Non-Markovian theory of activated rate processes. VI. Unimolecular reactions in condensed phases

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The non-Markovian theory of activated rate processes developed by Carmeli and Nitzan is applied to investigate unimolecular reactions in condensed phases with particular emphasis on the molecular size (number of internal degrees of freedom) dependence of the effect of solvent friction on the reaction rate. The model consists of one reaction coordinate coupled to $n - 1$ nonreactive modes. The molecule solvent interaction is treated within the context of the generalized Langevin equation. The reaction dynamics may be roughly described as two consecutive processes: the well (energy diffusion) dynamics where it is assumed that fast intramolecular vibrational relaxation and slower overall molecular energy diffusion dominate the process, and the barrier dynamics where it is assumed that the motion along the reaction coordinate is only weakly coupled to the nonreactive modes. This model leads to a result for the reaction rate which, as in the one-dimensional case, is obtained as the inverse of the sum of two times: the barrier crossing time and the energy diffusion time. The latter is very sensitive to molecular size and becomes extremely short for large molecules. Correspondingly, the Kramers turnover region is predicted to occur for low molecular weight solvent in the high pressure gas phase, as was found in recent experiments. For higher viscosities the rate is dominated by the barrier crossing time with a large (larger for larger molecules) transition state rate plateau and with a falloff for high viscosities. Recent interesting results by Straub *et al.* which have pointed out the dominance of spatial diffusion in the well for extremely high viscosities (overdamped well motion) are argued to be irrelevant for most molecular situations.

I. INTRODUCTION

In a recent series of papers[1,2] we have explored several aspects of the theory of activated processes in condensed phases. The starting point of this study was Kramer's treatment[3] of escape of a Brownian particle from a potential well. We have extended Kramers theory to the non-Markovian regime for the whole friction range and have used the modified theory to analyze several experimental observations. Many authors have also over the years extended Kramers theory in these and other directions.[4]

On the experimental side, interest in unimolecular reactions in condensed phases has been increasing over the last decade. Of particular relevance to the present papers are measurements of the rate as a function of the strength of the reactant molecule–solvent interaction (as expressed, e.g., by solvent viscosity).[5-14] Time resolved spectroscopy has been utilized to study photochemical isomerization of *trans*-stilbene,[5,11] diphenyl butadiene,[6,7] DODCI,[8] binaphthyl,[9,10] and triphenyl methane[12] in various solvents. High pressure NMR technique has been used to study solvent effects on the rate of ring inversion in cyclohexane[13] and difluorocyclohexane.[14] In another important development the isomerization of *t*-stilbene and of DPB have been studied also in supersonic jet expansions[15-20] thus making it possible to directly compare chemical dynamics in solution and in isolation conditions. Combining these results with high pressure gas phase kinetic data it has become possible now to study activated chemical rate process throughout all the relevant friction (or other measure of the molecule–environment coupling)

range—from the isolated (beam) condition through the low pressure gas phase, to the high pressure gas phase and to the liquid phase up to pressure of several kbar. Such studies have now been completed for the *t*-stilbene isomerization[11,21(a)] and somewhat less complete results are available also for DPB.[7,21(b)] Hochstrasser and co-workers[22] have recently carried out such measurements (for *t*-stilbene) in ethane above its critical temperature, thus maintaining the solvent as a uniform fluid throughout the relevant viscosity range. A different but related experiment is the photo dissociation and atom recombination in the reaction $Br_2 \rightleftharpoons 2Br$, carried out by Troe and co-workers[23] in different inert gases in pressure range 1–7000 bar.

In addition to yielding a large body of data about the systems studied, these experiments have raised several issues of interest from the standpoint of general theory. These are:

(a) The viscosity (η) dependence of the rate k in some of the studied systems (stilbene in alkanes,[5] DPB in alkanes,[6] and DODCI in alcohols[8]) is weaker (i.e., $k \sim \eta^{-\alpha}$, $0 < \alpha < 1$) than predicted by the Kramers' theory. In others (stiff stilbene in alkanes,[5] stilbene in alcohols,[24] and DPB in alcohols[25]) the "usual" η^{-1} dependence was observed. These observations were interpreted[5,8,26] as arising from the non-Markovian nature of the molecule–solvent coupling in systems involving high curvature barriers.[1(d),27,28] While this interpretation is plausible other possibilities cannot be excluded: Schroeder and Troe[29] have pointed out that pressure dependence of the barrier height could in principle lead to the observed viscosity dependence without invoking the non-Markovian nature of the dynamics. Similar conclusions

0021-9606/87/052734-16$02.10   © 1987 American Institute of Physics

have been reached by Akesson, Sundstrom, and Gilbro in their study of the isomerization of the dye diethyl tetramethylindocarbocyanine iodine.[30]

(b) For some unimolecular reactions involving large molecules in supersonic beams the microcanonical RRKM theory appears to overestimate (by about one order of magnitude) the rate. This has been reported for t-stilbene[18(b),31] and for A-$(CH_2)_3$-ϕ, where A is anthracene and ϕ is N,N-dimethylaniline.[32] This obviously cannot be a conclusive statement since there are many unknown parameters in the calculation. Obviously the RRKM rate can be made smaller by postulating transition state frequencies larger than the corresponding frequencies near the bottom of the reactant well [in Refs. 18(b), 31, and 32 the two sets of frequencies were taken equal]. This has been recently demonstrated by Troe for both t-stilbene[33(a)] and PBD.[33(b)] Alternatively simple modifications of the RRKM theory can be invoked to explain the discrepancy. If fast intramolecular vibrational energy redistribution occur only within subspaces of the full phase space while those subspaces are only weakly connected, the rate can be either larger or smaller than that predicted by the RRKM theory depending on whether the reaction coordinate and the pumped mode belong to the same subspace or not.[34]

More significant for our discussion is the observation, for t-stilbene, that in low viscosity solvents the isomerization rate is larger by about one order of magnitude than that predicted from infinite pressure extrapolation of the observed beam rates, or that observed in low pressure host gas environments.[18(a),21,33(a)] (Though there are data in support of the existence of a similar phenomenon in PDB[22] a recent analysis by Troe, Amirav, and Jortner[33(b)] has led these authors to conclude that this is not the case.) The interpretation of this observation is still an open question: Syage, Felker, and Zewail[18(b)] (see below) have suggested that the difference arises from nonadiabatic effects which are more pronounced in the gas phase because of the larger velocity along the reaction coordinate. Courtney and Fleming[21] suggest that the difference may arise from slow intramolecular energy relaxation in the beam and in low pressure gases. In other words the gas phase reaction may be in the energy controlled regime and therefore slower than the fully equilibrated process in low viscosity solvents.[35] Troe and co-workers[11,29,33(a)] suggest that the difference has no dynamic origin and reflects solvent influence on the potential energy surface.

(c) The crossover from energy controlled dynamics to diffusion controlled dynamics and the range of validity of the statistical approach (transition state theory, TST) has been the focus of several recent studies. Kramers' theory[1-4] predicts this transition as a function of solvent "friction" where the rate increases with friction in the low friction limit (energy controlled dynamics inside the reactant well) and becomes inversely proportional to friction in the high friction limit (diffusion controlled dynamics on the barrier). The quantitative aspects of the Kramers theory have been modified by taking non-Markovian behavior (frequency dependent friction) into account (see paper III and J. T. Hynes in Ref. 4). Still a turnover region, a maximum of the rate as a

function of solvent friction (viscosity, collision rate, etc.) is expected to exist: Obviously the thermal unimolecular rate vanishes in the zero pressure limit and is a decreasing function of solvent viscosity in liquid solutions. Although there have been some reports of experimental observation of energy controlled dynamics and of the turnover in solutions,[10,12,13] other experiments[21-23] indicate that for large molecules the turnover region may be in the intermediate pressure gas phase. Schroeder and Troe[30] have recently suggested that some of the apparent observations of turnover in solutions may be due to pressure dependence of the potential surface, in particular the threshold energy (barrier height). A similar suggestion was recently made by Hicks et al.[36] for reactions involved substantial charge redistribution. These authors found that the barrier height for the isomerization of p-dimethylaminobenzonitrile depends on solvent polarity which is in turn affected by the same factors (temperature, pressure, composition) which affect the viscosity.

(d) The possible role of nonadiabatic effects in the unimolecular isomerization processes discussed above has been recently brought up by Syage, Felker, and Zewail.[18(b)] The excited state potential barrier for many of the photoisomerization reactions considered above is believed to result from an (avoided?) crossing between the optically active S_1 state and a higher (in the reactant geometry) state which for stilbene has a minimum at the perpendicular configuration.[37] Nevertheless, most of the discussions of these isomerization processes have chosen to disregard the possible role played by the upper potential surface (thus tacitly assuming that the energy gap between the two adiabatic surfaces is large compared to kT). Recently Frauenfelder and Wolynes[38] have discussed the possible effects of nonadiabaticity on the viscosity dependence of chemical rate processes in liquids, and Syage et al. have offered such effects as a possible explanation for the larger rate observed in the liquide phase (relative to gas phase) photoisomerization of t-stilbene. This question deserves more experimental and theoretical study.

The present work is a continuation of the effort[1] to develop Kramers' model into a useful theoretical tool for the study of unimolecular reactions in condensed media. Here I limit myself to adiabatic reactions (one potential surface) and generalize the non-Markovian version of Kramers' theory[1,4] to take into account the interaction between the reactive mode and the nonreactive molecular modes in a large molecule. Some results of this work have been presented in an earlier communication.[39]

Many of the earlier applications of the Kramers' theory or of similar collisional theories to chemical dynamics in condensed phases have used the original, one-dimensional Kramers' theory.[3] Multidimensional generalizations of this theory which focus on the dynamics near the barrier (saddle point in the multidimensional case) have been derived by several workers,[40,44] and were recently generalized by Grote and Hynes[44] and by van der Zwan and Hynes[45] to the non-Markovian regime. These studies lead to an expression for the escape rate out of a multidimensional potential well of the form

$$k = k_{TST} \frac{\lambda_0}{\omega_B}, \tag{1.1}$$

where k_{TST}, the transition state theory rate is given by[47]

$$k_{\mathrm{TST}} = \frac{\omega_R}{2\pi} \frac{Q^{(B)}}{Q} \exp(-\beta E_B). \qquad (1.2)$$

In Eqs. (1.1) and (1.2) E_B is the barrier energy, $\beta = (k_B T)^{-1}$, ω_B is the frequency characterizing the barrier along the reactive mode, Q and $Q^{(B)}$ are the equilibrium partition functions for the system of nonreactive modes in the well and on the barrier, respectively, and ω_R is the reactive mode frequency in the well. The factor λ_0/ω_B in Eq. (1.1) measures the dynamical correction to the statistically originated k_{TST}. In the Markovian limit it is given by the Kramers' result[3]

$$\frac{\lambda_0}{\omega_B} = \left[\left(\frac{\gamma}{2\omega_B}\right)^2 + 1\right]^{1/2} - \frac{\gamma}{2\omega_B}, \qquad (1.3)$$

where γ is the friction. For the non-Markovian case[1(c),27,28] λ_0 is the smallest (positive) root of the equation

$$\lambda^2 + \lambda \hat{Z}(-i\lambda) - \omega_B^2 = 0, \qquad (1.4)$$

where $\hat{Z}(\omega)$ is the Fourier–Laplace transform of the friction Kernel [see Eq. (2.1)]

$$\hat{Z}(\omega) = \int_0^\infty dt\, e^{-i\omega t} Z(t); \quad \hat{Z}(0) = \gamma. \qquad (1.5)$$

The result (1.1) is based on the assumption that the escape rate is dominated by equilibrium distribution in the well and by the dynamics near the saddle point. As the friction (γ or Z) goes to 0, $\lambda_0/\omega_B \to 1$ and $k \to k_{\mathrm{TST}}$. This expression therefore cannot describe the turnover into the well dominated dynamics. This failure results from the assumption of thermal equilibrium in the well, inherent in the results (1.1) and (1.2).

