Multi-coincidence in cascade Auger decay processes

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Abstract. Two-electron emission following inner shell ionization of rare-gas atoms by synchrotron radiation has been investigated experimentally with a magnetic bottle electron time of flight spectrometer. The detection in coincidence of a photoelectron with all Auger electrons allows a complete understanding of inner shell hole decay. This method has been applied to the study of single and double Auger decays following Xe 4d, Ar 2p and Kr 3d inner shell ionization. The double Auger decay scheme reveals direct double Auger process but is dominated by cascade processes involving inner-valence electrons in a first step followed by autoionization. Post collision interaction (PCI) associated to distorted Auger spectra and double photoionization paths in the vicinity of Xe 4d threshold, is also discussed.

1. Introduction

Several deexcitation pathways are possible after inner shell ionization. Relaxation by emission of an Auger electron is an important process which provides a fingerprint of the system studied.

When a hole is created in a deep inner shell, Auger decay is in competition with radiative decay by X-ray emission [1]. Both processes can populate states with remaining inner shell vacancies that will undergo further Auger decay leading, finally, to multiply charged ions. But such process also occurs for shallow inner shells for which X-ray decay is negligible. If the energy of the initial excited ion (with inner shell hole) is higher than the triple (or higher) ionization threshold as for Xe 4d [2], Ar 2p [3] and Kr 3d [4] it is possible to observe, in addition to the “normal” single Auger process, a process where two Auger electrons are emitted. These decays occur by two ways: 1- a direct process observed for the first time by Krause in 1965 [5] where the two electrons are ejected at the same time and share continuously the available excess of energy, 2- a sequential process, where the doubly charged ion state populated in the first Auger decay is autoionizing and releases a second electron. This double Auger process is less intense than “normal” single Auger decay but is not negligible.
The limited understanding of such processes comes from the difficulty to study them with conventional electron spectroscopy (i.e. using electrostatic analyzers). They involve low energy peaks and also a continuous energy distribution which is difficult to separate from background. The best way to observe these processes is to measure all the electrons in coincidence [6-8]. A complete picture of these processes is difficult to obtain by conventional coincidence techniques using electrostatic analyzers due to a low angular acceptance. In this case, only coincidences between two electrons have been realized so far, even if three or more electrons are involved. Major improvements were done by measuring coincidences between electrons and ions, including analysis of the final charge of the ion [9] but the identification of the decay paths is still difficult. Only a complete experiment where all the electrons are detected allows to disentangle these processes of inner shell ionization and consecutive multiple ionization. We will present such apparatus (HERMES for High Energy Resolution Multi Electron Spectrometer) in this paper with selected results in rare gas atoms: single and double Auger decays and also PCI effect in single Auger process.

2. Experiment

We have used a magnetic bottle time of flight spectrometer. Such apparatus was initially developed by J.H.D. Eland [10] with a pulsed helium lamp. Two spectrometers of this type have been implemented on synchrotron radiation: a first one in Europe was used at Super ACO (Orsay, France) and later at BESSY II (Berlin, Germany) and a second one in Japan at Photon Factory (Tsukuba). The single (or two) bunch mode provided by these synchrotron radiation facilities gives a period between bunches of 120 ns at Super ACO, 634 ns at Photon Factory and 800.5 ns at BESSY II and is necessary for electrons time of flight measurements. The total length of the magnetic bottle was 2.5 m to fit in synchrotron environment while keeping a good energy resolution (the longer the time of flight, the better the energy resolution). The principle of the magnetic bottle electron time of flight spectrometer (MBS) was described elsewhere [2, 3, 7, 10-14] and is briefly recalled here. A conical shaped permanent magnet (FeNdB) placed close to the interaction region creates a strongly divergent magnetic field of about 0.5 T at 1 mm from the tip of the magnet. The resulting magnetic mirror configuration collects all electrons on almost the full solid angle. The trajectories of the electrons are parallelized [14] after a few centimeters and the electrons are guided in the field (0.5 to 1 mT) of a long solenoid. The electrons fly along this solenoid towards a multi-hit detector (micro channel plates with delay line position encoding or phosphor screen). The scheme of the set-up is shown in Fig 1.

