Two-photon-induced excited-state nonlinearities

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Abstract: We report a theoretical investigation of laser-pulse-duration dependence of excited-state nonlinearities induced by two-photon absorption (2PA). We investigate the spatiotemporal characteristics of the transmitted pulses caused by 2PA-induced excited-state absorption, which strongly depends on laser pulse duration. By taking into account 2PA cross-section, excited-state photophysical properties, as well as laser pulse duration, we quantitatively determine the effective fifth-order nonlinearities caused by excited-state absorption and refraction. The results are capable of predicting the magnitude of 2PA-induced excited-state nonlinearities on the time scales where laser pulse duration is less than or comparable to the lifetime of 2PA-induced excited states. We also develop Z-scan theories for quickly yet unambiguously estimation of 2PA coefficient, third-order nonlinear refraction index, and excited-state absorption and refraction cross-sections.

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References and links


fifth-order nonlinearities, including the inherent $\chi^3$ susceptibility of the medium and some nonlinearities equivalent to the fifth-order nonlinearities (i.e., sequential $\chi^3 : \chi^{(1)}$ effect), such as excited-state nonlinearities in organic molecules [1] and free-carrier nonlinearities in semiconductors [10]. Recently, investigations of fifth-order nonlinearities have attracted basic as well as applied research, such as spatiotemporal spinning solitons supported by third- and fifth-order nonlinearities [16], optical limiting originated from both two-photon absorption (2PA) and 2PA-induced excited-state absorption (ESA) [6, 9], and infrared detector and optical reshaping based on free-carrier absorption (FCA) [17, 18]. Consequently, the identification of the physical mechanisms responsible for the competing processes of the simultaneous third- and fifth-order nonlinearities, the separation of their contributions, and the unambiguous determination of photophysical parameters are crucial for fundamental research and technological applications.

Under the excitation of intense laser pulses, experimental observations have revealed that many organic molecules exhibit 2PA-induced excited-state nonlinearities [1-9]. Furthermore, this nonlinear effect depends partly on the laser duration and partly on the material itself. Most
theoretical investigations have focused a case where laser pulse duration is less than the lifetime of 2PA-induced excited states [10]. When laser pulse duration is comparable to the lifetime of 2PA-induced excited states, however, data analyses require numerical methods [11, 12]. Hence, it is greatly desirable to develop an analytical theory for the analysis of laser-pulse-duration dependence of excited-state nonlinearity caused by 2PA.

In this work, we theoretically investigated a laser-pulse-duration dependence of excited-state absorption and refraction induced by 2PA. We analyzed the spatiotemporal distortions of the transmitted pulses caused by 2PA-induced excited states. We determined the analytical results for the effective fifth-order nonlinear coefficients originated from excited-state absorption and refraction, which depend on 2PA cross-section, excited-state photophysical properties, as well as laser pulse duration. This theory provides a quantitative analysis of 2PA-induced excited-state nonlinearities on the time scales where laser pulse duration is less than or comparable to the lifetime of 2PA-induced excited states. We also developed Z-scan theories for unambiguously yet high-efficiency evaluation of 2PA coefficient, third-order nonlinear refraction index, and excited-state absorption and refraction cross-sections.

2. Theory

Many of the strongest 2PA organic molecules are hybrid chromophores where the 2PA is accompanied by excited-state nonlinearities. The photodynamics in this kind of hybrid systems can be simplified as follows. The system simultaneously absorbs two identical photons, promoting an electron from the ground state to the first excited state. Subsequently, the electron can be excited to higher-lying state by absorbing another single photon, resulting in 2PA-induced ESA. At the same time, 2PA populates new electric states, which could be an excited bound state in an organic molecule. Significant population redistribution produces an additional change in the refractive index, leading to 2PA-induced excited-state refraction (ESR). Under the thin-sample approximation and the slowly varying envelope approximation, the propagation of the electric field within the nonlinear medium is monitored by [10]

\[
\frac{\partial I}{\partial z'} = -\alpha_0 I - \alpha_2 I^2 - \sigma_a N_e I,
\]

\[
\frac{\partial \Delta \phi}{\partial z'} = k\gamma_1 I + k\sigma_r N_e,
\]

\[
\frac{\partial N_e}{\partial t} = \frac{\alpha_2 I^2}{2\hbar\omega} - \frac{N_e}{\tau_e},
\]

where \(z'\) is the propagation length inside the sample; \(\alpha_0, \alpha_2, \gamma_1\) are the linear absorption coefficient, the 2PA coefficient, and the third-order nonlinear refractive index, respectively; \(\sigma_a\) and \(\sigma_r\) are the absorptive and refractive cross-sections of excited states, respectively; \(\tau_e\) represents the lifetime of 2PA-induced excited states; \(N_e\) is the population density of excited states created by 2PA; \(k = 2\pi/\lambda\) is the wave vector in free space; and \(\hbar\omega\) is the incident photon energy.

