J. Phys. B: At. Mol. Opt. Phys. **30** (1997) L197–L205. Printed in the UK PII: S0953-4075(97)80418-X

LETTER TO THE EDITOR

Evidence for resonant effects in high-order ATI spectra

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Received 23 December 1996

Abstract. We have observed resonant phenomena in the intense-field ionization of argon that do not easily fit into the standard models of above-threshold ionization. High-resolution angle-resolved measurements of the energy region around 6–10 times the ponderomotive potential U_P in the ATI electron spectrum show at least three separate series of peaks, each with a distinct intensity threshold for their onset. These series do not shift in energy and have characteristic values of intensity for their appearance, pointing to an intensity-selective resonant enhancement effect. In order to further investigate this phenomenon, we have observed VUV fluorescence photons from the focal region following ionization. Current theories for the creation of high-energy electrons do not seem to explain these phenomena without significant modifications. We discuss possible physical mechanisms and implications for extending the standard model.

Above-threshold ionization (ATI) in noble gases produces highly structured electron spectra, consisting of one or more series of regularly spaced narrow energy peaks. Most low-energy (less than 10 eV) features of these spectra have been successfully explained by considering the dynamics of a single-active-electron (SAE) wavepacket driven by the laser field in the presence of a static ion potential [1–3]. When the ionization probability per optical cycle is not too high, the spectrum is dominated by narrow peaks due to excited states which AC Stark shift into multiphoton resonance with the laser. For higher intensities, most electrons are emitted below an energy of twice the ponderomotive energy $2U_P$, which is the maximum energy a free classical electron can extract from the laser field if it starts from rest [4]. U_P is the classical wiggle energy for a free electron in an oscillating field ($U_P = (e^2F^2)/(4m_e\omega^2)$), which amounts to about 3.5 eV in our experiment at 6×10^{13} W cm^{-2}.

Recent experiments [5–8] have discovered an additional region of enhanced ionization in the high-energy part of the electron spectrum above 20 eV, separated from the low-order peaks by a gap of several eV. The energies of electrons in the enhanced region significantly exceed $2U_P$. In this energy region, the electron spectrum often shows a non-monotonic decrease or 'plateau' [3, 5, 7–10]. One explanation for this enhancement within the SAE framework involves rescattering of the photoelectrons that are driven back by the laser field to re-encounter their parent ion [11–13]. This process can produce electrons with the observed energies (up to $11U_P$). In this, and other models that neglect the (Coulomb) electron–ion interaction up to the very moment of collision, virtually all rescattering happens

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0953-4075/97/060197+09$19.50

on the first encounter, because later encounters are strongly suppressed due to spreading of the initial wavepacket.

Our high-resolution experiments in argon now show that the ATI peaks in the plateau region actually consist of a set of three sub-peaks with features that do not easily fit current models. In contrast to previous observations of these peaks, the sub-peak energies do not shift with laser intensity or direction of emission. Their narrow widths and separate, very sudden onsets with laser intensity suggest a resonant enhancement mechanism reminiscent of the Rydberg resonances observed in the lower-order ATI peaks.

To obtain further information about the ionization dynamics, we performed time-correlated photon counting (TCPC) on the fluorescence from the laser focus. To our knowledge, this is the first use of TCPC in ATI experiments.

Our experiments were conducted with a 10 Hz amplified Ti:sapphire laser system capable of producing 790 nm, 120 fs pulses at energies up to 8 mJ. A 7 mm portion of this beam with a flat-top spatial intensity profile and polarization along the direction of the detector was focused with a 350 mm focal length lens into a vacuum chamber backfilled with 1×10^{10} to 1×10^{12} cm^{-3} (3×10^{-7}–3×10^{-5} Torr) of argon. The gas density was adjusted to avoid degradation of electron energy resolution due to space charge.

