



## Rate of Reaction of Electron Transfer over a Long Range and Mediated by a Solvent

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We present a simple quantum mechanical model for solvent bridge-mediated long-range nonadiabatic electron-transfer reaction rate. A perturbation theory using a one-electron model is employed to treat the electronic transition element that includes donor, acceptor and bridge unit wave functions. Reaction-coordinate activation is treated by high-temperature approximation. The pre-exponential factor in the rate coefficient becomes dependent on the distance between donor and acceptor; the decay length depends strongly on the driving force and is effective at a large range if the level of energy of the donor is nearly that of the bridge. This condition is satisfied for a process of electron transfer with excited donor molecules or in the highly exothermic regime.

According to a simple model calculation, the non-existence of an "inverted" regime in highly exothermic reaction is favored for solvent media with large relative permittivity and low-lying HOMO (highest occupied molecular orbital) or LUMO (lowest unoccupied molecular orbital). In the normal regime in which the driving force ( $\Delta G^\circ$ ) is positive or nearly zero this effect at large-range is negligible, and transfer of the electron occurs mostly at the distance of contact.

### INTRODUCTION

The electron-transfer (ET) reaction has played an important role in chemical systems and in such complicated biological processes as respiration and photosynthesis. These reactions have been actively investigated both theoretically and experimentally. Investigating the redox reaction of inorganic metal complexes, Taube<sup>1,2</sup> showed the importance of primary structure in determining electron-transfer pathways, distinguished "outer-sphere" and "inner-sphere" reaction, and explored the role of the ligand in determining rate of electron-transfer reactions.

Early theories were nonadiabatic;<sup>3</sup> that is, the rate coefficient depends explicitly on the orbital overlap of the reactants, and the change of nuclear configuration was not specifically calculated. Marcus<sup>4</sup> developed a classical theory of electron transfer in which the transfer is assumed to be adiabatic; that is, the reactants must be near each other to enhance the coupling of their electronic orbitals, and the electronic coupling is assumed to be strong enough that the probability of electronic transmission is unity so that it no longer appears in the expression for the rate coefficient. The change of solvent configuration was treated by classical dielectric polarization theory, Hush, Sutin and others further refined.<sup>5-7</sup> Levich and Dogonadze described

quantum-mechanically the change of nuclear mode.<sup>8,9</sup> Later theoretical advances were made by Ulstrup,<sup>10</sup> Jortner et al.,<sup>11</sup> Schmidt,<sup>12</sup> Hopfield,<sup>13</sup> and others. In the adiabatic theory of electron transfer, the rate coefficient of homogeneous reactions of electron transfer,



in which  $\text{ox}_1$  or  $\text{red}_2$  is varied, is predicted first to increase with decreasing standard Gibbs energy of reaction  $\Delta G^\circ$ , for small  $\Delta G^\circ$ . It is expected then to achieve a maximum when the reorganization energy is approximately equal to the Gibbs-energy change, and thereafter decline as  $\Delta G^\circ$  continues to become smaller. This region of declining rate was termed the inverted region. The existence of an inverted region was first predicted on the basis of Marcus's theory.<sup>4</sup> Quantum-mechanical correction for vibrational motions given by perturbation theories predicts a smaller but significant inversion. The difference arises from nuclear tunneling.

In the inverted region, the sharp crossing of potential surfaces makes the electron transfer event more likely non-adiabatic, as discussed in early theories of electron transfer.<sup>8,14,15</sup> The effect of the region of inversion was also predicted in nonadiabatic theory, with a different pre-ex-



ponential factor that involves an electronic coupling matrix element.

The results of measured rates of electron transfer in the highly exothermic region seem uncertain. The effect of the region of inversion was formerly not readily observed, but in recent experiments it has been observed.

From fluorescence quenching, Rehm and Weller,<sup>16</sup> Scandola and coworkers<sup>17</sup> found no inverted region in the highly exothermic region for many excited aromatic compounds in acetonitrile, but a diffusion-limited rate. Similar results were obtained in photoinduced electron-transfer reactions between aromatic compounds and amines in acetonitrile.<sup>18</sup>

This experimental evidence indicates the need for revisions to classical (and quantum-mechanical) treatments of highly exothermic reactions for which modified treatments of the pre-exponential factor in rate is needed. Although there has been much discussion of this problem and progress has been made,<sup>19-25</sup> many questions remain.

A much larger rate of reaction than that predicted by classical theory was obtained when long-range electron transfer through the solvent was allowed.<sup>18</sup> The following conditions are more favorable to electron transfer through a long distance.

(a) The existence of low-lying LUMO of solvent molecules increases the electronic coupling between donor and acceptor molecules at larger separation.

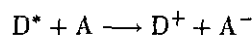
(b) A smaller energy gap between the HOMO of donor and the LUMO of solvent molecule also increases the probability of electron tunneling. In the highly exothermic region this condition is applicable, especially if the donor is in excited state.

Many experiments provide evidences of transfer of electrons through a large distance of 1.0 - 3.0 nm. For instance, the rate of oxidation of ferrocyanide by oxidized bacteriochlorophyll dimer (Bchl)<sub>2</sub><sup>+</sup> is about 10<sup>6</sup> s<sup>-1</sup>; ΔG° for the reaction is 43.5 kJ mol<sup>-1</sup>.<sup>26</sup> From EPR measurements, the distance between centers of ferrocyanide and (Bchl)<sub>2</sub><sup>+</sup> is at least 2.5 nm, corresponding to a separation 1.2-1.8 nm between edges.<sup>27</sup>

For electron transfer between two electrodes separated by absorbed monolayer assemblies, Kuhn demonstrated that the current produced decreased with increasing distance between the two aluminum plates.<sup>28</sup> The thickness of the monolayer was variable by means of fatty acids in the series C<sub>14</sub> to C<sub>23</sub>. That the current was independent of temperature was taken as evidence of tunneling through a large range.

Further evidence comes from measurements of yield of ions in photo-induced electron transfer by means of the

transient-conductivity technique. By fitting the yield to Onsager diffusion theory, we found that the distance of electron transfer was as great as 1.7 nm in acetonitrile for the reaction,<sup>29</sup>

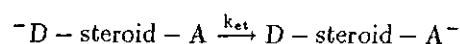


in which

D = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine or perylene

A = naphthalene.

