

The dependence of the rate constant for isomerization on the competition between intramolecular vibrational relaxation and energy transfer to the bath: A stochastic model

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A new stochastic model is introduced to emulate intramolecular vibrational relaxation in molecules undergoing isomerization. In this model the Hamiltonian flow is punctuated at random times by an exchange of vibrational kinetic energies. When applied to the study of the rate of barrier crossing, this model reproduces many of the salient features of rate processes in real molecules. For example when the mean time τ between kinetic energy exchange events is short compared to the crossing time of a well the model gives the Rice–Ramsperger–Kassel–Marcus (RRKM) rate constant. When τ is longer than the crossing time the rate constant is smaller than the RRKM value. In this paper the stochastic kinetic energy exchange model (SKEEM) combined with the Bhatnagar–Gross–Krook model for impulsive collisions with a bath is used to explore the dependence of the rate constant on collision rate. This model clarifies why at low collision rates the rate constant for barrier crossing reflects the full dimensionality of the molecule, whereas at higher collision rates the rate constant seems to reflect a lower dimensionality. © 1999 American Institute of Physics. [S0021-9606(99)50802-7]

I. INTRODUCTION

This paper focuses on the role of intramolecular vibrational relaxation (IVR) in determining the rate constant for activated barrier crossing in polyatomic molecules. Here the reaction coordinate can exchange energy with the other intramolecular degrees of freedom or with the solvent. In theoretical treatments, the coupling of the reaction coordinate to the bath is either treated stochastically through strong-collision models^{1–8} [such as the Bhatnagar–Gross–Krook (BGK) model], weak collision models^{9,10} (such as the Langevin–Kramers model), or explicit solvent models using molecular dynamics simulations. In the polyatomic molecule the intramolecular degrees of freedom are coupled nonlinearly. Interesting effects have been predicted due to these nonlinear couplings in the weak coupling regime^{11–14,7} (low collision rate for BGK dynamics, low friction constant for Langevin dynamics, or low solvent density for explicit solvent dynamics) where the energy associated with the reaction coordinate only rarely exceeds the activation energy. In this regime, energy excitation becomes the rate determining step in the kinetics. This is the so called energy diffusion (ED) regime.^{9,15,10} Theoretical treatments of this regime often make the tacit assumption that IVR is rapid compared to energy exchange with the bath. One can then show^{16,17} that the barrier crossing rate constant will depend linearly on the collision rate (BGK) or the friction coefficient (Langevin–Kramers). This may be true at very low collision rate or friction, but as these parameters are increased, IVR may become slower than energy transfer to the bath. What happens then? Previous studies have shown that the rate constant then becomes a nonlinear function of the collision rate or the fric-

tion coefficient.^{11–14,18} Its behavior may then reflect the full dimensionality of the polyatomic molecule at low collision rates or friction and a reduced dimensionality at higher values of these parameters. Similar behavior has more recently been shown to exist in explicit solvent models. We focus on these effects in this paper. We introduce a simple stochastic model for the microcanonical dynamics of the isolated polyatomic model and combine this new stochastic model with the BGK model for bath collisions. This stochastic model allows us to understand the behavior of the rate constant in terms of very simple physical principles because the model has very simple intramolecular dynamics with a well defined IVR rate. Nonlinear Hamiltonian dynamical systems by contrast have much more complicated intramolecular dynamics.

When a polyatomic molecule such as cyclohexane undergoes a conformation change (Boat \rightleftharpoons Chair) the reaction coordinate must pass over an energy barrier.^{7,19} The reaction coordinate is coupled both to other intramolecular degrees of freedom and to the bath. Let us consider what happens immediately after the reaction coordinate passes over the barrier. If it is not coupled to either intramolecular modes or to the bath, it will periodically recross the barrier with a period $T(E)$ depending on the total energy of the molecule (which is conserved) and no barrier crossing rate constant would exist. If it is only coupled to other intramolecular modes and not to the bath, it would exchange energy only with the other intramolecular modes through IVR on a time scale τ_{IVR} and, depending on the strength of its coupling to the other modes, it would exhibit a range of behaviors.

- (a) If its coupling strengths to the other intramolecular modes are strong, the reactive coordinate will lose energy to the other modes in a time (τ_{IVR}) short compared to its transit time $T(E)$ over either of the two

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potential energy basins corresponding to the Boat or Chair conformations. In this case of rapid IVR there will be no rapid barrier recrossings and the rate constant will be given by the Rice–Ramsperger–Kassel–Marcus (RRKM) rate theory.

- (b) On the other hand, if the coupling strengths to the other intramolecular degrees of freedom are not strong [$\tau_{\text{IVR}} \gg T(E)$], the reaction coordinate will rapidly recross the barrier one or more times before losing energy by IVR and the rate constant will be smaller than the RRKM rate constant. In addition, there will be the added complication that the phase space can be decomposed into regular regions filled with invariant tori and irregular regions.^{20,21} (The invariant tori are usually destroyed in the limit of large coupling strength.)

In the presence of a molecular bath the molecule will suffer random collisions leading to energy exchange between the molecular degrees of freedom and the bath. The time scale for these collisions will be defined by the time between collisions τ_{coll} . The barrier crossing kinetics will thus depend on several time scales: the crossing time of the stable wells $T(E)$; the time scale characterizing energy transfer between the reaction coordinate and the other intramolecular degrees of freedom τ_{IVR} ; and the time between collisions of the molecule and the bath τ_{coll} .

