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TEMPERATURE AND MAGNETIC FIELD INFLUENCES ON ANNIHILATION DELAYED FLUORESCENCE OF AROMATIC MOLECULES IN LANGMUIR-BLODGETT FILMS

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The temperature influence on an annihilation delayed fluorescence of aromatic molecules in Langmuir-Blodgett films was investigated. It is shown that the efficiency of migration of triplet excitons depends on temperature owing to inhomogeneous broadening of energetic levels caused by local inhomogeneity of film structure. From experimental data the quantities of scattering of Anthracene, 1,2-Benzanthracene and Fluoranthene triplet levels were determined. The influence of external magnetic field on delayed fluorescence characteristics was studied. On an incipient stage of luminescence decay the magnetic effect replicates that of crystals. In the course of time magnetic field effect on intensity of delayed fluorescence decreases.

Keywords: aromatic molecules; delayed fluorescence; Langmuir-Blodgett film; triplet-triplet annihilation

INTRODUCTION

In Ref. [1,2] properties of annihilation delayed fluorescence of aromatic molecules in Langmuir-Blodgett films was studied. Obtained delayed fluorescence spectra were analogous to those of crystals. The kinetics of annihilation delayed fluorescence decay had complicated form. The initial part of the kinetics was described by a power function and long-time part-exponential function. It was made comparison of experimental decay curve with curves calculated on the basis of different models of triplet-triplet annihilation in solid mediums. It was obtained that the initial part of the kinetics of delayed fluorescence decay coincided with curve for model of triplet exciton annihilation in crystals [3]. The long-time part of the kinetics of decay better conforms to percolation cluster model [4,5]. On the basis of that it was made the conclusion that Langmuir-Blodgett films of aromatic

molecules had structure inhomogeneity and consisted of microcrystalline and percolation clusters. The data about clusterization of aromatic molecules in Langmuir-Blodgett films have been obtained in Ref. [6].

It is known [7–10] that in condensed disordered mediums, such as glasses, polymers, alcohols etc., inhomogeneous broadening of energetic levels of impurity luminescence centres is observed. It is connected with structure heterogeneity of their local environment. As a result of this the dependence of efficiency of migration of excitation energy on medium temperature is observed. Starting from this, one can expect that in Langmuir-Blodgett films obtained on the basis of aromatic molecules and fatty acids the exciton processes of energy transfer will depend on temperature.

One of the interesting properties of annihilation delayed fluorescence is its dependence on external magnetic field. Magnetic effect was observed in crystals and liquid solutions [11,12]. The most exhaustive theory of external magnetic field influence on annihilation rate constant was evolved in Ref. [13]. One of the essential aspects of the theory is the question about role of repeated collisions of exciton pairs. Influence of the magnetic field on annihilation rate constant increases with growth repeated contacts. On that reason the role of system dimension is important. Exciton migration in three-dimensional lattice qualitatively differs from that in one and two-dimensional lattice. Reduction of dimension leads to increase of magnetic field influence.

Langmuir-Blodgett monolayers are two-dimensional structures. Therefore one can expect untraditional magnetic field influence on annihilation delayed fluorescence in them.

In this paper the results of investigation of temperature and magnetic field influences on the characteristics of annihilation delayed fluorescence of aromatic molecules in Langmuir-Blodgett films were presented.

EXPERIMENTAL METHODS

Multimolecular films of Anthracene, 1,2-Benzanthracene, Fluoranthene were used as objects of investigation. The films were prepared on non-luminescent quartz substrates using Langmuir-Blodgett setup. Twice-distilled deionized water was used. The surface tension of water was 72.8 dyn/cm at pH = 5.6 and T = 293 K. To receive stable monolayers on a water subphase the mixtures of these molecules with palmitic acid were used. Luminophore concentration was 50 mol%. The rate of movement of substrate through the monolayer was $2*10^{-3}$ cm/s. It was deposited 20 monolayers of molecules on the surface of substrate.

