121

Sonderdruck aus der Zeitschrift:

Berichte der Bunsen-Gesellschaft für physikalische Chemie (früher Zeitschrift für Elektrochemie)

Energy Distributions in Unimolecular Reactions*)

R. A. Marcus

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801, U.S.A.

Absorptionsspektren, Infrarot / Atom- und Molekularstrahlen / Energieübertragung / Quantenmechanik / Reaktionskinetik

The present paper describes results on modes of anharmonically coupled oscillators in a molecule, the role of energy exchange and near-degeneracy, and quasi-periodic versus ergodic theory of unimolecular reactions. The quasi-periodic one is a formal generalization of Slater's harmonic oscillator theory. Spectral decomposition of a classical trajectory for the molecule provides insight into the molecular spectrum, both in the low (quasi-periodic) and high (ergodic) energy regimes. The role of quantization of transition states in unimolecular reactions and a relation to vibrational adiabaticity are analyzed. Results obtained on energy distribution of translational energy of molecular beam reactions involving intermediate complexes and tight exit channel transition states are described together with the relation to intramolecular energy randomization.

Es werden Ergebnisse über Schwingungen anharmonisch gekoppelter Oszillatoren in einem Molekül, über die Rolle von Energieaustausch und Fast-Entartung, sowie über die Zusammenhänge zwischen quasiperiodischen und ergodischen Theorien unimolekularer Reaktionen beschrieben. Die quasiperiodische Theorie entspricht einer formalen Verallgemeinerung von Slaters Theorie für harmonische Oszillatoren. Die spektrale Zerlegung der klassischen Trajektorien für das Molekül ergibt Aufschlüsse über das Molekülspektrum bei niedrigen Energien (quasiperiodischer Bereich) und hohen Energien (ergodischer Bereich). Die Quantisierung der Übergangszustände in unimolekularen Reaktionen und die Beziehung zu schwingungsmäßiger Adiabasie werden analysiert. Ergebnisse über Translationsenergieverteilungen von Produkten aus Molekularstrahlreaktionen mit Zwischen-Komplexen und starren Übergangszuständen im Ausgangskanal werden ebenso beschrieben wie die Beziehung zu intramolekularer Energierandomisierung.

Introduction

This paper brings together aspects of unimolecular reaction rate theory and of the anharmonic low and high energy behavior of molecules: Anharmonically coupled oscillators in a molecule are considered first, using action-angle variables for the "quasi-periodic regime". A numerical method [1] for finding these variables is outlined. The variables themselves are generalizations of the usual amplitudes and phases of

---

*) Supported in part by the National Science Foundation and the Office of Naval Research.

harmonic oscillators, and so extend that description into the anharmonic regime. Qualitative implications are drawn for systems such as vibrationally-excited van der Waals' complexes and for near-harmonic oscillator unimolecular theories. A formal generalization of Slater theory is given.

The idea of a spectral decomposition of a classical trajectory, introduced in a study with Noid [2], is described. Application can be made to the low and high energy regimes for molecular spectra and thereby for multiphoton dissociation.

A third topic considered is the quantization of transition states, typically not analyzed but significant in its relation to unimolecular reaction rate theory. A role of vibrational adiabaticity and nonadiabaticity in quantization is described. Semiclassical theory and classical trajectories are used to obtain further information.

In a concluding section the interpretation of product energy distributions [3] in a reaction involving formation of an intermediate complex in a molecular beam is considered. The information which such data do or do not provide on energy randomization in the intermediate is discussed for loose and tight exit channel transition states. Particular reference is made to Worry's theoretical study [4] in this laboratory of the tight-transition-state-exit channel reaction [3]

$$\begin{aligned} F + (CH_3)_2C = CH_2 &\longrightarrow F(CH_3)_2CCH_2 \\ &\longrightarrow CH_3 + F(CH_3)C = CH_2 . \end{aligned} \tag{1}$$

Dynamical Considerations for Anharmonically Coupled Oscillators

There have been many trajectory studies of the behavior of dynamical systems whose Hamiltonians are similar to those of molecules. The astronomical literature in particular is replete with studies of anharmonically-coupled oscillators [5]. Such studies, in accordance with the fundamental theory of Kolmogorov, Arnold and Moser for nonlinear systems [6], illustrate that at low energies the motion of the system is quasi-periodic (i.e., multiply-periodic): any coordinate q_i depends on time only via "angle" variables w_i. It depends on w_i in a periodic manner with unit period:

$$q_i = q_i(w_1, \ldots, w_n, J_1, \ldots, J_n), \quad w_i = \nu_i t + \varphi_i , \tag{2}$$

where φ_i is the phase angle at zero time. The number of *nonzero* frequencies ν_i is equal to the number of degrees of freedom n in the nondegenerate case, and less than that number in the degenerate case. (In the degenerate case, some of the w_i's are therefore constants of the motion.) Canonically conjugate to these angle variables w_i are action variables J_i [7]. They are constants of the motion and, for vibrational problems, serve in effect as generalizations of the usual amplitudes for harmonic oscillator (normal mode) systems. This generalization for anharmonic systems is also applicable to systems which do not permit separation of variables. In a harmonic system with normal modes q_i one has

$$q_i = a_i \cos(2\pi \nu_i t + \varphi_i) \quad \text{(harmonic)} \tag{3}$$

where the amplitude a_i is related to the action J_i,

$$2\pi^2 \nu_i^2 a_i^2 = J_i \nu_i , \quad \text{(harmonic)} \tag{4}$$

both sides being expressions for the oscillator's energy.

