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Journal of Magnetic Resonance 169 (2004) 335–341

JMR
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Analysis of EPR-time profiles of transient radicals with unresolved spectra

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Received 29 December 2003; revised 14 May 2004
Available online 17 June 2004

Abstract

A method for analysing EPR-time profiles of transient radicals in solution with unresolved hyperfine structure is proposed. It is based on considering the magnetic field integral of the magnetization, i.e., the total EPR signal intensity, instead of single components of overlapping EPR transitions. For a radical system involving chemical kinetics, chemically induced electron polarization (CIDEP), and spin relaxation, an analytical solution is found for the evolution of the integral magnetization in the Laplace domain. The solution in the time domain is given for the case of negligible saturation, i.e., $\omega_1^2 T_1 T_2 \ll 1$. The formulae presented are suitable to avoid equivocal multi-parameter fits when analysing the results of time-resolved continuous-wave EPR experiments for the observables, which characterize the chemical kinetics, CIDEP, and electron spin relaxation of radical systems.

Keywords: Analysis of time-resolved EPR data; Free radicals; Radical kinetics; Electron spin relaxation; Chemically induced electron polarization

1. Introduction

Studies of the dynamics of radical systems, subject to chemical kinetics, chemically induced electron polarization (CIDEP), and spin relaxation, usually employ time-resolved EPR (TREPR) measurements after pulse radiolytic or flash photolytic radical generation [1,2]. The EPR signal amplitude in dependence on time then contains all information about the chemical kinetics and spin dynamics of the system and, therefore, is determined by a variety of parameters (reaction rate constants, electron spin polarizations, and relaxation times T_1, T_2, etc.), which are all more or less unknown. If continuous-wave TREPR is employed, the EPR-time profiles are commonly analysed in terms of extended Bloch equations [3–5], using the possibility to determine the spin dynamics separately from the chemical kinetics by analysing the Torrey oscillations at high incident microwave powers [6]. This approach avoids equivocal multi-parameter fits and has proven its efficiency in a variety of investigations [6–9]. However, this approach is only applicable for radical systems possessing well-separated single EPR transitions and fails for species, which exhibit unresolved EPR spectra enveloping an unknown hyperfine structure. The latter is often the case, especially for radicals with fast spin relaxation, where the EPR line width is comparable or larger than the hyperfine splitting.

We run into this problem recently [10], when trying to analyse CIDEP data from EPR-time profiles of thionine radicals which, under our conditions, exhibited only one broad EPR line enveloping the whole unknown hfi. There it was found, that in the simplest case of a radical system without chemical decay and large initial spin polarization $M_Z^0 \gg P_{\mathrm{eq}} R_0$ (R_0: radical concentration, P_{eq}: Boltzmann polarization) the initial spin polarization and its relaxation time can be rather well estimated from the variation of the total intensity of the EPR spectrum in the Laplace domain.

In this paper, we generalize that approach for radical systems undergoing chemical decay kinetics and exhibiting CIDEP of any magnitude. To do so, the extended Bloch equations for such a system are solved for the v-magnetization and integrated over the full frequency range. An analytical solution for the total EPR signal

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doi:10.1016/j.jmr.2004.05.014

intensity is found in the Laplace domain for a radical system subject to decay kinetics, CIDEP, and spin relaxation. A time domain solution is obtained under the condition $\omega_1^2 T_1 T_2 \ll 1$, i.e., if saturation is negligible. Thus, the final formulae describe the dependence of the integral electron spin magnetization on time t and/or the Laplace transformation parameter s. They are to be fitted in the time or Laplace domain, respectively, to the total experimentally observed signal intensity, i.e., the EPR-time profiles numerically integrated over the magnetic field.

2. Theory

We consider a system of reacting radicals in solution possessing an EPR spectrum, which is a superposition of several overlapping hyperfine components, each of them being describable by a set of extended Bloch equations [7]:

$$\begin{aligned}
\dot{u} &= -\frac{u}{T_2} - \Delta\omega \cdot v + F_1^{\mathrm{ex}}(t),\\
\dot{v} &= \Delta\omega \cdot u - \frac{v}{T_2} + \omega_1 M_Z + F_2^{\mathrm{ex}}(t),\\
\dot{M}_Z &= -\omega_1 \cdot v - \frac{M_Z}{T_1} + F_z(t) + F_3^{\mathrm{ex}}(t),
\end{aligned} \tag{1}$$

where

$$F_z(t) = \frac{1}{T_1} P_{\mathrm{eq}} R(t) + 2k_t R^2(t) P_F P_{\mathrm{eq}}, \tag{2}$$

u and v represent the perpendicular magnetization in the rotating frame, $\Delta\omega$ is the offset from resonance, ω_1 the microwave field amplitude, $R(t)$ the radical concentration, $P_{\mathrm{eq}}R(t)$ the equilibrium z-magnetization, and $T_{1,2}$ are the electron spin relaxation times. F_1^{ex}, F_2^{ex}, and F_3^{ex} describe the Heisenberg spin exchange between the radicals. The second order term in $F_z(t)$ accounts for the production of F-pair polarization in radical collisions due to the radical pair mechanism (RPM). $F_z(t)$ can be modified for each particular radical system by including the specific terms, which affect the z-magnetization of that system. The initial conditions for the equations are taken as $u(0) = v(0) = 0$, $M_z(0) = M_z^0$, the initial z-magnetization generated instantaneously at $t = 0$.

