Thesis for Candidates Degree (Troitsk: Institute of Spectroscopy, USSR Academy of Sciences, 1981)
10. Matveets Yu A, Semchishen V A *Kvantovaya Elektron.* **6** 848 (1979) [*Sov. J. Quantum Electron.* **9** 503 (1979)]
11. Matveets Yu A, Chekalin S V, Yartsev A P *Pis'ma Zh. Eksp. Teor. Fiz.* **43** 546 (1986) [*JETP Lett.* **43** 707 (1986)]; *Dokl. Akad. Nauk SSSR* **292** 724 (1987); Chekalin S V et al. *FEBS Lett.* **216** 245 (1987); Chekalin S V, Matveetz Yu A, Yartsev A P *Rev. Phys. Appl.* **22** 1761 (1987); Matveets Yu A et al. *Dokl. Akad. Nauk SSSR* **294** 1480 (1987); Matveets Yu A, Chekalin S V, Yartsev A P *Izv. Akad. Nauk SSSR Ser. Fiz.* **53** 1462 (1989)
12. Matveetz Yu A, Chekalin S V, Sharkov A V *J. Opt. Soc. Am. B* **2** 634 (1985); Sharkov A V et al. *Photochem. Photobiol.* **38** 109 (1983); Sharkov A V et al. *Biochim. Biophys. Acta* (*BBA*): *Bioenerg.* **808** 94 (1985); Sharkov A V et al. *Dokl. Akad. Nauk SSSR* **281** 466 (1985)
13. Chekalin S V et al. *J. Phys. Chem.* **92** 6855 (1988); Kozlov A A et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **47** 294 (1988) [*JETP Lett.* **47** 353 (1988)]
14. Lozovik Yu E et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **52** 851 (1990) [*JETP Lett.* **52** 221 (1990)]; Besel' I V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **59** 376 (1994) [*JETP Lett.* **59** 403 (1994)]
15. Afanas'eva N I et al. *Opt. Spektrosk.* **82** 808 (1997) [*Opt. Spectrosc.* **82** 750 (1997)]
16. Bezel I V et al. *Chem. Phys. Lett.* **218** 475 (1994)
17. Golovlev V V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **55** 441 (1992) [*JETP Lett.* **55** 450 (1992)]
18. Chekalin S V et al. *Phys. Rev. Lett.* **67** 3860 (1991); Gershenzon M E et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **52** 1189 (1990) [*JETP Lett.* **52** 602 (1990)]; Dobryakov A L et al. *Opt. Spektrosk.* **76** 975 (1994) [*Opt. Spectrosc.* **76** 871 (1994)]
19. Sekatskii S K et al. *J. Phys. Chem. A* **102** 4148 (1998); Sekatskii S K et al. *Zh. Eksp. Teor. Fiz.* **115** 1680 (1999) [*JETP* **88** 921 (1999)]; Sekatskii S K et al. *Nonlinear Opt.* **23** 157 (2000)
20. Sekatskii S K et al. *Appl. Phys. Lett.* **83** 4900 (2003)
21. Aseev S A et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **80** 645 (2004) [*JETP Lett.* **80** 568 (2004)]; Mironov B N et al. *Zh. Eksp. Teor. Fiz.* **128** 732 (2005) [*JETP* **101** 628 (2005)]
22. Balykin V I *Pis'ma Zh. Eksp. Teor. Fiz.* **81** 268 (2005) [*JETP Lett.* **81** 209 (2005)]
23. Apatin V M et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **80** 104 (2004) [*JETP Lett.* **80** 95 (2004)]; Apatin V M et al. *Chem. Phys. Lett.* **414** 76 (2005)
24. Razjivin A P et al. *Biologicheskie Membrany* **22** 55, 83 (2005); *Kvantovaya Elektron.* **35** 107 (2005) [*Quantum Electron.* **35** 107 (2005)]
25. Chekalin S, Kompanets V, Starodubtsev N *Proc. SPIE* **6181** 282 (2006)
26. Kompanets V O, Matveets Yu A, Chekalin S V *Kvantovaya Elektron.* **31** 393 (2001) [*Quantum Electron.* **31** 393 (2001)]
27. Vinogradov E A *Usp. Fiz. Nauk* **172** 1371 (2002) [*Phys. Usp.* **45** 1213 (2002)]; *Laser Phys.* **15** 954 (2005)
28. Kompanets V O et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **68** 320 (1998) [*JETP Lett.* **68** 344 (1998)]
29. Dement'ev D A et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **65** 388 (1997) [*JETP Lett.* **65** 402 (1997)]; *Opt. Commun.* **150** 38 (1998); Aseyev S A et al. *Proc. SPIE* **6181** 274 (2006)
30. Zagorulko K et al. *Opt. Express* **12** 5996 (2004)
31. Lozovik Yu E et al. *Laser Phys.* **9** 564 (1999)

