Isolated high-harmonic XUV photon absorption and NIR strong-field tunnel ionization

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Abstract. Extreme ultraviolet (XUV) pulses with a duration of tens of femtoseconds initiate 4s\textsuperscript{−1} or 4p\textsuperscript{−1} photoionization of krypton, which populates highly excited satellite states through the electron correlation. The excited ions are then tunnel ionized to Kr\textsuperscript{2+}4s\textsuperscript{−1}4p\textsuperscript{−1} or 4p\textsuperscript{−2} by a strong-field near-infrared (NIR) pulse of a similar duration. The XUV pulses are produced by high harmonic generation in a gas jet and we employ a state-of-the-art time-preserving monochromator to isolate individual XUV harmonic orders. An enhancement of the Kr\textsuperscript{2+} yield as a function of harmonic photon energy and XUV-pump NIR-probe delay is observed and compared with a two-step model, which allows the population of the satellite states to be inferred. Furthermore, relative 4s and 4p satellite excitation cross-sections are predicted at the photon energies studied. This proof-of-principle experiment demonstrates that isolated harmonics can be employed to pump specific electronic states, which will be highly complementary to synchrotron, attosecond and x-ray free-electron laser studies of complex systems.

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1. Introduction

In the solid state, ferromagnetism, magnetoresistance and superconductivity are mediated by electron correlation dynamics; on the atomic scale, this coupling is of vital significance to scattering or absorption, many chemical processes and fullerene formation. Narrowband synchrotron radiation is used to measure photon cross-sections as a function of energy from 10 eV to several keV with a typical resolution of a few thousand, allowing the influence of electron correlations to be observed. The Fourier analogue, time-resolved photoexcitation and detection, is now capable of tracking electron dynamics on the attosecond timescale [1, 2]. Resolving transient states is the key characteristic, rather than absolute resolution, typically $t/\Delta t \simeq 5 \text{fs}/100 \text{as}$. In this work, we undertake a novel investigation of atomic ionization dynamics using monochromated high harmonic extreme ultraviolet (XUV) radiation and ultrafast strong-field near-infrared (NIR) pulses. Krypton is $4s^{-1}$ or $4p^{-1}$ photoionized, populating satellite states via the electron correlation [3–8]. Subsequent tunnel ionization [9, 10] of the satellites allows the relative photoexcitation populations and relative cross-sections to be recovered in a pump–probe configuration. We show this unique simultaneous time- and energy-dependent measurement allows weak electron dynamics to be quantified, and is highly complementary to the studies of complex systems with synchrotron, attosecond and x-ray free-electron laser (XFEL) sources [11–15].

Depending on photon energy and flux, radiation absorption processes can be roughly categorized as linear (single photon) or nonlinear multiphoton. Synchrotron sources with a photon energy of tens to thousands of eV are an excellent probe of linear processes [8]. On the other hand, intense ultrafast lasers operating in the visible and NIR spectral regions can initiate nonlinear processes such as multiphoton and tunnel ionization, first theoretically discussed by Keldysh [9]. High harmonic generation (HHG) in a gas driven by an ultrafast NIR pulse is also highly nonlinear and allows ultrabroadband photon upconversion into the UV and XUV. Recently, HHG-derived attosecond XUV pulses have, in conjunction with phase-stable few-cycle NIR pulses, allowed time-resolved observation of tunnel ionization [16] and interference during photon excitation [17] in a linear–nonlinear combination. Strong-field XUV pulses are now accessible with XFELs, allowing nonlinear processes to be initiated for the first time [11, 13–15]; observations include the complete electron stripping of neon by creating ‘hollow atoms’ and x-ray induced transparency by core ionization [12].