Miller et al.<sup>30</sup> prepared steroidal derivatives with varied donors and acceptors at the ends and a widely varied driving force. Using pulse radiolysis, a radical anion was generated on the biphenyl chromophores. The decay of this radical is due mainly to the intramolecular electron transfer



These intramolecular processes were described as reactions for which the electron was transferred a large distance; the rigid saturated hydrocarbons with length exceeding 1.0 nm separated the donor and acceptor. Donors and acceptors at a rigidly fixed distance have been systematically varied.<sup>31-35</sup>

For trapped electrons produced in 2-methyltetrahydrofuran glass at 77 K with their subsequent transfer to acceptor molecules, electron tunneling occurred across an average distance 2.5 nm in 10<sup>-6</sup>s and 3.5 nm in 3 × 10<sup>-2</sup>s; benzonitrile was the acceptor.<sup>36</sup> The rate decreased exponentially with distance for electron transfer between some aromatic molecules in glassy solvents.<sup>36</sup>

Photo-induced electron transfer in the intramolecular exciplex pyrene-(CH<sub>2</sub>)<sub>3</sub>-(DMA)(*N,N*-dimethylaniline) depended strongly on solvent polarity; in strongly polar solvent such as acetonitrile, the photo-induced electron transfer took place rapidly (within 10 ps) in the extended form without formations of any "complex" between pyrene and DMA. The electron transfer in this system also takes place by the mechanism of weak interaction without close contact between the reactants.<sup>37</sup>

In such a process of electron transfer through a large distance, not is the solvent is not just a passive dielectric medium but also its molecular orbitals may play an important role in the transfer process. When solvent molecules play the role of bridge in their process, the conventional distinction between an "outer-sphere" and an "inner-sphere" mechanism may be ambiguous.

According to the standard theoretical treatment of

nonadiabatic electron transfer,<sup>9,11,16</sup> the Condon approximation is used to calculate the matrix element  $H_{12}$  for electron transfer; i.e. the value of  $H_{12}$  is assumed constant, independent of distance. The Condon approximation breaks down when the energy levels of the solvent bridge are involved in the electron transfer.<sup>38</sup> Onuchic et al. developed a detailed quantum-mechanical model involving electron, reaction coordinates and bath.<sup>38</sup> The result shows that  $H_{12}$  depends on both the driving force and the reorganization energy. The physical reason is that electronic coupling between the transferring electron and the bridge unit becomes enhanced for nuclear coordinates at the position of the "activated complex". For reactions of which the reorganization energy  $\lambda$  comes mainly from the dielectric mode of the solvent,  $\lambda$  increases with transfer distance.<sup>39</sup> The effect leads to a much enhanced rate of reaction at the highly exothermic region of inversion. Because

$$\text{rate} \propto A e^{-(\Delta G^\circ + \lambda)^2 / 4\lambda RT},$$

at  $-\Delta G^\circ > \lambda$  (region of inversion), increasing  $\lambda$  leads to a decreased barrier height.

Our objective was to develop a simplified model based on this idea to show that the inversion effect is much suppressed under conditions that are favorable to transfer an electron through a large distance.

We developed a theory of nonadiabatic electron transfer to elucidate various factors in the expression of the rate of transfer, such as change of activation energy (including change of Gibbs energy and reorganization energy) and coefficient of electron transmission (including oxidation potential and "O-O" transition energy of donor, Gibbs-energy change, reorganization energy and solvent bridge molecular orbital). In this theory, for which the first-order expression for the rate of nonadiabatic transfer is a limit, both the Franck-Condon factors of solvent reorganization and solvent bridge molecular orbital have significant roles.

## NONADIABATIC ELECTRON TRANSFER THEORY

The Fermi golden rule expression is used to calculate quantum mechanically the coefficient for the rate of nonadiabatic electron transfer. Because the process of electron transfer occurs so rapidly that nuclear coordinates remained fixed during the electron transfer, Born-Oppenheimer approximation is introduced to separate the electronic and nuclear motions, and the Condon approximation is used to calculate the electronic matrix element  $R_{ba}$  for the Born-Oppenheimer states. The rate of

electron transfer is thus equal to a product of electronic and nuclear factors. The electronic term expresses the electronic interaction between donor and acceptor. The nuclear factor is related to the nuclear activation barrier to electron transfer. The electron tunnels between donor and acceptor molecules in an "activated complex" of fixed nuclear geometric distortions, including both intramolecular bond length and non-equilibrium polarization of the solvent, with matching electronic energy of the donor and acceptor. The electronic factors limit the rate when the reorganization barrier is decreased by an exothermic reaction or when the reactants are far apart. According to perturbation theory in the lowest order, the element  $R_{ba}$  is calculated directly between the interacting donor and acceptor at the contact distance;  $R_{ba}$  is then independent of the solvent. One way to include the influence of the solvent on  $R_{ba}$  at long distance is to attach a dielectric permittivity to the coulombic operator calculate  $R_{ba}$ ;<sup>40</sup> this way lacks rigorous justification however. What one needs to consider is the electronic interactions between the valence level of the donor and the highest occupied bonding orbital or the lowest unoccupied orbital of the bridge molecules. If the interaction is strong enough the solvent acts as a tunneling bridge for the transferring electron. The transfer matrix element  $R_{ba}$  may be determined by the electronic structure of the solvent.

If the energy of the transferring electron is nearer the energy of the lowest occupied bonding orbital than that of the lowest unoccupied orbital of the bridge molecules, "hole transfer" is said to dominate the electron transfer process; conversely "electron transfer" is dominant.

Early treatments of bridge-mediated electron transfer employed one-electron models; Halpern and Orgel first identified the importance of orbital symmetry, overlap and energetics on the bridge-mediated electronic interaction.<sup>41</sup> McConnell used a model of one orbital per bridge site to describe electron exchange through a saturated bridge.<sup>42</sup> These models originated in earlier work of Kramers<sup>43</sup> and Anderson<sup>44</sup> who introduced the concept of superexchange to explain long-range antiferromagnetic coupling.

The rate of nonadiabatic electron transfer through a large distance depends critically on the electronic matrix element  $R_{ba}$  between donor and acceptor. Of three methods to calculate this matrix element, in one the interaction is assumed to occur directly through space and the presence of the bridge is ignored altogether. In the other methods all interactions are mediated by the intervening medium (bonds). The "medium" includes atomic or molecular species of any number between donor and acceptor. This medium may be protein, solvent molecule or

hydrocarbon chain. The donor-acceptor interaction through bonds depends on distance, energy, orbital symmetry, and detailed molecular structure of the bridge.<sup>45</sup> Of the two through-bond mechanisms, they differ in the treatment of interactions between neighboring bridge units. Strong electronic exchange is assumed in one case but weak electronic interaction between bridging groups in the others. Each method is an approximation of the correct interaction between donor and acceptor that is assisted by interactions with both bound and continuum states. We present an improved theory of electron transfer through a large distance that includes both through-bond weak interactions and interaction between donor and acceptor through space.

According to the Fermi golden rule, the coefficient  $k_e$  for the rate of electron between two transfer vibronic states (DA) and ( $D^+A^-$ ) is

$$k_e = \frac{2\pi}{\hbar} \sum_{v''} \sum_{v'} P_{av'} |\langle \Psi_{bv''} | \hat{V} | \Psi_{av'} \rangle|^2 \delta(E_{bv''} - E_{av'}) \quad (1)$$

in which  $\Psi_{bv''}$  and  $\Psi_{av'}$  represent the vibronic states of (DA) and ( $D^+A^-$ ), respectively, and  $P_{av'}$  is the Boltzmann factor.  $(E_{bv''} - E_{av'})$  denotes the difference of vibration-electronic energy near the crossing of the potential curves of (DA) and ( $D^+A^-$ ). With Born-Oppenheimer states, the distribution of vibronic energy of initial states at the limit of high temperature is through a broadened gaussian energy spectrum;<sup>13</sup> that is, the removal of an electron from the donor is characterized by a Gaussian distribution of energies  $D_D(E)$ . Similarly, there is an electron insertion spectrum  $D_A(E)$  that describes the distribution of changes of charges that result from insertion of an electron into the acceptor in various vibrational states.

