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Proton transfer in benzoic acid crystals: Another look using quantum operator theory

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We present a calculation of the rate of synchronous double proton transfer in benzoic acid crystals. Experiments on these systems have been performed over a wide range of temperatures (roughly 10–400 °K). Even though the energetic barrier for proton transfer is rather high, the observed activation energy is low, while kinetic isotope experiments seem to indicate classical transfer. The system exhibits significant quantum character even at high temperatures and we show that the observed low activation energies can be reproduced assuming that the reaction is “assisted” by a low-frequency intramolecular mode, as has been suggested in different contexts by Benderskii [V. A. Benderskii, S. Yu. Grebenshchikov, and G. V. Mil’nikov, *Chem. Phys.* **194**, 1 (1995)], Hynes [D. Borgis and J. Hynes, *J. Chem. Phys.* **94**, 3619 (1991)] and Silbey [A. Suarez and R. Silbey, *J. Chem. Phys.* **94**, 4809 (1991)]. We use our previous work on the quantum Kramers problem to perform a fully quantum calculation that incorporates symmetric coupling to the intramolecular mode and coupling to the condensed environment to all orders. We calculate the activation energies for hydrogen and deuterium transfer and we show that our results are in quantitative agreement with the experiment. © 1998 American Institute of Physics. [S0021-9606(98)50330-3]

I. INTRODUCTION

The theoretical study of quantum reaction rates in a condensed phase has been a topic of central importance in chemical physics for the last four decades. A seminal early theoretical model was due to Marcus¹ that was later reformulated in a quantum Hamiltonian formalism by Levich and Dogonadze.² In that view the environment changes configuration during the tunneling motion of the charge and the activation energy of the reaction is related to an environment reorganization energy. The environment is represented by a phenomenological one-dimensional coordinate. This theory is extremely important for the study of electron transfer, with the electron hopping from the ground state at the initial site to the ground state at the final site. A microscopic theory of charge transfer in a condensed phase that assumes a similar viewpoint is offered by the spin-boson Hamiltonian that has been solved analytically by Leggett and co-workers.³ In this model, the environment consists of modes that have a wide range of frequencies. Models for charge transfer in a liquid phase that included coupling of the charge to a continuous spectrum of polarization phonons had been studied earlier (see the recent review by Kuznetsov⁴).

The case of proton transfer in condensed phases introduces some new features compared to electron transfer. Because of the larger proton mass, several energy levels in the reactant well (and not only the ground state) are involved in the dynamics. What is needed is a quantum generalization of the classical Kramers theory,⁵ where a wave packet is propagated in time under the full Hamiltonian. Several such schemes for evolution in real time have appeared in the last several years: mixed quantum-classical methods,⁶ centroid methods,⁷ adiabatic path-integral methods⁸ and the method

developed by us, namely the exponential resummation of the evolution propagator.⁹

Carboxylic acid crystals provide a useful system for the application of theoretical models. Benzoic acid forms dimers linked by two hydrogen bonds and a synchronous two proton transfer leads to a tautomerization reaction, as is shown schematically in Fig. 1. The transfer of the two protons is assumed to be concerted, therefore it can be described by a single reaction coordinate. The reason for this assumption is that a synchronous proton transfer has been shown to be the dominant mechanism in the closely related *p*-toluic acid.¹² Since the proton transfer takes place between identical O atoms, the potential energy surface looks like a symmetric double well. In the crystalline phase the two tautomers become distinct and they acquire a small energy difference that is determined by the structure of the environment. In fact, spectroscopic analysis has shown that the asymmetry is of the order of only 35 cm⁻¹. This means that as the temperature is lowered, the activation energy is determined by the quantum dynamics and it does not become equal to the potential asymmetry until we reach very low temperatures. For these reasons, this system has been studied experimentally over a very wide temperature range, from 10 to 400 °K, which is uncharacteristic for reactions in solution.

