Photoionization of atomic copper in the region of the 3*p* inner-shell thresholds

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Vacuum ultraviolet photoionization of atomic copper is studied within nonrelativistic *R*-matrix theory. Special care is taken to provide an adequate description of the Cu II target states by means of a configuration interaction method. Using the fact that the *R*-matrix method allows for an estimate of the relative importance of the $l=0$ and $l=2$ channels in the $3p\rightarrow n,\varepsilon l$ photoionization, a complete assignment of the experimental photoabsorption spectrum obtained by Bruhn *et al.* [J. Phys. B **12**, 203 (1979)] is provided. Finally, the coupling of the $3p$ excitations to the dominating spectator decay channels is considered with respect to the resonance line shapes. [S1050-2947(98)02510-4]

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I. INTRODUCTION

The *R*-matrix theory of atomic photoionization (Burke and Berrington [1], Berrington *et al.* [2]) is a powerful method for treating electron correlation in discrete states and coupling between continuum channels in a unified manner (Starace [3]). The energy region near the $3p$ inner-shell thresholds for the atoms of the iron series poses a particular challenge because many-electron effects are known to play the leading role (Sonntag and Zimmermann [4]). Formidable complexity arises from the partially filled $3d$ shell of these atoms and the photoionization process is exceedingly difficult to describe theoretically. In contrast, the theoretical approach is much simplified for closed $3d$ shell ground-state configurations and so the neighboring elements, Cu $3d^{10}4s$ (Liu *et al.* [5], Combet Farnoux [6], Zangwill and Soven [7], Davis and Feldkamp [8]) and Zn $3d^{10}4s^2$ (Stener and Decleva [9], Adam *et al.* [10], Fliflet and Kelly [11]) have received considerable attention.

However, despite such investigations, an experimental high-resolution absorption spectrum of atomic copper in the region of the $3p$ thresholds (Bruhn *et al.* [12]) has never been fully interpreted theoretically, in particular, the $3p\rightarrow ns,md$ resonant photoionization spectrum. In this work we improve upon earlier studies (Liu *et al.* [5], Combet Farnoux [6], Zangwill and Soven [7], Davis and Feldkamp [8]) by including higher series members up to $n=7$ and $m=5$ through the introduction of the dominating spectator Auger decay channels. Since these Rydberg resonances contribute significantly to the absorption close to the $3p$ thresholds (Bruhn *et al.* [12]), accounting for them in the calculations is crucial for a thorough understanding of the cross section. Particular emphasis in our investigation is to provide an estimate of the relative importance of the $3p\rightarrow md$ excitations and accounting for them requires the inclusion of a large number of $3p^64smd3d^8$ Cu II final states populated by super Coster-Kronig (SCK) decay. Previous calculations (Combet Farnoux [6], Zangwill and Soven [7], Davis and Feldkamp [8]) mainly concentrated on $3p\rightarrow 4s$ excitation. However, Davis and Feldkamp obtained one-electron estimates of the $3p\rightarrow 4d,5d$ oscillator strengths but did not provide partial cross sections whilst Liu *et al.* [5] presented a many-body perturbation theory (MBPT) calculation including $3p\rightarrow 4s$, $5s$, and $4d$ photoexcitations. They obtained a relatively large $4d$ excitation strength which, as we shall see, is in conflict with our results.

II. METHOD

The present calculation follows closely our previous studies on neutral chromium (Donnelly *et al.* [13]) and singly ionized chromium (Donnelly *et al.* [14]). The orbital basis set used to describe the singly ionized copper target states was based on tabulated nonrelativistic Hartree-Fock orbitals ($1s$, $2s$, $2p$, $3s$, $3p$, $3d$, and $4s$) (Clementi and Roetti [15]) of the Cu II $3s^23p^64s^23d^8\ ^3F$ state. [Note that the $3d^8$ configurations are of special interest since they are populated by the dominating $M_{23}M_{45}M_{45}$ SCK decay of the $3p$ core excited states (Bruhn *et al.* [16], Chandesris *et al.* [17]).] Additional orbitals ($ns,n=5,6,7$; $4p$; $md,m=4,5,6$) were then determined by optimization of the energy of specific states using the configuration-interaction code CIV3 (Hibbert [18]) to determine the optimum parameters c_{jnl} and ζ_{jnl} in the orbital radial function representation

$$P_{nl}(r)=\sum_{j=1}^{k} c_{jnl}\left[\frac{(2\zeta_{jnl})^{2I_{jnl}+1}}{(2I_{jnl})!}\right]^{1/2} r^{I_{jnl}}e^{-\zeta_{jnl}r}.$$

