

# First passage times and the kinetics of unimolecular dissociation

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(Received 11 December 1980; accepted 18 June 1981)

Approximate solutions for multistep master equations describing the time evolution of product formation in multiphoton or thermal unimolecular reactions are investigated. In particular, a method based on fitting the first few moments of the passage time distribution associated with the given stochastic process to proposed simple expressions for the product yield function is studied. It is shown that reasonable agreement with the exact numerical solution of the corresponding master equation is obtained with a two parameter fit (using two passage time moments) and an excellent agreement is obtained with a three parameter fit (using three passage time moments). In no case studied does a need arise for more than a three-moment description and the quality of available experimental results makes the simpler two-moment description sufficient in most cases. Analytical solutions for the first and second passage time moments are obtained for simple discrete and continuous master equation models. Expressions for the incubation time and the reaction rate are obtained in terms of these solutions. The validity of discretizing a continuous master equation (which is an important simplifying step in evaluating the time evolution associated with multiphoton dissociations in the presence of collisions, or with thermal unimolecular reactions involving large molecules) is studied using both the approximate two-moment solutions and exact numerical solutions. It is concluded that a proper discretization of a continuous master equation may be carried out provided  $\epsilon \ll k_B T^*$ , where  $\epsilon$  is the discretization energy step,  $k_B$  the Boltzmann constant, and  $T^*$  the effective (density of states weighted) temperature. A larger discretization step can be used if only the incubation time is required. Using the approximately discretized master equation, we next calculate the effect of collisions on the incubation time and the rate of multiphoton dissociation using a model constructed to correspond to the unimolecular dissociation of tetramethyldioxethane. Incubation times are found to be less sensitive to collisions than the reaction rates. Finally, we investigate the applicability of the passage time moments method to describe the time evolution of product formation in a system whose dynamics is determined by a quantum mechanical Liouville equation. Again the two-moment description provides a reasonable and the three-moment approximation a good approximation to the exact solution. The three-moment approximations, however, cannot be used when the pressure (i.e., the dephasing rate) is too low.

## I. INTRODUCTION

The kinetic behavior of unimolecular reactions in large molecules is mostly described by the Pauli master equations. For example, the discrete model

$$\dot{p}_n = \sum_m A_{nm} p_m - \gamma_n p_n \quad (\text{I.1a})$$

in the particular form

$$\dot{p}_n = k_{n,n-1} p_{n-1} + k_{n,n+1} p_{n+1} - (k_{n-1,n} + k_{n+1,n}) p_n - \gamma_n p_n, \quad (\text{I.1b})$$

is used to describe photochemically (multiphoton) induced reactions<sup>1,2</sup> (where  $p_n$  is the probability that the molecule has absorbed  $n$  photons,  $\gamma_n$  are reaction rates, and  $k_{nm} = I\sigma_{nm}/\hbar\omega$ , where  $I$  is the light intensity and  $\sigma_{nm}$  is the cross section for the  $m \rightarrow n$  transition). A similar equation is used to describe thermal reactions in diatomic molecules.<sup>3-5</sup> The continuous form

$$\dot{p}(E) = \int A(E, E') p(E') dE' - \gamma(E) p(E), \quad (\text{I.2})$$

where  $p(E)$  is the probability of energy accumulation  $E$  in the molecule and  $A(E, E')$  is the (collisionally induced) rate for the  $E' \rightarrow E$  transition, is used to describe thermal reactions in polyatomic molecules.<sup>6,7</sup> Laser induced reactions in the presence of collisions in large mole-

cules are described by a combination of the processes entering into Eqs. (I.1) and (I.2). For small molecules (or for "region I"—the low energy discrete spectrum of large molecules) the full Liouville equation for the molecular density matrix has to be employed.

With Eq. (I.1) or (I.2) constituting the starting point, the objective in many past studies was to obtain an expression for the reaction rate in terms of the parameters entering into the rate matrices  $A_{nm}$  or  $A(x, y)$ . The usual procedure is to identify this rate with the largest (smallest in absolute value) eigenvalue of the rate matrix.<sup>8-11</sup> The rationale behind this procedure lies in the observation that in many cases this eigenvalue  $\lambda_0$  is well separated from the other eigenvalues ( $|\lambda_0| \ll |\lambda_1| < |\lambda_2| \dots$ ) which implies that steady state will be established on a timescale much shorter than the following reaction time. In such a situation the bulk of the process indeed proceeds with the steady state rate  $\lambda_0$ . This steady state rate may be calculated as the inverse mean first passage time (MFPT) for the steady state distribution. Indeed the time evolution is governed in this case by a single exponential  $P(t) = \exp(-k_{ss}t)$  [where  $P(t)$  is defined by Eq. II.3] so that the MFPT is  $\tau_{1^{ss}}^{-1} = \int_0^\infty P(t) dt = k_{ss}^{-1}$  (see Sec. II).

The assumption  $|(\lambda_0 - \lambda_1/\lambda_0)| \gg 1$  necessary for the steady state approach to be useful does not always hold. For multiphoton dissociation of large molecules it was estimated that about a third of the reaction occurs before steady state is established.<sup>12</sup> Furthermore it is possible

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to carry out experiments that focus on the transient regime, such as measurements of incubation times in unimolecular thermal<sup>13-16</sup> or multiphoton<sup>17-19</sup> reactions, or of the (closely related) fluence threshold in multiphoton dissociation of large molecules. A proper analysis of such cases requires a more detailed study of the solution [ $p_n(t)$  or  $p(X, t)$ ] of the master equation (1) or (2). Experimentally what is observed is the evolution of the reaction yield

$$Y(t) = \begin{cases} 1 - \sum_{n=0}^{\infty} p_n(t) \\ 1 - \int_0^{\infty} dx p(x, t) \end{cases} \quad (\text{I.3})$$

This is in turn analyzed in terms of an incubation time  $\theta$  which is the time elapsed between the onset of the reaction and the first observation of products, and of a rate  $k$  which characterizes the long time behavior of  $Y$  (see Fig. 1). The complete time evolution of  $Y(t)$  is of course determined by more than just three or two parameters; in principle by all the parameters which determine the rate matrix  $A$ . The purpose of the present paper is to express this time evolution using a *small* number of parameters which may be calculated from  $A$  and from the given initial distribution. This is achieved by realizing that the time dependence of  $Y(t)$  is determined mostly by the first few lower moments of the *passage time distribution* which are relatively easy to calculate. We use these few (2 or 3) moments as input parameters to fit reasonable approximations to the evolution function, from which we obtain expressions for the incubation time  $\theta$  and the rate  $k$  associated with the reaction.

It should be noted that other approaches to the calculation of the incubation time  $\theta$  exist in the literature. Dove and Troe,<sup>20</sup> following Brau, Keck, and Carrier<sup>21</sup> used a method based on the smallest eigenvalue (SEV) of the evolution operator. Denoting this eigenvalue by  $-\lambda_0$  and the corresponding eigenvector by  $u_0$ , the long time evolution of the system is given by [denoting  $P(t) = 1 - Y(t)$ ]

$$P(t) = [u_0^L \cdot p(0)] \exp(-\lambda_0 t), \quad (\text{I.4})$$

where  $u_0^L$  is the left eigenvector of the master equation corresponding to  $-\lambda_0$ , [ $u_0^L \cdot u_0 = 1$ ]. The evolution is now approximated to be given by

$$P(t) \cong P_A(t),$$

$$P_A(t) = \begin{cases} 1, & t \leq \theta \\ [u_0^L \cdot p(0)] \exp(-\lambda_0 t), & t \geq \theta \end{cases} \quad (\text{I.5})$$

From this an estimate for the incubation time  $\theta$  is

$$\theta = \frac{1}{\lambda_0} \ln[u_0^L \cdot p(0)]. \quad (\text{I.6})$$

Recently, Kelley, Zalotai, and Rabinovitch<sup>22</sup> have suggested a different estimate

$$\theta = \tau_1 - 1/\lambda_0, \quad (\text{I.7})$$

where  $\tau_1$  is the mean first passage time (first moment of

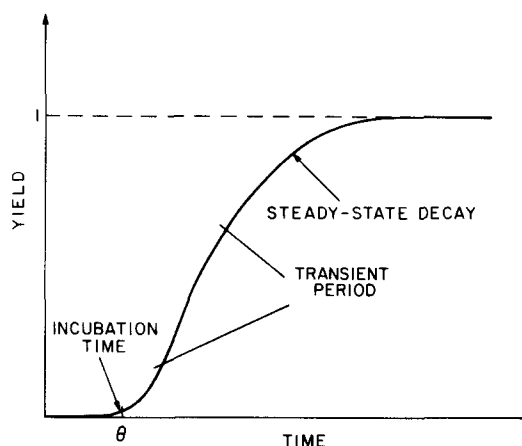


FIG. 1. A schematic view of the time evolution of product formation in multistep reaction system.

the passage time distribution) associated with the master equation.

Finally, Barker<sup>23</sup> has recently proposed that the passage time distribution function is closely reproduced by a log-normal distribution function

$$\Pi(t) \cong \frac{1}{t\sigma\sqrt{2\pi}} \exp\left[-\frac{\ln^2(t/\mu)}{2\sigma^2}\right]. \quad (\text{I.8})$$

This is a two parameter function which may be used if the parameters  $\sigma$  and  $\mu$  can be calculated, e.g., by evaluating the two lowest moments of the passage time distribution (see Sec. II).

