

Mechanism of energy transfer in molecular complexes

V.A. Pomogaev and V.Ya. Artyukhov

V.D. Kuznetsov Siberian Physical Technical Institute at the Tomsk State University

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To find possible ways for excitation, deactivation, and energy transfer, spectral and photophysical characteristics of molecular complexes: benzophenone/9,10-substituted anthracenes and 9,10-substituted anthracenes/naphthalene were calculated within the framework of the standard quantum-chemistry approach. Intermolecular $T \rightarrow S$ energy transfer in these systems occurs only in collision complexes at the van der Waals distance between molecules. Direct $S \rightarrow T$ energy transfer strongly yields the intramolecular process in substituted anthracenes/naphthalene complexes. Matrix elements of the single-electron spin-orbital operator were calculated in the multicenter approximation.

Introduction

The problem of electronic excitation energy transfer (EEET) and EEET mechanisms were studied experimentally and theoretically in many papers (see Ref. 1). Of great interest in photonics of molecules is the EEET between molecules being at a small distance from each other (collisional complexes). As molecules come within very short distance from each other, their electron shells overlap and joint molecular orbitals are formed, what can favor strengthening of the spin-orbital coupling and intensification of $S \leftrightarrow T$ EEET.

To study photophysical processes occurring in the collisional complexes, we have considered the following bimolecular systems: benzophenone/anthracene (B/A), benzophenone/9,10-dichloroanthracene (B/DCA), benzophenone/9,10-dibromoanthracene (B/DBA) and anthracene/naphthalene (A/N), 9,10-dichloroanthracene/naphthalene (DCA/N), and 9,10-dibromoanthracene/naphthalene (DBA/N). The interest in these complexes was motivated by the results presented in Refs. 2–6, which assumed $S \leftrightarrow T$ EEET. The properties of all components of these systems are studied quite thoroughly, and the results of interaction between them are described in the references cited above.

The $T \rightarrow S$ energy transfer was found from chemiluminescence of the complexes of oxidized hydrocarbons with 9,10-substituted anthracenes.^{2–4} Chemical reactions yield oxidation products in excited electronic states. For example, the process of diphenylmethane oxidation in benzol solution yields benzophenone molecules excited in the triplet state, as follows from its weak phosphorescence. It was observed experimentally that the intensity of chemiluminescence increases due to fluorescence of substituted anthracenes added to the solution. This follows from the fact that intensification of chemiluminescence was accompanied by the appearance of a band corresponding to the acceptor fluorescence band. Excitation of anthracenes becomes possible, in the authors' opinion, because of the nonradiative EEET from the triplet level of benzophenone to the S_1 state of the anthracene.

The $S \rightarrow T$ energy transfer was accepted for explanation of fluorescence quenching in the complexes of 9,10-substituted anthracenes with the naphthalene.⁶ After a thorough study of the lifetimes of the fluorescent state of the anthracene derivatives, it was concluded that quenching of fluorescence at addition of naphthalene is caused by the nonradiative $S \rightarrow T$ EEET, because the acceptor's singlet levels have higher energy than the donor's singlet levels, whereas the triplet ones have lower energy.

In both of the cases, the resonance-exchange mechanism of the EEET according to Ferster–Deckster theory was proposed to explain the observed processes. In this paper, we use the quantum-chemistry approach described in Ref. 7 to study the peculiarities of photoprocesses in the systems mentioned above.

Models and calculation technique

A very efficient method for studying molecular complexes is the model of a “supermolecule,” in which the molecular system is considered as a single supermolecule without separation into fragments. In such an approach, the EEET is interpreted as a consequence of the intrasystem photophysical processes. In this case, it is possible to determine the contribution of molecules D and A to the formation of spectral-luminescent characteristics of the complex. The model also allows separation, to a certain degree, of the intermolecular and intramolecular photoprocesses based on estimation of the contributions coming from the system components to the formation of single-electron molecular orbitals and wave functions of the electronic states.

When modeling a chemically uncoupled bicomponent system, it is a very urgent problem to select the mutual arrangement of molecules (conformation of the system). Since the energy transfer occurs in collisional complexes, the mutual arrangement of molecules in a complex is arbitrary. Therefore, we have studied spectral-luminescent properties of several types of fixed, static molecular complexes. For every type of a complex, the ways of excitation and deactivation were determined.

