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Coupling an ion trap with synchrotron radiation is shown here to be a powerful approach to measure photoionization cross sections on ionic species relaxed in their ground state. The photoionization efficiency curve of $Xe^+$ ions stored in a Fourier transform ion cyclotron resonance ion trap was recorded at ELETTRA in the 20–23 eV photon energy range. Absolute cross sections were derived by comparison of the photoionization yield of $Xe^+$ with measurements from the ASTRID merged-beam experiment. Multiconfiguration Dirac-Fock calculations were performed for the interpretation of these new data.

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We describe an experimental study on the photoionization of a $Xe^+$ ion prepared in the pure $5p^5\ ^2P_{3/2}$ ground level, coupling for the first time a Penning ion trap with a monochromatized soft x-ray (XUV) synchrotron radiation beam.

Advances in atomic spectroscopy represent valuable and direct assets in the field of plasma diagnostics, allowing a deeper characterization of both thermodynamics and transport properties of hot matter. The determination of the relative populations of atoms and molecules in various ionization and excitation states inside the plasma requires knowledge of the cross sections and production rates for many atomic processes, as well as transition energies and transition probabilities in ions. Beyond the intrinsic interest in fundamental physics, studies of ion photoionization are relevant to different subjects such as astrophysics, planetary sciences, and, more generally, all applications of energetic plasmas. Additionally, since photoabsorption is the main path for energy diffusion inside plasmas, accurate cross sections are needed for the description of radiation transfer in hot dense plasmas.

Because of a lack of experimental data, parameters of photoionization processes in multiply charged ions are mainly derived from theoretical calculations, which imply sophisticated atomic models. In this way, the *R*-matrix method was employed to calculate the photoionization cross sections for ions with atomic number up to 26, in order to deduce the opacity of stellar envelopes (Opacity Project [1] and Iron Project [2]). A critical comparison of theoretical data with experimental results is thus highly desirable and particularly useful for a validation of approximate methods of accounting for electron correlation. High quality experimental data are thus mandatory, including absolute photoionization cross section measurements on well-characterized ionic species. The main obstacle to ion photoionization experiments is the difficulty of producing ''clean'' targets of ions with a high enough density to compensate for both the relatively low flux of available XUV photon sources and the low value of photoionization cross sections. During the 1980s, merged-beam techniques were developed at the Daresbury laboratory, in order to allow measurement of absolute photoionization cross sections on a large variety of ion samples [3]. After production in an ion source and selection by a magnetic separator, an ion beam is merged with a beam of monochromatic synchrotron radiation. Though initially limited to singly charged ions [4], the advance of third-generation synchrotron radiation facilities has allowed the extension of these studies to multiply charged ions [5], favoring an increase in the number of experimental studies. Unfortunately, ions are often generated in the source in a large number of excited states, with relaxation times that may be longer than the typical flight time from the source to the interaction chamber (a few microseconds). It is extremely difficult to ascertain the relative populations of the different electronic states in the ionic target, and, thus, the possibility of irradiating a mixture of ions in undefined electronic states strongly limits the merged-beam method. Most of the time, comparison of experimental intensities to a theoretical photoionization cross section is required either close to threshold [6,7] or at well-resolved resonances [8]. So far, the contribution of ground state ions in merged-beam experiments could be disentangled from that of metastable states in the experimental data only in the two most favorable cases of $O^+$ [9,10] and $Sc^{++}$ [11].

 

Here we describe an alternative experimental approach that directly measures photoionization cross sections of ionic species in their ground state. In our method, a Fourier transform-ion cyclotron resonance (FT-ICR) ion trap is coupled to a third-generation synchrotron radiation beam line. In contrast with merged-beam methods, ions can be stored in the trap for a time long enough to allow complete radiative decay to the ground state before irradiation takes place. In the past, the concept of coupling a FT-ICR to a light source was successfully applied in ion spectroscopy studies by infrared multiphoton dissociation on the infrared free electron laser CLIO in Orsay [12] and at FELIX in Rijnhuizen [13]. There have been only a few attempts to couple an ion trap with a beam of XUV light. Kravis *et al.* [14] obtained the charge distribution of photoions resulting from broadband synchrotron radiation irradiation of $Ar^{2+}$ ions stored in a Penning ion trap. Epp *et al.* [15] used instead the ultrabrilliant light from the free electron laser in Hamburg to demonstrate the feasibility of laser spectroscopy on $Fe^{23+}$ ions produced in an electron beam ion trap.

