Proton-Enhanced Relaxation in Low-Symmetry Paramagnetic Complexes ($S=1$): Beyond the Solomon–Bloembergen and Morgan Theory. 1. The Smoluchowsky Distortion Model of the ZFS Interaction

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Westlund, P.-O. and Larsson, P. T., 1991. Proton-Enhanced Relaxation in Low-Symmetry Paramagnetic Complexes ($S = 1$): Beyond the Solomon–Bloembergen and Morgan Theory. 1. The Smoluchowsky Distortion Model of the ZFS Interaction. – Acta Chem. Scand. 45: 11–18.

A model describing paramagnetic enhanced proton relaxation (PER) in low-symmetry complexes is developed. The theoretical framework valid in the slow-motion region for the electron spin system is reviewed and related to the Solomon–Bloembergen–Morgan theory. The dynamic model of a low-symmetry paramagnetic complex comprises a static and a transient ZFS interaction. Calculations of NMRD dispersion curves are presented for complexes of paramagnetic ions with electron spin quantum number $S = 1$. The dipole–dipole cross-correlation functions are shown to play an important role in the low-field region where the ZFS interaction is larger than the Zeeman interaction. The calculations of dispersion curves cover the range from the Redfield region to the slow-motion region and are compared with analogous results obtained using the Bloembergen–Morgan approach. The results indicate that an appropriate model for many low-symmetry complexes must include a model similar to the restricted pseudo-rotation of the principal frame of the ZFS interaction in order to average the electron spin – nuclear spin dipole–dipole coupling, implying a low and constant PER effect in the low-field region. This fact may explain the partial success of fitting the Bloembergen–Morgan expressions to the experimental dispersion curves for low-symmetry complexes.

Introduction

Nuclear spin relaxation times in diamagnetic liquids are often reduced markedly when small concentrations of some paramagnetic species are added. This effect is usually called paramagnetic enhanced relaxation (PER). The interpretation of PER is usually based on the Solomon–Bloembergen–Morgan (SBM) theory[1–4] or low-field approaches with similar assumptions as in the SBM theory.[5–7] The SBM theory incorporates the effect of the electron spin relaxation on the nuclear spin relaxation of octahedral (high-symmetry) complexes. In biological systems, on the other hand, a paramagnetic hexaaqua complex $[M(H_2O)_6]^{n+}$ is expected to become permanently distorted owing to the perturbation of the charged interfaces of the macromolecules, or the bilayer, and the solvent. Some of the water in the first hydration shell may be replaced by other ligands or be subject to hindered motion. The result of such a perturbation is a low-symmetry environment of the paramagnetic ion when averaged over the local motions of the surrounding molecules, and which is manifested in a static ZFS interaction. Consequently the PER effect in a heterogeneous system, where the paramagnetic ion is located in a low-symmetry environment, may be quite different and is not taken into account in the SBM theory. Thus, for an

important class of systems, i.e. for all heterogeneous systems where the electron spin relaxation rate is relevant, the PER effect is not theoretically well-described.

The SBM relaxation description is condensed into a set of equations describing the relaxation rates of the nuclear spin ($I = 1/2$) when coupled via nuclear spin – electron spin dipole–dipole interaction and scalar interaction to an electron spin S [eqns. (1) and (2)]. In this set, interaction

$$\frac{1}{T_{1M}} = 2A^{DD}\left(3\,\frac{\tau_{C1}}{(1+\omega_I^2\tau_{C1}^2)} + 6\,\frac{\tau_{C2}}{[1+(\omega_I+\omega_S)^2\tau_{C2}^2]}\right.$$

$$\left.+\,\frac{\tau_{C2}}{[1+(\omega_I-\omega_S)^2\tau_{C2}^2]}\right) + 2A^{SC}\left(\frac{\tau_{E1}}{(1+\omega_I^2\tau_{E1}^2)}\right) \tag{1}$$

$$\frac{1}{T_{2M}} = A^{DD}\left(4\tau_{C1} + 3\,\frac{\tau_{C1}}{(1+\omega_I^2\tau_{C1}^2)} + 13\,\frac{\tau_{C2}}{(1+\omega_S^2\tau_{C2}^2)}\right)$$

$$+\,A^{SC}\left(\tau_{E1} + \frac{\tau_{E2}}{(1+\omega_S^2\tau_{E2}^2)}\right) \tag{2}$$

constants for the dipole–dipole and the scalar interaction are given by eqns. (3a) and (3b). The first term in both

$$A^{DD} = \frac{S(S+1)}{15}\gamma_I^2\gamma_S^2 \, r_{IS}^{-6} \tag{3a}$$

$$A^{SC} = \frac{S(S+1)A^2}{3} \tag{3b}$$

equations arises from the nuclear spin – electron spin dipole–dipole interaction (DD) and is characterized by the correlation times τ_{C1} and τ_{C2}. The second term arises from the scalar interaction (SC) and is characterized by the correlation times τ_{E2} and τ_{E2}. The correlation times are defined by eqn. (4). The electron spin relaxation times τ_{1S} and τ_{2S}

$$\tau_{C1}^{-1} = \tau_R^{-1} + \tau_{1S}^{-1} + \tau_M^{-1}$$

$$\tau_{C2}^{-1} = \tau_R^{-1} + \tau_{2S}^{-1} + \tau_M^{-1}$$
$$\tag{4}$$
$$\tau_{E1}^{-1} = \tau_{1S}^{-1} + \tau_M^{-1}$$

$$\tau_{E2}^{-1} = \tau_{2S}^{-1} + \tau_M^{-1}$$

are determined within the Redfield theory and given by eqns. (5) and (6), where Δ refers to the transient ZFS

$$\tau_{1S}^{-1} = \frac{\Delta^2}{5}\left(\frac{\tau_v}{(1+\omega_S^2\tau_v^2)} + 4\frac{\tau_v}{(1+4\omega_S^2\tau_v^2)}\right) \tag{5}$$

$$\tau_{2S}^{-1} = \frac{\Delta^2}{10}\left(3\tau_v + \frac{5\tau_v}{1+\omega_S^2\tau_v^2} + \frac{2\tau_v}{1+4\omega_S^2\tau_v^2}\right) \tag{6}$$

interaction. The molecular reorientational modulation of the dipole–dipole interaction is characterized by the correlation time τ_R and the modulation of the transient ZFS interaction is characterized by τ_v. The correlation time τ_M refers to the lifetime of the diamagnetic nuclei in the complex.

