Selective excitation of resonance-enhanced multiphoton-ionization photoelectron spectroscopy via a cubic phase modulation

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Resonantly enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PS) has proven to be a well-established tool to study the excited-state structure. However, femtosecond-induced REMPI-PS suffers from poor selectivity between neighboring excited states due to the large spectral bandwidth. In this paper, we present a feasible scheme to realize the selective excitation of $(2+1)$ REMPI-PS in sodium atoms. We show that, by shaping the femtosecond laser pulse with a cubic phase modulation, a high-resolution $(2+1)$ REMPI-PS is obtained, and the $(2+1)$ REMPI-PS signal from one excited state is enhanced while that from the other excited state is effectively suppressed. Furthermore, we explain the physical control mechanism of the selective excitation of $(2+1)$ REMPI-PS by considering the two-photon power spectrum.

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I. INTRODUCTION

Resonantly enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PS), involving a resonant single- or multiple-photon absorption to an excited state followed by other photons that ionize the atom or molecule, is one of the most important nonlinear spectroscopic techniques [1]. Currently, the REMPI-PS has been widely applied to studying the photoionization and photodissociation dynamical process of the excited states [2–9], which can determine for which excited state the electrons are created. Nanosecond- or picosecond-induced REMPI-PS has proven to be an excellent technique to investigate the excited-state or Rydberg-state structure [9]. However, for femtosecond-induced REMPI-PS, several excited states falling within the broad spectrum of the femtosecond laser pulse will be simultaneously excited, thus leading to low spectral resolution and poor selectivity between the neighboring excited states, and this greatly limits the further application of the femtosecond-induced REMPI-PS. Recently, the femtosecond pulse-shaping technique has proven to be an effective method to manipulate the REMPI-PS [1,10–15]. Krug *et al.* demonstrated that the $(2+1+1)$ REMPI-PS in a sodium (Na) atom can be enhanced or suppressed by a chirped phase modulation [10]. Wollenhaupt *et al.* showed that the slow and fast photoelectrons of $(1+2)$ REMPI-PS in a potassium (K) atom can be selectively excited by a sinusoidal, chirped, or phase step modulation [1,11–14]. We showed that the $(1+2)$ REMPI-PS in a K atom can be narrowed by a cubic phase modulation [15].

The coherent control strategy with the femtosecond pulse-shaping technique is dominated by the quantum interference of different excitation pathways connecting the initial and final states, and so the main challenge is how to create a constructive or destructive interference among these different excitation pathways by properly designing the spectral phase and/or amplitude distribution. In this paper, we first theoretically show that the selective excitation of $(2+1)$ REMPI-PS in Na atoms can be realized by shaping the femtosecond laser pulse with a cubic phase modulation. Our results indicate that the $(2+1)$ REMPI-PS can be greatly narrowed and a high-resolution $(2+1)$ REMPI-PS is obtained, and the $(2+1)$ REMPI-PS signal from one excited state is enhanced while that from the other excited state is effectively suppressed. Moreover, the selective excitation of $(2+1)$ REMPI-PS is explained by the two-photon power spectrum.

II. THEORETICAL MODEL

Figure 1 shows the schematic diagram of the $(2+1)$ resonantly enhanced three-photon ionization process in a Na atom. The transition from ground state $3s$ to excited state $8d$ or $9d$ is coupled by nonresonant two-photon absorption, and the populations in excited states $8d$ and $9d$ are ionized by single-photon absorption. We consider that the laser pulse duration is much smaller than the lifetime of the excited state and only ground state $3s$ is initially populated. Thus, the $(2+1)$ REMPI-PS can be approximated as [1,11–14]

$$P(E_v) \propto \int_{-\infty}^{+\infty} E(t) C_{8d(9d)}(t) \times \exp\left[\frac{i(E_v + E_I - E_{8d(9d)}t)}{\hbar}\right] dt, \qquad (1)$$

where E_I is the ionization energy from ground state $3s$, $E_{8d(9d)}$ is the eigenenergy of excited state $8d$ or $9d$, and $C_{8d(9d)}$ represents the time-dependent probability amplitude in excited state $8d$ or $9d$, which can be obtained by second-order time-dependent perturbation theory in weak laser field and is written as [16]

$$C_{8d(9d)}(t) \propto \int_{-\infty}^{t} E^2(t') \exp\left[i\omega_{8d(9d)}t'\right] dt', \qquad (2)$$

where $\omega_{8d(9d)}$ is the transition frequency from ground state $3s$ to excited state $8d$ or $9d$.

