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Level structure of the $3d^94s6p$, $3d^94s4f$, $4d^95s7p$, and $4d^94s4f$ configurations in copper and silver

M. Aslam Baig,* A. Rashid, and M. Hanif
Atomic and Molecular Physics Laboratory, Department of Physics, Quaid-i-Azum University, Islamabad, Pakistan

W. Dussa, Ishaq Ahmad, and J. Hormes
Physikalisches Institut der Universität Bonn, Nussallee-12, D-5300 Bonn, Federal Republic of Germany

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High-resolution photoabsorption spectra of copper and silver are reported in the d-subshell excitation region that reveal well-resolved level structure for the $3d^94s6p$, $3d^94s4f$, $4d^95s7p$, and $4d^95s4f$ configurations. A consistent set of level assignments is suggested within the framework of the J_cK coupling scheme. The fine-structure splittings in the $4f$ excited levels are reported.

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High-resolution photoabsorption spectroscopy in conjunction with synchrotron radiation plays an important role in measuring weak structure, line shapes, and relative intensities of the spectral lines which might get obscured due to the presence of impurity lines in the continuum emitted by conventional light sources. This limitation of conventional light sources results, in some cases, in misleading identifications of the observed transitions. A controversial identification exists in the literature for some of the transitions in the d-subshell excitation spectra of silver [1,2]. Cantu *et al.* [2] recorded the spectra at a reciprocal dispersion of 2.78 Å/mm using a 3-m vacuum spectrograph, flash-pyrolysis technique for the silver vapors and Garton-type flash tube or BRV source as the background source of continuum, whereas Connerade and Baig [1] recorded the spectra at a reciprocal dispersion of 8.15 Å/mm using a 1-m spectrograph, an inductively heated furnace, and synchrotron radiation as a continuum. The data of Connerade and Baig [1], although taken at lower resolution, provided all of the nine expected electric dipole transitions in the $4d^95s5p$ configuration of silver. The identifications were also supported by the *ab initio* Hartree-Fock calculations. It was remarked that the level assignments for the $3d^94s5p$ configuration in copper given by Tondello [3] needed to be revised.

Subsequently, Heinzmann, Wolcke, and Kessler [4] investigated the autoionizing resonances in silver using a spin-polarization technique and confirmed the level assignments suggested by Connerade and Baig [1]. Recently, Müller, Schmidt, and Zimmermann [5] reinvestigated the photoionization spectra of silver and copper using an atomic beam and monochromated synchrotron radiation and again the identifications for the $4d^95s5p$ configuration suggested by Connerade and Baig [1] were adopted. These studies have established the identifications for the $4d^95s5p$ configuration in silver but the situation in copper remains unclear.

Recently, Baier *et al.* [6] reported the lifetimes and Stark mixing of the autoionizing states of copper in the configurations $3d^94s6s$ and $3d^94s4d$ using a combination of collisional and laser excitation. The autoionizing levels of $4d^94s(nl)$ $(nl=5p,6s,5d,7s,6d)$ configurations in silver have been studied by Baier *et al.* [7] by a combination of discharge and laser excitation.

In order to resolve the discrepancies and to provide a consistent interpretation for the d-subshell excitation spectra of copper and silver, we have reinvestigated the spectra at a much higher resolution and dispersion than available to the previous investigators [1–3]. This Brief Report deals with the leading members of the $d\rightarrow f$ transitions and the accompanied $d\rightarrow p$ transitions: the excited states $3d^94s(^3D_{3,2,1})6p$ and $4f$ and $4d^95s(^3D_{3,2,1})7p$ and $4f$ for copper and silver, respectively. All the expected electric dipole transitions within the framework of the J_cK coupling scheme have been observed and identified. The fine-structure splittings for the $4f$ excited states are reported.

The spectra were recorded using a 3-m spectrograph equipped with a 6000 lines/mm holographic grating and synchrotron radiation emitted by the 2.5-GeV electron accelerator as the background source of continuum. The reciprocal dispersion of the spectrograph was 0.51 Å/mm and a 15-μm slit width was used during the experiment. The absorption column was obtained by using an induction furnace some 40 cm long heated to 1700–2000 K. The heating element was a tantalum tube of 15-mm inner diameter, 0.2-mm wall thickness, and 40-cm length, inside which about 5 gm of spectroscopically pure copper or silver was loaded in a tungsten boat.

