

Phase shift of quantum oscillations in the recombination luminescence of spin-correlated radical ion pairs

V.M. Grigoryants, B.M. Tadjikov, O.M. Usov, Yu.N. Molin

Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russian Federation

Received 10 August 1995

Abstract

The phase shift of quantum oscillations observed in the recombination fluorescence of the (diphenylsulfide- d_{10})⁺ / (*p*-terphenyl- d_{14})⁻ radical ion pair in isooctane has been detected experimentally. The shift is caused by the delay in (diphenylsulfide- d_{10})⁺ formation in the reaction of solvent holes with a diphenylsulfide molecule. Comparison with a theoretical model has given for the rate constant of isooctane hole capture by diphenylsulfide molecules the value $(3.5 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which exceeds the diffusion-controlled one. The fraction of singlet-correlated pairs in the track has been estimated from the oscillation amplitude to be approximately 35%.

1. Introduction

Dynamic transitions between levels of different multiplicity are known to occur in spin-correlated radical pairs. The initial coherent state of a radical pair being nonstationary, singlet–triplet (S–T) oscillations arise in the system (see e.g. Refs. [1,2]). Recombination of radical ion pairs in nonpolar solvents gives rise to either singlet- or triplet-excited products ^{1,3}P*. Their multiplicity corresponds to that of the pair one (S, T) upon recombination which allows the direct observation of the spin dynamics in the pair by recombination fluorescence kinetics [3].

The S–T oscillations have been observed in the recombination of spin-correlated radical ion pairs forming under ionizing radiation in saturated hydrocarbons containing electron and hole acceptors [4–8]. Due to the conservation of spin angular momentum in the ionization process the primary pairs appear in the nonstationary singlet state. The capture of primary species by aromatic acceptors and subsequent recombination

leads to the formation of luminescing products.

In a static external magnetic field the dynamics of S–T transitions are governed by the Zeeman and hyperfine interactions (hfi) of the electron spins. Particularly, in the strong magnetic field region the transition frequencies coincide with the differences in the ESR spectrum frequencies of pair partners. Therefore, the conditions for observing oscillations are mostly favorable in systems with simple spectra, otherwise the oscillation pattern is a superposition of many modulation frequencies. Thus, hfi-induced quantum oscillations have been observed in the recombination of (tetramethylethylene)⁺ / (*p*-terphenyl- d_{14})⁻ pairs forming under radiolysis of a tetramethylethylene and *p*-terphenyl- d_{14} (PTP- d_{14}) solution in squalane [5]. The oscillations result from the hfi with the twelve equivalent protons in the tetramethylethylene cation. Therefore, the oscillation pattern observed corresponds to a superposition of multiple harmonics. An appropriate electron acceptor, *p*-terphenyl- d_{14} , was taken both as a counter-ion with narrow spectrum

widths (~ 1.5 G) as well as an effective luminescing agent P^* with short fluorescence lifetime.

The quantum oscillations induced by the difference in g -factors of pair partners have been recorded in the (diphenylsulfide- d_{10})⁺ / (PTP- d_{14})⁻ system [6]. Diphenylsulfide- d_{10} (DPS- d_{10}), a hole acceptor molecule with narrow cation spectrum and large g -factor shift, on the one hand, and a simple ESR spectrum of the system, resulting in a single oscillation frequency, on the other, have favoured the observation of large-amplitude oscillations. In both of the examples described, the oscillation pattern has corresponded to the ESR parameters of pair spectra. However, the observed oscillation amplitude has appeared to be less than that expected which could be explained by the contribution of non-correlated pairs to bulk luminescence arising from cross-recombination in the radiation track.

The quantum oscillations phenomenon could be employed to study the process of charge transfer from primary solvent holes to solute molecules. The ionization of a dilute solution results in a free electron and a solvent hole. The electrons are scavenged fast enough due to their high mobility whereas the holes are captured in much slower reactions that are assumed to be limited by molecular diffusion. As a result, oscillations in the secondary radical ion pair start with a delay. This delay is sure to lead to a phase shift of oscillations and related decrease of their amplitude. In earlier papers the oscillation amplitude has been reported to vanish with dilution of the solution of the holes acceptor. However, the phase shift has not yet been recorded [8]. Probably, the shift of oscillations did not exceed 2 ns which was beyond the time resolution of the apparatus used.