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Time-resolved EPR spectroscopy of nonequilibrium spin systems produced during spin-dependent photophysical and photochemical processes in condensed media

K M Salikhov

1. Introduction

The course of spin-dependent elementary acts may result in the formation of nonequilibrium polarization of electron spins exceeding the equilibrium spin polarization by several orders of magnitude. The physical nature of the nonequilibrium polarization formation is as follows. In elementary photophysical and photochemical events, it is not infrequent that the Hamiltonian of spin systems changes rapidly on a time scale of spin evolution times, and therefore the spins do not follow the variations in the spin Hamiltonian parameters adiabatically. For instance, in the rupture of a chemical bond, two free radicals form that inherit the spin state of the molecule. For these nonadiabatic processes, the disintegration of the molecule is, with respect to the spins of valence electrons, an abrupt switch of the spin Hamiltonian: a large value of the exchange integral in the molecule rapidly gives way to a relatively small value for two radicals at the distance equal to the sum of their Van der Waals radii; the g-factor of unpaired electrons changes simultaneously. The molecular spin Hamiltonian does not commute with the spin Hamiltonian of the two resultant radicals and therefore the electron spins of the radicals at the instant of radical pair production find themselves in a transient coherent state [1]. A similar situation occurs in the photo-induced electron transfer.

The above scheme of the transient spin state formation may formally be represented as follows. We let H_1 and ψ_n denote the spin Hamiltonian and eigenstates of the system *prior to* a phototransformation and H_2 and φ_p denote the spin Hamiltonian and eigenstates of the system *after* the phototransformation.. We assume that the phototransformation occurs in an excited state ψ_2 and the event proceeds nonadiabatically. In this situation, the phototransformation products (for instance, a pair of radicals resulting from molecular photodecay or an electron–hole pair produced in the phototransfer of an electron) are produced in the initial state with the wave function ψ_2, which is not an eigenfunction for the products because the spin Hamiltonians H_1 and H_2 do not commute, as a rule. This initial state can be represented as a linear superposition of the eigenstates of the products: $\varphi(0) = \psi_2 = \sum c_p \varphi_p$. The subsequent evolution of the electron spins is described by the wave function

$$\varphi(t) = \sum c_p \exp\left(-\frac{\mathrm{i}E_p t}{\hbar}\right) \varphi_p \,, \tag{1}$$

where E_p are the energy levels upon phototransformation.

Therefore, by inducing nonadiabatic transformations by a light pulse, it is possible to prepare ensembles of electron spin systems in transient coherent states.

In free-radical or electron–hole pairs, the evolution of wave packet (1) quite frequently proceeds on the nanosecond time scale [1]. Modern techniques of electron paramagnetic resonance (EPR) also permit observing the evolution of transient electron spin states with a nanosecond resolution. Directly observable in EPR experiments is the dipole spin polarization. In the phototransformation of diamagnetic molecules in the initial state ψ_2, the electron spins are not polarized, and therefore the EPR signal cannot be observed immediately in the products of nonadiabatic reactions. However, the spin dynamics are responsible for the formation of the EPR-observable polarization of electron spins.

We note that elementary photo-induced nonadiabatic reactions allow preparing ensembles of electron spins in the initial states unattainable when starting from the thermodynamic equilibrium. That is why the results of investigations of paramagnets at thermal equilibrium are not directly

applicable to the analysis of EPR data obtained in the study of transient photo-induced transformations.

