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ARTICLES

One-Dimensional Description of Multidimensional Electron Transfer Reactions in Condensed Phase

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We derive a one-dimensional energy diffusion equation for describing the dynamics of multidimensional electron transfer reactions in condensed phase, which is conceptually simpler and computationally more economic than the conventional approaches. We also obtain an analytical expression for the rate of electron transfer reactions for a general one-dimensional effective potential as well as an energy dependent diffusivity. As an illustrative example, we consider application to electron transfer in a contact ion pair system modeled through harmonic potentials consisting of two slow classical modes and a high frequency vibrational mode for which the numerical results calculated using the proposed one-dimensional approach are shown to be in good agreement with experimental results. The energy diffusion equation and the rate expression for electron transfer obtained from the present theory, therefore, open up the possibility of describing the dynamics of electron transfer in complex systems, through a simpler approach.

I. Introduction

Electron transfer (ET) reactions in condensed phase have been one of the most thoroughly investigated processes over the past decade. Recent years have witnessed an upsurge of experimental investigations on ET processes due to availability of spectroscopic techniques for dynamical measurements and the synthesis of tailor-made artificial electron donor−acceptor systems which have led to a wealth of new experimental results. In the traditional ET theory of Marcus,[1] it is assumed that the state, from which reaction occurs, is always in thermal equillibrium which is unperturbed by the reaction. In this theory, the ET rate constant depends on static aspects of the solvent effects but not explicitly on the dynamics of the solvent. The theory works well in many situations involving particularly the nonadiabatic ET processes where the electronic coupling between the localized reactant and product states is sufficiently weak and the ET rate is directly proportional to the electronic coupling. However, in many ET reactions, involving particularly the electronically adiabatic regime, the electronic coupling is sufficiently large and the solvent dynamical effects are very much pronounced. The work of Zusman,[2] Calef and Wolynes[3] and the unified approach of Hynes[4–7] have extended Marcus theory to treat the dynamics of ET reactions and to investigate the role of solvent dynamics in adiabatic ET. But in all these theories the effect of nonequilibrium aspects on the rate of ET reaction has not been taken into consideration. There are many situations e.g. photochemical ET reactions[8,9] where the system is initially in a nonequilibrum configuration rather than an equilibrium one. One usually proposes a model in which the system is assumed to be in the ground state and is brought to the nonequilibrium excited state by laser excitation. Subsequently, the ion pair formed at the higher level of excitation relaxes downward to the potential minimum of the excited-state surface due to relaxation of the polar solvent till its energy coincides with that of the ground state, when back ET reaction takes place. Thus, the ET reaction can occur from a completely nonequilibrium condition. Therefore, the main assumption in the Marcus theory that the initial distribution of the system is an equilibrium one may not hold for this system which leads to a marked deviation from the expected bell-shaped dependence of the logarithmic rate on the free energy gap (ΔG). Such deviation is referred to as the non-Marcus free energy gap (FEG) dependence of the rate. To explain the non-Marcus FEG dependence of the rate of ET reactions, one usually invokes a mechanism based on an interplay between solvent relaxation dynamics and electron transfer.

The ET reactions in general are associated with intrinsic multidimensional potential energy surfaces,[10] physical examples of which include bond breaking ET,[11] ET in a non-Debye solvent,[12] low frequency vibrational and solvent polarization mediated ET[13] etc. A multidimensional space description, based on Smoluchowski equation, is very cumbersome and highly involved, and hence a simpler description, such as a one-dimensional one for these multidimensional processes, is very important and significant. In our earlier work,[14] we have addressed a generalized one-dimensional energy diffusion approach for describing the dynamics of multidimensional processes in condensed phase. On the basis of a formalism originally due to Zwanzig, we obtained a one-dimensional kinetic equation for a properly selected relevant dynamical quantity and derived new analytical results for the dynamics of a multidimensional nonequilibrium solvation and diffusive escape from a potential well. We also derived a one-dimensional energy diffusion equation for a properly selected reaction

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coordinate for ET reactions and obtained an analytical expression for the ET rate constant where the effective potential is harmonic and the diffusivity is independent of the reaction cordinate. However, the rate expression cannot be easily derived in the same way as shown in our earlier work[14] if one considers a general effective potential and a reaction coordinate-dependent diffusivity in the kinetic equation. In this work, therefore, we have proposed an alternative approach to derive an analytical expression for the rate of ET reactions for a general effective potential and an energy-dependent diffusivity.

The organization of the rest of the paper is as follows. In the following section (section II), we derive the one-dimensional energy diffusion equation for multidimensional ET reactions. We then derive an analytical expression for the ET rate constant for a general effective potential and an energy-dependent diffusivity. In sections III and IV, as an illustrative example, we apply the proposed formalism to an ET reaction in a contact ion pair system modeled through harmonic potentials consisting of two slow classical modes and a high frequency vibrational mode where the system is prepared initially in a nonequilibrium state and obtain analytical expressions for the ET rate constant and the energy-dependent diffusivity. In section V, we present the calculated results based on the derived analytical expressions and compare them with experimental results. Section VI concludes with a brief summary.