In Sec. II we describe our method and compare it with the approximations based on Eqs. (I.6)–(I.8). In Sec. III we obtain analytical solution for the lower passage time moments for some simple discrete and continuous master equation models and use them to obtain expressions for the corresponding incubation times and reaction rates. In Sec. IV we discuss the validity of discretizing a continuous master equation which is used to simplify calculations of collision induced processes in large molecules. Results of model calculations on collision effects in multiphoton excitation of large molecules are also presented. Finally in Sec. V we investigate the applicability of our approach for quantum-mechanical evolution described by the quantum-mechanical Liouville equation, of which Eq. (I.1) constitutes a particular limit. Our conclusions are summarized in Sec. VI.

## II. THE PASSAGE TIME MOMENTS (PTM) METHOD

Given the master equation (1) or (2), our aim is to obtain the product yield function  $Y(t)$ , Eq. (3). We introduce the passage time distribution function<sup>24</sup>

$$\Pi(t) = \dot{Y}(t) = \begin{cases} -\sum_{n=0}^{\infty} \dot{p}_n(t) \\ -\int_0^{\infty} dx \dot{p}(x, t) \end{cases}, \quad (\text{II.1})$$

which is positive and satisfies  $\int_0^{\infty} dt \Pi(t) = 1$ . Its moments are

$$\tau_n = \int_0^\infty dt t^n \Pi(t) = n \int_0^\infty t^{n-1} P(t) dt, \quad (\text{II. 2})$$

where

$$P(t) = 1 - Y(t) = \begin{cases} \sum_{n=0}^{\infty} p_n(t) \\ \int_0^\infty dx p(x, t) \end{cases}. \quad (\text{II. 3})$$

The moments  $\tau_n$  are readily calculated<sup>24</sup> in the discrete case where  $P(t) = U \cdot p(t)$ ,  $U$  being a vector of unities  $U = (1, 1, \dots)$ :

$$\tau_n = nU \cdot \int_0^\infty \exp(\mathbf{A}t) p(0) t^{n-1} dt = (-1)^n n! U \cdot \mathbf{A}^{-n} p(0). \quad (\text{II. 4})$$

Thus only the inverse of the rate matrix  $\mathbf{A}$  and the initial distribution  $p(0)$  are needed to evaluate all the PTM's. For the continuous master equation there are also methods available to calculate the PTM's.<sup>24</sup>  $\tau_1$ , the mean passage time has been widely used for steady state rate calculations.<sup>8-11</sup>

To go beyond the steady state approximation we observe that the product yield function  $Y(t)$  is usually a smooth function of  $t$  (Fig. 1) which may be approximated by simple mathematical forms in terms of a small number of parameters. These parameters may in turn be calculated by fitting the approximate forms to yield the correct lower PTM's. The simplest approximation is

$$Y(t) \approx Y_A(t), \quad (\text{II. 5})$$

$$Y_A(t) = \begin{cases} 0, & t \leq \theta \\ 1 - \exp[-k(t - \theta)], & t \geq \theta \end{cases}. \quad (\text{II. 6})$$

The parameters  $k$  and  $\theta$  are chosen so that the approximate  $Y_A(t)$  yields the correct first and second PTM's as the exact  $Y(t)$ . This leads to

$$k^{-1} = \sqrt{\tau_2 - \tau_1^2}, \quad (\text{II. 7a})$$

$$\theta = \tau_1 - \sqrt{\tau_2 - \tau_1^2}. \quad (\text{II. 7b})$$

A better approximation is obtained by using a three parameter function

$$Y_A(t) = \begin{cases} 0, & t \leq \theta \\ 1 - \frac{k_1 \exp[-k_2(t - \theta)] - k_2 \exp[-k_1(t - \theta)]}{k_1 - k_2}, & t \geq \theta \end{cases}, \quad (\text{II. 8})$$

with the requirement that  $Y_A(t)$  now yields the correct three lower PTM's. This leads to

$$\theta = \tau_1 - x \sqrt{\tau_2 - \tau_1^2}, \quad (\text{II. 9a})$$

$$\frac{1}{k_1} = \frac{1}{2}(x + \sqrt{2 - x^2}) \sqrt{\tau_2 - \tau_1^2}, \quad (\text{II. 9b})$$

$$\frac{1}{k_2} = \frac{1}{2}(x - \sqrt{2 - x^2}) \sqrt{\tau_2 - \tau_1^2}, \quad (\text{II. 9c})$$

where  $x$  is the solution to the cubic equation

$$x^3 - 3x + \alpha = 0, \quad (\text{II. 10a})$$

and where

$$\alpha = \frac{\tau_3 - \tau_1^3 - 3\tau_1(\tau_2 - \tau_1^2)}{(\tau_2 - \tau_1^2)^{3/2}}. \quad (\text{II. 10b})$$

Note that Eq. (II. 10a) has, in general, three roots. Of these we are limited to real  $x$  satisfying  $1 \leq x \leq (\tau_1)/(\sqrt{\tau_2 - \tau_1^2})$  because  $\theta$  should be real and non-negative and  $k_1, k_2$  should have a positive real part  $\{k_{1,2} = \gamma \pm i\omega$  is in principle possible, in which case  $P_A(t) = 1 - Y_A(t) = \exp(-\gamma t) [\cos \omega t + (\gamma/\omega) \sin \omega t]$ . In the rare cases when such a result was obtained we found  $\gamma \gg \omega$  and no oscillations actually appear.

An alternative way to use the information contained in the PTM's is to use the first and second passage time moments for evaluating the parameters  $\mu$  and  $\sigma$  of the log-Gauss distribution function (I. 8). The moments of  $\Pi(t)$  given by Eq. (I. 8) are

$$\tau_n = \langle t^n \rangle = \int_0^\infty dt t^n \Pi(t) = \mu^n \exp[n^2 \sigma^2 / 2], \quad (\text{II. 11})$$

so that  $\mu$  and  $\sigma$  are obtained in terms of  $\tau_1$  and  $\tau_2$  in the forms

$$\sigma = [\ln(\tau_2/\tau_1^2)]^{1/2}, \quad (\text{II. 12})$$

$$\mu = \tau_1(\tau_1^2/\tau_2)^{1/2}. \quad (\text{II. 13})$$

Thus evaluating  $\tau_1$  and  $\tau_2$  we obtain an explicit expression for  $\Pi(t)$ , from which the product yield function is obtained by integration

$$Y(t) = \int_0^t \Pi(t') dt'. \quad (\text{II. 14})$$

In Fig. 2 we compare, using a model master equation the exact numerical solution for  $P(t) = 1 - Y(t)$  with approximate solutions based on the SEV approximation [Eqs. (I. 5)–(I. 7)] and on the PTM method with two moments [Eqs. (II. 6) and (II. 7) or Eqs. (I. 8) and (II. 12)–(II. 14)] and with three moments [Eqs. (II. 8) and (II. 9)]. Figure 2(a) shows the results obtained for a multiphoton excitation of a model large molecule in the absence of collisions while in Fig. 2(b) the same process has been considered under 100 Torr inert gas pressure. The model used for the collisionless process is the same one described before<sup>25</sup> for the multiphoton dissociation of tetramethyldioxethane (where real time monitoring of the dissociation product has been performed). The way in which collisional processes are incorporated is described in Sec. IV.

Comparing the results shown in Figs. 2(a) and 2(b) we see that already the two-moment approximation [(II. 6) and (II. 7)] gives a reasonable approximation to the exact results which is superior to the SEV approximation [(I. 5) and (I. 6)] or to the estimate given by (I. 7). Using two passage time moments with the log-Gauss distribution [Eqs. (I. 8), (II. 12), and (II. 13)] leads to an excellent agreement with the exact result in the collisionless case (in agreement with Barker's observation<sup>23</sup>); but gives a poor fit when collisions are important. The three-moment approximation [Eqs. (II. 8)–(II. 10)] is in almost complete agreement with the exact solution at all pressures. Similar results were obtained for all cases checked, with all approximations excluding the log-Gauss distribution becoming better as the separation