2. Charge separation at the initial stages of photosynthesis

Perhaps the most remarkable example of the formation of a nonequilibrium electron spin polarization is the spin behavior of electron – hole pairs produced at the initial stage of solar energy assimilation by photosynthetic systems (see, e.g., Ref. [2]). Charge separation occurs in the reaction center of a photosystem: from a chlorophyll P dimer in a singlet electron-excited state, within a time of 5 – 6 ps, the electron is transferred to the primary acceptor, a chlorophyll molecule, and then, in a time of the order of 100 ps, to the secondary electron acceptor, quinine Q. This reaction is nonadiabatic and the resultant electron – hole pair P^+Q^- inherits the singlet spin state of its predecessor, P^*. The distance between the electron and the hole in this pair is about 3 nm, and therefore the spin – spin interaction in frequency units is of the order 10^7 rad s^{-1} and manifests itself efficiently only for times longer than ~ 10 ns. For times shorter than 1 ns, this electron – hole pair may be treated as the realization of the Einstein – Podolsky – Rozen – Bohm (EPRB) pair [3]. A very important property of an EPRB pair consists in the spin state of the pair being correlated, although the spin – spin interaction is negligible. This correlation results from the interaction of pair partners in the past, at the P^* dimer.

Therefore, at the primary stage of photosynthesis, electron – hole pairs form in the singlet state:

$$|S\rangle = \frac{|+1/2,-1/2\rangle - |-1/2,+1/2\rangle}{\sqrt{2}}\,. \qquad (2)$$

The singlet state is 'dark' for EPR spectroscopy. The recording of EPR is not possible until spin dynamics or paramagnetic relaxation occur. The EPR spectroscopy of the separated charges in the photosynthesis reaction center yields unusual results [4 – 7]. Some prominent EPR features of the separated charges in the reaction center, which have already been discussed at the scientific sessions of the Physical Sciences Division of the Russian Academy of Sciences [8], are listed below.

(a) The EPR line intensities oscillate and build up with time when experiencing quantum beats with the frequency of singlet – triplet transitions in the electron – hole pair [4, 5, 8].

(b) The EPR spectrum is antiphase in structure: some lines correspond to absorption, other lines to emission [8]. The integral intensity of the EPR spectrum is zero. This signifies that the spin dynamics of an electron – hole pair produce a quadrupole polarization of the pair of electron spins, while the total dipole polarization of the two spins is equal to zero.

(c) The signal of primary spin echo has a phase that depends on the selectivity of spin excitation by the microwave pulses exciting the echo signal. In the case of nonselective spin excitation, the primary spin echo signal turns out to be shifted by $\pi/2$ relative to the echo signal of the same spin pair upon the establishment of thermal equilibrium [2, 6, 8].

(d) The primary spin echo signal can be obtained with the aid of only one microwave pulse if the electron transfer is initiated by a laser pulse [6, 8]. In this case, the electron transfer reaction produces a pair in spin-coherent state (2). Therefore, in principle, for the formation of a spin echo signal, there is no need for the first microwave pulse, which is intended to produce spins in a coherent state.

Furthermore, other interesting properties were revealed for the ensemble of electron – hole pairs produced in quantum-entangled state (1).

(e) When the microwave field amplitude B_1 is low enough, four antiphase lines are observed in the EPR spectrum, which correspond to single-quantum transitions in the system of two 1/2 spins. With an increase in B_1, the single-quantum transition lines broaden and a double-quantum transition line shows up at the center of the spectrum [9]. The double-quantum transition line of the spin-correlated pair is of the form of a dispersion curve rather than of an absorption curve [9]. This signifies that the single- and double-quantum transition signals in spin-correlated pairs are shifted by 90° in phase.

