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Electron transfer reactions in condensed phase: Effect of reversibility

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We propose a generalized one-dimensional kinetic equation for multidimensional reversible electron transfer (ET) reaction with a nonequilibrium situation as the initial condition. The rate constant for the forward reversible ET reaction obtained here consists of the rate for the corresponding irreversible ET reaction, and an extra term due to reversibility of the ET process which includes the rates of diffusion dynamics in the reactant and product wells. In order to understand the effect of reversibility, we consider back ET reaction in a system consisting of an electron donor-acceptor pair in a solvent modeled through low frequency solvent collective coordinates (multidimensional) characterized by the orientational polarization and slowly relaxing one-dimensional vibrational mode. We propose here a new generalized polarization energy functional corresponding to the extension of the continuum version for the same, which has opened up the possibility of inclusion of molecular nature of the solvent into the solvent reorganization energy. We then derive an exact expression for the ET rate for this model system. The numerical results calculated by using the proposed one-dimensional approach are shown to be in good agreement with the available experimental results. Non-Marcus free energy gap dependence of the rates observed here for the reversible and irreversible ET reactions are very close to each other in the barrierless region, while for other situations, the rate for the former process is found to be less than the latter. The extra term, which makes the difference between the rate constants for irreversible and reversible ET reactions, is found to be contributed by the diffusion dynamics from both reactant and product wells but the dominating contribution is provided mainly by the product well.

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I. INTRODUCTION

The study of electron transfer (ET) processes in condensed phase is ubiquitous in chemistry, physics, and biological sciences. The dynamics of these processes has recently received considerable scrutiny from the experimentalists as well as theoreticians [1–18]. The current phenomenal upsurge of interest in this field owes its origin to the experimental investigations on ET processes explored through widely available ultrafast spectroscopic techniques for dynamical measurements and the synthesis of tailor-made artificial electron donor-acceptor systems. In particular, the advent of femtosecond dynamics on the time scale of nuclear motion [19–21] has opened up new horizons in the exploration of ultrafast ET processes. Thus, the dynamics of ET processes in condensed phase has been a subject of renewed interest.

ET reaction constitutes one of the most important chemical processes in solution and it also plays a crucial role in the energy conversion mechanism in biological systems. A large amount of work in this field has been dedicated to the understanding of the diverse behavior of ET reactions exhibited by donor-acceptor pairs in solutions and also in organized media, much of which were attempted to be simplified within the traditional well-known ET theory of Marcus [1]. However, the study of solvent effects on outer sphere ET reactions has been a subject of much discussion. The works of Zusman [2], Calef and Wolynes [3], and the unified approach of Hynes [4] 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 aspect as well as the effect of reversibility on the rate of ET reaction has not been taken into consideration. There are many situations, e.g., photochemical ET reactions [22,23], where the system is initially in a nonequilibrium configuration rather than an equilibrium one.

Of particular interest is the possibility of reactions in the excited state, where the ET may take place in the highly nonequilibrium conditions. Furthermore, in principle, it is possible to take into account the backward processes even within the framework of such nonequilibrium situations. A complete picture of the ET reaction between two states, therefore, includes the effect of diffusion and reaction in both directions starting with nonequilibrium initial configuration of the system. If equilibrium is to prevail between the initial and the final states, the consideration of the presence of a reverse reaction is very much crucial and the survival probabilities obtained by taking into account such reversible ET differ from those for a reaction in a single direction.

The process of reversible ET with nonequilibrium initial configuration (say with delta function distribution), can arise from a system which is originally in the ground state and is brought to the nonequilibrium excited state by laser excitation. Subsequently, the system at the higher level of excitation relaxes downward toward the potential minimum of the excited-state surface due to relaxation of the polar solvent until its energy coincides with that of the ground state when

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back ET reaction takes place. Thus, the ET reaction can occur from a completely nonequilibrium condition. Depending on the magnitude of the intrinsic ET rate constant k_0, there is an interplay between the relaxation and ET at the crossing point. If k_0 is small, the system relaxes to the potential minimum of the excited-state surface and ET hardly occurs during relaxation to the equilibrium state, although the system passes through the intersection point in the course of relaxation. Only after reaching the minimum of the excited-state surface, thermal fluctuation of solvent molecules brings the system back to the crossing point again and ET reaction then takes place with intrinsic rate k_0. On the other hand, when k_0 is large, the back ET reaction occurs almost exclusively at the intersection point during its downward travel, in place of the relaxation of the system to the minimum of the excited-state surface. In the case of intermediate k_0, however, both the above processes start operating at the crossing point, viz. relaxation of the system to the potential minimum of the same state surface and back electron transfer at the crossing point. However, once the product is formed, it then starts crossing to the reactant surface again through the same intersection point. This process continues until the system finally reaches a dynamical equilibrium. At equilibrium, the ratio of the rate constants for the forward and backward reactions is known in terms of free energy change (ΔG) of the reaction. But it is not clear whether the rate constant for the forward direction for a reversible ET is identical with the same for an irreversible reaction. If they are not equal, then the question arises as to how they are related to each other. In order to answer these queries, what is needed is a microscopic kinetic equation for the distribution function in a relevant space for obtaining either of the two rate constants. The microscopic kinetic equation needed for an exact evaluation of the rate constant in either direction (say forward rate constant), in turn, involves diffusive motion in multidimensional potential wells. The situation can be further complicated if both the surfaces are multidimensional in nature and ET also takes place from the product to the reactant surface. Such complex situations are often encountered in various experiments. Theoretical studies of ET reaction rates in such multidimensional potential energy surfaces pose an interesting but formidable challenge due to tremendous complexity of the problem, since one has to solve a multidimensional Smoluchowski equation to understand the effect of dynamics on the rate of ET reaction. Our objective here is to address all those issues methodically and propose new alternatives.

The organization of the paper is as follows. In Sec. II, we provide a general kinetic equation in one-dimensional reaction coordinate space for multidimensional reversible ET reactions starting with nonequilibrium initial conditions. This is followed by details of the theoretical formulation for obtaining an exact analytical expression for the average forward rate constant for reversible charge recombination (CR) reactions starting with initially prepared nonequilibrium configuration for the system, in terms of a general effective potential and reaction-coordinate-dependent diffusivity. In Sec. III, as an illustrative example, we consider an application of the theory to reversible ET in an ion-pair system modeled through a generalized polarization energy functional (multidimensional) and harmonic one-dimensional vibrational coordinate. The objective here is to select the energy components corresponding to the generalized polarization energy functional and to provide a route to include the molecular effect through solvent reorganization energy into the ET rate. We then derive the expression for the effective potential in terms of the one-dimensional reaction coordinate and define a new generalized expression for solvent reorganization energy which has opened up a possibility of inclusion of the discrete molecular nature of the solvent. In Sec IV, we present details of the theoretical formulation for exact analytical expressions for the average forward rate constant of reversible ET reactions in terms of the general effective potential and reaction-coordinate-dependent diffusivity using the effective potentials derived in the previous section. In Sec. V, we provide some numerical results calculated by using the proposed one-dimensional approach and compare them with available experimental results. We do discuss the role of diffusion dynamics in the reactant and the product wells due to an extra term appearing in the rate expression. Sec. VI concludes with a brief summary.

II. THEORETICAL FORMULATION FOR ONE-DIMENSIONAL DESCRIPTION OF MULTIDIMENSIONAL REVERSIBLE ELECTRON TRANSFER REACTIONS

The phenomenological macroscopic kinetic equation for an irreversible ET reaction is given by

$$\frac{dN_1(t)}{dt} = -\,k'_{12}N_1(t) \tag{1}$$

where k'_{12} denotes the first order rate constant for ET reaction and can be obtained from the following equation defined as

$$k'^{-1}_{12} = \int_0^\infty dt\, N_1(t) = \lim_{S\to 0} \tilde{N}_1(s). \tag{2}$$

