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Activated chemistry in the presence of a strongly symmetrically coupled vibration

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In the gas phase, tunneling reaction rates can be significantly enhanced if the reaction coordinate is symmetrically coupled to a harmonic oscillation, as has been emphasized by Benderskii and co-workers [Adv. Chem. Phys. **88**, 1 (1994)]. This is due to the fact that the symmetric coupling leads to modulation of the barrier height. Similar effects have been observed in reactions in model condensed phase studies, as in the Hamiltonians that have been studied by Borgis and Hynes [J. Chem. Phys. **94**, 3619 (1991)] and Suarez and Silbey [J. Chem. Phys. **94**, 4809 (1991)]. All of these works assume that tunneling proceeds from the ground state. In this paper, we use the exponential resummation technique that we used in our recent work on the quantum Kramers problem, to study the case when there can be excitations to higher states and activated transmission over a barrier. We present a general methodology to exactly include direct coupling between the reaction coordinate and the symmetrically coupled promoting vibration and find that the rate of reactions in condensed phases is enhanced as in the case of tunneling from the ground state. This effect, however, is strongly modulated by loss of coherence induced by the condensed phase environment. © 1998 American Institute of Physics. [S0021-9606(98)50109-2]

I. INTRODUCTION

The Kramers model for chemical reactions in a condensed phase is a useful, but highly simplified picture of condensed phase chemistry. In particular, this model assumes that the reaction coordinate does not couple strongly to any substrate mode and that the coupling of all modes is of the same symmetry. It is well known that in complex substrates, certain motions have profound effects on reaction rates in the gas phase, as in the following example where the “fluctuation barrier preparation” is due to a symmetrically coupled vibration. Proton tunneling in tropolone is a system that has been studied both theoretically¹ and experimentally.² It has been found that the rate depends strongly on the symmetry of excited nonreactive vibrations. One would expect to see similar effects in the condensed phase. This paper explores these effects for the specific case of a symmetrically coupled oscillation. In particular, we will show how starting from the exact solution of the two-dimensional Hamiltonian Eq. (2.1) and using only the well-understood approximation Eq. (3.5), one can calculate numerically the reaction rate in the presence of a heat bath.

The character of the symmetry of the coupling of the reaction coordinate s to a nonreactive vibration Q has a profound effect on the reaction rate, which is more pronounced when there is a significant degree of tunneling. It is meaningful to talk about symmetry when the potential function for the uncoupled one-dimensional reaction potential is symmetric and in the following discussion we will assume that the potential energy surface is a quartic double well.

Usually, a bilinear coupling csQ is assumed. This is the antisymmetric case and the effect of the coupling is to induce asymmetry fluctuations to the potential energy surface. The probability of tunneling is maximum when the fluctuations

happen to restore the symmetry of the double well and it is often assumed that tunneling takes place instantaneously compared to the period of the Q vibration. This is the Franck–Condon approximation, which results in an effective tunneling splitting

$$\Delta_{\text{eff}} = \Delta_0 e^{-\Phi/2}, \quad (1.1)$$

where Φ is the Franck–Condon factor. In a golden rule calculation the rate is found to be proportional to Δ^2 , therefore Eq. (1.1) shows that the effect of antisymmetrically coupled vibrations is to always reduce the tunneling rate.

On the other hand, a symmetrically coupled vibration has the opposite effect on the tunneling rate. A classical argument for understanding the reason would be to assume a double well $as^4 - bs^2$ (the barrier height of a quartic double well is equal to $b^2/4a$) that is coupled to a harmonic oscillator Q through a term $cs^2Q(t)$. The effect of the coupling is to modulate the barrier height (without inducing any asymmetry) which becomes $[b - cQ(t)]^2/4a$. As Q oscillates, there are time spans for which the barrier is lowered significantly (assuming that the coupling c is large enough) and as a result the rate is enhanced.

