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Influence of magnetic field on delayed fluorescence of coumarin dye in Langmuir–Blodgett films

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ABSTRACT

The triplet–triplet annihilation (TTA) was studied in mixed Langmuir–Blodgett films of 7-decyloxy-3 (4′-ethoxyphenyl)-coumarin molecules and palmitic acid. The thermal activation of the TTA process is observed due to the inhomogeneous broadening of triplet energy levels. Modulation of the TTA rate constant in the external magnetic field for the multilayer films shows the dependence that is characteristic of crystals. Only negative magnetic effect is observed for the monolayers. Time dependence of the magnetic effect in conditions of high rate constant of triplet excitons migration is connected with the dominating contribution of ordered clusters or randomly oriented molecule clusters into the TTA process.

1. Introduction

Triplet–triplet annihilation (TTA) has been studied well enough in molecular crystals, liquids and amorphous materials [1,2]. TTA is the main channel of deactivation of triplet states with high concentrations of excited particles. TTA may have a significant impact on the efficiency of solar energy converters [3,4], electrophosphorescence light-emitting devices [5,6]. Therefore, it is important to study the features of TTA in thin organic films.

The effect of magnetic field on the annihilation of excitons migration and diffusely moving triplet molecules in crystals and liquids have been investigated and discussed in the works of Merrifield, Suna, Atkins and Evans [7–9]. These works prove the presence of the magnetic-field modulation of electroluminescence in organic light-emitting devices [10–12]. The influence of structural disorder in thin films on the properties of TTA is accounted in [13]. Considering the magnetic modulation of the annihilation fluorescence of the model system, the authors, based on Merrifield's model, have obtained expressions to estimate the overall annihilation probability.

The annihilation of triplet excitons in the mixed Langmuir–Blodgett (LB) films of non-amphiphilic aromatic molecules, such as anthracene and stearic acid, was studied in [14,15]. The observed nonexponential decay kinetics of the annihilation delayed fluorescence (ADF) is well described by a combination of formal-kinetic [16] and percolation [17] models. It has been suggested that the LB films of aromatic molecules are heterogeneous in the structure and consist of microcrystals and clusters with a disordered structure. The temperature studies [18,19] have shown the dispersion of the molecules' triplet levels due to non-homogenous film structure, which has its effect on the efficiency of triplet excitons migration. The research in magnetic fields [19,20] has revealed differences in the magnetic effect depending on the number of layers, temperature and time of signal detection of the annihilation delayed fluorescence.

This Letter presents the results of a research of the magnetic field effect and temperature on TTA in solid LB films of amphiphilic coumarin dye. In contrast to the films of aromatic molecules, in LB films of coumarin dye anisotropy of light absorption is observed. This is evidence of the dominating spatial molecules orientation in the monolayer. The specificity of triplet exciton wandering in the ordered structure of LB coumarin dye may be close to the dynamics of exciton migration in molecular crystals. This should lead to a magnetic effect characteristic of crystals and anisotropy of the of magnetic field effect on the ADF intensity. However, the received LB films would not be expected to strictly correspond to two-dimensional crystals, also they will demonstrate a structural disorder. In this case, a temperature dependence of ADF and magnetic effects corresponding to locally inhomogeneous structures should be expected.

2. Experiment procedure

Mixed thin films obtained by the LB technology, consisting of molecules of palmitic acid and amphiphilic coumarin dye (7-decyloxy-3 (4′-ethoxyphenyl)-coumarin) have been used as the research objects.

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Solid mixed film coumarin dye and palmitic acid were obtained by the Langmuir–Blodgett method [21]. Monomolecular films were formed on the surface of water/air in a Langmuir trough. Bidistilled deionized water was used as the subphase. Pure water was received with the help of the AquaMax 360 Basic Series water treatment system. The specific resistance of the water was 18.2 MΩ/cm. The surface tension of the water was 72.8 mN/m at pH = 5.6 and at the temperature of 17 °C. A two-component solution of the dye and palmitic acid in chloroform were spread onto the water subphase. The isotherms of monolayers compression were measured at the temperature of 20 °C. The monolayers were transferred to a substrate of nonluminescent quartz by the vertical method according to the X (monolayer) and Y types (2 and 10 layers) at the pressures of π_{tr} = 30 mN/m and the plate speed through the monolayer of 0.02 mm/s. The film consists of 1, 2 and 10 monolayers. Concentration of the dye molecules in the obtained films is equal to 33 mol% relative to the palmitic acid. The average coefficient of the monolayer transfer onto a solid substrate was equal to k_{tr} = 0.94.

