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Quantitative interpretation of the very fast electronic relaxation of most Ln^{3+} ions in dissolved complexes

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In a reference frame rigidly bound to the complex, we consider two Hamiltonians possibly at the origin of the very fast electronic relaxation of the paramagnetic lanthanide Ln^{3+} ions ($\text{Ln} = \text{Ce}$ to Nd , Tb to Yb), namely the mean (static) ligand-field Hamiltonian and the transient ligand-field Hamiltonian. In the laboratory frame, the bombardment of the complex by solvent molecules causes its Brownian rotation and its vibration-distorsion dynamics governing the fluctuations of the static and transient terms, respectively. These fluctuations are at the origin of electronic relaxation. The electronic relaxation of a Ln^{3+} ion is defined by the decays of the time correlation functions (TCFs) of the longitudinal and transverse components of the total angular momentum J of its ground multiplet. The Brownian rotation of the complex and its vibration-distorsion dynamics are simulated by random walks, which enable us to compute the TCFs from first principles. It is shown that the electronic relaxation is governed mainly by the magnitude of the transient ligand-field, and not by its particular expression. The range of expected values of this ligand-field together with the lower limit of relaxation time enforced by the values of the vibration-distortion correlation time in liquids give rise to effective electronic relaxation times which are in satisfactory overall agreement with the experimental data. In particular, these considerations explain why the electronic relaxation times vary little with the coordinating ligand and are practically independent of the external field magnitude.

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I. INTRODUCTION

Ln^{3+} complexes in solution play an important role in imaging techniques for biology and medicine.^{1–3} In particular, Gd^{3+} complexes have been extensively studied as efficient relaxation contrast agents in magnetic resonance imaging (MRI).^{4–8} Indeed, because of their high electronic spin value $S = 7/2$ and long^{9,10} electronic (e) relaxation time $T_{1e} \cong 10^{-8}$ s at the usual imaging fields, the Gd^{3+} ions create strong local dipolar fields that enhance the relaxation rates of the neighboring water protons very efficiently. The other paramagnetic Ln^{3+} ions display much shorter electronic relaxation times, typically of the order of 10^{-13} to 10^{-12} s^{11–17} so that they are much less efficient relaxation agents in MRI at the usual⁸ imaging fields. Hereafter, they will be referred to as fast relaxing Ln^{3+} ions. However, their fast electronic relaxation is very useful since it allows one to determine the geometry of their LnL complexes ($L = \text{ligand}$) from the induced paramagnetic dipolar shifts of the resonance frequencies of the ligand nuclei^{18–20} and to efficiently investigate the intermolecular interactions of these complexes with solvent and solute species.²¹ For a given ligand, the geometries of the LnL complexes of the various Ln^{3+} ions are generally very similar so that any LnL complex inducing appropriate shifts can serve as structural representative of the whole family.

Such cooperative properties of Ln^{3+} ions are important not only for Gd^{3+} -based MRI contrast agents, but also for many other Ln^{3+} ions such as Eu^{3+} or Yb^{3+} serving in luminescent probes.^{1,2}

Several experimental estimates of the electronic relaxation times of fast-relaxing Ln^{3+} ions are available in various complexes. All the values were obtained indirectly by interpreting the measured paramagnetic relaxation enhancements (PREs) of neighboring nuclear spins with the help of approximate models describing their relative motions with respect to the Ln^{3+} ion. In a pioneering work, Alsaadi *et al.*^{11,12} implicitly assumed that the electronic magnetization of complexed fast relaxing Ln^{3+} ions prepared in a non-equilibrium state returns to equilibrium according to a mono-exponential law characterized by a single relaxation time T_{1e} . They evaluated the relaxation times T_{1e} of the fast relaxing Ln^{3+} ions in several complexes dissolved in water from the PRE of the water protons at various temperatures and resonance frequencies. Using the popular Solomon, Bloembergen, Morgan (SBM) equations,^{4–7,18} they obtained T_{1e} values varying between 0.5×10^{-13} and 3.7×10^{-13} s. They found that these times are practically independent of the magnetic field intensity and slightly increase with decreasing temperature. This latter effect was attributed to a very small activation energy of T_{1e} of the order of 1 to 4 kJ mol⁻¹. The above authors also remarked that the PRE is roughly proportional to the number of water molecules bound to the metal and nearly independent of the chemical nature of the ligands and of the configuration (symmetry) of the complex.

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By avoiding the difficulty raised by the correct description of the dynamics of water around the metal ion, Aime *et al.*¹³ developed a more precise method for determining T_{1e} , which consists in measuring the intramolecular longitudinal and transverse PREs of several protons of the complexing ligand in D₂O. They tested their method with $\text{Ln}(\text{dota})(\text{H}_2\text{O})^-$ complexes ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}$; $\text{dota}^{4-} = 1,4,7,10\text{-tetraazacyclododecane-N, N', N'', N'''}\text{-tetraacetate}$). Applying the SBM equations to six different proton sites, they obtained remarkably coherent estimates 3.0×10^{-13} , 2.5×10^{-13} , and 1.4×10^{-13} s of T_{1e} at 295 K for Tb, Dy, and Ho, respectively, with an uncertainty of about 10%. They also confirmed a slight increase of T_{1e} with decreasing temperature. This approach was further applied to $\text{Ln}(\text{dotp})^{5-}$ complexes ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$; $\text{dotp}^{8-} = 1,4,7,10\text{-tetraazacyclododecane-1,4,7,10-tetrakis(methylenephosphonate)}$) for which the T_{1e} values are about two times longer than for $\text{Ln}(\text{dota})$.¹⁵ For Ln^{3+} aqua complexes and from new experimental values of the PREs of the water protons, Bertini *et al.*¹⁴ showed that the T_{1e} values are independent of the field magnitude up to 14.1 T. Finally, Vigouroux *et al.*¹⁶ derived T_{1e} estimates for the Ln^{3+} aqua ions in D₂O from the measured PREs of the protons of the tetramethylammonium cation $(\text{CH}_3)_4\text{N}^+$ used as outer-sphere probe. Their values are in overall agreement with previous determinations.

Up to now, for a given fast relaxing Ln^{3+} ion, there is no really convincing physical explanation of the mono-exponential return of the magnetization to equilibrium with a well-defined relaxation time T_{1e} and of the mechanisms leading to the observed T_{1e} values. A first attempt in that direction was performed in 1963 by Zapirov.²² He studied the Ce^{3+} and Pr^{3+} aqua ions, improperly approximated as octahedral complexes.²³ He assumed that the electronic relaxation is due to harmonic vibrations of the complex (normal modes) induced by collisions with the solvent molecules. Using reasonable adjusted parameters, he obtained values of T_{1e} of the right order of magnitude. However, the point charge model used for describing the fluctuating ligand-field created by the water molecules²⁴ is known to provide incorrect energy splittings because of the covalent nature of the metal-ligand bonding.²⁵ Moreover, because of the violence of the collisions, the deformations of the complex are unlikely described by linear combinations of harmonic normal mode vibrations. Three decades after Zapirov, when measuring the PRE of water protons due to various Ln^{3+} aqua ions up to 14.1 T, Bertini *et al.*¹⁴ could not observe any field dependence of T_{1e} . Therefore, following a suggestion of Zapirov, they inferred that the fast electronic relaxation of Ln^{3+} ions is due to an Orbach process,^{24,26,27} by analogy to what happens for these ions in solids, but they did not perform any calculation in that direction. Finally, they pointed out the need for a physical model for the electronic relaxation of Ln^{3+} complexes in solution.¹⁴

