Resonance-enhanced multiphoton-ionization photoelectron spectroscopy by a rectangular amplitude modulation

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In this Brief Report, we present a scheme to control the $(2+1)$ resonance-enhanced multiphoton-ionization (REMPI) photoelectron spectrum in cesium (Cs) atom by shaping the femtosecond laser pulse with a rectangular amplitude modulation. We show that the amplitude-shaped laser pulse can induce a hole in the $(2+1)$ REMPI photoelectron spectrum, and the position and width of the hole depend on the amplitude step position and amplitude modulation width. We also show that a high-resolution REMPI photoelectron spectrum and the fine energy-level structure of the excited states can be obtained by observing the holes in the $(2+1)$ REMPI photoelectron spectrum. We believe that these theoretical results can provide a feasible method to study the excited-state or Rydberg-state structure and the laser-induced photoionization dynamics.

With the advent of the ultrafast pulse shaping technique, now such a shaped laser pulse with almost arbitrary temporal distribution can be achieved by tailoring the femtosecond laser pulse in the frequency domain with a phase and/or amplitude modulation [1]. The coherent control strategy making use of the shaped femtosecond laser pulse, which is dominated by a constructive or destructive interference of different excitation pathways connecting the initial and final target states, has been successfully applied to controlling various nonlinear optical effects [2–11], such as two-photon absorption [2,3], coherent anti-Stokes Raman scattering [4,5], photoionization and photodissociation [6–8], molecular alignment and orientation [9,10], harmonic-order generation [11], and so on. The predesigned laser pulse can be favorable for a desired result for the simple quantum system and simple excitation processes [2–5,8–10], and the adaptive pulse shaping with learning algorithms is the dominant methodology in the cases of higher complexity [6,7,11].

Resonance-enhanced multiphoton-ionization (REMPI) photoelectron spectroscopy has been proven to be a well-established method to study the excited-state or Rydberg-state structure and the photoionization or photodissociation dynamical process [12–18]. The femtosecond laser pulse is an excellent tool to create the REMPI photoelectron spectroscopy because of its broad laser spectrum and high pulse intensity, while a main drawback for the femtosecond-induced REMPI photoelectron spectroscopy is low spectral resolution due to the broadband photoelectron spectrum. Recently, various methods by the femtosecond pulse shaping technique were proposed to narrow the REMPI photoelectron spectrum [19–27]. For example, Wollenhaupt *et al.* showed that the REMPI photoelectron spectrum in potassium (K) atom can be narrowed by the selective excitation of the slow and fast photoelectrons using a sinusoidal, chirped, or

phase-step modulation [19–23]. We showed that the REMPI photoelectron spectrum in cesium (Cs), sodium (Na), and K atoms can be tremendously narrowed by a cubic or π phase modulation [24–27]. These previous works aim to improve the spectral resolution by narrowing the photoelectron spectrum by the spectral phase modulation. However, in this Brief Report we propose a scheme to improve the spectral resolution by a spectral amplitude modulation. Our results show that, by a rectangular amplitude modulation, the $(2+1)$ REMPI photoelectron spectrum in Cs atom cannot be tremendously narrowed, but a hole in the $(2+1)$ REMPI photoelectron spectrum is created, and its position and width are correlated with the amplitude step position and amplitude modulation width; thus a high-resolution $(2+1)$ REMPI photoelectron spectrum and the fine energy-level structure of the excited states can be obtained by observing the holes in the $(2+1)$ REMPI photoelectron spectrum.

The schematic diagram of the $(2+1)$ resonance-enhanced multiphoton-ionization process in Cs atom induced by the femtosecond laser pulse $E(t)$ is shown in Fig. 1(a); here the transition from the ground state $6s$ to the excited state $7d$ is coupled by a nonresonant two-photon absorption, and the populations in the excited state $7d$ are ionized by a single-photon absorption. We consider this case 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 [19–23], the $(2+1)$ REMPI photoelectron spectrum can be approximated as

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

(1)

where E_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 second-order time-dependent

