Unified Interpretation of Exciplex Formation and Marcus Electron Transfer on the Basis of Two-Dimensional Free Energy Surfaces[†]

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The mechanism of exciplex formation proposed in a previous paper has been refined to show how exciplex formation and Marcus electron transfer (ET) in fluorescence quenching are related to each other. This was done by making simple calculations of the free energies of the initial (DA*) and final (D^+A^-) states of ET. First it was shown that the decrease in D−A distance can induce intermolecular ET even in nonpolar solvents where solvent orientational polarization is absent, and that it leads to exciplex formation. This is consistent with experimental results that exciplex is most often observed in nonpolar solvents. The calculation was then extended to ET in polar solvents where the free energies are functions of both D−A distance and solvent orientational polarization. This enabled us to discuss both exciplex formation and Marcus ET in the same D−A pair and solvent on the basis of 2-dimensional free energy surfaces. The surfaces contain more information about the rates of these reactions, the mechanism of fluorescence quenching by ET, etc., than simple reaction schemes. By changing the parameters such as the free energy change of reaction, solvent dielectric constants, etc., one can construct the free energy surfaces for various systems. The effects of free energy change of reaction and of solvent polarity on the mechanism and relative importance of exciplex formation and Marcus ET in fluorescence quenching can be well explained. The free energy surface will also be useful for discussion of other phenomena related to ET reactions.

1. Introduction

Fluorescence quenching by electron transfer (ET) has attracted much attention for many years. This is probably because ET is one of the most fundamental chemical reactions, and also because it is important in many chemical and biological processes. In their pioneering paper, Leonhardt and Weller[1] reported that solvent polarity strongly affects the mechanism of fluorescence quenching by ET: in polar solvents quenching occurs by full ET from the electron donor (D) to the excited acceptor (A) (D^+ and/or A^- ions are detected), but in nonpolar solvents only the formation of an excited-state charge-transfer complex (later named the exciplex) is observed (exciplex fluorescence is detected). Similar results were also reported for many other D−A systems.[2−4] In the 1990s a modification was made that for D−A pairs with smaller $-\Delta G^{\mathrm{AN}}$ values (ΔG^{AN} is the free energy change of ET in acetonitrile (AN) solvent), exciplex formation is responsible for quenching even in highly polar solvents such as AN.[5−7] In these papers it was reported that full ET occurs at distances longer than the contact distances of D and A to form a solvent-separated ion pair (SSIP). Studies of fluorescence quenching by ET have been extended to shorter times using picosecond and femtosecond spectroscopy.[8] Recently, it has been reported by measuring the rate of charge recombination of D^+ and A^- formed through ET quenching that in AN (a nonviscous solvent), ET quenching occurs at distances shorter than was thought, to form a loose ion pair (LIP) rather than to form a SSIP.[9,10] This has been attributed to the fast diffusion of D and A* compared to ET at longer distances in this solvent.

It has been established that full ET leading to free ion formation is explained by Marcus nonadiabatic theory. In Marcus theory, ET occurs when the free energies[11] of the initial and final states coincide as a result of change of solvent coordinate (coordinate representing solvent orientational polarization; see eq 6 below). Therefore, the solvent orientational polarization coordinate is relevant to this type of ET. On the other hand, the coordinate that is relevant to exciplex formation is not yet clear. Some exciplexes have been shown to have almost pure ion pair structure, i.e., they are strongly charge-separated.[13] In many cases exciplex formation occurs more efficiently in nonpolar solvents than in polar solvents. In the case of nonpolar solvent, solvent orientational polarization is absent. This indicates that some coordinate other than solvent orientational polarization is relevant to exciplex formation (or ET) in nonpolar solvent.

In previous papers[14−20] we reported quenching of fluorescence of cyanoanthracenes (A) by aniline derivatives (D). Measurements were made at quencher concentrations higher than ∼0.1 M where the fluorescence decay curves are nonexponential at short times (the transient effect in fluorescence quenching). At concentrations 0.1−0.3 M,[14−17] the measurements were made by picosecond time-correlated single photon counting in highly viscous solvents ethylene glycol (polar) and liquid paraffin (nonpolar). Viscous solvents were employed to make the transient effect more prominent, so that the ET parameters can be extracted from the experimental results. By analyzing the decay curves, the ET parameters and thus the distance dependence of the reaction rate were determined. The reactions were found to occur at distances longer than the contact distances.

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The effect of diffusion on ET was also studied by Fayer and co-workers.[21−24] In a recent paper they reported that the ET distance in viscous solvents is longer than the contact distances and it decreases with decreasing solvent viscosity.[24]

Recently, we have made measurements at quencher concentrations higher than 0.3 M in AN solvent by femtosecond upconversion.[18−20] The decay curves at longer times (longer than 2 ps) can be reproduced well using the parameters obtained in the picosecond experiment. At shorter times, however, we found an additional decay component that disappears in less than 2 ps and the decay curve cannot at all be reproduced by the above parameters (see Figures 1 and 2 of ref 18). This shows that the fluorescence of cyanoanthracenes is quenched by ET in two different ways simultaneously. When the donor *N*,*N*-dimethylaniline was used as solvent, the decay time (210 fs) of acceptor fluorescence was equal to the rise time (220 fs) of exciplex fluorescence. From this result it was concluded that the faster quenching is due to exciplex formation between D and A, which happen to be very close to each other when A is excited, and that the exciplex is formed directly upon quenching. Similar ultrafast fluorescence quenching in donor solvents has been found by several other groups,[26−31] and the dynamic behaviors of the exciplex have been reported.[30,31]

On the basis of these experimental results, we proposed a mechanism of exciplex formation in fluorescence quenching.[19,32] In this model (Figure 6 of ref 19), the mixing of the DA* and D^+A^- states at short distances as a result of strong interaction between D and A occurs to produce an exciplex state. The exciplex state can be reached when D and A* approach each other. This model can explain the experimental result that the exciplex is directly formed upon quenching of acceptor fluorescence.

