AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **131**, 154502 (2009); doi: 10.1063/1.3249964 View online: http://dx.doi.org/10.1063/1.3249964 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v131/i15 Published by the American Institute of Physics.

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Photoinduced homogeneous proton-coupled electron transfer: Model study of isotope effects on reaction dynamics

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(Received 30 June 2009; accepted 26 September 2009; published online 16 October 2009)

A model Hamiltonian for photoinduced homogeneous proton-coupled electron transfer reactions is presented, and the equations of motion for the reduced density matrix elements in an electron-proton vibronic basis are derived. This formalism enables a detailed analysis of the proton vibrational dynamics, as well as the dynamics of the electronic state populations, following photoexcitation. The application of this theory to model systems provides insight into the fundamental physical principles underlying these types of processes. The initial nonequilibrium state is prepared by vertical photoexcitation from the ground electronic state to a coherent vibrational mixture in the donor electronic state. This nonstationary state relaxes to the equilibrium distributions in the donor and acceptor electronic states via dynamical processes arising from nonadiabatic transitions between the donor and acceptor vibronic states concurrent with energy dissipation to the bath. During the initial stage, when the proton vibrational population in the donor state is distributed among higher vibrational states and the donor proton wavepacket is oscillating with large amplitude, the electronic state population dynamics exhibits virtually no hydrogen/deuterium isotope effect. After vibrational relaxation, when the proton vibrational population in the donor state becomes concentrated in the lower vibrational states and the donor proton wavepacket becomes more localized near the minimum of the donor potential, a significant hydrogen/deuterium isotope effect on the electronic state population dynamics is exhibited. These model system calculations lead to experimentally testable predictions about the qualitative behavior of these isotope effects. © 2009 American Institute of Physics. [doi:10.1063/1.3249964]

I. INTRODUCTION

The coupling of electron transfer reactions to proton motion plays a central role in a variety of biological charge transport and catalytic processes.^{1–6} Understanding such proton-coupled electron transfer (PCET) reactions is important for designing alternative renewable energy sources, such as artificial photosynthetic systems and solar fuel cells.^{7,8} These types of energy sources require the activation of molecules by light to induce the forming and breaking of bonds, often involving electron transfer accompanied by proton transfer reactions.

Numerous experimental studies focused on photoinduced PCET processes, where the PCET reaction is initiated by a laser pulse.^{9–20} In these experiments, the laser pulse photoexcites an electron within a redox complex comprised of an electron donor-acceptor pair separated by a hydrogenbonding interface. The electron transfer is often accompanied by proton transfer within the hydrogen-bonding interface to avoid high-energy intermediates. The electron transfer reaction kinetics can be monitored by ultrafast time-resolved spectroscopy. Evidence of proton tunneling may be observed in the form of a hydrogen/deuterium isotope effect on the reaction kinetics.

Theoretical approaches based on the nonadiabatic golden rule formalism have been developed and applied to a wide

range of thermally activated PCET reactions.^{1,6,21-27} Photoinduced PCET reactions, however, are essentially nonequilibrium processes. Following photoexcitation, the electron, proton, and coupled nuclear degrees of freedom are in a nonequilibrium configuration, and thermal equilibrium is achieved only after various relaxation processes. Modeling these processes is challenging due to the quantum mechanical nature of the tunneling proton^{28,29} and the dissipative effects of the solvent environment. Photoinduced ET reactions in condensed phase environments have been studied using a variety of approaches, such as the generalized master equation approach,^{30,31} quantum Fokker–Planck approach,^{32–37} Redfield theory,^{38–51} path integral influence functional approach,⁵²⁻⁶⁷ semiclassical theories,⁶⁸⁻⁷¹ multiconfiguration time-dependent Hartree method,⁷²⁻⁷⁶ mixed/quantum classical approaches.^{69,77-80} In principle, many of these approaches could be extended to study photoinduced PCET reactions.

In the present paper, we investigate photoinduced PCET processes using the reduced density matrix (RDM) formalism.^{44,81,82} Our model consists of donor and acceptor electronic states that are coupled to a bath representing the condensed phase environment. A laser pulse excites an electron from the ground electronic state of the system to the donor state. The subsequent electron transfer between the donor and acceptor electronic states is accompanied by a proton transfer reaction represented by a displacement of the

 $0021 \hbox{-} 9606/2009/131(15)/154502/11/\25.00

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proton potential. Modeling the high-frequency vibrational motion of the proton is challenging because it requires the inclusion of highly excited proton vibrational states. The RDM formalism enables us to study the time evolution of the populations of the donor and acceptor electronic states, as well as the dynamics of the associated proton vibrational wavepackets. Our objective is to elucidate the physical basis for the hydrogen/deuterium (H/D) isotope effect on the relaxation processes and to identify the key system properties that impact this isotope effect.

An outline of the paper is as follows. In Sec. II A, we present a model Hamiltonian for describing photoinduced homogeneous PCET reactions, and in Sec. II B we perform a canonical transformation of this model Hamiltonian to enable us to study model systems with strong coupling between the electronic states and the bath modes. In Sec. II C, we apply the RDM formalism to this canonically transformed model Hamiltonian in order to derive the master equations for the populations of the vibronic states following photoexcitation. Section II D describes the methodology for analysis of the proton vibrational wavepacket dynamics within the RDM formalism. In Sec. III, we utilize this theoretical formulation to investigate four model systems, analyzing the origin of the H/D isotope effect on the dynamics, as well as the impact of various system parameters on the PCET process. Concluding remarks are presented in Sec. IV.

II. THEORY

A. Model Hamiltonian for the PCET reaction

In this subsection, we define a model Hamiltonian that describes photoinduced homogeneous PCET processes. The reactive system includes two diabatic electronic states: the photoexcited donor state and the acceptor state. The electron transfer from the donor state to the acceptor state is strongly coupled to a proton transfer reaction. The proton potential energy curves are $U^{I}(r_{p})$ and $U^{II}(r_{p})$ in the donor and acceptor states, respectively, where r_{p} is the proton coordinate. A laser pulse is assumed to instantaneously excite an electron from the ground electronic state of the system to the donor state, followed by dynamical processes involving electron transfer between the donor and acceptor states. This model system is depicted in Fig. 1.

