

# Peculiarities of magnetic and spin effects in a biradical/stable radical complex (three-spin system). Theory and comparison with experiment.

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## **Abstract**

The field dependences of the biradical recombination probability in the presence of paramagnetic particle with spins  $S = 1$  and  $S = \frac{1}{2}$  have been calculated in terms of the density matrix formalism. To describe the effect of the “third” spin on the spin evolution in biradical, we have also considered spin exchange interaction between the added spin and one of the paramagnetic biradical centers. A characteristic feature of the calculated field dependences is the existence of several extrema whose positions and scales depend on the signs and values of the exchange integral in the system. The method proposed can be used to describe spin catalysis. It is shown that for the system with the third spin  $S = 1$  spin catalysis manifests itself stronger than in the case of spin  $S = \frac{1}{2}$ . The dependence of spin catalysis efficiency on the exchange interaction with the third spin has an extremum whose position is independent of the value of the spin added.

## Introduction

At present, the study of magnetic and spin effects in multi-spin systems is one of the most interesting problems of spin chemistry. In 1994, an increase in the cage effect in solution was observed experimentally for triplet radical pairs in the presence of a stable radical, i.e., the phenomenon of spin catalysis [1]. In addition, the effects of an added (so-called “third”) spin on magnetic field effects in radical ion pairs (RIP) [2,3] and of stable radicals on CIDNP formation in a radical pair (RP) [4] were discovered. These effects indicate that paramagnetic species can efficiently influence the processes of spin evolution in RP and RIP. In literature, several examples are available that demonstrate the effect of the “third” spin on the field dependences of magnetic field effects in biradicals [3, 5]. Thus, the existence of an additional paramagnetic species in a multi-spin system (a radical triad or tetrad) can not only lead to the well-known relaxation effects (mainly due to dipole-dipole interaction) [2], but can also affect spin dynamics directly.

The classical version of the existing theory [6] of radical pairs neglects the interaction with other paramagnetic centers of macrosystem. The analysis of spin and magnetic field effects in multi-spin systems require to improve the approaches to take into account the interaction of all electrons during the entire lifetime of radical triad or tetrad. Such an approach was used by Berdinsky and Buchachenko to describe spin catalysis [7]. However, their results do not describe magnetic field effects and their field dependences. A model suggested by Molin and Lukzen [8] describes magnetic field effect, but only concerns the case where paramagnetic particles are generated by radiolysis, which allows one to neglect molecular dynamics. The latter does not allow one to use this model for analyzing magnetic field effects in the case of thermal or photochemical generation of paramagnetic species.

In [9], we proposed the approach for calculating the probability of recombination in a three-spin system biradical/paramagnetic species in which a paramagnetic species is rigidly complexed near one of the biradical

centers. The approach was applied for calculating the probability of the recombination of a complex biradical/paramagnetic species with spin equal to  $S_3 = 1$ . In the present paper, we have extended this approach to the system with an additional paramagnetic species with spin  $S_3 = \frac{1}{2}$  to reveal the similarities and differences of these two cases.

## Model descriptons

The approach developed [9] allows us to describe the main peculiarities of magnetic field effects which appeared (as assumed in [5]) in complexes of silicon-centered biradicals with molecular oxygen formed by the photolysis of 7-silanorbornadiene in solution. In this process, the influence of the stable radical 4-OH-TEMPO on the rate of the quenching of triplet dimethylsililene (precursor of the aforementioned biradicals) was also found [10]. Therefore, our description of magnetic and spin effects in a three-spin system consisting of biradical and a “third” paramagnetic particle with spin  $S_3 = \frac{1}{2}$  is aimed to account for the effects observed.

The system under study is a bound radical triad consisting of two radical centers  $R_1$  and  $R_2$ , that form a covalent bond and yield the product, and  $R_3$  is a radical center rigidly bound to the radical center  $R_1$ . Between the  $R_1$ ,  $R_2$  and  $R_3$  centers there are exchange interactions  $J_1$  and  $J_2$ , respectively. Radical center  $R_1$  has a magnetic nucleus with a HFI constant  $a$ . Thus, the Hamiltonian of the system is of the form:

$$\hat{H} = g_1\beta B\hat{S}_{1z} + g_2\beta B\hat{S}_{2z} + g_3\beta B\hat{S}_{3z} + J_1\hat{S}_1\hat{S}_2 + J_2\hat{S}_1\hat{S}_3 + a\hat{S}_1\hat{I} \quad (1)$$

where  $g_1$ ,  $g_2$ ,  $g_3$ , are the g-factors of the electrons of the corresponding radical centers,  $S_1$ ,  $S_2$  and  $S_3$  are the electron spin operators,  $\beta$  is the Bohr magneton, and  $B$  is the induction of external magnetic field of the corresponding radical centers.

