Calculation of fluence-dependent dissociation probabilities in infrared multiple-photon photolysis

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Received July 31, 1979

Exact analytical expressions are derived for the expected dissociation yield in bulk infrared photolysis experiments; these results are based on a power-law fluence-dependent model of infrared multiple-photon dissociation as applied to the interaction of a focused, Gaussian-profiled pulsed laser with a medium.

In recent years infrared multiple-photon dissociation (MPD) has been extensively studied from both fundamental scientific and applications-oriented vantage points. The dissociation probability has been found to be a sensitive function of the laser fluence in regimes between threshold and saturation. An accurate quantitative characterization of this fluence dependence based on experimental observations is quite important and is particularly essential in assessing possible applications of MPD. Although some research on the relation of the observed bulk-reaction yield to laser fluence (or intensity) has been reported, such as the explanation of the 3/2 power law for MPD in tightly focused geometries,[1] formulas relating observed yields to a general fluence-dependent dissociation probability and beam geometry are apparently not available. This Letter derives these general equations.

Consider a laser that propagates centrally and axially through a cylindrical cell of length l and radius R and that is focused in the center of the cell. The transverse profile is taken to be Gaussian with (electric-field) confocal radius ω, so the radial dependence of the fluence, ϕ, is given by

$$\phi(r,z) = \phi(0,z)\exp[-2r^2/\omega^2(z)], \tag{1}$$

where r and z are the radial and longitudinal coordinates, respectively, which are measured from the center of the cell. $\phi(0,z)$ is readily related to the laser-pulse energy, E, and the beam parameters:

$$\phi(0,z) = \frac{2E}{\pi\omega^2(z)}. \tag{2}$$

The expression for the beam radius for a focused Gaussian-profiled laser is given by

$$\omega^2(z) = \omega_0^2\left[1+\left(\frac{\lambda z}{\pi\omega_0^2}\right)^2\right] = \omega_0^2\left[1+\left(\frac{z}{a}\right)^2\right], \tag{3}$$

where ω_0 is the radius at the focus ($z = 0$), λ is the wavelength, and a equals the conventional Rayleigh range ($a = \pi\omega_0^2/\lambda$). Any deviation from diffraction-limited behavior may be incorporated into Eq. (3) by suitably decreasing a.

Two empirical (and widely employed) models for the fluence dependence of the dissociation probability, $P(\phi)$, are considered:

$$\text{(Model I)} \quad P(\phi) = p\left(\frac{\phi}{\phi_{\text{sat}}}\right)^m \qquad \phi < \phi_{\text{sat}}$$

$$m = \text{integer} \tag{4a}$$

$$= p \qquad \phi \geq \phi_{\text{sat}}; \tag{4b}$$

$$\text{(Model II)} \quad P(\phi) = 0 \qquad \phi < \phi_{\text{crit}} \tag{5a}$$

$$= p \qquad \phi \geq \phi_{\text{crit}}. \tag{5b}$$

An integral power-law dependence is assumed in the first case; the dissociation probability saturates at p for fluences above ϕ_{sat}. The second case is actually a special case of Model I with $m \to \infty$ and $\phi_{\text{sat}} \to \phi_{\text{crit}}$ (which is the critical or threshold fluence). The predictions of the expected yield based on this simple model are easily derived from the yield equations obtained assuming Model I. The maximum dissociation probability at high fluences is p ($0 < p \leq 1$) in both cases. Under many conditions p is nearly unity; however, in the MPD of small molecules p may be much less than 1 because of rotational-level bottlenecking.[2]

The experimental-dissociation yield may be expressed in terms of an effective volume, V_{eff}, which is defined as the product of the observed fractional yield per pulse and the cell volume. V_{eff} may also be expressed in terms of $P(\phi)$ (Model I):

$$V_{\text{eff}} = 2\int_0^{l/2}\int_0^{2\pi}\int_0^R P(\phi) r\,dr\,d\theta\,dz, \tag{6}$$

where θ is the cylindrical angular coordinate.

V_{eff} may be obtained by first calculating the effective cross-sectional area, A_{eff}, which includes only the inner two integrations of Eq. (6):

$$A_{\text{eff}} = 2\pi\int_0^R P(\phi) r\,dr \tag{7a}$$

and

$$V_{\text{eff}} = 2\int_0^{l/2} A_{\text{eff}}\,dz, \tag{7b}$$

where cylindrical symmetry has just been invoked.

