ON THE ENERGY TRANSFER MECHANISM IN BIFLUOROPHORS

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Photochemical processes occuring in molecules of nonconjugate bifluorophors, i.e., the molecular systems composed of two monofluorophor molecules (the donor and acceptor of energy) coupled by the bridge CH_2 *bonds are studied. It is shown that transfer of energy from the donor to acceptor molecules occurs in the bifluorophor molecules as a result of intramolecular process of internal energy conversion.*

Determination of regularities in the relation of optical properties of molecules to their electron and spatial structure is a fundamental problem of physics of polyatomic molecules. Solution of this problem can be decisive in the progress of science and engineering branches connected with spectroscopy and luminescence of polyatomic molecules, as well as with photochemistry, quantum electronics, development of luminophors and dyes, etc.

Much progress has been achieved in this area. However, a variety of molecular systems and extremely complicated intra– and intermolecular interactions put forward new problems.

Thus, interest in a specific kind of polyatomic molecules, bifluorophors, has increased in recent years. The concept of a bilfluorophor is described in detail in Ref. 1, so in this paper we deal with nonconjugate bilfluorophors, which represent systems constructed of two different monofluorophor molecules coupled by the bridge $(CH_2)_n$ bonds not transferring electron conjugation. A bifluorophor consists of a donor molecule with the first excited singlet state ($S_{\rm ID}$) of higher energy than that of an acceptor molecule with a lower $S_{\rm IA}$ state. The lower excited state $T_{\rm ID}$ of the donor is usually higher than the state $T_{\rm IA}$ of the acceptor but in some cases the energy of the acceptor $T_{\rm IA}$ state can exceed the energy of the donor state $T_{\rm ID}$ in the latter case a monofluorophor molecule being a donor in a singlet–singlet energy transfer can become an acceptor in a triplet–triplet energy transfer.

It should be noted that bifluorophors are of great interest for quantum electronics (the use of them as active media for dye lasers enables one to substantially increase the efficiency of a conversion and to raise the photochemical resistance of active media, i.e., to prolong the laser lifetime), for developing systems of optical filtration and transformation of lamp and laser radiation, for constructing scintillation detectors for nuclear–physical setups, etc. In many aspects these applications are based on the principal feature of a bifluorophor, i.e., on a wide dispersion of the energy–spectra of electron–excited states of donor and acceptor molecules what causes very important peculiarities of intramolecular relaxation processes.

In this paper we consider the situation when the electron excitation of a bifluorophor in the absorption band of donor molecules is followed by the fluorescence of acceptor molecules, that is, a singlet–singlet energy transfer occurs.

An appreciable contribution to development of the concepts on energy transfer has been made by Vavilov,[2] Ermolaev,[3] and Galanin.[4] A quantum–chemical theory of nonradiative energy exchange between individual molecules had been developed by Förster[5] and then it was modified by Dexter.[6]

It should be noted that the Förster theory was developed for energy exchange between individual molecules in a condensed phase (not connected with chemical bonds) provided that there is equilibrium among the electron–excited states of a donor and an acceptor. Moreover, the donor's excited state must be formed by an optically allowed transition (the energy transfer with optically forbidden transitions is not described by this theory). The interaction Hamiltonian in the Förster theory is represented as a sum of interactions of outer electrons of a donor and an acceptor unbound molecules (induction–resonance and resonance–exchange mechanisms of energy transfer are well described in this case). Although the Förster theory has not been developed for describing the energy transfer between chemically bound molecules of a donor and an acceptor in a bifluorophor, it was successfully used for studying such systems.[3]

However, a detailed examination shows that in the Förster model it is possible to describe the energy transfer in bifluorophors with sufficiently far–spaced molecules of a donor and an acceptor (~ 10 Å and larger), i.e., in bifluorophors with long chains of bridge bonds. When the distances between donor and acceptor molecules in a biofluorophor is about 5 Å and smaller it is difficult, within the framework of the Förster model, to describe the energy transfer (it is difficult to define the concept, e.g., of an effective transfer radius R_0), since at small distances there occur the effects of overlapping of the inner and outer (σ–and π–) electron shells of a donor and an acceptor. In such a situation the interaction Hamiltonian must be written in a more general form which includes not only the interaction between outer electrons of a donor and an acceptor but also the interaction between electrons and nuclei.

The second important fact is that the models like that developed by Förster are to describe general behavior of energy transfer (e.g., they make it possible to calculate

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the rate constant and to study its dependence on R_0 and some spectral parameters of a donor and an acceptor as well) but they do not allow one to find the relation of energy transfer to the chemical structure of donor and acceptor molecules and a bifluorophor as a whole. This statement is even more correct in the case of bifluorophors with a short bridge ($\lesssim 5$ Å). In this connection it should be noted that there are not any general concept on the relation of spectroscopic and luminescent (lasing) properties of bifluorophors to their electron and spatial structures what prevents synthesizing bifluorophors with desired properties.

