

Electron- and nuclear-spin relaxation in an integer spin system, *tris*-(acetylacetonato)Mn(III) in solution

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Expressions are derived for the intermolecular contribution to the nuclear-spin relaxation rate in solutions containing dissolved paramagnetic ions with spin $S \geq 1$. The calculation assumes that the electron-spin Hamiltonian is dominated by a large axial zero-field splitting, and it accounts for effects of Zeeman interactions to first order. The expressions are used to analyze proton-spin relaxation of the acetone solvent in solutions of *tris*-(acetylacetonato)Mn(III)/acetone. The main objective was to measure electron-spin relaxation times of Mn(III), which in this complex is a high-spin, d^4 ion with integer spin $S = 2$. Spin-lattice relaxation measurements were conducted over a range of magnetic field strengths (0.28–1.1 T) where the zero-field splitting is large compared to the Zeeman energy. Electron-spin relaxation times of Mn(III) were found to be 8 ± 2 ps, with little dependence on temperature over the range 215–303 K and on magnetic field strength up to 1.1 T. Use of the assumption that Zeeman splittings dominate zero-field splittings (Solomon–Bloembergen–Morgan theory) resulted in computed electron-spin relaxation times that are too short by a factor of 3–4.

I. INTRODUCTION

The electron-spin energy levels and relaxation properties of paramagnetic ions with integer spin ($S = 1, 2$, etc.) have, in general, been sparsely studied due to the fact that the ESR spectra of these ions are frequently unobservable experimentally. In part, this results from the fact that the zero-field splittings are often larger than the Zeeman splittings at accessible magnetic field strengths. In addition, electron-spin relaxation times tend to be very short for these ions, further adding difficulties to direct observation of the resonance. Thus little direct information concerning spin relaxation times is available for these ions, particularly at noncryogenic temperatures.

An alternative approach to the measurement of electron-spin relaxation phenomena is through studies of the paramagnetic increment of nuclear-spin relaxation of ligand or solvent nuclei in the solution phase. Relatively low concentrations of paramagnetic ions can produce a potent relaxation mechanism for solvent nuclei due to the high magnetic moment of the electron. The nuclear relaxation rate depends on the spectral density function of the nuclear–electron magnetic interaction. When the electron-spin relaxation is rapid, this spectral density function is determined largely by electron-spin relaxation time, τ_S . Analysis of nuclear-spin relaxation of solvent nuclei in this way provides a probe of the electronic relaxation phenomena of the solute.

Nuclear relaxation in paramagnetic solutions is described in the well-known theory of Solomon¹ and Bloembergen and Morgan² (SBM). This theory assumes that the spin levels are split only due to Zeeman interactions, i.e., zero-field splittings (ZFS's) are ignored. This is appropriate when $\mathcal{H}_{\text{ZFS}} \ll \mathcal{H}_{\text{Zeeman}}$ (the Zeeman limit), as well as in systems where the ZFS is effectively motionally averaged by rapid molecular reorientation. SBM theory is notably successful in applications involving Mn(II), where the ZFS tends to be small even in sites of noncubic symmetry. For most other ions with $S \geq 1$, the ZFS is much larger and is

often not motionally averaged even in low molecular weight solution-phase complexes.

To analyze this latter situation, a suitable modification of the SBM theory is needed. Below, we derive appropriate expressions for the intermolecular relaxation contribution of nuclear spins due to dissolved paramagnetic ions of general spin S under the assumption that the ZFS is large compared to Zeeman splittings. In this case S is quantized along molecule-fixed, rather than space-fixed axes. In addition, molecular reorientation is assumed to be rapid enough to average the molecular axes on the time scale of nuclear relaxation, but not sufficiently rapid to motionally average the ZFS: in other words, for a system with axial symmetry we assume $D^{-1} < \tau_r < T_{1,\text{nuc}}$ and $D > \omega_S$, where $D = 2\pi cD'$ is the ZFS in rad s^{-1} and ω_S is the electronic Larmor frequency. These conditions frequently describe the situation for dissolved transition-metal complexes of moderate molecular weight at all but very high magnetic field strengths. Intramolecular relaxation in paramagnetic solutions under conditions of large ZFS and very slow molecular reorientation, $\tau_r > T_{1,\text{nuc}}$, has been studied previously for $S = 1$ (Ref. 3) and $S = 3/2$ (Ref. 4) ions.

The extended theory is used to analyze solvent proton relaxation in acetone solutions of the transition-metal complex *tris*-(acetylacetonate)Mn(III). Mn(III) in this system is a high-spin, d^4 ion with spin $S = 2$. The complex, which is uncharged, has been well characterized structurally,⁵ and with respect to its static zero-field splitting.⁶ The molecular symmetry is illustrated in Fig. 1. Mn(III)(AcAc)₃ is an octahedral *tris*-bidentate complex with nominal D_3 symmetry, which is lowered to C_2 by a Jahn–Teller distortion along a fourfold axis of the Mn(III) coordination sphere. The symmetry of the coordination sphere is dominated by the Jahn–Teller distortion and is nearly tetragonal, with two long (2.11 Å) and four short (1.94 Å) Mn–O bonds. This structure results in a relatively large zero-field splitting of -3.1 cm^{-1} ,⁶ which is probably nearly isotropic in the perpendic-

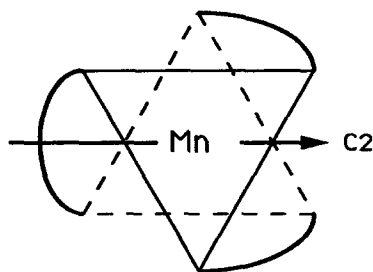


FIG. 1. Symmetry of the Mn(III)(AcAc)₃ complex. The D_3 nominal symmetry of the complex is lowered to C_2 by a tetragonal distortion of the Mn(III) coordination sphere. The axis of the Jahn-Teller distortion coincides with a two-fold axis of the D_3 point group.

ular plane. The measurements reported here characterize electronic and nuclear-spin relaxation in acetone solutions of Mn(III)(AcAc)₃ as a function of temperature and magnetic field strength.

