Magnetic resonance of short-lived intermediate complexes in the reaction of quenching of triplet excitons by radicals

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The method wherein magnetic resonance is detected by the change of the reaction yield (RYDMR) was used to study the intermediate triplet exciton + radical pairs in the reaction of quenching of the delayed fluorescence of crystals of charge transfer complexes (CTC) produced by gamma irradiation of the samples. The RYDMR spectrum of the pairs was calculated theoretically and was obtained experimentally by detecting the delayed-fluorescence intensity changes due to absorption of the resonant microwave power by intermediate pairs and the resultant change of their spin state. The pair lifetime determined from the line width is 6×10^{-9} sec. The measurements were made on the anthracene-dimethylpyromellitimide CTC at room temperature.

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1. INTRODUCTION

Numerous examples of condensed-phase reactions whose rates depend on the spin state of an intermediate complex produced in the course of the reaction have been recently observed. This dependence manifests itself in experiment as an influence of an external magnetic field on the yield of reaction products having a definite multipolarity, or on system parameters kinematically connected with this yield. Reviews of processes sensitive to magnetic fields can be found, for example, in Refs. 1 and 2. It was recently demonstrated that a resonant microwave field can be used to alter the spin state of intermediate complexes produced in collisions of triplet excitons[3,4] or of ion-radical pairs,[5,6] having lifetimes in the range 10^{-8}–10^{-9} sec and situated in a magnetic field. Since the change of the spin state of a pair leads to a change in the yield of the reaction products, the registration of the product yield as a function of the magnetic field intensity has made it possible, for the first time ever, to obtain the spectra of magnetic resonance detected by means of the reaction yields (hereafter abbreviated RYMDR), for triplet excitons contained in pairs, as well as the spectra of ion-radical pairs in an excited complex with charge transfer, by registering the microwave-induced changes in the fluorescence intensity[3,4] or in the photoconductivity.[6]

A reaction of importance in the photochemistry of molecular crystals is the quenching of triplet excitons when they collide with particles having a spin $\hbar/2$ (with free radicals):

$$^3T+{}^2R\rightarrow{}^1S_0+{}^2R. \tag{1a}$$

When account is taken of the formation of the intermediate state, the same reaction can be written in the form

$$^3T+{}^2R\underset{k_{-1}}{\overset{1/6k_1}{\rightleftharpoons}}{}^{2,4}[^3T^2R]_i\xrightarrow{k_2|B_i|^2}{}^1S_0+{}^2R. \tag{1b}$$

Here ^3T are the triplet excitons, ^2R are particles with spin $\hbar/2$, $^1S_0$ is the ground state of the crystal molecules, and $[^3T^2R]_i$ is an intermediate complex produced in one (the i-th) of the six possible spin states. The rate constants of the quenching process (γ_1), of the complex formation (k_1), of the decay of the complex into the initial particles (k_{-1}), and of formation of the reaction products from the complex ($k_2|B_i|^2$) are indicated. The yield of the reaction (1*b*) in a channel having a doublet multiplicity (with a total product-particle spin equal to $\hbar/2$) depends on how the doublet component of the spin function B_i is distributed over the six possible states of the intermediate complex $[^3T^2R]$. Observations of the influence of the constant magnetic field on the rate of the reaction (1) in molecular crystals[7] and in liquid solutions[8] show that the lifetime of the intermediate complex is much shorter than the spin-relaxation time, and consequently, as shown before,[3,4,5] it is possible in principle to alter the rate of the reaction (1) by using a resonant microwave field.

In the present study we obtained experimentally the RYDMR spectrum of the intermediate pair in the reaction (1b), as revealed by the changes ΔL of the intensity L of the delayed fluorescence due to the annihilation of the triplet excitons in the reaction

$$^3T+{}^3T\xrightarrow{\gamma_2}{}^1S_0+{}^1S_1, \tag{2a}$$

$$^1S_1\underset{L}{\rightarrow}{}^1S_0+h\nu, \tag{2b}$$

where $^1S_1$ is a singlet exciton. These changes are due to the influence of the resonant magnetic microwave field on the lifetime of the triplet excitons ^3T, which is determined by the rate of the reaction (1) and on which the intensity of the delayed fluorescence L depends.

We present the experimental results on the magnetic-resonance-mediated changes of the rate of the process (1), as well as a theory that describes these changes.

