Investigation of fractal properties of clusters of sorby molecules under anhygilation processes on inhomogeneous surface

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Abstract. The paper investigates the annihilation processes between the molecules of rose bengal dye, a donor of triplet energy, and the molecules of the aromatic hydrocarbon anthracene, an acceptor of triplet energy, adsorbed on the silica surface SiO₂ in the temperature range 218 ... 293, K. The rate constants of homo- and heteroannihilation of luminophore molecules in a wide temperature range are determined. It is established that the energy transfer processes in the initial (after photoexcitation) periods of phosphorescence decay are described by Inokuti-Hirayama equations, and the kinetics of phosphorescence decay becomes similar to the fractal one in the medium-time and long-time periods.

1. Introduction
General ideas about the photoprocess mechanisms in molecular systems can be obtained by studying model systems, for example, molecules of luminescent dye deposited on a solid surface [1]. The efficiency of the development of photoprocesses, including hetero- and homoannihilation, depends on the different environments of the luminescent molecules of the reagents, as well as on the interaction distance between the reagent molecules and the electron excitation energy transfer rate.

2. Statement of problem
It is necessary to study the effect of molecules distribution over an inhomogeneous surface on the nature of the photoprocesses between them and on the change in the magnitude of these kinetic parameters. Since the kinetics of photoprocesses is determined by the specific location of interacting molecules over a solid surface, by the change in the reagents concentration, and also by the change in the temperature of a matrix [2].

3. Theory
The paper investigates the kinetics of phosphorescence (PHOS) decay and delayed fluorescence (DF) of the rose bengal dye (BR) and aromatic hydrocarbon anthracene (An), respectively, sorbed on the porous surface of silicon dioxide at different concentrations of anthracene. The measurements have been performed with the help of a laser photolysis setup in the temperature range -100 °C ... 0°C. The concentration of dye molecules in the samples under study remained constant (5·10⁻⁵ mol/L), and the concentration of the An molecules varied in the range 5·10⁻⁵, mol/L ... 5·10⁻⁴, mol/L. The luminescence spectra of the samples were recorded by the method described in [3]. The BR dye was purified by recrystallization from an alcohol solution, and An was purified by zone melting. The dye molecules were sorbed from the dried alcoholic solution (C = 10⁻⁴, mol/L) to the surface of a wide porous silica (C – 80 silochromium, a powder with a grain size of 0.2 - 0.3, mm and a pore radius up to 40, nm) with addition of An dissolved in hexane. The concentration of An in the solution was C = 10⁻⁴, mol/L. Before sorption of luminophore molecules silochromium was evacuated for 30 minutes at a temperature of 120°C. At the same time, the physiosorbed water was removed from the surface to a concentration of 0.21 mol/100 Å². The process of sorption of luminophore molecules...
was performed in a vacuum cell. After sorption, before the luminescence measurements, the samples were pumped out at a temperature of +40°C for 4 h to the residual pressure in the cell of $P = 5 \times 10^{-5}$ mm Hg. Experimental studies were carried out on a laser photolysis setup: annihilation delayed fluorescence (ADF) and the dye phosphorescence were excited in the first absorption band by the second harmonic of the laser system based on the YAG:Nd$^{3+}$ crystal ($\lambda_{rad} = 532$ nm, $\tau_{0.5} = 10$ ns, pulse energy up to 50 mJ). Laser radiation at the principal frequency was filtered out by a glass light filter SZS-22, and the second-harmonic radiation was not absorbed by silochromium. The emission of ADF and phosphorescence of the adsorbates of luminophores was recorded with the help of a MS-80 diffraction monochromator and a FE′U-84 photomultiplier with an electronic gate. The time resolution of the installation is 100 ns. Low-temperature measurements were carried out in a quartz cryostat. The temperature of the sorbents varied in the range of –120°C… + 20°C and was measured with accuracy of ±2°C.

4. Results of experiments

Early studies of the kinetics of luminescence decay [4] of dye molecules (triplet energy donors) and aromatic hydrocarbons (triplet energy acceptors) on the silica surface under conditions of the electron excitation energy transfer between donors and acceptors of triplet energy made it possible to establish that the interaction of rose bengal and anthracene molecules occurs by the exchange mechanism.