Although the model is consistent with the above experimental result and gives some insight into the mechanism of exciplex formation, it is not sufficient for the following reasons. As described above, it is well-known that the solvent polarity strongly influences the exciplex formation processes. In the above model, however, the solvent plays practically no role and, consequently, the model cannot explain the influence of solvent. A new model is required to account for the solvent effect. In addition, the relation between exciplex formation and Marcus ET should be clarified. In a broad sense they are both electron transfer, but entirely different models have been used so far to explain their mechanisms. The model used to explain Marcus ET cannot explain exciplex formation, and the model we proposed for explaining exciplex formation cannot explain Marcus ET, either. It is desirable to develop a new model to explain the two types of ET in a unified manner and resolve these two problems.

In the present paper, we show that we can treat ET between D and A* (or between D* and A) in nonpolar and polar solvents in a unified manner by introducing solvent orientational polarization and D−A separation as the reaction coordinates for ET, and considering 2-dimensional free energy surfaces of the initial and final states as functions of the two coordinates. For simplicity we hereafter consider ET between D and A*. ET occurs when the free energies of the initial and final states coincide. The free energies of the initial and final states change when the solvent orientational polarization or the D−A separation changes. In nonpolar solvents, the solvent orientational polarization is zero, so coincidence between the free energies of the initial and final states is induced only by change of D−A separation. In polar solvents Marcus theory assumes that energy matching is induced by change of solvent orientational polarization. However, in the present more general framework of 2-dimensional free energy surfaces energy matching is induced in polar solvents not only by change of solvent orientational polarization but also by that of D−A separation.

Among various processes involved in the system of D and A*, we confine ourselves to reactions that lead to Marcus ET or exciplex formation. In this case, the minimal set of electronic states is locally excited state DA* and ion pair state D^+A^-. If we consider radiative processes or nonradiative processes other than ET, other electronic states also have to be included, as was done by Bixon et al.[35] and Gould et al.[13] Types of ET which can be treated in the present framework can be nonadiabatic and adiabatic ET. When D and A are very close to each other, the electronic coupling between DA* and D^+A^- states should be large, so ET near the contact distance should be adiabatic. In long-range ET the electronic coupling should be small, so long-range ET should be nonadiabatic.

The new model described in this paper can resolve the two problems mentioned above and will also be used to explain other phenomena related to ET.

2. Nonpolar Solvents: Exciplex Formation

The mechanism of exciplex formation that we proposed previously[19] is essentially that in nonpolar solvents, because the solvent plays practically no role in it. Here we first refine this model. In refs 18 and 19, some experiments were carried out in the donor solvent; i.e., A* molecules were surrounded by D molecules. In many fluorescence quenching experiments, however, the quencher concentration is not so high, and D and A* have to approach each other by diffusion. The free energy G_i of the initial state (DA*) does not depend on the D−A distance r, and we take it as 0. The free energy G_f of the final state (D^+A^-) as a function of r is given by eq 2 (in nonpolar solvents, G_i and G_f are equal to the energies of the initial and final states, respectively).

$$G_i = 0 \tag{1}$$

$$G_f = \Delta G = \Delta G^{AN} + \frac{e^2}{2}\left(\frac{1}{\epsilon_S} - \frac{1}{\epsilon_S^{AN}}\right)\left(\frac{1}{a} + \frac{1}{b} - \frac{2}{r}\right) \tag{2}$$

where ΔG and ΔG^{AN} are the free energy changes of ET in the nonpolar solvent and AN, and ϵ_S and ϵ_S^{AN} are static dielectric constants of the nonpolar solvent and AN, respectively. D and A are assumed to be spherical with radii of a and b (both are 3 Å in this paper), respectively. ΔG^{AN} is almost independent of r, because ϵ_S^{AN} is large enough (37.5) and the Coulomb attraction is strongly shielded.[36] In this paper it is assumed to be constant irrespective of r. The second term on the right-hand side of eq 2 represents the difference in the solvation energy plus Coulomb attraction energy between the nonpolar solvent and AN. At shorter distances, repulsive forces between D and A* (and D^+ and A^-) become important, but they are not incorporated in eqs 1 and 2. In eq 2 the free energy change for a D−A pair in an arbitrary solvent is expressed in terms of that for the same pair in AN. Theoretically, there is no necessity to do so. However, practically, it is in general easier to measure the free energy change in AN; so throughout this paper we specify the identity of a D−A pair by the free energy change for the pair in AN.

ET occurs when the free energies of the initial and final states coincide. In Marcus theory, the energy coincidence is realized by the change of solvent orientational polarization. This is impossible in nonpolar solvents, because the solvent molecules

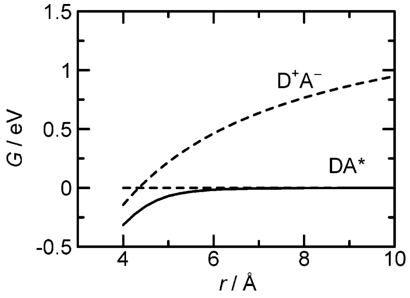


Figure 1. Free energy curves of a D−A pair with $\Delta G^{\mathrm{AN}} = -0.75$ eV in a nonpolar solvent ($\epsilon_{\mathrm{S}} = 1.88$). The broken and solid curves represent the diabatic and adiabatic curves, respectively. The parameter values assumed: molecular radii of D and A are 3 Å, J_0 and β in eq 5 are 0.23 eV at $r_0 = 4$ Å and 1.0 Å^{-1}, respectively. The same values are used throughout this paper. The ground state DA and the triplet states, D^{3}A* and^3(DA)*, to which the DA* or the exciplex state can decay are not shown here.

have no permanent dipole. Equations 1 and 2 are plotted as broken curves in Figure 1 for a D−A pair with $\Delta G^{\mathrm{AN}} = -0.75$ eV ($\epsilon_{\mathrm{S}} = 1.88$, $a = b = 3$ Å). The two curves intersect at a short distance.[37] This shows that ET can occur even in the absence of solvent polarization, if the interaction matrix element H_{12} (see eq 4 below) is sufficiently large. In the case of Figure 1, H_{12} is large enough because the two curves intersect at a small r. Hence ET would occur from D to A in nonpolar solvent, if ΔG^{AN} is around -0.75 eV. The intersection distance increases with $-\Delta G^{\mathrm{AN}}$. However, if the intersection distance remains sufficiently small for a certain range of ΔG^{AN}, ET can occur over that range of ΔG^{AN}. As explained above, the intermolecular distance is another important coordinate relevant to intermolecular ET reactions. This point has not been stressed so far.