Here, $N_1(t)$ represents the probability of finding the unreacted species in the reactant well at time t and $\tilde{N}_1(s)$ denotes its Laplace transform $[\tilde{N}_1(s) = \int_0^\infty dt \exp(-st)N_1(t)]$. In order to evaluate the rate constant k'_{12}, what is needed, is a microscopic kinetic equation for the distribution function in phase space or reaction-coordinate space, which is to be solved to obtain the distribution function and the latter is to be integrated over the relevant coordinates to obtain an expression for $N_1(t)$ and hence k'_{12} using Eq. (2). In order to construct the relevant microscopic kinetic equation, one needs to know the mechanism of the ET reaction. Let us consider an example of mechanism for back ET reaction from a nonequilibrium situation, a typical ET process (see Fig. 1) 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^-. The system is thus initially prepared in a constrained nonequilibrium state through photochemical excitation and in subsequent time, the constraint is removed as the system is no longer under laser field. The system then starts relaxing downward along its multidimensional potential energy surface (corresponding to the ion pair D^+A^-) through relaxation of the surrounding polar solvents until it meets that of the molecule DA at the critical geometrical configuration [3,24–26] determined by

$$H^r_{\rm sol}(\mathbf{R}) - H^p_{\rm sol}(\mathbf{R}) = \gamma^* = \Delta G_{\rm CR} - \lambda, \tag{3}$$

where back ET reaction takes place with an intrinsic rate constant k_0. The quantity $H_{\rm sol}^i(\mathbf{R})(i = r,p)$ represents the Hamiltonian corresponding to the solute-solvent and solvent-solvent interaction energy. Here $\mathbf{R}$ represents a set of geometrical coordinates for the relevant system. Here, $\Delta G_{\rm CR}$ corresponds to the free energy change of CR reaction and λ denotes the solvent reorganization energy. In the process of ET, the electron, which is originally localized at A^- corresponding to ion pair $\mathrm{D}^+\mathrm{A}^-$, will be delocalized to D^+ leading to the formation of the molecule DA when the critical configuration at the intersection point is reached as satisfied by Eq. (3).

The kinetic equation in Liouville space for the ET reaction as described above can now be written as

$$\frac{\partial\rho(\Gamma,t|\Gamma_0,0)}{\partial t} = -[iL + k_0\delta(A(\mathbf{R}) - \gamma^*)]\rho(\Gamma,t|\Gamma_0,0), \tag{4}$$

where $\rho(\Gamma,t|\Gamma_0,0)$ is the probability density defined in phase space Γ at time t when initially it is Γ_0 at $t = 0$. Here, L represents the Liouville operator in phase space and Γ denotes the corresponding phase space coordinates.

Now, $N_1(t)$ can be obtained by integrating the phase space distribution function $\rho(\Gamma,t|\Gamma_0,0)$ over the phase space coordinate, as given by

$$N_1(t) = \int d\Gamma\, \rho(\Gamma,t|\Gamma_0,0). \tag{5}$$

However, it is extremely difficult to solve Eq. (4) and obtain an expression for $N_1(t)$ through Eq. (5) due to the multidimensional nature of the problem. Another difficulty is that the configuration in phase space for the system prepared in a constrained nonequilibrium state under photochemical excitation is also unknown. Since $A(\mathbf{R})[=H_{\rm sol}^r(\mathbf{R}) - H_{\rm sol}^p(\mathbf{R})]$ is a scalar quantity and constraint is imposed on $A(\mathbf{R})$ at the initial time, it is, therefore, convenient to construct a distribution function, say, $g_1(\gamma,t|\gamma_0,0)$ in the reaction coordinate space $A(\mathbf{R})$defined as

$$g_1(\gamma,t|\gamma_0,0) = \int d\Gamma\, \rho(\Gamma,t|\Gamma_0,0)\delta[A(\mathbf{R}) - \gamma]. \tag{6}$$

Here, the initial constraint is imposed on $A(\mathbf{R})$ as $A(\mathbf{R}_0) = \gamma_0$ and $g_1(\gamma,t|\gamma_0,0)$ represents the probability distribution of the reaction coordinate $A(\mathbf{R})$ to have the value γ at time t with its initial value γ_0 at $t = 0$. In our earlier work [27], we have rigorously shown, using projection operator technique, how ET reaction dynamics defined in Liouville space Γ [Eq. (4)] can be mapped into the microscopic reaction-coordinate space $A(\mathbf{R})$. The one-dimensional kinetic equation for the distribution function $g_1(\gamma,t|\gamma_0,0)$ in reaction coordinate space $A(\mathbf{R})$ can be written [28] as

$$\begin{aligned}\frac{\partial g_1(\gamma,t|\gamma_0,0)}{\partial t}&\\ = Z(\gamma,t)g_1(\gamma,t|\gamma_0,0)&-k_0\delta(\gamma-\gamma^*)g_1(\gamma,t|\gamma_0,0),\end{aligned} \tag{7}$$

where $Z(\gamma,t)$ is defined as

$$\begin{aligned}Z(\gamma,t)f(\gamma,t) = &\int dc[i\Omega(\gamma,c)]f(c,t)\\ &- \int dc \int_0^t ds\, K(\gamma,c,s)f(c,t-s)\end{aligned} \tag{8}$$

and the frequency $\Omega(\gamma,c)$ and the memory kernel $K(\gamma,c,t)$ are defined, respectively, as

$$i\Omega(\gamma,c) = \frac{\langle iL\delta[A(\mathbf{R}) - \gamma],\delta[A(\mathbf{R}) - c]\rangle}{\langle\delta[A(\mathbf{R}) - c]\rangle}, \tag{9a}$$

$$K(\gamma,c,t) = \frac{\langle F(c,t),F(\gamma,0)\rangle}{\langle\delta[A(\mathbf{R}) - c]\rangle}. \tag{9b}$$

The random force $F(c,t)$ is defined as

$$F(c,t) = \exp[(1 - P_G)iLt](1 - P_G)iL\delta[A(\mathbf{R}) - c], \tag{10}$$

with the projection operator P_G given by

$$P_G = \int db \frac{(\cdots,\delta[A(\mathbf{R}) - b])}{\langle\delta[A(\mathbf{R}) - b]\rangle}\delta[A(\mathbf{R}) - b]. \tag{11}$$

Although the presence of the projection operator (P_G) makes it difficult to evaluate the memory kernel $K(\gamma,c,t)$ in general, for the situation of the reaction coordinate $A(\mathbf{R})$ varying slowly, Eq. (7) can be simplified in the Markovian limit as

$$\begin{aligned}\frac{\partial g_1(\gamma,t|\gamma_0,0)}{\partial t} = &\frac{\partial}{\partial\gamma}\left\{D_1(\gamma)\left[\frac{\partial g_1(\gamma,t|\gamma_0,0)}{\partial\gamma}\right.\right.\\ &\left.\left.+ g_1(\gamma,t|\gamma_0,0)\frac{\partial}{\partial\gamma}\{\beta V_1^{\rm eff}(\gamma)\}\right]\right\}\\ &- k_0\delta(\gamma - \gamma^*)g_1(\gamma,t|\gamma_0,0).\end{aligned} \tag{12}$$

Here, the γ-dependent diffusivity $D_1(\gamma)$ is defined as

$$\begin{aligned}&D_1(\gamma)\\ &= \int_0^\infty dt \frac{\int d\mathbf{R}\, \dot{A}(\mathbf{R},t)\, \dot{A}(\mathbf{R})\delta[A(\mathbf{R})-\gamma]\exp\left[-\beta H_{\rm sol}^r(\mathbf{R})\right]}{\int d\mathbf{R}\,\delta[A(\mathbf{R})-\gamma]\exp\left[-\beta H_{\rm sol}^r(\mathbf{R})\right]},\end{aligned} \tag{13}$$

where the dot corresponds to time derivative and $\beta\,(=1/k_BT)$ denotes the inverse temperature. The effective potential $V_1^{\rm eff}(\gamma)$ is a function of γ, and is given by

$$\begin{aligned}\exp\left[-\beta V_1^{\rm eff}(\gamma)\right] &= \beta^{-1}\langle\delta[A(\mathbf{R}) - \gamma]\rangle_r\\ &= \beta^{-1}\int d\mathbf{R}\,\delta[A(\mathbf{R}) - \gamma]\exp\left[-\beta H_{\rm sol}^r(\mathbf{R})\right].\end{aligned} \tag{14}$$

It is now clear from Eqs. (5) and (6) that $N_1(t)$ can also be obtained by integrating $g_1(\gamma,t|\gamma_0,0)$ over γ, viz.

