

Spin Relaxation Parameters in Recombining Radical Ion Pair (Diphenylsulfide- d_{10})⁺/(*p*-Terphenyl- d_{14})⁻ Obtained by OD ESR and Quantum Beats Techniques

V. A. Bagryansky¹, O. M. Usov¹, N. N. Lukzen², and Yu. N. Molin¹

¹Institute of Chemical Kinetics and Combustion, Novosibirsk, Russian Federation

²International Tomography Center, Novosibirsk, Russian Federation

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Abstract. Parameters of paramagnetic relaxation were determined by OD ESR and quantum beats techniques for a recombining pair of radical ions (DPS- d_{10})⁺/(PTP- d_{14})⁻ in *n*-hexane, isooctane, *cis*-decalin, and squalane solutions. The T_2 relaxation time determined by quantum beats technique is independent of solvent viscosity and magnetic field strength in the range 170–9600 G. These data are in agreement with the results obtained by OD ESR technique assuming fast T_1 relaxation for radical cation. Neglecting the contribution of radical anion relaxation, we obtained $T_{1c} = T_{2c} \cong 50$ ns for (DPS- d_{10})⁺.

1. Introduction

The method of optically detected electron spin resonance (OD ESR) is successfully used to observe the ESR spectra of short-lived radical ions resulting from the radiolysis of solutions (see, e.g., [1–3]). A geminate anion-cation pair is initially formed in a track as a singlet pair. In the static magnetic field of spectrometer, transitions to the triplet state occur under Zeeman and hyperfine interactions as well as relaxation processes. The products of radical recombination, depending on pair multiplicity at the moment of recombination, are formed in either singlet or triplet excited states. The observed fluorescence intensity is the lower the more probable is the singlet-triplet (S-T) transition. When the microwave (mw) field of spectrometer is in resonance with particular Zeeman transitions, this probability increases further which leads to a drop in recombination fluorescence intensity. Therefore the OD ESR signal is registered as a fluorescence drop upon passage through resonance. The resulting spectra are similar to the ESR spectra of radical ions participating in the processes.

An alternative method for studying spin-correlated radical ion pairs is the spectroscopy of quantum beats [4–7]. In this case, the kinetics of the recombination

fluorescence of radical-ion pairs is observed in the static external magnetic field without applying mw field. Dynamic S-T transitions lead to modulation of decay curves by the frequencies that are equal to the frequency differences between the ESR spectra components of radical cation and radical anion [8]. In the simplest case, when the spectra of these radical ions consist of single non-overlapping lines, the frequency of quantum beats characterizes the distance between the lines and the decay of beats amplitude reflects their width.

Perdeuterated diphenylsulfide (DPS-d₁₀) and *p*-terphenyl (PTP-d₁₄) dissolved in alkanes yield the OD ESR spectrum of a (DPS-d₁₀)⁺/(PTP-d₁₄)⁻ pair which consists of two non-overlapping lines and the spectroscopy of quantum beats for this system displays the damped oscillations [5]. In this paper we have compared the relaxation parameters of radical ions in the (DPS-d₁₀)⁺/(PTP-d₁₄)⁻ pair obtained by the OD ESR and quantum beats methods.

2. Experimental

Commercial *n*-hexane, isooctane, *cis*-decalin and squalane were repurified by passing through a column with activated silica gel. The $6 \cdot 10^{-2}$ M DPS-d₁₀ and 10^{-3} M PTP-d₁₄ solutions in these alkanes were degassed by a repeated freeze-pump-thaw cycle and were sealed in thin quartz cuvettes. All experiments were carried out at room temperature.

The OD ESR spectra were recorded under X-ray irradiation using an X-band ER-200 D Bruker spectrometer under stationary conditions as described in [1]. Fluorescence was recorded using a light filter ($\lambda < 360$ nm) under modulation conditions.

Recombination fluorescence kinetics was recorded by the photon counting technique as described in [4]. The radioactive isotope ⁹⁰Sr of about 5 μ Ci in activity was used as an ionization source.

