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Control of resonance enhanced multi-photon ionization photoelectron spectroscopy by phase-shaped femtosecond laser pulse

Shian Zhang,^{1,a)} Chenhui Lu,¹ Tianqing Jia,¹ Jianrong Qiu,² and Zhenrong Sun^{1,b)}

¹State Key Laboratory of Precision Spectroscopy, and Department of Physics, East China Normal University, Shanghai 200062, People's Republic of China

²State Key Laboratory of Luminescent Materials and Devices, and Institute of Optical Communication Materials, South China University of Technology, Wushan Road 381, Guangzhou 510640, People's Republic of China

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In this paper, we theoretically demonstrate that the (2+1+1) resonance enhanced multi-photon ionization photoelectron spectroscopy in sodium atom can be effectively controlled by shaping femtosecond laser pulse with a π phase step modulation in weak laser field, involving its total photoelectron energy, maximal photoelectron intensity, and spectroscopic bandwidth. Our results show that the total photoelectron energy can be suppressed but not enhanced, the maximal photoelectron intensity can be enhanced and also suppressed, and the photoelectron spectroscopy can be tremendously narrowed. These theoretical results can provide a feasible scheme to achieve the high-resolution photoelectron spectroscopy and study the excited state structure in atomic and molecular systems. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4762865>]

Resonance enhanced multi-photon ionization, which involves a resonant single or multiple photon absorption to an excited state followed by another photon that ionizes the atom or molecule, is a powerful technique applied to the atomic and molecular spectroscopy.¹ The resonance enhanced multi-photon ionization photoelectron spectroscopy (REMPI-PS) has proven to be an excellent tool to study the photo-ionization and -dissociation dynamical process of the excited states.^{2–10} In resonance enhanced multi-photon ionization process, REMPI-PS allows for the determination of the excited states in which the electrons are created, which offers valuable information on the electronic and vibrational characteristics in the excited states. Moreover, REMPI-PS can also identify the dynamical processes occurring in the excited states, which can determine the electrons deriving from the ionization of the neutral fragments or the dissociation of molecular ion.

The femtosecond laser pulse is a well-established tool in inducing the REMPI-PS because of its high laser intensity and broad laser spectrum, but the femtosecond-induced REMPI-PS is faced with an inevitable problem that is the poor spectral resolution due to large laser spectral bandwidth. Recently, femtosecond pulse shaping technique has shown a perfect method to control the REMPI-PS.^{11–16} For example, Wollenhaupt *et al.* showed the selective excitation of the slow and fast photoelectrons of the REMPI-PS in potassium (K) atom by various phase modulations, such as sinusoidal, chirped, and phase-step modulation.^{2,11–14} Krug *et al.* demonstrated the enhancement and suppression of the REMPI-PS in sodium (Na) atom by a chirped phase modulation.¹⁵ We showed that the photoelectron spectroscopic structure in (2+1) REMPI-

PS can be effectively manipulated by a spectral phase step modulation.¹⁶

The REMPI-PS is correlated with the time-dependent population of the final excited state, and so the population variation of the final excited state will affect the REMPI-PS. In our previous work of the (2+1) REMPI-PS,¹⁷ the population of the final excited state through non-resonant two-photon absorption can be suppressed but not enhanced by the phase-shaped femtosecond laser pulse. In this paper, we further extend our theoretical investigation. We consider this case of (2+1+1) REMPI-PS, the population of the final excited state through resonant-mediated (2+1) three-photon absorption can be suppressed and also enhanced by properly controlling the femtosecond laser pulse. With Na atom as our study model, we show that the π phase step modulation can provide a feasible scheme to control the (2+1+1) REMPI-PS in weak laser field, involving its total photoelectron energy, maximal photoelectron intensity, and spectroscopic bandwidth. Our results indicate that the total photoelectron energy can be suppressed but not enhanced, while the maximal photoelectron intensity can be suppressed and also enhanced, and the spectroscopic bandwidth can be greatly reduced.