In this paper, we employ ultrafast pulses of XUV radiation from a HHG source to initiate linear photoionization and investigate the time-evolution of satellite states excited by correlation...
dynamics by probing with nonlinear tunnel ionization. Importantly, this method is distinct from synchrotron and XFEL experiments as sub-cycle synchronization to a femtosecond strong-field laser pulse is straightforward [18]. Unlike attosecond observations of similar processes [16], selecting single harmonics from the broad XUV spectrum allows the photon energy to be discretely varied across a band of satellite states and a prominent photoionization threshold, akin to synchrotron or XFEL experiments. As the photon flux is reduced below that employed in attosecond XUV studies, in the present proof-of-principle experiment we opt to employ an ion time-of-flight mass spectrometer (TOFMS) to allow the dynamics to be inferred from the varying charge state yields as a function of delay between the single harmonic and tunnel ionizing pulses. Following this successful demonstration, it is clear that photoelectron spectroscopy is the ideal tool to observe the influence of the electron correlation in more complex systems.

Related linear studies of ionization in noble gases have been performed combining HHG–XUV photons and NIR pulses. In xenon, the interaction of a weak-field NIR pulse with picosecond-duration XUV pulses from the 17th or 21st harmonic orders (H17 or H21, where $H_1 = 1.56 \text{ eV}$) was studied, and the influence of the $5s^25p^5nl^2$ correlation satellites observed [19]. Pairs of multilayer mirrors have also been employed to isolate H19 or H25 in a momentum imaging spectrometer, allowing the interplay between ionization routes to be studied, again in xenon [20]. Very recently, ionization pathways have been interfered in helium illuminated with H11 or H13 (isolated using multilayer mirrors) and an intense NIR laser, where the combined influence of the XUV + NIR radiation dynamically modifies the electronic structure [21].

A general theme exists between [19–21] and this work, however while multilayer mirrors are highly efficient and preserve the duration of the reflected harmonic, they lack tunability. Selecting the energy of the XUV photon is key to combined time- and energy-resolved studies as it allows a subset of electron states to be pumped while retaining dynamic information within the transform limit.

2. Experimental technique

Our experimental apparatus, illustrated in figure 1, allows a single XUV harmonic to be selected from the UV to XUV photon flux resulting from HHG in a gas jet driven by a 30 fs NIR pulse. We use a state-of-the-art time-preserving monochromator in the off-plane geometry which combines a single flat grating and two focusing mirrors as detailed in [22, 23]. The high harmonic radiation co-propagates with the residual NIR onto the flat grating, whereby it is azimuthally dispersed around a cone centred at the point of incidence. Rotating the grating about an axis parallel to the propagation direction then allows harmonic selection at variable width slit further down the beamline.

The photon flux as a function of photon energy is presented in figure 2(a), recorded by placing a calibrated channel electron multiplier (CEM) after the monochromator exit slit. By measuring the CEM response as a function of grating angle, the selectivity of the monochromator is demonstrated. The bandwidth of the individual harmonics cannot be inferred from this measurement as the CEM response is a convolution of the bandwidth, spectral dispersion and finite source size. Ray tracing through the monochromator indicates the bandwidth of an isolated harmonic will be around 0.5 eV. The cut-off at 50 eV is the result
**Figure 1.** Schematic of XUV beamline including monochromator and NIR delay line. A 30 fs 2.4 mJ 800 nm pulse is interferometrically split 3 : 1 at beamsplitter (BS), the weaker beam is transmission focused into an argon gas jet (J1) to an intensity, \( I \approx 10^{13} \text{ Wcm}^{-2} \), generating broadband XUV photons by HHG. The time-preserving monochromator (toroidal mirror TM1, grating GR, toroidal mirror TM2) is optimized for the transmission of H13 to H29 and extracts a single harmonic from the XUV region of the spectrum. By changing the grating angle (rotating around dotted line), the transmitted wavelength is varied and the bandwidth is controlled by changing the slit width (SL). The single-harmonic XUV beam is reflection focused into the interaction region of an ion TOFMS by a grazing incidence toroidal mirror (TM3). The focus of the XUV beam is overlapped with a strong-field NIR pulse, generated by transmission focusing the stronger NIR beam from the 3 : 1 splitter from an annular mirror (HM) to an intensity in excess of \( 10^{13} \text{ Wcm}^{-2} \). The relative path length of the NIR and XUV beams is variable using a translation stage, which introduces a NIR–XUV delay with a sub-cycle resolution and stability. Krypton is effusively released into the interaction region of the TOFMS through jet J2. The dashed line indicates the extent of the vacuum chamber.

of the grating geometry rather than the HHG process, and the densely spaced peaks around 20 eV are due to the overlap of the second order with the first order peaks.

