Theoretical and experimental studies of three-photon-induced excited-state absorption

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We theoretically and experimentally study excited-state absorption (ESA) induced by three-photon absorption (3PA) under the excitation of ultrafast laser pulses. Based on five-level rate-equation theory, we obtain an analytical expression for the effective four-photon absorption coefficient that originates from both singlet-singlet (S-S) and triplet-triplet (T-T) ESA. We validate that the T-T ESA could be justifiably neglected in the femtosecond regime. Experimentally, we verify it in acetone solution of 2,4,5-trimethoxychalcone by performing femtosecond Z-scan measurements; at low excitation intensity, only 3PA is determined; and under the excitation of high intensity, however, we observe the concurrence of 3PA and 3PA-induced S-S ESA processes. © 2010 American Institute of Physics. [doi:10.1063/1.3327340]

Recently, investigations of multiphoton absorption (mPA) related processes, in particular, three- and four-photon absorption (3PA and 4PA), have received tremendous attention because of their potential applications in photonics and biophotonics.1-3 Furthermore, many researchers have indicated that under the excitation of high-power ultrafast-pulsed laser, a strong mPA process may considerably increase molecular populations in the excited states; and subsequently, the cascaded one-photon absorption (1PA) from an excited state may create an equivalent stepwise mPA:1PA process. This two-step (m+1)-photon absorption is a so-called mPA-induced excited-state absorption (ESA).4-9 Two-photon-induced ESA has been observed in a wide variety of materials, such as organic molecules,4 semiconductors,5 quantum dots,6 and nanocomposite films.7 However, reports of 3PA-induced ESA effect are sporadic in the literature. For instance, Penzkofer et al.8 observed the 3PA and subsequent ESA in CdS. Yoshino et al.9 and Chatopadhyay et al.10 revealed 3PA-induced ESA in polydiacetylenes and ZnO quantum dots, respectively.

As an intriguing type of nonlinear optical materials, chalcones have recently received extensively attention due to their high tendency to crystallize in noncentrosymmetric structure, significant frequency conversion property, and good third-order optical nonlinearity in nanosecond and femtosecond regimes.11-13 However, mPA related properties of chalcones have not been exploited so far.

In a previous report, we studied a three-level two-step 4PA process of singlet-singlet (S-S) ESA induced by 3PA under the excitation of ultrafast pulses.14 The triplet-triplet (T-T) ESA was neglected in the analysis. In this work, we develop a theory based on a five-level rate-equation model of 3PA-induced ESA under the excitation of ultrafast laser pulses. We demonstrate that the T-T ESA could be justifiably omitted in the femtosecond regime. Experimentally, we validate it by performing femtosecond Z-scan measurements in the near infrared region on 3PA-induced ESA in acetone solution of 2,4,5-trimethoxychalcone.

Figure 1 illustrates the proposed mechanism of 3PA-induced ESA. This model is similar to that used for three-level two-step 4PA but includes simultaneously ESA from both excited singlet and triplet states.14 The process of non-linear absorption (NLA) in the system is described as follows. The system simultaneously absorbs three identical photons, promoting electrons from $S_0$ to $S_1$. For an electron in $S_1$, there are three following possibilities: namely, (i) it may relax to $S_0$ or (ii) it may undergo a spin-flip transition to $T_1$ or (iii) it is promoted to $S_1$ by absorbing another photon. From $T_1$, the electron may relax to $S_0$ by another spin-flip transition or be promoted to $T_h$ by absorbing another photon. The attenuation of the pulse intensity as light propagates through an optically thin sample is described by

$$\frac{\partial I}{\partial z} = -\sigma_S N_S I^3 - \sigma_S N_S I - \sigma_T N_T I$$  \hspace{1cm} (1)

and the populations of states $N_{S_1}$ and $N_{T_1}$ are given by

$$\frac{\partial N_{S_1}}{\partial t} = \frac{\sigma_S I^3}{3h\omega} N_S - \frac{N_{S_1}}{\tau_S},$$ \hspace{1cm} (2a)

and

$$\frac{\partial N_{T_1}}{\partial t} = \frac{\sigma_T I^3}{3h\omega} N_T,$$ \hspace{1cm} (2b)

