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Longitudinal Electron Spin Relaxation Induced by Degenerate Electron Exchange as Studied by Time-Resolved Magnetic Field Effects

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T_1 paramagnetic relaxation of radical ions induced by degenerate electron exchange (DEE) reactions is studied theoretically and experimentally. Our theoretical analysis shows that T_1 relaxation time is well described by the Redfield theory at arbitrary values of the characteristic DEE time τ. Longitudinal relaxation of norbornane (NB) radical cation is studied by means of the time-resolved magnetic field effects (TR-MFE) technique; the rate constant of DEE involving $NB^{\bullet+}$ radical cation and NB neutral molecule is obtained. Advantages of the TR-MFE technique and its potential for measuring the short DEE times are discussed in detail.

1. Introduction

Degenerate electron exchange (DEE) is known to be typical for liquid phase when both radical ions $A^{\bullet+}$ or $D^{\bullet+}$ and their parent neutral molecules A or D are present in a solution. The DEE reactions

$$A^{\bullet-} + A \rightleftharpoons A + A^{\bullet-} \quad \text{or} \quad D^{\bullet+} + D \rightleftharpoons D + D^{\bullet+} \qquad (1.1)$$

are also often referred to as self-exchange reactions.[1] In the course of electron transfer from, say, D to $D^{\bullet+}$, the spin state of the magnetic nuclei coupled to the unpaired electron by hyperfine interaction (HFI) is randomly changed. As a consequence, DEE leads to paramagnetic relaxation of radical ion.

DEE-induced transverse relaxation at high external magnetic field is a subject of the numerous electron paramagnetic resonance (EPR) studies.[1−3] It is well-known that DEE may result in broadening of the EPR lines (slow spectral exchange limit) or collapse of the EPR spectrum into a single homogeneously broadened line of the width $1/T_2{}^0 + 2\Delta^2\tau$ (fast spectral exchange limit). Here $T_2{}^0$ is the transverse relaxation time in the absence of DEE, Δ^2 is the second momentum of the spectrum, and τ is the characteristic DEE time (correlation time of the DEE process). The value of τ^{-1} is equal to $k_{\mathrm{dee}}[\mathrm{D}]$, where k_{dee} is the DEE rate constant. DEE reactions induce not only transverse relaxation but longitudinal or T_1 relaxation as well, as has been pointed out by Cheng and Weissman.[4] Unfortunately, this phenomenon has not been studied yet in much detail. This kind of T_1 relaxation has been studied by Bagryanskaya et al.[5] by analyzing the chemically induced dynamic nuclear polarization in the switched external magnetic field. The manifestation of DEE-induced T_1 relaxation in microwave-induced quantum nutations in spin-correlated radical ion pairs was observed by Anishchik et al.[6]

The simplest and most natural way of estimating the DEE-induced relaxation times[5,7] is provided by the Redfield theory of spin relaxation.[8,9] According to this approach, the value of the DEE-induced longitudinal relaxation time, T_1^{dee}, is as follows:[9]

$$\frac{1}{T_1^{\mathrm{dee}}} = \frac{2\Delta^2\tau}{1+\omega^2\tau^2} \qquad (1.2)$$

where $\omega = g\beta B/\hbar$ is the Larmor precession frequency of the electron spin and Δ^2 is the second moment of EPR spectrum of radical ion involved in the DEE reaction at high magnetic field $B \gg \Delta$. This relation is believed to be valid in the limit of short correlation times τ (i.e., in the fast spectral exchange limit where $\Delta^2\tau^2 \ll 1$). In the opposite limit of long correlation times, the DEE-induced T_1 relaxation has not been studied so far. The present work is aimed at comprehensive theoretical and experimental study of T_1 relaxation caused by DEE in the wide region of the DEE times τ.

To study experimentally the DEE-induced T_1 relaxation, we shall utilize the technique of the time-resolved magnetic field effects (TR-MFE).[10−13] This is an efficient tool for studying magnetic properties of elusive radical species that are often beyond the reach of the conventional EPR spectroscopy. Earlier the TR-MFE studies allowed us to extract the HFI constants and *g*-factors of the short-lived intermediates formed in pulsed radiolysis of nonpolar solutions.[14−19] In the present work, we shall study electron exchange involving the radical cation of norbornane (NB, Scheme 1) in *n*-hexane solutions at a room temperature. $NB^{\bullet+}$ has four equivalent *exo*-protons in the six-membered ring with HFI constants of 6.5 mT,[20] whereas the HFI constants of the other protons are negligible. Therefore, we shall model the spin dynamics of NB taking account of only

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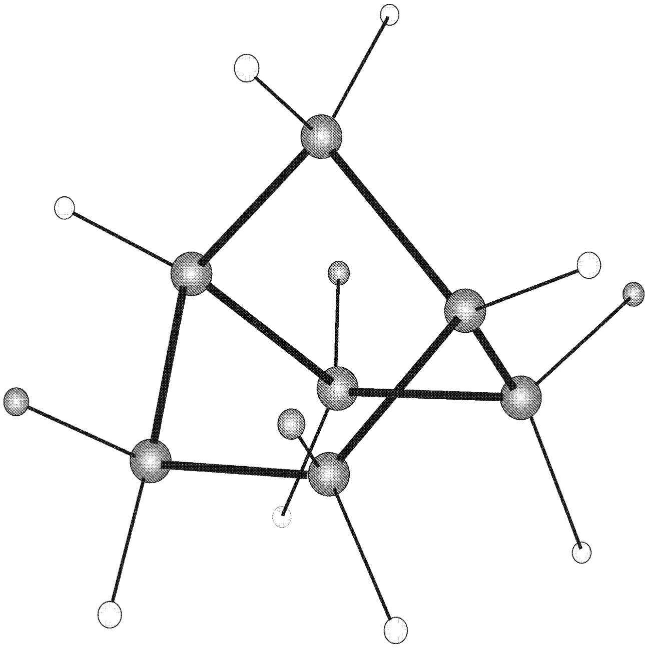
SCHEME 1: Structure of Norbornane (NB)[a]



[a] Four exo-protons in the six-membered ring are marked in gray.

four equivalent protons, so that the spin dynamics of NB radical cation can be treated analytically at arbitrary magnetic field strength. We shall analyze the manifestation of DEE reactions in the TR-MFE kinetics and discuss the potential of this technique for studying paramagnetic relaxation and DEE processes in solutions.