The application of the SBM theory is restricted to electron spin systems weakly coupled to the lattice and to the extreme narrowing condition for the electron spin system. The latter restriction is removed by the generalization to multi-exponential electron spin relaxation given by Luz et al.[8] Furthermore, the BM approach assumes that the nuclear and the electron spin systems are uncorrelated. This is only strictly true for octahedral complexes with relatively fast fluctuations compared with the molecular reorientation. However, for paramagnetic complexes with permanently low symmetry the ZFS interaction is also modulated by the molecular reorientational motion, together with the local, and often faster, symmetry-distorting motion of the ligands. The former dynamics is thus the same motion that modulates the electron–nuclear dipole–dipole coupling, and it has been shown that the correlation between the ZFS interaction and the dipole–dipole coupling may necessitate a large correction of the SBM description for nuclear T_{2M}.[9] Consequently, the nuclear spin – electron spin dipole–di-

pole correlation function is not separable into an electron spin correlation function and a pure reorientational correlation function.

We follow the theoretical framework developed in a number of papers,[9-17] applied to other types of systems, however. In Refs. 9 and 11–13 the paramagnetic system treated refers to the low-symmetric and rigid complexes with a ZFS interaction only modulated by molecular reorientation. In Refs. 10 and 14 we applied the theoretical framework to the other extreme, namely to octahedral complexes where only a transient and fast fluctuating ZFS interaction was present. In this paper we combine the two extreme cases into a model which comprises both a static and a transient ZFS interaction. We have confined the treatment to electron spin systems with spin quantum number $S = 1$ and to a specific dynamic model for the local symmetry-disrupting motion described as a low-frequency classical vibrational mode. This model is the classical analogue to the quantum-mechanical vibration model discussed in Ref. 18. The local symmetry-distorting motion is described by a Smoluchowski model,[10] and the molecular reorientation is described as an isotropic rotational diffusion motion. We focus on the cross-correlation effects and compare our results with the corresponding Bloembergen–Morgan results.

For the weak coupling, as for the slow-motion regime, we must rely on numerical results, which are presented in the form of NMRD dispersion curves showing how the nuclear spin–lattice relaxation rate T_{1M} varies with the static magnetic field B_0. This paper is organized as follows. In section 2 we review the fundamentals of the theoretical framework, and in section 3 the lattice model is described. The numerical results are then discussed, and in section 5 we summarize the results and conclusions of this work.

Nuclear spin relaxation theory

For nuclear spins (I) in a paramagnetic complex, the coupling to the lattice is predominantly via the interaction with the electron spin system. The interaction between a nuclear spin and an electron spin arises from electron spin – nuclear spin dipole–dipole coupling (H^{DD}) and Fermi contact scalar interaction (H^{SC}). In this paper we concentrate on the former mechanism since it is, in most cases, the dominant relaxation path for the nuclear spin system. The spin dipole–dipole interaction depends on the magnitudes of the nuclear and electron spins and on the separation and relative orientation of the spins. The 'lattice' (L) refers to the electron spin system (S) and other relevant degrees of freedom, e.g. the distortion motion of the complex symmetry and the molecular tumbling motion. The equation of motion is given by eqn. (7).

$$\frac{d}{dt}\varrho(t) = -i[L_I^0 + L_{IL}^{DD}(t) + L_{IL}^{SC}(t) + L_L]\varrho(t) \tag{7}$$

Following the formalism,[9-17] the analogous expressions to eqns. (1) and (2) describing the nuclear spin–lattice relaxation rate within the Redfield theory are given by eqn. (8).

$$\frac{1}{T_{1M}} = -2\text{Re}[K_{1,-1}^{DD}(\omega_I) + K_{1,-1}^{SC}(\omega_I) + 2K_{1,-1}^{DD-SC}(\omega_I)]$$

$$\frac{1}{T_{2M}} = -\text{Re}[K_{0,0}^{DD}(0) + K_{0,0}^{SC}(0) + 2K_{0,0}^{DD-SC}(0)] + \frac{1}{2T_{1M}} \quad (8)$$

The expressions now also include an additional term, representing a cross-correlation effect between the scalar and the dipole–dipole interactions, which is not very important and is not discussed further in this paper. The complex spectral density $K_{n,-n}$ is defined as the Fourier–Laplace transform of the correlation function $G(t)$. The dipole–dipole correlation function is given by eqn. (9).

$$G_{n,-n}^{DD}(\tau) = (-)^n \text{Tr}\{T_{-n}^1 [\exp(i\tau L_L) T_n^1 \sigma_L^{eq}]\} \quad (9)$$

The nuclear spin–lattice relaxation rate is thus given in terms of the Fourier–Laplace transform of the dipole–dipole correlation function. The nuclear spin – electron spin dipole–dipole interaction hamiltonian is most conveniently written in terms of first-rank irreducible tensor operators [eqn. (9)], where the lattice tensor operator T_n^1

$$H_{IL} = \sum_n (-1)^n I_n^1 T_{-n}^1 \quad (9)$$

representing the dipole–dipole interaction is defined by eqn. (10), and for the scalar interaction we have eqn. (11).

