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Magnetic field effects in the recombination fluorescence of a three-spin radical ion/biradical ion system

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Magnetosensitive radiofluorescence resulting from geminate recombination of a spin triad involving a radical ion and a biradical ion formed radiolytically in non-polar solutions has been investigated theoretically. The effect of exchange interaction in the biradical ion on the kinetics and yield of radiofluorescence has been studied. Hyperfine coupling in the radical ion and in the biradical ion has been taken into account. The existence of local fluorescence resonances at zero magnetic field and at a field close to the value of the exchange integral in the biradical has been predicted theoretically. The latter result provides a basis to determine the exchange integral in short-lived radiolytically generated biradical ions with high accuracy from experiment.

I. Introduction

Static magnetic fields are known to affect the recombination fluorescence (radiofluorescence) of radical ion pairs generated in solution by ionizing radiation. Under ionization and the subsequent reactions, spin correlated radical ion pairs ($S^{+\bullet}/e^-$), ($D^{+\bullet}/e^-$), ($S^{+\bullet}/A^{-\bullet}$) and ($D^{+\bullet}/A^{-\bullet}$) are formed. Here S is the solvent molecule, A and D are the molecules of electron and hole acceptors, respectively.^{1,2} The primary pairs ($S^{+\bullet}/e^-$) mainly arise in the singlet spin state. Since electron and hole capture occurs within short times of about several nanoseconds one can assume that the radical pairs ($D^{+\bullet}/e^-$), ($S^{+\bullet}/A^{-\bullet}$), ($D^{+\bullet}/A^{-\bullet}$) are also formed in the singlet spin state. The singlet-triplet (S - T) transitions in the radical pair and, hence, the kinetics and yield of radiofluorescence, are mainly determined by the hyperfine couplings of the unpaired electrons of the radical pair with the magnetic nuclei and by interaction of these electrons with an external magnetic field.³⁻⁷

Earlier analytical and numerical estimations⁸⁻¹¹ have shown that interradical dipole-dipole and exchange interactions have no effect on the spin evolution of radical ion pairs generated by ionizing radiation in solutions of normal viscosity. The reason is that radicals are spaced widely during the main time before recombination. However, in three-spin systems consisting of a biradical ion and a radical ion, exchange and dipole-dipole interactions in the biradical ion can substantially affect spin dynamics. An example of such a system is the radical triad in the photosynthetic reaction centre,¹² and another one is a photochemically generated radical pair combined with a stable radical.¹³ It should be noted that the term "spin triad", for the first time, was introduced by the authors of the work.¹⁴ More generally such systems can be considered as spin-catalytic systems.^{15,16}

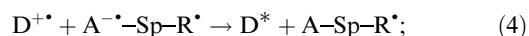
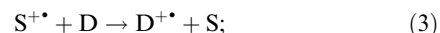
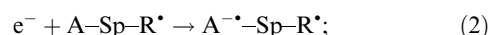
With the purpose of studying radiation-generated three-spin systems, the molecules $A-Sp-R^{\bullet}$ containing a stable radical moiety have been recently synthesized.¹⁷ Here A is a luminescing aromatic group, Sp is the molecular bridge, and R^{\bullet} is a stable nitroxide radical. Under ionization of hydrocarbon solution these molecules can serve as electron acceptors, i.e., they can capture an electron and form a spin-correlated radical ion/biradical ion pair of the type $S^{+\bullet}/(A^{-\bullet}-Sp-R^{\bullet})$ or $D^{+\bullet}/A^{-\bullet}-Sp-R^{\bullet}$. Preliminary experiments have shown, that the

presence of a paramagnetic centre R^{\bullet} changes the magnetic field effect in radiofluorescence significantly.

In this paper, magnetic field effects on the kinetics and yield of radiofluorescence in three-spin radical ion/biradical ion systems are investigated theoretically. We considered a model biradical having only one magnetic nucleus. The intensity of recombination fluorescence in a magnetic field is determined by the singlet state population of the two-spin system consisting of the radical ion and the radical ion centre of the biradical. We have obtained analytical expressions for the singlet state population in zero magnetic field, and also in the vicinity of $B \sim |J|$, where B is the strength of the magnetic field and J is the exchange integral in the biradical. Numerical calculations of the kinetics and yield of fluorescence have been performed, and their dependence on the magnetic field has been studied. It has been shown that both the kinetics and the yield of fluorescence exhibit resonance behaviour in the regions $B \sim 0$ and $B \sim |J|$, the latter will be referred to as a J -resonance.

II. Model of the radical ion/biradical ion pair (RIBIP)

The ionization and subsequent reactions that occur under irradiation of hydrocarbon solutions of $A-Sp-R^{\bullet}$ are as follows:



In reactions (1-5) the spin correlated $D^{+\bullet}/A^{-\bullet}$ pair incorporated in RIBIP $D^{+\bullet}/(A^{-\bullet}-Sp-R^{\bullet})$ is formed. The stable radical R^{\bullet} is in equilibrium spin state at the moment of RIBIP formation. The initial separation between the radical cation $D^{+\bullet}$ and the biradical anion $A^{-\bullet}-Sp-R^{\bullet}$ ranges up to some tens of ångströms. Following their formation, radical ions diffusionally approach each other in their mutual Coulombic attraction potential and finally recombine, see reactions (4) and (5).

Recombination of these pairs gives rise to the corresponding excited molecules. The spin multiplicity of the excited molecule D^* or luminophore group A^* coincides with that of the radical pair $D^{+\bullet}/A^{-\bullet}$ at the instant of recombination. Singlet excited molecules give rise to fluorescence, while triplet excited ones decay in a non-radiative way. In the absence of a hole acceptor D in the solution, the solvent radical cations $S^{+\bullet}$ take part in reactions (4) and (5) instead of the radical ion $D^{+\bullet}$.

Let us consider the following model of RIBIP and spin transitions in it. We take into account hyperfine interactions both in the radical ion $D^{+\bullet}$ and in the biradical. We assume that the exchange integral in the biradical is fixed, thus neglecting its modulation due to conformational motion of the molecular bridge Sp . We also shall not take into account paramagnetic relaxation, in particular, the relaxation induced by dipole–dipole interaction of biradical spins. In view of the results described in refs. 8–11, exchange and dipole–dipole interactions of radical ion $D^{+\bullet}$ with biradical paramagnetic centres $A^{-\bullet}$ and R^{\bullet} are also neglected. Under these assumptions the Hamiltonian of RIBIP is as follows:

$$\hat{H} = \sum_{i=1}^N a_i \hat{S}_D \hat{I}_i^D + g_D \beta \hbar^{-1} B \hat{S}_{Dz} + g_A \beta \hbar^{-1} B \hat{S}_{Az} + g_R \beta \hbar^{-1} B \hat{S}_{Rz} + J \hat{S}_A \hat{S}_R + A \hat{I} \hat{S}_R \quad (6)$$

where the z -axis is chosen along the magnetic field B . The indices D , A , R correspond to the radical centres $D^{+\bullet}$, $A^{-\bullet}$ and R^{\bullet} . The first term on the right hand side of eqn. (6) describes the hyperfine couplings in the radical ion $D^{+\bullet}$. The next three terms describe the Zeeman interaction of the unpaired electrons with an external magnetic field. The term $J \hat{S}_A \hat{S}_R$ describes the exchange interaction of the unpaired electrons in the biradical. Finally, the last term in (6) describes the hyperfine coupling of the unpaired electron of radical R^{\bullet} with the nucleus located on it. The effect of the location of the magnetic nucleus on radical $A^{-\bullet}$ will be also considered.

Let us assume for simplicity that the g -factors of the radicals are identical: $g_D = g_A = g_R = g$. Inequality of g -factors may play a vital part at strong magnetic fields when, for instance,

$$(g_A - g_R) \beta \hbar^{-1} B \geq A \quad (7)$$

The case of strong magnetic fields including unequal g -factors of radicals is considered later in section III.B. Let us assume, except where otherwise indicated, that the exchange integral J is positive and by far exceeds the hyperfine coupling constants both in the radical ion $D^{+\bullet}$ and in biradical, *i.e.* $J \gg A, a_i$. For the sake of definiteness we also suppose that the hyperfine coupling constant A is positive, $A > 0$.

