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Paramagnetic Proton Nuclear Spin Relaxation Theory of Low-Symmetry Complexes for Electron Spin Quantum Number $S = \frac{5}{2}$

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A generalization of the modified Solomon–Bloembergen–Morgan (MSBM) equations has been derived in order to describe paramagnetic relaxation enhancement (PRE) of paramagnetic complexes characterized by both a transient (Δ_t^{ZFS}) and a static (Δ_s^{ZFS}) zero-field splitting (ZFS) interaction. The new theory includes the effects of static ZFS, hyperfine coupling, and angular dependence and is presented for the case of electron spin quantum number $S = \frac{5}{2}$, for example, Mn(II) and Fe(III) complexes. The model gives the difference from MSBM theory in terms of a correction term δ which is given in closed analytical form. The theory may be important in analyzing the PRE of proton spin–lattice relaxation dispersion measurements (NMRD profiles) of low-symmetry aqua–metal complexes which are likely to be formed upon transition metal ions associated with charged molecular surfaces of biomacromolecules. The theory has been implemented with a computer program which calculates solvent water proton T_1 NMRD profiles using both MSBM and the new theory. © 1999 Academic Press

Key Words: paramagnetic relaxation enhancement; NMR dispersion; SBM theory; low symmetry; aqua–metal complexes.

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1. INTRODUCTION

In proton T_1 nuclear magnetic resonance dispersion (NMRD) experiments (*1*) solvent water proton spin–lattice relaxation times, T_1, are measured almost continuously over a large range of static magnetic field strengths ranging from typically 0.001 to 0.3 T (proton Larmor frequencies of 0.01–100 MHz). When these data are complemented with measurements at a couple of field strengths of superconducting magnets the NMRD profile probes both the ESR and the NMR time scales. Thus, by analyzing solvent water ^1H T_1 NMRD profiles one may obtain microscopic information on the electron spin subsystem, coordination number q, intermolecular electron–nuclear spin distances (r_{IS}), and the overall reorientation correlation time (τ_R). The modified Solomon–Bloembergen–Morgan (MSBM) theory (*2*) successfully describes paramagnetically enhanced solvent water proton spin–lattice relaxation (PRE) rates of *symmetrical* complexes (*3*). This is usually expressed as the enhancement of

relaxation divided by the concentration of paramagnetic ions, the relaxivity $R_1 = 1/(mT_{1p})$, measured in units of $(mMs)^{-1}$.

The relaxation enhancement is given by (*4, 5*)

$$\frac{1}{T_{1p}} = \frac{Pq}{T_{1M} + \tau_M},$$ [1]

where τ_M is the chemical exchange time, q is the number of water in the first hydration sphere of each metal ion, and P is the concentration of ions divided by the concentration of water

$$P = \frac{m}{[H_2O]} = \frac{m}{55.5 \times 10^3}$$ [2]

(with concentrations in mM).

When confined to nuclear spin–electron spin dipole–dipole coupling, the proton nuclear spin–lattice relaxation rate of water protons in the first hydration shell around the paramagnetic ion is given by a relatively simple expression (in s^{-1}):

$$\frac{1}{T_{1M}} = \frac{4}{3} \left(\frac{\mu_0}{4\pi} \right)^2 \hbar^2 \gamma_I^2 \gamma_S^2 \frac{S(S+1)}{r_{IS}^6} \tau_c^{DD}.$$ [3]

The physical constants have their usual meanings (*3–8*). S is the electron spin quantum number of the paramagnetic metal ion. The effective dipole–dipole correlation time τ_c^{DD} of Eq. [3] is defined as a weighted sum of spectral density functions s_σ^{DD}, $\sigma = \pm 1, 0$. Each spectral density function comprises effects from both molecular reorientation and electron spin relaxation processes (*2, 6–11*):

$$\tau_c^{DD} = Re\{0.1 \times s_1^{DD} + 0.3 \times s_0^{DD} + 0.6 \times s_{-1}^{DD}\}.$$ [4]

s_σ^{DD} is the Fourier–Laplace transform of the isotropic reorientation diffusion correlation function (of the paramagnetic complex) and

TABLE 1
Parameters for MSBM and Generalized MSBM

Theory	τ_c	τ_R	r_{IS}	A_{IS}	Δ_t^{ZFS}	Δ_s^{ZFS}	β_{LM}	q	Validity range
MSBM	Y	Y	Y	No	Y	No	No	6	High field
Ref. (9)	Y[a]	Y	Y	Y	Y	Y	No	$q \leq 6$	High field
This work	Y	Y	Y	Y	Y	Y	Y	$q \leq 6$	High field

[a] The electron spin relaxation description is approximate.

the electron spin correlation function, $\mathrm{tr}_S\{\hat{S}_\sigma^{1\dagger} e^{i\hat{L}_S\tau} \hat{S}_\sigma^1 \hat{\rho}_S^T\}$, at the nuclear Larmor frequency ω_I:

$$s_\sigma^{DD} = \frac{3}{S(S+1)} \int_0^\infty \mathrm{tr}_S\{\hat{S}_\sigma^{1\dagger} e^{i\hat{L}_S\tau} \hat{S}_\sigma^1 \hat{\rho}_S^T\} e^{-(i\omega_I + 1/\tau_R)\tau} d\tau$$

$$\equiv M_{\sigma\sigma}^{-1}. \qquad [5]$$

Here $\hat{L}_S$ is the Liouville superoperator governing the electron spin correlation function. The definition of $\hat{L}_S$ and how to determine the spectral density in terms of an inverted matrix **M** is presented in detail in Appendixes A–C. We then follow the same approach as in (11–14), however, now generalized to low-symmetry complexes. The need for a generalized SBM theory valid for biological systems was first recognized by Dwek (3) and the first attempt to consider the effect of a static zero-field splitting interaction was made by Bertini et al. (8).

The spectral density of Eq. [5] in the MSBM theory is

$$s_\sigma^{DD,MSBM} = \int_0^\infty e^{-\tau(1/T_{\sigma+1,S} - \sigma i\omega_S + i\omega_I + 1/\tau_R)} d\tau, \qquad [6]$$

where well-defined electron spin relaxation times T_{1S} and T_{2S} are assumed (extreme narrowing condition for the electron spin subsystem). The electron spin relaxation rates are described using Bloch–Wangsness–Redfield theory (15) and obtained in terms of the transient zero-field splitting interaction, Δ_t^{ZFS}, and its characteristic correlation time, τ_c. T_{1S} and T_{2S} of Eq. [6] are given by

$$\frac{1}{T_{1S}} = \frac{1}{5\tau_{S0}} \left(\frac{1}{1 + \omega_S^2\tau_c^2} + \frac{4}{1 + 4\omega_S^2\tau_c^2} \right) \qquad [7]$$

$$\frac{1}{T_{2S}} = \frac{1}{5\tau_{S0}} \frac{1}{2} \left(3 + \frac{5}{1 + \omega_S^2\tau_c^2} + \frac{2}{1 + 4\omega_S^2\tau_c^2} \right). \qquad [8]$$

In Eqs. [7] and [8] we use instead of the strength constant the electron spin relaxation rate in extreme narrowing $1/\tau_{0S} = ((\Delta_t^{ZFS})^2/5)[4S(S+1) - 3]\tau_c$. Notice that the SBM theory has no parameter reflecting a low-symmetry coordination of

the paramagnetic metal ion (3, 11). In Table 1 we have summarized the parameter space of SBM, the theoretical approach of Bertini et al. (8, 9), and compared it with the parameter space of the generalized theory of this work.

In Refs. (8, 9) the effect of zero-field splitting in slow tumbling systems is discussed using a slightly different approach. It is also a high-field theory which is thought to be approximately valid in the low-field regime. However, the main difference between our theory and their theory is that we treat the electron spin relaxation exact in the Redfield limit whereas Bertini et al. ignore the angle dependence of the electron spin relaxation matrix and the effect of nonextreme narrowing conditions. Second, we are able to derive the corrections to SBM due to nonextreme narrowing, static ZFS interaction, and hyperfine splitting in a consistent and compact form.