There have been several experimental studies of benzoic acid crystals. NMR spectroscopic studies have been done by Nagaoka and co-workers,¹⁰ Meyer-Ernst and co-workers¹¹ (who have also done isotope studies¹²) and recently by Horsewill and co-workers.¹³ Other studies have used inelastic neutron scattering¹⁴ and optical spectroscopy.¹⁵ The latter is useful at very low temperature where the NMR relaxation time is very long and the neutron scattering signal is very

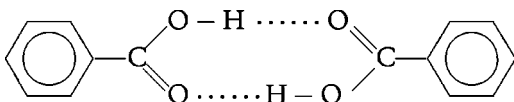


FIG. 1. Tautomerization reaction for the benzoic acid dimer: the synchronous two-proton transfer can be described by a single reaction coordinate.

weak. In addition, in optical spectroscopic methods a dye molecule that is used as a probe of the environment fortuitously lifts the small potential asymmetry, which allows the study of quantum dynamics down to very low temperature. The NMR experimental data have been interpreted using the theory of Look and Lowe.¹⁶ In this theory, the barrier height can be extracted from plots of the relaxation time T_1 vs the temperature. Analysis of the experimental data for benzoic acid has shown that distinct values of the barrier height are obtained in the low- and high-temperature limits. This is an indication that quantum tunneling plays a role.

Skinner and Trommsdorff¹⁷ studied in detail the low-temperature data. In this limit, the system can be described by a spin-boson Hamiltonian. In order to solve it they used a Redfield-theory-like approach and found that the data from the three kinds of experimental probes mentioned above are consistent with each other.

For the high-temperature limit they assumed over the barrier transfer. However, as we shall see in Sec. III, the transfer distance is very small (0.6 Å), which makes it favorable even for the relatively massive proton to tunnel. For this reason, one should not assume that at high temperatures the dynamics is purely classical. In the present work we will examine precisely the higher-temperature limit of the data. Several other workers have included quantum dynamics in this regime. The effect that theoretical studies have to explain is that the activation energy is much smaller than the energetic barrier height even at room temperature.

Meyer and Ernst¹⁸ used a master equation approach. They first tried to fit the experimental data using a one-dimensional potential energy surface (PES), but they found that this fitting leads to an energetic barrier for D transfer more than twice as high as the one for H transfer. For this reason they concluded that one should try to fit the results with a two-dimensional PES and they assumed that there is a single bath mode that is very strongly coupled to the reaction coordinate. We should stress that they assumed *antisymmetric* coupling between the proton and this bath mode. Using this two-dimensional surface they were able to fit the data in a satisfactory way. Scheurer and Saalfrank¹⁹ started from a similar Hamiltonian, but they used a density matrix formalism to study the quantum dynamics. However, they too had to use perturbation theory to include the coupling to the bath in order to calculate the off-diagonal relaxation matrix elements.

Both of these investigations were a first step in the right direction: they incorporated the fluctuating environment in the quantum dynamics of the proton. However, in the last few years it has been possible to tackle the full quantum particle plus bath Hamiltonian, without making any assumption of weak coupling between the proton and the bath. Therefore the first task that must be accomplished is to apply

to the benzoic acid dimer system the current exact quantum methods developed for the Kramers problem.

The above studies have another shortcoming. The work of Hynes,²⁰ Silbey²¹ and Benderskii²² has shown that the proton transfer rate is very sensitive to fluctuations of the transfer distance. The reason is that the wave function of the massive proton decays quickly with distance and small changes in the transfer distance can cause large changes in the overlap matrix elements. This fact had been recognized in earlier studies²³ (where it was usually referred to as “fluctuational barrier preparation”), but in these works the quantum problem was solved only in the framework of Fermi’s golden rule and the corner cutting limit was often assumed. Hynes and Silbey performed rigorous calculations in the deep tunneling limit and showed that intramolecular oscillations that affect the transfer distance can change significantly the activation energy predicted by Marcus’s model.

One approach that did include the oscillations of the O–O bond in the benzoic acid system was Ref. 24. However, some oversimplifications were made in that work: The quantum solution was obtained in an adiabatic approximation and the effect of the environment was modeled as a random force.

We are now in a position to summarize the ingredients of a full theory of proton transfer in benzoic acid crystals: (a) it must treat the bath quantum mechanically; (b) it must describe the coupled dynamics of proton and bath beyond a weak coupling approximation; (c) it must include the effect of a rate promoting intramolecular vibration. In another publication (Ref. 25) we have presented a theory that incorporates a rate promoting vibration in the quantum Kramers problem in a fashion that meets the requirements mentioned above. In Sec. II we will summarize our method and in Sec. III we will apply it to the benzoic acid dimer system.

