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INFLUENCE OF TEMPERATURE AND MAGNETIC FIELDS ON INTER LAYERS AND INTRA LAYER ANNIHILATION OF THE TRIPLET CENTRES IN NANOSCALE FILMS OF COUMARIN DYE

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The influence of temperature and magnetic field on delayed fluorescence of mixed Langmuir films of molecules 7-decyloxy-3 (4'-ethoxyphenyl)-coumarin and palimitic acid is investigated. In this films consist of microcrystals and clusters with non-crystalline structure. The annihilation is stipulated by interaction of molecules of different layers and most effective occurred at low temperatures at registration time till the 0.5 ms.

Keywords: delayed fluorescence, mixed Langmuir films, microcrystals, clusters, magnetic field.

At the present time, in connection with the development of nanotechnology, interest has intensified in photoprocesses nanodisperse medium. In small spatial regions such systems can form non-traditional modes of transport for molecular reactions. The reaction of spin-selective triplet-triplet annihilation (TTA), which runs on the exchange-resonance mechanism at distances of 1-10 nm between the reactants, and the modulation of its velocity by the magnetic field can be used as a sensitive tool for probing the structural features of the nanostructures and specific contact partners reaction in the dispersed systems of nanometer scale.

This paper presents the results of an experimental study of delayed luminescence properties of Langmuir-Blodgett (LB) films 7-decyloxy-3 (4'-ethoxyphenyl)-coumarin (coumarin dye). Structural formula of coumarin dye shown in Figure 1. Mixed thin films were prepared by the Langmuir-Blodgett technology. Concentration of the dye molecules in the obtained films is equal to 75 mol% relative to palimitic acid. The films are prepared by the method of vertical lift on solid substrates of nonluminescent quartz. The films were obtained with the number of layers 2 and 1. 1- layer film is a monolayer, obtained by the Z-type, 2- layer film obtained by the Y-type.

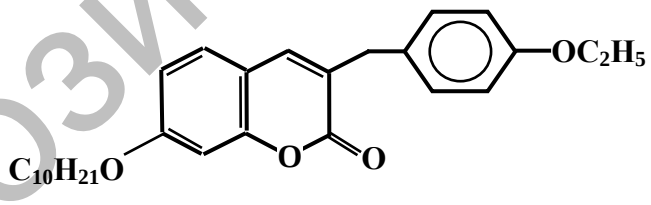

Fig. 1 – Structural formulas of the amphiphilic coumarin dye

A photoexcitation of the samples use a laser LCS-DTL-374QT with the generation wavelength of 355 nm, the energy of 5 μJ at a pulse duration τ=7 ns. Measurements are made with apparatus for the influence of magnetic field study on kinetics of delayed luminescence with registration in the photon-counting regime. A recording part of apparatus consist of a gated photomultiplier tube modules H7680, amplifier-discriminator C8744, photon counting board M8784. Registration is performed after 10 μs after excitation of the samples. At each time interval summing up signal of electronic pulses from the photomultiplier. A satisfactory signals are summed signal is not less than 500 excitation pulses. A signal of the kinetics usually is the accumulation of 1000 pulses. The temperature of sample was varied in the range T = 100-280 K, the external magnetic field - in the range H = 0-0,47 T. For measurements at different temperatures, the sample was placed in an evacuated optical cryostat. Temperature is controlleded out using differential copper-constantan thermocouple.

The value of magnetic field effect (MFE) is estimated by the relative change in the intensity of delayed fluorescence in the magnetic field (MF) and the absence of field of the formula:

$$g(B) = \frac{I_{MF} - I_0}{I_0} * 100\%, \quad (1)$$

where, I_{MF} intensity of delayed fluorescence (DF) in the field and I_0 - intensity of DF without field.