Another limiting form of unimolecular rates is common in treatments of gas phase unimolecular reactions. In its simplest form this is just the Lindeman theory and in its most elaborate version is obtained by adding microcanonical RRKM decay rates $k(E)$ into an energy master equation:

$$\frac{\partial P(E,t)}{\partial t} = \int dE'\, K(E,E') P(E') - k(E) P(E) \qquad (1.6)$$

$[k(E) = 0$ for $E < E_B]$. The overall reaction rate is

$$k = \int_{E_B}^\infty d\, E P(E) k(E). \qquad (1.7)$$

For high pressures $P(E) \to P_{\mathrm{eq}}(E)$ and Eq. (1.7) becomes the thermal RRKM rate, while for low pressure the rate is dominated by the energy exchange rates $K(E,E')$.

Troe[48] and Schroeder and Troe[29] have modified Kramers' result by combining Kramers' barrier solution with a Lindemann-type expression which describes the low collision rate limit. The so constructed expression takes the form[29]

$$k = \frac{k_{\mathrm{gas}} k_{\mathrm{diff}}}{k_{\mathrm{gas}} + k_{\mathrm{diff}}} F_{\mathrm{diff}}, \qquad (1.8)$$

where k_{gas} is an appropriate gas phase reaction rate [e.g., k of Eq. (1.7) if $K(E,E')$ in Eq. (1.6) are collisional energy transfer rates], k_{diff} is the Kramers' high friction (diffusion controlled) limit

$$k_{\mathrm{diff}} = k_{\mathrm{TST}} \frac{\omega_B}{\gamma}, \qquad (1.9)$$

and where F^{diff} is a "broadening function" of the form[49]

$$F^{\mathrm{diff}} = \left(1 + \frac{\gamma}{\omega_B}\right)\left[\sqrt{\frac{\gamma}{2\omega_B} + 1} - \frac{\gamma}{2\omega_B}\right]. \qquad (1.10)$$

The form (1.8) extrapolates between the gas phase and between the high friction liquid rates.

Two other recent papers are relevant to the present work. Borkovec and Berne[50] have evaluated the collisional rate coefficients $K(E,E')$ in Eq. (1.6) for a polyatomic molecule within the BGK model and have elucidated the effect of molecular size (number of coupled degrees of freedom) within this model. In the weak collision limit their treatment is equivalent to the Markovian–Kramers low friction limit.

Zawadzki and Hynes[51] have evaluated the energy relaxation rate of a polyatomic molecule whose interaction with the surrounding solvent is described by a generalized Langevin equation. To account for the whole friction range they use the construction (for a symmetric double well)

$$k = [k_B^{-1} + (k_W/2)^{-1}]^{-1}, \qquad (1.11)$$

where k_B is the barrier dominated rate [k of Eq. (1.1)] and where k_W is the energy relaxation rate in the well. Equation (1.11) is used to analyze molecular size effect on the transition from the low to high friction regimes.

The present paper is a detailed version of an earlier communication[39] which is also aimed at studying molecular size effects on the dynamics of unimolecular reactions in condensed media. While the final result may be cast in a form similar to Eq. (1.8) or (1.11), this result is derived (not constructed) from the generalized Langevin equation. This derivation makes it possible to track down the approximations involved in the forms (1.8) and (1.11), and provides more general forms for cases where these approximations breaks down.

Section II describes the model employed in this work while Sec. III presents the mathematical derivation of the rate expression and its analysis in limiting cases. Some numerical estimates are provided in Sec. IV. Section V discusses the results in view of recent experimental work.

II. THE MODEL

The starting point for the present treatment is a set of generalized Langevin equations (GLE) for the atomic (mass weighted) coordinates[45,46]

$$x_a = -\frac{\partial U}{\partial x_a} - \sum_b \int_0^t d\tau\, Z_{ab}(t-\tau)\dot{x}_b(\tau) + R_a(t), \qquad (2.1)$$

$$\langle R_a(t) R_b(t') \rangle = Z_{ab}(t-t')/\beta; \quad \beta = (k_B T)^{-1}, \qquad (2.2)$$

where $U(\{x\})$ ($\{x\} = x_1, x_2, ..., x_N$, N is the number of atoms) is the molecular potential surface, $Z_{ab}(t)$ and $R_a(t)$ ($a = 1,2,...,3N$) are the friction kernels and the random forces associated with the surrounding medium. Nondiagonal friction kernels may arise from hydrodynamical interactions between different atoms via the surrounding medium[45] and also from medium induced impulsive interactions

between molecular modes (see below). The mass weighted form (2.1) is obtained by scaling the regular atomic equations

$$m_a \ddot{\xi}_a = - W(\{\xi\})/\partial \xi_a$$

$$- \int_0^t d\tau \, z_{ab}(t-\tau) \xi_a(\tau) + \rho_a(t)$$

according to

$$\sqrt{m_a} \, \xi_a = x_a, \quad w\left(\left\{\frac{x}{\sqrt{m}}\right\}\right) = U(\{x\}), \quad z_{ab}/\sqrt{m_a m_b} = Z_{ab}$$

and

$$\rho_a/\sqrt{m_a} = R_a.$$

Also note that the indices a,b ($= 1,2,...,3N$) stand for both the atom and for the three Cartesian components of the atomic coordinate.

The chemical reaction is assumed to proceed when the molecule passes irreversibly from a region of configuration space identified as the reactant to a region identified as the product through a saddle point in the multidimensional potential surface. It is assumed that this saddle point is characterized by a local maximum of the potential along one degree of freedom (the "reaction coordinate") while the other intramolecular degrees of freedom maintain stable oscillations about their local minima. This saddle point constitutes the potential barrier to the reaction.

Near the barrier Eqs. (2.1) and (2.2) can be linearized and transformed to

$$\ddot{x}_R = \omega_B^2 x_R - \int_0^t d\tau \sum_j Z_{Rj}(t-\tau) \dot{x}_j(\tau)$$

$$- \int_0^t d\tau \, Z_{RR}(t-\tau) \dot{x}_R(\tau) + R_R(t), \quad (2.3)$$

$$\ddot{x}_j = -\omega_j^{(B)2} x_j - \int_0^t d\tau \sum_{j'} Z_{jj'}(t-\tau) x_{j'}(\tau)$$

$$- \int_0^t d\tau \, Z_{jR}(t-\tau) \dot{x}_R(\tau) + R_j(t), \quad (2.4)$$

$$\langle R_i(t) R_{i'}(t') \rangle = Z_{ii'}(t-t')/; \quad i,i' = \{j\}, R, \quad (2.5)$$

where x_R denote the reactive mode, $\{x_j\}$ is the set of $3N - 7$ nonreactive modes (the six overall translational and rotational coordinates are considered here as a part of the thermal environment), ω_B is the barrier frequency in the direction of the local maximum, and $\omega_j^{(B)}$ are the frequencies associated with the nonreactive modes near the barrier.

Turning to the reactant well region, great simplification is achieved by assuming that energy redistribution between intramolecular modes takes place on a time scale much shorter than the energy exchange between the molecule and its enviroment. This is generally believed to be the case for large molecules in low pressure gas phase but is not obvious for similar molecules in condensed phases at room temperature. However there are indications that this assumption is valid also in the latter case: Gottfried et al.[52] have observed intramolecular vibrational energy redistribution (IVR) rate in the S_1 state of anthracene in C_2Cl_4 to be within the temporal resolution of their apparatus (~ 2 ps), while cooling

the vibrationally excited molecule, i.e., energy transfer to the solvent was observed to proceed an order of magnitude slower (~ 25 ps). With this assumption the molecular motion in the reactant well is completely characterized (on the relevant time scale) by the time evolution of the total molecular energy E_T; the energies in the different modes are determined from E_T by statistical considerations.

Finally, as in the one-dimensional version of the theory,[1(c)] I assume that the well dynamics region (determined by the time evolution of E_T) and the barrier dynamics region (governed by the one-dimensional flux across the saddle point) overlap somewhere below the barrier. Furthermore, I assume that the reactive mode (defined near the barrier) keeps its identity below the barrier at least down to this overlap region.

The use of the GLE (2.1) as the starting point for the present treatment may raise questions concerning the generality of the model. Langevin equations are usually used in the context of Brownian motion where a heavy particle exchanges energy in small steps with a bath made of light particles. In the context of the master equation description of the energy evolution [Eq. (1.6)] this situation corresponds to the weak collision limit where $K(E,E')$ is strongly peaked about $E = E'$. Unlike the regular Langevin equation, the GLE may in principle describe processes involving strong collisions, however as in previous work[1(a)] I shall use reduction procedures which are valid only in the weak collision limit. This limit covers a large range of energy exchange processes in both condensed and gas phase systems. The choice of Kernel $Z(t)$ in Eqs. (2.1), (2.3), and (2.4) depends, of course, on the details of the interaction dynamics between the molecule and its environment. This issue has been recently discussed by Grote, van der Zwan, and Hynes.[53] In particular, following insight obtained from molecular dynamics simulations on liquid Ar,[54] these authors separate the friction Kernel into its collisional (short time) and hydrodynamical (long time) components. Hynes[55] has shown that for parabolic barrier crossing, the rate calculated from the GLE (2.3) with a friction kernel approximated by its collisional component is numerically very close to that calculated from the BGK collision model[56] for the same system.

Another objection to the present model may be made on the basis of an interesting observation made by Rosenberg, Berne, and Chandler.[57] These authors have performed molecular dynamics simulations for the isomerization of n-butane in liquid CCl_4 and observed that the computed rate does not change when the CCl_4 molecules are frozen in their initial configuration. As noted by the authors, for this system which is characterized by a large solvent to solute mass ratio ($m_{CH}/m_{CCl} = 0.11$), once the molecule has enough energy to react the dominant solvent effect is to cause energy transfer between intramolecular modes during collisions between the solute molecule and the surrounding solvent cage. In terms of the system's potential energy surface this process is associated with the occurrence of three body (two solute one solvent) and higher order interaction terms. Part of the dynamics associated with such terms will be reflected in the impulsive part of the nondiagonal friction Kernel $Z_{ab}(t)$ of

Eq. (2.1). In addition such interactions will lead to anharmonic coupling terms between the reactive and nonreactive modes in Eqs. (2.3) and (2.4). These [together with anharmonic interactions associated with the intramolecular potential surface that were neglected in Eqs. (2.3) and (2.4)] will give rise to an effective intramolecular friction affecting the motion of the reactive mode. Thus, the reduced reactive mode equations [Eq. (3.1)] is expected to remain formally the same, however the effective friction tensor Z_R will contain contributions associated with the energy exchange between the reactive and nonreactive modes. With this understanding the discussion in this paper remains unchanged.