The $4d$ and $5d$ orbitals were obtained by optimizing the energies of the $4s4d3d^8\ ^1F$ and $4s5d3d^8\ ^1F$ states, respectively, while the $5s$, $6s$, and $7s$ orbitals were obtained by optimizing the energies of the $4s5s3d^8\ ^3F$, $4s6s3d^8\ ^3F$, and $4s7s3d^8\ ^3F$ states, respectively. The $3d$ Hartree-Fock orbital was incapable of accurately representing the Cu II ground state and so a $\overline{6d}$ corrector orbital was introduced by optimizing the energy of the Cu II ground state using the configurations $[3p^63d^{10}+3p^64d3d^9+3p^65d3d^9+3p^6\overline{6d}3d^9]\ ^1S$. Finally, a real $4p$ orbital was determined by optimization of the energy of the $3p^64p3d^9\ ^3P^o$ state. The resulting parameters for these additional orbitals are obtainable from the authors.

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TABLE I. Target states and energies relative to the $3p^6 3d^{10}\ ^1S$ ground state of Cu II compared with experimental values (Sugar and Musgrove [19], Schmidt *et al.* [20]).

Theoretical energy (a.u.)	Experimental energy (a.u.)	Target state
0.000 000	0.000 000	$3p^6 3d^{10}\ ^1S$
0.114 140	0.103 195	$3p^6 4s(3d^9\ ^2D)\ ^3D$
0.130 743	0.119 670	$3p^6 4s(3d^9\ ^2D)\ ^1D$
0.449 422	0.305 128	$3p^6 4p(3d^9\ ^2D)\ ^3P^o$
0.470 619	0.335 323	$3p^6 4p(3d^9\ ^2D)\ ^1P^o$
0.461 659	0.435 430	$3p^6 4s^2(3d^8\ ^1G)\ ^1G$
3.047 148	2.778 676	$3p^5 4s 3d^{10}\ ^3P^o$
3.062 335	2.778 676	$3p^5 4s 3d^{10}\ ^1P^o$

A set of 50 Cu II target states selected from states of the form $3p^6 3d^{10}$, $3p^6 4s 3d^9$, $3p^6 4p 3d^9$, $3p^6 4s n s 3d^8$ ($n=4-7$), $3p^6 4s n d 3d^8$ ($n=4,5$), and $3p^6 4p^2 3d^8$ were included in the *R*-matrix wave-function expansion (A detailed list of the states used including energy levels are available from the authors on request.) Each of these target states is represented by a configuration-interaction expansion where the electron correlation configurations used in the target wave-function expansion are generated by the addition of one electron from the above orbital set to the basis distributions $3p^6 3d^9$ and $3p^6 4s 3d^8$. In addition to the configurations generated in this manner, the $3p^6 4p^2 3d^8$ and $3p^5 4s 3d^{10}$ configurations were also included in order to allow for the strong mixing between the $4p^2$ and $4s4d$ configurations and the possibility of $3p \rightarrow \varepsilon l$ excitation from the copper ground state, respectively. A total of 272 configurations were thus used to represent the target states and the results indicate strong mixing in the $3d^8$ final ionic states, especially among the $4s4d$, $4s5d$, and $4p^2$ electron configurations. Theoretical energies are compared to the only available experimental data (Sugar and Musgrove [19]) in Table I. The agreement between experiment and theory is satisfactory for the purposes of our calculation.

The *R*-matrix codes were utilized with 59 continuum orbitals for each value of continuum electron orbital angular momentum $l \leqslant 7$ with an *R*-matrix radius of 42.5 a.u. The $(N+1)$-electron configurations (representing the total e^- + Cu II system) were generated by adding two electrons from the orbital basis set to the basis distributions $3p^6 3d^9$ and $3p^6 4s 3d^8$ and one electron from the basis set to the distributions $3p^6 4p^2 3d^8$ and $3p^5 4s 3d^{10}$. This approach ensures a ''balanced'' calculation in which the set of target correlation configurations is consistent with the set of $(N+1)$-electron configurations. We note that the photoionization energy to get from the ground state of Cu I to the ground state of Cu II was found to be 0.3066 a.u.

