Non-Condon nature of fluctuating bridges on nonadiabatic electron transfer: Analytical interpretation

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(Received 18 September 2008; accepted 11 December 2008; published online 21 January 2009)

Rigorous expressions for the calculation of nonadiabatic electron transfer rates are presented in closed forms for donor-acceptor systems incorporated fluctuating bridges and their non-Condon electronic couplings. In high temperature limit, they show a similar property to the Marcus formula. However, the Marcus parabolic with respect to the driving force is shifted for the exponential coupling while it becomes an overlap of several Gaussian functions for the linear coupling. Furthermore, the effective couplings are exponentially and linearly dependent on temperature and the squared frequencies of bridge modes for the exponential and linear couplings, respectively.
 [DOI: 10.1063/1.3063095]

I. INTRODUCTION

Electron transfer (ET) process in donor-bridge-acceptor (D-B-A) systems has been one of the exciting areas of research. As the bridges are assumed to be rigid spacers the standard nonadiabatic ET rates in high temperature limit are given by the well-known Marcus formula,[1,2]

$$k = \frac{(T_{\mathrm{DA}}^{0})^{2}}{\hbar}\sqrt{\frac{\pi}{\lambda k_{B}T}}\exp\left[-\frac{(\lambda+\Delta G)^{2}}{4\lambda k_{B}T}\right]. \tag{1}$$

Here λ, T, and ΔG are reorganization energy, temperature, and driving force, respectively. T_{DA}^{0} is the effective electronic coupling between D and A states. In recent years the fluctuating effects of the bridges on ET in complex medium, such as solvent molecules, glasses, and proteins, have drawn much interest (see, for instance, Refs. 3–7). In these systems, the nuclear motions are commonly divided into two groups in respect of their effects on ET.[8,9] The first group corresponds to the modes that undergo reorganization in the course of transition. They mainly contain the donor and acceptor modes. The second one includes the modes that oscillate around their equilibrium positions during ET and represent the fluctuations of the bridges. An important property for the first group modes is that the electronic transition is dominated by the particular regime where the electronic energies of the D and A states are nearly the same. Thus, the Condon approximation is applicable for the transition. However, the second group modes are not limited to local positions during ET process. The electronic coupling can be influenced by these modes and may strongly depend on the nuclear coordinates of the bridges. In this case, the non-Condon effect begins to play a role and produces inelastic tunneling. Based on such a consideration, theoretical and experimental investigations have revealed rich information being significantly different from the prediction from Eq. (1).[8–18] For instance, the effective electronic coupling becomes temperature dependent when bridge dynamics is incorporated.[17] The conformational gating of the bridges greatly enhances the rates.[12,13,15,16] Several theoretical models have been proposed to deeply understand these phenomena.[8,9,19–21] Medvedev and Stuchebrukhov[9] treated the non-Condon couplings with exponential and linear forms and demonstrated that non-Condon effects can result in substantial enhancement of the rates in the inverted regime and qualitatively new distance dependence. Troisi *et al.*[19] expressed the rate in energy domain as a series of contributions of the decreasing importance from the fluctuating bridge without introducing explicit coupling forms. The leading term corresponds to the slow fluctuations, which is the same as the Marcus formula except that the squared coupling is substituted by its average value, and the other terms include the corrections due to finite time fluctuations. The rate formula is easily applied to realistic systems as long as the non-Condon effects are relatively small. Jang and Newton[21] investigated the torsional non-Condon effects on the basis of a generalized spin-boson Hamiltonian with a sinusoidal modulation coupling. They also extensively discussed possible applications to realistic systems.

In the present work, we use the non-Condon models considered by Medvedev and Stuchebrukhov[9] and present closed rate expressions. Although the rigorous formulas in the nonadiabatic limit have been proposed,[9] they are quite complicated in the implementation especially for multiple bridges because they require sum over all eigenstate quantum number of the systems. We start the rate expressions from time domain and present eigenstate-free formulas which should be convenient for both analytical and numerical calculations. Indeed, the rate formulas obtained can be expressed as the Marcus-type forms in the classical limit. Thus, the quantita-

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tively analytical relationship between the rates and the non-Condon coupling parameters is built naturally.

