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Relaxation theory of the electronic spin of a complexed paramagnetic metal ion in solution beyond the Redfield limit

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The relaxation of the electronic spin S of a paramagnetic metal ion with fully quenched orbital angular momentum in its ground state is investigated in an external magnetic field through a systematic study of the time correlation functions governing the evolution of the statistical operator (density matrix). Let ω_0 be the Larmor angular frequency of S. When the relaxation is induced by a time-fluctuating perturbing Hamiltonian $\hbar H_1(t)$ of time correlation τ_c, it is demonstrated that after a transient period the standard Redfield approximation is relevant to calculate the evolution of the populations of the spin states if $\|H_1\|^2 \tau_c^2 / (1 + \omega_0^2 \tau_c^2) \ll 1$ and that this transient period becomes shorter than τ_c at sufficiently high field for a zero-field splitting perturbing Hamiltonian. This property, proven analytically and confirmed by numerical simulation, explains the surprising success of several simple expressions of the longitudinal electronic relaxation rate $1/T_{1e}$ derived from the Redfield approximation well beyond its expected validity range $\|H_1\| \tau_c \ll 1$. It has favorable practical consequences on the interpretation of the paramagnetic relaxation enhancement of nuclei used for structural and dynamic studies. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2730831]

I. INTRODUCTION

Consider the electronic spin S of a molecule or ion having unpaired electrons and submitted to an external magnetic field $\mathbf{B}_0$ along the z axis in the laboratory (L) frame. The Hamiltonian $\hbar H(t)$ of the spin S is the sum of the Zeeman term $\hbar H_0 = g_S \mu_B B_0 S_z = \hbar \omega_0 S_z$ and of a time-fluctuating perturbing Hamiltonian $\hbar H_1^{(L)}(t)$ reflecting the structure of the species and its molecular motion.[1–29] The time fluctuations of $H_1^{(L)}(t)$ give rise to longitudinal and transverse electronic spin relaxations. In particular, the transverse relaxation is responsible for the broadening of the lines of the electron spin resonance (ESR) spectrum.[4,13,15–17,20–22,26] The width of a Lorentzian line is proportional to the transverse electronic relaxation rate $1/T_{2e}$. It is measurable if it is not too broad; i.e., for a sufficiently long transverse electronic relaxation time $T_{2e} > 10^{-10}$ s. To describe the evolution of a spin system the Redfield approximation of the statistical operator (density matrix) by a second-order expansion of the time-dependent perturbing Hamiltonian was a milestone[1] in the development of general and accurate relaxation theories. It was successfully applied to the interpretation of ESR spectra of free radicals[4,13,16] and low molecular weight Mn(II) and Gd(III) complexes in nonviscous solvents by using more and more realistic models of Hamiltonians and molecular motions.[15,17,20–22,26] Despite the rather limited number of situations where the electronic spins of paramagnetic solutes can be directly observed by ESR, the effects of these spins

are very important in NMR since they are a striking source of enhancement of the relaxation rates of the neighboring nuclei.[2,5–12,17–19,23] This enhancement is at the origin of two important applications: (i) the structural characterization of complexes of paramagnetic metals with small ligands or biomolecules through the relaxometric evaluation of the distances of the nuclei from the metal[8] and (ii) the use in magnetic resonance imaging[10–12] (MRI) of paramagnetic species as relaxation contrast agents to accelerate the relaxation rate of the neighboring protons, which improves the image contrast. Bloembergen and Morgan recognized early[2] that the paramagnetic relaxation enhancement (PRE) of a nuclear relaxation rate is often dramatically reduced by the relaxation of the electronic spin. Thus, a correct theoretical description of electronic spin relaxation is necessary for a sound interpretation of the PREs in terms of structural and dynamic molecular parameters. Here, we consider complexed paramagnetic metal ions M with fully quenched orbital angular momenta in their ground states such as[3] Ni(II) ($S=1$), Cr(III) ($S=3/2$), Mn(II) and Fe(III) ($S=5/2$), and Gd(III) ($S=7/2$). The perturbing Hamiltonian $\hbar H_1^{(L)}(t)$ is the zero-field-splitting (ZFS) Hamiltonian $\hbar H_{ZFS}^{(L)}(t)$, which can be conveniently expressed[20–23] as the sum $\hbar H_{ZFS}^{(L)}(t) = \hbar H_{ZFS,S}^{(L)}(t) + \hbar H_{ZFS,T}^{(L)}(t)$ of its static (S) and transient (T) parts $\hbar H_{ZFS,S}^{(L)}(t)$ and $\hbar H_{ZFS,T}^{(L)}(t)$. The static part is modulated by the Brownian rotation of the complex of rotational diffusion coefficient D^r and has a typical rotational correlation time value $\tau_2 \equiv 1/(6D^r) \geq 50$ ps. The transient part fluctuates because of the vibrations and distorsions of the complex and/or

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the pseudorotations[24] of the coordination polyhedron, with a vibrational (v) correlation time τ_v of the order of a few picoseconds. It is usually assumed that the Redfield approximation is applicable if the Redfield-limit inequalities[1,5–9] $|H_{ZFS,S}^{(L)}|\tau_2 \ll 1$ and $|H_{ZFS,T}^{(L)}|\tau_v \ll 1$ hold. These inequalities become particularly questionable either for slowly rotating complexes of long τ_2 or for paramagnetic metals, which can have large ZFS values $\cong 1$ cm^{-1}, such as[9] Ni(II), Cr(III), and Mo(III). Since the 1980s, considerable theoretical efforts have been made to properly describe the electronic relaxation and/or its effects on the PREs of nuclei beyond the so-called Redfield limit, i.e., outside the expected validity domain of the Redfield approximation. The Swedish school[5,6,25] has developed a stochastic superoperator Liouville approach based on the eigenfunction expansion of the propagator describing the molecular motion. Alternatively, several groups have proposed to simulate the suitable time correlation functions (TCFs) involving the components S_α ($\alpha=x,y,z$) of the electronic spin S by computing the time evolution of the electronic spin quantum states submitted to the random time-dependent total Hamiltonian.[16,18,19,22–24,26] In many cases, severe discrepancies were found between the rigorous values and the Redfield-limit predictions. Moreover, for a nuclear spin I located on the paramagnetic metal complex, it was shown that the often implicitly assumed[10–12] so-called decomposition approximation[27] fails; i.e., at low and intermediate field values a strong statistical correlation is observed[6,28] between the dynamics of the electronic spin quantum states induced by a static ZFS Hamiltonian and the motion of the I-S interspin vector $\mathbf{r}_{IS}$ responsible for the spatial dependence of the dipolar interaction. Clearly, rigorous but much more complicated methods seem necessary beyond the Redfield limit.

However, Monte Carlo simulations have shown that the simulated longitudinal TCF $G_\parallel(t) \equiv \langle S_z(t)S_z(0)\rangle$ displays a very simple monoexponential decay[23,29] in $\exp(-t/T_{1e})$ as predicted by the McLachlan expression derived from the Redfield formalism, far beyond its expected validity range. In general, for $S>1$, the normalized longitudinal TCF $G_\parallel^{nor}(t) \equiv G_\parallel(t)/G_\parallel(0)$ calculated within the Redfield theory is a weighted sum $G_\parallel^{nor}(t) = \sum_i w_i \exp(-t/T_{1e}^{(i)})$ of decreasing exponentials.[13,14,20] Introducing the McLachlan relaxation rate[13] $1/T_{1e}^{McLachlan} \equiv \sum_i w_i 1/T_{1e}^{(i)}$, the McLachlan approximation of $G_\parallel^{nor}(t)$ is defined as $\exp(-t/T_{1e}^{McLachlan})$, which has the same short-time decay $1-t/T_{1e}^{McLachlan}$ as the Redfield weighted sum. For instance, consider a second-order static or transient ZFS $\hbar H_{ZFS}$ of the form $H_{ZFS}^{(M)} = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$ in the molecular (M) frame of the complex and assume that it fluctuates with a correlation time τ_c in the (L) frame. Let $\Delta \equiv \sqrt{2D^2/3 + 2E^2}$ (rad s^{-1}) be the ZFS amplitude. The simulated longitudinal relaxation rate was found to be accurately given by the popular[9–12] McLachlan expression[2,13]

$$\frac{1}{T_{1c}^{McLachlan}} = \frac{1}{25}[4S(S+1)-3]\Delta^2\tau_c\left[\frac{1}{1+\omega_0^2\tau_c^2} + \frac{4}{1+4\omega_0^2\tau_c^2}\right]$$

$$= \frac{1}{2}\sum_{M,M_0} w_{MM_0}(E_M - E_{M_0})^2 \bigg/ \sum_{M_0} E_{M_0}^2, \qquad (1)$$

where E_M ($-S \leqslant M \leqslant S$) are the Zeeman energy levels and

w_{MM_0} are the transition probabilities per second of the spin system from the state $|M_0\rangle$ to the state $|M\rangle$. Because of its simplicity, this expression was extensively discussed and/or used by several authors, even in situations lacking of theoretical justification. Indeed, Bloembergen and Morgan[2] pointed out that it rests on the assumption of a spin temperature; namely, "if thermodynamic equilibrium is assumed at all times within the spin system one has only one single (longitudinal) relaxation time T_{1e}," but they emphasized that this assumption is "clearly not valid in the present case since it supposes an infinitely short transverse relaxation time." Nevertheless, they derived Eq. (1) from the concept of spin temperature and the Van Vleck formalism as proposed by Hebel and Slichter in the context of nuclear relaxation in conducting metals.[30] At this level of the discussion it should be pointed out that the McLachlan approximation of $G_\parallel^{nor}(t)$ is surprisingly very accurate for[14,29] $S=5/2$ and $7/2$ when the Redfield theory applies. Besides, in the formally analogous case of the quadrupolar relaxation of a nuclear spin $I>1$, Halle and Wennerström[31] showed that the longitudinal and transverse relaxation functions are both given by their McLachlan approximations even in nonextreme narrowing conditions, provided that the spectral density of the electric-field gradient fluctuations is weakly frequency dependent. In the present work dealing with electronic spins in a high field, the spectral densities of the fluctuating ZFS Hamiltonian depend strongly on the Larmor frequency, and the situation is opposite.

