

Product quantum state distributions in unimolecular reactions involving highly flexible transition states

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(Received 10 March 1986; accepted 8 July 1986)

An expression for the distribution of quantum states of the reaction products of unimolecular dissociations is obtained, based on statistical theory. A recently formulated RRKM-type treatment of unimolecular reactions with highly flexible transition states is used to obtain a distribution of quantum states of the products, by introducing an adiabatic approximation for motion from transition state to products. Any impulsive (nonadiabatic) exit channel effects are neglected thereby. Both the final yields of the quantum states of the products and the time evolution of these states are considered. The time evolution of the yield of the products can permit a direct test of non-RRKM effects and, additionally via the long-time component, of other aspects of RRKM theory. The long-time component of the yield of individual quantum states of the products then provides a test of the additional (here, adiabatic) approximation. Such tests are the more definitive the narrower the distribution of initial E 's and J 's of the dissociating molecule.

I. INTRODUCTION

In treatments of unimolecular reaction rates attention is usually focused on the dependence of the reaction rate on the energy of the dissociating or isomerizing molecule.¹ Also of interest has been the distribution of the reaction products among the various rotational-vibrational quantum states.²⁻¹² Energy distributions of the reaction products have been measured using a variety of initiation techniques, including chemical activation and infrared multiphoton dissociation.¹⁰ Overtone excitation methods (OH and CH) have also been used, permitting initiation with a more sharply defined energy.^{4,6-9,11} Theoretical calculations¹² for distributions (final yields) found in studies of Wittig,⁴ Crim,⁶ and their co-workers have been made using phase space theory (PST),^{2,4-6} some modified version of PST,⁵ and the statistical-adiabatic channel model (SACM).^{3,6} More recently, time-resolved rates of formation of the individual product states have been obtained by Zewail and co-workers using picosecond experiments and molecular beams.⁷⁻⁹

In the present paper we describe how, with some added assumptions, a recent implementation¹³ of RRKM theory for unimolecular dissociation rates can be applied to the problem of yields of the individual quantum states of the reaction products. Rates of formation of these states are also considered, as are (briefly) non-RRKM effects.

The RRKM theory of the rate of a unimolecular dissociation (or isomerization) of a molecule utilizes a characterization of the transition state and a statistical assumption for the probability per unit time that the system passes through it.¹ The theory also yields a distribution of the quantum states in the transition state. To then obtain a distribution of quantum states of the products some added assumption would be needed, namely for treating the motion after the system leaves the transition state. Only when the fragments

rotate freely in the transition state can such an additional assumption be avoided, since the distribution of the quantum states of the products is then the same as that in the transition state. In the present paper an adiabatic assumption is used for treating the dissociative process after passage through the transition state. The present treatment for quantum states of products can be regarded as complementary to, or competitive with, phase space and adiabatic channel theories, depending on one's point of view.

In Sec. II the treatment in Ref. 13 is adapted to this problem of calculating the distribution of products' quantum states. In the adaptation one possibility would have been to use classical trajectories to obtain the final distribution of product states for the so-called (largely classical) transitional modes, using the distribution in the transition state as initial conditions. An adiabatic approximation would perhaps be introduced for the remaining modes, the "conserved modes," which are usually of higher frequency and are treated quantum mechanically. This procedure appears to be fairly straightforward.^{12,14} A second approach, the one adopted in this article, is to introduce some simplifying dynamical approximation connecting the distribution of states in the transition state with those of the separated fragments. As already noted, an adiabatic approximation will be used for this purpose.

A main purpose of introducing such approximations is that they provide a basis for comparing and analyzing the experimental results, and for identifying thereby possible nonstatistical (non-RRKM) and nonadiabatic exit channel effects. Some recent comparisons⁴⁻⁶ with theory (PST or SACM in those instances) are described later. We also consider non-RRKM effects and their detection via time-resolved studies in Sec. III. The various results are discussed in Sec. IV and concluding remarks are given in Sec. V. The principal equations derived in the present paper are Eqs. (3), (7), (8), and (10). Equations (12) and (16) also play a role.

