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Multiple ionization of copper by electron impact

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Abstract. A pulsed crossed beam technique previously developed in this laboratory has been used to study the electron impact ionization of copper. Previous measurements have been very limited in scope and exhibit large discrepancies. Relative cross sections σ_n for the formation of 1 to 5 times ionized copper have been measured with high accuracy within the range 7.8–2100 eV. Individual cross sections have been obtained by normalization to absolute values of σ_2 obtained by Freund *et al* at energies below 200 eV using a fast crossed beam technique. Weak structures in σ_1 can be attributed to Auger decay processes following the creation of 3s subshell and L shell vacancies but there is a lack of other pronounced structures in σ_n for $n>1$ where many close-lying subshell vacancies are involved. At 2100 eV cross sections σ_5 are less than three orders of magnitude smaller than σ_1.

1. Introduction

In this laboratory (Shah *et al* 1987) we developed a crossed beam technique incorporating time-of-flight spectroscopy to study multiple ionization of atoms by electron impact over a wide energy range. In this method a pulsed beam of electrons is arranged to intersect a thermal energy beam of ground state atoms and, unlike most previous methods, ionization takes place in the absence of external electric or magnetic fields. Immediately after the transit of each pulse of electrons through the target atom beam, a pulsed electrostatic field is applied to extract product ions with high and equal efficiency prior to time-of-flight analysis and counting by a particle multiplier.

The method was originally developed for studies of the ionization of atomic hydrogen over a wide energy range but we have also used it successfully for studies of the multiple ionization of stable gas atoms (Shah *et al* 1988, McCallion *et al* 1992a) where the results of other methods sometimes exhibit large discrepancies. By the use of a specially developed high temperature oven source we have also started to apply this method to studies of the multiple ionization of metallic species (McCallion *et al* 1992b, Shah *et al* 1993). Although many metallic species are important in fusion energy research and astrophysical applications, existing data are often sparse and of a limited accuracy.

In the present work we have used the same experimental approach to study

$$e + Cu \rightarrow e + Cu^{n+} + ne \qquad (1)$$

and obtained data for cross sections σ_n for $n=1$ to 5 at impact energies ranging from near threshold to 2100 eV. Previous experimental measurements have been very limited in scope and exhibit large discrepancies. The measurements by Pavlov *et al* (1967) and

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Schroeer *et al* (1973) using crossed beam techniques provided only 'apparent' total cross sections $\Sigma n\sigma_n$ (based on measurements of the total slow ion product current) for energies up to 150 eV and 250 eV respectively. Measurements by Crawford (1968), which incorporated a mass spectrometer into a crossed beam arrangement, provided both total cross sections and cross sections σ_1 and σ_2 for impact energies up to 850 eV. In the most recent measurements by Freund *et al* (1990), a fast crossed beam technique was used to obtain cross sections σ_1 and σ_2 for energies up to 200 eV. In these measurements the electron beam was crossed with a 3 keV beam of Cu atoms prepared by charge transfer neutralization in a gas target. Measurement of the fractional yield of Cu^{n+} ions from a region where the collision volume and density profiles are well defined, then allowed absolute cross sections to be determined. Values of σ_1 and σ_2 measured by Freund *et al* (1990) exhibit a different energy dependence and differ substantially in magnitude from those obtained by Crawford (1968). While the fast crossed beam technique used by Freund *et al* (1990) is believed to be the most reliable, their measurements with Cu, in common with some other target species investigated, exhibit evidence of significant ionization below the σ_1 threshold energy. This indicates that their Cu beams contained a substantial admixture of metastable species. The effect of this unknown admixture on the measured cross sections is impossible to assess.

