Polarization control of multi-photon absorption under intermediate femtosecond laser field*

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It has been shown that the femtosecond laser polarization modulation is a very simple and well-established method to control the multi-photon absorption process by the light–matter interaction. Previous studies mainly focused on the multi-photon absorption control in the weak field. In this paper, we further explore the polarization control behavior of multi-photon absorption process in the intermediate femtosecond laser field. In the weak femtosecond laser field, the second-order perturbation theory can well describe the non-resonant two-photon absorption process. However, the higher order nonlinear effect (e.g., four-photon absorption) can occur in the intermediate femtosecond laser field, and thus it is necessary to establish new theoretical model to describe the multi-photon absorption process, which includes the two-photon and four-photon transitions. Here, we construct a fourth-order perturbation theory to study the polarization control behavior of this multi-photon absorption under the intermediate femtosecond laser field excitation, and our theoretical results show that the two-photon and four-photon excitation pathways can induce a coherent interference, while the coherent interference is constructive or destructive that depends on the femtosecond laser center frequency. Moreover, the two-photon and four-photon transitions have the different polarization control efficiency, and the four-photon absorption can obtain the higher polarization control efficiency. Thus, the polarization control efficiency of the whole excitation process can be increased or decreased by properly designing the femtosecond laser field intensity and laser center frequency. These studies can provide a clear physical picture for understanding and controlling the multi-photon absorption process in the intermediate femtosecond laser field, and also can provide a theoretical guidance for the future experimental realization.

Keywords: multi-photon absorption, laser polarization, femtosecond laser field

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1. Introduction

The multi-photon absorption manipulation, including absorption enhancement and suppression, is an important fundamental study for understanding the multi-photon excitation process and up-conversion luminescence mechanism. The ability to artificially manipulate the multi-photon absorption enhancement or suppression has potential applications in biology and medicine, such as fluorescence spectroscopy, three-dimensional fluorescence imaging or photodynamic therapy.[1–4] So far, several schemes have been proposed to manipulate the multi-photon absorption process in atomic, molecular or ionic system. The spectral phase modulation based on a femtosecond pulse shaping technique is a common method to control the multi-photon absorption process, such as π phase step modulation,[5,6] cosine or sinusoidal phase modulation,[7–9] V-shaped spectral phase modulation,[10,11] chirped phase modulation,[12] and so on. Furthermore, the femtosecond laser polarization modulation is considered as another flexible method, which has been successfully applied in the control of multi-photon ionization in I_2 or K_2,[13,14] multi-photon absorption in fluorescent dyes,[15,16] and up-conversion luminescence in rare earth ions,[17,18] and anti-Stokes Raman spectroscopy.[19]

The previous works mainly focused on the multi-photon absorption modulation in the weak femtosecond laser field.[5–7,20,21] Here, we further study the polarization control behavior of multi-photon absorption process in the intermediate femtosecond laser field. In a two-level quantum system, the excited state population can be induced by the non-resonant two-photon absorption in the weak femtosecond laser field. However, under the intermediate femtosecond laser field excitation, a higher nonlinear optical effect can also occur, i.e., four-photon absorption. In this work, we established a fourth-order perturbation theory model to study the polarization control behavior of this multi-photon absorption (i.e., involving both two-photon and four-photon transitions) in the intermediate femtosecond laser field. Our theoretical re-

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sults show that both the contributions of two-photon and four-photon transitions determine the final state absorption, while the constructive or destructive interference between the two excitation processes depends on the femtosecond laser center frequency. Moreover, the polarization control efficiencies of the two-photon and four-photon transitions are different, and the four-photon absorption can obtain the higher polarization control efficiency. In addition, the relative weight of the four-photon transitions in the whole excitation processes will increase with the increase of the femtosecond laser field intensity. Therefore, the polarization control efficiency of the whole multi-photon excitation process can be increased or decreased by properly designing the femtosecond laser field intensity and laser center frequency.

