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## Migration of Triplet Excitations in Chrysene Glass Films

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*Research results of delayed fluorescence decay kinetics in solid chrysene films deposited on quartz substrates in vacuum are presented. It is found that at the temperatures which are close to the temperature of liquid nitrogen, phosphorescence and annihilation delayed fluorescence decay kinetics are described by non-exponential function. The data obtained were discussed from the point of formal kinetics and percolation T–T annihilation models.*

**Keywords:** delayed fluorescence; disordered structures; exciton; phosphorescence; triplet–triplet annihilation

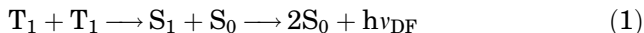
### INTRODUCTION

Efficiency of most photo processes in the molecular systems depends mainly on the energy transport to the reaction centers. Especially, it concerns the disordered solids because in these systems molecules have different surroundings, and energy of their interaction with the surrounding particles is the random variable, energy changed from the centre to centre. Therefore, regularity of the electronic excitation dynamics in such disordered systems as impurity molecular crystals, glasses, polymers, thin films will be differ from model approximation of the similar processes in homogenous mediums.

To study a transport of electronic excitation energy at triplet levels of organic molecules, the triplet–triplet annihilation (T–T) can be used:

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During the study of annihilation delayed fluorescence ( $h\nu_{DF}$ ), a constant of rate  $k_{ann}$  can be obtained for the T–T annihilation process, and its time dependence can be analyzed.

In the homogenous mediums the constant of rate of T–T annihilation does not depend on time. The regularity of the pair annihilation of the triplet excitons in homogenous mediums is well described in the way of formal kinetic approach, according to which the triplet decay is described by the following:

$$\frac{d[T]}{dt} = -k_1[T] - k_{ann}[T]^2, \quad (2)$$

and the delayed fluorescence intensity:

$$I_{DF} = \left( \frac{k_1^2}{k_{ann}} \right) \left\{ \left( 1 + \frac{k_1}{k_{ann}[T_0]} \right) \exp(k_1 t) - 1 \right\}^{-2} \quad (3)$$

where  $k_1/k_{ann}$  – the constants of the monomolecular decay and T–T annihilation, accordingly,  $[T_0]$  – the initial concentration of the triplet excitons.

In case of disordered structures  $k_{ann}$  stops to be a constant and becomes time dependent parameter. Reaction (1) for such systems is described by the [1]:

$$-\frac{d[T]}{dt} = k_1[T] + k_{ann}t^{-h}[T]^2 \quad (4)$$

and the delayed fluorescence intensity is determined as:

$$I_{DF} = k_{ann}t^{-h}[T]^2 \quad (5)$$

Parameter  $h$  characterizes the degree of the local heterogeneity of the medium and is connected to spectral dimension of the percolation cluster  $d_s$ ,

$$h = 1 - d_s/2, \quad 0 \leq h \leq 1. \quad (6)$$

The low limit,  $h=0$ , corresponds to the movement in the locally homogenous medium. The upper limit,  $h=1$ , characterizes movement in the locally inhomogeneous clusters. For strictly fractal medium  $d_s=1,33$ , and  $h=0,35$  [2,3].

Keeping in mind that intensity of phosphorescence ( $I_{Ph}$ ) is proportional to the density of triplet excitation, and the delayed fluorescence intensity ( $I_{DF}$ ) is proportional to the square of triplets concentration, the time

dependence  $k_{\text{ann}}(t)$  can be found from the following:

$$I_{\text{DF}}/I_{\text{Ph}}^2 \sim k_{\text{ann}}(t) \sim t^{-h}. \quad (7)$$

The diagram  $\ln(I_{\text{DF}}/I_{\text{Ph}}^2)$  from  $\ln(t)$  must be linear with a slope  $h$ . Dependence  $I_{\text{DF}}(t)$ ,  $I_{\text{Ph}}(t)$  can be obtained from the experiment directly.

