THE JOURNAL OF
PHYSICAL
CHEMISTRY A

© Copyright 2001 by the American Chemical Society VOLUME 105, NUMBER 41, OCTOBER 18, 2001

ARTICLES

Direct Measurement of Fast Electron Spin−Lattice Relaxation: Method and Application to Nitroxide Radical Solutions and Gd^{3+} Contrast Agents

V. A. Atsarkin,*,† V. V. Demidov,† G. A. Vasneva,† B. M. Odintsov,†,‡ R. L. Belford,‡
B. Radüchel,§ and R. B. Clarkson‡

Institute of Radio Engineering and Electronics, Russian Academy of Sciences, 101999 Moscow, Russia, Illinois EPR Research Center, Departments of Chemistry, Clinical Veterinary Medicine, and Medical Information Sciences, University of Illinois, Urbana, Illinois 61801, and Laboratory for Contrast Media Research, Schering AG, Berlin, Germany

Received: March 26, 2001; In Final Form: June 28, 2001

A modulation technique for direct measurement of extremely fast electron spin−lattice relaxation is described. The method is based on longitudinal magnetization detection. It is applied here to study the spin−lattice relaxation times T_{1e} in aqueous solutions of perdeuterated nitroxide radical ($T_{1e} \approx 200$ ns) with various concentrations as well as to two Gd DOTA complexes ($T_{1e} \approx 1.8-3.2$ ns), which can be employed as paramagnetic contrast agents in magnetic resonance imaging.

1. Introduction

Measuring the longitudinal (spin−lattice) relaxation time (T_1) is a powerful method to investigate the internal fields and molecular dynamics in condensed matter (see, for example, ref 1). The relaxation rate T_1^{-1} is proportional to the spectral density $J(\omega_o)$ of the internal field fluctuations at the magnetic resonance frequency ω_o. Electron spin−lattice relaxation of paramagnetic ions and free radicals serving as spin probes or spin-labels gives unique information about processes with correlation times $\tau_c < 10^{-10}$ s, which are too short to be measured by NMR techniques.

In many cases, however, such measurements are hampered by the fact that the electronic T_{1e} values are extremely short ($<10^{-7}$ s) and cannot be measured by ordinary cw and pulse EPR methods. Furthermore, since $T_{2e} \leq T_{1e}$, the EPR line width in fast-relaxing systems is broad, usually greater than 10 mT. In such a case, a quite impractical microwave power, $P > 1$ kW, is needed to achieve a saturation factor $s = (\gamma B_1)^2 T_{1e} T_{2e}$ of the order of unity, where γ is the magnetogyric ratio, B_1 is the half-amplitude of the microwave magnetic field, and T_{2e} is the transverse relaxation time.

The problem of measuring short T_{1e} values can be addressed by using a modulation technique suggested originally by Hérve and Pescia[2,3] and recently modified by Atsarkin et al.[4,5] The method is described in section 2. Section 3 shows the application of the technique in the measurement of T_{1e} in water solutions of the ^{15}N-perdeuteriotempone (PDT) radical. Since this radical system has been extensively studied by pulsed EPR methods, it provides a good benchmark to calibrate the new approach. Finally, section 4 presents new results concerning electron spin−lattice relaxation in aqueous solutions of two Gd^{3+} chelates that may be useful as paramagnetic contrast agents (PCA's) for magnetic resonance imaging (MRI).

---

* To whom correspondence should be addressed. Institute of Radio Engineering and Electronics Russian Academy of Sciences, 11, Mokhovaya Street, 101999 Moscow, Russia. Phone: (7095) 203-0156. Fax: (7095)-203-8414. E-mail: atsarkin@mail.cplire.ru.

† Institute of Radio Engineering and Electronics.

‡ Illinois EPR Research Center.

§ Laboratory for Contrast Media Research.

