Spectral luminescent study of orientation states of dye molecules adsorbed on a nonuniform surface

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Brownian reorientation motion of molecules results in an equilibrium of orientation states of adsorbed molecules. The character of the orientation equilibrium depends on the total concentration of adsorbed molecules. Since optical properties of molecules are sensitive to the intermolecular interaction with an adsorbent, each orientation state has an individual luminescence spectrum. A change in the equilibrium results in complicated concentration and temperature dependences of the spectra of adsorbed molecules. These dependences have been experimentally observed for several dyes adsorbed on microporous silicate glass. Equilibrium constants and fractal dimensions of the spatial distribution of dye molecules in porous matrices have been determined.

Key words: dye molecules, quantum efficiency of fluorescence, emission anisotropy, statistical equilibrium, mechanical equilibrium, microporous glass, orientation states, law of mass action.

The interaction between molecules and the surface determines many physicochemical and optical properties of adsorbed substances. The study of these properties is important for understanding processes of physical adsorption and because of the wide usage of new materials, in particular, those based on finely porous silicate glass activated by organic dyes. Studies of recent years showed that the behavior of dye molecules in silicate porous matrices[1] differs significantly from that in homogeneous condensed media, for example, in solutions. In particular, a multi-atomic dye molecule in the adsorbed state nearly loses the ability of translation due to the nonuniformity of the surface and high barriers of translational motion. At the same time, a dye molecule that is localized at a certain site of the surface, can execute not only small vibrations around different local orientation quasi-equilibrium states, but also Brownian reorientation motions characterized by the threshold energy and the average time of reorientation. However, both of these values can be so significant that the molecule would be "frozen" into the matrix to be in the non-equilibrium state for a rather long time, which is often longer than the lifetime of the electron excitation of adsorbed dye molecules.

The energy of the bond between a complex multiatomic molecule and the surface depends strongly on the degree of curvature of the surface and in many cases its absolute value turns out to be maximum on the regions of high curvature.[2,3] This results in the fact that finest accessible pores are filled first when adsorbate molecules are introduced into the porous matrix. As a result of the continuous saturation of fine pores, the mean energy of the interaction between a molecule and the surface, W, begins to depend on the total concentration of molecules, N, according to a law $\overline{W} = \overline{W}(N)$, which is characterized by curves with an acute angle in the range of low concentrations and a "plateau" at high concentrations (Fig. 1). In addition, a molecule in a pore can be deformed and can have changed optical parameters.[2]

Finally, molecules in the state of physical adsorption are characterized by the lower efficiency of the energy

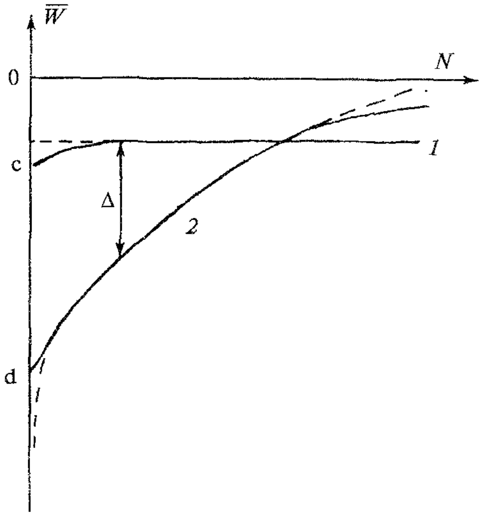

Fig. 1. Scheme of the change in the mean energy ($\overline{W}$) of the interaction between adsorbate molecules on a nonuniform surface and changes in concentration (N) for two orientation states 1 (*1*) and 2 (*2*).

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exchange with the medium than those in homogeneous media. This results in several phenomena during the optical excitation of adsorbed dye molecules: distortion of the universal ratio between absorption and fluorescence spectra;[4] a high level of intramolecular vibration excitations of electron-excited molecules during the Stokes excitation and, as a consequence, enhancement of processes of the internal and intersystem conversion;[5] abnormally weak temperature quenching of fluorescence during the anti-Stokes excitation;[6] and others. The nonradiative transfer of energy (NTE) of electron excitation over the molecule ensemble during the adsorption of dye molecules on porous glass differs from that in solutions. The fractal character of the spatial molecular distribution, which is inherent in dye molecules adsorbed on porous glass, results in basically nonlinear temperature dependences of the quantum yield and polarization of fluorescence, which can be expressed as[7]

$$\Phi = aN_A{}^{\gamma/3}, \qquad P = bN_D{}^{\gamma/3}, \tag{1}$$

in the range of relatively low concentrations. Here N_A and N_D are the concentrations of withdrawing and donating dye molecules, respectively; γ is the fractal dimension; and a and b are constants;

$$\Phi = B_0/B - 1, \quad P = r_0/r - 1,$$

where B is the quantum yield of fluorescence; r is the emission anisotropy; and B_0 and r_0 are their values at such low concentrations when NTE is absent.