The calculations were performed in the framework of the density matrix formalism by solving Liouville stochastic equations. Hamiltonian (1) commutates with the

projection of the total spin on the direction of the external magnetic field. Therefore, the ensemble of the wave functions of the triad can be divided into several subensembles with defined projections of total spin  $F$ . The calculations were carried out for each subensembles and the total recombination probability was a sum of the results with their statistic weights. Let the reactive state be singlet. Then for the singlet and triplet initial state of the biradical, the recombination probabilities respectively are

$$\begin{aligned} w^s &= \frac{U_0 \tau}{1 + U_0 \tau} \\ w^r &= \frac{1}{3} \frac{U_0 (\tau_p - \tau)}{1 + U_0 \tau} \end{aligned} \quad (2)$$

$\tau_p$  is total time of direct contacts between the active biradical centers,  $\tau$  is the lifetime of the system in the reactive state, i.e. when both of the active biradical centers are in the zone of direct contact and their electron spins form a singlet state if the spin evolution starts from the same singlet state.  $\tau = \text{Re}(\hat{g}_{ss,ss})$ , where  $\hat{g}(s)$  is the result of the Laplace transform of the spin evolution operator convolved with a function characterizing spatial motion and averaged over the reaction zone. All elements of the matrix  $\hat{g}(s)$  are expressed by means of function  $\hat{g}(s)$  which depends on mutual motion of the unpaired electrons in pair.

The two-position exponential model [11] is the most appropriate for the description of motion of the bond triad. On the one hand, this model is mathematically simple; on the other hand, it describes well the main point of cage effect.

In the frame of the model, two states of system are available. One is the state of direct contact—the radicals are located in the reaction zone. An escape of a RP from this state is described as a monomolecular decay with the characteristic time  $\tau_1$ . The other is the state where the radicals are in the cage, but out of the reaction zone. This state is characterized by two parameters –  $\tau_2$  is the time of return of the system into the reaction zone, and  $\tau_c$  – the time of RP decay.

Trivial solution yields expression

$$g(s) = \frac{(s + 1/\tau_2 + 1/\tau_c)}{s(s + 1/\tau_2 + 1/\tau_c) + 1/\tau_1(s + 1/\tau_c)}. \quad (3)$$

In the frame of the model we have [9]:

$$\tau = \tau_p \left( \sum_i Q_{ii}^4 + 2 \cdot \sum_{i>j} \frac{Q_{ii}^2 Q_{jj}^2}{n+1} \left( 1 + \frac{n}{1 + ((E_i - E_j)\tau_c)^2} \right) \right) \quad (4)$$

In this case,  $Q_{ii}$  is the expansion coefficient of the singlet state in the basis of eigen functions of the system,  $E_i$  is the energies of the eigen functions,  $n = \frac{\tau_c}{\tau_2}$  is the number of re-encounters in RP.

The dependences of the recombination probability of the system on the strength of external magnetic field were calculated providing that the initial biradical state was a triplet.

## Results and discussion

Figure 1 shows the calculated field dependences of the recombination probability for fixed  $J_1$  and various  $J_2$ .

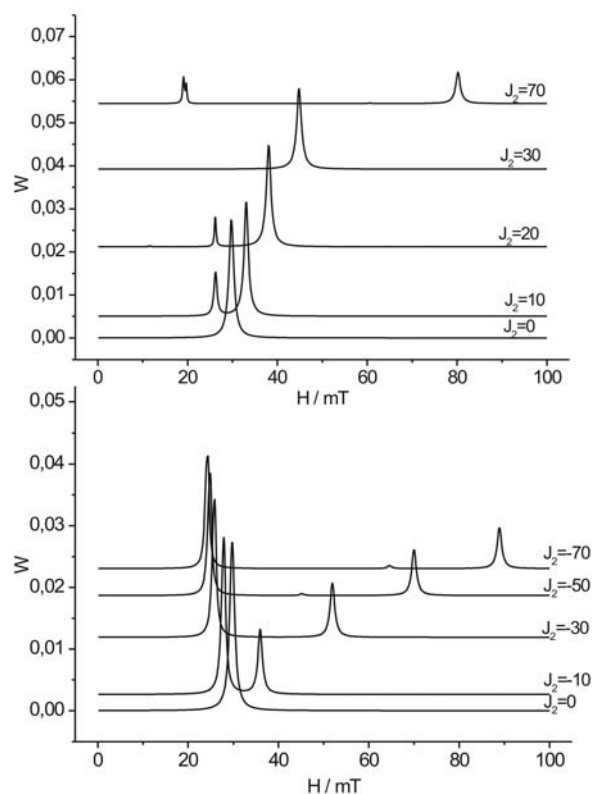


Figure 1 The field dependence of the recombination probability for the complex biradical/paramagnetic species with spin  $S_3 = \frac{1}{2}$  for various  $J_2$ .  $J_1 = 30$  mT,  $g_{B1B} = 2.0035$ ,  $g_{B2B} = 2.0040$ ,  $g_{B3B} = 2.0045$ ,  $U_0 \tau_c = 5$ , and  $n = 100$ .