^{a1} Contribution No. 7407.

It is planned to apply the present treatment in a subsequent paper.

II. THEORY

In RRKM theory the rate constant k_{EJ} for the dissociation of a molecule of energy E and total angular momentum J is given by^{1,13}

$$k_{EJ} = N_{EJ}^{\ddagger} / h\rho_{EJ}, \quad (1)$$

where ρ_{EJ} is the density of states of the dissociating molecule whose energy is equal to E and which has a total angular momentum J . The center-of-mass system of coordinates of the reacting molecule is used, so E excludes the translational energy of the center of mass. The quantity N_{EJ}^{\ddagger} is the minimum of $N_{EJ}(R)$, plotted as a function of the reaction coordinate R .^{13,15} Here, $N_{EJ}(R)$ is the number of quantum states of the dissociating molecule, at any R , having an energy less than or equal to E and an angular momentum J . The aim in the earlier papers in this series¹³ was to provide a calculation of $N_{EJ}(R)$ and hence of N_{EJ}^{\ddagger} and of k_{EJ} for highly flexible transition states. In these transition states the hindered rotational (vibrational) motions of the fragments can be strongly coupled to each other and to the orbital motion.

In PST one of the approximations is to neglect these angle-dependent interactions of the separating fragments. Thereby, the orbital angular momentum (quantum number l) becomes a constant of the motion between the value R^{\ddagger} of R in the transition state and $R = \infty$. One improvement over PST is to include^{1,3,13} the influence of the angle-dependent terms on N_{EJ}^{\ddagger} .

Two limiting approximations will be considered: In the first of these l is not required to be a constant of the motion between R^{\ddagger} and $R = \infty$. We then use an adiabatic approximation to relate the distribution of quantum states in the products ($R = \infty$) to that at R^{\ddagger} , yielding Eqs. (3) and (8). An alternative limiting approximation is to assume that l is a constant of the motion between R^{\ddagger} and $R = \infty$.¹⁶ An adiabatic approximation is then again employed, but now at each value of l , yielding Eqs. (7) and (8). This second treatment can be shown to reduce to PST, in the limit of vanishing angle dependence of the fragment-fragment potential. These two limiting situations presumably bracket the actual statistical behavior and, indeed, should approach each other when l becomes the dominant contribution to J which is a constant of the motion. In addition to assuming a statistical behavior for formation of the transition state, both limiting cases neglect impulsive (nonadiabatic) exit channel effects.

To introduce the adiabatic approximation we first note that when the energy eigenvalues for the degrees of freedom transverse to R are plotted vs R , each eigenvalue changes to some limiting value at $R = \infty$. In part, the change is due to the decreasing magnitude of the centrifugal and attractive potentials as R approaches infinity and, in part, the change is due to the changing nature of the levels themselves, because the angle-dependent interactions of the separating fragments decrease as R increases. The energies of the adiabatic states at R^{\ddagger} differ from those at $R = \infty$ because of both changes.

At a given J and E , an adiabatic approximation can be introduced as follows: The states lowest in energy at R^{\ddagger} correlate with the lowest states at $R = \infty$ of the same symmetry, because of the noncrossing rule for states of a given symmetry. For each (E, J) an energy E' is then defined,¹⁷ such that the number of states at $R = \infty$ with energy equal to or less than E' , $N_{E',J}^{\infty}$, equals N_{EJ}^{\ddagger} , the number of states in the transition state with energy less than or equal to E and for the given J ,

$$N_{EJ}^{\ddagger} = N_{E',J}^{\infty} \quad (\text{definition of } E'). \quad (2)$$

In the adiabatic approximation, because of the noncrossing rule, the states which constitute N_{EJ}^{\ddagger} also constitute $N_{E',J}^{\infty}$. In particular, the states lowest in energy at R^{\ddagger} are the lowest ones at $R = \infty$, with the same J , and similarly for successively higher tiers of states. [When there are states of different symmetry, their eigenvalues can cross when plotted vs R , and Eq. (2) would be applied and an E' defined for each symmetry.]