In fact the coupling to the Q oscillation reduces both the barrier height V_0 and the transfer distance D . For ground state tunneling the rate is proportional to the square of the tunneling splitting Δ^2 . For a quartic double well it is possible to calculate Δ analytically,³ with the result

$$\Delta \sim e^{-aDV_0^{1/2}}, \quad (1.2)$$

where a is a constant that depends on the mass and V_0 , D are the barrier height and the distance between the centers of the wells, respectively. Equation (1.2) suggests that in a discussion of rate enhancement we should take into account the

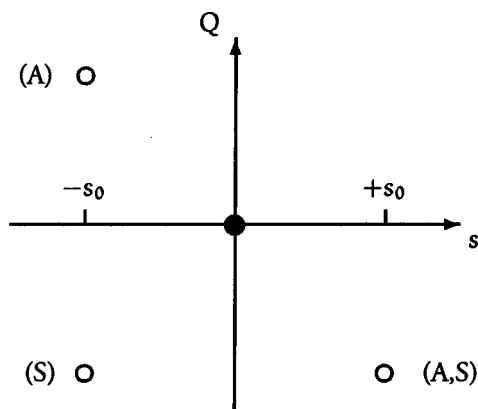


FIG. 1. Locations in the (s, Q) plane of the minima and saddle points of the two-dimensional potentials. The open circles are the positions of the minima for symmetric coupling (S) and antisymmetric coupling (A). The filled circle at the origin is the position of the saddle point for both types of coupling.

effects of the reduction of both the barrier height and the transfer distance. However, in a quartic double well these two quantities are related by

$$V_0 = \frac{1}{32} m \omega_0^2 D^2, \quad (1.3)$$

where ω_0 is the frequency of oscillations at the bottom of the well. Therefore for a quartic double well, the barrier height reduction and the barrier width reduction are one and the same effect and in the following discussion we shall always mention only the barrier height reduction. In fact, Eqs. (1.2) and (1.3) show that the logarithm of the rate increases linearly with the reduction of the barrier width, a fact that is the starting point of the calculations in Refs. 4 and 5.

We shall now pinpoint the crucial physical difference between the two types of coupling. Assume that the double well has the reaction well centered at $-s_0$ and the product well centered at $+s_0$.

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

$$\frac{1}{2} M \Omega^2 \left(Q + \frac{cs}{M \Omega^2} \right)^2. \quad (1.4)$$

During the reaction, the center of the Q oscillation shifts from $+cs_0/M\Omega^2$ to $-cs_0/M\Omega^2$, which leads to the Franck-Condon overlap factor in Eq. (1.1).

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

$$\frac{1}{2} M \Omega^2 \left(Q + \frac{cs^2}{M \Omega^2} \right)^2, \quad (1.5)$$

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

There is a further consequence of this difference, explained in Ref. 6, where the two-dimensional potential energy surfaces are plotted for both types of coupling. In both cases there is one saddle point and two minima (see Fig. 1):

(a) In the antisymmetric case, the minima are symmetric with respect to the origin of the (s, Q) plane (a consequence of the fact that the equilibrium position of the Q vibration is shifted after the transition). When we draw a straight reaction path that connects the minima (this is the one-dimensional static barrier), it passes near the saddle point. In other words, the minimum energy path is the same as the path in the static barrier.

(b) In the symmetric case, on the other hand, the two minima are symmetric with respect to the Q -axis (because the Q oscillation is not reorganized in the transition) and as a result the reaction path that connects the two minima with a straight line does not pass near the saddle point. The minimum energy path differs from the static barrier path and the true tunneling path lies between these two limits.³

We now turn our attention to multidimensional Hamiltonians and to reactions in condensed phases. Proton transfer in solution with coupling to a “rate promoting” vibration in the sense we discussed above, has been studied by Borgis and Hynes.⁴ They used a Marcus-like model with the important addition that the coupling matrix element between the reactant and product states is written as

$$\Delta \sim \Delta_0 e^{-\alpha Q}, \quad (1.6)$$

where Q is the deviation from equilibrium of the interatomic distance of the heavy atoms between which the proton hops. In this picture, Q is the rate promoting vibration. A typical value of the parameter α for proton transfer is $\alpha \sim 30 \text{ \AA}^{-1}$, which means that the rate (that is proportional to Δ^2 in Marcus’ theory) is very sensitive to variations of Q . In contrast, for electron transfer $\alpha \sim 1 \text{ \AA}^{-1}$ and the effects of coupling are not as dramatic. Borgis and Hynes solved for the coupled dynamics of the proton, the Q oscillation, and the phenomenological one-dimensional solvent using a perturbation theory approach. Recently,⁷ they have used a curve-crossing formulation to study their Hamiltonian and they reproduced their earlier results.