II. Theoretical Formalism

The description, which we have proposed recently in an earlier work,[14] is based on a kinetic equation for the probability distribution $P(\gamma, t|\gamma_0, 0)$ of a microscopic phase space function A constrained to have a value γ at time t with its initial value γ_0 at $t = 0$, which was originally obtained by Zwanzig[15] and subsequently modified by others and can be written[3] as

$$\frac{\partial P(\gamma, t|\gamma_0, 0)}{\partial t} = \frac{\partial}{\partial \gamma}\left\{\int_0^t D(\gamma, \tau) d\tau\left[\frac{\partial P(\gamma, t-\tau|\gamma_0, 0)}{\partial t} + P(\gamma, t-\tau|\gamma_0, 0)\frac{\partial}{\partial \tau}\{\beta V_{eff}(\gamma)\}\right]\right\} \quad (1)$$

Here time- and γ -dependent diffusivity $D(\gamma, t)$ is defined as $D(\gamma, t) = \langle \dot{A}(t)^{\cdot} \dot{A}(0)\, \delta(A(t) - \gamma)\rangle / \langle \delta(A(0) - \gamma)\rangle$ with the symbol $\langle\, \rangle$ denoting an equilibrium ensemble average and the dot corresponding to time derivative. The effective potential V_{eff}, a function of the γ coordinate, is defined as $\beta V_{\mathrm{eff}}(\gamma) = -\ln (N \langle \delta(A(0) - \gamma)\rangle)$, where β $(=1/k_BT)$ denotes the inverse temperature and $N = \int_{-\infty}^{+\infty} \mathrm{d}\gamma \exp[-\beta V_{\mathrm{eff}}(\gamma)]$. Here $P(\gamma, t|\gamma_0, 0)$ represents the probability of A to have the value γ at time t when its initial value is γ_0 at $t = 0$. Zwanzig's derivation[15] of eq 1 assumes $\mathrm{d}A/\mathrm{d}t$ to be small as has been discussed by him in detail. It has been recently shown[14] that this single kinetic equation can form the basis for a unified description of different dynamical problems through proper identification of the phase space function A.

In an ET process, the system moving initially on a multidimensional reactant potential energy surface (PES) crosses to the product PES at the intersection point. The ET reactions do occur with an intrinsic rate[10] k_0 (corresponding to $\gamma = 0$), i.e. when the reactant and product potential energies are equal and hence the relevant microscopic phase space function A for the ET reactions can be chosen to be the difference between the potential energy for the product (V^{P}) and that of the reactant (V^{R}), viz. $A = V^{\mathrm{P}} - V^{\mathrm{R}}$. Therefore, the kinetic equation for $P(\gamma, t|\gamma_0, 0)$ given by eq 1 should be modified for ET reactions by introducing a delta sink with strength k_0 to its right side. The modified kinetic equation, for ET reactions thus becomes

$$\frac{\partial P(\gamma, t|\gamma_0, 0)}{\partial t} = \frac{\partial}{\partial \gamma}\left\{\int_0^t D(\gamma, \tau)\, \mathrm{d}\tau\left[\frac{\partial P(\gamma, t-\tau|\gamma_0, 0)}{\partial \gamma} + P(\gamma, t-\tau|\gamma_0, 0)\frac{\partial}{\partial \gamma}(\beta V_{\mathrm{eff}}(\gamma))\right]\right\} - k_0\, \delta(\gamma)\, P(\gamma, t|\gamma_0, 0) \quad (2)$$

This is an important result since it provides a one-dimensional energy diffusion equation of the reactive system. However, the rate expression for the ET reactions involving energy dependent diffusivity from the above generalized kinetic equation (eq 2) cannot be obtained directly based on the method addressed in our earlier work.[14] We propose here altogether a different method to obtain an analytical expression for the rate of ET reactions. We start with eq 2 which, in the Markovian limit, can be rewritten as

$$\frac{\partial P(\gamma, t|\gamma_0, 0)}{\partial t} = \frac{\partial}{\partial \gamma}\left\{D(\gamma)\left[\frac{\partial P(\gamma, t|\gamma_0, 0)}{\partial \gamma} + P(\gamma, t|\gamma_0, 0)\frac{\partial}{\partial \gamma}(\beta V_{\mathrm{eff}}(\gamma))\right]\right\} - k_0\, \delta(\gamma) P(\gamma, t|\gamma_0, 0) \quad (3)$$

where $D(\gamma)$ is given by

$$D(\gamma) = \int_0^\infty dt\, D(\gamma, t) \quad (4)$$

The quantity of interest here is the mean passage time $\tau(\gamma_0)$, which is defined as

$$\tau(\gamma_0) = \int_0^\infty dt\, p(t, \gamma_0) \quad (5)$$

where $p(t, \gamma_0)$ defines the probability of finding the system at the reactant surface at time t when the system is initially ($t = 0$) prepared at $\gamma = \gamma_0$ and can be obtained from $P(\gamma, t|\gamma_0, 0)$ by integrating over γ, i.e.

