AP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **103**, 595 (1995); doi: 10.1063/1.470094 View online: http://dx.doi.org/10.1063/1.470094 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v103/i2 Published by the American Institute of Physics.

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Nonequilibrium photoinduced electron transfer

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(Received 15 November 1994; accepted 3 April 1995)

We consider photoinduced electron transfer, which is intrinsically a three-state system consisting of electronic ground, electronic excited (electron donor), and electron acceptor states. It is assumed that the bath consists of a collection of harmonic oscillators. Using an elementary time-dependent perturbation theory, it is found that the nonequilibrium Golden rule formula proposed by Coalson et al. [J. Chem. Phys. 101, 436 (1994)] can be rigorously obtained in a certain limit of our results. Invoking a stationary phase approximation, a simple result analogous to the Marcus expression is obtained, except for the presence of time-dependent reorganization energy. The multidimensional nature of the solvation coordinate system is discussed further. Finally a few numerical calculations are presented. © 1995 American Institute of Physics.

I. INTRODUCTION

Ultrafast laser techniques¹⁻³ developed in the last two decades enable direct measurement of population changes of either the electron donor or acceptor states 4-9 in electron transfer reactions in condensed media. By using a subpicosecond laser pulse, one can create a population state on the electron donor state, which is in this case coupled to the electronic ground state radiatively. There are two popular ways to detect the population changes in time. One of the two is to probe the transient absorption intensity of the donor state radiatively coupled to another electronic state.¹⁰ This transient absorption experiment is useful when there is an electronic state accessible by the optical field. The other method is to measure the stimulated or spontaneous emission intensity from the donor state. In contrast to the spontaneous emission measurement, the stimulated fluorescence measurement utilizes an additional pulse to stimulate the emission of photon from the acceptor state.¹¹ These two methods, transient absorption and light emission measurements, are basically related to the general pump-probe-type experiment. The former differs from the latter by the probing method. In some cases, interpretations of these results are difficult because one has to have a full knowledge of the potential surfaces and intramolecular dynamics of the target molecular system.

Most of the theoretical studies on electron transfer in condensed media are based on the assumption that the initial state is a thermal equilibrium state, which is stationary, on the donor surface. In this conventional situation a single solvation coordinate representing the fluctuating bath degrees of freedom by projecting their fluctuations onto a onedimensional coordinate is chosen. This solvation coordinate is collective in nature since it represents the multidimensional potential energy surfaces constructed by the bath degrees of freedom. However one of the remarkable outcomes of this reduction procedure is that one can use an approximate picture for the time evolution of the solvation coordinate, such as generalized Langevin equation (or equivalently generalized Fokker-Planck equation).¹²⁻¹⁷ Furthermore, as Marcus showed a long time ago, the electron transfer rate can be fully described by a single quantity, the classical solvent reorganization energy, in the classical (high temperature) limit.¹⁸ The solvent reorganization energy represents the magnitude of the overall coupling strength of the bath degrees of freedom with the electron transfer pair-thus we shall use these quantities as measures of coupling strength in this paper.

In contrast to this conventional situation, photoinduced electron transfer involves an additional ground state optically coupled to the donor state. Unless we ignore the initial relaxation process of the optically created wave packet on the donor surface, we cannot select a single solvation coordinate in this three-state system coupled to multidimensional bath degrees of freedom. The optical excitation step is governed by another solvation coordinate whose fluctuation induces broadening of spectra as well as relaxation of the nonequilibrium wave packet on the donor surface. One of the complexities is that the two coordinates, one associated with the optical transition and one with the electron transfer, are not necessarily correlated with each other. This actually induces a great deal of difficulties since we have to deal with a truly multidimensional solvation coordinate system in this case. As one can expect, only for times longer than the relaxation time on the donor surface, will the electron transfer rate reach its equilibrium value. In this paper we will explore this nonequilibrium nature of the photoinduced electron transfer in the nonadiabatic regime.

Recently Coalson et al.¹⁹ considered a similar problem. Instead of directly considering the optical process in their formulation, they proposed a nonequilibrium Fermi-Golden rule formula for the case when the initial preparation of the donor population is in the nonequilibrium state on the donor surface. They replaced the initial stationary state with nonequilibrium (time-dependent) state in the usual Golden rule formula. In order to test the nonequilibrium Golden rule formula, they carried out computer simulation studies with a spin-boson Hamiltonian used by Garg et al.¹⁶ We present in this paper a rigorous derivation of the nonequilibrium rate kernel for the nonequilibrium electron transfer process when the preparation of the donor population is performed by an ultrafast optical pulse. In some limiting case we show our results reduce to their so-called nonequilibrium Golden rule formula. We further show that a simplified analytic expression for the ET rate kernel can be obtained by using the stationary phase approximation. It turns out that the dimensionality of the solvation coordinate system plays a crucial role in understanding the nonequilibrium nature of the photo-induced ET. We present some simple numerical evaluations of our formal results to help understanding the resultant equations.

We organize this paper as follows. In Sec. II, we sketch the entire picture of the nonequilibrium ET process qualitatively. We next formulate the time-dependent nonequilibrium ET rate kernel by using elementary time-dependent perturbation theory. The nonequilibrium generalization of the Marcus expression for ET rate constant is obtained by invoking the stationary phase approximation. In Sec. IV, we present numerical results for a few cases. We finally summarize our results in Sec. V.

II. QUALITATIVE PICTURE

A three-state system consisting of an electronic ground state, an electronic excited state which acts as an electron donor state, and an electron acceptor state is considered. $|g\rangle$, $|D\rangle$, and $|A\rangle$ are the ground, donor, and acceptor states, respectively. It is assumed that the ground state $|g\rangle$ is radiatively coupled to the donor state $|D\rangle$ which is the electronic excited state. Furthermore, the donor state $|D\rangle$ is coupled to the acceptor state $|A\rangle$ by a nonzero electron exchange matrix element, Δ . Before we present a theoretical description of the nonequilibrium electron transfer in condensed media, we will briefly sketch the entire picture.

It is assumed that the system is initially in the ground state in thermal equilibrium with the bath. Therefore, the initial state is stationary and can be defined by the statistical distribution in the phase space. The bath is modeled by a collection of the harmonic oscillators, which are coupled to each state linearly. The potential energy surface of the electronically excited donor state is likely to be displaced from the potential energy surface of the ground state. Otherwise one may not expect any broadening of spectra induced by the bath degrees of freedom, since the Franck-Condon overlaps of harmonic modes with small displacements are small. A short laser pulse to create a population on the donor potential energy surface is introduced. It is assumed that the pulse duration time is short enough to ignore both electron transfer process from $|D\rangle$ to $|A\rangle$ and propagation of the nuclear wave packet on the donor surface during the pulse duration time. This condition can be met by using a femtosecond laser pulse when the time scales of the electron transfer and solvent modes are order of subpicosecond to picosecond. If the solvation time scale is comparable to the pulse duration time, one must relax these assumptions. In that case, we may have to consider the propagation effect of the nonequilibrium wave packet on the donor surface during the pulse duration time. We shall consider this case in another paper. The created wave packet on the donor potential energy surface tends toward a new thermal equilibrium state since the equilibrium positions of the nuclear degrees of freedom on the donor potential surface are different from those on the ground potential surface. In the mean time, the wave packet on the $|D\rangle$ state keeps leaking into the acceptor state by the nonzero



FIG. 1. Two cases of potential surfaces in one-dimensional solvation coordinate system. (a) and (b) correspond to $\theta=0$ and π , respectively (a detailed discussion on the dimensionality parameter is given in Sec. III F). 1. Initially the stationary nuclear wave packet is in a thermal equilibrium state on the ground potential surface. 2. At t=0 nonequilibrium wave packet is created on the donor surface by a resonant optical pulse. 3. Relaxation of the non-equilibrium wave packet completes for times longer than the relaxation time.

