ELSEVIER

29 September 1995

Chemical Physics Letters 244 (1995) 10–18

CHEMICAL
PHYSICS
LETTERS

Solvent dynamics-modified RRKM theory in clusters

R.A. Marcus

Noyes Laboratory of Chemical Physics [1], *California Institute of Technology, Pasadena, CA 91125, USA*

Received 17 July 1995; in final form 28 July 1995

Abstract

Kramers and RRKM theories are used to formulate a solvent dynamics-modified treatment of unimolecular reaction rates in clusters. The canonical Kramers' description is modified so as to apply to microcanonical systems. An entropic gradient, arising from all coordinates but the reaction coordinate q, and a q-dependent microcanonical vibrational temperature are introduced. A simple expression is obtained relating the rate constant to its RRKM value and permitting comparison with recent experiments. An application is also made to the Kramers' turnover region.

1. Introduction

In a recent and stimulating experiment Zewail and co-workers [1] have determined the dynamics of the photoinduced isomerization of trans-stilbene molecules, both with and without a cluster of n hexane molecules, with n varied from 1 to 5. The isomerization dynamics in each case showed a single exponential time decay, which was studied as a function of the excess vibrational energy of the photoexcited stilbene. Current discussions of stilbene isomerization include those in Ref. [2] and in references therein.

There are several possible effects of an adsorbed solvent molecule on the reaction rate of a photoexcited solute at a given initial energy of excitation. They include (1) collisional deactivation/activation (energy sharing), (2) a possible modification of the threshold energy for the reaction [3], and (3) a frictional effect associated with random forces. The first effect is well known in gas phase collisions.

In this Letter, an approximate theoretical expression is derived for a generic system of this type, focusing on effect (3). The simplest model consistent with a single exponential behavior is also included for any contribution of effects (1) and (2). The following assumptions or conditions are made regarding the photoexcited molecule, termed the solute:

(i) The photoexcitation conditions yield a wave packet comprised of many quantum states. (Other experimental conditions could yield, instead, a state-resolved preparation of a single quasi-eigenstate.)

(ii) The behavior of the solute molecule is microcanonical and is RRKM-like or, as defined later, diffusively-modified RRKM-like, with an energy determined by the initial excitation energy. For case (b) below it is the cluster which is microcanonical.

(iii) The radial and various librational or floppy motions of each solvent molecule adsorbed on the solute can cause or enhance a frictional effect on the velocity along the reaction coordinate. (The intramolecular vibrations of the solute might also contribute, though presumably to a lesser extent.)

(iv) The probable range of values of the momen-

---

[1] Contribution No. 9113.

SSDI 0009-2614(95)00899-3

tum p along the reaction coordinate q is 'thermal', rather than very 'hot', so permitting a statistical-like adjustment among the remaining coordinates during the itinerant motion along q and a Fokker–Planck-like treatment for both q and p.

There are several limiting cases regarding intramolecular vibrational relaxation within a cluster:

(a) the excitation energy remains, in effect, confined to the solute, and

(b) the excitation energy is immediately redistributed between the solute and, at least, the librational and radial modes of the solvent molecules in the cluster. The treatment given in Section 2 would include either of these two limiting cases, but the numbers of degrees of freedom contributing to $k_{\mathrm{RRKM}}(E)$ in Eq. (22) below would differ for the two cases.

For trans-stilbene, case (b) is probably favored, judging from data in solution, which show a thermalization of the initially excited solute molecule prior to isomerization. For the results in Ref. [1] the enhanced rate observed with a solvent molecule in the cluster in the threshold region is presumably due to the effect of the latter on the energy barrier [1]. However, the increasing depression of the rate observed at higher excess energies with increasing number of solvent molecules in the coordination shell is presumably due, instead, to two factors: an enhanced friction and, for case (b), a redistribution of the initial excitation energy among more modes. Both effects undoubtedly occur, and distinguishing between them in a cluster represents an interesting task, accomplished perhaps with studies varying the nature of the adsorbed solvent molecules and their number outside the inner coordination shell. Presumably, in any cluster of a solute attached to n solvent molecules ($n = 1, 2, \ldots$) mainly the molecules in the first coordination shell contribute to the interruptions, i.e. to the 'frictional effect'.

The present treatment blends the concepts of RRKM and Kramers' theories. Kramers' considered a one-dimensional system at a constant temperature [4]. An excellent extensive review of Kramers' theory and its extensions is given in Ref. [5]. A relation between Kramers' result, its Grote–Hynes memory modification [6], and a transition state/harmonic bath theory is described in Refs. [7–9].

The present treatment uses thermodynamic (statistical mechanical) microcanonical functions along the reaction coordinate, permitting the remaining coordinates to be involved, and in that particular sense is many-dimensional. There is some similarity in that respect to our earlier study of electron transfer reactions for canonical systems, which involved calculations of the free energy along the reaction coordinate [10] and to the work of Chandler and others (e.g. use of a 'potential of mean force' or 'free energy surface') for condensed phase reactions [11].