In the present experiment, a FT-ICR mass spectrometer is used to select trapped ions, store them before and during irradiation, and analyze the final mass to charge distribution of photoions. The mobile ion cyclotron resonance analyzer (MICRA) mass spectrometer was installed on the branch line of the gas phase beam line (ELETTRA, Trieste). MICRA is a simple and robust movable spectrometer, based on a 1.24 T permanent magnet, specifically designed to let a light beam pass through it [16]. The magnetic field allows for mass selection and detection in the mass to charge range 4–500 u, with an ultimate resolving power of 73 000 at the mass of a $Xe^+$ ion. The ICR cell is derived from a cubic cell with 2 cm between electrodes. Each of the two excitation plates is replaced by an open structure, thus providing optical access without interference from surfaces [16]. The density of ions, in the middle of the trap, is estimated to be of the order of $10^7$ $cm^{-3}$. The nominal pressure in the setup is in the low $10^{-9}$ mbar range. Figure 1 illustrates the time sequence realized for the acquisition of the data at each photon energy. In the first step, target ions are produced by ionization of Xe atoms in the gas pulse, with 25 eV kinetic energy electrons. After a delay of 1050 ms, the $Xe^+$ ions are irradiated for 1300 ms by monochromatized synchrotron radiation, and the mass spectrum of ions in the trap is recorded. Chopping of the synchrotron radiation beam is performed by using a home-built vacuum-compatible electromechanical chopper with a time response of 4 ms. It consists of a modification of a commercial solenoid pulsed valve (Parker-General Valve series 99), where the poppet is replaced by a small cylindrical metal shutter. The mass spectrum at each photon energy is obtained from the Fourier transform of an average of 60–100 cycles identical to the one shown on Fig. 1. It is important to note that, in the energy range considered here, neither the energy of the photons nor the electrons alone is sufficient to produce $Xe^{2+}$ ions from double ionization of Xe atoms (the threshold is at 33.1 eV [17]). We have checked that no $Xe^{2+}$ ions are produced when either the photon pulse or the electron pulse is missing in the cycle. Possible reduction of the $Xe^{2+}$ signal by a charge exchange reaction with neutral Xe does not significantly affect the determination of the relative cross section. In order to increase the photon flux, the photon energy resolution was kept close to 60 meV. The photon energy was calibrated against the $5s \rightarrow 6p$ and $5s \rightarrow 7p$ autoionization lines of neutral Xe [17].

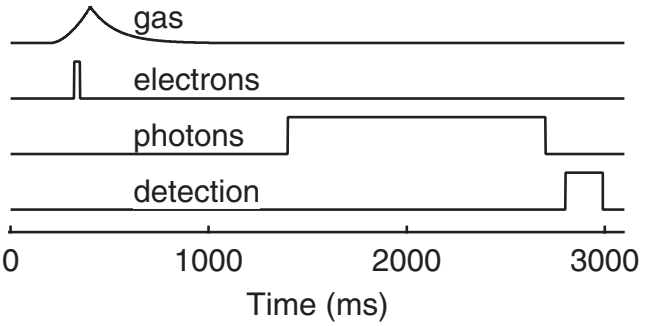


FIG. 1. Schematic representation of the $Xe^+$ ions preparation and irradiation timing procedure, repeated 60 times at each photon energy. The target ions are first produced by electron impact ionization of Xe atoms in the gas pulse and are subsequently photoionized by a pulse of monochromatic synchrotron radiation, with a delay of more than 1 s.

The $Xe^+$ photoionization spectrum, obtained in the 20–23 eV photon energy range with an energy step of 20 meV, is shown as the thick curve in the upper panel of Fig. 2. It represents the variation of the sum of the intensity of the three main isotopic components ($m = 129$, 131, and 132 u) of $Xe^{2+}$ ions as a function of the photon energy. All previous experiments on $Xe^+$ ions, realized using merged-beam setups [18–21], as well as the previous theoretical investigations [21,22] have focused on the higher energy region of $4d$ excitations, which is out of the range considered here. The tabulated positions of the different thresholds for the various terms of the $Xe^{2+}$ $5p^4$ configuration [17] are reported as vertical bars. The increase in the $Xe^{2+}$ photoyield at 20.9 eV is consistent with the first threshold expected for the direct photoionization process:

$$Xe^+ 5p^5\,{}^2P_{3/2} + h\nu \rightarrow Xe^{2+}5p^4 + e^-. \qquad (1)$$

Above the continua produced by process (1), prominent lines are observed. In the FT-ICR spectrum, the negligible signal below 20.9 eV demonstrates that most of the ions in the trap are stored in their ground state at the moment of the irradiation. The $5p^5\,{}^2P_{1/2}$ metastable $Xe^+$ ion has a lifetime of 48.7 ms [23]. As expected, the delay of 1050 ms between production and irradiation of the ions in the trap is

