

EXCITED STATES OF INTERMOLECULAR ELECTRON-DONOR-ACCEPTOR SYSTEMS AND INTERNAL GEOMETRY OF COMPLEX' COMPONENTS

I. DEPERASIŃSKA* AND A. SOBIERAJ

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

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In this work we present the results of semiempirical AM1 calculations of the energy of electron-donor-acceptor system in the ground and excited states with full optimization of the complex geometry (in terms of both: intermolecular and intramolecular coordinates). A comparison of these results with those obtained for separated acceptor and donor molecules enables the estimation of the energetic effects of changes in internal structure of donor and acceptor which accompany the process of formation and stabilization of excited charge-transfer state. It is shown that energies corresponding to those changes are comparable with the energy of intermolecular interactions between donor and acceptor molecules.

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1. Introduction

An electron-donor-acceptor (EDA) complex [1] is formed in the ground state as a result of dynamic equilibrium



between the electron acceptor (A) and electron donor (D) and the complex (AD). In the case of organic molecules A and D an (AD) complex is essentially a large-size "supermolecule" and hence a modelling of the properties of EDA complexes with the use of advanced methods of quantum chemistry is very frequently performed only in terms of intermolecular coordinates at frozen geometrical structures of the

*e-mail: deper@ifpan.edu.pl, fax: (48-22) 843-09-26

donor and acceptor molecules [2-7] — thus bypassing the problem of internal structure of complex' components. Such an assumption may be acceptable in the case of very weak complexes (this is often the case of EDA system in the ground state) but it may be insufficient for the description of the excited charge-transfer (CT) states in which interactions between A and D are relatively strong [1-4, 6, 7]. The experimental investigations of the excitation and fluorescence spectra of EDA systems indicate that vibrational frequencies of the component molecules are changing upon the formation of the complex [3, 6, 8]. This means that the internal structure of complex' components changes, however an estimation of the contribution of energy due to such changes to the energy of formation of CT state has been discussed only occasionally [9-11] and still remains an open question.

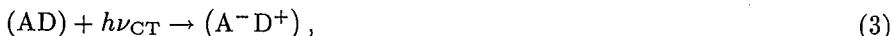
This problem is the central issue of the present study and is quantitatively treated for the EDA system of 1,2,4,5-tetracyanobenzene (TCNB) and diethylaniline (DEA). We investigate the energetic effects of the changes of the internal structure of complex' components for two well-known ways of formation and stabilization of CT state of EDA system, namely for:

(i) the exciplex reaction [2, 3, 6] which takes place between the primarily excited acceptor (donor) molecule and unexcited donor (acceptor) molecule



where $h\nu_A$ is the excitation energy of isolated acceptor molecule and (A^-D^+) denotes CT state of EDA system;

(ii) the relaxation of excited EDA complex (i.e. where the process of relaxation begins after the excitation of EDA complex in its ground state):



where $h\nu_{CT}$ is the excitation energy of complex.

2. Outline of the analysis procedure

The potential energy of EDA system in a given electronic state (m) can be described as a sum of the potential energies of intramolecular interactions in the acceptor and in the donor molecules and the intermolecular donor-acceptor interactions

$$E_{\text{tot}}^m(Q_A, Q_D, Q_{AD}) = E_A^m(Q_A, Q_D, Q_{AD}) + E_D^m(Q_A, Q_D, Q_{AD}) + E_{AD}^m(Q_A, Q_D, Q_{AD}), \quad (4)$$

where Q_A , Q_D represent sets of intramolecular (internal) coordinates for the acceptor and donor, respectively and Q_{AD} is the set of intermolecular coordinates for the donor-acceptor system. Thus, Eq. (4) describes the potential energy surface (PES) of the complex in the multidimensional space of both intermolecular and intramolecular coordinates. The minimum of energy of PES for m -th electronic state of the complex can be determined in the course of the optimization procedure and corresponds to a particular set of coordinates (Q_A^m, Q_D^m, Q_{AD}^m). It should be born in mind that due to the presence of the intermolecular interactions in the system the internal structures of the donor and acceptor molecules (described by

(Q_A^m) and (Q_D^m) intramolecular coordinates, respectively) can be different from the structures of the isolated (non-interacting) molecules of the acceptor and donor molecules (described for instance by the (q_A^m) and (q_D^m) coordinates, respectively).