2. Theoretical model

As shown in Fig. 1(a), when a two-level atomic system interacts with the intermediate femtosecond laser field, the final excited state can be populated by two excitation processes, i.e., two-photon and four-photon transitions. Here, the two-photon process is that the population in the ground state $|g\rangle$ is pumped to the final state $|f\rangle$ by simultaneously absorbing two photons via the virtual state $|i\rangle$. For the four-photon transition process, the transition pathways include all the contributions of the non-resonant Raman parts via the virtual state $|i\rangle$ and $|n\rangle$, where the four photons involve three absorbed photons and one emitted photon. One can see that the two-photon process is non-resonant two-photon absorption (i.e., 1 and 2), while the four-photon process is a resonance-mediated four-photon absorption (i.e., 1, 2, 3, and 4). Here, the $A_{\rm f}(\omega_{\rm fg})$ is used to express the transition amplitude of final excited state $|f\rangle$, while $A_{\rm f}^{(2)}$ and $A_{\rm f}^{(4)}$ are two-photon and four-photon transition amplitudes. Thus, the transition amplitude $A_{\rm f}(\omega_{\rm fg})$ of the final excited state $|f\rangle$ should involve both the contributions of the two-photon and four-photon transitions. Here, we construct a fourth-order perturbation theory to describe the two-photon and four-photon absorption processes under the intermediate femtosecond laser field, which includes the second-order and fourth-order perturbation terms, i.e., $A_{\rm f}^{(2)}$ and $A_{\rm f}^{(4)}$. The second-order term $A_{\rm f}^{(2)}$ (i.e., non-resonant two-photon absorption) involves all the ground-to-final non-resonant two-photon excitation pathways, and can be described as[5]

$$A_f^{(2)} = \frac{\mathrm{i}}{\hbar^2}|E_0|^2 A^{(2)}(\omega_{\rm fg}), \tag{1}$$

with

$$A^{(2)}(\Omega) = \mu_{\rm fg}^{(2)} \int_{-\infty}^{\infty} \widehat{E}(\omega)\widehat{E}(\Omega-\omega)\,\mathrm{d}\omega, \tag{2}$$

where $\mu_{\rm fg}^2$ is the dipole moment matrix elements, and $\omega_{\rm fg}$ is the transition frequency of $|g\rangle \to |f\rangle$. The spectral laser field is written as $E(\omega) = |E(\omega)|\exp[\mathrm{i}\phi(\omega)]$, and $E(\omega)$ and $\phi(\omega)$ are the spectral amplitude and phase at the frequency ω. Here, we use the normalized spectral field $\hat{E}(\omega) = |E(\omega)|/|E_0|$ to represent the laser field shape, and E_0 is the maximal spectral amplitude. The fourth-order term $A_{\rm f}^{(4)}$ (i.e., resonance-mediated four-photon absorption) interferes with all the ground-to-final four-photon transition pathways with three absorbed photons and one emitted photon. The four-photon absorption can be divided into two parts: on-resonant and near-resonant parts. In the on-resonant four-photon absorption process, the population in the ground state $|g\rangle$ is first pumped to the excited state $|f\rangle$ or ground state $|g\rangle$ and then further pumped to the excited state $|f\rangle$ by absorbing three photons and emitting one photon. For the near-resonant four-photon absorption process, the population in the ground state $|g\rangle$ is directly pumped to the excited state $|f\rangle$ without passing through the two states $|f\rangle$ or $|g\rangle$ with three absorbed photons and one emitted photon. Thus, the four-order term $A_{\rm f}^{(4)}$ can be approximated as[22–24]

$$A_{\rm f}^{(4)} = A_{\rm f}^{(4){\rm on-res}} + A_{\rm f}^{(4){\rm near-res}}, \tag{3}$$

with

$$A_{\rm f}^{(4){\rm on-res}} = \frac{\mathrm{i}}{\hbar^4}|E_0|^4\left[\mathrm{i}\pi A^{(2)}(\omega_{\rm fg})A^{({\rm R})}(0)\right], \tag{4}$$

$$A_{\rm f}^{(4){\rm near-res}} = \frac{\mathrm{i}}{\hbar^4}|E_0|^4\left[-\wp\int_{-\infty}^{\infty}\mathrm{d}\delta\frac{1}{\delta}A^{(2)}(\omega_{\rm fg}-\delta)A^{({\rm R})}(\delta)\right], \tag{5}$$

where $A^{({\rm R})}(\delta)$ interfere with all the Raman transitions that are all of non-resonant nature, and can be defined as