Photoexcitation of the samples was effected by the third harmonic of a neodymium laser LCS-DTL-374-QT (λ = 355 nm, τ = 7 ns, E = 5 μJ). Registration of spectral–kinetic characteristics was carried out in a photon counting mode. Measurements of the intensity (I) emission were performed in 0.01 ms after the excitation of samples. At each time interval the signal of electronic pulses from the photomultiplier was summed up. A satisfactory signal is of not less than 500 excitation pulses, on average accumulation of 1000 pulses was done. The temperature of the samples varied in the range of T = 90–300 K, the external magnetic field varied in the range of H = 0–0.72 T. To do measurements at different temperatures, the sample was placed in an evacuated optical cryostat. The temperature was controlled by using differential copper-constantan thermocouple.

The value of magnetic field effect was estimated by relative change in the intensity of delayed fluorescence in the magnetic field and in the absence of the field by following equation:

$$g(B) = \frac{I_B - I_0}{I_0} \times 100\% \quad (1)$$

where I_B and I_0 is the intensity of delayed fluorescence in the field and without the field, respectively.

In carrying out magnetic measurements, the following procedure was used: at a given value of the magnetic field induction the repeated measurements of the signal from 5 to 7 times were carried out, then the signal was summarized and then, the dispersion of values was calculated. Furthermore, the Student's criterion was used. The error of measurement defined in this way is 2%.

To determine the dependence of $g(B)$ based on the LB film, measurements of the magnetic effect (ME) were made by rotating the substrate relative to the magnetic induction vector. Initially, the magnetic lines of force have been directed in parallel to the substrate plane φ = 0°. Furthermore, the rotation of the substrate around the axis in the center of the substrate with respect to the lines of force by reaching the angle $\varphi \rightarrow \pm 90°$ was carried out (Figure 1).

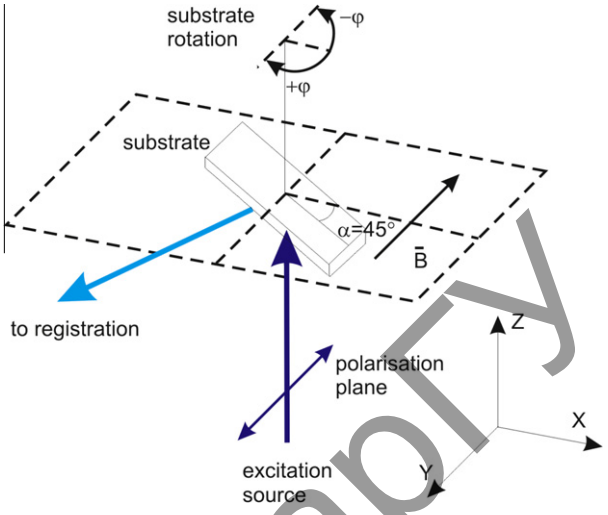

Figure 1. Layout of a quartz substrate with a dye film relative to the magnetic induction vector in measurements of magnetic effect by rotating the substrate.

3. Results and discussion

3.1. The phase state of monolayers at the water–air interface

The value of the monolayer surface pressure (π) dependence on the molecular area (A) were measured to study the phase state of monolayers on the water surface. π–A isotherms of palmitic acid and coumarin dye monolayers and their mixtures are shown in Figure 2. In the inset of Figure 2 is shown structural formula of a 7-decyloxy-3 (4′-ethoxyphenyl)-coumarin. Extrapolation to zero surface pressure the area per molecule for palmitic acids is found to be about 0.22 nm^2 (curve 1) and it represents a typical compression isotherm of palmitic acids [22]. The isotherm of pure dye (curve 3) shows that a monolayer of amphiphilic coumarin is liquid. At the pressure close to the collapse pressure (π = 28–32 mN/m) the monolayer becomes more condensed with the specific molecular area of A = 0.28 ± 0.05 nm^2. This value is close to the calculated value A_{calc} = 0.34 nm^2, when a plane of a molecule fragment, consisting of a benzene ring and the group OC_2H_5 (ethoxyphenyl part) is parallel to the water surface, and the molecule remainder is oriented in the gas phase at a certain angle. The value A_{calc} was estimated from the geometric dimensions (including the Van der Waals' radius of atoms) of coumarin dye molecule into the vacuum by molecular mechanics method (MM2).

