Two-photon-induced excited-state absorption: Theory and experiment

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We develop an open-aperture (OA) Z scan and nonlinear transmission theory of two-photon-induced excited-state absorption, under the excitation of spatial Gaussian laser pulses with temporal Gaussian and hyperbolic secant profiles. The found analytic expressions allow us to straightforwardly fit the OA Z-scan trace and the nonlinear transmission curve, for convenient extraction of the nonlinear absorption coefficients. As a test, the two-photon-induced excited-state absorption in a chalcone derivative of 3,4-dimethoxy-4′-fluorochalcone is explored by performing femtosecond Z-scan measurement and is analyzed by our theory. © 2008 American Institute of Physics. [DOI: 10.1063/1.2841713]

Optical materials exhibiting strong two-photon absorption (2PA) have recently received considerable attention, due to their numerous potential applications, such as fluorescence imaging,1 up-conversion lasing,2 and optical limiting.3 Under the excitation of intense laser pulses, the 2PA process may be accompanied by excited-state absorption (ESA). The 2PA-induced ESA process has been demonstrated by nonlinear transmission and open-aperture (OA) Z-scan experiments4 on many materials, including charge-transfer salts,5,6 nanocomposites,7 and organic molecules.8,9 However, the existing Z-scan theories are inadequate to deal with this effect. Although several approaches5,6,10,11 have been proposed, no satisfactory theory is available to identify and separate the contributions of 2PA and ESA. It is well-known that 2PA is a third-order nonlinear absorption (NLA) process, while ESA can be considered as a fifth-order NLA or three-PA (3PA) process in theoretical treatment.6 Due to the requirements of various ultrafast photonic devices, evaluating the suitable materials with high performances (such as ultrafast time response and the large nonlinearity) is always a challenging subject. Therefore, it is highly desirable to develop a theory, which allows us to conveniently and precisely extract the nonlinear information of measured samples from the ultrafast-pulsed Z-scan experimental data. Here, we present analytic expressions for directly and simultaneously evaluating the 2PA coefficient and ESA cross section from the Z-scan measurements under the excitation of ultrafast laser pulses. As a test, the NLA property of a chalcone derivative of 3,4-dimethoxy-4′-fluorochalcone (which is abbreviated as VFC) is measured by performing femtosecond-pulsed OA Z-scan technique and analyzed by our analytic expressions.

As well-known, a simplified five-level model can adequately explain NLA phenomena in many materials. However, this model becomes problematic in understanding the NLA behavior in some polyatomic molecule systems.5–9 Therefore, Sutherland et al.6 proposed an improved five-level model [as illustrated in the inset (a) of Fig. 1]. In particular, simultaneous absorption of two photons promotes an electron from $S_0$ to $S_1$, instead of a single photon absorption. From $S_1$, the electron will experience one of three possible processes as follows: (i) relaxes to $S_0$, (ii) undergoes a spin-flip transition to $T_1$, and (iii) is promoted to $S_3$ by absorbing another single photon. For an excited electron in $T_1$, there are only two possibilities that it may relax to $S_0$ by another spin-flip transition or be promoted to $T_h$ by absorbing another single photon. Sutherland et al.6 simplified their five-level system and further proposed a so-called one-step 3PA model; however, this 3PA model is not very suitable in dealing with our experimental data, as we demonstrate below.

Here, we present a three-level two-step 3PA model, as illustrated in the inset (b) of Fig. 1, in which $S_1$ and $T_1$ ($S_h$ and $T_h$) are combined to $S_{T_1}$ ($S_{T_h}$). In our model, the system simultaneously absorbs two photons, promoting an electron from $S_0$ to $S_{T_1}$. Subsequently, the electron can be excited to $S_{T_h}$ by absorb-
Table I. Coefficients $a_n$, $b_n$, and $c_n$ for temporal Gaussian and sech pulses when $0 \leq q_0 \leq \pi$ and $0 \leq p_0 \leq \pi$.