The paper is arranged as follows. In Sec. II, we present the closed expressions of rates for the exponential and linear electronic couplings. The semiclassical and classical limits of the rates are discussed in Sec. III, and the concluding remarks are given out in Sec. IV.

II. RIGOROUS RATE EXPRESSIONS IN THE NONADIABATIC LIMIT

The Hamiltonian regarding to a D-A system with fluctuating bridges can be written as

$$H = |D\rangle(H_D + H_B)\langle D| + |A\rangle(H_A + H_B)\langle A| + [|D\rangle H_{DA}\langle A| + H.c.]. \tag{2}$$

Here, H_D and H_A are the Hamiltonians for the first group modes. H_B is for the second group modes. H_{DA} is the electronic coupling between D and A states. For nonadiabatic ET reactions, i.e., the electronic coupling is weak enough that the perturbation theory is applicable to calculate the transition probability from the D to the A states, Fermi's golden rule predicts the ET rates as

$$k = \frac{2\pi}{\hbar}\sum_{ii'}\sum_{jj'} P_{Di}P_{i'}\langle Di,i'|H_{DA}(Q)|Aj,j'\rangle|^2 \times \delta(E_{Di} + E_{i'} - E_{Aj} - E_{j'}), \tag{3}$$

where T is temperature, $|Di\rangle$, $|Aj\rangle$ and E_{Di}, E_{Aj} are the vibrational eigenfunctions and eigenenergies in the D and the A states, respectively, i and j with prime correspond to the bridge modes, Q represents the nuclear coordinates of bridges, and initial probabilities P_{Di} and $P_{i'}$ are given by

$$P_{Di} = \exp(-\beta E_{Di})/Q_d, \tag{4}$$

$$P_{i'} = \exp(-\beta E_{i'})/Q_b, \tag{5}$$

respectively, where $\beta = 1/k_bT$ and Q_d and Q_b are the corresponding partition functions. By using the Fourier transform of the delta function in Eq. (3) and assuming that the electronic coupling only depends on the coordinates of the bridge molecules, one can obtain an alternate rate expression,

$$k = \frac{1}{\hbar^2}\int dt C_{DA}(t)C_B(t), \tag{6}$$

in time domain, with

$$C_{DA}(t) = \frac{1}{Q_D}\mathrm{tr}[e^{-\beta H_D}e^{iH_Dt/\hbar}e^{-iH_At/\hbar}] \tag{7}$$

and

$$C_B(t) = \frac{1}{Q_B}\mathrm{tr}[e^{-\beta H_B}e^{iH_Bt/\hbar}H_{DA}(Q)e^{-iH_Bt/\hbar}H_{DA}(Q)]. \tag{8}$$

It is clear that $C_{DA}(t)$ is the usual correlation function of the ET theory and the non-Condon contribution to the rate is incorporated into $C_B(t)$. Equation (6) together with Eqs. (7) and (8) has been adopted by Teklos and Skourtis,[22] Medvedev and Stuchebrukhov,[9] and others to investigate ET rates. It has been successfully used in theoretical studies of ET by Skourtis and Beratan[5] and more recently by Berlin *et al.*[23]

For the multimodes of the D and A states with frequencies ω_i and shifts x_{0i}, and the B state with frequencies ω_j', the Hamiltonians are explicitly given by

$$H_D = \sum_i \left(\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2x_i^2\right), \tag{9}$$

$$H_A = \sum_i \left(\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2(x_i - x_{i0})^2\right), \tag{10}$$

$$H_B = \sum_j \left(\frac{p_j^2}{2m_j'} + \frac{1}{2}m_j'\omega_j'^2Q_j^2\right), \tag{11}$$

where x_i represent the nuclear coordinates of the D and the A modes, m_i and m_j' are masses for the D-A and the B modes, respectively. p_i and p_j are relevant momentum operators. With above Hamiltonians, the full quantum expression of $C_{DA}(t)$ is well known (see, for instance, Refs. 3 and 24), and it has an explicit form

$$C_{DA}(t) = \exp(i\Delta Gt/\hbar)\Pi_i \times \exp\{-S_i[(2n_i+1) - n_ie^{-i\omega_it} - (n+1)e^{i\omega_it}]\}, \tag{12}$$

where $n_i = 1/(\exp(\beta\omega_i) - 1)$, ΔG is the driving force, and Huang–Rhys factors $S_i = \lambda_i/\hbar m_i\omega_i$ with the reorganization energy $\lambda_i = \frac{1}{2}m_i\omega_i^2x_{0i}^2$.