In our case, the terms F_1^{ex}, F_2^{ex}, and F_3^{ex} in Eq. (1) can be omitted, because we are interested only in the total electron spin magnetization, which is not affected by Heisenberg spin exchange. Thus, the Laplace transformation reads:

$$\begin{aligned}
s\tilde{u} &= -\frac{\tilde{u}}{T_2} - \Delta\omega \cdot \tilde{v}\\
s\tilde{v} &= \Delta\omega \cdot \tilde{u} - \frac{\tilde{v}}{T_2} + \omega_1 \tilde{M}_Z\\
s\tilde{M}_Z &= -\omega_1 \cdot \tilde{v} - \frac{\tilde{M}_Z}{T_1} + M_Z^0 + \tilde{F}_z
\end{aligned} \tag{3}$$

with the solution for $\tilde{v}$:

$$\tilde{v}(s, \Delta\omega) = \frac{\omega_1 T_1 (M_z^0 + \tilde{F}_z)}{(1 + sT_1) \cdot \left[s + T_2^{-1} + \frac{\Delta\omega^2}{s + T_2^{-1}} + \frac{\omega_1^2}{s + T_1^{-1}}\right]}. \tag{4}$$

The signal $S(t, \Delta\omega)$ monitored in continuous-wave TREPR is proportional to $v(t, \Delta\omega)$ convoluted with the response function of the spectrometer $f_{\mathrm{R}}(t)$

$$S(t, \Delta\omega) = w \cdot C \cdot f_{\mathrm{R}}(t) \otimes v(t, \Delta\omega), \tag{5}$$

where w is the weight of the hyperfine component and C the sensitivity factor of the spectrometer. Assuming an exponential response function with response time τ_{R}

$$\left.\begin{aligned} t < 0 &: f_{\mathrm{R}}(t) = 0\\ t \geqslant 0 &: f_{\mathrm{R}}(t) = \tfrac{1}{\tau_{\mathrm{R}}} \exp(-\tfrac{t}{\tau_{\mathrm{R}}}) \end{aligned}\right\}, \tag{6}$$

the Laplace transform of the response function is $\tilde{f}_{\mathrm{R}}(s) = (1 + s\tau_{\mathrm{R}})^{-1}$ and, hence, Laplace transformation of Eq. (5) into $\tilde{S}(s, \Delta\omega) = w \cdot C \cdot \tilde{f}_{\mathrm{R}}(s) \cdot \tilde{v}(s, \Delta\omega)$ leads to

$$\tilde{S}(s, \Delta\omega) = \frac{w \cdot C \cdot \omega_1 T_1 (M_z^0 + \tilde{F}_z)}{(1 + s\tau_{\mathrm{R}})(1 + sT_1) \cdot \left[s + T_2^{-1} + \frac{\Delta\omega^2}{s + T_2^{-1}} + \frac{\omega_1^2}{s + T_1^{-1}}\right]}. \tag{7}$$

Assuming equal relaxation times $T_{1,2}$ for all hyperfine components, integration of $\tilde{S}(s, \Delta\omega)$ over the whole frequency range $-\infty < \Delta\omega < \infty$ of the spectrum then results in the total EPR signal intensity

$$\tilde{I}(s) = \frac{C\pi\omega_1 T_1 (M_z^0 + \tilde{F}_z)}{(1 + s\tau_{\mathrm{R}})(1 + sT_1)} \cdot \sqrt{\frac{1}{1 + \frac{T_1 T_2 \omega_1^2}{(1 + sT_1)(1 + sT_2)}}}. \tag{8}$$

If saturation is negligible, i.e., under the conditions $\omega_1^2 T_1 T_2 \ll 1$, the solution can be approximated by

$$\tilde{I}(s) = \frac{C\pi\omega_1 T_1 (M_z^0 + \tilde{F}_z)}{(1 + s\tau_{\mathrm{R}})(1 + sT_1)}. \tag{9}$$

For this case, the inverse Laplace transformation gives an elegant solution in the time domain, namely

$$I(t) = \frac{C\pi\omega_1}{1 - \frac{\tau_{\mathrm{R}}}{T_1}} \left[M_z^0 \left(\mathrm{e}^{-\frac{t}{T_1}} - \mathrm{e}^{-\frac{t}{\tau_{\mathrm{R}}}}\right) + \left(F_z(t) \otimes \left(\mathrm{e}^{-\frac{t}{T_1}} - \mathrm{e}^{-\frac{t}{\tau_{\mathrm{R}}}}\right)\right)\right] \quad \text{for } T_1 \neq \tau_{\mathrm{R}}, \tag{10}$$

where the second term on the right-hand side involves all parameters of the radical system because of the convolution integral of the exponential functions with $F_z(t)$.

