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Energy Gap Law of Electron Transfer in Nonpolar Solvents[†]

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We investigate the energy gap law of electron transfer in nonpolar solvents for charge separation and charge recombination reactions. In polar solvents, the reaction coordinate is given in terms of the electrostatic potentials from solvent permanent dipoles at solutes. In nonpolar solvents, the energy fluctuation due to solvent polarization is absent, but the energy of the ion pair state changes significantly with the distance between the ions as a result of the unscreened strong Coulomb potential. The electron transfer occurs when the final state energy coincides with the initial state energy. For charge separation reactions, the initial state is a neutral pair state, and its energy changes little with the distance between the reactants, whereas the final state is an ion pair state and its energy changes significantly with the mutual distance; for charge recombination reactions, vice versa. We show that the energy gap law of electron-transfer rates in nonpolar solvents significantly depends on the type of electron transfer.

I. Introduction

Electron transfer in polar solvents has been extensively studied on the basis of the Marcus equation.[1,2] In nonpolar solvents, when fluorescence is quenched by electron transfer, often an exciplex is formed, and a new emission from the exciplex is detected.[3] Although the bell shape of the energy gap law for the back electron transfer from triplet exciplexes in weakly polar solvents is observed,[4,5] Marcus theory is originally developed for the electron transfer in polar solvents, and it becomes less appropriate as the static dielectric constants of solvents decrease. In the exciplex, the donor and the acceptor seem to be more or less in contact. However, this does not indicate that the electron transfer in nonpolar solvents occurs at contact distance because the ions may have been attracted to each other by the unscreened strong Coulomb force after electron transfer has occurred at remote distances. To avoid this complexity, donor−acceptor pairs that are connected by semi-flexible groups to reduce the translational motion of reactants were also studied.[6−8]

Recently, the transient effect in fluorescence quenching in a viscous nonpolar liquid paraffin was measured.[9] The results indicate the occurrence of long-range electron transfer rather than exciplex formation. In general, the mechanism of electron transfer depends on the free energy change. When the free energy change is large, the long-range electron transfer occurs, whereas exciplex formation prevails when the free energy change is small.

Electron transfer in weakly polar solvents has been studied theoretically by several groups.[10−15] In weakly polar solvents, one cannot describe electron transfer in terms of orientational fluctuations of permanent dipoles, as in polar solvents. Density fluctuations, detailed interaction between solvent and solute molecules and their motions becomes increasingly important for less polar solvents.[11−13] Electron transfer in ideal nonpolar solvents where the electrostatic interaction between solvents and solutes is absent is not fully understood, although the situation looks much simpler than electron transfer in weakly polar solvents. In polar solvents, the reaction coordinate is given in terms of the electrostatic potentials from solvent permanent dipoles at solutes. In ideal nonpolar solvents, fluctuation of an electrostatic potential from solvents is absent. However, the energy of ion pair states changes significantly with the distance between the ions due to the unscreened strong Coulombic potential. The electron transfer occurs when the final state energy coincides with the initial state energy. For charge separation, the initial state is a neutral pair, and its energy changes little with the distance between the reactants, but the final state is an ion pair and its energy changes significantly with the mutual distance; for charge recombination, vice versa. We investigate the energy gap law of electron transfer in nonpolar solvents for charge separation and charge recombination reactions. The strong distance dependence of an ion pair state in a nonpolar solvent is important for the energy coincidence of the initial and the final states.

II. Charge Separation

The rate of electron transfer in polar solvents is controlled by fluctuations in electrostatic potentials produced at solutes by the surrounding polar solvent molecules.[1,16] However, in ideal nonpolar solvents in which the contribution from the orientational polarization is ignored, such fluctuations are absent. Therefore, the theory of electron transfer in such ideal nonpolar solvents cannot be formulated in terms of fluctuations in the electrostatic potentials from solvent molecules. For charge separation reactions, reactants are neutral in the initial state, and the electrostatic interaction energy between them is neglected. The initial energy of the system may be assumed constant, E_{AB}, independent of the mutual distance except at short distances, where the molecular interaction between the reactants is important. In the final state, one of the solutes has a positive charge, e, and the other has a negative charge, $-e$. The energy of the final state is given by

$$E_{A^+B^-}(r) = E_{AB} + \mathrm{IP} - \mathrm{EA} - \frac{e^2}{2}\left(1 - \frac{1}{\epsilon_{op}}\right)\left(\frac{1}{a} + \frac{1}{b} - \frac{2}{r}\right) - \frac{e^2}{r} \tag{1}$$

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where IP and EA stand for the ionization potential of the donor and the electron affinity of the accepter molecules, respectively. The fourth term on the right-hand side stands for the solvation energy of the ion pair due to the electronic polarization, where e is the electronic charge, $\epsilon_{\rm op}$ is the optical dielectric constant, r is the interionic distance, and a and b are the radii of the ions. $-e^2/r$ is the Coulomb attractive energy between the ion pair. The final state energy fluctuates with time as the distance between the reactants changes. Let $\Delta E(r)$ denote the energy gap between the two states; namely, $\Delta E(r) \equiv E_{\rm A^+B^-}(r) - E_{\rm AB}$. The electron transfer occurs when the final state energy coincides with the initial state energy. The distance, R, at which energy coincidence occurs is given by

$$R = \frac{e^2}{\epsilon_{\rm op}\Delta E_\infty} \tag{2}$$

where ΔE_∞ is the energy gap between the two states at infinity and given by

$$E_\infty = \mathrm{IP} - \mathrm{EA} - \frac{e^2}{2}\left(1 - \frac{1}{\epsilon_{\rm op}}\right)\left(\frac{1}{a} + \frac{1}{b}\right) \tag{3}$$

In polar solvents, the solvent coordinate is usually taken as a reaction coordinate. However, it has already been pointed out that the donor−acceptor distance is also an important reaction coordinate.[17,18] In nonpolar solvents, the donor−acceptor separation is the most important reaction coordinate because in this case, the solvent coordinate is absent. The transition probability at the intersection R is given according to the Landau−Zener theory by[19]

$$P(R) = 1 - \exp\left[-2\pi J(R)^2 \Big/ \left(\hbar v \left|\frac{\mathrm{d}\Delta E(R)}{\mathrm{d}R}\right|\right)\right] \tag{4}$$

where $J(R)$ is the interaction energy at the intersection R. This energy is often called the transfer integral. v is the velocity of relative motion at R. Let $\varphi(r)$ denote the distribution of acceptors around a donor. Then, the frequency that the system crosses the intersection point is given by $\varphi(R)v$. Since the electron-transfer rate is equal to the frequency at which the system crosses the intersection point multiplied by the transition probability, it is given by[16]

$$k(R) = \int_{-\infty}^{\infty} \varphi(R) v P(R) u(v)\, \mathrm{d}v \tag{5}$$

where $u(v)$ is the distribution function of v. For nonadiabatic reactions, the transfer integral is small, and eq 4 can be approximated by

$$P(R) = 2\pi J(R)^2 \Big/ \left(\hbar v \left|\frac{\mathrm{d}\Delta E(R)}{\mathrm{d}R}\right|\right) \tag{6}$$