10.1021/jp0111158 CCC: $20.00 © 2001 American Chemical Society
Published on Web 09/22/2001

2. Method of Measuring T_{1e}

The basic idea and some essential features of the experimental method are as follows. A sample under study is positioned in the resonator of an EPR spectrometer and irradiated by microwaves at frequency $\omega \approx \omega_0$. The microwave power should provide a small saturation factor $s \sim 10^{-2}-10^{-4}$ or even less; in fact, $P \sim 0.1-0.5$ W is quite sufficient. Before entering the cavity, the microwave power is subjected to a large amplitude modulation at a frequency Ω which should be, where possible, of the order of $T_{1e}{}^{-1}$, the expected relaxation rate. As a result, the saturation factor is modulated as well, producing corresponding oscillations of the longitudinal spin magnetization M_z. Generally, the oscillating part of M_z can be written as

$$M_z(t) = u\cos(\Omega t) + v\sin(\Omega t) \tag{1}$$

where u and v are the amplitudes of the in-phase and out-of-phase components relative to the modulation wave-form. This oscillating magnetization induces a corresponding radio frequency (r.f.) voltage in a specially designed pick-up coil wound around the sample (or around the resonator). The coil is tuned to Ω and has its axis along the external magnetic field $\mathbf{B_0}||z$. Then the r.f. signal (proportional to dM_z/dt) is amplified and lock-in detected to separate the values of U and V, which are related to the u and v components of the longitudinal magnetization, respectively. Finally, the U and V values are accumulated and processed; as shown below, these quantities allow the determination of T_{1e}.

The easiest way to evaluate U and V is to restrict consideration to the case when the off-diagonal elements of the density matrix of the spin system can be neglected during the whole measurement procedure. In our case, the following inequalities should be fulfilled:

$$T_{2e} \ll \mathrm{T}_{1e}; \quad \Omega \mathrm{T}_{2e} \ll 1; \quad \gamma B_1 \ll T_{2e}{}^{-1} \tag{2}$$

Evidently, this means that the transverse relaxation is the fastest process, and the experiment is being performed on a time scale $t \gg T_{2e}$ that satisfies conditions of the spin temperature approximation (see, for example, refs 1 and 6). In such a case, the U and V values can be found from the solution of the conventional rate equations slightly modified in accordance with the amplitude modulation of B_1. The M_z value is simply proportional to the difference in the spin energy level populations. The corresponding calculations were performed in refs 2 and 3 where a complex expression for $M_z(t)$ in the quasi-steady-state regime was given. Using this expression and supposing hereafter that

$$s \ll 1 \tag{3}$$

one obtains[4]

$$U = AM_0(\gamma\, B_1)^2 g(\omega)\frac{\Omega\, T_{1e}}{1+\Omega^2 T_{1e}^2} \tag{4}$$

$$V = AM_0(\gamma\, B_1)^2 g(\omega)\frac{\Omega^2\, T_{1e}^2}{1+\Omega^2 T_{1e}^2} \tag{5}$$

where A is an instrumental factor accounting for the microwave power, modulation index, receiver amplification and so on; M_0 is the static spin magnetization; and $g(\omega)$ is the form factor of the EPR absorption line. Thus, one has

$$\frac{V}{U} = \Omega T_{1e} \tag{6}$$

so the T_{1e} value of interest can be determined readily. The ratio given by eq 6 is simply $\tan(\varphi)$, where φ is the phase lag caused by the longitudinal spin relaxation. Thus, in a sense, this version of the method (called the "phase version") resembles the pulse saturation-recovery technique. As seen from eq 6, to determine the T_{1e} value it is sufficient to perform measurements of U and V at a single modulation frequency. This is an essential advantage of our technique as compared with the original version[2,3] (see also refs 7 and 8), where the frequency dependence $M_z(\Omega)$ should be obtained over a wide range of Ω. It should be noted, however, that the single-frequency "phase version" works only in the case of a single-exponential relaxation process. Otherwise, additional measurements must be made at various Ω values. For instance, for biexponential relaxation, two different modulation frequencies should be used, and so on. Generally, the whole relaxation process (in the time domain) is related to the frequency dependence $M_z(\Omega)$ through the Fourier transformation.

