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A. N. Faidysh [a] & A. S. Gaevsky [a]

[a] Department of Physics, Kiev University, Kiev, USSR

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Influence of Triplet Exciton Annihilation on Quantum Efficiency and Phosphorescence Decay Law in Benzophenone Crystals

A. N. FAIDYSH and A. S. GAEVSKY

Department of Physics
Kiev University
Kiev, USSR

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Abstract—The influence of triplet (T) exciton annihilation on the quantum efficiency (B) and phosphorescence decay law ($\mathcal{J}(t)$) in two benzophenone crystal modifications at 77 °K has been studied. Comparison of theory with the experimentally determined exciting light intensity dependence of B and $\mathcal{J}(t)$ in crystals of different thickness enabled to determine the annihilation rate constant (μ) and to estimate the T-exciton diffusion coefficient ($\mathscr{D}_T$). The determined values of μ are $(5 \pm 2) \times 10^{-15}$ cm^3 sec^{-1} for x-benzophenone, $(1.3 \pm 0.7) \times 10^{-13}$ cm^3 sec^{-1} for α-benzophenone and the estimated values of $\mathscr{D}_T - (3.75 \pm 1.25) \times 10^{-9}$ cm^2 sec^{-1}, $(1.05 \pm 0.55) \times 10^{-7}$ cm^2 sec^{-1} for x- and α-benzophenone respectively. It is suggested that the smallness of μ and $\mathscr{D}_T$ in these crystals is due to the localization of excitation in the carbonyl group of the benzophenone molecule.

1. Introduction

Exciton migration in organic crystals influences greatly their luminescence, photoconduction and photochemical reactions.$^{(1-26)}$ Therefore the determination of the main parameters characterizing exciton migration is of great importance not only for knowledge of the properties of energy transport mechanism of electron excitation but for understanding of some regularities in the stated phenomena as well. In the organic crystals there may arise both singlet and triplet excitons. In the investigated crystals of anthracene, phenanthrene, naphthalene, stilbene, diphenyl the value of singlet exciton diffusion length (l_0) ranges approximately by a factor of several times. For anthracene crystals $l_0 \simeq 1 \times 10^{-5}$ cm,$^{(2,3,5)}$ and the exciton diffusion coefficient $\mathscr{D} \simeq 10^{-2}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$. Much more difference between l_0 and $\mathscr{D}$ is observed for triplet excitons in different crystals. Triplet exciton migration has been studied most carefully for anthracene and benzophenone crystals. In anthracene crystals the order of magnitude of $\mathscr{D}_T$ is $10^{-4}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$,(19,20,22–26) and in α-benzophenone crystals $\mathscr{D}_T \simeq 10^{-7}$ to $10^{-8}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$.(21) The difference in dependence of $\mathscr{D}$ for singlet and triplet excitons on crystal properties seems to reflect differences in the character of intermolecular interactions responsible for arising of exciton states.

It should be, however, noted that l_0 and $\mathscr{D}_T$ in anthracene and benzophenone crystals have been determined by different methods. In anthracene crystals $\mathscr{D}_T$ was determined mainly from delayed fluorescence resulting from triplet exciton annihilation, and in benzophenone crystals from quenching of phosphorescence caused by trapping of triplet excitons with impurity molecules.

In this connection it is also desirable to study exciton migration in pure benzophenone crystals by the effect of exciton annihilation on the phosphorescence quantum efficiency.

With this purpose a careful study of the quantum efficiency and phosphorescence decay law dependences on exciting light intensity with benzophenone crystals of different thickness has been carried out by the authors. A number of experiments were also performed in order to find out the reasons for the small value of $\mathscr{D}_T$ in benzophenone crystals compared with that of anthracene.

2. Experimental

Benzophenone under investigation was carefully purified by recrystallization in acetone, multiple distillation in vacuum and zone melting. Benzophenone crystals purity was checked by phosphorescence spectra.(27) Benzophenone crystals may be found in different modifications.(27,28,36) In this work the main investigations were performed on x-benzophenone films obtained when liquid benzophenone, melted between two quartz windows, was quickly dipped into liquid nitrogen. This choice has been caused by the fact that the quantum efficiency (B) and phosphorescence decay time (τ) in x-benzophenone is 7 times more than that in the stable α-modification and thus better conditions to study T-exciton annihilation are created. The earlier investigations(27,37) showed that when phosphorescence was excited by a DRSh-1000 lamp, producing maximum illumination (L) at the sample, about 6×10^{16} phot. $\text{cm}^{-2}\,\text{sec}^{-1}$, 16000 time changing of L had not noticeably altered the phosphorescence quantum efficiency. Therefore in this work for excitation of phosphorescence we used an ISSh-500 pulse lamp, its radiation power being a few orders of magnitude higher than that of the DRSh-1000 lamp. The benzophenone phosphorescence was excited by the light of 310–380 nm via a filter. L could be diminished by means of a calibrated set of diaphragms.