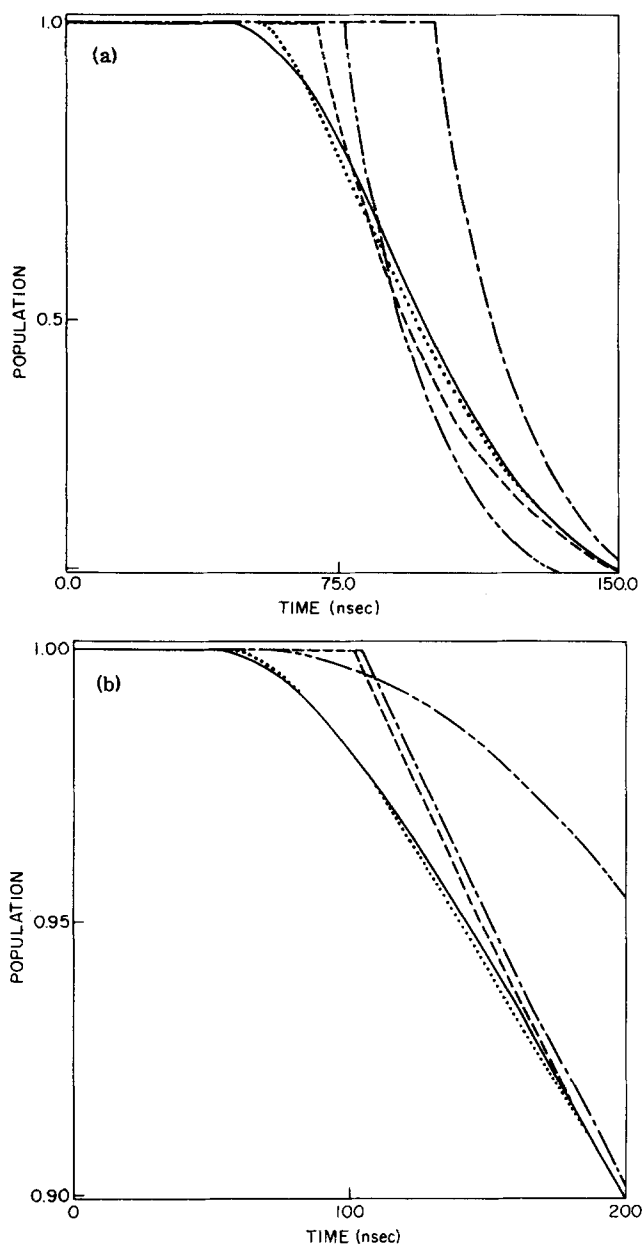


FIG. 2. A comparison of several methods used in the analysis of product formation in multistep reaction process. Here the remaining reactant population,  $P(t) = 1 - Y(t)$  is plotted vs time. (a) collisionless multiphoton dissociation; (b) multiphoton dissociation in the presence of collisions as described in the text. Full line—exact numerical result. Dotted line—three-moment fit to Eqs. (II.8) and (II.9). Dashed line—a two-moment fit to Eqs. (II.6) and (II.7). Dash-dotted line—a fit based on the SEV method [Eqs. (I.5)–(II.7)]. The dash-two-dot line in (a) is based on Eq. (I.7) while a similar line in (2b) results from a two-moment fit to the log-Gauss distribution. In (a) the result from a two-moment fit to the log-Gauss distribution coincides with the exact line. In (b) the result from Eq. (I.7) coincides with the SEV (dash-dotted) curve.

between the smallest (in absolute value) eigenvalue of the rate matrix and the other eigenvalues increases.<sup>26</sup>

In Fig. 3 an analysis of experimental data for the yield versus fluence in the collisionless multiphoton dissociation of  $SF_6$  [Fig. 3(a)],<sup>27–29</sup>  $C_2F_4S_2$  [Fig. 3(b)],<sup>30</sup> and

$CF_3I$  [Fig. 3(c)],<sup>31</sup> in terms of the expressions (II.6) or (II.8) is presented.<sup>32</sup> In such experiments the laser intensity is not constant in time so that the rate matrix  $A$  in Eq. (I.1) is time dependent. However, as discussed before<sup>25</sup> it is possible to consider an equivalent constant intensity situation on a transformed time axis provided that the dissociation is assumed to depend only on the laser fluence. When this is done, the fluence replaces

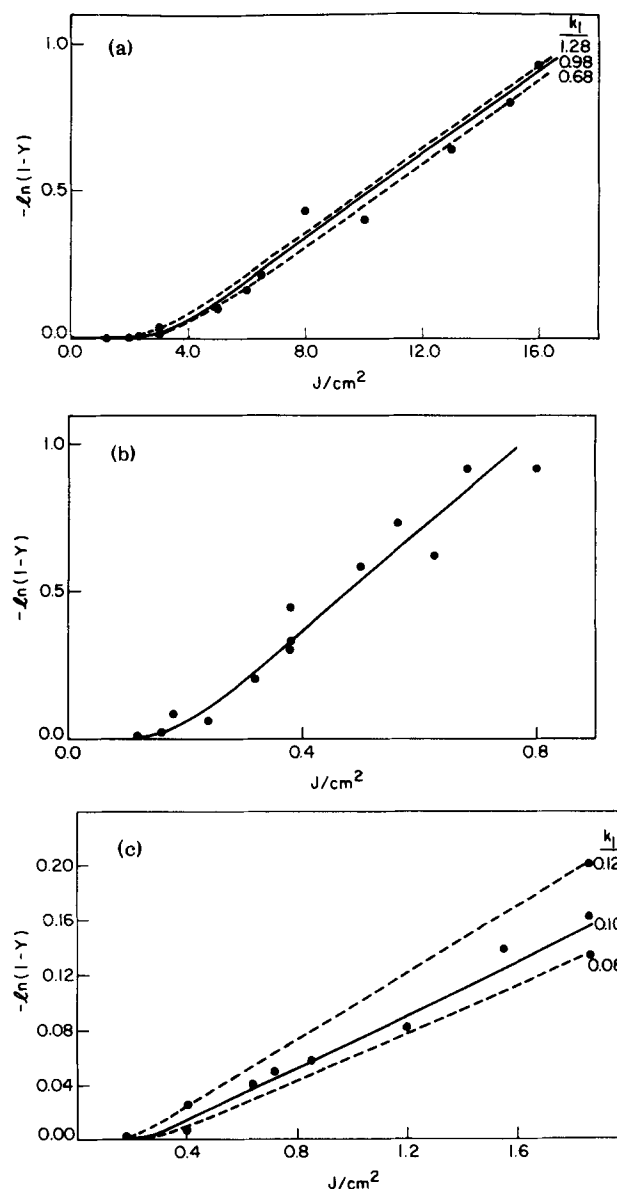


FIG. 3. Dissociation yield [expressed in terms of  $\ln(1 - Y)$ ] vs fluence for several collisionless multiphoton dissociation reactions. (a)  $SF_6$ . Experimental points were taken from Refs. 27–29. The best fit to a function of the form (II.8) is obtained using  $\theta = 2 \text{ J/cm}^2$ ,  $k_2 = 0.07 \text{ (J/cm}^2\text{)}^{-1}$ , and  $k_1 = 0.98 \text{ (J/cm}^2\text{)}^{-1}$ . Also shown are two curves based on Eq. (II.8) with the same  $\theta$  and  $k_2$  and with  $k_1 = 0.68 \text{ (J/cm}^2\text{)}^{-1}$ , and  $1.28 \text{ (J/cm}^2\text{)}^{-1}$ . (b)  $C_2F_4S_2$ . The experimental points are from Ref. 30. The best fit to (II.8) is obtained with  $\theta = 0.12 \text{ J/cm}^2$ ,  $k_2 = 1.68 \text{ (J/cm}^2\text{)}^{-1}$ , and  $k_1 = 18.5 \text{ (J/cm}^2\text{)}^{-1}$ . (c)  $CF_3I$ . The experimental points are from Ref. 31. The best fit to the functions (II.5) and (II.6) is obtained using  $\theta = 0.18 \text{ J/cm}^2$  and  $k = 0.1 \text{ (J/cm}^2\text{)}^{-1}$ . Also shown are curves corresponding to the same  $\theta$  with  $k = 0.08$  and  $0.12 \text{ (J/cm}^2\text{)}^{-1}$ .

time in Eqs. (II.6)–(II.9), the incubation time becomes the threshold fluence, and the rates  $k$  measure the progress of dissociation per unit fluence. It is seen from Fig. 3 that the two parameter function provide a good fit to the experimental results in most cases and that given the quality of the available experimental results nothing beyond the three parameter fit is sensible. The fit thus obtained is directly related to properties of the rate matrix moments of the passage time (or fluence) distribution by Eqs. (II.7) or (II.9) and (II.10). As noted by Barker,<sup>23</sup> the log-normal distribution also fits well these collisionless cases and the parameters  $\sigma$  and  $\mu$  thus obtained may be again used to calculate the two lowest passage time moments. We should keep in mind that these fits are meaningful, in terms of passage time moments, only provided that fluence and time may be considered to be equivalent as mentioned above, i.e., when the effects of the discrete level structure in “region I” may be disregarded.

We end this section with the following comments:

(a) The time  $\theta$  and the rates  $k$  [Eq. (II.6)] or  $k_1$ ,  $k_2$  [Eq. (II.8)] are directly measurable as the incubation time and the rate associated with the unimolecular reaction. In this section we have related these quantities to the (relatively easy to calculate) passage time moments associated with the given kinetic equation.

(b) While Eq. (II.6) is the simplest approximation to  $Y(t)$ , dividing the evolution into an incubation and a steady state part, Eqs. (I.8) and (II.8) provide simple ways to include also the transient regime. Other ways are possible. In particular Quack<sup>33</sup> and Troe<sup>34</sup> have considered functions of the form

$$Y(t) \simeq Y_A(t) = 1 - \exp\left[-\int_0^t k(\tau) d\tau\right] \quad (\text{II.15})$$

with a time dependent rate [becoming a constant  $k(t) \rightarrow k$  (steady state) at long time].  $k(t)$  is then chosen as a few parameter function, e.g.,<sup>28</sup>  $k(t) = k[1 - \exp(-t/\tau)]^n$ , where  $k$ ,  $\tau$ , and  $n$  are parameters determined by fitting experimental results. Our form (II.8) as well as the log-Gauss function (I.8) has the advantage of mathematical simplicity which enables us to relate the empirically determined parameters with the PTM's. The form (II.8) has in addition an appealing underlying physical picture: expression (II.8) corresponds to the case where following an incubation period  $\theta$  the system behaves as an effective two-level system satisfying the kinetic scheme

$$\begin{aligned} \dot{p}_1(t) &= -r_1 p_1(t) + r_2 p_2(t), \\ \dot{p}_2(t) &= r_1 p_1(t) - (r_2 + \gamma) p_2(t), \end{aligned} \quad (\text{II.16})$$

where  $p_1(0) = 1$ ,  $p_2(0) = 0$ , and where  $k_1$  and  $k_2$  of Eq. (II.8) are the eigenvalues of the rate matrix appearing in Eq. (II.16). The success of this fit implies that for practical purposes the unimolecular reaction involving a multilevel system may be described effectively by a two level system subjected to an incubation period.