Up to now, the interactions between D and A other than Coulomb interaction have been neglected. This is a good approximation at long distances. At short distances, however, quantum-mechanical interactions cannot be neglected. In such cases, the DA* and D$^+$A$^-$ states are no longer pure eigenstates but are mixed with each other near the intersection distance. The mixing will be strong if the energy levels of the two states are close to each other (or the two curves intersect) as in the case of Figure 1. The resulting state ϕ is given by the following equation:

$$\phi = c_1\psi_1 + c_2\psi_2 \tag{3}$$

where ψ_1 and ψ_2 are the wavefunctions of the diabatic states and ϕ represents the adiabatic state. Because in the present case ψ_1 and ψ_2 are DA* and D$^+$A$^-$ states, the interaction is classified as charge-transfer interaction. The interaction is complex and it is not easy to accurately evaluate the interaction energy. Here we just make a simple calculation that is still useful for discussing the ET mechanism.

If the energies of ψ_1 and ψ_2 are E_1 and E_2 ($E_1 \leq E_2$), respectively, the energies of the new (adiabatic) states are given by the following equation.[39]

$$\begin{aligned} E_{\pm} &\approx \frac{E_1 + E_2}{2} \pm \frac{\sqrt{{\Delta_{12}}^2 + 4{H_{12}}^2}}{2} \\ \Delta_{12} &= |E_1 - E_2| \\ H_{12} &= \langle \psi_1 | H | \psi_2 \rangle \end{aligned} \tag{4}$$

The overlap integral $S_{12} = \langle \psi_1 | \psi_2 \rangle$ was neglected. H_{12} is the electronic coupling matrix element and is assumed to decrease exponentially with distance.

$${H_{12}}^2 = {J_0}^2 \exp[-\beta(r - r_0)] \tag{5}$$

The result of calculation based on eq 4 is shown by the solid curve in Figure 1 for $J_0 = 0.23$ eV[40] at $r_0 = 4$ Å and $\beta = 1$ Å^{-1}. Only the low-energy branch (with energy E_-) is shown, because ET occurs along that branch. Indeed, the energy changes significantly at short distances and the ET reaction becomes adiabatic. The energy difference $E_1 - E_-$ is the stabilization energy due to the charge-transfer force, and it increases with increasing H_{12} and decreasing Δ_{12}.

The adiabatic state given by eq 3 and shown by the solid curve in Figure 1 is a mixture of the DA* and D$^+$A$^-$ states. This is the exciplex state.[41−45] The electronic structure of the exciplex changes with distance. At distances longer than the intersection distance, the DA* state is lower in energy than the D$^+$A$^-$ state, and the exciplex state is more like the DA* state, whereas at shorter distances, it is more like the D$^+$A$^-$ state. When D and A* approach each other from long distances to short distances through the intersection point, the exciplex state changes from almost neutral to an ionic one. This implies that the decrease in D−A distance induces (adiabatic) ET from D to A to form the ionic exciplex. This clearly shows that even in the absence of solvent orientational polarization, ET (exciplex formation) can occur with the change in intermolecular distance. Thus the well-known experimental result that exciplex formation is efficient in nonpolar solvents can be understood.

The effect of mutual orientation of D and A, which has not been considered so far, can also be important for ET and exciplex formation. The effect will be large for aromatic molecules with planar structures. The importance of mutual orientation of D and A* on (ultrafast) ET at short distances has been discussed in some recent papers.[29−31] The effect of mutual orientation on ET and exciplex formation mainly arises from the dependence of H_{12} on the orientation. It therefore depends strongly on the shapes and molecular structures of D and A. It is difficult to express H_{12} in a general form such as eq 5 used for the dependence on the distance. The effect of mutual orientation on ET and exciplex formation will not be discussed in detail in this paper, but some comments will be given where necessary.

If Δ_{12} is small, the mixing can occur even when the two curves do not intersect with each other, i.e., even when the D$^+$A$^-$ state is higher in energy than the DA* state (see Figure 2). In this case, the mixing again stabilizes the exciplex state relative to the DA* state to form a weak (both in the degree of charge transfer and in the stabilization energy) exciplex.

If $-\Delta G^{\mathrm{AN}}$ is larger, the two diabatic curves intersect at longer distances (Figure 3) where H_{12} is smaller. When D and A* approach by diffusion from long distances and pass the

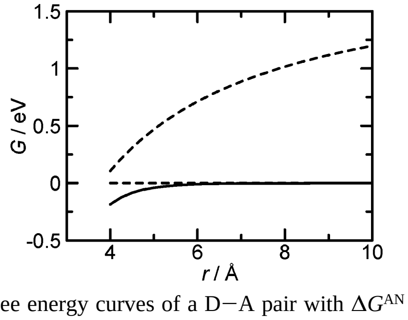


Figure 2. Free energy curves of a D−A pair with $\Delta G^{\mathrm{AN}} = -0.5$ eV in a nonpolar solvent ($\epsilon_{\mathrm{S}} = 1.88$). The exciplex can be formed even when the two states do not intersect.

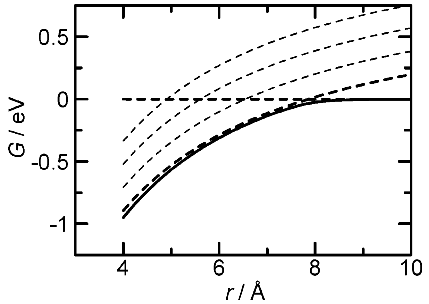


Figure 3. Free energy curves of a D−A pair with $\Delta G^{\mathrm{AN}} = -1.5$ eV in a nonpolar solvent ($\epsilon_{\mathrm{S}} = 1.88$). Thin broken lines are the free energy curves of the vibronic D^+A^- states.

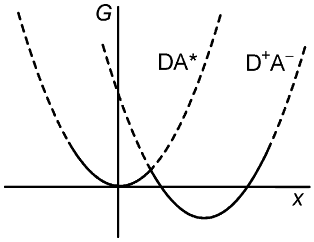


Figure 4. Cross section of the surfaces represented by eqs 7 and 8 at a given value of *r*. Solid curves: parts of the above curves which are relevant to nonadiabatic ET reaction.

intersection point, the system can either stay in the DA* state or jump to the D^+A^- state depending on the rates of diffusion and ET. The rate of ET at that distance in nonpolar and polar solvents may not be much different, because H_{12} is almost the same in both solvents. Such long-distance ET in a nonpolar, highly viscous solvent has already been reported.[17] In such cases, ET is nonadiabatic and the product formed has almost an ion pair structure (full ET). The words "nonadiabatic", "long-range", etc. have been used to characterize Marcus ET induced by solvent polarization. However, ET described in Figure 3 also has such characteristics.