The use of ground state thermal energy Cu beams in the present measurements obviates the problem of metastable contamination inherent in the fast crossed beam method used by Freund *et al* (1990). However, absolute cross section determination is much more difficult mainly because of the difficulty in accurately determining the absolute flux of the Cu beam. Methods based on the condensation technique previously used by Pavlov *et al* (1967), Schroeer *et al* (1973) and Crawford (1968) involve assumptions which are difficult to accurately justify. For this reason, our measurements have been limited to an accurate determination of the relative cross sections σ_n for $n=1$ to 5. However, as in the case of our recent measurements on Fe (Shah *et al* 1993), we have suggested that normalization of our data to the absolute values of σ_2 measured by Freund *et al* (1990) is a reasonable procedure.

2. Experimental approach

2.1. General description

A detailed description of the crossed beam apparatus and the measurement procedure has been given previously (Shah *et al* 1987, McCallion *et al* 1992b) so that only a summary of the essential features is necessary here.

The electron gun provided pulses of 200 ns duration at a repetition rate of about 10^5 pulses/s (equivalent to between 1 and 3 nA in the continuous mode) with very small angular divergence. The electron beam intersected at 90° the beam of Cu atoms effusing from an oven source (Shah *et al* 1993). The crossed beam region was differentially pumped and maintained at a pressure of about 5×10^{-8} torr.

In the interaction region the electron beam had a diameter not exceeding 2 mm while the Cu beam was 6×6 mm^2. As in our previous work careful checks were made to ensure that the effective collision volume was insensitive to the point of intersection of the two beams.

The electron beam current was recorded by a screened Faraday cup located beyond the crossed beam region. A continuous indication of the Cu atom beam intensity was obtained by the use of a simple pulsed electron gun operating at 30 eV. The beam from this gun was arranged to intersect the Cu beam at a point beyond the main crossed beam region and the resulting Cu^+ product signal recorded by a channeltron was used to monitor the Cu atom beam flux.

As in our previous work, product Cu^{n+} ions were extracted from the crossed beam region, accelerated through a potential difference of 5 kV then identified and distinguished from background gas product ions by their different times of flight to a particle multiplier operated as a single particle counter. It was important to ensure that Cu^{n+} ions were extracted with high and equal efficiency independent of the primary beam energy. A pulsed extraction field of 15 V cm^{-1} applied between two high transparency grids on either side of the crossed beam region was found to be sufficient to ensure complete collection. This extraction field was subject to a variable delay which could be adjusted according to the transit time of the trailing edge of the electron pulse through the target beam (Shah *et al* 1987).

A time-to-amplitude converter operating with start pulses from the extraction field pulse generator and stop pulses from the particle multiplier provided time-of-flight

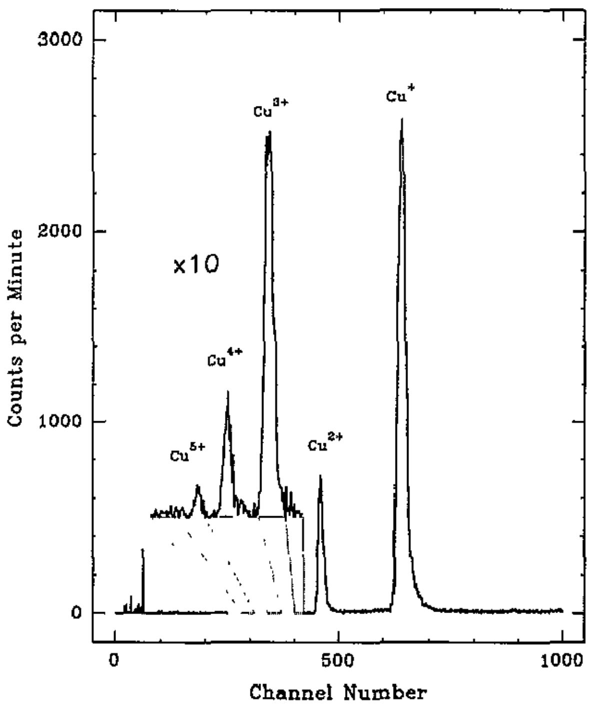

Figure 1. Time-of-flight spectrum showing Cu^{n+} product ions formed in collisions of 1600 eV electrons with Cu atoms.

spectra of the type shown in figure 1 in which the separate Cu^{n+} ion products for up to $n=5$ could be discerned. No attempt was made to separate the 69% abundant ^{63}Cu isotope from the 31% abundant ^{65}Cu isotope.