The main advantage of the present approach lies in the approximate relation found between the experimentally measurable parameters and the PTM's which are rela-

tively easy to calculate. In fact, for some simple models we can obtain analytical expressions for the PTM's which in turn yield useful approximate expressions for  $k$  and  $\theta$ . We demonstrate such solutions in the next section.

### III. EVALUATION OF PASSAGE TIME MOMENTS

There are general procedures outlined for the evaluation of PTM's associated with either the Fokker-Planck (FP) or the discrete master equation. In most practical uses, only the first moment (mean passage time) was obtained. In this section we evaluate  $\tau_1$  and  $\tau_2$  [and thereby  $k$  and  $\theta$ , Eqs. (II.6) and (II.7)] for two simple model master equations: one continuous and the other discrete in the state variable.

#### A. A continuous model

Consider Eq. (I.2) with the rate matrix  $A(x, y)$  given by

$$A(x, y) = \begin{cases} \frac{\nu}{\alpha + \beta} \exp[(x - y)/\alpha], & x < y \\ \frac{\nu}{\alpha + \beta} [\alpha + \beta - \alpha \exp(-y/\alpha)] \delta(x - y), & x = y \\ \frac{\nu}{\alpha + \beta} \exp[(y - x)/\beta], & x > y \end{cases} \quad (\text{III.1})$$

$A$  is conservative,  $\int_0^\infty dx A(x, y) = 0$ . This model has been used by several workers<sup>6,7,20,35</sup> to describe thermal excitation of large molecules where  $x(y)$  is the internal energy of the molecule,  $\alpha$  and  $\beta$  are the average energy loss and gain, respectively, per collision, and  $\nu$  is the number of collisions per unit time. When supplemented by dissociation rates above some energy threshold this constitutes a model for thermal unimolecular reaction. We adopt the simple scheme (low pressure limit) where the dissociation rate at the threshold  $E_0$  is much larger than the collisional energy transfer rate so that a molecule is dissociated immediately after its energy surpasses  $E_0$ . In this case, Eq. (I.2) is solved with Eq. (III.1) in the range  $x = 0 \cdots E_0$ , where  $x = 0$  is a reflecting and  $x = E_0$  is an absorbing barrier. The method described below is similar to that used to obtain passage time moments for the FP equation.<sup>24</sup>

Let  $P(y, t|x)$  be the probability to be in state  $y$  in time  $t$  after starting in state  $x$  at time 0. This is the solution  $p(y, t)$  to Eq. (I.2), given the initial condition

$$p(y, 0) = \delta(x - y). \quad (\text{III.2})$$

Note that  $p(y, t|x) = 0$  for  $y \geq E_0$ . Defining

$$Y(x, t) = 1 - \int_0^{E_0} dy p(y, t|x), \quad (\text{III.3})$$

this is the product yield function subjected to the initial condition  $p(y, 0) = \delta(x - y)$ .  $Y(x, t)$  satisfies the master equation

$$\frac{\partial Y(x, t)}{\partial t} = \int_0^{E_0} dy Y(y, t) A(y, x), \quad (\text{III.4})$$

with the boundary conditions  $Y(x, 0) = 0$  and  $Y(x, \infty) = 1$ , given  $x < E_0$  [ $Y(x, t) = 1$  for all  $t$  for  $x \geq E_0$ ].

$\tau_n(x)$ , the  $n$ th passage time moment subjected to Eq. (III. 2) is defined by [cf. Eq. (II. 2)]

$$\tau_n(x) = \int_0^\infty t^n \dot{Y}(x, t) dt = n \int_0^\infty t^{n-1} [1 - Y(x, t)] dt, \quad (\text{III. 5})$$

which with Eq. (III. 4) implies

$$n\tau_{n-1}(x) = \int_0^{E_0} \tau_n(y) A(y, x) dy. \quad (\text{III. 6})$$

This enables us to obtain a differential equation for the function

$$f_n(x) = \tau_n(x) \exp(-x/\beta) \quad (\text{III. 7})$$

in the form

$$\begin{aligned} (\alpha + \beta) \frac{n}{\nu} \left[ \frac{d^2 f_{n-1}(x)}{dx^2} + \frac{\alpha + \beta}{\alpha\beta} \frac{df_{n-1}(x)}{dx} \right] \\ = \frac{d^2}{dx^2} [g(x)f_n(x)] + \frac{\alpha + \beta}{\alpha\beta} \frac{d}{dx} [g(x)f_n(x)] + \frac{\alpha + \beta}{\alpha\beta} f_n(x), \end{aligned} \quad (\text{III. 8})$$

where  $g(x)$  is the diagonal part of  $A(x, y)$

$$g(x) = \alpha + \beta - \alpha \exp(-x/\alpha). \quad (\text{III. 9})$$

We assume that  $E_0 \gg \alpha, \beta$ .  $x$  varies in the range  $0 \cdots E_0$  and in most of this range we can replace Eq. (III. 9) by

$$g(x) \cong \alpha + \beta. \quad (\text{III. 10})$$

Inserting this into Eq. (III. 8) results in

$$\frac{d^2 \tau_n}{dx^2} - \frac{1}{\gamma} \frac{d\tau_n}{dx} = \frac{n}{\nu} \left[ \frac{d^2 \tau_{n-1}}{dx^2} - \frac{1}{\gamma} \frac{d\tau_{n-1}}{dx} - \frac{1}{\alpha\beta} \tau_{n-1} \right], \quad n > 0 \quad (\text{III. 11a})$$

or equivalently

$$\frac{d^2 \tau_n}{dx^2} - \frac{1}{\gamma} \frac{d\tau_n}{dx} = -\frac{n!}{\nu_n} \frac{1}{\alpha\beta} \sum_{k=0}^{n-1} \frac{\nu^k}{k!} \tau_k(x), \quad (\text{III. 11b})$$

where

$$\frac{1}{\gamma} = \frac{1}{\beta} - \frac{1}{\alpha}. \quad (\text{III. 12})$$

Equation (III. 11b) is supplemented by the boundary conditions

$$\tau_0(x) = 1 \quad \text{for } x \in [0, E_0], \quad (\text{III. 13a})$$

$$\tau_n(E_0) = 0 \quad \text{for } n > 0, \quad (\text{III. 13b})$$

$$\left( \frac{d\tau_n}{dx} \right)_{x=0} = 0 \quad \text{for } n > 0. \quad (\text{III. 13c})$$

Equation (III. 13a) expresses the normalization of the passage time distribution while Eq. (III. 13b) and (III. 13c) are properties of the absorbing and the reflecting barriers respectively.<sup>36</sup> The solution of Eqs. (III. 11) and (III. 13) is obtained as a recursion relation

$$\begin{aligned} \tau_n(x) = \frac{n}{\nu} \tau_{n-1}(x) + \frac{n}{\nu(\alpha - \beta)} \\ \times \left[ c - \exp\left(\frac{x}{\gamma}\right) \int_0^x \exp\left(-\frac{y}{\gamma}\right) \tau_{n-1}(y) dy - \int_x^{E_0} \tau_{n-1}(y) dy \right], \end{aligned} \quad (\text{III. 14})$$

with

$$c = \exp\left(\frac{E_0}{\gamma}\right) \int_0^{E_0} \exp\left(-\frac{y}{\gamma}\right) \tau_{n-1}(y) dy. \quad (\text{III. 15})$$

Equations (III. 13), (III. 14), and (III. 15) may now be used to obtain the desired set of PTM's. The results for the first two moments are

$$\tau_1(x) = \frac{\gamma [\exp(E_0/\gamma) - \exp(x/\gamma)] + x - E_0}{\nu(\alpha - \beta)}, \quad (\text{III. 16a})$$

$$\begin{aligned} \tau_2(x) = \left\{ \left[ \gamma^2 \exp(E_0/\gamma) + \gamma(2\gamma + \alpha - \beta) \right] [\exp(E_0/\gamma) - \exp(x/\gamma)] + \gamma x [\exp(E_0/\gamma) + \exp(x/\gamma)] \right. \\ \left. - \gamma E_0 [3 \exp(E_0/\gamma) - \exp(x/\gamma)] + (x - E_0) \left[ \frac{1}{2}(x - E_0) + \gamma + \alpha - \beta \right] \right\} / \left[ \frac{1}{2} \nu^2 (\alpha - \beta)^2 \right] \end{aligned} \quad (\text{III. 16b})$$