Under this approximation, the rate is expressed as

$$k(R) = \begin{cases} \dfrac{2\pi J(R)^2}{\hbar}\varphi(R)\dfrac{R^2\epsilon_{\rm op}}{e^2} & \text{for } R \ge r_0 \\ 0 & \text{for } R < r_0 \end{cases} \tag{7}$$

where r_0 is the contact distance of solutes. The distance dependence of the transfer integral is approximated as an exponentially decreasing function if the electron transfer occurs by tunneling,

$$J(r) = J_0 \exp[-\beta(r - r_0)/2] \tag{8}$$

where β is the attenuation coefficient. There are two possibilities for electronic interaction between donor and acceptor. They may interact directly or through intervening solvents. In this paper, we do not analyze this problem. We just assume the value of β = 1 (Å^{-1}). By substituting eq 8 into eq 7, we obtain

$$k(R) = \begin{cases} \dfrac{2\pi\, J_0^2 \exp[-\beta(R - r_0)]}{\hbar}\varphi(R)\dfrac{R^2\epsilon_{\rm op}}{e^2} & \text{for } R \ge r_0 \\ 0, & \text{for } R < r_0 \end{cases} \tag{9}$$

A. Kinetic Control Case. If the translational diffusion of donors and acceptors is sufficiently fast compared with electron transfer at R, the distribution $\varphi(r)$ of acceptors around a donor remains an equilibrium distribution and given by

$$\varphi_{\rm eq}(r) = 4\pi r^2 \tag{10}$$

This case is referred to as the kinetic control case. Substituting eq 10 in eq 9, the second-order electron-transfer rate is given by

$$k(\Delta E_\infty) = \begin{cases} \dfrac{8\pi^2 e^6 J_0^2 \exp[-\beta e^2/(\epsilon_{\rm op}\Delta E_\infty) + \beta r_0]}{\hbar \epsilon_{\rm op}^3 \Delta E_\infty^4} & \text{for } 0 < \Delta E_\infty \le e^2/(\epsilon_{\rm op} r_0) \\ 0 & \text{for } \Delta E_\infty \le 0 \text{ and } e^2/(\epsilon_{\rm op} r_0) < \Delta E_\infty \end{cases} \tag{11}$$

In the above treatment, the intramolecular vibration is not included. In the presence of intramolecular vibration, the electron transfer is accompanied by the emission or absorption of vibrational quanta. We generalize eq 9 by taking into account vibrational mode. For simplicity, we include only one vibrational mode with frequency ν.

The theory for taking into account the intramolecular vibration is well developed.[20,21] The energy coincidence is now accounted for by including emission or absorption of quanta (see Figure 1). The result is given by

$$k(\Delta E_\infty) = \frac{2\pi}{\hbar} \sum_{i \ge i_{\rm min}}^{i \le i_{\rm max}} J_0^2 \exp[-\beta(R_i - r_0)] F_i \varphi(R_i) \frac{R_i^2 \epsilon_{\rm op}}{e^2} \tag{12}$$

$$F_i = \exp(-s)\exp[ih\nu/(2k_{\rm B}T)] I_{|i|}(z) \tag{13}$$

where $i_{\rm min}$ is the minimum integer greater than $-\Delta E_\infty/(h\nu)$, $i_{\rm max}$ is the maximum integer less than or equal to $[-\Delta E_\infty + e^2/(\epsilon_{\rm op} r_0)]/(h\nu)$, and

$$R_i = \frac{e^2}{\epsilon_{\rm op}(\Delta E_\infty + ih\nu)} \tag{14}$$

$I_{|i|}(z)$ is the modified Bessel function of the first kind,[22] s is the Debye−Waller factor with a coupling constant Λ of the Huang−Rhys factor, and the average number of phonons, n,

$$s = \Lambda(2n + 1) \qquad n = 1/[\exp\{h\nu/(k_{\rm B}T)\} - 1] \tag{15}$$

$$z = 2\Lambda\sqrt{n(n + 1)} \qquad \Lambda = \lambda/(h\nu) \tag{16}$$

where the vibration reorganization energy is denoted by λ.

When the vibrational quantum is much larger than thermal energy, the electron transfer occurs from the lowest vibrational level, and eq 12 reduces to

$$k(\Delta E_\infty) = \frac{2\pi}{\hbar} \sum_{i \ge \max(0, i_{\min})}^{i \le i_{\max}} J_0^2 \exp[-\beta(R_i - r_0) - \Lambda] \frac{\Lambda^i}{i!} \varphi(R_i) \frac{R_i^2 \epsilon_{\mathrm{op}}}{e^2} \quad (17)$$

where max(x, y) denotes the maximum of two values, x and y. The summation gives nonzero values only when $i_{\max} \ge 0$, which comes from the condition on the free energy difference, $\Delta E_\infty \le e^2/(\epsilon_{\mathrm{op}} r_0)$.

In the kinetic control case, the second-order electron-transfer rate constant is given by

$$k(\Delta E_\infty) = \frac{8\pi^2 \epsilon_{\mathrm{op}}}{e^2 \hbar} \sum_{i \ge i_{\max}}^{i \le i_{\max}} J_0^2 \exp[-\beta(R_i - r_0)] F_i R_i^4 \quad (18)$$

with F_i and R_i given by eqs 13 and 14, respectively. When the tunneling occurs from the lowest vibrational state, the result is given by

$$k(\Delta E_\infty) = \frac{8\pi^2 \epsilon_{\mathrm{op}}}{e^2 \hbar} \sum_{i \ge \max(0, i_{\min})}^{i \le i_{\max}} J_0^2 \exp[-\beta(R_i - r_0) - \Lambda] \frac{\Lambda^i}{i!} R_i^4 \quad (19)$$

with the same R_i given by eq 14.