As seen from eqs 4–6, the V component tends to zero at $\Omega T_{1e} \ll 1$. In this case, the V/U ratio cannot be measured with the proper accuracy and the method breaks down. Practically, in the vicinity of X-band microwave frequency, Ω cannot exceed 10^7-10^8 Hz because of the finite band-pass of the microwave resonator (quality factor $Q \geq 10^2$). Hence, the "phase version" is restricted to $T_{1e} \geq 10^{-8}$ s. To measure shorter relaxation times, another version has been developed[4] called the "amplitude version". In this case ($\Omega T_{1e} \ll 1$), only the U component is to be measured. However, an additional measurement of the nonsaturated EPR absorption signal is carried out:

$$\mathrm{G}_{\mathrm{EPR}} = CM_0(\gamma B_1)^2 g(\omega) \tag{7}$$

where C is another instrumental factor. This signal must be recorded in the same microwave resonator and, wherever possible, under the same conditions (except for the microwave power, which can be changed) as those employed in the measurement of U. As a result, one can write

$$\frac{U}{G_{\mathrm{EPR}}} = \frac{A}{C}\Omega T_{1e} \tag{8}$$

This equation is sufficient to find T_{1e}, provided the A/C ratio is known. To determine A/C, one performs an additional calibration experiment using a reference paramagnetic sample with a well-characterized EPR spectrum and a known value of T_{1e}.

In fact, the "amplitude version" is based on the determination of the saturation factor and in this sense resembles the conventional cw saturation techniques. It should be noted that both "phase" and "amplitude" versions can be performed simultaneously in many cases, thus providing an independent check on the measured T_{1e} value.

Application of both "phase" and "amplitude" versions of the modulation method allows determination of T_{1e} values ranging from 10^{-6} to 10^{-10} s. Applications of these techniques in studies of electron spin–lattice relaxation in some high-temperature superconductors and related materials as well as in conducting fullerides are described in refs 4, 5, and 9–11.

Consider now a more complicated case when the "spin temperature" conditions of eq 2 are not fulfilled; such a situation is rather typical of liquids and exchange-coupled systems with relatively narrow EPR lines and T_{1e}, $T_2 \geq 10^{-7}$ s. Note that, in this case, the conventional pulse and cw methods of measuring T_{1e} are usually applicable. Nevertheless, it is worthwhile to present here the results based on solution of the Bloch equations and not limited by eq 2.[3] The generalized expressions for U and V are rather complex, so we restrict ourselves to the case of $\omega = \omega_0$ and obtain[5]

$$U(w_0) = AM_0(\gamma B_1)^2 g(w_0)\frac{\Omega T_{1e}\left[1 - \frac{\Omega T_{2e}}{2}(\Omega T_{1e} - \Omega T_{2e})\right]}{(1 + \Omega^2 T_{1e}^2)(1 + \Omega^2 T_{2e}^2)} \tag{9}$$

$$V(w_0) = AM_0(\gamma B_1)^2 g(w_0)\frac{\Omega T_{1e}\left[\Omega T_{1e} + \frac{\Omega T_{2e}}{2}(1 + \Omega^2 T_{1e} T_{2e})\right]}{(1 + \Omega^2 T_{1e}^2)(1 + \Omega^2 T_{2e}^2)} \tag{10}$$

One can see that T_{1e} can be determined from the $V(\omega_0)/U(\omega_0)$ ratio, provided T_{2e} is known from the EPR line width. As to the line shape of the longitudinal magnetization response at $\omega \neq \omega_0$, generally it does not coincide with g(ω), the distortions being especially strong at ΩT_{1e}, $\Omega T_{2e} \geq 1$.

Before discussing the experimental results, we note one more advantage of the method. Since these techniques measure relaxation of the total longitudinal magnetization, in many cases the result does not depend on cross-relaxation processes conserving M_z. Another interesting feature of the method is related to the case of $S > {}^1/_2$ paramagnetic centers with fine structure in the EPR spectrum. It can be shown (see, for example, ref 12) that if the partial relaxation rates between any energy levels i, j are governed by the magnetic dipole selection rules

$$W_{ij} = S(S + 1) - m_i(m_i + 1), \quad m_i - m_j = \pm 1 \tag{11}$$

where m_i is a magnetic quantum number; the relaxation of the total longitudinal magnetization is described by a single exponential. Its characteristic rate $T_{1e}{}^{-1}$ is the smallest root of the secular equation describing joint relaxation of all $2S + 1$ energy levels. This is just the T_{1e} value that is measured by this modulation method (for experimental results, see refs 10 and 11).

