Unimolecular dissociation as diffusion with a radiation boundary condition

Noam Agmon

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Unimolecular dissociation as diffusion with a radiation boundary condition

Noam Agmon[a)]

Department of Physical Chemistry and The Fritz Haber Center for Molecular Dynamics,[b)] The Hebrew University, Jerusalem 91904, Israel

Unimolecular decomposition of an isolated polyatomic molecule is discussed in terms of a diffusion equation with a radiation boundary condition, instead of a master equation with an absorbing boundary. This gives a short-cut to evaluating the mean first passage time. More important, it results in simple models, such as the model of diffusion in a linear potential solved here. This model is analytically solvable for the probability distribution and the survival probability, and may be helpful in analyzing future experiments.

I. INTRODUCTION

Unimolecular dissociation[1] has been modeled[2] by a stochastic (random walk) process on a vibrational energy ladder with an absorbing boundary condition (BC) at the upper step (i.e., dissociation occurs immediately when the molecule first reaches this step). The mean first passage time τ (i.e., the average time for reaching this upper dissociative step) has been interpreted as the reciprocal rate constant for decomposition. More recently, Proccacia, Mukamel, and Ross (PMR)[3] and Seshadri, West, and Lindenberg (SWL)[4] have elaborated this model. They have derived an expression for τ for an isolated polyatomic molecule, discussing the conditions under which it simplified to the well known statistical (e.g., RRKM[1]) result, where the rate constant is proportional to the density of states in the transition state (here the upper vibrational step).

We contend that these results do not correctly explain the wide applicability[1] of RRKM. In order to do so the model should have a "radiation"[5,6] (rather than an absorbing) BC. This means that dissociation from the upper step occurs with a finite (instead of infinite) rate constant κ. As is evident intuitively, it is the limit of small κ in comparison to the ladder process rate which would lead to a RRKM-like expression.

The Master equation used[3,4] for describing the evolution of the probability distribution p_n of the vibrational states $n = 0,1,...,N$ in the dissociating mode is of the nearest-neighbor type

$$\partial p_n/\partial t = W_{n,n-1}p_{n-1} + W_{n,n+1}p_{n+1}$$
$$- (W_{n-1,n} + W_{n+1,n})p_n. \qquad (1)$$

$W_{n,m}$ is the transition frequency (transition probability per unit time) for transitions from state m to n. For the ground state, $n = 0$, one assumes a "reflection" BC, $W_{0,-1} = W_{-1,0} = 0$, so that population cannot be gained from or lost to the states $n < 0$. At the dissociation level $n = N$, an "absorption" BC was imposed: $W_{N-1,N} = 0$, while $W_{N,N-1} \neq 0$, so that population reaching $n = N$ is trapped there forever.

The Master equation (1) can be written in a matrix form

$$d\mathbf{p}/dt = -\mathbf{Lp}, \qquad (2)$$

where $\mathbf{p} = (p_0,...,p_N)$ and $\mathbf{L}$ is a $(N+1)\times(N+1)$ tridiagonal matrix whose elements are $L_{n,n\pm1} = -W_{n,n\pm1}$ and $L_{n,n} = W_{n-1,n} + W_{n+1,n}$. $\mathbf{L}$ is a "stochastic" matrix in the sense that its columns sum to zero, $\Sigma_n W_{n,m} = 0$.

For the above mentioned ladder process the transition frequencies were assumed[3] to be of the general form

$$W_{n+1,n} = f_n (p_{n+1}^e/p_n^e)^{1/2},$$
$$W_{n,n+1} = f_n (p_n^e/p_{n+1}^e)^{1/2}, \qquad (3)$$

where $\mathbf{p}^e$ is the equilibrium distribution in the absence of absorption, which is proportional to the density of states[1] for the remaining $s-1$ degrees of freedom in the molecule

$$p_n^e = Z^{-1}\left(\frac{\epsilon-n}{\epsilon}\right)^{s-1}. \qquad (4)$$

ϵ is proportional to the total energy and Z is a normalization constant, $\Sigma_{n=0}^{N-1}p_n^e = 1$. The transition probabilities (3) obey the condition of detailed balance

$$W_{n+1,n}p_n^e = W_{n,n+1}p_{n+1}^e. \qquad (5)$$

The probability distribution $\mathbf{p}$ is usually not accessible experimentally. Therefore, interesting quantities are the "survival probability" (the probability for not reacting up to time t)

$$Q(t) = \sum_{n=0}^{N-1} p_n(t) \qquad (6)$$

and the mean first passage time[7] (the average time for absorption in $n = N$)

$$\tau = \int_0^\infty Q(t)dt. \qquad (7)$$

All quantities above depend, of course, on the initial distribution $p_n(0) = p_n^0$. We are particularly interested in the solution where the initial distribution is concentrated in a given state $0 \leqslant n_0 \leqslant N$, $p_n^0 = \delta_{n,n_0}$. From such solutions $\mathbf{p}(t\,|n_0)$, known sometimes as Green's functions, one can construct the solution for an arbitrary initial distribution $\mathbf{p}^0$,

$$p_n(t\,|\mathbf{p}^0) = \sum_{n_0=0}^{N-1} p_{n_0}^0 p_n(t\,|n_0). \qquad (8)$$

