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CONDENSED-MATTER SPECTROSCOPY

Kinetics of Photoreactions with Participation of Molecular Oxygen in Langmuir–Blodgett Films

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Abstract—The influence of molecular oxygen on the luminescence of organic molecules (dyes and aromatic hydrocarbons) in Langmuir–Blodgett films is studied. Experimental luminescence kinetics curves are compared with theoretical curves calculated in terms of different mathematical models. It is shown that the best agreement with experiment is achieved using a model that takes into account the frontal diffusion of excited oxygen molecules to the interphase surface.

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INTRODUCTION

Processes occurring near interphase boundaries and in heterophase systems comprise a promising scientific field due to the development of nanotechnologies and heterogeneous catalysis and the wide application of dispersed systems. The kinetics of reactions involving electronically excited molecules forming on the surfaces of solid adsorbents considerably differs from the kinetics of the same reactions in bulk phases. The differences are related to the lower dimensionality of the system and its heterogeneity. At present, the specific features of the kinetics of photoreactions in quasi-homogeneous unbounded systems have been studied in detail. Situations in which the interaction between electronically excited molecules occurs in a system with a bounded geometry, in structured media, and in near-surface layers coated with surfactants are less studied.

In this work, we study the kinetics of photoreactions occurring between organic dye molecules and mobile oxygen molecules in a polymer film deposited by the Langmuir–Blodgett (LB) technology onto a solid substrate.

The excitation of adsorbed luminophore molecules by a laser pulse beam leads to a series of elementary intramolecular transitions, after which the molecules pass to the metastable excited triplet (T) state. When O_2 molecules diffuse into the regions occupied by Tcenters, the electronic excitation energy is nonradiatively transferred from the excited triplet molecule to the O_2 molecule according to the reaction

$$T + {}^3\Sigma_g^-(O_2) \rightarrow S_0 + {}^1\Delta_g(O_2), \qquad (1)$$

with simultaneous formation of the singlet electronic state ${}^1\Delta_g(O_2)$. As a result, the dye molecule nonradiatively decays to the unexcited S_0 state. When stage (1) is completed, the formed singlet oxygen molecules may interact with other triplet centers according to the scheme

$$T + {}^1\Delta_g(O_2) \rightarrow S_1 + {}^3\Sigma_g^-(O_2), \qquad (2)$$

which results in the formation of the fluorogenic S_1 state of the dye. Therefore, the two-stage process (1), (2) is accompanied by delayed fluorescence of luminophore molecules.

In this work, the luminescence signals of adsorbents measured at different air pressures are processed and interpreted using mathematical models taking into account the specific features of oxygen migration in LB layers.

EXPERIMENTAL TECHNIQUE

Solid LB films were synthesized from dye and polymer molecules analogously to the process described in [1]. Mixed LB films were prepared based on amphiphilic polyampholyte and heptadecyl ether of rose bengal (amphiphilic analogue of rose bengal dye). Monomolecular films were formed on the water–air interface in a Langmuir tube. We used bidistilled deionized water with the specific resistance R = 18 MΩ/cm. The water surface tension was 72.8 mN/m at pH = 5.6 and a temperature of 20°C. Mixed monolayers were deposited from a 1 : 4 mixture of ethanol with chloroform. The compression isotherms of monolayers were measured at a temperature of 20°C. The monolayers were transferred as Y-type films onto nonluminescent quartz substrates by the vertical method at transfer pressure π_t = 28 mN/m and a 0.02-mm/s rate of movement of the plate through