Thus, the first step of the procedure must be the full optimization of the geometry of the TCNB-DEA complex (and separately of its components) which in this work is performed within the semi-empirical AM1 method [12] with configuration interactions for microstates. This leads to:

(i) the optimized structures (Q_A^m, Q_D^m, Q_{AD}^m) of the complex in the ground (S_0) and first excited (S_1) singlet states, (i.e., for either $m = S_0$ or S_1) — hereafter these structures are abbreviated as G_{AD} and V_{AD} , respectively,

(ii) the optimized structures of each isolated complex' components (q_A^m) and (q_D^m) in their ground, excited and ionic states, (i.e., $m = S_0, S_1$, and J , respectively) — hereafter these structures are abbreviated as G, V , and J , respectively.

The second step is the analysis of the PES of the excited state of the complex for both the exciplex reaction (2) and direct excitation of EDA complex (3).

3. Results

3.1. Optimized structures

The AM1 geometrical structures of the complex, optimized in the ground state (G_{AD}) and in the lowest excited state (V_{AD}), are shown in Fig. 1. It is seen that:

(i) the relative orientations of the donor and acceptor molecules in the G_{AD} and V_{AD} structures of the complex are distinctly different (e.g. the intermolecular distances are 3.8 and 4.8 Å for V_{AD} and G_{AD} structure, respectively),

(ii) the conformations of $-N(C_2H_5)$ group of DEA are different in both considered cases — this is a clear example of the changes of the internal geometry of the complex' components related to different interactions in the ground and excited states of the complex.

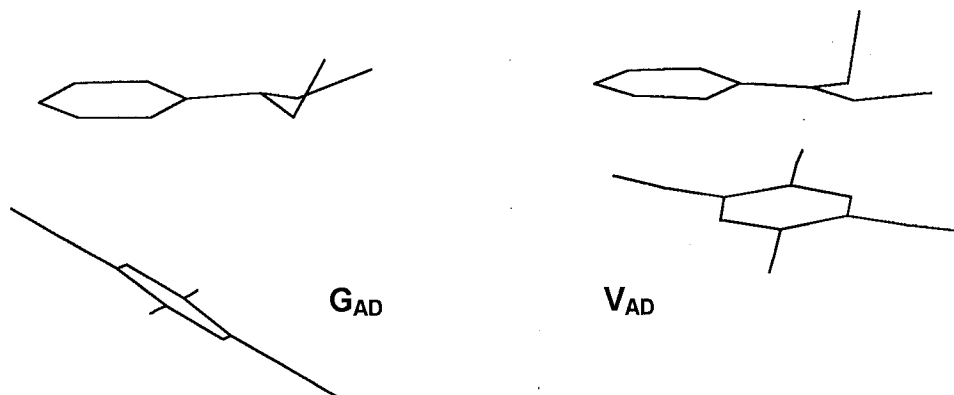


Fig. 1. Geometrical structures of TCNB-DEA complex calculated by AM1 method: G_{AD} (optimized in the ground S_0 state) and V_{AD} (optimized in the excited S_1 state).

The optimized structures of each isolated complex' component in their ground, excited and ionic states (i.e., $m = S_0, S_1$, and J states — hereafter these structures are abbreviated as G, V, and J, respectively) have been carried out earlier [7, 13]. The analysis of the ground state G-structures of isolated donor and acceptor molecules has shown that for all practical purposes their geometries are the same as the geometries found for G_{AD} structure of their complex (i.e. $Q_A^{S_0} \cong q_A^{S_0}$ and $Q_D^{S_0} \cong q_D^{S_0}$).

For each optimized structure of the complex and of isolated donor and acceptor molecules in a given, specified electronic state one can calculate the full energy diagram. In Table I the results of calculations of energy levels for G_{AD} and V_{AD} optimized structures of TCNB-DEA complex are collected and similarly Table II collects the results of calculated energies of the various electronic states (i.e., ground, excited, and ionic) of discussed geometrical structures of the donor (DEA) and acceptor (TCNB) molecules.

TABLE I

Results of AM1 calculations for TCNB-DEA system — the energies of the complex in different electronic states for G_{AD} and V_{AD} geometrical structures (in bold — energy of this state in which a given structure was optimized). Zero of the energy scale corresponds to the energy of separated donor and acceptor molecules in their optimized ground states. In the last column — transition energies between S_0 and S_i states — abbreviations CT (charge-transfer) and LE (locally excited) describe character of transition [2, 7, 9] (in italic — energies of CT transitions).

