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## Feature Article

### Quantum Beats in Recombination of Spin-correlated Radical Pairs

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The present paper is a review of the current studies of quantum beats in recombination of spin-correlated radical pairs in solutions as well as of future applications of quantum beats technique for studying these pairs. Examples are given of the use of this method for determining the hf constants and relaxation times of short-lived radical ions, for finding the rate constants of the reactions of alkane radical cations and for estimating a fraction of singlet-correlated pairs in the tracks of ionizing particles. The potentialities of this method, its advantages and limitations are discussed.

#### Introduction

As short-lived intermediate states, radical pairs participate in many reactions in solutions. That is why they have long drawn attention of researchers.<sup>1,2</sup> Upon dissociation or ionization of a molecule, the radicals arise in solutions in pairs. For free valency to disappear, the radicals must encounter in solution or, in other words, must form a radical pair which can recombine or take part in other reactions. One of the peculiarities of the reactions of radical pairs is the so-called cage effect, *i.e.* a high probability of reverse recombination of two radicals, forming in the solution.

For the last 20-30 years, with the appearance of spin chemistry, a quickly developing scientific area, radical pairs have roused extraordinary interest.<sup>3,4</sup> Then, it has been made clear that the radical pairs are responsible for the unusual phenomena such as the chemical polarization of electron and nuclear spins, the influence of permanent and oscillating magnetic fields on chemical reactions, magnetic isotopic effect, etc.

It is commonly assumed that two radicals form a radical pair till the probability of their reaction with each other exceeds that of the reaction with other particles. A radical pair can decay due to either the recombination (disproportionation), called usually the cage recombination, or the separation of radicals via their diffusion (escape into the bulk) or, finally, the reaction of radicals with other particles (radical acceptors).

One of the most interesting properties of radical pair is the dependence of the probability of its recombination on the spin multiplicity of a pair which follows from the conservation of the total electron spin in the elementary chemical act. Studies of magnetic field and spin effects in reactions of radical pairs led to an important conclusion that the spin multiplicity can vary during radical pair lifetime. These variations take usually the form of dynamic quantum oscillations (beats) between the singlet and triplet states of a pair. These dynamic transitions modulate the probability of various channels of radical pair reactions and account for the variety of the observed magnetic field and spin effects. A study of these effects gives information about the structure, reactions, molecular and spin dynamics of short-lived radical pairs.

This review is devoted to both the direct observation of quantum beats in recombination of radical ion pairs and the applications of quantum beats technique for studying these pairs in solutions.

#### Spin-correlated Radical Pairs

When a molecule dissociates (is ionized) under thermal excitation, light, or ionizing radiation, radical pairs arise in the spin-correlated state, *i.e.* they preserve spin multiplicity of their precursor. The ionization of a ground-state molecule or the dissociation of a singlet-excited molecule gives rise to a singlet pair in which the partner spins are antiparallel and the total electron spin  $S$  is zero. Dissociation of the triplet-

excited molecule causes the formation of a triplet pair with total electron spin  $S=1$ .

When there is no exchange interaction between pair partners (which holds for the systems below), the behavior of pair spins in nonviscous solutions is described by the spin-Hamiltonian

$$H = \beta_e H_0 (g_1 S_{1z} + g_2 S_{2z}) + \hbar \sum_i a_{1i} \mathbf{S}_1 \cdot \mathbf{I}_{1i} + \hbar \sum_k a_{2k} \mathbf{S}_2 \cdot \mathbf{I}_{2k} \quad (1)$$

where the first term is determined by the Zeeman interaction of unpaired electrons (spins  $S_1$  and  $S_2$ ) with external magnetic field  $H_0$  and the second and third terms depend on the isotropic hyperfine interactions (hfi) of each unpaired electron with its magnetic nuclei (spins  $I_{1i}$  and  $I_{2k}$ ). The spin-Hamiltonian parameters (the  $g$ -factors of radicals and the hyperfine couplings constants  $a_{1i}$  and  $a_{2k}$ ) are often known from ESR spectroscopy of free radicals.

A particular feature of this Hamiltonian is that the states of the pair with a given spin multiplicity (singlet or triplet) are not its eigenstates. This is the difference between the radical pair and the molecules for which due to great intramolecular electron exchange interaction the singlet and triplet states are stationary. In other words, in terms of quantum mechanics, the spin-correlated radical pair appears in the coherent state subject to oscillations between the singlet and triplet states. Oscillation frequencies are determined by the parameters of spin-Hamiltonian (1), *i.e.* the difference in the  $g$ -factors of radicals and hfi constants. For organic radicals the typical oscillation periods vary from several nanoseconds to several tens of nanoseconds. In this case, the coherence is destroyed with time by the processes of spin relaxation.

A pattern of quantum oscillations is particularly simple when the system studied is placed in high magnetic field. In this case, the spin-correlated pair oscillates between the singlet and one of the triplet states  $T_0$  with a zero projection of total electron spin onto direction of external magnetic field. Due to the Zeeman splitting in high magnetic field the triplet states  $T_+$  and  $T_-$  do not mix with a singlet state of the pair. For a singlet born radical pair with a given configuration of nuclear spins the spin population  $\rho_{ss}(t)$  of the singlet state obeys the expression below