When the adiabatic approximation is introduced the probability $p_i(EJ)$ that the system is in any of the final quantum states with an energy E_i in the i th internal coordinate of the products is given by

$$p_i(EJ) = N_{E'-E_i,J}^{\infty} / N_{E',J}^{\infty}, \quad (3)$$

where $N_{E'-E_i,J}^{\infty}$ includes all quantum states at $R = \infty$ with given J , with an energy E_i localized in the i th coordinate, and with an energy equal to or less than E' . For each EJ the sum of the $p_i(EJ)$'s over E_i equals unity.

As an alternative to Eq. (2) we have, for the case that l is a constant of the motion between R^{\ddagger} and $R = \infty$, the relation

$$N_{EJ}^{\ddagger} = N_{E',Jl}^{\infty} \quad (\text{definition of } E'), \quad (4)$$

where $N_{E',Jl}^{\infty}$ is the number of states in $N_{E',Jl}^{\infty}$ with the given l . $N_{E',Jl}^{\infty}$ is the number of states at $R = \infty$ with the given J and l , with an energy E_i localized in the i th coordinate, and with an energy equal to or less than E' . In the adiabatic approximation the states that constitute $N_{E',Jl}^{\infty}$ in Eq. (4) also constitute $N_{E',Jl}^{\infty}$. The N_{EJ}^{\ddagger} in Eq. (1) equals the sum over these $N_{E',Jl}^{\infty}$'s.

$$N_{EJ}^{\ddagger} = \sum_l N_{E',Jl}^{\infty}. \quad (5)$$

When the adiabatic approximation is introduced the probability $p_i(EJl)$ that for the given l the system is in any of the final quantum states with an energy E_i is

$$p_i(EJl) = N_{E'-E_i,Jl}^{\infty} / N_{E',Jl}^{\infty}, \quad (6)$$

where $N_{E'-E_i,Jl}^{\infty}$ includes all quantum states at $R = \infty$ with an energy localized in the i th coordinate, with a given J and l , and with an energy equal to or less than E' . For each EJl the sum of the $p_i(EJl)$'s over E_i equals unity.

The distribution function for l in the transition state is $N_{E',Jl}^{\infty} / N_{EJ}^{\ddagger}$ so that the probability $p_i(EJ)$ that the i th coordinate at the given E and J has an energy E_i is $N_{E',Jl}^{\infty} / N_{EJ}^{\ddagger}$ multiplied by the $p_i(EJl)$ in Eq. (6) and summed over l . Thereby, one obtains

$$p_i(EJ) = \left(\sum_l N_{E'-E_i,Jl}^{\infty} \right) / N_{EJ}^{\ddagger} \quad (7)$$

instead of Eq. (3). A sum of the $p_i(EJ)$'s over the E_i 's equals unity.

In the following treatment $p_i(EJ)$ is given by Eq. (3) or (7), accordingly as l is not or is required to be a constant of the motion, respectively.

We consider an ensemble of molecules that are excited at $t = 0$ with an optical pulse, and consider those molecules whose E 's and J 's after this excitation permit them to react sooner or later. The distribution function $P_i(\infty)$ for the final yield of the product having an energy E_i in the i th coordinate is obtained as the product of the $p_i(EJ)$ given by Eq. (3) or (7) and p_{EJ}^0 , integrated over E and summed over J . Here, $p_{EJ}^0 dE$ is the probability that the parent molecule which ultimately does react is formed with an energy in the range $(E, E + dE)$ and with a given J . This quantity p_{EJ}^0 involves a convolution of the original energy and J distribution, the absorption coefficient, and the laser profile. We now have

$$P_i(\infty) = \sum_{J=0}^{\infty} \int_0^{\infty} p_i(EJ) p_{EJ}^0 dE. \quad (8)$$