As is shown in Table 1 three extra parameters are introduced. First the hyperfine splitting (A_{IS}) is included, which is important in analyzing Mn^{2+} complexes. Second, we introduce the static ZFS interaction (Δ_s^{ZFS}), which reflects an average low coordinate symmetry, i.e., lower symmetry than the octahedral coordination of a hexa aqua complex. Such an average distortion of the coordination shell may be indicated in an MSBM analysis by a small coordination number ($q < 6$). However, then one assumes that lowering the coordination symmetry does not influence the electron spin relaxation rates and the extracted intermolecular electron–nuclear spin distance r_{IS}. In the context of our generalized theory we are able to investigate the validity of these assumptions. However, we assume slow tumbling complexes so that the static ZFS interaction influences only the electron spin energy levels and not the electron spin relaxation rates through a reorientation-modulated ZFS time correlation function, as seen from Eqs. [7] and [8]. We can then use the Redfield theory, which is valid when $\Delta_t^{ZFS}\tau_v < 1$ and $\Delta_s^{ZFS}\tau_R > 1$, implying the static limit of the electron spin system. If the complexes are small and the reorientation very fast, so that $\Delta_s^{ZFS}\tau_R \ll 1$, there is a rotationally modulated contribution to Eqs. [7] and [8] which is readily included in the generalized SBM equations (13). In the case when $\Delta_s^{ZFS}\tau_R \approx 1$ this contribution has to be analyzed with the slow motion theory (7, 11).

The third new parameter is the angle β_{LM} between the

laboratory and molecular frames of reference. The electron relaxation is sensitive to this angle, as shown in the appendixes. When the reorientation of the complex is slow compared to the electron spin relaxation time, as we assume in this work, the angle is constant on the time scale of the ESR experiment. In other words, the electron spin will relax so fast that the angle β_{LM} will not change during the relaxation and we can treat it as a constant in this respect. If the sample is macroscopically oriented, all molecules have the same orientation and only one angle β_{LM} describes the system. Otherwise we have a distribution of angles and an averaging over angles should be performed. If the distribution is isotropic we have a normal powder sample, but arbitrary distributions can be treated with the theory. If the reorientation is fast, the reorientation correlation function must be taken into account, and then there is no angle dependence.

We derive a generalization of Eq. [3] by introducing correction terms to the three spectral densities of the MSBM theory (cf. Eq. [4]). The simple form of MSBM equations is then preserved and the added correlation terms are derived in closed analytical form. The generalized theory then has the form

$$\frac{1}{T_{1M}} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \hbar^2 \gamma_I^2 \gamma_S^2 \frac{S(S+1)}{r_{IS}^6}$$

$$\times \text{Re}\{0.1|d_{00}^2(\beta_{LM})|^2 M_{11}^{-1}$$

$$+ 0.3|d_{01}^2(\beta_{LM})|^2 M_{00}^{-1}$$

$$+ 0.6|d_{02}^2(\beta_{LM})|^2 M_{-1-1}^{-1}\}, \qquad [9]$$

where the MSBM spectral densities are replaced by the full solution of the spectral density of Eq. [5] and $d_{0m}^2(\beta_{LM})$ are reduced Wigner rotation matrix elements (12). The deviation from the MSBM theory is accommodated by correction terms (δ_σ), obtained from the inversion of the matrix $\mathbf{M}$ (cf. Eq. [5]). The matrix elements of $\mathbf{M}^{-1}$ are given as $M_{\sigma\sigma}^{-1} = s_\sigma^{DD,MSBM}(1 + \delta_\sigma)$, which are derived in detail in Appendixes A–C (13).

The effective dipole–dipole correlation time τ_c^{DD} of Eq. [4] now becomes

$$\tau_c^{DD} = \text{Re}\{0.1 \times s_1^{DD,MSBM}(1 + \delta_1) + 0.3 \times s_0^{DD,MSBM}$$

$$\times (1 + \delta_0) + 0.6 \times s_{-1}^{DD,MSBM}(1 + \delta_{-1})\} \quad [10]$$

and the relation between Eq. [3] and Eq. [9] may be written

$$\frac{1}{T_{1M}} = \frac{1}{T_{1M}^{MSBM}} + \Delta_{sum}. \qquad [11]$$

We now focus on the importance of the correction term

$$\Delta_{sum} = \text{Re}\{0.1 \times s_1^{DD,MSBM}\delta_1 + 0.3$$

$$\times s_0^{DD,MSBM}\delta_0 + 0.6 \times s_{-1}^{DD,MSBM}\delta_{-1}\}, \quad [12]$$

which is calculated for a number of different situations corresponding to different biochemical systems.

2. THEORY AND NUMERICAL CALCULATIONS

The correction terms derived in Appendixes A–C are given in terms of Redfield relaxation matrix elements. The spectral density containing electron spin–lattice relaxation is angle dependent and written as

$$s_0^{DD}(\beta_{LM}) = s_0^{DD,MSBM}(\beta_{LM})(1 + \delta_0(\beta_{LM})), \qquad [13]$$

where the correction term is given by

$$\delta_0(\beta_{LM}) = \frac{B'^2}{C'A' - B'^2 - D'^2(A'/E')}, \qquad [14]$$

where the matrix elements A', B', etc., are given in Appendix C. They are angle dependent through the model spectral densities of Eq. [36] given in Appendix B. The corresponding expression including electron spin–spin relaxation depends on the angle β_{LM} between the Z axes of the laboratory frame (Z_L) and the molecular-fixed frame (Z_M). These spectral densities are given by

$$s_{\pm1}^{DD}(\beta_{LM}) = s_{\pm1}^{DD,MSBM}(1 + \delta_{\pm1}(\beta_{LM})) \qquad [15]$$

$$s_{\pm1}^{DD}(\beta_{LM}) = \frac{3}{S(S+1)}$$

$$\times \int_0^\infty \text{tr}_L\{\hat{S}_{\pm1}^{1\dagger} e^{i\hat{L}\,s(\beta_{LM})\tau}\hat{S}_{\pm1}^1\hat{\rho}_S^{T,eq}\}e^{-i\omega_I\tau}d\tau, \quad [16]$$

where $\hat{S}_{\pm1}^1$ is a standard electron spin vector operator of the laboratory-fixed frame (L), and

$$\delta_{\pm1}(\beta_{LM}) = \frac{G^2Z - Y - 2FJHL}{CX - G^2Z + Y}, \qquad [17]$$

where the matrix elements A, B, etc., are given in Appendix B and X, Y, and Z are defined in Eqs. [41]–[43].

In the general case, when one perform a powder average, the correction term $\Delta_{sum}(\omega_I)$ becomes

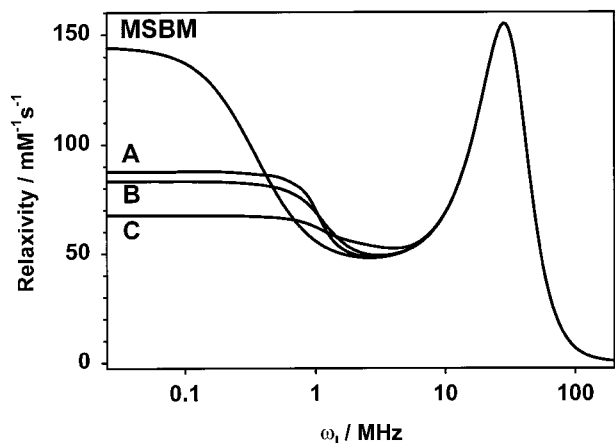**FIG. 1.** Proton T_1 NMRD profiles for three different static ZFS interactions Δ_s^{ZFS}. In (A) $\Delta_s^{ZFS} = 0.01$ cm^{-1}, in (B) $\Delta_s^{ZFS} = 0.025$ cm^{-1}, and in (C) $\Delta_s^{ZFS} = 0.1$ cm^{-1}. Other parameters are $\Delta_t^{ZFS} = 0.025$ cm^{-1}, $\tau_c = 10.0$ ps, $q = 2$, $r_{IS} = 2.8$ Å, $\tau_M = 10$ ns, $\tau_R = 100$ ns, and the hyperfine coupling constant $A_{IS} = 0.0074817$ cm^{-1}. The corresponding MSBM NMRD profile is also shown.

$$\Delta_{sum}(\omega_I) = \sum_{m_I} \int_0^\pi P(\beta_{LM})$$

$$\times \left[0.3 \frac{B'^2}{C'A' - B'^2 - D'^2(A'/E')} \right.$$

$$\left. + 0.7 \frac{1}{C} \frac{G^2Z - Y - 2FJHL}{CX - G^2Z + Y} \right]$$

$$\times \sin(\beta_{LM})d\beta_{LM}. \qquad [18]$$

It should be noted that all the different terms A', A, etc., depend on β_{LM} and ω_S (which in turn depends on m_I) through the spectral densities given in Appendix B.