II. THEORY

A. The ligand-field Hamiltonian

Each of the different fast relaxing paramagnetic Ln^{3+} ions has a ground electronic multiplet $^{2S+1}L_J$ characterized by

a total orbital momentum L , a total spin S , and a total angular momentum $J \neq 0$.^{24,25} It has $L \neq 0$, so that the ligand-field Hamiltonian H_{lig} , which acts on its $4f$ electrons and is due to their Coulomb interactions with the nuclei and electrons of its ligand(s), has a direct effect at the first order of perturbation, giving rise to a total splitting of the multiplet energy levels of the order of a few hundreds of cm^{-1} . By contrast, Gd^{3+} has a degenerated ground state $^8S_{7/2}$ with $L = 0$, on which the ligand-field has no direct perturbation effect at the first order, but only indirect effect of higher orders through the spin-orbit coupling. This indirect effect is conveniently described by a zero-field splitting (ZFS) Hamiltonian H_{ZFS} acting on the ground multiplet $^8S_{7/2}$ and giving rise to a total splitting of the energy levels of about $0.3\text{--}1 \text{ cm}^{-1}$. Despite their very different magnitudes, the ligand-field and ZFS terms H_{lig} and H_{ZFS} stem from electrostatic interactions acting on $4f$ electrons so that they can be expressed as homogeneous polynomials of even order $k \leq 6$ in the components J_x, J_y, J_z of \mathbf{J} and S_x, S_y, S_z, S_z of \mathbf{S} , respectively.²⁴ The electronic relaxation of the fast relaxing Ln^{3+} and of Gd^{3+} is due to the fluctuations in the laboratory (L) frame of the ligand-field and ZFS Hamiltonians, respectively. A convenient description of these fluctuating Hamiltonians rests on their definition in a molecular (M) frame rigidly bound to the mean conformation of the complex. This description amounts to neglecting the possibility of several equilibrium conformations. In the (M) frame, the ligand-field $H_{\text{lig}}^{(M)}(t)$ is the sum of its time average called the static ligand-field $H_{\text{lig},S}^{(M)}$ and of its fluctuating part $H_{\text{lig},T}^{(M)}(t)$ called the transient ligand-field.^{10,28–32}

$$H_{\text{lig}}^{(M)}(t) = H_{\text{lig},S}^{(M)} + H_{\text{lig},T}^{(M)}(t). \quad (1)$$

Then, the formalism extensively developed for describing the electronic relaxation of Gd^{3+} applies to that of the fast relaxing Ln^{3+} by replacing the spin \mathbf{S} of Gd^{3+} by the total angular momentum \mathbf{J} of Ln^{3+} . It is convenient to express the ligand-field Hamiltonians in terms of the components t_k^q of the normalized (nor) Racah spherical tensors,^{33,34} which are homogeneous polynomials of order k in the components J_x, J_y, J_z of \mathbf{J} . The operators t_k^q are defined by their matrix elements in the standard basis $|JM\rangle$ of the ground multiplet. These elements are given in terms of $3j$ -symbols by

$$\langle JM' | t_k^q | JM \rangle = (-1)^{J-M'} \sqrt{2k+1} \begin{pmatrix} J & k & J \\ -M' & q & M \end{pmatrix}. \quad (2)$$

Note that the t_k^q are also normalized with

$$\text{tr } t_k^{q\dagger} t_{k'}^{q'} = \delta_{kk'} \delta_{qq'}, \quad (3)$$

where tr is the trace over the $(2J+1)$ states $|JM\rangle$ of the ground multiplet. The static ligand-field term reads as

$$H_{\text{lig},S}^{(M)} = \sum_{k=2,4,6} H_{\text{lig},S,k}^{(M)} = \sum_{k=2,4,6} B_{S,k} \sum_{q=-k}^k b_{S,k}^q t_k^q, \quad (4)$$

where the real energy parameters $B_{S,k}$ describe the magnitudes of the contributions of order k . In Eq. (4), the normalized complex coefficients $b_{S,k}^q$ are determined so that the linear combinations $\sum_q b_{S,k}^q t_k^q$ are invariant under the local symmetry group of the complex with $\sum_q |b_{S,k}^q|^2 = 1$.

Here, we use the t_k^q instead of the usual Buckmaster (Buck) tensor operators T_k^q defined as³⁴

$$T_k^q = \sqrt{A_k(J)} t_k^q \quad (5)$$

with

$$A_k(J) = (k!)^2 \frac{(2J+k+1)!}{2^k(2k+1)!(2J-k)!}. \quad (6)$$

When $H_{lig,S}^{(M)}$ in Eq. (4) is expanded as a sum of T_k^q , the energy parameters $B_{S,k}$ should be replaced by their Buckmaster counterparts $B_{S,k}^{Buck} = B_{S,k}/\sqrt{A_k(J)}$. The interest of employing the t_k^q is that the total splitting Δ_S of the multiplet J due to the Hamiltonian $H_{lig,S}^{(M)}$ is, as discussed hereafter, approximately equal to its norm $\|H_{lig,S}\|$ simply given by

$$\|H_{lig,S}\| = \left[\text{tr} \left(\left(H_{lig,S}^{(M)} \right)^\dagger H_{lig,S}^{(M)} \right) \right]^{1/2} = \left[\sum_{k=2,4,6} B_{S,k}^2 \right]^{1/2}. \quad (7)$$

When only one contribution $H_{lig,S,k}^{(M)}$ is involved, we have $\|H_{lig,S}\| \equiv |B_{S,k}|$.

Typically, for an axial symmetry of the complex, the various contributions of $H_{lig,S}^{(M)}$ read as

$$\begin{cases} H_{lig,S,2}^{(M)} = B_{S,2} t_2^0 = \frac{B_{S,2}}{\sqrt{6A_2(J)}} [3J_z^2 - J(J+1)] \\ H_{lig,S,4}^{(M)} = B_{S,4} t_4^0 \\ H_{lig,S,6}^{(M)} = B_{S,6} t_6^0 \end{cases}, \quad (8)$$

while for a cubic symmetry the 4th and 6th order contributions are

$$\begin{cases} H_{lig,S,4}^{(M)} = B_{S,4} \sqrt{\frac{7}{12}} \left[t_4^0 + \sqrt{\frac{5}{14}} (t_4^4 + t_4^{-4}) \right] \\ H_{lig,S,6}^{(M)} = B_{S,6} \sqrt{\frac{1}{8}} \left[t_6^0 - \sqrt{\frac{7}{2}} (t_6^4 + t_6^{-4}) \right] \end{cases}. \quad (9)$$

In crystals, the total amplitudes of the ligand-field splitting Δ_S of the ground multiplets range between 100 and 500 cm^{-1} for all the Ln^{3+} ions,^{35,36} except Gd^{3+} , for which the $^8S_{7/2}$ ground level has its orbital angular momentum fully quenched, and Eu^{3+} with $J=0$ in its 7F_0 ground state. It is expected that the ligand-field remains of similar magnitude for a complex in solution.