A second measurable quantity, is the time evolution of the population $P_i(t)$ of individual quantum states of the products,^{7,8} as distinct from their final yields $P_i(\infty)$. This time-evolving distribution function $P_i(t)$ is defined as the probability that the product fragments at $R = \infty$ and at time t have an energy E_i in the i th coordinate. We denote by $p_{EJ}(t)dE$ the probability at time t of finding the parent molecule with energy $(E, E + dE)$ and with a specified J after the excitation. Since these molecules disappear with a rate constant k_{EJ} , the rate $dP_i(t)/dt$ is given by

$$\frac{dP_i}{dt} = \sum_{J=0}^{\infty} \int_0^{\infty} p_i(EJ) k_{EJ} p_{EJ}(t) dE. \quad (9)$$

Further, $p_{EJ}(t)$ equals $p_{EJ}^0 \exp(-k_{EJ}t)$. Equation (9) then yields

$$P_i(t) = \sum_{J=0}^{\infty} \int_0^{\infty} p_i(EJ) p_{EJ}^0 (1 - e^{-k_{EJ}t}) dE, \quad (10)$$

where $p_i(EJ)$ is given by Eq. (3) or (7). As t tends to infinity, this $P_i(t)$ approaches the final yield $P_i(\infty)$ given by Eq. (8).

We have considered until now the case where RRKM theory^{1,13} can be used to calculate the distribution of quantum states in the transition state. We consider in the next section the case where the intramolecular energy redistribution is not instantaneous, and hence where non-RRKM effects appear. In such a case if one assumes a kinetic model¹⁸ one finds there that time-resolved studies may still permit the application of the above results, though only to data obtained at sufficiently long times.

III. NON-RRKM EFFECTS

The existence of an intramolecular energy redistribution slow enough to influence an observable is sometimes termed a non-RRKM effect. Indirect information on the latter has been obtained from pressure effects on chemical activation studies.^{19,20} In recent time-resolved studies^{7-9,21} a biexponential behavior has been reported in some cases^{8,9,21,22} and one interpretation of the latter has been that

it represents a non-RRKM effect. (An alternative possibility, at the present time, is that the behavior is due to there being contributions to the rate from a distribution of E 's and J 's.⁹) Classical trajectory calculations have also sometimes yielded an apparently slow intramolecular relaxation,²³ though in some cases tunneling corrections may be important in reducing the time for intramolecular energy transfer.¹⁴

Kinetic models for intramolecular energy transfer have been used in various studies, e.g., Refs. 8, 18, 20, and 24-26. One such treatment¹⁸ was used to interpret the detailed results of a trajectory study.²³ We shall utilize results obtained in this kinetic treatment, and recall some relevant ones in which the role played by the RRKM rate constant k_{RRKM} was discussed.¹⁸ We consider a subdivision of the phase space of the parent molecule, the populations in each being N_1 and N_2 , such that the products are formed from N_1 and such that first-order kinetic equations can be written for N_1 and N_2 with rate constants k_j :



Let the initiation step be such that different amounts of N_1 and N_2 , N_1^0 and N_2^0 , are initially populated. The surviving population $N(t)/N(0) = [N_1(t) + N_2(t)]/[N_1^0 + N_2^0]$ is found to be

$$N(t)/N(0) = ce^{-\lambda_1 t} + (1-c)e^{-\lambda_2 t}, \quad (12)$$

where c is a constant given later. It depends on N_1^0, N_2^0 and on the rate constants k_1 to k_3 . The eigenvalues λ_1 and λ_2 of the first-order kinetic equations arising from the scheme in Eq. (11) have a sum and a product given by¹⁸

$$\lambda_1 + \lambda_2 = k_1 + k_2 + k_3, \quad \lambda_1 \lambda_2 = k_1 k_3. \quad (13)$$