The operators $\hat{c}_r^{\dagger}, \hat{c}_r, \hat{c}_k^{\dagger}, \hat{c}_k$ are the fermionic creation and annihilation operators for the donor and acceptor electronic states $|r\rangle$ and $|k\rangle$. The energies ϵ_r and ϵ_k denote the electronic energies of the photoexcited donor and acceptor states relative to the ground state. The donor and acceptor states are coupled by the constant electronic coupling term V_{rk} , which is assumed to be independent of the nuclear degrees of freedom. The intramolecular degrees of freedom of the molecule (except for the transferring proton) and the surrounding solvent molecules are modeled as a harmonic bath, where x_i and p_i are the position and momentum coordinates of the *i*th harmonic oscillator mode with masses and frequencies m_i and ω_i , respectively. The bath responds to the change in



FIG. 1. Depiction of the photoinduced homogeneous PCET model system. The ground, donor, and acceptor state proton potentials U^0 , U^I , and U^{II} with minima at r_p^0 , r_p^1 , and r_p^{II} are depicted in green, blue, and red, respectively. The energies ε_r and ε_k of the donor and acceptor electronic states are indicated. Prior to photoexcitation, the proton wavepacket is in the ground vibrational state of the ground electronic state. Photoexcitation from the ground electronic state to the donor electronic state is depicted by the green arrow. The initial wavepacket following photoexcitation is a coherent vibrational mixture in the donor electronic state. The red and blue arrows indicate the relaxation processes arising from nonadiabatic transitions between the bath. The blue arrow corresponds to proton vibrational relaxation in the donor state via the indirect mechanism involving nonadiabatic transitions, and the red arrow corresponds to the PCET reaction. The blue and red wavepackets depict the final equilibrium populations in the donor and acceptor states following the dynamical relaxation processe.

charge distribution of the system, and the coupling constants c_i describe the coupling between the bath and the occupation of the donor electronic state.

The Hamiltonian of the entire model system has the following form:

$$\begin{aligned} \hat{H} &= \hat{T}_p + (\boldsymbol{\epsilon}_r + U^{\mathrm{I}}(r_p))\hat{c}_r^{\dagger}\hat{c}_r + (\boldsymbol{\epsilon}_k + U^{\mathrm{II}}(r_p))\hat{c}_k^{\dagger}\hat{c}_k \\ &+ (V_{rk}\hat{c}_r^{\dagger}\hat{c}_k + V_{rk}^{\ast}\hat{c}_k^{\dagger}\hat{c}_r) \\ &+ \sum_i \left\{ \frac{p_i^2}{2m_i} + \frac{m_i\omega_i^2}{2} \left(x_i + \hat{n}_r \frac{c_i}{m_i\omega_i^2} \right)^2 \right\}, \end{aligned}$$
(1)

where \hat{T}_p is the proton kinetic energy and $\hat{n}_r = \hat{c}_r^{\dagger} \hat{c}_r$ is the occupation number operator associated with the donor state. The system-bath coupling parameters are described by the spectral density function⁸³

$$J(\omega) = \frac{\pi}{2} \sum_{i} \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i).$$
(2)

The above Hamiltonian can be rewritten in terms of the harmonic oscillator ladder operators \hat{b}_i^{\dagger} and \hat{b}_i :

$$\begin{aligned} \hat{H} &= \hat{T}_p + (\boldsymbol{\epsilon}_r + U^{\mathrm{I}}(r_p))\hat{c}_r^{\dagger}\hat{c}_r + (\boldsymbol{\epsilon}_k + U^{\mathrm{II}}(r_p))\hat{c}_k^{\dagger}\hat{c}_k \\ &+ (V_{rk}\hat{c}_r^{\dagger}\hat{c}_k + V_{rk}^*\hat{c}_k^{\dagger}\hat{c}_r) + \sum_i \hbar \omega_i \left(\hat{b}_i^{\dagger}\hat{b}_i + \frac{1}{2}\right) \\ &+ \hat{n}_r \sum_i \frac{\hbar c_i}{\sqrt{2\hbar m_i \omega_i}} (\hat{b}_i^{\dagger} + \hat{b}_i) + \hat{n}_r^2 \sum_i \frac{c_i^2}{2m_i \omega_i^2}. \end{aligned}$$
(3)

This model does not include direct coupling between the proton vibrational mode and the bath. The proton vibrational mode is indirectly coupled to the bath, however, because the proton vibrational mode is coupled to the electronic states, which in turn are coupled to the bath. Thus, although this model does not include a direct mechanism for proton vibrational relaxation, it does include an indirect mechanism for proton vibrational relaxation via nonadiabatic transitions between the donor and acceptor states. Typically the electron transfer reaction is more strongly coupled to the bath than the proton transfer reaction because the electron transfers over a much longer distance. In this case, the proton vibrational relaxation is expected to occur on a faster timescale for the indirect mechanism than for the direct mechanism, and therefore the neglect of the direct coupling between the proton vibrational mode and the bath does not significantly impact the ultrafast dynamical relaxation of the electronic state populations.

B. Canonically transformed Hamiltonian

In this subsection, we derive the canonically transformed Hamiltonian that allows us to study model systems with strong system-bath coupling. A straightforward application of the RDM formalism to the Hamiltonian given in Eq. (3) would restrict the treatment to the weak system-bath coupling case due to the perturbative treatment of the systembath interaction term. In order to capture the effects of the strong interaction between the electronic state and the bath modes, we apply the small polaron transformation⁸⁴ to the Hamiltonian of Eq. (3):

$$\widetilde{H} = e^{-\hat{n}_r \hat{\upsilon}} \widehat{H} e^{\hat{n}_r \hat{\upsilon}},\tag{4}$$

where

$$\hat{v} = -\sum_{i} \frac{c_i}{\sqrt{2\hbar m_i \omega_i^3}} (\hat{b}_i^{\dagger} - \hat{b}_i).$$
⁽⁵⁾

The transformed Hamiltonian has the following form:

$$\begin{split} \widetilde{H} &= \widehat{T}_p + (\epsilon_r + U^{\mathrm{I}}(r_p))\widehat{c}_r^{\dagger}\widehat{c}_r + (\epsilon_k + U^{\mathrm{II}}(r_p))\widehat{c}_k^{\dagger}\widehat{c}_k \\ &+ (V_{rk}e^{-\widehat{v}}\widehat{c}_r^{\dagger}\widehat{c}_k + V_{rk}^*e^{\widehat{v}}\widehat{c}_k^{\dagger}\widehat{c}_r) + \sum_i \hbar\omega_i (\widehat{b}_i^{\dagger}\widehat{b}_i + \frac{1}{2}). \end{split}$$
(6)

This canonical transformation removes the linear coupling between the electronic states and the bath. Instead, we have a renormalized electronic coupling term, which is often denoted the bath-dressed electronic coupling term.⁵⁵ Furthermore, this transformation introduces a shift in the donor electronic level, $\epsilon_r \rightarrow \epsilon_r - \lambda_s$, where the solvent reorganization energy λ_s is defined as

$$\lambda_s = \frac{1}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} = \sum_i \frac{c_i^2}{2m_i \omega_i^2}.$$
(7)

The presence of the counter-term $\hat{n}_r^2 \lambda_s$ in the Hamiltonian of Eq. (3) cancels this level shift. A related canonically transformed model Hamiltonian has been used to describe equilibrium electrochemical PCET.⁸⁵