The central result[3,4,7b] for the mean first passage time starting from n_0, $\tau(n_0)$, for a nearest-neighbor Master equation with detailed balance is

$$\tau(n_0) = \sum_{n=n_0}^{N-1}\left(\sum_{l=0}^{n}p_l^e\right)/(p_n^e W_{n+1,n}). \qquad (9)$$

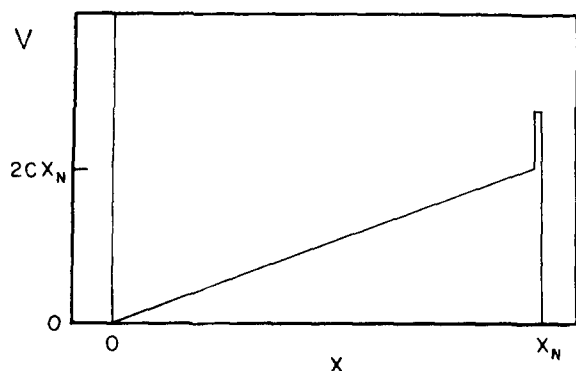0021-9606/84/105049-06$02.10 © 1984 American Institute of Physics 5049

FIG. 1. A demonstration of the potential and boundary conditions in the DE (27). The left boundary is represented by an infinitely high wall, whereas the right boundary is a thin wall of finite height followed by an infinitely deep well.

This result has served as a basis for the discussion of the conditions for the applicability of the statistical RRKM theory. PMR[3] mention (p. 3247) three such conditions for which the last term in Eq. (9) is dominant and $\tau(n_0)$ reduces to a ratio of density of states

$$\tau(n_0) \approx (p_{N-1}^e \, W_{N,N-1})^{-1} \tag{10}$$

whose magnitude is determined by the last upward transition frequency $W_{N,N-1}$:

(i) All transition frequencies are similar, a condition not likely to hold generally.

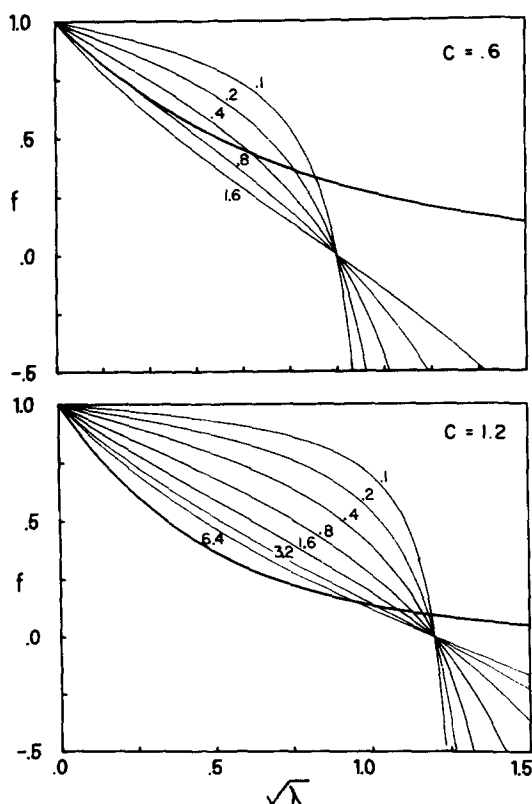(ii) The total energy is small, $\varepsilon \approx N$, as demonstrated in

FIG. 2. Graphical solution for λ_0 from Eq. (33). The thick line is f_r, and the thin lines are f_i for the designated values of κ. In this work $x_N = 1$ and $D = 1$.

Figs. 1 and 2 in PMR. This restriction is too strict for a theory with such wide applicability as RRKM.[1]

(iii) $W_{N,N-1}$ is much smaller than all other transition frequencies, which is nonphysical if all these frequencies are given by a smooth continuous function as in Eq. (3).

To remedy this situation, SWL[4] have discussed a second order approximation of Eq. (9) as a correction for RRKM. This, we feel, only confuses, since as we argue below the RRKM limit is determined by the rate κ out of state N, not by the transition from $N-1$ to N.

II. THE DIFFUSION EQUATION APPROACH

The diffusion equation (DE), which has found wide applicability in physics and chemistry,[5,6,8] describes the evolution of the probability distribution $p(x)$, due to fluctuations ("entropic" effects) and a force field derived from a potential $V(x)$. The one dimensional DE with a nonconstant diffusion coefficient $D(x)$, can be written as a continuity condition

$$\partial p/\partial t = -\partial j/\partial x \tag{11}$$

with the flux $j(x)$ given by

$$-j(x) = D(x)[\partial p/\partial x + \beta V' p]. \tag{12}$$

In Eq. (12) a prime denotes differentiation with respect to x and β is a constant (for a thermal heat bath it is $1/k_B T$).