When $-\Delta G^{\mathrm{AN}}$ is large, the effect of intramolecular vibrations on ET should also be considered. The thin broken lines in Figure 3 show the free energy curves of the D^+A^- state with intramolecular vibrational quanta. The curves with more vibrational quanta intersect with the DA curve at shorter distances. The initial DA state is considered to be effectively in the vibrational ground state. Therefore, when the final D^+A^- state with more vibrational quanta is formed, the Franck−Condon factor should be in general small. This is unfavorable for ET. However, because H_{12} increases exponentially with decreasing distance, intersection at shorter distances favors ET. The effect of intramolecular vibrations is not important in the cases described by Figures 1 and 2, because the free energy curves of the D^+A^- state with vibrational quanta do not intersect with the DA curve outside the contact distance.

Theoretical expressions of the second-order ET rate in ideal nonpolar solvent are reported by Tachiya and Seki.[46] They treated the intermolecular distance as reaction coordinate, as was done in the present paper, and calculated the rate of charge separation, charge recombination and charge shift reactions.

3. Solvents with Permanent Dipoles: Competition of Exciplex Formation and Marcus ET

In the previous section, we pointed out the importance of intermolecular distance as a reaction coordinate in intermolecular ET in nonpolar solvent. In solvents with permanent dipoles (hereafter referred to simply as polar solvents), not only the intermolecular distance *r* but also the solvent orientational polarization is important as reaction coordinate. The free energies of the DA* and D^+A^- states are functions of distance *r* and solvent orientational polarization *x*, which can be given by

$$x = e\Delta V = e(V_{\mathrm{D}} - V_{\mathrm{A}}) \tag{6}$$

where V_{D} and V_{A} are the electrostatic potentials at the positions of D and A generated by the solvent dipoles. The free energies are given by[12,47]

$$G_{\mathrm{i}} = \frac{1}{4\lambda}x^2 \tag{7}$$

$$G_{\mathrm{f}} = \frac{1}{4\lambda}(x - 2\lambda)^2 + \Delta G \tag{8}$$

λ and ΔG are the solvent reorganization energy and the free energy change of ET, respectively, and are given by eqs 9 and 10:

$$\lambda = \frac{e^2}{2}\left(\frac{1}{\epsilon_{\mathrm{op}}} - \frac{1}{\epsilon_{\mathrm{S}}}\right)\left(\frac{1}{a} + \frac{1}{b} - \frac{2}{r}\right) \tag{9}$$

$$\Delta G = \Delta G^{\mathrm{AN}} + \frac{e^2}{2}\left(\frac{1}{\epsilon_{\mathrm{S}}} - \frac{1}{\epsilon_{\mathrm{S}}^{\mathrm{AN}}}\right)\left(\frac{1}{a} + \frac{1}{b} - \frac{2}{r}\right) \tag{10}$$

ϵ_{op} and ϵ_{S} are the optical and static dielectric constants of the solvent, respectively, and $\epsilon_{\mathrm{S}}^{\mathrm{AN}}$ is the static dielectric constant of AN. Equations 7 and 8 are functions of *x* and *r* and represent 2-dimensional surfaces. They are also functions of mutual orientation of D and A, but its effect is not taken into account, as already mentioned. The surfaces represented by eqs 7 and 8 intersect with each other. The cross section of the two surfaces at a given *r* value consists of two parabolas that intersect with each other, as shown by the broken curves in Figure 4. Marcus nonadiabatic ET occurs along these curves and the parts drawn by solid curves are important in discussing ET. Figure 5a shows the corresponding parts of the 2-dimensional surfaces in AN solvent ($\epsilon_{\mathrm{op}} = 1.8$ and $\epsilon_{\mathrm{S}} = 37.5$) for a D−A pair with $\Delta G^{\mathrm{AN}} = -0.25$ eV. The left-side valley is the free energy surface of the DA* state, and the right-side one is that of the D^+A^- state. The free energy surfaces in large and small *x* regions are artificially cut by the plane $G = 0.15$ eV so that one can see the inside of the valleys. Figure 5b shows the surface obtained by mixing the DA* and D^+A^- states corresponding to the same *x* and *r* values (the parameter values are the same as those in nonpolar solvent). At short distances the surface in (b) is smoother than that in (a), and the former clearly shows the "exciplex region" (indicated in Figure 5b) where the two states are mixed significantly. ET occurs when the D−A distance and/or solvent orientational polarization change. As in the case of nonpolar solvent, significant mixing occurs when the energies of the two states are close enough at short distances. In this region, ET occurs adiabatically. Because the parameters in eqs 7−10, which depend on the solvent, are just ϵ_{op} and ϵ_{S}, Figure 5 can also be used for D−A pairs in solvents other than AN, as long as they have e_{op} and ϵ_{S} values similar to those of AN.

As described above, the cross section of the two surfaces at a given value of *r* are two parabolas, as shown in Figure 4, that are used to explain nonadiabatic ET. Let us consider a cross section at a given value of *x*. The cross section at $x = 0$ eV is