The usual RRKM rate constant k_{RRKM} for this system, i.e., the k_{EJ} in Eq. (2), can be defined when none of the k_j 's in Eq. (11) vanishes. It equals^{18,27(a)}

$$k_{\text{RRKM}} = \frac{k_1 k_3}{k_2 + k_3}. \quad (14)$$

It then follows from Eqs. (13) and (14) that when the smaller of the two eigenvalues, λ_2 say, is much less than λ_1 , and when $k_1 \ll k_2 + k_3$, the larger eigenvalue approaches $k_2 + k_3$, which is the rate constant for the equilibration of N_1 and N_2 in Eq. (11b), and λ_2 approaches k_{RRKM} :

$$\lambda_1 \simeq k_2 + k_3, \quad \lambda_2 \simeq k_{\text{RRKM}} \quad (\lambda_1 \gg \lambda_2 \text{ and } k_1 \ll k_2 + k_3). \quad (15)$$

Thus, when there is a non-RRKM effect described by the first-order processes in Eq. (11), the time decay of the dissociating molecule is not a single exponential, but the long-time component is described by k_{RRKM} under the conditions given in Eq. (15). A similar result is expected for a larger phase space decomposition, as seen, for example, in Ref. 12 when there were three components N_1, N_2, N_3 to the phase space.^{27(b)} Implications of Eqs. (12) and (15) for time-resolved studies are discussed later.

The value of c in Eq. (12) can be shown to be given by

$$c = \frac{k_1 f_1^0 - \lambda_2}{\lambda_1 - \lambda_2}, \quad (16)$$

where $f_1^0 = N_1^0 / (N_1^0 + N_2^0)$. When $\lambda_1 \gg \lambda_2$, Eq. (12) shows that there will be a rapid initial decay of $N(t)/N(0)$, equal in amount to c . When $\lambda_1 \gg \lambda_2$, Eq. (16) yields

$$c \approx \frac{k_1}{\lambda_1} \left[f_1^0 - \frac{k_3}{k_1 + k_2 + k_3} \right]. \quad (17)$$

According to this result, c is small if $k_1 \ll \lambda_1$, and doubly small if, at the time the initial fractional population f_1^0 has its equilibrium value $k_3 / (k_2 + k_3)$. There is then roughly a single exponential decay, $\exp(-\lambda_2 t)$; a not unexpected result since the fast exponential $c \exp(-\lambda_1 t)$ in Eq. (12) then represents the preliminary intramolecular equilibration.

However, there will be some systems for which the scheme in Eqs. (11)–(15) will clearly be inapplicable. For example, in the dissociation of van der Waals' complexes $I_2 \cdots X$, where the I_2 in the complex is initially excited to a high vibrational state the distribution of the I_2 states in the products is highly nonstatistical. Frequently the transfer of even one vibrational quantum of the excited I_2 to the $I_2 \cdots X$ bond serves to rupture the latter,²⁸ so that the system never explores the total amount of phase space. That is, the scheme (11a) and (11b) is inadequate for such systems. Again, if there is in a system any significant number of nondissociating states, the scheme in (11a) and (11b) is not applicable. [The existence of quasiperiodic (trapped) trajectories is not necessarily evidence of such states.¹⁴]

IV. DISCUSSION

We consider first the final yields $P_i(\infty)$ of quantum states of products, represented by Eq. (8), and next the time evolution $P_i(t)$ represented by Eq. (10) and any non-RRKM effects given by Eqs. (12) and (16).