One of the effective approaches to the solution of this problem can be a study of the initial photon–induced processes based on the quantum–chemical calculations of properties of a bifluorophor molecule as a unique molecular system (without division into donor and acceptor molecules). In this case the interaction Hamiltonian involves the terms of electron–electron, electron–nuclear, and spin–orbital interactions. Thus, it is possible to describe radiation and nonradiative transitions and to extract quantitative information about the dynamics of populations of different electron–excited states.

Analysis of a total wave function of a bifluorophor in each specific case provides the determination of corresponding contributions coming from donor and acceptor molecules, individual atoms and groups of atoms as well as their roles in the formation of spectral and luminescent characteristics of biofluorophors. In this method we remove such restrictions of the Förster model as $\kappa_R > \kappa_t$ (κ_t and κ_R are the rate constants of energy transfer and vibrational relaxation in an electron–excited state), the requirement of a many stage nature of energy transfer (donor excitation → vibrational relaxation and (or) other intramolecular relaxation processes in the donor molecule → energy transfer → radiation and conversion of electron energy in the acceptor), the requirement that an optical transition to the excited state of the donor is permitted, and other restrictions of this model due to chemical unboundness of donor and acceptor molecules existing at sufficiently large distances in the condensed phase.

In this paper devoted to the study of mechanisms of energy transfer in complicated molecular systems we consider the possibilities of quantum chemistry methods when examining such processes.

The properties of bifluorophor molecules were calculated using the semi–empirical quantum–chemical method INDO/S with the spectroscopic parameterization.[7] The nature of electron–excited states was analyzed based on the calculated coefficients of expansion of molecular orbitals over the atomic $2S$, $2P_x$–, $2P_y$–, and $2P_z$–orbitals and wave functions of electron–excited states over the corresponding Slater configurations as well as using indices of localization of electron excitation on fragments[8]:

$$L_A^{(i)} = \frac{\sum\limits_{\mu \in M} |\Delta q_\mu^{(i)}|}{\sum\limits_{\upsilon \in M} |\Delta q_\upsilon^{(i)}|}\,, \tag{1}$$

where Δq_μ^i is the change of electron density of an atom μ during electron excitation from the ground to i th electron state.

Summation in the numerator of Eq. (1) is carried out over atoms of the fragment A (in our case, over atoms of one of monofluorophors of a bifluorophor) while the summation in the denominator is done over all atoms of the molecular system (M).

The efficiency of intercombination conversion was determined based on calculations of matrix elements of the operator of spin–orbital interaction in single– and multicenter approximations.[9]

The rate constant of internal conversion involving the electron states g and f was estimated by the formula

$$\kappa_{g\,f} = \Omega_{g\,f}\,\kappa_{g\,f}^{(0)}\,, \tag{2}$$

where $\kappa_{g\,f}^{(0)}$ is the rate of the $g \to f$ internal conversion in a single configuration approximation,[10] $\Omega_{g\,f}$ is the factor describing overlapping of the wave functions of the electron states g and f

$$\begin{aligned}\Omega_{g\,f} = N_{\mathrm{CH}} \sum_{\alpha=1}^{N_{\mathrm{CH}}} \Bigg\{ & \sum_{\substack{i\to\kappa\\ j\to\kappa}} A_{i\kappa}^{(g)}\; B_{j\kappa}^{(f)}\, (c_{is}\, c_{js} + \\ & + c_{ix}\, c_{jx} + c_{iy}\, c_{jy} + c_{iz}\, c_{jz} + c_{i\mathrm{H}}\, c_{j\mathrm{H}})_\alpha + \\ & + \sum_{\substack{i\to\kappa\\ i\to l}} A_{i\kappa}^{(g)}\, B_{il}^{(f)}\, (c_{\kappa s}\, c_{ls} + c_{\kappa x}\, c_{lx} + c_{\kappa y}\, c_{ly} + c_{\kappa\mathrm{H}}\, c_{l\mathrm{H}})_\alpha + \\ & + \sum_{i\to\kappa}^{i,\ \kappa} A_{i\kappa}^{(g)}\, A_{i\kappa}^{(f)} (c_{is}^2 + c_{ix}^2 + c_{iy}^2 + c_{iz}^2 + c_{i\mathrm{H}}^2)_\alpha \Bigg\}\,, \end{aligned} \tag{3}$$

where N_{CH} is the number of C–H bonds, $A_{i\kappa}^{(g)}$ is the coefficient of the contribution coming from the electron configuration $|i \to \kappa>$ into the electron state g; c_{is}, c_{ix}, c_{iy}, c_{iz}, and $c_{i\mathrm{H}}$ are the coefficients of expansion of the ith molecular orbital (MO) over $2S$, $2P_x$, $2P_y$, $2P_z$, and $1S_{\mathrm{H}}$ atomic orbitals (AO); i and j are the occupied MO, κ and l are the vacant MO, and $1S_{\mathrm{H}}$ are the AO of a hydrogen atom.