Figure 1(a) shows the excitation scheme of the (2+1+1) resonance enhanced multi-photon ionization process in Na atom. Here, 3s, 4s, and 7p represent the ground state, intermediate excited state, and final excited state, respectively. The transition from the 3s state to the 4s state is coupled by non-resonant two-photon absorption and the transition from the 4s state to the 7p state is coupled by single-photon absorption, and finally the populations in 7p state are ionized by single-photon excitation. Thus, the (2+1+1) REMPI-PS $P(E_v)$ can be approximated as^{2,11–14}

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

^{a)}sazhang@phy.ecnu.edu.cn.

^{b)}zrsun@phy.ecnu.edu.cn.

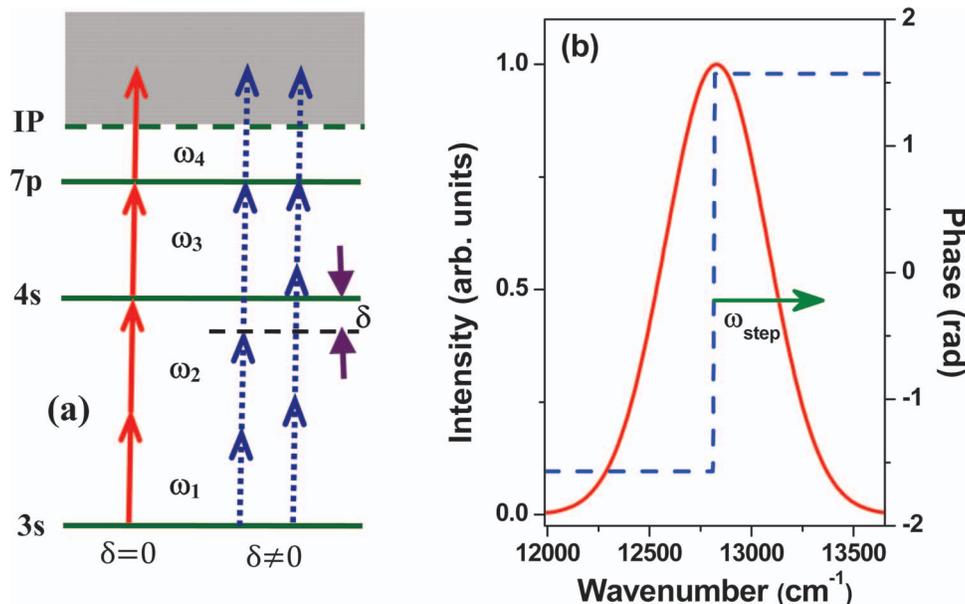


FIG. 1. (a) The schematic diagram of the (2+1+1) resonance enhanced multi-photon ionization process in Na atom. (b) The laser spectrum modulated by a π phase step modulation with the function of $\Phi(\omega) = \frac{\pi\sigma(\omega-\omega_{\text{step}})}{2}$.

where E_I is the ionization energy from the 3s state, E_{7p} is the eigenenergy of the 7p state, and $C_{7p}(t)$ describes the time-dependent probability amplitude in the 7p state. In weak laser field, $C_{7p}(t)$ can be approximated by third-order time-dependent perturbation theory as^{17,18}

$$C_{7p}(t) = \frac{\mu_{4s-7p}\mu_{3s-4s}^2}{\hbar^3} [C_{7p}^{(2+1)\text{on-res}}(t) + C_{7p}^{(2+1)\text{near-res}}(t)], \quad (2)$$

where μ_{4s-7p} is the state $4s \rightarrow 7p$ dipole matrix element and μ_{3s-4s}^2 is the state $3s \rightarrow 4s$ effective non-resonant two-photon dipole coupling. The two terms $C_{7p}^{(2+1)\text{on-res}}(t)$ and $C_{7p}^{(2+1)\text{near-res}}(t)$ are given by

$$C_{7p}^{(2+1)\text{on-res}}(t) = i\pi S_{\omega_{3s-4s}}^{(2)}(t) S_{\omega_{4s-7p}}^{(1)}(t), \quad (3)$$