Such an approach provides for an insight to be made into the dynamic pattern of possible EEET from the donor to the acceptor under conditions of continuous motion of molecules. The minimum (contact) distance between the interacting molecules was determined by the van der Waals spheres of the closest atoms belonging to different molecules.⁸ Thus, the minimum distance for oxygen is 2.9 Å at interaction with carbon, 3.0 with chlorine, 3.1 with bromine, and 2.5 Å with hydrogen. The contact distance is 3.3 Å between the closest carbon atoms, 3.5 between carbon and chlorine, 3.6 between carbon and bromine, and smaller than 3 Å between hydrogen with these elements.

The quantum-chemistry calculations of the considered systems have been carried out within the framework of the Partial Neglect of Differential Overlap (PNDO) method with a spectroscopic parameterization.⁷ Calculations of the energy levels and rate constants of photochemical processes were tested with various molecules and have demonstrated close agreement with the experimental data. Earlier we have applied this approach to the study of intermolecular photoprocesses in systems of the second type.⁹ The sandwich-type conformation was studied, and it was shown that in this conformation the $S \rightarrow T$ processes do not compete with the intramolecular processes of degradation of the donor's S_1 state. At the same time, the use of "standard" system of parameters of the computational method did not allow correct calculation of the quantum yield of the anthracene fluorescence and fluorescence of the substituted anthracenes (at the close common agreement with the experimental data on optically observable electronic states). In this paper, we have corrected some parameters. As a result, the

scheme of energy levels became somewhat different (changes in the scheme are considered below), and this allowed us to estimate correctly the quantum yield of fluorescence γ_{fl} of A, DCA, and DBA as 27, 33, and 3%, respectively. The calculated values agree well with the data from Ref. 4.

Because the $S \leftrightarrow T$ EEET is assumed in the systems under study, the problem of calculation of the rate constant of intersystem crossing (k_{ST}) seems to be rather urgent. Taking into account that the geometric structure of bimolecular systems has rather a complicated character for calculation of matrix elements of the single-electron spin-orbital interaction operator, we applied the software for calculation of matrix elements in the multicenter approximation,^{10,11} that allows such calculations to be performed for systems of arbitrary geometry.

Calculated results and discussion

Benzophenone/anthracene systems

From the quantum-chemistry calculations, we have found the scheme of the electron energy levels and photochemical processes in the B/A, B/DCA, and B/DBA complexes (Fig. 1). The electron energy levels have common numbering all over the complex; assignment of a level to a particular molecule is given in parentheses: a means anthracene or substituted anthracenes, b denotes benzophenone, and n denotes naphthalene; the nature of a state is given after comma. The rate constants of photophysical processes affecting the EEET and the transfer efficiency $\gamma_{tr} = k_{TS}/(k_{TS} + k_{TT})$ for different conformations of the complex and the distances between molecules are given in Table 1.

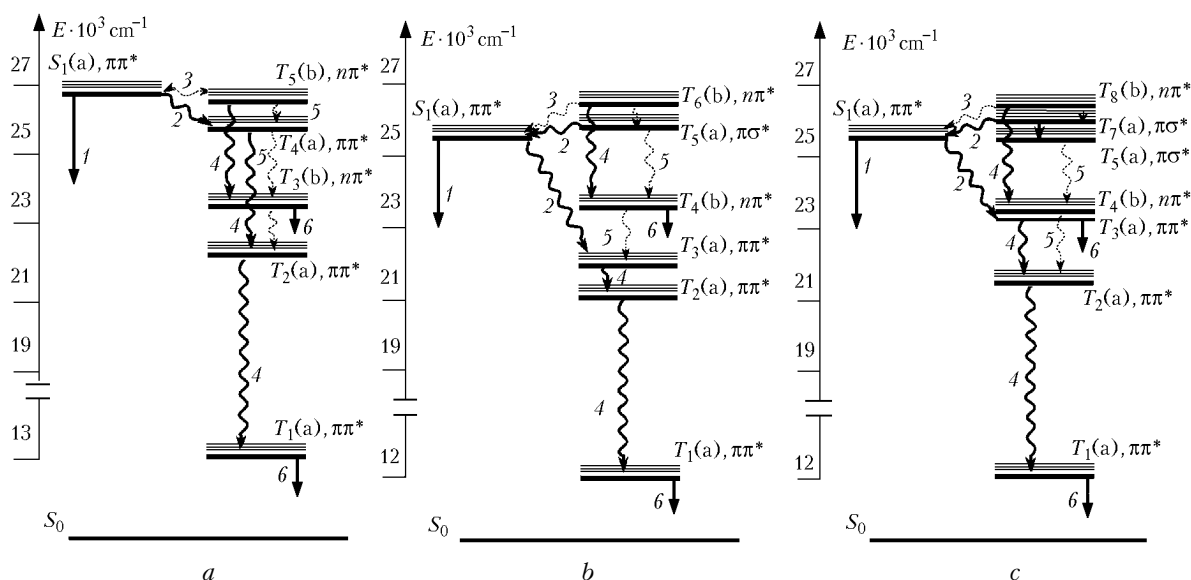
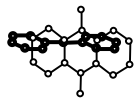
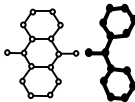
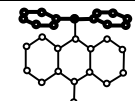


