

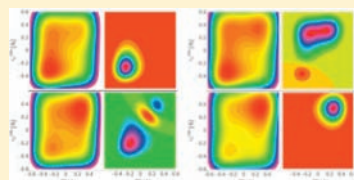
Theoretical Analysis of Proton Relays in Electrochemical Proton-Coupled Electron Transfer

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S Supporting Information

ABSTRACT: The coupling of long-range electron transfer to proton transport over multiple sites plays a vital role in many biological and chemical processes. Recently the concerted proton-coupled electron transfer (PCET) reaction in a molecule with a hydrogen-bond relay inserted between the proton donor and acceptor sites was studied electrochemically. The standard rate constants and kinetic isotope effects (KIEs) were measured experimentally for this double proton transfer system and a related single proton transfer system. In the present paper, these systems are studied theoretically using vibronically nonadiabatic rate constant expressions for electrochemical PCET. Application of this approach to proton relays requires the calculation of multidimensional proton vibrational wave functions and the incorporation of multiple proton donor–acceptor motions. The decrease in proton donor–acceptor distances due to thermal fluctuations and the contributions from excited electron–proton vibronic states play important roles in these systems. The calculated KIEs and the ratio of the standard rate constants for the single and double proton transfer systems are in agreement with the experimental data. The calculations indicate that the standard PCET rate constant is lower for the double proton transfer system because of the smaller overlap integral between the ground state reduced and oxidized proton vibrational wave functions, resulting in greater contributions from excited electron–proton vibronic states with higher free energy barriers. The theory predicts that this rate constant may be increased by modifying the molecule in a manner that decreases the equilibrium proton donor–acceptor distances or alters the molecular thermal motions to facilitate the concurrent decrease of these distances. These insights may guide the design of more efficient catalysts for energy conversion devices.



I. INTRODUCTION

The coupling of long-range electron transfer to proton transport over multiple sites plays a critical role throughout biology. These coupled processes occur in many biological systems, such as photosystem II,^{1–3} cytochrome c oxidase,^{4–7} and ribonucleotide reductase.^{8–10} The design of biomimetic systems for artificial photosynthesis and other energy conversion processes requires an understanding of the coupling of electron transfer to proton translocation over hydrogen-bonded networks. A variety of model systems have been designed to study proton-coupled electron transfer (PCET) reactions that involve the coupling of electron transfer to a single proton transfer reaction. These types of model systems have been studied experimentally and theoretically with both homogeneous and electrochemical approaches.^{11–34} PCET processes involving proton transport over multiple proton transfer sites have been studied less extensively.

Recently Costentin et al. reported the synthesis and characterization of a molecule in which a hydrogen-bond relay is inserted between the proton donor and acceptor sites in a PCET system.³⁵ This PCET process involves two proton transfers and is depicted as System II in Figure 1. In ref 35, cyclic voltammetry was used to determine the standard rate constant and the kinetic isotope effect (i.e., the ratio of the standard rate constants for hydrogen and deuterium). A major advantage of the electrochemical approach is that it provides exquisite control over the energetics by varying the overpotential. The analysis in ref 35

indicates that the electron and two proton transfer reactions occur by a concerted mechanism without any stable intermediates. For comparison, the analogous process involving a single proton transfer, depicted as System I in Figure 1, was also studied. The standard rate constant was found to be a factor of 16 greater for System I than for System II, and the kinetic isotope effect (KIE) was determined to be 1.7 and 2.4 for Systems I and II, respectively. The results were interpreted using an expression for the standard rate constant corresponding to adiabatic electron transfer. The smaller standard rate constant for System II was explained in terms of a larger inner-sphere reorganization energy, which involves movements of the heavy atoms. This interpretation provides useful insight but does not account for the nuclear quantum effects, such as hydrogen tunneling, and does not explain the experimentally observed KIE.³⁶

In this paper, we provide an alternative interpretation of these experimental data within the framework of a vibronically nonadiabatic rate constant expression that includes the nuclear quantum effects of the transferring proton(s).^{31,37–39} To examine these specific systems, we devised a theoretical approach for calculating the heterogeneous rate constants of electrochemical PCET reactions involving proton relays. This treatment requires the calculation of multidimensional proton vibrational wave

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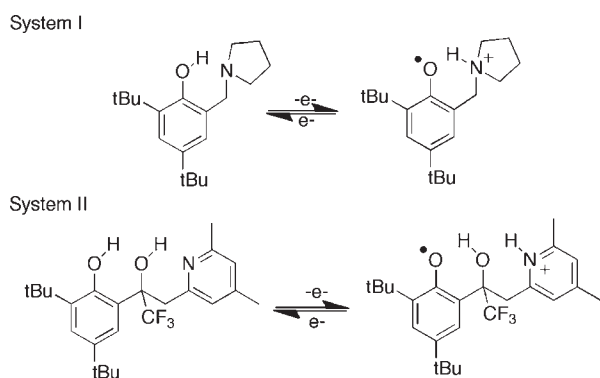


Figure 1. Electrochemical PCET reaction for System I, which involves single proton transfer, and System II, which involves double proton transfer.

functions representing the transferring protons,⁴⁰ the incorporation of the proton donor–acceptor motions for all proton transfer reactions, and the inclusion of excited electron–proton vibronic states. Our calculated KIEs and ratio of standard rate constants for Systems I and II are in qualitative agreement with the experimental data. The calculations indicate that the rate constant is lower for System II than for System I because of the smaller overlap integral between the ground state reduced and oxidized proton vibrational wave functions for the double proton transfer system, resulting in greater contributions from excited vibronic states with higher free energy barriers. In addition, our theoretical calculations provide insight into the fundamental physical principles underlying these types of processes and thus may assist in the design of more efficient proton relay systems in artificial photosynthesis, solar cells, and electrochemical fuel cells. Note that increasing the efficiency of proton relays could be detrimental in some biological systems involving proton pumps.^{7,9} In such cases, the objective may be to maintain the appropriate balance of relative rates among the various steps in the reaction mechanism.

An outline of this paper is as follows. In Section IIA, we present the expressions for the anodic and cathodic rate constants. In Section IIB, we summarize the computational strategy for calculating the standard rate constants, with particular emphasis on the methodology for including the proton donor–acceptor motions and for generating the proton potential energy surfaces and corresponding proton vibrational wave functions. The results of our calculations for the experimentally studied systems as well as an analysis of the underlying physical concepts are presented in Section III. The conclusions of this study are presented in Section IV.

II. METHODS

A. Heterogeneous Rate Constant Expressions. The electrochemical experiments indicate that the proton transfers concertedly with the electron transfer between the molecule and the electrode, as supported by the measurement of a KIE for the standard rate constant determined with cyclic voltammetry.^{35,41} Thus, the electrochemical PCET process of interest is the transfer of an electron between a solvated solute complex and an electrode, along with the simultaneous transfer of one or more protons within the solute complex. This process can be described in terms of nonadiabatic transitions between the electron–proton vibronic states of the reduced solute complex and the oxidized solute complex.^{42,43} Each electron–proton vibronic state is

expressed as the product of a diabatic electronic state representing the reduced or oxidized solute complex and an associated proton vibrational state. Expressions for the heterogeneous anodic and cathodic rate constants have been derived in various limits.^{42,43}

