Quantum beats in recombination of spin-correlated radical ion pairs with equivalent protons

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Abstract

Quantum beats caused by the hyperfine coupling (hfc) with magnetically equivalent protons were observed in the recombination fluorescence of the singlet-correlated pairs of secondary radical ions generated in cyclohexane solutions by ionizing radiation. In agreement with theoretical predictions, the ratio $I_H(t)/I_0(t)$ of fluorescence decay kinetics in high and zero magnetic fields showed narrow peaks for the radical cations with an even number of the equivalent protons. To generate radical pairs, p-terphenyl-d_{14} was used as an electron acceptor while the solvent holes were trapped by octamethyl-1,4-cyclohexadiene, tetramethylethylene, 9,10-octalin, cis-decalin, hexamethylbenzene, durene, p-diethylbenzene, p-xylene, or benzene. When diisopropylamine was used as a hole acceptor, a trough was observed instead of the strongest peak. The position of the strongest peak (trough) is determined by the value of hfc constant only and is independent of the number of protons. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Radical pairs arising in solution upon dissociation of molecules under heat, light or ionizing radiation are usually formed in a spin-correlated (singlet or triplet) state. These states are not eigenstates, because hyperfine coupling (hfc) and the g-factor difference in the radical pair result in a mixing of singlet and triplet states. Therefore, the spin-correlated pairs undergo dynamic transitions (quantum beats) between singlet and triplet states [1,2] which lead to a modulation of the yield of their recombination product in a given spin state [3–7].

The most convenient pairs for observing quantum beats are the radical ion pairs arising from radiolysis of liquid alkanes with additions of acceptors of electrons and solvent radical cations (holes). A considerable proportion of these pairs is formed in the singlet-correlated state and undergoes geminate recombination on the nanosecond time scale [8]. The pairs recombining in the singlet state produce singlet-excited molecules, which can be monitored by time-resolved fluorescence methods.

After a pulsed generation of radical ion pairs, the oscillating component of fluorescence is observed against the background of a smoothly decaying curve, which describes the kinetics of

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geminate pair recombination. This background may be easily excluded if hfc is negligible and the beats are determined by a difference in the *g*-factors of radical partners. To this end, the fluorescence decay curve in a high magnetic field is divided by the reference curve obtained in zero or weak magnetic fields [5]. This approach is assumed to fail for hfc-induced beats, because in zero or weak magnetic fields, hfc gives a more complex pattern of oscillations than in high fields. We have found, however, that for pairs with magnetically equivalent nuclei, this method also leads to a simple pattern of oscillations allowing straightforward qualitative interpretation and a simple quantitative treatment.

2. Theoretical background and model calculations

Let us consider an ensemble of identical radical ion pairs instantaneously formed in a non-polar solvent at $t = 0$, the fraction of singlet correlated pairs being equal to θ. Assuming that the singlet and triplet pairs recombine by the same kinetic law and the recombination fluorescence is instantaneous, the observed fluorescence decay is

$$I(t) \propto F(t)\left[\theta\rho_{ss}(t) + \tfrac{1}{4}(1-\theta)\right], \qquad (1)$$

where $F(t)$ is the rate of pair recombination, and $\rho_{ss}(t)$ is the singlet state population of the singlet-born spin-correlated pair. The population is determined both by dynamic spin evolution and spin relaxation, and depends on the strength of the applied magnetic field. The term in the square brackets takes into account the contribution of the singlet component of spin-uncorrelated pairs to fluorescence with the assumption of the same recombination kinetics for spin correlated and uncorrelated pairs [9]. As mentioned above, the unknown function $F(t)$ is excluded by taking the ratio,

$$\frac{I_H(t)}{I_0(t)} = \frac{\theta\rho_{ss}^H(t) + \tfrac{1}{4}(1-\theta)}{\theta\rho_{ss}^0(t) + \tfrac{1}{4}(1-\theta)}, \qquad (2)$$

where subscript and superscript H or 0 refer to high or zero magnetic fields, respectively.

