Incubation times in the multiphoton dissociation of polyatomic molecules

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The incubation period revealed in the multiphoton dissociation of molecules by intense infrared lasers is discussed. It is found experimentally that large excess of added foreign gas affects the incubation period to a much smaller degree than the overall yield. A rate equations model is presented, including both the laser intensity and collisional effects. Exact numerical solution is compared with a simple analytical approximation, based on the passage time moments method. Agreement with experimental results is quite satisfactory, indicating that the role of collisions in the case discussed (tetramethyldioxetane dissociation) is primarily vibrational relaxation of excited molecules.

INTRODUCTION

A considerable amount of work has been carried out in an effort to elucidate the microscopic mechanisms which govern multiphoton excitation (MPE) and multiphoton dissociation (MPD) of large molecules. The fact that these multistep processes are affected by many molecular parameters, most of them unknown, while the number of directly observable quantities is quite limited has been the main source of difficulty in these attempts. Another (closely related) problem lies in the fact that most measurements made to date monitor time averaged molecular properties (e.g., mean energy absorbed or dissociated yield) following an IR pulse or a train of pulses. In such experiments the instantaneous dynamical evolution of the molecules is often obscured. It appears that more direct information is needed, particularly that which can be obtained by real time measurements. These measurements can be conveniently based on monitoring electronically excited dissociation products by their fluorescence, or ground state products by laser induced fluorescence as has recently been reported by several laboratories.[1-3]

The possibility to follow real time MPE dynamics implies that transient phenomena associated with this process can be observed. Such transients result (a) from the nonstationary (pulsed) nature of the excitation source and (b) from the inherent molecular evolution. The first cause may be eliminated in cases where the molecular evolution is determined solely by the field energy and not by its intensity, simply by considering the molecular evolution as a function of the "effective time" t_e $= \tau_p \int_0^t I(t')dt'/\int_0^\infty I(t')dt'$, where τ_p is a measure of the pulse duration. The evolution dynamics as a function of t_e corresponds to excitation by a rectangular pulse with duration τ_p and intensity $\tau_p^{-1} \int_0^\infty I(t)dt$.

Turning now to the inherent molecular evolution, we note that the transient behavior is associated with the relaxation of the molecular distribution towards its steady state in the presence of the radiation field. This

relaxation period has been termed "incubation time" in the literature on thermal reactions.[4,5] From the practical point of view, however, the incubation time is observed as the time elapsed between the onset of the radiation field and the first observation of the monitored species (e.g., dissociation product). Quack[6] has recently shown that taking a proper account of incubation times is essential in the analysis of intensity dependence in MPD yield and that their presence may account for at least part of the nonlinear dependence of yield on intensity observed in many experiments and generally attributed to lower discrete molecular spectrum.

Another aspect of real time measurements lies in the ability to study collisional effects separately within and after the laser pulse. It should be mentioned that some pressure effects reported in the literature (in particular those associated with self collisions of the excited molecule) may have resulted from collisions occurring after the pulse,[1] and therefore may be irrelevant to the analysis of collisional effects on the up-pumping process.

In this paper we use an approximate technique for calculating incubation times associated with MPD assuming that the latter is described by a simple master equation. This analysis is compared to recent results obtained for MPD of tetramethyldioxethane (TMD).[1] We also present preliminary results showing the foreign gas pressure effect on the transient MPD behavior and analyze the observed behavior by a simple generalization of the kinetic model. The main results of the present study are as follows: (a) Incubation times are proportional to the inverse averaged intensity, corresponding to the existence of an energy threshold in the MPD process. They are also approximately proportional to the molecular dissociation energy. (b) Incubation times are only weakly dependent on foreign gas pressure (in the experiments reported below no dependence is found for 0–200 torr added N_2 within the experimental accuracy). (c) The dissociation rate (and thus the yield) decreases moderately with increasing pressure.