The study of the effect of changes in the concentration of energy acceptor molecules on the flow of photoprocess is an important aspect in the investigation of energy transfer process in condensed media. It was established earlier that the change in the number of interacting molecules in the system is mainly characterized by the location of molecules of triplet energy acceptors near the triplet energy donors, as well as by the peculiarity of their interaction. In paper [5] the authors formulate «the problem of spheres» that helps to consider a random distribution of molecules over a solid surface. The use of the model makes it possible to consider the process of energy transfer with respect to the location of the reagent molecules on the surface. To describe the distribution behavior using «the problem of spheres» is to find the critical value of the concentrations of interacting reagent molecules in order to detect an infinite cluster formed as a result of the energy transfer process. The formation of the infinite cluster is due, first of all, to a change in the concentration of molecules deposited on the porous surface of the sorbent. With an increase in the number of so-called nodes through which the triplet energy is transferred, the probability of detecting the infinite cluster increases. Otherwise, the process of energy migration between the reagent molecules occurs through micro-clusters.

In order to study the influence of the reagent molecules environment on the photoprocess development, the rate constant of mono-deactivation of molecules of the triplet energy acceptors ($K_{An}$) at different concentrations of anthracene molecules on the surface was calculated. The graphical results are shown in Figure 1.
Figure 1. Dependence of the rate constant of mono-deactivation of anthracene molecules on the concentration of acceptor molecules on the silica surface.

As can be seen from Figure 1, the dependence $K_0$ has a minimum in the entire investigated temperature range at $C_{An}=10^{-4}$, mol/L. This concentration of acceptor molecules can be considered as critical, corresponding to the transition from the reagents distribution in the form of micro-clusters to the infinite cluster. When the acceptor concentration is less than $C_{An}=10^{-4}$, mol/L, with a decrease in the temperature of the medium, the rate constant of mono-deactivation of the triplet energy acceptor molecules decreases. In this case, the processes of electron excitation energy transfer take place in micro-clusters formed on the surface.

The analysis of the radius of the quenching sphere ($R_0/R$) (where $R_0$ is the critical energy transfer radius, $R$ is the distance between the interacting molecules) at different concentrations of the reagent molecules and the matrix temperature (Figure 2) is a confirmation of the change in the reagents distribution on the surface. The $R_0/R$ calculation was performed using the Inokuti-Hiroshima model by varying the $C/C_0$ value ($C_0$ is the initial concentration of the reagents, $C$ is the concentration of molecules in the excited state) [6].

Figure 2. Dependence of the ratio of the quenching spheres radii on the concentration of the triplet energy acceptors molecules on the silica surface.

It can be seen from the plots in Figure 2 that when the concentration of acceptors increases, the radius of the quenching sphere decreases sharply (an increase in $R_0/R$ in Figure 2) and reaches a minimum at $C_{An}=10^{-4}$, mol/L. A subsequent increase in the acceptor concentration does not lead to a change in the radius of the quenching sphere, which confirms the above assumption about the formation of the infinite cluster of sorbed molecules of rose bengal dye and anthracene on the surface of SiO$_2$.

This change in the dependence of $R_0/R$ on the concentration of anthracene molecules is due to the medium microscopic inhomogeneity that appears as a result of the clusters growth as the concentration of anthracene molecules increases [7].

That is, the concentration of electron excitation energy donor molecules remains constant, and the more efficient flow of heteroannihilation processes leads to a spatial separation of the reagents and, accordingly, to the formation of clusters of molecules of the same class [8]. Therefore, the appearance of cluster formations on an inhomogeneous surface makes it possible to determine the efficiency of electron excitation energy transfer.

5. Discussion
To determine the influence of structural features of the used materials on the kinetics of the luminescence flow we calculated the parameter of inhomogeneous medium $h$ with the help of Kopelman model at anthracene concentrations in the system $C_{An1}=10^{-4}$, mol/L, $C_{An2}=5 \times 10^{-4}$, mol/L, $C_{An3}=5 \times 10^{-5}$, mol/L. The numerical values of $h$ are presented in Table 1.