Let us consider radical pairs in which one of the radicals has no hfc and the other has isotropic hfc with equivalent protons, their *g*-factors being equal. Assuming that the electron relaxation times are independent of the nuclear spin projections, the expression for the population of the singlet state of the spin-correlated pair in high magnetic field ($H \gg a$) has the following form [10]:

$$\rho_{ss}^H(t) = \frac{1}{4} + \frac{1}{4}e^{-t/T_1} + \frac{1}{2}e^{-t/T_2}\left[\cos\left(\frac{at}{2}\right)\right]^n. \qquad (3)$$

Here, n is the number of magnetically equivalent protons (or other spin-1/2 nuclei), a is an hfc constant given in angular frequency units, T_1 and T_2 are the longitudinal and transverse relaxation times. The parameters T_1 and T_2 are harmonic average $T^{-1} = (T_a)^{-1} + (T_c)^{-1}$ of relaxation times T_a and T_c for isolated radical anion and cation, respectively [11].

To derive a similar equation for a zero magnetic field, we use the condition of conservation of the total nuclear spin for equivalent nuclei [1]. Thus, the equation for the singlet state population of a pair involving a single magnetic nucleus with spin I [1]

$$\rho_{ss}^0(t) = 1 - 4\frac{I(I+1)}{(2I+1)^2}\left[\sin\left(\frac{(2I+1)at}{4}\right)\right]^2 \qquad (4)$$

should be averaged over the values I of total spin of n equivalent protons determined by probabilities,

$$P_I = \frac{(2I+1)^2}{2^n(n+1)}C_{(n/2)-I}^{n+1}, \qquad (5)$$

where $C_{(n/2)-I}^{n+1}$ is a binomial coefficient. Summing up Eq. (4) weighted by coefficients (5) and taking into account paramagnetic relaxation, we obtain Eq. (6) for the singlet population of the pair with n equivalent protons in zero magnetic field:

$$\rho_{ss}^0(t) = \frac{1}{4} + \frac{1}{4}e^{-t/T_0}\left\{\frac{n+3}{n+1} + \frac{2n(n+2)}{n+1}\right.$$
$$\left. \times \left[\cos\left(\frac{at}{2}\right)\right]^{n+1} - 2n\left[\cos\left(\frac{at}{2}\right)\right]^{n-1}\right\}. \qquad (6)$$

The factor describing paramagnetic relaxation in zero magnetic field with characteristic time T_0 is

introduced into Eq. (6) so that, at longer delay times, the population tends to 1/4.

It follows from Eqs. (3) and (6) that expressions for spin populations contain the terms oscillating with multiple frequencies. The simple relationship between these oscillation frequencies give the well-defined characteristic features of the $I_H(t)/I_0(t)$ curves. Fig. 1 illustrates the results of calculations for the pairs with an even number of equivalent protons neglecting spin relaxation. The existence of multiple frequencies gives a simple oscillation pattern for ρ_{ss}^H and ρ_{ss}^0 with a period $4\pi/a$. In this case, all the high-field harmonics with frequencies $a, 2a, 3a, \ldots, na$ have the maximum at time $\tau = 2\pi/a$, while the zero-field harmonics with frequencies $a/2, 3a/2, 5a/2, \ldots, (n+1)a/2$ have the minimum at this time. As a result, the ρ_{ss}^H/ρ_{ss}^0 ratio

has a strong peak located at $\tau = 2\pi/a$ whose position is determined by the hfc constant but is independent of the number of equivalent protons. The larger the number of protons, the higher is the peak amplitude and the smaller is the peak width. At shorter times, a weaker peak is seen. Its relative intensity and the time of appearance decrease with an increasing number of equivalent protons. According to simulations, in the limit of large n, its position and shape are described by Schulten's quasi-classical model [12]. Another weak peak is "symmetric" about the strongest one (Fig. 1).

When the number of equivalent protons is odd, the pattern of beats displays similar features, however at time $\tau = 2\pi/a$, a trough occurs instead of the strong peak (Fig. 2).

