Traces on ion yields and electron spectra of Ar inner-shell hollow states with Free-Electron Lasers

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We explore the formation by Free-Electron-Laser radiation of Ar hollow states with two or three inner-shell holes. We find that even charged Ar ion states can be more populated than odd charged Ar ion states. This depends on the pulse intensity and the number of energetically accessible inner-shell holes. Fully accounting for fine structure, we demonstrate that one electron spectra bare the imprints of Ar hollow states with two inner-shell holes. Moreover, we show how the Auger spectra of these hollow states can be extracted from two-electron coincidence spectra.

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The advent of extreme ultraviolet and X-ray Free-Electron Lasers (FELs) allows the exploration of novel states of matter. One fascinating aspect of FELs is that the laser boils away electrons from the inside out giving rise to hollow atoms and molecules. To monitor the femtosecond time-scale dynamics of these hollow states one needs to identify the ionization pathways that lead to their formation. Understanding the processes leading to the formation of hollow states will allow these states to be employed as the basis for a new type of spectroscopy for chemical analysis [1–4]. It will also assist in achieving atomic resolution in diffraction patterns from biological molecules interacting with FEL-radiation [5–6].

We consider Ar interacting with FEL radiation. For each additional inner-shell hole that becomes energetically accessible, a link of a PC and an AV transition is added to the ionization pathways. Even charged Ar ion states are primarily populated by chains of these links. P stands for a single-photon ionization of an electron and A for an Auger decay with an electron from a higher orbital, denoted as the subscript in A, dropping to fill in a hole. C and V stand for a core and a valence electron, respectively. We show that when hollow states with two inner-shell holes are formed, the ion yield of Ar\(^{2+}\) is larger than the ion yield of Ar\(^{2n+}\), with \(n = 1, \ldots, h\) and \(h\) the number of holes. This is true for all intensities. However, when three inner-shell holes are energetically accessible, additional transitions become available. These are Coster-Kronig Auger (AC) transitions [7] where the hole and the electron dropping in to fill the hole occupy sub-shells with the same \(n\) and different \(l\) numbers. As a result, we find that it is only for higher intensities that the yield of the even charged Ar ion states is larger than the yield of the odd charged Ar ion states.

Focusing on two inner-shell holes, we demonstrate how to identify the formation of the Ar\(^{2+}\)(2p\(^{-2}\)) hollow state [8][10]. We show that the yield of Ar\(^{4+}\), which bare the imprint of Ar\(^{2+}\)(2p\(^{-2}\)), is not sufficient for identifying this hollow state. The reason is that Ar\(^{4+}\) is populated by competing ionization pathways, however, not all of these pathways contribute to the formation of the hollow state. Unlike in the ion yields, we find that in the one electron spectra these competing pathways leave different traces and we can thus discern the formation of Ar\(^{2+}\)(2p\(^{-2}\)). We also show how to extract the Auger spectrum of the hollow state from two-electron coincidence spectra.

We first describe the rate equations we use to obtain our results [11][12]. We account for the general case when multiple states lead to state j, for example, i → j → k and i' → j → k. To compute the contribution of the state i to the yield \(\mathcal{I}_{(j(i))}^{(q-1)}\) of the ion state j with charge \(q - 1\) we solve the rate equations:

\[
\frac{d}{dt} \mathcal{I}_{(j(i))}^{(q-1)}(t) = (\sigma_{i-j} J(t) + \Gamma_{i-j}) \mathcal{I}_{(j(i))}^{(q-2)}(t) - \sum_{k'} (\sigma_{j-k'} J(t) + \Gamma_{j-k'}) \mathcal{I}_{(j(i))}^{(q-1)}(t) - \sum_{k'} (\sigma_{j-k'} J(t) + \Gamma_{j-k'}) \mathcal{I}_{(j(i))}^{(q-1)}(t)
\]