A primary motivation for the present work, aside from the inherent physical interest, lies in its relevance to the NMR study of two important Mn(III)-containing redox-active manganese enzymes. One of these is the tetramangano metal center which functions as the active site of oxygen evolution in photosystem II of the photosynthetic membrane. The other is the manganese-containing pseudocatalase of *Lactobacillus Plantarum*. These enzyme systems contain polynuclear manganese centers, the redox chemistry of which is mirrored, in a specific and sensitive manner, in paramagnetic increments in the solvent ¹H relaxation rate (NMR-PRE).^{7,8} In a different context, interest in the NMR-PRE induced by Mn(III) has been stimulated by current interest in the use of Mn(III) complexes as contrast agents in magnetic resonance imaging.⁹ While an adequate theoretical basis exists for analyzing NMR-PRE data from Mn(II) oxidation states, current theory is much less satisfactory for Mn(III) and Mn(IV). Similarly, the available experimental electron-spin relaxation data in model systems, while ample for Mn(II), is quite sparse for both Mn(III) and Mn(IV). Two recent studies have examined the use of Mn(III) in this context, the present study provides a useful basis for evaluating data in the biological systems.

II. EXPERIMENT

Tris-(acetylacetonato) Mn(III) (Aldrich Chemical) was dissolved in benzene, filtered, and recrystallized by adding petroleum ether to a concentration of 70% v/v petroleum ether/benzene.¹⁰ Recrystallization required about 4 h at room temperature. Uniform dark brown crystals, 1–2 mm long, were precipitated and redissolved in acetone. The solutions were transferred to 7 mm glass tubes, degassed by five freeze-thaw cycles, and sealed under vacuum.

NMR spin-lattice relaxation times were measured at ¹H frequencies of 12.34, 20.63, 32.54, and 42.24 MHz using an apparatus described previously.¹¹ Reported T_1 's, measured using the phase-shifted triplet sequence,¹¹ are the average of five determinations. Probe temperature was controlled with a stream of dry nitrogen and maintained within ± 1 °C.

III. THEORETICAL

In this section we calculate the increment in the intermolecular spin-lattice relaxation rate ($1/T_{1,inter} \equiv R_{1p}$, of solvent nuclei due to dissolved paramagnetic ions of general spin $S \gg 1$). The ZFS is assumed to be large relative to the Zeeman energy, $\mathcal{H}_{ZFS} \gg \mathcal{H}_Z$. In this situation, the electron spin is quantized along molecule-fixed, rather than along laboratory-fixed axes.

Relaxation is assumed to result from magnetic dipole coupling between I and S . Intermolecular scalar coupling can also provide a relaxation pathway, in some cases quite efficient, but this contribution is neglected here. Whether scalar relaxation can be neglected in any practical situation must be considered carefully. For solutions of organic radicals, scalar relaxation is frequently important, sometimes dominant over dipolar relaxation, as has been shown by electron-nuclear NOE experiments.¹² The main interest in the present study concerns solutions of transition-metal complexes in which solvent is excluded from the first coordination sphere of the metal ion by the presence of strongly donating ligands. In this case, only outer-sphere scalar coupling is possible, and we expect this to be small. A quantitative description of intermolecular scalar relaxation has been given by Hubbard.¹³

The electron-nuclear dipolar Hamiltonian can be written as a scalar product of two first-rank spherical tensors,¹⁴

$$\hbar \mathcal{H}_{dip} = \frac{\alpha}{r^3} \sum_q 3^{-1/2} (-1)^{1-q} I_q^1 F_{-q}^1. \quad (1)$$

The I_q^1 are the components of the first-rank spherical tensor formed by the nuclear-spin operators

$$I_{\pm}^1 = \mp 2^{-1/2} I_{\pm}, \quad (2a)$$

$$I_0^1 = I_z, \quad (2b)$$

and F^1 is a first-rank spherical tensor formed from the direct product of spherical tensors of the electron-spin and polar spatial variables, $F^1 = \{S^1 \otimes C^2\}^1$.

The S_q^1 are defined as

$$S_{\pm}^1 = \mp 2^{-1/2} S_{\pm}, \quad (3a)$$

$$S_0^1 = S_z, \quad (3b)$$

the $C_m^2(\theta, \phi)$ are Racah's normalized spherical harmonics of spherical rank 2 and order m :

$$C_m^2(\theta, \phi) = \left(\frac{4\pi}{5}\right)^{1/2} Y_{2,m}(\theta, \phi), \quad (4)$$

and $\alpha = (-30^{1/2}) \gamma_I \gamma_S \hbar$. [Note that the superscripts in Eqs. (2)–(4) are ranks, not powers, of the spherical tensors. To avoid confusion, powers of operators will be written with parentheses, e.g., $(S_0^1)^n$.] Using this form for the dipolar Hamiltonian, the nuclear relaxation rate can be written³

$$\frac{1}{T_1} = - \left(\frac{3^{-1}\alpha^2}{\hbar^2}\right) \int_0^\infty \left\langle \frac{F_{+1}^1(t) F_{-1}^1(0)}{r^3} \frac{F_{-1}^1(0)}{r_0^3} \right\rangle e^{-i\omega_I t} + \left\langle \frac{F_{-1}^1(t) F_{+1}^1(0)}{r^3} \frac{F_{+1}^1(0)}{r_0^3} \right\rangle e^{i\omega_I t} dt. \quad (5)$$

Expanding the products $F_{\pm 1}^1(t) F_{\mp 1}^1(0)$ gives

$$F_{\pm 1}^1(t)F_{\mp 1}^1(0) = \frac{3}{5} [6^{-1} S_{\pm 1}^1(t)S_{\mp 1}^1(0)C_0^2(t)C_0^2(0) + 2^{-1} S_0^1(t)S_0^1(0)C_{\pm 1}^2(t)C_{\mp 1}^2(0) + S_{\mp 1}^1(t)S_{\pm 1}^1(0)C_{\pm 2}^2(t)C_{\mp 2}^2(0)]. \quad (6)$$

These expressions are all written in the laboratory coordinate frame, with H_0 along z . They can be used directly, after taking appropriate ensemble averages, to calculate T_1 in the Zeeman limit. In the ZFS limit, S is quantized along molecule-fixed axes, and it is necessary to transform from the laboratory frame to the molecular-axis system which diagonalizes \hat{S} .