In the presence of paramagnetic relaxation, there is damping of beats. In addition, a background is observed (see simulations in Section 4). Similar changes may result from chemical
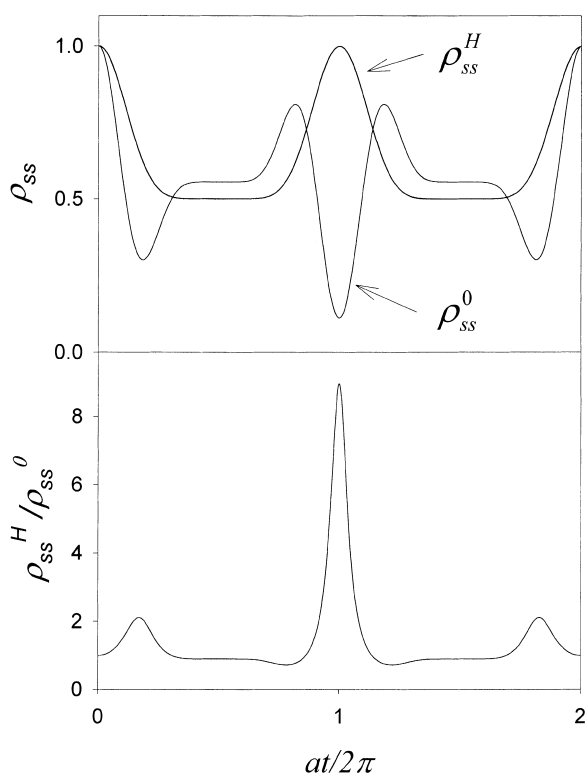

Fig. 1. The calculated time dependence of singlet state population in high and zero magnetic fields (top) and their ratio (bottom) for a singlet born radical pair with eight equivalent protons in one of the radicals.
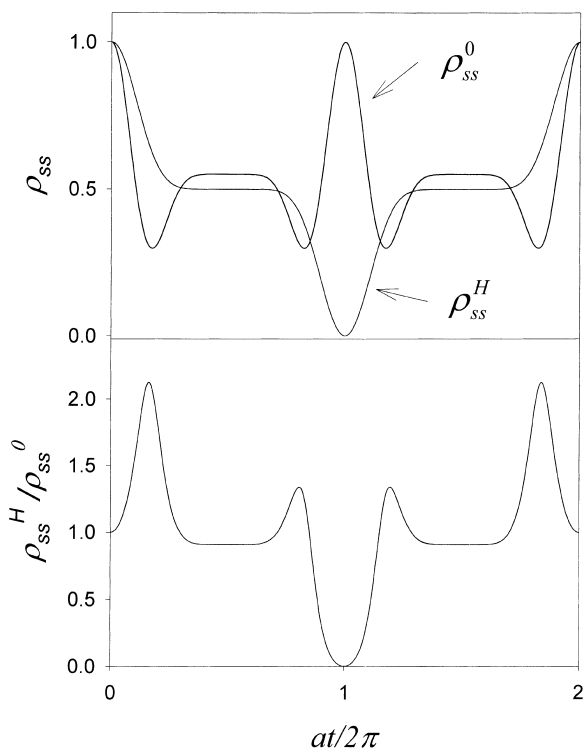

Fig. 2. The same as in Fig. 1, but for nine equivalent protons.

transformation of radical ions, e.g. from formation of dimer radical cations, which is typical for aromatic and olefin radical cations [13]. It is noteworthy that the relaxation (reaction) does not actually shift the main peak (trough) whose position is determined by the hfc constant only.

Let us discuss the case of an arbitrary number of magnetic nuclei with different spins but with accidentally coinciding hfc constants. For example, consider a radical cation that has identical hfc constants for three protons and a ^{14}N ($I = 1$) atom, as in (diisopropylamine)$^{+\bullet}$ [14] (see Section 4). Eq. (3) for $\rho_{ss}(t)$ may be generalized for any number of nonequivalent magnetic nuclei with arbitrary spin [10]. In this particular case, we obtain

$$\rho_{ss}^H(t) = \frac{1}{4} + \frac{1}{4}e^{-t/T_1} + \frac{1}{6}e^{-t/T_2}$$
$$\times (1 + 2\cos at)\left[\cos\left(\frac{at}{2}\right)\right]^3. \qquad (7)$$