In general, the Hamiltonian contains nonlinear terms and the Hamiltonian flow is complicated, requiring extensive numerical simulation. To gain insight into reactive dynamics simple two degree of freedom systems have been studied in detail. One such system is the DeLeon–Berne Hamiltonian which consists of a quartic double well, coupled to a Morse oscillator.²⁰ In this model the energy barrier in the quartic double well is an exponential function whose argument is proportional to the displacement of the Morse oscillator, with the proportionality constant being the coupling strength. It is of interest to understand how this model behaves at fixed total energy for different coupling strengths. Simulations showed that for strong coupling strengths the barrier crossing dynamics is well described by the RRKM theory. This means that for trajectories starting at the transition state with energy $E > E_a$, where E_a is the activation energy, the energy in the reactive coordinate is transferred to the other mode fast enough that the molecule gets trapped in one of the wells and remains there for a long enough time for the two modes to equipartition before the reactive coordinate can be reactivated and recross the transition state to the other well. For lower coupling strengths the reactive dynamics are more complicated because the phase space will now subdivide into regular and irregular parts. The model is dynamically very rich and has been used in other studies.²²

The De Leon–Berne model has been used to probe the competition between IVR and energy transfer to a collisional bath as a model for how solvents effect rate constants.^{11–14} Two different models of the collisional bath (gas or liquid) were used. In one model the effect of the bath was modeled by random impulsive (strong) collisions during which the velocities in the molecule are thermalized (the so-called BGK model^{1–3}) and in the other model the molecule experi-

ences a systematic frictional force and a randomly fluctuating force (the so called Langevin dynamics model of weak collisions).¹³ Using the reactive flux^{23,24} absorbing boundary technique^{25,26} to calculate the rate constant for barrier crossing, it was found that the rate constant at very low collision rate increases with collision rate with a slope given by the full two dimensions of the molecule but at higher collision rate it behaves as though the dimensionality of the molecule is between two and one dimensions.

We wish to understand how the barrier crossing rate constant depends on these different time scales. Unfortunately, molecular dynamics simulations of reacting molecules in explicit or stochastic solvents have not been able to provide the kind of insight we seek because it is very difficult to determine τ_{IVR} . Thus we seek guidance by devising a simple stochastic molecular model that has all of the processes described above. We call this model the stochastic kinetic energy exchange model (SKEEM). Combining this model with the BGK model for molecular collisions with the bath allows us to gain considerable insight into the competition between IVR and bath collisions in determining the rate constant for barrier crossing.

II. STOCHASTIC KINETIC ENERGY EXCHANGE MODEL (SKEEM)

To better understand the physical behavior described above, we have devised a stochastic model to describe the microcanonical dynamics of the molecule, the SKEEM, which can be combined with BGK dynamics to account for bath collisions. To our knowledge this is the first such stochastic microcanonical dynamical model. SKEEM for a two degree of freedom system is defined by the following:

- (1) The Hamiltonian is separable into reactive and nonreactive degrees of freedom.
- (2) The dynamics generated by this separable Hamiltonian is punctuated by random intramolecular energy transfer events (a Poisson process) where the mean time between these events is $\tau = \gamma^{-1}$ and the probability that the molecule will evolve for a time t without suffering an energy transfer event is

$$p_0(t) = e^{-\gamma t}. \quad (1)$$

- (3) The kinetic energy after an energy transfer event (indicated by a') is related to the kinetic energy before the energy transfer event as follows:

$$T'_x = T_y, \quad (2)$$

$$T'_y = T_x. \quad (3)$$

- (4) The potential energies are not changed during an energy transfer event.
- (5) An energy transfer event changes the magnitude of the velocities of the two degrees of freedom according to:

$$|v'_x| = \left(\frac{2}{m_x} T'_x \right)^{1/2} \quad (4)$$

$$|v'_y| = \left(\frac{2}{m_y} T'_y \right)^{1/2}. \quad (5)$$

but does not change the direction of the velocities. (This can be modified if desired.) An important feature of this

model is that the total energy is conserved during each energy transfer event. From Eqs. (2) and (3) we see that

$$T'_x + T'_y = T_x + T_y \quad (6)$$

Thus, the total kinetic energy is conserved during the event and because the potential energy of each degree of freedom is unchanged during the event, the total energy is conserved. It is a simple matter to extend this model to higher dimensional systems. In fact there are several possible models. One could define different mean times for the energy exchange between each pair of modes so that when the system is advanced to each of the sampled event times the kinetic energies corresponding to the specific pair of modes in that event are transformed according to Eqs. (2) and (3). This would allow for a multiplicity of mode specific IVR relaxation times. Another possibility is to define one mean free time between events and to define an event to be such that the kinetic energies of all the distinct pairs of modes are updated (exchanged) independently.

It is worth commenting on the fact that other SKEEM type models are possible. For example in place of the total kinetic energy exchange one can invoke the following kinetic energy transformation in place of Eqs. (2) and (3):

(3') The kinetic energy after an energy transfer event (indicated by a') is related to the kinetic energy before the energy transfer event as follows:

$$T'_x = \xi T_x + (1 - \xi) T_y, \quad (7)$$

$$T'_y = (1 - \xi) T_x + \xi T_y, \quad (8)$$

where ξ is a number between 0 and 1. Once chosen, this number can be held fixed at 0, as above, or it can jump between 0 and 1 with a specified probability.

(4') The values of ξ for different energy transfer events are uncorrelated.

