Polarization and phase control of two-photon absorption in an isotropic molecular system*

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We theoretically and experimentally study the polarization and phase control of two-photon absorption in an isotropic molecular system. We theoretically show that the two-photon transition probability decreases when the laser polarization changes from linear through elliptical to circular, and the laser polarization does not affect the control efficiency of two-photon transition probability by shaping the spectral phase. These theoretical results are experimentally confirmed in coumarin 480. Furthermore, we propose that the combination of the laser polarization with the spectral phase modulation can further increase the control efficiency of the two-photon absorption.

Keywords: two-photon absorption, laser polarization, spectral phase modulation

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1. Introduction

A coherent control strategy provides a powerful method with which to steer a quantum system towards a preselected target state by the light-matter interaction,[1,2] and the primary experimental tool is the spectral phase and/or amplitude modulation.[3] With the development of the ultrafast pulse shaping technique, now it is possible to obtain such a pulse with an almost arbitrary temporal distribution by tailoring the spectral phase and/or amplitude in the frequency domain. So far, the coherent control strategy by manipulating the spectral phase and/or amplitude has been widely applied to various nonlinear optical processes, involving multiphoton absorption,[4−8] photo-ionization, and photodissociation,[9−11] coherent anti-Stokes Raman scattering,[12−15] high-harmonic generation,[16] and so on. In previous studies, the laser electric field was usually considered as being scalar, while it is vector. Since the quantum system is a three-dimensional object, the laser polarization should have a significant effect on these nonlinear optical processes. Therefore, the spectral phase and/or amplitude modulation combining with the laser polarization can further increase the control degree and efficiency.

The laser polarization effect (i.e., linear versus circular polarization) on the two-photon absorption (TPA) or two-photon fluorescence (TPF) has been well studied in theory and experiment, such as the polarization dependence of the TPA rate in randomly oriented molecules,[17] the polarization effect on TPA in organic molecules,[18,19] or the polarization-dependent TPA effect in chiral molecules.[20] A very recent study by Nag and Goswami[21] demonstrated that the TPF intensity in non-chiral isotropic fluorescent dye decreases when the laser polarization changes from linear through elliptical to circular. However, the theoretical model and the physical control mechanism are still unclear. In this paper, we expect to further address these problems. We theoretically study the dependence of the two-photon transition probability on the laser polarization in an isotropic molecular system, and experimentally confirm it in coumarin 480. Furthermore, we show that the laser polarization does not affect the control efficiency of TPF intensity by manipulating the spectral phase, and suggest that the control efficiency of the TPF intensity can be further

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increased by combining the laser polarization with the spectral phase modulation.

2. Theoretical model

We consider the nonlinear interaction of a linearly polarized laser field $\boldsymbol{E}(t)$ with an isotropic molecular system, and the non-resonant two-photon transition probability (i.e., a transition without the intermediate state) that can be approximated based on the second-order perturbation theory as[4,22]

$$P_2 \propto \int_{-\infty}^{+\infty} G(\omega_0) \left| \int_{-\infty}^{+\infty} \boldsymbol{E}^2(t) \exp(\mathrm{i}\omega_0 t)\, \mathrm{d}t \right|^2 \mathrm{d}\omega_0, \tag{1}$$

where ω_0 is the single-photon transition frequency from the ground state to the final excited state, and $G(\omega_0)$ is the line-shape function that is correlated with the molecular absorption. When a laser field with the linear polarization $\boldsymbol{E}(t) = A(t)\cos(\omega t)\boldsymbol{e}_x$ propagates through a quarter-wave plate ($\lambda/4$ wave plate), the output laser field can be expressed as

$$\begin{aligned} \boldsymbol{E}_{\lambda/4}(t) = {} & A(t)\cos(\theta)\cos(\omega t)\,\boldsymbol{e}_x \\ & + A(t)\sin(\theta)\cos(\omega t + \pi/2)\,\boldsymbol{e}_y, \end{aligned} \tag{2}$$

where θ is the angle between the input laser polarization direction and the $\lambda/4$ wave plate optical axis. The output laser is linearly polarized for $\theta = m\pi/2$ ($m = 0$, 1, 2...), circularly polarized for $\theta = (2m+1)\pi/4$, and elliptically polarized for other rotation angle θ. Thus, P_2 can be further written as

