

On the theory of unimolecular reactions: Application of mean first passage time to reaction rates^{a)}

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We apply the theory of first passage times to the process of collision free unimolecular decomposition of large molecules at a given total energy. The theory is intermediate between the dynamical and statistical theories. We find that the rate of decomposition is given in terms of a series, the leading term of which has the form used in the RRKM theory. We analyze the conditions for which this term is dominant, and find that when the molecule is large or the total energy is low or the rate of decomposition is small, our expression coincides with the phase space approach. We show that the separation of time scales (energy redistribution vs decomposition) is large when the same conditions are met. Our analysis reduces to the Montroll-Shuler model for the decomposition of a diatomic molecule in a bath of inert atoms, in the appropriate limits.

I. INTRODUCTION

The goal of the theory of unimolecular reactions¹⁻³ is to predict absolute rates of decomposition of large molecules with various energies of activation, as well as the distribution of fragments among the possible reaction channels. Although in principle a large amount of information about the molecule is required for this purpose, it is often sufficient to use phase space theories (usually the RRKM theory)¹⁻³ which simplify the description enormously. The basic idea is that the phase space is divided into distinct "molecular" and "fragment" regions with an "activated complex" in between. The complex is assumed to be in quasiequilibrium with the reactant molecule and thus the probability of finding the molecule in the "complex" configuration $p_c(E)$ is proportional to its volume in phase space:

$$p_c(E) = \frac{\rho_c(E)}{\rho_M(E)}, \quad (1)$$

where $\rho_c(E)$ and $\rho_M(E)$ are the densities of states of the complex and the molecule, respectively, with energy E . The unimolecular rate at a given energy is then

$$K(E) = v p_c(E), \quad (2)$$

where v is a velocity associated with the crossing of the complex configuration. Finally, the experimental unimolecular rate at temperature T is given by

$$K(T) = \int dE K(E) p(E), \quad (3)$$

where $p(E)$ is the probability of finding the molecule with energy E ,

$$p(E) = \rho_M(E) \exp(-\beta E) \left(\int dE \rho_M(E) \exp(-\beta E) \right)^{-1}. \quad (4)$$

The validity of the statistical theories depends heavily on the assumption that the fragmentation (reaction) process is much slower than the relaxation rate of the in-

ternal degrees of freedom. If the assumption holds then the distribution of energy among the internal molecular states is not affected by the slow fragmentation and the population of the complex configuration can be calculated with equilibrium statistical mechanics. This is the meaning of Eqs. (1) and (2).

RRKM theory has been widely applied to a large number of systems.^{1,2} It is often capable of predicting orders of magnitude of rates as well as product state distributions. In recent years there have been developed some new experimental techniques which provide detailed information regarding the behavior of unimolecular reactions. These techniques include chemical activation experiments,⁴ molecular beam studies,⁵ and infrared chemiluminescence.⁶ They showed in several cases serious deviations from statistical behaviors. Another area which has been developed in recent years and which provides much information regarding unimolecular behavior is that of multiphoton molecular processes.⁷ In these experiments molecules are being driven by strong infrared laser fields up to dissociation under collision free conditions. Here there may occur deviation from statistical behavior when the laser field is strong enough to compete with intramolecular relaxations.

In this paper we make use of the theory of stochastic processes⁸⁻¹⁰ to describe the energy randomization and dissociation of a large molecule. The stochastic level of discussion is simpler and less detailed than the level of complete dynamical solution. It is intermediate between the statistical and full dynamical treatments. It allows us to introduce to the theory a desired amount of dynamical information, as well as nonequilibrium effects.

We choose a single molecular degree of freedom to be the "relevant" part associated directly with the decomposition. The rest of the molecular degrees of freedom are assumed to be weakly correlated with the dynamics of the decomposition. We choose a stochastic model for the populations of the various levels of the relevant mode and estimate the rate of decomposition using the method of mean first passage time. The model is applicable to chemical activation⁴ and multiphoton studies⁷ where an "initial" state of the relevant

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mode may be obtained. For applying the model to thermally activated reactions one has to add the dynamics of energy changing collisions. Our main goals are as follows:

(1) To present a stochastic formulation of unimolecular reactions which contains dynamical information in the form of transition probabilities.

(2) To use the mean first passage time concept¹¹ for estimating the following time scales: (a) the time scale for energy redistribution (τ_r) within the molecule after some specific preparation, and (b) the time scale for dissociation (τ_d). The result for τ_d , in the form of a series, shows that when some conditions are met (such as no bottleneck in the dynamics of the system), one of the terms in the series becomes the leading one and is in the form of the RRKM result. We derive, however, closed expressions for the rest of the series, and we can analyze the conditions for which the leading term becomes the dominant one.

(3) To show that the assumption of the separation of these two time scales is strongly linked with the conditions that cause the leading term in the expansion mentioned in (2) to become dominant. In other words, we show that subject to the same conditions $\tau_d/\tau_r \ll 1$. The meaning of this is that irrespective of the way in which the molecule is prepared, it undergoes a rapid intramolecular energy randomization prior to the decomposition. Intuitively, this is of course consistent with the picture underlying the phase space theories.