$$N_1(t) = \int_{-\infty}^{+\infty} d\gamma\, g_1(\gamma,t|\gamma_0,0), \tag{15}$$

and hence the rate constant k'_{12} through Eq. (2). Using the Green's function technique, one can easily solve Eq. (12) to obtain a formal expression for k'_{12} given by

$$k_{12}^{\prime -1} = \left[k_1^{\rm TST}(\gamma^*)\right]^{-1} + \left[k_1^d(\gamma^*,\gamma_0)\right]^{-1}, \tag{16}$$

where the intrinsic transition rate $k_1^{\rm TST}(\gamma^*)$ and nonequilibrium relaxation dynamics rate $k_1^d\,(\gamma^*,\gamma_0)$ are defined, respectively, as

$$\left[k_1^{\rm TST}(\gamma^*)\right]^{-1} = \frac{1}{k_0 g_1^{\rm eq}(\gamma^*)}, \tag{17}$$

$$\left[k_1^d(\gamma^*,\gamma_0)\right]^{-1} = \frac{\int_0^\infty dt\left[g_1^0(\gamma^*,t|\gamma^*,0) - g_1^0(\gamma^*,t|\gamma_0,0)\right]}{g_1^{\rm eq}(\gamma^*)}, \tag{18}$$

with $g_1^{\mathrm{eq}}(\gamma^*)[=g_1^0(\gamma^*,\infty|\gamma^*,0)]$ representing the stationary distribution given by

$$g_1^{\mathrm{eq}}(\gamma^*) = \frac{\exp\left[-\beta V_1^{\mathrm{eff}}(\gamma^*)\right]}{\int_{-\infty}^{+\infty} d\gamma\ \exp\left[-\beta V_1^{\mathrm{eff}}(\gamma)\right]}. \tag{19}$$

The macroscopic kinetic equation, defined in Eq. (1), is valid as long as the barrier height for the reverse reaction is very large. However, the effect of reversibility on $N_1(t)$ becomes significant when the barrier heights for both the processes are comparable. In these cases, the modified macroscopic kinetic equations are given by

$$\frac{dN_1(t)}{dt} = -k_{12}N_1(t) + k_{21}N_2(t), \tag{20a}$$

$$\frac{dN_2(t)}{dt} = -k_{21}N_2(t) + k_{12}N_1(t), \tag{20b}$$

where k_{12} and k_{21} denote, respectively, the rate constants for forward and backward reactions and $N_1(t) = \int_{-\infty}^{\infty} d\gamma\ g_1(\gamma,t|\gamma_0,0)$ and $N_2(t) = \int_{-\infty}^{\infty} d\gamma\ g_2(\gamma,t|\gamma_0,0)$. Here, $g_2(\gamma,t|\gamma_0,0)$ is the probability distribution of the reaction coordinate $A(\mathbf{R})$ to have the value γ at time t with its initial value γ_0 at $t=0$ at the product surface. Now, taking the Laplace transform of both Eqs. (20a) and (20b), one can easily obtain an expression for $N_1(t)$ in the Laplace plane as

$$\tilde{N}_1(s) = \frac{s + k_{21}}{s^2 + s\,(k_{12} + k_{21})}, \tag{21}$$

which on inverse Laplace transformation, leads to the expression

$$\frac{[N_1(t) - (1-\alpha)]}{\alpha} = \exp\left[-\,(k_{12}+k_{21})\,t\right], \tag{22}$$

where the parameter α can be expressed in terms of the forward and backward rate constants k_{12} and k_{21} as

$$\alpha = \frac{k_{12}}{(k_{12}+k_{21})}. \tag{23}$$

Now, using the relation $k_{12}/k_{21} = \exp[-\beta\Delta G_{\mathrm{CR}}]$, Eqs. (22) and (23), after some algebra, leads to the expression for the rate constant k_{12} [30] given by

$$k_{12}^{-1} = \lim_{s\to 0}\frac{(1+\exp[\beta\Delta G_{\mathrm{CR}}])}{\alpha}\left[\tilde{N}_1(s) - \frac{(1-\alpha)}{s}\right], \tag{24}$$

where ΔG_{CR} represents the free energy of ET reaction. It is apparent from Eqs. (2) and (24) that the rate constant k'_{12} defined in Eq. (2) for an irreversible reaction is different from the same k_{12} defined in Eq. (24) for a reversible reaction. But, it is not clear whether the rate constant k_{12} is greater or smaller than k'_{12}. In this connection, another important question that arises is whether k_{12} really consists of two parts—one from irreversible rate k'_{12} and another from the collection of dynamical quantities, i.e., rates of diffusion dynamics in reactant as well as product potential surfaces. In order to answer all these queries, first we need a microscopic kinetic equation in reaction coordinate space (γ) for the reversible ET reaction. In the case of reversible ET reaction, the kinetic equation for the probability distribution $g_i(\gamma,t|\gamma_0,0)$ given by Eq. (12) should be modified by considering a delta sink of strength k_0 both for the forward as well as the backward processes. The modified kinetic equations for reversible ET reactions thus become

$$\begin{aligned}\frac{\partial g_1(\gamma,t|\gamma_0,0)}{\partial t} &= \frac{\partial}{\partial\gamma}\left\{D_1(\gamma)\left[\frac{\partial g_1(\gamma,t|\gamma_0,0)}{\partial\gamma}\right.\right.\\ &\quad \left.\left. + g_1(\gamma,t|\gamma_0,0)\frac{\partial}{\partial\gamma}\left\{\beta V_1^{\mathrm{eff}}(\gamma)\right\}\right]\right\}\\ &\quad - k_0\delta(\gamma-\gamma^*)[g_1(\gamma,t|\gamma_0,0) - g_2(\gamma,t|\gamma_0,0)],\end{aligned} \tag{25}$$

$$\begin{aligned}\frac{\partial g_2(\gamma,t|\gamma_0,0)}{\partial t} &= \frac{\partial}{\partial\gamma}\left\{D_2(\gamma)\left[\frac{\partial g_2(\gamma,t|\gamma_0,0)}{\partial\gamma}\right.\right.\\ &\quad \left.\left. + g_2(\gamma,t|\gamma_0,0)\frac{\partial}{\partial\gamma}\left\{\beta V_2^{\mathrm{eff}}(\gamma)\right\}\right]\right\}\\ &\quad - k_0\delta(\gamma-\gamma^*)[g_2(\gamma,t|\gamma_0,0) - g_1(\gamma,t|\gamma_0,0)],\end{aligned} \tag{26}$$

where $g_1(\gamma,t|\gamma_0,0)$ and $g_2(\gamma,t|\gamma_0,0)$ are the probability distributions corresponding to the diffusive motion along the one-dimensional reaction coordinate γ in the respective potential wells of the reactant and product state in the presence of a delta sink of strength k_0 located at the transition point γ^*. Here, $D_1(\gamma)$ and $D_2(\gamma)$ denote, respectively, the reaction-coordinate (γ)-dependent diffusivities in the reactant and product states, and $V_1^{\mathrm{eff}}(\gamma)$ and $V_2^{\mathrm{eff}}(\gamma)$ are the corresponding effective potentials. The initial condition, which we have considered here, is the nonequilibrium configuration, i.e., $g_1(\gamma,t=0|\gamma_0,0) = \delta(\gamma-\gamma_0)$ as the initial condition for the reactant and $g_2(\gamma,t=0|\gamma_0,0) = 0$ for the product. The rate constant k_{12} can now be obtained using Eqs. (15) and (24), along with Green's function [29] technique and the procedure discussed in [30]. The final expression for k_{12} obtained in terms of the nonequilibrium relaxation dynamics rate $k_1^d(\gamma^*,\gamma_0)$ in the reactant well, well dynamics rate $k_i^d(\gamma^*)$, and intrinsic transition state rate $k_i^{\mathrm{TST}}(\gamma^*)$, is given by

$$k_{12}^{-1} = k_{12}'^{-1} + \frac{\exp(\beta\Delta G_{\mathrm{CR}})}{k_1^d(\gamma^*,\gamma_0)}\left\{1 + \frac{k_1^d(\gamma^*,\gamma_0)}{k_2^d(\gamma^*)} - \frac{k_1^d(\gamma^*,\gamma_0)}{k_1^d(\gamma^*)}\right\}, \tag{27}$$

where the well dynamics rate $k_i^d(\gamma^*)$ is defined as

$$\left[k_i^d(\gamma^*)\right]^{-1} = \frac{\int_0^\infty dt\left[P_i^0(\gamma^*,t|\gamma^*,0) - P_i^{\mathrm{eq}}(\gamma^*)\right]}{P_i^{\mathrm{eq}}(\gamma^*)}. \tag{28}$$

The explicit form of $k_1^d(\gamma^*,\gamma_0)$ is given as

$$\begin{aligned}\left[k_1^d(\gamma^*,\gamma_0)\right]^{-1} &= \int_{\gamma^*}^{\gamma_0} d\gamma\,\frac{\exp\left[\beta V_1^{\mathrm{eff}}(\gamma)\right]}{D_1(\gamma)}\\ &\quad\times\left\{C_1 - \int^{\gamma} d\gamma'\ \exp\left[-\beta V_1^{\mathrm{eff}}(\gamma')\right]\right\},\end{aligned} \tag{29}$$

where the expressions for $C_1$are given by

$$C_1 = \frac{1}{2}\int_{-\infty}^{\infty} d\gamma\ \exp\left[-\beta V_1^{\mathrm{eff}}(\gamma)\right] \quad \text{for} \quad \gamma_0 > \gamma^* \tag{30}$$

and

$$C_1 = -\frac{1}{2}\int_{-\infty}^{\infty} d\gamma\ \exp\left[-\beta V_1^{\text{eff}}(\gamma)\right] \quad \text{for} \quad \gamma_0 < \gamma^*. \tag{31}$$