3. OD ESR Measurements

The OD ESR spectra for all the solvents consist of two lines. The distance between them (8.9 ± 0.2 G) coincides with that given in [5]. The low-field line was shown [5] to belong to the (DPS-d₁₀)⁺ radical cation and the high-field one – to the (PTP-d₁₄)⁻ radical anion. The widths of both lines depend on mw power. In order to eliminate the saturation effect, the distance ΔH_{pp} between the points of the maximum slope was measured for each line for four values of mw power in the range of 11 to 270 mW. Further, the $(\Delta H_{pp})^2$ value was extrapolated by a linear function to zero power [9]. The obtained values of ΔH_{pp}^+ and ΔH_{pp}^- , belonging, respectively, to cation and anion lines, are listed in Table 1. The values calculated for the difference between the *g*-factors for all cases were $\Delta g = 0.0053 \pm 0.0002$ which is close to the published value of

Table 1. Relaxation parameters of radical ions in different solvents.

Solvent	ΔH_{pp}^+ (G)	ΔH_{pp}^- (G)	Γ_c (10^7 s^{-1})	Γ_a (10^7 s^{-1})	T_2^{-1a} (10^7 s^{-1})	T_2^{-1b} (10^7 s^{-1})
<i>n</i> -hexane	1.9 ± 0.3	1.9 ± 0.3	2.8 ± 0.5	1.7 ± 0.5	2.6 ± 0.2	2.1 ± 0.2
isooctane	1.6 ± 0.1	1.9 ± 0.2	2.4 ± 0.1	1.6 ± 0.3	1.8 ± 0.1	1.5 ± 0.1
<i>cis</i> -decalin	1.3 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	1.7 ± 0.3	1.8 ± 0.1	1.5 ± 0.1
squalane	1.3 ± 0.1	2.3 ± 0.1	1.9 ± 0.1	2.5 ± 0.2	1.8 ± 0.2	1.6 ± 0.2

^a In the case (i), when $T_1^{-1} = T_2^{-1}$.

^b In the case (ii), when $T_1^{-1} = 0$.

0.0055 [10]. The available [10] hfi constants of $(\text{DPS-d}_{10})^+$ and $(\text{PTP-d}_{14})^-$ radicals allow one to calculate the second moments of the spectra of deuterated radical ions and to estimate the linewidths $\Delta H_{pp}^+ = 0.6 \text{ G}$, $\Delta H_{pp}^- = 1.35 \text{ G}$. The widths observed exceed substantially these values which testifies to a considerable contribution of homogeneous broadening. The rate constant of ion-molecular charge exchange for the $(\text{DPS-d}_{10})^+$ cation in the most viscous solvent (squalane) may be estimated to exceed $10^9 \text{ M}^{-1}\text{s}^{-1}$ [9]. For the concentrations used this conforms to the case of exchange-narrowed spectrum. Thus, the width of the $(\text{DPS-d}_{10})^+$ line is fully determined by homogeneous broadening whereas that of the $(\text{PTP-d}_{14})^-$ one depends on both the homogeneous contribution and unresolved hfi.

It is shown [11] that within the range of small H_1 values the individual lines of the OD ESR spectrum, corresponding to a given nuclear configuration, display the Lorentzian

$$\Gamma_{a,c} = \tau_d^{-1} + T_{2a,c}^{-1}, \quad (1)$$

where the indices a or c refer to either radical anion or cation; τ_d is the pair recombination time under assumption of the exponential decay; T_{2a} and T_{2c} are the T_2 relaxation times of radical ions. In this paper, however, the T_1 relaxation is neglected, i.e., actually the case of $T_{1a,c} \gg T_{2a,c}$ is considered. To allow for the influence of longitudinal relaxation, it is suffice to substitute the expression $\langle b_z(t) \rangle = b_z(0)\exp(-t/T_{1b})$ to formulas (11) of [11] which is an approximate solution to the Bloch equation for the Spin operator z -component of a radical-partner in the Heisenberg representation (here $b_z(t)$ is the operator of radical cation spin if the lineshape of radical anion is calculated and vice versa). Generalizing further the calculations performed in the paper cited, for Eq. (1) we get