The isotherm of the mixed monolayer (curve 2) is similar in shape to dye isotherm. However, it is characterized by lower values of the area per molecule within the monolayer. Estimation of molecular area by extrapolating the isotherm of the mixed monolayer at zero pressure yields $A \approx 0.25$ nm^2. The value obtained indicates the formation of close-packed monolayer at the interface, which retains the same orientation of the luminophore molecule as in individual monolayer of coumarin dye.

3.2. Absorption and fluorescence spectra

The absorption and fluorescence spectra of coumarin dye in ethanol with concentration of 10^{-5} mol/l (curves 1, 3) and in LB film with the dye concentration C = 33 mol% (curves 2–4) are shown in Figure 3a. The Figure 3a shows that the absorption spectrum of an ethanol solution of the dye contains two peaks at 240 and 345 nm. In the absorption spectra of LB film there are also two absorption maxima. In the spectrum of LB film the long-wavelength peak is hypochromic shifted at 25 nm, and the short-wavelength peak is not changed significantly. The fluorescence spectrum of the solution has a maximum at 445 nm. The maximum of the fluorescence spectrum of LB film is shifted to short-wavelengths at 20 nm. The obtained absorption and fluorescence spectra are identical to the coumarin dye spectral data of related chemicals compounds [23,24].

3.3. The orientation of dye molecules on the substrate surface

Measurements of the polarization of the absorption band and quantum-chemical calculations were carried out to establish the

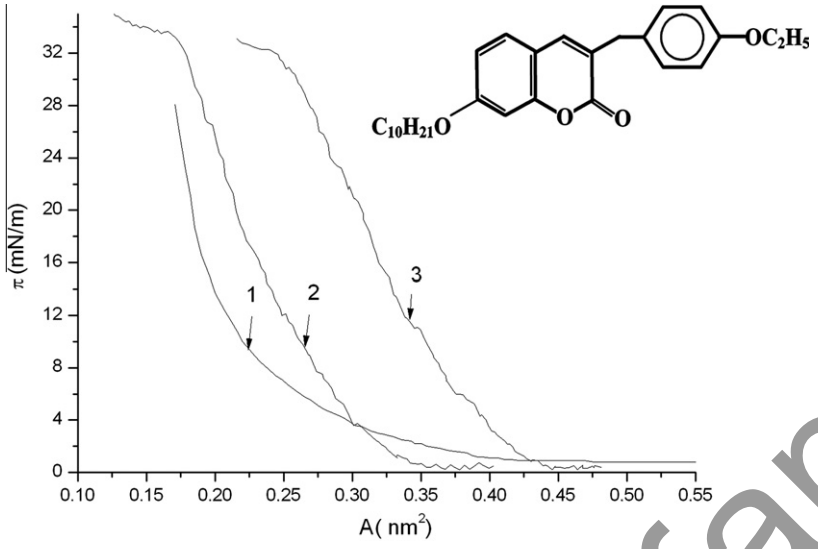

Figure 2. Isotherms of monolayers compression: 1 – palmitic acid, 2 – coumarin dye: palmitic acid (33:67 mol%), 3 – coumarin dye. Structural formula of amphiphilic coumarin dye inserted.

spatial geometry of the dye molecules in the monolayer on the substrate surface. Optimization of the geometry of the dye molecule in the force field MM + showed that the atoms of the coumarin nucleus and etoxyphenyl part are located in one plane and have no significant deviations from this plane. Calculation of energy levels of the ground and excited electronic states of transition dipole moments of the dye molecule was performed in the approximation of Pariser–Parr–People, taking into account the configuration interactions. The obtained values of the energies of the lower excited singlet $E_S = 3.51$ eV (352 nm) and the triplet state $E_T = 2.35$ eV (528 nm) do agree with the experimental result. The value of S–T splitting has a low value of the $E_{S-T} = 1.16$ eV, which agrees well with data on S–T splitting given for oxygen molecules [25]. Variation of the torsion angle between the coumarin nucleus of the molecule and its etoxyphenyl part leads to minor changes in the value of singlet energy level and major changes in the value of the triplet level T_1.