electron exchange matrix element. The most effective channel in this electron transfer process is that the wave packet on $|D\rangle$ state reaches the curve crossing point between the potential surfaces of the donor and acceptor states. This is because in this region of the phase space, the two states are isoenergetic and the Franck-Condon overlaps are maxima. We will refer to this curve crossing region between the donor and acceptor surfaces as the exit channel. In the case of an underdamped wave packet, which means that the mean position of the wave packet undergoes an oscillating motion on the harmonic potential surface of the $|D\rangle$ state, one may expect that the donor state wave packet gets close to the curve crossing point periodically. This is the case when the electron transfer process is strongly coupled to a few underdamped vibrational modes.²⁰ On the other hand, if the electron transfer system is coupled to a large number of degrees of freedom, even though each of them could be underdamped, the superposition of these oscillating features makes the time evolution of the average position of the wave packet overdamped. In any case, regardless of the position of the donor state wave packet, there is nonzero probability between the donor wave packet and the exit channel. Here the probability is time-dependent because of the nonstationarity of the initial wave packet. Furthermore, its magnitude is dependent on the potential energy surfaces as well as temperature. Obviously the electron transfer rate is proportional to the magnitude of the overlap between the nuclear wave packet and the exit channel in the phase space.

Consider the time immediately after a wave packet is created on the donor state. For the sake of simplicity let us consider a one-dimensional coordinate system, where one solvation coordinate can describe both optical broadening, relaxation of the nonequilibrium wave packet, and electron transfer. If the center of the nonequilibrium wave packet is located far away from the exit channel [see Fig. 1(a)], we expect to see a small electron transfer rate, and vice versa. In this situation, the time-dependent electron transfer rate increases in time until the wave packet reaches its thermal equilibrium on the donor potential surface. On the other



FIG. 2. Model contour plots of three two-dimensional potential surfaces. The q_1 coordinate is chosen to represent the collective nuclear degrees of freedom associated with the electron transfer between $|D\rangle$ and $|A\rangle$ —note that it is parallel with the line connecting two minima of $|D\rangle$ and $|A\rangle$, which is shown by a dashed line. The initial nonequilibrium wave packet (shown by thicker ellipsoids) is created on the donor surface at the origin of (q_1, q_2) coordinate system and relaxes toward the minimum of the donor surface as shown by a thick dashed arrow.

hand, if the initial wave packet is created close to the exit channel [see Fig. 1(b)], closer than the minimum of the donor potential surface, we expect the electron transfer rate decreases in time until the wave packet reaches its thermal equilibrium state. As an example of a two-dimensional case, in Fig. 2, we draw contour plots of three harmonic wells associated with three states. The created nonequilibrium wave packet is shown by thicker ellipsoids. This twodimensional wave packet relaxes toward the minimum of the donor surface as drawn by the dashed arrow. During this relaxation, there is nonzero leakage of the donor population via electron transfer mechanism. We can, therefore, expect that after the relaxation time, the electron transfer rate should not depend on time because we are looking at a two-level electron transfer process where the initial state is in a thermal equilibrium state on the donor state. In Sec. III, we shall formulate this picture to serve as a reasonable model for the realistic electron transfer induced by the optical excitation.

III. FORMULATION

We first consider the total Hamiltonian of the composite system,

$$H = H_0 + V(t) + J, \tag{1}$$

where

$$H_{0} = |g\rangle h_{g}\langle g| + |D\rangle h_{D}\langle D| + |A\rangle h_{A}\langle A|,$$

$$V(t) = \mu E(t) \cos \omega t |D\rangle \langle g| + \mu^{*} E^{*}(t) \cos \omega t |g\rangle \langle D|,$$
(2)

$$J = \Delta |A\rangle \langle D| + \Delta^* |D\rangle \langle A|.$$

Here, for example, h_g represents the nuclear Hamitonian of the ground state. The ground state $|g\rangle$ is radiatively coupled to the donor state $|D\rangle$ by the coupling potential V(t). The central frequency of the optical field is ω , and the time profile is determined by E(t). μ is the dipole matrix element, which could be dependent on coordinates of the nuclear degrees of freedom. We will keep this coordinate dependence of the dipole matrix element until the last stage of our derivation. The donor and acceptor states are coupled by J, where the coupling strength is determined by Δ .

We assume that the bath consists of harmonic oscillators coupled to each level linearly,

$$H_{0} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \epsilon_{Dg} & 0 \\ 0 & 0 & \epsilon_{Ag} \end{bmatrix} + \frac{1}{2} \sum_{\alpha} \begin{bmatrix} p_{\alpha}^{2} + \omega_{\alpha}^{2} x_{\alpha}^{2} & 0 & 0 \\ 0 & p_{\alpha}^{2} + \omega_{\alpha}^{2} (x_{\alpha} - d_{\alpha}/\omega_{\alpha}^{2})^{2} & 0 \\ 0 & 0 & p_{\alpha}^{2} + \omega_{\alpha}^{2} (x_{\alpha} - a_{\alpha}/\omega_{\alpha}^{2})^{2} \end{bmatrix}.$$
(3)

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The energy of the isolated ground state is assumed to be zero. ϵ_{Dg} and ϵ_{Ag} are the energy gaps between the donor and ground states and the acceptor and ground states, respectively. When we consider the harmonic oscillators on the ground state as a reference, the harmonic modes coupled to the donor and acceptor states are displaced by d_{α} and a_{α} , respectively.

A. Definitions of spectral densities

The nuclear Hamiltonians, Eq. (3), contains linear coupling terms representing energy fluctuations induced by bath degrees of freedom. Since we only consider linear terms with respect to the bath harmonic coordinates, our model Hamiltonian includes neither any phonon-induced excitation transfer effects nor molecular vibrational relaxation. However, we believe it is still useful enough to understand the role of the bath degrees of freedom in the electron transfer process when the initial wave packet created by the optical field is in a nonequilibrium situation. The magnitude of the coupling strength of bath degrees of freedom is determined by the displacements of harmonic modes, for example, $d_{\alpha}/(2\omega_{\alpha}^2)$. These coupling strengths are in turn related to the time scale of the relaxation rate as well as energetics of potential energy surfaces. We find that it is useful to define spectral densities representing the coupling strengths of harmonic modes as

$$\rho_{Dg}(\omega) = \sum_{\alpha} \frac{d_{\alpha}^{2}}{2\omega_{\alpha}^{3}} \,\delta(\omega - \omega_{\alpha}),$$

$$\rho_{Ag}(\omega) = \sum_{\alpha} \frac{a_{\alpha}^{2}}{2\omega_{\alpha}^{3}} \,\delta(\omega - \omega_{\alpha}),$$

$$\rho_{AD}(\omega) = \sum_{\alpha} \frac{(a_{\alpha} - d_{\alpha})^{2}}{2\omega_{\alpha}^{3}} \,\delta(\omega - \omega_{\alpha}).$$
(4)

The first spectral density, $\rho_{Dg}(\omega)$, is fully responsible to the broadening effect of the optical spectra. The last one,

J. Chem. Phys., Vol. 103, No. 2, 8 July 1995

 $\rho_{AD}(\omega)$, is associated with the *equilibrium* ET process. Because we are considering a nonequilibrium situation, it is necessary to include all three spectral densities as we will show in the following sections. Note that in general $\rho_{AD}(\omega) \neq \rho_{Ag}(\omega) - \rho_{Dg}(\omega)$. This unequality gives us a hint that multidimensionality will play a role in the ET of the three-state system. *Our goal is eventually to describe the nonequilibrium ET rate in terms of the three spectral densities*.

