Appl. Phys. B26, 111–116 (1981)

Applied
Physics

Focusing Effect of a Laser Beam on the Power Dependence of Multiphoton Processes

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Received 7 July 1980/Accepted 11 May 1981

Abstract. The effect of focusing a laser beam on the intensity (I) dependence of multiphoton processes was examined. A general method is given to deduce a genuine intensity dependence from the focused-beam experiment. In addition, some typical examples were examined in detail. For the dependence of the type of I^n, an apparent relation of $I^{3/2}$ appears only when there is a change of dependence as $I^n \rightarrow I^m$, with $n > 3/2$ and $m < 3/2$. A genuine intensity dependence can be obtained directly from the focused beam experiment if n does not change throughout the irradiated volume, or if the condition $n > 3/2 > m$ does not hold. The case of gradually decreasing n, as is common for the infrared multiphoton reaction probability (P), was also analyzed taking the Arrhenius-type dependence, $P \propto \exp(-\Theta/I)$, as an example. A simple method is proposed to obtain a genuine relation between P and I for this type of intensity dependence.

PACS: 82.50

Dissociation of molecules upon irradiation with intense infrared laser radiation has been the subject of considerable interest in the last decade, in relation to its application to vibrational photochemistry and to isotope separation [1, 2]. Many of these experiments employ a focused laser beam in order to achieve a high radiation field. It was first pointed out by Speiser and Kimel [3], in the case of self-focusing, that the apparent intensity dependence is of $I^{3/2}$ irrespective of a true intensity dependence of the process. Later Fuss and Cotter claimed that the 3/2 law holds generally in the case of external focusing with a lens [4]. Speiser and Jortner analyzed a dependence of the type of I^n, assuming a constant n below a certain critical intensity (I_t) and a saturation of the reaction probability ($n = 0$) above I_t. Their result shows that the existence of the saturation gives rise to the 3/2 dependence [5].

Although there are some experimental evidences for the appearance of the 3/2 law in the case of SF_6 and SF_4 [4, 6, 7], we are still confronted with the following problems: 1) Why do many other molecules not exhibit this type of dependence? 2) Is the saturation assumed in [5] an essential condition for the 3/2 dependence to appear? 3) All the experimental result hitherto reported for the infrared multiphoton dissociation probability shows that n decreases gradually upon increasing the laser intensity. How does focusing affect this type of intensity dependence? In view of these questions, and of the increasing use of the multiphoton excitation in the ultraviolet region, it seems to be necessary to reexamine critically the applicability of the focused beam experiment. To do this we assume a smooth hyperbolic trajectory of the light beam with a finite beam cross section at the focus, the size of which is determined by the focal length and the beam divergence of a source laser. We shall begin with examining the change of power density upon propagation in a reaction cell, then analyze the effect of focusing and give a general procedure to deduce a genuine intensity dependence from the apparent experimental result. Finally we examine the case of a sharp transition of the intensity dependence, $I^n \rightarrow I^m$, for various values of n and m, and the case of a gradually changing n, taking the Arrhenius-type dependence, $\exp(-\Theta/I)$, as an example.

Results and Discussion

In Fig. 1 illustrated is the geometry of a focused light beam. The axis z is taken in the direction of light

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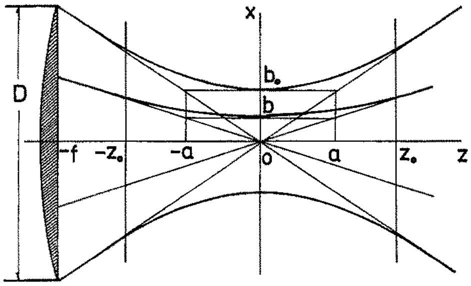