$$T_n^1(t) = (-1)^{1+n} 3^{1/2} \sum_q \begin{pmatrix} 2 & 1 & 1 \\ n-q & q & -n \end{pmatrix} S_q^1 F_{n-q}^2 [\Omega(t)] \quad (10)$$

$$T_n^{SC} = AS_n^1 \quad (11)$$

In eqn. (10) we have a $3-j$ symbol; S_q^1 is a first-rank standard electron–spin vector operator, and F_{n-q}^2 is a stochastic time-dependent rank-two tensor function containing the geometry-dependent part of the spin dipole–dipole interaction. It is related to the second-rank Wigner matrix elements through eqn. (12).

$$F_{n-q}^2 [\Omega(t)] = -(10)^{1/2} \gamma_S \gamma_I \frac{1}{r_{IS}^3} D_{0,n-q}^2 [\Omega(t)] \quad (12)$$

Substituting eqns. (10) and (12) into the dipole–dipole correlation function results in eqn. (13) for the dipole–

$$G_{n,-n}(\tau) = 30 \, \gamma_S^2 \gamma_I^2 r_{IS}^{-6} \sum_p \sum_q \begin{pmatrix} 2 & 1 & 1 \\ n-p & p & -n \end{pmatrix} \begin{pmatrix} 2 & 1 & 1 \\ n-q & q & -n \end{pmatrix}$$
$$\times \text{Tr}_L\{[S_q^1 D_{0,n-q}^2(\Omega)]^\dagger \, e^{i\tau L_L} S_p^1 D_{0,n-p}^2(\Omega) \, \sigma_L^{eq}\} \quad (13)$$

dipole correlation function, and for the scalar time correlation function we obtain eqn. (14).

$$G_{n,-n}^{SC}(\tau) = A^2 \text{tr}_L [(-)^n S_{-n}^1 \, e^{i\tau L_L} \, S_n^1 \sigma_L^T] \quad (14)$$

In order to determine the nuclear spin relaxation rate, the Fourier–Laplace transform of the correlation functions of eqns. (13) and (14) must be determined. In the next section we turn our attention to this problem, and first we define the Liouville lattice superoperator governing the dynamics of the correlation function.

The lattice degrees of freedom

The Liouville lattice superoperator may be written as a sum of the following Liouville superoperators [eqn. (15)]. L^0 is

$$L_L = L_{Zeeman}^0 + L_{ZFS} + i\Gamma_q + i\Gamma_\Omega \quad (15)$$

generated by the electron Zeeman interaction $H_S = g_S B_0 S_Z$. L_{ZFS} is generated by the ZFS interaction specifying the coupling between the electron spin system, the stochastic time-dependent distortion coordinate and the reorientational degrees of freedom [eqn. (16)], where a_0 is the

$$H_{ZFS}(t) = \sum_n (-1)^n S_n^2$$
$$\times \sum_m a_0^2(t) D_{0,m}^2[\Omega_{PM}(t)] D_{m,-n}^2[\Omega_{ML}(t)] \quad (16)$$

principal component of the ZFS interaction assuming a cylindrical symmetry of the interaction. In order to relate it to the classical subsystem, the principal component is expanded in terms of a coordinate $q(t)$ [eqn. (17)]. The

$$a_0^2(t) = \langle a_0^2 \rangle + \left\langle \frac{\partial a_0^2}{\partial q} \right\rangle q(t) \quad (17)$$

permanent ZFS interaction [eqn. (18)] refers to the first

$$H_{ZFS}^{Static}(t) = \sum_n (-1)^n S_n^2$$
$$\times \sum_m \langle a_0^2 \rangle \overline{D_{0,m}^2[\Omega_{PM}(t)]} D_{m,-n}^2[\Omega_{ML}(t)] \quad (18)$$

term of eqn. (17), which is only modulated by the molecular reorientational motion. The transient ZFS interaction due to the linear term is given by eqn. (19), and the root

$$H_{ZFS}^{Trans}(t) = \sum_n (-1)^n S_n^2$$
$$\times \sum_m \left\langle \frac{\partial a_0^2}{\partial q} \right\rangle q(t) \overline{D_{0,m}^2[\Omega_{PM}(t)]} D_{m,-n}^2[\Omega_{ML}(t)] \quad (19)$$

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mean-square value of the ZFS interaction is defined by eqn. (20).

$$\langle H^2_{ZFS}(t)\rangle^{1/2} = \left(S^2 \langle a_0^{(2)}\rangle^2 + \left\langle \frac{\partial a_0^{(2)}}{\partial q}\right\rangle^2 S^2 \frac{k_B T}{K}\right)^{1/2}$$

$$= (\Delta_0^2 + \Delta_1^2)^{1/2} \tag{20}$$

In eqns. (18) and (19) we have also indicated with the bar an average over the motion of the principal frame of the ZFS relative to the reorientational diffusion frame. We then introduced an order parameter S in eqn. (20) representing this partial average. The molecular reorientational motion is treated in the classical approximation and is represented by a Markov operator Γ_Ω, representing isotropic rotational diffusion (R), [eqn. (21)], where D_R is

$$\Gamma_{\Omega_{ML}} = D_R \, \nabla^2_{\Omega_{ML}} \tag{21}$$

the isotropic rotational diffusion constant retated to the rotational correlation time $1/\tau_R = 6D_R$. The fluctuation of the distortion coordinate $q(t)$ of the distortion space (D) is described by a Smoluchowski diffusion operator Γ_S [eqn. (22)].

$$\Gamma_S = D \left(\frac{\partial V(q)}{\partial q}\bigg/ k_B T \frac{\partial}{\partial q} + \frac{\partial^2 V(q)}{\partial q^2}\bigg/ k_B T + \frac{\partial^2}{\partial q^2}\right) \tag{22}$$

In order to proceed, a basis set of operators spanning the Liouville space is now introduced. A complete basis set is constructed as a direct product basis set formed by the eigenoperators (eigenfunctions) of the operators and functions representing the subsystems (S), (R) and (D). The electron spin part of this basis set is defined by eqn. (23),

$$|\Sigma,\sigma) = \sum_m (-)^{S-m-\sigma}(2\Sigma+1)^{1/2} \binom{S \quad S \quad \sigma}{m+\sigma \, -m \, -\sigma} |S,m+\sigma\rangle\langle S,m| \tag{23}$$

where $|S,m\rangle$ is a Hilbert space eigenvector of the standard electron vector operators S^2 and S_Z.