$$C_{7p}^{(2+1)\text{near-res}}(t) = -\rho \int_{-\infty}^{+\infty} \frac{1}{\delta} S_{\omega_{3s-4s}-\delta}^{(2)}(t) S_{\omega_{4s-7p}+\delta}^{(1)}(t) d\delta, \quad (4)$$

with

$$S_{\omega_{\text{ex}}}^{(i)}(t) = \int_{-\infty}^t E^i(t') \exp(i\omega_{\text{ex}} t') dt', \quad (5)$$

where ρ is the Cauchy principal value, and δ is the detuning. One can see that the first term $C_{7p}^{(2+1)\text{on-res}}(t)$ in the square brackets of Eq. (2) only depends on the spectral components of the laser pulse at the resonance frequencies ω_{3s-4s} and ω_{4s-7p} , while the second term $C_{7p}^{(2+1)\text{near-res}}(t)$ integrates over the contributions of all other spectral components.

The different excitation pathways of the (2+1+1) resonance enhanced four-photon ionization process are shown schematically in Fig. 1(a). Each excitation pathway is either on resonance ($\delta = 0$) or near resonance ($\delta \neq 0$) with the 4s state. On-resonant excitation pathway corresponds to the

combination of the four photons of frequencies ω_1 , $\omega_{3s-4s} - \omega_1$ (i.e., ω_2), ω_{4s-7p} (i.e., ω_3) and ω_4 . However, near-resonant excitation pathway corresponds to the combination of the four photons of frequencies ω_1 , ω_2 , $\omega_{4s-7p} - \delta$ (i.e., ω_3) and ω_4 . Thus, it is easy to verify that the on-resonant term in Eq. (1) is maximized by the transform-limited laser pulse for all values of $P(E_v)$, while the near-resonant term integrates over both negative ($\delta < 0$) and positive ($\delta > 0$) contributions, and therefore the transform-limited laser pulse induces a destructive interference among these four-photon excitation pathways. A feasible way to enhance $P(E_v)$ at a given kinetic energy E_v is to apply a phase inversion that induces a constructive interference instead of the destructive interference.

The π phase step modulation, as a typical phase inversion, has proven to be well-established tool to control various nonlinear optical processes, such as two-photon absorption,^{19,20} coherent anti-Stokes Raman scattering,^{21,22} and multi-photon ionization.¹¹ Here we employ it to control the (2+1+1) REMPI-PS. The π phase step modulation can be defined by the function of $\Phi(\omega) = \frac{\pi\sigma(\omega-\omega_{\text{step}})}{2}$, where $\sigma(\omega - \omega_{\text{step}})$ denotes the signum function which takes the values of ∓ 1 for $\omega \lesseqgtr \omega_{\text{step}}$, and thus $\Phi(\omega)$ is characterized by a phase jump from $-\pi/2$ to $\pi/2$ at the step position ω_{step} . This spectral phase step modulation is shown in Fig. 1(b). Thus, the modulated laser field in frequency domain $E_{\text{mod}}(\omega)$ can be given by $E_{\text{mod}}(\omega) = E(\omega) \times \exp[\frac{i\pi\sigma(\omega-\omega_{\text{step}})}{2}]$, where $E(\omega)$ is the Fourier transform of the unmodulated laser field $E(t)$, and the modulated laser field in time domain $E_{\text{mod}}(t)$ is given by the convolution of the unmodulated laser field $E(t)$ with $\frac{\exp(i\omega_{\text{step}}t)}{\pi t}$, i.e., $E_{\text{mod}}(t) = E(t) \otimes \frac{\exp(i\omega_{\text{step}}t)}{\pi t}$. By substituting $E_{\text{mod}}(t)$ into Eqs. (1)–(5), the REMPI-PS $P(E_v)$ induced by the π phase step modulation can be obtained.