Eastes [1] and Noid [1] in this laboratory discovered for the first time a numerical method for obtaining the J_i's and w_i's for nonseparable systems with smoothly varying potential energy. Semiclassical eigenvalues were obtained by quantizing the J_i's,

$$J_i = (n_i + \delta_i)h , \tag{5}$$

where n_i is a quantum number and δ_i is a known constant, usually 0, 1/2 or 1, depending on the degree of freedom.

An example of a trajectory where the coordinates q_i are two in number, x and y, and where the frequencies ν_i are rather different is given in Fig. 1. The method Noid used to obtain the J_i was to first obtain a Poincaré surface of section [8] from the trajectory: Denoting the momenta conjugate to x and y by p_x and p_y, one notes the value of p_x and x each time the trajectory crosses the $y = 0$ plane with p_y positive. The plot of this p_x versus x, as in Fig. 2, yields the value of J for this degree of freedom J_x, by calculating the area under the curve

$$J_x = \oint p_x \, dx . \tag{6}$$

Similarly, a plot of p_y versus y values when the trajectory crosses the $x = 0$ plane with positive p_x yields J_y from the area

$$J_y = \oint p_y \, dy . \tag{7}$$

When the unperturbed ν_i are degenerate a trajectory such as that in Fig. 3 was obtained. To treat this system Noid introduced a curvilinear surface of section and was able to calculate the action integrals and semiclassical eigenvalues [2a, 9]. Implications of the extensive energy exchange in Fig. 3 for unimolecular theory are given in a later section.

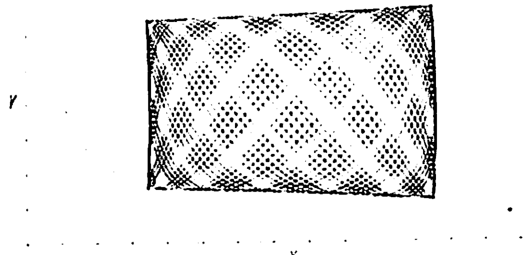


Fig. 1

A typical quasi-periodic trajectory for systems with the Hamiltonian $\frac{1}{2}(p_x^2 + p_y^2 + 4\pi^2\nu_x^2 x^2 + 4\pi^2\nu_y^2 y^2) + \lambda x(y^2 + \eta x^2)$, with $\nu_x \neq \nu_y$. On the oval line the potential energy equals the total energy

Trajectories in the case where the frequencies were rather different show little energy exchange between the motions in the x and y directions [1], the maximum x-amplitude varying little during the motion, as in Fig. 1. In marked contrast, trajectories found for the case where the unperturbed frequencies were equal (Fig. 3) showed extensive energy exchange between the x- and y-coordinates, the amplitude of the x-motion sometimes being large and sometimes small [9]. This extensive energy exchange was caused by a small amount of anharmonic coupling, and has a far-reaching consequence for harmonic oscillator theories of unimolecular reactions. This previously neglected consequence is described in a later section.

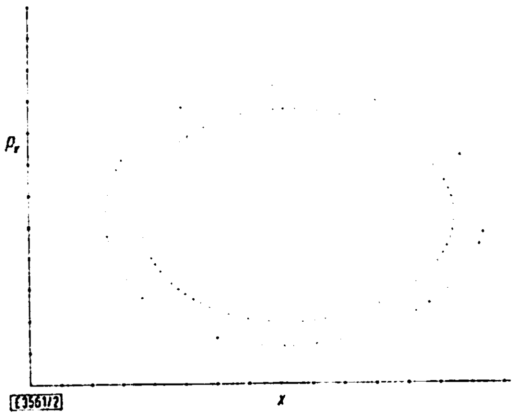


Fig. 2
A Poincaré surface of section for trajectories such as those in Fig. 1. The different ellipses correspond to different trajectories, each differing in J_x but having the same total energy

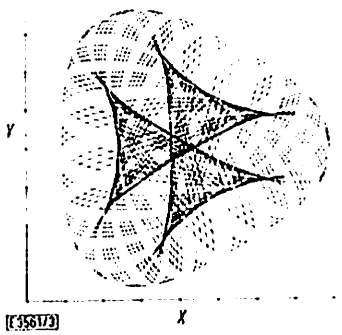


Fig. 3
A quasi-periodic trajectory for systems with the Hamiltonian as in Fig. 1 but with $\nu_x = \nu_y$

The slightness of the energy exchange in the quasi-periodic regime, when the unperturbed oscillator frequencies were incommensurate, may explain the stability of the vibrationally-excited van der Waals' $Cl_2^{\ddagger}-Cl_2$ complex described elsewhere in this symposium [10]. Here, $Cl_2^{\ddagger}$ is vibrationally-excited. The vibration frequency of the Cl_2 bond being very different from that of the Cl_2-Cl_2 bond, one expects little energy exchange in the quasiperiodic regime.

