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CONDENSED-MATTER SPECTROSCOPY

Effect of Magnetic Field on Triplet Excitons Annihilation in Langmuir–Blodgett Films

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Abstract—We study the effect of an external magnetic field on annihilation of triplet excitons of aromatic molecules in Langmuir–Blodgett films. Differences in the magnetic effect in relation to the number of layers, temperature, and recording time of annihilation delayed fluorescence are determined.

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INTRODUCTION

Langmuir–Blodgett (LB) films are organized molecular ensembles, which are formed by transferring monolayers of organic molecules from the water–air interface to a solid substrate. Characteristic features of these films are a specified spatial orientation of molecules in the layer and a strictly fixed thickness. Due to these structural features, LB films possess specific interesting properties, which can be used in nanophotonics, molecular electronics, etc.

In [1, 2] annihilation of triplet excitons of aromatic molecules in LB films has been studied. It was found that the observed nonexponential decay kinetics of annihilation delayed fluorescence can be well described by a combination of formally kinetic [3] and percolation [4] models. It was assumed that LB films of organic molecules are inhomogeneous in structure and consist of microcrystalline and percolation clusters. Temperature studies of [5, 6] showed that triplet levels in LB films are inhomogeneously broadened, which affects the migration efficiency of triplet excitons.

More detailed information on specifics of random walks and contacting of reagents in systems with inhomogeneous structure can be extracted from studies of the modulation of the triplet–triplet annihilation rate constant by an external magnetic field [7]. The spatial divergence of partners that failed to react with each other during their first contact is an important stage of spin-selective pair annihilation of triplets. During this time period, the combined spin state of a coherent pair of particles, which can be affected by an external magnetic field, can change. Upon repeated contact, if a necessary fraction of the spin component is ensured, a favorable reaction outcome can be reached. The probability of the repeated contact of reagents directly depends on the dimension of the system and the migration and interaction efficiency of excitons. Reducing the dimension of the system increases the probability of the repeated contact of particles [3]. Taking this into account, one can expect that, by modulating the rate of pair annihilation of triplets with a magnetic field, it may become possible to obtain additional information on particular features of the structure of LB films.

EXPERIMENTAL

As objects of study, we used thin films that consisted of a mixture of stearic acid and 1,2-benzanthracene, which were obtained using the Langmuir–Blodgett technology. The films were prepared by the vertical lift method on solid substrates made of non-luminescent quartz. The concentration of 1,2-benzanthracene molecules in films was 75 mol % with respect to stearic acid.

Measurements were performed on a setup designed for studying the effect of a magnetic field on the kinetics of delayed fluorescence in the photon-counting mode. As an excitation source, we used an ILGI-503 nitrogen laser with a pulse energy of 1 μJ at a wavelength of 337 nm. Measurements were performed either in 2 μs or in 0.5 ms after the excitation of the object of study. To determine the magnitude of the effect produced by the magnetic field, the fluorescence decay kinetics was measured in the presence and absence of the magnetic field. Initially, a series of five to ten measurements was performed in the absence of the field. After that the electromagnet was switched on, the kinetics of the delayed fluorescence annihilation was measured at least five times for each value of the field induction. The magnitude of the magnetic effect was estimated from a relative change in the intensity of the delayed fluorescence in the presence and in the absence of the magnetic field by the formula

$$g(B) = (I(B) / I(0) - 1)100\%,$$

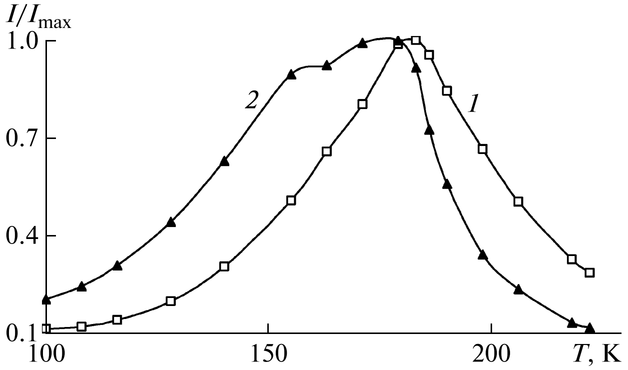

Fig. 1. Temperature dependence of delayed fluorescence intensity of ten-layer LB 1,2-benzanthracene film measured in (*1*) 2 μs and (*2*) 0.5 mS after excitation.

