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ARTICLE *in* CHEMICAL PHYSICS LETTERS · OCTOBER 1983

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THE INDUCTION OF QUANTUM BEATS BY HYPERFINE INTERACTIONS IN RADICAL-ION PAIR RECOMBINATION

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Received 18 July 1983

Quantum beats were detected in the recombination of spin-correlated radical-ion pairs. These beats are induced by singlet-triplet transitions in a pair due to hyperfine interactions. Singlet radical-ion pairs were generated by radiolysis of hydrocarbons involving acceptors of electrons and holes. The singlet pair recombination was detected by the luminescence of the product (singlet-excited molecules). The beat frequencies measured for (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ and (durene)⁺/(paraterphenyl-*d*₁₄)⁻ pairs correspond to the hfi constants in the cation radicals. The character of the beats differ in high and zero magnetic fields and their shape depends upon the solvent.

1. Introduction

The influence of hyperfine interactions (hfi) between an unpaired electron and magnetic nuclei upon radical-pair reactions has lately received widespread attention [1]. This influence forms the basis for a mechanism of external magnetic field effects upon radical reaction rates [2], and results in an isotropic effect of a new type — the so-called “magnetic isotopic effect” [3,4]. This phenomenon also underlies the recently developed highly sensitive method of optically detected electron spin resonance (ODESR) of radical pairs in solution [5].

An important effect of hfi is that the radical pair recombination probability changes in a periodic manner with a frequency determined by the hfi constant.

The origin of oscillations in the reaction probability can be readily explained for a one-nuclear radical pair (spin 1/2) with equal radical *g*-factors in a high magnetic field. If at the initial moment the pair is in a certain (e.g. singlet) spin-correlated state, the hfi induces its oscillations between the singlet and triplet states with a frequency $\omega = \gamma a/2$, where *a* is the hfi constant. As a result, the probability of radical recombination, featuring as a rule the singlet state only, must oscillate in time. In the more general case of both spin states being reactive, it is the probability of generating a product with

a definite spin multiplicity that must vary in time.

In real systems, radical pairs may have a great number of nonequivalent magnetic nuclei. In this case, harmonic oscillations between singlet and triplet states occur also in each radical pair. However, the whole radical-pair ensemble is characterized by a complex set of frequencies which makes the oscillations practically unobservable due to their superposition. The situation is more favourable if the magnetic nuclei of a radical pair are equivalent and hence the singlet-triplet oscillations in different pairs occur with multiple frequencies. The superposition of such oscillations must result in beats (sharp rises or falls) of the reaction probability.

The requisite condition for experimental observation of quantum beats in radical-pair recombination is a simultaneous formation of an ensemble of such pairs in a definite spin state. This condition is realized if geminate radical pairs are generated by a short pulse of either light or ionizing radiation. In this case, the pulse duration must be less than the singlet-triplet oscillation period.

The problem of quantum beats in radical recombination was previously discussed by Klein and Woltz [6] who detected nonmonotonic time variations of magnetic field effects in radical-ion recombinations. However, owing to the complex system studied, they failed to relate the experimental data to hfi parameters.

In the present work, we observe directly the quantum beats in radical-ion recombination kinetics and demonstrate an attractive fit of the experimental data to theoretical calculations.

We have investigated the recombination of the geminate singlet radical-ion pairs (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ generated by radiolysis of a solution of tetramethylethylene and paraterphenyl-*d*₁₄ in a non-polar solvent as a result of trapping free electrons and holes in an ionizing particle track. A tetramethylethylene radical cation has 12 equivalent hydrogen magnetic nuclei, while the hfi in a deuterated paraterphenyl radical anion is rather weak. The singlet pair-recombination product (singlet-excited paraterphenyl molecules) was detected by fluorescence. The information on the fluorescence kinetics was gained separately for each ionizing particle track, ensuring the simultaneous formation of an ensemble of geminate radical pairs.