Another quantity of interest in this context is the well dynamics rate $k_i^d(\gamma^*)$ and its explicit form is given as

$$\begin{aligned}\left[k_i^d(\gamma^*)\right]^{-1} = \frac{1}{2A_i}\Bigg[& g_i(-\infty)\int_{\gamma^*}^{-\infty} d\gamma \frac{\exp\left[\beta V_1^{\text{eff}}(\gamma)\right]}{D_i(\gamma)} F_i(\gamma) + g_i(\infty)\int_{\gamma^*}^{\infty} d\gamma \frac{\exp\left[\beta V_i^{\text{eff}}(\gamma)\right]}{D_i(\gamma)} G_i(\gamma) \\ & + \int_{-\infty}^{\gamma^*} d\gamma\ g_i(\gamma)\frac{\exp\left[\beta V_i^{\text{eff}}(\gamma)\right]}{D_i(\gamma)} F_i(\gamma) - \int_{\gamma^*}^{\infty} d\gamma\ g_i(\gamma)\frac{\exp\left[\beta V_i^{\text{eff}}(\gamma)\right]}{D_i(\gamma)} G_i(\gamma)\Bigg],\end{aligned} \tag{32}$$

where A_i, $g_i(\gamma)$, $F_i(\gamma)$, and $G_i(\gamma)$ are, respectively, given by

$$A_i = [g_i(\infty) - g_i(-\infty)], \tag{33}$$

$$g_i(\gamma) = \int^{\gamma} d\gamma'\ \exp\left[-\beta V_i^{\text{eff}}(\gamma')\right], \tag{34}$$

$$F_i(\gamma) = A_i + 2g_i(\gamma), \tag{35}$$

$$G_i(\gamma) = A_i - 2g_i(\gamma). \tag{36}$$

It is important to note here that Eq. (24) does not reveal whether the rate constant for reversible reaction can be separated into two parts contributed, respectively, by irreversibility and reversibility of the ET reaction. However, the rate constant given by Eq. (27) based on microscopic kinetic equations results in two terms consisting of contribution (first term) solely due to irreversible ET reactions and an extra term (second term) due to the effect of reversibility. It is also clear from Eqs. (27), (29), and (32) that an explicit expression for $V_i^{\text{eff}}(\gamma)$ is needed in order to account for the effect of reversibility, and details of derivation of the expressions for the required quantities are discussed in the following section.

III. EVALUATION OF EFFECTIVE POTENTIAL $V_i^{\text{eff}}(\gamma)$ IN REACTION COORDINATE SPACE

Before deriving the explicit expression for $V_i^{\text{eff}}(\gamma)$ ($i = 1,2$ for r,p), we now consider the typical ET process as already described in Sec. II. In the initial (before ET) state of the ion pair (D$^+$A$^-$), D and A have a positive charge e and a negative charge $-e$, respectively. Thus, the energy of the initial state is the interaction energy between the dipoles of the solvent molecules plus the interaction energy between the ion pair (D$^+$A$^-$) and the surrounding solvent. On the other hand, in the final (after ET) state, both D and A are neutral, and hence the interaction energy between the neutral solute (DA) and the solvent may be neglected. Therefore, the energy of the final state is only due to the interaction energy between the permanent dipoles of the solvent molecules. We propose here expressions corresponding to the continuum version of the interaction energies $H_P^r[\mathbf{P}(\mathbf{r})]$ and $H_P^p[\mathbf{P}(\mathbf{r})]$ of the donor-acceptor pair (D$^+$A$^-$ / DA) with the surrounding solvent before and after ET, respectively, which are given here in terms of orientation polarization function $\mathbf{P}(\mathbf{r})$ as

$$\begin{aligned}H_P^r[\mathbf{P}(\mathbf{r})] &= \int f(\mathbf{r})\mathbf{P}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r} \\ &\quad + \int_{\substack{|\mathbf{r}-\mathbf{r}_D|>a \\ |\mathbf{r}-\mathbf{r}_A|>b}} \mathbf{P}(\mathbf{r})\cdot\left[\frac{e(\mathbf{r}-\mathbf{r}_D)}{|\mathbf{r}-\mathbf{r}_D|^3} - \frac{e(\mathbf{r}-\mathbf{r}_A)}{|\mathbf{r}-\mathbf{r}_A|^3}\right] d\mathbf{r} \\ &= \int f(\mathbf{r})\mathbf{P}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r} + \int \mathbf{P}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})d\mathbf{r},\end{aligned} \tag{37}$$

$$H_P^p[\mathbf{P}(\mathbf{r})] = \int f(\mathbf{r})\mathbf{P}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r}. \tag{38}$$

Here, $\mathbf{r}_D$ and $\mathbf{r}_A$ stand for the positions of the donor and acceptor, of radii a and b, respectively, and the second term on the right-hand side of Eq. (37) stands for the interaction energy between the charges and the polarization field, while the function $f(\mathbf{r})$ appearing in the Eqs. (37) and (38) takes into account the effect of finite size of the solvent molecules. To include the effect of size, one may consider the equilibrium situation, for which the minimization of $H_P^r[\mathbf{P}(\mathbf{r})]$ establishes the relation between $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$, i.e., $\mathbf{P}(\mathbf{r}) = \mathbf{E}(\mathbf{r})/f(\mathbf{r})$. This provides a scheme to obtain $f(\mathbf{r})$, through the knowledge of $\mathbf{P}(\mathbf{r})$ obtainable from molecular theory, based on, for example, density functional theory where the effect of molecular nature has been included, or simulation results. The advantage of using the above mentioned Hamiltonian over the density functional theory is that here one can obtain an analytical expression for $V_i^{\text{eff}}(\gamma)$, which contains $f(\mathbf{r})$. As the ET reaction is assumed to proceed on a multidimensional surface, the theoretical description that we propose here for the ET system of interest consists of a multidimensional space spanned by the low frequency solvent collective coordinates (multidimensional) characterized by the orientational polarization function $\mathbf{P}(\mathbf{r})$. In addition to it, we also consider here a low frequency harmonic molecular vibrational mode which we describe by the coordinate Q. Thus, the Hamiltonians H_{sol}^r and H_{sol}^p for the ion pair (D$^+$A$^-$) and neutral solute (DA), respectively, are given as

$$\begin{aligned}H_{\text{sol}}^r = H_P^r[\mathbf{P}(\mathbf{r})] + H_V^r(Q) &= \int f(\mathbf{r})\mathbf{P}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r} \\ &\quad + \int \mathbf{P}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})d\mathbf{r} + \frac{1}{2}(Q+Q_0)^2,\end{aligned} \tag{39}$$

$$H_{\text{sol}}^p = H_P^p[\mathbf{P}(\mathbf{r})] + H_V^p(Q) = \int f(\mathbf{r})\mathbf{P}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r} + \frac{1}{2}Q^2. \tag{40}$$

The microscopic reaction coordinate $A[\mathbf{P}(\mathbf{r}),Q]$ defined for the ET reaction is given by

$$A[\mathbf{P}(\mathbf{r}),Q] = \left(H^{r}_{\mathrm{sol}} - H^{p}_{\mathrm{sol}}\right) = A_P[\mathbf{P}(\mathbf{r})] + A_V(Q), \tag{41}$$

where

$$A_P[\mathbf{P}(\mathbf{r})] = \int \mathbf{P}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})d\mathbf{r}, \tag{42}$$

$$A_V(Q) = QQ_0 + \tfrac{1}{2}Q_0^2. \tag{43}$$

The probability of the reaction coordinate $A[\mathbf{P}(\mathbf{r}),Q]$ to have the value γ, when the system is in the reactant-product state, is given by

$$\exp\left[-\beta V_i^{\mathrm{eff}}(\gamma)\right] = \beta^{-1}\left\langle\delta\left(A[\mathbf{P}(\mathbf{r}),Q]-\gamma\right)\right\rangle_i, \tag{44}$$

where $\langle\delta(A[\mathbf{P}(\mathbf{r}),Q]-\gamma)\rangle_i$ represents the ensemble average with respect to the reactant-product well. Now, using Eq. (42), one can decouple the ensemble average $\langle\delta(A[\mathbf{P}(\mathbf{r}),Q]-\gamma)\rangle_i$ into a product of two terms, one corresponding to averaging over the multidimensional polarization mode and the other representing averaging over the vibrational mode leading to the final expression, given by

$$\exp\left[-\beta V_i^{\mathrm{eff}}(\gamma)\right] = \beta^{-1}\int_{-\infty}^{\infty} d\gamma_1 \int_{-\infty}^{\infty} d\gamma_2\, \delta(\gamma_1+\gamma_2-\gamma) \times \langle\delta(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1)\rangle_i \langle\delta[A_V(Q)-\gamma_2]\rangle_i. \tag{45}$$