$$p(t, \gamma_0) = \int_{-\infty}^{+\infty} d\gamma P(\gamma, t|\gamma_0, 0) \quad (6)$$

In order to have an analytical expression for $\tau(\gamma_0)$, what we need is a differential equation for the function $p(t, Z_0)$. But it is clear from eqs 3 and 6 that it is not possible to obtain an equation for $p(t, \gamma_0)$ by merely integrating both sides of eq 3 over γ. Therefore, it will be advantageous if one can write a differential equation equivalent of eq 3 in the variable γ_0. This is indeed possible by using the substitution

$$P(\gamma, t|\gamma_0, 0) = \exp[-\beta V_{\mathrm{eff}}(\gamma)]\, U(\gamma, t|\gamma_0, 0) \quad (7)$$

in eq 3 along with the reciprocity relation[16–18]

$$U(\gamma, t|\gamma_0, 0) = U(\gamma_0, t|\gamma, 0) \quad (8)$$

which leads, after some algebra, to the differential equation

$$\frac{\partial P(\gamma, t|\gamma_0, 0)}{\partial t} = \exp[\beta V_{eff}(\gamma_0)]\frac{\partial}{\partial \gamma_0}\left[D(\gamma_0)\exp[-\beta V_{eff}(\gamma_0)] \times \frac{\partial P(\gamma, t|\gamma_0, 0)}{\partial \gamma_0}\right] - k_0\delta(\gamma_0)P(\gamma, t|\gamma_0, 0) \quad (9)$$

Now integrating both sides over γ, one obtains

$$\frac{\partial p(t, \gamma_0)}{\partial t} = \exp[\beta V_{\mathrm{eff}}(\gamma_0)]\frac{\partial}{\partial \gamma_0}\left[D(\gamma_0) \exp[-\beta V_{\mathrm{eff}}(\gamma_0)] \times \frac{\partial p(t, \gamma_0)}{\partial \gamma_0}\right] - k_0\, \delta(\gamma_0)\, p(t, \gamma_0) \quad (10)$$

which, on further integration over time, and using the boundary condition $p(0, \gamma_0) = 1$, leads to the differential equation

$$\exp[\beta V_{\mathrm{eff}}(\gamma_0)]\frac{\partial}{\partial \gamma_0}\left[D(\gamma_0)\exp[-\beta V_{\mathrm{eff}}(\gamma_0)]\frac{\partial \tau(\gamma_0)}{\partial \gamma_0}\right] - k_0\,\delta(\gamma_0)\,\tau(\gamma_0) = -1 \quad (11)$$

Integrating both sides over γ_0 for $\gamma_0 > 0$, we obtain

$$\frac{\partial \tau(\gamma_0)}{\partial \gamma_0} = \frac{\exp[\beta V_{eff}(\gamma_0)]}{D(\gamma_0)}\left[C - \int^{\gamma_0} d\gamma \exp[-\beta V_{eff}(\gamma)]\right] \quad (12)$$

where C is an arbitrary constant of integration, which can be evaluated, for example, by employing a boundary condition defined as

$$\left[\left(\frac{\partial \tau(\gamma_0)}{\partial \gamma_0}\right)_{(0+\varepsilon)} - \left(\frac{\partial \tau(\gamma_0)}{\partial \gamma_0}\right)_{0}\right] = \frac{k_0}{2D(0)}\tau(0) \quad (13)$$

where ε is a very small positive number.

In order to obtain an analytical expression for $\tau(0)$ we first write an exact Green's function solution[19] of eq 3 as

$$P(\gamma,\ t|\gamma_0,\ 0) = P_0(\gamma,\ t|\gamma_0,\ 0) - k_0\int_0^t \mathrm{d}t' P_0(\gamma,\ t-t'|0,\ 0)\,P(0,\ t'|\gamma_0,\ 0) \quad (14)$$

where the function $P_0(\gamma, t|\gamma_0, 0)$ is the solution of eq 3 in absence of the sink term. Both $P(\gamma, t|\gamma_0, 0)$ and $P_0(\gamma, t|\gamma_0, 0)$ correspond to the same initial condition, which we consider here to be $P(\gamma, t) = P_0(\gamma, t) = \delta(\gamma - \gamma_0)$ at $t = 0$. Taking the Laplace transform of eq 14 and after rearrangement we obtain

$$\tilde{P}(0,\ s|\gamma_0,\ 0) = \frac{\tilde{P}_0(0,\ s|\gamma_0,\ 0)}{1 + k_0\tilde{P}_0(0,\ s|0,\ 0)} \quad (15)$$

where

$$\tilde{P}(\gamma, s|\gamma_0, 0) = \int_0^\infty dt \exp[-st]P(\gamma, t|\gamma_0, 0) \quad (16)$$