2.1. Limit of fast relaxation

If the radical decay is slow and the electron spin relaxation sufficiently fast (T_1^{-1}, $T_2^{-1} \gg 2k_t R_0$) to consider the radical concentration as being approximately constant, $R(t) \approx R_0$, during the relaxation process, the solution can be further simplified by neglecting in Eqs. (1) and (2) the second order term in the radical concentration, i.e., $F_z(t) \approx T_1^{-1} P_{\mathrm{eq}} \mathrm{R}_0$. The solution (10) in the time domain for the case $\omega_1^2 T_1 T_2 \ll 1$ then becomes

$$I(t) = \frac{C\pi\omega_1}{1 - \frac{\tau_{\mathrm{R}}}{T_1}} \left(M_z^0 - P_{\mathrm{eq}} \mathrm{R}_0\right) \left(\mathrm{e}^{-\frac{t}{T_1}} - \mathrm{e}^{-\frac{t}{\tau_{\mathrm{R}}}}\right) + C\pi\omega_1 P_{\mathrm{eq}} \mathrm{R}_0 \left(1 - \mathrm{e}^{-\frac{t}{\tau_{\mathrm{R}}}}\right). \tag{11}$$

This is a generalization of the formula presented previously for the Laplace domain [10].

3. Discussion

As an example, we consider a chemical system consisting of only one sort of radicals, which have been generated instantaneously in low viscous solution by e.g., pulse radiolysis or laser flash photolysis. The radicals may possess an initial net polarization due to the triplet mechanism, which can be accounted for by the initial condition M_z^0 in the Bloch equations (Eq. (1)). S–T_0 mixing in geminate and free diffusional radical pairs will produce a pure multiplet type polarization which does not affect the intensity of the total EPR spectrum, as it cancels in the integration over the magnetic field. Therefore, as long as there is no noticeable S–T_- mixing (what is true in most cases), radical collisions do not lead to the formation of net polarization and so the second term on the right hand side of Eq. (2) can be set zero, i.e., $F_z(t) = T_1^{-1} P_{\mathrm{eq}} R(t)$. Assuming that the radicals decay by self-termination, the concentration $R(t)$ is described by $R(t) = R_0/(1 + 2k_t R_0 t)$. With

$$\tilde{R} = -\frac{1}{2k_t} \exp\left(\frac{s}{2k_t R_0}\right) Ei\left(-\frac{s}{2k_t R_0}\right), \tag{12}$$

where $Ei(x) = \int_{-\infty}^{x} \frac{e^t}{t} \mathrm{d}t$, we can rewrite the formulae (8)–(10) in a parametric form as

$$\tilde{I}(s) = \frac{AT_1 - B\tau_0 \exp(s\tau_0) Ei(-s\tau_0)}{(1 + s\tau_{\mathrm{R}})(1 + sT_1)} \cdot \sqrt{\frac{1}{1 + \frac{T_1 T_2 \omega_1^2}{(1+sT_1)(1+sT_2)}}}, \tag{13}$$

which for $\omega_1^2 T_1 T_2 \ll 1$ becomes

$$\tilde{I}(s) = \frac{AT_1 - B\tau_0 \exp(s\tau_0) Ei(-s\tau_0)}{(1 + s\tau_{\mathrm{R}})(1 + sT_1)} \tag{14}$$

with the time domain solution

$$I(t) = \frac{1}{1 - \frac{\tau_{\mathrm{R}}}{T_1}} \left[A\left(\mathrm{e}^{-\frac{t}{T_1}} - \mathrm{e}^{-\frac{t}{\tau_{\mathrm{R}}}}\right) + \frac{B}{T_1} \left(\left(1 + \frac{t}{\tau_0}\right)^{-1} \otimes \left(\mathrm{e}^{-\frac{t}{T_1}} - \mathrm{e}^{-\frac{t}{\tau_{\mathrm{R}}}}\right) \right) \right], \tag{15}$$

where $A = C\pi\omega_1 M_z^0$, $B = C\pi\omega_1 P_{\mathrm{eq}} R_0$, and $\tau_0 = (2k_t R_0)^{-1}$.

