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Relationship between four-state delineation and two-state delineation in electron transfer reactions and excitation transfer

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Abstract

The method of obtaining the transition rate between the initial and final states of the whole system which is usually applied to electron transfer reactions is called the two-state delineation. On the other hand, the method of obtaining the transition rate by the resonance mechanism between de-excitation of a donor and excitation of an acceptor which is usually applied to excitation transfers is called the four-state delineation. We prove that a clear relationship exists between formulas obtained by the two-state and four-state delineations. Based on this relationship, we can suggest some erroneous points when one uses the two-state delineation for the electron transfer reaction in some molecular systems.

Keywords: Two-state delineation; Four-state delineation; Energy gap law; Spectral overlap law; Electron transfer reactions; Excitation transfer; Non-linear response effect

1. Introduction

Intermolecular electron transfer (ET) reactions in various molecular environments take place due to a weak electrostatic interaction between donor and acceptor. In such reactions, at the moment of electron transfer, the energy of the initial state of the system must coincide with that of the final state. Namely, the electron tunneling mechanism works in the ET reaction [1].

Let us denote the initial state of ET as (DA) and the final state as (D^+A^-), where D and A represent donor and acceptor, respectively. We schematically write the potential energy surfaces as given in Fig. 1. The abscissa is a coordinate corresponding to intramolecular vibrations of D and A and motions of surrounding solvent molecules. Here, the solvent does not only stand for polar solvents but also various molecular environments including protein media. The multidimensional coordinates are expressed as one-dimensional coordinate for convenience of drawing. The crossing point T is the transition state. (In reality, T is the hypersurface produced by the crossing of the potential energy surfaces of the initial and final states in the multidimensional coordinates.) The ET reaction proceeds by thermal activation from the minimum O of the initial state to T and passes through it and relaxes to the minimum O′ of the final state. Since it is the transition between the two states of the initial and final states, we call it the two-state delineation.

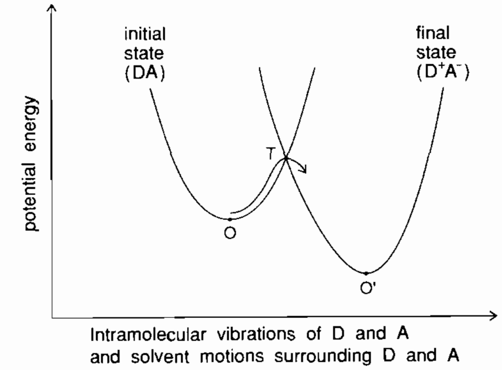

Fig. 1. Potential energy surfaces based on the two-state delineation for the ET reaction $DA \rightarrow D^+A^-$. The ET proceeds by way of $O \rightarrow T \rightarrow O'$.

On the other hand, we can also write the potential energy surfaces as given in Fig. 2. The abscissa is split into two coordinates; one is intramolecular vibrations of D and motions of the solvent surrounding D, and the other is intramolecular vibrations of A and motions of the solvent surrounding A. Strictly speaking, solvent motions cannot be separated into the one surrounding D and the one surrounding A due to the long range character of electrostatic interactions [2]. However, this separation will be approximately correct when D and

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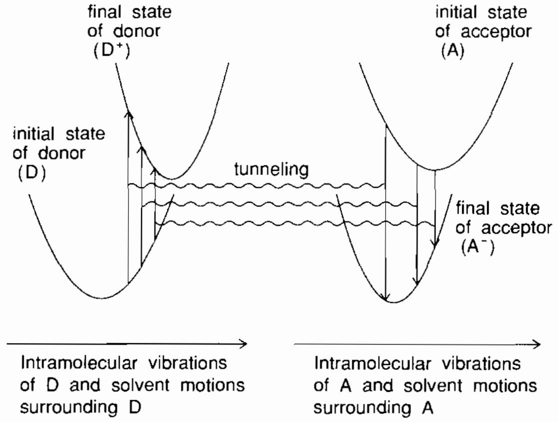

Fig. 2. Potential energy surfaces based on the four-state delineation for the ET reaction $DA \rightarrow D^+A^-$. The ET proceeds by simultaneous transitions of $D \rightarrow D^+$ and $A \rightarrow A^-$.

