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We have developed a theoretical formulation for evaluating the nonadiabatic electron-transfer (ET) rate constant in condensed medium which takes into account both inelastic electron tunneling and nuclear quantum effects. The derived formula allows us to calculate the ET rate as a function of the free-energy gap between the ET donor and acceptor states using the information on the spectral density associated with environmental polarization fluctuation and the temporal correlation function of electronic tunneling matrix element. Model calculations have been performed illustratively.

I. INTRODUCTION

The standard Marcus theory [1] for the long-range electron-transfer (ET) rate constant has provided a wealth of useful insights into electronic excitation reactions observed in condensed and biomolecular systems. This theory usually relies on the Condon approximation in which the degrees of freedom of nuclear and electronic motions are separately treated and also describes the nuclear motion classical-mechanically. Thus, the classical Marcus expression gives the logarithm of ET rate constant as a parabolic function of the energy gap between ET donor and acceptor states. Although this theoretical description has been successful to a considerable extent, some experimental results have been reported [1–4] concerning the deviation from the theoretical prediction.

In the recent developments in the theories for the long-range ET reactions, the inelastic, non-Condon effects have attracted much attention [4–8] in which a dynamic coupling between the electronic and nuclear degrees of freedom plays an essential role. For instance, Nishioka *et al.* [6] proposed a theoretical framework to describe the inelastic effect in terms of a convolution form of the power spectrum for the auto-correlation function of the electronic tunneling matrix element and the ordinary Franck-Condon factor. According to their numerical analysis for ET in a protein system, the calculated rate constants showed much weaker dependence on the energy gap compared to the Marcus formula especially in the inverted region [1,4], which is due to the dynamical interference between the electronic tunneling and the conformational fluctuation in protein. This observation has thus demonstrated a way to provide an underlying mechanism accounting for the discrepancies between theory and experiment. On the other hand, it has been known [4,9–11] that the enhancement of ET rate constant relative to the Marcus estimate in the inverted region could be explained by taking into account the quantum effect [12–14] associated with the nuclear dynamics.

In the present work, we propose a theoretical framework for describing the ET rate constant in condensed media, where the inelastic electron tunneling and nuclear quantum effects are taken into account. Through illustrative calculations on the basis of derived formula, we quantitatively analyze the interplay of these two effects concerning their influence on the magnitude of ET rate constant.

II. THEORY

We start from a general expression for the long-range ET rate from donor D to acceptor A on the basis of the Fermi golden rule as [6,15]

$$k_{DA} = \frac{2\pi}{\hbar} \langle \sum_v |\langle \Psi_{iu}(\vec{r},\vec{R})|\hat{T}^{DA}|\Psi_{fv}(\vec{r},\vec{R})\rangle_{\vec{r},\vec{R}}|^2 \delta(E_{iu}-E_{fv})\rangle_T, \tag{1}$$

where

$$\Psi_{iu}(\vec{r},\vec{R}) = \psi_i(\vec{r},\vec{R})\chi_{iu}(\vec{R}) \tag{2}$$

and

$$\Psi_{fv}(\vec{r},\vec{R}) = \psi_f(\vec{r},\vec{R})\chi_{fv}(\vec{R}) \tag{3}$$

refer to the initial and final vibronic wave functions, respectively, under the Born-Oppenheimer approximation ($\hbar$ is the Planck constant). The coordinates $\vec{r}$ and $\vec{R}$ are for electrons and nuclei, $\psi_i(\vec{r},\vec{R})$ and $\psi_f(\vec{r},\vec{R})$ are the initial and final electronic wave functions, $\chi_{iu}(\vec{R})$ and $\chi_{fv}(\vec{R})$ are the vibrational wave functions in the initial (iu) and final (fv) vibronic states, respectively; $\hat{T}^{DA}$ is the electron-tunneling operator, E_{iu} and E_{fv} are the energies of the vibronic states iu and fv, and the brackets $\langle\,\rangle_{\vec{r},\vec{R}}$ and $\langle\,\rangle_T$ represent the integral over $\vec{r}$ and $\vec{R}$ and the thermal average over the initial vibrational state u, respectively. Making the Fourier transformation of the δ function in Eq. (1), we find an expression in the time domain [6,15–17]

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$$k_{DA} = \frac{1}{\hbar^2} \left\langle \int_{-\infty}^{\infty} dt \langle \chi_{iu}(\vec{R}) | e^{iH_i t/\hbar} T_{DA}(\vec{R}) e^{-iH_f t/\hbar} T_{AD}(\vec{R}) \right.$$
$$\left. \times | \chi_{iu}(\vec{R}) \rangle_{\vec{R}} \right\rangle_T, \tag{4}$$

where

$$T_{DA}(\vec{R}) = \langle \psi_i(\vec{r},\vec{R}) | \hat{T}^{DA} | \psi_f(\vec{r},\vec{R}) \rangle_{\vec{r}} \tag{5}$$

and H_i and H_f are the nuclear (vibrational) Hamiltonians corresponding to the electronic states i and f, respectively.

