$4d$ Photoionization of Free Singly Charged Xenon Ions

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Electron spectroscopy in direct $4d$ photoionization of free Xe$^+$ ions has been realized for the first time, applying various timing and coincidence techniques to suppress and to monitor on line the strong fluctuating background. The ionization energies of $4d_{5/2}$ and $4d_{3/2}$ electrons of Xe$^+$($5p^5\,{}^2P_{3/2}$) and Xe$^+$($5p^5\,{}^2P_{1/2}$) were determined and compared to calculated RHF(CI) values and to corresponding results of neutral Xe($5p^6\,{}^1S_0$) atoms to study the influence of the outer-shell electron occupation on the $4d^{-1}$ inner-shell process. [S0031-9007(99)08598-1]

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The influence of the valence electron structure of matter on inner-shell excitation processes is the fundamental effect of one of the major techniques for the investigation of solids, surfaces, and thin films, that is, core level shift spectroscopy using vacuum ultraviolet (VUV) radiation or x rays. Basically, this effect can be studied by comparing inner-shell spectra of free atomic systems along isonuclear series, generating a well-defined preparation of the valence electron states by laser excitation or by studying free positive ions of different initial charges. However, VUV photoionization experiments on beams of free positive ions are rare because they are difficult to carry out [1]. In particular, the detection of photofragments like photoions or photoelectrons is hampered by a low signal due to the low target density that can be reached within an ion beam and which is 5 orders of magnitude lower compared to the ordinary gas phase or surface experiments. On the other hand, this low signal is superimposed by a fluctuating background due to ion-ion and ion-residual gas collisions, which usually is much higher compared to the signal.

Because of these difficulties, photoelectron spectroscopy on free positive ions first of all succeeded only on Ca$^+$, using highly brilliant undulator radiation at a photon energy of 33.2 eV, that is, the resonance energy for the very strong $3p \rightarrow 3d$ autoionizing resonance in Ca$^+$ [2,3]. Later, in order to suppress and to monitor on line the background signal in electron spectra of free positive ions, various timing and coincidence techniques have been developed which allowed the first observation and identification of $3p$ resonances in excited metastable (Ca$^+$)* [4]. Now, these techniques make it possible to measure even an electron spectrum obtained by direct continuum excitation of a free positive ion target with a cross section expected to be 1 to 2 orders of magnitude lower. In the present study, we chose the $4d$ inner-shell photoionization of Xe$^+$: [Kr]$4d^{10}5s^25p^5$ to compare with the corresponding process in the isonuclear electronic system of atomic Xe: [Kr]$4d^{10}5s^25p^6$ [5,6] and to study the influence of the $5p$ outer-shell occupation.

Results on the ion spectra of Xe$^+$ using synchrotron radiation in the spectral range of the $4d$ excitation have been presented already by Sano *et al.* [7]. O'Sullivan *et al.* [8] investigated the $4d$ excitation along the isonuclear series I, I$^+$, and I^{2+} by photoabsorption in a laser-produced plasma. Iodine is located just one element before xenon in the periodic table. Hence, atomic I: [Kr]$4d^{10}5s^25p^5$ is isoelectronic to Xe$^+$ in the ground state. Electron spectroscopy results on the $4d^{-1}$ multiplet of atomic iodine were presented by Tremblay *et al.* [9] and Nahon *et al.* [10]. In this context we present for the first time electron spectroscopy data on the $4d^{-1}$ multiplet of Xe$^+$.

Our experiments were performed at the electron storage ring BESSY. A beam of free Xe$^+$ ions was extracted from an electron impact ion source. The Xe$^+$ ion beam was electrostaticly preseparated and focused onto the interaction zone where it crossed a monochromatized beam of undulator radiation. At the point of intersection the Xe$^+$ density was in the range of 10^6 cm^{-3} and the photon flux amounted to 10^{12} to 10^{13} photons per sec. Photoionized Xe$^+$ ions, i.e., Xe^{2+} and Xe^{3+} ions, were analyzed electrostaticly and detected by a microchannel plate detector. Electrons emitted from the interaction zone were analyzed by a 360° cylindrical mirror analyzer and also detected by a microchannel plate detector. The BESSY bunch clock signal was used when working in the single bunch mode which provides pulsed undulator radiation of a 4.8-MHz repetition rate. The bunch clock signal allowed us to gate for the electron signal between the bunches (bunch-gate method). Thus, various types of spectroscopy on free positive ions could be realized: ion-yield spectroscopy, electron spectroscopy, bunch-gate electron spectroscopy, and (bunch-gate) electron-ion coincidence spectroscopy. By the bunch-gate methods, as well as by the coincidence technique, a suppression and on-line monitoring of the strong fluctuating background signal in electron spectra were realized [4]. Finally, using a gas inlet system, also rare gas electron spectra could be measured.