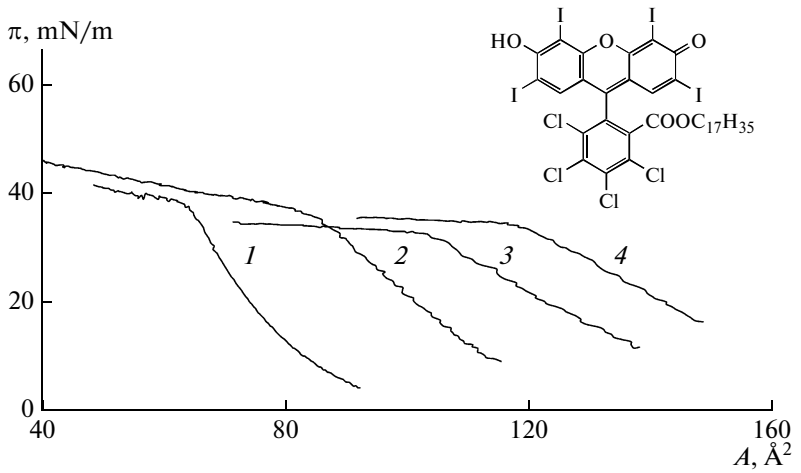

Fig. 1. Compression isotherms of (*1*) a polyampholyte layer and (*2–4*) mixed monolayers with dye-to-polymer concentration ratios of (*2*) 10 : 90, (*3*) 25 : 75, and (*4*) 50 : 50 mol %. The inset shows the structural formula of polyampholyte.

the monolayer. The dye concentration was 10 mol %, and the film thickness was equal to 20 monolayers.

The isotherms of mixed dye and polyampholyte layers differ from the isotherms of individual components (Fig. 1). The surface pressure begins to increase at lower specific areas per molecule. For a monolayer with a 10 : 90 molar ratio of the dye and polymer, the monolayer collapse pressure is 36 mN/m at the specific area 122 Å^2/molecule. For a monolayer with the molar ratio 25 : 75, the collapse pressure decreases to 34 mN/m at the specific area 155 Å^2/molecule. We may suggest that the increase in the specific area with increasing concentration of dye molecules in mixed monolayers is related to the aggregation of luminophore molecules due to van der Waals interactions.

The mixed LB films based on amphiphilic polyampholyte and 1,2-benzanthracene (1,2-BA) molecules were prepared in a similar way. The monolayers were transferred onto nonluminescent quartz substrates by the vertical method as Y-type films at transfer pressure $\pi_t = 44$ mN/m and a 0.02-mm/s rate of movement of the plate through the monolayer. The luminophore concentration was 75 mol %, and the film thickness was equal to 20 monolayers.

The spectral-kinetic characteristics of the films were measured using an automated setup in the photon counting mode [2]. The films with rose bengal molecules were photoexcited by the second harmonic of an LCS-DTL-374QT pulsed neodymium laser ($\lambda_{las} = 532$ nm, $\tau_{pulse} = 7$ ns, $E = 60$ μJ). The long-term luminescence signal was recorded in the photon counting mode by an H7680-01 photomultiplier and an M8784 Counting Board (Hamamatsu). The luminescence of 1,2-BA was excited by an ILGI-503 nitrogen laser ($\lambda_{las} = 337.1$ nm, $\tau_{pulse} = 15$ ns, $E = 60$ μJ).

The LB films were placed into a quartz vacuum cell pumped out to residual pressure $P = 10^{-5}$ mmHg. Then, the cell was controllably filled with air. The measurements were performed at room temperature.

The absorption and fluorescence spectra of rose bengal LB films are presented in Fig. 2, and their characteristics are listed in Table 1. Figure 2 shows that the absorption spectrum of the film with the dye concentration of 10 mol % consists of two bands peaking at 526 and 489 nm. An increase in the concentration leads to an increase in the optical density in both bands. Simultaneously, the wavelengths of the spectral maxima slightly shift to shorter wavelengths. With increasing concentration, the film absorption at a wavelength of 486 nm considerably increases com-

Table 1. Characteristics of the absorption and fluorescence spectra of mixed LB films of rose bengal and polyampholyte

Dye concentration, mol %	λ_{max}^{abs}, nm	$\Delta\lambda_{1/2}^{abs}$, nm	λ_{max}^{fl}, nm	$\lambda_{1/2}^{fl}$, nm	$\frac{I_{max}^{mono}}{I_{max}^{dimer}}$
10	526	74	568	59	1.29
25	520	90	575	65	1.11
50	519	96	575	55	1.06
75	517	104	576	45	1.01