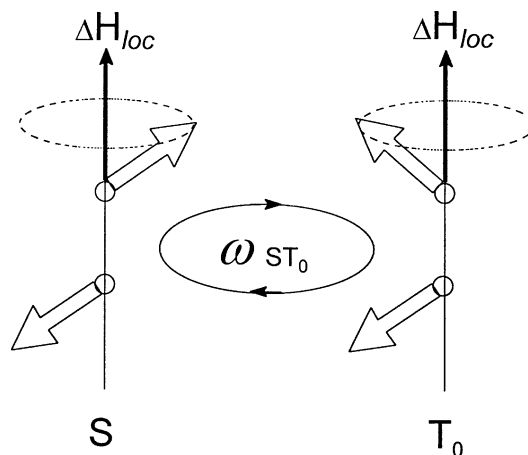
$$\rho_{ss}(t) = \cos^2(\omega_{ST} t/2) \quad (2)$$

where the frequency of  $ST_0$  quantum oscillations is determined by the expression

$$\omega_{ST} = \left| \beta_e \hbar^{-1} H_0 (g_1 - g_2) + \sum_i a_{1i} m_{1i} - \sum_k a_{2k} m_{2k} \right| \quad (3)$$

Here  $m_{1i}$  and  $m_{2k}$  are the projections of corresponding nuclear spins onto the direction of external magnetic field. As follows from the formula, the frequency of quantum beats depends on the difference in the frequencies of line positions in the ESR spectra of pair partners.

Since different nuclear configurations result in different frequencies, a general pattern of quantum beats for the entire ensemble of pairs can be rather complex and is simple only in two cases. When hyperfine couplings are negligibly small, the oscillations occur at frequency, depending on both



**Figure 1.** Vector diagram, explaining the appearance of  $S$ - $T_0$  oscillations in a radical pair in high external magnetic field. Oscillations arise if spins precess at different Larmor frequencies due to the difference  $\Delta H_{loc}$  of local magnetic fields.

the difference in  $g$ -factors and external magnetic field. In another simple case where all magnetic nuclei are equivalent and  $\Delta g=0$ , the oscillations occur at multiple frequencies and their superposition with corresponding weights gives sharp peaks in the curve of the total population of a given spin state of the pair.

The appearance of quantum oscillations in high magnetic field can be illustrated using a vector diagram (Figure 1). A pair, arising from a singlet state, can pass to the  $T_0$  state and back if the Larmor precession frequencies of two spins are unequal. The frequency difference may originate from the difference of both the  $g$ -factors and the local hyperfine fields.

In weak magnetic field ( $H_0 < a\hbar/g\beta_e$ ) the singlet term mixes up with all three triplet sublevels thus complicating the problem of description of quantum oscillations which, for the general case, can be solved only numerically. The analytical solution (rather cumbersome) is available if each of two radicals contains one nucleus with hyperfine couplings.<sup>3</sup> A compact analytical expression is derived for zero magnetic field for the radical pair with one magnetic nucleus with spin  $I$

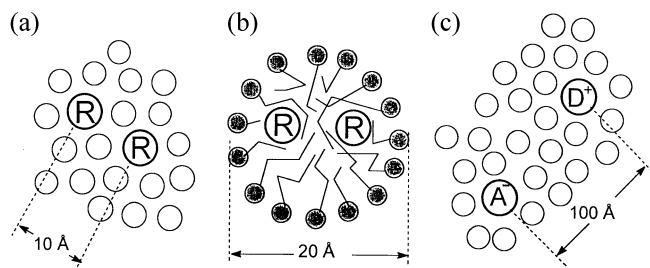
$$\rho_{ss}(t) = 1 - [4I(I+1)/(2I+1)^2] \sin^2(\omega_{ST} t/2) \quad (4)$$

where

$$\omega_{ST} = (2I+1)a/2 \quad (5)$$

To describe spin dynamics for several equivalent nuclei in one radical, it is sufficient to average expression (4) over parameter  $I$  which, in this case, corresponds to the possible values of the total nuclear spin.

For direct experimental observations of the influence of quantum beats on radical pairs recombination, it is necessary that the lifetime of a pair would be longer or comparable with the typical periods of quantum beats. Pair lifetimes depend on the initial distance between the radicals and on the character of their mutual diffusion. Two uncharged radicals in homogeneous solutions (Figure 2a) should be consid-

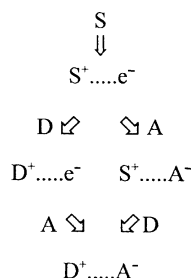


**Figure 2.** The schematic view of pair of uncharged radicals in homogeneous solution (a), in micelle (b), and of radical ion pair in the track of ionizing particles (c). The scale is approximate.

ered as the radical pair if the distance in-between does not exceed the double radical diameter. When the distances are larger, the probability of radical encounter becomes smaller than that of their diffusion into the bulk. The lifetime of these radical pairs in nonviscous solvents amounts to fractions of a nanosecond. For two radicals, captured in micelle (Figure 2b), the distance between pair radicals is determined by micelle size. The lifetime of this pair can be by one-two orders of magnitude larger than that in the homogeneous solution due to both the large size of the cage and the smaller molecular mobility. Finally, for the radical ion pair in the tracks of ionizing particles (Figure 2c) the size of the radical cage depends on the Onsager radius.<sup>5</sup> For nonpolar solvents it equals several hundreds of Angstroms and the time of diffusional approach of partners is tens to hundreds of nanoseconds.

### Some Experimental Peculiarities

Among the above types of spin-correlated radical pairs the singlet radical ion pairs are most convenient for observing quantum beats. They can be readily produced by ionizing alkane solutions, containing electron and hole acceptors.<sup>6,7</sup> The formation of pairs in these solutions obeys the scheme below

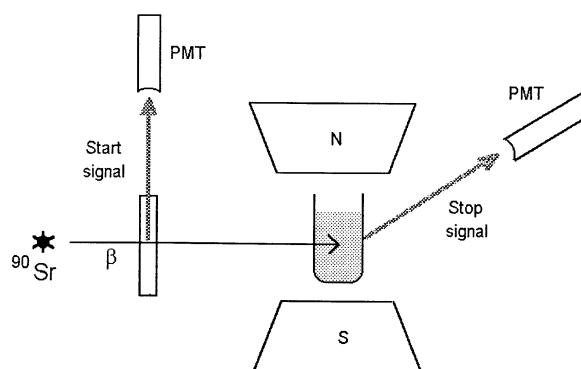


In this case S is the solvent molecule; A is the electron acceptor; D is the hole acceptor.