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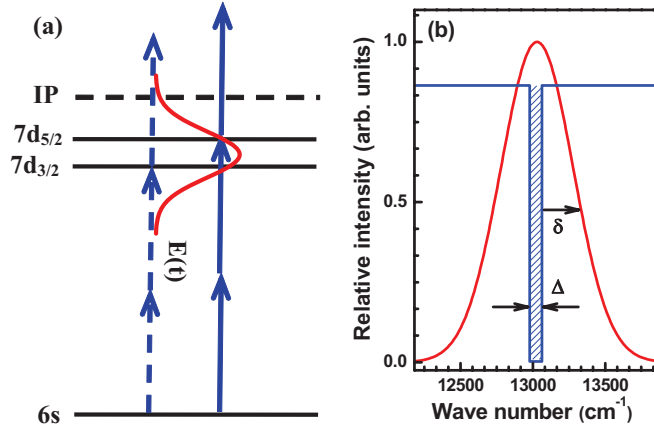†zrsun@phy.ecnu.edu.cn

FIG. 1. (Color online) (a) The schematic diagram of the $(2+1)$ resonance-enhanced multiphoton-ionization process in Cs atom. (b) The laser spectrum modulated by a rectangular amplitude modulation, where these frequency components in the window are cut off while those out of the window are preserved.

perturbation theory [28], and is given by

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

where ω_{7d} is the transition frequency from the ground state $6s$ to the excited state $7d$.

The spectral phase modulation, such as sinusoidal, chirped, cubic, or π function, has been proven to be enormously successful in controlling the REMPI photoelectron spectroscopy [19–27]. Here, we use a rectangular amplitude modulation to control the $(2+1)$ REMPI photoelectron spectroscopy, and the simple amplitude modulation is shown in Fig. 1(b), where δ and Δ represent the amplitude step position and amplitude modulation width, respectively. The amplitude-shaped laser pulse in the frequency domain can be written as $E_{\text{mod}}(\omega) = E(\omega) \times A(\omega)$, where $E(\omega)$ is the unshaped laser pulse in the frequency domain, and $A(\omega)$ is the amplitude modulation function with $A(\omega) = 1 - \text{rect}[(\omega - \delta)/\Delta]$; here $\text{rect}[(\omega - \delta)/\Delta]$ is 1 for $|\omega - \delta| < \Delta/2$, 1/2 for $|\omega - \delta| = \Delta/2$, and 0 for $|\omega - \delta| > \Delta/2$. Thus, by the rectangular amplitude modulation, these frequency components in the rectangular widow are cut off while those out of the window are preserved. In our simulation, with Cs atom as our study model, the transition frequencies from the ground state ω_{7d} to the excited states $7d_{3/2}$ and $7d_{5/2}$ are $\omega_{7d_{3/2}} = 26\,048$ cm^{-1} and $\omega_{7d_{5/2}} = 26\,068$ cm^{-1}, and the ionization energy is $E_I = 3.89$ eV, corresponding to the frequency of $31\,375$ cm^{-1}. The laser central frequency is set to be $\omega_L = 13\,029$ cm^{-1}; thus its two-photon frequency (i.e., $2\omega_L$) is in the middle of the two transition frequencies $\omega_{7d_{3/2}}$ and $\omega_{7d_{5/2}}$, and the laser pulse duration is set to be $\tau = 50$ fs.

We first study the effect of the amplitude modulation width Δ on the $(2+1)$ REMPI photoelectron spectrum. Figure 2 presents the $(2+1)$ REMPI photoelectron spectra only through the excited state $7d_{3/2}$ induced by the shaped laser pulse with the amplitude step position $\delta = 13\,029$ cm^{-1} for the amplitude modulation width $\Delta = 5$ (red solid line), 20 (green dashed line), and 50 cm^{-1} (blue dotted line). As can be seen,
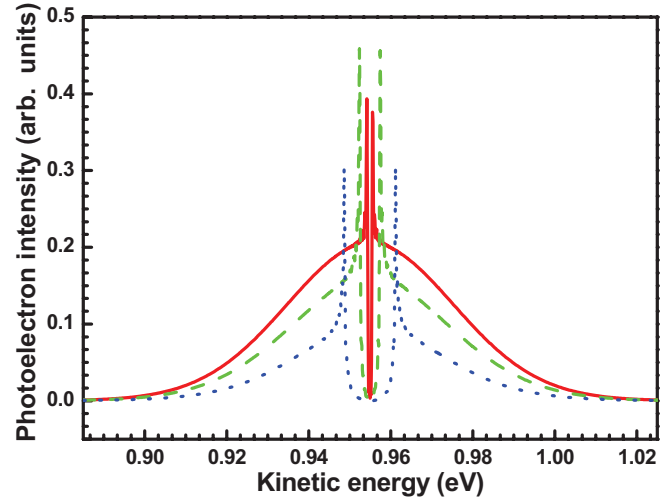

