Partial-wave analysis of multiphoton ionization of sodium by femtosecond laser pulses of 800 nm wavelength in over-the-barrier ionization regime

A. Bunjac, D. B. Popović, and N. S. Simonović

Institute of Physics, University of Belgrade, P.O. Box 57, 11001 Belgrade, Serbia

Multiphoton ionization of sodium by laser pulses of 800 nm wavelength and 57 fs duration is studied in the range of laser peak intensities belonging to over-the-barrier ionization regime. Photoelectron momentum distributions (PMD) and the energy spectra are determined numerically by solving the time dependent Schrödinger equation. The calculated spectra agree well with the spectra obtained experimentally by Hart et al. [Phys. Rev. A 93, 063426 (2016)]. The contributions of photoelectrons with different values of the orbital quantum number in the PMD are determined by expanding the photoelectron wave function in terms of partial waves. Partial wave analysis of the spectral peaks related to Freeman resonances has shown that each peak has photoelectron contributions from different ionization channels which are characterized by different photoelectron energies and different symmetries of released photoelectron wave-packets. These findings are justified by calculating the populations of excited states during the pulse. Our analysis indicates that the contribution of specific ionization channels in the total photoelectron yield might be selectively increased by varying to some extent the values of pulse parameters used here.

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I. INTRODUCTION

Strong-field ionization of the alkali-metal atoms has been studied intensively over the past ten years, both experimentally and theoretically including ab initio numerical calculations [1, 2, 3]. A specific feature of this group of atoms – a low ionization potential, which ranges from \( I_p \approx 3.89 \text{ eV} \) (cesium) to 5.39 eV (lithium), causes that a considerably smaller number of photons of a given energy \( h\omega \) is required for their photoionization than for the ionization of other atoms. For example, with the laser wavelength of around 800 nm ( \( h\omega \approx 1.55 \text{ eV} \) ) it takes four photons to ionize an alkali-metal atom, unlike to the case of frequently used noble gases where this number is of the order of ten. Since for a dipole transition requiring \( N \) photons the lowest order perturbation theory predicts that the photon absorption rate \( W \) is proportional to the \( N \)-th power of the laser intensity \( I \) ( \( W \sim I^N \) if \( I \ll I_a \), where \( I_a = 3.50945 \times 10^{16} \text{ W/cm}^2 \) is the atomic unit value for intensity, see e.g. [12]), measurable effects in experiments with multiphoton ionization (MPI) of alkali can be observed at relatively low laser intensities, available in table-top laser systems.

The perturbative treatment, however, is not applicable at higher intensities which can be achieved today. One indication of the nonperturbative regime is the so-called above threshold ionization (ATI) [4, 10, 12] in which the atom absorbs more photons than the minimum required. Under these conditions the photoelectron spectra (PES, electron yield versus their excess energy \( \epsilon \) ) were seen to consist of several peaks, separated by the photon energy \( h\omega \), and appearing at energies \( \epsilon^{(s)} = (N_0 + s)h\omega - I_p \), where \( N_0 \) is the minimum number of photons needed to exceed the ionization potential \( I_p \) and \( s = 0, 1, \ldots \) is the number of excess (“above-threshold”) photons absorbed by the atom. (For the alkali-metal atoms and the laser of 800 nm wavelength, \( N_0 = 4 \).) By increasing the intensity over a certain value, \( W \) does not follow further the prediction \( I^{N_0+s} \) of the perturbation theory.

At even larger intensities, the electric component of the laser field becomes comparable with the atomic potential, opening up another ionization mechanism – the tunnel ionization. In this case the field distorts the atomic potential forming a potential barrier through which the electron can tunnel. Multiphoton and tunneling ionization regimes are distinguished by the value of Keldysh parameter [13] which can be written as \( \gamma = \sqrt{I_p/(2U_p)} \), where \( U_p = e^2F^2/(4m_\epsilon\omega^2) \) is the ponderomotive potential of ejected electron with mass \( m_\epsilon \) and charge \( e \). The value of the electric field \( F \) in the expression for \( \gamma \) corresponds to the peak value of laser intensity. Multiphoton and tunneling regimes are characterized by \( \gamma \gg 1 \) (high-intensity, long-wavelength limit) and \( \gamma \ll 1 \) (low-intensity, short-wavelength limit), respectively. The transition regime at \( \gamma \approx 1 \) for alkali-metal atoms is reached at considerably lower intensities than for other atoms, again due to the small ionization potential \( I_p \). The experiments accessing the strong-field regime with alkali [3, 6, 7, 9] have revealed that the commonly used strong-field ionization models in the form of a pure MPI or tunnel ionization cannot be strictly applied. The problem, however, goes beyond by using an ab-initio numerical method for solving the time-dependent Schrödinger equation (TDSE).

