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DEPENDENCE OF THE EFFICIENCY OF TRIPLET-TRIPLET ENERGY TRANSFER ON THE DISTANCE BETWEEN THE DONOR AND ACCEPTOR

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The triplet-triplet and singlet-singlet energy transfer is investigated both experimentally and theoretically in the anthracene – Nile red system. Quantum-chemical investigations of the special features in the formation of electronically excited states and photoprocesses in the donor-acceptor pair are performed. It is demonstrated that atypical distance dependence of the efficiency of triplet-triplet energy transfer in the Langmuir–Blodgett multilayered thin films is caused by additional quenching of donor particles due to the process of energy transfer to acceptor centers by the inductive-resonant mechanism.

Keywords: energy transfer, Langmuir–Blodgett film, quantum-chemical calculations.

The triplet-triplet (T-T) electronic excitation energy transfer discovered by Terenin and Ermolaev [1] in the 50s of the XX century is caused by the exchange-resonant interactions between the excited and unexcited molecules spaced at a distance not exceeding several nanometers [2]. Therefore, the efficiency of energy transfer is extremely sensitive to the spacing and mutual orientation of the energy donor and acceptor. Investigations of organic compounds in which the donor and acceptor chromophores were fixed in a rigid insulating chain have demonstrated that the T-T energy transfer is possible only when the spacing does not exceed 1–1.2 nm [2]. However, because of the existence of conformations of molecules in which the donor and acceptor parts are in the van-der-Waals contact, the estimated efficiency of T-T energy transfer as a function of the spacing in such compounds can be not entirely correct [2].

To study experimentally the influence of the orientational and distance factors on the efficiency of intermolecular energy transfer, the technology of the Langmuir–Blodgett (LB) films can be used which allows donor-acceptor systems to be formed when particle spacing and their mutual orientation are strictly fixed.

In [3] the T-T energy transfer between anthracene (donor) and rhodamine C (acceptor) layers was observed by the LB method. Migrating triplet anthracene excitons, leaving the surface layer of anthracene, transferred their energy to dye molecules. Investigations demonstrated that sensitized delayed fluorescence of the acceptor is annihilation in nature. In the subsequent studies, results of experimental investigations of the process of T-T energy transfer between 1.2-benzantracene molecules and amphiphilic analog of rhodamine C [4] and in the anthracene – amphiphilic Nile red pair [5] located in different layers of the LB films were presented. All dyes-acceptors have low quantum yields into the triplet state in the case of direct photoexcitation.

In [5, 6] it was established that the efficiency of triplet energy transfer from the donor to the acceptor depended on the temperature because of inhomogeneous broadening of triplet levels of the energy donor. The dependence of the donor luminescence quenching on the distance between the donor and acceptor layers demonstrated that the energy was transferred at distances much larger than it followed from the exchange resonant nature of the T-T energy transfer [7].

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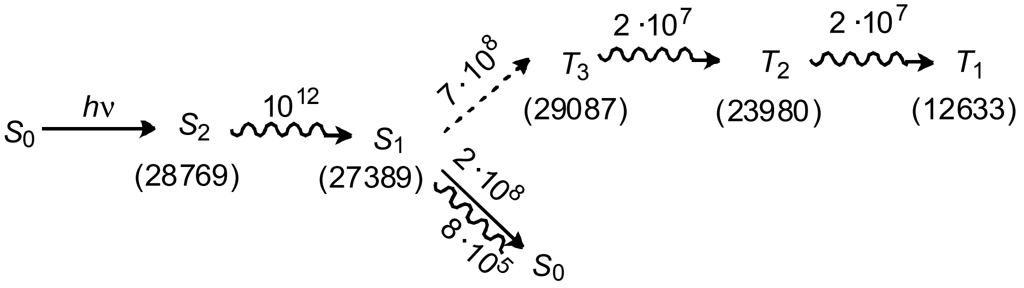

Fig. 1. Scheme of photophysical processes in the anthracene molecule.

To explain the obtained distance dependence of the T-T energy transfer, quantum-chemical investigations of the formation of electronically excited states in the anthracene – Nile red system are performed in the present paper, and the photophysical constants of this donor-acceptor pair are estimated. The examined molecules are theoretically calculated by the semiempirical quantum-chemical method of intermediate neglect of differential overlap (INDO) with special spectroscopic parameterization [6]. To calibrate the molecule parameters by this method, experimental data obtained in hydrocarbon (*inert*) solvents are used. Therefore, the calculated characteristics of molecules must be compared with the data for nonpolar aproton solvents where specific intermolecular interactions can be neglected. The constants of photophysical processes are estimated according to [8]. The efficiency of T-T energy transfer is estimated from the rate constant of internal conversion between the corresponding states of the donor and acceptor molecules according to [9, 10].