The present theoretical work was aimed to investigate to what extent Eq. (1) and the several simple expressions of the longitudinal electronic relaxation rate derived previously[23,29] are valid for various paramagnetic metal ions. Thus, simple field-dependent criteria for applying the longitudinal relaxation equations of the Redfield limit beyond their expected validity range will be proposed. Indeed, besides its effects on the efficiency of a MRI contrast agent,[10–12] the longitudinal electronic relaxation time has become an interesting source of information about a metal complex since (i) it is directly measurable by ESR techniques at the X band[32] when it is longer than a few nanoseconds, and (ii) it can be derived at various other field values from outer-sphere (OS) PRE measurements by using the simple and universal time decay in $t^{-3/2}$ of the dipolar intermolecular TCF.[33] Furthermore, at high field, the popular Solomon, Bloembergen, and Morgan (SBM) expression[2,8–12] of the intramolecular PRE accounts for the electronic relaxation through an effective correlation time τ_{c1} involving the rotational correlation time τ_2 and the McLachlan electronic relaxation time of Eq. (1) derived within the Redfield limit. The possibility of extending the validity of the SBM theory beyond the Redfield limit will be examined since this extension would considerably simplify the structural characterization of a paramagnetic metal complex by intramolecular PRE studies. Finally, ESR has been impressively developed during the last decade towards the high-frequency domain[34] enabling the accurate determination of the ZFS of large amplitudes ($D \geqslant 1$ cm^{-1}) of many transition metal ions. This new information also calls for an electron spin relaxation theory beyond the Redfield limit.

The paper is organized as follows: Sec. II is devoted to

the theory of the electronic spin relaxation of a complexed metal ion in the presence of a large "static" ZFS Hamiltonian of second order beyond the Redfield approximation. The evolution of the statistical operator (density matrix) is expressed in terms of the TCFs of spherical tensor operators. This section also incorporates selected known results in order to provide a complete theoretical framework suitable for deriving the time decay of the TCFs and interpreting their simulated values. Such an interpretation is carried out in Sec. III where "exact" representative TCFs are obtained by simulating the time evolution of the quantum states of the electronic spin due to the Brownian rotational dynamics of the metal complex. The extension of the theory to other fluctuating Hamiltonians $\hbar H_1(t)$, its validity domain, and its practical applications to the paramagnetic relaxation enhancement of nuclei are discussed in Sec. IV.

II. RELAXATION THEORY BEYOND THE REDFIELD LIMIT

Consider a representative ensemble of N_{sys} random realizations (systems) j of the metal complex submitted to a spin Hamiltonian $\hbar H_j(t)$. The unitary operator $U_j(t)$, which governs the time dependence of the quantum states of the electronic spin S, is the solution of the Schrödinger equation[35]

$$i\frac{dU_j(t)}{dt} = H_j(t)U_j(t),\qquad(2)$$

with the initial condition $U_j(0)=1$. The TCF $G_\parallel(t)$ $\equiv\langle S_z(t)S_z(0)\rangle$ is proportional to the average of the traces of the operators $U_j(t)^\dagger S_z U_j(t)S_z$ calculated over the N_{sys} realizations. In order to understand to what extent the function $G_\parallel(t)$ can be derived from the system of the Redfield longitudinal relaxation equations, we will study the evolution of the statistical operator (density matrix) of the electronic spin submitted to a large static (S) second-order ZFS Hamiltonian $H_{ZFS,j}^{(L)}(t)$, which fluctuates because of the Brownian rotation of the complex. The index S is omitted in the notation $H_{ZFS,j}^{(L)}(t)$ for simplification. In the laboratory (L) frame the spin Hamiltonian of the realization j is

$$H_j(t) = H_0 + H_{ZFS,j}^{(L)}(t).\qquad(3)$$

Introducing the components T_2^q of the usual Racah spherical tensor operator[36] of rank 2 as $T_2^0 \equiv \sqrt{3/2}[S_z^2 - S(S+1)/3]$, $T_2^{\pm1} \equiv \mp(1/2)(S_zS_\pm + S_\pm S_z)$, and $T_2^{\pm2} \equiv S_\pm^2/2$, the static (S) ZFS Hamiltonian in a suitable (M) frame can be written as

$$H_{ZFS}^{(M)} = \sum_{q=-2}^{2} C_2^q T_2^q,\qquad(4)$$

where the coefficients C_2^q are $C_2^0 = \sqrt{2/3}D_S$, $C_2^{\pm1}=0$, and $C_2^{\pm2} = E_S$. Let R_t be the rotation transforming the (L) frame into the chosen molecular (M) frame at time t. In the (L) frame, the ZFS Hamiltonian of a realization j of the spin system is of the form[35]

$$H_{ZFS}^{(L)}(t) = \sum_{q=-2}^{2} x_q(t)T_2^q \quad \text{with } x_q(t) \equiv \sum_{q'=-2}^{2} D_{qq'}^2(R_t)C_2^{q'},$$
$$(5)$$

with the quantities $D_{qq'}^2(R_t)$ being the elements of the Wigner matrix $D_2(R_t)$ associated with the rotation R_t. In Eq. (5) the index j is omitted to simplify the notation. Let $\tau_2 = \tau_c$ be the rotational correlation time of the metal complex. The values of τ_2 and of the magnitude $\Delta_S \equiv \sqrt{2D_S^2/3 + 2E_S^2}$ of H_{ZFS} can have arbitrary values, even such as $\Delta_S\tau_2 \gg 1$, so that the Redfield approximation is not justified.

Let $\sigma(0)$ be the statistical operator describing the properties of the spin S at initial time $t=0$. At time t the statistical operator $\sigma(t)$ is given by the evolution operator E of an ensemble of subensembles,[6,37] where each subensemble is defined as a large number of metal complexes submitted to the same time-dependent total Hamiltonian. Thus, $\sigma(t)$ depends on $\sigma(0)$ as[35]

$$\sigma(t) \equiv E[\sigma(0)] = \frac{1}{N_{sys}}\sum_{j=1}^{N_{sys}} U_j(t)\sigma(0)U_j(t)^\dagger.\qquad(6)$$

In practical computations the number N_{sys} of independent complexes is taken in the range of 2000–5000. The time evolution of $\sigma(t)$ can be expressed in terms of a set of TCFs, which generalize the longitudinal TCF $G_\parallel(t)$ and are derived from the normalized components t_k^q of the Racah spherical tensors defined as follows. Taking the z axis of the (L) frame to be along the magnetic field $\mathbf{B}_0$, the operators t_k^q ($0 \le k \le 2S, -k \le q \le k$) are defined on the basis of the eigenstates $|M\rangle$ ($\equiv|SM\rangle$) of the spin S with the help of the $3j$ coefficients[35] as

$$\langle SM'|t_k^q|SM\rangle = (-1)^{S-M'}\sqrt{2k+1}\begin{pmatrix} S & k & S \\ -M' & q & M \end{pmatrix}.\qquad(7)$$

The subset of $2k+1$ operators t_k^q ($-k \le q \le k$) are the components of a spherical tensor of order k. The $(2S+1)^2$ operators t_k^q, which are orthonormal for the Hermitian product $\mathrm{tr}(A^\dagger B)$ of two operators A and B, i.e., $\mathrm{tr}(t_k^{q\dagger}t_{k'}^{q'}) = \delta_{kk'}\delta_{qq'}$, form an orthonormal basis of the space of the spin operators of dimension $(2S+1)^2$. The norm of an operator A is $\|A\| \equiv [\mathrm{tr}(A^\dagger A)]^{1/2}$. The usual tensor components[36] T_k^q used in Eq. (4) and the reduced matrix element $\langle S\|T_k\|S\rangle$ given by Eq. (26) of Ref. 20 are related to the tensors t_k^q by

$$T_k^q = \sqrt{A_k(S)}t_k^q$$

with $A_k(S) \equiv \langle S\|T_k\|S\rangle^2/(2k+1)$

$$= (k!)^2\frac{(2S+k+1)!}{2^k(2k+1)!(2S-k)!}.\qquad(8)$$

Because the t_k^q form an orthonormal basis for the spin operators, $\sigma(t)$ can be expanded as

$$\sigma(t) = \sum_{k=0}^{2S} \sum_{q=-k}^{k} \sigma_k^q(t) t_k^q \quad \text{with } \sigma_k^q(t) = \text{tr}[t_k^{q\dagger}\sigma(t)]. \quad (9)$$

Replacing $\sigma(t)$ by its expression (6), the coefficients $\sigma_k^q(t)$ defined in Eq.(9) become

$$\sigma_k^q(t) = \text{tr}\left[t_k^{q\dagger} \frac{1}{N_{\text{sys}}} \sum_{j=1}^{N_{\text{sys}}} U_j(t)\sigma(0)U_j(t)^\dagger \right]. \quad (10)$$

Replacing $\sigma(0)$ by its expansion (9) at $t=0$, we get

$$\sigma_k^q(t) = \sum_{k',q'} g_{kk'}^{qq'}(t)\sigma_{k'}^{q'}(0), \quad (11)$$

where the TCFs $g_{kk'}^{qq'}(t)$ are defined as

$$g_{kk'}^{qq'}(t) \equiv \frac{1}{N_{\text{sys}}} \sum_{k=1}^{N_{\text{sys}}} \text{tr}[t_k^{q\dagger} U_j(t) t_{k'}^{q'} U_j(t)^\dagger]. \quad (12)$$

These TCFs are normalized in the sense that their values at $t=0$ are

$$g_{kk'}^{qq'} = \delta_{kk'}\delta_{qq'} \quad (13)$$

because of the orthonormality of the spherical tensors t_k^q. They also verify the general symmetry property

$$g_{kk'}^{-q,-q'}(t) = (-)^{q+q'} g_{kk'}^{qq'}(t)^*. \quad (14)$$

The previously defined TCFs $G_\parallel(t) \equiv \langle S_z(t)S_z\rangle$ and $G_\perp(t) \equiv \langle S_+(t)S_-\rangle$ are involved in the OS PRE of nuclei.[23,33] The theoretical electron paramagnetic resonance (EPR) spectrum is obtained[3,15,20,21] from the transverse TCF $G_\perp(t)$. The normalized forms of these TCFs are readily expressed in terms of the $g_{kk'}^{qq'}(t)$ as

$$G_\parallel^{\text{nor}}(t) \equiv G_\parallel(t)/G_\parallel(0) = g_{11}^{00}(t)$$

$$\text{and } G_\perp^{\text{nor}}(t) \equiv G_\perp(t)/G_\perp(0) = g_{11}^{11}(t)^*. \quad (15)$$

The applicability of the Redfield longitudinal relaxation equations to the calculation of $G_\parallel(t)$ rests on three properties PA, PB, and PC, stated hereafter and demonstrated in Appendixes A, B, SA, SB, and SC of the Supplementary Material.[38] Property PA states simplifying symmetry properties of the TCFs which result from the invariance of the whole statistical ensemble of the N_{sys} realizations of the system under the rotations R of a subgroup G of the full rotation group $O(3)$. Property PB rests on property PA and states that the populations $\sigma_{MM}(t)$ of the states $|M\rangle$ can be obtained by solving the usual master equation under precise conditions of time and field. Property C reminds that this master equation is identical to the Redfield master equation though the two equations are obtained from different time-dependent perturbation approximations.