In Figure 2, we show the energy gap law of the rates in the kinetic control case. Here, $\epsilon_{\mathrm{op}} = 2$, $\beta = 1$ ($Å^{-1}$), $J_0 = 100$ (cm^{-1}) and $r_0 = 6$ ($Å$). In the presence of vibrational mode, we set $\lambda = 0.3$ (eV), $h\nu = 1500$ (cm^{-1}), $k_B T = 0.025$ (eV). In the case of no vibrational mode, the rate is given by eq 11, which is shown in Figure 2. Equation 11 indicates that the rate increases with increasing E_∞ up to $\Delta E_\infty = \beta e^2/(4\epsilon_{\mathrm{op}})$ and then decreases according to $1/\Delta E_\infty{}^4$. Electron transfer does not occur for $\Delta E_\infty > e^2/(\epsilon_{\mathrm{op}} r_0)$. If the maximum position, $\Delta E_\infty = \beta e^2/(4\epsilon_{\mathrm{op}})$ is smaller than $e^2/(\epsilon_{\mathrm{op}} r_0)$; namely, if $r_0 < 4/\beta$, the rate has a maximum at $\Delta E_\infty = \beta e^2/(4\epsilon_{\mathrm{op}})$. However, for the realistic values of $\beta \sim 1[1/Å]$ and $r_0 = 6$ Å, this condition is not satisfied, and the rate does not have a maximum, as shown in Figure 2.

In the presence of vibrational mode, electron-transfer takes place at various positions, R_i, defined by eq 14. If $h\nu$ is much larger as compared with thermal energy, electron transfer occurs from the lowest vibrational state. In this case, eq 18 is simplified to eq 19. The result of eq 19 practically coincides with that of eq 18 for $\Delta E_\infty \le e^2/(\epsilon_{\mathrm{op}} r_0)$ (not shown).

In the presence of vibrational mode, if electron transfer occurs to vibrationally excited states, the energy coincidence between the initial and final states occurs at shorter distances as compared with the case of the vibrationally ground state. This increases the transfer integral and, therefore, the rate constant. Although the values of the Franck−Condon factor have also to be considered in the presence of the vibrational mode, inclusion of the vibrational mode in general increases the rate constant.

Although the result of eq 19 is zero for $E_\infty > e^2/(\epsilon_{\mathrm{op}} r_0)$, the result of eq 18 is not zero for $E_\infty > e^2/(\epsilon_{\mathrm{op}} r_0)$. This is because in the model on which eq 18 is based, vibrationally excited states are also populated in the initial state, and electron transfer from these states is energetically possible, even for $E_\infty > e^2/(\epsilon_{\mathrm{op}} r_0)$.

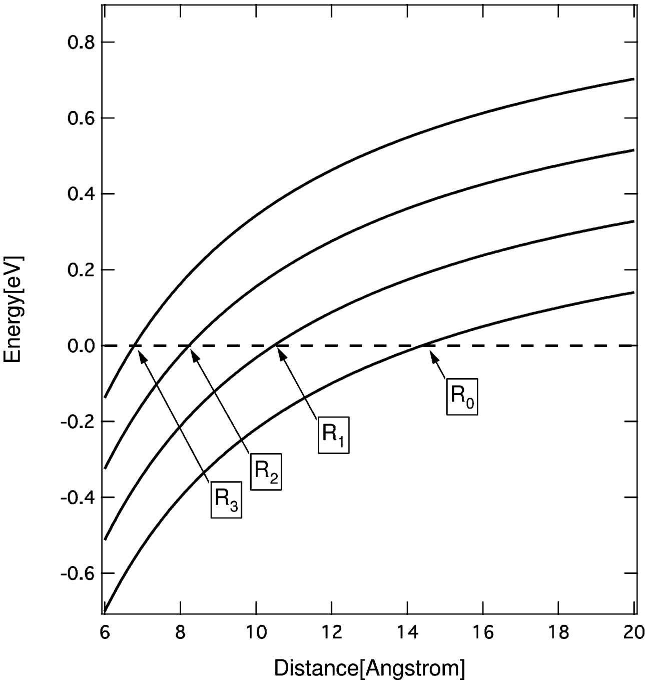

Figure 1. The energy of the final state and the initial state for the charge separation reaction against the distance between the reactants, where $\Delta E_\infty = 0.5$ (eV). The other values of the parameters are the same as those of Figure 2. The dashed line represents the initial state. The solid lines represent the final states. The solid lines from bottom to top represent the ground state and first, second, and third excited states of the vibrational mode, respectively.

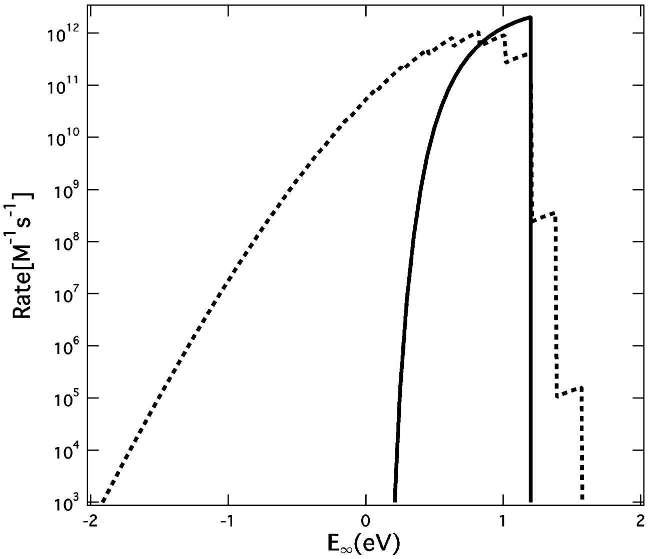

Figure 2. Second-order rates of charge separation reactions as functions of the energy difference in the kinetic control case. The dashed line indicates the rate in the presence of a high frequency intramolecular vibrational mode, eq 18. The solid line indicates the rate in the case of no vibrational mode, eq 11.

