Double resonance microwave transitions in intermediate complexes in the annihilation of triplet excitons

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Using the method of magnetic resonance detected by the change of the reaction yield (RCDMR) at room temperature, we have observed, for the first time ever, two-step microwave transitions between the Zeeman levels of the intermediate two-triplet state produced in the course of annihilation of triplet excitons in anthracene-tetracyanbenzene crystals. The lifetime of this state is 1.4×10^{-7} sec.

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The collision of triplet excitons that diffuse in molecular crystals leads, as is well known,[1] to the formation of an intermediate two-particle state, the electronic transitions from which to the final products conserve spin. These final products are singlet excitons that are detected by the emission that accompanies their radiative deactivation (by the so-called delayed fluorescence). It was shown recently[2,3] that production of magnetic-resonance transitions between the Zeeman levels of the short-lived two-triplet complex leads to a change in the intensity of the delayed fluorescence. By registering these spectra we can obtain the spectrum of the electron paramagnetic resonance of the short-lived pair (with a lifetime $r\sim10^{-7}$–10^{-10} sec), called the RCDMR spectrum, which practically coincides with the EPR spectrum of the triplet excitons. The use of the RCDMR spectrum uncovers extensive possibilities for the study of the dynamics of triplet excitons at room temperature.

Figure 1 shows the diagram of the Zeeman levels of a two-triplet complex in a strong magnetic field, obtained by adding the energies of the Zeeman levels of two equivalent non-interacting triplet excitons. The diagram shows from which of the triplet exciton levels, $|+\rangle$, $|0\rangle$ or $|-\rangle$, each of the levels of the two-triplet complex is formed. The state corresponding to the two central levels in Fig. 1 are superpositions of a quintuplet and a singlet state:

$$|00\rangle = \frac{1}{\sqrt{3}}|S\rangle + \sqrt{\frac{2}{3}}|Q_0\rangle \text{ and } \frac{1}{\sqrt{2}}\{|+-\rangle + |-+\rangle\} = \frac{1}{\sqrt{3}}|Q_0\rangle - \sqrt{\frac{2}{3}}|S\rangle$$

The rate of formation of the final products in the singlet state is determined by the population of these levels. If all the triplet-exciton levels are equally populated, each of the levels of the two-triplet complex is occupied at a rate $G=K_1n^2/9$, where K_1 is the rate constant of the exciton collisions and n is the exciton concentration. If the exciton spins are polarized the complex levels are occupied at unequal rates. In the first case, the resonant transitions due to the microwave power will increase the population of

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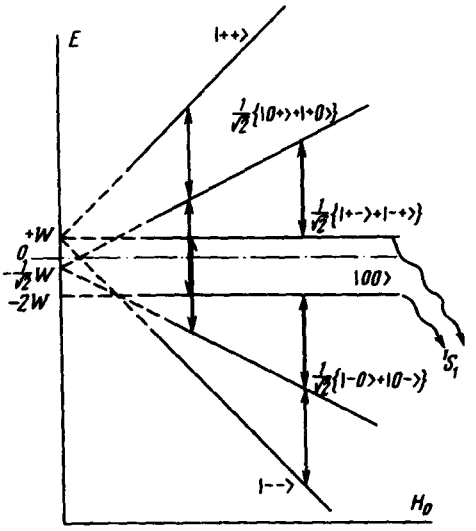

FIG. 1. Diagram of Zeeman levels of a two-triplet complex in a strong magnetic field.

the central levels with the singlet components, since their population is lower than that of the quintuplet components that go off to the reaction-product channel. This manifests itself in an increase of the intensity of the delayed fluorescence under the influence of the microwave power. In the second case, reversal of the sign of the change of the delayed-fluorescence intensity is possible if the polarization causes the levels with the singlet components to be populated to a greater degree than the pure quintuplet levels.

The magnetic resonance transitions in one of the triplet excitons making up the complex are marked by thick arrows in the diagram of Fig. 1. The probability that such a transition will occur within the lifetime τ of the complex is $P=2K_c\tau$, where

$$K_c = \frac{1}{4}\left(\frac{g\beta}{\hbar}H_1\right)^2 \frac{\tau(1-|S|^2)}{1+(\omega-\omega_0)^2\tau^2}$$

is the rate constant of the resonant transitions in a microwave magnetic field of intensity H_1; ω_0 is the resonant frequency of the microwave oscillations. At intensities $H_1=1$ Oe, we have $P(\omega_0)\propto 10^{14}\tau^2$, which approaches unity at $\tau\approx 10^{-7}$ sec. Under these conditions, realization of identical transitions in each of the triplet excitons making up the intermediate complex becomes sufficiently probable. This double transition corresponds in the diagram of Fig. 1 to transitions from the levels $|++\rangle$ (in a weak field H_0) and $|--\rangle$ (in a strong field H_0) to the level $|00\rangle$, which contains a singlet component. To observe such transitions by delayed fluorescence it is necessary to satisfy three conditions: 1) high microwave oscillation power ($H_1\gtrsim 1$ Oe); 2) relatively long lifetime of the intermediate complex ($\tau\approx 10^{-7}$ sec); and 3) a difference between the populations of the levels $|++\rangle$ and $|0+\rangle$ (or $|--\rangle$ and $|0-\rangle$). The last condition requires polarization of the triplet-exciton spins. The double transitions, as seen from Fig. 1, should appear at the same value of the magnetic field intensity H_0 of the spectrometer as the single transitions.