2. PROCEDURE AND RESULTS

We used crystals of complexes with charge transfer, namely anthracene-dimethylpyromellitimide (A-DMPI). The processes occurring in these complexes, accompanying the excitation in the singlet-singlet absorption band and leading to rapid and delayed fluorescence of

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the crystals as well as to photoconductivity and to a dependence of these properties on the intensity of the constant magnetic field, were investigated previously.[9,10] These complexes are convenient for the study of processes in which triplet excitons participate, since the yield of the triplet excitons when the crystals are excited in the charge-transfer band is large and amounts to 0.37 per absorbed optical photon.[9] The triplet excitation is localized on the molecules of the donar (anthracene) and migrate over the planes containing these molecules (over the *bc* planes[11]). The lifetime of the triplet excitons in the employed crystals, determined from the fall-off of the delayed fluorescence, is 1.8 msec.[10] The crystal structure of the complexes was investigated in Ref. 11. The RYDMR spectrum of pairs of triplet excitons that are intermediate states in the reaction (2) was registered for these complexes earlier.[4]

The needle-shaped crystals of the complexes measured $3 \times 0.1 \times 0.1$ mm. To register the RYDMR spectrum, use was made of a set of randomly placed crystals (~0.002 g) in a quartz ampul filled with argon. The ampul with the crystals was placed at the maximum of the magnetic microwave field H_1 of the RYDMR spectrometer resonator. A brief description of the RYDMR spectrometer follows.

This was a homodyne magnetic-resonance spectrometer of the reflex type with the modulation of microwave power (or of the magnetic field) and with detection of the magnetic-resonance signals by the change of the yield of the reaction products in the samples (by photoconductivity, fluorescence, or light absorption). In the present study the RYDMR spectra were obtained by registering the change of the fluorescence intensity under conditions of resonant absorption of modulated microwave power by the sample.[5] A block diagram of the RYDMR spectrometer is shown in Fig. 1.

The microwave generator was an *X*-band klystron with 10 W output power. The microwave power was modulated to obtain the envelope of the RYDMR signal; the modulation was effected with a ferrite switch at a repetition frequency 10^3 Hz; the switch, in turn was controlled by the generator that stabilized the modulation of the microwave power. The klystron frequency was stabilized against the frequency of the working resonator by an automatic frequency control (AFC) system with strobing and maintaining the error signal level in the time when, at 100% modulation of the microwave power, only the reference power is received by the balance detector. The AFC error signal was converted to a frequency 3×10^5 Hz by a semiconductor modulator and was fed to a synchronous AFC amplifier.

The strobint block ensured, at the end of each "positive" half-cycle of the microwave power modulation, the selection and maintenance of the error signal and its transmission to the klystron power-supply block. The electromagnet was fed from a stabilization and control block with linear-stepwise scanning, thus ensuring correspondence between the storage channel address and the magnetic field. The magnet stabilization coefficient was 10^5. The rate of linear scanning of the magnetic field was 5×10^{-3}–10^2 G/sec.

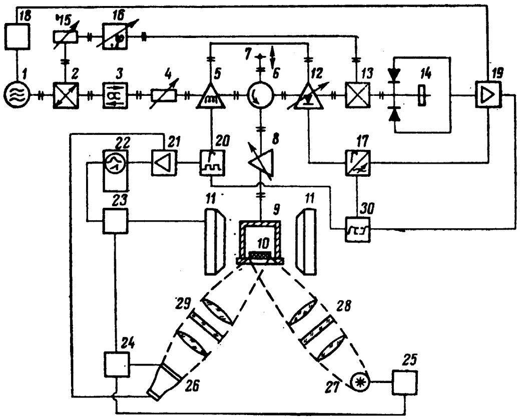

FIG. 1. 1—Microwave generator; 2, 13—directional couplers; 3—gyrator; 4, 15—attenuators; 5—ferrite switch; 6—circulator; 7—piston; 8—matching unit; 9—resonator; 10—sample; 11—electromagnet; 16—phase shifter; 17—generator for AFC; 18—power pack for microwave generator; 19, 20—synchronous amplifiers for AFC and for the RYDMR signal; 30—generator to stabilate the microwave-power modulation; 22—recording instrument; 23, 24, 25—blocks for stabilization and control of the magnetic field, the photomultiplier, and the light source, respectively; 26—photomultiplier; 27—light source; 28, 29—system of lenses and filters; 30—strobing block of AFC system.

The resonator used in the spectrometer could be either a rectangular tunable cavity or a dielectric resonator, with respective modes H_{10n} and H_{110}. The loaded Q of the resonators was 3×10^3. To expose the sample to light and ensure the possibility of registering the fluorescence signal, a number of slits were cut in the end faces and the side walls of the rectangular cavities. The light source can be a high-pressure gas-filled lamp (such as DKSSh-150 or DRSh-100), with their current stabilized (stabilization coefficient ~10^4).

