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Manipulation of Resonance-Enhanced Multiphoton-Ionization Photoelectron Spectroscopy by Two Time-Delayed Femtosecond Laser Pulses *

LU Chen-Hui(卢晨晖), ZHANG Shi-An(张诗按)**, SUN Zhen-Rong(孙真荣)

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

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We theoretically demonstrate that the (2+1) resonance-enhanced multiphoton-ionization (REMPI) photoelectron spectrum in a cesium (Cs) atom can be effectively manipulated by two time-delayed femtosecond laser pulses, involving its photoelectron spectral structure and photoelectron energy. We show that the photoelectron spectrum exhibits interference fringes and the fringe spacing is determined by the time delay of the two laser pulses, and the photoelectron energy is periodically modulated and the modulation period is determined by the two-photon transition frequency of the excited state. Finally, we utilize the power spectrum of the two time-delayed laser pulses and the two-photon transition probability of the excited state to respectively explain the modulations of the photoelectron spectrum and photoelectron energy.

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Quantum coherent control by shaping the femtosecond laser pulse opens up a new opportunity to manipulate photophysical, photochemical and photobiological processes because of its ability to exert microscopic control on quantum systems, which is implemented by the quantum interference of different excitation pathways connecting the initial state and the desired final state via the spectral phase and/or amplitude modulation in frequency domain or the pulse trains.[1–4] Nowadays, the quantum control strategy has been successfully applied in the control of various nonlinear optical processes, such as resonant or non-resonant multiphoton absorption,[5–8] high-harmonic generation,[9] coherent anti-Stokes Raman scattering spectroscopy,[10–14] photoionization and photodissociation,[15–18] and so on.

Resonance-enhanced multiphoton-ionization (REMPI) photoelectron spectroscopy has been proven to be a well-established tool to characterize the excited state structure and to study the photoionization and photodissociation dynamical processes.[19–28] However, femtosecond-induced REMPI photoelectron spectroscopy suffers from poor spectral resolution because of its broad spectral bandwidth. Recently, the femtosecond pulse-shaping technique has shown an excellent method to control the REMPI photoelectron spectrum and to achieve the valuable information from the modulated photoelectron spectrum.[29–37] For example, Wollenhaupt *et al.* realized the selective excitation of the slow and fast photoelectrons in the REMPI photoelectron spectrum by a sinusoidal, chirped or jumped phase modulation and obtained the selective population of the dressed states.[29–33] We realized the narrowing of the REMPI photoelectron spectrum by cubic or π phase modulation and obtained the fine structure of the excited states.[34–37] However, in this study we propose two time-delayed femtosecond laser pulses to manipulate the (2+1) REMPI photoelectron spectrum in Cs atoms. The Cs atom is a ideal model system that was widely used to study the quantum coherent control in various nonlinear optical processes,[38–40] where the physical dynamics can be well analyzed on the basis of theoretical evaluation, and thus more complicated quantum systems may become controllable and understandable. It is shown that the two time-delayed laser pulses can induce an interference fringe structure in the photoelectron spectrum and the fringe spacing is determined by the time delay of the two laser pulses. It is also shown that the photoelectron energy can be periodically modulated by varying the time delay of the two laser pulses and the modulation period is determined by the two-photon transition frequency of the excited state. Finally, the power spectrum of the two time-delayed laser pulses and the two-photon transition probability of the excited state are used to explain the modulations of the photoelectron spectrum and photoelectron energy, respectively.

