First Observation of Photoelectron Spectra Emitted in the Photoionization of a Singly Charged-Ion Beam with Synchrotron Radiation

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The first measurement of photoelectron spectra emitted in the photoionization of a singly charged-ion beam by synchrotron radiation is reported. A Ca^+-ion beam is resonantly photoionized by the monochromatized photon beam of the SU6 undulator of the SuperACO Storage Ring at 33.20 eV photon energy. The values observed for the kinetic energy and for the intensity of the photoelectron line are in good agreement with the predicted values. The success of this feasibility experiment opens up wide opportunities for similar photoionization and Auger studies on multiply charged ions.

We report here the results of an experiment aiming to explore the feasibility of a new class of studies, i.e., using photoelectron specterometry to study the photoionization of a positively charged-ion beam with synchrotron radiation. Because of the formidable difficulties encountered in such an experiment, a resonant photoionization process was chosen since photoionization cross sections are greatly enhanced by the existence of an intermediate excited autoionizing state. More precisely, the results presented in the Letter show, for the first time, photoelectron spectra emitted in the interaction of a monochromatic photon beam of synchrotron radiation produced by an undulator with a singly charged-ion beam. Ca^+ ions were selected because the energy and the cross section for photoionization of the $3p^64s\,^2S$ state via the $3p^53d4s\,^2P$ autoionizing state are known from previous photoabsorption [1] ($h\nu = 33.20$ eV) and photoion [2] ($\sigma \sim 2200$ Mb) spectrometry measurements. Also, the excitation energy of this resonance is in the tuning range of the SU6 undulator of the SuperACO Storage Ring in Orsay. We have obtained quantitative data which demonstrate the feasibility to study photoionization of multiply charged ions by this new technique for the next ten to fifteen years, especially when the new storage rings presently under construction, such as the Advanced Light Source in Berkeley, the European Synchrotron Radiation Facility in Grenoble, or the Advanced Photon Source in Argonne, come into operation.

Scientific justification for initiating new studies of the interaction processes between photons and multiply charged ions results from the fact that, except for a few measurements on mostly singly charged species, there is practically no data measured for inner-shell photoionization on ion targets, while they are of great importance for the understanding of astrophysical and laser-produced plasmas. From a theoretical point of view, there are many calculations, mostly based on one-electron models [3], predicting the behavior of photoionization parameters along various isoelectronic or isonuclear sequences, but these results are yet to be tested.

Previous experimental studies on the interaction of photons with positively charged ions were mostly dedicated to *photoabsorption* experiments [1,4–7] and, more recently, to *photoion* spectrometry [2,8]. In these later experiments, absolute cross sections were measured for a large number of autoionization resonances in a merged photon-ion-beam apparatus. However, when several channels are open into the continuum, only photoelectron spectrometry provides detailed insight into the photoionization process by allowing the measurement of branching ratios and partial photoionization cross sections for the various photoionization processes and the various subshells of a many-electron atom [9,10], and the study of nonradiative relaxation (autoionization and Auger decays) of a hole created in inner-shell ionization of the atom. However, the low density of ions focused in the small source volume of an electron analyzer (in the 10^7-ions/cm^3 range, i.e., lower by 3 to 4 orders of magnitude compared to the currently used densities of neutral-atom samples in similar investigations) makes it extremely

difficult to observe these electrons. Moreover, the transmission of an electron spectrometer is less than 1%, as compared to nearly 100% in the case of ion spectrometry, while the length of the interaction region is about 1 and 10 cm, respectively. This explains why it was absolutely necessary to have access to an undulator to get the highest flux of photons available from synchrotron radiation.

The experimental setup is shown in Fig. 1. In short, a 20-keV Ca$^+$-ion beam of about 35 μA was focused, after magnetic selection and electrostatic deflection, into the source volume of a cylindrical mirror electron analyzer (CMA). The monochromatized photon beam emitted in the SU6 undulator was also focused into the source volume of the CMA. The electrons emitted in the interaction were analyzed at an angle close to the magic angle.