$C_B(t)$ is significantly affected by the concrete electronic coupling form. According to the McConnell superexchange mechanism,[25,26] H_{DA} can be reasonably assumed to have an exponential expression

$$H_{DA}(\mathbf{Q}) = \prod_i C_ie^{-\alpha_iQ_i}, \tag{13}$$

where C_i and α_i are constants and $\mathbf{Q}$ represent the nuclear coordinates of the bridges. Molecular dynamical simulations,[8,10,27,28] however, have found that $H_{DA}(\mathbf{Q})$ can strongly oscillate and even change sign. In this case, $H_{DA}(\mathbf{Q})$ may be modeled to a linear dependence of the bridge coordinates,

$$H_{DA}(\mathbf{Q}) = \prod_i (C_i + D_iQ_j), \tag{14}$$

where C_i and D_i are constants. In this paper, we consider above two kinds of couplings.

A. Exponential coupling

We start from a single bridge mode, i.e., $H_{DA}(Q) = Ce^{-\alpha Q}$, Eq. (8) in the configuration space can be expressed as follows:

$$C_B(t) = 1/Q_B\int\int dQdQ'H_{DA}(Q)H_{DA}(Q')\langle Q|e^{-\tau_1H_B}|Q'\rangle \times \langle Q'|e^{-\tau_2H_B}|Q\rangle, \tag{15}$$

where $\tau_1 = \beta - it/\hbar$ and $\tau_2 = it/\hbar$. Consider the mode having a

frequency ω' and a mass m'. The coordinate matrices of the exponential propagator can be evaluated analytically by

$$\langle Q|e^{-\tau H_b}|Q'\rangle = \left(\frac{m'\omega'}{2\pi \sinh(\omega'\tau)}\right)^{1/2} \exp\left\{-\frac{m'\omega'}{2\sinh(\omega'\tau)} \times[(Q^2+Q'^2)\cosh(\omega'\tau)-2QQ']\right\}. \quad (16)$$

Inserting Eq. (16) and the concrete coupling form into Eq. (15) and introducing new variables $x=(Q+Q')/2$ and $y=Q-Q'$, we can cast Eq. (15) into two independent integrals,

$$C_B(t) = 1/Q_B C^2 \left(\frac{m'\omega'}{2\pi \sinh(\omega'\tau_1)}\right)^{1/2} \times \left(\frac{m'\omega'}{2\pi \sinh(\omega'\tau_2)}\right)^{1/2} I_1 I_2, \quad (17)$$

with

$$I_1 = \int dx \exp\left\{-x^2 m'\omega'\left[\frac{\cosh(\omega'\tau_1)-1}{\sinh(\omega'\tau_1)} + \frac{\cosh(\omega'\tau_2)-1}{\sinh(\omega'\tau_2)}\right] - 2\alpha x\right\}, \quad (18)$$

$$I_2 = \int dy \exp\left\{-y^2 \frac{m'\omega'}{4}\left[\frac{\cosh(\omega'\tau_1)+1}{\sinh(\omega'\tau_1)} + \frac{\cosh(\omega'\tau_2)+1}{\sinh(\omega'\tau_2)}\right]\right\}. \quad (19)$$

I_1 and I_2 are standard Gaussian integrals and can be easily calculated. By using $Q_B = 1/(2\sinh(\beta\omega'/2))$ and after some algorithms, we finally obtain a closed expression of Eq. (15) as follows:

$$C_B(t) = C^2 \exp\left\{\frac{\hbar\alpha^2}{2m'\omega'}[(2n'+1) + n'e^{i\omega t} + (n'+1)e^{-i\omega t}]\right\}, \quad (20)$$

where $n' = 1/(e^{\beta\omega'}-1)$. For the multiple bridge modes, $C_B(t)$ can be obtained through $C_{B,i'}(t)$ of the individual mode by $C_B(t) = \Pi_{i'} C_{B,i'}(t)$. Thus the rigorous nonadiabatic ET rates are evaluated from Eq. (6) together with Eqs. (12) and (20).

