Inner-shell resonances in metastable Ca^+ ions

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Electron spectroscopy experiments have been developed by applying coincidence techniques to handle strong background covering a weak signal on photoelectron spectroscopy of free positive ions with synchrotron radiation. $3p$ inner-shell resonances in $3d$ excited metastable Ca^+ could be identified and tentatively assigned. [S1050-2947(97)02005-2]

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Photoionization of free positive ions in the spectral range of the vacuum ultraviolet (VUV) is a rather actual and interesting field of research [1,2]. Comparing VUV photoionization of free atoms and free positive ions along isonuclear and isoelectronic sequences gives well-defined information about the interaction between valence-shell configuration and inner-shell excitation. Those interactions, e.g., cause binding and Auger energy shifts upon condensation of free atoms to solids [3], and they are applied in core level shift photoelectron spectroscopy to study chemical structure of solids, surfaces and thin films [4]. Moreover, the field of inner-shell photoionization of free positive ions is directly linked to plasma physics, solar physics, and astrophysics.

VUV-photoabsorption experiments on free positive ions started in the 1970s using laser and laser-induced plasmas to generate VUV radiation as well as the ionic targets [5,6]. However, to obtain partial cross sections by detection of photofragments, i.e., photoions and photoelectrons, ion-beam experiments must be performed, because within a plasma or ion source the ion- and electron-emission background cannot be handled. But even beam experiments are hampered by a very high background due to ion-ion and ion–residual-gas collisions compared to a weak signal due to the extremely low ion density that can be reached within an ion beam ($n<10^8$ cm^{-3}) [7–10]. In the mid-1980s synchrotron radiation (SR) was used to realize photoion spectroscopy on different positive ion species profiting from a 4π angular acceptance for the photoions and a large interaction region by merging ion and SR beam [7]. A similar experiment has been presented recently [8]. Despite the low angular and spatial acceptance of electron analyzers, electron spectroscopy of free positive ions (Ca^+) could be realized in 1990 [9], profiting from the high VUV-photon flux of undulator radiation and the high cross section ($\sigma\cong 2000$ Mb) of the Ca^+: $3p\rightarrow 3d$ excitation at 33.2-eV photon energy [7]. Even angular distribution of the emitted electron on the decay of this resonance state has been investigated recently [10].

In order to expand electron spectroscopy studies to processes of lower cross sections, additional techniques are needed to increase the signal-to-background ratio, apart from working with the highest photon flux and the lowest residual gas pressure as possible. In this context we present two different photoelectron spectroscopy experiments applying coincidence techniques as background filter and allowing for on-line monitoring of the usually strongly fluctuating signal background. Figure 1(a) shows a scheme of the experimental setup. A Ca^+ ion beam is extracted by a voltage of 2 kV from a discharge ion source. After electrostatic preseparation the beam is focused onto the interaction zone where it crosses a beam of monochromatized undulator radiation from the electron storage ring BESSY. At the point of intersection the Ca^+ density is in the range of 10^6 cm^{-3}. The photon flux at 33-eV photon energy amounts to 10^{13} photons per second in a bandpass of 0.1 eV. Emitted electrons as well as ionized ions are analyzed electrostatically and detected by microchannel plates.

In our first experiment, an electron-ion coincidence has been realized by using the electron signal as start and the signal of ionized ions as stop for a time-to-amplitude converter (TAC), as shown in Fig. 1(b). In the resulting time spectrum pairs of electrons and ionized ions that arise from the same ionization process form a discrete peak due to their