Writing this transformation in terms of the Wigner rotation matrices gives $S_q^1 = \sum_q \hat{S}_q^1 \mathcal{D}_{q'q}^1(\alpha\beta\gamma)$, where S_q^1 and \hat{S}_q^1 are tensor components along laboratory and molecular axes, respectively. This gives

$$F_{+1}^1(t)F_{-1}^1(0) = \frac{3}{5} \left[6^{-1} \sum_{q'} \sum_{q''} \hat{S}_{q'}^1(t) \hat{S}_{q''}^1(0) \mathcal{D}_{q'+1}^1(t) \mathcal{D}_{q''-1}^1(0) \frac{C_0^2(t)}{r^3} \frac{C_0^2(0)}{r_0^3} \right. \\ \left. + 2^{-1} \sum_{q'} \sum_{q''} \hat{S}_{q'}^1(t) \hat{S}_{q''}^1(0) \mathcal{D}_{q_0'}^1(t) \mathcal{D}_{q_0''}^1(0) \frac{C_{+1}^2(t)}{r^3} \frac{C_{-1}^2(0)}{r_0^3} \right. \\ \left. \times \left[+ \sum_{q'} \sum_{q''} \hat{S}_{q'}^1(t) \hat{S}_{q''}^1(0) \mathcal{D}_{q'-1}^1(t) \mathcal{D}_{q''+1}^1(0) \frac{C_{+2}^2(t)}{r^3} \frac{C_{-2}^2(0)}{r_0^3} \right] \right]. \quad (7)$$

(The Euler angles are omitted from the Wigner rotational matrix elements for brevity.) In calculating the required time correlation function $\langle F_{+1}^1(t)F_{-1}^1(0) \rangle$, the averages over molecular orientations $\langle \mathcal{D}_{q_1q_1'}^1(t) \mathcal{D}_{q_2q_2'}^1(0) \rangle$, over spin variables $\langle \hat{S}_{q'}^1(t) \hat{S}_{q''}^1(0) \rangle$, and over diffusional motions $\langle C_q^2(t)C_{-q}^2(0) \rangle$ are needed. When the Zeeman splitting is small, the variables of $\hat{S}_{q'}^1(t)$, $\mathcal{D}_{q'q}^1(\alpha\beta\gamma)$, and $C_q^2(t, \theta, \phi)$ are uncorrelated and the averages can be taken separately. Using the orthogonality relations of the Wigner rotation matrices and assuming an exponential form for the reorientational time correlation function gives

$$\langle \mathcal{D}_{q_1q_1'}^1(t) \mathcal{D}_{q_2q_2'}^1(0) \rangle = \langle \mathcal{D}_{q_1q_1'}^1(0) \mathcal{D}_{q_2q_2'}^1(0) \rangle e^{-t/\tau_R} = 3^{-1} e^{-t/\tau_R} \delta_{q_1', -q_2'} \delta_{q_1'', -q_2''}. \quad (8)$$

Substituting (8) in (7) contracts the double summation, giving

$$\langle F_{+1}^1(t)F_{-1}^1(0) \rangle = (-1) \frac{3}{5} \frac{e^{-t/\tau_R}}{3} \left[6^{-1} \frac{C_0^2(t)}{r^3} \frac{C_0^2(0)}{r_0^3} - 2^{-1} \frac{C_{+1}^2(t)}{r^3} \frac{C_{-1}^2(0)}{r_0^3} + \frac{C_{-2}^2(t)}{r^3} \frac{C_{+2}^2(0)}{r_0^3} \right] \\ \times [\langle \hat{S}_{+1}^1(t) \hat{S}_{-1}^1(0) \rangle - \langle \hat{S}_0^1(t) \hat{S}_0^1(0) \rangle + \langle \hat{S}_{-1}^1(t) \hat{S}_{+1}^1(0) \rangle]. \quad (9)$$

To compute the time correlation functions of the spin, $\langle \hat{S}_q^1(t) \hat{S}_{-q}^1(0) \rangle$, we write $\hat{S}_q^1(t)$ in the Heisenberg representation, $\hat{S}_q^1(t) = e^{i\mathcal{H}_S t} \hat{S}_q^1(0) e^{-i\mathcal{H}_S t}$. The electron-spin Hamiltonian ($H_S = \hbar \mathcal{H}_S$) is a sum of Zeeman and ZFS interactions,

$$\mathcal{H}_S = \mathcal{H}_{ZFS} + \mathcal{H}_Z = D(\hat{S}_Z^2 - (1/3)S(S+1)) + E((\hat{S}_X^2 - \hat{S}_Y^2) + g\beta_0 H_0 \hbar^{-1} S_Z). \quad (10)$$

To simplify the calculation, the ZFS tensor is assumed to be diagonal and uniaxial in the molecular system ($D \neq 0, E = 0$), and the Zeeman energy is (for the moment) neglected, giving

$$\mathcal{H}_S \cong D \left(\hat{S}_Z^2 - \frac{S(S+1)}{3} \right) = \left(\frac{3}{2} \right)^{1/2} D S_0^2 \equiv \omega S_0^2. \quad (11)$$

Using the commutation relations

$$[S_{\pm 1}^1, S_0^2] = (\mp 2)^{-1} c_{2,0}^{\pm} (2S_0^1 \mp 1) S_{\pm 1}^1,$$

$\hat{S}_{\pm 1}^1(t)$ can be evaluated directly in the Heisenberg representation to give

$$\hat{S}_{\pm 1}^1(t) = e^{i\omega S_0^2 t} \hat{S}_{\pm 1}^1 e^{-i\omega S_0^2 t} = e^{\pm i\omega c_{2,0}^{\pm} (2S_0^1 \mp 1) t/2} \hat{S}_{\pm 1}^1. \quad (12)$$