We have already noted the relation between the present treatment and PST: In the limit of vanishing angle-dependent interactions of the fragments the treatment based on Eqs. (4) and (7) reduces to PST. There is frequently a need for having some inclusion of the angle-dependent terms so as to explain the absolute values of the high pressure bimolecular association rate constants, which can sometimes show marked deviations from the loose transition state (PST) value.²⁹

In the presence of angle-dependent interactions, the final distribution of product states deduced from Eq. (8) and Eq. (3) or (7) may differ from that in PST: The spacing of the energy levels at R^\ddagger is larger than at $R = \infty$, since the energy levels of hindered rotations are more widely spaced than those of free rotations. Thereby, the energy drop $E - E'$ in Eq. (2), or for a given l in Eq. (4), will be greater than in PST. As a consequence, the higher rotational-vibrational states will be less accessible than they would be in PST. Thereby, the distribution of the final states is shifted to lower energies when angle-dependent terms at R^\ddagger become significant. A similar behavior has been noted for SACM.⁶

Wittig *et al.* have compared their data⁴ on the yields of

various rotational-vibrational states of the CN and NO products of the dissociation of NCNO with PST.⁵ They found excellent agreement when the excitation energy was below that leading to vibrational excitation of the products. At higher energies, the agreement was still comparatively good, though an improved agreement was obtained using some assumed modification of PST (their "SES" method).

In an experimental study⁶ of the dissociation of H_2O_2 induced by OH overtone excitation³⁰ the population of the rotational states j_i of OH was compared with PST and SACM values. Current with new experimental studies of the rates⁸ a new examination of the comparison PST, is under way.³¹ For comparison, it is planned to make a similar analysis of the experimental data using the present treatment.

We consider next the time evolution of the population $P_i(t)$ of the i th energy level. Such a time evolution was recently studied for the formation of rotational states j_i of CN in a picosecond study of the dissociation of NCNO.⁷ The formation of each was a single exponential. The rate constant for this formation differed for the two j_i 's studied.⁷ A possible explanation within the framework of statistical theory arises, but only when there is a distribution of initial E 's and J 's. In this case the time evolution of each j_i can differ from that of other j_i 's, because the integrand in Eq. (10) can peak in the vicinity of some E and J which depends upon j_i , as one sees as follows:

The initial distribution function p_{EJ}^0 can be factored into a term which is a function of the vibrational energy $E - E_J$ and independent of J , and a term dependent on J . Here, E_J denotes the initial rotational energy of the parent molecule (which depends on K , the projection of J along a body-fixed symmetry axis, but for purposes of the present illustration only we average over K). The rate constant k_{EJ} appearing in Eq. (9) increases with increasing $E - E_J$. Because of a centrifugal effect, k_{EJ} also increases with increasing J at fixed $E - E_J$. Since a larger $E - E_J$ at fixed J favors the tendency to form states of larger j_i the typical k_{EJ} in the ensemble in Eq. (9) for the states with large j_i will be higher than that for those for lower j_i 's. Moreover, at fixed $E - E_J$, very low values of J tend to discriminate against the formation of large j_i 's. Thus, the two effects can cause the position of the peak in the integrand in Eq. (9) to depend on j_i . Related effects are expected to occur in PST and SACM as well.

The time evolution of the dissociation of H_2O_2 has been studied in picosecond experiments using an excitation of the fifth OH overtone.⁸ The behavior was biexponential. One source of deviations from a single-exponential time evolution is the non-RRKM effect described in Sec. III, and we consider it now. It is seen there, assuming a particular first-order kinetic model, that the decay is the sum of exponentials, as in Eq. (12), rather than a single exponential and that under the conditions given in Eq. (15) the longest time constant for the decay is predicted to be $1/k_{RRKM}$ and the shorter one to be $k_2 + k_3$. In the case of the experiment in Ref. 8, the two time constants were approximately 600 and 60 ps.³¹ (Strictly speaking, it was not the total H_2O_2 decomposition that was monitored but rather the formation of a particular quantum state of OH.) The 600 ps could be regarded as being in the vicinity of a calculated value of $1/$

k_{RRKM} ,⁸ but, as the authors indicate, a more detailed calculation of the latter should be made, e.g., as in Ref. 13 and taking into account the range of initial E 's and J 's.