In zero magnetic field, only a numerical solution for describing spin dynamics is possible in general case. However, for magnetic nuclei with different spins but identical hfc constants, an analytical solution may be obtained by the method used for deriving Eq. (6): it is necessary to determine the weight coefficients of the states with different values of the total nuclear spin and to find the weighted average of Eq. (4). A lengthy calculation yield

$$\rho_{ss}^0(t) = \tfrac{1}{4} + \tfrac{1}{576}e^{-t/T_0}[173 + 54\cos(at)$$
$$+ 135\cos(2at) + 70\cos(3at)]. \qquad (8)$$

Simulation of quantum beats using Eq. (8) reveals the same oscillation behavior as for the pair with five equivalent protons but with minor differences in the form of peaks and troughs. This similarity is of little surprise because in both cases, the total nuclear spin has the same set of values.

3. Experimental

The fluorescence kinetics were recorded as described in Ref. [3]. The reaction mixture was irradiated either by X-ray pulses emitted by molybdenum target with duration of about 2 ns

fwhm or by fast electrons $E = 0.54$ and 2.25 MeV from a ^{90}Sr–^{90}Y source with an activity of about 5 µCi. The time resolutions of the setups were 3 and 1 ns.

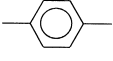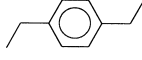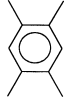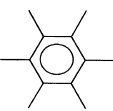Cyclohexane (Fluka) was used as a solvent. It was treated with aqueous $KMnO_4$, stirred with concentrated H_2SO_4, washed with water, dried over Na mirror, distilled and passed through a column filled with alumina containing 10 wt.% of $AgNO_3$, and then stored over metallic cesium. Octamethyl-1,4-cyclohexadiene was obtained from Novosibirsk Institute of Organic Chemistry. Other chemicals were obtained from Aldrich and used as supplied. Cyclohexane solutions containing 3×10^{-3}–10^{-2} M of hole acceptors and 10^{-4}–10^{-3} M of p-terphenyl-d_{14} (PTP-d_{14}) were degassed by freeze–pump–thaw cycles and sealed in quartz cuvettes. The measurements were performed at 20°C.

4. Results and discussion

Various hole acceptors (Table 1), whose radical cations have an even number of equivalent protons, have been chosen to test and illustrate the proposed method of observing hfc beats. Cyclohexane was used as a solvent since the mobility of cyclohexane holes substantially exceeds that of molecular ions [15] thus providing fast formation of acceptor radical cations. The acceptor concentration was chosen to make the time of hole capture comparable with or shorter than the time resolution of our fluorimeters. For 3×10^{-3} M of added acceptor the trapping time is about 1 ns for typical rate constant 3×10^{11} $M^{-1}s^{-1}$ of mobile hole trapping in cyclohexane [15,16]. The actual time delay in the formation of acceptor radical cation is even shorter than 1 ns since the cyclohexane holes are very short lived due to fast geminate recombination. Therefore, the approximation of instantaneous formation of the radical cations may be used in simulations.

The PTP-d_{14} radical anion, whose hfc constants are small and make negligible contribution to the spin evolution, served as geminate partner. Since PTP can trap both electrons and holes, its concentration was in all cases much lower than that of

Table 1
Calculated and observed positions of the main peaks in quantum beats

Acceptor	n[a]	A (G)	τ (ns)	
			calculated[b]	observed
(cis) [decahydronaphthalene structure]	4	50 [20]	7.1	8
[octahydronaphthalene structure]	8	24 [21]	14.9	15.1
[tetramethylethylene structure]	12	17.6 [22]	21.6	22
[octamethyl-1,4-cyclohexadiene structure]	12	–	–	54
[benzene structure]	6	4.4 [23]	81	–
[p-xylene structure]	6	16.7 [24]	21.3	20.5
[diethylbenzene structure]	4	–	–	21.4
[tetramethylbenzene structure]	12	10.8 [3]	33.1	33.5
[hexamethylbenzene structure]	18	6.5 [25]	54.9	56

