Appl. Phys. B 53, 268–270 (1991)

Applied Physics B Photophysics and Laser Chemistry

IR Multiple-Photon Dissociation by a Focused Uniform Beam

An Improved Analytical Method Based on a CLND Model

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Received 15 May 1991/Accepted 13 June 1991

Abstract. An improved analytical method is presented in which the reaction yield in the IR multiple-photon dissociation by a focused uniform beam is expressed in a generalized form as a function of fluence. The analytical solution is derived for a real focusing geometry by assuming the cumulative log-normal distribution (CLND) for the functional form of the dissociation probability vs. fluence. Also presented is a shortcut analytical method with simple and convenient algebraic expressions which approximate the exact analytical solution, thereby speeding up the analysis of experimental data.

PACS: 82.20.Wt, 33.80.Wz, 42.60.Kg

Since Barker and Baldwin [1–3] reported that the cumulative log-normal distribution (CLND) function satisfactorily described the dissociation probabilities (q) of molecules over a wide fluence (Φ) range in single-frequency IR multiple-photon dissociation (IRMPD), the two-parameter model based on the CLND function has been used and tested in the analysis of reaction yields in IRMPD by a focused beam. Takeuchi et al. [4, 5] compared the CLND model with the power-law model and showed that, when both models were normalized to give the same results in a sufficiently low Φ region, the power-law model overestimated the reaction yields near the fluence region where saturation of dissociation occurred. Nicol et al. [6] compared the exponential model in addition to the above two models and concluded that the CLND model was superior. Thus the practical CLND model is one of the most accurate two-parameter models reported that can be incorporated in analytical methods for the IRMPD in an optically thin medium.

The analytical methods with the CLND model, however, have proved to be inconvenient or tedious to use: Nicol's method necessitates a parameter fitting to a number of experimental data to extract the two CLND parameters [6]. In an improved method by Takeuchi et al. where CLND parameters are conveniently estimated [4], a tedious numerical integration is still necessary to calculate the reaction volume. The most sophisticated approach may thus be to first solve for the non-dimensional reaction volume as a function of the non-dimensional fluence based on the CLND model and secondly approximating the solution by well-suited algebraic expressions.

Such an approach was successfully employed in the analytical method for a Gaussian transverse beam geometry [5]. For a uniform beam geometry, however, only a method based on the power-law model was reported [7]. In the present paper we derive a mathematical solution based on the CLND model for a focused transversely uniform beam geometry, and express the solution in simple equations for convenient use.

1. Exact Analytical Solution

Figure 1 schematically illustrates the dimensions of a batch irradiation experiment with a weakly focused geometry. The beam radius at a distance z from the focal point is given by,

$$r^2 = r_f^2(1 + z^2/a^2) \tag{1}$$

where a is the Rayleigh range. The local fluence of the transversely uniform beam is thus

$$\Phi(z) = E_0/\pi r^2 \tag{2}$$

where E_0 is the pulse energy entering the irradiation cell.

According to the CLND formulation [1–3], the dissociation probability (q) can be expressed as

$$q(\Phi) = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\ln \Phi} \exp\left(- \frac{(\ln \Phi - \ln \Phi_s)^2}{2\sigma^2} \right) d \ln \Phi \tag{3}$$

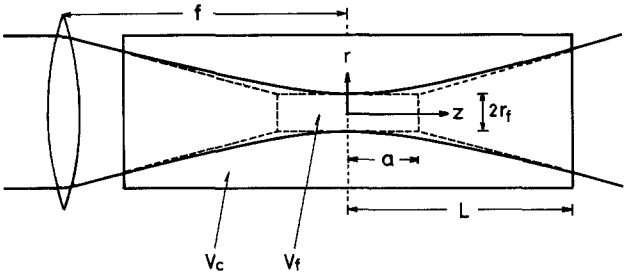

Fig. 1. Dimensions of a batch irradiation experiment with a weakly focused geometry

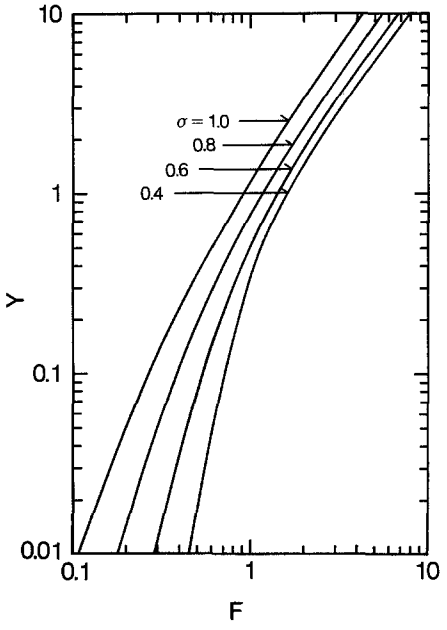

Fig. 2. Numerical results for non-dimensional reaction volume Y as a function of non-dimensional fluence F for various values of the standard deviation, σ. The CLND model is used to calculate Y for a focused, transversely uniform beam geometry

or

$$q(\Phi) = \frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^A \exp(-t^2)dt \tag{4}$$

where

$$A = \frac{1}{\sqrt{2}\sigma} \ln(\Phi/\Phi_s). \tag{5}$$

The σ is the standard deviation, and Φ_s is the characteristic fluence required to give a dissociation probability of 1/2. The reaction volume (V_R) is obtained by integrating the $q(\Phi)$ over the cell volume (V_c),

$$V_R = \int_{V_c} q(\Phi)dV$$

$$= 2\int_0^L q(\Phi)\pi r^2 dz. \tag{6}$$

The V_R is related to the specific dissociation rate, b, obtained experimentally;

$$b \equiv V_R/V_c$$

$$= -(1/t)\ln(1-X) \tag{7}$$

where X is the fraction converted after t-pulse irradiation. By introducing the non-dimensional distance, $k(\equiv z/a)$, V_R is calculated from (1, 2, 4–6) as

$$V_R = 2\pi r_f^2 a \int_0^{L/a} \times \left[\frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^A \exp(-t^2)dt\right](1+k^2)dk. \tag{8}$$

