A theory for nonisothermal unimolecular reaction rates

Eli Pollak, Peter Talkner and A. M. Berezhkovskii

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN
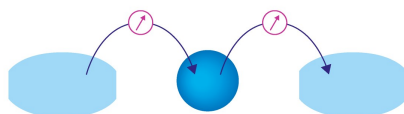
A theory for nonisothermal unimolecular reaction rates

Eli Pollak and Peter Talkner[a)]
Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovot, Israel

A. M. Berezhkovskii[b)]
Department of Physical Chemistry, Hebrew University, Jerusalem, Israel

A simple expression is derived for the survival probability of a reactive chemical species which is initially prepared at a temperature which differs from its surrounding. The competition between relaxation of reactants back to the external equilibrium and the possibility of reaction may prevent the usual single exponential kinetics for the survival probability. The theory is accurate for activated reactions with moderate ($V^{\ddagger}/k_B T \geq 3$) to high reduced barrier heights. It is especially relevant for multidimensional systems where the characteristic energy at which a molecule dissociates is greater than the barrier height. © *1997 American Institute of Physics.* [S0021-9606(97)00633-8]

I. INTRODUCTION

One of the most powerful approximations in the theory of chemical reaction rates is based on equilibrium statistical mechanics. In transition state theory, one assumes that the distribution of reactants is thermal with temperature T. The thermal rate of reaction $k(T)$ is then estimated by considering the equilibrium flux through a dividing surface leading from reactants to products. In unimolecular rate theory,[1–3] one estimates an energy dependent rate $k(E)$ by assuming that the reactants are microcanonically distributed. One then uses the classical RRK or quantum mechanical RRKM expressions to estimate the energy dependent rate. The thermal decay rate is just the Boltzmann averaged microcanonical rate, weighted by the density of states.

The thermal rate of reaction implies an exponential relaxation of the survival probability $S(t)$:

$$\frac{dS(t)}{dt} = -k(T)S(t). \tag{1.1}$$

If the interaction of the system with the bath is not especially weak, thermal equilibrium of reactants at temperature T will be maintained throughout the duration of the process and the (variational) transition state theory estimate for the thermal rate will be valid.

The topic of this paper is a richer situation, in which reactants are prepared initially in a canonical distribution at temperature T_0 but they are in contact with an environment whose temperature T is different from T_0. Such a situation may be realized in experimental situations. Consider the laser excitation of a molecule—say trans-Stilbene—in the presence of a medium, liquid or gas, whose temperature is T. The molecule is excited say, from the ground S_0 to the excited S_1 state. As noted by Gershinsky and Pollak,[4] depending on the laser frequency, the temperature of the excited state molecule T_0 after excitation may differ significantly from the temperature T of the ground state and the environ-

ment. In this nonequilibrium case, two processes occur simultaneously. One is the reequilibration of reactants changing their temperature from T_0 to the environmental temperature T. At the same time, reaction may occur, leading to the disappearance of the reactants. If the exchange of energy between the molecule and the environment is fast compared to the reaction time, then equilibration will occur prior to reaction and the rate will be given by $k(T)$. If, however, the reequilibration rate of reactants is slow in comparison with the reaction rate, the rate of reaction will be given by $k(T_0)$. This rate may differ substantially from $k(T)$ because of the Boltzmann factor $e^{-V^{\ddagger}/k_B T}$ characteristic of activated rate processes whose activation energy is $V^{\ddagger}$. The challenge is thus to understand how the survival probability depends on the equilibration rate, the initial difference of temperatures, and the reaction rate.

We will show that typically, the temperature of reactants changes in time according to the law:

$$T(t) = T + (T_0 - T)e^{-\langle \gamma \rangle t}, \tag{1.2}$$

where $\langle \gamma \rangle$ is an averaged friction coefficient which characterizes the intermolecular energy transfer rate between reactants and the medium. The time dependence of the survival probability is then found to be governed by the deceptively simple expression:

$$S(t) = e^{-\int_0^t dt' \, k[(T(t'))]}. \tag{1.3}$$

The rest of this paper will deal with the derivation of Eqs. (1.2) and (1.3). Langevin dynamics are assumed for the reacting multidimensional system with N degrees of freedom. If the friction coefficients are large when compared to the escape rate, then reactants will rapidly decay to the bath temperature T and nothing of great interest will occur. It is thus reasonable to consider the dynamics mainly in the weak to moderate friction limit for which the Langevin equations of motion may be reduced to an energy diffusion equation.[5,6] The possibility of reaction modifies the standard energy diffusion equation and one must add a sink term.[7–9] The diffusion equation in the presence of a sink has been studied previously by Agmon and Hopfield,[10] and Weiss[11] in a dif-

ferent context. The thermal rate constant for multidimensional systems in the energy diffusion limited regime has been considered by a number of authors.[7–9,12,13]

In Sec. II we provide a general formalism for exact solution of the diffusion equation in the presence of a sink term. This solution is guided by the perturbation theory approach described in Ref. 14. The theory is then applied in Sec. III, to the specific case of a harmonic molecule with N degrees of freedom, whose energy dependent escape rate is given by the classical RRK formula. The results of Sec. III may be considered as the nonisothermal generalization of classical unimolecular rate theory. Extension to the quantum case is easily achieved by employing quantum densities of states and the quantum mechanical RRKM rate expression for the energy dependent unimolecular decay rate.