In our simulation, the transition frequency from the 3s state to the 4s state in the Na atom is $\omega_{3s-4s} = 25740 \text{ cm}^{-1}$,

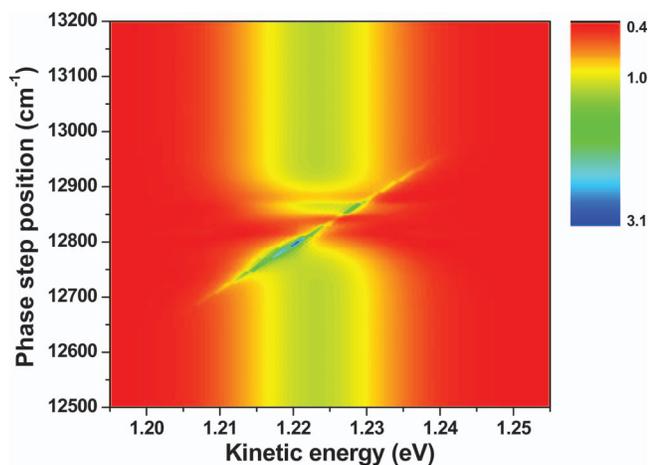


FIG. 2. The (2+1+1) REMPI-PS as the function of the π phase step position with the laser pulse duration of 180 fs.

and the transition frequency from the 4s state to the 7p state is $\omega_{4s-7p} = 12\,800\text{ cm}^{-1}$. The ionization energy from the 3s state is $E_I = 5.14\text{ eV}$, corresponding to the frequency of $41\,456\text{ cm}^{-1}$. The laser central frequency is set to be $\omega_0 = 12\,820\text{ cm}^{-1}$, and its pulse duration (full width at half maximum (FWHM)) is $\tau = 180\text{ fs}$, corresponding to the spectral bandwidth (FWHM) of $\sim 85\text{ cm}^{-1}$. Figure 2 shows the simulated (2+1+1) REMPI-PS in Na atom as the function of the π phase step position. All data are normalized by the maximal photoelectron intensity excited by the transform-limited laser pulse. It can be seen that the photoelectron spectroscopy is strongly modulated by this simple spectral phase modulation, involving its total photoelectron energy, maximal photoelectron intensity, and spectroscopic bandwidth. Next we will respectively discuss the control of these parameters characterizing the photoelectron spectroscopy.

The total photoelectron energy can directly reflect the multi-photon ionization efficiency. We firstly demonstrate the control of the total photoelectron energy by the π phase step modulation, as shown in Fig. 3. Here, the total photoelectron energy is obtained from the photoelectron spectroscopy by $E_p = \int_0^{+\infty} P(E_v) dE_v$. As can be seen, the total photoelectron energy cannot be enhanced, but can be tremendously suppressed by about 71%, which indicate that the π phase step modulation is an effective method to suppress the multi-photon ionization efficiency. As shown in Eq. (1), the photoelectron spectroscopy $P(E_v)$ relies on the time-dependent probability amplitude in the 7p state $C_{7p}(t)$. For comparison, we calculate the transition probability in the 7p state by $P_{7p} = |C_{7p}(t \rightarrow \infty)|^2$, and the calculated result is shown in the inset of Fig. 3. One can see that the transition probability P_{7p} can be greatly enhanced and also completely suppressed by the π phase step modulation. Obviously, this evolution behavior is different from the total photoelectron energy. We believe that no enhancement for the total photoelectron energy is due to the reduction of the laser intensity in the shaped pulse, and no complete suppression results from the time-dependent absorption of the 7p state in the ionization process since the absorption and ionization processes employ the same laser pulse.