The dipole moments of transitions and the values of the basic spectroscopic characteristics of electron transitions, obtained from the calculation are given in Table 1.

From the calculations it follows that the electronic transition from the ground state to the first excited singlet state ($S_0 \rightarrow S_1$) is polarized along the molecular *X*-axis. Changes in the orientation of the substrate with a layer of LB relative to linearly polarized light showed that the optical density of the absorption at a wavelength of 350 nm has maximum value at the location of the *X*-axis perpendicular to the plane of the substrate. The layout of the coumarin dye and palmitic acid molecules in the LB layer is shown schematically in Figure 4.

3.4. Annihilation delayed fluorescence

When the coumarin dye LB films was excited by laser pulses at $T = 100$ K both delayed luminescence ($\lambda_{max} = 460$ nm) and phosphorescence ($\lambda_{max} = 530$ nm) were observed. Phosphorescence with a maximum at 540–550 nm was observed for 4-methyl 3-phenyl coumarin dye in the work [23].

The observed delayed fluorescence is resulted from annihilation of migrating triplet excitons:

$$T_1 + T_1 \rightarrow S_1 + S_0 \rightarrow 2S_0 + h\nu_{DF} \quad (2)$$

The observed annihilation delayed fluorescence **(ADF)** occurs for deoxygated ethanol solutions of dye as well.

Decay kinetics of ADF of LB film has a non-exponential form (Figure 3b). In the chosen temperature range the initial part of kinetic curves ($t < 0.5$ ms) is approximated by exponential function, and the long-term – by the exponent. For single-layer film the power coefficient n varies from 0.3 to 1.0 in the temperature range 100–220 K. For the two-layer film index *n* changes in the range from 0.6 to 1.0 at the same temperature range. The lifetime calculated from the exponential decay kinetics of ADF equal to 2.91, 2.88, 2.63 ms for 1, 2 and 10-layer films, respectively (Figure 3b, curve 1, 2, 3, respectively). Lifetime of a phosphorescence is equal to 12 ms (Figure 3b, curve 4).

The energy spread of T-levels in the LB films is founded in [15,18]. It occurs due to the different environments of the triplet molecules. The broadening of the triplet energy levels requires thermal activation of triplet exciton migration and is manifested in the temperature dependence of the intensity of ADF. The dependence of the ADF (curves 1–3) and phosphorescence (curve 4) coumarin dye of LB films on temperature is shown in Figure 5a. Intensity of phosphorescence decreases exponentially with the increase in the temperature.

Temperature dependence of the intensity ADF for all films has two peaks. The first maximum is at the interval $T = 115$–125 K, while the second is at $T = 200$–220 K. Some difference in the size and shape of the intensity maxima is observed at different intervals. The presence of two maxima in the temperature dependence

Table 1
Transition dipole moments and spectroscopic characteristics of the electronic transitions of coumarin dye.

Transition dipole moments			$\bar{\nu}$, cm^{-1}	λ, nm	F	Transition $S_0 \rightarrow S_n$
M_x	M_y	M_z				
1.660	0.254	0.0	28 442	351.597	0.870	$S_0 \rightarrow S_1$
0.720	0.086	0.0	42 369	236.024	0.242	$S_0 \rightarrow S_5$

