

Manifestation of quantum coherence upon recombination of radical ion pairs in weak magnetic fields. Systems with equivalent nuclei

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Abstract

Magnetsensitive radiofluorescence has been used to study the magnetic field effect at fields of the order of hyperfine ones during the recombination of spin-correlated radical ion pairs in non-polar solutions. For radical pairs, in which hyperfine interactions are essential only for equivalent nuclei in one of the pair partners, additional local maxima of fluorescence intensity in characteristic 'multiple' fields were observed. These maxima arise from the coherent nature of the radical pair initial state: different stationary states interfere in the fields where energy levels of the radical pair cross.

1. Introduction

Static magnetic fields are known to have an effect on chemical reactions involving short-lived paramagnetic particles, e.g. radicals and radical ions being the intermediates in many chemical transformations [1,2]. Magnetic field and spin effects observed in radical reactions originate from singlet–triplet (S–T) transitions between the levels of a radical pair driven by hyperfine interaction (hfi) with magnetic nuclei of the radicals and by the difference in their Larmor precession frequencies. The transitions result in a change in the yield of products of given multiplicity.

The magnetic field dependence of reaction yield (MARY spectrum) is typically a smooth monotonic

curve without any sharp features. Theory [3] predicts, however, the appearance of sharp extrema in weak magnetic fields for long-lived spin-correlated pairs. The positions of these extrema are determined by the crossing of radical pair energy levels.

An initial radical pair (singlet or triplet) is formed in a coherent state [4] which is the superposition of stationary states evolving with their particular frequencies. Let ω_1 and ω_2 be the frequencies of the two stationary states involved. Then for a singlet-born radical pair the probability of finding the system in the singlet state behaves as

$$P_S \sim |\exp(i\omega_1 t) + \exp(i\omega_2 t)|^2 \\ \sim 1 + \cos[(\omega_1 - \omega_2)t]. \quad (1)$$

The oscillating term results from the interference of stationary states. In the region of level crossing ($\omega_1 = \omega_2$) the oscillating term becomes constant and

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is not averaged down to zero, i.e. for a long-lived radical pair the average population of the singlet state \bar{P}_S is larger than in the case of the level splitting ($\omega_1 \neq \omega_2$). Therefore, the crossing of the radical pair levels results in the sharp decrease of the S–T conversion rate which can be observed as local extrema in the MARY spectrum. Extrema positions H^* are determined by the set of hyperfine interaction constants in both radicals of the pair. For the particular case of zero field $H^* = 0$ the effect of interference must arise for an arbitrary set of magnetic nuclei in one of the radicals, if the hfi constants of the second partner are negligibly small. This has been verified experimentally as a local maximum of the fluorescence yield in non-polar solutions of luminophors under ionizing radiation [3,5].

For radical pairs, in which hyperfine interactions are essential only for equivalent nuclei in one of the pair partners, local extrema in non-zero fields could also be observed. In this case their position is determined by the single hyperfine interaction constant a_{hf} , possible values for the total spin of the sub-ensembles of equivalent nuclei I ($I > 1$) and its projection m ($0 < m < I$),

$$H^* = a_{\text{hf}} I(I+1)/2m. \quad (2)$$

The appearance of the features in non-zero fields has been predicted theoretically [3,6] but they have not yet been observed experimentally.

This Letter reports the recombination fluorescence in weak magnetic field for ion radical pairs with equivalent nuclei generated in non-polar solution by ionizing radiation. It is experimentally demonstrated that for radical pairs, with hyperfine interaction only being essential for equivalent nuclei in one of the partners, fluorescence maxima are observed in fields at multiples of a_{hf} (the word ‘multiple’ means here that $pH^* = qa_{\text{hf}}$, p, q – integers). This phenomenon opens additional possibilities for identifying short-lived radicals (by MARY spectra).

2. Experimental

Magnetic field effects under X-irradiation were recorded under stationary conditions as described in Ref. [7]. The experimental apparatus and sample preparation procedure have been described previously [5].