Figure 1 shows the schematic diagram of the (2+1) resonance-enhanced multiphoton-ionization process in the Cs atom induced by two time-delayed femtosecond laser pulses with $E(t) = E_A(t) + E_A(t - T_d)$. Here the transition from the ground state $6s$ to the excited state $7d$ is excited by non-resonant two-photon absorption, and finally the populations in the excited state $7d$ are ionized by single-photon absorption. We assume that only the ground state $6s$ is initially populated and the laser pulse duration is much smaller than the lifetime of the excited state $7d$. Based on Wollenhaupt's theory,[29–33] the (2+1) REMPI photoelectron spectrum can be approximated to

$$P^{(2+1)}(E_v) \propto \int_{-\infty}^{+\infty} E(t) C_{7d}(t) \exp\left[\frac{i(E_v + E_I - E_{7d})}{\hbar}\right] dt, \quad (1)$$

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**Corresponding author. Email: sazhang@phy.ecnu.edu.cn

where $E_{\rm I}$ is the ionization energy from the ground state $6s$, E_{7d} is the eigenenergy of the excited state $7d$, and $C_{7d}(t)$ is the time-dependent probability amplitude in the excited state $7d$, which can be obtained by the second-order time-dependent perturbation theory,[40] and given by

$$C_{7d}(t) \propto \int_{-\infty}^{+\infty} [E(t)]^2 \exp(i\omega_{7d}t')dt', \qquad (2)$$

where ω_{7d} is the transition frequency from the ground state $6s$ to the excited state $7d$. By transforming Eq. (1) into the frequency domain, $P^{(2+1)}(E_v)$ can be further written as

$$P^{(2+1)}(E_v) \propto |A^{(2+1)}_{\rm on-res}(E_v) + A^{(2+1)}_{\rm near-res}(E_v)|^2, \qquad (3)$$

where $A^{(2+1)}_{\rm on-res}(E_v)$ and $A^{(2+1)}_{\rm near-res}(E_v)$ represent the on- and near-resonant components, respectively, and are given by

$$A^{(2+1)}_{\rm on-res}(E_v) = i\pi E\Big[\frac{E_v + E_{\rm I}}{\hbar} - \omega_{7d}\Big] S^{(2)}(\omega_{7d}), \qquad (4)$$

$$A^{(2+1)}_{\rm near-res}(E_v) = -\wp \int_{-\infty}^{+\infty} \frac{1}{\Delta} E\Big[\frac{E_v + E_{\rm I}}{\hbar} - \omega_{7d} - \Delta\Big] \times S^{(2)}(\omega_{7d} + \Delta)d\Delta, \qquad (5)$$

with

$$S^{(2)}(\Omega) = \int_{-\infty}^{+\infty} E(\omega)E(\Omega - \omega)d\omega, \qquad (6)$$

where $E(\omega)$ is the Fourier transform of $E(t)$ with $E(\omega) = A(\omega)\exp[i\Phi(\omega)]$, and $A(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and phase in the frequency domain, respectively; $\wp$ is Cauchy's principal value operator and Δ is the detuning of the non-resonant two-photon absorption. The on-resonant term $A^{(2+1)}_{\rm on-res}(E_v)$ interferes all on-resonant three-photon excitation pathways ($\Delta = 0$) with the frequencies of ω, $\omega_{7d} - \omega$ and $[(E_v + E_{\rm I})/\hbar] - \omega_{7d}$, while the near-resonant term $A^{(2+1)}_{\rm near-res}(E_v)$ interferes all other near-resonant three-photon excitation pathways ($\Delta \neq 0$) with the frequencies of ω, $\omega_{7d} - \omega + \Delta$ and $[(E_v + E_{\rm I})/\hbar] - \omega_{7d} - \Delta$. The different excitation pathways of on- and near-resonant three-photon ionization processes are presented in Fig. 1. Therefore, $P^{(2+1)}(E_v)$ is the result of both the inter- and intra-group interferences involving on- and near-resonant three-photon excitation pathways (see Eq. (3)).

