

Effect of Temperature on Triplet Exciton Migration in Langmuir–Blodgett Films

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Abstract—The effect of temperature on delayed annihilation fluorescence of aromatic molecules in Langmuir–Blodgett films has been studied. It is shown that because of the inhomogeneous broadening of energy levels caused by local nonuniformities in the film structure, the migration efficiency of triplet excitons is temperature dependent. Experimental data were used to calculate the scatter in the triplet level energies of the anthracene, 1,2-benzanthracene, and fluoranthene molecules. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

It is known that condensed disordered media, such as glasses, polymers, alcohols, etc., exhibit inhomogeneous broadening of the levels of luminescent impurity centers [1–6]. This phenomenon originates from the structural nonuniformity of their local environment. As a result, the excitation migration efficiency becomes dependent on the temperature of the medium.

It was shown that the nonexponential decay kinetics of the delayed annihilation fluorescence of aromatic molecules in Langmuir–Blodgett films is caused by the inhomogeneous distribution of the triplet molecules [7, 8]. An analysis of experimental data made within theoretical models of triplet–triplet annihilation in solids showed the films to consist of microcrystalline and percolation clusters. Clusterization of aromatic molecules in Langmuir–Blodgett films was observed also in [9]. Thus, one could expect that excitonic energy transfer processes in Langmuir films based on aromatic molecules and fatty acids would be thermally activated.

We are reporting here on a study of the effect of temperature on the characteristics of delayed annihilation fluorescence of aromatic molecules in Langmuir–Blodgett films.

EXPERIMENTAL

The subjects of the study were multimolecular films of anthracene, 1,2-benzanthracene, and fluoranthene. The technique employed in film preparation was described in [7]. The luminescence characteristics were measured in the photon-counting regime. A nitrogen laser operating at a wavelength of 337.1 nm was used for photoexcitation. The pulse energy was 3 mJ, and the pulse duration, 10 ns. The films were placed in an optical cryostat with automatic temperature control. To prevent oxygen quenching of the triplet states of the molecules under study, the residual air pressure in the cry-

ostat was maintained at 10^{-4} mm Hg. The operation of the setup, data accumulation, and processing were computer controlled (Pentium II processor).

RESULTS AND DISCUSSION

Figure 1 presents the temperature dependence of the delayed annihilation fluorescence intensity in anthracene, 1,2-benzanthracene, and fluoranthene Langmuir films. The instantaneous luminescence intensity was measured as 50 μ s after the pump pulse. The luminescence intensity in the anthracene and fluoranthene films is seen to remain constant in the temperature region from 90 to 173 K. After this, the yield of delayed fluorescence starts to rise abruptly. For

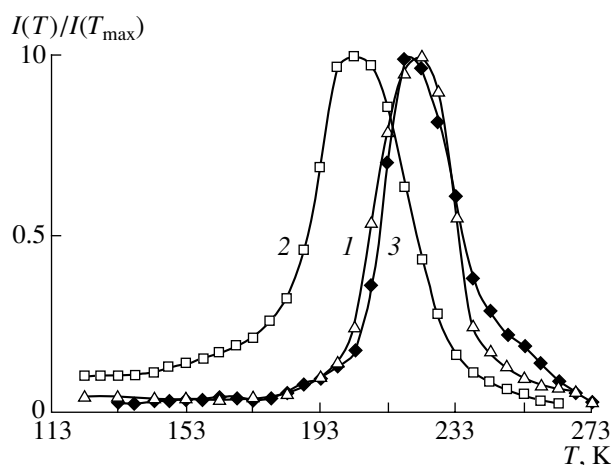


Fig. 1. Temperature dependence of the delayed fluorescence intensity of aromatic molecules in Langmuir–Blodgett films. $I(T)$ —luminescence intensity plotted vs. temperature; $I(T_{\max})$ —same quantity at the temperature of maximum luminescence yield. (1) Anthracene, (2) 1,2-benzanthracene, (3) fluoranthene.

anthracene, the luminescence intensity reaches a maximum at $T = 218$ K, and for fluoranthene, at $T = 223$ K. Increasing the film temperature still higher brings about luminescence quenching. The 1,2-benzanthracene films reveal qualitatively the same pattern. For this molecule, the luminescence yield reaches a maximum at $T = 203$ K. The maximum intensity of delayed fluorescence exceeds in these substances about tenfold or more the fluorescence intensity at $T = 90$ K.