![Figure 1. Scheme of HERMES experiment.](image)

The electrons time of flight are measured with respect to the light pulse by a time to digital converter with a 250 ps time resolution. The magnetic bottle spectrometer collects all the electrons emitted from almost (> 98%) 4π solid angle from 0 to about 200 eV with an excellent energy
resolution: $\Delta E/E = 1.6\%$ (see Fig 1 of reference [3]). Due to the parallelization process in the strong inhomogeneous magnetic field, the initial angular information of the emitted electrons is lost. The time of flight of electrons is only obtained modulo the light pulse period, but this limitation applies only to the first electron: after its detection, the time of flight of successive electrons is no longer limited in time. A small repelling potential is applied to the magnet in order to collect zero energy electrons on the detector in a finite time (typically less than 5µs). The dead time of the detector (~20ns) forbids detection of electrons with the same kinetic energies. Time to energy conversion and calibration are performed using photoelectrons peaks of well known energy. Some additional calibration points can be taken into account, provided by known Auger transitions for the rare gases studied. Time to energy conversion is given by a simple formula $t = t_0 + D/\sqrt{E-E_0}$ where $t$ is the time of flight of the electron, $E$ its energy, $D$ is proportional to the time of flight length ; $t_0$ and $E_0$ are adjustable parameters. Some corrective terms can be added to the formula to take into account deviations from this formula due to patch potentials.

3. Results

All the processes presented here have a common start: inner shell ionization. A photon of appropriate energy interacts with a rare gas atom and ejects a photoelectron ($e_{ph}$) from an inner shell. The resulting excited ion has different possibilities to release the excess of energy. The purpose of this paper is to focus on Auger decays following core hole ionization. Single and double Auger processes, leading respectively to double and triply ionized atoms are given by the next equation. In the single Auger process, only one Auger electron ($e_A$) is emitted, whereas in double Auger decays, two electrons ($e_{A1}$ and $e_{A2}$) are emitted after the photoelectron. Higher ionized states, not shown here, can also be obtained after multiple Auger decays if the process is energetically possible.

$$h\nu + A \rightarrow A^+ + e_{ph} \rightarrow A^{2+} + e_{ph} + e_A$$

$$\rightarrow A^{3+} + e_{ph} + e_{A1} + e_{A2}$$

Our measurements allow filtering the events against the energy of the photoelectron deduced from its time of flight. The photoelectron is the first signature of the core hole and we can sort and visualize the events (single and double Auger processes) according to which core hole is created. We will show selected examples of inner shell ionization of rare gases: Ar 2p, Kr 3d and Xe 4d. We will also present the PCI effect in the case of Kr 3d single Auger process.

3.1. Auger decays of the Argon 2p hole

The first example we will discuss is the Auger decay of the 2p holes in Argon. A 337 eV photon energy was chosen to ionize 2p inner shell (2p holes have binding energies of 248.628 eV ($2p_{3/2}$) and 250.776 eV ($2p_{1/2}$) [15]). Doubly and triply (and even higher) charge states of Argon are accessible after Auger relaxation since the Ar$^{2+}$ and Ar$^{3+}$ thresholds are found respectively at 43.389 eV and 84.124 eV [16].

After inner shell ionization, we can sort the events depending on the photoelectron time of flight (our apparatus resolution is high enough to resolve the $2P_{1/2}, 3/2$ photoelectron peaks around 90 eV, which are separated by 2.15 eV [15]) and transform those times of flight in energies as described above.

3.1.1. Single Auger decay of argon 2p hole

Single Auger process is the main decay channel after 2p inner shell ionization. We can summarize it as followed:

$$h\nu (337 \text{ eV}) + \text{Ar} \rightarrow \text{Ar}^{+} (2p^{-1}) + e^-_{ph} \rightarrow \text{Ar}^{2+} + e^-_{ph} + e^-_{\text{Auger}}$$

Fig 2 presents the single Auger spectra. We show the total Auger spectrum (bottom part) and the ones obtained after filtering of the photoelectron time of flight ($2P_{3/2}$ on top, $2P_{1/2}$ in the middle).
The single Auger spectra shown in Fig 2 are not comparable with high resolution data (ref [17] for instance) but our coincidence set-up allows the filtering the spectra associated to different sub shells. At this resolution (around 3 eV for the energy range of those spectra) it is not possible to identify clear differences between the components except the 2p_{1/2, 3/2} spin-orbit shift of the Auger lines. Auger lines are visible corresponding to Ar^{2+} states lying around 86 eV and 95 eV binding energies. Since the Ar^{3+} threshold is 84.124 eV, these states can be involved in cascade double Auger processes.

![Figure 2. Auger spectra following Ar 2p inner shell ionization.](image)

3.1.2. Double Auger decay of argon 2p hole

The double Auger process leads to triply charged Argon states, with emission of two Auger electrons:

\[ \text{hv (337 eV)} + \text{Ar} \rightarrow \text{Ar}^{2+}(2p^0) + e^{-}_{\text{ph}} + \text{Ar}^{3+} + e^{-}_{\text{Auger}1} + e^{-}_{\text{Auger}2} \]

Fig 3 figures the energy map of the double Auger decay following Ar 2p inner shell ionization. The 2D map presents the distribution of the two Auger electrons filtered by 2p_{1/2} (left part) or 2p_{3/2} (right part) when three electrons are detected in coincidence. X-axis shows \(E_{A1}-E_{A2}\), the difference of kinetic energy of the two Auger electrons, whereas Y-axis figures the \(E_{A1}+E_{A2}\) sum. Projection on Y-axis gives directly the spectra of final Ar^{3+} states (side parts).