To end Sec. I note again that the assumption of fast intramolecular energy redistribution in the reactant well introduced the number n of molecular modes as an important parameter of the theory. In a broader context n is taken to be the number of strongly coupled molecular modes and it is assumed that the reaction coordinate is part of this set. In liquid solvents n is expected to be equal to the total number $3N - 7$ of modes. In the low pressure gas phase n can be smaller, and the possible slow energy transfer between different regions of the molecular phase space (disregarded in the present model) may have a substantial influence on the reaction rate.[58]

III. EVALUATION OF THE STEADY STATE RATE

In what follows I evaluate the steady state rate for the model described in Sec. II. The calculation follows that described for the one-dimensional case (paper III): First the steady state fluxes associated with the barrier and with the well motion are obtained; second the solutions for the two regions are combined such as to satisfy appropriate boundary conditions. Finally the overall rate is obtained from the combined solution.

A. Barrier dynamics

Starting from the set of Eqs. (2.3) and (2.4) which are linearized about the saddle point, I follow Grote and Hynes[45] and derive a single equation for the reactive mode by formally solving Eq. (2.4) then inserting the solution for $x_j(t)$ into Eq. (2.3). The result is

$$\ddot{x}_R(t) = \omega_B^2 x_R - \int_0^t d\tau \, Z_R(t-\tau)\dot{x}_R(\tau) + \rho_R(t),$$
(3.1)

$$\langle \rho_R(t)\rho_R(t')\rangle = Z_R(t)/\beta,$$
(3.2)

where $Z_R(t)$ is given in terms of its inverse Laplace transform $\hat{Z}_R(s) = \int_0^\infty dt\, e^{-st} Z_R(t)$:

$$\hat{Z}_R(s) \equiv \hat{Z}_{RR}(s) - \sum_j \sum_{j'} Z_{Rj}(s) M_{jj'}(s) Z_{j'R}(s),$$
(3.3)

$$\hat{M}(s) \equiv \left[s\mathsf{I} + \hat{Z}(s) + \frac{1}{s}\Omega^2 \right]^{-1},$$
(3.4)

$$\Omega^2 \equiv \begin{pmatrix} \omega_1^2 & & 0 \\ & \omega_2^2 & \\ 0 & & \ddots \end{pmatrix}.$$
(3.5)

Here I is the unit matrix and Ω^2 is the frequency square

matrix in the space of nonreactive modes. Equation (3.1) leads to the following expression for the steady state probability distribution of the reactive mode near the barrier[1(c),27,28] (from now on I drop the index R from x_R, v_R, and E_R—the reactive mode position velocity and energy, and use it only when necessary to avoid confusion)

$$P^{(B)}(x,v) = F\frac{Q_{n-1}(x,v)}{2\pi\hbar Q_n}e^{-\beta E(x,v)}$$

$$\times \left[\sqrt{\frac{\pi}{2\bar{\alpha}\beta}} + e^{v-|\Gamma|x}\, dz\, e^{-1/2\beta\bar{\alpha}z^2} \right],$$
(3.6)

where the constant F will be determined by the boundary conditions, where

$$\bar{\alpha} = \frac{\omega_B^2}{\Gamma^2 - \omega_B^2},$$
(3.7)

$$E(x,v) = E_B + \tfrac{1}{2}v^2 - \tfrac{1}{2}\omega_B^2 x^2,$$
(3.8)

$$\Gamma = -\frac{\omega_B^2}{\lambda_0},$$
(3.9)

λ_0 is the largest (real and positive) root of the equation

$$\lambda^2 - \omega_B^2 + \lambda Z(\lambda) = 0,$$
(3.10)

and where Q_n and $Q_{n-1}(x,v)$ are, respectively, the molecular partition function and the partition function corresponding to the $n-1$ nonreactive modes, given that the reactive mode is held in position x and velocity v:

$$Q_n = \int_0^\infty dE_T\, \rho_n(E_T)e^{-\beta E},$$
(3.11)

$$Q_{n-1}(x,v) = \int_0^\infty dE_{n-1}\, \rho_{n-1}(E_{n-1})|x,v)e^{-\beta E_{n-1}}.$$
(3.12)

$\rho_n(E)$ is the molecular density of states per unit energy. $\rho_{n-1}(E|x,v)$ is the density of states associated with the $n-1$ nonreactive modes given that the reactive mode is in state (x,v). The notations E_T and E_{n-1} for the integration variables keep track of the meaning of E_T as the total molecular energy and E_{n-1} as the energy associated with the nonreactive modes [the energy of interaction between the reactive and nonreactive modes is assumed small and is neglected in Eq. (3.12)].[59]

The steady state molecular distribution near the saddle point may be now written as

$$P_M^{(B)}(x,v;E_{n-1}) = P^{(B)}(x,v)P_{n-1,\text{eq}}^{(B)}(E_{n-1}|x,v),$$
(3.13)

$$P_{n-1,\text{eq}}^{(B)}(E_{n-1}|x,v)$$
$$= \frac{1}{Q_{n-1}(x,v)}\rho_{n-1}(E_{n-1}|x,v)\exp(-\beta E_{n-1}),$$
(3.14)

where, again, the coupling between the reactive and nonreactive modes near the barrier is taken to be weak so that the flux along the reactive coordinate does not disturb much the (otherwise equilibrium) distribution in the nonreactive subsystem.

The steady state flux along the reaction coordinate is obtained from

$$j^{(B)} = \int_{-\infty}^{\infty} dE_{n-1} \int_{-\infty}^{\infty} dv \, v P_M^{(B)}(x,v;E_{n-1})$$

$$= \int_{-\infty}^{\infty} dv \, v P^{(B)}(x,v). \qquad (3.15)$$

Using Eq. (3.6) and replacing near the barrier $Q_{n-1}(x,v)$ by $Q_{n-1}(E_B)$ (to be denoted by $Q_{n-1}^{(B)}$) lead to

$$j^{(B)} = \frac{Q_{n-1}^{(B)}}{2\pi\hbar Q_n} F^{\beta - 3/2} \sqrt{\frac{2\pi}{\bar{\alpha} + 1}} e^{-\beta E_B}. \qquad (3.16)$$

If the thermal relaxation within the reactant well is fast, the constant F in Eq. (3.6) can be determined by the requirement that $P^{(B)}(x,v) \to P_{eq}(x,v)$ as $x \to -\infty$. This and Eq. (3.6) lead to $F = \sqrt{\alpha\beta/2\pi}$. Using also Eqs. (3.7)–(3.10) to get $\sqrt{\bar{\alpha}/(\bar{\alpha}+1)} = \lambda_0/\omega_B$ and the relation

$$Q_n = \frac{1}{\hbar} \int_0^{\infty} dE \frac{Q_{n-1}(E) e^{-\beta E}}{\omega_R(E)} \simeq \frac{Q_{n-1}^{(0)}}{\beta\hbar\omega_R(0)}, \qquad (3.17)$$

where $Q_{n-1}^{(0)}$ denotes the partition function associated with the subsystem of nonreactive modes when the reactive mode is in its ground state, Eq. (3.16) leads to the result of Hynes and co-workers[45,46] for the barrier dominated rate r_B:

$$r_B = j^{(B)} = \frac{\lambda_0}{\omega_B} \frac{\omega_R(0)}{2\pi} \frac{Q_{n-1}^{(B)}}{Q_{n-1}^{(0)}} e^{-\beta E_B}. \qquad (3.18)$$

In the Markovian limit, $Z_R(t) = 2\gamma_R \delta(t)$ and $\hat{Z}_R(\lambda) = \gamma_R$. Equation (3.17) then yields the well-known Markovian multidimensional result.[40,44] If, moreover, $Q_{n-1}^{(B)} = Q_{n-1}^{(0)}$ (i.e., the nonreactive subsystem is not affected by the state of the reactive mode) this becomes the Kramers one-dimensional result.

The result (3.18) corresponds to the case where the thermal relaxation in the reactant well is fast. In the general case the deviation of the well distribution from equilibrium has to be considered.

B. Well dynamics

As in the one-dimensional treatment[1(a),4] the atomic motion in the reactant well is assumed to be characterized by a time-scale separation between the slow energy variable and the fast changing phases. However, in accordance with our model assumption (Sec. II) it is the total molecular energy which is assumed to be (relatively) slow. Individual mode energies fluctuate rapidly and are estimated only by statistical consideration.

In order to make contact later with the barrier dynamics we need $P^{(w)}(E)$—the probability that the reactive mode has energy E. We note in passing that $P^{(w)}(E)$ is meaningful only provided that the reactive mode (defined near the barrier) keeps its identity in the well region. I show below that it is enough that this will be so high in the well, below the barrier region.

The probability $P^{(w)}(E)$ can be expressed in terms of $P_M^{(w)}(E_T)$—the probability distribution for the total molecular energy E_T, and the conditional probability distribution $P^{(w)}(E|E_T)$ for the reactive mode to have energy E given that the total molecular energy is E_T:

$$P^{(w)}(E) = \int_0^{\infty} dE_T \, P_M^{(w)}(E_T) P^{(w)}(E|E_T). \qquad (3.19)$$

Note that $P^{(w)}(E|E_T) = 0$ for $E_T < E$ so the lower bound in the intergration can be taken E.

The assumption of complete statistical distribution of energy within the n strongly coupled modes leads immediately to the following expression for $P^{(w)}(E|E_T)$[60]:

$$P^{(w)}(E|E_T) = \frac{1}{\hbar\omega_R(E)} \frac{\rho_{n-1}(E_T - E)}{\rho_n(E_T)}. \qquad (3.20)$$

To find the distribution $P_M^{(w)}(E_T)$ of the molecular energy, I need a diffusion equation for E_T which is a generalization of the one-dimensional equation[1(a)]

$$\frac{\partial P(E,t)}{\partial t} = \frac{\partial}{\partial E}\left[D(E)\left(k_B T \frac{\partial}{\partial E} + 1\right)\omega(E) P(E,t)\right]. \qquad (3.21)$$

The required generalization of Eq. (3.21) to the multidimensional case is

$$\frac{\partial P_M^{(w)}(E_T,t)}{\partial t} = \frac{\partial}{\partial E_T}\left[D(E_T)\left(k_B T \frac{\partial}{\partial E_T} + 1\right)\right.$$
$$\left. \times \rho_n^{-1}(E_T) P_M^{(w)}(E_T,t)\right], \qquad (3.22)$$

where $D(E_T)$ is related now to the rate of molecular energy dissipation at $T = 0$:

$$\left(\frac{dE_T}{dt}\right)_{T=0} = -D(E_T)\rho^{-1}(E_T). \qquad (3.23)$$

An explicit expression for $D(E_T)$ can be obtained from Eq. (2.1) which leads to

$$\left(\frac{dE_T}{dt}\right)_{T=0} = -\int_0^t d\tau \sum_a \sum_b z_{ab}(t-\tau)\dot{x}_a(t)\dot{x}_b(\tau). \qquad (3.24)$$