3. Electron Spin−Lattice Relaxation in Aqueous Solutions of Nitroxide Radicals

To check the modulation technique on a system important in chemical and biological applications, we chose the well-known and thoroughly investigated nitroxide radical ^{15}N perdeuteri-otempone (PDT) radical in water.

A ^{15}N isotopic substitution was used to simplify the EPR spectrum, which consists of two hyperfine components ($I_{^{15}\mathrm{N}} = {}^1/_2$). A set of aqueous solutions was prepared with nitroxide concentrations c ranging from 1.6 to 100 mM/L. Note that the concentration dependence of T_{1e}, in this system, has not been heretofore investigated and is of obvious chemical interest.

All experiments were carried out at room temperature (295 K). Figure 1 shows a typical EPR spectrum taken at X-band ($\omega/2\pi = 9.4$ GHz) on a Bruker ER-200 spectrometer (curve a). To measure T_{1e}, the homemade apparatus previously described[4,5] was used,. The microwave power ($P \approx 200$ mW) was modulated at $\Omega/2\pi = 373$ kHz or 1.6 MHz. A specially designed 3λ/2 coaxial microwave cavity ($Q \approx 150$) was employed, having its axis parallel to $\mathbf{B_0}$ and the walls transparent to r.f. field at the modulation frequency. Samples under study consisted of 20 mm^3 of the water solution in a toroidal container placed at the maximum of the microwave magnetic field $\mathbf{B_1} \perp \mathbf{B_0}$. The pick-up coil was wound on the coaxial cavity and tuned to the modulation frequency. After amplification and lock-in detection, the U and V signals were digitally averaged for 3 min to achieve acceptable signal-to-noise ratio. To obtain the line shape of the longitudinal response (i.e., the field dependence of the signal during the sweep through the EPR resonance), a conventional magnetic modulation technique was used, employing detection of the first derivatives, dU/dB_0 and dV/dB_0. An example is also shown in Figure 1 (curves b and c).

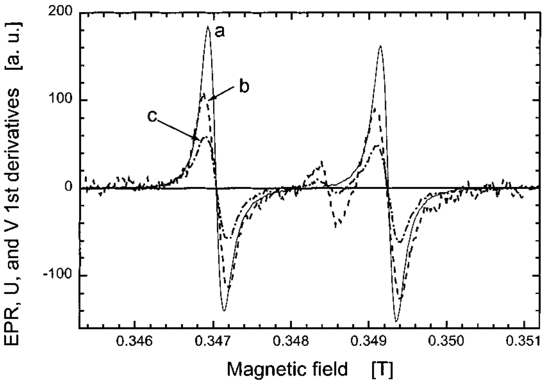


Figure 1. Magnetic field derivatives of the in-phase (U, the b curve) and out-of-phase (V, the c curve) components of the longitudinal magnetization response to the modulation of the microwawe power (at $\Omega/2\pi = 373$ kHz) for the 25 mM/L aqueous solution of ^{15}N PDT nitroxide radical. Both b and c curves are shown on the same scale.The solid curve a is the EPR spectrum (in arbitrary units). The line at 0.3484 T is the reference (DPPH).