For fixed proton donor–acceptor distance R , the anodic and cathodic nonadiabatic rate constants are^{42–44}

$$k_a(\eta; R) = \sum_{\mu, \nu} P_\mu \frac{(V^{\text{el}} S_{\mu\nu})^2}{\beta^2 \hbar} \sqrt{\frac{\pi}{k_B T \lambda}} \rho_M \int d\varepsilon [1 - f(\varepsilon)] \exp\left[-\frac{(\Delta \tilde{U}_{\mu\nu} + \varepsilon - e\eta + \lambda)^2}{4\lambda k_B T}\right] \quad (1)$$

$$k_c(\eta; R) = \sum_{\mu, \nu} P_\nu \frac{(V^{\text{el}} S_{\mu\nu})^2}{\beta^2 \hbar} \sqrt{\frac{\pi}{k_B T \lambda}} \rho_M \int d\varepsilon f(\varepsilon) \exp\left[-\frac{(-\Delta \tilde{U}_{\mu\nu} - \varepsilon + e\eta + \lambda)^2}{4\lambda k_B T}\right] \quad (2)$$

where the summations are over vibronic states μ of the reduced solute complex and vibronic states ν of the oxidized solute complex. P_μ and P_ν are the Boltzmann probabilities for the vibronic states μ and ν , respectively, $f(\varepsilon)$ is the Fermi distribution function for the electronic states in the electrode, and ρ_M is the density of states at the Fermi level, which is assumed to be a constant in the vicinity of the Fermi level. Moreover, V^{el} is the electronic coupling, β^2 is a parameter of magnitude $\sim 1\text{--}3 \text{ \AA}^{-1}$ representing the exponential decay of the electronic coupling with the distance between the molecule and the electrode, $S_{\mu\nu}$ is the overlap integral between the proton vibrational wave functions μ and ν , and λ is the reorganization energy. The quantity $\Delta \tilde{U}_{\mu\nu}$ is defined to be $\Delta \tilde{U}_{\mu\nu} = \Delta U_{\mu\nu} + k_B T \ln(Q^{\text{II}}/Q^{\text{I}})$, where $\Delta U_{\mu\nu}$ is the energy difference between vibronic states ν and μ , and Q^{I} and Q^{II} are the total partition functions of the reduced and oxidized solute complexes, respectively, in bulk solution. Note that the term $k_B T \ln(Q^{\text{II}}/Q^{\text{I}})$ is required to satisfy detailed balance⁴² and becomes simply $-\Delta U_{00}$ for the special case of harmonic proton potentials with identical frequencies (i.e., the effect of this term for this special case is that the vibronic energies are calculated relative to their respective ground states). In eqs 1 and 2, the overlap integral $S_{\mu\nu}$ and $\Delta \tilde{U}_{\mu\nu}$ depend on the proton donor–acceptor distance R . For simplicity, we assume that all other quantities are independent of R .

Previously we derived rate constant expressions including the effects of the proton donor–acceptor motion,^{42,43} but these expressions are based on the assumption that the overlap integral $S_{\mu\nu}$ decreases exponentially with the proton donor–acceptor distance R . Unfortunately, for many systems this assumption is not valid, so these expressions are not applicable. In these cases, the effects of the R mode can be included by thermally averaging over the proton donor–acceptor distances:^{45,46}

$$k_a(\eta) = \int P_a(R) k_a(\eta; R) dR \quad (3)$$

$$k_c(\eta) = \int P_c(R) k_c(\eta; R) dR \quad (4)$$

where $P_a(R)$ and $P_c(R)$ are probability distribution functions for the anodic and cathodic processes, respectively. The harmonic probability distributions are of the form:

$$P(R) = \frac{\exp[-k_{\text{eff}}(R - \bar{R})^2/2k_B T]}{\int_{-\infty}^{\infty} \exp[-k_{\text{eff}}(R - \bar{R})^2/2k_B T] dR} \quad (5)$$

These distributions depend on an effective force constant k_{eff} and equilibrium proton donor–acceptor distance R , which may be different for the reduced and oxidized complexes. Anharmonic probability distributions can be determined numerically by calculating normalized Boltzmann probabilities obtained from the energies of the relevant structures. Note that this thermal averaging procedure is based on the Born–Oppenheimer separation of the proton motion and the slower proton donor–acceptor motion.

In this paper, the standard rate constant is defined to be the heterogeneous rate constant for the overpotential at which the anodic and cathodic rate constants are equal, assuming equal concentrations of the reduced and oxidized solute complexes. Our previously derived analytical expressions satisfy detailed balance, and the anodic and cathodic rate constants are identical at zero overpotential.^{42,43} These analytical expressions were derived for models with fixed proton donor–acceptor distances (i.e., eqs 1 and 2) or for models in which the overlap integrals are assumed to decrease exponentially with this distance. The more general expressions in eqs 3 and 4, however, are not necessarily identical for zero overpotential because the probability distribution functions may be different for the anodic and cathodic processes, and the overlap integrals are not assumed to exhibit any specific type of dependence on the proton donor–acceptor distance or to be the same for the anodic and cathodic processes. For example, the equilibrium proton donor–acceptor distances and associated frequencies may differ for the reduced and oxidized complexes, and the shapes of the proton potentials may change significantly with the proton donor–acceptor distance. In this case, the standard rate constant can be calculated by determining the overpotential $\eta = \eta_0$ at which the anodic and cathodic rate constants are equal (i.e., numerically determining the appropriate constant shift of the formal electrode potential for a specified system). This constant shift effectively accounts for differences in the total partition functions of the systems corresponding to the anodic and cathodic processes.

This scheme can be extended to proton relay systems. For a double proton transfer system, the proton potential energy surfaces and corresponding proton vibrational wave functions depend on the coordinates of both protons. For simplicity, each proton may be assumed to move in one dimension, and the overlap integral $S_{\mu\nu}$ is calculated between the initial and final two-dimensional proton vibrational wave functions. Typically the two proton coordinates are strongly coupled, so the two-dimensional proton vibrational wave functions are not simply products of two one-dimensional proton vibrational wave functions. In addition, the anodic and cathodic rate constants in eqs 1 and 2 depend on both proton donor–acceptor distances R_1 and R_2 (i.e., $S_{\mu\nu}$ and $\Delta\tilde{U}_{\mu\nu}$ depend on both proton donor–acceptor distances). In addition, the probability distribution functions $P_a(R_1, R_2)$ and $P_c(R_1, R_2)$ also depend on both distances, and the integration in eqs 3 and 4 is over both coordinates, neglecting kinetic coupling. In general, these probability distribution functions are not simply the product of two one-dimensional probability distribution functions.

B. Calculation of Heterogeneous Rate Constants. Calculation of the standard heterogeneous rate constants and corresponding KIEs requires the proton potential energy surfaces, which provide $S_{\mu\nu}$, $P_{\mu\nu}$ and $\Delta\tilde{U}_{\mu\nu}$, and the probability distribution functions for both the anodic and cathodic processes. The solvent reorganization energy can be calculated from dielectric continuum models. The density of states, electronic coupling, and parameter β' are required for the calculation of absolute rate constants but not the KIEs or the ratio of rate constants for related systems. In this section, we describe the computational methods used to calculate the required input quantities for the application of this theory to Systems I and II.

1. Proton Donor–Acceptor Motion. To describe the proton donor–acceptor motion for single proton transfer, we express the deviation of the proton donor–acceptor distance R from its equilibrium value as a linear combination of normal mode coordinates. The

expansion coefficients c_i are determined by projecting the normal mode vectors onto the proton donor–acceptor axis. Evaluation of the time correlation function of the deviation δR , assuming the classical harmonic oscillator form, leads to an expression for an effective force constant k_{eff} that includes contributions from all normal modes:

$$k_{\text{eff}} = \left[\sum_{i=1}^{3N} \frac{c_i^2}{k_i} \right]^{-1} \quad (6)$$

where the summation is over all normal modes with force constants k_i . The derivation of this expression is provided in Supporting Information. This effective force constant corresponds to the second derivative of the electronic energy curve calculated by displacing the proton donor–acceptor distance from equilibrium and performing a constrained geometry optimization, where the displaced proton donor–acceptor distance is fixed. In other words, this effective force constant corresponds to the harmonic probability distribution function along R for which all other degrees of freedom respond instantaneously to changes in R .