It is seen that Eq. (13) has five parameters A, B, T_1, T_2, and τ_0, which depend on the radical system, whereas Eq. (14) and its time domain transform (15) have only four ones, A, B, T_1, and τ_0. It is noteworthy, that for negligible saturation, $\omega_1^2 T_1 T_2 \ll 1$, the time profile of the integrated EPR signal becomes independent of the value of T_2, what is clearly not the case for on-resonance time profiles [11], as is demonstrated in Fig. 1. Fig. 2 gives the Laplace transforms $\tilde{I}(s)$ corresponding to the time dependent intensities $I(t)$ in Fig. 1B.

Several different series of experiments should be carried out to obtain the parameters via a fitting procedure of the above formulae to the experimental TREPR data. It is always advisable first to minimize the number of free variable parameters by applying low microwave field amplitudes ω_1 to come into the range $\omega_1^2 T_1 T_2 \ll 1$, where the influence of T_2 on the integrated EPR-time profiles is minor. It is also recommendable to perform

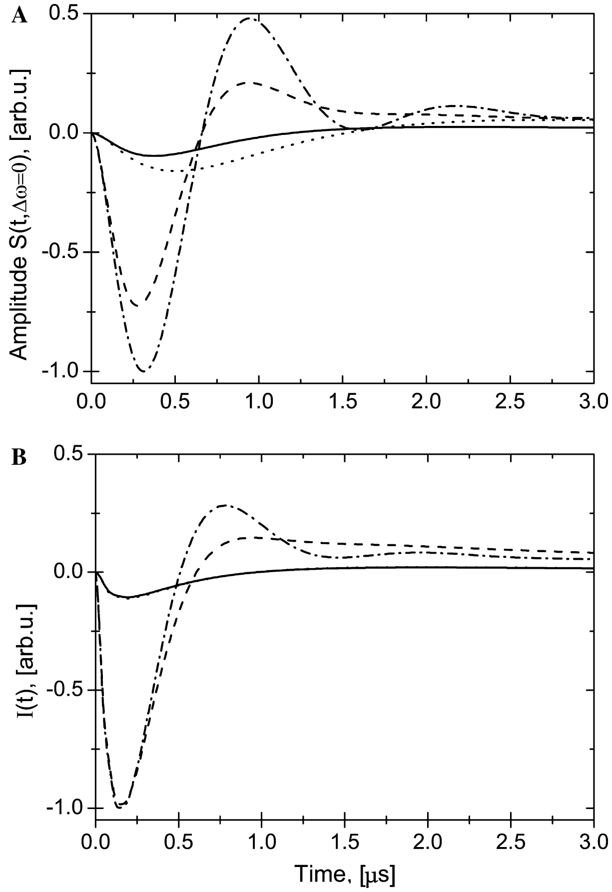

Fig. 1. (A) On-resonance time profiles of an EPR amplitude $S(t, \Delta\omega = 0)$ calculated numerically from extended Bloch equations, written for radicals produced instantaneously in solution and decaying via recombination (see Section 3). Parameters used: $T_1 = 5 \times 10^{-7}$ s, $R_0 = 10^{-4}$ M, $k_t = 5 \times 10^9$ M^{-1} s^{-1}, $\tau_{\mathrm{R}} = 10^{-7}$ s as well as: (—) $T_2 = 2 \times 10^{-7}$ s, $\omega_1 = 0.5 \times 10^6$ s^{-1}; (···) $T_2 = 5 \times 10^{-7}$ s, $\omega_1 = 0.5 \times 10^6$ s^{-1}; (---) $T_2 = 2 \times 10^{-7}$ s, $\omega_1 = 5 \times 10^6$ s^{-1}; and (-·-) $T_2 = 5 \times 10^{-7}$ s, $\omega_1 = 5 \times 10^6$ s^{-1}. (B) Time profiles of the total EPR signal intensity $I(t)$ calculated numerically with the same parameters as in (A). Initial conditions for both cases were $u(0) = v(0) = 0$ and $M_z(0) = -3P_{\mathrm{eq}} R_0$.

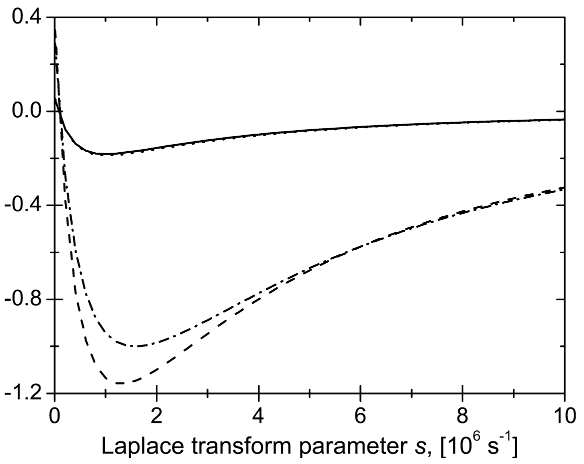

Fig. 2. Laplace transforms $\tilde{I}(s)$ of the time profiles presented in Fig. 1B.

the experiments with different initial radical concentrations R_0 to vary the initial chemical life time of the radicals $\tau_0 = (2k_tR_0)^{-1}$ in a predefined way.