Invoking the model assumption: slow variation of E_T relative to the relaxation time associated with $Z_{ab}(t-\tau)$ (the latter is essentially the characteristic solvent relaxation time), and averaging the product $\dot{x}_a(t)\dot{x}_b(\tau)$ over all initial phases assuming further that the averaged product $\overline{\dot{x}_a(t)\dot{x}_b(\tau)}$ depends only on $t-\tau$, I get from Eqs. (3.23) and (3.24):

$$D(E_T) = \rho_n(E_T)\int_0^{\infty} dt \sum_a \sum_b Z_{ab}(t) \overline{[\dot{x}_a(t)\dot{x}_b(0)]}_{E_T}. \qquad (3.25)$$

Equation (3.25) may be used for evaluating $D(E_T)$ using simulations based on Eq. (2.1). Such simulations will yield the correlation function $\overline{[\dot{x}_a(t)\dot{x}_b(0)]}_{E_T}$. The average is over the initial phase and the subscript E_T denotes the fact that the total molecular energy does not change during these simulations. For a small molecule $\overline{\dot{x}_a(t)\dot{x}_b(0)}$ can be evaluated in the absence of molecule-thermal bath coupling (so that E_T is obviously constant). This is the lowest order approximation in the molecule bath coupling to Eq. (3.25). For large molecules the coupling to the environment may strongly affect intramolecular energy redistribution and should be included in evaluating $\overline{\dot{x}_a(t)\dot{x}_b(0)}$ using Eq. (2.1). Our model assumptions still imply that E_T does not

change appreciably during the relevant time for this calculation [i.e., the relaxation time associated with $Z_{ab}(t)$]. Equation (3.25) has also been derived by Zawadzki and Hynes,[51] and its Markovian equivalent has been obtained by Borkovec and Berne.[50]

The Smulochowski-type equation (3.22) is of the same formal form as the equivalent equation (3.21) of the one-dimensional case. Its general steady state $(\partial P_M^{(w)}/\partial t = 0)$ solution is

$$P_{M,ss}^{(w)}(E_T)$$
$$= \frac{1}{Q_n}\rho_n(E_T)e^{-\beta E_T}\left[A_1 + A_2\int_{E_T}^{E_{1T}}dE'\frac{e^{\beta E'}}{D(E')}\right]$$
(3.26)

and the steady state flux $[j = D(k_B T\partial/\partial E + 1)\rho_n^{-1}P_{M,ss}^{(w)}]$ is

$$j^{(w)}(E_T) = \frac{A_2}{Q_n\beta}.$$
(3.27)

In Eq. (3.32) A_1, A_2, and E_{1T} are constants to be determined by the boundary conditions. Note that only two of these are independent. At equilibrium $A_2 = 0$ and $A_1 = 1$.

The expressions for $P^{(w)}(E|E_T)$ [Eq. (3.20)] and for $P_M^{(w)}(E|E_T)$ [Eq. (3.26)] are now used with Eq. (3.19) to get the reactive mode steady state distribution $p^{(w)}(E)$. This calculation (Appendix A) yields

$$P_{ss}^{(w)}(E) = \frac{Q_{n-1}(E)e^{-\beta E}}{\hbar\omega_R(E)Q_n}\left[A_1 + A_2\int_E^{E_1}dE'\frac{e^{\beta(E'+\bar\epsilon)}}{D(E'+\bar\epsilon)}\right],$$
(3.28)

where

$$E_1 = E_{1T} - \bar\epsilon$$
(3.29)

and where $\bar\epsilon$ is the value of ϵ for which the expression $\rho_{n-1}(\epsilon)e^{-\beta\epsilon}$ achieves its maximum value. In the high barrier high temperature limit it is approximately equal to the thermal energy in the nonreactive modes

$$\bar\epsilon \simeq (n-1)/\beta.$$
(3.30)

Note that, in this approximation, if E is the energy in the reactive mode, $\bar E + \bar\epsilon$ is approximately the corresponding total molecular energy.

The steady state flux $j^{(w)}(E)$ associated with the reactive mode steady-state distribution (3.28) is the same as that [Eq. (3.27)] associated with the total energy distribution (3.26)[61]:

$$j^{(w)}(E) = \frac{A_2}{Q_n\beta}.$$
(3.31)

C. The combined solution

The assumption that relaxation within the reactant well is fast so that $P^{(w)}(E)$ is well described by a Boltzmann distribution (i.e., $A_2 = 0$) leads to the barrier dominated rate [Eq. (3.21)]. When this assumption does not hold the unknown constants F in Eq. (3.6) and A_1, A_2, and E_1 in Eq. (3.28) have to be determined by matching these barrier and well solutions together. To this end I follow the procedure of

Carmeli and Nitzan[1(c)] and choose to match the solutions at some point $(x_1, v_1 = 0)$ corresponding to an energy E_1 in the reactive mode $(E_1 = E_B - 1/2\omega_B x_1^2)$. I assume that there is at least one such point where both the barrier and the well solutions are valid. Since E_1 in Eq. (3.28) can be chosen arbitrarily, I choose it to be this matching energy. At this point I require that the well steady state distribution [Eq. (3.28)] and the corresponding barrier distribution [Eq. (3.11)] are equal:

$$\frac{\omega_R(E_1)}{2\pi}P^{(w)}(E_1) = P_B(x_1, v_1 = 0)$$
(3.32)

[the $\omega/2\pi$ term arises from the $(xv)\to(E\phi)$ transformation together with the observation that in the well the ϕ distribution is $(2\pi)^{-1}$]. Similarly the energy derivatives are taken to be equal at this point:

$$\left[\frac{\partial}{\partial E}P^{(B)}(x,v=0)\right]_{x_1} = \frac{1}{2\pi}\left\{\frac{\partial}{\partial E}[\omega(E)P^{(w)}(E)]\right\}_{E_1}.$$
(3.33)

Finally the steady-state fluxes [Eqs. (3.16) and (3.31)] should be the same:

$$j^{(B)} = j^{(w)}.$$
(3.34)

The three conditions Eqs. (3.32)–(3.34), together with the requirement that the overall distribution is normalized, are just sufficient to determine the three unknown constants A_1, A_2, and F and the matching point energy E_1. Equations (3.32)–(3.34) lead to

$$\frac{A_2}{F} = Q_{n-1}^{(B)}\beta^{-1/2}\sqrt{\frac{2\pi}{\bar\alpha+1}}e^{-\beta E_B},$$
(3.35)

$$\frac{A_1}{F} = \pi\hbar\beta^{-1/2}\sqrt{\frac{2\pi}{\bar\alpha}}$$
$$+ [1 + \mathrm{erf}(\sqrt{\bar\alpha+1}\beta(E_B - E_1)],$$
(3.36)

and

$$\frac{Q_{n-1}^{(B)}}{(\bar\alpha+1)D(E_1+\bar\epsilon)}\left[\frac{\bar\alpha(E_B-E_1)}{\pi\beta}\right]^{1/2}e^{\beta[\bar\alpha(E_B-E_1)+\bar\epsilon]} = 1.$$
(3.37)

Equation (3.37) may be solved for E_1. To see its significance consider the limits of large and small molecule. For $n = 1$ $\bar\epsilon = 0$, $Q_{n-1} = 1$ and $\hbar D(E) = \omega^{-1}\int_\infty^\infty dt Z(t)$ $\times \dot x(t)\dot x(0) = \omega\epsilon E$ [$\epsilon(E)$ is defined in paper III; see also Eq. (30) of Ref. 2(c)]. In this limit Eq. (3.37) reduces to Eq. (3.19) of paper III. For a particular model of the memory Kernel the resulting E_1 is displayed as a function of friction in Fig. 2 of paper III. Generally $E_1 \to E_B$ for small friction and $E_1 \to 0$ when the friction becomes very large.

In the opposite limit of large n, both factor $Q_{n-1}^{(B)} e^{\beta\epsilon}$ and $D(E_1 + \bar\epsilon)$ increase rapidly with the number of degrees of freedom. Their ratio however depends only weakly on n so that E_1 will not be very sensitive to molecular size (see Sec. IV).[62]

The last step in evaluating the steady state distribution is the calculation of the normalization constant

$$\mathcal{N} = \int_{-\infty}^{\infty} d\{x^{n-1}\}d\{v^{n-1}\}\int_{-\infty}^{x_B} dx \int_{-\infty}^{\infty} dv \, P_M(x,v)$$

$$= \int_0^{\infty} dE_T \, \rho_n(E_T)P_M(E_T), \qquad (3.38)$$

where $\{x^{n-1}\}$ and $\{v^{n-1}\}$ denote the sets of coordinates and velocities of the nonreactive modes. The reaction rate is given by the steady state flux divided by $\mathcal{N}$:

$$r = j/\mathcal{N}. \qquad (3.39)$$

The evaluation of $\mathcal{N}$ is described in Appendix B. The result is

$$\mathcal{N} = \frac{\pi\hbar A_2\eta e^{\beta E_B}}{Q_{n-1}^{(B)}} + \frac{A_2\tau_1}{Q_n\beta} + \frac{\pi(2-\eta)A_2 e^{\beta E_B}}{Q_n Q_{n-1}^{(B)}} \frac{\omega_B}{\lambda_0} \int_{E_1}^{\infty} dE_T \int_{E_1}^{E_T} dE \frac{e^{-\beta E_T}\rho_{n-1}(E_T - E|E)}{\omega_R(E)}$$

$$+ \frac{A_2}{Q_n} \int_0^{E_1} dE_T \, \rho_n(E_T)e^{-\beta E_T} \int_{E_1}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} + \frac{A_2}{\hbar Q_n} \int_{E_1}^{\infty} dE_T \int_0^{E_1} dE \frac{e^{\beta E_T}\rho_{n-1}(E_T - E|E)}{\omega_R(E)} \int_E^{E'} dE' \frac{e^{\beta(E'+\bar{\epsilon})}}{D(E'+\bar{\epsilon})}, \qquad (3.40)$$

where

$$\tau_1 = \beta \int_{E_{0T}}^{E_1} dE' \frac{e^{\beta E'}}{D(E')} \int_0^{E'} dE_T \, \rho_n(E_T)e^{-\beta E_T}, \qquad (3.41)$$

$$\eta = 1 + \text{erf}\left[\sqrt{(\bar{\alpha}+1)\beta(E_B - E_1)}\right], \qquad (3.42)$$

$$E_{1T} = E_1 + \bar{\epsilon}, \qquad (3.43)$$

and where E_{0T} is some arbitrary source point on the energy axis near the bottom of the reactant well. τ_1 is the mean first passage time for a molecule that starts with total energy E_{0T} to reach the total energy E_1. For $E_{0T} \ll E_B$ the choice of E_{0T} does not affect the result.