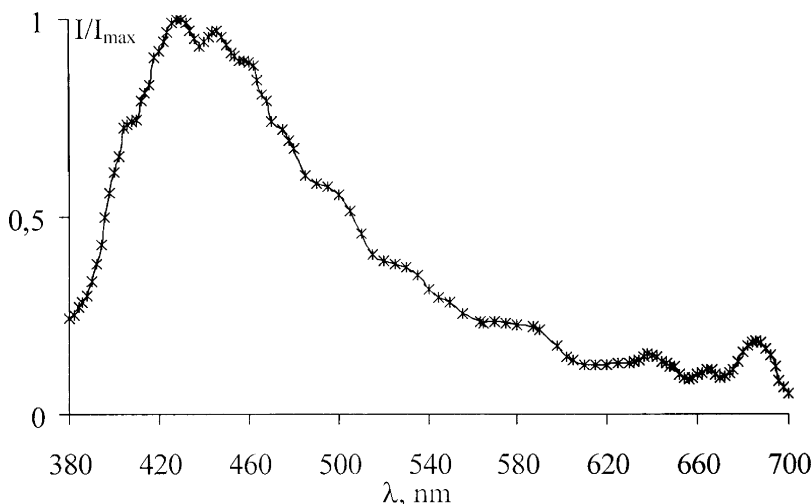
This article describes the results obtained from T–T annihilation in the chrysene molecular films.

## EXPERIMENTAL METHODS

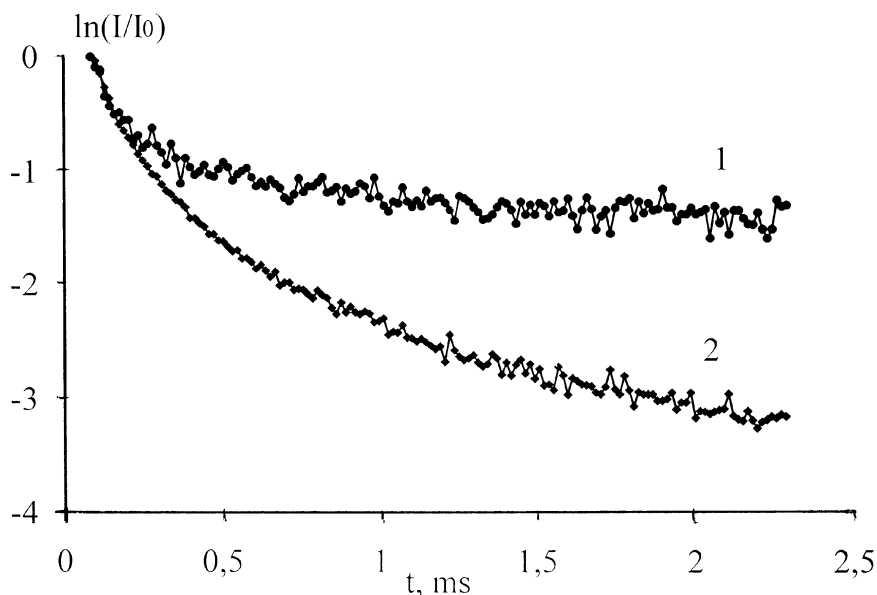
The films were obtained by vapor deposition of chrysene in vacuum on nonluminescent glass. The temperature of the glass was supported equal to liquid nitrogen. The pressure in camera was  $3 \cdot 10^{-5}$  torr. Measurements of spectra and long-lived luminescence decay kinetics of the glassy films was performed by method of photon counting. Photoexcitation was done by radiation of the nitrogen laser at the wave length  $\lambda = 337.1$  nm with impulse energy  $E = 3$  mJ. The time of impulse was  $\tau = 10$  ns.

## RESULTS AND DISCUSSION

In the Figure 1 a spectrum of long-lived luminescence of chrysene glass film at  $T = 90$  K is shown. In the long wavelength part of the spectrum



**FIGURE 1** The spectrum of long-lived luminescence of glass chrysene films.



**FIGURE 2** Decay kinetics of phosphorescence (1) and annihilation delayed fluorescence (2) of glass chrysene film at  $T = 90$  K.

in the region 600–700 nm the radiation corresponding to its phosphorescence is observed. In short wavelength part (400–500 nm) luminescence coinciding with its fast fluorescence is observed. This radiation corresponds to the delayed fluorescence, which appears due to T–T annihilation.