2. Nuts and Bolts of the TR-MFE

In the TR-MFE experiment, radiolytic impact on solution of electron acceptors A and hole acceptors D rapidly produces radical ion pairs (RIP) in spin-correlated singlet state $^1[A^{\bullet+} \ldots D^{\bullet+}]$. One on the charge (electron or hole) acceptors is a luminophor with sufficient fluorescence quantum yield and short fluorescence time τ_f. Typically, in nonpolar solutions RIP recombines from its singlet and triplet states at the same rate. Before its recombination occurs, RIP may change its spin state due to HFI, difference in *g*-factors of radical ions, and paramagnetic relaxation. The quantity measured in experiment is the fluorescence intensity $I(t)$ of *singlet* RIP recombination product. If τ_f is short enough, the fluorescence intensity can be described as follows:

$$I(t) \propto F(t)\left(\theta\rho_{SS}(t) + \frac{1-\theta}{4}\right) \tag{2.1}$$

where $F(t)$ is the RIP recombination rate, θ is the fraction of recombining RIPs that are initially in a spin-correlated singlet state (contribution of geminate pairs to $I(t)$), and $\rho_{SS}(t)$ is the singlet state population in these pairs at the instant of time t. The remaining fraction $(1 - \theta)$ of RIPs recombine in non-correlated spin state. Time dependence of $\rho_{SS}(t)$ provides important information on RIP spin dynamics and opens the principal opportunity to measure magnetic resonance parameters of radical ions as well as their paramagnetic relaxation rates. Unfortunately, the analysis of the measured fluorescence intensity $I(t)$ is complicated by the presence of recombination function $F(t)$ that is often unknown and changes with changing the solvent viscosity and polarity, properties of radical ions involved, etc. To get rid of the function $F(t)$, it is convenient to analyze the TR-MFE that is defined as a ratio of the fluorescence kinetics in the presence, $I_B(t)$, and in the absence, $I_0(t)$, of external magnetic field.[12,16] The expression for the TR-MFE on recombination fluorescence intensity takes the form:

$$\frac{I_B(t)}{I_0(t)} = \frac{\theta\rho_{SS}^{B}(t) + \frac{1-\theta}{4}}{\theta\rho_{SS}^{0}(t) + \frac{1-\theta}{4}} \tag{2.2}$$

Thus defined, the TR-MFE is determined merely by spin evolution of RIP, and its analysis gives the knowledge of paramagnetic properties of the short-lived radical ions composing the spin-correlated RIP. Sometimes it is convenient to present the TR-MFE in the following way:

$$\frac{I_B(t) - I_0(t)}{I_0(t)} = \frac{I_B(t)}{I_0(t)} - 1 \tag{2.3}$$

To extract reliable EPR data from the TR-MFE, its is necessary to compare the experimental results with model calculation of the RIP spin dynamics. The problem of calculating time behavior of the singlet state population in the absence of DEE is greatly simplified by introducing the so-called spin correlation tensors.[21] The expression for $\rho_{SS}(t)$ for initially singlet-correlated RIP can be written as follows:

$$\rho_{SS}(t) = \frac{1}{4} + \sum_{i,k} T_{ik}^{A}(t)T_{ik}^{D}(t) \tag{2.4}$$

where the components of spin tensors of $A^{\bullet-}$, $T_{ik}^{A}(t)$, and of $D^{\bullet+}$, $T_{ik}^{D}(t)$, are defined as follows:

$$T_{ik}^{A}(t) = \langle \mathrm{Tr}\{\hat{S}_{Ai}(t)\hat{S}_{Ak}(0)\}\rangle \quad \text{and} \quad T_{ik}^{D}(t) = \langle \mathrm{Tr}\{\hat{S}_{Di}(t)\hat{S}_{Dk}(0)\}\rangle \tag{2.5}$$

Here $i, k = x, y, z$, $\hat{S}_A(t)$, and $\hat{S}_D(t)$ are the electron spin operators of radical ions, Tr denotes the trace over the electron spin states, $\langle \ldots \rangle$ stands for the average over their nuclear spin configurations. Analytical expressions for the spin tensor components at arbitrary magnetic field B can be obtained for the radical ions having either a set of magnetically equivalent nuclei with isotropic HFI constants or small unresolved HFI constants.[21-23] Here we restrict ourselves solely to radical ions having equivalent nuclei. Let us present here the known expression for T_{zz} component of the spin tensor for radical ion having n equivalent spins $^1/_2$ nuclei with HFI constants a:[16]

$$T_{zz} = \frac{1}{2}\mathrm{e}^{-t/T_1{}^0}\langle f_J(t)\rangle = \frac{1}{2}e^{-t/T_1{}^0}\sum_J P_J f_J(t) \tag{2.6}$$

where $T_1{}^0$ is the longitudinal paramagnetic relaxation time in the absence of DEE:

$$P_J = \frac{(2J+1)^2 n!}{2^n (n/2 - J)!(n/2 + J + 1)!} \tag{2.7}$$

is the statistical weight of the nuclear state with spin J, and $f_J(t)$ is as follows:

$$f_J(t) = 1 - \frac{a^2}{2J+1}\sum_{m=-J}^{J}\frac{J(J+1) - m(m+1)}{R_m{}^2}(1 - \cos(R_m t)) \tag{2.8}$$

Here

$$R_{\mathrm{m}} = \sqrt{\omega^2 + a\omega(2m+1) + a^2\left(J+\frac{1}{2}\right)^2} \qquad (2.9)$$

and $\omega = g\beta B/\hbar$ is the Larmor precession frequency of the electron spin of the corresponding radical ion. As follows from (2.5) $T_{zz}(t)$ describes the evolution of the longitudinal electron spin components of radical ions. Therefore, to study the longitudinal DEE-induced relaxation we focus on the time-behavior of $T_{zz}(t)$. Here we do not present expression for all the rest spin tensor components, since for the case under study we neglect all the contributions from the transverse spin evolution to the TR-MFE. The reasons for this will become apparent later.