Now integrating eq 14 over γ, taking the Laplace transform of the resulting equation and finally combining with eq 15, we obtain

$$\tilde{p}(s,\ \gamma_0) = \frac{1 + k_0[\tilde{P}_0(0,\ s|0,\ 0) - \tilde{P}_0(0,\ s|\gamma_0,\ 0)]}{s[1 + k_0\tilde{P}_0(0,\ s|0,\ 0)]} \quad (17)$$

Since $k^{-1} = \tau(\gamma_0) = \lim_{s\to 0}\tilde{P}(s, \gamma_0)$, we obtain from eq 17 the result

$$k^{-1} = \frac{1}{k_0 P_{st}(0)} + \frac{\int_0^\infty dt[P_0(0, t|0, 0) - P_0(0, t|\gamma_0, 0)]}{P_{st}(0)}, \quad (18)$$

where $P_{st}(0) = P_0(0, \infty|0, 0)$. In eq 18, by substituting $\gamma_0 = 0$, we obtain the desired expression given by

$$\tau(0) = \frac{1}{k_0 P_{st}(0)} \quad (19)$$

Here $P_{st}(0)$ represents the stationary distribution in the variable $\gamma = 0$ and is given by

$$P_{st}(0) = \frac{\exp[-\beta V_{eff}(0)]}{\int_{-\infty}^\infty d\gamma \exp[-\beta V_{eff}(\gamma)]} \quad (20)$$

By combining eqs 12, 13 and 20, we obtain an expression for C, given by

$$C = \frac{1}{2}\int_{-\infty}^\infty \mathrm{d}\gamma \exp[-\beta V_{\mathrm{eff}}(\gamma)] \quad (21)$$

Now integrating both sides of eq 12 from $0 + \varepsilon$ to γ_0 and taking the limit $\varepsilon \to 0$, we obtain

$$\tau(\gamma_0) = \tau(0) + \int_0^{\gamma_0} \mathrm{d}\gamma\, \frac{\exp[\beta V_{\mathrm{eff}}(\gamma)]}{D(\gamma)}\left[C - \int^{\gamma} \mathrm{d}\gamma' \exp[-\beta V_{\mathrm{eff}}(\gamma')]\right] \quad (22)$$

which is an important new result for the mean passage time $\tau(\gamma_0)$. The overall ET rate constant k is defined as the reciprocal of the mean passage time $\tau(\gamma_0)$ $(= k^{-1})$. It can also be written as

$$k^{-1} = k_{TST}^{-1} + k_d^{-1} \quad (23)$$

where k_{TST} $(= 1/\tau(0))$ represents the rate calculated based on the transition state theory (TST)[1] and k_{d} is the rate for well dynamics defined below as

$$k_d^{-1} = \int_0^{\gamma_0} d\gamma \frac{\exp[\beta V_{eff}(\gamma)]}{D(\gamma)}\left[C - \int^{\gamma} d\gamma' \exp[-\beta V_{eff}(\gamma')]\right] \quad (24)$$

If one neglects the effect of energy dependent diffusivity and considers the effective potential $\beta V_{\mathrm{eff}}(\gamma)$ to be harmonic, eq 22 reduces to the rate expression shown in the earlier works.[14,20] Therefore, the analytical expression for ET reactions derived here is more general. It may also be noted that if one assumes $D(\gamma)$ to depend weakly on γ in eq 3, the present one-dimensional description of a multidimensional ET can be shown by proper coordinate transformation to be identical to the Zusman equation[2] for forward ET reaction proposed earlier only for one-dimensional process.

III. Nonequilibrium Electron Transfer

As an illustrative example, we now consider a typical ET reaction, where a molecule DA is excited from the ground state with an ultrashort laser pulse, leading to the formation of the ion-pair D^+A^-. Thus, the ion-pair is initially produced in a completely nonequilibrium configuration and then relaxes downward along its potential energy surface (corresponding to D^+A^-) through relaxation of the surrounding polar solvent till it meets the PES of the molecule DA, where the back ET reaction takes place. We consider here a simple theoretical model for the ET system of interest consisting of a multidimensional space spanned by the low frequency solvent polarization (X) and the vibrational coordinate[21] (Q) or two low frequency solvent collective coordinates.[12] Therefore, for the back ET reaction $D^+A^- \rightarrow DA$, we consider a standard low frequency harmonic oscillator model[12,21] potential for D^+A^- and DA systems defined respectively as

$$V^{\mathrm{R}}(Q,\ X,\ n_{\mathrm{R}}) = \frac{1}{2}Q^2 + \frac{1}{2}X^2 + n_{\mathrm{R}}h\nu_q \quad (25)$$

and

$$V^{\mathrm{P}}(Q,\ X,\ n_{\mathrm{P}}) = \frac{1}{2}(Q - Q_0)^2 + \frac{1}{2}(X - X_0)^2 + \Delta G + n_{\mathrm{P}}h\nu_q, \quad (26)$$

and the phase space function $A(t)$ is given by

$$A(t) = \lambda_{\mathrm{T}} + (n_{\mathrm{P}} - n_{\mathrm{R}})h\nu_q + \Delta G - (XX_0 + QQ_0) \quad (27)$$