In this Letter, predictions are made of the relation between the energy-dependent rate constants of the bare and solvent-adsorbed solute. In Section 2, pertinent unimolecular considerations are given. The Kramers' type equation is adapted so as to obtain the microcanonical phase space distribution of the microcanonical solute. The key final equations are Eq. (22) and its overdamped limit, Eq. (23). The evaluation of the 'frictional coefficient' is discussed in later sections, together with its experimental estimation and a rough molecular interpretation. An application of the present work to the Kramers' turnover problem is given in Section 6. Concluding remarks are made in Section 7. The use of a microcanonical description for calculating spectra of hot molecules is related to the present analysis and is described in the Appendix.

2. Unimolecular rate constant

In a nonstationary state of an anharmonic system the vibrational energy of the solute interchanges intramolecularly among its vibrational modes, including the mode which is the reaction coordinate q. Repeated impacts between the solute and any solvent molecules in its coordination shell in the cluster also interrupt the q-motion and so can enhance any diffusive nature of the latter. We consider the reaction rate of the 'solute' molecule in a cluster of $n = 0, 1, 2, \ldots$ solvent molecules.

2.1. Quasi-equilibrium (RRKM) case

To use as a starting point for the subsequent frictional calculations, we first recall the derivation of the RRKM rate constant [12,13]. The momentum conjugate to q is denoted by p. The number of quantum states accessible to a solute whose energy lies in $(E,\ E+\mathrm{d}E)$ and whose q and p lie in $(q,\ q+\mathrm{d}q)$ and $(p,\ p+\mathrm{d}p)$ is denoted by $\rho_v^{\mathrm{e}}(E_v,\ q)\mathrm{d}E\,\mathrm{d}q\,\mathrm{d}p/h$, where ρ_v^{e} is the density of vibrational states and is a function of E_v, the energy in all coordinates other than q. It depends on E_v at the given q and, because the shape of the potential energy surface for the vibrations depends on q, on q itself. The semiclassical number of quantum states for the given infinitesimal q and p intervals is $\mathrm{d}q\,\mathrm{d}p/h$.

The equilibrium probability of finding the system with the above specifications is $\rho_v^{\mathrm{e}}\,\mathrm{d}q\,\mathrm{d}p\,\mathrm{d}E/h\rho(E)\mathrm{d}E$, where $\rho(E)$ is the density of quantum states arising from all coordinates in the parent molecule. Dividing by $\mathrm{d}q$ to find the probability per unit length along q, multiplying by the velocity $\dot{q}$ to calculate the contribution to the reaction probability flux, we note that $\dot{q}\,\mathrm{d}p$ equals $\mathrm{d}E_q$, where E_q is the q-kinetic energy at q. Upon integrating over all E_q and thereby over all accessible E_v at the given E, the integrated reaction probability flux at the transition state $q^\dagger$ is the rate constant,

$$k_{\mathrm{RRKM}} = \int_0^{E_v^{\max}(q^\dagger)} \rho_v^{\mathrm{e}}(E_v, q^\dagger)\,\mathrm{d}E_v/h\rho(E), \tag{1}$$

since $-\mathrm{d}E_v$ equals $\mathrm{d}E_q$ at the given E when we write

$$E = E_v(q) + U(q) + \tfrac{1}{2}p^2. \tag{2}$$

$U(q)$ is the potential energy along q, and $E_v^{\max}(q^\dagger) = E - U(q^\dagger)$. We have used a mass-weighted q, for notational brevity, so that $\dot{q} = p$, and $E_q = \frac{1}{2}p^2$.

Thereby,

$$k_{\mathrm{RRKM}}(E) = N(E, q^\dagger)/h\rho(E), \tag{3}$$

where $N(E,\ q^\dagger)$ is the number of energetically accessible vibrational quantum states at $q = q^\dagger$. The $q^\dagger$ is obtained variationally by minimizing $N(E,\ q)$ (cf. Ref. [13] and references cited therein). A recent review of unimolecular reaction theory is given in Ref. [14].

This derivation is readily modified to include all vibrational-rotational states of the molecule consistent with the given total angular momentum J and with any constraints on those states, thereby yielding [10,11]

$$k_{\mathrm{RRKM}}(E, J) = N(E, J, q^\dagger)/h\rho(E, J). \tag{4}$$

However, for brevity of presentation the J symbol will be suppressed.

We next consider a modification of Eq. (3) which allows for frictional effects of the solvent molecules attached to the solute in the cluster. The treatment has the practical goal of obtaining a simple expression which can be easily related to experiments, and in the comparison serve to illustrate various issues. The single-exponential behavior observed in Ref. [1] was a factor in avoiding for the present the adapting to the microcanonical case more elaborate and more general treatments. In the literature a different approach for a microcanonical system has been given by Tucker and Pollak [15].

2.2. Nonequilibrium systems

We consider the frictional effect on the phase space distribution function, $P(E,\ q,\ p,\ t)$ of the solute. This P is the probability *density* for finding the system in $(q,\ q+\mathrm{d}q)$, $(p,\ p+\mathrm{d}p)$ and $(E_v,\ E_v+\mathrm{d}E_v)$. For the quasi-equilibrium system P was $\rho_v^{\mathrm{e}}(E_v,\ q)/h\rho$. We consider the steady-state case.