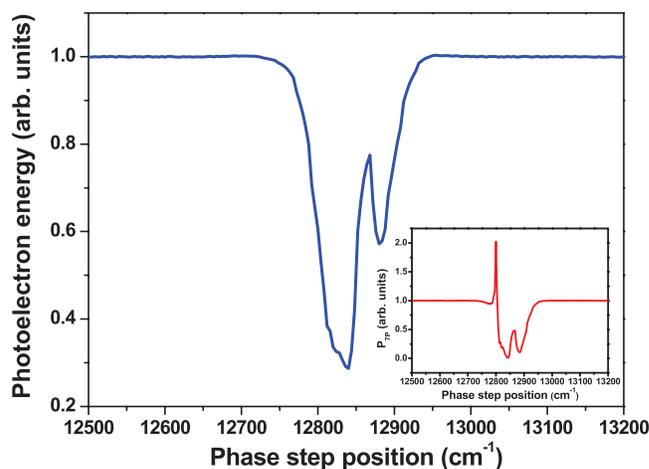


FIG. 3. The total photoelectron energy as the function of the π phase step position. Inset shows the transition probability in 7p state P_{7p} versus the π phase step position.

How to increase the photoelectron intensity and improve signal-to noise ratio is always researchers' active question. Therefore, we present the maximal photoelectron intensity as the function of the π phase step position, as shown in Fig. 4. Here, the maximal photoelectron intensity means the maximal amplitude of the photoelectron spectroscopy. As can be seen, the maximal photoelectron intensity can be enhanced and also suppressed. Since the total photoelectron energy cannot be enhanced (see Fig. 3), the photoelectron intensity enhancement can only occur at some special kinetic energies. The maximal photoelectron intensity is enhanced by a factor of 3.1 at the π phase step position of $12\,800\text{ cm}^{-1}$, while the laser intensity at this position is reduced by about 39%. Inset shows the temporal intensities of the transform-limited pulse (red solid line) and the shaped pulse with the π phase step position of $12\,800\text{ cm}^{-1}$ (green dashed line). The shaped pulse is the double-humped pulse shape with the reduction of the laser intensity and the broadening of the pulse duration. The

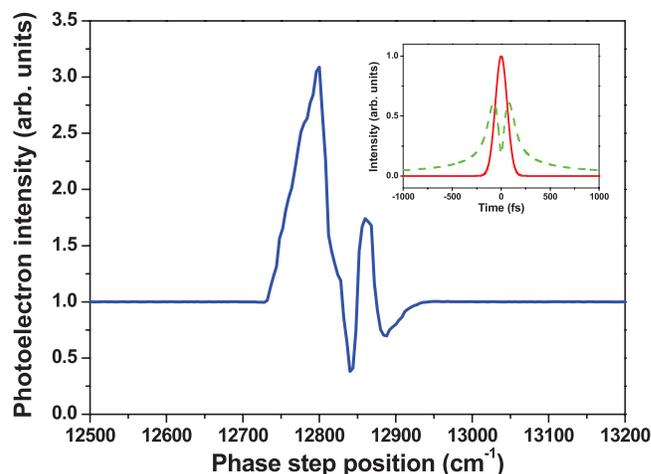


FIG. 4. The maximal photoelectron intensity as the function of the π phase step position. Inset shows the temporal intensities of the transform-limited pulse (red solid line) and the shaped pulse with the π phase step position $\omega_{\text{step}} = 12\,800\text{ cm}^{-1}$ (green dashed line).

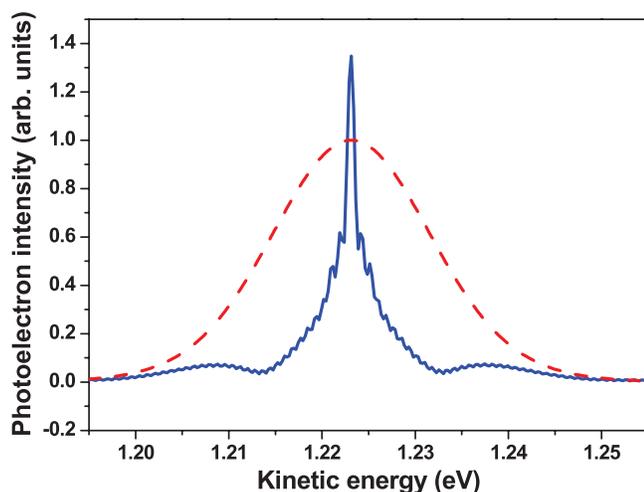


FIG. 5. The (2+1+1) REMPI-PS induced by the transform-limited laser pulse (red dashed line) and the shaped laser pulse with the π phase step position $\omega_{\text{step}} = 12820 \text{ cm}^{-1}$ (blue solid line).

phenomenon reflects the nature of the quantum coherent control that lower laser intensity can generate higher photoelectron intensity by the constructive interferences of different excitation pathways.