The photoexcitation LB films coumarin dye at T = 100 K was observed for a long luminescence spectrally identical to the normal fluorescence band of the film. Maximum of spectrum is at 460 nm. The results of previous studies have shown that delayed fluorescence can be attributed to the annihilation delayed fluorescence (ADF) [1].

The DF kinetics (λ = 460 nm) measured at different temperatures. All kinetics curve are characterized by nonexponential form in the entire range of measurements. Numerous experiments with mixed LB films of aromatic molecules and fatty kinetics of triplet-triplet annihilation shown a good approximation for the initial part of kinetic curve (up to 0.5 ms) in the classical model according to the dependence of the form $I_{DF} \sim t^n$ and for long-term part of kinetics over 0,5 ms by the percolation model in the process of random walks [2, 3].

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The fast component is approximated by the power function. In the chosen temperature range power factor *n* is in the range from 0,3 to 1,0 (Figure 2).). For the 1-layer film power factor varies from 0.3 to 1.0 when the temperature changes from 110 K to 220 K (Table 1). For a 2-layer film index *n* ranges from 0.6 to 1.0 when the temperature changes from 100 K to 220 K, and at low temperatures up to 180 K, the following law: the exponent n for the single-layer film 2 times less than for 2-layer. With increasing temperature indicators are aligned and at 220 K, they are approximately equal to 1.

The temperature dependence of the kinetic curve by percolation model shows that the curve can be divided into two components - the initial part of the curve with the time of registration to 100 microseconds and a portion of the curve with the time of registration of more than 100 ms (Figure 3). The change in temperature has little effect on the parameter h of the initial part of the curve, the value is normalized 0.42 ± 0.10. This is true both for the 1-layer film, and for 2-layer film. Parameter h long-term part of the kinetic curve depends on temperature and it varies from 0.5 to 0.83 by the temperature changes from 110 K to 220 K for 1-layer film and from 0.55 to 1 for 2-layer film in this temperature range. When the temperature increases further the long-term part of the kinetic curve practically disappears. Increasing the parameter h with increasing temperature indicates a random walk of the electronic excitation in a locally inhomogeneous medium.

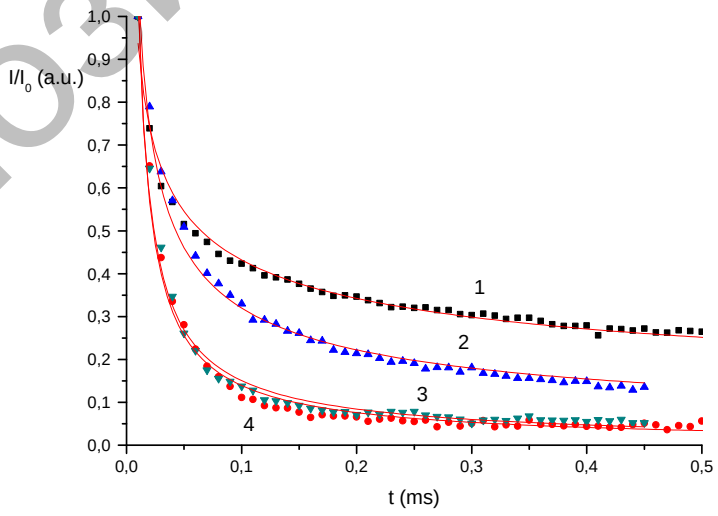

Fig. 2. Description of the initial part of the kinetic decay curve ADF LB films of coumarin by a power function: a) 1-layer LB film of 1 - T = 100 K, n = 0,40, 2 - T = 220 K, n = 0,86, b) 2 -layer LB film of 3 -