With respect to quantum beat observations, these pairs have the following favorable properties:

1) The probability of their recombination is close to unity because for most pairs, the initial distances between the partners are within the Onsager radius.

2) The singlet and triplet pairs give different recombination products, *i.e.* either the singlet or triplet excited mole-



**Figure 3.** Experimental scheme of quantum beats detection on recombination fluorescence in external magnetic field. Photons emitted by scintillator and sample after fast electron passage, are recorded by photomultiplier tubes (PMT).

cules. In this case the singlet channel of pair recombination is readily detected by the excited product fluorescence.

3) Exchange interactions between pair radicals are negligibly small over the entire trajectory of their motion because the recombination event (electron transfer) occurs in nonpolar solvents at fairly large distances of about 20 Å.

4) The times of diffusional approach of radical ions in the pairs  $D^+ \dots A^-$  and  $S^+ \dots A^-$  are large enough and exceed the typical periods of quantum beats.

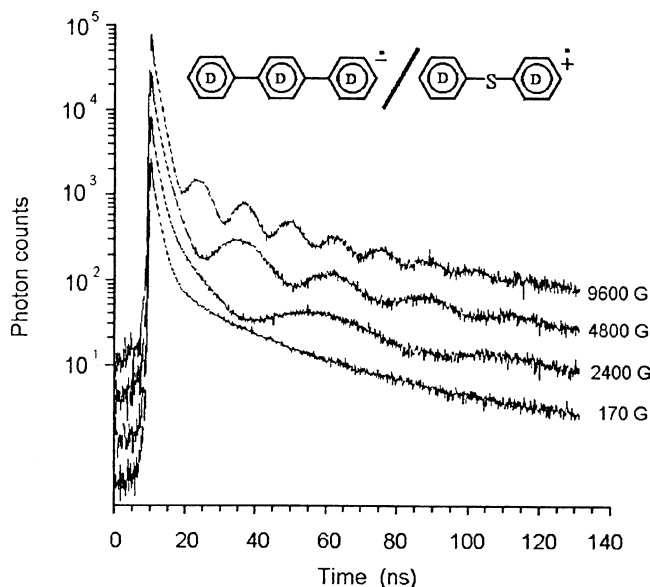
The method of photon counting is usually used to detect quantum beats by recombination product fluorescence. The sample to which the external magnetic field can be applied is ionized by fast electrons from a radioactive source (Figure 3). The electron first passes through a scintillator, giving a starting signal on a photomultiplier. From this point on, the time is counted. The second photomultiplier records a photon from the sample which is emitted with some delay, determined by the time of pair recombination. In this case, it is important that the time of excited molecule fluorescence would be much smaller than the oscillation period. Therefore, as an acceptor, we choose a molecule with a short fluorescence time, namely, the *p*-terphenyl molecule ( $\tau_{fl}=1.2$  ns). The number of photon counts, as a function of delay, is accumulated in a multichannel analyzer. To obtain a good signal-to-noise ratio it is necessary to accumulate the signal for an hour or more. The accumulation time can be reduced several times using pulsed cyclic sources of radiation, *e.g.* the pulsed X-ray sources. For details, see review.<sup>8</sup>

Studying quantum beats by recombination product fluorescence, it is necessary to remember that the kinetics of the decay of luminescence intensity  $I(t)$  (assuming very short fluorescence time and the absence of instrumental broadening) is determined by the product of two functions

$$I(t) \sim F(t) \rho_{ss}(t) \quad (6)$$

where  $F(t)$  is the rate of geminate recombination of pairs. Thus, the oscillating component is observed at the background of a quickly decaying  $F(t)$  function (Figure 4).

The oscillating component  $\rho_{ss}(t)$  is readily determined when the beats depend on the difference in the *g*-factors



**Figure 4.** The curves of recombination fluorescence decay for solution of  $10^{-3}$  M *p*-terphenyl- $d_{14}$  and  $3 \times 10^{-2}$  M diphenylsulphide- $d_{10}$  in isoctane in various magnetic fields. For convenience the curves are displaced relative to each other. The oscillating component is related to the recombination of the singlet-correlated pairs (diphenylsulphide- $d_{10}$ )<sup>+</sup>/*p*-terphenyl- $d_{14}$ )<sup>-</sup>; the oscillation frequency depends on the difference in the *g*-factors of radical ions and decreases with decreasing magnetic field strength. The curve in field of 170 G can be used as the reference curve to reveal the oscillating component.

of pair partners and hyperfine couplings are of no essence. To this end, we analyze the ratio between two decay curves<sup>9</sup>

$$I_H(t)/I_{\text{ref}}(t)$$

where  $I_{\text{ref}}(t)$  is the reference curve, obtained in relatively low magnetic fields in which a change in  $\rho_{\text{ss}}(t)$  within the observation time can be neglected. It is undesirable to use zero magnetic field to get the reference curve because in zero field even the weak hyperfine couplings can complicate substantially the pair spin evolution.

