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Measurement of the Longitudinal Relaxation Time by Continuous-Wave, Nonlinear Electron Spin Resonance Spectroscopies

F. Cianflone,*,† F. Francia,* and D. Leporini*,†,[1]

*Dipartimento di Fisica, Università di Pisa, Piazza Torricelli 2, Pisa I-56100, Italy; and
†Istituto Nazionale di Fisica Della Materia, Unità di Pisa, Italy

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We characterize a continuous-wave, nonlinear electron spin resonance spectroscopy which detects the longitudinal component of the magnetization. It is demonstrated that the signal is proportional to the Laplace transform of a relaxation function with decay time equal to the longitudinal relaxation time T_1. The conclusion is reached by comparing T_1 to the effective time $T_1^{(\mathrm{eff})}$ being drawn by progressive saturation for a nitroxide radical dissolved in supercooled *o*-terphenyl. © 1998 Academic Press

INTRODUCTION

Magnetic resonance spectroscopies may be grouped into two broad families involving continuous-wave (CWE) or transient experiments (TE). These experiments are often aimed at the study of the relaxation phenomena driving the magnetization to the thermal equilibrium (*1, 2*). In suitable limits the decays of the longitudinal and transverse components of the magnetization with respect to the static magnetic field B are characterized by single rates T_1^{-1} and T_2^{-1}, respectively (*1*). Longitudinal and transverse relaxation times are measured by various TEs, whereas CWEs provide information on longitudinal relaxation less directly (*1–4*).

It is well known that the lineshape of *linear* CWEs is the Laplace transform of the relaxation function $\psi(t)$ of suitable TEs (*1*). $\psi(t)$ describes the equilibrium recovery after the removal of the external disturbance. For example, the lineshape of the customary linear electron spin resonance (ESR) spectroscopy is the Laplace transform of the relaxation of the transverse magnetization which is created by rotating the equilibrium magnetization by a $\pi/2$ pulse.

No conclusive evidence exists in favor of CWEs whose lineshape is the Laplace transform of relaxation functions with decay rates T_1^{-1}. The present paper addresses the topic in the field of ESR where CWEs are of current use. It will be shown that the above feature is ensured by proper *nonlinear* ESR spectroscopies.

To the best of the authors' knowledge only few attempts tackling the above question were reported. Pescia, following a scheme by Whitfield and Redfield (*5*), developed a modulation technique whose linewidth was successfully compared to T_1 which was drawn by progressive saturation (*6*). The comparison took into examination only spin systems with $S = \frac{1}{2}$ and, therefore, is not conclusive. Moreover, it is well known that progressive saturation measures an *effective* T_1, $T_1^{(\mathrm{eff})}$, arising from the sum of all relaxation paths including nuclear and cross relaxation between observed levels. $T_1^{(\mathrm{eff})}$ usually differs from T_1 but for two-level systems the equality $T_1 = T_1^{(\mathrm{eff})}$ holds. Then, it becomes impossible to assess which ''kind'' of longitudinal relaxation the Pescia experiment is sensitive to. As a relevant example of T_1-sensitive CWE the saturation transfer spectroscopy developed by Hyde and co-workers must also be quoted (*7*).

Starting from a different standpoint, some of the present authors and their associates investigated the nonlinear susceptibility of a spin system under *weak,* multiple irradiation (*8*). A number of different spectroscopies were developed to characterize the second- and third-order nonlinear susceptibilities. In particular, the second-order susceptibility was studied by the longitudinally detected ESR (LODESR) (*8*).

In the LODESR experiment two σ-polarized microwave fields (MW) oscillating at frequencies $\nu_i = \omega_i/2\pi$ and amplitudes B_i, $i = 1, 2$, are present. Owing to the nonlinear spin-microwave interaction, under resonance condition ($\omega_{1,2} \approx \omega_0$, ω_0 being the Larmor angular frequency) a longitudinal dynamic magnetization comes out which induces a signal in coils with axis parallel to the static magnetic field $B = \omega_0/\gamma$, γ being the gyromagnetic factor. The signal exhibits Fourier components at $\Delta\omega \equiv |\omega_1 - \omega_2|$ and harmonics. The subsequent phase-detection at $\Delta\omega$ yields the LODESR signal L^{LODESR}. The dependence of L^{LODESR} on B and $\Delta\omega$ is usually studied by sweeping B with constant $\Delta\omega$ to detect the line-

[1] To whom correspondence should be addressed. Fax: 39-50-48277. E-mail: leporini@ipifidpt.difi.unipi.it.