At high temperature the total rate of electron transfer is written<sup>11-13</sup>

$$k_e = \frac{2\pi}{\hbar} \int D_D(E) |R_{ba}(E)|^2 D_A(E) dE \quad (2)$$

Integrations is over all possible electronic energies  $E$  that lie within the overlap of  $D_D(E)$  and  $D_A(E)$ .  $R_{ba}$  represents the electronic matrix element involved in electron transfer

$$R_{ba} = \langle \Phi_b | \hat{V} | \Phi_a \rangle, \quad (3)$$

in which  $V$  is the perturbation that mixes acceptor electronic state of donor and acceptor  $\Phi_b$  is the electronic

wave function of the final state ( $D^+A^-$ ) in which the transferring electron is localized at A and  $\varphi_a$  is the electronic wave function of the initial state (DA). The interaction between donor and acceptor is mediated by mixing localized states with bridge states. In simpler theories,  $\varphi_a$  is taken to be the state  $\varphi_a$  localized on D.

When the temperature is great enough that vibrational states are taken as a continuum, the electron spectral function for removal of the electron has the form,

$$D_D(E) = \left( \frac{1}{4\pi\lambda_D kT} \right)^{\frac{1}{2}} \cdot \exp \left[ \frac{-(E - \Delta E_D - \lambda_D)^2}{4\lambda_D kT} \right] \quad (4)$$

Similarly, the spectral function for electron insertion is

$$D_A(E) = \left( \frac{1}{4\pi\lambda_A kT} \right)^{\frac{1}{2}} \cdot \exp \left[ \frac{-(E + \Delta E_A + \lambda_A)^2}{4\lambda_A kT} \right], \quad (5)$$

in which  $\Delta E_D$  is the ionization energy of a donor in the solvent (including stabilization energy of the solvent) and  $\Delta E_A$  is the electron affinity of an acceptor in the solvent;  $\lambda_D$  and  $\lambda_A$  are reorganization energy parameters of the donor and acceptor. The total reorganization energy  $\lambda$  is equal to  $\lambda_D + \lambda_A$ . The separation of reorganization energy  $\lambda$  into  $\lambda_D$  and  $\lambda_A$  is obvious for intramolecular vibrational modes where vibrational energy is clearly identified in intramolecular local motion. For solvent interaction of electron and dipole, this separation is less obvious as  $\lambda$  becomes dependent on distance. Kestner et al. considered explicit interactions between the electron and dipole and showed that this separation is possible. We used a method due to Marcus in the Appendix also to show this separation.

To calculate  $R_{ba}$ , we represent  $\varphi_a$  as a perturbation series,

$$\varphi_a = \Phi_a + \frac{1}{E - H_0} V \Phi_a + \frac{1}{E - H_0} V \frac{1}{E - H_0} V \Phi_a + \dots \quad (6)$$

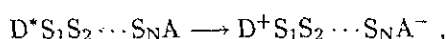
in which  $\Phi_a$  is the electronic wave function of initial state (DA) without a contribution from the solvent bridge,  $E$  is the energy of the transferring electron,  $H_0$  is the unper-

turbed hamiltonian operator.

Eqs. (3) and (6) become rewritten as follows

$$R_{ba} = V_{ba} + \sum_m \frac{V_{bm}V_{ma}}{E - E_m} \quad (7)$$

For the electron transfer,



the intermmediate state  $\Phi_m$  is a mixture of

$$\begin{aligned} \phi_1 &= \Phi_D + S_1^- S_2 \cdots S_N A \\ \phi_2 &= \Phi_D + S_1 S_2^- \cdots S_N A \\ &\dots\dots\dots \\ \phi_N &= \Phi_D + S_1 S_2 \cdots S_N^- A ; \end{aligned}$$

that is

$$\Phi_m = \sum_{n=1}^N C_{mn} \phi_n \quad (8)$$

The secular equations are

$$\begin{aligned} C_{m1}(H_{11} - E_m) + C_{m2}H_{12} + \cdots + C_{mN}H_{1N} &= 0 \\ C_{m1}H_{21} + C_{m2}(H_{22} - E_m) + \cdots + C_{mN}H_{2N} &= 0 \\ \dots\dots\dots \\ C_{m1}H_{N1} + \cdots + C_{mN}(H_{NN} - E_m) &= 0 . \end{aligned} \quad (9)$$

Using the approximation of interaction between only nearest neighbours,

$$\begin{cases} H_{nn+1} = H_{nn-1} = \beta \\ H_{nn} = E_c \end{cases} \quad (10)$$

we obtain

$$\begin{cases} E_m = E_c + 2\beta \cos \frac{m\pi}{N+1} \\ C_{mn} = \left( \frac{2}{N+1} \right)^{\frac{1}{2}} \sin \frac{mn\pi}{N+1} \end{cases} \quad (11)$$

Substituting Eq. (11) into Eq. (7) yields

$$R_{ba} = V_{ba} + \beta_D \beta_A \left( \frac{2}{N+1} \right) \sum_{m=1}^N \frac{(-1)^m \sin^2 \frac{m\pi}{N+1}}{E_c - E + 2\beta \cos \frac{m\pi}{N+1}} \quad (12)$$

in which

$$\beta_D = \langle \phi_1 | \hat{V} | \Phi_a \rangle ; \quad \beta_A = \langle \Phi_b | \hat{V} | \phi_N \rangle \quad (13)$$

For  $N = 1$

$$R_{ba} = V_{ba} - \frac{\beta_D \beta_A}{(E_c - E)} \quad (14)$$

and  $N = 2$

$$R_{ba} = V_{ba} + \frac{\beta_D \beta_A \beta}{(E_c - E)^2 - \beta^2} \quad (15)$$

or approximately, with  $\beta$  taken to be a small quantity,

$$R_{ba} = V_{ba} - \frac{\beta_D \beta_A \beta}{(E_c - E)^2} \quad (16)$$

In general, we expect that approximately

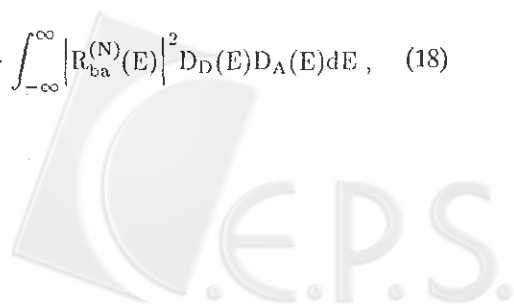
$$R_{ba} = V_{ba} + (-1)^N \frac{\beta_D \beta_A \beta^{N-1}}{(E_c - E)^N} \quad (17)$$

