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Preferential decay of 3*p* core excited valence and Rydberg states of atomic copper

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The detection of Cu^+ and Cu^{2+} ions, after excitation of the *M* shell of atomic copper in the 40–125-eV photon energy range (with synchrotron radiation) has allowed us to point out a preferential decay of the Rydberg states $3p^5 3d^{10} 4snd$ (and ns) into double-ionization channels ($3d^9$, $3d^8 4s$ final ionic states) in contrast with the relaxation of the valence resonance $3p^5 3d^{10} 4s^2$ into single-ionization ways (satellite $3d^8 4s^2 \epsilon l$ channels).

Soft x-ray absorption in an atom or a molecule leading to the resonant excitation of a core electron into an unfilled valence or Rydberg orbital has recently attracted much attention[1–4] mainly due to the site and chemical selectivity of such excitation processes. However, the counterpart of these well-selected primary excitations is the very complicated electronic relaxation processes which make these resonances decay to numerous electronic states of the singly or multiply charged[4] ions. Within this context it is of particular interest to compare the relaxation of valence and Rydberg resonances issued from the same core level.

We report the first evidence of an almost complete specific decay of valence and Rydberg resonances into singly and doubly charged ions, respectively, by studying the photoexcitation of the 3*p* core electron of atomic copper.

Photoionization studies[5,6] of copper [(core) $3s^2 3p^6$-$3d^{10} 4s$] have been stimulated by the photoemission studies[7] of resonant satellites observed near the 3*p* thresholds of copper embedded in a matrix, i.e., Cu-phthalocyanine. These experiments were supported by the remarkable photoabsorption studies in the *M* shell of atomic and metallic Fe, Co, Ni, and Cu performed by Brühn, Sonntag, and Wolff.[8] Surprisingly, neither the experimental studies[5–7] nor the theoretical analysis[9] dealing with the interpretation of these correlation effects took care of the double-photoionization process. A double-photoionization study of atomic copper is reported here.

The single- and double-ionization yield measurements were performed at the SUPERACO positron storage ring at Orsay with the setup already described.[10] The dispersed synchrotron beam (bandwidth ≈0.3 eV) is focused onto the interaction zone where it crosses a beam of atomic Cu. The Cu^+ and Cu^{2+} ions are detected with a time-of-flight (TOF) mass spectrometer. A constant pressure of argon is added in the ionization region in order to check at a fixed 70-eV energy the stability of copper pressure. Because of the well-known partition of the total photoionization cross section[11] of Ar, the intensity of the Ar^+ line is used as a reference to measure the Cu^+ yield.[12] Results concerning the Cu^+ yield and Cu^{2+}/Cu^+ ratio are displayed in Fig. 1. Values for the Cu^+ and Cu^{2+} cross sections, after a normalization of the Cu^+

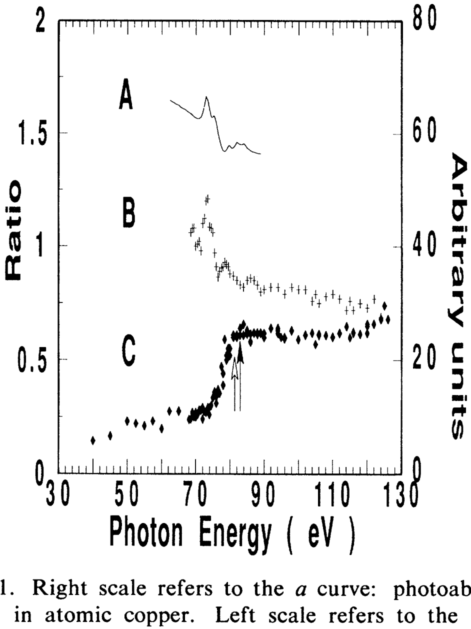

FIG. 1. Right scale refers to the *a* curve: photoabsorption (Ref. 8) in atomic copper. Left scale refers to the *b* and *c* curves. Curve *b*: $Cu^+(h\nu)/Cu^+$ (70 eV). The curve *b* displays one set of experiment performed with a 0.5-eV photon energy step. Curve *c*: Cu^{2+}/Cu^+. In the 68–96-eV photon energy range the curve *c* displays three sets of data recorded with a 0.2-eV interval. The arrows correspond to our calculated positions of the $3p(^2P_{3/2})$ and $3p(^2P_{1/2})$ thresholds (Ref. 14).

yield with the total-absorption cross section[8] at 70-eV photon energy, are shown in Fig. 2.

Comparing the relative Cu^+ ionic-yield curve *b* of Fig. 1 to the photoabsorption data curve *a* of Fig. 1, three points can be noticed.