An alternative but related approach has been taken by Silbey and Suarez in their study⁵ of hydrogen hopping in solids. Instead of a Marcus model, they used the spin-boson Hamiltonian⁸ with a tunneling splitting that has the form Eq. (1.6). The environment as described in the spin-boson Hamiltonian not only has slow dynamics (as in the Marcus model) but fast modes as well. Compared to the work of Borgis and Hynes, this detail leads to subtle questions of convergence of the rate that are discussed in Ref. 5.

Finally, we would like to mention an intriguing work⁹ where an analogy was drawn between coupling of a tunneling reaction coordinate to a harmonic oscillator and the stochastic resonance problem.

The structure of the rest of the paper is as follows. In the next section we briefly summarize some results and concepts from the work of Benderskii and co-workers on ground state tunneling in two-dimensional systems. The main part of the paper is Sec. III which discusses reactions in condensed phases. In the first part of Sec. III we present briefly our earlier results for the quantum Kramers problem, using the exponential resummation technique. Then we show how that method can be extended to incorporate the effect of a rate

promoting vibration in the quantum Kramers problem. Finally, we conclude with the discussion of certain enzymatic proton transfer reactions that show anomalously large kinetic isotope effects, which might be caused by the effects we discuss in this paper.

II. TUNNELING IN TWO-DIMENSIONAL POTENTIALS

The Hamiltonian we will study has the following form:

$$H_{2d} = \frac{1}{2}m\dot{s}^2 + as^4 - bs^2 + \frac{1}{2}M\dot{Q}^2 + \frac{1}{2}M\Omega^2Q^2 + cQ(s^2 - s_0^2) + \frac{c^2s_0^4}{2M\Omega^2}. \quad (2.1)$$

This Hamiltonian describes a reaction coordinate s in the symmetric double well $as^4 - bs^2$ that is coupled to a harmonic oscillator Q . The coupling is symmetric for the reaction coordinate and is assumed to have the form cs^2Q . The origin of the Q oscillations is taken to be at $Q=0$ when the reaction coordinate is at $\mp s_0$ (centers of the reactant/product wells), which explains the presence of the term $-cs_0^2Q$. This potential has two minima at $(s, Q) = (\pm s_0, 0)$ and one saddle point at $(s, Q) = (0, +cs_0^2/M\Omega^2)$.

This Hamiltonian has been studied by Benderskii and co-workers in Ref. 10 using instanton techniques [in a later paper¹¹ they used the Herring–Lifshitz formula to calculate semiclassical wave functions for the Hamiltonian (2.1)]. We will now mention some of their conclusions.

One has to distinguish between two physical pictures:

(a) The fast-flip limit (also called in the literature¹² the “sudden approximation,” “corner-cutting,” “large curvature,” or “frozen bath” approximation) 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 (also known as the “adiabatic” or the “small curvature” approximation¹³) 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 the above discussion more quantitative by introducing the parameter $B \equiv c^2/2aM\Omega^2$ and the dimensionless frequency¹⁰

$$\nu \equiv 2\frac{\Omega}{\omega_b}, \quad (2.2)$$

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

$$\begin{aligned} \nu &<< \sqrt{1-B} \quad (\text{fast flip/corner cutting}), \\ \nu &>> \sqrt{1-B} \quad (\text{slow flip/adiabatic}). \end{aligned} \quad (2.3)$$

In most cases $B \ll 1$, so that the conditions (2.3) are equivalent to $\nu \ll 1$ (or $\gg 1$).

Before we proceed, we must make an important observation. If $B \sim 1$, then the slow-flip condition may be satisfied even if ν is small, provided that the coupling c is large

enough. This was called the “strong fluctuation” limit in Ref. 10 and is relevant to the transfer of heavy particles.³

Benderskii and co-workers used the techniques of Ref. 14 and wrote the classical action for the Hamiltonian (2.3) by expanding¹⁵ the propagation kernel in imaginary time $\exp(-\Omega|t|)$ in power series in the fast-flip limit, or by replacing it by a δ -function in time in the slow-flip limit.

The instanton method takes into account only the dynamics of the lowest energy doublet. This is a valid description at low temperature. What happens at higher temperature, when excitations to higher states in the double well are possible? This leads to the question that is the focus of this paper: What is the effect of a symmetrically coupled vibration on the calculations of the quantum Kramers problem that have been performed recently^{16–19} for potentials where tunneling proceeds from excited states? The new physical feature introduced in the quantum Kramers problem is a new time scale in addition to the two frequencies shown in Eq. (2.2), namely the decay time of the flux-flux correlation function, as discussed in the next section after Eq. (3.4). As we will show, this new time scale makes the distinction between the corner cutting and the adiabatic limit in Eq. (2.3) to be of limited relevance to the dynamics of reactions in condensed phases.