The optical focus was at one end of a horizontal 1 m field-free time-of-flight (TOF) spectrometer. The electron detector at the other end consisted of a 3 inch diameter microchannel plate (MCP) with a collection half-angle of 38 mrad, allowing simultaneous angle and energy resolution. The electrons reaching the detector represent a sum over the entire focal volume. Time-of-flight data were acquired with a digitizing oscilloscope triggered with variable time delay and discriminated and analysed by computer. The time resolution achieved was typically 500 ps, resulting in a theoretical energy resolution of about 50 meV in the 10 eV regime, down to 4 meV in the 1 eV regime. The experimental resolution is somewhat lower and is limited by uncertainties in the trigger timing and by energy drifts due to contact potentials varying during the run. We could nevertheless determine the relative energy spacings between peaks in the spectrum to less than 10 meV by considering electron peaks from multiple ATI orders.

In order to reduce sensitivity to laser power fluctuations when measuring effects occurring in a very narrow intensity region, the energy of each laser pulse was measured and the electron signal was collected and binned according to intensity. This relative measurement also allowed absolute intensity calibration by observing the onset of resonances in the well known low-energy part of the spectrum. This allowed us to determine the absolute peak intensity of the laser to within approximately 7%. The relative intensity of laser shots, however, could be measured much more accurately with our shot-to-shot measurement, to less than 1%. In this experiment our bins were chosen to cover a range of 3% of the total intensity.

Photon data were collected with a 1 cm diameter uncoated MCP mounted 3 cm from the focal region, which provided a collection angle of 0.5 sr. The MCP is insensitive to photons below an energy of 6.2 eV, but has a wavelength-dependent photoelectron yield of around 10% in the vacuum ultraviolet, so that we could estimate the effective detection efficiency of the system to be between 0.1 and 1% for photon wavelengths below 300 nm. The time resolution here was limited to 0.5 ns due to the finite transient response time of the measurement system.

In the ‘short-pulse regime’ [14], where the laser pulse is shorter than the time it takes the electron to leave the laser focus, the low-energy electron spectrum is dominated by resonance enhancements (figure 1). For argon, these enhancements occur as the g states, and later the f states, come into resonance with the ground state dressed by 11 or 12

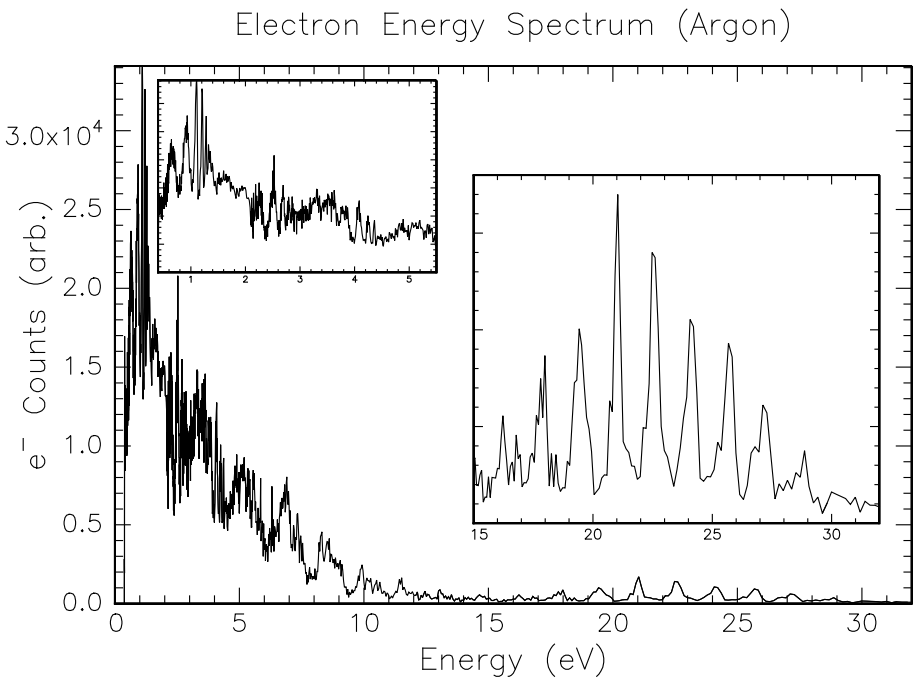

Figure 1. ATI spectrum for argon at an intensity of about 7×10^{13} W cm^{-2}. The left-hand inset shows the region of low-order Rydberg resonances with an expanded energy scale. The right-hand inset shows the region of high-energy electrons which are the focus of this paper.