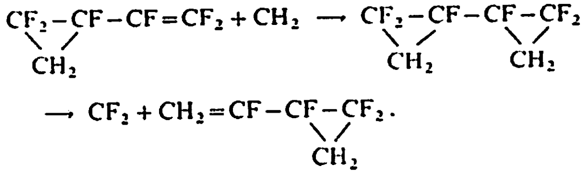
Trajectory studies in the astronomical literature [5] reveal that at higher energies the dynamical system behaves in an ergodic-like manner, yielding a shotgun pattern on the surface of section instead of the regular pattern in Fig. 2. There is, as yet, no rigorous theory for treating systems in the ergodic or nearly ergodic regime, unlike the quasi-periodic regime at low energies (and low couplings), but action variables J_i can no longer be rigorously defined (or evaluated). The onset of ergodicity has been treated in Chirikov's theory of overlapping resonances [11], as well as by other methods.

In the case of unimolecular reactions Bunker and coworkers have compared their results on trajectory studies of lifetimes of decomposing or isomerizing molecules with an ergodic-like theory (RRKM), obtaining reasonable agreement in most cases [12]. A typical relaxation time for intramolecular energy transfer was of the order of 10^{-11} sec [12a] for the systems studied. Some of the work is reviewed by Bunker elsewhere in this symposium. Recently, McDonald at Illinois has added CH_3Cl to the trajectory list of systems studied [13].

$$CH_3 + Cl \rightleftarrows CH_3Cl^* . \qquad (8)$$

The intramolecular relaxation time was about 1 psec, and the vibration initially the most excited in the formation of CH_3Cl was the CH_3-Cl one, while the vibrations transverse to the CH_3-Cl axis were initially those least excited, as one might expect. In the case of a truly head-on collision, the complex lasted only one vibration since there was no time for energy exchange between the newly formed CH_3-Cl bond and the other coordinates. The method used in the analysis was the spectral method of Noid and the writer [2], described in the next section.

Experimentally, in their now-classic experimental investigations, Rabinovitch and coworkers [14] found an intramolecular relaxation time of the order of one picosecond for systems such as



$$\underset{\diagdown\,\diagup\atop CH_2}{CF_2-CF}-CF=CF_2 + CH_2 \longrightarrow \underset{\diagdown\,\diagup\atop CH_2}{CF_2-CF}-\underset{\diagdown\,\diagup\atop CH_2}{CF-CF_2} \longrightarrow CF_2 + CH_2=CF-\underset{\diagdown\,\diagup\atop CH_2}{CF-CF_2} . \qquad (9)$$

They determined whether there was any preference for the CF_2 to be emitted from a particular ring. (The deuterium isotope was used to distinguish the possibilities.)

Fourier Analysis (Spectrum) of a Classical Trajectory for a Molecule

Recently, in a semiclassical study of eigenvalues of anharmonically coupled systems, it occurred to Noid and the writer that one could obtain the classical (and so approximate quantum) spectrum directly from the trajectory, for purposes of comparing with the observed spectrum [2]: One merely calculates from the trajectory the appropriate autocorrelation function and then computes the Fourier transform.

One sees from Equation (2) that in the quasi-periodic regime such a spectrum should consist of sharp lines, peaked at the ν_i's, at the overtones and at the combination frequencies. The sharpness of the spectrum has nothing to do with any approximation of harmonic vibrations or with any approximation of separation of variables, and should apply equally to the spectrum of any molecule that is in the quasi-periodic regime.

In the ergodic regime there are no well-defined variables J_i and w_i, and classically at least one would expect the sharpness to decrease. It is interesting, therefore, to compute the spectrum of a high energy molecule obtained from a classical mechanical trajectory. Such spectra obtained by Koszykowski and Noid [15] indicated a broadening of the formerly sharp lines and the appearance of an underlying continuum. Comparisons with a quantum mechanically calculated spectrum of a high energy molecule should be of interest and are in progress.

One can also compute the transient spectra from trajectories of molecules undergoing unimolecular reaction [13]. Several observations are given in a paper by McDonald and the writer [13]. In particular, the extensive energy exchange between anharmonically coupled modes, degenerate in zeroth order, is clearly evident from the spectrum, the sum of the energy in those modes remaining constant. Again, for purposes of comparing lifetimes with those estimated from RRKM theory, a determination of the spectrum can yield a check on the fundamental frequencies used in the calculation.

The above results bear on multiphoton dissociation, the subject of many recent investigations [16]. The multiphoton absorption is believed to occur stepwise in a particular mode (in the quasi-periodic regime) followed, at high energies, by absorption by a quasi-continuum, and by energy randomization or quasi-periodicity, and dissociation. Trajectory studies are in progress [17].

Degenerate Modes and Slater Theory

The extensive energy sharing which was seen earlier to occur between harmonic modes which are degenerate in the unperturbed case and which are anharmonically coupled, as in Fig. 3, has major consequences for Slater's [18] theory: For a pair of unperturbed harmonic oscillators of the same frequency the trajectory is a closed orbit, an ellipse. Thus, only one dimension in coordinate space is covered by the trajectory. However, as Fig. 3 illustrates, the trajectory for the anharmonically coupled oscillator pair covers densely a two-dimensional region. (The ellipse precesses.) Similarly, it covers four dimensions in phase space instead of the two in the unperturbed degenerate case.