So far, intramolecular vibration is assumed to be high. When intramolecular vibration is small, $|\Delta E_\infty| \gg h\nu$ and $\lambda \gg |\Delta E_\infty| \sinh[h\nu/(2k_B T)]$, the result is approximated by

$$k(\Delta E_\infty) = \frac{2\pi}{\hbar} \int_{r_0}^{\infty} \frac{J_0^2 \exp[-\beta(r - r_0)]}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta E_\infty - e^2/(\epsilon_{\mathrm{op}} r) + \lambda)^2}{4\lambda k_B T}\right) 4\pi r^2 \, \mathrm{d}r \quad (20)$$

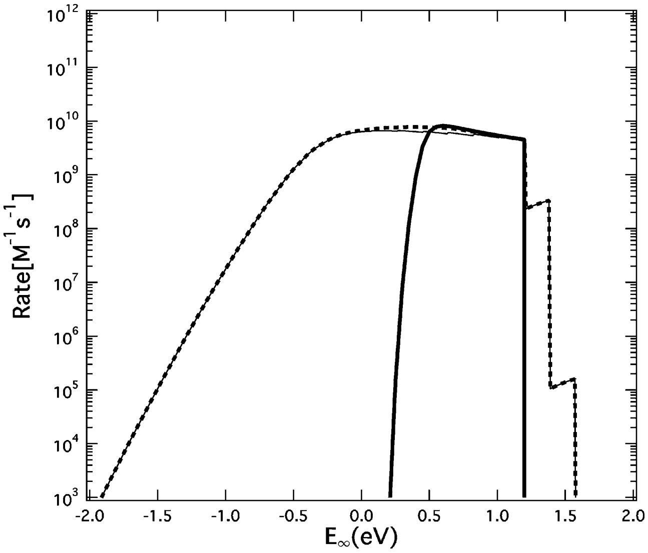

Figure 3. Second-order rates of diffusion-mediated charge separation as functions of the energy difference. The dashed line indicates the rate in the presence of a high frequency intramolecular vibration, eq 26. The thick, solid line indicates the rate in the absence of intramolecular vibration, eq 23. The thin solid line indicates the Padé approximation for the diffusion-mediated case, eq 29.

B. Diffusion-Mediated Case. If the translational diffusion of donors and acceptors is not sufficiently fast as compared with electron transfer, the distribution $\varphi(r)$ of acceptors around a donor is not an equilibrium distribution. In this case, if we denote $\varphi(r) = 4\pi r^2 f(r)$, $f(r)$ satisfies[23]

$$D\nabla^2 f(r) - k(r, \Delta E_\infty)f(r) = 0 \tag{21}$$

where D is the sum of the diffusion coefficients of the donor and the acceptor. The boundary conditions are given by $\partial f(r)/(\partial r)|_{r_0} = 0$ and $f(\infty) = 1$. This case is referred to as the diffusion-mediated case. The rate $k(\Delta E_\infty)$ is expressed in terms of the Green's function of the diffusion operator in eq 21; namely, $g(r, r') = 1/(4\pi D r_>)$, where $r_> = r$ for $r > r'$ and $r_> = r'$ for $r \le r'$.

In the absence of vibrational mode, the sink term is given by

$$k(r, \Delta E_\infty) = \frac{2\pi}{\hbar}J_0^2 \exp[-\beta(r - r_0)]\, \delta\left(\Delta E_\infty - \frac{e^2}{\epsilon_{\mathrm{op}} r}\right) \tag{22}$$

The steady-state rate constant of diffusion-mediated electron transfer is obtained as

$$k(\Delta E_\infty) = \begin{cases} 1/[1/k_{\mathrm{eq}}(\Delta E_\infty) + 1/k_{\mathrm{D}}(\Delta E_\infty)] & \text{for } 0 < \Delta E_\infty \le e^2/(\epsilon_{\mathrm{op}} r_0) \\ 0 & \text{for } \Delta E_\infty \le 0 \text{ and} \\ & \quad e^2/(\epsilon_{\mathrm{op}} r_0) < \Delta E_\infty \end{cases} \tag{23}$$

where $k_{\mathrm{eq}}(\Delta E_\infty)$ is given by eq 11 and $k_{\mathrm{D}}(\Delta E_\infty) = 4\pi DR$ is expressed as

$$k(\Delta E_\infty) = \begin{cases} \dfrac{4\pi e^2 D}{\epsilon_{\mathrm{op}}\Delta E_\infty} & \text{for } 0 < \Delta E_\infty \le e^2/(\epsilon_{\mathrm{op}} r_0) \\ 0 & \text{for } \Delta E_\infty \le 0 \text{ and } e^2/(\epsilon_{\mathrm{op}} r_0) < \Delta E_\infty \end{cases} \tag{24}$$

In the presence of the intramolecular vibrational mode, the sink term is given by

$$k(r, \Delta E_\infty) = \frac{2\pi}{\hbar}J_0^2 \exp[-\beta(r - r_0)] \sum_{i \ge i_{\min}}^{i \le i_{\max}} F_i\, \delta\left(ih\nu + \Delta E_\infty - \frac{e^2}{\epsilon_{\mathrm{op}} r}\right) \tag{25}$$

The steady-state, diffusion-mediated rate is expressed as[24−26]

$$k_2(\Delta E_\infty) = I^{\mathrm{T}}(E + \Gamma(\Delta E_\infty))^{-1}\phi(\Delta E_\infty) \tag{26}$$

Here, $\phi(\Delta E_\infty)$ and $\Gamma(\Delta E_\infty)$ are the vector and the matrix with the components

$$\phi_i(\Delta E_\infty) = \frac{2\pi}{\hbar}J_0^2 \exp[-\beta(R_i - r_0)]F_i\varphi_{\mathrm{eq}}(R_i)\frac{R_i^2\epsilon_{\mathrm{op}}}{e^2} \tag{27}$$

$$\Gamma_{i,j}(\Delta E_\infty) = \frac{8\pi^2\epsilon_{\mathrm{op}}}{e^2\hbar}J_0^2 \exp[-\beta(R_i - r_0)]F_i R_i^4 g(R_i, R_j) \tag{28}$$

for $i_{\min} \le i,j \le i_{\max}$ and $\varphi_{\mathrm{eq}}(r) = 4\pi r^2$. I^{T} is the transpose of the unit vector of the same dimension as that of $\phi(\Delta E_\infty)$, and E is the unit matrix with the same dimension as that of $\Gamma(\Delta E_\infty)$. On the other hand, the result of Padé approximation is given by[27,28]

$$k_{\mathrm{pd}}(\Delta E_\infty) = 1/[1/k_{\mathrm{eq}}(\Delta E_\infty) + 1/k_{\mathrm{Dpd}}(\Delta E_\infty)] \tag{29}$$

where $k_{\mathrm{eq}}(\Delta E_\infty)$ is given by eq 18 and

$$k_{\mathrm{Dpd}}(\Delta E_\infty) = k_{\mathrm{eq}}^2(\Delta E_\infty)/\sum_{i,j \ge i_{\min}}^{i,j \le i_{\max}} \frac{8\pi^2\epsilon_{\mathrm{op}}}{e^2\hbar}J_0^2 \exp[-\beta(R_i - r_0)]F_i R_i^4 g(R_i, R_j)\phi_j(\Delta E_\infty) \tag{30}$$