In our simulation, the transition frequency from the ground state $6s$ to the excited state $7d$ in the Cs atom is $\omega_{7d} = 26058\,{\rm cm}^{-1}$, and the ionization energy is $E_{\rm I} = 3.89\,{\rm eV}$, corresponding to the frequency of $31375\,{\rm cm}^{-1}$. The laser central frequency is set to be $\omega_L = \omega_{7d}/2 = 13029\,{\rm cm}^{-1}$, and the laser pulse duration is set to be $\tau = 30\,{\rm fs}$. Figure 2 shows the (2+1) REMPI photoelectron spectra induced by the two laser pulses with the time delay of $T_d = 0$ (a), 100 (b), 200 (c) and 300 fs (d) calculated from Eq. (3). As can be seen, when the two laser pulses are separated, the photoelectron spectrum is strongly modulated, which exhibits the interference fringes, and the fringe spacing decreases with the increase of the time delay of the two laser pulses. It can be found that the fringe spacing Ω and the time delay T_d satisfy the relation $\Omega = 2\pi\hbar/T_d$, which has been authenticated in terms of the final state interference of free electron wavepackets.[41]

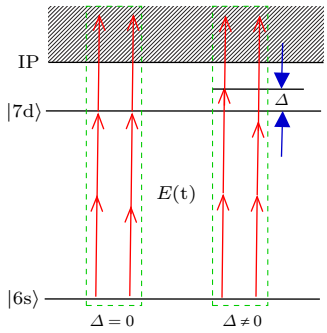

Fig. 1. (Color online) The schematic diagram of the (2 + 1) resonance-enhanced multiphoton-ionization process in the Cs atom induced by two time-delayed laser pulses with $E(\omega) = {\rm FFT}[E_A(t) + E_A(t - T_d)]$.

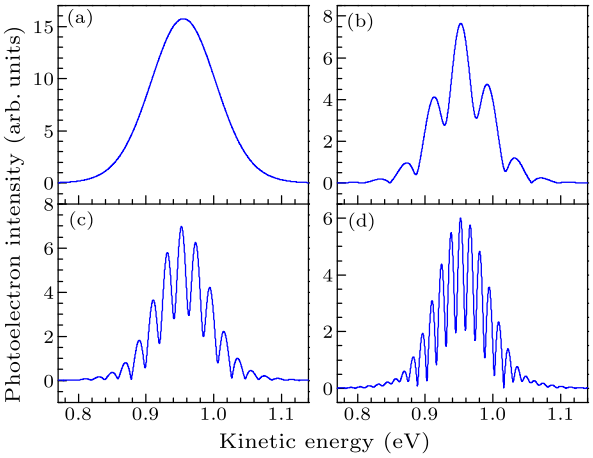

Fig. 2. (Color online) The (2 + 1) REMPI photoelectron spectra induced by the two laser pulses with the time delay of $T_d = 0$ (a), 100 (b), 200 (c) and 300 fs (d).

The photoelectron energy can directly reflect the multiphoton ionization efficiency, and therefore we demonstrate the control of the photoelectron energy by varying the time delay of the two laser pulses. Figure 3 presents the photoelectron energy E_p as the function of the time delay T_d of the two laser pulses (a), together with the extend views at small (b) and large (c) time delays. All data are normalized so that a single laser pulse generates a unity signal. Here, the photoelectron energy is obtained by $E_p = \int_0^{+\infty} |P^{(2+1)}(E_v)|^2 dE_v$. As can be seen, the photoelectron energy E_p is periodically modulated with the increase of time delay T_d, but the modulation period is different at small and large time delays. The modulation period is 2.66 fs at the small time delays (see Fig. 2(b)), corresponding to $2/\omega_{7d}$,

and is 1.33 fs at large time delays (see Fig. 2(c)), corresponding to $1/\omega_{7d}$. Since the modulation period is determined by the transition frequency ω_{7d}, it can provide a well-established method to study the excited state structure. Moreover, one can see that the photoelectron energy E_p can be enhanced or suppressed at small time delays, while can be enhanced but not suppressed at large time delays. That is to say, the photoelectron energy E_p induced by a laser pulse can be enhanced or suppressed by applying another time-delayed laser pulse. Actually, this modulation of the photoelectron energy E_p can be intuitively explained as follows. When the two laser pulses are overlapped at small time delays, the optical contribution is dominant because of the optical interference. When the two laser pulses are completely separated at large time delays, the optical contribution will disappear, and only quantum contribution occurs because of the quantum interference that is generated by the constructive or destructive interference between the two different optical pathways induced by the two time-delayed laser pulses.