II. THEORY OF REACTION RATES IN CONDENSED PHASES

A. Quantum Kramers problem

The modern era of the study of the Kramers problem⁵ began 35 years ago with the proof by Zwanzig²⁶ that the dynamics of a particle that obeys Langevin’s equation is equivalent to the problem defined by the Hamiltonian

$$H = H_{\text{ID}}(s) + \sum_{i=1}^N \left[\frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \left(q_i - \frac{c_i s}{m_i \omega_i^2} \right)^2 \right], \quad (2.1)$$

where $H_{\text{ID}}(s)$ is the uncoupled particle Hamiltonian and ω_i , m_i , c_i are, respectively, the frequency, mass and coupling constant of the normal modes of the environment. The important feature of this Hamiltonian is that the reaction coordinate is coupled to the bath via bilinear terms $c_i s q_i$. At first sight it seems that one would have to know the parameters ω_i , m_i and c_i for all N modes of the bath. Fortunately, the dynamics of the proton is determined only by the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_{i=1}^N \frac{c_i^2}{m_i \omega_i^2} \delta(\omega - \omega_i), \quad (2.2)$$

which is usually approximated by the phenomenological expression

$$J(\omega) = \gamma \omega_c \left(\frac{\omega}{\omega_c} \right)^n e^{-\omega/\omega_c}, \quad (2.3)$$

where ω_c is the frequency cutoff of the bath modes, γ is the friction and the exponent n is determined by details of the coupling, e.g., $n = 1$ (ohmic case) corresponds to a Markovian process. The usual case of coupling to acoustic phonons of the solid (which is the relevant model for the benzoic acid dimer crystal) corresponds to $n = 3$.

B. The two-dimensional potential

Let us assume that the potential energy surface (PES) for the reaction coordinate s is a double well $as^4 - bs^2$. We also assume that s is coupled to a harmonic mode Q . There are two ways to model this coupling, depending on the symmetry with respect to s .

- Antisymmetric coupling csQ (the choice of Meyer and Ernst¹⁸); in this case the Q mode is just one of the bath modes of Eq. (2.1) that we might prefer to treat separately because it is strongly coupled to the reaction coordinate.
- Symmetric coupling cs^2Q : This case has been studied by Oxtoby²⁷ and later in a series of papers²² by Benderskii and co-workers and leads to rate enhancement.

There is a profound physical difference between the two cases as we have explained in detail in Ref. 25. We mention briefly the main points.

(a) In the antisymmetric case, the Q -dependent part of the potential is

$$\frac{1}{2}M\Omega^2 \left(Q + \frac{cs}{M\Omega^2} \right)^2. \quad (2.4)$$

During the transfer of the particle from the reactant well centered at $-s_0$ to the product well centered at $+s_0$, the center of the Q oscillation shifts from $+cs_0/M\Omega^2$ to $-cs_0/M\Omega^2$, which leads [the same is true for the other bath modes in Eq. (2.1)] to a Frank-Condon overlap factor that reduces the rate.

(b) In the symmetric case on the other hand, the Q -dependent part of the potential is

$$\frac{1}{2}M\Omega^2 \left(Q + \frac{cs^2}{M\Omega^2} \right)^2, \quad (2.5)$$

the Q oscillator is not reorganized after the transition (the center of the oscillation remains at $-cs_0^2/M\Omega^2$) and there is no Frank-Condon factor.

These points are illustrated in Fig. 2. In addition, if we write an effective one-dimensional potential for the reaction coordinate as

$$as^4 - bs^2 + cs^nQ, \quad (2.6)$$

that fluctuates in time as Q oscillates, we have the following pictures.

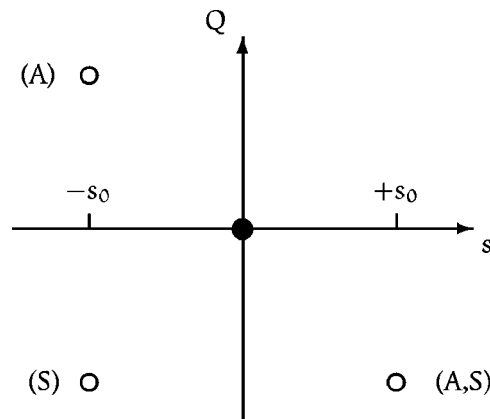


FIG. 2. Locations in the (s, Q) plane of the minima and saddle points of the two-dimensional potentials. The open circles are the positions of the minima for symmetric coupling (S) and antisymmetric coupling (A). The filled circle at the origin is the position of the saddle point for both types of coupling.

(a) In the antisymmetric case ($n = 1$) we have a double well with asymmetry fluctuations. The result is always a reduction of the rate (because of the Frank-Condon factor mentioned above).

(b) In the symmetric case ($n = 2$) we have a double well whose barrier height and transfer distance fluctuate. This leads to enhancement of the rate and justifies the term ‘‘rate promoting vibration’’ for the Q oscillation.