Table 1
hfi parameters of ion radicals

Radical ion	Isotropic hfi constant (G)		Ref.
(cis-decalin) ^{•+}	4H	50	[10]
(C ₆ F ₄ D ₂) ^{•+}	4F	41	[11]
	2D	< 1	
(C ₆ F ₆) ^{•+}	6F	133.6	[12]
(TEA) ^{•+}	N	21.6	[7]
	6H(CH ₂)	21.6	
(Δ9,10-octalin) ^{•+}	8H	24	[13]
(durene) ^{•+}	12H(CH ₃)	11.5	[7]
(TME) ^{•+}	12H	17.2	[14]

The solvents – squalane (99%, Fluka), cis- and trans-decalin (decahydronaphthalene) (99%, Aldrich) and cyclohexane (99%, Aldrich) – were purified by passing through a column with activated silica gel. Cyclohexane was distilled prior to the column. The purity was tested by UV-absorption spectra [8]. The solvents used had optical density equal to unity, at wavelengths 215–225 nm.

Triethylamine (TEA), tetramethylbenzene (durene), tetrafluorobenzene-*d*₂ (TFB), hexafluorobenzene (HFB), Δ9,10-octalin (1,2,3,4,5,6,7,8-octahydronaphthalene), cis-decalin and tetramethylethylene (TME) were used as electron and hole acceptors. The hfi parameters of their radical ions are given in Table 1. Durene (> 99%, Fluka) and TME (TCI-EP) were used without further purification. TEA was distilled. Fluorinated substances were supplied by the Novosibirsk Institute of Organic Chemistry and used without further purification.

3. Theory

The spin state of an ensemble of radical pairs is described by the density matrix $\rho(t)$ being the solution of the equation ($\hbar \equiv 1$)

$$\partial\rho/\partial t = -i[\hat{\mathcal{H}}, \rho], \quad (3)$$

with the spin-Hamiltonian ($g_1 \approx g_2 \equiv g$)

$$\begin{aligned} \hat{\mathcal{H}} = & g\beta H(S_{1z} + S_{2z}) + \sum_i a_i S_1 \cdot I_{1i} \\ & + \sum_j a_j S_2 \cdot I_{2j}, \end{aligned} \quad (4)$$

where the first term is the Zeeman energy of unpaired electrons in an external magnetic field, and the sums describe the hfi in pair radicals [1]. For a radical pair with equivalent nuclei Eq. (3) has been solved analytically [3]. Assuming exponential decay kinetics, the yield of singlet products of recombination is given by the Laplace image of singlet state population $\rho_{ss}(t)$,

$$G_S = \frac{1}{\tau} \int_0^{\infty} \rho_{ss}(t) e^{-t/\tau} dt = p \mathcal{L}[\rho_{ss}(t)], \quad (5)$$

where $1/\tau$ is denoted by p .

Taking the explicit expression for $\rho_{ss}(t)$ from Ref. [3], one obtains

$$G_S = \sum_{I_1=0}^{M_1} \sum_{I_2=0}^{M_2} W_1(I_1) W_2(I_2) \tilde{\rho}_{ss}(p, I_1, I_2), \quad (6)$$

where the summation with statistical weights $W_1(I_1)$, $W_2(I_2)$ is carried out over the nuclear sub-ensembles with total spins I_1 and I_2 for the first and second radicals, respectively, M_1 and M_2 are the maximal values of total nuclei spins in the partners. For example, for a radical pair containing $N_1 = 6$ and $N_2 = 0$ equivalent protons in the first and second radicals one obtains: $M_1 = 3$, $W_1(0) = \frac{5}{64}$, $W_1(1) = \frac{27}{64}$, $W_1(2) = \frac{25}{64}$, $W_1(3) = \frac{7}{64}$, $M_2 = 0$, $W_2(0) = 1$. Assuming a singlet initial state of a radical pair, the yield of singlet products for every particular sub-ensemble reads as