In Figure 2 annihilation delayed fluorescence decay curves are presented at  $T = 90$  K. From the Figure it is seen, that in common case, both kinetic curves are non exponential. The initial part of annihilation delayed fluorescence decay is well described by power dependence  $I_{DF} \sim t^{-n}$ . At the further times ( $t > 0.5$  ms) delayed fluorescence decay corresponds to exponent with  $\tau_{DF} = 1.33$  ms. In the case of phosphorescence the most part of the decay curve is described by the exponent function.

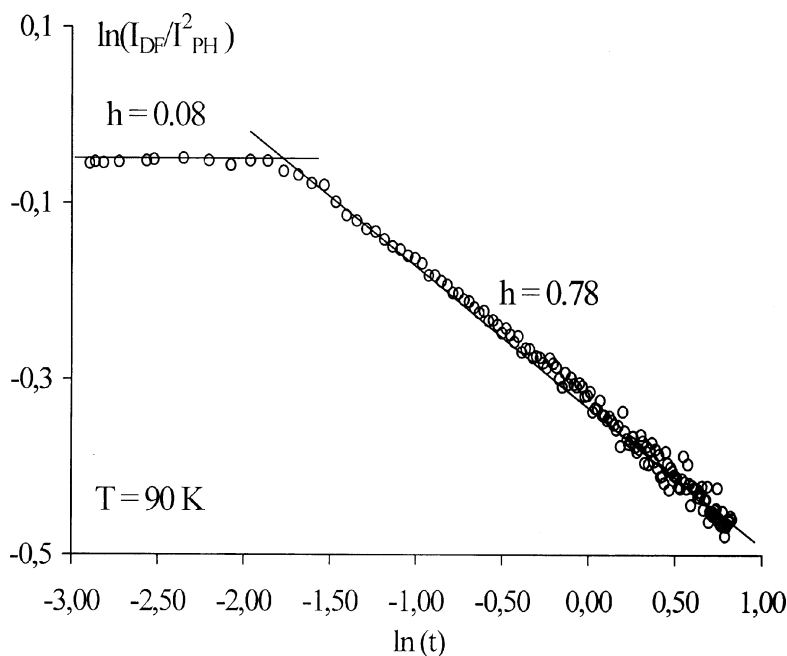
Non-exponential dependence is observed only for the small area in the initial part of the curve ( $\tau < 80 \mu s$ ). Duration of phosphorescence calculated from the exponential part of the curve is  $\tau_{Ph} = 2.5$  ms. The twofold difference of phosphorescence and delayed fluorescence lifetime shows that, delayed fluorescence appears as a result of T–T annihilation.

The comparison of the initial part of the experimental delayed fluorescence decay curve with the theoretical, built by the formula (3) is

made. The constant of rate of pair annihilation  $k_{\text{ann}}$  of the triplet molecules, at which the best coincidence of the experimental curve with the calculated one was observed equals to  $4.5 \cdot 10^9 \text{ s}^{-1} \text{ cm}^3$  and qualitatively agrees with the value of the constant of rate of bimolecular annihilation of the triplet excitons in molecular crystals [4].

In the Figure 3 dependence  $\ln(I_{\text{DF}}/I_{\text{PH}}^2)$  from  $\ln(t)$  is shown. It is seen, that all over investigated time interval two time areas can be stressed, in which the given dependence is linear. In millisecond range the slope of the dependence corresponds to  $h=0.78$ . The obtained value  $h$  shows that at given temperature of film, the movement of the triplet exciton has a local character. Geometry of the molecule ensemble in this area is close to the geometry of the percolation cluster. The similar data were obtained for solid naphthalene and chrysene melted [1,5].

In time interval less than 0.5 ms the same linear dependence is observed, but with a smaller slope. The obtained value  $h$  is close to zero and corresponds to migration of exciton in the locally homogenous area. This is consistent with the data obtained on the basis of analysis of the initial part of kinetic curve using a formal kinetic model.

