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Modulation on optical limiting and two-photon absorption behavior of a molecular medium by two-color ultrashort laser pulses

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Abstract. The dynamical behavior of two-color ultrashort laser pulse propagating in a molecular medium 4,4'-bis(di-*n* -butylamino)stilbene (BDBAS) has been studied by employing an iterative predictor-corrector finite-difference time domain (FDTD) technique to solve the Maxwell-Bloch equations. The results indicate that the spectrum of electric field shows oscillation feature around the two-photon resonant frequency when the delay time exists due to the interaction between two sub-pulses. The optical limiting window turns narrower and the saturation value of output intensity gets larger with the presence of delay time compared with no delay time case. The dynamical TPA cross section is smaller with the increase of delay time. The studies suggest a method to modulate the nonlinear optical properties of the medium by controlling the delay time of the two-color pulse.

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Key words: optical limiting, two-photon absorption, Maxwell-Bloch equations, two-color pulse

1 Introduction

During the past few decades, advances in ultrafast laser technology have made the generation of extremely short and intense pulses with only few optical periods in the visible region to be possible[1]. At the same time, studies on the intense fields-nonlinear materials interaction[2-4] and new mechanisms for generating shorter pulses were demonstrated theoretically[5]. High power laser sources have motivated an extensive research for the design of optical limiting (OL) system in order to protect sensors and human eye. There are several different mechanisms lead to OL behavior, such as reverse saturable

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absorption (RSA)[6], nonlinear refraction, optically induced scattering[7], and most importantly, two-photon absorption (TPA)[8]. Based on the *ab initio* level, several methods have been developed to calculate the intrinsic TPA cross section[9-10]. However, the actual TPA cross section of the medium is measured in laser field, which means its value is strongly dependent on the dynamical parameters of the pulse, such as pulse width, pulse intensity[8,11]. In recent years, lots of attentions are paid on developing approaches for modulating the OL behavior and TPA cross section.

Currently, there is a growing interest to investigate coherent control of nonlinear optical process with two strong laser fields, leading to numbers of interesting phenomena, such as controlling ionization, spontaneous radiation, population inversion, high-order harmonic generation (HHG) and so on. He *et al.* studied the HHG in argon using 800 nm and 400 nm laser fields simultaneously. They found that the interference of the two-color field could strongly modulate the intensity and divergence of the emitted even and odd harmonics, which is a function of the relative delay between the two fields[12]. Wu *et al.* demonstrated that the THz generation from a two-color pulse composed of the fundamental and second-harmonic waves can be coherently controlled by field-free molecular alignment[13]. Song *et al.* theoretically investigated the two-color interference effects for ultrashort laser pulses propagating in a two-level medium and the formation of higher spectral components[14]. The studies above motivate us to modulate the OL and TPA of the organic molecular materials using two-color pulses. The overlap and interference effects between the two pulses would lead to mutually interaction while propagating, and the relative phase and delay time between the two laser pulses can be used to modulate the nonlinear process.

In this paper, we study the dynamical behavior of two-color ultrashort laser pulse in a cascade three-level molecular BDBAS medium by solving the Maxwell-Bloch equations beyond the slowly-varying envelope approximation and the rotating-wave approximation. The spatial evolution properties of the pulse are analyzed, and the OL as well as dynamical TPA cross sections of the medium are given.

2 Theoretical methods

2.1 Maxwell-Bloch equations for a three-level system

The theoretical details are referred to in Ref. [15-16]. Here, we just list the main formulations. We treat the electromagnetic classically, and the molecule quantum mechanically. Then the electromagnetic radiation can be described by Maxwell equations, and the molecular system can be depicted by Bloch equations.

Starting with the density matrix equation with relaxation effect:

$$\dot{\rho}_{mn} = -\frac{i}{\hbar}[\hat{H},\rho]_{mn} - \gamma_{mn}(\rho_{mn} - \rho^0_{mn}) \tag{1}$$

where γ_{mn} is the relaxation rate of the density matrix element ρ_{mn}. $\hat{H}$ is the Hamilton of

the system, which can be expressed as (within the dipole approximation)

$$\hat{H}=\hat{H}_0+\hat{H}'=\hat{H}_0-\hat{\mu}\cdot E \tag{2}$$

where $\hat{H}_0$ is the free Hamilton of the system, $-\hat{\mu}$ is the dipole operator.