photons, respectively. The resonances that appear in the electron spectrum at an intensity of around 3×10^{13} W cm^{-2}, when the Rydberg series sweeps through 11-photon resonance, are assigned to g rather than d states, because they appear to have near-zero quantum defect and no members below $n = 5$ are present. Resonance-enhanced peaks, together with some non-resonant ionization features and broader peaks due to unresolved resonances with more deeply bound s, p or d states reappear at multiples of the photon energy.

The higher-energy region around 18–40 eV shows a large secondary maximum in the ATI envelope. At the laser intensities used in this work, 5–8$\times 10^{13}$ W cm^{-2}, this corresponds to a range of 5 to more than 11 times the ponderomotive potential U_P. This basic high-order enhancement (HOE) feature, similar to the plateau discovered by Paulus *et al* [9] at shorter wavelength (620 nm) or the spectral features seen by DiMauro and co-workers and by Mohideen *et al* in helium [6, 13], thus falls in the energy range expected for backscattered electrons.

The spectrum around this energy shows a significant structural change in a narrow intensity region. Previously published work [5] reports the peaks shifting as a function of laser intensity and angle. In contrast to these observations, our experiment shows that the peaks in the plateau region actually are the envelopes of three sub-peaks, which do not shift in energy as a function of laser intensity, but remain fixed, similar to resonances in low-energy ATI (see figure 2). The energy separation between the sub-peaks in each ATI order is independent of the order, though their magnitude ratios are not. Thus corresponding sub-peaks form individual ATI series, spaced by the photon energy, each series having its own smooth envelope and its own offset from a multiple of $\hbar\omega$.

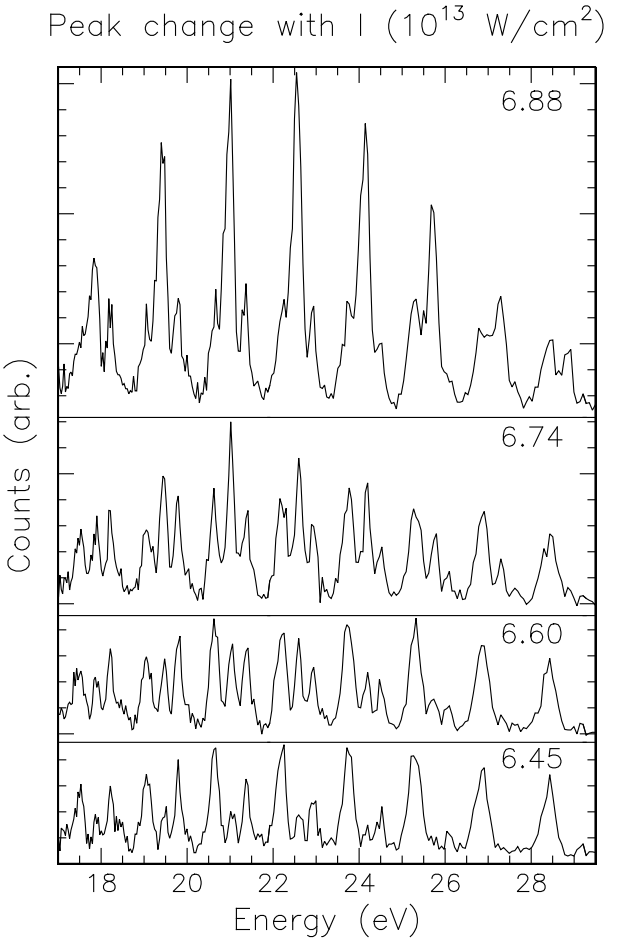

Figure 2. ATI electron spectrum in argon in the 15–35 eV range, over the intensity range 6.45×10^{13}–6.88×10^{13} W cm^{-2}.