Fig. 1. The focused beam geometry employed in the present work. The classical light trajectory is expressed by (1). The beam is cylindrically symmetric and is assumed to be uniform within a cross section characterized by radius b_0 at the focal point

propagation with $z=0$ at the focal point. Entrance and exit windows of the reaction cell are located at $z=-z_0$ and $z=z_0$, respectively. The intensity distribution is assumed to be uniform within the beam cross section, characterized by the beam diameter b_0 at focus. Each trajectory of light is determined by the relation,

$$x^2=(b/a)^2(z^2+a^2) \tag{1}$$

with $|b|\leqq b_0$. Parameter a is defined by

$$a\equiv 2fb_0/D, \tag{2}$$

where f and D are the focal length and the diameter of unfocused beam, respectively. Parameter b_0 is determined by

$$b_0\simeq f\theta, \tag{3}$$

where θ is the laser beam divergence (half angle). Photon flux ϕ along the trajectory going through $x=b$ at $z=0$ is given by

$$\phi=cn\chi, \tag{4}$$

$$\chi\equiv 1+(b/a)^2z^2/(z^2+a^2), \tag{5}$$

where c and n are the light velocity and the photon density, respectively.
Let us suppose that photons are absorbed by molecules as

$$dn/dt=-g(n). \tag{6}$$

Combining (4) and (6), it is shown that n changes as

$$\begin{aligned} n^{-1}(dn/dz)=&-g(n)\chi^{1/2}/cn-2z/(z^2+a^2)\\ &+b^2\chi^{-1}z/(z^2+a^2) \end{aligned} \tag{7}$$

upon propagation in a reaction cell. Under normal experimental condition, one can put $b^2/(z^2+a^2)\ll 1$. Hence (7) is approximated to be

$$n^{-1}(dn/dz)\simeq -g(n)/cn+2z/(z^2+a^2). \tag{8}$$

Transforming n to I, the light intensity per unit cross section, and putting $I=I_0$ at $z=-z_0$, one obtains

$$I/I_0=(z_0^2+a^2)(z^2+a^2)^{-1}\exp\left\{-\int_{-z_0}^{z}[h(I)/I]\,dz\right\}, \tag{9}$$

where $h(I)\equiv h\nu g(n)$. For $h(I)=\alpha I$, (9) results in the Lambert-Beer law corrected for the focusing effect. It is to be noted that parameter a is an effective length of the focal region (HWHM).
Now we turn to examine how the multiphoton reaction probability is affected by focusing. If the reaction probability at each point is denoted by $P(I)$, the total probability in a reaction cell is

$$P=\int_{\Pi}P(I)\,dV, \tag{10}$$

where the integration is performed over the irradiated volume Π. Neglecting the light absorption for the sake of simplicity,

$$I=I_0(z_0^2+a^2)(z^2+a^2)^{-1}. \tag{11}$$

Since $dV=\pi x^2\,dz$, (1) and (11) give

$$dV=\pm(\pi/2)ab_0^2I_f^2I^{-3}(I_f/I-1)^{-1/2}\,dI, \tag{12}$$

where + and − correspond to $z>0$ and $z<0$, respectively, and I_f is the intensity at focus defined by

$$I_f\equiv(\tau^2+1)I_0, \tag{13}$$

$$\tau\equiv z_0/a. \tag{14}$$

From (10) and (12),

$$P=\pi ab_0^2I_f^{3/2}\int_{I_0}^{I_f}P(I)\,W(I)\,dI, \tag{15}$$

where

$$W(I)\equiv I^{-3}(I^{-1}-I_f^{-1})^{-1/2}. \tag{16}$$

Equation (15) can be transformed into the following form

$$P=2\pi ab_0^2\int_0^{\tau}(1+t^2)P[I_f/(1+t^2)]\,dt. \tag{17}$$

The irradiated volume in a reaction cell is calculated to be

$$\begin{aligned} V&=\pi\int_{-z_0}^{z_0}x^2\,dz\\ &=2\pi ab_0^2/\alpha, \end{aligned} \tag{18}$$

where

$$\alpha\equiv 3/\tau(\tau^2+3). \tag{19}$$

Hence the average reaction rate in a unit volume, $\bar{P} \equiv P/V$, is given by

$$\bar{P} = \alpha \int_0^{\tau} (1+t^2) P[I_f/(1+t^2)]\, dt . \tag{20}$$

A general formula can be obtained from (17) to determine $P(I_0)$ from P

$$P(I_0) = [\alpha(\tau^2+1)V]^{-1} [\partial P/\partial \tau]_{I_f = \mathrm{const}} . \tag{21}$$

One can deduce the genuine dependence $P(I)$ on the basis of (21) by changing τ as well as I_0.

Now let us examine a few special forms of $P(I)$ which seem to be important in the multiphoton experiment:

(a) $P(I) = kI^n$.