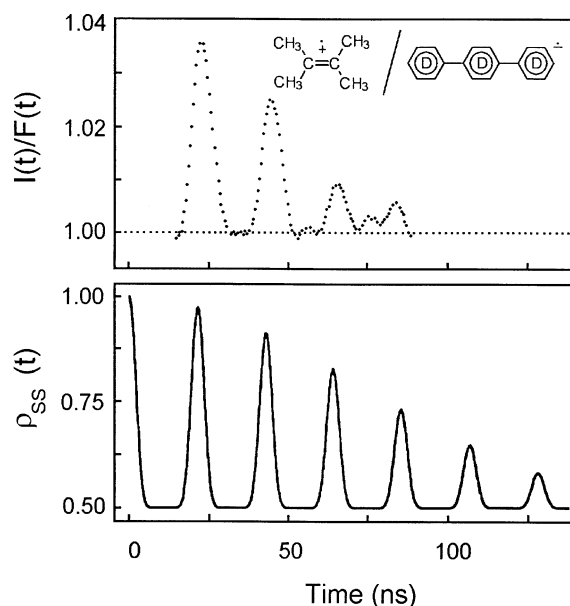
Compared to the  $\Delta g$ -beats, it is impossible to obtain the experimentally smooth reference curve for hfi-beats. In either zero or weak external field the hfi gives a complex pattern of oscillations. Therefore in first experiments<sup>10</sup> a smooth reference curve  $F(t)$  was chosen using a semi-empirical method. However, as established later,<sup>11,12</sup> for the hfi beats of equivalent nuclei the procedure of dividing of the curves, obtained in high and zero fields, is rather useful despite the existence of an oscillating component in both of the curves. Due to simple relationships between beat frequencies in this case, a simple oscillation pattern, allowing a qualitative interpretation and simple quantitative treatment, appears in the  $I_H(t)/I_0(t)$  curves. The most characteristic feature of these systems is the existence of a strong peak at time  $\tau = 2\pi/a$ , determined by a hfi constant,  $a$ , independent of the number of equivalent protons.<sup>12</sup>

## Applications of Quantum Beats Technique

Formally, a pattern of quantum beats can be characterized by the parameters such as a set of oscillation frequencies, the oscillation decay time, the phase shift of oscillations, and, finally, their amplitude. Each parameter contains useful information about the nature and properties of radical pairs. The oscillation frequencies, as follows from the above relationships, are related to the splittings in the ESR spectrum of pair partners. The decay of oscillations is determined by the ESR line widths of pair partners and, thus, contains information about their spin relaxation times. Actually, a pattern of quantum beats is the Fourier-transformation of the ESR spectrum. The phase shift is related to the time delay of the studied pair formation from its precursor. Finally, a decrease in the amplitude of oscillating component, compared to the calculated one, indicates usually that some pairs either originate in the spin-uncorrelated state or participate in cross-recombination in which the spin correlation is absent.

**ESR spectrum parameters.** In the pioneering works on the observation of quantum beats the radical pairs were generated whose ESR spectra were known or could be obtained independently, using, *e.g.* the method of optically detected ESR (OD ESR).<sup>13</sup> These experiments<sup>10,14</sup> show a fair agreement between the observed beat frequencies and the splittings in the ESR spectra of a pair.

Figure 5 exemplifies the experimental and calculated curves of the beats for the (tetramethylethylene)<sup>+</sup>/*p*-terphenyl- $d_{14}$ )<sup>-</sup> radical ion pair obtained by Anisimov *et al.*<sup>10</sup> The beats are determined by hyperfine couplings with 12 equivalent protons of tetramethylethylene radical cation. In the sec-



**Figure 5.** The experimental curve of quantum beats in the recombination fluorescence of (tetramethylethylene)<sup>+</sup>/*p*-terphenyl- $d_{14}$ )<sup>-</sup> pairs in *trans*-decalin in the field  $H_0 = 3300$  G, determined as a ratio of  $I(t)$  to the smoothed function  $F(t)$ , which imitates the pair lifetime distribution. The calculated curve  $\rho_{\text{ss}}(t)$  of singlet state population is shown at the bottom.

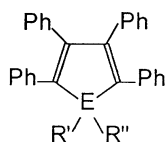
**Table 1.** Experimental and calculated parameters for quantum beats in the recombination of radical ion pairs ( $H_0 = 3300$  G)

Radical-ion pair	Solvent	HFI constant on equivalent protons, ESR $a$ (G)	Calculated beat period, $T = 2\pi/\gamma a$ (ns)	Experimental beat period (ns)
(tetramethylethylene) <sup>+</sup> / ( <i>p</i> -terphenyl- <i>d</i> <sub>14</sub> ) <sup>-</sup>	<i>trans</i> -decalin	16.5	21.6	22±0.5
	<i>cis</i> -decalin			22±0.5
	squalane	16.6	21.5	22±0.5
	pentadecane			22±0.5
(durene) <sup>+</sup> / ( <i>p</i> -terphenyl- <i>d</i> <sub>14</sub> ) <sup>-</sup>	<i>trans</i> -decalin	10.8	33.1	33.5±0.5

ond pair partner (*p*-terphenyl-*d*<sub>14</sub> radical anion) the hfi constants are small and cause just a decay of oscillation amplitude. A faster decay of oscillations, compared to the calculated one, is likely to depend on the processes of spin relaxation neglected in simulation. Table 1 compares the experimental periods of beats with those calculated from the hfi constants known for the studied radical cations. It is seen that within experimental errors these values coincide.