(f) Among the promising investigative methods is optical detection of the EPR spectra of spin-correlated electron – hole pairs (ODEPR) [10]. The gist of the method is as follows. In the recombination of a pair, recombination luminescence can occur. The intensity of this luminescence depends on the spin dynamics in the pair, specifically on singlet – triplet transitions in the pair. By recording the intensity variation of recombination fluorescence or phosphorescence as a function of the microwave field frequency, it is possible to obtain the ODEPR spectrum of the pair. The double-quantum transition line is missing from the ordinary EPR spectrum when the spins of the pair do not interact. In the ODEPR spectrum of *spin-correlated pairs*, the double-quantum transition line manifests itself even in the absence of the spin – spin interaction in the pair [11, 12]. Shown in Fig. 1 by way of illustration are the ODEPR spectra calculated for several values of the microwave field amplitude B_1. The calculations were done for a model situation with the spin – spin interaction in the electron – hole pair assumed to be zero. With increasing B_1, a narrow double-quantum transition line shows up at the center of the ODEPR electron – hole pair spectrum. For high B_1 values, the peak intensity of the double-quantum transition line in the ODEPR spectrum behaves as B_1^4 and flattens out for high B_1 values [12]. Therefore, a double-quantum transition line may emerge in the ODEPR spectrum of electron – hole pairs even when the spin – spin interaction can be neglected. In this situation, the occurrence of double-quantum transition lines is caused by the spin – spin interaction in the past, prior to the instant of pair production [12].

The manifestations of spin dynamics in the electron – hole pair in the reaction center of photosynthetic systems are just one example of the features of nonequilibrium electron spin polarization in spin-dependent photophysical and photochemical processes. The polarization formation scenario is that as a result of spin-selective molecular process, a spin-correlated pair of paramagnetic particles is formed and a coherent spin state is prepared. The spin dynamics in spin-correlated pairs produce a nonequilibrium polarization of electron spins, which characteristically shows up in EPR experiments.

3. Triplet – triplet exciton annihilation

The charge separation in a reaction center is a monomolecular process. The polarization of electron spins may also occur in the course of spin-dependent biomolecular processes. As an example, we mention the mechanism of excited triplet state polarization induced by the mutual annihilation of triplets. It has been known [13] that a pair of interacting excitons in molecular crystals may annihilate due to the

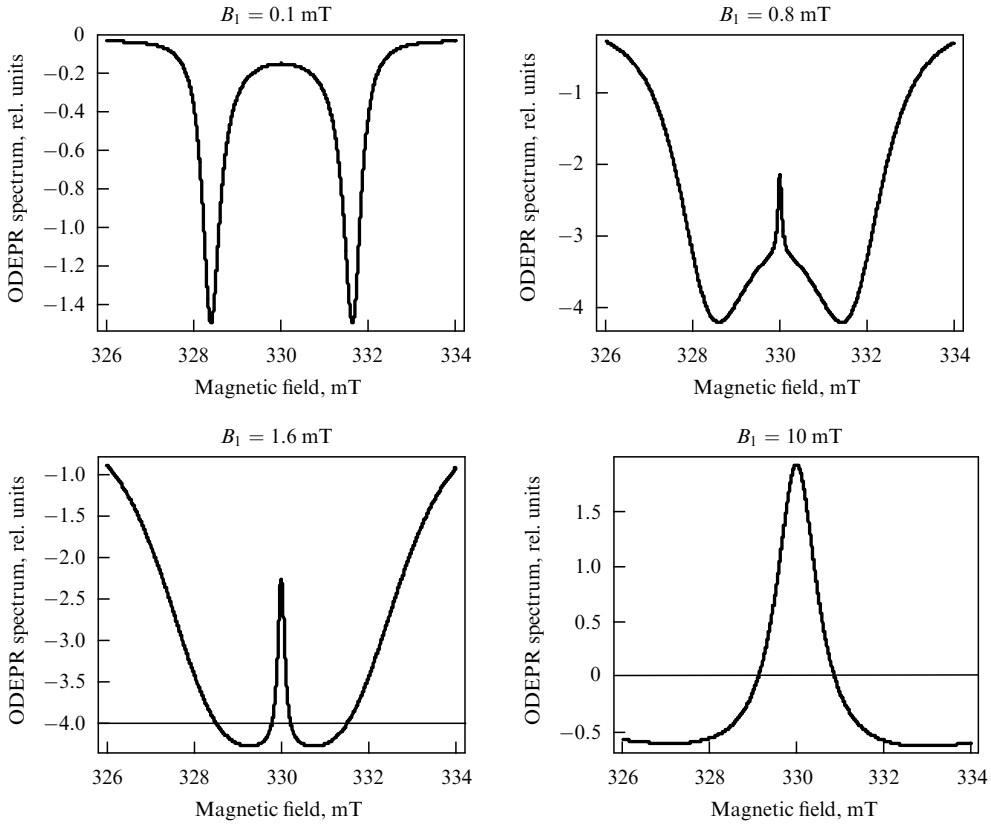

Figure 1. ODEPR spectra for a model system of electron – hole pairs calculated for different values of the microwave field induction B_1. The calculations neglected the spin – spin interaction, and the difference in g-factors was taken to be equal to 0.02.

energy transfer from one molecule of the pair to the other with the formation of a singlet excited state, resulting in delayed fluorescence. This annihilation of triplets is a spin-selective process.