$1/T_{1M}^{MSBM}(\omega_I)$ of Eq. [11] becomes

$$\frac{1}{T_{1M}^{MSBM}(\omega_I)} = \sum_{m_I} \int_0^\pi P(\beta_{LM}) \left[\frac{0.3}{A'(\omega_I, m_I, \beta_{LM})} \right.$$

$$\left. + \frac{0.7}{C(\omega_I, m_I, \beta_{LM})} \right] \sin(\beta_{LM})d\beta_{LM}, \qquad [19]$$

where $P(\beta_{LM})$ is a distribution function of the angle β_{LM} describing the orientation of the macromolecule relative to the laboratory frame. If the sample is macroscopically well oriented, the distribution function is a delta function and the integral is eliminated. The relaxivity will in this case depend on the angle β_{LM}, as shown below. When the hyperfine splitting is zero ($A_{IS} = 0$) then the sum over m_I is absent.

We now turn to a number of numerical calculations which

aim to illustrate the magnitude of the correction term for a couple of cases.

2.1. Mn Proteins

In the literature there are numerous articles using the MSBM theory in order to characterize binding sites of hydrated transition metal ions with $q < 6$ binding to biomolecules (3, 16–20). In these cases a coordination of lower symmetry is expected, which is however only considered by the hydration number q ($q < 6$). In our new theory, as well as in Ref. (8), a reinterpretation of the NMRD profiles also gives information about coordination symmetry in terms of a static ZFS interaction.

In Fig. 1 three T_1 NMRD profiles are displayed for theoretical Mn^{2+} cases and compared with the MSB profile. The hyperfine interaction strength constant was set to $A_{SI} = 0.0074817$ cm^{-1}, and the static ZFS interaction is varied from 0.01 (A) and 0.025 (B) to 0.1 (C) cm^{-1}. In Fig. 2 the same parameters are used except for the hyperfine interaction which we have omitted. Compared to the SBM NMRD profile (dotted line) the effect of the static ZFS interaction is to lower the relaxation enhancement at low fields. The other model parameters are $\Delta_t^{ZFS} = 0.025$ cm^{-1}, $\tau_c = 10.0$ ps, $q = 2$, and $r_{IS} = 2.8$ Å.

In Fig. 3 we display the effect of anisotropic motions. Instead of one correlation time $\tau_c = 10$ ps, we use $\tau_\perp = 10$ ps and a faster motion $\pi_\parallel = 3$ ps. In (A) $\Delta_s^{ZFS} = 0$, in (B) $\Delta_s^{ZFS} = 0.025$ cm^{-1}, and in (C) $\Delta_s^{ZFS} = 0.1$ cm^{-1}. The effect of anisotropic dynamics may be clearly seen in the "dip" region at Larmor frequencies of 1–10 MHz. All other parameters have the same values as in Fig. 2.

In Fig. 4 the relative correction term $\Delta_{sum}/(T_1^{MSBM})^{-1}$ is displayed for the cases displayed in Fig. 2. It is clearly shown that the correction term Δ_{sum} grows in importance as the proton
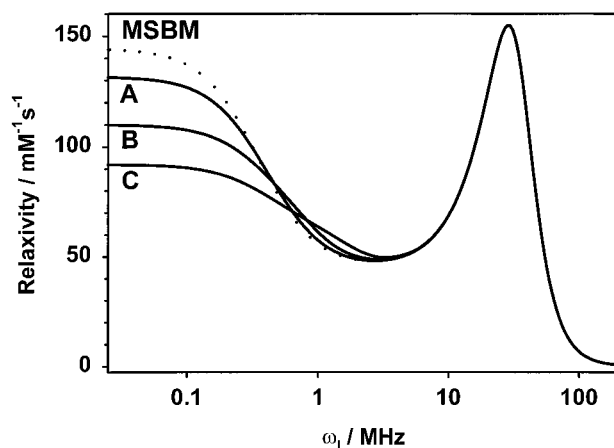

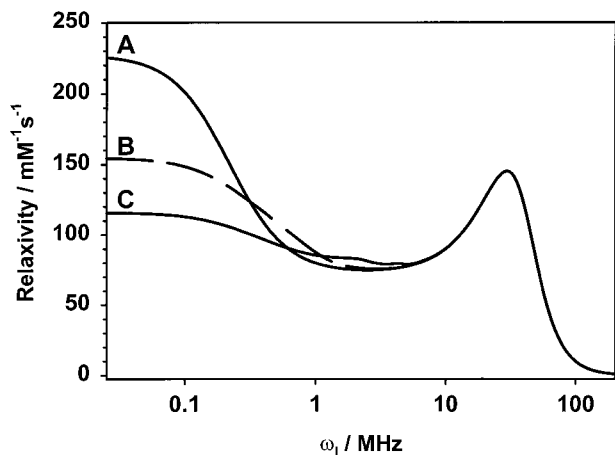**FIG. 2.** The same cases as in Fig. 1 are shown, but without hyperfine coupling, $A_{IS} = 0$.

FIG. 3. The effect of an anisotropic motion on the NMRD profile is shown. Here, $\tau_\perp = 10$ ps and $\pi_\parallel = 3$ ps. In (A) $\Delta_s^{ZFS} = 0$, in (B) $\Delta_s^{ZFS} = 0.025$ cm^{-1}, and in (C) $\Delta_s^{ZFS} = 0.1$ cm^{-1}. All other parameters are as in Fig. 2.

FIG. 5. The proton T_1 NMRD profile of Fig. 2B ($\Delta_s^{ZFS} = 0.025$ cm^{-1}) is calculated using the high-field version of the theory; i.e., only the electron spin–lattice spectral density s_0 is considered (Eq. [20]).

Larmor frequency gets smaller starting from ≈ 3 MHz. It first grows to about $+10$–13% and then at lower frequencies the presence of a static ZFS interaction makes the correction term as large as $\approx -40\%$ depending on the magnitude of the static ZFS interaction Δ_s^{ZFS}. There is also a correction due to a nonextreme narrowing condition or nonexponential electron spin relaxation at about 30–100 MHz, with a maximum value of about 9%. With hyperfine interaction present the correction term at low field is even larger. It should be noted that the correction term presented is calculated as a correction to T_{1M}. For fast chemical exchange, τ_M is very small, and the same relative corrections will also apply to T_{1p} (the measured relaxivity).