Measuring of luminescence characteristics was performed by method of photon counting. Photoexcitation was carried out by radiation of nitrogen

laser with wavelength 337.1 nm. The energy of impulse was 3 mJ and duration was 10 ns. The films were placed into optical cryostat with automatic temperature regulation. The cryostat was placed between electromagnet poles to investigate magnetic effects. The value of magnetic effect was estimated under the relative change of delayed fluorescence intensity in magnetic I(B) and zero field I(0) fields by formula:

$$g(B) = \frac{I(B) - I(0)}{I(0)} * 100\% \quad (1)$$

Operation control of setup, accumulation of data and their handling were automated and managed with computer PC Pentium II.

RESULTS AND DISCUSSION

Figure 1 shows temperature dependence of annihilation delayed fluorescence of Langmuir-Blodgett films of Anthracene, 1,2-Benzanthracene and Fluoranthene. Measuring of instantaneous luminescence intensity was carried out in 50 μs after excitation impulse. For Anthracene and Fluoranthene films one can see, that luminescence intensity remains stationary value within temperature range of 90−173 K. Then the considerable increase of delayed fluorescence yield begins. For Anthracene the luminescence intensity reaches peak value at $T = 218$ K, and for fluoranthene – at $T = 223$ K. Further increase of film temperature leads to luminescence quenching. In case of 1,2-Benzanthracene films it is qualitatively observed the same picture. Its luminescence yield reaches peak value at $T = 203$ K. For the all objects the ratio of maximum yield of delayed fluorescence intensity to that at $T = 90$ K is approximately 10 and more times.

Being at low temperatures the initial part of the kinetics of decay of a delayed fluorescence is approximated by a power function ($I \sim t^{-n}$), and long-time part-exponential function. In an interval of temperatures, where the intensity of luminescence remains a stationary value, the kinetics of decay also practically does not vary. In the field of temperature increase of delayed fluorescence intensity the exponential part of a kinetics of decay is extinguished, and at reaching a maximum of intensity of luminescence practically disappears. The exponent (n) of the initial part of the decay curve grows in accordance with temperature increase. At the temperature of maximal delayed fluorescence intensity value n is close to 2.

It is known, that temperature increase strengthens intra- and intermolecular processes, leading to nonradiative death of triplet centres. It leads to delayed fluorescence quenching. However, one can see that film heating results in luminescence increase. Intensity reaches peak value at definite temperature. To explain obtained results it is necessary to suppose

