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Étude par spectroscopie Auger de l'interaction post-collisionnelle d'ions solvatés ionisés en couche K

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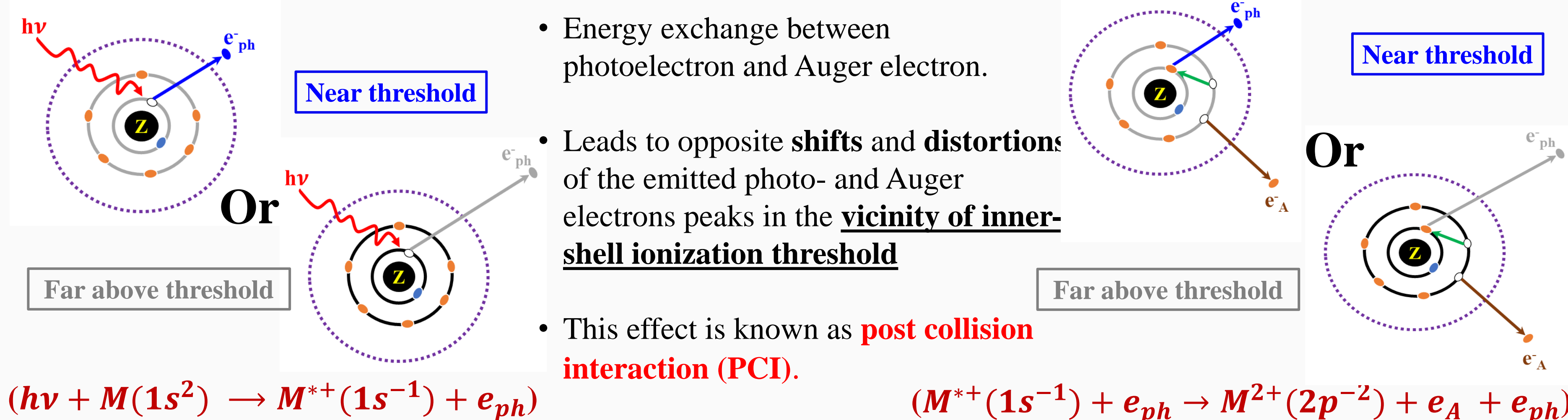
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PCI of the KLL transition

- Inner-shell photoionization of the 1s orbital leads to the emission of a photoelectron and to the creation of a short-lived unstable $1s^{-1}$ state that can relax by emission of a subsequent Auger electron and leads to a final $2p^{-2}$ state.
- For a photon energy just above the 1s ionization threshold : a **strong coulombic interaction** between the Auger electron, the photoelectron and the ionic core exists.
- The photoelectron undergoes a fast change of the ionic charge ($+1 \rightarrow +2$) when the Auger electron overtakes it and is slowed down. Conversely, the Auger electron is accelerated when overtaking the photoelectron.

