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ARTICLES

Semiclassical Treatment of Thermally Activated Electron Transfer in the Inverted Region under the Fast Dielectric Relaxation

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The previously formulated semiclassical theory (Zhao, Liang, and Nakamura, *J. Phys. Chem. A* **2006**, *110*, 8204) is used to study electron transfer in the Marcus inverted case by considering multidimensional potential energy surfaces of donor and acceptor. The Zhu−Nakamura formulas of nonadiabatic transition in the case of Landau−Zener type are incorporated into the approach. The theory properly takes into account the nonadiabatic transition coupled with the nuclear tunneling and can cover the whole range from weak to strong coupling regime uniformly under the assumption of fast solvent relaxation. The numerical calculations are performed for the 12-dimensional model of shifted harmonic oscillators and demonstrate that the reaction rate with respect to the electronic coupling shows a maximum, confirming the adiabatic suppression in the strong coupling limit. The adiabatic suppression is dramatically reduced by the effect of nuclear tunneling compared to the case that the Landau−Zener formula is used. The possible extension and applications to the case of the slow solvent dynamics are discussed.

1. Introduction

Electron transfer (ET) constitutes a ubiquitous and fundamental phenomenon in physics, chemistry, and biology.[1] Despite the long history of the investigation of ET process because of its crucial importance in many fields, theoretical studies are still very much challenging, because we have to incorporate various quantum mechanical effects such as nonadiabatic transition coupled with nuclear tunneling, quantum interference, and coupling to environment.

In the early treatments, the environmental fluctuation is commonly assumed to be faster than the ET dynamics and the thermal equilibrium distribution is maintained in the donor state. Under this assumption, certain limiting cases of ET are relatively well understood. In the weak electronic coupling regime, for instance, the reactions, being named as the nonadiabatic limit, can be well treated by the Fermi Golden rule.[1,2] In the strong electronic coupling limit where the reactions are called “adiabatic”, on the other hand, the well-known transition state theory (TST)[3,4] is applicable in the Marcus normal region. The intermediate region between the nonadiabatic and the adiabatic limits has still presented a challenging subject for theoretical studies. Besides, in the strong electronic coupling regime, the ET process is frequently connected to the solvent relaxation dynamics and the electronic coupling itself may not be a sufficient factor to justify the usage of nonadiabatic or adiabatic theory.

If the solvent relaxation is very slow compared with the ET process, multiple crossings of the transition region become possible even in the weak coupling regime. Ultimately, the reactions can become independent of the electronic coupling; i.e., they become solvent controlled adiabatic reactions, although they are still nonadiabatic in the absence of solvent dynamics. On the basis of the original works independently done by Zusman[5] and Burshtein and co-workers,[6] a large number of theoretical approaches have been proposed to treat the competition between solvent relaxation and electronic transition (see for instance, ref 7 and references therein). Yet, the true adiabatic process is different from the nonadiabatic one with slow solvent polarization modes. Several works have clarified the differences.[8−10]

The solvent dynamics has also been extensively investigated with the spin-boson model (dissipative two-state system). Various methods to deal with the multidimensional dynamics have been used, such as the path-integral Monte Carlo technique,[11,12] the quantum/classical hybrid method with the multiconfiguration time-dependent Hartree (MCTDH) method,[13] and the semiclassical initial value representation theory.[14]

In the limit of fast dielectric relaxation, on the other hand, the ET rate is independent of the relaxation properties of the solvent. In this limit, the ET thermal rate constants can be estimated by the traditional thermal equilibrium formulation without solving the dynamics equations explicitly. The well-known Marcus formula and the quantum perturbation theory are based on this equilibrium assumption. Very recently, we have formulated the semiclassical approach[15] based on the generalized nonadiabatic TST[16] and the Zhu−Nakamura (ZN) formulas of nonadiabatic transition. The proposed ET formula

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is composed of the two factors: the Marcus high temperature formula and a prefactor to that. The latter contains the thermally averaged ZN nonadiabatic transition probability and takes care of the nonadiabatic effects properly including the nuclear tunneling. Thus the formula is a kind of extension of the Marcus–Hush formula[3] and can cover the whole range of electronic coupling strength from nonadiabatic to adiabatic limit. Numerical tests in the Marcus normal region not only confirmed the accuracy but also demonstrated the applicability to multidimensional systems.[15] The major points of our present treatment can be summarized as follows. (1) The solvent relaxation is assumed to be fast. (2) Multidimensional potential energy surfaces of donor and acceptor are explicitly considered, and thus the Marcus normal and inverted cases are clearly differentiated. (3) The nonadiabatic transitions are treated by the analytical ZN formulas[17−19] that can cover the crossover region from nonadiabatic to adiabatic regimes and can treat the classically forbidden transitions properly, which cannot be done by other methods such as those based on the Landau–Zener (LZ) theory except for the quantum mechanical numerical simulations including the perturbation theory in the weak electronic coupling limit.

