

Quantum-classical Liouville dynamics of proton and deuteron transfer rates in a solvated hydrogen-bonded complex

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Proton and deuteron transfer reactions in a hydrogen-bonded complex dissolved in a polar solution are studied using quantum-classical Liouville dynamics. Reactive-flux correlation functions that involve quantum-classical Liouville dynamics for species operators and quantum equilibrium sampling are used to calculate the rate constants. Adiabatic and nonadiabatic reaction rates are computed, compared, and analyzed. Large variations of the kinetic isotope effect (KIE) for this reaction have been observed in the literature, which depend on the nature of the approximate calculation used to estimate the proton and deuteron transfer rates. Our estimate of the KIE lies at the low end of the range of previously observed values, suggesting a rather small KIE for this reaction. © 2008 American Institute of Physics. [DOI: [10.1063/1.2907847](https://doi.org/10.1063/1.2907847)]

I. INTRODUCTION

Proton transfer reactions occurring in the condensed phase play an important role in many chemical and biological processes.^{1–4} Knowledge of their rates is therefore necessary for an understanding of the time scales encountered in these processes. Under many conditions the thermal de Broglie wavelength of the proton is comparable to the distance over which it transfers. Thus, a quantum mechanical rate theory which correctly describes the reactive dynamics of the proton and its coupling to an environment is required.

Since condensed phase proton transfers often take place in complex environments with very large numbers of degrees of freedom, full quantum mechanical descriptions are not computationally feasible. However, since the particles comprising the environment are often heavy, they can be modeled to a high degree of accuracy by classical mechanics. In this case, mixed quantum-classical formalisms^{5–8} that combine a quantum mechanical treatment of the proton with a classical description of the environment provide practical ways of studying proton transfer processes. Mean field^{9–11} and surface-hopping^{12–15} schemes have been constructed in this spirit. The retention of quantum coherence is a limitation of such algorithms, and approximate methods have been developed to incorporate decoherence effects.^{16–18} The approach adopted in this article, which naturally takes decoherence into account,¹⁹ is based on the quantum-classical Liouville equation,^{8,20–29} which specifies the evolution of the density matrix for a quantum mechanical subsystem coupled to a classical environment.

Quantum mechanical rates of condensed phase reactions can be determined by evaluating time correlation functions of the fluxes of reactant and product chemical species.^{30,31} The computation of such correlation functions involves sam-

pling initial conditions from quantum equilibrium distributions and quantum time evolution of chemical species operators. Both the equilibrium and dynamical parts of the calculation present challenges for applications to condensed phase systems and a number of computational schemes have been proposed to compute the structure and dynamics.^{12,32–51} Our description of the quantum dynamics is based on quantum-classical Liouville evolution^{20,52} and on approximations to the quantum equilibrium structure which incorporate nonadiabatic effects.^{51,53–56}

In this work, we study an intermolecular proton transfer reaction in a bulk polar solvent of the form $AH-B \rightleftharpoons A^- - H^+B$. The model under study, which was constructed by Azzouz and Borgis,⁵⁷ describes a hydrogen-bonded phenol (*A*) trimethylamine (*B*) complex dissolved in methyl chloride. The proton transfer rate constant and kinetic isotope effect (KIE) have been computed for this model using a wide variety of techniques.^{16,57–63} The specific forms of the interaction potentials, parameter values used, and the remaining details of the model can be found in Refs. 16, 64, and 65. In a previous work, we calculated the proton transfer rate constant for this model with the *AB* distance constrained at $R_{AB}=2.7$ Å. Here we consider the more general situation in which the complex vibrates and calculate the corresponding rate constant and KIE.

The article is organized as follows: Section II presents the expression for the time dependent reaction rate coefficient that forms the basis for the simulations. Section III outlines the techniques used to simulate the quantum-classical Liouville evolution of the species variable, describes the rare event sampling scheme used in the evaluation of the rate, and illustrates the method used to obtain the free energy surfaces. The main results of the study are presented in Sec. IV. The results are briefly discussed in Sec. V.

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The Appendix contains details of the derivation of the spectral density function, which enters into the expression for the rate constant.

II. QUANTUM-CLASSICAL RATE THEORY

The rate constant calculations are based on an expression for the time dependent rate coefficient of the proton transfer reaction $A \rightleftharpoons B$

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}} \sum_{\alpha} \sum_{\alpha' \geq \alpha} (2 - \delta_{\alpha'\alpha}) \int dX \times \text{Re} \left[N_B^{\alpha\alpha'}(X, t) W_A^{\alpha'\alpha} \left(X, \frac{i\hbar\beta}{2} \right) \right], \quad (1)$$

which is written in terms of a partial Wigner representation of the bath degrees of freedom and a representation of the protonic degrees of freedom in adiabatic states.⁵⁴ Here the bath phase space variables (coordinates and momenta, respectively) are denoted by $X = (R, P)$, n_A^{eq} is the equilibrium density of species A and $\beta = 1/k_B T$ is the inverse temperature. In this partial Wigner transform representation,⁶⁶ the Hamiltonian $\hat{H}$ of the system is $\hat{H}_W = P^2/2M + \hat{h}(R)$, where $\hat{h}(R)$ is the protonic Hamiltonian in the field of fixed bath particles with mass M . The adiabatic basis states $\{|\alpha; R\rangle\}$ are the solutions of the eigenvalue problem $\hat{h}(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$, where $\{E_\alpha\}$ are the adiabatic energies. In this expression for the rate coefficient, $N_B^{\alpha\alpha'}(X, t)$ is the time evolved species B (product) operator, while $W_A^{\alpha'\alpha}(X, i\hbar\beta/2)$ is the spectral density function that contains all information on the quantum equilibrium structure.

