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Quantum beats in the recombination fluorescence of radical ion pairs caused by the hyperfine coupling in radical anions

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Abstract

The ratios of the radiofluorescence decay curves for *n*-decane solutions of 1,2,3,4-tetraphenylcyclopenta-1,3-diene and its silicon and germanium analogs (siloles and germoles) in high and zero magnetic fields have an oscillating component caused by singlet–triplet evolution of the pair S^+/A^-, where S^+ is the solvent hole and A^- is the radical anion of the acceptor (a compound added). It is shown that the beats are due to the hyperfine couplings (hfc) with either the protons of CH_2, SiH_2 and GeH_2 moieties or chlorine atoms in the $GeCl_2$ and GeClMe moieties of radical anions. The hfc constants in the anions and spin relaxation times of radical ion pairs were obtained by fitting the experimental curves.

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1. Introduction

The singlet-correlated radical ion pairs are known to be formed upon radiolysis of liquid hydrocarbons containing acceptors of electrons and holes [1]. The majority of pairs recombine geminately within a nanosecond time domain. Before recombination, the pairs undergo quantum oscillations between singlet and triplet states [1,2], resulting in modulation of the yield of their recombination product in a particular spin state. In a high magnetic field, the frequencies of beats are defined by the differences between the spin resonance frequencies of the partners of radical ion pair that can be caused by the difference in their *g* factors and hyperfine interactions.

The well-resolved oscillations of the recombination product yields in the external magnetic field were detected only in the simplest cases where the beats were caused either by the difference in *g* factors of radical ions [3] or by hyperfine couplings (hfc) with equivalent protons in radical cations [4]. The beats were recorded by fluorescence, accompanying the recombination of radical ion pairs from the singlet state.

In the case of Δg beats, the oscillating component of the fluorescence decay curve is easily re-

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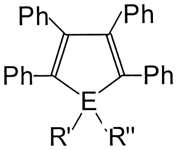
vealed through dividing a high field curve by a reference curve obtained in either a zero or weak magnetic field where the oscillations are absent. This approach allowed the use of the Δg beats to determine both the rate constants of the capture of solvent holes by acceptors [5] and the fraction of spin-correlated radical ion pairs in the tracks of fast electrons [6].

Unlike Δg beats, for the hfc beats it is impossible to obtain a smooth reference curve. In zero or weak external magnetic fields the hfc results in a complicated pattern of oscillations, which can be analytically described for the systems with simple hyperfine structure only [2]. This hampers the separation and the analysis of the oscillating component in fluorescence decay. In the case of hfc beats from radical cations another problem arises related to the contradictory requirement on the concentration of a positive charge acceptor. On the one hand, this concentration should be high enough to provide fast formation of the desired radical cation. On the other hand, at a high acceptor concentration the oscillations are destroyed because of spin dephasing due to ion–molecular charge transfer.

We were able to overcome these difficulties [7] by choosing 1,2,3,4-tetraphenylcyclopenta-1,3-diene (**1**) and its silicon- and germanium-containing analogs — the phenyl derivatives of silole (**2**), germole (**3**), dichlorogermole (**4**) and chloromethylgermole (**5**) — as electron acceptors for detection of the hfc beats.



E=C, R'=R"=H (**1**)
Si, R'=R"=H (**2**)
Ge, R'=R"=H (**3**)
Ge, R'= R"=Cl (**4**)
Ge,R'=CH_3,R"=Cl (**5**)

In the radical anion of parent compound **1**, the hfc constant with the two equivalent protons of the CH_2 group is 25.3 G whereas the couplings with other protons are small [8]. Therefore one can expect that the hfc beats in these systems will have a simple pattern in both high and zero magnetic fields and the oscillations in the curve obtained by division of fluorescence decay kinetics in high field by that in zero field will be described by a simple expression. Moreover, compared to radical cations, a high rate of radical anion generation can be easily achieved due to a high diffusion mobility of the primary free electrons. This allows us to detect the well-resolved beats and to obtain the hfc constants of the short-lived radical anions of organosilicon and organogermanium compounds **2**–**5**. The rates of spin relaxation in the radical ion pairs were estimated from the damping of the beats.