EXPERIMENTAL RESULTS

The experimental setup was described in an earlier paper[1] where the inverse linear dependence of the incu-

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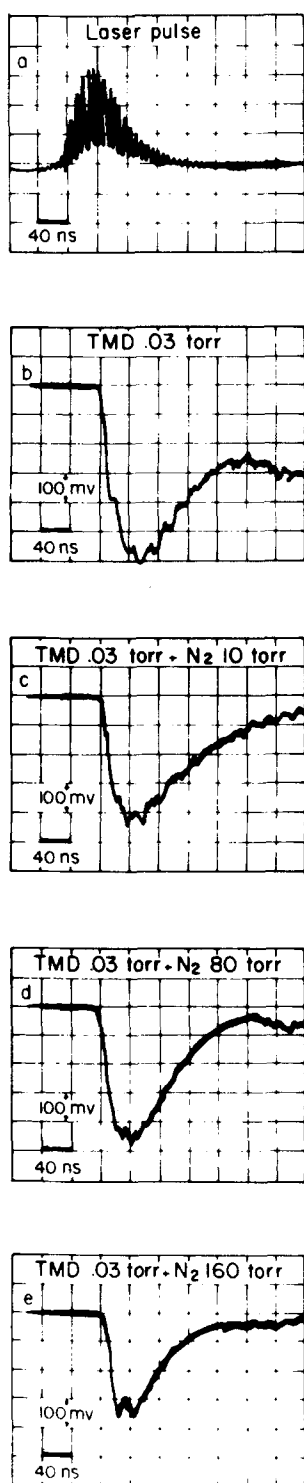
FIG. 1. The effect of added nitrogen on TMD multiphoton induced chemiluminescence. TMD pressure is 30 mTorr in all cases. The incubation period, defined as the time interval between the laser pulse onset and the chemiluminescence onset, is 80 nsec in all cases. Note that the postlaser chemiluminescence, clearly observed in the pure TMD case, is completely absent in the presence of nitrogen. Luminescence intensity is shown with the same arbitrary units in all cases.

bation time on the averaged pulse intensity under collisionless conditions and the existence of an energy threshold of ~30–35 mJ per pulse (100 J/cm^2 in the focused region) was also reported.

The effect of added inert gas on TMD multiphoton dissociation is shown in Fig. 1. Molecular nitrogen, found to be very effective in quenching the reaction occurring after the termination of the laser pulse,[7] was used. As Fig. 1 shows, the intensity of luminescence due to reaction occurring during the laser pulse is only moderately

affected. (In contrast, afterpulse chemiluminescence is completely quenched with 25 Torr of N$_2$). The incubation period is seen to be constant up to 160 Torr of added N$_2$, within experimental error.

Similar results to those reported here for TMD were obtained also for the multiphoton dissociation of SiF$_4$,[7] only there the product fluorescence yield is strongly reduced by increasing the N$_2$ pressure. It should be kept in mind however that collisions may quench the fluorescence by inducing radiationless relaxation in the product.

THEORETICAL ANALYSIS AND DISCUSSION

The inverse linear dependence of the incubation time on the averaged pulse intensity suggests that the bottom discrete levels (region I)[8] of the molecular vibrational manifold may be disregarded. This is indeed reasonable as we are dealing with a molecule of 54 vibrational degrees of freedom at room temperature. The radiative evolution and the consecutive dissociation may therefore be described by the master equation

$$\frac{d\mathbf{P}(t)}{dt} = \mathbf{K}\mathbf{P}(t) , \tag{1}$$

where $\mathbf{P} = (P_1 \circ \circ \circ P_n \cdots)$, P_n being the fraction of molecules that has absorbed n IR photons; and where

$$K_{nm} = k_{n-n+1}\delta_{m,n+1} + k_{n-n-1}\delta_{m,n-1} - (k_{n+1-n} + k_{n-1-n} + \gamma_n)\delta_{nn} , \tag{2}$$

in which k_{n-m} are the laser induced transition rate constants (linear in the laser intensity I) between molecular energy regimes corresponding to n and m absorbed photons and where γ_n is the dissociation rate of a molecule which has absorbed n photons. ($\gamma_n = 0$ for $n < N$, and N is determined by the dissociation threshold.) In the presence of collisions Eq. (1) should be replaced by an equation of the form

$$\frac{\partial P(E, t)}{\partial t} = \int_0^\infty dE' L(EE')P(E't) , \tag{3}$$

with

$$L(EE') = A(EE') + k(E, E + h\omega)\delta(E + h\omega - E') + k(E, E$$
$$- h\omega)\delta(E - h\omega - E') - \left[\int_0^\infty A(E'E)dE' + k(E + h\omega, E)\right.$$
$$\left. + k(E - h\omega, E) + \gamma(E)\right]\delta(E - E') , \tag{4}$$

where $A(EE')$ is the (continuous) collisional rate matrix,[9] while the k and γ functions are extensions of the radiative and dissociation rates of Eq. (2) in an obvious notation [note that $k(E - h\omega, E) = 0$ for $E < h\omega$].