Equation (20) gives

$$\bar{P} = \alpha k S_{1-n}(\tau) I_f^n , \tag{22}$$

where $S_{\pm k}(\tau)$ is defined by

$$\begin{aligned} S_k(\tau) &\equiv \int_0^{\tau} (1+t^2)^k\, dt \\ &= \sum_{j=0}^{k} (2j+1)^{-1}\, {}_kC_j\, \tau^{2j+1} \quad (k \geqq 0) , \end{aligned} \tag{23}$$

$$\begin{aligned} S_{-k}(\tau) &\equiv \int_0^{\tau} (1+t^2)^{-k}\, dt \\ &= [(2k-3)!!/(k-1)!] [2^{1-k} \arctan(\tau) \\ &\quad + \sum_{j=0}^{k-1} [(k-j-1)!/(2k-2j-1)!!] 2^{-j} \\ &\quad \cdot \tau(\tau^2+1)^{j-k} \\ &\quad - [(k-1)!/(2k-1)!!]\, \tau(\tau^2+1)^{-k}] \quad (k \geqq 1) . \end{aligned} \tag{24}$$

Similar expressions can be obtained for half-integer values of k.

(b) $P(I) = k_n I^n \quad (I < I_t)$

$\quad = k_m I^m \quad (I > I_t)$.

In this case the rate is expressed by

$$\bar{P} = (\alpha/2) I_f^{3/2} \left[\int_{I_0}^{I_t} k_n I^n W(I)\, dI + \int_{I_t}^{I_f} k_m I^m W(I)\, dI \right] \tag{25}$$

with $k_n I_t^n = k_m I_t^m$. Defining parameter $x \equiv I_f/I_t$, normalized rate $\bar{P}' \equiv \bar{P}/k_n I_t^n$ is given by

$$\bar{P}' = \alpha S_{1-n}(\tau) x^n \quad (x \leqq 1) \tag{26}$$

$$\bar{P}' = \alpha\{[S_{1-n}(\tau) - S_{1-n}(\sqrt{x-1})] x^n + S_{1-m}(\sqrt{x-1}) x^m\} \quad (1 < x < 1+\tau^2) , \tag{27}$$

$$\bar{P}' = \alpha S_{1-m}(\tau) x^m \quad (x \geqq 1+\tau^2) . \tag{28}$$

(c) $P(I) = \exp(-\Theta/I)$.

A direct integration of (20) gives

$$\begin{aligned} \bar{P} = (\alpha/2)\, \{ &\sqrt{\pi x}(1+x/2) \exp(-1/x)\, \Phi(\tau/\sqrt{x}) \\ &- \tau x \exp[-(\tau^2+1)/x]\} , \end{aligned} \tag{29}$$

where $x \equiv I_f/\Theta$ and $\Phi(z)$ is the probability integral defined by

$$\Phi(z) \equiv (2/\sqrt{\pi}) \int_0^{z} \exp(-t^2)\, dt . \tag{30}$$

Following discussions can be made on the basis of these results:

1) From (2), (3), and (14), one obtains

$$\tau = D z_0 / 2\theta f^2 . \tag{31}$$

One may distinguish two modes of detections; (I) one is to observe a signal from the focal region only, and (II) the other is to obtain a reaction probability by analyzing a whole reaction product in the irradiated volume. The former realizes in the detection of emission which is normally confined to the focal region, or in the optoacoustic (OA) experiment in which the signal is restricted to the focal region by placing apertures [8]. In this case $z_0 \sim a$ so that $\tau \sim 1$. In the latter case, typical values, $D = 1.5$ cm, $\theta = 2$ mrad. and $z_0 \sim f/2$ give $\tau = 37.5$, 18.8, 1.9, and 0.2 for $f = 5$, 10, 100, and 1000 cm, respectively.

2) In case (a), where the light intensity dependence does not change throughout the region under investigation, genuine dependence n can be obtained from (22) by plotting $\log P$ against $\log I_f$ (or $\log I_0$).

3) The apparent reaction rate in the case other than (a) is affected more or less by focusing, as indicated in (20). A general method to deduce a genuine dependence $P(I)$ from observed P is to utilize (21). Experimentally this means to change z_0 (e.g., the cell length) for a fixed focal length. This is a rather tedious but general procedure which can be applied to detection mode II.