The radiofluorescence intensity $I(t)$ at time t can be written as:¹⁸

$$I(t) \sim \rho_{DA,SS}(t) F(t) \quad (8)$$

Here $\rho_{DA,SS}(t)$ is the singlet state population of the pair $D^{+\bullet}/A^{-\bullet}$ at time t , $F(t)$ is the radical pair lifetime distribution function. The quantity $F(t)dt$ gives the amount of recombined radical pairs or, which is the same, the amount of recombination products formed for a time interval from t to $t+dt$. The function $F(t)$ is determined by the initial inter-radical distance distribution in the radical pairs and by the diffusion in the mutual Coulombic attraction potential. It does not depend on the dynamics of the spin system. The finite fluorescence lifetime of the recombination product should be also taken into account. After correction for the lifetime of the excited state τ_{fl} the expression for the intensity of fluorescence $I(t)$ takes the form (see also ref. 19):

$$I(t) \sim \frac{1}{\tau_{fl}} \int_0^t \rho_{DA,SS}(t-\tau) F(t-\tau) \exp(-\tau/\tau_{fl}) d\tau, \quad (9)$$

We shall assume that the following inequality holds true:

$$J\tau_{fl} \gg 1 \quad (10)$$

The population $\rho_{DA,SS}(t)$ of the singlet state of the pair $D^{+\bullet}/A^{-\bullet}$ is given by the following expression:¹⁹

$$\rho_{DA,SS}(t) = \frac{1}{4} - \text{Tr}(\hat{S}_D \hat{S}_A \rho(t)) \quad (11)$$

$$\hat{S}_D \hat{S}_A = \hat{S}_{Dx} \hat{S}_{Ax} + \hat{S}_{Dy} \hat{S}_{Ay} + \hat{S}_{Dz} \hat{S}_{Bz}$$

where $\rho(t)$ is the density matrix of the three-spin system RIBIP, \hat{S}_D , \hat{S}_A , \hat{S}_{Dx} , \hat{S}_{Ax} , \hat{S}_{Dy} , \hat{S}_{Ay} , \hat{S}_{Dz} , \hat{S}_{Bz} are electron spin operators of radical ions $D^{+\bullet}$ and $A^{-\bullet}$. Neglect of spin interactions between $D^{+\bullet}$ and $A^{-\bullet}$ essentially simplifies the calculation, since in that case the spin evolution of the radical ion and the biradical ion can be calculated separately and the following expression is valid:²⁰

$$\rho_{DA,SS}(t) = \frac{1}{4} + \frac{1}{4} T_{ik}^D(t) T_{ik}^A(t) \quad (12)$$

Here $T_{ik}^D(t)$ and $T_{ik}^A(t)$ ($i, k = x, y, z$) are the time-dependent tensor components related to the Heisenberg evolution of the spin operators of radicals $D^{+\bullet}$ and $A^{-\bullet}$ in the following way:

$$S_{Di}(t) = T_{ik}^D(t) S_{Dk}(0)$$

$$S_{Ai}(t) = T_{ik}^A(t) S_{Ak}(0) \quad (13)$$

($i, k = x, y, z$)

In eqns. (12) and (13) summation over repeating indices is implied. The second equality in eqn. (13) implies that averaging-out over spin states of the radical R^{\bullet} is already performed. We consider two limiting cases for the hyperfine structure of the radical ion $D^{+\bullet}$. The first case the hyperfine couplings in the radical ion $D^{+\bullet}$ are negligible, that is, the EPR spectrum of $D^{+\bullet}$ consists of a single line. In the second case the radical ion $D^{+\bullet}$ has a broad inhomogeneous EPR spectrum due to unresolved hyperfine structure. The only non-zero elements of T_{ik}^D in the absence of the external magnetic field (*i.e.* at $B = 0$) and for the absence of hyperfine couplings in the radical ion $D^{+\bullet}$ ^{20,21} are:

$$T_{xx}^D = 1, T_{yy}^D = 1, T_{zz}^D = 1, \quad (14)$$

(notice that the tensor components T_{ik}^D , $i, k = x, y, z$ differ by a factor of 2 from the ones defined in^{20,21}). For T_{ik}^D in a magnetic field B we have:

$$T_{xx}^D = \cos(\omega_0 t); \quad T_{xy}^D = -\sin(\omega_0 t)$$

$$T_{yx}^D = \sin(\omega_0 t); \quad T_{yy}^D = \cos(\omega_0 t); \quad T_{zz}^D = 1, \quad (15)$$

Here $\omega_0 = g\beta\hbar^{-1}B$ is the Larmor frequency.

Let us consider now the case when the radical ion $D^{+\bullet}$ has a broad hyperfine structure with the second moment σ^2 given by:

$$\sigma^2 = \sum_i \frac{1}{3} I_i^D (I_i^D + 1) a_i^2,$$

Here I_i^D is the spin of the i -th magnetic nucleus in the radical ion $D^{+\bullet}$. After a time of the order of $1/\sigma$, the tensor components $T_{ik}^D(t)$ become time-independent. Their stationary values, as can be easily found from eqns. (7)–(9) in ref. 21 are equal to:

$$T_{xx}^D = T_{yy}^D = \frac{1}{3} e^{-(\omega_0^2/2\sigma^2)} + I \left(\frac{\omega_0}{\sigma} \right);$$

$$T_{zz}^D = 1 - \frac{2}{3} e^{-(\omega_0^2/2\sigma^2)} - 2I \left(\frac{\omega_0}{\sigma} \right),$$

$$I(q) = -\frac{1}{\sqrt{2\pi}} \int_0^\infty e^{-(x^2+q^2)} \times \left[\frac{e^{xq}}{q^2} \left(\frac{1}{xq} - 1 \right) - \frac{e^{-xq}}{q^2} \left(\frac{1}{xq} + 1 \right) + \frac{2}{3} x^2 \right] dx \quad (16)$$

In the particular case of zero magnetic field one has (see also ref. 20):

$$T_{xx}^D = \frac{1}{3}, \quad T_{yy}^D = \frac{1}{3}, \quad T_{zz}^D = \frac{1}{3}, \quad (17)$$

In a strong magnetic field, well above hyperfine coupling constants, there is only one nonzero element of the tensor T_{ik}^D :

$$T_{zz}^D = 1, \quad (18)$$

Having eqns. (14–18), to calculate the singlet state population $\rho_{DA,SS}(t)$ we need the corresponding quantities, T_{ik}^A , for the spin of A^{\bullet} . The time evolution of the operator \hat{S}_A is given by:

$$\hat{S}_A(t) = \exp(i\hat{H}_{bir}t)\hat{S}_A(0)\exp(-i\hat{H}_{bir}t) \quad (19)$$

Here \hat{H}_{bir} is the biradical spin Hamiltonian:

$$\hat{H}_{bir} = \omega_0\hat{S}_{Az} + \omega_0\hat{S}_{Rz} + J\hat{S}_A\hat{S}_R + A\hat{I}\hat{S}_R \quad (20)$$

To simplify the notation further (except as otherwise noted) ω_0 , J , A are all measured in mT, then, for instance, ω_0 can be identified with B . The tensor components T_{ik}^A of the spin of radical centre A^{\bullet} can be evaluated in the following way:

$$T_{ik}^A = \text{Tr}(\hat{S}_{Ai}(t)\hat{S}_{Ak}(0)), \quad (i,k = x,y,z) \quad (21)$$

here $\hat{S}_{Ai}(t)$ are the x , y , z projections of vector $\hat{S}_A(t)$ defined in eqn. (19). Operators $\hat{S}_{Ai}(t)$ and $\hat{S}_{Ak}(0)$ are considered in the basis of products of spin states of the radical centres A^{\bullet} and R^{\bullet} . The trace over A^{\bullet} spin states is also taken in this basis. It should be emphasized that eqns. (12) and (21) are valid only in the case of equal population of spin states of the radical centre R^{\bullet} at the initial moment of time. This is true for not too strong magnetic fields, when it is possible to neglect the Boltzmann difference of spin level populations of the radical R^{\bullet} .

In several cases considered below we managed to obtain analytical expressions for $T_{ik}^A(t)$, and, hence, for $\rho_{DA,SS}(t)$.

III. Results and discussion

Neglecting spin–spin interactions between radical ion D^{+*} and biradical A^{\bullet} – Sp – R^{\bullet} allows one to express the spin dynamics of the system through independent dynamics of the radical ion and the biradical. Thus for understanding the behavior of a joint radical ion/biradical spin system in an external magnetic field, it will suffice to consider the biradical spin states with varying the magnetic field. There are three regions of magnetic fields where the spin dynamics of the biradical and, hence, that of RIBIP, differ from each other significantly. The weak magnetic field region extends from zero magnetic field to fields comparable with the hyperfine coupling constant A in the radical R^{\bullet} . The second region covers strong magnetic fields where Larmor frequencies considerably exceed the hyperfine coupling constant, yet the spin system is far from the region of J -resonance, *i.e.* the following inequalities hold true: $\omega_0 = B \gg A$ and $|B - J| \gg A$, the latter meaning that B can be both above or below J . The third region is the J -resonance region, where $|B - J| \sim A$.