The transmitted XUV pulse duration depends on the number of grating rulings illuminated, and is comparable to, or shorter than, the NIR drive pulse duration. So, for a NIR drive pulse duration of 30 fs, the duration of individual harmonic pulses is expected to be approximately 20 fs. One of the goals of this work is to demonstrate that the duration of isolated harmonics has been preserved on transmission through the monochromator. The vacuum propagation requirement for XUV radiation leads us to select atomic electronic processes to

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Figure 2. (a) XUV harmonic spectrum measured on a channel-electron multiplier inserted into the beamline after the monochromator as the photon energy is selected, corrected for CEM sensitivity (electrons per photon) and dispersion as a function of angle. (b) Energy level diagram for krypton showing relevant electronic transitions: the XUV harmonics (violet arrows) photoionizes to 4p−1 or 4s−1Kr+, populating excited satellite states through shake-up or configuration interaction (CI) with a bound 4p electron (green arrows). The NIR strong field pulse then tunnel ionizes the satellite states (red arrows) leaving the Kr2+ ion in the 4p−2 or 4s−14p−1 states. (c) 4s−1 (red) and 4p−1 (green) photoionization partial cross sections as a function of photon energy from the respective thresholds of 13.99 and 27.50 eV. The cross-sections are an amalgamation of experimental and theoretical results [3–8] with the uncertainty indicated by the shaded area.

demonstrate the ultrafast nature of the monochromated HHG–XUV, which is then probed with a 30 fs NIR pulse derived from the same pulse used to drive the HHG process. The monochromated XUV beam is focused into the interaction region of an ion TOFMS [24] where

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it overlaps the strong-field NIR pulse focused to an intensity in excess of $10^{13} \text{ Wcm}^{-2}$ in the same volume. The NIR and XUV pulse arrival times are controlled with an optical delay line, facilitating sub-cycle resolution and interferometric stability [18].

Krypton is effusively released directly into the interaction region of the TOFMS to a local density of $2 \times 10^{11} \text{ cm}^{-3}$. Over the H21, H23, H25 and H27 photon range (32.8–42.1 eV), krypton is either 4p$^{-1}$ or 4s$^{-1}$ photoionized as illustrated in figure 2(b), with the photoionization partial cross-sections shown in figure 2(c). During photoionization, bound 4p electrons have a small probability of being excited into unoccupied orbitals [3, 4, 6, 7] populating satellite states, as discussed below. Following single photon ionization and the population of a range of satellite states, the NIR strong-field pulse then initiates tunnel ionization of the excited electrons and the TOFMS records the final charge of ions extracted from the focal volume. We first outline the theoretical treatment the present a comparison with experimental observations then discuss the implications of these results. Finally, single-photon double-ionization (SPDI) is discussed as an additional demonstration of future possibilities.

3. Theoretical methodology

The intensity of the NIR pulse is insufficient to cause significant Stark-shifting of the satellite states towards the continuum hence the XUV photoionization and NIR tunnel ionization are treated separately. A complete TDSE-treatment of this pump–probe experiment is not performed in this work and it is hoped that such a treatment is attempted to confirm our findings. Rather, we make use of recent experimental measurements of XUV ionization by a synchrotron source using high-resolution photoelectron spectroscopy. A modern treatment of strong-field ionization valid over a range of Keldysh parameters is then used to describe the tunnelling of the populated satellite states into the field-modified continuum.