It is interested to find that $C_{DA}(t)$ [Eq. (12)] and $C_B(t)$ [Eq. (20)] have a very similar structure and $\hbar\alpha^2/2m'\omega'$ acts as the Huang–Rhys factor. This factor is the same as κ defined by Medvedev and Stuchebrukhov[9] [see Eq. (3.7) in their paper]. Compared with their formulas, the present rate expression avoids the sum over the vibrational quantum numbers of the bridges but uses time integral. This property is much useful especially for the calculation of the rates with multiple bridges.

B. Linear coupling

For the linear electronic coupling with the form of Eq. (14), the correlation function $C_B(t)$ for a bridge mode has four terms

$$C_B(t) \equiv \frac{1}{Q_B}\mathrm{tr}[e^{-\beta H_B} e^{iH_B t/\hbar} C e^{-iH_B t/\hbar} C] + \frac{1}{Q_B}\mathrm{tr}[e^{-\beta H_B} e^{iH_B t/\hbar} C e^{-iH_B t/\hbar} DQ] + \frac{1}{Q_B}\mathrm{tr}[e^{-\beta H_B} e^{iH_B t/\hbar} DQ e^{-iH_B t/\hbar} C] + \frac{1}{Q_B}\mathrm{tr}[e^{-\beta H_B} e^{iH_B t/\hbar} DQ e^{-iH_B t/\hbar} DQ]. \quad (21)$$

One immediately knows that the first term is C^2 and the second and third terms are zero because their integrands in the coordinate representations are odd functions. To calculate the fourth term, the same techniques used for the exponential coupling can be adopted although they are tedious. Here, we propose an alternative approach. It is easy to show that

$$1/Q_B\ \mathrm{tr}[e^{-\beta H_B} e^{iH_B t/\hbar} Q e^{-iH_B t/\hbar} Q] = 1/2 \lim_{\alpha\to 0}\frac{\partial^2}{\partial\alpha^2}\{1/Q_B\ \mathrm{tr}[e^{-\beta H_B} e^{iH_B t/\hbar} e^{-\alpha Q} e^{-iH_B t/\hbar} e^{-\alpha Q}]\} - 1/Q_B\ \mathrm{tr}[e^{-\beta H_B} Q^2]. \quad (22)$$

Here, the term in $\{\cdots\}$ is the correlation function for the exponential coupling. Taking the second derivative over α from Eq. (20), we obtain

$$\frac{\partial^2}{\partial\alpha^2}\{\cdots\} = \frac{\hbar}{m'\omega'}[(2n'+1) + n'e^{i\omega' t} + (n'+1)e^{-i\omega' t}]. \quad (23)$$

By using $\mathrm{tr}[e^{-\beta H_B} Q^2]/Q_B = \hbar(2n'+1)/2m'\omega'$ and Eq. (23), we can explicitly express Eq. (21) as follows:

$$C_B(t) = C^2 + \frac{\hbar D^2}{2m'\omega'}[n'e^{i\omega' t} + (n'+1)e^{-i\omega' t}]. \quad (24)$$

Thus the exact nonadiabatic rates can be calculated combining together Eqs. (6), (12), and (24).

It should be addressed that Eq. (24) is rigorous for the linear coupling. However, one may naturally expect that the correlation function for the linear coupling ($C_{linear}(t)$) with the coupling of $1-\alpha Q$ should be an approximation from that for the exponential coupling ($C_{expo}(t)$). Indeed, if one expands the exponential term in Eq. (20) with respect to α^2 to the first order, then $C_{linear}(t) \approx C_{expo}(t)$ is obtained with neglecting of $(\hbar\alpha^2/2m'\omega')(2n'+1)$.

III. SEMICLASSICAL AND CLASSICAL LIMITS

The closed forms of the rates in Sec. II are easy to implement numerically. However, it should be interesting to consider their semiclassical and classical limits. In such cases, the time integrations can be carried out and the effects of the non-Condon parameters on the rates may be found out.