We have tried these two variants. The model in which ξ jumps between 0 and 1 is essentially equivalent to the complete energy exchange model except for a transformation of the time scale for the relaxation.

The dynamics generated by SKEEM is easily simulated. For the determination of the rate constant one must calculate the reactive flux.^{23,24} This is done by sampling the positions and velocities of the molecule from a velocity weighted microcanonical distribution function with the reactive coordinate constrained to be at the transition state. For each of these initial states, the times for the energy transfer events are sampled from the Poisson distribution. The molecule then moves on the separable potential until the time of the first collision at which time the velocities of the two degrees of freedom are assigned according to item (5) above. Starting with the new velocities, the molecule now moves on the separable potential until the next event and the process is repeated seriatim. These trajectories can be used to determine the reactive flux

$$k(t) = \frac{1}{X_A X_B} \langle \dot{y} \delta(y) \theta[y(t)] \rangle_E, \quad (9)$$

where y is the reaction coordinate and X_A and X_B are the equilibrium mole fractions of reactant and product, respectively.

It is a simple matter to introduce the effect of solvent by using a BGK collisional bath in which the molecule suffers impulsive collisions.^{1,2} Then, starting with the initial state of the molecule, one samples the times for the energy exchange events as in SKEEM and one samples the times for collisional events with the bath from the Poisson distribution $P_0(t) = e^{-\alpha}$ as specified by the BGK model. The mean time between collisions is $\tau_{\text{coll}} = \alpha^{-1}$. There are now two kinds of events: an energy exchange event and a bath collisional event. Starting with the initial state the molecule moves on the separable Hamiltonian until the first event. If the first event is an energy exchange event then transform the molecular velocities according to SKEEM. If the first event is a bath collisional event then transform the molecular velocities according to BGK; that is, sample new velocities from the Maxwell distribution function. Now repeat for the next event, etc. This model can also be modified to allow for different degrees of freedom to experience different collision rates with the bath, thus allowing for the possibility that some molecular degrees of freedom within a large polyatomic molecule may be shielded from collisions with the bath. For the calculation of the reactive flux, sample the initial state of the molecule from the canonical (constant temperature) ensemble with the reaction coordinate fixed at the transition state. This can be accomplished in the manner outlined in Ref. 11–14. For each of these starting points run trajectories as just specified. This SKEEM-BGK model is very easy to implement.

III. SKEEM-BGK APPLIED TO THE DE LEON-BERNE MODEL

The De Leon–Berne Hamiltonian²⁰ is

$$H = 4(x^2 + y^2) + 4y^2(y^2 - 1)e^{-z\lambda x} + \lambda_3(1 - e^{-\lambda x})^2 + 1, \quad (10)$$

where the reaction coordinate y moves on a quartic double well and the coordinate x moves on a Morse potential. This potential can be decomposed into a separable part:

$$U_0(x, y) = \lambda_3(1 - e^{-\lambda x})^2 + 4y^2(y^2 - 1) + 1, \quad (11)$$

and a coupling part:

$$U_{\text{coup}}(x, y) = 4(e^{-z\lambda x} - 1)y^2(y^2 - 1). \quad (12)$$

Thus z is the coupling strength. For $z=0$ the Berne–De Leon potential is separable. It is the separable potential $U_0(x, y)$ that will be used in SKEEM simulations. Then the energy exchange step in SKEEM will mimic the effect of the coupling potential given in Eq. (12). In the full De Leon–Berne potential the coupling arises from the dependence of the barrier height on x , the displacement from equilibrium of the Morse oscillator. Energy is measured in units of the barrier height corresponding to $x=0$. λ_3 is the dissociation of the Morse oscillator in these units and λ is the range parameter of the Morse potential. The quartic has two minima at $y = \pm 1/\sqrt{2}$ and a maximum at $y=0$. These extremal points, and therefore the saddle point ($x=0$, $y=0$) do not depend on x .

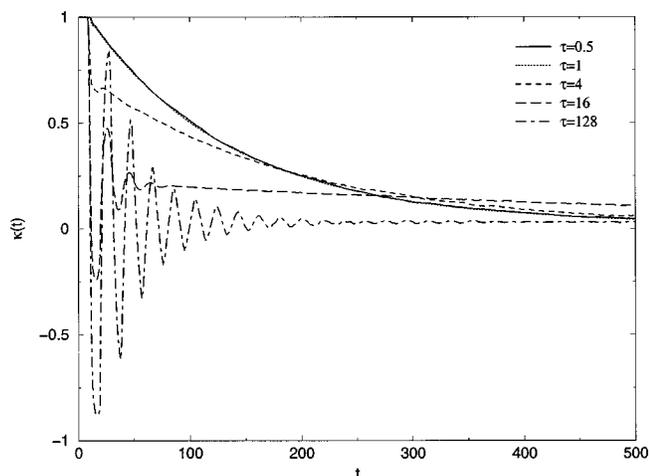


FIG. 1. Reactive flux dependence on time for different τ . SKEEM simulation in microcanonical ensemble, $E=1.02$.

We fix $\lambda_3=10$ in order to guarantee that the dissociation energy will be much larger than the barrier to conformation change.