[a] Number of equivalent protons.
[b] $\tau_{calc} = 2\pi/\gamma A$.

hole acceptors. At the lowest concentration of PTP-d_{14} used, 10^{-4} M, the rate of electron trapping is not too fast. For a typical rate constant, 3×10^{12} $M^{-1} s^{-1}$, of electron trapping by aromatic molecules in cyclohexane [17], the electron trapping time is about 3 ns. This time delay does not disturb the spin evolution of the radical ion pair since the ESR spectra of both PTP-d_{14} radical anion and electron are rather narrow with the nearly identical g-factors. Again, the actual time of radical anion formation is shortened by very fast geminate recombination of the electrons.

Fig. 3 shows experimental curves for non-aromatic hole acceptors under irradiation by fast electrons. X-ray irradiation gives similar results, but a smaller amplitude of the magnetic field effect. In all of these cases, a peak at $\tau = 2\pi/a$ is observed. Its position corresponds to that calculated from the known hfc constants of the radical cation (Table 1). The first peak is much weaker in all of the systems studied except for octamethyl-1,4-cyclohexadiene. For 9,10-octalin, the third and the fourth peaks can also be observed. An additional feature of unknown origin is observed at $t \sim 15$ ns when *cis*-decalin is used as a hole acceptor. The
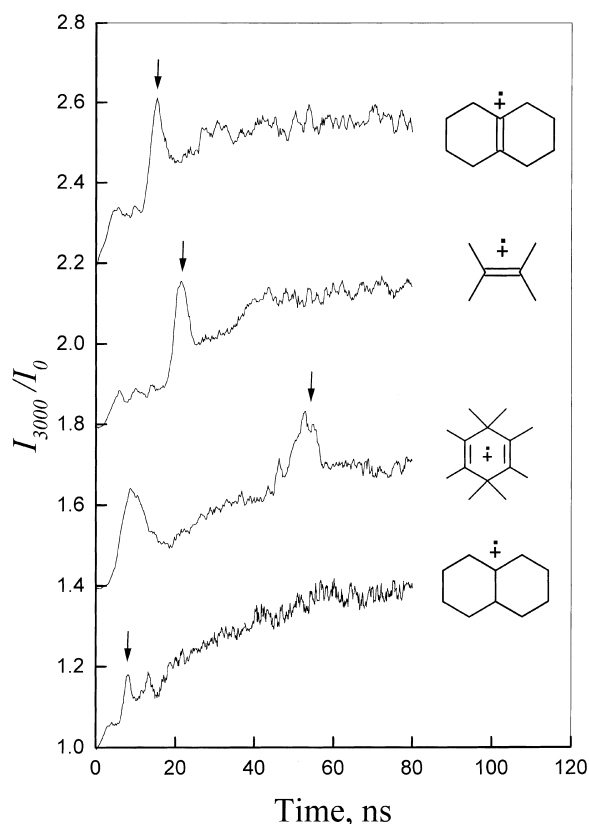

Fig. 3. Time dependence of the ratio of fluorescence intensities at 3000 G and in zero magnetic field for cyclohexane solutions (top to bottom): 10^{-4} M PTP-d_{14} and 6×10^{-3} M 9,10-octalin; 10^{-4} M PTP-d_{14} and 3×10^{-3} M tetramethylethylene; 10^{-4} M PTP-d_{14} and 3×10^{-3} M octamethyl-1,4-cyclohexadiene; 10^{-3} M PTP-d_{14} and 10^{-2} M *cis*-decalin. The arrows show the positions of the second (main) peak. The curves are shifted vertically by 0.4 units relative to each other for convenience.

shapes of $I_H(t)/I_0(t)$ kinetics indicate considerable effect of paramagnetic relaxation (and/or reaction) on the spin evolution: the smooth baseline grows in and the peak amplitudes decay with time.

Fig. 4 presents the kinetics obtained for substituted benzenes as hole acceptors. In all of these cases, with the exception of benzene itself, the first and second peaks were observed. Their amplitude (as well as the magnetic effect) are much lower than in previously examined systems. This is probably due to fluorescence from the excited PTP-d_{14} formed by energy transfer from the long-lived singlet excited benzenes.