This Letter reports the observation of the phase shift of oscillations in the (DPS- d_{10})⁺ / (PTP- d_{14})⁻ pair. It is demonstrated that from the phase shift measurements one can find the rate constant of hole capture by acceptor molecules and also estimate their lifetime in the net solvent.

2. Theoretical model

Assuming the electron to be captured instantaneously, the formation of radical ion pairs under ionizing radiation and their recombination yielding

excited products can be described by [9]



where S is the solvent molecule; P and D are acceptors of electrons (PTP- d_{14}) and holes (DPS- d_{10}), respectively. The yield of fluorescing products depends on the S–T evolution in the radical pairs, and the multiplicity of the excited products $^1,^3P^*$ formed corresponds to that of the pair (S, T) at the moment of recombination. The fluorescence from the singlet excited state has been studied by experiment.

Let particles of type '1' (holes) be captured by acceptor molecules '2' (diphenylsulfide) with time τ_0 while particle '3' (PTP⁻) is formed instantaneously. It is also known that the radical-cations of alkanes are unstable at room temperature and disappear via reactions of deprotonation [10]. Neglecting pair recombination, the corresponding time-dependent concentrations of cations with regard to the hole decay time τ_1 are read as (supposing $C^{(1)}(0) = 1$)

$$C^{(1)}(t) = e^{-k_0^* t}, \quad (5)$$

$$C^{(2)}(t) = \frac{k_0}{k_0^*} (1 - e^{-k_0^* t}), \quad (6)$$

where $k_0 = 1/\tau_0 = k[D]$; k is the rate constant of bimolecular hole capture, $[D]$ is the DPS concentration and τ_0^* is the mean hole lifetime, $k_0^* = (\tau_0^*)^{-1} = (\tau_0)^{-1} + (\tau_1)^{-1}$.

In the presence of ion–molecular capture, the population of the system spin states is more convenient to describe by a density matrix depending on reagent concentration: $\sigma^{(k)}(t) = \rho^{(k)}(t)C^{(k)}(t)$, where $\rho(t)$ covers only spin components. The matrix obeys the equations [11]

$$\dot{\sigma}^{(1)} = i\hat{L}^{(1)}\sigma^{(1)} - k_0^*\sigma^{(1)}, \quad (7)$$

$$\dot{\sigma}^{(2)} = i\hat{L}^{(2)}\sigma^{(2)} + k_0\sigma^{(1)}, \quad (8)$$

where the components of the diagonal spin tensor $T^{(k)}$ describe the motion of spin 1/2 in the basis (S_+, S_-, S_z),

$$e^{i\tilde{L}^{(k)}t} = T^{(k)}(t). \quad (9)$$

In the absence of hfi or upon its averaging by fast ion-molecular charge transfer the radical's correlation tensor just corresponds to the rotation of spin with Larmor frequency, $\omega_k = g_k\beta H$ in the external magnetic field H [12],

$$T^{(k)}(t) = \frac{1}{2} \begin{pmatrix} e^{i\omega_k t} & 0 & 0 \\ 0 & e^{-i\omega_k t} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (10)$$

A simple form of expression (10) is determined by specific experimental conditions when narrow-spectra deuterated compounds are taken as acceptors. It is also assumed that the hyperfine structure of the solvent holes S^+ is averaged down by fast ion-molecular charge transfer. In this approach both the influence of the partners linewidth as well as relaxation terms are neglected. The validity of such a simplification will be mentioned below in discussions. A full expression for $T^{(k)}(t)$ can be found in, for example, Ref. [13].