4) Case (b) assumes a sudden change of dependence as $n \to m$ at a certain threshold intensity I_t. The 3/2 dependence appears in the region $1 < x < \tau^2 + 1$, as illustrated in Fig. 2 for $\tau = 18.8$, a typical value in detection mode II. In Fig. 3 illustrated is the effect of changing τ. It can be seen that the 3/2 region almost disappears for $\tau \leqq 1$ (i.e., $z_0 \leqq a$).

5) For $m = 0$, our result is equivalent to that of Speiser and Jortner [5]. However, it is more general in that the 3/2 region is shown to appear only when inequalities $n > 3/2$ and $m < 3/2$ hold simultaneously.

6) For $n \leqq 3/2$ or $m \geqq 3/2$, one obtains a genuine intensity dependence even in the focused beam experiment, as can be seen in Fig. 2. An apparent threshold for $n \to m$ would be observed at $x = \tau^2 + 1$ for the former

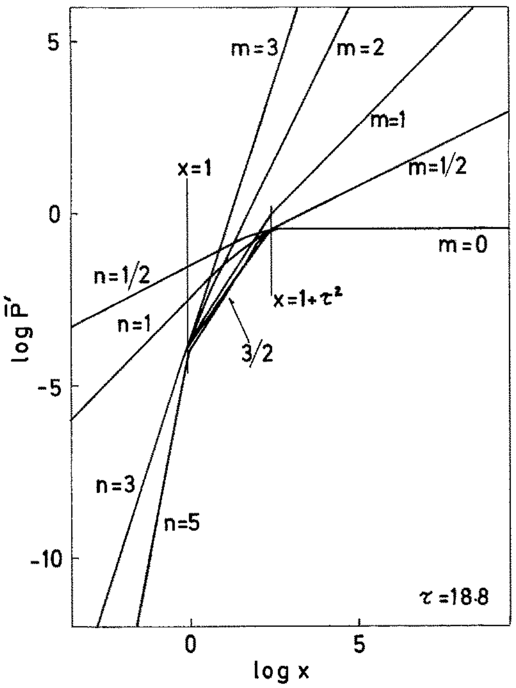

Fig. 2. Apparent light intensity dependence in the focused beam experiment calculated by the use of (26)–(28) with $\tau=18.8$. A change of the intensity dependence, $I^n \rightarrow I^m$, is assumed to exist at $I=I_t$

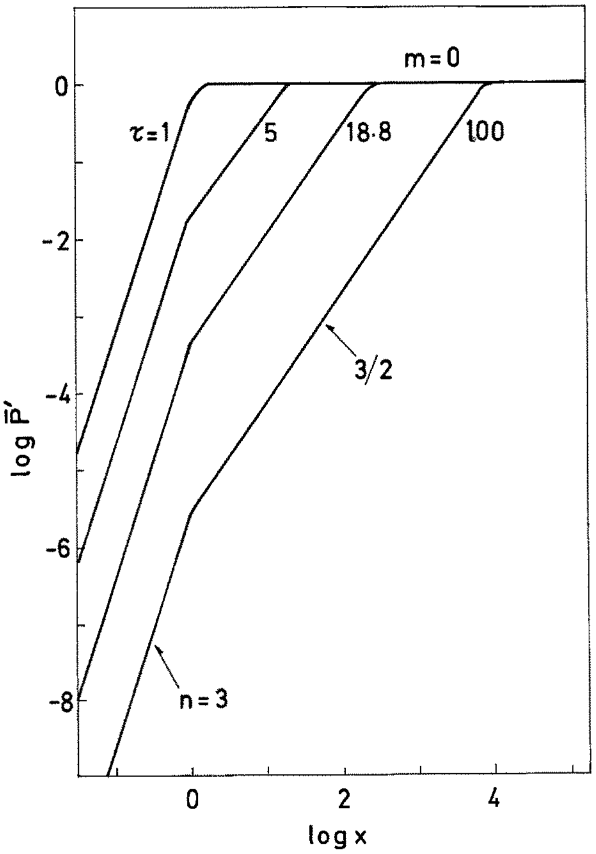

Fig. 3. Effect of changing τ for the $n=3 \rightarrow m=0$ transition. Values of τ are 1, 5, 18.8, and 100