Femtosecond-induced REMPI-PS is not an appropriate tool for high resolution studies because of its broad photoelectron spectroscopy. Figure 5 shows the (2+1+1) REMPI-PS induced by the transform-limited laser pulse (red dashed line) and the shaped laser pulse with the π phase step position $\omega_{\text{step}} = 12820 \text{ cm}^{-1}$ (blue solid line). One can see that the photoelectron spectroscopy can be tremendously narrowed by the π phase step modulation. The spectroscopic bandwidth (FWHM) is about 0.0201 eV for the transform-limited laser pulse, while is only about 0.0012 eV for the shaped laser pulse, which is narrowed by a dozen times. It can be found that the narrowing of the photoelectron spectroscopy results from the photoelectron intensity enhancement at special kinetic energy, which is of a similar nature to that obtained for the narrow-band coherent anti-Stokes Raman spectroscopy by Oron *et al.*²² Recently, the spectral narrowing of the REMPI-PS by the π phase step modulation has been experimentally observed in potassium (K) atom.²³ It is evident that the π phase step modulation can provide an excellent method to narrow the femtosecond-induced REMPI-PS. If multiple excited states are simultaneously excited, a high-resolution REMPI-PS can be achieved.

Figure 6 shows the (2+1+1) REMPI-PS induced by the shaped laser pulse with the π phase step position $\omega_{\text{step}} = 12780$ (red solid line), 12800 (green dashed line), and 12820 cm^{-1} (blue dotted line). The maximal photoelectron intensities for the π phase step position $\omega_{\text{step}} = 12780$, 12800, and 12820 cm^{-1} occur at the kinetic energies of 1.218 204, 1.220 674, and 1.223 144 eV, respectively. It can be seen that the maximal photoelectron intensities for different π phase step positions are obtained at different kinetic energies, while the energy difference between the photon energy at this phase step position (i.e., $E_{\omega_{\text{step}}}$) and the kinetic energy corresponding to the maximal photoelectron intensity (i.e., $E_{\text{v}}^{\text{max}}$)

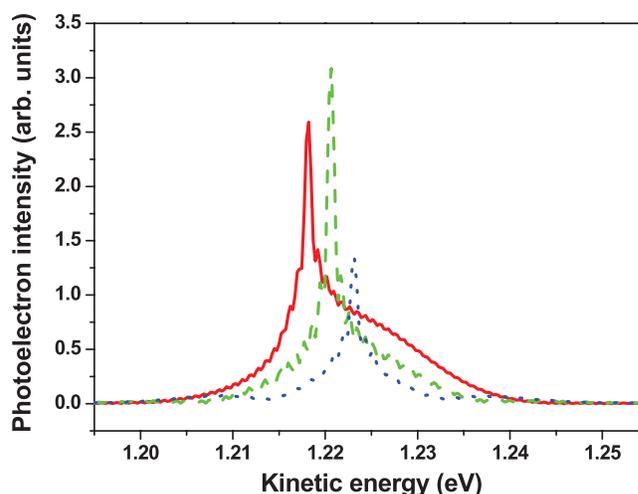


FIG. 6. The (2+1+1) REMPI-PS induced by the shaped laser pulse with the π phase step position $\omega_{\text{step}} = 12780$ (red solid line), 12800 (green dashed line), and 12820 cm^{-1} (blue dotted line).