The spectra were photographed on Kodak SWR plates with exposure time ranging between 5 and 10 min. The absorption spectra of H_2 [8] and Kr [9] were used as reference wavelength standards. We used a third-order Chebychev polynomial fit (internal consistency ± 0.002 Å) to calculate the wavelengths. Other experimental details are the same as described in our previous papers [10–12].

The spectra recorded on the photographic plates were digitized with a computer-controlled microdensitometer. The transmission of the blackened photographic plate was measured in steps of 5 μm using a slit width of 10 μm at the photomultiplier. One photographic plate of 20-cm length covers a spectral range of roughly 120 Å. The digitized spectrum therefore consists of about 40 000 data points. As the response curve of the photographic emulsion is nonlinear, the plotted profile is not proportional to the absorption cross section. Relative intensities, however, are correct when lines on the same exposure are compared that lie on the linear part of the response curve.

The densitometric trace of the spectra of copper, 1259–1304 Å, and silver, 1053–1077 Å, are reproduced in Figs. 1 and 2, which show the level structure of the d-p and d-f transitions. The observed spectra show that the splitting between the substates formed by coupling a Rydberg electron to the d^9s ion core is much smaller than the splitting in the ionic states. Therefore, the J_cK coupling is more appropriate for the level designation. In this coupling scheme the orbital angular momenta of the core electrons are strongly coupled with the orbital angular momentum of the excited electron forming K quantum number. This K is then weakly coupled with the spin quantum number of the excited electron resulting in the total J quantum number. The levels are designated as $[\{(l_1s_1)j_c,l_2\}K,s_2]_J$. For the level assignments, the level structure is grouped according to the parent ion levels $(^3D_{3,2,1})$.

The lowest-lying levels are built on the $d^9s(^3D_3)$ parent ion configuration, which gives rise to one p, $[2]^0_{3/2}$, and three f, $[0]^0_{1/2}$, $[1]^0_{1/2,3/2}$, and $[2]^0_{3/2}$, levels allowed in the J_cK coupling and indeed one strongly autoionizing resonance and three sharp resonances are observed around 1300 Å in copper and around 1072 Å in silver. The levels of the investigated configurations $3d^94s6p$ and $3d^94s4f$ and $4d^95s7p$ and $4d^95s4f$ of copper and silver, respectively, lie above the first-ionization limit. By configuration interaction with the continuum states $\varepsilon p[1]^0_{1/2,3/2}$ caused by the Coulomb interaction, $d \rightarrow p$ levels can autoionize. The f levels are forbidden to autoionize because coupling of the $d^{10}(^1S_0)$ ionic state with an electron can produce only $\varepsilon p[1]_{1/2,3/2}$ continua. From the measurements of the linewidths of the $(^3D)4f$ transitions ($\Gamma = 5 \pm 2$ cm^{-1} and 3.5 ± 1.5 cm^{-1}) in copper and silver, we have estimated the lifetimes to be 6.6×10^{-12} and 9.5×10^{-12} sec, respectively. The shorter lifetime of these levels is consistent with the selection rules of autoionization, which show that the nf levels can autoionize by spin-orbit interaction.

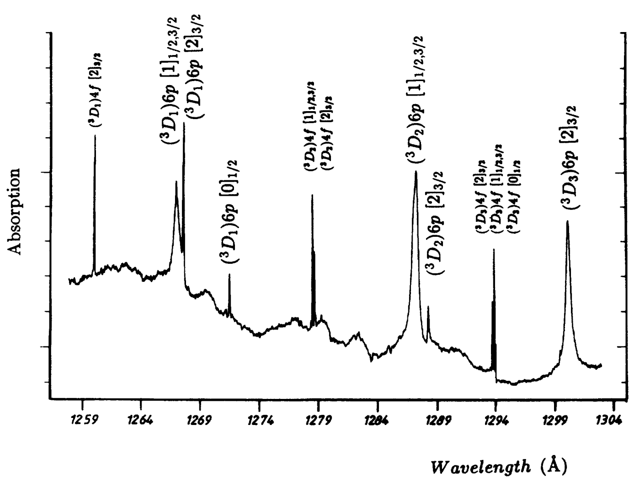

FIG. 1. Densitometric trace of the level structure of the $3d^94s(^3D_{3,2,1})6p$ and $3d^94s(^3D_{3,2,1})4f$ configurations in copper.