The fluorescence signal was registered with a photomultiplier. Measures were taken to stabilize the photomultiplier operation; it was placed 1 m away from the electromagnet and a double screen shielded it against external fields. The power supply to the photomultiplier divider was optimized; photomultiplier power packs with high stabilization coefficients (10^5) were chosen; the photomultiplier load was carefully matched to the RYDMR signal-recording amplifier.

The spectrometer sensitivity is limited primarily by the photomultiplier noise limit. The main contribution to the photomultiplier noise when a signal is registered at 10^3 Hz is due to the shot noise of the current and of the amplifier that registers the RYDMR signal. If the light flux exciting the fluorescence is 10^5 photons/sec-cm^2, then the RYDMR signal can be registered if the sample contains only 10^4–10^5 pairs of paramagnetic particles at room temperature.

The sample was illuminated in the wavelength band $350 < \lambda < 510$ nm. The sample fluorescence was registered at wavelengths $\lambda > 520$ nm. The fluorescence had two components, fast and delayed. The delayed component, a small fraction (~3%) of the total fluorescence, was due to emission of the singlet excitons produced in process (2). The radicals were produced in the sample by bombardment with ^{60}Co gamma rays at room temperature and in an inert-gas atmosphere. The irradiation dose power was 0.01 Mrad/min. Irradiation of the samples decreased the intensity of the delayed fluorescence (by up to 50%). We attribute this decrease to the quenching of the triplet excitons by the radiolysis products, particularly by the free radicals. Since the lifetime of the triplet excitons in the non-irradiated samples is known, it is possible to estimate the concentration of the defects produced by the irradiation:

$$[R]\leqslant\left(\frac{k_0}{\gamma_1}\right)=5\cdot 10^{13}\ \mathrm{cm}^{-3}.$$

It was assumed for this estimate that the rate constant of the quenching of the triplet excitons is $\gamma_1 = 10^{-11}$ cm^3/sec and $(k_0)^{-1} = 2\times 10^{-3}$ sec. Such a concentration corresponds to not more than 10^{11} particles in the entire volume of the sample, and is insufficient for the study of radicals by the usual electron paramagnetic resonance method.

However, the RYDMR spectra of the irradiated samples differed from the initial spectra.

Figure 2 (curve 1) shows the RYDMR spectrum of a non-irradiated sample, determined from the change of the intensity of the delayed fluorescence of the sample. It corresponds to the spectrum of magnetic resonance of triplet excitons in random oriented crystals. The sample contained a small number of crystals (~50). The spectrum shows therefore lines belonging to the RYDMR spectra of individual crystals.

The same figure shows a typical RYDMR spectrum obtained with samples exposed to a dose of 0.2 Mrad (curve 2).

Figure 3 shows the central part of the spectrum, taken at a lower sweep of the spectrometer magnetic field. The sample irradiation led to the appearance, in the RYDMR spectrum, of a single line with Lorentz shape but of negative sign, superimposed on the initial spectrum, whose intensity was decreased somewhat. That this is indeed a superposition of spectra and not a change in the shape or structure of the initial spectrum is attested by the passage of the central line through the zero line of the spectrum, i.e., the reversal of the polarity of the combined spectrum in the region where the new line appears. The line position corresponds to a g-factor smaller than the g-factor of the triplet excitons by 2×10^{-2} times.

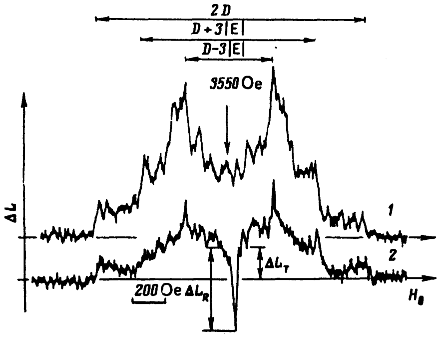

FIG. 2. Magnetic-resonance spectra of short-lived pairs of paramagnetic particles (RYDMR spectra) in a polycrystalline sample of the charge-transfer complex A-DMPI (ΔL is the change of intensity of the delayed fluorescence of the sample); 1—non-irradiated sample, the spectrum corresponds to a pair of triplet excitons of anthracene; 2—the same sample but irradiated by a dose of 0.3 Mrad. The central line in the spectrum is due to absorption of microwave power by the radicals in the triplet exciton + radical pairs. D and E are parameters of the tensor of fine splitting of the triplet excitons. Spectrum sweep rate 50 Oe/min, registration time constant $\tau=1$ sec, $T=300$ K.