If the NIR pulse precedes the XUV pulse, the NIR intensity ($I_{\text{NIR}} < 2 \times 10^{13} \text{ Wcm}^{-2}$) is only sufficient to produce Kr$^+$ in the lowest lying electronic states with a probability of the order $10^{-4}$ per shot. As a result, subsequent XUV photoionization is essentially negligible as very few Kr$^+$ ions are generated, so in this case the Kr$^{2+}$ yield would be below the detection limit of the TOFMS. Furthermore, direct tunnel ionization to Kr$^{3+}$ in the NIR has a probability around seven orders of magnitude lower than Kr$^+$. The only route to generating significant amounts of Kr$^{2+}$ is through XUV photoionization, followed by excitation of high-lying satellites which are then tunnel ionized.

The satellite states populated during photoionization of Kr by synchrotron radiation have been studied extensively with high-resolution photoelectron spectroscopy [3–8]. There is a general agreement on state assignment, however the mechanisms leading to the population of these states are disputed, especially in the vicinity of photoionization thresholds [4, 6–8]. A number of experimental studies have observed that some satellite lines follow the photon energy dependence of the 4s$^{-1}$ main line [4, 7, 8, 25, 26] and [4] also observed that a second group of satellite lines follow 4p$^{-1}$.

In the case of Kr, the distinction between 4s$^{-1}$ or 4p$^{-1}$ following allowed Caló et al to differentiate between different photoexcitation mechanisms. After absorbing an XUV photon with sufficient energy to eject at least one electron, the major route to additional excitation is through the shake-up mechanisms, classified into direct and conjugate shake-up (DSU and CSU). DSU sees exchange of energy between the photoelectron and excited electron, whereas in CSU there is an exchange of energy and angular momentum. DSU and CSU are distinguished.
according to which electron (ejected or excited) removes the majority of the photon momentum. CSU is dominant at or near threshold as there is a significant overlap between the initial bound and final continuum states, while DSU is strongest when the photon energy is tens or hundreds of eV above threshold. Satellites can also be populated by the CI, caused by the strong Coulomb interaction between the mixing of the single-hole and two-hole one-electron configurations, and tend to exhibit a structured influence from threshold to high photon energies.

Cross-sections for excitation during the photoionization of Kr are unknown at the photon energy range in this work, therefore the state assignment of [4] is employed, and we assume the main-line-following behaviour extends to a lower photon energy. This treatment relies on extrapolating the photon energy dependence, however it is hoped that this proof-of-principle experiment will initiate further studies in this area, clarifying the validity of this assumption.

To predict the Kr$^{2+}$ yield following the XUV and NIR pulses, we use the photoexcitation cross-sections $\sigma_{4s}$ and $\sigma_{4p}$ as fitting parameters, which are varied as a function of XUV photon energy. The XUV pulse duration is also known as a function of harmonic order, which is the result of the reduced harmonic emission duration and increasing divergence with increasing harmonic. Taking the photoelectron spectrum at 68.5 eV from [4], we scale the satellite peak intensities for those states identified to follow the behaviour of the 4s$^{-1}$ or 4p$^{-1}$ main lines by varying $\sigma_{4s}$ and $\sigma_{4p}$. Essentially, the population of the satellite states is predicted if the extrapolation to lower photon energy were to hold in the case of our assigned values of $\sigma_{4s}$ and $\sigma_{4p}$.

The rate of harmonic-induced satellite population is then predicted as a function of time through the XUV pulse; at each time-step (0.02 fs) the tunnel ionization of the cumulative satellite population is then predicted by an established strong-field ionization theory [10]. Importantly, this theory applies at arbitrary Keldysh parameter so is valid for all satellite states even in the vicinity of the ionization threshold. The rate of Kr$^{2+}$ production throughout the XUV and NIR pulses is then integrated to produce a yield as a function of XUV–NIR pulse delay. Finally, this process is repeated across the focal volume in the TOFMS, allowing a volume-weighted XUV-pump NIR-probe Kr$^{2+}$ yield to be generated for comparison with the experimental observations. To find the best fit $\sigma_{4s}$ and $\sigma_{4p}$ excitation cross sections and isolated harmonic pulse durations, the least-squares fit between experiment and theory is calculated for a range of all three fitting parameters and the best-fit compared with experiment.