Consider the simplest situation that $C_{DA}(t)$ decays much more rapidly than $C_B(t)$. $C_B(t)$ may be approximately replaced by $C_B(0)$, and Eq. (6) becomes

$$k \approx \frac{1}{\hbar^2}\langle H_{\mathrm{DA}}^2\rangle \int dt C_{\mathrm{DA}}(t), \tag{25}$$

where $\langle H_{\mathrm{DA}}^2\rangle$ $(\equiv C_{\mathrm{B}}(0)=1/Q_{\mathrm{B}}\ \mathrm{tr}[e^{-\beta H_{\mathrm{B}}}H_{\mathrm{DA}}(Q)^2])$ represents the effect of structural averaging of the bridge conformation and neglects the inelastic ET by the bridge fluctuations. Its values are $C^2\exp[\hbar\alpha^2/m'\omega'\coth(\beta\omega'/2)]$ and $C^2+(\hbar D^2/2m'\omega')\coth(\beta\omega'/2)$ for the exponential and linear couplings, respectively. These values are explicitly dependent on temperature and the frequency of bridge modes as well as the coupling strength. It should be addressed that $\langle H_{\mathrm{DA}}^2\rangle$ for the linear coupling cannot be obtained by the linear expansion of that for the exponential coupling because a 0.5 factor is missing if doing it. In the classical limit, Eq. (25) is nothing but the Marcus formula except that the electronic coupling H_{DA}^2 is replaced by $C_{\mathrm{B}}(0)$.

However, the fluctuations of the bridge, donor, and acceptor modes usually have comparable relaxation times as demonstrated by molecular dynamical simulations.[8,10] One has to treat both $C_{\mathrm{B}}(t)$ and $C_{\mathrm{DA}}(t)$ in a similar way. In the semiclassical limit, the time integration in Eq. (6) can be explicitly carried out by using saddle point techniques. Here we use a simpler approximation, which is used to derive the Marcus formula (1), i.e., we expand exponential terms $\exp(\pm i\omega t)$ to the second order of time.

For the exponential coupling, the semiclassical approximation reads

$$k = \frac{\prod_{i'} C_{i'}^2}{\hbar^2}\exp\left[\sum_{i'} 2S'_{i'}(2n'_{i'}+1)\right] \times \sqrt{\frac{2\pi}{\sum_i S_i(2n_i+1)w_i^2+\sum_{i'} S_{i'}(2n'_{i'}+1)w_{i'}'^2}} \times \exp\left[-\frac{\left(\sum_i S_i\omega_i-\sum_{i'} S_{i'}\omega'_{i'}+\Delta G\right)^2/\hbar}{2\left(\sum_i S_i(2n_i+1)w_i^2+\sum_{i'} S_{i'}(2n'_{i'}+1)w_{i'}'^2\right)}\right]. \tag{26}$$

Here i and i' correspond to the D-A and the B modes, respectively, and a Huang–Rhys–type factor $S'_{i'}$ with a value of $\hbar\alpha_{i'}^2/2m'_{i'}\omega'_{i'}$ for the i′th bridge mode has been introduced.

In the classical (high temperature) limit, n_i and $n_{i'}$ can be further approximated by $1/(\hbar\beta\omega_i)$ and $1/(\hbar\beta\omega'_{i'})$. In this case, the rates can be compactly expressed as follows:

$$k = \frac{1}{\hbar}(\overline{H_{\mathrm{DA}}^e})^2\sqrt{\frac{\pi}{k_BT(\lambda+\lambda')}}\exp\left(-\frac{(\lambda-\lambda'+\Delta G)^2}{4k_BT(\lambda+\lambda')}\right). \tag{27}$$

Here, prefactor $\overline{H_{\mathrm{DA}}^e}$ is given by $(\overline{H_{\mathrm{DA}}^e})^2=\Pi_{i'}C_{i'}^2\exp[(2k_bT/m'_{i'})(\alpha_{i'}/\omega'_{i'})^2]$. λ is the total reorganization energy of the D-A system and $\lambda'=\Sigma_{i'}\lambda'_{i'}=\Sigma_{i'}(\hbar\alpha_{i'})^2/2m'_{i'}$.