In order to apply the RDM formalism, the transformed Hamiltonian $\tilde{H} = \hat{H}_S + \hat{H}_B + \hat{V}$ is now partitioned into a system Hamiltonian

$$\hat{H}_{S} = \hat{T}_{p} + (\boldsymbol{\epsilon}_{r} + U^{\mathrm{I}}(r_{p}))\hat{c}_{r}^{\dagger}\hat{c}_{r} + (\boldsymbol{\epsilon}_{k} + U^{\mathrm{II}}(r_{p}))\hat{c}_{k}^{\dagger}\hat{c}_{k}, \qquad (8)$$

a bath Hamiltonian

$$\hat{H}_B = \sum_i \hbar \omega_i \left(\hat{b}_i^{\dagger} \hat{b}_i + \frac{1}{2} \right), \tag{9}$$

and a perturbative term

$$\hat{V} = V_{rk} e^{-\hat{v}} \hat{c}_r^{\dagger} \hat{c}_k + V_{rk}^* e^{\hat{v}} \hat{c}_k^{\dagger} \hat{c}_r$$
(10)

corresponding to the bath-dressed electronic coupling.⁵⁵ At finite temperature, the effect of this coupling term can be quantified by an effective tunneling matrix element $\Delta_{\rm eff} = V_{rk} tr(\hat{\rho}_B e^{-\hat{v}})$,⁸³ which can be evaluated for a harmonic bath as $\Delta_{\text{eff}} = V_{rk} \exp\{-\sum_i (c_i^2/4\hbar m_i \omega_i^3) \coth(\hbar \beta \omega_i/2)\}$, where $\beta = 1/k_B T$. This effective coupling is smaller than the bare electronic coupling element V_{rk} for finite temperatures and large magnitudes of the system-bath coupling strength. As a result, the perturbative treatment of the bath-dressed electronic coupling term is valid if the bare electronic coupling element V_{rk} is reasonably small. Note that the perturbative treatment of the system-bath coupling in Eq. (3) is restricted to small system-bath coupling, whereas the perturbative treatment of the bath-dressed coupling in Eq. (6) is restricted to small electronic coupling but is valid for strong systembath coupling. Thus, this canonical transformation enables us to treat the strong system-bath coupling case with the RDM formalism described in the next subsection.

C. RDM formalism for photoinduced PCET

In the RDM formalism, the state of the system and bath at any time *t* is described by the total density matrix $\hat{\rho}(t)$, and the time evolution of this density matrix is given by the quantum Liouville equation⁸⁶

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H},\hat{\rho}(t)].$$
(11)

The reduced density operator $\hat{\sigma}(t)$ is obtained by taking the trace over the bath degrees of freedom:⁸²

$$\hat{\sigma}(t) = tr_B\{\hat{\rho}(t)\}.$$
(12)

The total density matrix is assumed to factorize into the RDM and the bath density matrix at all times. Furthermore, the bath is assumed to remain in thermal equilibrium [i.e., $\hat{\rho}_B = e^{-\beta \hat{H}_B}/tr(e^{-\beta \hat{H}_B})$] throughout the process. Thus, $\hat{\rho}(t) = \hat{\sigma}(t) \otimes \hat{\rho}_B$.

In this formalism, the interaction term is treated perturbatively up to second order, and the equations of motion of the RDM are obtained in the basis of system eigenstates. The matrix elements of the RDM in this basis are given by $\sigma_{\mu\nu}(t) = \langle \mu | \hat{\sigma}(t) | \nu \rangle$, where $\hat{H}_S | \mu \rangle = E_{\mu} | \mu \rangle$. The equations of motion for these matrix elements are known as the Redfield equations.^{38,42,44,81} The RDM equations of motion can be further simplified by employing the secular approximation,^{81,82} which decouples the equations of motion for the diagonal (i.e., population) and off-diagonal (i.e., coherence) elements of the RDM. The resulting equations of motion for the diagonal RDM elements are known as the Pauli master equations.⁸² In standard Redfield theory, the perturbative

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term is usually assumed to be the system-bath coupling, so this theory has been limited to weak system-bath coupling. The canonical transformation described in the previous subsection allows us to treat the strong system-bath coupling that is typical for PCET reactions.

In this subsection, we apply the RDM formalism to the canonically transformed model Hamiltonian given in Eq. (6). The photoinduced homogeneous PCET process is described in terms of nonadiabatic transitions between mixed electron-proton vibronic states of the photoexcited donor state with proton potential $U^{II}(r_p)$ and the acceptor state with proton potential $U^{II}(r_p)$. The RDM of the system is represented in the electron-proton vibronic basis. The proton vibrational states for the potentials $U^{II}(r_p)$ and $U^{II}(r_p)$ can be calculated by solving the following Schrödinger equations:

$$[\hat{T}_{p} + U^{\mathrm{I}}(r_{p})]\chi^{\mathrm{I}}_{\mu}(r_{p}) = E^{\mathrm{I}}_{\mu}\chi^{\mathrm{I}}_{\mu}(r_{p}),$$

$$[\hat{T}_{p} + U^{\mathrm{II}}(r_{p})]\chi^{\mathrm{II}}_{\nu}(r_{p}) = E^{\mathrm{II}}_{\nu}\chi^{\mathrm{II}}_{\nu}(r_{p}).$$
(13)

The eigenstates of the system Hamiltonian are denoted $|r\rangle|\chi^{I}_{\mu}\rangle$ and $|k\rangle|\chi^{II}_{\nu}\rangle$ when the photoexcited electron is in the donor and acceptor states, respectively.

The diagonal matrix elements of the RDM in the electron-proton vibronic basis are given by

$$\sigma_{r\mu,r\mu}(t) = \langle \chi^{\mathrm{I}}_{\mu} | \langle r | \hat{\sigma}(t) | r \rangle | \chi^{\mathrm{I}}_{\mu} \rangle,$$

$$\sigma_{k\nu,k\nu}(t) = \langle \chi^{\mathrm{II}}_{\nu} | \langle k | \hat{\sigma}(t) | k \rangle | \chi^{\mathrm{II}}_{\nu} \rangle,$$
(14)

where $\sigma_{r\mu,r\mu}(t)$ is the population of the vibronic state $|r\rangle|\chi_{\mu}^{I}\rangle$, and $\sigma_{k\nu,k\nu}(t)$ is the population of the vibronic state $|k\rangle|\chi_{\nu}^{II}\rangle$. The equations of motion for the diagonal RDM elements are given by

$$\dot{\sigma}_{r\mu,r\mu}(t) = \sum_{\nu} W_{r\mu,k\nu}(t)\sigma_{k\nu,k\nu}(t) - \sum_{\nu} W_{k\nu,r\mu}(t)\sigma_{r\mu,r\mu}(t),$$

$$\dot{\sigma}_{k\nu,k\nu}(t) = \sum_{\mu} W_{k\nu,r\mu}(t)\sigma_{r\mu,r\mu}(t) - \sum_{\mu} W_{r\mu,k\nu}(t)\sigma_{k\nu,k\nu}(t),$$
(15)