A major simplification of Eq. (3) may be achieved if the average energy transferred per collision is much smaller than the total energy interval of interest (e.g., the dissociation energy). In this case we can approximately represent the effect of collisions by discrete jumps. This leads back to Eqs. (1) and (2) with modified rates $\bar{k}_{nm}$ replacing the pure radiative rates k_{nm} in Eq. (2). It can be readily shown that the proper choice
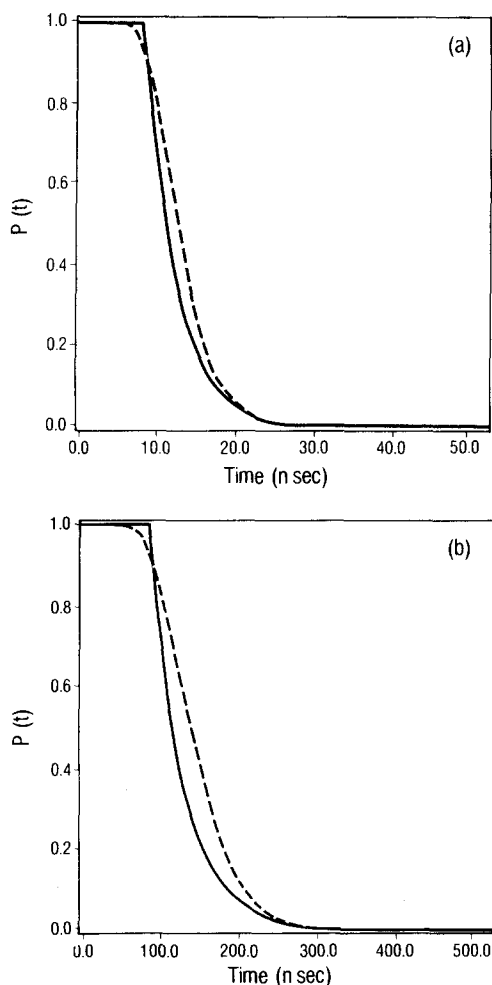
FIG. 2. Model calculation of the dissociation rate as a function of ω_R. Solid line: exact numerical solution of Eq. (1) using the parameters of Table I. Dashed line: approximate solution using the PTM method [Eqs. (11) and (12)]. (a) ω_R = 0.25 cm^{-1}; (b) ω_R= 0.07 cm^{-1}.

for the $\bar{k}_{nm}$ rates is

$$\bar{k}_{n+1-n} = k_{n+1-n} + \frac{M\beta(n\hbar\omega)}{\hbar\omega} , \tag{5a}$$

$$\bar{k}_{n-1-n} = k_{n-1-n} + \frac{M\alpha(n\hbar\omega)}{\hbar\omega} , \tag{5b}$$

where ω is the IR photon frequency, M is the number of collisions per unit time inducing vibrational relaxation in the excited molecule, and where $\beta(E)$ and $\alpha(E)$ are, respectively, the average vibrational energy transfer per collision into and out of the vibrationally excited molecule having energy E above the ground state. $\alpha(E)$ and $\beta(E)$ are related to $\Delta(E)$, the total average vibrational energy loss per collision sufferred by a molecule of energy E, by

$$\Delta(E) = \langle \Delta E \rangle_E = \beta(E) - \alpha(E) \quad (<0) . \tag{6}$$

Another relation between $\alpha(E)$ and $\beta(E)$ is obtained from the detailed balance condition. In the exponential model for the collisional rate matrix[9] one obtains

$$\frac{1}{\beta(E)} - \frac{1}{\alpha(E)} = \frac{1}{k_B T} - \mu(E) , \tag{7}$$

where

$$\mu(E) = \frac{d \ln \rho(E)}{dE} , \tag{8}$$

$\rho(E)$ being the vibrational density of states of the molecule at energy E.

