

The Rhombic Effect of Zero-Field Splitting on the Nuclear Relaxation Times. Quenching of the Electron Spin Angular Momentum

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The effect of zero-field splitting (ZFS) on the nuclear relaxation rates, T_{1M}^{-1} and T_{2M}^{-1} , is investigated under the condition that the static ZFS is larger than the energy uncertainty of the ZFS levels. It is shown that the rhombic term E of ZFS drastically reduces the nuclear relaxation rates of a paramagnetic molecule with an integer electron spin quantum number. In this case the nuclear relaxation time is independent of the external magnetic field strength. This signifies quenching of an electron spin angular momentum, which was predicted by N. Bloembergen and L. O. Morgan (*J. Chem. Phys.* 34, 842, 1961). It is suggested that the true value for the correlation time of lanthanide ion complexes could be much longer than the accepted value, 10^{-13} s. © 1990 Academic Press, Inc.

The effect of the electron-nucleus dipolar interaction on the nuclear relaxation rates can be described by the well-known Solomon equation (1, 2). In the Solomon equation, it is assumed that the S manifold is split by the electron Zeeman energy alone, with an isotropic g factor. If g is anisotropic, for example, for each orientation of the molecule in the magnetic field, the system experiences a particular g value and then the relaxation equation must be modified (3, 4). Furthermore, when $S > \frac{1}{2}$, the effect of spin-orbit coupling results in zero-field splitting (ZFS) which alters the spacing of the spin levels (5, 6). If the ZFS energy is smaller than the electron Zeeman energy, it will introduce only a small perturbation. However, when the ZFS is large compared to both the electron Zeeman energy $\hbar\omega_S$ and the EPR linewidth, its presence may severely alter the nuclear relaxation equations (4, 7).

Recently the effect of ZFS on the nuclear relaxation rates has attracted the attention of a number of authors (8-17). In the treatment suggested by the Stockholm authors (8-12), the electron spin is included in the lattice and the nuclear relaxation times are numerically calculated directly from the spectral densities without invoking the concept of electron spin relaxation times, which is valid in the slow motion regime for the electron spin. In the treatment suggested by the Florence authors (13-15), the electron spin is assumed to be coupled to the lattice through a mechanism whose correlation time is short compared to the electron relaxation time, so that the electron spin system is still in the Refield limit (18) and can be described by a single relaxation time τ_S . Analytical equations for the dipolar contribution to the nuclear relaxation rates in the limit case of the ZFS much larger than the electron Zeeman interaction have been derived.

In the treatments of both the Stockholm and the Florence groups, however, a ZFS tensor is assumed to have an axial symmetry, which is hardly acceptable in actual systems of paramagnetic metal ions complexed to organic ligands. The present paper investigates the effect of the rhombic symmetry of ZFS on the nuclear relaxation rates, T_{1M}^{-1} and T_{2M}^{-1} , in which it is assumed that the static ZFS is larger than the energy uncertainty of the ZFS levels and the electron spin system can be described by a single relaxation time τ_S .

THEORY

(i) *Nuclear longitudinal relaxation time.* In the general formalism of Kubo and Tomita (19) the nuclear longitudinal relaxation rate T_{1M}^{-1} is given in the laboratory fixed axis system x, y, z by

$$T_{1M}^{-1} = \int_0^{\infty} \langle [I_z, \mathcal{H}'(\tau)] [\mathcal{H}'(0), I_z] \rangle d\tau / \hbar^2 \langle I_z^2 \rangle, \quad [1]$$

where

$$\mathcal{H}'(\tau) = e^{(i/\hbar)\mathcal{H}_0\tau} \mathcal{H}' e^{-(i/\hbar)\mathcal{H}_0\tau} \quad [2]$$

and

$$\mathcal{H}_0 = \mathcal{H}_{ZFS} + \hbar\omega_S S_z + \hbar\omega_I I_z. \quad [3]$$

The ZFS interaction Hamiltonian \mathcal{H}_{ZFS} is given as a static energy in the molecular axis system x', y', z' by

$$\mathcal{H}_{ZFS} = D[S_z'^2 - \frac{1}{3}S(S+1)] + E(S_x'^2 - S_y'^2). \quad [4]$$