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shape $L^{\mathrm{LODESR}} = L_a$ or, vice versa, by sweeping $\Delta\omega$ with constant B to detect the lineshape $L^{\mathrm{LODESR}} = L_d$.

The analysis of the LODESR experiment for a two-level system in terms of Bloch equations led to the result that the line L_d has the width T_1^{-1} (*8*). However, owing to the simplified theory, a clear-cut conclusion on the relation between T_1 and the observed linewidth was not reached.

A general theory of the nonlinear response of a spin system subjected to external fields has been recently proposed by one of the present authors (*9*). It takes into full account the quantum-mechanical character of the spin–radiation interaction and makes use of a stochastic picture of the spin–bath interaction. The work extends the well-known result of linear response theory, which relates the susceptibility to the Laplace transforms of proper relaxation functions, by writing the nth-order nonlinear susceptibility in terms of the product of Laplace transforms of n relaxation functions ψ. The analysis of second-order susceptibilities showed that, under fairly general conditions (see below), one of the two relaxation functions describing the LODESR signal decays at rate T_1^{-1}.

Guided by the above indications, we carried out new measurements and proved that the LODESR signal has a ''linewidth'' T_1^{-1} even in *multilevel* paramagnetic systems. The paper is organized as follows. In the next section the relevant theory is presented. Then, the experimental aspects are detailed and the results are discussed. Finally, the conclusions are summarized.

THEORY

The present study deals with paramagnetic systems with spin $S = \frac{1}{2}$ coupled to a nucleus with magnetic dipole I. ω_I will denote the hyperfine splitting constant ($\omega_I \ll \omega_0$). The amplitude of the MW fields in the LODESR spectroscopy is extremely low and the lineshape L^{LODESR} may be written as (*9*)

$$L^{\mathrm{LODESR}} = B_1 B_2 \mathrm{Re}\{\psi_+(i\omega_1)\}|\psi_z(i\Delta\omega)|. \qquad [1]$$

$\psi_k(z)$ is a relaxation function to be interpreted as the Laplace transform of the correlation function $\psi_k(t) \equiv \langle S_k^\dagger(t) S_k\rangle$ of the kth spherical component of the spin ($k = \pm, z$) (*1*). $\Delta\omega \equiv |\omega_1 - \omega_2|$. $A^\dagger$ is the Hermitean conjugate of A. S_+ is the usual raising operator and $S_- = S_+^\dagger$. $Re\{A\}$ and $|A|$ mean the real part and the modulus of A, respectively. $\langle A\rangle$ denotes the weighted average of A on the heat bath and the degrees of freedom of the spin system. One important point is that the time evolution of the relaxation functions $\psi_k(t)$ is governed by the total Hamiltonian in absence of external fields, i.e., $B_{1,2} = 0$. Then, Eq. 1 is a natural generalization of the linear response theory to nonlinear CWEs. Equation [1] holds provided that the relaxation of $\psi_z(t)$ takes place on time scales longer than the microscopic correlation times τ (time scale separation). In this regime $\psi_z(t)$ may be expressed by a sum of exponentials with proper relaxation times. Time scale separation occurs if the strength Δ of the interactions relaxing the magnetization is smaller than the Larmor frequency ω_0 (*10*). The special case of the exponential damping of $\psi_z(t)$, namely

$$\psi_z(t) = \exp(-t/T_1) \qquad [2a]$$

or, equivalently,

$$|\psi_z(i\Delta\omega)| = T_1/\sqrt{(\Delta\omega T_1)^2 + 1} \qquad [2b]$$

is worth noting. Even in presence of hyperfine coupling, it suffices that the correlation functions of the interactions relaxing the magnetization are decreasing functions of time, and their correlation times τ are longer than ω_0^{-1} (*9, 10*). These conditions, which are not surprising in view of the inequality $\omega_I \ll \omega_0$, are easily met in the X-band ESR ($\omega_0^{-1} \approx 1.6 \times 10^{-11}$ s).