The solvent polarization reaction coordinate^{67,68}

$$\xi(R) \equiv \Delta E(R) = \sum_{i,a} z_a e \left(\frac{1}{|R_i^a - s|} - \frac{1}{|R_i^a - s'|} \right) \quad (2)$$

is used to monitor the progress of the proton transfer reaction. Here $z_a e$ ($e = 1.602 \times 10^{-19}$ C) is the charge on atom a , s and s' are the two positions of the proton within the AHB complex that correspond to the stable covalent and ionic configurations, respectively, and the sums run over all solvent molecules i and atoms a . Given this reaction coordinate, the species operator that characterizes the B metastable state is $\hat{N}_B = \theta(\xi(R) - \xi^\ddagger)$, where θ is the Heaviside function. The metastable A species is defined in an analogous manner. The dividing surface that separates the A and B species is located at $\xi(R) = \xi^\ddagger$. The time evolution of the species operator is assumed to be governed by quantum-classical Liouville dynamics.

The calculation of the quantum equilibrium structure, although a difficult problem, is far more tractable than that of the quantum time evolution of a many-body system. The mathematical details and approximations which enter into the calculation of the spectral density function are given in the Appendix. In the limit of high temperature, the result is

$$W_A^{\alpha\alpha}(X, i\hbar\beta/2) = \frac{1}{(2\pi\hbar)^\nu} \delta(\xi(R) - \xi^\ddagger) e^{-\beta H_\alpha(R)} \times \left\{ \frac{P}{M} \cdot \nabla_R \xi(R) + D_\alpha(R) \right\}, \quad (3)$$

where ν denotes the coordinate space dimension and $D_\alpha(R)$ is

$$D_\alpha(R) = \frac{\beta\hbar^2}{2} \sum_{\alpha_2} [e^{-(\beta/2)E_\alpha(R)} - e^{-(\beta/4)(E_{\alpha_2}(R) + E_\alpha(R))}] \times [e^{-(\beta/4)E_{\alpha_2}(R)} - e^{-(\beta/4)E_\alpha(R)}]^2 e^{\beta E_\alpha(R)} \times \frac{P}{M} \cdot d_{\alpha\alpha_2}(R) \frac{\nabla_R \xi(R)}{M} \cdot d_{\alpha\alpha_2}(R). \quad (4)$$

The nonadiabatic coupling matrix element, $d_{\alpha\alpha'}(R)$, is defined below Eq. (A10) in the Appendix. When $\alpha \neq \alpha'$, the term $N_B^{\alpha\alpha'} W_A^{\alpha'\alpha}$ yields a negligible contribution to the rate coefficient. Due to the nature of the species operator ($\hat{N}_B$)_W(R) = $\theta(\xi(R) - \xi^\ddagger)$, the off-diagonal matrix element of the observable, $N_B^{\alpha\alpha'}(R, t)$, is zero initially and remains very small (compared to its diagonal counterpart) for all times. Thus, when $W_A^{\alpha'\alpha}$ is multiplied by a very small number, the product will also be very small. Hence, we can safely drop the off-diagonal part of the rate coefficient from the formula. At low temperatures, other approximations to the equilibrium spectral density function must be considered.

Substituting Eq. (3) into Eq. (2), we obtain the expression for the rate coefficient used in our computations

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}(2\pi\hbar)^\nu Z_Q} \sum_{\alpha} \int dX N_B^{\alpha\alpha}(X, t) \times \left\{ \frac{P}{M} \cdot \nabla_R \xi(R) + D_\alpha(R) \right\} \delta(\xi(R) - \xi^\ddagger) e^{-\beta H_\alpha(X)}, \quad (5)$$

where it can be shown that

$$n_A^{\text{eq}} = [1/(2\pi\hbar)^\nu Z_Q] \sum_{\alpha} \int dX \theta(\xi^\ddagger - \xi(R)) e^{-\beta H_\alpha(X)}$$

and $Z_Q = [1/(2\pi\hbar)^\nu] \sum_{\alpha} \int dX e^{-\beta H_\alpha(X)}$ in the high temperature limit. Equation (5) provides a well-defined formula involving sampling from the barrier top. If the time scale of the chemical reaction is much longer than that of the microscopic dynamics, one can extract the rate constant k_{AB} from the plateau value of $k_{AB}(t)$. When nonadiabatic effects are important, the term $D_\alpha(R)$ (which is of order $|d_{\alpha\alpha'}|^2$) contributes significantly to the rate coefficient. However, in the limit of weak nonadiabatic coupling (i.e., when $|d_{\alpha\alpha'}|$ is very small), the first term in Eq. (3) dominates and the expression for the rate coefficient reduces to the simpler form

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}(2\pi\hbar)^\nu Z_Q} \sum_{\alpha} \int dX N_B^{\alpha\alpha}(X, t) \times \frac{P}{M} \cdot \nabla_R \xi(R) \delta(\xi(R) - \xi^\ddagger) e^{-\beta H_\alpha(X)}. \quad (6)$$

III. COMPUTATIONAL METHODOLOGY

The adiabatic evolution of the species variable, $N_B^a(X, t)$, in Eq. (6) was carried out by solving the time independent Schrödinger equation of the proton for fixed values of the classical bath coordinates. Using Newton's equations of motion, the classical bath coordinates were evolved on the ground state adiabatic potential energy surface. The details of the solution are given in Ref. 64. These classical equations of motion were integrated using the velocity Verlet, SHAKE (Ref. 69), and RATTLE (Ref. 70) algorithms with a time step of 1 fs to yield a new bath configuration.