The general character of the field dependences, i.e., the existence of several extrema of the recombination probability, remains the same as for  $S_3 = 1$  [9]. There are, however, some qualitative and quantitative distinctions.

When  $J_2 \lesssim J_1$ , the main extremum is located in a lower field as compared with the case of  $S_3 = 1$ . The number of extrema also decreases, probably, due to a simpler structure of terms because of the smaller total spin  $F$  of the system.

The extrema in the field dependence of the recombination probability arise in the fields of anticrossings of the system terms (Figure 2).

Let us consider the term structures of the two systems in two extreme cases:  $J_2 \ll J_1$  and  $J_2 \gg J_1$  to understand the origin of the differences between these two cases and predict the positions of extrema.

Figure 3 shows the terms of the biradical/paramagnetic

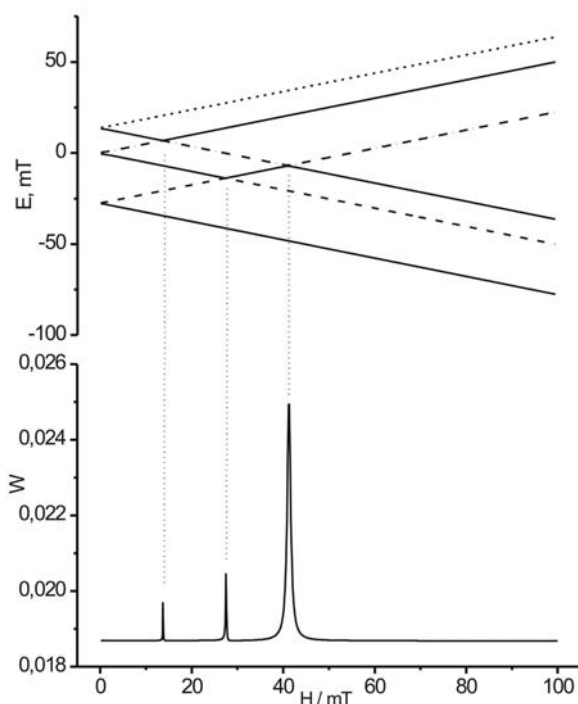


Figure 2 The structure and dependence of the terms of the system biradical/paramagnetic species  $S_3 = \frac{1}{2}$  on external magnetic field.

The subensemble with the total projection  $F_z = \frac{1}{2}$  and its contribution to recombination probability.  $J_1 = 30$  mT, and  $J_2 = 25$  mT. The remaining parameters are the same as in Figure 1.

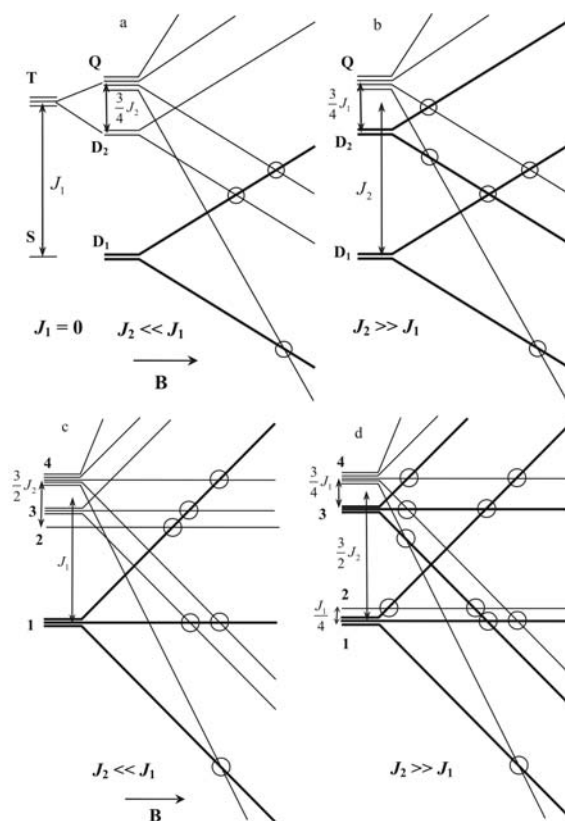


Figure 3 The structure and dependence of the terms of the system biradical/paramagnetic species on external magnetic field.