Geometric structure		Electronic state	Energy in S_i state [cm^{-1}]	Energy of transition between S_0 and S_i states [cm^{-1}]	
G_{AD}	Optimization of the complex geometry in the ground state S_0	S_0	- 390		
		S_1	32620	<i>33010</i>	CT
		S_2	33710	34100	LE
		S_3	35590	35980	LE
		S_4	37580	<i>37970</i>	CT
V_{AD}	Optimization of the complex geometry in the excited state S_1	S_0	2540		
		S_1	27350	<i>24810</i>	CT
		S_2	33370	<i>30830</i>	CT
		S_3	36500	33960	LE
		S_4	37550	35010	LE

Since all energy levels in such diagrams correspond to the same (unchanged) geometry of the molecule (or complex), the differences of the electronic energy between the levels are formally corresponding to the energies of Franck-Condon transitions. However, such energy diagrams have a physical meaning reflected in the observed spectroscopic properties of the molecules under considerations. For example, transitions from the ground (S_0) state to the excited (S_m) states in the

TABLE II

Results of AM1 calculations for TCNB and DEA molecules. Zero energy for each molecule corresponds to the energy of S_0 state for G geometry (results of calculations for G-structures were discussed in our previous works [7, 13]).

Molecule	Geometric structure	A_A , electron affinity I_D , ionization potential	Electronic state	Energy in S_i state [cm^{-1}]	Energy of transition between S_0 and S_i states [cm^{-1}]
TCNB	G	Optimization in th. ground state $A_A = 2.16$ eV	S_0	0	
			S_1	34040	34040
			S_2	35950	35950
	V	Optimization in the excited state $A_A = 2.20$ eV	S_0	330	
			S_1	33710	33380
			S_2	35770	35440
J	Optimization in the ionic state $A_A = 2.27$ eV	S_0	450		
		S_1	34300	33850	
			S_2	35510	35060
DEA	G	Optimization in the ground state $I_D = 8.28$ eV	S_0	0	
	J	Optimization in the ionic state $I_D = 7.80$ eV	S_0	980	

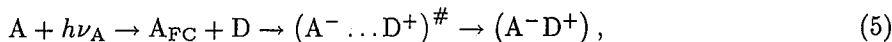
diagrams for the G-type structures correspond to the absorption spectra while the emission spectra can be correlated with the transitions from the first excited (S_1) state to the ground (S_0) state in the diagrams for V-type of structures.

The analysis of the data of Tables I and II leads to the following immediate conclusion — the stabilization energy of the complex in G_{AD} structure in the ground state is 390 cm^{-1} (cf. Table I). As was mentioned earlier the geometries of both the isolated donor and acceptor molecules are practically the same as those in G_{AD} structure of their complex and this leads to the conclusion that this value of the energy of formation is practically determined by the intermolecular interactions between the donor and acceptor. In general, such small values of the energy of formation are characteristic of weak van der Waals complexes [3, 6].

In the case of the V_{AD} structure of the complex the estimation of the energy related to the formation of CT excited state is not that straightforward due to the fact that one should take into account two different reaction schemes of the formation of relaxed CT state (either reaction (2) or reaction (3)) which start from different initial geometrical structures of complex' components and follow different pathways on the PES of the system.

3.2. Exciplex reaction and the changes of internal structure of complex' components

An exciplex reaction takes place between the primarily excited acceptor (donor) molecule and unexcited donor (acceptor) molecule and the reaction scheme (2) can be written as



where $h\nu_A$ is the excitation energy of isolated acceptor molecule, A_{FC} denotes acceptor in the excited Franck–Condon state and the reaction proceeds through the transient state $(A^- \dots D^+)^\#$ known also as an “encounter complex” [14]. The electronic and geometrical structures of this transient state are not well-specified and are the key problems in the discussion of kinetics and dynamics of the photoinduced intermolecular electron (charge) transfer processes [10, 13–18]. However, in the discussion of the energetics of reaction (5) the important factors are its initial and final states.