Property PA. In the presence of an external field $\mathbf{B}_0 \neq 0$, because of the rotational invariance of the spin system about the $\mathbf{B}_0$ direction z, the only nonvanishing TCFs are for $q=q'$, i.e.,

$$g_{kk'}^{qq'}(t) = g_{kk'}^{qq}(t)\delta_{qq'} \quad (16)$$

When $\mathbf{B}_0$ vanishes, the TCFs further simplify because the system remains invariant under the full rotation group. (i) They are different from zero, only for $k=k'$ and $q=q'$, and (ii) they are independent of the index q. More precisely, they verify the equalities $g_{kk'}^{qq'}(t) = g_{kk}^{00}(t)\delta_{kk'}\delta_{qq'}$. As shown in Appendixes A and SA (Ref. 38), these symmetry relations result from the following evolution property of the statistical operator $\sigma(t)$ defined by Eq. (6): Assume that the whole statistical ensemble of the N_{sys} realizations of the system is globally invariant under a rotation R of associated quantum rotation matrix[35] $\mathbf{R}$. Let $\hat{R}(\xi) = \mathbf{R}\xi\mathbf{R}^\dagger$ be the rotation of an operator ξ. Then, the transformation of $\sigma(t)$ under $\hat{R}$ at time t is simply given by the evolution of the transformation of $\sigma(0)$ under the same rotation; namely, the following commutation property holds: $\hat{R}E[\sigma(0)] = E\hat{R}[\sigma(0)]$.

In order to introduce property PB the statistical operator $\sigma(t)$ is expanded in the orthonormal basis of the $(2S+1)^2$ operators $|M'\rangle\langle M|$ as

$$\sigma(t) = \sum_{M,M'} \sigma_{M'M}(t)|M'\rangle\langle M|, \quad (17)$$

where the coefficients

$$\sigma_{M'M}(t) \equiv \text{tr}[(|M'\rangle\langle M|)^\dagger\sigma(t)] = \langle M'|\sigma(t)|M\rangle \quad (18)$$

of the expansion of $\sigma(t)$ are simply its matrix elements in the basis $|M\rangle$. Now, substituting the expansion (17) for $\sigma(t)$ in the definition (9) of $\sigma_k^q(t)$, we have

$$\sigma_k^q(t) = \sum_{\substack{M,M' \\ M'-M=q}} (-1)^{S-M'}\sqrt{2k+1}\begin{pmatrix} S & k & S \\ -M' & q & M \end{pmatrix}\sigma_{M'M}(t). \quad (19)$$

According to the orthogonality properties[35] of the $3j$ symbols, this system of linear equations can be inverted and the coefficients $\sigma_{MM'}(t)$ are easily seen to be the linear combinations

$$\sigma_{M'M}(t) = \sum_{k=|q|}^{2S} (-1)^{S-M'}\sqrt{2k+1}\begin{pmatrix} S & k & S \\ -M' & q & M \end{pmatrix}\sigma_k^q(t) \quad (20)$$

of the $2S+1-|q|$ coefficients $\sigma_k^q(t)$ with $q=M'-M$. The matrix $\sigma_{M'M}(t)$ can be decomposed into bands indexed by q, defined by $M'-M=q$, and parallel to the main diagonal of the matrix. The consequence of Eqs. (20), (11), (16), and (19) is that the elements $\sigma_{M'M}(t)$ of a band of index q at time t depend only on their values at time $t=0$. In other words, the elements of different bands have independent evolutions. It should be noted that this property, which is also a consequence of the secular approximation[37] of the Redfield master equation, has been derived from the global rotational invariance of the time-dependent total Hamiltonians acting on the system. In particular, this property holds for the populations $\sigma_{MM}(t)$ which are the diagonal elements of $\sigma_{M'M}(t)$ corresponding to $q=0$ and which evolve independently of the off-

diagonal terms associated with $q \neq 0$. Then, it becomes possible to derive a master equation for describing the evolution of the diagonal part of $\sigma(t)$ after a surprisingly short transient period. This is the practical statement of property PB proven in Appendix B of Ref. 38.

Property PB. The fluctuations of the ZFS Hamiltonian $H_{ZFS}^{(L)}(t)$ give rise to random time variables $\langle M|H_{ZFS}^{(L)}(t)|M_0\rangle$ of stationary TCFs,

$$k_{MM_0}(\tau) \equiv \overline{\langle M|H_{ZFS}^{(L)}(t)|M_0\rangle \langle M|H_{ZFS}^{(L)}(t-\tau)|M_0\rangle^*}. \quad (21)$$

Within the elementary theory of population evolution[35,37,39,40] consider the transition probabilities w_{MM_0} per unit time from a state $|M_0\rangle$ to a state $|M\rangle$ $(M \neq M_0)$, which are induced by the fluctuations of $H_{ZFS}^{(L)}(t)$, and the probability of no transition $w_{M_0M_0}$ per unit time defined as

$$w_{MM_0} = \begin{cases} 2\,\mathrm{Re}\int_0^\infty \exp(i\omega_{MM_0}\tau)k_{MM_0}(\tau)d\tau & \text{if } M \neq M_0 \\ -\sum_{M \neq M_0} w_{MM_0} & \text{if } M = M_0, \end{cases} \quad (22)$$

with $\omega_{MM_0} \equiv (M-M_0)\omega_0$. According to Eqs. (4) and (29) of Ref. 20, the transition probabilities are given by

$$w_{MM_0} = 2A_2(S)\begin{pmatrix} S & 2 & S \\ -M & M-M_0 & M_0 \end{pmatrix}^2 \Delta_S^2 \frac{\tau_2}{1+(\omega_{MM_0}\tau_2)^2} \quad (23)$$

with $A_2(S) \equiv \dfrac{(2S+3)(2S+2)(2S+1)2S(2S-1)}{5!}$.

Note that the value of w_{MM_0} is proportional to the squared norm $\|H_{ZFS}^{(L)}(t)\|^2 = A_2(S)\Delta_S^2$ of the fluctuating ZFS Hamiltonian. Let $\mathbf{W} = (w_{MM_0})$ be the transition probability matrix. First, assume that the field B_0 is high enough for the two inequalities

$$\varepsilon_S \equiv \max_{M \neq M_0}(w_{MM_0})\tau_2 < 1/4 \quad \text{and} \quad \Delta_S < \omega_0/4 \quad (24)$$

to hold. Then, after a short initial transient period $0 \leq t \leq 4\pi/\omega_0$, the diagonal part $\sigma_{\mathrm{diag}}(t) \equiv (\sigma_{MM}(t))$ of the populations $\sigma_{MM}(t)$ of the density matrix is given for $t \geq t_{\min} \cong 4\pi/\omega_0$ by the simple evolution equation

$$\sigma_{\mathrm{diag}}(t) = \exp[\mathbf{W} \times (t+\tau_2)]\sigma_{\mathrm{diag}}(0) \quad (25)$$

to within a relative error of about ε_s^2. In Eq. (24), the first factor 1/4 related to ε_s ensures that the relative error of about ε_s^2 is typically less than 5% and the second factor 1/4 related to Δ_s implies that according to Appendix B of Ref. 38 the probability $P_{MM_0}^{\mathrm{mod}}(t)$ can be accurately approximated by Eqs. (B18)–(B20), which lead to Eq. (25). Of course, both factors are somewhat flexible. The relevance of the validity condition (24) will be checked by simulation in Secs. III and IV. Second, if $\varepsilon_S \ll 1$, the standard master equation $d\sigma_{\mathrm{diag}}/dt = \mathbf{W}\sigma_{\mathrm{diag}}$ applies at any field. Besides, the theory of ZFS-modulated Zeeman transition frequencies developed in Appendix B of Ref. 38 provides the analytical expressions

(B23) of $\sigma_{MM}(t)$ during the initial transient period $0 \leq t \leq 4\pi/\omega_0$.

Finally, the link with the Redfield relaxation theory[1] is given by property PC recalled in Appendix SC of Ref. 38.

Property PC. The master equation $d\sigma_{\mathrm{diag}}/dt = \mathbf{W}\sigma_{\mathrm{diag}}$ and the Redfield master equation for the longitudinal relaxation, which both give the evolution of the populations $\sigma_{MM}(t)$ within the Redfield limit, are identical.

According to Eq. (25), the time evolution of the populations and of the related "longitudinal" TCFs such as $G_\parallel^{\mathrm{nor}}(t)$ is simply obtained by replacing the time argument t of the Redfield expressions by a shifted time $t+\tau_2$. For instance, if the McLachlan formula of $G_\parallel^{\mathrm{nor}}(t)$ is an accurate approximation of its Redfield expression, as for the spin values[14,29] $S = 1, 5/2, 7/2$, this TCF can be simply approximated as

$$G_\parallel^{\mathrm{nor}}(t) = \exp[-(t+\tau_2)/T_{1e,S}^{\mathrm{McLachalan}}], \quad (26)$$

where $1/T_{1e,S}^{\mathrm{McLachalan}}$ is given by Eq. (1) with $\Delta = \Delta_S$, $\tau_c = \tau_2$.

In the next section the applicability of the theory is examined by numerical simulation of the TCFs of various spin systems.

III. COMPARISON WITH NUMERICAL EXPERIMENTS

In this section the electronic relaxation of complexed paramagnetic metal ions of increasing spin values is investigated. The exact TCFs are computed by solving the Schrödinger equation [Eq. (2)] for Brownian rotational trajectories of the metal complex as previously described[22,23] and compared with the Redfield predictions. We will focus our attention on the high field domain where the inequality $w_{MM_0}\tau_2 \ll 1$ or condition (24) hold for $M \neq M_0$ together with the inequality $\Delta_S\tau_2 \geq 1$. Then, the Redfield or time-shifted Redfield approximations should be applicable to the TCFs $g_{kk'}^{qq'}(t)$ with $q = 0$ (general longitudinal relaxation) according to the theory of Sec. II, although the usual Redfield validity condition is not satisfied. For low and intermediate magnetic field values where the inequalities (24) do not hold with $\Delta_S\tau_2 \geq 1$, the actual electronic relaxation as derived from exact Monte Carlo simulations is expected to deviate from the Redfield predictions for all the TCFs. This point shown previously[23] will not be discussed in this section. To simplify the notation the Redfield expressions of the TCFs will be given in terms of the spectral density

$$j(\omega) \equiv \Delta_S^2\tau_2\frac{1}{1+\omega^2\tau_2^2}. \quad (27)$$

The calculation of the Redfield TCFs is detailed in Appendix SD of Ref. 38 where the required Redfield relaxation matrices are also tabulated for $S = 1$ and $3/2$.