The reorientational space is spanned by the infinite set of orthonormal Wigner rotation matrix elements [eqn. (24)].

$$|L,K,M) = \left(\frac{2L+1}{8\pi^2}\right)^{1/2} D^L_{K,M}(\Omega) \tag{24}$$

Finally, the complete set of Smoluchowsky eigenfunctions is formed from the eigenfunctions of the harmonic oscillator, i.e. the Hermite functions φ_i.[10] The complete basis set of the Liouville space is thus formed as a direct product of the electron spin operators, the reorientational functions and the Smoluchowsky eigenfunctions [eqn. (25)].

$$O(\Sigma,\sigma,L,M,i) = |\Sigma,\sigma)\otimes|L,M)\otimes|i) \tag{25}$$

The dipole–dipole correlation function of eqn. (13) is determined by expanding the dipole operators in terms of the complete basis set, eqn. (26), where the coefficients of

$$S^1_q D^2_{0,n-q}(\Omega_R) = \sum_\nu C_\nu \hat{O}_\nu$$

$$\sigma_L S^1_p D^2_{0,n-p}(\Omega_R) = \sum_\mu D_\mu \hat{O}_\mu \tag{26}$$

the C and D vectors are given by eqn. (27).

$$C_\nu = \mathrm{Tr}_L\{\hat{O}^\dagger_\nu S^1_q D^2_{0,n-p}(\Omega_R)|0)\}$$

$$D_\mu = \mathrm{Tr}_L\{\hat{O}^\dagger_\mu \sigma_L S^1_q D^2_{0,n-p}(\Omega_R)|0)\} \tag{27}$$

From eqns. (13), (26) and (27), the dipole–dipole correlation function may be written as eqn. (28), where the

$$G^{DD}_{n,-n}(\tau) = 30 \, \gamma^2_S \gamma^2_I r^{-6}_{IS}$$

$$\times \sum_p \sum_q \binom{2 \quad 1 \; 1}{-n-q \, q \, n} \binom{2 \quad 1 \; 1}{-n-p \, p \, n} [C]^\dagger [D] e^{\tau[M]} \tag{28}$$

Liouville supermatrix is denoted $[M] = i\,O\dagger L_L\,O$ written in the operator representation. Eqn. (28) defines a submatrix of dimension nine of the full and infinite correlation matrix M determined by the Liouville operators of eqn. (15).

We close this section by investigating the SBM approach in the context of the model used in this paper. By "the BM approach" we refer to the separation of the electron spin system and the reorientational motion of the nuclear spin – electron spin dipole–dipole interaction. The first assumption we have to make in order to obtain the SBM equations is that the Liouville superoperator L_{ZFS} governing the relaxation of the electron spin is independent of molecular reorientation. Then the dipole–dipole correlation function of eqn. (28) may be separated into a reorientational part and an electron spin part, according to eqns. (29) and (30).

$$G^{DD}_{1,-1}(\tau) = 30 \, \gamma^2_I \gamma^2_S r^{-6}_{IS}$$

$$\times \sum \sum \binom{2 \quad 1 \; 1}{-1-q \, q \, 1}^2 \mathrm{tr}_R\{D^2_{0,-1-q}(\Omega)e^{\tau\Gamma}D^2_{0,-1-q}(\Omega)\sigma^T_R\}\,.$$

$$\times \mathrm{tr}_S\{S^1_q{}^\dagger e^{i\tau L'}\sigma^T_S S^1_q\}$$

$$= \frac{1}{5}\,\gamma^2_I\gamma^2_S r^{-6}_{IS}\,e^{-6D\tau}6\mathrm{tr}_S\{S^1_{-1}{}^\dagger e^{i\tau L'}S^1_{-1}\sigma^T_S\}$$

$$+ 3\mathrm{tr}_S\{S^1_0{}^\dagger e^{i\tau L'}S^1_0\sigma^T_S\} + \mathrm{tr}_S\{S^1_1{}^\dagger e^{i\tau L'}S^1_1\sigma^T_S\} \tag{29}$$

$$G^{DD}_{0,0}(\tau) = \frac{1}{5}\,\gamma^2_S\gamma^2_I r^{-6}_{IS}\,e^{-6D_R\tau}\{3\mathrm{tr}_S\{S^1_{-1}{}^\dagger e^{i\tau L'}S^1_{-1}\sigma_S\}$$

$$+ 4\mathrm{tr}_S\{S^1_0{}^\dagger e^{i\tau L'}S^1_0\sigma_S\} + 3\mathrm{tr}_S\{S^1_1{}^\dagger e^{i\tau L'}S^1_1\sigma_S\}\} \tag{30}$$

The SBM approach [eqns. (29) and (30)] thus makes it possible to express the nuclear spin – electron spin dipole–dipole correlation functions in terms of pure electron spin–lattice and spin–spin relaxation rates and a reorientation correlation function.

