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COMPUTER MODELLING AND DESCRIPTION OF STABLE MOLECULAR CLUSTER FORMATION DYNAMICS IN DISPERSION MATRIX USING MULTIFRACTAL ANALYSIS

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The paper presents the results of computer simulation of the processes of energy transfer of electronic excitation and annihilation in dispersed molecular matrices. The dispersed molecular matrices with different types of initial distribution of interacting molecules had been investigated. Multifractal analysis of the distribution of interacting molecules in the matrix under study at various time intervals of kinetic dependencies was done. It was shown the formation of stable molecular structures in the transfer of electron excitation and annihilation energy leads to a change in the generalized fractal dimensions, the order parameter, and the information entropy. The values of these parameters are influenced by the temperature of the matrix, the initial distribution of interacting molecules, the number of cluster nodes.

***Keywords**:* heteroannihilation, electronic excitation, cluster, multifractal analysis, disperse matrix, orderliness, possibility interrelation, donor-acceptor pair, transfer of electronic excitation energy, fractal dimension, order parameter.

Introduction

Investigation of the influence of the structural organization of dispersed molecular matrices on the nature of the photophysical processes taking place in them, and, first of all, the processes of electron energy transfer, is a topical task of modern condensed-state physics. As it is known, in the conditions of external influences in the exchange of the system with the environment, energy, matter and information [1] in the dispersive matrices, spatial and / or time structures are formed. The formation of molecular structures and interactions between them lead to a change in the physicochemical properties of the matrix as a whole, and, accordingly, to a change in the dynamics of the processes occurring in it and the dynamic properties of the final structures [2-5]. The changes occurring in the structure of dispersed matrices as a result of the intermolecular interactions taking place in it can be judged from the change in the kinetics of the luminescence. At the same time, an important addition to the experimental results can be the results of computer simulation and multifractal analysis, which allow obtaining numerical characteristics of the molecular structures formed in the system.

1. Methodics of modelling

When studying the dynamics of the formation of molecular structures in dispersed matrices during the transfer of electron excitation energy and annihilation, we used a surface model based on a planar square lattice measuring 500*500, representing a set of nodes and bonds. Modeling of annihilation was carried out in the temperature range of the matrix from 193K to 273K with the probability of interaction of 100% corresponding to the instantaneous reaction in donor-acceptor pairs with a size equal to one interstitial distance. The computational experiment was carried out at different degrees of surface coverage by the donor (σ1) and acceptor molecules (σ2) (from σ = σ1 = σ2 = 0.4% to σ = σ1 = σ2 = 0.8%), which allowed modeling to take into account the transfer electron excitation energy from the dono subsystem to the annihilation event.

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Investigation of the formation conditions of molecular structures was carried out at the initial cluster, chaotic and multifractal distributions of donor molecules in the simulated matrix. The concept of molecular connectivity in the theory of dynamic percolation [7, 8] is based on the model of the cluster distribution of donor molecules over the surface [6]. When generating the cluster distribution in the model proposed by us in accordance with the given degree of coverage of the modeled surface, the number of randomly distributed disjoint connected clusters was specified. The number of molecules in the cluster S (cluster size) changed from $S_{min} = 1$, which corresponded to the single-particle distribution, up to $S_{max} = 1000$ - for the degree of coverage $\sigma = 0.4\%$ and $S_{max} = 2000$ - for the coverage ratio $\sigma = 0.8\%$ corresponding to the maximum possible number of molecules in the cluster. The distribution of the acceptor molecules over the simulated surface for all types of the initial distribution of the donor molecules was given randomly.

Multifractal parametrization of structural characteristics of the investigated molecular matrix was carried out through discrete time intervals, determined by the number of iterations N [8]. The physical meaning of the concept of iteration used in the work allows us to consider iteration as a quantity proportional to time and to analyze the kinetic dependencies in conditional time units.

2. Results and discussion

The efficiency of intermolecular interaction processes in a dispersed molecular matrix depends on the fractality of molecular clusters and their mutual arrangement, which is explained by the "anomalousness", in comparison with euclide structures, of transport and annihilation processes [9-12]. The formation of molecular structures leads to a change in the intermolecular distances, the relative orientation and relative motion of the interacting molecules, and, consequently, to a change in the probability of intermolecular interactions [13] and the development of several kinetic regimes simultaneously [14]. The predominance of any of these regimes is determined by local intermolecular interactions that discourage the system from spatial uniformity. Conversely, an increase in the efficiency of transport processes with an increase in the temperature of the matrix and an increase in the number of mixed pairs of interacting molecules with a decrease in cluster size lead to a rapid destruction of fluctuations in the medium. As a result, the distribution of interacting molecules in the matrix under study can be considered to be homogeneous, and, accordingly, the kinetic dependences can be described on the basis of a simple formal-kinetic approach.

