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High-resolution resonance-enhanced multiphoton-ionization photoelectron spectroscopy of Rydberg states *via* spectral phase step shaping

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Femtosecond-induced resonance-enhanced multi-photon ionization (REMPI) photoelectron spectroscopy of the Rydberg states is faced with low spectral resolution due to the broadband laser spectrum. In this paper, we theoretically demonstrate that a high-resolution (2 + 1) REMPI photoelectron spectrum of the Rydberg states in a sodium (Na) atom can be obtained by shaping a femtosecond laser pulse with a spectral phase step modulation. Our results show that, by using a phase-shaped femtosecond laser pulse, some narrowband holes or peaks in the REMPI photoelectron spectrum can be created, and the positions of these holes or peaks are correlated with the eigenenergies of the Rydberg states. Thus, by observing these holes or peaks in the REMPI photoelectron spectrum, both the high-resolution REMPI photoelectron spectrum and the energy-level diagram of the Rydberg states can be obtained.

Rydberg states are the states of an atom or molecule in which the electrons have been excited to the high principal quantum number orbits, which usually can be obtained by electron impact excitation,[1] charge exchange excitation,[2] or optical excitation.[3] Because of their novel properties of extreme sensitivity to electric and magnetic fields, long energy-level lifetime, and large electric dipole moment and magnetic susceptibility, the Rydberg states have attracted extensive attention from physicists and chemists, and have been widely applied in various research fields, such as plasma,[4] astrophysics,[5] and quantum information.[6]

Resonance-enhanced multi-photon ionization (REMPI) photoelectron spectroscopy has been proven to be a well-established tool to study the Rydberg states.[7–14] A femtosecond laser pulse is an ideal excitation source to use in the REMPI photoelectron spectroscopy of the Rydberg states because of its broad laser spectrum and high pulse intensity. However, a major drawback of femotseond-induced REMPI photoelectron spectroscopy is low spectral resolution because of the large bandwidth of the photoelectron spectrum. Therefore, how to achieve high-resolution REMPI photoelectron spectroscopy of the Rydberg states is a question that requires researchers' attention. Recently, with the advent of the femtosecond pulse shaping technique by controlling the spectral phase and/or amplitude in the frequency domain, the coherent control strategy using the shaped femtosecond laser pulse has been shown to be an effective method to narrow the REMPI photoelectron spectrum of the excited states and therefore improve the photoelectron spectral resolution.[15–23] In this paper, we propose a spectral phase step modulation to achieve high-resolution (2 + 1) REMPI photoelectron spectroscopy of the Rydberg states in a sodium (Na) atom. We show that some narrowband holes or peaks in the REMPI photoelectron spectrum can be created by the phase-shaped femtosecond laser pulse and these holes or peaks are related to the Rydberg states, and therefore both the high-resolution REMPI photoelectron spectrum and the energy-level diagram of the Rydberg states can be obtained by observing these holes or peaks in the REMPI photoelectron spectrum.

Fig. 1(a) shows a schematic diagram of the (2 + 1) resonance-enhanced multiphoton ionization process of the Rydberg states in a Na atom pumped by a femtosecond laser pulse $E(t)$, the transitions from the ground state $|3s>$ to the Rydberg states $|ms>$ and $|nd>$ are excited by a non-resonant two-photon absorption, and then the populations in the Rydberg states are ionized by absorbing the other photon. We assume that the laser pulse duration is much smaller than the lifetime of the Rydberg states and only the ground state $|3s>$ is initially populated. Thus, the (2 + 1) REMPI photoelectron spectrum $P(E_v)$ can be approximated based on Wollenhaupt's theory as[15–19]