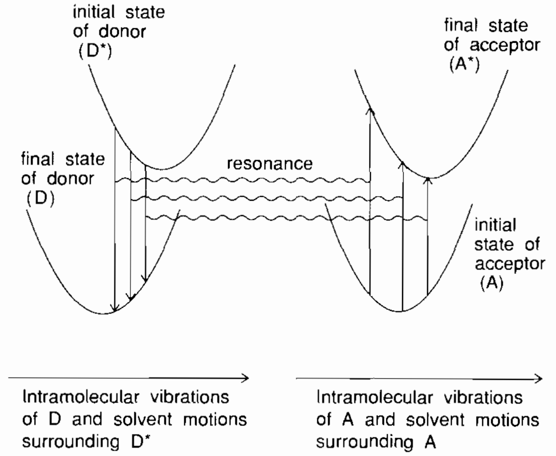

Fig. 3. Potential energy surfaces based on the four-state delineation for the excitation transfer $D^*A \rightarrow DA^*$. The excitation transfer proceeds by the resonance transition of $D^* \rightarrow D$ and $A \rightarrow A^*$.

A are considerably separated in a highly polar solvent. In this case, the ET proceeds by the simultaneous transitions of $D \rightarrow D^+$ and $A \rightarrow A^-$ at the points where the two transition energies coincide with each other. We call this the four-state delineation of the ET reaction.

The four-state delineation in the excitation transfer reaction $(D^*A) \rightarrow (DA^*)$ is usually treated by the Förster mechanism [3]. In this case, potential energy surfaces are written as given in Fig. 3. Excitation transfer proceeds by the resonance of virtual emission of a photon in D^* and virtual absorption of a photon in A.

We can also write the potential energy surfaces for excitation transfer in the two-state delineation by replacing (DA) and (D^+A^-) by (D^*A) and (DA^*), respectively, in Fig. 1.

The question arises as to the relationship between the rate formulas obtained by the two-state and four-state delineations. In this paper, we elucidate mathematically the mutual relation of the formulas obtained by the two-state and four-state delineations. We discuss the significance of the energy gap law in the two-state delineation and the overlap law in the four-state delineation under some specific molecular conditions.

2. Relation between two-state and four-state delineations

2.1. ET reaction

First, starting from the two-state delineation, we derive the ET rate formula in the four-state delineation. The initial (I) and final (F) states of the reaction are expressed using a diabatic basis as follows

$$\Phi_{\mathrm{I}u}(\mathrm{DA})=\psi_{\mathrm{I}}(r,Q)\chi_{\mathrm{I}u}(Q) \tag{1}$$

$$\Phi_{\mathrm{F}v}(\mathrm{D^+A^-})=\psi_{\mathrm{F}}(r,Q)\chi_{\mathrm{F}v}(Q) \tag{2}$$

where ψ and χ are the electronic and vibrational wavefunctions, r, Q, u and v are the electronic and nuclear coordinates, vibrational states of the initial and final states, respectively. These vibrations include the solvent motions as well as the intramolecular vibrations of donor and acceptor molecules. Using the Fermi's golden rule, the ET rate W_{EL} based on the two-state delineation is written as

$$W_{\mathrm{EL}}=\frac{2\pi}{\hbar}\sum_u B_u \sum_v |\langle\Phi_{\mathrm{I}u}|V_{\mathrm{es}}|\Phi_{\mathrm{F}v}\rangle|^2\delta(E_u-E_v+\Delta E) \tag{3}$$

where E_u and E_v are vibrational energies of the u and v states, ΔE is the energy difference between the initial and final states, B_u is the normalized Boltzmann factor

