

Possible Mechanisms of Intermolecular Charge Transfer and Electron Transfer Processes in the Excited Electronic State

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Mechanisms of intermolecular charge transfer and electron transfer processes in the electronically excited states of solute molecules have been discussed in relation to the exciplex formation and fluorescence quenching reactions in solution. A new model for the electron transfer process has been proposed and studied by the quantum mechanical method. Some naive and intuitive concepts of the electron transfer process have been given a more rigorous theoretical basis. An experiment which can test this model has been suggested. Furthermore, the possible connections among the very weak CT complex formation, exciplex formation and the electron transfer reaction have been discussed in general on the basis of the theoretical considerations.

Mechanismen für den intermolekularen Ladungs- und Elektronenübergang bei gelösten Molekülen in elektronisch angeregten Zuständen werden im Zusammenhang mit der Bildung von Exciplexen und der Fluoreszenzlöschung diskutiert. Für den Elektronenübergang wird ein neues Modell vorgeschlagen, das quantenmechanisch untersucht wird. Dadurch wird einigen einfachen und intuitiven Vorstellungen zum Elektronenübergang eine breitere theoretische Grundlage gegeben. Zur Überprüfung des Modells wird ein Experiment vorgeschlagen. Ferner werden auf der Grundlage theoretischer Überlegungen mögliche Zusammenhänge zwischen der Bildung eines sehr schwachen "charge transfer"-Komplexes, der Bildung eines Exciplexes und dem Elektronenübergang diskutiert.

Les mécanismes de transfert de charge intermoléculaire et de transfert d'électrons dans les états électroniques excités de molécules solutées sont discutés en relation avec la formation d'exciplex et les réactions d'extinction de fluorescence en solution. On propose et on étudie quantitativement un nouveau modèle pour les processus de transfert d'électrons. Il donne une base théorique plus rigoureuse à certains représentations naïves et intuitives du transfert d'électron. On suggère une expérience pour étudier la validité de ce modèle. Enfin les rapports possibles entre la formation de complexes CT très faibles, la formation d'exciplex et la réaction de transfert d'électrons a été discutée de façon générale sur la base de considérations théoriques.

Introduction

It has been believed for a long time that the intermolecular electron transfer process in the electronic excited state is one of the most important mechanisms of the fluorescence quenching reactions in solution [1]. However, very clear-cut and conclusive experimental proofs for this mechanism were quite scarce. On the other hand, the intermolecular electron transfer (redox) reactions

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in solution have been studied in detail, both theoretically and experimentally, mainly in the case of metal ions and metal complexes [2].

By the measurements of the absorption spectrum of the transiently produced anion radical of perylene, Leonhardt and Weller [3] have given for the first time an experimental evidence that the intermolecular electron transfer causes the fluorescence quenching in the perylene-*N,N*-dimethylaniline (DMA) system in polar solvents. They have further shown that in nonpolar solvents perylene forms the CT type complex only in the excited state with DMA and the complex can fluoresce weakly. Since then, many works have been performed [4–7] to elucidate the mechanism of the formation and decomposition process and to investigate the electronic structures of the CT type complexes formed only in the excited electronic state (exciplex), and much informations concerning this phenomenon have been obtained.

In any way, the observations concerning the behaviours of the exciplex fluorescence suggest that the exciplex formed in a polar solvent by the encounter collision between the fluorescer and the quencher molecule shifts to a very polar complex and further becomes a solvated ion-pair and/or completely dissociated ion radicals during the lifetime of the excited state, thus completing the quenching process. Such a process may certainly be one of the most important mechanisms of the fluorescence quenching due to the charge transfer and electron transfer interactions. However, the actual mechanisms of the fluorescence quenching appear to be quite diverse.

It does not appear to be true that the electron transfer occurs always via the formation of a “complex” where the interaction between the electron donor and the acceptor is considerable. Contrary to this, it seems also to be possible that the electron transfer occurs by very weak interaction in a quite loose encounter complex. Weller and co-workers have proposed a model of a loose complex from which the solvent shared ion-pair arises by the electron transfer. However, their experimental criterion for this mechanism seems to involve rather complicated and uncertain factors. Therefore, it will be necessary and important to classify systematically the charge transfer and electron transfer processes into several possible cases on the basis of theoretical considerations. We shall try here to present such a classification and propose a new model for the electron transfer process in the excited state.