Using the argument leading to Eq. (1) the rate constant in this case is

$$k_{\mathrm{rate}} = \int P(E, q^\dagger, p)\,p\,\mathrm{d}p, \tag{5}$$

where the integral is now over all p. We seek an expression for P.

It will be convenient to define a Boltzmann-type vibrational entropy $S_v(E_v,\ q)$ associated with the equilibrium distribution of the vibrational states of all coordinates but q,

$$S_v(E_v, q) = k_{\mathrm{B}} \ln \rho_v^{\mathrm{e}}(E_v, q) + \text{const.} \tag{6}$$

This constant does not enter into Eqs. (7)–(9) below, since only derivatives of S_v appear there. The explicit dependence of S_v on q at a given E_v is due to the dependence of the shape of the multidimensional potential energy surface for these vibrational coordinates on q. Bearing Eq. (2) in mind, we shall sometimes write $S_v(E_v,\ q)$ as $S_v(E,\ q,\ p)$, and $\rho_v^{\mathrm{e}}(E_v,\ q)$ as $\rho_v^{\mathrm{e}}(E,\ q,\ p)$.

We define a microcanonical vibrational temperature T_v for all coordinates contributing to E_v,

$$T_v(E, q, p) = 1/(\partial S_v/\partial E_v)_q = 1/(\partial S_v/\partial E)_{q,p}, \tag{7}$$

where the derivative is calculated at the particular E, q and p, of interest. Since p is assumed to be typically small in the present formulation, only the dependence of T_v on q will be stressed. At the given E and q it will be written as $T_v(q)$, for brevity.

We introduce a Kramers-type equation, which we have modified so as to be appropriate for the present microcanonical system, i.e. at fixed E,

$$\frac{\partial P}{\partial t} = -T_v\left(\frac{\partial S_v}{\partial q}\right)\frac{\partial P}{\partial p} - p\frac{\partial P}{\partial q} + \zeta\frac{\partial}{\partial p}\left(pP + k_B T_v\frac{\partial P}{\partial p}\right). \tag{8}$$

Eq. (8) differs from the standard Kramers' phase-space differential equation [4] in two respects. The constant temperature T in the latter is replaced by a $T_v(q)$ and the usual mechanical force $-\partial U/\partial q$ is replaced by $T_v(q)\partial S_v/\partial q$. These changes are designed to permit the $\rho_v^e(E, q, p)/h\rho(E)$ in Eq. (1) to be a solution of Eq. (8) for P. In fact, differentiation of ρ_v^e in Eq. (6), and making use of Eqs. (2) and (7), shows that

$$\frac{\partial \rho_v^e}{\partial p} = -\frac{\rho_v^e p}{k_B T_v}, \quad \frac{\partial \rho_v^e}{\partial q} = \frac{\rho_v^e}{k_B}\frac{\partial S_v}{\partial q}, \quad \frac{\partial \rho_v^e}{\partial t} = 0, \tag{9}$$

which in turn shows that Eq. (8) for P is indeed identically satisfied by $\rho_v^e(E, q, p)/h\rho(E)$.

The method of Kramers [4] is used to solve Eq. (8) in the steady-state case, a case which is consistent with a single-exponential decay. (A relaxation treatment, with a single exponential decay constant λ, would yield in an alternative procedure an eigenvalue problem to be solved for λ and P.) For the steady-state case we set

$$P(E,q,p,t) = \rho_v^e(E,q,p)W(E,q,p)/h\rho(E) \tag{10}$$

and solve for the unknown function $W(E, q, p)$.

So defined, this W should approach unity when q approaches the reactant's region of q-space ($q \sim 0$), since the value of P there can be approximated by its equilibrium value ρ_v^e/hp. The W in Eq. (10) can be expected to depart from this value of unity mainly when q is near or greater than $q^\dagger$. Therefore, the S_v is first expanded in the vicinity of $q = q^\dagger$:

We note that in variational RRKM theory $N(E, q)$ is a minimum at $q = q^\dagger$. For complex molecules the minimum in the density of states ρ_v^e, and hence in S_v^e, occurs at a value of q very close to $q^\dagger$ (as is also seen later from Eq. (20) since $T_v(q)$ there varies little with q near $q^\dagger$). We have on that basis, expanding in powers of $q - q^\dagger$ and of p (and in this case the limits on p in Eq. (3) can be replaced by $\pm\infty$)

$$S_v(E,q,p) = S_v(E,q^\dagger,0) + \frac{\omega^{\dagger 2}(q-q^\dagger)^2}{2T_v^\dagger} - \frac{p^2}{2T_v^\dagger} + \ldots \quad (q \approx q^\dagger, p\,\text{small}), \tag{11}$$

where $T_v^\dagger$ and $\omega^{\dagger 2}$ denote $T_v(q^\dagger)$ and $T_v\,\mathrm{d}^2S_v/\mathrm{d}q^2$ at $q = q^\dagger$, respectively. We have used $(\partial S_v/\partial(p^2))_{E,q} = (\partial S_v/\partial E_v)_q(\partial E_v/\partial(p^2))_{E,q} = -1/2T_v^\dagger$ and neglected $\partial S_v/\partial q$ at $q^\dagger$. (If the latter were included in the expansion in Eq. (11), only a minor modification would be needed in Eq. (13) below, but this extra complexity seems unwarranted at this point.)