2.2. *Cross section measurements and normalization*

Measurements were made for electron impact energies ranging from 7.8 eV to 2100 eV. As in our previous work, a small correction was applied to the indicated electron energy to allow for the effect of contact potentials and filament misalignment in the electron gun. This was determined from a linear extrapolation of the observed Cu^+ yield to the known threshold energy of 7.72 eV for single ionization. Although no specific claim is made for the energy spread of our electron beam, an indication that this was small was provided by the very small observed signals below threshold (cf Shah *et al* 1987). At each particular electron energy the Cu^+, Cu^{2+}, Cu^{3+}, Cu^{4+} and Cu^{5+} yields were determined from the average of several measurements of the area of the appropriate peak in the time-of-flight spectrum. Cross sections σ_n were then determined from the expression.

$$\sigma_n = S_n / k\mu \tag{2}$$

where S_n is the Cu^{n+} yield per unit electron beam intensity and μ is the effective target thickness of the Cu atoms. The constant k is the overall detection efficiency of the Cu^{n+} ions which, on the basis of checks of the type described previously (cf Shah *et al* 1993) was believed to be independent of n.

Relative cross sections σ_n for different values of n could be determined with an estimated accuracy within ±5%. However, in order to determine absolute values from equation (2) it is necessary to be able to determine $k\mu$. In our previous studies of the multiple ionization of Mg (McCallion *et al* 1992b) we effectively determined $k\mu$ by normalizing our relative values of σ_1 to the absolute values measured by Freund *et al* (1990) using the fast crossed beam technique in an overlapping energy range. However, as noted earlier, the σ_1 measurements of Freund *et al* (1990) for Cu exhibit evidence of distortion due to the presence of metastable atoms in their target beams. For this reason, as in the case of our recent measurements on Fe (Shah *et al* 1993), we have normalized the present relative cross sections to the σ_2 rather than the σ_1 values measured by Freund *et al* (1990) for energies up to 200 eV. It seems likely that, as in the case of Fe (Jacobs *et al* 1980), Cu^{2+} production will be dominated by Auger processes resulting from cascade decay of a single vacancy in the *nl* subshells. The values of σ_2 measured by Freund *et al* (1990) should therefore be much less susceptible to the influence of metastable atoms than their measurements of σ_1. The excellent agreement in energy dependence between their values and the present values of σ_2 (see section 3) provides further support for this view.

3. Results and discussion

Figure 2 shows our measured cross sections σ_n for $n=1$ to 5 normalized in the way described by fitting our relative cross sections σ_2 to the low energy absolute values of σ_2 measured by Freund *et al* (1990). As a result, the values of σ_1 measured by Freund *et al* (1990) are about 15% larger than our values at 200 eV and the difference becomes progressively larger as the impact energy decreases in a way that is consistent with the presence of metastable atoms in their Cu beam.

Individual values of σ_n for $n=1$ to 5 are shown in table 1 together with estimated uncertainties assessed at the 67% confidence level which reflect the degree of reproducibility of the measurements in terms of the experimental parameters and statistical fluctuations. The absolute accuracy of our cross sections depends on the validity of our normalization procedure and the accuracy of the values of σ_2 measured by Freund *et al* (1990) but cannot be better than ±14%.