T = 100 K, n = 0,40, 4 - T = 150 K, n = 0,86

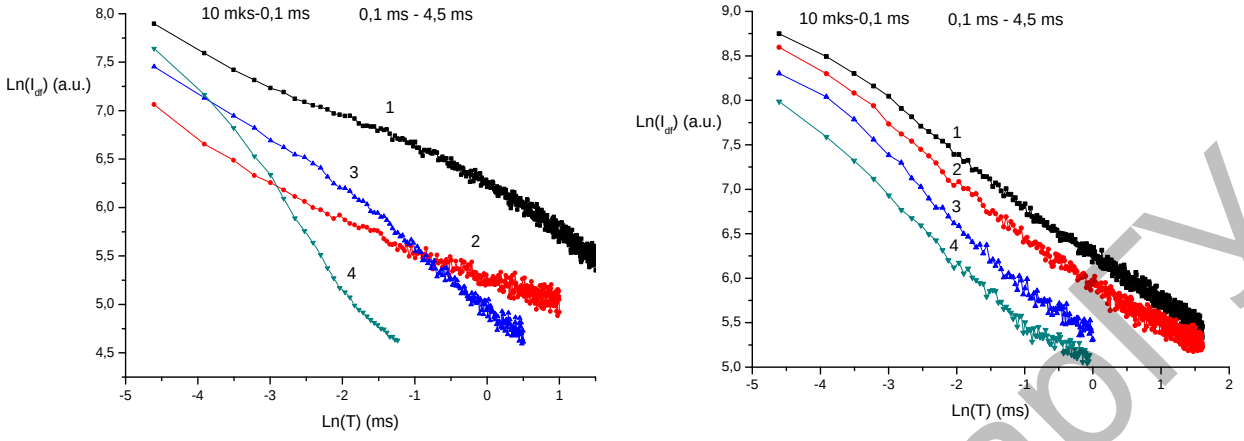

Fig. 3. The treatment of the kinetic curve for LB films of coumarin by percolation model: a) 1-layer LB film: 1 – T = 100 K, n = 0,40, 2 – T = 150 K, n = 0,86, 3 – T = 180 K, n = 0,41, 4 –T = 230 K, n = 0.76. b) 2-layers LB film: 1 – T = 100 K, n = 0.40, 2 – T = 150 K, n = 0.86, 3 – T = 180 K, n = 0.41 , 4 –T = 230 K, n = 0.76

Table 1. The calculated values of parameters n and h for a 1- layer and 2-layer LB films at different temperatures

T, K	100	110	120	130	140	150	160	170	180	190	200	210	220
1- layer LB films													
n		0.32	0.36	0.38	0.38	0.44	0.40	0.49	0.56	0.82	0.92	0.97	1.01
h		0.51	0.52	-	0.26	0.29	0.34	0.45	0.55	0.84	0.88	0.83	0.83
2-layers LB films													
n	0.64	0.67	0.69	0.69	0.64	0.70	0.75	0.81	0.80	0.92	1.01	1.00	1.09
h	0.55	0.53	0.52	0.47	0.46	0.54	0.67	0.64	0.58	0.92	1.07	0.97	-

The presence, two sections of the kinetic curve with different values of h indicates the presence of clusters in the films of coumarin molecules with different structures. In the time interval from 0 to 0.1 ms form of kinetic curve is determined by migration of triplet excitations in clusters with "crystalline" structure. Long-term part of the kinetics curve is formed as a result of the annihilation of triplets in percolation clusters with a higher local in homogeneity. A large change in *n* as compared with the change of *h* for a 1- layer and 2-layer films is described. The interlayer annihilation gives a greater contribution to the initial part of kinetic curve, compared with the long part of the kinetic curve.

Figure 4 shows the temperature dependence of intensity of the annihilation-type delayed fluorescence of Langmuir films of coumarin in different periods of registration. Measurement of the emission intensity is carried out after 10 μs. The curve of the intensity of ADF of temperature dependence for the 1 - and 2-layer film has two peaks. The first maximum occurs at T = 115 K, and the second at T = 220 K. For a 1-layer and 2-layer films was some differences in the magnitude of intensity peaks at 220 K. For a 1-layer film have higher growth intensity of ADF the compared to a 2-layer film.