The distribution of dye molecules is fractal in porous glass, which also manifests itself in the regularities of light scattering[8] and absorption[9] on activated porous glasses.

It has been established recently that a physically adsorbed complex multi-atomic molecule can have more than one position of stable equilibrium on a dielectric surface.[2,3,10] This fact is very substantial and determines the properties of a substance in the adsorbed state. Each of these positions corresponds to the orientation relative to the surface and the orientation mobility, the energy, and a set of optical parameters. The latter is caused by the fact that intermolecular forces, which differ for different orientations of an anisotropic molecule, participate in the formation of optical properties of a molecule. Thus, one can speak about different orientation states of one multi-atomic molecule on the surface of an adsorbent. Some model concepts (called the theoretical model in further discussions), which allow one to describe the distribution of dye molecules over different orientation states, and spectral effects, which are caused by the peculiarities of this distribution, are presented below.

Theoretical model

Brownian reorientation motion of adsorbate molecules can transform molecules from one discrete orientation state to another. The question about the conditions of the steady-state equilibrium of orientation states is the most important problem. Specific features of this equilibrium under conditions of the nonuniform surface are considered below.

Let us consider the case of two discrete orientation states (with indices 1 and 2). It has been mentioned that the energy of the interaction between a molecule and the surface has a wide set of values for each orientation state, depending on the surface curvature at the point of localization of the molecule. Let $\bar{W}_1$ and $\bar{W}_2$ be the averaged values of the energies (Fig. 1). The relative fraction of molecules in two states, $\sigma = N_1/N_2$, will be determined by the Boltzmann factor $G\cdot\exp(-\Delta/kT)$, where $\Delta = \bar{W}_1 - \bar{W}_2$, G is the ratio of degeneracy multiplicities of the two states (with account for all degrees of freedom of a molecule on the surface). The values $\bar{W}_1$ and $\bar{W}_2$ are the increasing functions of the total concentration

$$N = N_1 + N_2 \tag{2}$$

of adsorbed molecules. It is evident that these functions are different for different orientation states. One may expect that the degeneracy multiplicity, G, also depends on N. As a result, the multiplier σ also becomes a function of N. The N-power series expansion of the $\sigma(N)$ function results in the following equation

$$\sigma(N) = \sigma_0 + q_1N + q_2N^2 + ...,$$

where σ_0, q_1, and q_2 are coefficients of the power series. In the majority of cases of dye molecules studied, σ_0 can be considered to be fairly low value and can be neglected. In fact, at $N \to 0$ dye molecules are concentrated on the regions of the surface of high curvature at the values of the energy determined by points c and d in Fig. 1. The energies, which at least three to four times differ from one another (the corresponding estimations are given in Ref. 3), correspond to these points. This gives for $\sigma_0 < \exp(-3) \approx 0.05$. Confining to the linear term, we obtain

$$\frac{N_1}{N_2 N} = q_1, \tag{3}$$

where N_1 and N_2 are the numbers of molecules in 1 cm^3 of the substance in states 1 and 2 and q_1 is the constant.

It can be easily seen that Eq. (3) is similar to the law of mass action. In the case considered, it expresses the ratio between concentrations of adsorbed molecules in two discrete states of the steady-state equilibrium.

The q_1 value has a sense of the equilibrium constant, and the total concentration of adsorbed molecules coincides with the concentration of occupied regions of adsorption. The concentration of molecules in each state can be easily found from formulas (2) and (3)

$$N_1 = \frac{q_1 N}{1+q_1 N}N, \quad N_2 = \frac{1}{1+q_1 N}N \cdot \tag{4}$$

It can be seen that the fractions N_1/N and N_2/N are redistributed in the whole range of values (0—1) on going from low ($N < q_1^{-1}$) to high ($N > q_1^{-1}$) concentrations as N increases.

It should be mentioned that Eq. (3) is approximate and is valid only when one linear term can be used in the expansion of $\sigma(N)$ over N.