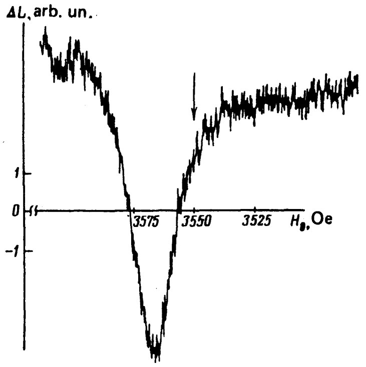

FIG. 3. Central part of the RYDMR spectrum of irradiated sample of A-DMPI (of spectrum 2 on Fig. 2). Spectrum sweep rate 2 Oe/min, $\tau=1$ sec, $T=300$ K. Line shape - Lorentzian, width ~20 Oe at half-height. The arrow indicates the center of the RYDMR spectrum of a pair of triplet excitons.

To determine the nature of the single line that appears on the spectra of the irradiated samples, it is important to know the dependence of the height of the RYDMR spectrum line on the intensity of the exciting light. This dependence (points) is shown in Fig. 4. It corresponds to an almost linear change of the height of the central line on the light intensity, and becomes stronger at lower intensities. The spectrum sideband heights depend quadratically on the light intensity. The line shape is independent of the level of the employed microwave power (in the range from several watts to dozens of milliwats); it remains Lorentzian, with a width ~20

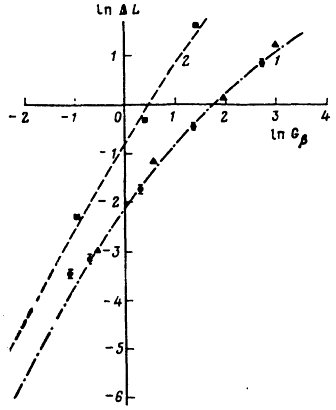

FIG. 4. Intensities of the radical line (ΔL_R—curve 1) and of the triplet line (ΔL_T—curve 2) vs. the intensity of the exciting light. The curves were plotted in accord with Eq. (15), and ΔL for each of the curves is given in arbitrary units. The experimental points were made to fall on the calculated curves by special choice of the exciting-light intensity units.

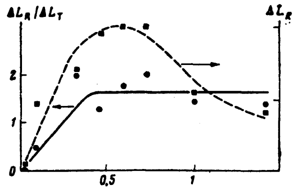

FIG. 5. Intensity of the central line ΔL_R and the ratio $\Delta L_R/\Delta L_T$ in the spectrum of an irradiated A-DMPI sample vs. the irradiation dose. The values of ΔL_R and ΔL_T are shown in Fig. 1.

Oe at half-height (the lifetime of the corresponding correlated triplet-radical pair is 6×10^{-9} sec).

Figure 5 shows the dependence of the amplitude of the central line of the RYDMR spectrum on the gamma dose to which the sample is exposed.

3. DISCUSSION

The main result of the action of gamma rays on the CTC crystals, obtained in this paper, is the appearance of a negative line at the center of the RYDMR spectrum as revealed by the change of the intensity of the delayed fluorescence. The height of this line increased with the irradiation dose (up to 0.3 Mrad). In addition, irradiation decreased the height of the lines of the positive part of the spectrum. The observed changes in the RYDMR spectrum are due to the appearance of new intermediate pairs of paramagnetic particles, whose spin state affects the delayed-fluorescence yield. We propose that these are $[^3T^2R]$ pairs in the course of the extinction of the triplet excitons by the radicals (1b). To prove this assumption, we consider the magnetic-resonance transitions in this pair, as well as those singularities of its RYDMR spectrum which can be used for a comparison of the experimental results with the calculation.

Connection of rate constant γ_1 of the reaction (1) with the distribution of the doublet component over the spin states of the intermediate complex

In the scheme of reaction (1b), the rate of formation of the $[^3T^2R]$ pairs in the i-th spin state when the particles ^3T and ^2R are not polarized is equal to $\frac{1}{6}k_1[T][R]$, where $[T]$ and $[R]$ are the concentrations of the free triplet excitons ^3T and the radicals ^2R. The pair $[^3T^2R]$ can either decay into initial particles (the rate constant of this process is equal to k_{-1} and does not depend on the spin state of the pair), or can be transformed into the reaction products. Since the total spin of the final products is equal to $\hbar/2$ and the reaction conserves spin, the rate constant of this transformation is equal to $k_2|B_i|^2$, i.e., it depends on the amplitude of the doublet component B_i in the given spin state. The total rate constant of the process (1) is defined as

$$\gamma_1=\frac{1}{6}k_1\sum_{i=1}^{6}\frac{k_2|B_i|^2}{k_{-1}+k_2|B_i|^2}. \tag{3}$$

The changes $\Delta\gamma_1$ of the constant γ_1 under the influence of the resonant microwave field with magnetic component $\mathbf{H}_1\perp\mathbf{H}_0$ can be calculated on the basis of the general approach to bimolecular reactions that conserve spin, an approach developed earlier.[3,4] According to this approach, the intermediate complex is regarded as a particle that has a system of energy levels, each of which has its own lifetime τ_i and its own rate constant of decay with formation of reaction products. The effect of the microwave power on the reaction rate constant γ_1, which is a function of the stationary populations of the levels of the complex, is taken into account in this case as a change of these populations.