The nonadiabatic evolution of the species variable in Eq. (5) is governed by the quantum-classical Liouville equation.²⁰ We used the sequential short-time propagation algorithm to solve this equation in conjunction with the momentum jump approximation. The details of these methods are given elsewhere.^{64,71} In addition, we placed a filter on the species variable such that if its magnitude exceeds some threshold, the value of the species variable is set equal to the threshold value. The purpose of this filter is to prevent the excessive accumulation of weight factors at long times, which magnifies the “sign problem” associated with an oscillatory integrand. Within the regime that the filter is effective (i.e., regime in which the product of the weight factors is not excessively large), the threshold value was increased until the value of the observable converged within statistical uncertainty. In simple spin-boson models, for which our quantum-classical dynamics algorithm has been shown⁷¹ to reproduce exact quantum results,^{37,72,73} it has been confirmed that the expectation value obtained using this approximation agrees with the exact one at long times.⁷⁴

Since our molecular dynamics simulations are carried out in Cartesian coordinates with intramolecular bond constraints, constraint forces must be applied to the molecules in conjunction with the nonadiabatic coupling forces. This is required so that the adjusted velocities do not have any components along the intramolecular bonds. For a rigid diatomic molecule, the adjusted velocities can be calculated according to

$$v'_i = v_i + \frac{h}{M_i} \tilde{d}_{\alpha\beta}^i, \quad (7)$$

where h is the quantity in square brackets given in Eq. (36) of Ref. 64 (with $\hat{d}_{\alpha\beta}^i$ replaced by $\tilde{d}_{\alpha\beta}^i$) and $\tilde{d}_{\alpha\beta}^i \equiv \hat{d}_{\alpha\beta}^i - \lambda_{ij} \hat{R}_{ij}$ (the hat denotes a normalized vector). Here the subscripts i and j label the atoms in the diatomic molecule and $\hat{R}_{ij}$ is the unit bond vector between them. In order to determine λ_{ij} , we need to satisfy the following constraint:

$$\dot{\sigma}_{ij} = \hat{R}_{ij} \cdot (v'_i - v'_j) = 0, \quad (8)$$

where $\sigma_{ij} = R_{ij}^2 - d_{ij}^2$ with d_{ij} being the desired constrained distance. After substituting Eq. (7) into the constraint and noting that $\hat{R}_{ij} \cdot (v_i - v_j) = 0$, we obtain

$$\lambda_{ij} = \hat{R}_{ij} \cdot \left(\frac{\hat{d}_{\alpha\beta}^i}{M_i} - \frac{\hat{d}_{\alpha\beta}^j}{M_j} \right) / \left(\frac{1}{M_i} + \frac{1}{M_j} \right). \quad (9)$$

This scheme was used in Ref. 64. Another description of constraints in the context of Dirac brackets is given in Ref. 75 and the relation between these methods remains to be established.

A. Rare event sampling scheme

In order to describe the rare event sampling scheme, we consider the computation of the adiabatic rate coefficient using Eq. (6) and restricting the sum to one adiabatic state. The adiabatic rate coefficient can be written in the form

$$k^{\text{ad}}(t) = \frac{\langle \dot{\xi}(0) \theta(\xi(t) - \xi^\ddagger) \delta(\xi(0) - \xi^\ddagger) \rangle}{n_A^{\text{eq}} n_B^{\text{eq}}}. \quad (10)$$

For nonadiabatic dynamics, the same rare-event sampling scheme is used but the time evolution of the species operator is carried out using full quantum-classical dynamics. The angular brackets $\langle \cdots \rangle$ are defined as

$$\langle \cdots \rangle \equiv \frac{\int dX \cdots e^{-\beta H_1}}{\int dX e^{-\beta H_1}}, \quad (11)$$

where the ground-state adiabatic Hamiltonian is $H_1 = \sum_i P_i^2 / 2M_i + E_1(R)$. The ensemble average needed to compute the rate coefficient is conditioned on the reaction coordinate being on the $\xi = \xi^\ddagger$ dividing surface. For highly activated rate processes, this would pose a problem since the system would rarely visit the barrier top. To circumvent this difficulty, the conditional average can be computed using a “blue moon” ensemble⁷⁶ of initial configurations in which the value of the reaction coordinate is fixed at the barrier top value [i.e., $\xi(R) = \xi^\ddagger$]. Using this ensemble, the expression for $k^{\text{ad}}(t)$ takes the form

$$k^{\text{ad}}(t) = \left(\frac{\langle D^{-1/2} \dot{\xi}(0) \theta(\xi(t) - \xi^\ddagger) \rangle_{\xi^\ddagger}}{\langle D^{-1/2} \rangle_{\xi^\ddagger}} \right) \left(\frac{P_1(\xi^\ddagger)}{n_A^{\text{eq}} n_B^{\text{eq}}} \right), \quad (12)$$

where $\langle \cdots \rangle_{\xi^\ddagger}$ denotes an average over the ξ -constrained ensemble and $P_1(\xi^\ddagger)$ is the probability density of the system being in the ground adiabatic state and the reaction coordinate being on the $\xi = \xi^\ddagger$ dividing surface. The factor $D^{-1/2}$ [not to be confused with D_α in Eq. (4)] removes the bias introduced by the blue moon sampling and its general form is given in Eq. (21) of Ref. 77. Its specific form for the proton transfer system under investigation is given by

$$D = \sum_i \left\{ \frac{1}{M_{\text{CH}_3}} \left(\frac{\partial \xi}{\partial R_{i,\text{CH}_3}} \right)^2 + \frac{1}{M_{\text{Cl}}} \left(\frac{\partial \xi}{\partial R_{i,\text{Cl}}} \right)^2 - \mu \left[\frac{1}{M_{\text{CH}_3}} \left(\hat{r}_i^{\text{rel}} \cdot \frac{\partial \xi}{\partial R_{i,\text{CH}_3}} \right) - \frac{1}{M_{\text{Cl}}} \left(\hat{r}_i^{\text{rel}} \cdot \frac{\partial \xi}{\partial R_{i,\text{Cl}}} \right) \right]^2 \right\} + \sum_{\alpha=A,B} \frac{1}{M_\alpha} \left(\frac{\partial \xi}{\partial R_\alpha} \right)^2, \quad (13)$$

where the index i runs over solvent molecules, $\hat{r}_i^{\text{rel}}$ is the unit

bond vector for molecule i , and $\mu = M_{\text{CH}_3} M_{\text{Cl}} / (M_{\text{CH}_3} + M_{\text{Cl}})$. The details related to the computation of the first factor in Eq. (12) are given in Ref. 64.