Spin correlation tensor formalism also allows one to take into consideration the spectral exchange effectively leading to electron spin relaxation. However, particular expressions for the tensor components should be modified as has been done by Knapp and Schulten.[24] Calculations of the DEE-induced spin evolution of RIP based on their results are given in the following section.

3. Theory

Expression for the DEE-Induced T_1 Relaxation Time. Above all we are interested in the DEE-induced longitudinal relaxation at high external magnetic field. T_1 relaxation is known to manifest itself in the long-time decay of the TR-MFE kinetics.[10,12,16,25] If the dynamic evolution of the transverse spin components and the T_2 relaxation as well as the spin dynamics at zero magnetic field proceed much faster than T_1 relaxation (i.e., if the longitudinal spin relaxation is the slowest process in the system), at long times the TR-MFE is expressed merely via the *zz*-components of the spin tensors T^{A}_{zz} and T^{D}_{zz}, and the its kinetics takes the form:

$$\frac{I_{\mathrm{B}}(t)}{I_0(t)} - 1 \approx 4\theta T^{\mathrm{A}}_{zz}(B,t)T^{\mathrm{D}}_{zz}(B,t) \qquad (3.1)$$

This expression is valid at times much longer than T_2 at high field and spin relaxation time at zero field. To obtain it we assumed that at long times $\rho^0_{\mathrm{SS}} \rightarrow {}^1/_4$ and $T^{\mathrm{D}}_{ik}(B,t) \rightarrow 0$ for $ik \neq zz$. Henceforth, we shall restrict ourselves to the assumption of slow T_1 relaxation as compared to other relaxation processes. This assumption is valid for NB radical cation (vide infra).

As a consequence, for our purpose it is enough to calculate these *zz*-components in the presence of DEE for radical ion having a set of equivalent spin ${}^1/_2$ magnetic nuclei. To do this, let us first estimate $T_{zz}(t)$ from eq 2.6 at high magnetic fields $\omega \gg a$ in the absence of DEE. Inasmuch as $\omega \gg a$, $R_m \approx \omega$ and $f_J(t)$ in eq 2.8 can be approximated as follows:

$$f_J(t) \approx 1 - \frac{1}{2J+1}\frac{a^2}{\omega^2}(1-\cos\omega t)\sum_{m=-J}^{J}[J(J+1) - m(m+1)]$$

$$= 1 - \frac{a^2}{\omega^2}\frac{2J(J+1)}{3}(1-\cos\omega t) \qquad (3.2)$$

Here we used that

$$\sum_{m=-J}^{J} m = 0, \quad \sum_{m=-J}^{J} m^2 = \frac{J(J+1)(2J+1)}{3} \qquad (3.3)$$

One should note that the approximation of $R_m \approx \omega$ is rather crude since it completely ignores that in different nuclear states $T_{zz}(t)$ contains cosine terms with different frequencies. As a consequence, at sufficiently long times the phases of $\cos(R_m t)$ are different for different m and J and the right expansion of R_m in $\cos(R_m t)$ is as follows: $R_m \approx \omega + (2m+1)a/2$. At the same time, we are interested in the effective falloff time of $T_{zz}(t)$ but not in the beats in $T_{zz}(t)$ and find it reasonable for our purpose to approximate R_m as ω.

As a result, we arrive at the following expression for $T_{zz}(t)$:

$$T_{zz}(t) = \frac{1}{2}\exp(-t/T_1{}^0)\{1 - \gamma(1-\cos\omega t)\} \qquad (3.4)$$

where

$$\gamma = \frac{2a^2}{\omega^2}\sum_J P_J\frac{J(J+1)}{3} = \frac{2\Delta^2}{\omega^2} \qquad (3.5)$$

Here Δ^2 is the second momentum of the radical ion EPR spectrum.

The Laplace transform of this expression is as follows:

$$\tilde{T}_{zz}(s) = \frac{1}{2}\left(\frac{1-\gamma}{p} + \gamma\frac{p}{p^2+\omega^2}\right) \qquad (3.6)$$

Hereafter, a tilde denotes the Laplace-transformed quantity, s is the Laplace variable ($\tilde{f}(s) = \int_0^\infty f(t)\exp(-st)\,\mathrm{d}t$) and $p = s + 1/T_1{}^0$.

As has been emphasized above in the presence of DEE, the spin correlation tensor formalism is still useful. In the Laplace domain, the tensor components in the presence, $\mathcal{T}$, and in the absence, T, of exchange are bound by the following relation:[24]

$$\tilde{\mathcal{T}}_{ik}(s) = \frac{\tilde{T}_{ik}(s+1/\tau)}{1 - 2\dfrac{\tilde{T}_{ik}(s+1/\tau)}{\tau}} \qquad (3.7)$$

where τ is the DEE time.

Thus, applying these relations, one can obtain that *zz*-component of the spin tensor in the presence of DEE takes the form:

$$\tilde{\mathcal{T}}_{zz}(s) = \frac{1}{2(p+\nu)}\,\frac{1 - \gamma\dfrac{\omega^2}{(p+\nu)^2+\omega^2}}{\dfrac{p}{p+\nu} + \dfrac{\gamma\omega^2}{(p+\nu)^2+\omega^2}} \qquad (3.8)$$

where $\nu = 1/\tau = k_{\mathrm{dee}}[\mathrm{D}]$ is the DEE frequency. Above all we are interested in the expession for $\tilde{\mathcal{T}}_{zz}(s)$ in the high field limit (i.e., at $\gamma \ll 1$) that is as follows:

$$\tilde{\mathcal{T}}_{zz}(s) = \frac{1}{2}\,\frac{1}{p + \dfrac{\gamma\nu\omega^2}{(p+\nu)^2+\omega^2}} \qquad (3.9)$$

Despite the fact that, strictly speaking, the time behavior of $\tilde{\mathcal{T}}_{zz}$ cannot be approximated by monoexponential function, its Laplace transform value at $s = 0$ may serve to obtain a reasonable estimate for the falloff time of the longitudinal magnetization (i.e., the effective overall T_1 value). As a