$S_3 = \frac{1}{2}$  : a, b;  $S_3 = 1$  : c, d. The remaining parameters are similar to those in Figure 1.

species system with spins  $S_3 = \frac{1}{2}$  and  $S_3 = 1$  for the cases of strong and weak  $J_2$ . The wave functions are represented by a linear combination of singlet and triplet states of the biradical interacting with the third species. Expressions for the wave functions were derived from numerical solution of equations for the eigen values and eigen vectors of the Hamiltonian in the singlet-triplet basis of the biradical and the third species. Transitions arising in the region of anticrossing (Table 1) can be due flip of the spin of biradical  $S_1$  induced by HFI. Let us consider the biradical-radical system. In the case of weak interaction (Figure 3, a) the singlet state of the biradical converts into the doublet state  $D_1$ , the triplet states mix up and fall into the quartet  $Q$  and doublet  $D_2$  states shifting in energy by  $\frac{J_2}{4}$  and  $-\frac{J_2}{2}$ , respectively. The system can get into the reactive state at a field where anticrossing of two terms

occurs, provided that one of the terms includes the reactive singlet state of the biradical. In Figure 3, such terms are denoted by a thick line. When  $J_2 \ll J_1$ , the transitions in the system occur at the anticrossing of the  $Q$  and  $D_2$  levels with  $D_1$  in the fields  $J_1 + \frac{J_2}{4}$  and  $J_1 - \frac{J_2}{2}$ .

Analyzing the composition of multiplicative functions composing the terms (Table 2), we conclude that the extrema in the field dependences of the recombination probability cause  $S-T_-$  transitions.

In the opposite case,  $J_2 \gg J_1$  (b), the terms  $D_1$  and  $D_2$  change their composition.  $D_1$  consists mainly of the triplet states with a small addition of the singlet one.  $D_2$  mainly includes singlet states (Table 2). As a result, the  $S-T_-$  transitions occur between  $D_1$  and  $D_2$ ,  $Q$  and  $D_1$ ,  $Q$  and  $D_2$  in the fields  $\frac{3}{4}J_1$ ,  $J_2 + \frac{J_1}{4}$  and  $J_2 - \frac{J_1}{2}$ , respectively (Table 1). The greatest efficiency of the transitions in the approximation of long-lived pairs should be observed for the greatest difference in the singlet state component in anticrossing terms. Thus, far from anticrossing of terms, the fractions of the singlet state in  $D_1$ ,  $D_2$ , and  $Q$  are  $\frac{1}{4}$ ,  $\frac{3}{4}$ , and 0, respectively (Table 2). Therefore, for  $J_2 \ll J_1$

Table 1 Position of extrema of recombination probability field dependence for the case of weak and strong interaction.

	$S_3 = \frac{1}{2}$		$S_3 = 1$	
	$J_2 \ll J_1$	$J_2 \gg J_1$	$J_2 \ll J_1$	$J_2 \gg J_1$
Extrema position	$J_1 + \frac{J_2}{4}$ $J_1 - \frac{J_2}{2}$	$\frac{3}{4}J_1$ $J_2 + \frac{J_1}{4}$ $J_2 - \frac{J_1}{2}$	$J_1 - J_2$ $J_1 \pm \frac{J_2}{2}$	$\frac{J_1}{4}, \frac{3}{4}J_1$ $\frac{3}{2}J_2 \pm \frac{J_1}{4}$ $\frac{3}{2}J_2 - \frac{J_1}{2}$

the main extremum is observed upon the anticrossing of  $D_2$  and  $Q$  states in weaker fields.

For  $S_3 = 1$  in the extreme case  $J_2 \ll J_1$  (Figure 3, c), the triplet functions of the biradical are distributed between two multiplets, (3) and (4), and a single term (2), which differ in energy at  $J_2$  and  $\frac{J_2}{2}$  and are  $J_1$  apart from the multiplet of the singlet states of the biradical (1). Thus, the anticrossings involving the reactive states of (1) that give the extrema of recombination probability, occur in the fields close to  $J_1$ :  $J_1 - J_2$ ,  $J_1 \pm \frac{J_2}{2}$ . When  $J_2 \gg J_1$  (d),

Table 2 Expansion coefficient of the eigen function of triad biradical/paramagnetic species with spin  $S_3 = \frac{1}{2}$