$$\Gamma_{a,c} = \tau_d^{-1} + T_{2a,c}^{-1} + T_{1c,a}^{-1}. \quad (2)$$

Thus, in the case of exponential kinetics the width of the individual line of OD ESR spectrum is determined by the sum of three inverse times: recombination time, the time T_2 of the radical considered and the time T_1 of radical-

partner. A geminate recombination kinetics rate $F(t)$ of radical ions is essentially non-exponential and has a long-time asymptotic behavior $F(t) \sim t^{-1.5}$. In [12] the arguments are given that testify to the absence of the contribution of recombination to the OD ESR linewidth in this very case. Thus, in the range of low mw power, the line belonging to the radical cation has the form of the Lorentzian curve with a width $\Gamma_c = T_{2c}^{-1} + T_{1a}^{-1}$ and the linewidth of a given hf component of radical anion is $\Gamma_a = T_{1c}^{-1} + T_{2c}^{-1}$. By assuming the lineshape to be Lorentzian, parameter Γ_c was determined from the value of ΔH_{pp}^+ . The value of Γ_a was obtained by numerical modeling of the ESR spectrum of the $(\text{PTP-d}_{14})^-$ radical using the available hfi constant [10] and choosing the parameter Γ_a of Lorentzian broadening so that the calculated and observed values of ΔH_{pp}^- coincided.

Table 1 summarizes the relaxation parameters Γ_c and Γ_a for various solvents.

4. Quantum Beats

Additional information about relaxation times has been extracted using the quantum beats technique. To this end, the fluorescence decay kinetics of the same samples was analyzed for two values of static magnetic field strength H , 170 G and 9600 G. Expression for the probability $P(S \rightarrow S)$ to find a singlet born pair in the singlet state [8, 13] may be generalized using Eq. (135) in [14] to take into account spin relaxation

$$P(S \rightarrow S) = \frac{1}{4} \left[1 + \exp(-t/T_1) + 2 \exp(-t/T_2) \exp\left(-0.5(\sigma_a^2 + \sigma_c^2)t^2\right) \cos(\Delta g \beta H t / \hbar) \right], \quad (3)$$

here $T_1^{-1} = T_{1c}^{-1} + T_{1a}^{-1}$, $T_2^{-1} = T_{2c}^{-1} + T_{2a}^{-1}$, σ_a and σ_c are the second moments of the hfi contours of radical cation and anion lines, respectively; Δg is the difference between the g -factors of radical ions. The radical cation spectrum is narrowed upon exchange, which results in $\sigma_c = 0$, while the calculated value of the second moment of radical anion ESR spectrum is $\sigma_c = 1.19 \cdot 10^7 \text{ s}^{-1}$. Then the rate of the formation of the singlet recombination product of a radical ion pair with allowance for relaxation has the form:

$$W(t) = \frac{1}{2} F(t) \Theta \left[1 + \exp(-t/T_1) + 2 \exp(-t/T_2 - 0.5\sigma_a^2 t^2) \cos(\Delta g \beta H t / \hbar) \right] + \frac{1}{4} F(t) (1 - \Theta), \quad (4)$$

where $F(t)$ is the recombination rate; Θ is the fraction of singlet spin-correlated pairs. The last term in Eq. (4) takes into account recombination of non-correlated pairs. The recombination fluorescence intensity $I(t)$ is the convolution of $W(t)$ function with an exponential function

$$I(t) = \tau^{-1} \int_0^t W(t') \exp\left(-\frac{t-t'}{\tau}\right) dt' , \quad (5)$$

where $\tau = 1.2$ ns is the PTP-d₁₄ fluorescence time [7]. As follows from Eq. (5), the $W(t)$ function may be determined from the form of kinetics $I(t)$ and its time-derivative $\dot{I}(t)$