The yield of singlet products of recombination in reactions (2) and (4) is given by the expressions

$$G_k(t) = \frac{1}{4} C^{(k)}(t) + \frac{1}{2} [2 \operatorname{Re}(\sigma_{++}^{(k)}(t) e^{-i\omega_3 t}) + \sigma_{zz}^{(k)}(t)], \quad (11)$$

where ω_3 is the Larmor frequency of the PTP anion. From formulae (5)–(11) one could obtain

$$G_1(t) = \frac{1}{2} e^{-k_0^* t} + \frac{1}{2} e^{-k_0^* t} \cos(\omega_{13} t), \quad (12)$$

$$G_2(t) = \frac{k_0}{k_0^*} [R(t) + \frac{1}{2} \cos \varphi \cos(\omega_{23} t - \varphi)], \quad (13)$$

$\varphi = \arctan(\omega_{21}\tau_0^*)$, where $\omega_{ij} = \omega_i - \omega_j$, and $R(t)$ is the smooth function,

$$R(t) = \frac{1}{2}(1 - e^{-k_0^* t}) - \frac{1}{2} e^{-k_0^* t} \cos^2 \varphi. \quad (14)$$

Thus, the yield of singlet pairs oscillates with time and the value of phase shift is determined by the capture rate, the hole decay time and g -factor shift upon hole capture,

$$\omega_{21} \cot \varphi = k[D] + (\tau_1)^{-1}. \quad (15)$$

Consequently, the hole capture and decay rate constants could be extracted from the slope and cut-off of the concentration dependence.

When the hole lifetime τ_0^* is prolonged, the phase shift of oscillations φ tends to $\pi/2$ and their amplitude drops to zero. Note that oscillations appear in both the hole recombination channel (12) and acceptor recombination (13) and the experimentally observed pattern is a superposition of them both. However, since the difference in the g -factors of the alkane holes and the p -terphenyl anion as counterion is not large ($\omega_{13} < \omega_{23}$) the quantum oscillations induced by primary pairs are found to be observed only at high magnetic fields (~ 18 kG [7]). Moreover, the contribution of this channel to the total fluorescence emission exponentially vanishes with the time of hole capture so that at longer times only secondary pair oscillations are observed.

Expression (15) serves as a basis for the method presented of the direct evaluation of the time of capture of primary solvent holes by acceptors with a lower ionization potential. The experimentally measured magnitude of the phase shift φ unambiguously determines the capture rate constant since g -factor values of the corresponding radical ions are available from the literature.

3. Experimental

Recombination fluorescence was recorded by the photon counting technique as described in Ref. [5]. The radioactive isotope ^{90}Sr of about $5 \mu\text{Ci}$ in activity was used as ionization source. Electrons arrived at the sample along the magnetic field direction.

To observe the oscillation phase shift the apparatus was modified in order to increase the long-term stability of all equipment parameters and to improve the time resolution. To this goal, a magnet system was made consisting of a Varian E-3 electromagnet and power supply unit controlled by a Hall probe. Using pole concentrators the field up to 9600 G was obtained in a magnet gap with inhomogeneity being not more than 2 G at the sample site. Field calibration and its long-term stability were checked with an NMR magnetometer. Employing fast microchannel PMT tubes (ELDI) with a single-photon pulse risetime < 200 ps (from 0.1 to 0.9 of maximum amplitude) and short (~ 10 cm) lightguides has improved the time resolution up to 700 ps (fwhm). Eventually, the attained reproducibility of fluorescence kinetics curves allowed

one to extract the time shift of oscillations to within ~ 200 ps.

The fluorescence time of the excited recombination products P^* was measured using the same apparatus. For these measurements a cuvette section was modified to excite solution fluorescence by Čerenkov light pulses arising upon passage of fast electrons through a 45 mm thick quartz converter totally blocking ionizing radiation of the radioactive source.

Solutions were prepared using as acceptors diphenylsulfide- d_{10} and p -terphenyl- d_{14} whose isotopic purity ($\sim 99\%$) was controlled by NMR. Isooctane (99%, FLUKA) was used as a solvent. Diphenylsulfide was purified by distillation.

Particular attention was paid to solvent purification. The initial chemical purification of the solvent was performed by treating it with a mixture of sulfuric and nitric acids at room temperature. The traces of unsaturated solutes were transferred into the corresponding nitro compounds then separated by distillation with sodium. Chemically purified solvent was additionally passed through a chromatographic column with aluminum oxide. The isooctane used has optical density 1 at 205 nm.

Samples were degassed by repeated freeze–pump–thaw cycle and sealed in thin quartz cuvettes. All experiments were carried out at room temperature.