$S_3 = \frac{1}{2}$	1: $J_2 \ll J_1$	2: $J_2 = 2J_1$	3: $J_2 \gg J_1$	4: $ J_2  \gg J_1, J_2 < 0$
$DB_{1B}$	$ S\alpha\rangle$ $ S\beta\rangle$	$\sqrt{\frac{1}{2}} S\alpha\rangle - \sqrt{\frac{1}{2}}\Phi_1^+$ $\sqrt{\frac{1}{2}} S\beta\rangle + \sqrt{\frac{1}{2}}\Phi_1^-$	$\sqrt{\frac{1}{4}} S\alpha\rangle - \sqrt{\frac{3}{4}}\Phi_1^+$ $\sqrt{\frac{1}{4}} S\beta\rangle + \sqrt{\frac{3}{4}}\Phi_1^-$	$\sqrt{\frac{3}{4}} S\alpha\rangle + \sqrt{\frac{1}{2}}\Phi_1^+$ $\sqrt{\frac{3}{4}} S\beta\rangle - \sqrt{\frac{1}{2}}\Phi_1^-$
$DB_{2B}$	$\Phi_1^+$ $\Phi_1^-$	$\sqrt{\frac{1}{2}} S\alpha\rangle + \sqrt{\frac{1}{2}}\Phi_1^+$ $\sqrt{\frac{1}{2}} S\beta\rangle - \sqrt{\frac{1}{2}}\Phi_1^-$	$\sqrt{\frac{3}{4}} S\alpha\rangle + \sqrt{\frac{1}{4}}\Phi_1^+$ $\sqrt{\frac{3}{4}} S\beta\rangle - \sqrt{\frac{1}{4}}\Phi_1^-$	$\sqrt{\frac{1}{4}} S\alpha\rangle - \sqrt{\frac{3}{4}}\Phi_1^+$ $\sqrt{\frac{1}{4}} S\beta\rangle + \sqrt{\frac{3}{4}}\Phi_1^-$
$Q$			$ T_+\alpha\rangle$ $\Phi_2^+$ $\Phi_2^-$ $ T_+\beta\rangle$	

$$\Phi_1^+ = \sqrt{\frac{1}{3}}|T_0\alpha\rangle - \sqrt{\frac{2}{3}}|T_+\beta\rangle; \quad \Phi_1^- = \sqrt{\frac{1}{3}}|T_0\beta\rangle + \sqrt{\frac{2}{3}}|T_+\alpha\rangle$$

$$\Phi_2^+ = \sqrt{\frac{2}{3}}|T_0\alpha\rangle - \sqrt{\frac{1}{3}}|T_+\beta\rangle; \quad \Phi_2^- = \sqrt{\frac{2}{3}}|T_0\beta\rangle + \sqrt{\frac{1}{3}}|T_+\alpha\rangle$$

$|S\rangle$  and  $|T\rangle$  are the states of a biradical,  $|\alpha\rangle$  and  $|\beta\rangle$  are the states of  $S_3$ .

as for  $S_3 = \frac{1}{2}$ , multiplets (1) and (3) change their composition and (1) mainly consist of triplet states with a small admixture of the singlet state, and (3) is mainly the triplet state. As a result, in the field dependence we observe two groups of extrema, i.e., the major one is observed in lower field at  $\frac{J_1}{4}$  и  $\frac{3}{4}J_1$  and the minor one at  $\frac{3}{2}J_2 \pm \frac{J_1}{4}$  and  $\frac{3}{2}J_2 - \frac{J_1}{2}$  (Table 1). In the intermediate case,  $J_2 \sim J_1$ , the extremum at  $\frac{3}{2}J_2 - \frac{J_1}{2}$  manifests itself as a separate one and is strong enough.

When  $J_2 = J_1$ , the field dependence is simplified. For  $S_3 = 1$  we observe a few small extrema and only one large extremum at  $\frac{3}{2}J_1$ . For  $S_3 = \frac{1}{2}$  the extremum at  $\frac{3}{2}J_1$  is the only one.

Thus, in both of the systems, the main extremum moves to a higher field with increasing  $J_2$ . When  $J_2 \sim J_1$ , the low-field extrema increase, and with  $J_2 \gg J_1$  the main extrema are in low field.

It is worth noting that for both of the systems the widths of the extrema are quite different. Thus, if the high-field extrema exhibit the expected width, close to HFI constant  $a$ , the low-field ones are more narrow by a factor of up to 2. In all cases, we observed either the  $|S\rangle \leftrightarrow |T_-\rangle$  or  $|S\rangle \leftrightarrow |T_+\rangle$  transitions caused by HFI.

As for  $S_3 = 1$  [9], in the system under study, far from particular points, the recombination probability depends on  $J_2$  (spin catalysis) (Figure 4). However, in the system with  $S_3 = \frac{1}{2}$ , the spin catalysis is less effective.

Transitions corresponding to spin catalysis are caused by exchange interaction with the third species. As follows from Table 2, the transitions in terms  $D_1$  and  $D_2$  corresponding to spin catalysis occur in the subensembles  $\{|S\alpha\rangle, |T_0\alpha\rangle, |T_+\beta\rangle\}$  and  $\{|S\beta\rangle, |T_0\beta\rangle, |T_-\alpha\rangle\}$ . Here,  $|S\rangle$  and  $|T\rangle$  are the states of biradical,  $|\alpha\rangle$  and  $|\beta\rangle$  are the