Here $\langle\delta(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1)\rangle_i$ and $\langle\delta[A_V(Q)-\gamma_2]\rangle_i$ represent, respectively, the ensemble averages over polarization and vibrational modes. In order to evaluate the effective potential $\beta V_i^{\mathrm{eff}}(\gamma)$ ($i = 1{,}2$ for r,p), the ensemble averages $\langle\delta(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1)\rangle_i$ and $\langle\delta[A_V(Q)-\gamma_2]\rangle_i$ are to be calculated individually with respect to the ith potential energy surface, since ET is considered to occur from the ith surface to the jth surface for a single direction. The quantity $\langle\delta(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1)\rangle_r$ contains the term $A_P[\mathbf{P}(\mathbf{r})]$, a functional of orientational polarization $\mathbf{P}(\mathbf{r})$, which has a distribution of Boltzmann type, viz., $\exp\{-\beta H_P^r[\mathbf{P}(\mathbf{r})]\}$ due to thermal fluctuation of the solvent molecules. Therefore, $A_P[\mathbf{P}(\mathbf{r})]$ will have a distribution that can be calculated by discretizing the integrals involved in the ensemble average $\langle\delta(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1)\rangle_r$, i.e., writing the ensemble average in the following form:

$$\langle\delta\left(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1\right)\rangle_r = \frac{\left[\int d\mathbf{P}(\mathbf{r}_i)\exp\left[-\beta\sum_{i=1}^{\infty}d\mathbf{r}_i\left\{f(\mathbf{r}_i)\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{P}(\mathbf{r}_i)+\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{E}(\mathbf{r}_i)\right\}\right]\left[\delta\left(\sum_{i=1}^{\infty}d\mathbf{r}_i\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{E}(\mathbf{r}_i)-\gamma_1\right)\right]\right]}{\int d\mathbf{P}(\mathbf{r}_i)\exp\left[-\beta\sum_{i=1}^{\infty}d\mathbf{r}_i\left\{f(\mathbf{r}_i)\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{P}(\mathbf{r}_i)+\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{E}(\mathbf{r}_i)\right\}\right]}, \tag{46}$$

and expressing the delta function in Fourier space, viz.,

$$\delta\left(\sum_{i=1}^{\infty}d\mathbf{r}_i\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{E}(\mathbf{r}_i)-\gamma_1\right) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}dk\,\exp\left(ik\left[\sum_{i=1}^{\infty}d\mathbf{r}_i\mathbf{P}(\mathbf{r}_i)\cdot\mathbf{E}(\mathbf{r}_i)-\gamma_1\right]\right). \tag{47}$$

After some algebra, this leads to the expression

$$\langle\delta\left(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1\right)\rangle_r = \left(\frac{\beta}{4\pi\lambda_S}\right)^{1/2}\exp\left[-\frac{\beta}{4\lambda_S}(\gamma_1+2\lambda_S)^2\right], \tag{48}$$

where the generalized solvent reorganization energy λ_S is defined as

$$\lambda_S = \frac{1}{4}\int d\mathbf{r}\frac{\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})}{f(\mathbf{r})}. \tag{49}$$

Equation (49) reveals that the effect due to molecular nature is incorporated into the solvent reorganization energy through $f(\mathbf{r})$. The evaluation of the ensemble average $\langle\delta[A_V(Q)-\gamma_2]\rangle_r$ over the vibrational coordinate can be obtained as

$$\langle\delta\left[A_V(Q)-\gamma_2\right]\rangle_r = \frac{\int dQ\,\delta\left[\left(QQ_0+\frac{1}{2}Q_0^2\right)-\gamma_2\right]\exp\left[-\frac{\beta}{2}(Q+Q_0)^2\right]}{\int dQ\,\exp\left[-\frac{\beta}{2}(Q+Q_0)^2\right]} = \left(\frac{\beta}{4\pi\lambda_V}\right)^{1/2}\exp\left[-\frac{\beta}{4\lambda_V}(\gamma_2+\lambda_V)^2\right], \tag{50}$$

where $\lambda_V(=\frac{1}{2}Q_0^2)$ is the vibrational reorganization energy. Now, combining Eqs. (45), (48), and (50), one can have a probability distribution for the reaction coordinate $A[\mathbf{P}(\mathbf{r}),Q]$ to have the value γ in the reactant surface defined as

$$\beta^{-1}\left\langle\delta\left(A[\mathbf{P}(\mathbf{r}),Q]-\gamma\right)\right\rangle_r = \exp\left[-\beta V_1^{\mathrm{eff}}(\gamma)\right] = (4\pi\beta\lambda_T)^{-1/2}\exp\left[-\frac{\beta}{4\lambda_T}(\gamma+2\lambda_S+\lambda_V)^2\right]. \tag{51}$$

Here, the total reorganization energy $\lambda_T(=\lambda_S+\lambda_V)$ is contributed by the low frequency solvent and vibrational reorganization energies λ_S and λ_V, respectively.

The ensemble average $\langle\delta(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1)\rangle_p$ over the polarization mode in the product surface (DA plus solvent environment) can be obtained similarly by writing the ensemble average in discretized form as

$$\langle\delta\left(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1\right)\rangle_p=\frac{\left[\int d\mathbf{P}\left(\mathbf{r}_i\right)\exp\left[-\beta\sum_{i=1}^{\infty}d\mathbf{r}_i\left\{f\left(\mathbf{r}_i\right)\mathbf{P}\left(\mathbf{r}_i\right)\cdot\mathbf{P}\left(\mathbf{r}_i\right)\right\}\right]\left[\delta\left(\sum_{i=1}^{\infty}d\mathbf{r}_i\mathbf{P}\left(\mathbf{r}_i\right)\cdot\mathrm{E}\left(\mathbf{r}_i\right)-\gamma_1\right)\right]\right]}{\int d\mathbf{P}\left(\mathbf{r}_i\right)\exp\left[-\beta\sum_{i=1}^{\infty}d\mathbf{r}_i\left\{f\left(\mathbf{r}_i\right)\mathbf{P}\left(\mathbf{r}_i\right)\cdot\mathbf{P}\left(\mathbf{r}_i\right)\right\}\right]},\tag{52}$$

which on further simplification leads to the result

$$\langle\delta\left(A_P[\mathbf{P}(\mathbf{r})]-\gamma_1\right)\rangle_p=\left(\frac{\beta}{4\pi\lambda_S}\right)^{1/2}\exp\left[-\frac{(\gamma_1)^2}{4k_BT\lambda_S}\right].\tag{53}$$

The evaluation of the quantity $\langle\delta[A_V(Q)-\gamma_2]\rangle_p$ over the vibrational mode in the product surface leads to the result

$$\langle\delta\left[A_V(Q)-\gamma_2\right]\rangle_p=\frac{\int dQ\,\delta\left[\left(QQ_0+\frac{1}{2}Q_0^2\right)-\gamma_2\right]\exp\left[-\frac{\beta}{2}Q^2\right]}{\int dQ\,\exp\left[-\frac{\beta}{2}Q^2\right]}=\left(\frac{\beta}{4\pi\lambda_V}\right)^{1/2}\exp\left[-\frac{\beta}{4\lambda_V}(\gamma_2-\lambda_V)^2\right].\tag{54}$$

With the combination of Eqs. (45), (53), and (54), one can obtain a probability distribution for the reaction coordinate $A[\mathbf{P}(\mathbf{r}),Q]$ to have the value γ in the product surface defined as

$$\exp\left[-\beta V_2^{\mathrm{eff}}(\gamma)\right]=(4\pi\beta\lambda_T)^{-1/2}\exp\left[-\frac{\beta}{4\lambda_T}(\gamma-\lambda_V)^2\right].\tag{55}$$

It is now clear from Eqs. (51) and (55) that the effective potentials $V_i^{\mathrm{eff}}(\gamma)$ in reaction coordinate space (γ) for the reactant and product states can be defined as

$$\beta V_1^{\mathrm{eff}}(\gamma)=\frac{\beta}{4\lambda_T}(\gamma+2\lambda_S+\lambda_V)^2,\tag{56}$$

$$\beta V_2^{\mathrm{eff}}(\gamma)=\frac{\beta}{4\lambda_T}(\gamma-\lambda_V)^2.\tag{57}$$

The transition point γ^* in the reaction coordinate space (γ) is defined as

$$\gamma^*=(\Delta G_{\mathrm{CR}}-\lambda_T).\tag{58}$$

The analytical expression derived here based on a different approach for the effective potentials $V_i^{\mathrm{eff}}(\gamma)$ can be used to evaluate the rate of ET reaction in the following section.