2. Experimental

The fluorescence decay kinetics were measured by single photon counting on an X-ray nanosecond fluorometer [9]. The solution was irradiated with X-ray pulses from a molybdenum target of ca. 2 ns duration on a base. The X-ray pulse was generated by an electron gun triggered by a signal (60–80 kHz) of an external generator. This signal was also the start signal for a time-amplitude converter of the registration system. The stop signal came from a photomultiplier tube registering the fluorescence of the irradiated sample. The width of instrument function of the apparatus was ca. 3 ns. The accuracy of the zero time moment, which was identified with the center of the X-ray pulse, was ± 0.5 ns. The zero magnetic field was set to within ± 1 G. All luminophores used had a fluorescence lifetime shorter than 1 ns. The fluorescence was recorded without any light filters.

Tetraphenylcyclopentadiene **1** [10], silole **2** [11], germole **3** [12] and dichlorogermole **4** [13] were synthesized according to the published methods. Chloromethylgermole **5** was obtained by the reaction of the dilithium salt of 1,2,3,4-tetraphenylbutadiene with $MeGeCl_3$ as described in Ref. [13] (yield 45%, m.p. 138°C). The solvent *n*-decane was treated with $KMnO_4$, shaken with concentrated H_2SO_4, washed with water and dried over Al_2O_3.

The samples of 10^{-3} M acceptors solution in *n*-decane were degassed by repeated freeze–pump–

thaw cycles and sealed in thin-walled quartz cuvettes. All experiments were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the ratios $I_H(t)/I_0(t)$ of the fluorescence kinetics in the external magnetic fields. $H=$ 3000 G and zero magnetic fields for the 10^{-3} M solutions of **1**–**3** in *n*-decane. The clearly defined oscillations of a similar shape but with different periods were detected for all compounds. A relatively high intensity of the second peak, despite the damping of oscillations, is the characteristic feature of the curves. One can note that the first peak appears somewhat earlier than it could be expected for the oscillations with a single frequency. The data on the solutions of germoles **4** and **5** are presented in Fig. 2. Here the beats are less clearly defined and the second peak is rather weak. The characteristic feature of all curves is the damping of the magnetic field effect with a typical time of ca. 100 ns.

Measurements in the range of magnetic fields from 100 to 3000 G for compounds **1** and **3** have shown that the magnetic field strength variation does not affect the period of the beats. Thus the beats are caused by hyperfine couplings and the difference in the *g* factors of radical ions is not essential.

At an acceptor concentration of 10^{-3} M, the capture of the *n*-decane radical cation (hole) which is diffusion controlled [14], needs approximately 100 ns, while the electron capture requires 1 ns (capture rate constant is $\sim 10^{12}$ M^{-1} s^{-1} [14]). Therefore one can assume that under our conditions the main contribution to the recombined fluorescence is given by the S^+/A^- pairs and the contribution of the A^+/A^- pairs is not important (S is the *n*-decane molecule; A is the acceptor molecule). The shape of the oscillations is retained when the concentrations of compounds **1** and **3** were decreased to 10^{-4} M. This is an additional argument in support of the conclusion.

Since the periods and shapes of the oscillations for the systems studied are different, they should be caused by hfc in radical anions rather than in *n*-decane radical cation. In the case of radical anion $(\mathbf{1})^-$, the beats are evidently caused by the dominant splitting of the protons of the CH_2 group [8]. One can reasonably suggest that in the other compounds studied, the beats are caused by hfc in similar fragments. Additional qualitative arguments in support of this