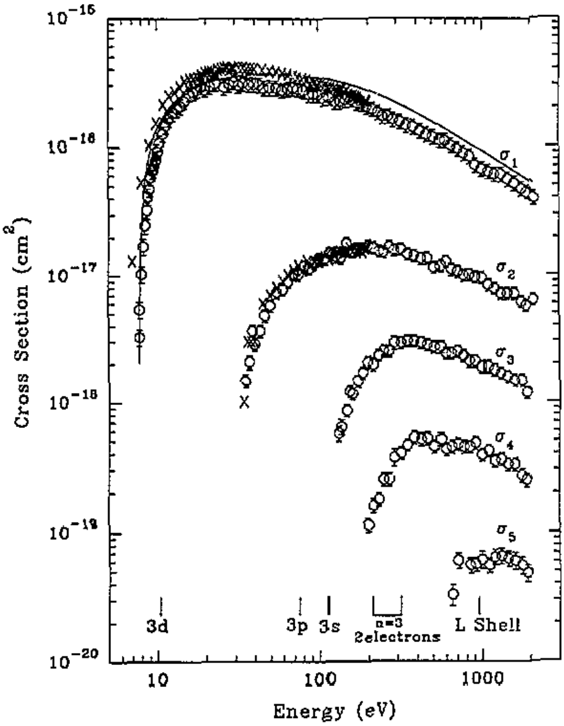

Figure 2. Cross sections σ_n for n times ionization of copper by electrons. O, $\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5$, present data; ×, σ_1, σ_2, Freund *et al* (1990); —, σ_1, Lotz (1970) empirical formula.

Cross sections σ_1 measured by Crawford (1968) in the range 45-850 eV attain a peak value of 3.4×10^{-16} cm^2 at 80 eV whereas the corresponding values measured by Freund *et al* (1990) attain a peak value of 4.1×10^{-16} cm^2 at a markedly different energy of 30 eV. In the case of σ_2, values measured by Crawford (1968) attain a peak value of 6.7×10^{-17} cm^2 at 140 eV and differ considerably from the peak value of 1.6×10^{-17} cm^2 observed at 200 eV by Freund *et al* (1990). These large discrepancies must reflect the quite different experimental arrangement used by Crawford (1968) to collect and analyse the products of ionization. In particular, the presence of an electric field in the collision region is a potential problem for accurate measurements at low electron impact energies. In this context, it is also worth noting that cross sections $\Sigma n\sigma_n \simeq \sigma_1$ measured by Pavlov *et al* (1967) at energies from threshold to 150 eV and by Schroeer *et al* (1973) at energies from 40 eV to 250 eV are also markedly different in both magnitude and energy dependence. Cross sections measured by Pavlov *et al* (1967) attain a peak value of 3.1×10^{-16} cm^2 at 29 eV while those obtained by Schroeer *et al* (1973) attain a peak value of 7.7×10^{-16} cm^2 at 100 eV. The measurements of Freund *et al* (1990) are considered to be the most reliable of the previous measurements and only these are included for comparison in figure 2.

As in the case of our previous results for Fe, cross sections σ_n for Cu can be seen to attain peak values at progressively higher energies as n increases. At our high energy 2100 eV limit, cross sections decrease by less than an order of magnitude as n increases. Indeed, at 2100 eV σ_5 is only three orders of magnitude smaller than σ_1, a result

Table 1. Cross sections σ_n for the production of n times ionized iron by electron impact.

