Highly selective population of two excited states in nonresonant two-photon absorption*

Zhang Hui(张 晖), Zhang Shi-An(张诗按)†, and Sun Zhen-Rong(孙真荣)

State Key Laboratory of Precision Spectroscopy and Department of Physics, East China Normal University, Shanghai 200062, China

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A nonresonant two-photon absorption process can be manipulated by tailoring the ultra-short laser pulse. In this paper, we theoretically demonstrate a highly selective population of two excited states in the nonresonant two-photon absorption process by rationally designing a spectral phase distribution. Our results show that one excited state is maximally populated while the other state population is widely tunable from zero to the maximum value. We believe that the theoretical results may play an important role in the selective population of a more complex nonlinear process comprising nonresonant two-photon absorption, such as resonance-mediated (2+1)-three-photon absorption and (2+1)-resonant multiphoton ionization.

Keywords: nonresonant two-photon absorption, selective population, coherent control

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Following its advent, the femtosecond laser has been widely used in various fields, including physics, chemistry, biology and engineering. However, due to its broad-width spectrum, the femtosecond laser brings a new question to the investigation of light-matter interaction, i.e., several excited states falling within the broad spectrum of the femtosecond pulses can be simultaneously excited, thereby resulting in the poor selectivity between neighbouring excited states. It is crucial for the selective population of the specific state to enhance the signal contrast. Fortunately, quantum coherent control by the ultrafast pulse shaping technique provides an excellent method to steer a quantum system toward a desired state by light-matter interaction. In a weak laser field, quantum control is dominated by the interference among different optical pathways connecting the initial and the final states and therefore the challenge is how to induce the instructive or destructive interference among the different pathways by properly constructing a phase distribution. With the development of the ultrafast pulse shaping technique, it is now possible to obtain such a pulse with an almost arbitrary temporal distribution by the amplitude and/or phase modulation in the frequency domain. Recently, a quantum control strategy based on the ultrafast pulse shaping technique, including an open-loop scheme with a simple spectral phase pattern or a closed-loop scheme based on a certain learning algorithm, has been employed to realize the selective population of the specific state in an atom and a molecule,[1−17] such as the selective excitation of femtosecond coherent anti-Stokes Raman scattering,[1−4] the selective population of a dressed state,[5−8] the selective excitation and ionization of a multilevel system in alkali atoms,[9−16] and the selective multiphoton excitation of two distinct electronically and structurally complex dye molecules.[17]

As a typical nonlinear optical effect, the coherent control of the nonresonant two-photon absorption (i.e. a resonant two-photon transition without intermediate state) in an atomic system by shaping the femtosecond laser pulse has been widely investigated in theory and experiment.[18−26] Recently, the selective two-photon excitation at a special excited state has aroused great interest. Präkelt *et al.*[26] demonstrated that maximizing two-photon excitation at a single resonant frequency and simultaneously minimizing it elsewhere can be realized using binary phase

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†Corresponding author. E-mail: sazhang@phy.ecnu.edu.cn

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shaping. In a previous study, the state-selective excitation was usually performed by simultaneously manipulating the two states, and finally one of the states was selectively excited according to their control efficiency. As one state was maximally suppressed or excited, the other state population was fixed. That is to say, the control degree in the state-selective excitation was invariable. However, in this paper, we theoretically demonstrate a highly selective population between two excited states in a nonresonant two-photon absorption process by properly designing the spectral phase shape. Here, one excited state is maximally populated while the other state population is widely tunable from zero to a maximum value.

The weak interaction of the laser field $E(t)$ with a three-level atomic system is schematically shown in Fig. 1, where $|g\rangle$ and $|f_i\rangle$ $(i = 1, 2)$ are the ground and final excited states, respectively. $|g\rangle \rightarrow |f_i\rangle$ is coupled by the laser field $E(t)$ with two-photon excitation and the pulse spectrum is sufficiently broad to cover the two excited states $|f_1\rangle$ and $|f_2\rangle$. We assume that the laser pulse is much shorter than the lifetime of the excited state and that the population is initially in the ground state $|g\rangle$. The two-photon transition (TPT) probability P_{f_i} of the two excited states can be written as[16,18,19]

