

# Characteristics of mutual annihilation of triplet excitons in various spin states

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Mutual annihilation of triplet excitons with the spin angular momentum projection parallel and antiparallel to an external magnetic field of 6 T was investigated at 2 K in a molecular crystal of 4,4'-dichlorobenzophenone. The characteristics of the annihilation processes in various spin states of excitons, and also an anisotropy of the rate constants in a magnetic field, are attributed to spin relaxation in an intermediate pair complex.

## 1. INTRODUCTION

The rate of mutual annihilation of triplet excitons in organic molecular crystals is governed by the probability of finding an intermediate complex of two colliding excitons in each of the nine spin states.<sup>1</sup> In turn, this probability depends on the spin state of annihilating excitons, temperature, and also the magnitude and orientation of the external magnetic field.<sup>1-3</sup>

The majority of theoretical and experimental results on the subject of exciton–exciton annihilation (EEA) have been obtained for a quasiequilibrium distribution of populations between the spin states of triplet excitons. When spin-polarized triplet excitons (with a nonequilibrium distribution of the populations) participate in the EEA process, the spin states of an intermediate complex become populated selectively in accordance with the rule of spin conservation in the annihilation process.<sup>1,2</sup> This circumstance makes it possible to investigate in greater detail the EEA processes by determining the annihilation rate constants for excitons in specific spin states; it can also be used to find the influence of spin relaxation process on the annihilation. It should be pointed out that in the case of selective population of the spin states of triplet excitons it is possible to influence the EEA spin channels by a magnetic field.

If the exciton spin relaxation rates are sufficiently low, it is possible to populate the spin states of triplet excitons selectively by the application of an external magnetic field to an investigated crystal along various directions.<sup>4</sup> This spin polarization effect of triplet excitons under optical pumping conditions is a consequence of a general property of organic crystals, viz., the spin selectivity of intercombination transitions in zero field.<sup>5,6</sup>

We shall report an investigation of mutual annihilation of triplet excitons in spin states corresponding to the directions of projections of the spin angular momentum antiparallel (state  $|+\rangle$ ) and parallel (state  $|-\rangle$ ) to an external magnetic field. We shall report the first results of a study of the characteristics of mutual annihilation of excitons in the states  $|+\rangle$  and  $|+\rangle$ , and  $|+\rangle$  and  $|-\rangle$ . The data on the annihilation of excitons in other spin states in benzophenone crystals were published earlier.<sup>7-9</sup>

## 2. EXPERIMENTAL METHOD

We investigated single crystals of 4,4'-dichlorobenzophenone (DCBP) the unit cell of which contains four molecules magnetically equivalent along all the directions of an external magnetic field.<sup>10</sup>

Single crystals of DCBP were grown from the melt by

the Bridgman method from well-purified materials. Optical excitation was provided by periodic pulses from an LGI-21 laser (pulse duration about 10 nsec, emission wavelength 337.1 nm) corresponding to a singlet-singlet absorption band. Fast intercombination inversion ( $\approx 10^{11}$  sec<sup>-1</sup>—see Ref. 11) was followed by selective population of spin states of an exciton triplet. The polarization vector of the exciting light was directed at right-angles to a monoclinic axis **b** of a crystal and in this weak absorption case<sup>12</sup> the distribution of excitation in a sample could be regarded as homogeneous. All the measurements were carried out in a magnetic field of 6 T at a temperature of 2 K. The EEA processes in a DCBP crystal were observed during the initial stages of the decay of the phosphorescence originating from separate Zeeman states under strong optical excitation conditions. The decay kinetics and the Zeeman phosphorescence spectra were recorded by the photon counting method accumulating the data in the memory of an AI-256-6 amplitude analyzer supplemented by a specially developed time encoding device.

Various experimental geometries were used in the study of the exciton phosphorescence in a magnetic field. In the Faraday geometry an external magnetic field was directed along the **a'** crystallographic axis of a monoclinic DCBP crystal,<sup>10</sup> whereas in the Voigt geometry the field was directed along the **c** axis (the **c** axis lies in the **bc** cleavage plane of a crystal). In both cases an external magnetic field was perpendicular to the **b** monoclinic axis of the crystal, which was collinear with the principal magnetic axes **z** of all four molecules inside the unit cell.

## 3. RESULTS OF MEASUREMENTS AND DISCUSSION

Two Zeeman phosphorescence bands were observed for the external magnetic field directions used in the present study and these bands corresponded to radiative transitions from the states  $|+\rangle$  and  $|-\rangle$  polarized along the **b** axis (the zero-field phosphorescence was also polarized along the **b** axis), as shown in Fig. 1.