Fig. 1. Schemes of electronic states and photochemical processes in molecular complexes: benzophenone/anthracene (a), benzophenone/9,10-dichloranthracene (b), and benzophenone/9,10-dibromanthracene (c): fluorescence (1), intersystem crossing (2), singlet-triplet energy transfer (3), internal conversion (4), triplet-triplet energy transfer (5), and phosphorescence (6). Thin lines are for the processes arising in the collisional complex, and thick lines are for the continuous processes. The processes of vibrational relaxation are omitted.

Table 1. Rate constants of the processes in benzophenone/9,10-substituted anthracene

Complexes Processes Conformation	B/A			B/DCA			B/DBA		
	$k_{T_5 \rightarrow T_3}$	$k_{S_1 \leftrightarrow T_5}$	$\gamma_{tr}, \%$	$k_{T_6 \rightarrow T_4}$	$k_{T_6 \rightarrow S_1}$	$\gamma_{tr}, \%$	$k_{T_8 \rightarrow T_4}$	$k_{T_4 \rightarrow S_1}$	$\gamma_{tr}, \%$
	$1.0 \cdot 10^{10}$	$7.3 \cdot 10^8$	7	$6.1 \cdot 10^9$	$9.9 \cdot 10^8$	14	$7.2 \cdot 10^9$	$1.2 \cdot 10^9$	15
	$1.0 \cdot 10^{10}$	$3.9 \cdot 10^9$	28	$2.8 \cdot 10^{10}$	$1.5 \cdot 10^9$	5	$2.1 \cdot 10^{10}$	$1.1 \cdot 10^9$	5
	$2.0 \cdot 10^{10}$	$7.1 \cdot 10^9$	26	$2.2 \cdot 10^{10}$	$3.2 \cdot 10^9$	13	$1.8 \cdot 10^{10}$	$2.4 \cdot 10^9$	12
5 Å	$2.3 \cdot 10^{10}$	$8.8 \cdot 10^8$	4	$2.2 \cdot 10^{10}$	$4.2 \cdot 10^8$	2	$2.0 \cdot 10^{10}$	$5.6 \cdot 10^8$	3
20 Å	$2.3 \cdot 10^{10}$	0	0	$2.1 \cdot 10^{10}$	$5.9 \cdot 10^4$	0	$2.3 \cdot 10^{10}$	$5.9 \cdot 10^4$	0

In Ref. 4 it was noted that the excited triplet state of benzophenone in the B/A complex is lower than the S_1 state of anthracene, and populating the latter through $T \rightarrow S$ EEET is only possible from some vibrational sublevel. The efficiency of this process depends on the temperature. For two other complexes, the $T \rightarrow S$ EEET is exothermic, because the excited benzophenone triplets are above the S_1 states of substituted anthracenes.

From Fig. 1a it is seen that the second triplet level of the benzophenone, $T_3(b)$, actually is lower than $S_1(a)$, and the EEET efficiency for the B/A complex can be estimated only by the maximum value (Table 1 for this compound gives the efficiency in the case of energy transfer from the zero vibrational sublevel).