The DE can be written, in analogy with the discrete case [Eq. (2)] as

$$\partial p/\partial t = -\mathcal{L}(p), \tag{13}$$

where $\mathcal{L}$ is the "diffusion operator" whose definition is evident from Eqs. (11) and (12). Although, when solving the DE numerically one would often convert it to a finite difference form[9,10] [Eq. (2)] the opposite is true for analytic analysis.[11] In the latter case it is better to write a nearest-neighbor Master equation with detailed balance in an equivalent DE form.

We discretized the DE as follows[10]: x is divided into intervals of constant length $\Delta x = x_{n+1} - x_n$ (actually x_n is n). For any function $f(x), f_n = f(x_n)$ and $f'_n = (f_{n+\frac{1}{2}} - f_{n-\frac{1}{2}})/\Delta x$. Hence

$$
\begin{aligned}
(\Delta x)^2 \partial p_n/\partial t = &\, D_{n-\frac{1}{2}}[1 - \tfrac{1}{2}\beta(V_n - V_{n-1})]p_{n-1} \\
&+ D_{n+\frac{1}{2}}[1 - \tfrac{1}{2}\beta(V_{n+1} - V_n)]p_{n+1} \\
&- \{D_{n-\frac{1}{2}}[1 - \tfrac{1}{2}\beta(V_{n-1} - V_n)] \\
&+ D_{n+\frac{1}{2}}[1 - \tfrac{1}{2}\beta(V_n - V_{n+1})]\}p_n \tag{14}
\end{aligned}
$$

which is equivalent to Eq. (1) with transition probabilities given by [cf. Eq. (3)]

$$W_{n+1,n} = D_{n+\frac{1}{2}} \exp[-\tfrac{1}{2}\beta(V_{n+1} - V_n)]/(\Delta x)^2,$$

$$W_{n,n+1} = D_{n+\frac{1}{2}} \exp[-\tfrac{1}{2}\beta(V_n - V_{n+1})]/(\Delta x)^2. \tag{15}$$

(We have used a first order Taylor expansion for the exponent.) The equilibrium distribution is, of course

$$p_n^e = Z^{-1} \exp(-\beta V_n). \tag{16}$$

For small Δx, $D_{n+\frac{1}{2}}$ can be replaced by D_n. In the application to the vibrational ladder model, f_n of Eq. (3) is identified with $D_n/(\Delta x)^2$, both Δx and β are taken as unity, and [cf. Eq. (4)]

$$V(x) = -(s-1)\ln(1 - x/\epsilon). \tag{17}$$

As boundaries we take $x = 0$ and $x = x_N$. At the left

boundary we have reflection

$$j(0,t) = 0 \qquad (18)$$

but at the right boundary we impose, instead of an absorption BC, $p(x_N) = 0$, a "radiation"[5,6] BC

$$j(x_N,t) = \kappa p(x_N,t). \qquad (19)$$

This BC is intermediate between reflection and absorption [these two limits are realized for $\kappa = 0$ and $\kappa = \infty$, respectively. Note that the sign of κ should be inversed for a radiation BC at $x = 0$, since there $j(x)$ is directed inwards, whereas at $x = x_N$ it is outwards flux].

One can now readily apply the theory of first passage time[7,12–14] for the DE. This theory starts (in one of its versions) by the observation that the transition (conditional) probability $p(x,t\,|x_0)$ obeys the backward equation

$$\partial p(x,t\,|x_0)/\partial t = -\mathcal{L}^{\dagger}_{x_0}(p), \qquad (20)$$

where $\mathcal{L}^{\dagger}_{x_0}$ is the adjoint diffusion operator in x_0,

$$\mathcal{L}^{\dagger}_{x} = \left[-\frac{\partial}{\partial x} + \beta V' \right] D(x) \frac{\partial}{\partial x}. \qquad (21)$$

From this follows immediately that $Q(t\,|x_0)$ also obeys the backward equation and therefore that $\tau(t\,|x_0)$ is the solution of

$$\mathcal{L}^{\dagger}(\tau) = 1. \qquad (22)$$

In the discrete case $\mathcal{L}^{\dagger}$ is $\tilde{L}$, the transpose of L, and the first passage problem reduces to solving a set of nonhomogeneous linear equations, $\tilde{L}\tau = 1$. (Since $(\tilde{L})^{-1} = \tilde{L}^{-1}$ this is also equivalent to[7] $\tau_n = \Sigma_m L^{-1}_{mn}$).