B. Perturbational approach to evaluation of timedependent populations

In order to obtain perturbation results on the nonequilibrium ET rate, we shall consider the case of nonadiabatic limit and elementary time-dependent perturbation theory will be used. Throughout this paper, we will retain only terms proportional to $|\mu|^2$ and all the higher-order terms with respect to the electronic dipole interaction will be ignored.

To calculate the transition amplitudes we next consider the time-evolution operator

$$U(t,t_{0}) = \exp_{+} \left\{ -i \int_{t_{0}}^{t} d\tau \ H(\tau) \right\}$$

= $e^{-iH_{0}(t-t_{0})} \exp_{+} \left\{ -i \int_{t_{0}}^{t} d\tau [\tilde{V}(\tau) + \tilde{J}(\tau)] \right\}$
= $e^{-iH_{0}(t-t_{0})} u(t,t_{0}),$ (5)

where the Heisenberg operators $\tilde{V}(t)$ and $\tilde{J}(t)$ in the interaction picture with respect to the zeroth-order Hamiltonian are

$$\tilde{V}(t) = e^{ih_g(t-t_0)}\mu \ e^{-ih_D(t-t_0)}E(t)\cos \ \omega t |D\rangle\langle g|$$

$$+ e^{ih_D(t-t_0)}\mu^* \ e^{-ih_g(t-t_0)}E^*(t)\cos \ \omega t |g\rangle\langle D|,$$
(6)
$$\tilde{J} = e^{ih_A(t-t_0)}\Delta \ e^{-ih_D(t-t_0)}|A\rangle\langle D|$$

$$+e^{ih_D(t-t_0)}\Delta * e^{-ih_A(t-t_0)}|D\rangle\langle A|.$$

Here $u(t,t_0)$ in Eq. (5) is obviously defined as above. We can expand this evolution operator in the interaction picture as

$$u(t,t_{0}) = \exp_{+} \left\{ -i \int_{t_{0}}^{t} d\tau [\tilde{V}(\tau) + \tilde{J}(\tau)] \right\}$$
$$= 1 - i \int_{t_{0}}^{t} d\tau [\tilde{V}(\tau) + \tilde{J}(\tau)]$$
$$- \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' [\tilde{V}(\tau) \tilde{V}(\tau') + \tilde{V}(\tau) \tilde{J}(\tau')$$
$$+ \tilde{J}(\tau) \tilde{V}(\tau') + \tilde{J}(\tau) \tilde{J}(\tau')] + \cdots .$$
(7)

By using the time-evolution operator we can now calculate the transition probability in time. First consider the population at the donor state,

$$P_{D}(t) = \langle \psi_{0} | \langle g | \exp_{-} \left\{ i \int_{t_{0}}^{t} d\tau H(\tau) \right\} | D \rangle \langle D |$$

$$\times \exp_{+} \left\{ -i \int_{t_{0}}^{t} d\tau H(\tau) \right\} | g \rangle | \psi_{0} \rangle$$

$$= \langle \psi_{0} | \langle g | u^{+}(t,t_{0}) | D \rangle \langle D | u(t,t_{0}) | g \rangle | \psi_{0} \rangle, \qquad (8)$$

where $|\psi_0\rangle$ denotes the initial nuclear wave function on the ground state in the thermal equilibrium. Thus the matrix element of $|\psi_0\rangle$ shown above is identical to trace over the thermal bath degrees of freedom. Inserting Eq. (7) into Eq. (8) we find the time-dependent population at the donor state is, perturbatively, given by

$$P_{D}(t) = \frac{1}{2} \operatorname{Re} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' \ E^{*}(\tau) E(\tau') \\ \times \langle \psi_{0} | e^{ih_{g}\tau} \mu^{*} \ e^{-ih_{D}(\tau-\tau')} \mu \ e^{-ih_{g}\tau'} | \psi_{0} \rangle e^{i\omega(\tau-\tau')} \\ + P_{D}(\mu^{2}\Delta^{2}, t) + O(\mu^{2}\Delta^{4}).$$
(9)

Here we invoked the rotating wave approximation, which assumes that terms oscillating with frequencies of $\pm(\omega_{Dg}+\omega)$ are ignored because integrals over those highly oscillating function is negligibly small. The lowest order contribution to the population of the donor state is obviously induced by the optical excitation. The next higher order term one should consider is proportional to $\mu^2 \Delta^2$, and its magnitude is exactly identical to the lowest order term for the population of the acceptor $P_A(t)$ with opposite sign [see Eq. (13)]. This is because the whole population is conserved. Because the acceptor is not radiatively coupled to the ground state, the lowest order term contributing to $P_A(t)$ is also proportional to $\mu^2 \Delta^2$. Here we should mention that we have not considered spontaneous loss of donor population via radiative or nonradiative channels except for the electron transfer process. In other words, we assume that the lifetime of the donor state induced by other channel is sufficiently long compared to that induced by the electron transfer.

Changing the integration variable in Eq. (9) to $t_1 = \tau - \tau'$, we can rewrite the population of the donor state as

$$P_{D}(t) = \frac{1}{2} \operatorname{Re} \int_{-\infty}^{t} d\tau \int_{0}^{\infty} dt_{1} E^{*}(\tau) E(\tau - t_{1}) \\ \times \langle \psi_{0} | e^{ih_{g}t_{1}} \mu^{*} e^{-ih_{D}t_{1}} \mu | \psi_{0} \rangle e^{i\omega t_{1}} \\ + P_{D}(\mu^{2}\Delta^{2}, t) + O(\mu^{2}\Delta^{4}), \qquad (10)$$

where $t_0 = -\infty$. If we further assume that the pulse duration time is sufficiently short enough to ignore any nuclear dynamics, i.e., we assume that $E(t) = E_0 \delta(t)$ where E_0 is a product of the pulse amplitude and its duration, then the population of the donor state is simply given by

$$P_D(t) = \frac{1}{2} |E_0|^2 |\mu|^2 \theta(t) + P_D(\mu^2 \Delta^2, t) + O(\mu^2 \Delta^4), \quad (11)$$

where $\theta(t)$ is a step function.

J. Chem. Phys., Vol. 103, No. 2, 8 July 1995

Next consider the population of the acceptor state by calculating the transition amplitude,

$$P_{A}(t) = \langle \psi_{0} | \langle g | \exp_{-} \left\{ i \int_{t_{0}}^{t} d\tau H(\tau) \right\} | A \rangle$$
$$\times \langle A | \exp_{+} \left\{ -i \int_{t_{0}}^{t} d\tau H(\tau) \right\} | g \rangle | \psi_{0} \rangle.$$
(12)

Likewise, inserting the time-evolution operator into the above equation, the lowest order term is given by

$$P_{A}(t) = 2 \operatorname{Re} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' \int_{t_{0}}^{\tau} dT \int_{t_{0}}^{T} dT' E^{*}(\tau') E(T')$$

$$\times \cos \omega \tau' \cos \omega T' F(\tau, \tau', T, T') + O(\mu^{2} \Delta^{4}),$$
(13)

where

$$F(\tau,\tau',T,T') \equiv \langle \psi_0 | e^{ih_g \tau'} \mu^* e^{ih_D(\tau-\tau')} \Delta e^{-ih_A(\tau-T)}$$
$$\times \Delta e^{-ih_D(T-T')} \mu e^{-ih_g T'} | \psi_0 \rangle.$$

It is useful to rewrite Eq. (13) by using the following identities:

$$\int_{t_0}^{\tau} d\tau' = \int_{t_0}^{T'} d\tau' + \int_{T'}^{T} d\tau' + \int_{T}^{\tau} d\tau',$$
$$\int_{t_0}^{T} dT' \int_{T'}^{T} d\tau' = \int_{t_0}^{T} d\tau' \int_{t_0}^{\tau'} dT',$$

and

$$\int_T^{\tau} d\tau' \int_{t_0}^{\tau} dT = \int_{t_0}^{\tau} d\tau' \int_{t_0}^{\tau'} dT.$$

