

Energy-diffusion-limited unimolecular reactions in condensed phases

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Unimolecular reactions of polyatomic molecules in condensed phases in the low-friction regime where the reaction rate is controlled by the energy transfer rate between the molecule and the media are investigated. It is assumed that the intramolecular degrees of freedom are strongly coupled and thus the microcanonical rate of the molecule is described by statistical theories. The generalized Kramers' model is employed and the rate constant is calculated by numerically solving the general energy-diffusion equation, which we refer to as the "exact" result. Using a simple model system that employs the harmonic approximation, we demonstrate the dependence of the "exact" rates on the number of molecular degrees of freedom and compare them with those obtained by assuming the low-friction limit. It is shown that the "exact" rates may be orders of magnitude smaller for high-dimensional systems even at extremely low friction, indicating that the commonly used solutions obtained in the low-friction limit are not applicable to large molecules. To investigate the practical aspects of applying the generalized Kramers' theory to treat reactions of polyatomic molecules in condensed phases, we study the reaction of a large molecule (dimethylnitramine) in liquid xenon. This study suggests that the energy-diffusion-controlled region may be experimentally observable for polyatomic systems, and that the theory may provide a practical means of obtaining the rate constants for such processes.

I Introduction

Most modern studies of reactions in condensed phases are based on Kramers' theory,^{1–3} in which a reaction is considered as a barrier crossing in a one-dimensional potential along the reaction coordinate influenced by a heat bath that constitutes the remaining degrees of freedom of both reacting and solvent molecules. The effect of the bath on the reaction coordinate is described by a random fluctuating force. Thus, the process is described by the Langevin equation. Kramers discussed three regimes for the dynamical influence of a bath on the reaction. In the low-friction regime, the friction is not sufficiently strong to maintain an equilibrium distribution. Energy transfer to the reaction coordinate is the slower process and thus the rate-limiting step, and the rate constant is proportional to the friction. In the intermediate and high friction regimes, the rate is determined by the barrier passage kinetics. When the friction is strong enough to maintain an equilibrium distribution but weak enough not to disturb the barrier passage, the rate constant is given by transition-state theory (TST). As the friction increases sufficiently to induce recrossings, the rate decreases with increasing friction.

A unimolecular reaction of a polyatomic molecule with n strongly coupled degrees of freedom in the low-friction regime, where the reaction is controlled by the energy transfer between the molecule and the solvent, is the subject of this study. There have already been extensive studies on generalizing Kramers' one-dimensional model to multidimensional systems (see ref. 3 and references therein). The usual approach is to start from the Fokker–Planck equation in energy space with an additional term accounting for chemical reaction, and then employ the steady-state approximation to obtain the constant flux. However, analytical solutions are generally not available for energies above the barrier. An approximate solution can be obtained in the low-friction limit when the rate of energy supply to the reaction coordinate is much smaller than the rate of reaction. In this case, the reaction is so effective in removing particles above the barrier that the barrier can be

considered as a perfect sink. Then the absorbing boundary condition can be employed and an analytical expression for the reaction rate obtained. Some low-order corrections to this low-friction limit rate have also been worked out.⁴ It was concluded that the reaction rate rises so rapidly with friction as the number of degrees of freedom increases that the transition to the TST region occurs at extremely low friction, thus the energy-diffusion-controlled region is experimentally observable only for small molecules. However, those studies were based on the assumption that the microcanonical rate of the molecule rises sharply in the barrier region, which obviously does not hold for large systems. As the molecule increases in size there is an increase in the number of modes that share the total energy and less energy will be present in the reaction coordinate, and hence a slower increase in the rate with energy. This can also be seen, for example, from the RRK (Rice–Ramsperger–Kassel) expression (see below); the rate constant rises less rapidly as the number of degrees of freedom increases.

The main purpose of the present work is to provide a more rigorous study of reactions in the low-friction regime and further explore the prospect of applying the generalized Kramers' theory to unimolecular reactions of polyatomic molecules in condensed phases. A general energy-diffusion equation is employed to obtain the rate constants. A model system of a set of harmonic oscillators is used to provide comparisons between the accurate rates and that obtained by assuming the low friction limit. Then, a model of a relatively large molecule (dimethylnitramine) embedded in liquid xenon is used to investigate the practicability of the energy diffusion theory for treating unimolecular reactions in condensed phases.