On the way to understanding the fast electronic relaxation of complexed Ln^{3+} ions in solution, the first useful result is that the ratio $\Delta_S/\|H_{lig,S}\|$ of the total splitting Δ_S arising from a pure $H_{lig,S}^{(M)}$ Hamiltonian and the norm of this term is always close to unity as shown in Table I for Tb^{3+} , Er^{3+} , and Yb^{3+} in axial or cubic symmetry. Thus, the norms $\|H_{lig,S}\|$ also range between 100 and 500 cm^{-1} for all the Ln^{3+} ions.

The transient ligand-field $H_{lig,T}^{(M)}(t)$ results from the deformations (distortions) of the complex, which are induced by its collisions with the solvent molecules and are generally nicknamed “vibrations” (v). The exact description of these deformations is very difficult because they are not limited by any symmetry requirement and their time variation is

TABLE I. Ratios $\Delta_S/\|H_{lig,S}\|$ of the total splitting Δ_S of a static ligand-field Hamiltonian $H_{lig,S}$ of pure order k divided by the norm $\|H_{lig,S}\|$ of this Hamiltonian for selected Ln^{3+} ions in axial or cubic symmetry.

Ln^{3+}	$\text{Tb}^{3+} (J=6)$	$\text{Er}^{3+} (J=15/2)$	$\text{Yb}^{3+} (J=7/2)$
$k=2$ axial	0.80	0.74	0.93
$k=4$ axial	0.75	0.72	0.89
$k=6$ axial	0.82	0.73	0.86
$k=4$ cubic	0.70	0.62	0.98
$k=6$ cubic	0.91	0.74	0.78

unknown. For this reason, we adopt a semi-classical model in which the deformations are treated as very fast random pseudo-rotations^{37–39} of the complex in the (M) frame. A similar approach was already successively used for describing the electronic relaxation of Gd^{3+} complexes in solution due to a transient ZFS.^{10,30,31} Then, by analogy with expression (4), the transient ligand-field reads in a molecular frame (M') different from (M) as

$$H_{lig,T}^{(M')} = \sum_{k=2,4,6} H_{lig,T,k}^{(M')} = \sum_{k=2,4,6} B_{T,k} \sum_{q=-k}^k b_{T,k}^q t_k^q. \quad (10)$$

The transformation of $H_{lig,T}^{(M')}$ to $H_{lig,T}^{(M)}(t)$ is performed by using the quantum rotation operator $\mathbf{R}(t)$ associated with the 3D pseudo-rotation $\mathcal{R}(t)$ transforming (M) into (M') according to the relation,

$$H_{lig,T}^{(M)}(t) = \mathbf{R}'(t) H_{lig,T}^{(M')} (\mathbf{R}'(t))^{-1}. \quad (11)$$

The transient correlation times of the terms of order k of $H_{lig,T}^{(M)}(t)$ due to the Brownian pseudo-rotation are^{7,28,40}

$$\tau_{v,k} = \frac{1}{D_V k(k+1)} = \frac{6\tau_{v,2}}{k(k+1)}. \quad (12)$$

D_V (s^{-1}) being a formal pseudo-rotational diffusion coefficient. In order to describe the fluctuations of the transient ligand-field, the pseudo-rotation formalism is preferred because of its simplicity to the Ornstein-Uhlenbeck process which was initially used in our simulation method.⁴¹ Indeed, both approaches assume that the transient motions (here, pseudo-rotations) and actual rotations are independent. They lead to identical results within the Redfield approximation.

The splitting between the various ligand-field levels of all the investigated Ln^{3+} ions is typically of about a few tens of cm^{-1} .^{24,25,35,36} It is generally much larger than the Zeeman coupling even at rather high field. The situation is very similar to that of Gd^{3+} at very low fields when the ZFS of the order of 0.1 cm^{-1} dominates the Zeeman interaction.

The values of $\tau_{v,k}$ for the investigated Ln^{3+} complexes are expected to be similar to those involving the Gd^{3+} complexes,^{28,29,42} i.e., of the order of 10^{-13} – 10^{-12} s, since the distortions-vibrations mechanisms are caused by nearly identical collision dynamics with the solvent for all the Ln^{3+} complexes. The correlation time $\tau_{v,2}$ can also be approximated as the inverse of the collision frequency between the complex and the solvent molecules. Assuming a Maxwellian distribution of speed of the molecules and using simple collision models, this frequency is easily estimated to be about

10^{13} s^{-1} for a spherical complex 0.7 nm in diameter in water at room temperature. This estimate is confirmed by molecular dynamics simulation.^{42,43}

It is not easy to know the energy parameters $B_{T,k}$. In solids, Scott and Jeffries^{24,44} considered that they are comparable to the static parameters $B_{S,k}$. This assumption is supported by the results of Newman and Ng²⁵ who showed that the amplitudes of the static coefficients $B_{S,k}$ are multiplied by a factor ranging from 1.5 ($k = 2$) to 3 ($k = 6$) for a 10% decrease of the metal-ligand distance. These parameter variations were experimentally corroborated by the study of the optical spectra modifications induced by a high hydrostatic pressure up to $1.5 \times 10^{10} \text{ N m}^{-2}$ for Pr^{3+} in LaOCl .⁴⁵ Such a value also corresponds to the instantaneous pressure of about $2 \times 10^{10} \text{ N m}^{-2}$ induced by the collision of a water molecule on a complex at room temperature when assuming an inversion of the average speed of that molecule over a penetration depth of 0.01 nm. All these arguments show that the $B_{T,k}$ and $B_{S,k}$ parameters should be of similar magnitudes.

B. The relaxation mechanisms

The electronic relaxation of the considered Ln^{3+} ions due to the Hamiltonian $H_{lig}^{(M)}(t)$ defined by Eq. (1) results from the fluctuations of both its static $H_{lig,S}^{(L)}(t)$ and transient $H_{lig,T}^{(L)}(t)$ contributions in the laboratory frame (L).^{9,10,30–32,37–39} These contributions are

$$H_{lig,S}^{(L)}(t) = \mathbf{R}(t) H_{lig,S}^{(M)}(t) \mathbf{R}(t)^{-1}, \quad (13)$$

$$H_{lig,T}^{(L)}(t) = \mathbf{R}(t) H_{lig,T}^{(M)}(t) \mathbf{R}(t)^{-1}, \quad (14)$$

where $\mathbf{R}(t)$ is the quantum rotation operator associated with the true random rotation $\mathfrak{R}(t)$ of the complex, transforming (L) into (M). The correlation times of this rotational Brownian motion are^{7,28,40}

$$\tau_k = \frac{1}{D_R k(k+1)} = \frac{6\tau_2}{k(k+1)}. \quad (15)$$

D_R being the rotational diffusion constant of the complex. It should be noted that the time evolution of the actual rotation $\mathfrak{R}(t)$, hence of $\mathbf{R}(t)$ in Eq. (14), is much slower than that of the pseudo-rotation $\mathfrak{R}'(t)$, hence of $\mathbf{R}'(t)$ in Eq. (11), so that the actual Brownian rotation of the complex has negligible effects on the fluctuations of the transient ligand-field term $H_{lig,T}^{(L)}(t)$.