$$W(t) = I(t) + \tau \dot{I}(t) . \quad (6)$$

Equations (4)–(6) give

$$\begin{aligned} \frac{W(t)}{W_0(t)} &= \frac{I(t) + \tau \dot{I}(t)}{I(t) + \tau \dot{I}_0(t)} \\ &= \frac{1 + \Theta \exp(-t/T_1) + 2\Theta \exp(-t/T_2 - 0.5\sigma_a^2 t^2) \cos(\Delta g 9600 t / \hbar)}{1 + \Theta \exp(-t/T_1) + 2\Theta \exp(-t/T_2 - 0.5\sigma_a^2 t^2) \cos(\Delta g 170 t / \hbar)} , \end{aligned} \quad (7)$$

where the values of $W(t)$ and $I(t)$ refer to the 9600 G field and those of $W_0(t)$ and $I_0(t)$ belong to the 170 G one. Using Eq. (7) we determined the unknown parameters of the right-hand side by the least-squares fit (LSF). To decrease the influence of error introduced upon numerical differentiation of noisy experimental kinetics, the $\dot{I}(t)$ and $\dot{I}_0(t)$ values were estimated by differentiating the smoothed curves $I(t)$ and $I_0(t)$.

Figure 1 shows the curve obtained by this method. The damped oscillations are clearly observed with a 12.5 ns period which coincides with the expected cosine period in the numerator of Eq. (7). The relaxation parameters in the numerator of Eq. (7) belong to a high field and those in the denominator to the low field. With a considerable dependence of relaxation times on field strength, the oscillation maxima would be located along the convex curve because in this case the terms in the denominator that depend on relaxation parameters would decay more rapidly than those in the numerator. Actually, the peaks are situated along the horizontal straight-line which makes us assume the absence of the field-dependence of relaxation times in the range 170–9600 G. Experimental data have been treated in the framework of this assumption confirmed by comparison between the quantum beats and the OD ESR data belonging to the lower field $H \cong 3400$ G:

The parameters were determined by approximating the experimental dependence $W(t)/W_0(t)$ by Eq. (7) using the LSF. According to the theory of ESR relaxation [15], the assumption of spin relaxation rate independence of magnetic field strength in the range 170–9600 G holds for the following two cases:

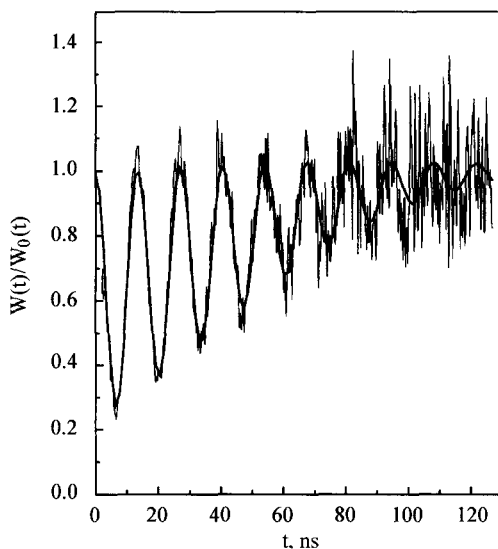


Fig. 1. Quantum beats in recombination fluorescence of pair $(\text{DPS-d}_{10})^+ / (\text{PTP-d}_{14})^-$. Acceptors are dissolved in isoctane. $W(t)$ is determined for a 9600 G field (see the text). The jagged line – experiment, the solid line – simulation by Eq. (7).

- (i) $9600\tau_c\gamma \ll 1$, where τ_c is the correlation time responsible for relaxation, γ is the gyromagnetic ratio. In this case, the T_1 and T_2 values coincide;
- (ii) $170\tau_c\gamma \gg 1$. This is the case of slow T_1 relaxation.

In both cases three parameters are varied: T_2^{-1} , Δg and Θ . These approximations are exemplified in Fig. 1 by the solid lines and for cases (i) and (ii), the curves, corresponding to the optimal parameters, coincide. It has appeared that for cases (i) and (ii), the values of Δg and Θ parameters coincide within experimental error. For all solvents $\Delta g = 0.0054 \pm 0.0001$ which is in agreement with the value obtained using the OD ESR method. The fraction of spin-correlated pairs $\Theta = 0.6 \pm 0.2$ coincides with the previously published value [16]. The values of T_2^{-1} parameter for both of the cases are listed in Table 1. In case (i) the values are slightly higher than those in case (ii).