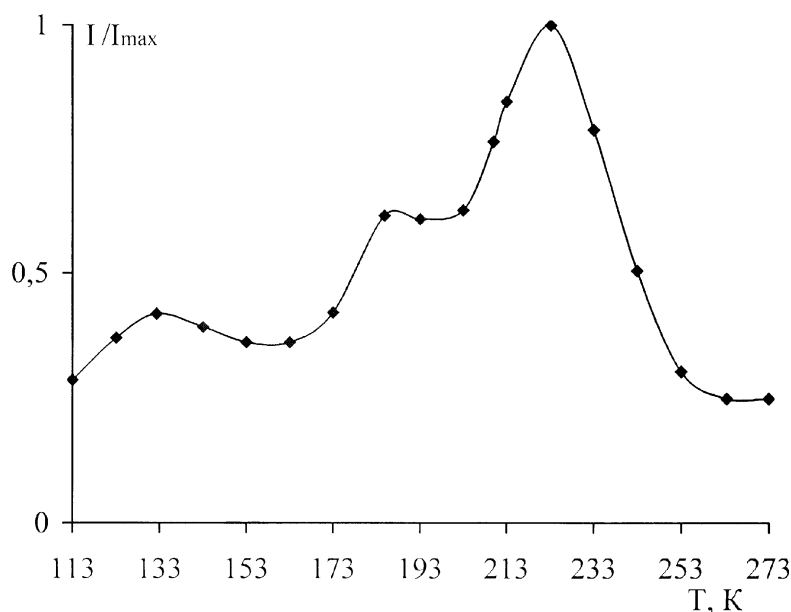


**FIGURE 3** Dependence  $\ln(I_{\text{DF}}/I_{\text{PH}}^2)$  from  $\ln(t)$  at temperature of the film  $T = 90 \text{ K}$ .

With the temperature increase, the reduction of delayed fluorescence lifetime calculated is observed, from exponential part of decay kinetics of phosphorescence and delayed fluorescence. The exponent  $n$  of the initial part of the decay curve increases while the temperature rises, and  $h$  is decreasing. This certifies that area of exciton migration increases. At temperature higher than 250 K the annihilation which is characteristic of homogeneous system is observed. Temperature dependence of  $h$  parameter shows transition from exciton migration in the percolation cluster ( $h=0.78$ ) to the movement in homogenous medium ( $h \rightarrow 0$ ).

Thus, analysis of annihilation delayed fluorescence decay kinetics shows that chrysene film structure is inhomogeneous. The major contribution to the kinetics of the initial part of the decay curve is done by the microcrystalline parts of the film. At the time  $t > 0.2$  ms delayed fluorescence is observed mainly from clusters with fractal properties.

With a change of film temperature together with change of delayed fluorescence decay kinetics the change of intensity was observed. In Figure 4 temperature dependence of annihilation delayed fluorescence of chrysene film is shown. Measurement of (instant) delayed fluorescence intensity was done in  $50 \mu\text{s}$  after excitation impulse. It is seen,



**FIGURE 4** Temperature dependence of the delayed fluorescence intensity.



that in the temperature range from 90 K to 273 K the delayed fluorescence intensity has 3 maxima. Maxima are observed at the temperatures 113 K, 183 K and 223 K. The further increase of the temperature leads to the delayed fluorescence quenching.