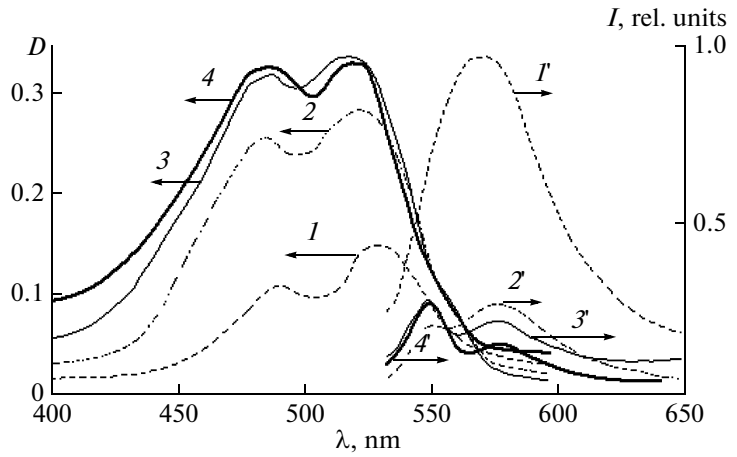

Fig. 2. (*1*–*4*) Absorption and (*1'*–*4'*) fluorescence spectra of mixed LB films of rose bengal and polyampholyte with dye concentrations of (*1*) 10, (*2*) 25, (*3*) 50, and (*4*) 75 mol %.

pared to the absorption at 526 nm. The halfwidth of the absorption spectra of films is almost twice as large as the halfwidth of the ethanol solution spectrum (Table 1).

The fluorescence spectra are insignificantly shifted to longer wavelengths and broadened compared to alcohol solutions. The most intense emission was exhibited by a film with a dye concentration of 10 mol %. An increase in the luminophore concentration leads to fluorescence quenching. It should be noted that the emission spectra of films with dye concentrations of 50 and 75 mol % consist of two bands.

The observed behavior of the absorption and fluorescence spectra testifies to molecular aggregation in the mixed LB films of rose bengal and polyampholyte.

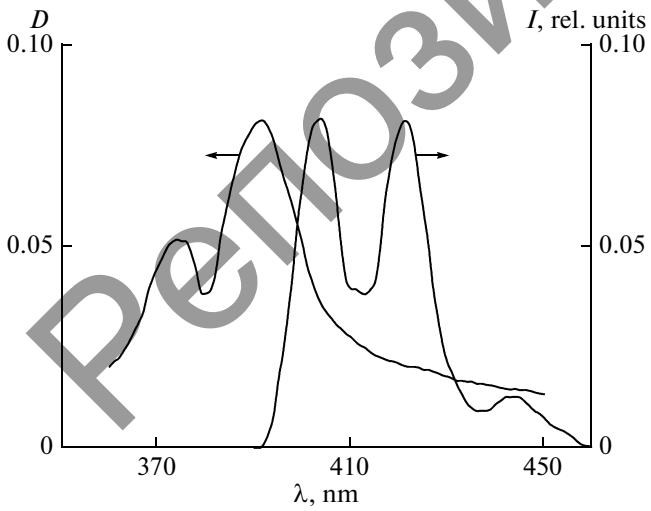

Fig. 3. Absorption and fluorescence spectra of mixed LB films of 1,2-BA and polyampholyte with a luminophore concentration of 75 mol %.

These aggregates are luminescent, which is well seen from the spectra of films with dye concentrations of 50 and 75 mol %. For experiments on the influence of oxygen, we chose films with a dye concentration of 10 mol %.

The luminophore concentration in mixed films of 1,2-BA and polyampholyte polymer was 75 mol %. Films with this concentration of luminophore exhibit intense fluorescence, and the absorption and fluorescence spectra (Fig. 3) show no aggregation at this concentration of 1.2-BA. The spectra obtained correspond to the absorption and fluorescence spectra of 1,2-BA molecules in condensed media [3].

MATHEMATICAL MODELS OF CROSS-ANNIHILATION LUMINESCENCE KINETICS

Within the formal kinetic approach, the cross annihilation of electronically excited molecules (1), (2) is described based on equations for the volume-average concentrations of triplet centers $n_T(t)$ and excited oxygen molecules $n_\Delta(t)$, which is acceptable in the case of a fast oxygen migration in the near-surface layer. Phosphorescence signal intensity $I_{ph}(t)$ is proportional to the concentration of triplet centers $n_T(t)$, while the intensity $I_{DF}(t)$ of the delayed cross-annihilation fluorescence in bilinear with respect to the $n_T(t)$ and $n_\Delta(t)$ concentrations [4, 5],