In the present paper, we extend this previous work[15] to the Marcus inverted case in the fast dielectric relaxation limit. In the inverted region the ET is different from the normal case, because it always requires the nonadiabatic transition and there is no adiabatic path between the donor and acceptor states. Naturally, the strong electronic coupling suppresses the ET rate as noticed in many works.[20−26] Recently, several approaches[22,24−26] based on the LZ nonadiabatic transition probability were proposed to study this adiabatic suppression. However, the LZ theory essentially neglects the nuclear tunneling and does not work at energies close to and lower than the potential curve crossing.

In the present work, we use the ZN formulas to treat the nonadiabatic transition in the inverted ET reaction and discuss the effect of the nuclear tunneling. In the ZN theory for the inverted ET, the transition probability is given by the two sets of analytical formulas: for the energy region (1) lower than and (2) higher than the potential curve crossing point (see details in Appendix). [The potential curve crossing corresponding to this case is called the Landau–Zener type in which the two diabatic potentials cross with the same sign of slopes. The normal case, on the other hand, is called the nonadiabatic tunneling type.[18]] Despite the formulas being quite different from those in the normal case, the nonseparability of the electronic and nuclear tunneling effects are properly incorporated in them. It has been demonstrated to overcome the defects of the LZ formula and to work well in the wide range of coupling strength and energy.

In the numerical simulation, we use the same shifted harmonic oscillator model with 12 degrees of freedom as used in the previous work[15] for the purpose of comparison with other available approaches. The different exothermicity ΔG is used to make the reaction system to be the inverted case. The Monte Carlo techniques are employed to perform the multidimensional integrations as before.[15]

Despite the present work being limited to the fast dielectric relaxation, this approach can incorporate the solvent dynamics and the possible extensions will be discussed in the paper.

The paper is organized as follows. In section 2, we present a brief description of the present semiclassical approach and its relation to the well-known Marcus theory. Section 3 illustrates its numerical applications to the ET rate in the inverted region. We investigate the nuclear tunneling contribution by comparing the LZ and ZN formulas. Section 4 is the conclusion. The possible extensions of the approach to the case of slow solvent relaxation will be briefly discussed there.

2. Semiclassical Model of Electron Transfer

In this section, we briefly explain our semiclassical theory of ET[15] within the framework of the nonadiabatic TST[16] and some important points of the ZN formulas. Without loss of generality, the ET can be described by the two-level electronic Hamiltonian

$$\hat{H} = \begin{bmatrix} \hat{H}_1 & H_{AB} \\ H_{AB} & \hat{H}_2 \end{bmatrix} \tag{1}$$

where $H_{1(2)} = K + V_{1(2)}$ is the nuclear Hamiltonian for the donor (acceptor) state and H_{AB} is the electronic coupling. It should be noted that the potentials $V_{1(2)}$ are not limited to the harmonic oscillators and the coupling H_{AB} may depend on the nuclear coordinates. Starting from the quantum mechanical flux-side correlation function,[27] one may get a semiclassical expression for the ET rate[16]

$$k = Z_{mod} Z_{cl}^{-1} \sqrt{\frac{1}{2\pi\beta}} \int d\mathbf{Q}\, e^{-\beta V_1(\mathbf{Q})} P_T(\beta,\mathbf{Q}) |\nabla S(\mathbf{Q})| \delta(\xi_0 - S(\mathbf{Q})) \tag{2}$$

Here $Z_{cl} = \int d\mathbf{Q}\, e^{-\beta V_1(\mathbf{Q})}$ is the classical partition function of the donor, Z_{mod} is the quantum mechanical correction of the partition function (its definition is explicitly given in ref 16), $\mathbf{Q}$ represents the nuclear Cartesian coordinates of N degrees of freedom, and $\xi = \xi_0 = S(\mathbf{Q}) = 0$ determines the crossing seam surface between the donor and acceptor. The variable ξ is introduced to define the free energy. The effective transition probability $P_T(\beta,\mathbf{Q})$ at a given temperature T is evaluated from the nonadiabatic transition probability $P_{ZN}(E,\mathbf{Q})$ by

$$P_T(\beta,\mathbf{Q}) = \beta \int_0^\infty dE\, e^{-\beta(E - V_1(\mathbf{Q}))} P_{ZN}(E,\mathbf{Q}) \tag{3}$$

where E represents the total energy along the direction normal to the crossing seam surface at the nuclear coordinate $\mathbf{Q}$. We implement $P_{ZN}(E,\mathbf{Q})$ by the ZN formulas in the case of Landau–Zener type of potential curve crossing.[17,18,19]

The basic physical idea behind eq 2 is the surface hopping due to nonadiabatic transition,[28−31] which has been widely used in the study of nonadiabatic chemical reactions. The crossing seam surface $S(\mathbf{Q})$ is determined by

$$S(\mathbf{Q}) = V_1(\mathbf{Q}) - V_2(\mathbf{Q}) = 0 \tag{4}$$

i.e., the crossing surface between the donor and acceptor potentials.

