ANALYTICAL RESOLUTION OF NONLINEAR OPTICAL ABSORPTION IN POLYMER

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Abstract

Many organic materials reveal strong nonlinear optical absorption property when exposed to strong light. It is mainly caused by Two-photon absorption (TPA) or excited state absorption (ESA). In this article, dependence of Two-photon absorption coefficient on occupation density is considered in the rate equation. An analytical resolution to describe the contributions of TPA and ESA simultaneously is derived.

Keywords: Excited state absorption; Two-photon absorption; Third-order nonlinear

1. Introduction

Nonlinear optical absorption material possesses optical limiting properties. Its optical absorption increases as the incident beam intensity increases while exhibiting higher transmittance at low intensity. The mechanism of this is mainly based on excited state absorption (ESA) and two-photon absorption (TPA). Sometimes only one of them has effect on a certain material[1,2,3]. And sometimes both of them are involved in these nonlinear processes[4,5]. It depends on materials and incident light property (intensity and wavelength)[6-8]. Most reported papers used rate equation and experiment date get numerical conclusion of absorption coefficients. The TPA coefficients β were considered constant in rate equation[4,5]. The relationship between β and ground state occupation density (N_0)is neglected. But in the strong absorption district, N_0 is great changed with incident light intensity. It has significant influence in TPA coefficients. In this paper, β is considered the product of TPA cross section $\sigma^{(2)}$ and N_0. We use rate equation obtain analytical resolution of nonlinear absorption caused by ESA and TPA. Their relative contribution is discussed.

2. Theory Evaluation of nonlinear absorption and discussion

Energy system of molecular can be classified by singlet levels S_m and triplet levels T_m . Many nonlinear absorption experiments are proceeded with shot pulse laser. When the time constant of intersystem crossing from singlet to triplet is larger than the width of pulse duration, transfer from singlet to triplet can be ignored. So our model is based on three-energy lever (singlet levels only)[8]. The absorption could be (a)from ground state S_0 to first exited state S_1—linear absorption; (b)from first exited state S_1 to higher exited state S_2—excited state absorption(c)directly from ground state S_0 to exited state S_2.—two photon absorption. Optical exitations and subsequent relaxations can be expressed by rate equations as

$$\frac{dN_0}{dt} = -\sigma_{01} N_0 \frac{I}{\hbar\omega} - \sigma^{(2)} N_0 \frac{I^2}{2\hbar\omega} + \frac{1}{\tau_{10}} N_1, \qquad (1)$$

$$\frac{dN_1}{dt} = \sigma_{01} N_0 \frac{I}{\hbar\omega} - \sigma_{12} N_1 \frac{I}{\hbar\omega} - \frac{1}{\tau_{10}} N_1 + \frac{1}{\tau_{21}} N_2, \qquad (2)$$

$$\frac{dN_2}{dt} = \sigma_{12} N_1 \frac{I}{\hbar\omega} + \sigma^{(2)} N_0 \frac{I^2}{2\hbar\omega} - \frac{1}{\tau_{21}} N_2, \qquad (3)$$

$$N = N_0 + N_1 + N_2, \qquad (4)$$

and the changes of intensity inside the sample is given by

$$\frac{dI}{dz} = -\sigma_{01} N_0 I - \sigma_{12} N_1 I - \sigma^{(2)} N_0 I^2, \qquad (5)$$

where N_0, N_1, N_2 are the corresponding population densities in the different states; N is total particle

density; τ_{10} , τ_{21} are relaxation time from S_1 to S_0 and S_2 to S_1 respectively; σ_{01} is ground state one photon absorption cross section, σ_{12} is excited state absorption cross-section; $\sigma^{(2)}$ is ground state two photons absorption cross section. I is intensity of light. Generally $\tau_{21} << \tau_{10}$, so N_2 is very small compared with N_0 and N_1. Equation (4) can be simplified as

$$N \approx N_0 + N_1 . \qquad (6)$$

If the pulse duration of incident light is longer than excited state lifetimes, we can get stable resolution of populations

$$N_0 = \frac{N}{1 + \frac{\sigma_{01}\tau_{10}}{\hbar\omega} I + \frac{\sigma^{(2)}\tau_{10}}{2\hbar\omega} I^2} , \qquad (7)$$

$$N_1 = \frac{\left(\frac{\sigma_{01}\tau_{10}}{\hbar\omega} I + \frac{\sigma^{(2)}\tau_{10}}{2\hbar\omega} I^2 \right) N}{1 + \frac{\sigma_{01}\tau_{10}}{\hbar\omega} I + \frac{\sigma^{(2)}\tau_{10}}{2\hbar\omega} I^2} , \qquad (8)$$

According to Beer's law equation $\frac{dI}{dz} = -\alpha I$ and (5), we have absorption efficient

$$\alpha = \sigma_{01} N_0 + \sigma_{12} N_1 + \sigma^{(2)} N_0 I$$

$$= \sigma_{01} N \frac{1 + \left(\frac{\tau_{10}\sigma_{12}}{\hbar\omega} + \frac{\sigma^{(2)}}{\sigma_{01}} \right) I + \frac{\sigma_{12}\tau_{10}\sigma^{(2)}}{2\hbar\omega\sigma_{01}} I^2}{1 + \frac{\sigma_{01}\tau_{10}}{\hbar\omega} I + \frac{\sigma^{(2)}\tau_{10}}{2\hbar\omega} I^2} \qquad (9)$$