Classification of the Electron Donor-Acceptor Interactions between the Fluorescer and the Quencher Molecules

Roughly speaking, the electron donor-acceptor interactions between the fluorescer and the quencher molecules may be classified into the following cases according to the strength of the interaction [8].

a) *Strong Interaction*: The CT complex formation occurs in the excited state. The CT complex (exciplex) may be either fluorescent or non-fluorescent. In non-polar solvents, if the exciplex is non-fluorescent, the fluorescence quenching occurs by the encounter collision and, in this case, the collision complex is the exciplex formed by strong interactions. If the same system (non-fluorescent

case) is studied in polar solvents, its electronic structure will be influenced by the interaction with the surrounding polar solvent molecules. In a sufficiently polar solvent, the exciplex will have a very polar electronic structure.

b) *Very Weak Interaction*: The electron donor-acceptor interaction is extremely weak compared with the case of the exciplex formation by strong interaction. Nevertheless, the interaction between the fluorescer and the quencher will be sufficiently large for the intermolecular electron transfer process to occur producing the ion radicals. Although the charge transfer and the electron transfer occur by an "adiabatic process" in the case of the strong interaction, the electron transfer in the case of the very weak interaction occurs by a "non-adiabatic" electronic transition. Namely, in the former case, the reaction proceeds on the "adiabatic" potential energy surface while in the latter case, the very loose encounter complex (initial state) and the ion-pair state (final state) can be regarded as isolated from each other because of the very weak electronic interaction between them. For the same donor-acceptor system, the "non-adiabatic" process can occur by a weaker interaction than that necessary for the "adiabatic" process. Therefore, the former process may occur at a larger distance between the donor and acceptor than that where the latter process can occur.

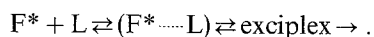
The above classification is the same as that for the intermolecular electronic excitation transfer. This analogy may be valid formally.

Whether the exciplex formed by the strong interaction is fluorescent or not depends on the electronic structure of the complex itself and also on the relative positions of the energy levels of the relevant states, i. e., $E_1 = E(F^* + L)$, $E_2 = E(\text{exciplex})$, $E_3 = E(F_s^\pm \cdot L_s^\mp)$ and $E_4 = E(F_s^\pm + L_s^\mp)$, where E_3 is the energy of the solvated ion-pair and E_4 is the energy of the dissociated ion radicals.

In the case of the pyrene-TCNE system, the complex formed by the excited pyrene and TCNE is non-fluorescent [10] while the fluorescence property of the pyrene-DMA exciplex may be determined by the relative values of the E_i 's which depend considerably on the extent of the solute-solvent interactions. Of course, E_3 and E_4 values may be affected profoundly by the solvent polarity.

In order that the exciplex is stable and can be fluorescent, it is at least necessary that $E_3, E_4 > E_2 < E_1$ and $E_1 < E_3, E_4$, and the energy differences between E_2 and other E_i 's must be larger than the thermal energy of the system. The exciplex reaction proceeds on the "adiabatic" potential energy surface and any activation energy specific to the reaction may not be necessary because, as F^* and L approach to each other by the diffusional motion, they will be only stabilized gradually by the intermolecular interaction. Thus, the reaction will be diffusion-controlled.

For a bimolecular reaction in solution, one usually assumes a encounter complex which changes to the further products in the course of the reaction. Accordingly, in the case of the exciplex formation, the reaction scheme may be written as,



However, for the exciplex formation by strong interaction, it may be physically rather meaningless to differentiate between the encounter complex and the exciplex.

Possible Long Range Effect in the Electron Transfer Process

The typical quenching reactions studied hitherto are all diffusion controlled fast reactions, where the bimolecular rate constant k in the Stern-Volmer equation is proportional to the effective diffusion coefficient $D=(D_{F^*} + D_L)$.