II. THE MEAN FIRST PASSAGE TIME

A stochastic description of physical phenomena may be applied whenever we are interested in partial information regarding the dynamics of a large system. We thus define our variables of interest (which do not specify completely the state of the system) and describe their temporal evolution using a stochastic master equation. The concept of "first passage time" is useful whenever we deal with a stochastic process on a space Q that can be decomposed into two nonoverlapping subspaces V and \bar{V} , $V + \bar{V} = Q$. The initial condition is that the stochastic random variable is in V , and the first passage time is defined as the time elapsing before passage to \bar{V} for the first time. We now denote the probability that the random variable is still in V at time t (given that it started at some point y) by $p_v(y, t)$,

$$p_v(y, t) = \int_V p(x, t) dx. \quad (5)$$

Let the passage time be T ; $\eta(y, t) dt$ is the probability that $t < T < t + dt$ given that the motion started at y . Obviously,¹¹

$$\eta(y, t) = -\frac{\partial p_v(y, t)}{\partial t}. \quad (6)$$

The mean first passage time is the average (first moment) of this distribution

$$\langle T \rangle = \int_0^\infty t \eta(y, t) dt = \int_0^\infty p_v(y, t) dt, \quad (7)$$

where the last step is achieved by integration by parts.

Suppose now that we have a discrete stochastic model on the energy levels of, say, a molecular mode. Let us assume further that it is a nearest neighbor model confined to the levels 0 to N , where N can be a dissociative level. Then the stochastic equations can be written generally as

$$\begin{aligned} \dot{p}_0 &= L_{10} p_1 - L_{01} p_0, \\ \dot{p}_1 &= L_{01} p_0 - (L_{10} + L_{12}) p_1 + L_{21} p_2, \\ \dot{p}_2 &= L_{12} p_1 - (L_{21} + L_{23}) p_2 + L_{32} p_3, \\ &\vdots \\ \dot{p}_N &= L_{N-1, N} p_{N-1} - (L_{N, N-1} + L_{N, N+1}) p_N. \end{aligned} \quad (8)$$

In such a scheme the state 0 is called a reflecting barrier (meaning that $L_{0,-1} = 0$) and N is an absorbing barrier (meaning that $L_{N, N+1}$ exists, whereas $L_{N+1, N} = 0$). Thus as $t \rightarrow \infty$ all the population is absorbed in the $N+1$ state. Clearly, in this case¹¹

$$p_v(t) = p_0(t) + p_1(t) + \cdots + p_N(t), \quad (9)$$

where $p_j(t)$ are the solutions of Eqs. (8) with the initial condition $p_j(0) = \delta_{j,r}$ and

$$\langle T(N, r) \rangle = \int_0^\infty [p_0(t) + p_1(t) + \cdots + p_N(t)] dt \quad (10)$$

is the mean first passage time for the system initially at the r th level to escape through the absorbing barrier N . The general expression for $\langle T(N, r) \rangle$ is derived in Appendix A and follows the recent work by Oppenheim, Shuler, and Weiss.¹²

In the next section we apply the concept of mean first passage time to the unimolecular decomposition of a large molecule under collision-free conditions. The mean first passage time furnishes information only about the rate of decomposition. It is not directly connected with the distribution of nascent products. The advantage of the concept is in the simplicity of the calculation and the transparency of the results.

III. THE DYNAMICS OF UNIMOLECULAR DECOMPOSITION

A stochastic treatment of chemical reactions was first done by Kramers¹³ and has since been studied extensively.¹⁴ The first application of the mean first passage time to unimolecular decomposition was the Montroll-Shuler model¹⁵ for the decomposition of a truncated harmonic oscillator. They used the Landau-Teller transition probabilities to evaluate the mean first passage time for its dissociation. They further discussed the question of conditions for the mean first passage time to coincide with the dissociation rate obtained from phase space considerations.

We consider here a polyatomic molecule with $s+1$ modes. We focus our attention on one of the modes involved in the dissociation and consider the stochastic process of transition between the levels of that mode induced by the intramolecular couplings to the other s modes. The dissociating mode can be a normal mode or preferably a local (bond) mode.¹⁶

$$\begin{aligned}
\chi_{r+1} &= \frac{1}{L_{N,N+1}} \left(\frac{\epsilon - \gamma - 1}{\epsilon - N} \right)^{s-1} + \frac{1}{L_{N-1,N}} \left(\frac{\epsilon - \gamma - 1}{\epsilon - N + 1} \right)^{s-1} + \cdots + \frac{1}{L_{r+1,r+2}} \left(\frac{\epsilon - \gamma - 1}{\epsilon - \gamma - 1} \right)^{s-1} + 0, \\
\chi_{r+2} &= \frac{1}{L_{N,N+1}} \left(\frac{\epsilon - \gamma - 2}{\epsilon - N} \right)^{s-1} + \frac{1}{L_{N-1,N}} \left(\frac{\epsilon - \gamma - 2}{\epsilon - N + 1} \right)^{s-1} + \cdots + 0 + 0, \\
&\vdots \\
\chi_N &= \frac{1}{L_{N,N+1}} \left(\frac{\epsilon - N}{\epsilon - N} \right)^{s-1} + 0 + \cdots + 0 + 0.
\end{aligned} \tag{25}$$

The summation is now performed on the columns instead of on the rows. Thus, we represent $\langle T(r, N) \rangle$ as a sum on terms, each of which is a summation of a column of the matrix (25):

$$\langle T(r, N) \rangle = \sum_{k=0}^{N-r} A_k, \tag{26}$$

$$\begin{aligned}
A_k &= \frac{1}{L_{N-k, N-k+1}} \sum_{l=0}^{N-k} \frac{\theta_l}{\theta_{N-k}} = \frac{1}{L_{N-k, N-k+1}} \sum_{l=0}^{N-k} \left(\frac{\epsilon - l}{\epsilon - N + k} \right)^{s-1} \\
&= \frac{1}{F(n)} \sum_{l=0}^{N-k} \left(\frac{\epsilon - l}{\epsilon - N + k - 1} \right)^{s-1}.
\end{aligned} \tag{27}$$