\mathcal{H}' represents the time-dependent perturbation Hamiltonian for the nuclear spin system due to the dipolar interaction between electronic and nuclear spins and can be expressed as the scalar product of nuclear and electronic spin operators in the molecular frame. That is,

$$\mathcal{H}' = \sum_{i=-1}^{+1} (-1)^i I_{i'} F_{-i'}, \quad [5]$$

where

$$I_{\pm 1'} = \mp \frac{1}{\sqrt{2}} I_{\pm'}, \quad I_{0'} = I_z' \quad [6]$$

and

$$\begin{aligned} F_{\pm 1'} &= \mp \sqrt{2} (-\frac{1}{4} S_{\pm'} \phi^{(0)} + S_z' \phi^{(\pm 1)} + S_{\mp'} \phi^{(\pm 2)}), \\ F_{0'} &= S_{+'} \phi^{(-1)} + S_z' \phi^{(0)} + S_{-'} \phi^{(1)}. \end{aligned} \quad [7]$$

Here $I_{\pm'} = I_{x'} \pm iI_{y'}$, $S_{\pm'} = S_{x'} \pm iS_{y'}$, and the ϕ 's have the form of spherical harmonics which are given by

$$\begin{aligned}
\phi^{(\pm 2)} &= \frac{3}{4} \hbar a \sin^2 \theta e^{\pm 2i\varphi}, \\
\phi^{(\pm 1)} &= \frac{3}{2} \hbar a \sin \theta \cos \theta e^{\pm i\varphi}, \\
\phi^{(0)} &= \hbar a (3 \cos^2 \theta - 1),
\end{aligned} \tag{8}$$

where $a = (\mu_0/4\pi)\gamma_1 g \mu_B r^{-3}$ and r, θ , and φ are the polar coordinates of the nucleus, with respect to the molecular axis system, from the electronic spin at the origin.

In order to evaluate T_{1M}^{-1} we need to transform I_z in Eq. [1], written in the laboratory system, into the nuclear spin operators in the molecular axis system at $t = 0$ with the Wigner rotation matrix. Then, Eq. [1] is changed to

$$\begin{aligned}
T_{1M}^{-1} &= \frac{1}{8\pi^2} \sum_{i=-1}^{+1} (-1)^i \int_0^{2\pi} d\alpha \int_0^\pi C_i(\beta) \sin \beta d\beta \int_0^{2\pi} d\gamma \\
&\quad \times \int_0^\infty \langle [I_{i'}, \mathcal{H}'(\tau)] [\mathcal{H}'(0), I_{-i'}] \rangle d\tau \left/ \frac{1}{3} \hbar^2 I(I+1) \right., \tag{9}
\end{aligned}$$

where

$$C_{\pm 1} = \frac{1}{2} \sin^2 \beta, \quad C_0 = \cos^2 \beta. \tag{10}$$

α, β , and γ are the Euler angles between the molecular coordinate at $t = 0$ and the laboratory coordinate defined by the external magnetic field. The exact evaluation of T_{1M}^{-1} from Eq. [9] would require detailed information on the reorientational dynamics for the molecule and the electron spin in addition to the eigenfunctions and eigenvalues of \mathcal{H}_0 as a function of the Euler angles. To proceed further we approximately calculate Eq. [9] as follows:

(a) The molecular axes at time τ differ from those at $t = 0$ on account of molecular reorientation. Precisely, the molecular axes at τ must be transformed into the molecular axes at $t = 0$ and then the ensemble average $\langle [I_{i'}, \mathcal{H}'(\tau)] [\mathcal{H}'(0), I_{-i'}] \rangle$ should be calculated according to the molecular reorientation process. However, we simply introduce the factor $e^{-\tau/\tau_r}$ into the ensemble average of the product $\mathcal{H}'(\tau)\mathcal{H}'(0)$ and in return we replace the molecular axes at τ by those at $t = 0$.

(b) The rate of molecular rotational motion τ_r^{-1} is assumed to be much larger than ω_1 . The last term of \mathcal{H}_0 given by Eq. [3], $\hbar\omega_1 I_z$, is ignored. This is the extreme narrowing condition for the nuclear spin system.

(c) It is assumed that the electron spin system can be described by a single electronic relaxation time τ_S without argument about the particular electron spin relaxation mechanism.