$$I_{ph}(t) \sim n_T(t), \quad I_{DF}(t) \sim n_T(t)n_\Delta(t),$$

where

$$n_T(t) = n_{T0}\exp\left[-\frac{t}{\tau_T} - 4\pi D_\Sigma r_0 n_{ox}\left(t + 2r_0\sqrt{t/\pi D_\Sigma}\right)\right], \quad (3)$$

$$n_\Delta(t) = K_\Sigma n_{ox}\int_0^t n_T(\tau) \times \exp\left[\frac{\tau - t}{\tau_\Delta} - (K_\Sigma + K_\Delta)\int_\tau^t n_T(\tau'|n_{ox})d\tau'\right]d\tau. \quad (4)$$

In these expressions, τ_T and τ_Δ are the lifetimes of the excited T and $^1\Delta_g$ states, n_{ox} is the concentration of unexcited O_2 molecules in the gas phase ($n_{ox} \gg n_\Delta$), $K_\Sigma = 4\pi D_\Sigma r_0$ is the bimolecular rate constant of energy transfer from T centers to oxygen molecules in the $^3\Sigma_g^-$ state, K_Δ is the rate constant of cross annihilation of T and $^1\Delta_g$ excitations, r_0 is the effective quenching radius of T centers, and D_Σ is the diffusion coefficient of unexcited oxygen molecules. In calculations, we take $K_\Delta = K_\Sigma$.

If a surfactant layer is characterized by a low mobility of oxygen in the direction perpendicular to the aligned molecules and the adsorption well is very shallow, then oxygen molecules may move only along the normal to the surface and attack the triplet organic molecules from the gas phase (the Eley–Riedel mechanism [6]). In this case, the concentration of excited oxygen molecules is the solution of a kinetic equation in partial derivatives and the delayed fluorescence intensity is determined not only by the product of the $n_T(t)$ and $n_\Delta(t)$ concentrations, but also by the probability $W(t-\tau)$ for an oxygen molecule to remain localized within the surfactant layer to the time moment t [5, 7],

$$I_{DF}(t) \sim n_T(t) K_\Sigma n_{ox}\int_0^t [\tilde{n}_T(\tau)/b] \times \exp\left(\frac{\tau - t}{\tau_\Delta} - (K_\Sigma + K_\Delta)\int_\tau^t n_T(\tau'|n_{ox})d\tau'\right)W(t-\tau)d\tau, \quad (5)$$

where $(W(t-\tau) = b[\pi D_\Delta(t-\tau)]^{-1/2}$, D_Δ is the singlet oxygen diffusion coefficient, b is the LB layer thickness, and $\tilde{n}_T(t)$ is the surface concentration of triplet centers.

An oxygen molecule captured by an adsorption well in the near-surface layer can move within this layer; i.e., lateral (quasi-two-dimensional) diffusion of O_2 occurs. Reactions (1) and (2) in this case obey the Langmuir–Hinshelwood kinetic scheme [6]. In the case of a very shallow adsorption well, desorption of singlet oxygen molecules can be considered as free diffusion along the normal to the surface and we return to the Eley–Riedel model. In the case of strong capture and lateral migration of oxygen molecules in the layer, the pulse shape of the cross-annihilation delayed fluorescence is determined from the integral of the pair distribution function $g_\Delta(r,t)$ of singlet oxygen over the surface with respect to the center of the local generation of the $^1\Delta_g$ excitation, i.e., with respect to the T center position before its quenching [7–9]. In this case, the experimentally recorded intensity $I_{DF}(t)$ of the cross-annihilation delayed fluorescence can be written in the form

$$I_{DF}(t) = \phi p_s K_\Delta \tilde{n}_T(t)\int_R^\infty g_\Delta(r,t)2\pi r dr. \quad (6)$$

Here,

$$g_\Delta(r,t) = \int_0^t \rho_\Delta(r|t,\tau)2bG(0,t-\tau)\left(\frac{dn_\Delta}{dt}\right)_{t=\tau}^{+} d\tau.$$