Energy (eV)	σ_1 (10^{-16} cm^2)	σ_2 (10^{-17} cm^2)	σ_3 (10^{-18} cm^2)	σ_4 (10^{-19} cm^2)	σ_5 (10^{-20} cm^2)
7.8	0.06 ± 0.01				
8.0	0.11 ± 0.02				
8.2	0.17 ± 0.03				
8.4	0.25 ± 0.04				
8.6	0.33 ± 0.05				
8.8	0.42 ± 0.06				
9.0	0.48 ± 0.06				
9.2	0.59 ± 0.08				
9.4	0.67 ± 0.09				
9.5	0.68 ± 0.09				
9.6	0.73 ± 0.10				
9.8	0.79 ± 0.10				
9.9	0.82 ± 0.11				
10.1	0.93 ± 0.12				
10.5	1.09 ± 0.14				
11.0	1.28 ± 0.17				
11.5	1.48 ± 0.20				
12.0	1.66 ± 0.22				
12.7	1.83 ± 0.24				
13.5	1.98 ± 0.26				
14.2	2.07 ± 0.28				
15.0	2.28 ± 0.30				
16.0	2.61 ± 0.33				
17.0	2.66 ± 0.34				
18.0	2.77 ± 0.35				
19.0	2.92 ± 0.37				
20.0	2.80 ± 0.36				
21.5	2.95 ± 0.37				
23.0	3.12 ± 0.40				
26.0	2.93 ± 0.37				
28.0	3.08 ± 0.39				
30.0	3.21 ± 0.41				
32.0	3.02 ± 0.38				
34.0	3.13 ± 0.40				
35.0		0.15 ± 0.02			
37.0	3.08 ± 0.39	0.21 ± 0.03			
38.5		0.37 ± 0.04			
40	3.08 ± 0.39	0.29 ± 0.03			
43	3.04 ± 0.39	0.37 ± 0.04			
46	2.88 ± 0.37	0.49 ± 0.05			
50	2.90 ± 0.37	0.59 ± 0.07			
55	2.89 ± 0.37	0.75 ± 0.08			
60	2.77 ± 0.35	0.79 ± 0.09			
65	2.83 ± 0.36	0.91 ± 0.10			
70	2.89 ± 0.37	1.05 ± 0.12			
75	2.84 ± 0.36	1.04 ± 0.11			
81	2.76 ± 0.35	1.21 ± 0.13			
88	2.58 ± 0.33	1.16 ± 0.13			
94	2.58 ± 0.33	1.27 ± 0.14			
100	2.55 ± 0.32	1.37 ± 0.15			
108	2.39 ± 0.30	1.35 ± 0.15			
117	2.41 ± 0.31	1.49 ± 0.16			
126	2.25 ± 0.29	1.40 ± 0.15			
131			0.57 ± 0.08		

Table 1. (continued)

Energy (eV)	σ_1 (10^{-16} cm^2)	σ_2 (10^{-17} cm^2)	σ_3 (10^{-18} cm^2)	σ_4 (10^{-19} cm^2)	σ_5 (10^{-20} cm^2)
136	2.25±0.29	1.37±0.15	0.64±0.09		
147	2.32±0.29	1.78±0.19	0.86±0.10		
153			1.22±0.13		
159	2.33±0.30	1.54±0.17	1.17±0.13		
172	2.21±0.28	1.60±0.17	1.47±0.16		
186	2.15±0.27	1.62±0.17	1.71±0.19	0.055±0.008	
200	2.05±0.26	1.69±0.18	2.04±0.22	0.11±0.01	
216	1.94±0.25	1.63±0.18	1.96±0.21	0.16±0.02	
233	1.84±0.23	1.54±0.17	2.28±0.25	0.18±0.02	
250	1.72±0.22	1.52±0.16	2.49±0.27	0.25±0.03	
270	1.72±0.22	1.67±0.18	2.50±0.27	0.25±0.03	
290	1.63±0.21	1.58±0.17	2.87±0.33	0.37±0.06	
320	1.57±0.20	1.60±0.17	2.86±0.31	0.40±0.04	
350	1.47±0.19	1.46±0.16	3.04±0.33	0.46±0.05	
385	1.43±0.18	1.42±0.15	3.00±0.33	0.53±0.06	
425	1.33±0.17	1.35±0.15	2.91±0.32	0.51±0.06	
465	1.25±0.16	1.36±0.15	2.77±0.30	0.52±0.06	
510	1.20±0.15	1.15±0.12	2.70±0.29	0.45±0.05	
560	1.13±0.14	1.18±0.13	2.70±0.29	0.51±0.06	
600	1.12±0.14	1.28±0.14	2.44±0.27	0.43±0.05	
650	1.03±0.13	1.11±0.12	2.40±0.26	0.45±0.05	3.3±0.6
710	0.97±0.12	1.07±0.12	2.45±0.26	0.47±0.05	6.1±0.8
770	0.90±0.11	1.00±0.11	2.30±0.25	0.45±0.05	
840	0.85±0.11	1.01±0.11	2.07±0.22	0.45±0.05	5.6±0.7
910	0.73±0.09	0.97±0.11	2.11±0.23	0.48±0.05	5.7±0.7
1000	0.68±0.09	0.96±0.10	1.94±0.21	0.39±0.04	6.2±0.9
1100	0.65±0.08	0.85±0.09	1.93±0.21	0.42±0.05	5.6±0.7
1200	0.62±0.08	0.79±0.09	1.81±0.20	0.35±0.04	6.5±0.8
1320	0.62±0.08	0.72±0.08	1.66±0.18	0.36±0.04	6.6±0.9
1450	0.57±0.07	0.72±0.08	1.59±0.17	0.33±0.04	6.3±0.9
1600	0.53±0.07	0.72±0.08	1.50±0.16	0.33±0.04	6.1±0.9
1775	0.48±0.06	0.62±0.07	1.47±0.16	0.27±0.03	5.6±0.8
1900	0.45±0.06	0.58±0.06	1.25±0.14	0.25±0.03	4.9±0.7
2100	0.40±0.05	0.64±0.07			

