Dynamics of two-photon-induced three-photon absorption in nanosecond, picosecond, and femtosecond regimes

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Based on five-level rate-equation theory, we develop the laser-pulse-duration dependence of two-photon-absorption-induced singlet and triplet excited-state absorptions (ESAs). We present analytical expressions for the effective three-photon absorption coefficients caused by both singlet and triplet ESAs under the pulsed excitation on time scales from femtoseconds to microseconds. We demonstrate that the triplet ESA is predominant with longer laser pulses (microseconds to tens of nanoseconds) and that the resultant nonlinear absorption (NLA) can be adequately interpreted by a simplified four-level model. Under the excitation of picosecond laser pulses, generally speaking, the competition between singlet and triplet ESAs is observable. In this instance, the photodynamics of the system can be understood by a five-level model. In the femtosecond regime, however, a three-level model is validated in the prediction of NLA, because the triplet ESA becomes negligible. © 2010 Optical Society of America

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During the past decade, two-photon absorption (2PA) related processes have received tremendous attention because of their intriguing applications in nonlinear optics and biophotonics [1]. Under the excitation of intense laser pulses, however, a strong 2PA 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 (2PA:1PA) three-photon absorption (3PA) process, as shown in Fig. 1. It has been revealed that the 2PA-induced 3PA dephasing times are governed by

\[ \frac{\partial I}{\partial z'} = - \alpha_2 I^2 - \sigma_S N_S I - \sigma_T N_T I, \]

and the time derivatives of populations of states \( S \) and \( T \) are governed by

\[ \frac{\partial N_{S_1}}{\partial t} = \frac{\alpha_2 I^2}{2\hbar \omega} \frac{N_{S_1}}{\tau_S}, \]

\[ \frac{\partial N_{T_1}}{\partial t} = \frac{\phi_T}{\tau_T} N_{S_1} - \frac{N_{T_1}}{\tau_T}, \]

where \( \tau' \) is the propagation length inside the sample; \( \alpha_2 \) is the 2PA coefficient; \( \sigma_S \) and \( \sigma_T \) are the singlet–singlet and triplet–triplet cross sections, respectively; \( \tau_S \) and \( \tau_T \) are the singlet and triplet lifetimes, respectively; \( \phi_T \) is the triplet quantum yield; and \( \hbar \omega \) is the
incident photon energy. It should be noted that we ignore both $S_h$ and $T_h$ states, because their lifetimes are much faster than the pulse durations we used in the analysis.

For the laser pulses with a Gaussian temporal profile, we have $I(t) = I_0 \exp(-t^2/\tau^2)$, where $\tau$ is the half-width at $e^{-1}$ of the maximum of pulse. Solving Eqs. (2) and (3), the population densities of $S_1$ and $T_1$ are given by

$$N_{S_1}(t) = \frac{\alpha_2 I_0^2}{2\hbar \omega} G(t),$$

$$N_{T_1}(t) = \frac{\phi T \alpha_2 I_0^2}{2h \omega \tau_S} \int_{-\infty}^{t} G(t') \exp((t' - t)/\tau_T) dt',$$

where

$$G(t) = \int_{-\infty}^{t} \exp(-2t'^2/\tau^2) \exp((t' - t)/\tau_S) dt'.$$

It can be seen that the population evolvement of $S_1$ and $T_1$ in time depends strongly on both the pulse duration and the lifetimes of excited states.

Applying time averaging technique as we reported recently [13] and taking into account the cumulative effects of 2PA-induced singlet and triplet ESAs, Eq. (1) can be revised as

$$\frac{\partial I(r,z;t)}{\partial t} = -\alpha_2 I^2(r,z;t) - (\alpha_S + \alpha_T) I^3(r,z;t),$$

where

$$\alpha_S = \frac{\sigma_S \alpha_2 \sqrt{3}}{2h \omega \sqrt{\pi \tau_S}} \int_{-\infty}^{\infty} \exp(-t^2/\tau_S^2) G(t) dt,$$

$$\alpha_T = \frac{\sigma_T \phi T \alpha_2 \sqrt{3}}{2h \omega \sqrt{\pi \tau_T}} \int_{-\infty}^{\infty} \exp(-t^2/\tau_T^2) G(t) dt.$$