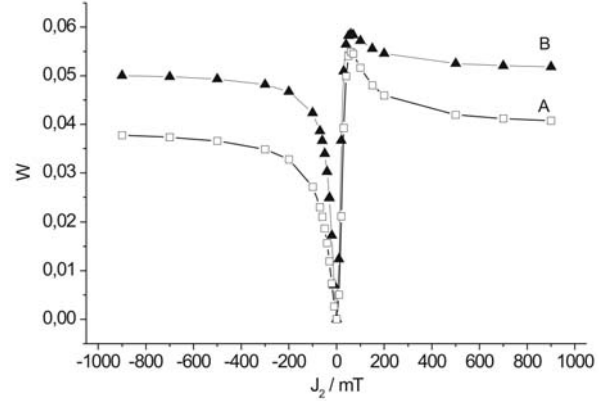


Figure 4 The dependence of recombination probability in zero field on  $J_2$  for (a)  $S_3 = \frac{1}{2}$ , (b)  $S_3 = 1$ .  $J_1 = 30$  mT. The remaining parameters are similar to those in Figure 1.

states of  $S_3$ . The interaction  $J_2$  occurs between all multiplicative functions included in the subensembles. It is concluded then that, unlike the extrema of the field dependence of recombination probability, the spin catalysis is caused by the  $S-T_0$ ,  $S-T_-$ , and  $S-T_+$  transitions. Figure 4 demonstrates the dependence of the biradical recombination probability in zero field (spin catalysis efficiency) on the exchange interaction with the added spin. Note that in both of the cases ( $S_3 = 1, \frac{1}{2}$ ), the dependence of the spin catalysis efficiency on  $J_2$  has an extremum which corresponds to  $J_2 = 2J_1$  (see the Figure 4). The origin of the extremum can be elucidated by considering the system of terms. Figure 5 shows the system of terms for  $S_3 = \frac{1}{2}$ . Table 2 summarizes the terms in the singlet-triplet basis. There is the interaction  $J_2$  between  $S$  and  $\Phi_I$  which mixes and separates them. At  $J_2 = 2J_1$ , where the  $S$  state is distributed equally among the terms (Table 2), the  $T$ - $S$  transitions in the system are most efficient. When the system is on a term, the recombination probability should be proportional to the probability to find it in the reactive singlet state,  $C_S^2$ . On the other hand, since the initial state of the system was the triplet one, the population of the term is proportional to  $\sum C_T^2$ . Thus, summing up the populations of the terms,

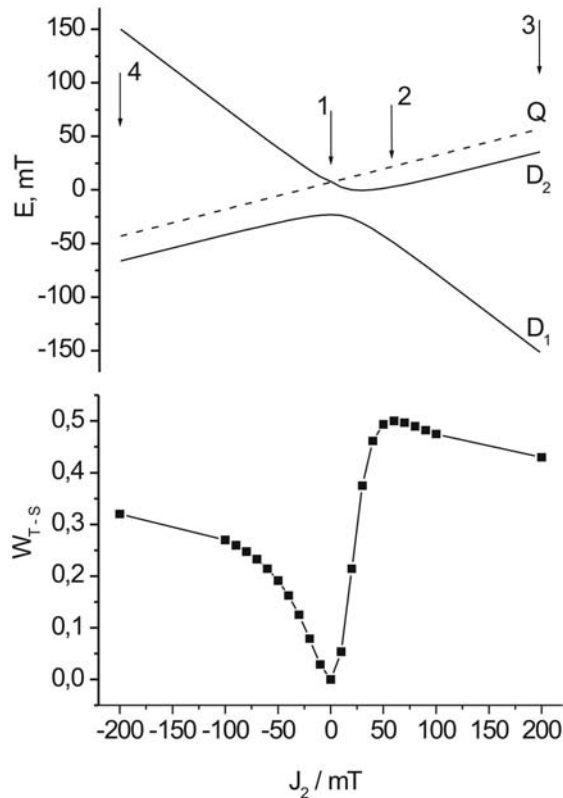


Figure 5 The dependence of the term splitting of the system (a) and estimates of recombination probability in zero field (b) on  $J_2$  for  $S_3 = \frac{1}{2}$ . The remaining parameters are similar to those in Figure 1.

we estimate the recombination probability as  $W_{T-S} = \sum (C_S^2 \sum C_T^2) = \sum C_S^2 (1 - C_S^2)$ . Thus, for  $C_S^2 = 0.5$  we observe the maximum recombination probability. Table 2 shows that these conditions are satisfied for  $J_2 = 2J_1$ . The form of the estimated dependence,  $W_{T-S}$  (Figure 5), is also similar to the form of the calculated  $W$  (Figure 4). It is worth noting that in contrast to the field dependence of recombination probability, in this case the interaction between the terms, which is the exchange integral, is a variable parameter. Therefore, the extremum in  $W$  and  $W_{T-S}$  corresponds not to the position of the anticrossing of the  $D_2$  and  $D_1$  terms where they are most close to each other, but to the position in which the parameter of mixing, i.e., the exchange integral to term separation ratio  $\frac{J_2}{\Delta E}$ , has a maximum.