We have calculated the properties of some molecules of bifluorophors with a common structure formula D–$(\mathrm{CH_2})_n$–A. Here the molecule of coumarine 120(K) was taken as an acceptor molecule (A) and molecules of paraterphenyl, biphenyl, phenyl, and naphthalene (H) were taken as a donor D. As an illustration we consider the calculations carried out for the bifluorophor ≪H–$(\mathrm{CH_2})_n$–K≫.

Depicted in Fig. 1 are the schemes of singlet electron–excited states of the naphthalene, coumarine, and bifluorophor molecules ≪H–$(\mathrm{CH_2})_n$–K≫. Table I gives the data on the degree of localization of the electron excitation and the electron charges on fragments of a bifluorophor molecule. Analysis of these results shows that the electron–excited states of bifluorophor are combined and contain the contributions from naphthalene and coumarine molecules. (It should be noted that such a situation is common for other bifluorophors.) Thus, though the molecules of naphthalene and coumarine are coupled by $\mathrm{CH_2}$–group (it is usually considered that it does not transfer the electron conjugation) the electron–excited states of bifluorophor must be treated as the states of a unique molecular system with different degree of excitation localization on the fluorophor fragments. The resolved electron states of naphthalene and coumarine molecules contributing to the formation of intense long–wave absorption bands of these molecules (S_2 state of a naphthalene molecule and S_1 and S_2 states of a coumarine molecule) are exhibited with a higher degree of excitation localization in a bifluorophor molecule. Just this situation causes the additivity of absorption spectra of fluorophors resulting in the absorption spectrum of the bifluorophor as a unique molecule (see Fig. 2). There is a good agreement between the calculated positions of electron states and the experimental absorption spectra of the molecules under study. It should also be noted that the oscillator strength of the $S_0 - S_1$ transition in a bifluorophor molecule is higher than that in the acceptor molecule (Figs. 1 and 2).

TABLE I. The degrees of excitation localization (L, %) and change distribution (Q, e) over the fragments of naphtalene (H) *and coumarine 120* (K) *and* CH_2*–group in a bifluorophor* $H–(CH_2)_n – K$.

States		$n = 1$			$n = 2$			$n = 4$		
		H	CH_2	K	H	CH_2	K	H	CH_2	K
S	Q	–0.010	0.143	–0.127	–0.011	0.142	–0.132	–0.029	0.156	–0.130
S_1	L	2	3	95	1	4	95	0	4	96
	Q	–0.041	0.183	–0.142	–0.010	0.186	–0.176	–0.027	0.199	–0.172
S_2	L	1	5	94	1	5	94	0	5	95
	Q	–0.017	0.197	–0.180	–0.012	0.200	–0.188	–0.029	0.211	–0.182
S_3	L	51	3	46	69	5	26	88	9	3
	Q	–0.300	0.161	0.139	–0.113	0.157	–0.044	–0.048	0.172	–0.124
S_4	L	69	4	27	83	7	10	92	8	0
	Q	–0.104	0.154	–0.050	–0.040	0.157	–0.117	–0.045	0.171	–0.126

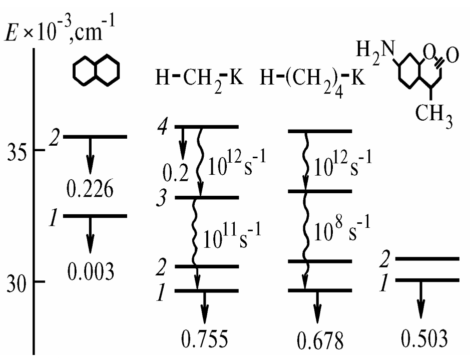

FIG. 1. Schemes of electron–excited states and processes of internal conversion in bifluorophor molecules.