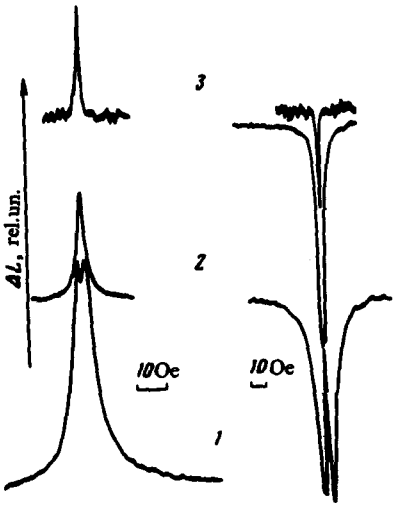

FIG. 2. Dependence of the spectral-line shape of the magnetic resonance of a two-triplet complex with lifetime 1.4×10^{-7} sec on the microwave oscillation power. Ordinates—delayed-fluorescence intensity change due to the microwave transitions: 1—total power ($\sim$3 W), 2—attenuation 10 dB, 3—attenuation 20 dB. In the measurements, the spectrometer magnetic-field vector $\mathbf{H}_0$ was in the (ab) plane of the crystal. For the spectra on the left-hand side $\mathbf{H}_0\|\mathbf{b}$ ($\alpha=0$). For the spectra on the right-hand side $\alpha=-45°$.

In the present study, the search for the double transitions was carried out by using as an example the reaction of annihilation of triplet excitons in crystals of the anthracene-tetracyanbenzene (A-TCNB) complex. The choice of this complex ensures satisfaction of the last two conditions. In fact, the spin-lattice relaxation time for this complex is large ($T_1=1.5\times10^{-6}$ sec[4]), and the diffusion of the triplet excitons is two-dimensional–this makes it possible to expect the lifetime τ of the two-triplet complex to come close to the spin-lattice relaxation time T_1. In addition, it is known that in these crystals the triplet excitons localized on the anthracene donor molecules are polarized.[4] The exciton polarization manifested itself in a reversal of the sign of the lines of the RCDMR spectrum.

We registered the RCDMR spectrum of single-crystal A-TCNB measuring $0.2\times1\times2$ mm at various microwave-oscillation power levels and for different orientations of the crystal relative to the magnetic field H_0 of the spectrometer. The crystal fluorescence was excited with a DKSSh-150 xenon lamp in the wavelength range $350<\lambda<530$ nm with intensity 10^{15} kV/cm^2 sec. By synchronous detection from the output of the photomultiplier, we registered the alternating component of the delayed fluorescence ΔL at the frequency of the amplitude modulation of the microwave power (1000 Hz).[5] Figure 2 shows the RCDMR spectra for two orientations of the crystal at different microwave-oscillation power levels. It was observed that at the "anomalous" negative polarity of the RCDMR spectrum there appears, against the background of the broad line, a narrow line of opposite polarity. With decreasing microwave power level, the narrow line decreases in intensity and vanishes. At positive polarity we also observed, against the background of the normal line, a narrow line of opposite sign, which vanished with decreasing microwave power, but its intensity was

much lower than that of the fundamental line. The narrow lines that cut through broader peaks of opposite polarity and vanish with decreasing microwave power are interpreted by us as lines due to double transitions in the two-triplet complexes. This is also confirmed by the shape of the double line on Fig. 2, which is well described by the difference between two equal-amplitude lines, one of which has a Lorentz shape and the other corresponds to its square:

$$\Delta L(H_0) \sim [1+4(\frac{H_0-H_{res}}{\Delta H_{1/2}})^2]^{-1} - [1+4(\frac{H_0-H_{res}}{\Delta H_{1/2}})^2]^{-2}.$$

The distance between the extremum points yields, by calculation, the width $\Delta H_{1/2}$ of the Lorentz line at half-height. This distance coincides with the width $\Delta H_{1/2}=6$ Oe for the undistorted positive line registered at the same power level.

Lowering of the microwave-power level led also to a decrease in the width of the RCDMR spectral lines. At maximum power (approximately 3 W) the line width $\Delta H_{1/2}$ was 10 Oe, and the width limit at approximately one-thirtieth of the power was 0.8 Oe. The spectral line had a Lorentz shape at low power, the lifetime of the two-triplet pair calculated from the line width was 1.4×10^{-7} sec. Thus, the results demonstrate the possibility of observing transitions due to absorption of two microwave quanta in short-lived intermediate complexes. A study of two-quantum transitions makes it possible to determine the degree of population of the levels $|++\rangle$ and $|--\rangle$ in comparison with the level $|00\rangle$, i.e., to obtain information on the polarizations of the triplet-exciton spins. Thus, at the crystal orientation corresponding to the spectrum shown in Fig. 2 on the right-hand side, the populations of the Zeeman levels of the triplet excitons are related like $n_+\approx n_- > n_0$.

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