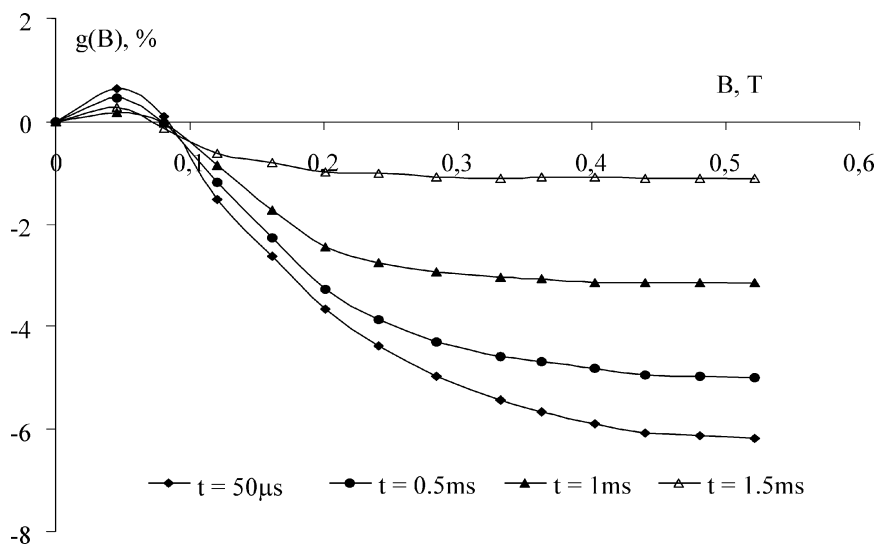
For explanation of the obtained data we have to assume, that in vacuum deposited films of chrysene inhomogeneous broadening of  $T_1$  level takes place. At low temperatures a migrating exciton is captured by those traps which have low lying  $T_1$  levels. Heating a film releases excitons from the traps and increases the efficiency of their migration over triplet levels of equal energy. An increase of migration efficiency results in its turn, an increase of the number of triplet pair annihilation events, which becomes manifest in an enhancement of the delayed fluorescence. The decrease of the luminescent intensity after a certain critical temperature is connected with domination of the non-radiative channels of triplet-centre decay with temperature increase. Presence of three temperature maxima, apparently, associated with existence of three types of chrysene molecules clusters with different dispersion value of  $T_1$  levels. Inhomogeneous broadening of energy levels was observed in inhomogeneous mediums such as glasses, polymers, Langmuir-Blodgett films [6–9].

For the temperature interval where the delayed annihilation fluorescence intensity increase is observed inhomogeneous triplet level broadening in conditions of, one can write

$$I_{DF} = I_0 \exp(-\Delta E/kT), \quad (8)$$

where  $I_0$ —delayed fluorescence intensity at  $T=90$  K, and  $\Delta E$ —is triplet level dispersion. From the dependence  $\ln(I_{DF}/I_0)$  from  $1/T$  the values of  $\Delta E$  were determined. For temperature intervals, where enhancement of the delayed fluorescence intensity was observed, the following values of  $\Delta E$  were obtained: 186, 216, 344  $\text{cm}^{-1}$ . The data obtained are close in magnitude to the inhomogeneous broadening of the triplet levels of aromatic molecules [7,10].

Figure 5 demonstrates influence of external magnetic field on the delayed annihilation fluorescence intensity of chrysene film in the different times of signal recording from the beginning of laser impulse. It is seen, that at  $t=50$  mks the obtained dependence has a classical form, typical for molecular crystals. With an increase of registered time of delayed fluorescence intensity, the magnetic effect decreases. In  $t=1.5$  ms its magnitude is almost 1%. Character of the magnetic field influence on annihilation delayed fluorescence on initial stages of decay proves that chrysene film has crystal areas. The decrease of



**FIGURE 5** Magnetic field influence on the delayed fluorescence intensity of glass chrysene film at  $T = 90\text{ K}$ .

magnetic effect in millisecond interval, perhaps, is explained by the reduction of concentration of triplet excitons at the moment of signal measurement.

## CONCLUSION

Summarizing the data obtained, we can conclude, that in glass chrysene films kinetics of annihilation of triplet excitons is determined by processes, which occur at the different time interval. In microsecond interval annihilation is well described on the basis of classical formal kinetic theory, when the constant of the annihilation rate does not depend on time. In millisecond interval dependence of  $k_{\text{ann}}$  from time by the power law is observed. The exponent of power of  $h$  characterizes local inhomogeneity of medium. At  $T = 90\text{ K}$  migration of exciton has local character. With an increase of temperature, area of migration is broadening and transition to exciton movement in the homogenous system is observed.

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