Let us consider how our results agree with the experimental data available in literature. Thus, in [12], the  $\text{Ln}^{3+}$  ions present in solution were established to substantially affect the distribution of the products of dibenzylketone (DBK) photolysis in micella. In [13], the dependence of the ratio of the recombination rate constants with and without  $\text{Ln}^{3+}$  ion process vs.  $\text{Ln}^{3+}$  ion spin is given. This dependence is well approximated by a linear dependence. On the other hand, the studies on the  $^{13}\text{C}$  CIDNP of DBK photolysis in micellas point out the existence of an exchange interaction between radicals in a pair recorded in the micella [14]. Thus, the effect of  $\text{Ln}^{3+}$  ions can be interpreted in terms of the formation of a radical triad. In this case, the diffusing  $\text{Ln}^{3+}$  ions approach the micella which contains a radical pair. However, since the  $\text{Ln}^{3+}$  ions do not enter the micella, the effective exchange interaction between the  $\text{Ln}^{3+}$  ions and the radicals in the micella should be much smaller than that between the radicals in the micella. In the framework of our model, this condition corresponds to the relation  $J_2 \gg J_1$ . For this case, the dependence of the efficiency of the calculated spin catalytic effect on the added spin is also close to the linear one (Figure 6). Thus, our model well describes qualitatively the results reported in papers [12,13] in terms of the concept of spin triads.

The influence of spin triads on the magnetic field effect formation can be demonstrated using photodecomposition

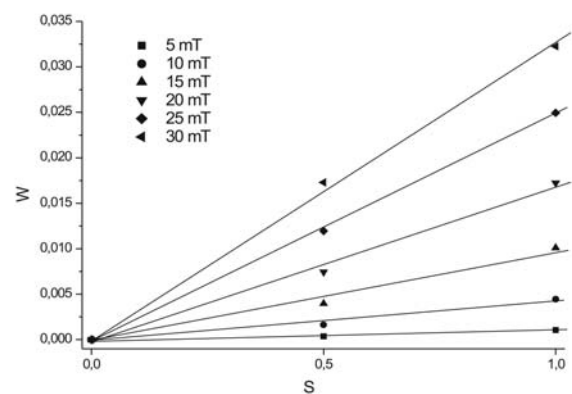


Figure 6 The efficiency of spin catalysis (recombination probability in zero field) for various values of  $J_2$  for added spins  $S_3 = \frac{1}{2}$  and  $S_3 = 1$ .  $J_1 = 50$  mT. The remaining parameters are similar to those in Figure 1.

of 7-silanonorborene (SNBD) [5,10]. Thus it has been established that the process involves the primary photodecomposition of SNBD into tetraphenylanthracene (TPN), and dimethylsilene (DMS) in the triplet state. Further DMS attacks the initial SNBD to form 1,6-biradical (BR) by introducing DMS via the Si-C bond of SNBD. The product of its decay is TPN. When photolysis is performed in external magnetic field, the yield of TPN demonstrates MFE. It has been established [5] that the S-T evolution in BR is the magnetosensitive stage responsible for the MFE recorded. In the absence of additional reagents, the field dependence of MFE exhibits an extremum in a field of about 25 mT. In the presence of oxygen, the MFE extremum shifts to a higher field and increases its scale substantially [5]. The addition of the stable 4-OH-TEMPO radical causes no shift in the field dependence extremum. However, as the TEMPO concentration increases, the MFE scale first decreases and then changes its sign [10].

In [10], the effect of triplet oxygen was assigned to the formation of the BR.- oxygen complex. Indeed, in [9], we demonstrated that considering this complex as a spin triad, then at certain sets of parameters of the spin triad the calculation can describe both the shift of extremum to higher field and the increase in the MFE scale

The absence of the MFE extremum shift after the addition of TEMPO indicates that the latter does not form complexes with BR in which there would be considerable exchange interaction between TEMPO and the paramagnetic BR centers. At the same time, a decrease in MFE down to the change of sign found in the presence of TEMPO [9], which indicates a change in the predominant multiplicity of BR, allows us to assume that DMS undergoes the T-S conversion before the reaction with initial SNBD. In the framework of this assumption, the influence of TEMPO is essentially its interaction with BR precursor, DMS, which accelerates its conversion into the singlet state. This corresponds to those of the discussed results that concern spin catalysis.