II Theory

Consider a general case of a polyatomic molecule of n strongly coupled degrees of freedom embedded in a heat bath where the effect of the bath on the molecule is described by a random fluctuating force. In the weak-collision regime where

the energy transfer per collision is small compared to $k_B T$, a Kramer–Moral expansion⁵ of the master equation^{6–8} leads to the energy-diffusion equation that governs the evolution of the energy distribution function $P(E, t)$ of the molecule^{6,9,10}

$$\frac{\partial P(E, t)}{\partial t} = \frac{\partial}{\partial E} \left[D(E) P_{\text{eq}}(E) \frac{\partial}{\partial E} \frac{P(E, t)}{P_{\text{eq}}(E)} \right] - k(E) P(E, t) \quad (1)$$

Here $k(E)$ is the microcanonical rate constant, $\beta = 1/k_B T$, $P_{\text{eq}}(E)$ is the equilibrium distribution

$$P_{\text{eq}}(E) = \rho(E) e^{-\beta E} \quad (2)$$

with $\rho(E)$ being the density of states, and $D(E)$ is the energy diffusion coefficient, which is simply the second moment of the transition kernel

$$D(E) = \frac{1}{2} \int dE' K(E', E) (E' - E)^2 \quad (3)$$

The steady-state solution $P_{\text{ss}}(E)$ of eqn. (1) can be obtained analytically in the low-friction limit when the intermolecular energy flow is much slower than the reaction and is hence the rate-limiting step. In this case, particles above the barrier height can be considered to disappear instantly, *i.e.*, the absorbing boundary condition $P_{\text{ss}}(E_b) = 0$ (where E_b is the barrier height) can be employed. The reaction rate constant is then obtained by solving eqn. (1) for the constant flux j below the barrier

$$j = -D(E) P_{\text{eq}}(E) \frac{\partial}{\partial E} \frac{P_{\text{ss}}(E)}{P_{\text{eq}}(E)} \quad (4)$$

Integrating eqn. (4) with the use of the absorbing boundary condition $P_{\text{ss}}(E_b) = 0$ yields

$$j \int_E^{E_b} \frac{dE}{D(E) P_{\text{eq}}(E)} = \frac{P_{\text{ss}}(E)}{P_{\text{eq}}(E)} \quad (5)$$

which leads to the usual expression for the rate constant^{9–11}

$$k = \frac{j}{\int_0^{E_b} P_{\text{ss}}(E) dE} = \left[\int_0^{E_b} P_{\text{eq}}(E) dE \int_E^{E_b} \frac{dE'}{D(E') P_{\text{eq}}(E')} \right]^{-1} \quad (6)$$

This expression can be easily evaluated once the energy diffusion coefficient $D(E)$ is known. Assuming constant friction, $D(E)$ is given by¹⁰

$$D(E) = \frac{k_B T \xi}{\rho(E)} \int_0^E dE' \rho(E') \quad (7)$$

where ξ is the friction coefficient and $\rho(E)$ the density of states of the molecule.

For simplicity, consider the molecule as n harmonic oscillators with one corresponding to the reaction coordinate truncated at E_b . In the case the density of states is

$$\rho(E) = \frac{E^{n-1}}{(n-1)! \prod_{i=1}^n h\nu_i} \quad (8)$$

Substituting eqn. (8) into eqn. (7) gives the energy diffusion coefficient for a set of n harmonic oscillators

$$D(E) = \frac{k_B T \xi E}{n} \quad (9)$$

Combining eqn. (2), (6), (8) and (9), and assuming $\beta E_b \gg 1$ (deep well), the rate constant can be approximated as^{10,12}

$$k = \xi \frac{(\beta E_b)^n}{(n-1)!} e^{-\beta E_b} \quad (10)$$

Eqn. (10) clearly shows that the rate constant increases linearly with increasing friction and should turn over to the TST limit $\nu e^{-\beta E_b}$ at some value of ξ . It is also clear that, for a polyatomic molecule with a large number of degrees of freedom, the initial rise of the rate with friction in the low-friction region is very rapid and hence the turnover to k_{TST} occurs at extremely low friction values. Thus, it has been argued^{10,12} that this energy-diffusion-controlled region may not be experimentally observable except for small molecules.