Here, we approximate expression (4) using the short-time approximation [6,17] so that the tunneling and nuclear dynamics are separately described. We then obtain [6,15–18]

$$k_{DA} = \frac{1}{\hbar^2} \left\langle \int_{-\infty}^{\infty} dt T_{DA}^{qc}(t) T_{AD}^{qc}(0) I(t) \right\rangle_T, \tag{6}$$

where

$$I(t) = \langle \chi_{iu}(\vec{R}) | e^{iH_i t/\hbar} e^{-iH_f t/\hbar} | \chi_{iu}(\vec{R}) \rangle_{\vec{R}} \tag{7}$$

and

$$T_{DA}^{qc}(t) = e^{iH_i t/\hbar} T_{DA}^{qc}(0) e^{-iH_i t/\hbar} \tag{8}$$

is the time-dependent quantum-classical electronic tunneling matrix element evaluated for Eq. (5) along the nuclear trajectory on the initial diabatic surface. Further, employing a factorization based on the decorrelation approximation [17], we obtain

$$k_{DA} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \langle T_{DA}^{qc}(t) T_{AD}^{qc}(0) \rangle_T \langle I(t) \rangle_T. \tag{9}$$

The function $\langle I(t) \rangle_T$ can be calculated quantum mechanically employing the single-mode model [19] in which the fluctuation of medium is approximated by a phonon mode and the classical limit thereof is then reduced to the Marcus formula [1] for the ET rate. On the other hand, the function $\langle I(t) \rangle_T$ can also be expressed in terms of the spectral density $J(\omega)$ associated with the fluctuation of medium. A standard expression [4,9–11,13,14] is then given by

$$\langle I(t) \rangle_T = \exp\left[-\frac{i}{\hbar}(\Delta G + \lambda)t - \frac{1}{\hbar^2} \int_0^t d\tau \int_0^\tau d\tau' C(\tau') \right], \tag{10}$$

where ΔG is the free-energy gap between the initial and final states, λ is the reorganization energy, and

$$C(t) = \frac{2\hbar}{\pi} \int_0^\infty d\omega J(\omega) \left[\coth\left(\frac{\hbar\omega}{2k_B T}\right) \cos \omega t - i \sin \omega t \right] \tag{11}$$

is the bath autocorrelation function, which is essentially the solvation time-correlation function. Using a relationship between the reorganization energy and the spectral density as [4,10,11,18]

$$\lambda = \frac{2}{\pi} \int_0^\infty \frac{d\omega}{\omega} J(\omega), \tag{12}$$

we further find

$$\langle I(t) \rangle_T = \exp[-Q_2(t) - iQ_1(t) - (i\Delta G t)/\hbar], \tag{13}$$

with

$$Q_1(t) = \frac{2}{\pi\hbar} \int_0^\infty \frac{d\omega}{\omega^2} J(\omega) \sin \omega t \tag{14}$$

and

$$Q_2(t) = \frac{2}{\pi\hbar} \int_0^\infty \frac{d\omega}{\omega^2} J(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right)(1 - \cos \omega t). \tag{15}$$

Here, introducing a power spectrum of $\langle T_{DA}^{qc}(t) T_{AD}^{qc}(0) \rangle_T$ as

$$P(\varepsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \langle T_{DA}^{qc}(t) T_{AD}^{qc}(0) \rangle_T \exp\left(\frac{i\varepsilon t}{\hbar}\right), \tag{16}$$

we further rewrite Eq. (9). Then, according to a model proposed by Nishioka *et al.* [6] who paid attention to the detailed balance condition, we employ an approximate expression as

$$P(\varepsilon) = \frac{2}{1 + \exp(-\varepsilon/k_B T)} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \langle T_{DA}(t) T_{AD}(0) \rangle_T$$
$$\times \exp(i\varepsilon t/\hbar). \tag{17}$$