Using the method of multifractal analysis, the values of generalized Renyi fractal dimensions D_q and the order parameter Δ characterizing the changes in the structural organization of the molecular matrix and depending on the efficiency of intermolecular interactions taking place in the system are calculated in the work. A detailed analysis of the obtained values has shown that the transfer of the energy of electron excitation and hetero annihilation lead to a change in the generalized fractal dimensions. Moreover, the ordering of the entire system is violated, as evidenced by the differences in the left branches of the spectrum of the generalized fractal dimensions D_q ($q < 0$). The observed changes in the spectra of the generalized fractal dimensions in the transfer of the electron excitation and hetero annihilation energy make it possible to infer the formation of local molecular ordered structures (clusters) in matrices with initial multifractal and chaotic distributions, within which the order is preserved, but in this case the ordering of the entire system is violated, which is consistent with the literature data [15, 16].

It is established that for a cluster distribution of donor molecules, the generalized fractal dimensions remain constant throughout the time interval under consideration. Consequently, while the distribution of donor molecules retains a cluster character, the intermolecular interactions that occur on the surface do not lead to a change in the fractal properties of the matrix, and, accordingly, to a change in the parameters of inhomogeneity and ordering. For similar interactions in matrices with a single-particle distribution of the donor molecules, the generalized fractal dimensions vary linearly, and for chaotic distribution, they are graded according to a power law.

Similar regularities in the variation of generalized fractal dimensions are observed throughout the temperature range under study, for all considered values of the degree of surface coverage. It should be noted that the values of the generalized fractal dimensions depend on the number of connected nodes forming the cluster, and the sharpest change in the generalized fractal dimensions in intermolecular interactions is observed with the initial chaotic distribution of interacting molecules. Thus, the results of multifractal analysis of the distribution of interacting molecules have shown that the observed changes in the structural organization of the matrix as a result of the transfer of electron excitation energy and its annihilation depend on the nature of the initial distribution.

A similar conclusion follows also from an analysis of the values of the order parameter calculated on different time intervals of the kinetic dependencies. It is established that with a chaotic distribution of interacting molecules over the surface, the degree of ordering of the matrix is smaller than for a matrix with multifractal and cluster distributions. In this case, while the topology and dimensions of the clusters distributed over the surface formed by the donor molecules remain constant, the order parameter does not change.

The destruction of molecular clusters as a result of the transfer of the electron excitation energy through the donor subsystem and its annihilation is accompanied by a change in the order parameter. The processes of formation and destruction of molecular clusters can occur at different time intervals and depend on the nature of the initial distribution of interacting molecules. For example, in the case of the initial multifractal distribution, the formation of molecular clusters as a result of heteroannihilation is observed at a long-term region of kinetic dependences. Moreover, as follows from the results of multifractal analysis, as the spatial separation of interacting molecules as a result of the transfer of electron excitation energy and its annihilation, molecular clusters formed on the surface uniformly fill the entire simulated surface. This process is accompanied by an increase in the degree of order and the achievement of a certain constant value. The clusters formed on the surface have characteristic dimensions. The fractal dimension of such clusters remains constant, which allows us to consider them to be stable. The formation of stable fractal clusters observed in the work is consistent with the literature data [6, 8]. The time of formation of stable fractal clusters depends on the nature of the initial distribution of interacting molecules and the features of the structural organization of the molecular matrix at different time intervals.

Thus, for matrices with different types of initial distribution of interacting molecules over the surface, there are characteristic dependences of the change in the order parameter as a result of the transfer of the electron excitation energy and its annihilation.

The destruction of clusters during heteroannihilation or the formation of a random set of clusters of different sizes and topologies as a result of migration of the electron excitation energy through the donor subsystem leads to a deviation from the dependences obtained on the basis of formal-kinetic equations. This is confirmed by the obtained kinetic dependences for matrices with initial chaotic and multifractal distribution of interacting molecules, for the description of which it is necessary to use a fractal-kinetic approach that allows to take into account the topological features of matrix-forming inhomogeneously distributed local structural elements.

Conclusion

Multifractal analysis of the structural organization of the investigated matrix and the obtained values of the ordering parameters Δ and the information entropy S_{inf} showed that the order parameter of the matrix Δ depends on the size of the molecular clusters formed on the surface as a result of heteroannihilation and increases with the cluster size. Thus, multifractal analysis makes it possible to establish the presence of correlations between the kinetic parameters characterizing the change in the structural organization of the matrix as a result of intermolecular interactions and the structural organization of the molecular matrix quantitatively described by the order parameter Δ.

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The calculated values of the order parameter of matrices with different types of initial distribution (the random distribution of donor molecules unconnected to clusters and the random distribution of microclusters of a given size formed by donor molecules) at different matrix temperatures allowed us to establish that for an initial non-cluster random distribution the degree of ordering of the matrix is less than random distribution of clustered donor molecules. With increasing cluster sizes and uniform filling of the simulated surface, the degree of ordering increases. Regardless of the degree of surface coverage by interacting molecules, an increase in the degree of order in the distribution of reagents leads to a decrease in the generalized fractal dimensions of D_q and the information entropy of the system.

The conducted multifractal analysis of the distribution of interacting molecules in a dispersive matrix at various time intervals of kinetic dependencies has shown that the transfer of electron excitation energy and heteroannihilation lead to the formation of stable molecular structures in disperse matrices. This is confirmed by the dependence of the change in generalized fractal dimensions, characteristic for each type of initial distribution of interacting molecules, the ordering of the whole system and the information entropy.

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