As is known, in zero magnetic field an excited triplet state of a DCBP molecule is split by internal molecular magnet interactions.<sup>13</sup> Filling of a triplet state by optical pumping, as well as radiative and nonradiative decay of a triplet in this molecule all occur practically via one spin state  $|z\rangle$  (Ref. 13) because of the strong anisotropy of the spin-orbit interaction which lifts the forbiddenness of intercombination transitions.<sup>6</sup> Therefore, only two bands are observed in the Zeeman phosphorescence spectra for field directions **B** $\parallel$ **b**(**z**).

Since the rates of exciton spin relaxation in a magnetic

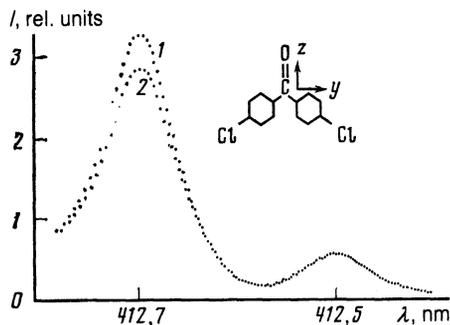


FIG. 1. Zeeman phosphorescence spectra recorded at 2 K in a magnetic field 6 T using exciting light of intensities  $10^{13}$  photons/cm<sup>2</sup> (1) and  $1.5 \times 10^{14}$  photons/cm<sup>2</sup> (2). The spectra were normalized to the short-wavelength component at  $\lambda_{\text{max}} = 412.5$  nm. The inset shows a molecule of 4,4'-dichlorobenzophenone.

field of 6 T at a temperature of 2 K are known to be relatively low [ $\approx (0.5-1) \times 10^4$  sec<sup>-1</sup> according to Ref. 12], we can assume that during the measurement time only the excitons in the spin states  $|+\rangle$  and  $|-\rangle$  participate in the EEA process. Estimates indicate that the populations of excitons in the state  $|0\rangle$  and the contribution of these excitons to the EEA process can be ignored. The time dependences of the populations of the spin states  $|+\rangle$  and  $|-\rangle$  are described by a system of nonlinear equations

$$\begin{aligned} \frac{dn_+}{dt} &= -(k+W+k_+)n_+ - \gamma_{+-}n_+ - \gamma_{++}n_+^2, \\ \frac{dn_-}{dt} &= -(k+k_-)n_- + W_{+-}n_+ - \gamma_{+-}n_+n_- - \gamma_{--}n_-^2, \end{aligned} \quad (1)$$

where  $n_+$  and  $n_-$  are the populations of the  $|+\rangle$  and  $|-\rangle$  states;  $k$  is the rate constant of the exciton capture by  $X$  traps, is independent of the magnetic field, and has been measured by us earlier;  $k_+$  and  $k_-$  are the rate constants of deactivation of the spin states  $|+\rangle$  and  $|-\rangle$  to the ground state ( $k_+ = k_- \ll k$ —see Refs. 6 and 8);  $W = W_{+0} + W_{+-}$ , where  $W_{+0}$  and  $W_{+-}$  are the rates of exciton spin relaxation between the states  $|+\rangle$  and  $|0\rangle$ , and  $|+\rangle$  and  $|-\rangle$ , respectively;  $\gamma_{+-}$ ,  $\gamma_{++}$ , and  $\gamma_{--}$  are the rate constants representing the mutual annihilation of triplet excitons in the spin states  $|+\rangle$  and  $|-\rangle$ ,  $|+\rangle$  and  $|+\rangle$ , and  $|-\rangle$  and  $|-\rangle$ . The system of equations (1) ignores the rates of exciton spin relaxation between the spin states  $|0\rangle$  and  $|+\rangle$  and  $|-\rangle$  and  $|+\rangle$ , in view of their smallness (due to the Boltzmann factor) in a magnetic field of 6 T at a temperature 2 K.