$$P_{f_i} = \frac{\mu^4_{f_i,g}}{\hbar^4\bar{\omega}^2}\left|\int_{-\infty}^{\infty} E^2(t)\exp(\mathrm{i}\omega_i t)\,\mathrm{d}t\right|^2 = \frac{\mu^4_{f_i,g}}{\hbar^4\bar{\omega}^2}\left|a_{f_i}\right|^2, \quad (1)$$

with

$$a_{f_i} = \int_{-\infty}^{\infty} A\left(\frac{\omega_i}{2}+\Omega\right)A\left(\frac{\omega_i}{2}-\Omega\right) \times \exp\left[\mathrm{i}\left(\Phi\left(\frac{\omega_i}{2}+\Omega\right)+\Phi\left(\frac{\omega_i}{2}-\Omega\right)\right)\right]\mathrm{d}\Omega, \quad (2)$$

where $\mu^2_{f_i,g}$ is the effective nonresonant two-photon dipole coupling for the transition $|g\rangle \rightarrow |f_i\rangle$,[16] $\hbar\bar{\omega}$ is an approximately weighted average energy,[18] a_{f_i} is the amplitude of the excited states $|f_i\rangle$, ω_i is the single-photon transition frequency from $|g\rangle$ to $|f_i\rangle$, and $E(\omega) = A(\omega)\exp[\mathrm{i}\Phi(\omega)]$ is the Fourier transform of $E(t)$, with $A(\omega)$ and $\Phi(\omega)$ being the spectral amplitude and phase, respectively.

As can be seen from Eq. (2), a_{f_i} is the result of coherent summation of all the two-photon pathways and it is a positive value for the photon pairs with the phase relation of $\Phi(\omega_i/2+\Omega)+\Phi(\omega_i/2-\Omega) = 0$ and a negative value for those photon pairs with the phase relation of $\Phi(\omega_i/2+\Omega)+\Phi(\omega_i/2-\Omega) = \pi$. For the transform-limited pulse (i.e., $\Phi(\omega_i/2+\Omega) = \Phi(\omega_i/2-\Omega) = 0$) or the shaped pulse with antisymmetric spectral phase distribution around the two-photon transition frequency $\omega_i/2$ (i.e., $\Phi(\omega_i/2+\Omega) = -\Phi(\omega_i/2-\Omega)$), all two-photon pairs are of positive contribution and therefore P_{f_i} is a maximum. However, other phase distributions can reduce and even eliminate it. A simple method to completely eliminate P_{f_i} is to induce the destructive interference by introducing half-photon pairs with the positive contribution and the others with the negative contribution.

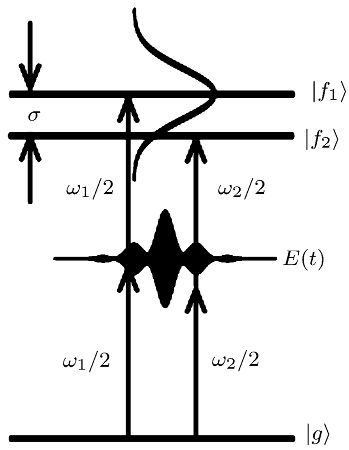

Fig. 1. Schematic diagram of three-energy-level system for nonresonant two-photon absorption, and $|g\rangle \rightarrow |f_1\rangle$ and $|g\rangle \rightarrow |f_2\rangle$ are coupled by laser field $E(t)$. The laser spectrum is broad enough to cover the two excited states, and the population is initially in the ground state $|g\rangle$.

Since the two-photon transition probability is independent of the antisymmetric phase distribution around the two-photon transition frequency, it provides a feasible project to realize the selective population of two excited states in the two-photon transition process. By rationally designing the spectral phase, one excited state is always pumped by the shaped pulse with antisymmetric phase distribution and the other one can be excited by the shaped pulse with various phase distributions. Here, we consider the case where the excited state $|f_1\rangle$ is of selective population and the excited state $|f_2\rangle$ is of suppressive population. In our simulation, the parameters of the model system are set as follows. The laser centre frequency is 12500 cm^{-1} with a spectral bandwidth (FWHM) of 500 cm^{-1}. The single-photon transition frequencies ω_1 and ω_2 from the ground state $|g\rangle$ to the excited states $|f_1\rangle$ and $|f_2\rangle$ are, respectively, 25000 cm^{-1} and 24850 cm^{-1}, and the separation between the two excited states is 150 cm^{-1}. The two effective dipole moments $\mu^2_{f_1,g}$ and $\mu^2_{f_2,g}$ are equal.