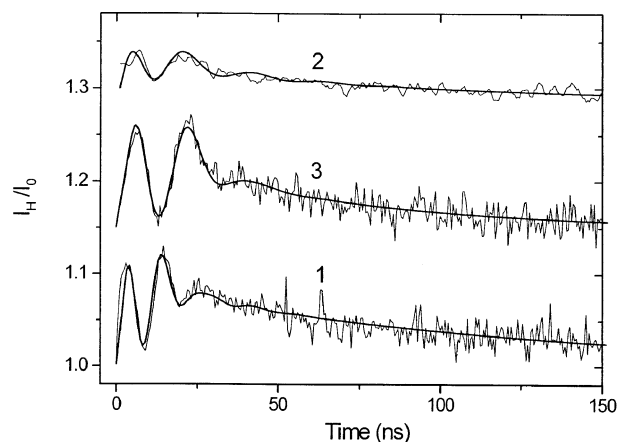
Studying the beats caused by the difference in *g*-factors, Veselov *et al.* have obtained the same good agreement between the frequencies and the data of ESR spectroscopy<sup>9,14</sup> for the pairs (diphenylsulphide)<sup>+</sup>/*p*-terphenyl-*d*<sub>14</sub>)<sup>-</sup> and (diethylsulphide)<sub>2</sub><sup>+</sup>/*p*-terphenyl-*d*<sub>14</sub>)<sup>-</sup>. In the S<sup>+</sup>/*p*-terphenyl-*d*<sub>14</sub>)<sup>-</sup> pairs, in which S<sup>+</sup> is the radical cation (hole) of a solvent (squalane or pentadecane), the beats are also caused by the difference in *g*-factors.<sup>9</sup> They, however, decay very quickly so that only the first minimum is observed in the  $I_H(t)/I_{ref}(t)$  curves. Nevertheless, it was demonstrated that the curves obtained in various magnetic fields are best simulated using the values of *g*-factors of the solvent hole measured by the OD ESR method.

Recently, Bagryansky *et al.*<sup>11,15</sup> were the first to use the quantum beats technique to determine the unknown hfi constants of short-lived radical ions. Radical ion pairs were generated in decane 10<sup>-3</sup> M solutions of 1,2,3,4-tetraphenylcyclopentadiene and its silicon and germanium analogs:



- E=C, R'=R''=H (1)  
 Si, R'=R''=H (2)  
 Ge, R'=R''=H (3)  
 Ge, R'=R''=Cl (4)  
 Ge, R'=CH<sub>3</sub>, R''=Cl (5)

When low acceptor concentrations are used, the main contribution to the pattern of beats is made by the (decane)<sup>+</sup>/A<sup>-</sup> pairs in which A is either **1**, **2**, **3**, **4** or **5**. It was shown that the beats are due to the hyperfine couplings with either the protons of CH<sub>2</sub>, SiH<sub>2</sub>, and GeH<sub>2</sub> moieties (Figure 6) or chlorine atoms in the GeCl<sub>2</sub> and GeClMe moieties of radical anions.

**Figure 6.** The ratio of fluorescence decay curves in high (3000 G for **1** and **2** and 1000 G for **3**) and zero magnetic fields for 10<sup>-3</sup> M solutions of **1-3** in decane. The curves are 0.15 apart in vertical for convenience. Smoothed curves are obtained by computer simulation.

Later, Bagryansky *et al.* have managed to choose conditions (viscous squalane solvent, low temperatures), under which they observed the OD ESR spectra of the (squalane)<sup>+</sup>/A<sup>-</sup> pair and determined the hfi constants in radical anions.<sup>16</sup> The results of independent measurements of hfi constants by both the beats and ESR coincide (Table 2).

The decay of quantum beats is determined by the same factors as the ESR line width, *i.e.* spin relaxation and unresolved hyperfine structure. Spin relaxation leads to the decay of oscillating terms by the exponential law  $\exp(-t/T_2)$ , in which  $T_2^{-1}$  is the total rate of pair partners transverse relaxation. The contribution of unresolved hfi to the decay is of the  $\exp(-t^2\sigma^2/2)$  type, where  $\sigma^2$  is the contribution of hfi to the second moment of the line contour. Bagryansky *et al.*,<sup>17</sup> using the (diphenylsulphide-*d*<sub>10</sub>)<sup>+</sup>/*p*-terphenyl-*d*<sub>14</sub>)<sup>-</sup> pair as an example, have confirmed a good agreement between the data on the decay of beats and the line widths in the OD ESR spectrum of this pair. In this case, the time  $T_2$  was determined to be about 50 ns which was attributed to relaxation in the sulfur-containing radical cation.

**Phase shift and hole capture rate.** Since the formation of the secondary D<sup>+</sup>...A<sup>-</sup> pairs occurs with some delay, this can cause a phase shift in quantum oscillations. The scattering of phase shifts also leads to the decrease of oscillation amplitude. The delay is mainly determined by the trapping time of

**Table 2.** HFI constants for radical anions (**1**)<sup>-</sup> - (**5**)<sup>-</sup> obtained from OD ESR spectra and from quantum beats

Molecule	Atom	$a$ (G) OD ESR	$a$ (G) Quantum beats
( <b>1</b> )	H(2)	24.6	25.0
( <b>2</b> )	H(2)	17.0	15.6
( <b>3</b> )	H(2)	15.4	15.0
( <b>4</b> )	Cl(2)	7.0	7.0
( <b>5</b> )	Cl	12.4	11.4

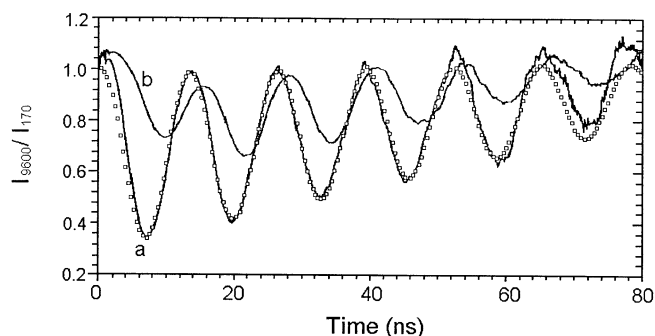
solvent hole (or another molecular radical cation) with the acceptor molecule D. Due to high electron mobility, its capture by acceptor A is much more quicker. Under these conditions, the phase shift  $\phi$  is related to the concentration [D] of the hole acceptor via a simple relationship