If the relaxation is fast enough in comparison with the radical decay (T_1^{-1}, $T_2^{-1} \gg 2k_tR_0$), it is possible to separate completely the electron relaxation processes from the chemical kinetics. In that case, the *fast relaxation limit* considered above is useful. Rewriting Eq. (11) in parametric form we obtain

$$I(t) = \frac{A-B}{1-\frac{\tau_R}{T_1}} \times \left(e^{-\frac{t}{T_1}} - e^{-\frac{t}{\tau_R}}\right) + B \times \left(1 - e^{-\frac{t}{\tau_R}}\right). \qquad (16)$$

It is seen that Eq. (16) contains only three unknown parameters, A, B, and T_1. This solution is very easy to use in practice and suitable to determine relaxation time T_1 and initial electron magnetization M_z^0. Keeping the condition $\omega_1^2T_1T_2 \ll 1$ satisfied, one can obtain the values of M_z^0 and T_1 by least square fitting of Eq. (16) with only three variable parameters A, B, and T_1 to the experimental time profile of the total EPR intensity. The initial magnetization of the radicals M_z^0 is calculated from the relation $A/B = M_z^0/P_{\mathrm{eq}}R_0$ in units of the initial equilibrium magnetization. If the sensitivity factor C of the spectrometer is known, M_z^0 and R_0 can be determined separately from the parameters A and B, respectively. Afterwards, the more general formulae (13)–(15) can be applied to analyse experimental data measured under conditions, where T_1^{-1}, $T_2^{-1} \sim 2k_tR_0$, and $\omega_1^2T_1T_2 \sim 1$. This will then yield in addition the transverse relaxation time T_2 and the recombination rate constant k_t of the radicals.

We have performed two "virtual experiments" by numerical simulations, to check the above equations and to demonstrate their usefulness in the data analysis. We have assumed radicals with two equivalent hyperfine interacting spins 1/2 yielding an only partially resolved EPR spectrum because of $a = 4.4 \times 10^6$ rad/s (0.025 mT) and $T_2 = T_1 = 500$ ns. The radical system was further assumed to be produced instantaneously at time zero with an initial concentration of $R_0 = 10^{-4}$ M and a positive initial net polarization $M_z^0 = 5P_{\mathrm{eq}}R_0$. The rate constant for decay by radical termination was chosen as $k_t = 5 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Two TREPR spectra have been calculated numerically from the Bloch equations, one for low (**1**) and the other (**2**) for high microwave field amplitude. Their integration over the microwave frequency yields the total EPR intensity $I_1(t)$ and $I_2(t)$, respectively. Let us be interested in determining the initial net polarization M_z^0, the relaxation times T_1, T_2 and the radical decay rate constant k_t of that radical system. T_1 and $k_t = (2\tau_0R_0)^{-1}$ can be obtained by first using Eq. (15) to fit the EPR intensity $I_1(t)$ of the unsaturated spectrum **1**. Then, keeping T_1 and k_t fixed, Eq. (13) can be applied to estimate T_2 by fitting the Laplace transformed EPR intensity of the second spectrum **2,** simulated at partial saturation. The initial polarization M_z^0 is obtainable from both fits in two ways, from the parameter A as $M_z^0(A) = A/C\pi\omega_1P_{\mathrm{eq}}R_0$ and as $M_z^0(A,B) = A/B$ (here M_z^0 is expressed in units of the initial equilibrium magnetization $P_{\mathrm{eq}}R_0$).

First, the unsaturated spectrum **1** is analysed, part of which is plotted in Fig. 3. The spectrum has been generated on the time scale from 0 to 20 μs with steps of 10 ns and covers the microwave frequency range $\omega_0 \pm 1.06 \times 10^8$ rad/s (±0.6 mT) with steps of 1.76×10^6 rad/s (0.01 mT). $\omega_0 = 6 \times 10^{10}$ rad/s was chosen for the position of the centre line and $\omega_1 = 0.5 \times 10^6\,\mathrm{s}^{-1}$ ($\omega_1^2T_1T_2 \approx 0.06 \ll 1$) for the microwave field amplitude. A Gaussian distributed noise was added to the spectrum so that the signal-to-noise ratio was equal to 25 at maximum signal amplitude. Then, the noisy spectrum was numerically integrated over the frequency giving a time profile of the total EPR intensity $I_1(t)$, which is plotted in Fig. 4. Starting at approximately its maximum, $I_1(t)$ was fitted with Eq. (15) in the time interval from 250 ns to