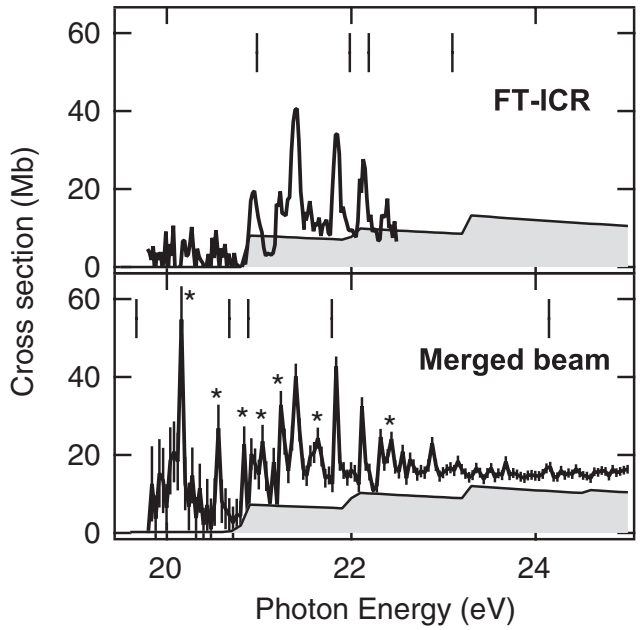


FIG. 2. Variation of the photoionization cross sections of the $Xe^+$ ion over the 20–25 eV photon energy range. The present experimental results (thick lines) obtained with the FT-ICR ion trap (upper panel) and the merged-beam experiment (lower panel) are compared with the results of our MCDF calculations for the direct photoionization cross sections (thin lines). The error bars on the lower spectrum give the statistical uncertainty on each point. For a better comparison, the calculated curves have been shifted by 1 eV towards the high photon energy. The vertical bars give the position of the various ionization thresholds for ions in the ground and metastable levels, in the upper and lower panel, respectively [17].

thus long enough to allow for the radiative decay to the ground state of all metastable ions.

Since the density of ions in the trap cannot be precisely determined, only relative values of the cross section can be derived at present. In order to convert our measurement to absolute figures, we have compared them with an analogous photoionization experiment that we performed at the merged-beam facility in Aarhus [24]. In that experiment, the $Xe^+$ ions were produced in a 10 GHz permanent magnet electron cyclotron resonance ion source (ECRIS). After extraction using an acceleration voltage of 2 kV, the ions were selected by a dipole magnet and merged with the synchrotron radiation beam over a length of about 50 cm. The calibration of the photon energy was performed on the energy of the $2s \rightarrow 3p$ and $2s \rightarrow 4p$ transitions in neutral Ne [17] measured in an ionization chamber. The bandpass of the monochromator was of the order of 50 meV. The lower panel of Fig. 2 shows the spectrum obtained in the energy range 20–25 eV with an energy step of 40 meV and by counting of the number of $Xe^{2+}$ ions after the interaction of the $Xe^+$ ion beam with the photons. The error bars give the statistical error on each data point. When combined with the estimated systematic error in the 10%–15% range [24], the result is a total relative uncertainty around 20% of the cross sections presented in Fig. 2. Additional uncertainty in the trap measurements, due mainly to the fluctuation of the gas pulse density, is of the order of a few percent after averaging the number of cycles performed at each photon energy. In addition to the previously observed lines, new ones, marked with an asterisk, appear. The most intense is below 20.9 eV and reveals an overwhelming contribution of $Xe^+$ ions in the $5p^5\ ^2P_{1/2}$ metastable level. The various ionization thresholds for ions in this level are given by the vertical bars in Fig. 2 [17].