If one defines the free energy profile by

$$F_i(\xi) = e^{-\beta F_i(\xi)} = \int d\mathbf{Q}\, e^{-\beta V_i(\mathbf{Q})} |\nabla S(\mathbf{Q})| \delta(\xi - S(\mathbf{Q})) \tag{5}$$

and assumes F_i to have the parabolic shapes, eq 2 can then be cast into an improved Marcus formula[15]

$$k = \kappa k_{Marcus} \tag{6}$$

with

$$\kappa = \frac{\hbar\omega}{2\pi H_{AB}^2} \sqrt{\frac{\lambda}{\pi\beta}} \bar{P}_T(\beta,\xi_0) \tag{7}$$

where k_{Marcus} is the celebrated Marcus formula given by In the

$$k_{\mathrm{Marcus}} = \frac{{H_{\mathrm{AB}}}^2}{\hbar}\sqrt{\frac{\pi\beta}{\lambda}}\mathrm{e}^{-(\beta(\lambda+\Delta G)^2)/4\lambda} \tag{8}$$

prefactor κ, the key quantity $\bar{P}_T(\beta,\xi_0)$ is given by

$$\bar{\mathrm{P}}_T(\beta,\xi_0) = \frac{\int \mathrm{d}\mathbf{Q}\ \mathrm{e}^{-\beta V_1(\mathbf{Q})}|\nabla S(\mathbf{Q})|\delta(\xi - S(\mathbf{Q}))P_T(\beta,\mathbf{Q})}{\int \mathrm{d}\mathbf{Q}\ \mathrm{e}^{-\beta V_1(\mathbf{Q})}|\nabla S(\mathbf{Q})|\delta(\xi - S(\mathbf{Q}))} \tag{9}$$

This represents the effective nonadiabatic transition probability averaged over the seam surface. In the evaluation of eq 9, we first find a point on the crossing seam surface by numerical approach such as the Monte Carlo technique. At this point, we decide the hopping direction normal to the crossing seam surface and evaluate the nonadiabatic transition probability along the hopping direction which is averaged over the Boltzmann energy distribution. Finally, $\bar{P}_T(\beta,\xi_0)$ can be obtained by taking the average over all points on the crossing seam surface.

If one uses the conventional transition state approximation, eq 9 can be further simplified. In this case, $P_T(\beta,\mathbf{Q})$ over the seam surface is assumed to be constant and the value is replaced by the nonadiabatic transition probability at the saddle point Q_0. Then, eq 9 becomes

$$\bar{\mathrm{P}}_T(\beta,\xi_0) = \beta\int_0^{\infty}\mathrm{d}E\ \mathrm{e}^{-\beta E}P_{\mathrm{ZN}}(E,Q_0) \tag{10}$$

At high temperatures and weak electronic coupling limit, $P_{\mathrm{ZN}}(E,Q_0)$ can be given by the Taylor expansion of the ZN formula as

$$P_{\mathrm{ZN}}(E,Q_0) \approx \frac{2\pi {H_{\mathrm{AB}}}^2}{\hbar|\Delta F|\sqrt{2E}} \tag{11}$$

where ΔF is the slope difference of the two diabatic potentials at the crossing point. Combining eqs 11, 10, and 7, one can easily find $\kappa = 1$. Thus, eq 6 goes back to the original Marcus formula in the nonadiabatic (weak electronic coupling) limit. When the coupling strength becomes strong enough, the $P_{\mathrm{ZN}}(E,Q_0)$ goes to zero because two adiabatic potentials split far from each other. Because the rate constant increases quadratically with the electronic coupling strength in the weak coupling regime and becomes zero in the limit of strong coupling, one expects that the rate takes a maximum at a certain electronic coupling strength.