From Eqs. (9)–(11) we then have in the steady-state case

$$-\omega^{\dagger 2}(q-q^\dagger)\frac{\partial W}{\partial p} - p\frac{\partial W}{\partial q} - \zeta p\frac{\partial W}{\partial p} + \zeta k_B T_v^\dagger\frac{\partial^2 W}{\partial p^2} = 0 \quad (q \sim q^\dagger), \tag{12}$$

where, in the vicinity of $q = q^\dagger$, $T_v(q)$ has been replaced by $T_v^\dagger$, its typical value there.

To introduce a similarity transformation, which reduces the partial differential equation in two variables to an ordinary differential equation in one variable, we write [4]

$$W = W(u), \quad u = p - \alpha(q - q^\dagger). \tag{13}$$

Eq. (13) is seen to be a solution to Eq. (12) only if α is chosen to satisfy

$$\alpha = \tfrac{1}{2}\zeta \pm \sqrt{\left(\tfrac{1}{2}\zeta\right)^2 + \omega^{\dagger 2}}. \tag{14}$$

After one integration of Eq. (12) $W(u)$ satisfies the first-order ordinary differential equation

$$\frac{\mathrm{d}W(u)}{\mathrm{d}u} = C\exp\left[-(\alpha - \zeta)u^2/2\zeta k_B T\right], \tag{15}$$

where C is the integration constant. For $W(u)$ to converge as $u \to \pm\infty$ $\alpha - \zeta$ must be positive, so the positive root in Eq. (14) is selected. The appropriate solution of Eq. (15) is that which tends to zero as q becomes large and positive and hence as u becomes large and negative. Using this boundary condition the integration of Eq. (15) yields

$$W(u) = C\int_{-\infty}^{u} \exp\left[-(\alpha-\zeta)z^2/2\zeta k_B T_v^\dagger\right] \mathrm{d}z. \tag{16}$$

The remaining constant C is chosen so that W approaches unity when q is near zero.

In the vicinity of $q=0$, the upper limit in Eq. (16) is essentially $+\infty$, since the $q-q^\dagger$ in Eq. (13) becomes large and negative in the reactant's region. Since W is close to unity there, C can then be evaluated and $W(u)$ becomes

$$\begin{aligned} W(u) &= \left[(\alpha-\zeta)/2\pi\zeta k_B T_v^\dagger\right]^{1/2} \\ &\quad\times\int_{-\infty}^{u} \exp\left[-(\alpha-\zeta)z^2/2\zeta k_B T_v^\dagger\right] \mathrm{d}z. \end{aligned} \tag{17}$$

The Kramers'-type distribution function described by Eqs. (10) and (17) shows a smooth depletion of the population of negative p's in the vicinity of $q=q^\dagger$ and for $q>q^\dagger$. We also note from Eq. (17) that when ζ becomes very small, the integrand for $W(u)$ at $q=q^\dagger$ serves as a delta-like function at $z=0$, making $W(p)$ equal to zero if $p<0$ and equal to unity if $p>0$. In that case Eq. (5), with Eqs. (10) and (17), reduces to the quasi-equilibrium case, Eq. (1), as expected.

The rate constant k_{rate} can be calculated using Eq. (5) for the reactive flux crossing $q=q^\dagger$, with P given by Eqs. (10) and (17). From Eqs. (6) and (11) we first have

$$\rho_v^e(E,q^\dagger,p) = \rho_v^e(E,q^\dagger,0)\exp\left(\frac{-p^2}{2k_B T_v^\dagger}\right), \tag{18}$$

whence Eqs. (5), (10) and (17) yield

$$k_{\text{rate}} = \rho_v^e(E,q^\dagger,0)\sqrt{\frac{\alpha-\zeta}{\alpha}}\,\frac{k_B T_v^\dagger}{h\rho}. \tag{19}$$

However, using Eq. (18), $N(E,q)$ is given by

$$\begin{aligned} N(E,q) &= \int_0^{p_{\max}} \rho_v^e(E,q,p)\,\mathrm{d}\left(\tfrac{1}{2}p^2\right) \\ &= \rho_v^e(E,q,0)k_B T_v(q), \end{aligned} \tag{20}$$

which, with Eq. (19), yields

$$k_{\text{rate}} = \sqrt{\frac{\alpha-\zeta}{\alpha}}\,\frac{N(E,q^\dagger)}{h\rho} = \sqrt{\frac{\alpha-\zeta}{\alpha}}\,k_{\text{RRKM}} \tag{21}$$

and so, from Eq. (14),

$$k_{\text{rate}} = (1/\omega^\dagger)\left[\sqrt{\left(\tfrac{1}{2}\zeta\right)^2+\omega^{\dagger 2}} - \tfrac{1}{2}\zeta\right]k_{\text{RRKM}}. \tag{22}$$