The two-dimensional Hamiltonian that we need in order to describe the effect of an intramolecular oscillation that enhances the rate is therefore^{25,22,28}

$$H_{2D} = \frac{1}{2}ms^2 + as^4 - bs^2 + \frac{1}{2}M\dot{Q}^2 + \frac{1}{2}M\Omega^2Q^2 + cQ(s^2 - s_0^2) + \frac{c^2s_0^4}{2M\Omega^2}. \quad (2.7)$$

This Hamiltonian has been extensively studied by Benderskii and co-workers.²² It is useful to clarify the terminology that is commonly used.

(a) The ‘‘fast-flip’’ limit, or ‘‘sudden approximation,’’ or ‘‘corner-cutting,’’ or ‘‘large curvature,’’ or ‘‘frozen bath’’ approximation, all refer to the case where the reaction coordinate follows the minimum energy path, but before it reaches the saddle point it tunnels along the s coordinate in a time that is short compared to the time scale of the Q vibration.

(b) The ‘‘slow-flip’’ limit, or ‘‘adiabatic,’’ or ‘‘small curvature’’ approximation, refer to the case in which the Q vibration adiabatically follows the s coordinate and tunneling takes place along the minimum energy path (i.e., at the saddle point).

We can make this distinction more quantitative by introducing the dimensionless frequency

$$\nu \equiv 2 \frac{\Omega}{\omega_b}, \quad (2.8)$$

where $\omega_b \equiv \sqrt{2b/m}$ is the inverted barrier frequency. Then the two limits mentioned above correspond to

$$\begin{aligned} \nu \ll 1 & \quad (\text{fast flip/corner cutting}), \\ \nu \gg 1 & \quad (\text{slow flip/small curvature}). \end{aligned} \quad (2.9)$$

C. Two-dimensional potential coupled to a bath

We now describe how to couple the two-dimensional Hamiltonian Eq. (2.7) to a harmonic bath, similar to the Zwanzig Hamiltonian Eq. (2.1). There are two limiting cases, low and high temperature.

In the low-temperature limit (or when the transferred particle is an electron which has very small mass), only the lowest doublet is occupied [so the Hamiltonian Eq. (2.1) can be approximated by the spin-boson Hamiltonian or by the Marcus model] and there is a small parameter, the tunneling splitting Δ , which can be used in a perturbative treatment. Hynes²⁰ (in the framework of Marcus's model) and Silbey²¹ (in the framework of the spin-boson Hamiltonian) assumed that the effect of the modulation of the potential by the intramolecular mode can be captured by an effective tunneling splitting

$$\Delta = \Delta_0 e^{-\alpha \delta D}, \quad (2.10)$$

where Δ_0 is the splitting of the uncoupled system, δD is the reduction of the transfer distance of the fluctuating double well and α is a parameter that for proton transfer has a value in the range of 25–35 Å⁻¹.

In the high-temperature limit on the other hand, more energy levels besides those in the lowest doublet participate in the dynamics, and the perturbative methods of Hynes and Silbey cannot be used. What is needed is a way to solve the full quantum Kramers problem Eq. (2.1), with the one-dimensional Hamiltonian H_{1D} replaced by the two-dimensional Hamiltonian Eq. (2.7). In a recent paper²⁵ we proposed a scheme that accomplishes this task. Since it is based on our earlier work on the Kramers problem with a one-dimensional PES, we will first summarize our method for that case.

D. Solution of the quantum Kramers problem

The quantum reaction rate is calculated using the Miller–Schwartz–Tromp rate formula²⁹ by an integration of the flux-flux correlation function:

$$k = \frac{1}{Z^r} \int_0^{+\infty} dt C_f(t_c), \quad (2.11)$$

where k is the rate, Z^r is the partition function for the reactants and $t_c = t - i\beta/2$ is the complex time.