Using these results and Eqs. (II. 5)–(II. 7) we obtain

$$Y(x, t) \approx \begin{cases} 0, & t < \theta(x) \\ 1 - \exp\{-k(x)[t - \theta(x)]\}, & t > \theta(x) \end{cases} \quad (\text{III. 17})$$

with

$$k^{-1}(x) \approx \frac{\left\{ \gamma^2 \left[ \exp\left(\frac{2E_0}{\gamma}\right) - \exp\left(\frac{2x}{\gamma}\right) - 4\gamma(E_0 \exp\left(\frac{E_0}{\gamma}\right) - x \exp\left(\frac{x}{\gamma}\right)) \right] \right\}^{1/2}}{\nu(\alpha - \beta)}, \quad (\text{III. 18})$$

$$\theta(x) \approx \frac{\gamma \left[ \exp\left(\frac{E_0}{\gamma}\right) - \exp\left(\frac{x}{\gamma}\right) \right] + x - E_0 - \left\{ \gamma^2 \left[ \exp\left(\frac{2E_0}{\gamma}\right) - \exp\left(\frac{2x}{\gamma}\right) - 4\gamma(E_0 \exp\left(\frac{E_0}{\gamma}\right) - x \exp\left(\frac{x}{\gamma}\right)) \right] \right\}^{1/2}}{\nu(\alpha - \beta)}. \quad (\text{III. 19})$$

In obtaining Eqs. (III. 18) and (III. 19) we have used again the assumption  $E_0 \gg \alpha, \beta, \gamma$ . The incubation time  $\theta$  and the rate  $k$  are seen to depend on the initial state  $x$ ,  $\theta(E_0)$  and  $k^{-1}(E_0)$  vanish as expected. We note that  $\tau_1(x)$  and  $\tau_2(x)$  are practically exact for  $x > \alpha, \beta$  while otherwise they involve the approximation introduced by Eq. (III. 10). For  $x = 0$  we obtain

$$\begin{aligned} \theta(0) &= \frac{E_0}{\nu(\alpha - \beta)}, \\ k^{-1}(0) &= \frac{\gamma \exp(E_0/\gamma)}{\nu(\alpha - \beta)}. \end{aligned} \quad (\text{III. 20})$$

We note in passing that the result for  $\theta(0)$  agrees with that obtained by Dove and Troe<sup>20</sup>

$$\theta = - \int_0^{E_0} \frac{dx}{\nu \langle \Delta E(x) \rangle} \approx \frac{E_0}{\nu(\alpha - \beta)},$$

where  $\langle \Delta E(x) \rangle \approx \beta - \alpha$  is the averaged energy per collision transferred into the molecule.

The results (III. 20) may be rewritten in a somewhat more physically appealing form by using the detailed balance condition

$$\frac{A(x, y)}{A(y, x)} = \frac{\rho(x)}{\rho(y)} \exp\left[\frac{y-x}{k_B T}\right], \quad (\text{III. 21})$$

where  $\rho(x)$  is the density of states at energy  $x$ ,  $T$  the temperature, and  $k_B$  the Boltzmann constant, to get

$$\frac{1}{\gamma} = \frac{1}{\beta} - \frac{1}{\alpha} = \frac{1}{k_B T} - \frac{\ln \rho(x) - \ln \rho(y)}{x-y}. \quad (\text{III. 22})$$

If we adopt an exponential model for  $\rho(x)$ ,

$$\rho(x) \propto \exp(x/\mu), \quad (\text{III. 23})$$

we get

$$\frac{1}{\gamma} \approx \frac{1}{k_B T} - \frac{1}{\mu} \equiv \frac{1}{k_B T^*}, \quad (\text{III. 24})$$

where  $T^*$  denotes an "effective temperature." Equations (III. 18) and (III. 19) may be now written in the form

$$\theta(0) = \frac{E_0}{\nu |\langle \Delta E \rangle|}, \quad (\text{III. 25})$$

$$k(0) = \frac{\nu |\langle \Delta E \rangle|}{k_B T^*} \exp(-E_0/k_B T^*). \quad (\text{III. 26})$$

$k$  is here obtained in an Arrhenius form with activation

energy  $E_0$ , while  $\theta$  is the activation energy divided by the rate of energy exchange by the molecule.

## B. A discrete model

Next we consider a discrete model suitable for collisionless multiphoton dissociation of large molecules. The rate equation is (I. 1) with

$$A_{nm} = k_{n, n+1} \delta_{m, n+1} + k_{n, n-1} \delta_{m, n-1} - (k_{n+1, n} + k_{n-1, n} + \gamma_n) \delta_{nm}. \quad (\text{III. 27})$$

$n$  denotes the energy content of the molecule in terms of a discrete number of quanta. We again assume that  $\gamma_n = 0$  for  $n < N$  and that it is much larger than all  $k_n$  for  $n \geq N$ , so that all dissociation occurs at the threshold  $n = N$ . Furthermore, we simplify the model by taking

$$\left. \begin{aligned} k_{n+1, n} &\equiv k_+ \\ k_{n-1, n} &\equiv k_- \end{aligned} \right\} \text{independent of } n. \quad (\text{III. 28})$$

We also assume

$$p_n(t=0) = \delta_{n,0}. \quad (\text{III. 29})$$

The PTM's are calculated for this model by extending a method<sup>24</sup> used to calculate the first moment (the mean first passage time). The results for the first two moments are

$$\begin{aligned} \tau_1 &= \sum_{n=0}^N p_n(0) = k_+^{-1} \frac{\eta}{\eta^N (\eta-1)^2} [N\eta^{N+1} - (N+1)\eta^N + 1] \\ &= \frac{N\eta^{N+1} - (N+1)\eta^N + 1}{k_+ (\eta-1)^2 \eta^N}, \end{aligned} \quad (\text{III. 30})$$

$$\tau_2 = \frac{N(N+1)\eta^{2N+2} - 2(N^2 + N + 2)\eta^{2N+1} + N(N+1)\eta^{2N} + 2(3N+2)\eta^{N+1} - 2(3N+1)\eta^N + 2}{k_-^2 (\eta-1)^4 \eta^{2N}}, \quad (\text{III. 31})$$

where

$$\eta = k_+ / k_-. \quad (\text{III. 32})$$

The same procedure as described in Ref. 24 may be continued to obtain higher moments.

Equations (III. 30) and (III. 31) may be used with Eq. (II. 7) to obtain the incubation time and the reaction rate within the scheme (II. 6). For the interesting case  $N \gg 1$  we obtain

$$\theta = \begin{cases} \frac{N}{k_- - k_+}, & \eta < 1 \\ \frac{N}{k_+ - k_-}, & \eta > 1 \\ (3 - \sqrt{6})N^2 / 6k_+, & \eta = 1 \end{cases} \quad (\text{III. 33})$$

and

$$k = \begin{cases} \eta^N (1 - \eta)(k_- - k_+), & \eta < 1 \\ \frac{\eta - 1}{\eta + 1} \frac{1}{\sqrt{N}} \frac{k_+ - k_-}{\sqrt{N}}, & \eta > 1 \\ \frac{\sqrt{6}k_+}{N^2}, & \eta = 1 \end{cases} \quad (\text{III. 34})$$

These results can be used for a quick, zero order estimate of the incubation time and rate associated with infrared multiphoton dissociation of large molecules.<sup>25</sup>

## IV. DISCRETIZATION OF A CONTINUOUS MASTER EQUATION

In applying the master equation to describe the evolution of a large molecule excited by IR radiation in the presence of a collisional heat bath, we encounter the necessity to combine a discrete process described by Eq. (I. 1) with a continuous process Eq. (I. 2). A considerable simplification of the problem is achieved if the continuous kernel can be discretized in some specified way.

The rationale behind discretizing a continuous ME lies in the observation that we are interested only in processes which involve many collisional steps so that the energy transfer probability per collision may be important only in some averaged way. Thus, given the transition rate kernel  $A(x, y)$  in Eq. (I. 1) we replace it by the kernel  $B(x, y)$ ,

$$B(x, y) = k_-(y)\delta(x - y + \epsilon) + k_+(y)\delta(x - y - \epsilon) - [k_-(y) + k_+(y)]\delta(x - y). \quad (\text{IV. 1})$$

Here  $k_-$  and  $k_+$  denote transition rates in the downward and upward directions, respectively, and  $\epsilon > 0$  is a discrete energy step.  $k_-$  and  $k_+$  are chosen so that some averaged properties of  $A(x, y)$  are maintained in  $B(x, y)$ . In a recent work,<sup>25</sup> we have determined  $k_-$  and  $k_+$  from the requirements

$$k_+(y) \int_y^\infty (x - y)\delta(x - y - \epsilon) dx = \int_y^\infty (x - y)A(x, y) dx, \\ k_-(y) \int_0^y (x - y)\delta(x - y + \epsilon) dx = \int_0^y (x - y)A(x, y) dx. \quad (\text{IV. 2})$$

For the model (III. 1) this implies

$$k_+(y) = \frac{\nu\beta^2}{(\alpha + \beta)\epsilon}, \quad (\text{IV. 2a}) \\ k_-(y) = \begin{cases} 0, & y < \epsilon, \\ \frac{\nu\alpha^2}{(\alpha + \beta)\epsilon} \left[ 1 - \left( \frac{y}{\alpha} + 1 \right) \exp(-y/\alpha) \right], & y > \epsilon \end{cases} \quad (\text{IV. 2b})$$