The first term in this series, A_0 , is

$$A_0 = \frac{1}{L_{N, N+1}} \left(\frac{1}{\epsilon - N} \right)^{s-1} \sum_{l=0}^N (\epsilon - l)^{s-1}, \tag{28}$$

which can be written in the form

$$A_0 = \frac{1}{L_{N, N+1}} \frac{\rho_T(E)}{\rho(N, E)}, \tag{29}$$

where

$$\rho_T(E) = \sum_{l=0}^N \rho(l, E). \tag{30}$$

A_0^{-1} is thus the statistical expression for the unimolecular rate constant.²²

We further note that A_0 is independent of r , i.e., the starting point for the stochastic process. This is consistent with the assumption underlying the RRKM theory that intramolecular equilibrium occurs prior to the dissociation, so that the dissociation rate is independent of the initial state of the molecule. A_0 is also independent of the absolute values of the transition probabilities $[F(n)]$ in Eqs. (17)] but depends only on their ratios G_n (21) (and, of course, on $L_{N, N+1}$). This is again in accord with the RRKM assumptions, as $F(n)$ determines how the molecule approaches its steady state—a question which is immaterial once we assume that the molecule is in equilibrium.

From Eqs. (26) and (27) we see that if all the $L_{j, j+1}$ are of the same order of magnitude, A_0 is the largest term in the sum. This arises since (i) A_0 contains the largest number of positive terms; (ii) the denominator in all these terms, $1/(\epsilon - N + k)$, is the smallest for $k=0$.

On the other hand, it is also clear that in general there is not any reason for the largest term A_0 to be much larger than the following terms, or for the series (26) to be quickly converging. However, having explicit

expressions for the other terms (A_k , $k \neq 0$) in this formulation, we can now state some conditions that insure that $A_0 \gg \sum_{k=1}^{N-r} A_k$, i.e., conditions for the applicability of the statistical theory. These conditions are as follows:

(i) s is very large and all the transition probabilities $L_{j, j+1}$ are comparable. In this case the ratio between a typical term in A_0 to a typical term in A_k ($k \neq 0$) is $0[(\epsilon - N + k)/(\epsilon - N)]^{s-1} \gg 1$, which causes A_0 to be the dominant term in the expansion (26).

(ii) $\epsilon \approx N$ or $\epsilon - N \approx 0$, that is, the absorbing barrier has an energy comparable to the total available energy. In this case A_0 is dominant.

(iii) $L_{N, N+1} \ll L_{j, j+1}$ for every j . This condition is intuitively appealing because it means that the motion is almost trapped in the space $0 - N$ and the levels equilibrate before the decomposition. The consistency with a statistical approach is obvious.

A direct way of assessing this "trapping" of the motion is provided by considering the time scales that are involved in the evolution of the system. In the next section we show that the conditions for A_0 to be dominant are the same as those for a separation of time scales in the stochastic evolution.

B. Separation of time scales

The observation that the starting point r as well as the details of the stochastic transition probabilities $[F(n)]$ do not appear in the leading term (A_0) of the passage time strongly suggests that when the leading term is indeed dominant there is also a separation of time scales. Whatever the starting point, on a short time scale the system approaches internal equilibrium and only on longer time scales does a diffusion towards the absorbing barrier lead to decomposition. To demonstrate that this is indeed the case, we consider here the mean first passage time for sliding down and arriving at the level 0, starting at an arbitrary point r . This time is a measure for the rate of equilibration. The calculation is similar to the previous one, except that now the state 0 is absorbing and N is reflecting. As in the previous analysis, we use Eq. (A29) and get the expression

$$\langle T(r, 0) \rangle = \sum_{k=1}^r \tilde{A}_k, \tag{31}$$

where

$$\bar{A}_k = \frac{1}{L_{k,k-1}} \sum_{l=k}^N \frac{\bar{\theta}_l}{\bar{\theta}_k}, \quad (32)$$

and where $\bar{\theta}_j$ is defined by (A20).

It is easy to verify that all the ratios of $\bar{\theta}$'s in Eq. (32) are smaller than 1. Thus we can bound the passage time for sliding down very easily by taking the minimal value of L as L_{\min} and substituting 1 for all the ratios of θ 's. Thus

$$\langle T(r, 0) \rangle < \frac{1}{L_{\min}} \left((N+1)r - \frac{(n+1)r}{2} \right). \quad (33)$$

Actually an even cruder bound is sufficient; r can be as big as N and the negative term can be rejected, so that then

$$\langle T(r, 0) \rangle < \frac{N(N+1)}{L_{\min}}. \quad (34)$$

We found in the previous section that the passage time to reach N is bounded from below

$$\langle T(r, N) \rangle > \frac{1}{L_{N,N+1} p_N} \quad (35)$$

and thus

$$\frac{\langle T(r, N) \rangle}{\langle T(r, 0) \rangle} > \frac{L_{\min}}{L_{N,N+1} p_N N(N+1)}. \quad (36)$$

Clearly, the conditions that make this ratio large are that either $L_{N,N+1} \ll L_{\min}$ or that p_N is very small. The last condition is met if s , the number of modes, is very large, or if $\epsilon \approx N$. Thus we see that the same conditions that guarantee a separation of time scales guarantee that A_0 is the dominant term in the series (26). When

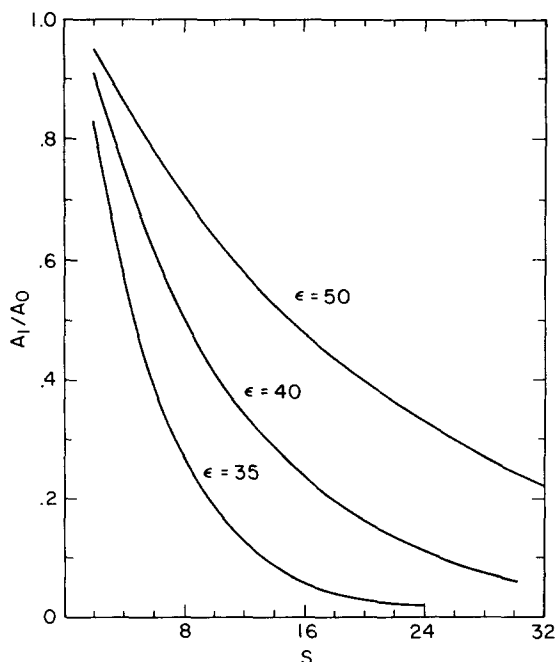


FIG. 1. The ratio of the second to first term in the expansion (26), as a function of the number of molecular modes. As the molecule becomes larger, the first term becomes dominant. When the total energy (ϵ) of the molecule increases, the importance of the correction terms increases.