$$B_u=\exp(-E_u/k_{\mathrm{B}}T)\Big/\sum_u \exp(-E_u/k_{\mathrm{B}}T) \tag{4}$$

and V_{es} and k_{B} are the electrostatic interaction energy between donor and acceptor and Boltzmann factor, respectively. Applying the Condon approximation, we can factorize Eq. (3) as

$$W_{\mathrm{EL}}=A_{\mathrm{EL}}\sum_u B_u \sum_v |\langle v|u\rangle|^2\delta(E_u-E_v+\Delta E) \tag{5}$$

where A_{EL} is related to the electron tunneling matrix element

$$A_{\mathrm{EL}}=\frac{2\pi}{\hbar}\left|\langle\psi_I|V_{\mathrm{es}}|\psi_F\rangle\right|^2 \tag{6}$$

and $|\langle v|u\rangle|^2$ is the total Franck–Condon factor.

In the following, we adopt the harmonic oscillator approximation for all the vibrations. We classify the vibrations into four kinds of modes (qd), (qa), (sd) and (sa) which represent quantum modes (q mode) due to intramolecular vibrations of donor and acceptor, solvent modes (s mode) due to solvent motions around donor and acceptor, respectively. Then, we can write the vibrational energies as the sum of each class of modes as

$$E_u = E_{u(\mathrm{qd})} + E_{u(\mathrm{qa})} + E_{u(\mathrm{sd})} + E_{u(\mathrm{sa})} \tag{7}$$

$$E_v = E_{v(\mathrm{qd})} + E_{v(\mathrm{qa})} + E_{v(\mathrm{sd})} + E_{v(\mathrm{sa})} \tag{8}$$

Similarly, the Franck–Condon factor and the Boltzmann factor can be written as products

$$\begin{aligned}|\langle u|v\rangle|^2 = {} & |\langle u(\mathrm{qd})|v(\mathrm{qd})\rangle|^2 \times |\langle u(\mathrm{qa})|v(\mathrm{qa})\rangle|^2 \\ & \times |\langle u(\mathrm{sd})|v(\mathrm{sd})\rangle|^2 \times |\langle u(\mathrm{sa})|v(\mathrm{sa})\rangle|^2\end{aligned} \tag{9}$$

$$B_u = B_{u(\mathrm{qd})} B_{u(\mathrm{qa})} B_{u(\mathrm{sd})} B_{u(\mathrm{sa})} \tag{10}$$

Substituting Eqs. (9) and (10) into Eq. (5), we obtain

$$\begin{aligned}W_{\mathrm{EL}} = A_{\mathrm{EL}} & \int_{-\infty}^{\infty} \mathrm{d}\epsilon_1 \int_{-\infty}^{\infty} \mathrm{d}\epsilon_2 \int_{-\infty}^{\infty} \mathrm{d}\epsilon_3 \\ & \int d\epsilon_4 F_{\mathrm{d}}(\epsilon_1) F_{\mathrm{a}}(\epsilon_2) S_{\mathrm{d}}(\epsilon_3) S_{\mathrm{a}}(\epsilon_4) \\ & \times \delta(\Delta E - \epsilon_1 - \epsilon_2 - \epsilon_3 - \epsilon_4)\end{aligned} \tag{11}$$

where

$$\begin{aligned}F_{\mathrm{d}}(\epsilon_1) = \sum_{u(\mathrm{qd})} B_{u(\mathrm{qd})} \sum_{v(\mathrm{qd})} & |\langle u(\mathrm{qd})|v(\mathrm{qd})\rangle|^2 \delta(\epsilon_1 \\ & + E_{u(\mathrm{qd})} - E_{v(\mathrm{qd})})\end{aligned} \tag{12}$$