$$\begin{aligned} P_2 \propto {} & \left[\cos^4(\theta) + \sin^4(\theta)\right] \int_{-\infty}^{+\infty} G(\omega_0) \\ & \times \left| \int_{-\infty}^{+\infty} \left[A(t)\cos(\omega t)\right]^2 \exp(\mathrm{i}\omega_0 t)\, \mathrm{d}t \right|^2 \mathrm{d}\omega_0 \\ \propto {} & \left[\cos^4(\theta) + \sin^4(\theta)\right] \int_{-\infty}^{+\infty} G(\omega_0) \\ & \times \left| \int_{-\infty}^{+\infty} E\left(\frac{\omega_0}{2} + \Omega\right) E\left(\frac{\omega_0}{2} - \Omega\right) \mathrm{d}\Omega \right|^2 \mathrm{d}\omega_0 \\ \propto {} & \left[\cos^4(\theta) + \sin^4(\theta)\right] \int_{-\infty}^{+\infty} G(\omega_0) \\ & \times \left| \int_{-\infty}^{+\infty} A\left(\frac{\omega_0}{2} + \Omega\right) A\left(\frac{\omega_0}{2} - \Omega\right) \right. \\ & \times \exp\left\{ \mathrm{i} \left[\Phi\left(\frac{\omega_0}{2} + \Omega\right) \right.\right. \\ & \left.\left. + \Phi\left(\frac{\omega_0}{2} - \Omega\right) \right] \right\} \mathrm{d}\Omega \Bigg|^2 \mathrm{d}\omega_0, \end{aligned} \tag{3}$$

where $E(\omega) = A(\omega)\exp[\mathrm{i}\Phi(\omega)]$ is the Fourier transform of $E(t)$, and $A(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and phase, respectively. As can be seen from Eq. (3), the two-photon transition probability P_2 in the isotropic molecular system is correlated with the $\lambda/4$ wave plate rotation angle θ (i.e., the laser polarization). It is easy to verify that P_2 reaches a maximal value for $\theta = m\pi/2$ (the linear polarization) and minimal value for $\theta = (2m+1)\pi/4$ (the circular polarization). Therefore, when the laser polarization changes from linear through elliptical to circular, P_2 is reduced. Furthermore, it can be seen that the laser polarization (linear or circular polarization) does not affect the control efficiency of P_2 by manipulating the spectral phase $\Phi(\omega)$.

3. Experimental results and discussion

To demonstrate the polarization and phase control of the non-resonant TPA in the isotropical molecular system, we perform the experiment in coumarin 480, which is purchased from the Exciton Company and used without further purification. In our experiment, coumarin 480 is dissolved in methanol solution, and its concentration is 1×10^{-4} mol/L. The experimental arrangement is shown in Fig. 1. A Ti-sapphire mode-locked regenerative amplifier (Spectra-physics, Spitfire) is used as an excitation source with a pulse width of about 50 fs, a central wavelength of 800 nm, and a repetition rate of 1 kHz. The output laser pulse is sent into a programmable 4-f configuration zero-dispersion pulse shaper, which is composed of a pair of diffraction gratings with 1200 lines/mm, a pair of concave mirrors with focal length of 200 mm, and a one-dimensional liquid-crystal spatial light modulator (SLM-256, CRI), and the spatial light modulator (SLM) is placed in the Fourier plane and used to control the spectral phase and/or amplitude in frequency domain. A $\lambda/4$ wave plate is used to vary the laser polarization from linear through elliptical to circular, and *vice versa*. The phase- and polarization-shaped laser pulse is focused into a 10-mm quartz cuvette full of coumarin 480 by using a lens of 500-mm focal length, and the laser intensity at the focus is estimated to be $\sim1.3\times10^{11}$ W/cm^2. The two-photon fluorescence (TPF) is perpendicularly collected and measured by a spectrometer with charge-coupled device (CCD).

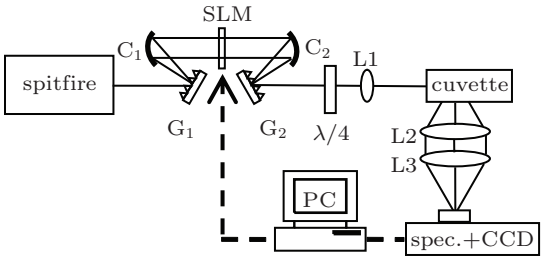

Fig. 1. Schematic diagram of the experimental arrangement. Here, an SLM is used to modulate laser spectral phase and a $\lambda/4$ wave plate is employed to vary the laser polarization.