The conditions leading to Eqs. [1, 2] may be summarized by the chain of inequalities $T_1 \gg \tau \gg \omega_0^{-1}$. It takes very little to understand that they ensure that $\psi_+(i\omega_1)$ does not change appreciably on frequency intervals comparable to $1/T_1$. In fact, they imply that $\min\{1/T_2, 1/\tau\} \gg 1/T_1$. Therefore, if $\Delta\omega = |\omega_1 - \omega_2|$ is swept, the LODESR signal, Eq. [1], reduces to

$$L^{\mathrm{LODESR}} = L_d \cong C|\psi_z(i\Delta\omega)| = CT_1/\sqrt{(\Delta\omega T_1)^2 + 1}, \qquad [3]$$

where C is a constant. Equation [3] shows that by sweeping $\Delta\omega$, i.e., the offset of the frequencies of the MW fields, the LODESR signal, L_d, yields the spectral profile of $|\psi_z(i\Delta\omega)|$ which has a width T_1^{-1}.

EXPERIMENTAL

The homebuilt X band spectrometer for both linear and nonlinear ESR and the programmable temperature controller are detailed elsewhere (*8*). The controller ensures stabilities as high as 10^{-3} K and step resolution of 10^{-2} K. The measurements have been carried out on the stable radical TEMPO ($S = \frac{1}{2}$, $I = 1$, $\omega_0/\omega_I \approx 200$ at X band) dissolved in the glass former o-terphenyl (OTP) in concentration $c = 5 \times 10^{-3}$ M/liter (*4*). Samples were degassed in N_2 flow and then sealed under N_2 atmosphere in quartz tubes of 3 mm i.d.

Due to the high viscosity of OTP (about 10 P at $T = 300$ K) and the TEMPO dilution, exchange and dipolar broadening are negligible in the investigated temperature range. This conclusion was also supported by two indepen-