Quite generally, consider a real sample containing N_{sys}^{real} identical paramagnetic Ln^{3+} complexes (systems) j ($1 \leq j \leq N_{sys}^{real}$) with total angular momentum J . The longitudinal and transverse time correlation functions (TCFs) describing their relaxation are^{9,10,30–32}

$$G_{//}(t) = \frac{1}{N_{sys}^{real}} \sum_{j=1}^{N_{sys}^{real}} \frac{1}{2J+1} \text{tr} [U_j(t)^\dagger J_{zj} U_j(t) J_{zj}], \quad (16)$$

$$G_{\perp}(t) = \frac{1}{N_{sys}^{real}} \sum_{j=1}^{N_{sys}^{real}} \frac{1}{2J+1} \text{tr} [U_j(t)^\dagger J_{+j} U_j(t) J_{-j}], \quad (17)$$

where $U_j(t)$ is the unitary time evolution operator acting on the system j and the trace tr is taken over the $(2J+1)$ states $|JM\rangle$ of the J multiplet. It can be shown that the decays of $G_{//}(t)$ and $G_{\perp}(t)$ are identical to the evolution towards equilibrium of the macroscopic magnetizations $M_z = -g_J \mu_B \langle J_z \rangle$ and $M_{\pm} = -g_J \mu_B \langle J_x \pm iJ_y \rangle$ after a perturbation. Therefore, the usual electronic relaxation times T_{1e} and T_{2e} are provided by the evolution of $G_{//}(t)$ and $G_{\perp}(t)$ when they decay mono-exponentially. In what follows, in order to compare the relaxation of different Ln^{3+} ions, it is convenient to introduce the normalized TCFs defined as

$$\begin{cases} G_{//}^{nor}(t) = G_{//}(t)/G_{//}(0) \\ G_{\perp}^{nor}(t) = G_{\perp}(t)/G_{\perp}(0) \end{cases} \quad (18)$$

Consequently, in the laboratory frame (L) with an external magnetic field B_0 along the z direction, the full Hamiltonian of the Ln^{3+} system is a time-dependent random operator $H(t)$ given by

$$H(t) = \hbar \omega_J J_z + H_{lig,S}^{(L)}(t) + H_{lig,T}^{(L)}(t), \quad (19)$$

where $\hbar \omega_J J_z = g_J \mu_B B_0 J_z$ is the time-independent Zeeman term and $H_{lig,S}^{(L)}(t)$, $H_{lig,T}^{(L)}(t)$ represent the time-fluctuating ligand-field terms defined by Eqs. (13) and (14).

C. The longitudinal relaxation rate

The evaluation of the longitudinal electronic relaxation of the Ln^{3+} ions will be successively studied through the approximate analytical Redfield theory and a numerical Monte-Carlo simulation method.

1. The Redfield approach

In the framework of the Redfield approximation, we had calculated the electronic relaxation rate R_{1e} due to a fluctuating static ZFS Hamiltonian $\sum_{k=2,4,6} B_k^{Buck} \sum_{q=-k}^k b_k^q T_k^q$ acting on a spin S .^{28,40} From our previous results,⁴⁶ replacing the spin S by the Ln^{3+} total angular momentum J and using the normalized tensors t_k^q , it is easy to derive the contribution $R_{1e,S}$ of a fluctuating static ligand-field term $\sum_{k=2,4,6} B_{S,k} \sum_{q=-k}^k b_{S,k}^q t_k^q$ to R_{1e} . This contribution is

$$R_{1e,S} = \frac{6}{(2J+1)J(J+1)(2k+1)} \sum_{k=2,4,6} \left(\frac{B_{S,k}}{\hbar} \right)^2 \tau_k \times \sum_{n=1}^k \frac{n^2}{1 + (n \omega_J \tau_k)^2}, \quad (20)$$

where τ_k is given by Eq. (15). The contribution $R_{1e,T}$ of a fluctuating transient ligand-field term $\sum_{k=2,4,6} B_{T,k} \sum_{q=-k}^k b_{T,k}^q t_k^q$ to R_{1e} is given by an expression similar to Eq. (20) obtained by replacing $B_{S,k}$ by $B_{T,k}$ and τ_k by $\tau_{v,k}$ with $\tau_{v,k} \ll \tau_k$.^{28,32,41,42,47} At zero external field, according to Eqs. (7), (12), (15), and (20), the

rates $R_{1e,S}$ and $R_{1e,T}$ take the very simple forms

$$R_{1e,S}(B_0 = 0) = \frac{1}{T_{1e,S}}(B_0 = 0) = \frac{6\tau_2}{(2J+1)J(J+1)} \times \left(\frac{\|H_{lig,S}\|}{\hbar} \right)^2, \quad (21)$$

$$R_{1e,T}(B_0 = 0) = \frac{1}{T_{1e,T}}(B_0 = 0) = \frac{6\tau_{v,2}}{(2J+1)J(J+1)} \times \left(\frac{\|H_{lig,T}\|}{\hbar} \right)^2, \quad (22)$$

fully determined by the norms of the ligand-field Hamiltonians, independently of the relative magnitudes of the contributing terms of order k . In other words, within the Redfield approximation, two static ligand-field terms of different orders $k_1 \neq k_2$ with the same amplitude $|B_{S,k_1}| = |B_{S,k_2}|$ induce the same relaxation rates at $B_0 = 0$ T. This is also true for transient ligand-field terms. Note that the norm is independent of the reference frame of the ligand-field Hamiltonian so that its superscript (M), (M'), or (L) indicating this frame can be dropped.

The validity of the Redfield approximation is limited by the loosely defined conditions $\|H_{lig,S}\|\tau_2/\hbar < 1$ and $\|H_{lig,T}\|\tau_{v,2}/\hbar < 1$.^{9,10,37–39} According to previous discussion the norm of the static and transient ligand-field Hamiltonians range between 100 and 500 cm^{-1} . Since the rotational correlation time τ_2 is of the order of 100 ps or longer, we have $\|H_{lig,S}\|\tau_2/\hbar > 2000$ and the Redfield theory does not apply. Besides, as $\tau_{v,k}$ is expected to be of the order or shorter than 0.1 ps, we have $\|H_{lig,T}\|\tau_{v,2}/\hbar \leq 10$ and the Redfield equation (22) is expected to only provide rough estimates of $T_{1e,T}$. However, the importance of Eq. (22) will be shown in Sec. III since it yields an upper limit of R_{1e} rather close to the simulated values.

2. Numerical simulation

The simulation (sim) of the TCFs $G_{//}(t)$, $G_{\perp}(t)$ defined by Eqs. (16) and (17), is carried out by replacing the real number $N_{sys}^{real} \cong N_{Avogadro}$ of Ln^{3+} systems by a much smaller, but still significant number $N_{sys}^{sim} \cong 500$ to 100 000 of replicas which initially have representative random initial isotropic orientations and vibrational configurations (here, isotropic pseudo-orientations) and then undergo rotational and vibrational Brownian motions. This procedure has been applied several times to Gd^{3+} complexes.^{9,10,30–32,41,46} Its practical implementation has been carefully explained recently.³² When compared to the alternative methods used for computing the electronic spin relaxation,^{10,39,48} the main features of the present approach are the statistical simulation in the time domain of the evolution of the electronic states of the J multiplet and the direct use of the Schrödinger equation for obtaining this evolution. More precisely, for each system j ($1 \leq j \leq N_{sys}^{sim}$), the evolution operator $U_j(t)$ at time $t = (L-1)\Delta t$ with L integer ($1 \leq L \leq NT$) is the discrete numerical solution

of the Schrödinger equation,

$$i\hbar \frac{dU_j(t)}{dt} = H_j(t)U_j(t) \quad (23)$$

with $U_j(0) = 1$, $H_j(t)$ being the Hamiltonian of Eq. (19) for the system j . The value of $H_j(t)$ at time t is generated through successive rotations and pseudo-rotations.^{32,49} Details on the statistical convergence and computing time of the present simulations are given in the supplementary material.⁵⁰