Taking the the largest peak in figure 2 as a reference, the energy offsets for the peak just below and above it in energy are measured to be -0.406 eV and 0.334 ± 0.005 eV, respectively. All peaks are narrow enough to be clearly resolved and remain so for the range of intensities we examined, up to the point where peak broadening due to space-charge effects in the laser focus becomes significant. Their widths range from 0.25 to 0.5 eV.

The envelopes themselves also have different widths and their centres appear offset from each other by several eV. The set formed by the lowest energy peaks of the triplet has the largest envelope width, about 13 eV full width half maximum (FWHM) versus about 8 eV for the remaining two peaks. Its envelope maximum is at 22 eV, with the other two centres appearing around 20 and 19 eV for the middle and higher energy peaks, respectively. Furthermore, each set has a different threshold laser intensity for its appearance onset in the spectrum. The lowest-energy peak of the triplet dominates the spectrum at intensities below 6.5×10^{13} W cm^{-2}, with the others falling below the detection limit up to 6.3×10^{13} W cm^{-2}. At about 6.4×10^{13} W cm^{-2} the other two sets start to appear, with the rightmost peak initially remaining the largest of the three. However, above

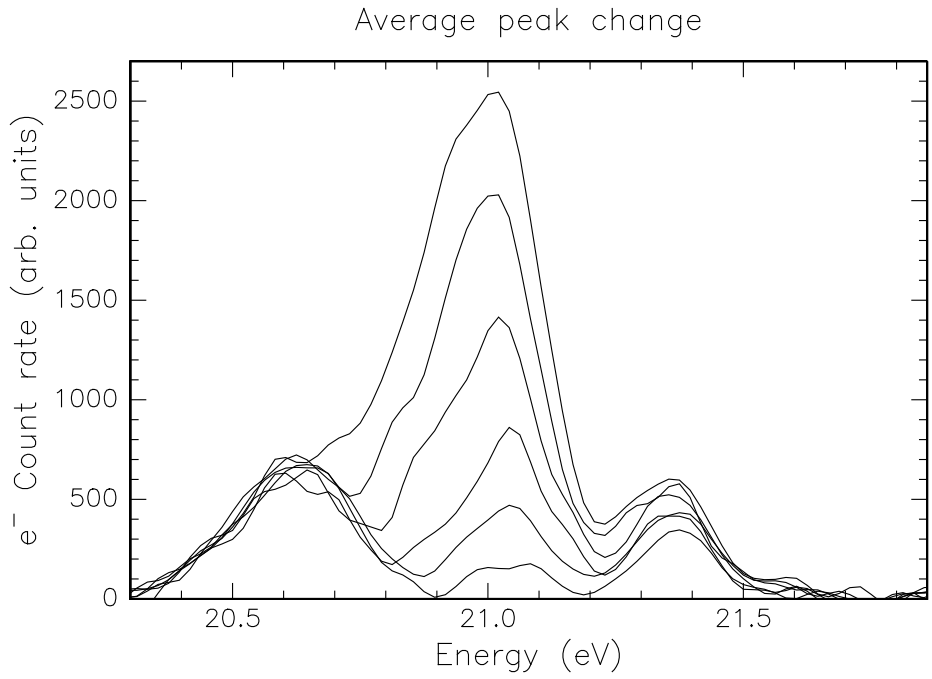

Figure 3. High-resolution plot showing the variation in shape and height of the individual sub-peaks. Each trace is the average of the five ATI orders between 18.5 and 26.5 eV in the high-energy part or the electron spectrum, taken at one laser intensity. The intensities for the individual traces range from 6.45×10^{13}–7.35×10^{13} W cm^{-2}.

