J. Phys. B: At. Mol. Phys. **18** (1985) 3011-3016. Printed in Great Britain

Electron impact double ionisation of Ar^{+} and Ar^{4+} ions†

A Müller‡, K Tinschert‡, C Achenbach‡‖, R Becker§ and E Salzborn‡

‡ Institut für Kernphysik, Universität Giessen, D-6300 Giessen, West Germany

§ Institut für Angewandte Physik, Universität Frankfurt, D-6000 Frankfurt, West Germany

Received 17 December 1984

Abstract. Employing an improved crossed-beams technique described in the preceding paper, cross sections $\sigma_{q,q+2}$ for electron impact double ionisation of Ar^{q+} ions ($q = 1$ and $q = 4$) were measured for electron energies from threshold to about 700 eV. The improved experimental accuracy allowed contributions of L-shell ionisation-autoionisation to $\sigma_{1,3}$ to be identified for Ar^{+}. With increasing q the relative importance of the L-shell contribution to $\sigma_{q,q+2}$ strongly increases. As a result the cross section $\sigma_{4,6}$ for Ar^{4+} is by far dominated by the L-shell contribution at energies above 350 eV. Calculations on the basis of semi-empirical and semiclassical theories are made to compare the relative strengths of direct double ionisation and inner-shell ionisation with subsequent electron emission.

1. Introduction

Electron impact multiple ionisation of multiply charged ions was first studied experimentally by Müller and Frodl (1980). In this investigation of Ar^{q+} ions ($q = 1, 2, 3$) contributions to the multiple ionisation cross section were identified resulting from two-step processes in which the ionisation of an L-shell electron is followed by various electron rearrangement processes leading to the ejection of additional electrons. The relative probabilities of these indirect processes were found to increase with increasing ion charge state q and with increasing number of electrons removed in a single electron impact.

Because of limited accuracy it was not possible in that experiment to see the expected L-shell effect on the cross section $\sigma_{1,3}$ and it was not possible to make a measurement for double ionisation of Ar^{4+} ions. However, with our improved experimental technique the cross sections $\sigma_{1,3}$ and $\sigma_{4,6}$ for Ar^{+} and Ar^{4+} ions, respectively, could be measured absolutely with good precision. In both cases the contributions of the L shell can be clearly identified. The cross sections $\sigma_{4,6}$ for Ar^{4+} are in agreement with recently published data of Pindzola *et al* (1984).

2. Experimental technique

The new experimental technique described in detail in the preceding paper (Müller *et al* 1985) was used for the present measurements. Briefly, a magnetically analysed beam of 10 keV Ar^{+} or 40 keV Ar^{4+} ions is passed through an electron gun which can be

† Work supported by Deutsche Forschungsgemeinschaft.

‖ Present address: Daimler-Benz AG, Stuttgart, West Germany.

moved perpendicularly up and down across the ion beam covering a range from complete overlap to complete separation of both beams. The rate of ionised ions analysed with a second magnet and the current of the parent ion beam are measured as a function of the electron gun position, while the constant velocity of the electron gun movement is also controlled. Independently absolute cross sections can be determined without further measurement of background or beam overlap factors. The uncertainties of a single cross section measurement are due to counting statistics and the systematic errors of measured particle currents (±3%), particle velocities (±1%), detector efficiency (±3%) and amplitude of electron gun displacement (±0.6%). The total uncertainty is the quadrature sum of counting statistics on the signal at 95% confidence level and systematic uncertainties in each of the measured parameters estimated at a comparable level of confidence.

3. Results and discussion

The cross section data for electron impact double ionisation of Ar^+ and Ar^{4+} ions are listed in table 1 together with the total experimental uncertainty including the statistical error at 95% confidence level. The measured cross section $\sigma_{1,3}$ is shown in figure 1 as a function of the electron impact energy. With the improved accuracy of our present technique it is now possible to identify the expected contribution of L-shell ionisation-autoionisation to double ionisation of Ar^+: above an electron energy of 260 eV a structure in the cross section which was not found previously becomes clearly visible. Below 260 eV the cross section $\sigma_{1,3}$ is apparently determined by direct ionisation of two outer-shell electrons. The observed threshold of the measured cross section corresponds to the minimum energy (68.3 eV) necessary for the ejection of two electrons from an Ar^+ ion in the ground state.