$$\begin{aligned}F_{\mathrm{a}}(\epsilon_2) = \sum_{u(\mathrm{qa})} B_{u(\mathrm{qa})} \sum_{v(\mathrm{qa})} & |\langle u(\mathrm{qa})|v(\mathrm{qa})\rangle|^2 \delta(\epsilon_2 \\ & + \mathrm{E}_{u(\mathrm{qa})} - E_{v(\mathrm{qa})})\end{aligned} \tag{13}$$

$$\begin{aligned}S_{\mathrm{d}}(\epsilon_3) = \sum_{u(\mathrm{sd})} B_{u(\mathrm{sd})} \sum_{v(\mathrm{sd})} & |\langle u(\mathrm{sd})|v(\mathrm{sd})\rangle|^2 \delta(\epsilon_3 \\ & + E_{u(\mathrm{sd})} - E_{v(\mathrm{sd})})\end{aligned} \tag{14}$$

$$\begin{aligned}S_{\mathrm{a}}(\epsilon_4) = \sum_{u(\mathrm{sa})} B_{u(\mathrm{sa})} \sum_{v(\mathrm{sa})} & |\langle u(\mathrm{sa})|v(\mathrm{sa})\rangle|^2 \delta(\epsilon_4 \\ & + E_{u(\mathrm{sa})} - E_{v(\mathrm{sa})})\end{aligned} \tag{15}$$

Eq. (11) indicates that W_{EL} can be expressed by a convolution of four kinds of partial Franck–Condon factors F_{d}, F_{a}, S_{d} and S_{a}.

Integrating Eq. (11) by ϵ_4 and putting $\epsilon_3 = \epsilon - \epsilon_1$, we obtain

$$W_{\mathrm{EL}} = A_{\mathrm{EL}} \int_{-\infty}^{\infty} \mathscr{F}_{\mathrm{d}}(\epsilon) \mathscr{F}_{\mathrm{a}}(\Delta E - \epsilon)\, \mathrm{d}\epsilon \tag{16}$$

where

$$\mathscr{F}_{\mathrm{d}}(\epsilon) = \int_{-\infty}^{\infty} F_{\mathrm{d}}(\epsilon_1) S_{\mathrm{a}}(\Delta E - \epsilon - \epsilon_1)\, \mathrm{d}\epsilon_1 \tag{17}$$

$$\mathscr{F}_{\mathrm{a}}(\Delta E - \epsilon) = \int_{-\infty}^{\infty} F_{\mathrm{a}}(\epsilon_2) S_{\mathrm{a}}(\Delta E - \epsilon - \epsilon_2)\, \mathrm{d}\epsilon_2 \tag{18}$$

Here, we put

$$f_{\mathrm{d}}^{\mathrm{em}}(\epsilon') = \mathscr{F}_{\mathrm{d}}(E_{\mathrm{d0}} - \epsilon') \tag{19}$$

$$f_{\mathrm{a}}^{\mathrm{in}}(\epsilon') = \mathscr{F}_{\mathrm{a}}(\epsilon' - E_{\mathrm{a0}}) \tag{20}$$

where E_{d0} is the difference between the zero point energy levels of D^+ and D, and E_{a0} is the difference between the zero point energy levels of A and A^-. They are related to ΔE by

$$\Delta E = E_{\mathrm{d0}} - E_{\mathrm{a0}} \tag{21}$$

Putting $\epsilon = E_{\mathrm{d0}} - \epsilon'$ and substituting Eqs. (19) and (20) into Eq. (16) we obtain the ET formula in the four-state delineation as follows.

$$W_{\mathrm{EL}} = A_{\mathrm{EL}} \int_{-\infty}^{\infty} f_{\mathrm{d}}^{\mathrm{em}}(\epsilon') f_{\mathrm{a}}^{\mathrm{in}}(\epsilon')\, \mathrm{d}\epsilon' \tag{22}$$

From the definition of Eqs. (19) and (20), we find that $f_{\mathrm{d}}^{\mathrm{em}}$ and $f_{\mathrm{a}}^{\mathrm{in}}$ represent an electron emitting spectrum of donor and an electron inserting spectrum of acceptor, respectively [4]. Therefore Eq. (22) states that the ET rate is proportional to the overlap of the two spectra $f_{\mathrm{d}}^{\mathrm{em}}$ and $f_{\mathrm{a}}^{\mathrm{in}}$. This is called the spectral overlap law.