The polarization of spin $S = 1$ states is specified by the polarization operators T_{LM} ($L = 0, 1, 2$; $-L \leqslant M \leqslant L$) [14]. The operators T_{1M} define the dipole moment of the triplet:

$$T_{1,+1} = -\frac{S_X + \mathrm{i}S_Y}{2}\,,\qquad T_{1,0} = \frac{S_Z}{\sqrt{2}}\,,\qquad T_{1,-1} = \frac{S_X - \mathrm{i}S_Y}{2}\,. \tag{3}$$

The operators T_{2M} are equivalent to the quadrupole moment tensor

$$Q_{ik} = \frac{1}{2}\left(S_i S_k + S_k S_i - \frac{4}{3}\,\delta_{ik} I\right), \tag{4}$$

where $i, k = X, Y, Z$ and I is the unit operator. For instance,

$$T_{20} = \left(\frac{3}{2}\right)^{1/2} Q_{ZZ} = \left(\frac{3}{2}\right)^{1/2}\left(S_Z^2 - \frac{S(S+1)}{3}\right).$$

The average value of the dipole moment characterizes the integral intensity of the EPR spectrum of the triplet state. The average value of the quadrupole moment characterizes the form of the EPR spectrum [15]. For instance, when the dipole moment is equal to zero and the quadrupole moment is nonzero, the two lines in the EPR spectrum of a triplet are in antiphase: one line corresponds to absorption (A) and the other to emission (E), i.e., an antiphase EPR spectrum of the A/E or E/A type is expected.

When two triplet excitons meet, their total spin may be equal to 0, 1, or 2. The triplet – triplet annihilation may occur only in singlet pairs. As a result, the triplet pairs that escape annihilation are enriched with the states with the total spin 1 or 2, i.e., in the triplet or quintet states of the pair, respectively. The total spin moment of the pair of colliding triplets A and B is to be denoted by $\mathbf{S} = \mathbf{S}_\mathrm{A} + \mathbf{S}_\mathrm{B}$. Immediately upon collision, the triplet pairs that have escaped mutual annihilation have the density matrix

$$\rho(0) = \frac{1}{9}(P_1 + P_2) \equiv \frac{1}{9}\left\{\frac{2}{3}\,\mathbf{S}^2 - \frac{1}{12}\,\mathbf{S}^4\right\}, \tag{5}$$

where $P_1 = \mathbf{S}^2(6I - \mathbf{S}^2)/8$ and $P_2 = \mathbf{S}^2(\mathbf{S}^2 - 2I)/24$ are the operators for the projection on the triplet-pair states with the respective total spin 1 and 2. In the state with density matrix (5), the pair of triplets turns out to be spin-correlated. The average value of the scalar product of the spin moments of the pair partners $\mathbf{S}_\mathrm{A}$ and $\mathbf{S}_\mathrm{B}$ is in fact nonzero:

$$\langle(\mathbf{S}_\mathrm{A}\mathbf{S}_\mathrm{B})\rangle = \mathrm{Tr}\left\{\rho(0)(\mathbf{S}_\mathrm{A}\mathbf{S}_\mathrm{B})\right\} = \frac{2}{9}\,. \tag{6}$$

The subsequent spin dynamics in these spin-correlated pairs form the dipole and quadrupole polarization of each of the triplets of the pair [15]. The spin dynamics in triplet pairs are determined by the spin Hamiltonian that includes the