4. Results and discussion

As shown in figure 3, a clear time-dependent enhancement in the experimental Kr$^{2+}$ yield is observed as a function of XUV-pump NIR-probe delay, with a varying amplitude and gradient depending on the isolated harmonic order. These observations are compared to the theoretical predictions integrated over the focal volume, and the corresponding tunnel ionization contribution from each satellite state presented.

We systematically vary the $\sigma_{4s}$ and $\sigma_{4p}$ trial photoexcitation cross-sections and XUV pulse duration to predict the Kr$^{2+}$ yield. Unlike our previous studies of atomic and molecular dynamics [27], the focal volume is characterised experimentally, i.e. measurements are made of the spot throughout the spectrometer source region. The grazing incidence optics in the XUV beamline cause a nonaxisymmetric focus, and as quantified recently in [28], removing a significant portion of a laser pulse with an annular optic causes a shift of the NIR focus with
Figure 3. Kr$^{2+}$ yield following XUV-pump and NIR-probe as a function of delay and harmonic order. Comparison of measured and predicted yields for (a) H21 (32.8 eV), (b) H23 (35.9 eV), (c) H25 (39.0 eV) and (d) H27 (42.1 eV) XUV pump with NIR probe at an intensity of $2 \times 10^{13}$ W cm$^{-2}$. Each point is a 2500-shot average, recorded at a laser repetition rate of 1 kHz. A 4-point FWHM Gaussian weighted average is applied to the data (solid magenta) to highlight the underlying variation. The predicted total Kr$^{2+}$ yield (black) is comprised of the 4s (red) and 4p (green) satellite contributions and the grey shading represents the uncertainty associated with varying $\sigma_{4s}$, $\sigma_{4p}$ and the XUV duration. For H21–H27, XUV pulse durations of 24, 26, 26 and $28 \pm 2$ fs, respectively, produce the best fit. Below each yield graph, the predicted Kr$^{2+}$ tunnel ionization yield from the satellite states are shown on a colour logarithmic plot.
Figure 4. Relative populations of satellite states predicted by the modelling and fitting routine discussed in the text. For harmonic orders (a) H21 to (d) H27, the populations of the satellite states identified in table 1 are presented as a function of binding energy. These states are derived from [4] and the populations are predicted by the photoexcitation cross-sections in figure 5, which produces the theoretical yield curve shown in figure 3 following tunnel ionization by the NIR pulse as predicted by [10]. The vertical dashed line represents the photon energy, excitation above which we assume is energetically forbidden.

respect to the zero-order of the monochromated beam. Despite some statistical noise in the Kr$^{2+}$ yield presented in figure 3, a change in the step size from H21 to H27 is seen, which the theoretical treatment reproduces very successfully. Furthermore the changing shape of the rising edge of the step is reproduced: H21 exhibits a sharp gradient change and H23 to H27 exhibit a successively less acute gradient. This is the result of the 4s satellite states becoming populated later in the XUV pulse and a changing distribution of population with XUV energy.

The best-fit satellite state populations as a function of binding energy and harmonic order are presented in figure 4, and the peak assignments employed in figures 3 and 4 are identified in table 1, taken directly from [4], and are only those satellite states that have been observed to exhibit a significant variation in intensity with photon energy.
Table 1. Kr$^+$ satellite energies and states populated following XUV photoionization identified by [4] to exhibit a photon energy dependence. The peak number corresponds to figures 3 and 4; peaks 1 to 10 are populated by shake-up following 4p photoionization and peaks 11 to 25 are populated by the CI following 4s photoionization.