According to the one-electron approximation,  $\beta_D$  simply expresses the electronic interaction between a localized donor and the solvent,  $\beta_A$  and  $\beta$  are interpreted similarly.  $V_{ba}$  represents the interaction through-space between the donor and the acceptor.  $N$  is the number of intervening sites (identical bridging units) between  $D$  and  $A$ .  $N$  signifies the distance between the donor and acceptor; that is,  $N = (R - R_c)/l$ ,  $l$  being the length of a bridging unit.  $R_c$  is the distance of effective contact of the two reactants,

From Eqs. (2) and (17), we separately consider the  $N$ th-order contribution to the coefficient of the rate of electron transfer

$$k_e^{(N)} = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} |R_{ba}^{(N)}(E)|^2 D_D(E) D_A(E) dE \quad (18)$$

in which



$$R_{\text{ba}}^{(N)}(E) = \left( \frac{\beta_D \beta_A}{\beta} \right) \left( \frac{\beta}{E - E_c} \right)^N \quad (19)$$

Substituting Eqs. (4) and (5) into Eq. (18), we rewrite Eq. (18) as

$$k_e^{(N)} = \frac{2\pi}{h} \left( \frac{1}{4\pi\lambda kT} \right)^{\frac{1}{2}} \exp\left( \frac{-(\Delta E + \lambda)^2}{4\lambda kT} \right) \cdot \int_{-\infty}^{\infty} \left( \frac{\beta_D \beta_A}{\beta} \right)^2 \left( \frac{\beta}{|E - E_c|} \right)^{2N} \cdot \exp\left[ \frac{-(E - E^*)^2}{4\lambda kT} \right] dE \quad (20)$$

in which  $E^*$  is the most probable energy of the transferring electron for the transfer.  $E^*$  is given by

$$E^* = \frac{(\lambda_A \Delta E_D - \lambda_D \Delta E_A)}{\lambda_A + \lambda_D}$$

$$\bar{\lambda} = \frac{\lambda_A \lambda_D}{(\lambda_A + \lambda_D)}$$

$$\lambda = \lambda_A + \lambda_D \quad (21)$$

In the final theoretical expressions, Eqs. (20) and (21), for the rate of electron transfer,  $\Delta E$  is the energy of reaction. In most applications the change of Gibbs energy  $\Delta G^\circ$  replaces  $\Delta E$ . Marcus had justified this replacement for a nonadiabatic process without superexchange by a semi-classical analysis of the Franck-Condon factor.<sup>46</sup> For many applications, the change of entropy is practically small and hence negligible in the process of electron transfer. Thus, we let

$$\Delta E = \Delta E_D + \Delta E_A$$

$$\cong \Delta G^\circ \quad (22)$$

$\Delta G^\circ$  represents the overall change of Gibbs energy of the electron-transfer reaction. A rigorous justification of this replacement in Eq. (21) is unavailable at present and further analysis of the vibration-rotational modes of the bridges would be necessary.

Because varied reaction paths over the saddle point in the energy surface produce different total energies at the transition structure, the common assumption of transition-state theory is that most reaction crosses the barrier at its

lowest point; hence the energy of the transition structure is at saddle point. According to this saddle-point method, one can replace approximately the integral in Eq. (20) by one term. Eq. (20) is approximated as

$$k_e^{(N)} = \frac{2\pi}{h} \left( \frac{1}{4\pi\lambda kT} \right)^{\frac{1}{2}} \left( \frac{\beta_D \beta_A}{\beta} \right)^2 \cdot \left( \frac{\beta}{E^* - E_c} \right)^{2N} \exp\left[ \frac{-(\Delta G^\circ + \lambda)^2}{4\lambda kT} \right] \quad (23)$$

This result corresponds to the classical Marcus quadratic form.<sup>4</sup>

When the system is at the saddle crossing point of the two multi-dimensional harmonic potential surface, the vertical ionization energy  $V_o$  of the donor of an electron to an adjacent bridging unit is

$$V_o = E^* - E_c$$

$$= (\Delta E_D - E_c) - \frac{\lambda_D}{\lambda} (\Delta E_D + \Delta E_A)$$

$$= (IP_D - \lambda_D - E_c) - \frac{\lambda_D}{\lambda} \Delta G^\circ$$

$$= V_o^\circ - \frac{\lambda_D}{\lambda} (\Delta G^\circ + \lambda) \quad (24)$$

and

$$V_o^\circ = IP_D - E_c \quad (25)$$

$V_o^\circ$  is the vertical ionization energy for removal of an electron from donor to adjacent bridging unit with nuclear coordinates in their equilibrium configurations. We estimate it as the difference between the ionization potential  $IP_D$  of the donor and the orbital energy of the bridge  $E_c$ .  $V_o$  is the corresponding quantity with nuclear coordinates in their activated complex.  $\Delta E_D$  is the sum of ionization potential and solvation energy due to the donor; the latter is  $-\lambda_D$ . Eq. (24) was previously given in a simplified treatment<sup>47</sup> and more rigorously.<sup>45d</sup>

For the reaction of transfer of the photo-electron, the donor is in the excited state; its O-O transition energy is  $E_D^*$ ;  $V_o^\circ$  in Eq. (25) is replaced by

$$V_o^\circ = IP_D - E_D^* - E_c \quad (26)$$

The electron transition element in the pre-exponen-



tial factor Eq. (23) is placed in the conventional form  $H^2 \exp[-\alpha(R-R_C)]$ ; then Eq. (23) adopts the familiar form,

$$k_e^{(N)} = \frac{2\pi}{\hbar} H^2 \exp[-\alpha(R-R_C)] \left( \frac{1}{4\pi\lambda kT} \right)^{\frac{1}{2}} \cdot \exp \left[ \frac{-(\Delta G^\circ + \lambda)^2}{4\lambda kT} \right] \quad (27)$$

in which

$$H = \frac{\beta_D \beta_A}{\beta} \quad (28)$$

$$\alpha = \frac{2}{\ell} \ln \frac{V_o}{\beta} \quad (29)$$

The decay factor  $\alpha$  depends on the ratio of  $V_o$ , the vertical ionization energy of the donor to the bridge at the configuration of the "activated complex", and  $\beta$ . A smaller value of  $V_o/\beta$  leads to electron transfer at a larger distance. The transfer distance factor  $\alpha$  here depends on reorganization energy  $\lambda$ . If  $\lambda$  were contributed mainly by dielectric polarization,  $\alpha$  would be strongly dependent on distance. In fact, the electronic coupling depends exponentially on  $R$ . This effect is significant in sample calculations of the next section. Eqs. (28) and (29) were used by Miller and Beitz in treating electron transfer at large distance using superexchange, but  $V_o$  was considered by them as independent of  $\lambda$ .<sup>36a</sup>