IV. SKEEM-BGK SIMULATIONS: ALL TRAJECTORIES ARE IRREGULAR

A. SKEEM simulations of microcanonical and canonical processes absence of the bath

The De Leon–Berne potential²⁰ with $\lambda=1.95$, $z=2.3$, and $\lambda_3=10.0$ was shown to be “completely” chaotic. Moreover it was shown that the microcanonical reactive flux exhibited “no” rapid recrossings. The rate for activated barrier crossings for this strongly coupled case was shown to be in accord with the RRKM theory. It is of interest to apply SKEEM to this case. In applying SKEEM we remove the coupling by setting $z=0$. The coupling is then emulated by the mean time τ between kinetic energy exchanges. In Fig. 1 the reactive flux is shown for different values of τ . From the oscillations of the reactive flux for very large τ we can esti-

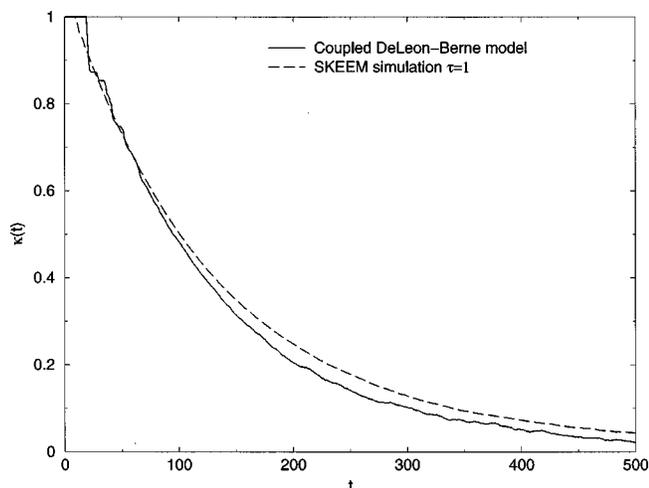


FIG. 2. The reactive flux dependence on time for the original De Leon–Berne model with strong mode coupling $z=2.3$ (solid line) and SKEEM simulation with $\tau=1$ (dashed line).

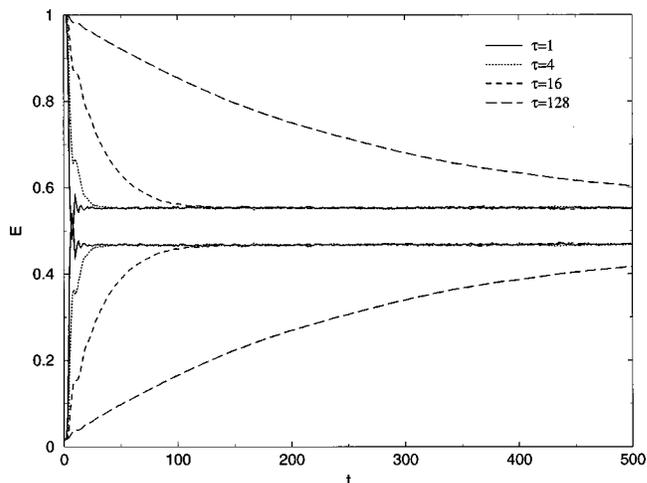


FIG. 3. The dependence of internal mode energies on time in a SKEEM simulation (microcanonical ensemble $E=1.02$) for different values of τ . The initial value of the y mode energy, $E_y=T_y+U_y(y)$ is close to $E_a=1$ (the four curves in the upper part of the graph). The energy for the x mode, $E_x=T_x+U_x(x)$, is equal to $E-E_y$ (the four curves in the lower part of the graph).

mate the period for recrossing of the barrier to be $T(E) \approx 10$. Thus for $\tau \ll 10$ the kinetic energy should be equipartitioned before the reactive trajectories can recross the barrier. We see that for $\tau=0.5$ and 1.0 this is the case, but for larger values of τ the reactive flux starts to exhibit recrossing events leading to a dephasing decay to a plateau value. The recrossing period $T(E)$ is thus seen to be the cause of the short “molecular time scale” often referred to in discussions of the reactive flux. When $\tau \ll T(E)$ the reactive flux predicted by SKEEM decays exponentially and the rate constant for this decay is $k(E)=7.5 \times 10^{-3}$. The microcanonical rate constant $k_{\text{RRKM}}(E)=(X_A X_B)^{-1} \langle \dot{y} \delta(y) \theta(\dot{y}) \rangle_E = 7.2 \times 10^{-3}$ for the uncoupled De Leon–Berne potential is easy to compute and we find that the decay rate of the reactive flux is identical to the RRKM rate constant as separately calculated; that is $k(E)=k_{\text{RRKM}}(E)$, as expected.

How well does the SKEEM model emulate molecular dynamics of the fully coupled De Leon–Berne potential in the strong coupling limit? To answer this, in Fig. 2 we compare the microcanonical reactive flux for $E=1.02$ (only slightly larger than the activation energy $E_a=1.0$) for the fully coupled De Leon–Berne potential with the SKEEM simulation of the uncoupled potential with $\tau=1$. Clearly, for this case, the SKEEM model emulates the fully coupled system very closely.