The general formalism presented in Sec. II is solved perturbatively in Sec. IV. The important conclusion of this section is that the small parameter of the expansion is found to be $\kappa = e^{-(V^\ddagger)/(k_B T)}$ and that Eq. (1.3) is accurate to order κ^2. This of course implies that for most cases of physical interest, Eq. (1.3) is highly accurate. In Sec. V we apply the theory to a simplistic model of the unimolecular isomerization of trans-Stilbene in the S_1 state. The paper ends with a discussion of the limitations of the theory, its importance especially when dealing with multidimensional systems, possible extensions, and further applications.

II. FORMAL SOLUTION OF THE ENERGY DIFFUSION EQUATION WITH A SINK TERM

A. Preliminaries

The reacting molecule, with N degrees of freedom, is described by a Hamiltonian H with (mass weighted) coordinates x_i and associated momenta p_i. The coupling of the molecule to its surrounding is described in terms of N coupled Langevin equations of motion:

$$\ddot{x}_i(t) = -\frac{\partial V(\underline{x})}{\partial x_i} - \sum_{j=1}^{N} \gamma_{ij}\dot{x}_j + R_i(t). \tag{2.1}$$

Here $V(\underline{x})$ is the potential surface of reactants, γ_{ij} are the friction coefficients, and $R_i(t)$ are Gaussian random forces whose correlation functions are given by:

$$\langle R_i(t)R_j(t')\rangle = 2k_B T\gamma_{ij}\delta(t-t'), \tag{2.2}$$

where $\delta(x)$ is the Dirac δ function. Note that the temperature appearing in Eq. (2.2) is the bath temperature T; it is independent of the dynamics of the system.

The dynamics of the isolated molecule is such that it decays at any energy E with the rate $k(E)$. In the "weak friction limit," where the coupling of the system to the bath is weak, one may replace the Langevin equations of motion with an energy diffusion equation. The probability $P(E,t)$ that the molecule has an energy E at time t is then governed by the energy diffusion equation:

$$\frac{\partial P(E,t)}{\partial t} = \frac{\partial}{\partial E}\left[D(E)\left(k_B T\frac{\partial}{\partial E}+1\right)\frac{1}{\rho(E)}P(E,t)\right]$$
$$-k(E)P(E,t)\equiv[\mathbf{L}(T)-k(E)]P(E,t). \tag{2.3}$$

The sink term $k(E)P(E,t)$ accounts for the fact that at any moment in time the molecule may disappear with the rate $k(E)$. The identity on the right hand side defines the Fokker–Planck operator $\mathbf{L}(T)$ in the absence of the sink. The energy diffusion coefficient $D(E)$ is found to be:[7,9]

$$D(E) = \sum_{i=1}^{N}\gamma_{ii}\int_0^E dE'\,\rho(E'), \tag{2.4}$$

where $\rho(E)$ is the microcanonical density of states of the reactant molecule.

The survival probability of the molecule $S(t)$ is defined as:

$$S(t) = \int_0^\infty dE P(E,t). \tag{2.5}$$

The boundary condition is that initially the survival probability is unity, or in other words the probability distribution $P(E,0)$ is normalized:

$$S(0) = 1 = \int_0^\infty dE P(E,0). \tag{2.6}$$

Integrating the energy diffusion equation over all energies, noting that $D(0)=0$, that $P(E,t)\to 0$ as $E\to\infty$, and using the definition of the survival probability, it is straightforward to write down a deceptively simple exact equation for the time derivative of the survival probability:

$$\frac{dS(t)}{dt} = -k(t)S(t). \tag{2.7}$$

All of the dynamics is hidden in the time-dependent rate constant $k(t)$ defined as

$$k(t) = \frac{\int_0^\infty dE k(E)P(E,t)}{\int_0^\infty dE P(E,t)}. \tag{2.8}$$

To obtain the survival probability one must first solve for the probability distribution $P(E,t)$.

B. Formal solution for the survival probability

Before solving the Fokker–Planck equation in the presence of the sink, one should consider the easier problem—solution of the equation without the sink. The formal solution of the equation is well-known, one can find, using standard methods,[15] all the eigenvalues, and eigenfunctions of the Fokker–Planck operator $\mathbf{L}(T)$. The lowest eigenvalue is 0, the associated normalized eigenfunction is the equilibrium distribution of the reactants in the absence of reaction at the bath temperature T, denoted $P_{eq}(E)$:

$$\int_0^\infty dE P_{eq}(E) = 1. \tag{2.9}$$

We are interested in a specific solution of the unperturbed equation, namely the time-dependent distribution $P_{eq}(E,t)$ whose boundary condition is that at time $t=0$ it is the equilibrium solution at temperature T_0 different from T. As $t \to \infty$, $P_{eq}(E,t) \to P_{eq}(E)$ and it becomes the equilibrium distribution at the temperature T. $P_{eq}(E,t)$ is thus a specific solution of the time-dependent equation

$$\frac{\partial P_{eq}(E,t)}{\partial t} = \mathbf{L}(T) P_{eq}(E,t). \qquad (2.10)$$