In Fig. 5 the NMRD profile Fig. 2B is displayed together with that obtained using the high-field version of Eq. [9]
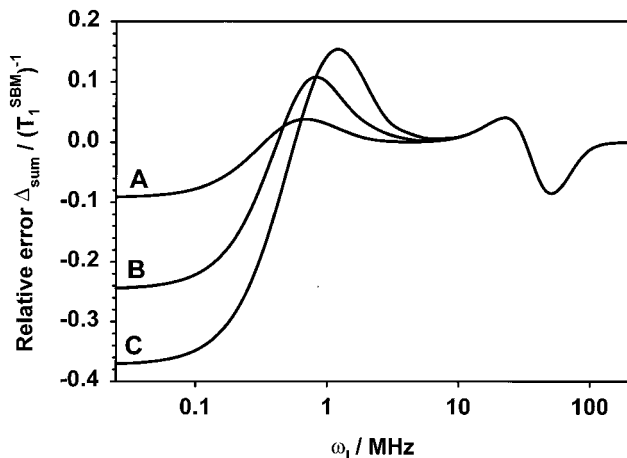

FIG. 4. The relative correction terms $\Delta_{sum}/(T_1^{MSBM})^{-1}$ are shown for the cases displayed in Fig. 2.
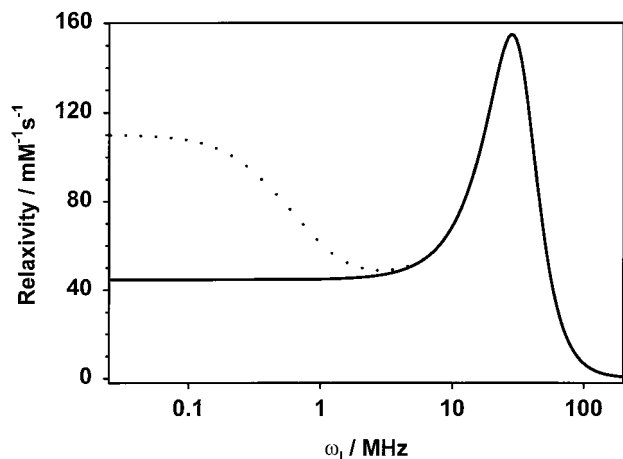
$$\frac{1}{T_{1M}^{hf}} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \hbar^2 \gamma_I^2 \gamma_S^2 \frac{S(S+1)}{r_{IS}^6} \text{Re}\{0.3 \times M_{00}^{-1}\}. \quad [20]$$

Here the spectral densities containing electron spin–spin relaxation processes have been excluded because of non extreme narrowing conditions. This NMRD profile shows no effects of low-symmetry coordination since only the electron spin–lattice relaxation process is active.

Proton T_1 NMRD profiles are more informative than high-field measurements since they are very sensitive to the presence of a static ZFS interaction and consequently to low-symmetry coordination. This information is not present in the high-field region ($\omega_I > 10$ MHz) where low-symmetry coordination influences mainly the coordination number q. The correction term, however, becomes extremely important and actually dominates the relaxivity at lower fields.

When ^{1}H NMRD profiles are interpreted using the SBM theory, the coordination number q is difficult to extract in accordance with high-field data. This difficulty also influences the extracted distance r_{IS} between the water proton and the paramagnetic electron spins since it comes as a scaling of the magnitude of the relaxivity, q/r_{IS}. This type of difficulty has been discussed in the controversial interpretation of high-field data and water proton NMRD data of Mn(II)-carboxy peptidase A and concanavalin A (*16, 18–20*). Either one relies solely on high-field data as in Navon (*18*) or one tries to use high-field SBM theory analyzing the entire NMRD profile as in Koenig and Brown (*20*). Koenig and Brown write ". . . *we can readily argue that the resulting fits to the proton data are not too bad, and can ascribe deviations to the intrinsic complexities of the theory, realizing that zero-field splittings have not been properly considered*" (p. 433 in Ref. (*20*)). So, here we will briefly discuss the latter approach, however, in the context
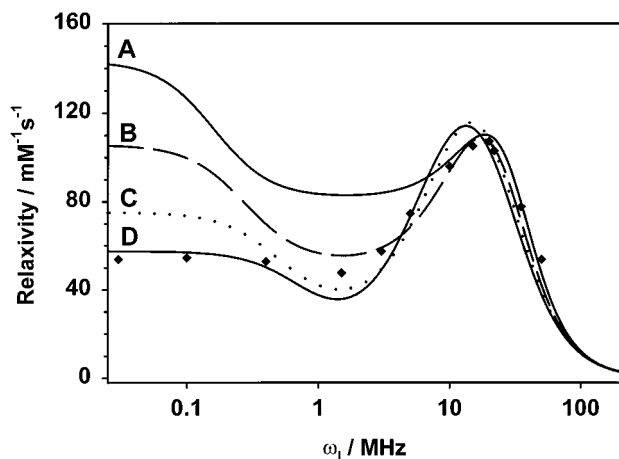
FIG. 6. The paramagnetic contribution of bound Mn^{2+} to the solvent proton T_1 NMRD profiles in a solution of Mn^{2+}–Con A. The diamonds are the experimental values found in Ref. (20). The theoretical NMRD profiles are obtained using the best fit parameters of Ref. (20) varying only τ_c and τ_M. The following parameters are used: (A) $\tau_c = 10$ ps and $\tau_M = 170$ ns, (B) $\tau_c = 20$ ps and $\tau_M = 190$ ns, (C) $\tau_c = 40$ ps and $\tau_M = 190$ ns, and (D) $\tau_c = 59$ ps and $\tau_M = 205$ ns. All parameters are listed in Table 2.

of a generalized SBM theory. We then think that the ZFS interaction is now properly considered to about 1 MHz proton frequency.

In Fig. 6D we display the best fit and the experimental values (diamonds) of Koenig and Brown (20) of paramagnetic relaxivities of solvent protons in solutions of Mn^{2+}–Con A. In trying to fit the high-field SMB theory to the entire NMRD profile, the electron spin relaxation rates seem to be overestimated. This means that $\tau_c = 59$ ps is too long keeping τ_{S0} constant. If we shorten τ_c as is displayed in Figs. 6A–6C to about 10 ps the theoretical NMRD profile is improved at proton frequencies $\omega_I < 10$ MHz. At high fields the NMRD profile conforms very well with the experimental values but at low fields the fit is very bad. However, one should remember that part of this low-field region is outside the validity range of the high-field SMB theory. Mn^{2+}–Con A is expected to be a low-symmetric complex since one expect a coordination number of $q = 2$.

In Fig. 7 we also compare the experimental NMRD profile of Koenig and Brown (20) with three theoretical NMRD profiles where the correlation time τ_c of the transient ZFS interaction and the exchange time τ_M have been changed from the best fit values of Ref. (20). We use $\tau_c = 30$ ps which is considerably shorter than their best fit value of $\tau_c = 59$ ps. This theoretical NMRD profile also conforms quite well to the experimental data at high fields, indicating correlation times more like a perturbed hydration shell. Figures 7A–7C display the effect of a static ZFS interaction, lowering the relaxivity at frequencies below 5 MHz. The effect of a static ZFS interaction clearly removes the large discrepancy at low fields. Figure 7C is an NMRD curve with a static ZFS $\Delta_S^{ZFS} = 0.1$ cm^{-1} and

displays a good fit in the whole region of high fields $[1, \infty]$ MHz. With these NMRD profiles we want to indicate the fitting philosophy starting with the generalized SBM theory with $\Delta_S^{ZFS} = 0.0$ and consider only high-field data, and then add the static ZFS interaction to the model when data below ≈ 5 MHz are considered. An ESR lineshape analysis when possible would be helpful in finding reasonable values for τ_c and τ_{S0}.

The parameters of Koenig (20) and our NMRD profiles are summarized in Table 2. A problem similar to the one we discussed here may also be encountered in interpreting water proton T_1 NMRD profiles of Mn(II)–aqua complexes at low temperature and in high-viscosity solutions.