For nuclear spin 1/2 the spin level diagrams of the *biradical* for these three regions are represented in Fig. 1. The spin wave functions corresponding to these levels are defined as direct products of the electron spin functions in the singlet-triplet basis and the nuclear spin functions in Zeeman basis, α_N , β_N . For convenience, for each region of magnetic field, these spin functions are arranged in two columns, corresponding to different nuclear spin projections. Generally speaking, these functions are not eigenfunctions of the biradical spin Hamiltonian (20). Thus, the RIBIP Hamiltonian has non-zero matrix elements between some of them. These couplings are marked on the diagram by dashed lines if consideration of non-zero Hamiltonian matrix elements is essential. This is the case if the value of a matrix element between two spin functions is

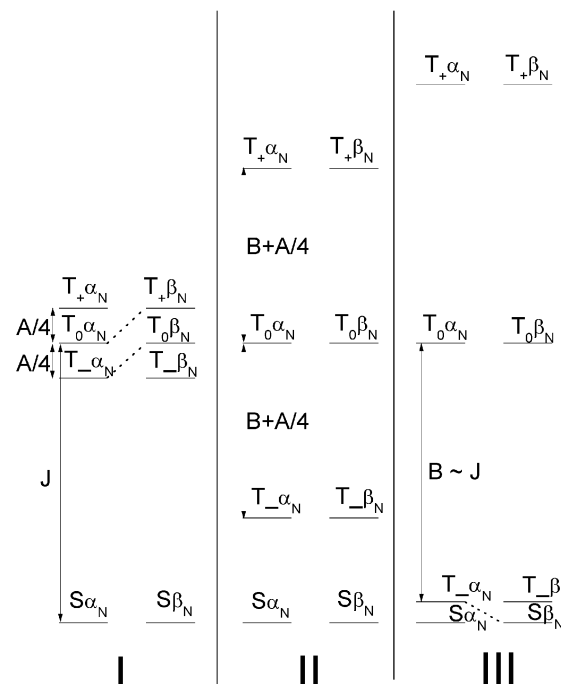


Fig. 1 Spin level scheme for a biradical ion in magnetic field for: (I) $B = 0$; (II) $B, |B - J| \gg A$; (III) $|B - J| \sim A$ (see text for details).

comparable with the energy difference between these two levels. For instance, for zero (or weak, of the order of the hyperfine coupling constant) magnetic field, the matrix element between $T_{0\alpha_N}$ and $T_{-\beta_N}$, as well as between $T_{-\alpha_N}$ and $T_{0\beta_N}$ states is equal to $A/2\sqrt{2}$ and is comparable with the energy gap between the two states ($A/4$ in zero magnetic field). Alternatively, though there is a non-zero matrix element of $A/4$ between $T_{0\alpha_N}$ and S_{α_N} , as well as between the $T_{0\beta_N}$ and S_{β_N} , it can be neglected for any value of B , since the energy difference between these levels equals J which exceeds this matrix element by far. This mixing is therefore energy forbidden. In strong magnetic fields, but far from J -resonance (region II) the states $T_{0\alpha_N}$ and $T_{-\beta_N}$, as well as $T_{-\alpha_N}$ and $T_{0\beta_N}$ no longer mix up. Thus all the states depicted in Fig. 1 for region II become eigenstates of the biradical spin Hamiltonian. To be more precise, spin functions of these states are eigenfunctions with the accuracy of the order A/J or A/ω_0 in spin function amplitudes. In this region of magnetic fields, both values A/J and A/ω_0 are considered to be much less than unity.

In the region of J -resonance, when $|B - J| \sim A$, there is essential mixing between the $T_{-\alpha_N}$ and S_{β_N} states. Thus, one may expect that when passing from region II to region III and again to region II (with further increasing of the magnetic field) recombination fluorescence exhibits resonance behaviour.

A. Spin dynamics in zero and weak magnetic fields

For $B = 0$ we managed to obtain an analytical expression for the singlet state population $\rho_{DA,SS}(B = 0, t)$. In the absence of hyperfine coupling in the radical ion D^{+*} and for a spin-1/2 nucleus located on radical ion R^{\bullet} , the expression for the singlet state population is:

$$\rho_{DA,SS}(B = 0, t) = \frac{1}{4} + \frac{3}{8}\Phi_1$$

$$\text{Here } \Phi_1 = \frac{1}{9\Omega^2} [(10\Omega^2 - 3J^2) + 3J^2 \cos(\Omega t) + 2(2\Omega^2 + 2A\Omega - \Omega J) \cos\left(\frac{A+J-\Omega}{2}t\right) + 2(2\Omega^2 - 2A\Omega + J\Omega) \cos\left(\frac{A+\Omega+J}{2}t\right)] \quad (22)$$

and $\Omega = (A^2 + J^2 - AJ)^{1/2}$.

When the spin-1/2 nucleus is located on A^{••}, one obtains:

$$\rho_{\text{DA,SS}}(B=0, t) = \frac{1}{4} + \frac{3}{8} \Phi_2$$

$$\begin{aligned} \text{Here } \Phi_2 = & \frac{1}{9\Omega^2} \left[(3A^2 + 3J^2 + 4\Omega^2) + 3(A-J)^2 \cos(\Omega t) \right. \\ & + 2(2\Omega^2 - A\Omega - J\Omega) \cos\left(\frac{A+J-\Omega}{2}t\right) \\ & \left. + 2(2\Omega^2 + A\Omega + J\Omega) \cos\left(\frac{A+\Omega+J}{2}t\right) \right] \end{aligned} \quad (23)$$

For a radical ion D^{••} having a broad hyperfine structure and for location of the magnetic nucleus on R[•], the singlet state population is given by:

$$\rho_{\text{DA,SS}}(B=0, t) = \frac{1}{4} + \frac{1}{8} \Phi_1 \quad (24)$$

while for a magnetic nucleus located on A^{••}

$$\rho_{\text{DA,SS}}(B=0, t) = \frac{1}{4} + \frac{1}{8} \Phi_2 \quad (25)$$

where Φ_1 and Φ_2 are the same as in (22) and (23).

It should be emphasized, that expressions (22–25) are valid for arbitrary values (not only for $J \gg A$) and signs of J and A .

For a considered case of strong exchange interaction, *i.e.*, when $J \gg A$, one can easily obtain: $\Omega \approx J - A/2$. Consequently, $\rho_{\text{DA,SS}}(B=0, t)$ given by eqns. (22)–(25) involves harmonics with frequencies close to J . As we suppose that $J\tau_0 \gg 1$, these high-frequency harmonics, when integrating according to formula (9) are averaged to zero and their contribution in fluorescence kinetics $I(t)$ can be neglected. Thus it makes sense to analyze only the slowly changing part (in the time scale $1/J$) of $\rho_{\text{DA,SS}}(t)$. Denoting the slow part as $\bar{\rho}_{\text{DA,SS}}(t)$, for the absence of hyperfine coupling in D^{••} we obtain the following simple expression for $\bar{\rho}_{\text{DA,SS}}(t)$:

$$\bar{\rho}_{\text{DA,SS}}(B=0, t) = \frac{13}{24} + \frac{1}{12} \cos\left(\frac{3}{4}At\right) \quad (26)$$

irrespective of whether the magnetic nucleus is located on A^{••} or on R[•].

For a broad hyperfine structure of radical ion D^{••} we have:

$$\bar{\rho}_{\text{DA,SS}}(B=0, t) = \frac{25}{72} + \frac{1}{36} \cos\left(\frac{3}{4}At\right) \quad (27)$$

again independent of where the magnetic nucleus is located in the biradical.

It was shown,²² that oscillation frequencies of singlet state population (or population of any other state) are equal to the differences of stationary energies of the spin system (in the absence of or neglecting paramagnetic relaxation). If spin-spin couplings between radical ion and biradical can be neglected, a spin eigenfunction of the radical + biradical system is given by the product of a spin eigenfunction of the biradical and that of the radical ion, and the energy of the three-spin eigenstate is equal to the sum of the energies of biradical and radical ion spin eigenstates. By using this approach it can easily be shown that the oscillation frequency of the singlet state population in zero magnetic field is equal either to $\frac{3}{4}A$ or to the value close to J , which is in agreement with eqns. (22)–(27).

It is of interest to compare the obtained results for singlet state population $\bar{\rho}_{\text{DA,SS}}(B=0, t)$ with those in the absence of exchange interaction in the biradical. Substitution of $J=0$ into eqns. (22)–(25) yields the following results for the singlet state population. For the absence of hyperfine coupling in D^{••}

$$\bar{\rho}_{\text{DA,SS}}(B=0, t) = \frac{5}{8} + \frac{3}{8} \cos At \quad (28)$$

and for the broad hyperfine structure in D^{••}:

$$\bar{\rho}_{\text{DA,SS}}(B=0, t) = \frac{3}{8} + \frac{1}{8} \cos At \quad (29)$$

Eqns. (28) and (29) reproduce the well-known results for radical ion pairs.^{4,21,23,24} Thus, the strong exchange interaction manifests itself as a decrease of the oscillation frequency in zero field from A to $\frac{3}{4}A$.