At low temperatures, the initial part of the delayed fluorescence decay kinetics is described by a power law, $I \sim t^{-n}$, and the longer part, by an exponential. Within the temperature region where the luminescence intensity remains constant, the decay kinetics also practically does not vary. At the temperatures corresponding to the rise of the delayed fluorescence, the exponential part of the kinetics falls off, to practically disappear when the luminescence intensity reaches a maximum. The exponent n for the initial part of the decay curve grows with temperature. At the temperature corresponding to the maximum delayed fluorescence intensity the value of n is close to 2.

It is known that increasing the temperature intensifies the intra- and intermolecular processes giving rise to nonradiative destruction of the triplet centers. If the nonradiative quenching process was prevailing, one would observe the delayed fluorescence to decrease both in duration and in intensity of luminescence. We see, however, that as a film is heated, the luminescence increases to reach a maximum intensity at a certain temperature. To interpret these data, one has to assume that the T_1 levels of aromatic molecules in the Langmuir–Blodgett films have a scatter in energy. At low temperatures, the migrating exciton is captured by the traps with lower 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 in the migration efficiency results, in its turn, in an increase in the number of triplet pair annihilation events, which becomes manifest in an enhancement of the delayed fluorescence intensity. The drop of the luminescence intensity after a certain critical temperature has been reached is associated with the nonradiative triplet-center decay channels becoming dominant with increasing temperature.

The temperature dependence of the delayed annihilation fluorescence intensity can be used to derive the triplet level energy dispersion. For the temperature interval where the delayed annihilation fluorescence intensity is observed to grow under inhomogeneous triplet-level broadening, one can write

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

where I_0 is the delayed fluorescence intensity at $T = 90$ K, and ΔE is the triplet level dispersion. Figure 2 plots the relations from which the values of ΔE were obtained for the samples under study. The dispersion in energy of the triplet levels of anthracene, 1,2-benzanthracene,

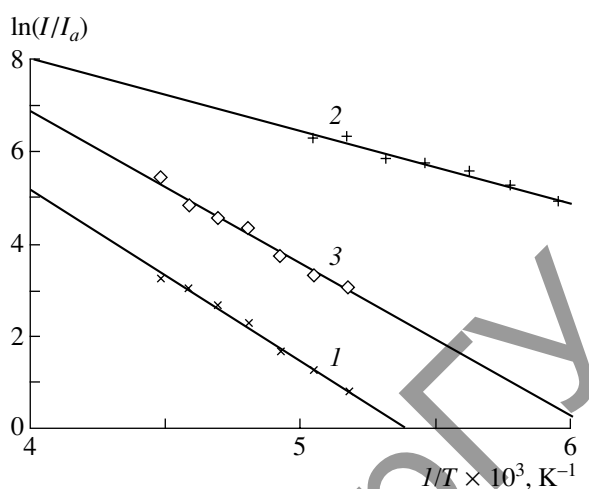


Fig. 2. Determination of the inhomogeneous broadening of the triplet levels. I —delayed luminescence intensity as a function of temperature; I_a —same quantity at $T = 90$ K. (1) anthracene, (2) 1,2-benzanthracene, (3) fluoranthene.

and fluoranthene in Langmuir–Blodgett films was found to be 518, 270, and 470 cm^{-1} , respectively. The data obtained are close in magnitude to the inhomogeneous broadening of the triplet levels of benzophenone in polymethyl methacrylate ($\Delta E = 450 \text{ cm}^{-1}$) and of benzaldehyde in solid ethanol ($\Delta E = 490 \text{ cm}^{-1}$) [5, 6].

These results give us grounds to maintain that the triplet levels of aromatic molecules in Langmuir films exhibit inhomogeneous broadening. This results in the triplet exciton migration efficiency becoming dependent on the film temperature.

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