In the case of the singlet-singlet electronic excitation transfer from pyrene to perylene in fluid solution, it has been shown that the bimolecular fluorescence quenching reaction due to the excitation transfer is a diffusion-controlled collision process when the value of the diffusion coefficient is relatively large while it is faster than the diffusion-controlled collision process at relatively low values of the diffusion coefficient and the rate constant k is proportional to $D^{3/4}$ [11], in accordance with the theoretical study [12]. This result shows that the dependence of the reaction probability on the distance between the energy donor and acceptor molecules is not of the hard core type but of a long range type, i. e., the dipole-dipole interaction type.

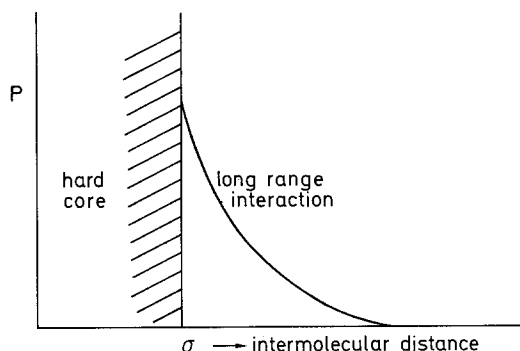


Fig. 1. Relation between the probability of an electron transfer reaction and the intermolecular distance

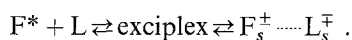
One may suppose that, because the quenching reactions we are discussing here are not the simple excitation transfer but the electron transfer reactions for which the overlap between the electron clouds of F^* and of L is essentially important, the long range effect may not be working in the present case. However, in the case of the pyrene-TCNE system in acetonitrile, the bimolecular rate constant of the fluorescence quenching determined by the fluorescence decay time measurements does not appear to be proportional to D at relatively small values of D , but it is proportional to D^m ($m < 1$) [10]. This fact seems to indicate that the dependence of the electron transfer probability on the distance between F^* and L cannot be regarded as being of the hard core type but involves a long range one as indicated in Fig. 1.

In any way, the above-described facts clearly show that the electron transfer process in the fluorescence quenching reaction is quite different from that in the

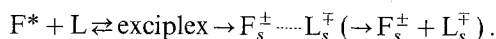
redox reactions such as the ferric-ferrous exchange [2] and the reactions between strongly solvated ions in polar solvents, in general. In the case of these redox reactions, the high solvation energies of the ions play important roles for the determination of the reaction rate, and the activation energy specific to the reaction arises due to the rearrangements in the solvation state as it has been discussed by Marcus and others [2]. Therefore, these redox reactions of the solvated ions are generally much slower than the fluorescence quenching processes.

Now, let us consider the change of the structure of the CT type complex formed in the excited state, when the solvent is changed from a non-polar to a very polar one. We are concerned here mainly with electrostatic interactions such as dipole-dipole and dipole-polarization forces, etc. between the solute and solvent molecules, although, in actual systems, not only these electrostatic forces but also more specific and short range forces, even if they are weaker than the electrostatic ones, may be working. For example, some of them may be very weak charge transfer forces.

Generally speaking, if F^* or L or both of them have a little permanent dipole-moment, E_1 will be a little lowered by the interaction with the polar solvent molecules. However, the extent of this energy lowering for E_1 may certainly be much smaller than those for E_3 and E_4 . The behaviour of E_2 seems to be somewhat complicated because, even if the interaction between the exciplex and the polar solvent molecules will lower E_2 , the solvation which makes the exciplex more ionic might weaken the interaction due to the electronic delocalization between the partners in the exciplex. The latter effect may not lower E_2 but raise it. In other words, because of the direct participation of solvent molecules in the exciplex formation, the structure of the exciplex will become more and more resembled to that of the solvated ion-pair as the solvent polarity is increased. Therefore, since $E_3 > E_2$ in a nonpolar solvent as well as in a slightly polar solvent, E_2 may not necessarily be lowered but raised when the solvent polarity is increased. Thus, in moderately polar solvents, E_2 and E_3 will become quite close to each other because E_2 will become slightly higher while E_3 may become much lower in a polar solvent than in a less polar solvent. When E_2 becomes close to E_3 in a moderately polar solvent, although E_4 is still considerably higher than E_3 , the following reaction may become possible.



In this case, the exciplex and the solvated ion-pair can co-exist. In a more polar solvent where $E_2 > E_3$ or E_4 , the solvated complex will immediately shift to the solvated ion-pair or dissociate into the solvated ion radicals leading to a complete quenching of the fluorescence.