where \(\sigma_{i-j}\) and \(\Gamma_{i-j}\) are the single-photon absorption cross section and the Auger decay rate from the initial state i to the final state j, respectively. J(t) is the photon flux, which is modeled with a Gaussian function. Atomic units are used in this work. For details on how we compute \(\Gamma_{k-j}\), see [11]. The first term in Eq. [1] accounts for the formation of the state j with charge \(q - 1\) through the single-photon ionization and the Auger decay of the state i with charge \(q - 2\). The second term in Eq. [1] accounts for the depletion of state j by single-photon ionization and Auger decay to the state \(k'\) with charge \(q\). In addition, we compute the photo-ionization \(\mathcal{P}_{(j(i))}^{(q)}\) and the Auger \(\mathcal{A}_{(j(i))}^{(q)}\) yields, with \(q\) the charge of the final state k. These yields provide the probability for observing two electrons with energies corresponding to the transitions i → j and j → k. Using these yields, we obtain the coincidence two-electron spectra. The one electron spectra, that is, the transition yields from an initial state j with charge \(q - 1\) to a final state k with charge \(q\) and the ion yields of the state j and of all the states with charge \(q - 1\)
FIG. 1. Ion yields of Ar$^{n+}$ for a pulse of $5\times 10^{15}$ W cm$^{-2}$ intensity, 10 fs duration and different photon energies. For each photon energy, the number of accessible inner-shell holes is different: (a) 200 eV, no inner-shell holes; (b) 260 eV, a single 2p inner-shell hole; (c) 315 eV, two 2p inner-shell holes. (d) 360 eV, three 2p and a combination of two 2p and one 2s inner-shell holes. Highlighted in red is the contribution of Coster-Kronig Auger transitions. (e) for 315 eV and (f) for 360 eV show the contribution of pathways that are differentiated by the maximum number of core holes in any state along each pathway: light grey corresponds to zero maximum number of core holes, grey to one, black to two and striped black lines to three.

are given by

$$P_{j\rightarrow k}^{(q)} = \sum_{i} P_{j(i)\rightarrow k}^{(q)} \quad A_{j\rightarrow k}^{(q)} = \sum_{i} A_{j(i)\rightarrow k}^{(q)} \tag{2}$$

$$T_{j}^{(q-1)} = \sum_{i} T_{j(i)}^{(q-1)} \quad I_{j}^{(q-1)} = \sum_{j} I_{j}^{(q-1)}. \tag{3}$$

In Fig. 1 we compute the yields of the Ar$^{n+}$ ion states for four photon energies and for a high pulse intensity of $5\times 10^{15}$ W cm$^{-2}$. We do so accounting only for the electronic configuration of the ion states in the rate equations and without including fine structure. We first consider a photon energy sufficiently low, 200 eV, that single-photon ionization events do not lead to the formation of inner-shell holes. In Fig. 1(a), we show that the Ar$^{n+}$ ion states are populated in descending order. For 260 eV, a single 2p inner-shell hole is accessible by a P$_C$ process from neutral Ar. A P$_C$ is a much more likely transition than a P$_V$ one. As a result, for all intensities, the population going through Ar$^+(2p^{-1})$ is much larger than the population ending up in or going through Ar$^+(3v^{-1})$. In addition, since the P$_C$ photo-ionization is followed by an A$_V$ decay—P$_C$A$_V$ pathway—the ion yield of Ar$^{2+}$ is higher than the ion yield of Ar$^+$, see Fig. 1(b). For 315 eV, two 2p inner-shell holes are accessible by two P$_C$ events, see Fig. 2(a). As for 260 eV, Ar$^{3+}$ has a larger population than Ar$^+$. In addition, P$_C$A$_V$P$_C$A$_V$ and P$_C$P$_C$A$_V$A$_V$ are now energetically allowed pathways that populate Ar$^{4+}$, see Fig. 2(a). Since, Ar$^{3+}$ is populated by pathways involving at least one P$_V$ process, Ar$^{4+}$ has a larger population than Ar$^{3+}$, see Fig. 1(c). For 360 eV, three 2p inner-shell holes or a combination of one 2s and two 2p inner-shell holes are accessible through three P$_C$ events, see Fig. 2(b). Pathways involving three P$_C$ and three A$_V$ transitions, such as P$_C$A$_V$P$_C$A$_V$P$_C$A$_V$, are now energetically allowed and populate Ar$^{6+}$. For 200 eV, 260 eV and 315 eV the odd charged states are populated only by pathways that include at least one P$_V$ process. In contrast, for 360 eV, pathways that include Coster-Kronig Auger transitions between the 2s and 2p sub-shells are energetically allowed. These path-
as does not necessarily involve a PV event. For instance, in Fig. 2(b), we show the P_{CV}A_{V} pathway that includes a Coster-Kronig transition (AC) and populates Ar^{3+}. When no Coster-Kronig transitions are present, the most probable pathways populating the Ar^{2n−1+} states and those populating the Ar^{2n} states have the same number of P events, with n = 1, ..., h. Thus, for 260 eV and for 315 eV, the yield of the Ar\textsuperscript{2n−1+} states is less than the yield of the Ar\textsuperscript{2n} states for all intensities. However, when a Coster-Kronig transition is present some of the most probable pathways populating the Ar\textsuperscript{2n−1+} states have one P transition less than the most probable pathways populating the Ar\textsuperscript{2n} states. As a result, the yield of the Ar\textsuperscript{2n−1+} states is larger/smaller than the yield of the Ar\textsuperscript{2n} states for low/high intensities. For a high pulse intensity of 5 × 10\textsuperscript{15} W cm\textsuperscript{−2}, in Fig. 1(d), we show that the ion yields of Ar\textsuperscript{4+} and Ar\textsuperscript{5+} are larger than the ion yields of Ar\textsuperscript{3+} and Ar\textsuperscript{4+}, respectively.