Figure 2 shows the normalized TPF intensity of coumarin 480 as a function of $\lambda/4$ wave-plate rotation angle θ, together with the theoretical curve calculated from Eq. (3) (solid line). All data are normalized by the linear-polarization pulse excitation. Since coumarin 480 is composed of isotropic molecules, the direction iflaser polarization does not affect the TPF intensity as expected, such as the horizontal linear polarization ($\theta = 0$ or π) and vertical linear polarization ($\theta = \pi/2$ or $3\pi/2$), or the right circular polarization ($\theta = \pi/4$ or $5\pi/4$) and left circular polarization (θ=$3\pi/4$ or $7\pi/4$). With the increase of the $\lambda/4$ wave plate rotation angle θ, the TPF intensity presents a periodical modulation, and approaches to a minimum value at $\theta = (2m + 1)\pi/4$ (the circular polarization) and a maximum value at $\theta = m\pi/2$ (the linear polarization).

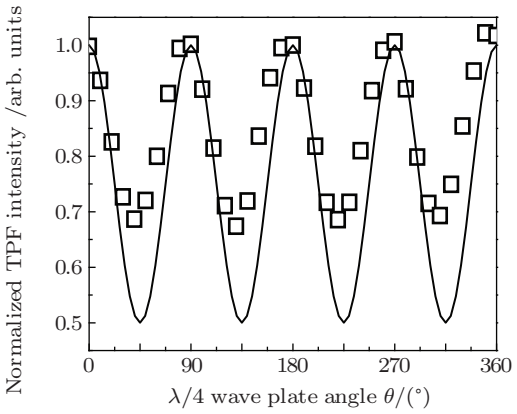

Fig. 2. Normalized TPF intensity of coumarin 480 as a function of $\lambda/4$ wave plate rotation angle θ, together with the theoretical curve calculated from Eq. (3) (solid line). The TPF intensity achieves a minimum value at $\theta = (2m + 1)\pi/4$ (circular polarization) and a maximum value at $\theta = m\pi/2$ (linear polarization).

It is obvious that the experimental observations are consistent with the above theoretical prediction, but the control efficiency obtained in the experiment is smaller than that calculated in theory. To explore the difference between the experiment and the theory, we measure the UV-visible absorption spectra of coumarin 480 as shown in Fig. 3. As can be seen in the figure, two broad absorption bands appear around 218 nm and 391 nm, thus the excitation process in our experiment should be considered as a resonance-mediated (2+1) three-photon absorption process. Therefore, we believe that the decrease of control efficiency of TPF intensity due to the variation of the laser polarization should be attributed to the absorption of the higher excited state.

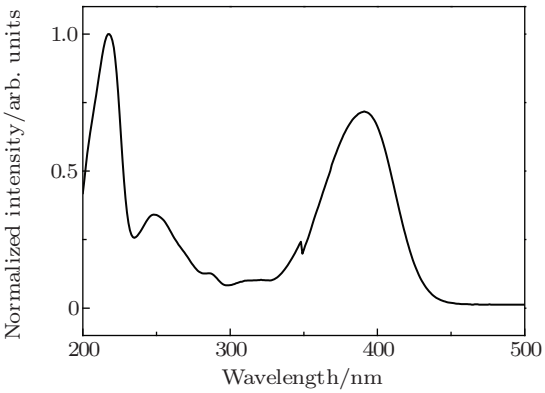

Fig. 3. Normalized UV-visible absorption spectrum of coumarin 480, with two broad absorption bands being around 218 nm and 391 nm.

Spectral phase modulation can vary the temporal distribution of laser intensity, and therefore it is usually employed to control the TPF intensity.[4–6] Next, we investigate the laser polarization effect on the control efficiency of TPF intensity by manipulating the spectral phase. Here, we modulate the spectral phase using a sinusoidal modulation function $\Phi(\omega) = \alpha \sin[2\beta\pi(\omega - \omega_{\min})/(\omega_{\max} - \omega_{\min})]$, where α and β represent the modulation amplitude and modulation period number, and $\omega_{\max}$ and $\omega_{\min}$ are the maximal and minimal frequency of the laser spectrum, and the spectral phase modulation is schematically plotted in the inset of Fig. 4. Figure 4 shows the curves of normalized TPF intensity of coumarin 480 versus modulation period number β for $\alpha = \pi$ with the linear polarization (squares) and the circular polarization (circles). The data for the linear and circular polarizations are both normalized by the transform-limited pulse excitation. As can be seen in the figure, with the increase of modulation period number β, the TPF intensities for linear and circular polarizations evolve in the same manners, showing a fast following by a slow decrease process. That is to say, the laser

polarization does not change the control efficiency of the TPF intensity by manipulating the spectral phase, which is in good agreement with the above theoretical expectation.