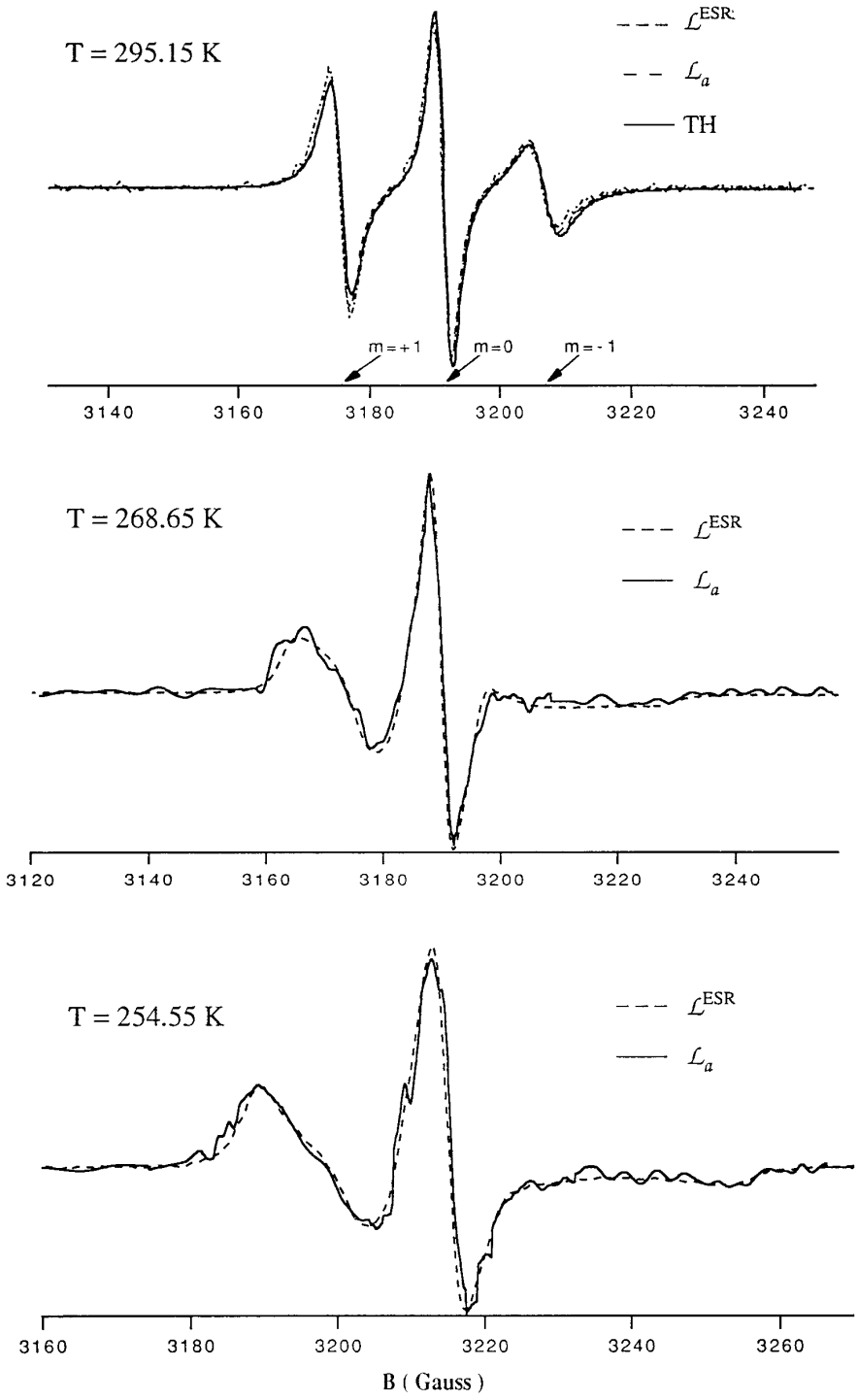

FIG. 1. Comparing the differentiated lineshapes of linear ESR L^{ESR} and LODESR L_a. $\nu_1 - \nu_2 = 42$ kHz. For the case at $T = 295.15$ K the arrows mark the points where $T_1^{(eff)}(m)$ and $T_1^{-1}(m)$ are measured, and the solid line is the best fit according to the Redfield theory of the ESR lineshape.

dent measurements. First, we compared the ESR lineshapes of two samples with TEMPO concentration 5×10^{-3} and 3×10^{-4} M/liter at $T = 297.55$ K without detecting any change. Then, we compared the T_1^{-1} values, as measured by the LODESR signal L_d, of two samples with TEMPO concentration 5×10^{-3} and 1×10^{-3} M/liter at $T = 295.32$ K (at lower concentrations the signal-to-noise ratio becomes poor). The two values were found to be equal within the experimental errors. The negligible role of the dipolar interaction is also understood by evaluating the amplitude of the

dipolar field on one tagged radical due to the closest radicals. For the concentration $c = 5 \times 10^{-3}$ M/liter two radicals are spaced apart about 10 OTP molecules, i.e., 7.4 nm, being the OTP Van der Waals radius $r_{OTP} = 0.37$ nm (*11*). Then, the contribution due to a single radical is about 2.2 μT. Assuming 10 nearest neighbors, the total dipolar field is about 20–30 μT.

The spin relaxation of the radical is driven by the interplay between the rotational Brownian motion of TEMPO and the anisotropic Zeeman and hyperfine tensors, yielding fluctuating fields with $0.5\ \text{mT} \leq \Delta \leq 2.6\ \text{mT}$ (*4*). These fields fairly exceed the dipolar contribution. The principal components of the Zeeman and hyperfine tensors to be used in the numerical simulations were drawn by careful simulation of the ESR powder spectrum recorded at $T = 100$ K.

RESULTS AND DISCUSSION

The LODESR measurements we carried out examined some specific predictions of Eqs. [1] and [3].