The time correlation functions $\langle \hat{S}_{+q}^1(t) \hat{S}_{-q}^1(0) \rangle$ are then readily computed,

$$\langle \hat{S}_0^1(t) \hat{S}_0^1(0) \rangle = \frac{1}{3} S(S+1) e^{t/\tau_S}, \quad (13)$$

$$\langle \hat{S}_{\pm 1}^1(t) \hat{S}_{\mp 1}^1(0) \rangle = (-2^{-1}) (2S+1)^{-1} \sum_m |c_{S,m}^{\pm}|^2 e^{\pm iD(2m+1)t} e^{-t/\tau_{S,m}}. \quad (14)$$

$c_{S,m}^{\pm}$ is the coefficient of the raising operator $\hat{S}_{+1} |S, m\rangle = c_{S,m}^+ |S, m+1\rangle$ and the sum is over transitions of the S spin system. For an integer spin, the transition frequencies of S can be written simply in terms of the ZFS parameter D , $\omega_m = (2m+1)D$. For a half-integer spin, the situation is somewhat more complex since in this case the central transition, $\Delta m_S = (+1/2 \leftrightarrow -1/2)$, is not affected by the ZFS and occurs at the Zeeman frequency in lowest order. This situation is considered further below.

$\tau_{S,m}$ is the spin relaxation time of the transition at ω_m . In general, an integer spin S possesses S distinct relaxation times. For large ZFS ions these usually cannot be measured individually, and we will employ a single averaged parameter τ_S .

McLachlan¹⁵ has derived a simple expression for an averaged relaxation time of this type.

One further time correlation function is needed to compute $(1/T_{1,inter})$, namely that describing the relative motions of the nuclear and electronic spins due to molecular diffusion:

$$\left(\frac{4\pi}{5}\right)G_i(t) = \frac{C_q^2(t) C_{-q}^2(0)}{r^3 r_0^3} = \int_{\bar{r}} \int_{\bar{r}_0} \frac{C_q^2(t) C_{-q}^2(0)}{r^3 r_0^3} P(\bar{r}_0|\bar{r},t) g(r_0) d\bar{r}_0 d\bar{r}. \quad (15)$$

(The factor $4\pi/5$ arises from the definition of the C_q^2 [Eq. (4)] and is written explicitly in Eq. (15) to maintain consistency with Abragam's¹⁶ notation.) $G_i(t)$ has been derived previously in both open and closed form based on solutions of the classical diffusion equation^{13,16,17} or from random-flight models.¹⁸ Hwang and Freed¹⁹ have derived a convenient analytic expression for $G_i(t)$ using the Smoluchowski equation with boundary conditions that account for effects of excluded volume of the diffusing pair. In the subsequent analysis we use their spectral density function,

$$J(\omega) = 2 \operatorname{Re} \int_0^\infty G(t) e^{i\omega t} dt, \quad (16)$$

modified to account for effects of spin relaxation²⁰ and for molecular reorientation of the solute:

$$J_F(\omega) = \frac{8}{27} \frac{N}{dD_i} \times \operatorname{Re} \left[\frac{1 + \frac{1}{4}(i\omega\tau_D + \tau_D/\tau_c)^{1/2}}{1 + (i\omega\tau_D + \tau_D/\tau_c)^{1/2} + \frac{2}{3}(i\omega\tau_D + \tau_D/\tau_c) + \frac{1}{3}(i\omega\tau_D + \tau_D/\tau_c)^{3/2}} \right]. \quad (17)$$

In this expression, D_i is a sum of self-diffusion coefficients of solvent and solute, $D_i = D_1 + D_2$, N is the number density of paramagnetic ions in solution, and d is the distance of closest approach of I and S . τ_D and τ_c are correlation times, defined as

$$\tau_D = d^2/D_i, \quad (18a)$$

$$\tau_c^{-1} = \tau_r^{-1} + \tau_s^{-1}. \quad (18b)$$

Writing $\langle \mu_e^2 \rangle = g^2 \beta^2 S(S+1)$ for the squared magnetic moment of S , we have from Eq. (5),

$$\frac{1}{T_{1,inter}} = \frac{10}{3} (\gamma_I^2 \langle \mu_e^2 \rangle) \left(\frac{4\pi}{5}\right) [3^{-1} J(\omega_I)] \times \left\{ + 2^{-1} [S(S+1)(2S+1)]^{-1} \sum_m |c_{S,m}^+|^2 [J(\omega_I + \omega_m) + J(\omega_I - \omega_m)] \right\}. \quad (19)$$

The limiting behavior of Eq. (19) can be evaluated in the extreme narrowing region, where $J(\omega) \rightarrow J(0)$, by using the relation

$$(2S+1)^{-1} \sum_m |c_{S,m}^+|^2 = \frac{2}{3} S(S+1).$$

This gives

$$\frac{1}{T_{1,inter}} = \frac{8\pi}{3} \gamma_I^2 \langle \mu_e^2 \rangle J(0),$$

which equals Abragam's result in the corresponding limit (Ref. 16, pp. 300–304).

We particularize Eq. (19) to the situation of a high-spin, d^4 ion ($S=2$) in the ZFS limit, which describes the specific chemical situation of interest, Mn(III) (AcAc)₃. In the ZFS limit, there are four electronic spin transitions, two with $\omega_1 = D$, $|c^+|^2 = 6$, and two with $\omega_2 = 3D$, $|c^+|^2 = 4$. Writing $J(\omega) = J_F(\omega)$ and taking account that $\omega_I \ll \omega_m$, Eq. (19) can be written as

$$R_{1,inter} = (8\pi/9) \gamma_I^2 \langle \mu_e^2 \rangle \{ J_F(\omega_I) + 10^{-1} [12J_F(D) + 8J_F(3D)] \}. \quad (20)$$

For Mn(III), $|\langle \mu_e^2 \rangle|^{1/2}$ to a good approximation equals the spin-only value of the magnetic moment, which is 4.90 B.M.