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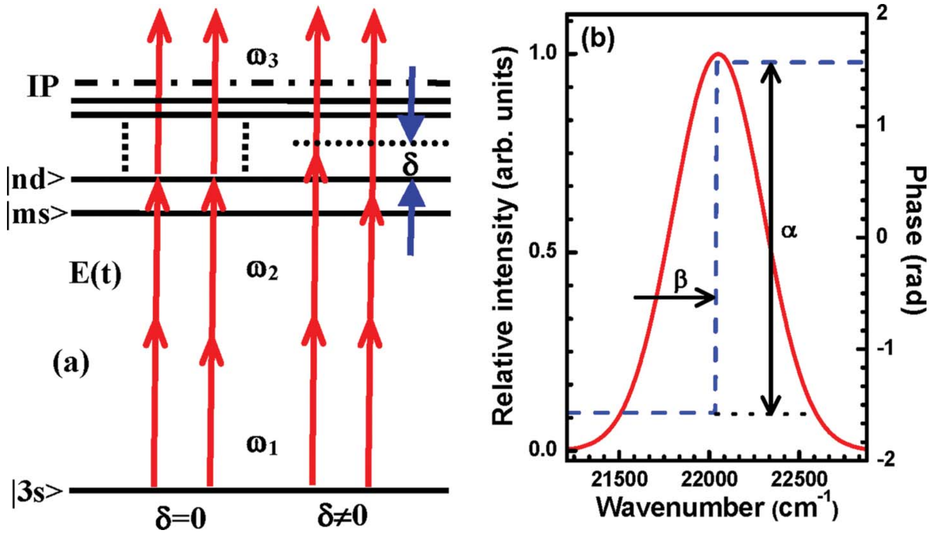

Fig. 1 (a) The (2 + 1) resonance-enhanced multiphoton-ionization process of Rydberg states in a Na atom. (b) The laser spectrum is modulated by a spectral phase step modulation, where α and β represent the modulation depth and step position, respectively.

$$P(E_\mathrm{v}) \propto \int_{-\infty}^{+\infty} E(t) C_\mathrm{Ryd}(t) \exp\left[\frac{\mathrm{i}(E_\mathrm{v}+E_\mathrm{I}-E_\mathrm{Ryd})t}{\hbar}\right]\mathrm{d}t, \quad (1)$$

where E_Ryd is the eigenenergy of the Rydberg states, E_I is the ionization energy from the ground state |3s>, and $C_\mathrm{Ryd}(t)$ is the time-dependent probability amplitude in the Rydberg states. Based on second-order time-dependent perturbation theory in a weak laser field,[24] $C_\mathrm{Ryd}(t)$ can be written as

$$C_\mathrm{Ryd}(t) \propto \int_{-\infty}^{t} E^2(t') \exp[\mathrm{i}\omega_\mathrm{Ryd} t']\mathrm{d}t', \quad (2)$$

where ω_Ryd is the transition frequency from the ground state |3s> to the Rydberg states.

In our simulation, we consider the Rydberg states of a Na atom including the highly excited states |*m*s> (*m* is integer number, 11–18) and |*n*d> (*n* is integer number, 9–17), and their corresponding transition frequencies are listed in Table 1. The ionization energy of a Na atom is E_I = 5.14 eV, corresponding to a frequency of 41 456 cm^{-1}. The laser central frequency is set to be ω_L = 20 250 cm^{-1}, and its pulse duration (full width at half maximum) is τ = 50 fs. Here, we utilize a spectral phase step modulation to control the (2 + 1) REMPI photoelectron spectrum, and this simple phase modulation is shown in Fig. 1(b), where α and β represent the modulation depth and step position, respectively. Mathematically, the phase step modulation can be defined by the formula $\Phi(\omega) = \alpha\sigma(\omega - \beta)/2$, where $\sigma(\omega - \beta)$ is the signum function which takes the values of -1 for $\omega < \beta$ and 1 for $\omega > \beta$, thus $\Phi(\omega)$ is characterized by a phase jump from $-\alpha/2$ to $\alpha/2$ at the step position β. Thus, the phase-shaped laser field in frequency domain $E_\mathrm{shape}(\omega)$ can be written as $E_\mathrm{shape}(\omega) = E(\omega) \times \exp[\mathrm{i}\alpha\sigma(\omega - \beta)/2]$, where $E(\omega)$ is the Fourier transform of the unmodulated laser field $E(t)$, and the phase-shaped laser field in time domain $E_\mathrm{shape}(t)$ is given by $E_\mathrm{shape}(t) = E(t) \times \cos(\alpha/2) + E(t) \otimes \exp(\mathrm{i}\beta t)/(\pi t) \times \sin(\alpha/2)$. The temporal intensity profile of the shaped laser field by varying the modulation depth α and the step position β has been explicitly discussed in ref. 15. By substituting $E_\mathrm{shape}(t)$ into eqn (1) and (2), the (2 + 1) REMPI photoelectron spectrum $P(E_\mathrm{v})$ induced by the phase-shaped laser pulse can be obtained.