In the next section we shall show how the technique of exponential resummation of the evolution operator that has been developed in our group^{19,20} can naturally incorporate the effect of a symmetrically coupled vibration.

III. QUANTUM KRAMERS PROBLEM

We now turn our attention to the Hamiltonian

$$H = \frac{1}{2}m\dot{s}^2 + as^4 - bs^2 + \sum_{i=1}^{N+1} \left[\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2q_i^2 \right] - \sum_{i=1}^{N+1} c_iq_if_i(s), \quad (3.1)$$

which describes a particle in a double well that is coupled to a bath of harmonic oscillators through the coupling functions $c_iq_if_i(s)$. In the case of bilinear coupling, $f_i(s) = s$ and Eq. (3.1) reduces to the usual quantum Kramers problem.

Let us now assume that one of the harmonic modes [e.g., the $(N+1)$ -th mode in Eq. (3.1)] is symmetrically coupled to the reaction coordinate, while all the others are coupled antisymmetrically. Then, Eq. (3.1) can be rewritten as

$$H = H_{2d}(s, Q) + \sum_{i=1}^N \left[\frac{p_i^2}{2m_i} + \frac{1}{2}m_i\omega_i^2 \left(q_i - \frac{c_is}{m_i\omega_i^2} \right)^2 \right], \quad (3.2)$$

where H_{2d} is given by Eq. (2.1). As we mentioned earlier, the effect of the symmetrically coupled oscillation is to change the height of the barrier of the double well, while the effect of the antisymmetrically coupled oscillations is to induce asymmetry fluctuations to the double well.

We will assume that the Q vibration is not directly coupled to the bath of harmonic oscillators. This assumption is similar to the approach employed by Silbey and Suarez⁵ who used a tunneling splitting that depends on the oscillating

transfer distance Q in their spin-boson Hamiltonian. Borgis and Hynes⁴ also made this assumption in the context of Marcus' theory.

After this assumption is made, it is possible to calculate the quantum rate for the Hamiltonian Eq. (3.2). We shall now show how starting from our previous work¹⁹ on the quantum Kramers problem we can accommodate the effect of the symmetrically coupled Q mode.

The rate will be calculated using the Miller–Schwartz–Tromp rate formula,²¹ by an integration of the correlation function

$$k = \frac{1}{Z_r} \int_0^{+\infty} dt C_f(t_c), \quad (3.3)$$

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

$$C_f = \frac{1}{4m^2} \int dq \int dq' \left[\frac{\partial^2}{\partial s \partial s'} \right] \left| \langle s' q' | e^{-i(H_s + H_q + f)t_c} | s q \rangle \right|^2 \Big|_{s=s'=0}, \quad (3.4)$$

where H_q is the bath Hamiltonian, q is a N -dimensional coordinate that describes the bath, and $f = \sum_{i=1}^N c_i q_i s$. The interaction of the reaction coordinate with the bath destroys phase coherence and as a result the correlation function decays to zero after some time and this fact introduces the new time scale we mentioned at the end of the previous section.

The numerical evaluation of Eq. (3.4) becomes feasible when we use the exponential resummation form of the evolution operator²⁰

$$e^{-i(H_s + H_q + f)t} \approx e^{-iH_s t} e^{-i(H_q + f)t} e^{+i(H_s + f)t} e^{-iH_s t}. \quad (3.5)$$

Using this result, the correlation function Eq. (3.4) can be rewritten as

$$C_f = \frac{1}{4m^2} \int dq \int dq' \left[\frac{\partial^2}{\partial s \partial s'} \right] \int ds_\alpha \int ds_\beta \times \langle s' | e^{-iH_s t} | s_\alpha \rangle \langle q' | e^{-i(H_q + f)t} | q \rangle \times \langle s_\alpha | e^{+i(H_s + f)t} | s_\beta \rangle \langle s_\beta | e^{-iH_s t} | s \rangle \Big|_{s=s'=0}. \quad (3.6)$$