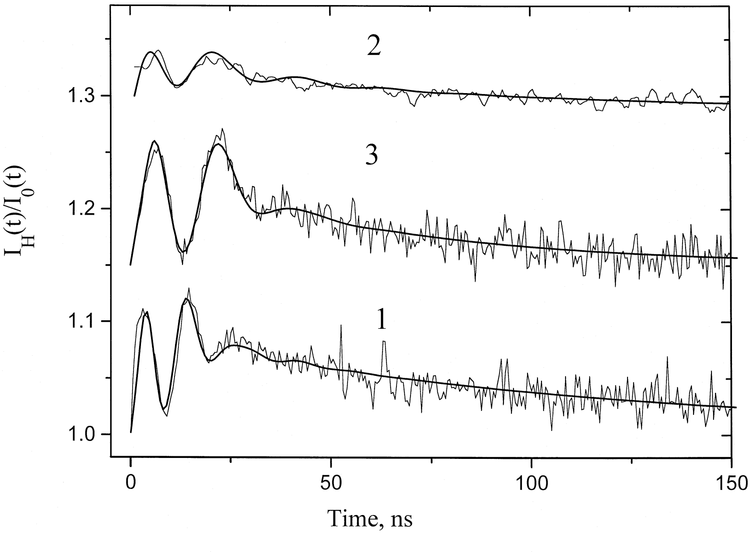


Fig. 1. Ratio of fluorescence decay curves in high (3000 G for **1** and **2** and 1000 G for **3**) and zero magnetic fields. The curves are vertically spaced 0.15 apart for convenience.

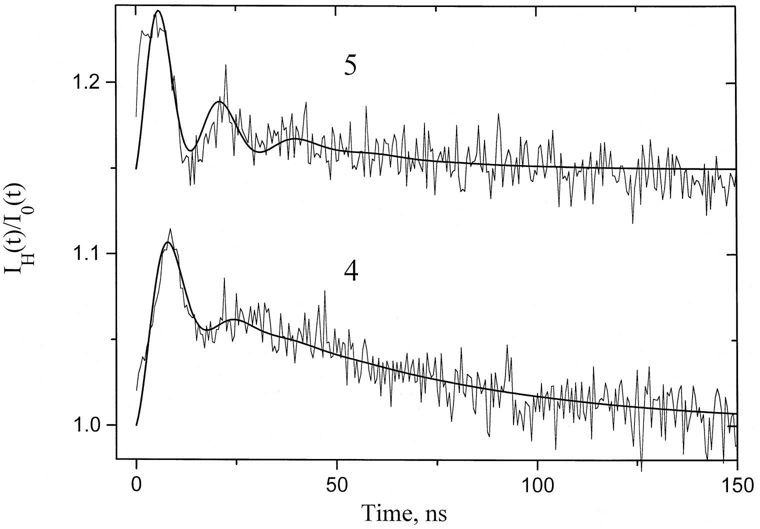


Fig. 2. Ratio of the fluorescence decay curves in high ($H = 3000$ G) and zero magnetic fields for **4** and **5**. The curves are vertically spaced 0.15 apart for convenience.

suggestion follow from the consideration of the spin dynamics of a radical ion pair neglecting spin relaxation (Fig. 3). For a radical pair in which one of the partners has no magnetic nuclei and another has a hyperfine coupling with two equivalent protons, the frequency of the singlet–triplet oscillations in a high magnetic field is equal to a and in zero field is equal to $1.5a$, where a is an hfc constant in the units of angular frequency [2]. The calculated ratio of the singlet populations in high and zero magnetic fields (Fig. 3a) has characteristic features which manifest themselves in the experimental curves shown in Fig. 1. The first peak appears slightly earlier than the expected one for harmonic oscillations and its intensity is less than that of the second peak. For the splitting on a chlorine nucleus (each of ^{35}Cl and ^{37}Cl isotopes has spin $3/2$) all the peaks on the spin dynamics curve (Fig. 3b) are equal in intensity. Accordingly, the second peak on the experimental curves (Fig. 2) is less pronounced.

The experimental curves were simulated assuming that (i) radical ions have the same g factors, (ii) in the radical anions of compounds **1**–**3** the hyperfine coupling with only two equivalent protons is essential while in the radical anions of dichlorogermol **4** and chloromethylgermole **5** — only that with chlorine nuclei (the difference in hfc constants for the two isotopes was ignored), (iii) the ESR spectrum of the solvent radical cation (hole) is a homogeneously broadened singlet line. Such a spectrum can result from hole migration over the solvent molecules.