Table 1 The Rydberg states of a Na atom and their corresponding frequencies

ω_{9d}	ω_{11s}	ω_{10d}	ω_{12s}	ω_{11d}	ω_{13s}	ω_{12d}	ω_{14s}	ω_{13d}
40 090	40 271	40 349	40 482	40 540	40 641	40 685	40 764	40 799
ω_{15s}	ω_{14d}	ω_{16s}	ω_{15d}	ω_{17s}	ω_{16d}	ω_{18s}	ω_{17d}	Units
40 861	40 888	40 938	40 961	41 002	41 020	41 053	41 069	(cm^{-1})

Fig. 2 shows the REMPI photoelectron spectrum induced by the unshaped laser pulse (a), together with the contribution of each Rydberg state listed in Table 1 (b). Only a single

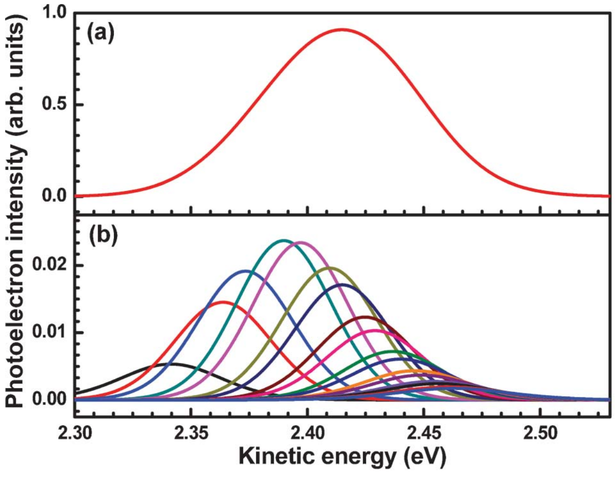

Fig. 2 The REMPI photoelectron spectrum induced by the unshaped laser pulse (a), together with the contribution of each Rydberg state listed in Table 1 (b).

broadband photoelectron spectrum for the unshaped laser pulse is observed (see Fig. 2(a)), that is to say, the contribution of each Rydberg state in the photoelectron spectrum is indistinguishable. The essential origin is that the broadband femtosecond laser spectrum and the small energy separation of the Rydberg states result in the broadband photoelectron spectra of each Rydberg state overlaping with the photoelectron spectra of the neighboring Rydberg states, as shown in Fig. 2(b). To study the Rydberg state structure or the photoionization dynamical process in the Rydberg states, it is crucial to achieve a high-resolution REMPI photoelectron spectrum of the Rydberg states. Therefore, our research goal is to distinguish between the contributions of each Rydberg state in the whole photoelectron spectrum by spectral phase step modulation.