This effect of anharmonicity has far-reaching consequences for any harmonic oscillator theory of unimolecular reactions such as Slater's. In his treatment of a molecule as a collection of harmonic oscillators Slater was required to assume that if a molecule was symmetrical, and so had a vibrational degeneracy, that symmetry (and degeneracy) was preserved throughout the decomposition or isomerization step of the molecule [19a]. In practice, as in cyclopropane, the distortion of the molecular geometry during the isomerization is so great that this symmetry is typically destroyed. Thus, the assumption of this continued degeneracy is not correct. One immediate consequence of the assumption is that if there are n vibrations and the degree of degeneracy is m, the unperturbed trajectory covers densely a configuration space of only $n-m$ dimensions instead of n dimensions, and a phase space of $2(n-m)-1$ dimensions instead of $2n-1$. The system thereby more easily reaches the critical region, the "transition state", of the phase space and has a shorter lifetime. In fact, the first order Slater rate constant k_a for reaction of a molecule of given energy E, averaged over vibrational phases and vibrational amplitudes behaves as [19b]

$$k_a(E) \propto [(E-E_0)/E]^{n-m-1}, \quad \text{(Slater)} \tag{10}$$

where $E-E_0$ is the excess energy. However, since it is found (Fig. 3) in the trajectory of a pair of coupled oscillators that even a small anharmonicity causes an extensive sharing between formerly degenerate oscillators, and so causes the system to cover densely the larger dimensional phase space, this anharmonic coupling yields instead of (10),

$$k_a(E) \propto [(E-E_0)/E]^{n-1}. \quad \text{(Quasi-periodic, anharmonic)} \tag{11}$$

The motion in this system is still in the quasi-periodic regime. One can distinguish between this energy exchange and ergodicity. The former is a "periodic" or more precisely quasi-periodic exchange while the latter is not. The former's motion covers less phase space than the latter's (but both in $2n-1$ dimensions). Nevertheless, for the ergodic case one has

$$k_a(E) \propto [(E-E_0)/E]^{n-1}, \quad \text{(ergodic)} \tag{12}$$

which is of the same *form* as (11) rather than (10).

We conclude this section with a brief statement of a formal quasi-periodic generalization of Slater theory for nondegenerate systems. The usual stationary state arguments and strong collision assumption yield for the unimolecular rate constant

$$k_{uni} = \int k_a(\underset{\sim}{J})\rho(\underset{\sim}{J})\mathrm{d}\underset{\sim}{J}/(1 + k_a(\underset{\sim}{J})/\omega), \tag{13}$$

where $\underset{\sim}{J}$ is the totality of some zeroth order action variables (one per oscillator), $\rho(\underset{\sim}{J})$ is the equilibrium Boltzmann probability of finding $\underset{\sim}{J}$ in $(\underset{\sim}{J}, \underset{\sim}{J}+\mathrm{d}\underset{\sim}{J})$ per unit $\mathrm{d}\underset{\sim}{J}$, and ω is the collision frequency at the prevailing pressure. (The $\underset{\sim}{J}$'s in a unimolecular reaction can't be strictly true action variables: quasi-periodicity is only an approximation here, since the ultimate act of decomposition of real molecules clearly cannot be a quasi-periodic one!) Slater gives an explicit expression for $k_a(\underset{\sim}{J})$, using a harmonic oscillator approximation, and for $\rho(\underset{\sim}{J})$. He employs amplitudes instead of actions, but they are simply related to each other in the harmonic oscillator approximation as in Equation (4). When k_a depends on the J's only via E, as it does in the ergodic case, one can convert (13) by integration to the RRKM form

$$k_{uni} = \int k_a(E)\rho(E)\mathrm{d}E/(1 + k_a(E)/\omega). \tag{14}$$

When there is a degree of degeneracy equal to m in the quasi-periodic case $\mathrm{d}\underset{\sim}{J}$ in (13) would be $\mathrm{d}J_1 \ldots \mathrm{d}J_{n-m}$ instead of $\mathrm{d}J_1 \ldots \mathrm{d}J_n$ [19a]. Such degeneracy typically disappears in the anharmonic case, as already noted, and so one can expect to use $\mathrm{d}J_1 \ldots \mathrm{d}J_n$ for $\mathrm{d}\underset{\sim}{J}$ in (13) in most generalizations of Slater-type theory.

It will be interesting to compare the results of (13) and (14) for some system with incommensurate frequencies, to see how different the quasi-periodic and ergodic predictions can be, when extensively averaged as they are in those equations. Only when $k_a(\underset{\sim}{J})$ shows relatively little fluctuation with $\underset{\sim}{J}$ for a given E can the two expressions yield somewhat similar numerical results at various ω's (pressures).

