

Variation of Fractality of Sorbed Molecule Clusters under Annihilation Processes

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Abstract – To find out the dependencies of changing rate of the interacting triplet excited molecule number on sizes of formed clusters, the analysis of change of the nonuniformity parameter connected to fractal dimension of clusters as a result of hetero-annihilation interactions is organized and presented in this paper. The analysis of experimental kinetic dependencies and the results of computer modeling have shown that the areas in which the annihilation process efficiency increases were formed on the sorbent surfaces; they had local high concentrations of reagents. Herewith, the increase of concentration of the acceptor molecules caused the change of the local surrounding of dye molecules does not lead to the growth of cluster sizes.

1. Introduction

The regularities of electron excitation dynamics in unordered systems greatly differ from similar processes in a uniform medium. This is connected with that in unordered molecular systems the rate and the efficiency of photo-physical processes are defined by geometry of support surface of the molecular systems, spatial distribution of interacting molecules, energy of the interaction of activator molecules with nearest surrounding which accidentally changes from the centre to the centre [1]. Electronic excitation energy transfer in these systems leads to the spatial division of reagents and the formation of fractal clusters. The geometry of clusters being formed will define the kinetics of the luminescence decay.

To find out the influence of cluster fractality upon kinetics of annihilation luminescence the analysis of kinetic dependencies of annihilation delayed fluorescence (ADF) and phosphorescence (Phos) of the molecules of bengal pink dye (BP) and anthracene aromatic hydrocarbon (An) sorbed on a fractal surface of wide porous silica is presented in the paper in wide temperature range from 173 to 293 K at different concentrations of anthracene. The measurements have been performed on a laser photolysis plant. The concentration of dye molecules has been remained constant ($7.4 \cdot 10^{-4}$ mol/nm²) in studying samples, the concentration of the anthracene molecules has been changed from $3.9 \cdot 10^{-1}$ mol/nm² to $3.9 \cdot 10^{-2}$ mol/nm². Proportions of the cover degree of the sorbent surface by BP and An molecules have been 1:1, 1:4, 1:40. The kinetics of luminescence of samples have been registered with the help the methods described in the work [2].

2. Results and discussion

Triplet states of dye molecules have being induced by light pulse were a donor of triplet energy concerning anthracene molecules, which triplet state generation have being realized only as a result of nonradiative triplet-triplet energy transfer. Kinetics of delayed fluorescence of anthracene and dye (Fig. 1) which was observed under mentioned above conditions qualitative differs from similar kinetic dependencies for mono-component systems [3].

Herewith ADF intensity of donor and acceptor grows on a certain time period. Time of the phosphorescence growth is distinguished for each component and it is changed at different matrix temperatures and proportions of donor and acceptor concentrations (Fig. 1).

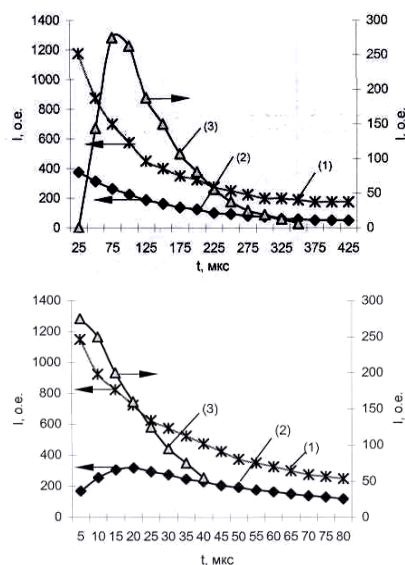


Fig. 1. The oscillogramms of BP phosphorescence decay (curve 1), BP delayed fluorescence (curve 2) and An delayed fluorescence (curve 3) at proportions of donor and acceptor concentrations 1:4 (a), 1:1 (b), and temperatures 293 K (a), 218 K (b)

The observed ADF kinetics is the result of hetero-annihilation processes, which lead to nonlinear mode of deactivation. Non-exponential character of the ADF decay (Fig. 2) and temporal dependence of the annihilation rate constant are the effect of nonlinearity of deactivation processes that leads to necessary taking into account the interparticle distribution and the topology of fractal clusters being formed.