In Fig. 1(a) an electron spectrum of Xe$^+$ is displayed measured at a photon energy of 103.3 eV that shows the $4d^{-1}$ multiplet of Xe$^+$ (Xe$^+$: [Kr]$4d^{10}5s^25p^5 \rightarrow$ Xe^{2+}: [Kr]$4d^95s^25p^5 + \varepsilon l$). To correct for the background signal, bunch gate as well as the electron-ion

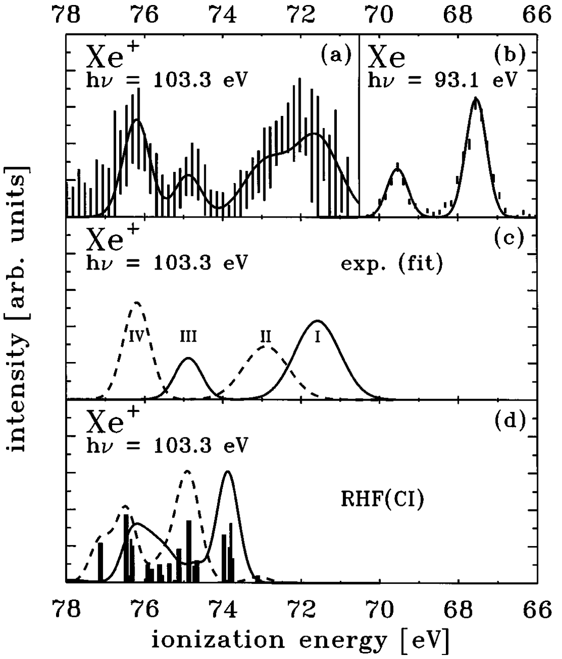

FIG. 1. Electron spectrum of ionic Xe$^+$ taken at 103.3-eV photon energy (a), fitted by a superposition of two Gaussian-type doublet structures that are also shown individually (c) and compared to a RHF(CI) calculation [11] to the $4d^{-1}$ multiplet of Xe$^+$ (d). Starting from Xe$^+$: [Kr]$4d^{10}5s^25p^5\,{}^2P_{3/2}$ (solid line) and Xe$^+$: [Kr]$4d^{10}5s^25p^5\,{}^2P_{1/2}$ (dashed line), respectively, the calculated spectra have been convoluted with the experimental bandpass (0.6 eV). For comparison the electron spectrum of atomic Xe taken at 93.1-eV photon energy is shown (b), fitted by one Gaussian-type doublet structure.

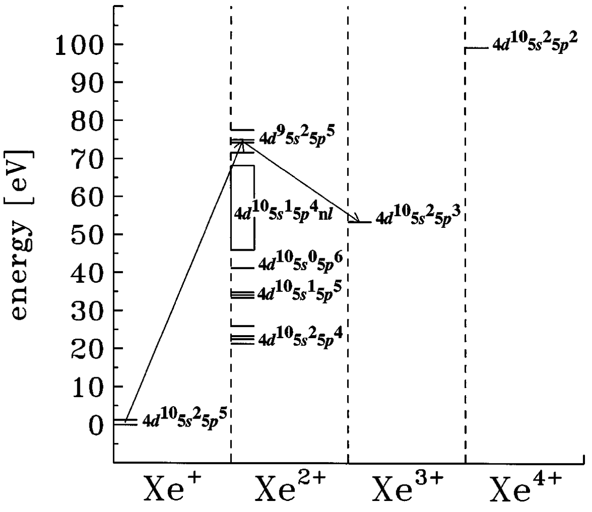

FIG. 2. Energy level diagram of ionic xenon based on published data [12–14], a calculation in the RHF(CI) approximation [11], and the present experimental results. The arrows indicate the $4d^{-1}$ photoionization process on Xe$^+$ with subsequent Auger decay into a Xe^{3+} final state.

coincidence technique was applied, while the ion analyzer was tuned to accept Xe^{3+} ions only. From the energy level diagram in Fig. 2 it is obvious that the $4d^{-1}$ hole states (Xe^{2+}: [Kr]$4d^95s^25p^5$) are located above the Xe^{3+} threshold but below the Xe^{4+} threshold. Hence, the $4d^{-1}$ ionization process of Xe$^+$ exclusively leads to the formation of Xe^{3+} in the final state by subsequent Auger decay (Xe^{2+}: [Kr]$4d^95s^25p^5 \longrightarrow$ Xe^{3+} + $\varepsilon_{\mathrm{Auger}}$), provided that charge conserving fluorescence decay can be neglected as demonstrated recently for atomic Xe [15]. The absolute uncertainty of the kinetic energy measurement of emitted electrons and, hence, of the ionization energy scale in Fig. 1(a) amounts to ±0.5 eV due to a fluctuating space charge retarding of the emitted electrons within the ion beam that is correlated with ion beam instabilities.