An ISP-28 spectrograph with photoelectric arrangement and a Sl-19 oscillograph at the output were used for the investigation of phosphorescence and quantum efficiencies. With the capacitance switched on parallel at the input of the oscillograph ($RC = 3 \times 10^{-2}$ sec), deflection on the screen was proportional to the luminescence pulse integral. The preliminary studies showed that energy distribution in the phosphorescence spectrum did not depend on L (Fig. 1).

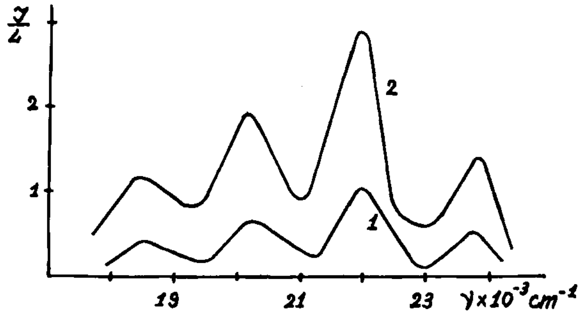

Figure 1. x-benzophenone phosphorescence spectra at 77 °K. (1) at $L = L\text{max}$; (2) $L = L\text{max}/720$.

Therefore all the measurements of emission intensity were made in the region of the second band maximum of benzophenone phosphorescence ($\sim 21800\ \text{cm}^{-1}$). In order to reduce the effect of scattered exciting light a ZhS-11 filter, transmitting this phosphorescence region and strongly absorbing the exciting light was put in front of the spectrograph entrance slit.

To determine the triplet state lifetime (τ), with exponential phosphorescence decay law, the luminescence intensity curve was straightened on the oscillograph screen, by applying the signal from an exponential voltage generator ($u = u_0 e^{-t/RC}$) to the input of the horizontal deflection plates of the oscillograph. The generator enabled to get signals with RC from 10^{-5} to 10^{-2} sec. The exciting light pulse was used in order to synchronize the triggering of the exponential generator. For studying the rate of decay at the initial and final portions of the phosphorescence decay curve the delay of the onset of the exponential voltage with respect to the exciting pulse for times of 1×10^{-5} to 5×10^{-3} sec was applied.

3. Results

In order to determine the exciton annihilation rate constant we studied the exciting light intensity (L) dependence of the quantum efficiency and phosphorescence decay law for pure benzophenone crystals. The quantum efficiency was determined as the ratio of the number of photons in the phosphorescence pulse to the number of absorbed photons during the exciting light pulse

$$B = \frac{\dfrac{1}{\tau_r}\displaystyle\int_0^\infty \mathrm{d}t \int_0^d C_T(x,t)\,\mathrm{d}x}{(1 - e^{-Kd})\displaystyle\int_0^{t_p} L(t)\,\mathrm{d}t} \tag{1}$$

where $C_T(x,t)$—T-exciton concentration, τ_r—their radiation lifetime, K—exciting light absorption coefficient, t_p—exciting light pulse duration, d—crystal thickness.

The number of photons falling on 1 cm² of sample surface at exciting pulse time was determined through comparison of the intensities of anthracene solution in benzene (77 °K) excited with the ISSh-500 and DRSh-1000 lamps, the intensity of the latter being determined by a IF-68-IM calorimeter. Under our conditions the maximum value of $S = \int_0^{t_p} L(t)\,\mathrm{d}t$ was equal to $S_{\max} = (9 \pm 3) \times 10^{14}$ phot. cm^{-2}. The study of the dependence of B on S was performed on the x-benzophenone films whose thickness was approximately equal to 5 μ, 20 μ and 100 μ. For each film thickness measurements were made on several samples and then the average value of B/B_0

TABLE 1 Exciting Light Intensity Dependence of Relative Quantum Efficiency of x-benzophenone Phosphores