$$A^{({\rm R})}(\delta) = \left(\mu_{gig}^{(2)} + \mu_{\rm fif}^{(2)} + \mu_{\rm fnf}^{(2)}\right)\int_{-\infty}^{\infty}\widehat{E}(\omega+\delta)\widehat{E}^{*}(\omega)\,\mathrm{d}\omega, \tag{6}$$

where $\wp$ is the Cauchy principal value, and $\mu_{\rm gig}^2$, $\mu_{\rm fif}^2$, and $\mu_{\rm fnf}^2$ are the effective non-resonant Raman coupling via the virtual state $|i\rangle$ and $|n\rangle$. In our theoretical simulation, the two-level atomic system parameters are set as follows, the transition frequency of $|g\rangle \to |f\rangle$ is 25000 cm^{-1}, and the ratio of $\mu_{\rm fg}^2$, $\mu_{\rm gig}^2$, $\mu_{\rm fif}^2$, and $\mu_{\rm fnf}^2$ can be set on the basis of the actual system, and here we set 1:1:1:1. The femtosecond laser pulse has the Gaussian shape with the central frequency of 12500 cm^{-1} and the pulse duration of 80 fs.

As can be seen, for the transform-limited (TL) femtosecond laser field (i.e., $\phi(\omega) = 0$), the two-photon transition amplitude $A_{\rm f}^{(2)}$ is an imaginary quantity (see Eq. (1)), while four-photon transition amplitude $A_{\rm f}^{(4)}$ is a complex quantity, where the on-resonant part $A_{\rm f}^{(4){\rm on-res}}$ is real (see Eq. (4)), and the near-resonant part $A_{\rm f}^{(4){\rm near-res}}$ is imaginary (see Eq. (5)). Obviously, the two-photon absorption $A_{\rm f}^{(2)}$ and the near-resonant four-photon absorption $A_{\rm f}^{(4){\rm near-res}}$ can occur with destructive or constructive interference. Moreover, δ is the detuning from the excited state $|f\rangle$ (or ground state $|g\rangle$) (see Eq. (5)), and

thus the femtosecond laser center frequency will determine the sign of the near-resonant four-photon part $A_f^{(4)near-res}$. When the signs of two-photon absorption $A_f^{(2)}$ and the near-resonant four-photon absorption $A_f^{(4)near-res}$ are opposite, the destructive interference between two-photon and four-photon excitation pathways can occur, and *vice versa*. Furthermore, it can be seen that the second-order term $A_f^{(2)}$ is proportional to $|E_0|^2$ (see Eq. (1)), while the fourth-order term $A_f^{(4)}$ is proportional to $|E_0|^4$ (see Eqs. (3)–(5)), and therefore the relative weight of the four-photon absorption contribution in the whole excitation process will increase with the increase of the femtosecond laser intensity.

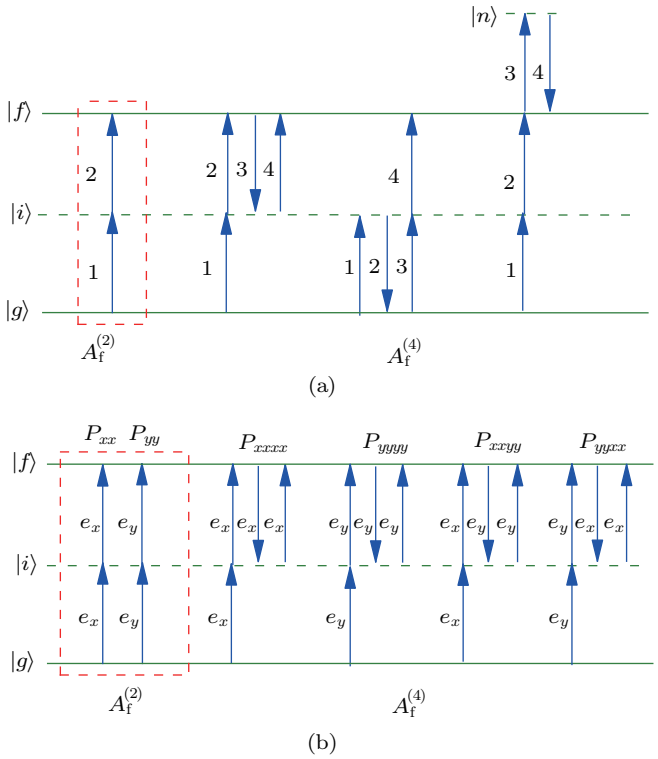


Fig. 1. (color online) (a) The non-resonant two-photon and four-photon transition processes in the two energy level system. (b) The possible excitation pathways of non-resonant two-photon and on-resonant four-photon transition under the polarization modulated femtosecond laser field.