B. Free energy calculation

The numerator of the second factor of Eq. (12) is related to the free energy at the barrier top. Without restriction to the ground adiabatic state we have

$$\begin{aligned} P_\alpha(\xi') &= \frac{\int dX \delta(\xi(R) - \xi') e^{-\beta H_\alpha}}{\sum_\alpha \int dX e^{-\beta H_\alpha}} \\ &= \frac{\int dX \delta(\xi(R) - \xi') e^{-\beta H_\alpha}}{\int dX e^{-\beta H_\alpha}} \frac{\int dX e^{-\beta H_\alpha}}{\sum_\alpha \int dX e^{-\beta H_\alpha}} \\ &\equiv P(\xi' | \alpha) p_\alpha, \end{aligned} \quad (14)$$

where $P(\xi' | \alpha)$ is the conditional probability density of ξ' given that the system is in quantum state α and p_α is the probability that the system is in state α . The free energy along a reaction coordinate $\xi(R)$, $W_\alpha(\xi')$, corresponding to an adiabatic surface α with Hamiltonian $H_\alpha = P^2/2M + E_\alpha(R)$ is given by (using an additive constant)⁶⁴

$$\beta W_\alpha(\xi') = -\ln \frac{P(\xi' | \alpha)}{P_u} - \ln \frac{p_\alpha}{p_1}, \quad (15)$$

where $P_u = (\sum_\alpha \int d\xi' e^{-\beta W_\alpha(\xi')})^{-1}$ is the uniform probability density of ξ' and

$$\frac{p_\alpha}{p_1} = \frac{\int dX e^{-\beta(E_\alpha - E_1)} e^{-\beta H_1}}{\int dX e^{-\beta H_1}}. \quad (16)$$

This factor is related to the relative probability that the system is in state α , regardless of the value of ξ , and can be determined from a long adiabatic trajectory on the ground state surface.

Averages of any function $f(\xi(R))$, $\langle f(\xi(R)) \rangle_\alpha$, [such as those in the second factor of Eq. (12)] are computed by numerical integration of the free energy corresponding to an adiabatic surface α ,

$$\langle f(\xi(R)) \rangle_\alpha = \int d\xi' f(\xi') e^{-\beta W_\alpha(\xi')} P_u. \quad (17)$$

IV. RESULTS

The protonic and deuteronic free energy profiles, constructed by binning $\xi = \Delta E$ in long (2.5 ns) adiabatic dynamics trajectories on the ground and first excited state surfaces, are shown in Fig. 1. Both sets of ground state curves have sharply defined barrier regions and approximately harmonic stable wells. Here, $\Delta E^\ddagger = 0.0138 \text{ eC/\AA}$ is the value of ΔE at the transition state. It is evident from the plots that the minimum of the (ionic) product state is lower in free energy than that of the (covalent) reactant state as a result of the stabilizing effect of the polar solvent. Thus, the complex spends more time in the ionic configuration than in the covalent configuration, whereas in the gas phase it is primarily found

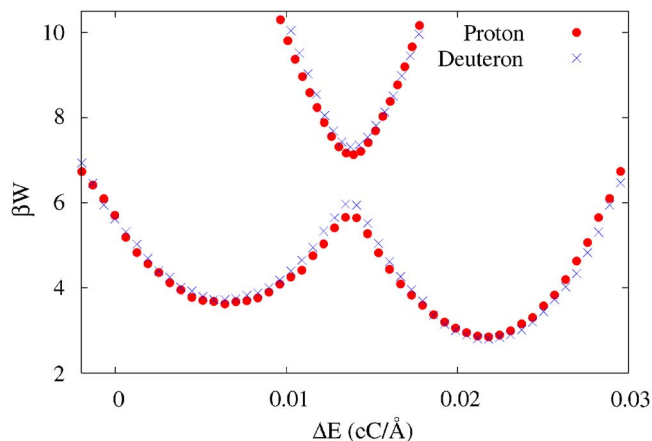


FIG. 1. (Color online) Ground and excited state free energy (βW) profiles along the ΔE coordinate for the proton and deuteron transfer reactions.

in the covalent configuration. The equilibrium constant, $K_{\text{eq}} = n_i^{\text{eq}}/n_c^{\text{eq}}$, is ≈ 1.9 . In contrast, the free energy in the first excited state has a single-well structure.

Several differences between the protonic and deuteronic free energy curves are worth noting. They differ with respect to the forward and reverse barrier heights, and the energy gap between the ground and excited state surfaces at $\Delta E^\ddagger = 0.0138 \text{ eC/\AA}$ as follows: $\Delta W_1^f = 2.09 \text{ kT}$, $\Delta W_1^r = 2.88 \text{ kT}$, and $\Delta W_{12} = 1.41 \text{ kT}$ for the proton transfer, and $\Delta W_1^f = 2.31 \text{ kT}$, $\Delta W_1^r = 3.23 \text{ kT}$, and $\Delta W_{12} = 1.29 \text{ kT}$ for the deuteron transfer. As expected, the barrier heights for the deuteron transfer are larger since the deuteron is heavier than the proton. Also, since ΔW_{12} is smaller for the deuteron, the nonadiabatic coupling at the barrier top will on average be stronger for the deuteron than for the proton.