A similar procedure can be performed for the double proton transfer system. In this case, however, we express deviations of both proton donor–acceptor distances R_1 and R_2 from their equilibrium values in terms of the normal mode coordinates with expansion coefficients $c_i^{(1)}$ and $c_i^{(2)}$, respectively. A single effective force constant for the double proton transfer system can be derived by following an analogous procedure for the time correlation function of $\delta R_1 + \delta R_2$. The resulting effective force constant is

$$k_{\text{eff}} = \left[\sum_{i=1}^{3N} \frac{(c_i^{(1)})^2 + (c_i^{(2)})^2 + 2c_i^{(1)}c_i^{(2)}}{k_i} \right]^{-1} \quad (7)$$

Our implementation includes only the symmetric mode, where both R_1 and R_2 increase or decrease concurrently by the same amount. In this case, the effective force constant corresponds to the second derivative of the electronic energy curve calculated by displacing both proton donor–acceptor distances from their equilibrium distances by the same amount and performing a constrained geometry optimization, where both displaced proton donor–acceptor distances are fixed. In other words, this effective force constant corresponds to the harmonic probability distribution function for which all other degrees of freedom respond instantaneously to changes in R_1 and R_2 . In this treatment, we include only the impact of the symmetric mode because we expect this mode to exert the greatest influence on the rate constants for concerted double proton transfer. In general, however, other modes will also contribute and could be included. The derivations of the effective force constant expressions, along with the expansion coefficients for Systems I and II, are provided in Supporting Information.

2. Proton Potential Energy Surfaces. We generated the reduced and oxidized structures to be used for calculating the anodic and cathodic rate constants, respectively, by performing a series of constrained geometry optimizations. For System I, we generated a series of reduced structures obtained by displacing R from its equilibrium value in the optimized structure by increments of 0.05 Å and performing constrained optimizations with R fixed. We performed the same procedure to obtain a series of oxidized structures. For System II, a similar procedure was performed in which both proton donor–acceptor distances were increased or decreased from their equilibrium values by the same amount. In this approach, the reduced structure moves along an effective mode (i.e., a linear combination of normal modes) corresponding to the instantaneous response of all other modes to changes in the proton donor–acceptor distance(s) for the anodic process. The oxidized structure moves along an analogous effective mode for the cathodic process.

We generated the proton potentials for the anodic and cathodic rate constants of System I using the following procedure. For the anodic rate constant, we removed an electron from the reduced system, transferred

the proton to the acceptor, and optimized the hydrogen position with all other nuclei fixed for each reduced structure generated along R . The proton coordinate axis was defined to be the line that connects the hydrogen position in its reduced and oxidized state for each reduced structure. To calculate the proton potentials, we performed a series of single-point energy calculations, where the hydrogen was moved along a grid spanning this proton coordinate axis, for both the reduced and oxidized states. Using these proton potentials, we calculated the proton vibrational wave functions for the reduced and oxidized states and determined the overlaps and other quantities required to calculate the anodic rate constant. The proton potentials and associated proton vibrational wave functions for the cathodic rate constants were generated in an analogous manner, using the oxidized structures generated along R .

We generated the two-dimensional proton potentials for the anodic and cathodic rate constants of System II using a similar procedure. In this case, however, both protons were on their donors for the reduced state, and both protons were on their acceptors for the oxidized state. One proton coordinate axis was defined to be the line connecting the first hydrogen in its optimized positions on its donor and acceptor for the reduced and oxidized states, and a second proton coordinate axis was defined analogously for the second hydrogen. A two-dimensional grid was defined in terms of these two axes, and a series of single-point energy calculations, where the two hydrogen atoms were moved to sample all points on the two-dimensional grid, was performed for both the reduced and oxidized states. Subsequently, the two-dimensional proton vibrational wave functions were calculated for the reduced and oxidized states. This procedure was used to generate the proton potentials and the associated wave functions of the reduced and oxidized states for both the anodic and cathodic rate constants (i.e., for both the reduced and oxidized structures).

We used both harmonic and anharmonic probability distributions in our calculations. The harmonic probability distribution function was based on the effective force constant defined in eqs 6 and 7 for the single and double proton transfer systems, respectively. The anharmonic probability distribution was determined by calculating the energies of the structures generated along this effective mode (i.e., the structures obtained from the series of constrained optimizations) and using these energies to calculate normalized Boltzmann probabilities. The numerical integration in eqs 3 and 4 was performed over the coordinate δR , the deviation of the proton donor–acceptor distance from its equilibrium value, for the single proton transfer system and over the coordinate $2\delta R$, the sum of equal deviations of both proton donor–acceptor distances from their equilibrium values, for the double proton transfer system.

3. Summary of Strategy for Calculations.

- Step 1: Optimize the reduced and oxidized structures. Generate a set of reduced structures along R for the anodic process and a set of oxidized structures along R for the cathodic process.
- Step 2: Determine the proton coordinate axes by optimizing the hydrogen position for the oxidized state of the reduced structures and the reduced state of the oxidized structures.
- Step 3: Generate the proton potentials for the reduced and oxidized states of each reduced structure. Generate the proton potentials for the reduced and oxidized states of each oxidized structure.
- Step 4: Calculate the proton vibrational wave functions corresponding to the proton potentials generated in Step 3 and use them to determine the overlap integrals, vibronic state energy differences, and Boltzmann probabilities of the vibronic states.
- Step 5: Calculate the anodic rate constant using eq 1 for each R value (based on the reduced structures). Calculate the cathodic rate constant using eq 2 for each R value (based on the oxidized structures).
- Step 6: Calculate the total anodic rate constant as a function of η using the results from Step 5, together with the anodic probability

distribution function, by numerically integrating eq 3. Calculate the total cathodic rate constant as a function of η analogously using eq 4.

- Step 7: Determine the value of $\eta = \eta_0$ at which the total anodic and cathodic rate constants are equal. The resulting rate constant is the standard rate constant.

4. *Computational Details.* We generated the structures and calculated the associated proton potential energy surfaces by performing density functional theory (DFT) calculations with the B3LYP functional^{47,48} and the 6-31G(d,p) basis set^{49–52} using Gaussian03.⁵³ For these calculations, the *t*Bu groups in Figure 1 were replaced by methyl groups. As shown in Supporting Information, the proton potentials were nearly identical using other density functionals, such as M06-2X,⁵⁴ and larger basis sets, and the methyl substitution does not significantly impact the results. All geometry optimizations were performed in the gas phase. We also performed frequency analyses in the gas phase to determine the effective force constants along the proton donor–acceptor coordinate(s). We generated the proton potentials using the polarized continuum model (PCM)^{55,56} with the universal force field (UFF)⁵⁷ to include the effects of the acetonitrile solvent. For the single proton transfer system, the proton potential energy curves were calculated by moving the hydrogen along a one-dimensional grid and performing single-point energy calculations with all other nuclei fixed. For the double proton transfer system, the two-dimensional proton potential energy surfaces were generated analogously, where each hydrogen moved along a one-dimensional grid. In both cases, the proton vibrational wave functions were calculated with the discrete variable representation method, neglecting the kinetic coupling between the two proton coordinates for the calculation of the two-dimensional proton vibrational wave functions.⁵⁸

5. *Reorganization Energies.* We calculated the solvent reorganization energy using the procedure described in ref 59. In our implementation, the solute complex was placed in a spherical cavity on the surface of the electrode. The diameter of the cavity was estimated as the distance between the two atoms furthest apart in the optimized reduced structure. The resulting cavity radii were 5.06 and 5.18 Å for Systems I and II, respectively. The dielectric constant of the solvent surrounding the spherical cavity was chosen to correspond to acetonitrile. Using this procedure, the solvent reorganization energy was calculated to be 8.5 and 8.7 kcal/mol for Systems I and II, respectively. This treatment may slightly underestimate the solvent reorganization energy because the molecule may not be located directly on the electrode. As shown in Supporting Information, the KIEs and the ratio of the rate constants do not depend strongly on the solvent reorganization energy within the range of 8–12 kcal/mol. For consistency, we used a value of 8.5 kcal/mol for all calculations presented in this paper. Note that the analysis in ref 35 used a solvent reorganization energy of 18.0 kcal/mol, as calculated from a dielectric continuum model for homogeneous charge transfer reactions.⁶⁰ The solvent reorganization energy is expected to be approximately twice as large for homogeneous as for electrochemical electron transfer reactions,⁶¹ so these two calculated values are consistent.