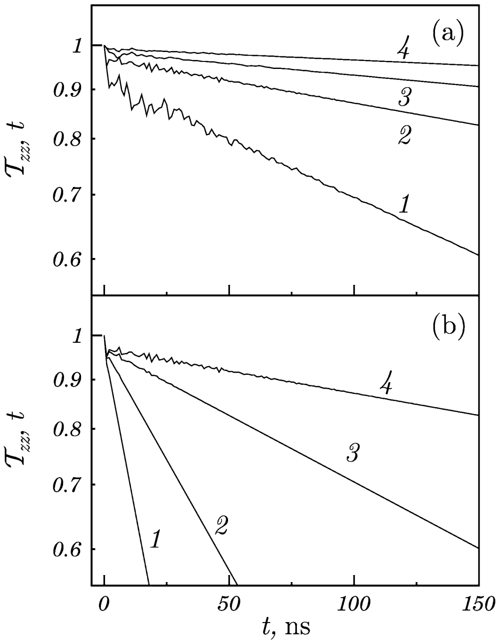


Figure 1. Numerical simulations of $\mathcal{T}_{zz}$ time dependence as presented in semilogarythmic coordinates. Panel a shows $\mathcal{T}_{zz}$ at fixed $\tau = 30$ ns for magnetic field B of 30 mT (1); 50 mT (2); 70 mT (3); and 100 mT (4). Panel b shows $\mathcal{T}_{zz}$ for $B = 50$ mT with different τ equal to 1 ns (1); 3 ns (2); 10 ns (3); and 30 ns (4). $\mathcal{T}_{zz}(t)$ curves are normalized to 1 at $t = 0$.

consequence, we obtain the following expression for the T_1 relaxation rate:

$$\frac{1}{T_1} = \frac{\mathcal{T}_{zz}(t=0)}{\tilde{\mathcal{T}}_{zz}(s=0)} = \frac{1}{T_1^{\,0}} + \frac{1}{T_1^{\mathrm{dee}}} \tag{3.10}$$

where the DEE-induced relaxation time T_1^{dee} is of the form:

$$\frac{1}{T_1^{\mathrm{dee}}} = \frac{\gamma\tau\omega^2}{1+\omega^2\tau^2} = \frac{2\Delta^2\tau}{1+\omega^2\tau^2} \tag{3.11}$$

To obtain this expression we have taken $\nu T_1^{\,0} \gg 1$, which is reasonable in our case, otherwise the T_1^{dee} value also depends on $T_1^{\,0}$. The expression (eq 3.11) that is valid in both fast and slow exchange limits as well as in the intermediate regime exactly coincides with that of the Redfield theory. Therefore, the Redfield theory estimate for the DEE-induced T_1 relaxation time can be used at arbitrary values of τ. To confirm this, we shall perform numerical simulations of the longitudinal relaxation in the presence of DEE processes.

Numerical Simulations of the DEE-Induced T_1 Relaxation. We performed the numerical simulations assuming radical ion involved in exchange to have four equivalent nuclei with spin $^1/_2$ with HFI constants equal to 6.5 mT, thereby modeling the radical cation of NB.[20,26] To evaluate the spin tensor components in the presence of DEE, $\mathcal{T}_{zz}(t)$, we first calculated the Laplace transform of T_{zz} from eq 2.6. Then we evaluated $\tilde{\mathcal{T}}_{zz}(s)$ according to eq 3.7 and numerically performed the backward Laplace transformation.

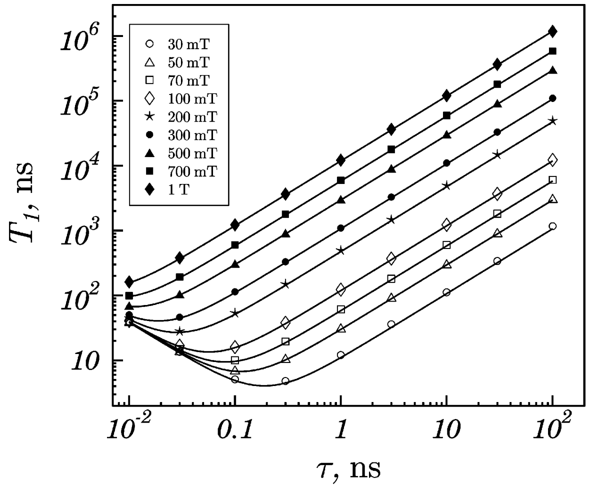


Figure 2. Calculated DEE-induced T_1 relaxation time vs the DEE time τ at different magnetic fields. Numerical simulations have been performed at magnetic fields 30 mT, 50 mT, 70 mT, 100 mT, 200 mT, 300 mT, 500 mT, 700 mT, and 1 T. Lines show the dependencies $T_1(\tau)$ as predicted by the Redfield theory.

The characteristic behavior of $\mathcal{T}_{zz}(t)$ is depicted in Figure 1, where panel a shows the evolution of the longitudinal magnetization with fixed DEE time equal to $\tau = 30$ ns at different magnetic fields, while in panel b $\mathcal{T}_{zz}(t)$ is shown at fixed magnetic field (50 mT) with varied DEE time τ. As is readily seen $\tilde{\mathcal{T}}_{zz}(t)$ at $t \gtrsim \tau$ can well be approximated as a monoexponential function and its characteristic falloff time can easily be obtained. The value of the falloff time in the presence of DEE can be considered as the DEE-induced T_1 relaxation time, T_1^{dee}. Thus defined, the values of T_1^{dee} can be compared with the Redfield theory predictions (eq 3.11) at different magnetic fields and DEE times. Such a comparison is shown in Figure 2. Numerical simulations are in excellent agreement with theoretical estimates in a wide range of B and τ. In general, the dependence $T_1^{\mathrm{dee}}(\tau)$ is a non-monotonic curve with a minimum reached at $\tau = 1/\omega$. At the descending branch of the curve T_1^{dee} is proportional to $1/\tau$ (at $\omega^2\tau^2 \ll 1$), while at the ascending branch of the dependence $T_1^{\mathrm{dee}}(\tau)$, one obtains $T_1^{\mathrm{dee}} \propto \tau$ (at $\omega^2\tau^2 \gg 1$).