The second term of \mathcal{H}_0 in Eq. [3], $\hbar\omega_S S_z$, is transformed into the molecular axis system at $t = 0$, and we choose the molecular z' axis at $t = 0$ as the quantization axis for the electron spin. \mathcal{H}_0 is written in the molecular axis system at $t = 0$ as

$$\mathcal{H}_0 = \mathcal{H}_{ZFS} + \hbar\omega_S S_{z'} \cos \beta + \hbar\omega_S S_{x'} \sin \beta \cos \alpha + \hbar\omega_S S_{y'} \sin \beta \sin \alpha. \tag{11}$$

With this \mathcal{H}_0 , Eq. [2] can be rewritten as

$$\begin{aligned}\mathcal{H}'(\tau) &= \sum_{i=-1}^{+1} (-1)^i I_{i'} F_{-i'}(\tau), \\ F_{i'}(\tau) &= e^{(i/\hbar)\mathcal{H}_0\tau} F_{i'} e^{-(i/\hbar)\mathcal{H}_0\tau}.\end{aligned}\quad [12]$$

Using the commutation rule

$$[I_{\pm 1'}, I_{\mp 1'}] = \mp I_{0'}, \quad [I_{\pm 1'}, I_{0'}] = \mp I_{\pm 1'}.$$

T_{1M}^{-1} becomes

$$\begin{aligned}T_{1M}^{-1} &= \frac{1}{4\pi} \hbar^{-2} \int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \int_0^\infty d\tau [2C_1(\beta) \langle F_{0'}(\tau) F_{0'}(0) \rangle \\ &\quad - (C_0(\beta) + C_1(\beta)) \langle F_{1'}(\tau) F_{-1'}(0) + F_{-1'}(\tau) F_{1'}(0) \rangle].\end{aligned}\quad [13]$$

Let the eigenket for \mathcal{H}_0 be $|n\rangle$ and its eigenvalue be $\hbar\omega_n$. Taking the ensemble average for both the molecular orientation and the electron spin orientation at τ with respect to those at $t = 0$, we obtain

$$\begin{aligned}T_{1M}^{-1} &= \frac{1}{32\pi} a^2 (2S + 1)^{-1} \int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \sum_{mn} J(\omega_{mn}) \{ |\langle m | S_z' | n \rangle|^2 \\ &\quad \times [8C_1(3 \cos^2\theta - 1)^2 + 36(C_0 + C_1) \sin^2\theta \cos^2\theta] \\ &\quad + |\langle m | S_{+}' | n \rangle|^2 [(C_0 + C_1)(3 \cos^2\theta - 1)^2 \\ &\quad + 36C_1 \sin^2\theta \cos^2\theta + 9(C_0 + C_1) \sin^4\theta] \},\end{aligned}\quad [14]$$

where

$$J(\omega) = \int_0^\infty (e^{i\omega\tau} + e^{-i\omega\tau}) e^{-\tau/\tau_C} d\tau = 2\tau_C / (1 + \omega^2\tau_C^2),\quad [15]$$

$$\tau_C^{-1} = \tau_r^{-1} + \tau_S^{-1},\quad [16]$$

and

$$\omega_{mn} = \omega_m - \omega_n.\quad [17]$$

In the limiting condition of weak field, $\omega_S\tau_C \ll 1$, \mathcal{H}_0 is approximately equal to \mathcal{H}_{ZFS} , and ω_{mn} 's become independent of α and β . T_{1M}^{-1} is given by

$$\begin{aligned}T_{1M}^{-1} &= \frac{1}{3} a^2 (2S + 1)^{-1} \sum_{nm} \{ \tau_C / (1 + \omega_{nm}^2\tau_C^2) \} [|\langle n | S_z' | m \rangle|^2 \\ &\quad \times (2 + 6 \cos^2\theta) + |\langle n | S_{+}' | m \rangle|^2 (5 - 3 \cos^2\theta)].\end{aligned}\quad [18]$$

(ii) *Nuclear transverse relaxation time.* In the formalism of Kubo and Tomita the nuclear transverse relaxation rate T_{2M}^{-1} is given in the laboratory axis system by

$$\begin{aligned}T_{2M}^{-1} &= \int_0^\infty \langle [I_1, \mathcal{H}'(\tau)] [\mathcal{H}'(0), I_{-1}] + [I_{-1}, \mathcal{H}'(\tau)] [\mathcal{H}'(0), I_1] \rangle d\tau / \\ &\quad \hbar^2 \langle I_1 I_{-1} + I_{-1} I_1 \rangle,\end{aligned}\quad [19]$$