The ions are produced in a plasma discharge ion source [11,12] which was developed at the Institut de Physique Nucléaire in Orsay. The ions are extracted and, after focusing by an electrostatic quadrupole, a first magnet (M1) selects the ionic species of interest and focuses the desired q/m isotope on a collimating slit (2×30 mm^2). Then, the ions are deflected by a 45° toroidal electrostatic deflector which makes the ion beam collinear to the axis of the CMA and to the photon beam. After focusing of the ion beam, with electrostatic quadrupoles, into the source volume of the CMA, where the focus is 4 mm wide and 2 mm high, the ions exit the CMA and are refocused by a quadrupole at the entrance of a second magnet (M2) which deflects singly and doubly charged ions into two Faraday cups. A long-lived $3\,^1D$ ($\sim$0.77 sec) Ca$^+$ metastable ionic state might be present in the ion beam, but, since we are discriminating against electron energies, the autoionization line due to the decay of this core-excited metastable ion would appear at a different photon energy.

The photon beam is produced in the 1.33-m (16 undulations) SU6 undulator [13] of SuperACO ($K = 1.85$ at the minimum gap of 38 mm). After monochromatization with a toroidal grating monochromator, the photon beam is focused into the source volume of the CMA. A gold foil, connected to an electrometer, could be inserted in the photon beam to measure the variation of its intensity. A

pneumatic chopper was introduced after the second mirror in order to modulate the photon beam.

The CMA is basically the same electron analyzer already used for photoelectron spectrometry studies of atoms in the ground state [10,14] and, later on, in some laser-excited states [15,16]. However, it was slightly modified for this experiment. A collinear geometry was chosen to minimize the Doppler broadening of the photoelectron lines. Because of the high velocity of the ions, the electrons transmitted through the slits of the CMA are emitted at an angle higher than the magic angle (e.g., 60° for 20-eV electrons in the laboratory frame). The resolution of the CMA was fixed, for this experiment, at 2.1% in the constant-resolution mode, which means that the contribution of the electron spectrometer function to the FWHM of the autoionization line is 0.4 eV. Three high-counting-rate RTC channeltrons were placed in the focal plane of the photoelectrons at 120° from each other. A polarized grid, biased up to -6 eV, was placed in front of the channeltrons to protect them against the high rate of low-energy electrons. The residual pressure in the CMA was 1×10^{-7} Torr. The best overlap between the photon beam and the ion beam into the source volume of the CMA was achieved using a removable double-sided Faraday cup. The data acquisition was controlled by computer.

The photoionization process used in this feasibility experiment can be written as

$$\text{Ca}^+ 3p^6 4s\,^2S + h\nu_R \rightarrow \text{Ca}^{+*} 3p^5 3d4s\,^2P$$

$$\rightarrow \text{Ca}^{++} 3p^6\,^1S + e^-.$$
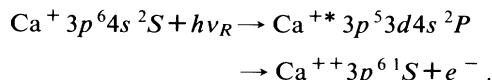
The whole process can be described as the resonant photoionization of the $4s$ electron. $h\nu_R$ is known to be equal to 33.20 eV. Setting the monochromator at 33.17-eV energy (taking into account the $+0.03$-eV Doppler shift of the radiation in the ion frame) was obtained, first within 0.1 eV, by using the photoelectron lines produced by photoionization of the $2p$ subshell of Ne. These photolines were also used to determine the bandpass (BP) of the monochromator (about 0.3 eV with the 1-mm slits used in this experiment) and to optimize the use of the undulator for 33.17-eV photon energy. We determined the gap of the undulator spacing which provided the highest photon flux at 33.17 eV (43 mm, $K = 1.51$) by
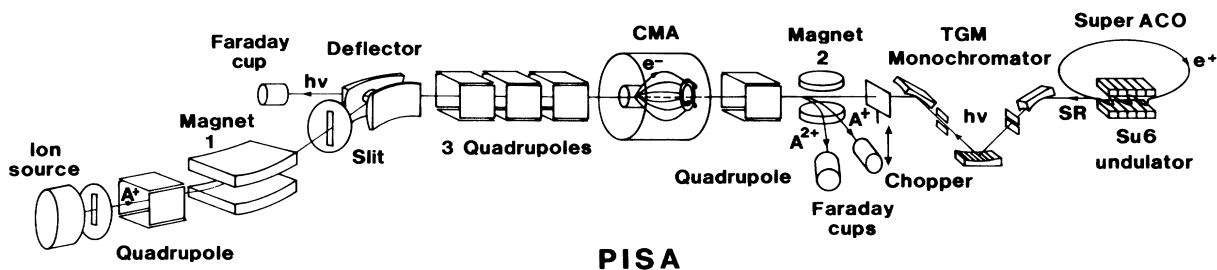

FIG. 1. Layout of the experimental setup. See text for description. Ions propagate from left to right, photons travel the other way. Both beams are focused into the source volume of the CMA.

measuring the variation, versus gap value, of the intensity of the Ne $2p$ photoline produced at this photon energy. Final tuning, within 0.01 eV, of the monochromator was obtained by setting the photon energy to the maximum of the constant-ionic-state (CIS) curve as described later.