In any way, when the exciplex can be formed by the encounter collision and the reaction proceeds on an "adiabatic" energy surface, the non-fluorescent solvated ion-pair or the solvated ion radicals may be formed via the exciplex. However, when E_3 and E_4 become considerably lower than E_1 , there arises at the same time the possibility of a "non-adiabatic" electron transition as it will be discussed below.

A Theoretical Treatment of the Electron Transfer Process

Now, the wave functions for the exciplex may be written in general as follows,

$$\Psi_e \approx \sum_i a_i(s) \Phi_i(r, s) + \sum_j a_j(s) \Phi_j(r, s) + \sum_k a_k(s) \Phi_k(r, s) + \sum_l a_l(s) \Phi_l(r, s) + a_n(s) \Phi_n(r, s), \quad (1)$$

where r and s represent, respectively, the coordinates of the electrons and the nuclear configurations including the surrounding solvent molecules, Φ_i and Φ_j represent various locally excited configurations $F^* \cdot L$ and $F \cdot L^*$, respectively, and, Φ_k and Φ_l represent various electron transfer configurations $F^- - L^+$ and $F^+ - L^-$, respectively. Φ_n represents the ground configuration corresponding to the structure $F \cdot L$.

Certainly,

$$|a_n| \ll \sum_i |a_i| \quad \text{or} \quad \sum_j |a_j| \quad \text{and} \quad |a_n| \ll \sum_k |a_k| \quad \text{or} \quad \sum_l |a_l|.$$

Owing to the strong solute-solvent interactions, the weight of Φ_k or Φ_l in Ψ_e may become larger and those of Φ_i and Φ_j may become smaller in a polar solvent than in a less polar solvent. According to this interpretation, it is essentially important that the solvent molecules participate directly in the formation of the exciplex even in slightly polar solvents. This finally leads to the formation of the solvated ion-pair or to the dissociation into the solvated ion radicals in a moderately or strongly polar solvent. The nuclear coordinate s including those of the surrounding solvent molecules, which appear in Eq. (1), symbolizes this important effect of the solute-solvent interaction.

Because, even in a non-polar solvent, the exciplex has a considerably polar structure with a dipole moment larger than $10 D$ [4, 5], it seems to be probable that $\sum_i |a_i|$ or $\sum_j |a_j|$ is approximately equal to $\sum_k |a_k|$ or $\sum_l |a_l|$ in that solvent. Then, in a polar solvent, $\sum_k |a_k|$ or $\sum_l |a_l|$ will become larger than $\sum_i |a_i|$ or $\sum_j |a_j|$, which means the decrease of the binding energy due to an electron delocalization between F and L . Moreover, the strong interaction with the solvent may presumably increase a little the intermolecular distance in the exciplex, which further makes the binding energy smaller. If $\sum_i |a_i|$ or $\sum_j |a_j|$ is a little larger than $\sum_k |a_k|$ or $\sum_l |a_l|$ for a exciplex in the non-polar solvent, the interaction of the exciplex with slightly polar solvent molecules may increase a little the weight of the electron transfer configurations, which will lead to the enhancement of the electron delocalization between F and L to some extent. This increase of the electron delocalization will bring out a little increase of the binding energy. In a more polar solvent, however, the binding energy will decrease again in accordance with the mechanism described above for a more polar exciplex.

The extent of the configuration interaction as indicated in Eq. (1) decreases and especially, the contributions from the higher excited configurations to Ψ_e will decrease as the electronic delocalization interaction becomes weaker. Therefore, in a rough approximation, the exciplex wave function in a sufficiently polar

solvent may be written as,

$$\begin{aligned}\psi_e &\sim c_1(s)\Phi_i^0(r,s) + c_2(s)\Phi_k^0(r,s), \\ \psi_e &\sim c_1(s)\Phi_i^0(r,s) + c_2(s)\Phi_l^0(r,s),\end{aligned}\quad (2)$$

where Φ_i^0 represents the lowest energy configuration among Φ_i 's and, Φ_k^0 or Φ_l^0 are the electron transfer configurations which can interact with Φ_i^0 and are close to Φ_i^0 energetically.