We also calculated the inner-sphere (i.e., solute) reorganization energy as $(E_{\text{red state}}^{\text{ox geom}} - E_{\text{red state}}^{\text{red geom}} + E_{\text{ox state}}^{\text{red geom}} - E_{\text{ox state}}^{\text{ox geom}})/2$, where the reduced and oxidized states correspond to the neutral and cationic molecules, respectively. The second (fourth) term was calculated at the optimized reduced (oxidized) geometry. The first (third) term was calculated at the optimized oxidized (reduced) geometry with the transferring hydrogen(s) optimized for the reduced (oxidized) state. Using this expression, we calculated inner-sphere reorganization energies of 9.7 and 10.0 kcal/mol for Systems I and II, respectively. Thus, both the inner- and outer-sphere reorganization energies are nearly identical for Systems I and II. Note that the constrained geometry optimization procedure for each proton donor–acceptor distance implicitly includes some effects of inner-sphere reorganization, so we do not include it explicitly in our rate constant calculations.

Table 1. KIEs for Systems I and II and Ratio of Standard Rate Constants, k_I/k_{II} , Obtained Experimentally³⁵ and Calculated with the Harmonic and Anharmonic Probability Distribution Functions

	system I KIE	system II KIE	k_I/k_{II}
experiment	1.7	2.4	16
harmonic	1.9	2.2	15
anharmonic	1.9	1.9	13

In ref 35 a value for the total reorganization was obtained by fitting the experimental temperature-dependent kinetic data to a single exponential rate constant expression. The resulting values were 24.5 and 31.4 kcal/mol for Systems I and II, respectively. These values cannot be directly compared to the values used in our calculations because the rate constant expressions in eqs 1 and 2 are linear combinations of exponential terms arising from summing over the reactant and product vibronic states. For comparison to the experimental temperature dependence, we calculated the standard rate constant at 294, 303, and 312 K, fit an Arrhenius plot of these three points to a line, and determined an effective reorganization energy by equating the Arrhenius slope to $\lambda_{\text{eff}}/4R$, neglecting the temperature dependence of the prefactor. The resulting effective reorganization energies are 17 and 25 kcal/mol for Systems I and II, respectively. These values are in qualitative but not quantitative agreement with the values obtained from the slightly different temperature dependence analysis in ref 35. In general, fitting the results from a multiexponential expression to a single-exponential expression should be viewed in only a qualitative manner. As shown in Supporting Information, the KIEs and the ratio of the rate constants are relatively insensitive to the reorganization energy.

6. Limitations of the Computational Strategy. The computational strategy described above invokes numerous approximations. A significant approximation is the treatment of the motion of each proton in one dimension. Another significant approximation for the double proton transfer system is the reduction of the two proton donor–acceptor motions to a single symmetric motion. For concerted proton transfers, the symmetric motion is expected to exert the greatest effect on the rate constant because both proton donor–acceptor distances must decrease for the protons to transfer simultaneously. Nevertheless, in some cases the antisymmetric mode may need to be included. Furthermore, the generation of the structures through constrained optimizations relies on the assumption that the other modes respond instantaneously to the proton donor–acceptor motion. Since the other modes correspond mainly to minor changes in bond lengths and angles for these systems, this assumption appears to be physically reasonable, but for certain types of systems, additional modes may need to be treated separately. In an alternative scheme, the reduced and oxidized structures could be generated by following the dominant normal mode coordinate (i.e., the one that contributes the most to the symmetric motion of the proton donor–acceptor distances). Thus, a variety of strategies could be implemented. Finally, the electronic structure methods also have errors associated with them, requiring benchmarking studies as provided in Supporting Information.

III. RESULTS

The calculated KIEs for Systems I and II, along with the ratio of the standard rate constants for these two systems, are presented in Table 1. The results are provided for calculations using both the harmonic and anharmonic probability distribution functions along the proton donor–acceptor mode. All of the calculated KIEs are within 0.5 of the experimental values.³⁵ The better agreement of the results obtained using the harmonic

Table 2. Proton Donor–Acceptor Distances and Force Constants of Dominant Normal Mode and Effective Mode Corresponding to Proton Donor–Acceptor Motion for Optimized Reduced and Oxidized Structures of Systems I and II

	R_{OO} (Å)	R_{ON} (Å)	k_{dom}^a (au)	k_{eff}^b (au)
I - reduced	—	2.71	0.0157	0.0275
I - oxidized	—	2.63	0.0218	0.0336
II - reduced	2.60	2.68	0.0221	0.0156
II - oxidized	2.52	2.64	0.0257	0.0184

^a Force constant of normal mode with dominant contribution to proton donor–acceptor motion for System I and with greatest contribution to symmetric proton donor–acceptor motion for System II. ^b Effective force constant corresponding to proton donor–acceptor motion for System I, using eq 6, and to symmetric proton donor–acceptor motion for System II, using eq 7, including contributions from all normal modes.

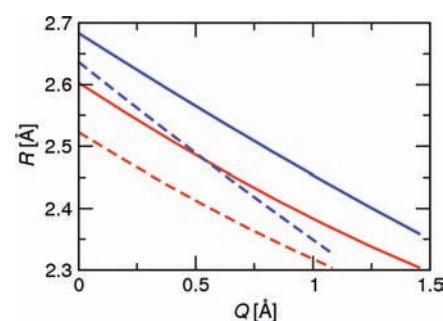


Figure 2. Dependence of the proton donor–acceptor distances R_{OO} (red) and R_{ON} (blue) on the normal mode coordinate with the dominant contribution to the symmetric proton motion for the optimized reduced (solid line) and oxidized (dashed line) structures of System II.

probability distribution function with the experimental data may be due to the errors associated with the DFT B3LYP energies of structures far from equilibrium in the anharmonic treatment. With the harmonic treatment, the calculated KIEs of 1.9 and 2.2 for Systems I and II agree well with the experimental values of 1.7 and 2.4, respectively, and the calculated ratio of the standard rate constants, k_I/k_{II} , of 15 is in excellent agreement with the experimental value of 16.

Previously the moderate KIEs were interpreted as indicating that these PCET reactions are adiabatic, but our analysis indicates that such moderate KIEs are obtained within a nonadiabatic treatment. The qualitative agreement between theory and experiment suggests that this nonadiabatic treatment adequately describes these processes. Moreover, the small magnitudes of the overlap integrals between the ground state reduced and oxidized proton vibrational wave functions at the equilibrium geometries indicate that the ground state vibronic coupling (i.e., the product of the electronic coupling and the overlap integral) is much smaller than the thermal energy $k_B T$ for physically reasonable values of the electronic coupling. This observation implies that a ground state vibronically adiabatic treatment would not be suitable for these systems. The remainder of this section focuses on analyzing the underlying physical principles for these types of electrochemical PCET processes, particularly the proton relay system.