where $W_{r\mu,k\nu}(t)$ is the probability of transition from the eigenstate $|k\rangle|\chi_{\nu}^{II}\rangle$ to the eigenstate $|r\rangle|\chi_{\mu}^{II}\rangle$ at time *t*, and $W_{k\nu,r\mu}(t)$ denotes the reverse transition probability.⁸² Using the formalism described in Ref. 82 in conjunction with the stationary Redfield tensor approximation, ^{44,81} the time-dependent transition probabilities are of the form:

$$W_{r\mu,k\nu} = \frac{1}{\hbar^2} |V_{rk}|^2 |\langle \chi_{\nu}^{\rm II} | \chi_{\mu}^{\rm I} \rangle|^2 \int_{-\infty}^{\infty} d\tau e^{-i(\epsilon_r - \epsilon_k + E_{\mu}^{\rm I} - E_{\nu}^{\rm II})\tau/\hbar} \langle e^{\hat{v}(\tau)} e^{-\hat{v}(0)} \rangle,$$
(16)

$$W_{k\nu,r\mu} = \frac{1}{\hbar^2} |V_{rk}|^2 |\langle \chi_{\nu}^{\mathrm{II}} | \chi_{\mu}^{\mathrm{I}} \rangle|^2 \int_{-\infty}^{\infty} d\tau e^{i(\epsilon_r - \epsilon_k + E_{\mu}^{\mathrm{II}} - E_{\nu}^{\mathrm{II}})\pi/\hbar} \langle e^{\hat{v}(\tau)} e^{-\hat{v}(0)} \rangle.$$

The populations of the donor and acceptor states at time *t* are obtained by summing over the proton vibrational states:

$$P_r(t) = \sum_{\mu} \sigma_{r\mu,r\mu}(t), \quad P_k(t) = \sum_{\nu} \sigma_{k\nu,k\nu}(t).$$
 (17)

The quantity $\langle e^{\hat{v}(\tau)}e^{-\hat{v}(0)}\rangle = tr(\hat{\rho}_B e^{i\hat{H}_B\tau/\hbar}e^{\hat{v}}e^{-i\hat{H}_B\tau/\hbar}e^{-\hat{v}})$ is denoted the bath correlation function, where $\hat{\rho}_B$ is the equilibrium bath density operator given by the Boltzmann distribution for the bath Hamiltonian \hat{H}_B in Eq. (9). Following the procedure described in Ref. 84, the bath correlation function can be evaluated exactly using the bosonic creation and annihilation operator algebra:

$$\langle e^{\hat{v}(\tau)} e^{-\hat{v}(0)} \rangle = \exp\left\{-\sum_{i} \frac{c_i^2}{2\hbar m_i \omega_i^3} \left(\coth\left[\frac{\hbar\beta\omega_i}{2}\right] (1 - \cos(\omega_i \tau)) + i\sin(\omega_i \tau) \right) \right\}.$$
(18)

In the continuum limit for the bath modes, the bath correlation function can be rewritten in terms of the spectral density as

$$\langle e^{\hat{\upsilon}(\tau)} e^{-\hat{\upsilon}(0)} \rangle = \exp\left\{-\frac{1}{\pi\hbar}\mathcal{Q}(\tau)\right\},\tag{19}$$

where

$$Q(\tau) = \int_{0}^{\infty} d\omega \frac{J(\omega)}{\omega^{2}} \Biggl\{ \operatorname{coth}\left[\frac{\hbar\beta\omega}{2}\right] (1 - \cos(\omega\tau)) + i\sin(\omega\tau) \Biggr\}.$$
(20)

In this paper, we choose the bath spectral density to have Ohmic form with an exponential cutoff^{83}

$$J(\omega) = \eta \hbar \omega e^{-\omega/\omega_c}.$$
 (21)

This model is specified by the cutoff frequency ω_c and the friction constant η . The dimensionless Kondo parameter $\alpha = 2 \eta / \pi$ characterizes the strength of the system-bath coupling. For the Ohmic bath, the classical reorganization energy is $\lambda_s = \hbar \eta \omega_c / \pi$. For this Ohmic spectral density, an exact analytical expression can be derived for $Q(\tau)$ given in Eq. (20):

$$Q(\tau) = \eta \hbar \ln[1 + i\omega_c \tau] - \eta \hbar \ln\left[\Gamma\left(\Omega + \frac{i\tau}{\hbar\beta}\right)\Gamma\left(\Omega - \frac{i\tau}{\hbar\beta}\right) \middle/ \Gamma^2(\Omega)\right],$$
(22)

where $\Omega = 1 + (1/\hbar\beta\omega_c)$ and $\Gamma(z)$ is the Euler Gamma function⁸⁷ of a complex variable.

The transition probability elements in the RDM equations of motion given in Eq. (15) are calculated with Eq. (16) using Eq. (22) to calculate the bath correlation function. To solve these equations, we need to specify the initial populations of all vibronic states, $\sigma_{r\mu,r\mu}(0)$ and $\sigma_{k\nu,k\nu}(0)$. At time zero, the laser pulse instantaneously excites an electron from the ground electronic state of the system to the donor state. The proton potential corresponding to the ground electronic state is denoted by $U^0(r_p)$. Since the excitation is assumed to be instantaneous, the initial proton wavepacket in the donor state, which has proton potential $U^1(r_p)$, corresponds to the equilibrium configuration of the potential $U^0(r_p)$. This process is depicted schematically in Fig. 1.

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If thermal excitations are negligible, we can assume that the proton is in the ground vibrational state $|\chi_0^0\rangle$ for the proton potential $U^0(r_p)$ prior to photoexcitation. In this case, the RDM at zero time is

$$\hat{\sigma}(0) = |r\rangle |\chi_0^0\rangle \langle \chi_0^0 | \langle r|.$$
(23)

The corresponding RDM elements at zero time are

$$\sigma_{r\mu,r\mu'}(0) = \langle \chi^{\mathrm{I}}_{\mu} | \langle r | \hat{\sigma}(0) | r \rangle | \chi^{\mathrm{I}}_{\mu'} \rangle = \langle \chi^{\mathrm{I}}_{\mu} | \chi^{0}_{0} \rangle \langle \chi^{0}_{0} | \chi^{\mathrm{I}}_{\mu'} \rangle, \quad (24)$$

and are given by products of the proton vibrational wave function overlaps. Since the photoexcited electron is in the donor state at zero time, the initial populations of all vibronic states corresponding to the acceptor state are zero. Thus, the population of the donor state is unity at time zero [i.e., $P_r(0)=1$].

The initial population following photoexcitation, as given by Eq. (23), is far from the equilibrium distribution $\hat{\sigma}^{eq} = e^{-\beta \hat{H}_S/tr}(e^{-\beta \hat{H}_S})$, where \hat{H}_S is defined in Eq. (8). During the time evolution of the RDM elements, the transition probabilities $W_{r\mu,k\nu}$ and $W_{k\nu,r\mu}$ drive the system toward this thermal equilibrium distribution, and $\hat{\sigma}(t \to \infty) = \hat{\sigma}^{eq}$. Note that the system Hamiltonian \hat{H}_S does not include the ground electronic state, so the thermal equilibrium distribution spans only the donor and acceptor electronic states. Electronic relaxation down to the ground electronic state is expected to occur on a much longer timescale.