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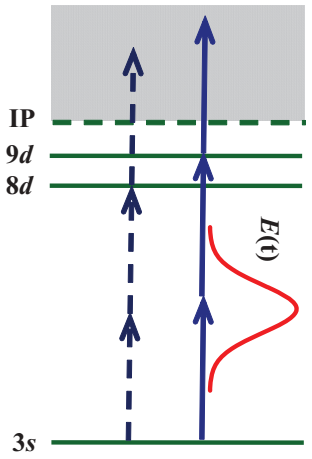

FIG. 1. (Color online) The schematic diagram of the $(2+1)$ resonantly enhanced three-photon ionization process in a Na atom. The transition from ground state $3s$ to excited state $8d$ or $9d$ is pumped by nonresonant two-photon absorption, and the populations in excited states $8d$ and $9d$ are ionized by single-photon absorption.

In our simulation, the transition frequencies from ground state $3s$ to excited states $8d$ and $9d$ in the Na atom are $\omega_{8d} = 39\,728$ cm^{-1} and $\omega_{9d} = 40\,090$ cm^{-1}, respectively. The ionization energy from ground state $3s$ is $E_I = 5.14$ eV, corresponding to a frequency of 41 456 cm^{-1}. The laser central frequency is $\omega_L = 19\,955$ cm^{-1}, its two-photon frequency (i.e., $2\omega_L$) is almost in the middle of the two transition frequencies, ω_{8d} and ω_{9d}, and the pulse duration (full width at half maximum) is $\tau = 50$ fs. Here, we utilize a cubic phase modulation to control the $(2+1)$ REMPI-PS, and this method has been successfully applied in controlling $(1+2)$ REMPI-PS in K atoms [15]. This cubic phase modulation can be defined by the function $\Phi(\omega) = \alpha(\omega - \omega_{\text{step}})^3$, where α is the modulation amplitude and ω_{step} is the phase step position. Figure 2 presents the laser spectrum modulated by this cubic spectral modulation in the frequency domain [Fig. 2(a)] and its corresponding temporal intensity distribution [Fig. 2(b)]. One can see that the shaped laser pulse is an asymmetric profile with an intense initial pulse proceeded by a pulse sequence with decaying amplitude. The effects of the modulation amplitude α and the phase step position ω_{step} on the shaped laser pulse have been explicitly described in our previous work [15].

III. RESULTS AND DISCUSSION

Figure 3 shows the $(2+1)$ REMPI-PS (green solid lines) induced by the transform-limited laser pulse [Fig. 3(a)] and the shaped laser pulse with $\alpha = 2 \times 10^5$ fs^3 and $\omega_{\text{step}} = 19\,955$ cm^{-1} [Fig. 3(b)], together with the contribution by only excited state $8d$ (red dashed lines) or $9d$ (blue dotted lines). As can be seen, only a single broad photoelectron spectrum is observed for the transform-limited laser pulse, while the photoelectron spectrum can be greatly narrowed for the shaped laser pulse, and the larger modulation amplitude α yields the narrower photoelectron spectrum. Furthermore, two distinct photoelectron peaks are observed, which are related to the two