This equation reduces to Eq. (1) when $\zeta/2\omega^\dagger$ becomes small. When $\zeta/2\omega^\dagger$ becomes large, it yields, instead,

$$k_{\text{rate}} = \frac{\omega^\dagger}{\zeta}k_{\text{RRKM}} \quad (\zeta/2\omega^\dagger \gg 1). \tag{23}$$

Eqs. (22) and its limiting case Eq. (23) are the desired equations.

To compare with the Kramers' canonical expression, we consider a cluster so large that $\omega^\dagger$ and ζ are independent of energy. Eq. (22) is then multiplied by $\rho(E)\exp(-E/k_B T)\mathrm{d}E/Q$, where Q is the partition function for the coordinates involved in ρ, integrated over E, and summed over J (when $\rho(E)$ denotes $\rho(E, J)$) to then yield

$$k_{\text{rate}}(T) = \frac{1}{\omega^\dagger}\left[\sqrt{\left(\tfrac{1}{2}\zeta\right)^2+\omega^{\dagger 2}} - \tfrac{1}{2}\zeta\right]k_{\text{RRKM}}(T). \tag{24}$$

Eq. (24) has the same form as Kramers' original canonical result [4]. However, the variational transition-state rate constant on the right, denoted by $k_{\text{RRKM}}(T)$, is more general than the Kramers' $(\omega_0/2\pi)\exp(-U^\dagger/k_B T)$, which is a special case of the former.

3. Other aspects: collisional effects, reaction threshold energy

A photoexcited molecule may, when it is in a cluster of n ($n = 1$, 2, ...) solvent molecules, lose some of its energy to a solvent molecule, particularly to the latter's librations and radial translation. When there is a complete redistribution to such modes we have case (b) referred to in Section 1. Then, the $k_{\text{RRKM}}(E)$ in Eq. (22) is calculated using these extra coordinates, and the energy E is the sum of the initial vibrational excitation energy of the solute and the relevant initial energy of the modes of the solvent cluster.

Another effect of a solvent molecule attached to the solute is its influence on the threshold energy ϵ_0 for reaction. For this reason it is useful in comparisons with experiment to reexpress k_{RRKM} in terms of the energy ϵ in excess of ϵ_0, ϵ_0 being the energy at the lowest quantum state of the transition state. With $E = \epsilon_0 + \epsilon$ we have

$$k_{\mathrm{RRKM}}(\epsilon_0 + \epsilon) = \frac{N(\epsilon_0 + \epsilon, q^{\dagger})}{h\rho(\epsilon_0 + \epsilon)}. \qquad (25)$$

The $N(\epsilon_0 + \epsilon,\ q^{\dagger})$ is more sensitive to ϵ than $\rho(\epsilon_0 + \epsilon)$. Other quantities in Eq. (21) are relatively weakly dependent on ϵ, and apart from ζ are independent of the solvent molecule(s) adsorbed on the solute.

Regardless of whether or not ϵ_0 varies with the nature and number n of the solvent molecules in the cluster, a comparison of $k_{\mathrm{rate}}(E)$'s at the same excess energy ϵ is predicted from Eqs. (23) and (25) to yield ratios of those k_{rate}'s which are approximately ϵ-independent in case (a) of Section 1 (no redistribution to solvent modes). An experimental test of this result is being made by Zewail and co-workers [1]. For case (b) the parallelism is modified by the change in number of relevant coordinates with the number of solvent molecules and by the dependence of E on the initial energy in the modes of the solvent molecules. Evidence of the latter effect is found in Ref. [1].

If the motion of the bare molecule along q toward the transition state is diffusive, due to the random nature of the interaction of q with the other vibrational modes of the solute, and so if it itself obeyed Eq. (22), the same type of parallelism for the k_{rate}'s would again be predicted.

4. Independent estimate of ζ

We consider next the photoexcitation at low energies, e.g. at energies below the reaction threshold, of a solute that is bare or is attached to adsorbed solvent molecules. In the case of a suitable Franck–Condon factor a wave packet associated with the q-motion could be prepared experimentally and perhaps found to exhibit a damped oscillatory decay. A damped oscillatory decay has been observed for q in the bare cis-stilbene molecule, reflecting the interaction of q with some modes of the phenyl groups, all modes damped by other modes in stilbene [16].

We let the wave packet be initially concentrated at some time designated as $t = 0$. One can test experimentally whether the q-motion and its subsequent damping interaction by 'intramolecular' collisions with a solvent molecule in the cluster can be modeled with the Langevin equation for the damped Brownian motion of a harmonic oscillator, e.g. Ref. [17]. The latter is the stochastic equation corresponding to the Kramers' equation when a harmonic oscillator form of the force term is used.

$$\ddot{q} + \zeta\dot{q} + \omega^2 q = A(t). \qquad (26)$$

$A(t)$ is the random force and ω the angular frequency of the harmonic q-motion. The correlation function for the random force depends on the temperature [15] and so will differ in the regions $q \sim 0$ and $q \sim q^{\dagger}$.