Assuming that the incident electromagnetic field is polarized along the x-axis and propagates along the z-axis to an input interface of the medium at z=0. Then the Maxwell equations can take the form

$$\begin{aligned}\frac{\partial E_x}{\partial z}&=-\mu_0\frac{\partial H_y}{\partial t}\\ \frac{\partial H_y}{\partial z}&=-\frac{\partial P_x}{\partial t}-\varepsilon_0\frac{\partial E_x}{\partial t}\end{aligned} \tag{3}$$

where μ_0 and ε_0 are the permeability and permittivity of free space, respectively.

The Maxwell equations and the Bloch equations couple to each other by the macroscopic polarization P_x

$$P_x=N<\hat{\mu}_x>=Ntr(\hat{\mu}_x\hat{\rho}) \tag{4}$$

where N is the molecular density.

2.2 Formula for the dynamical TPA cross section

The differential equation that describes pulse propagation in the presence of linear and second order absorption can be written as[17]

$$dI/dz+\alpha I+\beta I^2=0 \tag{5}$$

where α denotes the linear absorption coefficient and β is the TPA coefficient. The analytical solution of eq. (5) is

$$I_z=\frac{\alpha I_0\exp(-\alpha z)}{\alpha+\beta I_0(1-\exp(-\alpha z))} \tag{6}$$

Assuming $\beta=\beta_0+cI_0$, where β_0 is the steady-state TPA coefficient and c is a constant[18], eq. (6) can be reformed as follows

$$\frac{1}{T}=\frac{I_0}{I_z}=\exp(\alpha z)+\frac{[\exp(\alpha z)-1]\beta_0}{\alpha}I_0+\frac{c[\exp(\alpha z)-1]}{\alpha}I_0^2 \tag{7}$$

where T is the intensity transmission at the propagation distance of z. The values of α and β_0 can be estimated by fitting eq. (7). The molecular TPA cross section σ_{tp} is related to β_0 by

$$h\nu\beta_0=\sigma_{tp}N \tag{8}$$

where $h\nu$ is the input photon energy.

3 Computational details

We employ a FDTD approach for solving the full-wave Maxwell-Bloch equations. The BDBAS molecule is used as the nonlinear medium (Fig. 1). Time-dependent DFT/B3LYP method implemented in DALTON package[19] is employed to obtain the parameters of the molecule. Electronic structure calculations show that the molecule has only one charge transfer state (the first excited state S_2) in the optical region with a transition dipole moment between the ground state S_1 and the first excited state S_2 of $3.747\times10^{-29}C\cdot m$. The transition dipole moment between S_2 and the fourth excited state S_3 is $4.154\times10^{-29}C\cdot m$. The permanent dipole moments of these states are also equal to zero because of the molecule's symmetrical characteristic. The excitation energies of S_2 and S_3 states are $\hbar\omega_{21}$=3.41eV and $\hbar\omega_{31}$=4.20eV, respectively. In order to describe the interaction between the molecule and ultrashort pulse in the low energy region, a cascade three-level system including the ground state S_1, the first excited state S_2 and the fourth excited state S_3 is modeled as shown in Fig. 1. The molecule is assumed to be rest in its ground state S_1 and there is no coherence between states before the laser pulse is switched on, namely, $\rho^0_{11}=1$, $\rho^0_{22}=\rho^0_{33}=0$ and the non-diagonal elements $\rho^0_{mn}=0$ $(m\neq n)$. The decay rates of the density matrix elements are all be chosen as $\gamma_{mn}=1.0\times10^{13}/s$. The molecular density is taken as $N=7.0\times10^{25}/m^3$.

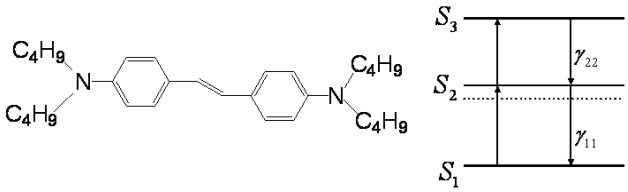
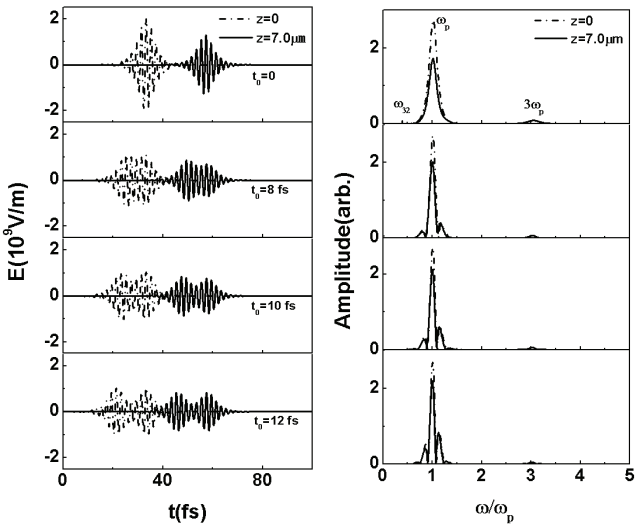


Figure 1: Molecular structure of BDBAS (left) and the scheme of transitions (right).