Indeed, DMS can be represented as a biradical in which both of the unpaired electrons are located at different

orbitals of the same atom. The difference in the energies of the S and the T states for a close analog of DMS, SiH<sub>2</sub>, is known to be  $\Delta E = 16.8 \text{ kcal/mole} \cong 6500 \text{ T}$  [15]. These values are in the range of from 19 to 29.4 kcal/mole [16] and from 13.7 to 28.6 kcal/mole [17] for GeH<sub>2</sub> and Ge(CH<sub>3</sub>)<sub>2</sub>. It is expected then that for DMS,  $\Delta E$  is also amounts to several thousands tesla. Thus, the interaction with the third species (TEMPO) can cause transition to the singlet state. The aforementioned theoretical calculations indicate that for  $J_2 \ll J_1$  the extrema in the field dependence can manifest themselves in fields close to  $J_1$  (Table 1). Thus, in the magnetic field range up to 100 mT, no dependence of MFE on the field should be observed. The spin catalysis in this system is sure to exist because it is independent of MF. Spin triad is a short-lived encounter complex in this case, which is not identical to the model under study. However, the model describes the processes in the system correctly.

Thus, the photolysis of SNBD in the presence of various paramagnetic additions has presented a unique opportunity to observe the two effects of the third spin considered in the present paper, i.e., the influence of paramagnetic admixtures on the field dependence of magnetic field effect and the spin catalysis effect.

In addition, this calculation method is in agreement with other calculations available in literature. Thus, in the extreme case, for  $J_1 = 0$  and the number of re-encounters  $n = 1$ , the system under study is similar to that studied by Lukzen and co-authors [8]. They theoretically considered a three-spin system which can be experimentally obtained under the irradiation of the spatially separated donor and acceptor and a spin label, calculated the spin dynamics of such a radical triad and described the  $J$ -resonance, i.e., the extremum of the recombination probability in the field close to the value of exchange interaction between the acceptor radical anion and the stable radical bound to it. Under the given conditions (Figure 7), the calculated field dependence of the recombination probability is of the form similar to that in [8]. The field dependence exhibits both the main extremum of  $J$ -resonance and a narrow



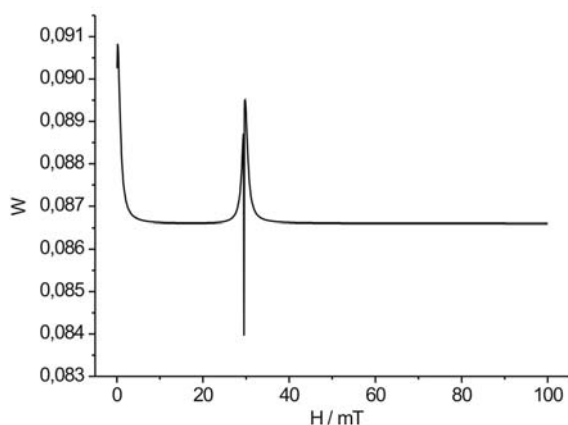


Figure 7 The field dependence of recombination probability for the complex biradical/paramagnetic species with spin  $S_3 = \frac{1}{2} J_2 = 30$  mT,  $J_1 = 0$  mT. The remaining parameters are similar to those in Figure 1.

extremum with an opposite sign. This latter extremum is also described in [8] for the case where the donor radical cation ( $D^{+*}$ ) has no substantial HFI, and is assigned by the authors to the competition of spin evolution in both  $D^{+*}$  and biradical anion.

Thus, in the present work, the method used earlier to calculate recombination probability in a three-spin system biradical/paramagnetic species was extended to the case of the added paramagnetic particle with spin  $S_3 = \frac{1}{2}$ . We analyzed the results from the calculations of the field dependences of the recombination probability for systems with the electron spin of the added particle  $S_3 = 1$  and  $S_3 = \frac{1}{2}$ . In both of the cases, we observed similar

behavior of field dependences with varying values and signs of exchange interactions in the system. One of the most characteristic features of the calculated field dependences is the existence of several extrema whose positions and scales depend on the signs and values of the exchange integrals in the system. Introducing exchange interaction with the third particle, we found a shift in the position of the main extremum. With  $J_2 \sim J_1$  for the system with  $S_3 = 1$  the main extremum was observed in

a field stronger than that for  $S_3 = \frac{1}{2}$ . For  $J_2 \gg J_1$  the main extremum for both of the systems is near  $\frac{3}{4}J_1$ . In

real systems, exchange integrals are not constants as assumed in calculations, which is sure to lead to a broadening of the extrema. As a result, with  $J_2 \ll J_1$  and  $J_2 \gg J_1$  we should experimentally observe one extremum and for  $J_2 \sim J_1$  even two or three wide extrema for

$S_3 = \frac{1}{2}$  and 1, respectively. It is also shown that the spin catalysis (the field independent recombination probability) is also manifested with different efficiency in the systems studied. For the system with  $S_3 = 1$  it is much stronger. In addition, the dependence of the spin catalysis efficiency on  $J_2$  is of extreme character and the position of the extremum  $\tilde{J}_2 = 2J_1$  is independent of the values of the spin added.

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