Finally, at a sufficiently high laser intensity, the field strength overcomes the atomic potential. This can be considered as the limiting case of tunnel ionization when the barrier is suppressed below the energy of atomic state. This regime is usually referred to as over-the-barrier ionization (OBI). Such a barrier suppression takes place independently of the value of Keldysh parameter. For neu-
tral atoms the threshold value of field strength for OBI is estimated as $F_{\text{OBI}} \approx \frac{I_0^2}{4}$ (in atomic units). $F_{\text{OBI}}$ values for alkali, determined more accurately, are given in Ref. 14. The corresponding laser intensities can be obtained by formula $I = I_a F^2$, where $F$ is expressed in atomic units and $I_a$ is the above introduced atomic unit for intensity. For noble gas atoms irradiated by the laser of wavelength from the visible light domain, OBI was occurring well into the tunneling regime 15. This is, however, not a general rule. For atoms with low ionization potentials, as the alkali-metal atoms are, the OBI threshold, compared to that for hydrogen or noble gases, is shifted to significantly lower values of the field strength. For example, the laser peak intensity that corresponds to the OBI threshold for sodium is about 3.3 TW/cm$^2$ ($F_{\text{OBI}} = 0.0097$ a.u. 14), whereas the value of Keldish parameter for the sodium atom interacting with the radiation of this intensity and 800 nm wavelength is $\gamma = 3.61$. Thus, the OBI threshold in this case belongs to the MPI regime. Previous experiments and theoretical studies have already mentioned this peculiar situation for sodium and other alkali 5 7 9. In addition, it is demonstrated that at intensities above the OBI threshold the atomic target is severely ionized before the laser’s peak intensity is reached 6. Thus, the ionization occurs at the leading edge of the pulse only, that is equivalent to the ionization by a shorter pulse.

A remarkable feature of the photoelectron spectra obtained using short (sub-picosecond) laser pulses is the existence of substructures in ATI peaks, known as Freeman resonances. The mechanism which is responsible for occurrence of these substructures is the dynamic (or AC) Stark shift 10,11,16 which brings the atomic energy levels into resonance with an integer multiple of the photon energy. Freeman et al. 17,18 have shown that when atomic states during the laser pulse transiently shift into resonance, the resonantly enhanced multiphoton ionization (REMPI) 11,12,19 takes place, increasing the photoelectron yield, and one observes peaks at the corresponding values of photoelectron energy. Thus, the peaks in the PES can be related to the REMPI occurring via different intermediate states.

The resonant dynamic Stark shift of energy levels corresponding to sodium excited states $nl$ ($n \leq 6$), relative to its ground state (3s) energy, is recently calculated for the laser intensities up to 7.9 TW/cm$^2$ and wavelengths in the range from 455.6 to 1139 nm 8. These data are used to predict the positions of REMPI peaks in the PES of sodium interacting with an 800 nm laser pulse. Freeman resonances in the PES of alkali-metal atoms have been studied in papers 10,16, mentioned at the beginning of Introduction, where a number of significant results have been reported.

The dynamic Stark shift also appears as an important mechanism in the strong-field quantum control of various atomic and molecular processes 20,22. Focusing on the MPI of atoms, a particular challenge would be the selective ionization of an atom through a single energy level which could produce a high ion yield. By increasing simply the laser intensity one increases the yield, but also spreads the electron population over multiple energy levels 18 and, in turn, reduces the selectivity. Krug et al. 7 have shown in the case of multiphoton ionization of sodium that chirped pulses can be an efficient tool in strong-field quantum control of multiple states. Hart et al. in their paper 7 claim that improved selectivity and yield could be achieved by controlling the resonant dynamic Stark shift via intensity of the laser pulse of an appropriate wavelength (∼800 nm).

In this paper we study the photoionization of sodium by the laser pulse of 800 nm wavelength and 57 fs duration with the peak intensities ranging from 3.5 to 8.8 TW/cm$^2$, which belong to OBI domain in the MPI regime and which have been used in the experiment by Hart et. al. 7. Using the single-active-electron approximation we calculate the corresponding photoelectron momentum distribution (PMD) and the PES by solving numerically the TDSE and perform a similar analysis as it has been done in Refs. 10,19. In order to make a deeper insight into the ionization process, in addition, we perform a partial-wave analysis of the calculated PMD. In the next section we describe the model and in Sec. III consider the excitation scheme and ionization channels. In Sec. IV we analyze the calculated photoelectron momentum distribution and energy spectra. A summary and conclusions are given in Sec. V.

