{-1} = (5/2)(k(0) + k(\omega_D)) \qquad [A3.1]$$

$$(\tau_{S,\hat{z}})^{-1} = 4\,k(0) + k(\omega_D) \qquad [A3.2]$$

$S = 3/2$:

$$(\tau_{S,\hat{x}})^{-1} = (6/5)(3\,k(0) + 7\,k(2\omega_D)) \qquad [A3.3]$$

$$(\tau_{S,\hat{z}})^{-1} = 12\,k(2\omega_D) \qquad [A3.4]$$

$S = 2$:

$$(\tau_{S,\hat{x}})^{-1} = (1/10)(81\,k(0) + 15\,k(\omega_D)$$
$$+ 24\,k(2\omega_D) + 90\,k(3\omega_D)) \qquad [A3.5]$$

$$(\tau_{S,\hat{z}})^{-1} = (1/10)(72\,k(0) + 6\,k(\omega_D)$$
$$+ 96\,k(2\omega_D) + 36\,k(3\omega_D)) \qquad [A3.6]$$

$S = 5/2$:

$$(\tau_{S,\hat{x}})^{-1} = (2/35)(168\,k(0) + 152\,k(2\omega_D)$$
$$+ 200\,k(4\omega_D) + 40\,k(6\omega_D)) \qquad [A3.7]$$

$$(\tau_{S,\hat{z}})^{-1} = (2/35)(320\,k(2\omega_D) + 80\,k(4\omega_D)$$
$$+ 160\,k(6\omega_D)) \qquad [A3.8]$$

$S = 1$ (orthorhombic zfs tensor):

$$(\tau_{S,\hat{x}})^{-1} = (3/2)\,k(0) + k(2\omega_E) + (5/4)(k(\omega_D - \omega_E)$$
$$+ k(\omega_D + \omega_E)) \qquad [A3.9]$$

$$\tau_{S,\hat{y}} = \tau_{S,\hat{x}} \qquad [A3.10]$$

$$(\tau_{S,\hat{z}})^{-1} = 4\,k(2\omega_E) + (1/2)(k(\omega_D - \omega_E) + k(\omega_D + \omega_E)).$$
$$[A3.11]$$

APPENDIX 4

Zfs-Limit Formulae for the NMR-PRE

The following formulae describe the zfs-limit R_{1p} NMR-PRE. It should be noted that in the zfs limit, $R_{1p} = R_{2p}$, since the dipolar field of S is uncorrelated with the laboratory axes. R_{1p} can be written as the sum of a longitudinal contribution, $R_{1\hat{z}}$, arising from the time correlation function, $\overline{\langle S_{\hat{z}}(0)S_{\hat{z}}(t)\rangle}$, of $\langle S_{\hat{z}}\rangle$, plus a transverse contribution, $R_{1\hat{x}}$, arising from $\overline{\langle S_{\hat{x}}(0)S_{\hat{x}}(t)\rangle}$. These two contributions depend respectively on thermal relaxation of $\langle S\rangle$ along $\hat{z}$ and $\hat{x}$. Assuming level-averaged electron spin relaxation, $R_{1\hat{z}}$ and $R_{1\hat{x}}$ depend respectively on the quantities $\tau_{S,\hat{z}}$ and $\tau_{S,\hat{x}}$ of Appendix 3.

Thus the zfs-limit NMR-PRE is

$$R_{1p} = R_{2p} = R_{1\hat{z}} + R_{1\hat{x}},$$

with $R_{1\hat{z}}$ and $R_{1\hat{x}}$ given by Eqs. [A4.1]–[A4.8]. These expressions assume slow Brownian reorientation and a cylindrical quadratic zfs tensor $(D \neq 0, E = 0)$, and electron spin transition frequencies are assumed much larger than the nuclear spin transition frequencies. The nuclear gyromagnetic ratio is γ_I, and c_{d} is a constant,