IV. EVALUATION OF RATE OF ELECTRON TRANSFER REACTION

Before deriving an expression for the rate of forward ET reaction, we first introduce a new variable z_1 given by

$$\gamma=z_1-2\lambda_S-\lambda_V\tag{59}$$

to evaluate the diffusion rate constant $k_1^d(\gamma^*,\gamma_0)$ defined in Eqs. (29)–(31). During photo excitation of the molecule DA in a solvent environment [corresponding to the effective potential $V_2^{\mathrm{eff}}(\gamma)$ of the system] we consider the initial value of the reaction coordinate as $\gamma_0=\lambda_V$, which is obtained by minimizing $V_2^{\mathrm{eff}}(\gamma)$ [Eq. (57)] with respect to the variation of γ. The ion pair $\mathrm{D}^+\mathrm{A}^-$ is now formed [corresponding to the effective potential $V_1^{\mathrm{eff}}(\gamma)$] after photoexcitation at this initial value, i.e., $\gamma=\gamma_0=\lambda_V$, which can be expressed in z_1 coordinate as $z_1^0=2\lambda_T$, by substituting $\gamma=\gamma_0=\lambda_V$ and $z_1=z_1^0$ in Eq. (59). During relaxation of the ion-pair $(\mathrm{D}^+\mathrm{A}^-)$ system in the downhill potential $V_1^{\mathrm{eff}}(z_1)$, the coordinate z_1 which started with initial value z_1^0 corresponding to the initial nonequilibrium solvent configuration, changes in subsequent time in the direction toward the minimum energy configuration of the ion-pair $(\mathrm{D}^+\mathrm{A}^-)$ system in a solvent environment. However, during relaxation when the system reaches the configuration corresponding to the value of the reaction coordinate determined by the condition $A[P(r),Q]=\gamma=\gamma^*=(\Delta G_{\mathrm{CR}}-\lambda_T)$ [the same in z_1 coordinate is $z_1=z_1^*=\lambda_T+(\Delta G_{\mathrm{CR}}-\lambda_V)$], ET occurs at a rate proportional to $k_0[=(4\pi^2/h)J^2]$, where J is the electronic coupling matrix element. Now, considering the model potential $\beta V_1^{\mathrm{eff}}(z_1)=(\beta/4\lambda_T)z_1^2$ in z_1 coordinate and using Eqs. (17), (19) and (29)–(31), we derive the intrinsic transition state theory rate $k_1^{\mathrm{TST}}(z_1^*)$ and nonequilibrium relaxation dynamics rate $k_1^d(\mathrm{z}_1^*,z_1^0)$ given by

$$\left[k_1^{\mathrm{TST}}(z_1^*)\right]^{-1}=k_0^{-1}(4\pi\lambda_Tk_\beta T)^{1/2}\exp\left[\frac{\beta}{4\lambda_T}(\Delta G_{\mathrm{CR}}+\lambda_S)^2\right],\tag{60}$$

$$\left[k_1^d\left(z_1^*,z_1^0\right)\right]^{-1}=(\pi\lambda_Tk_BT)^{1/2}\int_{\Delta G+\lambda_S}^{2\lambda_T}dz_1\frac{\exp\left(\frac{\beta}{4\lambda_T}z_1^2\right)}{D_1(z_1)}\times\{1-\mathrm{erf}[z_1/(4\lambda_Tk_BT)^{1/2}]\},\tag{61}$$

where $\mathrm{erf}(z_1)$ is the error function. The rate constant k_{12}' can now be expressed in terms of the above two rate constants as

$$k_{12}'^{-1}=\left[k_1^{\mathrm{TST}}(z_1^*)\right]^{-1}+\left[k_1^d\left(\mathrm{z}_1^*,z_1^0\right)\right]^{-1}.\tag{62}$$

In order to obtain the effect of reversibility on the rate constant k_{12}, one needs to calculate the additional quantities, viz., the well dynamics rates $k_1^d(z_1^*)$ and $k_2^d(z_2^*)$ for the reaction coordinate $A[\mathbf{P}(\mathbf{r}),Q]$ undergoing diffusive motion in the respective effective potentials $V_1^{\mathrm{eff}}(\gamma)$ and $V_2^{\mathrm{eff}}(\gamma)$. While evaluating $k_1^d(z_1^*)$, we use the same coordinate transformation as defined by Eq. (59), whereas for $k_2^d(z_2^*)$, we introduce the new transformation given by

$$z_2=\gamma-\lambda_V,\tag{63}$$

with the transition point in z_2 coordinate given by $z_2^*=-\lambda_T+(\Delta G_{\mathrm{CR}}-\lambda_V)$. Now, using Eqs. (32)–(36), and after a lengthy algebra we obtain the well dynamics rate constants given by

$$\left[k_i^d(z_i^*)\right]^{-1} = \frac{1}{2}\left(\int_{z_i^*}^{\infty} dz_i^0 \exp\left[-\frac{\beta}{4\lambda_T}\left(z_i^0\right)^2\right]\int_{z_i^*}^{z_i^0} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i\left(z_i\right)}\{1-\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\} - \int_{-\infty}^{z_i^*} dz_i^0 \exp\left[-\frac{\beta}{4\lambda_T}\left(z_i^0\right)^2\right]\int_{z_i^*}^{z_i^0} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i\left(z_i\right)}\{1+\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}\right), \tag{64}$$

which can be further simplified as

$$\left[k_i^d(z_i^*)\right]^{-1} = \frac{1}{2}\left(\frac{\pi\lambda_T}{\beta}\right)^{1/2}\left[\int_0^{\infty} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i\left(z_i\right)}\{1-\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}^2 + \int_0^{z_i^*} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i(z_i)}\{1+\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}^2 \quad \text{for} \quad z_i^* > 0 + \int_{z_i^*}^{\infty} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i(z_i)}\{1-\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}^2\right] \tag{65}$$

and

$$\left[k_i^d(z_i^*)\right]^{-1} = \frac{1}{2}\left(\frac{\pi\lambda_T}{\beta}\right)^{1/2}\left[\int_0^{\infty} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i\left(z_i\right)}\{1-\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}^2 + \int_0^{|z_i^*|} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i\left(z_i\right)}\{1+\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}^2 \quad \text{for} \quad z_i^* < 0. + \int_{|z_i^*|}^{\infty} dz_i \frac{\exp\left(\frac{\beta}{4\lambda_T}z_i^2\right)}{D_i\left(z_i\right)}\{1-\mathrm{erf}[z_i/(4\lambda_T k_\beta T)^{1/2}]\}^2\right] \tag{66}$$

The forward rate constant k_{12} can now be expressed in terms of the above rate constants as

$$k_{12}^{-1} = k_{12}'^{-1} + \exp\left(\beta\Delta G_{\mathrm{CR}}\right)\left\{\frac{1}{k_1^d\left(z_1^*,z_1^0\right)} + \frac{1}{k_2^d(z_2^*)} - \frac{1}{k_1^d(z_1^*)}\right\}. \tag{67}$$

Equation (67) provides an expression for the forward rate constant k_{12} for reversible back ET reactions, when the system is initially prepared in a nonequilibrium state and it also takes into account the backward process described by the extra term [second term in Eq. (67)] appearing in the equation. Hence, this extra term arises due to reversibility of the ET process and consists of population ratio [$\exp(\beta\Delta G_{\mathrm{CR}})$] of the reactant and product and diffusive rates in the respective potential wells. The first term in the parentheses of the second part of Eq. (67) represents the first passage time [31] $[k_1^d(z_1^*,z_1^0)]^{-1}$, i.e., the time taken for the reaction coordinate created at z_1^0 at initial time in the reactant well to execute the diffusive motion in a downhill potential, to finally get adsorbed at the transition point z_1^*. The second term $[k_2^d(z_2^*)]^{-1}$ and third term $[k_1^d(z_1^*)]^{-1}$ in parentheses, on the other hand, characterize the time taken for the reaction coordinate created at initial time at z_2^* and z_1^*, respectively, with localized distribution, to subsequently undergo diffusive motion to reach the broad distribution governed by the canonical distribution. It may also be noted here that the analytical results for the average forward rate constant k_{12} cannot be obtained directly by solving the multidimensional Liouville equation (4) and in fact, the numerical evaluation through this equation becomes increasingly difficult for higher dimensionality. On the contrary, the investigation of multidimensional reversible ET as a one-dimensional problem, as shown here, leads to an analytical expression for the average forward rate constant k_{12} and also the same for irreversible reaction. In order to understand the effect of reversibility, we now numerically evaluate k_{12} for various physical parameters and discuss the various issues raised in Sec. II.