In an earlier paper¹⁹ we found that after a lengthy calculation, the correlation function for the Kramers problem Eq. (3.6) can be shown to be equal to

$$C_f = C_f^0 B_1 Z_{\text{bath}} - \int_0^\infty d\omega \kappa_f^0 J(\omega) B_2(\omega) Z_{\text{bath}}. \quad (3.7)$$

In this equation, $J(\omega)$ is the spectral density of the bath, 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. 19) and

$$\kappa_f^0 = \frac{1}{4m^2} |\langle s=0 | e^{-iH_s t_c} | s=0 \rangle|^2. \quad (3.8)$$

We shall now explain how the result Eq. (3.7) is modified when we make the substitution

$$H_s \rightarrow H_s + H_Q + c(s^2 - s_0^2)Q \quad (3.9)$$

in Eq. (3.4). In order to calculate the quantum rate for the new Hamiltonian we proceed in four steps.

First step: We evaluate the matrix element [which corresponds to the first matrix element in Eq. (3.6)]

$$\langle s' Q' | e^{-i[H_s + H_Q + c(s^2 - s_0^2)Q]t} | s_\alpha Q \rangle. \quad (3.10)$$

In order to calculate this matrix element we need to diagonalize the Hamiltonian Eq. (2.1). We diagonalized the two-dimensional Hamiltonian in two steps:

(i) We used a basis set consisting of 200 harmonic eigenfunctions in order to diagonalize the double well Hamiltonian for the uncoupled s degree of freedom.

(ii) We used the eigenfunctions that correspond to the lowest 30 states obtained in the previous step, along with 30 eigenfunctions for the harmonic Hamiltonian H_Q to form a 30×30 basis set. We then used this basis set to form a 900×900 matrix from the Hamiltonian Eq. (2.1), which we diagonalized using the EISPACK package.

Once we are able to calculate matrix elements like the one in Eq. (3.10), we can calculate the modified [i.e., those that correspond to the new Hamiltonian Eq. (3.9)] functions \tilde{C}_f^0 and $\tilde{\kappa}_f^0$. For the calculations of these functions one needs to integrate out the nonreactive degree of freedom which leads to integrals of the type

$$\int dQ \int dQ' |\langle sQ | e^{-iH_{2d}t_c} | s'Q' \rangle|^2, \quad (3.11)$$

where H_{2d} is the right-hand side of Eq. (3.9). As is well known one can expand the propagator in a series as

$$\langle sQ | e^{-iH_{2d}t} | s'Q' \rangle = \sum_i \Psi_i^{(2d)}(s, Q) \Psi_i^{(2d)}(s', Q') \times e^{-iE_i^{(2d)}t_c}, \quad (3.12)$$

where $\Psi_i^{(2d)}$ are the eigenfunctions of H_{2d} . Each of these eigenfunctions can be expanded in terms of the basis specified in step (ii) above:

$$\Psi_i^{(2d)}(s, Q) = \sum_{l,m} c_{l,m}^i \psi_l^{(1d)}(s) \phi_m^{ho}(Q), \quad (3.13)$$

where $\psi_l^{(1d)}(s)$ are the eigenfunctions of the one-dimensional double well Hamiltonian H_s and $\phi_m^{ho}(Q)$ are harmonic eigenfunctions of H_Q . Using Eqs. (3.12) and (3.13) it is straightforward to show that

$$\begin{aligned} & \int dQ \int dQ' |\langle sQ | e^{-iH_{2d}t_c} | s'Q' \rangle|^2 \\ &= \sum_{m,m'} \left| \sum_i \sum_{l,l'} c_{l,m}^i c_{l',m'}^i \psi_l^{(1d)}(s) \psi_{l'}^{(1d)}(s') e^{-iE_i^{2d}t_c} \right|^2. \end{aligned} \quad (3.14)$$

Second step: We shall turn our attention now to the nonadiabatic correction, which consists of the last two operators of Eq. (3.6), as modified after the substitution Eq. (3.9):

$$e^{+i[H_s+H_Q+c(s^2-s_0^2)Q+f]t}e^{-i[H_s+H_Q+c(s^2-s_0^2)Q]t}. \quad (3.15)$$

It is by forming the matrix elements of these operators that we obtain the functions $B_1, B_2(\omega)$ in Eq. (3.7). For each operator of this equation, we apply the resummation Eq. (3.5) with the result

$$\begin{aligned} & [e^{+i[H_s+c(s^2-s_0^2)Q+f]t}e^{+iH_Qt}e^{-i[H_Q+c(s^2-s_0^2)Q]t}e^{+iH_Qt}] \\ & \times [e^{-iH_Qt}e^{+i[H_Q+c(s^2-s_0^2)Q]t}e^{-iH_Qt} \\ & \times e^{-i[H_s+c(s^2-s_0^2)Q]t}]. \end{aligned} \quad (3.16)$$