The function $\rho_\Delta(r, t-\tau)$ is the probability density of finding a $^1\Delta_g(O_2)$ excitation at instant t at distance r from the point of its creation at moment τ. This function satisfies the planar diffusion equation with the reaction term corresponding to the excitation cross annihilation [7–9]. The solution of this equation is

$$\rho_\Delta(r|t,\tau) = G_S(r,r_0|t-\tau) \times \exp\left[\frac{\tau - t}{\tau_\Delta} - \int_\tau^t \frac{4\pi D_\Delta^{(2)}}{\ln(D_\Delta^{(2)}\tau'/r_0^2)}\tilde{n}_T(\tau')d\tau'\right]. \quad (7)$$

Here, $G_S(r,r_0|t-\tau)$ is the polar Green function for the planar diffusion equation,

$$G_S(r,r_0|t) = \frac{1}{4\pi D_\Delta^{(2)} t}\exp\left(-\frac{r^2 + r_0^2}{4D_\Delta^{(2)}t}\right)I_0\left(\frac{rr_0}{2D_\Delta^{(2)}t}\right),$$

$D_\Delta^{(2)}$ is the two-dimensional diffusion coefficient of $^1\Delta_g(O_2)$ excitations in the monolayer; and $I_0(x)$ is the imaginary-argument Bessel function. The time derivative

$$\left(\frac{dn_\Delta}{dt}\right)^+ = \left[K_\Sigma^{(3)} + \frac{4\pi D_\Sigma^{(2)} kb}{\ln(D_\Sigma^{(2)}t/r_0^2)}\right]n_{ox}^{(3)}\tilde{n}_T(t) \quad (8)$$

denotes the generation rate of surface-average density n_Δ for $^1\Delta_g(O_2)$ excitations. The superscripts in parentheses indicate spatial dimensionality d of corresponding values.

DISCUSSION

Figure 4 presents the time dependence of the rose bengal phosphorescence intensity at a partial pressure of 0.01 mmHg above the sample surface, which is nonexponential at the initial stage (to 30 μs). The phosphorescence intensity calculated within the Smolukhovskii model (3) shows no satisfactory coincidence with experimental data. The best coincidence is achieved on the assumption that the LB film has a

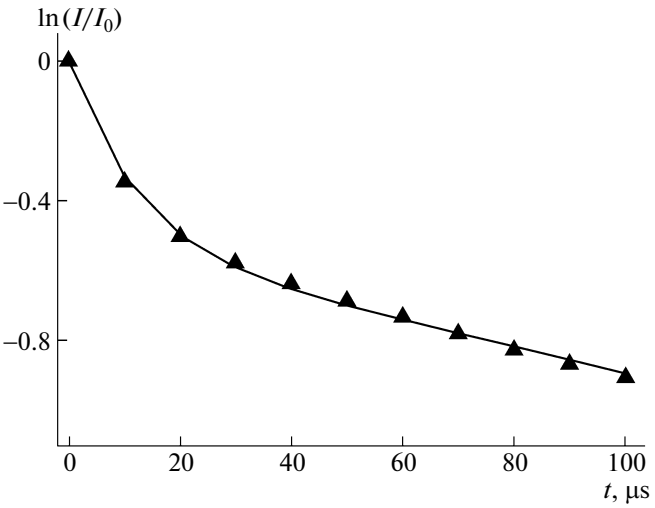

Fig. 4. Fluorescence decay kinetic of rose bengal in an LB film at an oxygen pressure of 0.01 mmHg.

microheterogeneous structure consisting of regions with different mobility for migrating quenchers, since the slowing of the phosphorescence decay with time points to the occurrence of slow relaxation processes [4]. In the case of an inhomogeneous distribution of dye molecules in the film, the phosphorescence intensity can be written in the form

$$I_{\text{ph}}(t) = I_0 \exp[-t/\tau_T]\{A\exp[-K_1(t+\sqrt{t/K_2})] + (1-A)\exp[-K_1'(t+\sqrt{t/K_2'})]\}, \quad (9)$$

where A is the fraction of dye molecules falling into the region of a relatively high mobility of oxygen molecules and $K_1 = 4\pi D_1 r_0 n_{ox}$ and $K_2 = \pi D_1/4r_0^2$ are the quasi-molecular rate constant and efficiency of diffusion motions in the Smolukhovskii model, respectively. The K_1' and K_2' constants for microregions with a low mobility of oxygen molecules are determined in a similar way. The triplet state lifetime is known from