For a weak (less than hyperfine coupling constant A) non-zero magnetic field the analytical expressions for $\rho_{\text{DA,SS}}(t)$ are rather cumbersome even if one neglect energy forbidden transitions between singlet and triplet biradical spin states. Therefore for this range of magnetic fields we have performed numerical calculations with exact consideration of all terms of the RIBIP Hamiltonian, eqn. (6). Let us define the fluorescence intensity $I(t)$ as a product of singlet state population $\rho_{\text{DA,SS}}(B, t)$ and the normalized exponential recombination function $F(t) = (1/\tau_0)\exp(-t/\tau_0)$. In its turn let us define the function $\bar{I}(t)$ as a product of the slowly changing part of the singlet state population $\bar{\rho}_{\text{DA,SS}}(B, t)$ and the exponential recombination function $F(t) = (1/\tau_0)\exp(-t/\tau_0)$. Computation of $\bar{\rho}_{\text{DA,SS}}(B, t)$ was performed by the formula:

$$\bar{\rho}_{\text{DA,SS}}(B, t) = \frac{1}{2} [\rho_{\text{DA,SS}}(B, t) + \rho_{\text{DA,SS}}(B, t + \pi/J)] \quad (30)$$

where the kinetics $\rho_{\text{DA,SS}}(B, t)$ and $\rho_{\text{DA,SS}}(B, t + \pi/J)$ were being calculated numerically. It is easy to show that harmonics with frequency J in $\rho_{\text{DA,SS}}(B, t)$ become equal to zero in $\bar{\rho}_{\text{DA,SS}}(B, t)$. Also, the amplitude of harmonics with frequencies χ close to J (*i.e.* $(\chi - J)/J \ll 1$) in $\rho_{\text{DA,SS}}(B, t)$ is multiplied by a small quantity $(\chi - J)/J$ in $\bar{\rho}_{\text{DA,SS}}(B, t)$. Obviously $I(0) = F(0) = 1/\tau_0$, since $\rho_{\text{DA,SS}}(0) = 1$. The numerically calculated decays of fluorescence intensity $\bar{I}(t)$ in $I(0)$ units are presented in Fig. 2 for a number of magnetic field strengths and recombination lifetime $\tau_0 = 50$ ns. The kinetics of Fig. 2 have been calculated for the absence of hyperfine couplings in the radical ion D^{••} and for a hyperfine coupling constant $A = 3$ mT and an exchange integral $J = 500$ mT. As is seen from Fig. 2, the oscillation frequency of fluorescence kinetics in zero magnetic field is higher than that in a strong magnetic field (at $B = 60$ mT $\gg A = 3$ mT) and as it will be shown in the following subsection, their ratio is equal to three. Also it is easy to see,

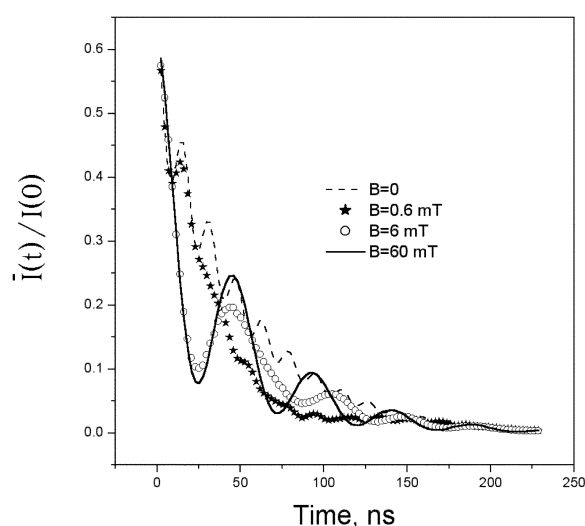


Fig. 2 Fluorescence kinetics in weak magnetic fields. The radical ion D^{••} does not contain magnetic nuclei. Recombination function $F(t) = (1/\tau_0)\exp(-t/\tau_0)$, $\tau_0 = 50$ ns, hyperfine coupling constant $A = 3$ mT, $J = 500$ mT. $\bar{I}(t)$ is the slowly changing part of fluorescence intensity.

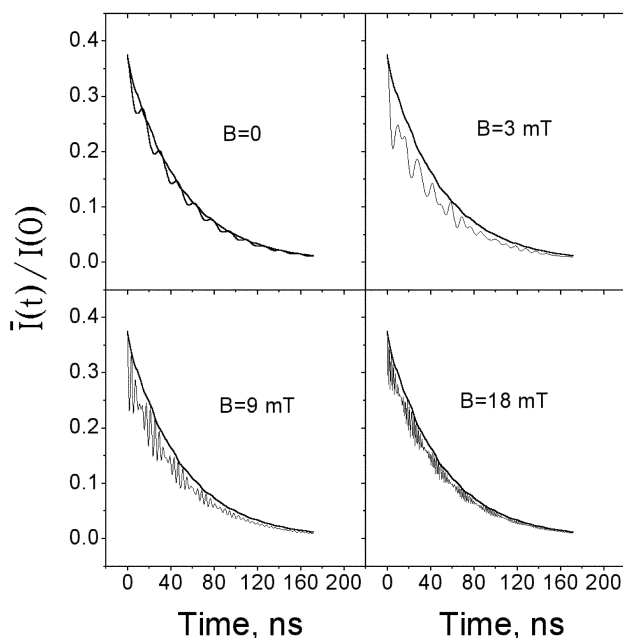


Fig. 3 Fluorescence kinetics in weak magnetic fields. The radical ion $D^{+\bullet}$ has a broad hyperfine structure with second moment $\sigma^2 = 10^2 \text{ mT}^2$. Recombination function $F(t) = (1/\tau_0)\exp(-t/\tau_0)$, $\tau_0 = 50 \text{ ns}$, hyperfine coupling constant $A = 3 \text{ mT}$, $J = 500 \text{ mT}$. $\bar{I}(t)$ is the slowly changing part of fluorescence intensity.

that with increasing magnetic field, the fluorescence kinetics $I(t)$ at short times resembles the one in a strong magnetic field.

Fig. 3 presents kinetic curves $\bar{I}(t)/I(0)$ for the case when the radical ion $D^{+\bullet}$ has a broad hyperfine structure. The second moment σ^2 of the hyperfine structure was chosen equal to 10^2 mT^2 . For calculations of T_{ik}^D , $i, k = x, y, z$ the relation (16) was employed. On each plot of Fig. 3 alongside with fluorescence kinetics for magnetic fields from $B = 0$ to $B = 18 \text{ mT}$, kinetics for a strong magnetic field $B = 60 \text{ mT}$ (thick line) is also shown. Since harmonics with frequencies close to J are numerically filtered, the value $\bar{\rho}_{DA,SS}(t)$ for $B = 60 \text{ mT}$ practically does not depend on time and as it will be shown below, is close to the value $\frac{3}{8}$. Thus the kinetics $\bar{I}(t)/I(0)$ for a strong magnetic field actually follows (with a factor $\frac{3}{8}$) the exponential function $\exp(-t/\tau_0)$.

As is seen from the plots of Fig. 3 for magnetic fields of the order of several times the hyperfine coupling constant A , the kinetics contain both high and low frequencies and essentially differ from that in zero or strong magnetic field. The presence of these high-frequency oscillating components is determined by contribution of terms of the type $T_{xx}^D T_{xx}^A$ and $T_{yy}^D T_{yy}^A$ to $\bar{\rho}_{DA,SS}(t)$ (see (12)). As the magnetic field increases, at $B > \sigma$, this contribution decreases and tends to zero, since $T_{xx}^D, T_{yy}^D \rightarrow 0$. As is clearly seen from Fig. 3, the frequencies of oscillations increase, but their amplitudes decrease with increasing magnetic field, the curves “nestle up” to the one for $B = 60 \text{ mT}$.