From the calculated values of electronic levels of the B/DCA and B/DBA complexes, it is seen (Figs. 1b and c) that the state $T_4(b)$, in both cases, is below $S_1(a)$. This result also agrees with the data from Ref. 5. The EEET efficiency depends on the mutual arrangement of molecules and the distance between them, rather than on temperature (see Table 1). This can be established from variation of k_{ST} , which is responsible for EEET. Already at a distance of 5 Å the efficiency of energy transfer decreases drastically, and at 20 Å EEET is completely absent. The $T \rightarrow T$ EEET also takes place in collisional complexes. The allowance for this process leads either to some decrease in the fluorescence intensity [$T_5(b) \rightarrow T_4(a)$ in Fig. 1a, $T_6(b) \rightarrow T_5(a)$ in Fig. 1b, and $T_8(b) \rightarrow T_7(a)$ in Fig. 1c] or to intersystem crossing [$T_5(a) \rightarrow S_1(a)$ in Fig. 1b and $T_7(a) \rightarrow S_1(a)$ in Fig. 1c], that results in the transition of the substituted anthracenes to the fluorescent state.

It is seen from Fig. 1 that further energy degradation in the anthracenes excited to the S_1 state follows the channels that are ordinary for these molecules, in which intramolecular processes of emission and intersystem crossing to the triplet level closest to the excited state (processes 1 and 2) prevail. Taking into account the

possibility of the $T \rightarrow S$ transfer, the high quantum yield of fluorescence for anthracene and substituted anthracenes gives grounds for speaking about an increase in the luminescence efficiency. It is seen from the above-said that the chemiluminescence actually occurs in collisional complexes. Only for the benzophenone/anthracene system this process is hampered by the endothermic character of the $T \rightarrow S$ energy transfer and the presence of the $T \rightarrow T$ transfer and is unlikely at low temperatures.

Anthracene/naphthalene systems

As was noted above, earlier we have already studied the complexes of 9,10-substituted anthracene with naphthalene.⁹ The use of corrected parameters has changed (decreased) the position of the triplet state (T_3 in anthracene) having good spin-orbital coupling with the S_1 state. In this case, the channel of the $S_1 \rightarrow T_3$ conversion becomes the main channel of quenching the fluorescence of an isolated anthracene molecule (according to the well known Ermolaev–Sveshnikova rule).

From the results shown in Fig. 2 and in Tables 2 and 3, it is seen that the presence of the $T_4(a)$ level lying below the fluorescent state allows us not only to estimate really the quantum yield of the anthracene fluorescence, but also to study fluorescence quenching in complexes based on its variations.

The efficiency of fluorescence in the DCA/N complex (Fig. 2b) was also affected by the rise of the $T_5(\pi\sigma^*)$ level, for which the very strong spin-orbital coupling with the S_1 state was noticed earlier in Ref. 9. In the DBA/N complex (Fig. 2c), on the contrary, the level $T_5(\pi\sigma^*)$ went down and the additional channel of $S_1 \rightarrow T_5$ conversion arose, thus causing a sharp decrease in the efficiency of fluorescence in this system (see Table 3).