Table 1. Numerical values of the parameter of inhomogeneity of the medium depending on temperature at different concentrations of anthracene.

| $T, \text{K}^\circ$ | $h_{(\text{near})}$ | $h_{(\text{distant})}$ | $h_{(\text{near})}$ | $h_{(\text{distant})}$ | $h_{(\text{near})}$ | $h_{(\text{distant})}$ |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
|                     | $C=5 \times 10^{-5}$, mol/L | $C=10^{-4}$, mol/L | $C=5 \times 10^{-4}$, mol/L |
| 193 (-80)           | 0.56 (50…200, μs) | 2.2 (200…800, μs) | 1.27 (25…200, μs) | 4.6 (200…350, μs) |
| 213 (-60)           | 0.82 (20…50, μs)  | 0.79 (4…20, μs)  |
| 218 (-55)           | 0.83 (5…50, μs)  |
| 233 (-40)           | 1.1 (35…75, μs)  | 4.9 (75…90, μs)  | 2.5 (3…17, μs)  | 19.9 (17…19, μs) |
| 237 (-36)           | 1.14 (5…30, μs)  | 2.85 (30…45, μs) | 1 (50…85, μs)  | 1.8 (85…100, μs) |
| 253 (-20)           | 2.85 (30…45, μs) | 1 (50…85, μs)  | 1.8 (85…100, μs) |
| 259 (-14)           | 0.7 (4…14 μs)    |
| 263 (-10)           | 0.7 (4…14 μs)    |
| 265 (-8)            | 1.31 (4…20 μs)   | 1.4 (35…55 μs)  | 0.8 (55…95 μs)  | 0.54 (2…18 μs) |
| 273(0)              | 1.31 (4…20 μs)   | 1.4 (35…55 μs)  | 0.8 (55…95 μs)  | 0.54 (2…18 μs) |
| 293(20)             | 0.83 (250…450 μs) |

From the table data it follows that the studied systems are characterized by a complex dependence of $h$ on temperature. Analyzing the calculated values, we see that for the anthracene concentration $C_{An1}=5 \times 10^{-5}$, mol/L, in the low-temperature region (193, K…213, K) a sharp increase in $h$ is observed, which corresponds to processes in inhomogeneous media ($h \to 1$). In the temperature region $T = 265, \text{K}$ a drop in the decreasing direction for the parameter $h$ is observed. This fact describes the processes occurring in systems with a homogeneous distribution of the reagent molecules on the sorbent surface ($h \to 0$). With an increase in the anthracene concentration (up to the value of $C_{An2}=5 \times 10^{-4}$, mol/L) the growth of $h$ is observed in the temperature range from 232, K to 253, K. Such range of the values of the medium inhomogeneity parameter is due to the fact that with an increase in the anthracene concentration the system is transformed from a homogeneous to a heterogeneous one, in which the processes of triplet energy transfer and triplet-triplet annihilation are observed [9]. The heterogeneity of the system is also characterized by the formation of clusters consisting of molecules whose triplet excitation lifetime is determined by the size of these clusters. Therefore, the character of the change in the parameter $h$ is closely related to the values $K_i$ and $R_o/R$. 
Figure 3. Dependence of the rate constant of electron excitation energy transfer between the dye molecules and aromatic hydrocarbon on the temperature of the samples at different concentrations of anthracene.

Figure 4. Dependence of the radius of the quenching sphere on the temperature of the samples at different concentrations of aromatic hydrocarbon.

Thus, comparing the numerical data of the kinetic parameters with the value of the parameter $h$, we can find out that the condition $h \rightarrow 1$ characterizes the slowing of the kinetics in the processes of DF and PHOS. This is also confirmed by the fact that, for example, in the temperature range from 232, K to 253, K, for the anthracene concentration in the system $C_{An}=5 \times 10^{-4}$, mol/L an increase in the value of $h$ is observed, while the value of the rate constant for transfer of the triplet energy decreases [10]. By analyzing the curves describing the temperature dependence of the kinetic parameters when the
concentration of acceptors in the system changes, it is established that the shape of the curves determines the system sensitivity to rearrangements on the surface, i.e. sensitivity to the fractal dimension of clusters formed in the system.

6. Conclusion

Thus, based on the conducted research, it is established that the flow of photophysical processes in the inhomogeneous media does not obey the formal kinetic model. On a porous surface molecules are sorbed according to the «island» mechanism, which leads to a microscopically inhomogeneous distribution of adsorbed molecules. The inhomogeneity of the surface itself and the structures formed from the sorbed molecules indicates that the given system can have fractal properties. The paper shows the importance of the method described above; having applied it we analyze the deactivation process at different moments, taking into account the influence of various factors, for example, the surface temperature, which influences the diffusion of reagents. The mechanism of photoprocesses, which occurs between sorbed molecules on the surface forming homogeneous and heterogeneous structures with fractal characteristics, is determined.

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