A detailed quantum theoretical calculation of cross sections for multiple ionisation is presently not available. Gryzinski (1965) has calculated direct double ionisation of atoms and ions by a semiclassical approach. This approach considers two possibilities for double ionisation: the incident electron hits a target electron which is ejected and the projectile electron, although with reduced energy, again has a certain probability to eject a second electron from the same atom. It is also possible that the first ejected electron hits a second target electron which also becomes ionised. The sum of these two contributions yields the direct double ionisation cross section and was calculated to be

$$\sigma_{q,q+2}=\frac{\sigma_0^2}{P_1^2P_2^2}\frac{n_e^{5/3}(n_e-1)}{4\pi\bar{R}^2}g\left(\frac{E}{P_1+P_2}\right) \tag{1}$$

with $\sigma_0=6.56\times10^{-14}\ \mathrm{eV^2\,cm^2}$. P_1 and P_2 are the ionisation potentials of the considered ion A^{q+} and the ion $A^{(q+1)+}$, respectively, n_e is the number of equivalent electrons in the outermost shell of A^{q+}, $\bar{R}$ is the gas kinetic radius of the shell and g is a general function given by Gryzinski (1965).

We have applied equation (1) to direct double ionisation of Ar^+ using $P_1=27.6$ eV and $P_2=40.7$ eV from Moore (1970), $n_e=5$ for the 3p shell and $\bar{R}=0.67\times10^{-10}$ m from calculated shell radii (Fraga *et al* 1976). The resulting cross section is far too large. It is displayed in figure 1 after multiplication by a factor $\frac{1}{4}$. At least, however, the Gryzinski model seems to give a reasonable representation of the shape of the direct double ionisation cross section.

Table 1. Electron impact double ionisation cross sections $\sigma_{1,3}$ and $\sigma_{4,6}$ for Ar^+ and Ar^{4+} ions, respectively. Estimated total uncertainties are given including the statistical error at 95% confidence level.

