Abstract. We compare advantages and drawbacks of the two techniques mainly used for the experimental study of gas phase photoionization processes on ionic targets in combination with synchrotron radiation, the merged beam and ion trap. The comparison will be illustrated by recent results obtained on atomic and small molecular positively charged ions using both techniques at SOLEIL, the French synchrotron radiation facility.

1. Introduction
Photoionization (PI) of ionic species is a key process for the modeling of many plasmas, including laboratory plasmas, planetary ionospheres and astrophysical plasmas. The knowledge of PI cross sections is required over extended ionic charge stages and photon energies, both parameters of increasing magnitude with increasing plasma temperature. Until recently, relatively few experiments were performed on PI processes, facing the difficulty to combine a high density ionic target with a high flux of X ray radiation. Therefore, most of the data on these processes are known from models using more or less sophisticated approximations for the description of electron correlation effects [1-3]. Only the advent of high photon flux available at synchrotron radiation facilities has allowed the experiments to develop. First, merged beam setups have been used, allowing the determination in absolute values of PI cross sections for ions with charge stage up to 9 [4,5]. One difficulty of this technique consists in an ionic target often composed of a mixture of ions in the ground and metastable states. During the last five years, a new approach showed rapid expansion: the use of ion traps. It has allowed already the measurements of PI cross sections on relaxed ions [6], on more highly charged ions [7] and large molecular ions and clusters [8,9].
We present here our recent results obtained at SOLEIL, the French synchrotron radiation facility, on the PI of atomic and small molecular positively charged ions, using both a merged beam setup and an ion trap. To conclude, we will summarize the advantages and drawbacks of the two techniques.

2. Merged beam technique
The merged beam technique was first developed by Peart et al [10] for the study of electron impact processes on atomic ions. It was adapted later by Lyon et al [11] for measuring PI cross sections at the Daresbury synchrotron radiation source. The principle is to merge a beam of ions, produced in an ion source and charge over mass selected using a magnetic device, with a monochromatic synchrotron radiation beam. After the interaction, the charge of the ions is analyzed, the parent ions being collected in a Faraday cup and the ions which have increased their charge by one (or several) unit(s) during the interaction with the photons (the so-called photoproducts) are counted. Compared to similar studies on neutral species, the main advantage is a target density easy to measure, allowing determination of PI cross sections in absolute values. In return, the target density is five or six orders of magnitude lower and a high background is often produced by collisional ionization processes between the fast ion beam and the residual gas in the interaction chamber. To improve the signal to noise ratio, high photon flux is mandatory, requiring the use of undulators as synchrotron radiation source. A long interaction region (20-50 cm) is also welcome, and ultra-high vacuum is requested. Once these conditions are achieved, 10 to 20% accuracy is typically obtained on the cross section measurements, the main contribution to the uncertainty coming from photon flux determination and statistics when the signal/noise ratio is low.

**Figure 1:** Single (blue dots) and double (red dots) measured absolute PI cross sections for Sm$^{3+}$ ion, compared to the results of a UTA code (black curves).