When the electronic interaction between F^* and L is very small in a very polar solvent, the Φ^0 's in Eq. (2) may be regarded as isolated stationary states, respectively. Then, the probability P of the electronic transition, $F^* \cdots L \rightarrow F^\pm \cdots L^\mp$, can be given by

$$P = \frac{2\pi}{\hbar} |\langle \Phi_i^0 | \mathcal{H} | \Phi_f^0 \rangle|_{\rho_f}^0 = \frac{2\pi}{\hbar} |\beta|^2 \rho_f, \quad (3)$$

where ρ_f is the final state level density. It is necessary that the final state of the electronic transition is continuous for the formula of Eq. (3) to be defined. This condition is satisfied by the quite many vibrational energy levels in the ions, the solute-solvent interaction energy as well as the thermal energy of the surrounding solvent molecules.

Let us examine now the evaluation of the matrix element β for several simple cases where F is an alternant hydrocarbon molecule and L is a closed shell molecule. We denote the MO's of F and L as indicated in Fig. 2, where the ψ_m 's are the highest occupied orbitals.

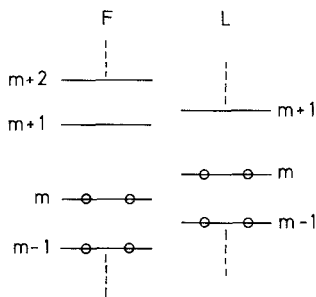


Fig. 2. Numbering of MO's and the electronic configuration for the ground state pair $F \cdot L$

The hamiltonian \mathcal{H} can be separated into the one electron core part $\mathcal{H}_c = \sum f_c$ and the electron repulsion part $G = \sum g$. The matrix elements between the Φ_i^0 's and the Φ_j^0 's can be calculated by the standard method. For example

$$\begin{aligned}\langle \Phi_i^0(^1L_a) | \mathcal{H} | \Phi_j^0(F^+ - L^-) \rangle &= \langle \psi_{m+1}^F | f_c | \psi_{m+1}^L \rangle + \sum_{\lambda_k \neq \psi_{m+1}^F} \{ \langle \psi_{m+1}^F \lambda_k | g | \psi_{m+1}^L \lambda_k \rangle \\ &\quad - \langle \psi_{m+1}^F \lambda_k | g | \lambda_k \psi_{m+1}^L \rangle \} + \langle \psi_m^F \psi_{m+1}^F | g | \psi_{m+1}^L \psi_m^F \rangle\end{aligned}\quad (4)$$

$$\begin{aligned}\langle \Phi_i^0(^1L_a) | \mathcal{H} | \Phi_j^0(F^- - L^+) \rangle &= - \langle \psi_m^F | f_c | \psi_m^L \rangle \\ &\quad - \sum_{\lambda_k \neq \psi_m^F} \{ \langle \psi_m^F \lambda_k | g | \psi_m^L \lambda_k \rangle - \langle \psi_m^F \lambda_k | g | \lambda_k \psi_m^F \rangle \} \\ &\quad + \langle \psi_m^L \psi_{m+1}^F | g | \psi_{m+1}^F \psi_m^F \rangle,\end{aligned}\quad (5)$$

$$\begin{aligned}
\langle \Phi_i^0(^1L_b) | \mathcal{H} | \Phi_f^0(F^+ - L^-) \rangle &= (1/\sqrt{2}) \cdot [\langle \psi_{m+2}^F | f_c | \psi_{m+1}^L \rangle \\
&+ \sum_{\lambda_k \neq \psi_{m+2}^F} \{ \langle \psi_{m+2}^F \lambda_k | g | \psi_{m+1}^L \lambda_k \rangle \\
&- \langle \psi_{m+2}^F \lambda_k | g | \lambda_k \psi_{m+1}^L \rangle \} \\
&+ \langle \psi_{m+1}^F \psi_m^F | g | \psi_{m+1}^L \psi_{m-1}^F \rangle + \langle \psi_m^F \psi_{m+2}^F | g | \psi_{m+1}^L \psi_m^F \rangle \\
&- 2 \langle \psi_{m+1}^F \psi_m^F | g | \psi_{m-1}^F \psi_{m+1}^L \rangle, \tag{6}
\end{aligned}$$