By sweeping the static magnetic field B with constant $\Delta\omega$, we detected the lineshape $L^{\text{LODESR}} = L_a$. According to Eq. [1], L_a is proportional to the lineshape of low-power ESR (*1, 3, 4*):

$$L^{\text{ESR}} \propto \text{Re}\{\psi_+(i\omega_1)\}|_{\omega_1=\gamma B}. \qquad [4]$$

In order to scrutinize this prediction, L_a has been differentiated and then compared with the first derivative of L^{ESR}. The comparison of different temperatures is shown in Fig. 1. For $T = 295.15$ K Fig. 1 also shows the fit of L^{ESR} and L_a with the three Lorentzians predicted by the Redfield theory (*1, 3, 4*) which were convoluted with a Gaussian lineshape of width $w = 0.07$ mT to account for the residual broadening. TEMPO is assumed to rotate with isotropic diffusion constant D. The pattern of L^{ESR} and the best-fit value of the correlation time $\tau = 1/6D = 1.6 \times 10^{-9}$ s point to a moderately fast reorientation of TEMPO.

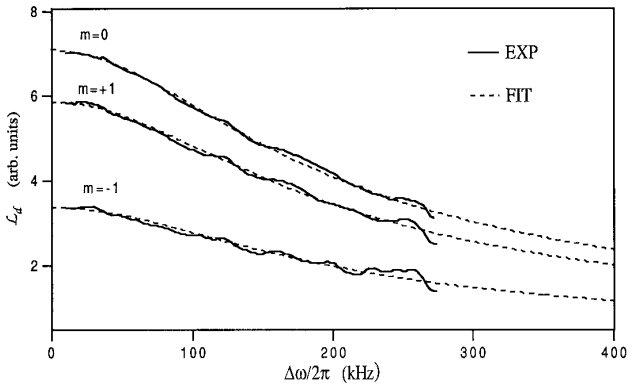

FIG. 2. LODESR signal L_d at $T = 295.15$ K for the three hyperfine components. The static magnetic field B is set at the values marked in Fig. 1. The dashed line is the best fit according to Eq. [3].

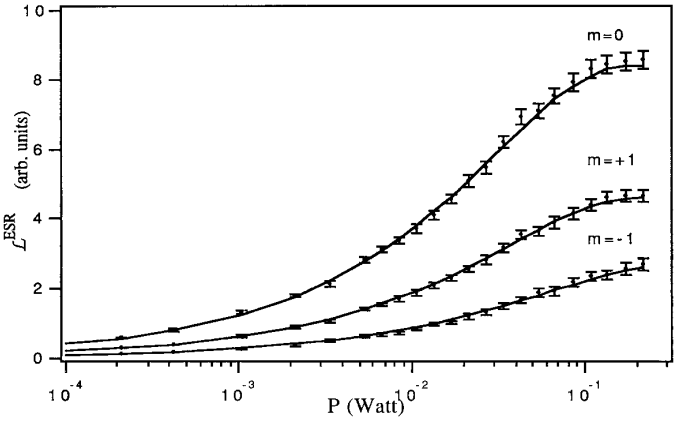

FIG. 3. Saturation curve of L_m^{ESR} for the three hyperfine components. $T = 295.15$ K. The solid line is the best fit according to Eq. [6]. The only adjustable parameter is $T_1^{(\text{eff})}(m)$. See text for details.

Of major relevance to the purposes of the present paper is to prove that, according to Eq. [3], the LODESR signal, measured when $\Delta\omega = |\omega_1 - \omega_2|$ is swept, L_d, yields the longitudinal relaxation time.

To achieve this, the LODESR lineshape L_d was recorded by sweeping $\Delta\omega$ for each line of the ESR lineshape. The magnetic field B was set to the maximum absorption of each of the three hyperfine components of the ESR lineshape, $m = \pm 1, 0$ (see Fig. 1). The best-fit of L_d with Eq. [3] yields $T_1(m)$. The fits for the three hyperfine components at $T = 295.15$ K are shown in Fig. 2.