2.2. Angular Dependence

In ordinary MSMB theory, the paramagnetic ion is assumed to be in an isotropic liquid, so that all angular dependence is averaged out by fast isotropic motions. In this generalized theory, the angle β_{LM} between the laboratory reference frame and the molecular reference frame appears in the expression for the spectral densities, Eq. [36], through the reduced Wigner rotation matrix elements $d_{kn}^2(\beta_{LM})$ (12). As can be seen from Eq. [9], the electron T_1 contribution to the relaxivity includes only a $d_{01}^2(\beta_{LM})$ element, which is equal to zero when $\beta_{LM} = 0°$ or $90°$. This means that the T_1 part of the relaxivity can be *eliminated* in a macroscopically oriented sample by changing the angle to one of these values. The T_2 part cannot be eliminated in this way, since it includes both $d_{00}^2(\beta_{LM})$ and $d_{02}^2(\beta_{LM})$ elements, and there is no angle that will simultaneously make these two elements zero.

This effect is shown in Fig. 8. $\Delta_s^{ZFS} = 0.025$ cm^{-1}, $\Delta_t^{ZFS} = 0.025$ cm^{-1}, $\tau_c = 10.0$ ps, $q = 1$, and $r_{IS} = 2.8$ Å in all cases.
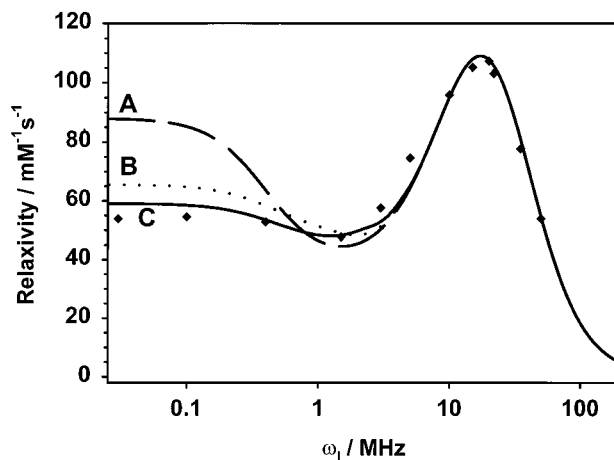

FIG. 7. The effect of static ZFS interaction for the paramagnetic contribution of bound Mn^{2+} to the solvent proton T_1 NMRD profiles in a solution of Mn^{2+}–Con A. The parameters are as in Fig. 6 except for $\tau_R = 8$ ns, $\tau_c = 30$ ps, and $\tau_M = 180$ ns, and the static ZFS interaction. In (A), $\Delta_s^{ZFS} = 0$, in (B) $\Delta_s^{ZFS} = 0.05$ cm^{-1}, and in (C) $\Delta_s^{ZFS} = 0.1$ cm^{-1}.

TABLE 2
Comparison of SBM Best Fit (20) and the Generalized SBM Theory

Figure	τ_R/ns	r_{IS}/Å	τ_M/ns	τ_c/ps	A_{IS}/MHz	Δ_t^{ZFS}/cm^{-1}	Δ_s^{ZFS}/cm^{-1}	q	T/K
6A	14	2.8	170	10	—	0.0135	—	2	—
6B	14	2.8	190	20	—	0.0135	—	2	—
6C	14	2.8	190	40	—	0.0135	—	2	—
6D (20)	14	2.8	205	59	—	0.0135	—	2	298
7A	8	2.8	180	30	—	0.0135	0.000	2	—
7B	8	2.8	180	30	—	0.0135	0.025	2	—
7C	8	2.8	180	30	—	0.0135	0.100	2	—

In Fig. 8A, the isotropic case is shown, in (B) the angle is 90°, and in (C) the angle is 30°

3. SUMMARY

In this work we give a generalized SBM theory for $S = \frac{5}{2}$ which is valid for low-symmetry coordination of water molecules around a paramagnetic metal ion binding to a biomacromolecule. It is assumed that the reorientational motion is too slow to be important for the relaxation of the electron spin system. The electron spin relaxation then becomes angle dependent which has been accounted for in the theory. The theory derived is valid for nonextreme narrowing conditions for the electron spin system with a static ZFS interaction present. It should be noted that, like the SBM theory, this is not a low-field theory. We assume that the Zeeman interaction dominates over the ZFS and hyperfine interactions. Therefore, one should be careful when the theory is used at low fields ($< \approx 1$ MHz). For example, with a ZFS strength $\Delta_t^{ZFS} = 0.05$ cm^{-1}, the theory is strictly valid only for field strengths $B_0 > 0.02$ T, or $\omega_I > \approx 1$ MHz. In our figures, we have extended the plots into low fields, thus slightly outside the validity range of the theory.

The expressions for the paramagnetically enhanced nuclear spin–lattice relaxation rate is derived in a closed analytical form. However, in order to obtain the enhanced nuclear spin–lattice relaxation rate for an isotropic solution one must perform an average over β_{LM} angles. The theory provides an extra parameter Δ_s^{ZFS} which may reflect changes in the average symmetry of the first hydration shell of the paramagnetic ions upon binding to biomacromolecules. NMRD profiles for macroscopically oriented samples are also investigated where it is shown that electron spin–lattice relaxation enhancement may be removed for a macroscopically well-oriented sample with the director at 0° and 90° relative to the static magnetic field.

A computer program in which the closed analytical expressions are implemented to give the first MSBM-like theory of proton T_1 NMRD profiles, which is valid for both nonextreme narrowing conditions for the electron spin system and low-symmetry coordination, has been developed. The relaxivity from the scalar interaction is also included in the computer program.

Computer program. A Fortran computer program developed according to the theory presented in this work is available upon request by e-mail to Perolof.Westlund@chem.umu.se.

APPENDIX A

The Lattice Dynamics

Consider the spectral density of Eq. [5]

$$s_\sigma^{DD}(i\omega_I, \beta_{LM}) = \frac{3}{S(S+1)}$$

$$\times \int_0^\infty \text{tr}_S\{\hat{S}_\sigma^{1\dagger} e^{i\hat{L}_S(\beta_{LM})\tau} \hat{S}_\sigma^1 \hat{\rho}_S^T\} e^{-(i\omega_I + 1/\tau_R)\tau} d\tau$$

$$\equiv M_{\sigma\sigma}^{-1}. \qquad [21]$$

First, we must define the propagator or the Liouville superop-
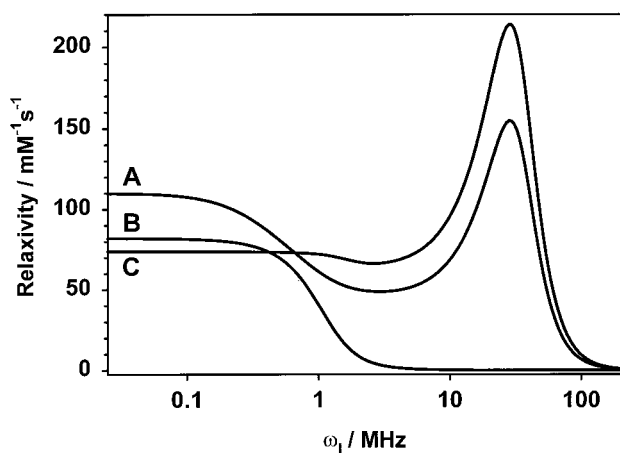

FIG. 8. The proton T_1 NMRD profile is calculated for macroscopically oriented samples. The isotropic (not oriented) NMRD profile is shown in (A). The angle β_{LM} is in (B) 90° and in (C) 30°. All other parameters are the same as those for Fig. 2B.

erator governing the time dependence of the electron spin correlation function. Lowering the coordination symmetry and decreasing the ZFS correlation time increase the electron spin relaxation and may also lower the PRE effect. Taking this into account in formulating the Hamiltonian model, the electron spin Liouvillian $\hat{L}_S(\beta_{LM})$ is given by

$$\hat{L}_S(\beta_{LM}) = \hat{L}_0^{Zeeman} + \hat{L}_0^{hyperfine}$$
$$+ \hat{L}_0^{ZFS}(\beta_{LM}) + i\hat{R}_{ZFS}(\beta_{LM}). \qquad [22]$$

$\hat{L}_S(\beta_{LM})$ governs the time dependence of the electron spin correlation functions and contains a Zeeman term, a hyperfine interaction term, a static secular ZFS term, and a Redfield superoperator $\hat{R}_{ZFS}$. The latter is generated by the transient part of the ZFS interaction, since we are focusing on slowly tumbling complexes of electron spin systems with $S = \frac{5}{2}$. Let us focus on Eq. [22] and first consider the time-independent Liouville operators.