Then Eq. (13) can be written as

$$P_{A}(t) = 2 \operatorname{Re} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} dT \int_{t_{0}}^{T} dT' \int_{t_{0}}^{T'} d\tau' E^{*}(\tau') E(T') \cos \omega \tau' \cos \omega T' F(\tau, \tau', T, T') + 2 \operatorname{Re} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} dT \int_{t_{0}}^{T} d\tau' \int_{t_{0}}^{\tau'} dT' E^{*}(\tau') E(T') \cos \omega \tau' \cos \omega T' F(\tau, \tau', T, T') + 2 \operatorname{Re} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' \int_{t_{0}}^{\tau'} dT \int_{t_{0}}^{T} dT' E^{*}(\tau') E(T') \cos \omega \tau' \cos \omega T' F(\tau, \tau', T, T') + O(\mu^{2} \Delta^{4}).$$
(14)

In comparison to Eq. (13), there are time orderings of integration variables in Eq. (14). For example, the first and second terms contain two consecutive interactions with the external field to create a diagonal density matrix element on the donor state, and the remaining second-order perturbations by the electron exchange matrix elements create population on the acceptor state. On the other hand, the third term includes a different time ordering. The actions of external field perturbation and electron exchange perturbation are altered. Therefore, as long as the pulse duration time is sufficiently short compared to the time scale of the electron transfer rate, we can safely ignore the contribution from the third term in Eq. (14). It is worth mentioning that the latter contribution has a complete analog in the nonlinear four-wave mixing spectroscopies known as the coherent artifact.²¹ This phenomenon is usually induced when the two laser pulses overlap in time so that there are mixed time ordering of the field– system interactions in the four-wave mixing spectroscopy.²² In terms of four-wave mixing spectroscopic language, we use an external laser pulse to pump the population of the ground state up to the donor state, and then probe the population of the donor state by the second-order interaction with the electron exchange perturbation. This is therefore more closely related to the spontaneous fluorescence measurement where the probing step involves actions of the vacuum field operator which are not controlled by experimentalist. Likewise, one has no control on the action of electron exchange perturbation in our ET problem either.

We now change the integration variables in Eq. (14) as $t_1 \equiv T' - \tau'$ and $t_2 \equiv \tau - T$ in the first term and $t_1 \equiv \tau' - T'$ and $t_2 \equiv \tau - T$ in the second term, respectively, and also let $t_0 = -\infty$. Equation (14) can be rewritten as

$$P_{A}(t) = \frac{1}{2} \operatorname{Re} \int_{-\infty}^{t} d\tau \int_{0}^{\infty} dt_{2} \int_{-\infty}^{\tau-t_{2}} dT' \int_{0}^{\infty} dt_{1} E^{*}(T'-t_{1})E(T')e^{-i\omega t_{1}}F(\tau,\tau'=T'-t_{1},T=\tau-t_{2},T') + \frac{1}{2} \operatorname{Re} \int_{-\infty}^{t} d\tau \int_{0}^{\infty} dt_{2} \int_{-\infty}^{\tau-t_{2}} d\tau' \int_{0}^{\infty} dt_{1} E^{*}(\tau')E(\tau'-t_{1})e^{i\omega t_{1}}F(\tau,\tau',T=\tau-t_{2},T'=\tau'-t_{1}) + O(\mu^{2}\Delta^{4}).$$
(15)

It should be noted that the two time periods, t_1 and t_2 , are associated with the time evolutions of the off-diagonal density matrix elements which are likely to be highly oscillating with frequencies determined by the energy differences between states. Therefore it is natural to evaluate the integrals over these highly oscillating periods by using the stationary phase approximation. As mentioned before, it is assumed that the time profile of the external field is effectively a delta function, $E(t) = E_0 \delta(t)$. With this approximation, we find

$$P_{A}(t) = |E_{0}|^{2} \operatorname{Re} \int_{0}^{t} d\tau \int_{0}^{\tau} dt_{2} \langle \psi_{0} | \mu^{*} e^{ih_{D}\tau} \Delta e^{-ih_{A}t_{2}} \\ \times \Delta e^{ih_{D}t_{2}} e^{-ih_{D}\tau} \mu | \psi_{0} \rangle + O(\mu^{2} \Delta^{4}).$$
(16)

As a result of the ultrafast optical pulse, the same wave packet, $\mu |\psi_0\rangle$, is created on the donor state at time zero. Then it propagates on the donor surface for time τ . Defining the nonequilibrium wave packets as $|\psi(\tau)\rangle \equiv e^{-ih_D\tau}\mu |\psi_0\rangle$, we find the generalized Fermi–Golden rule expression including the nonequilibrium effect. This problem has recently been discussed by Coalson *et al.*,¹⁹ based on the approximations of (i) ignoring nuclear dynamics during the pulse duration time and (ii) ignoring the contribution from the mixed timeordering term that is the third in Eq. (14). Here we have presented a rigorous basis for the nonequilibrium photoinduced electron transfer reaction.

C. Populations and cumulant approximation

We next calculate time-dependent population of the donor state. The donor population created by the optical excitation was calculated by considering the second-order term with respect to the dipole matrix element [see Eq. (11)]. As mentioned before, the next higher order term contributing to $P_D(t)$, which is proportional to $\mu^2 \Delta^2$, is identical to the population of the acceptor state to this order except for the opposite sign, i.e., $P_D(\mu^2 \Delta^2, t) = -P_A(\mu^2 \Delta^2, t)$. Therefore the time-dependent population of the donor state is approxi- $P_D(t) = P_D(\mu^2, t) - P_A(\mu^2 \Delta^2, t)$ mately given by $+O(\mu^2 \Delta^4)$. Using these results, Eqs. (11) and (16), we find that the population of the donor state can be approximately written by exponentiating the expression to find

$$P_D(t) \cong \frac{1}{2} |E_0|^2 |\mu|^2 \exp\left\{-\int_0^t d\tau \, k_f(\tau)\right\},\tag{17}$$

where the forward rate kernel representing the transition rate per unit time from donor to acceptor is

$$k_{f}(\tau) = \frac{2}{|\mu|^{2}} \operatorname{Re} \int_{0}^{\tau} dt_{2} \langle \psi(\tau) | \Delta \ e^{-ih_{A}t_{2}} \Delta \ e^{ih_{D}t_{2}} | \psi(\tau) \rangle.$$
(18)

It is possible to derive this equation more formally than we have done here, using the partial-ordering procedure (POP)²³ and truncating at the second-order cumulant. This leads to the identical expression for $P_D(t)$. Here we assume that the exothermicity of the electron transfer from donor to acceptor is large enough to ignore the backward transition rate. However as shown by the authors recently,²⁴ it is a straightforward exercise to include the contribution from the backward

transfer process. Furthermore, the exponentiation approximation we introduced is exact when we consider a second-order cumulant approximation to the solution of the linear stochastic differential equation.²⁴ However we will not pursue this in this paper since here we only focus on the simple case of very large exothermic reaction to make the whole picture as simple as possible.