In the calculation of the reactive flux a set of initial dynamical states are sampled with the reaction coordinate constrained to be at the transition state $y=0$ and the SKEEM rules are applied to generate the trajectory. It is of interest to study how the energy in the reaction coordinate is transferred to the nonreactive degree of freedom. In Fig. 3, the top four curves show how the average energy in the reaction coordinate decays as a function of the time for four different values of τ and the bottom four curves show how the corresponding average energy of the nonreactive mode grows. Since the potentials are anharmonic and different, the y mode decays

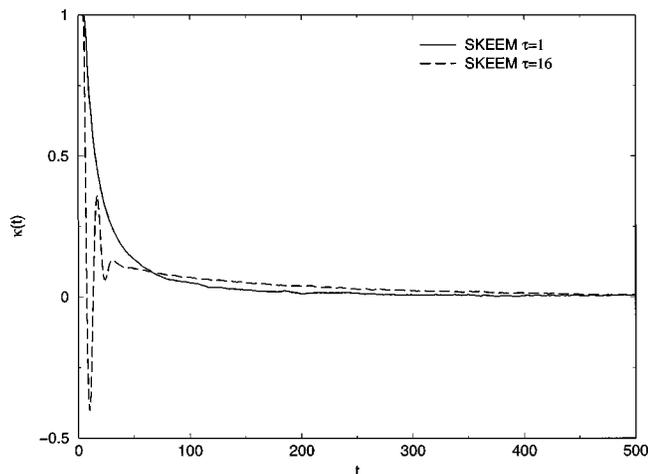


FIG. 4. The dependence of the reactive flux on time in canonical ensemble, as predicted by SKEEM with $\tau=1$ and 16 for a temperature of $\beta^{-1}=0.1$. No BGK collisions are introduced in this calculation.

to a different energy than the x mode. From these curves we can conclude that the intramolecular vibrational relaxation time τ_{IVR} is roughly double the time between kinetic energy exchanges; that is, $\tau_{\text{IVR}} \approx 2\tau$.

So far we have presented SKEEM results in the microcanonical ensemble. It is a simple matter to use SKEEM to compute reactive fluxes in the canonical ensemble

$$\kappa(t) = \langle \theta[y(t)] \rangle_+ - \langle \theta[y(t)] \rangle_-, \quad (13)$$

where the subscripts $+$ and $-$ correspond to trajectories initially moving from the TST towards the product side and the reactant side respectively. One samples the initial states at the TST from a weighted canonical distribution function and uses the SKEEM rules to generate trajectories starting from these initial states. In Fig. 4 the canonical reactive fluxes for two different values of τ are presented. Again for $\tau=1$ we do not observe recrossings but for large $\tau=16$ the fast dephasing decay is the indicator of rapid barrier recrossings. Thus there is a fast "molecular time scale" dephasing decay followed by a slow activated recrossing decay. In this, as in the previous microcanonical simulations, the activation energy $E_a=1$. The temperature here is 0.1 so that $\beta E_a=10$.

B. SKEEM-BGK simulations of the canonical reactive flux

In the following simulations, a set of TST canonical initial states are sampled and the SKEEM plus BGK rules are applied to generate trajectories corresponding to each of these initial states for $\beta E_a=10$. Figure 5 shows a set of reactive fluxes generated in this way for a collision rate $\alpha=1/8$ along with the reactive flux calculated for the fully coupled De Leon–Berne potential using full molecular dynamics of the molecule punctuated by BGK collisions. Again we see that SKEEM-BGK with $\tau=1$ does a pretty good job of emulating the fully coupled system. There is not too much evidence of recrossing events. The plateau values give the canonical rate constants. For the SKEEM-BGK flux, $\tau_{\text{IVR}}=2$ and the time between collisions in the BGK model is $1/\alpha=8$. Thus the time between BGK collisions is longer than

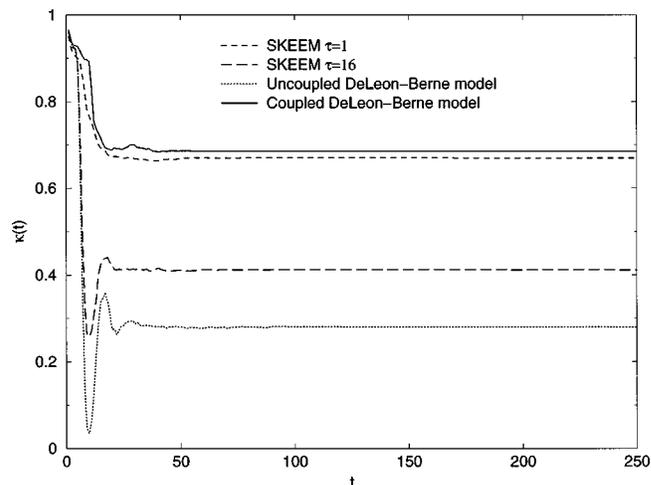


FIG. 5. An example of time dependent reactive flux in the presence of solvent (BGK model), collision frequency $\alpha=1/8$. Well defined plateau values of κ can be determined.

the time it takes for the constant energy system to equipartition by IVR. Both of these times are shorter than the mean recrossing time. The SKEEM-BGK result for $\tau=16$ gives evidence of the dephasing decay typical of recrossing events and has a much smaller plateau value and correspondingly smaller rate constant than for $\tau=1$. The lower curve represents the BGK simulation for the y coordinate without SKEEM. This is a purely one-dimensional calculation. We see that the rate constant for SKEEM-BGK with $\tau=16$ gives a rate constant between the fully two-dimensional rate constant found using $\tau=1$ and the rate constant for the one-dimensional system.

These curves already give evidence that when the IVR time scale is short to the time between bath collision so that the reaction coordinate can equipartition with the nonreactive degree of freedom before it can lose energy to the bath, the rate constant will be given by a rate constant typical of a two-dimensional canonical rate constant. On the other hand when the time scale for IVR is close to the time between collisions and the reaction coordinate cannot equipartition before it can lose energy to the bath, the rate constant will be smaller than that predicted by the two-dimensional system.