4. Experimental Section

The luminescence of n-hexane solutions was detected by the single photon counting technique using an X-ray fluorimeter described elsewhere.[27] The duration of the ionizing pulse was about 2 ns. The light was collected using an optical band-pass filter (260−390 nm). The sample cuvette was describe elsewhere.[27] To decrease the influence of instrumental drift, the fluorescence decays were registered for periods of 250 s, alternatively, with and without the external magnetic field. Zero magnetic field was adjusted to within 0.05 mT, strong field was up to 1 T. n-Hexane ("Reactiv", Russia, 99.2%) was stirred with concentrated sulfuric acid, washed with water, and passed several times through a 1 m column of activated alumina. With the gas chromatography we revealed that n-hexane available contained 2-methylpentane (0.2%) and 3-methylpentane (0.5%) as the main impurities. Other impurities were present in amounts up to 0.05%, and they were not identified. The presence of hexane isomers was believed not to influence significantly on the obtained results due to rather high values of their ionization potential.[28] Norbornane (NB, 98%) and p-terphenyl-d_{14} (pTP, 98%) were used as received from Aldrich. Prepared solutions of NB before the addition of pTP were stored over sodium. The solutions were degassed by repeated freeze−pump−thaw cycles. All presented measurements were made at 293 ± 0.5 K.

5. Results

In pulsed-radiolytic experiments on n-hexane solutions of NB (shown in Scheme 1), and pTP, solvent holes resulting from

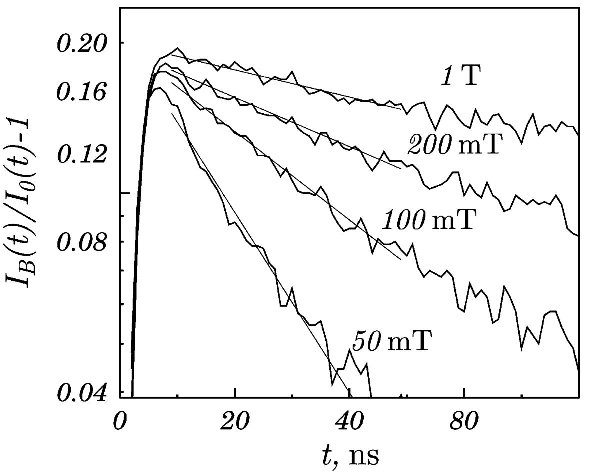


Figure 3. Experimentally observed TR-MFE in the system NB + *p*TP in *n*-hexane at different magnetic fields. Concentration of NB is 0.2 M, and that of *p*TP is 30 μM. Straight lines show the exponential approximations of the TR-MFE curves in the range from 10 to 50 ns.

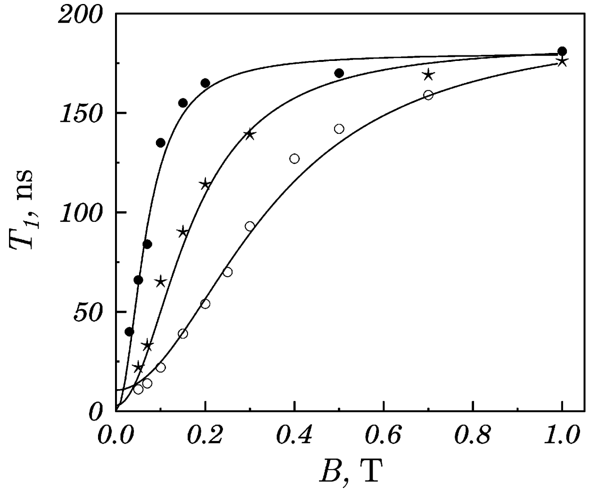


Figure 4. Experimental dependence of T_1 on the strength of external magnetic field at different concentrations of NB: [NB] = 0.04 M (●); [NB] = 0.2 M (★); [NB] = 0.6 M (○). Solid lines show the approximation of the dependencies by the Redfield theory with $\Delta = 6.5$ mT.

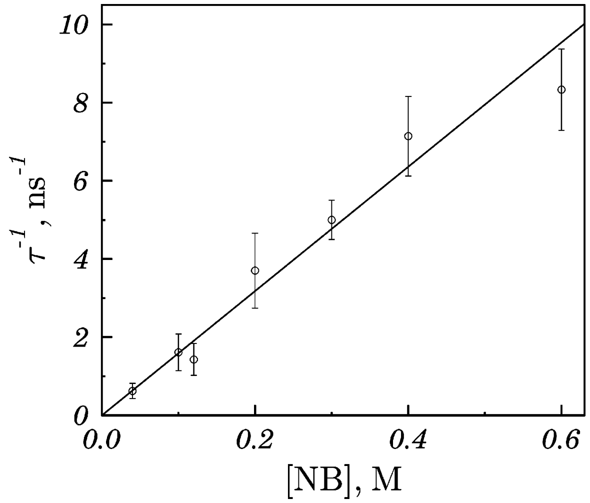


Figure 5. Experimental dependence of the inverse DEE time τ^{-1} on NB concentration. Solid line shows the linear approximation of the measured dependence for $k_{\mathrm{dee}} = 1.5 \times 10^{10}$ M^{-1}·s^{-1}.