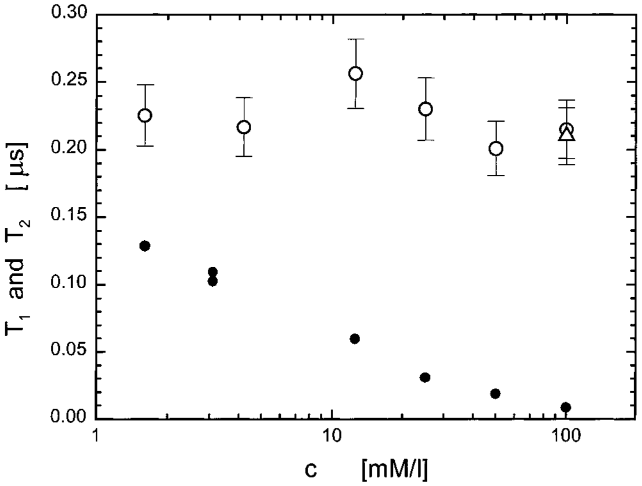


Figure 2. Concentration dependencies of longitudinal (T_{1e}, open symbols) and transverse (T_{2e}, filled symbols) relaxation times in aqueous solutions of ^{15}N PDT nitroxide radical. ○: $\Omega/2\pi = 373$ kHz. △: $\Omega/2\pi = 1.6$ MHz.

The T_{1e} values obtained by means of the V/U ratio (the "phase version", see section 2) are plotted against the nitroxide concentration in Figure 2 together with T_{2e} data determined from the EPR line widths, approximated as

$$T_{2e} = \frac{2}{\sqrt{3}}(\gamma \Delta B_{\mathrm{PP}})^{-1} \tag{12}$$

where ΔB_{pp} is the EPR peak-to-peak line width of a hyperfine component. Note that at higher concentrations $c > 40$ mM/L, the width of a component becomes comparable with the hyperfine splitting (2.2 mT), so eq 12 is only approximate.

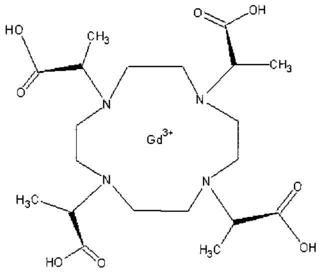
As seen from Figure 2, the conditions of eq 2 are fairly well fulfilled in the range of concentrations studied, so the simplified expressions of eqs 4−6 were used in most cases. (Small corrections from eqs 9 and 10 were made only for the lowest concentrations.) For a check on the data, the same measurements were repeated at different values of Ω; as seen in Figure 2, the results obtained at both 320 kHz and 1.6 MHz are the same, thus supporting the validity of our approach.

Figure 2 shows that while T_{2e} displays a strong concentration dependence, the T_{1e} values are practically independent of nitroxide concentration. The value of $T_{1e} = (0.23 \pm 0.0.02)$ μs measured here is in good agreement with a value of $T_{1e} = 0.37$ μs measured by a conventional pulse saturation-recovery method in ref 13 for $c = 0.5$ mM/L. The small difference between the two measurements may be related to differences in sample preparation and, perhaps, to some ambiguity in the application of the saturation-recovery method at $T_{1e} \sim T_{2e}$.

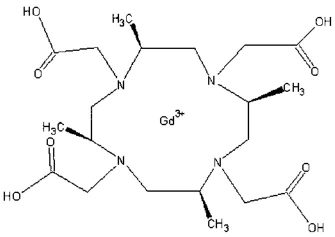
4. Electron Spin−Lattice Relaxation in Paramagnetic Contrast Agents (Gd Chelates)

Paramagnetic contrast agents (PCA's) are widely used in magnetic resonance imaging (MRI). Gd^{3+} complexes are the most frequently employed PCA's (see, for example, ref 14). When introduced into biological tissues or organs, they shorten the nuclear spin−lattice relaxation time of surrounding protons and so improve the contrast of MR images. The efficiency of a PCA can depend strongly on the electron spin−lattice relaxation time T_{1e} of the paramagnetic complex, particularly when the agent is tumbling slowly, as is the case for new blood-pool agents that associate with serum proteins. Up to now, however, information on T_{1e} in these systems has been available only from theoretical estimates derived from nuclear spin relaxation measurements, or from extrapolations from T_{2e} values derived from EPR line shape studies; experimental determination of T_{1e} in Gd^{3+} PCA solutions could not be performed because of extremely fast relaxation rates combined with rather broad EPR line widths. As shown above, this is just the case when the modulation technique of measuring T_{1e} can be useful.