A. Spin $S=1$ (Ni^{2+})

It is assumed that the electronic spin relaxation is caused by the time fluctuations of an axial static ZFS with typical parameters $\Delta_S = \sqrt{2/3}D_S = 1$ cm$^{-1} = 2\pi \times 3 \times 10^{10}$ rad s^{-1}, $E_S = 0$. The rotational correlation time is taken to be $\tau_2 = 100$ ps and corresponds to a complex of moderate molecular weight in a standard solvent. The field value $B_0 = 7.05$ T is that of a routine NMR spectrometer operating at the proton

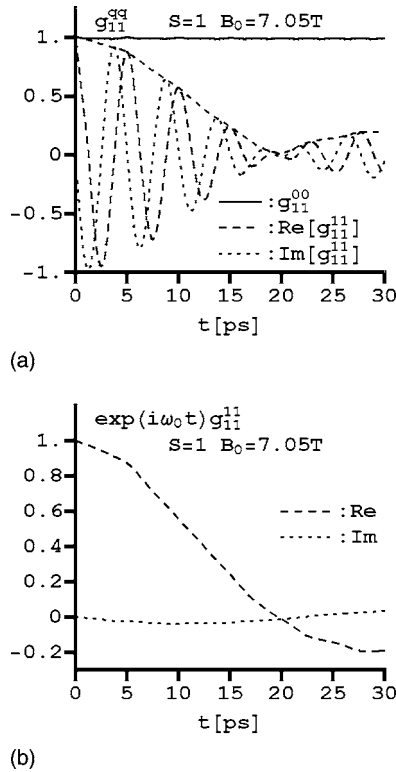FIG. 1. $S=1$ and $B_0=7.05$ T. The simulated longitudinal and transverse time correlation functions (TCFs) $g_{11}^{00}(t)=G_\parallel^{nor}(t)$ and $g_{11}^{11}(t)=G_\perp^{nor}(t)^*$ for a static ZFS Hamiltonian of parameters $\Delta_S=\sqrt{2/3}D_S=1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2=100$ ps. (a) Comparison of the overall behaviors of the TCFs. (b) On the absence of fast oscillations of $\exp(i\omega_0t)g_{11}^{11}(t)$.

resonance frequency of 300 MHz. We have $\Delta_S\tau_2=18.8$, $\omega_0\tau_2=124$, $w_{10}\tau_2=w_{0,-1}\tau_2=4.6\times10^{-3}$, and $w_{1,-1}\tau_2=2.3\times10^{-3}$. The short-time drops of the longitudinal TCFs induced by the time shift $\mathbf{W}\tau_2$ in Eq. (25) are expected to be of the order of 1% or less, so that the standard Redfield TCFs $g_{kk}^{00}(t)$ should reproduce the simulation results very accurately.

First, direct inspection of the TCFs $g_{kk'}^{qq'}(t)$ computed by Monte Carlo simulations shows that they vanish for $q\neq q'$ as stated by Eq. (16) of property PA. The exact longitudinal and transverse simulated TCFs $g_{11}^{00}(t)$ and $g_{11}^{11}(t)$ are displayed in Fig. 1. The simulated $g_{11}^{00}(t)$ of Fig. 1(a) is in excellent agreement with its Redfield counterpart,

$$g_{11}^{00}(t) = \exp(-t/T_{1e,S}^{McLachlan}) \tag{28}$$

with $\dfrac{1}{T_{1e,S}^{McLachlan}} = \dfrac{1}{5}[j(\omega_0) + 4j(2\omega_0)],$

as expected from the theory of Sec. II. The Redfield expression of $g_{11}^{11}(t)$ is

$$g_{11}^{11}(t) = \exp[-i(\omega_0 + \omega_{11}^{11})t]\exp(-t/T_{2e,S}^{McLachlan}) \tag{29}$$

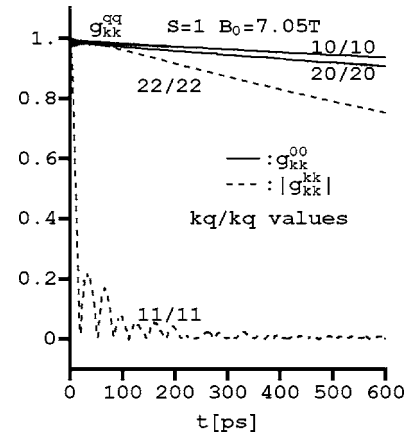with $\dfrac{1}{T_{2e,S}^{McLachlan}} = \dfrac{1}{10}[3j(0) + 5j(\omega_0) + 2j(2\omega_0)],$

FIG. 2. $S=1$ and $B_0=7.05$ T. The simulated time decays of the TCFs $g_{kk}^{00}(t)$ and of the moduli $|g_{kk}^{kk}(t)|$ for a static ZFS Hamiltonian of parameters $\Delta_S=\sqrt{2/3}D_S=1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2=100$ ps.

$$\omega_{11}^{11} = \frac{1}{10}\omega_0\tau_2[j(\omega_0) + 4j(2\omega_0)].$$

In Eq. (29), $1/T_{2e,S}^{McLachlan}$ is the transverse relaxation rate and ω_{11}^{11} is a dynamic shift[15,21,37] arising from the imaginary part of the complex spectral density of the rotational TCF.[20,21] According to Fig. 1(a), the simulated TCF $g_{11}^{11}(t)$ has the same rapid oscillatory behavior in $\exp(-i\omega_0t)$ as the Redfield TCF of Eq. (29). This is better shown in Fig. 1(b) since the simulated function $\exp(i\omega_0t)g_{11}^{11}(t)$ does not display any rapid oscillations. Furthermore, because of the term $j(0)$ in $1/T_{2e,S}^{McLachlan}$, the Redfield theory predicts that $g_{11}^{11}(t)$ should have a much faster decay than $g_{11}^{00}(t)$. Only the qualitative trend of this prediction is verified by the simulated functions shown in Fig. 1(a). Indeed, the Redfield $g_{11}^{11}(t)$ has a relaxation time $T_{2e,S}^{McLachlan}=0.94$ ps, which is more than one order of magnitude shorter than the characteristic decay time of about 15 ps of the simulated $g_{11}^{11}(t)$. Furthermore, the numerical data of Fig. 2 show that the simulated modulus $|g_{11}^{11}(t)|$ has an oscillating damped behavior, whereas the Redfield approximation predicts that it should be a purely monoexponential decaying function $\exp(-t/T_{2e,S}^{McLachlan})$. This underlines the inadequacy of the Redfield approximation for $q\neq0$. The Redfield TCFs

$$g_{22}^{00}(t) = \exp(-t/T_{22e}^{00}) \quad \text{with} \quad \frac{1}{T_{22e}^{00}} = \frac{3}{5}j(\omega_0), \tag{30}$$

$$|g_{22}^{22}(t)| = \exp(-t/T_{22,e}^{22}) \quad \text{with} \quad \frac{1}{T_{22e}^{22}} = \frac{1}{5}[j(\omega_0) + 2j(2\omega_0)], \tag{31}$$

$$g_{12}^{00}(t) = g_{12}^{11}(t) = 0 \tag{32}$$

can be used to test this approximation further. Again, the exact decay of the simulated $g_{22}^{00}(t)$ is very accurately given by Eq. (30), but only the trend of the decay of the simulated $|g_{22}^{22}(t)|$ with respect to those of the other TCFs is very roughly estimated by Eq. (31). Indeed, the Redfield $|g_{22}^{22}(t)|$ has a relaxation time $T_{22e}^{22}=14.5$ ns, which is one order of
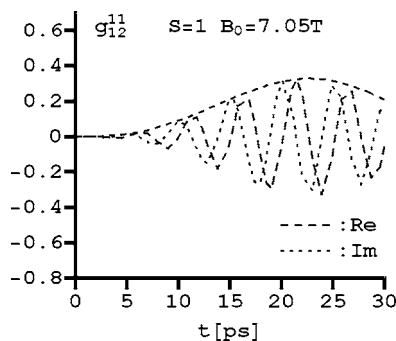
FIG. 3. $S=1$ and $B_0=7.05$ T. The simulated TCF $g_{12}^{11}(t)$ for a static ZFS Hamiltonian of parameters $\Delta_S=\sqrt{2/3}D_S=1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2=100$ ps. The Redfield approximation of this function is zero.

magnitude longer than the characteristic decay time of about 2 ns of the simulated $|g_{22}^{22}(t)|$. To be complete, it is interesting to analyze the very small drops of the simulated longitudinal TCFs $g_{kk}^{00}(t)$ calculated at short time, but hardly apparent at the scale of Fig. 2. For instance, the simulated $g_{11}^{00}(t)$ has the same decay rate as the Redfield function (28), apart for a transient behavior of duration shorter than $\tau_2=100$ ps and much shorter than $T_{1e_S}^{\text{McLachlan}}=10.9$ ns. During the transient period the simulated $g_{11}^{00}(t)$ decreases more rapidly than the Redfield function (28), so that at the beginning of the Redfield regime $t>t_{\min}$, with $t_{\min}<\tau_2$, the simulated $g_{11}^{00}(t)$ is about 1% smaller than its Redfield counterpart. Note the reasonable order of magnitude of this relative difference of about $\tau_2/T_{1e}^{\text{McLachlan}}$. This is in complete agreement with the theory of Sec. II. Finally, Eq. (32) correctly predicts that the simulated $g_{12}^{00}(t)$ vanishes to within the statistical noise of the simulation results, but does not give the right behavior of the simulated $g_{12}^{11}(t)$, which is significantly different from zero as shown by Fig. 3.

B. Spin $S=3/2$ (Cr^{3+})

The static ZFS is defined by $\Delta_S=\sqrt{2/3}D_S=1$ cm$^{-1}=2\pi\times3\times10^{10}$ rad s^{-1}, $E_S=0$. The rotational correlation time is $\tau_2=100$ ps. The field value is $B_0=7.05$ T. We have $\Delta_S\tau_2=18.8$ and $\omega_0\tau_2=124$, and the values of the products $w_{MM_0}\tau_2$ $(M\neq M_0)$ are $w_1\tau_2=w_{-1/2,-3/2}\tau_2=0.028$ and $w_2\tau_2=w_{1/2,-3/2}\tau_2=0.007$. They are larger than those for $S=1$, but still much smaller than 1. The short-time drops of the longitudinal TCFs induced by the time shift $\mathbf{W}\tau_2$ in Eq. (25) are expected to be of the order of a few percent, so that this equation should be used to calculate TCFs $g_{kk}^{00}(t)$ suitable to reproduce the simulation results very accurately.