$$\omega \cot \phi = k [D] + k_{\text{dec}} \quad (7)$$

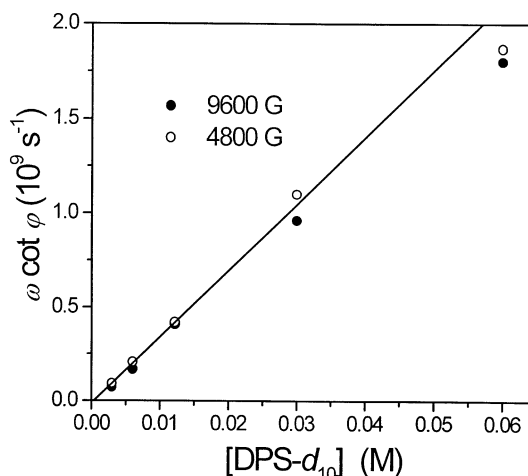
if the ESR spectra of all radical ions are the narrow singlets and the hole capture by the acceptor is followed by a change in the  $g$ -factor. In this case,  $\omega = \Delta g \beta_e H_0 / \hbar$  is the difference in the Larmor frequencies of  $S^+$  and  $D^+$ ;  $k$  is a bimolecular reaction rate constant of solvent hole trapping by acceptor D; and  $k_{\text{dec}}$  is a monomolecular rate constant of hole decay in any reactions other than the trapping by D. In this case, we extract the hole capture and the decay rate constants from the slope and intercept of the concentration dependence.

Attempts to record the phase shift of quantum oscillations, made in early works, have not been successful. Grigoryants *et al.*<sup>18</sup> have succeeded recently in detecting the phase shift of oscillations due to an increase in time resolution of the apparatus up to 0.7 ns. The phase shifts were observed in various solvents for the radical pair (diphenylsulphide- $d_{10}$ )<sup>+</sup>/ $(p$ -terphenyl- $d_{14}$ )<sup>-</sup>, in which the beats are determined by the difference in  $g$ -factors. The hyperfine couplings in this pair are insignificant owing to the use of deuterated acceptor molecules. It is assumed then that in the  $S^+$  radical cations the effective  $hfi$  are also small due to the fast electron exchange over solvent molecules.

Figure 7 exemplifies the experimental curves of oscillations for two different concentrations of diphenylsulphide- $d_{10}$  in isooctane. It is seen that as the concentration decreases, the phase shift appears and the oscillation amplitude decreases. In this case, in terms of the theoretical model,  $\cot \phi$  increases linearly with concentration of hole acceptor (Figure 8), and the measurements, made in various magnetic fields, give consistent results. The rate constant of isooctane hole capture by diphenylsulphide molecules was determined from the slope to be  $(3.5 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  which



**Figure 7.** The ratio between the fluorescence decay curves in high (9600 G) and weak (170 G) magnetic fields for recombination of (diphenylsulphide- $d_{10}$ )<sup>+</sup>/ $(p$ -terphenyl- $d_{14}$ )<sup>-</sup> pairs in isooctane. The concentration of  $p$ -terphenyl- $d_{14}$  is  $10^{-3} \text{ M}$ . It is seen that as the concentration of the hole acceptor, diphenylsulphide- $d_{10}$ , decreases from 0.12 M (curve a) to 0.012 M (curve b), the phase shift in oscillations appears and the oscillation amplitude decreases. Points: the theoretical fit to curve (a).

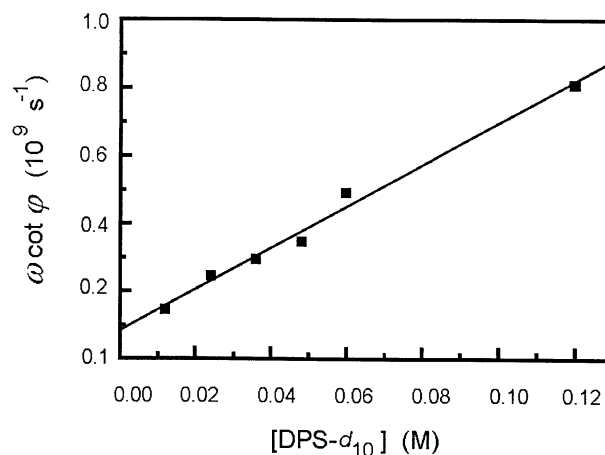


**Figure 8.** The dependence of  $\omega \cot \phi$  on the concentration of diphenylsulphide- $d_{10}$  (DPS- $d_{10}$ ) in isooctane at 9600 G and 4800 G.

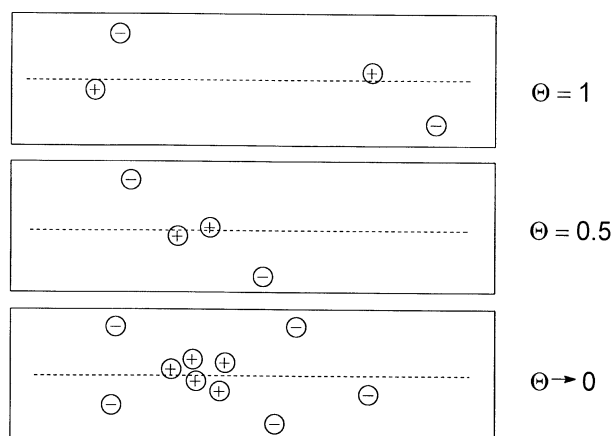
exceeds the value of the diffusion controlled reaction rate constant. Since the straight line passes through the origin of coordinates, we have managed to estimate only the lower limit for hole lifetime ( $\tau \geq 15 \text{ ns}$ ).