Our previous study showed that the photoelectron intensity at a given kinetic energy in the (2 + 1) REMPI photoelectron spectrum can be suppressed or enhanced by varying the modulation depth α of the spectral phase step modulation,[20] and so this can provide a feasible scheme to achieve a high-resolution REMPI photoelectron spectrum of the Rydberg states. Fig. 3(a) and 4(a) show the REMPI photoelectron spectra induced by the shaped laser pulse with the step position β = 20 250 cm^{-1} for the modulation depth $\alpha = 0.2\pi$ and 1.5π, respectively. As can be seen, the photoelectron spectra structures are strongly modulated by the spectral phase step modulation, seventeen narrowband holes in the photoelectron spectrum are observed when the modulation depth is $\alpha = 0.2\pi$, while seventeen narrowband peaks in the photoelectron spectrum are observed when the modulation depth is $\alpha = 1.5\pi$. By separately observing the photoelectron spectra of the seventeen Rydberg states listed in Table 1, as shown in Fig. 3(b) and 4(b), it can be verified that the seventeen holes or peaks in the photoelectron spectra come from the contributions of the seventeen Rydberg states. Obviously, the photoelectron spectra of the seventeen Rydberg states are indistinguishable, but the seventeen holes or peaks in the whole photoelectron spectra associated with the seventeen Rydberg states are distinguishable. Consequently, by observing these holes or peaks in the photoelectron spectra, the high-resolution REMPI photoelectron spectrum of the Rydberg states can be obtained.

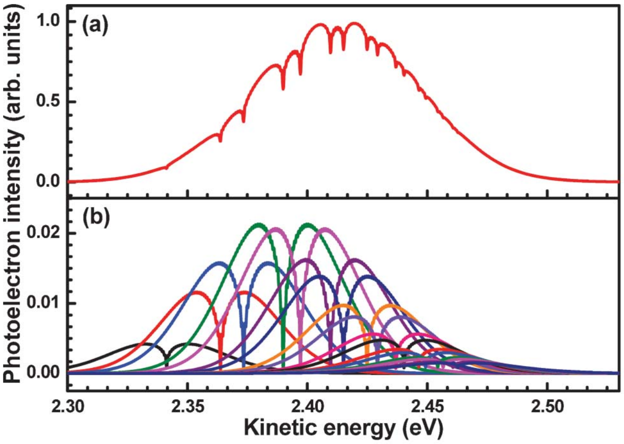

Fig. 3 The REMPI photoelectron spectrum induced by the shaped laser pulse with the step position β = 20 250 cm^{-1} and $\alpha = 0.2\pi$ (a), together with the contribution of each Rydberg state (b).

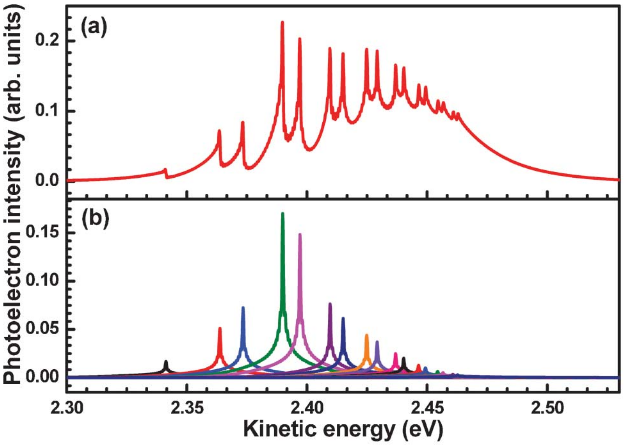

Fig. 4 The REMPI photoelectron spectrum induced by the shaped laser pulse with the step position β = 20 250 cm^{-1} and $\alpha = 1.5\pi$ (a), together with the contribution of each Rydberg state (b).