V. RESULTS AND DISCUSSION

In general, the visualization of ET reaction in a multidimensional space from a nonequilibrium initial situation is very difficult. Hence, it is extremely tricky to visualize the initial geometrical coordinates in the multidimensional space for the nonequilibrium ion pair D^+A^- produced initially in solvent after the molecule DA is excited from the ground state with an ultrashortlaser pulse. The system then relaxes downward along its multidimensional potential energy surface (corresponding to D^+A^-) through the relaxation of the surrounding polar solvent until it meets that of the molecule DA, where back ET

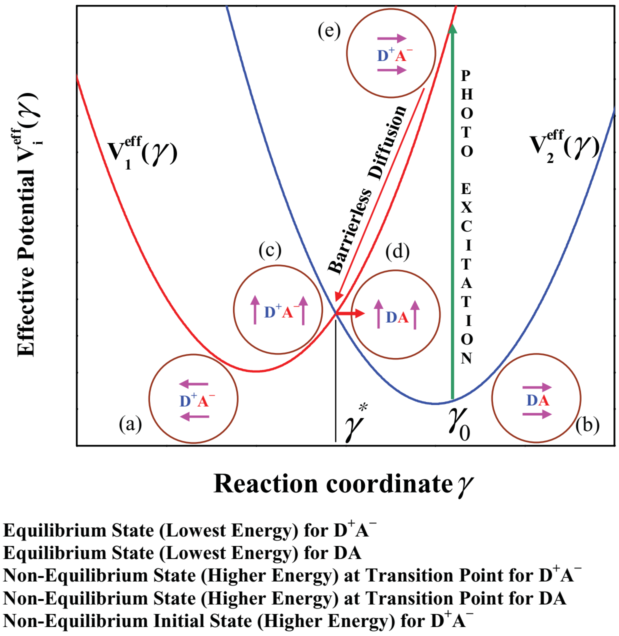

FIG. 1. (Color online) Potential energy curves for the reactant and product in an ET reaction. The abscissa stands for the one-dimensional reaction coordinate γ and the ordinate stands for the effective potential $V_i^{\text{eff}}(\gamma)$. It represents both the processes, i.e., relaxation of the excited state to its potential minimum and the back ET: (a) Equilibrium state (lowest energy) for D^+A^-, (b) equilibrium state (lowest energy) for DA, (c) nonequilibrium state (higher energy) at transition point for D^+A^-, (d) nonequilibrium state (higher energy) at transition point for DA, and (e) nonequilibrium initial state (higher energy) for D^+A^-.

reaction takes place with the geometrical coordinates satisfying the constraint $A(R) = \Delta G_{\text{CR}} - \lambda_S$. The visualization of this critical point in the multidimensional space is also equally difficult. However, the kinetic equation developed here deals with one-dimensional reaction coordinate γ, which makes it easy to understand ET reaction in this one-dimensional space. In Fig. 1, we have plotted the effective potential $V_i^{\text{eff}}(\gamma)$ against the one-dimensional reaction coordinate γ, for the initial value taken by γ corresponding to the minimum of the potential $V_2^{\text{eff}}(\gamma)$ for the system DA in solvent environment as given by $\gamma = \gamma_0 = \lambda_V$. This is the initial nonequilibrium configuration for the ion pair D^+A^- in the reaction coordinate space. The ion pair D^+A^- formed at the nonequilibrium state undergoes barrierless diffusion along its potential surface $V_1^{\text{eff}}(\gamma)$ in solvent environment until it reaches the transition point $\gamma = \gamma^* = (\Delta G_{\text{CR}} - \lambda_T)$, where ET reaction takes place with intrinsic rate constant k_0.

We have calculated here the average forward ET rate constant k_{12} using Eqs. (67), (60)–(62), (65), and (66) for an ion pair (D^+A^-) in acetonitrile solvent as a function of the free energy change ΔG_{CR} of the reaction. We assume the reaction coordinate $A[P(r),Q]$ to decay exponentially with relaxation time τ. We further assume here that $D_i(z_i)$ weakly depends on z_i, i.e., $D_i(z_i) \approx D_i$ and it can be shown within this approximation that $D_1 = D_2 = D = 2\lambda_T/\beta\tau$. Now, we first consider the simple theoretical model for the ET system of interest consisting of a multidimensional space spanned only by low frequency solvent collective coordinates (multidimensional) described by the orientational polarization function $\mathbf{P}(\mathbf{r})$. In order to understand the effect of reversibility on k_{12}, we have calculated both k_{12} and k'_{12} exclusively for the polarization mode and plotted the results in Fig. 2 along with available experimental data [22] for the best fitted values of the reorganization energy $\lambda_S = 1.4$ eV and $J = 0$ .1eV for this mode. The solvent relaxation time of acetonitrile is taken [32] as $\tau = 0.3$ ps at temperature $T = 300$ K. Here, Fig. 2 reveals a quite interesting fact that the effect of reversibility characterized by an extra term in Eq. (67) decreases with an increase in exothermicity $(-\Delta G_{\text{CR}})$ of the reaction, and continues to be minimum at the barrierless region (where the rate of forward ET reaction is maximum) but happens to be more and more significant on further increase of $-\Delta G_{\text{CR}}$. This reversibility effect on the overall rate of the forward ET reaction depends on the contributions from the population ratio $[\exp(\beta\Delta G_{\text{CR}})]$ of the reactant and product, and the effective diffusive motion $([k_1^d(z_1^*,z_1^0)]^{-1} + [k_2^d(z_2^*)]^{-1} - [k_1^d(z_1^*)]^{-1})$ comprising nonequilibrium relaxation dynamics $[k_1^d(z_1^*,z_1^0)]^{-1}$, well dynamics $[k_1^d(z_1^*)]^{-1}$ in the reactant well, and well dynamics $[k_2^d(z_2^*)]^{-1}$ in the product well. The population ratio [i.e., $\exp(\beta\Delta G_{\text{CR}})$] decreases with an increase of $-\Delta G_{\text{CR}}$, whereas the effective diffusive motion increases resulting in a decrease in the combined effect, which becomes minimum at the barrierless region. However, on further increase of $-\Delta G_{\text{CR}}$, the effective diffusive motion increases at a much faster rate as compared to its variation before reaching the barrierless region, although the population ratio $\exp(\beta\Delta G_{\text{CR}})$ decreases resulting in an increase in the combined effect, thereby showing an opposite trend, i.e., an increase in the effect of reversibility with an increase of $-\Delta G_{\text{CR}}$. The present numerical study for the effect of back ET on the free energy gap (FEG) dependence of the rate also shows that although the diffusion dynamics in the reactant well, viz., $[k_1^d(z_1^*,z_1^0)]^{-1}$ and $[k_1^d(z_1^*)]^{-1}$

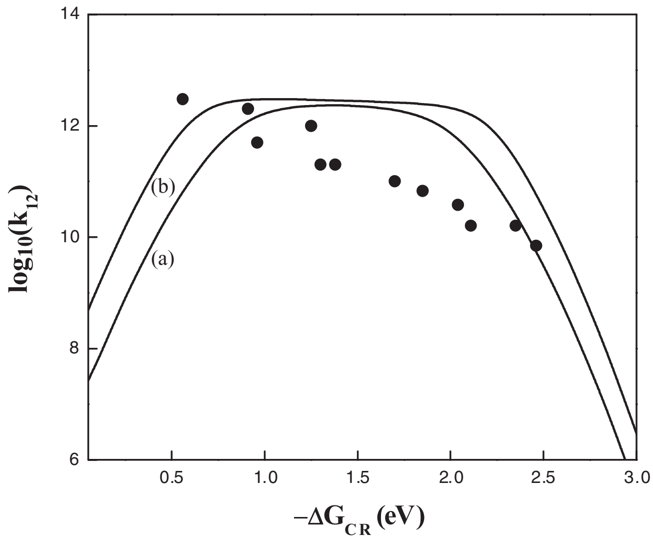

FIG. 2. Dependence of the average forward rate constant k_{12} of back ET in ion pairs on the free energy change ΔG_{CR} for (a) reversible and (b) irreversible (reaction in a single direction) reactions. The parameters used are $\tau = 0.3$ ps, $\lambda_S = 1.4$ eV, $J = 0.1$ eV, and $T = 300$ K. The experimental data (●) correspond to the ET rate constant k_{12} and are taken from Ref. [22].

as well as the same in the product well, viz., $[k_2^d(z_2^*)]^{-1}$ contribute to the effective diffusion dynamics, the most dominating contribution coming from the product well, i.e., from $[k_2^d(z_2^*)]^{-1}$.