One can now loosely treat the sink term as a perturbation and suggest that a zeroth order approximation for the time-dependent rate constant defined in Eq. (2.8) is

$$k_{eq}(t) = \int_0^\infty dE k(E) P_{eq}(E,t), \qquad (2.11)$$

where we have also used the fact that $\int_0^\infty dE P_{eq}(E,t) = 1$ for all times. The associated approximate survival probability is then

$$S_{eq}(t) = e^{-\int_0^t dt\, k_{eq}(t')}. \qquad (2.12)$$

This result will turn out to be the central approximation of this paper, but further work needs to be done to justify it.

Given the approximate survival probability $S_{eq}(t)$, one writes down the exact probability distribution $P(E,t)$ as a sum of two terms:

$$P(E,t) \equiv P_{eq}(E,t) S_{eq}(t) + \Delta P(E,t). \qquad (2.13)$$

By definition, the boundary conditions on $\Delta P(E,t)$ are such that

$$\Delta P(E,0) = \Delta P(E,\infty) = 0 \qquad (2.14)$$

for all energies E. Using this definition and the Fokker–Planck Eq. (2.3), one obtains an inhomogeneous Fokker–Planck equation for the function $\Delta P(E,t)$:

$$\frac{\partial \Delta P(E,t)}{\partial t} = [\mathbf{L}(T) - k(E)] \Delta P(E,t)$$
$$+ [k_{eq}(t) - k(E)] P_{eq}(E,t) S_{eq}(t). \qquad (2.15)$$

A solution of the equation may be obtained by finding all the eigenvalues (k_m) and associated eigenfunctions $[\psi_m(E)]$ of the Fokker–Planck operator with the sink term:

$$[\mathbf{L}(T) - k(E)] \psi_m(E) = k_m \psi_m(E). \qquad (2.16)$$

The normalization of these eigenfunctions may be shown to be:[15]

$$\int_0^\infty dE \psi_m(E) \psi_n(E) / P_{eq}(E) = \delta_{nm}. \qquad (2.17)$$

At this point one expands the function $\Delta P(E,t)$ in terms of the eigenfunctions:

$$\Delta P(E,t) = \sum_m a_m(t) \psi_m(E), \qquad (2.18)$$

where the initial condition [cf. Eq. (2.14)] implies that for any m:

$$a_m(0) = 0. \qquad (2.19)$$

Inserting this expansion into the inhomogeneous Fokker–Planck Eq. (2.15), multiplying by $\psi_m(E)/P_{eq}(E)$, and integrating over energy, one finds a simple first order differential equation for the mth time-dependent coefficient:

$$\frac{da_m(t)}{dt} - k_m a_m(t) = S_{eq}(t) \int_0^\infty dE \psi_m(E) [k_{eq}(t) - k(E)]$$
$$\times P_{eq}(E,t)/P_{eq}(E) \equiv h_m(t). \qquad (2.20)$$

This equation is readily solved:

$$a_m(t) = \int_0^t dt'\, e^{k_m(t-t')} h_m(t'). \qquad (2.21)$$

Since the eigenvalues k_m are negative and the approximate survival probability $S_{eq}(t)$ decays exponentially at long times, one finds that $a_m(t) \to 0$ as $t \to \infty$. We have thus presented a formally exact solution for the time-dependent probability distribution $P(E,t)$, and thus for the survival probability in terms of the eigenfunctions and eigenvalues of the two Fokker–Planck operators $\mathbf{L}(T)$ and $\mathbf{L}(T) - k(E)$.

This methodology will be applied in the next section to the specific case in which the reacting molecule may be described by a collection of N harmonic normal modes—corresponding to the standard RRK and RRKM treatments.

III. NONISOTHERMAL RRK AND RRKM THEORY

The well-known statistical energy dependent rate expression used in RRKM theory is:

$$k(E) = \frac{N^\ddagger(E)}{2\pi\hbar\rho(E)}, \qquad (3.1)$$

where $\rho(E)$ is the microcanonical density of states of reactants:

$$\rho(E) = \mathrm{Tr}\ \delta(E - H). \qquad (3.2)$$

In RRKM theory, the *Trace* operation is over the Hilbert space of the reactants, in classical mechanics it is an integration over the N dimensional phase space of the reactants, weighted by $(2\pi\hbar)^{-N}$.

