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T_{1e} in Four Gd^{3+} Chelates: LODEPR Measurements and Models for Electron Spin Relaxation

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In a previous paper, we reported the first longitudinally detected electron paramagnetic resonance (LODEPR) measurements of fast T_{1e} values in aqueous solutions of two Gd^{3+} chelates, and we included predicted values for these relaxation times, based on zero field splitting (ZFS) parameters derived from multifrequency EPR data on the two systems [Atsarkin, V. A.; Demidov, V. V.; Vasneva, G. A.; Odintsov, B. M.; Belford, R. L.; Radüchel, B.; Clarkson, R. B. *J. Phys. Chem.* **2001**, *105*, 9323–9327]. The model used in that analysis was derived from the original work of Hudson and Lewis and did not explicitly consider the static and dynamic parts of the ZFS. A more comprehensive model for relaxation in these $S = 7/2$ systems has been recently published. Here, we reexamine the multifrequency data in light of this new model, recalculate the ZFS parameters, and calculate new predictions for T_{1e} , which much more closely agree with experimental values. Additionally, the LODEPR T_{1e} values for two standard chelates, $[Gd(DOTA)(H_2O)]^-$ and $[Gd(DTPA)(H_2O)]^{2-}$ are reported, together with predicted relaxation times. Both the importance of the new model and the validity of the LODEPR values are strengthened by these data.

1. Introduction

Measurement of fast electron spin relaxation has been experimentally challenging since the inception of EPR. With the advent of pulsed EPR, longitudinal relaxation rates (T_{1e}) often have been measured by these direct methods. Among the most popular techniques are inversion–recovery (IR)¹ and saturation–recovery (SR)². Unfortunately, the use of these approaches requires that T_{2e} must be long enough to observe an electron spin–echo, and this places a lower limit on the measurement of fast relaxation at $T_{2e} \sim 1$ ns. For the measurement of faster relaxing paramagnetic systems, longitudinally detected (LOD) EPR methods can be useful.^{3–6}

Recently, we published an account of the application of LODEPR for the measurement of T_{1e} in aqueous solutions of Gd^{3+} chelates at an experimental frequency of 9.5 GHz (X band), where the observed longitudinal relaxation times varied between 1.7 and 4.0 ns.⁷ In that account, we described a calculation of T_{1e} values based on zero field splitting (ZFS) parameters evaluated from cw multifrequency EPR spectra of the compounds. That calculation made use of an approach originally developed by Hudson and Lewis for evaluating the Redfield relaxation matrix in $S = 7/2$ systems,⁸ and modified for fitting ZFS parameters (Δ , τ_v) from the peak-to-peak multifrequency EPR line widths (ΔB_{pp}).⁹ T_{1e} values calculated for X band from the ZFS parameters made use of longitudinal relaxation matrix elements provided by Powell et al.¹⁰ The predicted values were all shorter than the observed values in these systems.

Since publishing that work, Rast et al. have published a more complete treatment of electron spin relaxation in $S = 7/2$ systems,^{11,12} explicitly considering static and dynamic ZFS interactions. We have now utilized this more complete theoretical model, implemented without recourse to the high-field approximation that was used in the previous work (ref 9), and have recalculated ZFS parameters from the original multifrequency EPR data. Furthermore, we have now measured T_{1e} for two other chelates, $[Gd(DTPA)(H_2O)]^{2-}$ and $[Gd(DOTA)(H_2O)]^-$, and have compared these experimental values with relaxation times calculated from literature values for the complexes.^{11,12} Values of T_{1e} calculated for X band are in much better agreement with experimental values than those previously reported and give greater confidence that the experimental LODEPR method is a useful approach for studying fast longitudinal electron spin relaxation in these Gd^{3+} systems.

2. Theoretical Methods

The relaxation of an $S > 1/2$ electron spin system is explained by the modulation of a general time-dependent spin Hamiltonian $H_1(t)$ of the form:¹³

$$\hat{H}_1(t) = \sum_{k,\eta} B^{k\eta} \sum_{q=-k}^{+k} b_q^{k\eta} \hat{T}_q^k \quad (1)$$

where \hat{T}_q^k is an irreducible spin tensor of order k ($k = 2, 4, \text{ or } 6$ for a crystal field acting upon f electrons in the case of Gd^{3+}),¹⁴ $B^{k\eta}$ is a real coefficient describing the magnitude of the interaction, and the $b_q^{k\eta}$ are complex coefficients of the development of the Hamiltonian as a sum of linear combinations of spin tensors, chosen to be orthonormal. More specifically, if the modulation is partly due to molecular tumbling [isotropic