4. Results and discussion

Figs. 1a–1d depict the experimental radiofluorescence decay curves $I_H(t)$ of the 10^{-3} M PTP- d_{14} and 3×10^{-2} M DPS- d_{10} solutions in isooctane taken at room temperature in various magnetic fields. For convenience the curves are shifted arbitrary along the vertical axis. In strong magnetic fields (Figs. 1a–1c) the oscillation pattern can be observed on curves whose frequency is proportional to field strength and coincides with the calculated one for the pair $(DPS-d_{10})^+ / (PTP-d_{14})^-$. As follows from Fig. 1d, the curve taken in the field of 170 G bears no oscillations ($\omega_{ij}t \ll 1$) and could be used as a reference to get the oscillating components in curves 1a–1c.

The phase shift was analyzed in terms of the relation $I_H(t)/I_{170}(t)$. Figs. 2a and 2b exemplify the time profiles I_{9600}/I_{170} obtained from experimental curves for two different concentrations of diphenylsulfide in

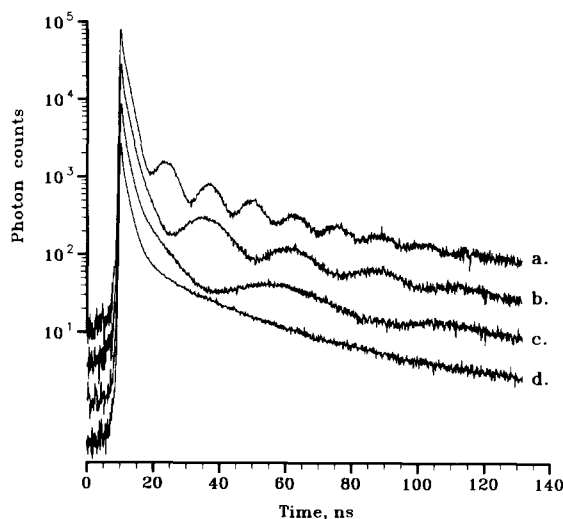


Fig. 1. Recombination fluorescence intensity curves of the 10^{-3} M p -terphenyl- d_{14} and 3×10^{-2} M diphenylsulfide- d_{10} solutions in isooctane at room temperature for magnetic fields: (a) 9600 G, (b) 4800 G, (c) 2400 G, (d) 170 G.

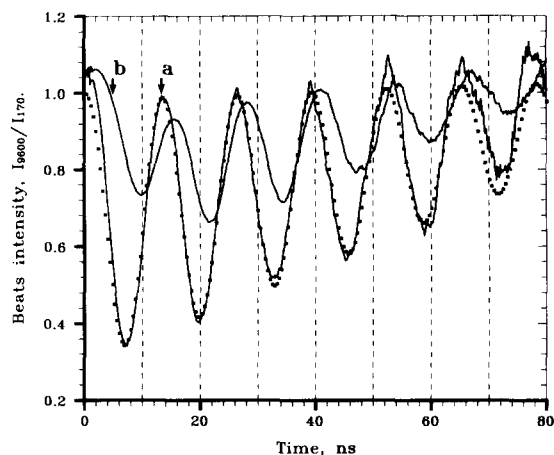


Fig. 2. Quantum oscillations $I_{9600}(t)/I_{170}(t)$ for 10^{-3} M p -terphenyl- d_{14} solutions in isooctane at diphenylsulfide- d_{10} concentrations: (a) 1.2×10^{-1} M, (b) 1.2×10^{-2} M. Solid lines: experiment; points: theoretical fit to curve (a).

solution. At a high DPS concentration (curve 2a) the oscillation depth reaches 70% and the corrected phase shift (see below) is actually absent. In agreement with the theoretical model, the oscillation phase shift has been observed at low acceptor concentrations (curve 2b) accompanied by a decrease in their amplitude.

The phase shift φ was determined by fitting the calculation curves to the experimental one. To compare

theoretical expressions (12) and (13) with experimental data the following items should be pointed out.