For comparison, Fig. 1(b) shows the well-known corresponding $4d^{-1}$ multiplet of atomic Xe: [Kr]$4d^{10}5s^25p^6 \longrightarrow$ Xe$^+$: [Kr]$4d^9({}^2D_{3/2,5/2})5s^25p^6 + \varepsilon l$ measured at 93.1 eV photon energy. The spectrum has been fitted by a Gaussian-type doublet structure with a constant width equal to the combined bandpass of the monochromator and the electron analyzer (0.6 eV). In contrast to that rather simple spin-orbit doublet, the $4d^{-1}$ multiplet of Xe$^+$, shown in Fig. 1(a), is more complex. One reason for that might be the coexistence of the two initial fine structure state Xe$^+$: [Kr]$4d^{10}5s^25p^5\,{}^2P_{1/2,3/2}$ within the ion beam that are separated by 1.3 eV [12]. In fact, the $4d^{-1}$ multiplet of Xe$^+$ can be fitted fairly well by a superposition of two almost identical Gaussian-type doublet structures, as demonstrated in Fig. 1(a). The components of that fit are shown individually in Fig. 1(c) and compared to the results of a relativistic Hartree-Fock [RHF(CI)] calculation [14] to the $4d^{-1}$ multiplet, starting from Xe$^+$: [Kr]$4d^{10}5s^25p^5\,{}^2P_{3/2}$ and Xe$^+$: [Kr]$4d^{10}5s^25p^5\,{}^2P_{1/2}$, respectively [Fig. 1(d)]. The calculation confirms the general feature of the measured $4d^{-1}$ multiplet of Xe$^+$, consisting of a superposition of two doublet structures. A corresponding assignment is given in Table I. According to this interpretation, the five $5p$ electrons of Xe$^+$ act as a kind of "spectator" during $4d$ photoionization, and each of the two observed doublet structures almost represents the $4d^{-1}\,{}^2D_{3/2,5/2}$ spin-orbit splitting, in Xe^{2+}: [Kr]$4d^95s^25p^5({}^2P_{1/2})$ and in Xe^{2+}: [Kr]$4d^95s^25p^5({}^2P_{3/2})$, respectively. The relative energy levels of the corresponding states are also given in Table I and shown in Fig. 2. However, the broadening of the observed line components in Fig. 1(a), compared to the experimental bandpass, and the complex multiplet of the RHF(CI) calculation in Fig. 1(d) indicate the influence of intermediate coupling. Obviously the corresponding multiplet components due to the coupling between the open $4d$ and $5p$ shells in the $4d^95s^25p^5$ configuration are not resolved in the experiment. Intermediate coupling was found to well describe the $4d^{-1}$ multiplet of atomic iodine I: [Kr]$4d^{10}5s^25p^5$ [9,10] that in the ground state is isoelectronic to Xe$^+$. In analogy to Xe$^+$, the $4d^{-1}$

TABLE I. Assignment of the line structures in Fig. 1.

		Initial state		Ionization state	
Line No.	Ionization energy [eV]	Xe^+: [Kr]...	Relative energy [eV][a]	Xe^{2+}: [Kr]...	Relative energy [eV][a]
I	71.6 ± 0.5	$4d^{10}5s^25p^5\,{}^2P_{3/2}$	0.0	$4d^9({}^2D_{5/2})5s^25p^5({}^2P_{3/2})$	71.6 ± 0.5
II	72.9 ± 0.5	$4d^{10}5s^25p^5\,{}^2P_{1/2}$	1.3 [11]	$4d^9({}^2D_{5/2})5s^25p^5({}^2P_{1/2})$	74.2 ± 0.5
III	74.9 ± 0.5	$4d^{10}5s^25p^5\,{}^2P_{3/2}$	0.0	$4d^9({}^2D_{3/2})5s^25p^5({}^2P_{3/2})$	74.9 ± 0.5
IV	76.2 ± 0.5	$4d^{10}5s^25p^5\,{}^2P_{1/2}$	1.3 [11]	$4d^9({}^2D_{3/2})5s^25p^5({}^2P_{1/2})$	77.5 ± 0.5

[a] To ground state [Kr]: $4d^{10}5s^25p^5\,{}^2P_{3/2}$ of Xe^+.

multiplet of I consists of a doublet structure too, but the separation of the two line groups is less pronounced.