We note that eqn. (6) is an overestimate of the rate for finite friction because of the absorbing boundary condition $P_{\text{ss}}(E_b) = 0$. Since the absorbing boundary condition is based on the assumption that the reaction is so fast that the particles can be considered to instantly react when they reach the barrier, it can be easily seen to be less valid for larger molecules from the RRK expression for the microcanonical rate

$$k(E) = \nu \left(1 - \frac{E_b}{E} \right)^{n-1} \quad (11)$$

For $n > 1$, $k(E)$ starts from zero at $E = E_b$ and rises less rapidly with energy as n increases, indicating that the use of an infinite $k(E)$ at $E = E_b$ implied by the absorbing boundary condition might severely overestimate the rate for large n even when the friction is very low. The main purpose of this work is to investigate this matter and provide a more rigorous study of reactions in the energy-diffusion regime for polyatomic molecules.

In general, the solution of the energy-diffusion equation, eqn. (1), can be expanded as⁹

$$P(E, t) = \sum_m a_m \exp(-\mu_m t) \phi_m(E) \quad (12)$$

where μ_m and $\phi_m(E)$ are the eigenvalues and eigenfunctions of the equation

$$-\mu \phi(E) = \frac{\partial}{\partial E} \left[D(E) P_{\text{eq}}(E) \frac{\partial}{\partial E} \frac{\phi(E)}{P_{\text{eq}}(E)} \right] - k(E) \phi(E) \quad (13)$$

If the lowest eigenvalue μ_0 is appreciably smaller than all the others, then at times $t \gg 1/\mu_1$, $P(E, t)$ is dominated by contribution from the ground state, that is,

$$P(E, t) = a_0 e^{-\mu_0 t} \phi_0(E) \quad (14)$$

and consequently μ_0 is the rate. Thus the calculation of the rate requires finding the lowest eigenvalue of eqn. (13).

To solve eqn. (13), it is more convenient to eliminate the first derivative term so that it becomes a one-dimensional Schrödinger-like equation.¹³ This is accomplished by defining a new function $\chi(E)$

$$\chi(E) = \left(\frac{D(E)}{P_{\text{eq}}(E)} \right)^{1/2} \phi(E) \quad (15)$$

Substituting $\chi(E)$ into eqn. (13), we have

$$\mu \chi(E) = -D(E) \chi''(E) + \left\{ k(E) + \frac{D(E)}{2} \left[\frac{(P_{\text{eq}} D(E))''}{P_{\text{eq}} D(E)} - \frac{1}{2} \left(\frac{(P_{\text{eq}} D(E))'}{P_{\text{eq}} D(E)} \right)^2 \right] \right\} \chi(E) \quad (16)$$

which is a one-dimensional Schrödinger-like equation with a variable mass $1/2D(E)$.

For the sake of simplicity, in the present study we treat the reacting molecule as a set of n harmonic oscillators and use the RRK expression for the microcanonical rate $k(E)$. Employing eqn. (8) for the density of states and eqn. (9) for the diffusion coefficient, eqn. (16) in the harmonic limit becomes

$$\mu \chi(E) = -D(E) \chi''(E) + \left\{ k(E) + \frac{D(E)}{2} \left[\frac{\beta^2}{2} - \frac{\beta n}{E} + \frac{n(n-2)}{2E^2} \right] \right\} \chi(E) \quad (17)$$

where $\beta = 1/k_B T$ and n is the number of degrees of freedom. We solve eqn. (17) numerically to obtain the eigenvalues, and the lowest one is the reaction rate. We note that there have also been some related studies (for example, ref. 11, 14 and 15) in which the master equation was solved to obtain the rate.