For the external two-color laser pulse, the initial electric field is

$$\begin{aligned}E(z,t=0)=&F_1\,\mathrm{sech}[1.76((z+z_0)/c)/\tau_{p1}]\cos[\omega_{p1}(z+z_0)/c]\\&+F_2\,\mathrm{sech}[1.76(t_0+(z+z_0)/c)/\tau_{p2}]\cos[\omega_{p2}(t_0(z+z_0)/c)]'\end{aligned}\tag{9}$$

where F_1 and F_2 are the peak amplitudes of the two sub-pulses, τ_{p1} and τ_{p2} are the full width at half maximum (FWHM) of the two sub-pulses intensity envelopes, ω_{p1} and ω_{p2} are the frequencies of the two sub-pulses, respectively. And t_0 is the delay time between them. The choice of z_0 ensures that the laser pulse penetrates negligibly into the medium at $t=0$. In our simulation, the carrier wave frequencies ω_{p1} and ω_{p2} take the value of half of the frequency between S_1 and S_3 states, *i.e.*, the two photon resonant frequency $(\omega_{p1}=\omega_{p2}=\omega_{31}/2=\omega_p)$. The FWHM of the two pulses are all set as 5 fs.



(a) (b)

Figure 2: (a) Evolution of electric fields of pulse with different delay time $t_0 = 0$, 8 fs, 10 fs and 12 fs at the propagation distance of $z = 0$ (dash dot line) and $z = 7.0$ μm (solid line). $F_1 = F_2 = 1.0 \times 10^9$ V/m. (b) The spectra corresponding to (a).

4 Numerical results and analysis

4.1 Propagation of the two-color ultrashort laser pulse in BDBAS

We firstly model the propagation of two-color laser pulse with the same pulse peak amplitudes of $1.0 \times 10^9 V/m$ but with different delay time of 0, 8 fs, 10 fs and 12 fs in the medium. Fig. 2(a) depicts the electric field at the input surface of the nonlinear medium (dash dot line) and at the distance of 7.0 μm (solid line). It can be seen that without any delay between two sub-pulses, the propagation is the same as one-color case. We can explain it from the external laser pulse field expression (9), which can be simplified into an one-color laser pulse when $t_0 = 0$. Taken the delay time into consideration, the two sub-pulses show an obvious separate feature, and the overlap between two sub-pulses leads to obvious modification of the electric field temporal shape. The pulse intensity in the propagation decreases because the interaction between the electric and the medium leads to more and more energy transfer from the pulse into the medium. The corresponding spectra are shown in Fig. 2(b). As one can see, except for the base frequency ω_p, new frequency components ω_{32} appears during the propagation of the pulse. Besides, odd harmonic components $3\omega_p$ appear, while the even harmonic components are restrained because of the symmetry of the molecule. When the delay time exists, the frequency component ω_{32} turns weaker which indicates less population decay from level S_3 to S_2, and the oscillation feature around ω_p occurs due to the interference between the two separated sub-pulses.

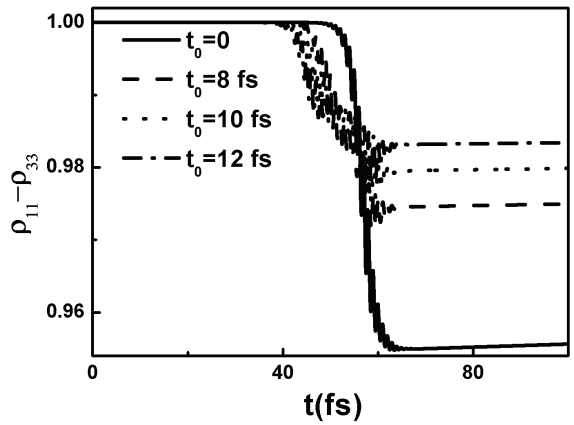


Figure 3: Population differences of molecules with different delay time of 0, 8 fs, 10 fs and 12 fs at the propagation distance of 7.0μm.