The photoelectron spectral modulation in Fig. 3(a) and 4(a) can be explained as follows. In the frequency domain, the different excitation pathways of the (2 + 1) resonance-enhanced three-photon ionization process are schematically shown in Fig. 1(a). Each excitation pathway is either on resonance (*i.e.*, $\delta = 0$) or near resonance (*i.e.*, $\delta \neq 0$) with these Rydberg states. The on-resonant excitation pathway corresponds to the combination of the three photons with frequencies of ω_1, $\omega_{\mathrm{Ryd}} - \omega_1$ (*i.e.*, ω_2) and ω_3, while the near-resonant excitation pathway corresponds to the combination of the three photons with frequencies of ω_1, $\omega_{\mathrm{Ryd}} - \omega_1 + \delta$ (*i.e.*, ω_2) and $\omega_3 - \delta$. It is easy to verify that the on-resonant term is maximized by the transform-limited laser pulse for all values of $|P(E_{\mathrm{v}})|^2$, while the near-resonant term integrates over both positive (*i.e.* $\delta > 0$) and negative ($\delta < 0$) contributions, and therefore the transform-limited laser pulse induces a destructive interference. The spectral phase step modulation (see Fig. 1(b)), which produces a phase inversion, can control the constructive or destructive interference at a given kinetic energy E_{v} by varying the modulation depth α. That is to say, the shaped laser pulse by the spectral phase step modulation can induce a hole or peak in the photoelectron spectrum of each Rydberg state, and these hole or peak positions are different for different Rydberg states (see Fig. 3(b) and 4(b)). Therefore, when the photoelectron spectra of these Rydberg states are coherently superimposed, these holes or peaks corresponding to these Rydberg states will emerge in the full photoelectron spectrum.

To achieve a high-resolution REMPI photoelectron spectrum of these Rydberg states, it is crucial to narrow these holes or peaks as much as possible. Our theoretical calculations find that the bandwidths of these holes or peaks (Full Width at Half

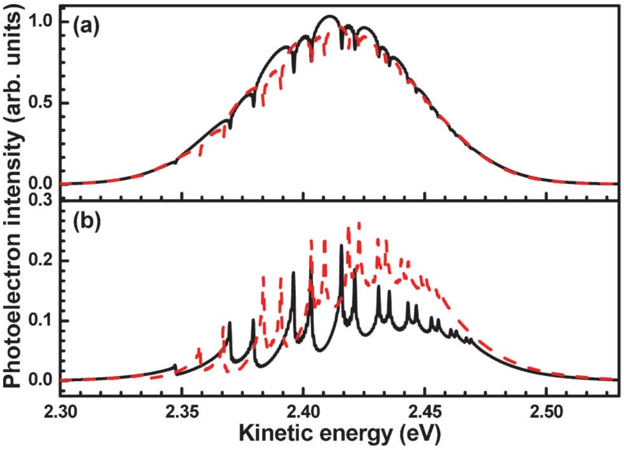

Fig. 5 The REMPI photoelectron spectra induced by the shaped laser pulse with modulation depths of $\alpha = 0.2\pi$ (a) and 1.5π (b) for the step positions $\beta = 20\,200$ (red dashed line) and 20 300 cm^{-1} (black solid line).

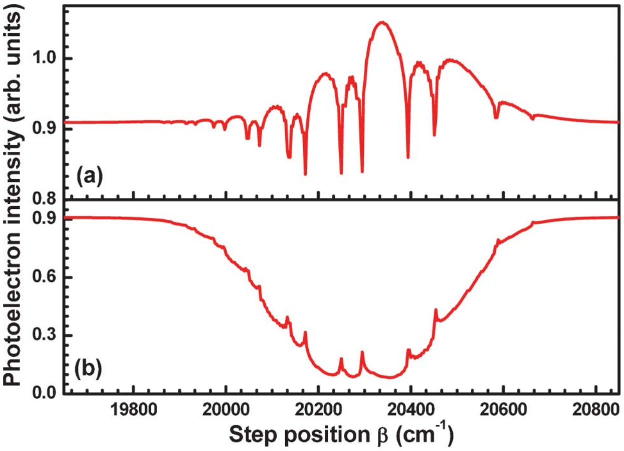

Fig. 6 The photoelectron intensity at the kinetic energy of $E_v = 2.415$ eV as the function of the step position β with the modulation depth $\alpha = 0.2\pi$ (a) and 1.5π (b).

Maximum (FWHM)) depend on the laser spectral resolution in the phase step, and higher laser spectral resolution can yield narrower holes or peaks. Therefore, increasing the laser spectral resolution in the phase step can improve the photoelectron spectral resolution. In our simulation, the laser spectral resolution in the phase step is 1.67 cm^{-1}, and the bandwidths of the hole and peak in the photoelectron spectrum for the Rydberg state |11d> are about 2.6 and 0.8 meV (see Fig. 3(b) and 4(b)). Obviously, compared with the holes, inducing the peaks in the photoelectron spectrum can lead to higher spectral resolution (see Fig. 3(a) and 4(a)).