[in Ref. 25 we have replaced Eq. (IV. 2b) by  $k_-(y) = \nu\alpha^2/(\alpha + \beta)$ , which is equal to the value given by Eq. (IV. 2b) in most of the energy range]. The choice (IV. 2) suffers from the drawback of not satisfying the detailed balance condition which, for Eq. (IV. 1) and for the thermal reaction case takes the form

$$\frac{k_+(x)}{k_-(x + \epsilon)} = \frac{\rho(x + \epsilon)}{\rho(x)} \exp\left(-\frac{\epsilon}{k_B T}\right) = \exp(-\epsilon/k_B T^*). \quad (\text{IV. 3})$$

In order to satisfy this requirement we choose  $k_-$  and  $k_+$  so that

$$k_-(y) - k_+(y) = \nu \langle \Delta E(y) \rangle / \epsilon, \quad (\text{IV. 4})$$

$$k_-(y)/k_+(y) = \exp(\epsilon/k_B T^*), \quad (\text{IV. 5})$$

where  $\langle \Delta E(y) \rangle$  is the average total energy transferred per collision from state  $y$ , and where  $T^*$  is defined in Eq. (III. 24). The definitions (IV. 4) and (IV. 5) are model independent. For our model (III. 1),  $\langle \Delta E(y) \rangle = \alpha - \beta$  for  $y$  sufficiently large and  $\nu \langle \Delta E(y) \rangle / \epsilon$  is the difference between the terms appearing on the right-hand side of Eq. (IV. 2). Equations (IV. 4) and (IV. 5) lead to

$$k_+(y) = \frac{\nu |\langle \Delta E(y) \rangle|}{\epsilon [\exp(\epsilon/k_B T^*) - 1]}, \quad (\text{IV. 6a})$$

$$k_-(y) = \frac{\nu |\langle \Delta E(y) \rangle| \exp(\epsilon/k_B T^*)}{\epsilon [\exp(\epsilon/k_B T^*) - 1]}. \quad (\text{IV. 6b})$$

Taking  $|\langle \Delta E(y) \rangle| \cong \alpha - \beta$  independent of  $y$ , we can use Eqs. (III. 33) and (III. 34) to get  $k$  and  $\theta$ . We note from Eq. (IV. 5) that the parameter  $\eta$  [Eq. (III. 32)] is  $< 1$ , so that Eqs. (III. 33), (III. 34), and (IV. 6) lead to

$$\theta = \frac{E_0}{\nu |\langle \Delta E \rangle|}, \quad (\text{IV. 7})$$

$$k = \frac{\nu |\langle \Delta E \rangle|}{K_B T^*} \exp(-E_0/K_B T^*) \times \frac{k_B T^*}{\epsilon} [1 - \exp(-\epsilon/k_B T^*)], \quad (\text{IV. 8})$$

where  $E_0 = N\epsilon$  is the dissociation energy.

The validity of this discretization method may be now assessed by comparing the results (IV. 7) and (IV. 8) to the results (III. 25) and (III. 26) obtained from the analogous continuous model.<sup>37</sup> We see that the results for the incubation time are identical while those for the rates become identical for  $\epsilon \ll k_B T^*$ . For  $\epsilon \sim k_B T^*$  the discrete model underestimates the reaction rate. In Ref. 25 we have used a discretization procedure with  $\epsilon = \hbar\omega$  in order to incorporate the collisional transitions into the radiative rate matrix. This approach is expected to be reliable for the calculation of incubation times, while a better model, utilizing a smaller step size ( $\epsilon = \hbar\omega/n$ ,  $n = 10$  for  $T = 300$  K) is expected to give more reliable results for the rates. In such a model the radiative rates connect levels which lie  $n$  steps apart and the order of the rate matrix is  $n$  times larger than the original purely radiative rate matrix. Still it is much easier to solve numerically such a model than the complete model combining the discrete equation (I. 1) with the continuous equation (I. 2). Following this observation we conclude that a suitably discretized model constitutes the best way to approach the problem of collisional effects in the (quasi) continuous level regimes of multiphoton excitation of large molecules.

## V. MODEL CALCULATIONS

In this section we present results of some model calculations which were performed in order (a) to compare results obtained using the PTM method with exact solutions of the master equation, and (b) to get a feeling for the pressure and light intensity dependence of the incubation time  $\theta$ , the rate ( $k$  or  $k_1, k_2$ ) and the reaction yield  $Y$  in multiphoton dissociation reactions.

Our model is based on the master equation used previously to simulate IR multiphoton dissociation of tetramethyldioxethane (TMD), only the collisional rate coefficients of Ref. 25 were replaced by those given by Eq. (IV. 6). Tables of the density of states and the RRKM rate constants used are provided in Ref. 25. The rates which enter into the master equation are given by

$$k_{n+1-n} = \Gamma_{n+1, n} + k_+, \quad (\text{V. 1a})$$

$$k_{n-1-n} = \Gamma_{n-1, n} + k_-. \quad (\text{V. 1b})$$

The collisional rates  $k_+$  and  $k_-$  were obtained from Eq. (IV. 6) using (unless otherwise specified)  $T = 300$  K,  $T^* = 420$  K, and  $|\langle \Delta E \rangle| = 100$  cm<sup>-1</sup>, with the collision rate  $\nu$  estimated as  $\sim 10^{-4} P$  where  $P$  is the pressure expressed in Torr. The forward radiative rates were taken to be energy independent and are expressed as  $\omega_R^2/\Gamma^{(a)}$ , where  $\omega_R$  is the Rabi frequency for the 0-1 transition and where  $\Gamma^{(a)}$  is the anharmonic width of the optically active mode, estimated here to be 50 cm<sup>-1</sup>. The backward radiative rates are calculated using the detailed balance relation  $k_{n+1, n}/k_{n, n+1} = \rho_{n+1}/\rho_n$ . The dissociation threshold for TMD is at 10 IR (CO<sub>2</sub>) photon absorption steps. The master equation was truncated after 27 such steps. The passage time moments were calculated numerically using Eq. (II. 4).

In Fig. 4 we present the results of a test calculation in



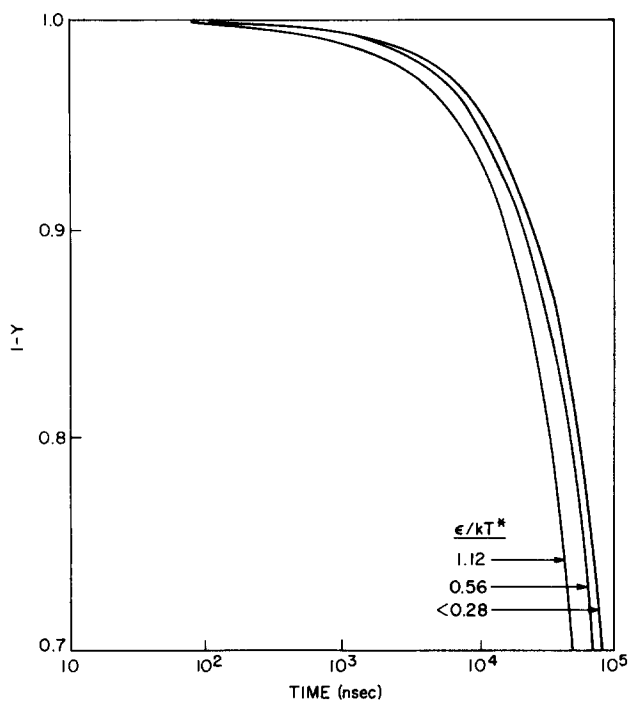


FIG. 4. Remaining reactant population  $P(t) = 1 - Y(t)$  plotted vs time in a thermal reaction model for TMD.  $T = 1500$  K. The different curves correspond to  $\epsilon/k_B T^* = 1.12$ , 0.56, and 0.28 where  $\epsilon$  is the discrete energy step. Curves with smaller ratio of  $\epsilon/k_B T^*$  coincide with the 0.28 curve.

in which, for a purely thermal reaction, we compare the result obtained with different choices of the discretization interval  $\epsilon$ . The same model molecule and the same collisional model as described above were used in this calculation. The temperature  $T$  was taken as 1500 °K, and  $\epsilon$  was chosen to vary in different calculations. The results converge for smaller  $\epsilon$ , and for  $\epsilon/k_B T^*$  smaller than 0.28 no significant difference exists between re-

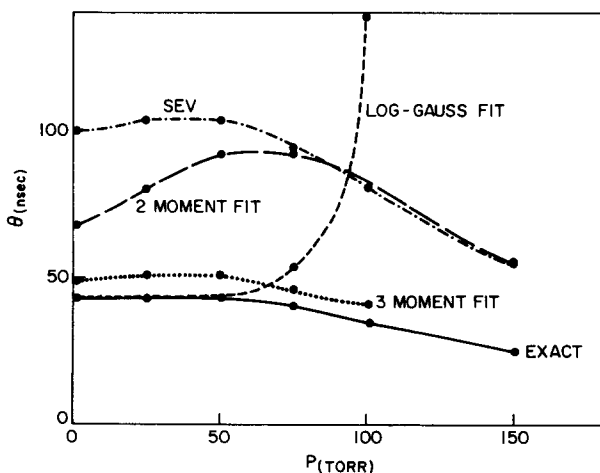


FIG. 5. Incubation time as a function of pressure obtained by an exact numerical solution (where  $\theta$  was taken as the time where 0.5% of the reactant disappeared) and by different approximation methods. The Rabi frequency is  $\omega_R = 0.21$  cm<sup>-1</sup>.