Here, the total reorganization energy $\lambda_{\mathrm{T}}(= \lambda_{\mathrm{v}} + \lambda_{\mathrm{s}})$ is contributed by the low frequency vibrational and solvent reorganization energy $\lambda_v = (1/2)Q_0^2$ and $\lambda_s = (1/2)X_0^2$ respectively, while ΔG represents the free energy change of the ET reaction and ν_q is the frequency for the high-frequency vibrational mode with the quantum numbers n_R and n_P referring to the reactant and product, respectively. For this model, the effective potential $V_{eff}(\gamma)$ can be expressed as

$$\beta V_{eff}(\gamma) = [\beta/(4\lambda_T)][\lambda_T + \Delta G + (n_P - n_R)h\nu_q - \gamma]^2 \tag{28}$$

and the diffusivity $D(\gamma, t)$ is given by

$$D(\gamma, t) = \frac{(Q_0)^2 < \dot{Q}(t)\dot{Q}(0)\delta(A(t) - \gamma)>}{<\delta(A(0) - \gamma)>} + \frac{X_0^2 < \dot{X}(t)\dot{X}(0)\delta(A(t) - \gamma)>}{<\delta(A(0) - \gamma)>}. \tag{29}$$

Here, for evaluating the mean potential $\beta V_{eff}(\gamma)$, an ensemble average has been evaluated with respect to the reactant potential energy surface, since ET is considered to occur from the reactant surface to the product surface and in obtaining eq 29 for $D(\gamma, t)$, the cross velocity contribution has been assumed to be small. Now using the variable $Z = [\lambda_T + \Delta G + (n_P - n_R)h\nu_q - \gamma]$, one can write the two-dimensional Smoluchowski equation

$$\frac{\partial P(Z, t|Z_0, 0)}{\partial t} = \frac{\partial}{\partial Z}\left\{D(Z)\left[\frac{\partial P(Z, t|Z_0, 0)}{\partial Z} + P(Z, t|Z_0, 0)\frac{\partial}{\partial Z}(\beta V_{eff}(Z))\right]\right\} - k_0\delta(Z - Z^*)\, P(Z, t|Z_0, 0) \tag{30}$$

and considering the model potential $\beta V_{eff} = (\beta/4\lambda_T)Z^2$, obtain the analytical rate expressions for k_d^{-1} and k_{TST}^{-1} $(=\tau(Z^*))$ given respectively as

$$k_d^{-1} = (\pi\lambda_T k_B T)^{1/2}\int_{Z^*}^{Z_0} dZ\, \frac{\exp[Z^2/(4\lambda_T k_B T)]\,[1 - erf(Z/(4\lambda_T k_B T)^{1/2})]}{D(Z)} \tag{31}$$

and

$$k_{TST}^{-1} = k_0^{-1}(4\pi\lambda_T k_B T)^{1/2} \exp\left[\frac{(\lambda_T + \Delta G + (n_P - n_R)h\nu_q)^2}{4\lambda_T k_B T}\right] \tag{32}$$

where $erf(Z)$ represents the error function. Here $Z^* = \lambda_T + \Delta G + (n_P - n_R)h\nu_q$ at $\gamma = 0$, $Z_0 = 2\lambda_T$ at $\gamma = \gamma_0$ $(t = 0)$ and ΔG stands for the free energy change of charge recombination reactions. k_0 is the instrinsic reaction rate between the initial n_R-th and the final n_P-th vibrational states of the reactant and the product. The expression for k_0 can be written, using the Franck−Condon factor,[22] as

$$k_0 = \exp(-S)n_R!\,n_P! \times \left[\sum_{r=0}^{\min(n_R,n_P)} \frac{(-1)^{n_R+n_P-r}S^{(n_R+n_P-2r)/2}}{r!\,(n_R - r)!\,(n_P - r)!}\right]^2 V_{el}^{\,2} \tag{33}$$

where the electron-vibrational coupling strength is $S = \lambda_h/h\nu_q$ with λ_h as the reorganization energy for the high frequency mode and the electronic coupling matrix element V_{el} is given in terms of the transfer integral J as $V_{el}^2 = (4\pi^2/h)J^2$. Equations 23, 31 and 32 are used here to study the rate of ET reactions.