It follows from Eq. (26) that the correlation function for the q-motion $C(t) = \langle q(t)q(0)\rangle$ obeys the standard equation, using the usual stipulation that $q(0)$ and $A(t)$ are uncorrelated, i.e. that $\langle q(0)A(t)\rangle = 0$,

$$\ddot{C}(t) + \zeta\dot{C}(t) + \omega^2 C(t) = 0. \qquad (27)$$

The latter has the well known solution for the initial condition $\dot{q} = 0$

$$C(t) = \langle q^2(0)\rangle \exp(-\tfrac{1}{2}\zeta t) \times \cos\left\{\left[\omega^2 - \left(\tfrac{1}{2}\zeta\right)^2\right]^{1/2} t\right\}. \qquad (28)$$

This $C(t)$ reduces to the usual $\langle q^2(0)\rangle \cos(\omega t)$ for the underdamped oscillator ($\frac{1}{2}\zeta \ll \omega$) and to $\langle q^2(0)\rangle \exp(-\zeta t)$ for the overdamped one ($\frac{1}{2}\zeta \gg \omega$). When this motion can be studied experimentally by direct observation of a wave packet, a value of ζ can be estimated by fitting the damped oscillatory behavior to Eq. (28). A molecular estimate of ζ could be obtained independently by fitting that equation to a computer simulation of the q-motion. However, estimates of ζ in the vicinity of $q = 0$ at low energies need not represent the ζ at higher energies, and so may or may not agree with the ζ estimated by comparing Eq. (23) with the experimental data. Estimates of the value of ζ in solution have been also made using the translational or rotational diffusion constants of the solute in the solution [18,19].

Of particular interest is the behavior along q in the transition state region. The barrier is now inverted and the solution for $C(t)$ in the vicinity of $q = q^{\dagger}$ can be obtained by replacing the ω in Eq. (26) by $\mathrm{i}\omega^{\dagger}$, where $\omega^{\dagger}/2\pi$ would be the frequency associated with the inverted parabola at $q = q^{\dagger}$. When the initial conditions are $\dot{q} = 0$, and $q(0) = q^{\dagger}$, the correlation function is then obtained from Eq. (28) by replacing ω by $\mathrm{i}\omega$ and $q(O)$ by q. (The ensemble still involves varying the initial conditions for all other coordinates and momenta.) We then have

$$\begin{aligned} C(t) &= \langle q^{\dagger} q(t) \rangle \\ &= q^{\dagger 2} \exp\left(-\tfrac{1}{2}\zeta t\right) \\ &\quad \times \cosh\left\{ \left[\omega^{\dagger 2} + \left(\tfrac{1}{2}\zeta\right)^2 \right]^{1/2} t \right\}. \end{aligned} \tag{29}$$

By fitting the results of simulations for $C(t)$ to Eq. (29), values of ζ and $\omega^{\dagger}$ could be estimated in the transition state region and the former compared with the estimate of ζ near $q = 0$ at low energies.

Since at low energies the vibrational modes are separable (normal modes), the excitation of only a normal mode in that regime for the bare molecule would yield $\zeta = 0$. At higher energies the nonseparability leads to a dissipation and so to a finite ζ. When some superposition of normal modes is excited at low energies, a quasi-decay (and hence an effective ζ) could occur even in the harmonic regime, but with long time recurrences. Clearly, experiments with wave packet excitation at low and at high energies, and in the absence and presence of adsorbed solvent molecules, is of much interest.

5. Molecular interpretation of ζ

In the case of a free Brownian motion the velocity autocorrelation function [15] is of the form $\langle \dot{q}(0)\dot{q}(t) \rangle = \langle \dot{q}(0)^2 \rangle \exp(-\zeta t)$, which can be used to obtain a very crude molecular model for ζ: In a short time $t = \Delta t$, $\dot{q}(t)$ equals $\dot{q}(0) + \Delta\dot{q}$. Expanding the exponent yields $\langle \dot{q}(0)\Delta\dot{q} \rangle \approx -\zeta\Delta t \langle \dot{q}(0)^2 \rangle$. But $\Delta\dot{q}$ will typically be in the opposite sense from $\dot{q}(0)$, since each impact leads to a rebound, and will be roughly proportional to $\dot{q}(0)$. If Δt is chosen to be small enough that only one impact occurs between solute and solvent during Δt, then $\Delta\dot{q}\Delta t/\dot{q}(0)$ will depend on the frequency ν_{c} of the impacts between a single adsorbed solvent molecule in the coordination shell, the number n_{c} of solvent molecules in that shell, and the detailed geometry and masses (appropriate masses for the coordinates). By choosing $\Delta t = 1/\nu_{\mathrm{c}} n_{\mathrm{c}}$ only a single solute–solvent collision in the cluster occurs in Δt. If as a rough estimate one sets $\Delta\dot{q} \sim -\gamma\dot{q}(0)$, where $0 < \gamma \leqslant 1$, it then follows that

$$\zeta \sim \gamma \nu_{\mathrm{c}} n_{\mathrm{c}}. \tag{30}$$

Eq. (30) neglects the difference in effectiveness of different positions of the molecules in the inner coordination shell. In the case of a bare solute in a fluid, treated as collection of hard spheres, Eq. (30) would be replaced by

$$\zeta \sim \gamma \nu_{\mathrm{c}} g(d), \tag{31}$$

where $g(d)$ is the radial pair distribution function at contact.