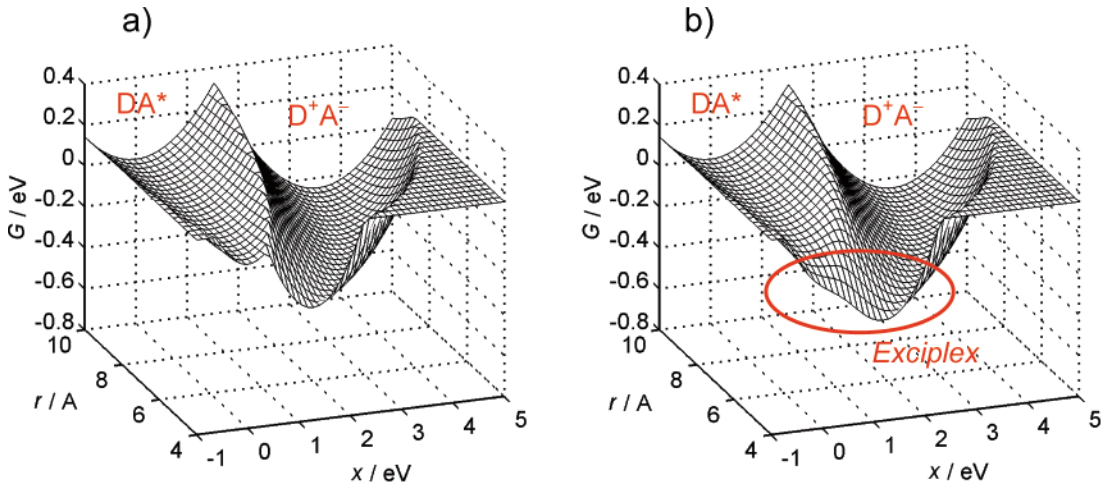


Figure 5. 2-Dimensional free energy surfaces for a D−A pair with $\Delta G^{AN} = -0.25$ eV in AN. Only the parts relevant to ET reactions are shown: (a) mixing of the two states not taken into account; (b) mixing taken into account. The circle shows the “exciplex region”. The ground state DA and the triplet states, D^3A^* and$^3(DA)^*$, to which the DA*, D^+A^-, and exciplex states can decay are not shown.

two curves that are almost the same as those shown in Figure 1 for a nonpolar solvent. This is because at $x = 0$ eV the solvent is not polarized. In this case we have from eqs 7 and 8

$$G_i = 0 \tag{11}$$

$$G_f = \Delta G + \lambda = \Delta G^{AN} + \frac{e^2}{2}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_S^{AN}}\right)\left(\frac{1}{a} + \frac{1}{b} - \frac{2}{r}\right) \tag{12}$$

Equation 11 is the same as eq 1, and eq 12 is very similar to eq 2. The only difference is that ϵ_S in eq 2 is replaced by ϵ_{op} in eq 12. For all nonpolar solvents $\epsilon_S = \epsilon_{op} \approx 2$, and for all solvents $\epsilon_{op} \approx 2$. So eq 12 is almost the same as eq 2, and the exciplex curves obtained by mixing the G_i and G_f curves are also very similar. This implies that, if Marcus ET does not occur for some reason in a polar solvent, exciplex formation occurs in a manner similar to that in a nonpolar solvent with similar ϵ_{op}. Namely, in polar solvents, ET can occur with the decrease in D−A distance (motion along the r-axis) as in nonpolar solvents.

The short distance region of Figure 5b shows the free energy surface of the exciplex state. The free energy of the exciplex system changes with x. The equilibrium position with respect to x is close to the bottom of the D^+A^- state for each r value. Figure 6 shows the contour plot of Figure 5b. We see that the free energy surface of the exciplex system has a weak downward slope toward shorter distances. This is due to the charge-transfer force originating from the mixing of the DA* and D^+A^- states at short distances. The exciplex has the equilibrium structure at $r \sim 4$ (or 3.5) Å and $x \sim 1$ eV (see Figure 5b). This is consistent with the experimental results of Kikuchi et al.[5] and Gould et al.[6] that exciplex fluorescence is observed even in highly polar AN solvent, if D−A pairs with $-\Delta G^{AN} < 0.4$ eV are selected (see the next section). Because in many cases solvent orientational polarization is faster than fluorescence emission, fluorescence is mainly emitted from the equilibrium structure of the exciplex.

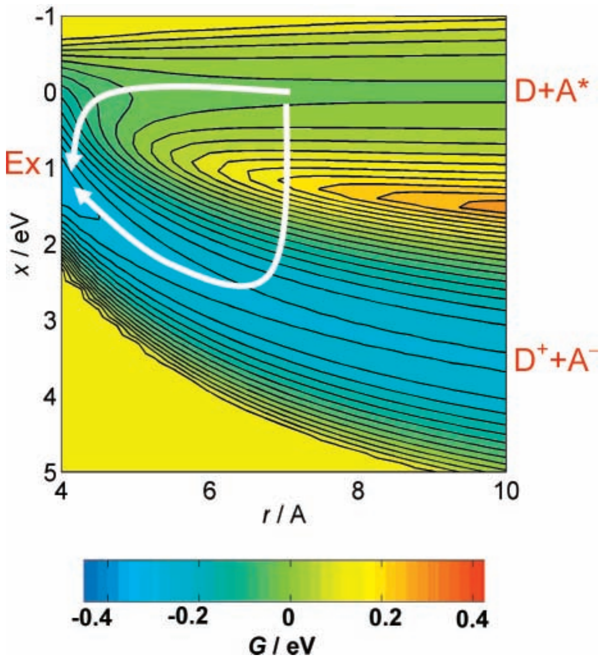
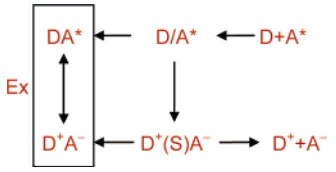


Figure 6. Contour plot of Figure 5b. Upper and lower arrows indicate route 1 and route 2 to reach the equilibrium structure of the exciplex, respectively. (See section 4.1.)

SCHEME 1: Reaction Scheme of Fluorescence Quenching by ET[7,25,a]



[a] D/A* and $D^+(S)A^-$ denote the encounter pair and the SSIP, respectively. The species described inside the box is the exciplex (Ex).