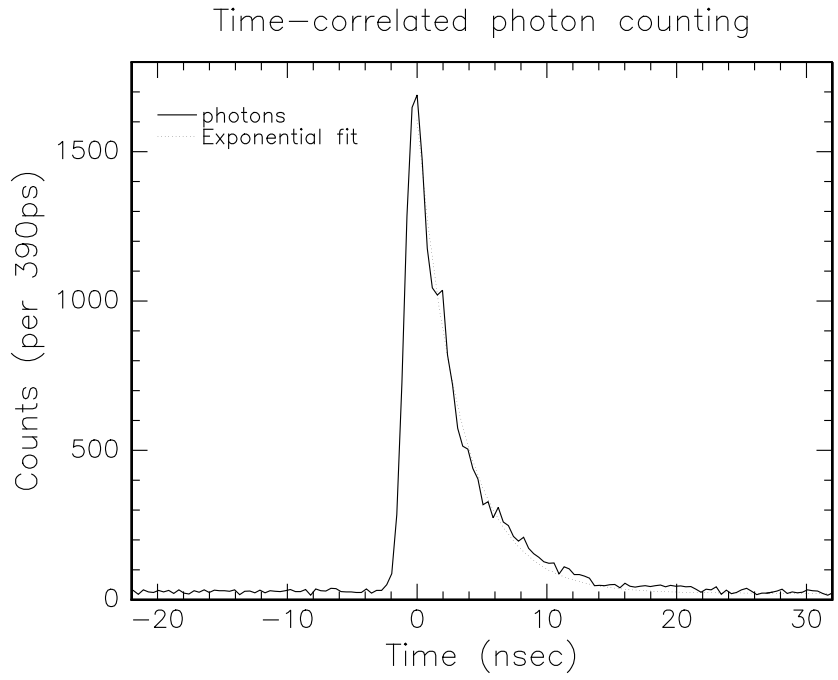

Figure 4. Time-gated photon counting histogram for multiphoton excitation of argon at an intensity of 7×10^{13} W cm^{-2} and a gas density of 3×10^{11} cm^{-3}.

6.7×10^{13} W cm^{-2}, the central sub-peak starts to dominate and eventually completely overshadows the other sets.

The different intensity and saturation behaviour of each set can be explained if one considers the effect of spatial averaging over the focal volume. This behaviour shows that, similar to low-energy ATI resonances, the peaks only occur at very specific values of peak laser intensity. At higher laser pulse energies the signal then comes from regions in the focal volume where the peak intensity reaches the resonance intensity.

An analysis of the peak triplet with high resolution shows that as the laser intensity changes, the maximum of each sub-peak remains fixed in energy to within our uncertainty. The widths of the left and right sub-peak similarly remain constant, the central peak, however, shows a broadening which extends only towards low energy.

It is interesting to note that the set first appearing in the spectrum is the one whose envelope is centred at the highest energy and has the greatest width. The amount of field dressing would suggest that the production intensity of this peak would have to be higher than the others. Nevertheless, it appears in the spectrum at lower laser intensities. The other two resonances have similar envelope widths and centres. The fact that the lowest-energy member of each triplet is produced at the lowest intensity (when the Stark-shifted ionization potential is lowest) shows that it must have a different order than the other two sub-peaks and a comparison of the appearance intensities suggests that it corresponds to ionization with one photon less than the other two.

The absolute energies of the subpeaks at high energies are difficult to determine precisely, due to the timing uncertainties in the experiment, as mentioned above. Accounting for these uncertainties determines the energy to about ± 0.2 eV in the high-energy region of the energetic electrons. However, the appearance onset of the middle sub-peak in that region coincides in intensity with the appearance onset of the 4f peak in the low-order spectrum, to within our uncertainty of around 0.1×10^{13} W cm^{-2}. Both peaks are therefore created at the same (ponderomotively shifted) ionization potential, to within an uncertainty of 60 meV. Consequently, the centre sub-peaks must be an integer number of photon energies (± 60 meV) above the 4f peak. The calibration of the electron spectrum thus obtained agrees with the previous, less accurate one obtained by direct conversion of the time-of-flight data.

Our measurements of fluorescence photons from the laser focus show a decrease over time in the number of photons produced, which can be fitted to a single exponential decay curve with a width of 3.6 ± 0.7 ns. The only VUV fluorescence line with this lifetime in excited neutral argon is the 3d–3p decay. Assuming a purely ponderomotive Stark shift, this state comes into 11-photon resonance with the ground state at a laser intensity of 5.5×10^{13} W cm^{-2} and decays with a 3.7 ns lifetime by emitting an 87 nm photon.