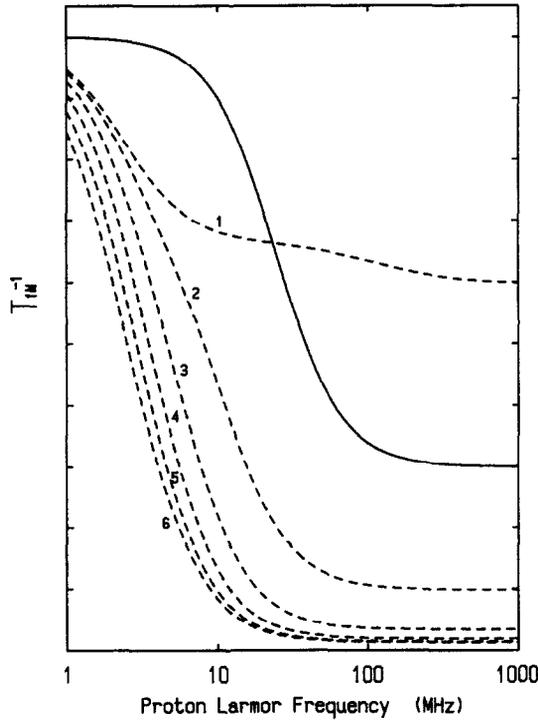


FIG. 1. Field dependence of T_{1M}^{-1} calculated according to Eq. [14] (---) for $S = 1$, $\theta = 0$, $\tau_C = 10^{-11}$ s, $D = 10h\omega_S$, and several values of E ; the field dependence predicted by the Solomon equation is also reported (—). The magnitudes of E are as follows: 1, $E = 0$; 2, $E = h\omega_S$; 3, $E = 2h\omega_S$; 4, $E = 3h\omega_S$; 5, $E = 4h\omega_S$; 6, $E = 5h\omega_S$.

where $I_{\pm 1} = \mp(I_x \pm iI_y)/\sqrt{2}$. Transforming the laboratory axis system into the molecular coordinate system at $t = 0$, we obtain

$$T_{2M}^{-1} = \frac{1}{8\pi} \hbar^{-2} \int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \int_0^\infty d\tau [(1 + C_0) \langle F_{0'}(\tau) F_{0'}(0) \rangle - (1 + C_1) \langle F_{1'}(\tau) F_{-1'}(0) + F_{-1'}(\tau) F_{1'}(0) \rangle]. \quad [20]$$

Taking the ensemble average for both the molecular orientation and the electron spin orientation, T_{2M}^{-1} becomes

$$T_{2M}^{-1} = \frac{1}{32\pi} a^2 (2S + 1)^{-1} \int_0^{2\pi} d\alpha \int_0^\pi \sin \beta d\beta \sum_{mn} J(\omega_{mn}) \left\{ |\langle m | S_z' | n \rangle|^2 \times [2(1 + C_0)(3 \cos^2 \theta - 1)^2 + 18(1 + C_1) \sin^2 \theta \cos^2 \theta] + |\langle m | S_{+}' | n \rangle|^2 \left[\frac{1}{2} (1 + C_1)(3 \cos^2 \theta - 1)^2 + 9(1 + C_0) \sin^2 \theta \cos^2 \theta + \frac{9}{2} (1 + C_1) \sin^4 \theta \right] \right\}. \quad [21]$$

In the limit of $\omega_S \tau_C \ll 1$, we get $T_{1M} = T_{2M}$.

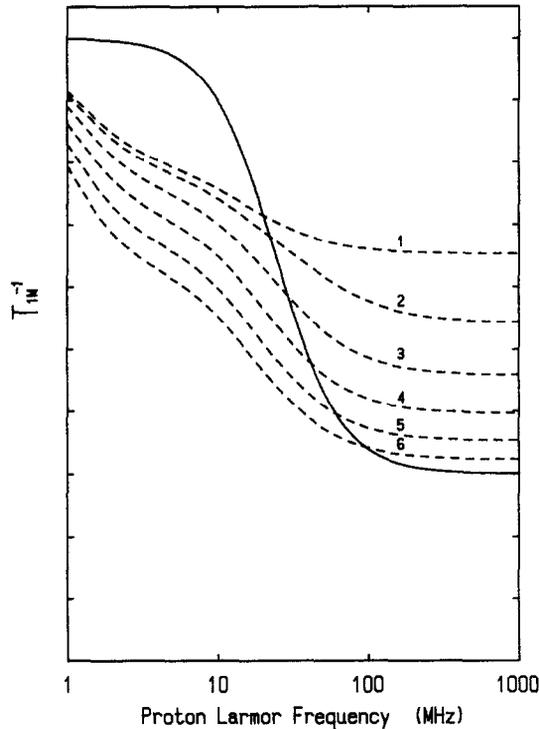


FIG. 2. Field dependence of T_{1M}^{-1} calculated according to Eq. [14] (---) for $S = \frac{3}{2}$, $\theta = 0$, $\tau_C = 10^{-11}$ s, $D = 10\hbar\omega_S$, and several values of E ; the field dependence predicted by the Solomon equation is also reported (—). The magnitudes of E are as follows: 1, $E = 0$; 2, $E = \hbar\omega_S$; 3, $E = 2\hbar\omega_S$; 4, $E = 3\hbar\omega_S$; 5, $E = 4\hbar\omega_S$; 6, $E = 5\hbar\omega_S$.