$$\begin{aligned}
\langle \Phi_i^0(^1L_b) | \mathcal{H} | \Phi_f^0(F^- - L^+) \rangle &= (1/\sqrt{2}) \{ 2 \langle \psi_m^L \psi_{m+2}^F | g | \psi_{m+1}^F \psi_m^F \rangle \\
&- \langle \psi_m^L \psi_{m+2}^F | g | \psi_m^F \psi_{m+1}^F \rangle \\
&- \frac{3}{2} \langle \psi_m^L \psi_{m+1}^F | g | \psi_{m+1}^F \psi_{m-1}^F \rangle \\
&- \frac{1}{2} \langle \psi_m^L \psi_{m+1}^F | g | \psi_{m-1}^F \psi_{m+1}^F \rangle \}. \tag{7}
\end{aligned}$$

In Eqs. (4)–(7),

$$\langle \psi_p | f_c | \psi_q \rangle = \int \psi_p(i) f_c(i) \psi_q(i) dv(i)$$

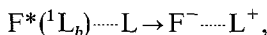
and

$$\langle \psi_p \psi_q | g | \psi_r \psi_s \rangle = \int \psi_p^*(i) \psi_q^*(j) (e^2/r_{ij}) \psi_r(i) \psi_s(j) dv(ij).$$

Although we have not made any numerical evaluation of the matrix elements in Eqs. (4)–(7) for a specific system, both the core part, $\langle \psi_p | f_c | \psi_q \rangle$, and the electron interaction part may play an important role in the electron transfer process.

Roughly speaking, the matrix elements of Eqs. (4)–(7) are proportional to the intermolecular overlap of the MO's of F and L, respectively. Therefore, the value of $|\beta|$ may be much larger than that of the matrix element for the triplet-triplet excitation transfer where the electron exchange integral is the most effective. Therefore, the $|\beta|$ value of Eq. (3) will have the nature of a much longer range interaction than the corresponding matrix element for the triplet-triplet excitation transfer where the contribution of the electron exchange integral (proportional to the square of the intermolecular overlap) is the most dominant.

Because the core part is absent in Eq. (7), this matrix element may be much smaller than the others, which seems to indicate that the long range electron transfer process of the type,



seems to be improbable compared to the other cases. However, if it is possible that $\Phi_f^0(F^- - L^+)$ is not the ground state of the ion-pair but an excited singlet state, the core part can remain non-vanishing. For example, we assume the following wavefunction.

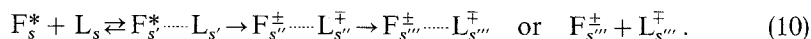
$$\Phi_f^0(F^- - L^+) = (1/\sqrt{2}) \{ \dots \psi_{m-1}^L \bar{\psi}_{m-1}^L \psi_m^L \bar{\psi}_{m+2}^F \dots \psi_{m-1}^F \bar{\psi}_{m-1}^F \psi_m^F \bar{\psi}_m^F | \tag{8}$$

Then we have, $-\dots \psi_{m-1}^L \bar{\psi}_{m-1}^L \bar{\psi}_m^L \psi_{m+2}^F \dots \psi_{m-1}^F \bar{\psi}_{m-1}^F \psi_m^F \bar{\psi}_m^F \}$.

$$\begin{aligned}
\langle \Phi_i^0(^1L_b) | \mathcal{H} | \Phi_f^0(F^- - L^+) \rangle &= (1/\sqrt{2}) [- \langle \psi_m^F | f_c | \psi_m^L \rangle - \sum_{\lambda_k \neq \psi_m^F} \{ \langle \psi_m^F \lambda_k | g | \psi_m^L \lambda_k \rangle - \langle \psi_m^F \lambda_k | g | \lambda_k \psi_m^L \rangle \} \\
&+ \langle \psi_{m+2}^F \psi_m^F | g | \psi_m^L \psi_{m+2}^F \rangle - \langle \psi_m^L \psi_{m+1}^F | g | \psi_{m+2}^F \psi_{m-1}^F \rangle \\
&- \frac{1}{2} \langle \psi_{m+2}^F \psi_m^L | g | \psi_{m-1}^F \psi_{m+1}^F \rangle + \frac{1}{2} \langle \psi_m^F \psi_m^L | g | \psi_{m+1}^F \psi_{m-1}^F \rangle \\
&+ \frac{1}{2} \langle \psi_m^L \psi_{m+1}^F | g | \psi_{m-1}^F \psi_{m+2}^F \rangle]. \tag{9}
\end{aligned}$$

In the above discussions, we have assumed that the energy is conserved in the course of the electron transition process and this may be possible because there is no strong solvation of the reactant, $F^* \cdots L$.