In Eq. (17), k_B and T refer to the Boltzmann constant and the temperature, respectively, and the quantum-classical T_{DA}^{qc} has been replaced by the classical T_{DA}. Thus, making use of the convolution of the Fourier transforms, we finally obtain the expression of ET rate as

$$k_{DA} = \frac{2\pi}{\hbar^2} \int_{-\infty}^{\infty} d\varepsilon \frac{2}{1 + \exp(-\varepsilon/k_B T)} \frac{1}{2\pi\hbar}$$
$$\times \int_{-\infty}^{\infty} dt \langle T_{DA}(t) T_{DA}(0) \rangle_T \exp\left(\frac{i\varepsilon t}{\hbar}\right) \frac{1}{2\pi}$$
$$\times \int_{-\infty}^{\infty} d\tau \exp[-Q_2(\tau) - iQ_1(\tau)] \exp\left[-i\frac{(\Delta G + \varepsilon)}{\hbar}\tau\right], \tag{18}$$

where $T_{AD}(0) = T_{DA}(0)$ is noted. On the basis of Eq. (18), we can evaluate the ET rate constant k_{DA} as a function of the free-energy gap ΔG when we have $\langle T_{DA}(t) T_{DA}(0) \rangle_T$ and $J(\omega)$.

III. CALCULATION AND DISCUSSION

The spectral density $J(\omega)$ is associated with the fluctuation of medium surrounding the donor and acceptor of ET. It can be evaluated through the molecular-dynamics simulation in the case of biomolecular systems [11] and can be related to the dielectric properties of solvent in the case of solution systems [14,18,20]. In the latter case, the spectral density may be expressed by
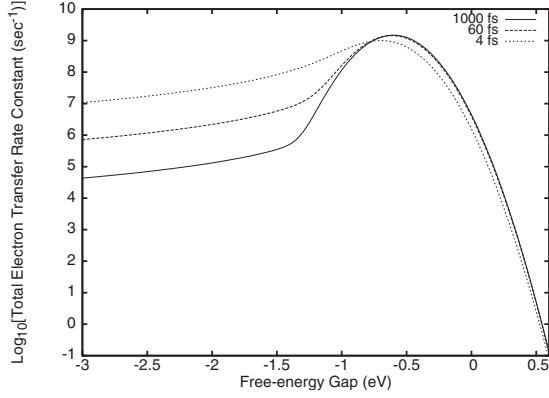
FIG. 1. ET rate constant $k_{DA}(\Delta G)$ calculated by Eq. (18) in the case of $\lambda=0.6$ eV for $\tau_c=4$ fs (dotted line), 60 fs (dashed line), and 1000 fs (solid line).

$$J(\omega) = (\lambda/c_p)[\text{Im } \epsilon(\omega)]/|\epsilon(\omega)|^2 \qquad (19)$$

in terms of the dielectric function $\epsilon(\omega)$ and the Pekar factor [4,14,18]

$$c_p = \frac{2}{\pi}\int_0^\infty \frac{d\omega}{\omega} \frac{\text{Im } \epsilon(\omega)}{|\epsilon(\omega)|^2}. \qquad (20)$$

Thus, for a given set of $\epsilon(\omega)$ and λ, we can obtain $J(\omega)$. In the following analysis, we employ the dielectric function of water for simplicity whose real and imaginary parts have been tabulated [10,14].

As for the estimate for $\langle T_{DA}(t)T_{DA}(0)\rangle_T$, it is possible [6] to calculate it through the application of quantum chemical method to conformational ensemble. In the model calculations below, however, considering an observation [6] that this function may show a simple exponential dependence on time, we employ an approximate form as

$$A(t) = [\langle T_{DA}(t)T_{DA}(0)\rangle_T - \langle T_{DA}\rangle_T^2]/(\langle T_{DA}^2\rangle_T - \langle T_{DA}\rangle_T^2), \qquad (21)$$

with

$$A(t) = \exp[-\gamma|t|] \qquad (22)$$

and $\gamma=1/\tau_c$. Given the values of $\langle T_{DA}^2\rangle_T$, $\langle T_{DA}\rangle_T^2$, and τ_c, we can thus carry out the t integration in Eq. (18) analytically. In the following test calculations, we employ tentative values of $\langle T_{DA}^2\rangle_T=8.82\times10^{-8}$ eV^2 and $\langle T_{DA}\rangle_T^2=0.405\langle T_{DA}^2\rangle_T=3.57\times10^{-8}$ eV^2 according to Nishioka *et al.* [6]