RESULTS AND DISCUSSION

The field dependence of T_{1M}^{-1} for the two cases $S = 1$ and $S = \frac{3}{2}$ is shown in Figs. 1 and 2, respectively. Figure 1 shows that the rhombic term E of ZFS drastically reduces the T_{1M}^{-1} for $S = 1$. For large D and E the nuclear relaxation time is independent of the external magnetic field strength. On the other hand, it is shown in Fig. 2 that the T_{1M}^{-1} for $S = \frac{3}{2}$ is insensitive to the magnitude of E . The field dependence of T_{2M}^{-1} for $S = 1$ and $S = \frac{3}{2}$ is shown in Figs. 3 and 4, respectively. We notice that T_{2M}^{-1} gives the same field dependence as that of T_{1M}^{-1} and that the profile of the curves of T_{1M}^{-1} and T_{2M}^{-1} vs field strength strongly depends on the existence of Kramer's degeneracy.

We can explain the above results about the effect of the rhombic parameter E on T_{1M}^{-1} and T_{2M}^{-1} under the condition that the ZFS energy is much larger than $\hbar\omega_S$. Let the eigenket for S_z be $|M\rangle$ and its eigenvalue be M . We define the symmetric electron spin functions as

$$\begin{aligned} |M_S\rangle &= (|M\rangle + |-M\rangle)/\sqrt{2}, & M \neq 0 \\ |O_S\rangle &= |0\rangle, \\ |M_A\rangle &= (|M\rangle - |-M\rangle)/\sqrt{2}, & M \neq 0. \end{aligned} \quad [22]$$

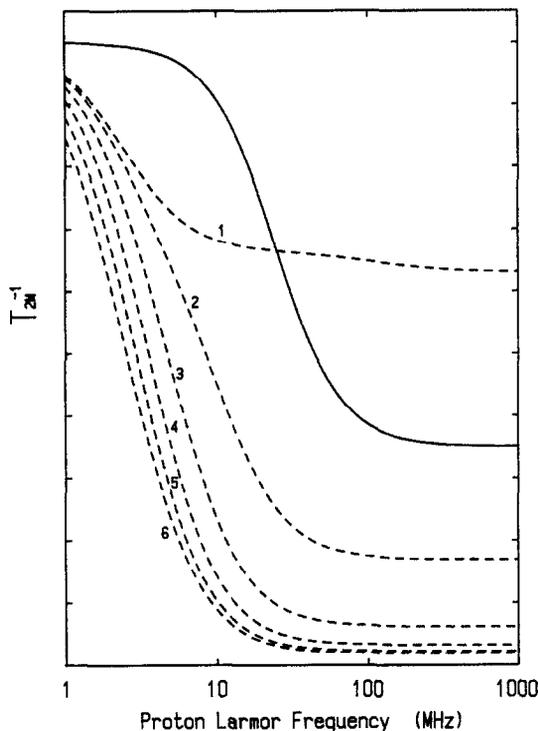


FIG. 3. Field dependence of T_{2M}^{-1} calculated according to Eq. [21] (---) for $S = 1$, $\theta = 0$, $\tau_C = 10^{-11}$ s, $D = 10\hbar\omega_S$, and several values of E ; the field dependence predicted by the Solomon equation is also reported (—). The magnitudes of E are as follows: 1, $E = 0$; 2, $E = \hbar\omega_S$; 3, $E = 2\hbar\omega_S$; 4, $E = 3\hbar\omega_S$; 5, $E = 4\hbar\omega_S$; 6, $E = 5\hbar\omega_S$.