III Results and discussion

Our main interest is to provide a more rigorous study of energy-diffusion-controlled reactions and further explore the prospect of applying the energy-diffusion theory to reactions in condensed phases. We first present the results of a model study that demonstrate the dependence of the rates on the number of degrees of freedom of the molecule, and compare the accurate rates with that obtained in the low-friction limit. We then study a test case—unimolecular dissociation of dimethylnitramine in liquid xenon—to investigate the applicability of the theory to practical problems.

A Dependence of reaction rates on the number of degrees of freedom

The usual approach for computing the rate constants in the energy-diffusion regime is to calculate the constant steady-state flux j by solving eqn. (1), but, in general, there are no analytical solutions for energies above the barrier. An analytical expression can be obtained in the low-friction limit by imposing the absorbing boundary condition $P(E_b) = 0$. This boundary condition implies that the reaction occurs very fast once the barrier is reached, and is hence valid only when the microcanonical rate $k(E)$ rises sharply in the barrier region. Obviously, this is true only for small systems. As the system gets larger, more modes will share the total energy and thus less energy will go into the reaction coordinate, resulting in smaller rates. From statistical theories such as the RRK expression, it is also clear that $k(E)$ rises less rapidly in the barrier region with increasing n .

To obtain the reaction rate more accurately, we have numerically computed the eigenvalues of the general equation, eqn. (17), assuming the system is a set of harmonic oscillators and using the RRK expression for $k(E)$ [eqn. (11)]. In our calculations the second eigenvalues are at least an order of magnitude larger than the lowest ones, showing that the lowest eigenvalues accurately represent the true rates. Fig. 1 shows the scaled rate constants ($\kappa = k/k_{\text{TST}}$) as a function of friction coefficient ξ (in fs^{-1}) for $n = 3, 10$ and 30 . The parameters used are $\nu = 0.2 \text{ fs}^{-1}$, $k_B T = 4 \text{ kcal mol}^{-1}$, and $E_b = 40 \text{ kcal mol}^{-1}$. It is clear that as n increases the rate rises more

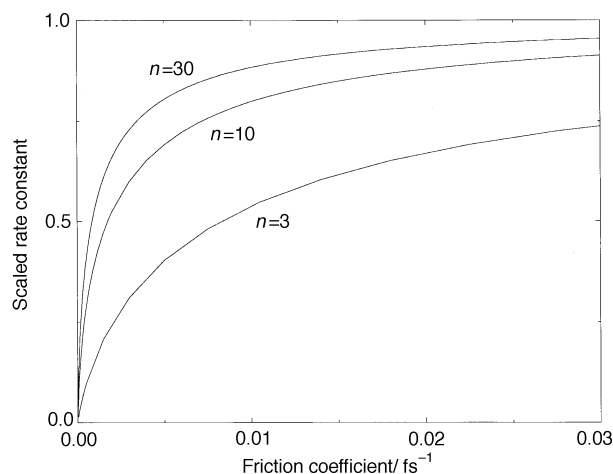


Fig. 1 Scaled rate constants $\kappa = k/k_{\text{TST}}$ versus friction coefficient ξ for a model system of n harmonic oscillators. The results are for $n = 3, 10$ and 30 . The parameters used are $\nu = 0.2 \text{ fs}^{-1}$, $k_B T = 4 \text{ kcal mol}^{-1}$ and $E_b = 40 \text{ kcal mol}^{-1}$.

rapidly and approaches the TST value at lower value of ξ . But the rise is far less rapid than that predicted by employing the low-friction limit, as demonstrated in Fig. 2, where comparisons of the rate constants, obtained by employing the RRK expression for $k(E)$ (solid curves) and by using an infinite “barrier” (dashed curves), are given. (An infinite “barrier”, meaning $k(E) = \infty$ for $E \geq E_b$, was used to represent a fast microcanonical rate implied in the low-friction limit.) Note that a much smaller scale is used in Fig. 2 than in Fig. 1. It is evident that for a large system the true rate could be overestimated by orders of magnitude even at extremely low friction, and it actually approaches the TST value at much higher friction than predicted by employing the low-friction limit. Therefore, the previous conclusion^{10,12} based on the result in the low-friction limit that for large systems the energy-diffusion-controlled regime would occur at too low friction to be experimentally accessible may not be valid.