which indicates the strong influence of Auger decay processes in multiple ionization. At 1000 eV total cross sections for Cu, Fe and Ar (Shah *et al* 1993, McCallion *et al* 1992b) have the not greatly different values of 0.78×10^{-16} cm^2, 0.73×10^{-16} cm^2 and 0.81×10^{-16} cm^2 respectively. The corresponding respective ratios of σ_3/σ_2 are 0.20, 0.27 and 0.20 and of σ_4/σ_2 are 0.041, 0.059 and 0.045. These not greatly different ratios indicate that multiple ionization is determined primarily by Auger processes with similar branching ratios following the creation of inner shell vacancies.

Threshold energies for removal of one of the 3s, 3p or an L shell electron (Henke *et al* 1982) or the 3d electron (estimated from Moore 1970) are included in figure 2. Also shown is a narrow band of threshold energies between 210 eV and 315 eV calculated by Koike (1993) for double ionization of two $n=3$ electrons. This assumes removal of either two 3s electrons, one 3s plus one 3p electron or two 3p electrons. Weak structures in σ_1 around 160 eV and 1300 eV indicate extra contributions arising from 3s subshell and L shell vacancies respectively. However the lack of pronounced structures in σ_n for $n>1$ (unlike our results for Fe) seems likely to reflect blurring out effects resulting from contributions arising from the creation of many close lying subshell vacancies. The comparatively flat maximum in σ_1 may also reflect contributions arising from removal of any one of the ten 3d electrons in Cu.

There have been no detailed theoretical studies of the ionization of Cu by electron impact. However, included in figure 2 are predictions of σ_1 based on the well known Lotz (1970) empirical formula. This includes only direct ionization and provides no estimate of contributions arising through autoionization. Although at high energies the predicted values can be seen to be too large, they are in reasonable accord with our experimental values over the full energy range. These values from Lotz (1970) are in much better accord with experiment than values based on an earlier prediction by Lotz (1969).

4. Conclusions

Previous experimental studies of the ionization of copper have been very limited in scope and exhibit large discrepancies. The present measurements of σ_n for $n=1$ to 5 which range from near threshold to 2100 eV are of high relative accuracy. The fast crossed beam technique previously used by Freund *et al* (1990) is considered to be inherently reliable but subject to some uncertainties in this case, due to the presence of metastable atoms in their target beams. However normalization of our data to the σ_2 rather than the σ_1 values of Freund *et al* (1990) is believed to minimize such uncertainties.

The absence of clearly defined structure in cross sections σ_n for $n>1$ unlike our previous measurements for Fe is believed to indicate that many close lying subshell vacancies are involved in the multiple ionization process.

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