Table 2. Parameters of theoretical models providing agreement with experimental data

Models, parameters	Formal kinetic approach	Frontal diffusion model	Lateral diffusion model
K_Σ, cm^3/s	5.0×10^{-10}	4.5×10^{-10}	1.5×10^{-10}
K_Δ, cm^3/s	5.0×10^{-10}	4.5×10^{-10}	
D_Σ, cm^2/s	4.0×10^{-4}	3.6×10^{-4}	1.2×10^{-4}
D_Δ, cm^2/s	4.0×10^{-4}	3.6×10^{-4}	2.5×10^{-7}
n_{T0}, cm^{-3}	5.0×10^{14}	8×10^{13}	2.5×10^{16}
b, nm		40	40
Other parameters	$n_{ox} = 1.3 \times 10^{14}$ cm^{-3}, $\tau_T = 1000$ μs, $\tau_\Delta = 40$ μs, $r_0 = 1$ nm		

independent measurements to be 1 ms. As a result of the procedure of fitting of experimental and calculated fields, we found all the free parameters of the problem, namely, the ratio $A = 0.4$ and rate constants $K_1 = 10^5$ s^{-1}, $K_2 = 2.8 \times 10^{10}$ s^{-1}, $K_1' = 2.7 \times 10^3$ s^{-1}, and $K_2' = 7.3 \times 10^6$ s^{-1}, which ensure the best agreement of the model with experiment. Assuming the effective quenching radius of T centers r_0 to be 1 nm and using K_1 and K_2, we obtain diffusion coefficient $D_1 = 3.6 \times 10^{-4}$ cm^2/s and oxygen concentration $n_{ox} = 2.2 \times 10^{14}$ cm^{-3}. The oxygen concentration thus determined corresponds to the air pressure above the sample of 0.01 mmHg. The second pair of the constants found from the fitting procedure is $D_2 = 9 \times 10^{-8}$ cm^2/s and $n_{ox} = 2.4 \times 10^{16}$ cm^{-3}. The anomalously high concentration of oxygen molecules in the regions with a low mobility can be associated with temporary capture of O_2 molecules by structured fragments of surfactants.

Figure 5 (curve *1*) presents the experimental time dependence of the delayed fluorescence intensity for a rose bengal LB film with oxygen concentration $n_{ox} = 1.3 \times 10^{14}$ cm^{-3}. Since the signal decays for times of ~50 μs, the intensity can be theoretically described using only the first pair of K_1 and K_2 constants responsible for the fast fluorescence quenching. The time dependences of the delayed fluorescence intensity (curves *2–4*) were calculated within the above-considered mathematical models. The parameters of these models providing the best agreement between the theory and experiment are given in Table 2. Figure 5 shows that all the calculated curves describe rather well the observed shape of the luminescence pulse. However, the formal kinetic approach, which is usually used for consideration of homogeneous media, is based on the assumption on a fast motion of oxygen molecules in an LB layer, which seems hardly probable in this case because the films used in our experiments have a complex layered structure. In addition, the results of processing of the phosphorescence kinetics also testify to the existence of different regimes of oxygen migration in the layer. The oxygen diffusion coefficient in the film determined in the course of optimization has an overestimated value, which is more typical for the gas phase. Comparison of the results calculated by the lateral diffusion model with experiment shows good agreement in the case in which the diffusion coefficient of oxygen in the excited singlet state is lower than the diffusion coefficient in the ground state by approximately three orders of magnitude. This fact can be explained only on the assumption that singlet oxygen, due to its high chemical activity, can react with polyampholyte or can be captured by this polymer without formation of covalent bonds, which seems improbable. It should also be noted that the obtained diffusion coefficient of oxygen in the ground state also has an overestimated value untypical