## RESULTS

The coefficient of the total rate of electron transfer  $k_q$  includes both the first-order contribution,  $k_e$  (transfer through space) and another of high order rate for electron transfer  $k_e^{(N)}$ ; that is,

$$k_q = k_e \left( \begin{array}{l} \text{through-space} \\ \text{nonadiabatic term} \end{array} \right) + \sum_N k_e^{(N)} (\text{high-order term}) \quad (30)$$

in which

$$k_e = \frac{2\pi}{\hbar} |V_{ba}|^2 \left( \frac{1}{4\pi\lambda kT} \right)^{\frac{1}{2}} \cdot \exp \left[ \frac{-(\Delta G^\circ + \lambda)^2}{4\lambda kT} \right] \quad (31)$$

The high-order rate terms of the rate of electron transfer are integrated over all space. Therefore the total rate coefficient of electron transfer is written as

$$k_q = k_e + k_h \quad (32)$$

in which

$$k_h = \frac{2\pi}{\hbar} \left( \frac{\beta_D \beta_A}{\beta} \right)^2 \int_{R_c+\ell}^{\infty} \left( \frac{\beta}{V_o} \right)^{2N} \cdot \left( \frac{1}{4\pi\lambda kT} \right)^{\frac{1}{2}} \exp \left[ \frac{-(\Delta G^\circ + \lambda)^2}{4\lambda kT} \right] \cdot 4\pi R^2 dR \quad (33)$$

In the integrand,  $\lambda$  and  $N$  depend on distance.

The rate coefficient of electron transfer depends on the distance of electron tunneling, the reorganization energy, the driving force of the reaction, the ionization energy and the O-O transition energy of the donor in the case of an excited reactant and the molecular orbital energy of the solvent bridge.

We made a detailed numerical calculation of the rate based on Eq. (32), investigating the influence of various parameters in Eq. (32). The results are plotted as  $\log(k_q)$  versus  $\Delta G^\circ$  in Figs. 1-3.

To calculate the parameter for reorganization energy  $\lambda_A$  and  $\lambda_D$ , we use the conventional dielectric model. This model is reasonable for our previous experimental system involving an excited aromatic compound and an amine.<sup>18</sup> We have  $\lambda_D$  and  $\lambda_A$  as (see appendix),

$$\lambda_X = (\Delta e)^2 \left( \frac{1}{2r_x} - \frac{1}{2R} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon} \right), \quad X = D \text{ or } A \quad (34)$$

in which  $\Delta e$  is the charge transferred in the reaction,  $n$  is the refractive index of the medium,  $\epsilon$  is the static dielectric permittivity of the medium,  $r_D$  and  $r_A$  are the radii of the two reactants, and  $R$  is the distance through which the electron transfer.

### The Effect of Ionization Energy of the Donor

The dependence of the rate of electron transfer on electron couplings, solvent polarity and reduction potential of donor and acceptor varies with details of the model. We examined numerically various factors that control the rate. Our calculations were performed with parameters appropriate to photo-electron transfer in acetonitrile.<sup>18</sup>

We chose  $\beta = \beta_D = \beta_A = 0.03$  eV; only the product  $\beta_D\beta_A$  appears in the final rate expression. This choice seems reasonable as a qualitative estimate because electron coupling between nonbonding  $\pi$ -electrons should be smaller than  $\sigma$ -electrons (0.1 eV) and stronger than the van der Waals interaction (0.001 eV). The parameter  $V_{ba}$  was chosen to be  $V_{ba} = 0.02$  eV, so that the long range effect is not dominated by direct donor-acceptor transfer. The other solvent parameters were chosen as  $l = 0.3$  nm,  $\epsilon = 37.5$ ,  $n = 1.3441$ ,  $E_c = 1$  eV. (approximately valid for acetonitrile). The radii were chosen as  $r_D = r_A = 35$  nm; these values seem typical of the aromatic molecules used in experiments. Fig. 1. displays as an example of the effect of changing the ionization energy of the donor;  $IP_D$  was varied in the range 2-5 eV.

In Fig. 1, the line A represents the coefficient of the first-order rate coefficient of electron transfer according to nonadiabatic electron transfer. The lines B, C, D, represent the coefficient of the total rate of electron transfer according to Eq. (32) with the ionization energy of the donor

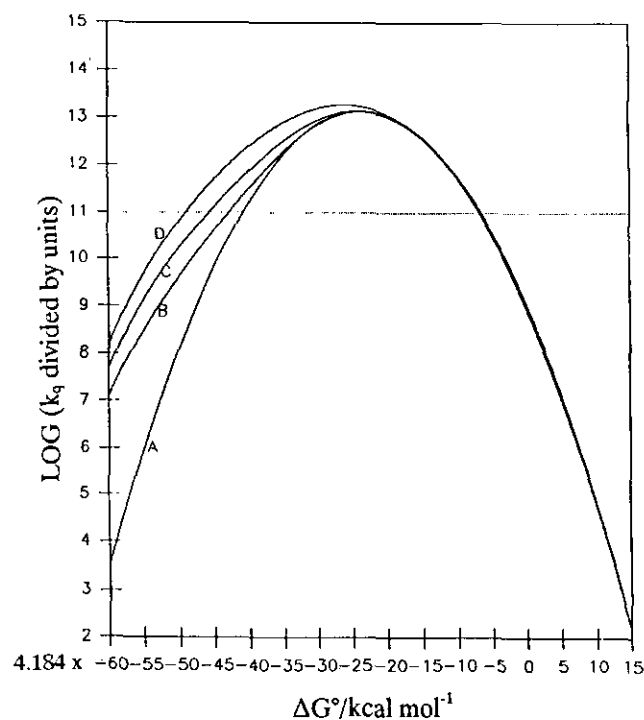


Fig. 1. Plots of  $\log(k_q)$  for varied values of  $\Delta G^\circ$ . The line A represents a first-order rate coefficient of electron transfer according to nonadiabatic electron transfer. The lines B, C, D, represent the total rate coefficient of electron transfer according to Eq. (39) with donor ionization energy being 5 eV, 3 eV, 2 eV, respectively. The dotted line represents a possible diffusion limit; other parameters are defined in the text.

being 5, 3 and 2 eV, respectively. The dotted line represents a possible diffusion controlled limit in a normal solvent.