$$c_{\text{d}} = -g_{\text{e}}\beta_{\text{e}}(\mu_0/4\pi);$$

g_{e}, β_{e}, and μ_0 are the electron g factor, the Bohr magneton, and the permeability of space. The electron-nuclear (S–I) interspin vector is $\mathbf{r}_{IS}$ of length r_{IS}. The angular functions, $\Phi(\theta_{\hat{z}})$ and $\Phi(\theta_{\hat{z}})$, describe the dependence of the NMR-PRE on the polar angle $\theta_{\hat{z}}$ between $\mathbf{r}_{IS}$ and the unique axis of the zfs tensor,

$$\Phi_1(\theta_{\hat{z}}) = 3^{-1}(1 + P_2(\cos\theta_{\hat{z}}))$$

$$\Phi_2(\theta_{\hat{z}}) = 6^{-1}(2 - P_2(\sin\theta_{\hat{z}})),$$

where $P_2(x)$ is the second-order Legendre polynomial. The spectral density functions,

$$j_r(\omega) = \frac{\tau_{S,r}}{1 + (\omega\tau_{S,r})^2} \quad (r = \hat{x}, \hat{z}),$$

depend on the level-averaged electron spin relaxation times, $\tau_{S,\hat{z}}$ and $\tau_{S,\hat{x}}$, defined along molecule-fixed $\hat{x}$ and $\hat{z}$ directions. Functional forms for $\tau_{S,\hat{z}}$ and $\tau_{S,\hat{x}}$ are given by the following:

$S = 1$:

$$R_{1\hat{z}} = (8/3)(\gamma_I c_{\text{d}})^2 r_{IS}^{-6}\Phi_1(\theta_{\hat{z}})j_{\hat{z}}(\omega_I) \qquad [A4.1]$$

$$R_{1\hat{x}} = (16/3)(\gamma_I c_{\text{d}})^2 r_{IS}^{-6}\Phi_2(\theta_{\hat{z}})j_{\hat{x}}(\omega_D) \qquad [A4.2]$$

$S = 3/2$:

$$R_{1\hat{z}} = 5(\gamma_I c_{\text{d}})^2 r_{IS}^{-6}\Phi_1(\theta_{\hat{z}})j_{\hat{z}}(\omega_I) \qquad [A4.3]$$

$$R_{1\hat{x}} = (\gamma_I c_{\mathrm{d}})^2 r_{IS}^{-6} \Phi_2(\theta_{\hat{z}})(6 j_{\hat{x}}(2\omega_D) + 4 j_{\hat{x}}(\omega_I)) \quad [\text{A4.4}]$$

$S = 2$:

$$R_{1\hat{z}} = 8(\gamma_I c_{\mathrm{d}})^2 r_{IS}^{-6} \Phi_1(\theta_{\hat{z}}) j_{\hat{z}}(\omega_I) \qquad [\text{A4.5}]$$

$$R_{1\hat{x}} = (4/5)(\gamma_I c_{\mathrm{d}})^2 r_{IS}^{-6} \Phi_2(\theta_{\hat{z}})(6 j_{\hat{x}}(3\omega_D) + 12 j_{\hat{x}}(\omega_D)) \qquad [\text{A4.6}]$$

$S = 5/2$:

$$R_{1\hat{z}} = (35/3)(\gamma_I c_{\mathrm{d}})^2 r_{IS}^{-6} \Phi_1(\theta_{\hat{z}}) j_{\hat{z}}(\omega_I) \qquad [\text{A4.7}]$$

$$R_{1\hat{x}} = (2/3)(\gamma_I c_{\mathrm{d}})^2 r_{IS}^{-6} \Phi_2(\theta_{\hat{z}})(10 j_{\hat{x}}(4\omega_D)$$
$$+ 16 j_{\hat{x}}(2\omega_D) + 9 j_{\hat{x}}(\omega_I)). \qquad [\text{A4.8}]$$

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