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SELECTIVE MULTIPHOTON IONIZATION OF SODIUM BY FEMTOSECOND LASER PULSES

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Abstract. Multiphoton ionization of sodium by femtosecond laser pulses of 800 nm wavelength is studied in the range of laser peak intensities from 3.5 to 8.8 TW/cm^2. Photoelectron probability distributions and the energy spectra are determined numerically by solving the time dependent Schrödinger equation. The calculated spectra agree well with recent experimental results. A partial wave analysis of the spectral peaks related to Freeman resonances has shown that under specific conditions the resonantly enhanced multiphoton ionization may be realized through a single energy level.

1. INTRODUCTION

A remarkable feature of the photoelectron energy spectra (PES) obtained at the multiphoton ionization (MPI) of atoms using short (sub-picosecond) laser pulses is the existence of the so-called Freeman resonances. The mechanism which is responsible for occurrence of these spectral structures is the dynamic (or AC) Stark shift which brings the atomic energy levels into resonance with an integer multiple of the photon energy. Freeman et al. (1987) have shown that when atomic states during the laser pulse transiently shift into resonance, the resonantly enhanced multiphoton ionization (REMPI) takes place, increasing the photoelectron yield, and one observes peaks at the corresponding values of photoelectron energy. Thus, the peaks in the PES are related to the REMPI occurring via different intermediate states. A particular challenge would be the selective ionization of the atom through a single energy level which could produce a high ion yield. By increasing the laser intensity one increases the yield, but also spreads the electron population over multiple energy levels and, in turn, reduces the selectivity. Hart et al (2016) have shown that improved selectivity and yield could be achieved by controlling the resonant dynamic Stark shift of sodium states via intensity of the laser pulse of an appropriate wavelength.

Here we study the MPI of the sodium atom by the laser pulse of 800 nm wavelength and 57 fs full width at half maximum (FWHM) with the peak intensities ranging from 3.5 to 8.8 TW/cm^2, which are the same values as used in the experiment by Hart et al. Using the single-active-electron approximation we calculate the photoelectron probability distribution and the PES by solving numerically the time dependent Schrödinger equation (TDSE). In order to make a deeper insight into the ionization process, we perform, in addition, a partial-wave analysis of the photoelectron outgoing wave.

2. THE MODEL, ENERGY SCHEME AND PHOTOIONIZATION CHANNELS

Within the single-electron model the dynamics of the valence (active) electron of sodium atom in an alternating electric field $F(t)$ is described by Hamiltonian (in atomic units)

$$H = \frac{\mathbf{p}^2}{2} + V_{\text{core}}(r) - F(t)z. \tag{1}$$

The effective core potential $V_{\text{core}}(r)$ describes the interaction of the valence electron with the atomic core (inner electrons + atomic nucleus). For this purpose we use the Hellmann's pseudopotential $V_{\text{core}}(r) = -1/r + A\,e^{-ar}/r$. The parameters $A = 21$ and $a = 2.54920$ provide the correct value for the ionization potential of lithium $I_{\text{p}} = 5.1391\,\text{eV} = 0.18886\,\text{a.u.}$ and reproduce approximately the energies of singly-excited states (see Fig. 1).

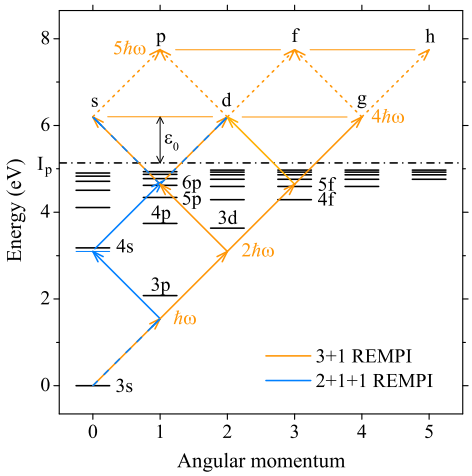

Figure 1: The unperturbed energy levels (short black lines) corresponding to singly excited states of sodium (Sansonetti, 2008) relative to its ground state (3s) and possible four-photon and five-photon absorption pathways (arrows) from the ground state to continuum for the radiation of 800 nm wavelength ($\hbar\omega \approx 1.55\,\text{eV}$). The continuum boundary is drown by the dash-dot line and ϵ_0 is the excess energy of photoelectrons produced in the nonresonat four-photon ionization.