| Peak No. | Energy (eV) | State                           |
|---------|-------------|---------------------------------|
| 1       | 35.88       | ($^1$D)5d($^2$G$_{9/2}$)+($^3$P)7p |
| 2       | 34.95       | ($^1$S)5p($^2$P$_{3/2}$)        |
| 3       | 32.63       | ($^1$D)5p($^2$P$_{3/2}$)        |
|         |             | ($^1$D)4d($^2$D$_{3/2}$)        |
| 4       | 31.65       | ($^3$P)5p($^2$S$_{1/2}$)        |
| 5       | 31.61       | ($^3$P)5p($^2$D$_{3/2}$)        |
| 6       | 31.57       | ($^3$P)5p($^4$S$_{3/2}$)        |
| 7       | 31.37       | ($^3$P)5p($^2$P$_{3/2}$)        |
| 8       | 31.22       | ($^3$P)5p($^2$P$_{1/2}$)        |
| 9       | 31.16       | ($^3$P)5p($^2$S$_{1/2}$)        |
| 10      | 30.65       | ($^3$P)5p($^4$D$_{3/2}$)        |
| 11      | 39.47       | ($^1$D)10d($^2$D$_{3/2}$)       |
| 12      | 39.31       | ($^1$D)9d($^2$D$_{3/2}$)        |
| 13      | 38.99       | ($^1$D)8d($^2$S$_{1/2}$)        |
| 14      | 38.55       | ($^1$D)7d($^2$S$_{1/2}$)        |
| 15      | 37.84       | ($^1$D)6d($^2$S$_{1/2}$)        |
| 16      | 36.48       | ($^1$D)5d($^2$S$_{1/2}$)        |
| 17      | 34.39       | ($^1$S)6s($^2$S$_{1/2}$)        |
| 18      | 34.15       | ($^3$P)5d($^2$D$_{1/2}$)+($^4$P$_{1/2}$)+($^2$F$_{7/2}$)+($^4$F$_{7/2}$) |
| 19      | 34.07       | ($^3$P)6s($^2$P$_{1/2}$)+($^4$P$_{3/2}$)+($^4$D$_{3/2}$) |
| 20      | 33.94       | ($^1$D)4d($^2$S$_{1/2}$)        |
| 21      | 32.08       | ($^1$S)5s($^2$S$_{1/2}$)        |
| 22      | 30.23       | ($^3$P)4d($^2$P$_{1/2}$)+($^2$P$_{1/2}$) |
| 23      | 30.06       | ($^3$P)4d($^2$P$_{1/2}$)+($^2$P$_{1/2}$)+($^4$F$_{5/2}$)+($^1$D)4d($^2$P$_{1/2}$) |
| 24      | 28.70       | ($^3$P)5s                        |
| 25      | 28.27       | ($^3$P)5s                        |

In addition to the variation of photoexcitation cross section with harmonic order, the XUV photon energy and photoionization cross sections place limits on the satellite states populated, and, as the harmonic order is varied, the ease with which the NIR pulse can initiate tunnel ionization. This is illustrated in figure 4 where the cumulative Kr$^+$ populations are presented for all satellite states following the XUV pulse only, and are equivalent to the photoelectron spectrum expected following the harmonic pulse. For H21, a limited group of low-lying satellite states are energetically permitted; H23 sees this limitation reduced. In H25, only a small number of high-lying 4s-following states cannot be accessed and for H27, the full range of states are available. The energy considerations of the populated satellite states is approximate: if the XUV photon energy lies below the main line and satellite state, shake-up or CI are treated as impossible; however, this is worthy of future theoretical investigation, particularly in light of [21]. Comparing figure 4 with the tunnelling contributions in figure 3 indicates that, as expected, tunnel ionization favours highly lying states with a large population.
Figure 5. (a) Relative photoexcitation cross-sections recovered from the XUV-pump NIR-probe measurements by the modelling and fitting procedure as compared to the 4s\(^{-1}\) and 4p\(^{-1}\) photoionization cross-sections. The uncertainties are estimated by varying the trial 4s and 4p photoexcitation cross sections until an appreciable change in the regression fit to the experimental Kr\(^{2+}\) yield is found. (b) The non-time-correlated residual Kr\(^{2+}\) yield from figure 2 is presented as a function of harmonic order, indicating the onset of direct double ionization for H25 and H27. The shaded region indicates that direct double ionization is energetically unfavourable and the error bars indicates 2 s.d. where the XUV and NIR pulses are well separated in time.