In Figure 3, we show the steady-state rate constant of diffusion-mediated charge separation. We assume the diffusion coefficient of $D = 10^{-5}$[cm^2/s]. The other parameters are the same as those in Figure 2. In the case of no vibrational mode, the rate is given by eq 23. In the presence of intramolecular vibration, the rate is given by eq 25. The exact result in the presence of the vibrational mode is also compared with that by the Padé approximation. In the Padé approximation, the correlation among sinks is not fully taken into account. The slight deviation of the result of Padé approximation from the exact result is due to the correlation among reactive sinks at various distances of reactants. The correlation among sinks at various distances is a signature of the long-range nature of electron transfer.

III. Charge Recombination

A. Kinetic Control Case. For charge recombination reactions, in the initial state, one of the solutes has a positive charge, e, and the other has a negative charge, $-e$, and the energy of the system can be expressed by eq 1. In the final state, the energy of the system is constant, independent of the mutual distance. The initial state energy fluctuates with time as the distance between the reactants changes. The electron transfer occurs when the initial state energy coincides with the final state energy (see Figure 4). The energy gap between the two states is defined as $\Delta E(r) \equiv E_{\mathrm{AB}} - E_{\mathrm{A^+B^-}}(r)$. In the case of no vibrational mode, the distance at which energy coincidence occurs is given by

$$R = -\frac{e^2}{\epsilon_{\mathrm{op}}\Delta E_\infty} \tag{31}$$

where the energy gap ΔE_∞ at infinity is expressed as

$$\Delta E_{\infty} = \mathrm{EA} - \mathrm{IP} + \frac{e^2}{2}\left(1 - \frac{1}{\epsilon_{\mathrm{op}}}\right)\left(\frac{1}{a} + \frac{1}{b}\right) \tag{32}$$

Note that the sign is different between eqs 2 and 31 and between eqs 3 and 32. In the presence of a vibrational mode, the energy coincidence occurs at

$$R_i = -\frac{e^2}{\epsilon_{\mathrm{op}}(\Delta E_{\infty} + ih\nu)} \tag{33}$$

In the case of no vibrational mode, the rate is given by eq 9, whereas in the presence of a vibrational mode, it is given by eq 12, which reduces to eq 17 when the vibrational quantum is much larger than thermal energy, and so the electron transfer occurs from the lowest vibrational level. Note, however, that the distribution $\varphi(r)$ of acceptors around a donor in charge recombination is different from that in charge separation.

In the charge recombination, the equilibrium distribution of acceptors around a donor is given by

$$\varphi_{\mathrm{eq}}(r) = 4\pi r^2 \exp(r_c/r) \tag{34}$$

where r_c is the Onsager distance defined by[28]

$$r_{\mathrm{c}} = \frac{e^2}{\epsilon_{\mathrm{op}} k_{\mathrm{B}} T} \tag{35}$$

In the case of no vibrational mode the rate is given by

$$k(\Delta E_{\infty}) = \begin{cases} \dfrac{8\pi^2 e^6 {J_0}^2}{\hbar {\epsilon_{\mathrm{op}}}^3 {\Delta E_{\infty}}^4} \\ \exp\left(\dfrac{\beta e^2}{\epsilon_{\mathrm{op}}\Delta E_{\infty}} + \beta r_0 - \dfrac{r_{\mathrm{c}}\epsilon_{\mathrm{op}}\Delta E_{\infty}}{e^2}\right) & \text{for } -e^2/(\epsilon_{\mathrm{op}} r_0) \le \Delta E_{\infty} < 0 \\ 0 & \text{for } \Delta E_{\infty} < -e^2/(\epsilon_{\mathrm{op}} r_0) \text{ and } 0 \le \Delta E_{\infty} \end{cases} \tag{36}$$

In the presence of a vibrational mode, the rate is given by

$$k(\Delta E_{\infty}) = \frac{8\pi^2 \epsilon_{\mathrm{op}}}{e^2 \hbar} \sum_{i \ge i_{\mathrm{min}}}^{i \le i_{\mathrm{max}}} J_0^2 \exp[-\beta(R_i - r_0) + r_c/R_i] F_i R_i^4 \tag{37}$$

where i_{min} is the minimum integer greater than or equal to $[-\Delta E_{\infty} - e^2/(\epsilon_{\mathrm{op}} r_0)]/(h\nu)$, i_{max} is the maximum integer less than $-\Delta E_{\infty}/(h\nu)$ and R_i given by eq 33. When the tunneling occurs from the lowest vibrational state, the rate is given by

$$k(\Delta E_{\infty}) = \frac{8\pi^2 \epsilon_{\mathrm{op}}}{e^2 \hbar} \sum_{i \ge \max(0, i_{\mathrm{min}})}^{i \le i_{\mathrm{max}}} J_0^2 \exp[-\beta(R_i - r_0) + r_c/R_i - \Lambda] \frac{\Lambda^i}{i!} R_i^4 \tag{38}$$

In Figure 5, we present results for $\epsilon_{\mathrm{op}} = 2$, $J_0 = 100$ (cm^{-1}), $\beta = 1$ (Å^{-1}), $\lambda = 0.3$ (eV), $h\nu = 1500$ (cm^{-1}), $k_{\mathrm{B}}T = 0.025$ (eV), and $r_0 = 6$ (Å). In the case of no vibrational mode, the electron transfer occurs in the range $-e^2/(\epsilon_{\mathrm{op}} r_0) \le \Delta E_{\infty} < 0$. In the presence of vibrational mode, electron transfer to the vibrational excited states is possible even for $\Delta E_{\infty} < -e^2/(\epsilon_{\mathrm{op}} r_0)$. Because of large Onsager radius $r_{\mathrm{c}} = 288$ (Å) for $\epsilon_{\mathrm{op}} = 2$, the factor in the equilibrium distribution, $\exp(r_c/r)$ becomes 7×10^{20} at the contact distance. Roughly speaking, the concentration of acceptors at the contact distance is 7×10^{20} times larger as compared to that at infinity. The second-order rate is usually defined in reference to the concentration at infinity. This is the reason for the high values of the rates. If we define the rate in reference to the concentration at the distance at which electron transfer actually occurs, the values in Figure 5 should be divided by the factor 7×10^{20}. According to Figure 5, the rate in the