We now invoke the *classical Condon approximation that* the dipole operator and the electron exchange operator, μ and Δ , respectively, do not depend on the nuclear coordinates. The forward transfer rate kernel, Eq. (18), is then

$$k_{f}(\tau) = 2 \operatorname{Re} \Delta^{2} \int_{0}^{\tau} dt_{2} \langle \psi^{0}(\tau) | e^{-ih_{A}t_{2}} e^{ih_{D}t_{2}} | \psi^{0}(\tau) \rangle,$$
(19)

where we define $|\psi^0(\tau)\rangle \equiv e^{-ih_D\tau}|\psi_0\rangle$. If we replace the upper bound of the integration over t_2 with ∞ , we recover Coalson *et al.*'s result, termed the nonequilibrium Golden rule formula [Eq. (2-12) in Ref. 19]. We see that our derivation is useful in extending beyond the short-pulse approximation. Rewriting the nuclear Hamiltonians, h_D and h_A , in the interaction representation with respect to h_g we can rewrite the forward transfer rate kernel as

$$k_{f}(\tau) = 2 \operatorname{Re} \Delta^{2} \int_{0}^{\tau} dt_{2} \left\langle \exp_{-} \left\{ i \int_{0}^{\tau} ds \ U_{Dg}(s) \right\} \right.$$
$$\times \exp_{+} \left\{ -i \int_{\tau-t_{2}}^{\tau} ds \ U_{Ag}(s) \right\}$$
$$\times \exp_{+} \left\{ -i \int_{0}^{\tau-t_{2}} ds \ U_{Dg}(s) \right\} \left. \right\rangle$$
$$\times \exp\{-i \epsilon_{AD} t_{2} - i \lambda_{AD}^{g} t_{2}\}, \qquad (20)$$

where the zero-centered difference potential is defined, in the interaction picture,

$$U_{mn}(s) = e^{ih_g s} (h_m - h_n - \langle h_m - h_n \rangle) e^{-ih_g s}$$

for $m, n = g, D, A$.

Here the angular bracket represents a thermal average over the nuclear degrees of freedom in the equilibrium ground state. $\exp_+(\exp_-)$ denotes positive (negative) time-ordered exponential. ϵ_{AD} is the energy difference between the isolated acceptor and donor states, $\epsilon_{AD} = \epsilon_{Ag} - \epsilon_{Dg}$. Because of the system–bath interaction, from Eq. (3) the solvation energies of the donor and acceptor states are $\int d\omega \rho_{Dg}(\omega)\omega$ and $\int d\omega \rho_{Ag}(\omega)\omega$, respectively. In Eq. (20), the corresponding reorganization energy is given by

$$\lambda_{AD}^{g} = \langle h_{A} - h_{D} \rangle - \epsilon_{AD} = \int d\omega [\rho_{Ag}(\omega) - \rho_{Dg}(\omega)] \omega.$$
(21)

It should be noted that the reorganization energy (difference in the solvation energies of the donor and acceptor states), λ_{AD}^g , is evaluated over the Hamiltonian of the ground state instead of that of the donor state—the superscript *g* of λ_{AD}^g means that the thermal average is carried out over the Hamiltonian of the ground state. We may expect that the reorganization energy approaches to that evaluated over the donor Hamiltonian as the nonequilibrium population created on the donor state by the optical excitation reaches its equilibrium state on the donor potential surface. It now turns out to be useful to rewrite various reorganization energies in terms of spectral densities defined in Eqs. (4),

$$\lambda_{Dg}^{g} = \int d\omega \ \rho_{Dg}(\omega)\omega, \quad \lambda_{Ag}^{g} = \int d\omega \ \rho_{Ag}(\omega)\omega,$$
$$\lambda_{AD}^{D} = \int d\omega \ \rho_{AD}(\omega)\omega, \text{ and } \lambda_{AD}^{g} = \lambda_{Ag}^{g} - \lambda_{Dg}^{g}. \tag{22}$$

Once again we emphasize that there are two different reorganization energies, λ_{AD}^D and λ_{AD}^g , associated with the electron transfer pair. Of the two, the former appears in the conventional electron transfer process since it is evaluated over the equilibrium distribution of the donor nuclear degrees of freedom.

We next evaluate the nonlinear correlation function given in Eq. (20) by using the cumulant expansion method and truncating higher order terms than the second. The forward transfer rate kernel is then

$$k_{f}(\tau) = 2 \operatorname{Re} \Delta^{2} \int_{0}^{\tau} dt_{2} \exp\{-i\epsilon_{AD}t_{2} - i\lambda_{AD}^{g}t_{2} - \varphi_{AD}(t_{2}) + i \operatorname{Im}[\varphi_{Dg}(\tau) + \varphi_{AD}(\tau) - \varphi_{Ag}(\tau)]\}$$
$$\times \exp\{-i \operatorname{Im}[\varphi_{Dg}(\tau - t_{2}) + \varphi_{AD}(\tau - t_{2}) - \varphi_{Ag}(\tau - t_{2})]\}, \qquad (23)$$

where

$$\varphi_{mn}(t) = \int_0^t d\tau \int_0^\tau d\tau' \langle U_{mn}(\tau) U_{mn}(\tau') \rangle$$

= $-i\lambda_{mn}^l t + \int d\omega \ \rho_{mn}(\omega) \coth(\beta \omega/2)$
 $\times (1 - \cos \omega t) + i \int d\omega \ \rho_{mn}(\omega) \sin \omega t$, (24)

where l = g when mn = Dg or Ag, and l = D when mn = AD. Note that we need to consider all three spectral densities to completely describe the forward transfer rate kernel, whereas the equilibrium electron transfer rate is determined by a single spectral density, $\rho_{AD}(\omega)$. As can be seen in Eq. (23), the imaginary parts of the double integration of correlation functions changes the phase of the integrand in Eq. (23). As the initial wave packet on the donor state propagates toward an equilibrium position (potential minimum) on the donor state, the reorganization energy associated with the electron transfer changes in time τ .

D. Stationary phase approximation (Laplace method)

Although Eq. (23) can be easily calculated numerically, we will invoke the stationary phase approximation to the integral given in Eq. (23). Since during the time period of t_2 in the integrand of Eq. (23), the whole integrand is highly oscillating, it is suitable to take short-time expansion of the

exponent in the integrand with respect to t_2 to find the stationary phase point.²⁴ The integral, Eq. (23), then reduces to

$$k_{f}(\tau) = 2 \operatorname{Re} \Delta^{2} \int_{0}^{\tau} dt_{2}$$

$$\times \exp\{-\frac{1}{2} \langle U_{AD}^{2} \rangle t_{2}^{2} - i [\epsilon_{AD} + \lambda_{AD}^{g} - Q(\tau)] t_{2}\},$$
(25)

where the time-dependent reorganization energy $Q(\tau)$ is defined in terms of three spectral densities,

$$Q(\tau) = \int d\omega \{ \rho_{Ag}(\omega) - \rho_{AD}(\omega) - \rho_{Dg}(\omega) \} \omega (1 - \cos \omega \tau).$$
(26)

The mean square fluctuation amplitude $\langle U_{AD}^2 \rangle$ is given by

$$\langle U_{AD}^2 \rangle = \int d\omega \ \rho_{AD}(\omega) \coth(\beta \omega/2) \omega^2.$$
 (27)

 $\sqrt{\langle U_{AD}^2 \rangle}$ is a characteristic quantity representing the magnitude of the bath fluctuation energy. As shown in the definition, Eq. (27), $\sqrt{\langle U_{AD}^2 \rangle}$ is strongly dependent on temperature. When the temperature is much larger than any harmonic oscillator energy, the mean square fluctuation amplitude is directly related to the reorganization energy as $\langle U_{AD}^2 \rangle \cong 2k_B T \lambda_{AD}^D$. This limit is usually referred to the classical or high temperature limit in the literature.¹²

When the mean square root fluctuation amplitude of the coupled bath degrees of freedom $\sqrt{\langle U_{AD}^2 \rangle}$ is much larger than the time scale of $Q(\tau)$, we can approximately replace the integration limit with ∞ instead of τ in Eq. (25). In this case, we find

$$k_{f}(\tau) = \sqrt{\frac{2\pi}{\langle U_{AD}^{2} \rangle}} \exp\left\{-\frac{\left[\epsilon_{AD} + \lambda_{AD}^{g} - Q(\tau)\right]^{2}}{2\langle U_{AD}^{2} \rangle}\right\}.$$
 (28)

This result is exceptionally simple. Note that Eq. (28) is precisely of the same form with the Marcus' expression for an equilibrium electron transfer rate except that the reorganization energy is replaced with τ -dependent one,²⁶ so we shall refer this result as *nonequilibrium generalization of the Marcus ET rate constant*. We also emphasize that Eq. (28) includes the complicated multidimensional nature of the solvation coordinate system via time-dependent function Q(t)which is in turn determined by the three spectral densities. Thus we believe that we have accomplished our goal of expressing the nonequilibrium ET rate kernel in terms of spectral densities.