D. Proton dynamics during photoinduced PCET

In this subsection, we describe the methodology for analysis of the proton vibrational dynamics within the RDM formalism. The probability density of the proton at a position r_p in the electronic state *i* is given by $\langle r_p | \hat{\sigma}_{ii}(t) | r_p \rangle$ where $\hat{\sigma}_{ii}(t) = \langle i | \hat{\sigma}(t) | i \rangle$. In the previous subsection, the RDM equations of motion were expressed in the electron-proton vibronic basis. We can express the proton probability density $\sigma^{(r)}(r_p, t)$ at a position r_p for the donor electronic state in terms of the diagonal and off-diagonal RDM elements:

$$\begin{aligned} \sigma^{(r)}(r_p,t) &= \langle r_p | \hat{\sigma}_{rr}(t) | r_p \rangle \\ &= \sum_{\mu} |\chi^{\rm I}_{\mu}(r_p)|^2 \sigma_{r\mu,r\mu}(t) \\ &+ \sum_{\mu \neq \mu'} \chi^{\rm I}_{\mu}(r_p) \chi^{\rm I}_{\mu'}(r_p) \sigma_{r\mu,r\mu'}(t). \end{aligned}$$
(25)

Similarly, the proton probability density $\sigma^{(k)}(r_p, t)$ at a position r_p for the acceptor electronic state is

$$\sigma^{(k)}(r_p,t) = \langle r_p | \hat{\sigma}_{kk}(t) | r_p \rangle = \sum_{\nu} |\chi^{\mathrm{II}}_{\nu}(r_p)|^2 \sigma_{k\nu,k\nu}(t).$$
(26)

The proton probability density for the donor state has contributions from the coherences because of the nonzero offdiagonal RDM elements at zero time. The off-diagonal RDM elements for the acceptor electronic state are initially zero and remain zero at all times.

The equations of motion for the off-diagonal RDM elements of the donor electronic state are given by 82

$$\sigma_{r\mu,r\mu'}(t) = \sigma_{r\mu,r\mu'}(0) \exp\{-i\omega_{r\mu,r\mu'}t - \gamma_{r\mu,r\mu'}t\},\qquad(27)$$

where the frequencies are $\omega_{r\mu,r\mu'} = E^{I}_{\mu} - E^{I}_{\mu'}$ and the dephasing rate coefficients are

$$\gamma_{r\mu,r\mu'} = \sum_{\alpha} \left(\Gamma^+_{r\mu,k\alpha,k\alpha,r\mu} + \Gamma^-_{r\mu',k\alpha,k\alpha,r\mu'} \right), \tag{28}$$

with

$$\Gamma_{r\mu,k\alpha,k\alpha,r\mu}^{+} = \frac{1}{\hbar^{2}} |V_{rk}|^{2} |\langle \chi_{\alpha}^{\mathrm{II}} | \chi_{\mu}^{\mathrm{I}} \rangle|^{2} \\ \times \int_{0}^{\infty} d\tau e^{i(\epsilon_{r} - \epsilon_{k} + E_{\mu}^{\mathrm{I}} - E_{\alpha}^{\mathrm{II}})\tau/\hbar} \langle e^{\hat{v}(\tau)} e^{-\hat{v}(0)} \rangle,$$

$$\Gamma_{r\mu',k\alpha,k\alpha,r\mu'}^{-} = \frac{1}{\hbar^{2}} |V_{rk}|^{2} |\langle \chi_{\alpha}^{\mathrm{II}} | \chi_{\mu'}^{\mathrm{I}} \rangle|^{2} \\ \times \int_{0}^{\infty} d\tau e^{-i(\epsilon_{r} - \epsilon_{k} + E_{\mu'}^{\mathrm{I}} - E_{\alpha}^{\mathrm{II}})\tau/\hbar} \langle e^{\hat{v}(\tau)} e^{-\hat{v}(0)} \rangle^{*}.$$

$$(29)$$

To facilitate the calculation of the proton probability density, we use the high-temperature approximation for the bath correlation function in Eq. (18), which can therefore be expressed in terms of the solvent reorganization energy λ_s :

$$\langle e^{\hat{v}(\tau)}e^{-\hat{v}(0)}\rangle = \exp\left\{-\frac{\lambda_s\tau^2}{\hbar^2\beta} - \frac{i\tau\lambda_s}{\hbar}\right\}.$$
(30)

With this approximation, the Redfield tensor elements in Eq. (29) and the transition probability elements in Eq. (16) can be evaluated analytically, thereby simplifying the numerical propagation of the equations of motion for both the offdiagonal and the diagonal RDM elements given in Eqs. (27) and (15), respectively. For the model systems studied, the evolution of these equations of motion using the approximate bath correlation function given in Eq. (30) leads to very similar electronic state population dynamics as obtained with the exact bath correlation function given in Eqs. (19) and (22).

III. MODEL CALCULATIONS

In this section, we use the RDM approach outlined in the previous section to study the dynamics of photoinduced homogeneous PCET. The calculations of the PCET dynamics were performed for four different models with the parameters of the proton potentials and energy bias between the electronic states given in Table I. The proton potentials $U^0(r_p)$, $U^{I}(r_p)$, and $U^{II}(r_p)$ corresponding to the ground, donor, and acceptor states, respectively, were chosen to be harmonic potentials with frequencies ω^0 , ω^{I} , and ω^{II} , and minima located at r_p^0 , r_p^{I} , and r_p^{II} . The displacement between the minima of the proton potentials $U^{I}(r_p)$ and $U^{II}(r_p)$ for the donor and acceptor electronic states was chosen to be 0.5 Å, corresponding to a typical proton transfer reaction at a hydrogen-bonded interface.

The parameters of the harmonic bath were chosen to represent a homogeneous environment with a strong systembath coupling given by $\eta = 12\pi$ and a high bath cutoff frequency of $\omega_c = 600 \text{ cm}^{-1}$. These parameters correspond to a bath with relaxation time $\tau_c \sim 1/\omega_c \approx 55$ fs and reorganiza-

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TABLE I. Parameters for the four models of photoinduced PCET.