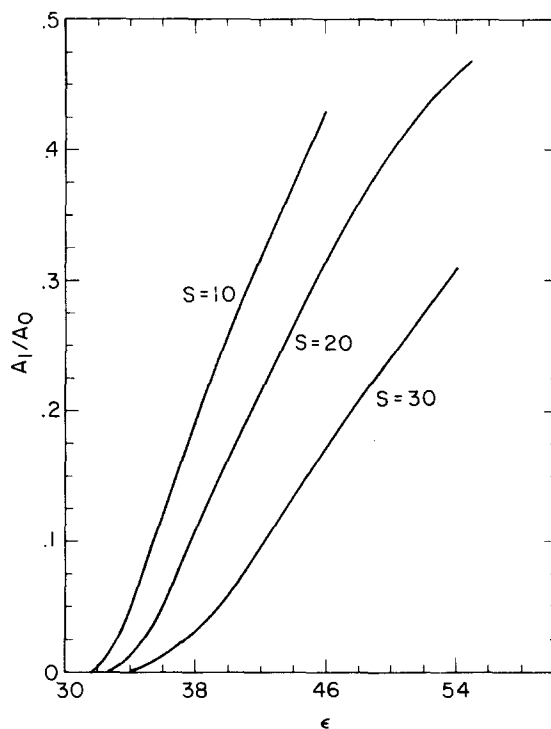


FIG. 2. The ratio of the second to first terms in the expansion (26) as a function of total energy (ϵ). As the energy is lowered, the first term becomes dominant. An increase in the size of the molecules (s) reduces the effect of increasing energy.

($T(r, N) \gg T(r, 0)$), we see that the leading term in the MFPT is independent of the starting point r and of $F(n)$. Provided these conditions hold, on short time scales the system equilibrates in the given mode and forgets its initial state before starting the decomposition process. We note, however, that our general expression (26) does depend on r and $F(n)$ and we have here simple correction terms for the RRKM expressions, which depend on the nature of the initial preparation and on the details of the stochastic model.

It is useful to give some estimations of the magnitude of the correction terms to A_0 . As an example consider a situation where the reduced energy of the molecule is $\epsilon = 30$ and the reduced energy necessary for dissociation is $N = 20$. The ratio of every two terms in A_1 and A_0 (except for the last, of course) is [see (25)] $[(\epsilon - N)/(\epsilon - N + 1)]^{s-1} (L_{N,N+1}/L_{N-1,N})$. If $L_{N,N+1} \approx L_{N-1,N}$ this ratio is $\sim (10/11)^{s-1}$. We can ask what is the value of s for which A_1 is less than 10% of A_0 . We find that $s \approx 20$ is sufficient to insure this. For $s = 15$, A_1 is still some 25% of A_0 . If ϵ is lower (say, 25), then $s = 13$ is sufficient to guarantee that A_1 is about 10% of A_0 . On the other hand, if ϵ is 40 we need s to be as big as 50 to guarantee the same thing. Obviously if $L_{N,N+1}$ is much smaller than $L_{N-1,N}$, A_0 is dominant even for quite small molecules.

These considerations are summarized graphically in Figs. 1 and 2. Figure 1 shows A_1/A_0 for a given activation and total energy as a function of s .

As ϵ is increased compared to N , s must be increased in order to guarantee that A_0 is indeed appreciably

larger than A_1 . Figure 2 shows the same ratio A_1/A_0 for a given molecule with fixed s and N , as a function of the total energy. The smaller s is, the greater the influence of increasing the total energy on the ratio A_1/A_0 .

C. Reduction to the Montroll-Shuler model

The derivation of the master equation (Appendix B) depends on the fact that s is sufficiently large, so that when we focus our attention on one mode, the rest of the molecule can be treated as a "bath." If we let s now grow indefinitely, while fixing the amount of energy per mode, we should recapture the picture of a harmonic oscillator dissociating through a coupling to a heat bath. In other words, if we take the limit $s \rightarrow \infty$, $\epsilon \rightarrow \infty$ and $\epsilon/s = 1/\beta\omega$, where $\beta = 1/kT$, we should obtain from our model the results of Montroll and Shuler.¹⁵ The limit guarantees that the bath is so large that it is unaffected by the state of the system. Consider then a typical ratio that appears in the previous formulation,

$$\frac{\theta_i}{\theta_j} = \left(\frac{\epsilon - i}{\epsilon - j} \right)^{s-1} = \left(1 + \frac{j-i}{\epsilon - j} \right)^{s-1}. \quad (37)$$

Using the equipartition we can write $\epsilon = s/\beta\omega$ and take the limit specified above,

$$\lim_{\substack{s \rightarrow \infty \\ \epsilon \rightarrow \infty \\ s/\epsilon = \beta\omega}} \frac{\theta_i}{\theta_j} = \left\{ \left[1 + \frac{1}{(j-i)\beta\omega} \right] \frac{s}{(j-i)\beta\omega} \right\}^{(j-i)\beta\omega} \\ = \exp[(j-i)\beta\omega]. \quad (38)$$