The general relaxation properties of the TCFs $g_{kk'}^{qq'}(t)$ computed by Monte Carlo simulation are now investigated and compared with the Redfield predictions. After taking the general symmetry property [Eq. (14)] into account the number of nontrivial ($k\neq0$, $k'\neq0$) different TCFs $g_{kk'}^{qq'}(t)$ is reduced to 135. This number should further decrease to the extent that the TCFs vanish for $q\neq q'$, as stated by Eq. (16) of property PA. This property is checked by computing the maximum of the moduli $|g_{kk'}^{qq'}(t)|$ for $q\neq q'$ as a function of time. This function displayed in Fig. 4 is zero to within the
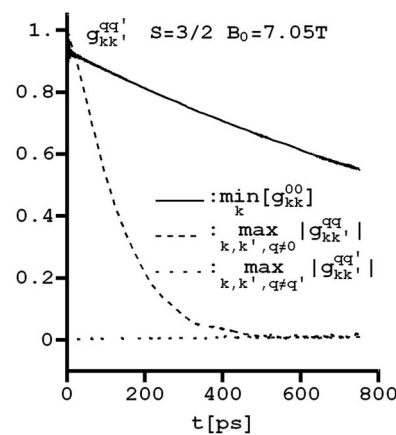
statistical noise of the simulation results. Another interesting property, already observed for $S=1$, is that all the "transverse" TCFs $|g_{kk'}^{qq}(t)|$ with $q\neq0$ decay much more rapidly than any of the longitudinal TCF $g_{kk}^{00}(t)$. This difference of decays is equivalent to the fact that the maximum function $\max_{k,k',q\neq0}|g_{kk'}^{qq}(t)|$ vanishes much more rapidly with time than the minimum function over the k values $\min_k[g_{kk}^{00}(t)]$, as shown in Fig. 4. In Sec. II, it was proven that the evolution of the populations $\sigma_{MM}(t)$ governed by the longitudinal TCFs $g_{kk'}^{00}(t)$ and the evolution of the off-diagonal terms $\sigma_{M'M}(t)$ $(M'\neq M)$ governed by the transverse TCFs $g_{kk'}^{qq}(t)$ $(q\neq0)$ are independent. This property is consistent with the fact that the two families of TCFs have different characteristic evolution times. It can be further explored by comparing the simulated TCFs $|g_{kk}^{kk}(t)|$ and $g_{kk}^{00}(t)$ plotted in Fig. 5 with one another and with the Redfield predictions. For that purpose define the auxiliary electronic relaxation rates

FIG. 4. $S=3/2$ and $B_0=7.05$ T. The overall time decays of the simulated TCFs $g_{kk'}^{qq'}(t)$ for a static ZFS Hamiltonian of parameters $\Delta_S=\sqrt{2/3}D_S=1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2=100$ ps.
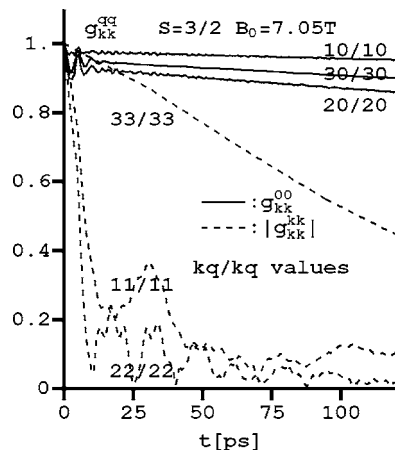

FIG. 5. $S=3/2$ and $B_0=7.05$ T. The simulated time decays of the TCFs $g_{kk}^{00}(t)$ and of the moduli $|g_{kk}^{kk}(t)|$ for a static ZFS Hamiltonian of parameters $\Delta_S=\sqrt{2/3}D_S=1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2=100$ ps.

$$\frac{1}{T_{1e}^{(1)}} \equiv \frac{12}{5} j(\omega_0) \text{ and } \frac{1}{T_{1e}^{(2)}} \equiv \frac{12}{5} j(2\omega_0). \tag{33}$$

As for $S=1$, the decays of the three simulated longitudinal TCFs $g_{kk}^{00}(t)$ are well predicted by those of their Redfield counterparts,[14,20,21]

$$g_{11}^{00}(t) = \tfrac{1}{5} \exp(-t/T_{1e}^{(1)}) + \tfrac{4}{5} \exp(-t/T_{1e}^{(2)}), \tag{34}$$

$$g_{22}^{00}(t) = \exp(-t/T_{22e}^{00}) \text{ with } \frac{1}{T_{22e}^{00}} \equiv \frac{1}{T_{1e}^{(1)}} + \frac{1}{T_{1e}^{(2)}}, \tag{35}$$

$$g_{33}^{00}(t) = \tfrac{4}{5} \exp(-t/T_{1e}^{(1)}) + \tfrac{1}{5} \exp(-t/T_{1e}^{(2)}), \tag{36}$$

apart from a transient behavior of duration shorter than $\tau_2 = 100$ ps and much shorter than the relaxation times $T_{1e}^{(1)}$, $T_{1e}^{(2)}$, and T_{22e}^{00}. Moreover, as shown by Fig. S2 of Appendix B,[38] the transient behavior of the simulated TCFs $g_{kk}^{00}(t)$ is fully predicted by Eq. (B23), which simplifies to Eq. (25) after the initial transient period. On the contrary, the decays of the simulated transverse TCFs markedly differ from those predicted by the Redfield approximation. For instance, the modulus of the Redfield TCF $g_{33}^{33}(t)$ given by

$$|g_{33}^{33}(t)| = \exp(-t/T_{33,e}^{33}) \quad \text{with } \frac{1}{T_{33e}^{33}} = \frac{6}{5}[j(\omega_0) + j(2\omega_0)] \tag{37}$$

has a relaxation time $T_{33e}^{33} = 2.9$ ns, which is one order of magnitude longer than the characteristic decay time of about 150 ps of the simulated $|g_{33}^{33}(t)|$. As $g_{22}^{22}(t)$ for $S=1$, the TCF $g_{33}^{33}(t)$ decays more slowly than the other transverse TCFs since it is the autocorrelation function of an operator, here t_3^3, which has a single nonzero matrix element in the basis $|M\rangle$. Thus, the maximum function $\max_{k,k',q\neq0}|g_{kk'}^{qq}(t)|$ would decay significantly more rapidly in the absence of $|g_{33}^{33}(t)|$. Despite the inadequacy of the Redfield approximation to predict the correct decays of the transverse TCFs $g_{kk'}^{qq}(t)$ ($q\neq0$), it still provides their oscillatory behaviors in $\exp(-iq\omega_0 t)$, as shown by the absence of rapid oscillations of the simulated functions $\exp(iq\omega_0 t)g_{kk'}^{qq}(t)$.

Finally, two additional features of the simulated longitudinal TCFs can serve to further demonstrate the accuracy of the time-shifted Redfield theory for these functions. First, the Redfield transcorrelation function

$$g_{13}^{00}(t) = \tfrac{2}{5}[\exp(-t/T_{1e}^{(1)}) - \exp(-t/T_{1e}^{(2)})] \tag{38}$$

is a negative function with a minimum value of -0.189 at $t = t_{\min} = 3.35$ ns. The time-shifted TCF $g_{13}^{00}(t+\tau_2)$ has the same minimum value occurring at a time shifted by $-\tau_2$, i.e., $t_{\min} = 3.25$ ns. Its simulated counterpart is nearly identical with a minimum value of -0.180 at $t=t_{\min}$ between 3.15 and 3.2 ns. Second, the biexponential decay [Eq. (34)] of the time-shifted (t-shift) Redfield $g_{11}^{00}(t+\tau_2)$ is fully reproduced by the Monte Carlo (MC) simulation, as shown in Fig. 6. Note that the time-shifted expression $g_{11}^{00,\mathrm{McLachlan}}(t+\tau_2)$ of the McLachlan approximation, with
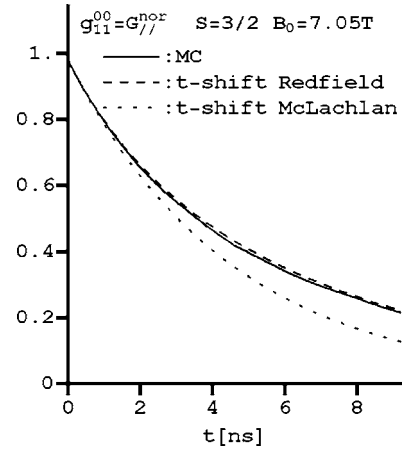

FIG. 6. $S=3/2$ and $B_0=7.05$ T. The Monte Carlo (MC) simulated TCF $g_{11}^{00}(t)$ compared with the time-shifted biexponential Redfield TCF derived from Eq. (34) for a static ZFS Hamiltonian of parameters $\Delta_S = \sqrt{2/3}D_S = 1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2 = 100$ ps. The time-shifted McLachlan approximation derived from Eq. (39) is less accurate.

$$g_{11}^{00,\mathrm{McLachlan}}(t) = \exp(-t/T_{1e}^{\mathrm{McLachlan}}) \tag{39}$$

$$\text{with } \frac{1}{T_{1e}^{\mathrm{McLachlan}}} \equiv \frac{1}{5}\frac{1}{T_{1e}^{(1)}} + \frac{4}{5}\frac{1}{T_{1e}^{(2)}},$$

is not as accurate as the time-shifted Redfield function deduced by Eq. (34). Furthermore, in Fig. S4 of Appendix SD of Ref. 38 it is shown that the simulated TCF $g_{11}^{00}(t) = G_\parallel^{\mathrm{nor}}(t)$ keeps a very similar time behavior for a given magnitude Δ_S of the static ZFS irrespective of the presence of the largest possible rhombic terms $|E_S| = |D_S|/3$.

It should be added that the relaxation time T_{1e}^{sim} (nanosecond) reported in Table I of our recent study[23] was derived from the short-time decay of the simulated TCF $G_\parallel^{\mathrm{nor}}(t) = g_{11}^{00}(t)$. It can be compared to the McLachlan relaxation time previously[23] denoted by T_{1e}^{analyt}. A good agreement between the simulated and McLachlan values supports the validity of the Redfield approximation, but does not presume a monoexponential decay of the TCF as it was incorrectly stated[23] for $S=3/2$.