As an example, we consider a system with singlet-singlet (S-S) and triplet-triplet (T-T) transitions. The electronic transitions are described by the rate equations:

$$\frac{\partial N_{S_1}}{\partial t} = \frac{\sigma_S I^3}{3h\omega} N_S - \frac{N_{S_1}}{\tau_S},$$ \hspace{1cm} (2a)

and

$$\frac{\partial N_{T_1}}{\partial t} = \frac{\sigma_T I^3}{3h\omega} N_T,$$ \hspace{1cm} (2b)

FIG. 1. (Color online) Five-level diagram of 3PA-induced ESA.
\[ \frac{\partial N_{T_1}}{\partial t} = \frac{\varphi_T}{\tau_S} N_S - \frac{N_{T_1}}{\tau_T}, \]  
\[ N_{S_0} = N - N_{S_1} - N_{T_1}, \]

where \( \varphi \) is the propagation length inside the sample; \( \sigma_S, \sigma_T \), and \( \varphi_T \) are the absorption cross-sections for molecular 3PA, excited S-S state, and excited T-T state, respectively; \( \tau_S \) and \( \tau_T \) are the singlet and triplet state lifetimes, typically of picosecond and nanosecond time scales, respectively; \( \varphi_T \) is the triplet quantum yield; and \( \hbar \omega \) is the incident photon energy. In this analysis, we ignore the populations on both \( S_0 \) and \( T_0 \) because relaxation times from all higher-lying states \( (S_0 \) and \( T_0) \) to the \( S_1 \) and \( T_1 \) states are extremely fast. Besides, we assume that the \( S_0 \) state is not sufficiently depleted for the light irradiances used, therefore \( N_{S_0} \ll N \) and \( N_{T_1} \ll N \), we set \( N_{S_0} = N \). Under the excitation of ultrafast laser pulses, we note the fact \( \tau_T \gg \tau_S \gg \tau \), where \( \tau \) is the half-width at \( e^{-1} \) of the maximum for the pulse duration. Thus the population densities of \( S_1 \) and \( T_1 \) are given by

\[ N_{S_1}(t) = \frac{\sigma_S N}{3 \hbar \omega} \int_{-\infty}^{t} \varphi(r') dt', \]
\[ N_{T_1}(t) = \frac{\varphi_T}{\tau_S} \int_{-\infty}^{t} N_{S_1}(r') dt'. \]

Assuming a temporal Gaussian profile for the incident pulses and following an approach we presented recently,\(^{14}\) we could revise Eq. (1) as

\[ \frac{\partial I(r,z,t)}{\partial t} = -\alpha_y \Phi(r,z,t) - (\alpha_S + \alpha_T) \tilde{I}(r,z,t), \]

where

\[ \alpha_S = \frac{\sigma_S \omega}{3 \hbar \omega}, \]
\[ \alpha_T = \frac{\sigma_T \varphi_T \omega}{3 \hbar \omega}, \]

Here \( \alpha_3 = \sigma_3 N \) is the 3PA coefficient; \( \alpha_S \) and \( \alpha_T \) are the effective 4PA coefficients for the cumulative nature of 3PA-induced ESA, which arise from S-S and T-T ESA, respectively. It is clear that the values of both \( \alpha_S \) and \( \alpha_T \) strongly depend on laser pulse duration. Taking the typically values of \( \alpha_S \approx 10^{-17} \text{cm}^{-1} \), \( \alpha_T \approx 10^{-16} \text{cm}^{-1} \), \( \tau_S \approx 10 \text{ ps} \), and \( \tau_T \approx 100 \text{ fs} \), we estimate \( \alpha_3 \approx 10^{-5} \alpha_S \). Apparently, the T-T ESA becomes negligible and hence, is justifiably omitted in the femtosecond regime. In this instance, the S-S ESA plays a dominant role in the whole 3PA-induced ESA process. Consequently, a simplified three-level model can adequately explain NLA under the excitation of femtosecond pulses.\(^{14}\)

The sample that we studied experimentally is 2,4,5-trimethoxychalcone (labeled 2,4,5TA, its structure is displayed by the inset in Fig. 2), which was synthesized by the condensation reaction.\(^{15}\) Fig. 2 shows the linear absorption spectrum of 2,4,5TA in acetone with a concentration of \( 5 \times 10^{-4} \text{ M} \). The contributions to the spectrum from both liquid cell and solvent (acetone) were subtracted. Clearly, 2,4,5TA exhibits a strong linear absorption band with a peak at \( \lambda_{\text{abs}} = 347 \text{ nm} \) and is highly transparent in the near infrared range. As examples, we perform the Z-scan measurements at different laser intensities \( I_0 \) with carbon disulfide as a standard and the experimental uncertainty should be within \( \pm 10\% \). We also carried out the Z-scan measurements on the pure acetone, confirming that the measured NLA mainly originates from 2,4,5TA.