The final state of reaction (5) is the charge-transfer excited S_1 state of V_{AD} optimized structure. Its energy is 27350 cm^{-1} (cf. Table I). In the initial state of this reaction the substrates, i.e., an excited acceptor (A_{FC}) and donor in its ground state (D), have both the geometries and energies relevant to G-type optimized structures of isolated (and separated, noninteracting) molecules — thus the total energy of the initial state is 34040 cm^{-1} (cf. Table II). The difference between these two energies is equal to 6690 cm^{-1} and may be treated as the exciplex' formation energy released upon the interactions within the EDA system. As mentioned in the Introduction such interactions are optimizing not only the structure of the complex (relative orientation of the donor and acceptor) but also the internal structure of the components of the complex. The estimation of the individual contributions connected with the inter- and intramolecular geometry changes can be performed by means of analysis of potential energy surfaces of excited S_1 states corresponding to relevant optimized structures of the complex and its components. In order to simplify the problem we limit the analysis of PES to their cross-sections along the main intermolecular coordinate, which describes intermolecular A–D distance. The results of this analysis are collected in Fig. 2, which illustrates the potential energy curves of excited S_1 states for:

(1) exciplex in V_{AD} structure (full optimization of inter- and intramolecular coordinates),

(2) exciplex which is formed by A^* and D molecules in “frozen” geometries corresponding to the G-structures of isolated molecules

(3) exciplex which is formed by A^* molecule in “frozen” geometry corresponding to its V- structure and D molecule in “frozen” geometry corresponding to its G-structures.

Cases 2 and 3 are reflecting two possible initial states of reaction (5) as inferred and established by the spectroscopic investigations of jet-cooled exciplexes [10, 15–17]. In the case 2 the exciplex formation process is considered to begin from the non-relaxed excited Franck–Condon state of A^* , i.e., the electron transfer process is a rapid one and it is followed by reorganization of the ion pair.

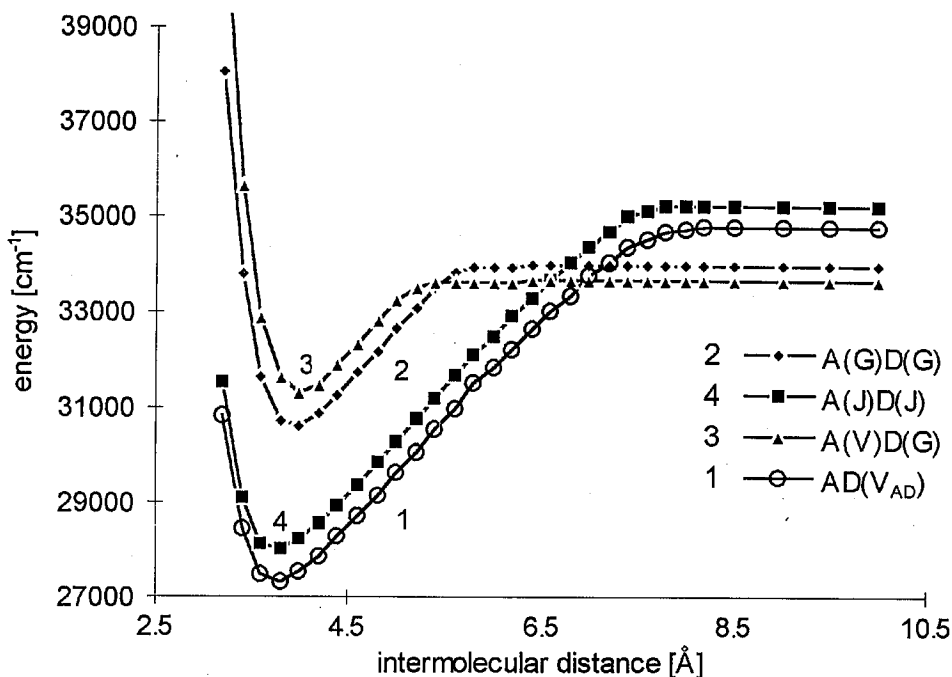


Fig. 2. Cross-sections of the potential energy curves in the excited S_1 state of TCNB-DEA complex along the intermolecular distance for different internal geometries of component molecules. In all cases the angular intermolecular orientation of the donor and acceptor is the same and as the intermolecular orientation determined for V_{AD} structure of the complex. (The energies of minima are: 27350 cm^{-1} , 30600 cm^{-1} , 31400 cm^{-1} , and 28050 cm^{-1} for curves 1, 2, 3, and 4, respectively.).

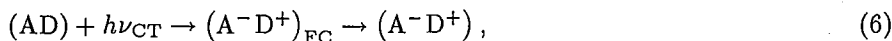
In the case 3 the process of formation begins from the relaxed excited state of A^* , i.e., the electron transfer process is a slow one, and takes place after the vibronic relaxation within the A^* .