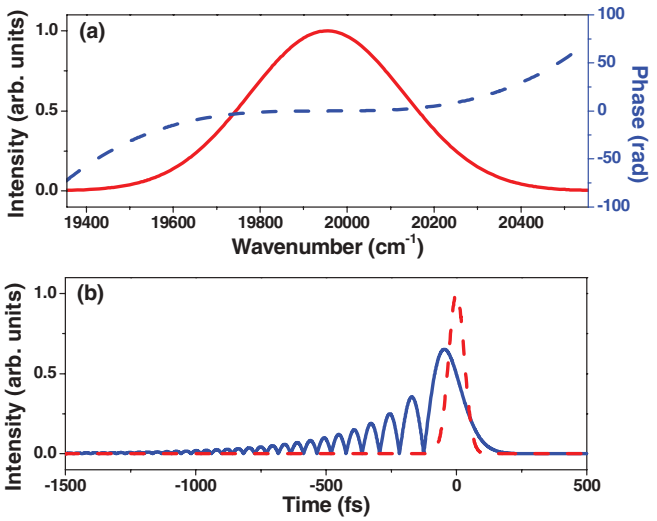

FIG. 2. (Color online) (a) The laser spectrum modulated by a cubic phase modulation. (b) The temporal intensity profile of the transform-limited laser pulse (red dashed line) and the shaped laser pulse by the cubic phase modulation with modulation amplitude $\alpha = 5 \times 10^4$ fs^3 and phase step position $\omega_{\text{step}} = 19\,955$ cm^{-1} (blue solid line).

excited states, $8d$ and $9d$. That is to say, the $(2+1)$ REMPI-PS signals between the two excited states can be differentiated from their indistinguishable photoelectron spectra, and this phenomenon is the same as that obtained in $(1+2)$ REMPI-PS [15]. Obviously, this cubic phase modulation provides an effective method to narrow the $(2+1)$ REMPI-PS and achieve a high-resolution photoelectron spectrum.

Since the $(2+1)$ REMPI-PS signals between the two excited states, $8d$ and $9d$, can be differentiated by varying the modulation amplitude α, their selective excitation is possible to realize by supplementally controlling the phase step position

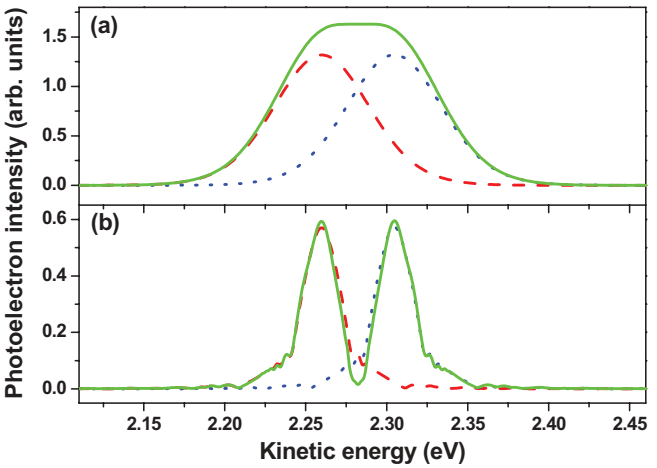

FIG. 3. (Color online) The $(2+1)$ REMPI-PS (green solid lines) induced by (a) the transform-limited laser pulse and (b) the shaped laser pulse with modulation amplitude $\alpha = 2 \times 10^5$ fs^3 and phase step position $\omega_{\text{step}} = 19\,955$ cm^{-1}, together with the contribution only from excited states $8d$ (red dashed lines) and $9d$ (blue dotted lines).