In order to study the ΔG dependence of ET rate constant k_{DA}, we have performed the calculations based on Eq. (18) for the cases of $T=300$ K, $\lambda=0.1$, 0.6, and 1.0 eV, and $\tau_c=4$, 60, and 1000 fs. In the present calculations, we have relied on the saddle-point method [9,10] for the evaluation of τ integration in Eq. (18). The calculated results for $k_{DA}(\Delta G)$ are illustrated in Fig. 1 only for the case of $\lambda=0.6$ eV. We observe in the figure a remarkable deviation of ET rate from the Marcus parabola [1] in the inverted region ($\Delta G<-\lambda$), which is more significant for smaller value of τ_c. It is noted that the deviation from the Marcus parabola is observed also in the normal region, $\Delta G>-\lambda$ (see below).

Next, we investigate the role of the nuclear quantum effect in the calculation of ET rate constant. If we consider the
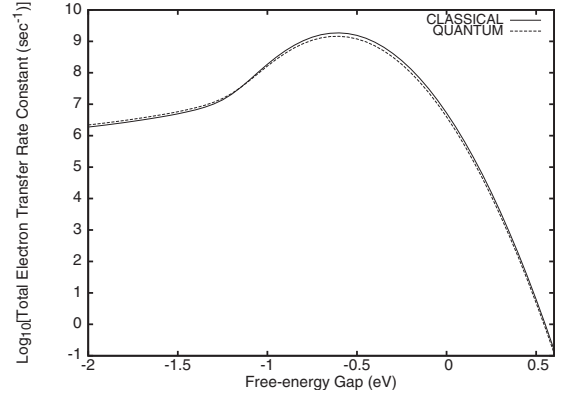

FIG. 2. Comparison of ET rate constants calculated by Eq. (18) (dashed line) and Eq. (23) (solid line) in the case of $\tau_c=60$ fs and $\lambda=0.6$ eV.

classical limit for the description of nuclear motions associated with the spectral density, Eq. (18) is reduced to the following expression [6] when we employ Eqs. (21) and (22):

$$k_{DA}^{cl} = WR \exp[-(\Delta G+\lambda)^2/4\lambda k_B T] + W(1-R)(1/\pi)$$

$$\times\int_{-\infty}^\infty d\varepsilon \frac{2}{1+\exp(-\varepsilon/k_B T)} \frac{\hbar\gamma}{\varepsilon^2+\hbar^2\gamma^2}$$

$$\times\exp[-(\Delta G+\lambda+\varepsilon)^2/4\lambda k_B T] = k_{DA1}^{cl} + k_{DA2}^{cl}. \qquad (23)$$

Here,

$$W = (2\pi/\hbar)(\langle T_{DA}^2\rangle_T/\sqrt{4\pi\lambda k_B T}) \qquad (24)$$

and

$$R = \langle T_{DA}\rangle_T^2/\langle T_{DA}^2\rangle_T \qquad (25)$$

have been introduced. We compare in Fig. 2 the ET rate constants between those calculated by Eq. (18) and by Eq. (23) for the case of $\tau_c=60$ fs and $\lambda=0.6$ eV. As seen in the figure, both the calculated values of k_{DA} by the quantum and classical expressions are virtually identical, which indicates the dominance of the inelastic effect over the nuclear quantum effect. The comparisons in the cases of $\lambda=0.1$ and 1.0 eV show analogous results (data not shown). To think of the reason for this fact, we focus on the second term in Eq. (23), k_{DA2}^{cl}, which describes the inelastic effect of ET. In the limits of $\Delta G\to-\infty$ and $\Delta G\to\infty$, we find

$$k_{DA2}^{cl} \to 4W(1-R)\sqrt{\frac{\lambda k_B T}{\pi}} \frac{\hbar\gamma}{(\Delta G+\lambda)^2+\hbar^2\gamma^2} \qquad (26)$$

and

$$k_{DA2}^{cl} \to 4W(1-R)\sqrt{\frac{\lambda k_B T}{\pi}} \frac{\hbar\gamma}{(\Delta G+\lambda)^2+\hbar^2\gamma^2}$$

$$\times\exp[-(\Delta G+\lambda)/(k_B T)], \qquad (27)$$

respectively. These asymptotic behaviors significantly enhance the ET rate relative to that by the Marcus expression, thus essentially dominating over the ET rate even with the inclusion of the nuclear quantum effect associated with $J(\omega)$.