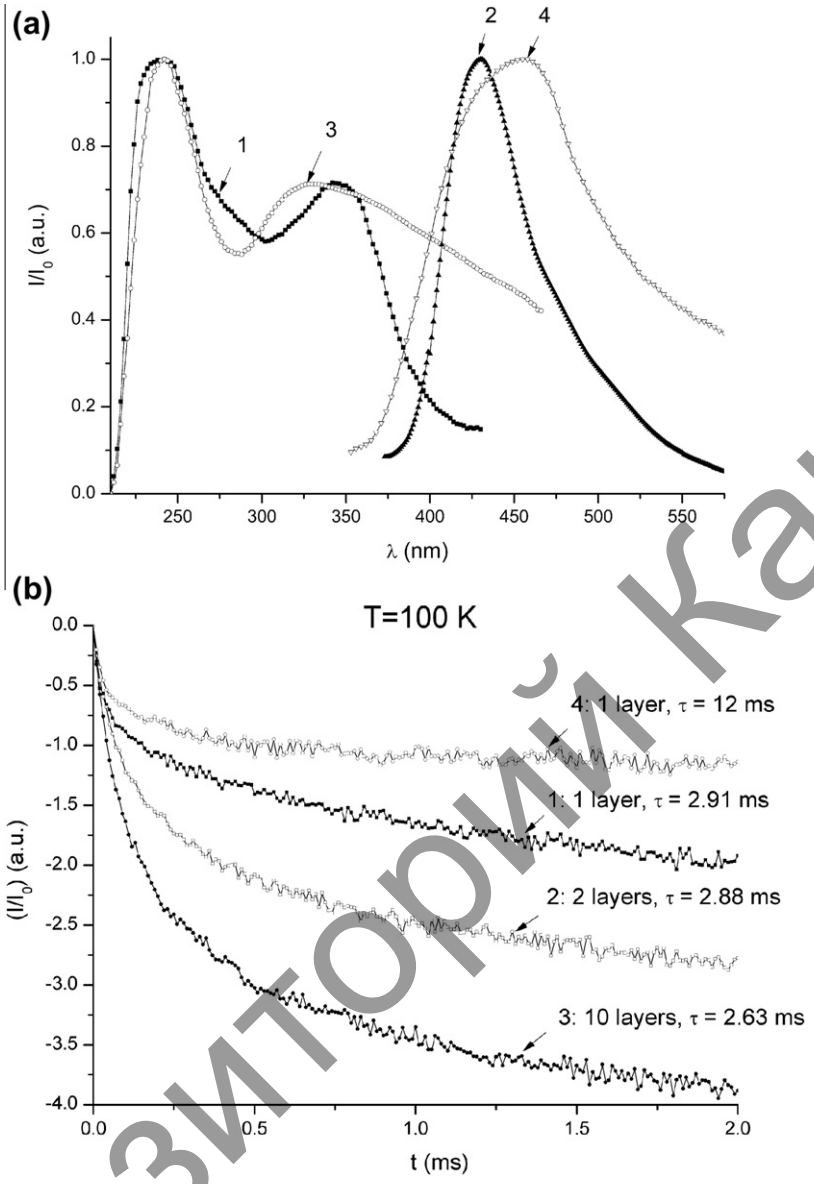

Figure 3. (a) The absorption (1,3) and fluorescence (2,4) spectra of coumarin dye in ethanol (1,2) and LB film (3,4). The concentration of the dye in ethanol – 10^{-5} mol/l in the LB film – 33 mol%. (b) Decay kinetics of ADF (1–3) and phosphorescence (4) of coumarin LB films, T = 100 K.

of ADF indicates the existence in the films of two types of traps of triplet energy with different depth.

Investigation of the effect of the magnetic field (MF) on the kinetics of ADF of coumarin LB films was carried out at different temperatures. Determination of the magnetic effects $g(B)$ was carried out by measuring the light intensity in different time intervals after excitation.

The dependence of $g(B)$ on the substrate plane rotation angle φ relative to magnetic induction vector $\dot{B}$ is shown in Figure 6. The resulted dependence is different from the analogous dependence for crystals, such as anthracene [7], but has a similar dependence with the crystal p-terphenyl [26].

The curves of the magnetic effect for LB films at 100 K are shown in Figure 7a. Type of dependence of $g(B)$ on the magnetic field B for 2 and 10 layer films is about the same (curves 2,3) and is characteristic of crystals [7]. The maximum value of the positive effect is in the range of 10–15%, and negative −2–4%. Magnitude of the positive magnetic effect decreases with decreasing number of layers. Negative magnetic effect is observed only for single-layer film (curve 1). The maximum value is 12%.

According to the work of [13] the large value of a positive magnetic effect for the 10 layer film shows a higher order of its structure in comparison with the two layer film. The absence of a positive magnetic effect for the monolayer films shows that structure is presented in the larger disorder than the multilayered films.

The magnetic effect varies with the increase in the temperature. The time dependence is observed for values of $g(B)$. Magnetic dependences at film temperature T = 120 K are shown in Figure 7b. The magnetic dependence form is preserved for 2 and 10 layer films at t = 0.01 ms (curves 2,5) for T = 100 K. But at the same time the decrease in the positive effect and growth of negative values of $g(B)$ occurs. The single-layer film magnitude of the magnetic effect increases to 18% (curve 1).