We investigated the conformation with molecules oriented in parallel planes one above the other. The distance between the donor and acceptor molecules varied from 4.6 to 22.3 Å. The choice of the minimum distance was determined by contact of the van-der-Waals spheres of luminophore molecules having parallel orientation. The geometry of individual molecules was chosen according to [11].

Results of calculation of the electronically excited states of the anthracene molecule correlated well with the literature data [4, 12]. An analysis of the energy states and rate constants of the photophysical processes in the anthracene molecule demonstrated that upon excitation with a nitrogen laser pulse ($\lambda = 337.2$ nm (29656 cm^{-1})), the transition of the molecule to the S_2 state took place. The excited molecule via the process of internal conversion (IC) fast relaxed to the state S_1 with the rate $k(S_2 \rightarrow S_1) = 6{\cdot}10^{12}$s^{-1}. Calculations of the rate constants for the intersystem crossing (ISC) demonstrated the presence of molecule transition from the state S_1 to the state T_3 ($k_{\mathrm{ST}} = 7{\cdot}10^8$ s^{-1}) in agreement with the results presented in [13]. As a result of the process of internal conversion, the molecule successively goes from the state T_3 to states T_2 and T_1.

The general scheme of transformation of the electronic excitation energy in the anthracene molecule is shown in Fig. 1, where the straight arrows indicate the radiative decay, the wavy arrows indicate the IC, and the dashed arrows indicate the ISC; the energy of the excited states, in cm^{-1}, is indicated in the parenthesis, and the corresponding rate constants, in s^{-1}, are indicated above the arrows.

Results of calculation of the spectral characteristics of the Nile red molecule are in agreement with the data presented in [14]. The calculated energy (~21000 cm^{-1}) of the S_1 state is greater than its value (~18000 cm^{-1}) observed in the experiment. The difference between the calculated energy of the electronically excited S_1 state of the dye and its experimental value demonstrates the fact that Nile red possesses solvatochromic properties and is strongly affected by the solvent [14].

Let us consider the relaxation channels for the excited electronic states of Nile red upon optical excitation of molecules in the long-wavelength absorption band. From the S_1 state, the effective process of ISC to the T_4 state of $n\pi^*$ nature is observed [14]. In addition, the nonradiative transition to the ground state is possible. The general scheme of the process of energy transformation is shown in Fig. 2.

When modeling the donor-acceptor complex, the general form of the wave functions Ψ_p of the excited electronic states in a bimolecular system constructed from the singly excited configurations Φ_{ik} is written as follows [15]:

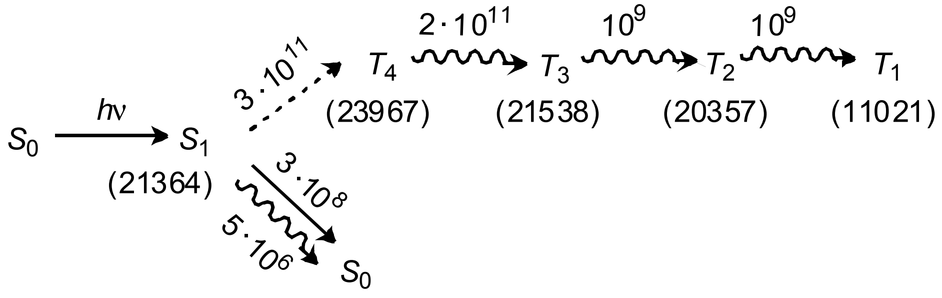

Fig. 2. Scheme of photophysical processes in the Nile red molecule.

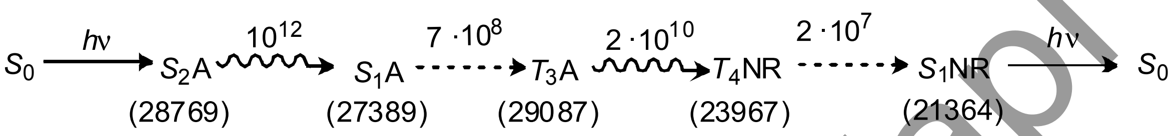

Fig. 3. Scheme of the electronic states and photophysical processes in the anthracene – Nile red system.