While deriving Eq. (9) from the set of linear equations can be complicated,[3] Eq. (22) is readily integrated[13,14] in the continuous case to give

$$\tau(x_0) = [\kappa p^e(x_N)]^{-1}$$
$$+ \int_{x_0}^{x_N} \left[\int_0^x p^e(y)dy \right] [D(x)p^e(x)]^{-1} dx. \qquad (23)$$

This integration can be performed for particular choices of $D(x)$. For example, for $D(x) = ax$, $a = $ const, and $p^e(x)$ as in Eq. (4) (this is an analogy to the Landau–Teller transition frequencies used in Ref. 2), one has

$$\tau(x_0) = [\kappa p^e(x_N)]^{-1} + \frac{\epsilon}{as}\Bigg\{(x_N - x_0)/\epsilon$$
$$+ \left[\left(\frac{\epsilon}{\epsilon - x_N}\right)^{s-2} - \left(\frac{\epsilon}{\epsilon - x_0}\right)^{s-2} \right]/(s-2)$$
$$+ \cdots + \left[\frac{\epsilon}{\epsilon - x_N} - \frac{\epsilon}{\epsilon - x_0} \right] + \ln\frac{\epsilon - x_0}{\epsilon - x_N} \Bigg\}. \qquad (24)$$

Comparing Eqs. (23) and (9) we see that PMR[3] and SWL[4] have considered only the second term in Eq. (23), which is the continuous analog of Eq. (9) when we substitute $D(x)p^e(x) \rightarrow D_{n+\frac{1}{2}}p^e_{n+\frac{1}{2}}$. It is, however, the first term which reduces to RRKM when $\kappa \ll D$. Mathematically, this difference is rather subtle since in the discrete case, a "radiation" BC at $n = N$ is equivalent to an absorbing boundary at $n = N + 1$ with $W_{N+1,N} \equiv \kappa$. Physically, there is a difference, since here κ is a parameter *independent* of the transition frequencies $W_{n,n\pm1}$, Eq. (3).

More generally, there may be several vibrational states

from which reaction may proceed (e.g., all states behind a "centrifugal barrier"[1]). In such a case reaction is introduced via a function $\kappa(x)$, and one has a typical case of diffusion "perpendicular to the reaction coordinate."[10] As discussed for such cases,[10] the overall kinetics is determined by the interplay of reaction and diffusion, i.e., the relative magnitudes of $\kappa(x)$ and $D(x)$. When $D \gg \kappa$ relaxation precedes reaction and the total population decays exponentially with a rate constant

$$\tau^{-1} = \int p^e(x)\kappa(x)dx. \qquad (25)$$

When $\kappa(x) = \kappa\delta(x - x_N)$ this becomes just the first term in Eq. (23). When $\kappa \gg D$ reaction precedes relaxation and the decay of the total population (the survival probability Q) is multiexponential. In this limit, when the diffusion operator has closely spaced eigenvalues (the spacing is almost proportional to D), the second term in Eq. (23) becomes signficant. But in this same limit of deviation from "statistical" behavior, τ alone no longer determines the time evolution of $Q(t)$. Hence one should now be interested not only in a theory for τ but (primarily) for Q. This is missing in the PMR–SWL approach. In the next section we present an analytic model which yields also an expression for the survival probability.

III. AN ANALYTICALLY SOLVABLE MODEL

For a large total energy ϵ, we can approximate the potential of Eq. (17) by

$$V(x) \approx \frac{s-1}{\epsilon}x. \qquad (26)$$

Hence we take as a model of unimolecular dissociation a diffusion process (with a constant diffusion coefficient D) in a constant force field[8]

$$D^{-1}\partial p/\partial t = \partial^2 p/\partial x^2 + 2c\partial p/\partial x, \quad 0 \leqslant x \leqslant x_N, \qquad (27)$$
$$\partial p/\partial x + 2cp = 0 \quad \text{at } x = 0,$$
$$\partial p/\partial x + (2c + \kappa/D)p = 0 \quad \text{at } x = x_N,$$
$$p(x,0) = \delta(x - x_0), \quad 0 < x_0 < x_N.$$

Evidently, $c \equiv (s-1)/2\epsilon$ is inversely proportional to the total energy. (c, κ, and D are positive.) Figure 1 demonstrates schematically the potential with the BC's.