$$\tilde{\rho}_{ss}(p, I_1, I_2) = \frac{1}{4(2I_1 + 1)(2I_2 + 1)} \times \sum_{m_1=-I_1}^{I_1} \sum_{m_2=-I_2}^{I_2} \Theta(m_1, m_2), \quad (7)$$

where the contributions from all projections $m_{1,2}$ of total spins $I_{1,2}$ are summed up. An analytical expression for $\Theta(m_1, m_2)$ is given in Appendix A.

Fig. 1 shows theoretically calculated dependences of singlet product yield G_S versus external magnetic field for a singlet-born radical pair with 12 equivalent protons in one of the pair partners. Curve (a) is the calculated dependence, (b) its smooth background, (c) their difference, $a_{hf}\tau = 40$. Along with the pronounced maximum at zero field additional

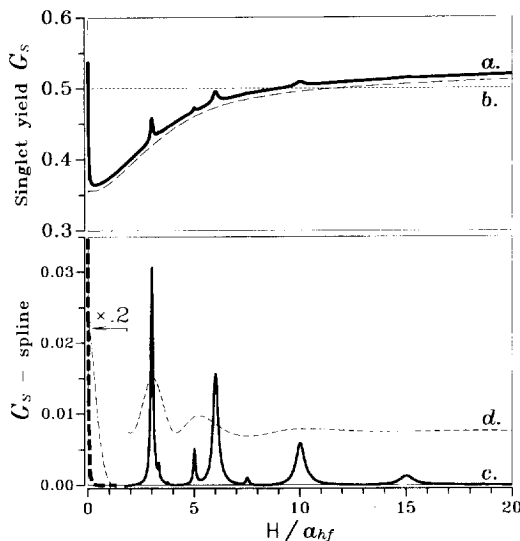


Fig. 1. Theoretically calculated dependences of singlet product yield G_S (absolute values) versus external magnetic field H for a singlet-born radical pair with twelve equivalent protons in one of the pair partners. The second partner contains no magnetic nuclei. There is a pronounced maximum for zero field. (a) Calculated dependence for $a_{hf}\tau = 40$; (b) its smooth background (smoothing spline); (c) only sharp peaks are left by subtracting the spline, the zero field feature is reduced fivefold; (d) 'sharp' peaks at $a_{hf}\tau^* = 2$ (a_{hf} is the hfi constant, τ is the lifetime of exponential decay).

maxima in the characteristic 'multiple' fields are predicted. First, the largest one is situated in the field $H^* = 3a_{hf}$.

It is worth mentioning that the amplitude of this peak is about five times less than that at zero field, which may explain the failure of the previous attempts to observe the features [3]. The features at higher fields have greater width and are more sensitive to a decrease in the lifetime of the spin-correlated pair. Curve (d) shows the field dependence for a shorter lifetime of the spin-correlated pair ($a_{hf}\tau = 2$). The maxima broaden and decrease in amplitude, the maxima at $H^* = 5a_{hf}$ and $H^* = 6a_{hf}$ merge, the features at higher fields vanish and disappear.

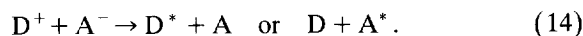
For an arbitrary number of equivalent protons N_p in one of the pair partners the positions of the maxima are given by formula (2) [6]. For $N_p = 1, 2$ only a zero field maximum is expected, additional maxima appear for $N_p \geq 3$. For an even N_p the first peak is situated at triple the hfi constant and corre-

sponds to the contribution of sub-ensembles with total spin $I = 2, 3$. E.g. for $N_p = 4$ one should expect the only non-zero feature at $H^* = 3a_{hf}$, and for $N_p = 6$ two peaks are expected in the spectrum: at $H^* = 3a_{hf}$ and $H^* = 6a_{hf}$. For $N_p = 8$ three more peaks arise at $H_p = \frac{10}{3}a_{hf}, 5a_{hf}, 10a_{hf}$. Thus, spectral information about the pair partners could be extracted from the product yield field dependence, and direct identification of short-lived radicals by their MARY spectra becomes possible.