We first employ a piecewise phase jump to modulate the laser spectrum as shown in Fig. 2, symbols δ and $\varDelta$ represent the modulation amplitude and each segment spectral width, respectively. Here, each segment spectral width $\varDelta$ is set to be four times of $\omega_1/2-\omega_2/2$, i.e., $\varDelta = 300\ \mathrm{cm}^{-1}$, thus all photon pairs make a positive contribution to a_{f_1} and the photon pairs modulated by the phase, labeled with a solid line, make a positive contribution to a_{f_2}, but those modulated by the phase labeled with a dotted line make a positive or negative contribution, which depends on the modulation amplitude δ. Figure 3 shows P_{f_1} (solid line) and P_{f_2} (dashed line) each as a function of the modulation amplitude δ. All the data are normalized by the population in excites state $|f_1\rangle$ induced by the transform-limited pulse. We note an invariable value in P_{f_1} but a strong variation in P_{f_2}. The P_{f_2} achieves a minimum at the modulation amplitude $\delta = \pi$. That is to say, the shaped pulse at that modulation amplitude induces the two-photon absorption for $|g\rangle \rightarrow |f_2\rangle$ with a destructive instead of a constructive interference.

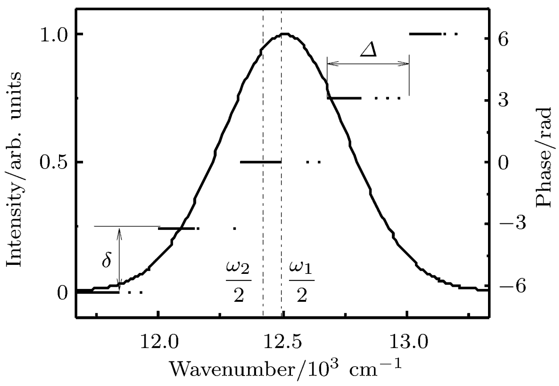

Fig. 2. Schematic diagram of the piecewise phase jump applied to the laser spectrum. δ and $\varDelta$ represent the modulation amplitude and each segment spectral width, respectively. Here, each segment spectral width $\varDelta$ is set to be four times of $\omega_1/2 - \omega_2/2$.

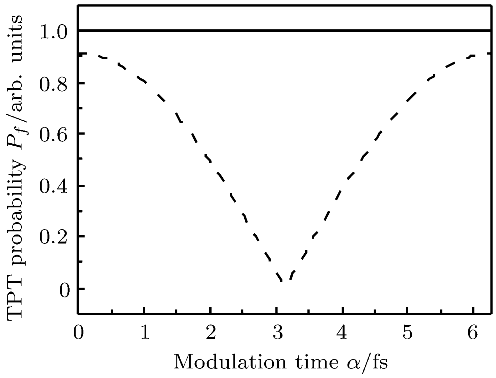

Fig. 3. The TPT probability P_{f_1} (solid line) and P_{f_2} (dashed line) each as a function of modulation amplitude δ.

The shaped pulse with sinusoidal phase modulation is a well-established method in quantum control because it is convenient to obtain the symmetric or antisymmetric phase distribution or the controllable pulse sequences. So it is usually used as a tool to analyse a physical control mechanism or test novel control strategies, such as the control of two-photon transition (TPT) probability[18] and the selective population of dressed state.[5–8] In the present paper, we employ a shaped pulse with sinusoidal phase modulation to study the selective population of the two excited states $|f_1\rangle$ and $|f_2\rangle$ by the two-photon transition as shown in Fig. 4. We set $\varPhi(\omega) = \alpha \sin[\beta(\omega - \omega_1/2)]$, where α is the amplitude of the phase modulation function and β is the frequency of the sinusoidal oscillation. Thus, the spectral phase for $|g\rangle \rightarrow |f_1\rangle$ always has an antisymmetric distribution in controlling α and β, and so it does not change P_{f_1}.