Fig. 1 shows the net contribution due to the electron transfer through space. In the region ( $\Delta G^\circ > -\lambda$ ), the rate of electron transfer is controlled by the activation energy mostly according to a first-order process in which short-range electron transfer dominates. We used<sup>16</sup> a form like Eq. (31) to fit experimental data in the normal region; the result is consistent in that the reorganization energy agrees closely with values given by Eq. (34). In contrast, in the highly exothermic region, ( $\Delta G^\circ < -45$  kcal mol<sup>-1</sup>), the rate of electron through space transfer is less important than the high-order mechanism of electron transfer, occurs mainly through the solvent. The long-range process is favored because the energy gap between donor and solvent in the activated complex becomes smaller. The smaller the ionization energy of the donor, the more the higher-order process of electron transfer contributes, and the greater the average distance of electron transfer. For donors having a small ionization energy, such as TMPD (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine), the electron transfer large distance occurs at about 1.8 nm.<sup>29</sup>

Even for the same overall change of Gibbs free energy

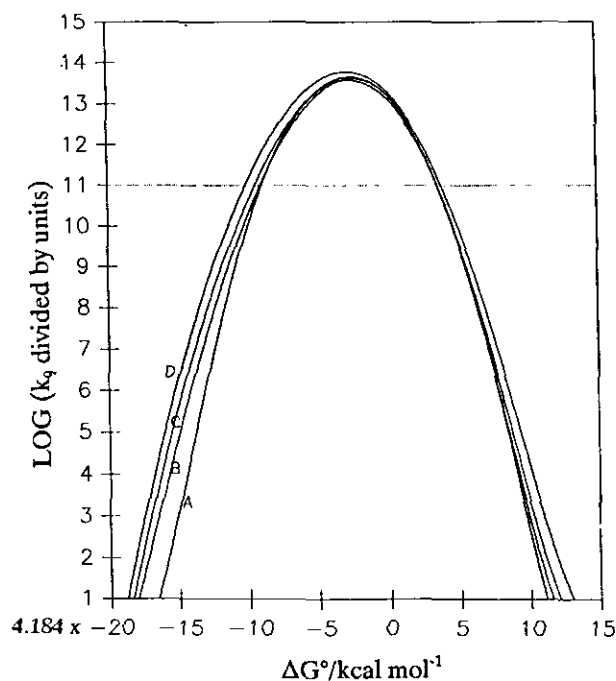


Fig. 2. Plots of  $\log(k_q)$  for different values of  $\Delta G^\circ$ . The calculation is performed by decreasing the dielectric permittivity of the solvent ( $\epsilon = 2$ ). The line, B, C, D, have same meaning as in Fig. 1 with donor ionization energy being 5, 3, 2 eV, respectively; other parameters are the same as Fig. 1.



for electron transfer, the system with a smaller ionization energy of the donor results in a greater coefficient of the rate of electron transfer. This effect is due to stronger coupling with the solvent bridge, consistent with previous results.<sup>18</sup>

For an excited donor, varying the O-O transition energy is also equivalent to varying the ionization energy in Eq. (25). According to Fig. 1, the greater the O-O transition energy of the donor, the larger is the contribution of the high-order process of electron transfer and the greater the coefficient of the rate of electron transfer. From photo-conductivity experiments,<sup>29</sup> an excited donor, such as perylene, results in electron transfer through a long distance (about 1.6 nm).

In experimental systems,<sup>16,18</sup> to reach the highly exothermic region ( $\Delta G^\circ < -35 \text{ kcal mol}^{-1}$ ) the donors, such as naphthalene, must be in an excited state (with tetracyanoethylene as acceptor). The O-O transition energy of naphthalene is so large (about 4 eV) that the process of electron transfer through a long distance is dominant. Therefore, to find the inverted region in the highly exothermic region in acetonitrile in such a system is difficult.

In general, in reaction having  $\Delta G^\circ \ll 0$ , the energy gap between donor and solvent does not necessarily

become smaller. The condition  $\Delta G^\circ \ll 0$  is produced by having the level of the acceptor much lower than the donor with a fixed level of the donor. In this case, the rate of electron transfer is expected to fall into the inverted region. This case may apply for photoinduced electron transfer in photosynthetic molecular models.<sup>48</sup> Joran et al. measured the rates of electron transfer for zinc meso-phenyloctamethylporphyrins coupled to variously substituted quinones via a dicyclooctane spacer.<sup>48</sup> They fixed the oxidation potential of the donor and the distance of transfer and adjusted exothermicity by varying the levels of the acceptor; they observed a decrease of rate in the inverted region.

#### The Effect of Relative Permittivity of the Solvent

The calculation was performed for the relative permittivity of the solvent decreased to  $\epsilon = 2$  (Fig. 2); other parameters were kept the same as for Fig. 1. The lines B, C, D have the same significance as in Fig. 1 with the ionization energy of the donor being 5, 3 and 2 eV respectively. In all regions processes of high order contribute much less relative to the case of Fig. 1. The distance of electron transfer is almost the distance of contact. The decay factor of the transfer distance  $\alpha$  is exceeded  $20 \text{ nm}^{-1}$  for all cases in Fig. 2.

We compare the contribution of the high-order process in varying solvent polarity in the highly exothermic regions in Figs. 1 and 2. The greater the polarity of the solvent becomes, the more the high-order process contributes, and the greater the average distance of electron transfer. This result is consistent with our experimental results.<sup>18,29</sup> We found a small decrease in rate in the region of inversion in photo-induced transfer in cyclohexane. For a non-polar solvent we expected to find a much smaller distance of transfer.

#### The Effect of Decreasing the Energy of the Bridge Units

For a polar solvent, decreasing the energy of the bridge unit increased the distance of transfer. In Fig. 3,  $\log(k)$  vs  $\Delta G^\circ$  is plotted for  $E_c = 2.5 \text{ eV}$ ,  $IP_D = 5 \text{ eV}$ ,  $\epsilon = 37.5$  with the excitation energy  $E_D^*$  of the donor being 3 eV (E), 2.5 eV (D), 2 eV (C) and 1 eV (B) respectively. To simulate the experimental results, we included the effect of the diffusion-controlled limit; that is, we plotted

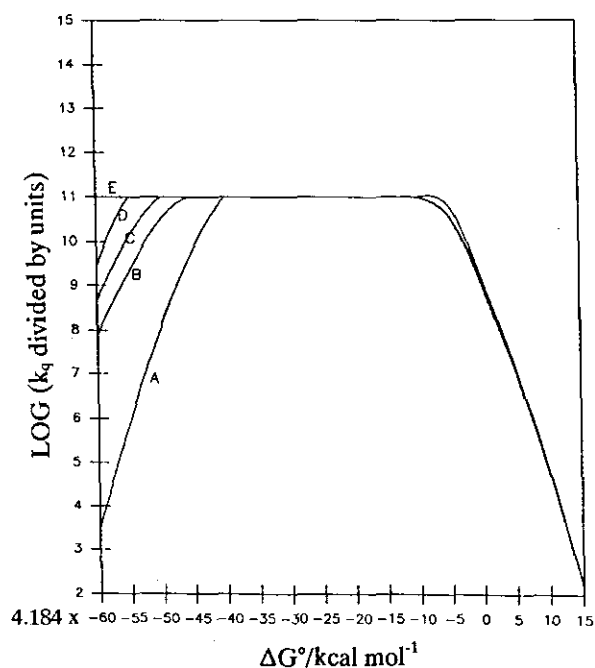


Fig. 3. Plots of  $\log(k)$  of varied of  $\Delta G^\circ$ . For  $E_c = 2.5 \text{ eV}$ ,  $IP_D = 5 \text{ eV}$ ,  $\epsilon = 37.5$  with donor excitation energy  $E_D^*$  being 3 eV (E), 2.5 eV (D), 2 eV (C), 1 eV (B) respectively; other parameters are the same as in Fig. 1.

$$k = \frac{k_d}{1 + k_d/k_q} \quad (35)$$

and took the diffusion-controlled rate  $k_d = 1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ . Curve A in Fig. 3 represents the result of the theory of

electron transfer through space; an inversion effect exists for  $\Delta G^\circ < -35 \text{ kcal mol}^{-1}$ . When  $E_D^*$  was increased to 3 eV, the inverted region completely disappeared.