To obtain the integrated density of states $N^\ddagger$ at the barrier, one must first identify the unstable mode at the barrier to isomerization. Defining the Hamiltonian $H^\ddagger$ as the full Hamiltonian at the barrier, but excluding the unstable mode, and the associated density of states $\rho^\ddagger(E) = \mathrm{Tr}\ \delta(E - H^\ddagger)$, one obtains the integrated density of states at the barrier as:

$$N^\ddagger(E) = \int_0^E dE \rho^\ddagger(E). \qquad (3.3)$$

The thermal rate constant is given by the expression

$$k(T) = \frac{\int_0^\infty dE k(E) \rho(E) e^{-E/k_B T}}{\int_0^\infty dE \rho(E) e^{-E/k_B T}}. \qquad (3.4)$$

In the simplest possible form of the theory, the two Hamiltonians $H, H^\ddagger$ are taken to be a sum of N and $N-1$,

independent harmonic oscillators with frequencies ω_j and $\omega_j^{\ddagger}$, respectively. Classically this implies that:

$$\rho_{\text{RRK}}(E) = \left[\prod_{j=1}^{N} \frac{1}{\hbar\omega_j}\right] \frac{E^{N-1}}{(N-1)!}. \tag{3.5}$$

The integrated density of states at the barrier is:

$$N_{\text{RRK}}^{\ddagger}(E) = \left[\prod_{j=1}^{N-1} \frac{1}{\hbar\omega_j^{\ddagger}}\right] \frac{(E-V^{\ddagger})^{N-1}}{(N-1)!} \theta(E-V^{\ddagger}), \tag{3.6}$$

where $\theta(x)$ is the unit step function. Combining Eqs. (3.5) and (3.6) leads to the well-known RRK expression for the energy dependent rate:

$$k_{\text{RRK}}(E) = \frac{1}{2\pi} \frac{\prod_{j=1}^{N} \omega_j}{\prod_{j=1}^{N-1} \omega_j^{\ddagger}} \left(\frac{E-V^{\ddagger}}{E}\right)^{N-1} \theta(E-V^{\ddagger}). \tag{3.7}$$

Using Eq. (3.4) one finds that the thermal rate is:

$$k_{\text{RRK}}(T) = \frac{1}{2\pi} \frac{\prod_{j=1}^{N} \omega_j}{\prod_{j=1}^{N-1} \omega_j^{\ddagger}} e^{-V^{\ddagger}/k_B T} \equiv k_{\text{RRK}} e^{-V^{\ddagger}/k_B T}. \tag{3.8}$$

Denoting the averaged friction coefficient [cf. Eq. (2.4)] as:

$$\langle\gamma\rangle = \frac{1}{N} \sum_{i=1}^{N} \gamma_{ii}, \tag{3.9}$$

one finds that the energy dependent diffusion coefficient is given within the RRK framework as:

$$D_{\text{RRK}}(E) = \langle\gamma\rangle \left[\prod_{j=1}^{N} \frac{1}{\hbar\omega_j}\right] \frac{E^N}{(N-1)!}. \tag{3.10}$$

Inserting these expressions into the definition of the Fokker–Planck operator [c.f. Eq. (2.3)], gives us the RRK Fokker–Planck operator as:

$$\mathbf{L}_{\text{RRK}}(T) = \langle\gamma\rangle \frac{\partial}{\partial E} E^N \left(k_B T \frac{\partial}{\partial E} + 1\right) E^{-(N-1)}. \tag{3.11}$$

The equilibrium distribution is readily found to be:

$$P_{\text{eq}}(E) = \left(\frac{1}{k_B T}\right)^N \frac{E^{N-1}}{(N-1)!} e^{-E/k_B T}. \tag{3.12}$$

The first step in finding the survival probability is finding the solution $P_{\text{eq}}(E,t)$ for the time-dependent Fokker–Planck equation, in the absence of the sink term. This solution is well-known.[16] One inserts the ansatz that the time dependence occurs only through the temperature $T(t)$ of the equilibrium distribution

$$P_{\text{eq}}(E,t) = \left(\frac{1}{k_B T(t)}\right)^N \frac{E^{N-1}}{(N-1)!} e^{-E/k_B T(t)} \tag{3.13}$$

into the Fokker–Planck Eq. (2.10), to find the amazingly simple equation:

$$\frac{dT(t)}{dt} = -\langle\gamma\rangle[T(t)-T]. \tag{3.14}$$

This equation is readily integrated and one finds the result given in Eq. (1.2).

It is now a matter of simple algebra to find that the time-dependent equilibrium rate [c.f. Eq. (2.11)] is:

$$k_{\text{eq}}(t) = k_{\text{RRK}} e^{-V^{\ddagger}/k_B T(t)}, \tag{3.15}$$

where the preexponential term k_{RRK} has been introduced in Eq. (3.8). Our final expression for the survival probability is thus:

$$S_{\text{eq}}(t) = \exp\left[-k_{\text{RRK}} \int_0^t dt\, e^{-V^{\ddagger}/[k_B(T+(T_0-T)e^{-\langle\gamma\rangle t})]}\right]. \tag{3.16}$$

We shall see in the next section that this result is accurate as long as $V^{\ddagger}/k_B T > 1$.