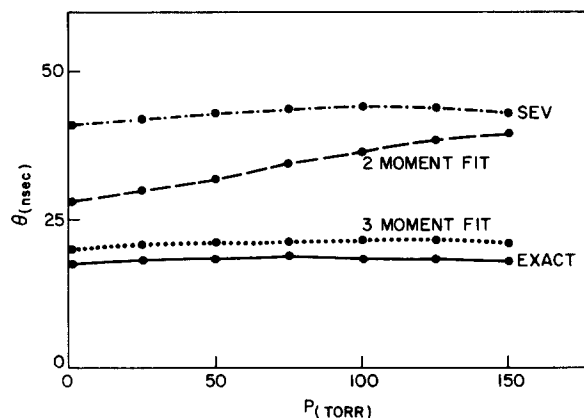


FIG. 6. As Fig. 5 with  $\omega_R = 0.34$  cm<sup>-1</sup>.

sults obtained for different choices of the discretization interval.

In the rest of the calculation presented in this section we choose  $\epsilon = \hbar\omega$ . The temperature in all high pressure calculations was taken 300 °K. According to the discussion in Sec. IV we expect the results for the incubation times  $\theta$  to be quantitatively correct within the model, while those for the rates and yields to provide a qualitative feeling for these properties.

Figures 5 and 6 represent the pressure dependence of  $\theta$  at two different IR intensities. The dependence of yield on pressure is shown for a particular rectangular pulse in Fig. 7 while its intensity dependence at fixed fluence at zero and finite pressures is demonstrated in Fig. 8.

This numerical study leads to the following conclusions:

(a) the PTM method provides a reliable tool for studying unimolecular reactions governed by a master equa-

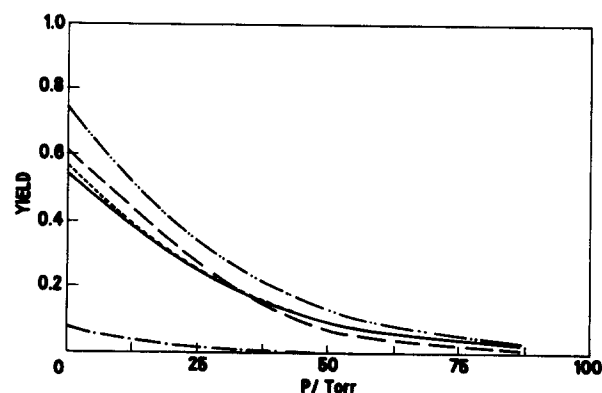


FIG. 7. Reaction yield vs pressure for the model TMD reaction described in the text. The full, dotted, dashed, and the dash-dotted curves correspond to yields obtained in an exact calculation, a three-moment fit, a two-moment fit, and the SEV approximation, respectively, all immediately after a 100 ns pulse. The dash-two-dot line corresponds to the long time yield (including post-pulse dissociation).  $\omega_R = 0.21$  cm<sup>-1</sup>.

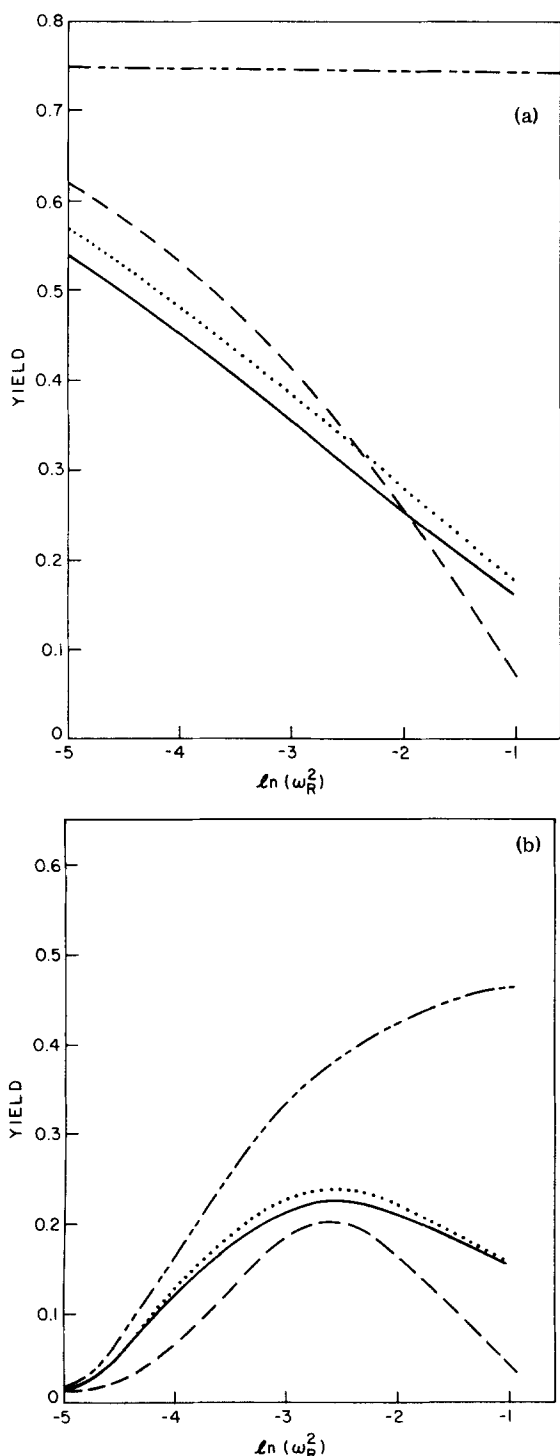


FIG. 8. Yield vs intensity for the TMD model reaction. Pulse duration is  $\tau_p = 0.7/\omega_R^2$  ( $\tau_p$  in ns and  $\omega_R$  in  $\text{cm}^{-1}$ ). (a)  $P$  (pressure) = 0; (b)  $P = 100$  Torr. Line code is same as in Fig. 7.

tion. A two-moment description provides a rough qualitative picture which is sufficient in many cases and is somewhat superior to the SEV method. The three-moment approximation leads to an almost quantitative agreement with the exact solution and is sufficient for all practical purposes.

(b) The incubation time in multiphoton dissociation of large molecules is independent of pressure at low pres-

sure where the processes are dominated mostly by the radiative transitions. A mild dependence on pressure is observed up to moderate pressures (where  $\Gamma_{n-1,n} \sim k_-$ ). At the high pressure limit,  $\theta$  becomes inversely proportional to the pressure [as seen from the result (III.24) for the purely collisional process].

(c) The rates [ $k$  of Eq. (II.6) or  $k_1, k_2$  of Eq. (II.8)] are more strongly dependent on the pressure than the corresponding incubation time  $\theta$ . In particular, the steady state rate is a decreasing function of pressure. We note that for the purely thermal case the opposite is true [c.f. Eq. (IV.25)] however for the values of dissociation threshold and temperature considered here the purely thermal rate is practically zero.

(d) The incubation time and the reaction yield for a given pulse duration and intensity is well described by the PTM approach using Eqs. (II.6) or (II.8). As seen from Figs. (2), (8), and (9) this approach is superior to estimates based on the SEV method. The log-Gauss distribution reproduces well the exact results only in the zero pressure limit. It should be noted that a comparison between the exact and the approximate results for the yield has to be done immediately following the pulse as none of the approximate methods can handle in its present form a situation (as seen, e.g., in Fig. 8) where a substantial part of the dissociation occurs after the pulse.

(e) The dependence of yield mostly on pulse fluence (rather than on the intensity and duration separately) observed and interpreted for collisionless multiphoton excitation governed by excitation (with rates proportional to the IR intensity) in the quasicontinuous and continuous ranges of the molecular spectrum is no longer expected when collisions play a significant part in the evolution. As seen in Fig. 8(b) the yield rises with intensity at fixed fluence, then slowly saturates. The dependence on intensity is of course understandable since the rate matrix is no longer essentially proportional to the light intensity. The initial rise of yield with intensity at fixed fluence results from the competition between the radiative excitation and the collisional loss. The latter occurs on a fixed timescale and its role is reduced when the photochemical timescale is shortened.

These conclusions are expected to hold generally. Details of the time evolution and the dependence of the incubation time, the rates and yield on the parameters characterizing the pulse and on the pressure will of course vary.

## VI. APPLICATION OF PASSAGE TIME MOMENTS IN QUANTUM MECHANICAL EVOLUTION

First passage times were introduced and so far used for processes described by either the master or the Fokker-Planck equation. The concept applies of course equally well to time evolution governed by the Schrödinger or the quantum-mechanical Liouville equation. In this section we explore the possibility to use the method described in Sec. II for an approximate evaluation of a quantum-mechanical evolution.

Our model consists of  $N$  levels of energies

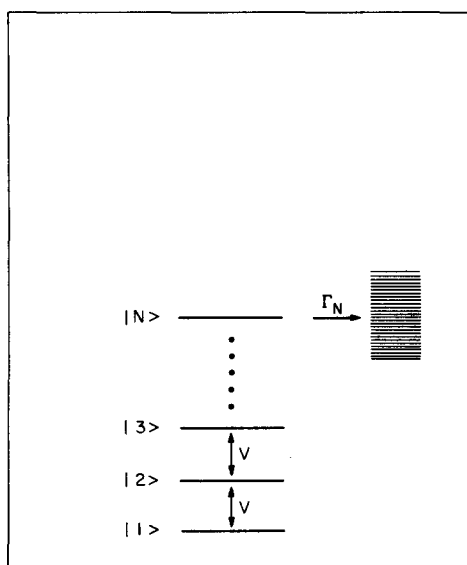


FIG. 9. A schematic model for multiphoton excitation in an  $N$  level system.  $V$  is the radiative coupling. Dissociation (or decay to an intramolecular quasicontinuum) takes place from the upper level.