Figs. 5 and 6 exhibit the observed curves for octamethyl-1,4-cyclohexadiene and for 9,10-
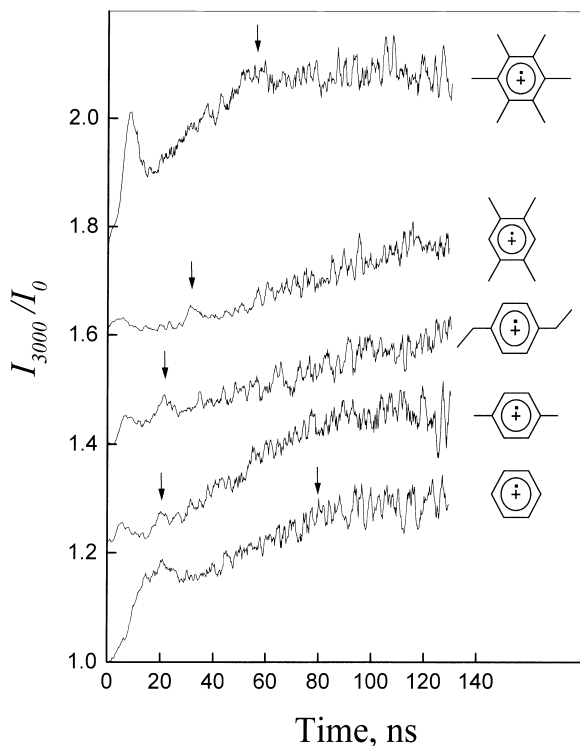

Fig. 5. Time dependence of the ratio of fluorescence intensities in a field 3000 G and in zero field for cyclohexane solutions of 10^{-4} M PTP-d_{14} and 3×10^{-3} M octamethyl-1,4-cyclohexadiene. Smooth curves are simulations with $n = 12$, $A = 6.9$ G, $T_1 = \infty$, $\theta = 0.33$, and $T_2 = T_0 = 25$ ns (—), $T_2 = T_0 = 12.5$ ns (- - -), $T_2 = T_0 = 50$ ns ($\cdots$).