Several factors cancel out, the final result being

$$e^{+i[H_s+cs^2Q+f]t}e^{-i[H_s+cs^2Q]t}. \quad (3.17)$$

This result is a consequence of the fact that the nonadiabatic correction due to coupling between s and Q is of higher order for the symmetric degree of freedom, that is if the *antisymmetric* coupling vanishes ($f=0$) then the nonadiabatic correction to the *symmetrically* coupled propagator Eq. (3.15) vanishes.

Equation (3.17) shows that the nonadiabatic correction, i.e., the last two matrix elements of Eq. (3.6), is affected in the following way: the factor cs^2Q modifies the barrier frequency ω_b in a fashion that will be specified in the discussion of the third step below.

Third step: The functions $B_1, B_2(\omega)$ depend on the barrier frequency ω_b . For a quartic double well as^4-bs^2 , it is $\omega_b=\sqrt{2b/m}$, while the barrier height is $V_0=b^2/4a$. The symmetric coupling cs^2Q changes ω_b and V_0 to the new values

$$\omega'_b=\sqrt{2(b-cQ)/m}, \quad V'_0=(b-cQ)^2/4a. \quad (3.18)$$

In Sec. II we mentioned that possible tunneling trajectories lie between $Q=0$ (static barrier) and $Q=cs_0^2/M\Omega^2$ (saddle point). After a binomial expansion of the quantities in Eq. (3.18) it is easy to show that $\delta V_0/V_0 \sim 4\delta\omega_b/\omega_b$. This means that even for significant reductions $\delta V_0/V_0$ of the barrier height (e.g., 10%–20%), the reduction $\delta\omega_b/\omega_b$ of the barrier frequency is small (3%–5% for the values mentioned above). This allows us to use the “bare” barrier frequency ω_b in the nonadiabatic correction Eq. (3.16) and, as a consequence, in the functions B_1 and $B_2(\omega)$ in Eq. (3.7).

Fourth step: We are now ready to calculate the transmission coefficient Γ which is defined as the ratio of the quantum rate k over the uncoupled *multi*-dimensional 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):

$$\Gamma \equiv \frac{k}{k_{\text{TST}}} = \frac{(1/Z_r) \int_0^\infty dt \tilde{C}_f(t_c)}{(Z^\#/Z_r) e^{-\beta V_0}}, \quad (3.19)$$

where $Z^\#$ is the part of the partition function with the reaction coordinate excluded, evaluated at the transition state. We can write it as $Z^\#=Z_{Q\text{ bath}}$, 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. (3.7) and (3.19) we find that

TABLE I. Values of the transmission coefficient Γ for two values of the dimensionless friction ρ at $T=200$ K. The uncoupled potential has barrier height 0.004 75 a.u., transfer distance 2.8 a.u., and barrier frequency 707 cm^{-1} . The transverse oscillation has mass 100 000 a.u. and frequency 0.001 14 a.u. (0.0057 a.u.) for $\nu=1$ ($\nu=5$). The coupling is $c=0.0058$ a.u. (0.029 a.u.) for $\nu=1$ ($\nu=5$). The spectral density is ohmic with an exponential cutoff 100 cm^{-1} . The transmission coefficient Γ_0 for the uncoupled case is also shown.

ν	ρ	Γ_0	Γ
1.0	0.9	1.7	7.7
1.0	0.6	1.5	7.0
5.0	0.6	1.5	9.2

$$\Gamma = \frac{e^{\beta V_0}}{Z_Q} \int_0^\infty dt \left[\tilde{C}_f^0 B_1 - \int_0^\infty d\omega \tilde{\kappa}_f^0 J(\omega) B_2(\omega) \right]. \quad (3.20)$$

The bath functions $B_1, B_2(\omega)$ are the same as in the uncoupled (to the Q vibration) double well case, while the functions $\tilde{C}_f^0, \tilde{\kappa}_f^0$ were evaluated in the first step Eq. (3.10) for the two-dimensional potential.