Results and discussion

The numerical results are presented in this section in the form of dispersion curves, where the reduced spectral density function $K(\omega)$ is plotted as a function of the static magnetic field B_0 or $\log(-\omega_S \tau_R)$. The reduced spectral density is normalized according to eqn. (31). The value of

$$K(\omega_I) = \frac{K_{n,n}^{DD}(n\omega_I)}{\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 r_{IS}^{-6} \tau_R} \tag{31}$$

the reduced spectral density is thus restricted to the interval [0,1]. $K(\omega)$ is composed of a sum of spectral densities $k_{p,q}$ forming a $3 \otimes 3$ submatrix of the Fourier–Laplace transformed full correlation matrix. From section 2 it follows that the reduced spectral density is given by eqn. (32),

$$K(\omega_I) = \sum_p \sum_q \binom{2 \quad 1 \ 1}{n-q \ q \ -n} \binom{2 \quad 1 \ 1}{n-p \ p \ -n} 4 \, k_{p,q}^{DD}(\omega_I) \tag{32}$$

where the separate reduced spectral densities are given by eqn. (33). The reduced spectral density represents an effec-

$$k_{p,q}^{DD}(\omega_I) = \int_0^\infty \langle 0|(2,n-p|(1,p|e^{i\tau L_L}|1,q)|2,n-q)|0\rangle e^{i\omega_I\tau} d\tau \tag{33}$$

tive dipole–dipole correlation time normalized against the reorientational correlation time. Thus, when $K(\omega) = 1$ there is an effective dipole–dipole correlation time equal to τ_R. In the following we focus on the dipole–dipole contribution to T_{1M} and leave out the spectral density $K_{0,0}$, which is equal to 1 over the whole parameter space, and the scalar contribution, which is small.[11]

The set of parameters that determine the reduced spectral densities $k_{p,q}(\omega)$ is quite large. The ZFS interaction parameters of eqn. (20) that are given in square brackets $[\Delta_0, \Delta_1]$ refer to the static and the linear transient ZFS interaction, respectively. The Smoluchowsky distortion dynamics has a characteristic correlation time τ_S, and the tumbling of the whole paramagnetic ion–macromolecule complex is characterized by the correlation time τ_R. The correlation times are given in curly brackets, $\{\tau_R, \tau_S\}$. It should be noted that no explicit characterizations of the electron spin relaxation rates in terms of electron spin relaxation times enter the parameter space.

Figs. 1(A) and 1(B) show the variation of the reduced spectral densities $k_{p,q}$ with the dimensionless variable $\log(\omega_S\tau_R)$. The dotted lines representing the cross-spectral
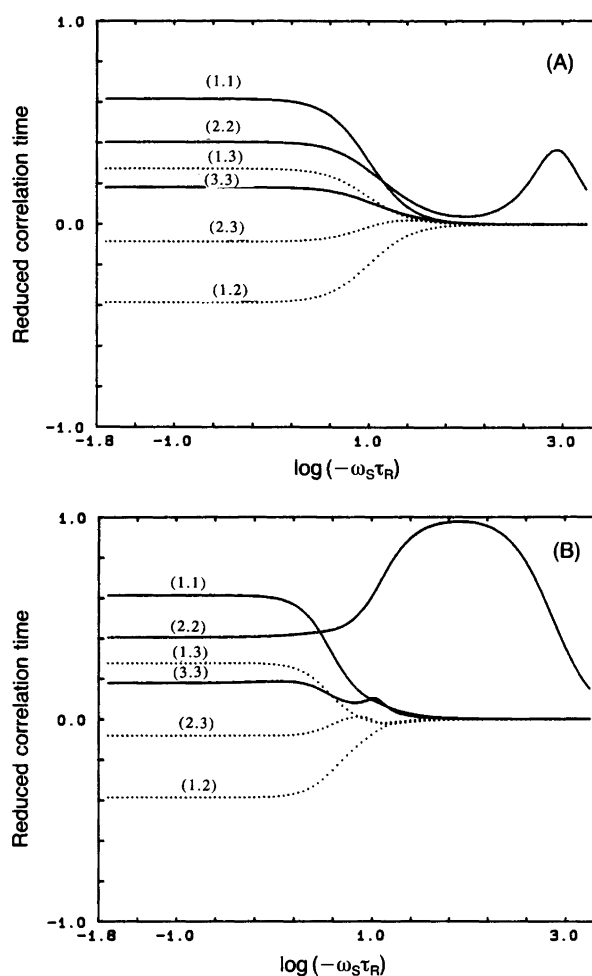

Fig. 1. $k_{p,q}^{DD}(\omega_I)$ given for the Smoluchowsky distortion model (A) [0.0, 10], {100, 1.0} and for the static ZFS model (B) with [0.5, 0.0] {100, 1.0}.

densities are denoted by the set of indices (α,β) $(\alpha = p+2,$ $\beta = q+2,$ $p,q = -1,0,1)$, and the solid lines represent the diagonal spectral densities (α,α). If we multiply the low-field values by the corresponding weight factor of eqn. (32) they add upp to 1. The low-field behaviour of the Smoluchowsky distortion model [Fig. 1(A)] is exactly the same as for the static ZFS model [Fig. 1(B)]. Only the (2.2) diagonal spectral density changes when the stochastic fluctuation of the ZFS interaction amplitude is introduced. This term $k_{0,0}$ reduces to $\tau_{1S}/(\tau_{1S}+\tau_R)$ in the SBM approximation and strong narrowing condition. Fig. 1 reveals the importance of cross-correlation times of the dipole–dipole coupling in the low-field region.