It may also be noted that analytical results for the ET rate constant k cannot be obtained by directly solving the two-dimensional Smoluchowski equation and in fact, the difficulty for numerical evaluation through this equation increases drastically with increasing the dimensionality. On the contary, the investigation of two-dimensional ET as a one-dimensional problem, as shown here, leads to an analytical expression for the rate constant. The investigation of two-dimensional ET as a one-dimensional problem leading to an analytical expression for the rate constant, as shown here, is only illustrative and it is straightforward to use the present approach to formulate the treatment of ET reactions involving more than two-dimensional space as a one-dimensional problem and obtain analogues of eqs 3 and 22. Although harmonic oscillator model is used in this work, the theory developed is general and can be applied to general situation as well.

IV. Evaluation of Energy and Time-Dependent Diffusivity

In order to study the ET rate constant using eqs 31 and 32, what we need is an explicit expression for $D(Z, t)$, for which we first substitute $\gamma = (\lambda_T + (n_P - n_R)h\nu_q + \Delta G) - Z$ in eq 29 to obtain

$$D(Z, t) = \frac{(Q_0)^2\langle \dot{Q}(t)\,\dot{Q}(0)\,\delta(A(t) + Z - (\lambda_T + (n_P - n_R)h\nu_q + \Delta G))\rangle}{\langle \delta(A(0) + Z - (\lambda_T + (n_P - n_R)h\nu_q + \Delta G))\rangle} + \frac{X_0^{\,2}\langle \dot{X}(t)\,\dot{X}(0)\,\delta(A(t) + Z - (\lambda_T + (n_P - n_R)h\nu_q + \Delta G))\rangle}{\langle \delta(A(0) + Z - (\lambda_T + (n_P - n_R)h\nu_q + \Delta G))\rangle} \tag{34}$$

We then assume $Q(t)$ and $X(t)$ to decay exponentially with relaxation times τ_v and τ_s respectively and eq 34 thereby simplifies to

$$D(Z, t) = \frac{2}{\beta}\left(\frac{\lambda_T}{B}\right)^{1/2}\frac{\exp[-\beta Z^2/(4B)]}{\exp[-\beta Z^2/(4\lambda_T)]} \times [\{\lambda_v f_1(t) \times (1/\tau_v)^2 K_1\} + \{\lambda_s f_2(t)\,(1/\tau_s)^2 K_2\}] \tag{35}$$

where B, K_1 and K_2 are given by

$$B = \lambda_v f_1^{\,2}(t) + \lambda_s f_2^{\,2}(t) \tag{36}$$

$$K_1 = \left[1 - \frac{\lambda_v f_1^{\,2}(t)}{B}\left(1 - \frac{\beta Z^2}{2B}\right)\right] \tag{37}$$

$$K_2 = \left[1 - \frac{\lambda_s f_2^{\,2}(t)}{B}\left(1 - \frac{\beta Z^2}{2B}\right)\right] \tag{38}$$

with $f_1(t) = \exp(-t/\tau_v)$ and $f_2(t) = \exp(-t/\tau_s)$.

V. Results and Discussion

The rate expression derived here is quite general and involves the energy dependent diffusivity. We have calculated the rate constant k of back ET reactons using eqs 23, 31 and 32 for contact ion pairs (CIP) in acetonitrile solvent as a function of the free energy change ΔG of the reaction. We assume here $X(t)$ and $Q(t)$ to decay exponentially with relaxation times τ_s and τ_v respectively. The solvent ralaxation time of acetonitrile is taken[23] as $\tau_s = 0.3$ ps at temperature $T = 300$ K. For simplicity, we consider the relaxation time (τ_v) for the other mode to be same as τ_s. We consider here $\nu_q = 10^{14}$/s and the reorganization energy[24] for this high frequency mode $\lambda_h = 0.893$ eV. Since we assume the energy ralaxation in the high frequency

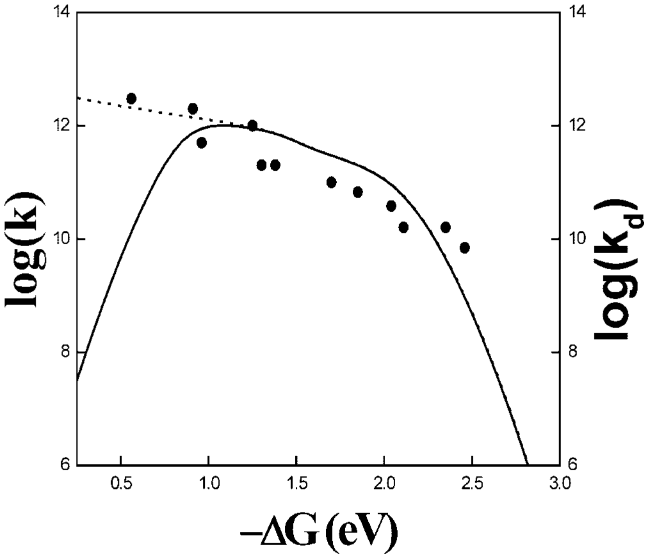

Figure 1. Plot of the total rate constant k of back electron transfer for contact ion pairs (CIP) and the well dynamics rate constant k_d as a function of the free energy change ($-\Delta G$). The parameters used are $\tau = 0.3$ ps, $\nu_q = 10^{14}$/s, $\lambda_v = \lambda_s = 0.55$ eV, $\lambda_h = 0.893$ eV, $J = 0.1$ eV and $T = 300$ K. The solid line (—) and the dotted line (•••) correspond to the calculated results for k and k_d respectively. The experimental data (●) correspond to the ET rate constant k and are taken from ref 8.