Usov *et al.*<sup>19</sup> have applied the quantum beats method for studying hole reactions in a viscous squalane solvent. Molecular diffusion in this solvent is substantially retarded due to its high viscosity. Shkrob *et al.*<sup>20</sup> have recently demonstrated in their pulse radiolysis experiments that the mobility of squalane holes exceeds considerably the mobility of molecular ions and, accordingly, the rate constants of hole trapping by acceptors exceed the diffusion controlled rate constant by almost order of magnitude. This behavior, so as that found earlier by Warman *et al.*<sup>21</sup> in cyclic alkanes, was assigned to the predominant contribution of fast hole hopping to the solvent cation mobility.

The results of measurements of phase shifts in squalane<sup>19</sup> are shown in Figure 9. The rate constant of hole capture was determined from the slope to be  $6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  which confirms conclusion on the high mobility of holes in squalane.



**Figure 9.** The dependence of  $\omega \cot \phi$  on the concentration of diphenylsulphide- $d_{10}$  (DPS- $d_{10}$ ) in squalane. The concentration of  $p$ -terphenyl- $d_{14}$  is  $10^{-3} \text{ M}$ . Note the non-zero cut off.



**Figure 10.** The scheme of radiation track fragments in the condensed phase, containing isolated radical ion pairs, double pairs, and multi-pair spurs. The assumed fraction of singlet-correlated pairs  $\theta$  for these fragments is also shown in the Figure.

Compared to isooctane, for squalane there is a non zero cut-off on the ordinate. The rate constant of squalane hole decay is estimated from the intercept to be  $(8.3 \pm 2) \times 10^7 \text{ s}^{-1}$  which is in fair agreement with experiments on pulse radiolysis.<sup>20</sup>

The phase shifts of quantum beats have been studied in other alkanes as well.<sup>22</sup> As expected, in linear alkanes the rate constants of hole trapping by acceptors, determined from the shifts, were close to the diffusion-controlled ones. In cyclic alkanes, cyclohexane, *cis*-decalin, and *trans*-decalin, the observed phase shifts had an intermediate value between that expected for the highly mobile holes and that assumed for molecular ions. In this case, both types of ions are likely to take part in the formation of diphenylsulphide radical cation.

**The fraction of singlet spin-correlated pairs.** The fraction of spin-correlated pairs is a very important characteristic of primary radiation chemical and photochemical events. The scale of magnetic field and spin polarization effects as well as the product composition are the functions of this quantity.

In irradiated solutions this fraction is substantially below unity because of the complex structure of the radiation track (Figure 10). While isolated pairs are believed to be singlet correlated, for a double pair the fraction might be as low as 1/2 due to cross recombination. For multi-pair spurs the spin correlation might be completely lost.

There are several approaches<sup>6,23</sup> trying to determine the fraction of spin-correlated radical ion pairs in radiolysis. The transient emission and absorption<sup>23</sup> suffer, however, from the lack of exact data on the extinction coefficients and luminescence quantum yields of intermediate products. The magnetic field effect technique<sup>6</sup> needs a detailed knowledge of spin evolution in zero field which is a problem in most cases. The quantum beats technique seems to be free from these limitations.

When applying quantum beats technique, it is essential that only the spin-correlated pairs contribute to the oscillat-

**Table 3.** The fraction  $f_s$  of the singlet channel of recombination  $f_s = \theta + 0.25(1 - \theta)$

Solvent	Method		
	Magnetic field effect <sup>6</sup>	Transient emission and absorption <sup>23</sup>	Quantum oscillations <sup>24,25</sup>
Hexane		0.5	0.65
Isooctane		0.5	0.66
Cyclohexane	0.65	0.5	0.60
<i>trans</i> -Decalin			0.52
<i>cis</i> -Decalin			0.52
Squalane	0.65		0.40
			0.60 <sup>a</sup>

<sup>a</sup>90 °C

ing component of spin evolution. Therefore formula (2) is substituted by

$$\rho_{ss}(t) = \theta \cos^2(\omega_{ST} t/2) + 0.25(1 - \theta) \quad (8)$$

where  $\theta$  is the fraction of singlet spin-correlated pairs. The second term in this formula takes into account the time-independent contribution of uncorrelated pairs.

To determine the fraction of singlet-correlated pairs on irradiated alkanes Usov *et al.*<sup>24</sup> have applied quantum beats to the same radical ion pairs (diphenylsulphide- $d_{10}$ )<sup>+</sup>/(*p*-terphenyl- $d_{14}$ )<sup>-</sup> used to study the phase shifts. The initial amplitude  $A$  of decaying oscillations for the  $I_H(t)/I_{ref}(t)$  ratio is related, in this case, to the fraction of spin-correlated pairs via the formula below

$$\theta = A/(4-3A) \quad (9)$$

The fraction of spin correlated pairs can be determined either from the oscillation amplitude extrapolated to zero time or by computer simulation of the entire oscillation curve. Two methods gave consistent results.

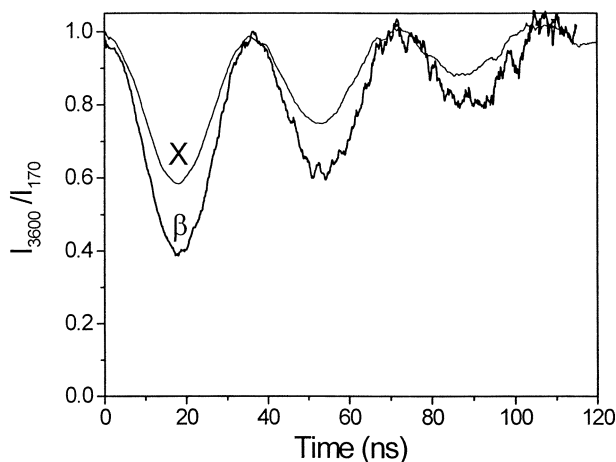
The results for different alkanes irradiated by fast electrons are compared in Table 3 with those obtained by other techniques. To this end, the fraction of singlet recombination  $f_s$

$$f_s = \theta + 0.25(1 - \theta) \quad (10)$$

is given in the Table for all cases. This value contains an extra singlet contribution from uncorrelated pairs.