The background due to low-energy scattered electrons, and to collisional ionization processes with molecules present in the residual gas, was found to be very high, from 5000 to 10000 counts/sec. But the main problem arises from the variations of the ion-beam intensity. Short-term variations of this intensity were due to numerous discharges occurring randomly in the ion source and producing a complete blowout of the spectrum under accumulation. Long-term variations of the ion beam produced variations in the background of amplitude higher than the expected intensity of the photoelectron signal. Operating the chopper with a modulation frequency of 0.25 Hz, the photon-induced spectrum at each kinetic energy was immediately obtained by instantaneous subtraction, in each channel, of the spectra measured with and without synchrotron radiation. The effect of discharges in the ion source was eliminated by the computer, which rejected, after accumulation in each channel, the measured electron flux each time the fluctuations of the ionic current exceeded 2%. In that way, it was possible to accumulate a photoelectron spectrum for 40–50 sec/channel.

Figure 2 shows two typical examples of the photoelectron spectra we have regularly obtained with this procedure. The ion-beam current was typically about 35 μA and the averaged beam current in SuperACO was 200 mA. In the top part of the figure, one sees the photoelectron spectrum which is measured when the monochromator is tuned to the energy of the resonance, i.e., to 33.17 eV in the laboratory frame (33.20 eV in the ion frame). A very intense electron peak appears at about 19.2-eV kinetic energy. The ionization energy of the Ca$^+$ ion being 11.87 eV, the kinetic energy of the autoionization electrons in the ion frame is equal to 21.30 eV. However, two corrections must be applied to this value. The first one is due to the potential created by the ionic current itself. It has the effect of retarding the electrons while they are leaving the ion beam. For a 35-μA ionic current, the shifted energy position of the Ne $2p$ photoelectron line ejected by 33.20-eV photons with and without the ion beam going through the CMA was measured to be 5.3 ± 0.5 eV, in good agreement with our predicted value of 5 eV. Thus, the electrons are ejected in the ion frame with an energy of $15.7 + 1.2 = 16.9$ eV, $+1.2$ eV being due to contact potentials in the CMA. The second correction is due to the velocity of the ions in the laboratory frame. In the case of 16.9-eV electrons, we deduced from geometrical considerations a kinetic energy of the electrons in the laboratory frame of 19.1 ± 0.2 eV, again in excellent agreement with the 19.2 ± 0.1-eV measured value. The width of the autoionization line is about 0.8 eV, indicating a space-charge–induced broadening of a few tenths of
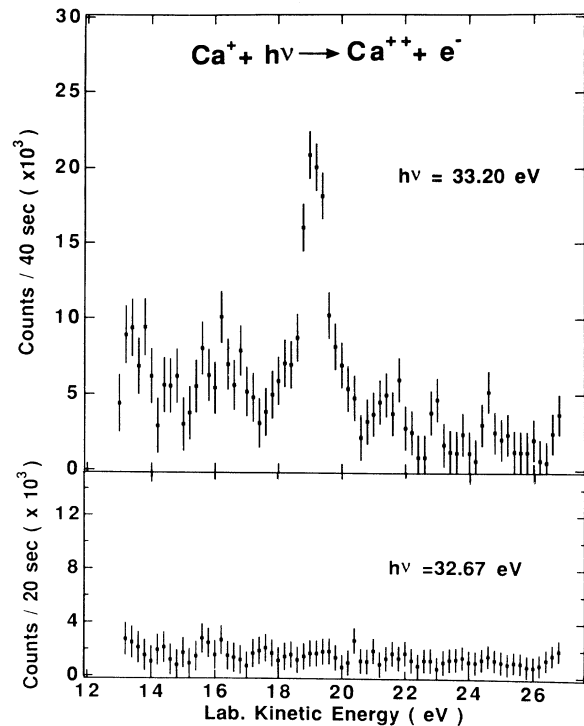