The values of the decay factor  $\alpha$  for the transfer distance decrease greatly from the normal region to the highly exothermic region for case E. For the highly exothermic region,  $\alpha$  is not constant but depends on distance. For  $E_D^* = 3 \text{ eV}$  (case E), and  $\Delta G^\circ = -60 \text{ kcal mol}^{-1}$ ,  $\alpha = 9.0 \text{ nm}^{-1}$  at  $R = 1 \text{ nm}$  whereas  $\alpha < 1.0 \text{ nm}^{-1}$  at  $R = 1.4 \text{ nm}$ , i.e. the most efficient transfer distance is around 1.4 nm. For  $E_D^* = 3 \text{ eV}$ ,  $\Delta G^\circ > -30 \text{ kcal mol}^{-1}$ , the decay factor  $\alpha$  of the distance of transfer is larger than  $20 \text{ nm}^{-1}$ ; the distance of transfer is nearly the distance of contact.

## CONCLUSION

We have developed a simple quantum-mechanical model to treat the dependence of the rate of electron-transfer on distance, reorganization energy, and driving force of the donor/acceptor couple. The electron transition elements are sensitive to the electronic energies of the donor, acceptor, and bridge. The effect of transfer through a large distance increases the rate in the inverted region to the extent of its disappearance for realistic parameters.<sup>18</sup>

In their calculation of electron transfer in a highly exothermic homogeneous outer-sphere reaction, Marcus and Siders chose an exponential dependence of the matrix element  $R_{ab}$  without explicit consideration of the role of the electronic orbitals of the solvent.<sup>49</sup> The prediction of an inverted region in the plot of rate coefficient vs  $\Delta G^\circ$  is related to the shape of the spectral overlaps in Eq. (2).

Having explained the disappearance of the inverted region we would like to comment on the observation of the region in some experiments. It seems they falls into three types. In the first, either the process of electron transfer occurred across a rigid saturated hydrocarbon spacers<sup>33</sup> or in a glassy medium (MTHF or isooctane).<sup>33,36</sup> In either case the coupling of the electronic states was weak due to the high-lying intermediate HOMO levels. According to our calculation (Fig. 2), we expect an inverted region in the highly exothermic region. Farid and co-workers measured the rate of return transfer of electron within photo-produced geminate radical ion pairs,  $k_{ET}$ .<sup>50</sup> It shows rate fall-off in the region of increasing exothermicity. This result is not in conflict with our theory because the geminate radical pair recombines in the solvent cage before separation. The distance of transfer is expected to be short as the original process of electron transfer of geminate-pair

production is within short range. A first-order theory is expected to suffice. In the work of Lewitzka and Leohmannsreoben,<sup>51</sup> also an inverted region was observed for geminate charge recombination for a reaction in acetonitrile solvent. In recent work of McCleskey, Winkler and Gray,<sup>52</sup> they observed inverted fall-off behavior for recombination electron transfer while it remains diffusion limited in forward electron transfer even where it is highly exothermic. In the experimental system<sup>18</sup> the donor-excited process of electron transfer in acetonitrile is much more favorable for the disappearance of the region of inversion because of the transfer through a large distance. In the third type of electron transfer, the large  $\Delta G^\circ < 0$  is adjusted by low acceptor energy level while keeping the donor level relatively low as may have been observed.<sup>48</sup> We expect a system of this kind to show an inverted behavior.

Our theory is relevant to biological electron transfer for which the effect at long range seems to be the norm.<sup>51</sup> McLendon reviewed the process of electron transfer in proteins and model systems;<sup>52</sup> he conjectured that one is expected to consider coupling between the donor and acceptor via appropriate orbitals in the intervening medium. Detailed quantum mechanical study on electron transfer in the protein system appears prohibitively complex. Model systems would be interesting both theoretically and experimentally. Further work to investigate the following effects are of interest: (a) Direct determination of the spectral distribution functions  $D_D(E)$  and  $D_A(E)$  in Eq. (2) may be possible by photo-electron spectroscopy. (b) Experimental measurements are needed of the dependence on distance of rate of electron transfer like those of Miller et al. With various bridges,<sup>36b</sup> one can elucidate the decay of electronic coupling. (c) Electron transfer with a photo-excited donor indicates the effects of the solvent in the highly exothermic region. (d) Quantum Monte Carlo simulations on a model system are useful.

Kakitani and Mataga proposed<sup>53</sup> an explanation of the behaviour  $k_{ET}$  vs  $\Delta G^\circ$  in the inverted region. Their idea is based on the effect that dielectric saturation of the solvent leads to diverse curvatures of the potential-energy surfaces of reactant and products. By this means they explained the larger width of  $k_{ET}$  vs  $\Delta G^\circ$  for quenching of fluorescence by separation of charge. Marcus used<sup>36</sup> the analogies between the intensity of the charge-transfer spectral line vs its frequency and the plot  $k_{ET}$  vs  $\Delta G^\circ$  to examine the cases for partial dielectric saturation. This theory relies on the decreased activation energy due to dielectric saturation or change of vibrations in the highly exothermic region in contrast to the present theory. There

are insufficient experiments to guide the choice of these theoretical constructs. Further theoretical and experimental work on the role of solvent in electron transfer is desirable.

A more nearly complete theoretical treatment of the role of solvent is expected to include more detailed description of the role of the dipolar solvent in determining reorganization energy, the effect of electron exchange in the tunneling of electron (the role of valence orbitals of solvent) and the effect of dynamic friction due to solvent relaxation. The latter effect was omitted from our work; it is expected limit the rate when the rate is rapid. This effect may be important for biological electron-transfer.<sup>57</sup> Theories of the frictional effect on the nonadiabatic process of electron transfer at large distances are developing rapidly.<sup>58</sup>

We considered only the electronic factor; in the highly exothermic region, the Franck-Condon overlap may vary substantially, and the efficiency of transfer may be enhanced when the gap of energy between the states is small. This effect merits further study.