By considering the first-order expansion of the expression (9), we get that the effective third-order nonlinear absorption coefficient (β_{eff})

$$\beta_{eff} = \sigma_{01} N \left[\frac{\tau_{10}}{\hbar\omega} (\sigma_{12} - \sigma_{01}) + \frac{\sigma^{(2)}}{\sigma_{10}} \right] \qquad (10)$$

The first term in the right of Eq. (10) related to ESA and the second related to TPA. When incident intensity is very high the relationship between α and I is complicated by ESA and TPA according to Eq. (9). Two-step exited state absorption process competes with one step two-photon process. Calculated dependence of absorption coefficient α on I for the samples with different exited

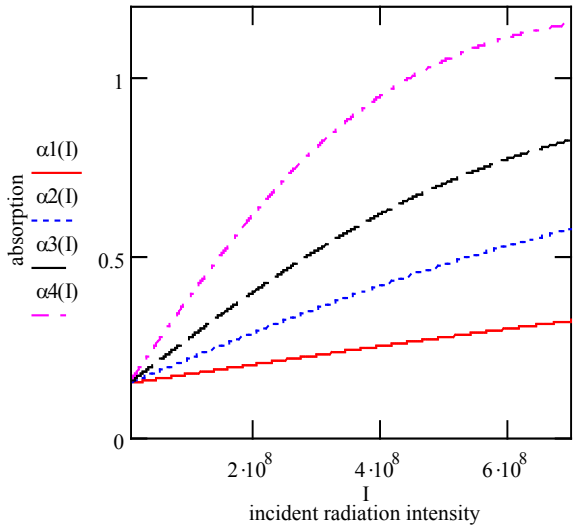

Fig.1 Calculated dependence of absorption coefficient on incident intensity for different TPA cross-section, $\sigma^{(2)} : 2.5\times10^{-27}, 10\times10^{-27}, 20\times10^{-27}, 40\times10^{-27}\ cm^4/W$ for curve $\alpha1, \alpha2, \alpha3, \alpha4$ respectively. $\sigma_{12} = 10\times10^{-18} cm^2$

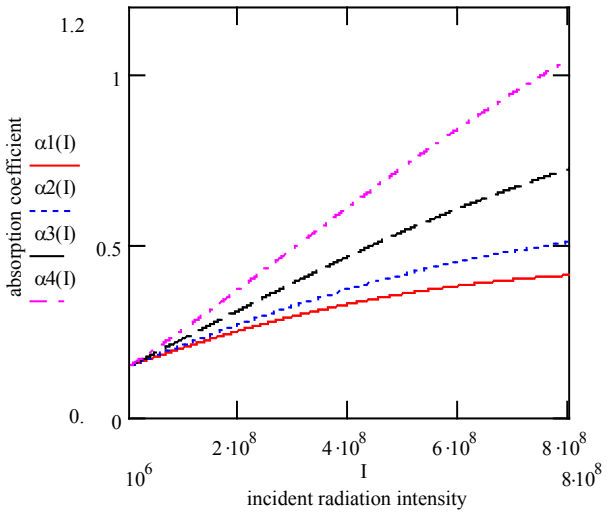

Fig2. Calculated dependence of absorption coefficient on incident intensity for different ESA cross-section, $\sigma_{12} = 0.5\times10^{-18}, 5.0\times10^{-18}, 15\times10^{-18}, 30\times10^{18} cm^2$ for curve $\alpha1, \alpha2, \alpha3, \alpha4$ respectively. $\sigma^{(2)} = 10\times10^{-27}$

state absorption cross sections(σ_{12}) and TPA cross sections($\sigma^{(2)}$) is shown in Fig.1 and fig.2. Parameters used for the simulations is: dopant concentration $N = 1.0 \times 10^{-4}\ mol/l$; $\sigma_{01} = 2.5 \times 10^{-18}\ cm^2$; $\tau_1 = 20\ ps$; $\omega = 1.78 \times 10^{15}\ s^{-1}$ (corresponding wavelength 1064nm). Other parameters are shown in the figue

A very clear feature is that at low intensities a constant coefficient is observed meaning that a linear absorption is present. When intensities exceed $10^6\ W/cm^2$ absorption coefficient increases in this situation. In Fig.1, we take $\sigma_{12} = 10 \times 10^{-18}\ cm^2$ for all four curves. α increase with I linearly for curve1 to curve3. But for very large TPA cross section $\sigma^{(2)}$ the changes of α slow down (curve4). It can be explained with TPA saturation. In fig 2, we take $\sigma^{(2)} = 10 \times 10^{-27}\ \ cm^4/W$. Curve 2 to curve 4 are straight. For lower ESA cross section (curve 1 for $\sigma_{12} < \sigma_{01}$), it rise with I linearly at first and slowdown because of one photon absorption saturation.

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