Figure 1 shows an example of PI cross section that we have measured recently for Sm$^{3+}$ ion between 80 and 200 eV photon energy using the merged beam setup permanently installed on the PLEIADES beam line at SOLEIL. The ions were produced using an Electron Cyclotron Resonance Ion Source (ECRIS). Single PI (corresponding to the detection of Sm$^{4+}$ ions, blue curve and filled points) and double PI (corresponding to detection of Sm$^{5+}$ ions, red curve and open points) have been obtained. Electronic configuration of Sm$^{3+}$ ion in its ground state is [Kr] 4d$^{10}$ 5s$^2$ 5p$^6$ 4f$^5$. The large structure centered around 145 eV in the single PI cross section corresponds mainly to photoexcitation...
of a 4d inner-shell electron to the partially filled 4f subshell, leaving a Sm$^{3+}$ ion in highly excited states [Kr] 4d$^9$ 5s$^2$ 5p$^6$ 4f$^6$ which will further decay via autoionization to the energetically open continua. Because of the high temperature of the plasma in the ECRIS, all the states with the same configuration as the Sm$^{3+}$ ground state, extending on an excitation energy range larger than 6 eV, are populated in the source and have lifetime long enough to contribute to our spectra. Combined with the presence of open 4d and 4f subshells in the Sm$^{3+}$ 4d$^9$ 5s$^2$ 5p$^6$ 4f$^6$ intermediate states, all this leads to a huge number of allowed 4d → 4f photoexcitations. Due to the large number of transitions and their large natural width resulting from the very fast decay via super Coster-Kroning transition to the Sm$^{4+}$ [Kr] 4d$^{10}$ 5s$^2$ 5p$^4$ 4f$^4$ ground configuration, the line spacing is statistically lower than their natural width and only very broad structures, called Unresolved Transition Arrays (UTA), can be observed. We are trying to reproduce our observations using the statistical model developed by J. Bauche [12], assuming a statistical population of the initial states. Very preliminary results, not including yet the effect of electron correlations, are shown on Figure 1 (black continuous line). The agreement of theory with experiment is rather satisfactory. However, the experimental UTA profile is broader and asymmetric compared to the calculated profile. One explanation might be that the Sm$^{3+}$ [Kr] 4d$^{10}$ 5s$^2$ 5p$^6$ 4f$^6$ states are metastable and contribute also to the measured spectra, broadening the structure on the low energy side. Calculated 4d → 4f UTA starting from the metastable configuration is also shown as the dashed line on Figure 1.

Double PI channel in mainly populated via cascade Auger decay. It is weak at the energy of the 4d → 4f UTA because few Sm$^{4+}$ configurations, involving one or two holes in the 5s subshell, are open above the Sm$^{3+}$ thresholds. It is more intense at higher energy, where more excited 4d → nf, n>4 excitations are involved.

3. Ion trap

Contribution of ions in various metastable state is a quite general problem in the merged beam experiments, especially when using high temperature plasma ion source like ECRIS. It makes more difficult the interpretation of the experimental spectra and their comparison with theoretical predictions, in particular because the relative population of the different states is most of the time unknown. A commonly used procedure to minimize the contribution of metastable states is to store the ions before interaction, for a time long enough allowing them to radiatively decay into the ground state. The first coupling of an ion trap with synchrotron radiation was performed by Kravis et al in the 90's at NSLS facility in Brookhaven, using a Penning ion trap to measure broadband PI of Ar$^{2+}$ ion [13,14]. To demonstrate the feasibility that a PI experiment on cooled ions can be performed in association with synchrotron radiation, we brought a small movable Fourier Transform Ion Cyclotron Resonance (FT-ICR) ion trap first at ELETTRA [6], then on the DESIRS beam line at SOLEIL [15]. In this device, 1.2 T magnetic fields produced by permanent magnet is combined with an electrostatic potential to trap the ions inside a 2 cm$^3$ cubic cell [16]. FT-ICR traps are widely used for mass spectrometry studies on large molecules, often using superconducting magnets to produce very high magnetic fields. Nevertheless, even our small trap is able to achieve 70,000 mass resolving power.

Figure 2 shows PI cross sections measured for Xe$^+$ ion between 19.5 and 23 eV photon energy. The upper spectrum was obtained with the ASTRID merged beam setup [5]. The sharp lines correspond to photoexcitations of a 5p electron to empty nd or ns orbitals, leaving a Xe$^+$ ion in 5p$^1$ nd,ns highly excited levels which will decay via autoionization to the ground state of Xe$^{2+}$ ion [6,17]. The vertical bars above the spectrum indicate the position of the Xe$^+$$^2$P$^1/2$ ionization thresholds [18]. A strong signal is visible at lower photon energy than the first ionization threshold at 20.98 eV, clearly demonstrating the contribution of Xe$^+$ ions in metastable states to our spectrum. Actually, only the Xe$^+$$^2$P$^1/2$ term is metastable, with a lifetime of 48.7 ms [19], and lines observed below 20.98 eV can be attributed to photoexcitation of a 5p electron starting from this $^2$P$^1/2$ excited term.
Figure 2: Comparison of the PI cross sections measured on Xe$^+$ ion with a merged beam setup (upper panel) and a FT-ICR trap (middle panel). Combination of the two spectra allows estimating the cross section for ions in the pure metastable state (lower panel).