Spin wave functions of intermediate triplet–radical complex

To calculate $\Delta\gamma_1$ it is necessary to establish the spin wave functions of a triplet radical pair in a strong magnetic field $\mathrm{H}_0 \gg D,\ E,\ a,$ where D and E are the parameters of the fine-splitting tensor of the triplet excitons, and a is the constant of the hyperfine splitting of the radicals. These functions are determined by solving a wave equation in which the triplet–radical pair Hamiltonian $\mathscr{H}_{TR}$ is equal to the sum of the Hamiltonians of the single triplet exciton ($\mathscr{H}_T$) and of the radical ($\mathscr{H}_R$):

$$\mathscr{H}_{TR}=\mathscr{H}_T+\mathscr{H}_R=g_T\beta\mathrm{H}_0S_T+S_T\hat{D}S_T+g_R\beta\mathrm{H}_0S_R+\sum_m a_mS_RI_m. \tag{4}$$

The first term corresponds here to the energy of interaction of the magnetic moment of the triplet exciton with the external magnetic field, the second to the tensor of the spin-spin interaction of the electrons in the triplet exciton, while the third and fourth terms describe respectively the Zeeman interaction of the magnetic moment of the radical with the field H_0 and the spin-nucleus interaction in the radical.

If the energy levels are not degenerate, the wave eigenfunctions of the pair take the form:

$$|\pm 1, \pm{}^1/_2\rangle=|Q;\ \pm{}^3/_2\rangle$$

is a function of the pure quadruplet state with spin projections $\pm(3/2)\hbar$ on the direction of the field H_0:

$$|\pm 1, \mp{}^1/_2\rangle=({}^1/_3)^{1/2}|Q;\ \pm{}^1/_2\rangle\mp({}^2/_3)^{1/2}|P;\ \pm{}^1/_2\rangle,$$

$$|0, \pm{}^1/_2\rangle=({}^2/_3)^{1/2}|Q;\ \pm{}^1/_2\rangle\pm({}^1/_3)^{1/2}|P;\ \pm{}^1/_2\rangle$$

are functions representing mixtures of quadruplet and doublet states with spin projections $\pm(1/2)\hbar$ on H_0. Here $|Q;\ \pm3/2\rangle$, $|Q;\ \pm1/2\rangle$ are the spin wave functions of the triplet + radical pair in a pure quadruplet state Q, and their projections on H_0 are respectively $\pm(3/2)\hbar$ and $\pm(1/2)\hbar$; $|P;\ \pm1/2\rangle$ are the spin wave functions of the pair in the pure doublet state P, and their projections on the external magnetic field H_0 are $\pm(1/2)\hbar$. In the indicated mixed states, the amplitude B_i of the doublet components are $\mp(2/3)^{1/2}$ and $\pm(1/3)^{1/2}$, respectively.

The energy-level scheme of the complex situated in a strong magnetic field H_0 is shown in Fig. 6. The arrows T and R on the diagram mark the transitions between levels under the influence of the resonant microwave field in the triplet excitons and the radicals. The $|0, +1/2\rangle \rightarrow |0, -1/2\rangle$ transition is not shown, since it does not change the population of the levels that

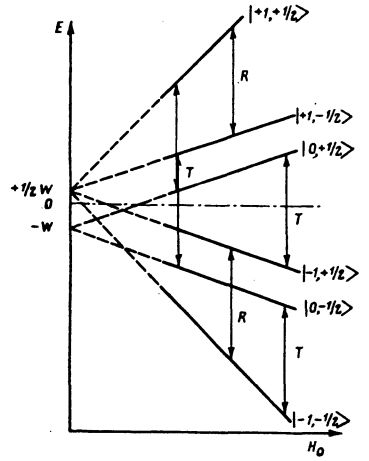

FIG. 6. Energy-level diagram of triplet exciton + radical pair of paramagnetic particles in a strong magnetic field. The energy W is determined by the fine splitting in the triplet excitons and depends on the orientation of the crystal relative to the direction of the constant magnetic field H_0. The figure indicates the wave functions of each level and those Zeeman transitions in the triplet excitons (T) and radicals (R) which lead to a change in the rate constant of reaction (1a).

contain a doublet component of the spin wave function.