$E_n (n=1 \cdots N)$  consecutively coupled by photons of frequency  $\omega$  (Fig. 9). The upper level decays with an associated width  $\Gamma_N$  to form a product. The radiative coupling elements are  $V_{n,n+1}$ . In addition we have collision induced dephasing imposing a decay rate  $\gamma_{nn'}$  on a nondiagonal element of the density matrix  $\rho$ .  $\rho$  denotes the density matrix of the "dressed" system-radiation field levels with the corresponding energies  $\bar{E}_n = E_n + (N-n)\hbar\omega$ . The time evolution in the rotating wave approximation is governed by the Liouville equation

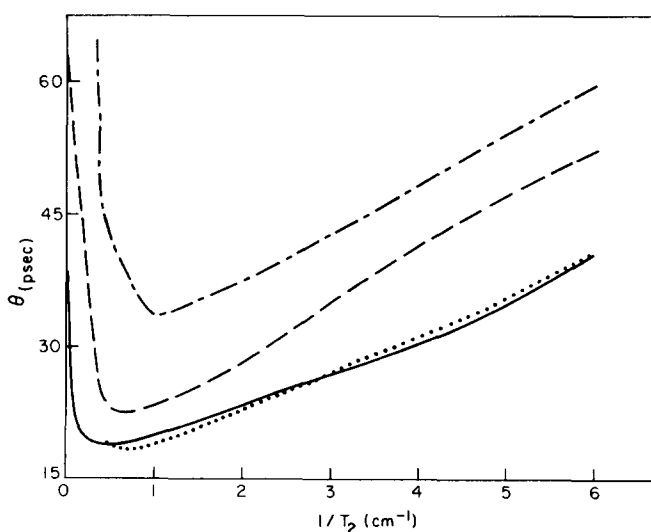


FIG. 10. Incubation time vs dephasing rate in the five-level system described in the text. The full, dotted, dashed, and dash-dotted curves correspond to the exact numerical solution, a three-moment fit, a two-moment fit to Eqs. (II. 6) and (II. 7) and a two-moment fit to the log-Gauss distribution, Eq. (I. 8), respectively.

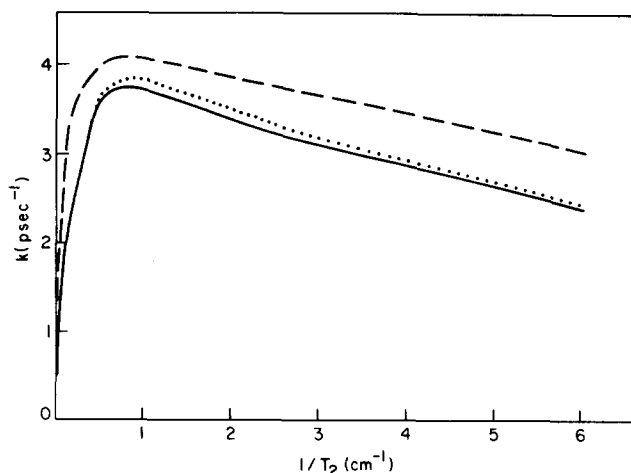


FIG. 11. Steady state rate constant vs dephasing rate in the five-level system described in the text. Line codes are as in Fig. 10.

$$\dot{\rho} = -iL\rho, \quad (\text{VI. 1})$$

where

$$L_{i,j;i,j} = \bar{E}_i - \bar{E}_j - \frac{1}{2}i(\Gamma_i\delta_{iN} + \Gamma_j\delta_{jN}) - i\gamma_{ij},$$

$$L_{i,j\pm 1;i,j} = iV_{j\pm 1,j},$$

and

$$L_{i\pm 1,j;i,j} = iV_{i,i-1}. \quad (\text{VI. 2})$$

This model has been widely used in atomic and molecular physics. In particular it has been used to describe the time evolution within the discrete level region in multiphoton excitation of molecules, as well as for multiphoton ionization of atoms. As is well known, it yields the regular master equation in the limit of fast dephasing (when  $\gamma_{ij}^{-1}$  are the shortest timescales).

Equations (II. 1)–(II. 4) [with Eqs. (II. 1) and (II. 3) in their discrete versions] which define the passage time distribution and moments still hold, where of course

$$\dot{\rho}_n = \rho_m. \quad (\text{VI. 3})$$

In Figs. 10 and 11 we present the results of calculations made on a five level system where the moments are calculated using Eq. (II. 4). The parameters chosen are  $V_{i,i\pm 1} = 1 \text{ cm}^{-1}$  for all  $i$ ,  $E_{i,i-1} = 1 \text{ cm}^{-1}$  for all  $i$ ,  $\Gamma_5 = 0.126 \text{ cm}^{-1}$ , and  $\gamma_{ij} = (1 - \delta_{ij})\gamma$ , independent of  $i$  and  $j$ . Dephasing is expected to initially assist the process as the corresponding broadening of the levels compensates for the off resonance energy gap. For  $\gamma$  larger than the detuning the evolution is essentially master-equationlike with rates becoming inversely proportional to  $\gamma$  for larger  $\gamma$  and the process is inhibited. Correspondingly,  $\theta$  and  $k^{-1}$  pass through a minimum as functions of  $\gamma$  as is seen in the figures.

Turning now to a comparison of the exact and the PTM solutions we see that the three-moment approximation for  $\theta$  and  $k$  agrees well with the exact solutions; however, for  $\gamma$  smaller than  $0.5 \text{ cm}^{-1}$  no physical solution to Eqs. (II. 9) and (II. 10) was obtained. The two-moment solution is obtained for all  $\gamma$  and provides a reasonable ap-

proximation to the exact results. The log-Gauss distribution function [with the parameters  $\mu$  and  $\sigma$  in Eq. (I.8) determined from the two lowest PTM's] is seen to work poorly and deviates by over a factor of 2 from the exact result

## VII. CONCLUSIONS

In this work we have investigated several subjects related to the solution of master (and Liouville) equations for unimolecular reactions.

(a) The validity of replacing a continuous master equation (corresponding to thermal activation of large molecules where the energy is essentially a continuous variable) by a discrete master equation where energy is taken to change in discrete steps  $\epsilon$ , has been investigated. Our result indicate that procedure is valid for the calculation of incubation times. However to reproduce the complete time evolution  $\epsilon$  must be much smaller than  $kT^*$  where  $T^*$  is the effective temperature [Eq. (III.24)]. In a set of test computations for a particular molecular model, we have found that the discrete model reproduces well the exact results for  $\epsilon/kT^* \lesssim 0.28$ .

(b) Several approximation schemes for the time dependent product yield function  $Y(t)$  were investigated. These schemes are based on postulated forms for  $Y(t)$  which contain a small number of parameters. These parameters are obtained from the relatively easy to calculate lower moments of the passage time distribution. The two parameters log-Gauss distribution seems to work well for collisionless multiphoton dissociation but fails at higher collision rates. The three parameter rate model, Eqs. (II.8)–(II.10), works well consistently under all conditions while the simpler two parameter model, Eqs. (II.5), and (II.6) provides an easy route for rapid estimates. Even this simpler scheme is superior to estimates based on the smallest eigenvalue (and the corresponding eigenvector) of the master equation.

(c) The PTM methods provide also reasonable-to-good approximations to solutions of dissociation models based on the quantum-mechanical Liouville equation. Obviously there is a limit to the validity of simple models like (II.6) and (II.8) which can never reproduce quantum-mechanical oscillations, but under conditions where such oscillations are absent, good agreement is obtained in most cases.

In addition, we have found analytical expressions for the first and second passage time moments for some simple master equation models, both discrete and continuous. These results has been used to obtain analytical results for the incubation time and the reaction rates for these simple models. We have previously used<sup>25</sup> such simple analytical results to investigate the pressure and intensity dependence of the incubation time and the rate of multiphoton dissociation of tetramethyldioxethane.

In our view, the most important conclusion of the present work is that a small number (2–3) of parameters (which are of course functions of pressure, temperature, light intensity, etc.) are sufficient for describing the full

time evolution of the product yield function in unimolecular reactions. With the current quality of available experimental results, two parameters are enough in the large majority of cases. These two parameters can be calculated using the PTM method.

This conclusion is reminiscent of the general success of the information theory approach to chemical kinetics. This success is again associated with the fact that for most relevant observables, a few moments of the distribution function usually contain sufficient relevant information on the process studied. We have chosen not to work in the framework of information theory because the constraints imposed by given passage time moments are not easy to implement within this framework.

After completion of this work we received articles by Baldwin and Barker<sup>38</sup> in which they use passage time moments to fit the parameters of the log-Gauss distribution in a way similar to what we describe in Sec. II.

## ACKNOWLEDGMENTS

This research was supported in part by the U.S. – Israel Binational Science Foundation, Jerusalem. We thank Dr. Peter Salamon for helpful discussions.

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