(i) The resonant enhancement of the Cu^+-ion signal resulting from the excitation of a $3p(^2P_{3/2})$ electron in the unfilled 4*s* shell followed by a super-Coster-Kronig decay is observed at 73.1 eV, in agreement with the previous observations.[5,6] We may also notice that at 73.1 eV the enhancement of the intensity is about 22% and only 12% in the total absorption curve. Our data, which provide the total Cu^+ yield, are compatible with the last photoemission study of atomic copper,[6] although the latter ones concern only the on-resonance intensity (24%) of the satellite relative to the 3*d* lines. This statement means that the autoionization process in the 3*d* main decay channels is very weak. The separation of the spin-orbit components $^2P_{3/2,1/2}$ (curve *b*, Fig. 2) is found to be 2 eV, which is at least 0.2 eV lower than the previously published values.[8,13]

(ii) Out of both resonances corresponding to the $3p \rightarrow 4s$ excitations, the Cu^+ ionic-yield curve shows a gradual decrease throughout the whole photon energy range 70–124 eV, in agreement with the variation[8] of the 3*d* cross section which represents the major contribution of single photoionization since the 4*s* cross section is negligible.

(iii) Between 80 and 85 eV we do not observe the bump clearly recognized in the photoabsorption curve *a* of Fig. 1. The Cu^{2+}/Cu^+ ratio displayed in curve *c* of Fig. 1 increases slightly within the 40–75-eV photon energy range while in the interval 75–81 eV the rate of increase is much larger. In the region 81–126 eV the Cu^{2+}/Cu^+ ratio is almost constant.

It is important to notice that the large enhancement of the Cu^{2+}/Cu^+ between 75 and 81 eV cannot be completely explained by the decrease in the Cu^+-ion signal since we observe, in the 77–80-eV interval, a corresponding enhancement in the Cu^{2+} curve (curve *c*) displayed in Fig. 2. This experimental finding suggests two possibilities.

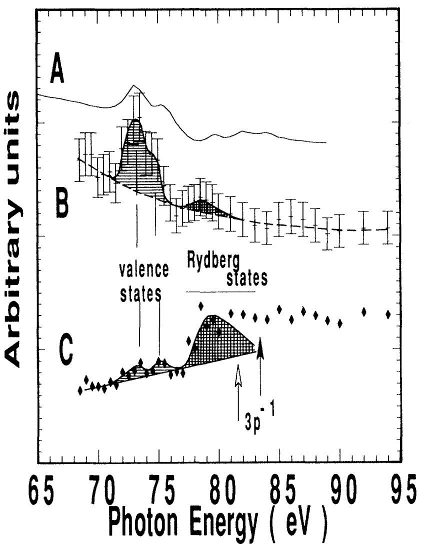

FIG. 2. Curve *a*: photoabsorption data (Ref. 8); curve *b*: Cu^+ cross section with 7% error bars; curve *c*: Cu^{2+} cross section. The solid curved line across the data guides the eye and gives an upper limit of the possible resonant shakeoff process. The arrows are as in Fig. 1, curve *c* (Ref. 14).

On one hand, the $3p^{-1}(^2P_{3/2})$ threshold is located around 77 eV. But this threshold energy would be too low in comparison with our 81.5-eV calculated[14] value. Our calculated $^2P_{3/2}$, $^2P_{1/2}$ threshold energies at, respectively, 81.5 and 83.6 eV can be compared to the 82.5- and 84.8-eV values previously reported in the literature[8] and we will not retain this explanation. Or, on the other hand, the enhancement of the Cu^{2+} cross section is due to the decay of both $3p^5 3d^{10} 4sns$ ($n \geq 5$) and $3p^5 3d^{10} 4snd$ ($n \geq 4$) series of excited neutral Rydberg states converging to the 3*p* thresholds. We do not observe resonant structures but a gradual unresolved increase of the Cu^{2+} yield because the experimental band pass used is large compared to the spacing of these excited states.

The notable feature of the results in Fig. 2 (curves *b* and *c*) is that the valence core excited states $3p^5(^2P)$-$3d^{10}4s^2$ of neutral copper preferentially decay to singly charged Cu^+ ions, whereas the Rydberg core excited states $3p^5(^2P)3d^{10}4sns(nd)$ mainly decay to doubly charged Cu^{2+} ions. According to these findings, we show in Fig. 3 the possible decay pathways of neutral Cu resonances. The Cu ($3p^5 3d^{10} 4s^2$) valence states mainly decay to singly charged ion states. The Rydberg states $3p^5 3d^{10} 4snl$ can decay through resonant spectator Auger transition into singly ionized states $3d^8 4snl$ that converge to the $3d^8 4s$ states of doubly charged ions. We have reported in Fig. 3 the respective positions of these levels, without being able to reproduce any precise assignment. Nevertheless, according to this diagram it is clear that the intermediate singly ionized states $3d^8 4snl$ may autoionize into the various continua $3d^9 \epsilon l''$, only a few (the highest ones) also being able to produce excited doubly charged ions $3d^8 4s$ of Cu^{2+}. An alternative decay to this two-step process lies in the direct production of Cu^{2+} ions through a resonant shakeoff process. Its existence and intensity have been discussed intensively in several papers[4,16,17] devoted to the decay of the $4d^9 nl$ Rydberg states below the 4*d* thresholds of xenon. In the case of xenon, the most recently published work[4] emphasizes the increase of the resonant shakeoff contribution as a function of *n* in contrast with a decrease of the two-step process. Further studies on copper, both theoretical and experimental (by using photoelectron spectroscopy), are necessary to disentangle the respective contribution of the resonant spectator Auger decay (followed by autoionization) and of the shakeoff process.