The quantum oscillation results are seen to correlate well with the published data. It is seen also that the fraction does not vary much among alkanes. The only exception is a very viscous solvent, squalane, in which the quantum beats give a substantially lower  $f_s$ -value as compared to other techniques. It was found, however,<sup>25</sup> that for squalane the oscillation amplitude increases up to the normal value with increasing temperature. Obviously, the quantum beats technique has some limitations at high viscosity. The reason is not clear yet. On the other hand, at low viscosity the method seems to be quite reliable and universal.

The quantum beats technique was also used by Anishchik *et al.*<sup>26</sup> to compare the tracks of X-rays and fast electrons



**Figure 11.** The ratio  $I_{3600}/I_{170}$  of fluorescence intensities at 3600 G and 170 G for 0.12 M diphenylsulfide- $d_{10}$  and  $10^{-3}$  M  $p$ -terphenyl- $d_{14}$  solution in *cis*-decalin. A higher ionization density in the tracks of slow secondary electrons under X-ray irradiation causes a decrease in oscillation amplitude compared to fast electrons.

(Figure 11). As expected, the X-rays show much lower oscillation component which corresponds to a higher track density for the secondary X-ray electrons. The measured fraction of singlet correlated pairs for X-rays is by a factor of two smaller than that for fast electrons.

### Conclusion

Finally, it might be noted that at the present time the main experimental and theoretical approaches are worked out and some trends of the application of this technique are assigned. These include the determination of the ESR spectra parameters of short-lived radical pairs, the study of fast reactions, involving these pairs, and the estimation of the fraction of spin-correlated pairs.

The main advantage of the method in studying radical ion pairs, recombining with fluorescence, is its high sensitivity and time resolution. Because of luminescence recording, the quantum beats technique, so as the OD ESR method, allows these pairs to be studied at stationary concentrations up to 100 particles per sample which is by many orders of magnitude lower than the sensitivity limit of the conventional ESR method. The advantage of quantum beats technique over the OD ESR method is its higher (more than order of magnitude) time resolution. In OD ESR it is limited by the time of electron spin flip around a microwave magnetic field of the ESR spectrometer (to several Gauss) whereas in the case of quantum beats, this limit is determined by hyperfine fields (usually, tens of Gauss) or by the difference in radical  $g$ -factors. Therefore, in the case of ESR technique, the lifetime limitation amounts to tens of nanoseconds, whereas the quantum beats method allows it to be extended to nanoseconds. Moreover, the analysis of phase shifts makes it possible to get information about precursors (the primary radical pairs) with shorter lifetimes because the available equipment

allows one to determine the shifts to within fractions of a nanosecond.

The future development and application of the method will depend on the range of systems and problems that are now only put forward but not exhausted. The method is sure to be used for obtaining spectroscopic information about radical ions that were not investigated in liquid solutions by the ESR method due to their short lifetime. They can include alkane radical cations, radical anions of halogen-containing compounds, radical ions of organoelement compounds, etc. The use of phase shifts for measuring rate constants of very fast reactions, particularly, of the reactions of highly mobile solvent holes and quasifree electrons is under development. Owing to its universality, the quantum beats method can be widely used for determining a fraction of spin-correlated pairs and for studying the influence of various factors on the fraction of geminate recombination of pairs in the tracks of ionizing particles. At the present time, a great body of theoretical papers exceeds that of reliable experimental data. The method offers interesting and new possibilities for determining the relaxation times of short-lived radical particles. This information is actually unavailable in the literature although it is highly needed for interpreting experimental results for spin polarization and magnetic field effects in radical reactions.

The obvious limitation of the above studies is the necessity of selecting radical ion pairs with simple ESR spectra. Actually, this limitation is caused by insufficient time resolution determined by both the apparatus function of the setup and the non zero fluorescence time of luminophor. Improving resolution, we could get spectral information about the systems with a more complex set of hyperfine couplings. Therefore, to develop further the recording technique is an urgent problem. Certain success can be gained however using the available equipment by choosing luminophors with a shorter fluorescence time.

The quantum beats technique has been used to study only radical ion pairs, produced by ionizing radiation. Probably, it can be extended to the radical ion pairs, resulting from photoionization in solutions. The interpretation of results in this case is likely to be more simple due to the use of monochromatic sources of ionization and the absence of the effect of pair cross-recombination typical of the ionizing track. At the same time, the mechanisms of pair formation under photoionization are insufficiently studied and the use of quantum beats method can give additional information about these primary events.

Compared to radical ion pairs whose recombination is followed by fluorescence, the approaches to the observation of quantum beats in the recombination of uncharged radicals are not obvious. The use of other methods of detection, *e.g.* optical absorption, causes substantial losses in sensitivity. A real candidate for such studies could be the radical pairs in micelles which have rather long lifetimes. However, there is another problem related to spin exchange between pair partners which destroys spin coherence.<sup>27</sup> Note that the spin exchange between partners can lead to the appearance of



quantum beats in its recombination if the exchange integral does not change with time or is averaged by fast motions.<sup>28</sup> As has been shown by Buchachenko and Berdinsky,<sup>29</sup> in these conditions the beats can be also caused by exchange interaction with the third paramagnetic particle. These theoretical predictions have not been realized experimentally. Another type of quantum beats, observed experimentally but omitted in this review, are the beats induced by resonance microwave radiation.<sup>30-33</sup> The range of the applications of this phenomenon for studying spin-correlated radical pairs is to be determined.

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