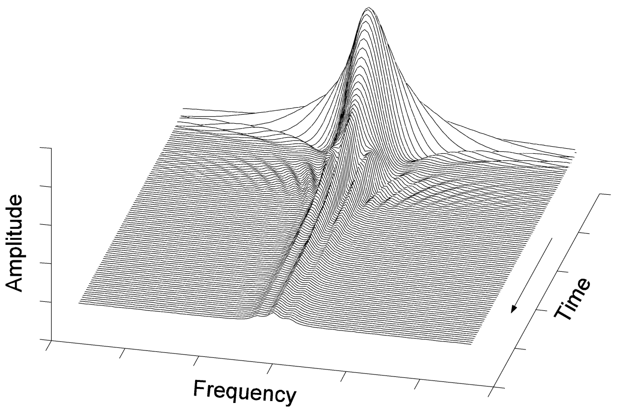

Fig. 3. **1:2:1** Triplet TREPR spectrum numerically simulated with the parameters: hfs $a = 4.4 \times 10^6$ rad/s, $\tau_R = 100$ ns, $T_1 = T_2 = 500$ ns, $\omega_1 = 0.5 \times 10^6\,\mathrm{s}^{-1}$, $R_0 = 10^{-4}$ M, and $k_t = 5 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Initial condition were $u(0) = v(0) = 0$ and $M_z(0) = 5P_{\mathrm{eq}}R_0$. Sensitivity C was chosen so that $C \cdot P_{\mathrm{eq}} = 1$.

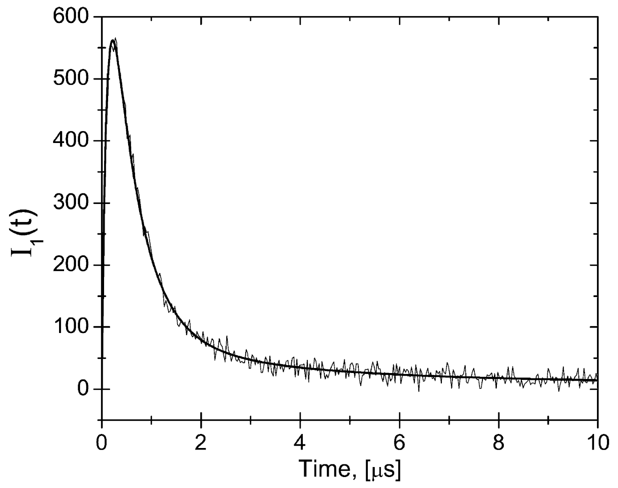

Fig. 4. Time profile of the total EPR signal intensity $I_1(t)$ (noisy trace), obtained by numerical integration over the frequency of a noisy ($S/N = 25$) spectrum with the same parameters as in Fig. 3. Solid line is its least squares fit with Eq. (15) (see text).

20 μs, using parameters A, B, T_1, and τ_0 as variable parameters. The resulting optimal values of the parameters and their 95%-confidence intervals became $T_1 = 486 \pm 35\,\text{ns}$, $k_t = (5.29 \pm 30) \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$, $M_z^0(A) = 5.49 \pm 0.14$, and $M_z^0(A,B) = A/B = 3.93 \pm 1.2$. The "dynamic" parameters T_1 and k_t are estimated with good accuracy close to the exact values ($T_1 = 500\,\text{ns}$, $k_t = 5 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$). However, the scale parameter M_z^0 shows a considerable error, especially when estimated from A/B. This is because the decay of the signal is more sensitive to the dynamic parameters than to the scale ones. If we keep $T_1 = 486\,\text{ns}$ and $k_t = 5.29 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$ fixed and fit Eq. (15) to $I_1(t)$ once again with only two free parameters A and B, but over the full time domain from 0 to 20 μs, the optimal values become $M_z^0(A) = 5.09 \pm 0.03$ and $M_z^0(A,B) = 4.95 \pm 0.09$, much closer to the exact value of 5. Such a separate determination of the dynamic (T_1, k_t) and scale parameters (M_z^0) is advisable, because the direct fit with four variable parameters over the whole time scale from 0 to 20 μs leads to worse estimations of some parameters: $T_1 = 524 \pm 26\,\text{ns}$, $k_t = (3.77 \pm 1.00) \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$, $M_z^0(A) = 5.06 \pm 0.04$, and $M_z^0(A,B) = 6.53 \pm 1.3$. This is because the parameters k_t and B are coupled. Thus, from the first "experiment" we have determined $T_1 = 486\,\text{ns}$ and $k_t = 5.29 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$ for the longitudinal relaxation time and the decay rate constant.