The spectrum recorded with the FT-ICR trap is shown on the middle panel of Figure 2. The Xe$^+$ ions were produced directly inside the trap by electron impact, a pulse of electrons ionizing a pulse of xenon gas. The ions were trapped for 1 sec, allowing the metastable species to decay, and then irradiated by the monochromatized synchrotron radiation. The signal below 20.98 eV has clearly vanished, demonstrating that we measured the PI cross section of Xe$^+$ ion in the pure ground state. As it is not possible to determine the density of ions inside the trap, the cross section is only obtained in relative value. It was normalized on the measurements performed with the merged beam setup, assuming for the latter a statistical population of the ground and metastable terms.

From the difference between the two spectra, we can derive the cross section for the ions in the pure metastable state, assuming once again a statistical population of the two terms in the merged beam spectrum. It is shown on the bottom panel of Figure 2. The cross section in the high energy part is dominated by the direct PI process and is not expected to be of very different magnitude for the ions in the ground and metastable terms, contrary to what is observed. However, it should be noted that the two spectra were recorded on two different beam lines, with slightly different resolution, and there is also contribution of higher orders light diffracted by the monochromator on the ASTRID beam line.

As stated earlier, owing to very high $m/z$ resolution, FT-ICR ion traps are particularly well suited for the study of molecular ions. Only studies on CO$^+$ ions [20,21] and some endohedral ions [22,23], have been performed up to now on molecular ions using merged beam setups. One difficulty is that often doubly-charged molecular ions (so-called dications) are generally unstable with respect to dissociation into two singly charged ions, due to the coulombic repulsion which dominates the long range interaction between the two fragments. Nevertheless, short range covalent bonding can overcome the repulsive coulombic forces and metastable or even stable molecular dications are observed. For example, in CO$_2^{2+}$ lifetimes up to 4s have been measured [24]. Figure 3 gives the variation of the cross section we have measured for CO$_2^{2+}$ ion with the FT-ICR ion trap. Detection of the dications was performed in the 10-1000 ms time window after their production by the photons, in such a way only dications in long lived states can be detected. This first result on molecular ion has been obtained in the very last hour of our last beam time on DESIRS beam line. Although very preliminary, it is
consistent already with the electronic state energies of the dication measured by Slattery et al [25], shown as the vertical bars on Figure 3.

4. Conclusion

We have given examples of PI cross sections of ionic species measured at SOLEIL synchrotron radiation facility using two different techniques, the merged beam and ion trapping, and we have tried to show their complementarities. Merged beam setups are perfectly adapted for the determination of cross sections in absolute values, but interpretation of their results is often obscured by metastable ions contribution. In contrast, ion traps provide with relative cross sections on cold ions, which can be normalized using the absolute values. Merged beam technique is in use since the 80’s and has been applied to the study of singly (both positively and negatively) and multiply-charged atomic ions, with charge stage up to 9 [26]. At present, such setups are in operation in the USA (ALS) [27], Denmark (ASTRID) [5] and in France (SOLEIL) [28,29], and one is under commissioning in Germany (PETRA). They are huge setups requiring a permanent installation on a synchrotron radiation beam line, and can support several detection techniques like ion and electron spectrometry [30,31]. In contrast, ion traps are light and easily movable, but limited to mass spectrometry, often with a very high mass resolution making them a perfect tool for the study of molecular ions. They have been in fast development during the last five years, mainly at SOLEIL in France and BESSY II in Germany. Different traps have been used: FT-ICR for the study of singly-charged atomic and small molecular ions as shown in this paper, linear traps for the study of singly-charged atomic ions [32], large molecular [9] and metallic clusters ions [8], RF trap for the study of large molecular ions of biological interest [33-35], electron beam ion trap (EBIT) for the study of highly-charged atomic ions [7,36]. To finish, let us note the construction of an electrostatic ring to store the ions at ASTRID II in Denmark, which will combine some of the advantages of both merged beam setup and ion trap.

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