It is reasonable to assume that the equilibrium constant q_1 depends on temperature. If this dependence is presented by the classical isochore equation

$$\frac{d}{dT}(\ln q_1) = \frac{\Delta}{kT^2} ,$$

then integrating at N = const gives

$$q_1 = q_0 \exp(-\frac{\Delta}{kT}) , \tag{5}$$

where q_0 is the limiting value of q_1. Of course, the relationship

$$\frac{N_1}{N_2} = G \exp(-\frac{\Delta}{kT}) . \tag{6}$$

corresponds to Eq. (5).

Results and Discussion

The validity of the approach presented was experimentally checked by temperature and concentration dependences of parameters of fluorescence spectra of several organic dyes adsorbed on porous glass. A finely porous glass matrix was prepared by acidic treatment of samples of liquating sodium borosilicate glass of a certain composition[12] and comprised a spongy framework consisting of nearly pure silica with through pores.[12] The average diameter of pores of the matrices used was about 8 nm. Dyes (see Table 1) were introduced by diffusion from solution followed by removing the solvent by evaporation. The concentration of dye molecules in the matrix was controlled by spectrophotometry and was varied from 10^{14} to 10^{19} cm^{-3}.

There are strong grounds to believe that when there are several orientation states of adsorbed complex molecules, each of them corresponds to its own quantum yield of fluorescence. In fact, the value of the quantum yield of fluorescence is determined by several factors: rates of internal and intersystem conversion specified by intermolecular interactions; the degree of conjugation of multiple bonds in chromophore groups of molecules, whose value can be affected by the distortion of the molecular configuration during adsorption; the nonradiative energy transfer, which shortens the lifetime of a molecule and thus affects the yield and polarization of fluorescence; finally, by the direct effect of induction-resonance interactions between electron-excited and nonexcited molecules on the efficiency of processes of nonradiative energy degradation in an electron-excited molecule; and by several other factors, which depend considerably on orientations of molecules.

Table 1. Parameters of dye molecules adsorbed on porous glass (T = 293 K)

Dye	q_1/cm^3	γ	B_1	B_2
Oxazine 17	$9.5 \cdot 10^{-18}$	1.1	0.35	0.90
Coumarin 7	$3.7 \cdot 10^{-17}$	1.7	0.70	0.01
Coumarin 30	$1.2 \cdot 10^{-16}$	3.0	0.72	0
Phenalemine 160	$1.1 \cdot 10^{-16}$	3.0	0.35	0.70
Rhodamine 6G	—	1.0	0.95	

Let us consider the temperature dependence of the quantum yield (at N = const). The temperature dependence of the quantum yield of fluorescence for the population of molecules of one-type is well known: it is monotonic and is approximately described by the Mott formula:

$$B = [1 + F \exp(-\frac{Q}{kT})]^{-1} ,$$

where F and Q are empirical constants. The values of these constants are sensitive to the intermolecular interaction and therefore are different for different orientation states. When two orientations coexist, the resulting quantum yield of fluorescence per molecule is determined as

$$B = \frac{B_1 N_1 + B_2 N_2}{N_1 + N_2} = \frac{B_1 \frac{N_1}{N_2} + B_2}{\frac{N_1}{N_2} + 1} . \tag{7}$$

Taking into account Eq. (6) and using the Mott formula, this results in the nonmonotonic function $B(T)$. In the cases of adsorbed cumarins, such a dependence was in fact found,[13] and it is illustrated by an example of oxazine 17 in Fig. 2. The data obtained suggest not only the existence of two orientation states of adsorbates

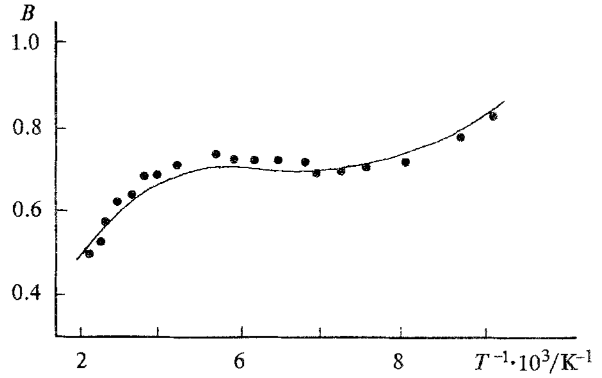

Fig. 2. Temperature (T) dependence of the quantum yield of fluorescence (B) of oxazine 17 in porous glass. Experimental points and a curve plotted from formulas (6)—(7) at fixed values of $F_1 = F_2 = 4$, $G = 2$, Q_1 = 1.67 kJ mol^{-1}, Q_2 = 8.37 kJ mol^{-1}, Δ = 1.08 kJ mol^{-1}, $N = 10^{17}$ cm^{-3}, and a wavelength of the exciting light of 582 nm are presented.

mentioned, but also the validity of the prerequisites made (formula (7)), which served as a basis for explaining the temperature redistribution of molecules between the states.