When $G_{//}^{nor}(t)$ has a mono-exponential decay $G_{//}^{nor}(t) = \exp(-t/T_{1e})$ with a longitudinal relaxation time T_{1e} , we have $\int_0^\infty \exp(-t/T_{1e})dt = T_{1e}$. In the general case when the decay of $G_{//}^{nor}(t)$ deviates from a simple exponential law, T_{1e} is replaced by an effective relaxation time T_{1e}^{eff} defined as

$$T_{1e}^{eff} = \int_0^\infty G_{//}^{nor}(t) dt. \quad (24)$$

III. RESULTS AND DISCUSSION

We focus on the simulation of the relaxation behavior of Yb^{3+} complexes because its rather low value of $J = 7/2$ reduces the computation time. Since the experimental electronic relaxation is almost independent of the magnetic field B_0 , all results are discussed for $B_0 = 0$ T unless explicitly stated otherwise.

In Fig. 1, we display the TCFs $G_{//}^{nor}(t)$ of a YbL complex induced by either a purely static ligand-field Hamiltonian $H_{lig,S}^{(L)}(t)$ or a purely transient ligand-field Hamiltonian $H_{lig,T}^{(L)}(t)$. We assume that $H_{lig,S}^{(L)}(t)$ derives from the axial Hamiltonian $H_{lig,S,2}^{(M)}$ of order 2 given by Eq. (8) with a reasonable norm $\|H_{lig,S}\| = B_{S,2} = 320 \text{ cm}^{-1}$ ($B_{S,2}^{Buck} = 20 \text{ cm}^{-1}$) and a rotational correlation time $\tau_2 = 100$ ps. We also assume that $H_{lig,T}^{(M)}(t)$ stems from a similar axial term of order 2, $H_{lig,T}^{(M')} = B_{T,2}t_2^0$, with the same norm $\|H_{lig,T}\| = B_{T,2} = 320 \text{ cm}^{-1}$ and a vibrational correlation time $\tau_{v,2} = 0.1$ ps. We observe that the static ligand-field induces an oscillatory

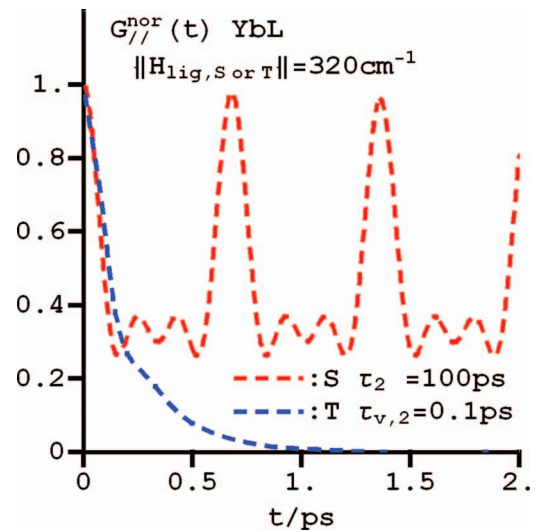


FIG. 1. Time evolution of $G_{//}^{nor}(t)$ of a YbL complex induced by either a purely axial static (S) ligand-field Hamiltonian $H_{lig,S}$ of order 2 or a purely axial transient (T) ligand-field Hamiltonian $H_{lig,T}$ of order 2.

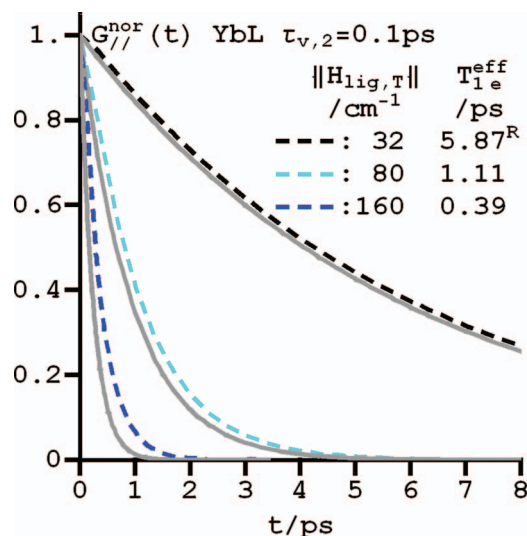


FIG. 2. Time evolution of $G_{||}^{nor}(t)$ of a YbL complex induced by a purely axial transient ligand-field Hamiltonian $H_{lig,T}$ of order 2 with various magnitudes $\|H_{lig,T}\|$ and a vibrational correlation time $\tau_{v,2} = 0.1$ ps. The Redfield predictions are represented by grey lines. The superscript R indicates a result of the Redfield theory.

behavior of $G_{||}^{nor}(t)$ with a decay of characteristic time significantly longer than 1 ps, which is much too slow for explaining the very fast experimental electronic relaxation. By contrast, the purely transient ligand-field leads to a monotonous decrease of $G_{||}^{nor}(t)$ with an effective electronic relaxation time $T_{1e}^{eff} = 0.19$ ps, in agreement with the observed values for Yb^{3+} complexes.^{11,12,14-16}

Because of the weak contribution of the static ligand-field fluctuations to the electronic relaxation, we will concentrate on the effects of various realistic purely transient ligand-field Hamiltonians.

In Fig. 2, the simulated TCFs $G_{||}^{nor}(t)$ are compared to their analytical counterparts of the Redfield theory for a purely transient axial term $H_{lig,T}^{(M')} = H_{lig,T,2}^{(M')} = B_{T,2}t_2^0$ of order 2 with vibrational correlation time $\tau_{v,2} = 0.1$ ps and increasing norm $\|H_{lig,T}\| = B_{T,2} = 32, 80$, and 160 cm^{-1} , corre-

sponding to $\|H_{lig,T}\|\tau_{v,2}/\hbar = 0.6, 1.5$, and 3 , respectively. For the smallest ligand-field 32 cm^{-1} , the simulation nearly reproduces the mono-exponential decay predicted by the Redfield theory with $T_{1e}^{eff} \cong T_{1e}^{Redfield} = 5.87$ ps calculated from Eq. (22). For the intermediate value 80 cm^{-1} , the simulated TCF slightly deviates from its Redfield counterpart leading to $T_{1e}^{eff} = 1.11$ ps instead of $T_{1e}^{Redfield} = 0.94$ ps. Finally, for the highest ligand-field 160 cm^{-1} , we get $T_{1e}^{eff} = 0.39$ ps and $T_{1e}^{Redfield} = 0.23$ ps, showing the limit of applicability of the Redfield approximation.