For comparison with Eq. (30), we note that in the case of hard sphere translational collisions between two similar molecules, each of mass m (Enskog theory), in a dilute gas ζ equals $\frac{8}{3}\rho\sigma^2(2\pi k_{\mathrm{B}}T/m)^{1/2}$ (e.g. Ref. [20] using $\zeta = k_{\mathrm{B}}T/mD$), while the gas phase collision frequency ν equals $4\rho\sigma^2(\pi k_{\mathrm{B}}T/m)^{1/2}$, so leading to $\zeta = \frac{2}{3}\nu$ for this simple molecular collision. This result can be compared with the $\zeta = \gamma\nu_{\mathrm{c}}$ for the corresponding case ($n_{\mathrm{c}} = 1$) in Eq. (30).

6. Application to the Kramers' turnover observation

Kramers noted that in a unimolecular reaction there should be a turnover in the reaction rate as a function of the pressure [4]. Experimental evidence for this effect now exists [21,22] and there have been many treatments or extensions of Kramers' original arguments, e.g. reviewed in Ref. [5]. At low pressures the reaction rate is proportional to the number of activating collisions, and hence to the pressure of the ambient gas. Kramers described this feature in terms of an 'energy diffusion' mechanism [4], using a frictional force coefficient ζ to treat the exchange of energy with the surrounding medium. The expression for the rate constant in that 'energy diffusion' regime was proportional to ζ, which increased with increasing concentration of the ambient gas. At higher pressures, in a different regime, an enhanced ζ reduces the reaction rate, and so the rate passes through a maximum as a function of ζ. A formulation which treats the regime bridging these two limits has been given, for example, by Büttiker et al. [23] and by others cited in Ref. [5].

For this Kramers' turnover problem we consider first the 'strong' collision formulation for the unimolecular reaction rate. The canonical unimolecular rate constant is given by [12,14]

$$k_{\text{uni}}(T) = \int_0^\infty \frac{k_{\text{rate}}(E)[\rho(E)/Q(T)]}{1 + k_{\text{rate}}(E)/Zc} \times \exp(-E/k_B T)\,\mathrm{d}E, \tag{32}$$

where $\rho(E)$ appeared in Eq. (3), $Q(T)$ is the partition function of the reactant (apart from its three translations), Z is the deactivating collision frequency, per unit c, and c is the concentration of molecules in the surrounding medium (i.e., Zc is the frequency of deactivating collisions). The $k_{\text{rate}}(E)$ is given by Eq. (22). We have suppressed the angular momentum symbol J for notational brevity in the (E), which would read (E, J) and then there would be a sum over all J. Instead of Eq. (32), treatments for the 'weak collision' case, e.g. Ref. [14] and references therein, can be used.

There are seen to be two effects of collisions: one is their activating–deactivating role, represented in the denominator in Eq. (32). The other is the frictional effect represented in Eq. (22). Both effects appear in Eq. (32) and in its 'weak collision' counterpart. In those equations the chemists' conventional view of the activating and deactivating effects of collisions is used in preference to Kramers' phenomenological 'energy diffusion' description.

Eq. (32), with Eq. (22), displays a Kramers' turnover behavior. If there were a solute–solvent clustering at high densities at the prevailing temperature T, Eq. (32) could be modified to allow for these physical clusters.

7. Concluding remarks

The present problem of the unimolecular reaction rate of a bare molecule or of one attached to any specific number of solvent molecules in a cluster raises a variety of interesting features: to what extent, during the lifetime of the system, can (as assumed in this Letter) for practical purposes a simple, diffusive-like model be used for motion along the reaction coordinate in the interaction between the solute and the solvent? Does a diffusive model, reflecting interactions between q and the other modes, apply even to a bare solute (with a smaller ζ than in the solvent case)? Can one observe experimentally the diffusive motion at a subthreshold energy by direct experimental observation of a damped oscillatory wave packet, for the bare and for the clustered solute? What is the value for γ in Eq. (30), estimated from a comparison of Eqs. (22), (23) and (30) with the data? Can an effect of the 'temperature' of the radial and librational motions and other bulk motions of the solvent molecules on the damped oscillatory decay be observed?

There are fundamental questions on the detailed dynamics for which suitable experiments may provide some answers and stimulate further studies.