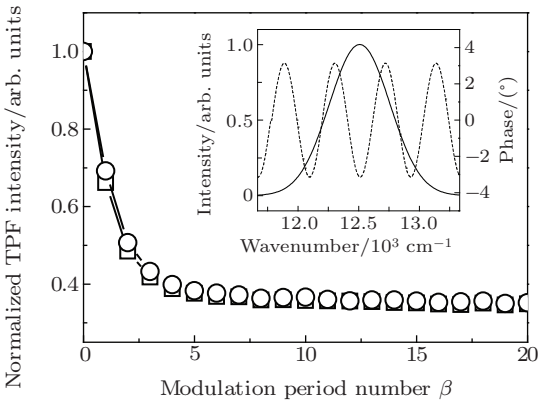

Fig. 4. Curves of normalized TPF intensity of coumarin 480 versus modulation period number β for $\alpha = \pi$ with the linear polarization (squares) and the circular polarization (circles). Inset shows the schematic diagram of the sinusodial phase modulation $\Phi(\omega) = \alpha \sin[2\beta\pi(\omega - \omega_{\min})/(\omega_{\max} - \omega_{\min})]$ applied to the laser spectrum.

As shown in Figs. 2 and 4, the TPF intensity can be effectively controlled by manipulating the laser polarization or the spectral phase, and the laser polarization does not affect the control efficiency of the TPF intensity by manipulating the spectral phase, thus the control efficiency of the TPF intensity can be further increased by combining the laser polarization and the spectral phase modulation. Accordingly, we can conclude that the combination of the laser polarization and the spectral phase modulation can provide an excellent tool for controlling various nonlinear optical processes.

4. Conclusion

In this paper, we theoretically and experimentally investigated the control of the non-resonant TPA in an isotropic molecular system by varying the laser polarization and the spectral phase. Our theoretical results indicate that when the laser polarization changes from linear through elliptical to circular, the two-photon transition probability decreases. We experimentally validated the two-photon absorption dependence on the laser polarization in coumarin 480. Furthermore, we showed that the laser polarization does not affect the control efficiency of the TPF intensity by manipulating the spectral phase, and proposed that combining the laser polarization and spectral phase modulation can further increase the control efficiency of the TPF intensity.

References

[1] Nuernberger P, Vogt G, Brixner T and Gerber G 2007 *Phys. Chem. Chem. Phys.* **9** 2470
[2] Silberberg Y 2009 *Ann. Rev. Phys. Chem.* **60** 277
[3] Weiner A M 2000 *Rev. Sci. Instrum.* **71** 1929
[4] Meshulach D and Silberberg Y 1999 *Phys. Rev.* A **60** 1287
[5] Amitay Z, Gandman A, Chuntonov L and Rybak L 2008 *Phys. Rev. Lett.* **100** 193002
[6] Zhang S A, Zhang H, Yang Y, Jia T Q, Wang Z G and Sun Z R 2010 *J. Chem. Phys.* **132** 094503
[7] Zhang S A, Wang Z G and Sun Z R 2008 *Chin. Phys.* B **17** 2914
[8] Zhang H, Zhang S A, Wang Z G and Sun Z R 2010 *Chin. Phys.* B **19** 113208
[9] Langhojer F, Cardoza D, Baertachy M and Weinacht T 2005 *J. Chem. Phys.* **122** 014102
[10] Bartelt A F, Feurer T and Wöste L 2005 *Chem. Phys.* **318** 207
[11] Papastathopoulos E, Strehle M and Gerber M 2005 *Chem. Phys. Lett.* **408** 65
[12] Oron D, Dudovich N, Yelin D and Silberberg Y 2002 *Phys. Rev. Lett.* **88** 063004
[13] Konradi J, Singh A K and Materny A 2006 *J. Photochem. Photobio.* A **180** 289
[14] Zhang S A, Zhang H, Wang Z G and Sun Z R 2010 *Chin. Phys.* B **19** 043201
[15] Zhang S A, Zhang H, Jia T Q, Wang Z G and Sun Z R 2010 *J. Chem. Phys.* **132** 044505
[16] Bartels R, Backus S, Zeek E, Misoguti L, Vdovin G, Christov I P, Murnane M M and Kapteyn H C 2000 *Nature* **406** 164
[17] Nascimento M A C 1983 *Chem. Phys.* **74** 51
[18] Wang C K, Macak P, Luo Y and Agren H 2001 *J. Chem. Phys.* **114** 9813
[19] Macak P, Luo Y, Norman P and Agren H 2001 *J. Chem. Phys.* **113** 7055
[20] Toro C, De Boni L, Lin N, Santoro F, Rizzo A and Hernandez F E 2010 *Chem. Eur. J.* **16** 3504
[21] Nag A and Goswami D 2010 *J. Chem. Phys.* **132** 154508
[22] Zhang S A, Zhang H, Lu C H, Jia T Q, Wang Z G and Sun Z R 2010 *J. Chem. Phys.* **133** 214504