From the temperature dependence of the ADF can determine the dispersion of the triplet levels. If the intensity of the ADF is increase in same temperature range, and this fact is explaining of inhomogeneous broadening of the of the triplet levels (IB), then we can write:

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

where I_0 - intensity of the DF at T = 100 K, I_{DF} - subsequent intensity values AZF, and ΔE the variance of the triplet levels.

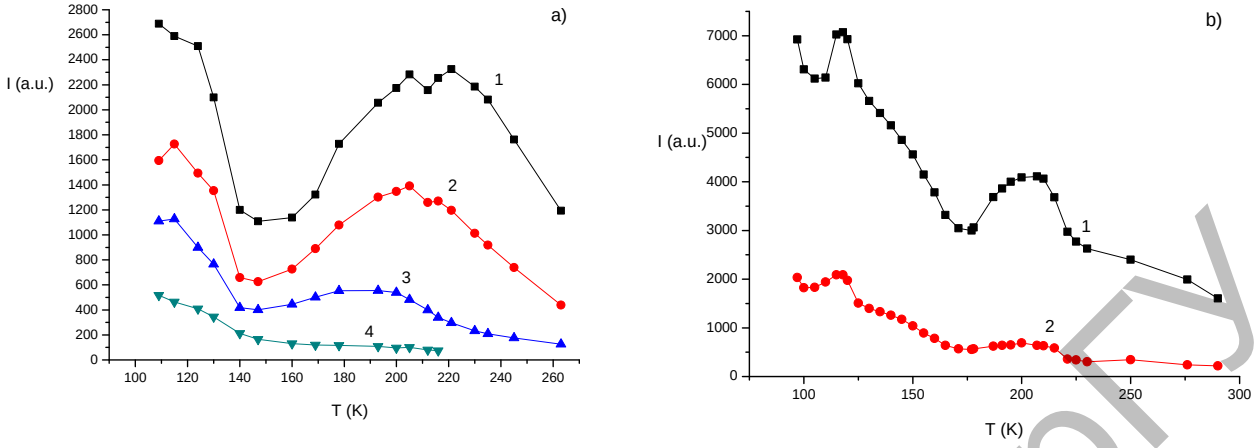

Fig. 4. Dependence of the delayed fluorescence intensity of Langmuir-Blodgett films of coumarine dye on the temperature at different time delay after initiation of registration: a) 1-layer LB film: 1 – 10 μs, 2 – 50 μs, 3 – 0,1 ms, 4 – 1 ms; b) 2-layers LB film: 1 – 10 μs, 2 – 0,1 ms

Figure 5 shows the dependence of which is determined by the value ΔE for the 1-layer and 2-layer LB films. From these results, it follows that the dispersion of the triplet levels for clusters of 1-layer LB film is ΔE_{115K} = 511 cm^{-1}, ΔE_{220K} = 370 cm^{-1}, and for clusters of 2-layer ΔE_{115K} = 176 cm^{-1}, ΔE_{220K} = 296 cm^{-1}.

The data obtained suggest that in films there are clusters with different structures. And the maximum at 115 K can be attributed to the clusters with "crystal" structure, and the maximum at 220 K can be attributed to the percolation clusters. The variance of the energy levels of the percolation clusters of 1-layer film and a 2-layer do not differ significantly. This suggests similar rates of local heterogeneity of both films. For clusters with a "crystal" structure of the dispersion of the triplet energy levels are significantly different. The variance of the 1-layer film is much larger than for 2-layer. This fact indicates that the variance of the T-energy levels of these clusters is a big contribution is nearby monolayer.