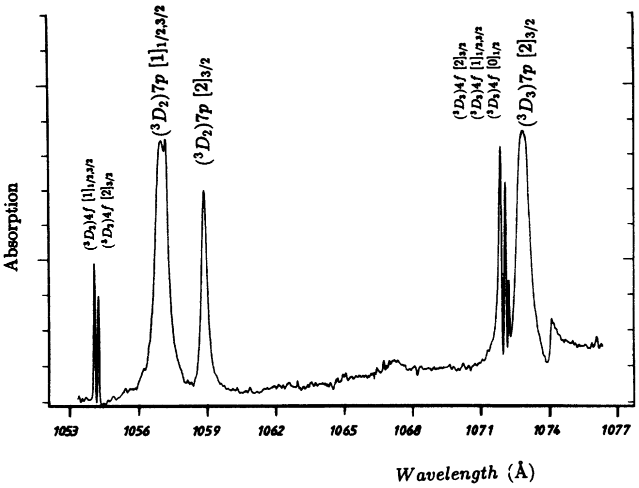

FIG. 2. Densitometric trace of the level structure of the $4d^95s(^3D_{3,2})7p$ and $4d^95s(^3D_{3,2})4f$ configurations in silver.

The np levels possessing $J = \frac{3}{2}$ show pronounced autoionization as compared to the $J = \frac{1}{2}$ levels, which in fact facilitates the J-value assignments.

The widths of the autoionizing resonances were extracted using Fano's [13] relation for an isolated autoionizing resonance:

$$\sigma = \sigma_a \frac{(\varepsilon + q)^2}{1 + \varepsilon^2} + \sigma_b ,$$

where σ_a is the part of the continuum that interacts with the discrete state, σ_b is the part that does not, and q is the line-shape parameter. The quantity ε describes an energy variable from the resonance energy E_R in units of the resonance width "Γ" of the autoionizing resonance:

$$\varepsilon = \frac{(E - E_R)}{\Gamma/2} .$$

The widths of the autoionizing resonance $3d^94s(^3D_3)6p[2]^0_{3/2}$ in copper is 27 ± 2 cm^{-1} (lifetime $\simeq 19 \times 10^{-14}$ sec), whereas the corresponding transition in silver $4d^95s(^3D_3)7p[2]^0_{3/2}$ has 42 ± 3 cm^{-1} full width at half maximum (lifetime 13×10^{-14} sec).

The next parent ion configuration $d^9s(^3D_2)$ possesses two p, $[1]^0_{1/2,3/2}$ and $[2]^0_{3/2}$, and two f, $[1]^0_{1/2,3/2}$ and $[2]^0_{3/2}$, levels provided that the K components are resolved. In copper the observed peak at 1288 Å can safely be assigned as $3d^94s(^3D_2)6p[2]^0_{3/2}$ and a strong peak at 1387 Å, which is a composite of two overlapping resonances, is assigned as $3d^94s(^3D_2)6p[1]^0_{1/2,3/2}$. An identical situation is present in the corresponding transitions in silver at 1057 and 1056 Å (see Fig. 2). The two J components corresponding to $np[1]^0_{1/2,3/2}$ levels in silver are about 19 cm^{-1} apart as compared to 14 cm^{-1} in copper.

The level structure built on the $(^3D_1)$ parent ion level contains three p levels: $[0]^0_{1/2}$, $[1]^0_{1/2,3/2}$, and $[2]^0_{3/2}$, and

TABLE I. Level structure of the $3d^94s(^3D_{3,2,1})\,6p$ and $4f$ configuration in Cu I.

Level assignments (J_cK coupling)	Wavelengths (Å)	Effective quantum numbers	Tondello's [3] assignments (LS coupling)
$(^3D_3)6p[2]^0_{3/2}$	1300.18	3.868	$(^3D_3)6p\ ^4P_{3/2}$
$4f[0]^0_{1/2}$	1293.98[a]	3.969	$(^3D_3)4f$
$[1]^0_{1/2,3/2}$	1293.875	3.971	
$[2]^0_{3/2}$	1293.719	3.974	
$(^3D_2)6p[2]^0_{3/2}$	1288.285[b]	3.815	$(^3D_2)4f$
$[1]^0_{1/2,3/2}$	1287.309	3.830	$(^3D_2)6p\ ^4P_{1/2}$
	1287.079[a]	3.833	
$4f[2]^0_{3/2}$	1278.625[a]	3.972	
$[1]^0_{1/2,3/2}$	1278.478[a]	3.975	
$(^3D_1)6p[0]^0_{1/2}$	1271.451[a]	3.784	
$[2]^0_{3/2}$	1267.542	3.845	$(^3D_1)6p\ ^4D_{1/2}$
$[1]^0_{1/2,3/2}$	1266.948	3.855	$(^3D_1)6p\ ^4P_{1/2}$
$4f[2]^0_{3/2}$	1259.999	3.973	$(^3D_1)4f$

[a] Absent from Tondello's [3] line list.