Numerical calculations demonstrate that the presence of magnetic nuclei in both partners diminishes the effect. For example, introducing a nucleus with a small a_{hf} in the second partner results in peaks splitting with corresponding decrease in amplitude, while many nuclei cause the smashing of features. The presence of nuclei in the first partner that could not be included in the set of equivalent nuclei has the same effect.

4. Results and discussion

The generation of radical ion pairs under X-radiation of non-polar solutions and their recombination with the formation of excited molecules can be described by the scheme [9]



Here S is the solvent molecule; D and A are hole and electron acceptors, respectively. Primary S^+/e^- pairs form in the singlet state (because of cross-recombination the share of spin-correlated pairs is less than 1). The yield of fluorescing products depends on the singlet–triplet evolution in radical pairs, and the multiplicity of forming excited products D^*, A^* corresponds to the pair multiplicity at the moment of recombination. In the experiment fluorescence from the singlet excited state has been studied.

As has already been mentioned, the coherence effects must be large upon the recombination of

radical ion pairs with negligibly small hfi in one of the partners. The reactions of the recombination of electrons and solvent holes (when their hfi are small or averaged down by fast charge transfer) with the corresponding counterions (reactions (12) and (13)) meet these requirements. Fluorinated substances (tetra- and hexa-fluorobenzene) were used as electron acceptors, and substances with low ionization potential and negative electron affinity (e.g. durene) served as hole acceptors. Substances that can capture both the solvent holes and electrons were avoided.

Fig. 2 shows the field dependences of the fluorescence intensity for solutions of different acceptors with equivalent nuclei in non-polar hydrocarbons (first derivatives, due to the use of the magnetic field modulation technique). Besides the pronounced inversion at zero field all the curves show an additional feature in the field equal to triple the hfi constant, having the shape of the local maximum derivative. Their positions are marked by arrows. For convenience the ESR stick diagram of the corresponding radical ion is shown above every experimental curve. The hfi parameters of the radical ions are given in Table 1. As has been mentioned above, for a system with an integer total spin (e.g. with an even number of protons) the first maximum must appear on the triple hfi constant (formula (8)). The curves shown in Fig. 2 correspond to radical pairs with four equivalent protons (c), four (b) and six (a) equivalent fluorine nuclei, eight (e) and twelve (f) equivalent protons. The splitting on the nitrogen nucleus in triethylamine radical cation coincides with that on six methylene protons ($a(N) = a(6H_{CH_2}) = 21.6$ G). Formally, system (d) can also be considered as a system with integer total spin. Thus, the observed additional features can be identified with the theoretically predicted interference maxima in non-zero fields. The dashed curves (Figs. 2a, 2d and 2f) are an attempt to describe the shape of the experimental field dependences in an exponential decay approximation (with a single lifetime). Although the curves describe the features positions and amplitudes fairly well, the experimentally observed broad background (Figs. 2d and 2f) is not reproduced in the calculations. The use of a more realistic power law decay kinetics does not mend the situation. This discrepancy between theory and experiment may be connected with the secondary reactions of pair part-

ners (e.g. reactions of radical cation charge transfer) leading to the loss of spin coherence or with the contribution of other radical pairs to the MARY curves.

Although the theory predicts the existence of several additional maxima for $N_p \geq 4$, only the first most intensive one is observed in the curves of Fig. 2. This can be attributed to the lower relative intensities of the higher field peaks and to their stronger lifetime broadening as well as to a poor signal-to-noise ratio.