If we relax the delta-function approximation to an optical pulse envelope, we expect to see the time-dependent change of the Gaussian width in Eq. (28). This is analogous to the time-dependent change of the time-resolved fluorescence width in liquid. We will discuss this case elsewhere.

We next investigate some limiting cases of Eq. (28) to give some insights and to check its consistency with other known results. Consider the case when τ is very small (but larger than the inverse of $\sqrt{\langle U_{AD}^2 \rangle}$) so that $Q(\tau)$ is negligibly small. In this case, the initial wave packet involved in the electron transfer process does not have enough time to significantly propagate on the donor surface, hence the corresponding reorganization energy should be equal to λ_{AD}^g —this is the solvation energy difference when the nuclear configuration of the bath coordinates is identical to that of the equilibrium distribution on the potential surface of the ground state. As we allow the wave packet propagate on the donor potential energy surface for time τ , the reorganization energy changes in time by $\lambda_{AD}^g - Q(\tau)$. Finally for a long time τ , $Q(\tau)$ approaches to an asymptotic value:

$$\lim_{\tau\to\infty} Q(\tau) = \lambda_{AD}^g - \lambda_{AD}^D$$

In this long time limit, the relevant reorganization energy reduces to λ_{AD}^D , which is the solvation energy difference evaluated over the equilibrium distribution of the bath degrees of freedom on the donor surface not the potential surface of the ground state. This can be understood simply: For such a long time τ , the wavepacket created on the donor surface reaches thermal equilibrium on the donor surface so that there is a constant rate of leaking of the donor population into the acceptor surface by the second-order electron transfer mechanism. Thus we have shown that the generalized result, Eq. (28), reaches the known equilibrium value (Marcus expression) after the relaxation time on the donor surface.

Finally it should be noted that as temperature decreases the stationary phase approximation used in this section becomes invalid, since the short-time approximation by a Gaussian [see Eq. (25)] is not reliable. In case of the low temperature regime, we should use Eq. (23) to calculate the nonequilibrium ET rate kernel instead of Eq. (28), even though Eq. (23) contains an undesirable additional integration.

E. Further simplification: Two orthogonal solvation coordinates

Our results, Eqs. (17) with (28), are valid regardless of the shapes and magnitudes of the three spectral densities. In other words, those results can be applied to multidimensional situations by inserting appropriate forms for the three spectral densities. We cannot, in general, obtain two orthogonal solvation coordinates to fully describe the three-state system, since there is no simple way to include the complicated cross correlation effect. However it will still be useful to extract two orthogonal coordinates to simplify the whole picture. Particularly, when we assume that the functional forms of the three spectral densities are the same, we may find two orthogonal solvation coordinates representing multidimensional bath fluctuations. This is because the potential energy surfaces associated with the three states can be described by two-dimensional harmonic wells with same curvatures. We explain the procedure of finding two orthogonal coordinates below.

When we used interaction representations of the donor and acceptor nuclear Hamiltonians in Eq. (20), we considered three time-dependent difference potentials, $U_{Dg}(t), U_{AD}(t)$, and $U_{Ag}(t)$, which are all collective coordinates. Among the three variables, $U_{AD}(t)$ is directly related to the electron transfer between $|D\rangle$ and $|A\rangle$, so we will choose $U_{AD}(t)$ as the primary coordinate, q_1 . Now there are two remaining variables, $U_{Dg}(t)$ and $U_{Ag}(t)$, but from the definition $U_{Ag}(t) = U_{AD}(t) + U_{Dg}(t)$, only one is independent. Therefore, we can choose either $U_{Dg}(t)$ or $U_{Ag}(t)$ as the other coordinate. We take $U_{Dg}(t)$, since this variable is directly responsible for the spectroscopic broadening effects. Although there are two representative coordinates, $U_{AD}(t)$ and $U_{Dg}(t)$, these two are not orthogonal to each other. Thus we use Schmidt orthogonalization method to obtain two orthogonal coordinates. We consider

$$q_1 \equiv U_{AD}(t),$$

$$q_2 \equiv U_{Dg}(t) + \gamma U_{AD}(t).$$
(29)

Here we should determine γ satisfying $\langle q_1 q_2 \rangle = 0$. By inserting $U_{Ag}(t) = U_{AD}(t) + U_{Dg}(t)$ and using the fact that $\langle U_{AD}U_{Dg} \rangle = \frac{1}{2} (\langle U_{Ag}^2 \rangle - \langle U_{AD}^2 \rangle - \langle U_{Dg}^2 \rangle)$, we find

$$\gamma = \frac{\langle U_{AD}^2 \rangle + \langle U_{Dg}^2 \rangle - \langle U_{Ag}^2 \rangle}{2 \langle U_{AD}^2 \rangle}.$$
(30)

This quantity is fully determined by the mean square fluctuation amplitudes. In order to obtain Eq. (30), we try to make $q_1(t)$ and $q_2(t')$ orthogonal to each other at equal time, t=t'. Here the approximation we introduce is that $\langle q_1(t)q_2(t')\rangle \approx 0$ for all t and t', which we shall refer as orthogonalization approximation. In terms of the two orthogonal coordinates we can rewrite the three difference potentials as $U_{Ag} = (1-\gamma)q_1 + q_2$, $U_{Dg} = -\gamma q_1 + q_2$, and $U_{AD} = q_1$. Inserting these into Eq. (23) and using the orthogonal property of the two coordinates q_1 and q_2 , the time-dependent rate kernel can be recast in the form

$$k_{f}(\tau) = 2 \operatorname{Re} \Delta^{2} \int_{0}^{\tau} dt_{2} \exp\{-i\epsilon_{AD}t_{2} - i\lambda_{AD}^{g}t_{2} - \varphi_{AD}(t_{2}) + 2i\gamma \operatorname{Im}[\varphi_{AD}(\tau) - \varphi_{AD}(\tau - t_{2})]\}.$$
(31)

By introducing the orthogonality approximation discussed above the resulting formula becomes dependent on one correlation function, $\varphi_{AD}(t)$. Furthermore by applying the stationary phase approximation to the integral and replacing the integration limit with infinity, we find that the nonequilibrium rate kernel becomes

$$k_{f}(\tau) = \sqrt{\frac{2\pi}{\langle U_{AD}^{2} \rangle}} \exp\left\{-\frac{\left[\epsilon_{AD} + \lambda_{AD}^{g} + 2\gamma Q_{AD}(\tau)\right]^{2}}{2\langle U_{AD}^{2} \rangle}\right\},$$
(32)

where

$$Q_{AD}(\tau) = \int d\omega \ \rho_{AD}(\omega) \,\omega (1 - \cos \omega \tau). \tag{33}$$

As can be seen in Eq. (32), the factor γ plays a critical role in determining the magnitude of the nonequilibrium rate kernel. As we will show in the following section, this factor is a sensitive function of the dimensionality of the solvation co-ordinates.

As briefly discussed in the Introduction, since we have to deal with three states, we have found that the multidimensional solvation coordinate system can be reduced to a twodimensional one by using the Schmidt orthogonalization method. We next show the importance of the dimensionality of the solvation coordinate system.