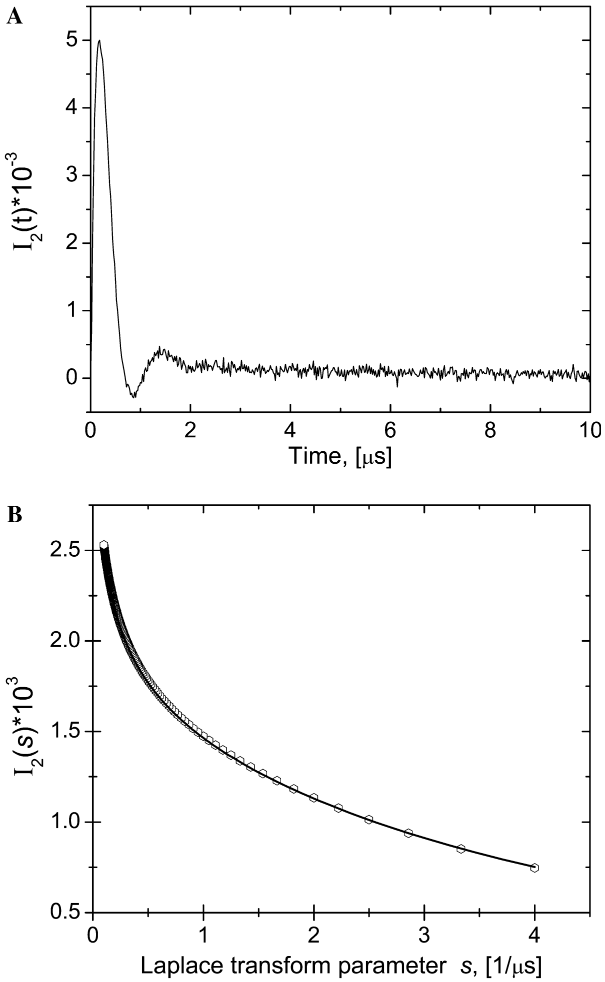

Fig. 5. (A) Time profile of the total EPR signal intensity $I_2(t)$, calculated numerically for high microwave field amplitude $\omega_1 = 5 \times 10^6\,\text{s}^{-1}$ ($\omega_1^2 T_1 T_2 \approx 6$). The other parameters are the same as in Figs. 3 and 4. (B) Laplace transform $\tilde{I}_2(s)$ (open circles) of the time profile presented in (A) and its Laplace domain least squares fit with Eq. (13) (see text).

To find out the transverse relaxation time T_2 we need the time profile of the EPR intensity at high microwave field amplitude. The spectrum **2** has been simulated with $\omega_1 = 5 \times 10^6\,\text{s}^{-1}$ ($\omega_1^2 T_1 T_2 \approx 6$) in the same way as **1**, but for a longer time scale from 0 to $t_0 = 50\,\mu\text{s}$, to allow the radicals to decay. In Fig. 5A the first 10 μs of the EPR intensity $I_2(t)$ is presented, obtained from integration of spectrum **2** over the frequency. We have to make a numerical Laplace transformation of it, to analyse it with Eq. (13). The result is given in Fig. 5B. For each value of s, the transform $\tilde{I}_2(s)$ was obtained by numerical integration of the product $I_2(t)e^{-s \cdot t}$ over time from 0 to 50 μs. The scale for s was chosen so that $1/s$ varied from 0.25 to 10 μs with steps of 50 ns. It does not make sense to use shorter values of $1/s$, because the value of $I_2(t)e^{-s \cdot t}$ would decay very fast and, therefore, would not be sensitive to the original signal $I_2(t)$ but to the noise at early times. The upper value of $1/s$ was chosen much longer than $T_1 = T_2 = 0.5\,\mu\text{s}$ and $\tau_0 = (2k_tR_0)^{-1} = 1\,\mu\text{s}$. It was limited to 10 μs to make sure that $I_2(t)e^{-s \cdot t}$ has decayed sufficiently close to zero at time $t_0 = 50\,\mu\text{s}$. The resulting fit of Eq. (13) to $\tilde{I}_2(s)$ in the Laplace domain is depicted in Fig. 5B as solid line. It led to the optimum values $T_2 = 517\,\text{ns}$, $M_z^0(A) = 4.97$, and $M_z^0(A,B) = 4.74$. The confidence intervals were very narrow but do not indicate the real error of parameter estimates, because the Laplace transform is a smoothed function. Thus, combining the two "experiments" we have found the parameters $T_1 = 486\,\text{ns}$, $T_2 = 517\,\text{ns}$, $k_t = 5.29 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$, and $M_z^0 = 4.94$ as average of the four values obtained from the first and second experiment. These estimates are rather close to the exact values $T_1 = T_2 = 500\,\text{ns}$, $k_t = 5 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}$, and $M_z^0 = 5$, what proves the correctness of the formulae and demonstrates their usefulness in analysing TREPR data.