We consider a linearly polarized laser pulse of the form

$$F(t) = F_{\text{peak}} \sin^2(\pi t/T_{\text{p}}) \cos(\omega t), \quad 0 < t < T_{\text{p}} \tag{2}$$

(otherwise $F(t) = 0$). Here ω, F_{peak} and T_{p} are the frequency of laser field, the peak value of its electric component and the pulse duration ($2\times$ FWHM), respectively. Due to the axial symmetry of the system, the magnetic quantum number m of the valence electron is a good quantum number and we set $m = 0$ (the ground state value).

The photoionization process is simulated by calculating the evolution of the wave function of valence electron $\psi(\mathbf{r}, t)$, which is initially ($t = 0$) chosen to be the lowest eigenstate of Hamiltonian (1) (then $F = 0$) that describes the sodium ground state. The evolution is calculated by integrating the TDSE (see Bunjac et al., 2017).

Fig. 1(a) shows the lowest energy levels corresponding to singly-excited states of sodium and possible multiphoton absorption pathways during the interaction of the atom with a laser radiation of 800 nm wavelength ($\hbar\omega = 0.05695$ a.u. ≈ 1.55 eV). At this wavelenghth there are three dominant REMPI channels: (i) (3+1)-photon ionization via excitation of 5p, 6p and 7p states, giving rise to photoelectrons with s and d-symmetry; (ii) (3+1)-photon ionization via excitation of 4f, 5f and 6f states, producing photoelectrons with d and g-symmetry; (iii) (3+1+1)-photon ionization via nearly resonant two-photon transition 3s $\rightarrow$ 4s and subsequent excitation of P-states, giving rise to photoelectrons with s and d-symmetry.

3. PARTIAL WAVE ANALYSIS

In order to determine the PES, the outgoing part of the active electron wave function $\psi(\mathbf{r}, t)$ at a time $t > T_p$ is transformed from the coordinate to momentum representation $\bar{\psi}(\mathbf{k}, t)$ by the Fourier transform and expanded in terms of partial waves

$$\bar{\psi}(\mathbf{k}) = \sum_l \Phi_l(k) Y_{l0}(\vartheta), \tag{3}$$

where $Y_{l0}(\vartheta)$ are the spherical harmonics with $m = 0$ and $\Phi_l(k) = \int Y^*_{l0}(\vartheta)\, \bar{\psi}(\mathbf{k})\, \mathrm{d}\Omega$ are the corresponding radial functions. Using the representation of $\bar{\psi}$ in cylindrical coordinates, the radial functions can be calculated as

$$\Phi_l(k) = 2\pi \int_0^\pi \bar{\psi}(k \sin\vartheta, k\cos\vartheta)\, Y_{l0}(\vartheta)\, \sin\vartheta\, \mathrm{d}\vartheta. \tag{4}$$

According to partial wave expansion (3), the radial probability density of photoelectrons in momentum space is the sum $w(k) = \sum_l w_l(k)$, where

$$w_l(k) = |\Phi_l(k)|^2\, k^2 \tag{5}$$

are the partial probability densities. These quantities for $l = 0, \ldots, 5$, as functions of the photoelectron excess energy $\epsilon = \hbar^2 k^2 / 2m_e$, are shown in the left column of Fig. 2 for three values of the laser peak intensity: 3.5, 4.9 and 8.8 TW/cm^2. The corresponding total probability densities w represent the PES for these three values of laser intensity. They are shown in the right column of Fig. 2 together with the corresponding spectra obtained experimentally (Hart et al., 2016).

The spectra, both the calculated and experimental, exhibit a typical above threshold ionization (ATI) structure with prominent peaks separated by the photon energy $\hbar\omega \approx 1.55$ eV. Fig. 2 shows the peaks corresponding to lowest three orders of ATI (MPI by $4 + s$ photons, $s = 0, 1, 2$) which are located approximately at $\epsilon = 0.8\,\mathrm{eV} + s\hbar\omega$. The partial wave analysis recovers the character of these peaks. We see in Fig. 2 (left) that for the photoelectron energies around the main peak ($s = 0$, $\epsilon \approx 0.8$ eV) and around the second-order ATI peak ($s = 2$, $\epsilon \approx 3.9$ eV) dominant contributions in the total probability density come from the partial waves with even l (s, d, g-waves). Thus, the photoelectrons with these energies are generated by absorbing an even number of photons ($N = 4$ and 6). Contrarily, in the vicinity of the first-order ATI peak ($s = 1$, $\epsilon \approx 2.35$ eV) the partial waves with even l are suppressed and those with odd l (p, f, h-waves) dominate. Therefore, in this case odd number of photons is absorbed (here $N = 5$).