We have also observed the ions produced during the ATI process in this intensity region. Both Ar^{+} and Ar^{2+} were observed, but no correlation with the onset of electron production at the various resonance intensities seems to exists. The appearance of Ar^{2+} at modest intensities has previously been attributed to non-sequential ionization [15]; no sequential ionization should be observed in the intensity region where the resonances appear and become prominent.

Our observation of sharp structure in high-order ATI peaks does not fit easily into current models of ATI. The intensity region of interest, where the marked structure change occurs, corresponds to a Keldysh parameter γ of 1.4. Such a low value of γ allows a significant amount of tunnelling, especially if we take into account the fact that the Coulomb tail of the atomic potential (neglected in Keldysh's original treatment) significantly lowers the tunnelling barrier. At the highest intensities we studied (in argon, with an ionization potential IP of 15.76 eV) the barrier is suppressed to an energy of about -11.5 eV and the

tunnelling probability amounts to about 10^{-4} per optical cycle. Previous ATI experiments carried out at similar values of the Keldysh parameter have demonstrated that the low-order ATI peaks closely follow the predictions of semiclassical tunnelling models of ATI [16]. The appearance of high-energy electrons can be predicted from such models, once rescattering of the emitted electron is considered [6, 11]. On the other hand, sharp energy structure, which must be associated with relatively long-lived resonant states, does not readily appear in such theories. Significant modifications of these models appear to be necessary.

Since neutral argon is a closed-shell system, all excited levels have energies far above the ground state; therefore excited states have at least one electron in a Rydberg state. At the relevant intensities, such Rydberg states are in a highly non-perturbative situation, as indicated by their extrapolated perturbative lifetimes, which are of the order of a few femtoseconds. In the tunnelling picture, the saddle point of the electron potential, created by the core plus laser field occurs at a radius r of about 5 au, at the intensities where our high-order enhancements occur. Even in the field-free unperturbed case, most excited states in argon have an expectation value for the radius r of 9 au or greater, and live both outside and above the potential barrier at this intensity. Based on such calculations, one should expect any of these states to ionize in much less than one Kepler orbital period; long-lived resonances are not expected.

Yet our observations are very much at odds with this. The narrowness of the individual resonant peaks in the data suggests a homogeneous lifetime of at least 10 optical cycles. Furthermore, the 3d state observed in the fluorescence experiment is evidently stable against photoionization, although it is certainly well into the over-the-barrier regime at its resonance intensity.

Assigning the particular resonance responsible for each of the observed ATI series in the plateau proves difficult. The basic choice is between resonances embedded in the continuum near the centre of the ATI envelope, producing the plateau by laser-assisted autoionization, or bound states. In the latter case, the plateau would result from high-order ATI of those bound states, making it more difficult to explain the position and shape of the envelope. Most types of continuum-embedded resonances that seem plausible present a number of problems. We consider several possibilities.

Resonances of weakly bound states built on a core with a 3s hole ($(3s)(3p)^6(nl)$, $nl = 4s, 4d, \ldots$) would decay through an Auger-like mechanism to $(3s)^2(3p)^5$. In the presence of the laser field, laser-assisted Auger decay [17] would occur and the Auger line would be dressed with a number of sidebands (due to the decay being accompanied by absorption or emission of a number of photons) to produce a set of peaks.

For this scenario, we must consider how the 3s hole could be formed. The applied laser field is too weak to let an electron tunnel directly out of the 3s orbital. A more likely mechanism is formation by recapture of a tunnelling electron accelerated in the course of its quiver motion. This could liberate just enough energy (up to a maximum of $\mathrm{IP} + 3.17U_P$, about 28 eV in our experiment) to promote the 3s electron to an (nl) state, provided that recapture occurred near a zero crossing of the field. Although this might seem plausible, it is not clear how such a core-excited neutral could live long enough. The (nl) electron formed in the inelastic collision is so loosely bound that it would be pulled away by the laser immediately afterwards, with a drift energy of around $2U_P$, instead of being available for autoionization. Thus, even if impact excitation of a 3s electron occurred, it would lead mainly to the production of excited Ar^+ ions. Such ions are even more stable than neutral argon atoms and would survive the pulse to fluoresce later with a 5 ns lifetime. No such fluorescence was observed in the TCPC.