The flux-flux correlation function C_f is given by

$$\begin{aligned} C_f = & \frac{1}{4m^2} \int dq \int dq' \\ & \times \left[\frac{\partial^2}{\partial s \partial s'} \left| \langle s' q' | e^{-i(H_{1D} + H_q + f)t_c} | s q \rangle \right|^2 \right]_{s=s'=0}, \end{aligned} \quad (2.12)$$

where H_q is the bath Hamiltonian, q is an N -dimensional coordinate that describes the bath and $f = \sum_{i=1}^N c_i q_i s$, i.e.,

$H_{1D} + H_q + f$ is the Zwanzig Hamiltonian Eq. (2.1). The interaction of the reaction coordinate with the bath destroys phase coherence and as a result the correlation function decays to zero leading to the introduction of a new time scale to the problem. The numerical evaluation of Eq. (2.12) can be accomplished by use of the exponential resummation form of the evolution operator⁹

$$e^{-i(H_{1D} + H_q + f)t} \approx e^{-iH_{1D}t} e^{-i(H_q + f)t} e^{+i(H_{1D} + f)t} e^{-iH_{1D}t}. \quad (2.13)$$

After some long algebra,⁹ the final result for the correlation function is found to be equal to

$$C_f = C_f^0 B_1 Z_{\text{bath}}^\# - \int_0^\infty d\omega \kappa_f^0 J(\omega) B_2(\omega) Z_{\text{bath}}^\#. \quad (2.14)$$

In this equation, $J(\omega)$ is the spectral density of the bath Eq. (2.2), C_f^0 is the correlation function for the *uncoupled* one-dimensional problem, B_1 and B_2 are functions that depend on the characteristics of the bath and on the barrier frequency ω_b (the detailed forms of these functions are given in Ref. 9), $Z_{\text{bath}}^\#$ is the bath partition function when s is at the transition state and

$$\kappa_f^0 = \frac{1}{4m^2} |\langle s=0 | e^{-iH_{1D}t_c} | s=0 \rangle|^2. \quad (2.15)$$

Equation (2.14) is a one-dimensional integral that can be easily calculated numerically and then substituted into Eq. (2.11) for the calculation of the rate. It is more useful to calculate a more intuitive physical quantity, the transmission coefficient which gives an indication of the degree of the quantum character of the reaction and is defined as

$$\Gamma_{1D} = \frac{k}{k^{\text{TST}}}, \quad (2.16)$$

where k^{TST} is the rate as calculated by the classical transition state theory (TST):⁵

$$k^{\text{TST}} = \frac{k_B T}{2\pi} \frac{Z_{\text{bath}}^\#}{Z^r} e^{-\beta V_0}, \quad (2.17)$$

where V_0 is the barrier height. Fortunately, when we calculate the ratio Eq. (2.16) the quantities $Z_{\text{bath}}^\#$ and Z^r cancel out and we do not need to compute them. We should emphasize that the subscript “1D” in Eq. (2.16) refers to the fact that the PES is one dimensional, but the proton is still coupled to a bath.

E. Solution of the quantum Kramers problem with a rate promoting vibration

We now substitute in Eq. (2.12) the one-dimensional double well Hamiltonian by the two-dimensional problem Eq. (2.7). The calculation is lengthy and explained in detail in Ref. 25. We mention the final result for the transmission coefficient Γ_{2D} which is defined as the ratio of the quantum rate k_{2D} over the *multidimensional* transition state theory result k_{TST} (i.e., k_{TST} is the TST rate when the reaction coordinate is coupled to the N -dimensional bath *and* to the Q oscillation):

$$\Gamma \equiv \frac{k}{k_{\text{TST}}} = \frac{(1/Z^r) \int_0^\infty dt \tilde{C}_f(t_c)}{(Z^\# / Z^r) e^{-\beta V_0}}, \quad (2.18)$$

where $Z^\#$ is the part of the partition function with the reaction coordinate excluded, evaluated at the transition state. We can write it as $Z^\# = Z_Q Z_{\text{bath}}^\#$, where Z_Q is the partition function for the harmonic vibration Q with frequency Ω that is coupled symmetrically to the reaction coordinate. Combining Eqs. (2.14) and (2.18) we find that

$$\Gamma_{2D} = \frac{e^{\beta V_0}}{Z_Q} \int_0^\infty dt \left[\tilde{C}_f^0 B_1 - \int_0^\infty d\omega \tilde{\kappa}_f^0 J(\omega) B_2(\omega) \right]. \quad (2.19)$$

The bath functions $B_1, B_2(\omega)$ are the same as in the uncoupled (to the Q vibration) case, while the functions with the tilde have the same definition as in the one-dimensional case, except that the evolution propagator is now related to the two-dimensional Hamiltonian H_{2D} .

Equation (2.19) is our final result for the quantum Kramers problem with a symmetrically coupled vibration. We should emphasize once again that the effect of this vibration *cannot* be approximated by treating the rate promoting vibration Q as one of the bath modes with the requirement that is strongly coupled to the reaction coordinate. The effect of the Q vibration is not due to the strength of the coupling, but due to the different symmetry of the coupling compared to the coupling to the other bath modes.