Equation (3) can be solved to give the result as

\[
N_e(t) = \frac{\alpha_2}{2\hbar\omega} G(t) I^2(t),
\]

where

\[
G(t) = \frac{1}{F(t)} \int_{-\infty}^{t} I^2(t') \exp\left[-(t-t')/\tau_e\right] dt'.
\]

Substituting Eq. (4) into Eqs. (1) and (2) give

\[
\frac{\partial I}{\partial z'} = -\alpha_0 I - \alpha_2 I^2 - \sigma_a \sigma_r G(t) I^2(t),
\]

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\[
\frac{\partial \Delta \phi}{\partial z'} = k \gamma I + k \frac{\sigma_2 \alpha_2}{2 \hbar \omega} G(t) I^2(t).
\]  

(7)

For a 2PA-induced ESA process, Gao et al. [19] have theoretically found, depending on the material itself, the transmitted pulse profiles will be distorted in both time and space. Afterward, Liu et al. [20] experimentally observed this result in carbon disulfide. In the following, we demonstrate that the degree of temporal and spatial distortion also strongly depends on the laser pulse duration. In the analysis, we assume that the spatiotemporal profiles of incident pulses are Gaussian. We investigate the spatiotemporal characteristics of the transmitted pulses by taking the typical parameters of organic materials [1, 19] as:

- \( L = 0.2 \) cm,
- \( \alpha_0 \approx 0 \),
- \( \alpha_2 = 0.1 \) cm/GW,
- \( \sigma_a = 6.2 \times 10^{-18} \) cm²,
- \( \tau_e = 500 \) ps,
- \( \lambda = 532 \) nm,
- \( \omega_0 = 19 \) μm,
- \( I_0 = 20 \) GW/cm²,

where \( L \), \( \lambda \), \( \omega_0 \), and \( I_0 \) are the thickness of the sample, the laser wavelength, the waist radius, and the on-axis peak intensity, respectively. For the sake of comparison, we also plot the results for input laser pulse and the transmitted intensity caused by purely 2PA, as shown in Fig. 1 by the solid and dashed lines, respectively. The pulse-duration dependence of transmitted intensities as a function of time at \( r = 0 \) is shown in Fig. 1(a), here time on x-coordinate is normalized to the half-width at \( e^{-1} \) of the maximum of pulse, \( \tau \). It can be seen that both the peak and the trailing edge of the pulse shifts in time as after the pulse propagates through the sample. Furthermore, the peak of the pulse shifts toward the leading edge of the pulse because there is more absorption at the trailing edge under the excitation of longer pulse duration. Figure 1(b) illustrates the transmitted intensity as a function of radius at \( t = 0 \) under the different pulse duration. Obviously, the initial Gaussian beam configuration becomes flat-topped beam under the longer pulse excitation, while the Gaussian profile nearly holds if \( \tau \ll \tau_e \). That is, illuminated by longer pulse duration, the material exhibits stronger 2PA-induced ESA effect and then increases the absorption occurring in the center of the pulse. Obviously, 2PA process is dominant in the femtosecond time domain; ESA becomes significant for nanosecond and longer pulse excitation; while the competition between 2PA and 2PA-induced ESA is observable in the picosecond regime. To confirm the physical mechanism of 2PA-induced ESA and obtain the lifetime of 2PA-induced excited states, one could perform transient transmittance measurements as we reported recently [9].