In Figs. 2(A) and 2(B) the dispersion curves for a set of increasing static ZFS interaction values are shown. This case represents a set of rigid low-symmetry complexes. In Fig. 2(A) the x-axis shows the range of $\log(\omega_S\tau_R)$ values, and in Fig. 2(B) the analogous Solomon–Bloembergen–Morgan curve shows the range of the corresponding static magnetic field ($\tau_R = 100$ ps). The first dispersion is due to $\omega_S\tau_R > 1$, but is modified to appear at higher fields as the
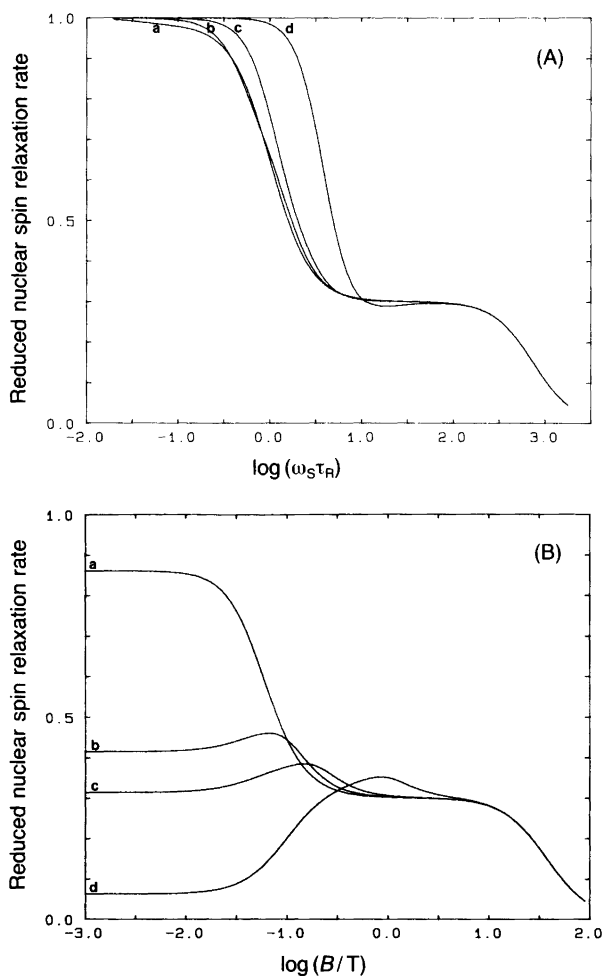
Fig. 2. (A) The dispersion curves $K_1 -_1(\omega)$ for a set of static ZFS interaction strengths. The parameter space is defined as $\{\tau_R, \tau_S\}$ (ps) and $[\Delta_0, \Delta_1]$ (cm^{-1}). $\{100,1.0\}$ (a) [0.001,0.0], (b) [0.05,0.0], (c) [0.1,0.0], (d) [0.5,0.0]. The dispersion curves in (B) correspond to the Bloembergen–Morgan approach.

ZFS interaction increases owing to the modification of the electron spin energy levels. In Figs. 3(A) and 3(B) the effect of the transient ZFS interaction strength is shown, thus representing flexible complexes. Notice that the low-field region is not modified compared to Fig. 1(A), but only the high-field region. The SBM curves (B-curves) show a qualitatively different behaviour. The low-field region is considerably lower in these cases, indicating a more effective averaging of the nuclear spin – electron spin dipole–dipole interaction owing to electron spin relaxation. The striking features of the Smoluchowsky distortion model are the high low-field values, corresponding to an effective dipole–dipole correlation time equal to τ_R. In Fig. 4 the dispersion curves are shown for the case of both a static and a transient ZFS interaction. The transient ZFS interaction is held constant at 4 cm^{-1}, and the static ZFS interaction is increased from 1 to 2 cm^{-1}, which may be expected for an increasing distortion of the paramagnetic complex. The high-field and low-field regions are not sensitive to the

changes; only the SBM $\omega_S \tau_R = 1$ dispersion is transferred to higher fields. How can this behaviour be rationalized? When the electron spin is fixed in the ZFS frame, no averaging of the nuclear spin – electron spin dipole–dipole interaction on a timescale faster than the molecular reorientation is present. In most experimental investigations, as shown in Fig. 5 (taken from Ref. 19), the low-field region indicates a fast averaging of the dipole–dipole interaction.[15,20] The dispersion curve then shows a constant region at low field [$K(\omega) \ll 1$] and an increase of the effective dipole–dipole correlation time [$K(\omega) \to 1.0$] at higher field. The model presented is essentially determined by eqns. (18) and (19). However, with small modifications some of the restrictions may be lifted, and in Table 1 we have summarized the changes.

First, we assumed that the principal frames of the ZFS interaction and the diffusion tensor coincide. This restriction is lifted in Fig. 6 and was further discussed in showing that the smallest value in the low-field region is 0.25.[15] When the Zeeman energy becomes comparable with the ZFS interaction, the electron spin relaxation introduces an
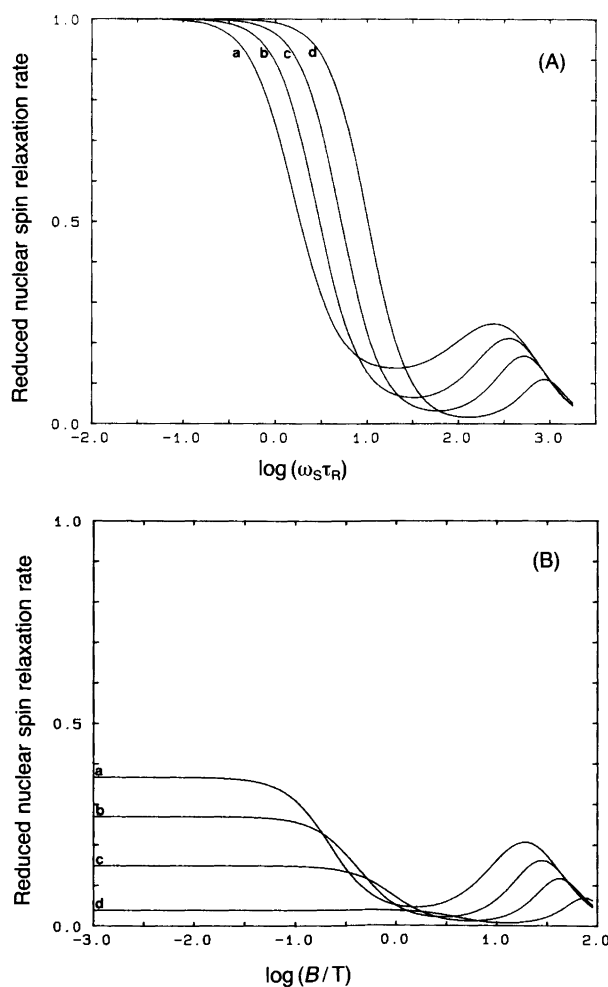