Equation (1) can now be solved for any given molecular model. Such a model is characterized by the radiative absorption cross section $\sigma(E)$ and the density of states $\rho(E)$ for a molecule with vibrational energy E above the ground state {so that $k_{n+1-n} = \sigma(n\hbar\omega)I/\hbar\omega$ and $k_{n-n+1} = k_{n+1-n}\rho(n\hbar\omega)/\rho[(n+1)\hbar\omega]$} by the dissociation rate constants $\gamma(E)$ and by the average energy loss per collision $\Delta(E)$. The general case has to be computed numerically. However, approximate analytical results for the incubation time and the dissociation rate may be obtained for simplified models by the passage time moments (PTM) method.[10]

In the simplest version of this method we calculate the two lowest moments τ_1 and τ_2 of the distribution of passage times $\pi(t)$ [$\pi(t)dt$ is the probability that the molecule will dissociate in the time interval $t \cdots t+dt$].[11] Denote

$$P(t) = 1 - \int_0^t \pi(t')dt' ; \tag{9}$$

then it is easily realized that

$$P(t) = \sum_n P_n(t) . \tag{10}$$

In terms of $P(t)$ the passage time moments are given by[11]

$$\tau_n(t) \equiv \int_0^\infty t^n \pi(t)dt = n \int_0^\infty t^{n-1}P(t)dt . \tag{11}$$

The calculated τ_1 and τ_2 are used to fit the parameters k and θ of the function

$$P_A(t) = \begin{cases} 1 , & t \le \theta , \\ \exp[-k(t-\theta)] , & t \ge \theta . \end{cases} \tag{12}$$

$P_A(t)$ is an approximation to $P(t)$. In this approximation θ and k are identified as the incubation time and as steady state dissociation rate, respectively. θ and k are obtained in terms of τ_1 and τ_2 in the form

$$k^{-1} = (\tau_2 - \tau_1^2)^{1/2} , \tag{13}$$

$$\theta = \tau_1 - (\tau_2 - \tau_1^2)^{1/2} . \tag{14}$$

Some results comparing the exact numerical solution of the master equation and the approximation obtained by this version of the PTM method are shown in Fig. 2. Obviously, one can improve the PTM results by calculating higher moments of the passage time distribution and fitting to a function $P_A(t)$ with more parameters. The calculation of several such moments is considerably easier than a full solution of the master equation.

Consider now a rate process governed by a master equation of the form (1) and (2) and characterized by the following features: (a) All forward rates are equal $k_{n+1-n} = k_+$ and all backward rates are equal $k_{n-1-n} = k_-$; and (b) dissociation first occurs from the level $n = N + 1$

and its rate is so fast relative to k_+ that the levels $n \geq N+1$ are not populated. For this model $P(t) = \sum_{n=0}^{N} P_n(t)$ and we obtain[12]

$$\tau_1 = \frac{1}{k_-} \frac{N\eta^{N+1} - (N+1)\eta^N + 1}{(\eta - 1)^2 \eta^N} , \tag{15}$$

$$\tau_2 = \left(\frac{1}{k_-}\right)^2 \frac{N(N+1)\eta^{2N+2} - 2(N^2+N+2)\eta^{2N+1} + N(N+1)\eta^{2N} + 2(3N+2)\eta^{N+1} - 2(3N+1)\eta^N + 2}{(\eta-1)^4 \eta^{2N}} , \tag{16}$$

where $\eta = k_+/k_-$. The corresponding θ and k are obtained from Eqs. (13) and (14).

When the rates k_+ and k_- are determined mostly by the collisional process we usually have (except for extremely high temperatures) $\eta < 1$ and then for the usual case where $N \gg 1$, Eqs. (13)–(16) yield

$$\theta \cong \frac{N}{k_-(1-\eta)} , \qquad k^{-1} \cong \frac{1}{k_-\eta^N(1-\eta)^2} . \tag{17}$$

In the opposite case where the rates are determined mostly by the radiative transitions, $\eta > 1 [\sim \rho(E + \hbar\omega)\rho(E)]$ and Eqs. (13)–(16) result in (for $N \gg 1$)

$$\theta = \frac{N}{k_-(\eta-1)} , \qquad k^{-1} \simeq \left[\frac{\eta+1}{(\eta-1)^3}\right]^{1/2} \frac{\sqrt{N}}{k_-} . \tag{18}$$

Finally, it is interesting to note that for $\eta = 1$ ($k_+ = k_- \equiv k_+$) one obtains $\theta \simeq [(3 - \sqrt{6})/6]N^2/k_+$ and $k^{-1} \simeq (1/\sqrt{6})N^2/k_+$.