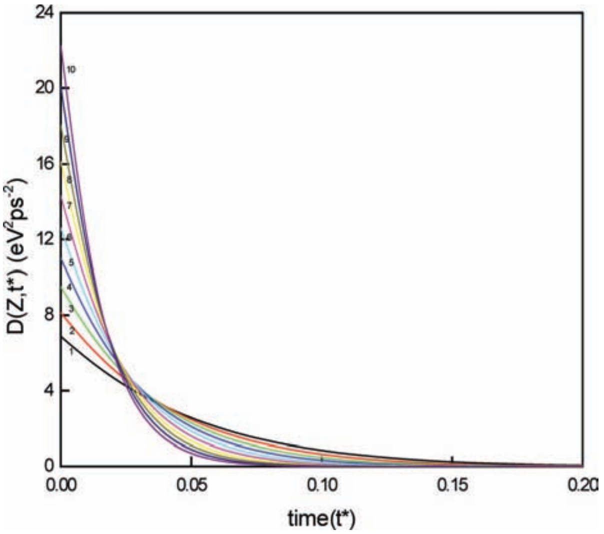

Figure 2. Plot of the calculated values of diffusivity $D(Z, t^*)$ vs time t^* ($=t/\tau$) for different values of Z. The value of ΔG used is -2.5 eV, and values of all the other parameters used remain the same as in Figure 1. The plots are for various values of Z (in eV units): (1) -1.08, (2) -1.18, (3) -1.28, (4) -1.38, (5) -1.48, (6) -1.58, (7) -1.68, (8) -1.78, (9) -1.88, (10) -1.98.

vibrational mode is very fast, therefore, we consider that after excitation the system reaches to the lowest vibrational state of the reactant surface and then back ET reaction takes place with a rate constant k_0. It is clear from eq 33 that the intrinsic rate decreases with increase in the vibrational quantum number of the product surface, and therefore, we have considered here only the rate with maximum contribution, i.e. $n_R = 0$ and $n_P = 1$ for the systems D^+A^- and DA respectively, although contribution from other vibrational states of the product surface can also be included. To explain the experimental results for the rate constant of back ET, Tachiya and Murata[16] had considered only single mode diffusive motion in the X coordinate and used the reorganization energy $\lambda_s = 1.5$ eV, but this value is quite high and cannot be easily rationalized. However, the ET reaction is multidimensional in nature and the reorganization energy might be contributed by different modes and not necessarily arise from one single mode as they have considered in their investigation. In the present theory of a one-dimentional description of a two-dimensional ET, the total reorganization energy is contributed by two modes. For simplicity, we assume an equal contribution from each of the two slowly relaxing modes X and Q corresponding to the reorganization energies λ_s and λ_v respectively. Figure 1 compares the calculated energy gap dependence of the rate for the best fitted values of λ_s (=0.55 eV) and J (=0.1 eV) with the experimental data[8] on back ET in CIP based on the proposed theory and the above approximations. The numerical values of these parameters used here are much less than the values taken by Tachiya and Murata[16] ($\lambda_s = 1.5$ eV and $J = 0.3$ eV) and are even less than the values used ($\lambda_s = 0.75$ eV and $J = 0.3$ eV) in our previous work.[14] However, the value of J for CIP is reasonably significant as expected and the back ET reaction occurs with almost unit probability during the course of the relaxation. Thus, the reaction can occur from a completely nonequilibrium condition and an interplay between k_{TST} and k_d leads to a non-Marcus FEG dependence of the rate of the ET reactions, as is clear from Figure 1 and hence, the total rate of ET reaction is strongly dependent on the initial nonequilibrium configuration as well as the solvent relaxation dynamics. Therefore, one can see that the non-Marcus FEG dependence of the back ET process in CIP is explained fairly well by the present theory with much smaller value of coupling strength, of the order of 0.1 eV. In order to understand the relative contribution of k_d to the total rate constant k, we have also plotted k_d in Figure 1.