In real situations the electronic spin of the metal ion undergoes the fluctuations of the static and transient ZFS Hamiltonians simultaneously. In this case the analysis of the simulated TCFs within the framework of the theory of Sec. II is obscured by the presence of the transient ZFS, the correlation time τ_v of which is short enough for the Redfield theory to be at least approximately valid. For that reason it was preferred to handle a purely static ZFS until now. However, in view of the applications to real systems, it is worth testing the applicability of the Redfield theory in a limiting situation where both the static and transient ZFSs have large magnitudes. This will be done now without entering the details.

The purely axial static ZFS is defined by $\Delta_S = \sqrt{2/3}D_S = 3$ cm^{-1} $= 5.6 \times 10^{11}$ rad s^{-1}, $E_S=0$. The rotational correlation time is $\tau_2=100$ ps. The transient ZFS is also purely axial and defined by $\Delta_T = \sqrt{2/3}D_T = 3$ cm^{-1} $= 5.6 \times 10^{11}$ rad s^{-1}, $E_T=0$. The vibrational correlation time is $\tau_v=1$ ps. The field
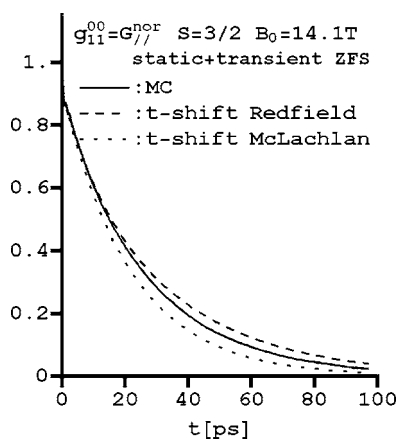
FIG. 7. $S=3/2$ and $B_0=14.1$ T. The decay of the Monte Carlo (MC) simulated TCF $g_{11}^{00}(t)$ for a general ZFS Hamiltonian including a static part of parameters $\Delta_S=\sqrt{2/3}D_S=1$ cm^{-1} and $E_S=0$, fluctuating with a rotational correlation time $\tau_2=100$ ps and a transient part of parameters $\Delta_T=\sqrt{2/3}D_T$ $=3$ cm^{-1} and $E_T=0$, fluctuating with a vibrational correlation time τ_v $=1$ ps. The time-shifted Redfield and McLachlan approximations derived from generalizations of Eqs. (34) and (39) and detailed in Appendix SD of the Supplemental Material (Ref. 38) are also displayed.

value $B_0=14.1$ T is that of a commercial high-performance NMR spectrometer operating at the proton resonance frequency of 600 MHz. We have $\Delta_S\tau_2=56.5$, $\omega_0\tau_2=248$, and $\Delta_T\tau_v=0.56$, $\omega_0\tau_v=2.48$. The transition probabilities w_{MM_0} are $w_1\tau_2=w_{-1/2,-3/2}\tau_2=0.062$ and $w_2\tau_2=w_{1/2,-3/2}\tau_2=0.016$ for the static ZFS, and $w_1\tau_v=w_{-1/2,-3/2}\tau_v=0.053$ and $w_2\tau_v$ $=w_{1/2,-3/2}\tau_v=0.015$ for the transient ZFS. For both ZFS Hamiltonians they are not negligible with respect to 1, but still significantly smaller than 1. The fluctuations of the transient ZFS were represented by the popular model of random pseudorotations.[24] In Fig. 7 the simulated longitudinal TCF $g_{11}^{00}(t)$ is compared to the time-shifted forms of the Redfield and McLachlalan approximations derived from Eqs. (34) and (39), respectively, and explicitly given by Eqs. (SD5) and (SD6) of Appendix SD.[38] The agreement is quite satisfactory with both approximations. In the presence of both static and transient ZFS Hamiltonians the auxiliary Redfield relaxation rates of Eq. (33) become $1/T_{1eS+T}^{(1)}=1/T_{1eS}^{(1)}+1/T_{1eT}^{(1)}$ and $1/T_{1eS+T}^{(2)}=1/T_{1eS}^{(2)}+1/T_{1eT}^{(2)}$ with obvious notations. The transient contributions are easily computed with the help of a spectral density of the form (27) where τ_v replaces τ_2. Because $\omega_0\tau_2=248\gg\omega_0\tau_v=2.48$ the transient contributions are 100 times larger than the static ones and the Redfield electronic relaxation is largely dominated by the fluctuations of the transient ZFS. The McLachlan relaxation rate is $1/T_{1eS+T}^{McLachlan}\equiv(1/5)1/T_{1eS+T}^{(1)}+(4/5)1/T_{1eS+T}^{(2)}=4.6\times10^{10}$ s^{-1}. Since $\Delta_T\tau_v=0.56$, the usual Redfield condition $\Delta_T\tau_v\ll1$ is not clearly satisfied. Nevertheless, the inequalities (24) hold and the Redfield rates govern the relaxation after a transient period of the order of 1 ps, during which the theoretical $g_{11}^{00}(t)$ has a rapid drop of $\tau_2/T_{1eS}^{McLachlan}+\tau_v/T_{1eT}^{McLachlan}=0.05$ $+0.045=0.095$ from 1 to about 0.9, in very good agreement with the simulated behavior.

C. Spin $S=5/2$ (Mn^{2+}) and $S=7/2$ (Gd^{3+})

For these ions with an orbital angular momentum $L=0$, the magnitude Δ_S of the static ZFS is significantly smaller
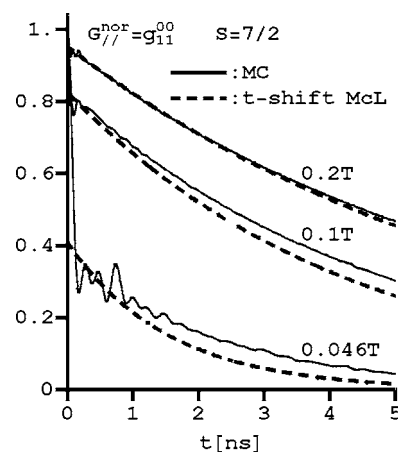

FIG. 8. $S=7/2$. Comparison at various field values of the Monte Carlo (MC) simulated TCF $G_\parallel^{nor}(t)=g_{11}^{00}(t)$ with the time-shifted McLachlan (t-shift McL) expression (40) for a model of the macromolecular P760-Gd(III) complex.

than in the case of Ni^{2+} and Cr^{3+}. Typically, if Mn^{2+} is in a weakly distorted tetrahedral or octahedral symmetry[3] and for any coordination of Gd^{3+}, we have $\Delta_S\lesssim0.1$ cm^{-1}. Then, the validity condition (24) of the Redfield formalism holds not only for fast rotating complexes with $\Delta_S\tau_2<1$ at any field B_0, but also for slowly rotating complexes as far as B_0 >0.2 T and $\Delta_S<\omega_0$.

We had already observed[23,29] that the simulated longitudinal TCFs, $G_\parallel^{nor}(t)=g_{11}^{00}(t)$, of various Gd^{3+} complexes have the quasi monoexponential decays predicted by the McLachlan approximation of the Redfield theory, with a relaxation rate accurately given by Eq. (1), even if $\Delta_S\tau_2>1$. This *a priori* surprising result is now well understood through the present theory of relaxation leading to the much less restrictive applicability condition (24). Moreover, according to Eq. (26), the time evolution of $G_\parallel^{nor}(t)$ should be described by the very simple time-shifted McLachlan type expression

$$G_\parallel^{nor}(t) = g_{11}^{00}(t)$$
$$= \exp[-(t+\tau_2)/T_{1e,S}^{McLachlan}-(t+\tau_v)/T_{1e,T}^{McLachlan}],$$
(40)

which, according to Eq. (24), should be accurate to within a relative error of $\varepsilon_S^2+\varepsilon_T^2$ with $\varepsilon_S\equiv\max_{M\neq M_0}(w_{MM_0,S})\tau_2$ and $\varepsilon_T\equiv\max_{M\neq M_0}(w_{MM_0,T})\tau_v$. As a rule of thumb, since the relaxation rates $1/T_{1e,S}^{McLachlan}$ and $1/T_{1e,T}^{McLachlan}$ are linear combinations of the transition probabilities $w_{MM_0,S}$ and $w_{MM_0,T}$, the accuracy parameters ε_S and ε_T can be estimated as ε_S $\cong\tau_2/T_{1e,S}^{McLachlan}$ and $\varepsilon_T\cong\tau_v/T_{1e,T}^{McLachlan}$. These properties are checked in Fig. 8 by comparing the time-shifted (t-shift) expression (40) of $G_\parallel^{nor}(t)$ with the simulation results for the P760-Gd(III) complex in water at various field values B_0.[23] The ZFS parameters of this complex are $\Delta_S=0.35$ $\times10^{10}$ rad s^{-1}, $\tau_2=1.7$ ns, $\Delta_T=0.43\times10^{10}$ rad s^{-1}, and τ_v $=0.54$ ps. The initial drops of the simulated TCFs are accurately predicted even at a field as low as 0.046 T. As B_0 takes the increasing values 0.046, 0.1, and 0.2 T, the relaxation