n-hexane ionization are rapidly captured by NB (in 1 ns at NB concentration of about 30 mM), while the electrons are captured by *p*TP only, which was added in very low concentration of 3×10^{-5} M to avoid scavenging positive charges by this solute. Fluorescence of excited *p*TP formed in recombination of the singlet RIPs $\mathrm{NB}^{\bullet+}/p\mathrm{TP}^{\bullet-}$ was measured to monitor the TR-MFE kinetics. The radical ions of perdeuterated *p*TP has very small HFI constants,[29] and its contribution into spin dynamics of RIP is truly negligible (i.e., the TR-MFE is determined solely by the spin dynamics in $\mathrm{NB}^{\bullet+}$ radical cation). Figure 3 shows the characteristic TR-MFE curves for the system $\mathrm{NB}^{\bullet+}/p\mathrm{TP}^{\bullet-}$ in *n*-hexane. The growth of the MFE kinetics during the first few nanoseconds that is due to the HFI in $\mathrm{NB}^{\bullet+}$ radical cation is quite typical in the TR-MFE. In the case under study at high magnetic field, the evolution of the transverse magnetization components due to DEE and HFI is much faster than that of the longitudinal magnetization. The same holds for spin evolution at zero magnetic field: at $B = 0$ the RIP spin states are completely mixed by HFI and DEE after 10 ns. As a consequence, at $t > 10$ ns the TR-MFE curves are determined solely by the evolution of the longitudinal magnetization. As is readily seen from Figure 3, the TR-MFE curves within time range from 10 to 50 ns exhibit exponential behavior, which depends on the magnetic field strength. The falloff times that are, in essence, the effective T_1 relaxation times can easily be extracted. For all experimental kinetics, we obtained that the parameter θ is practically *B*- and τ-independent (as is expected) and falls into the range of 0.2−0.21. This encourages us that the effective T_1 relaxation times are extracted correctly from the experimental TR-MFE kinetics. At $t > 100$ ns the falloff times of the TR-MFE at different field is approximately the same (not shown in Figure 3). A possible reason for the decay may be the reaction of $\mathrm{NB}^{\bullet+}$ with unknown impurities. We have measured the TR-MFE at different external magnetic fields and different NB concentration. The dependence of T_1 on the external magnetic field strength *B* measured at three different concentrations of NB is shown in Figure 4. The experimentally observed dependence of TR-MFE kinetics on NB concentration indicates that the RIP spin dynamics is strongly affected by the DEE reaction involving radical cation of NB:

$$\mathrm{NB}^{\bullet+} + \mathrm{NB} \rightleftharpoons \mathrm{NB} + \mathrm{NB}^{\bullet+} \tag{5.1}$$

The obtained T_1 times were treated by eq 3.10 with the T_1^{dee} dependence on τ and ω given by the Redfield theory formula (eq 3.11). At very strong *B* values, the T_1 relaxation time tends to that in the absence of exchange, $T_1{}^0$, approximately equal to 180 ns.

Fitting the experimental dependencies by formulas 3.10 and 3.11 with $\Delta = 6.5$ mT, we obtain the DEE correlation time value τ. The inverse value $\tau^{-1} = \nu$ depends on NB concentration (Figure 5) linearly. This is a clear indication that the longitudinal spin relaxation of $\mathrm{NB}^{\bullet+}$ is mainly due to DEE, and the slope of the dependence allows one to obtain the value of the DEE rate constant k_{dee}. Our analysis yields $k_{\mathrm{dee}} = (1.5 \pm 0.3) \times 10^{10}$ M^{-1}·s^{-1}, which is close to the half of the diffusion-controlled limit of bimolecular collisions rate constant in *n*-hexane at room temperature.[30] This result is in full correspondence with theoretical predictions:[31] the rate constant of diffusion-controlled DEE is equal to $k_{\mathrm{D}}/2$ owing to the DEE reversibility (eq 1.1). Here $k_{\mathrm{D}} = 4\pi RD$ is the diffusional rate constant (*R* is the closest approach distance of neutral NB and its radical cation $\mathrm{NB}^{\bullet+}$ equal to the sum of their radii, *D* is their mutual diffusion coefficient equal to the sum of individual diffusion coefficients).

In the analysis presented above, Δ is assumed to be known and is equal to the 6.5 mT. However, this value of Δ has been found for NB radical cation in the frozen matrixes at temperature of 100 K and in solution at 180 K,[20,26] whereas we performed all the experiments at a room temperature. Unfortunately, we did not manage to obtain the optically detected EPR spectrum of NB radical cation under our experimental conditions. If one takes both τ and Δ as fitting parameters and analyzes the measured T_1 using the Redfield theory, the value of the latter will be somewhat lower. The Δ values will be within a range of 4.5−5.5 mT with the accuracy of approximately 1 mT with the tendency to the increase with decreasing NB concentration. At the same time, the k_{dee} value remains approximately the same. Although the experimental accuracy is insufficient to discriminate between $\Delta = 6.5$ mT and 5.5 mT, we can suggest two reasons for lowering of the Δ value in the case under study. The first possible explanation for lowering of the Δ value is dimerization of $\mathrm{NB}^{\bullet+}$ and formation of $\mathrm{NB}_2^{\bullet+}$ radical cation with spin density delocalization. The latter may then participate in the ion-molecular change transfer reaction with the neutral NB molecule. Another probable reason of lowering of the Δ value is the thermally activated redistribution of the electron spin density leading to the decrease of Δ value.[26] Unfortunately, there is no reliable EPR data in the radical cation species of NB at our experimental conditions that can provide unambiguous information about the Δ value.

6. Discussion

The present analysis reveals that the conventional Redfield theory for T_1 in the presence of spectral exchange is valid at both short and long correlation times τ. Although the evolution of the Z-component of the electron spin magnetization is not purely exponential, the Redfield theory provides a good estimate of the effective T_1 relaxation time. The limiting values of the DEE-induced longitudinal relaxation time, $1/T_1^{\mathrm{dee}}$, are as follows:

$$\frac{1}{T_1^{\mathrm{dee}}} = 2\Delta^2\tau \quad \text{at } \omega^2\tau^2 \ll 1 \tag{6.1a}$$

$$\frac{1}{T_1^{\mathrm{dee}}} = \frac{2\Delta^2}{\omega^2\tau} \quad \text{at } \omega^2\tau^2 \gg 1 \tag{6.1b}$$

The value of T_1^{dee} at $\omega^2\tau^2 \ll 1$ exactly coincides with that of T_2^{dee} in the fast exchange limit. This is quite common in paramagnetic relaxation: if the correlation time of the random process that causes spin relaxation is very small ($\omega^2\tau^2 \ll 1$, limiting narrowing regime), the values of T_1 and T_2 coincide and are given by eq 6.1a.