Such a preferential decay of core excited valence and Rydberg states is expected to exist in some other atoms and molecules, although it is generally less pronounced as in the case of atomic copper. In some cases such as closed-shell atoms (i.e., rare gases), where only Rydberg states exist, or 3*d* excited rubidium,[18] where transition to valence states are not allowed, this effect could not be observed. For the first series of transition metals (Mn, Fe, Co, and Ni) whose 3*d* subshell is at least half filled, the

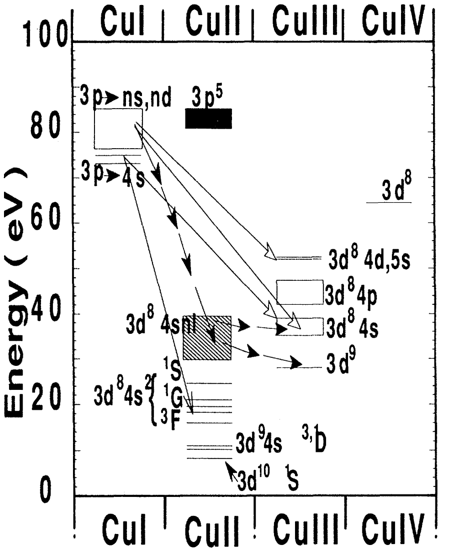

FIG. 3. Energy-level diagram of copper and its ions with excitation and decay paths of the $3p \rightarrow ns,nd$ resonances. The positions of the two neutral excited states $3p^5(^2P_{3/2,1/2})3d^{10}4s^2$ are obtained from the present work. In the Cu II spectrum the positions of the resonant satellites $3d^84s^2\,{}^3F,{}^1G,{}^1S$ are obtained from Ref. 6 and the $3d^84snl$ states lie inside the hatched rectangle, without any particular assignment for the various overlapping *LS* coupling terms. The black rectangle indicates the region of the calculated $3p$ thresholds (Ref. 14). In the Cu III and Cu IV spectra the levels are obtained from Moore (Ref. 15). The Cu III configurations $3d^9$, $3d^84s$, $3d^84p$, and $3d^85s,4d$ have numerous multiplet terms lying inside each of the empty rectangles. The solid arrows represent the resonant process observed in the photoemission experiments (Refs. 5–7). The dashed and the empty arrows show the main resonant two-step process and the resonant shakeoff process, respectively.

enhancement of the doubly-charged-ion yield below the $3p$ thresholds[19] may be related to the preferential decay of the $3p$ core excited Rydberg states. In molecules, this preferential decay effect is evidenced, for example, by the relative enhancement of the zero kinetic-energy electrons emitted by the $1s$ core excited Rydberg state of N_2 as compared to the $1s$ core excited valence states,[20] or by the valence versus Rydberg selectivity observed in the ion mass spectra of the $1s$ core excited N_2 (Refs. 1 and 21) and O_2.[22]

By studying this pronounced preferential decay of the $3p$ core excited Rydberg states of copper, the attention is focused on the shakeoff contribution to the total photoabsorption cross section above the $3p$ thresholds. Above 85 eV, the $3p$ holes decay via Super-Coster-Kronig process and consequently Cu^{2+} ions are detected. It is equivalent to say that the Cu^{2+} ionic yield is the sum of the double-photoionization cross section (shakeoff) plus the single photoionization in the $3p$ shell. On the other hand, Yeh and Lindau[23] report Hartree-Fock-Slater (HFS) calculations of the $3p$ photoionization cross section which undergoes a Cooper minimum above 100 eV. The $3p$ cross section $\sigma(3p)$ is almost flat between 100 and 120 eV but increases to reach a maximum value at 160 eV before decreasing monotonically again. In the 100–120-eV energy range the HFS model predicts the $\sigma(3p)$ to be about 10% of the $\sigma(3d) \approx \sigma(Cu^+)$. By simply combining this information with our measured Cu^{2+}/Cu^+ ratio around 100–120 eV (0.62, as shown in Fig. 1), we obtain a rough estimation of the shakeoff contribution in this photon energy range: i.e., $\sigma(\text{shakeoff}) \approx 0.62 \times \sigma(Cu^+) - 0.1 \times \sigma(Cu^+) \approx 0.5 \times \sigma(Cu^+)$. This result means that the shakeoff contribution is continuously increasing from the double-ionic thresholds, as it is suggested by the background line in the Cu^{2+} cross section shown in curve *c* of Fig. 2.

In conclusion, we have brought evidence of a specific decay of excited states of copper, below the $3p$ threshold. According to whether the excitation leads to a Rydberg or to a valence state (i.e., transition to an unfilled valence orbital), the final product is a doubly or a singly charged ion. Much further experimental and theoretical work is needed to understand in detail this effect which is especially pronounced in copper but may also exist in other atomic and molecular systems.

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