In Fig. 3, we show the variations of $G_{||}^{nor}(t)$ and T_{1e}^{eff} with both the magnitude of $H_{lig,T}^{(M')} = B_{T,2}t_2^0$ and of the vibrational correlation time $\tau_{v,2}$. An increase of $\tau_{v,2}$ by a factor of 8 from 0.05 to 4 ps induces a variation of T_{1e}^{eff} less than about 50%. Moreover, an increase of $\|H_{lig,T}\|$ by a factor of 2 leads to a decrease of T_{1e}^{eff} by a factor significantly smaller than the value of 4 predicted by the Redfield equation (22). This reduction factor drops from 2.8 to 1.4 as $\tau_{v,2}$ increases from 0.05 to 4 ps. Consequently, the changes of $\tau_{v,2}$ and $\|H_{lig,T}\|$ have much less impact on T_{1e}^{eff} than on its Redfield counterpart and the impact of $\|H_{lig,T}\|$ even drops as $\tau_{v,2}$ becomes longer.

In Fig. 4, we study how the symmetry and the order of the transient ligand-field Hamiltonian affect $G_{||}^{nor}(t)$ and T_{1e}^{eff} . For fixed values of $\|H_{lig,T}\| = 320 \text{ cm}^{-1}$ and $\tau_{v,2} = 0.1$ ps, we have calculated the decay of $G_{||}^{nor}(t)$ successively for the axial Hamiltonians of pure order 2, 4, or 6 defined in Eq. (8), for the cubic Hamiltonians of pure order 4 or 6 defined in Eq. (9), and for various sums of these terms with equal weights. We observe that the symmetry and tensorial order of the transient ligand-field have modest influence on the shape of the decay of $G_{||}^{nor}(t)$ and on the values of T_{1e}^{eff} which hardly vary by a factor of 2. In all situations, the Redfield approximation predicts the same too fast decay with a relaxation time $T_{1e}^{Redfield} = 0.06$ ps, which is too short by a factor ranging between 2 and 4.

Although we have shown in Fig. 1 that a pure static ligand-field Hamiltonian $H_{lig,S}^{(L)}(t)$ is not an effective

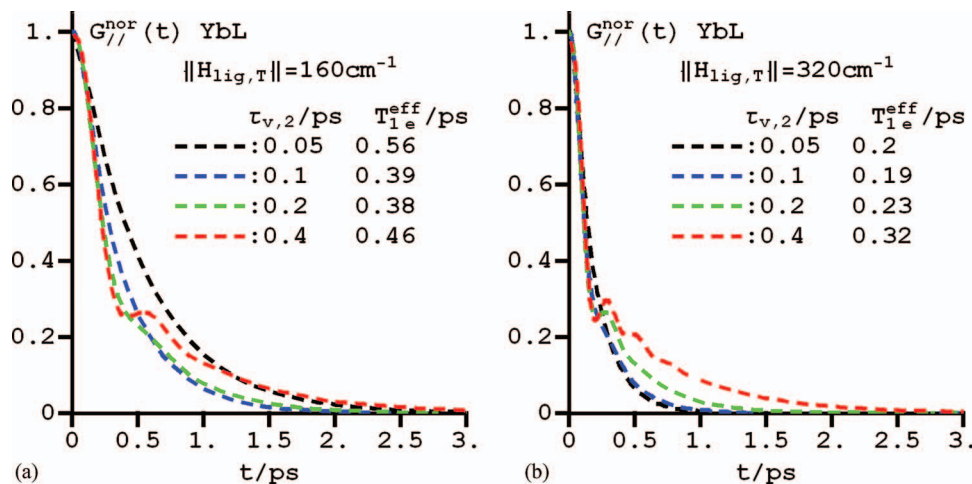


FIG. 3. Time evolution of $G_{||}^{nor}(t)$ of a YbL complex induced by a purely axial transient ligand-field Hamiltonian $H_{lig,T}$ of order 2 for various correlation times $\tau_{v,2}$. (a) $\|H_{lig,T}\| = 160 \text{ cm}^{-1}$, (b) $\|H_{lig,T}\| = 320 \text{ cm}^{-1}$.

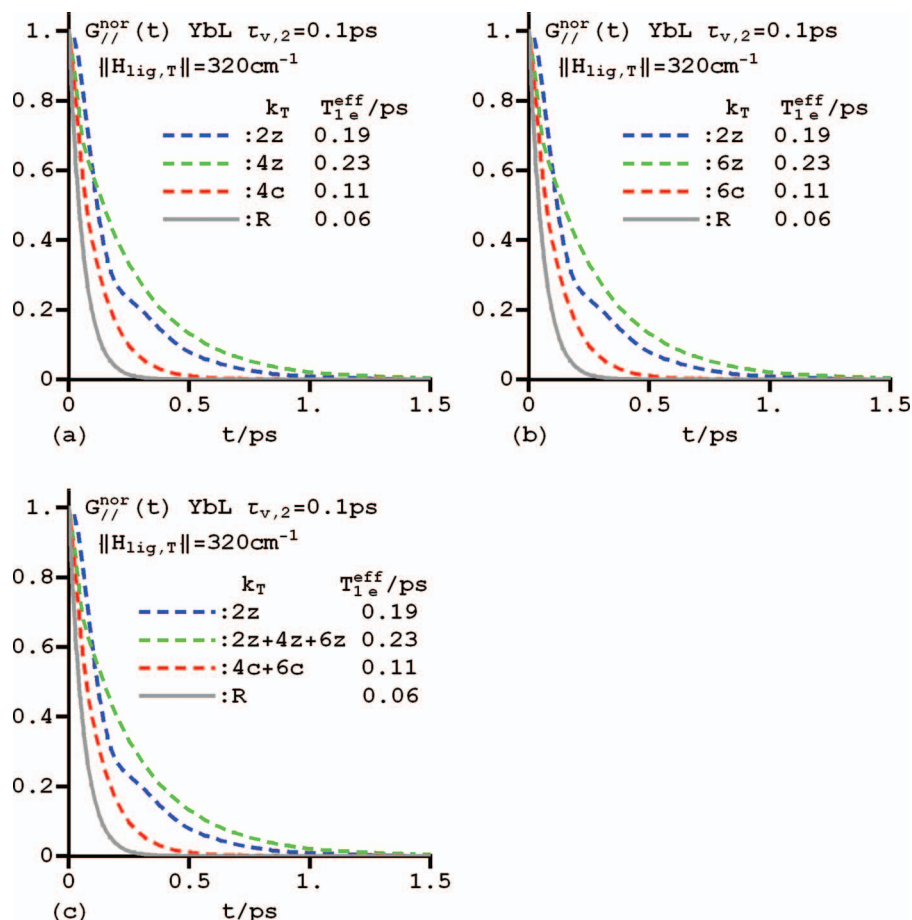


FIG. 4. Time evolution of $G_{||}^{nor}(t)$ of a YbL complex induced by various transient ligand-field terms $H_{lig,T}$ of fixed magnitude $\|H_{lig,T}\| = 320 \text{ cm}^{-1}$ and vibrational correlation time $\tau_{v,2} = 0.1 \text{ ps}$. Notations: 2z, 4z, and 6z are axial Hamiltonians of pure order 2, 4, or 6; 4c and 6c are cubic Hamiltonians of pure order 4 or 6; 2z + 4z + 6z is the sum of the axial Hamiltonians of order 2, 4, and 6 with equal weights; 4c + 6c is the sum of the cubic Hamiltonians of order 4 and 6 with equal weights; and R is the result of the Redfield theory. Changes of the evolution of $G_{||}^{nor}(t)$ due to (a) terms of order 4, (b) terms of order 6, and (c) mixture of terms.

relaxation mechanism, it is interesting to determine the modifications brought by the inclusion of this term in the total ligand-field Hamiltonian $H_{lig}^{(L)}(t)$. In Fig. 5, we display $G_{||}^{nor}(t)$ for fixed norms $\|H_{lig,S}\| = \|H_{lig,T}\| = 320 \text{ cm}^{-1}$ and correlation times $\tau_2 = 100 \text{ ps}$, $\tau_{v,2} = 0.1 \text{ ps}$. The transient term $H_{lig,T}^{(M')} = B_{T,2}t_2^0$ is axial of order 2 while axial and cubic Hamiltonians of various pure order k_S are considered for the static term. It is clear that the values of T_{le}^{eff} vary by less than 40% with respect to the purely transient case ($k_S = 0$), except in the very particular situation of a pure cubic static term of order 6. Note that for any pure static ligand-field with $\|H_{lig,S}\| = 320 \text{ cm}^{-1}$, the Redfield equation (21) leads at zero field to the unphysical value $T_{le}^{Redfield} = 0.06 \times 10^{-3} \text{ ps}$, which is three orders of magnitude shorter than the simulated and experimental values.