II. THE MODEL

Singly-excited states and the single ionization of the alkali-metal atoms are, for most purposes, described in a satisfactory manner using one-electron models. This follows from the structure of these atoms, which is that of a single valence electron moving in an orbital outside a core consisting of closed shells. In that case the valence electron is weakly bound and can be considered as moving in an effective core potential $V_{\text{core}}(r)$, which at large distances $r$ approaches the Coulomb potential $-1/r$. One of the simplest models for the effective core potential, applicable for the alkali-metal atoms, is the Hellmann pseudopotential 24 which reads (in atomic units)

$$V_{\text{core}}(r) = \frac{1}{r} + \frac{A}{r} e^{-ar}.$$  

The parameters $A = 21$ and $a = 2.54920$ 14 provide the correct value for the ionization potential of sodium $I_p = 5.1391$ eV = 0.18886 a.u. and reproduce approximately the energies of singly-excited states 23 (deviations are less than 1%). The associated eigenfunctions are one-electron approximations of these states and have the form $\psi_{nlm}(r) = R_{nl}(r)Y_{lm}(\Omega)$. Radial functions $R_{nl}(r)$ can be determined numerically by solving the corresponding radial equation.

Here we use this single-active-electron approximation to study the single-electron excitations and ionization of
the sodium atom in a strong laser field. Assuming that the field effects on the core electrons can be neglected (the so-called frozen-core approximation [14]), the Hamiltonian describing the dynamics of valence (active) electron of the sodium atom in an alternating field, whose electric component is \( F(t) \cos \omega t \), reads (in atomic units)

\[
H = -\frac{1}{2} \nabla^2 + V_{\text{core}}(r) - F(t) z \cos \omega t. \tag{2}
\]

We consider the linearly polarized laser pulse whose amplitude of the electric field component (field strength) has the form

\[
F(t) = F_{\text{peak}} \sin^2(\pi t/T_p), \quad 0 < t < T_p \tag{3}
\]

[otherwise \( F(t) = 0 \)]. Here \( \omega \), \( F_{\text{peak}} \) and \( T_p \) are the frequency of the laser field, the peak value of \( F \) and the pulse duration, respectively. Since the system is axially symmetric, the magnetic quantum number \( m \) of the active electron is a good quantum number for any field strength. In the sodium ground state (when \( F = 0 \)) the orbital and the magnetic quantum number are equal to zero and in our calculations we set \( m = 0 \).

The photoionization process is simulated by solving numerically the TDSE for the active electron wave function \( \psi(r, t) \) (i.e. by calculating its evolution), assuming that at \( t = 0 \) the atom is in the ground state represented by the lowest eigenstate of Hamiltonian (2) for \( F = 0 \). We have used the second-order-difference (SOD) scheme [20] that is for this purpose adapted to cylindrical coordinates \((\rho, \varphi, z)\) [5, 27]. Due to the axial symmetry of the system, Hamiltonian (2) and the electron’s wave function do not depend on the azimuthal angle and the dynamics reduces to two degrees of freedom \((\rho, z)\). The calculations were performed on 1000 \( \times \) 2000 grid in the wave-packet propagation domain \( \rho \leq 500 \text{ a.u.}, -500 \text{ a.u.} \leq z \leq 500 \text{ a.u.} \).

III. ENERGY SCHEME AND PHOTOIONIZATION CHANNELS

Fig. 1 shows the lowest energy levels corresponding to singly-excited states of sodium and possible multi-photon absorption pathways during the interaction of the atom with a laser radiation of 800 nm wavelength (\( \hbar \omega \approx 1.55 \text{ eV} \)). At this wavelength there are two dominant REMPI channels: (i) \((3+1)\)-photon ionization via excitation of 5p, 6p and 7p states (including \( 2+1+1 \) process via nearly resonant two-photon transition \( 3s \Rightarrow 4s \) and subsequent excitation of P-states), giving rise to photoelectrons with s and d-symmetry, and (ii) \((3+1)\)-photon ionization via excitation of 4f, 5f and 6f states, giving rise to photoelectrons with d and g-symmetry [2, 21].