rates $1/T_{1e,S}^{\text{McLachlan}}$ are 5.25×10^8, 1.11×10^8, 0.28×10^8 s^{-1} and strongly decrease with field, whereas $1/T_{1e,T}^{\text{McLachlan}} = 1.20 \times 10^8$ s^{-1} is constant. The associate accuracy parameters $\varepsilon_S \cong \tau_2/T_{1e,S}^{\text{McLachlan}}$ are 0.89, 0.19, and 0.05, whereas ε_T is negligible. Then, the predicted relative error ε_S^2 of expression (40) of $G_\parallel^{\text{nor}}(t)$ has the values 0.79, 0.036, and 0.0025. These predicted errors can be compared with the real errors defined as follows. The integrals $I \equiv \int_0^{5 \text{ ns}} G_\parallel^{\text{nor}}(t)dt$ of $G_\parallel^{\text{nor}}(t)$ given by the MC simulation and Eq. (40) are calculated over the simulation time interval, and the real error is defined as the relative difference $(I_{t\text{-shift McL}} - I_{\text{MC}})/I_{\text{MC}}$ of these integrals. The real errors are 0.26, 0.06, and 0.005 at 0.046, 0.1, and 0.2 T. Clearly, the predicted errors give reasonable estimates of the accuracy of the theory in its expected validity range $\varepsilon_S < 1/4$. Surprisingly, Eq. (40) is still reasonably accurate at 0.046 T for $\varepsilon_S \cong 1$, as shown in Fig. 8 and the fact that $I_{t\text{-shift McL}}$ is just 26% smaller than I_{MC}. On the other hand, the integral $I_{\text{McLachlan}}$ derived from the standard McLachlan expression is 82% larger than I_{MC}. Another useful feature of Eq. (40) is that the initial value of $G_\parallel^{\text{nor}}(t)$ given by $\exp(-\varepsilon_S - \varepsilon_T)$ with $\varepsilon_S \cong \tau_2/T_{1e,S}^{\text{McLachlan}}$ and $\varepsilon_T \cong \tau_v/T_{1e,T}^{\text{McLachlan}}$ becomes independent of the correlation times τ_2 and τ_v at sufficiently high field. Indeed, for $\lambda = S$, T, according to Eq. (1), $\varepsilon_\lambda \to (2/25)(4S(S+1)-3)(\Delta_\lambda/\omega_0)^2$ as $B_0 \to \infty$. This property is nicely illustrated in Fig. 3 of a recent work by Åman and Westlund[26] for a Gd(III) complex of ZFS parameters $\Delta_S = 0.4$ cm^{-1}, $\tau_2 = 100$ and 1000 ps, $\Delta_T = 0.04$ cm^{-1}, and $\tau_v = 10$ ps. For the fast rotating complex with $\tau_2 = 100$ ps, the accuracy parameter ε_S is $\varepsilon_S = 0.56$ at $B_0 = 1.25$ T (Q band) and Eq. (40) predicts $G_\parallel^{\text{nor}}(0) = 0.57$ in reasonable agreement with the simulated value in the range of 0.65–0.70. Furthermore, for the slowly rotating complex with $\tau_2 = 1000$ ps, the initial value of the simulated $G_\parallel^{\text{nor}}(t)$ is the same as for the fast rotating complex. The same property was found far beyond the expected validity range of the present theory at the lower fields 0.339 T (X band) and even 0.107 T (S band) by Åman and Westlund[26] and clearly deserves further investigation.

IV. DISCUSSION

A. Extension of the theory

When the static ZFS is simply a sum of second-order tensorial operators, the "high-field" time-shifted Redfield formalism and the standard Redfield theory are applicable, respectively, if Eq. (24) and the inequality $\varepsilon_S \equiv \max_{M \neq M_0}(w_{MM_0})\tau_2 \ll 1$ hold. When the static ZFS involves terms of the fourth or sixth orders, the above conditions are easily extended. Using the notations of Rast et al.[20] for a kth order ZFS Hamiltonian ($k = 2,4,6$) of magnitude a_k ($a_2 = \Delta_S$) and corresponding rotational correlation time $\tau_k = 6\tau_2/[k(k+1)]$, the above applicability conditions are loosely summarized as

$$w_{MM_0}^{(k)}\tau_k = 2A_k(S)\begin{pmatrix} S & k & S \\ -M & M-M_0 & M_0 \end{pmatrix}^2 a_k^2$$

$$\times \frac{\tau_k^2}{1+(\omega_{MM_0}\tau_k)^2} \ll 1$$

$$\text{with } A_k(S) \equiv \frac{(k!)^2(2S+k+1)!}{2^k(2k+1)!(2S-k)!}, \qquad (41)$$

with $\sqrt{A_k(S)}$ being the proportionality factor between T_k^q and t_k^q defined in Eq. (8). Note that $w_{MM_0}^{(k)}$ is proportional to the squared norm $\|H_{\text{ZFS}}^{(L)}(t)\|^2 = A_k(S)a_k^2$ of the fluctuating ZFS Hamiltonian of kth order. As an example, consider the case of the static ZFS Hamiltonian of the Gd^{3+} aquo complex derived from an analysis of the full ESR spectra[21] and of static ZFS parameters $a_2 = \Delta_S = 0.38 \times 10^{10}$ rad s^{-1}, $a_4 = 0.024 \times 10^{10}$ rad s^{-1}, $a_6 = 0.021 \times 10^{10}$ rad s^{-1}, and $\tau_2 = 23.3$ ps in H$_2$O at 298 K. At $B_0 = 0$ T, the transition probabilities $w_{MM_0}^{(k)}$ are $w_{-5/2,-7/2}^{(2)}\tau_2 = 0.2$ and $w_{MM_0}^{(k)}\tau_k \ll 1$ for $k = 4,6$. Because $w_{-5/2,-7/2}^{(2)}\tau_2$ is not much smaller than 1, the McLachlan approximation should be inaccurate near $B_0 = 0$ T. Indeed, it predicts a longitudinal relaxation time $T_{1e}^{\text{McLachlan}} = 0.096$ ns, which is significantly shorter than the simulated value[41] by 30%. This could be expected from Eqs. (B13) and (B14) of Appendix B (Ref. 38) which indicate that the relaxation probabilities $P_{MM_0}(t)$ are significantly smaller than their Redfield limits $w_{MM_0}(\omega_{MM_0})t$ for an initial period of time longer than τ_2, so that the exact simulated relaxation appears slower than the Redfield relaxation during this initial period. As $B_0 \to 0$, the theory of ZFS-modulated Zeeman transition frequencies developed in Appendix B of Ref. 38 does not apply so that the rate of longitudinal relaxation is not given by the Redfield theory for times shorter than τ_2. Briefly, the Redfield theory holds only if the products $w_{MM_0}^{(k)}\tau_k$ are really much smaller than 1. On the other hand, in the field region $B_0 \geqslant 0.2$ T with $\omega_0 \gg a_2 = \Delta_S$, the Redfield theory was found to be accurate[41] even if the value 0.12 of $w_{-5/2,-7/2}^{(2)}\tau_2$ at $B_0 = 0.2$ T is just somewhat smaller than its value 0.2 at zero field.

Obviously, the approach can be extended to a relaxation mechanism induced by a transient fluctuating ZFS of magnitude Δ_T with a vibrational correlation time τ_v. Using the pseudorotation model[24] of vibrations, condition (24) transforms into the appropriate inequalities by replacing Δ_S and τ_2 by Δ_T and τ_v, respectively. An open question is the range of possible values of τ_v, which was found shorter than 5 ps in previous studies.[20,21]

Similarly, consider the electronic relaxation due to the g anisotropy modulation[7] as for Cu^{2+} ($S = 1/2$) complexes. For example, in axial symmetry, setting $g \equiv (g_\parallel + 2g_\perp)/3$ and $\Delta g \equiv g_\parallel - g_\perp$, condition (41) becomes for a spin S,

$$\frac{1}{15}S(S+1)\left(\frac{\Delta g}{g}\right)^2 \frac{(\omega_0\tau_2)^2}{1+(\omega_0\tau_2)^2} \ll 1. \qquad (42)$$

Note that the average of the squared norm $\overline{\|H_{g \text{ anisotropy}}(t)\|^2}$ of the g-anisotropy Hamiltonian over all the orientations of the complex is of the order of $(1/15)S(S+1)(\Delta g/g)^2\omega_0^2$. For a typical situation[3] such as $\Delta g = 0.2$ and $\tau_2 \geqslant 30$ ps, the usual

Redfield condition $\Delta g \omega_0 \tau_2 \ll 1$ does not hold for $B_0 \geq 1$ T since $\Delta g \omega_0 \tau_2 \geq 1$. However, since $(\Delta g/g)^2 \ll 1$, inequality (42) is satisfied at any field value and the Redfield formalism can be safely used to calculate the longitudinal TCF.

Finally, the extension of the theory to deal with magnetically coupled electronic spins[7–9] should be envisaged. The evolution of the statistical operator will no longer be represented by the simple expansion (11) which results from straightforward Wigner algebra. It will depend on the much more numerous TCFs of the components of irreducible tensor operators made from an appropriate basis of coupled spin states with the help of sophisticated angular momentum techniques well developed by several authors for the purpose of atomic physics.[42–44]

B. Validity of the Redfield relaxation theory

It is generally accepted that the electronic spin relaxation due to a fluctuating Hamiltonian $\hbar H_1(t)$ of correlation time τ_c is properly described by the Redfield theory under the condition $|H_1|\tau_c \ll 1$ denoted as[23,29] (RA1), where the magnitude $|H_1|$ of $H_1(t)$ is somewhat loosely defined.[6] In previous papers,[23,29] it was already observed that the difference between the simulated longitudinal TCF $G_{\parallel}^{nor}(t)$ and its McLachlan approximation of the Redfield theory increases as the field B_0 tends to zero and that this growing discrepancy is accompanied by oscillations of larger and larger amplitudes. Since condition (RA1) is field independent, we erroneously attributed this failure of the Redfield theory to an increase of the mixing between the longitudinal TCF and the transverse TCF causing the oscillations. Indeed, the secular approximation condition $\omega_0 \gg |H_1|^2 \tau_c$ denoted as (RA2), which is compatible with Eq. (41) for $\omega_0 \gg |H_1|$ and sufficient to ensure the independent evolution[37] of these TCFs, is less and less true as $B_0 \to 0$. Now, because of the global dynamic rotational symmetry of the spin systems about the field direction, $G_{\parallel}^{nor}(t) = g_{11}^{00}(t)$ evolves independently of all the TCFs $g_{kk'}^{qq'}(t)$, with $q \neq 0$ as stated by property PA. Clearly, the reason invoked for resorting to condition (RA2) is not justified. Furthermore, as shown in Appendix B of Ref. 38, the transient oscillations of $G_{\parallel}^{nor}(t)$ at a field $B_0 > 0$ result simply from a rigorous calculation of the population changes at short time. The present discussion confirms that condition (RA2) is not relevant in explaining the surprising accuracy of the high field longitudinal relaxation rates of the Redfield theory and is not required for applying this second-order perturbation formalism as recently stated by Åman and Westlund.[26]

The meaning of the Redfield-limit validity condition (RA1) can be further analyzed. This condition stems from the expansion of the time derivative $d\sigma(t)/dt$ of the whole statistical operator as a series[37,44] of multiple commutators involving the product of $H_1(t)$ by $H_1(t_1) \times \cdots \times H_1(t_n)$ $(n \geq 1)$ integrated over the time variables $t_1, \ldots, t_n$. Inequality (RA1) is just a loose condition of convergence of this series accounting for the loss of correlation between the values of $H_1(t), H_1(t_1), \ldots, H_1(t_n)$ over times of the order of τ_c. The complicated algebraic nature of the series used to calculate the evolution of the whole statistical operator makes it

difficult to derive more precise convergence criteria, and the search for a rigorous definition of $|H_1|$ is not justified. On the contrary, the evolution of the diagonal elements of the density matrix, i.e., the population of the Zeeman states, is based on a much simpler algebra from which the accuracy of the theory can be reasonably estimated. Indeed, the transition probability theory developed in Appendix B of Ref. 38 rests on the approximate Eq. (B7). This equation introduces a relative error on $\overline{|c_{j,M}(t)|^2}$ of the order of $(w_{MM_0}t)^2$ $(M \neq M_0)$ since it only keeps the changes in $w_{MM_0}t$ in the successive approximation of the mean values of the squared coefficients of the states $U_j(t)|M_0\rangle$ evolving from $|M_0\rangle$, so that the correction in $(w_{MM_0}t)^2$ of $|\langle M_0|U_j(t)|M_0\rangle|^2 = 1 + O(w_{MM_0}t) \cong 1$ is neglected, hence the relative error in $(w_{MM_0}t)^2$. Now, it is well known[37,44] and quantitatively shown by Eqs. (B13) and (B14) that the master equation describing the population evolution only applies for $t \gg \tau_c$, say, $t \geq 5\tau_c$. Therefore, the relative error inherent in this master equation is limited to about $(5w_{MM_0}\tau_c)^2$. An accuracy goal of 1% should be obtained for $(5w_{MM_0}\tau_c)^2 \leq 0.01$, i.e., $w_{MM_0}\tau_c \leq 0.02$ for $M \neq M_0$. Note that the high-field condition (24) is less stringent by an order of magnitude.