The reaction rate may now be obtained from Eqs. (3.27) and (3.40). To simplify the resulting rate note that the ratios between the flux $j = A_2/(Q_n\beta)$ and between the first and third terms of Eq. (3.40) contain the term r_B—the barrier dominated rate [Eq. (3.18)]. The final result for the rate is thus

$$r = \{[(2/\tilde{\eta})r_B]^{-1} + \tau\}^{-1}, \qquad (3.44)$$

$$r_B = \frac{\lambda_0}{\omega_B} \frac{\omega_R(0)}{2\pi} \frac{Q_{n-1}^{(B)}}{Q_{n-1}^{(0)}} e^{-\beta E_B}, \qquad (3.45)$$

$$\tilde{\eta} = \eta + (2-\eta)\frac{1}{Q_n} \int_{E_1}^{\infty} dE_T \, e^{-\beta E_T}$$

$$\times \int_{E_1}^{E_T} dE \frac{\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)}, \qquad (3.46)$$

$$\tau = \tau_1 + \tau_2 + \tau_3, \qquad (3.47)$$

where τ_1 is given by Eq. (3.41),

$$\tau_2 = \beta \int_0^{E_1} dE_T \, \rho_n(E_T)e^{-\beta E_T} \int_{E_1}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}, \qquad (3.48)$$

$$\tau_3 = \beta \int_{E_1}^{\infty} dE_T \int_0^{E_1} dE \frac{e^{-\beta E_T}\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)}$$

$$\times \int_E^{E'} dE' \frac{e^{\beta(E'+\bar{\epsilon})}}{D(E'+\bar{\epsilon})}. \qquad (3.49)$$

In the one-dimensional case $E_{1T} = E_1$, $\tau_2 = \tau_3 = 0$ and $\tau = \tau_1$. In Appendix C I show that for deep wells,

$$\tau \lesssim \beta Q_n \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}, \qquad (3.50)$$

where the equality is a reasonable approximation. The right-hand side of Eq. (3.50) is a good approximation to

$$\beta \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')} \int_0^{E'} dE \, e^{-\beta E}\rho_n(E). \qquad (3.51)$$

This is the mean first passage time to reach from the bottom of the well to the energy $E_{1T} = E_1 + \bar{\epsilon} = E_1 + (n-1)/\beta$. Thus τ corresponds approximately to this mean first passage time, in analogy to the one-dimensional case.

In the one-dimensional case $\rho_{n-1} = 0$ so $\tilde{\eta}$ in Eq. (3.45) is equal to the factor η as already obtained in paper III. For a very large molecule the double integral in Eq. (3.46) can be approximated by

$$\int_0^{\infty} dE_T \, e^{-\beta E_T} \int_0^{E_T} dE \frac{\rho_{n-1}(E_T - E|E)}{\hbar\omega_R(E)} = Q_n \qquad (3.52)$$

because most of the contribution to Eq. (3.52) comes from energy regions $E_T, E \gg E_1$. In this case $\tilde{\eta} = 2$.

Equations (3.44)–(3.49) are the final equations for the reaction rate. Next I discuss these results.

IV. DISCUSSION

The escape rate from the polyatomic reactant well has been obtained in the form

$$r = \{[(2/\tilde{\eta})r_B]^{-1} + \tau\}^{-1}. \qquad (4.1)$$

τ is given by Eqs. (3.47)–(3.49) which for large barriers may be approximated by

$$\tau \sim \beta Q_n \int_0^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}; \quad \beta = (k_B T)^{-1} \qquad (4.2)$$

which is approximately the mean first passage time for the reactant to reach the energy

$$E_{1T} = E_1 + \bar{\epsilon}. \qquad (4.3)$$

$\bar{\epsilon}$ is defined as the energy where $\rho_{n-1}(\epsilon)e^{-\beta\epsilon}$ achieves its maximum, and in the high temperature large barrier limit is equal to the energy in the nonreactive modes $\bar{\epsilon} \simeq (n-1)/\beta$ (n is the number of strongly coupled internal degrees of freedom). $\tilde{\eta}$ is given by

$$\bar{\eta} = \eta + (2 - \eta)\frac{1}{Q_n} \int_{E_1}^{\infty} dE_T \, e^{-\beta E_T} \int_{E_1}^{E_T} dE$$

$$\times \frac{\rho_{n-1}(E_T - E \mid E)}{\hbar \omega_R(E)}, \qquad (4.4a)$$

$$\eta = 1 + \mathrm{erf}\sqrt{(\bar{\alpha} + 1)\beta(E_B - E_1)}. \qquad (4.4b)$$

$\bar{\alpha}$ is given by Eqs. (3.8)–(3.10), E_1 is the solution of Eq. (3.37) whose typical dependence on the solvent friction is shown in Fig. 1. In particular $E_1 \to E_B$ in the low friction limit and $E_1 \to 0$ when $\gamma \to \infty$. Q_n is the equilibrium partition function of the n-mode system; $D(E)$, given by

$$D(E) = \rho_n(E) \int_0^{\infty} dt \sum_a \sum_b Z_{ab}(t) \, \overline{[\dot{x}_a(t)\dot{x}_b(0)]}_{E_T}, \qquad (4.5)$$

is related to the rate of energy damping by the reactant molecule

$$\left(\frac{dE}{dt}\right)_{T=0} = -D(E)\rho_n^{-1}(E). \qquad (4.6)$$

Finally r_b is the barrier dominated rate given by

$$r_B = \frac{Q_{n-1}^{(B)}}{2\pi\hbar\beta Q_n} \frac{\lambda_0}{\omega_B} e^{-\beta E_B} \simeq \frac{\omega_R(0)}{2\pi} \frac{Q_{n-1}^{(B)}}{Q_{n-1}^{(0)}} \frac{\lambda_0}{\omega_B} e^{-\beta E_B}. \qquad (4.7)$$

A few comments should be made concerning these results.

(a) As in the simpler one-dimensional case, the result [Eq. (4.1)] exhibits a smooth transition from a well dominated rate τ^{-1} to a barrier dominated rate r_B. For very weak solvent interactions the denominator in the right-hand side of Eq. (4.1) is dominated by the energy accumulation time τ, and the rate is given by $r \sim \tau^{-1}$. When solvent interactions become stronger τ decreases and at the same time $\bar{\eta}$ approaches 2, so r becomes dominated by r_B. Note that the low friction limit of r_B is the transition state expression for the transition rate. Also note that the way in which the rate depends on solvent friction changes with the molecular size. In the large molecule limit (large n) $\bar{\eta}$ becomes 2 as discussed in the previous section. Also in this limit τ can be neglected (see below) unless the friction is so low that E_1 is equal to E_B. Equation (4.1) can therefore be written

$$r = \left[r_B^{-1} + \beta Q_n \int_0^{E_B + \bar{\epsilon}} dE' \frac{e^{\beta E'}}{D(E')} \right]^{-1}. \qquad (4.8)$$

In this form the rate is given as the inverse of the sum of two times: the barrier crossing time r_B^{-1} and a time characteristic to the energy relaxation rate within the reactant well.

(b) The calculation which leads to Eq. (4.1) is based on a single well (dissociation) model. Its extension to a double well (isomerization) situation can be carried out in complete analogy to the similar extension of the one-dimensional problem described in paper IV.[63] For a large molecule the result is simply

$$r_{R \leftarrow L} = \left[r_{B,R \leftarrow L}^{-1} + \tau_L + q_e \tau_R \right]^{-1}, \qquad (4.9)$$

$$\tau_w \simeq \beta Q_w \int_0^{E_{1T}^{(w)}} dE' \frac{e^{\beta E'}}{D_w(E')} \quad (w = L,R), \qquad (4.10a)$$

$$E_{1T}^{(w)} = E_{1w} + \bar{\epsilon}_w, \qquad (4.10b)$$

$$q_e = Q_L/Q_R. \qquad (4.11)$$

The subscripts $W(=R,L)$ in Eqs. (4.9)–(4.11) denote quantities related to the right (R) or left (L) wells. Thus Q_R is the partition function, n_r is the number of strongly coupled modes, and $D_R(E)$ is the relaxation function in the right well. $r_{R \leftarrow L}$ and $r_{B,R \leftarrow L}$ are, respectively, the overall and the barrier dominated transition rates from left to right. As discussed in paper IV, the appearance of τ_R in the expression for $r_{R \leftarrow L}$ is associated with the back scattering of trajectories from the far wall of the product well.

(c) As discussed with respect to the one-dimensional model and in recent experimental papers, the rate equation (4.1) goes through a maximum when the friction grows from zero. For extremely small damping the rate is given by τ^{-1} with $E_1 = E_B$ which grows linearly with the friction while for large damping the rate is dominated by r_B which decreases with increasing friction.[64] While the situation here is qualitatively similar to the one-dimensional case, the quantitative behavior is quite different. The barrier term in Eqs. (4.1) [or Eq. (4.8)] and (4.7) is not much different: The additional factor Q_{n-1}^B/Q_{n-1} is, for isomerization reactions, of order 0.1–10. The relaxation time τ may however be orders of magnitude different. To see this take as a rough estimate for τ (which holds for $E_{1T} \gg k_B T$) the expression

$$\tau \simeq \frac{Q_n e^{\beta E_{1T}}}{D(E_{1T})} \simeq Q_n e^{n-1} \frac{e^{\beta E_1}}{D(E_{1T})} \qquad (4.12)$$

and use[65]

$$D(E) = \rho(E) E k_{VR}(E), \qquad (4.13)$$

where $k_{VR}(E)$ is the vibrational energy relaxation rate of the molecule at total vibrational energy E. Using also the classical approximations for Q_n and ρ (with ω—a characteristic molecular frequency)

$$Q_n \left[\frac{kT}{\hbar\omega} \right]^n; \quad \rho(E) = \frac{(E/\hbar\omega)^{n-1}}{\hbar\omega(n-1)!} \qquad (4.14)$$

leads to

$$\tau = \left\{ k_{VR}(E_{1T}) \frac{(\beta E_1 + n - 1)^n}{(n-1)!} e^{-\beta[E_1 + (n-1)/\beta]} \right\}^{-1}. \qquad (4.15)$$

For $n = 1$ this yields $\tau = (k_{VR}\beta E_1 e^{-\beta E_1})^{-1}$ which is exactly the low friction generalized Kramers' result (the friction γ is replaced here by the more general k_{VR} which incorporates non-Markovian effects if present. In this low friction limit $E_1 = E_B$). This results both because of the larger k_{VR} expected for larger molecules and because of the explicit n dependence in Eqs. (4.15)–(4.17). Equation (4.1) then implies that the turnover from well dynamics to barrier dynamics dominated rate occurs for large molecules at much smaller solvent viscosities (or pressure in the gas phase) than for small molecules. This point was discussed in Refs. 39, 50, and 51. Since for this small friction the barrier dominated rate is identical to the TST rate, it may be concluded that for large molecules a plateau in the rate vs solvent friction, where $r = r_{TST}$, should be observed. It should be kept in mind that identifying this plateau value with r_{TST} rests on the assumption that the number n of strongly interacting modes is equal to the total number of internal degrees of freedom, and that energy redistribution among these modes

occurs instantaneously relative to other relevant times. If this is not the case, rates larger or smaller than r_{TST} may be observed depending on whether or not the reaction coordinate belong to the group of directly pumped modes. This may explain some of the recent observations on the isomerization rates of t-stilbene and of diphenylbutadiene.[67]

(d) In the large molecule limit I have shown that $\tilde{\eta}$ in Eq. (4.1) becomes 2 so that the rate r is always smaller than r_B, and therefore also bounded by the transition state rate r_{TST} (assuming that n is equal to the total number of degrees of freedom). Equation (4.1) was also shown to yield in the one-dimensional limit the results of paper III which has similar properties. In the general case I did not succeed to prove that the form [Eq. (4.1)] is bounded by r_{TST}, though this was the case for all the numerical checks. Obviously, provided than n is equal to the total number of internal degrees of freedom, the rate r should be bounded by r_{TST} and any possible deviation of Eq. (4.1) from this will be the result of the approximations employed in the derivation.