In Fig. 6, we compare the decays of $G_{||}^{nor}(t)$ for three Ln^{3+} complexes YbL, TbL, and ErL for which the ground multiplet has a total angular momentum $J = 7/2, 6$, and $15/2$, respectively. Two situations are studied. First, we simply consider the influence of an axial transient ligand-field $H_{lig,T}^{(M')} = B_{T,2}t_2^0$ of order 2 with the norm $\|H_{lig,T}\| = 320 \text{ cm}^{-1}$ which was shown to be representative of the electronic relaxation

behavior. Second, we add a purely cubic static ligand-field $H_{lig,S}^{(M)} = H_{lig,S,4}^{(M)}$ of order 4 with the same norm 320 cm^{-1} . In all cases, T_{le}^{eff} increases by a factor of 3 when J is doubled. For Yb^{3+} , Tb^{3+} , and Er^{3+} , the values of $T_{le}^{Redfield}$ for the purely transient ligand-field are 0.06, 0.25, and 0.48 ps, respectively. These values are shorter than their simulated counterparts $T_{le}^{eff} = 0.19, 0.42$, and 0.65 ps , with differences that significantly reduce with increasing J . These values are also rather similar to their simulated counterparts $T_{le}^{eff} = 0.11, 0.21$, and 0.35 ps including the effects of the purely cubic static ligand-field, with deviations by less than 40% for Tb^{3+} and Er^{3+} .

We also checked⁵⁰ that the decay of $G_{||}^{nor}(t)$ is practically independent of the magnetic field B_0 up to 5 T and then slightly slows down with increasing field. The values of T_{le}^{eff} lengthen by less than a few percents from 0 to 23.5 T in agreement with the experimental data.^{11–14} Note that the upper limit 23.5 T of the investigated field values is the maximal field of the commercial high-resolution spectrometers, giving rise to a proton resonance frequency of 1 GHz.

As shown in Ref. 50, Fig. S5, it is worth mentioning the weak relaxation effects of an additional axial transient ligand-field $H_{lig,T,b}^{(M_b)} = B_{Tb,2}t_2^0$ of order 2 with norm $\|H_{lig,T,b}\|$

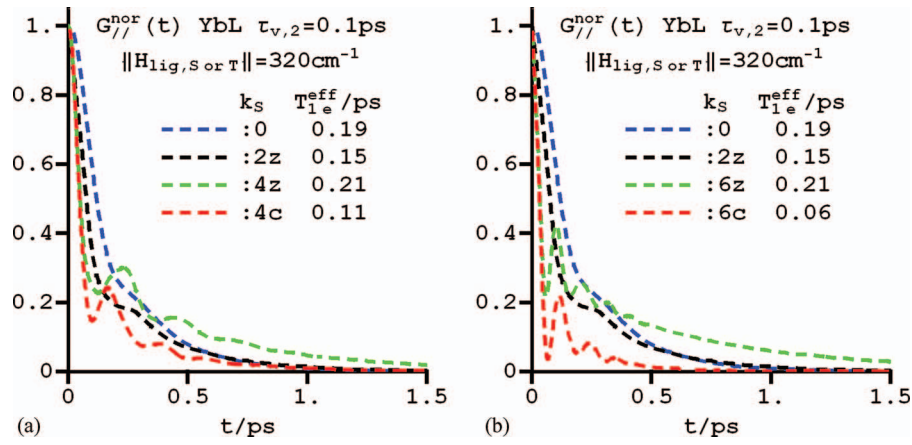


FIG. 5. Time evolution of $G_{\perp}^{\text{nor}}(t)$ of a YbL complex induced by an axial transient ligand-field $H_{\text{lig},T}$ of order 2 with norm $\|H_{\text{lig},T}\| = 320 \text{ cm}^{-1}$ to which static ligand-fields of axial and cubic symmetry of various orders k_s are added. The correlation times are $\tau_2 = 100 \text{ ps}$ and $\tau_{v,2} = 0.1 \text{ ps}$. Notations: 0 is a purely axial transient Hamiltonian; 2z, 4z, and 6z indicate the addition of axial static ligand-fields of pure order 2, 4, or 6; 4c and 6c indicate the addition of cubic static ligand-fields of pure order 4 or 6. (a) Effects of static terms of order 4; (b) effects of static terms of order 6.

$= 320 \text{ cm}^{-1}$ and correlation time $\tau_{vb,2} = 1 \text{ ps}$, which is superimposed to the reference axial transient ligand-field $H_{\text{lig},T,a}^{(M'_a)} = B_{Ta,2}t_2^0$ of order 2 with norm $\|H_{\text{lig},T,a}\| = 320 \text{ cm}^{-1}$ and correlation time $\tau_{va,2} = 0.1 \text{ ps}$. From $B_0 = 0$ to 23.5 T, this additional ligand-field provides an acceleration of the electronic relaxation rate $1/T_{1e}^{\text{eff}}$ by less than 40% whereas the Redfield theory predicts an acceleration by a factor of more than 30. Similarly, if the additional ligand-field $H_{\text{lig},T,b}^{(M'_b)}$ with norm 320 cm^{-1} has a very short correlation time $\tau_{vb,2} = 0.01 \text{ ps} \ll \tau_{va,2}$, its contribution to the relaxation can be calculated within the Redfield theory and also provides a small acceleration of $1/T_{1e}^{\text{eff}}$ by less than 40%. This indicates that the reference transient ligand-field $H_{\text{lig},T,a}^{(M'_a)}$ with norm 320 cm^{-1} as well as the other transient ligand-fields of similar norm give rise to an almost optimal relaxation mechanism for the correlation time $\tau_{va,2} = 0.1 \text{ ps}$.