A second source of deviation from a single exponential is the possible existence of an initial distribution of E 's and J 's.

V. CONCLUDING REMARKS

In summary, equations are given for the distribution of final yields and for the time evolution of quantum states of products, using RRKM theory and an adiabatic approximation for the motion after the system leaves the transition state region [Eqs. (3), (7), (8), and (10)]. Alternative adiabatic approximations are given, according as l is or is not required to be a constant of the motion. Because of the sensitivity of k_{EJ} in the exponent in Eq. (10) to E and J , the time evolution given by Eq. (10) may provide a more sensitive test for deviations from statistical models than the final yields given by Eq. (8). Another feature of time-resolved studies, when the behavior is not a single exponential, is that they may permit a separate evaluation of RRKM and non-RRKM effects. In particular, we saw that, assuming a kinetic model and the conditions in Eq. (15), the behavior at long times can be compared with statistical theory, whereas the behavior at short times depended on the intramolecular redistribution rate. The interpretation is the less ambiguous the narrower the initial distribution of E 's and J 's.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the support of this research by the National Science Foundation and helpful discussions with my colleague, Ahmed Zewail. I am also particularly indebted to my collaborator, David Wardlaw, whose critical reading of the manuscript led to significant improvements.

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- ¹¹References to the overtone excitation work of Haas, Houston, and others are given in Ref. 5.
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- ¹⁴Some caution is needed, of course, in drawing any conclusions about the lifetimes of real dissociating molecules from classical trajectory data. A variety of quantum effects which can influence these lifetimes may occur, for example, nuclear tunneling can occur between pairs of quasiperiodic (trapped) trajectories [recent examples appear in E. L. Sibert III, J. T. Hynes, and W. P. Reinhardt, *J. Chem. Phys.* **77**, 3595 (1982); T. Uzer, D. W. Noid, and R. A. Marcus, *ibid.* **79**, 4412 (1983); and S. M. Lederman, V. Lopez, G. A. Voth, and R. A. Marcus, *Chem. Phys. Lett.* **124**, 93 (1986)], and between trapped and untrapped trajectories. A second quantum effect is the usual one associated with counting of the density of states, and a third concerns quantum implications of any apparent classical chaos, i.e., the size of the latter relative to \hbar [cf. R. A. Marcus, *Faraday Discuss. Chem. Soc.* **75**, 103 (1983), and references cited therein]. The suggested use of classical trajectories mentioned in the text involves the fate of the separating fragments after passage through the transition state, and not the lifetime of the molecule prior to reaching the transition state.
- ¹⁵See, for example, R. A. Marcus, *J. Chem. Phys.* **45**, 2630 (1966). Compare comment on this paper in the introductory section of Ref. 13(a). References to a use of this variational criterion for microcanonical ensembles by Hase, Quack, and Troe, and Garrett and Truhlar are given in Ref. 13(a) (Refs. 3 and 4 there), and a related minimum density criterion of Benker and Pattengill is also noted there. This variational approach is nowadays termed microcanonical variational transition state theory. A comprehensive recent review of applications of variational transition state theory is given in D. G. Truhlar and B. C. Garrett, *Annu. Rev. Phys. Chem.* **35**, 159 (1984).
- ¹⁶An example where l has been found, on the average, to be a good constant of the motion in trajectory calculations, even when angle-dependent terms were present, occurred for a model system HC₂ in W. L. Hase and R. J. Wolf, in *Potential Energy Surfaces and Dynamics Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981), p. 37, Table 7.
- ¹⁷This E' should not be confused with the E' notation used in Ref. 13. There, E' denoted at each R the value of $E - V_{min} - E_{zp}$, where V_{min} is the potential energy minimum at that R and E_{zp} is the zero-point energy of the conserved degrees of freedom at that R .
- ¹⁸R. A. Marcus, W. L. Hase, and K. N. Swamy, *J. Phys. Chem.* **88**, 6717 (1984).
- ¹⁹J. D. Rynbrandt and B. S. Rabinovitch, *J. Chem. Phys.* **54**, 2275 (1971).
- ²⁰For example, A. B. Trenwith, B. S. Rabinovitch, and F. C. Wolters, *J. Chem. Phys.* **76**, 1586 (1982), and references cited therein. I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.* **12**, 166 (1979).
- ²¹J. W. Perry, N. F. Scherer, and A. H. Zewail, *Chem. Phys. Lett.* **103**, 1 (1983).
- ²²The case of a biexponential decay in which the fast (a few ps) component involves a decay of quantum beats is discussed in Y. Fujimura, Y. Nomura, and T. Nakajima, *Chem. Phys. Lett.* **124**, 283 (1986).
- ²³See, for example, for a model system HC₂, W. L. Hase, R. J. Duchovic, K. N. Swamy, and R. J. Wolf, *J. Chem. Phys.* **80**, 714 (1984).
- ²⁴F. Lahmani, A. Tramer, and C. Tric, *J. Chem. Phys.* **60**, 4431 (1974).
- ²⁵M. J. Davis, *J. Chem. Phys.* **83**, 1016 (1985), who also discusses a method for finding the phase space bottleneck for intramolecular redistribution of vibrational energy.
- ²⁶The kinetic model in Ref. 20 and in D. L. Bunker, *J. Chem. Phys.* **40**, 1946 (1964) differs from that given by the present Eqs. (11)–(13), in that the energy in the former equilibrates intramolecularly in a first-order process, rather than the populations in phase space.
- ²⁷(a) More precisely, a quantity $k_{mic}(0)$ appears, instead of k_{RRKM} , in Eq. (15) of Ref. 18; $k_{mic}(0)$ is the microcanonical rate constant at zero time. However, it equals k_{RRKM} when, as assumed in transition state theory,