$\frac{L\text{max}}{L}$		1.0	1.6	2.5	3.9	6.0	9.6	16	25	40	63	100	160	240
100 μ	B/B_0 exp.	0.54	0.62	0.71	0.80	0.85	0.90	0.96	0.98	1.00	1.02	1.00	0.99	1.00
	B/B_0 theor.	0.55	0.64	0.71	0.78	0.85	0.91	0.95	0.98	0.99	1.00	1.00	1.00	1.00
30 μ	B/B_0 exp.	0.45	0.54	0.63	0.71	0.75	0.85	0.94	0.99	1.01	1.00	1.00	0.99	1.02
	B/B_0 theor.	0.45	0.56	0.62	0.70	0.79	0.88	0.94	0.98	0.99	1.00	1.00	1.00	1.00
5 μ	B/B_0 exp.	0.36	0.44	0.53	0.63	0.72	0.83	0.89	0.94	0.97	0.99	1.00		
	B/B_0 theor.	0.36	0.45	0.54	0.64	0.72	0.81	0.87	0.90	0.95	0.98	0.99		

was determined where B_0 was the value of B at $S = 1/100 \cdot S_{\max}$. The results of the dependence of B/B_0 on S at 77 °K are presented in Table 1. As may be seen from the table in thin films 100 time increasing of S results in about 3 time decreasing of B. At small exciting light intensity B practically takes on the constant value independent of S.

Changing of S influences the phosphorescence decay law as well. At $L < 10^{17}$ phot. $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$ phosphorescence intensity decay after the end of the exciting pulse occurs according to the exponential law with $\tau \approx (2 \text{ to } 3) \times 10^{-3}$ sec. Increasing of S results in decay rate increasing which has a non-exponential character at the initial stage. At the end of the luminescence pulse when exciton concentration becomes small decaying occurs according to the exponential law approximately with the same τ as for $S \to 0$. Phosphorescence nonlinearity caused by T-exciton annihilation is displayed more strongly in α-benzophenone at 77 °K than that in x-benzophenone. In the films with $d = 5\ \mu$ 720 time decreasing of S results in approximately 8 time increasing of B/B_0, and at $d = 100\ \mu \sim$ in 3 time.

Addition of naphthalene impurity to α-benzophenone crystal decreases greatly S dependence of B. Thus, for instance, at $d = 20\ \mu$ in pure α-benzophenone 720 time decreasing of S results in approximately 5.5 time increasing of B/B_0, and with naphthalene impurity of 10^{-4} g/cm^3 concentration increasing is equal only to 2.8. Such an influence of impurity is due to decreasing of concentration of T-excitons since they are trapped by naphthalene molecules.(29)

4. Discussion

The observed exciting light intensity dependence of the quantum efficiency and phosphorescence decay law is due to T-exciton annihilation. Under exciton annihilation a transition from the triplet to the ground singlet state occurs in one molecule and in the other a transition occurs from the first to a higher triplet or excited singlet state. In both cases a fast radiationless transition back to the lower triplet level takes place because of the strong intersystem crossing between the excited singlet and first triplet level in benzophenone As a result of the mentioned processes each annihilation act leads to the loss of one triplet excitation and thus increasing of exciting light intensity which is accompanied by increasing of probability of annihilation results in decreasing of the phosphorescence quantum efficiency. The exciting light intensity dependence of the quantum efficiency and phosphorescence decay law is defined by the kinetics of the processes of population and deactivation of the triplet state. For the general case the equation defining T-exciton concentration at distance x from the crystal surface takes on the form

$$\frac{dC_T(x,t)}{dt} = KLe^{-Kx}\,\frac{C - C_T(x,t)}{C} + \mathscr{D}_T\frac{d^2C_T(x,t)}{dx^2} - \frac{C_T(x,t)}{\tau} - \mu C_T^2(x,t) \tag{2}$$

where C is the concentration of molecules in the ground state, $C_T(x,t)$—concentration of molecules in the triplet state, i.e. T-exciton concentration, τ—triplet exciton life-time, μ—triplet exciton annihilation rate constant. In benzophenone crystals the exciton concentration gradient is small due to the smallness of K (for $\lambda = 365$ nm, $k \approx 600$ cm^{-1}) and therefore we can neglect exciton flux to the crystal surface as well as the influence of exciton diffusion on the distribution of exciton concentration through the crystal thickness. Since in the experiments performed the excitation pulse time t_p is over two orders less than phosphorescence emission time, in estimating the quantum efficiency one may neglect radiation during t_p time, i.e. in Eq. (1) time counting may be started after the excitation is ceased.