The experimental values of  $\gamma_{++}$ ,  $\gamma_{--}$ , and  $\gamma_{+-}$  were determined in several stages. During the first stage the kinetics of phosphorescence decay from single Zeeman states was determined at such an exciting light intensity ( $\approx 10^{13}$  photons/cm<sup>2</sup>) that the contribution of nonlinear terms in the system (1) could be ignored. Consequently, the experimental curves representing the decay of the phosphorescence from the states  $|+\rangle$  and  $|-\rangle$  (Figs. 2 and 3) could be approximated by solutions of a system of linear equations

$$\begin{aligned} n_+ &= n_+^0 \exp[-(k+W)t], \\ n_- &= \frac{n_-^0}{W} \{ (W+W_{+-}) \exp(-kt) - W_{+-} \exp[-(k+W)t] \}, \end{aligned} \quad (2)$$

$$(3)$$

where  $n_+^0$  and  $n_-^0$  are the initial populations ( $n_+^0 = n_-^0$ );  $k_+$  and  $k_-$  will be ignored here and later. The decay of the phosphorescence from the  $|+\rangle$  state was exponential, indi-

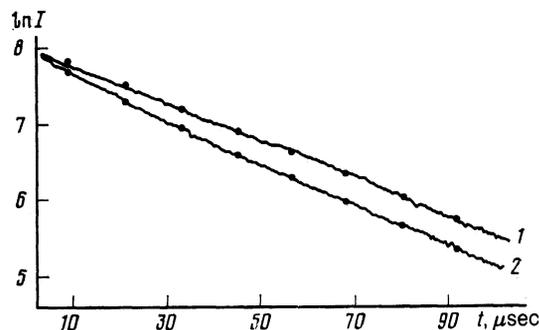


FIG. 2. Kinetics of decay of the phosphorescence from the  $|+\rangle$  spin state in a magnetic field of 6 T when the intensity of the exciting light was  $10^{13}$  photons/cm<sup>2</sup> (1) and  $1.5 \times 10^{14}$  photons/cm<sup>2</sup> (2). The points on curve 1 are the results of approximation by Eq. (2), whereas those on curve 2 represent the solution of the system of equations (1).

cating that there was no EEA at these intensities of the exciting light. When the experimental curves were approximated on a computer, the variable parameters were  $W$  and  $W_{+-}$ , which were determined from a minimum of the rms deviation by the method of least squares and were used in subsequent calculations. The values of  $W_{+-}$  and  $W_{+0}$  found from this approximation agreed, within the limits of the experimental errors, with the values of the same parameters obtained directly using a more rigorous method,<sup>14</sup> in which an allowance was made for the spin relaxation rates  $W_{0-}$ ,  $W_{-0}$ , and  $W_{-+}$ . The values of  $W_{+-}$  and  $W_{+0}$  are given in Table I.

In the second stage we used a computer to solve numerically the system of equations (1) using the values of  $W$  and  $W_{+-}$  found as described above. The variable parameters were now the EEA rate constants  $\gamma_{++}$ ,  $\gamma_{--}$ , and  $\gamma_{+-}$ . This solution was used to approximate the phosphorescence decay curves in the case of strong optical excitation ( $1.5 \times 10^{14}$  photons/cm<sup>2</sup>). The initial stages of these curves were characterized by annihilation-induced deviations from the exponential curve (in the case of the  $|+\rangle$  state) or a sum of two exponential curves (in the case of the state  $|-\rangle$ ), as demonstrated in Figs. 2 and 3.

It should be pointed out that the best fit between the model and experimental curves obtained by the least-squares method was not always unambiguous when there

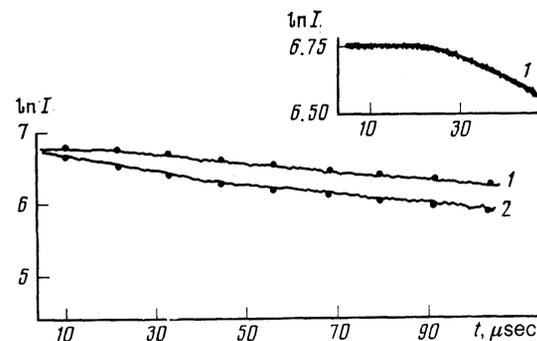


FIG. 3. Kinetics of decay of the phosphorescence from the spin state  $|-\rangle$  at a temperature 2 K in a magnetic field of 6 T when the intensity of the exciting light was  $10^{13}$  photons/cm<sup>2</sup> (1) and  $1.5 \times 10^{14}$  photons/cm<sup>2</sup> (2). The points on curve 1 are the results of an approximation by Eq. (3), whereas those on curve 2 are the solution of the system of equations (1). The inset shows the initial part of curve 1.

TABLE I. Rate constants of mutual annihilation of triplet excitons  $\gamma_{ij}$  ( $\text{cm}^3/\text{sec}$ ) and of exciton spin relaxation  $W_{ij}$  ( $\text{sec}^{-1}$ ) for different directions of external magnetic field  $\mathbf{B}$  ( $B = 6 \text{ T}$ ,  $T = 2 \text{ K}$ ,  $i, j = +, -, 0$ ; crystallographic axes designated in accordance with Ref. 10).