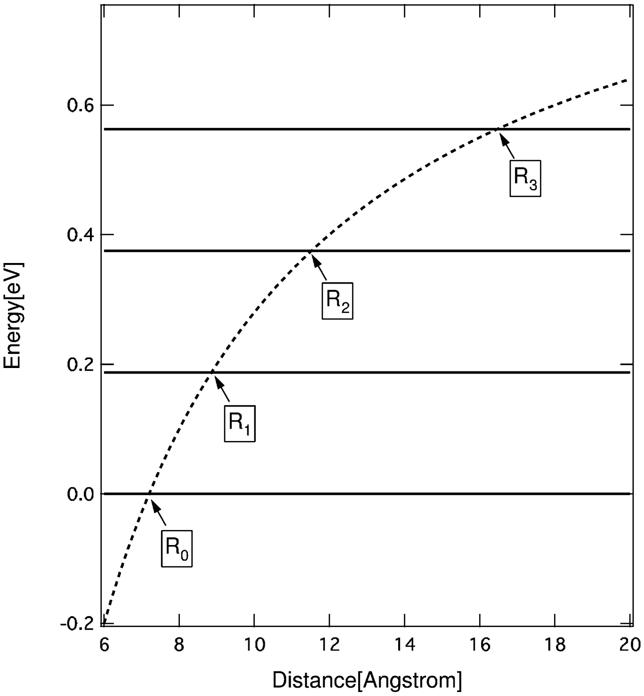

Figure 4. The energy of the final state and the initial state for the charge recombination reaction against the distance between the reactants, where $\Delta E_{\infty} = -1$ (eV). The other values of the parameters are the same as those of Figure 5. The dashed line represents the initial state. The solid lines represent the final states. The solid lines from bottom to top represent the ground state and first, second, and third excited states of the vibrational mode, respectively.

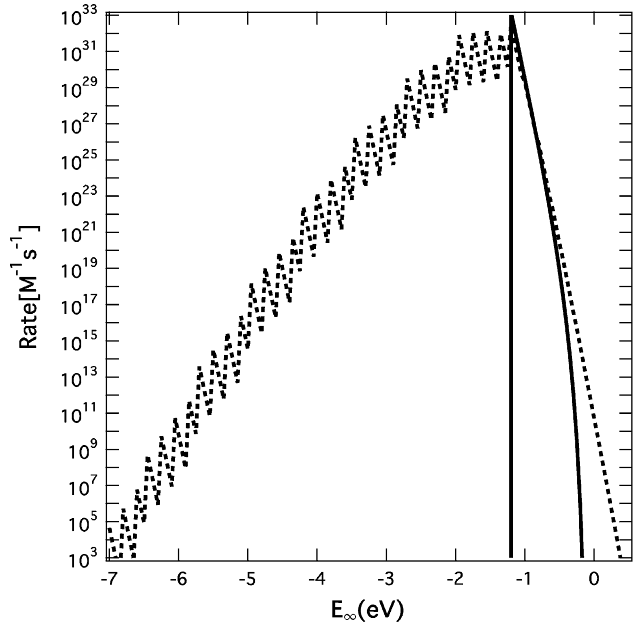

Figure 5. Second-order rates of charge recombination reactions as functions of the energy difference in the kinetic control case. The dashed line indicates the rate in the presence of a high frequency intramolecular vibration, eq 37. The solid line indicates the rate in the case of no vibrational mode, eq 36.

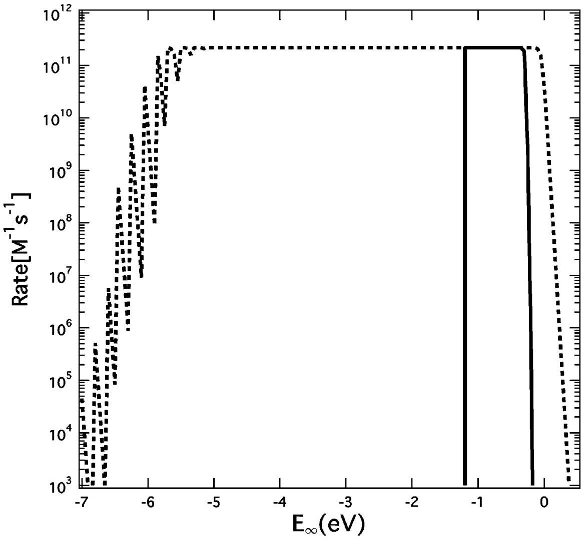

Figure 6. Second-order rates of diffusion-mediated charge recombination as functions of the energy difference. The dashed line indicates the rates in the presence of a high frequency intramolecular vibration, eq 26, where $\varphi_{\rm eq}(r)$ is given by eq 34. The solid line indicates the rate in the case of no vibrational mode, eq 23, where $k_{\rm eq}(\Delta E_\infty)$ is given by eq 36 and $k_{\rm D}(\Delta E_\infty)$ is given by eq 43.

case of no vibrational mode is zero for $\Delta E_\infty < -e^2/(\epsilon_{\rm op} r_0)$. The reason is as follows: The distance at which the energy coincidence occurs decreases with decreasing ΔE_∞. For $\Delta E_\infty < -e^2/(\epsilon_{\rm op} r_0)$, this distance becomes smaller than r_0. In the presence of a vibrational mode, the rate is not zero, even for $\Delta E_\infty < -e^2/(\epsilon_{\rm op} r_0)$. This is because if electron transfer occurs to vibrationally excited states of the final state, the distance at which the energy coincidence occurs increases as compared to electron transfer to the vibrational ground state of the final state and becomes larger than the contact distance. If the frequency of vibrational mode is high, this distance change is large. In charge recombination, the distribution $\varphi_{\rm eq}(r)$ is very high near the contact distance. Therefore, even if electron transfer occurs to a highly vibrationally excited-state of the final state, the rate can be very high, as shown in Figure 5, if the energy coincidence occurs near the contact distance.