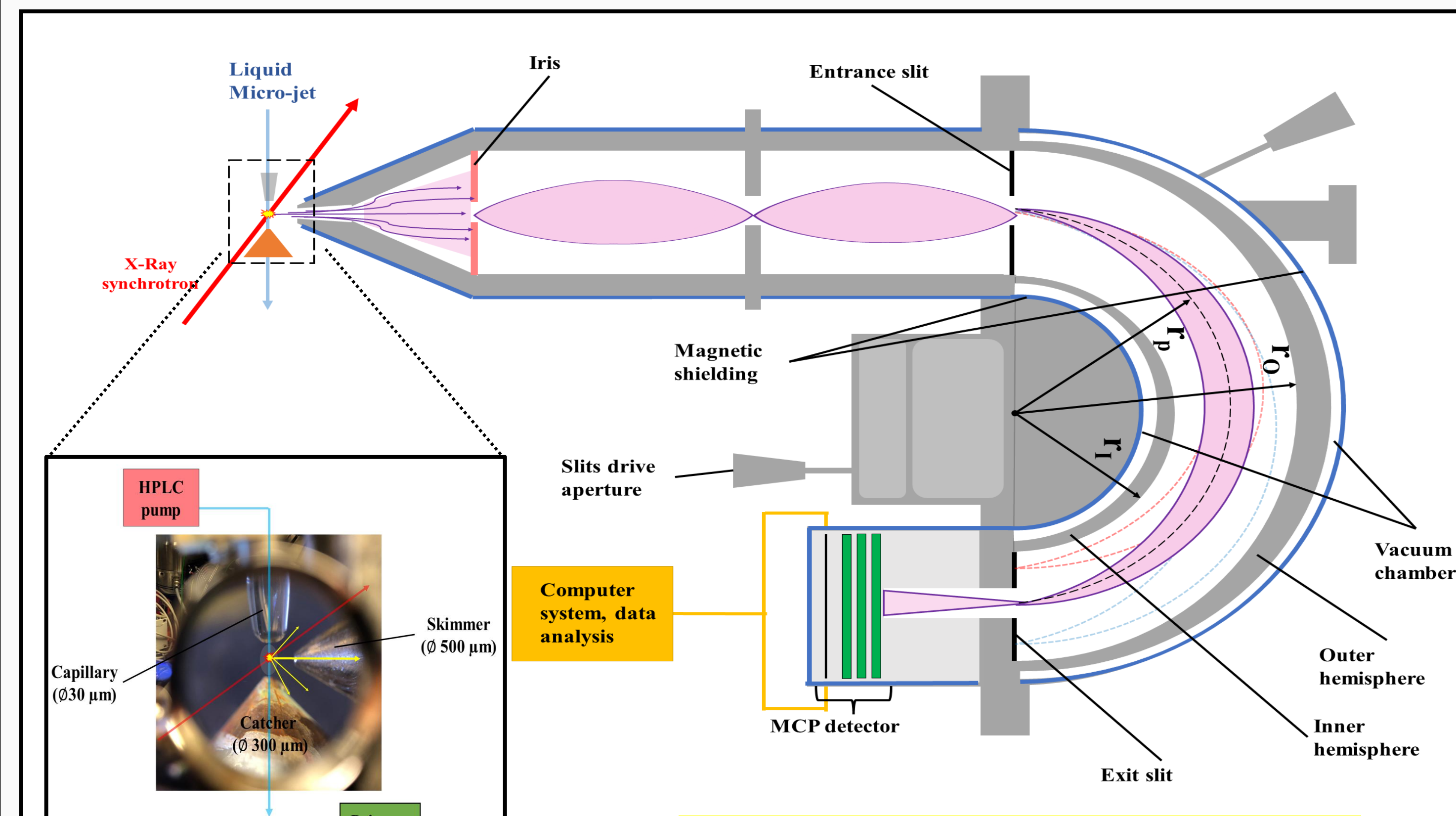


Screening effect and motivation

- In the **gas phase** and **tender X-ray** domain (1-5 keV), the PCI effect was studied on Argon [1]. A maximum shift (0.8 eV) of the main KLL Auger peak (¹D) is observed and decreases while increasing photon energy.
- In solid phase (surface and bulk), the energy shift could be also influenced by the modification of the effective charge of the residual ion [2]
- Hence, applied to the **aqueous phase**, we chose to study by Auger spectroscopy, the PCI effect on different **isoelectronic ions** to Argon : hydrated Cl^- , K^+ , Ca^{2+} .

Experimental Set-Up

- Experiments were conducted at the GALAXIES [3] beamline (2.3 – 12 keV) of the SOLEIL synchrotron (France) with a **liquid micro-jet** [4] adapted for the HAXPES [5] photoemission end-station.



Drawing of the principle of a hemispherical analyzer

- HAXPES resolution : 375 meV
- KCl and CaCl₂ solutions were prepared at 0.5 M in water
- Degassing and filtering of the solutions were systematically performed

Picture took @ GALAXIES in December 2020

Experimental results in water

- To evaluate the PCI shift, we focused our study onto the $2p^{-2}$ (¹D) peak (the most intense and well isolated) as a function of the photon energy.
- We calibrated the photon energy.
- We defined the Excess Energy (EE) : photon energy minus the **ionization potential** of the ion targeted : $\text{EE} = h\nu - \text{IP}$; the Energy Shift (ES) : shift of the Auger ¹D peak recorded close to the threshold relative to the position of the same peak recorded far above the threshold : $\text{ES} = E_k(\text{D}) - E_k(\text{D})_{\text{unshifted}}$

Comparison with theory

- **Van der Straten** calculations type were performed by our colleagues S. Sheinerman and L. Gerchikov [6]