It is interesting to note that Eq. (27) has a very similar structure to the Marcus formula [Eq. (1)]. $\overline{H_{\mathrm{DA}}^e}$ acts as an effective electronic coupling strength. It explicitly depends on the coupling parameters $C_{i'}$, $\alpha_{i'}$ as well as the bridge mode frequencies $\omega_{i'}$ and temperature, and is sensitive very much to the ratio of $\alpha_{i'}$ and $\omega_{i'}$ because of its exponential dependence. For a given bridge, this effective coupling increases exponentially with increasing of temperature. From Eq. (27), it is also seen that the λ' plays a similar role to λ. Compared with the Marcus formula, the maximum rate with respect to ΔG is shifted from $\Delta G=-\lambda$ to $\Delta G=\lambda'-\lambda$. Despite the driving force dependence of the rates has the Marcus parabolic shape, it is $4\sqrt{k_BT\ln 2}(\sqrt{\lambda+\lambda'}-\sqrt{\lambda})$ broader. For a symmetric ET reaction, i.e., $\Delta G=0$, the barrier is lowered by $\lambda\lambda'/(\lambda+\lambda')$.

Equation (27) has an advantage that it reveals the analytical relationship between the rates and the non-Condon parameters. In applications, one has to consider its validity. Although the exponential coupling model is predicted by the McConnell superexchange mechanism, it may be physically reasonable when $\hbar\omega' \gg k_BT$. In high temperature limit $(\hbar\omega' \ll k_BT)$ the population of the bridge modes can be distributed in the high vibrational excited states, which leads to the dramatic exponential increase in the electronic coupling for $Q_{i'}<0$. This is not only unphysical but also contradicts the nonadiabatic limit considered in the present work. One way to remedy this problem is to include anharmonic bridge modes as considered by Medvedev and Stuchebrukhov.[9] To guarantee Eq. (27) validity, therefore, one must use a small enough $\alpha_{i'}$. Here we roughly estimate its values. At a given temperature, the energy of the motion of the bridge mode is about k_BT and the corresponding classical turning point is $Q_0=\sqrt{2k_BT/m'\omega'^2}$. If the linear expansion of the exponential coupling at Q_0 is still valid Eq. (27) should be less problematic, which leads to $\alpha<\sqrt{m'\omega'^2/2k_BT}$.

For the linear coupling, since $C_{\mathrm{B}}(t)$ itself is the sum of exponential terms we only make an approximation for $C_{\mathrm{DA}}(t)$, i.e., expand $\exp(\pm i\omega t)$ in Eq. (12) to the second order as before. For a single mode, the correlation function becomes

$$C(t) \approx (C^2+S'n'e^{i\omega' t}+S'(n'+1)e^{-i\omega t}) \times \exp[i\Delta Gt/\hbar+iS\omega t-1/2(2n+1)S\omega^2t^2], \tag{28}$$

where $S'=\hbar D^2/2m'\omega'$. Thus the semiclassical rates can be obtained by simple Gaussian integrations, and it has a form

$$k = \frac{1}{\hbar^2}\sqrt{\frac{2\pi}{(2n+1)S\omega^2}}\{C^2e^{-(S\omega+\Delta G/\hbar)^2/2(2n+1)S\omega^2} + S'n'e^{-(S\omega+\omega'+\Delta G/\hbar)^2/2(2n+1)S\omega^2} + S'(n'+1)e^{-(S\omega-\omega'+\Delta G/\hbar)^2/2(2n+1)S\omega^2}\}. \tag{29}$$

By using the classical approximations of n and n', we get

$$k = \frac{C^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_BT}}\exp\left[-\frac{(\lambda+\Delta G)^2}{4\lambda k_BT}\right] + \frac{\overline{H_{\mathrm{DA}}^2}}{\hbar}\sqrt{\frac{\pi}{\lambda k_BT}}\left(\exp\left[-\frac{(\lambda+\hbar\omega'+\Delta G)^2}{4\lambda k_BT}\right] + \exp\left[-\frac{(\lambda-\hbar\omega'+\Delta G)^2}{4\lambda k_BT}\right]\right), \tag{30}$$