Note, that for strong exchange interaction the singlet states $S\alpha_N$ and $S\beta_N$ are spin eigenstates of the biradical spin Hamiltonian for all magnetic fields, excluding the J -resonance region. Their account in spin evolution, obviously, causes oscillations in $\rho_{DA,SS}(t)$ with frequency J which are filtered numerically for kinetics in Fig. 3. As the values T_{ik}^D are considered to be time independent (for a broad hyperfine structure in $D^{+\bullet}$), the low frequencies of $I(t)$ are determined by the energy differences $(\mathcal{E}_i - \mathcal{E}_j)$ only, where $\mathcal{E}_i, \mathcal{E}_j$ are energies of the spin eigenstates of the biradical, which are determined exclusively by triplet state mixing. Finding \mathcal{E}_i is rather

straightforward, and they are equal to:

$$\begin{aligned}\mathcal{E}_1 &= B + J/4 + A/4, \\ \mathcal{E}_2 &= \frac{B - A/4}{2} + \frac{J}{4} + \frac{1}{2} \sqrt{\left(B - \frac{A}{4}\right)^2 + \frac{A^2}{2}}, \\ \mathcal{E}_3 &= \frac{B - A/4}{2} + \frac{J}{4} - \frac{1}{2} \sqrt{\left(B - \frac{A}{4}\right)^2 + \frac{A^2}{2}}, \\ \mathcal{E}_4 &= -\frac{B + A/4}{2} + \frac{J}{4} + \frac{1}{2} \sqrt{\left(B + \frac{A}{4}\right)^2 + \frac{A^2}{2}}, \\ \mathcal{E}_5 &= -\frac{B + A/4}{2} + \frac{J}{4} - \frac{1}{2} \sqrt{\left(B + \frac{A}{4}\right)^2 + \frac{A^2}{2}}, \\ \mathcal{E}_6 &= -B + J/4 + A/4,\end{aligned}\quad (31)$$

For $B \gg A$ the difference $(\mathcal{E}_i - \mathcal{E}_j)$ can take six non-zero values: $A/2, \omega_0 - A/4, \omega_0 + A/4, 2\omega_0, 2\omega_0 - A/2, 2\omega_0 + A/2$. Therefore for $B \gg A$ the $\bar{I}(t)$ kinetics can contain up to six harmonics, their amplitudes being not small, as long as $B \leq \sigma$.

B. Spin dynamics in a strong magnetic field far from the J -resonance region

In a strong magnetic field, *i.e.* much exceeding the hyperfine coupling constants in both radical ion and biradical, the non-secular part of the hyperfine coupling in the Hamiltonian, eqn. (6), can be completely neglected, as flip-flop transitions with simultaneous inversion of electron and nuclear spins are energy forbidden. This is true for all strong magnetic fields, excluding the region of J -resonance, when $|B - J| \sim A$ (case III in Fig. 1) which we shall consider in the following subsection. On neglecting the non-secular part of hyperfine couplings it is obvious, that the RIBIP spin Hamiltonian, \hat{H}_{RIBIP} can be put in the following form:

$$\hat{H}_{\text{RIBIP}} = \omega_D \hat{S}_{Dz} + \omega_A \hat{S}_{Az} + \omega_R \hat{S}_{Rz} + J \hat{S}_A \hat{S}_R \quad (32)$$

for any number of magnetic nuclei in the radical ion and the biradical. For instance, for the considered model of biradical one has: $\omega_A = \omega_0$, $\omega_R = \omega_0 \pm A/2$, depending on the nuclear spin projection $I_z^R = \pm \frac{1}{2}$ (for a spin-1/2 nucleus located on R^\bullet). The frequency ω_D equals ω_0 in the absence of hyperfine coupling in the radical ion $D^{+\bullet}$, and $\omega_D = \omega_0 + \sum_{i=1}^N a_i I_{iz}^D$ in the presence of magnetic nuclei, where I_{iz}^D are the z -projections of i -nuclear spin in the radical ion $D^{+\bullet}$.

The RIBIP Hamiltonian also has the same form, eqn. (32), in the case of unequal g -factors of the radicals $D^{+\bullet}$, A^{\bullet} and R^\bullet .

Starting from Hamiltonian, eqn. (32), we obtain the following analytical expression for $\rho_{DA,SS}(B, t)$:

$$\begin{aligned}\rho_{DA,SS}(B, t) &= \frac{1}{4} + \frac{1}{8Q^2} \left\{ 2\nu^2 + J^2 + Q(Q - \nu) \cos\left(\frac{\omega_A + \omega_R - 2\omega_D - J - Q}{2}t\right) \right. \\ &\quad + Q(Q - \nu) \cos\left(\frac{\omega_A + \omega_R - 2\omega_D + J - Q}{2}t\right) + J^2 \cos(Qt) \\ &\quad + Q(Q + \nu) \cos\left(\frac{\omega_A + \omega_R - 2\omega_D - J + Q}{2}t\right) \\ &\quad \left. + Q(Q + \nu) \cos\left(\frac{\omega_A + \omega_R - 2\omega_D + J + Q}{2}t\right) \right\} \quad (33)\end{aligned}$$

where $Q^2 = (\omega_A - \omega_R)^2 + J^2$, $\nu = \omega_A - \omega_R$. Then for $\bar{\rho}_{DA,SS}(B, t)$ from eqn. (33) we obtain:

$$\bar{\rho}_{DA,SS}(B, t) = \frac{3}{8} + \frac{1}{4} \cos\left(\frac{\omega_A + \omega_R - 2\omega_D}{2}t\right) \quad (34)$$

Eqns. (33) and (34) are also valid for negative J . As it follows from eqn. (34) for a one-nucleus biradical in the absence of hyperfine coupling in the radical ion $D^{+\bullet}$ the singlet state

population $\bar{\rho}_{\text{DA,SS}}(B, t)$ is given by:

$$\bar{\rho}_{\text{DA,SS}}(B, t) = \frac{3}{8} + \frac{1}{4} \cos\left(\frac{A}{4}t\right) \quad (35)$$

independent of the position of the magnetic nucleus in the biradical.

Thus, oscillation frequencies of $\bar{\rho}_{\text{DA,SS}}(B, t)$, and consequently of $\bar{I}(t)$, in zero and high magnetic field differ by a factor of three (see also Fig. 2) and are equal to $\frac{3}{4}A$ and to $A/4$, respectively.

In another case when the radical ion $\text{D}^{+\bullet}$ has a broad hyperfine structure, the cosine in eqn. (34) is averaged to zero, and for $\bar{\rho}_{\text{DA,SS}}(B, t)$ we obtain the result announced in the preceding subsection:

$$\bar{\rho}_{\text{DA,SS}}(B, t) = \frac{3}{8} \quad (36)$$

In the absence of exchange interaction, substituting $J = 0$ in eqn. (33), we obtain for the absence of hyperfine coupling in the radical ion $\text{D}^{+\bullet}$ the well-known result:²⁵

$$\rho_{\text{DA,SS}}(B, t) = \bar{\rho}_{\text{DA,SS}}(B, t) = \frac{1}{2} + \frac{1}{2} \cos(\omega_A - \omega_D)t \quad (37)$$

When the spin-1/2 nucleus is located on A^{\bullet} , we have:

$$\rho_{\text{DA,SS}}(B, t) = \bar{\rho}_{\text{DA,SS}}(B, t) = \frac{1}{2} + \frac{1}{2} \cos\left(\frac{A}{2}t\right) \quad (38)$$

Therefore exchange interaction in high magnetic fields manifests itself as a decrease of the oscillation frequency of singlet state population $\bar{\rho}_{\text{DA,SS}}(B, t)$ from $A/2$ to $A/4$.

For a radical ion $\text{D}^{+\bullet}$ with a broad hyperfine structure, and in the absence of exchange interaction, the singlet state population $\rho_{\text{DA,SS}}(B, t)$ quickly reaches its stationary value:

$$\rho_{\text{DA,SS}}(B, t) = \bar{\rho}_{\text{DA,SS}}(B, t) = \frac{1}{2} \quad (39)$$

Therefore exchange interaction decreases this stationary value from 1/2 to 3/8.

C. Spin dynamics in the J -resonance region

In a magnetic field close to the value of the exchange integral (within the accuracy of the hyperfine coupling constant A) it is important to take into account mixing of $T_{-}\alpha_N$ and $S\beta_N$ states (case III in Fig. 1) with matrix element $A/2\sqrt{2}$.