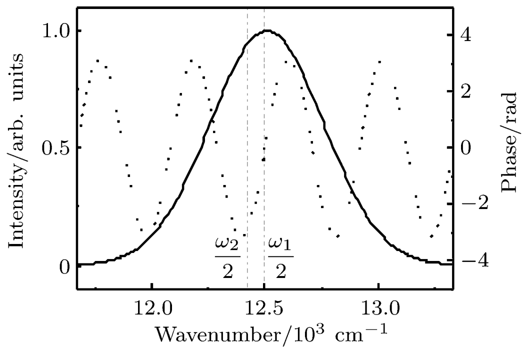

Fig. 4. The schematic diagram of the sinusodial phase modulation ($\varPhi(\omega) = \alpha \sin[\beta(\omega - \omega_1/2)]$) applied to the laser spectrum, where α is the amplitude of the phase modulation function, and β is the frequency of the sinusoidal oscillation.

Figure 5 shows P_{f_1} (solid line) and P_{f_2} (dashed line) each as a function of the modulation time β for $\alpha = \pi$ (Fig. 5(a)) and the modulation amplitude α for $\beta = 80$ fs (Fig. 5(b)). All the data are also normalized by the population in excite state $|f_1\rangle$ excited by the transform-limited pulse. As can be seen, controlling α and β does not change P_{f_1} but does enormously affect P_{f_2}. With the increase of the modulation time β, the P_{f_2} is periodically modulated and can be continuously tuned from zero to a maximum value. The zero P_{f_2} corresponds to the dark pulse that induces a destructive interference in the different two-photon pathways. The maximal P_{f_2} results from the shaped pulse with the antisymmetric phase distribution around $\omega_2/2$. As the modulation amplitude α increases, P_{f_2} reduces, accompanied by oscillation, and it is completely eliminated at some values of α.

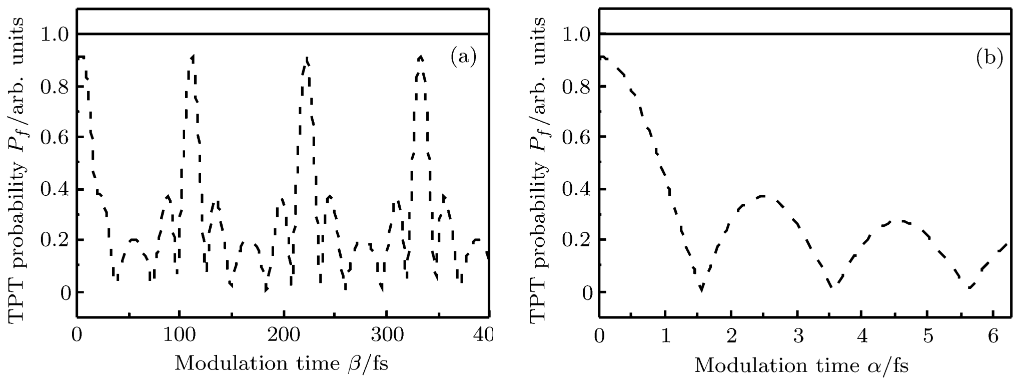

Fig. 5. The TPT probabilities P_{f_1} (solid line) and P_{f_2} (dashed line) each as a function of the modulation time β for $\alpha = \pi$ (a) and the modulation amplitude α for $\beta = 80$ fs (b).

The α value for the first disappearance of the P_{f_2} depends on the separation of the excited state $|f_2\rangle$ from the excited state $|f_1\rangle$ and a larger separation results in a smaller α value. Based on the above observation and analysis, we can conclude that by manipulating the modulation amplitude α or the modulation time β, the shaped pulse is always optimal for the P_{f_1} but can completely eliminate the P_{f_2} or reconstruct it as that obtained by the transform-limited pulse.

In summary, we theoretically demonstrated a highly selective population of two excited states in a nonresonant two-photon absorption process based on the invariance of two-photon transition probability to the antisymmetric phase distribution around the two-photon transition frequency. By properly designing the spectral phase shape of the exciting pulse, one excited state is maximally populated while other state populations can be continuously tuned from zero to a maximum value. These schemes can be applied iteratively to the selective population of multiple excited states once the excited states are identified.

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