III. PROTON TRANSFER RATE IN BENZOIC ACID DIMER CRYSTALS

We shall now apply the theory of Sec. II to the benzoic acid dimer crystal system. First we shall specify the appropriate parameters explaining which ones have been determined experimentally and the reason for making a particular guess for the ones that are unknown.

A. Bath

We assume that the protons are coupled to acoustic phonons of the crystal, which means that the exponent in Eq. (2.3) is equal to $n=3$. The bath frequency cutoff (which in a crystal is the Debye frequency) is known¹⁷ from experiments and is equal to $\omega_c = 80 \text{ cm}^{-1}$. The friction coefficient γ of Eq. (2.3) is not known. Skinner and Trommsdorff¹⁷ estimate an upper bound for γ equal to 0.83. We have chosen a value $\gamma=0.8$ for our calculations and we have checked that the results are not sensitive to changes in the value of γ .

B. PES

The transfer distance is known experimentally:¹³ the O–H bond length is 1.03 Å and the O–O bond length equal to 2.66 Å, which means that the transfer distance is equal to 0.6 Å. The bond frequency ω_{OH} is experimentally known and is equal to 2890 cm^{-1} . The barrier height is not known. Meyer and Ernst¹⁸ in their two-dimensional fitting used barrier heights equal to 0.008–0.009 a.u. (5 kcal/mol, 1760 cm^{-1}), but these values were a consequence of their choice to couple the reaction coordinate antisymmetrically to the Q vibration. One artifact of approximating the PES by a double well potential $as^4 - bs^2$ is that once we specify the values of

the barrier height and the transfer distance, the full PES is specified. For the value of the barrier height that Meyer and Ernst chose, the well frequency is equal to 1980 cm^{-1} which is 30% lower than the experimental value of the O–H bond frequency. Since the energy doublets in a double well are separated by a spacing roughly equal to the well frequency, it is important for the accurate description of the quantum dynamics to use a reasonable value for this quantity. For this reason, we used a barrier height equal to 0.013 a.u. (8.1 kcal/mol, 2850 cm^{-1}) which corresponds to a well frequency 2650 cm^{-1} .

C. Rate promoting vibration

The frequency of the O–O bond oscillation is not known exactly, so we have followed Ref. 24 and set $\Omega = 120 \text{ cm}^{-1}$, which is a typical value for an intramolecular oscillation of heavy atoms. We should mention that the results depend only on the ratio $c^2/(M\Omega^2)$, therefore there is effectively only one fitting parameter, the coupling c (assuming that the frequency Ω is smaller than $k_B T$ so that the mode is thermally excited). For this value of Ω , the dimensionless frequency ν in Eq. (2.8) is equal to 0.13, which means that in a pure two-dimensional problem we would be in the fast-flip (corner-cutting) limit. The mass of the Q vibration is not known (since the heavy atoms are coupled to the rest of the crystal), so we follow Ref. 24 and set $M_Q = 100m_H$ which is a reasonable value since it is equal to the mass of several C atoms. The coupling c of the reaction coordinate to the Q vibration is not known. We chose a value $c = 0.08$ a.u. which in the two-dimensional problem (without the presence of the bath) would lead to a 90% reduction of the barrier height at the saddle point compared to the height of the static barrier. This reduction is not as large as it appears to be at first sight, since for this value of the dimensionless frequency ν , the instanton trajectory in the two-dimensional potential is close to the static barrier and not to the saddle point.

Using these parameters we have calculated the activation energies for H and D transfer. Because the calculation uses an expansion in a series of two-dimensional wave functions it requires substantial CPU time. In particular, the CPU time required on a RS/6000 workstation for the calculation of Eq. (2.14) is 10 s, while 2 h were required for the corresponding calculation Eq. (2.18) of the two-dimensional case. Since we need to calculate several time steps until the correlation function decays so that the integral of Eq. (2.11) can be calculated with confidence, the obvious way to calculate the activation energy by repeating the calculation at several values of temperature, is prohibitively long. On the other hand, we will demonstrate a way to extract the two-dimensional activation energy E_{2D} from a calculation at one value of temperature only.

As we mentioned earlier, the TST result is equal to

$$k_{\text{TST}} = \frac{k_B T}{2\pi} \frac{Z_{\text{bath}}^\#}{Z^r} e^{-\beta V_0}, \quad (3.1)$$

where the activation energy is equal to the barrier height V_0 .