For the moment, assume that $\phi(0,z) > \phi_{\text{sat}}$. If r_{sat} is that radius at which $\phi = \phi_{\text{sat}}$, then within this radius $P = p$; r_{sat} is determined from Eqs. (1) and (2):

0146-9592/79/120403-03$0.50/0

$$r_{\mathrm{sat}}^2 = \frac{\omega^2(z)}{2} \ln\left[\frac{2E}{\pi\omega^2(z)\phi_{\mathrm{sat}}}\right]. \tag{8}$$

Therefore, in a circular section in which $\phi(0,z) \geq \phi_{\mathrm{sat}}$,

$$A_{\mathrm{eff}} = \pi r_{\mathrm{sat}}^2 p + 2\pi \int_{r_{\mathrm{sat}}}^{R} P(\phi) r\,dr \tag{9a}$$

$$= \pi r_{\mathrm{sat}}^2 p + \pi \frac{\omega^2(z)}{2m} p, \tag{9b}$$

where the last form is obtained from Eqs. (1), (4a), and (8); it is assumed that the laser fluence is vanishingly small at the cell radius. However, if $\phi(0,z) < \phi_{\mathrm{sat}}$, then Eq. (9a) is utilized with $r_{\mathrm{sat}} = 0$:

$$A_{\mathrm{eff}} = \frac{\pi\omega^2(z)p}{2m}\left[\frac{2E}{\pi\omega^2(z)\phi_{\mathrm{sat}}}\right]^m. \tag{10}$$

If $\bar{z}$ is defined as the longitudinal coordinate at which $\phi(0,z) = \phi_{\mathrm{sat}}$, then Eq. (9b) is valid for $|z| \leq \bar{z}$, whereas Eq. (10) is correct for $|z| \geq \bar{z}$. $\bar{z}$ may be expressed as

$$\bar{z} = a(\eta - 1)^{1/2} \tag{11}$$

with

$$\eta \equiv \frac{2E}{\pi\omega_0^2\phi_{\mathrm{sat}}}. \tag{12}$$

η is the ratio of the peak fluence at the focus to the saturation fluence. If $\eta < 1$, then $\bar{z}$ is taken to be 0, whereas if $\bar{z} > l/2$ it is set equal to $l/2$.

These expressions for A_{eff} are now substituted into Eq. (7b):

$$V_{\mathrm{eff}} = 2p\int_0^{\bar{z}}\left[\pi r_{\mathrm{sat}}^2 + \pi\frac{\omega^2(z)}{2m}\right]dz + 2p\int_{\bar{z}}^{l/2}\frac{\pi\omega^2(z)}{2m}\left[\frac{2E}{\pi\omega^2(z)\phi_{\mathrm{sat}}}\right]^m dz \tag{13a}$$

$$= 2p\int_0^{a(\eta-1)^{1/2}}\left\{\frac{\pi\omega_0^2}{2}\left[1+\left(\frac{z}{a}\right)^2\right]\ln\left[\frac{\eta}{1+\left(\frac{z}{a}\right)^2}\right] + \frac{\pi\omega_0^2}{2m}\left[1+\left(\frac{z}{a}\right)^2\right]\right\}dz + 2p\int_{a(\eta-1)^{1/2}}^{l/2}\frac{\pi\omega_0^2}{2m}\left[1+\left(\frac{z}{a}\right)^2\right]\left[\frac{\eta}{1+\left(\frac{z}{a}\right)^2}\right]^m dz. \tag{13b}$$

Equation (13b) is derived from Eq. (13a) using Eqs. (3), (8), (11), and (12). For an unfocused beam, V_{eff} equals lA_{eff}, where the appropriate form of A_{eff} is employed [either Eq. (9b) or Eq. (10)] and the actual beam waist, ω_0, is substituted for $\omega(z)$; in this special case, the result will agree with that obtained by using the prescription for averaging functions over Gaussian beams presented by Kolodner *et al.*[3]

Equation (13b) involves standard integrals, which are straightforwardly evaluated, leading to (for $m \geq 2$)

$$V_{\mathrm{eff}} = \pi\omega_0^2 ap\left\{\frac{4m+3}{3m}(\eta-1)^{1/2} + \frac{2m+3}{9m}(\eta-1)^{3/2} - \frac{4}{3}\arctan(\eta-1)^{1/2} + \frac{\eta^m}{m}\left[\frac{x}{2m-3}\sum_{k=1}^{m-2}\frac{1}{2^k}\frac{(2m-3)!!}{(2m-2k-3)!!}\times\frac{(m-k-2)!}{(m-2)!}\frac{1}{(1+x^2)^{m-k-1}} + \frac{(2m-5)!!}{2^{m-2}(m-2)!}\arctan x\right]\Bigg|_{x=(\eta-1)^{1/2}}^{l/2a}\right\}. \tag{14}$$

If $\eta < 1$, then each $(\eta - 1)$ is replaced by zero. The m-independent portions of the first three terms in the curly brackets are derived from the πr_{sat}^2 expression in Eq. (13a), whereas the m-dependent parts of the first two terms come from the $\pi\omega^2(z)/(2m)$ expression in the same equation. These three cited terms are absent if $\eta < 1$. The last term comes from the $l/2 > z > \bar{z}$ integration in Eq. (13a). The appropriate values of ϕ_{sat}, m, and p in the Eq. (4) probability function can now be determined, for example graphically, by using Eq. (14). The first two parameters affect the shape of the V_{eff} versus ϕ plot, whereas the last variable is only an overall multiplying factor.