The type of magnetic dependence changes at estimation of $g(B)$ on the long-term part (t = 1 ms) of ADF kinetics. Only negative magnetic effect is observed for all films (curves 1,3,5). At varying registration time in the range from 0.01 to 1 ms curves having an intermediate position between the curves 2–3 and 4–5 are observed. The similar time dependence magnetic effect was observed for LB films of aromatic molecules [20].

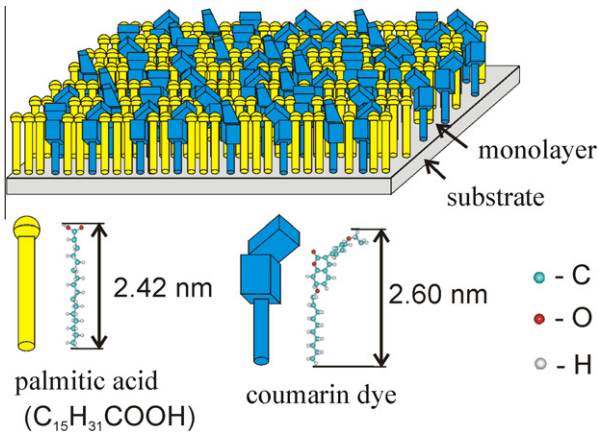

Figure 4. Schematic representation of monolayer LB films.

The resulted time dependence of the magnetic effect suggests that the coumarin dye LB films consist of ordered clusters and clusters with randomly oriented molecules. In ordered clusters TTA proceeds similar to triplet annihilation in crystals. They give the largest contribution to the intensity of ADF at initial moments of time after excitation. The randomly oriented molecules clusters give the dominant contribution to the kinetics of ADF at t_{reg} = 1 ms.

Temperature dependence of the magnetic effect for 2 and 10 layer films under weak and strong fields are shown in Figure 5b. By comparing the temperature dependence on the intensity of ADF and the magnetic effect shows that the correlation exists between them. At T = 120 K, the efficiency of exciton migration is much increased compare to the temperature of the film T = 100 K. The migrating exciton attends more T-centers during the lifetime of the triplet state. This leads to enhancement of the annihilation process in clusters with randomly oriented molecules and the shift of the curve of the magnetic effect down the Y-axis. It was expected that at the second temperature peak, when ejection of excitons from deeper traps occurred, the curve of the magnetic effect moves further down. However, as seen in Figure 5b, the $g(B)$ curve is shifted upwards relative to the curve for T = 120 K.

The resulting temperature dependence of magnetic effect is consistent with the results of [26], according to which the temperature shifts of the magnetic effect curve is associated with redistribution of the ratio between the triplet–singlet or triplet–quintet pair states for the time of the trapped exciton.