Performing SKEEM-BGK simulations for different BGK collision rates α and determining the plateau times of the reactive flux allows us to determine the canonical rate constant as a function of α for different values of the τ_{IVR} . Because the rate constant decreases as α decreases and can become very small, we use the absorbing boundary reactive flux method,^{25,26} according to which the rate constant is given by

$$\kappa = \frac{T}{2-T}, \quad (14)$$

where T is the fraction of trajectories that become rapidly trapped in the product well. In Fig. 6 the dependence of the canonical rate constant on the BGK collision rate α is compared for the fully coupled De Leon–Berne potential with BGK collisions, the SKEEM model ($\tau=1$) with BGK colli-

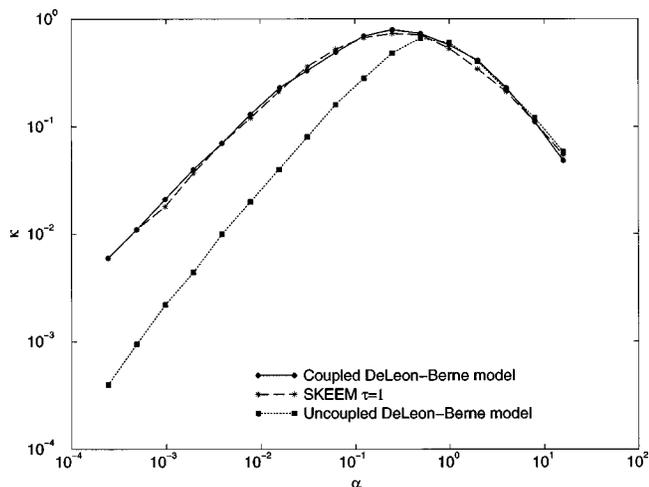


FIG. 6. The dependence of the canonical rate constant (from the reactive flux plateau) on the BGK frequency. The solid line corresponds to the original De Leon–Berne model, with a large value of coupling coefficient $z = 2.3$. The dotted line corresponds to the same model, but with switched off mode coupling, $z = 0$. The dashed line is the result of SKEEM simulation with $\tau = 1$.

sions, and the one-dimensional model with BGK collisions (denoted uncoupled De Leon–Berne model in the figure). This curve covers several decades in both the collision rate and the reaction rate. It is clear from this model that the SKEEM-BGK model is in excellent agreement with the fully coupled BGK dynamics first studied by Borkovec and Berne. It is also clear that the rate constant for the one-dimensional system is much smaller.

A question posed long ago is the following: How does the rate constant vary with bath collision rate? In Fig. 7 we compare the dependence predicted by SKEEM-BGK for $\tau = 16, 64,$ and 128 with the dynamics of the fully coupled De Leon–Berne potential with BGK collisions and with the one-dimensional De Leon–Berne potential with BGK collisions. In the latter two cases, the rate constants reflect the full dimensionality of the molecule (two dimensions for the strongly coupled De Leon potential and one dimension for the uncoupled De Leon–Berne potential). Plate (c) gives a comparison between the SKEEM-BGK simulation for the case where $\tau = 128$. In this case we see that at a very low collision rate where the time between collisions of the molecule with the bath α^{-1} is much longer than the IVR time τ_{IVR} of the molecule, the rate constant appears to be two dimensional. As the collision rate is increased until the time between collisions is short compared to the IVR time, the rate constant becomes one dimensional. As the collision rate is made even larger, the rate constant follows the one-dimensional curve, reaches a turnover (the so called Kramers turnover¹⁰), and finally decreases with collision rate as predicted by the spatial diffusion regime. For smaller τ or τ_{IVR} this transformation from two- to one-dimensional behavior occurs at a higher collision rate and becomes obscured by the turnover regime. Thus the effect should be seen in systems with very slow IVR times. This is just the behavior predicted a decade ago.^{11–14}

It is of interest to determine whether simple connection

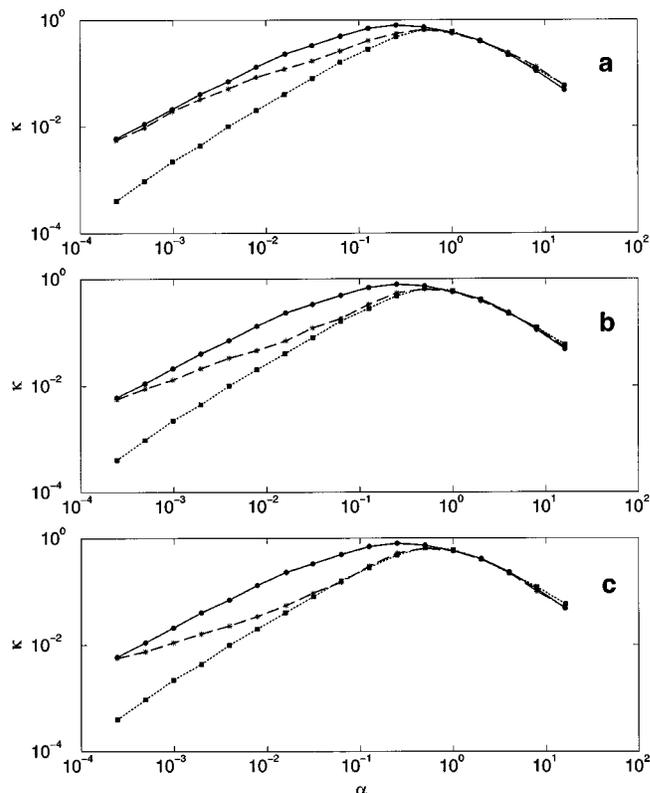


FIG. 7. The dependence of the canonical rate constant on the BGK collision frequency, for different values of the SKEEM parameter τ : $\tau = 16, 64,$ and 128 [dashed lines in panels (a) (b), and (c) respectively]. The solid line corresponds to the original De Leon–Berne model, with a large value of coupling coefficient $z = 2.3$. The dotted line corresponds to the same model, but with switched off mode coupling, $z = 0$.