Scenarios involving doubly excited states seem to suffer from similar problems with the excitation mechanisms and lifetime in the laser field. The dominant product in this case would be doubly ionized argon, and although we observed some Ar^{2+}, the intensity dependence of its production does not correlate with any of the plateaus.

We do, however, have some evidence from the TCPC signal that some $(3p)^5(3d)$ excited states are formed, but do not ionize. Lifetimes large enough to make such survival possible would be more than sufficient to cause narrow resonances. The Auger scenario, however, seems to be problematic, not so much due to the involvement of Rydberg electrons, but due to the difficulty of extracting enough energy from the laser field to excite the deeply bound 3s electron to the (Stark-shifted) 3d orbital.

At the intensity at which the last observed high-order enhancement onset occurs, around 6.6×10^{13} W cm^{-2}, inelastic rescattering of an ionized 3p electron could make an energy of 28.0 eV available for promotion of a 3s to a 3d state, which requires 27.4 eV in the field-free case. However, if the 3d state Stark shifts by more than just 0.6 eV (at a ponderomotive shift of 3.9 eV), this energy would no longer be sufficient. Excitation to higher lying states (that tend even more to shift ponderomotively) would be more unlikely. The high-order resonance observed at lower intensities would require an unusually large negative Stark shift exceeding U_P in this picture.

This problem does not occur in the following scenario. A singly excited Rydberg state ($(3p)^5(nl)$ configuration) could get excited and resonantly trapped in a Kramers–Henneberger (KH) state [18]. An electron tunnelling out of the argon ground state emerges with zero kinetic energy on the other side of the barrier. There, a significant fraction of the created wavepacket will consist of lower Rydberg (excited) states ($n = 4$–6 in argon) due to good wavefunction overlap. Population in those states could build up resonantly if the wavepackets from tunnelling events in consecutive field cycles interfere constructively. Since the phase relation between consecutively emitted wavepackets is determined by the phase evolution of the ground state, which again is determined by the Stark shift of the latter with respect to the threshold, this process is very intensity selective.

Resonant trapping in a KH state would then enhance the probability for rescattering by forcing the electron to remain near the atom until it is removed by such an event. This would increase production of electrons in all ATI orders at the resonance intensity, but the enhancement (and thus the peak–valley contrast in the ATI spectrum) would be most pronounced in the energy range for which backscattering is a prerequisite. In the low-energy part of the spectrum electrons can be produced by straightforward tunnelling (without any re-encounters) which makes the enhancement less pronounced there.

We have observed resonant and highly intensity-selective substructure in the high-energy part of the argon ATI electron spectrum. This resonant substructure does not easily fit current theories of above-threshold ionization. The fact that enhancement of this process occurs with such a high energy selectivity shows that states are involved that live for many (10) optical cycles. Quivering Rydberg states, adiabatically stabilized, are the most likely candidates. The presence of VUV fluorescence does indeed indicate that excited states can survive in the intense field.

All of the proposed mechanisms involve interaction with the ion core upon rescattering. If the production of high-energy electrons can be taken to be a measure for the number of high-energy impacts on the ion core, the experiment shows that such impacts are almost exclusively due to resonant ionization occurring at very specific intensities. In that case, other processes depending on high-energy impacts, such as harmonic generation, are likely to be similarly affected. However, due to the higher laser intensities and gas pressures required for efficient production, these effects might be difficult to observe.

We gratefully acknowledge discussions with L Van Woerkom, P Hansch and D W Schumacher. This work is supported by the National Science Foundation. HGM participated through the Fellows Program of the Centre for Ultrafast Optical Science at the University of Michigan. PHB thanks the Miller Institute at the University of California at Berkeley and the John Simon Guggenheim Memorial Foundation for support during the preparation of this work.

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