Before concluding this section, the following two points are clarified about the ZN formulas: (1) inclusion of the tunneling effect and (2) the wide applicability of the formulas. It is obvious that the nuclear tunneling plays an important role in the nonadiabatic transition at energies lower than the crossing point, because the tunneling from the turning point to the crossing point is needed for the electronic transition to occur at the crossing point. This tunneling effect is represented by the factor δ_{ZN} in the corresponding ZN formula (see eqs A-20−A-28 in the Appendix). The factor σ_{ZN} there is responsible for the electronic transition. The accuracy and wide applicability of the ZN formulas have been tested extensively.[18] Not only the ordinary two-state problems but also various multichannel problems have been successfully treated by the ZN formulas in a wide range of coupling strengths. Even the heavy overlapping resonances in multichannel systems have been nicely reproduced in comparison with the quantum mechanically exact numerical solutions.[32−34] Within the TSH (trajectory surface hopping) approach to multidimensional chemical reactions the ZN formulas are found to produce far better agreement with the exact quantum mechanical numerical solutions than the LZ formula not only in the gas phase[35−37] but also in the condensed phase.[38]

TABLE 1: Frequencies and Reorganization Energies of 12 Dimensional Harmonic Oscillator Model

ω_i (cm^{-1})	λ_i (cm^{-1})
462	3038
511	1372
584	775
602	1039
628	2125
677	1196
1007	269
1169	638
1252	351
1334	625
1403	275
1548	100

3. Numerical Results

For the numerical simulation we have chosen the same model as that used in ref 15. The model is composed of a collection of shifted harmonic oscillators. It should be noted that the harmonic oscillators are used just for simplicity and the potential functions can be general, because the ZN formulas are applicable to general potentials.

The Hamiltonian can be written as

$$H_1 = \sum_i \frac{{P_i}^2}{2} + V_1 \tag{12}$$

and

$$H_2 = \sum_i \frac{{P_i}^2}{2} + V_2 + \Delta G \tag{13}$$

with

$$V_1 = \frac{1}{2}\sum_i {\omega_i}^2 {Q_i}^2 \tag{14}$$

and

$$V_2 = \frac{1}{2}\sum_i {\omega_i}^2 (Q_i - Q_{0i})^2 \tag{15}$$

where H_1 and H_2 correspond to the donor and acceptor, respectively. The parameters ω_i and reorganization energies $\lambda_i = {}^1/_2({\omega_i}^2\ {Q_{0j}}^2)$ are listed in Table 1. In the present simulations, the exothermicity ΔG of the reaction is set to a negative value so as to make the ET to occur in the inverted region.

The reaction coordinate ξ thus is defined as

$$\xi = V_1 - (V_2 + \Delta G) = \sum_j\left({\omega_j}^2 Q_j - \frac{1}{2}\omega^2 {Q_{0j}}^2\right) - \Delta G \tag{16}$$

and the crossing seam surface corresponds to $\xi = \xi_0 = 0$.

In the numerical simulations, the Monte Carlo technique is used to evaluate the multidimensional integrals. All the detailed numerical procedures can be found in refs 15 and 38.

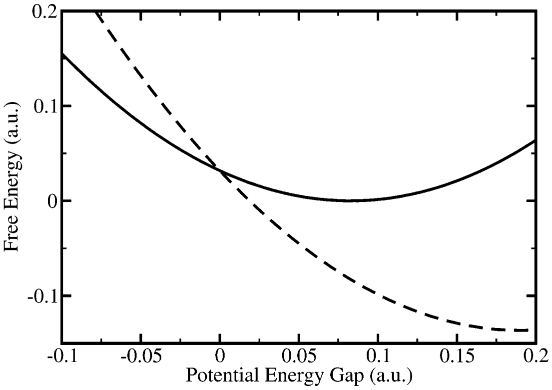

Figure 1. Diabatic free energy profiles corresponding to the potentials defined by eq 5: (—) donor; (---) acceptor.

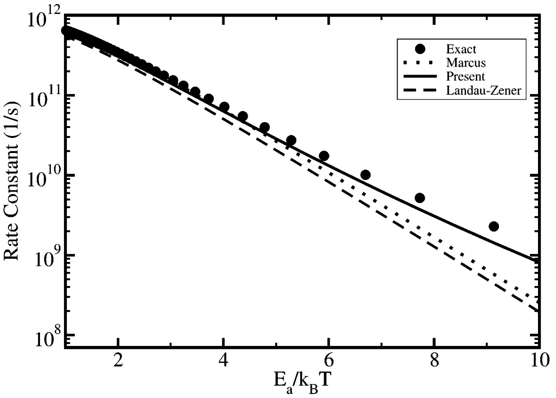

Figure 2. Arrhenius plot of the ET rate in the weak electronic coupling (H_{AB} = 0.001 au): (●) perturbation theory; (—) present approach (eq 6); (···) Marcus's high temperature theory (eq 8); (---) Landau–Zener theory.

Figure 1 shows the free energy curves with respect to reaction coordinate ξ at $\Delta G = -40\omega_0 = -0.1365$ au. Here, ω_0 is the effective frequency.[15] The corresponding crossing free energy is 0.032 au. Those curves are precisely parabolic. We have compared our numerical results with those from the analytical formula. Our numerical values are in excellent agreement with those from the analytical formulas, which demonstrates the accuracy of the present Monte Carlo technique in the inverted region (the analytical values are not shown in Figure 1 because of indistinguishability).