Along with the results on ET rates, it would be of interest to look at the behavior of the intermediate quantities, the diffusivities $D(Z, t)$ and $D(Z)$. The calculated values of $D(Z, t^*)$ for $\tau = \tau_v = \tau_s = 0.3$ ps at $T = 300$ K are plotted in Figure 2 against the scaled time t^* ($=t/\tau$) for different values of Z. It is clear from the figure that $D(Z, t)$ is strongly dependent on Z at small time but is only weakly dependent on Z at long time. Sumi and Marus[10] and Tachiya and Murata[16] in their one-dimensional theory of ET proposed a simple exponential model for $D(Z, t)$ ($=(2\lambda_s/\beta\tau_s^2)\exp(-t/\tau_s)$) containing only the parameters λ_s and τ_s whereas our expression of $D(Z, t)$ (eq 35) contains more parameters allowing for a nonexponential dependence on time. Since the quantity $D(Z)$ is explicitly appearing in the well dynamics rate constant k_d, it is also of interest to study the variation of $D(Z)$ as a function of Z. It is for this purpose that we have plotted this quantity as a function of Z in Figure 3, from which it is clear that $D(Z)$ is sharply peaked near the reaction zone and is otherwise weakly dependent on Z.

VI. Concluding Remarks

In this work, we have presented, using Zwanzig's formalism, a conceptually simpler and computationally economic one-dimensional energy diffusion approach to study the ET reactions. We derive an analytical expression for the rate of ET reactions considering a general effective potential and an energy dependent diffusivity. If one neglects the high frequency vibration mode and the effect of energy dependent diffusivity, the present theory reproduces the earlier rate expression shown in a previous work[14] for a harmonic effective potential. Therefore, an analytical expression derived here is more general. As an illustrative example, we have considered here ET reactions for nonequilibrium situation and derived an analytical expression for the

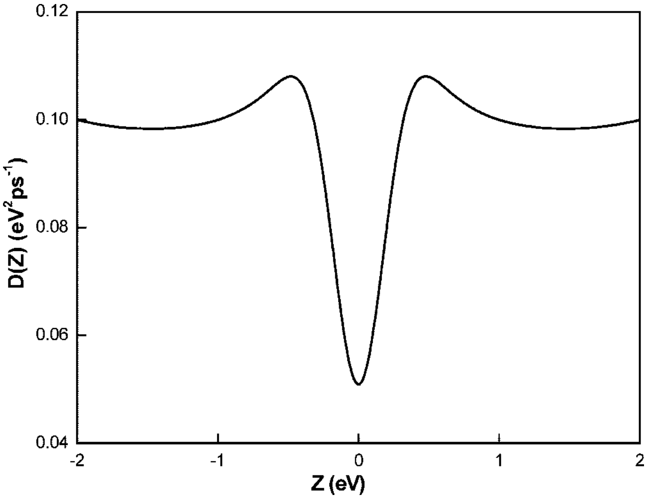

Figure 3. Plot of the calculated values of $D(Z)$ as a function of Z. The value of ΔG used is -2.5 eV, and values of all the other parameters used are the same as in Figure 1.

rate of ET where the total rate constant is explicitly dependent on various physical parameters of the system. We are here able to explain the rate of electron transfer reaction for CIP using much smaller and reasonable values of the solvent reorganization energy λ_s (=0.55 eV) and electron transfer integral J (of the order of 0.1 eV), in contrast to the earlier works where the larger values of λ_s (=1.5 eV) and J (=0.3 eV) had to be invoked to explain the experimental results. In our earlier study,[14] although we had not considered the effect of high frequency vibration mode and energy dependent diffusivity, we found a good agreement of the calculated rate constant values of ET reaction with the experimental results using the reorganization energy values $\lambda_s = \lambda_v = 0.75$ eV which are still quite high for the two low frequency modes Q and X. Although Gayathri and Bagchi[13] have been able to explain the rate of the same ET reactions using smaller values of the solvent reorganization energy λ_s and electron transfer integral J, they evaluated the rate numerically using multidimensional Smoluchowski equation which is very cumbersome and highly involved whereas we have obtained an analytical expression for the ET rate constant which is not only easy to evaluate but also comprises many static and dynamical parameters and hence, it is possible to predict the rates of ET reactions in complex systems which are multidimensional in nature. The investigation of two-dimensional ET as a one-dimensional problem leading to an analytical expression for the rate constant, as shown here, is however only illustrative, and it is straightforward to use the present approach to formulate the treatment of ET reactions involving more than two-dimensional space as a one-dimensional problem and obtain analogues of eqs 3 and 22. In the case of a delocalized sink, one may replace the localized $\delta(\gamma)$ sink of eq 3 by a generalized sink function[19] $S(\gamma)$. Although harmonic oscillator model is used in this work, the theory developed is general and can be applied to the general situation as well. In addition, the situation can be further complicated when both the surfaces are multidimensional in nature and ET does take place[25] from the product to the reactant surface. Such complex situations are often encountered in various experiments. It is of interest to develop a one-dimensional theory for such complicated ET processes, and work in this direction is in progress.

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