FIG. 2. Top: Photoelectron spectrum measured in the photoionization of a 20-keV, 35-μA Ca$^+$-ion beam with 33.20-eV (33.17 in the laboratory frame) photons. The Ca$^+$ photoelectron line appears at 19.2 eV. The weaker electron line at 16 eV arises from photoionization of the $^1b_1$ state of H$_2$O. The averaged current in SuperACO was 200 mA. The error bars are larger than the statistical error on the count numbers, because the number of electrons in each channel results from the subtraction of two large numbers [$(1–2) \times 10^5$]. Bottom: Photoelectron spectrum obtained under the same experimental conditions, except for the photon energy, which is detuned from the maximum of the resonance by 0.5 eV. Only the H$_2$O photoelectron line is still visible around 16-eV kinetic energy, because the direct $4s$ photoionization cross section of Ca$^+$ is very weak (1–2 Mb) at this photon energy.

an eV. This broadening was seen to be dependent on the ion density. On the left of the main electron line in Fig. 2, one observes a low-intensity structure which is due to the photoionization of the $^1b_1$ state of H$_2$O. In the bottom part of Fig. 2, we show the photoelectron spectrum which is observed when the photon energy is shifted by about 0.5 eV. Clearly, the Ca$^+$ photoelectron line has disappeared.

The counting rate at the maximum of the peak is about 500 counts/sec, as can be seen in Fig. 2. Using this value, we can estimate an order of magnitude for the cross section in order to check the consistency of all experimental parameters. At 20 keV, 35-μA Ca$^+$ ions have a density d in the source volume (having a section of 2×4 mm^2) of about 8×10^7/cm^3. Then, the total number per second n of ionization events produced in the source volume is $N \times \sigma \times d \times l$, where N is the photon flux in the natural
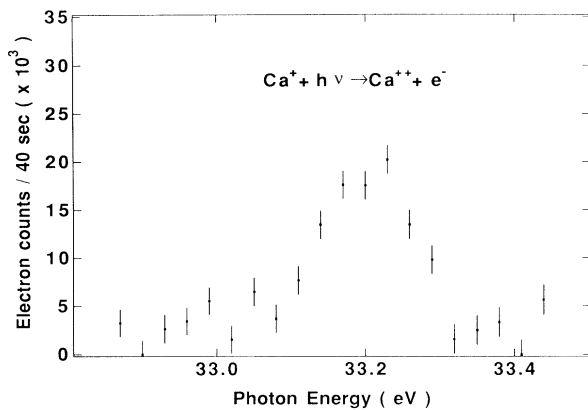
FIG. 3. Constant-ionic-state spectrum in the photon energy range of the resonance. The energy interval between each point is 0.03 eV. Error bars represent the statistical error.

width of the resonance (≈ 0.1 eV) [2], σ the cross section, and l the averaged length of the source volume seen by the CMA. $N = 2 \times 10^{13}$/sec with 200 mA in the machine, $l = 10$ mm, and thus n is equal to $(8.7 \times 10^{20})\sigma$. Using the value of the transmission of the spectrometer, which is measured from the intensity of the Ne $2p$ photoelectron lines, to be about 1% and the expression of the photoelectron line intensity [17], we obtain an estimated value of 3×10^{-15} cm^2 for σ, within a factor of 2, in reasonable agreement with the previously measured value [2] of 2.2×10^{-15} cm^2.

Finally, we show, in Fig. 3, the spectrum recorded in the constant-ionic-state mode. In this mode, the pass electron energy in the CMA is scanned, simultaneously to the photon energy, by regular steps (0.03 eV). The resulting curve is the excitation function of the resonance whose maximum is proportional to the oscillator strength.

To conclude, we have measured photoelectron spectra resulting from the photoionization of a singly charged-ion beam with undulator synchrotron radiation. In the present experimental conditions, the method is limited to the study of resonances with high cross sections. The next step is to build new experimental chambers with ultrahigh-vacuum techniques, to improve the detection efficiency, and, possibly, to increase the ion-beam current focused in the source volume of the CMA. With a reasonably expected gain of about a factor of 4 in total, the counting rate at the top of a photoelectron line should reach about 1 count/Mb sec. Having a residual gas pressure in the 10^{-10}-Torr range would drastically reduce the electron background. Thus, with the present ion and photon sources, it should be possible to study many resonant photoionization processes in singly charged ions, as well as Auger decay of core-excited ions using the white light emitted by the undulator. To go futher, i.e., to study direct photoionization processes into the continuum and multiply charged ions, another ion source is needed. This new source should be able to provide high ion-beam currents, at least in the 100-μA range for low-charge-state (1-5) ions, in the source volume of the CMA. Presently, the best ion source seems to be an electron-cyclotron-resonance ion source which would be optimized to deliver high currents of low-charge-state ions [7].

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