Fig. 4. The same as in Fig. 3 for cyclohexane solutions of 10^{-4} M PTP-d_{14} and 3×10^{-3} M of hole acceptors (from the top to bottom): hexamethylbenzene; durene; p-diethylbenzene; p-xylene; benzene. The arrows denote positions of the second (main) peak. For benzene, the expected position is marked. The curves are shifted vertically by 0.2 units relative to each other for convenience.
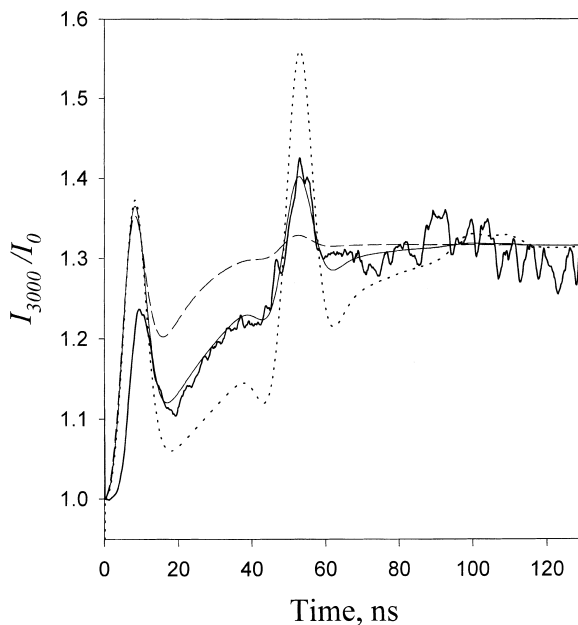
octalin and simulation of the experimental results. In these simulations, Eq. (1) was convoluted with the exponential fluorescence decay kinetics under the assumption that $F(t)$ decay slower than fluorescence ($\tau_{fl} = 1.2$ ns for PTP-d_{14} [6]). This approximation is not valid at short times (a few nanoseconds), when $F(t)$ decays very steeply. The hfc constants for (9,10-octalin)$^{+\bullet}$ was taken from the literature while that for (octamethyl-1,4-cyclohexadiene)$^{+\bullet}$ was estimated from the position of the second peak. The hfc constants in PTP-d_{14} radical anion and smaller hfc couplings in the radical cations were ignored. The fraction of spin-correlated radical ion pairs was determined from the $I_H(t)/I_0(t)$ ratio at $t > 50$ ns. The relaxation time T_1 that determines the long-term decay kinetics was $\geqslant 500$ ns. The two remaining free parameters T_0 and T_2 were assumed to be equal. This assumption corresponds to spin relaxation induced by degenerate electron exchange between a hole acceptor molecule and its radical cation with a rate
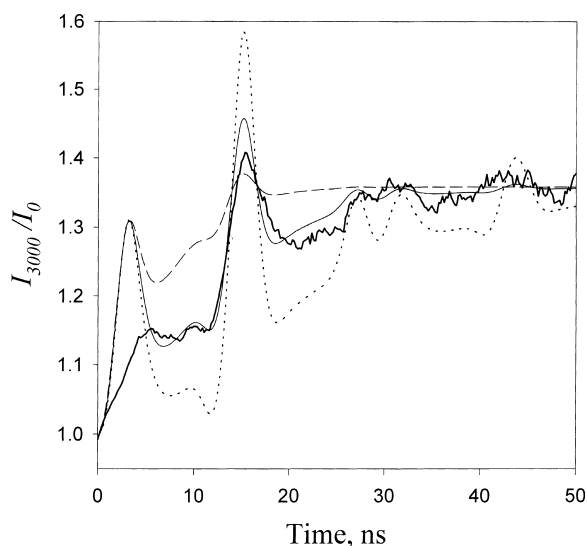
Fig. 6. The same as in Fig. 5 for cyclohexane solutions of 10^{-4} M PTP-d_{14} and 6×10^{-3} M of 9,10-octalin. Smooth curves are simulations with $n = 8$, $A = 24.9$ G, $T_1 = \infty$, $\theta = 0.36$, and $T_2 = T_0 = 9$ ns (—), $T_2 = T_0 = 4.5$ ns (- - -), $T_2 = T_0 = 18$ ns ($\cdots$).

that is much lower than the EPR spectrum width of the radical cation [18].

In our simulations, we ignored the possible contribution of dimer radical cations to the quantum beats dumping. Pulse radiolysis experiments [13] show that diene and olefin radical cations react in solution with their parent molecules with the rates close to the diffusion-controlled ones and hence dimerization should be taken into account. On the other hand, OD ESR studies [19] demonstrate that in similar systems the degenerate electron exchange is several times faster than the dimerization and therefore makes a predominant contribution. In any event one should consider $T_2 = T_0$ as an effective parameter, which may contain a contribution from dimerization or other reactions.

For octamethyl-1,4-cyclohexadiene, the simulations reproduced well the main features of the experimental kinetics. The optimum $T_2 = T_0 = 25$ ns (Fig. 5, solid curve) corresponds to the rate constant 1.3×10^{10} M^{-1} s^{-1} for the degenerate electron exchange, which is close to that expected for diffusion controlled reaction of cations in

cyclohexane. One can see, however, that the first peak is about two times lower than in our simulations, and its maximum is slightly shifted to longer times. The twofold decrease or increase of $T_2 = T_0$ (Fig. 5) does not change substantially the amplitude of the first peak, while the disagreement for other regions becomes obvious. The independent variation of T_0 and T_2 does not noticeably improve the fitting quality. We believe that the decrease in the amplitude of the first peak is caused by the prompt luminescence, which is independent of the external magnetic field. Such a luminescence within the range of a few nanoseconds may arise, e.g., from the PTP-d_{14} molecules excited by Cherenkov light or energy transfer from the excited solvent molecules. Recombination of radical ion pairs with small hfc constants, like e$^-$/(PTP-d_{14})$^{+\bullet}$ or (PTP-d_{14})$^{-\bullet}$/(PTP-d_{14})$^{+\bullet}$ may result in a similar effect.