The time-dependent survival probability was derived explicitly for the classical RRK model, based on independent harmonic oscillators. It is well-known[1–3] that the quantum density of states, as well as RRKM energy dependent rate expression, may be well represented using the classical RRK energy dependence, except that one must replace the true dimensionality of the system N with an effective exponent N_{eff}, which is usually much smaller than N. Moreover, in the harmonic limit, the quantum mechanical energy diffusion process is described rather well in terms of the Fokker–Planck operator. All this implies that a reasonable quantum approximation for the survival probability would be to use the classical time-dependent temperature as given in Eq. (1.2), inserted into the quantum mechanical thermal rate expression.

IV. PERTURBATION THEORY

In this section we shall show that the approximate expression for the survival probability given by Eqs. (1.2) and (1.3) is quite accurate for a large range of conditions. This will be done by obtaining a perturbation theory expansion for the survival probability. The derivation is technical, so that the cursory reader is encouraged to skip it and consider the practical applications as described in the next section.

Initially, we will consider the sink term to be the "small" term. The exact meaning of "small" will become evident later on. We thus write

$$k(E) = \kappa \tilde{k}(E), \tag{4.1}$$

where the dimensionless constant κ will be the expansion parameter. Our basic assumption is that the eigenvalues and eigenfunctions of the Fokker–Planck operator $\mathbf{L}(T)$ [c.f. Eq. (2.3)], denoted as k_m^0 and $\psi_m^0(E)$ respectively, are known. Standard perturbation theory then leads to the following results for the eigenvalues (k_m) of the operator $\mathbf{L}(T) - k(E)$:

$$k_m = k_m^0 - \kappa \int_0^\infty dE\, \hat{k}(E)\psi_m^0(E)^2/P_{\text{eq}}(E) + o(\kappa^2)$$

$$\equiv k_m^0 + k_m^1 + o(\kappa^2). \tag{4.2}$$

The expansion up to first order for the eigenfunctions ($\psi_m(E)$, $m \neq 0$) is:

$$\psi_m(E) = \psi_m^0(E)$$

$$+ \kappa \sum_{n \neq m} \frac{[\int_0^\infty d\,E \psi_n^0(E) \widetilde{k}(E) \psi_m^0(E)/P_{eq}(E)]}{k_n^0 - k_m^0}$$

$$\times \psi_n^0(E) + o(\kappa^2)$$

$$\equiv \psi_m^0(E) + \psi_m^1(E) + o(\kappa^2). \qquad (4.3)$$

One already notes that the first order correction to the eigenfunction (ψ_m^1) is exponentially small. Any eigenfunction of the operator $\mathbf{L}(T)$ usually has the form of a polynomial in E multiplied by the Boltzmann factor e^{-E/k_BT}. The rate $k(E)$ is typically negligible for energies below the barrier height $V^\ddagger$. Therefore the integral appearing in Eq. (4.3) will give a term which is of the order of $e^{-V^\ddagger/k_BT}$.

We are interested in deriving the leading order correction to the ''zeroth order'' survival probability $S_{eq}(t)$. For this purpose, it is necessary to use the expansion of the function $\Delta P(E,t)$ in powers of the perturbation parameter κ. We will use the notation:

$$\Delta S(t) = \int_0^\infty dE \Delta P(E,t)$$

$$= \sum_m a_m(t) \int_0^\infty dE [\psi_m^0(E) + \psi_m^1(E) + o(\kappa^2)]. \qquad (4.4)$$

For any $m \neq 0$, the orthonormality of the eigenfunctions of the operator $\mathbf{L}(T)$ [c.f. Eq. (2.17)] implies that

$$\int_0^\infty dE \psi_m^0(E) = 0; \quad m \neq 0. \qquad (4.5)$$

Similarly:

$$\int_0^\infty dE \psi_m^1(E) = -\frac{1}{k_m^0} \int_0^\infty dE \psi_m^0(E) k(E); \quad m \neq 0. \qquad (4.6)$$

We may therefore write:

$$\Delta S(t) = a_0(t) - \sum_{m \neq 0} a_m(t) \left[\frac{1}{k_m^0} \int_0^\infty dE \psi_m^0(E) k(E) + o(\kappa^2) \right]. \qquad (4.7)$$

The next step is to write down the expansion of the time-dependent coefficients $a_m(t)$. From Eq. (2.21) one notes that this involves both the expansion of the eigenvalue k_m as well as the function $h_m(t)$ defined in Eq. (2.20). Starting with the latter, we note that the leading order term in the expansion of $h_0(t)$ is:

$$h_0(t) = S_{eq}(t) \sum_{n \neq 0} \frac{1}{k_n^0} \int_0^\infty dE \psi_n^0(E) k(E)$$

$$\times \int_0^\infty dE \psi_n^0(E) \frac{P_{eq}(E,t)}{P_{eq}(E)} [k_{eq}(t) - k(E)]. \qquad (4.8)$$

The time-dependent coefficient $a_0(t)$ is proportional to h_0, so that the contribution of $a_0(t)$ to the survival probability is of the order of κ^2, or equivalently of the order of $e^{-2V^\ddagger/k_BT}$, which is very small.