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<th>$b_n$</th>
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Equation (2) is valid for $\gamma > 0$ [reverse saturable absorption (RSA)]. $q$ and $p$ are given by $q=\gamma_0/(1+z^2/\gamma_0^2)$ and $p=p_0/(1+z^2/\gamma_0^2)$, respectively, where $q_0=\beta L_{\text{eff}}$ and $p_0=(2\gamma_0^2L_{\text{eff}})^{1/2}$ are the on-axis peak phase shifts caused by the third- and fifth-order nonlinear absorption processes, respectively. Here, $L_{\text{eff}}$ is the on-axis peak intensity at the waist, $\gamma_0=\pi a_0^2/\lambda$ the Rayleigh length, $L_{\text{eff}}=1-[1-\exp(-\alpha L)]/\alpha$, and $L_{\text{eff}}=1-[1-\exp(-2\alpha L)]/2\alpha$. When considering the temporal profile [Gaussian or hyperbolic secant (sech)] of the spatial Gaussian laser pulses, the coefficients $a_n$, $b_n$, and $c_n$ in Eq. (3) are listed in Table I. We have confirmed that all the empirical formulas [Eqs. (2)-(6)] have an error of 0.5% at the utmost with respect to the exact numerical results when $0 \leq q_0 \leq \pi$ and/or $0 \leq p_0 \leq \pi$. For the pure 2PA ($\gamma=0$) and 3PA ($\beta=0$), Eq. (2) degenerates into the following forms, respectively:

$$T(z) = (a_0 + b_0 q_0) \ln(1 + q_0) / q_0 (1 + c_0 q_0)$$

and

$$T(z) = \ln\left[1 + \frac{1}{p_0} \frac{1}{p_0} \frac{1}{p_0} \sum_{n=0}^{\infty} a_n p^n - 1\right].$$

Of course, Eq. (2) can also be used to describe the intensity-dependent nonlinear transmission. Setting $z=0$ in Eq. (2), we yield $T(0)$ as a function of $I_{00}$.

$$T(0) = \frac{\ln(1 + q_0)}{q_0} \frac{\ln\left[1 + \frac{1}{p_0} \frac{1}{p_0} \frac{1}{p_0} \sum_{n=0}^{\infty} a_n p^n - 1\right]}{f(0)}$$

where $f_0=f(q_0, p_0)$. For the pure 2PA ($\gamma=0$) and 3PA ($\beta=0$) models, Eq. (5) is simplified to two forms as follows:

$$T(0) = (a_0 + b_0 q_0) \ln(1 + q_0) / q_0 (1 + c_0 q_0)$$

and

$$T(0) = \ln \left[1 + \frac{1}{p_0} \frac{1}{p_0} \frac{1}{p_0} \sum_{n=0}^{\infty} a_n p^n - 1\right].$$

In Eqs. (2) and (5), there are two free parameters, $\beta$ and $\gamma$. The value of $\beta$ is unambiguously determined from the measurements at the low intensity because ESA could be safely ignored in this case. With the aid of the obtained $\beta$, the value of $\gamma$ can be extracted from the $Z$-scan or nonlinear transmission measurements at the high intensity by the use of Eq. (2) and (5). As evidence, Fig. 1 shows the nonlinear transmission curves fitted by Eq. (5) and by Sutherland’s theory, and the experimental data for the AF350 solution. By using $\beta=0.064$ cm/GW obtained from independent measurements, we have determined $\gamma=12.5 \pm 0.3$ cm$^3$/GW$^2$, which is in good agreement with the result reported previously.

We devote to investigating the NLA (or nonlinear transmission) property of a chalcone derivative of VFC (its structure is shown by the inset in Fig. 2), which was synthesized by the Claisen-Schmidt condensation method. The linear absorption measurement shows that VFC is transparent in the near infrared region. The laser source used for the OA Z-scan experiments was a Ti:sapphire regenerative amplifier (Quantix, Titan) with a 130 fs pulse duration at 780 nm wavelength and 1 kHz repetition rate. The laser pulses had near-Gaussian spatial and temporal profiles. The sample was an acetone solution of VFC with a concentration of 0.2 mol/l. The solution was contained in a 2-mm-thick quartz cell. We also performed the Z-scan measurements on the pure acetone, validating that the measured NLA originates from VFC only.