As we can see in Fig 3, direct double Auger process is also clearly observed by a continuous energy distribution between the two electrons for a selected final state (horizontal line). But these lines reveal several spots where most of the coincidence counts are concentrated. That means that the double Auger decays are dominated by cascade processes. The Ar^{2+} states involved in this cascade are mainly states with 3s^2 configurations [3].
3.2. Auger decay of the Krypton 3d hole

We will now focus on Auger decays following Krypton 3d inner shell ionization. As double (Kr$^{2+} \ 3p_2$ (4s$^2$4p$^2$) at 38.358 eV [16]) and triple (Kr$^{3+} \ 5S (4s^24p^3))$ at 75.308 eV [16, 18]) ionization thresholds are below the Kr$^+$ 3d$^{-1}$ states (93.788 eV for 3d$^{5/2}$ and 95.038 eV for 3d$^{3/2}$ [15]), the first excited states of Kr$^{2+}$ and Kr$^{3+}$ can be populated by deexcitation and electronic rearrangement after 3d inner shell ionization. Both single and double Auger processes will be discussed in more details elsewhere [4], here we will just present some selected results about double Auger decay.

In our study, 140 eV photons were used, allowing to ionize krypton in 3d shell while keeping a good resolution for photoelectrons (important to separate 3d$^{5/2}$ and 3d$^{3/2}$ photoelectrons). At this photon energy, the photoelectrons kinetic energy around 45eV does not coincide with any Auger electron energy.

Around 45 eV the resolution of our apparatus is good enough (about 0.7 eV) to resolve the 3d photoelectron peaks separated by 1.25 eV [15] and we can easily filter the events associated to 3d$^{3/2}$ and 3d$^{5/2}$ inner shell ionization. After that we convert the times of flight values into energies as described previously.
3.2.1. Single Auger decay of krypton 3d hole

Single Auger decay after krypton 3d hole is given by the following equation:

\[ h\nu (140 \text{ eV}) + \text{Kr} \rightarrow \text{Kr}^+ (3d^{1+}) + e^-_{\text{ph}} \rightarrow \text{Kr}^{2+} + e^-_{\text{ph}} + e^-_{\text{Auger}} \]

Fig 4 presents the single Auger spectra after 3d inner shell ionization. The total Auger spectrum (bottom part) and the filtered spectra (3d\(3/2\) on top, 3d\(5/2\) in the middle) are presented.

Even if the spectra presented in Fig 4 are not comparable in terms of energy resolution with those presented in references [19, 20], according to the filtering of the process possible with our coincidence method, it is possible to visualize filtered spectra for the single Auger process and to know which states of Kr\(^{+}\) are populated after which core hole and to extract the branching ratio for overlapping peaks issued from different inner shells (that would be difficult to extract from the total Auger spectrum). More details will be given in reference [4].

In the low energy part of those spectra, we can see some peaks which have the same kinetic energies in the two channels while most of the Auger peaks are just shifted by the 3d\(3/2\)-5/2 spin-orbit splitting. These peaks are due to double Auger process when Kr\(^{5+}\) states are populated from the two sub shells and emit a second electron in their decay to Kr\(^{3+}\).

3.2.2. Double Auger decay of krypton 3d hole

The double Auger process following creation of a 3d hole is less documented than the single Auger process. This process leads to triply charged krypton ion, with emission of two Auger electrons:

\[ h\nu (140 \text{ eV}) + \text{Kr} \rightarrow \text{Kr}^+ (3d^{1+}) + e^-_{\text{ph}} \rightarrow \text{Kr}^{3+} + e^-_{\text{ph}} + e^-_{\text{Auger1}} + e^-_{\text{Auger2}} \]

Fig 5 (central parts) presents the energy correlation map between the two Auger electrons filtered by the 3d\(3/2\) (right panel) or 3d\(5/2\) (left panel) photoelectron, when three electrons are detected in coincidence. Axes are defined as in Fig 3 (X-axis: \(E_{A1} - E_{A2}\), Y-axis: \(E_{A1} + E_{A2}\)).
The horizontal lines correspond to the Kr$^{3+}$ states $4p^{-3}$ ($4S, 2D, 2P$) $4p^{-2}$ $4s^{-1}$ ($4P_{5/2, 3/2, 1/2}$ and $2D_{5/2, 3/2}$). Fig 5 is decomposed as follow: left part for 3d$^{3/2}$ ionization and right part for 3d$^{5/2}$ ionization. The projection on $E_{A1}+E_{A2}$ gives the energy of the Kr$^{3+}$ states (side parts).