From the relative 4s and 4p photoionization cross-sections, figure 2(c), it might appear that the photoionization and excitation will be dominated by the 4p contribution, however two important factors must be considered. Firstly, there are many more high-lying satellites populated through 4s photoionization which will be far more readily tunnel ionized by the NIR (figures 3 and 4). This tips the balance in favour of the 4s states, particularly for H25 and H27. Secondly, without the influence of both the 4s- and 4p-following states, the best-fit XV pulse duration would approach 45 fs. The emission harmonic time is principally governed by the time within the pulse that significant tunnel ionization occurs in the argon gas jet (J1 in figure 1). For a 30 fs NIR drive pulse, harmonics 21 to 27 are caused by tunnelling in the central 12 to 8 fs of the pulse at the dominant intensity in the focal volume. For the plane grating employed in this work, we expect a full-width temporal response of 10 to 8 fs [23], calculated by ray-tracing paths from J1 to the exit slit through the monochromator. There is a requirement therefore that two processes are occurring: an XUV pulse with a duration of 45 fs would appear unlikely and our predicted XUV durations of 24 to 28 fs seem much more in line with the ray-tracing predictions.

The photoexcitation cross-sections employed to generate the fit presented in figure 3 are shown in figure 5(a), where the error bars are directly drawn from our estimate of the

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experimental uncertainty. By requiring that the predicted Kr$^{2+}$ yield lie within 2-sigma of the flat upper and lower sections of the measured yield step, and by varying the XUV pulse duration between 15 and 45 fs, we include only those XUV durations that cause a minimal variation of the least-squares fit.

An absolute comparison between photoionization and excitation cross sections cannot be performed as normalization to previous observations has not been possible, however relative comparisons reveal the energetic trends. Comparing the $\sigma_{4s}$ and $\sigma_{4s}$ satellite photoexcitation cross-sections to the $4s^{-1}$ and $4p^{-1}$ main-line photoionization cross-sections, it appears that the $4p$ satellite follows the energy dependence of the $4p^{-1}$ main line, which is most likely the result of DSU and CI dominating, as this route is $\simeq 20$ eV above threshold. This confirms the observations [4, 7] at a significantly lower photon energy despite using a radically different experimental configuration. The $4s$ satellite exhibits a distinct divergence from the $4s^{-1}$ cross-section although a minimum is predicted. The separation between the $4s^{-1}$ and satellite states ranges from 0 to 13 eV hence DSU, CSU and the CI are all possible however CSU is expected to dominate. CSU is the result of multi-electron interactions and is unlikely to be well approximated by the main line. This is, to our knowledge, the first example of the recovery of excitation partial cross sections with an ultrafast source.

5. Single-photon double-ionization

An interesting by-product of the measurement presented in figure 3 is the first observation of SPDI at threshold using a harmonic source, shown in figure 5(b). A single H25 or H27 photon can directly initiate generate a double 4p subshell vacancy, as apparent from figure 2(b). As presented in figure 3, for H21 and H23 the Kr$^{2+}$ yield is zero when the NIR pulse precedes the XUV pulse, however for H25 and H27, there is a clear Kr$^{2+}$ offset that exhibits no time dependence. The XUV intensity is not sufficient to permit two-photon effects, therefore the remaining route is SPDI. This further demonstrates the usefulness of this technique as it facilitates the selective population of electronic states across an ionization threshold, which will be of major importance when examining more electronically complex systems. We envisage using the monochromated XUV flux to populate specific electronic states, which when coupled with photoelectron spectroscopy, will allow the evolution of molecular and solid state systems to be investigated with unprecedented fidelity.

6. Conclusion

This proof-of-principle experiment has demonstrated how isolated harmonics from a time-preserving monochromatic ultrafast XUV source coupled with a strong-field probe can be employed to probe atomic excitation and ionization. Such a technique is highly complementary to current and emerging techniques involving attosecond and XFEL sources, with wide-ranging future possibilities for driving molecular and solid state systems far from equilibrium.

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