In this communication, we report on T_{1e} measurements in two chelate complexes of Gd^{3+}, both 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 3, and are designated **1** and **2**. The Gd^{3+} complexes were synthesized by Schering AG, Berlin. Aqueous solutions were prepared at various concentrations, with and without a pH 7.4 buffer. To search for an environmental effect on the Gd^{3+}-chelate relaxation, two types of samples were prepared: (i) free liquid and (ii) the same amount of the solution absorbed into filter paper. Measurements were performed at 295 K with the same experimental setup as described in section 3, with the modulation frequency $\Omega/2\pi = 1.6$ MHz. As an example, Figure 4 shows the field dependence of the U signal taken point by point through the resonance region together with the EPR absorption line. Because of extremely rapid relaxation, the "amplitude version" of the modulation method was used (see eq 8). Calibration was made with a reference particle of α,α′-diphenyl-β-picrylhydrazyl (DPPH) −not shown in Figure 4, with T_{1e} (DPPH) $= 5.0 \times 10^{-8}$ s as measured previously by means of the "phase version" of the same technique. Our value of T_{1e} for DPPH is in good agreement with the published values for this standard ($T_{1e} = T_{2e} = 6.7 \times 10^{-8}$ s).[15]



Compound (1)



Compound (2)

Figure 3. Chemical structures of the two gadolinium compounds studied in this work.

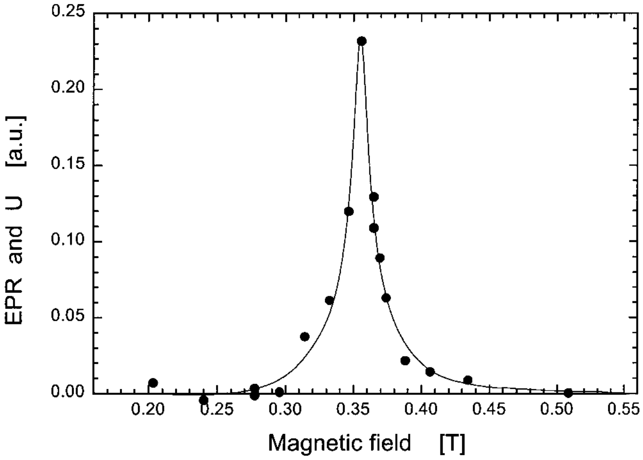


Figure 4. Magnetic field dependencies of the in-phase component of the longitudinal magnetization response (*U*, points) and the EPR absorption (solid curve) for aqueous solution of Gd DOTA compound (**2**) at $c = 60$ mM/L (a free liquid sample). Both signals are normalized to the maximum value.

TABLE 1: Sample Characterization and Relaxation Data for Gd DOTA PCAs

compound	c (mM/l)	buffer added	ΔB_{pp} (mT)	T_{2e} (ns)	T_{1e} (ns) (free liquid)	T_{1e} (ns) (in filter paper)
1	30	yes	15.5	0.42		2.2
1	35	no	15.5	0.42	1.7	2.6
1	70	no	15.5	0.42	1.9	2.3
2	26	yes	7.7	0.86		3.9
2	30	no	7.7	0.86	3.3	3.7
2	60	no	7.7	0.86	3.2	4.0

Table 1 presents the sample parameters, EPR line widths, T_{2e} as calculated using eq 12, and the measured T_{1e} data. The overall experimental error of the absolute T_{1e} values depends on the calibration procedure and so is rather large (about ±30%). Nevertheless, accuracy in comparing different samples measured under the same conditions is considerably better. As one can estimate from the spread of the experimental data (Table 1), it is within ±10%. As seen from Table 1, that the electron spin−