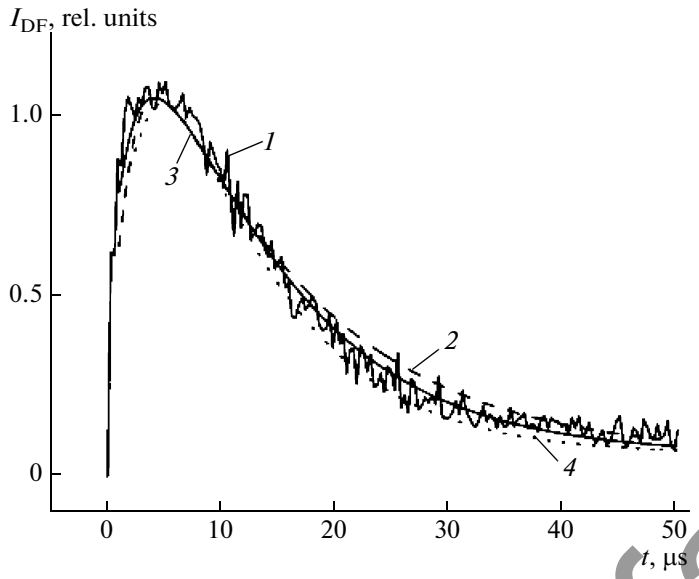

Fig. 5. Comparison of the (*1*) experimental curve of the delayed fluorescence decay of rose bengal LB films with the theoretical curves obtained within the (*2*) models of formal kinetics, (*3*) frontal oxygen diffusion, and (*4*) lateral oxygen diffusion.

for solid films. The best agreement with experiment is achieved by the model taking into account the frontal diffusion of oxygen. This model suggests that triplet centers undergo vertical attack by singlet oxygen molecules from the gas phase. Therefore, the diffusion coefficients obtained within this model can be taken to be reliable. In addition, the structure of the used LB films allows one to think that the regions most easily accessible for migrating quenchers are mainly the outer layers and the aligned polyampholyte chains form a kind of vertical channel of a sort for motion of oxygen with a rather high diffusion coefficient.

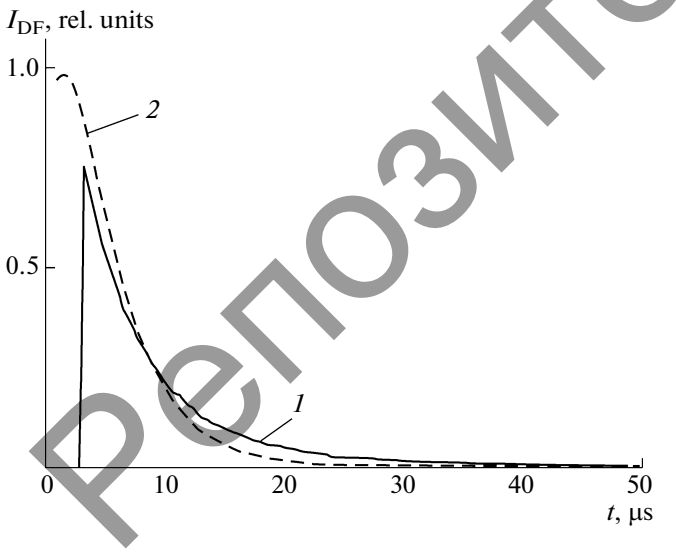

Fig. 6. Comparison of the (*1*) experimental curve of the delayed fluorescence decay of 1,2-BA LB films with the (*2*) theoretical curve obtained within the model of frontal oxygen diffusion. The model parameters are $n_{ox} = 3.0 \times 10^{18}$ cm^{-3}, $n_{T0} = 1.0 \times 10^{15}$ cm^{-3}, $D_\Delta = 5.0 \times 10^{-8}$ cm^2 s^{-1}, $\tau_T = 1200$ μs, and $K_\Sigma = K_\Delta = 6.2 \times 10^{-14}$ cm^3 s^{-1}.

The performed comparison of the theoretical calculations of the delayed fluorescence intensity with experiment for LB films with 1,2-BA also demonstrates the best agreement in the case of model with the frontal diffusion (Fig. 6).

Thus, in this work, we experimentally and theoretically studied the effect of molecular oxygen on the kinetics of phosphorescence and delayed fluorescence of the molecules of organic luminophores incorporated into polymer films deposited by LB technology. The experimental kinetic curves are compared with the theoretical curves calculated by models based on different schemes of cross-annihilation reactions (1) and (2). It is found that the best agreement with experiment for the used LB films is obtained by the model of frontal oxygen diffusion.

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