5. Comparison of OD ESR and Quantum Beats Results

In the framework of hypothesis (i) on the relaxation rate independence of magnetic field strength with $T_1 = T_2$ the equality $T_2^{-1} = 0.5(\Gamma_c + \Gamma_a)$ must hold. Figure 2 shows a comparative diagram of the values of both T_2^{-1} determined for case (i) and $(\Gamma_c + \Gamma_a)$. This equality is approximately valid. In the case of slow T_1 relaxation (ii), the equality $T_2^{-1} = \Gamma_c + \Gamma_a$ would be true which strongly contradicts the experiment.

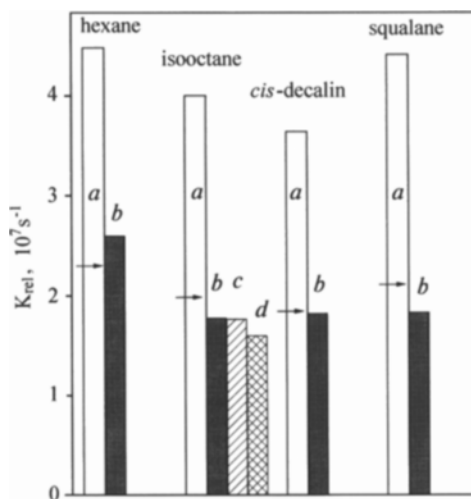


Fig. 2. Comparative diagram of relaxation parameters of the pair: *a* is the $(T_a^{-1} + T_c^{-1})$ value equal to the sum of four inverse relaxation times determined by the OD ESR method in the field of 3400 G (arrow denotes a half of this value); *b* is the T_2^{-1} value equal to the sum of inverse T_2 relaxation times determined by the quantum beat method in a 9600 G field using the assumption $T_1^{-1} = T_2^{-1}$; *c* is the same as *b* but for a 4800 G field; *d* the same as *b* but for a 2400 G field.

Additional verification of the relaxation rate independence of magnetic field strength has been obtained from quantum beats in fields 4800 and 2400 G for the solutions of acceptois in isooctane. The value of T_2^{-1} in these cases coincided with the value determined in a 9600 G field (see Fig. 2). Thus, $T_2^{-1} = T_{2c}^{-1} + T_{2a}^{-1}$ is independent of magnetic field strength in the range 170–9600 G and coincides with a half of the value $T_a^{-1} + T_c^{-1} = T_{1c}^{-1} + T_{1a}^{-1} + T_{2c}^{-1} + T_{2a}^{-1}$ determined using the OD ESR method in the field of about 3400 G. This gives the equality $T_{2c}^{-1} = T_1^{-1} \cong 2 \cdot 10^7 \text{ s}^{-1}$ in this range. The data of Brocklehurst [17] have been used to estimate the upper limit $T_{1a}^{-1} \leq 10^6 \text{ s}^{-1}$ of the T_1 relaxation rate for $(\text{PTP-d}_{14})^-$. Thus, our results testify to the equality between the T_1 and T_2 relaxation times for the $(\text{DPS-d}_{10})^+$ radical cation. These times are about 50 ns and are independent of solvent viscosity which, in our experiments, was varied by 60 times. The correlation time of paramagnetic relaxation which is necessary for the relaxation rate independence of the magnetic field strength up to 9600 G was estimated to be $\tau_c \ll 10^{-11} \text{ s}$. A feasible mechanism to provide such relaxation is the modulation of spin-orbital interaction by the vibrations of $(\text{DPS-d}_{10})^+$ radical ion fragments (the Altschuller-Valiev mechanism [18]).

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Author's address: Dr. Victor A. Bagryansky, Institute of Chemical Kinetics and Combustion, Institutskaya Str. 3, Novosibirsk 630090, Russian Federation