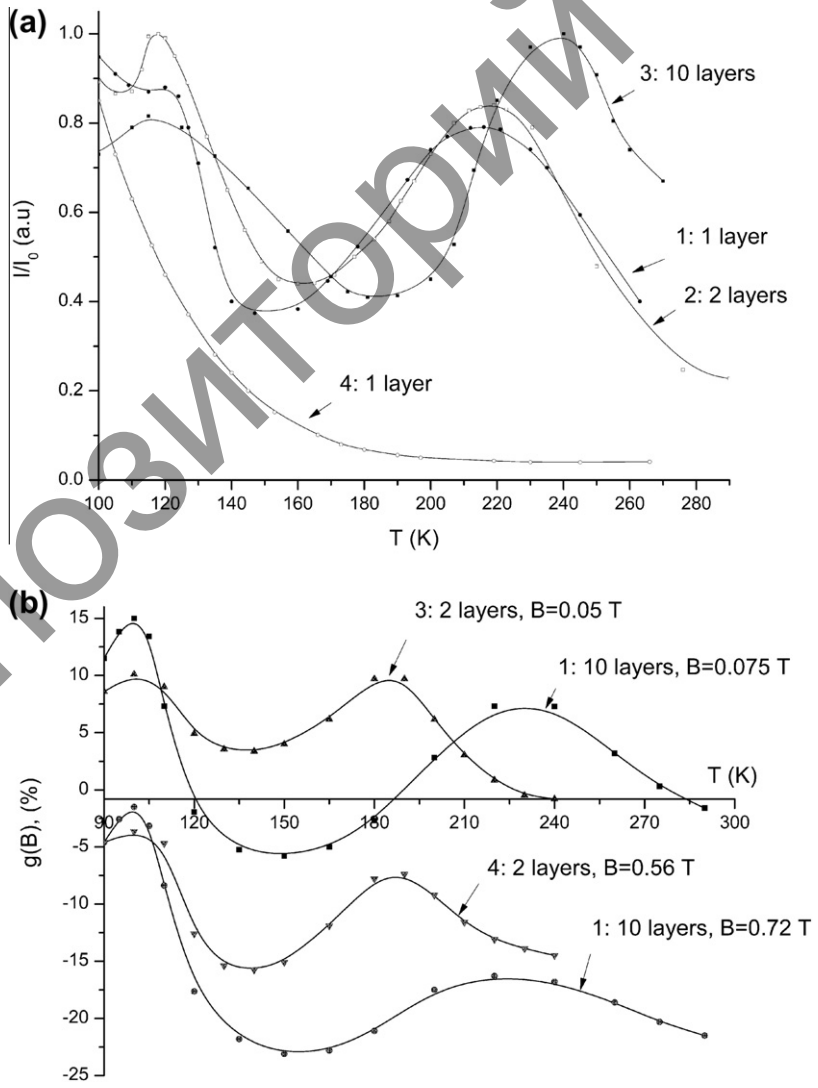

Figure 5. (a) The dependence of intensity of ADF (1–3) and phosphorescence (4) of coumarin LB films on the temperature. (b) The dependence of the magnetic effect on the temperature.

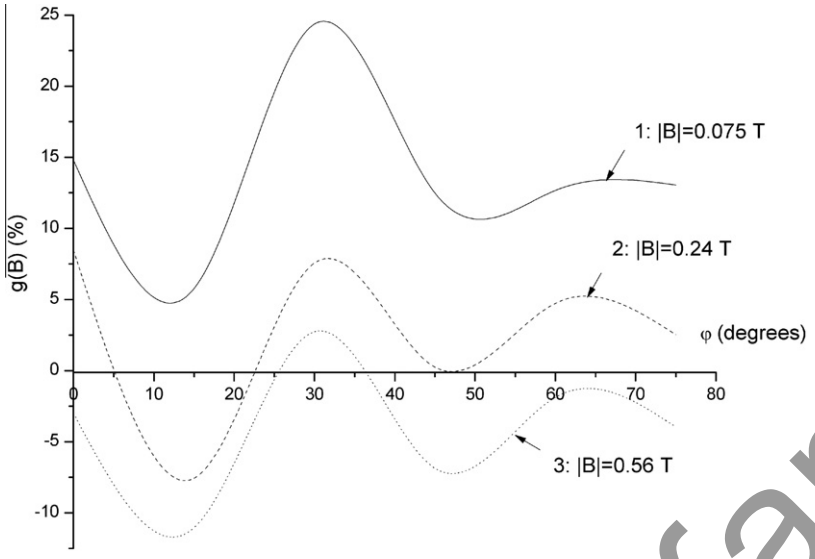

Figure 6. Anisotropy dependence of ADF magnetic field at $T = 100$ K.