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Brownian rotation described by a time-dependent Wigner matrix $D_{pq}^k(\Omega(t))$ with correlation time $\tau_k = 1/\{k(k+1)D_R\}$, D_R being the rotational diffusion constant], and partly to vibrations that affect the coordination sphere geometry (described by time-dependent Hamiltonian coefficients $C^{2\eta}(t)$, limited to 2nd order, and a single correlation time τ_v), the Hamiltonian may be rewritten in the laboratory frame as eq 2:^{11,12}

$$\hat{H}_1^L(t) = \sum_{k,\eta} B^{k\eta} \sum_{p,q=-k}^{+k} b_q^{k\eta} T_p^k D_{pq}^k(\Omega(t)) + \sum_{\eta} C^{2\eta}(t) \sum_{p,q=-2}^{+2} c_q^{2\eta} \hat{T}_p^2 D_{pq}^2(\Omega(t)) \quad (2)$$

The Hudson–Lewis approach⁸ is formally a special case of this more general theory, with a development limited to 2nd order, and only one ZFS contribution (either static or dynamic). Now the Redfield theory of relaxation¹⁵ allows us to calculate the relaxation matrix elements from the spectral densities $J_{\alpha\alpha'\beta\beta'}$ (eq 3) associated with the spin states α , α' , β , and β' (for transverse relaxation, $\alpha = \alpha' + 1$ and $\beta = \beta' + 1$, whereas for longitudinal relaxation $\alpha = \alpha'$ and $\beta = \beta'$):

$$R_{\alpha\alpha'\beta\beta'} = J_{\alpha\beta\alpha'\beta'}((\alpha' - \beta')\omega) + J_{\beta'\alpha'\beta\alpha}((\beta - \alpha)\omega) - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\alpha\gamma\beta\gamma'}((\beta - \gamma)\omega) - \delta_{\alpha\beta} \sum_{\gamma} J_{\gamma\alpha'\gamma'\beta'}((\gamma - \beta')\omega) \quad (3)$$

The spectral densities may be evaluated either explicitly from the matrix elements of the irreducible tensors (see for example Poupko et al.¹⁶ for a development to 2nd order of $S = 3/2$, $5/2$, and $7/2$) or by taking advantage of the Wigner–Eckart theorem to yield eq 4:

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \sum_k \frac{1}{2k+1} |\langle S || T^k || S \rangle|^2 \left(\frac{\tau_k}{1 + \omega^2 \tau_k^2} + i \frac{\omega \tau_k^2}{1 + \omega^2 \tau_k^2} \right) \times \sum_t (B^{k\eta})^2 (-1)^{S-\alpha} \begin{pmatrix} S & k & S \\ -\alpha & \alpha - \alpha' & \alpha' \end{pmatrix} (-1)^{S-\beta} \begin{pmatrix} S & k & S \\ -\beta & \beta - \beta' & \beta' \end{pmatrix} \quad (4)$$

where

$$\langle S || T^k || S \rangle = \sqrt{\frac{(k!)^2 (2S+k+1)!}{2_k (2k)! (2S-k)!}}$$

is the reduced matrix element and

$$\begin{pmatrix} S & k & S \\ -\alpha & \alpha - \alpha' & \alpha' \end{pmatrix}$$

is a $3j$ symbol. A similar spectral density with a correlation time $\tau_v = 1/(1/\tau_2 + 1/\tau_v)$ is obtained for the transient part. The complete longitudinal and transverse relaxation matrixes may thus be written as the sum of the static 2nd, 4th, and 6th order, and the dynamic 2nd order ZFS contributions, in terms of just a few adjustable parameters:

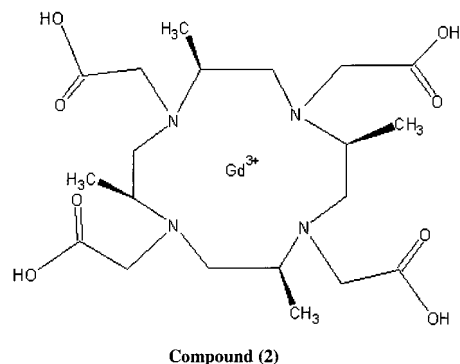
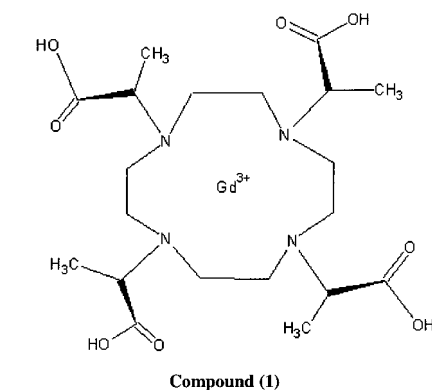


Figure 1.

$$-a_k = [\sum_{\eta} (B^{k\eta})^2]^{1/2}$$

and the associated correlation time $\tau_k = 1/\{k(k+1)D_R\}$

$$-a_{2T} = [\sum_{\eta} (C^{2\eta}(0))^2]^{1/2}$$

and the associated correlation time τ_v .