Orientation of $\mathbf{B}$	$\gamma_{+-}$	$\gamma_{++}$	$\gamma_{--}$	$\gamma_{00}$	$W_{+0} = W_{0-}$	$W_{+-}$
$\mathbf{B} \parallel \mathbf{a}'$	$(2.9 \pm 0.1) 10^{-12}$	$(6.5 \pm 1.5) 10^{-13}$	$< 5 \cdot 10^{-14}$	—	$(8 \pm 1) 10^3$	$(40.5 \pm 0.5) 10^3$
$\mathbf{B} \parallel \mathbf{c}$	$(1.25 \pm 0.05) 10^{-12}$	$(1.75 \pm 0.25) 10^{-13}$	$< 3 \cdot 10^{-14}$	—	$(5.5 \pm 1.5) 10^3$	$(8 \pm 1) 10^3$
$\mathbf{B} \parallel \mathbf{b}$	—	—	—	$(2.8 \pm 1) 10^{-12}$ [9]	$(7.5 \pm 0.5) 10^3$ [9]	—

were more than two variable parameters. This was because in the presence of an experimental scatter of the results the global minimum of the rms deviation could be insufficiently definite, since under these conditions we could have a whole set of local minima without any physical meaning. In our case a number of circumstances helped us to make this approximation more reliable. Firstly, it was known<sup>8,15</sup> that mutual annihilation of excitons with the same spin projections (parallel or antiparallel to the magnetic field) should be strongly suppressed compared with the annihilation of excitons with different spin projections. Consequently, we could expect the inequalities  $\gamma_{+-} \gg \gamma_{++}$ ,  $\gamma_{--}$  to be obeyed. This was a serious restriction on the range of possible values of the variable quantities. Secondly, the experimental conditions and the selected model made it possible to approximate the phosphorescence decay kinetics directly for the upper and lower spin states of a triplet exciton. Then, the global minima of the rms deviation for both curves should exist in the same range of parameters ( $\gamma_{+-}$ ,  $\gamma_{++}$ ,  $\gamma_{--}$ ). If in the case of independent variation of the rate constants we found minima of two curves for two different sets of parameters, we regarded these minima as local and the rate constants as physically meaningless.

We used this approach to determine the range of values of the rate constants of mutual annihilation ( $\text{cm}^3/\text{sec}$ ) of spin-polarized triplet excitons for two orientations of an external magnetic field:

$$\begin{aligned} \gamma_{+-} &= (2.9 \pm 0.1) 10^{-12}; \quad \gamma_{++}, \gamma_{--} < 8 \cdot 10^{-13} \quad (\mathbf{B} \parallel \mathbf{a}'), \\ \gamma_{+-} &= (1.2 \pm 0.1) 10^{-12}; \quad \gamma_{++}, \gamma_{--} < 2 \cdot 10^{-13} \quad (\mathbf{B} \parallel \mathbf{c}). \end{aligned} \quad (4)$$

The third stage involved refinement of the values of  $\gamma_{+-}$ ,  $\gamma_{++}$ , and  $\gamma_{--}$ . We used here additional experimental results. We recorded the Zeeman phosphorescence spectra (Fig. 1) at exciting light intensities of  $10^{13}$  and  $1.5 \times 10^{14}$  photons/ $\text{cm}^2$  under the same conditions as in the case of the phosphorescence decay study. It was found that an increase in the exciting light intensity increased the ratio of the intensities of the maxima of the Zeeman components ( $R_e$ ). This result could be readily explained in the qualitative sense by assuming that  $\gamma_{++} > \gamma_{--}$ . We determined more accurately the constants  $\gamma_{++}$  and  $\gamma_{--}$  by assuming various values of these quantities in a numerical (computer) integration of the solutions of the system (1):

$$I_- = k_-^r \int_0^\infty n_-(t) dt, \quad I_+ = k_+^r \int_0^\infty n_+(t) dt, \quad (5)$$

where  $I_-$  and  $I_+$  are the calculated intensities of the Zeeman phosphorescence components  $| - \rangle$  and  $| + \rangle$ ;  $k_-^r$  and  $k_+^r$  are the rate constants of the radiative decay of these compo-

nents ( $k_-^r = k_+^r$ ). We then ensured the best agreement between the calculated parameter  $\Delta R_m$ , representing the relative change in  $R_m = I_-/I_+$  on increase in the intensity, with the experimental values  $\Delta R_e$ . Using the limits of variation of the parameters  $\gamma_{++}$  and  $\gamma_{--}$  determined earlier and the values of  $\gamma_{+-}$  from Eq. (4), we found that the rate constants under investigation had the following values ( $\text{cm}^3/\text{sec}$ ):

$$\begin{aligned} \gamma_{++} &= (6 \pm 1) 10^{-13}; \quad \gamma_{--} < 5 \cdot 10^{-14} \quad (\mathbf{B} \parallel \mathbf{a}'), \\ \gamma_{++} &= (1.5 \pm 0.5) 10^{-13}; \quad \gamma_{--} < 3 \cdot 10^{-14} \quad (\mathbf{B} \parallel \mathbf{c}). \end{aligned} \quad (6)$$