(e) An interesting difference exists between the low friction limit of the rate obtained in the present work and between the low friction rates calculated by other workers.[50,51] Borkovec and Berne[50] as well as Zawadzki and Hynes identify this limit rate as the inverse mean first passage to reach from the bottom of the reactant well to the reactive mode barrier energy E_B. The rate is then given by the inverse of Eq. (4.15) with $E_{1T} = E_1 + (n - 1)/\beta$ replaced by E_B. In the present work, the low friction rate is obtained as the inverse mean first passage time to reach the energy $E_B + (n - 1)/\beta$. Mathematically this is obtained as a consequence of our connecting procedure: the flux across the reaction barrier was assumed in Sec. III to take place with the nonreactive modes at thermal equilibrium [Eq. (3.14)]. This implies that the products are formed with their internal degrees of freedom at equilibrium while taking E_B as absorbing barrier implies that the products are formed with zero internal energy.

It should be stressed that the correct mathematical low friction limit is that corresponding to E_B as an absorbing barrier: if the friction (or the gas phase pressure) is low enough, the molecule will spend enough time near E_B so that a fluctuation in internal energy distribution that leads to reaction will occur. Such a fluctuation is less likely for a larger molecule. For a large molecule, we expect that a range of friction/pressure exists for which the rate still obeys low friction dynamics but the effective absorbing barrier (effective threshold) is considerably higher than E_B. Such "chemical shifts" of the effective threshold are well known.[66] Our model implicitly assumes that this shift is $(n - 1)/\beta$.

(f) The results (4.1)–(4.15) stress the number of strongly coupled modes n as an important parameter of the theory which together with the activation barrier height and the solvent frequency dependent friction determine the reaction rate. The barrier height and the friction can in principle be determined by independent measurements (Arrhenius temperature dependence of the rate in the transition state regime and molecular vibrational relaxation rates). The number of strongly coupled degrees of freedom is an undetermined parameter of the theory. In this respect our situa-

tion is similar to that of the RRKM theory, and in fact the present results may be viewed as a unification of the RRKM and the generalized Kramers' theories of chemical reaction rates. Using n as a fitting parameter has been a traditional way of applying the RRKM theory to interpretation of experimental data. Because of the large sensitivity of the calculated rate to n (both in the RRKM theory and in its present extension) such a fitting can at best lead to very crude estimates. An interesting possibility is to estimate n from transition state (high pressure gas phase) data and to use the so obtained number of strongly coupled modes to predict the full range pressure/viscosity dependence. Such a procedure may work if intramolecular energy distribution is dominated by intramolecular interactions. More likely we may find that the number of strongly coupled modes is pressure dependent at low pressures as discussed at the end of Sec. II. (See also Ref. 69. In this paper Borkovec et al. describe a model in which molcular mode–mode coupling seems to effectively *decrease* with increasing pressure. However the model does not include the possibility of collision induced energy transfer between the modes, a process which may dominate the relaxation behavior of large molecules.) In any case, it is obviously important to get experimental information on the parameter n in the different pressure/viscosity regimes. The present results provide a theoretical framework for such studies.

(g) Very recently it was shown by Straub, Borkovec, and Berne[70] that in highly non-Markovian situations and for high friction the barrier dominated rate r_B as derived by Grote and Hynes[27] (see also Hanggi and Mojtabai[28] and paper III) does not provide a proper description of the overall escape rate out of the reactant well, as obtained by the simulation. These observations have been subsequently explained by Okuyama and Oxtoby.[71] Qualitatively the origin of this behavior can be understood by considering the model memory function used by Straub et al.[70]:

$$\ddot{x} = -\frac{1}{m}\frac{\partial v(x)}{\partial x} - \int_0^t d\tau\, Z(t - \tau)\dot{x}(\tau) + \frac{1}{m}R(t),$$
(4.16)

$$\langle R(0)R(t)\rangle = mk_B T Z(t)$$
(4.17)

with

$$Z(t) = \frac{\gamma}{\tau_c}e^{-t/\tau_c}; \quad \tau_c = \alpha\gamma.$$
(4.18)

The potential $V(x)$ is characterized by the well bottom ω_0 and the barrier ω_B frequencies. As γ increases so does the bath correlation time τ_c. However, provided that $\alpha\omega_B^2 > 1$ the reactive frequency λ_0 (defined in Sec. III) remains finite as $\gamma \to \infty$, so that the barrier crossing rate r_B also remains finite. On the other hand the relaxation rate associated with the overdamped well motion vanishes in this limit[71] so that as in the $\gamma \to 0$ situation the well dynamics becomes rate determining and dominates the overall rate.

It should be noted that this limit involves a very strong molecule–solvent interaction which substantially changes the intramolecular motion.[69] There is no spectroscopical evidence for such an effect even in high viscosity solvents or for molecules imbedded in solid matrices. In the present work

(as in our previous work) I have made the assumption that the well motion is underdamped and is not qualitatively changed by the solvent interaction. Moreover I have assumed that at such energies where the motion may not be underdamped the system is close enough to the barrier to make it possible to describe the latter as an inverted parabola. These assumptions will obviously break down in the situation considered by Straub et al.[70]

(h) While the model employed in the present work provides a reasonable picture of a unimolecular reaction involving a large molecule in solution, other ingredients not considered here may play a role in some systems. The possible role played by intramolecular friction (nonlinear coupling between the reaction coordinate and other nonreactive modes near the barrier) has been discussed in the Introduction. Agmon[7] has recently discussed a model in which the rate is controlled by diffusion perpendicular to the reaction coordinate and has shown that such a model can give rise to the fractional power dependence of the rate on solvent viscosity, similar to what is predicted by the non-Markovian theories.

(i) The results listed above are based on several approximations. Some are essential parts of the model: The assumption that intramolecular relaxation is much faster in the well region than intermolecular energy exchange, the decoupling between the reactive coordinate and the nonreactive mode in the barrier region and the assumption that a unimolecular rate is well defined (which is valid if $E_B \gg k_B T$). Other approximations serve to simplify the results. Thus Eq. (4.2) is the large barrier approximation to Eq. (3.58) while Eqs. (3.42) for $\bar{\epsilon}$ and Eq. (4.15) for τ are based on the assumption that temperature is high enough to permit the use of classical statistical thermodynamics in evaluating the molecular distribution. While these approximations served to illustrate the essential points in the theory they are not valid in many practical situations. In the much studied isomerization of trans-stilbene for example, the barrier to isomerization is ~ 1150 cm^{-1} while the largest molecular frequencies are in the 3000 cm^{-1} range. The theory may be applied to such situations by avoiding the simplifying classical approximation and resorting instead to numerical integrations.

It is interesting to estimate some of the parameters of the theory. In Fig. 1 I plot, for t-stilbene, the transition energy E_1, which roughly separates between the well-controlled and the barrier-controlled regimes, as a function of friction γ [related to the solvent viscosity η through $= 6\pi \eta a/m$, where a and m are the radius and mass of the moving particle. In this calculation the vibrational density of states is obtained by direct counting, using the normal modes of stilbene as calculated by Warshel.[73] The reaction coordinate is taken, following Troe,[33(a)] as the 88 cm^{-1} mode. The barrier frequency ω_B is taken the same 88 cm^{-1}. $\bar{a} = \lambda^2/(\omega_B^2 - \lambda^2)$ where λ, the largest root of $\lambda^2 - \omega_B^2 + \lambda \widehat{Z}(\lambda) = 0$, is calculated using the simplified memory Kernel $Z(t) = (\gamma/\tau_c)e^{-t/\tau_c}$ [whence $\widehat{Z}(\lambda) = \gamma(1 + \lambda \tau_c)^{-1}$] with τ_C chosen equal to ω_B^{-1}.[74] The function

$$D(E) = \rho(E) \int_0^\infty dt \sum_a Z_a(t) \, \overline{[\dot{x}_a(t)\dot{t}_a(0)]}_E$$

can be calculated by assuming that $\overline{\dot{x}_a(t)\dot{x}_a(0)} = \overline{x_a^2}$ Re $e^{-\kappa t - i\omega t}$ with some characteristic κ and ω. Putting $\Sigma_a \dot{x}_a^2 = E$ leads to

$$D(E) = \gamma \rho(E)E \frac{\tau_c \kappa + 1}{\omega^2 + (\tau_c \kappa + 1)^2}. \qquad (4.19)$$

In the actual calculation displayed in Fig. 1 I have used $D(E) = 0.1\gamma \rho(E)E$.

As mentioned above, the high temperature expression $\bar{\epsilon} = (n - 1)/\beta$ cannot be used in the present case. Instead $\bar{\epsilon}$ was computed as the energy for which $\rho_{n-1}(E)e^{-\beta E}$ attains its maximum. For $T = 300$ K this yields $\bar{\epsilon} = 1870$ cm^{-1}. In Fig. 1 I also show the E_1 vs γ curves for molecules which are substantially larger and substantially smaller than stilbene but with the same reactive modes. In Fig. 1 the different sizes are expressed by the different room temperature partition functions of the nonreactive subsystems. E_1 is surprisingly quite insensitive to the molecular size [see also discussion following Eq. (3.49)].