It is easily seen in Fig. 2 that the intermolecular equilibrium distances corresponding to the minima of energy of curve 1 and/or 2 are very close to the equilibrium distance for curve 3 (they differ by *ca.* $0.1\text{--}0.2\text{ \AA}$). Therefore, we can assume that the energy of intermolecular interactions (which control the changes of the exciplex structure along the intermolecular distance coordinate) is practically the same in all three cases under consideration. With this assumption the energy differences of the minima of either curves 1 and 2 or curves 1 and 3 can be identified as the energy connected with the changes of the internal structure of A and D upon the formation of exciplex. Since the energy of minimum of curve 2 is 30600 cm^{-1} and that of curve 3 is 31400 cm^{-1} (cf. Fig. 2) while the energy of minimum of curve 1 is 27350 cm^{-1} we arrive at the value of $\sim 3200\text{--}4000\text{ cm}^{-1}$ as the contribution connected with the changes of internal structure of A and D to the total exciplex' formation energy (which equals $\sim 6700\text{ cm}^{-1}$ as found above). At first glance such a contribution from the changes of internal structure of the complex' components which is almost 50-60% of the total energy of formation

of exciplex might seem surprisingly large. One should remember, however, that although the electronic configuration in both initial states (curve 2 or 3) of the reaction (5) is of charge transfer character, the electron has been transferred (or redistributed) between A and D with their internal geometries "frozen" as molecular geometries (in G or V molecular structures). On the other hand CT character of excited exciplex (S_1 state of V_{AD} structure) is inherently connected with the geometrical structures of its components of ionic type (J-type molecular structures, cf. Table II). This is clearly demonstrated if one takes into account the case illustrated by curve 4 in Fig. 2, which corresponds to the case of exciplex formed by A and D molecules in "frozen" geometries of the ionic J-structures of isolated molecules. And although this case cannot be treated as the initial state for the exciplex formation reaction (one could roughly identify such a state with the "encounter complex"), it is seen that the energy related to the changes of internal structures of complex' components is only 700 cm^{-1} (energy difference between the minima of curves 4 and 1).

3.3. Relaxation of excited EDA complex and changes of internal structure of complex' components

As defined by Eq. (3) another way of creation of excited CT state of EDA system is realized by the direct excitation of ground-state-stable EDA complex and in more detailed fashion the reaction scheme can be rewritten as



where $(A^-D^+)_{FC}$ is initially excited Franck-Condon CT state which subsequently relaxes to the (A^-D^+) excited CT state. As discussed in Sec. 3.1 the excited Franck-Condon state of the complex (reached upon absorption) is the S_1 excited state in G_{AD} structure while the excited CT state (initial for the emission) is the S_1 excited state optimized in V_{AD} structure. Thus, the energy difference between the S_1 states in both structures can be formally treated as the relaxation energy connected with the transition (radiationless) from G_{AD} to V_{AD} structure.

According to data of Table I the relaxation energy equals 32620 cm^{-1} (G_{AD}) $- 27350 \text{ cm}^{-1}$ (V_{AD}) = 5270 cm^{-1} . Similarly to the above-discussed case of exciplex formation also in this case the value of relaxation energy has two contributions connected either with the changes of inter- or intramolecular geometrical structures of the system. These contributions can be found by means of analysis of the pathways along intra- and intermolecular coordinates between the points on PES of the S_1 excited state of the system. In the case under consideration these points are defined by:

- (a) energy of the excited Franck-Condon state of G_{AD} structure, and
- (b) energy of the minimum of excited V_{AD} structure,

which are specified just above.

In order to simplify the problem we reduce the multidimensional PES to the two-dimensional space, for two kinds of generalized coordinates, intermolecular $Q_{AD} = \{Q_{AD}\}$ and intramolecular $Q_{IN} = \{Q_A, Q_D\}$. The generalized coordinates are created by the composition of linear change of all coordinates of a given type between two specified points of PES of S_1 . With such a procedure the reaction

pathway between G_{AD} and V_{AD} points can be separated into paths followed along the intramolecular and intermolecular coordinates, as shown on the sector of calculated PES reproduced in Fig. 3. It is seen that there are two possible ways of the transition from G_{AD} to V_{AD} point:

(1) from G_{AD} to A along the intermolecular coordinate Q_{AD} (i.e., for $Q_{IN} = \text{const}$) and then from A to V_{AD} along the intramolecular coordinate ($Q_{AD} = \text{const}$). The energy connected with the first path is *ca.* 3100 cm^{-1} and the energy with the second path is *ca.* 2100 cm^{-1} .