To gain an insight on the NLA property of the sample, we perform the Z-scan measurements at different laser intensities \( I_0 \). Note that \( I_0 \) is the one within the sample. All Z-scans display a symmetric valley with respect to the focus, typical of an induced positive NLA effect. As examples, Z-scans at low and high intensities are shown in Fig. 3. Analysis of Z-scans using 3PA theory\(^{14}\) reveals the following: (i) the NLA coefficient \( \alpha_{\text{com}} \) is nearly constant at low excitation intensities below \( I_C = 150 \pm 10 \text{ GW/cm}^2 \), which implies that 2,4,5TA indeed exhibits 3PA in nature; (ii) as the intensity exceeds \( I_C \), however, as shown in the inset of Fig. 3, the measured \( \alpha_{\text{com}} \) values increase with increasing intensity, suggesting the simultaneous occurrence of 3PA and higher-order NLA. Using the Z-scan theory of 3PA-induced ESA,\(^{14}\) we obtain 3PA coefficient of \( \alpha_3 = (2.2 \pm 0.1) \times 10^{-4} \text{ cm}^3/\text{GW} \) and the effective 4PA coefficient of \( \alpha_4^{\text{eff}} = (5.5 \pm 0.8) \times 10^{-6} \text{ cm}^3/\text{GW}^3 \). In Fig. 3, the solid line calculated by these two parameters is in good agreement with the measured data.
agreement with the experimental data, confirming that our analysis is reasonable. The 3PA cross-section $\sigma_{3PA}$ is evaluated to be $(1.22 \pm 0.03) \times 10^{-78}$ cm$^6$ s$^2$ by $\sigma_{3PA} = \alpha_3(\hbar \omega)^2/N$, where $N=N_A d_0 \times 10^{-3}$ is the number of molecules in cm$^{-3}$, $N_A$ is the Avogadro’s number, and $d_0$ is the concentration in mol/L (M). The value of $\sigma_{3PA}$ is comparable with that of other organic molecules.\textsuperscript{1} The S-S cross-section was estimated as $\sigma_S = (8.7 \pm 1.7) \times 10^{-17}$ cm$^2$ by Eq. (5a), which is one order of magnitude larger than the findings for semiconductors.\textsuperscript{8} Besides, the observed $I_C$ can be understood as the critical intensity due to the critical population of $S_1$.

Based on the above analysis, the observed NLA effect in 2,4,5TA can be understood as follows. For 2,4,5TA molecule as a polyatomic molecular system, its electronic structure can be simplified as Fig. 1. At low intensity, the dominant NLA is the 3PA process caused by the transition from $S_0$ to $S_1$. Consequently, the population of $S_1$ is insufficient to promote electrons from $S_1$ to $S_n$. Note that the possibility of the electron transition from $S_1$ to $T_1$ is negligible in the femtosecond regime, as our theoretical analysis [see Eq. (5)] points out. As the intensity exceeds $I_C$ (see the inset of Fig. 3), i.e., the population of $S_1$ exceeding a critical value, the electrons located at $S_1$ partially relax to $S_0$ and the remainder are rapidly excited into $S_0$ by absorbing another photon before it relaxes to $S_0$, resulting in the simultaneous occurrence of 3PA and 3PA-induced S-S ESA, which is consistent with our observation.

In summary, we have theoretically investigated 3PA-induced ESA in the femtosecond regime and derived the effective 4PA coefficient that arises from both S-S and T-T ESA. Experimentally, we have observed 3PA-induced S-S ESA in acetone solution of 2,4,5-trimethoxychalcone by performing Z-scan measurements under intense femtosecond laser excitation in the near infrared region.

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