![Fig. 1. Pulse-width dependence of transmitted intensity with \( L = 0.2 \) cm, \( \alpha_0 \approx 0 \), \( \alpha_2 = 0.1 \) cm/GW, \( \sigma_a = 6.2 \times 10^{-18} \) cm², \( \tau_e = 500 \) ps, \( \lambda = 532 \) nm, \( \omega_0 = 19 \) μm, and \( I_0 = 20 \) GW/cm². (a) Intensity as a function of time at \( r = 0 \), (b) intensity as a function of radius at \( t = 0 \).](image)

To characterize the optical nonlinearities of a material, time averaging techniques have been extensively exploited in Z-scan experiments [21]. In the theoretical treatment, integrating Eq. (6) over time, one yields the attenuation of the pulse fluence. The ESA term on the right-hand
side will contain an integral, \( \int_{-\infty}^{+\infty} G(t)I^3(t)dt \). The equation is unchanged if we replace this integral with \( \langle G \rangle \int_{-\infty}^{+\infty} I^3(t)dt \), where

\[
\langle G \rangle = \frac{\int_{-\infty}^{+\infty} G(t)I^3(t)dt}{\int_{-\infty}^{+\infty} I^3(t)dt} \tag{8}
\]

is the temporal average of \( G(t) \) weighted by intensity distribution \( I^3(t) \).

As well-known, the 2PA-generated ESR is an effective fifth-order process. The refraction index change related to fifth-order nonlinearity in Eq. (7) can be written as

\[
n_4(t) = \frac{\sigma_2 \alpha_2}{2\hbar \omega} G(t)I^2(t) \tag{9}
\]

Applying the time-averaged \( \langle n_4(t) \rangle \), one can readily extend the quasi-steady-state result to include the cumulative nature of 2PA-induced ESR [21]

\[
\langle n_4(t) \rangle = \frac{\int_{-\infty}^{+\infty} n_4(t)I(t)dt}{\int_{-\infty}^{+\infty} I(t)dt} \tag{10}
\]

In Z-scan measurements, time averages of refraction index should be a reasonable approximation. We assume, therefore, \( n_4(t) \) in Eq. (10) is approximately replaced by \( n_4(t) = \gamma_2^{\text{eff}} I^2(t) \), where \( \gamma_2^{\text{eff}} \) is the effective fifth-order nonlinear refraction index. Compared with the time-averaged index change \( \langle n_4(t) \rangle \) originated from both cumulative nonlinearity and effective nonlinearity, we determine the effective fifth-order nonlinear refraction index as follows

\[
\gamma_2^{\text{eff}} = \frac{\sigma_2 \alpha_2}{2\hbar \omega} \langle G \rangle \tag{11}
\]

In solving Eqs. (6) and (7), the transmitted intensity is numerically solved and then it is integrated spatially and temporally to give the transmitted energy. A reasonable approximation to the transmitted energy can be obtained as follows: (i) replacing \( G(t) \) with its corresponding time average \( \langle G \rangle \) in Eq. (8); (ii) solving Eqs. (6) and (7) to determine the transmitted intensity; and (iii) integrating over space and time to yield the transmitted energy. For the laser pulses with a Gaussian temporal profile, we write \( I(r,z,t) = I(r,z) \exp(-t^2/\tau^2) \), where \( \tau \) is the half-width at \( e^{-1} \) of the maximum of pulse. With the above approximations, we could revise Eqs. (6) and (7) as

\[
\frac{\partial I(r,z,t)}{\partial z'} = -\alpha_0 I(r,z,t) - \alpha_2 I^2(r,z,t) - \alpha_3^{\text{eff}} I^3(r,z,t), \tag{12}
\]

\[
\frac{\partial \Delta \phi(r,z,t)}{\partial z'} = k_\gamma I(r,z,t) + k_\gamma^{\text{eff}} I^2(r,z,t), \tag{13}
\]

where

\[
\alpha_3^{\text{eff}} = \frac{\sigma_2 \alpha_2}{2\hbar \omega} \frac{\sqrt{3}}{\sqrt{\pi} \tau} \int_{-\infty}^{+\infty} \exp \left( \frac{t^2}{\tau^2} \right) \left\{ \int_{-\infty}^{t} \exp \left( \frac{-t^2}{\tau^2} \right) \exp \left( \frac{-t'-t}{\tau_e} \right) dt' \right\} dt, \tag{14}
\]

\[
\gamma_2^{\text{eff}} = \frac{\sigma_2 \alpha_2}{2\hbar \omega} \frac{\sqrt{3}}{\sqrt{\pi} \tau} \int_{-\infty}^{+\infty} \exp \left( \frac{t^2}{\tau^2} \right) \left\{ \int_{-\infty}^{t} \exp \left( \frac{-t^2}{\tau^2} \right) \exp \left( \frac{-t'-t}{\tau_e} \right) dt' \right\} dt. \tag{15}
\]

Here \( \alpha_3^{\text{eff}} \) and \( \gamma_2^{\text{eff}} \) are the effective fifth-order nonlinear absorption and refraction coefficients caused by 2PA-induced ESA and ESR, respectively. Eqs. (14) and (15) predict that the magnitudes of excited-state nonlinearities caused by 2PA depend on the 2PA coefficient, ESA or ESR cross-sections, the lifetime of 2PA-induced excited states, and laser pulse duration.