Of course, the solvation state in Φ_f^0 is not the most stable one, but an unstable non-equilibrium one. Therefore, the electron transition may be followed by a very rapid relaxation process of the solvation state into the most stable equilibrium one, completing the quenching process. Thus, it may be possible to express the whole process of the electron transfer reaction between F^* and L as follows.

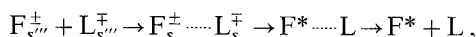


The diffusion equation for the encounter and electron transfer process may be written as,

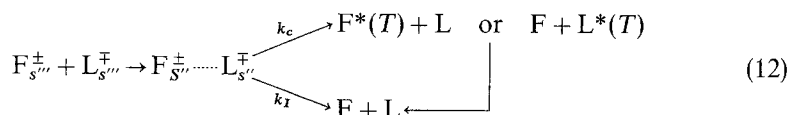
$$-\frac{\partial f(R, t)}{\partial t} = -D \nabla^2 f(R, t) + \sum_i P(|R - R_i|) f(R, t), \quad (11)$$

where $f(R, t)$ is the distribution function for F^* and $P(|R - R_i|)$ is the electron transfer probability as given by Eq. (3). $P(|R - R_i|)$ depends on the intermolecular distance $|R - R_i|$ between F^* and L . The long range part in P will give the relation, $k \propto D^m$ ($m < 1$), as we have discussed already.

In some cases, the ion-radicals $F_{s'''}^{\pm}$ and $L_{s'''}^{\mp}$ will undergo further chemical reactions to give some products. However, we shall discuss here only the simplest case where the electron transfer reaction occurs between $F_{s'''}^{\pm}$ and $L_{s'''}^{\mp}$, finally giving the ground state molecules F and L . Since the energy of the ion-radicals in the equilibrium solvation state is much lower than that of the final state of the electron transition, $F_{s'''}^{\pm} \cdots L_{s'''}^{\mp}$, the reverse electron transfer reaction,



may occur very hardly. Therefore, it is more favourable for the electron transfer reaction between the ion-radicals to give the ground state molecules F and L . It is also possible that the reaction product is the triplet state which lies much lower than the fluorescent state. Because the phosphorescence yield in the fluid solution is negligibly small, the triplet state product may return to the ground state by a radiationless transition. Then, the reaction scheme for this reverse electron transfer may be written as follows.



The rates of these electron transfer reactions may not be so large as that of the fluorescence quenching reaction between the neutral molecules F^* and L , in general, because of the activation energies due to the rearrangements of solvent molecules. Although detailed kinetic studies on the electron transfer reactions of this sort are quite scarce, it has been shown that the bimolecular rate constant for the reaction between the *N,N*-dimethyl-2-naphthylamine (DMNA) cation radical and the dimethyl-isophthalate (DMP) anion radical or the phthalic anhydride (PA) anion radical in formamide is ca. 10^4 – 10^5 l/mol sec [13]. These

ion radicals were produced by an electron transfer from the excited DMNA to the ground state DMP or PA in this very polar solvent. Thus, the rate constant of the electron transfer reaction between the ions in this case is considerably smaller than that in the case of the neutral molecules in the fluorescence quenching reactions.