3. Results and discussion

In order to show the influence of femtosecond laser center frequency on the interference between two-photon and four-photon excitation pathways, we theoretically calculate the transition amplitude of non-resonant two-photon and near-resonant four-photon part (i.e., $A_f^{(2)}$ and $A_f^{(4)near-res}$) by varying the femtosecond laser center frequency with the laser intensity of 1×10^{11} W/cm^2, and the calculated results are shown in Fig. 2. Obviously, when the femtosecond laser center frequency is changed from 12300 cm^{-1} to 12500 cm^{-1}, the signs of non-resonant two-photon (blue dashed line) and near-resonant four-photon absorption amplitude (red dotted line) are opposite, and therefore can induce a destructive interference. However, their signs are the same for the laser center frequency changing from 12500 cm^{-1} to 12700 cm^{-1}, and thus can create a constructive interference between two-photon and four-photon transition pathways. Therefore, the femtosecond laser center frequency modulation can provide a feasible scheme to manipulate the constructive or destructive interference of the two-photon and four-photon transitions, and finally affect the excited state absorption.

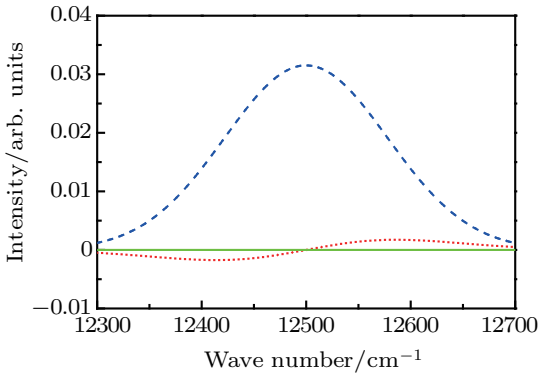


Fig. 2. (color online) The transition amplitude of non-resonant two-photon (blue dashed line) and near-resonant four-photon part (red dotted line) by varying the laser center frequency with the femtosecond laser field intensity of 1×10^{11} W/cm^2, together with a horizontal line (green solid line) equaling to 0.

Previous studies have shown that the femtosecond laser polarization is a well-established tool to control the multi-photon absorption. Here, we apply the femtosecond laser polarization strategy to our theoretical model. In experiment, the laser polarization modulation was usually obtained by propagating a linearly polarized laser field through a quarter wave ($\lambda/4$) plate. Mathematically, the polarization modulated femtosecond laser field in the space can be decomposed into two orthogonal directions (i.e., e_x and e_y), and is given by

$$E_{\lambda/4}(t) = \cos(\theta)E(t)e_x + \sin(\theta)E(t)e_y, \tag{7}$$

where θ is the angle between the input laser polarization direction and the optical axis of the quarter wave plate. One can verify that the output laser is linear polarization for $\theta = m\pi/2$ ($m = 0,1,2\ldots$), circular polarization for $\theta = (2m+1)\pi/4$, and elliptical polarization for other angle θ. Figure 1(b) shows the possible excitation pathways of non-resonant two-photon and one of on-resonant four-photon transition processes excited by the polarization modulated femtosecond laser field. In the non-resonant two-photon transition process, the two photons should come from the same polarization direction (e.g., e_xe_x and e_ye_y). However, the four photons in the on-resonant four-photon transition process can come from different polarization directions (e.g., $e_xe_xe_ye_y$ and $e_ye_ye_xe_x$,) or the same polarization direction (e.g., $e_xe_xe_xe_x$ and $e_ye_ye_ye_y$), but the four photons in the near-resonant four-photon transition process should come from the same polarization direction (e.g., $e_xe_xe_xe_x$ and $e_ye_ye_ye_y$). Therefore, the polarization modulated