Fig. 5 shows the REMPI photoelectron spectra induced by the shaped laser pulse with modulation depths of $\alpha = 0.2\pi$ (a) and 1.5π (b) for the step positions $\beta = 20\,200$ (red dashed line) and 20 300 cm^{-1} (black solid line). One can see that, by varying the step position β, the positions of these holes or peaks in the photoelectron spectrum will shift, but the energy difference between the photon energy at the step position E_β and the electron kinetic energy at these holes or peaks $E_v^{\text{hole(peak)}}$ remains unchanged, and is exactly equal to the energy difference between the ionization energy E_I and the eigenenergies of the Rydberg states E_{Ryd}, *i.e.*, $E_\beta - E_v^{\text{hole(peak)}} = E_I - E_{\text{Ryd}}$. Therefore, if the ionization energy E_I is known, the eigenenergies of the Rydberg states E_{Ryd} can be determined by observing these holes or peaks in the photoelectron spectrum using the spectral phase step modulation, which can provide a good method to study the energy-level diagram of the Rydberg states.

Since the positions of these holes or peaks in the REMPI photoelectron spectrum are correlated with the step position β and the eigenenergies of the Rydberg states E_{Ryd}, an alternative way to achieve a high spectral resolution of the Rydberg states is by measuring the photoelectron intensity at a given kinetic energy by scanning the step position β. Fig. 6 shows the photoelectron intensity at the kinetic energy of $E_v = 2.415$ eV as a function of the step position β with modulation depths of $\alpha = 0.2\pi$ (a) and 1.5π (b). Again, seventeen distinct holes are observed when the modulation depth $\alpha = 0.2\pi$ and seventeen distinct peaks are observed when the modulation depth $\alpha = 1.5\pi$. Based on the relation $E_\beta - E_v^{\text{hole(peak)}} = E_I - E_{\text{Ryd}}$, it is easy to verify that the seventeen holes or peaks are related to the seventeen Rydberg states listed in Table 1. Furthermore, it can be found that the separation of these holes or peaks is exactly equal to the frequency difference of the Rydberg states, and so this can provide an excellent method to directly determine the energy separation of the Rydberg states.

Finally, we analyzed the feasibility of our present scheme by experiment. Two important issues for our scheme must be addressed, one is the spectral phase step modulation of the femtosecond laser pulse and the other is the instrument used to measure the photoelectron spectrum with high energy resolution. With the advent of the ultrafast pulse shaping technique, the spectral phase modulation of the femtosecond laser pulse with an almost arbitrary shape can be obtained by a programmable 4*f*-configuration zero-dispersion pulse shaper combined with a one-dimensional liquid-crystal spatial light modulator.[25] Recently, the spectral phase step modulation based on the femtosecond pulse shaping system has been successfully applied in experiment to control the REMPI photoelectron spectrum in a strong laser field.[15] In a real experiment, the energy resolution of the photoelectron spectrum using a Scienta R4000 analyzer can be up to 360 μeV,[26] which could completely meet the experimental requirements of our scheme.

In conclusion, we have proposed a feasible scheme to obtain the high-resolution (2 + 1) REMPI photoelectron spectrum of the Rydberg states in a Na atom by shaping a femtosecond laser pulse with a spectral phase step modulation. It was shown that the phase-shaped laser pulse can create holes and peaks in the REMPI photoelectron spectrum, and the positions of these holes or peaks are correlated with the eigenenergies of the Rydberg states. Therefore, the high-resolution REMPI photoelectron spectrum and the energy-level diagram of the Rydberg states can be obtained by observing these holes or peaks in the photoelectron spectrum. We believe that these theoretical results can provide a prediction for an experimental study and are expected to be applied in the study of photoionization dynamical process in the Rydberg states.

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