The expression for the probability of finding a singlet-born pair in the singlet state at high magnetic field $W_H(t)$ [1,2] can be generalized using equation (135) in Ref. [15] to take into account electron spin relaxation. For the zero field probability $W_0(t)$ in the case of a number of equivalent nuclei it is possible to divide all the radical pairs into sub-ensembles. Each sub-ensemble is assumed to have a magnetic nucleus with one of the possible values of the total spin of all the equivalent nuclei [2]. The evident condition $W_0(t) \to_{t\to\infty} (1/4)$ was used in the case of zero field. The relaxation rates were assumed to be independent of nuclear spin configuration, both in high and zero magnetic fields.

In terms of these suggestions the probabilities $W_H(t)$ and $W_0(t)$ for a pair of compounds **1**–**3** with EH_2 (E = C, Si Ge) moieties obeys the equations:

$$W_H(t) = \frac{1}{4}\left[1 + e^{-t/T_1} + 2e^{-t/T_2}\cos^2\frac{at}{2}\right] \qquad (1)$$

$$W_0(t) = \frac{1}{4} + \frac{1}{12}e^{-t/T_0}\left[5 + 4\cos\frac{3at}{2}\right] \qquad (2)$$

for high and zero magnetic fields, respectively.

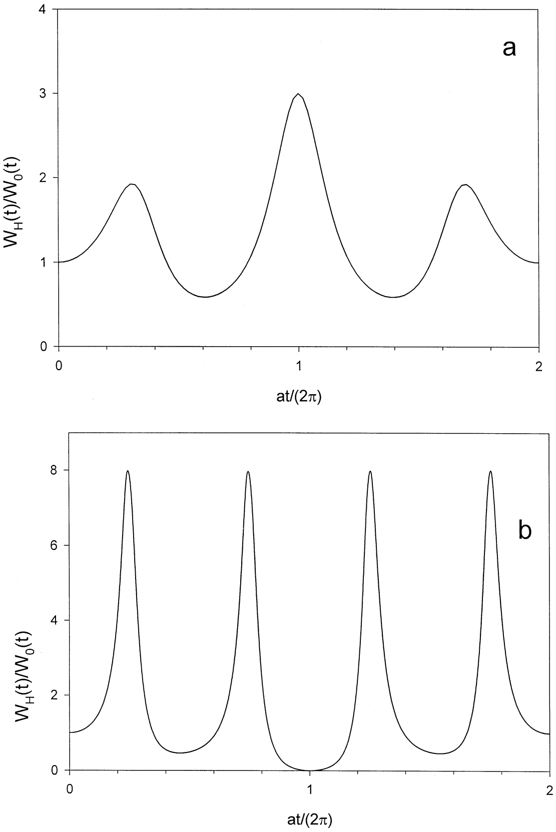


Fig. 3. The ratio of singlet populations in high and in zero magnetic fields for a singlet born pair: (a) for two equivalent nuclei of spin 1/2 for one of the partners; (b) for one nucleus of spin 3/2. The pattern is periodically reproduced since spin relaxation is neglected.

For one nucleus with spin 3/2, the corresponding equations take the forms:

$$W_H(t)=\frac{1}{4}\left[1+\mathrm{e}^{-t/T_1}+2\mathrm{e}^{-t/T_2}\cos\frac{at}{2}\cos(at)\right] \tag{3}$$

$$W_0(t)=\frac{1}{4}+\frac{3}{32}\mathrm{e}^{-t/T_0}[3+5\cos(2at)] \tag{4}$$

and for two equivalent nuclei with spin 3/2, we get

$$W_H(t)=\frac{1}{4}\left[1+\mathrm{e}^{-t/T_1}+2\mathrm{e}^{-t/T_2}\cos^2\frac{at}{2}\cos^2(at)\right] \tag{5}$$

$$W_0(t)=\frac{1}{4}+\frac{1}{420}\mathrm{e}^{-t/T_0}\left[127+35\cos\frac{3at}{2}+63\cos\frac{5at}{2}+90\cos\frac{7at}{2}\right] \tag{6}$$

Here $(T_1)^{-1}$ is the sum of the rates of longitudinal relaxation and, $(T_2)^{-1}$ is the sum of the rates of transverse relaxation of the radical ions in a pair in a high magnetic field, and $(T_0)^{-1}$ is the sum of the rates in zero field.

