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Photoelectron spectroscopy on ions beam: Study of the Auger decay of the $4d \rightarrow nf$ ($n=4,5$) resonances in Xe^{5+} ion.

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We have studied, for the first time by electron spectroscopy, the Auger decay of the $4d \rightarrow nf$ ($n = 4, 5$) resonances in Xe^{5+} ion. By detecting in coincidence the Auger electrons with the resulting Xe^{6+} ions, we unravel the contribution of the different final ionic states to the total cross section measured by ion spectroscopy. A strong intensity of $5s5p$ satellite lines has been observed, up to four times stronger than the $5s^2$ main lines. This unexpected behavior is confirmed by MCDF calculations. This technique provides the most stringent test for theoretical models and allows to disentangle the contribution of ions in the ground and metastable states in the target beam.

Since the 70's, taking benefit of the parallel development of synchrotron radiation sources and electron spectrometers, photoelectron spectroscopy, used alone or in conjunction with mass spectrometry, has proven to be a unique tool for the study of electron correlation effects and to perform chemical analysis in all kind of targets, going from free atoms and molecules to solids [1][2]. However, all the attempts performed up to now to apply this technique to ionic species have encountered limited success. The main reason is due to the very low density of the ionic targets which can be focused into the source volume of an electron spectrometer, typically five or six orders of magnitude lower than what is usually achieved with a gas phase target.

Photoionization of multiply-charged ions is a key process to understand and describe the energy transport in high energy density plasmas like laser produced and X-ray photoionized plasmas. The need for accurate photoionization cross sections is shared by various research fields such as modelling of astrophysical and laboratory plasmas created using high-energy laser pinch machine or tokamak. Most of our knowledge on photoionization processes is obtained still today from theoretical models, providing a large amount of data, collected in databases [3][4][5][6]. The validity of these calculated data, which strongly depends on how the electron correlation effects are treated by the models, stays up to now largely untested by experiment. The first experimental works were based on photoabsorption measurements in laser produced plasmas [7], providing relative photoabsorption cross section for low-charged ions. More recently, ion-photon merged-beam setups at synchrotron radiation (SR) facilities allowed the determination of absolute single and multiple photoionization cross sections for selected ions using ion spectrometry [8][9]. One limitation of both techniques is that they give only information on the global response of the electrons cloud to the photon excitation. Another one is that the ionic targets are most of the time composed of ions not only in the ground state, but also in several metastable states produced during the ion target production. The relative population determination of the ions in the various states requires most of the time the use of theoretical data, weakening *de facto* the intended test of the theoretical results. In addition, the presence in the target of ions in various initial states often produces overlapping structures in the photoionization spectra. The use of electron spectroscopy allows to overcome these limitations, providing a stringent test of the theoretical models. By analyzing the electron kinetic energy, new information is brought on the contribution of the various subshells of the ion to the photoionization process, as well as on the non-radiative decay (autoionization, Auger effect) of the ion photoexcited in inner-shell, providing a deep insight of the electron correlation effects.

The electron spectroscopy experiment feasibility on an ionic target was demonstrated at Super-ACO storage ring in the case of a resonant photoionization process. The electron line emitted during the autoionizing decay of the $3p \rightarrow 3d$ giant resonance in Ca^+ ion was observed [10]. The success of this experiment was favored by the huge cross section of the photoexcitation process (2000 Mb) and the existence of only one dominant decay channel.. Electron-ion coincidence technique was also performed at BESSY to improve the signal to noise ratio in the electron spectra, but with the draw-

back of a very low counting rate [11][12]. Since these pioneering experiments, a few electron spectra were obtained on ionic species at free electron laser facilities [13,14], taking advantage of the very high photon brilliance produced by these devices, several orders of magnitude higher than what is available at an undulator beam line on a storage ring light source. Nevertheless, even with such light sources photoelectron spectroscopy on ionic species is far to be a routine.

In this letter, we report the very first measurements of electron spectra obtained on multiply-charged ion using a conventional third generation SR light source. The decay channels of the $4d \rightarrow 4f$ and $4d \rightarrow 5f$ resonances in Xe^{5+} ion were recorded. The experiments were carried out with the photon-ion merged-beam setup [15] at the PLEIADES beam line [16] of the SOLEIL synchrotron light source. Multi-configuration Dirac-Fock (MCDF) calculations were performed for the interpretation of the spectra.

The ions are produced in an electron cyclotron resonance ion source (ECRIS) by heating ^{129}Xe isotopic gas with a 12.4 GHz radio-frequency wave. The Xe^{5+} ions are produced both in the $[\text{Kr}]4d^{10}5s^25p^2P_{1/2}$ ground level and the $^2P_{3/2}$ metastable level. After acceleration to 4 keV kinetic energy and magnetic selection, the ions are focused into the source volume of a cylindrical mirror electron analyzer (CMA) composed of three coaxial cylinders with the axis collinear to the counter propagating ion and photon beams [17]. The typical ionic current in the source volume is 1.2 μA . The photon beam is produced in the HU80 undulator of the PLEIADES beam line and, after monochromatization, is focused into the source volume of the CMA. After photon interaction, the charge of the ions is analyzed by a dipole magnet, the Xe^{6+} photoions being counted using micro-channel plates. The photoelectrons are detected by eight channeltrons placed at equidistant azimuthal angles between the two inner cylinders on the focal plane of the CMA [17].