At $\omega^2\tau^2 \gg 1$, the result (eq 6.1b) can be understood as follows.[32] Let us consider a radical ion having one magnetic spin $^1/_2$ nucleus with HFI constant a at high magnetic field. Let us imagine that at $t = 0$ spin system is prepared in $|\alpha_e\beta_N\rangle$ electron−nuclear spin state. Here α and β denote the spin states with projections $^1/_2$ and $-^1/_2$ on Z-axis, respectively, while the subscripts e and N denote the electron and the nuclear spins. Since the state $|\alpha_e\beta_N\rangle$ is not an eigenstate of the spin Hamiltonian (the pure eigenstate also contains a small admixture of the state $|\beta_e\alpha_N\rangle$), HFI mixes $|\alpha_e\beta_N\rangle$ with $|\beta_e\alpha_N\rangle$ state. The degree of this mixing is proportional to a^2/ω^2. The mixing of the two states proceeds coherently (dynamic mixing): the population of $|\alpha_e\beta_N\rangle$ state oscillates with the frequency approximately equal to ω, and its maximal value is equal to 1 (reached at $t = 0$, $2\pi/\omega$, $4\pi/\omega$. etc.), while the minimal value is $1 - a^2/\omega^2$ (reached at $t = \pi/\omega$, $3\pi/\omega$, $5\pi/\omega$, etc.). Although the magnetic field causes the flips of electron spins (accompanied by the flops of the nuclear spins), it does not cause any stochastic evolution (relaxation) of the two states. In the presence of electron exchange the situation is different. DEE destroys the coherence between the states $|\alpha_e\beta_N\rangle$ and $|\beta_e\alpha_N\rangle$. Just as any other relaxation process it makes the mixing of the two states stochastic and tends to equalize the population of the two states. Single DEE event *irreversibly* transfers approximately a^2/ω^2 fraction of $|\alpha_e\beta_N\rangle$ to the population of $|\beta_e\alpha_N\rangle$ spin state. The resulting DEE induced relaxation rate can be estimated as the product of the degree of mixing of the two states, a^2/ω^2, and the frequency of the DEE events, $\nu = 1/\tau$. This is valid only in the case where $\nu \ll \omega$ (the frequency of the DEE events is much smaller than that of the coherent mixing). As a result, the following estimate can be obtained:

$$\frac{1}{T_1^{\mathrm{dee}}} \propto \frac{a^2}{\omega^2}\nu = \frac{a^2}{\omega^2\tau} \propto \frac{\Delta^2}{\omega^2\tau} \tag{6.2}$$

that coincides to coefficient with the result (eq 6.1b). Equation 6.1b gives a more general result for $n \geq 1$ magnetic nuclei.

In general, T_1 relaxation is due to the combined effect of dynamic mixing of the states having different Z-projections of the electron spin at the frequency ω and DEE that makes this mixing stochastic. We have to emphasize that for the T_1 relaxation the conditions of slow and fast exchange should be revised as compared to those for the T_2 relaxation. As long as the T_2 relaxation is concerned, ν should be compared with the width of the EPR spectrum; thus, the fast exchange limit is reached at $\Delta^2\tau^2 \ll 1$, whereas at $\Delta^2\tau^2 \gg 1$ the spectral exchange is slow. However, for the T_1 relaxation ν should be compared with the frequency of dynamic mixing that is approximately ω at high magnetic field and is much greater than the EPR spectrum width. Therefore, for the DEE-induced T_1 relaxation it is reasonable to consider the limit $\omega^2\tau^2 \ll 1$ as a fast exchange limit (eq 6.1a), whereas at $\omega^2\tau^2 \gg 1$ a slow exchange limit is reached (eq 6.1b). Although the present work only deals with radical ions having a set of magnetically equivalent nuclei, we anticipate that the Redfield theory estimate is valid for non-equivalent nuclei as well.

It is important to emphasize that the TR-MFE technique opens new possibilities for measuring short DEE times τ as compared to the conventional and optically detected EPR. First, in the standard EPR experiment to determine the exchange rate the line shapes and widths are studied that are often strongly affected by the inhomogeneous line broadening, whereas the TR-MFE gives a possibility to measure directly the T_1 relaxation time and determine the τ value. Since the fast phase relaxation affects only the ascending branch the TR-MFE kinetics (first 10 ns for NB + pTP system) the longitudinal relaxation is observed in a different time scale and can be analyzed separately. Second, in the TR-MFE technique T_1 relaxation times can be measured in a wide range of magnetic fields that is often hardly realizable in the EPR techniques. Another evident advantage of the TR-MFE technique is that changing the magnetic field strength one can adjust the T_1 value to fall into the range that is convenient for measurements. For example, in the limit $\omega^2\tau^2 \gg 1$ the ratio of T_1^{dee} and T_2^{dee} is as follows:

$$\frac{T_1^{\mathrm{dee}}}{T_2^{\mathrm{dee}}} = \omega^2\tau^2 \gg 1 \tag{6.3}$$

(i.e., T_1^{dee} relaxation time is much greater than T_2^{dee} and can be determined from experiment by using eq 3.1). Increasing external magnetic field strength B one can make T_1^{dee} time as long as it is needed. Accordingly, even at very short τ reliable values of T_1^{dee} can still be obtained, and the DEE time can be determined.

7. Concluding Remarks

The present work describes the results of comprehensive theoretical and experimental study of the T_1 electron spin relaxation induced by DEE at high external magnetic fields. Our theoretical analysis shows that the T_1 relaxation time in the presence of DEE can be described by the conventional Redfield theory. Suffice to say, this estimate of T_1 is valid both in the fast exchange and in the slow exchange limits. The behavior of T_1 in both limits is discussed in detail. Analytical estimates are confirmed by the rigorous numerical simulations of the longitudinal spin relaxation. To study experimentally the DEE-induced T_1 relaxation, we utilize the technique of the TR-MFE. For a particular system norbornane + *p*-terphenyl-d_{14} in *n*-hexane, the TR-MFE at $t > 10$ ns is determined solely by T_1 spin relaxation. The measured T_1 dependence on the DEE time τ and external magnetic field strength B is described by the Redfield theory, and the DEE time is determined. This allows us to obtain the DEE rate constant k_{dee} of about 1.5×10^{10} $\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$.