Zeeman interaction of the triplets with the magnetic field B_0, the energy of splitting in the zero magnetic field (ZFS), and the exchange interaction $H_{\rm ex}$ between the triplets:

$$H = \beta g_{\rm A}\mathbf{B}_0\mathbf{S}_{\rm A} + \mathbf{S}_{\rm A}\hbar D\mathbf{S}_{\rm A} + \beta g_{\rm B}\mathbf{B}_0\mathbf{S}_{\rm B} + \mathbf{S}_{\rm B}\hbar D\mathbf{S}_{\rm B} + H_{\rm ex}\,, \tag{7}$$

$$H_{\rm ex} = -\hbar J\left(\frac{1}{2} + 2\mathbf{S}_{\rm A}\mathbf{S}_{\rm B}\right),$$

where $g_{\rm A,B}$ are the g-factors of the triplets, D is the ZFS tensor, and J is the exchange integral of the interaction between two triplet excitons in a spin-correlated pair. The principal values $-X$, $-Y$, and $-Z$ of the ZFS tensor D are expressed in terms of the parameters D and E: $D = (1/2)(X+Y) - Z$, $E = -(1/2)(X-Y)$. In this system, the total pair spin $\mathbf{S}^2 \equiv (\mathbf{S}_{\rm A} + \mathbf{S}_{\rm B})^2$ is not an integral of motion because $[H, \mathbf{S}^2] \neq 0$. Consequently, the spin dynamics in spin-correlated pairs of triplets change the total spin of the pair. As a result, the polarization of spins of the pair partners changes.

The spin polarization of the triplet excitons under discussion was first considered in Ref. [15]. We mention some results obtained for short-lived spin-correlated pairs of triplets. The nonzero projection $\langle S_B \rangle$ of the dipole moment of a triplet exciton on the direction of the external magnetic field shows up in the fourth order of the time-dependent perturbation theory. The dipole polarization of the triplet depends on the crystal orientation in the external magnetic field. For instance, when the magnetic field is aligned with the Z axis of the ZFS tensor, we obtain

$$\langle S_B \rangle = -\frac{16}{27}\, J\gamma B_0 E^2 t^4\,, \tag{8}$$

where t is the lifetime of a spin-correlated pair of triplets. When the field is aligned with the X axis of the ZFS tensor, the dipole polarization is

$$\langle S_B \rangle = -\frac{4}{27}\, J\gamma B_0 (D+E)^2 t^4\,. \tag{9}$$

A nonzero quadrupole moment of a triplet already appears in the second order of the perturbation theory:

$$\langle Q_{ZZ} \rangle = -\frac{8}{27}\, DJt^2\,, \qquad \langle Q_{XX} - Q_{YY} \rangle = -\frac{8}{9}\, EJt^2\,. \tag{10}$$

Therefore, the mutual annihilation of triplets leads to the production of spin-correlated pairs of triplets that have escaped mutual annihilation. The spin dynamics in spin-correlated pairs transforms the mutual ordering of the spins in a pair to the dipole and quadrupole polarization of individual triplets. The necessary condition for the formation of spin polarization caused by triplet – triplet annihilation is the spin – spin interaction between two triplet excitons in a spin-correlated pair. When the distance between the excitons lengthens to the extent that the spin – spin interaction may be neglected, the formation of spin polarization of the triplets ceases. But the separated triplets retain the polarization formed during their encounter and interaction. The manifestation of this spin polarization mechanism was experimentally proven in the investigation of the time evolution of the EPR spectra of triplet excitons in mixed molecular crystals [16]. Plotted by way of illustration in Fig. 2 is the time evolution of the intensity of low-field (Fig. 2a) and high-field (Fig. 2b) components in the EPR spectrum of triplet excitons in a phenazine/tetracyanquinodimethane crystal for $T = 300$ K. It can be seen from Fig. 2 that for the times of the order of 1 μs, the well-known polarization of electron spins of triplet excited states, which emerges due to the spin selectivity of a nonradiative intramolecular singlet – triplet transition [17], manifests itself. And for the times of the order of several dozen microseconds, the nonequilibrium polarization caused by the biomolecular process of triplet – triplet annihilation shows up. Observed in this case is the A/E type spectrum, which is indicative of the emergence of nonequilibrium quadrupole polarization.