Theoretically, if the multiphoton ionization occurs by absorbing \( N \) photons, the excess energy of ejected electrons in the weak field limit is \( 
\epsilon(0) = N \hbar \omega - I_p \). At stronger fields, however, the dynamic Stark shift of the ground state \((\delta E_{\text{gr}})\), as well as that of the continuum boundary \((\delta E_{\text{cb}})\), change effectively the ionization potential \( I_p \) to \( I_p - \delta E_{\text{gr}} + \delta E_{\text{cb}} \) and the excess energy becomes dependent on the field strength (see the inset in Fig. 1). Within quadratic approximation \( \delta E \approx -\alpha(\omega) F^2/4 \) one has [3]

\[
\epsilon(F) \approx N \hbar \omega - I_p - \left( \alpha_{\text{stat}}^{\text{stat}} + \frac{e^2}{m_e \omega^2} \right) \frac{F^2}{4}, \tag{4}
\]

where the dynamic polarizability \( \alpha(\omega) \) in the ground state and at the continuum boundary is approximated by its static value for the sodium ground state \( \alpha_{\text{stat}}^{\text{stat}} = 162.7 \text{ a.u.} \) [28] and its asymptotic value in the high frequency limit \( \alpha_{\text{cb}}(\omega) \approx -e^2/(m_e \omega^2) \), respectively. Thus, \( \delta E_{\text{cb}} \approx U_p \), where \( U_p \) is the ponderomotive potential of the active electron, whereas \( \delta E_{\text{gr}} \approx -0.53 U_p \).

Formula (1) for \( N = N_0 \) (here \( N_0 = 4 \)) and \( F = F_{\text{peak}} \) gives the energy of photoelectrons whose contribution in the total yield is maximal, i.e. the position of main non-resonant peak in the PES. However, if we enter the field strength values \( F_{\text{nl}} \) at which the atomic levels \( nl \) shift into resonance with the laser field, the same formula estimates the positions of REMPI peaks \( \epsilon^{(nl)} \) in the spectrum. The field strengths at which \( 4f, 5p, 5f \) and \( 6p \) states
shift into the three-photon resonance with the laser field of 800 nm wavelength are determined in a previous work [3]. They are given in Table I together with the corresponding values for $\epsilon^{(nl)}$ obtained by formula (4). Note that the atomic states will be transiently shifted into resonance twice during the pulse, once as the laser pulse "turns-on" and again as the pulse "turns-off". Of course, the condition for this is that $F_{\text{peak}} > F_{nl}$. Notice that for the 3+1 REMPI via atomic state $nl$ (which energy is then in the three-photon resonance with the laser filed, i.e. $E_{nl} = -I_p + \delta E_{F} + 3\hbar \omega$) formula (4) reduces to $\epsilon^{(nl)} = E_{nl} - U_p + \hbar \omega$. Since the dynamic Stark shift for the high lying levels takes approximately the same value as that for the continuum boundary, the photoelectron energy at the 3+1 REMPI via considered state will be (see Table I)

$$\epsilon^{(nl)} \approx E_{nl}^{(0)} + \hbar \omega, \quad (5)$$

where $E_{nl}^{(0)}$ is the energy of the state $nl$ for the field-free atom. The positions of REMPI maxima in the PES are, therefore, almost independent on the peak intensity of the laser pulse, in contrast to the position of the nonresonant four-photon ionization maximum $\epsilon(F_{\text{peak}})$. Since usually $\delta E_{F} + \delta E_{gr} > 0$ (at least for P and F states, see the inset in Fig. 1), the states which can be shifted into three-photon resonance are those with $E_{nl}^{(0)} \leq 3\hbar \omega - I_p$. As a consequence the REMPI maxima are in the spectrum located below the theoretical value for photoelectron energy in the weak field limit ($\epsilon^{(nl)} \leq \epsilon^{(0)}$).

| state $(nl)$ | $E_{nl}^{(0)}$ (eV) | $F_{nl}$ (a.u.) | $\epsilon^{(nl)}$ (eV) | $E_{nl}^{(0)} + \hbar \omega$ (eV) |
|-------------|-----------------|----------------|----------------|-----------------|
| 4f          | -0.851          | 0.0105         | 0.707          | 0.699           |
| 5p          | -0.795          | 0.0092         | 0.789          | 0.755           |
| 5f          | -0.545          | 0.0043         | 1.001          | 1.005           |
| 6p          | -0.515          | 0.0028         | 1.035          | 1.035           |
| 6f          | -0.378          | -              | -              | 1.172           |
| 7p          | -0.361          | -              | -              | 1.189           |