In the presence of low-frequency vibration, the rate is given by

$$k(\Delta E_\infty) = \frac{2\pi}{\hbar}\int_{r_0}^{\infty} {\rm d}r\, \frac{J_0^2 \exp[-\beta(r-r_0)]}{\sqrt{4\pi\lambda k_{\rm B}T}} \exp\left(-\frac{(\Delta E_\infty + e^2/(\epsilon_{\rm op} r) + \lambda)^2}{4\lambda k_{\rm B}T}\right)\varphi(r) \quad (39)$$

where $\varphi(r)$ is given by $\varphi_{\rm eq}(r)$ of eq 34.

B. Diffusion-Mediated Case. In the diffusion-mediated electron transfer, the distribution $4\pi r^2 f(r)$ of acceptors around a donor satisfies

$$D\nabla\cdot\left[\nabla - \left(\nabla\frac{r_{\rm c}}{r}\right)\right] f(r) - k(r, \Delta E_\infty) f(r) = 0 \qquad (40)$$

where D is the sum of the diffusion coefficients of the donor and the acceptor. The boundary conditions are given by $[\partial f(r)/\partial r - (\nabla r_c/r) f(r)]|_{r_o} = 0$ and $f(\infty) = 1$. The steady-state rate $k(\Delta E_\infty)$ is expressed in terms of the Green's function of the diffusion operator in eq 40; namely,[29]

$$g(r, r') = \frac{\exp(r_c/r)}{4\pi D r_c}[1 - \exp(-r_c/r_>)] \qquad (41)$$

where $r_> = r$ for $r > r'$ and $r_> = r'$ for $r \le r'$.

In the absence of a vibrational mode, the sink term is given by

$$k(r, \Delta E_\infty) = \frac{2\pi}{\hbar} J_0^2 \exp[-\beta(r - r_0)]\, \delta\left(\Delta E_\infty + \frac{e^2}{\epsilon_{\rm op} r}\right) \quad (42)$$

The diffusion-mediated reaction rate in the absence of intramolecular vibration is given by eq 23, where $k_{\rm eq}(\Delta E_\infty)$ is given by eq 36 and $k_{\rm D}(\Delta E_\infty)$ is given by[30]

$$k_{\rm D}(\Delta E_\infty) = \begin{Bmatrix} 4\pi D r_c/[1 - \exp(r_c \epsilon_{\rm op} \Delta E_\infty/e^2)], & \text{for } -e^2/(\epsilon_{\rm op} r_0) \le \Delta E_\infty < 0 \\ 0 & \text{for } \Delta E_\infty < -e^2/(\epsilon_{\rm op} r_0) \text{ and } \\ & 0 \le \Delta E_\infty \end{Bmatrix} \quad (43)$$

In the presence of an intramolecular vibrational mode, the sink term is given by

$$k(r, \Delta E_\infty) = \frac{2\pi}{\hbar} J_0^2 \exp[-\beta(r - r_0)] \sum_{i \ge i_{\min}}^{i \le i_{\max}} F_i \delta\left(ih\nu + \Delta E_\infty + \frac{e^2}{\epsilon_{\rm op} r}\right) \quad (44)$$

In the presence of a vibrational mode, the rate is given by eq 26 with the same vector and matrix as eqs 27 and 28. The result of Padé approximation is given by eq 29, with $k_{\rm eq}(\Delta E_\infty)$ given by eq 36. In these equations, the distribution in charge recombination, eq 34, has to be used for $\varphi_{\rm eq}(r)$ instead of that in charge separation.

In Figure 6, we show the steady-state rate constant of diffusion-mediated charge recombination for $D = 10^{-5}$[cm^2/s]. Due to the large Onsager radius, eq 43 is well approximated as $k_{\rm D} = 4\pi D r_{\rm c} = 2.2 \times 10^{11}$[M^{-1} s^{-1}], which is independent of ΔE_∞. Therefore, whenever the rates are larger than $k_{\rm D}(\Delta E_\infty)$, they become independent of ΔE_∞. The large Onsager radius also implies that the distribution of acceptors around a donor is very high at the contact distance. This indicates that electron transfer proceeds effectively at or near the contact distance, although it is possible at several distances if a vibrational mode is included. Accordingly, the correlation among sinks far away from the contact is negligibly small. This is the reason the result of Padé approximation coincides with that of the exact solution (not shown). In the Padé approximation, correlation among sinks is not fully taken into account. However, in the present case, it gives a very accurate result since the correlation among sinks is small.

IV. Summary and Conclusions

We have studied electron-transfer reactions in ideal nonpolar solvents in which permanent dipoles and higher multipoles are absent. In nonpolar solvents, the energy of the ion pair state changes significantly with the distance between the ions. Accordingly, significant energy fluctuation is induced when the distance between the reactants fluctuates. Electron transfer occurs when the final state energy coincides with the initial state energy. In charge separation reactions, the final state is an ion pair state, and its energy fluctuates significantly when the distance between the reactants fluctuates. In charge recombination reactions, the initial state is an ion pair state, and its energy changes significantly with the distance. In both cases, the energy coincidence between the initial and final states is induced by the change in the distance between the reactants. The distance at which the energy coincidence occurs depends on the energy gap, ΔE_∞, between the initial and final states at infinity.

In charge separation reactions, the energy coincidence occurs only for $0 < \Delta E_\infty \leq e^2/(\epsilon_{op}r_0)$ in the absence of a vibrational mode. Outside this energy gap region, electron transfer does not occur. For $\Delta E_\infty \leq 0$, the energy coincidence is energetically not possible in the absence of a vibrational mode. However, if electron transfer occurs to vibrationally excited states of the final state, the energy coincidence becomes possible. Therefore, in the presence of a vibrational mode, electron transfer can occur even for $\Delta E_\infty \leq 0$. For $\Delta E_\infty > e^2/(\epsilon_{op}r_0)$, the energy coincidence occurs at distances smaller than the contact distance, r_0. However, if the initial state is vibrationally excited, the distance at which the energy coincidence occurs increases and becomes larger than r_0. Therefore, in the presence of a vibrational mode, electron transfer can occur even for $\Delta E_\infty > e^2/(\epsilon_{op}r_0)$. These effects of the vibrational mode are clearly shown in Figure 2, which also shows that the full width at a height of 10^{-6} times the maximum of the energy gap law in the presence of a vibrational mode is a few times larger than that in the case of no vibrational mode.