Here $\alpha_S$ and $\alpha_T$ are the effective 3PA coefficients originating from singlet and triplet ESAs, respectively. If the triplet ESA process is ignored, Eq. (7) becomes the one as we discussed previously [13]. Generally speaking, to obtain both $\alpha_S$ and $\alpha_T$, one should appeal to numerical integration. Fortunately, we find the quasi-analytical expressions for both $\alpha_S$ and $\alpha_T$ at different conditions and summarize in Table 1. As listed in Table 1, when $\tau >> \tau_S$ and $\tau >> \tau_T$, the coefficients caused by singlet and triplet ESAs are independent of the pulse duration; that is, the ESA effects depend on the instantaneous irradiance. Table 1 also shows pulse-duration dependence of the effective 3PA coefficients ($\alpha_S$ and $\alpha_T$) under the extreme conditions of $\tau \ll \tau_S$ and $\tau \ll \tau_T$. In this instance, the NLA is a cumulative effect and may be assumed to be fluence dependent rather than irradiance dependent.

Taking the typical parameters of organic materials [2,10] as $\alpha_2 = 2.3 \times 10^{-2}$ cm/GW, $\alpha_S = 1.3 \times 10^{-17}$ cm$^2$, $\sigma_T = 6.5 \times 10^{-17}$ cm$^2$, $\phi_T = 0.05$, $\tau_S = 2.5$ ps, $\tau_T = 200$ ns, and $\hbar \omega = 1.6$ eV, we have investigated both singlet and triplet ESAs coefficients obtained by numerical simulation at different pulse durations, as shown by the scatters in Fig. 2. For comparison, we also plot the corresponding analytical results (see Table 1) of $\alpha_S$ and $\alpha_T$, as shown in Fig. 2 by the solid lines. Apparently, our analytical solutions are in well agreement with the numerical simulations.

For nanosecond and longer pulsed excitation, as illustrated in Fig. 2, 2PA and 2PA-induced singlet and triplet ESAs, rather than a pure 2PA process, simultaneously make contributions to the observed signal. In this case, because the contribution from excited triplet state is much greater than that of excited singlet state, we can simplify the energy diagram as a...
To verify the validity of the presented theory, we have compared the analytical solutions with the experimental results. Using the reported parameters \( \alpha_2 = 0.8 \text{cm/GW}, \quad \sigma_S = 6.0 \times 10^{-11} \text{cm}^2, \quad \sigma_T = 1.2 \times 10^{-16} \text{cm}^2, \quad \tau_S = 1.8 \text{ns}, \quad \tau_T = 110 \text{ns}, \quad \phi_T = 0.10, \quad \hbar \omega = 2.34 \text{ eV} \) for 4-propyl 4’-butyl diphenyl acetylene [11] and Eqs. (8) and (9), we evaluate \( \alpha_2^{\text{eff}} = \alpha_S + (\alpha_S + \alpha_T) I_0 \) to be 0.90 cm/GW at \( I_0 = 1.00 \text{ GW/cm}^2 \) for \( \tau = 13.8 \text{ ps} \) and 5.2 cm/GW at \( I_0 = 0.11 \text{ GW/cm}^2 \) for \( \tau = 3.6 \text{ ns} \), respectively, which are closer to the reported values of \( \alpha_2^{\text{eff}} = 0.95 \) and 5.6 cm/GGW [11]. Besides, we find that our theory could adequately interpret the observations in the femtosecond regime [9,10]. The above discussion indicates that the presented theory can well describe the experimental results on different time scales.

In summary, we have investigated 2PA-induced 3PA under the excitation of laser pulses on a wide range of time scales. We have presented analytical expressions for the effective 3PA coefficients caused by both excited singlet and triplet states. We have discussed the contributions of both singlet and triplet ESAs in the nanosecond, picosecond, and femtosecond time scales.

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References