Effects of Zeeman couplings. To introduce effects of small Zeeman couplings into the analysis, the relevant spin Hamiltonian (11) is

$$\begin{aligned} \mathcal{H}_S &= \mathcal{H}_{ZFS} + \mathcal{H}_Z \\ &= D(\hat{S}_Z^2 - \frac{1}{3}S(S+1)) + g\beta_0 H_0 \hbar^{-1} S_z \\ &= \left(\frac{3}{2}\right)^{1/2} DS_0^2 + g\beta_0 H_0 \hbar^{-1} \sum_q \hat{S}_q^1 \mathcal{D}_{q0}^1, \end{aligned} \quad (21)$$

with $\mathcal{H}_Z \ll \mathcal{H}_{ZFS}$, \mathcal{H}_Z , and thus also the time correlation functions $\langle \hat{S}_q^1(t) \hat{S}_{-q}^1(0) \rangle$, depend explicitly on molecular orientation through $\mathcal{D}_{q0}^1(\alpha\beta\gamma)$, which complicates the averaging process. However, the form of Eqs. (13) and (14) is fairly simple to lowest order in the Zeeman perturbation as long as molecular reorientation is slow compared to spin relaxation of S , $\tau_r \gg \tau_s$. In this situation the motion of the electron spin can be treated adiabatically.

A general expansion of the time correlation functions $\langle \hat{S}_q^1(t) \hat{S}_{-q}^1(0) \rangle$ can be obtained³ from an iterative solution of the equation of motion for $\hat{S}_q^1(t)$,

$$\frac{d\hat{S}_q^1(t)}{dt} = -i[\hat{S}_q^1, \hat{\mathcal{H}}_S], \quad (22)$$

using a suitable interaction representation. For this purpose we set $\hat{\mathcal{H}}_S = \hat{\mathcal{H}}_0 + \hat{V}$, where $\hat{\mathcal{H}}_0$ is the diagonal part of $\hat{\mathcal{H}}_S$,

$$\hat{\mathcal{H}}_0 = D\left(\frac{3}{2}\right)^{1/2} \hat{S}_0^2 + g\beta_0 H_0 \hbar^{-1} \hat{S}_0^1 \mathcal{D}_{00}^1 \quad (23)$$

and

$$\hat{V} = g\beta_0 H_0 \hbar^{-1} (\hat{S}_{+1}^1 \mathcal{D}_{+10}^1 + \hat{S}_{-1}^1 \mathcal{D}_{-10}^1). \quad (24)$$

To lowest order in $g\beta_0 H_0 / \hbar D$,

$$\begin{aligned} \langle \hat{S}_{+1}^1(t) \hat{S}_{-1}^1 \rangle &= \langle e^{i\mathcal{H}_0 t} \hat{S}_{+1}^1 e^{-i\mathcal{H}_0 t} \hat{S}_{-1}^1 \rangle \\ &= \sum_m \langle m | \hat{S}_{+1}^1 \hat{S}_{-1}^1 | m \rangle e^{i\omega_m t} e^{-t/\tau_{S,m}} \\ &= (-2^{-1})(2S+1)^{-1} \\ &\quad \times \sum_m |c_{S,m}^+|^2 e^{\pm i\omega_m t} e^{-t/\tau_{S,m}}, \end{aligned} \quad (25)$$

where the ω_m are transition frequencies of \mathcal{H}_0 . For a general spin S , Eqs. (13), (14), and (19) remain valid in the presence of small Zeeman splittings, but the electronic transition frequencies are modified by inclusion of the \hat{z} component of the Zeeman energy:

$$\omega_m = (2m+1)D + g\beta_0 H_0 \hbar^{-1} \mathcal{D}_{00}^1(\alpha\beta\gamma). \quad (26)$$

Lindner³ has solved Eq. (22) to second order in $g\beta_0 H_0 / \hbar D$ for a spin $S=1$, using an iterative approach. Her result to first order is equivalent to Eq. (26).

With the inclusion of Zeeman interactions, the ω_m depend on $\mathcal{D}_{00}^1 = \cos(\beta)$, where β is the polar angle between the laboratory and molecular frames. The average over molecular orientations is straightforward when τ_r is long relative to τ_S , in which case the time correlation function $\langle \hat{S}_{+1}^1(t) \hat{S}_{-1}^1(0) \rangle$ can be calculated with respect to fixed molecular axes. For integer spin, the Zeeman term produces a spread of electronic transition frequencies ω_m about the central value determined by the ZFS, $\omega_m = D(2m+1)$. The transition at ω_I is unaffected. We have not attempted to carry out this average explicitly in Eq. (16), since the exact form of $J(\omega)$ in this case is complicated and is likely to be of little practical utility. Qualitatively, the first-order effects of Zeeman splittings on Eq. (19) are simple; namely, the electronic transitions at ω_m are broadened, while the transition at ω_I is unaffected.

IV. RESULTS AND DISCUSSION

A. Relaxation in the ZFS and Zeeman limits

Figure 2 illustrates certain quantitative aspects of the spectral density function $J(\omega)$ of Eq. (17) and some characteristic differences between the ZFS and Zeeman limits. $J(\omega)$ is specified by two parameters, one describing translational diffusion τ_D , the other, τ_c , describing fluctuations in the local dipolar field of S . In the Zeeman limit, the dipolar fluctuation results solely from spin relaxation, $\tau_c = \tau_S$. In the ZFS limit, S is quantized along molecule-fixed axes, and τ_c contains contributions from both spin relaxation and molecular reorientation [Eq. (18b)]. Figure 2 shows plots of the reduced spectral density function, $j(\omega) \equiv J(\omega)/J(0)$, vs $\omega\tau_D$. Individual curves correspond to specific values of the ratio τ_c/τ_D . The purely translational part of $J(\omega)$, corresponding to $\tau_c/\tau_D \gg 1$, consists of a very broad dispersion, the width of which reflects the spectrum of dipolar couplings due to translational motions. For translational diffusion, the effective dipolar correlation time of a pair of spins increases as the square of their separation,²¹ thus producing a broad