III. RESULTS AND DISCUSSION

Photoabsorption cross sections were then evaluated using the length formulation of the dipole matrix element. A free-electron-energy mesh of 2×10^{-3} a.u. was used. Due to the difference in both the energies of the $3p^5 4s 3d^{10}\ ^1P^o$ and $^3P^o$ target states obtained theoretically (caused by limitations in computer resources enforcing a lack of inclusion of correlation in the $3p^5$ core) compared to the (weighted average) energies obtained from the measured $M_{23}M_{45}M_{45}$ Auger spectrum (Schmidt *et al.* [20]) the overall position of the theoretical spectrum will differ from experiment. We have thus shifted the calculated spectrum by 7.92 eV so that the position of the first of these thresholds agrees with experiment.

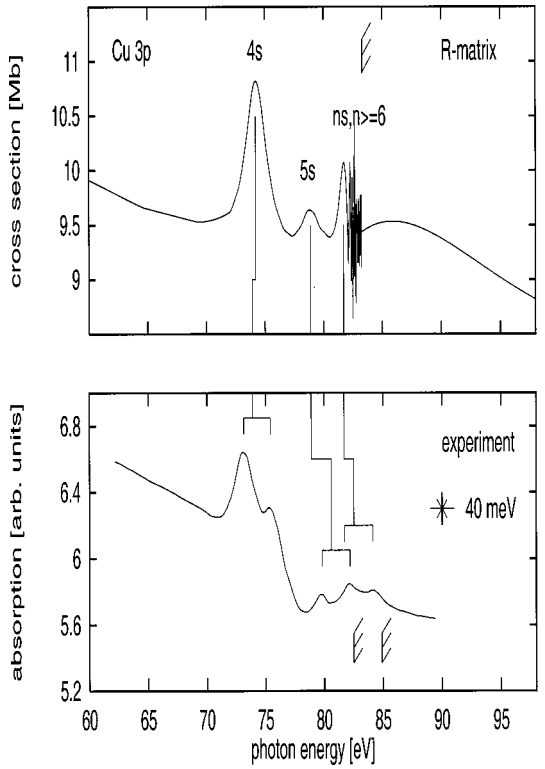

FIG. 1. Upper part: Total *R*-matrix cross section in the region of the $3p$ thresholds. Lower part: High-resolution photoabsorption spectrum recorded photographically (Bruhn *et al.* [12]).

The *R*-matrix total cross section is displayed in the upper part of Fig. 1. The dominating $3p \rightarrow 4s$ resonance at about 74 eV is accompanied by two smaller resonances at higher energies belonging to $3p \rightarrow 5s$ excitation and a superposition of $3p \rightarrow 6s, 7s, \ldots$ resonances. We note that the assignment given above is based on the total neglect of the *d*-type against the *s*-type $3p \rightarrow nl$ excitations. The justification for this approximation is provided later.

For comparison the measured photoabsorption spectrum (Bruhn *et al.* [12]) is displayed in the lower part of Fig. 1. The analysis of the spectrum is complicated by (i) the $3p$ core-hole lifetime width of about 2 eV and (ii) the spin-orbit splitting of the $3p$ hole of about 2.4 eV, resulting in very broad and strongly overlapping resonances. In comparison the splitting introduced by the coupling of the Rydberg electrons to the $3p$ hole is small and can be neglected. In order to account for the spin-orbit splitting of the $3p$ core hole in the calculated spectrum in an approximate way, we assume every resonance to be split into two lines, weighted $\frac{2}{3}:\frac{1}{3}$ and displaced by 2.4 eV from each other. In this way the dominating $3p \rightarrow 4s$ excitation is seen to be very well reproduced by the calculations concerning both the width of about 2 eV as well as the resonance strength relative to the underlying $3d$ continuum. The assignment of the smaller absorption

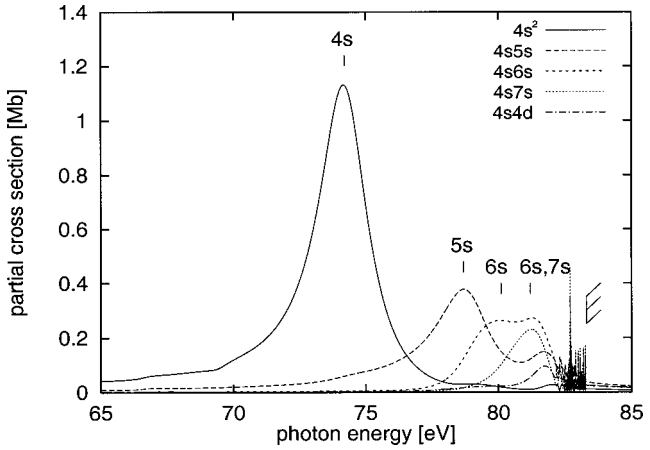

FIG. 2. Calculated partial cross sections belonging to the final ionic states $3p^6 4snl(3d^8\ ^1G)\ ^3G$ ($nl=4s,5s,6s,7s,4d$) of SCK decay of the $3p\rightarrow nl$ excitations.