One way to ascertain if $T_1(m)$ is the ''true'' longitudinal relaxation time is to compare the latter to the effective time $T_1^{(\text{eff})}(m)$ determined by progressive saturation measurements (*12, 13*). In fact, in the regime of TEMPO rotational motion of our interest ($\tau \gg \omega_0^{-1}$) $T_1(m)$ and $T_1^{(\text{eff})}(m)$ are expected to be little dependent on m and with a ratio

$$T_1(m)/T_1^{(\text{eff})}(m) = (2I + l) \qquad [5]$$

For TEMPO ($I = 1$) the expected ratio is 3. Equation [5] does not rely on a particular spin-relaxation model but only on the different natures of the time constants $T_1(m)$ and $T_1^{(\text{eff})}(m)$. The former is a genuine relaxation time, the latter may be seen as a steady-state impedance representing the reaction of the m transition to the MW field (*1, 3*). The precision of the progressive saturation measurements is in general not particularly high but in the validity range of Redfield/Bloch theory good results are found (*13*).

$T_1^{(\text{eff})}(m)$ was measured as follows. The saturated mth line of the ESR lineshape L_m^{ESR} was fitted to the Voigt lineshape (*1*):

$$L_m^{\text{ESR}}(B) = \int g(B' - B_m) \times \frac{1}{[\gamma(B - B')T_2(m)]^2 + 1 + \alpha^2 QP\gamma^2 T_1^{(\text{eff})}(m)T_2(m)}\, dB. \qquad [6]$$

TABLE 1
Temperature Dependence of T_1 (m) and $T_1^{(\mathrm{eff})}$ (m)

T (K)	$1/T_1^{(\mathrm{eff})}$ (+1) (KHz)	$1/T_1^{(\mathrm{eff})}$ (0) (KHz)	$1/T_1^{(\mathrm{eff})}$ (−1) (KHz)	$1/T_1$ (+1) (KHz)	$1/T_1$ (0) (KHz)	$1/T_1$ (−1) (KHz)	τ (s)
289.91	2225 ± 66	2237 ± 67	2250 ± 66	740 ± 25	745 ± 20	710 ± 25	2.2×10^{-9}
292.15	2330 ± 70	2325 ± 70	2390 ± 72	802 ± 25	800 ± 25	785 ± 20	1.9×10^{-9}
295.15	2670 ± 80	2670 ± 80	2640 ± 79	910 ± 25	885 ± 25	910 ± 35	1.6×10^{-9}

Note. The table also lists the rotational correlation time τ of the TEMPO radical dissolved in OTP as drawn by numerical simulation of the ESR lineshape.

$g(x)$ is Gaussian centered at $x = 0$ with second moment w which accounts for the inhomogeneous broadening. B_m is the magnetic field where L_m^{ESR} is maximum. $T_2^{-1}(m)$ is the homogeneous linewidth in the limit of low MW power. P is the MW power feeding the resonating cavity with quality factor $Q = 5530 \pm 60$. α is defined as the amplitude of the rotating component of the MW field divided by $\sqrt{QP}$. $T_2^{-1}(m)$ and w were measured by fitting the low-power ESR lineshape (see Fig. 1), α was measured by the method of perturbing metal sphere (*14*). It was found $\alpha = (1.71 \pm 0.02) \times 10^{-2}$ Gauss/W$^{1/2}$, corresponding to a rotating component with amplitude 1.27 Gauss at $P = 1$ W. $T_1^{(\mathrm{eff})}(m)$, which is the only adjustable parameter, was drawn by fitting Eq. [6] to the saturation curve, namely the curve $L_m^{\mathrm{ESR}}(B_m)$ vs P. The results are shown in Fig. 3 for $T = 295.15$ K.