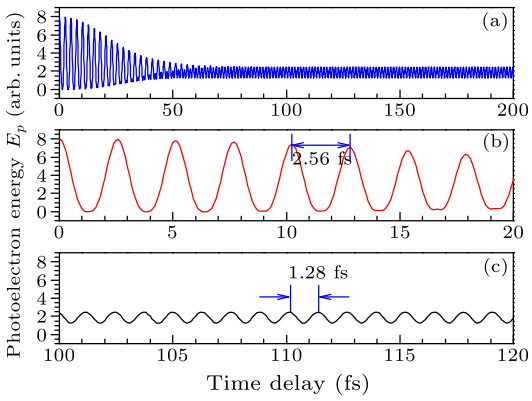

Fig. 3. (Color online) The photoelectron energy E_p as a function of the time delay T_d of the two laser pulses (a), together with the extended views at small (b) and large (c) time delays.

The power spectrum of the modulated laser field can provide a good method to explain the control mechanism of the REMPI photoelectron spectral modulation.[34,35] Here, we also utilize the power spectrum of the two time-delayed laser pulses to explain the interference fringes of the photoelectron spectrum in Fig. 2. Figure 4 presents the power spectrum of the two laser pulses $E(\omega)$ with the time delay of $T_d = 0$ (a), 100 (b), 200 (c) and 300 fs (d). Here the power spectrum of the two time-delayed laser pulses $E(\omega)$ is obtained by the Fourier transform with $E(\omega) = \mathrm{FFT}[E_A(t) + E_A(t - T_d)]$. One can see that the power spectrum $E(\omega)$ also exhibits the interference fringes when the two laser pulses are separated, and the fringe spacing also decreases with the increase in the time delay T_d. This evolution behavior is the same as the photoelectron spectrum in Fig. 2, and the fringe numbers for the power spectrum and photoelectron energy are equal at the same time delay T_d. Obviously, the power spectrum of the two time-delayed laser pulses can well explain the modulation of the photoelectron spectrum in Fig. 2.

Since the photoelectron energy E_p depends on the populations in the excited state $7d$, as shown in Eq. (1), we use the two-photon transition probability S_{7d} of the excited state $7d$ to explain the modulation of the photoelectron energy in Fig. 3. Her the two-photon transition probability S_{7d} is obtained by

$$S_{7d} = |C_{7d}(t \to \infty)|^2. \tag{7}$$

The two-photon transition probability amplitude C_{7d} can be separately described by the optical and quantum contributions, the optical contribution is due to the optical interference when the two laser pulses are overlapped, and the quantum contribution is attributed to the quantum interference when the two laser pulses are separated. Thus, the two-photon transition probability S_{7d} can be further approximated to

$$S_{7d} \propto |C_{7d}^{\mathrm{opt}}(T_d) + C_{7d}^{\mathrm{qum}}(T_d)|^2, \tag{8}$$

with

$$C_{7d}^{\mathrm{opt}}(T_d) = 2\exp\left[\frac{-T_d^2}{2\tau^2}\right]\exp\left(-\frac{i\omega_{7d}T_d}{2}\right), \tag{9}$$

$$C_{7d}^{\mathrm{qum}}(T_d) = 1 + \exp(-i\omega_{7d}T_d), \tag{10}$$

where $C_{7d}^{\mathrm{opt}}(T_d)$ and $C_{7d}^{\mathrm{qum}}(T_d)$ represent the optical and the quantum contributions, respectively. It is easy to verify from Eq. (9) that the optical contribution $C_{7d}^{\mathrm{opt}}(T_d)$ will disappear when the two time-delayed laser pulses are completely separated, and thus Eq. (8) can be further simplified at small and large time delays, and written as

$$S_{7d}(T_d \ll \tau) \propto 4 \times [1 + \cos(\omega_{7d}T_d/2)]^2, \tag{11}$$