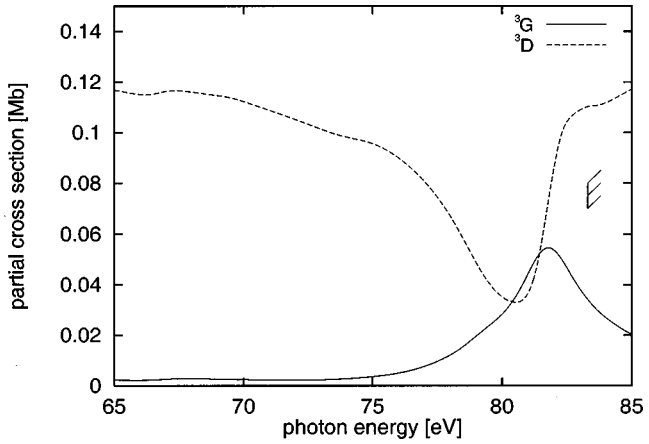

FIG. 3. Calculated $3p^6 4s4d(^3D)(3d^8\ ^1G)\ ^3L_{\rm ion}+\varepsilon l$ partial cross sections for $L_{\rm ion}=2$ and $L_{\rm ion}=4$ both displaying the $3p\rightarrow 4d$ resonance, but with very different line shapes. The cross sections have been convoluted with a Lorentzian of 2-eV width corresponding to the $3p$ core-hole lifetime in order to get rid of sharp structure near the threshold.

resonances at higher photon energies poses the main problem. By noting that the spacing between the $3p\rightarrow 5s$ and $3p\rightarrow ns$, $n\geqslant 6$, resonances in the *R*-matrix cross section coincides with the spin-orbit splitting, the threefold structure above the $3p\rightarrow 4s$ resonance in the absorption spectrum becomes plausible. We thus interpret the three small absorption resonances in the experimental spectrum at photon energies of (i) 79.80 eV, (ii) 82.13 eV, and (iii) 84.13 eV as mainly belonging to excitations (i) $3p_{3/2}\rightarrow 5s$, (ii) $3p_{1/2}\rightarrow 5s$ superimposed on $3p_{3/2}\rightarrow ns$, $n\geqslant 6$, and (iii) $3p_{1/2}\rightarrow ns$, $n\geqslant 6$. The assignment of the first of these is in agreement with the original publication (Bruhn *et al.* [12]) while an assignment of the higher resonances has not been previously given.

One brief remark concerns the sharp structure in the *R*-matrix cross section approaching the $^{1,3}P^o$ thresholds, which has no counterpart in the high-resolution ($\Delta E\approx 40$ meV) absorption spectrum. Perhaps the calculations have not taken full account of the SCK decay of these resonances. However, since the narrowness of these features implies a very small strength it is safe to ignore them in the present case. A similar consideration applies also to the $3p\rightarrow ns$, $n\geqslant 6$, resonances, which appear to be sharper and taller than the preceding $3p\rightarrow 5s$ resonance.

The foregoing analysis is based on the result that the contribution of the $3p\rightarrow n,\varepsilon s$ series strongly dominates over the $3p\rightarrow m,\varepsilon d$ series close to the $3p$ thresholds. This finding is illustrated in Fig. 2 where selected *R*-matrix partial cross sections belonging to the $3p^6 4sns(^3S)(3d^8\ ^1G)\ ^3G$ ($n=5,6,7$) and $3p^6 4s4d(^3D)(3d^8\ ^1G)\ ^3G$ final ionic states are presented. The $3p^6 4sns3d^8\varepsilon l$ cross sections are strongly enhanced by the $3p\rightarrow ns$ excitations followed by the dominating spectator decay. We note that the decay of the $3p\rightarrow 4s$ resonance is well studied both experimentally (Bruhn *et al.* [16], Chandesris *et al.* [17]) and theoretically (Liu *et al.* [5], Combet Farnoux [6], Zangwill and Soven [7], Davis and Feldkamp [8]). In comparison there is only a small enhancement of the corresponding partial cross section by the $3p\rightarrow 4d$ resonance. The evident dominance of the $3p\rightarrow ns$ channels below the threshold is explained by the delayed onset of the $3p\rightarrow m,\varepsilon d$ oscillator strength caused by the centrifugal barrier in the *d*-electron radial potential for nuclear charge $Z=29$ (Rau and Fano [21], Manson and Cooper [22]). Our results are in agreement with a one-electron calculation giving a relative oscillator strength $f_{3p\rightarrow 4d}/f_{3p\rightarrow 5s}$ of 17% (Davis and Feldkamp [8]). In contrast MBPT (Liu *et al.* [5]) predicts the Cu $3p\rightarrow 4d$ resonance to be nearly as strong as the $3p\rightarrow 5s$ resonance.