Change of the rate constant γ_1 of the quenching of the triplet excitons by radicals under the influence of magneto-resonant transitions in an intermediate complex

We calculated $\Delta\gamma_1$ with the aid of the previously proposed[3,4] stationary kinetic scheme. An exact calculation with the aid of the equation for the spin density matrix of the complex, performed for the reaction of annihilation of triplet excitons,[12] has shown that the kinetic scheme provides a correct quantitative and qualitative description of the spectrum of the resonant change of the rate constant far from the level degeneracy of the intermediate complex.

In the absence of a microwave field, the stationary population of the i-th level is

$$n_i={}^1/_6k_1[T][R]\tau_i,$$

where

$$\tau_i=(k_{-1}+k_2|B_i|^2)^{-1}. \tag{5}$$

Application of a microwave field produces transitions between the levels $i \leftrightarrow j$ with a rate constant (with probability calculated per second):

$$k_{ij}=k_c\langle i|S_x|j\rangle^2 l(\tau_{ij}, H_0, H_{0\,\text{res}})\ [\text{sec}^{-1}], \tag{6a}$$

where

$$k_c=(g\beta/\hbar)^2\text{H}_1^2\ [\text{sec}^{-2}],$$

S_x is the operator of spin projection on the x axis, which is perpendicular to H_0, and determines the transition probability; $\lambda(\tau_{ij}, H_0, H_{0\,\text{res}})$ is the absorption-line shape function;

$$\tau_{ij}=2\tau_i\tau_j(\tau_i+\tau_j)^{-1}=1/(k_{-1}+{}^1/_2k_2(|B_i|^2+|B_j|^2))$$

is the average lifetime for the levels i and j; $H_{0\,\text{res}}$ is the resonant value of the magnetic field of the spectrometer H_0 (at a constant frequency of the microwave field); for a Lorentzian line we have

$$l=\frac{1}{\pi}\frac{\tau}{(g\beta/\hbar)^2(H_0-H_{0\,\text{рез}})^2\tau^2+1}\ [\text{sec}]. \tag{6b}$$

We did not take into account here the hyperfine splitting of the absorption line of the radicals, $a=0$. If $a\neq 0$, the radical absorption line shape is the sum of the Lorentzians for all m spin-nuclear sublevels of the radical. At $k_{ij}\ll k_{-1}$ the changes of the rate constant $\Delta\gamma_1$ are connected with Δn_i by a relation obtained by substituting (5) in (3):

$$\Delta\gamma_1=\frac{1}{[T][R]}\sum_{i=1}^{6}\Delta n_i k_2|B_i|^2. \tag{7}$$

The change $\Delta\gamma_{1R}$ is due to absorption of microwave power by the radical and is caused by the transitions between the levels $|\pm1, \pm1/2\rangle \leftrightarrow |\pm1, \mp1/2\rangle$:

$$\Delta\gamma_{1R}=\frac{1}{6}k_1\frac{2}{9}\frac{\varepsilon^2}{(1+{}^2/_3\varepsilon)^2}\frac{k_c l(k_{-1}+{}^1/_3k_2, H_0)}{k_{-1}}, \tag{8}$$

where $\varepsilon=(k_2/k_{-1})$.

The calculation of the change of $\Delta\gamma_{1T}$ due to the magnetic-resonance transitions between the triplet-exciton levels in the triplet-doublet complex leads, when account is taken of the contribution from each of the two transitions, to the formula

$$\Delta\gamma_{1T}=\frac{1}{6}k_1\frac{1}{18}\frac{\varepsilon^2}{(1+{}^1/_3\varepsilon)^2}\frac{k_c}{k_{-1}}\Big[l\Big(k_{-1}+\frac{1}{6}k_2, H_0\Big) + \frac{1}{(1+{}^2/_3\varepsilon)^2}l\Big(k_{-1}+\frac{1}{2}k_2, H_0\Big)\Big]. \tag{9}$$

The formulas (8) and (9) already take into account the amplitude values $|B_i|^2=2/3$ and $1/3$ and the values of the matrix elements $\langle i|S_x|j\rangle^2$.

Thus, the $\Delta\gamma_1$ spectrum has three lines of positive polarity, one from the radicals and two, of equal intensity, from the triplet excitons. The ratio of their amplitudes $(\Delta\gamma_{1R}/\Delta\gamma_{1T})\to 2$ at $a=0$ and as $\varepsilon\to 0$. The foregoing calculations are correct far from the level degeneracy of the triplet-radical pair. Formula (8) yields a numerical estimate of $\Delta\gamma_{1R}$. At $\varepsilon=1$ and $k_{-1}=2\times 10^{-8}$ sec we get $\Delta\gamma_{1R}=\frac{1}{6}k_1H_1^2\cdot 1.5\cdot 10^{-4}$ cm³/sec, as well as the ratio

$$\frac{\Delta\gamma_{1R}}{\gamma_1}=\frac{1}{\pi}\frac{\varepsilon}{(3+2\varepsilon)^2}\frac{k_c}{k_{-1}^2}=10^{-4}H_1^2. \tag{10}$$