We examined the structures and normal modes of the reduced and oxidized systems. The proton donor–acceptor distances for the optimized reduced and oxidized structures for Systems I and II

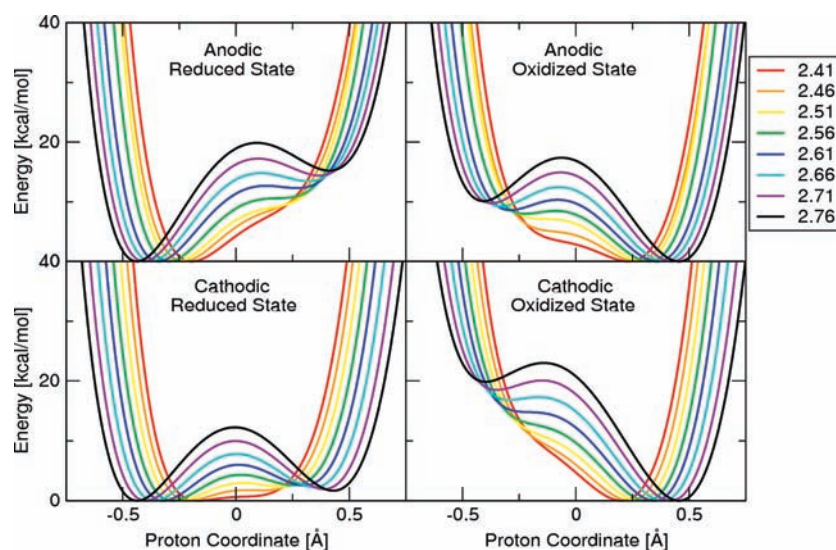


Figure 3. Proton potential energy curves for the reduced and oxidized states of the anodic and cathodic processes for System I. The proton potential energy curves are depicted as functions of the proton coordinate for a series of structures generated from constrained optimizations at fixed proton donor–acceptor distances. The fixed O–N distances are listed in the color key. The anodic and cathodic potential energy curves were calculated from different structures corresponding to constrained optimizations of reduced and oxidized structures, respectively.

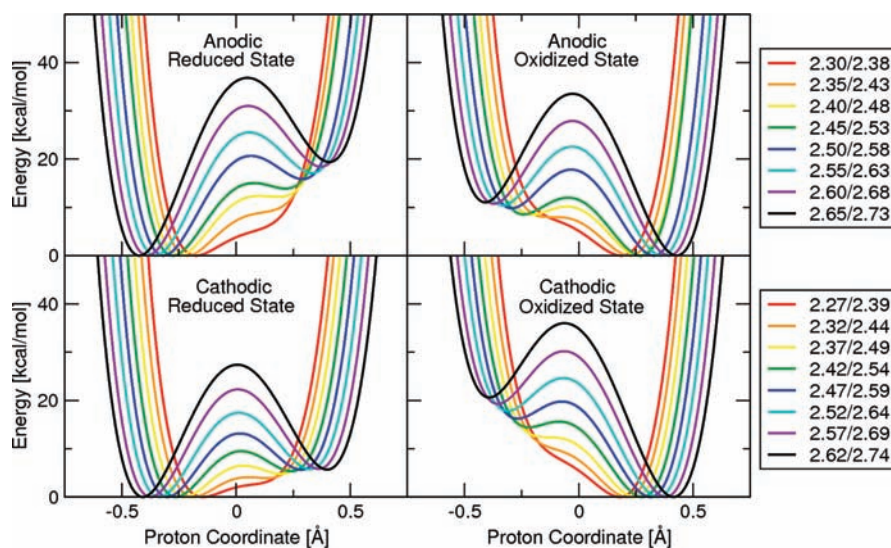


Figure 4. Diagonal slices of the proton potential energy surfaces for the reduced and oxidized states of the anodic and cathodic processes for System II. The proton potential energy curves are depicted as functions of a proton coordinate corresponding to both transferring protons moving together along their respective axes for a series of structures generated from constrained optimizations at fixed proton donor–acceptor distances. The fixed O–O/O–N distances are listed in the color key for the anodic (top) and cathodic (bottom) processes. The anodic and cathodic potential energy curves were calculated from different structures corresponding to constrained optimizations of reduced and oxidized structures, respectively.

are provided in Table 2. In all cases, the proton donor–acceptor distances are smaller for the oxidized structure than for the reduced structure. For System II, the O–N distance is greater than the O–O distance in both the reduced and oxidized structures. Table 2 also provides the force constant of the normal mode with the dominant contribution to the proton donor–acceptor motion for the reduced and oxidized structures. For System II, this dominant normal mode has the greatest contribution to the symmetric proton donor–acceptor motion, where both distances increase and decrease together. The dependence of the proton donor–acceptor distances on this dominant normal mode coordinate for System II is illustrated in Figure 2.

In addition, Table 2 provides the effective force constant for the proton donor–acceptor motion(s) including contributions from all normal modes. For System II, this effective force constant corresponds to the symmetric proton donor–acceptor motion. This symmetric motion is expected to be the most important mode for this system because experiments indicate that both protons transfer simultaneously,³⁵ requiring the concerted decrease of both proton donor–acceptor distances.

As illustrated in Figures 3 and 4, the shape of the proton potential energy surface depends strongly on the proton donor–acceptor distance(s). Figure 3 depicts the one-dimensional proton potential energy curves for System I. The anodic and cathodic

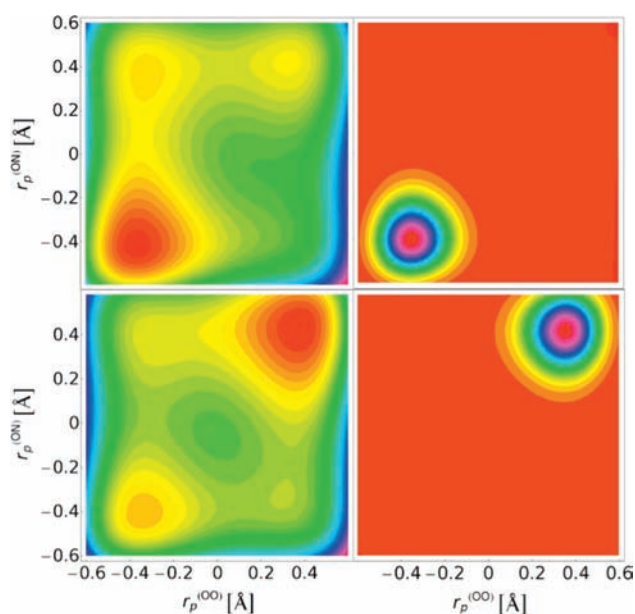


Figure 5. Two-dimensional proton potential energy surfaces (left panels) and ground state hydrogen vibrational wave functions (right panels) for the reduced (top panels) and oxidized (lower panels) states of System II at the optimized reduced geometry. The coordinate $r_p^{(OO)}$ represents the position of the hydrogen transferring between the two oxygens, and the coordinate $r_p^{(ON)}$ represents the position of the hydrogen transferring between the oxygen and nitrogen, where each hydrogen moves along a one-dimensional axis. In each panel, the progression of colors from the maximum to the minimum value is as follows: magenta, blue, green, yellow, orange, and red.

potential energy curves were calculated from different structures corresponding to constrained optimizations of reduced and oxidized structures, respectively. Figure 4 depicts a one-dimensional slice along the diagonal of the two-dimensional proton potential energy surfaces for System II. This slice corresponds to the two protons moving simultaneously by the same amounts. Figure 5 depicts the two-dimensional proton potential energy surfaces for the reduced and oxidized states at the optimized reduced geometry as well as the associated ground state proton vibrational wave functions. Note that the proton vibrational wave functions and all input quantities for calculating the rate constants were determined from the full two-dimensional potential energy surfaces. The diagonal slices in Figure 4 are depicted only to illustrate the impact of the proton donor–acceptor distances on the proton potential energy surfaces.