(i) A simple form of expression (10) was obtained by neglecting the unresolved hyperfine structure of both the $(\text{PTP-}d_{14})^-$ and $(\text{DPS-}d_{10})^+$ spectra as well as the relaxation processes induced by resonance charge transfer. Such a simplification is determined by specific experimental conditions where the deuterated compounds with narrow spectra have been chosen as acceptors. This approximation is sufficient for determining the phase shift φ and allows clear analytical expressions. Evidently, the introduction of the unresolved spectrum width and ion–molecular charge transfer cause the decay of oscillations (see e.g. Ref. [7]). These processes can readily be taken into account when deducing expression (10). Therefore, a full computation procedure has been used to process experimental data [13]. Indeed, as follows from Fig. 2, the experimentally observed oscillation pattern displays some decay that is likely to be assigned to these reasons.

(ii) In the radiation track, the singlet-correlated pairs compose just a fraction Θ of the total number of recombining pairs (see e.g. Ref. [14]). Therefore, a fraction of singlet-recombining pairs is

$$W_S(t) = [G_1(t) + G_2(t)] \Theta + \frac{1}{4}(1 - \Theta). \quad (16)$$

The last term conforming to the contribution of uncorrelated pairs reflects the fact that the fraction of the singlet component among these pairs is constant and amounts to $\frac{1}{4}$. As seen from Fig. 2a, even at high DPS concentrations the oscillation amplitude fails to reach 100% which allows one to estimate the fraction of spin-correlated pairs in the track $\Theta \approx 35\%$. The value obtained is slightly lower than those obtained from magnetic field effects [14] and corresponds to the data obtained by optical methods [15].

(iii) The theoretical expression for the observed fluorescence decay $I(t)$ is given by the convolution,

$$I(t) = (\tau_{\text{fl}})^{-1} \int_0^t \exp\left(-\frac{t-\xi}{\tau_{\text{fl}}}\right) W_S(\xi) F(\xi) d\xi, \quad (17)$$

where $F(t) \propto t^{-3/2}$ is the kinetics of the radical ion pair recombination independent of magnetic field strength [16], and τ_{fl} is the P* fluorescence time.

It was checked numerically that the explicit form of the $F(t)$ function is insignificant for determining the magnitude of the phase shift φ , whereas the fluorescence time is highly essential for consideration (see Table 1). As already mentioned, to get the oscillating component the kinetics have been accumulated twice for each sample: in a strong magnetic field (e.g. $H = 9600$ G) and in a reference magnetic field $H_{\text{ref}} = 170$ G. The result has been presented as the ratio of these two curves: $I_H(t)/I_{\text{ref}}(t)$. For this approach the following expansion holds:

$$I_H/I_{\text{ref}} = W'_H(t)/W'_{\text{ref}}(t) + \mathcal{O}(\alpha\tau_{\text{fl}}), \quad (18)$$

where $\alpha = (1/F)(\partial F/\partial t)$ is the slope of function $F(t)$, $W'(t)$ is given by the convolution

$$W'(t) = (\tau_{\text{fl}})^{-1} \int_0^t \exp\left(-\frac{t-\xi}{\tau_{\text{fl}}}\right) W_S(\xi) d\xi, \quad (19)$$

and $F(t)$ drops out from the equation. Therefore, the phase shift φ can be found by using the approximate expression (18). With $\tau_{\text{fl}} \rightarrow 0$ the accuracy of expression (18) increases. Thus, it is desirable to use fast luminophores.

The luminophore fluorescence time τ_{fl} was measured on the same samples. In the absence of diphenylsulfide the fluorescence time of PTP- d_{14} was found to be $\tau_{\text{fl}}^0 = 1.23 \pm 0.04$ ns which is in agreement with the known value of 1.19 ns [17]. The fluorescence time decreases with diphenylsulfide concentration according to the relation,

$$(\tau_{\text{fl}})^{-1} = k_Q[\text{D}] + (\tau_{\text{fl}}^0)^{-1}. \quad (20)$$

The obtained value of the fluorescence quenching rate constant k_Q appeared to be close to the diffusion-controlled one $k_Q = 4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The values obtained for the fluorescence time have then been used to determine the phase shift angle φ and the hole lifetime τ_0^* . Convolution (19) was performed numerically. The values of the g -factors, 2.0028 for $(\text{PTP-}d_{14})^-$ and 2.0040 for the isooctane radical cation, necessary for the calculations, have been taken in accord with literature data [18]. The value of 2.0086 for the $(\text{DPS-}d_{10})^+$ g -factor deduced from the oscillation frequency was in agreement with that found from its OD ESR spectrum. The experimental data are listed in Table 1. As follows from the table, neglecting the P* fluorescence time gives anomalously large values of φ that