F. Dimensionality of solvation coordinate system

Although we showed that the two orthogonal coordinates can be extracted from the general multidimensional coordinate system, we have not discussed the possible implication of the two dimensionality of the solvation coordinate system. One of the questions arising immediately is that how large the fluctuation amplitudes of the two solvation coordinates we chose are. Particularly, these quantities are important in determining the probability of finding nuclear configuration maximizing the Franck–Condon overlap for ET.

As we shall show later it is useful to introduce a dimensional parameter, θ , defined by

$$\langle U_{Ag}^2 \rangle = \langle U_{AD}^2 \rangle + \langle U_{Dg}^2 \rangle - 2\sqrt{\langle U_{AD}^2 \rangle \langle U_{Dg}^2 \rangle} \cos \theta.$$
(34)

This relationship among the mean square fluctuation amplitudes can be viewed as a triangle with three sides of $\sqrt{\langle U_{Ag}^2 \rangle}$, $\sqrt{\langle U_{AD}^2 \rangle}$, and $\sqrt{\langle U_{Dg}^2 \rangle}$. The angle between the two sides, $\sqrt{\langle U_{Dg}^2 \rangle}$ and $\sqrt{\langle U_{AD}^2 \rangle}$, is the dimensionality parameter θ . The width of the q_1 distribution is determined by the square root of mean square fluctuation amplitude of U_{AD} , that is to say, $\langle q_1^2 \rangle = \langle U_{AD}^2 \rangle$. The mean square fluctuation amplitude of q_2 is written, in terms of the dimensionality parameter θ , by

$$\sqrt{\langle q_2^2 \rangle} = \sqrt{\langle U_{Dg}^2 \rangle} |\sin \theta|. \tag{35}$$

Although only $\sqrt{\langle U_{Dg}^2 \rangle}$ appears in Eq. (35), the square root of the mean square fluctuation amplitude of q_2 is determined by all three quantities, $\sqrt{\langle U_{Dg}^2 \rangle}$, $\sqrt{\langle U_{AD}^2 \rangle}$, and $\sqrt{\langle U_{Ag}^2 \rangle}$.

In case when $\gamma = 0$ or equivalently $\theta = \pi/2$, $\langle q_2^2 \rangle$ is solely determined by $\langle U_{Dg}^2 \rangle$, therefore the two fluctuating coordinates, $U_{Dg}(t)$ and $U_{AD}(t)$, are orthogonal to each other. Consequently, fluctuations of $U_{Dg}(t)$, which is associated with optical broadening effect and relaxation of the nonequilibrium wave packet on the donor surface, do not affect the electron transfer rate associated with fluctuations of $U_{AD}(t)$. That is, nonequilibrium preparation of the nuclear wave packet on the donor surface does not affect to the ET rate at all. On the other hand, when θ is equal to 0 or π , the solvation coordinate system is in one-dimensional situation, that is to say, we need only one solvation coordinate in order to describe both the optical excitation and the electron transfer. In this one-dimensional limit, the fluctuation amplitude along the q_2 axis is zero, as can be seen in Eq. (35), so that we can justify that a one-dimensional solvation coordinate can fully describe both optical transition and electron transfer. The difference between the two cases, $\theta = 0$ and $\theta = \pi$, is the alignment of the potential energy surfaces in the one-dimensional solvation coordinate system (see Fig. 1).

As can be seen in Eq. (35), the mean square fluctuation amplitude of q_2 is determined by a projection of the mean square fluctuation amplitude of $U_{Dg}(t)$. This can be reinterpreted by noting that the projection of $\sqrt{\langle U_{Dg}^2 \rangle}$ onto the primary coordinate, q_1 , is determined by $\sqrt{\langle U_{Dg}^2 \rangle} |\cos \theta|$. Therefore, when $\theta = \pi/2$, there is no projection of the $U_{Dg}(t)$ onto

coordinate system. (a) and (b) correspond to $\theta=0$ and π , respectively. See figure caption of Fig. 1 for the stepwise explanation.

the solvation coordinate associated with ET so that there is no effect of fluctuations of $U_{Dg}(t)$ on ET rate kernel. On the other hand, when $\theta=0$ or π , there are maximum influences of nonequilibrium preparation on the ET process.

IV. NUMERICAL CALCULATIONS

In this section we present numerical calculations of the time-dependent populations and rate kernel for various situations. In order to calculate these quantities we need to define the spectral densities. The spectral densities are assumed to be the following form:

$$\rho(\omega) = \eta \omega^3 \exp(-\omega/\omega_c). \tag{36}$$

 η 's associated with each spectral density are determined by the classical reorganization energies we use. For the sake of simplicity we will consider the classical (high temperature) limit only where the mean square fluctuation amplitude is proportional to the classical reorganization energy by $\langle U_{AD}^2 \rangle = 2\lambda_{AD}^{D}k_BT$ for example. Therefore, from Eq. (34), there is a relationship among the three classical reorganization energies,

$$\lambda_{Ag}^{g} = \lambda_{AD}^{D} + \lambda_{Dg}^{g} - 2\sqrt{\lambda_{AD}^{D}\lambda_{Dg}^{g}} \cos \theta.$$
(37)

We will consider that the two among the three reorganization energies are given and the remaining one is determined by the relationship given above.

We first calculate the time-dependent rate kernel, Eq. (28) with spectral densities of the same form defined in Eq. (36) with $\omega_c = 10 \text{ cm}^{-1}$. The electron exchange matrix element is assumed to be 30 cm⁻¹, throughout the numerical calculations. Two reorganization energies, λ_{Dg}^g and λ_{AD}^D are 1000 and 200 cm⁻¹, respectively. The remaining reorganization energy, λ_{Ag}^g , should be calculated from Eq. (37) when we specify the dimensionality (θ) of the system. The energy gap (ϵ_{AD}) between the isolated acceptor and donor is -500 cm^{-1} . Since $\epsilon_{AD} + \lambda_{AD}^D < 0$, potential surfaces of the electron transfer pair are in the so-called inverted regime (see Fig. 3). We now present the time-dependent rate kernel, Eq. (28), in Fig. 4(a). The dashed curve corresponds to the case of θ =0





FIG. 4. (a) Time-dependent ET rate kernels, Eq. (28), are calculated for three cases when θ =0 (dashed curve), $\pi/2$ (solid curve), and π (dotted curve). (b) Donor populations are calculated for θ =0 (dashed curve), $\pi/2$ (solid curve), and π (dotted curve). (c) Semilogarithmic plots of the donor populations are shown. The spectral densities are given by Eq. (36) with ω_c =10 cm⁻¹. η 's associated with each spectral density are determined by the classical reorganization energies from the definitions in Eq. (22). λ_{AD} =200 cm⁻¹ and λ_{Dg} =1000 cm⁻¹. λ_{Ag} is determined by using the relationship among the three classical reorganization energies [see Eq. (37)]. In this case, λ_{Ag} for θ =0, $\pi/2$, and π are 305.6, 1200, and 2094.4 cm⁻¹, respectively. ϵ_{AD} = -500 cm⁻¹. T=300 K.