Under the extreme condition of \( \tau_e \ll \tau \), the solution of Eqs. (14) and (15) can be derived as follows

\[
\alpha_3^{\text{eff}} = \frac{\sigma_2 \alpha_2 \tau_e}{2\hbar \omega}, \tag{16}
\]

\[
\gamma_2^{\text{eff}} = \frac{\sigma_2 \alpha_2 \tau_e}{2\hbar \omega}. \tag{17}
\]
In the limit of $\tau_e \gg \tau$, we find

$$\alpha_{3}^{\text{eff}} = \sqrt{\frac{3\pi}{8} \frac{\sigma_3 \alpha_2 \tau}{2\hbar\omega}},$$

(18)

$$\gamma_{2}^{\text{eff}} = \sqrt{\frac{3\pi}{8} \frac{\sigma_1 \alpha_2 \tau}{2\hbar\omega}}.$$  

(19)

In particular, we reduce empirical expressions as follows:

$$\alpha_{3}^{\text{eff}} = \frac{\sigma_3 \alpha_2 \tau}{2\hbar\omega} \sqrt{\frac{0.59 (\tau/\tau_e)^{3/2}}{1 + 0.59 (\tau/\tau_e)^{3/2}}},$$

(20)

$$\gamma_{2}^{\text{eff}} = \frac{\sigma_1 \alpha_2 \tau}{2\hbar\omega} \sqrt{\frac{0.59 (\tau/\tau_e)^{3/2}}{1 + 0.59 (\tau/\tau_e)^{3/2}}}.$$  

(21)

The above two expressions are in agreement with exact numerical results within 2.5% for $\tau/\tau_e > 0.1$.

In experiments, researchers reported that 2PA-induced excited-state nonlinearities are observable only above an intensity threshold [2, 7, 13]. This experimental finding can be understood as follows. At low intensity, third-order nonlinear effect is dominant because the population of the first excited state is not so sufficient that the electrons at the first excited state can be excited to higher-lying state with an observable effect. At excitation intensity exceeding a critical value, the interplay between third- and effective fifth-order nonlinearities occurs. It should be emphasized that Eqs. (12) and (13) are applicable only above a critical intensity. Using the steady-state condition in Eq. (3), the critical intensity can be estimated as

$$I_c = \frac{2\hbar\omega N^c_e}{\alpha_2 \tau_c},$$

(22)

where $N^c_e$ is the critical population of the first excited state.

The popular yet effective technique to investigate optical nonlinearities of a material is Z-scan measurements [21]. By performing the open- and closed-aperture Z scans, one could extract the sign and magnitude of nonlinear absorption and refraction coefficients, respectively. To simulate Z-scan traces, we assume that the profiles of input pulses are Gaussian beam in time and space. In solving Eq. (12), the transmitted intensity is numerically calculated. By integrating over time and space, the open-aperture Z-scan is obtained [8]. The simulation of closed-aperture Z-scan is less straightforward. By numerically solving Eqs. (12) and (13) together, the field distribution at the exit surface of the sample can be derived. Then the irradiance configuration at the far-field aperture can be evaluated using the Huygens-Fresnel principle with spatial and temporal integrals to give the closed-aperture Z-scan trace. The related Z-scan theory can be found elsewhere [10-12]. Furthermore, the Z-scans using Eqs. (12) and (13) are good agreement with the ones reported by Zhang et al. [11], which indicates that our theory is reasonable. It should be noted that the difference between the magnitude of the effective third-order nonlinearities measured in the nanosecond regime and in the femtosecond for two similar samples could be several orders of magnitude [9, 22]. This fact may imply that, in the nanosecond regime, both third-order nonlinearities and 2PA-induced excited-state nonlinearities, rather than a pure third-order process, simultaneously make contributions to the observed signal. Under the excitation of femtosecond laser pulses, however, the third-order effect is a dominant mechanism of whole nonlinear process.