It is also noted here that the nuclear quantum effect slightly enhances [4,9–11] the ET rate in the inverted region ($\Delta G < -\lambda$), while it gives a minor contribution in the present case. This result may partly be attributed to a simple exponential form of $A(t)$, Eq. (22), employed in the model calculations above, in which the contributions from fast oscillatory modes are missing. In this connection, if we employ

$$A(t) = \cos \Omega_0 t \qquad (28)$$

instead of Eq. (22), we can take into account the effect of the interaction between electron and modulating vibration with the frequency Ω_0. These effects of vibrational modulation on the ET reaction have been discussed in detail by Dahnovsky [8].

Incidentally, it should be remarked that there would be alternative choices [21] for the correction factor, $F_0(\varepsilon) = 2/[1 + \exp(-\varepsilon/k_BT)]$, introduced in Eq. (17), which relates the quantum-classical correlation function $P(\varepsilon)$ to the classical one obtained through molecular-dynamics simulation. Examples would be

$$F_h(\varepsilon) = (\varepsilon/k_BT)/[1 - \exp(-\varepsilon/k_BT)] \qquad (29)$$

and

$$F_s(\varepsilon) = \exp[\varepsilon/(2k_BT)], \qquad (30)$$

which are referred to as the harmonic and Schofield approximations, respectively, and satisfy the detailed balance condition [6] as well as $F_0(\varepsilon)$. If we would employ F_h or F_s instead of F_0, the asymptotic forms, Eqs. (26) and (27), would become

$$k_{DA2}^{cl} \to 2W(1-R)\sqrt{\frac{\lambda}{\pi k_BT}}\frac{\hbar\gamma|\Delta G + \lambda|}{(\Delta G + \lambda)^2 + \hbar^2\gamma^2} \qquad (31)$$

and

$$k_{DA2}^{cl} \to 2W(1-R)\sqrt{\frac{\lambda}{\pi k_BT}}\frac{\hbar\gamma(\Delta G + \lambda)}{(\Delta G + \lambda)^2 + \hbar^2\gamma^2}\exp\left(-\frac{\Delta G + \lambda}{k_BT}\right) \qquad (32)$$

in the case of F_h or

$$k_{DA2}^{cl} \to 2W(1-R)\sqrt{\frac{\lambda k_BT}{\pi}}\frac{\hbar\gamma}{(\Delta G)^2 + \hbar^2\gamma^2}\exp\left(-\frac{2\Delta G + \lambda}{4k_BT}\right) \qquad (33)$$

(the identical form for $\Delta G \to -\infty$ and ∞) in the case of F_s, respectively. Thus, this ambiguity should be investigated more extensively in future studies.

IV. CONCLUSION

We have developed a theoretical formulation for ET rate constant in condensed medium which takes into account both the inelastic electron tunneling and nuclear quantum effects. Using the derived formula, Eq. (18), we can calculate the ET rate constant k_{DA} in condensed or biomolecular systems as a function of the energy gap ΔG once we obtain the spectral density $J(\omega)$ and the temporal correlation function of electronic tunneling $\langle T_{DA}(t)T_{DA}(0)\rangle_T$ through the molecular-dynamics and quantum-chemical calculations. In the present paper, as an example, we have performed model calculations for k_{DA} by employing model forms for $J(\omega)$ and $\langle T_{DA}(t)T_{DA}(0)\rangle_T$ to study the cooperative contributions due to the inelastic electron tunneling and nuclear quantum effects. We have thus found a significant enhancement of ET rate compared to the (elastic and classical) Marcus estimate in the inverted region ($\Delta G < -\lambda$). We have also found the deviation of ET rate from the Marcus expression in the normal region ($\Delta G > -\lambda$) as well. In addition, the classical-limit calculations of ET rate without inclusion of the nuclear quantum effect yielded the results that showed very similar behaviors to those by the quantum calculations based on the spectral density. This can be ascribed to the reason that the inelastic tunneling effect is dominant in the regions of large $|\Delta G|$, as seen in the asymptotic behaviors of ET rate expression. Finally, it is remarked that the recent advances in *ab initio* methodologies for fast calculations of electronic states of biomolecular systems [22] would facilitate the estimate of the temporal correlation function of electronic tunneling even for large protein, which was a formidable task previously.

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