The precision of our measurements was insufficient to determine the lower limit of the rate constant  $\gamma_{--}$ , which was considerably less than  $\gamma_{++}$  and  $\gamma_{+-}$ . The upper limit for  $\gamma_{--}$  and the lower for  $\gamma_{++}$  were assumed to correspond to a reduction in  $\Delta R_m$  by twice the experimental error, i.e., about 10%.

We were thus able to use spectroscopic and kinetic measurements to determine the rate constants of mutual annihilation of triplet excitons in identical ( $\gamma_{++}$ ,  $\gamma_{--}$ ) and different ( $\gamma_{+-}$ ) spin states. The results obtained are collected in Table I, which includes also the results taken from Ref. 9, representing the rate constant  $\gamma_{00}$  of mutual annihilation of triplet excitons in the  $|0\rangle$  state and the rate of exciton spin relaxation  $W_{0-} = W_{+0}$  between the states  $|0\rangle$  and  $| - \rangle$  in a magnetic field directed so that  $\mathbf{B} \parallel \mathbf{b}$ .

An unexpected result was the difference between the EEA rate constants  $\gamma_{++}$  and  $\gamma_{--}$ . Clearly, this difference is associated with the processes of spin relaxation in an intermediate complex. When the rates of spin relaxation are comparable with the rates of formation and decay of an intermediate complex or are higher than the latter rates, the annihilation of excitons via the  $| + + \rangle$  state are more effective than via the  $| - - \rangle$  state because of the transfer of excitation from the state with the highest energy  $| + + \rangle$  to other states of an intermediate complex, that can participate in the annihilation process. This circumstance should reduce  $\gamma_{--}$  compared with  $\gamma_{++}$  (in the absence of spin relaxation in an intermediate complex their values should be the same).

It should be pointed out that the EEA via the states  $| + + \rangle$  and  $| - - \rangle$  should be forbidden,<sup>15</sup> because—in accordance with the spin conservation rule—the final stage of the annihilation process should be in the form of excited quintet states, which are not observed in organic crystals in the range of energies of interest to us. The occurrence of the annihilation of triplet excitons with identical directions of the spins (parallel and antiparallel to an external magnetic field) is clearly associated with intermolecular interactions, which do not commute with the total spin operator of the colliding excitons.<sup>8</sup>

It is clear from Table I that the EEA rate constants depend on the direction of the external magnetic field. A possible explanation of the anisotropy of  $\gamma_{+-}$  in a magnetic field is the phenomenon of "resonances in a strong field" (Refs. 1 and 2) due to crossing of the  $|00\rangle$  state with the states  $2^{-1/2}\{|+-\rangle + |-+\rangle\}$  and  $2^{-1/2}\{|+-\rangle - |-+\rangle\}$ . However, estimates obtained in accordance with the resonance conditions of Refs. 1 and 2:

$$S = D(\cos \gamma - 1/3) + E(\cos^2 \alpha - \cos^2 \beta) = 0,$$

where  $D$  and  $E$  are the parameters of the fine-structure tensor taken from Ref. 12 and  $\alpha$ ,  $\beta$ , and  $\gamma$  are the angles between  $\mathbf{B}$  and the principal axes of this tensor calculated on the basis of Ref. 7, demonstrate that an approach to resonance (reduction in the parameter  $S$ ) does not agree with the experimental observation of an increase in  $\gamma_{+-}$ .

On the other hand, interpretation of the experimental results is self-consistent if we assume that the EEA rates (including  $\gamma_{++}$  and  $\gamma_{--}$ ) depend on spin relaxation in an intermediate complex and then the anisotropy of this relaxation affects the annihilation rate constants when the orientation of the magnetic field is altered.

It therefore follows that the rate of mutual annihilation of spin-polarized triplet excitons in organic crystals subjected to strong magnetic fields at low temperatures depend strongly on the projection of the exciton spin along the direc-

tion of the external magnetic field and on the processes of spin relaxation in an intermediate complex.

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