FIG. 2. (Color online) The $(2+1)$ REMPI photoelectron spectra only through the excited state $7d_{3/2}$ induced by the shaped laser pulse with the amplitude step position $\delta = 13\,029$ cm^{-1} for the amplitude modulation width $\Delta = 5$ (red solid line), 20 (green dashed line), and 50 cm^{-1} (blue dotted line).

the photoelectron spectrum can be strongly modulated by the simple amplitude modulation, and a hole and two peaks around the hole are observed. The photoelectron intensities at the two peaks can be greatly enhanced, and this result is similar to that obtained by the π phase-step modulation [24,26]. However, the photoelectron intensity at the hole is completely suppressed, and the width of the hole depends on the amplitude modulation width Δ, which decreases with the decrease of the amplitude modulation width Δ. Thus, a very narrow hole can be obtained by applying a small amplitude modulation width Δ, and the width (the full width at half depth) is only ~ 0.9 meV for the amplitude modulation width $\Delta = 5$ cm^{-1}.

Next we show the $(2+1)$ REMPI photoelectron spectral modulation by varying the amplitude step position δ. Figure 3 presents the $(2+1)$ REMPI photoelectron spectra only through the excited state $7d_{3/2}$ induced by the shaped laser pulse with the amplitude modulation width $\Delta = 5$ cm^{-1} for the amplitude step position $\delta = 12\,979$ (red solid line), $13\,029$ (green dashed line), and $13\,079$ cm^{-1} (blue dotted line). One can see that these holes for the amplitude step positions $\delta = 12\,979, 13\,029$, and $13\,079$ cm^{-1} occur at the kinetic energies of $E_v = 0.9492, 0.9554$, and 0.9618 eV, respectively. Obviously, the positions of these holes for different amplitude step positions δ are obtained at different kinetic energies E_v, but the energy difference between the photon energy at this amplitude step position (i.e., E_δ) and the kinetic energy corresponding to the hole (i.e., E_v^{hole}) is a fixed value, which is just equal to the ionization energy from the excited state $7d_{3/2}$ (i.e., $E_I^{7d_{3/2}}$), where $E_I^{7d_{3/2}} = E_I - E_{7d_{3/2}}$. That is to say, the four parameters, the eigenenergy of the excited state $7d_{3/2}$ $E_{7d_{3/2}}$, the photon energy at the amplitude step position E_δ, the ionization energy from the ground state $6s$ E_I, and the kinetic energy corresponding to the hole E_v^{hole}, exist in the relation of

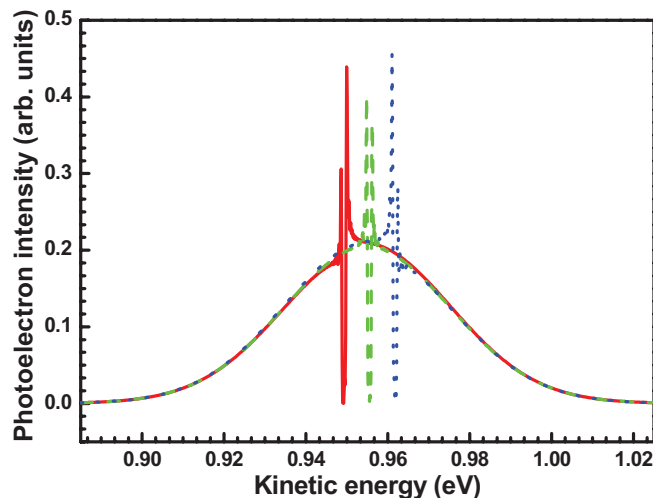$$E_{7d_{3/2}} + E_\delta = E_I + E_v^{\text{hole}}. \qquad (3)$$

FIG. 3. (Color online) The $(2+1)$ REMPI photoelectron spectra only through the excited state $7d_{3/2}$ induced by the shaped laser pulse with the amplitude modulation width $\Delta = 5$ cm^{-1} for the amplitude step position $\delta = 12\,979$ (red solid line), 13 029 (green dashed line), and 13 079 cm^{-1} (blue dotted line).

Thus, by observing the hole in the $(2+1)$ REMPI photoelectron spectrum induced by the rectangular amplitude modulation, the eigenenergy of the excited state $7d_{3/2}$ $E_{7d_{3/2}}$ can be determined, which can provide a good way to study the excited-state or Rydberg-state structure.