The time evolution according to Eq. (1) was calculated using an exact (numerical) method and the PTM approximation. Input parameters to the master equation were taken as follows: $k_{n-n+1} = k_{n+1-n} \times \{\rho(n\hbar\omega)/\rho[(n+1)\hbar\omega]\}$; $k_{n+1-n} = \omega_R^2/\Gamma_a$, where ω_R is the Rabi frequency (proportional to the IR field strength) for the 0–1 transition and where Γ_a is a measure of the width associated with the optically active mode in the quasicontinuum, and Γ_a was chosen to be 50 cm^{-1} for all excitation energies; the density of states function $\rho(E)$ was calculated using the Whitten–Rabinovitch[13] formula for the species $R_4(CO)_2$ with frequencies appropriate for the TMD molecule without however counting the methyl CH bonds. The dissociation energy was taken to be $\sim 10\hbar\omega$ (approximating the known activation energy of TMD) and the dissociation rates were calculated using a crude RRKM scheme for TMD (again disregarding the CH bonds). A summary of input parameters is given in Table I. The master equation was truncated after 27 photon absorption steps.

Figures 2(a) and 2(b) show the results of these calculations for $\omega_R = 0.25$ and 0.07, respectively. Both exact and PTM calculations are seen to reproduce the experimental curve (Fig. 1) reasonably well. Obviously, the definition of the incubation period is somewhat ambiguous, as it depends on the sensitivity of the measurement.[14] However, as Figs. 2(a) and 2(b) show, a sharp increase in dissociation rate is clearly obtained after a finite period of time, strongly dependent on laser power (here represented by ω_R). The duration of the delay indicates a weak dipole moment of the 0–1 transition (of the order of 0.01 D). This is in agreement with the observed infrared intensities of TMD at about 10.2 μ.

The result of a similar calculation based on RRKM dissociation rates smaller by a factor of 10 than those in Table I are shown in Fig. 3. The numerical solution of the full master equation enables us to look also at the yield of dissociation from different energy regions. The result for this choice of parameters indicates that the maximum dissociation yield corresponds to molecules that have absorbed 16 photons. Also, in Fig. 3 we display the result of a calculation done for a truncated model. Only 16 photon absorption steps are considered; γ_n is taken zero for $n < 16$ and very large for $n = 16$ so that all dissociation occurs from this energy regime. The close agreement between the results of the two calculations (the somewhat shorter incubation time obtained for the more realistic model reflects the fact that in

TABLE I. Parameters for IR dissociation of TMD. Molecular frequencies were taken to be (cm^{-1}) 4×980, 4×700, 4×50, 3×450, and 3×880 (the vibrations associated with the CH bonds are not included). Dissociation energy $= 9500$ cm^{-1}, photon frequencies $= 950$ cm^{-1}, and n is the number of photon absorbed (corresponding to excess molecular vibrational energy $n\hbar\omega$). $k_{n+1-n} = 6.2 \times 10^{-4}$ cm^{-1} for all n, $\omega_R = 0.07$ cm^{-1}.