MCDF calculations, including Breit and QED corrections as well as nucleus finite size effects, were performed based on a full intermediate coupling regime in a jj-basis [18]. Photoexcitation cross sections are carried out for the two levels ($J=1/2, 3/2$) of the Xe^{5+} ($[\text{Kr}] 4d^{10} 5s^2 5p$) ground configuration in the 90-115 eV photon energy range. Only electric dipole transitions are computed using the Babushkin gauge. Four $[\text{Kr}] 4d^9 5s^2 5p n f$ configurations are used to describe final states where $n=4$ to 7. Radial

wavefunctions are obtained from the trace minimization of the Hamiltonian matrix. The same set of radial wavefunctions are used to compute autoionization rates connecting the photoexcited levels ($J=1/2$, $3/2$, and $5/2$) to the five $[\text{Kr}] 4d^{10} 5s^2$ ($J=0$) and $[\text{Kr}] 4d^{10} 5s 5p$ ($J=0$, $2x1$, and 2) levels of Xe^{6+} .

The experimental and calculated photoionization cross sections in the photon energy ranges of the $4d \rightarrow 4f$ and $4d \rightarrow 5f$ resonances are shown on Fig. 1. Because the overlap between the ions and photons beam is not measured in the present experiment, only relative cross sections are determined. The absolute scales are obtained by normalization on our previous absolute measurement of the resonances strength [19]. The photon energy is calibrated on the position of the $\text{Kr } 3d \rightarrow np$ ($n=5$ to 7) resonances [20] measured simultaneously in an ionization chamber. The present measurements are in good agreement with the cross sections previously measured with higher band width (BW) [21] [19] [22]. MCDF calculations for the Xe^{5+} ions in the $J = 1/2$ and $J = 3/2$ initial levels are displayed on the lower panels. The calculated Lorentzian lines have been convolved by a Gaussian profile with a full width at half maximum (FWHM) equal to the experimental BW, 75 meV and 90 meV for the $4d \rightarrow 4f$ and $4d \rightarrow 5f$ transitions, respectively. For easier comparison with experiment, the theoretical results for the $4d \rightarrow 5f$ transitions have been shifted by 1.5 eV towards higher energy. The theoretical spectra are reconstructed by weighting the calculated cross sections for the two initial levels in order to obtain the best overall agreement with the experimental cross section for the $4d \rightarrow 4f$ structure. This procedure leads to an estimation of the relative population equal to 45% for the $J = 1/2$ and 55% for the $J = 3/2$ levels. Our calculations reproduce quite well the position and strength of the $4d \rightarrow 4f$ structure but underestimate the complexity of the $4d \rightarrow 5f$ one. They demonstrate that each structure is composed of large number of transitions, issued from both the ground and metastable levels in an undistinguishable way by the ion spectrometry experiment.

On each panel of Fig. 1, the vertical arrows indicate the photon energy where electron spectra have been measured and where they were simulated by the MCDF calculations. The photoelectron spectrum recorded at 94.43 ± 0.02 eV, the top of the $4d \rightarrow 4f$ structure, is shown on the upper panel of Fig. 2. It represents the variation of the sum of the eight channeltron signals as a function of the kinetic energy of the electrons in the frame of the Xe^{5+} ions. A strong and slowly decreasing background is observed. It is produced by collisions between the Xe^{5+} beam and the residual gas in the interaction

chamber or metallic surfaces. The three tiny lines above the background, marked with vertical bars, are due to photoionization in the 4d subshell of neutral residual Xe gas. They are useful to calibrate the CMA energy scale. In order to reduce the background, we detected the photoelectrons signal in coincidence with the Xe^{6+} photoion signal. The result is shown on the middle panel of Fig. 2. After subtraction of the false coincidences, the background and the lines due to the neutral Xe are efficiently suppressed, while three new lines are now clearly visible. The resonant photoionization process of Xe^{5+} ions at this photon energy can be represented by the simplified scheme:

The main decay channel of the 4d hole is the recombination $4f \rightarrow 4d$ accompanied by the emission of an outer 5p or 5s electron. By convention, the line arising from the emission of the 5p electron is called main line, the Xe^{6+} ion being left in its $5s^2 \ ^1S_0$ ground state. Those coming from the emission of a 5s electron, the Xe^{6+} ion being left in its first excited levels $5s5p \ ^1P_1, \ ^3P_{0,1,2}$, are called satellite lines. The vertical bars above the spectrum give the expected position of the electron lines deduced from the tabulated energy levels of the Xe^{6+} ions [23]. The two higher lines at 28.2 and 30.2 eV kinetic energy can be identified as the main lines starting from the Xe^{5+} ion in the $J = 1/2$ et $J = 3/2$ levels, respectively. The line at 15.9 eV kinetic energy is a satellite which corresponds to the Xe^{6+} ion left in one of the $5s5p \ ^3P$ final level starting from the $\text{Xe}^{5+} \ J = 3/2$ level and/or $\text{Xe}^{5+} \ J = 1/2$. To go further, we have reconstructed the electron spectrum from our MCDF results. The spectrum is displayed on the bottom panel of Fig. 2, and is normalized to have the same total number of counts than the experimental spectrum. The vertical lines to zero give the energy and the strength of the calculated lines starting from the two initial levels. For better comparison with experiment, the eight of the lines is multiplied by the electron kinetic energy to simulate the CMA transmission [24]. The black curve is the reconstructed spectrum obtained as the sum of the lines after convolution by a Gaussian profile with 0.8 eV FWHM representing the experimental broadening. The numbers above the lines indicate, both for the experimental and theoretical spectra, the relative strength of the line normalized to the sum of the strengths, after correction for the CMA transmission. Apart a shift of the energy of the lines, our calculations satisfactorily reproduce the experimental spectrum, in particular the strong intensity of the satellite line, and show it is mainly due $\text{Xe}^{5+} \ ^2P_{3/2} \rightarrow \text{Xe}^{6+} \ ^3P_2$ transitions. The strong satellite line calculated at 13.6 eV and corresponding to the

1P_1 final level starting from the ions in the metastable state is not observed experimentally.

The coincidence spectra recorded at the two maxima of the $4d \rightarrow 5f$ structure are given on Figures 3 and 4 respectively, together with the MCDF reconstructed electron spectra. Comparison with the calculated cross section of Fig. 1 suggests that the two maxima correspond mainly to the excitation of the ground $Xe^{5+} \ ^2P_{1/2}$ (Fig. 3 at 108.34 ± 0.02 eV) or the excited $Xe^{5+} \ ^2P_{3/2}$ state (Fig. 4 at 108.62 ± 0.02 eV). The experimental electron spectra confirm this prediction at 108.62 eV, but show a non-negligible contribution of the $J = 3/2$ level at 108.34 eV. One remarkable feature is the almost complete vanishing of the main lines in the coincidence spectrum at 108.34 eV, all the intensity being concentrated in the satellite lines. The calculations overestimate the contribution of the main lines at this energy while they reproduce quite well the experimental spectrum at 108.62 eV, with this time a slight underestimation of the intensity of the main line at 43.8 eV.

To conclude, we have measured for the first time the Auger decay channels of the $4d \rightarrow nf$ ($n = 4, 5$) resonances in Xe^{5+} ions using the electron-ion coincidence technique. For both resonances, the $5s5p$ satellite lines show a stronger intensity than the $5s^2$ main lines. In particular, at 108.34 eV the satellite lines are 3 to 4 times more intense than the main lines. MCDF calculations reproduce the general behavior of the electron spectra, with some notable differences in the relative intensity of the lines. In addition, electron spectroscopy allows to partly disentangle the contribution of the ions in the ground and metastable levels in the Xe^{5+} target.

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Figure 1: (Color online) Xe^{5+} photoionization cross sections in the vicinity of the $4d \rightarrow 4f$ (left panels) and $4d \rightarrow 5f$ (right panels) resonances obtained in experiment (upper panels) with 75 and 90 meV bandwidth, respectively (thick green curves) and MCDF calculations (lower panels) for the $5p\ ^2P_{1/2}$ and $5p\ ^2P_{3/2}$ levels (red dotted and blue solid curves, respectively), and for a mixture of 45% ground and 55% metastable ions (thick solid green curves).

Figure 2: (color online) Photoelectron spectra obtained at the top of the $4d \rightarrow 4f$ structure (94.43 eV, BW = 75 meV). Electron kinetic energies were converted from the laboratory frame to the Center of Mass (CM) frame by taking into account the Doppler effect due to their emission from the fast Xe^{5+} ions. Upper panel: experimental electron spectrum. Middle panel: Coincidence spectrum. Lower panel: MCDF reconstructed spectrum. The vertical red and blue lines give the energy and the strength of the calculated electron lines for the $J = 1/2$ and $J = 3/2$ initial levels, respectively.

Figure 3: (color online) Top panel: Coincidence spectrum measured at the first maximum of the $4d \rightarrow 5f$ structure ($h\nu = 108.34 \text{ eV}$, $\text{BW} = 90 \text{ meV}$). Bottom panel: reconstructed MCDF electron spectrum.

Figure 4: (color online) Top panel: Coincidence spectrum measured at the second maximum of the $4d \rightarrow 5f$ structure ($h\nu = 108.62$ eV, BW = 90 meV). Bottom panel: reconstructed MCDF electron spectrum.