To solve Eq. (27) we first define

$$q(x,t) \equiv p(x,t)\exp(cx). \qquad (28)$$

This transforms it to a Schrödinger-like equation

$$D^{-1}\partial q/\partial t = \partial^2 q/\partial x^2 - c^2 q \equiv -\mathcal{H}(q) \qquad (29)$$

with boundary conditions

$$\partial q/\partial x + cq = 0 \quad \text{at } x = 0, \qquad (30a)$$
$$\partial q/\partial x + bq = 0 \quad \text{at } x = x_N, \qquad (30b)$$

where $b \equiv c + \kappa/D > 0$. We search for eigenfunctions of the operator $\mathcal{H}$ with eigenvalues μ_n. These can be of the form

$$q_0(x) = \exp(-\sqrt{\lambda}_0 x) - a_0\exp(\sqrt{\lambda}_0 x), \qquad (31a)$$
$$q_n(x) = \cos(\sqrt{\lambda_n}x) - a_n\sin(\sqrt{\lambda_n}x), \quad n = 0,1,2.... \qquad (31b)$$

For small κ, q_0 is in the form (31a) and the lowest eigenvalue is $\mu_0 = c^2 - \lambda_0$. In particular, when $\kappa = 0$, $q_0 = \exp(-cx)$ is

the equilibrium distribution. For large κ the lowest eigenfunction is sometimes of the form (31b). The higher eigenfunctions are always of this form and correspond to the eigenvalues $\mu_n = c^2 + \lambda_n$. We will justify these conclusions below.

First we solve for λ_0 and a_0. By using the BC(30) for Eq. (31a),

$$c - \sqrt{\lambda_0} = a_0(c + \sqrt{\lambda_0}), \tag{32a}$$

$$(b - \sqrt{\lambda_0}) e^{-\sqrt{\lambda_0}x_N} = a_0(b + \sqrt{\lambda_0}) e^{\sqrt{\lambda_0}x_N}. \tag{32b}$$

Hence λ_0 is determined from

$$f \equiv (\sqrt{\lambda_0} - c)(\sqrt{\lambda_0} + b)[(\sqrt{\lambda_0} + c)(\sqrt{\lambda_0} - b)]^{-1}$$
$$= e^{-2\sqrt{\lambda_0}x_N}. \tag{33}$$

This is demonstrated in Fig. 2. The solution $\lambda_0 = 0$ implies $a_0 = 1$ and $q_0 = 0$, so it can be ruled out. There can be at the most one additional solution for $c \geqslant \sqrt{\lambda_0} > 0$. Since the right-hand side of Eq. (33), $f_r(\sqrt{\lambda})$, is a concave function of $\sqrt{\lambda}$ (decreasing from 1 to 0 as $\sqrt{\lambda} \to \infty$), the left-hand side $f_l(\sqrt{\lambda})$ is convex $(f_l'' < 0)$, decreasing to zero at $\sqrt{\lambda} = c$, and $f_l(0) = f_r(0)$, they will intersect once more if $f_l'(0) > f_r'(0)$. (Both derivatives are negative.) This implies that the validity range of Eq. (31a) is

$$\begin{array}{ll} 0 \leqslant \kappa < Dc^2x_N/(1 - cx_N) & \text{when } cx_N < 1, \\ 0 \leqslant \kappa < \infty & \text{when } cx_N \geqslant 1. \end{array} \tag{34}$$

Also, the eigenvalue $\mu_0 = c^2 - \lambda_0$ is always positive, as should be when the total population is depleted. In the special case $\kappa/D = 0$ we have $\lambda_0 = c^2$. This corresponds to the equilibrium distribution $p^e(x) \propto e^{-2cx}$, which has a zero eigenvalue. In the limit $\kappa/D \to c^2x_N/(1 - cx_N)$, one has $\lambda \to 0$. The lowest eigenfunction becomes linear (up to normalization) $q_0 = c^{-1} - x$, with an eigenvlaue $\mu_0 = c^2$.

We can deduce from Eq. (33) an approximation for μ_0 when κ/D is small (the "statistical limit"). Since when $\kappa/D \ll c$, $\sqrt{\lambda_0} \approx c$, we may replace $b \equiv c + \kappa/D$ by c in the term $\sqrt{\lambda_0} + b$ (but not in the term $\sqrt{\lambda_0} - b$) and also replace $\sqrt{\lambda_0}$ by c in the exponent in the right-hand side of Eq. (33). This leads to

$$\mu_0 = c^2 - \lambda_0 \approx 2c\kappa e^{-2cx_N}/D(1 - e^{-2cx_N}) = (\kappa/D)p^e(x_N), \tag{35}$$

where $p^e(x)$ is the equilibrium distribution for no reaction, $\kappa = 0$. Under these conditions the lowest eigenvalue of $\mathscr{L}$, $D\mu_0$, is independent of D.[10] Equation (35) is just the approximation (25), or the first term in Eq. (23). When Eq. (35) is valid, $(D\tau)^{-1}$ approximately equals to the lowest eigenvalue and $Q(t) \approx e^{-t/\tau}$. This is no longer true for larger κ/D, when higher eigenvalues contribute to the expansion.