This result can be used in Eq. (26) for the mean first passage time,

$$\langle T(r, N) \rangle = \sum_{k=0}^{N-r} A_k. \quad (39)$$

Choosing $F(n) = n + 1$ as in the Landau-Teller dynamics, A_k is transformed to

$$A_k = \frac{1}{N-k+1} \sum_{l=0}^{N-k} \exp[(N-k-l)\beta\omega] \\ = \frac{1}{N-k+1} \frac{\exp[\beta\omega(N-k+1)] - 1}{\exp(\beta\omega) - 1}. \quad (40)$$

Changing indices in the summation (40) we get

$$\langle T(r, N) \rangle = \sum_{l=r+1}^{N+1} \frac{\exp(-\beta\omega)}{l} \frac{\exp(\beta\omega l) - 1}{1 - \exp(-\beta\omega)}. \quad (41)$$

This result coincides with the expression obtained by Montroll and Shuler,¹⁵ who derived it using Landau-Teller dynamics. This agreement is an example of a more general observation²³ that the ratio of transition probabilities G_j contains a large amount of information on the time scales involved in a stochastic problem.

We note that when the term with $l = N + 1$ in (41) is the leading term we recover the phase space result

$$\langle T(r, N) \rangle = \frac{1}{N+1} \frac{\exp(\beta\omega N)}{1 - \exp(-\beta\omega)}. \quad (42)$$

III. DISCUSSION

We have presented a stochastic model for unimolecular reactions which consists of the following steps:

(1) We focus our attention on a single molecular mode and describe the time evolution of its levels using a stochastic master equation. The stochastic transition probabilities (17) contain two kinds of information: the ratios $G_j = L_{j,j+1}/L_{j+1,j}$ are determined by the equilibrium state of the molecule whereas the absolute value of the transition probabilities [$F(n)$ in (27)] is additional information on how internal equilibrium is achieved.

(2) The formalism of mean first passage time is then used to evaluate the rate of redistribution of energy among the molecular states and the rate of unimolecular decomposition.

(3) The general result for the rate of unimolecular reaction is a sum of many terms. The first term (A_0) is independent of the initial state of the molecule and of the details of the stochastic model (F_n). This term is equal to the result of statistical theories.

(4) Under certain limiting conditions (large molecule, low energy, low rate of dissociation) the first term (A_0) becomes dominant and we recover the RRKM result. We note also that under the same conditions there is a separation of time scales in the problem, i.e., the time scale for intramolecular relaxation becomes very short compared to the unimolecular rate. This is again consistent with the RRKM assumptions.

(5) When the molecule becomes very large, it acts as a heat bath on the relevant mode and our expressions reduce to those of Montroll and Shuler.

The present model allows us to discuss the limitations of statistical theories of unimolecular reactions and provides explicit expressions for correction terms when these theories are not applicable.^{3-6,23} The model also enables us, through the explicit dependence on r and $F(n)$, to incorporate dynamical information regarding the "preparation" stage of the activated molecule and the transition probabilities. Thus it is particularly useful for experiments such as chemical activation or multiphoton processes and laser chemistry in which much information is available.

Finally, we wish to comment on the problem of ergodicity in unimolecular reactions. The treatment presented above assumes tacitly that all the transition probabilities $L_{j,j+1}$ (except for $L_{N,N+1}$, perhaps) are comparable in magnitude. Thus there are no disconnected subspaces in the molecular phase space. This assumption is not necessarily valid and we may imagine one transition probability, say, $L_{p,p+1}$, to be very small. Thus the motion on the subspaces $[0, p]$ and $[p+1, N]$ are effectively uncoupled. The role of A_0 as a leading term is lost now, and from (26) and (27) we see that A_p may become the leading or the dominant term. Thus we see that it is possible to assess problems of non-ergodicity by identifying an appropriate term in the expansion (26).

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APPENDIX A: CLOSED EXPRESSIONS FOR THE MEAN FIRST PASSAGE TIME

We start with the birth and death master equation:

$$\begin{aligned} \frac{d p_0}{d t} &= L_{10} p_1 - L_{01} p_0, \\ \frac{d p_1}{d t} &= L_{01} p_0 - (L_{10} + L_{12}) p_1 + L_{21} p_2, \\ &\vdots \\ \frac{d p_N}{d t} &= L_{N-1, N} p_{N-1} - (L_{N, N-1} + L_{N, N+1}) p_N, \end{aligned} \quad (\text{A1})$$

where the state 0 is a reflecting barrier whereas the state N is absorbing. We wish to evaluate the mean first passage time $\langle T(r, N) \rangle$ for a system started at a state r to arrive at the state N .

$\langle T(r, N) \rangle$ is given by¹¹

$$\langle T(r, N) \rangle = \sum_{j=0}^N P_j^*(0), \quad (\text{A2})$$

where

$$P_j^*(s) = \int_0^\infty d\tau p_j(\tau) \exp(-s\tau). \quad (\text{A3})$$

Here $p_j(\tau)$ are the solutions of Eqs. (A1) with the initial conditions $p_j(0) = \delta_{j,r}$ and $p_j^*(s)$ are their Laplace transforms. Performing a Laplace transformation on (A1) and substituting $s=0$, we get the following equations for P_j^* :

$$\begin{aligned} L_{01} P_0^* &= L_{10} P_1^*, \\ (L_{10} + L_{12}) P_1^* &= L_{01} P_0^* + L_{21} P_2^*, \\ (L_{r, r-1} + L_{r, r+1}) P_r^* &= L_{r-1, r} P_{r-1}^* + L_{r+1, r} P_{r+1}^* + 1, \\ (L_{N, N-1} + L_{N, N+1}) P_N^* &= L_{N-1, N} P_{N-1}^*. \end{aligned} \quad (\text{A4})$$