	Model A	Model B	Model C	Model D
$\overline{\epsilon_r - \epsilon_k}$ (eV)	1	0	0	0
r_p^0 (Å)	-0.5	-0.5	-0.5	-0.15
r_{p}^{I} (Å)	0	0	0	0
r_{p}^{II} (Å)	-0.5	-0.5	-0.5	-0.5
ω^0 (cm ⁻¹) ^a	3000	3000	2500	3000
$\omega^{\rm I}~({\rm cm^{-1}})^{\rm a}$	3000	3000	3000	3000
ω^{II} (cm ⁻¹) ^a	3000	3000	2500	3000

^aThe frequencies are given here for hydrogen with mass 1 amu. Note that the frequencies will change for deuterium, which has a mass of 2 amu, because the force constants of the harmonic potentials remain fixed.

tion energy $\lambda_s = \hbar \eta \omega_c / \pi = 0.892$ eV. These parameters ensure that the bath relaxes to equilibrium on a faster timescale than the electronic state population decay of the system due to PCET. Thus, the underlying assumptions of our theoretical formalism, such as the Markovian and the stationary Redfield tensor approximations, are valid for these parameters. In addition, the secular approximation, which relies on fast solvent relaxation and strong system-bath coupling, is valid for these parameters. As discussed above, we found that the results calculated in the high-temperature limit are nearly identical to those calculated without this approximation. In this regime, the bath impacts the population decay primarily through the reorganization energy, which depends on the product of the bath cutoff frequency and the system-bath coupling, and the results are qualitatively similar for smaller bath cutoff frequencies with the same reorganization energy. The calculations were performed at 300 K, and the electronic coupling was chosen to be $V_{rk}=0.03$ eV, which is small compared to the characteristic proton vibrational frequency of $\sim 3000 \text{ cm}^{-1} = 0.37 \text{ eV}.$

The RDM elements were evolved in time by employing two different numerical approaches. In both approaches, the master equation given in Eq. (15) was cast in the form

$$\frac{\partial}{\partial t}\vec{P}(t) = \mathbf{L}\vec{P}(t), \qquad (31)$$

where the relaxation matrix **L** is composed of the transition probabilities $W_{r\mu,k\nu}$ and $W_{k\nu,r\mu}$, and $\vec{P}(t)$ is the column vector with entries $\sigma_{r\mu,r\mu}(t)$ and $\sigma_{k\nu,k\nu}(t)$. In the first approach, the solution to the above equation was calculated as⁴²

$$\vec{P}(t) = e^{\mathbf{L}t}\vec{P}(0) = \mathbf{J}e^{\mathbf{D}t}\mathbf{J}^{-1}\vec{P}(0),$$
(32)

where **J** is the eigenvector matrix and **D** is the eigenvalue matrix of the diagonalizable matrix **L**. Thus, the population of each state obtained from this approach is a sum of exponential terms. In the second approach, we employed an efficient numerical method based on the modified Arnoldi iteration scheme.⁸⁸ The results of the two approaches are identical for the model systems studied.

The number of proton vibrational states required for convergence is determined by the temperature, the frequencies of the proton harmonic potentials, and the displacement between the donor and acceptor proton potentials. For each model, we included enough vibrational states to ensure that the donor state population is unity at zero time and that the trace of the RDM is conserved during the time propagation. For models A, B, and D, we included 30 vibrational states for hydrogen and 35 vibrational states for deuterium for each electronic state. For model C, we included 40 states for hydrogen and 45 states for deuterium for each electronic state.

In the following subsections, we present the results of our calculations and analyses of the PCET dynamics for the four model systems. In all cases, the initial state is prepared by vertical photoexcitation from the ground vibrational state on the ground electronic surface to a coherent vibrational mixture in the donor electronic state. We analyze the dynamics of relaxation from this initial nonstationary state to the equilibrium distribution in the donor and acceptor states. Although this model does not include direct coupling between the proton vibrational mode and the bath, the proton vibrational population can redistribute to lower proton vibrational states by an indirect mechanism involving nonadiabatic transitions between the donor and acceptor vibronic states. Our analysis focuses on the origin of the hydrogen/deuterium (H/D) isotope effect on the dynamics of the electronic state populations. We also examine the role of various system parameters in determining the key dynamical characteristics of the PCET process. The parameters considered include the electronic bias between the donor and acceptor states, the frequencies of the proton potentials, and the displacement of the initial proton wavepacket from the donor state minimum.

A. Model with electronic energy bias

In this subsection, we consider model A for the exergonic PCET process with the energy bias $\epsilon_r - \epsilon_k = 1.0$ eV between the donor and acceptor electronic states. The frequencies of the ground, donor, and acceptor state proton potentials are identical, as given in Table I. The minima of the ground and acceptor electronic states U^0 and U^{II} are chosen to be the same and are shifted -0.5 Å from the minimum of the donor state potential U^{I} , which is at $r_{p}=0$. Thus, the initial proton vibrational wavepacket created in the donor electronic state by vertical photoexcitation from the ground state is localized around the ground state potential minimum, which is identical to the acceptor state potential minimum. In the donor electronic state, this initial proton wavepacket is represented by a nonstationary coherent mixture with the vibrational populations distributed among the higher vibrational states. Figure 2 depicts the proton vibrational population distribution of the donor state at t=0 ps, t=5 ps, and t=200 ps. At zero time, this distribution has a maximum at μ =11 for H and μ =15 for D, as shown in Fig. 2(a).

During the initial stage of the time evolution, the proton vibrational wavepacket in the donor state exhibits coherent oscillations with a time period of ~11 fs for H and ~15 fs for D. The coherent oscillatory motion of the H and D wavepackets in the donor state during the initial stage of the dynamics is depicted in Fig. 3. At zero time, the proton wavepacket is localized around r_p =-0.5 Å, the minimum of the acceptor potential U^{II} . At short times, the proton wavepacket oscillates about r_p =0, the minimum of the donor potential U^{I} , with an amplitude of 0.5 Å, as determined by the initial wavepacket. During this initial stage, the proton populations



FIG. 2. Population distribution for the H (red) and D (blue) vibrational states in the donor electronic state at (a) t=0 ps, (b) t=5 ps, and (c) t=200 ps for model A.

in the donor state are distributed among highly excited proton vibrational states, as shown in Fig. 2(a). Note that the coherent oscillations are absent in the acceptor state because only the diagonal RDM elements contribute to the acceptor proton probability density, as indicated by Eq. (26).

Figure 4 depicts the time evolution of the proton vibrational wavepacket for the donor and acceptor states for both hydrogen and deuterium on a longer timescale. In this figure, the wavepacket is plotted at time steps corresponding to every ten periods of the coherent oscillations shown in Fig. 3, so only the proton wavepacket at the left turning point is illustrated. Figure 4 indicates that the amplitude of the coherent oscillations is initially 0.5 Å but decreases over time as the coherent oscillations are damped due to vibrational relaxation. As discussed above, the vibrational relaxation process in this model occurs through the indirect mechanism of energy dissipation from the proton vibrational mode into the bath via nonadiabatic PCET transitions. This relaxation process leads to redistribution of the vibrational populations to the lower proton vibrational states, as well as the damping of the coherent oscillations.

By ~ 5 ps, the population maximum has shifted down to the first and second excited vibrational states, as shown in Fig. 2(b). In addition, the amplitude of the coherent oscillations has been damped considerably, so the wavepacket is oscillating over a smaller region closer to the minimum of the donor potential $U^{\rm I}$, as shown in Fig. 4(a). After a dephasing time of ~ 10 ps for H and ~ 15 ps for D, the coherent oscillations in the donor state are completely damped, and



FIG. 3. Coherent oscillations of the (a) H and (b) D vibrational wavepacket in the donor electronic state for model A.