2.2. Excitation transfer

We can formulate the excitation transfer rate W_{EX} in parallel with the ET rate W_{EL} above. We start from the two-state delineation based on the Born–Oppenheimer representation. We can write W_{EX} as

$$W_{\mathrm{EX}} = A_{\mathrm{d\text{–}d}} \sum_u B_u \sum_v |\langle u|v\rangle|^2 \delta(E_u - E_v + \Delta E) \tag{23}$$

Here, $A_{\mathrm{d\text{–}d}}$ is related to the dipole–dipole interaction matrix element

$$A_{\mathrm{d\text{–}d}} = \frac{2\pi}{\hbar} \left| \langle \psi_{\mathrm{I}} | V_{\mathrm{d\text{–}d}} | \psi_{\mathrm{F}} \rangle \right|^2 \tag{24}$$

$$\langle \psi_{\mathrm{I}} | V_{\mathrm{d\text{–}d}} | \psi_{\mathrm{F}} \rangle = \frac{1}{n^2 R_{\mathrm{da}}^3} \left[\vec{m}_{\mathrm{d}} \cdot \vec{m}_{\mathrm{a}} - \frac{3}{R_{\mathrm{da}}^2} (\vec{m}_{\mathrm{d}} \cdot \vec{R}_{\mathrm{da}})(\vec{m}_{\mathrm{a}} \cdot \vec{R}_{\mathrm{da}}) \right] \tag{25}$$

where $\vec{m}_{\mathrm{d}}$, $\vec{m}_{\mathrm{a}}$, $\vec{R}_{\mathrm{da}}$ and n are the transition dipole moments of donor and acceptor, the distance between them and the refractive index of solvent, respectively.

For the convenience of the following discussion we rewrite Eq. (23) as

$$W_{\mathrm{EX}} = A_{\mathrm{EX}} |\vec{m}_{\mathrm{d}}|^2 \cdot |\vec{m}_{\mathrm{a}}|^2 \sum_u B_u \sum_v |\langle u|v\rangle|^2 \delta(E_u - E_v + \Delta E) \tag{26}$$

where A_{EX} is a function of n, R_{da} and relative orientation of vectors $\vec{m}_{\mathrm{d}}$ and $\vec{m}_{\mathrm{a}}$.

After a manipulation similar to that above, we obtain the formula of the excitation transfer rate in the four-state delineation as follows:

$$W_{\mathrm{EX}}=A_{\mathrm{EX}}\int_{-\infty}^{\infty} f_{\mathrm{d}}^{\mathrm{fl}}(\epsilon')\cdot f_{\mathrm{a}}^{\mathrm{ab}}(\epsilon')\,\frac{\mathrm{d}\epsilon'}{(\epsilon')^4} \tag{27}$$

where

$$f_{\mathrm{d}}^{\mathrm{fl}}(\epsilon')=|\vec{m}_{\mathrm{d}}|(\epsilon')^3\mathscr{F}_{\mathrm{d}}(E_{\mathrm{d0}}-\epsilon') \tag{28}$$

$$f_{\mathrm{a}}^{\mathrm{ab}}(\epsilon')=|\vec{m}_{\mathrm{a}}|^2(\epsilon')\mathscr{F}_{\mathrm{a}}(\epsilon'-E_{\mathrm{a0}}) \tag{29}$$

From the definition, $f_{\mathrm{d}}^{\mathrm{fl}}(\epsilon')$ represents the fluorescence spectrum of donor and $f_{\mathrm{a}}^{\mathrm{ab}}(\epsilon')$ the absorption spectrum of acceptor [3]. Therefore, Eq. (27) states that the excitation transfer rate is proportional to the overlap of the two spectra $f_{\mathrm{d}}^{\mathrm{fl}}(\epsilon')$ and $f_{\mathrm{a}}^{\mathrm{ab}}(\epsilon')$. This spectral overlap law was first provided by Förster [3].