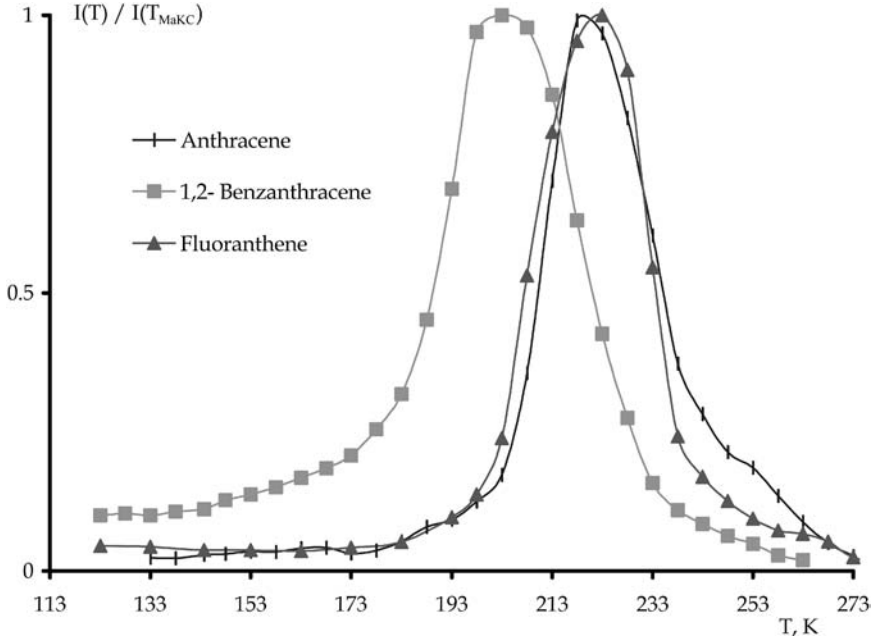

FIGURE 1 Temperature dependence of delayed fluorescence intensities of aromatic molecules in Langmuir-Blodgett films. I(T) – luminescence intensity at different temperatures; $I(T_{max})$ – luminescence intensity at temperature of maximum luminescence yield.

that there is scattering of T_1-levels. At low temperatures migratory exciton is captured by the traps which have lower T_1-level. Film heating leads to exciton release from traps and promotes increase of efficiency of their migration on triplet levels of identical energy. The increase of migration efficiency, in turn, leads to rise of pair annihilation of triplet excitons. That is exhibited in delayed fluorescence intensity increase. Luminescence intensity decrease at higher temperatures than some critical temperature is connected to prevalence of nonradiating channels of triplet centres decay.

From temperature dependence of annihilation delayed fluorescence intensity one can find the value of inhomogeneous broadening of triplet levels. For temperature interval in which the increase of annihilation delayed fluorescence intensity in condition of inhomogeneous broadening of triplet levels is observed one can use the ratio:

$$I_{DF} = I_0 \exp(-\Delta E/kT), \tag{2}$$

Where I_0 is delayed fluorescence intensity at T = 90 K, I_{DF}-delayed fluorescence intensity at different temperatures, ΔE is the value of dispersion of triplet levels. Figure 2 shows dependencies from which the values ΔE for studied objects have been determined. It follows from obtained results that value of dispersion of Anthracene, 1,2-Benzanthracene, Fluoranthene triplet levels in Langmuir-Blodgett films is 518 cm^{-1}, 270 cm^{-1} and 470 cm^{-1} accordingly.

Figure 3 shows annihilation delayed fluorescence intensity of Langmuir-Blodgett films of 1,2-Benzanthracene as a function of induction of magnetic field. The film temperature was 90 K. Concentration of 1,2-Benzanthracene was 75 mol%. Annihilation delayed fluorescence intensity was measured at wavelength 420 nm. Measurements of magnetic effect were performed in different time (t_{reg}) after excitation laser impulse.

Curve 1 (Fig. 3) demonstrates intensity increase of delayed fluorescence at 2–4% at change of induction of magnetic field from 0 T till 0.05 T. Further rise of magnetic induction leads to monotonous increase of luminescence intensity. When induction of magnetic field B > 0.35 T luminescence intensity decreases up to value which is equal to 80–85% of intensity in zero field approximately. Observed dependence is close to dependence