formulas can be used to infer the full collision rate dependence of the rate constant.^{10,27} Borkovec and Berne have shown^{28,11} that for the strong collision models the dependence of the rate constant on collision rate at low collision rate energy diffusion limit can be approximated by

$$\kappa_{\text{ED}} = \alpha \tilde{\kappa}^{(0)}(\alpha), \quad (15)$$

where $\tilde{\kappa}^{(0)}(\alpha)$ is the Laplace transform of the time dependent canonical reactive flux of the isolated molecule (no BGK collisions) evaluated for the Laplace variable equal to the collision rate ($s = \alpha$). Here the subscript ED indicates the energy diffusion limit. In the high collision or spatial diffusion (SD) limit the transmission coefficient is known to depend on collision rate α as²

$$\kappa_{\text{SD}} = \frac{\omega_B}{\alpha}, \quad (16)$$

where ω_B is the imaginary frequency of the barrier. A connection formula that appears to be valid when there is no long memory friction time in the system (a condition satisfied here) is

$$\frac{1}{\kappa} = \frac{1}{\kappa_{\text{ED}}} + \frac{1}{\kappa_{\text{SD}}} + 1, \quad (17)$$

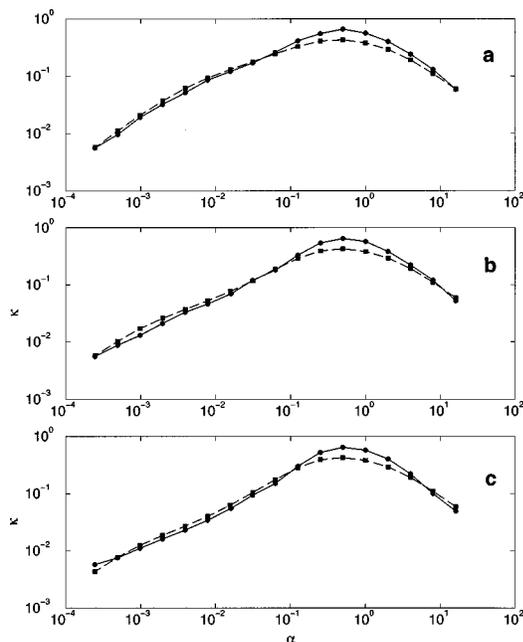


FIG. 8. Comparison of the dependence of the canonical rate constant on BGK collision frequency for the SKEEM-BGK simulation results (solid line) with theoretical predictions from Eq. (17) (dashed line): panels (a), (b), and (c) correspond, respectively, to $\tau=16$, 64, and 128.

where unity comes from the TST rate constant. According to this formula, the smallest transmission coefficient is rate limiting and dominates the overall rate constant.

In Fig. 8 we compare the predictions of this connection formula with the full SKEEM-BGK simulations for three cases: $\tau=16$, 64, and 128 in panels (a), (b), and (c), respectively. It should be clear from this comparison that the connection formula, while approximate, does a very reasonable job in predicting the change in apparent dimensionality with increasing α as well as the Kramers turnover region.

V. SKEEM-BGK SIMULATIONS: REGULAR AND IRREGULAR TRAJECTORIES

Berne and De Leon²⁰ have shown that when the coupling strength is not strong, the phase space decomposes into regular and irregular regions, the regular region being filled with invariant tori. Clearly, SKEEM, being an entirely stochastic model, will destroy all invariant tori given by the separable potential. SKEEM will thus not be able to model this aspect of weakly coupled systems. Nevertheless, one can modify SKEEM to model some of the features of the weakly coupled De Leon–Berne system. For a given value of coupling strength z the measure of the phase space containing invariant tori will be μ_{reg} and the measure of the phase space containing irregular trajectories will be $1 - \mu_{\text{reg}}$. Thus when sampling initial phase points for the trajectories one can sample a random number and assign the labels irreg or reg to the given initial state in accordance with the value of μ_{reg} . Then one applies the SKEEM rules to generate trajectories only for the irregular initial states. The trajectories for the regular initial states do not have any kinetic energy exchanges and will thus be quasiperiodic because they are gen-

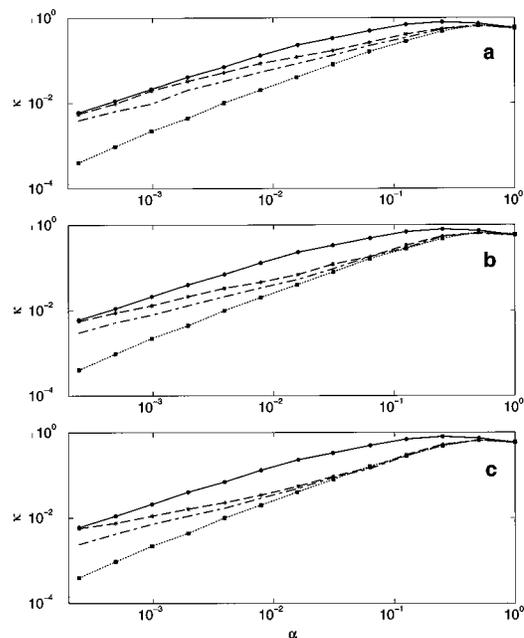


FIG. 9. The dependence of the transmission coefficient on BGK collision frequency for an equal mixture of regular and irregular trajectories (dotted-dashed line). The solid line corresponds to the original De Leon–Berne model, with a large value of coupling coefficient $z=2.3$. The dotted line corresponds to the same model, but with switched off mode coupling, $z=0$. The dashed lines in panels (a), (b), and (c), correspond, respectively, to different values of the SKEEM parameter τ : $\tau=16$, 64, and 128.

erated on a separable potential. This procedure does not preserve the important feature of Hamiltonian dynamics that two distinct trajectories cannot cross.