In order to interpret our experimental data, we have performed multiconfiguration Dirac-Fock (MCDF) calculations using the code developed by Bruneau [25]. To calculate the direct photoionization cross sections, we considered all of the levels with configuration $Xe^+\ 5p^5$ in the initial state and $Xe^{2+}\ 5p^4$ in the final ionic state. For each initial state, the photoionization cross sections were calculated with a regular interval of the photon energy of 1 eV. For photoexcitation, two calculations including 66 levels constructed from the configurations $Xe^+\ 5s^2\ 5p^5$, $Xe^+ 5s^1 5p^5 np$ ($n = 6, 7, 8$), and $Xe^{2+}\ 5s^2\ 5p^4$ and 601 levels from the configurations $Xe^+ 5p^4 ns$, $Xe^+ 5p^4 nd$ ($n = 6, 7, 8$), $Xe^+\ 5p^3\ 5d\ 6p$, $Xe^+\ 5p^3\ 6s\ 6p$, $Xe^+\ 5p^3\ 6p\ 6d$, and $Xe^{2+}\ 5s^2\ 5p^4$were performed. The length form of the electric-dipole operator was used. Our calculations for the direct photoionization cross section of $Xe^+$ assumes a statistical mixing of 2/3 $Xe^+$ ions in the ground level and 1/3 in the metastable level, and they are shown in the lower panel of Fig. 2 as the thin curve filled in gray to zero. For a better comparison with the experimental data, the theoretical curve has been shifted by 1 eV towards higher energy. It reproduces rather well the continuum part of the experimental cross section, showing that the relative population of the ions is compatible with a statistical ratio. Such a distribution is expected due to the high electronic temperature of the plasma in the ECRIS, relative to the low excitation energy of the metastable level, as it was already observed in a similar experiment on the $Ne^+$ ions produced in an ion source with a plasma temperature even lower than in ECRIS [26]. The absolute scale displayed for the experimental spectrum recorded with the FT-ICR trap has been obtained by normalization on the integrated intensity of the 3 resonant structures observed at 21.4, 21.8, and 22.1 eV in both spectra, after subtraction of the continuous background and taking into account the different relative population of ions in the ground level. The intensity of the continuum part of the experimental cross section measured with the FT-ICR trap is in good agreement with the calculated cross section for direct photoionization of $Xe^+$ ions in the ground level, shown as the thin curve in the upper panel of Fig. 2. It is noteworthy that the intensity of the direct photoionization cross section is strongly perturbed at threshold by the presence of an interfering resonant struc-

ture and that, in the energy range considered here, it is 4 times lower than the cross section for neutral xenon [27].

Concerning the identification of the lines observed above the continua, our 601 levels calculations indicate that the resonances embedded in the continua correspond to resonant photoionization of a $5p$ electron following processes of the type

$$\mathrm{Xe}^{+}5p^5\,{}^2P_{3/2} + h\nu \rightarrow \mathrm{Xe}^{+*}5p^4nd(n \geq 7) \rightarrow \mathrm{Xe}^{2+}5p^4 + e^-, \quad (2)$$

responsible for the Rydberg series converging to the various $Xe^{2+}$ $5p^4$ thresholds. Because of the large number of overlapping series and the extreme sensitivity of the position of the resonances to the number of levels introduced in the calculations, no identification of the individual lines was possible. The 66 levels calculations show that the $5s \rightarrow np$ excitations do not contribute to the spectrum in this energy range. The energy of the $5s \rightarrow 5p$ excitation is below the threshold and around 14.5 eV, while the $5s \rightarrow np$ excitations with $n \geq 6$ are above 26.2 eV. We observe no effect of the trapping magnetic field of 1.24 T on the position of the lines. The MCDF code has been used to quantify the magnetic field effect on both $Xe^{+}$ $5p^5$ and $Xe^{2+}$ $5p^4$ levels. Each ionic charge state has been separately considered. For each $M_J$ value, the energies of the sublevels have been calculated by diagonalization of the Hamiltonian matrix including contributions of the magnetic field interaction evaluated on the basis of unperturbed wave functions. The shift produced by a field of 1.24 T has a maximum amplitude of 0.15 meV for $Xe^{+}$ $5p^5$ and 0.21 meV for $Xe^{2+}$ $5p^4$. Such values are well below the resolution of our experiments.

In summary, our experimental work demonstrates that the implementation of an ion trap setup at a third-generation synchrotron radiation beam line allows the measurement of the photoionization cross section of ionic species in their ground state. Comparison of the photoionization spectra of $Xe^{+}$ ions obtained at ELETTRA in the 20–23 eV photon energy range using the trap with the ASTRID merged-beam experiment has allowed the extraction of the pure ground state ionization cross section on an absolute scale. MCDF calculations reproduce well the intensity of the direct photoionization cross section and show the negligible effect of the external magnetic field. Further developments are foreseen combining the tandem mass spectrometry capability of ion traps within cell photochemistry on mass-selected ions. This will open new opportunities for studies of interest in many different fields, including spectroscopy and dynamics of atomic and molecular ions, mass-selected ionic clusters, multiply charged molecular and cluster ions, or fragmentation of large biomolecules.

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