$$\Psi_p = \sum_{ik\in 1} A_{ik}\Phi_{ik} + \sum_{jl\in 2} A_{jl}\Phi_{jl} + \sum_{il} A_{il}\Phi_{il} + \sum_{jk} A_{jk}\Phi_{jk} \quad . \qquad (1)$$

In Eq. (1) it has been assumed that the subscripts i and k of the molecular orbitals (MO) denote the first molecule (for example, donor) of the bimolecular system, and the subscripts j and l denote the second molecule (acceptor). The wave function of the pair has this form both with and without allowance for the intermolecular interaction. The first two sums in Eq. (1) correspond to monomolecular excitations of molecules 1 and 2. The third and fourth sums contain the configurations corresponding to the electron transition from the occupied MO of one molecule to the free MO of another molecule.

Generally, the function Ψ_p should contain all terms presented in Eq. (1). However, an analysis of delocalization of a concrete excited state of the bimolecular system demonstrated that in most cases, the main contribution to the formation of Ψ_p is brought by one of the sums in Eq. (1). For example, for the state mostly localized on the 1st molecule, we have $|A_{ik}|^2 \gg |A_{jl}|^2$, $|A_{il}|^2$, and $|A_{jk}|^2$. In the examined system, such localization is determined fairly unambiguously. Therefore, below we designate the electronic states of the system by letters A (anthracene), NR (Nile red), or their combination.

The scheme of the photophysical processes in the donor-acceptor anthracene – Nile red system is shown in Fig. 3. The distance between the planes of anthracene and Nile red molecules was equal to 0.46 nm.

The electronically excited states of the donor-acceptor system represent superposition of the corresponding energy levels of its individual components. The T-T electronic energy transfer, according to [5], proceeds as follows. Upon excitation of the donor-acceptor system, the anthracene molecule goes to the electronically excited state S_2. As a result of internal conversion, the molecule goes to the state S_1, as described above. From the donor state S_1, the process of ISC to the T_3 anthracene state proceeds. The triplet-triplet energy transfer occurs by the mechanism of internal conversion between the triplet anthracene state T_3 and the Nile red state T_4. After that, as a result of ISC, the S_1 state of the acceptor is formed from the T_4 state and then relaxes to the ground S_0 state with emission of a photon.

However, as demonstrated the results of our calculations, singlet-singlet (S-S) energy transfer (Fig. 4) can be realized in the pair anthracene – Nile red in addition to the triplet energy transfer. The efficiency of electronic excitation energy transfer in this case was estimated from the rate constant of internal conversion between the S_1 state of the anthracene molecule and S_4 state of the Nile red molecule.

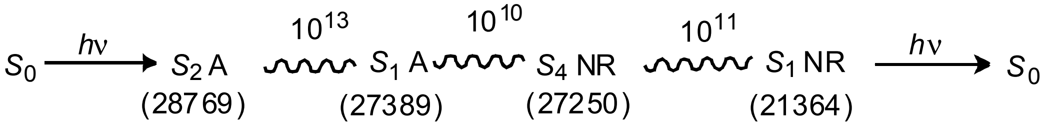

Fig. 4. Scheme of photophysical processes in the system anthracene – Nile red.