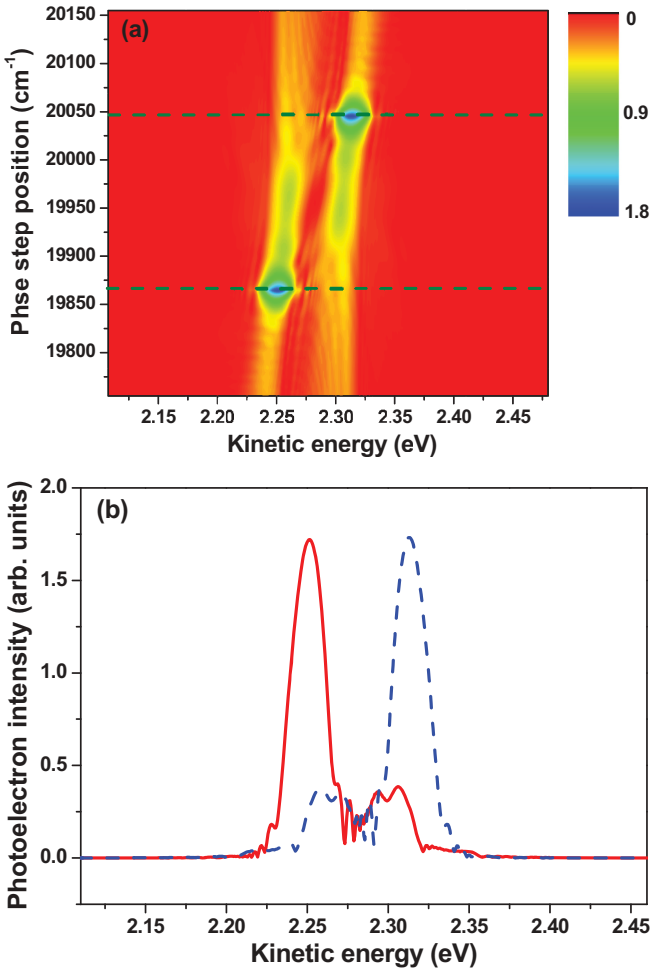

FIG. 4. (Color online) (a) The $(2+1)$ REMPI-PS as a function of the phase step position ω_{step} with modulation amplitude $\alpha = 2 \times 10^5$ fs^3. (b) The $(2+1)$ REMPI-PS for phase step position $\omega_{\text{step}} =$ 19 865 (red solid line) and 20 045 cm^{-1} (blue dashed line).

ω_{step}. Figure 4(a) shows the $(2+1)$ REMPI-PS as a function of the phase step position ω_{step} with the modulation amplitude $\alpha = 2 \times 10^5$ fs^3. It can be seen that the photoelectron spectrum is strongly modulated and that one photoelectron peak is enhanced while the other one is effectively suppressed; that is to say, the two photoelectron peaks can be selectively excited. The low-energy photoelectron peak is maximally enhanced at $\omega_{\text{step}} = 19\,865$ cm^{-1}, while the high-energy photoelectron peak is maximally enhanced at $\omega_{\text{step}} = 20\,045$ cm^{-1} (labeled with olive dashed lines). Figure 4(b) presents the $(2+1)$ REMPI-PS for the phase step position $\omega_{\text{step}} = 19\,865$ (red solid line) and 20 045 cm^{-1} (blue dashed line). The low-energy photoelectron peak is enhanced by ~30%, while the high-energy photoelectron peak is suppressed by ~71% at $\omega_{\text{step}} =$ 19 865 cm^{-1}, and the opposite behavior is observed at $\omega_{\text{step}} =$ 20 045 cm^{-1}. Since the two photoelectron peaks are correlated with excited states $8d$ and $9d$, this result illustrates that the $(2+1)$ resonantly enhanced three-photon ionization process can be selectively excited by the cubic phase modulation.

As can be seen in Eq. (1), the photoelectron spectrum $|P(E\nu)|^2$ depends on the time-dependent population

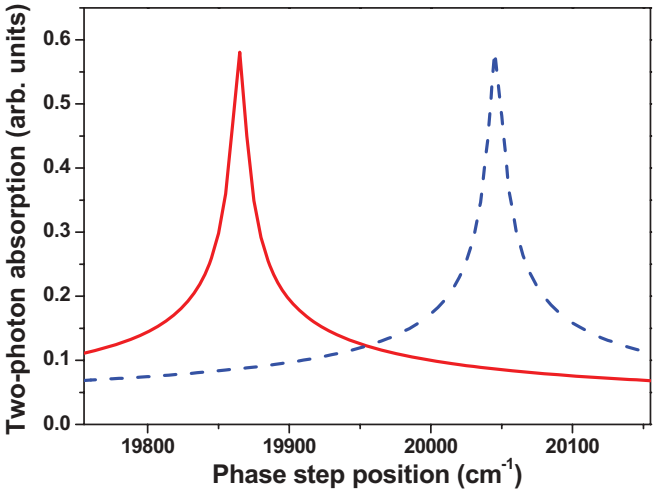

FIG. 5. (Color online) The two-photon transition probability in excited states $8d$ and $9d$, P_{8d} (red solid line) and P_{9d} (blue dashed line), as a function of the phase step position ω_{step} with modulation amplitude $\alpha = 2 \times 10^5$ fs^3.