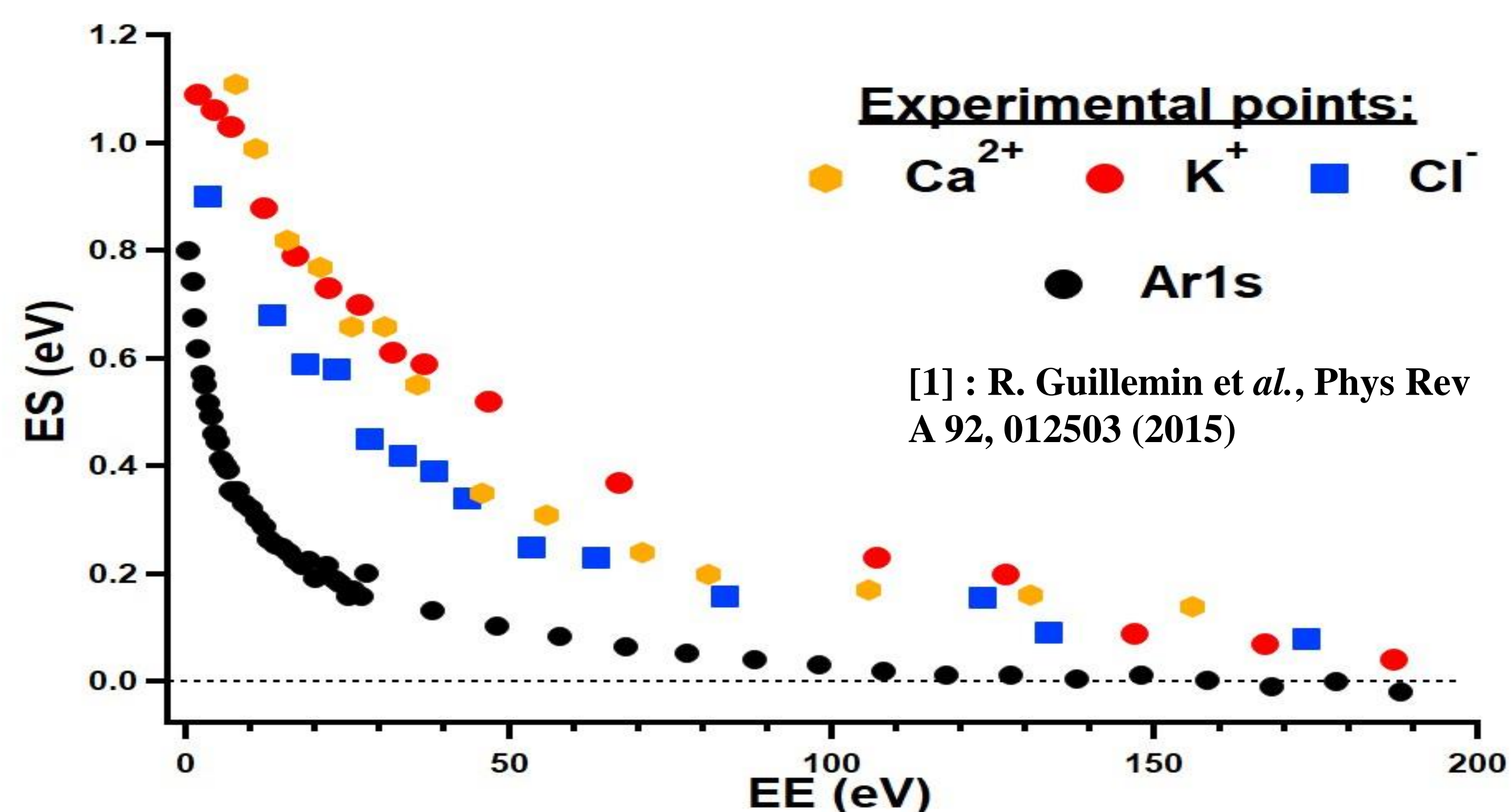
$$ES = \frac{\Gamma_{tot} \cdot C}{2} \times \frac{e^2}{h} \quad \text{with: } C = \frac{1}{\epsilon} \left(\frac{1}{v_{ph}} - \frac{1}{|v_A - v_{ph}|} \right) \quad [7]$$

- The total width depends on the ionic autoionization width Γ_a and the photoelectron **damping term** Γ_d in the water. This later is expressed as a function of the velocity of the photoelectron and of the **electron mean free path**, l

$$\Gamma_{tot} = \Gamma_a + \Gamma_d = \Gamma_a + \frac{\hbar v_{ph}}{l} \quad \text{With: } v_{ph} = \sqrt{2EE/m} \quad [8]$$

PCI shift in water

- A decrease of the PCI effect **slower** than the argon case (due to screening effect and to the reduced mean free path)
- Shift just above threshold **greater** for ions than for Ar (1 eV versus 0.8 eV)
- A **charge/ size effect**



PCI shift the ¹D KLL peaks for the ions Cl⁻, K⁺ et Ca²⁺ in water in comparison with the results obtained for Ar in the vicinity of the 1s ionization thresholds of each studied ion.

References

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Conclusions and perspectives

- Our study shows a **PCI effect** in the KLL Auger decay of several ions isoelectronic to argon, studied in aqueous phase. The position of the ¹D peak maximum in the Auger spectra shows a shift of a value larger than the one observed on gas phase Argon. The PCI shift in the aqueous case decreases slowly with photon energy.
- An initial **charge effect** is observed.
- A solvent effect is observed
- Theoretical investigations of the PCI effect show that the model depends on an additional term linked to the mean free path of the medium.