In charge recombination reactions, the energy coincidence occurs only for $-e^2/(\epsilon_{op}r_0) \leq \Delta E_\infty < 0$ in the absence of a vibrational mode. For $\Delta E_\infty < -e^2/(\epsilon_{op}r_0)$, the energy coincidence occurs at distances smaller than the contact distance, r_0. However, if electron transfer occurs to vibrationally excited states of the final state, the distance at which the energy coincidence occurs increases and becomes larger than r_0. For $\Delta E_\infty \geq 0$, the energy coincidence is energetically not possible in the absence of a vibrational mode. However, if the initial state is vibrationally excited, the energy coincidence becomes possible. Therefore, in the presence of a vibrational mode, electron transfer can occur even for $\Delta E_\infty < -e^2/(\epsilon_{op}r_0)$ or $\Delta E_\infty \geq 0$, as shown clearly in Figure 5, which also shows that the full width at a height of 10^{-6} times the maximum of the energy gap law in the presence of a vibrational mode is several times larger than that in the case of no vibrational mode. The second-order charge recombination rate constant in Figure 5 is abnormally high. The reason is explained in the following way: Because of the large Onsager distance, the concentration of acceptors at the contact distance in the neighborhood of which electron-transfer effectively occurs is orders of magnitude higher that that at infinity. However, the second-order rate constant is usually defined in reference to the concentration at infinity. This is the reason the charge recombination rate constant in Figure 5 is abnormally high. If we define the second-order rate constant in reference to the concentration at the contact distance, the magnitude of the rate constant is not abnormal.

We have also calculated the diffusion-mediated rate constants of charge separation and charge recombination reaction (Figures 3 and 6). In the presence of a vibrational mode, the diffusion-controlled plateau of the charge separation reaction extends over a range of a couple of electron volts, whereas that of charge recombination reactions extends over a range of several electron volts.

There are few experimental data on electron-transfer reactions in nonpolar solvents that can be compared with our theory. At present, our work is conceptually important as the basic theory of electron-transfer reactions in nonpolar solvents. In our theory, the donor−acceptor distance plays the role of the reaction coordinate, in contrast with Marcus theory, in which the solvent polarization is taken as the reaction coordinate. We hope that our theory will stimulate experimental work on electron-transfer reactions in nonpolar solvents and help to deepen our understanding of the problem.

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References and Notes

(1) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(2) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(3) Leonhardt, H.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 791.

(4) Levin, P. P.; Pluzhnikov, P. F.; Kuzmin, V. A. *Chem. Phys. Lett.* **1988**, *147*, 283.

(5) Kuzmin, M. G.; Soboleva, I. V.; Dolotova, E. V. *J. Phys. Chem. A* **2007**, *111*, 206.

(6) Verhoeven, J. W.; Scherer, T.; Willemse, R. J. *Pure Appl. Chem.* **1993**, *65*, 1717.

(7) Wegewijs, B.; Ng, A. K. F.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 6.

(8) Jäger, W.; Schneider, S.; Verhoeven, J. W. *Chem. Phys. Lett.* **1997**, *270*, 50.

(9) Burel, L.; Mostafavi, M.; Murata, S.; Tachiya, M. *J. Phys. Chem. A* **1999**, *103*, 5882.

(10) Kim, H. J.; Hynes, J. T. *J. Phys. Chem.* **1990**, *94*, 2736.

(11) Matyushov, D. V. *Chem. Phys.* **1996**, *211*, 47.

(12) Leontyev, I. V.; Tachiya, M. *J. Chem. Phys.* **2005**, *123*, 224502.

(13) Leontyev, I. V.; Tachiya, M. *J. Chem. Phys.* **2007**, *126*, 064501.

(14) Burshtein, A. I.; Frantsuzov, P. A.; Zharikov, A. A. *Chem. Phys.* **1991**, *155*, 91.

(15) Balagura, O. V.; Ivanov, A. I. *Khim. Fiz.* **1992**, *11*, 1338.

(16) Tachiya, M. *J. Phys. Chem.* **1993**, *97*, 5911.

(17) Iwai, S.; Murata, S.; Katoh, R.; Tachiya, M.; Kikuchi, K.; Takahashi, Y. *J. Chem. Phys.* **2000**, *112*, 7111.

(18) Murata, S.; Tachiya, M. *J. Phys. Chem. A* **2007**, *111*, 9240.

(19) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*, 3rd ed.; Elsevier: Oxford, 1977.

(20) (a) Huang, K.; Rhys, A. *Proc. R. Soc.* **1950**, *204A*, 406. (b) Kubo, R.;. Toyozawa, Y. *Prog. Theor. Phys.* **1955**, *13*, 160. (c) Lax, M. *J. Chem. Phys.* **1952**, *20*, 1752. (d) Levich, V. G.; Dogonadze, R. R. *Dokl. Akad. Nauk SSSR* **1959**, *124*, 123.

(21) Lin, S. H. *J. Phys. Chem.* **1966**, *44*, 3759. Kestner, N. R.; Logan J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148. Ulstrup J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. Efrima S.; Bixon, M. *Chem. Phys. Lett.* **1974**, *25*, 34. Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. Bixon, M.; Jortner, J. *Adv. Chem. Phys.* **1999** *106*, 35. Kuznetsov, A. M.; Ulstrup, J. *Electron Transfer in Chemistry and Biology; An Introduction to the Theory*; John Wiley & Sons Ltd.: West Sussex, 1999. Sumi, H. Adiabatic versus Non-Adiabatic Electron Transfer. In *Electron Transfer in Chemistry 1 Principles and Theories Methods and Techniques*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 1, p 64. Barzykin, A. V.; Frantsuzov, P. A.; Seki, K.; Tachiya, M. *Adv. Chem. Phys.* **2002**, *123*, 511.

(22) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1972.

(23) Tachiya, M.; Murata, S. *J. Phys. Chem.* **1992**, *96*, 8441.

(24) Szabo, A.; Lamm, G.; Weiss, G. *J. Stat. Phys.* **1984**, *34*, 225.

(25) Samanta, A.; Ghosh, S. K. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1993**, *47*, 4568.

(26) Seki, K.; Barzykin, A. V.; Tachiya, M. *J. Chem. Phys.* **1999**, *110*, 7639.

(27) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1973**, *58*, 4009.

(28) Rice, S. A. Diffusion-Limited Reactions. In *Comprehensive Chemical Kinetics*; Bamford, C. H.; Tipper, C. F. H.; Compton, R. G., Eds.; Amsterdam: North-Holland/American Elsevier, 1985; Vol. 25, and references cited therein.

(29) Hong, K. M.; Noolandi, J. *J. Chem. Phys.* **1978**, *68*, 5163.

(30) Debye, P. *J. Electrochem. Soc.* **1942**, *82*, 265.