2.3. Physical meaning of the two-state delineation and four-state delineation

Let us consider the physical meaning of the two kinds of delineations.

The formula of Eq. (16) is still based on the two-state delineation. On the other hand, we can rewrite Eq. (22) of the four-state delineation as

$$W_{\mathrm{EL}}=A_{\mathrm{EL}}\int_{-\infty}^{\infty}\mathscr{F}_{\mathrm{d}}(E_{\mathrm{d0}}-\epsilon')\mathscr{F}_{\mathrm{a}}(\epsilon'-E_{\mathrm{a0}})\,\mathrm{d}\epsilon' \tag{30}$$

Comparing Eq. (16) with Eq. (30), we find that Eq. (16) contains one parameter ΔE, while Eq. (30) contains two parameters E_{d0} and E_{a0}. That is, one redundant parameter is involved in the four-state delineation of the ET rate formula. Mathematically, this redundancy was introduced by means of Eq. (21). The two factors of the integrand of Eq. (30), $\mathscr{F}_{\mathrm{d}}(E_{\mathrm{d0}}-\epsilon')\equiv f_{\mathrm{d}}^{\mathrm{em}}(\epsilon')$ and $\mathscr{F}_{\mathrm{a}}(\epsilon'-E_{\mathrm{a0}})\equiv f_{\mathrm{a}}^{\mathrm{in}}(\epsilon')$, have clear physical meanings. That is, by introducing one redundant parameter in the four-state delineation, the spectral overlap law of the two well-defined spectra could be derived. In contrast to this, Eq. (16) is mathematically clear, e.g. the convolution of the two Franck–Condon factors of donor and acceptor. However, its physical meaning is less clear, i.e. the integrand of Eq. (16) is not directly related to the observable quantity.

It will be needless to say that the above discussion applies more clearly to the excitation transfer.

3. Energy gap law

The ET rate depends on the energy gap ΔE. This phenomenon is called the energy gap law. In most cases, the two-state delineation is more convenient to investigate the energy gap law than the four-state delineation, because only one parameter ΔE is involved in the former formula. However, the four-state delineation can be more useful in some cases. In the following, we show these concretely.

For this purpose, we adopt the harmonic vibration approximation, and treat the q mode quantum mechanically and s mode classically. In many cases, force constants of the q mode and s mode will not change significantly between the initial and final states, which we treat now. We start from the four-state delineation of Eq. (22) or Eq. (30). Putting $\epsilon_2=\epsilon-\epsilon_1$, we obtain

$$W_{\mathrm{EL}}(\Delta E)=A_{\mathrm{EL}}\int_{-\infty}^{\infty}F(\epsilon)S(\Delta E-\epsilon)\,\mathrm{d}\epsilon \tag{31}$$

where

$$F(\epsilon)=\int_{-\infty}^{\infty}F_{\mathrm{d}}(\epsilon_1)F_{\mathrm{a}}(\epsilon-\epsilon_1)\,\mathrm{d}\epsilon_1 \tag{32}$$

$$S(\Delta E-\epsilon)=\int_{-\infty}^{\infty}S_{\mathrm{a}}(\Delta E-\epsilon-\epsilon_3)\,\mathrm{d}\epsilon_3 \tag{33}$$