Another question concerns the turnover from energy controlled to barrier diffusion controlled rate, namely the location of the maximum in the rate vs friction dependence. Even though the present theory uses the generalized Langevin equations as its starting point, the observation that for large molecules τ becomes extremely short for any appreciable solvent interaction suggests that this turnover may take place in the gas rather than in the liquid phase. The interpretation of τ of Eq. (4.1) as the mean first passage time for the molecule to reach the energy $E_B + \bar{\epsilon}$ makes it possible to increase the applicability of this result by making the plausible assumption that maintains this physical meaning also in
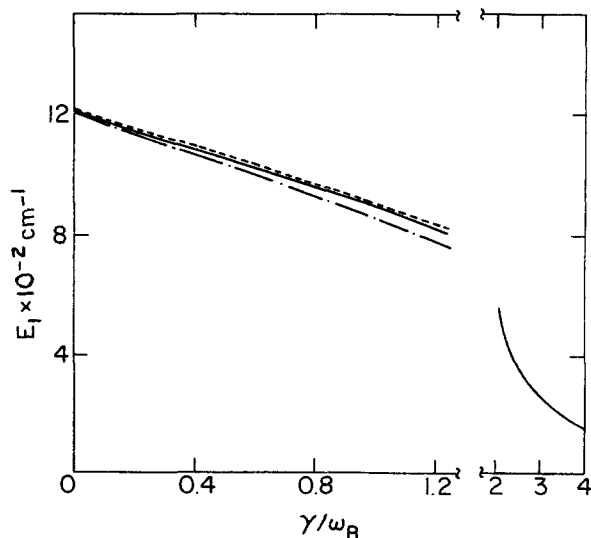

FIG. 1. The transition energy E_1 [solution of Eq. (3.49)] for trans-stilbene (full curve) calculated using parameters described in the text. The dashed line corresponds to a molecule with the same reactive mode parameters and with partition function of the nonreactive subsystem larger by a factor of 5 than that of the t-stilbene. The dotted dashed line corresponds to a similar molecule with partition function of the nonreactive subsystem smaller by a factor of 5 than that of t-stilbene.

situations when the present model and Eq. (4.15) cease to be valid. In the gas phase Eq. (1.6) with $k(E) = 0$ may be a better description of the well dynamics than the generalized Langevin equation (2.1). Using for $K(E,E')$ in Eq. (1.6) the popular exponential model $K(E,E') = (v/(\alpha + \beta))$ $\times \exp[(E - E')/\alpha]$ for $E < E'$ and $K(E,E') = [v/(\alpha + \beta)] \times \exp[(E' - E)/\beta]$ for $E > E'$, where α and β are the mean energy transfer per collision in the upward and downward directions, respectively, and where v is the collision rate leads[75,76] to the following approximate expression for the mean first passage time to reach an energy E:

$$\tau(E) = \frac{k_B T_e \exp(E/k_B T_e)}{v(\alpha - \beta)},\qquad (4.20)$$

where T_e is an effective temperature defined from $\rho(E)$ $\times e^{-E/kT} = \text{const } e^{-E/kT_e}$. A rough estimate of the collision rate corresponding to the turnover of the rate vs friction dependence may be obtained by equating $\tau(E)$ to the TST rate. For stilbene the latter is measured (k_∞ in the gas phase) to be $2 \times 10^9 \text{ s}^{-1}$ at room temperature. Taking (again for stilbene) $E = E_B$ 1150 cm^{-1}, taking for v the gas kinetic value $v \simeq (10^6 P_{\text{Torr}}) \text{ s}^{-1}$ and choosing as reasonable room temperature estimates $\alpha = 500$ cm^{-1} and $\beta = 200$ cm^{-1} [detailed balance requires that $\beta^{-1} - \alpha^{-1} = (k_B T_e)^{-1}$] lead to $P_{\text{turnover}} \simeq 70$ atm. The value measured by Fleming and co-workers[67] in methane is about 90 atm. This calculation serves to indicate that the turnover region for large molecules should be looked for in the high pressure gas phase or in very low viscosity liquids. For smaller molecules this pressure (viscosity) is expected to be higher. A trajectory study by Montgomery et al.[57] for the isomerization rate of n-butane in a Lennard-Jones solvent with parameters corresponding to CCl$_4$ places the turnover regime in the liquid.

To end this discussion it should be remembered that apparent turnover behavior may be the result of pressure dependence of the reaction barrier height (see Sec. I) and therefore observation of turnover behavior cannot be taken by itself to indicate the existence of the mechanism discussed in this paper.

In this paper I have developed the non-Markovian theory of activated rate processes to the large molecule regime. The dependence of unimolecular rates on solvent interaction has been shown to be very sensitive to molecular size. The crossover from the energy controlled well dynamics to the diffusion controlled barrier crossing has been estimated to occur for moderately large molecules in the high pressure gas phase.

Note added in proof: In a recent paper, Straub and Berne [J. Chem. Phys. **85**, 2999 (1986)] have presented as a paradox the difference between the result (4.15) obtained as the low friction limit of the rate associated with a system of n strongly coupled modes and between the low friction rate obtained from a non-Markovian one mode model.[1(a),2(a)] According to these authors, the two models should be physically equivalent because it is always possible to reduce a system of many modes to a one reactive mode with non-Markovian thermal interactions. Still as is evident from Eq. (4.15), the temperature dependence of the preexponential term is strongly dependent on the number of modes. They offer a

resolution to this "paradox" by suggesting that the elimination procedure which leads to the generalized Langevin equation for the single reaction coordinate is valid only when the eliminated modes are overdamped.

I disagree with this suggestion. As was shown by Carmeli and Nitzan,[1(a),2(a)] the single mode rate expression is valid if the reactive mode energy changes slowly relative to the timescale associated with the dynamics of the thermal bath (the bath correlation time). Equation (4.15) is valid for a set of n strongly coupled modes—strongly coupled in the sense that they exchange energy rapidly so that the total energy is the only slow variable. If in such situations, we eliminate $n - 1$ modes, the energy evolution of the remaining one changes on the time scale which characterizes the other modes which now constitute the bath, and the time separability does not hold. On the other hand, such time separability does not require that the eliminated modes will be overdamped—only that the coupling between the reaction coordinate and these modes is weak enough. A simple example of such a situation is the vibrational relaxation of a diatomic molecule inbedded in a solid matrix, due to coupling to the lattice phonons. These phonon modes that were eliminated from the full dynamical description are not overdamped. Still (one mode) energy equation of the form (3.21) (or its quantum analog) provides a valid description of this process.

APPENDIX A: EVALUATION OF THE REACTIVE MODE WELL DISTRIBUTION

Inserting Eqs. (3.26) and (3.20) into Eq. (3.19) leads to

$$P^{(w)}(E) = \frac{e^{-\beta E}}{\hbar \omega_R(E) Q_n} I(E),\qquad (A1)$$

$$I(E) = \int_E^\infty dE_T \rho_{n-1}(E_T - E) e^{-\beta(E_T - E)}$$
$$\times \left(A_1 + A_2 \int_{E_T}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}\right).\qquad (A2)$$

Note that at equilibrium where $A_2 = 0$ and $A_1 = 1$, $I(E)$ becomes

$$\int_0^\infty dE' \rho_{n-1}(E'|E) e^{-\beta E'} = Q_{n-1}(E)$$

(here the dependence of ρ_{n-1} on the reactive mode energy E was written explicitly) so that

$$P_{\text{eq}}^{(w)}(E) = \frac{Q_{n-1}(E)}{\hbar \omega_R(E) Q_n} e^{-\beta E}.\qquad (A3)$$

To simplify $I(E)$ change variable $E_T - E = \epsilon$,

$$I(E) = \int_0^\infty d\epsilon \rho_{n-1}(\epsilon|E) e^{-\beta E}$$
$$\times \left(A_1 + A_2 \int_{E+\epsilon}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}\right)\qquad (A4)$$

and notice that the term $\rho_{n-1}(\epsilon|E) e^{-\beta E}$ is strongly peaked at some $\epsilon (\equiv \bar{\epsilon})$ while the remaining term in the integrand i

constant at equilibrium and monotonously decreasing with increasing ϵ. Therefore,

$$I(E) \simeq Q_{n-1}(E)\left(A_1 + A_2 \int_{E+\bar{\epsilon}}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}\right). \quad (A5)$$

Equations (A1) and (A5) lead after changing variables $(E' \rightarrow E' + \bar{\epsilon}, E_{1T} \rightarrow E_1 + \bar{\epsilon})$ to Eq. (3.40). $\bar{\epsilon}$ is given approximately by

$$\bar{\epsilon} \simeq \frac{\int_0^\infty d\epsilon \, \epsilon \rho_{n-1}(\epsilon) e^{-\beta\epsilon}}{\int_0^\infty d\epsilon \, \rho_{n-1}(\epsilon) e^{-\beta\epsilon}} \simeq (n-1)/\beta, \quad (A6)$$

where the second equality holds for high T.

$$P_M = \begin{cases} \dfrac{A_0 \rho_n(E_T)}{Q_n} e^{-\beta E_T}; & E_T \leqslant E_{0T} \\[4mm] \dfrac{\rho_n(E_T)}{Q_n} e^{-\beta E_T}\left(A_1 + A_2 \displaystyle\int_{E_T}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}\right); & E_1 \geqslant E_T \geqslant E_{0T} \end{cases} \quad (B1)$$

Continuity of the distribution at $E_T = E_{0T}$ leads to

$$A_0 = A_1 + A_2 \int_{E_{0T}}^{E_{1T}} dE' \frac{e^{\beta E'}}{D(E')}. \quad (B2)$$

For $E_T > E_1$ we do not have an exact expression of P_M. I propose the following approximation:

$$P_M(E_T) = \int dx \int dv \int dE_{n-1} P_M(x,v;E_{n-1})$$
$$\times \delta[E(x,v) + E_{n-1} - E_T], \quad (B3)$$

where

$$P_M(x,v;E_{n-1})$$
$$= P(x,v) \frac{\rho_{n-1}[E_{n-1}|E(x,v)]e^{-\beta E_{n-1}}}{Q_{n-1}[E(x,v)]} \quad (B4)$$

and where

$$P(x,v) = P^{(w)}[E(x,v)] \frac{\omega_R[E(x,v)]}{2\pi}; \quad E_T > E_1 > E(x,v) \quad (B5)$$

and

$$P(x,v) = \lim_{x \to -\infty} P^{(B)}(x,v); \quad E_T > E(x,v) > E_1. \quad (B6)$$

Note that in Eq. (B4) I assume that the density of states and the partition function of the nonreactive subsystem depend on the state of the reactive mode only through its energy $E(x,v)$.

In Eq. (B5) $P^{(w)}(E)$ is given by Eq. (3.28). The meaning of the right-hand side of Eq. (B6) is

$$P^{(B)}(x,v) \xrightarrow{x \to -\infty} \frac{Q_{n-1}[E(x,v)]}{Q_n} F\sqrt{\frac{2\pi}{\bar{a}\beta}} e^{-\beta E(x,v)}, \quad (B7)$$

where F is determined by the continuity condition (3.34). This yields

APPENDIX B: EVALUATION OF $\mathcal{N}$ [EQ. (3.50)]

The calculation of the normalization constant $\mathcal{N}$ [Eq. (3.38)] follows closely the similar calculation presented for the one-dimensional case in Appendix B of paper III. In what follows E denotes the reactive mode energy and E_1 is the reactive mode energy at the joining point of the barrier and the well distributions [solution of Eq. (3.37)]. E_T is the total molecular energy and $E_{1T} = E_1 + \bar{\epsilon}$. Finally $E_{n-1} = E_T - E$ is the energy in the nonreactive subsystem. The computation is facilitated by introducing a source point (see paper III) E_{0T} near the bottom of the reactant well. The molecular distribution function in the range $0 < E_T < E_1$ is then

$$P(x,v) = A_2 \frac{Q_{n-1}[E(x,v)]}{Q_n Q_{n-1}^{(B)}} \frac{\omega_B}{\lambda_0} e^{\beta[E_B - E(x,v)]};$$
$$E(x,v) > E_1. \quad (B8)$$

The rationale for these approximations is as follows. First, near the barrier (where the normal modes are nearly uncoupled) the fact that the reactive flux flows along the reactive mode implies that the distribution in the nonreactive subsystem is Boltzmann like. Second, the approximation (B7) for the reactive mode (which is the same as was used in the one-dimensional case, paper III) is sufficient as a crude estimate because in this range of high reactive mode energy (for large n E_1 is close to E_B in all situations where the well is not in equilibrium, see Sec. IV) and the contribution of Eq. (B7) to $\mathcal{N}$ is therefore quite small.