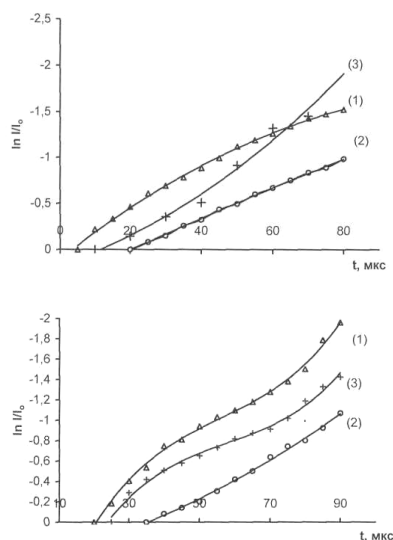


Fig. 2. The semi-logarithmic kinetics dependencies of intensity of the phosphorescence BP Phos (1), BP ADF (2), An ADF (3) on time of the luminescence: a) $T=218$ K; b) $T=253$ K; proportions of BP and An concentrations are a) 1:1, b) 1:4

For this purpose the calculation of the h_{exp} nonuniformity parameter is organized for different time periods of experimental kinetic curve. The nonuniformity parameter is related to fractal dimension (f) and Hausdorff dimension (D_0) according to the formula:

$$h = 1 - f \quad h = 1 - \frac{\ln(D_0 + 1)}{\ln(D_0 + 3)} \quad (1)$$

Calculated values of h_{exp} were compared with results of the calculation of h_{mod} which has been obtained from computer modeling of pairwise interactions in two-component systems by the probabilistic cellular automata method described in the work [4], and multifractal analysis of the reagent distributions formed at different iterations (Fig. 3). To compare the results of experiment and modeling the non-dimensional value kt was used, where k is a reaction rate constant being defined at the distant-temporal section of a kinetic curve. Adaptability of such simulation is motivated in the works [5, 6, 7].

As one can see in Fig. 3 h_{mod} and h_{exp} are weakly changed for the observation time in the all temperature range. Herewith the numerical values of h_{exp} parameter are greater than h_{mod} . Besides, h_{exp} parameter decreases while h_{mod} increases according to the reduction of the reagent concentration as a result of pairwise interactions. It is possible to suppose that observed differences of the temporal dependencies of h_{mod} and h_{exp} are related with the fact that h_{exp} unlike h_{mod} characterizes both geometric and energetic nonuniformity, connected with the variations of energy and probability of annihilation interactions in pairs for observation time. The hetero-annihilation interactions will tend to increase of geometric nonuniformity and reduction of energetic one (the curves 1 and 2 in the Fig. 3). The

energetic nonuniformity was not taken into account at the computer modeling.

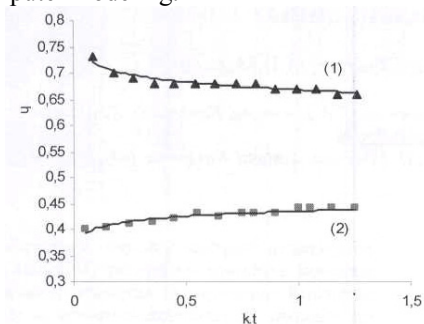


Fig. 3. The temporal dependencies of h_{exp} and h_{mod} nonuniformity parameters of the medium (curve 1, curve 2) at temperature 218 K and proportion of reagent concentration 1:1

Increase of geometric nonuniformity can be explained by making analysis of the reagent distribution at different iterations. Supposing that reagents are chaotically allocated on the surface at the initial time moment, one can note that the formation of clusters of each kind particles occurs as a result of interaction; it leads to appearance of the depleted areas on the sorbent surface. As a result, the efficiency of the interaction processes must increase in areas where clusters being localized. Herewith according to the reduction of the number of interacting reagents, sizes of the depleted areas increase, but clusters sizes do not change noticeably.

3. Conclusion

Thereby, analysis of the experimental kinetic dependencies and results of computer modeling indicate that the areas are formed with local high concentration of reagents on sorbent surface, in which the efficiency of the annihilation processes increases. Increase of the acceptor molecular concentration leading to change of the local surrounding of the dye molecules does not tend to the increase of clusters sizes.

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