Finally, we have analysed the simulated EPR intensity $I_1(t)$ also by using Eq. (16) despite the fact that the condition T_1^{-1}, $T_2^{-1} \gg 2k_tR_0$ for the *fast relaxation limit* is not satisfied, as in our example $\tau_0 = (2k_tR_0)^{-1} = 2T_1 = 2T_2$. From the fit of Eq. (16) to $I_1(t)$ in the time interval from 250 ns to 2.5 μs, we obtained the parameters $T_1 = (590 \pm 15)$ ns, $M_z^0(A) = 5.09 \pm 0.07$, and $M_z^0(A,B) = 16.4 \pm 1.3$. Though the *fast relaxation limit* is not given, $M_z^0(A)$ comes out surprisingly correct and T_1 is overestimated by only 20%. $M_z^0(A,B)$ gives a completely wrong estimate of M_z^0, because the parameter B is coupled with the radical kinetics and is considerably underestimated in the *fast relaxation limit*.

Recently, we have successfully applied relation (16) to investigate the fast electron spin relaxation of some benzoyl type radicals possessing unresolved EPR spectra [12].

3.1. Accuracy of the approximations

3.1.1. Initial conditions

Initial conditions in integrating the Bloch equations have been $u(0) = v(0) = 0$, $M_z(0) = M_z^0$. This is an approximation in so far as the process of generation of the initial radical magnetization is actually not instantaneous but determined, for example, in flash photolysis experiments by the duration of the laser pulse, as well as the lifetime of the excited precursor state. Therefore, the formulae given are good approximations only if $\Delta\tau \ll T_1,\ T_2,\ (2k_tR_0)^{-1}$, where $\Delta\tau$ is the characteristic time of the initial generation of radical magnetization. Otherwise, the radical generation process would have to be included in a rate law for the radical concentration.

3.1.2. Criterion $\omega_1^2 T_1 T_2 \ll 1$

This criterion defines the applicability of the formulae (9)–(11) as well as (14)–(16). It seems to be sufficient to work with microwave powers fulfilling the condition $\omega_1^2 T_1 T_2 \leqslant 0.1$ (vide infra).

3.1.3. Fast relaxation limit

(i) The limit is a good approximation when the radical concentration is about constant, $R(t) \approx R_0$, during the relaxation process. If the radicals decay by self-termination this means that $2k_tR_0t \ll 1$ for all times $t \leqslant 5T_1$, as the relaxation will be essentially completed after $5T_1$. This leads to the condition: $T_1 \ll (10k_tR_0)^{-1}$. We tested the accuracy of the approximation by fitting Eq. (16) to time profiles of EPR line intensities, which were calculated numerically from the extended Bloch equations for a system of equivalent radicals with decay by self-termination. The fitting yielded about 6% error in T_1 and 15% error in the parameter A/B for traces calculated with $T_1 = (50k_tR_0)^{-1}$, and deviations of about 3 and 10% in T_1 and A/B, respectively, for traces calculated with $T_1 = (100k_tR_0)^{-1}$.

(ii) *Criterion* $\omega_1^2 T_1 T_2 \ll 1$. We have also calculated from the Bloch equations exact time profiles of EPR line intensities for a constant radical concentration and have fitted Eq. (16) to them for different values of $\omega_1^2 T_1 T_2$. For $\omega_1^2 T_1 T_2 = 0.1$ we found deviations in T_1 and A/B of 5 and 8%, respectively, which decreased to 3 and 5%, respectively, when $\omega_1^2 T_1 T_2 = 0.05$.

(iii) *Optimum fitting interval.* The optimum fitting interval for Eq. (16) was found to be $T_1/2 \leqslant t \leqslant 5T_1$. In this region, the fitting procedure with Eq. (16) should yield the best results, because it is less sensitive to uncertainties in the initial conditions and the radical kinetics on the early and later time scale, respectively.

4. Conclusion

Time-resolved continuous-wave EPR spectroscopy can be used to investigate quantitatively chemical kinetics, electron spin relaxation, and initial net spin polarization of reactive radicals in solution also in cases, where the transient species exhibit unresolved EPR spectra enveloping an unknown hyperfine structure. In those cases, the experimental EPR-time profiles can be analysed without using equivocal multi-parameter fits by considering the dependence on time of the total intensity of the EPR spectrum. From several measurements, partially under conditions of negligible saturation and low initial radical concentrations, approximate values for the electron spin relaxation times $T_{1,2}$, the rate constants of the chemical kinetics of the radicals, and their initial net spin polarization can be determined, which are accurate within a few percent.

Acknowledgments

The authors would like to thank S. Milikisyants for fruitful discussions and the Swiss National Science Foundation for financial support.

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