FIG. 4. Time evolution of the vibrational wavepacket for (a) H in the donor state, (b) H in the acceptor state, (c) D in the donor state, and (d) D in the acceptor state for model A. The wavepacket was plotted with a time step of $10 \times 2\pi/\omega^{I}$, so only the oscillating wavepacket at the left turning point is depicted.

the donor wavepacket is localized around the $U^{\rm I}$ minimum. Figure 4 illustrates that the proton wavepackets in the donor and acceptor states are localized around the minima of their potentials $U^{\rm I}$ and $U^{\rm II}$, respectively, at ~10 ps for H and ~15 ps for D. By 200 ps, the vibrational population in the donor state relaxes to the ground vibrational state for H and to the ground and first excited states for D, as illustrated in Fig. 2(c). In the long time limit, the population of the donor state is virtually zero, and the entire population is in the acceptor state with the acceptor proton wavepacket localized around the minimum of the acceptor potential $U^{\rm II}$.

This analysis of the PCET dynamics provides a qualitative explanation for the H/D isotope effect on the dynamics of the populations of the donor and acceptor electronic states. Figure 5(a) depicts the population dynamics of the donor electronic state for H and D. The population dynamics exhibits virtually no H/D isotope effect during the initial time period of \sim 5 ps. During this initial stage, the proton vibrational population in the donor state is distributed in higher vibrational states, and the left turning point of the



FIG. 5. Population decay of the donor electronic state for H (red solid line) and D (blue dashed line) for (a) model A, (b) model B, (c) model C, and (d) model D.

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oscillating donor proton wavepacket is near the minimum of the acceptor potential U^{II} . By ~5 ps, the proton vibrational population in the donor state is concentrated in lower vibrational states due to the indirect vibrational relaxation process, and the donor proton wavepacket is more localized near the minimum of the donor potential U^{I} . As a result, a significant H/D isotope effect on the population decay of the donor acceptor state is evident beyond ~5 ps.

Figure 5(a) illustrates that the population of the donor electronic state decreases with time. Since the electronic energy bias significantly favors the acceptor electronic state at equilibrium, the population of the donor state reaches a very small value and the entire population accumulates in the acceptor state on the nanosecond timescale. Note that these equilibrium populations are the same for H and D because the frequencies of the harmonic potentials U^{I} and U^{II} are identical.

B. Symmetric model

In this subsection, we consider model B, which is identical to model A described in the previous subsection except that the donor and acceptor electronic levels are degenerate (i.e., $\epsilon_r - \epsilon_k = 0$), corresponding to a symmetric PCET system. The initial dynamics of the nonstationary proton vibrational wavepacket in the donor electronic state exhibits qualitatively similar behavior to that exhibited in model A. As in model A, initially the proton vibrational population in the donor state is distributed among highly excited proton vibrational states. Moreover, the proton vibrational wavepacket in the donor state exhibits the coherent oscillatory motion with a time period of ~ 11 fs for H and ~ 15 fs for D and an initial amplitude of 0.5 Å, with dephasing time of ~ 10 ps for H and ~ 15 ps for D. By ~ 5 ps, the proton vibrational population has relaxed to lower vibrational states, and the proton wavepacket in the donor state is more localized near the donor potential minimum U^{I} . In contrast with model A, however, the electronic state populations of the donor and acceptor states in model B reach thermal equilibrium (i.e., $P_r = P_k = 0.5$) on the much shorter time scale of ~6 ps, although the vibrational relaxation processes continue and the individual populations of the vibrational states and coherences still change beyond this time.

The time evolution of the electronic state populations does not exhibit a significant H/D isotope effect for the entire time of relaxation to equilibrium for this model, as illustrated in Fig. 5(b). As in model A, the H/D isotope effect is not observed during the first ~ 5 ps of the time evolution because the proton vibrational population in the donor state is distributed among the higher vibrational states, and the left turning point of the oscillating donor proton wavepacket is near the acceptor potential minimum. The H/D isotope effect is expected to be observed only after the proton vibrational population relaxes to the lower vibrational states and the wavepacket in the donor state is localized near the donor potential minimum. By that time, however, the electronic state populations are already near their equilibrium values of 0.5, which are the same for H and D. As a result, no H/D isotope effect on the electronic state population dynamics is observed. Furthermore, in contrast with model A, the equilibrium populations of the donor and acceptor states are equal. At equilibrium, the donor proton wavepacket is localized around the U^{I} minimum, and the acceptor proton wavepacket is localized around the U^{II} minimum.

C. Model with different proton frequencies in the donor and acceptor states

In this subsection, we consider model C, which is identical to model B except that the proton vibrational frequencies in the ground and acceptor electronic states are chosen to be 2500 cm⁻¹, while the frequency in the donor state remains 3000 cm⁻¹. This model is not symmetric, so the equilibrium population of the donor electronic state is different for H and D. Specifically, in the case of zero electronic energy bias, the equilibrium population of the donor electronic state is $P_r^{eq} = Z^{I}/(Z^I + Z^{II})$, where Z^I and Z^{II} are the vibrational partition functions for harmonic oscillators with frequencies ω^I and ω^{II} , respectively. For model C, the equilibrium populations of the donor electronic state are $P_r^{eq} = 0.23$ and $P_r^{eq} = 0.29$ for H and D, respectively. In the other models studied, $Z^I = Z^{II}$ because $\omega^I = \omega^{II}$, and the equilibrium populations are the same for H and D.

Figure 5(c) depicts the time evolution of the donor electronic state population decay for H and D. The population decay exhibits a distinct isotope effect after ~ 5 ps of evolution. As in models A and B, at ~ 5 ps the proton vibrational population in the donor state becomes concentrated in lower vibrational states and the donor proton vibrational wavepacket begins to localize near the donor U^{I} minimum. The total population relaxation time for model C is on the nanosecond timescale. Note that thermal equilibrium of the electronic state populations for model B is attained on a similar timescale as vibrational relaxation to the lower proton vibrational states, whereas thermal equilibrium of the electronic state populations for models A and C is attained on the longer nanosecond timescale. As a result, an isotope effect on the population decay is observed for models A and C but not for model B. A qualitative difference between model C and the other models is that the equilibrium populations are isotope dependent for model C due to the different frequencies of the donor and acceptor proton potentials.

