## Scientific session of the Division of General Physics and Astronomy of the Academy of Sciences of the USSR (25 October 1989)

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A scientific season of the Division of General Physics and Astronomy of the Academy of Sciences of the USSR was held on October 25, 1989 at the S. I. Vavilov Institute of Physics Problems. The following reports were presented at the session:

1. K. M. Salikhov. Polarization of electron spins and EPR spectrum of a photosynthesis reaction center.

2. I. S. Aranson, K. A. Gorshkov, A. S. Lomov, and M. I. Rabinovich. Nonlinear dynamics of the localized states of multidimensional fields.

3. V. E. Zakharov. Trends in nonlinear physics. Summaries of two of the reports are published below.

4. K. M. Salikhov. Polarization of electron spins and EPR spectrum of a photosynthesis reaction center. The primary charge separation in photosynthesis occurs at a reaction center (RC): a pair of ion radicals is formed. The EPR spectrum obtained for this system with the help of the time-resolved EPR method reveals chemical (nonequilibrium) polarization of electron spins (CPE). Figure 1a shows schematically the type of spectrum observed for a reaction center. The real spectrum is a superposition of spectra of reaction centers of this type having different orientation relative to the external magnetic field  $B_0$ .

The lines referring to different ion-radicals  $R_1$  and  $R_2$ are split into two components owing to the spin-spin (exchange and dipole-dipole) interaction. The fact that the spectrum contains absorption and emission lines has a simple explanation: the spins of the partners in the radical pairs (RPs) studied are already mutually ordered at the moment the pairs are formed. In addition, unexpectedly, lines in the spectrum (see Fig. 1a) have the same intensity. According to the published ideas regarding chemical polarization of electron spins in radical pairs different lines should have different intensities, as shown in Fig. 1b.

In the report a new interpretation of the polarization of electron spins of ion radicals at a reaction center and its manifestation in the time-resolved EPR spectra is given.

In the situation of the reaction center under discussion here ion-radical pairs are formed in the singlet state. This means that initially the spins  $S_1$  and  $S_2$  of the partners of the pair are mutually ordered:  $\langle S_{1u} S_{2u} \rangle = -1/4$ , where u = x, y, and z. In the course of evolution of the spins in radical pairs the mutual ordering of the spins changes and other types of order appear. For example, the spins can become aligned in a definite manner relative to external fields; this is the mechanism of the chemical polarization of electron spins. In the theory of the CPE the following sequence of events was usually studied: creation of spin-correlated radical pairs  $\rightarrow$  evolution of spins under the action of the Hamiltonian  $H_0$  of the isolated radical pairs  $\rightarrow$  decomposition of radical pairs into independent radicals -> switching on of a microwave field  $H_1$  and recording of the EPR spectra. It is shown precisely for this case that under the action of  $H_0$  the

spins of the partners in the pair are aligned relative to the constant external magnetic field, nonzero values of  $\langle S_{1z} \rangle$  and  $\langle S_{2z} \rangle$  appear, and the spins are oppositely polarized, i.e.,

$$\langle S_{1z} \rangle = - \langle S_{2z} \rangle \neq 0.$$

As a result in a microwave field one of the spins radiates while the other absorbs. This model can be employed to describe radical pairs in solutions, where the partners of the pairs separate over times of the order of nanoseconds. In the case of a reaction center the EPR spectrum of a radical pair and not the EPR spectrum of isolated radicals is measured. For this reason the action of  $\hat{H}_0$  and the microwave field must be taken into account simultaneously. Such an analysis gives results which are in complete agreement with the observed spectrum: in the linear-response limit all lines must have the same intensity.

The intensity of lines at exact resonances is proportional to the quantity

$$J = \omega_1 \frac{\Delta \omega^2}{16R^2 \sin \varphi} \left[ \cos \left( \omega_1 t \sin \varphi \right) - \cos \left( 2Rt \right) \right] \sin \left( \omega_1 t \sin \varphi \right)$$

or

$$J' = \omega_1 \frac{\Delta \omega^2}{16R^2 \cos \varphi} \left[ \cos \left( \omega_1 t \cos \varphi \right) - \cos \left( 2Rt \right) \right] \sin \left( \omega_1 t \cos \varphi \right),$$

where  $\Delta \omega$  is the difference of the Zeeman frequencies of the



FIG. 1. a) Schematic diagram of the experimentally observed EPR spectrum of a radical pair. b) The spectrum that should be observed according to the existing theory of chemical polarization in radical pairs.

spins,  $R^2 = (\Delta \omega^2 + B^2)/4$ , B fixes the nonsecular part of the spin-spin interaction,

$$\begin{split} \hat{H}_{0} &= \omega_{A} \hat{S}_{12} + \omega_{B} \hat{S}_{22} + A \hat{S}_{12} \hat{S}_{22} + B \left( \hat{S}_{1x} \hat{S}_{2x} + \hat{S}_{1y} \hat{S}_{2y} \right) \\ \Delta \omega &= \omega_{A} - \omega_{B}, \\ \cos \varphi &= \left( \frac{1}{2} + \frac{B}{4R} \right)^{1/2}, \quad \sin \varphi = \left( \frac{1}{2} - \frac{B}{4R} \right)^{1/2}, \end{split}$$

and  $\omega_1$  is the amplitude of the microwave field.

As  $t \to 0$  the intensities of all lines approach zero, since the initial state of the radical pair is a singlet state. An interesting result is obtained for comparatively small  $\omega_1 t$  $(\omega_1 t \leq 1)$ . In this case

$$J \approx J' \approx \frac{\Delta \omega^2}{8R^2 \sin^2(Rt)} (\omega_1 t) \omega_1.$$

All lines have the same intensity. Here the first factor is the probability that the radical pair passes into the triplet state and  $\omega_1 t$  is the angle of nutation. This result could have been expected, since the microwave field acts only on the triplet states of the radical pair.

For reaction centers with different orientation the quantities  $\Delta \omega$ , *B*, and hence *R* also are different. For this reason for  $t > \langle \Delta R^2 \rangle^{-1/2}$  we can set  $\langle \cos(2Rt) \rangle \approx 0$ . Then

$$J \approx \omega_1 \frac{\Delta \omega^2}{16R^2} \frac{\sin(2\omega_1 t \sin \varphi)}{2 \sin \varphi}$$
  
and  
$$J' \approx \omega_1 \frac{\Delta \omega^2}{16R^2} \frac{\sin(2\omega_1 t \cos \varphi)}{2 \cos \varphi}$$

The intensities of all lines depend on  $\omega_1$  and the time, and two lines  $\sim J$  while the two other lines  $\sim J'$ .

Norris, Turnauer, and others have proposed an explanation for the fact that the intensities of the lines in the EPR spectrum of a reaction center are equal. Their explanation depends on the populations of the levels of the radical pair and the scheme of transitions between the levels. In the report it is shown that the approach in the linear-response limit is justified, if there is enough time for the coherence of the states of the radical pair to be destroyed owing to the spread in the values of R. The necessary condition for this is  $t > \langle \Delta R^2 \rangle^{-1/2}$ .

I thank D. Shtelik and J. Norris for a discussion of this problem.

The book: K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, and A. L. Buchachenko, *Spin Polarization and Magnetic Effects in Radical Reactions*, Elsevier, Amsterdam 1984 deals with material relevant to the subject of this report.