A. Adiabatic rate coefficient

In Fig. 2, we show the time dependent adiabatic rate coefficients $k^{\text{ad}}(t)$ [from Eq. (10)] for the proton and deuteron transfer reactions. The results were obtained from averages over 16 000 trajectories. After a sharp fall from the transition state theory value in a few tenths of a picosecond, one observes a slower decay to a plateau, characteristic of the

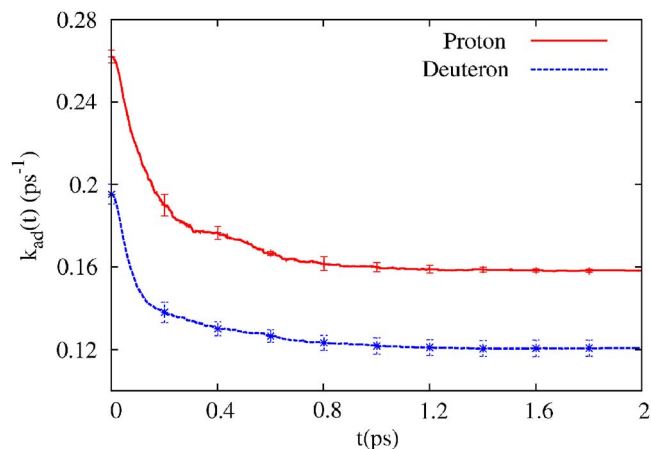


FIG. 2. (Color online) Adiabatic rate coefficients for the proton and deuteron transfer reactions as a function of time.

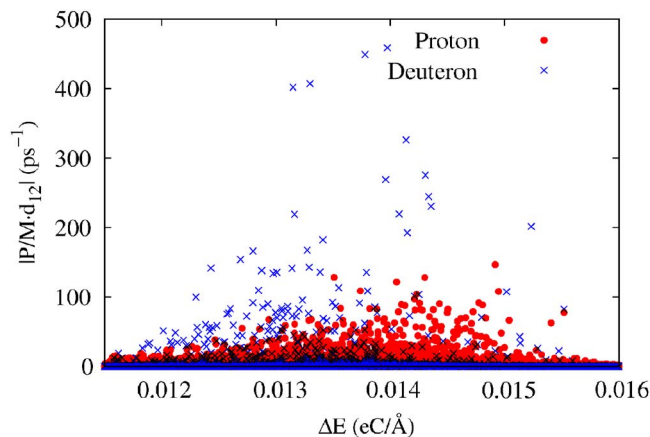


FIG. 3. (Color online) $|P/M d_{12}|$ vs ΔE for the proton and deuteron systems.

charge transfer process. To eliminate the slow decay of $k^{\text{ad}}(t)$ to zero on the time scale of the charge transfer process, we introduced absorbing boundaries in the trajectories at the well minima of the free energy potential. The proton and deuteron transfer rate constants obtained from the plateau of $k^{\text{ad}}(t)$ are $k_P^{\text{ad}} = 0.158 \text{ ps}^{-1}$ and $k_D^{\text{ad}} = 0.121 \text{ ps}^{-1}$, respectively, giving rise to a kinetic isotope effect of $\text{KIE}^{\text{ad}} = k_P^{\text{ad}}/k_D^{\text{ad}} = 1.3$. The transmission coefficients for the proton and deuteron transfers were estimated to be $\kappa_P^{\text{ad}} = 0.60$ and $\kappa_D^{\text{ad}} = 0.62$, respectively.

B. Nonadiabatic rate coefficient

Coupling between the solvent motions and the quantum protonic degree of freedom can induce quantum transitions among the protonic adiabatic states. In this case the dynamics is no longer confined to the ground state surface and a full nonadiabatic treatment of the reaction dynamics is necessary.

To obtain insight into the nature of the nonadiabatic dynamics of the proton and deuteron transfer reactions, we have examined the nonadiabatic coupling strength, $|P/M d_{12}(R)|$, which determines the probability of a nonadiabatic transition from the ground to the first excited adiabatic state, at phase space configurations drawn from a long adiabatic trajectory on the ground state surface. In Fig. 3, we see that the deuteron system attains higher values of the nonadiabatic coupling than the proton system in the barrier-top region ($0.01 \text{ eC}/\text{\AA} \leq \Delta E \leq 0.016 \text{ eC}/\text{\AA}$), where the likelihood of a nonadiabatic transition is highest. This suggests that the deuteron transfer will be more nonadiabatic than the proton transfer. This is consistent with the fact that there is a smaller mass scale disparity between the deuteron and the other particles in the system than in the case of the proton.

We now turn to the results of the time dependent nonadiabatic rate coefficient $k(t)$ calculated using Eq. (5) [where $k(t) = k_{AB}(t)/n_B^{\text{eq}}$]. Given that nonadiabatic transitions predominantly occur only in the vicinity of the barrier top, we have used the window $0.01 \text{ eC}/\text{\AA} \leq \Delta E \leq 0.016 \text{ eC}/\text{\AA}$ around the barrier top $\Delta E^\ddagger = 0.0138 \text{ eC}/\text{\AA}$, outside which nonadiabatic transitions are not allowed in the simulations. It is useful to decompose the rate coefficient into its ground ($\alpha=1$)

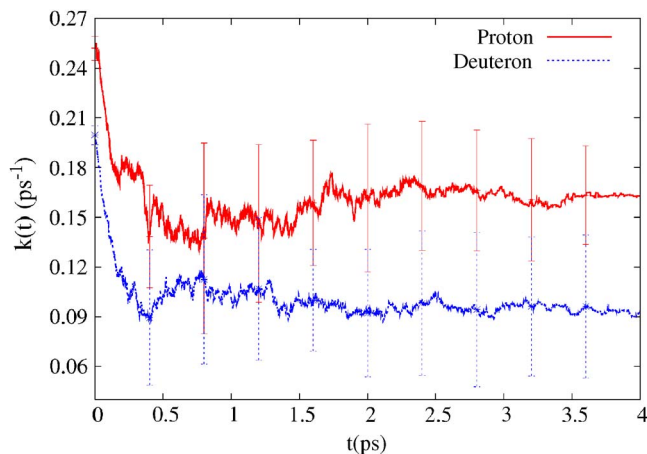


FIG. 4. (Color online) Ground state contributions to the time dependent nonadiabatic rate coefficient for the proton and deuteron transfer reactions.