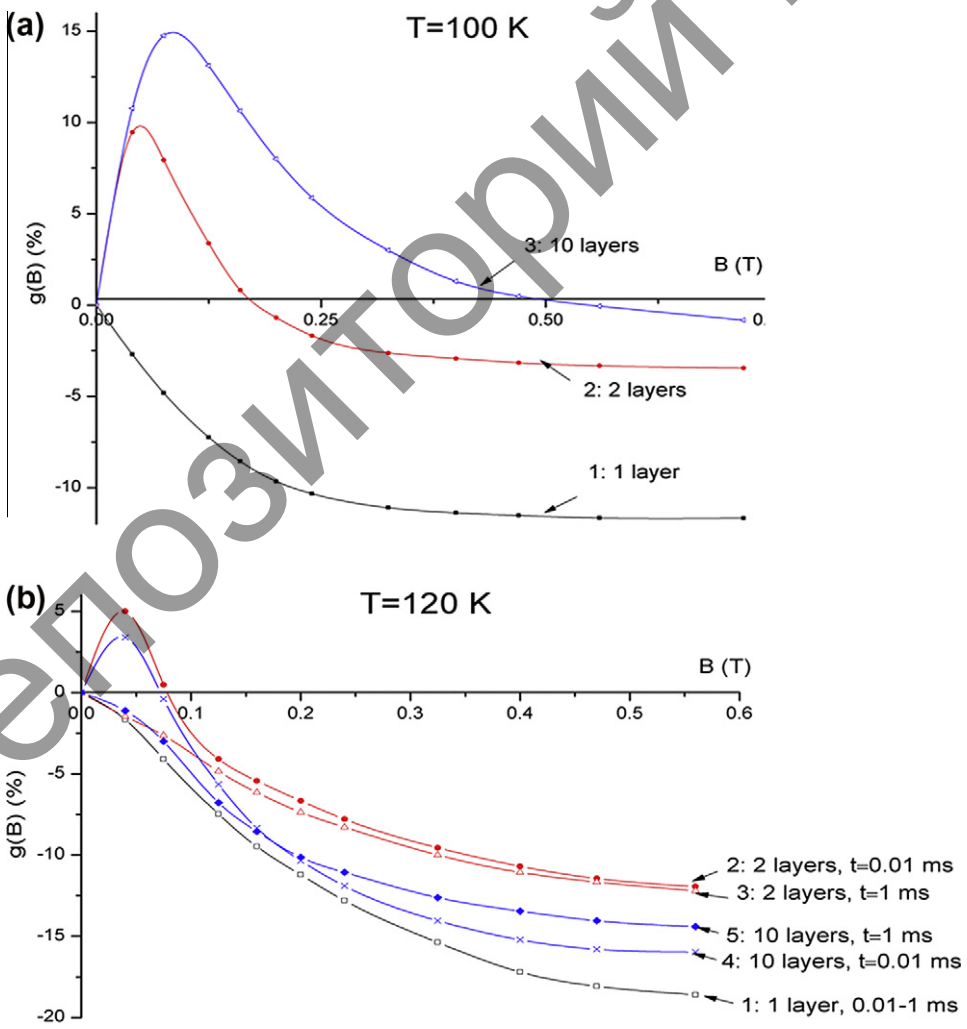

Figure 7. (a) Effect of the magnetic field on the ADF coumarin dye LB films at the temperature of 100 K. (b) Time dependence of the magnetic effect.

4. Conclusions

Our results demonstrate that TTA process is the one way of deactivation of T_1 centers in Langmuir–Blodgett films of the coumarin dye. TTA is the intra-layer and inter-layer process. The existing of the inhomogeneity of the films leads to the existence two types of structures with different values of the inhomogeneous broadening of triplet energy levels. TTA process realized in these structures with different thermal activation energy.

Modulation of the TTA rate constant by the external magnetic field at $T = 100$ K for multilayer films shows the dependence as for crystals. Monolayers shows only the negative magnetic effect. The large magnitude of the positive magnetic effect shows a higher order structure for the 10 layer film compared to the two layer film. The absence of a positive magnetic effect for the monolayer films shows that structure is present in the largest disorder.

Changing the magnetic effect occurs with increasing temperature for the multilayer films. The dependence of $g(B)$ from the time of registration ADF signal was observed. When the signal was recorded up to 0.5 ms, the magnetic effect remains positive but decreases in magnitude. At the time of registration of more than 0.5 ms the positive part of the magnetic effect is absent. It becomes completely negative.

The resulting time dependence of the magnetic effect indicates that the coumarin dye LB films consist of clusters of ordered and chaotic distribution of molecules. In clusters with ordered molecules TTA triplet annihilation is similar to triplet annihilation in crystalline environments. The triplet annihilation in these clusters gives the largest contribution to the intensity of the ADF at the initial moments after excitation. The dominant contribution to the kinetics of ADF give clusters with a disordered distribution of molecules when $t_{reg} \geqslant 0.5$ ms.

The temperature dependence of $g(B)$ correlates with the temperature dependence of the ADF intensity. This fact is additional evidence of the important role of thermal activation of triplet excitons migration in the clusters with the orderly and chaotic distribution of molecules.

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