The mixing of these states has a resonance dependence on B in passing through the region $B \sim J$. Neglecting the energy forbidden transitions, such as $S\alpha_N \leftrightarrow T_0\alpha_N$, for the absence of hyperfine coupling in the radical ion $\text{D}^{+\bullet}$ one can obtain the following analytical expression for the singlet state population:

$$\begin{aligned} \rho_{\text{DA,SS}}(t) = & \frac{3}{8} + \frac{1}{16} \left\{ 3 \cos \frac{At}{4} + \cos \left(J + \frac{A}{4} \right) t \right. \\ & + \sin^2 \varphi \left[\cos \left(E_2 + \frac{A}{4} - \frac{J}{4} \right) t \right. \\ & + \cos \left(E_2 - \frac{A+J}{4} \right) t + \cos \left(E_1 + \omega_0 - \frac{J}{4} \right) t \\ & + \cos \left(E_1 + \omega_0 + \frac{3J}{4} \right) t \left. \right] + \cos^2 \varphi \left[\cos \left(E_1 - \frac{J-A}{4} \right) t \right. \\ & + \cos \left(E_1 - \frac{A+J}{4} \right) t + \cos \left(E_2 + \omega_0 - \frac{J}{4} \right) t \\ & + \cos \left(E_2 + \omega_0 + \frac{3J}{4} \right) t \left. \right] + \cos Jt \\ & + \sin^2 \varphi \cos \left(E_2 - \frac{J}{4} \right) t + \cos^2 \varphi \cos \left(E_1 - \frac{J}{4} \right) t \left. \right\} \\ & - \frac{1}{64} \frac{A^2}{Z^2} (1 - \cos Zt) \end{aligned} \quad (40)$$

where

$$\begin{aligned} Z = & \sqrt{\left(\omega_0 - J + \frac{A}{4} \right)^2 + \frac{A^2}{2}}; \\ \cos^2 \varphi = & \frac{1}{2} \left(1 + \frac{\omega_0 - J + \frac{A}{4}}{Z} \right); \\ \sin^2 \varphi = & \frac{1}{2} \left(1 - \frac{\omega_0 - J + \frac{A}{4}}{Z} \right); \\ E_1 = & - \left(\frac{J}{4} + \frac{\omega_0}{2} + \frac{A}{8} \right) + \frac{1}{2} Z; \\ E_2 = & - \left(\frac{J}{4} + \frac{\omega_0}{2} + \frac{A}{8} \right) - \frac{1}{2} Z; \end{aligned} \quad (41)$$

For a radical ion $\text{D}^{+\bullet}$ with a broad hyperfine structure, the expression for the singlet state population is much simpler:

$$\begin{aligned} \rho_{\text{DA,SS}}(t) = & \frac{3}{8} + \frac{1}{16} \left[\cos^2 \varphi \cos \left(E_1 - \frac{J}{4} \right) t \right. \\ & + \sin^2 \varphi \cos \left(E_2 - \frac{J}{4} \right) t \left. \right] \\ & - \frac{1}{64} \frac{A^2}{Z^2} (1 - \cos Zt) + \frac{1}{16} \cos Jt \end{aligned} \quad (42)$$

For the derivation of eqn. (42) we used eqn. (18) for T_{zz}^D , which implies $B \gg \sigma$. It is obvious, that in the absence of hyperfine coupling in $\text{D}^{+\bullet}$ the eqn. (40) well describes spin dynamics for a magnetic field $B \gg A$, i.e., for regions II and III in Fig. 1. For a broad hyperfine structure of $\text{D}^{+\bullet}$ eqn. (42) describes spin dynamics well for $B \gg \max(A, \sigma)$. But applicability of both eqn. (40) and eqn. (42) has a restriction on time t . When deriving eqns. (40) and (42) we neglected the energy-forbidden transitions, such as $S\alpha_N \leftrightarrow T_0\alpha_N$. Their consideration would give a correction to frequencies in eqns. (40) and (42) of the order A^2/J , A^2/ω_0 . It is obvious that these corrections can be neglected at instant t , if the conditions $(A^2/J)t \ll 1$, $(A^2/\omega_0)t \ll 1$ are met. Thus the eqns. (40) and (42) well describe the singlet state population kinetics in the time domain: $t < \min(J/A^2, \omega_0/A^2)$, where J , A , ω_0 are taken in frequency units. This conclusion is verified by comparison of calculations using (40) with exact numerical calculations taking account of all terms of RIBIP Hamiltonian. Such a comparison for $B = J = 500$ mT and $A = 3$ mT shows excellent coincidence up to 200 nanoseconds. This is in a good agreement with the above stated criteria, since in this case $J/A^2 = 315$ ns. Calculations with the same values of B and J but with $A = 1$ mT give coincidence for much longer time up to 1200 ns. This is also in good agreement with the criteria, since $J/A^2 = 2840$ ns in this case.

Note, that for $J < 0$ the J -resonance occurs at $B \sim |J|$, and its appearance is due to resonance mixing of $S\alpha_N$ and $T_{+}\beta_N$ states. To adjust eqns. (40) and (41) for $J < 0$ one has to replace in eqns. (40) and (41): $J \rightarrow |J|$ and $A \rightarrow -A$.

It is easy to see that in the region of J -resonance $\rho_{\text{DA,SS}}(t)$ contains both low- and high-frequency harmonics, the latter with frequency close to J . This is true not only for the region of J -resonance, but for any strong magnetic field $B \gg \max(A, \sigma)$. Indeed, to analyze harmonics in eqns. (40) and (42) in magnetic fields far from J -resonance, i.e. when $|\omega_0 - J| \gg A$, we consider the variation of $\sin^2 \varphi$ and $\cos^2 \varphi$ with the magnetic field. It is easy to see, that to the left of the J -resonance $\cos^2 \varphi$ tends to zero and $\sin^2 \varphi \sim 1$, and, on the contrary, to the right of the resonance $\cos^2 \varphi \sim 1$, $\sin^2 \varphi \sim 0$. Analyze now, for instance, the term $\sin^2 \varphi \cos(E_2 + A/4 - J/4)t$ in eqn. (40). When $\omega_0 < J$ (both close to the resonance or far from it), the frequency $E_2 + A/4 - J/4$ is close (by absolute value) to J and $\sin^2 \varphi \sim 1$. For $\omega_0 > J$ and $|\omega_0 - J| \gg A$ this frequency tends to ω_0 , but

$\sin^2 \varphi \sim 0$, so one can neglect the term $\sin^2 \varphi \cos(E_2 + A/4 - J/4)t$ in this region. Thus, the term $\sin^2 \varphi \cos(E_2 + A/4 - J/4)t$ either oscillates with high-frequency J , or is negligible.

A similar analysis for other terms in eqns. (40) and (42) leads to the conclusion that the frequency spectrum of the kinetics as given by eqns. (40) and (42) in strong magnetic fields contains either low-frequency components (frequencies comparable with the hyperfine coupling constant A), or high-frequency components with frequencies close to J (to within the hyperfine coupling constant A). Components with other frequencies are negligible in amplitude.

Keeping only low-frequency harmonics in eqn. (40) (i.e. filtering harmonics with frequencies close to J) one can obtain the following expression for $\bar{\rho}_{\text{DA,SS}}(t)$:

$$\begin{aligned} \bar{\rho}_{\text{DA,SS}}(t) = & \frac{3}{8} + \frac{1}{16} \left\{ 3 \cos \frac{At}{4} + \sin^2 \varphi \cos \left(E_1 + \omega_0 - \frac{J}{4} \right) t \right. \\ & \left. + \cos^2 \varphi \cos \left(E_2 + \omega_0 - \frac{J}{4} \right) t \right\} \\ & - \frac{1}{64} \frac{A^2/2}{Z^2} (1 - \cos Zt) \end{aligned} \quad (43)$$

Performing the same procedure for eqn. (42), we obtain an even simpler expression for $\bar{\rho}_{\text{DA,SS}}(t)$:

$$\bar{\rho}_{\text{DA,SS}}(t) = \frac{3}{8} - \frac{1}{64} \frac{A^2/2}{Z^2} (1 - \cos Zt) \quad (44)$$

The last term $(1/128)(A^2/Z^2)(1 - \cos Zt)$ in eqns. (43) and (44) exhibits a resonance at $\omega_0 = J - A/4$ and coincides with the quantum dynamics of a two-level EPR spin system in the rotating frame to within a numerical factor.²⁶

One can establish the following correspondence with a EPR two-level spin system: the value $(\omega_0 - J + A/4)$ corresponds to the splitting between spin levels in the rotating (with the frequency of the resonant magnetic field) frame, whereas the matrix element $A/2\sqrt{2}$ between the states corresponds to the amplitude of the resonant magnetic field (see²⁶). It is obvious that in our case this two-level system comprises the pair of spin states $T_{-\alpha}$ and $S\beta$.

In Fig. 4 there are represented numerically calculated dependences $\bar{I}(t)/I(0)$ for a set of magnetic fields B , for the absence of hyperfine coupling (Fig. 4a) and for a broad hyperfine structure (Fig. 4b) in the radical ion $D^{+\bullet}$. One can see that the form of the kinetic curves distinctly changes upon the passage through the resonance region $B \sim J$.