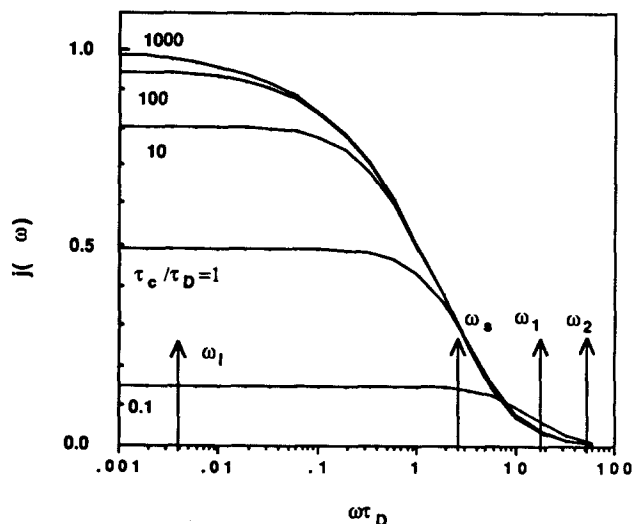


FIG. 2. Plots of the reduced spectral density function, $j(\omega) \equiv J_F(\omega)/J_F(0)$, vs $\omega\tau_D$ where $J_F(\omega)$ is given by Eq. (17). Theoretical curves corresponding to specific τ_c/τ_D ratios are shown. Arrows show the nuclear (ω_I) and electronic transition frequencies at 0.48 T, based on a parameters appropriate to Mn(III)(AcAc)₃. ω_S is the electronic Larmor frequency at 0.48 T, and $\omega_1 = D$ and $\omega_2 = 3D$ are zero-field splittings for an $S=2$ ion with an axial ZFS of $|D'| = 3.1 \text{ cm}^{-1}$. Positions of the transition frequencies are based on a value of $\tau_D = 33 \text{ ps}$ (see text).

dispersion in the spectral density function. As τ_c becomes comparable to or less than τ_D , the dispersion sharpens and its midpoint moves to higher frequency. In the limit $\tau_c/\tau_D \ll 1$, $J_F(\omega) = (2/3)N\tau_c/d^3$ (Ref. 18) and is independent of translational motion.

The nuclear relaxation rate depends on the spectral density function at the nuclear and electronic transitions, $J(\omega_I)$ and $J(\omega_m)$. The positions of these transitions are indicated in Fig. 2 for the system of specific experimental interest here, namely Mn(III)(AcAc)₃/acetone studied at a ¹H frequency of 20.5 MHz (0.48 T). τ_D in this system is taken to be 33 ps, corresponding to a temperature of 25 °C (see below).

A principal difference between the ZFS and Zeeman limits is that τ_c is usually much shorter in the former (ZFS limit) than in the latter, thereby reducing $J(\omega)$ and $R_{1\rho}$ relative to the value given by SBM theory. In part, this results from the effects of molecular reorientation, which contributes to τ_c only in the ZFS limit as described above. In addition, electron-spin relaxation is typically very rapid for large ZFS ions, resulting in a further shortening of τ_c . For ions with $S \gg 1$, τ_S^{-1} generally results from thermal modulation of the ZFS splittings and scales with the square of the ZFS tensor, $D^2 = X^2 + Y^2 + Z^2 = (2/3)D^2 + 2E^2$.¹³ Thus τ_S is expected to be very short for large ZFS ions, and the τ_c/τ_D ratio is expected to be of order unity or less. Under these conditions ($\tau_c/\tau_D \leq 1$), SBM theory severely overestimates $J(\omega)$ (see Fig. 2).

Further error results from misassignment of the electronic transition frequencies, i.e., the use of $J(\omega_S)$ as opposed to $J(\omega_m)$. When the τ_c/τ_D ratio is large, this may produce only modest effects, at least at moderate to high magnetic field strengths, because the electronic transitions under these conditions make only a minor contribution to

$1/T_{1,inter}$. At low τ_c/τ_D ratios (which are characteristic of large ZFS ions), the error becomes much more serious because of the increasing relative importance of the $J(\omega_S)$ term. Figure 2 illustrates these points in the specific case of Mn(III)(AcAc)₃. For this system, SBM theory overestimates $J(\omega_S)$ severalfold, resulting in an underestimate of τ_S by a factor of 3–4 (see below). In the large ZFS limit, the results are not very sensitive to the specific value of the ZFS parameter D , since the contribution of $J(\omega_m)$ to $1/T_{1,inter}$ is relatively small.

B. Spin relaxation in the Mn(III)(AcAc)₃/acetone system

Spin-lattice relaxation times of the methyl resonance of the acetone solvent were measured in a 5.1 mM Mn(III)/(AcAc)₃ solution. Figure 3 shows paramagnetic enhancements of the solvent relaxation rate, $R_{1p} = R_{1,obs} - R_{1,solv}$, plotted as a function of temperature at magnetic field strengths of 20.63 and 12.34 MHz. Data were also obtained at field strengths of 32.54 and 42.24 MHz. These data were used with Eqs. (17)–(19) to measure electron-spin relaxation times of Mn(III).

Calculation of the spectral density function [Eq. (17)] required dynamical information appropriate to Mn(AcAc)₃. For the self-diffusion coefficient D_1 for the acetone solvent at 25 °C, a value based on ¹H spin-echo studies was used.²² The temperature dependence of D_1 from 0–70 °C has been measured.²² Rather than extrapolate these values down to 217 K, we assumed the temperature dependence to be that of T/η , as given by the Stokes–Einstein equation, and used literature values²³ for $\eta(T)$. The self-diffusion coefficient D_2 of the solute was calculated from the Stokes–Einstein equation, $D_i = kT/6\pi\eta a$, using a radius $a = 5 \text{ \AA}$ estimated from molecular models. This gave a value of $D_2 = 1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25 °C, which is reasonable in light of the measured value for the acetone solvent

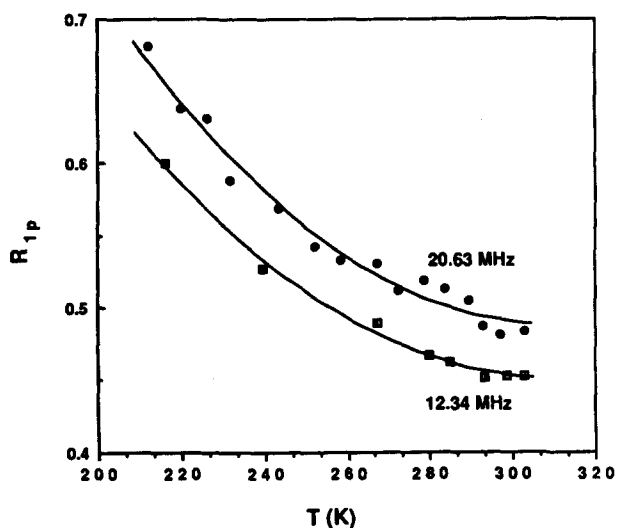


FIG. 3. R_{1p} for the acetone methyl protons in a 5.1 mM solution of Mn(III)(AcAc)₃ in acetone. Data are shown as a function of temperature at proton frequencies of 12.34 MHz (□) and 20.63 MHz (●).