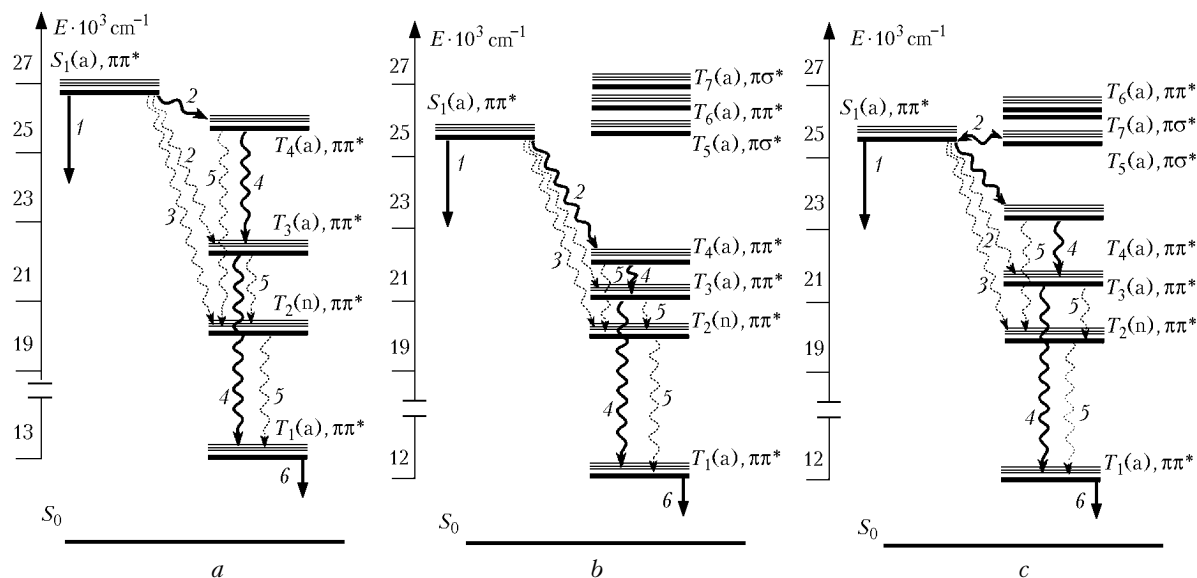


Fig. 2. Schemes of electronic states and photochemical processes in molecular complexes: anthracene/naphthalene (a), 9,10-dichloranthracene/naphthalene (b), and 9,10-dibromanthracene/naphthalene (c): fluorescence (1), intersystem crossing (2), singlet-triplet energy transfer (3), internal conversion (4), triplet-triplet energy transfer (5), and phosphorescence (6). Thin lines are for the processes arising in the collisional complexes, and thick lines are for the continuous processes. The processes of vibrational relaxation are omitted.

Table 2. Rate constants of the processes in 9,10-substituted anthracene with naphthalene

Complexes Processes Conformations	A/N					DCA/N				
	k_r	$k_{S_1 \rightarrow T_4}$	$k_{T_3 \rightarrow T_2}$	$k_{T_3 \rightarrow T_1}$	$\gamma_{fl}, (\%)$	k_r	$k_{S_1 \rightarrow T_4}$	$k_{T_3 \rightarrow T_2}$	$k_{T_3 \rightarrow T_1}$	$\gamma_{fl}, \%$
	$8.3 \cdot 10^7$	$5.7 \cdot 10^8$	$7.1 \cdot 10^8$	$1.2 \cdot 10^8$	10	$8.8 \cdot 10^7$	$6.7 \cdot 10^8$	$1.1 \cdot 10^9$	$1.4 \cdot 10^8$	12
	$6.1 \cdot 10^7$	$9.7 \cdot 10^8$	$1.1 \cdot 10^9$	$1.8 \cdot 10^8$	6	$7.7 \cdot 10^7$	$4.6 \cdot 10^8$	$1.0 \cdot 10^9$	$1.8 \cdot 10^8$	14
	$6.8 \cdot 10^7$	$4.5 \cdot 10^8$	$5.3 \cdot 10^8$	$9.5 \cdot 10^7$	13	$8.4 \cdot 10^7$	$4.0 \cdot 10^8$	$3.1 \cdot 10^8$	$1.5 \cdot 10^8$	14
	$1.3 \cdot 10^8$	$3.3 \cdot 10^8$	$2.5 \cdot 10^7$	$1.3 \cdot 10^8$	28	$1.4 \cdot 10^8$	$2.5 \cdot 10^8$	$1.2 \cdot 10^3$	$1.5 \cdot 10^8$	35
5 Å	$1.1 \cdot 10^8$	$4.2 \cdot 10^8$	7.5	$1.2 \cdot 10^8$	21	$1.1 \cdot 10^8$	$3.4 \cdot 10^8$	$8.3 \cdot 10^2$	$1.5 \cdot 10^8$	25
20 Å	$1.3 \cdot 10^8$	$3.5 \cdot 10^8$	0	$1.2 \cdot 10^8$	27	$1.4 \cdot 10^8$	$2.8 \cdot 10^8$	0	$1.5 \cdot 10^8$	33