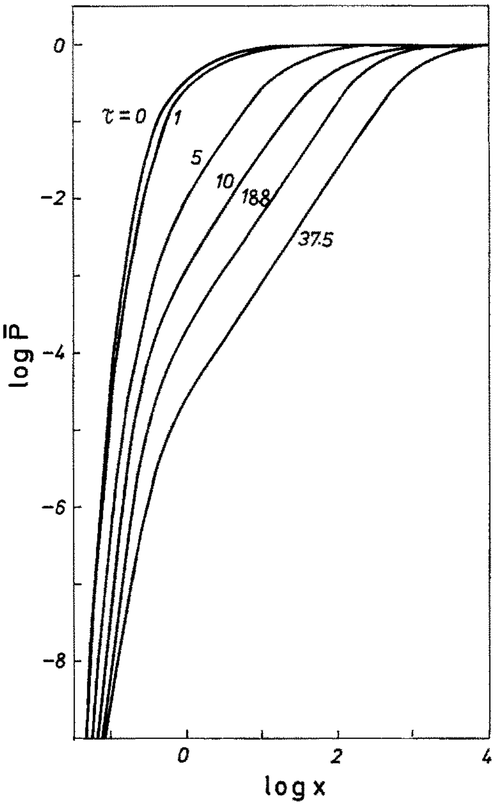

Fig. 4. Logarithmic plot of (29). The curve for $\tau=0$ corresponds to the true dependence, $P(I)=\exp(-\Theta/I)$.

and at $x=1$ for the latter, corresponding to $I_0=I_t$ and $I_f=I_t$, respectively.

7) The above-mentioned type of dependence, cases (a) and (b), may be applied to the OA measurement [9–12]. The case (b) result must give an apparent critical intensity at $x=\tau^2+1$, i.e., $I_0=I_t$, since $n \leqq 1$ for usual OA experiments. This means that all the volume being detected is irradiated with a light intensity above I_t.

8) Most of the intensity dependences hitherto reported for the multiphoton process show a gradually decreasing slope in the logarithmic plot of reaction probability versus laser intensity. This type of dependence should be expanded in the form;

$$P(I)=\sum_n k_n I^{-n} \tag{32}$$

rather than in positive powers of I. As can be seen from the comparison of Figs. 4 and 5, the Arrhenius relation assumed in case (c) is a typical analytical formula of this type. It should be noted in this connection that an Arrhenius relation

$$P(I) \propto \exp(-\Theta/I^\nu) \tag{33}$$

seems to be more common in the multiphoton process than previously recognized. In (33), Θ is the apparent

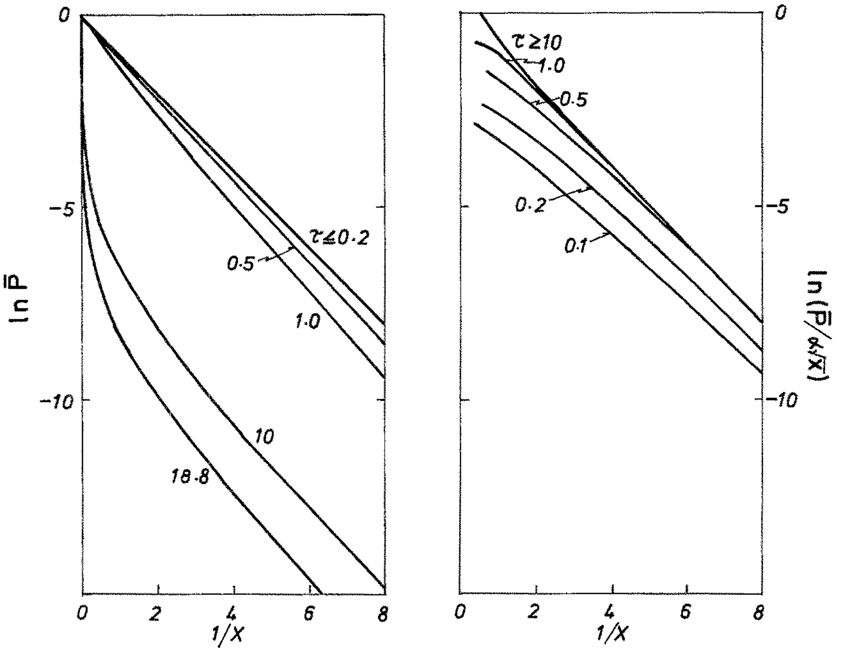

Fig. 5. The Arrhenius plots of (29) (left) and of $\bar{P}/\alpha\sqrt{x}$ versus x (right)