amplitude in excited states $8d$ and $9d$ [i.e., $C_{8d(9d)}(t)$], and therefore the population variation in excited states $8d$ and $9d$ will affect the photoelectron intensity. We present the two-photon transition probability in excited states $8d$ and $9d$, P_{8d} (red solid line) and P_{9d} (blue dashed line), as a function of the phase step position ω_{step} with modulation amplitude $\alpha = 2 \times 10^5$ fs^3, as shown in Fig. 5. Here, P_{8d} (P_{9d}) is obtained with $P_{8d(9d)} = |C_{8d(9d)}(t \to \infty)|^2$. One can see that P_{8d} is the maximal value at $\omega_{\text{step}} = 19\,865$ cm^{-1}, while P_{9d} is the maximal value at $\omega_{\text{step}} = 20\,045$ cm^{-1}, and this observation is the same as the photoelectron intensity in Fig. 4. This further confirms that the photoelectron intensity modulation in Fig. 4 occurs because of the variation of the transition probability in excited states $8d$ and $9d$.

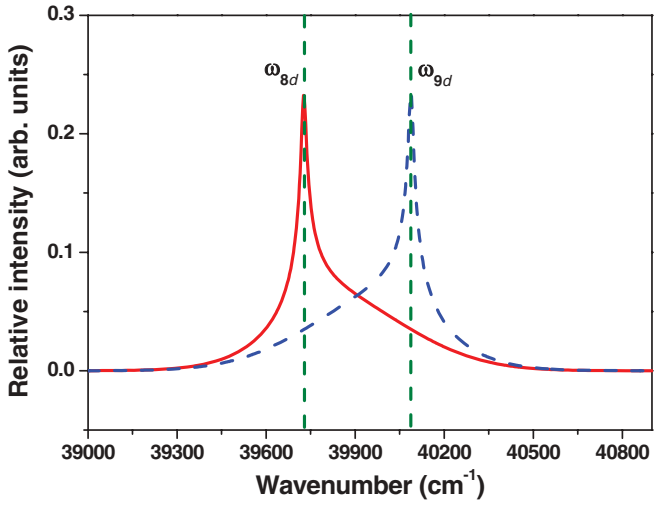

FIG. 6. (Color online) The two-photon power spectra of the shaped laser pulse with modulation $\alpha = 2 \times 10^5$ fs^3 for phase step position $\omega_{\text{step}} = 19\,865$ (red solid line) and 20 045 cm^{-1} (blue dashed line).

A previous study showed that the two-photon power spectrum provides an excellent tool to explain the coherent control of nonresonant two-photon absorption induced by the shaped laser pulse [17]. Here, we also employ the same method to explain the physical control mechanism of the selective excitation of $(2+1)$ REMPI-PS since the populations in ground state $3s$ are pumped to excited states $8d$ and $9d$ by nonresonant two-photon absorption and then ionized. Figure 6 shows the two-photon power spectra of the shaped laser pulse with the modulation $\alpha = 2 \times 10^5$ fs^3 for the phase step position $\omega_{\text{step}} = 19\,865$ (red solid line) and $20\,045$ cm^{-1} (blue dashed line). The two-photon power spectra for $\omega_{\text{step}} = 19\,865$ and $20\,045$ cm^{-1} are greatly narrowed, and their maximal values are at $39\,728$ and $40\,090$ cm^{-1}, respectively, which correspond to the two transition frequencies ω_{8d} and ω_{9d} (labeled with olive dashed lines). Thus, the selective excitation of $(2+1)$ REMPI-PS in Fig. 4 can be intuitively understood as follows. Due to the narrowing and movement of the two-photon power spectrum by the cubic phase modulation, the optical pathway through excited state $8d$ is mainly excited for $\omega_{\text{step}} = 19\,865$ cm^{-1}, while the optical pathway through excited state $9d$ is mainly excited for $\omega_{\text{step}} = 20\,045$ cm^{-1}, as shown in Fig. 1.

IV. CONCLUSIONS

In summary, we have theoretically demonstrated that the $(2+1)$ REMPI-PS in Na atoms can be selectively excited by shaping the femtosecond laser pulse with a cubic phase modulation. Our results showed that the $(2+1)$ REMPI-PS signals between neighboring excited states can be differentiated from their indistinguishable photoelectron spectra, and one is enhanced while the other one is effectively suppressed. Moreover, the two-photon power spectrum was used to explain the physical control mechanism of the selective excitation of $(2+1)$ REMPI-PS. We believe that these results are a very promising application in the study of excited-state or Rydberg-state structure.

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