Defining the focal volume (V_f) by $V_f \equiv 2\pi r_f^2 a$, we arrive at the non-dimensional reaction volume $Y(\equiv V_R/V_f)$;

$$Y = \int_0^{L/a} \left[\frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^A \exp(-t^2)dt\right](1+k^2)dk \tag{9}$$

$$A = \frac{1}{\sqrt{2}\sigma} \ln[F/(1+k^2)] \tag{10}$$

where F is the non-dimensional fluence defined by,

$$F \equiv \Phi_f/\Phi_s. \tag{11}$$

Equations (9–11) are generalized expressions for the relation between Y and F under a focused uniform beam geometry. The upper limit, L/a, in the integration in (9) is the non-dimensional cell length which can be replaced with ∞ in most cases. The results of numerical calculations are shown in Fig. 2 for various values of σ.

2. Shortcut Analytical Procedure

Although (9–11) are expressed in a generalized form, deconvolution of experimental data using these equations to determine the CLND parameters, σ and Φ_s, is not very simple. Takeuchi et al. [4] derived a convenient relationship between the standard deviation (σ) and the slope of the $\log q$ vs. $\log \Phi$ plot (n) well below the saturation of dissociation ($q \leq 0.1$);

$$\sigma = 2.2/n. \tag{12}$$

The assumption on which (12) is based should be noted before use: the above relationship was obtained by fitting the CLND and power-law models at two points giving $q = 0.01$ and 0.1 [4]. Thus an experimental value of n should be determined from data to give $0.01 \leq q \leq 0.1$ in order for (12) to be valid.

Even when σ is evaluated from (12), the deconvolution to determine Φ_s is still tedious because the iteration from Y to F contains a numerical integration in (9). Thus we approximate the relation between Y and F in (9–11) by

Table 1. Coefficients in (13–15) for various values of σ

	$\sigma = 1.0$ ($n = 2.2$)	$\sigma = 0.8$ ($n = 2.8$)	$\sigma = 0.6$ ($n = 3.7$)	$\sigma = 0.4$ ($n = 5.5$)
A_0	−0.116	−0.157	−0.118	−0.059
A_1	2.057	1.211	0.466	−0.042
A_2	−0.773	−0.275	0.191	0.460
B_0	1.287	1.280	1.239	1.080
B_1	−2.918	−2.971	−2.743	−1.920
B_2	2.742	2.686	2.153	0.795
B_3	−0.981	−0.927	−0.645	−0.024
B_4	1.047	0.703	0.517	0.419
C_0	16.42	6.166	4.210	2.729
C_1	3.303	3.746	4.878	7.284

algebraic expressions similar to those in [5] as follows:

$$Y = A_0F + A_1F^2 + A_2F^3 \quad \text{for} \quad F < 1, \tag{13}$$

$$Y = B_0 + B_1/F + B_2/F^2 + B_3/F^3 + B_4F^{3/2} \quad \text{for} \quad F \geq 1. \tag{14}$$

The fifth term in (14) represents the 1.5th power dependence of Y upon F where $F \gg 1$. For extremely low Y regions ($10^{-3} < Y < 10^{-2}$), it is recommended to use,

$$Y = C_0F^{C_1}. \tag{15}$$

Table 1 summarizes the coefficients in (13–15) for various values of σ. The values of Y approximated with these equations are accurate to within 0.5% for (14) and 5% for (13) and (15). Since the coefficients do not vary too steeply with σ or n (Table 1), the values of Y for another σ (or n) are also calculable by using the coefficients A_0–A_2, B_0–B_4, and C_0–C_1 interpolated from Table 1. Now the non-dimensional fluence, F, is calculated from the experimental Y value by iteration with a simple computational method (e.g., Newton's method). Then the Φ_s from (11) and the σ are used to calculate the dissociation probability as a function of fluence by using (3), or (4) and (5).

3. Conclusion

The improved analytical method presented above for the IRMPD by a focused uniform beam is based on very realistic assumptions, i.e., a real (hyperbolic) focusing geometry and the CLND model for $q(\Phi)$. A similar method of Herman [8] is based on a less accurate power-law model for $q(\Phi)$, and furthermore, has the limitation that the parameter, n, must be an integer. Thus we believe our method, together with that for a Gaussian beam geometry [5], to be the most accurate and convenient one now available for the analysis of IRMPD under optically thin conditions.

Acknowledgement. The authors wish to express their gratitude to Mr. E. Suzuki of Power Reactor & Nuclear Fuel Development Corporation, Japan, for his help with the numerical calculations in this work.

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Printers: Brühlsche Universitätsdruckerei, Giessen

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