MODULATION BEATS OF SIGNAL OF DOUBLE ELECTRON–ELECTRON RESONANCE IN SPIN ECHO FOR BIRADICAL SYSTEMS

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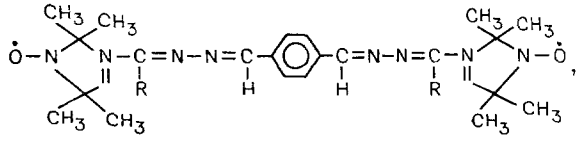
The method of double electron–electron resonance in the electron spin echo has been used to investigate biradical systems in the solid phase. Time-dependent oscillations in the amplitude of the echo signal have been observed, these oscillations being related to dipole–dipole and exchange interaction of unpaired electrons in the biradical. The distance between the radical fragments in these biradicals has been determined.

By means of double electron–electron resonance in the spin echo (DEERSE) that was described in detail in [1], it is possible to determine the parameters of dipole–dipole interaction between paramagnetic centers in the solid phase, centers that have lines in the ESR spectrum that differ substantially in frequency. In this method, a spin system consisting of interacting paramagnetic centers of two types is acted upon not only by the pulses shaping the signal of the electron spin echo, but also a rather strong UHF pulse at the resonance frequency of the spins of the second type. This results in a change in the local magnetic fields at the sites of the spins forming the echo signal, the scale of the change being determined by the magnitude of the dipole–dipole interaction between the partners. The decrease in amplitude of the echo signal in comparison with its magnitude in the absence of the saturated pulse is observed experimentally, and from this, conclusions can be drawn as to the magnitude of the dipole–dipole interaction of the spins. The sequence of actions of the pulses forming the echo and the pumping pulse is shown in Fig. 1.

In [1], this method was used to determine the distribution function for the distances between hydrogen atoms and hydroquinone radicals formed by photolysis of frozen aqueous solutions of sulfuric acid with added hydroquinone. It is of interest to examine the possibility of using this method to determine the distances between identical radicals that have a sufficiently broad ESR spectrum in the solid phase. Of particular importance in this respect may be stable nitroxyl radicals, which are widely used as spin labels in the investigation of various systems.

With these objectives, in the present work, we have used DEERSE in a study of dipole–dipole interaction between radical fragments of stable biradicals (I) and (II) with the following structure:



where R = H in (I) and R = CH_3 in (II).

These biradicals have a relatively rigid chain connecting the radical fragments, and they are characterized by relatively weak exchange interaction between the unpaired electrons [2].

The biradicals (I) and (II) in toluene solution were glassed by freezing down to 77°K in these studies. For comparison, analogous experiments were performed under the same conditions on solutions of the stable radicals

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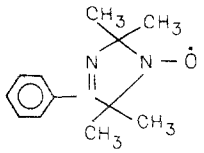

(III)

EXPERIMENTAL PROCEDURES

In this work we used the biradicals (I) and (II) that had been synthesized and purified in accordance with procedures described in [2]. The samples were placed in a Dewar condenser (chilled with liquid nitrogen), located at the antinode of the magnetic fields of a bimodal UHF generator.

The DEERSE unit, which was similar to that used in [1], was built up from a coherent electron spin echo spectrometer in the three-centimeter range [3]. This unit differed from that described in [1] in that the UHF loops of both modes of the bimodal resonator were completely separated; and for observation of the echo signal with respect to both modes, two separate registration systems were used.

The ESR spectra of our samples are typical for stable radicals of this type in the solid phase, and they have an overall extent of approximately 230 MHz. The frequency of the UHF vibrations of the pulses shaping the spin echo signal differed from the frequency of the pumping pulse by approximately 95 MHz. Thus it was possible, by observing the spin echo signal on the low-field edge of the ESR spectrum, to excite a considerable fraction of the spins (15-20% of the total number) pertaining to the central part of the ESR spectrum of these radicals. The length of the pulses shaping the spin echo signal was approximately 60 nsec, and the length of the pumping pulse was 30 nsec.

The dependence of the spin echo signal amplitude on T was determined by varying the position of the pumping pulse relative to the pulses shaping the echo, with a fixed value of τ.

RESULTS AND DISCUSSION

A study of the dependence of the spin echo signal amplitude on the position of the saturating pulse showed that there is a substantial difference in the behavior of the echo signals from the stable radicals and from the biradicals.

In the case of frozen solutions of the stable radicals (III), the usual exponential dependence of the echo signal amplitude on T is observed (Fig. 2):

$$V_p = V_0 \exp(-bT), \tag{1}$$

where V_p is the amplitude of the echo when the pumping pulse is turned on; V_0 is the amplitude of the echo signal in the absence of a pumping pulse. The magnitude of b in (1) depends on the concentration of radicals and on the parameters of the saturating pulse. Such behavior of the echo signal is due to dipole–dipole interaction of the spins participating in echo formation with randomly located spins excited by the pumping pulse. This mechanism of echo signal decay was described in [1], and in the present case it is not of any interest.

Substantial differences in the behavior of the spin echo signal appear when the change is made to the biradicals (see Fig. 2). It will be noted that in addition to the dependence of the type of (1), there are oscillations of the echo signal amplitude, the appearance of these oscillations being related to interaction between radical fragments belonging to the same biradical.