Table 1
Oscillation phase shift versus diphenylsulfide concentration observed and corrected with regard to the time of luminophore fluorescence

[D] (10^{-2} M) ^a	τ_{fl} (ns) ^b	Δt_{obs} (ns) ^c	φ_{obs} (grad) ^d	τ_0^* (ns) ^e	φ (grad) ^f
0	1.23	–	–	–	–
0.3	1.21	4.7 (6.6)	100 (73)	10 (9)	75 (60)
0.6	1.19	4.0 (4.6)	90 (52)	5.5 (4.1)	65 (39)
1.2	1.15	3.1 (3.4)	68 (38)	2.5 (2.4)	44 (25)
3	1.05	2.0 (1.9)	43 (19)	1.0 (.9)	21 (9)
6	.92 (1.5)	1.5 (1.5)	32 (.6)	.6 (.6)	13

Magnet field strength is 9600 (4800) G.

^a DPS concentration. ^b Luminophore fluorescence time interpolated according to (20). ^c Observed oscillations delay time.

^d Observed phase shift. ^e Hole lifetime. ^f Corrected phase shift.

exceed the theoretical limit of 90° . Fig. 2 gives a theoretical fit for curve 2a (dots) according to (18). Comparison testifies to a fair agreement between the theoretical model and experimental data. The divergence observed at short times (<5 ns) is especially noticeable at minor DPS concentrations. It can be assigned to several facts, e.g. to the difference in the yields of the excited products of recombination P^* in reactions (2) and (4) as well as to the additional fluorescence of the luminophore resulting from direct excitation by the Čerenkov light. Note that similar reasons make it difficult to analyze the amplitude drop with decreasing DPS concentration.

The experimentally obtained dependence of $(\tau_0^*)^{-1} = \omega_{21} \cot \varphi$ on DPS concentration is shown in Fig. 3. The closed circles correspond to the values obtained in a field of 9600 G, and the open ones to those obtained in a field of 4800 G. As expected, the values of τ_0^* obtained are independent of magnetic field strength. Within experimental accuracy the data coincide and fall onto the straight line passing through the zero point. Its slope gives the capture constant and the ordinate cut-off gives the constant of hole decay (expression (15)). Experimental error is determined by the reproducibility of the oscillation time shift in fluorescence kinetics (~ 200 ps). The rate constant of isooctane hole capture by diphenylsulfide molecules obtained by this method was found to be $k = (3.5 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which is twice

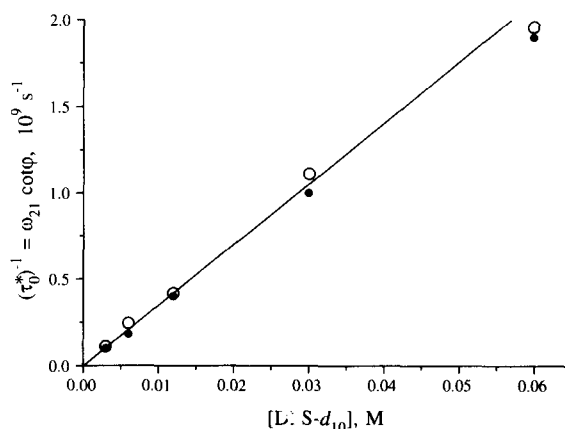


Fig. 3. Dependence of the isooctane hole lifetime $(\tau_0^*)^{-1} = \omega_{21} \cot \varphi$ on diphenylsulfide- d_{10} concentration. Closed circles: the data obtained in a field of 9600 G; open circles correspond to a field of 4800 G. Solid line: linear approximation.

the diffusion-controlled value $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ obtained from isooctane viscosity. This excess can be related to a large radius of charge transfer between solvent hole and acceptor because such a reaction can follow the tunneling mechanism from the distances exceeding the sum of the van der Waals reagent radii. It is, however, not inconceivable that a solvent hole displays high mobility when moving in a hopping fashion over same matrix molecules (resonance charge transfer). Within the experimental error the straight line passes through the axis origin. This gives

an estimate for hole lifetime from below $\tau_1 \geq 15$ ns which is in accord with the values obtained by the method of pulse radiolysis for the cations of linear and branched alkanes (see e.g. Ref. [17]).