B Dimethylnitramine in liquid xenon

To further study the application of energy-diffusion theory to unimolecular reactions of polyatomic molecules in condensed phases, we have chosen a model system of a relatively large molecule (dimethylnitramine) in liquid Xe. The molecule behaves statistically at low energies, as shown in ref. 16.

The intramolecular potential energy surface of the molecule is given in ref. 16. The intermolecular interactions are taken to be the pairwise Lennard-Jones 12-6 potentials

$$V_{\text{LJ}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (18)$$

The parameter values for the interaction between A and B atoms were calculated using the combination rules¹⁷

$$\sigma_{\text{A-B}} = \frac{1}{2} (\sigma_{\text{A}} + \sigma_{\text{B}}) \quad (19)$$

and

$$\epsilon_{\text{A-B}} = (\epsilon_{\text{A}} \epsilon_{\text{B}})^{1/2} \quad (20)$$

The values for σ and ϵ were taken from ref. 17 and 18. The Lennard-Jones potential parameters used in this study are given in Table 1.

The liquid was modeled by 256 Xe atoms with a density $0.1 \sigma^{-3}$ atom \AA^{-3} . Periodic boundary conditions were imposed in all three directions. The Lennard-Jones potentials

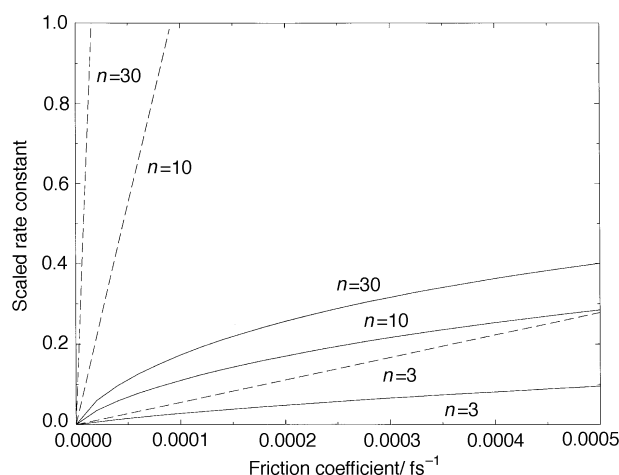


Fig. 2 Comparisons of the scaled rate constants obtained by using the RRK expression for $k(E)$ (solid curves) and by using $k(E) = \infty$ for $E \geq E_b$ (dashed curves). The parameters used are the same as those in Fig. 1. It is clear that the calculated rates employing the low-friction limit do not represent the true rates for high-dimensional systems even at very low frictions.

Table 1 Lennard-Jones potential parameters

Atom pair	$\epsilon/\text{kcal mol}^{-1}$	$\sigma/\text{\AA}$
Xe-Xe	0.461	3.98
Xe-H	0.089	3.40
Xe-C	0.217	3.67
Xe-N	0.185	3.65
Xe-O	0.238	3.47

were truncated at 2.7σ . Ensembles of 1500 trajectories were used for each set of calculations.

The only quantity to be evaluated before solving the energy-diffusion equation is the diffusion coefficient $D(E)$, which is a measure of the energy-transfer rate between the bath and the molecule. It can be obtained by monitoring the change of energy in the molecule⁹