In order to understand the effect of reversibility with an increase in the number of participating modes, we now consider an ET system of interest which consists of a multidimensional space spanned by an additional slowly relaxing molecular vibrational (Q) mode (harmonic) along with the low frequency solvent polarization mode (multidimensional). Here, the total reorganization energy λ_T is contributed by the corresponding reorganization energies λ_V (vibrational mode) and λ_S (solvent polarization mode). For simplicity, we assume here an equal contribution from each of the reorganization energies, i.e., $\lambda_V = \lambda_S$. In Fig. 3, we have compared the calculated FEG dependence of the rate of reversible and irreversible ET reactions for the best fitted values of $\lambda_S = \lambda_V = 1.0$ eV and $J = 0.05$ eV, with available experimental data [22] on back ET reaction. The values of all the other parameters used here remain the same as in Fig. 2. Although the numerical values of the parameters [$\lambda_S = \lambda_V = 1.0$ eV and J(=0.05 eV)] used here are even lower than the values [$\lambda_S = 1.4$ eV and J(=0.1 eV)] taken in explaining the ET processes described in Fig. 2, the calculated results are in better agreement (see Fig. 3) with the available experimental results than the same calculated (see Fig. 2) considering only the polarization mode. It is thus clear from Figs. 2 and 3 that the effect of reversibility is more prominent (see Fig. 2) for the model of ET system of interest described by polarization mode only in comparison to that (see Fig. 3) described by both the modes, i.e., polarization as well as vibrational modes. It is the extra vibrational mode which makes the diffusion dynamics much faster than that for the system containing only polarization mode.

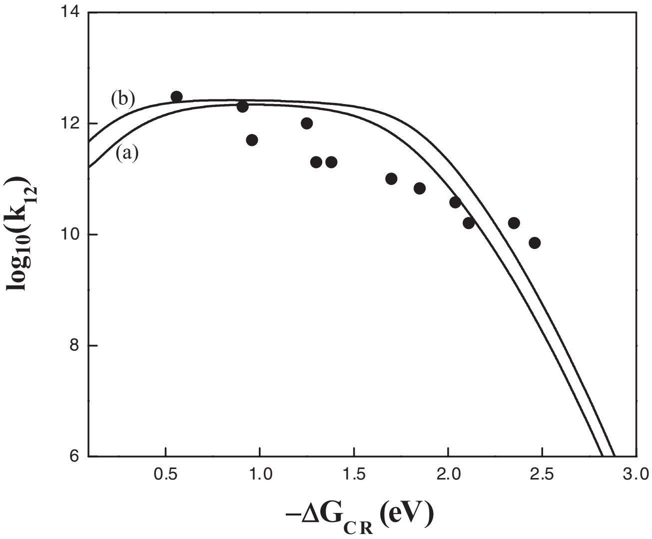

FIG. 3. Dependence of the average forward rate constant k_{12} of back ET in ion pairs on the free energy change ΔG_{CR} for (a) reversible and (b) irreversible (single direction) reactions described by additional vibrational modes at the values of reorganization energy $\lambda_S = \lambda_V = 1.0$ eV and transfer integral $J = 0.05$ eV. The values of all the other parameters used remain the same as in Fig. 2. The experimental data (●) correspond to the ET rate constant k_{12} and are taken from Ref. [22].

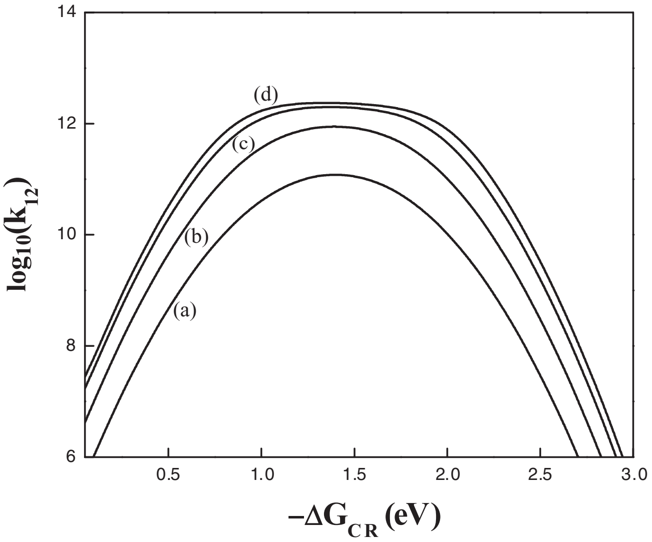

FIG. 4. Dependence of the average forward rate constant k_{12} of back ET in ion pairs on the free energy change ΔG_{CR} for various values of the electronic coupling J: (a) 0.003 eV, (b) 0.01 eV, (c) 0.03 eV, and (d) 0.3 eV. The parameters used are $\tau = 0.3$ ps, $\lambda_S = 1.4$ eV, and $T = 300$ K.

Earlier studies for irreversible ET reactions have shown that with an increase in the electronic coupling parameter J, there is a transition of the rate from the symmetric bell shape as predicted by Marcus to an asymmetric shape. Therefore, it is interesting to know whether a similar transition may be observed or not for the reversible ET reactions. In this context, we have calculated here the ET rates at various values of the electronic coupling parameter J and plotted k_{12} in Fig. 4. The figure shows that with an increase in J, there is a gradual change from a symmetric behavior of the FEG dependence of the rate to an asymmetric behavior. When the value of J is small, FEG dependence of the rate becomes symmetric as predicted by Marcus. However, when the value of J for ET system of interest is reasonably significant, the average rate k_{12} is controlled by the initial nonequilibrium configuration as well as the solvent relaxation dynamics and an interplay involving $k_1^{\mathrm{TST}}(z_1^*)$, $k_1^d(z_1^*,z_1^0)$, and $k_i^d(z_i^*)$ ($i = 1,2$ for r,p), leads to a non-Marcus FEG dependence of the rate of the reversible ET reactions. The interplay between $k_1^{\mathrm{TST}}(z_1^*)$ and $k_1^d(z_1^*,z_1^0)$ solely on the reactant surface is, however, responsible for having a non-Marcus FEG dependence of the rate of irreversible ET reaction. Therefore, one can observe that the presence of non-Marcus FEG dependence of the back ET process in a reversible ET reaction for the ion-pair system in solvent can be explained by the present theory with a significant value of the coupling strength.

VI. CONCLUDING REMARKS

We have proposed here a generalized one-dimensional kinetic equation for multidimensional reversible ET reaction with a nonequilibrium situation as the initial condition. The rate constant for the forward reversible ET reaction obtained here consists of two distinct contributions, the first one being from irreversible ET and the second one from diffusion dynamics both from reactant and product wells due to reversibility of the processes. In order to understand the effect of reversibility, we have considered back ET reaction in a system of interest modeled through low frequency solvent collective coordinates (multidimensional) characterized by orientational polarization function and also a slowly relaxing harmonic one-dimensional molecular vibrational mode. We have proposed a generalized polarization energy functional corresponding to the continuum version for the same, which resulted in a generalized expression for solvent reorganization energy where the molecular effect is incorporated into the rate of ET explicitly through the function $f(\mathbf{r})$. We have then derived an exact analytical expression for the ET rate for this model system. However, we have separately studied the rates of reversible ET as a function of the free energy change for the system of interest modeled through polarization mode only, as well as for the system described by an extra vibrational mode along with polarization function. The numerical results calculated by using the proposed one-dimensional approach are shown to be in good agreement with the available experimental results. It may also be noted that the results are found to have a fairly better concurrence with the available experimental results for the system of interest modeled through multidimensional polarization function and one-dimensional molecular vibrational mode (harmonic). Non-Marcus free energy gap dependence of the rate observed here for both reversible and irreversible ET reactions are very close to each other in the barrierless region, while in other regions, the rate for the former process is found to be less than the latter. The extra term, which makes the difference between the rate constants for irreversible and reversible ET reactions, is found to be contributed by the diffusion dynamics from reactant as well as product wells, although the contribution is mainly dominated from the product well.

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