and excited ($\alpha=2$) state contributions. The ground state proton transfer rate coefficient $k_P^1(t)$ (for which trajectories with six nonadiabatic transitions were found to be sufficient for convergence) was obtained from an average over 20 000 trajectories. From the long time decay of $k_P^1(t)$ shown in Fig. 4, a rate constant of $k_P^1 = 0.163 \text{ ps}^{-1}$ was extracted. This result is over two times larger than that obtained in our previous study of this model which fixed R_{AB} , indicating that the vibration of the AB complex significantly enhances the proton transfer rate. The contribution from the first excited state was determined to have a negligible effect on the overall rate constant. The transmission coefficient was estimated to be $\kappa_P \approx 0.65$.

The ground state contribution to the deuteron transfer rate coefficient $k_D^1(t)$ (for which trajectories with eight nonadiabatic transitions were found to be sufficient for convergence) was obtained from an average over 30 000 trajectories. From the long time decay of $k_D^1(t)$ shown in Fig. 4, a value of $k_D^1 = 0.093 \text{ ps}^{-1}$ was extracted. Again, the first excited state contribution was determined to have a negligible effect on the overall rate constant. The transmission coefficient was estimated to be $\kappa_D \approx 0.47$. Based on the ground state contributions to the proton and deuteron transfer rate constants, the kinetic isotope effect is $\text{KIE} = 1.8$, although accounting for the statistical uncertainty in our simulation results, the KIE may be as large as 4.

References 61 and 63 contain comprehensive tables that compare the rate constants and kinetic isotope effects for this model system calculated with various approaches. The rate constants vary by over two orders of magnitude depending on which computational method was used. Our proton transfer rate constant is in best agreement with the surface-hopping results of Kim and Hammes-Schiffer,⁶² the semi-classical variational transition state theory with multidimensional tunneling results of McRae *et al.*⁶¹ and the quantum transition state theory results of Yamamoto and Miller.⁶³ However, our deuteron transfer rate constant is almost a factor of 2–5 times larger than the previously largest rate constant obtained in Ref. 62.

The kinetic isotope effects for this model vary widely across the different methods (ranging from 3.9 to 47), due

mainly to the large variation in the deuteron transfer rate. Our kinetic isotope effect is on the low end of the range of the previously calculated values. Unfortunately, there is no absolute benchmark for the value of the KIE that can be used for comparison. The previously calculated estimates of the KIE were based on a variety of methods including quantum transition state theory (QTST),⁶³ quantum-classical surface-hopping molecular dynamics^{16,62} and generalized Langevin equation approaches.^{59–61} The QTST approaches obtain deuteron transfer rates that are lower than our result by about an order of magnitude. Since quantum transition state effects are accounted for by our spectral density function, such a large decrease in the rate from this effect would have been reflected in the D_α factor [see Eq. (4)], which signals the importance of quantum equilibrium dispersion in the reaction coordinate. While more accurate expressions for the spectral density can in principle be constructed and used in our calculations, the magnitude of D_α was observed to be very small, suggesting that our quantum equilibrium sampling is adequate.

The difficulty in identifying the sources of discrepancy between the various methods lies in the fact that they have disparate theoretical origins and utilize different approximations to the full quantum dynamics. Of all these methods, the surface-hopping approach is most closely related in spirit and implementation to ours, but it still differs significantly in that mean-surface dynamics is absent and quantum coherence effects are treated differently. Our value for the KIE is also closest and within statistical uncertainty to that obtained using surface-hopping molecular dynamics, which yielded a KIE of 4.7 ± 1.5 .⁶²

A number of factors make the deuteron transfer rate difficult to estimate. We observed bath configurations with large nonadiabatic coupling strengths for the deuteron transfer, but these configurations were rare and, most of the time, the protonic nonadiabatic couplings were higher, as shown in Fig. 3. These rare configurations are difficult to sample and, as a result, make the accurate sampling of nonadiabatic transitions difficult. If we were better able to sample these rare events, it is possible that we would observe a further decrease in the deuteron rate. The error bars in our calculations were estimated by block averaging using a reasonable number of blocks to obtain a reliable estimate of the error in the mean. However, filtering can introduce a systematic error in the result. While we have carried out tests to measure the effectiveness of the filter in reducing fluctuations without compromising the result, the use of a filter adds some uncertainty to our rate coefficient values. Within our statistical uncertainty, we predict a relatively small value of the KIE for this model.