$$D(E) = \frac{1}{2} \frac{\langle \Delta E^2 \rangle}{\Delta t} \quad (21)$$

Within the harmonic approximation, $D(E)$, as shown in eqn. (9), is linearly dependent upon temperature T and energy E . We thus first studied the dependence of $D(E)$ on T and E . The energies were chosen to be small so that the harmonic approximation is valid. Fig. 3 shows typical plots of $\langle \Delta E^2 \rangle$ as a function of time;¹⁹ they are for $E = 47 \text{ kcal mol}^{-1}$ and $T = 500$, 1000 and 1500 K. The energy diffusion coefficient $D(E)$ is just the slope of the initial portion of the curve. The calculated results for $D(E)$ are plotted in Fig. 4 as a function of energy at a fixed temperature $T = 500 \text{ K}$, panel (a), and as a function of temperature at a fixed energy $E = 47 \text{ kcal mol}^{-1}$, panel (b). They agree with the prediction of eqn. (9) that $D(E)$ is linearly dependent on T and E . Thus, eqn. (9) and (17) were used to determine the rate constants. The number of vibrational degrees of freedom of dimethylnitramine is 30, and the N—N bond is the reaction coordinate with a dissociation energy of $46.17 \text{ kcal mol}^{-1}$. The RRK expression for $k(E)$ was used with the frequency factor $\nu = 0.2 \text{ fs}^{-1}$ taken from ref. 16. The friction constants obtained by least-squares fitting of the results of Fig. 4(a) and Fig. 4(b) are $1.9 \times 10^{-3} \text{ fs}^{-1}$ and $1.5 \times 10^{-3} \text{ fs}^{-1}$, respectively, so the average value $1.7 \times 10^{-3} \text{ fs}^{-1}$ was used. To check whether this friction is in the energy-diffusion region, we plot in Fig. 5 the scaled rate, $\kappa = k/k_{\text{TST}}$, as a function of friction. It is clear that the energy-diffusion-controlled region occurs at lower frictions for the present case. Nevertheless, our results suggest that this region may be experimentally observable for systems with fewer degrees of freedom or lower barriers. For example, if βE_b was 10, as used in the model study described in the preceding section, then a friction of $1.7 \times 10^{-3} \text{ fs}^{-1}$ obtained for the present case would be close

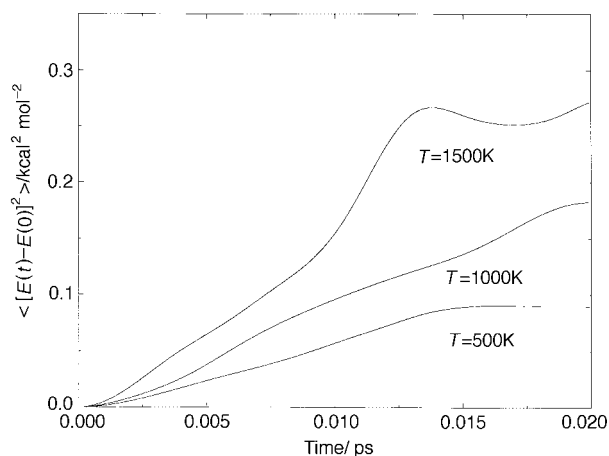


Fig. 3 Plots of $\langle \Delta E(t)^2 \rangle$ as a function of time for $T = 500$, 1000 and 1500 K, respectively. $E(0) = 47 \text{ kcal mol}^{-1}$.