We note that the entire calculation was made for unpolarized triplet excitons and radicals. When polarized excitons are quenched, an appreciable increase of $\Delta\gamma_1/\gamma_1$ can be observed in comparison with the calculated value, as well as a reversal of the sign of $\Delta\gamma_1$, depending on the orientation of the crystal relative to H_0.[13] A negative $\Delta\gamma_1$ is obtained if the level populations of the triplet excitons with magnetic-moment projections on H_0 equal to ±1 are larger than the population of the states with zero projection.

The calculations do not take into account the contribution of the spin-spin relaxation to the width of the spectral lines, since the pairs considered had lifetimes shorter than the time of spin relaxation in the system. This assumption is justified both by the very existence of the RYDMR spectrum of these pairs, and by the fact that the width of the RYDMR spectral line, namely

20 Oe, is much larger than typical widths of the EPR spectral lines of these particles, which equal 1–2 Oe.

Magnetic-resonance spectrum of intermediate complexes of reactions (1) and (2), as revealed by delayed fluorescence

In the method used here to observe the RYDMR spectrum, we measured the delayed-fluorescence intensity change ΔL produced by the microwave field. The rate constant γ_2 of this process also changes under the influence of the resonant magnetic field. Therefore the registered RYDMR spectrum consists of two superimposed spectra, corresponding to the changes of γ_2 and γ_1. The last rate constant, in parallel with the reaction (1), determines the lifetime of the triplet excitons. To obtain a complete kinetic scheme that makes it possible to calculate the intensity of the delayed fluorescence, it is necessary to introduce on top of processes (1a) and (2) also the process of formation of triplet excitons via the triplet channel of annihilation of the triplet excitons:

$$^3T+{}^3T\xrightarrow{\gamma_3}{}^3T+{}^1S_0. \tag{11}$$

This channel, the existence of which was demonstrated experimentally,[14] must be taken into account under conditions when the rates of processes (1a) and (2a) are commensurate.

The solution of the kinetic equation for the concentration of the triplet excitons

$$\frac{d[T]}{dt}=G-(\gamma_2+\gamma_3)[T]^2-(k_0+\gamma_1[R])[T]=0 \tag{12}$$

makes it possible to express $L=(1/2)\gamma_2[T]^2$ as a function of the rate of formation of the excitons G and the rate constants given in the scheme:

$$L=\frac{1}{2}\frac{\gamma_2}{\gamma_2+\gamma_3}\frac{1}{\beta}((1+G\beta)^{1/2}-1)^2,\quad \beta=\frac{4(\gamma_2+\gamma_3)}{(k_0+\gamma_1[R])^2}. \tag{13}$$

The differentiation of (14) with respect to γ_1 and γ_2 leads to a dependence of the line amplitudes on the intensity G of the exciting light for the experimentally observed RYDMR spectrum $\Delta L(H_0)$ in the form

$$\begin{gathered}\Delta L=\Delta L_T+\Delta L_R,\\ \Delta L_T=\frac{1}{2}\frac{\gamma_2}{\gamma_2+\gamma_3}\frac{1}{\beta}\Big[\frac{\Delta\gamma_2\gamma_3}{\gamma_2(\gamma_2+\gamma_3)}((1+G\beta)^{1/2}-1)^2\\ +\Big(\frac{\Delta\gamma_2}{(\gamma_2+\gamma_3)}-\frac{2\Delta\gamma_{1T}[R]}{(k_0+\gamma_1[R])}\Big)\Big(2(1+G\beta)^{1/2}-2-\frac{G\beta}{(1+G\beta)^{1/2}}\Big)\Big],\\ \Delta L_R=-\frac{\gamma_2}{\gamma_2+\gamma_3}\frac{1}{\beta}\frac{\Delta\gamma_{1R}}{(k_0+\gamma_1[R])}\Big(2(1+G\beta)^{1/2}-2-\frac{G\beta}{(1+G\beta)^{1/2}}\Big).\end{gathered} \tag{14}$$

It is known from experiment that[1,2] $\gamma_2\ll\gamma_3$ and that $\gamma_1[R]<k_0$. This enables us to simplify (14):

$$\begin{gathered}\Delta L_T\sim\Delta\gamma_2(H_0)((1+G\beta)^{1/2}-1)^2,\\ \Delta L_R\sim-\Delta\gamma_{1R}(H_0)\Big(2(1+G\beta)^{1/2}-2-\frac{G\beta}{(1+G\beta)^{1/2}}\Big).\end{gathered} \tag{15}$$

It follows from (14) and (15) that the RYDMR spectrum determined from the change of the delayed fluorescence should consist of two parts, one positive and corresponding to triplet excitons in accord with the line positions (at least if the radical concentration is low), and the second negative and corresponding the EPR spectrum of the radicals. On should expect that, if polycrystalline samples are used, the part of the spectrum corresponding to the triplet excitons will broaden and will occupy a magnetic-field region of width $2D$. Since the EPR spectrum of the radicals is isotropic, the radical line is preserved at the center of the spectrum also in the case of polycrystals.