D. MARY spectra

The J -resonance at region $B \sim J$ is especially well pronounced in the yield of fluorescence $I_{\text{fl}}(B)$, defined as:

$$I_{\text{fl}}(B) = \int_0^\infty I(t) dt \quad (45)$$

Assume for simplicity the recombination function $F(t)$ to be an exponential function

$$F(t) = \frac{1}{\tau_0} \exp(-t/\tau_0)$$

Then the contribution $\Delta I_{\text{fl}}(B)$ of the term $(1/128)(A^2/Z^2)(1 - \cos Zt)$ in eqns. (43) and (44) to MARY (magnetic field effect on reaction yield) spectrum is as follows:

$$\Delta I_{\text{fl}}(B) = -\frac{1}{64} \frac{A^2/2}{(\omega_0 - J + A/4)^2 + \left(\frac{1}{\tau_0^2} + A^2/2 \right)} \quad (46)$$

It is easy to see that, apart from the sign, this contribution is described by a Lorentzian function with a minimum (because of a negative sign) in the magnetic field $B = (J - A/4)$. The width of the resonance is determined by the inverse of the

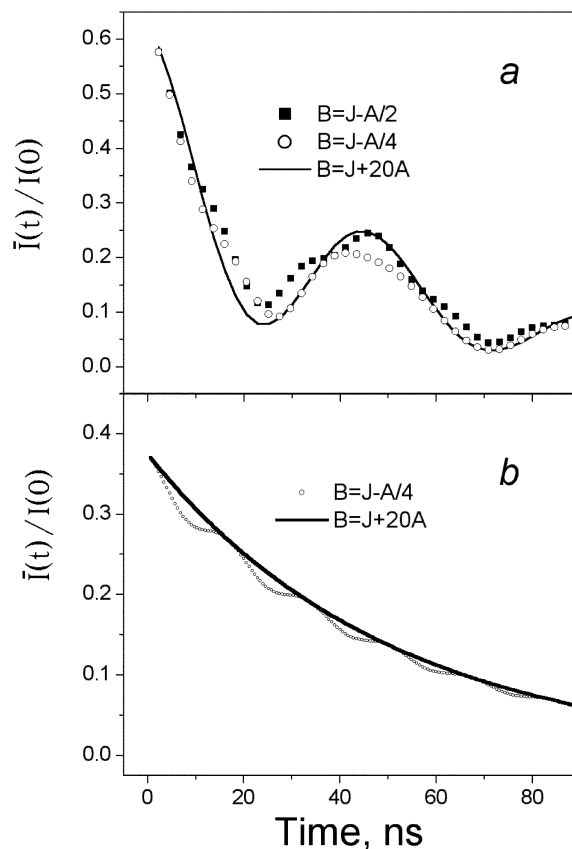


Fig. 4 Fluorescence kinetics in the J -resonance region: a. The radical ion $D^{+\bullet}$ does not contain magnetic nuclei. b. Radical-ion $D^{+\bullet}$ has broad hyperfine structure with second moment $\sigma^2 = 10^2 \text{ mT}^2$. Recombination function $F(t) = 1/\tau_0 \exp(-t/\tau_0)$, $\tau_0 = 50 \text{ ns}$, hyperfine coupling constant $A = 3 \text{ mT}$, $J = 500 \text{ mT}$. $\bar{I}(t)$ is the slowly changing part of fluorescence intensity.

RIBIP lifetime $1/\tau_0$ and the hyperfine coupling constant A . The fact that the resonance occurs at a magnetic field $B = (J - A/4)$, instead of $B = J$ is due to the energy shift of the state $T_{-\alpha_N}$ by the value of $A/4$ because of contribution of the secular part of hyperfine coupling, $A I_z S_{Az}$. While for $\bar{\rho}_{\text{DA,SS}}(t)$ in eqn. (44) the MARY spectrum is described to within a constant by a Lorentzian function, for the kinetics determined by eqn. (43), i.e. for the absence of hyperfine coupling in the radical ion $D^{+\bullet}$, the MARY spectrum has a more complex form. For $F(t) = (1/\tau_0) \exp(-t/\tau_0)$ we have the following expression for the MARY spectrum $I_{\text{fl}}(B)$:

$$\begin{aligned} I_{\text{fl}}(B) = & \frac{3}{8} + \frac{1}{16} \left\{ \frac{3}{1 + \frac{A^2 \tau_0^2}{16}} + \frac{\sin^2 \varphi}{1 + \Omega_1^2 \tau_0^2} \right. \\ & \left. + \frac{\cos^2 \varphi}{1 + \Omega_2^2 \tau_0^2} - \frac{1}{8} \frac{A^2 \tau_0^2}{1 + Z^2 \tau_0^2} \right\} \end{aligned} \quad (47)$$

here

$$\Omega_1 = E_1 + \omega_0 - \frac{J}{4}, \quad \Omega_2 = E_2 + \omega_0 - \frac{J}{4}$$

Let us analyze the magnetic field dependence of frequencies Ω_1 , Ω_2 in the J -resonance region. When passing through the resonance with increasing magnetic field, frequency Ω_1 starts to rise, but at the same time (far from the J -resonance) the factor $\sin^2 \varphi$ tends to zero and makes the contribution of the term containing this frequency insignificant. A similar effect occurs for Ω_2 , but in this case its high-frequency contribution is hampered by the factor $\cos^2 \varphi$.

From these two frequencies Ω_1 , Ω_2 only one, Ω_1 , turns to zero, it occurs at $\omega_0 = J - A/2$.

The linear expansion of Ω_1 in the vicinity of $\omega_0 = J - A/2$ gives:

$$\Omega_1 = \frac{1}{3} \left(\omega_0 - J + \frac{A}{2} \right),$$

Substitution of this expansion in (47) gives for $I_{\text{fl}}(B)$:

$$I_{\text{fl}}(B) = \frac{3}{8} + \frac{1}{16} \left\{ \frac{3}{1 + \frac{A^2 \tau_0^2}{16}} + \frac{\sin^2 \varphi}{1 + \frac{1}{9} \left(\omega_0 - J + \frac{A}{2} \right)^2 \tau_0^2} + \frac{\cos^2 \varphi}{1 + \frac{1}{9} \left(\omega_0 - J + \frac{A}{2} \right)^2 \tau_0^2} - \frac{1}{8} \frac{A^2 \tau_0^2}{1 + Z^2 \tau_0^2} \right\} \quad (48)$$

Now it is clearly seen that the second term in eqn. (48) is a Lorentzian function with a maximum at $\omega = J - A/2$ and with the width determined by inverse of the lifetime $1/\tau_0$, in contrast to the fourth term in eqn. (48) described by a Lorentzian function with its centre at $\omega = J - A/4$ and with the width of the order of $\max(A, 1/\tau_0)$. Note, that these resonances are opposite in sign. Thus, if, for instance, $A > 1/\tau_0$ then the MARY spectrum in the J -resonance region is described by a wide resonant trough centered at $\omega_0 = J - A/4$ with a width of A , and overlapped by a narrow resonant peak centered at $\omega_0 = J - A/2$.

The occurrence of this narrow resonant line is caused, obviously, by the concurrence of the Larmor frequency ω_0 of the radical ion $D^{+\bullet}$ (in the absence of hyperfine coupling in $D^{+\bullet}$) with one of the frequencies determining spin evolution of biradical at $B = J - A/2$. In other words, the frequency spectrum of $\hat{\rho}_{\text{DA,ss}}(t)$ is determined by differences²² $(E_i - E_j)/\hbar$, where E_i , E_j are the energies of stationary states of the combined radical ion and biradical spin system. In a

magnetic field $B = J - A/2$, two spin levels of this system cross. This causes appearance of the narrow line, as it generally takes place for MARY spectra in case of level crossing.^{22,23}

This conclusion is illustrated by Fig. 5 representing the results of numerical calculations of fluorescence yield $I_{\text{fl}}(B)$ defined by eqn. (45), with the consistent account of all terms of RIBIP Hamiltonian. The recombination function $F(t)$ was taken as $F(t) = (1/\tau_0)\exp(-t/\tau_0)$, with $\tau_0 = 50$ ns. Calculations were carried out with a step of 0.1 mT, for a range of magnetic field from zero up to 550 mT. The exchange integral was equal to $J = 500$ mT, and the hyperfine coupling constant $A = 3$ mT. The solid line corresponds to a broad hyperfine structure of the radical ion $D^{+\bullet}$, the dashed line to the absence of hyperfine coupling in the radical ion $D^{+\bullet}$. In both cases the broad resonance trough occurs at $B = J - A/4$. In addition, in the absence of hyperfine coupling in $D^{+\bullet}$, a narrow resonant peak centered at $B = J - A/2$ appears in complete accordance with the earlier conclusions. A pronounced change of $I_{\text{fl}}(B)$ occurs within the change of the magnetic field from zero up to the value of the order of the hyperfine coupling constant. This is a MARY resonance in zero magnetic field. The amplitude of the resonance in zero field essentially exceeds that for the J -resonance.