The method of the TR-MFE, despite being indirect, is a promising technique for studying the longitudinal electron spin relaxation and measuring the T_1 relaxation times of the short-lived radical ions. It allows one to extract very short DEE times τ from T_1 measurements. As far as the T_1 relaxation is concerned, the TR-MFE technique has certain advantages as compared to the conventional EPR. For radical ions undergoing DEE and rapid transverse electron spin relaxation (like the $\mathrm{NB}^{\cdot+}$ radical cation), the TR-MFE method allows one to obtain reliable data on the characteristic times of DEE.

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References and Notes

(1) (a) Grampp, G.; Landgraf, S.; Rasmussen, K. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 1897. (b) Telo, J. P.; Grampp, G.; Shohoji, M. C. B. L. *Phys. Chem. Chem. Phys.* **1999**, *1*, 99.

(2) Larsen, H.; Pedersen, S. U.; Pedersen, J. A.; Lund, H. *J. Electroanal. Chem.* **1992**, *331*, 971.

(3) Shulten, K. *Advances in Solid State Physics*; Treusch, J., Ed.; Vieweg: Braunschweig, 1982; Vol. XXII, pp 61−83.

(4) Cheng, C. P.; Weissman, S. I. *J. Phys. Chem.* **1976**, *80*, 872.

(5) Bagryanskaya, E. G.; Gorelik V. R.; Sagdeev, R. Z. *Chem. Phys. Lett.* **1997**, *264*, 655.

(6) Anishchik, S. V.; Borovkov, V. I.; Ivannikov, V. I.; Schebolaev, I. V.; Chernousov, Yu. D.; Lukzen, N. N.; Anisimov, O. A.; Molin; Yu. N. *Chem. Phys.* **1999**, *242*, 319.

(7) (a) Kubarev, S. I.; Sheberstov, S. V.; Shustov, A. S. *Dokl. AN USSR* **1987**, *292*, 401. (b) Kubarev, S. I.; Sheberstov, S. V.; Shustov, A. S. *Sov. Chem. Phys.* **1987**, *6*, 1327.

(8) Redfield, A. G. *Adv. Magn. Reson.* **1965**, *1*, 1.

(9) Abragam, A. *Principles of Nuclear Magnetism*; Clarendon Press: Oxford, 1961.

(10) Brocklehurst, B. *Radiat. Phys. Chem.* **1997**, *50*, 213.

(11) (a) Molin, Yu. N. *Bull. Korean Chem. Soc.* **1999**, *20*, 7. (b) Molin, Yu. N. *Mendeleev Commun.*, **2004**, *No. 3*, 85.

(12) Bagryansky, V. A.; Borovkov, V. I.; Molin, Yu. N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 924.

(13) Brocklehurst, B. *Chem. Soc. Rev.* **2002**, *31*, 301.

(14) Usov, O. M.; Grigoryantz, V. M.; Tadzhikov, B. M.; Molin, Yu. N. *Radiat. Phys. Chem.* **1997**, *49*, 237.

(15) Brocklehurst, B. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1079.

(16) Bagryansky, V. A.; Usov, O. M.; Borovkov, V. I.; Kobzeva, T. V.; Molin, Yu. N. *Chem. Phys.* **2000**, *255*, 237.

(17) Borovkov, V. I.; Bagryansky, V. A.; Yeletskikh, I. V.; Molin, Yu. N. *Mol. Phys.* **2002**, *100*, 1379.

(18) Borovkov, V. I.; Bagryansky, V. A.; Molin, Yu. N.; Egorov, M. P.; Nefedov, O. M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2027.

(19) Bagryansky, V. A.; Ivanov, K. L.; Borovkov, V. I.; Lukzen, N. N.; Molin, Yu. N. *J. Chem. Phys.* **2005**, *122*, 224503.

(20) Werst, D. W.; Trifunac, A. D. *J. Phys. Chem.* **1988**, *92*, 1093.

(21) Schulten, K.; Wolynes, P. G. *J. Chem. Phys.* **1978**, *68*, 3292.

(22) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Akad. Kiado: Budapest, 1984.

(23) Saik, V. O.; Lukzen, N. N.; Grigoryants, V. M.; Anisimov, O. A.; Doktorov, A. B.; Molin, Yu. N. *Chem. Phys.* **1984**, *84*, 421.

(24) Knapp, E.-W.; Schulten, K. *J. Chem. Phys.* **1979**, *71*, 1878.

(25) Mashnin, A. S.; Anishchik, S. V.; Borovkov, V. I.; Yeletskikh, I. V.; Anisimov, O. A.; Molin, Yu. N. *Appl. Magn. Reson.* **2001**, *20*, 473.

(26) Okazaki, M.; Toriyama, K. *J. Phys. Chem.* **1993**, *97*, 8212.

(27) Anishchik, S. V.; Grigoryants, V. M.; Shebolaev, I. V.; Chernousov, Yu. D.; Anisimov, O. A.; Molin, Yu. N. *Prib. Tech. Eksp.* **1989**, *No. 4*, 74 (in Russian).

(28) Webbook. Internet Interface to NIST databases. http://webbook.nist.gov.

(29) Berndt, A.; Jones, M. T.; Lehnig, M.; Lunazzi, L.; Placucci, G.; Stegmann, H. B.; Ulmschneider, K. B. In *Numerical Data and Functional Relationship in Science and Technology*; Fisher, H., Hellwege, K.-H., Eds.; Landolt-Bornstein New Series, Group II, Vol. 9 part d1; Springer-Verlag: Berlin−Heidelberg−New York, 1980.

(30) Borovkov, V. I.; Velizhanin, K. A. *Chem. Phys. Lett.* **2004**, *394*, 441.

(31) Doktorov, A. B.; Ivanov, K. L.; Lukzen, N. N.; Morozov, V. A. *J. Chem. Phys.* **2002**, *117*, 7995.

(32) Lukzen, N. N. Private communication, unpublished results.