A feature of the RYDMR spectrum of the system in question is that the heights of the spectral lines belonging to the triplets and to the radical have different dependences on the intensity of the light that generates the triplet excitons. The reason is that at high intensities, when the loss of the triplet excitons is due to their mutual annihilation, the effect of the collisions between the triplets and the radicals on the lifetime is decreased. Curves 1 and 2 of Fig. 5 were calculated from formulas (15) and show the height variation of different lines in the RYDMR spectrum as functions of the exciting-light intensity. By choosing the parameter β it becomes possible to reconcile the experimental and calculated relations.

4. CONCLUSION

A comparison of the experimental results with the deductions of the theory shows that there is a general agreement between the registered and calculated spectra. The dependence of the height of the central line of the spectrum on the light intensity has a dependence intermediate between $\Delta L_R\propto G^2$ and $\Delta L_R\propto G^{1/2}$.

At the same time, the dependence of the height of the triplet-exciton lines on the light intensity lies in the region where $\Delta L_T\propto G^2$.

It can thus be regarded as proved that the observed RYDMR spectrum is determined by transitions in the short-lived pair $[{}^3T{}^2R]$. The pair lifetime estimated from the width of the central line of the spectrum is 6×10^{-9} sec.

The line is Lorentzian apparently because in all cases the motion of the triplet excitons is quasi-two-dimensional, i.e., the time of jump between the planes of the exciton motion is much longer than the time of jump in the plane of motion. In this case the decay constant k_{-1} of the complex is determined mainly by the time of jump between the planes.[2] This allows us to estimate the smallest diffusion coefficient of the triplet excitons (in a direction perpendicular to the plane of fast motion of the excitons).

The use of the RYDMR method to study intermediate stages in the reactions of interaction between paramagnetic particles uncovers great prospects for the identification of the mechanisms of processes such processes as recombination of electrons and ions, autoionization, and recombination of radicals. Besides the identification of the paramagnetic particles themselves, the method makes it possible to determine the lifetimes of the correlated intermediate state and the singularities of motion of paramagnetic particles.

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Reversal of the wave front of light in the case of depolarized pumping

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Some specific features of the reversal (or reproduction) of the wave front during stimulated scattering of light, which are due to the inhomogeneity of the pump polarization state, are considered. It is found that there are four linearly independent solutions for the scattered field with a structure correlated with the structure of the pump field. The growth rates are determined and the form of the solutions is investigated in detail. It is shown that the polarization inhomogeneity is favorable for reproduction of the wave front in the case of forward stimulated scattering. For backward stimulated scattering, the pumping depolarization impairs the quality of the wave front reversal (the reaction of the scattered wave on the pump is neglected).

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1. INTRODUCTION

The reversal of the wave front in backward stimulated scattering (SS) of light in pump beams $E_L(\mathbf{r},z)$ with a highly developed transverse structure[1] consists of the fact that the preferred gain is possessed by the configuration of the scattered field $E_s(\mathbf{r},z)$ that is the complex conjugate of the pump field, i.e.,

$$E_s(\mathbf{r},z)=\mathrm{const}\cdot E_L^*(\mathbf{r},z). \tag{1a}$$

Similarly, in forward scattering a configuration of the form

$$E_s(\mathbf{r},z)=\mathrm{const}\cdot E_L(\mathbf{r},z) \tag{2a}$$

should possess a large gain. These effects were investigated later in a number of researches (see, for example, Refs. 2–17 and papers cited therein); however, the theory and the experiments pertained to radiation with a definite state of polarization that is the same at all points $(\mathbf{r},z)$ of the scattering medium. On the other hand, it is well known that the inhomogeneity of the pump polarization leads to a number of specific features of the SS process—see for example, Refs. 18–20. In the present work, we examine how the appearance of reversal (in backward SS) or reproduction (in forward SS) of the wavefront takes place when the pump polarization is modulated randomly over the cross section.

The following results are obtained in the present work for the most interesting case of scattering of the scalar type. For forward SS, the phenomenon of reproduction with account of depolarization differs in general little from the case of homogeneous polarization of the pumping, and the relation (2) is essentially generalized to

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