The proton potential energy curves for System I are asymmetric double well potentials, where the donor well is lower in energy for the reduced state, and the acceptor well is lower in energy for the oxidized state. The presence of higher energy minima on the opposite side (i.e., the acceptor side for the reduced state and the donor side for the oxidized state) allows excited proton vibrational wave functions to become localized on the opposite side. For System II, additional higher energy minima corresponding to single proton transfer may be present. For these systems, the assumption that the overlap between the reduced and oxidized proton vibrational wave functions decreases exponentially with the proton donor–acceptor distance is not valid, and we need to use the thermally averaged procedure described above for including the proton donor–acceptor motion. Furthermore, Figures 3 and 4 illustrate that the separation

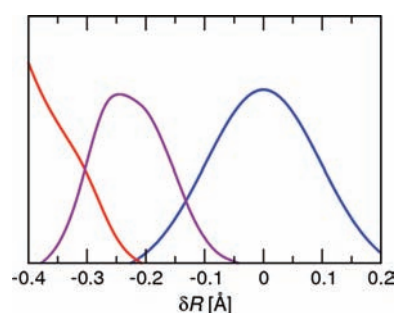


Figure 6. Harmonic probability distribution function $P_a(R)$ (blue), heterogeneous standard rate constant $k_a(\eta_0; R)$ (red), and the product of these two quantities (i.e., the integrand of $k_a(\eta_0)$) (purple) for the anodic process of System I. The quantities are depicted as functions of δR , the deviation of the proton donor–acceptor distance from its equilibrium value. The y-axis has no label because the quantities are scaled arbitrarily so they can be viewed on the same graph. The curves were obtained from a splining procedure for the discrete data points separated by 0.05 Å.

between the two minima and the potential energy barrier decrease significantly as the proton donor–acceptor distance decreases. Thus, the overlap integrals between the reduced and oxidized proton vibrational wave functions and the relative energies among the vibronic states will depend strongly on the proton donor–acceptor distance(s).

The dominant proton donor–acceptor distance in the PCET process is determined by a balance between the probability distribution function, which has a maximum at the equilibrium distance, and the heterogeneous rate constant, which typically increases as the proton donor–acceptor distance decreases relative to its equilibrium value. Figure 6 depicts the probability distribution function $P_a(R)$ for the harmonic treatment, the rate constant $k_a(\eta_0; R)$ calculated from eq 1, and the product of these two quantities (i.e., the integrand of the total anodic rate constant $k_a(\eta_0)$ given in eq 3) for System I. This figure illustrates that the dominant proton donor–acceptor distance (i.e., the distance with the greatest contribution to the total anodic rate constant) is ~ 0.25 Å smaller than the equilibrium proton donor–acceptor distance because of the dramatic increase in the rate constant as this distance decreases. The complete set of these plots for the anodic and cathodic processes of Systems I and II with both the harmonic and anharmonic treatments of the probability distribution functions is provided in Supporting Information. In general, the dominant proton donor–acceptor distance(s) are different for the anodic and cathodic processes and for hydrogen and deuterium transfer.

Table 3 provides an analysis of the main contributions to the rate constants at the dominant proton donor–acceptor distance(s) for Systems I and II with the harmonic probability distribution function. The analogous table for the anharmonic probability distribution function is provided in Supporting Information. Figures 7 and 8 depict the corresponding proton potential energy surfaces and proton vibrational wave functions. The contribution of each pair of reduced/oxidized vibronic states is determined predominantly by a balance between the free energy barrier and the overlap integral between the reduced and oxidized proton vibrational wave functions. The anodic and cathodic free energy barriers are determined from the exponential terms of the form $\exp[-\Delta G^\ddagger/k_B T]$ in eqs 1 and 2, respectively. For all of the cases considered here, the Boltzmann probability favors the ground

Table 3. Analysis of Main Contributions to Anodic and Cathodic Standard Rate Constants for Dominant Proton Donor–Acceptor Distance(s) for Systems I and II with Hydrogen and Deuterium^a

	μ/ν	$\Delta U_{\mu\nu}$ (kcal/mol)	$\Delta G_{\mu\nu}^{\ddagger}$ (kcal/mol)	$S_{\mu\nu}^2$	% contribution
I - anodic - H ^b	0/0	0.0	1.00	0.043	62
	0/1	3.71	2.68	0.46	36
I - cathodic - H ^c	1/0	-1.59	4.81	0.89	99
I - anodic - D ^d	0/0	0.0	0.89	0.0041	14
	0/1	3.07	2.16	0.15	54
	0/2	5.03	3.26	0.47	27
I - cathodic - D ^e	1/0	-1.52	5.02	0.93	100
II - anodic - H ^f	0/0	0.0	0.86	0.0002	10
	0/1	4.95	3.15	0.018	23
	0/3	7.39	4.82	0.59	53
II - cathodic - H ^g	1/0	-2.55	5.89	0.35	80
	2/0	-3.84	7.01	0.46	19
II - anodic - D ^h	0/5	8.05	5.37	0.64	77
II - cathodic - D ⁱ	1/0	-4.00	7.10	0.84	98

^a μ and ν correspond to the reduced and oxidized vibronic states, respectively; $\Delta U_{\mu\nu}$ is the energy difference between oxidized vibronic state ν and reduced vibronic state μ ; $\Delta G_{\mu\nu}^{\ddagger}$ is the free energy barrier for the anodic or cathodic rate constant given by eqs 1 or 2, respectively, for $\varepsilon = 0$; $S_{\mu\nu}$ is the overlap integral between reduced proton vibrational wave function μ and oxidized proton vibrational wave function ν ; and % contribution is the percentage contribution to the overall standard rate constant, where contributions less than 10% are excluded. All results in this table were obtained with the harmonic probability distribution function; analogous results for the anharmonic probability distribution function are given in Table S3 of Supporting Information. ^b $R_{\text{ON}} = 2.46 \text{ \AA}$, $\eta_0 = 0.1156 \text{ V}$. ^c $R_{\text{ON}} = 2.66 \text{ \AA}$, $\eta_0 = 0.1156 \text{ V}$. ^d $R_{\text{ON}} = 2.46 \text{ \AA}$, $\eta_0 = 0.1305 \text{ V}$. ^e $R_{\text{ON}} = 2.71 \text{ \AA}$, $\eta_0 = 0.1305 \text{ V}$. ^f $R_{\text{OO}} = 2.45 \text{ \AA}$, $R_{\text{ON}} = 2.53 \text{ \AA}$, $\eta_0 = 0.1340 \text{ V}$. ^g $R_{\text{OO}} = 2.47 \text{ \AA}$, $R_{\text{ON}} = 2.59 \text{ \AA}$, $\eta_0 = 0.1340 \text{ V}$. ^h $R_{\text{OO}} = 2.45 \text{ \AA}$, $R_{\text{ON}} = 2.53 \text{ \AA}$, $\eta_0 = 0.1317 \text{ V}$. ⁱ $R_{\text{OO}} = 2.52 \text{ \AA}$, $R_{\text{ON}} = 2.64 \text{ \AA}$, $\eta_0 = 0.1317 \text{ V}$.

reduced and oxidized vibronic states for the anodic and cathodic processes, respectively. In other words, the initial state is typically the ground vibronic state for these cases. In this regime, the free energy barrier increases as the quantum number of the final state (i.e., the oxidized vibronic state for the anodic process and the reduced vibronic state for the cathodic process) increases.