To see what happens when some of the trajectories are regular, SKEEM-BGK simulations are performed on the separable ($z=0$) De Leon–Berne potential²⁰ with $\lambda=1.95$ and $\lambda_3=10.0$, where the fraction of regular trajectories is taken to be $\mu_{\text{reg}}=0.50$ for the three SKEEM times $\tau=16$, 64, and 128, the same cases studied above. The dependence of the transmission coefficient on α for these three cases is shown in Fig. 9. Figure 9 shows three panels with four curves in each. Two of the curves represent the one- and two-dimensional results, one of the curves represent what happens when there are no regular trajectories ($\mu_{\text{reg}}=0$), and the remaining curve shows the behavior when half the trajectories are regular ($\mu_{\text{reg}}=0.5$). This behavior is consistent with the above analysis. We see that when there are regular trajectories, the low collision rate behavior of κ is different from the case when there are no regular trajectories ($\mu_{\text{reg}}=0$). Instead of showing the full dimensionality (two dimensions) of the De Leon–Berne potential, the low collision rate behavior appears to be between the curves corresponding to one- and two-dimensional behavior. This was also seen in our previous simulations of the weakly coupled De Leon–Berne potential using BGK stochastic dynamics.^{11–14} This observation can be understood easily in terms of the SKEEM-BGK model. Since the regular and irregular trajectories are completely independent of each other the reactive flux, when there are no collisions with the bath, can be expressed as

$$\kappa^{(0)}(t) = \mu_{\text{reg}} \kappa_{\text{reg}}^{(0)}(t) + \mu_{\text{irreg}} \kappa_{\text{irreg}}^{(0)}(t). \quad (18)$$

Equation (18) can then be combined with the Eq. (15) so that

$$\kappa_{\text{ED}} = \alpha [\mu_{\text{reg}} \tilde{\kappa}_{\text{reg}}(\alpha) + \mu_{\text{irreg}} \tilde{\kappa}_{\text{irreg}}(\alpha)]. \quad (19)$$

Since at a low collision rate (low α) $\tilde{\kappa}_{\text{reg}}(\alpha=0)$ is essentially one dimensional (zero coupling with no SKEEM) and $\tilde{\kappa}_{\text{irreg}}(\alpha=0)$ is essentially two dimensional, the weighted average of these two transmission coefficients will be bounded from above by the two-dimensional rate constant and from below by the one-dimensional result. Since the diffusion controlled limit at high α does not depend on dimensionality, Eq. (19) can be combined with the connection formula given by Eq. (17) to predict the dependence of κ on α from a low to a high collision rate for the case when regular trajectories are present.

VI. SUMMARY

In order to better understand the effect of IVR on barrier crossing kinetics, a new microcanonical stochastic dynamics model called SKEEM, in which at random times the kinetic energies of different pairs of intramolecular modes are exchanged, was applied to a ‘‘molecule’’ interacting through the two-dimensional uncoupled De Leon–Berne potential. For isolated molecules, SKEEM was shown to generate reactive dynamics qualitatively similar to what is observed in the Hamiltonian dynamics (nonstochastic) of the fully coupled De Leon–Berne potential. The rate constant generated by SKEEM was shown to depend on the mean time τ between kinetic energy exchanges. This time also determines the IVR time and it was found for the system simulated here that $\tau_{\text{IVR}} \approx 2\tau$. For small τ or τ_{IVR} the rate constant was shown to be equal to the RRKM rate constant and as τ or τ_{IVR} was increased the rate constant monotonically decreased.

The reaction dynamics of the ‘‘molecule’’ in solvent was modeled by the thermalizing impulsive collisions occurring at random times, this is the BGK model of collisions with collision rate α . SKEEM was combined with BGK collisions in order to model the reacting molecule in solvent. The rate constant predicted by this model as a function of α displays many of the features observed in the full nonlinear dynamics of the fully coupled De Leon–Berne potential. As α was increased from zero, the rate constant increased first lineally with α with a slope given by RRKM theory with the full dimensionality of the molecule. When $\alpha \approx 1/\tau$ the slope of the curve switched to a smaller slope typical of a molecule with fewer degrees of freedom. At still larger α the rate constant exhibited a Kramers turnover and thereafter decreased with increasing α consistent with diffusion control.

This dependence of the rate constant on collision rate was well described by a connection formula relating the rate constant to rate constants for the energy diffusion regime [approximated by Eq. (15)] for the the spatial diffusion regime and for the transition state approximation.²⁹ A simple scheme for using SKEEM-BGK to model Hamiltonian systems with regular and irregular trajectories was discussed and analyzed. It was shown that when the fraction of regular trajectories is large ($\approx 50\%$) the rate constant at very low collision rate falls between the two- and one-dimensional limits.

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