2. Experimental

Time measurements of the recombination fluorescence intensity were made using a single-photon counting technique on apparatus similar to that described earlier [6,7]. The ⁹⁰Sr isotope with an activity of some 10 μCi served as a source of fast electrons. The sample and the radioactive source were placed between the poles of an electromagnet. The decay curves of the recombination fluorescence were stored in a multichannel analyzer and processed thereafter by a LSI-11 mini-computer. To remove oxygen, argon was bubbled through the sample before the experiment. The solvents were purified by passing through a column containing activated silica gel. Trans- and cis-decaline were separated from a commercial mixture by a chromatographic technique. Tetramethylethylene, durene, and perdeuteroparaterphenyl were not purified further.

3. Results and discussion

Fig. 1 depicts the time dependence of the logarithm of the recombination fluorescence intensity $I(t)$ observed in a trans-decaline solution involving 1.3×10^{-2} M tetramethylethylene and 10^{-3} M paraterphenyl-*d*₁₄, irradiated by fast electrons in high (3300 G) and zero

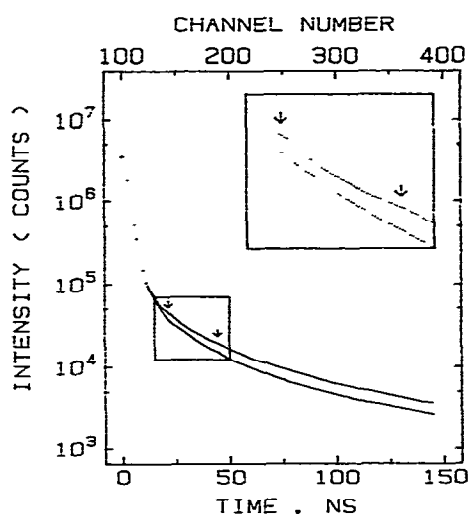


Fig. 1. Time evolution, $I(t)$, of the fluorescence intensity in a fast-electron-irradiated solution of 1.3×10^{-2} M tetramethylethylene and 10^{-3} M paraterphenyl-*d*₁₄. The upper curve corresponds to $H = 3300$ G, the lower one to zero field. The arrows mark the moments of periodical rises in the fluorescence intensity.

magnetic fields. The arrows mark moments of periodic rises in the intensity $I(t)$. The signal-to-noise ratio depends on the number of counts, and is sufficiently high for the beats to be reliably identified. It is difficult, however, to observe them on the scale employed since they are superimposed on the smooth luminescence curve which falls off rapidly and reflects the pair-life-time distribution before collisions, $F(t)$. Fig. 2 shows the ratio $I(t)/F(t)$ for a high magnetic field. To calculate this ratio, the smooth curve $F(t)$ is analytically simulated as a sum of exponential and power functions. The numerical parameters of the functions are chosen by a computer so that the areas between the beat peaks (see fig. 2) lie on the same level. The signal-to-noise ratio is increased by the procedure of smoothing the original curve over 11 channels.

Fig. 3 shows experimental results obtained for the same system in a zero magnetic field. Quantum oscillations were also observed for the radical-ion pair (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ in some other solvents and for the pair (durene)⁺/(paraterphenyl-*d*₁₄)⁻ in trans-decaline (table 1).

The beat period can be calculated with the weak hfi in paraterphenyl-*d*₁₄ radical anions neglected. Since a

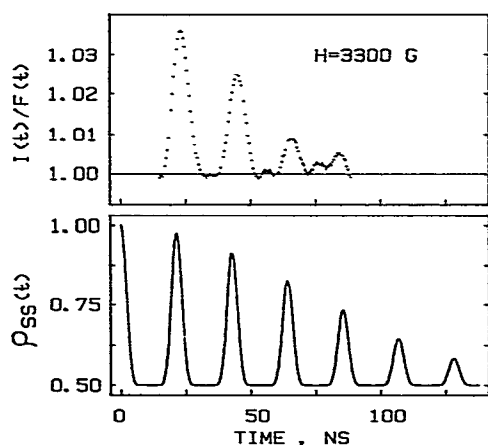


Fig. 2. Top: The experimental curve of quantum beats in the recombination of (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ pairs in trans-decaline, determined as the ratio of $I(t)$ to the smoothed function $F(t)$ which imitates the pair-lifetime distribution before collisions. Bottom: The calculated curve of singlet-state population, $\rho_{ss}(t)$. Both top and bottom curves are for high magnetic fields.