Similarly one finds that for $m \neq 0$,

$$h_m(t) = S_{eq}(t) \int_0^\infty dE \psi_m^0(E) \frac{P_{eq}(E,t)}{P_{eq}(E)} [k_{eq}(t) - k(E)]. \qquad (4.9)$$

This means that for any $m \neq 0$ the leading term in the expansion of the coefficient $a_m(t)$ is of the order of $e^{-2V^\ddagger/k_BT}$. In other words, the leading order term for $\Delta S(t)$ is of the order of $e^{-2V^\ddagger/k_BT}$, which is exponentially small.

Finally, we note that as $t \to \infty$, all the coefficients decay as $S_{eq}(t)$. This implies that for all times $\Delta S(t)$ is exponentially small when compared to $S_{eq}(t)$ and may thus be ignored. In other words, as long as $V^\ddagger/k_BT \geqslant 3$ one may safely ignore the correction terms.

V. A MODEL APPLICATION

The theory developed in this paper was motivated by the observation that the isomerization reaction of trans-Stilbene from the S_1 state may be accompanied by an initial cooling of trans-Stilbene prior to isomerization. Specifically, Balk and Fleming[17] found that the lifetime of gas phase Stilbene when pumped at the fundamental S_0 to S_1 transition frequency was approximately 700 psec at $T = 300$ K. In the experiment, the S_0 Stilbene was prepared from a thermal distribution at $T = 300$ K. This measurement was somewhat of a surprise, since the lifetime in liquid ethane at the same temperature was measured to be approximately 30 psec.[18] Gershinsky and Pollak[4] suggested that this discrepancy was due to laser cooling of the Stilbene molecule upon excitation to a temperature of 200 K. In the liquid, they argued that the liquid surrounding causes a fast reequilibration and heating of the cold S_1 molecule back to the liquid temperature of 300 K. This is then followed by isomerization. In the gas phase, there is no liquid and so one measures the much slower $T = 200$ K rate.

A first challenge is to verify that indeed in the liquid it is plausible to assume that the heating of the trans-Stilbene molecule is sufficiently fast so that one effectively measures the $T = 300$ K rate. Perhaps more interesting is to provide a picture of the simultaneous thermal equilibration and decay of the molecule in the hope that the combination of the two processes could be detected experimentally. It is also of interest to present characteristic plots of the survival probability for reactants which are initially hot or cold relative to their surrounding.

To model the Stilbene reaction we chose the following dimensionless representation for the thermal rate:

$$\frac{k(T)}{\langle \gamma \rangle} = k_\infty e^{-V^\ddagger/k_BT}. \qquad (5.1)$$

It is also useful to scale the time in terms of the damping constant ($t \to \langle \gamma \rangle t$). The Stilbene isomerization at $T = 300$ K is reasonably well modeled by choosing $V^\ddagger/k_BT = 6$ and k_∞
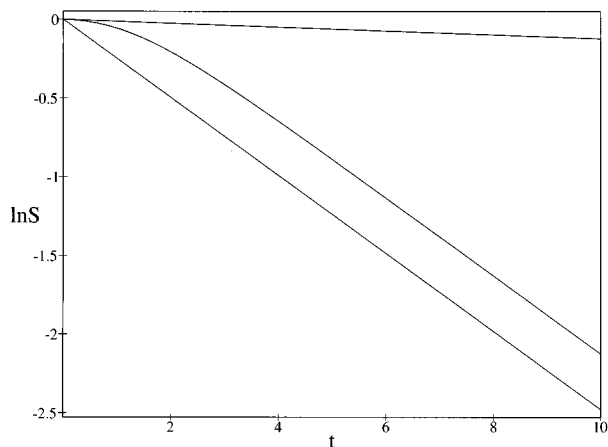
FIG. 1. Nonisothermal decay plot for initially cold reactants. The logarithm of the survival probability, as given in Eq. (3.16), is plotted versus reduced time. The initial and final temperatures are 200 and 300 K, respectively, the reduced barrier height is taken to be $V^{\ddagger}/k_B T = 6$, and the reduced prefactor $k_{\infty} = 100$. For additional details, see text.

$= 100$. This corresponds to a dimensionless rate of ~ 0.25, or if we assume a damping constant $\hbar \langle \gamma \rangle = 1$ cm^{-1}, this gives a lifetime $[1/k(T)]$ of 20 psec.

In Fig. 1, we plot the survival probability as a function of reduced time on a logarithmic scale. The upper line corresponds to the case $T = T_0 = 200$ K, the bottom line corresponds to the case $T = T_0 = 300$ K, and the middle line shows the result for the case $T_0 = 200$ and $T = 300$ K. The high temperature limit is obtained for $t \geqslant 3$. By this time approximately half of the population has disappeared. In other words, a careful measurement of the survival probability should show a nonexponential decay, starting with a slow decay characteristic of the lower temperature and ending with a fast decay characteristic of the higher temperature.