We consider first the eigenstates and eigenvalues of \mathcal{H}_{ZFS} . \mathcal{H}_{ZFS} connects states of the same symmetry. Therefore, the eigenfunctions of \mathcal{H}_{ZFS} are linear combinations of $|M_S\rangle$ or $|M_A\rangle$ states. We denote the eigenstates consisting of $|M_S\rangle$ states by $|s\rangle$ and those consisting of $|M_A\rangle$ states by $|a\rangle$. S_z has nonzero matrix elements only between $|s\rangle$ and $|a\rangle$ states, so it has no diagonal elements. Because \mathcal{H}_{ZFS} combines the states differing by ± 2 in M , S_z also has no diagonal elements. Therefore, the diagonal terms, $n = m$, in Eqs. [14] and [21] will disappear. We find the following results: If either $E = 0$ or S is a half integer, the corresponding two eigenstates of $|s\rangle$ and $|a\rangle$ have the same energy. However, if $E \neq 0$ and S is an integer, no eigenstates of \mathcal{H}_{ZFS} are degenerate. If both D and E parameters are much larger than $\hbar\omega_S$, the energy differences, ω_{mn} 's, are so large compared to ω_S that T_{1M}^{-1} and T_{2M}^{-1} are drastically reduced and are independent of the field strength. This signifies quenching of the electron spin angular momentum, which was first suggested by Bloembergen and Morgan (20). However, our work is the first which derives exactly the electron spin angular momentum quenching.

The quenching of the electron spin may be effective in some lanthanide shift reagents. Using the Solomon equation, a very short τ_S , 10^{-13} s, is necessary to account for well-resolved NMR spectra of lanthanide shift reagent complexes (21). The τ_S of

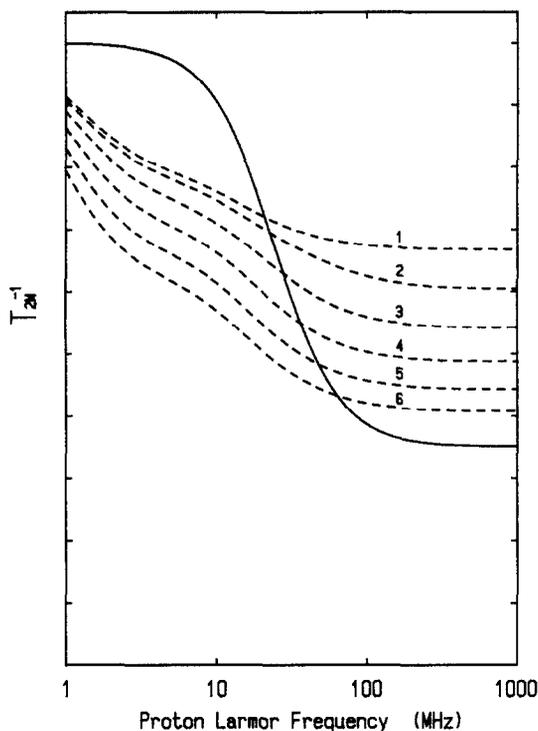


FIG. 4. Field dependence of T_{2M}^{-1} calculated according to Eq. [21] (---) for $S = \frac{3}{2}$, $\theta = 0$, $\tau_c = 10^{-11}$ s, $D = 10\hbar\omega_S$, and several values of E ; the field dependence predicted by the Solomon equation is also reported (—). The magnitudes of E are as follows: 1, $E = 0$; 2, $E = \hbar\omega_S$; 3, $E = 2\hbar\omega_S$; 4, $E = 3\hbar\omega_S$; 5, $E = 4\hbar\omega_S$; 6, $E = 5\hbar\omega_S$.

10^{-13} s is shorter than the correlation time for the symmetry distortion of aqua complexes of metal ions τ_V , which is of the order of 10^{-12} s (12, 17). Such a short τ_S is strange and difficult to explain. On account of a large LS coupling in a lanthanide ion complex, the magnetic moment runs parallel with the total angular momentum \mathbf{J} . We must replace \mathbf{S} by \mathbf{J} in our theoretical approach for lanthanide ion complexes. In a lanthanide ion complex with an integer J value and large ligand field coefficients¹ (22), ZFS will necessarily reduce T_{1M}^{-1} and T_{2M}^{-1} , and the true value for τ_S could be much larger than the accepted value, 10^{-13} s. If we tentatively assume a τ_c of 10^{-11} s and ligand field coefficients of 5 cm^{-1} , our theory presents the T_{1M}^{-1} and T_{2M}^{-1} values of the same order of magnitude as those estimated from the Solomon equation assuming 10^{-13} s for τ_c .

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¹ For the $\text{S}_m(\text{thd})_3$ chelate the authors of Ref. (22) obtained $D = 95 \text{ cm}^{-1}$ and $E = -84 \text{ cm}^{-1}$.

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