For the results in Fig. 3 double ionization (DI) and double Auger (DA) decays are not accounted for. These are both processes where two electrons are ejected in one step. Some of the pathways DI and DA give rise to have one P process less compared to pathways where only one electron is ejected at each ionization step. As a result, the contribution of these two processes is less for high intensities. Moreover, these two processes are significantly less likely than the ionization processes we currently account for in our calculations. For instance, the probability for a DA decay from a 2p hole in Ar is roughly 10% of the probability for a single Auger decay.

For 260 eV and 315 eV, we plot as a function of intensity the yield of Ar\textsuperscript{4+} and Ar\textsuperscript{5+}, respectively. For 315 eV, the single-photon ionized electrons from a valence shell (3s or 3p) escape with energy between 214 eV and 300 eV. The P\textsuperscript{(q)}\textsubscript{j−i}k yields for valence shell electons do not necessarily involve a PV event. For instance, in Fig. 2(b), we show the P_{CV}A_{V} pathway that includes a Coster-Kronig transition (AC) and populates Ar^{3+}. When no Coster-Kronig transitions are present, the most probable pathways populating the Ar\textsuperscript{2n−1+} states and those populating the Ar\textsuperscript{2n} states have the same number of P events, with n = 1, ..., h. Thus, for 260 eV and for 315 eV, the yield of the Ar\textsuperscript{2n−1+} states is less than the yield of the Ar\textsuperscript{2n} states for all intensities. However, when a Coster-Kronig transition is present some of the most probable pathways populating the Ar\textsuperscript{2n−1+} states have one P transition less than the most probable pathways populating the Ar\textsuperscript{2n} states. As a result, the yield of the Ar\textsuperscript{2n−1+} states is larger/smaller than the yield of the Ar\textsuperscript{2n} states for low/high intensities. For a high pulse intensity of 5 × 10\textsuperscript{15} W cm\textsuperscript{−2}, in Fig. 1(d), we show that the ion yields of Ar\textsuperscript{4+} and Ar\textsuperscript{5+} are larger than the ion yields of Ar\textsuperscript{3+} and Ar\textsuperscript{4+}, respectively.

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trons are very small and not visible in Fig. 4. Moreover, the Auger electrons escape with energies between 150 eV and 240 eV. Thus, Auger electrons are well separated from single-photon ionized electrons. The most probable Auger and single-photon ionization transitions are depicted in Fig. 4. During the transition: i) \( \text{Ar}^+ (2p^{-1}) \rightarrow \text{Ar}^{2+} (3e^{-2}) \) the first Auger electron is ejected along \( \text{P}_{\text{C}}\text{C}_{\text{A}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) with energy from 173 eV to 208 eV \[14\]. ii) \( \text{Ar}^+ (2p^{-2}) \rightarrow \text{Ar}^{3+} (2p^{-1}3e^{-2}) \) the first Auger electron is ejected along \( \text{P}_{\text{C}}\text{C}_{\text{A}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) with energy from 181 eV to 241 eV and iii) \( \text{Ar}^{3+} (2p^{-2}3e^{-2}) \rightarrow \text{Ar}^{4+} (3e^{-4}) \) the second Auger electron is ejected along \( \text{P}_{\text{C}}\text{C}_{\text{A}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) with energy from 140 eV to 198 eV. Thus, the Auger transition ii) that bares the imprint of \( \text{Ar}^{2+} (2p^{-2}) \) can be clearly discerned only for energies above 208 eV. For smaller energies Auger transitions i) and ii) strongly overlap. During the transitions: iv) \( \text{Ar} \rightarrow \text{Ar}^+ (2p^{-1}) \) the first photo-ionized electron is ejected along \( \text{P}_{\text{C}}\text{C}_{\text{A}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) and \( \text{P}_{\text{C}}\text{A}_{\text{V}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) with energy from 65 eV to 67.5 eV, v) \( \text{Ar}^+ (2p^{-1}) \rightarrow \text{Ar}^{2+} (2p^{-2}) \) the second photo-ionized electron is ejected along \( \text{P}_{\text{C}}\text{C}_{\text{A}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) with energy from 1 eV to 25 eV and vi) \( \text{Ar}^{2+} (3e^{-2}) \rightarrow \text{Ar}^{3+} (2p^{-1}3e^{-2}) \) the second photo-ionized electron is ejected along \( \text{P}_{\text{C}}\text{C}_{\text{A}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) with energy from 22 eV to 41 eV. From 22 eV to 25 eV there is an overlap between photo-ionization transitions v) and vi). However, transition v) is orders of magnitude larger than vi). Since transition v) bares the imprint of \( \text{Ar}^{2+} (2p^{-2}) \), we can clearly identify the formation of the hollow state from the one-electron spectra.