"activation intensity" which is determined by the activation energy (E_A) of the dissociation process as well as by the light absorption probability and the collisional pumping rate, whenever it is important. Hence Θ may be high even for a lower activation energy if the probability of pumping up the molecular vibrational levels is low. Nevertheless, the condition $I^{\nu}=\Theta$ is equivalent to $\hbar\omega\langle n\rangle = E_A$, where $\hbar\omega$ is the photon energy, $\langle n\rangle$ is the average number of quanta stored in a molecule. There are experimental evidences for the applicability of (33) in the case of ammonia, ethylene and hexaflueroacetone [8, 9, 13]. Many other multiphoton results usually given in a logarithmic plot, including those obtained under low pressures, can be replotted in the form of (33) with appropriate ν values. This is reasonable in view of the facts that the reaction rate reflects only the internal distribution of the parent molecule *above* the reaction barrier and that a molecular beam experiment indicates the distribution to be thermal [14, 15]. The thermal distribution realizes even under a collision-free condition because of a rapid intramolecular energy transfer in the higher vibrational-rotational continuum. This conclusion holds irrespectively of the distribution *below* the barrier, whereas the mechanism of light absorption is reflected in ν [8].

9) In Fig. 4 are shown results of numerical calculation on case (c) for various values of τ. It is shown again that the 3/2 dependence manifests itself in the range $I_f/\Theta = 1 \sim \tau^2+1$ for larger values of τ. It should be noted that the 3/2 region starts at $I_f \sim \Theta$, i.e., $\hbar\omega\langle n\rangle$ at focus is equal to E_A. The same result is given in Fig. 5 in a form of the Arrhenius plot. It is indicated that the genuine dependence (a slope of unity) is obtained for smaller values of τ ($\tau \ll 1$), whereas the slope deviates from unity on increasing τ. However, the figure indicates that detection mode I ($\tau \sim 1$) gives a slope within an error of 10%, which is reasonably good in view of the errors expected in conventional experiments of chemical kinetics. Even higher values of τ seem to give a slope with a similar accuracy if one uses lower light intensities ($I_f \ll \Theta$).

10) In Fig. 5 shown also is a plot of $\ln(\bar{P}/\alpha\sqrt{x})$ versus $1/x$. This type of plot seems to be useful in analyzing data for larger τ values, since it gives a genuine slope for $\tau \geq 1$ except for very high light intensities ($I_f \geq \Theta$). In an actual analysis one may try two kinds of plots, $\ln\bar{P}$ versus $1/I_f$ and $\ln(\bar{P}/\sqrt{I_f})$ versus $1/I_f$, estimate Θ, and confirm either of the plots, $\ln\bar{P}$ versus $1/x$ or $\ln(\bar{P}/\alpha\sqrt{x})$ versus $1/x$ to give a unit slope.

11) It is not necessary to assume a sudden onset of saturation to explain the 3/2 dependence observed for SF_6 and SF_4 [4, 6, 7]. Rather it may be attributed to case (c) as illustrated in Fig. 4. The τ values must be large since short focal lengths were employed in these experiments. The dependence has been observed solely for these molecules probably because they have low Θ values owing to a higher light absorption probability and to a higher density of vibrational-rotational states.

12) As a conclusion, one can easily obtain a genuine dependence in cases (a) and (b), which are often met in the OA measurement, by carefully avoiding the 3/2 region. For case (c), it is recommended to determine ν in (32) by use of the OA technique, then perform the analysis given in 8) and 9) above. Alternatively one may plot $\log P$ versus $1/\langle n\rangle$, thereby avoiding uncertainties in the determination of ν.

13) There is no simple method at present to obtain a true dependence for the general form of (32). Therefore, in the case that the Arrhenius relation does not hold, one has to use a long focal length to achieve the condition $\tau \ll 1$, or, alternatively, to perform an analysis on the basis of (21).

14) The present result can be applied generally in analyzing the focused beam experiment. It can be applied not only to the reaction probability in the infrared multiphoton process but also to the emission intensity of the reaction products and to the OA measurement. It is also applicable to the ultraviolet multiphoton dissociation and/or ionization experiments.

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