Fig. 3. The dispersion curves $K_{1,-1}(\omega)$ for a set of transient ZFS interactions with $\{100,1.0\}$ (a) [0.0, 1.0], (b) [0.0, 2.0], (c) [0.0,4.0], (d) [0.0,10.0].
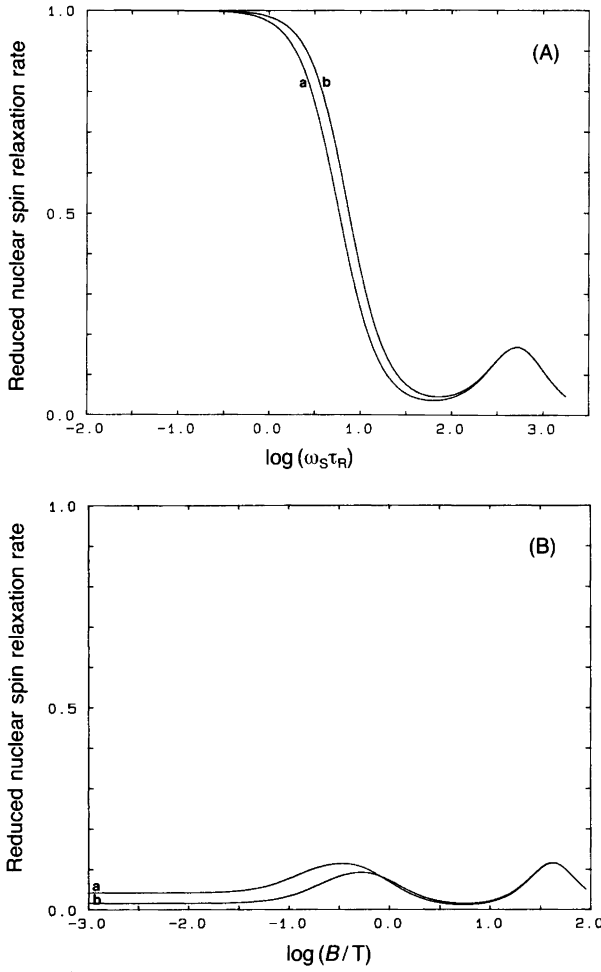
Fig. 4. The dispersion curves $K_{1,-1}(\omega)$ defined by the parameters (100,1.0) (a) [1.0,4.0] and (b) [2.0,4.0] for the low-symmetry Smoluchowsky model (A) and the analogous Bloembergen–Morgan model (B).
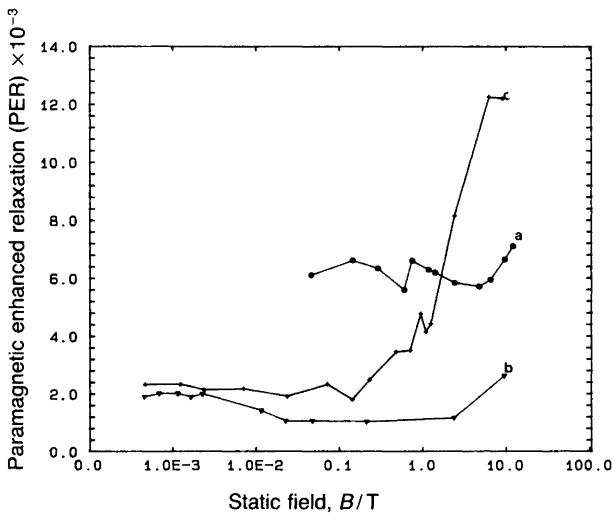
Table 1. Modifications of eqns. (17) and (18).

$D^2_{0,m}[\Omega_{PM}(t)] = d^2_{0,0}[\beta_{PM}(t)] = S$		Figs. 1–4
$D^2_{0,m}[\Omega_{PM}(t)] = D^2_{0,m}(0,90,0)$		Fig. 5
$D^2_{0,m}[\Omega_{PM}(t)] = 1$ and $a^{2(P)}_0 = 0$, $a^{2(P)}_{[2]} \neq 0$.		Fig. 6
$D^2_{0,m}[\Omega_{PM}(t)] = 1$ and $a^{2(P)}_0 \neq 0$, $\eta \neq 0$		Fig. 7

averaging of the dipole–dipole coupling, and for higher Zeeman interactions the electron spin motion slow down, which is manifested by an increase in $K(\omega)$. Secondly, we assumed a cylindrical symmetry of the ZFS interaction; this restriction is lifted in Fig. 7. However, the main characteristics of the low-field limit still remain unchanged. In the low-field limit we can rewrite the dipole–dipole correlation function according to eqn. (34), where the electron spin

$$G^{DD}(t) = \sum_{m'} \sum_{m} \text{tr}_L \{S^1_m D^2_{0,n-q}(\Omega_R)D^1_{n,q}[\Omega_{LP}(t)]$$

$$\times e^{i\tau^{L_L}} S^1_{m'} D^2_{0,n-p}(\Omega)D^1_{m',p}(\Omega)\} \qquad (34)$$

operators are now taken in the principal frame of the ZFS interaction. The Liouville lattice operator is given by eqn. (35).

$$L_L = L_{ZFS} + L_{Zeeman}(t) - i\Gamma_R - i\Gamma_{PR} \qquad (35)$$

Here we have added a Markov operator describing the motion of the principal frame of the ZFS relative to the laboratory frame. Now, ignoring the Zeeman term, we can separate the correlation function into two correlation functions representing the overall motion of the complex and the independent motion of the principal frame of the ZFS [eqn. (36)].