Our data demonstrate several important trends: Going from Xe to Xe^+, the center of gravity of the $4d^{-1}$ multiplet is shifted by (5.5 ± 1.0) eV towards higher ionization energy. Obviously the screening of the $4d^{-1}$ hole by the $5p$ subshell is weaker in the case of ionic Xe^+ because of the one missing $5p$ electron. Moreover, from the point of view of a jj-coupling scheme the $4d^{-1}$ ${}^2D_{3/2,5/2}$ spin-orbit energy increases from 2.0 eV for Xe to 3.3 eV for Xe^+. The $5p^{-1}\,{}^2P_{1/2,3/2}$ spin-orbit energy increases from 1.3 eV for Xe^+ in the ground state to 2.6 eV in the presence of a $4d$ hole. Going from Xe^+ to isoelectronic I, the center of gravity of the $4d^{-1}$ multiplet is shifted by about 15.5 eV towards lower ionization energy due to the lower nuclear charge by one elementary unit in the case of iodine.

In conclusion, photoelectron spectroscopy on direct continuum excitation of a free positive ion target was realized. The influence of outer-shell occupation on inner-shell excitation was studied by the example of $4d$ photoionization along the isonuclear series Xe, Xe^+. In comparison to isoelectronic iodine, the $4d^{-1}$ multiplet of Xe^+ was discussed in terms of different coupling mechanisms.

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[1] F. J. Wuilleumier, in *Correlations and Polarization in Electronic and Atomic Collisions and (e,2e) Reactions*, edited by P. J. O. Teubner and E. Weingold, IOP Conf. Proc. No. 122 (Institute of Physics and Physical Society, London, 1992), p. 203.

[2] J. M. Bizau, D. Cubaynes, M. Richter, F. J. Wuilleumier, J. Obert, J. C. Putaux, T. Morgan, E. Källne, S. Sorensen, and A. Damany, Phys. Rev. Lett. **67**, 576 (1991).

[3] S. Al Moussalami, J. M. Bizau, B. Rouvellou, D. Cubaynes, L. Journel, F. J. Wuilleumier, J. Obert, J. C. Putaux, T. Morgan, and M. Richter, Phys. Rev. Lett. **76**, 4496 (1996).

[4] A. Gottwald, S. Anger, J.-M. Bizau, D. Rosenthal, and M. Richter, Phys. Rev. A **55**, 3941 (1997).

[5] B. Kämmerling, H. Kossmann, and V. Schmidt, J. Phys. B **22**, 841 (1989).

[6] U. Becker, D. Szostak, H. G. Kerkhoff, M. Kupsch, B. Langer, R. Wehlitz, A. Yagishita, and T. Hayaishi, Phys. Rev. A **39**, 3902 (1989).

[7] M. Sano, Y. Itoh, T. Koizumi, T. M. Kojima, S. D. Kravis, M. Oura, T. Sekioka, N. Watanabe, Y. Awaya, and F. Koike, J. Phys. B **29**, 5305 (1996).

[8] G. O'Sullivan, C. McGuinness, J. T. Costello, E. T. Kennedy, and B. Weinmann, Phys. Rev. A **53**, 3211 (1996).

[9] J. Tremblay, M. Larzilliere, F. Combet-Farnoux, and P. Morin, Phys. Rev. A **38**, 3804 (1988).

[10] L. Nahon, A. Svensson, and P. Morin, Phys. Rev. A **43**, 2328 (1991).

[11] R. P. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).

[12] Ch. E. Moore, in *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circular No. 467 (U.S. GPO, Washington, DC, 1971), Vol. III.

[13] H. Siegbahn and L. Karlsson, in *Handbuch der Physik*, edited by W. Mehlhorn (Springer-Verlag, Berlin/Heidelberg/New York, 1982), Vol. 31.

[14] H. Aksela, S. Aksela, and H. Pulkkinen, Phys. Rev. A **30**, 865 (1984).

[15] T. Luhmann, Ch. Gerth, M. Groen, M. Martins, B. Obst, M. Richter, and P. Zimmermann, Phys. Rev. A **57**, 282 (1998).