Concluding remarks

In the above consideration we did not take into account several essential factors affecting the evolution of RIBIP spin system. The first of these is a possible presence of several magnetic nuclei in the biradical. To consider this effect we performed numerical calculations of MARY spectra for a biradical with a ^{14}N nucleus ($I = 1$) located in the stable radical centre R^\bullet , and many other magnetic nuclei with smaller hyperfine coupling constants located at the radical centre A^\bullet . Hyperfine coupling with the nitrogen was taken into account accurately, while hyperfine couplings with the other nuclei were considered in the so-called semiclassical approximation. Such a model biradical corresponds well enough to biradical anions formed under ionization of solutions containing derivatives of anthracene, terphenyl or tolan having a stable nitroxyl radical centre moiety. Such compounds were recently synthesized and investigated.¹⁷ The calculated MARY spectra in weak magnetic fields and in the J -resonance region are shown in Fig. 6. The hyperfine coupling constant and the second

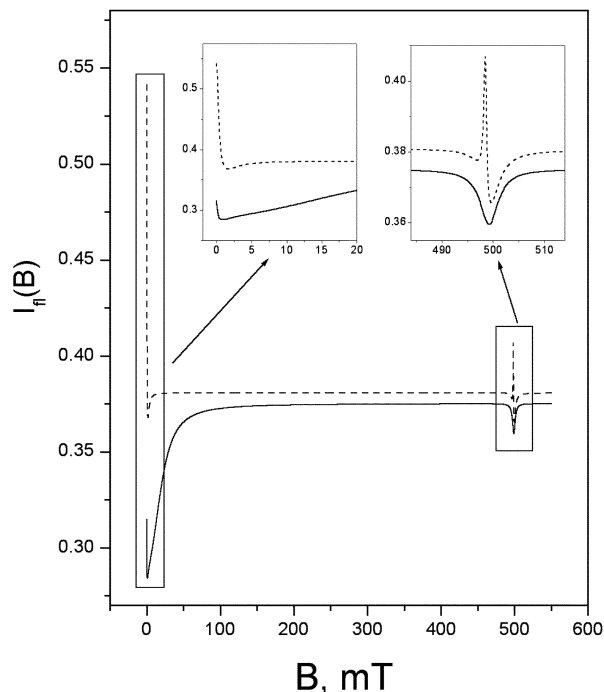


Fig. 5 MARY spectra for a biradical with one spin 1/2 magnetic nucleus. Recombination function $F(t) = 1/\tau_0 \exp(-t/\tau_0)$, $\tau_0 = 50$ ns, hyperfine coupling constant $A = 3$ mT, $J = 500$ mT. The radical ion $D^{+\bullet}$ has a broad (solid line) or narrow (dashed line) EPR spectrum.

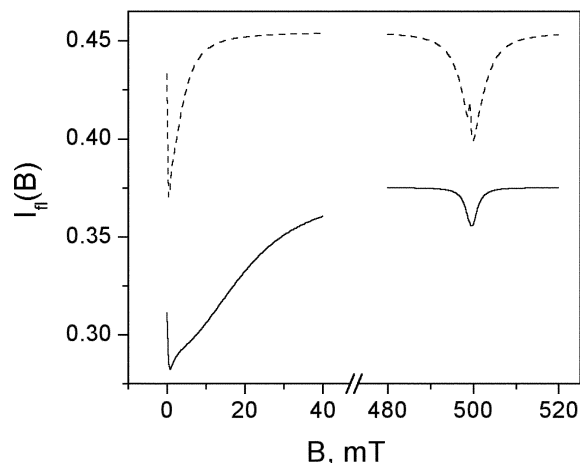


Fig. 6 MARY spectra for a biradical with one ^{14}N nucleus ($I = 1$) located in the stable radical centre R^\bullet (hyperfine coupling constant 1.4 mT) and many other magnetic nuclei with smaller hyperfine coupling constants (second moment of hyperfine structure $A^2 = 0.0068$ mT²) located in radical centre A^\bullet . The radical ion $D^{+\bullet}$ has broad (solid line) or narrow (dashed line) EPR spectrum.

moment of the hyperfine structure of $A^{\bullet-}$ were chosen as 1.4 mT and 0.0068 mT², respectively. These values are close to expected for a radical anion formed by a capture of electron by derivatives of perdeuterated *p*-terphenyl having a nitroxyl radical centre. The recombination function was taken the same as above: $F(t) = (1/\tau_0)\exp(-t/\tau_0)$ with $\tau_0 = 50$ ns. It is easy to see, that the calculations confirm the qualitative conclusions made above for the simplest model of a biradical having one magnetic nucleus.

The next factor not taken into account in the above consideration is the modulation of the exchange integral by conformational dynamics of the molecular bridge (the degree of this modulation depends, certainly, on the rigidity of this bridge). Consider first the effect of this modulation on radiofluorescence in passing from weak (zero) to strong magnetic fields. From the biradical spin level scheme of Fig. 1 it is seen, that the change of spin dynamics of the biradical in passing from weak to strong fields is caused by switching off the mixing of the pairs of triplet spin states, $T_0\alpha_N$ with $T_+\beta_N$, and $T_-\alpha_N$ with $T_0\beta_N$. In zero magnetic field they effectively mix up, while in strong magnetic fields this mixing is forbidden by energy. Obviously, if the biradical spends most of its time in conformations with $J \gg A$, the modulation of the exchange integral does not change the spin dynamics. Triplet levels are completely isolated from the singlet ones. Level splittings and matrix transition elements between them do not depend on the exchange integral. A modulation of the exchange integral can only affect high-frequency harmonics, of the order of J , in the singlet state population. In experiment they are filtered out automatically due to finite lifetime of the fluorescent excited state and to the limited time resolution of the experimental setup. We perform such a filtration analytically, or numerically, therefore, for instance, eqns. (26), (27), (35) and (36) for singlet state population $\bar{\rho}_{DA,SS}(t)$, still remain valid in the presence of modulation of the exchange integral.

For the J -resonance region, a modulation of the exchange integral is equivalent to the frequency migration in a two-level system, i.e., change of splitting between resonant levels. In the case considered, modulation of the exchange integral produces a modulation of the splitting (frequency migration) in the two-level system $S\beta_N$ and $T_-\alpha_N$. If the motion of the biradical molecular bridge is very slow, such that $\Delta_J^2\tau_{\text{bir}}^2 \gg 1$, where Δ_J^2 is the dispersion of the exchange integral and τ_{bir} is the characteristic correlation time, then the J -resonance line is an inhomogeneous broad line with the second moment Δ_J^2 centered at $B \sim \bar{J}$, where \bar{J} is the time averaged mean value of $J(t)$. In the other limiting case, when $\Delta_J^2\tau_{\text{bir}}^2 \ll 1$ (the case of strong narrowing) the shape of the J -resonance is Lorentzian with the same maximum position as for the slow motion, i.e., at $B \sim \bar{J}$ and with the width equal to $\Delta_J^2\tau_{\text{bir}}$.

The third factor not taken into account is paramagnetic relaxation of the electron spins. All the qualitative conclusions made for magnetic effects in recombination of radical ion pairs also hold true for the radical/biradical recombination. For instance, electron spin relaxation essentially changes the shape of the kinetic curves $I(t)$. As to MARY resonances, paramagnetic relaxation only slightly contributes to their width both in weak magnetic field and in the J -resonance region if $T_1 \gg \tau_0, A_{\text{eff}}^{-1}$, where A_{eff} is the characteristic value of the hyperfine coupling constant.

Thus, we believe that our conclusions made for a very simple model hold true for more realistic pairs, too.

The J -resonance in the radical/biradical recombination resembles to some extent the J -resonance of chemically-induced dynamic nuclear polarization (CIDNP) in the recombination of biradicals formed in photochemical reactions.^{27,28} However there are essential distinctions between them. In the case of CIDNP, the biradical is formed in a correlated spin state, whereas in the case of radical/biradical recombination the spin state of the biradical at the instant of its formation

is in equilibrium. Furthermore, in our case, the spin system actually is not a two-spin, as for CIDNP in biradicals, but a three-spin system. At the same time the theoretical analysis of this three-spin system is much easier and more transparent, than in the case of CIDNP. This is due to the fact that in the case of CIDNP spin dynamics is complicated by the conformational motion of the biradical, since recombination occurs only from the singlet spin state of the biradical (see refs. 27 and 28). In the system considered here, recombination occurs both from singlet and triplet states of the pair $D^{\bullet+}/A^{\bullet-}$. This circumstance strongly facilitates the theoretical analysis of such a system.

The performed analysis shows, that resonant changes of the kinetics as well as of the yield of the fluorescence resulting from radical ion/biradical recombination occur both close to zero magnetic field and in a magnetic field close to the value of exchange integral. The latter gives a principal opportunity to determine the exchange integral with high accuracy.

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