Electron energy (eV)	Cross section (10^{-19} cm^2)	Electron energy (eV)	Cross section (10^{-19} cm^2)
$\sigma_{1,3}$: $Ar^+ \rightarrow Ar^{3+}$			
57.5	-0.18 ± 0.51	210.0	42.7 ± 2.6
60.0	0.44 ± 1.58	220.0	42.3 ± 2.6
63.7	0.59 ± 0.49	230.0	42.2 ± 2.6
69.9	1.62 ± 0.50	240.0	41.0 ± 2.5
71.8	3.01 ± 0.47	250.0	39.4 ± 2.4
74.4	5.42 ± 0.54	260.0	38.8 ± 2.4
77.1	9.76 ± 0.83	270.0	37.6 ± 2.4
80.0	13.6 ± 1.1	280.0	38.3 ± 2.4
82.7	17.3 ± 1.3	290.0	38.6 ± 2.4
85.7	20.5 ± 1.4	300.0	37.6 ± 2.3
89.0	24.4 ± 1.5	310.0	37.7 ± 2.3
92.7	27.4 ± 1.7	320.0	37.3 ± 2.3
96.2	30.3 ± 1.9	330.0	37.1 ± 2.3
100.0	33.6 ± 2.1	340.0	37.3 ± 2.3
104.0	35.3 ± 2.2	350.0	37.3 ± 2.3
108.0	36.8 ± 2.3	365.0	37.0 ± 2.3
112.0	39.3 ± 2.4	380.0	37.1 ± 2.3
118.0	41.4 ± 2.6	395.0	35.6 ± 2.2
122.0	42.6 ± 2.6	410.0	36.2 ± 2.2
128.0	43.3 ± 2.7	430.0	36.3 ± 2.2
134.0	44.1 ± 2.7	450.0	34.8 ± 2.2
140.0	45.3 ± 2.8	470.0	34.9 ± 2.2
145.0	46.2 ± 2.9	490.0	33.6 ± 2.1
150.0	44.6 ± 2.8	510.0	33.8 ± 2.1
160.0	46.7 ± 2.9	530.0	33.3 ± 2.1
170.0	45.3 ± 2.8	550.0	31.8 ± 2.0
180.0	44.6 ± 2.8	575.0	30.9 ± 1.9
190.0	44.5 ± 2.8	601.0	28.7 ± 1.8
200.0	43.9 ± 2.7	650.0	27.3 ± 1.7
$\sigma_{4,6}$: $Ar^{4+} \rightarrow Ar^{6+}$			
160.0	0.08 ± 1.18	330.0	3.25 ± 0.66
170.0	1.15 ± 0.87	340.0	4.17 ± 0.72
180.0	-0.41 ± 2.48	360.0	4.82 ± 0.73
190.0	-1.44 ± 1.32	380.0	6.26 ± 0.93
210.0	-0.24 ± 0.62	400.0	6.63 ± 1.01
220.0	0.24 ± 1.06	410.0	8.22 ± 0.81
240.0	0.04 ± 0.06	430.0	8.78 ± 0.77
250.0	0.85 ± 0.64	460.0	9.92 ± 0.78
265.0	1.31 ± 0.61	480.0	10.4 ± 0.8
280.0	1.16 ± 0.69	500.0	9.89 ± 1.25
287.0	1.28 ± 0.46	520.0	11.2 ± 0.9
300.0	1.62 ± 0.75	550.0	11.5 ± 0.9
310.0	1.60 ± 0.48	600.0	11.6 ± 1.1
320.0	2.09 ± 0.60	630.0	12.0 ± 1.0
325.0	3.26 ± 0.51	660.0	12.3 ± 0.9

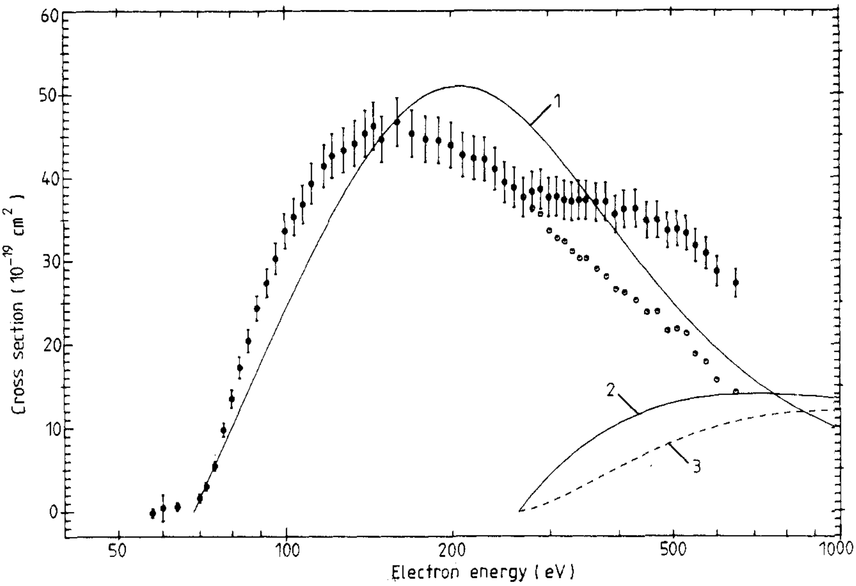

Figure 1. Electron impact double ionisation cross section $\sigma_{1,3}$ for Ar^+ ions: full circles, present measurement; full curve 1, direct double ionisation cross section calculated from semiclassical binary-encounter theory (equation (1)) multiplied by the factor $\frac{1}{4}$; full curve 2, L-shell contribution $\sigma_{1,3}(L)$ from equation (2) with σ_{2s} and σ_{2p} calculated from the Lotz formula; broken curve, L-shell contribution $\sigma_{1,3}(L)$ from equation (2) with σ_{2s} and σ_{2p} calculated from binary-encounter theory (Gryzinsky 1965) for single ionisation; open circles, difference between measured data points and full curve 2; i.e. the estimated contribution of direct double ionisation to the cross section $\sigma_{1,3}$ above the L-shell ionisation threshold.