C. Application to the paramagnetic relaxation enhancement of nuclei

As mentioned in the Introduction, in order to safely apply electronic spin relaxation theories to the MRI contrast agents and to the structural characterization of paramagnetic metal complexes, it is important to test the validity of the decomposition approximation[27] (DCA), which is inherent in the SBM formalism and used to calculate the intramolecular PREs. For this purpose we have compared the results of the SBM theory with those obtained through numerical simulations (i) using the decomposition approximation and (ii) performing an exact computation following the procedure proposed by Schaefle and Sharp [see Ref. 19, Eqs. (15) and (16)]. We considered the PRE of protons at distances $r_H = 3.1$ Å from the electron spin $S = 3/2$ of a complex characterized by $\tau_2 = 100$ ps, $\tau_v = 5$ ps, static and transient axial ZFS parameters of $\Delta_S = \sqrt{2/3}D_S = \Delta_v = \sqrt{2/3}D_v = 1$ cm^{-1}, and an external magnetic field $B_0 = 7.05$ T. The values of the intramolecular nuclear relaxation rate R_{1M} to be compared are $R_{1M}^{Solomon} = 40\,300$ s^{-1} for the Solomon approximation assuming infinite values of the electronic relaxation times, $R_{1M}^{SBM} = 28\,140$ s^{-1} for the SBM approximation using $1/T_{1e}^{McLachlan} = 4.6 \times 10^9$ s^{-1}, $R_{1M}^{DCA} = 28\,100$ s^{-1} for the decomposition approximation using the simulated TCF $G_{\parallel}^{nor}(t)$, and $R_{1M}^{exact} = 28\,600 \pm 800$ s^{-1} for the exact computation. As expected, there is a significant decrease of the PRE due to the electronic spin relaxation. Moreover, for this high field value, the decomposition approximation is very accurate and fully justified as well as the SBM theory.

We checked that this property is independent of the orientation of the vector $\mathbf{r}_H$ joining the metal center to the proton with respect to the principal axes of the static ZFS and remains valid for larger Δ_S values at least up to 3 cm^{-1} for sufficiently high field $B_0 \geq 14$ T. This result is obvious for a purely transient ZFS, the modulation of which is independent

of the whole rotation of the complex, but wrong in the presence of a strong static ZFS at low field values.[6,28] The applicability of the decomposition approximation was already shown in the high field region,[6,28] where the electronic relaxation does not quench the PRE. Here, it is observed in less restrictive high field situations where the effects of the electronic relaxation can be safely calculated by the Redfield formalism provided that condition (24) holds.

In the case of the OS PRE, the statistical correlation between the dynamics of the electronic spin quantum states induced by a static ZFS Hamiltonian and the spatial motion of the I-S interspin vector $\mathbf{r}_{IS}$ is expected to be negligible. Then, the rates of the OS PREs can be expressed as linear combinations of dipolar spectral densities $j_{2\mathrm{dir}}(\omega)$ [see Ref. 33, Eqs. (9)–(12)], where dir$=\parallel, \perp$ denotes a direction parallel or perpendicular to the field B_0 and indicates that the spectral density involves either the longitudinal TCF $G_{\parallel}^{\mathrm{nor}}(t)$ or the transverse TCF $G_{\perp}^{\mathrm{nor}}(t)$ of Eq. (15). At high field, if condition (24) holds, the effects of the electronic spin relaxation on the dipolar spectral densities $j_{2\mathrm{dir}}(\omega)$ can be calculated with the help of the (time-shifted) Redfield formalism. Indeed, on the one hand, it is applicable to $G_{\parallel}^{\mathrm{nor}}(t)$. On the other hand, $G_{\perp}^{\mathrm{nor}}(t)$ is of the form $\exp(i\omega_0 t)G_{\perp}^{\mathrm{nor,nro}}(t)$, where $G_{\perp}^{\mathrm{nor,nro}}(t)$ has no rapid oscillations (nro). Thus, the dipolar spectral densities involving $G_{\perp}^{\mathrm{nor,nro}}(t)$ vanish because of the rapid oscillations of $G_{\perp}^{\mathrm{nor}}(t)$ in $\exp(i\omega_0 t)$. Now, even if the decomposition approximation is somewhat inaccurate, for instance, because of strong anisotropic shape and/or electrostatic interactions between the species carrying the spins I and S, the previous calculations performed for the intramolecular PRE shows that the OS PRE rates can still be confidently calculated at high field by using the (time-shifted) Redfield formalism for describing the longitudinal electronic spin relaxation and neglecting the terms involving the transverse electronic spin relaxation.

Another important application of the longitudinal electronic relaxation T_{1e} occurs in the optimization of the Gd(III)-based MRI contrast agents. The residence time τ_{M} of the water molecules coordinated to the metal is a key factor governing the contrast efficacy.[10,11] It can be determined[11] from the transverse PRE of the water $^{17}\mathrm{O}$ nuclear spins, which is a simple analytical expression of τ_{M} and T_{1e}. For that purpose, τ_{M} and T_{1e} are assumed to be simple reasonable functions of physical parameters of the metal complex, which are adjusted in order to reproduce the measured PRE. The method is all the more accurate as the expression of T_{1e} is reliable. This was pointed out by Dunand *et al.*[45] who used a reliable determination of the fluctuating ZFS Hamiltonian obtained through the interpretation of careful EPR measurements within a valid formalism.[21,22] They derived values of τ_{M} for Gd(III)-based contrast agents, which were significantly different from those previously calculated with the help of a less precise description. The present theory provides a rigorous framework within which analytical McLachlan expressions of T_{1e} corresponding to the used ZFS Hamiltonian can be derived and safely employed in the fitting of the $^{17}\mathrm{O}$ nuclear relaxation.

V. CONCLUSION

When it was realized that the presence of a static zero-field-splitting (ZFS) Hamiltonian is necessary to interpret the ESR spectra of Gd(III) complexes,[20,21] the description of electronic spin relaxation beyond the Redfield approximation became a renewed challenge[5–7,16,18,19,22–24,28] because the time fluctuations of the static ZFS Hamiltonian induced by the Brownian rotation of the complex are often too slow for an *a priori* legitimate use of this approximation. The importance of the Gd(III)-based contrast agents in magnetic resonance imaging (MRI) and of many metal ions with fully quenched orbital angular moments in their ground states called for a reliable theory of the electronic spin relaxation due to a fluctuating Hamiltonian $\hbar H_1(t)$ which does not satisfy the validity condition $\|H_1\|\tau_c \ll 1$ of the Redfield approximation. Moreover, this approximation had been successfully applied without real justifications beyond its expected validity range. In this paper the electronic spin relaxation has been investigated by a thorough analytical and numerical study of all the time correlation functions governing the evolution of the statistical operator. It has been shown that the Redfield analytical theory of the longitudinal relaxation is valid even if $\|H_1\|\tau_c \gtrsim 1$, provided that $\|H_1\|$ is much smaller than the Larmor angular frequency ω_0. For a ZFS Hamiltonian $\hbar H_1(t)$, when the ratio $\|H_1\|/\omega_0$ increases, the longitudinal Redfield master equation with the time argument t replaced by the shifted time $t + \tau_c$ provides an accurate description of the relaxation up to quite large $\|H_1\|/\omega_0$ values. In particular, the time-shifted form of the popular McLachlan monoexponential expression of $\langle S_z(t)S_z(0)\rangle$, which is identical to the Redfield result for $S=1$ and surprisingly very close to it[14,23,29] for $S=5/2$ and $S=7/2$, can be safely employed. These key theoretical results of the present work are summarized by the easy-to-use Eqs. (25) and (40). The useful Solomon, Bloembergen, and Morgan equations describing the paramagnetic relaxation enhancements of nuclei located on the metal complex have been validated at high field together with their counterparts for nuclei carried by other species in the solution. Finally, it has been observed that the paramagnetic relaxation enhancements of nuclei can still be notably quenched by the electronic spin relaxation due to a large transient ZFS Hamiltonian even at high field. This calls for accurate classical[46,47] or quantum[48] theories of the molecular vibrations giving rise to the fluctuations of the transient ZFS Hamiltonian.

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[38] iSee EPAPS Document No. E-JCPSA6-126-008718 for Supplementary Material. Appendix A contains a general proof beyond the Redfield limit of the symmetry properties [Eq. (16)] of the time correlation functions (TCFs). In Appendix SA, the general symmetry properties of the TCFs at zero field are proven. In Appendix B the time evolution of the populations of the eigenstates of the Zeeman Hamiltonian H_0 is described by a new theory accounting for the time modulation of the Zeeman transition frequencies by the terms of the fluctuating zero-field-splitting (ZFS) Hamiltonian which commute with H_0. Appendix SB reports on mathematical techniques used to derive the analytical expressions of the population evolution discussed in Appendix B. The influence of the rhombicity of the static ZFS Hamiltonian is also studied in Appendix SB. Appendix SC is a reminder of the equivalence between the Redfield theory and the usual population evolution formalism within the Redfield limit. For the spins S=1 and S=3/2, Appendix SD provides the Redfield relaxation formalism used to calculate the Redfield TCFs which are compared with their simulated counterparts in the printed article. The longitudinal relaxation is also studied when the static ZFS Hamiltonian is rhombic. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

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