Equations (A4) are now solved recursively. We first define

$$\begin{aligned} P_j^* &= \theta_j P_0^* \quad j=0, 1, \dots, r, \\ P_j^* &= \theta_j P_0^* - \eta_j \quad j=r+1, r+2, \dots, N, \end{aligned} \quad (\text{A5})$$

where θ_j, η_j will be determined by the equations. The first r equations are satisfied if we choose

$$\theta_0 = 1,$$

$$\theta_j = G_0 G_1 \cdots G_{j-1}, \quad (\text{A6})$$

where

$$G_j \equiv \frac{L_{j, j+1}}{L_{j+1, j}}. \quad (\text{A7})$$

The $r+1$ st equation gives

$$\eta_{r+1} = \frac{1}{L_{r+1, r}}. \quad (\text{A8})$$

If we proceed to the next equation we see that the η 's satisfy the equations

$$\begin{aligned} L_{j+1, j} \eta_{j+1} &= (L_{j, j-1} + L_{j, j+1}) \eta_j - L_{j-1, j} \eta_{j-1}, \\ j &= r, r+1, \dots, \end{aligned} \quad (\text{A9})$$

which results in the following general expression for the η 's:

$$\begin{aligned} \eta_{r+k} &= \frac{1}{L_{r+k, r+k-1}} \left(1 + \frac{L_{r+k-1, r+k}}{L_{r+k-1, r+k-2}} \right. \\ &\quad \left. + \frac{L_{r+k-1, r+k} L_{r+k-2, r+k-1}}{L_{r+k-1, r+k-2} L_{r+k-2, r+k-3}} + \frac{L_{r+k-1, r+k} L_{r+k-2, r+k-1} L_{r+k-3, r+k-2}}{L_{r+k-1, r+k-2} L_{r+k-2, r+k-3} L_{r+k-3, r+k-4}} \cdots \right). \end{aligned} \quad (\text{A10})$$

Equation (A9) can be rearranged to yield

$$\eta_{r+k} = \frac{1}{L_{r+k-1, r+k}} \frac{\theta_{r+k}}{\theta_{r+k-1}} + \frac{1}{L_{r+k-2, r+k-1}} \frac{\theta_{r+k}}{\theta_{r+k-2}} + \cdots + \frac{1}{L_{r, r+1}} \frac{\theta_{r+k}}{\theta_r} \quad (\text{A11})$$

for every $k=1, 2, \dots, N-r$.

P_0^* is determined by the last equation,

$$(L_{N, N-1} + L_{N, N+1})(\theta_N P_0^* - \eta_N) = L_{N-1, N}(\theta_{N-1} P_0^* - \eta_{N-1}), \quad (\text{A12})$$

i. e.,

$$\begin{aligned} (L_{N, N-1} + L_{N, N+1}) \theta_{N-1} \frac{L_{N-1, N}}{L_{N, N-1}} P_0^* - L_{N-1, N} \theta_{N-1} P_0^* \\ = (L_{N, N-1} + L_{N, N+1}) \eta_N - L_{N-1, N} \eta_{N-1}; \end{aligned} \quad (\text{A13})$$

but the rhs of Eq. (A12) is exactly equal to $L_{N+1, N} \eta_{N+1}$ [see Eq. (A9)] and thus we get

$$P_0^* = \frac{\eta_{N+1}}{\theta_{N+1}}. \quad (\text{A14})$$

Our expression for $\langle T \rangle$, Eq. (A2), can be now rearranged [using (A5)] to the form

$$\langle T(r, N) \rangle = \sum_{j=0}^r \frac{\eta_{N+1}}{\theta_{N+1}} \theta_j + \sum_{j=r+1}^N \left(\frac{\eta_{N+1}}{\theta_{N+1}} \theta_j - \eta_j \right). \quad (\text{A15})$$

Let us consider now each sum in (A15) separately. Define ψ_j ,

$$\begin{aligned} \psi_j &= \frac{\eta_{N+1}}{\theta_{N+1}} \theta_j = \frac{1}{L_{N+1, N}} \frac{1}{G_N G_{N-1} \cdots G_j} + \frac{1}{L_{N, N-1}} \frac{1}{G_{N-1} \cdots G_j} + \frac{1}{L_{N-1, N-2}} \frac{1}{G_{N-2} G_{N-3} \cdots G_j} + \cdots + \frac{1}{L_{r+1, r}} \frac{1}{G_r G_{r-1} \cdots G_j} \\ &= \frac{1}{L_{N+1, N}} \frac{\theta_j}{\theta_{N-1}} + \frac{1}{L_{N, N-1}} \frac{\theta_j}{\theta_N} + \cdots + \frac{1}{L_{r+1, r}} \frac{\theta_j}{\theta_{r+1}} = \frac{1}{L_{N, N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1, N}} \frac{\theta_j}{\theta_{N-1}} + \cdots + \frac{1}{L_{r, r+1}} \frac{\theta_j}{\theta_r} \quad j=0, 1, \dots, r, \end{aligned} \quad (\text{A16})$$

and define χ_j ,

$$\begin{aligned}\chi_j &= \frac{\eta_{N+1}}{\theta_{N+1}} \theta_j - \eta_j \quad j = r+1, \dots, r \\ &= \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \dots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r} - \frac{1}{L_{j-1,j}} \frac{\theta_j}{\theta_{j-1}} \frac{1}{L_{j-2,j-1}} \frac{\theta_j}{\theta_{j-2}} + \dots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r} \\ &= \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \dots + \frac{1}{L_{j,j+1}} \frac{\theta_j}{\theta_j}.\end{aligned}\quad (\text{A17})$$