there is no recrossing of the transition state region by trajectories (Ref. 18). (b) In Eq. (20) of Ref. 18 the lowest eigenvalue is seen to equal k_{RRKM} , when the intramolecular rate constants k_3 and k_5 are sufficiently large, for then the reciprocals of the two larger eigenvalues in Eq. (20) there become negligible.

²⁸D. H. Levy, *Annu. Rev. Phys. Chem.* **31**, 197 (1980), and references cited therein.

²⁹For illustrative examples see C. J. Cobos and J. Troe, *J. Chem. Phys.* **83**, 1010 (1985); S. W. Benson, *Can. J. Chem.* **64**, 881 (1983); D. M. Wardlaw and R. A. Marcus, *J. Phys. Chem.* (in press). (For methyl recombination significant deviations due to angle-dependent interactions occur at high temperatures.) The effect of angle-dependent terms on high pressure recombination rate constants have been considered in numerous other ar-

ticles in the literature, for example, by Truhlar, Hase, and Bowers and their co-workers, listed in W. L. Hase and R. J. Duchovic, *J. Chem. Phys.* **83**, 3448 (1985) and in S. Mondro, S. VanderLinde, and W. L. Hase, *ibid.* **84**, 3783 (1986). A statistical-dynamical theory involving angle-dependent terms in the exit channel is given in R. A. Marcus, *J. Chem. Phys.* **62**, 1372 (1975) and in G. Worry and R. A. Marcus, *ibid.* **67**, 1636 (1977).

³⁰As already noted (Ref. 12) classical trajectory studies have also been reported for the dissociation of nonrotating H_2O_2 molecules. There were too few trajectories to characterize the lifetime distribution. It would be interesting, too, to include rotational and quantum effects. Trajectory calculations for intramolecular energy transfer in H_2O_2 have been given by B. G. Sumpter and D. L. Thompson, *J. Chem. Phys.* **82**, 4557 (1985).

³¹N. F. Scherer and A. H. Zewail (private communication).