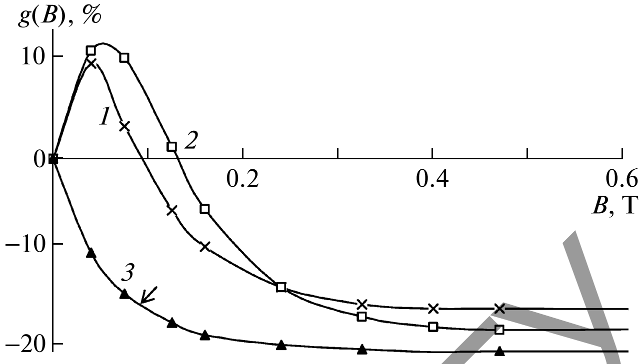

Fig. 2. Dependences of magnitude *g* of magnetic effect on magnetic induction for ten-layer LB 1,2-benzanthracene film measured at (*1*) 100 and (*2*, *3*) 190 K in (*1*, *2*) 2 μs and (*3*) 0.5 ms after excitation.

where $I(B)$ and $I(0)$ is the intensity of the delayed fluorescence in the field and without field, respectively, B is the magnetic induction.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the annihilation intensity of the delayed fluorescence of a Langmuir film of 1,2-benzanthracene. The fluorescence intensity was measured in 2 μs (curve *1*) and 0.5 ms (curve *2*) after the excitation. It can be seen from this figure that, upon heating the film, the fluorescence intensity increase and reaches a maximum at a certain temperature.

To explain these data, it should be assumed that, in LB films of organic molecules, there is a spread in T_1 levels. At low temperatures, a migrating exciton is captured by traps whose T_1 level is the most low-lying. Heating the film releases excitons from traps and facilitates an increase in the migration efficiency via triplet levels of the same energy. In turn, the increase in the migration efficiency causes an increase in the number of events of pair annihilation of triplets, which manifests as an increase in the intensity of the delayed fluorescence. The decrease in the fluorescence intensity above a certain critical temperature is related to the fact that, with increasing temperature, channels of nonradiative deactivation of triplet centers dominate.

The effect of the magnetic field on the delayed fluorescence annihilation kinetics of LB 1,2-benzanthracene films was studied at different temperatures. The magnetic field was directed tangentially to the substrate surface along its short side. The magnitude of the magnetic effect was estimated from the measurements of an instantaneous intensity in different time periods after the excitation. Figure 2 presents curves of the magnetic effect for a ten-layer film. At a temperature of the film of $T = 100$ K (curve *1*), the obtained dependence is characteristics of crystals of organic molecules. In a temperature range of 100–180 K, the magnitude of the magnetic effect does not depend on the measurement time, and the behavior of the curve remains the same.

At a temperature of the film of 190 K and a measurement time of $\tau = 2$ μs (curve *2*), the qualitative behavior of the curve of the magnetic effect does not change. It remains characteristic of crystalline systems. For the measurement time $\tau = 0.5$ ms (curve *3*), the shape of the curve unexpectedly changes, and the effect becomes typical of liquid solutions. As the measurement time is varied in the range from 2 μs to 0.5 ms, the shape of the observed curve is intermediate between curves *2* and *3*. This character of the magnetic dependence is also preserved with increasing temperature.

We found that, qualitatively, the experimental data on the effect of the magnetic field on the delayed fluorescence annihilation obtained for single- and ten-layer films coincide. However, as the number of layers in the film decreases, the magnitude of the magnetic effect increases. Thus, for the ten-layer film, the magnitude of the effect at a temperature of 100 K is 15%, whereas, for the single-layer film and the same temperature, the magnitude of the effect is 20%. This difference is seemingly related to the fact that the probability of a repeated contact between reagents in the single-layer film is considerably higher than in the multilayer film. It also follows from this that, in the multilayer film, an exciton can travel from layer to layer.

Therefore, our data indicate that LB films of organic molecules consist of microcrystals and clusters with a disordered structure. At initial time moments after the laser excitation, crystalline regions contribute most to the delayed fluorescence annihilation intensity because a large migration rate of excitons and orientation of spins of triplets facilitate a high probability of pair annihilation. The existence of microcrystalline structures is also confirmed by the shape of the dependence of the modulation of the rate of triplet–triplet annihilation on the induction of the external magnetic field. This shape is characteristic of crystals of organic molecules (the Merrifield model) [8]. With increasing temperature, the specifics of intracluster exciton walks becomes similar to the diffusion motion of particles in solutions and, in this case, the Atkins–Evans relaxation model [9] should be applied. According to this model, the total spin of a coherent pair of particles changes within the time period between their repeated contacts.

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