For simplicity, we consider one kind of q mode and s mode for each donor and acceptor. Quantum mechanical calculations for $F_{\mathrm{a}}(\epsilon_1)$ give [2,5]

$$F_{\mathrm{a}}(\epsilon_1)=\frac{1}{\hbar\langle\omega_{\mathrm{a}}\rangle}\exp[-S_{\mathrm{a}}(2\bar{v}_{\mathrm{a}}+1)] \times I_{|p_{\mathrm{a}}|}(2S_{\mathrm{a}}\sqrt{\bar{v}_{\mathrm{a}}(\bar{v}_{\mathrm{a}}+1)})\cdot[(\bar{v}_{\mathrm{a}}+1)/\bar{v}_{\mathrm{a}}]^{p_{\mathrm{a}}/2} \tag{34}$$

with

$$\bar{v}_{\mathrm{a}}=[\exp(\hbar\langle\omega_{\mathrm{a}}\rangle/k_{\mathrm{B}}T)-1]^{-1} \tag{35}$$

$$p_{\mathrm{a}}=\epsilon/\hbar\langle\omega_{\mathrm{a}}\rangle \tag{36}$$

$$S_{\mathrm{a}}=d_{\mathrm{a}}^2/2 \tag{37}$$

where I is the modified Bessel function of the first kind, d_{a} a displacement of the normal coordinate between the initial and final states of the q mode, $\langle\omega_{\mathrm{a}}\rangle$ the average frequency of the q mode of the acceptor. We obtain the same equation for F_{d} by replacing a with d in all the parameters. One can show that only when the following equation holds

$$\langle\omega_{\mathrm{d}}\rangle=\langle\omega_{\mathrm{a}}\rangle\equiv\langle\omega\rangle \tag{38}$$

can $F(\epsilon)$ be simplified as [6]

$$F(\epsilon)=\frac{1}{\hbar\langle\omega\rangle}\exp[-S(2\bar{v}+1)]\cdot I_{|p|}(S\sqrt{\bar{v}(\bar{v}+1)}) \times[(\bar{v}+1)/\bar{v}]^{p/2} \tag{39}$$

with

$$\bar{v}=[\exp(\hbar\langle\omega\rangle/k_{\mathrm{B}}T)-1]^{-1} \tag{40}$$

$$p=\epsilon/\hbar\langle\omega\rangle \tag{41}$$

$$S=d_a^2/2+d_d^2/2 \tag{42}$$

Eq. (39) is equivalent to the Franck–Condon factor of the q mode which can be obtained by the two-state delineation within the one mode approximation. However, when $\langle\omega_d\rangle \neq \langle\omega_a\rangle$ holds, we cannot express $F(\epsilon)$ by such a simple formula as Eq. (39). In such case, the four-state delineation of the q mode with one mode approximation is not equivalent to the two-state delineation with one mode approximation. As long as one bases on the two-state delineation, two quantum modes are necessary.

The Franck–Condon factor of the s mode is easily obtained as [4]

$$S_d(\epsilon_3)=\frac{1}{\sqrt{4\pi\Delta_d k_B T}}\exp\left[-\frac{(\Delta_d-\epsilon_3)^2}{4\Delta_d k_B T}\right] \tag{43}$$

$$S_a(\Delta E-\epsilon-\epsilon_3)=\frac{1}{\sqrt{4\pi\Delta_a k_B T}}\exp\left[-\frac{(\Delta_a-\Delta E+\epsilon+\epsilon_3)^2}{4\Delta_a k_B T}\right] \tag{44}$$

where Δ_d and Δ_a are the reorganization energies of the s mode around donor and acceptor, respectively. Substituting Eqs. (43) and (44) into Eq. (33), we obtain

$$S(\Delta E-\epsilon)=\frac{1}{\sqrt{4\pi\Delta_s k_B T}}\exp\left[-\frac{(\Delta_s-\Delta E+\epsilon)^2}{4\Delta_s k_B T}\right] \tag{45}$$

where

$$\Delta_s=\Delta_d+\Delta_a \tag{46}$$

Eq. (45) is equivalent to the Franck–Condon factor of the s mode which can be obtained by the two-state delineation within one mode approximation. In other words, the four-state delineation of the s mode has no merit over the two-state delineation as long as the force constants are the same between the initial and final states.