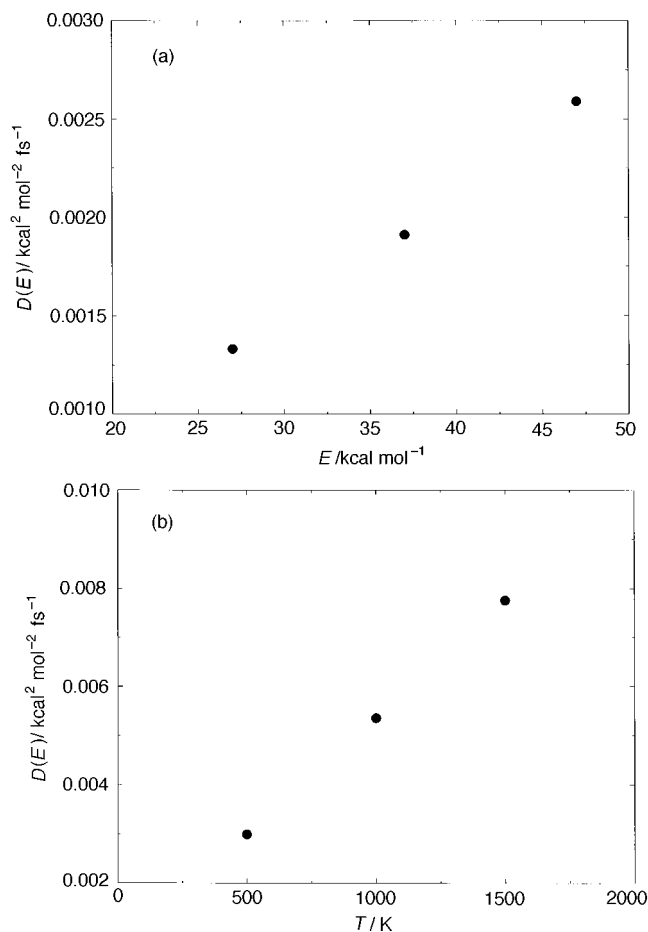


Fig. 4 The energy diffusion coefficient $D(E)$ for dimethylnitramine in liquid Xe. The density is $0.1/\sigma^3 \text{ atom \AA}^{-3}$. (a) $D(E)$ as a function of E , $T = 500 \text{ K}$. (b) $D(E)$ as a function of T , $E = 47 \text{ kcal mol}^{-1}$.

to the energy-diffusion-controlled region as can be seen in Fig. 1.

IV Concluding remark

We have investigated energy-diffusion-controlled unimolecular reactions in liquids by using the Kramers' model

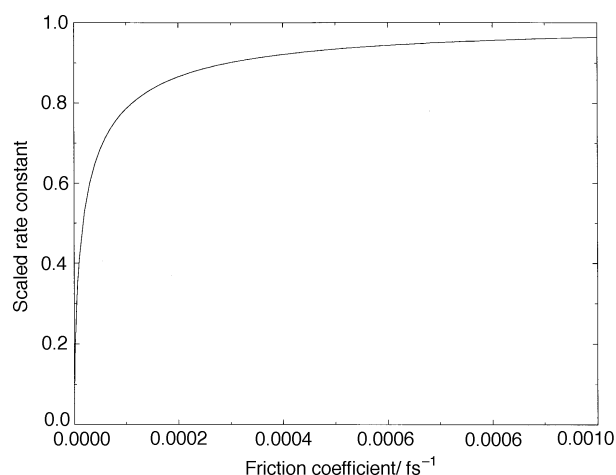


Fig. 5 Scaled rate constants $\kappa = k/k_{\text{TST}}$ versus friction. The potential parameters used correspond to the ring fission reaction in dimethylnitramine, $E_b = 46.17 \text{ kcal mol}^{-1}$, $\nu = 0.2 \text{ fs}^{-1}$, and $n = 30$. The temperature is 1500 K. It is clear that the calculated friction $1.7 \times 10^{-3} \text{ fs}^{-1}$ for dimethylnitramine in liquid Xe is beyond the energy-diffusion-controlled region.

generalized for multidimensional systems. The rate constants are evaluated by numerically solving the general energy-diffusion equation. We have used a model system consisting of a set of harmonic oscillators to study the effect on the rate of increasing the number of molecular degrees of freedom. We find that for high-dimensional systems, even at very low frictions, the exact rates may be overestimated by orders of magnitude by assuming the low-friction limit. This indicates that the transition to the TST region occurs at a much larger friction than previously believed and thus the energy-diffusion-controlled region may still be experimentally observable.

We have also used a more realistic system, a large molecule (dimethylnitramine) embedded in liquid Xe, to investigate the applicability of the generalized Kramers' model to practical problems. The calculated energy-diffusion constant $D(E)$ at low energies is linearly proportional to T and E , in agreement with Kramers' results in the harmonic limit. Although the friction constant obtained for this case is beyond the energy-diffusion-controlled region, our results suggest that this region may still be observable for a lower barrier or fewer degrees of freedom. This study sheds some new light on the applicability of the generalized Kramers' approach for studying reactions of polyatomic molecules in condensed phases. Since calculations of the energy diffusion coefficient $D(E)$ required relatively short time simulations, the approach may provide a practical method for computing the rates at considerable savings of computer time.

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