The problem of calculating (13) in approximations other than the harmonic oscillator one is a formidable one, because of the complexity of anharmonic modes and because of the problem of connecting those modes with motion in the vicinity of the transition state, with its highly distorted geometry. There is also the problem of zero-point energy in the transition state considered later. The latter places a marked lower bound on the phase space occupied by the "critical configuration" or transition state. When the high energy molecules are in an ergodic regime, such a development of quasi-periodic theory is of course unnecessary.

Quantization of Transition States

An assumption of transition state theory is that the states of the internal degrees of freedom in the transition state are quantized, *i.e., have discrete energies*. Because the *transition* state is a dynamical entity, one cannot automatically assume the existence of such quantization, although this topic has not really been analyzed. The subject of quantization of transition states is particularly important in the low pressure region in unimolecular reactions, since it determines (via "zero-point energy") the minimum energy needed by a molecule to reach the transition state and hence react. In turn, this second-order low pressure rate constant for the reaction depends on this minimum, in RRKM theory largely through a density of states of the energized molecule.

We consider now this quantization of transition states ABC^+ for the case of *long-lived* energetic molecules ABC (in Equation (16) later), first for the case of a loose transition state. An example is the dissociation of ethane,

$$C_2H_6 \longrightarrow 2CH_3, \tag{15}$$

where the methyl radicals rotate freely in the transition state, judging from the high collision efficiency for the reverse reaction of recombination of methyl radicals. In this reverse reaction there is therefore no coupling between the internal motions and the translational one before reaching the transition state from the separated CH_3's. Since the vibrations of CH_3 are quantized in the isolated state, they are fully quantized in the same freely rotating free state when they are in the transition state. Similar remarks apply to loose transition states in general.

We consider next the quantization of tight transition states, the analysis of which is more difficult, e.g., in

$$ABC \rightarrow ABC^* \rightarrow AB + C, \tag{16}$$

where ABC^* is the transition state. An example of such a *reaction is the second half of the chemical activation step in* Equation (1).

If, in the reverse reaction to (16), the internal motions were vibrationally adiabatic [20], i.e., retained the values of their vibrational quantum numbers n_i, or in the classical case their actions J_i, the vibrational levels of the transition state which identifiably arise from the vibrations of AB and of C would be quantized, since they are fully quantized in those species. (Adiabaticity preserves numerical values of quantum numbers and action variables.) If, on the other hand, a nonadiabaticity occurred before, between (AB, C) and ABC^* in the reverse reaction to (16), due to coupling between these vibrations and the reaction coordinate, the levels of the transition state would presumably be broadened. A possible semiclassical description is given later. There are also rotations of AB and of C which, when coupled with orbital motions of the AB, C pair, become bending vibrations in the transition state. Such a transformation is even less likely to be adiabatic, though may be on the average ("statistically adiabatic" [21]).

No unimolecular reaction has apparently been studied quantum mechanically, but relevant effects have been observed computationally for tight transition states in a bimolecular reactions. We consider it first, in particular the $H + H_2 \rightarrow H_2 + H$ reaction, which has a tight transition state. An analysis reveals nonadiabatic effects [22]. Such effects may be more extensive in bimolecular reactions than in unimolecular: A typical skewed-axis plot [23] for a unimolecular reaction is indicated in Fig. 4. In bimolecular reactions most of the very highly nonadiabatic effects (leading to population inversion for example) occur in "early downhill exothermic reactions" [24] and particularly in the curved region, near the acute angle of the skewed-axes. In unimolecular reactions, in contrast, this region is pre-empted by the ABC molecule as in Fig. 4 and the transition state ABC^* is situated in the (AB, C) exit channel.

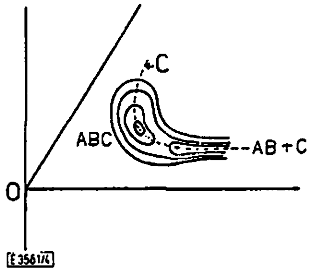


Fig. 4
A skewed-axis plot, in which the kinetic energy in the center of mass system has no cross-terms, for unimolecular Reaction (16). The x-axis is a scaled-distance between C and the center of mass of AB, and the y-axis is a scaled AB distance. The diagonal line is a scaled distance between A and the center of mass of BC

We turn nevertheless to the $H + H_2 \rightarrow H_2 + H$ reaction, a mildly nonadiabatic one, since it illustrates an analysis which can be used and ultimately applied to unimolecular reactions. Along the reaction path the H_2 vibration evolves into a symmetric stretching vibration of H_3 in the transition state and then into a vibration of the H_2 product. Vibrationally nonadiabatic effects occur because of coupling with the *curvilinear reaction coordinate: Classical trajectories* show that when the system has an initial translational-vibrational energy partitioning which is not quite such on the average to permit it to surmount the barrier, some systems surmount it while others do not, depending on the initial vibrational phase [25].