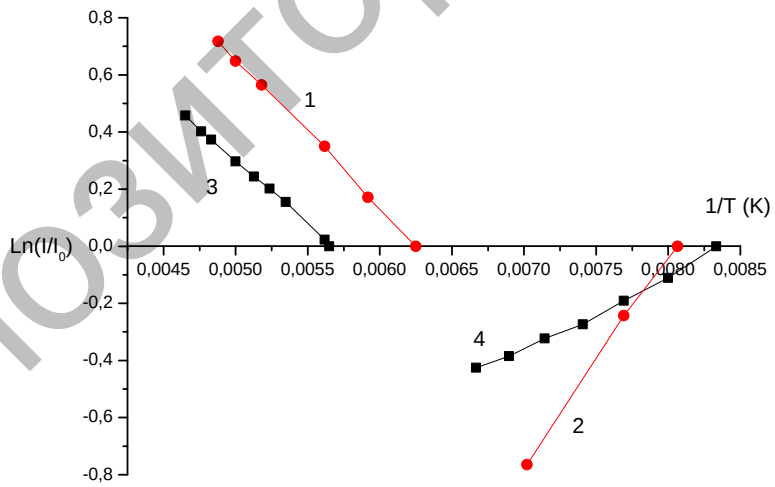

Fig. 5. Calculation of activation energy for the inhomogeneous broadening of energy levels: 1 – 1-layer LB film T_{max} = 220 K, 2 – 1-layer LB film T_{max} = 115 K, 3 – 2-layers LB film T_{max} = 220 K, 4 – 2-layers LB film T_{max} = 115 K

Investigation of the influence of magnetic field on the kinetics of ADF LB films was carried out at different temperatures. The magnetic field was directed along the tangent to the surface of the substrate along its short side. Evaluation of the magnetic effect was performed by measuring the "instantaneous" intensity across different time intervals after excitation. Figure 6 shows the curves of the magnetic effect for a 1-layer film at different temperatures registration. To all registered temperatures observed independence of the

magnetic effect on the time of registration. At low temperatures, the curve of light intensity on the field is not observed positive peak at low values of magnetic induction. With increasing temperature, the plots appear positive magnetic effect at 160 K. It reaches a value of about 3%.

The form of the magnetic effect changes qualitatively for a 2-layer film. The dependence of value on the time and temperature during registration is observed. Figure 7 shows the most characteristic curves of the magnetic effect. At 100 K at the initial stage of registration is a large quantity of a positive effect, which reaches 10%. With increasing magnetic induction is a transition to negative values of the ME, which does not exceed 3%. With increasing time of registration of the maximum positive effect at 0.1 T is significantly reduced. At the time of registration of more than 1 ms get negative ME. The ME at 0.47 T does not change the value. With increasing temperature to 120 K, the dependence of ME on the induction of the field is varies considerably. There is a decrease positive ME and increases the negative effect to a value of 12%. With increasing time of registration is a smooth decrease in positive effect. At time of registration of about 2.5 ms, it becomes negative. Measurements of the ME at higher temperatures show the dependence similar to the curves of figure 7 (b).

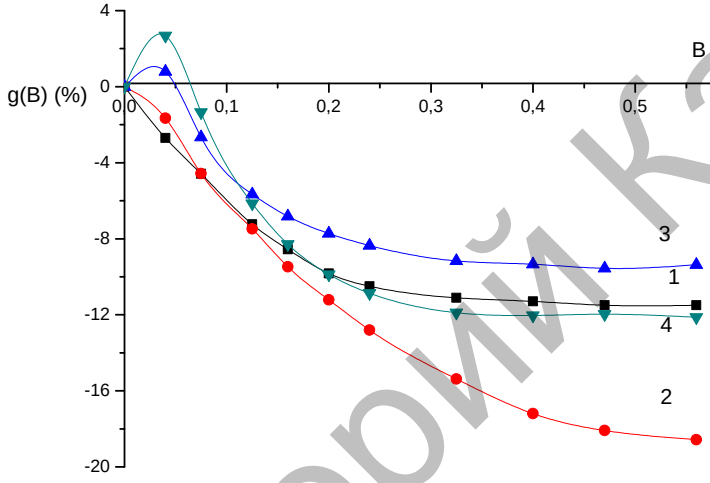

Fig. 6. Effect of magnetic field on the annihilation-type delayed fluorescence of the 1-layer Langmuir-Blodgett films of coumarin dye at various temperatures: 1 - 100 K, 2 - 115 K, 3 - 130 K, 2 - 160 K