There are three time-independent interactions: the Zeeman interaction

$$\hat{H}_0^{Zeeman} = -\gamma_S B_0 \hat{S}_0^1 \equiv \omega_S \hat{S}_z^1, \qquad [23]$$

the hyperfine interaction with the metal nucleus with spin quantum number I

$$\hat{H}_0^{hyperfine} = A_{IS} \hat{S}_0^1 \hat{I}_0^1, \qquad [24]$$

and finally the static ZFS interaction

$$\hat{H}_0^{ZFS} = \sum_n (-1)^n \hat{S}_n^2 \langle F_{-n}(t)^{2(L)} \rangle. \qquad [25]$$

Here, $\hat{S}_n^2$ is a standard second-rank electron spin operator and $\langle F_{-n}(t)^{2(L)} \rangle$ is a static ZFS tensor component of the laboratory frame. We may write the laboratory tensor components in terms of the ZFS principal components by introducing an intermediate frame (M) defining the molecular surface where the hydrated metal ion is "bound":

$$\langle F_{-n}(t)^{2(L)} \rangle = \sum_k [F_0(t)^{2(P)} \langle D_{k0}(\Omega_{PM}(t)) \rangle + F_2(t)^{2(P)}$$
$$\times \langle D_{k2}(\Omega_{PM}(t)) \rangle + F_{-2}(t)^{2(P)}$$
$$\times \langle D_{k-2}(\Omega_{PM}(t)) \rangle] D_{kn}^2(\Omega_{LM}). \qquad [26]$$

Now we assume threefold symmetry or more around the molecular-fixed director z_M and then $k = 0$ which considerably simplifies the static ZFS Hamiltonian:

$$\langle F_{-n}(t)^{2(L)} \rangle = [F_0(t)^{2(P)} \langle D_{00}(\Omega_{PM}(t)) \rangle + F_2(t)^{2(P)}$$
$$\times \langle D_{02}(\Omega_{PM}(t)) \rangle + F_{-2}(t)^{2(P)}$$
$$\times \langle D_{0-2}(\Omega_{PM}(t)) \rangle] D_{0n}^2(\Omega_{LM}). \qquad [27]$$

Rhombicity of the ZFS tensor is included in an effective ZFS parameter $\Delta_s^{ZFS} = \sqrt{\frac{2}{3}} D_s D_0^{PM} + 2E S_2^{PM}$. Here S_m^{PM} is an order parameter given by $S_m^{PM} = \langle d_{0m}^2(\beta_{PM}) \rangle$ and measures the flexibility of the complex. The order parameter S_m^{PM} introduces a partially averaged ZFS which thus measures an averaged low-symmetry coordination of the first hydration shell of the metal ion.

The secular approximation means that only the term commuting with the Zeeman interaction is considered. This is a good approximation since the other nonsecular terms only will contribute at higher order:

$$\hat{H}_0^{ZFS}(\beta_{LM}) = \Delta_s^{ZFS} d_{00}^2(\beta_{LM}) \hat{S}_0^2. \qquad [28]$$

In Eq. [28] the orientational dependence of the molecular-fixed frame (M) of a macromolecule or a molecular interface is given by $d_{00}^2(\beta_{LM})$ which is a reduced Wigner rotation matrix element (12). We assume for simplicity that the molecular frame (M) of the partially averaged ZFS interaction coincides with the r_{IS} vector of the dipole–dipole interaction. In practice, it is not possible to distinguish D_s, E, and S_m^{PM} in the calculations. The effect of noncoinciding dipole–dipole and static ZFS tensor frames also introduces a reduction in the NMRD profiles. This effect has been analyzed by Benetis and Kowalewski (21). It is straightforward to include the extra transformation matrix which thus will scale the paramagnetically enhanced relaxation contribution. But without knowing more about the structure of the hydration shell and the binding site of the paramagnetic metal ion we think that such an analysis must come at a later stage. The orientational dependence of the molecular-fixed frame (M) of a macromolecule or a molecular interface is given by $d_{00}^2(\beta_{LM})$, which is a reduced Wigner rotation matrix element (12).

The time-dependent ZFS interaction arises because of fluctuating symmetry of the first coordination shell of the paramagnetic metal ion, that is, the fluctuating symmetry of the hydration shell with an averaged symmetry lower than octahedral or tetrahedral symmetry. This lowering of symmetry may arise because some ligand water molecules are immobilized or have been replaced by molecular groups originating from a molecular interface or from the macromolecule to which the metal ion is bound. The molecular fluctuation of the first coordination sphere then generates a transient ZFS with zero mean average value. This is modeled by an electron spin ZFS Hamiltonian,

$$\Delta \hat{H}_1^{ZFS}(t, \beta_{LM}) = \hat{H}^{ZFS}(t) - \hat{H}_0^{ZFS}(\beta_{LM}). \qquad [29]$$

TABLE 3
Matrix Elements of $M_2(\beta_{LM}, m_I)$ for $S = \frac{5}{2}$

$$A = i(\omega_I \pm \omega_S(m_I)) + R_{11}^{22}(\beta_{LM}, m_I)$$

$$B = i(\omega_I \pm \omega_S(m_I)) + R_{11}^{44}(\beta_{LM}, m_I)$$

$$C = i(\omega_I \pm \omega_S(m_I)) + R_{11}^{11}(\beta_{LM}, m_I)$$

$$D = i(\omega_I \pm \omega_S(m_I)) + R_{11}^{33}(\beta_{LM}, m_I)$$

$$E = i(\omega_I \pm \omega_S(m_I)) + R_{11}^{55}(\beta_{LM}, m_I)$$

$$F = R_{11}^{24}(\beta_{LM}, m_I)$$

$$G = i4\sqrt{\tfrac{2}{5}}D_s S_{PM} d_{00}^2(\beta_{LM})$$

$$H = i6\sqrt{\tfrac{6}{35}}D_s S_{PM} d_{00}^2(\beta_{LM})$$

$$I = i\sqrt{\tfrac{100}{21}}D_s S_{PM} d_{00}^2(\beta_{LM})$$

$$J = i2\sqrt{\tfrac{2}{5}}D_s S_{PM} d_{00}^2(\beta_{LM})$$

$$K = R_{11}^{13}(\beta_{LM}, m_I)$$

$$L = R_{11}^{35}(\beta_{LM}, m_I)$$

Now, applying ordinary Bloch–Wangsness–Redfield theory (*15*), the transient ZFS interaction generates an angle-dependent relaxation supermatrix **R**. The relaxation matrix elements are listed in Table 3. In order to determine the paramagnetically enhanced nuclear spin relaxation in micro-heterogeneous systems, the angle-dependent spectral densities $k_\sigma(\omega_I, \beta_{LM})$, involving both types of electron spin relaxation processes (Eqs. [5]–[7]), have to be determined. However, a theoretical simplification may be introduced since it is the spectral densities and not the time autocorrelation functions which are the crucial objects to be determined. Therefore, by formally solving the Fourier–Laplace transforms it is possible to derive closed analytical expressions. This procedure is analogous to deriving NMR/ESR lineshape functions for high-spin systems. We then readily obtain closed analytical expressions for the spectral densities for arbitrary nuclear spin quantum numbers (*13, 14, 22*).