It should be noted here that, because the solvation energy depends largely on the structures of the ion radicals, it will show considerable variations from one reactant pair to another, which may result in large variations of the activation energy due to the rearrangements in the solvation state. If the charge of an ion radical is considerably localized at a small region of the radical, the solvation energy will be relatively large while it will be small if the charge is spread over the whole frame work of the ion radical. In the former case, the activation energy for the electron transfer reaction may be considerably large whereas it will be small in the latter case. In the case of the electron transfer reaction between the DMNA cation and the DMP or PA anion radicals, the charge seems to be rather well localized at each substituent group. Therefore, the solvation energy and, accordingly, the activation energy for the reaction will be large, leading to a slow electron transfer reaction. If the ion radicals are those of the ordinary alternant hydrocarbons, the solvation energy and the rearrangement energy of the solvation state will be small. In this case, it will be possible that the activation energy is sufficiently small so that the electron transfer reaction is almost diffusion-controlled. For example, the electron transfer reaction between the naphthalene anion radical and the neutral naphthalene molecule, which has been studied in detail by EPR spectral measurements [14], appears to be very rapid and almost diffusion-controlled.

Relations among Contact CT Interactions, Exciplex Formations and Electron Transfer Reactions

For the contact CT interactions [15], the electron transfer interaction is usually assumed to be quite similar to that indicated in Fig. 3. Namely, it is assumed that there is no electronic delocalization interaction between F and L in the ground state contact pair, F.....L, while there arises a small overlap between the orbitals of the pair F*.....L at the moment of the light absorption, which causes the electron transfer from F* to L or from L to F* in the contact pair. From the arguments given in the previous sections, one may suppose that the excited equilibrium state of the contact pair is very ionic, being almost equal to the ion-pair state. Then, the wave function for the ground state may be given approximately by $\Psi_g \approx \Phi_n(r, s)$ while that for the excited state seems to be written as,

$$\Psi_e \approx \sum_i a_i \Phi_i(r, s) + \sum_k a_k \Phi_k(r, s) \quad \text{or} \quad \Psi_e \approx \sum_i a_i \Phi_i(r, s) + \sum_l a_l \Phi_l(r, s)$$

where $|a_i| \ll |a_k|$ or $|a_l|$. Therefore, the intensity of the contact CT absorption band may be borrowed mainly from the local transitions, $\Phi_n \rightarrow \Phi_i$'s, because the transition moments of the $\Phi_n \rightarrow \Phi_k$ or the $\Phi_n \rightarrow \Phi_l$ transitions are rather small. Thus, the electronic structure of the excited contact CT pair seems to be rather similar to that of the exciplex. However, the absorption spectrum corresponding

to the exciplex fluorescence band has not been found out yet but it has been confirmed experimentally in the case of the pyrene-DMA exciplex, for example, that the ground state destabilization energy (Franck-Condon destabilization energy) is too large to populate sufficiently the $F \cdots L$ pair, for observing its characteristic absorption band [4, 10]. Therefore, further studies seem to be necessary to elucidate the true connection between the exciplex state and the excited state of the contact CT complex.

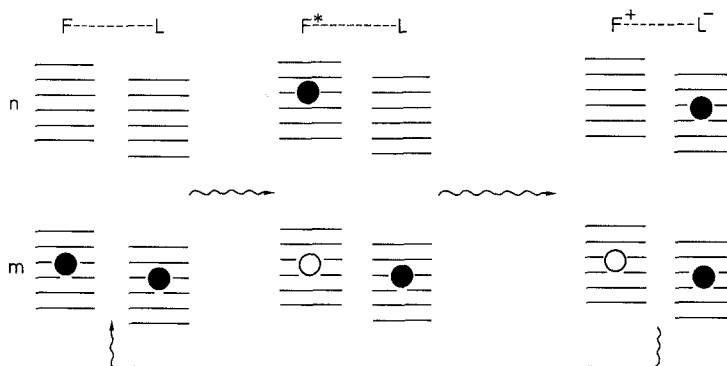


Fig. 3. A schematic representation of the electron transfer process

Since the electronic delocalization interaction in the contact pair is very weak, there arise some questions concerning the nature of the charge transfer process in the pair. If the interaction is not very weak, the excited electronic state of the pair may be described by the stationary state wave function composed by the superposition of locally excited configurations and the electron transfer configurations (strong interaction). However, if the interaction is very weak, there arises the possibility of an electron transition $F^* \cdots L \rightarrow F^\pm \cdots L^\mp$ by a very weak interaction mechanism. If such an electron transfer actually occurs, the contact CT absorption may produce directly the ion-pairs or ions. Although the circumstance for the actual systems may be some intermediate of these two extremes, there is probably a close connection between the contact CT absorption and electron transfer reaction in the excited state.

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