**IV. RESULTS**

**A. Photoelectron momentum distribution**

The photoelectron momentum distribution (PMD) is determined from the electron probability density in the momentum space $|\tilde{\psi}(k, t)|^2$ at $t = T_p$. Transformation of the wave function from the coordinate to momentum representation can be done by the Fourier transform. In our case, due to the axial symmetry of the problem, it is not necessary to calculate the full 3D Fourier transform. The PMD in the $(k_p, k_z)$-subspace has been obtained directly from the outgoing wave part of the function $\psi(\rho, z)$ by transformation

$$\tilde{\psi}(k_p, k_z) = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dz' e^{-i k_z z'} \int_0^{\infty} \rho d\rho J_0(k_p \rho) \psi(\rho, z). \quad (6)$$

In order to get a clear PMD, before the transformation one has to remove the atomic (bound) part of the active electron wave function $\psi(\rho, t)$ and leave only the outgoing wave. It is found that at $t = T_p$ two parts of $\psi(\rho, t)$ separate approximately at $r = 90$ a.u.

Fig. 2 shows the calculated PMD for the photoionization of sodium by 800 nm wavelength pulse of the form [3] with 57 fs duration for three values of the peak intensity: 3.5, 4.9 and 8.8TW/cm² (the corresponding field strength are: $F_{\text{peak}} = 0.0100, 0.0118$ and 0.0158 a.u.).

The radial ($k$) dependence of the PMD contains information about the photoelectron energies ($\epsilon = h^2 k^2/2m_e$). The dashed semicircles of radii $k_0 = 0.279$ a.u. ($\epsilon^{(0)} = 1.060$ eV) and $k_0' = 0.438$ a.u. ($\epsilon^{(0)}' = 2.610$ eV), drawn in the PMD plots, mark the asymptotic values of momenta (energies) of the photoelectrons generated in the nonresonant MPI with four and five photons, respectively, in the weak field limit. Compared to these values, the radial maxima of PMD determined numerically are shifted toward the origin of $(k_p, k_z)$-plane. (The related energy maxima are shifted to lower energies, see Sec. IV B) We point out that some of these maxima are related to the nonresonant MPI for different numbers of absorbed photons, while others can be attributed to the REMPI (Freeman resonances). The shift of nonresonant maxima $\delta k = h^{-1} \sqrt{2 m_e \epsilon(F_{\text{peak}})} - k_0$, referring to Eq. (4), is determined by the dynamic Stark shift of the ground state and the continuum boundary at the given laser peak intensity. The positions of Freeman resonances are, on the other hand, almost independent on the field strength, but they are also located below $k_0$ due to inequality $\epsilon^{(nl)} \leq \epsilon^{(0)}$ discussed at the end of Sec. III.

The angular structure of the PMD, the so-called photoelectron angular distribution (PAD), carries information about the superposition of accessible emitted partial waves, which, according to selection rules for the four-photon absorption, can be s, d and g-waves (see Fig. 1). Indeed, apart from the strong emission along the laser polarization direction ($\vartheta = 0^\circ$ and $180^\circ$), which can be attributed to all three partial waves, the PADs also show maxima at $\vartheta = 90^\circ$, which characterize d and g-waves and at $\vartheta \approx 45^\circ$ and $135^\circ$, which characterize the g-wave. Analogously, accessible emitted partial waves for the five-photon absorption can be p, f and h-waves (see Fig. 1).
functions. Using the representation \( \bar{\psi}(k) = \int Y_{l0}(\vartheta) \psi(k) \, d\vartheta \), the radial functions can be calculated as

\[
\Phi_l(k) = 2\pi \int_0^\pi \bar{\psi}(k \sin \vartheta, k \cos \vartheta) Y_{l0}(\vartheta) \sin \vartheta \, d\vartheta.
\]  

According to partial wave expansion \( \Phi_l(k) \) in terms of partial waves reads the sum \( w(k) = \sum_l w_l(k) \), where

\[
w_l(k) = |\Phi_l(k)|^2 k^2
\]

are the partial probability densities. These quantities for \( l = \ldots, 5 \), as functions of the photoelectron excess energy \( \epsilon = h^2k^2/2m_e \), are shown in Fig. 4 for three values of the laser peak intensity: 3.5, 4.9 and 8.8 TW/cm\(^2\). The corresponding total probability densities \( w \) are shown in Fig. 4(a). The graphs in Fig. 4(a) represent the photoelectron energy spectra (PES) for the considered three values of laser intensity. For comparison, the corresponding spectra obtained experimentally \( \bar{\psi} \) are shown in Fig. 4(b).