To evaluate the higher eigenvalues of $\mathscr{H}$, $\mu_n = c^2 + \lambda_n$, we apply the BC (30) to Eq. (31b):

$$a_n \sqrt{\lambda_n} = c, \tag{36a}$$

$$(b - a_n\sqrt{\lambda_n})\cos(\sqrt{\lambda_n}x_N) = (\sqrt{\lambda_n} + a_nb)\sin(\sqrt{\lambda_n}x_N). \tag{36b}$$

From which we find that

$$f \equiv \cot(\sqrt{\lambda_n}x_N) = D(\lambda_n + cb)/\sqrt{\lambda_n}\kappa. \tag{37}$$
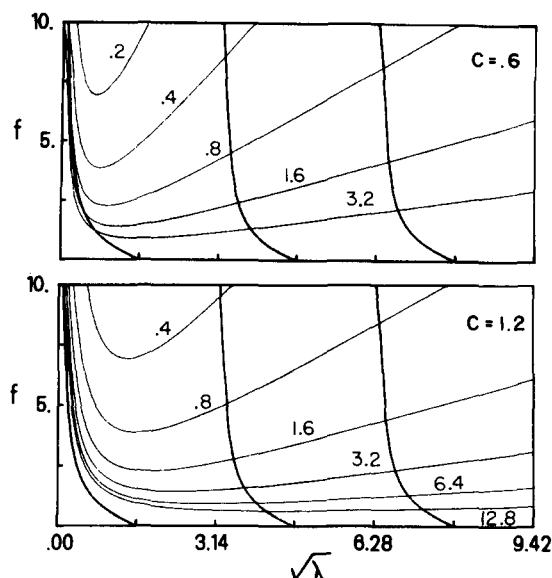
The determination of the eigenvalues from this equa-

FIG. 3. Graphical solution for λ_n from Eq. (37). The thick lines are the branches of the cotangent f_l. The thin lines are f_r for the designated values of κ. In this work $x_N = 1$ and $D = 1$.

tion is demonstrated in Fig. 3. From arguments similar to those following Eq. (33) we now conclude that the ground eigenfunction is of the form (31b) whenever Eq. (34) is violated. The higher eigenvalues are determined from the intersections of the right-hand side f_r with branches of the cotangent f_l. These occur at

$$n\pi \leqslant \sqrt{\lambda_n}x_N \leqslant (n + \tfrac{1}{2})\pi, \quad n = 1,2,\dots. \tag{38}$$

The left bound is obtained for $\kappa = 0$ (complete reflection), whereas the right bound is realized when $\kappa = \infty$ (complete absorption) and $c = 0$. When κ/D is small, the higher eigenvalues of $\mathscr{L}$, $D\mu_n$, are approximately equally spaced and proportional to D.[10]

Figure 4 shows the lowest eigenvalue μ_0 as a function of κ/D for several values of c. μ_0 increases with increasing κ and decreasing c. The tangents to the graphs at $\kappa/D = 0$ are of slopes $p^e(x_N)$, as given in the approximation (35). [This can be verified by direct differention of Eq. (33)].
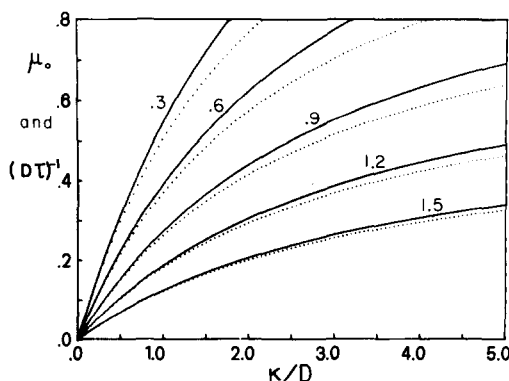
In order to calculate the probability distribution

FIG. 4. The lowest eigenvalue (as determined from Fig. 2 and the upper panel of Fig. 3), as a function of κ/D for the various designated values of c (full lines). The dotted lines are the inverse first passage time from $x_0 = 0$, Eq. (45) below.
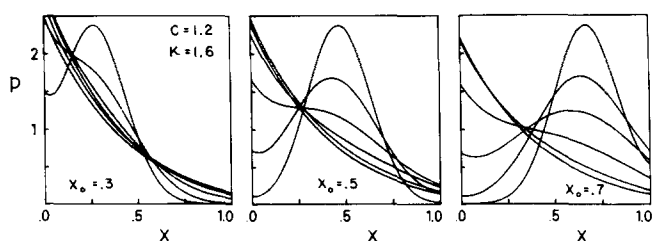
FIG. 5. The solution for the probability distribution $p(x,t\,|x_0)$ [Eq. (41)] for one combination of c and κ, and different initial distributions (different x_0). The time evolution of p, from an initial δ function to a final exponential with time-decreasing normalization constant, is shown for (in order of decreasing amplitude at x_0) $t = 0.01$, 0.02, 0.04, 0.08, 0.16, 0.32. In this work $x_N = D = 1$.