Since the position of the hole in the $(2+1)$ REMPI photoelectron spectrum depends on the amplitude step position δ, an alternative way to determine the eigenenergy of the excited state $7d_{3/2}$ $E_{7d_{3/2}}$ is to measure the photoelectron intensity at a given kinetic energy by scanning the amplitude step positions δ. Figure 4 presents the photoelectron intensity at the kinetic energy of $E_v = 0.9554$ eV only through the excited
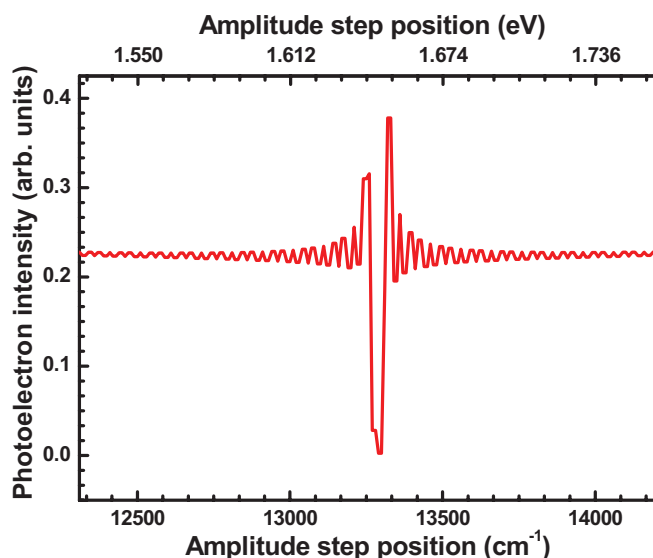

FIG. 4. (Color online) The photoelectron intensity at the kinetic energy of $E_v = 0.9549$ eV only through the excited state $7d_{3/2}$ as the function of the amplitude step position δ for the amplitude modulation width $\Delta = 5$ cm^{-1}.
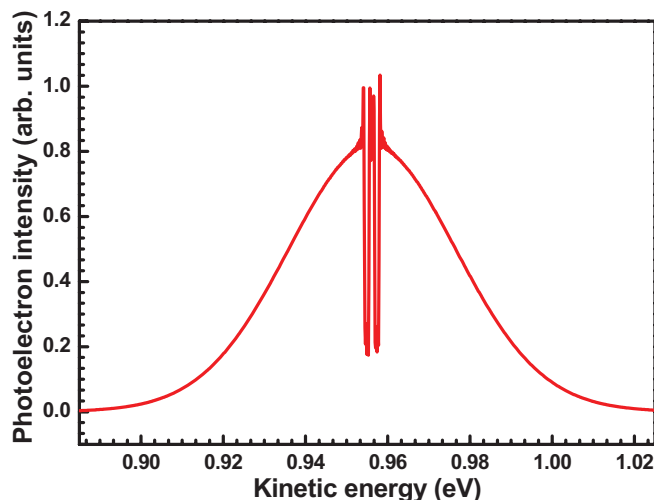

FIG. 5. (Color online) The $(2+1)$ REMPI photoelectron spectrum through both excited states $7d_{3/2}$ and $7d_{5/2}$ induced by the shaped laser pulse with the amplitude modulation width $\Delta = 5$ cm^{-1} and the amplitude step position $\delta = 13\,029$ cm^{-1}.

state $7d_{3/2}$ as the function of the amplitude step position δ for the amplitude modulation width $\Delta = 5$ cm^{-1}. It can be seen that the photoelectron intensity is completely suppressed at the amplitude step position $\delta = 13\,029$ cm^{-1}, and this result is in agreement with that obtained in Fig. 3.

As shown in Figs. 2 and 3, a very narrow hole in the $(2+1)$ REMPI photoelectron spectrum can be obtained by the rectangular amplitude modulation, and the position of the hole is correlated with the eigenenergy of the excited state; thus a high-resolution $(2+1)$ REMPI photoelectron spectrum through both excited states $7d_{3/2}$ and $7d_{5/2}$ can be achieved by observing the holes. Figure 5 presents the $(2+1)$ REMPI photoelectron spectrum through both excited states $7d_{3/2}$ and $7d_{5/2}$ induced by the shaped laser pulse with the amplitude modulation width $\Delta = 5$ cm^{-1} and the amplitude step position $\delta = 13\,029$ cm^{-1}. Two distinct holes are observed at the kinetic energy of $E_v = 0.9554$ and 0.9574 eV, respectively. It is easy to verify that the two holes are related to the two excited states $7d_{3/2}$ and $7d_{5/2}$ based on the relation of $E_{7d} + E_\delta = E_I + E_v^{\text{hole}}$. It is noteworthy that the photoelectron spectra through the two excited states $7d_{3/2}$ and $7d_{5/2}$ are indistinguishable, but the two holes associated with the two excited states $7d_{3/2}$ and $7d_{5/2}$ are distinguishable. Obviously, this high-resolution $(2+1)$ REMPI photoelectron spectrum by the rectangular amplitude modulation is different from that obtained by the cubic or π phase modulation, where the photoelectron spectrum is greatly narrowed [24–27].