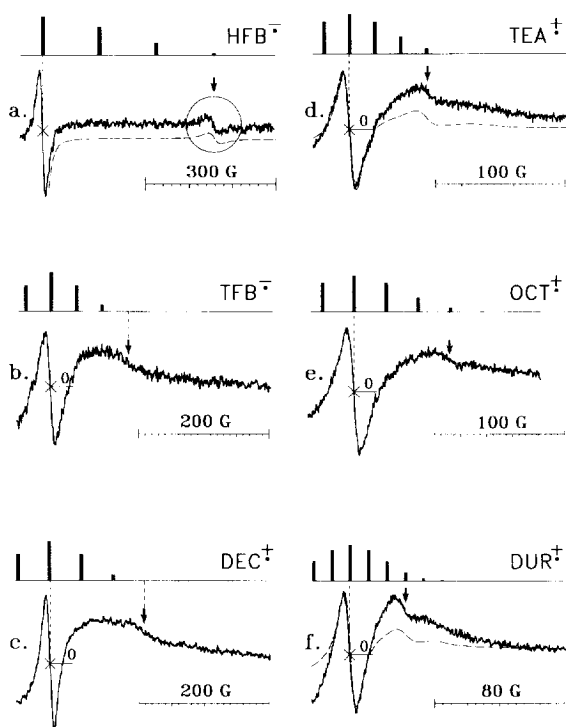


Fig. 2. Experimental dependences of fluorescence intensity (first derivative) versus external magnetic field for the solutions: (a) 2.5×10^{-2} M C_6F_6 in squalene, $T = 233$ K; (b) 10^{-2} M tetrafluorobenzene- d_2 in squalene, $T = 293$ K; (c) 10^{-3} M p -terphenyl- d_{14} + 10^{-2} M cis-decalin in cyclohexane, $T = 293$ K; (d) 2×10^{-2} M TEA in squalene, $T = 293$ K; (e) 5×10^{-4} M p -terphenyl- d_{14} + 10^{-1} M $\Delta 9,10$ -octalin in cis-decalin, $T = 293$ K; (f) 1.2×10^{-2} M duren in squalene, $T = 233$ K; p -terphenyl- d_{14} is used as a partner with narrow ESR spectrum, yielding a fluorescing excited product. Modulation amplitude 5 G. The arrows mark additional features at triple a_{hf} . Zero field is at the curves' centres of symmetry. Stick-diagrams show the ESR spectra, shifted to zero field. Dashed curves are attempts to describe the experiment with exponential decay of radical ion pairs.

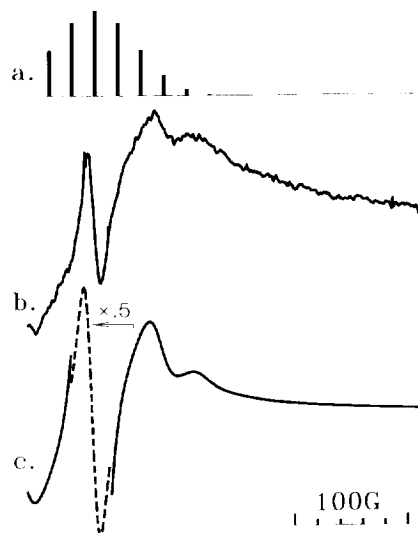


Fig. 3. Fluorescence intensity (first derivative) versus external magnetic field for the solution of 2×10^{-3} M TME + 10^{-4} M p -terphenyl- d_{14} in trans-decalin at 293 K. Along with the feature at triple a_{hf} a more distant one is observed. Modulation amplitude 10 G. (a) ESR stick-diagram of TME cation-radical, shifted to zero field; (b) experimental MARY spectrum; (c) calculated curve, $a_{hf}\tau = 10$, $a_{hf}T_2 = 30$, central dashed part multiplied by 0.5.