| N	$(n\hbar\omega)$ (cm)	k_{n-n+1} (cm^{-1})	$\gamma_n = \gamma(n\hbar w)$ (cm^{-1})
1	19.7	0.1×10^{-4}	
2	889	0.4×10^{-4}	
3	15.5×10^3	0.3×10^{-4}	
4	16.1×10^4	0.8×10^{-4}	
5	11.9×10^5	1.1×10^{-4}	
6	69.1×10^5	1.3×10^{-4}	
7	33.4×10^6	1.5×10^{-4}	
8	13.9×10^7	1.7×10^{-4}	
9	51.2×10^7	1.8×10^{-4}	
10	17.1×10^8	2.0×10^{-4}	4.1×10^{-6}
11	52.3×10^8	2.2×10^{-4}	3.04×10^{-5}
12	14.9×10^9	2.3×10^{-4}	1.43×10^{-4}
13	39.7×10^9	2.4×10^{-4}	5.00×10^{-4}
14	10.0×10^{10}	2.6×10^{-4}	1.38×10^{-3}
15	24.0×10^{10}	2.7×10^{-4}	3.25×10^{-3}
16	55.1×10^{10}	2.8×10^{-4}	6.74×10^{-3}
17	12.2×10^{11}	2.9×10^{-4}	1.26×10^{-2}
18	25.9×10^{11}	3.0×10^{-4}	2.18×10^{-2}
19	53.2×10^{11}	3.1×10^{-4}	3.53×10^{-2}
20	10.6×10^{12}	3.2×10^{-4}	5.41×10^{-2}
21	20.6×10^{12}	3.3×10^{-4}	7.91×10^{-2}
22	39.1×10^{12}	3.3×10^{-4}	1.11×10^{-1}
23	72.2×10^{12}	3.4×10^{-4}	1.51×10^{-1}
24	13.1×10^{13}	3.5×10^{-4}	2.00×10^{-1}
25	23.2×10^{13}	3.5×10^{-4}	2.57×10^{-1}
26	40.3×10^{13}		3.24×10^{-1}
27	68.8×10^{13}		4.01×10^{-1}
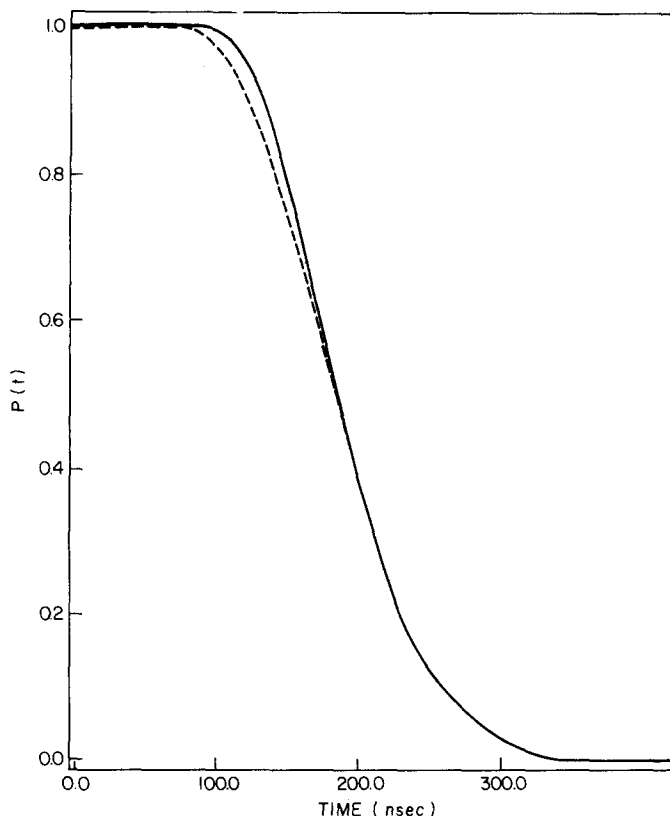
FIG. 3. Time evolution of TMD laser induced dissociation using RRKM rate constants (dashed line) and a step function distribution of rate constants, in which $\gamma(n) = 0$ for $n < 16$ and $\gamma(16) \ 3 \times 10^{11} \ \text{sec}^{-1}$ (solid line).

TABLE III. Effect of added inert gas.

P (Torr)	θ (nsec)	$\frac{1}{k}$ (nsec)
0.0	33.4	15.6
20.0	34.3	19.5
40.0	35.2	24.5
60.0	36.0	30.8
80.0	36.5	39.1
100.0	36.8	49.9
120.0	36.7	64.0
140.0	36.3	82.0
160.0	35.5	105.3
180.0	34.6	134.3
200.0	33.0	169.8

reality dissociation starts before the molecule absorbs 19 photons) suggests that this truncation (which is the essence of the approximate calculation described above) is valid. (Similar agreement is obtained in a calculation based on RRKM rates of Table I with a truncated model using 14 photon absorption steps).