Based on the combined origin of the electron excited states of a bifluorophor as a unique molecular system it is possible to consider the following scheme of the processes occurring in the bifluorophor molecule. After optical excitation due to strong absorption of donor (naphthalene) to the S_4 state of the bifluorophor a rapid internal conversion of the absorbed energy according to the scheme $S_4 \sim\to \Sigma_3 \sim\to S_2 \sim\to S_1$ occurs that results in the bifluorophor molecular transition to the S_1 state (localized in a coumarine fragment). In this case the $S_1 \to S_0$ fluorescence of the bifluorophor is in fact the fluorescence of coumarine (spectral shift of bifluorophor fluorescence maximum compared to that of the pure acceptor (see Fig. 2) is analogous to that when the CH_3– group is introduced into the acceptor molecule). Thus the energy transfer from the donor molecule to the acceptor one in a bifluorophor molecule can be interpreted in terms of intramolecular relaxation processes, in particular, internal energy conversion. The estimates of the constants of internal energy conversion rates by formulas (2) and (3) are depicted in Fig. 1.

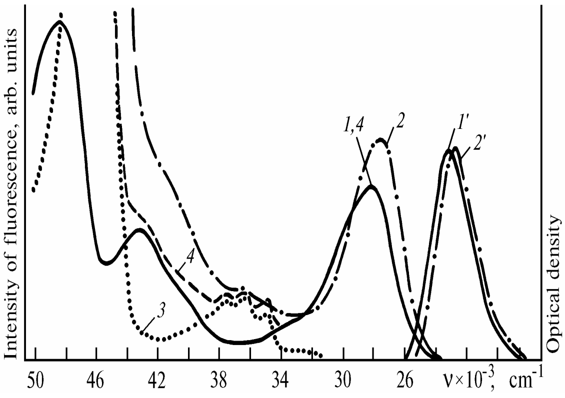

FIG. 2. Spectra of absorption (1–4) and fluorescence (1′– 2′) of coumarine 120 (1, 1′), naphthalene (3), bifluorophor (2, 2′), and of their equimolar mixture (4) in ethanol.

In our opinion special attention should be paid to the intermediate combined S_3 state through which the internal energy conversion $S_D \sim\rightarrow S_A$ takes place. As follows from Table I, the S_3 state of a bifluorophor is equally contributed to by the donor and acceptor molecules and is a coupling for the internal energy conversion $S_D \sim\rightarrow S_A$.

With increase of n (the number of CH_2–groups) the degree of excitation localization on individual molecular fragments increases. In particular, S_3 state with $n = 4$ is already localized mainly on the naphthalene fragment that results in a substantial reduction of overlapping of wave functions of S_3 and S_1 states and, correspondingly, in substantial slowing down of a general molecular deactivation process $S_3 \sim\rightarrow S_1$ in a bifluorophor (Fig. 1). Analysis of charge distribution (Table I) demonstrates that the S_3 state (to a smaller degree the S_4 state) with $n = 1$ is of a charge–transfer nature (~ 0.3 e is promoted from the coumarine fragments to the naphthalene ones); with the n increase the degree of charge transfer decreases and when $n = 4$ the values of charges of the fragments are approximately the same as that of the fragments in the ground state.

Thus, the calculational results show that internal energy conversion $S_D \sim\rightarrow S_A$ slows down with increase of the number of CH_2–groups. At the same time it is well known[3] that in biflourophors with a large number of CH_2–groups the processes of energy transfer can proceed at a sufficiently high rate. This is well described within the Förster model.

Taking into account what has been said above it is possible to conclude that at small distances between the molecules of a donor and an acceptor the processes of energy transfer mostly occur due to internal conversion, while with increase of a chain of nonconjugate bonds the Förster mechanism of energy transfer becomes prevailing. It should be noted in this connection that our experiments showed that the efficiencies of energy transfer in bifluorophors ≪paraterphenyl–CH_2–coumarine 120≫ and nnaphthalene–CH_2–coumarine 120. are similar ($K_t \sim 10^{11}-10^{12}\ s^{-1}$), while within the framework of the Förster model the transfer constant in the first bifluorophor must exceed that in the second bifluorophor by 2–3 orders of magnitude since the optical $S_1 \rightarrow S_0$ transition in the paraterphenyl molecule is permitted (the oscillator strength $f_{30} \simeq 1.5$), while in the naphthalene molecule $f_{10} \simeq 0.003$. This is an additional confirmation of the proposed mechanism of energy transfer in bifluorophors through intramolecular relaxation processes.

Thus the above analysis of quantum mechanical calculations allows one to draw the following conclusions. The bifluorophor molecules that are nonconjugate systems in the ground state after optical excitation come to electron–excited states which are the states of a unique molecular system with different degree of excitation localization in individual fragments. After optical excitation of a bifluorophor within the absorption band of a donor there occur rapid intramolecular relaxation processes (in particular, internal energy conversion) resulting in the transition of the bifluorophor molecule to the S_1 state localized on the acceptor from which the fluorescence occurs what can be treated as intramolecular energy transfer from the donor to the acceptor in the bifluorophor molecule.

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