The spectra, both the calculated and experimental, exhibit typical ATI structure with prominent peaks separated by the photon energy \( \hbar \omega \approx 1.55 \) eV. Fig. 4 shows the peaks corresponding to lowest three orders of ATI (MPI by \( 4 + s \) photons, \( s = 0, 1, 2 \)) which are located approximately at \( \epsilon = 0.8 \) eV + \( s\hbar \omega \). The partial wave analysis recovers the character of these peaks. We see in Fig. 4 that for the photoelectron energies around the threshold 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 \( l \) (p, f, h-waves) dominate. Therefore, in this case odd number of photons is absorbed (here \( N = 5 \)).

Each ATI peak, in addition, has an internal structure in the form of local peaks which can be attributed to the nonresonant MPI and to the REMPI via different excited states.

\[ \text{C. Nonresonant photoionization} \]

The position of the nonresonant threshold peak (four-photon ionization maximum) predicted by formula \( \epsilon(F_{\text{peak}}) \) for laser peak intensities 3.5, 4.9 and 8.8 TW/cm\(^2\) is \( \epsilon(F_{\text{peak}}) = 0.74 \) eV, 0.61 eV and 0.26 eV, respectively. This peak can be observed in Figs. 3 and 4(a). Since the energy of photoelectrons produced by the nonresonant MPI does not depend on \( l \), a feature of the nonresonant peak is that the maxima of contributing partial densities \( w_l \) have the same positions on the energy axis. At the laser peak intensity of 3.5 TW/cm\(^2\), however, the nonresonant peak overlaps with the most prominent REMPI
The position of this peak at intensities 4
and 8.8 TW/cm² is 0.69 eV and 0.43 eV (numerical values), respectively [see Figs. 3(b,c) and 4(a)]. A discrepancy between the values obtained by formula (4) and from numerical calculations is attributed to the approximative character of the former and to the fact that probability densities \( w_l \) are calculated shortly after the end of the pulse (not in the asymptotic domain). In addition, it should be mentioned that in experimental spectra the nonresonant peak is less prominent (almost invisible). This observation is reported also in an earlier work presenting a comparison between calculated and experimental data for the photoionization of lithium. Nonresonant peaks of the first and of the second ATI order can be observed in Fig. 4 too, at positions which are shifted by one and two-photon energy relative to the threshold peak at a given laser intensity.

**FIG. 3:** (Color online) Partial probability densities \( \Psi_l \) for \( l = 0, \ldots, 5 \) \((s, \ldots, h)\) as functions of the photoelectron energy \( \epsilon = \hbar^2 k^2 / (2m_e) \), which correspond to the outgoing waves shown in Fig. 2(a)-(c). The full vertical lines indicate the positions of nonresonant threshold (four-photon absorption) peak at the corresponding laser intensities, while the dashed lines mark the energies of two 3+1 REMPI channels (via 4f and 5p state) of the threshold peak.

**FIG. 4:** (Color online) (a) Total probability density for photoionization of sodium by the laser pulse with the same parameters as in Fig. 2 versus the photoelectron energy, calculated for three values of the laser peak intensity (3.5, 4.9, 8.8 TW/cm²). Vertical arrows show the positions of nonresonant threshold peak at the corresponding intensities, while the dashed lines mark 3+1 REMPI channels via 4f and 5p state. (b) Electron yield versus photoelectron energy determined in a recent experiment [7] for the same pulse parameters as in the calculations.
D. Resonantly enhanced multiphoton ionization

In contrast to the nonresonant peaks the positions of REMPI peaks (Freeman resonances), as explained in Sec. III, are almost independent on the laser peak intensity. We saw that photoelectrons belonging to the threshold peak reach the continuum along two pathways which involve the 3+1 REMPI via intermediate P and F states. For the most prominent peak at \( \epsilon \approx 0.8 \text{ eV} \) the corresponding intermediate states are 5p and 4f, whereas the subpeaks at \( \epsilon \approx 1 \text{ eV} \) and at \( \epsilon \approx 1.2 \text{ eV} \) [the positions in Fig. 3(b)] are related to 3+1 REMPI via states 6p and 5f and via states 7p and 6f, respectively. The corresponding values in Fig. 3(a) are slightly shifted upwards since the PMD and probability densities are calculated immediately after the end of the pulse.] Note, however, that for a pulse of 800 nm wavelength the transfer of population from the ground state to states 7p and 6f is only near resonant (\( E_{\text{FP}}, E_{\text{FP}} > 3h\omega - I_{\text{P}} \)), see the inset in Fig. 1 and, strictly speaking, the four-photon ionization via these states is not 3+1 REMPI (see the last paragraph of Sec. III). In this case formula (1) is not applicable, but the photoelectron energy can be estimated using relation (5).