These parameters, plus the natural g factor, determine the line shape. In this work, a simplified program, based on the FORTRAN code presented in ref 12, was used for the analysis of the peak-to-peak widths and central fields and the calculation of the longitudinal relaxation rates.

3. Experimental Section

Experimental methods have been discussed in the previous publication.⁷ Both new compounds that were studied are Gd^{3+} chelates, based on the DOTA ligand (1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane, $C_{20}H_{32}N_4O_8^{4-}$). The two compounds are shown in Figure 1 and are designated (1) and (2). Gd DTPA and Gd DOTA were obtained from Schering AG and were treated in an identical fashion.

4. Results and Discussion

Best-fit values for the multifrequency EPR data on the four compounds, making use of the improved theory of Rast et al. are shown in Table 1, together with values obtained by use of the older Hudson and Lewis approach. Simulations were made to second order for the static ZFS contribution, because only very small changes in the values were observed when the simulations were made to sixth order.

Close agreement between the values of a_2 for the second-order static ZFS in the Rast model and the phenomenological Δ from the earlier theory⁸ suggests that they may characterize the same interaction. However, one should be careful to avoid

TABLE 1: Summary of Best Fit Parameters from Multi-Frequency EPR Data

| compound | this work | | | | previous work ^{7,9} | | |
|---|-------------------------------------|--|--------------------|--------------------|--|---|---|
| | a_2 (10 ¹⁰ rad/sec) | a_{2T} (10 ¹⁰ rad/sec) | τ_R (psec) | τ_V (psec) | Δ (10 ¹⁰ rad/sec) | τ_V^\dagger (psec) ^a | R_0 (10 ⁸ sec ⁻¹) |
| 1 | 0.555 | 0.298 | 500 | 1.2 | 0.453 | 15.6 | 1.57 |
| 2 | 0.319 | 0.289 | 495 | 1.1 | 0.332 | 10.3 | 1.48 |
| [Gd(DOTA)(H ₂ O)] ⁻ [ref 12] | 0.35 | 0.43 | 491 | 0.54 | 0.331 | 12.6 | 0.76 |
| [Gd(DTPA)(H ₂ O)] ²⁻ [ref 11] | 0.92 | 0.43 | 395 | 1.33 | 0.89 | 24 | 0.76 |

^a τ_V^\dagger according to Hudson and Lewis [8].TABLE 2: Experimental and Calculated Room Temperature T_{1e} Values for Several Gd³⁺ Chelates in Aqueous Solution

| compound | conc (mM) | ΔB_{PP} (Gauss) | T_{1e} (ns) in water | T_{1e} (ns) predicted | T_{1e} (ns) previous ^{7,9} |
|--|--------------|----------------------------|---------------------------|----------------------------|--|
| 1 | 35 | 155 | 1.7 ± 0.2 | 1.8 | 1.0 |
| 1 | 70 | 155 | 1.9 ± 0.2 | 1.8 | 1.0 |
| 2 | 30 | 77 | 3.3 ± 0.3 | 3.9 | 1.7 |
| 2 | 60 | 77 | 3.2 ± 0.3 | 3.9 | 1.7 |
| [Gd(DOTA)(H ₂ O)] ⁻ | 100 | 125 | 4.7 ± 1.0 | 3.4 | 1.7 |
| [Gd(DTPA)(H ₂ O)] ²⁻ | 100 | 600 | 1.2 ± 0.4 | 0.64 | 0.3 |

direct comparison since the relevant correlation times ($\tau_2 = \tau_R/6$ and τ_V^\dagger respectively) are different.

Table 2 gives the experimental and predicted values for T_{1e} , calculated with the Rast model and the Hudson and Lewis model. Included in the table are values for compounds (**1**) and (**2**) measured at two different concentrations. Also included in the table are the previously unpublished values for [Gd(DOTA)(H₂O)]⁻ and [Gd(DTPA)(H₂O)]²⁻, which were measured by the same LODEPR procedure at a concentration of 100 mM.

Table 2 shows a very good agreement between experimental and theoretical values and demonstrates an improvement over values of T_{1e} calculated with the more approximate theory in ref 7. Although improvement in the precision of T_{1e} measurements remains a goal toward which we are working, these results already give us key information to help develop a better theoretical model for longitudinal relaxation in these systems.

The improved agreement between theory and experiment demonstrated here is important for two reasons — first, because it shows the improvement which a more comprehensive model of ZFS-induced electron spin relaxation makes in analyzing multi-frequency EPR data, and second, because it gives us

stronger reason to believe that the LODEPR technique used in this work can accurately measure T_{1e} in fast-relaxing paramagnetic systems.

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