Similarly, the eigenenergies of the two excited states $7d_{3/2}$ and $7d_{5/2}$, $E_{7d_{3/2}}$ and $E_{7d_{5/2}}$, can also be determined by scanning the amplitude step positions δ and measuring photoelectron intensity at a given kinetic energy. Figure 6 presents the photoelectron intensity at the kinetic energy of $E_v = 0.9554$ eV through both excited states $7d_{3/2}$ and $7d_{5/2}$ as the function of the amplitude step position δ with the amplitude modulation width $\Delta = 5$ cm^{-1}. One can see that the photoelectron intensity is tremendously suppressed at the amplitude step positions $\delta = 13\,009$ and 13 029 cm^{-1}. By the relation of
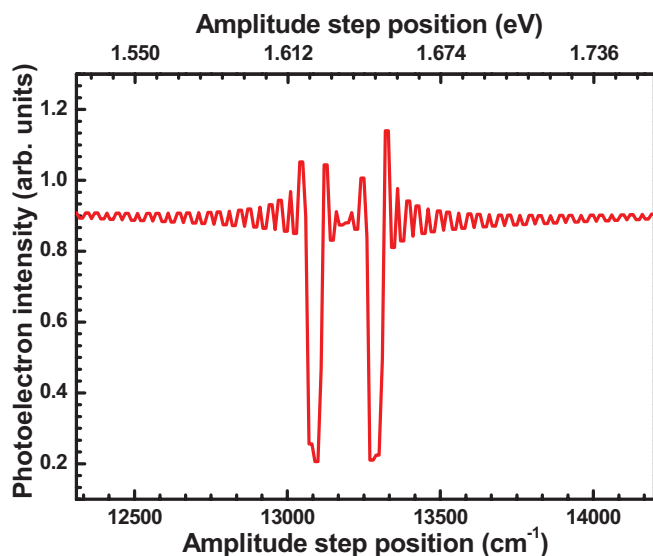
FIG. 6. (Color online) The photoelectron intensity at the kinetic energy of $E_v = 0.9549$ eV through both excited states $7d_{3/2}$ and $7d_{5/2}$ as the function of the amplitude step position δ with the amplitude modulation width $\Delta = 5$ cm^{-1}.

$E_{7d} = E_I + E_v^{\text{hole}} - E_\delta$, $E_{7d_{3/2}}$ and $E_{7d_{5/2}}$ can be calculated as $E_{7d_{3/2}} = 3.2295$ eV and $E_{7d_{5/2}} = 3.2319$ eV, corresponding to the frequencies of $26\,048$ and $26\,068$ cm^{-1}, which are consistent with the transition frequencies of the two excited states $7d_{3/2}$ and $7d_{5/2}$, $\omega_{7d_{3/2}}$ and $\omega_{7d_{5/2}}$. Furthermore, it can be found from Fig. 6 that the separation between the two positions of the photoelectron intensity suppression is 20 cm^{-1}, which is exactly equal to the transition frequency difference of the two excited state $7d_{3/2}$ and $7d_{5/2}$, $\omega_{7d_{5/2}} - \omega_{7d_{3/2}}$, so this method can be utilized to directly determine the energy-level separation of the excited states.

In summary, we have theoretically demonstrated that the $(2 + 1)$ REMPI photoelectron spectrum in Cs atom can be modulated by a shaped femtosecond laser pulse with a rectangular amplitude modulation. A hole in the photoelectron spectrum can be created by the amplitude-shaped laser pulse, and the position and width of the hole can be controlled by varying the amplitude step position and amplitude modulation width. Thus, by observing the holes in the $(2 + 1)$ REMPI photoelectron spectrum, a high-resolution $(2 + 1)$ REMPI photoelectron spectrum and the fine energy-level structure of the excited states can be achieved in spite of a broadband photoelectron spectrum. Our scheme can also be further applied to controlling the $(m + 1)$ REMPI photoelectron spectroscopy, and is expected to be significant for femtosecond-induced REMPI process and related applications in various fields.

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