(2) from G_{AD} to B along the intramolecular coordinate Q_{IN} (i.e., for $Q_{AD} = \text{const}$) and then from B to V_{AD} along the intermolecular coordinate ($Q_{IN} = \text{const}$). The energy connected with the first path is *ca.* 1800 cm^{-1} and the energy with the second path is *ca.* 3400 cm^{-1} .

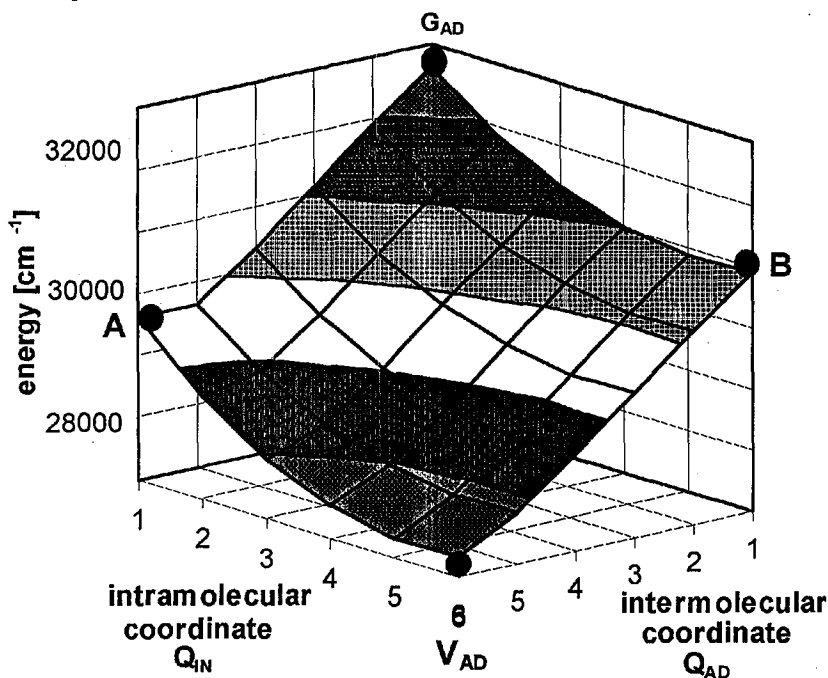


Fig. 3. Potential energy surface in the S_1 excited state of TCNB-DEA (see the text for details).

Thus, as could be expected, the total relaxation energy (a sum of both contributions) from the excited Franck-Condon CT state to the CT state is independent of the pathway between the initial and final points of PES. One can see, however, that the value of energy related to changes of either intramolecular or intermolecular coordinates depends on the pathway followed (i.e., case 1 or case 2). It is obvious that the differences of the energy value of particular contribution are not of physical importance as the changes of intra- and intermolecular coordinates in the real system are completed between the final and initial points (G_{AD} and V_{AD}) in more or less concerted way. What is important, however, is the fact that, sim-

ilarly to the above-discussed case of exciplex formation, also in the case of EDA complex the total energy of relaxation is clearly divided into two comparable contributions connected with the change of intermolecular structure of complex as well as with the changes of internal structures of the complex' components.

4. Concluding remarks

The present results are clearly demonstrating that in the process of the formation of the excited state of EDA system the changes of the electronic as well as of geometrical structure of the donor and acceptor molecules must be considered as equally important as the changes of the structure of their complex (changes in relative orientation of the donor and acceptor within the complex). We arrive at this conclusion as a result of analysis of potential energy surfaces of excited states of EDA system, which also reveals (cf. Secs. 3.2 and 3.3) the role of the initial states in the reaction of exciplex formation or in the relaxation of excited CT Franck-Condon state of EDA complex. The changes of the internal structure of the complex' components would control the main parameters of the charge (electron) transfer reaction, i.e., the ionization potential of donor and electron affinity of acceptor molecules. Therefore, they would influence the energetics and rate constants of the reaction and if taken into account may be of use in the understanding of the initial step of photoinduced charge-transfer reaction, i.e., in the understanding of the changes of electronic and geometrical structure of EDA system in a transient state (an encounter complex) of the reaction [10, 13-18], as well as the experimentally observed [6, 17, 19] departures from the so-called two-state kinetic model of exciplex formation [20].

Acknowledgments

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