TABLE I. Activation energies for H and D transfer at $\gamma=0.8$ and $T=300^\circ\text{K}$. Three values are shown: the activation energies calculated using a one- and two-dimensional Kramers problem and the experimental (Ref. 12) values. The values of energies are in atomic units (the values in kcal/mol are given in parentheses).

	E_{1D}	E_{2D}	Experiment
H	0.0054 (3.39)	0.0024 (1.51)	0.0023 a.u. (1.44 kcal/mol)
D	0.0083 (5.21)	0.0050 (3.14)	0.0048 a.u. (3.01 kcal/mol)

By analogy, we can define the quantum activation energies for the one- and two-dimensional quantum Kramers problems by

$$k = \frac{k_B T}{2\pi} \frac{Z_{\text{bath}}^\ddagger}{Z^r} e^{-\beta E_{1D}}, \quad k_{2D} = \frac{k_B T}{2\pi} \frac{Z_{\text{bath}}^\ddagger}{Z^r Z_Q} e^{-\beta E_{2D}}, \quad (3.2)$$

where Z_Q is the partition function for the Q vibration [see the remarks after Eq. (2.19)]. We should emphasize that by the terms one- and two-dimensional Kramers problem we mean a one- or two-dimensional PES coupled to a bath, in other words we are always considering reactions in a condensed phase. A simple manipulation of Eqs. (3.1), (3.2), (2.16), (2.17), (2.18) and (2.19) leads to

$$E_{2D} = E_{1D} - (k_B T) \ln \frac{\Gamma_{2D}}{\Gamma_{1D}} - (k_B T) \ln Z_Q. \quad (3.3)$$

Since the calculation for the one-dimensional quantum Kramers problem can be done in a few minutes it is easy to find the activation energy E_{1D} . Then, if we calculate the transmission coefficient Γ_{2D} for the two-dimensional Kramers problem for one value of temperature, we can find the activation energy E_{2D} using Eq. (3.3). In Table I we show the results of our calculations for temperature $T=300^\circ\text{K}$ and friction coefficient $\gamma=0.8$.

We have repeated the H calculation for friction $\gamma=1.0$ and found that the activation energy E_{2D} was equal to 0.0019 a.u., which means that the results depend only weakly on the friction parameter γ . The remarkable agreement with experiment shown in Table I is undoubtedly fortuitous but it is a strong indication that our model, for a reasonable choice of the parameters that are not known experimentally, makes predictions that are consistent with the experimental findings.

A question arises naturally regarding calculation of Skinner and Trommsdorff.¹⁷ Do we have to correct the model used in that work by including a rate promoting vibration? The model solved by Silbey²¹ is equivalent at low temperature to the model used in Ref. 17, plus coupling to a rate promoting vibration. Examination of the results of Ref. 21 shows that at low temperature the Q oscillation does not affect the one-phonon processes included in the calculation of Ref. 17.

We propose that the described model has an importance beyond fitting the benzoic acid dimer data and is useful as a general theory of proton transfer in condensed phases at intermediate temperatures. Benderskii and co-workers²² (for earlier studies by other workers see the review paper Ref. 28) have shown conclusively that in gas phase proton transfer

reactions one must take into account the vibration assisted tunneling effect due to heavy atom oscillations that modulate the transfer distance. This effect was included in the study of proton transfer in condensed phases by Hynes (for reactions in solutions) and Silbey (for solids). Both used a perturbative expansion in the tunneling splitting which is valid only at very low temperature. It is natural to extend these works at intermediate temperatures, which can be accomplished by incorporating a symmetrically coupled vibration into the Zwanzig Hamiltonian. The operator exponential resummation method we have used for the study of the quantum Kramers problem allows inclusion of a rate promoting vibration in a straightforward manner, with the details of the derivation presented in Ref. 25. Finally, we should mention that in Ref. 30 we have applied the theory we used in this paper to proton transfer in another system, to explain the large kinetic isotope effects observed in bovine serum amine oxidase.