Finally, we simulated the decays of $G_{\perp}^{\text{nor}}(t)$ defined by Eqs. (17) and (18) for each investigated complex. For a fast relaxing Ln^{3+} , the real part $\text{Re}[G_{\perp}^{\text{nor}}(t)]$ of $G_{\perp}^{\text{nor}}(t)$ cannot be

distinguished from $G_{\perp}^{\text{nor}}(t)$ and its imaginary part $\text{Im}[G_{\perp}^{\text{nor}}(t)]$ remains small up to $B_0 = 5 \text{ T}$ as shown in Fig. S4.⁵⁰ Then, by analogy with Eq. (24), it is possible to define an auxiliary (aux) transverse relaxation time,

$$T_{2e}^{\text{eff,aux}} = \int_0^{\infty} \text{Re}[G_{\perp}^{\text{nor}}(t)] dt, \quad (25)$$

which is nearly equal to T_{1e}^{eff} . This legitimates the introduction in the literature of a unique relaxation time $\tau_{s0} = T_{1e}^{\text{eff}} = T_{2e}^{\text{eff,aux}}$. However, with increasing field, $G_{\perp}^{\text{nor}}(t)$ shows faster and faster oscillations at the angular Larmor electronic frequency^{9,50} ω_J . The definition of the transverse relaxation time $T_{2e}^{\text{eff,aux}}$ in Eq. (25) becomes inappropriate when the associated period $2\pi/\omega_J$ stops being much longer than $T_{2e}^{\text{eff,aux}}$. Introducing the slowly varying modulated transverse TCF $G_{\perp}^{\text{nor,slow}}(t) = G_{\perp}^{\text{nor}}(t)e^{-i\omega_J t}$, it should be replaced by the more general definition,

$$T_{2e}^{\text{eff}} = \int_0^{\infty} \text{Re}[G_{\perp}^{\text{nor}}(t)e^{-i\omega_J t}] dt. \quad (26)$$

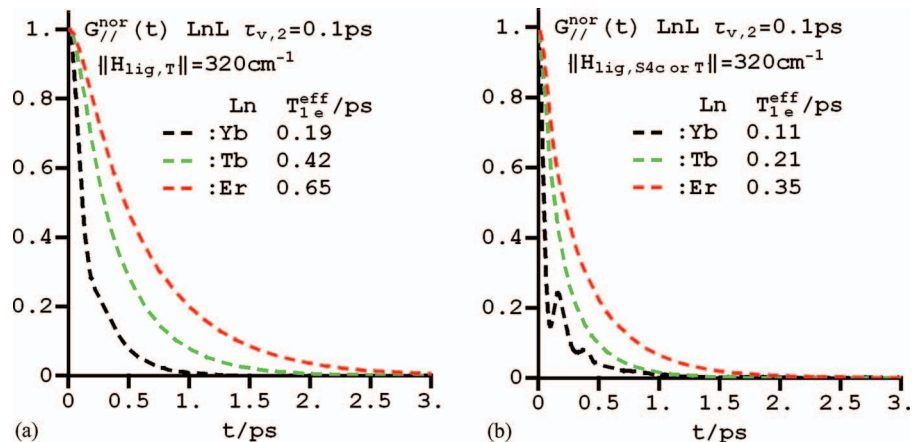


FIG. 6. Time evolution of $G_{\perp}^{\text{nor}}(t)$ of YbL, TbL, and ErL complexes induced by (a) a purely axial transient ligand-field $H_{\text{lig},T}$ of order 2 with $\|H_{\text{lig},T}\| = 320 \text{ cm}^{-1}$, and (b) the same transient ligand-field superimposed to a static cubic ligand-field $H_{\text{lig},S}$ of order 4 with $\|H_{\text{lig},S}\| = 320 \text{ cm}^{-1}$. The correlation times are $\tau_2 = 100 \text{ ps}$, and $\tau_{v,2} = 0.1 \text{ ps}$.

The values of T_{2e}^{eff} are very near to those of T_{1e}^{eff} and practically independent of the magnetic field B_0 up to 5 T and vary by less than a few percents up to 23.5 T (see Ref. 50, Fig. S4). This further justifies the introduction of a single relaxation time $\tau_{S0} \cong T_{1e}^{\text{eff}} \cong T_{2e}^{\text{eff}}$ for the fast relaxing Ln^{3+} . However, it should be kept in mind that τ_{S0} is only an effective electronic relaxation time in the rather frequent situations where $G_{\perp}^{\text{nor}}(t)$ deviates from a decreasing exponential function. In those situations, the approximation $T_{1e}^{\text{eff}} \cong T_{2e}^{\text{eff}}$ should be replaced by the less stringent equation,

$$G_{\perp}^{\text{nor}}(t) \cong G_{\perp}^{\text{nor}}(t)e^{i\omega_J t}, \quad (27)$$

which clearly appears by comparing⁵⁰ Figs. S3(a) with S3(b) and Figs. S4(a) with S4(b). Equation (27) holds because the fluctuations of the transient ligand-field, which satisfy $\omega_J \tau_{v,2} \ll 1$, are nearly in the extreme narrowing regime of the Redfield theory.⁵¹

All the simulation data were obtained for YbL, TbL, and ErL complexes, but equivalent results would be derived for the other Ln^{3+} complexes which have similar J values and ligand-field magnitudes.

IV. CONCLUSION

We have shown that the measured electronic relaxation times of fast relaxing Ln^{3+} complexes in solution are satisfactorily interpreted by the rapid modulation of the ligand-field due to the distortions of the complexes induced by the collisions with the solvent molecules occurring at a rate $1/\tau_{v,2}$ of about 10^{13} s^{-1} . We have pointed out that the effective electronic relaxation times T_{1e}^{eff} are essentially governed by the norm of this transient ligand-field and by its correlation time $\tau_{v,2} \cong 10^{-13} \text{ s}$, but neither by its symmetry nor by its specific tensorial form. In contrast, the modulation of the static ligand-field by the Brownian rotation of the complex has a minor influence. Because the magnitude of the transient ligand-field is significantly larger than the Zeeman energy, we have reproduced the field independence of the electronic relaxation and the equality of the effective longitudinal and transverse relaxation times. We have recovered the general tendency of the increase of T_{1e}^{eff} with the value of the total angular momentum J as already predicted by the Redfield approach. Through the simple Eq. (22), the latter has been shown to provide a lower limit of T_{1e}^{eff} , which is a reasonable estimate of this time only when the norm of the transient ligand-field is small enough ($\|H_{\text{lig},T}\| \leq 100 \text{ cm}^{-1}$). The fact that the electronic relaxation is nearly independent of the Ln^{3+} ion and of its coordinating ligand comes from four combined effects: (i) the norm of the transient ligand-field varies in a rather limited range from 100 to 500 cm^{-1} for all the Ln^{3+} ions so that T_{1e}^{eff} is near $\tau_{v,2}$, (ii) as pointed out by the Florence school^{26,27} the correlation time $\tau_{v,2} = 0.1 \text{ ps}$ should be a lower limit of T_{1e}^{eff} because “it is not conceivable that a modulation can induce a change in a physical property (here, the evolution of the states of the J multiplet) at a rate higher than the modulation rate itself,” (iii) the modest influence of the static ligand-field and of transient ligand-fields with correlation times significantly different from $\tau_{v,2}$, and (iv) the weak effect of the tensorial form

of the transient ligand-field as already suggested within the Redfield limit by Eq. (22). Consequently, for a given fast relaxing Ln^{3+} ion, the T_{1e}^{eff} values of its different complexes are in a narrow interval of width between 0.1 and 0.2 ps, so that they have a significant probability of being fortuitously equal for two complexes with different geometries and flexibilities. Finally, the slight observed decrease of T_{1e}^{eff} with increasing temperature can be explained by a decrease of its lower limit $\tau_{v,2}$ due to more frequent molecular collisions. Then, T_{1e}^{eff} can reach somewhat shorter values.

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