$D_1 = 4.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, at the same temperature.

Also required is a distance of closest approach, d . An examination of molecular models suggested that appropriate values lie in the range 4.0–4.5 Å. This parameter enters rather sensitively in the theory (as d^{-3} in the limit where $\tau_c/\tau_D \ll 1$) and is probably the dominant source of uncertainty in the analysis. A value of 4.3 Å was used for most of the calculations. The effect of varying d was explored, with results that are described below.

Figure 4 shows values of the correlation time τ_c calculated from Eqs. (17)–(19) using the data in Fig. 3. Values were nearly temperature independent, varying from 8 to 10 ps over the observed temperature range (215–303 K). To extract τ_S^{-1} from τ_c^{-1} , the reorientational correlation time τ_r was needed. This was estimated from Debye's expression for the reorientational diffusion time of a second-rank tensor, $\tau_r^{(2)} = (4\pi a^3 \eta / 3kT)$. The temperature dependences of τ_c , τ_S , τ_r , and τ_D are shown in Fig. 4. Clearly, τ_S is substantially shorter than both τ_r and τ_D and effectively controls the behavior of τ_c as well as of $J(\omega)$.

For the sake of comparison, parallel calculations of τ_S^Z , the electronic relaxation time in the Zeeman limit, were undertaken using SBM theory with the spectral density function of Eq. (17). τ_S^Z is consistently shorter, by a factor of 3 to 4, than the corresponding result in the ZFS limit.

To better estimate the accuracy of calculated τ_S values, we have plotted in Fig. 5 grids of theoretical curves of R_{1p} vs temperature, each computed at a fixed value of τ_S . These curves were calculated using values of τ_r and τ_D computed as described above. Experimental R_{1p} values are superimposed on this grid as open circles. Examination of the figure shows that τ_S is determined most sensitively at low temperature ($\sim 215 \text{ K}$). In the low-temperature regime, Eq. (17) is determined largely by τ_S and d , and is nearly independent of

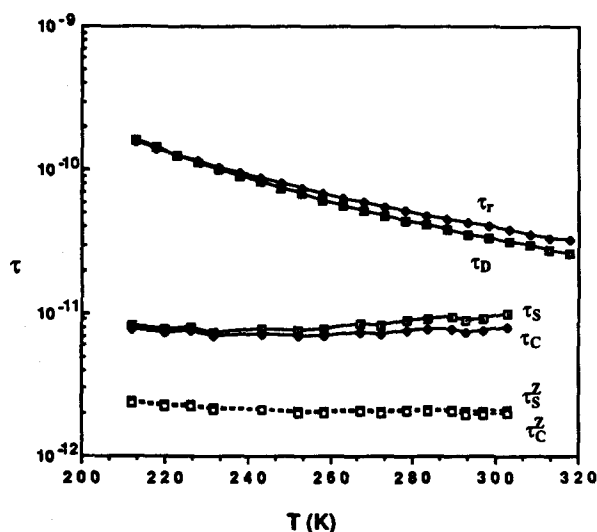


FIG. 4. Calculated correlation times for the Mn(III)(AcAc)₃/acetone system. (●), τ_c calculated for the data in Fig. 3 using Eqs. (17), (18), and (20) of the text. (□), τ_S , calculated from τ_c and Eq. (18b). (■), τ_D , calculated from the Stokes–Einstein equation; and (◆), τ_r , calculated from the Debye equation as described in the text. Dashed lines are τ_c (□) and τ_S (■) calculated from SBM theory in the Zeeman limit.

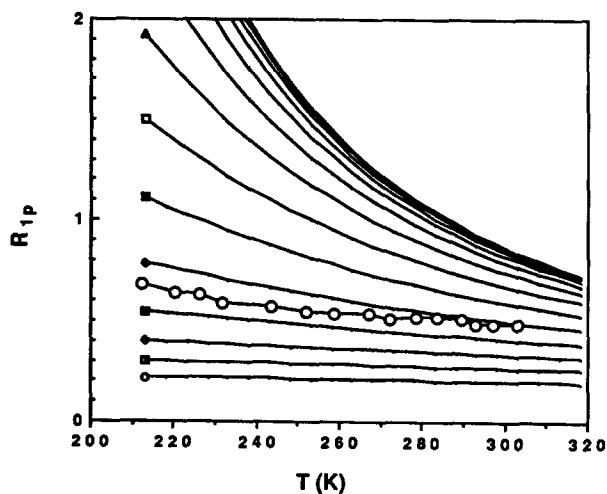


FIG. 5. Determination of τ_S from the proton relaxation increment, R_{1p} . Circles are measured R_{1p} values at 0.48 T (^1H frequency of 20.63 MHz). Theoretical curves, in order from bottom to top, correspond to τ_S values in ps of 1, 1.78, 3, 5.63, 10, 17.8, 30, 56.3, 100, 178, 300, 563, 1000, and 1780. Calculated curves are based on values of τ_D and τ_r as described in the text.

parameters describing molecular diffusion and reorientation (see above).

The greatest uncertainty in $J(\omega)$ at low temperature arises from the parameter d . The effect of varying d between 4.0 and 4.5 Å on the calculated τ_S is shown in Fig. 6. The overall uncertainty in τ_S is estimated to be $\pm 25\%$, increasing somewhat with rising temperature.

Figure 7 shows the magnetic field dependence of τ_S , measured at temperatures of 215 and 298 K. τ_S is essentially field independent between 0.34 and 1.09 T.

V. CONCLUSIONS

Measured values of τ_S lie in the range 8–10 ps, with little dependence on temperature over the liquid range of acetone and on magnetic field strength up to 1.1 T.