In Fig. 2, we show results for the opposite case; the initial temperature is $T_0 = 400$ K and the final temperature is as before, $T = 300$ K. Here, the initial decay is fast while the
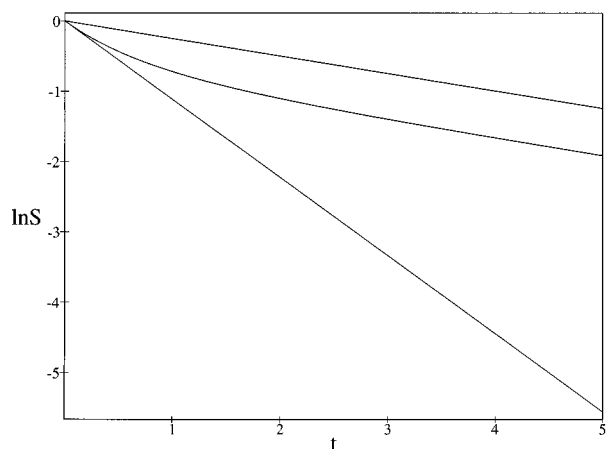

FIG. 2. Nonisothermal decay plot for initially hot reactants. The logarithm of the survival probability, as given in Eq. (3.16), is plotted versus reduced time. The initial temperature is 400 K. All other details are as given in Fig. 1.

final decay is slow. Presumably, by increasing the wavelength of the excitation laser, one could go from the low temperature to the high temperature case, observing a qualitative change in the shape of the survival probability, from the convex form of Fig. 1 to the concave form of Fig. 2.

The critical remaining question is the magnitude of the characteristic friction coefficient. Some preliminary computations[19] indicate that in liquid ethane at room temperature a characteristic value of $\langle \gamma \rangle$ is ~ 50 cm^{-1}. In our dimensionless units, this would reduce the prefactor k_{∞} from 100 to 2. The transition from the initial low temperature to the final liquid room temperature will still occur at $t \sim 3$, but the survival probability at this time would be almost unity; that is, any measurement of the decay would reveal a single exponential decay corresponding to the rate at the temperature of the liquid. As claimed in Ref. 4, in the liquid, the friction is strong enough to cause a rapid equilibration prior to decay.

Balk and Fleming also studied the isomerization reaction in the gas phase in the presence of methane gas. An increase in the pressure of the gas led to an increase of the rate. Gershinsky and Pollak explained this increase as due to the initial low temperature of the Stilbene molecule. Collisions heat the molecule, leading to an increased rate. At a pressure of 1 atm one finds[19] that the characteristic damping constant is 1 cm^{-1}, indicating that there are reasonable chances for observing nonexponential decay. Of course, the continuum theory presented in this paper is not rigorously applicable to the gas phase, where a binary collision theory should provide a better description.[20]

VI. DISCUSSION

A simple expression has been derived for the survival probability of reactants prepared at a temperature that differs from their surrounding. Two important conditions must hold for the theory to be valid. We have assumed throughout that the energy diffusion equation is an adequate representation of the energy relaxation of reactants. This implies a continuum medium—not a gas, and that the friction is weak. More precisely, the energy diffusion equation is valid provided that over a characteristic period of motion, the relative change of energy of the system is small. If ω is the characteristic frequency of the molecule, then the energy diffusion equation is valid if $\langle \gamma \rangle \leqslant \omega/2\pi$. This condition can be obtained in an inert liquid such as ethane or hexane, but would most certainly be violated in dipolar liquids. From a practical point of view, a large damping constant leads naturally to a fast relaxation towards the solvent equilibrium temperature. The result based on the weak friction assumption bridges naturally into the high friction limit.

The second condition is that the reduced barrier height $(V^{\ddagger}/k_B T)$ is not too small. If the barrier height is small, one must go to higher order in the perturbation theory. This is not too difficult. One finds easily enough that within the RRK formalism, the eigenfunctions of the adjoint Fokker–Planck operator ($\mathbf{L}^{\dagger}(T)$) are the Laguerre polynomials. A numerical solution for the survival probability is thus readily available.

This is not a purely academic exercise. For example, the decay of cis-Stilbene seems to occur with a low barrier, with a lifetime of ~ 1 psec.

There is a third limitation on the results presented in this paper. We have tacitly assumed that at any given instant, reactants are thermally distributed. We have not allowed for the extremely underdamped limit, where one would find a serious depletion of population in the vicinity of the barrier. In practice, this is not a severe restriction when dealing with polyatomic molecules. Even for small friction, the effective energy loss will go as

$$\frac{\langle \gamma \rangle}{\omega} \frac{1}{(N-1)!} \left(\frac{V^{\ddagger}}{k_B T} \right)^N ,$$

where N is the number of (effective) degrees of freedom of the reacting molecule. The extremely underdamped limit is thus usually not attained.

A different question is when should one expect to see a significant deviation from single exponential kinetics. As mentioned in the Introduction, if the relaxation rate is faster than the reaction rate, one will relax to the external temperature rapidly and the survival probability will decay with the thermal equilibrium rate constant. Only if the relaxation rate of temperature ($\langle \gamma \rangle$) is of the same order as the escape rate, will one be able to measure nonexponential kinetics. For a one degree of freedom system, this would imply the underdamped limit, in which the present theory is, as mentioned, no longer valid. If the number of degrees of freedom of the system is N, the condition for equilibration of reactants (within the RRK theory) is

$$\frac{\langle \gamma \rangle}{\omega} \frac{1}{(N-1)!} \left(\frac{V^{\ddagger}}{k_B T} \right)^N \geq 1 ,$$

where ω is the characteristic frequency of the system. In other words, the minimal value of the damping for which the theory is valid decreases significantly as the number of degrees of freedom increases.