Horizontal lines in the 2D map correspond to a constant energy sum (i.e. $E_{A1} + E_{A2}$ = constant) and provide information on Kr$^{3+}$ final states accessible after 3d$^{3/2}$ or 3d$^{5/2}$ inner shell ionizations since $E(Kr^{3+}) = E(Kr^{+}+(3d^{1}-1)) - (E_{A1}+E_{A2})$. The projection of the 2D map on the vertical axis (summation on $E_{A1}$) (side parts in Fig 5 correspond to the sum ($E_{A1} + E_{A2}$)) gives the energy of Kr$^{3+}$ states populated after double Auger decay and their relative population. The triple ionization threshold Kr$^{3+}$ $4S$ ($4s^{2}4p^{2}$) is found at 74.197 eV ± 20 meV, instead of 75.308 eV found in 1935 by Humphreys [16, 18] still referred by NIST which is incorrect. Our value is in good agreement with the 74.208 eV found by Viefhaus and co-workers [20]. Other Kr$^{3+}$ states are in good agreement with literature once referred to Kr$^{3+}$ ground states. The lines observed in 2D spectra in Fig 5 present a continuous background corresponding to direct double Auger where the two electrons share randomly the energy available. However these lines are clearly dominated by intense spots which reveal cascade double Auger decay, populating different intermediate states of Kr$^{2+}$ which are presumed to be states with major $4s^{-2}$ configuration or satellites states which correlate with those $4s^{-2}$ states. To summarize, double Auger process in those cases begins by a single Auger process involving only two 4s electrons that populates states with $4s^{-2}$ configuration, since these states lie above triple ionization threshold they generally decay by autoionization in the last step.

3.3. Post-Collision Interactions

In the previous examples, the photon energies were chosen to be sure that the energy of the photoelectron was not affected by the Auger process. Here, we will consider the case where the photoelectron exchanges energy with the Auger electrons. Reference [12] and [13] already present a complete overview of such processes in the case of Kr 3d. We will focus here our attention on PCI effect following Xe 4d ionization. Such results were recorded at Photon Factory and presented in reference [21] but the resolution was strongly improved for similar results recorded at BESSY II. A
photon energy of 70.2 eV was used, giving 2.7 eV as excess energy for the 4d$_{5/2}$ photoelectron. Fig 5 display the 4d$_{5/2}$ photoelectron taken in coincidence with different Auger electrons energies (8 eV in blue, 15 eV in red and 30 eV in black). The green line figures the position of the 4d$_{5/2}$ photoelectron without the PCI perturbation.

![Graph](image.png)

**Figure 5.** Energy map of the single Auger process following Xe 4d inner shell ionization affected by PCI effect. In that case, photon energy of 70.2 eV was used. Both theoretical (lines) and experimental (dots) curves are plotted.

We can clearly see the influence of the Auger electron kinetic energy on the PCI effect: the faster the Auger electron the stronger the PCI shift of the photoelectron. The theoretical spectra (lines) calculated by S. Sheinerman are also plotted and are in very good agreement without any additional energy convolution due to the improved experimental energy resolution which is now small compared to the PCI shift. Other excess energy spectra have been recorded and the associated calculations are in progress.

3.5. Conclusion

Results concerning the Auger decays of the Xenon 4d hole were not detailed in this paper. Reference [8] gives a complete overview of single Auger scheme, whereas reference [2] describes Xe 4d double Auger decay. To summarize emission of two Auger electrons: direct double Auger process is possible but cascade processes dominate that populate different intermediate excited states of Xe$^{2+}$, mainly those with 5s$^2$ configurations. Our coincidence set-up allowed to give a complete scheme of all the states involved in single and double Auger processes (see Fig 4 of reference [2]).

The few examples presented here have shown the power of our coincidence setup. This apparatus is helpful to consider complete Auger processes. It was possible to focus on the final states after single and double Auger processes and to correct the value of thresholds as in the case of Kr$^{3+}$. But it also allows to consider all the states ($A^+$, $A^{++}$) involved in single and double Auger processes, and also to isolate overlapping components in the Auger spectra due to different inner shells. To summarize, we can say that cascade Auger decay is the predominant process, compared to simple double Auger decay where the electrons share the available energy. Cascade Auger decay after a given “n” inner shell ionization comes from intermediate states populated by a two electron process involving two (n+1)s
electrons: for krypton 3d hole, mainly the 4s electrons participated; for argon 2p hole, two 3s electrons were involved; whereas for xenon 4d inner shell ionization, 5s electrons had a major contribution in the double Auger cascades.

Finally, the PCI effect in the vicinity of the Xe 4d state shows a clear effect on the Auger electron energy.

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