In the following, we consider on the basis of Figure 5 how ET reactions occur. Just after excitation, the system is in the DA* state. We assume, as in usual quenching experiments, that the quencher concentration is low enough, so that D and A* have to approach by diffusion to distances where ET can occur. Figure 5 shows that two types of ET reactions can occur. Marcus ET occurs when the system crosses over the barrier which separates the DA* and D^+A^- states. This is mediated by solvent orientational polarization and is slow when the barrier is high. It is faster at shorter distances, because the electronic coupling H_{12} increases with decreasing distance, and also because in the normal region the barrier is lower at shorter distances. On the other hand, exciplex formation occurs when D and A* approach each other along the r axis as in nonpolar solvents. This process has no barrier but it is slower in more viscous solvents. These two types of ET reactions occur competitively from within the valley of the DA* state. If at distances longer than the contact distance Marcus ET is faster than the diffusive approach of D and A*, fluorescence can be quenched by Marcus ET there and exciplex formation will be inefficient. This is the case of viscous solvents already reported.[15,24] On the other hand, if the diffusive approach is faster than Marcus ET, quenching will occur at shorter distances. So quenching occurs at shorter distances in nonviscous solvents than in viscous solvents.[15,24]

When D and A* approach sufficiently and their mutual orientation is more or less optimized, the exciplex will be formed (partial ET by state mixing) even if x does not change. As seen from Figure 5, the exciplex is not yet stabilized at this time with respect to the x coordinate. With the change of x, further charge is transferred from D to A and the exciplex will be stabilized to the equilibrium structure. Figure 5 shows that Marcus ET and exciplex formation are different not only in their reaction products but also in the reaction routes. The routes are not limited to two: there can be a variety of routes depending on the diffusion rate, solvent relaxation time, interaction energy, etc., even for fixed ΔG^{AN}. The relative importance of Marcus ET and exciplex formation, and hence the mechanism of fluorescence quenching, will change with the value of ΔG^{AN} (see the next section).

In Scheme 1 is shown a reaction scheme often used for fluorescence quenching by ET.[6] The scheme includes the diffusion of D and A* to form an encounter pair D/A*, formation of a solvent-separated ion pair (SSIP) $D^+(S)A^-$, formation of free ions, and exciplex formation. The species described inside the box is the exciplex denoted by Ex. Comparison of Figure 6 and Scheme 1 shows that they correspond well to each other. The encounter pair corresponds to the DA* state just before ET, with the intermolecular distance (more exactly, its distribution) dependent on the rate of diffusive approach of D and A*, and the exciplex state is formed by mixing of the DA* and D^+A^- states. In addition, Figure 6 shows that the reactions denoted by the horizontal arrows in Scheme 1 occur as a result of change in D−A distance, and the reaction denoted by the vertical arrow is induced by solvent polarization.

Recently, Kuzmin et al.[44] and Dosset et al.[45] made experimental studies of the exciplex formation processes. By analyzing the results, they obtained the thermodynamic and kinetic parameters and discussed the mechanism of exciplex formation. In the present paper we treated the D−A distance and the solvent orientational polarization as reaction coordinates for ET and expressed the free energy explicitly as a function of these two coordinates (Figures 5 and 6). This enabled us to understand ET in nonpolar vs polar solvents, and Marcus ET vs exciplex formation in a unified manner.

The mechanism of ET reactions is more precisely described using Figure 6. Figure 5 (or Figure 6) explicitly shows the relevant reaction coordinates for Marcus ET and exciplex formation. It shows the free energy change of electron-transfer semiquantitatively. It shows the energy and the structure (D−A distance) of the exciplex. When there are two routes for electron transfer, it shows which route is more likely to be taken. It shows that long-range ET is nonadiabatic, and exciplex formation is adiabatic.

4. Interpretation of Other Experimental Observations on the Basis of the 2-Dimensional Free Energy Surfaces

We have shown in the previous section that the 2-dimensional free energy surfaces are useful for discussing ET reactions. By changing the parameters such as ΔG^{AN} of the D−A pair, solvent dielectric constants, etc., it is possible to construct the free energy surfaces for various combinations of D−A pairs and solvents. Here we try to explain some experimental results on the basis of such surfaces.

4.1. Effect of ΔG^{AN} on the Quenching Mechanism in Highly Polar Solvents. It is known that the mechanism of fluorescence quenching changes from exciplex formation to SSIP formation (or opposite) under some conditions. One such example is found in AN solvent when $-\Delta G^{AN}$ of the D−A pairs increases from ~0 to >0.6 eV. It was believed until recently that in AN, quenching always occurs by SSIP formation. However, Kikuchi et al.[5] reported that quenching occurs by exciplex formation for D−A pairs with smaller $-\Delta G^{AN}$ values (around 0 eV). Gould et al.[6] measured the efficiency α that the exciplex is formed in the bimolecular quenching reaction in AN solvent. They found that $\alpha \sim 1$ when $-\Delta G^{AN} < 0.4$ eV but it sharply decreases with increasing $-\Delta G^{AN}$. They attributed this decrease to the increase of SSIP formation, which competes with exciplex formation. More recently, Vauthey[9,10] reported that, although there are two types of ion pairs, the difference in their structure (e.g., D−A distance) is smaller than was thought. He suggested that in nonviscous solvents the ion pairs formed by ET in fluorescence quenching are “tight” and “loose” ones, rather than “contact” (exciplex) and “solvent-separated” (SSIP) ones. In more viscous solvents, quenching seems to occur at longer distances. We reported that for D−A pairs with $-\Delta G^{AN} > 0.7$ eV in highly viscous ethylene glycol (EG) quenching occurs at distances longer than the contact distances,[14,15] and Gladkikh et al. reported that for a given D−A pair the quenching distance increases with solvent viscosity.[24]

The effect of ΔG^{AN} on the quenching mechanism can be elucidated by comparing the free energy surfaces of D−A pairs with different ΔG^{AN} values. We compare Figure 5 ($\Delta G^{AN} = -0.25$ eV) and Figure 7 ($\Delta G^{AN} = -0.75$ eV). The experimental result of Gould et al.[6] implies that in the case of $\Delta G^{AN} = -0.25$ eV the exciplex is formed with unit efficiency in the bimolecular quenching reaction from the DA* state, whereas in the case of $\Delta G^{AN} = -0.75$ eV the efficiency is almost 0.

As described in the previous section, exciplex fluorescence is emitted from the equilibrium structure of the exciplex, which occurs at $r \sim 3.5$ or 4 Å and $x \sim 1$ eV in the case of $\Delta G^{AN} = -0.25$ eV. There are two typical routes to the equilibrium structure of the exciplex (see Figure 6): In the first route (route 1) the D−A distance decreases to form the exciplex (motion along the r axis) and finally the equilibrium structure is attained by the change of solvent polarization (motion along the x-axis). In the second route (route 2) Marcus ET occurs by the change of solvent polarization (motion along the x-axis), and then D^+ and A^- formed by ET approach each other and finally attain the equilibrium structure (motion along the r axis). In the case of Figure 5, route 1 seems more probable to be taken than route 2, because the barrier between the DA* and D^+A^- states is rather high. Marcus ET (or motion along the x-axis) will occur only at very short distances where the reaction is almost barrierless. As described in the last section (Figure 6), the free energy surface of the exciplex system has a weak downward slope toward shorter distances because of the charge-transfer force. Consequently, the equilibrium structure of the exciplex will not dissociate to free ions once it is formed by route 1. This is the reason Gould et al. found $\alpha \sim 1$ when $-\Delta G^{AN} <$ 0.4 eV.