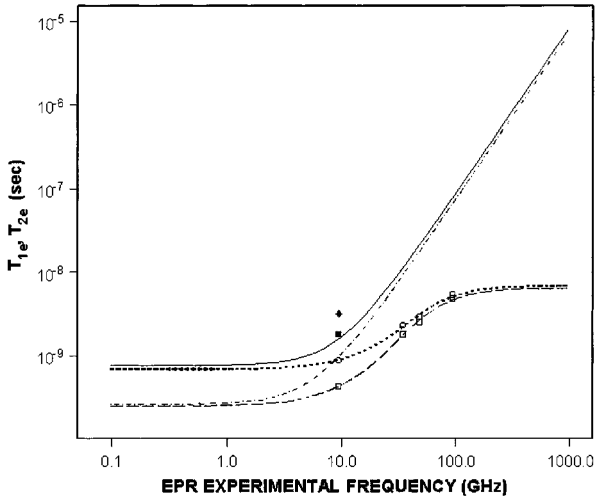


Figure 5. Experimental values for T_{1e} and $T_{2e,}$ together with predicted values, making use of Δ^2 and τ_v values obtained from fitting T_{2e} data by a method adapted from Hudson and Lewis[17,18] as described in the text. Compound **1**: (□) experimental T_{2e} values from line widths; (■) experimental T_{1e} value from longitudinal magnetization response. Dotted−dashed line (T_{1e}) and long dashed line (T_{2e}) represent predicted values. Compound **(2)**: (○) experimental T_{2e} values from line widths; (◆) experimental T_{1e} value from longitudinal magnetization response. Solid line (T_{1e}) and short dashed line (T_{2e}) represent predicted values.

lattice relaxation times (as well as the EPR line widths) in both Gd DOTA complexes do not depend on concentration or the presence of buffer in the range of concentrations studied. For the free liquid samples, one has on the average $T_{1e} = (1.8 \pm 0.1)$ ns and (3.2 ± 0.1) ns for the compounds **1** and **2**, respectively. The T_{1e} values for the samples dropped on filter paper are found to be about 1.2−1.4 times longer. With the current precision of the method, it is not possible to determine whether this difference is caused by interaction of the Gd DOTA molecules with cellulose or by experimental error.

Spin relaxation in the $S = {}^7/_2$ Gd^{3+} system is thought to be dominated by the stochastic modulation of the zero field splitting (ZFS).[16] In this mechanism, the magnitude of the static ZFS often is represented by the square of the trace of the ZFS tensor Δ^2 and the correlation time describing the modulation is denoted by τ_v. By studying the EPR line shapes of Gd^{3+} chelates in aqueous solution at several different microwave frequencies, important information can be obtained on the relationships between the ZFS and $T_{1,2e}$.[17] We have made careful multifrequency EPR studies of these two compounds in aqueous solutions at 9.5, 34.5, 48.2, and 94.5 GHz to study the magnetic field dependence of their line widths. Figure 5 shows the experimental values of T_{2e} obtained from the line widths, together with theoretical fitting of the data by a technique we have developed,[17] based on original work by Hudson and Lewis.[18] This approach allows the frequency dependence of ΔB_{PP} to be analyzed, and the values of the square of the trace of the zero field splitting tensor (Δ^2) and the correlation time associated with ZFS modulation in the system (τ_v) to be calculated. Best values for the two compounds were found to be, for compound **(1)** $\Delta^2 = 2.05 \times 10^{19}$ rad^2/s^2 and $\tau_v = 1.56 \times 10^{-11}$ s, and for compound **(2)** $\Delta^2 = 1.1 \times 10^{19}$ rad^2/s^2 and $\tau_v = 1.03 \times 10^{-11}$ s. The approach of Hudson and Lewis can be used to calculate T_{1e} as well as T_{2e}. Making use of the values of Δ^2 and τ_v obtained from the frequency dependence of the EPR line widths by the Hudson and Lewis method, relaxation matrix elements for T_{1e} given by Powell et al.[19] predicts values of T_{1e} of 1.0 ns for compound **1** and 1.7 ns for compound **2** at 9.5GHz. Figure 5 displays the experimental data for both T_{1e} and T_{2e}, together with the predicted values. The agreement between theory and experiment is reasonably good in this first instance of a direct measurement of T_{1e} in aqueous Gd^{3+} chelates; experimental T_{1e} values will help us to better understand the relationships between electron spin relaxation and the structure and environment of these important materials.