In order to further elucidate the influence of delay time on the medium, Fig. 3 shows the population differences between S_1 and S_3 of two-color laser pulse with different delay time of 0, 8 fs, 10 fs and 12 fs at the propagation distance of 7.0μm. It can be seen that as the delay time increases, the population difference between S_1 and S_3 turns smaller, indicating weaker TPA. For a shorter delay time, the particles excited by the former sub-pulse have more probability to be pumped onto S_3 by the secondary excitation of the latter sub-pulse, while for a longer delay time, they are likely to decay back to S_1 before the latter sub-pulse plays a role.

4.2 The OL and dynamical TPA cross section of two-color laser pulses

Fig. 4 shows the output fluence S_{out} versus the input fluence S_{in} of two-color pulses with different delay time 0, 8 fs, 10 fs and 12 fs at the distance of 7.0 μm. It is shown that without delay time, BDBAS has an evident OL behavior, namely, broad OL window and small output saturation value. However, the OL window turns narrower and the saturation value of output intensity gets larger with the presence of delay time compared with no delay time case, indicating weaker OL ability.

In Table 1, we listed the calculated TPA coefficient β_0 and dynamical TPA cross section σ_{tp} with different delay time of two-color pulse at different propagation distances using the linear fitting formula $\beta = \beta_0 + cI_0$. The values of dynamical TPA cross section are of the same order of magnitude with the intrinsic TPA cross section $\sigma_{tp} = 1430\ GM$. Compared with the experimental value $\sigma_{tp} = 9300\ GM$ [20], our calculated results are on the same order but somewhat smaller. The discrepancy mainly results from the experimental condition with the pulse duration of 5 ns and $\lambda = 600nm$ under which two-step TPA process takes place. Besides, we should notice that the dynamical TPA cross section is not a monotone function of the propagation distance. Therefore, the thickness of the

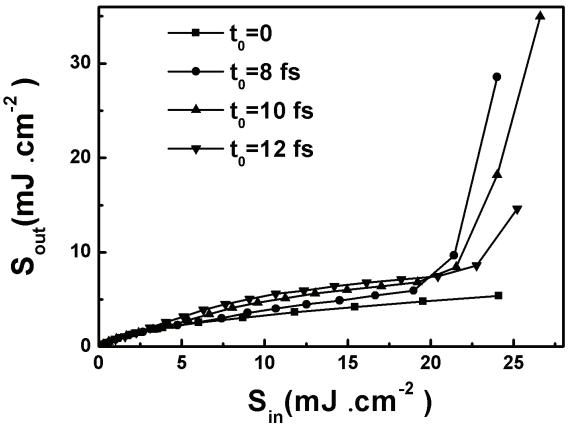


Figure 4: Output fluence S_{out} versus input fluence S_{in} with different delay time of 0, 8 fs, 10 fs and 12 fs at the distance of 7.0 μm.

medium should be taken into account when comparing the TPA cross sections of samples in different measurements. Moreover, the dynamical TPA cross section decreases with the increase of delay time, indicating the delay time between two-color sub-pulses can be used as a method to modulate the TPA cross section.

Table 1: Dependence of $\beta_0(10^{-10}$ m/W) and σ_{tp} (GM) (1GM=10^{-50} cm^{4}s/photon) on delay time of two-color pulse and the propagation distance.

t_0/fs	3.5 μm		7.0 μm		10.5 μm	
	β_0	σ_{tp}	β_0	σ_{tp}	β_0	σ_{tp}
0	0.190	915.65	0.186	898.01	0.207	995.68
8	0.187	902.59	0.138	663.34	0.203	980.70
10	0.104	503.18	0.067	325.37	0.059	282.83
12	0.060	286.56	0.020	98.04	0.010	49.19

5 Conclusions

We have provided dynamical analysis on the propagation and nonlinear properties for the two-color ultrashort laser pulses propagating in the organic molecular medium BDBAS by solving the Maxwell-Bloch equations using an iterative predictor-corrector FDTD method. By numerically simulating, it is concluded that the interference between two sub-pulses plays an important role on the evolution and spectrum of the electric field as well as the population difference of the medium. Taking the delay time into consideration, threshold for the breakdown of OL is smaller and the saturation of output intensity is higher. Moreover, the OL window turns wider and the output saturation value gets

larger with the increase of delay time between the two sub-pulses. The dynamical TPA cross section, which is dependent crucially on the sample thickness, is smaller with the increase of delay time. Our investigation provides a method to modulate the nonlinear optical properties of the medium by controlling the delay time of the two-color pulse.

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