Since the intensity of the next peak increases with the number of equivalent protons, we examined in more detail the TME cation radical with twelve equivalent protons ($a_{hf} = 17.2$ G). Fig. 3 depicts the field dependence for a 2×10^{-3} M TME solution in trans-decalin at 293 K. In this case an additional feature is observed which can be ascribed to a more distant maximum. Curve (b) shows the experimental MARY spectrum, curve (c) its theoretical simulation with exponential decay kinetics (for convenience the central dashed part is multiplied by 0.5).

The observation of additional local maxima in fields at multiples of the hfi constant opens the possibility of directly identifying the radicals involved in magnetosensitive reactions. This effect increases the informativity of MARY experiments and brings them closer to ESR methods. Thus, it becomes possible to create the technique of direct identification of short-lived radicals and to study their reactions using the spin coherence effect in radical ion pairs.

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Appendix

The analytical expression for function $\Theta(m_1, m_2)$ is

$$\Theta(m_1, m_2) = \left(f(m_1, m_2 - 1) + f(m_1 - 1, m_2) + \sum_{i,j=1}^8 \frac{\alpha_i \alpha_j p^2}{p^2 + (q_i - q_j)^2} \right), \quad (\text{A.1})$$

where

$$f(m_1, m_2) = \frac{1}{4} \sin^2(2\varphi_{m_1}) \sin^2(2\varphi_{m_2}) \times \left(1 - \frac{p^2}{p^2 + (2R_{m_1})^2} - \frac{p^2}{p^2 + (2R_{m_2})^2} + \frac{p^2/2}{p^2 + (2R_{m_1} + 2R_{m_2})^2} + \frac{p^2/2}{p^2 + (2R_{m_1} - 2R_{m_2})^2} \right), \quad (\text{A.2})$$

$$\alpha_1 = \cos^2\varphi_{m_1} \sin^2\varphi_{m_2-1}, \quad q_1 = -R_{m_2-1} - R_{m_1},$$

$$\alpha_2 = \sin^2\varphi_{m_1} \sin^2\varphi_{m_2-1}, \quad q_2 = -R_{m_2-1} + R_{m_1},$$

$$\alpha_3 = \cos^2\varphi_{m_1} \cos^2\varphi_{m_2-1}, \quad q_3 = R_{m_2-1} - R_{m_1},$$

$$\alpha_4 = \sin^2\varphi_{m_1} \cos^2\varphi_{m_2-1}, \quad q_4 = R_{m_2-1} + R_{m_1},$$

$$\alpha_5 = \cos^2\varphi_{m_2} \sin^2\varphi_{m_1-1}, \quad q_5 = -R_{m_1-1} - R_{m_2},$$

$$\alpha_6 = \sin^2\varphi_{m_2} \sin^2\varphi_{m_1-1}, \quad q_6 = -R_{m_1-1} + R_{m_2},$$

$$\alpha_7 = \cos^2\varphi_{m_2} \cos^2\varphi_{m_1-1}, \quad q_7 = R_{m_1-1} - R_{m_2},$$

$$\alpha_8 = \sin^2\varphi_{m_2} \cos^2\varphi_{m_1-1}, \quad q_8 = R_{m_1-1} + R_{m_2}, \quad (\text{A.3})$$

$$R_{m_k} = \frac{1}{2} \left[\omega^2 + a_k \omega (2m_k + 1) + a_k^2 (I_k + 1/2)^2 \right]^{1/2},$$

$$\omega = g\beta H, \quad (\text{A.4})$$

$$\cos^2\varphi_{m_k} = (1/2R_{m_k}) \left[R_{m_k} + \frac{1}{2}\omega + \frac{1}{4}a_k(2m_k + 1) \right],$$

$$\sin^2\varphi_{m_k} = 1 - \cos^2\varphi_{m_k}. \quad (\text{A.5})$$

$k = 1, 2$ refers to the first and second pair radicals, respectively, a_1, a_2 are their hfi constants.

The expressions above are given for the general case $a_{1,2} \neq 0$ and become much more simple when $a_1 = a_{\text{hf}}, a_2 = 0$.

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