Under above considerations after the exciting pulse is ceased, exciton concentration kinetics will be defined by the equation

$$\frac{dC_T(x,t)}{dt} = -\frac{C_T(x,t)}{\tau} - \mu C_T^2(x,t) \tag{3}$$

The solution of the equation takes on the form

$$C_T(x,t) = C_0(x)\,e^{-t/\tau}\,[1 + \mu\tau C_0(x)(1 - e^{-t/\tau})]^{-1} \tag{4}$$

where $C_0(x)$—T-exciton concentration at depth x at the moment when the exciting pulse is ceased. With neglect of the influence of spontaneous and annihilation deactivation of triplet excitation during a very short excitation pulse, C_0 will be equal to the number of photons absorbed at one pulse duration time, i.e.

$$C_0(x) = KS\,e^{-Kx}, \text{ where } S = \int_0^{t_p} L(t)\,dt \tag{5}$$

Then the total number of T-excitons (N_T) in the crystal at the moment after the exciting pulse is ceased will be equal:

$$N_T = \int_0^d C_T(x,t)\,\mathrm{d}x = \int_0^d \frac{KS\,\mathrm{e}^{-Kx}\mathrm{e}^{-t/\tau}\,\mathrm{d}x}{1+\mu\tau KS\,\mathrm{e}^{-Kx}(1-\mathrm{e}^{-t/\tau})} =$$

$$= \frac{\mathrm{e}^{-t/\tau}}{\mu\tau K(1-\mathrm{e}^{-t/\tau})}\ln\frac{1+\mu\tau KS(1-\mathrm{e}^{-t/\tau})}{1+\mu\tau KS\,\mathrm{e}^{-Kd}(1-\mathrm{e}^{-t/\tau})} \qquad (6)$$

The emission intensity will be proportional to this number, i.e. $\mathscr{T} = A\cdot N_T$. At $t=0$, according to (6), $\mathscr{T}_0 = AS(1-\mathrm{e}^{-Kd})$. Thus under the exciton annihilation, the phosphorescence decay law will take on the form

$$\frac{\mathscr{T}}{\mathscr{T}_0} = \frac{\mathrm{e}^{-t/\tau}}{\mu\tau KS(1-\mathrm{e}^{-Kd})(1-\mathrm{e}^{-t/\tau})}\ln\frac{1+\mu\tau KS(1-\mathrm{e}^{-t/\tau})}{1+\mu\tau KS\,\mathrm{e}^{-Kd}(1-\mathrm{e}^{-t/\tau})} \qquad (7)$$

At small S ($S \to 0$), i.e. when one may neglect exciton annihilation, the decay law, naturally, becomes exponential $\mathscr{T} = \mathscr{T}_0\mathrm{e}^{-t/\tau}$.

Exponentials will also be observed at late decay stage when $\mathrm{e}^{-t/\tau} \ll 1$:

$$\mathscr{T} = \mathscr{T}_0\frac{\mathrm{e}^{-t/\tau}}{\mu\tau KS(1-\mathrm{e}^{-Kd})}\ln\frac{1+\mu\tau KS}{1+\mu\tau KS\,\mathrm{e}^{-Kd}} \qquad (8)$$

The exciting light intensity dependence of the phosphorescence quantum efficiency can be obtained by substituting the expression for N_T from Eq. (6) into Eq. (1) and integrating the latter with respect to time. In so doing one obtains

$$\frac{B}{B_0} = \frac{1}{\mu\tau KS(1-\mathrm{e}^{-Kd})}\int_{\mu\tau KS\mathrm{e}^{-Kd}}^{\mu\tau KS}\frac{\ln(1+z)}{z}\,\mathrm{d}z \qquad (9)$$

where B_0, the value of B at $S \to 0$, is equal to $B_0 = \tau/\tau_r$. For thick crystals the value of this integral we determined graphically. For thin films when $\mathrm{e}^{-Kd} \to 1$, the S dependence of B is greatly simplified and

$$\frac{B}{B_0} = \frac{\ln(1+\mu\tau KS)}{\mu\tau KS} \qquad (10)$$

For thin films ($d = 5\ \mu$) as is seen from Table 1 a good agreement of theory (Eq. 10)) with the experimental data is obtained if one takes $\mu\tau KS_{\max} = 5$, since τ, K, $S_{\max}$ are known from the direct measurements, $\mu = 5 \times 10^{-15}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$. With this value of μ the theory (Eq. (9)) also reflects in a good way the crystal thickness dependence of the annihilation influence on the quantum efficiencies. For the phosphorescence decay the best agreement of the theory (Eq. (7)) and the experiment is obtained with $\mu \approx (2 \text{ to } 3) \times 10^{-15}\ \text{cm}^3\ \text{sec}^{-1}$ as is seen from Fig. 2.