[see Fig. 3(a)]. Since this is a one-dimensional case, we can draw the three potential surfaces with respect to a single coordinate. The nonequilibrium nuclear wave packet created on the donor surface tends to relax down to the minimum of the donor surface. The distance between the center of the nonequilibrium wave packet and the exit channel (curve crossing point between the donor and acceptor surfaces) becomes closer as time increases (it should be noted that the distance we have mentioned here should be considered as the magnitude of the time-dependent reorganization energy, so it should not be confused with the real distance). Therefore we expect that the time-dependent rate kernel increases in time and reaches its limiting value shown by the plateau in Fig. 4(a). On the other hand, when $\theta = \pi$, even though this is also a one-dimensional case, the position of the minimum of the ground state is different from that for $\theta = 0$ [see Fig. 3(b)]. Again the center of the nonequilibrium wave packet propagates on the donor surface to reach an equilibrium value. For a short time $(0 \le t \le 0.8 \text{ ps})$, the center of the nonequilibrium wave packet becomes closer to the exit channel. After it reaches the center of the exit channel, the distance between the center of the nonequilibrium wave packet and the exit channel increases so that the rate kernel decreases toward a limiting value [see dotted curves in Fig. 4(a)]. As the third example, we consider the case of $\theta = \pi/2$. We cannot draw three potential surfaces as Fig. 3, because the two dimensionality of potential surfaces are important (refer to Fig. 2, even though Fig. 2 is not precisely the relevant one). As we mentioned before, if $\theta = \pi/2$, the two solvation coordinates associated with optical transition (as well as relaxation of the nonequilibrium wave packet) and electron transfer are orthogonal so that there is no effect of nonequilibrium preparation of the donor population on the electron transfer rate. Therefore, the rate kernel, in this case, is a constant and identical to the equilibrium value [solid curve in Fig. 4(a)].

With the time-dependent rate kernels calculated above [shown in Fig. 4(a)], we calculate the donor populations in time. We normalize the initial donor population to be unity. The solid curve in Fig. 4(b) is corresponding to the case of $\theta = \pi/2$. Since the ET rate kernel is constant, the donor population is a simple exponential function with respect to time. If we assume that the relaxation of the nonequilibrium wavepacket can be ignored, we expect that the donor population decays as the solid curve. The dashed curve is corresponding to the case of $\theta = 0$. Because the magnitude of the rate kernel is small compared to the equilibrium value as shown by the dashed curve in Fig. 4(a), the donor population decreases very slowly for short time (0 < t < 2 ps). As time increases, the exponential decaying pattern is recovered. For $\theta = \pi$, the donor population [dotted curve in Fig. 4(b)] decays faster than the equilibrium case (or the case of $\theta = \pi/2$). This can be understood that the associated rate kernel [dotted curve in Fig. 4(a) becomes larger than the equilibrium value after 500 fs. Finally we present, in Fig. 4(c), semilogarithmic plots of donor populations to show nonexponential decaying patterns when the nuclear wave packet is in nonequilibrium situation.

In Fig. 5, we present similar numerical results except that the classical reorganization energies, λ_{Dg}^{g} and λ_{AD}^{D} , are 200 and 2000 cm⁻¹, respectively. Since $\epsilon_{AD} + \lambda_{AD}^{D} > 0$, this corresponds to the normal regime (see Fig. 1). In Fig. 5(a), the time-dependent rate kernels for $\theta=0$, $\pi/2$, and π , are shown by dashed, solid, and dotted curves, respectively. As can be seen in the potential surfaces in Fig. 1(a), we can understand the time dependence of the rate kernels for $\theta=0$ and π . In both cases, the limiting values approach to the equilibrium value, which is also identical to the rate kernel for $\theta = \pi/2$. Donor populations in time for the three cases are shown in Fig. 5(b). Also we find strong nonexponential patterns for short time (less than 2 ps). Semilogarithmic plots are shown in Fig. 5(c). Particularly, the decaying pattern [dashed curve in Fig. 5(c)] of $\theta = 0$ can be viewed as a double exponential with both fast and slow ones. We note that this behavior-initially the donor population decays quickly and then follows a slow exponential decay-has not been seen in Coalson *et al.*'s computer simulation studies. This is because they did not fully consider multidimensional aspect of the potential surfaces explicitly. The slow part of the decay is



FIG. 5. Similar plots are shown except that the two reorganization energies λ_{AD} and λ_{AD} are assumed to be 2000 and 200 cm⁻¹, respectively. Consequently, the remaining reorganization energies, λ_{Ag} , for $\theta=0$, $\pi/2$, and π are 935.1, 2200, and 3464.9 cm⁻¹, respectively. All the other parameters are the same with Fig. 4. (a) Time-dependent ET rate kernels, using Eq. (28), are calculated when $\theta=0$ (dashed curve), $\pi/2$ (solid curve), and π (dotted curve). (b) Donor populations are calculated when $\theta=0$ (dashed curve), $\pi/2$ (solid curve), and π (dotted curve). (c) Semilogarithmic plots of the donor populations are shown. Dashed, solid and dotted curves correspond to $\theta=0$, $\pi/2$, and π , respectively.

therefore related to the equilibrium ET rate constant, whereas the fast part of the decay is induced by the relaxation of the nonequilibrium wave packet on the donor surface.

In this section, although we presented very limited cases in the wide parameter space, we found that the resulting decaying patterns of donor populations in time are shown to be very sensitive with respect to the nonequilibrium natures of the photoinduced initiation of the ET in condensed media. Since the optical excitation step can be studied by various linear and nonlinear spectroscopic measurements, one can get detailed information on the mean square fluctuation amplitude, $\langle U_{Dg}^2 \rangle$, which is in turn related to the classical reorganization energy, λ_{Dg}^{g} . More specifically, the classical reorganization energy is approximately equal to the twice of the fluorescence Stokes shift. Thus half of the inputs we need can be obtained via spectroscopic measurements. Still we are suffering from the lack of direct experimental methods to obtain the mean square fluctuation amplitude directly associated with the electron transfer. These parameters can be, in principle, obtained by plotting equilibrium rate constants As shown conclusively in our model calculations, the short-time nonexponential decay of the donor population can be attributed to the nonequilibrium nature of the initial preparation of donor population by an ultrafast optical pulse. Both patterns, quick decay followed by slow exponential decay as well as slow decay followed by fast exponential decay, can be found in the photoinduced ET and are dependent on the multidimensional potential surfaces.

V. SUMMARY

In this paper, we presented a theoretical description of the photoinduced ET process in condensed media. Assuming that the bath consists of harmonic oscillators and that those harmonic modes are linearly coupled to the three states, we formulated the time-dependent ET rate kernel including nonequilibrium features of optical preparation of donor population. We assumed that the ultrafast laser pulse is short enough to ignore any electron transfer during the pulse duration time. In this case we can obtain a generalized expression for the nonadiabatic ET rate kernel that is identical to that discussed by Coalson et al.¹⁹ We further applied a stationary phase approximation within the cumulant method. We finally found a simple and interesting generalization of the Marcus expression of ET rate kernel, where the nonequilibrium nature is included via the time-dependent reorganization energy. In order to fully understand the nonequilibrium nature of the photoinduced ET, we discussed multidimensional aspects of the solvation coordinate system. In some limiting case we found that two orthogonal coordinates can be obtained by using the Schmidt orthogonalization method.

We believe that there are many directions to extend our work. One is to consider a finite pulse duration effect. In this case we cannot simply ignore the fully coherent contribution, where the time ordering is mixed. Furthermore, the propagation of the initial wave packet on the donor surface during the pulse duration time could be important if the relaxation time is comparable to the time scale of the pulse duration time. Another generalization is to develop either a fully phase space picture (e.g., Wigner distribution function) with two orthogonal coordinates and two conjugate momenta, or coordinate space picture with two coordinates. Then, the ET rate kernel should be given by an integral of the distribution functions over the phase space or over coordinate space. The picture emerging from these procedures show clearly that the conditional probability of finding the overlap between the distribution functions associated with the nonequilibrium wave packet and with the exit channel is directly proportional to the time-dependent ET rate kernel we discussed in this paper. Finally, in this paper, we have not specifically studied the effects of molecular vibrations on the dynamics. Formally, we can proceed in much the same spirit as above to take these effects into account.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation. M. C. thanks Professor Graham R. Fleming of the University of Chicago and Professor Shaul Mukamel of the University of Rochester for very helpful discussions.

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