The free energy surface of the D^+A^- state in Figure 7 is displaced toward lower energies by 0.5 eV compared with that in Figure 5. This causes a weaker mixing of the two states

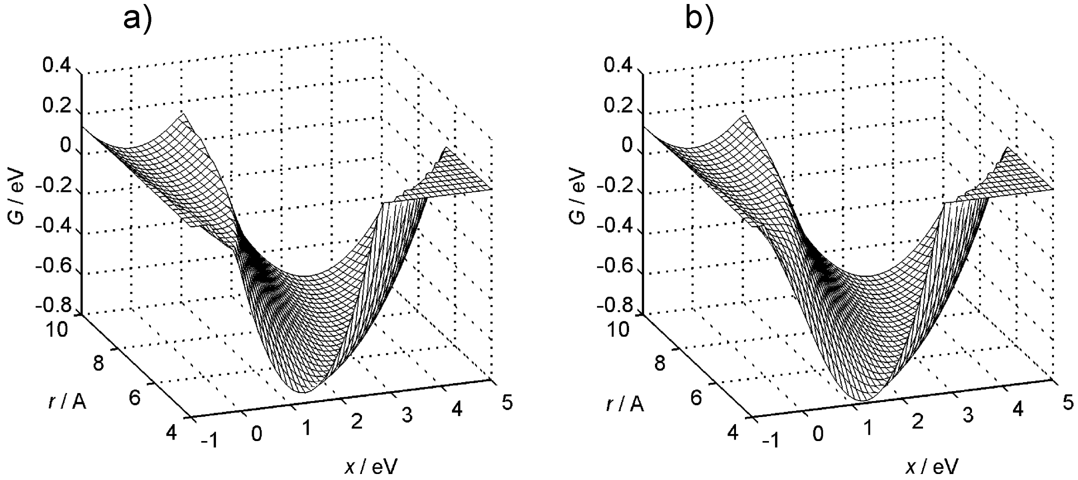


Figure 7. Free energy surfaces of a D−A pair with $\Delta G^{AN} = -0.75$ eV in AN solvent: (a) mixing not taken into account; (b) mixing taken into account.

because of the larger energy difference involved. Indeed, the energy difference for the equilibrium structure ($r = 4$ Å and $x = \lambda$) of the exciplex calculated from eq 4 is 0.88 eV (in the case of Figure 5) and 1.38 eV (Figure 7). Because the magnitude of H_{12} is similar in the two cases, this leads to a lower stabilization energy of the exciplex in the case of Figure 7 than in the case of Figure 5. For D−A pairs with $-\Delta G^{AN}$ values larger than that in Figure 7, the energy difference is larger and the charge-transfer force will be even smaller than in Figure 7. Therefore, the equilibrium structure of the exciplex, if it exists at all, will not be more stable than the ion pair state. This is one of the reasons exciplex fluorescence is not detected in these cases.

The most striking difference between Figures 5 and 7 is the height of the barrier between the DA* and D^+A^- states. The barrier is definitely lower in Figure 7 than in Figure 5, and route 2 seems more probable to be taken. In viscous solvents ET occurs at longer distances, as explainded before. In nonviscous solvents the diffusive approach of D and A* is faster than in viscous solvents, and the distance at which Marcus ET occurs shifts toward shorter distances. However, even in this case Marcus ET will occur at longer distances than in the case of Figure 5, because, as seen from Figure 7, Marcus ET becomes almost barrierless at distances longer than those in Figure 5. When Marcus ET becomes almost barrierless at some distance, it will occur there, and D^+ and A^- ions will be formed there. The ions formed at longer distances will not approach each other, because the charge-transfer force that stabilizes the exciplex works only at very short distances. This is another reason exciplex fluorescence is not detected. The ions are thought to be formed at distances longer than the contact distances even in nonviscous solvents. However, it is not certain from this qualitative discussion whether the ions are separated by solvent molecules when they are formed.

In addition to the D−A distance, the mutual orientation of D and A is important for ET reactions, because the rate of Marcus ET is proportional to H_{12}^2. The rate of Marcus ET will be higher for an orientation with larger H_{12}. However, the effect of orientation on the magnitude of H_{12}, and hence on the rate of Marcus ET, will be similar for the cases of Figures 5 and 7, as long as the D−A pairs have similar molecular structures. Therefore, the above conclusion as to the effect of ΔG^{AN} on the quenching mechanism in highly polar solvents will not be significantly changed by taking into account the mutual orientation of D and A.

We have explained the effect of ΔG^{AN} on the quenching mechanism in highly polar solvents on the basis of the free energy surfaces. Figures 5 and 7 are based on simplified calculations of the free energy surfaces and their accuracy is limited. However, even if more accurate calculations are made, the change in ET mechanism with ΔG^{AN} from exciplex formation to Marcus ET expected from Figures 5 and 7 is probably unchanged.

It has been reported[13] that the magnitude of the rate constant k_f of fluorescence emission of a series of exciplexes is larger for D−A pairs with smaller charge-transfer character, i.e., for pairs with smaller contribution of the D^+A^- state (and consequently larger contribution of the DA* state) in the mixing. Exciplex fluorescence is emitted from its equilibrium position with respect to both D−A distance and solvent polarization. Let us compare the contribution of the D^+A^- state at the equilibrium positions (the minima at $r = 4$ Å) in the cases of Figures 5 and 7. At these positions, (1) the D^+A^- state has lower energy in both cases and (2) the energy difference involved in the mixing is smaller in Figure 5a. Therefore, the contribution of the D^+A^- state is smaller in Figure 5. Accordingly, the exciplex formed in Figure 5 has a larger k_f value compared to that formed in Figure 7. This is another reason exciplex fluorescence has been detected for the case of Figure 5 and not detected for the case of Figure 7.