V. CONCLUSIONS

Rates of quantum mechanical reactive processes occurring in the condensed phase are difficult to compute because full quantum dynamical simulations of many-body systems are not feasible for large many body systems. Our simulations employ reactive-flux correlation function expressions that retain the quantum equilibrium structure of the system

and adopt a mixed quantum-classical Liouville description of the dynamics. In contrast to other investigations, we have chosen the solvent polarization to monitor the progress of the reaction. This reaction coordinate was shown to track the proton transfers between ionic and covalent species in the phenol-amine complex, indicating that the solvent plays an essential role in this quantum charge transfer process.⁶⁴

When coupling between the quantum and classical degrees of freedom induces transitions between the adiabatic states, the adiabatic approximation breaks down and nonadiabatic dynamics must be implemented. For the model system considered here, our simulations yield a proton transfer rate constant that is in good agreement with values obtained by several other approaches. The deuteron transfer rate constant that we calculated is larger than that obtained in other approaches, suggesting that the reaction may not be as sensitive to isotopic substitution as observed in some previous studies. Nonadiabatic dynamical effects led to an increase in the isotope effect. Although the proton transfer rate constant was not significantly affected by nonadiabatic dynamics, the deuteron transfer rate constant was reduced. This is consistent with the results in Fig. 3. This increase in the isotope effect due to nonadiabatic effects was also observed in previous studies.^{16,51,62}

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APPENDIX: DERIVATION OF THE SPECTRAL DENSITY FUNCTION

In this Appendix, we derive Eq. (3) starting from the general formula for the spectral density function

$$\begin{aligned}
 W_A^{\alpha'\alpha}(X, i\hbar\beta/2) &= \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \int dX' \frac{P'}{M} \cdot \nabla_{R'} \xi(R') \\
 &\times \delta(\xi(R') - \xi^\ddagger) \int dZ dZ' e^{-(i/\hbar)(P \cdot Z + P' \cdot Z')} \\
 &\times \langle \alpha'; R | \langle R + \frac{Z}{2} | e^{-(\beta/2)\hat{H}} | R' - \frac{Z'}{2} \rangle \\
 &\times \langle R' + \frac{Z'}{2} | e^{-(\beta/2)\hat{H}} | R - \frac{Z}{2} \rangle | \alpha; R \rangle. \quad (\text{A1})
 \end{aligned}$$

Equation (A1) can be simplified by performing integrations over all P' variables to obtain

$$\begin{aligned}
W_A^{\alpha'\alpha}(X, i\hbar\beta/2) &= \frac{i\hbar}{(2\pi\hbar)^{\nu}Z_Q} \int dZ dR' \\
&\times \left[\sum_j \int dZ'_j \frac{\nabla_{R'_j} \xi(R')}{M_j} (\partial \delta(Z'_j) / \partial Z'_j) \langle \alpha'; R | \langle R + \frac{Z}{2} | e^{-(\beta/2)\hat{H}} | R'_j - \frac{Z'_j}{2} \rangle \left(\prod_{k \neq j} |R'_k\rangle \langle R'_k| \right) \right. \\
&\times \left. \langle R'_j + \frac{Z'_j}{2} | e^{-(\beta/2)\hat{H}} | R - \frac{Z}{2} \rangle | \alpha; R \rangle \delta(\xi(R') - \xi^\ddagger) e^{-(i/\hbar)P \cdot Z} \right]. \quad (\text{A2})
\end{aligned}$$

The imaginary time propagators in $W_A^{\alpha'\alpha}(X, i\hbar\beta/2)$ can, in principle, be computed using quantum path integral methods³² or approximations such as linearization methods.^{43,49,78,79} Next, we show how one may construct approximate analytical expressions for this quantity, which are used to obtain the numerical results.

To proceed with the analytical calculation, we first partition the Hamiltonian into bath kinetic plus remainder terms as $\hat{H} = \hat{P}^2/2M + \hat{h}$. Approximating the propagator as $e^{-\beta\hat{H}} = e^{-\beta\hat{h}/2} e^{-\beta\hat{P}^2/2M} e^{-\beta\hat{h}/2} + \mathcal{O}(\beta^3)$ (which is valid at high temperatures), we can then evaluate the imaginary time propagators to obtain the following expression for $W_A^{\alpha'\alpha}(X, i\hbar\beta/2)$,

$$\begin{aligned}
W_A^{\alpha'\alpha}(X, i\hbar\beta/2) &= \frac{i\hbar}{(\pi\beta\hbar^2)^{\nu}(2\pi\hbar)^{\nu}Z_Q} \int dZ dR' \delta(\xi(R') - \xi^\ddagger) \\
&\times e^{-(i/\hbar)P \cdot Z} \sum_{\alpha_1, \alpha_2, \alpha_3, \alpha_4} \left\{ \left[\sum_j \int dZ'_j \frac{\nabla_{R'_j} \xi(R')}{M_j} (\partial \delta(Z'_j) / \partial Z'_j) e^{-M_j(Z'_j/2 + Z_j Z'_j)/\beta\hbar^2} \langle \alpha_1; R + \frac{Z}{2} | \alpha_2; R' - \frac{Z'_j}{2} \rangle \right. \right. \\
&\times \left. \langle \alpha_2; R' - \frac{Z'_j}{2} | \alpha_3; R' + \frac{Z'_j}{2} \rangle \langle \alpha_3; R' + \frac{Z'_j}{2} | \alpha_4; R - \frac{Z}{2} \rangle e^{-(\beta/4)E_{\alpha_2}(R' - Z'_j/2)} e^{-(\beta/4)E_{\alpha_3}(R' + Z'_j/2)} \right. \\
&\times \left. \left. \left[\prod_k M_k e^{-(M_k/\beta\hbar^2)(2R_k^2 + 2R_k'^2 - 4R_k R'_k + Z_k^2/2)} \right] \langle \alpha_4; R - \frac{Z}{2} | \alpha; R \rangle \langle \alpha'; R | \alpha_1; R + \frac{Z}{2} \rangle e^{-(\beta/4)E_{\alpha_1}(R + Z/2)} \right] \right\}. \quad (\text{A3})
\end{aligned}$$

To arrive at this expression, we used the fact that

$$\langle R | e^{-\beta P^2/4M} | R' \rangle = \sqrt{\frac{M}{\pi\beta\hbar^2}} e^{-M(R - R')^2/\beta\hbar^2}, \quad (\text{A4})$$

and a representation of $\hat{h}$ in the adiabatic basis,

$$e^{-\beta\hat{h}(R)} = \sum_{\alpha} |\alpha; R\rangle e^{-\beta E_{\alpha}(R)} \langle \alpha; R|. \quad (\text{A5})$$