For 9,10-octalin, the simulation (Fig. 6, solid curve) is less satisfactory. The first peak is shifted to longer times and is much weaker than calculated; the amplitude of the main (second) peak is also overestimated. However, its time position, as well as the positions of weaker peaks at longer times, are in agreement with the simulation. Obviously, the disturbing effect of the prompt luminescence is more significant for (9,10-octalin)$^{+\bullet}$, where peaks appear at earlier times. The estimates of the relaxation rates are less reliable for this system. The solid curve that corresponds to $T_2 = T_0 = 9$ ns (Fig. 6) seems to be optimum.

The range of acceptors with an odd number of equivalent protons is much more limited. Therefore, diisopropylamine (Fig. 7) has been taken as a hole acceptor to illustrate the features of quantum beats in spin systems with a half-integer total nuclear spin (a trough instead of a peak). For the (diisopropylamine)$^{+\bullet}$ the hfc constants with three protons, $A(2H) = 18$ G, $A(H) = 21.5$ G, and a nitrogen nucleus, $A(^{14}N) = 18.7$ G [14] are close. As shown in Section 2, the quantum beats in this case are similar to those in the system with an odd number of equivalent protons. Just as in Figs. 4 and 5, the first peak, as compared with the simulated one, displays lower intensity. The amplitude of the second peak is close to the simulated one with $T_2 = T_0 = 9.5$ ns, whereas the
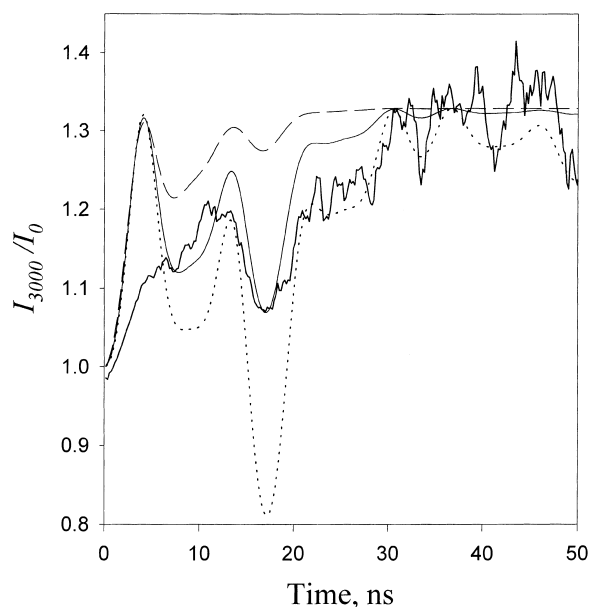
Fig. 7. The same as in Fig. 5 for cyclohexane solutions of 10^{-3} M PTP-d_{14} and 3×10^{-3} M diisopropylamine. Smooth curves are simulation with $A(3H) = A(^{14}N) = 21$ G, $\theta = 0.33$, $T_1 = \infty$, and $T_2 = T_0 = 9.5$ ns (—), $T_2 = T_0 = 4.75$ ns (- - -), $T_2 = T_0 = 19$ ns ($\cdots$).

background growth at $t \geqslant 20$ ns is better described when $T_2 = T_0$ is approximately twice higher. The additional problem with simulation may be the result of neglecting the hfc constants difference.

Table 1 summarizes the experimental and theoretical time delay of the second peak. The latter were estimated from the known hfc constant in the limit of $\tau_{fl} = 0$ and fast hole trapping. Experimental and calculated times are in fair agreement, within the experimental error (± 1 ns). In most cases, the second peak was observed at little longer delay times than expected. These systematic deviations could be accounted for by the finite rate of hole trapping and fluorescence time.

Thus, the method proposed can be used to detect quantum beats in recombination of spin-correlated radical ion pairs with magnetically equivalent protons. The position of the main (second) peak is determined by the hfc constant on the protons and does not depend on the number of these protons. The method gives the possibility to

determine the hfc constants and relaxation times for radical ion pairs with lifetimes of up to several nanoseconds.

Acknowledgements

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