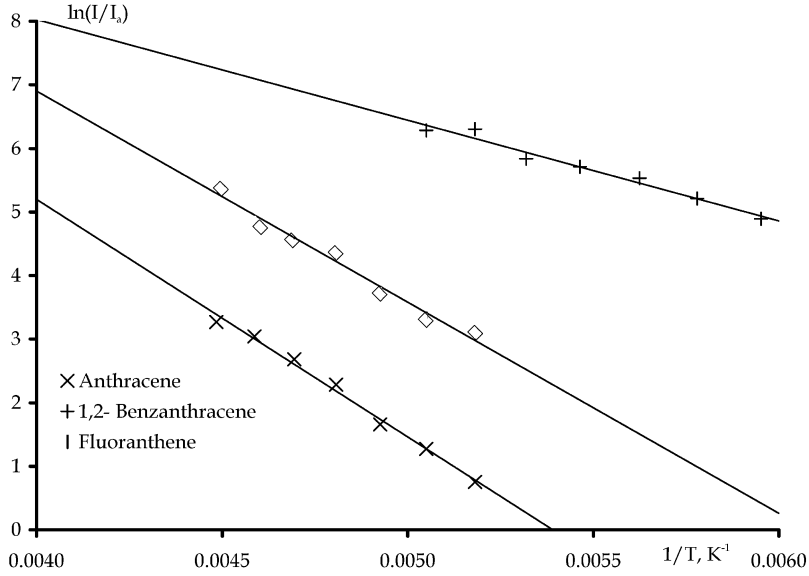

FIGURE 2 Determination of the value of inhomogeneous broadening of triplet levels. I – delayed fluorescence intensity at different temperatures; I_a – delayed fluorescence intensity at T = 90 K.

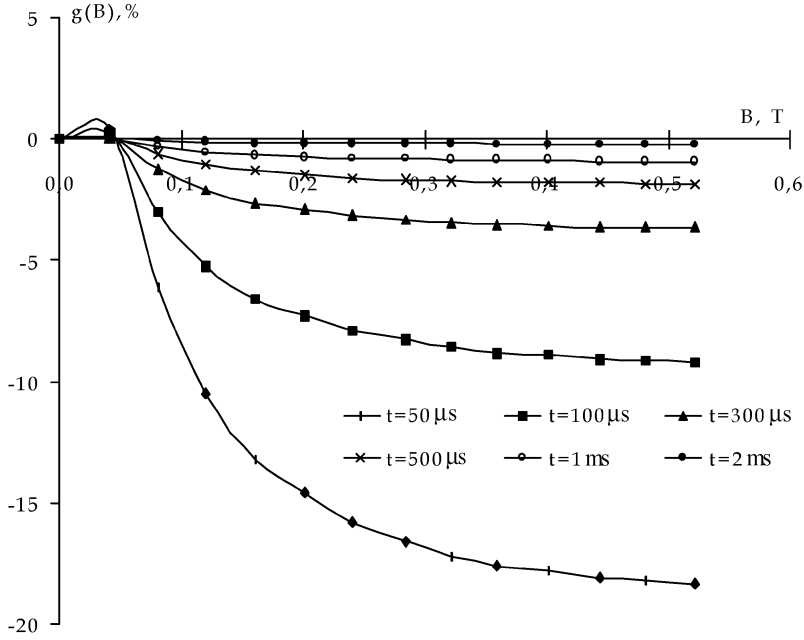

FIGURE 3 Magnetic field effect on delayed fluorescence of 1,2-Benzanthracene Langmuir-Blodgett films.

obtained for Anthracene crystals [9]. In increasing the time of beginning of signal registration from 50 μs till 1ms effect of magnetic field influence smoothly decreases. When $t_{reg} > 500$ μs magnetic field does not influence on delayed fluorescence practically. On film temperature increasing from 90 till 203 K qualitative changes do not take place.

In Ref. [6,7] there was performed analysis of kinetics of annihilation delayed fluorescence decay. It was shown that structure of Langmuir-Blodgett films of aromatic molecules was inhomogeneous. The initial part of the kinetics of decay is the result of annihilation in crystal areas. Long-time exponential decay is observed from percolation clusters. In microcrystals annihilation rate constant is stationary value. Whereas in percolation clusters it depends on time. Therefore coincidence of magnetic effect of initial part of Langmuir-Blodgett films kinetics of decay to magnetic effect for crystals. At the same time, it is difficult to say something definite about influence of the magnetic field on annihilation of triplet excitons in systems where annihilation rate constant depends on time.

CONCLUSION

According to obtained results inhomogeneous broadening of triplet levels in Langmuir-Blodgett films of aromatic molecules is observed. Therefore the efficiency of migration of triplet excitons depends on temperature. Character of the magnetic field influence on annihilation delayed fluorescence on initial stages of decay is analogous to that which is observed in crystals. The increase of magnetic effect at $t_{reg} > 50\,\mu s$ is evidence of different efficiency of modulation of annihilation rate constant by magnetic field in crystalline and percolation clusters.

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