The nuclear spin spectral densities of Eq. [5] and Eq. [7] may then be determined using the approach of Refs. (*13, 14, 22*). The expression for each of the spectral densities ($\sigma = \pm 1, 0$) is given by one element of the inverse of the matrix $M(\beta_{LM})$. The spectral density may be written (*13, 14*)

$$s_\sigma^{DD}(\omega_I, \beta_{LM}) \equiv \frac{3}{S(S+1)} \int_0^\infty \mathrm{tr}_L\{\hat{S}_\sigma^{1\dagger} e^{i\hat{L}_S(\beta_{LM})\tau} \hat{S}_\sigma^1 \hat{\rho}_S^{eq}\}$$

$$\times\ e^{-i\omega_I\tau}d\tau$$

$$= \int_0^\infty \mathrm{tr}_L\{\hat{O}_\sigma^{1\dagger} e^{-\hat{M}(\omega_I,\beta_{LM})\tau} \hat{O}_\sigma^1\}d\tau$$

$$= \mathrm{tr}_S\{\hat{O}_\sigma^{1\dagger}\hat{M}(\omega_I, \beta_{LM})^{-1}\hat{O}_\sigma^1\}, \qquad [30]$$

where $\mathrm{tr}_S\{\hat{O}_\sigma^{1\dagger}\hat{M}(\omega_I, \beta_{LM})^{-1}\hat{O}_\sigma^1\}$ denotes a matrix element of

the inverse of **M** which is determined by the superoperator $\hat{M}(\omega_I, \beta_{LM})$

$$\hat{M}(\omega_I, \beta_{LM}) = -i\hat{L}_S(\beta_{LM}) + i\omega_I\hat{1}. \qquad [31]$$

where $\hat{1}$ is the unity superoperator.

Here we have omitted the τ_R term, as the biomacromolecule–paramagnetic ion complex is assumed to reorient very slowly.

The electron spin operator representation chosen for $\hat{M}(\omega_I, \beta_{LM})$ is an irreducible spherical electron spin tensor operator basis set $\hat{O}_\sigma^\Sigma$

$$\hat{O}_\sigma^\Sigma = \sum_m \sqrt{2\Sigma + 1} \begin{pmatrix} S & S & \Sigma \\ m + \sigma & -m & -\sigma \end{pmatrix}$$

$$\times (-1)^{S-m-\sigma}|Sm + \sigma\rangle\langle Sm| \qquad [32]$$

expressed in terms of Zeeman eigenoperators $|Sm + \sigma\rangle\langle Sm|$ and where

$$\begin{pmatrix} S & S & \Sigma \\ m + \sigma & -m & -\sigma \end{pmatrix} \qquad [33]$$

is a 3j symbol (*12*).

For an electron spin quantum number $S = \frac{5}{2}$ in micro-heterogeneous systems all the statistical tensors of rank $\Sigma = 0$, 1, 2, 3, 4, 5 enter the theoretical description. The matrix **M** is then set up by adding the Redfield electron spin relaxation matrix in the irreducible spherical tensor spin operator representation to the static Liouville supermatrix which includes the electron Zeeman interaction, the hyperfine interaction, and the static ZFS interaction.

As mentioned above the theoretical approach means carrying out the Fourier–Laplace transform explicitly and thus solving the integral exactly, giving the result of the spectral density in terms of only one matrix element of M^{-1} for each block characterized by a hyperfine split ESR line. This is an approximation originating from taking only the scalar hyperfine coupling into account (cf. Eq. [24]).

APPENDIX B

The Electron Spin–Spin Spectral Density

In the spherical tensor representation of Eq. [32] of electron spin quantum number $S = \frac{5}{2}$ the spin–spin relaxation corresponds to $\sigma = \pm 1$. The **M** matrix is then denoted with an index, M_2, indicating its dependence on electron spin T_2 processes ($\sigma = \pm 1$). The M_2 matrix has the form

TABLE 4
Redfield Matrix Elements for $S = \frac{5}{2}$

$$R_{11}^{22}(\beta_{LM}, m_I) = \tfrac{5}{56}(33J_0 + 38J_1 + 76J_2 + 38iQ_1 - 5iQ_2)$$

$$R_{11}^{44}(\beta_{LM}, m_I) = \tfrac{5}{112}(39J_0 + 218J_1 + 233J_2 + 22iQ_1 + 17iQ_2)$$

$$R_{11}^{11}(\beta_{LM}, m_I) = \tfrac{1}{2}(3J_0 + 5J_1 + 2J_2 + iQ_1 + 2iQ_2)$$

$$R_{11}^{33}(\beta_{LM}, m_I) = \tfrac{1}{48}(123J_0 + 370J_1 + 497J_2 + 126iQ_1 - 3iQ_2)$$

$$R_{11}^{55}(\beta_{LM}, m_I) = \tfrac{5}{24}(3J_0 + 26J_1 + 16J_2 - 6iQ_1 + 9iQ_2)$$

$$R_{11}^{24}(\beta_{LM}, m_I) = \tfrac{45}{112}\sqrt{10}(J_0 + 2J_1 - 3J_2 + 2iQ_1 - iQ_2)$$

$$R_{11}^{13}(\alpha_{LM}, m_I) = \tfrac{9}{28}\sqrt{21}(J_0 - J_2 + 2iQ_1 - iQ_2)$$

$$R_{11}^{35}(\alpha_{LM}, m_I) = \tfrac{25}{336}\sqrt{14}(3J_0 + 14J_1 - 17J_2 + 6iQ_1 - 3iQ_2)$$

$$\mathbf{M}_2 \equiv \mathbf{M}_2(\omega_I, \beta_{LM}, m_I) = \begin{bmatrix} A & F & G & H & 0 \\ F & B & 0 & I & J \\ G & 0 & C & K & 0 \\ H & I & K & D & L \\ 0 & J & 0 & L & E \end{bmatrix}, \quad [34]$$

where the matrix elements are given in Table 3. It should be noted that the matrix elements both in Eq. [34] and in Eq. [49] all depend on β_{LM}. Elements on and next to the diagonal also depend on ω_S and m_I, and finally the diagonal elements depend on ω_I. To simplify the notation this dependence it not explicitly shown. In Eqs. [34] and [49], the matrix elements are ordered with even-rank elements first, with ranks in the order 2, 4, 1, 3, 5. The rank 1 element $C = (\mathbf{M}_2)_{33}$ corresponds to the spin vector and is the relevant element for spin relaxation. What we now need to calculate is the 33 element of the inverse matrix.

The electron spin energies are given by the Zeeman interaction and the hyperfine splitting as

$$i\omega_S(m_I) = i\omega_S^0 + im_I \times A_{IS}, \quad [35]$$

thus ignoring higher order terms. The Redfield relaxation matrix elements of Table 3 are written in the representation of Eq. [32] as $R_{\sigma\sigma}^{\Sigma'\Sigma} = \mathrm{tr}_S\{\hat{O}_\sigma^{\Sigma'\dagger}\hat{R}(\beta_{LM}, m_I)\hat{O}_\sigma^\Sigma\}$. The elements can be calculated using Eq. [3] in Ref. (22) and are listed in Table 4.

We have now reached the theoretical level where electron spin relaxation is expressed in terms of microscopic parameters describing the transient ZFS correlation function. Here also the intrinsic angle dependence becomes evident since the electron spectral densities have this angle dependence. The model electron spin spectral densities are given by

$$J_n(\beta_{LM}, n\omega_S(m_I)) \equiv -\frac{32(\Delta_t^{ZFS})^2}{25}\sum_k |d_{kn}^2(\beta_{LM})|^2$$

$$\times \frac{\tau_k}{1 + (n\omega_S(m_I)\tau_k)^2} \quad [36]$$

with the dynamic frequency shift Q_n defined by

$$Q_n(\beta_{LM}, n\omega_S(m_I)) \equiv -\frac{32(\Delta_t^{ZFS})^2}{25}\sum_k |d_{kn}^2(\beta_{LM})|^2$$

$$\times \frac{\tau_k^2 n\omega_S(m_I)}{1 + (n\omega_S(m_I)\tau_k)^2}. \quad [37]$$

We thus allow for anisotropic diffusion dynamics of the transient ZFS. Physically this anisotropy may be thought of as an effect of liberation and the spinning motion of the water ligands and a slower distortion motion are due to intercomplex M–O distance fluctuations. This model has been denoted the pseudo-rotation model (11, 23). The correlation times τ_k are defined as

$$\frac{1}{\tau_0} = \frac{1}{\tau_\perp}$$

$$\frac{1}{\tau_{\pm 1}} = \frac{5}{6\tau_\perp} + \frac{1}{6\tau_\parallel}$$

$$\frac{1}{\tau_{\pm 2}} = \frac{1}{3\tau_\perp} + \frac{2}{3\tau_\parallel}, \quad [38]$$

where the "fast" motion ($\tau_\parallel$) is expected to be in the range of 1–5 ps for hexa aqua complexes and the "perpendicular" motion ($\tau_\perp$) is much slower because it is more influenced by the molecular interface and may range from an isotropic (1–5 ps) case to very anisotropic dynamics, i.e., 5–300 ps.