(tetramethylethylene)⁺ radical cation has 12 equivalent protons and the g -values of the anion and cation practically coincide, the calculation is performed by summing the cosine curves with binomial intensity distributions and multiple frequencies, the lowest thereof being determined from $\omega = \gamma a$ (here a is the hfi constant for equivalent cation protons). With the hfi constant one can calculate the expected beat period, T . In the case

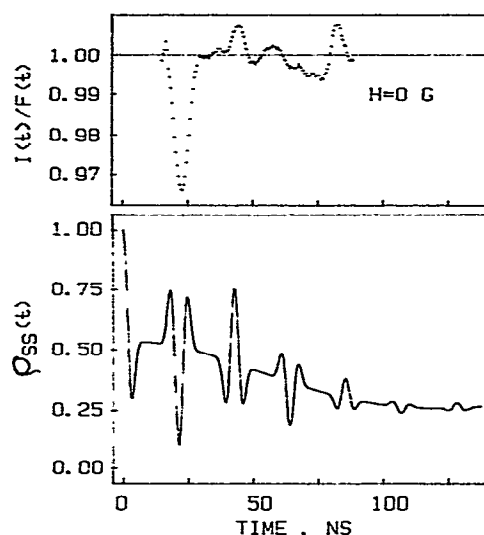


Fig. 3. Curves analogous to those in fig. 2 for the case of zero field.

of an even number of equivalent protons, it is determined as $T = 2\pi/\gamma a$.

We used the ODES method [5] to take ESR spectra of the radical pairs under study (fig. 4) and to measure hfi constants for tetramethylethylene radical cations in liquid trans-decaline and squalane. The values obtained were 16.5 and 16.6 G, respectively, which are close to the value (16.7 G) obtained in glassy 3-methylpentane by a standard ESR method [9]. We used the

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, a (G)	Calculated beat period $T = 2\pi/\gamma a$ (ns)	Experimental beat period (ns)
(tetramethylethylene) ⁺ /(paraterphenyl- <i>d</i> ₁₄) ⁻	trans-decaline	16.5	21.6	22 ± 0.5
	cis-decaline			22 ± 0.5
	squalane	16.6	21.5	22 ± 0.5
	<i>n</i> -pentadecane			22 ± 0.5
(durene) ⁺ /(paraterphenyl- <i>d</i> ₁₄) ⁻	trans-decaline	10.8 ^{a)}	33.1	33.5 ± 0.5

a) Ref. [8].

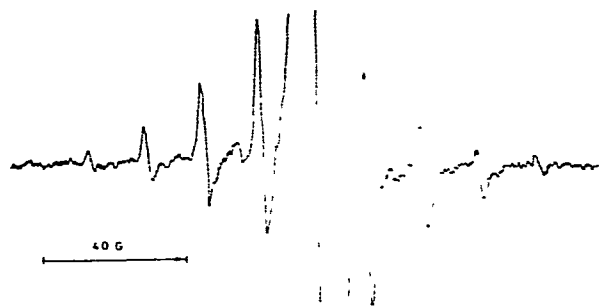


Fig. 4. ODESR spectrum of (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ radical-ion pairs in a squalane solution containing 10⁻² M tetramethylethylene and 10⁻³ M paraterphenyl-*d*₁₄ under X-irradiation at -10°C.

literature hfi constants in beat period calculations for a pair involving a durene radical cation. Table 1 shows the calculated and experimental values of beat periods. They are seen to agree within the experimental error.