In Figure 2, we present an Arrhenius plot of the ET rate against temperature. The electronic coupling is taken to be 0.001 au, which corresponds to weak coupling. The *x*-axis is scaled by the crossing potential energy E_a to make it easier to judge whether the thermal energy is higher or not than that. In this weak electronic coupling case, the quantum mechanical perturbation theory predicts the rigorous rate. Thus, it can be used to check the accuracy of the present approach in the nonadiabatic limit. The time-dependent perturbation theory is employed to calculate the reaction rate with the time integrations carried out numerically. The results are shown in Figure 2. Compared with this perturbation theory, the present approach is in very good agreement when E_a/κ_BT is greater than 5. Although it is expected that the present approach would become invalid in the deep tunneling regime because of the semiclassical treatment of the nonadiabatic transition and the transition state approximation, the error is only 30% even in the deep tunneling region ($E_a/\kappa_BT = 10$). For the comparison with other approximations, we also show the results from the LZ formula and the Marcus high temperature formula (eq 8). The LZ formula is given in the Appendix. As is clearly seen, both Marcus and LZ formulas predict 8–9 times smaller rate at $E_a/\kappa_BT = 10$. It should be noted that the LZ result cannot reach the exact value even at $E_a/\kappa_BT = 1$.

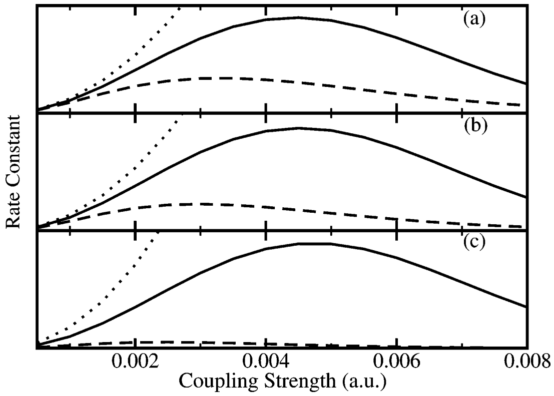

Figure 3. ET rate vs electronic coupling strength H_{AB} at three temperatures: (a) $E_a/\kappa_BT = 6.7$; (b) $E_a/\kappa_BT = 10.0$; (c) $E_a/\kappa_BT = 20.0$. Key: (—) present result (eq 6); (---) the results predicted from the Landau–Zener formula; (···) results from the perturbation theory.

The importance of the classically forbidden transitions at $E \leq E_a$ (crossing energy) is rather obvious, if we note that the Boltzmann factor exponentially increases as energy E decreases, where the ZN nonadiabatic transition probability is still appreciable, and the LZ probability is zero ($P_{LZ} = 0$) there.

To investigate the effect of nuclear tunneling in the strong electronic coupling case, we plot the ET rate against the electronic coupling strength H_{AB} from 0.001 to 0.008 au in Figure 3 at different temperatures.

From Figure 3, we also observe that the rate initially increases quadratically in the weak coupling regime, as predicted by the perturbation theory. As the coupling increases, the perturbation theory always overestimates the rate. This is different from the Marcus normal case where the perturbation theory does not necessarily provide the larger rate than the real one.[15] The rate predicted by the present approach reaches a maximum at a certain value of coupling strength and decreases with a further increase of the coupling. This behavior of the adiabatic suppression is the property peculiar to the inverted case, because the large electronic coupling makes adiabatic potentials separate far from each other and the nonadiabatic transition probability becomes small as a result. Comparing with the prediction from the LZ formula, the ZN formulas give a much larger rate, especially at low temperatures. The ratios of the maximal rates obtained from the ZN formulas and the LZ theory are 2.73 at $E_a/\kappa_BT = 6.7$, 3.85 at $E_a/\kappa_BT = 10$, and 17.29 at $E_a/\kappa_BT = 20$, respectively. We also observe that the maximal rate predicted by the LZ and ZN formulas locate at very different coupling H_{AB} values. With decreasing temperature, the coupling strength at the maximal rate predicted by the LZ formula shifts toward smaller value, but it remains nearly unchanged in the case of the ZN formulas. The corresponding coupling strength obtained from the ZN formulas is about 0.0045 au, whereas these values obtained from the LZ formula become 0.0035 au at $E_a/\kappa_BT = 6.7$, 0.003 au at $E_a/\kappa_BT = 10$, and 0.0025 au at $E_a/\kappa_BT = 20$, respectively. This interesting behavior can be understood from the energy dependence of the nonadiabatic transition probability P. In the case of the ZN formulas, we find that the probability becomes a maximum at a certain intermediate coupling strength at energies in the region around the crossing point E_a. Because the Boltzmann factor naturally shifts to the low-energy side as the temperature decreases, the maximum position of the ET rate is rather independent of temperature. In the case of the

LZ formula, on the other hand, the transition probability P_{LZ} is totally zero at $E \leq E_a$ and its peak moves toward E_a from the right as the coupling decreases. Because the Boltzmann factor shifts to the left as the temperature decreases, the maximum position of the ET rate moves to the smaller coupling.