Our final expression is thus

$$\langle T(r, N) \rangle = \sum_{j=0}^r \psi_j + \sum_{j=r+1}^N \chi_j, \quad (\text{A18})$$

$$\psi_j = \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \dots + \frac{1}{L_{r,r+1}} \frac{\theta_j}{\theta_r}, \quad (\text{A18}')$$

$$\chi_j = \frac{1}{L_{N,N+1}} \frac{\theta_j}{\theta_N} + \frac{1}{L_{N-1,N}} \frac{\theta_j}{\theta_{N-1}} + \dots + \frac{1}{L_{j,j+1}} \frac{\theta_j}{\theta_j}. \quad (\text{A18}'')$$

If we consider now the reverse problem in which the state 0 is absorbing and N reflecting we have

$$\langle T(r, 0) \rangle = \frac{\bar{\eta}_0}{\bar{\theta}_0} \sum_{j=0}^N \bar{\theta}_j - \sum_{j=0}^{r-1} \bar{\eta}_j, \quad (\text{A19})$$

where

$$\bar{\theta}_N = 1, \quad \bar{\theta}_j = \frac{1}{G_{N-1} \dots G_j}, \quad (\text{A20})$$

$$\bar{\eta}_{r-k} = \frac{1}{L_{r-k,r-k+1}} \left(1 + \frac{L_{r-k+1,r-k}}{L_{r-k+1,r-k+2}} + \dots + \frac{L_{r-k+1,r-k} \dots L_{r-1,r-2}}{L_{r-k+1,r-k+2} \dots L_{r-1,r}} \right), \quad (\text{A21})$$

$$\begin{aligned}\bar{\eta}_{r-k} &= \frac{1}{L_{r-k+1,r-k}} \frac{1}{G_{r-k}} + \frac{1}{L_{r-k+2,r-k+1}} \frac{1}{G_{r-k} G_{r-k+1}} + \dots + \frac{1}{L_{r,r-1}} \frac{1}{G_{r-k} G_{r-k+1} \dots G_{r-1}} \\ &= \frac{1}{L_{r-k+1,r-k}} \frac{\bar{\theta}_{r-k}}{\bar{\theta}_{r-k+2}} + \frac{1}{L_{r-k+2,r-k+1}} \frac{\bar{\theta}_{r-k}}{\bar{\theta}_{r-k+2}} + \dots + \frac{1}{L_{r,r-1}} \frac{\bar{\theta}_{r-k}}{\bar{\theta}_r}.\end{aligned}\quad (\text{A22})$$

We rearrange Eq. (A19) and write it in the form

$$\langle T(r, 0) \rangle = \sum_{j=0}^{r-1} \bar{\chi}_j + \sum_{j=r}^N \bar{\psi}_j, \quad (\text{A23})$$

where

$$\begin{aligned}\bar{\chi}_j &= \frac{\bar{\eta}_0}{\bar{\theta}_0} \bar{\theta}_j - \bar{\eta}_j, \\ \bar{\psi}_j &= \frac{\bar{\eta}_0}{\bar{\theta}_0} \bar{\theta}_j.\end{aligned}\quad (\text{A24})$$

Using Eq. (A22) we have

$$\bar{\eta}_0 = \frac{1}{L_{1,0}} \frac{1}{G_0} + \frac{1}{L_{2,1}} \frac{1}{G_0 G_1} + \dots + \frac{1}{L_{r,r-1}} \frac{1}{G_0 G_1 \dots G_{r-1}}. \quad (\text{A25})$$

Thus we get

$$\begin{aligned}\frac{\bar{\eta}_0}{\bar{\theta}_0} &= \frac{1}{L_{10}} G_{N-1} G_{N-2} \dots G_1 + \frac{1}{L_{21}} G_{N-1} \dots G_2 \\ &\quad + \dots + \frac{1}{L_{r,r-1}} G_{N-1} G_{N-2} \dots G_r.\end{aligned}\quad (\text{A26})$$

Substituting (A26) and (A20) in (A24) results in

$$\bar{\psi}_j = \frac{1}{L_{10}} \frac{\bar{\theta}_j}{\bar{\theta}_1} + \frac{1}{L_{21}} \frac{\bar{\theta}_j}{\bar{\theta}_2} + \dots + \frac{1}{L_{r,r-1}} \frac{\bar{\theta}_j}{\bar{\theta}_r}. \quad (\text{A27})$$

Similarly, from (A26), (A20), (A22), and (A24) we get

$$\begin{aligned}\bar{\chi}_j &= \frac{\bar{\eta}_0}{\bar{\theta}_0} \bar{\theta}_j - \bar{\eta}_j \\ &= \left(\frac{1}{L_{10}} \frac{\bar{\theta}_j}{\bar{\theta}_1} + \frac{1}{L_{21}} \frac{\bar{\theta}_j}{\bar{\theta}_2} + \dots + \frac{1}{L_{r,r-1}} \frac{\bar{\theta}_j}{\bar{\theta}_r} \right) \\ &\quad - \left(\frac{1}{L_{j+1,j}} \frac{\bar{\theta}_j}{\bar{\theta}_{j+1}} + \frac{1}{L_{j+2,j+1}} \frac{\bar{\theta}_j}{\bar{\theta}_{j+2}} + \dots + \frac{1}{L_{r,r-1}} \frac{\bar{\theta}_j}{\bar{\theta}_r} \right) \\ &\equiv \frac{1}{L_{10}} \frac{\bar{\theta}_j}{\bar{\theta}_1} + \frac{1}{L_{21}} \frac{\bar{\theta}_j}{\bar{\theta}_2} + \dots + \frac{1}{L_{j,j-1}} \frac{\bar{\theta}_j}{\bar{\theta}_j}.\end{aligned}\quad (\text{A28})$$