4.2. Solvent Effect on the Quenching Mechanism. There are many experimental results showing that in highly polar solvents fluorescence is quenched by full ET (D^+ and/or A^- are detected by transient absorption spectroscopy), whereas in nonpolar solvents exciplex formation is responsible for quenching (exciplex fluorescence is detected). Both the exciplex fluorescence yield and lifetime are found to decrease with an increase in solvent polarity (but the yield decreases more rapidly than the lifetime). These results show the importance of solvent polarity in fluorescence quenching.

The effect of solvent polarity can be incorporated in the free energy surfaces through ϵ_S and ϵ_{op}. Let us compare the surfaces for a D−A pair with $\Delta G^{AN} = -0.75$ eV in a nonpolar solvent (n-hexane, $\epsilon_S = \epsilon_{op} = 1.88$), in a weakly polar solvent ($\epsilon_S = 5$, $\epsilon_{op} = 1.8$, hereafter referred to as WP), and in a highly polar solvent (AN, $\epsilon_S = 37.5$, $\epsilon_{op} = 1.8$). The surface for n-hexane solvent is shown in Figure 1. Because of the low polarity of the solvent, the Coulomb interaction between D^+ and A^- is less shielded and $G(D^+A^-)$ decreases rapidly with decreasing r. This causes a sharp decrease in G(exciplex) at shorter

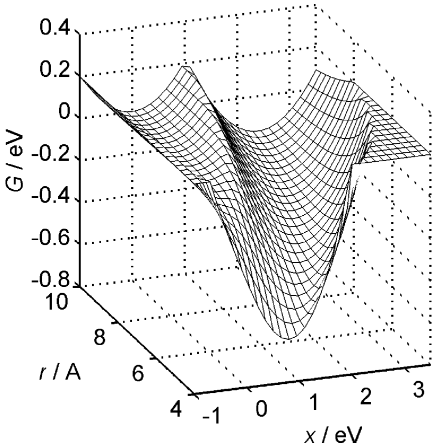


Figure 8. Free energy surface of a D−A pair with $\Delta G^{AN} = -0.75$ eV in a weakly polar solvent (WP, $\epsilon_S = 5$, $\epsilon_{op} = 1.8$).

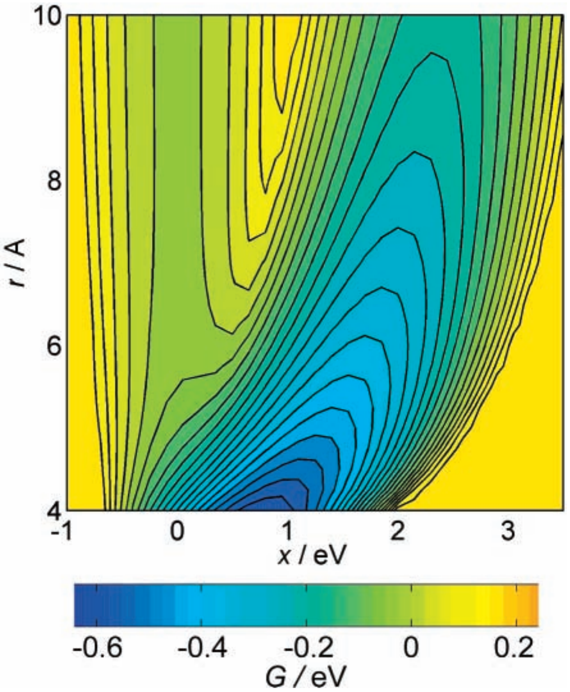


Figure 9. Contour plot of Figure 8 showing that the valley of the D^+A^- state has a downward slope toward shorter distances.

distances and quenching leads to exciplex formation, which is very often observed in experiment. The surfaces for AN are shown in Figure 7. It has been shown in the previous section that in this case Marcus ET occurs at distances longer than the contact distance.

Figure 8 shows the surfaces for WP solvent. We find that the height of the barrier between the two states in Figure 8 is not much different from that in Figure 7. Consequently, Marcus ET to form the D^+ and A^- ions will occur in WP with almost the same efficiency as in AN, if the rate of diffusive approach of D and A* is not very different in these solvents. The fate of the ion pairs formed by Marcus ET in WP (Figure 8) is different from that in AN (Figure 7). In WP the bottom of the valley of the D^+A^- state has a steep downward slope toward short distances as seen from Figures 8 and 9. This is because the Coulomb interaction is less shielded in WP than in AN. Charge-transfer force also works at very short distances, but its contribution to the slope is small compared to that of the Coulomb interaction. Anyway, the ions will recombine to form the exciplex more efficiently than in AN. Thus, among the above three solvents, exciplex formation is most efficient in *n*-hexane and the efficiency decreases in the order of WP > AN, as has been very often reported.

5. Conclusion

In this paper we dealt with fluorescence quenching by intermolecular ET from D to A* in solution. It is experimentally known that fluorescence is quenched by exciplex formation in nonpolar solvents and by Marcus ET and exciplex formation in polar solvents. By introducing the two-dimensional free energy surfaces we clarified why fluorescence is quenched by exciplex formation in nonpolar solvents and by Marcus ET and exciplex formation in polar solvents, depending on the value of the free energy change. In addition, it was elucidated how exciplex formation and Marcus ET are related to each other. Thus, the problems of the quenching mechanism pointed out in the Introduction have been resolved.

Fluorescence quenching by ET often leads to the formation of free ions in polar solvents. Braun et al.[48−50] studied the mechanism of free ion formation by measuring the fluorescence decay and transient photocurrent. The free energy surfaces presented in the present paper will also be useful for these processes.

Verhoeven et al.[51−53] published a series of papers dealing with intramolecular exciplex formation by the harpooning mechanism. In this case long distance ET occurs from D to A* to form the "extended CT state" (D^+A^- state). The extended CT state is then converted to the exciplex state (folded CT state) through the folding of the semirigid bridge. The first process is similar to that described in **3**. We did not discuss the second process (structural reorganization) as we treated just the case of intermolecular ET.

The importance of intramolecular modes in ET was pointed out by Jortner et al.[54] and by Sumi and Marcus.[55] The role of intramolecular modes in ET in solvent-free supermolecules was also discussed by Jortner et al.[56,57] To extend these works to the present more general framework of 2-dimensional free energy surfaces is a future task.

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