Together with the experimental curve $I(t)/F(t)$, figs. 2 and 3 show the curves $\rho_{ss}(t)$ of time evolution for the singlet-state population of radical pairs in high and zero fields. These are calculated by taking into account the hfi in both tetramethylethylene cations and paraterphenyl-*d*₁₄ anions. In a high magnetic field, the calculations followed the formula [10]

$$\rho_{ss}(t) = 0.5 + 0.5 \prod_{i,j} \{ \cos(\gamma a_i t / 2) \times \frac{1}{3} [1 + 2 \cos(\gamma a_j t)] \}.$$

where a_i and a_j are the hfi constants of protons and deuterons, respectively. The calculated $\rho_{ss}(t)$ in fig. 2 is obtained with $a_{i=1} = 16.6$ G and $a_j = 1,2,3,4 = 0.32, 0.09, 0.51$ and 0.15 G*. The $\rho_{ss}(t)$ calculations in a zero field are fairly elaborate. The anion hfi is taken into consideration by a semi-classical approximation [12].

As seen from figs. 2 and 3, the experimental curves are close to the calculated ones; the beat amplitude, however, is much lower in the former case. In a high

* The a_j values for entirely deuterated paraterphenyl were calculated by multiplying the a_j for non-substituted paraterphenyl [11] by the ratio $g_N(D)/g_N(H)$ (=0.1535) of the nuclear g_N -factors for the deuteron and proton.

field, e.g. at the moment of the first oscillation, $\rho_{ss}(t)$ must be twice as large as that between oscillations, while the fluorescence intensity observed increases only by some 3%. This discrepancy might be explained by the fact that the recombination fluorescence contains contributions from not only (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ pairs but also from some other pairs, such as (paraterphenyl-*d*₁₄)⁺/(paraterphenyl-*d*₁₄)⁻ and (solvent)⁺/(paraterphenyl-*d*₁₄)⁻, which smears the oscillations.

In a zero field, the experimental curves lack some details typical of the calculated ones because of insufficient time resolution of the apparatus. It should also be noted that the signal-to-noise ratio in the experimental curves is much lower at long times than at short times since the fluorescence intensity reduces in time (for the time moments corresponding to the first and the fourth beats, the number of counts differs by approximately an order of magnitude). Thus, the right-hand parts of the curves are substantially distorted by noise.

Fig. 5 shows quantum beats in the squalane solutions at concentrations of 1.7 × 10⁻² M tetramethylethylene and 10⁻³ M paraterphenyl-*d*₁₄ in a high magnetic field. It is seen that the beats are substantially broadened and of an asymmetrical shape as compared to those in the trans-decaline solution (fig. 2). Moreover, the maxima are slightly shifted towards long times. The beats in another solvent studied, *n*-pentadecane, are of the same character as those in squalane. The beats in cis-decaline are as narrow as in trans-decaline. Theoretical calculations show that the asymmetrical broadening of beat peaks might result from the time delay between the ionization moment and the capture of the

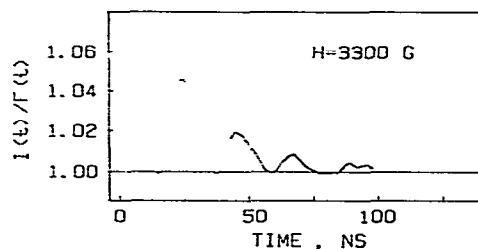


Fig. 5. Experimental curve of quantum beats in the recombination of (tetramethylethylene)⁺/(paraterphenyl-*d*₁₄)⁻ pairs in squalane at 3300 G, plotted in the same coordinates as in fig. 2. Concentrations: 1.7 × 10⁻² M tetramethylethylene, 10⁻³ M paraterphenyl-*d*₁₄.

newly formed holes by acceptors. This time delay violates the synchronism of singlet-triplet oscillations and thus leads to peak broadening. In cis- and trans-decalines, which are characterized by anomalously large hole mobility [13], the delay-induced broadening is lower than that in other solvents.

The phenomenon of quantum beats may be fairly promising for geminate radical-pair investigations. A frequency spectrum of the beats gives information on the hfi constants, its shape conveying information on the primary particle reaction rates.

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