$p(x,t\,|x_0)$ and the survival probability $Q\,(t\,|x_0)$ we first evaluate the following integrals:

$$Z_0 \equiv \int_0^{x_N} q_0^2(x)dx = (4\lambda_0)^{-1/2}\big[\,1 - e^{-2\sqrt{\lambda_0}\,x_N}$$
$$- a_0^2(1 - e^{2\sqrt{\lambda_0}\,x_N})\,\big] - 2a_0 x_N, \qquad (39a)$$

$$Z_n \equiv \int_0^{x_N} q_n^2(x)dx = \tfrac{1}{2}(a_n^2 + 1)x_N$$
$$+ (4\lambda_n)^{-1/2}\big[\,(1 - a_n^2)\cos(\sqrt{\lambda_n}\,x_N)\sin(\sqrt{\lambda_n}\,x_N)$$
$$- 2a_n \sin^2(\sqrt{\lambda_n}\,x_N)\,\big], \qquad (39b)$$

$$\gamma_0 \equiv \int_0^{x_N} e^{-cx} q_0(x)dx = 2(c + \sqrt{\lambda_0})^{-1}e^{-cx_N}\,sh\,(\sqrt{\lambda_0}\,x_N),$$
$$\qquad (40a)$$

$$\gamma_n \equiv \int_0^{x_N} e^{-cx} q_n(x)dx = (\lambda_n)^{-1/2}e^{-cx_N}\sin(\sqrt{\lambda_n}\,x_N). \quad (40b)$$

The range of validity for $n = 0$ is the same as in Eq. (31).

The eigenfunction expansion of the probability density is written in terms of the eigenfunctions $q_n(x)e^{-cx}$ of $\mathscr{L}$ with coefficients determined from the inner product of the initial distribution with the eigenfunctions $q_n(x)e^{cx}$ of $\mathscr{L}^\dagger$:
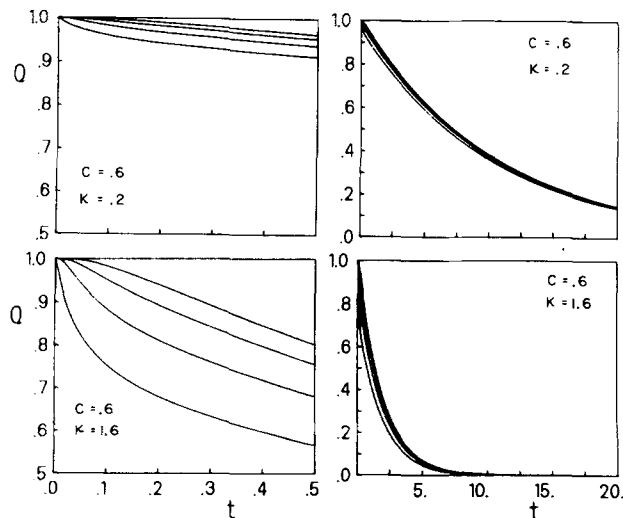

FIG. 6. The solution for the survival probability $Q\,(t\,|x_0)$ [Eq. (42)] for $c = 0.6$ and two values of κ. The four lines are for (top to bottom) $x_0 = 0.3, 0.5, 0.7,$ and 0.9. The left panels demonstrate short time behavior, whereas the right panels show the long time behavior. In this work $x_N = 1$ and $D = 1$.
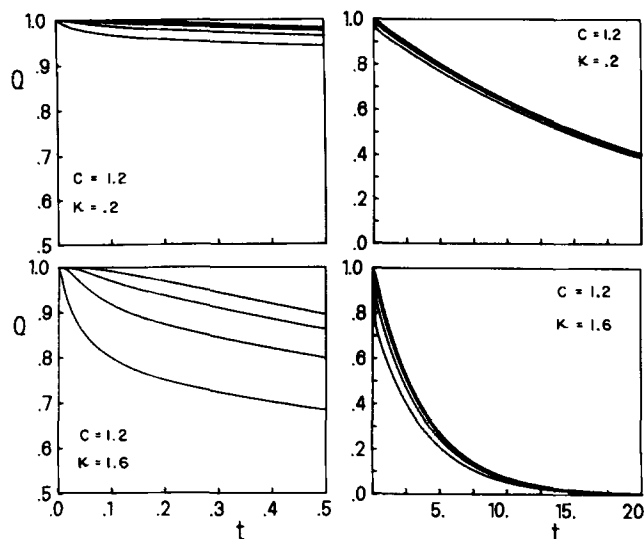

FIG. 7. Same as Fig. 6 for $c = 1.2$.

$$p(x,t\,|x_0) = e^{-c(x-x_0)} \sum_{n=0}^{\infty} Z_n^{-1} q_n(x_0)q_n(x)e^{-D\mu_n t}. \quad (41)$$

This solution, for some values of c, κ, and x_0 is demonstrated in Fig. 5.