is constant, which is equal to the ionization energy from the 7p state (i.e., E_{Δ}), where $E_{\Delta} = E_{\text{I}} - E_{7\text{p}}$. In other words, the photon energy at the phase step position $E_{\omega_{\text{step}}}$, the eigenenergy of the 7p state $E_{7\text{p}}$, the ionization energy E_{I} , and the kinetic energy corresponding to the maximal photoelectron intensity $E_{\text{v}}^{\text{max}}$ satisfy the relation of $E_{\omega_{\text{step}}} + E_{7\text{p}} = E_{\text{I}} + E_{\text{v}}^{\text{max}}$. Thus, it can be concluded that the maximal photoelectron intensity for the π phase step modulation occurs at the kinetic energy of $E_{\omega_{\text{step}}} + E_{7\text{p}} - E_{\text{I}}$.

Based on the relation of $E_{\omega_{\text{step}}} + E_{7\text{p}} = E_{\text{I}} + E_{\text{v}}^{\text{max}}$, if three among the four parameters are known, the another one can be obtained. For example, $E_{7\text{p}}$ can be calculated when $E_{\text{v}}^{\text{max}}$, E_{I} , and $E_{\omega_{\text{step}}}$ are known, which can be utilized to study the excited state structure. Similarly, when $E_{\text{v}}^{\text{max}}$, $E_{7\text{p}}$, and $E_{\omega_{\text{step}}}$ are given, E_{I} can be obtained, which can be used to determine the ionization energy.

By the π phase step modulation, the (2+1+1) REMPI-PS, involving its total photoelectron energy, maximal photoelectron intensity, and spectroscopic bandwidth, can be effectively controlled, as demonstrated above. Finally, we study the influence of the laser pulse duration on the control of the (2+1+1) REMPI-PS. Figure 7 shows the simulated (2+1+1) REMPI-PS as the function of the π phase step position with the laser pulse duration of 50 (a) and 100 fs (b). Comparing with Fig. 2, one can see that the evolutions of the (2+1+1) REMPI-PS for the three pulse durations are almost the same, that is to say, the laser pulse duration almost does not affect the control of the (2+1+1) REMPI-PS.

In summary, we have theoretically presented a scheme to control the (2+1+1) REMPI-PS in Na atom by the π phase step modulation. We showed that the total photoelectron energy can be suppressed but not enhanced, the maximal photoelectron intensity can be enhanced and also suppressed, and the photoelectron spectroscopic bandwidth can be tremendously reduced. We also showed that the excited state structure or ionization energy can be determined by measuring the (2+1+1) REMPI-PS with the π phase step modulation. Additionally, we demonstrated that the laser

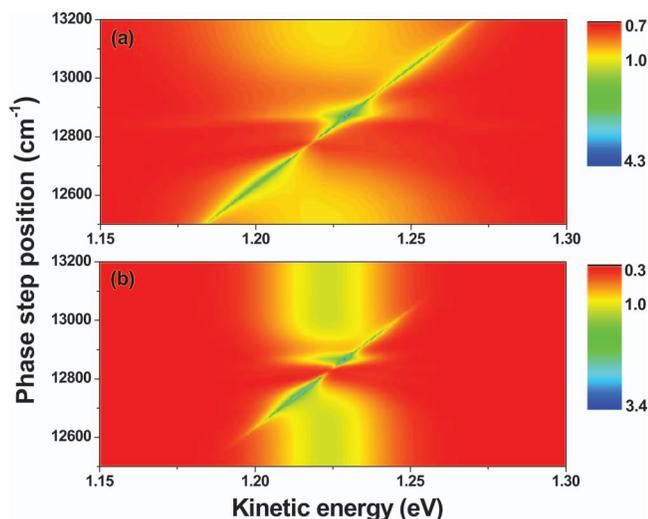


FIG. 7. The (2+1+1) REMPI-PS as the function of the π phase step position with the laser pulse duration of 50 (a) and 100 fs (b).

pulse duration almost does not affect the control of the (2+1+1) REMPI-PS. Of course, our scheme can be further applied in the control of photoelectron spectroscopy in various resonance enhanced multi-photon ionization processes.

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