In principle, both dipole–dipole and exchange interactions between the unpaired electrons of the biradical may be manifested in experiments on DEERSE. According to [2], the magnitude of the exchange interaction in the biradicals under investigation is less than 2 MHz, i.e., small in comparison with the difference between Zeeman frequencies of the spins forming the echo and the spins excited by the pumping pulse. Therefore, in calculating the behavior of the spin echo signal, we can limit ourselves to the spin Hamiltonian:

$$\hat{H} = \gamma^2\hbar r^{-3}(1 - 3\cos^2\theta)\hat{S}_{1z}\hat{S}_{2z} + \hbar J\hat{S}_{1z}\hat{S}_{2z} = \hbar a\hat{S}_{1z}\hat{S}_{2z}, \tag{2}$$

where γ is the gyromagnetic ratio; $\hbar$ is the Planck constant; r is the distance between radical fragments; θ is the angle between the direction of the external magnetic field and the vector r; J is the magnitude of the exchange interaction.

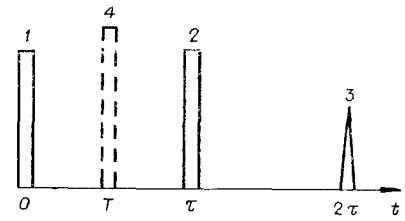

Fig. 1. Sequence of action of pulses (1, 2) forming echo signal (3), and pumping pulse (4).

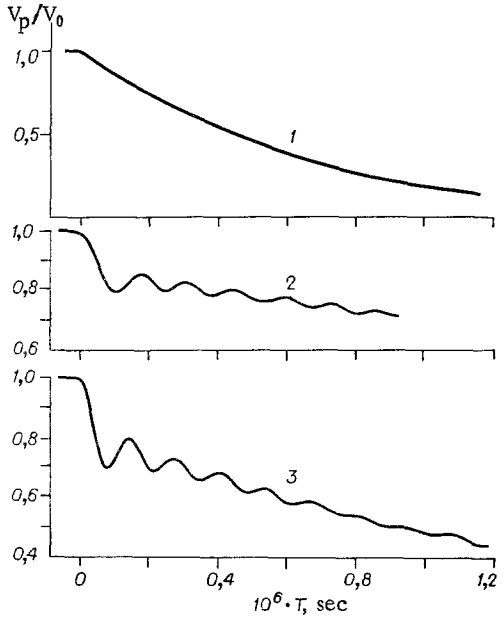

Fig. 2. Amplitude of spin echo signal as a function of position of pumping pulse: 1) stable radical (III); 2) biradical (I); 3) biradical (II).

The Hamiltonian (2) formally has the same form as in [1]; and for this Hamiltonian, calculations of the dependence of the spin echo were performed. Considering that these biradicals have a rigid structure, i.e., that the scatter with respect to distances r is sufficiently small, we can use the results of [1], taking the distribution function with respect to distances between the radical fragments in the form of a delta function. In this case, for the dependence of the spin echo signal, we obtain the expression

$$\frac{V_p}{V_0} = \exp(-bT)\left\{1 - p\left[1 - \left(\frac{\pi r^3 (C^2 + S^2)}{6\gamma^2 \hbar T}\right)^{1/2} \cos\left(\left(\gamma^2 \hbar r^{-3} + J\right) T - \operatorname{arctg}\left(\frac{S}{C}\right)\right)\right]\right\}, \quad (3)$$

where $C = \int_0^l \cos\left(\frac{\pi t^2}{2}\right) dt$ and $S = \int_0^l \sin\left(\frac{\pi t^2}{2}\right) dt$ are Fresnel integrals; $l = (6\gamma^2 \hbar T r^{-3})^{1/2}$; p, following [1], is the fraction of spins excited by the pumping pulse.

With an increase in the parameter l (it is sufficient to take $l > 3$), the Fresnel integrals S and C tend toward 0.5, and Eq. (3) can be represented approximately in the form

$$\frac{V_p}{V_0} = \exp(-bT)\left\{1 - p\left[1 - \left(\frac{\pi r^3}{12\gamma^2 \hbar T}\right)^{1/2} \cos\left[\left(\frac{\gamma^2 \hbar}{r^3} + J\right) T - \frac{\pi}{4}\right]\right]\right\}. \quad (4)$$

In comparing (4) with the experimentally observed spin echo dependence, it must be noted that the experimental value $p \approx 0.2$ is in complete agreement with the value calculated on the basis of Eq. (6) in [1], using real ESR spectra of the biradicals and real parameters of the pumping pulse.

Using (4), with the experimentally measured oscillation frequency of the spin echo signal we can determine the quantity $(\gamma^2\hbar r^{-3} + J)$. For the biradicals (I) and (II), the values obtained are practically identical, 7.2 and 7.5 MHz, respectively. Considering [2] that for these biradicals the magnitude of the exchange interaction J is less than 2 MHz, we can use the experimentally determined oscillation period to estimate the distance between the radical fragments of the biradicals. Considering the indeterminacy in the magnitude and sign of J, we find that such an estimate gives $r = (19 \pm 1.6) \cdot 10^{-8}$ cm. Substitution of this value of r into (4) gives the correct scale of timewise damping of oscillation amplitude, which indicates a small scatter (according to our estimates, not more than $0.5 \cdot 10^{-8}$ cm) with respect to the distances between the radical fragments.

In conclusion, let us note that modulation of primary electron spin echo signal decay as a result of dipole–dipole and exchange interaction was observed in [4]. The application of double electron–electron resonance opens up possibilities for studying these interactions in a broader circle of spin systems.

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