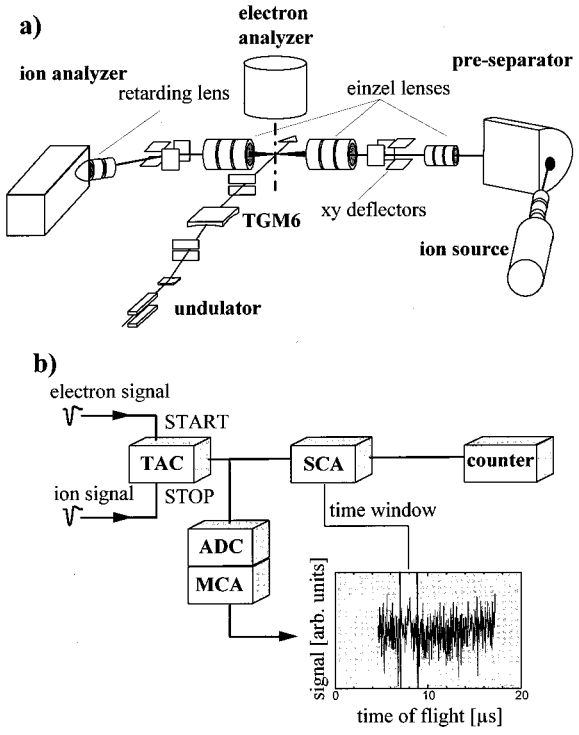

FIG. 1. (a) Setup for electron spectroscopy of free ions at BESSY. (b) Electron-ion coincidence electronics.

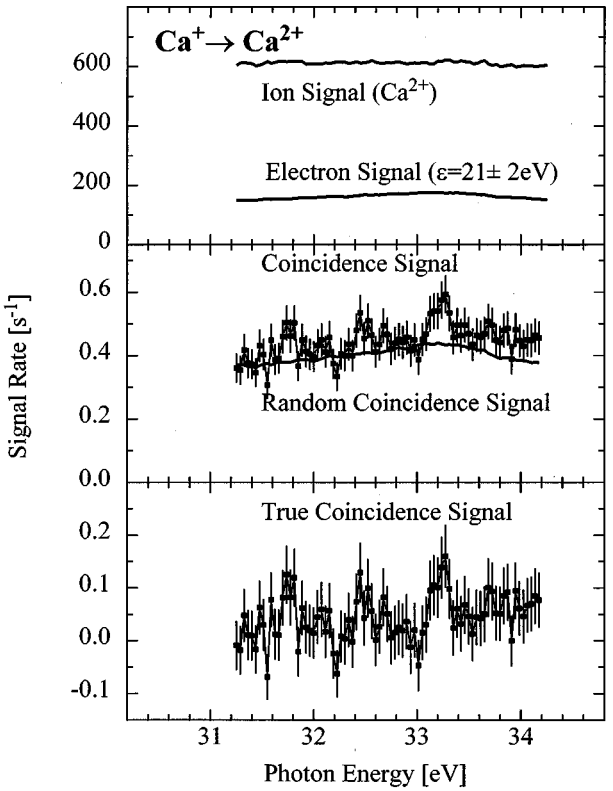

FIG. 2. Top: Rate for ionized Ca^+ ions (Ca^{2+}) and emitted electrons with 21 ± 2 -eV kinetic energy. Center: Rate of electron-ion coincidences and random coincidences [Eq. (1)]. Bottom: Rate of true coincidences.

time correlation. Peak position and width are mainly determined by the time of flight of the ions between interaction zone and ion detector. Uncorrelated background emissions in the electron and ion spectra only lead to random coincidences, arbitrarily distributed on the time scale. Hence setting a suitable time window by a single-channel analyzer (SCA), the major part of the background is suppressed and electron-ion coincidence rate can be measured as a function of the kinetic electron energy and/or photon energy. The remaining rate of random coincidences R_{rc} within the set time window $\Delta\tau$ can be calculated with the help of the electron and ion signal rates R_{el} and R_{ion}:

$$R_{rc}=R_{el}R_{ion}\Delta\tau. \tag{1}$$

For the results shown in Fig. 2 a small preliminary version of an electrostatic electron analyzer with an angular acceptance of 0.5% and an energy resolution of 13% has been used. In the top part, the rates for ionized Ca^+ ions (Ca^{2+}) and for emitted electrons with (21 ± 2)-eV kinetic energy are displayed as a function of the photon energy. The spectra are dominated by different types of background emission and a photoionization signal of Ca^+ is not apparent. The same signals have been used to realize simultaneously an electron-ion coincidence with a suitable time window. The result is shown in the center part of Fig. 2 in comparison to the calculated spectrum of random coincidences according to Eq. (1). The latter is a perfect on-line measured reference for uncorrelated background emission in the electron-ion coincidence spectrum and includes all fluctuations, e.g., due to instabilities of the ion source. Hence all structures in the difference spectrum shown in the bottom part of Fig. 2 correspond with true coincidences, i.e., photoionization signals of Ca^+. Despite the extremely low signal rate and the statistical uncertainty, the background filter effect of the method is evident. The signal-to-background ratio is estimated to be reduced from 1:40 to 1:4 in the electron signal by applying the electron-ion coincidence background filter. A corresponding preliminary spectrum has already been presented, but the data are given on an incorrect photon energy scale [2]. The already mentioned well-known strong $3p^{-1}\,3d$ resonance starting from ground-state $Ca^+(4s)$ arises at 33.2-eV photon energy as expected. The subsequent autoionization decay leads to the creation of a Ca^{2+} ion and the emission of a free electron in the final state:

$$Ca^+:3p^6 4s\ ^2S\rightarrow 3p^5 3d\ 4s\ ^2P\rightarrow Ca^{2+}:3p^6\ ^1S+\epsilon p. \tag{2}$$

The kinetic energy of the emitted electron is given by the difference between the resonance photon energy and the $Ca^+(4s)$: $4s^{-1}\ \epsilon p$ ionization energy ($\epsilon=\hbar\omega_{res}-I_{4s}=33.2-11.9$ eV [11]$=21.3$ eV). The additional resonance structures in the bottom part of Fig. 2, mainly the peak at 31.8-eV photon energy, may be interpreted as corresponding $3p$ excitation starting from $3d$ excited metastable $Ca^+(3d)$:

$$Ca^+:3p^6 3d\ ^2D\rightarrow 3p^5 nl(nl)'\ ^2(P,D,F)$$
$$\rightarrow Ca^{2+}:3p^6\ ^1S+\epsilon'(p,f\ ). \tag{3}$$

Here, the kinetic energy of the emitted electron only differs slightly from 21.3 eV ($\epsilon'=\hbar\omega'_{res}-I_{3d}=31.8-10.2$ eV [11]$=21.6$ eV), which means that both resonance processes, starting from $Ca^+(4s)$ [Eq. (2)] and from $Ca^+(3d)$ [Eq. (3)] are registered by the broad band electron analyzer at constant 21-eV pass energy. In photoabsorption spectra [12,13] as well as in photoion yield spectra [7] of Ca^+ a group of weak resonance structures between 31.5- and 33.0-eV photon energy has also been observed but, up to now, none of them has been identified to be due to $3p$ excitation starting from $Ca^+(3d)$.

To definitely clarify the origin of the resonances in Fig. 2 between 31.5 and 33.0-eV photon energy the experimental setup of Fig. 1(a) has been improved by replacing the preliminary broad band electron spectrometer by a 360° cylindrical mirror analyzer with an angular acceptance of 3% and an energy resolution of 1.4%. Moreover, our second background filter method (''bunch-gate method'') has been applied. Instead of the ion signal the BESSY bunch clock signal has been used for the coincidence electronics displayed in Fig. 1(b). Working in the BESSY single bunch mode the SR is pulsed with a repetition rate of 4.8 MHz and a pulse width of well below 200 ps. Thus in the resulting time spectrum photoelectrons form a discrete peak due to their time correlation with the SR pulses. Background emissions due to ion-ion and ion-residual gas collisions are not correlated with the SR pulses and lead to unstructured background in the time spectrum. Again, setting a suitable SCA time window the major part of the background is suppressed. By replacing the ion counting rate R_{ion} in Eq. (1) by the bunch rate $R_{bunch}=4.8$ MHz, again the remaining rate of background