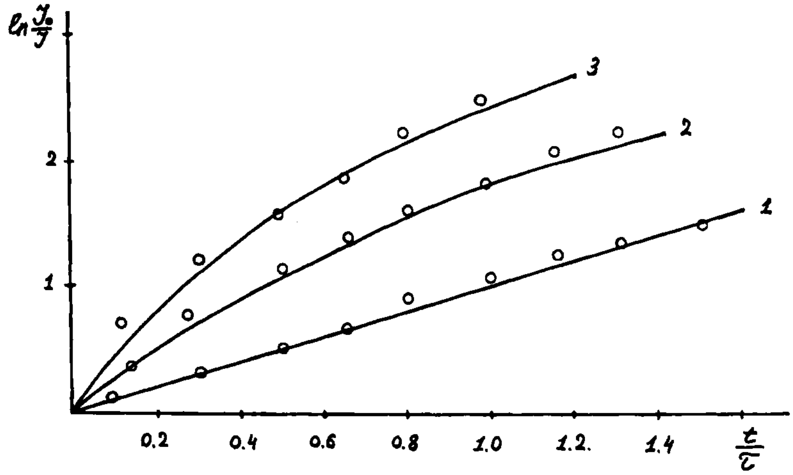

Figure 2. x-benzophenone phosphorescence decay at 77 °K.

The open circles are experimental, the solid curves theoretical: (1) $S = S_{\text{max}}/100$; (2) $S = S_{\text{max}}$, $d = 100\ \mu$; (3) $S = S_{\text{max}}$, $d = 5\ \mu$.

For the α-benzophenone thin films the agreement of the theory with the experiment is obtained if one takes $\mu \approx 1 \times 10^{-13}\ \text{cm}^3\ \text{sec}^{-1}$. Taking into consideration the accuracy of measurements of all the values which had to be known for the determination of μ, we considered the most probable value of μ for x-benzophenone to lie within the limits from 3×10^{-15} to $7 \times 10^{-15}\ \text{cm}^3\ \text{sec}^{-1}$, and for α-benzophenone from 6×10^{-14} to $2 \times 10^{-13}\ \text{cm}^3\ \text{sec}^{-1}$. For α-benzophenone this value of μ is almost an order of magnitude less than that given in(30) where it was determined from the difference of decay curves in the solution and in benzophenone crystal. This discrepancy seems to be mainly due to the difference in purity of benzophenone under investigation.

Knowing μ one can estimate the T-exciton diffusion coefficient from the equation $\mu = 8\pi \mathscr{D} R p$(17,31) where the value of R, the exchange forces action radius, is approximately equal to molecular dimensions,(32) and p—the probability of annihilation of excitons when they are approaching each other for this distance. The value of p is not exactly known, but if one takes it as one does in the case of exciton interaction with the impurity molecules, equal to $p = \frac{1}{2}$, thus for x-benzophenone one obtains $\mathscr{D}_T = (2.5 \text{ to } 5) \times 10^{-9}\ \text{cm}^2\ \text{sec}^{-1}$, and for α-benzophenone $\mathscr{D}_T = (0.5 \text{ to } 1.6) \times 10^{-7}\ \text{cm}^2\ \text{sec}^{-1}$. These values of $\mathscr{D}_T$ within the limits of accuracy of methods, applied to determine them, coincide with the values given in the beginning of this paper. Such a coincidence of data for $\mathscr{D}_T$ determined by different methods gives confidence in the correctness of its value and in the fact that its small value in regard to anthracene crystals is actually due to the peculiarities of benzophenone properties.

In the works(33,34) it was assumed that the smallness of $\mathscr{D}_T$ in benzophenone is mainly due to the localization of triplet excitation in the carbonyl groups of benzophenone molecules. In benzophenone crystals these carbonyl groups of neighbouring molecules are separated wide apart.(35) Since the exchange interaction depends exponentially on the distance between the interacting centres the increasing of distance between the chromophore groups caused by the localization of excitation must result in the considerable decreasing of the T-exciton migration rate.

The assumption about the strong influence of the localization of triplet excitation on the value of $\mathscr{D}_T$ in benzophenone crystals is confirmed as well by the following experimental results: (1) in liquid benzophenone $\mathscr{D}_T$ is about two orders of magnitude higher than that in α-benzophenone. Such increasing is apparently due to the possibility of considerable fluctuation approach of the carbonyl groups of neighbour molecules in the liquid phase;(33) (2) in α-benzophenone crystals the probability of T-exciton trapping by diacetyl impurity molecules in which excitation is also localized in the carbonyl groups is 10–20 times less than that by naphthalene or phenantrene molecules(38); (3) by the difference of $\mathscr{D}_T$ for two benzophenone crystals modifications which is probably due to the changes in molecule orientation and distance between their carbonyl groups.

The results of the experiments performed give ground to consider the properties of excitons resulting from the exchange interaction of molecules more sensitive to crystal peculiarities and particularly to the localization of excitation in certain groups than the properties of S-excitons resulting from the dipole–dipole molecular interaction.

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