The approximate results (17) and (18) suggest that the incubation time is linear in the ratio N/k. Table II shows a test of this result using the exact numerical solution for the model defined by Table I. We see that the linear dependence of the incubation time on the inverse intensity is maintained only approximately; however, in the experimentally relevant domain ($\theta = 100$–30 nsec) the product $\omega_R^2 \theta$ changes only by 10% when ω_R^2 changes by a factor of 4.

TABLE II. Incubation time vs intensity. Molecular parameters are given by Table I. The master equation was truncated after 27 photon absorption steps.[a]

ω_R (cm^{-1})	0.05	0.07	0.10	0.25	0.375	0.50
θ_{exact} (nsec)	116.7	63.7	31.8	6.8	3.0	1.75
θ_{PTM} (nsec)	150.8	84.2	44.1	9.0	4.1	2.4
$\omega_R^2 \times \theta_{\text{exact}}$	0.29	0.31	0.32	0.42	0.42	0.44

[a] θ_{exact} is determined from an exact numerical solution of the master equation as the point where the $P(t)$ curve (Fig. 2) visibly starts to bend down. θ_{PTM} is obtained from Eq. (14) using numerically calculated τ_1 and τ_2.

Finally, we consider the effect of an added inert gas. Table III shows the results of a calculation based on Eqs. (13)–(16) with $N = 19$ and

$$k_+ = (k_+)_{\text{rad}} + \frac{10^{-4}(P)_{\text{Torr}} \beta}{\omega} ,$$

$$k_- = (k_-)_{\text{rad}} + \frac{10^{-4}(P)_{\text{Torr}} \alpha}{\omega} .$$

α and β [Eqs. (6) and (7)] were chosen to be 222.3 and 122.3 cm^{-1}, respectively. The factor $10^{-4}(P)_{\text{Torr}}$ represents an estimate of the number of collisions per unit time. $(k_+)_{\text{rad}}$ and $(k_-)_{\text{rad}}$ were taken to be constants: 0.003 and 0.001 cm^{-1}, respectively. We see that, for these parameters, in the pressure range 0–200 Torr the incubation time is predicted to change only slightly while the steady state dissociation rate decreases by about an order of magnitude. Similar results are obtained from the exact numerical solution of Eq. (1) using Eq. (5) as well as from the approximation (19). It is interesting to note that the mean molecular energy at any time is greatly reduced due to the collisions. The incubation time θ is not strongly affected because the molecular distribution broadens and because it is the tail of the distribution which determines θ.[15] It should also be noted that while the general feature of the incubation time being considerably less sensitive to collisions than the steady state dissociation rate appears to hold for a broad range of parameters, the absolute dependence of θ and k on pressure varies with the choice of parameters. For example, in the extremely pressure dominated regime η becomes pressure independent and both θ and k^{-1} are inversely proportional to the pressure [cf. Eq. (17)].

In the present analysis we have taken the primary effect of collisions to be the induction of vibrational relaxation in the molecular quasicontinuum. This leads to a reduction in the dissociation yield in agreement with the experimental observation here and in previous works.[16]

Collisions can also help in overcoming a bottleneck effect in region I, by efficient rotational relaxation and, at high enough pressures, also by pressure broadening. These effects can lead to increased absorption efficiency and higher dissociation yields,[17] as well as to cancelation of intensity effects on the yields.[3] They can also

be easily incorporated into the model, as shown elsewhere.[12] The results of the present paper indicate that such bottleneck effects are probably less important in TMD, as expected for a very large molecule.

CONCLUSION

The presence and behavior of incubation times in multiphoton dissociation of molecules were analyzed within the formalism of the Pauli master equation. Approximate quantitative results can be obtained for any given molecular model (i.e., parameters) for an isolated and collisionally perturbed molecule. It should be realized that the definition and the calculation of incubation times are not limited to dissociation processes; any molecular level whose population may be monitored (e.g., by laser induced fluorescence) may constitute the threshold which is used to define and calculate the incubation time. Also, the method is not limited to the Pauli master equation and can be used for processes governed by the full Liouville equation (e.g., for evolution within a discrete manifold of molecular states).

ACKNOWLEDGMENTS

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