Equation (3.20) 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 reaction 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 other bath modes.

We used for the quartic double well as^4-bs^2 the set of parameters “DW2” of Refs. 16, 17, and 19. DW2 corresponds to a barrier height $V=0.004$ 75 a.u., a transfer distance $2s_0=2.8$ a.u., a frequency at the bottom of the well $\omega_0=0.0032$ a.u. (1000 cm^{-1}), and an inverted barrier frequency $\omega_b=707$ cm^{-1} (the mass of the transferred particle is $m=1837$ a.u.). The coupling of the reaction coordinate to the bath is assumed to be ohmic with a cutoff frequency $\omega_c=100$ cm^{-1} .

For the rate promoting vibration we made the following choice of parameters: $M=100$ 000 a.u. and $\Omega=0.001$ 14 a.u. For a pure two-dimensional potential (i.e., without the presence of the bath) these values correspond to a dimensionless frequency [see Eq. (2.2)] $\nu=1$, i.e., to a case for which the pure two-dimensional problem cannot be studied with the standard corner-cutting or adiabatic approximations. The coupling was $c=0.0058$ a.u. For the two-dimensional potential, this value corresponds to a 20% reduction of the barrier height at the saddle point.

We repeated the calculation for coupling $c=0.029$ a.u. and frequency $\Omega=0.0057$ a.u. For these parameters, the barrier height reduction of the pure two-dimensional problem is again 20% at the saddle point, but now the dimensionless frequency is $\nu=5$. In the pure two-dimensional problem, this would mean that the tunneling takes place at the saddle point, where the barrier is lowest.

The results of the calculation of the transmission coefficient Γ can be seen in Table I. We show the results for two

values of the dimensionless friction coefficient $\rho = \gamma/m\omega_b$ (γ is the friction and ω_b is the inverted barrier frequency). The calculations were done at $T=200$ K.

Compared to the calculations for two-dimensional Hamiltonians studied by Benderskii and co-workers, the coupling to the thermal bath changes qualitatively the results in two aspects:

(i) The enhancement is not as dramatic as in the deep tunneling case examined for two-dimensional Hamiltonians by Benderskii and co-workers, but it is still significant.

(ii) Because the coupling to the bath causes the correlation function to decay to zero quickly, the distinction made in two-dimensional problems (based on the separation between time scales of the tunneling motion and the Q oscillation) between the adiabatic and corner-cutting limits has much less significance when dissipation is present. As can be seen in Table I, the transmission factor for the “adiabatic” case $\nu=5$ (i.e., when the dynamics in the two-dimensional potential takes place where the barrier is lowest) is only slightly larger than the $\nu=1$ case.

IV. DISCUSSION

It is now well established both theoretically and experimentally that symmetrically coupled vibrations enhance the rate of reactions that proceed through tunneling from the ground state, not only in gas-phase reactions,^{1,2} but also in condensed phase reactions.^{4–7} This leads to the natural question: What is the effect of these rate promoting vibrations above the crossover temperature, when tunneling takes place from excited states and there is activated transfer over a barrier? In this paper we concentrated on reactions in condensed phases and assumed that one of the bath modes is coupled symmetrically to the reaction coordinate, while all the other modes antisymmetrically. We showed that the rate in condensed phases is affected even for moderate reduction of the effective barrier height at temperatures well above crossover, but that the distinction between the adiabatic and sudden regimes found in the gas phase is not nearly as sharp.

This raises another intriguing question: How are these results affected if the Q oscillation is damped (e.g., if it is coupled itself to the harmonic bath)? Some preliminary thoughts on this problem can be found in Ref. 22, where the preexponential factor of the rate was calculated for the Hamiltonian Eq. (2.1) coupled to an ohmic bath, using instanton techniques for the case where only the lowest doublet is occupied.

The results presented in this paper may be used to analyze more realistic chemical systems in which proton transfer is strongly modulated by intramolecular vibrations. One example of such a system may be the enzymatic proton transfer

experiments of Klinman and co-workers²³ who found anomalously large kinetic isotope effects (KIE) in certain enzymes, e.g., bovine serum amine oxidase (BSAO), which is an indication of tunneling. We have analyzed in detail these experiments elsewhere.²⁴ Another example is the anomalously low activated barrier to proton transfer in organic acid crystals.²⁵ This topic is currently under investigation in our group.

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