An analysis of System I clarifies the competing factors in these types of processes. For the anodic process with hydrogen, the main contributions arise from the 0/0 and 0/1 pairs of reduced/oxidized vibronic states. The 0/0 pair has a lower free energy barrier, while the 0/1 pair has a greater overlap integral because the excited proton vibrational wave function is more delocalized, as illustrated in Figure 7a. For the cathodic process with hydrogen, the main contribution arises from the 1/0 pair of reduced/oxidized vibronic states because the first excited proton vibrational wave function for the reduced state is localized on the acceptor side and therefore has a large overlap of nearly unity with the ground proton vibrational wave function for the oxidized state, as depicted in Figure 7b. Similar trends are observed for deuterium, although the relative contributions of the pairs of vibronic states for the anodic process are different.

System II exhibits qualitatively similar behavior, but the two-dimensional nature of the proton vibrational wave functions leads to the participation of higher excited vibronic states. In particular, the overlap between two-dimensional proton vibrational wave functions localized on opposite sides is typically smaller than the overlap between the one-dimensional counterparts, thereby favoring higher excited vibrational states with delocalized character for the double proton transfer system. The smaller overlap integral for two-dimensional wave functions can be understood qualitatively in the context of a pair of shifted two-dimensional harmonic oscillator potentials with no coupling between the two coordinates. Since the two-dimensional harmonic oscillator wave functions are simply products of two

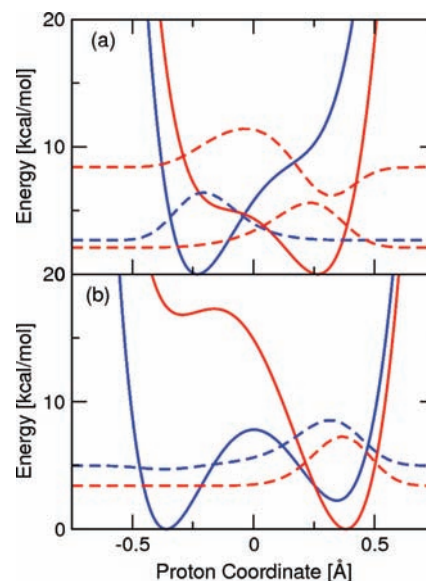


Figure 7. Proton potential energy curves and associated hydrogen vibrational wave functions for the reduced (blue) and oxidized (red) states of System I. These data are depicted for the main contributing pairs of reduced/oxidized vibronic states at the dominant proton donor–acceptor distance, as determined with the harmonic treatment of the probability distribution function: (a) the 0/0 and 0/1 pairs of reduced/oxidized vibronic states at $R_{\text{ON}} = 2.46 \text{ \AA}$ for the anodic process and (b) the 1/0 pair of reduced/oxidized vibronic states at $R_{\text{ON}} = 2.66 \text{ \AA}$ for the cathodic process.

one-dimensional harmonic oscillator wave functions, the overlap integral between the two-dimensional ground state wave functions is the square of the overlap integral between the corresponding one-dimensional ground state wave functions. Thus,

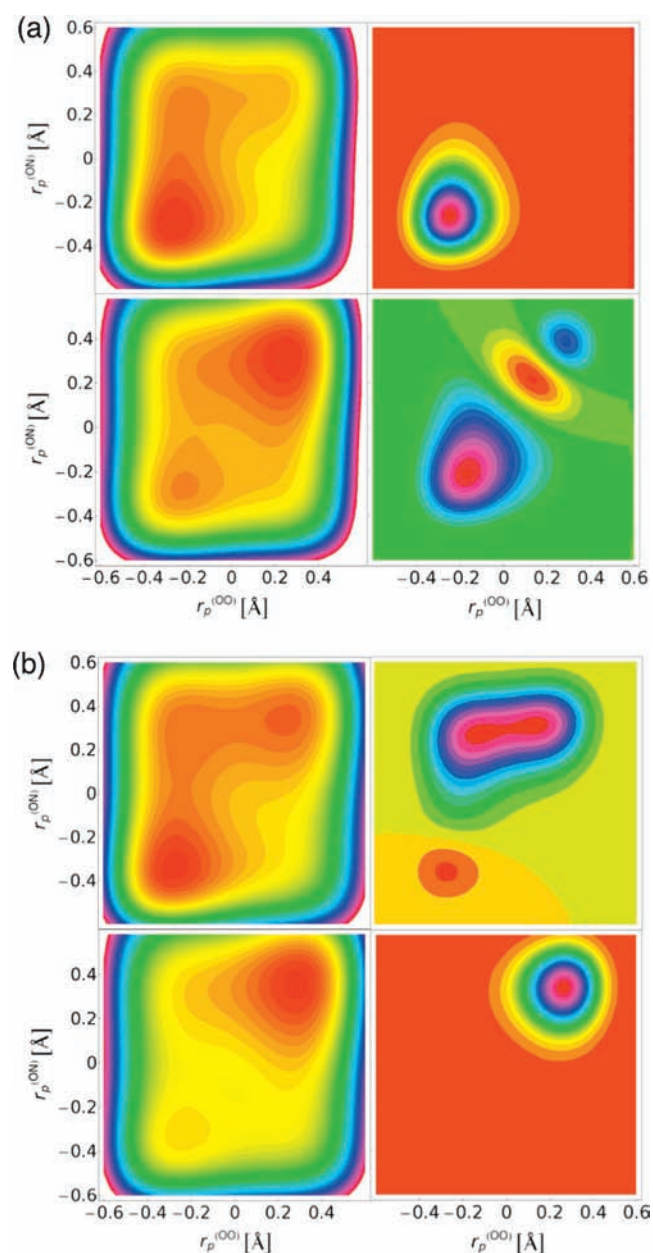


Figure 8. Two-dimensional proton potential energy surfaces (left panels) and associated hydrogen vibrational wave functions (right panels) for the reduced (top panels) and oxidized (lower panels) states of System II. These data are depicted for the main contributing pairs of reduced/oxidized vibronic states at the dominant proton donor–acceptor distances, as determined with the harmonic treatment of the probability distribution function: (a) the 0/3 pair of reduced/oxidized vibronic states at $R_{OO} = 2.45$ Å and $R_{ON} = 2.53$ Å for the anodic process and (b) the 1/0 pair of reduced/oxidized vibronic states at $R_{OO} = 2.47$ Å and $R_{ON} = 2.59$ Å for the cathodic process. In each panel, the progression of colors from the maximum to the minimum value is as follows: magenta, blue, green, yellow, orange, and red.

the two-dimensional overlap integral will be smaller than the corresponding one-dimensional overlap integral. As illustrated in Figure 5, the two proton coordinates are strongly coupled and hence are not separable in System II, but the qualitative trends concerning the overlap integrals for the one- and two-dimensional ground state proton vibrational wave functions are

still observed. For example, at the optimized reduced geometries, $S_{00}^2(\text{I-H}) = 7.4 \times 10^{-7}$, $S_{00}^2(\text{I-D}) = 3.1 \times 10^{-10}$, $S_{00}^2(\text{II-H}) = 3.0 \times 10^{-12}$, and $S_{00}^2(\text{II-D}) = 1.1 \times 10^{-18}$ for Systems I and II with H and D.