The electron spectral densities are determined from an inversion of the corresponding matrix. For the electron spin–spin relaxation with $\sigma = \pm 1$ we obtain

$$s_1^{DD}(\omega_I, \beta_{LM}, m_I) = \mathrm{tr}_S\{\hat{O}_1^{1\dagger}\hat{M}_2^{-1}(\omega_I, \beta_{LM}, m_I)\hat{O}_1^1\}, \quad [39]$$

where the exact solution of the spectral density of Eq. [39] is

$$\mathrm{tr}_S\{\hat{O}_1^{1\dagger}\hat{M}_2^{-1}(\omega_I, \beta_{LM}, m_I)\hat{O}_1^1\} = \frac{X - 2FJHL}{CX - G^2Z + Y}$$

$$= \frac{1}{C}\left(1 + \frac{G^2Z - Y - 2FJHL}{CX - G^2Z + Y}\right)$$

$$= \frac{1}{C}(1 + \delta_1(\omega_I, \beta_{LM}, m_I)), \quad [40]$$

where we have introduced

$$X = AZ + H^2(J^2 - BE) + 2EFHI + F^2(L^2 - DE) \quad [41]$$

$$Y = 2GK(BEH - EFI - HJ^2)$$

$$\quad + K^2(EF^2 - ABE + AJ^2) - 2FJL(CH - GK) \quad [42]$$

$$Z = BDE - EI^2 - DJ^2 - BL^2 + 2IJL. \quad [43]$$

Note that these terms all depend on ω_I, β_{LM}, and m_I. We also define a correction term

$$\delta_1(\omega_I, \beta_{LM}, m_I) = \frac{G^2 Z - Y - 2FJHL}{CX - G^2 Z + Y}, \qquad [44]$$

where we explicitly write the dependence of δ_1 on ω_I, β_{LM}, and m_I to stress this fact.

We obtain the spectral density independent of hyperfine splitting by a summation over hyperfine-dependent electron resonances

$$s_1^{DD}(\omega_I, \beta_{LM}) = \sum_{m_I} \text{tr}_S\{\hat{O}_1^{1\dagger}\hat{M}^{-1}(\omega_I, \beta_{LM}, m_I)\hat{O}_1^1\}. \quad [45]$$

In the case of extreme narrowing ($F = K = L = 0$) one may think that the SBM result ($1/C$) is recovered. However, this is not the case, since the static ZFS mixes even-rank electron spin tensor operators, and the following correction term is still present,

$$s_1^{DD}(\omega_I, \beta_{LM})$$
$$= \sum_{m_I} \frac{1}{C}\left(1 + \frac{G^2 U}{ACU - G^2 U + [J^2 - BE]CH^2}\right), \quad [46]$$

where we have defined

$$U = BDE - EI^2 - DJ^2. \qquad [47]$$

In deriving Eqs. [40] and [46] we obtain the first two of our main results, clearly displaying the correction terms to the MSBM theory.

APPENDIX C

The Electron Spin–Lattice Spectral Density

The spectral density which is dominated by electron spin–lattice relaxation is given by

$$s_0^{DD}(\omega_I, \beta_{LM}, m_I) = \frac{3}{S(S+1)}$$
$$\times \int_0^\infty \text{tr}_L\{\hat{S}_0^{1\dagger} e^{i\hat{L}_S(\beta_{LM}, m_I)\tau} \hat{S}_0^1 \hat{\rho}_S^{eq}\} e^{-\omega_I\tau} d\tau$$
$$= \text{tr}_S\{\hat{O}_0^{1\dagger}\hat{M}^{-1}(\omega_I, \beta_{LM}, m_I)\hat{O}_0^1\}. \qquad [48]$$

In this case only a 3×3 matrix has to be inverted since the

TABLE 5
Matrix Elements of M_1 for $S = \frac{5}{2}$ and Redfield Matrix Elements $R_{\sigma\sigma}^{\Sigma'\Sigma}$

$$R_{00}^{22}(\beta_{LM}, m_I) = \tfrac{15}{56}(22J_1 + 27J_2)$$
$$R_{00}^{44}(\beta_{LM}, m_I) = \tfrac{25}{56}(26J_1 + 23J_2)$$
$$R_{00}^{24}(\beta_{LM}, m_I) = \tfrac{25}{28}\sqrt{3}(J_1 - J_2)$$
$$A' = R_{00}^{11}(\beta_{LM}, m_I) + i\omega_I$$
$$C' = R_{00}^{33}(\beta_{LM}, m_I) + i\omega_I$$
$$E' = R_{00}^{55}(\beta_{LM}, m_I) + i\omega_I$$
$$B' = R_{00}^{13}(\beta_{LM}, m_I)$$
$$D' = R_{00}^{53}(\alpha_{LM}, m_I)$$
$$R_{00}^{11}(\beta_{LM}, m_I) = J_1 + 4J_2$$
$$R_{00}^{33}(\beta_{LM}, m_I) = \tfrac{1}{8}(82J_1 + 83J_2)$$
$$R_{00}^{55}(\beta_{LM}, m_I) = \tfrac{25}{8}(2J_1 + J_2)$$
$$R_{00}^{13}(\beta_{LM}, m_I) = \tfrac{9}{14}\sqrt{14}(J_1 - J_2)$$
$$R_{00}^{53}(\beta_{LM}, m_I) = \tfrac{25}{28}\sqrt{35}(J_1 - J_2)$$

even-rank tensor operators are decoupled from the odd-rank tensor operators. The M_1 ($\sigma = 0$) matrix is block diagonal:

$$M_1 \equiv M_1(\omega_I, \beta_{LM}, m_I)$$
$$= \begin{bmatrix} -R_{00}^{22} - i\omega_I & R_{00}^{24} & 0 & 0 & 0 \\ R_{00}^{24} & -R_{00}^{44} - i\omega_I & 0 & 0 & 0 \\ 0 & 0 & A' & B' & 0 \\ 0 & 0 & B' & C' & D' \\ 0 & 0 & 0 & D' & E' \end{bmatrix}. \quad [49]$$

The matrix elements of M_1 are expressed in terms of Redfield matrix elements and the nuclear spin Larmor frequency and are listed in Table 5, together with the Redfield matrix elements.

The inverted matrix element $(M_1^{-1})_{33}$ is given by

$$\text{tr}_S\{\hat{O}_0^{1\dagger}\hat{M}_1^{-1}(\omega_I, \beta_{LM}, m_I)\hat{O}_0^1\}$$
$$= \frac{1}{A'}(1 + \delta_0(\omega_I, \beta_{LM}, m_I)), \qquad [50]$$

where a correction term $\delta_0(\omega_I, \beta_{LM}, m_I)$ which is due to nonextreme narrowing has been introduced. It is thus equal to zero in the extreme narrowing regime,

$$\delta_0(\omega_I, \beta_{LM}, m_I) = \frac{B'^2}{C'A' - B'^2 - D'^2(A'/E')}. \quad [51]$$

This is our third main result of this paper and now we have two spectral densities of the PRE theory in closed form.

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