To see the quantum implications of this classical result we turn to semiclassical theory: The reaction probability can be obtained from an integral involving the wave function for the collision [26], and this wave function in turn involves in its phase an integral $\int p\,dq$ from the initial coordinates and momenta to the final ones. Because of the vibrational nonadiabaticity just cited, this $\int p\,dq$ integral will be real for some initial values of the vibrational w_i and complex-valued for others, when the system has an energy near that of the top of the barrier. In this threshold region, thereby, not all systems contributing to the wave function and starting in the lowest vibrational state of H_2 will behave as though they had exactly the same vibrational energy in the transition state H_3; some *will have less vibrational energy.*

The semiclassical conclusion [27] from such an argument is that the quantum reaction probability will exceed that of the usual transition state theory, a theory which requires that the transition state be (at low energies) in the zero-point H_3 vibrational state. The conclusion agrees with the findings: the numerical quantum reaction probability exceeds that calculated from transition state theory [28]. Further, since a "nonadiabatic leak" [22] thereby occurs both classically and quantum mechanically, the former should provide information on the latter. Specifically, on the previously mentioned semiclassical grounds, the quantum mechanical reaction probability P, in a plot of P versus initial translational energy, is expected to rise appreciably with increasing translational energy (~ 0.3, say) at the threshold energy for the classical reaction probability, and then (for a collinear collision) rise to its maximum value of unity. This result provides an interpretation of a numerical [29] comparison of classical and quantum results.

It is important to note that when the system has an energy placing it near the top of barrier these nonadiabatic effects can occur long before the system reaches a transition state configuration. I am not aware of it being treated adequately by any "local" (separable or nonseparable) transition state theory. Rather, it may be necessary to include the accumulated nonadiabatic effects incurred before reaching a transition state, as indicated above [30].

In the case of reactions in three dimensions there are of course additional effects not present in the one-dimensional collinear case. Whereas the zero-point energy in the collinear system decreased on formation of H_3, and nonadiabaticity resulted in enhanced rates, the three-dimensional reaction involves this decrease and also an increase due to formation of bending modes from rotations. It will be interesting to compare forthcoming 3-D results [31] with transition state theory in this case.

In summary, when the frequencies of any vibration are relatively unchanged when the system proceeds from the products in (16) to the transition state ABC^*, the vibrations are expected to be fully quantized. When the vibrations are strongly coupled to motion along the reaction coordinate between ABC^* and products, nonadiabatic effects can occur, probably resulting in some broadening of the quantized levels.

Molecular Beam Reactions Involving Complexes

In recent experiments the translational energy distribution of products of molecular beam reactions involving complexes has been measured [3], with a view to determining the extent of intramolecular energy randomization. In the case of a loose transition state there is no coupling between the internal degrees of freedom and the reaction coordinate when the system moves from ABC^* to products in (16). In such a case one can learn about the translational energy distribution in the transition state directly from the translational energy distribution in the products. Thereby, one learns about intramolecular energy randomization in the intermediate complex. In a reaction such as [3c]

$$\begin{aligned} F + ClRC = CR'R'' &\longrightarrow ClFRC\dot{C}R'R'' \\ &\longrightarrow Cl + FRC = CR'R'' \end{aligned} \tag{17}$$

the products' channel probably has a loose transition state. The translational energy distribution for this reaction agreed reasonably well with that expected from an energy randomization model (e.g., "RRKM theory plus angular momentum", or phase space theory) [3c].

Reaction (1) appeared instead to show a large discrepancy between theory and experiment [3a], as in Fig. 5 where the phase space theory result is compared with the experimental one. However, this reaction has a tight rather than a loose complex: the steric factor for addition of a methyl radical to an olefin is of the order of 10^{-3} rather than unity [32]. There are thereby exit channel effects, which are omitted in phase space theory. For example, the steric factor indicates that the rotations of CH_3 and of $FRC = CR'R''$ have become bending vibrations in the transition state for the products' channel. The translational energy distribution of the products is complicated by this interaction, and so does not, without further knowledge of the dynamical effects in this exit channel, provide immediate information about prior energy randomization.

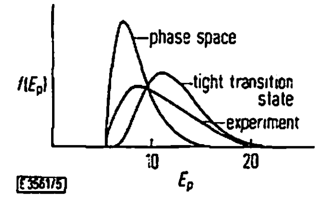


Fig. 5
Distribution function $f(E_p)$ of product translational energies E_p for Reaction (1), obtained by experiment, by phase space theory, and by the present analysis. E_p is in kcal/mol

Some idea of the dynamical coupling in the products' channel can be seen from the adiabatic correlation diagram in Fig. 6. The bending vibrational states of the transition state are more widely spaced than the rotational states of the products, and it is this difference which is ultimately responsible for the steric factor (and is related to an entropy of activation). In the formation of ABC^* from AB and C, the larger the excess translational energy, i.e., the translational energy of products E_p minus the potential energy barrier U^* and minus the centrifugal potential E_l^*, the better the chance that the system can surmount the *effective* potential energy barrier. Using this idea and microscopic reversibility, it was possible to construct a theory [33] for the translational energy distribution of products, for systems having tight transition states, as follows.