In Eqs. (12) and (13), there are four free parameters, namely $\alpha_2$, $\gamma_1$, $\alpha_{3}^{\text{eff}}$, and $\gamma_{2}^{\text{eff}}$. Both $\alpha_2$ and $\alpha_{3}^{\text{eff}}$ (then to $\sigma_3$) can be extracted by the best fittings between open-aperture Z scans and the Z-scan theory of 2PA-induced ESA [8]. By fitting to Z-scan theory [23], the value of $\gamma_1$ could be unambiguously evaluated from the closed-aperture Z-scan measurements at low intensities.
where excited-state nonlinearities could be safely ignored. With the aid of the measured $\alpha_2$ and $\gamma_1$, one may obtain $\alpha_3^{\text{eff}}$ and $\gamma_2^{\text{eff}}$ from the best fitting Z-scans at high intensity [11, 12].

There is another quick procedure to evaluate the nonlinear parameters. When weak nonlinear absorption is caused by both 2PA and a fifth-order nonlinear absorption, the valley in the open-aperture Z-scan is given by $T_V \simeq \alpha_2 I_0 L_{\text{eff}}^{(3)} / 23/2 + \alpha_3^{\text{eff}} I_0^2 L_{\text{eff}}^{(5)} / 33/2$, where $L_{\text{eff}}^{(3)}$ and $L_{\text{eff}}^{(5)}$ are the effective length related to the third- and fifth-order nonlinearities. Then the value of $T_V$ is divided by $L_{\text{eff}}^{(3)} / 23/2$ giving the total absorption change, $\Delta \alpha$. In computing $L_{\text{eff}}$, an effective linear absorption coefficient replaced by $\alpha_0 + \alpha_2 I_0$ should be adopted. We find that $\Delta \alpha / I_0$ is given by

$$\frac{(\Delta \alpha)}{I_0} = \alpha_2 + 0.544 \alpha_3^{\text{eff}} I_0.$$  \hspace{1cm} (23)

If there is no fifth-order absorption effect, plotting $\Delta \alpha / I_0$ as a function of $I_0$ should result in a horizontal line with $\alpha_2$ being the intercept with the vertical axis. As 2PA-induced ESA presents, one obtains a straight line with an intercept of $\alpha_2$ on the vertical axis and a slope of $\alpha_3^{\text{eff}}$.

To determine the contribution of purely nonlinear refraction, the closed-aperture Z-scan is approximatively divided by the open-aperture Z-scan. Then, the peak-valley transmittance difference, $\Delta T_{PV}$, is divided by $0.406(1 - S)0.25 k I_0 L_{\text{eff}} / \sqrt{2}$, where $L_{\text{eff}} = [1 - e^{-((\alpha_0 + \alpha_2 I_0) L)}] / (\alpha_0 + \alpha_2 I_0)$ and $S$ is the linear transmittance of the aperture in the far field [21]. This leads to a simple equation for the on-axis total change in the refractive index $\Delta n$, which is given by

$$\frac{(\Delta n)}{I_0} = \gamma_1 + 0.422 \gamma_2^{\text{eff}} I_0,$$  \hspace{1cm} (24)

By plotting $(\Delta n) / I_0$ as a function of $I_0$, the non-zero intercept on the vertical axis and the slope of the straight line are determined the third-order refraction and ESR indexes, respectively. If $\tau_c \gg \tau$, Eq. (24) can be written as $(\Delta n) / I_0 = \gamma_1 + 0.23 \sigma_2 \tau_2 / h \omega$, which is consistent with the one reported previously [10]. It should be emphasized that the above analytical theories are also applicable for 2PA-generated free-carrier nonlinearities in bulk and nano-scaled semiconductors as well.

### 3. Conclusion

In summary, we have presented a theoretical investigation of laser-pulse-duration dependence of excited-state nonlinearities caused by 2PA. We have demonstrated the spatiotemporal distortion in the transmitted pulse caused by 2PA-induced ESA. We have given the analytical expressions for the effective fifth-order nonlinear coefficients originated from ESA and ESR, which depend on 2PA cross-section, excited-state photophysical properties, and laser pulse duration. This theory is applicable for quantitative analysis of 2PA-induced excited-state nonlinearities on the time scales where laser pulse duration is less than or comparable to the lifetime of 2PA-induced excited states. Moreover, we have also developed Z-scan theories for unambiguously yet efficiently determinations of third-order nonlinearities and excited-state nonlinearities.

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