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The use of 2PA-induced ESA, pure 2PA, and pure 3PA models, respectively. The solid, dashed, and dotted lines are the theoretical fittings by the use of 2PA-induced ESA, pure 2PA, and pure 3PA models, respectively. The inset is the structure of VFC.

To carefully explore the NLA property of the sample, we perform the OA Z-scan measurements at different intensities. First, we apply Eq. (4a) for the pure 2PA model to fit the OA Z-scan traces by a single free parameter to extract the so-called nominal 2PA coefficient $\beta_{\text{nom}}$ at different intensities. The results show that $\beta_{\text{nom}}$ is a nearly linear increasing function of $I_{00}$, instead of an approximate constant, suggesting that the sample should exhibit RSA. From the OA Z-scan traces at different intensities, we easily yield the dependence of the nonlinear transmission $T(0)$ on the incident intensity $I_{00}$ for the acetone solution of VFC, as illustrated by the circles in Fig. 2. The experimentally measured curve $T(0)$ vs $I_{00}$ in Fig. 2 is fitted by using Eq. (5) with two variable parameters to extract both $\beta$ and $\gamma$. The best fit shown in Fig. 2 by the solid line indicates $\beta=(1.31 \pm 0.10) \times 10^{-2}$ cm/GW and $\gamma=(4.50 \pm 0.05) \times 10^{-4}$ cm$^3$/GW$^2$, from which, we evaluate the ESA cross section to be $\sigma_{\text{e}}=(1.76 \pm 0.17) \times 10^{-17}$ cm$^2$ by taking the excited-state lifetime $\tau \sim 1$ ps. This value of $\sigma_{\text{e}}$ is comparable with the result reported previously. In addition, we also fit the experimental data of $T(0)$ vs $I_{00}$ by Eq. (6a) and (6b) using a single variable parameter $\beta$ or $\gamma$, yielding $\beta=(3.11 \pm 0.16) \times 10^{-2}$ cm/GW or $\gamma=(1.51 \pm 0.05) \times 10^{-3}$ cm$^3$/GW$^2$. The dashed and dotted lines are the theoretical fitting curves by the use of the pure 2PA and 3PA models, respectively. Clearly, the solid line is in excellent agreement with the experimental data. However, there is a little deviation between the experimental data and the dotted line yielded by the effective one-step 3PA model; thereby, the NLA property of VFC would be misinterpreted if such a deviation was ignored.

Based on the above analysis, we conclude that the most possible physical mechanism is the 2PA-induced ESA (or two-step 3PA), instead of the pure 2PA or the effective one-step 3PA. For the VFC molecule as a polyatomic molecule system, its level structure can be simplified to a three-level model, as illuminated in the inset (b) of Fig. 1. When the system is excited by the relatively low power laser pulses, the dominant absorption is the 2PA process caused by the transition from $S_0$ to $S_1$. Under the excitation of high irradiance, the electron located at $S_1$ is rapidly excited into $S_0$ due to the single photon transition before it relaxes to the ground state $S_0$. Because the single photon absorption cross section of $S_1$ is greater than the 2PA cross section of $S_0$ (in other words, the density of electronic states of $S_1$ is larger than that of $S_0$), the 2PA-induced ESA results in a further reduction in the transmission of the system.

We present a three-level two-step 3PA model for a polyatomic molecule system. We find analytic expressions for both OA Z-scan trace and nonlinear transmission, which possess high accuracy for determination of the NLA coefficients with an advantage of time saving. Experimentally, we investigate the NLA property of a chalcone derivative (VFC) by performing both femtosecond OA Z-scan and nonlinear transmission measurements. Our analysis shows that the NLA in VFC originates from both 2PA and 2PA-induced ESA.

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