With the approximations (B5), (B6), and (B7) the distribution $P_M(x,v;E_{n-1})$ is a function of x and v only through $E(x,v)$. Using the transformation $\int dx \int dv f[E(x,v)] = \int dE\,[2\pi/\omega_R(E)]f(E)$. Equations (B3)–(B7) and (3.28) lead to

$$P_M(E_T) = \int dE\, P_M(E;E_T), \quad (B9)$$

where the joint probability distribution to have total energy E_T and reactive mode energy E is

$$P_M(E;E_T) = \frac{\rho_{n-1}(E_T - E|E)e^{-\beta E_T}}{\hbar\omega_R(E)Q_n}$$
$$\times \left(A_1 + A_2 \int_E^{E_1} dE' \frac{e^{\beta(E' + \bar{\epsilon})}}{D(E' + \bar{\epsilon})}\right)$$
$$(E_T > E_1 > E) \quad (B10)$$

and

$$P_M(E;E_T) = \frac{2\pi A_2 e^{\beta E_B}}{Q_n Q_{n-1}^{(B)}} \frac{e^{-\beta E_T} \rho_{n-1}(E_T - E|E)}{\omega_R(E)} \frac{\omega_B}{\lambda_0}$$
$$(E_T > E > E_1). \quad (B11)$$

The desired normalization constant is now obtained from

$$\mathcal{N} = \mathcal{N}_1 + \mathcal{N}_2 + \mathcal{N}_3 + \mathcal{N}_4, \tag{B12}$$

$$\mathcal{N}_1 = \int_0^{E_{0T}} dE_T \, P_M(E_T), \tag{B13}$$

$$\mathcal{N}_2 = \int_{E_{0T}}^{E_1} dE_T \, P_M(E_T), \tag{B14}$$

$$\mathcal{N}_3 = \int_{E_1}^{\infty} dE_T \int_{E_0}^{E_1} dE \, P_M(E;E_T), \tag{B15}$$

$$\mathcal{N}_4 = \int_{E_1}^{\infty} dE_T \int_{E_1}^{E_T} dE \, P_M(E;E_T), \tag{B16}$$

where Eq. (B1) is used to evaluate $\mathcal{N}_1$ and $\mathcal{N}_2$, Eq. (B10)—to evaluate $\mathcal{N}_3$ and Eq. (B11) is used to evaluate $\mathcal{N}_4$.

Equations (B1), (B13), and (B14) yield after some algebra,

$$\mathcal{N}_1 + \mathcal{N}_2 = \frac{A_1}{Q_n} \int_0^{E_1} dE_T \, \rho_n(E_T) e^{-\beta E_T} + \frac{A_2}{Q_n \beta} \tau + \frac{A_2}{Q_n}$$
$$\times \int_0^{E_1} dE_T \, \rho_n(E_T) e^{-\beta E_T} \int_{E_1}^{E_{1T}} dE' \, \frac{e^{\beta E'}}{D(E')}, \tag{B17}$$

where

$$\tau = \beta \int_{E_{0T}}^{E_1} dE_T \, \frac{e^{-\beta E_T}}{D(E_T)} \int_0^{E_T} dE' \, \rho_n(E') e^{-\beta E'} \tag{B18}$$

is the mean first passage time for a molecule that starts with total energy E_{0T} to reach the total energy E_1. Note that [using Eqs. (3.35) and (3.36), and the relation $\sqrt{\bar{a}/(\bar{a}+1)} = \lambda_0/\omega_B$]:

$$A_1 = \frac{\pi \hbar \eta}{Q_{n-1}^{(B)}} \frac{\omega_B}{\lambda_0} e^{\beta E_B} A_2 \tag{B19}$$

with

$$\eta = 1 + \text{erf}\left[\sqrt{(\bar{a}+1)(E_B - E_1)}\right]. \tag{B20}$$

Using Eqs. (B10), (B11), (B15), and (B16) together with Eqs. (B19) and (B20) we get

$$\mathcal{N}_3 + \mathcal{N}_4 = \frac{\pi \eta A_2 e^{\beta E_B}}{Q_n Q_{n-1}^{(B)}} \frac{\omega_B}{\lambda_0} \int_{E_1}^{\infty} dE_T \int_0^{E_T} dE \, \frac{e^{-\beta E_T} \rho_{n-1}(E_T - E \,|\, E)}{\omega_R(E)}$$
$$+ \frac{\pi(2 - \eta) A_2 e^{\beta E_B}}{Q_n Q_{n-1}^{(B)}} \frac{\omega_B}{\lambda_0} \int_{E_1}^{\infty} dE_T \int_{E_1}^{E_T} dE \, \frac{e^{-\beta E_T} \rho_{n-1}(E_T - E \,|\, E)}{\omega_R(E)}$$
$$+ \frac{A_2}{\hbar Q_n} \int_{E_1}^{\infty} dE_T \int_0^{E_1} dE \, \frac{e^{-\beta E_T} \rho_{n-1}(E_T - E \,|\, E)}{\omega_R(E)} \int_E^{E_1} dE' \, \frac{e^{\beta(E' + \bar{\epsilon})}}{D(E' + \epsilon)}. \tag{B21}$$

Using Eq. (B19) together with the relation

$$\rho_n(E_T) = \int_0^{E_T} dE \, \frac{\rho_{n-1}(E_T - E \,|\, E)}{\hbar \omega_R(E)}, \tag{B22}$$

the first term of Eq. (B17) and the first term of Eq. (B21) are easily shown to sum up to

$$\frac{\pi \hbar \eta A_2 e^{\beta E_B}}{Q_{n-1}^{(B)}} \frac{\omega_B}{\lambda_0}.$$

For a small molecule the second term in Eq. (B21) may be disregarded: If $E_1 \ll E_B$ then $\eta = 2$ and this term vanishes. If $E_1 \sim E_B$ [so that $\eta \sim 1$ and the coefficients of the integrals in the first and second terms of Eq. (B21) are identical] this term is much smaller than the first term of Eq. (B21). In either case the second term of Eq. (B21) may be neglected relative to the first one. This is no longer true for large molecules where most of the contribution to the integral $\int_0^{E_T} dE \, e^{-\beta E} \rho_{n-1}(E_T - E \,|\, E)/\omega_R(E)$ comes from the region $E_T > E > E_1$. Thus in general we should keep this term.

Using these considerations in combining Eqs. (B17) and (B21) finally leads to the result [Eq. (3.40)].

APPENDIX C: EVALUATION OF τ [EQS. (3.47)–(3.49)]

For deep enough walls τ_1 [Eq. (3.41)] is independent of E_{0T} and the latter may be replaced by zero. An upper limit on τ_1 is

$$\tau_1 \lesssim \beta \int_0^{E_1} dE' \, \frac{e^{\beta E'}}{D(E')} \int_0^{E_1} dE'' \, \rho_n(E'') e^{-\beta E''}. \tag{C1}$$

This is actually a good approximation to τ_1 because $e^{\beta E'}/D(E')$ is strongly peaked near the upper limit E_1.[68]

Using Eqs. (C1) and (3.58b) we get

$$\tau_1 + \tau_2 \lesssim \beta \int_0^{E_{1T}} dE' \, \frac{e^{\beta E'}}{D(E')} \int_0^{E_1} dE' \rho_n(E') e^{-\beta E'}, \tag{C2}$$

where again the equality is a good approximation for deep wells.

Consider now τ_3 [Eq. (3.48)]:

$$\tau_3 = \beta \int_{E_1}^{\infty} dE \, e^{-\beta E} \int_0^{E_1} dE' \, \frac{\rho_{n-1}(E - E' | E')}{\hbar \omega_R(E')}$$
$$\times \int_{E'}^{E_1} dE'' \, \frac{e^{\beta(E'' + \bar{\epsilon})}}{D(E'' + \bar{\epsilon})}. \tag{C3}$$

Integration by parts yields

$$\tau_3 = \beta \int_{E_1}^{\infty} dE \, e^{-\beta E} \int_0^{E_1} dE' \, \frac{e^{\beta(E' + \bar{\epsilon})}}{D(E' + \bar{\epsilon})}$$
$$\times \int_0^{E'} dE'' \, \frac{\rho_{n-1}(E - E'';E'')}{\hbar \omega_R(E'')}. \tag{C4}$$

Replacing E' in the upper limit of the E'' integration by E and using

$$\int_0^E dE'' \, \rho_{n-1}(E - E''|E'')/\hbar\omega_R(E'') = \rho_n(E)$$

leads to an upper bound on τ_3:

$$\tau_3 \lesssim \beta \int_{E_1}^\infty dE \, e^{-\beta E}\rho_n(E) \int_0^{E_1} dE' \, \frac{e^{\beta(E'+\bar{\epsilon})}}{D(E'+\bar{\epsilon})}$$

$$= \beta \int_{E_1}^\infty dE \, e^{-\beta E}\rho_n(E) \int_{\bar{\epsilon}}^{E_1 T} dE' \, \frac{e^{\beta E'}}{D(E')}$$

$$\lesssim \beta \int_0^{E_1 T} dE' \, \frac{e^{\beta E'}}{D(E')} \int_{E_1}^\infty dE \, e^{-\beta E}\rho_n(E). \qquad (C5)$$

For large βE_1 the equality in Eq. (C5) is a good approximation to τ_3. Equations (C2) and (C5) now yield

$$\tau \lesssim \beta Q_n \int_0^{E_1 T} dE' \, \frac{e^{\beta E'}}{D(E')}$$

which is Eq. (3.59)

ACKNOWLEDGMENTS

[1]The previous papers in this series are by B. Carmeli and A. Nitzan: (a) J. Chem. Phys. **79**, 393 (1983); (b) Isr. J. Chem. **22**, 360 (1982); (c) Phys. Rev. A **29**, 1481 (1984); (d) J. Chem. Phys. **80**, 3596 (1984); (e) Phys. Rev. A **32**, 2439 (1985). These will be referred to as papers I–V.

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[59]The factor $Q_{n-1}/2\pi\hbar Q_n$ which does not appear in the one-dimensional treatment [Refs. 1(d), 27, and 28] is needed for proper normalization in

the multi-dimensional case. To see this note that at equilibrium (3.6) becomes

$$^{\prime}\;P(x,v) = \frac{Q_{n-1}(x)}{2\pi\hbar Q_n}\,e^{-\beta E(x,v)}$$

and that

$$\int \frac{dx\,dv}{2\pi\hbar}\,Q_{n-1}\,e^{-\beta E(x,v)} = Q_n.$$

[60] Note that $\rho_{n-1}(E_T - E)$ should actually be written $\rho_{n-1}(E_T - E;E)$. The explicit E dependence comes from dependence of the frequencies of the nonreactive modes on the reactive mode energy E.

[61] This follows from the assumption that the intramolecular vibrational energy redistribution is fast on the relevant time scale.

[62] The opposite statement was erroneously made in Ref. 39.

[63] In Eq. (43) of ref. 1d the factor $e^{\Delta K/kT}$ should be emitted.

[64] It should be kept in mind that increasing the solvent viscosity does not necessarily imply stronger damping, because it may be accompanied with slower solvent motion (longer solvent relaxation time) and smaller effective friction due to the larger non-Markovian nature of the solvent molecule interaction.

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