The survival probability is now given by

$$Q\,(t\,|x_0) \equiv \int_0^{x_N} p(x,t\,|x_0)dx$$
$$= e^{cx_0} \sum_{n=0}^{\infty} Z_n^{-1} \gamma_n q_n(x_0)e^{-D\mu_n t}. \quad (42)$$

In particular, the normalization of the initial distribution $Q\,(0|x_0) = 1$ implies that

$$e^{cx_0} \sum_{n=0}^{\infty} Z_n^{-1} \gamma_n q_n(x_0) = 1. \qquad (43)$$

This serves as a convergence criterion for the expansion.

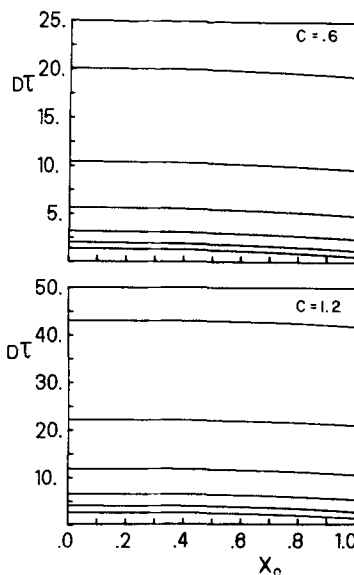Figures 6 and 7 demonstrate the solution (42) of the

FIG. 8. The average passage time as a function of x_0, Eqs. (44) or (45). The six different lines are for (top to bottom) $\kappa/D = 0.1, 0.2, 0.4, 0.8, 1.6,$ and 3.2.

survival probability for various values of c, κ, and x_0. There is more decay for small c, large κ, and x_0 which is closer to the reactive boundary x_N. The short time behavior, which is demonstrated in the left panels, is multiexponential, with several eigenvalues contributing to the expansion (42). Ultimately, only the lowest eigenvalue survives, and the decay becomes exponential, and independent of the initial conditions. This long time behavior is seen in the right panels.

Finally, the first passage time is given by

$$\tau(x_0) \equiv \int_0^\infty Q(t \mid x_0) dt$$

$$= D^{-1} e^{cx_0} \sum_{n=0}^\infty \gamma_n q_n(x_0) [Z_n \mu_n]^{-1}. \qquad (44)$$

In the limit when only the lowest eigenfunction contributes to the expansion $\tau(x_0) \to (D\mu_0)^{-1} \approx [\kappa p^e(x_N)]^{-1}$, and is independent of x_0 [Cf. Eq. (35)]. Alternatively, $\tau(x_0)$ is given by the integral (23),

$$2c\tau(x_0) = (e^{2cx_N} - 1)/\kappa$$

$$+ [(e^{2cx_N} - e^{2cx_0})/2c - (x_N - x_0)]/D \qquad (45)$$

Figure 8 shows the dependence of $\tau(x_0)$ on x_0 for several values of c and κ. This dependence is rather weak for large c or small κ/D, but becomes more pronounced for larger κ/D.

$\tau^{-1}(0)$ and μ_0 are compared in Fig. 4. They coincide for $\kappa/D \to 0$ but deviate with increasing κ/D. The latter are the conditions when many eigenfunctions contribute to the expansion and the short-time behavior of Q becomes multiexponential. Under these conditions, τ^{-1} cannot even describe the long-time exponential decay of the survival probability.

IV. CONCLUSION

We have discussed stochastic theories for the unimolecular decomposition of an isolated polyatomic molecule. In comparison to PMR[3] and SWL[4] we have noted that:

(i) Analytic properties of the solutions are better approached by a continuous diffusion equation, rather than by its discrete Master equation analog.

(ii) The boundary condition describing the dissociation should be of the radiation type, with an "intrinsic" rate constant κ, rather than of the absorption $\kappa = \infty$ type. It is in the limit of small κ when the results reduce to those of the statistical (RRKM) theories.

(iii) To discuss deviations from RRKM it is not enough to consider the full form of the first pasage time, since under

these conditions it does not adequately describe even the long time exponential decay of the survival probability. Therefore, one has to calculate the survival probability itself. Its time dependence is generally multiexponential at short times and turns gradually to a monoexponential decay at long times.

In addition, we have considered a model (valid, perhaps, for large total energies) of diffusion in a linear force field (responsible for relaxation of the oscillator), with a reflecting boundary for the lowest state and a radiation boundary condition for the upper dissociative state. This model is analytically solvable in terms of eigenfunctions (except that the eigenvalues have to be determined graphically or numerically). In spite of the simplicity of the model, it still has reasonable flexibility (through the parameters c and κ).

The interesting question is really in the experimental side. Is it possible by ultrashort laser techniques to follow transient kinetics of dissociation in isolated polyatomic molecules? Our results indicate that such experiments can yield more information on the intramolecular energy-transfer processes than measurements of "steady-state" rate constants alone.

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