These values of the overlap integrals for the optimized reduced geometries of Systems I and II also confirm the importance of including excited vibronic states and proton donor–acceptor motion. If the excited vibronic states and proton donor–acceptor motion were not included in the theoretical treatment, and all parameters except the overlap integrals were assumed to be the same for Systems I and II and for hydrogen and deuterium, then the ratio of the rate constants could be estimated as the ratio of the squares of the overlap integrals between the ground reduced and oxidized proton vibrational wave functions.⁵¹ Based on the values of the overlap integrals given above, the KIE for System I would be $\sim 10^3$, the KIE for System II would be $\sim 10^6$, and the ratio of the standard rate constants, k_I/k_{II} , for hydrogen would be $\sim 10^5$. These estimates are qualitatively incorrect, emphasizing the importance of including excited vibronic states and the proton donor–acceptor motion, thereby increasing the overlap integrals of the dominant contributions to the overall rate constant. Larger overlap integrals of the dominant contributions typically lead to more moderate KIEs³¹ and allow proton relay systems to have similar (or even larger) rate constants compared to those of related single proton transfer systems.

Figure 8 depicts the two-dimensional proton potential energy surfaces and associated hydrogen vibrational wave functions for the dominant contributions to the anodic and cathodic processes of System II. Note that each two-dimensional hydrogen vibrational wave function is labeled with a single quantum number. In Figure 8a, the 0/3 pair of reduced/oxidized vibronic states, with an overlap integral of 0.59, is depicted for the anodic process. In Figure 8b, the 1/0 pair of reduced/oxidized vibronic states, with an overlap integral of 0.35, is depicted for the cathodic process. For comparison, recall that $S_{00}^2 = 3.0 \times 10^{-12}$ for the ground state hydrogen vibrational wave functions at the optimized reduced geometry of System II. From a visual perspective, the overlaps between the reduced and oxidized proton vibrational wave functions depicted in Figure 8 are substantially greater than the overlap between the ground state proton vibrational wave functions depicted in Figure 5 for the optimized reduced geometry.

Analysis of the data provided in Table 3 enables a comparison between Systems I and II. For the anodic process with hydrogen, S_{00}^2 in System I is approximately the same magnitude as S_{01}^2 in System II, and S_{01}^2 in System I is approximately the same magnitude as S_{03}^2 in System II. For the anodic process with deuterium, S_{02}^2 in System I is approximately the same magnitude as S_{05}^2 in System II. In all of these cases, System II must access higher excited vibronic states to achieve similar overlap integrals. Qualitatively, the cathodic process for System II is similar to that for System I, where the 1/0 pair of reduced/oxidized vibronic states is the dominant contributor for both hydrogen and deuterium because of localization of the first excited two-dimensional proton vibrational wave function for the reduced state on the acceptor side, as depicted in Figure 8b. For the cathodic process with hydrogen, S_{10}^2 in System I is approximately twice the magnitude of both S_{10}^2 and S_{20}^2 in System II. For the cathodic process with deuterium, the magnitude of S_{10}^2 is slightly greater for System I than for System II. As for the anodic process, System II accesses vibronic states with greater free energy barriers, leading to a lower rate constant for System II than for System I.

IV. CONCLUSIONS

In this paper, we identified key physical characteristics of electrochemical PCET reactions involving proton relays and devised a theoretical treatment of these processes. We found that the coordinates of the transferring protons are strongly coupled and are not separable, thereby requiring the calculation of multidimensional proton vibrational wave functions. In addition, the proton donor–acceptor distances strongly impact the proton potential energy surfaces and the associated proton vibrational wave functions, necessitating the inclusion of the proton donor–acceptor motion for each proton transfer reaction. For concerted proton transfers, often the multiple proton donor–acceptor modes can be reduced to a single effective proton donor–acceptor mode corresponding to a symmetric motion in which all proton donor–acceptor distances decrease or increase concurrently. The excited electron–proton vibronic states play an important role in these types of processes, and the excited proton vibrational wave functions are typically delocalized or localized in a higher energy local minimum potential energy well. Moreover, the dominant proton donor–acceptor distances and contributing pairs of reduced/oxidized vibronic states may differ substantially for the anodic and cathodic processes. Both the anodic and cathodic processes must be studied to determine the standard heterogeneous rate constant.

These calculations assist in the interpretation of the experimental data. In ref 35 these systems were interpreted in the context of adiabatic electron transfer, and the smaller standard rate constant for the double proton transfer system than the single proton transfer system was attributed to a larger inner-sphere reorganization energy for the double proton transfer system.³⁶ The justification for applying the adiabatic electron transfer treatment to these systems was based on the relatively moderate KIEs. Our calculations indicate that moderate KIEs of 1.5–3.0 may arise within a nonadiabatic treatment because of significant contributions from excited electron–proton vibronic states associated with delocalized proton vibrational wave functions. According to our calculations, the smaller standard rate constant for the double proton transfer system is due to the smaller overlap integral between the ground state reduced and oxidized proton vibrational wave functions, leading to greater participation of excited vibronic states associated with higher free energy barriers. The decrease in the proton donor–acceptor distances due to thermal fluctuations and the contributions from excited electron–proton vibronic states enable this double proton transfer system to be only slightly slower than the related single proton transfer system.

These two theoretical analyses of the experimental data provide predictions that can be tested experimentally. The theoretical treatment in ref 35 predicts that the PCET rate constant of System II will be increased by maximizing the rigidity of the structure (i.e., minimizing the movements of the heavy atoms). The theoretical treatment described in the present paper predicts that the PCET rate constant will be increased by maximizing the dominant proton vibrational wave function overlap integrals. These overlap integrals could be enhanced by modifying the molecule in a manner that decreases the equilibrium proton donor–acceptor distances or alters the molecular thermal motions to facilitate the concurrent decrease of these distances. Experimentally testing these types of predictions is challenging, however, because of the complexity of

PCET processes and the difficulty associated with altering only a single property of an experimental system. Recent electrochemical experiments provide data on molecules differing from System II by the substituent at the alcohol functional carbon and methyl groups on the pyridine.⁶² Application of the present theoretical approach to these systems may provide additional insight into the balance between the hydrogen-bond accepting and donating characteristics of the central oxygen atom.

Understanding the fundamental physical principles underlying these types of model systems may assist in the design of catalysts coupling proton relays to electron transfer in electrochemical fuel cells, artificial photosynthetic systems, and solar cells. If the proton donor–acceptor distances were fixed at their equilibrium values, and only ground vibronic states contributed to the overall process, then proton relays would be expected to diminish the efficiency of PCET systems because of the smaller overlap integral between the reduced and oxidized proton vibrational wave functions. The PCET rate constant, however, is determined by a complex interplay between the overlap integral and the free energy barrier for all relevant pairs of vibronic states. In turn, these quantities and the relative contributions of the vibronic states are strongly influenced by the proton donor–acceptor distances and associated frequencies as well as the reorganization energies. The complexity of these processes prevents us from identifying a single design principle guaranteed to enhance efficiency. The general theoretical principles emerging from these types of studies, however, along with calculations focused on specific experimentally accessible systems, may guide the development of more efficient proton relay systems for energy conversion processes.

■ ASSOCIATED CONTENT

Supporting Information. Derivation of eqs 6 and 7 and normal mode expansion coefficients for Systems I and II; dependence of KIEs and ratio of standard rate constants on solvent reorganization energy; analog of Table 3 for the anharmonic probability distribution function; complete set of plots analogous to Figure 6 for the anodic and cathodic processes of Systems I and II with both harmonic and anharmonic probability distribution functions; benchmarking of basis sets and functionals for Systems I and II; full ref 53; and coordinates and energies of optimized reduced and oxidized structures of Systems I and II. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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