Static field, B/T

Fig. 5. The experimental complex–ligand proton PER of the complexes (a) Ni($H_2O)_6^{2+}$, (b) Ni($dpm)_2D_5NH_2)_2^{2+}$ and (c) Ni(R,S,R,S)1,2,8,11-tetramethyl-1,2,8,11-tetraazacyclotetra-decane)–($H_2O)^{2+}$(from Ref. 19).
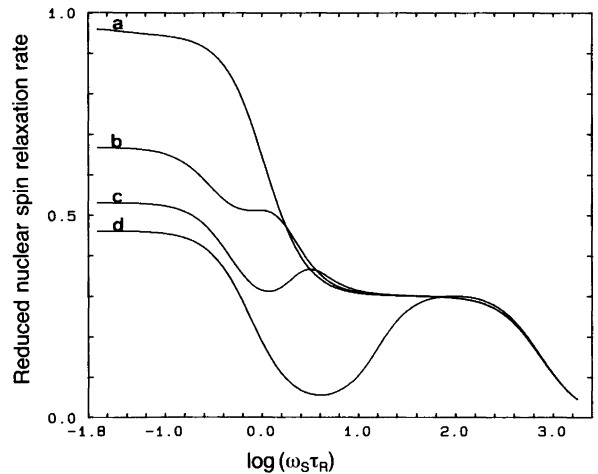

Fig. 6. The dispersion curves $K_{1,-1}(\omega)$ for a set of static ZFS interaction strengths where the tilt angle between the principal frame of the ZFS interaction and the reorientational diffusion frame is 90°. The parameter space is defined as $\{\tau_R,\tau_S\}$ (ps) and $[\Delta_0,\Delta_1]$ (cm^{-1}). $\{100,1.0\}$ (a) [0.001,0.0], (b) [0.05,0.0], (c) [0.1,0.0], (d) [0.5,0.0].
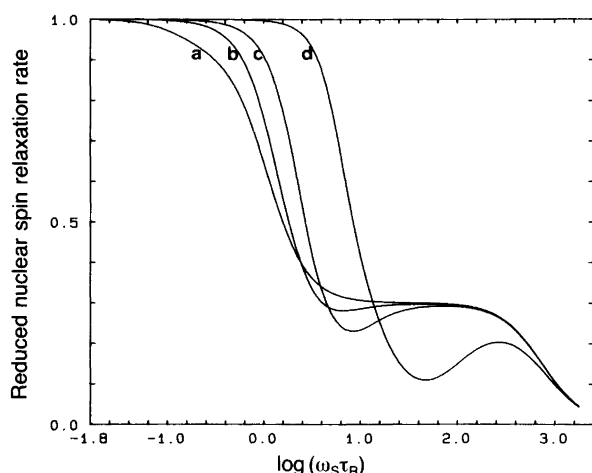
Fig. 7. The dispersion curves $K_{1,-1}(\omega)$ for a set of static ZFS interaction strengths with a noncylindrical ZFS hamiltonian. The parameter space is defined as $\{\tau_R,\tau_S\}$ $\{100,1.0\}$ (ps) and $[\Delta_0,\Delta_1]$ (cm^{-1}). (a) [0.001,0.0], (b) [0.05,0.0], (c) [0.1,0.0], (d) [0.5,0.0].

$$G^{DD}(t) = \frac{1}{15} e^{-(\tau_R^{-1}+\tau_{PR}^{-1})t} \sum_m \text{tr}_S \{S_m^{1\,\dagger} e^{iL_{ZFS}t} S_m^1 \sigma_S\} \tag{36}$$

However, assuming isotropic pseudorotation for the motion of the principal frame ignores the fact that the complex is of low symmetry, which should be reflected in the motion of the principal frame. Qualitatively, the argument is illustrative, and it gives a smallest value of the spectral density K in the low-field region. The spectral density results in the effective correlation time τ_{eff} and a low-field value τ_{eff}^{DD}/τ_R, where τ_{eff}^{DD} is given by eqn. (37). Assuming a

$$\tau_{eff}^{DD} = (\tau_R^{-1} + \tau_{PR}^{-1})^{-1} \tag{37}$$

pseudorotation of the ZFS interaction characterized by a correlation time of 10 ps, the low-field value is larger than 0.1.

Conclusions

The Smoluchowsky distortion model, together with the reorientational motion, forms a model describing PER effects in low-symmetry complexes. In this paper it is shown that the low-field regions of the NMRD curves are greatly affected by cross-dipole spectral densities and that they are also very sensitive to the orientational motion of the principal frame of the ZFS interaction relative to the r_{IS}-vector, a motion not present in the Smoluchowsky model. An appropriate model describing the low-field region in heterogeneous systems and for low-symmetry complexes seems to need restricted pseudorotation dynamics for the ZFS interaction in order to allow for a partial averaging of the dipole–dipole coupling in the low-field region. The Bloembergen–Morgan theory is not applicable to low-symmetry

complexes. However, experimental results may be interpreted as if the motion of the principal frame of the ZFS interaction is not strongly related to the symmetry of the complex. Thus the ZFS principal frame is allowed to undergo pseudoreorientation in some restrictive sense which yields a partial averaging of the dipole–dipole coupling but still reflects the low symmetry of the complex. The reorientational motion of the complex modulating the rest of the partially averaged ZFS interaction introduces minor changes to the NMRD profile. If so, it may explain the qualitatively correct prediction of the NMRD curves derived from the SBM theory. However, the problem merits further investigations in order to obtain a satisfactory theory to describe the experimental NMRD curves of low-symmetry complexes showing the characteristic constant and low values[19,20] at low static fields.

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