Here we focus on the threshold peak at 0.8 eV. Taking into account the possible ionization pathways (via states 5p and 4f) the electron outgoing wave in the energy domain of this peak can be written as the superposition of two wave-packets

\[
\psi = \tilde{\psi}^{(5p)} + \tilde{\psi}^{(4f)},
\]

which, according to diagram in Fig. 1, have forms

\[
\tilde{\psi}^{(5p)} = \Phi_0^{(5p)} Y_{00} + \Phi_2^{(5p)} Y_{20}, \tag{11}
\]

\[
\tilde{\psi}^{(4f)} = \Phi_2^{(4f)} Y_{20} + \Phi_4^{(4f)} Y_{40}. \tag{12}
\]

Since states 5p and 4f are shifted into the three-photon resonance at different field strengths (see Table III and Fig. 1), wave packets (11) and (12) are formed at different phases of the laser pulse and characterized by different mean energies (\( \approx 0.8 \text{ eV} \) and \( 0.7 \text{ eV} \), respectively, referring to Table III).

Expression (10) with components (11), (12) is compatible with the partial wave expansion of function \( \psi \). As Fig. 2 demonstrates, the outgoing wave in the domain of threshold peak decomposes into s, d and g-waves

\[
\hat{\psi} = \Phi_0 Y_{00} + \Phi_2 Y_{20} + \Phi_4 Y_{40}. \tag{13}
\]

Radial functions \( \Phi_l \) for considered values of the laser intensity are determined numerically using formula (8). Some parameters of these functions are given in Table III. The positions of maxima of \( |\Phi_l| \) confirm the existence of two ionization channels with different energies. Referring to Table III the photoelectrons with s and d-symmetry have higher expected energy (\( \approx 0.86 \text{ eV} \)) than those with g-symmetry (around 0.76 eV). A discrepancy between the values for \( \epsilon^{(nl)} \) in Tables II and III originates from the same reasons as explained in Sec. IV C.) Since the maximum of \( |\Phi_2| \) is close to that of \( |\Phi_0| \) we conclude that the majority of d-electrons are generated in the 3+1 REMPI via 5p state, i.e. their contribution in the wave packet (12) is minor (\( |\Phi_2^{(4f)}| \approx 0 \)). Taking into account the latest, the comparison between expansion (13) and expressions (10), (11), (12) gives \( \Phi_0^{(5p)} = \Phi_0, \Phi_2^{(5p)} \approx \Phi_2 \) and \( \Phi_4^{(4f)} = \Phi_4 \).

A similar analysis indicates that the subpeaks at \( \epsilon \approx 1 \text{ eV} \) and at \( \epsilon \approx 1.2 \text{ eV} \) should be related to 3+1 REMPI via states 5f and 6p and to 3+1 or 2+1+1 REMPI via state 6f and sequence 4s \( \rightarrow \) 7p, respectively. Thus, each of them includes contributions of two ionization channels of different energies (see Table III, as in the case of peak at \( \epsilon \approx 0.8 \text{ eV} \).

E. Selective enhancement of photoionization channels

By comparing the amplitudes of radial functions \( |\Phi_l| \) \( (l = 0, 2, 4) \) given in Table III (or alternatively the corresponding partial densities \( |w_l| \) shown in Fig. 3) it follows that the contribution of g-electrons in the peak at 0.8 eV is larger than the contributions of d and s-electrons. The electrons of g-symmetry also dominate in the peak around 1 eV, but the largest contribution in the peak around 1.2 eV is that of d-electrons (see Fig. 3). Dominant ionization channel for the peaks at 0.8 eV and 1 eV is, therefore, the 3+1 REMPI via states 4f and 5f, respectively. For the peak around 1.2 eV, however, dominant channel is the 2+1+1 REMPI via nearly resonant two-photon transition 3s \( \rightarrow \) 4s and subsequent excitation of state 7p. The populations of bound states \( nl \) of the unperturbed atom (i.e. transition probabilities \( |\langle nl|\psi(t)\rangle|^2 \), calculated during the laser pulse while solving the TDSE, justify these statements. Fig. 3 shows the populations of 3s, 4s and several P and F unperturbed states during 57 fs pulse of 800 nm wavelength and 3.5 TW/cm\(^2\) peak intensity. Although this intensity corresponds to the OBI threshold, still there is a significant population of ionized atoms at all phases of the pulse.
It can be seen that the population of states 4f and 5f is generally higher than that of states 5p and 6p, respectively, but the population of state 7p is higher than the population of state 6f. At higher laser intensities the atoms enter deeply in the OBI domain and in the second half of pulse the populations significantly drop down (not shown here) since the majority of atoms becomes quickly ionized.