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- ¹R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985).
- ²V. G. Levich and R. R. Dogonadze, *Dokl. Akad. Nauk. SSSR* **124**, 123 (1959).
- ³A. Leggett, S. Chakravarty, A. Dorsey, M. Fisher, A. Garg, and W. Zwerger, *Rev. Mod. Phys.* **59**, 1 (1987).
- ⁴A. M. Kuznetsov, *Charge Transfer in Physics, Chemistry and Biology* (Gordon & Breach, Reading, 1995).
- ⁵P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1991).
- ⁶S. Hammes-Schiffer and J. C. Tully, *J. Chem. Phys.* **101**, 4657 (1994).
- ⁷J. Cao and G. Voth, *J. Chem. Phys.* **105**, 6856 (1996).
- ⁸M. Topaler and N. Makri, *J. Chem. Phys.* **101**, 7500 (1994).
- ⁹S. D. Schwartz, *J. Chem. Phys.* **104**, 14394 (1996). For applications of the exponential resummation method see: S. D. Schwartz, *J. Chem. Phys.* **91**, 7621 (1989); **96**, 5952 (1992); **97**, 7377 (1992); **100**, 8795 (1994); **101**, 10436 (1994); **105**, 6871 (1996); D. Antoniou and S. D. Schwartz *ibid.* **103**, 7277 (1995); **104**, 3526 (1996).
- ¹⁰S. Nagaoka, T. Terao, F. Imashiro, A. Saika, N. Hirota, and S. Hayashi, *Chem. Phys.* **80**, 580 (1981); *J. Chem. Phys.* **79**, 4694 (1983).
- ¹¹B. H. Meier, F. Graf, and R. R. Ernst, *J. Chem. Phys.* **76**, 767 (1982); R. Meyer and R. R. Ernst, *ibid.* **86**, 784 (1987).
- ¹²A. Stöckli, B. H. Meier, R. Kreis, R. Meyer, and R. R. Ernst, *J. Chem. Phys.* **93**, 1502 (1990).
- ¹³A. J. Horsewill and A. Ikram, *Physica B* **226**, 202 (1996); D. F. Brougham, A. J. Horsewill, A. Ikram, R. M. Ibberson, P. J. McDonald, and M. Pinter-Krainer, *J. Chem. Phys.* **105**, 979 (1996).
- ¹⁴A. Stöckli, A. Furrer, Ch. Schönenberger, B. H. Meier, R. R. Ernst, and I. Anderson, *Physica B & C* **136**, 161 (1986).
- ¹⁵R. M. Hochstrasser and H. P. Trommsdorff, *Chem. Phys.* **115**, 1 (1987).
- ¹⁶C. C. Look and I. J. Lowe, *J. Chem. Phys.* **44**, 3437 (1966).
- ¹⁷J. L. Skinner and H. P. Trommsdorff, *J. Chem. Phys.* **89**, 897 (1988).
- ¹⁸R. Meyer and R. R. Ernst, *J. Chem. Phys.* **93**, 5518 (1990).
- ¹⁹C. Scheurer and P. Saalfrank, *J. Chem. Phys.* **104**, 2869 (1996).
- ²⁰D. Borgis and J. Hynes, *J. Chem. Phys.* **94**, 3619 (1991).
- ²¹A. Suarez and R. Silbey, *J. Chem. Phys.* **94**, 4809 (1991).
- ²²V. A. Benderskii, S. Yu. Grebenshchikov, and G. V. Mil'nikov, *Chem. Phys.* **194**, 1 (1995); and references cited therein.
- ²³C. P. Flynn and A. M. Stoneham, *Phys. Rev. B* **1**, 3966 (1970); Y. Kagan and M. I. Klinger, *Zh. Eksp. Teor. Fiz.* **70**, 255 (1976); A. M. Kuznetsov, *Elektrokimiya* **22**, 240 (1986); L. I. Trakhtenberg, *Zh. Fiz. Khim.* **54**,

- 1324 (1986); W. Siebrand, T. Wildman, and M. Zgierski, J. Am. Chem. Soc. **106**, 4083 (1984).
- ²⁴V. Sakun, M. Vener, and N. Sokolov, J. Chem. Phys. **105**, 379 (1996); N. Sokolov and M. Vener, Chem. Phys. **168**, 29 (1992).
- ²⁵D. Antoniou and S. D. Schwartz, J. Chem. Phys. **108**, 3620 (1998).
- ²⁶R. Zwanzig, J. Stat. Phys. **9**, 215 (1973).
- ²⁷S. Okuyama and D. W. Oxtoby, J. Chem. Phys. **88**, 2405 (1988).
- ²⁸V. Benderskii, D. Makarov, and C. Wight, Adv. Chem. Phys. **88**, 1 (1994).
- ²⁹W. Miller, S. D. Schwartz, and J. Tromp, J. Chem. Phys. **79**, 4889 (1983).
- ³⁰D. Antoniou and S. D. Schwartz, Proc. Natl. Acad. Sci. USA **94**, 12360 (1997).