The experimentally observed kinetics of the fluorescence decay is defined as

$$I(t)\propto F(t)\left[\theta W(t)+\frac{1}{4}(1-\theta)\right] \tag{7}$$

if fluorescence is considered to be instant. In Eq. (7) $F(t)$ is the rate of recombination of geminate pairs and θ is the fraction of spin-correlated pairs. The second term in the brackets takes into account the contribution of the singlet component of non-correlated pairs to the fluorescence. The unknown function $F(t)$ is excluded if we analyze the ratio

$$\frac{I_H(t)}{I_0(t)}=\frac{\theta W_H(t)+\frac{1}{4}(1-\theta)}{\theta W_0(t)+\frac{1}{4}(1-\theta)}\,. \tag{8}$$

This expression was used to simulate the experimental curves. The optimization was carried out over five parameters: a, T_0, T_1, T_2 and θ. The solid lines in Figs. 1 and 2 show the results of simulation according to expression (8) with the optimal parameters, the values of these parameters are given in Table 1. The consideration of weak splitting on the protons of phenyl groups (1.8 G on six protons [8]) has no effect on the simulation results. The introduc-

Table 1
Parameters of simulation of the curves shown in Figs. 1 and 2

Compound	a (G)	T_0 (ns)	T_1 (ns)	T_2 (ns)	θ
1	25.0 ± 0.4	8	110	9	0.23
2	15.6 ± 0.3	10	60	16	0.1
3	15.0 ± 0.3	6	120	17	0.04
4	7.0 ± 1	8	60	9	0.1
5	11.4 ± 1	7	30	12	0.07

tion of non-homogeneous broadening into the spectrum of the hole impairs agreement with experiment.

Note that the different parameters define the different features of the curves and therefore are substantially mutually independent. Thus, the hfc constant *a* defines the distance between the adjacent peaks, the long-time decay of the curve depends on the longitudinal relaxation time T_1, the fraction of spin-correlated pairs mostly determines the peak amplitudes and the short time T_0 provides a fast curve rising at the initial time. Statistics of simulations of various experimental realizations show that the hfc constant is reproduced with the best accuracy (see Table 1) whereas the accuracy of the determination of the other parameters does not exceed several tens of percent. The hfc values obtained were independent of both the acceptor concentration and the strength of the magnetic field. The relaxation time T_1 measured for germole **3** decreased with decreasing magnetic field strength (T_1 is equal to 120, 60, 30 and less then 10 ns at 3000, 1000, 400 and 100 G, respectively).

The hfc constant found for the radical anion **1** coincides within the experimental error with that obtained by ESR spectroscopy in tetrahydrofurane at 203 K [8]. The high value of this constant and small splitting of the protons of the phenyl groups show that the unpaired electron is predominantly localized in the π-system of cyclopentadienyl ring. One can suggest that the radical anions of the silicon and germanium analogs **2**–**5** have a similar structure. A detailed quantum-chemical analysis of the electronic structure of radical anions **1**–**5** along with the additional optically detected ESR spectral data will be published elsewhere [16].

The relaxation times obtained do not exhibit regular dependencies on the structure of the radical anions and their accuracy is not high. Therefore it is difficult to decide which of the partners (the solvent hole or the radical anon) makes the main contribution to the relaxation processes.

The typical value of the fraction of the spin-correlated pairs in *n*-alkanes obtained previously [6] by the methods of quantum beats and time-resolved magnetic effects is 20–25% for X-ray irradiation. This value is substantially higher than those in Table 1 (except for the radical anion of **1**). It is possible that under our conditions other processes, (apart from singlet pair recombination) independent of the external magnetic field, also contribute to luminescence which results in a decrease of the estimated θ value.

4. Conclusions

The results obtained show the possibilities of the method of quantum beats for the determination of hfc constants under conditions where a short lifetime of the radical anions makes it impossible to study them by the conventional ESR technique. The method of quantum beats can be easily generalized to systems with a greater number of equivalent nuclei since simulation in this cases is straightforward. Moreover, one can expect to get otherwise unavailable information about the relaxation times of alkane holes which can be used to estimate the rates of their migration over the solvent molecules.

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