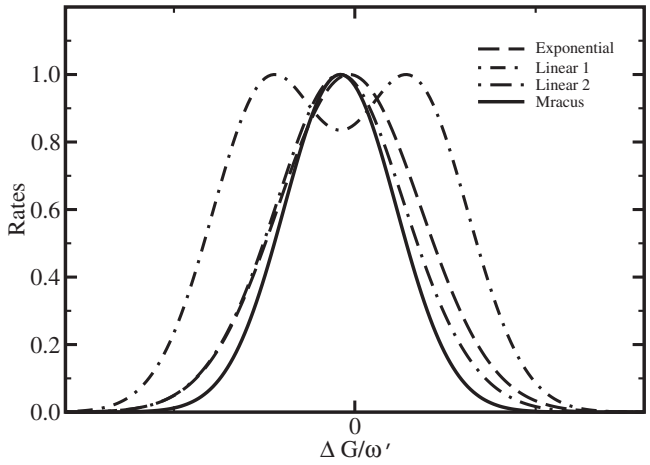

FIG. 1. The driving force dependence of the rates. Dashed line is for the exponential coupling [Eq. (27)], dot-long-dashed line for the linear coupling [Eq. (31)] with a $C+DQ$ form, dot-short-dashed line for the linear coupling with a DQ form, and solid line for no bridge [Eq. (1)].

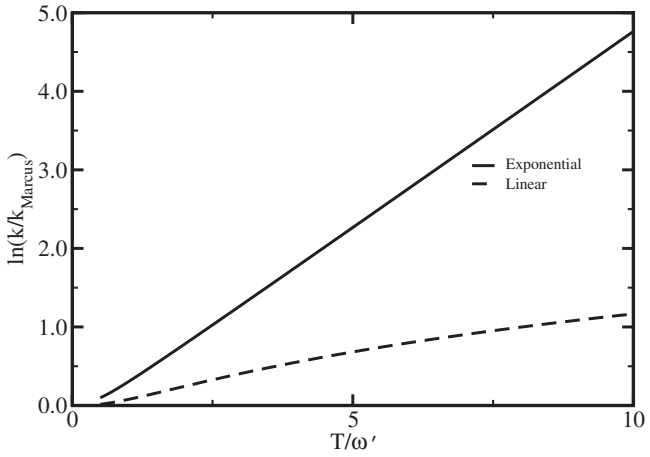

FIG. 2. The temperature dependence of the rates at $\Delta G=0$. Solid and dashed lines are for the exponential and linear couplings, respectively.

where the effective coupling strength $\overline{H_{\mathrm{DA}}^2}$ is defined as $k_BTD^2/2m'\omega'^2$. It is seen from Eq. (30) that the first term is the exact Marcus formula and other terms have the similar structures to the Marcus formula. However, in these two terms, the peaks of the Gaussian distributions with respect to the driving force are shifted with $\hbar\omega'$ and $-\hbar\omega'$, respectively, and the effective coupling explicitly depends on temperature and the frequency of the bridge mode.

For multiple bridge modes, the rates in the classical limit can be formally expressed as

$$k=\frac{1}{\hbar}\sqrt{\frac{\pi}{k_BT\lambda}}\sum_{j=1}^{3^{N'}}(\overline{H_{\mathrm{DA}}^j})^2e^{-(\lambda+\hbar\omega_j^c+\Delta G)^2/4k_BT\lambda}, \tag{31}$$

where N' is the total number of the bridge modes, ω_j^c represent all possible linear combinations of ω_i', $(i=1,2,\ldots N')$ including a zero value, and H_{DA}^j are the corresponding effective electronic couplings. The sum in Eq. (31) has $3^{N'}$ terms, in which the maximum and minimum ω_j^c are $\omega_{\max}=\Sigma_{i=1}^{N'}\omega_j'$ and $\omega_{\min}=-\omega_{\max}$, respectively, and the corresponding electronic couplings have the same value of $\Pi_{i'}k_BTD_{i'}^2/2m_{i'}'\omega_{i'}'^2$. Despite the effective electronic couplings have different forms in Eq. (31) two of them corresponding to the maximum and minimum ω_j^c have the most explicit change with respect to temperature and the frequencies of the bridge modes.