Acknowledgements

It is a pleasure to acknowledge stimulating discussions with my colleague, Ahmed Zewail, which prompted this work. It is also a pleasure to acknowledge the helpful comments of my student, Xueyu Song, and the support of this research by the National Science Foundation and the Office of Naval Research.

Appendix A

Relation to the calculation of absorption or fluorescence spectra of hot species

In the literature the absorption spectrum of a hot molecule of energy E is sometimes calculated using the canonical Boltzmann distribution for the population of the various vibrational states: A vibrational temperature T has been defined, for example, for hot product molecules in a stilbene isomerization [2], by equating the energy to the population-weighted canonical average energy, yielding

$$E = \sum_i h\nu_i \left[\exp(h\nu_i/k_B T) - 1\right]^{-1}, \qquad (A.1)$$

where E is the energy in excess of the zero-point energy. Eq. (A.1) has then been used as a definition of a vibrational temperature, and the probability of excitation of various optically active states is then calculated from the usual Boltzmann equation at this temperature T. Using Franck–Condon factors, the absorption spectrum is then calculated. Inasmuch as the hot spectrum is of interest in connection with the present analysis, we consider this topic in this research by the National Science Foundation and the Office of Naval Research.

For a microcanonical system, Eq. (A.1) is useful when the energy $\sum_i n_i h\nu_i$ of each important optically active state is much less than E. Otherwise, a microcanonical distribution should be used instead, and we consider this distribution next.

We note that all coordinates, including the reaction coordinate q, are involved in calculating the density of states $\rho(E)$. If an energy $\epsilon\{n\} = \sum_i n_i h\nu_i$ is used to populate an optically active state of the hot molecule, the remaining energy is $E - \epsilon\{n\}$. The number of states associated with this distribution in an energy range $E - \epsilon\{n\}$, $E - E\{n\} + \mathrm{d}E$, is defined as $\rho_{\{n\}}(E - E\{n\})\mathrm{d}E$. Like $\rho(E)$ it can be calculated by standard methods. The probability of having this optically active state is

$$\rho n = \rho_{\{n\}}(E - \epsilon\{n\})/\rho(E). \qquad (A.2)$$

This microcanonical expression would replace a canonical one, for example for the probability of finding n_i quanta in an optically active mode ν_i. One can expect that the use of the microcanonical distribution (A.2) would reduce the probability of large internal excitations of each mode, since it would reduce the number of states available for sharing the remaining energy among the other modes.

References

[1] A.A. Heikal, S.H. Chong, J.S. Baskin and A.H. Zewail, Chem. Phys. Letters 242 (1995) 380.
[2] R.J. Sension, S.T. Repinec, A.Z. Szarka and R.M. Hochstrasser, J. Chem. Phys. 98 (1993) 6291.
[3] J. Schroeder, D. Schwarzer, J. Troe and F. Voss, J. Chem. Phys. 93 (1990) 2393.
[4] H.A. Kramers, Physica 7 (1940) 284.
[5] P. Hanggi, P. Talkner and M. Borkovec, Rev. Mod. Phys. 62 (1990) 251.
[6] R.F. Grote and J.T. Hynes, J. Chem. Phys. 73 (1980) 2715.
[7] E. Pollak, J. Chem. Phys. 85 (1986) 865.
[8] P.G. Wolynes, Phys. Rev. Letters 47 (1981) 968.
[9] Yu.I. Dakhnovskii and A.A. Ovchinnikov, Phys. Letters A 113 (1985) 147.
[10] R.A. Marcus, J. Chem. Phys. 43 (1965) 679.
[11] D.C. Chandler, J. Chem. Phys. 68 (1978) 2959.
[12] R.A. Marcus, in: Chemische Elementaryprozesse, ed. H. Hartman (Springer, Berlin, 1968) p. 348.
[13] D.M. Wardlaw and R.A. Marcus, Advan. Chem. Phys. 70 (1988) 231.
[14] R.G. Gilbert and S.C. Smith, Theory of unimolecular and recombination reactions (Blackwell, Oxford, 1990).
[15] S.C. Tucker and E. Pollack, J. Stat. Phys. 66 (1992) 975.
[16] S. Pedersen, L. Bañares and A.H. Zewail, J. Chem. Phys. 97 (1992) 8801.
[17] R. Kubo, M. Toda and N. Hashitsume, Statistical physics II, 2nd Ed. (Springer, Berlin, 1991).
[18] Y.-P. Sun and J. Saltiel, J. Phys. Chem. 93 (1989) 8310.
[19] R.M. Bowman and K.B. Eisenthal, Chem. Phys. Letters 155 (1989) 99.
[20] D.A. McQuarrie, Statistical mechanics (Harper & Row, New York, 1976) p. 430.
[21] J. Schroeder, J. Troe and P. Vohringer, Z. Physik. Chem. 188 (1995) 287.
[22] M.Y. Lee, G.R. Holtom and R.M. Hochstrasser, Chem. Phys. Letters 118 (1985) 359.
[23] M. Büttiker, E.P. Harris and R. Landauer, Phys. Rev. B 28 (1983) 1268.