Our final result is thus

$$\langle T(r, 0) \rangle = \sum_{j=1}^{r-1} \bar{\chi}_j + \sum_{j=r}^N \bar{\psi}_j, \quad (\text{A29})$$

$$\bar{\chi}_j = \frac{1}{L_{10}} \frac{\bar{\theta}_j}{\bar{\theta}_1} + \frac{1}{L_{21}} \frac{\bar{\theta}_j}{\bar{\theta}_2} + \dots + \frac{1}{L_{j,j-1}} \frac{\bar{\theta}_j}{\bar{\theta}_j}, \quad (\text{A29}')$$

$$\bar{\psi}_j = \frac{1}{L_{10}} \frac{\bar{\theta}_j}{\bar{\theta}_1} + \frac{1}{L_{21}} \frac{\bar{\theta}_j}{\bar{\theta}_2} + \dots + \frac{1}{L_{r,r-1}} \frac{\bar{\theta}_j}{\bar{\theta}_r}. \quad (\text{A29}'')$$

APPENDIX B: DERIVATION OF THE MASTER EQUATION: TETRADIC FORMALISM

The tetradic analogue \tilde{u} of an ordinary operator u is defined by its action on an ordinary operator A as¹⁴

$$\tilde{u} \cdot A \equiv [u, A], \quad (\text{B1})$$

which may be written in the form

$$\begin{aligned}
 (\tilde{u}A)_{ij} &\equiv \sum_{kl} \tilde{u}_{ij,kl} A_{kl} \\
 &\equiv \sum_{kl} \langle\langle ij | \tilde{u} | kl \rangle\rangle \langle k | A | l \rangle. \quad (B2)
 \end{aligned}$$

Comparison of Eqs. (B1) and (B2) results in

$$\tilde{u}_{ij,kl} = u_{ik} \delta_{jl} - u_{jl}^* \delta_{ik}. \quad (B3)$$

Formally we can expand any tetradic operator in the form

$$\tilde{u} = \sum_{ijkl} |ij\rangle\langle ij| \tilde{u}_{ij,kl} \langle kl|. \quad (B4)$$

Thus, $|ij\rangle$ denotes a "state" in Liouville space, whereas $|ij\rangle\langle kl|$ represents a tetradic operator. The "scalar product" in this space is defined as

$$\langle\langle ij | kl \rangle\rangle = \text{Tr}(|j\rangle\langle i| |k\rangle\langle l|) = \delta_{ik} \delta_{jl}, \quad (B5)$$

where $i, j, k,$ and l belong to a complete orthogonal set. We thus see that tetradic operators are naturally defined in terms of four indices. In particular, if $u = H$ (the Hamiltonian of the system), then $\tilde{u} = L$ (the Liouvillian).

We consider now a polyatomic molecule and divide its modes into two groups:

(1) a group of relevant modes are the "system" which we wish to treat explicitly, and

(2) the rest of the modes are the "bath" which we wish to treat stochastically.

We thus partition the total Hamiltonian in the form

$$H = H_s + H_B + H' \equiv H_0 + H' \quad (B6)$$

where $H_s, H_B,$ and H' correspond to the Hamiltonian for the system, for the bath and their interactions, respectively. The eigenstates of H_0 is denoted by $(n\alpha)$, where n and α are the collections of system and bath quantum numbers, respectively. We define the tetradic projection operators

$$\begin{aligned}
 C &= \rho_{\text{Bath}}^0 \text{Tr}_{\text{Bath}}, \\
 D &= 1 - C, \quad (B7)
 \end{aligned}$$

where ρ_{Bath}^0 is the equilibrium density matrix for the bath. The density matrix of the system is

$$\sigma \equiv \text{Tr}_{\text{Bath}} \rho = \text{Tr}_{\text{Bath}} C \rho. \quad (B8)$$

We use the result of Zwanzig, which may be derived from the Liouville equation and the fact that C is a projection operator:

$$\frac{d\sigma}{dt} = -iL_s \sigma - i \int_0^t d\tau R(t-\tau) \sigma(\tau), \quad (B9)$$

$$R(t) = L' + L'D \exp[-iD(L_0 + L')D] DL'. \quad (B10)$$

We now assume

(1) the bath has a short correlation time (Markovian approximation), thus

$$\int_0^t d\tau R(t-\tau) \sigma(\tau) \approx \left(\int_0^\infty d\tau R(\tau) \right) \sigma(t); \quad (B11)$$

(2) the time evolution of the off-diagonal elements of σ includes many terms with random phases which are

assumed to cancel. Thus we may assume the coherences to be very small and ignore the contribution to the time evolution;

(3) R is expanded to second order in L' . Thus we get

$$\frac{dP_n}{dt} = \sum_m A_{n,m} P_m, \quad (B12)$$

where

$$P_n = \sigma_{nn}, \quad (B13)$$

$$A_{n,m} = \sum_{\alpha\beta} \pi \langle\langle n\beta n\beta L' \delta(L_0) L' | m\alpha m\alpha \rangle\rangle P(\alpha). \quad (B14)$$

Turning now to our special model, we consider a system with one mode where H' couples only states differing by one quantum number. If the matrix elements of L' are weakly dependent on the bath quantum number we get

$$\begin{aligned}
 A_{n+1,n} &= 2\pi |H'_{n,n+1}|^2 \rho_B(E - E_{n+1}), \\
 A_{n,n+1} &= 2\pi |H'_{n,n+1}|^2 \rho_B(E - E_n), \\
 A_{n,n} &= -A_{n+1,n} - A_{n-1,n}. \quad (B15)
 \end{aligned}$$

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has different frequencies from that of the molecule. Thus, Eq. (29) is more general than (28) and we can take $\rho(N, E)$ to be of any form compatible with the structure of the complex.

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