femtosecond laser field can induce several different excitation pathways of two-photon and four-photon absorption processes, and the transition amplitudes through these different excitation pathways can be written as

$$P_{xx} = \cos^2(\theta) \times A_{\rm f}^{(2)}, \tag{8}$$

$$P_{yy} = \sin^2(\theta) \times A_{\rm f}^{(2)}, \tag{9}$$

$$P_{xxxx} = \cos^4(\theta) \times A_{\rm f}^{(4)\rm near-res} + \cos^4(\theta) \times A_{\rm f}^{(4)\rm on-res}, \tag{10}$$

$$P_{yyyy} = \sin^4(\theta) \times A_{\rm f}^{(4)\rm near-res} + \sin^4(\theta) \times A_{\rm f}^{(4)\rm on-res}, \tag{11}$$

$$P_{yyxx} = \sin^2(\theta)\cos^2(\theta) \times {\rm A}_{\rm f}^{(4)\rm on-res}, \tag{12}$$

$$P_{xxyy} = \cos^2(\theta)\sin^2(\theta) \times {\rm A}_{\rm f}^{(4)\rm on-res}. \tag{13}$$

As can be seen that all the photons in Eqs. (8) and (10) (or Eqs. (9) and (11)) come from the same horizontal polarization direction (or the perpendicular polarization direction), and thus their excitation pathways can occur with the coherent interference. Therefore, the total transition probability $S_{\rm f}$ under the polarization modulated femtosecond laser field can be expressed as

$$S_{\rm f} = |P_{xx} + P_{xxxx}|^2 + |P_{yy} + P_{yyyy}|^2 + |P_{yyxx}|^2 + |P_{xxyy}|^2. \tag{14}$$

It can be seen that the total transition probability $S_{\rm f}$ includes both the two-photon and four-photon absorption contributions, and the destructive or constructive interference can occur between the two excitation processes (i.e., the two terms $|P_{xx} + P_{xxxx}|^2$ and $|P_{yy} + P_{yyyy}|^2$). Meanwhile, the two-photon and four-photon transition probabilities under the polarization modulated femtosecond laser field can also be respectively written as

$$S_{\rm f}^{(2)} = |P_{xx}|^2 + |P_{yy}|^2, \tag{15}$$

and

$$S_{\rm f}^{(4)} = |P_{xxxx}|^2 + |P_{yyyy}|^2 + |P_{yyxx}|^2 + |P_{xxyy}|^2. \tag{16}$$

One can see from Eqs. (15) and (16) that the two-photon and four-photon transition probability $S_{\rm f}^{(2)}$ and $S_{\rm f}^{(4)}$ are both correlated with the $\lambda/4$ wave plate rotation angle θ. In order to individually observe the polarization control efficiencies of the two-photon and four-photon transitions, we calculate the normalized two-photon and four-photon transition probabilities as the function of the $\lambda/4$ wave plate angle with the laser center frequency of 12500 cm^{-1} and the femtosecond laser field intensity of 1×10^{11} W/cm^2 based on Eqs. (15) and (16), and the simulated results are shown in Fig. 3. All traces are normalized by the TL pulse excitation. As can be seen, when the femtosecond laser polarization is changed from linear through elliptical to circular, both the two transition probabilities $S_{\rm f}^{(2)}$ and $\rm S_{\rm f}^{(4)}$ can be suppressed but not enhanced, and their maximal suppressions occur at the same position with $\theta = (2m+1)\pi/4$. However, the two-photon and four-photon transitions have the different polarization control degrees, and the polarization control efficiency of two-photon absorption is 50%, while that of four-photon absorption can be up to 75%. Here, we define the polarization control efficiency by the function of $\eta = 1 - I^{\rm min}/I^{\rm max}$, and $I^{\rm min}$ and $I^{\rm max}$ are the minimal and maximal transition probabilities.