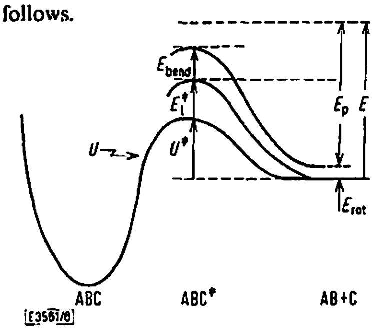


Fig. 6
Exit channel properties. Omitted for brevity is the vibrational energy of the other coordinates, which can be regarded as included in E_{bend} and E_{rot}

Microscanonical transition state theory [34] for a given total angular momentum yields

$$N_J^{\ddagger}(E - U^{\ddagger}) = \Sigma\, w_J = \int \cdots \int w_J \,\mathrm{d}l\,\mathrm{d}j_1\,\mathrm{d}j_2\,\mathrm{d}n\,, \tag{18}$$

where $N_J^{\ddagger}(E - U^{\ddagger})$ is the number of quantum states of the transition state when its total angular momentum quantum number is J and its total energy is E; j_1 and j_2 are rotational quantum numbers of the two products, l is the orbital angular quantum number, and n is the totality of remaining quantum numbers, including those involved with constructing a particular J from l, j_1 and j_2; w_J is the reaction probability for a given $(EJlj_1j_2n)$. Equation (18) presupposes, in its very nature, that an energy randomization has occurred in ABC. (All states in ABC* of the same E and J have equal a priori probability in $N_J^{\ddagger}$.)

The assumption made regarding w_J is that it depends on $(EJlj_1j_2n)$ only via the excess translational energy [33]:

$$w_J = w_J(E_p - E_l^{\ddagger} - U^{\ddagger}) \equiv w_J(E - E_{j_1j_2n} - E_l^{\ddagger} - U^{\ddagger}), \tag{19}$$

where $E_{j_1j_2n}$ is the rotational-vibrational energy of the products. Since $N_J^{\ddagger}$ is known for any model of the transition state, Equations (18) and (19) serve as an integral equation to be solved for the unknown function w_J. The solution of this equation was given for the case that $l \approx J$ in an earlier paper from this laboratory [33]. More recently, Gary Worry has obtained a solution for general l [4]. He first showed that in spite of the complicated limits on j_1,j_2 and l (triangle inequalities and energy bounds), one can write the integral as a convolution integral, because of the form (19) assumed for w_J. He showed thereby that

$$N_J^{\ddagger} = w_J * \rho_n * \rho_{j_1j_2lJ}\,, \tag{20}$$

where the ρ's, in effect, denote densities of states. Application of a Laplace transform then yielded a solution for w_J, which was used to obtain the translational energy distribution. The results involved a summing over all J consistent with the distribution of J's appearing in the entrance channel. The results are given in Fig. 5 (and are fairly close to some obtained with $l \approx J$). The E_p-distribution is shifted to higher translational energies, compared with phase space theory, since some of the bending vibrational energy of the tight transition state in the product channel has gone into translational energy E_p. The agreement with experiment [3a] may be considered to be within experimental error.

This type of agreement does not prove the assumptions made. It is possible that some other set of assumptions may also be in agreement. However, any assumptions must take into account the coupling that exists between the translational and internal motions in the case of a tight transision state, and one can no longer conclude (as had been done earlier) that energy randomization occurred only among a few modes.

The experiments themselves [3], together with those of McDonald and coworkers [35] on the vibrational energy distribution of products, have been an important development in providing information for theoretical analysis of unimolecular processes. The theory presented here can also be used to compute rotational and vibrational energy distributions of products and the angular distribution.

A portion of this research was performed while the writer was a Visiting Professor at Oxford and later an Alexander von Humboldt Awardee at the Technical University in Munich. He is particularly indebted to Professor Schlag (Munich) and Dr. Child (Oxford) for a wonderful sabbatical year.

References

[1] a) D. W. Noid and R. A. Marcus, J. chem. Physics *62*, 2119 (1975); b) cf. W. Eastes and R. A. Marcus, J. chem. Physics *61*, 4301 (1974). These papers give methods for obtaining action variables, but by measuring trajectory times from caustics they can be used to obtain angle variables also.

[2] a) D. W. Noid, Ph. D. Thesis, University of Illinois, April 1976; b) D. W. Noid and R. A. Marcus, J. chem. Physics (to be submitted).

[3] a) J. M. Parson, K. Shobotake, Y. T. Lee, and S. A. Rice, J. chem. Physics *59*, 1402 (1973); b) D. R. Herschbach, Faraday Discuss. Chem. Soc. *55*, 233 (1973) and references cited therein; D. L. King and D. R. Herschbach, Faraday Discuss. Chem. Soc. *55*, 331 (1973); c) Y. T. Lee, Ber. Bunsenges. physik. Chem. *78*, 135 (1974), and references cited therein; d) cf. P. J. Dadigan, H. W. Cruse, A. Schultz, and R. N. Zare, J. chem. Physics *61*, 4450 (1974); e) D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, Molec. Physics *29*, 1813 (1975).

[4] G. Worry and R. A. Marcus, J. chem. Physics (to be submitted).

[5] E. g., M. Henon and C. Heiles, Astron. J. *69*, 73 (1964); G. Contopoulos and M. Moutosoulas, Astron. J. *70*, 817 (1965); W. H. Jeffreys, Astron. J. *71*, 306 (1966); G. H. Walker and J. Ford, Physic. Rev. *188*, 416 (1969).

[6] J. Moser, Stable and Random Motions in Dynamical Systems, Annals of Mathematical Studies, No. 77, Princeton University, Princeton, N. J., 1973. and references cited therein.