It should be noted that the ZN theory is a semiclassical theory and it does not work well in the cases of extremely weak or strong diabatic (electronic) coupling, i.e., $a^2 > 1000$ or $a^2 < 0.01$ (see the definition of a^2 in the Appendix). Fortunately, however, at $a^2 > 1000$, the perturbation theory works well and can be easily manipulated numerically. In the case of extremely strong coupling, on the other hand, the ET rate is already negligibly small. In the present model, for instance, that corresponds to $H_{AB} \sim 0.015$, which is still in the validity range ($H_{AB} < 0.019$) of the ZN formulas.

4. Concluding Remarks

The semiclassical theory of ET with use of the Zhu−Nakamura (ZN) formulas of nonadiabatic transition has been completed under the assumption of fast solvent relaxation. Together with the previous paper[15] the final formula can cover both normal and inverted cases from the weak to strong electronic coupling regime. Its applicability to multidimensional systems has been numerically demonstrated by using the twelve-dimensional shifted harmonic oscillators model. Even some experimental data can be nicely reproduced.[39] The formula is composed of two factors: the Marcus high temperature formula and the prefactor to that. The latter contains the thermally averaged ZN transition probability and takes care of the nonadiabatic effects properly including the nuclear tunneling. This prefactor essentially involves the surface hopping mechanism. Under the assumption of fast solvent relaxation, the hopping direction can be uniquely determined by the geometry of the crossing seam surface of donor and acceptor potentials. The second important point to note is that the present prefactor is obtained by taking the thermal average of the nonadiabatic transition probability over the crossing seam surface. Thus, the microscopic nonadiabatic transition information is properly included. The third point to be noticed is that the electronically nonadiabatic transition and the nuclear tunneling are coupled and cannot be treated separately. The present theory based on the ZN formulas takes into account this effect properly. The present analysis showed that the LZ formula can produce quantitatively correct results only at very high temperatures. In the Marcus inverted case, the situation becomes worse. The LZ formula predicts too small rates and too strong adiabatic suppression.

As mentioned above, the present approach is limited to the case of fast bath relaxation in which the nonadiabatic transition is the “bottleneck” of the reaction. If the solvent relaxation is slow, on the other hand, the reaction becomes more complex. Various theories have been developed to treat this case. The one close to the present approach is the variational transition state theory proposed by Rips and Pollak and others.[24,40−42] They introduced the collective system-bath coordinate, which is characterized by a maximal mean-free path in the vicinity of crossing point. They have also demonstrated that the energy gap coordinate of the two electronic states provides a good description of the ET dynamics in the fast relaxation limit, which is consistent with the present approach, but cannot be appropriate in the strong solvent friction, and that the optimization approach has to be employed to find an effective coordinate. To incorporate the solvent dynamics into the present approach, we shall take into account both intramolecular and solvent modes on the same footing and either employ the optimized approach of Rips et al. or try to find the imaginary-frequency mode in the vicinity of crossing point on the adiabatic potentials. Because the imaginary-frequency mode is essentially separated from the other modes in the vicinity of the crossing seam and has a maximal mean free path along it, one can take its direction as the hopping direction. This has a similar property as the variational transition state theory, but the ZN formulas can take into account the nuclear tunneling effects properly.

In the very strong solvent friction limit, the dynamics satisfies the Smoluchowski equation. Sumi and Marcus[43] have introduced a sink function to take into account the contribution of high-frequency vibrational modes, assuming that the motion of high-frequency modes are much faster than the solvent motion. Thus, the motions of solvent and high-frequency modes are approximately separated and the sink function can be evaluated from statistical approach. The sink function is commonly used in the two limits: the Marcus nonadiabatic limit in the weak coupling case and the Marcus adiabatic limit in the very strong coupling case. In this sense, the present rate expression may be directly used as the sink function for the fast modes to cover from weak to very strong coupling regime properly both in normal and in inverted regions.

Finally, one more important point we have to keep in mind is the importance of the information on the free energy potential curves and coupling for realistic systems including the effects of solvent. This is crucial whenever we try to apply our theory to real systems. In this sense the method proposed by Hirata and his co-workers would be quite useful (see, for instance, ref 44 and references therein). The possible extensions mentioned above will be discussed in the future.