The interpretation of concentration dependences of fluorescence (at T = const) requires not only an account of the coexistence of adsorbate molecules in different orientation states, but also a combined consideration of NTE. In the case when these states are equivalent, the concentrations of withdrawing and donating molecules would be proportional to N.[14] As a result, according to Eq. (1), the quantum yield of fluorescence and emission anisotropy would change as $N^{\gamma/3}$ (Refs. 2, 3, and 10) as the concentration changes (however, it would be valid only in the range of fairly low concentrations). At high concentrations, the phenomenon is more complicated due to the direct effect of inductive-resonance interactions between electron-excited and non-excited molecules on their intramolecular parameters.[15] The existence of two orientation states results in the fact that the values of N_D and N_A depend on N in a more complicated way due to changes in the concentrations N_1 and N_2 as N changes. In fact,

$$N_D = N_1B_1 + N_2B_2 \text{ и } N_A = (N - N_D) + \alpha N_D,$$

where α is the so-called coefficient of light restitution to a donor, and N_1 and N_2 are described by formulas (4). In many cases, the dependences $\Phi(N)$ and $P(N)$ obtained experimentally in the range of moderate concentrations can be approximated by expressions similar to Eq. (1):

$$\Phi = AN^{K_\Phi},\ P = MN^{K_p}. \tag{8}$$

Plots on a logarithmic scale (Fig. 3), where curves (8) are rectified and the values of K_Φ and K_p are determined by the slopes, provide the most distinct demonstration of the possibility of this approximation. Since the parameters, which determine the run of curves (8) are analytically related to the physical parameters of the system (γ, q_1, α, B_1, and B_2,) the latter can be determined from the experimental data.

Thus, the experimental data on fluorescence spectra of dyes studied in porous glass confirms the fact that there is the equilibrium of discrete orientation states of complex multi-atomic molecules physically adsorbed on the nonuniform dielectric surface. The experimental data are in good accordance with the approximate theoretical relationships suggested in this work.

Some parameters of the systems studied, which have been obtained by the numerical estimations of the plots similar to those presented in Fig. 3, are listed in Table 1. It should be noted that rhodamine 6G is a special case: the values of K_Φ and K_p are equal for this dye. This means that they coincide with the value $\gamma/3$, and molecules of rhodamine 6G are oriented on the surface of pores of porous glass in a single way. Of course, in this case $B_1 = B_2$ and the orientation equilibrium is degenerate.

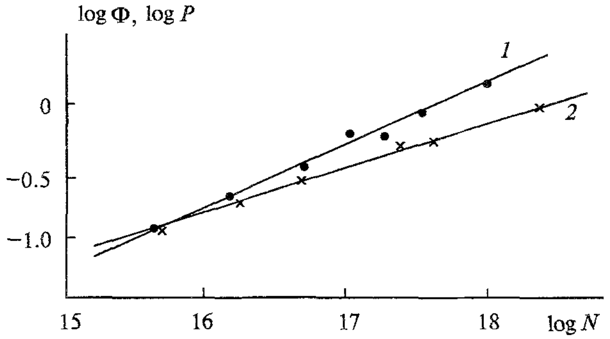

Fig. 3. Concentration (N) dependence of parameters of the quantum yield Φ (*1*) and anisotropy P (*2*) of fluorescence of oxazine 17 in porous glass on a logarithmic scale. Experimental points and straight lines with the slopes $K_\Phi = 0.42$ and $K_p = 0.33$ (T = 293 K) are presented.

It is noteworthy that fractal dimensions of the spatial distribution of molecules of various dyes in the porous matrix differ. It is likely that these differences are caused by the fact that the experimental results reflect not only the fractal structure of the population of all points of the surface of pores of the porous matrix, but rather provide the information about the peculiarities of these local regions of the surface on which molecules of one or another dye adsorb predominantly, depending on the size of molecules, their shapes, the existence of particular atomic groups, *etc.* In other words, in these experiments, different dye molecules serve as a peculiar kind of "probes", which make it possible to obtain information about the character of the spatial distribution (fractal dimension) of local regions of the surface of the porous structure depending on their properties, for example, on the local curvature of the surface.

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