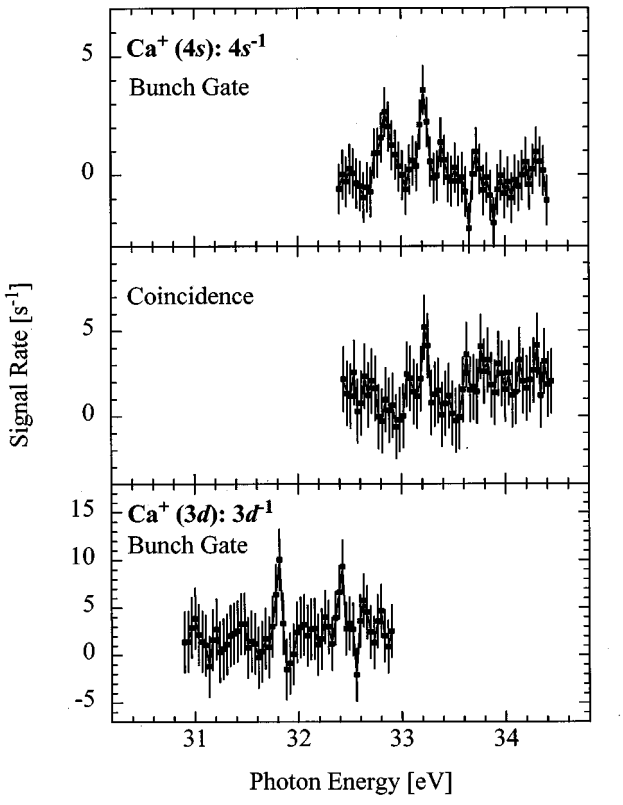

FIG. 3. Bunch-gate CIS spectrum (top) and electron-ion coincidence CIS spectrum (center) of the $Ca^+(4s)$: $4s\ \epsilon p$ photoemission process. Bottom: Bunch-gate CIS spectrum of the $Ca^+(3d)$: $3d^{-1}\epsilon(p,f)$ photoemission process.

emission within the set time window can be calculated, which represents an alternative perfect on line measured reference and has been subtracted from the signal.

In the top part of Fig. 3, a bunch-gate constant-ionic-state (CIS) spectrum of the $Ca^+(4s)$: $4s^{-1}\ \epsilon p$ photoemission process is shown. Both monochromator and electron analyzer have been scanned with a fixed energy difference corresponding to the $Ca^+(4s)$: $4s^{-1}\ \epsilon p$ ionization energy (I_{4s} $=11.9$ eV [11]). Again, the well-known $3p^{-1}\,3d$ ground-state resonance arises at 33.2 eV. However, the resonance structure at 32.9 eV is not due to photoionization of Ca^+ but can be explained by residual gas photoionization. This is proven by the center part of Fig. 3, which shows the result of a repetition of the measurement but by applying the electron ion coincidence technique instead of the bunch-gate method. Residual gas photoionization cannot lead to true electron-ion coincidences because the created photoions from atoms or molecules are not extracted and do not reach the ion detector. Accordingly, the peak at 32.9 eV disappears. The bunch-gate CIS spectrum at the bottom part of Fig. 3 has been measured with a constant difference of 10.2 eV between monochromator and electron analyzer energy, which corresponds to the $Ca^+(3d)$: $3d^{-1}\,\epsilon(p,f)$ ionization energy I_{3d} [11]. Resonances are observed at 31.8-, 32.4-, and around 32.7-eV photon energy in accordance to the resonance structures in Fig. 2. Therefore, these resonances have definitely been identified now to be due to resonance excitation in $Ca^+(3d)$. When comparing the relative signal rates of the resonances in Fig. 3 it seems that even the major part of the ions in our beam was excited to $Ca^+(3d)$.

$3p$ excitation in $Ca^+(4s)$ as well in $Ca^+(3d)$ is strongly influenced by electron correlations due to the $3d$ orbital collapse and accurate theoretical results to resonance energies and strengths are very difficult to obtain [14,15]. $Ca^+(3d)$ is excited by 1.70 eV [11] compared to $Ca^+(4s)$. Resonance excitation to $3p^5 3d4s\ ^2P$ starting from $Ca^+(3d)$ can therefore expect to be 1.70 eV below the $Ca^+(4s)$ resonance at 33.2 eV [Eq. (2)], i.e., at 31.5 eV, which is slightly below the observed $Ca^+(3d)$ resonances in Figs. 2 and 3. However, taking into account that not only a coupling in the excited state to ^2P is allowed but also to ^2D and ^2F, when starting from $Ca^+(3d)$ [Eq. (3)] the observed inner-shell resonances in $Ca^+(3d)$ may be assumed to be due to excitation into the $3p^5 3d4s4s\ ^2(P,D,F)$ multiplet.

In conclusion, we can state that under optimized but still realistic conditions, i.e., an increase of the photon flux by one and an increase of the ion density by two orders of magnitude, the presented techniques allow for systematic electron spectroscopy studies with synchrotron radiation on free positive ions, probably even outside of strong resonances.

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