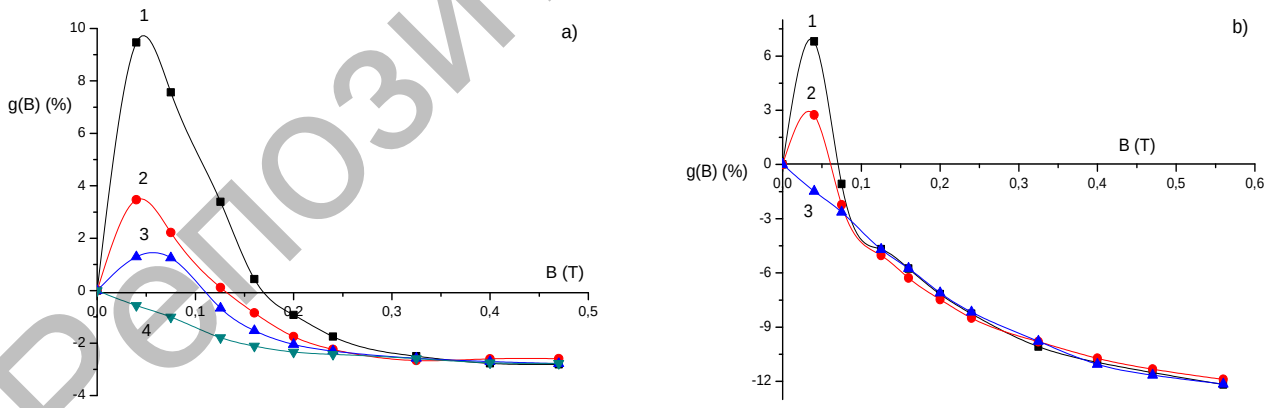

Fig.7. Effect of magnetic field on the annihilation-type delayed fluorescence of the 1-layer Langmuir-Blodgett films of coumarin dye at different times of registration and at various temperatures: a) T=100 K: 1 – 10 μs; 2 – 0,1 ms; 3 – 0,5 ms; 4 – 1 ms, b) T=120 K: 1 – 10 μs; 2 – 0,5 ms, 3 – 2,5 ms

A distinctive feature of this invistigation is the high value of the ME for a positive 2-layer film at a temperature close to liquid nitrogen temperature. One of the most credible explanation for this fact is the great influence of the intermolecular magnetic dipole-dipole interaction on the parameters of the zero-field splitting tensor (ZFS). Since the effect of high positive ME observed for 2-layer film, we can say that the intermolecular dipole-dipole interaction due to the interaction of molecules with different molecular layers of

the film. In [5] carried out theoretical invistigation influence of dipole-dipole interaction on the magnetic effect. The consequence of this effect is the shift of the curve ME up on the ordinate and the displacement of points of intersection with the horizontal axis toward larger values magnetic induction. Our experimental studies quite reliably described within this model. Additional measurements made when the angular relationships between ZFS tensor and magnetic induction vector, showed that the measurements were performed in the absence of resonance and a high positive ME for 2-layer film at 100 K observed for other magnetic field orientations with respect to the ZFS tensor .

Thus, the results of studies can describe some conclusions. In the resulting LB films of coumarin dyes exist clusters with a quasicrystalline structure and the associated percolation clusters. Comparison of kinetic data, temperature and magnetic measurements for 1- layer and 2-layer films shows that the processes of the interlayer annihilation occurs mainly at the initial part of the kinetic curve, and the further temporary registration is intralayer migration of triplet energy.

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