Fig. 2 (left column) shows that at the laser peak intensity of 3.5 TW/cm^2 dominant contribution in the main peak (around 0.8 eV) comes from d-electrons, while at the intensity of 8.8TW/cm^2 the electrons of g-symmetry dominate. In conclusion, by changing the laser intensity, one selects the main ionization channel – in the first case this is the 3+1 (or 2+1+1) REMPI via 5p state, while in the second case it is the 3+1 REMPI via 4f state.

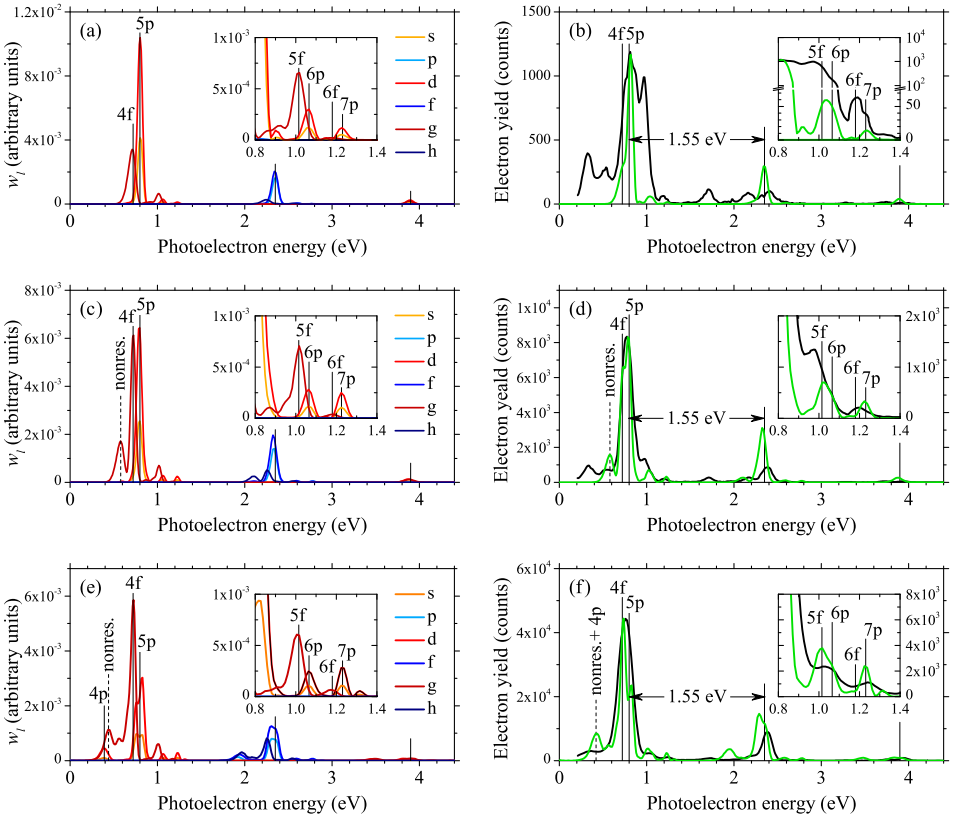

Figure 2: Partial probability densities w_l for $l = 0, \ldots, 5$ (left column) and the total probability density w (right column, green line) as functions of the photoelectron energy $\epsilon = \hbar^2 k^2/(2m_e)$ obtained at three values of the laser peak intensity: (a,b) 3.5 TW/cm^2, (c,d) 4.9 TW/cm^2, (e,f) 8.8 TW/cm^2. Experimental results (Hart et al., 2016) are represented by full black lines (right column). The full vertical lines mark the energies of two REMPI channels (via f and p states) of the threshold peak as well as the position of 5p subpeak in the higher order ATI peaks.

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