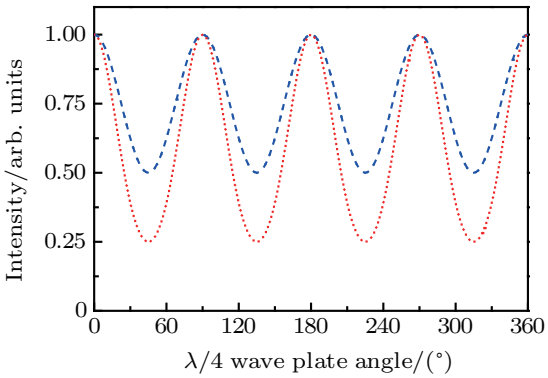


Fig. 3. (color online) The normalized two-photon (blue dashed line) and four-photon transition probability (red dotted line) by varying the quarter-wave plate angle with the laser center frequency of 12500 cm^{-1} and the laser intensity of 1×10^{11} W/cm^2.

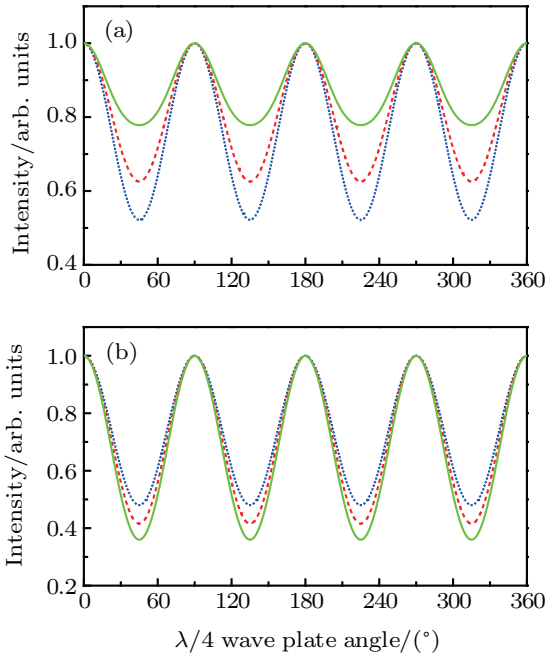


Fig. 4. (color online) The total transition probability by varying the quarter-wave plate angle with the laser intensities of 1×10^{10} (blue dotted lines), 5×10^{10} (red dashed lines), and 1×10^{11} W/cm^2 (green solid lines) and the laser center frequency of 12300 cm^{-1} (a) and 12700 cm^{-1} (b).

As shown above, the two-photon and four-photon transitions can induce the constructive or destructive interference and have the different polarization control degrees, and thus the total polarization control efficiency can be manipulated by properly designing the laser intensity and center frequency. Next, we study the effects of the laser intensity and center frequency on the polarization control efficiency, and the calculated results are shown in Fig. 4 with the laser intensities of

1×10^{10}, 5×10^{10}, and 1×10^{11} W/cm^2 and the laser center frequencies of 12300 cm^{-1} (see Fig. 4(a)) and 12700 cm^{-1} (see Fig. 4(b)). Here, all traces are normalized by the TL pulse excitation. As shown in Fig. 4(a), the polarization control efficiency is decreased with the increase of the laser intensity. The observation can be analyzed as follows: the four-photon absorption contribution increases with the increase of the laser intensity, and the destructive interference of two-photon and four-photon transitions results in the decrease of the polarization control efficiency. As shown in Fig. 4(b), the polarization control efficiency increases with the increase of the laser intensity. Similarly, the observation is attributed to the constructive interference of the two-photon and four-photon transitions. Obviously, by properly designing the femtosecond laser intensity and center frequency, the polarization control efficiency of the multi-photon absorption can be artificially manipulated.

4. Conclusions

In conclusion, we have theoretically constructed a fourth-order perturbation theory model to study the polarization control behaviors of the multi-photon absorption process in a two-level atomic system under the intermediate femtosecond laser field. It was shown that the whole excitation process involves the two-photon and four-photon absorption, and the two excitation processes can occur with the destructive or constructive interference that depends on the laser center frequency. Furthermore, it was also shown that the two-photon and four-photon transitions have the different polarization control efficiencies, and therefore the total polarization control efficiency can be increased or decreased by properly designing the laser intensity and center frequency. These theoretical results are very useful for understanding and controlling the multi-photon absorption process under the intermediate femtosecond laser field, and are also expected to be applied in some related areas, such as up-conversion luminescence and 3D fluorescence imaging.

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