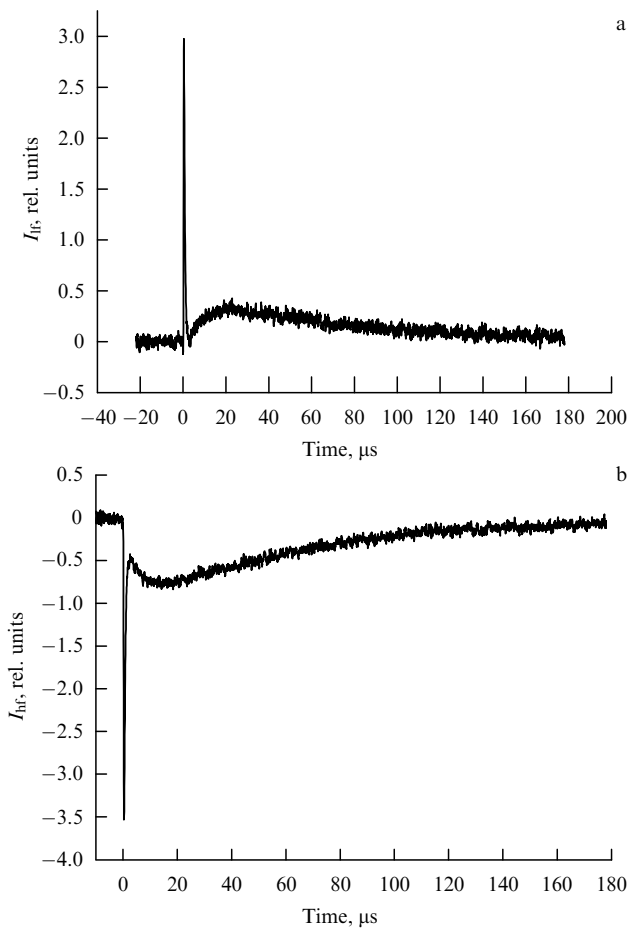

Figure 2. Time evolution of the low-field $I_{\rm lf}$ (a) and high-field $I_{\rm hf}$ (b) components of the EPR spectrum of triplets in a phenazine/tetracyanquinodimethane crystal for $T = 300$ K. The magnetic field B_0 is parallel to the principal X axis of the ZFS tensor of the triplet exciton.

4. Feasibility of using spin-dependent photo-induced processes in quantum computing

Of great interest is the possibility of using spin-dependent elementary photo-induced events in quantum computing. By way of example, we discuss the feasibility of quantum teleportation of an electron spin state with the quantum communication channel chosen as the spin-correlated electron – hole pairs produced due to photo-induced electron transfer.

Quantum teleportation was shown to be possible in Ref. [18]. Following the general teleportation scheme out-

lined in that work, the following protocol can be used in order to realize the quantum teleportation [19]. We imagine a molecular system containing three characteristic cofactors: A, B, and C. At the first stage, A is reduced, and in the system A^-BC, the electron spin in the anion radical A^- is prepared, employing microwave pulses, in a quantum-coherent state in the resonator of a pulsed EPR spectrometer. At the second stage, a light pulse produces the spin-correlated pair B^+C^- of ion radicals, yielding the three-spin system $A^-B^+C^-$. At the third stage, the A^-B^+ pair should recombine. This recombination is a spin-dependent process. As a rule, recombination is allowed for the singlet spin state in the pair A^-B^+. Eventually, we obtain the system ABC^-, in which the spin of the anion radical C^- is in the coherent state that is related to the coherent state of the anion radical A^- by the well-known unitary transformation. According to this protocol, we thus prepare the C^- electron spin in the coherent state by quantum teleportation of the coherence of another anion radical, A^-. To measure the coherent state of C^-, the methods of pulsed EPR spectroscopy can be used. To effect quantum teleportation, a photochemical process can therefore be used to produce the spin-correlated pair B^+C^-, a quantum communication channel, and to use the recombination of A^-B^+ for the projection of this pair on the singlet state.

To realize the above quantum teleportation protocol, there is good reason to use a natural photosynthetic reaction center (RC) or artificial RC models. A pair of separated charges P^+Q^- in the RC is a perfect quantum teleportation channel in a system of electron spins. The problem with this approach consists in the inclusion into the system of the reduced A^-, the carrier of the initial quantum state. Such a modification of the reaction center is basically possible.