Table 1 compares $T_1(m)$ and $T_1^{(\mathrm{eff})}(m)$ for different temperatures. In the temperature range of Table 1, $T_1 \gg \tau \gg \omega_0^{-1}$ which ensures that Eqs. [1] and [3] hold. Table 1 virtually covers the interval where the comparison between T_1 and $T_1^{(\mathrm{eff})}$ may be carried out quantitatively. The lower bound is set by the condition on which the Redfield–Bloch theory and then Eq. [6] hold, roughly $\tau < 5 \times 10^{-9}$ s. The upper bound is set by the requirement $\tau \gg \omega_0^{-1}$ and the need of a homogeneous contribution $T_2^{-1}(m)$ comparable or larger than w. The table shows that, as expected, both $T_1(m)$ and $T_1^{(\mathrm{eff})}(m)$ do not depend appreciably on m. The ratio $T_1(m)/T_1^{(\mathrm{eff})}(m)$ is listed in Table 2. It is found that in agreement with Eq. [5] $T_1 = 3T_1^{(\mathrm{eff})}$ within the experimental errors. The ratio $T_1(-1)/T_1^{(\mathrm{eff})}(-1)$ differs from 3 a little more than one standard deviation at the lowest temperature. We ascribed this deviation to the onset of slow-motion features in the ESR line with $m = -1$ which cannot be fully accounted for by the Redfield expression, Eq. [6].

TABLE 2
Temperature Dependence of the Ratio T_1 (m)/$T_1^{(\mathrm{eff})}$ (m)

T (K)	+1	0	−1
289.91	3.00 ± 0.13	3.00 ± 0.12	3.16 ± 0.14
292.15	2.91 ± 0.12	2.91 ± 0.12	3.04 ± 0.12
295.15	2.93 ± 0.12	3.02 ± 0.12	2.90 ± 0.14

The above study supports the conclusion that the parameter T_1 which is measured in the LODESR spectroscopy is just the longitudinal relaxation time.

CONCLUSIONS

The present paper reports on a continuous-wave nonlinear ESR spectroscopy (LODESR) which detects the longitudinal component of the magnetization. Under mild constraints ($T_1 \gg \tau \gg \omega_0^{-1}$ and the amplitude of the fluctuating magnetic fields $\Delta \ll \omega_0$) the LODESR signal was expressed in terms of the Laplace transform of the relaxation function $\psi_z(t) = \langle S_z(t) S_z \rangle$ and then related to the longitudinal relaxation time T_1. T_1, which plays the role of a kind of ''linewidth'' of the LODESR signal, may be measured by sweeping the frequency offset of the two microwaves ν_1 and ν_2. Strong support to the above conclusions was provided by progressive saturation measurements.

Some comments regarding the uses of T_1 measurements are also in order. First of all, T_1 provides a tool to measure the components at ω_0 of the random magnetic fields affecting the spin relaxation. This is particularly important for testing carefully specific models of spin relaxation, since T_2 and, more generally, the transverse relaxation is affected by the combined contributions of the components at zero, ω_0, and ω_I frequencies. It must be also pointed out that the longitudinal spin relaxation time T_1 is a robust quantity, since it is defined even in cases where the transverse relaxation cannot be described in terms of a simple exponential with decay time T_2 (*9, 10*). Moreover, inhomogeneous broadening may complicate the study of homogeneous transverse relaxation. Owing to the analytical expressions of T_1 which may be derived by Redfield theory (*1, 5*), the above remarks imply that the analysis of T_1 data does not usually require heavy numerical work. In practice, this means that T_1-sensitive methods become increasingly preferable to T_2-sensitive methods as the motion of the paramagnetic species slows. This feature and the finding that T_1 is quite sensitive to the

presence of oxygen in solution lead Hyde and associates to remarkable applications in the field of spin-label oximetry of biological systems (*15*). Also, the knowledge of T_1 and, in particular, its temperature dependence is expected to be of great help in improving the interpretation of saturation-transfer spectroscopy, a technique which is particularly well suited to investigate very slow rotational motions (*16*).

As a final remark we point out that the experiments described in the present paper compete well with the established pulse or step techniques to measure T_1 (e.g., inversion recovery, stimulated echoes, saturation recovery). Sample heating is completely negligible. Furthermore, the former require low-power standard microwave components and minor modifications of standard reflection ESR spectrometers, whereas the setup of the latter include a number of expensive microwave devices (e.g., GaAs-FET-amplifier, mixer, fast protection switches, limiters, fast boxcar integrator, and TWT amplifiers).

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