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A. Thermally Averaged Transition Probability Based on the Zhu−Nakamura Formulas in the Inverted Region

In this appendix, we explicitly present the Zhu−Nakamura (ZN) formulas used for the evaluation of thermally averaged transition probability (eq 3) in the inverted region

$$P_T(\beta,\mathbf{Q}) = \beta\int_0^{\infty} \mathrm{d}E\, \mathrm{e}^{-\beta(E-V_1(\mathbf{Q}))} P_{ZN}(E,\mathbf{Q}) \qquad \text{(A-1)}$$

where $V_1(\mathbf{Q})$ is the diabatic potential and $P_{ZN}(E,\mathbf{Q})$ is the nonadiabatic transition probability. Once the nuclear coordinate $\mathbf{Q}$ is specified on the crossing seam surface, we take the direction normal to the seam across $\mathbf{Q}$ by

$$\mathbf{n} = \nabla S(\mathbf{Q})/|\nabla S(\mathbf{Q})| \qquad \text{(A-2)}$$

and cut the potential energy surfaces along this direction to obtain one-dimensional potential curves. Because the Marcus inverted case is considered in the present model, the potential curves correspond to the Landau−Zener type as shown in Figure 4. In this case, Zhu and Nakamura have provided the analytical expressions of nonadiabatic transition probability. The expressions are based on the following two parameters on

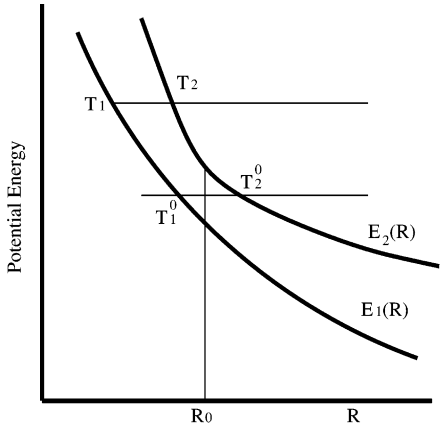

Figure 4. Schematic two state adiabatic potentials in the case of the inverted region.

the adiabatic potentials: and

$$a^2 = \sqrt{d^2 - 1}\frac{\hbar^2}{(T_2^0 - T_1^0)^2[E_2(R_0) - E_1(R_0)]} \qquad \text{(A-3)}$$

$$b^2 = \sqrt{d^2 - 1}\frac{E - [E_2(R_0) + E_1(R_0)]/2}{[E_2(R_0) - E_1(R_0)]^2} \qquad \text{(A-4)}$$

where

$$d^2 = \frac{[E_2(T_1^0) - E_2(T_1^0)][E_1(T_2^0)] - E_1(T_2^0)]}{[E_2(R_0) - E_1(R_0)]^2} \qquad \text{(A-5)}$$

where E is the incident energy, other parameters are shown in Figure 4. With parameter a^2 and b^2, the Landau−Zener formula for one passage of the crossing can be expressed as

$$p_{\mathrm{LZ}} = 1 - \exp\left(\frac{\pi}{4ab}\right) \qquad \text{(A-6)}$$

for $b^2 > 0$, and $p_{\mathrm{LZ}} = 0$ for $b^2 < 0$. The overall transmission probability is given by

$$P_{\mathrm{LZ}}(E) = 2p_{\mathrm{LZ}}(1 - p_{\mathrm{LZ}}) \qquad \text{(A-7)}$$

In the Zhu−Nakamura formulas, the electron and nuclear tunnelings are considered simultaneously. The overall transmission probability incorporates the phase and it is expressed as

$$P_{\mathrm{ZN}}(E) = 4p_{\mathrm{ZN}}(1 - p_{\mathrm{ZN}}) \sin^2(\psi_{\mathrm{ZN}}) \qquad \text{(A-8)}$$

where the probability p_{ZN} is for one passage of crossing, and ψ_{ZN} is the phase. p_{ZN} and ψ_{ZN} are given by two sets of formulas for $E > E_{\mathrm{X}}$ and $E < E_{\mathrm{X}}$, respectively, where E_{X} is the crossing energy.

(1) $E > E_{\mathrm{X}}$: The various quantities in eq A-8 are given by

$$p_{\mathrm{ZN}} = \exp\left[-\frac{\pi}{4a|b|}\left(\frac{2}{1 + \sqrt{1 + b^{-4}(0.4a^2 + 0.7)}}\right)^{1/2}\right] \qquad \text{(A-9)}$$

$$\sigma_0^{\mathrm{ZN}} = \frac{\sqrt{2}\pi}{4\sqrt{a^2}}\frac{F_-^{\mathrm{C}}}{{F_+}^2 + {F_-}^2} \qquad \text{(A-10)}$$

$$\psi_{\mathrm{ZN}} = \sigma_{\mathrm{ZN}} + \phi_{\mathrm{S}} \qquad \text{(A-11)}$$