Comparing Eq. (31) with Eq. (27), we find several obvious differences. The effective electronic coupling $(\overline{H_{\mathrm{DA}}^j})$ is quadratically dependent on $D_{j'}/\omega_{j'}$, rather than exponentially. For a given bridge, it is linearly proportional to temperature. Moreover, the parabolic shape dependence of the driving force is changed to the overlap of $3^{N'}$ Gaussian functions and the peak positions cover from $\Delta G=\lambda+\omega_{\max}$ to $-(\lambda+\omega_{\max})$.

To explicitly show these properties, Fig. 1 plots the driving force dependence of the rates with the linear and exponential couplings for a single bridge mode, respectively, as well as that from the Marcus formula. The maximum values of the rates are scaled to 1 for the comparison. The parameters used are $\lambda=0.2\omega'$, $\alpha=0.5\sqrt{\omega'}$, and $k_BT=1.5\omega'$, respectively, to guarantee the validity of the classical approximations. For the exponential electronic coupling, the peak is shifted as predicted by Eq. (27) and the width becomes wider compared with that from the Marcus formula. These properties have already been addressed in previous works (see, for instance, Ref. 9). However, the present work has presented an analytical form which correctly predicts these phenomena. For the linear coupling, we display the rates with two cases: $C+DQ(C=D)$ and DQ. They are drawn in Fig. 1 with dot-long-dashed and dot-short-dashed lines, respectively. In case 1, the peak position is the same as that from the Marcus formula, but the width becomes wider. The reason can be explained by the overlap of three Gaussian functions shown in Eq. (30). In case two or $C\ll D$, two symmetric peaks explicitly appear as expected because the intermediate peak (the Marcus peak) disappears. It is noted that two peaks have also been found for a sinusoidal modulation coupling[21] in a special situation where the peaks are asymmetric.

Figure 2 displays the temperature dependence of the rates at $\Delta G=0$. The rates are scaled by the Marcus one for the purpose of investigating rate slops. The linear coupling has a form of $C(1+Q)$. Obviously, the rate changes with respect to temperature are significantly different for the linear and exponential couplings. The rates increase exponentially with increasing of temperature for the exponential coupling, while the rates for the linear coupling show the linear property as expected.

IV. CONCLUDING REMARKS

We have presented rigorous nonadiabatic ET rate formulas for donor-acceptor systems incorporated fluctuating bridges for linear and exponential non-Condon couplings in closed forms. At high temperature limit, the analytical expressions of the non-Condon coupling parameter dependence of the rates are built. It is found that the effective coupling is much dependent on the coupling form, as well as the frequencies of bridge modes and temperature. The modifications for the Marcus parabolic shape are quantitatively predicted. The present analytical solutions may be used experimentally to judge the properties of bridge dynamics.

For instance, if the rates increase nearly exponentially with respect to temperature compared with these from the donor-acceptor system without bridges, the non-Condon coupling mostly depends exponentially on the nuclear coordinates of bridges. From the driving force dependence of the rates, one may expect the linear non-Condon coupling if several peaks appear or the parabolic width becomes wider than the Marcus's one, while the exponential coupling is assumed if the peak of the Marcus parabolic shape is shifted.

Exponentially, the anomalous energy gap law deviated from Marcus theory has been observed. The typical examples include ET for Ru-modified proteins[29] and the quenching of fluorescer molecules by quencher molecules.[30] The non-Condon coupling has been successfully used to explain such situations.[9,20] With a measurement of temperature dependence of the rates, the present formulas could further shed some light on bridge properties, such as mode frequencies and coupling parameters. More recently, several experiments have observed temperature dependence of electronic coupling in some systems, for example, C-shaped donor-bridge-acceptor systems[31] and the donor-acceptor system with oligo-*p*-phenyleneethynylene bridges.[32] The present approach may be also useful for these systems to investigate the non-Condon property coming from the bridge fluctuation. The work on this aspect is underway.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation of China (Grant Nos. 20673104, 20773115 and 20833004) and National Key Basic Research Foundation Program of China (Grant No. 2007CB815204).

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