Upon integrating Eq. (A3) over Z' , we obtain

$$\begin{aligned}
W_A^{\alpha'\alpha}\left(X, \frac{i\hbar\beta}{2}\right) &= \frac{i\hbar}{(\pi\beta\hbar^2)^{\nu}(2\pi\hbar)^{\nu}Z_Q} \int dZ dR' \sum_{\alpha_1 \alpha_4} e^{-(\beta/4)E_{\alpha_1}(R + (Z/2)) - (\beta/4)E_{\alpha_4}(R - (Z/2))} \langle \alpha'; R | \alpha_1; R + \frac{Z}{2} \rangle \langle \alpha_4; R \\
&- \frac{Z}{2} | \alpha; R \rangle \left[\sum_j \frac{\nabla_{R'_j} \xi(R')}{M_j} \left(\prod_k M_k \right) \left\{ \sum_{\alpha_2} e^{-(\beta/2)E_{\alpha_2}(R')} \frac{M_j Z_j}{\beta\hbar^2} \langle \alpha_1; R + \frac{Z}{2} | \alpha_2; R' \rangle \langle \alpha_2; R' | \alpha_4; R - \frac{Z}{2} \rangle \right. \right. \\
&+ \frac{1}{2} \sum_{\alpha_2 \alpha_3} \langle \alpha_2; R' | \frac{\partial}{\partial R'_j} | \alpha_3; R' \rangle \left[e^{-(\beta/4)E_{\alpha_2}(R')} - e^{-(\beta/4)E_{\alpha_3}(R')} \right]^2 \langle \alpha_1; R + \frac{Z}{2} | \alpha_2; R' \rangle \\
&\times \left. \left. \langle \alpha_3; R' | \alpha_4; R - \frac{Z}{2} \rangle \right\} \right] \delta(\xi(R') - \xi^\ddagger) \left[\prod_k e^{-(2M_k/\beta\hbar^2)(R_k - R'_k)^2} e^{-(M_k/2\beta\hbar^2)(Z_k + i\beta\hbar P_k/M_k)^2} e^{-\beta P_k^2/2M_k} \right]. \quad (\text{A6})
\end{aligned}$$

A classical treatment of the environmental coordinates is obtained by taking the limit

$$\lim_{\beta \rightarrow 0} \sqrt{\frac{2M_k}{\beta\hbar^2\pi}} e^{-(2M_k/\beta\hbar^2)(R_k - R'_k)^2} = \delta(R_k - R'_k). \quad (\text{A7})$$

In this limit Eq. (A6) simplifies to

$$\begin{aligned}
W_A^{\alpha' \alpha}(X, i\hbar\beta/2) = & \frac{i\hbar}{(\pi\beta\hbar^2)^{\nu}(2\pi\hbar)^{\nu}Z_Q} \left(\frac{\pi\beta\hbar^2}{2} \right)^{\nu/2} \int dZ \sum_{\alpha_1\alpha_4} e^{-(\beta/4)E_{\alpha_1}(R+(Z/2))-(\beta/4)E_{\alpha_4}(R-(Z/2))} \langle \alpha'; R | \alpha_1; R + \frac{Z}{2} \rangle \\
& \times \langle \alpha_4; R - \frac{Z}{2} | \alpha; R \rangle \left[\sum_j \frac{\nabla_{R_j} \xi(R)}{M_j} (\prod_k M_k) \left\{ \sum_{\alpha_2} e^{-(\beta/2)E_{\alpha_2}(R)} \frac{M_j Z_j}{\beta\hbar^2} \langle \alpha_1; R + \frac{Z}{2} | \alpha_2; R \rangle \right. \right. \\
& \times \langle \alpha_2; R | \alpha_4; R - \frac{Z}{2} \rangle + \frac{1}{2} \sum_{\alpha_2\alpha_3} \langle \alpha_2; R | \frac{\partial}{\partial R_j} | \alpha_3; R \rangle [e^{-(\beta/4)E_{\alpha_2}(R)} - e^{-(\beta/4)E_{\alpha_3}(R)}]^2 \langle \alpha_1; R + \frac{Z}{2} | \alpha_2; R \rangle \\
& \left. \left. \times \langle \alpha_3; R | \alpha_4; R - \frac{Z}{2} \rangle \right\} \right] \delta(\xi(R) - \xi^{\ddagger}) \left[\prod_k \frac{1}{\sqrt{M_k}} e^{-(M_k/2\beta\hbar^2)(Z_k + i\beta\hbar P_k/M_k)^2} e^{-\beta P_k^2/2M_k} \right]. \quad (\text{A8})
\end{aligned}$$

An approximate analytical expression may be obtained by expanding the overlap matrix elements and adiabatic energies E_{α} to linear order in Z ,

$$\langle \alpha'; R | \alpha_1; R + \frac{Z}{2} \rangle \approx \delta_{\alpha'\alpha_1} + \frac{1}{2} d_{\alpha'\alpha_1}(R)Z, \quad (\text{A9})$$

$$e^{-(\beta/4)E_{\alpha_1}(R+(Z/2))} \approx e^{-(\beta/4)E_{\alpha_1}(R)} \left\{ 1 - \frac{\beta}{8} \frac{\partial E_{\alpha_1}(R)}{\partial R} Z \right\}, \quad (\text{A10})$$

where $d_{\alpha'\alpha_1}(R) = \langle \alpha'; R | \nabla_R | \alpha_1; R \rangle$. The truncation to linear order in Z is valid for high temperatures since the factor $\exp^{-(M_k/2\beta\hbar^2)Z_k^2}$ restricts the integrand in Eq. (A8) to small values of Z_k . Finally, Eq. (A8) with $\alpha = \alpha'$ can be integrated over Z analytically to give Eq. (3).

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