It is clear from Eq. (14) that in the weak laser limit ($\eta \ll 1$) the observed yield obeys the same power-law dependence as does $P(\phi)$, whereas, in the tightly focused geometry, highly saturated regime ($\eta \gg 1$), the $\frac{3}{2}$ power law can dominate. Speiser and Jortner[1] have reached similar conclusions for non-Gaussian beams.

The expression for V_{eff} for the special case of $m = 3$ will be presented here because a cubic fluence dependence has been observed in the yield of MPD of several molecules[4] (below saturation) using lasers with relatively flat and decidedly non-Gaussian transverse profiles [so $V_{\mathrm{eff}}(\phi)$ behaves like $P(\phi)$]:

$$V_{\mathrm{eff}}^{m=3} = \pi\omega_0^2 ap\left\{\frac{5}{3}(\eta-1)^{1/2} + \frac{1}{3}(\eta-1)^{3/2} - \frac{4}{3}\arctan(\eta-1)^{1/2} + \frac{\eta^3}{6}\arctan\frac{l}{2a} - \frac{\eta^3}{6}\arctan(\eta-1)^{1/2} + \frac{\eta^3}{6}\frac{l/2a}{1+\left(\frac{l}{2a}\right)^2} - \frac{\eta^3}{6}\frac{(\eta-1)^{1/2}}{1+[(\eta-1)^{1/2}]^2}\right\}. \tag{15}$$

Finally, the effective volume for the probability function assumed in Model II [Eq. (5)] is straightforwardly obtained from Eq. (14) by letting $m \to \infty$:

$$V_{\mathrm{eff}}^{\mathrm{Model\ II}} = \pi\omega_0^2 ap\left[\frac{4}{3}(\eta-1)^{1/2} + \frac{2}{9}(\eta-1)^{3/2} - \frac{4}{3}\arctan(\eta-1)^{1/2}\right], \tag{16}$$

where now

$$\eta = 2E/(\pi\omega_0^2\phi_{\mathrm{crit}}).$$

This analysis can be refined in several ways. For instance, Model I could be altered to allow for a certain

power-law fluence dependence at fluences near threshold and a different one at higher fluences (below ϕ_{sat}); V_{eff} could then be calculated by using the procedures outlined above. In addition, note that Eq. (14) was derived under the assumption that the density of absorbing species, N, is small enough for the medium to be considered optically very thin. For use in assessing possible applications, it can be modified to include modest absorption (<15% per pass) by first linearizing the Beer's law absorption dependence of the laser-pulse energy, $E(z)$:

$$E(z) = E[1 - \alpha N(z + l/2)], \qquad (17)$$

where E is the input energy at the entrance window ($z = -l/2$) and α is the absorption coefficient, which is assumed to be fluence independent.[5]

Using the techniques described above, Eq. (14) is straightforwardly modified, to first order in αNl, to yield

$$V_{eff}^{mod} = \frac{V_{eff}^{+}}{2} + \frac{V_{eff}^{-}}{2} \qquad (\text{for } m\alpha Nl \ll 1), \qquad (18)$$

where $V_{eff}^{\pm}$ is V_{eff}, as defined in Eq. (14), with the η^m/m term multiplied by $(1 - m\alpha Nl/2)$ and all terms with $(\eta - 1)^{1/2}$ replaced by $[(\eta - 1)^{\pm}]^{1/2}$, where

$$[(\eta - 1)^{\pm}]^{1/2} = \left[\eta - 1 - \frac{\eta\alpha Nl}{2} + \left(\frac{\eta\alpha Na}{2}\right)^2\right]^{1/2} \mp \frac{\eta\alpha Na}{2}. \qquad (19)$$

η is still given by Eq. (12). When either $[(\eta - 1)^{\pm}]^{1/2}$ or the term in the (other) square root in Eq. (19) is negative, $[(\eta - 1)^{\pm}]^{1/2}$ is set equal to zero; whereas if $[(\eta - 1)^{\pm}]^{1/2} \geq l/2a$ it is then set equal to $l/2a$. Equation (18) may be further extended to optically thicker media by suitably modifying Eq. (17) and recalculating V_{eff} (Ref. 6); however, limitations in the assumption of a fluence-independent absorption coefficient will limit the accuracy of the results.

The results of MPD experiments on a given molecule obtained under varying conditions, perhaps in different laboratories, may now be compared by determining ϕ_{sat}, m, and p from either Eq. (14) or Eq. (18). Armed with the values of these parameters for a specific molecule, the expected yield can be accurately calculated for any other experiment, as long as the dissociation probability can be well characterized by Model I.

The author gratefully thanks J. Marling for valuable discussions regarding this work.

* This research was performed under the auspices of the U.S. Department of Energy under contract W-7405-Eng-48.

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5. For weakly focused beams in optically thin media, Eq. (17) is a good approximation. In multiple-photon absorption α actually decreases with increasing fluence, leading to several consequences in tightly focused or optically thick media, including (1) a more-complicated form for $E(z)$ than Eq. (17) because of both the focusing geometry and the non-Beer's law behavior of the transmitted fluence and (2) distortions in the Gaussian-beam propagation Eq. (3) since the wings absorb radiation more strongly than do the central regions (see Ref. 3).
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