## APPENDIX

In derivations of Eqs. (2), (4) and (5) from the golden rule the separation of the nuclear mode energy into contributions due to donor D, and acceptor A have the form,

$$\begin{aligned} \epsilon_D^+ &= (v + 1/2)\hbar\omega_D^+ \\ \epsilon_A^- &= (v + 1/2)\hbar\omega_A^- \\ \epsilon_D^{\delta+} &= (v + 1/2)\hbar\omega_D^{\delta+} \\ \epsilon_A^{\delta-} &= (v + 1/2)\hbar\omega_A^{\delta-} \end{aligned} \quad (\text{A-1})$$

Evaluation of the Franck-Condon factor with Boltzmann averaging at high temperature leads to Eqs. (2), (4) and (5).<sup>11</sup>

The separation of reorganization energy  $\lambda$  into  $\lambda_D$  and  $\lambda_A$  is thus formally assured. For the contribution of dielectric polarization energy, the implementation of this separation is not obvious. We have described a heuristic procedure due to Marcus to show this separation. The method is based on a thermodynamic charging process to evaluate the non-equilibrium Gibbs energy for a process of electron transfer



We consider a process of charging in two steps in a dielectric medium. We vary the charge of reactant "i" from  $e_i$  to  $e_i'$ ; we return the charge of reactant "i" from  $e_i'$  to  $e_i$  but with the orientational dipole fixed. Only the electronic polarization follows the discharging process.

$a_i$ : radius of reactant  $i$ ,  $i = 1$  donor  $i = 2$ , acceptor.

$R$ : distance between D and A.

$r_i$ : the center of molecule  $i$  relative to a position  $r$  in solvent.

$\varphi(r)$ : electric potential at  $r$ .

$n$ : refractive index of solvent.

In the charging process,

$$e_i^v = e_i + v(e_i' - e_i) \quad (\text{A-3})$$

with the potential at a position  $r$  given by

$$\varphi^v(r) = \frac{e_1^v}{\epsilon r_1} + \frac{e_2^v}{\epsilon r_2} \quad (\text{A-4})$$

The solvation energy of the donor is

$$\tilde{\varphi}_1^v(r) = \frac{e_2^v}{\epsilon R} + \frac{e_1^v}{a_1} \left( \frac{1}{\epsilon} - 1 \right) \quad (\text{A-5})$$

In Eq. (A-5), a self-energy (solvation in vacuum) is subtracted. The donor molecule is considered spherical with the charge at its surface.

For the process (A-2),  $e_1 = e_2 = 0$ , the reversible work of charging donor D is

$$W_1^D = \int_0^1 \left[ \frac{e_2^v}{\epsilon R} + \frac{e_1^v}{a_1} \left( \frac{1}{\epsilon} - 1 \right) \right] de_1^v \quad (\text{A-6})$$

With Eqs. (A-3) and (A-7), the result for  $W_1^D$  is given by (A-8)

$$\Delta e_i = e_i' - e_i \quad (\text{A-7})$$

$$\begin{aligned} W_1^D &= \int_0^1 \left[ \frac{e_2^v + v\Delta e_2}{\epsilon R} + \frac{e_1^v + v\Delta e_1}{a_1} \left( \frac{1}{\epsilon} - 1 \right) \right] \cdot \Delta e_1 dv \\ &= \frac{1}{\epsilon R} \left( e_2 \Delta e_1 + \frac{1}{2} \Delta e_1 \Delta e_2 \right) \\ &\quad + \frac{1}{a_1} \left( \frac{1}{\epsilon} - 1 \right) \left[ e_1 \Delta e_2 + \frac{1}{2} (\Delta e_1)^2 \right] \end{aligned} \quad (\text{A-8})$$

Similarly,  $W_1^A$  is given by

$$W_1^A = \frac{1}{\epsilon R} \left( e_1 \Delta e_2 + \frac{1}{2} \Delta e_1 \Delta e_2 \right) + \frac{1}{a_2} \left( \frac{1}{\epsilon} - 1 \right) \left[ e_2 \Delta e_2 + \frac{1}{2} (\Delta e_2)^2 \right] \quad (\text{A-9})$$

For the discharging process,  $v$  returns from 1 to 0 in Eq. (A-3), with only the component of electronic polarization responding to the process. We repeat the preceding calculation with  $n^2$  replacing the relative permittivity. The final results are

$$W_{II}^D = -\frac{1}{a_1} \left( \frac{1}{n^2} - 1 \right) e_1' \Delta e_1 - \frac{e_2' \Delta e_1}{\epsilon R} + \frac{1}{2} \frac{(\Delta e_1)^2}{a_1} \left( \frac{1}{n^2} - 1 \right) + \frac{1}{2} \frac{\Delta e_1 \Delta e_2}{n^2 R} \quad (\text{A-10})$$

$$W_{II}^A = -\frac{1}{a_2} \left( \frac{1}{n^2} - 1 \right) e_2' \Delta e_2 - \frac{e_1' \Delta e_2}{\epsilon R} + \frac{1}{2} \frac{(\Delta e_2)^2}{a_2} \left( \frac{1}{n^2} - 1 \right) + \frac{1}{2} \frac{\Delta e_1 \Delta e_2}{n^2 R} \quad (\text{A-11})$$

For the process (A-2), the Gibbs energy of total reorganization of charging and discharging and is thus

$$W_D = W_I^D + W_{II}^D = \left( \frac{(\Delta e_1)^2}{2a_1} + \frac{\Delta e_1 \Delta e_2}{2R} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (\text{A-12})$$

$$W_A = W_I^A + W_{II}^A = \left( \frac{(\Delta e_2)^2}{2a_2} + \frac{\Delta e_1 \Delta e_2}{2R} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (\text{A-13})$$

as given in Eq. (34).

Either from the quantum-mechanical evaluation of the FC factor or from the thermodynamic charging argument the separation of  $\lambda$  into  $\lambda_D$  and  $\lambda_B$  as in Eq. (34) is valid.

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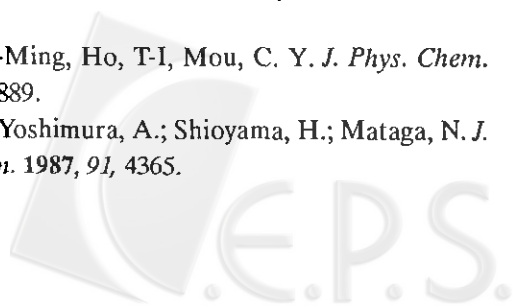
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## Key Words

Electron transfer reaction; Solvent effect.

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47. The main uncertainty of this calculation is the estimate of the parameters  $\beta$  and  $E_e$  of the solvent. In the gaseous phase the electron affinity of acetonitrile is nearly zero ( $10^{-4}$  eV) (K. D. Jordan, J. J.; Wendoloski, *Chem. Phys.* **1977**, *21*, 145). In the liquid state, the extra electron is stabilized by dipolar interactions. The relevant intermediate orbital for  $\text{CH}_3\text{CN}^-$  is probably an  $e^-$  weakly bound to nitrile carbon atoms. The dipolar stabilization energy should be less than 1 eV.  $\beta$  depends very sensitively on the diffuse tail of the wave function. Ab initio calculation of  $\beta$  with reasonable accuracy is difficult because most of the trial wave function is flexible enough for only the center part. For glassy MTHF, Onuchic et al. estimated<sup>38</sup>  $\beta$  to be 0.2 eV whereas other estimates fall in the range 0.1 - 0.001 eV. Our estimates of parameters are expected to be in the relevant range.
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