5. Conclusion

The modulation technique with lock-in detection of the longitudinal magnetization response allows direct determination of electron spin−lattice relaxation times T_{1e} as short as 10^{-7} to 10^{-10} s and so can be applied in many cases when the standard pulse and *cw* methods fail. For the first time, this technique has been successfully used for T_{1e} measurements in aqueous solutions of paramagnetic compounds. Both "phase" and "amplitude" versions of the modulation method are tested on perdeuterated nitroxide radicals and Gd DOTA complexes known as PCA materials. In both cases, we have found the measured T_{1e} values to be in agreement with previous published data and theoretical calculations. The modulation method thus appears to have considerable promise in chemical and biological applications of EPR.

Acknowledgment. The research was supported in part by a grant from Fogarty International Foundation (Grant 1RO3 TW00998-01), NIH (R.B.C.; Grants GM51630 and GM42208), Russian Foundation of Fundamental Research (Grant 99-02-16024), as well as from the U.S. Department of Energy (Grant DE FG22-96 PC 96205) and used facilities of the Illinois EPR Research Center (NIH Grants P41 RR01811 and R01 RR01811; R.L.B.).

References and Notes

(1) Slichter, P. C. *Principles of Magnetic Resonance*; Springer-Verlag: Berlin, 1980.

(2) Hérve, J.; Pescia, J. *C. R. Acad. Sci.* **1969**, *251*, 665.

(3) Pescia, J. *Ann. Phys.* **1965**, *10*, 389.

(4) Atsarkin, V. A.; Demidov, V. V.; Vasneva, G. A. *Phys. Rev.* **1995**, *B 52*, 1290.

(5) Atsarkin, V. A.; Vasneva, G. A.; Demidov, V. V. *Zh. Eksp. Teor. Fiz.* **1995**, *108*, 927 [English translation: *JETP* **1995**, *81*, 509].

(6) Abragam, A.; Goldman, M. *Nuclear Magnetism: Order and Disorder*; Clarendon Press: Oxford, 1982.

(7) Ablart, G.; Pescia, J. *Phys. Rev.* **1980**, *B 22*, 1150.

(8) Zinsou, P. K.; Vergnoux, D.; Ablart, G.; Pescia, J.; Misra, S. K.; Berger, R. *Appl. Magn. Reson.* **1996**, *11*, 487.

(9) Atsarkin, V. A.; Demidov, V. V.; Vasneva, G. A. *Phys. Rev.* **1997**, *B 56*, 9448.

(10) Atsarkin, V. A.; Demidov, V. V.; Vasneva, G. A. *Appl. Magn. Reson.* **1998**, *15*, 323.

(11) Atsarkin, V. A.; Vasneva, G. A.; Demidov, V. V.; Gutmann, M.; Böttger, G. *Pis'ma Zh. Eksp. Teor. Fiz.***1999**, *69*, 567 [English translation: *JETP Lett.* **1999**, *69*, 610].

(12) Walker, M. B. *Phys. Rev.* **1973**, *B 7*, 2920.

(13) Robinson, B. H.; Haas, D. A.; Mailer, C. *Science* **1994**, *263*, 490.

(14) Su, M. Y.; Muhler, A.; Lao, X. Y.; Nalcioglu, O. *Magn. Reson. Med.* **1998**, *39*, 259.

(15) Bloembergen, N.; Wang, S. *Phys. Rev.* **1954**, *93*, 72.

(16) Clarkson, R. B.; Smirnov, A. I.; Smirnova, T. I.; Kang, H.; Belford, R. L.; Earle, K.; Freed, J. *Mol. Phys.* **1998**, *95*, 1325.

(17) Clarkson, R. B.; Smirnov, A. I.; Smirnova, T. I.; Belford, R. L. *The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging*; Merbach, A., Toth, E., Eds.; Wiley: New York, Chapter 9.

(18) Hudson, A.; Lewis, J. W. E. *Trans. Faraday Soc.* **1970** *66*, 1297.

(19) Powell, D. H.; Merbach, A. E.; González, G.; Brücher, E.; Micskei, K.; Ottaviani, M. F.; Köhler, K.; von Zelewsky, A.; Grinberg, Ya. O.; Lebedev, Ya. S. *Helv. Chim. Acta* **1993**, *76*, 2129.