Finally let us briefly address the coupling of the $3p$ resonances to the dominating spectator satellite channels. To begin with the $3p\rightarrow ns$ excitations, as we have seen their SCK decay strongly *enhances* the corresponding partial cross sections, which, however, are very small off-resonance (see Fig. 2) because the $3p^6 3d^{10}4s\rightarrow 3p^6 3d^8 4sns\varepsilon l$ satellite process corresponds to $3d\rightarrow ns$ quadrupole shakeup. For the same reason the line shape of the $3p\rightarrow 4s$ resonance for example is seen (Fig. 2) to be almost symmetric. [Combet Farnoux [6,23] stressed that even the small asymmetry of the $3p\rightarrow 4s$ resonance (Fig. 2) is not due to interference with the shakeup channel but to final state coupling to the $3d$ continuum.] In contrast the $3p\rightarrow md$ excitations may lead to pronounced *suppression* (through spectral repulsion) of the corresponding partial cross sections, which may have appreciable strength even far from any resonance since $3p^6 3d^{10}4s\rightarrow 3p^6 3d^8 4smd\varepsilon l$ ionization constitutes $3d\rightarrow md$ monopole shakeup. Such behavior is seen for the $3p^6 4s4d(^3D)(3d^8\ ^1G)\ ^3D+\varepsilon l$ cross section displayed in Fig. 3. Here we want to stress that $3d\rightarrow md$ shakeup is appreciable only if the orbital angular momentum coupling of the *md* shakeup electron to the $3d^8$ shell of the ion core is not changed during shakeup, which implies $L_{\rm ion}=2$ in the final ionic state. Indeed, the $3p^6 4s4d(^3D)(3d^8\ ^1G)\ ^3G+\varepsilon l$ cross section where the $4d$ and $3d^8$ electrons recouple to $L_{\rm ion}=4$ is seen (Fig. 3) to be negligibly small well below resonance, resulting again in resonant enhancement of the cross section. We note that experimental verification of the given example by means of photoelectron spectroscopy may prove to be difficult because in addition to the small cross section, the final state splitting is of the order of 100 meV since the coupling of the $4s4d$ Rydberg electrons to the $3d^8$ core is weak and as a consequence high resolution would be necessary in any such experiment.

In conclusion, we have demonstrated that a proper description of the complex near-threshold $3p$ spectrum of atomic Cu mainly involves the *ns* resonance series, as well as a large number of final states populated by a super Coster-Kronig decay of the core excited state. The *nd* series, on the other hand, is weak. Here we have disentangled a peculiar dependence of the corresponding SCK partial cross section on the coupling of the *nd* electron to the $3d^8$ core that deserves further investigation. From the theoretical point of view the next step forward could be an *ab initio* treatment of the comparatively large spin-orbit splitting of the $3p$ hole in a fully relativistic calculation; such a calculation, however, presents a formidable challenge at the present time. Furthermore, our calculations indicate that, especially in the present case of broad and strongly overlapping resonances, a measurement of the total cross section does not provide enough information, but partial cross sections are needed that can be extracted by means of photoelectron spectroscopy. Up to now such partial cross sections have been measured only for the dominating $3p \rightarrow 4s$ resonance (Bruhn *et al.* [16], Chandesris *et al.* [17]). Therefore an extension of such measurements to the region of the higher resonances is very desirable for a detailed comparison with theory. On the basis of the calculated energies of the final ionic states we expect that photoelectron satellites at high binding energies (30 eV and more) above the ground state are populated by the decay of the higher resonances. This binding energy region has not been covered by earlier experiments (Bruhn *et al.* [16], Chandesris *et al.* [17]). In fact, for the neighboring element zinc (atomic charge $Z=30$) a strong enhancement of analogous satellites, at binding energies greater than 40 eV, upon excitation in the $3p_{3/2} \rightarrow 5s$ resonances has already been observed (Adam *et al.* [10]).

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