![FIG. 4. One electron spectra, for a pulse of \( 5 \times 10^{15} \) W cm\(^{-2}\) intensity, 10 fs duration and 315 eV photon energy.](image)

Finally, we show how to extract the Auger spectrum of \( \text{Ar}^{2+} (2p^{-2}) \) from two-electron coincidence spectra. Coincidence experiments have been performed extensively with synchrotron radiation \[16 \ 17\]. It is expected that coincidence experiments with FEL-radiation will take place in the near future \[16 \ 18\]. In anticipation of these experiments, in Fig. 5 we plot the coincidence spectra of a single-photon ionized electron and an Auger electron. This choice of electrons is based on the fact that single-photon ionized electrons are well separated in energy from Auger electrons, see Fig. 4. Moreover, we have already shown that for energies of a single-photon ionized electron (\( E_p \)) up to 25 eV we can clearly discern the second \( \text{P}_C \) event—previously denoted as transition v)—in the \( \text{P}_C\text{P}_{\text{C}}\text{A}_{\text{V}}\text{A}_{\text{V}} \) pathway. Indeed, as shown in Fig. 5 there is no trace of the \( \text{P}_C\text{A}_{\text{V}}\text{P}_{\text{C}}\text{A}_{\text{V}} \) pathway for \( E_p < 25 \) eV. Focusing on \( E_p < 25 \) eV, the energies of the Auger electron from 140 eV to 198 eV correspond to the transition \( \text{Ar}^{3+} (2p^{-1}3e^{-2}) \rightarrow \text{Ar}^{4+} (3e^{-4}) \), while from 181 eV to 241 eV correspond to the transition \( \text{Ar}^{2+} (2p^{-2}) \rightarrow \text{Ar}^{3+} (2p^{-1}3e^{-2}) \). It is this latter transition that corresponds to the Auger spectra of the \( \text{Ar}^{2+} (2p^{-2}) \) hollow state. In more detail, the Auger spectrum of the \( ^1\text{S}_0 \) fine structure state is the sum of the spectra corresponding to \( E_p \) around 1.4 eV and 3.6 eV. These two energies correspond to the \( ^2\text{P}_{1/2} \) and \( ^2\text{P}_{1/2} \) fine structure states of \( \text{Ar}^+ (2p^{-1}) \). The Auger spectrum of the \( ^3\text{D}_2 \) fine structure state is the sum of the spectra corresponding to \( E_p \) around 13.5 eV and 15.6 eV. Finally, it is more difficult to discern the Auger spectra of the \( ^3\text{P}_{0.1.2} \) fine structure states in the interval 20.2 eV< \( E_p < 24.6 \) eV. It is also mainly the Auger spectra of these \( ^3\text{P}_{0.1.2} \) states that overlaps in the energy interval from 181 eV to 198 eV with the Auger transition \( \text{Ar}^{3+} (2p^{-1}3e^{-2}) \rightarrow \text{Ar}^{4+} (3e^{-4}) \).

[FIG. 5. Coincidence spectra of an Auger and a photo-ionized electron. The pulse parameters are \( 5 \times 10^{15} \) W cm\(^{-2}\) intensity, 10 fs duration and 315 eV photon energy.](image)
we demonstrated how two-electron spectra carry infor-

mation regarding the Auger spectra of hollow states.

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