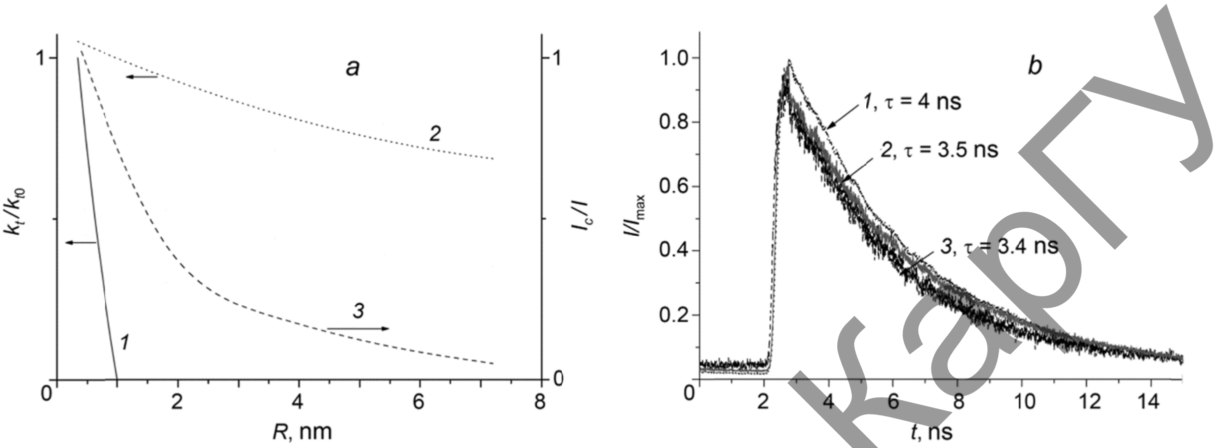

Fig. 5. *a*) Dependences of the rate constants of energy transfer on the distance between the planes of the donor and acceptor molecules. Here curve *1* is for the T-T energy transfer, curve *2* is for the S-S energy transfer, and curve *3* is for the experimental dependence of the efficiency of anthracene ADF quenching. *b*) Kinetics of the donor fluorescence decay (curves *1* and *2*) and of the sensitized acceptor fluorescence (curve *3*). Here curve *1* was obtained without acceptor, and curve *2* was obtained with acceptor at $\lambda_{exc} = 375$ nm.

As can be seen from Fig. 4, the S-S energy transfer occurs from the S_1 level of the donor to the S_4 level of the acceptor. Then the excitation energy quickly relaxes to the S_1 state of the dye molecule.

Figure 5*a* shows the calculated dependences of the rate constants of T-T (curve *1*) and S-S (curve *2*) energy transfer on the distance between the centers of the donor and acceptor molecules. Curve *3* shows the dependence of the efficiency of quenching of the annihilation delayed fluorescence (ADF) of anthracene on the distance between the donor and acceptor layers in the LB film [5].

From curve *1* in Fig. 5*a* it can be seen that the rate constant of T-T energy transfer fast decreases with increasing distance between the planes of molecules and vanishes at $R \approx 1$ nm. The efficiency of the S-S energy transfer changes slightly even for large distances between the interacting molecules (curve *2* in Fig. 5*a*). This behavior of the rate constant is typical for the process of electronic excitation energy transfer by the inductive-resonant mechanism [2]. The presence of the S-S energy transfer in the anthracene – Nile red pair was confirmed by both quenching of the fluorescence intensity of the donor for stationary excitation and the measured fluorescence decay kinetics of anthracene in the presence of dye molecules (curve *2* in Fig. 5*b*).

Experimental curve *3* in Fig. 5*a* characterizes the efficiency of intermolecular energy transfer as a function of the distance between the donor and acceptor layers. From the shape of curve *3* it follows that the T-T energy transfer dominates at short distances, and the experimental dependence is better described by curve *1* calculated for the energy transfer by the exchange-resonant mechanism. Experimental values of the efficiency of quenching of the donor triplets are nonzero even for large distances. The behavior of the curve for distances greater than the exchange interaction distance corresponds better to the dependence of the S-S rate constant (curve *2* in Fig. 5*a*).

The results obtained can be explained as follows. The intensity of the anthracene ADF is sensitive to the concentration of molecules in the T_1 state, since $I_{ADF} \sim [T]^2$ (here $[T]$ denotes the triplet molecule concentration). The concentration of the triplet anthracene molecules is determined by the ISC rate between the S_1 and T_3 states equal to $7\cdot10^8$ s^{-1}. The T-T energy transfer from the T_3 state of the anthracene to the T_3 state of Nile red is a competing process in relation to the formation of the T_1 state of anthracene molecules as a result of the $T_3 \rightarrow T_2 \rightarrow T_1$ transitions. It also causes quenching of the anthracene ADF intensity in the presence of Nile red molecules observed in the experiment. If in the same donor-acceptor pair the S-S energy transfer occurs, it will decrease the population of the T_1 state of the donor. As demonstrated the results of calculations, the rate constant of the S-S-energy transfer in the anthracene – Nile red pair is equal to 10^{10} s^{-1}. It is approximately by 2 orders of magnitude greater than the efficiency of forming anthracene triplets (the $S_1 \rightarrow T_3$ transition). This suggests that quenching of the anthracene ADF intensity observed in the experiment at distances greater than 1 nm is caused by a decrease in the concentration of anthracene triplets as a result of the S-S energy transfer.

Thus, the T-T and S-S energy transfer in multilayered thin films of aromatic molecules and dyes has been investigated both experimentally and theoretically. The quantum-chemical investigations of the special features in forming the electronically excited states and photoprocesses in the system anthracene – Nile red were performed. The atypical distance dependence of the efficiency of the T-T energy transfer in multilayered thin films was caused by additional quenching of the excited donor particles due to the process of energy transfer to acceptor centers by the inductive-resonant mechanism.

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