D. Model with the initial proton wavepacket localized near the donor potential minimum

In this subsection, we consider model D, which is the same as model B except the minimum of the ground state harmonic potential U^0 is at -0.15 Å, while the minimum of the donor state potential U^{I} remains at zero and the minimum of the acceptor state potential U^{II} remains at -0.5 Å. Thus, the nonstationary proton vibrational wavepacket in the donor state is localized closer to the minimum of the donor state potential U^{I} at zero time. As a result, the initial proton vibrational population distribution in the donor state, as depicted in Fig. 6, is predominantly concentrated in the ground and lowest two excited vibrational states for both H and D. As in the other models, the proton vibrational wavepacket in the donor state exhibits coherent oscillations with a



FIG. 6. Population distribution for the H (red) and D (blue) vibrational states in the donor electronic state at t=0 ps for model D.

period of ~ 11 fs for H and ~ 15 fs for D. For model D, however, the initial amplitude of the coherent oscillations of the proton wavepacket is only 0.15 Å, so the oscillations are restricted to a region near the donor potential minimum even in the early stages of the dynamics. This behavior is illustrated in Fig. 7, which depicts the time evolution of the proton vibrational wavepackets in the donor and acceptor electronic states, where only the oscillating wavepacket at the left turning point is illustrated for clarity.

In contrast with the other models, the coherent components of the initial wavepacket for model D arise predominantly from the lower proton vibrational states. Due to small proton vibrational wave function overlaps between the lower vibrational states, the dephasing rate coefficients given in Eq. (28) are very small, so the vibrational coherences have a long lifetime. Thus, the coherent oscillations of the proton wave function are damped on a timescale of hundreds of picoseconds. In this case, the indirect vibrational relaxation mechanism involving nonadiabatic transitions is insufficient to damp out the vibrational coherent oscillations. These oscillations might damp out faster if the model included an additional dissipation mechanism, such as direct coupling of the proton vibrational mode to the bath. Since the amplitude of the coherent oscillations is relatively small, however, this effect is not expected to significantly impact the overall population dynamics.



FIG. 7. Time evolution of the vibrational wavepacket for (a) H in the donor state, (b) H in the acceptor state, (c) D in the donor state, and (d) D in the acceptor state for model D. The wavepacket was plotted with a time step of $10 \times 2\pi/\omega^{I}$, so only the oscillating wavepacket at the left turning point is depicted. The wavepackets in (b) and (d) are scaled by a factor of 5 relative to those in (a) and (c).

Figure 5(d) depicts the population decay of the donor electronic state for H and D. In contrast with the other models, the H/D isotope effect is strongly pronounced from the start of the dynamical process. This early manifestation of the H/D isotope effect in model D is due to the initial distribution of the proton vibrational population among the lower vibrational states for the donor state and the localization of the initial donor vibrational wavepacket near the minimum of the donor state potential U^{l} . As illustrated in Fig. 7, the small amplitude of the coherent oscillations ensures that the donor proton vibrational wavepacket remains close to the minimum of the donor state potential at all times.

IV. CONCLUDING REMARKS

In this paper, we presented a model Hamiltonian for describing photoinduced homogeneous PCET reactions and developed a theoretical framework for studying the dynamics of the relaxation processes following photoexcitation. The model Hamiltonian includes shifted harmonic proton potentials for the donor and acceptor electronic states, as well as linear coupling between the electronic states and the harmonic bath. A canonical transformation of the model Hamiltonian enables the investigation of models with strong system-bath coupling. We derived the equations of motion for the diagonal and off-diagonal RDM elements in the electron-proton vibronic basis using a series of well-defined approximations. Numerical propagation of these equations of motion allows a detailed analysis of the proton vibrational dynamics, as well as the dynamics of the electronic state populations.

Our application of this theoretical formalism to four model systems provides insight into the fundamental physical principles underlying these types of processes. In these models, the initial nonequilibrium state was prepared by vertical photoexcitation from the ground vibrational state on the ground electronic surface to a coherent vibrational mixture in the donor electronic state. Following photoexcitation, this nonstationary state relaxes to the equilibrium distributions in the donor and acceptor states via dynamical processes arising from nonadiabatic transitions between the donor and acceptor vibronic states concurrent with energy dissipation to the bath modes. During the initial stage of the dynamics, the proton vibrational wavepacket in the donor state exhibits coherent oscillations with an amplitude dictated by the location of the initial proton wavepacket relative to the minimum of the donor state proton potential. When the initial proton wavepacket is shifted significantly from the minimum of the donor state proton potential, the proton vibrational population in the donor state is distributed among the higher vibrational states during this initial stage. Vibrational relaxation processes lead to redistribution of the vibrational populations to the lower proton vibrational states, as well as the damping of the coherent oscillations. After a certain dephasing time, the coherent oscillations in the donor state are completely damped, and the donor and acceptor proton wavepackets are localized around their respective proton potential minima. Eventually the overall populations of the electronic states reach thermal equilibrium.

Analysis of the proton wavepacket dynamics provides a qualitative explanation for the H/D isotope effect on the dynamics of the donor and acceptor populations. During the initial stage, when the proton vibrational population in the donor state is distributed in higher vibrational states and the proton wavepacket is oscillating with large amplitude, the electronic state population dynamics exhibit virtually no H/D isotope effect. The physical basis for this absence of H/D isotope effect is that the donor proton wavepacket has relatively high probability in the region of the acceptor proton potential minimum for both hydrogen and deuterium. After the proton vibrational population in the donor state becomes concentrated in the lower vibrational states and the donor proton wavepacket becomes more localized near the minimum of the donor potential, a significant H/D isotope effect on the electronic state population dynamics is exhibited. In this stage, the donor proton wavepacket has very low probability in the region of the acceptor proton potential minimum, and the difference between the probabilities of hydrogen and deuterium tunneling is significant.

This study leads to experimentally testable predictions concerning the H/D isotope effect on the dynamics of the electronic state populations. This theoretical model predicts that the H/D isotope effect on the population decay will not be observed when the timescale for attaining thermal equilibrium of the electronic state populations is similar to the timescale of proton vibrational relaxation. Conversely, when thermal equilibrium of the electronic state populations is attained on the longer nanosecond timescale, the H/D isotope effect is predicted to become evident on the picosecond timescale, after vibrational relaxation to the lower proton vibrational states. The relative timescales of these relaxation processes can be controlled by altering the energy bias between the donor and acceptor electronic states and the frequencies of the donor and acceptor proton potentials. Moreover, the final equilibrium populations of the electronic states will exhibit an H/D isotope effect when the frequencies of the proton potentials are different for the donor and acceptor states. In addition, the onset of the H/D isotope effect can be controlled by altering the initial photoexcited wavepacket. Specifically, the H/D isotope effect will be observed earlier in the dynamical relaxation process when the initial proton wavepacket is centered closer to the minimum of the donor state proton potential.

We also extended this theoretical formalism to ultrafast photoinduced PCET at a molecule-semiconductor interface.⁸⁹ The H/D isotope effects on the electronic state populations for these types of interfacial PCET systems have been studied experimentally with ultrafast time-resolved spectroscopy.⁹⁰ Feedback between experiment and theory will assist in the further development of these types of theoretical models.

ACKNOWLEDGMENTS

We are grateful for support of this work by NSF Grant Nos. CHE-07-49646 and CHE-08-02907 for Powering the Planet: A Chemical Bonding Center in the Direct Conversion of Sunlight into Chemical Fuel.

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