The populations of relevant states at different phases of the laser pulse can be well understood by analyzing the energy diagram for single-electron excitations and taking into account dynamic Stark shift of energy levels. From the level diagram shown in Fig. 4 one sees that three-photon transitions from the ground state to states 4f and 5p are not resonant with the radiation of 800 nm in the weak field limit, but these states shift into resonance at field strength $F \approx 0.01$ a.u. (see Table I), that is in the middle of laser pulse of 3.5 TW/cm$^2$ peak intensity. Fig. 5(a) shows that the population of states 4f and 5p increases rapidly right around $T_p/2$. Contrarily, three-photon transitions from the ground state to states 5f and 6p are near resonant with the radiation of 800 nm in the weak field limit. These states shift into the true resonance at small values of the field strength, which are reached two times during the pulse at its opposite sides, as it is visible in Fig. 5(b).

In a similar way we can analyze the transfer of the population from the ground state to P states via intermediate 4s state. Since the two-photon transition 3s $\rightarrow$ 4s is resonant with the radiation of 777 nm wavelength in the weak field limit, applying the laser pulse of 800 nm wavelength and 3.5 TW/cm$^2$ peak intensity will maximally populate the 4s state at the beginning of the pulse (around $T_p/4$, see Fig. 5), when the field is not strong enough to shift the state far from the resonance (see the inset in Fig. 1). On the other hand, the single-photon transitions 4s $\rightarrow$ 5p, 4s $\rightarrow$ 6p and 4s $\rightarrow$ 7p are in the weak field limit resonant with radiations of 1075 nm, 865 nm and 781 nm wavelength, respectively. Therefore, only the transition 3s $\rightarrow$ 4s $\rightarrow$ 7p is fully near resonant and has a significant rate. Since the dynamic Stark shift for P states increases with the field strength approximately with the same rate as for the 4s state (see the inset in Fig. 1), the transition 4s $\rightarrow$ 7p remains nearly resonant all the time and this part of transfer occurs during the rest of the pulse (see Fig. 5(c)).

We conclude this consideration with a speculation that for the laser pulse of a shorter wavelength, such that the 4s level during the pulse transiently shifts into resonance ($\lambda = 780$ nm or less), the 2+1+1 REMPI via 4s and subsequent excitation of a P-state may become more prominent process, increasing in this way the selectivity of ionization via specific state.

V. SUMMARY AND CONCLUSIONS

In this paper we studied the photoionization of sodium by laser pulses of 800 nm wavelength, 57 fs duration and 3.5 - 8.8 TW/cm$^2$ peak intensities. This falls into over-the-barrier ionization (OBI) domain occurring in the multiphoton ionization (MPI) regime. Using the single-active-electron approximation we calculated the photoelectron momentum distributions (PMD) by numerically solving the time dependent Schrödinger equation with these pulse parameters. The contributions of photoelectrons with different values of orbital quantum number l in the PMD are determined by expanding the photoelectron wave function in terms of partial waves. The corresponding partial probability densities $w_l$ depend on the photoelectron energy $\epsilon$ and the total density $\sum_l w_l(\epsilon)$ represents the photoelectron energy spectrum (PES). The spectra calculated for the above mentioned pulse parameters agree well with the spectra obtained experimentally.
Partial wave analysis of the spectral peaks related to Freeman resonances has shown that each peak has photoelectron contributions from different ionization channels which are characterized by different photoelectron energies and different symmetries of released photoelectron wave-packets. It is found that the most prominent peak around 0.8 eV is the overlap of two Freeman resonances related to resonantly enhanced multiphoton (3+1) ionization (3+1 REMPI) via the states 4f and 5p, but also has a contribution from the nonresonant four-photon ionization. The local peak around 1 eV is related to 3+1 REMPI via the states 5f and 6p, whereas the dominant ionization channel for the peak around 1.2 eV is 2+1+1 REMPI via the near resonant 4s state and subsequently excited 7p state. These findings are justified by calculating the populations of excited states during the pulse. Our analysis indicates that the contribution of specific ionization channels might be selectively increased using laser pulses of a shorter wavelength, at which the intermediate states are taken in a better resonance with the laser field.

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