[7] H. Goldstein, Classical Mechanics, Chap. 9, Addison Wesley, Reading, Mass., 1950.

[8] H. Poincaré, New Methods of Celestial Mechanics, Vol. 3 (1897) (Transl. NASA, Washington, D. C., 1967), Chap. 27, where the theory of the surface of sections is called the theory of consequents.

[9] D. W. Noid and R. A. Marcus, J. chem. Physics (to be submitted).

[10] D. A. Dixon and D. R. Herschbach, this symposium.

[11] B. V. Chirikov, Research Concerning the Theory of Nonlinear Resonance and Stochasticity (CERN Trans. 71–40, Geneva, Oct. 1971); G. M. Zaslavskii and B. V. Chirikov, Sov. Phys. Usp. *14*, 549 (1972).

[12] a) D. L. Bunker, J. chem. Physics *40*, 1946 (1964); b) D. L. Bunker and M. Pattengill, J. chem. Physics *48*, 772 (1968); c) cf. W. H. Hase and D. F. Feng, J. chem. Physics *64*, 651 (1976).

[13] J. D. McDonald and R. A. Marcus, J. chem. Physics *65*, 2180 (1976).

[14] J. D. Rynbrandt and B. S. Rabinovitch, J. physic. Chem. *75*, 2164 (1975); J. F. Meagher, K. J. Chan, J. R. Barker, and B. S. Rabinovitch, J. physic. Chem. *78*, 2535 (1974).

[15] M. Koszykowski, D. W. Noid, and R. A. Marcus, J. chem. Physics (to be submitted).

[16] R. V. Ambartzumian, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, JETP Lett. *20*, 273 (1974); D. M. Larsen and N. Bloembergen, Optics Comm. *17*, 254 (1976); V. S. Letokhov and C. B. Moore, Sov. J. Quantum Electronics *3*, 259 (1976) and references cited therein; M. J. Coggliola, P. A. Schultz, Y. T. Lee, and Y. R. Shen, Physics Rev. Letters (to be published) and references cited therein; J. P. Aldridge, J. H. Birely, C. D. Cantrell, and D. C. Cartwright, Physics Quant. Electr. *4*, 57 (1976).

[17] a) D. W. Noid, M. Koszykowski, and J. D. McDonald (unpublished); b) D. W. Noid, M. Koszykowski, and R. A. Marcus (unpublished).

[18] N. B. Slater, Theory of Unimolecular Reactions, Cornell University Press, New York 1959.

[19] a) Ref. [18], p. 152ff; b) Ref. [18], p. 92ff.

[20] M. A. Eliason and J. O. Hirschfelder, J. chem. Physics *30*, 1426 (1959); R. A. Marcus, J. chem. Physics *43*, 1598 (1965).

[21] R. A. Marcus, Discuss. Faraday Soc. *44*, 7 (1967).

[22] R. A. Marcus, Discuss. Faraday Soc. *44*, 87 (1967).

[23] Cf. S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, Chap. 3, for skewed-axes plots, McGraw-Hill, New York 1941.

[24] E. g., J. C. Polanyi, Faraday Discuss. Chem. Soc. *55*, 389 (1973).

[25] J. R. Stine and R. A. Marcus, to be published.

[26] Cf. R. A. Marcus, J. chem. Physics *59*, 5135 (1973) and references cited therein; cf. W. H. Miller, Adv. chem. Physics *25*, 69 (1974), and references cited therein.

[27] Nevertheless some caution should be observed in drawing precise conclusions from the integral expression which is, after all, an approximate one.

[28] E. Mortensen, J. chem. Physics *48*, 4029 (1968); D. G. Truhlar and A. Kuppermann, J. chem. Physics *56*, 2232 (1972).

[29] E. Mortensen, J. chem. Physics *49*, 3526 (1968). One can show from these results that the reaction occurs classically at energies below the vibrationally-adiabatic classical threshold energy, and hence shows a nonadiabaticity.

[30] In contrast, for energies well below the top of the barrier, the tunnelling region is a wide one, and a "local" transition state theory becomes a "global" one, when trajectories are used to calculate the tunneling. A very interesting analysis applicable to this large tunneling case, has been given by S. Chapman, B. C. Garrett, and W. H. Miller, J. chem. Physics *63*, 2710 (1975).

[31] Early 3-D results have been given by A. B. Elkowitz and R. E. Wyatt, J. chem. Physics *63*, 702 (1975); A. Kuppermann and G. C. Schatz, J. chem. Physics *62*, 2502 (1975).

[32] Cf. R. J. Cvetanovic and R. S. Irwin, J. chem. Physics *46*, 1694 (1967), Table II, where the Arrhenius pre-exponential factor is of the order of 10^{11} cc mol^{-1} sec^{-1}, which is about 10^{-3} of the collision frequency value (10^{14}).

[33] R. A. Marcus, J. chem. Physics *62*, 1372 (1975).

[34] R. A. Marcus, J. chem. Physics *45*, 2138 (1966).

[35] J. F. Durana and J. D. McDonald, J. chem. Physics *64*, 2518 (1976), and references cited therein.

E 3561