Table 3. Rate constants of the processes in the DBA/N complex

Processes Conformations	k_r	$k_{S_1 \rightarrow T_4}$	$k_{S_1 \leftrightarrow T_5}$	$k_{S_1 \rightarrow T_2}$	$k_{T_4 \rightarrow T_3}$	$k_{T_4 \rightarrow T_2}$	$k_{T_3 \rightarrow T_2}$	$k_{T_3 \rightarrow T_1}$	$k_{T_2 \rightarrow T_1}$	$\gamma_{fl}, \%$
		$8.2 \cdot 10^7$	$2.0 \cdot 10^9$	$3.6 \cdot 10^{10}$	$3.1 \cdot 10^5$	$2.3 \cdot 10^9$	$1.8 \cdot 10^8$	$1.2 \cdot 10^9$	$1.2 \cdot 10^8$	$1.3 \cdot 10^6$
	$8.0 \cdot 10^7$	$7.0 \cdot 10^8$	$6.1 \cdot 10^9$	$7.6 \cdot 10^5$	$6.7 \cdot 10^9$	$1.7 \cdot 10^6$	$2.4 \cdot 10^8$	$1.3 \cdot 10^8$	$3.7 \cdot 10^6$	1
	$8.7 \cdot 10^7$	$1.0 \cdot 10^9$	$1.3 \cdot 10^{10}$	$2.2 \cdot 10^7$	$6.4 \cdot 10^9$	$2.2 \cdot 10^6$	$2.8 \cdot 10^7$	$1.2 \cdot 10^8$	$7.9 \cdot 10^5$	0.1
	$1.3 \cdot 10^8$	$3.5 \cdot 10^8$	$2.5 \cdot 10^{11}$	$2.7 \cdot 10^6$	$7.2 \cdot 10^9$	2.4	$3.1 \cdot 10^2$	$1.3 \cdot 10^8$	$5.9 \cdot 10^3$	0
5 Å	$1.1 \cdot 10^8$	$5.1 \cdot 10^8$	$5.8 \cdot 10^9$	$2.8 \cdot 10^3$	$6.7 \cdot 10^9$	2.4	$6.3 \cdot 10^2$	$1.6 \cdot 10^8$	2.3	2
20 Å	$1.3 \cdot 10^8$	$4.2 \cdot 10^8$	$4.4 \cdot 10^9$	0	$6.8 \cdot 10^9$	0	0	$1.3 \cdot 10^8$	0	3

Analysis of the calculated rate constants of photophysical processes and quantum yields of fluorescence for different conformations of the complexes showed (see Tables 2 and 3) that quenching of fluorescence occurs not only due to the increase of k_{ST} of the approaching molecules, but also due to a decrease in the rate constant of radiative decay $k_r(S_1)$.

The EEET mostly follows the channel $T_3(a) \rightarrow T_2(n)$ at the minimum contact distances after transitions $S_1 \rightarrow T_4(a)$ and $T_4(a) \rightarrow T_3(a)$. The direct $S_1(a) \rightarrow T_2(n)$ transfer is inefficient even at the contact distances, what is reflected in Table 3. This allows us to draw the conclusion that quenching of the fluorescence is independent of EEET. This is indicated, in particular, by the fact that at the distance of 5 Å between molecules the probability of all the considered ways of EEET is very low, whereas the fluorescence quenching takes place.

At the contact distances, competition between $T_3(a) \rightarrow T_2(n)$ and $T_3(a) \rightarrow T_1(a)$ processes is possible, what can lead to appearance of naphthalenes excited to the triplet state (see Table 3). Similar probability exists in other systems considered, as well. At the distance of 20 Å, molecules have no marked resonance-exchange interaction and can be treated as isolated.

Conclusion

Thus, as a result of quantum-chemistry studies of photoprocesses in the selected systems, it was found that:

- in benzophenone/anthracenes systems, chemiluminescence actually intensifies due to the $T \rightarrow S$ EEET;
- in the anthracenes/naphthalene complexes, the fluorescence efficiency decreases due to the decrease of k_r and the growth of the spin-orbital interaction in the anthracene in the presence of naphthalene;

- the direct $S \rightarrow T$ transfer is unlikely at the contact distance between the interacting molecules;
- appearance of triplet naphthalenes is possible due to the $T \rightarrow T$ EEET.

It should be noted in conclusion that the differences in the relative arrangement of molecules and distances between them for all the considered systems affect the energy levels, but do not affect the general pattern of excitation deactivation in contact bimolecular complexes. At the distances longer than 5 Å, molecules interact only weakly and can be treated as isolated.

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