Denoting the thermal rate as $\langle \gamma \rangle k_{\infty} e^{-V^{\ddagger}/k_B T}$, one would find that the escape rate equals the damping constant when:

$$\frac{1}{k_{\infty}} \sim \frac{1}{(N-1)!} \left(\frac{V^{\ddagger}}{k_B T} \right)^N e^{-V^{\ddagger}/k_B T} . \tag{6.1}$$

Assuming that k_{∞} is of the order of unity, one finds that the condition given in Eq. (6.1) can be realized only if $N \geq V^{\ddagger}/k_B T$. In other words, nonexponential kinetics due to an initial nonequilibrium distribution is essentially associated with a finite barrier to reaction and a multidimensional reacting system.

The simple analytic formula given in Eq. (3.16) is based on the RRK model. Representing a polyatomic molecule in terms of a collection of independent harmonic oscillators would seem to be suspect. But in fact, one could argue that the result is more robust. One may analyze the range of energies of the molecule that contribute significantly to the decay. As the number of degrees of freedom of the molecule increases, the range becomes narrower. Approximating the energy dependence of the density of states over a narrow energy interval in terms of a power law dependence should not be too terrible. But this is all that is needed to write down an analytically soluble energy diffusion equation. In any case, these assumptions may be tested by comparing the theory with numerical results for a realistic model of a molecule, using Langevin dynamics.

A central assumption of the present theory is that initially the reactants are thermally distributed. Putting it differently, we are assuming that after the initial laser excitation, intramolecular vibrational redistribution (IVR) is much faster than anything else, leading to a microcanonical equilibrium of the reactants. If the effective number of degrees of freedom of the reactant is 5 or larger, then this distribution is well approximated as a thermal distribution. If however, IVR is slow, then the theory would become more complicated. It becomes necessary to solve the energy diffusion equation for the given initial condition.

Finally a word about quantum mechanics. In Sec. III, we argued loosely that Eq. (3.16) would still be valid except that one should replace the classical RRK expression for the rate with the appropriate quantum expression. In this way, one could include tunneling in the theory. The derivation of an energy diffusion equation for the quantum dynamics has been discussed in various places.[6,21,22] As mentioned, especially the analysis presented in Ref. 22 indicates that the Gaussian assumption inherent in the energy diffusion equation is quite good. In addition, as the molecule increases in size, the discreteness of its states becomes less important. An interesting question would be how quantum fluctuations in the rate $k(E)$ about its classical mean would affect the survival probability.

ACKNOWLEDGMENTS

[1] N. B. Slater, *The Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, New York, 1959).

[2] P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley, New York, 1972).

[3] W. Forst, *Theory of Unimolecular Reactions* (Academic, New York, 1973).

[4] G. Gershinsky and E. Pollak, J. Chem. Phys. (to be published).

[5] H. A. Kramers, Physica **7**, 284 (1940).

[6] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).

[7] M. Borkovec and B. J. Berne, J. Chem. Phys. **82**, 794 (1985).

[8] A. Nitzan, J. Chem. Phys. **86**, 2734 (1987).

[9] A. Nitzan and Z. Schuss, in *Activated Barrier Crossing*, edited by G. R. Fleming and P. Hänggi (World Scientific, Singapore, 1993), pp. 42–81.

[10] N. Agmon and J. Hopfield, J. Chem. Phys. **78**, 6947 (1983).

[11] G. H. Weiss, J. Chem. Phys. **80**, 2880 (1984), and references therein.

[12] B. J. Matkowsky, Z. Schuss, and E. Ban Jacob, SIAM J. of Appl. Math. **42**, 835 (1982).

[13] A. G. Zawadzki and J. T. Hynes, Chem. Phys. Lett. **113**, 476 (1985).

[14] M. Borkovec and B. J. Berne, J. Chem. Phys. **86**, 2444 (1987).

[15] H. Risken, *The Fokker–Planck Equation*, 2nd edition, Springer Series in Synergetics, Vol. 18, (Springer-Verlag, Berlin, 1989).

[16] H. C. Andersen, I. Oppenheim, K. E. Shuler, and G. H. Weiss, J. Math. Phys. **5**, 522 (1964).

[17] M. W. Balk and G. R. Fleming, J. Phys. Chem. **90**, 3975 (1986).

[18] J. Schroeder, D. Schwarzer, J. Troe, and F. Voss, J. Chem. Phys. **93**, 2393 (1990).

[19] G. Gershinsky, private communication.

[20] P. Talkner, A. M. Berezhkovskii, and E. Pollak (to be published).

[21] I. Rips and J. Jortner, Phys. Rev. B **34**, 233 (1986).

[22] I. Rips and E. Pollak, Phys. Rev. A **41**, 5366 (1990).