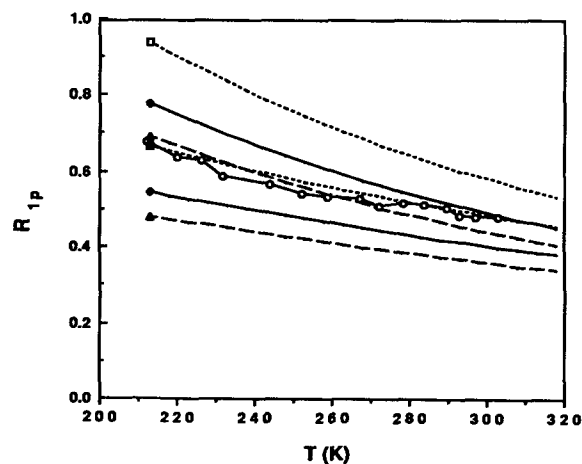


FIG. 6. Effect of variations of d , the distance of closest approach, on calculated τ_S values. O, experimental data; solid curves, $d = 4.3$ Å; short dashes, $d = 4.0$ Å; long dashes, $d = 4.5$ Å. For each value of d , two curves are plotted, the upper for $\tau_S = 10$ ps, the lower for $\tau_S = 5.63$ ps.

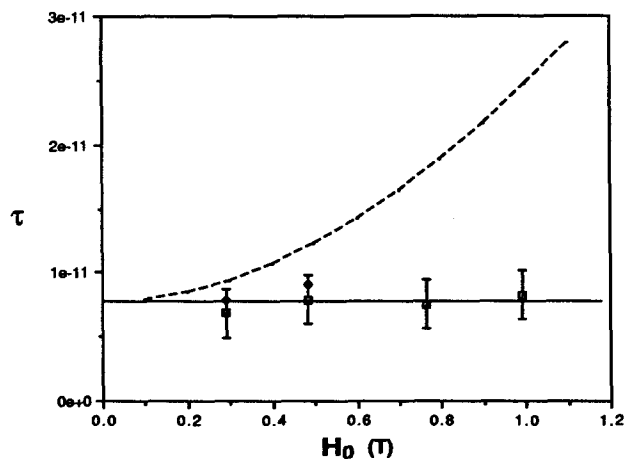


FIG. 7. Magnetic field dependence of τ_S at two temperatures, 215 K (□) and 298 K (◆). Also shown (dashed curve) is the field dependence of τ_S predicted in the Zeeman limit [Eq. (27)], where the ω_i are electronic Zeeman splittings at H_0 and $\tau_v = 5$ ps.

The accuracy with which τ_S can be measured for large ZFS ions depends upon the magnitudes of τ_r and τ_D , as shown in Figs. 4 and 5. The sensitivity of the NMR-PRE experiment to τ_S can be increased by selecting experimental conditions which lengthen these two parameters. The Stokes–Einstein and Debye equations suggest three variables of potential utility in this regard, namely, temperature, molar volume of the solute, and solution viscosity. The beneficial effect of low temperature on the determination of τ_S is evident in Fig. 5. R_{1p} is more sensitive to variations in τ_S at 213 K than at 298 K by a factor of about 3, primarily because of the temperature dependence of τ_D and τ_r , which vary as η/T . The results are not very sensitive to uncertainty in the ZFS parameter D , for which a value measured in the solid state was used. This is because relaxation contributions at the electronic transitions are small relative to those at ω_I (Fig. 2).

From Fig. 4, the temperature dependence of computed τ_S values is small, with τ_S increasing slightly, by about 15%, between 213 and 303 K. Al'tshuler and Valiev,²⁴ in their theory of paramagnetic salt solutions, have discussed the temperature dependence of τ_S , which they give as

$$\tau_S^{-1} \propto \overline{Q^2} \sum_i \frac{\tau_v}{1 + \omega_i^2 \tau_v^2}. \quad (27)$$

In this theory, relaxation of S results from vibrational modulation of the zero-field levels. $\overline{Q^2}$ is the mean-squared vibrational amplitude of modes which modulate the ZFS, τ_v is a mean damping time for those modes, and the sum is over $\Delta m_S = \pm 1, \pm 2$ transitions. For damping times the order of a few ps and with ω_i dominated by zero-field splittings, Eq. (27) reduces to

$$\tau_S^{-1} \propto \overline{Q^2} \sum \omega_i^{-2} \tau_v^{-1}.$$

Al'tshuler and Valiev take $\overline{Q^2} \propto \coth(\hbar\omega_0/2kT)$ for the mean-squared amplitude of a quantum-mechanical oscillator, with ω_0 a mean frequency of the relevant vibrational

modes, and they assume $\tau_v \propto T^{-1/2}$ for the temperature dependence of the damping time. This gives a temperature dependence of $\tau_S^{-1} \propto T^{1/2} \coth(\hbar\omega_0/2kT)$. Taking ω_0 to be of the order of 200–400 cm^{-1} , the predicted temperature dependence of τ_S in this model is very small, with τ_S shortening slightly with increasing temperature ($E_a \approx 2$ kJ). The observed temperature dependence in Fig. 4 is likewise very small, as predicted, although in the opposite direction. This disagreement is minor in view of the small magnitude of the temperature dependence, and it is not surprising considering uncertainties in the experimental measurement and crudeness in the theoretical model.

Figure 7 shows the measured τ_S values to be essentially magnetic field independent at field strengths up to 1.1 T. This is in marked contrast to the behavior often observed for the +II oxidation state of manganese, for which τ_S is normally found to be strongly field dependent over the same range.^{25–27} This difference clearly reflects characteristic differences of the Zeeman and ZFS limits. In the Zeeman limit, according to Eq. (27), τ_S is field dependent when $2\omega_S\tau_v \gg 1$. Quantitatively, the dashed curve in Fig. 7 illustrates the predicted field variation of τ_S that arises when $\tau_v = 5$ ps and when the ω_i are Zeeman splittings. In contrast, in the ZFS limit the ω_i , as well as τ_S , remain field independent at field strengths $H_0 \ll D\hbar/g\beta_0$, which includes the range of field variation studied here. The observed field independence of τ_S provides experimental confirmation of the applicability of the ZFS limit

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