Next, we consider other cases when the force constants of the initial and final states of the s mode are not equal [7]. Such a situation can happen when the charged donor or acceptor is strongly coupled with the polar solvent and dielectric saturation takes place [8,9]. The change of the force constant can be expected in a wider range of molecular environments including a protein environment [10]. Therefore, it would be better to call this phenomenon the non-linear response. Now, we consider the following simple, typical case of the self-exchange reaction in the presence of the non-linear response effect:

$$A^-A \longrightarrow AA^- \tag{47}$$

where A^- is the donor and A is the acceptor. In this case, the energy gap ΔE is zero. The Franck–Condon factor of the s mode in the four-state delineation was obtained as [11]

$$S(\epsilon)=C\int_0^\infty \exp(-\xi\cos y)\cosh\left(\sqrt{2}\eta\cosh\frac{y}{2}\right)\times\cosh\left(\sqrt{2}\eta\sinh\frac{y}{2}\right)\,dy \tag{48}$$

with

$$C=\frac{\sqrt{\beta(1+\beta)}}{\pi k_B T}\exp\left[-\left\{\frac{1}{2}\epsilon+\beta\left(\frac{1}{2}+\beta\right)\Delta\right\}\Big/k_B T\right] \tag{49}$$

$$\xi=\frac{(1+2\beta)|\epsilon|}{2k_B T} \tag{50}$$

$$\eta=\frac{\sqrt{\beta(1+\beta)\Delta|\epsilon|}}{k_B T} \tag{51}$$

$$\Delta\equiv\frac{1}{2}\Delta_d=\frac{1}{2}\Delta_a \tag{52}$$

$$\beta=\frac{k_n}{k_c-k_n} \tag{53}$$

where k_n and k_c are the force constants of solvent motion around the neutral and charged reactants, respectively. When $\beta\neq\infty$, the function $S(\epsilon)$ becomes infinity at $\epsilon=0$ and decays monotonically as $|\epsilon|$ departs from zero. Therefore, $S(\epsilon)$ is quite different from the Gauss function which is obtained when $\beta=\infty$ (or $k_n=k_c$) holds.

On the other hand, the Franck–Condon factor of the s mode in the two-state delineation with one mode approximation becomes Gaussian because the initial state is equivalent to the final state as seen in Eq. (47). Therefore, the rate obtained by the four-state delineation becomes quite different from that of the two-state delineation [11]. This fact indicates that when the non-linear response effect ($k_n\neq k_c$) works, the two-mode delineation with one mode approximation for the s mode leads to an erroneous result and so, at least, two modes for the s mode must be incorporated.

Similarly we can prove that the two-state delineation with one s mode is erroneous in the presence of the non-linear response effect in general for the charge shift reaction [11]

$$A^-B \longrightarrow AB^- \tag{54}$$

for the photoinduced charge separation reaction [7]

$$A^*B \longrightarrow A^-B^+ \tag{55}$$

and for the charge recombination reaction [12]

$$A^-B^+ \longrightarrow AB \tag{56}$$

4. Discussion

We have shown that as long as we consider the ET reaction due to a very weak interaction and the excitation transfer reaction by the Förster mechanism, both reactions can theoretically be treated by similar formulas. The energy gap law which is popular for the ET reaction is essentially based on the two-state delineation and the spectral overlap law which is popular for the excitation transfer is based on the four-state delineation. However, judging from the results of the present study, we can say that the energy gap law of the ET rate based on the four-state model becomes more important when the non-linear response effect exists and/or the average vibrational frequency of the donor differs significantly from that of the acceptor. On the other hand, we can say that the energy gap law of the excitation transfer will become quite useful when a large change of the dipole moment is induced by the excitation of A or de-excitation of D* and so a large change of the interaction between donor or acceptor and the solvent is brought about. In such cases, the energy gap law of excitation transfer becomes similar to that of the ET reaction; this energy gap law will be quite useful in studying the role of the solvent in excitation transfer.

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