$$S_{7d}(T_d \gg \tau) \propto 2 \times [1 + \cos(\omega_{7d}T_d)]. \tag{12}$$

One can see from Eqs. (11) and (12) that the two-photon transition probability S_{7d} is periodically modulated by varying the time delay T_d, and the modulation period is $2/\omega_{7d}$ at small time delays (i.e., $T_d \ll \tau$) and $1/\omega_{7d}$ at large time delays (i.e., $T_d \gg \tau$). Figure 5 presents the two-photon transition probability S_{7d} as a function of the time delay T_d of the two laser pulses calculated from Eq. (7) (a), together with the extend views at small (b) and large (c) time delays. Similarly, the two-photon transition probability S_{7d} also shows the periodical modulation with the increase in the time delay of the two laser pulses, and the modulation period is 2.56 fs (i.e., $2/\omega_{7d}$) at small time delays (see Fig. 5(b)) and 1.28 fs (i.e., $1/\omega_{7d}$) at large time delays (see Fig. 5(c)). This result is consistent with the above theoretical prediction in Eqs. (11) and (12), and is the same as the modulation of the photoelectron energy in Fig. 3. This further confirmes that the photoelectron energy modulation should result from the variation of the two-photon transition probability S_{7d} in the excited state $7d$.

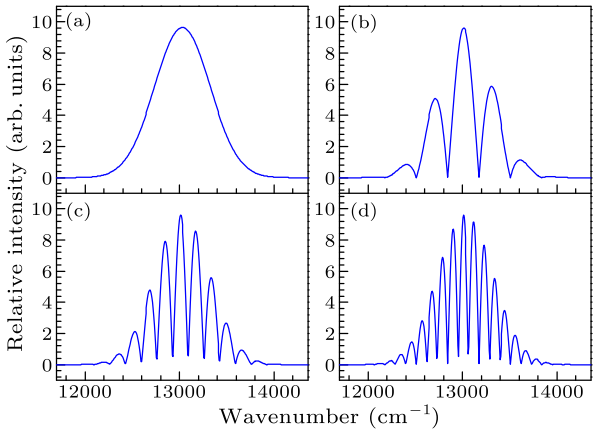

Fig. 4. (Color online) The power spectrum of the two laser pulses with the time delay of $T_d = 0$ (a), 100 (b), 200 (c) and 300 fs (d).

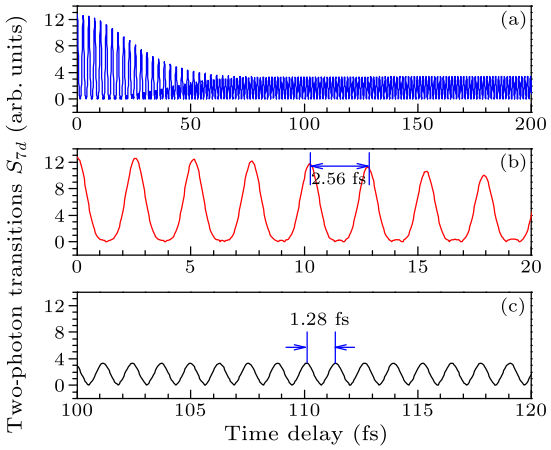

Fig. 5. (Color online) The two-photon transition probability S_{7d} as a function of the time delay T_d of the two laser pulses (a), together with the extended views at small (b) and large (c) time delays.

In summary, we have theoretically shown the manipulation of the (2+1) REMPI photoelectron spectrum in the Cs atom by two time-delayed femtosecond laser pulses. Our results show that the photoelectron spectrum exhibits interference fringes and its fringe spacing is determined by the time delay of the two laser pulses, the photoelectron energy is periodically modulated and the modulation period is determined by the two-photon transition frequency. Furthermore, the modulations of the photoelectron spectrum and photoelectron energy are well explained by the power spectrum of the two time-delayed laser pulses and the two-photon transition probability. We believe that these results provide a scheme to control and explain the REMPI photoelectron spectrum, involving its photoelectron spectral structure and photoelectron energy.

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