[b] We disagree with Tondello's assignment.

only one f level: $[2]^0_{3/2}$, and we have indeed observed these transitions. The two relatively sharp peaks around 1024 Å in Ag I and around 1266 Å in Cu I are interpreted as $np[0]^0_{1/2}$ and $[2]^0_{3/2}$ and the broad peak as $np[1]^0_{1/2,3/2}$, respectively. The very sharp peak at higher energy is assigned as the $4f[2]^0_{3/2}$ transition in copper and silver.

The effective quantum numbers for the $6p$ and $4f$ transitions in copper are 3.868 and 3.974, whereas for $7p$ and $4f$ transitions in silver are 3.943 and 3.967 (see Tables I and II). The quantum defects for the f electrons are nearly hydrogenic, which means that the f electrons are localized in the outer regions of the double-well potential for $l=3$ orbitals:

$$V_{\text{eff}}=V(r)+\frac{l(l+1)\hbar^2}{2mr^2}\ .$$

The *ab initio* Hartree-Fock calculations for the $3d^94snp$ ($n=4$, 5, and 6) and for the $4d^95snp$ ($n=5$, 6, and 7) configurations [14,15] show a sudden collapse of the exchange integral $G^1(sp)$. It is greater than the spin-orbit splitting of the nearly filled $3d$ and $4d$ subshells and drops from 24 188 to 2799 cm^{-1} for $n=4$ to $n=5$ and then to 992 cm^{-1} for $n=6$ in copper. In silver it drops from 30 236 to 3287 cm^{-1} and 1172 cm^{-1} for $n=5$, 6,

TABLE II. Level structure of the $4d^95s(^3D_{3,2,1})\,7p$ and $4f$ configuration in Ag I.

Level assignments (J_cK coupling)	Wavelengths (Å)	Effective quantum numbers	Cantu *et al.* [2] assignments (LS coupling)
$(^3D_3)7p[2]^0_{3/2}$	1072.77	3.943	$(^3D_3)7p\ ^4P_{3/2}$
$4f[0]^0_{1/2}$	1072.169	3.958	$(^3D_3)4f$
$[1]^0_{1/2,3/2}$	1072.018	3.962	$(^3D_3)4f$
$[2]^0_{3/2}$	1071.803[a]	3.967	
$(^3D_2)7p[2]^0_{3/2}$	1058.78[b]	3.851	$(^1D_2)6p\ ^2P_{1/2}$
$[1]^0_{3/2}$	1057.123	3.890	$(^3D_2)7p\ ^4P_{1/2}$
$[1]^0_{1/2}$	1056.914	3.895	$(^3D_2)7p\ ^2P_{1/2,3/2}$
$4f[2]^0_{3/2}$	1054.150	3.964	$(^3D_2)4f$
$[1]^0_{1/2,3/2}$	1053.974[b]	3.968	$(^1D_2)6p\ ^2D_{3/2}$
$(^3D_1)7p[0]^0_{1/2}$	1026.999	3.832	$(^3D_1)7p\ ^4F_{3/2}$
$[2]^0_{3/2}$	1026.499	3.844	$(^3D_1)7p\ ^4D_{3/2}$
$[1]^0_{1/2,3/2}$	1024.582	3.892	$(^3D_1)7p\ ^4D_{1/2}$
$4f[2]^0_{3/2}$	1021.751	3.967	$(^3D_1)4f$

[a] Absent from the line list of Cantu *et al.* [2].

[b] We disagree with the assignment of Cantu *et al.* [2].

and 7, respectively. These calculations suggest a change in coupling scheme with increasing n value and support our choice to use the J_cK coupling for the level designations.

In conclusion, the high-resolution photoabsorption data on the leading nf members and the accompanying np transitions demonstrate the importance of the J_cK coupling scheme for a consistent set of level assignments in copper and silver.

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[*] Also at the International Center for Theoretical Physics, Trieste, Italy.

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