Thus, in the present work the phase shift of luminescence quantum oscillations arising from the recombination of singlet-correlated radical ion pairs (DPS- d_{10})⁺/ (PTP- d_{14})⁻ has been observed. The shift is caused by the delay in (DPS- d_{10})⁺ formation in the reaction of isooctane solvent holes with diphenylsulfide molecules. Comparison with a theoretical model has allowed one to obtain the rate constant of isooctane hole capture and to estimate the fraction of singlet-correlated pairs in the track.

Acknowledgement

The authors are grateful to Dr. Ya.A. Ainbund and to the ELDI firm (68, M. Toreza pr., St-Peterburg, 194224, Russia, fax: 812-5899064) for the microchannel PMT, as well as Dr. A.I. Kruppa for valuable discussions. The work was supported by ISF, grants Nos. RCE000 and RCE300, and by INTAS, grant No. 93-1626.

References

- [1] K.M. Salikhov, Yu.N. Molin, R.Z. Sagdeev and A.L. Buchachenko, *Spin polarization and magnetic effects in radical reactions* (Elsevier, Amsterdam, 1984).
- [2] U.E. Steiner and T. Ulrich, *Chem. Rev.* 89 (1989) 51.
- [3] B. Brocklehurst, *J. Chem. Soc. Faraday Trans. II* 72 (1976) 1869.
- [4] J. Klein and R. Voltz, *Phys. Rev. Letters* 36 (1976) 1214; *Can. J. Chem.* 55 (1977) 2102.
- [5] O.A. Anisimov, V.L. Bizyaev, N.N. Lukzen, V.M. Grigoryants and Yu.N. Molin, *Chem. Phys. Letters* 101 (1983) 131.
- [6] A.V. Veselov, V.I. Melekhov, O.A. Anisimov and Yu.N. Molin, *Chem. Phys. Letters* 136 (1987) 263.
- [7] A.V. Veselov, V.L. Bizyaev, V.I. Melekhov, O.A. Anisimov and Yu.N. Molin, *Radiation Phys. Chem.* 34 (1989) 567.
- [8] A.V. Veselov, O.A. Anisimov and Yu.N. Molin, *Pulse radiolysis*, ed. Y. Tabata (CRC Press, Boca Raton, 1991) p. 27.
- [9] A.D. Trifunac and D.W. Werst, *Study of radical cations by time-resolved magnetic resonance, in radical ionic systems. Properties in condensed phases*, eds. A. Lund and M. Shiotani (Kluwer, Dordrecht, 1991) p. 19; O.A. Anisimov, *Ion pairs in liquids*, eds. A. Lund and M. Shiotani (Kluwer, Dordrecht, 1991) p. 285.
- [10] D.W. Werst and A.D. Trifunac, *J. Phys. Chem.* 92 (1988) 1093.
- [11] R. Ernst, G. Bodenhausen and A. Wokaun, *Principles of nuclear magnetic resonance in one and two dimensions* (Clarendon Press, Oxford, 1987).
- [12] E.-W. Knapp and K. Schulten, *J. Chem. Phys.* 71 (1979) 1878.
- [13] D.V. Stass, N.N. Lukzen, B.M. Tadjikov, V.M. Grigoryants and Yu.N. Molin, submitted for publication.
- [14] B. Brocklehurst, *Intern. Rev. Phys. Chem.* 4 (1985) 279.
- [15] M.C. Sauer and C.D. Jonah, *Radiation Phys. Chem.* 44 (1994) 281.
- [16] G.C. Abell, A. Mozumder and J.L. Magee, *J. Chem. Phys.* 56 (1972) 5422.
- [17] M.C. Sauer, C.D. Jonah and C.A. Naleway, *J. Phys. Chem.* 95 (1991) 730.
- [18] Fischer, ed., *Landolt-Börnstein, Numerical data and functional relationship in science and technology, Group II, Vol. 17, Subvol. f. Magnetic properties of free radicals* (Springer, Berlin, 1990).