5. Conclusion

That the electron spins play an important part in the making of chemical bonds has been well known since the emergence of the Heitler – London theory. For a long time, it was believed that the electron spin states are conserved in an elementary chemical event (Wigner's rule). However, time-resolved EPR experiments showed that short-lived intermediate states — spin-correlated pairs — form in the course of an elementary photochemical or photophysical event. The spin dynamics in these pairs manifest themselves in the unusual properties of the EPR signal. The study of spin polarization in the course of photo-induced processes has come to be an important part of a new scientific area — spin chemistry [20]. It is hoped that spin-dependent photo-induced processes will also find use in quantum computing.

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References

1. Salikhov K M *Chem. Phys. Lett.* **201** 261 (1993)
2. Angerhofer A, Bittl R *Photochem. Photobiol.* **63** 11 (1996)
3. Einstein A, Podolsky B, Rosen N *Phys. Rev.* **47** 777 (1935)
4. Salikhov K M, Bock C, Stehlik D *Appl. Magn. Reson.* **1** 195 (1990)
5. Kothe G et al., in *The Oji Intern. Conf. on Spin Chemistry, Tomakomai, Japan, 15–18 July 1991* (Ed. Y J I'Haya) (Tokyo, 1991) p. 420
6. Salikhov K M, Kandrashkin Yu E, Salikhov A K *Appl. Magn. Reson.* **3** 199 (1992)
7. Salikhov K M, Zech S G, Stehlik D *Mol. Phys.* **100** 1311 (2002)
8. (a) Salikhov K M *Usp. Fiz. Nauk* **160** (4) 77 1990 [*Sov. Phys. Usp.* **33** 299 (1990)]; (b) Salikhov K M, Kandrashkin Yu E *Usp. Fiz. Nauk* **166** 207 (1996) [*Phys. Usp.* **39** 191 (1996)]
9. Salikhov K M, Zech S, Stehlik D "Spin dynamics and EPR spectra of charge separated states in photosystem 1", in *30th Congress AMPERE on Magnetic Resonance and Related Phenomena, 23–28 July 2000, Lisbon, Portugal*
10. Molin Yu N et al. *J. Phys. Chem.* **84** 1853 (1980)
11. Salikhov K M, Sakaguchi Y, Hayashi H *Chem. Phys.* **220** 355 (1997)
12. Mursalimov L R, Salikhov K M *Appl. Magn. Reson.* **21** 223 (2001)
13. Kepler R G et al. *Phys. Rev. Lett.* **10** 400 (1963)
14. Varshalovich D A, Moskalev A N, Khersonskii V K *Kvantovaya Teoriya Uglovogo Momenta* (Quantum Theory of Angular Momentum) (Moscow: Nauka, 1975) [Translated into English (Singapore: World Scientific, 1988)]
15. Salikhov K M *Appl. Magn. Reson.* **26** 135 (2004)
16. Corvaja C et al. *Appl. Magn. Reson.* **28** 181 (2005)
17. Schmidt J *Chem. Phys. Lett.* **14** 411 (1972)
18. Bennett C H, Wiesner S J *Phys. Rev. Lett.* **69** 2881 (1992)
19. Salikhov K M *Proc. SPIE* **5833** 52 (2005)
20. Salikhov K M *10 Lektsii po Spinovoi Khimii* (10 Lectures on Spin Chemistry) (Kazan: Unipress, 2000)

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The role of electron paramagnetic resonance in the development of quantum electronics: facts and comments

A A Manenkov

1. Introduction

In 2004, the scientific community celebrated two milestones, 60 years of electron paramagnetic resonance (EPR) and 50 years of quantum electronics (QE).

Today, we have one more historic moment to celebrate, 60 years of the Zavoisky Kazan Physical-Technical Institute (KFTI). There is in fact a close historical connection between these three anniversaries. E K Zavoisky's 1944 discovery — and the subsequent development — of EPR has fundamentally influenced the making and development of quantum electronics, and the KFTI that bears Zavoisky's name is the leading research institute in the field of EPR. It is this historical connection that served as the stimulus for this paper.

The paper briefly reviews the early development of quantum electronics, including the formulation of its basic principles; the first ammonia-beam quantum oscillator (maser) and the first paramagnetic crystal-based quantum amplifiers (EPR masers); practical EPR maser schemes and their application; and progress from microwave EPR masers to optical quantum oscillators and amplifiers (lasers). The