$$\sigma_{\mathrm{ZN}} = \int_{T_1}^{R_0} K_1(R)\,\mathrm{d}R - \int_{T_2}^{R_0} K_2(R)\,\mathrm{d}R + \sigma_0^{\mathrm{ZN}} \qquad \text{(A-12)}$$

$$K_j(R) = \sqrt{2\mu/\hbar^2(E - E_j(R))} \qquad \text{(A-13)}$$

$$\phi_{\mathrm{S}} = -\delta_{\mathrm{ZN}}/\pi + \delta_{\mathrm{ZN}}/\pi \ln(\delta_{\mathrm{ZN}}/\pi) - \arg\Gamma(\mathrm{i}\delta_{\mathrm{ZN}}/\pi) - \pi/4 \qquad \text{(A-14)}$$

$$\delta_{\mathrm{ZN}} = \frac{\sqrt{2}\pi}{4\sqrt{a^2}}\frac{F_+^{\mathrm{C}}}{{F_+}^2 + {F_-}^2} \equiv \delta_0^{\mathrm{ZN}} \qquad \text{(A-15)}$$

$$F_\pm = \sqrt{\sqrt{(b^2 + \gamma_1)^2 + \gamma_2} \pm (b^2 + \gamma_1)} + \sqrt{\sqrt{(b^2 - \gamma_1)^2 + \gamma_2} \pm (b^2 - \gamma_1)} \qquad \text{(A-16)}$$

$$F_+^{\mathrm{C}} = F_+(b^2 \rightarrow [b^2 - 0.16b_x/\sqrt{b^4 + 1}]) \qquad \text{(A-17)}$$

$$F_-^{\mathrm{C}} = F_-\left(\gamma_2 \rightarrow \frac{0.45\sqrt{d^2}}{1 + 1.5\mathrm{e}^{2.2b_x|b_x|^{0.57}}}\right) \qquad \text{(A-18)}$$

$$b_x = b^2 - 0.9553 \qquad \gamma_1 = 0.9\sqrt{d^2 - 1} \qquad \gamma_2 = 7\sqrt{d^2}/16 \qquad \text{(A-19)}$$

(2) $E \leq E_{\mathrm{X}}$: One passage probability is given by

$$p_{\mathrm{ZN}} = [1 + B(\sigma_{\mathrm{ZN}}/\pi)\exp(2\delta_{\mathrm{ZN}}) - g\sin^2(\sigma_{\mathrm{ZN}})]^{-1} \qquad \text{(A-20)}$$

where

$$B(x) = \frac{2\pi x^{2x}\exp(-2x)}{x\Gamma^2(x)} \qquad \text{(A-21)}$$

$$\delta_{\mathrm{ZN}} = \int_{T_1}^{R_0} |K_1(R)|\,\mathrm{d}R - \int_{T_2}^{R_0} |K_2(R)\,\mathrm{d}R + \delta_0^{\mathrm{ZN}} \qquad \text{(A-22)}$$

$$\sigma_{\mathrm{ZN}} = \sigma_0^{\mathrm{ZN}} \qquad \text{(A-23)}$$

and

$$g = \frac{3\sigma_{ZN}}{\pi\delta_{\mathrm{ZN}}}\ln(1.2 + a^2) - 1/a^2 \qquad \text{(A-24)}$$

The local wave number $K_i(R)$ is defined by eq A-13. The quantities σ_0^{ZN} and δ_0^{ZN} are given by eqs A-10 and A-15. The phase ψ_{ZN} in eq A-8 is given by

$$\psi_{\mathrm{ZN}} = \arg(U) \qquad \text{(A-25)}$$

where

$$\mathrm{Re}\,U = \cos(\sigma_{\mathrm{ZN}})[\sqrt{B(\sigma_{\mathrm{ZN}}/\pi)}\mathrm{e}^{\delta_{\mathrm{ZN}}} - h\sin^2(\sigma_{\mathrm{ZN}})\mathrm{e}^{-\delta_{\mathrm{ZN}}}/\sqrt{B(\sigma_{\mathrm{ZN}}/\pi)}] \qquad \text{(A-26)}$$

$$\mathrm{Im}\,U = \sin(\sigma_{\mathrm{ZN}})[B(\sigma_{\mathrm{ZN}}/\pi)\mathrm{e}^{2\delta_{\mathrm{ZN}}} - h^2\sin^2(\sigma_{\mathrm{ZN}}) \times \cos^2(\sigma_{\mathrm{ZN}})\mathrm{e}^{-2\delta_{\mathrm{ZN}}}/B(\sigma_{\mathrm{ZN}}/\pi) + 2h\cos^2(\sigma_{\mathrm{ZN}}) - g]^{1/2} \qquad \text{(A-27)}$$

with

$$h = 1.8(a^2)^{0.23}\mathrm{e}^{-\delta_{ZN}} \qquad \text{(A-28)}$$

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