To calculate the L-shell contribution to double ionisation of Ar^+ we have used the approach of Müller and Frodl (1980)

$$\sigma_{q,q+2}(L) = 0.89\ \sigma_{2p} + 0.047\ \sigma_{2p} + 0.052\ \sigma_{2s} \tag{2}$$

where for Ar atoms and Ar^{q+} ions equal probabilities of rearrangement processes subsequent to L-shell ionisation are assumed. σ_{2p} and σ_{2s} are the cross sections for creating a single hole in the 2p and 2s subshells, respectively. The factor 0.89 gives the relative contribution of a single Auger process following the ionisation of the 2p subshell, the factor 0.047 represents the contribution of an Auger process connected with a shake-up transition, e.g. $2s^22p^53s^23p^5 \rightarrow 2s^22p^63s^23p^2nl + e$. Only 5.2% of 2s ionisation leads to a single Auger process and thus contributes to $\sigma_{1,3}$.

The cross sections σ_{2p} and σ_{2s} can be easily calculated either from the Lotz formula (Lotz 1968) or from the binary-encounter approximation (Gryzinski 1965) for single ionisation (see preceding paper). We used ionisation potentials of 263 eV for the 2p subshell and 327 eV for the 2s subshell (see Müller and Frodl 1980). The resulting L-shell contributions $\sigma_{1,3}(L)$ to $\sigma_{1,3}$ are also shown in figure 1.

By subtracting $\sigma_{1,3}(L)$ calculated with the Lotz formula from the measured cross section points one obtains the open circles in figure 1. These open circles together with the data points at electron energies below the L-shell threshold form a smooth cross section function which can be regarded as the direct double ionisation contribution to $\sigma_{1,3}$ for Ar^+. This indicates that the L-shell contribution is well represented by equation (2) when the semi-empirical Lotz formula is used to calculate the cross sections for the single ionisation of the 2s and 2p subshells.

Figure 2 shows cross sections for double ionisation of Ar^{4+} ions by electron impact. The present data (full circles) are compared with recent data (open squares) of the Oak Ridge group (Pindzola *et al* 1984). The agreement of both sets of experimental data is well within the quoted uncertainties.

Again we have calculated the direct double ionisation cross section $\sigma_{4,6}$ with the Gryzinski method (equation (1)) using $P_1 = 75.0$ eV, $P_2 = 91.0$ eV (Moore 1970), $n_e = 4$ for the M shell and $\bar{R} = 0.63 \times 10^{-10}$ m (Fraga *et al* 1976). Below the L-shell ionisation threshold the prediction is in much better agreement with the experiment than in the Ar^{+} case and was considered a useful estimate for direct double ionisation for all electron energies investigated. As a next step $\sigma_{4,6}(L)$ was calculated according to equation (2) with extrapolated L-shell ionisation potentials of 320 eV for the 2p subshell and 420 eV for the 2s subshell. The results both from the Lotz formula and the Gryzinski theory were added separately to the direct double ionisation cross section $\sigma_{4,6}$. In the case of the Lotz formula used for σ_{2s} and σ_{2p} the final result is in very good agreement with the experiment. This investigation shows that the cross section $\sigma_{4,6}$ is by far dominated by the indirect process of L-shell ionisation with subsequent emission of a single electron at energies above the 320 eV threshold for this process. A distorted-wave calculation of σ_{2p} by Pindzola *et al* (1984) is nearly identical to the Lotz results, and confirms these considerations.

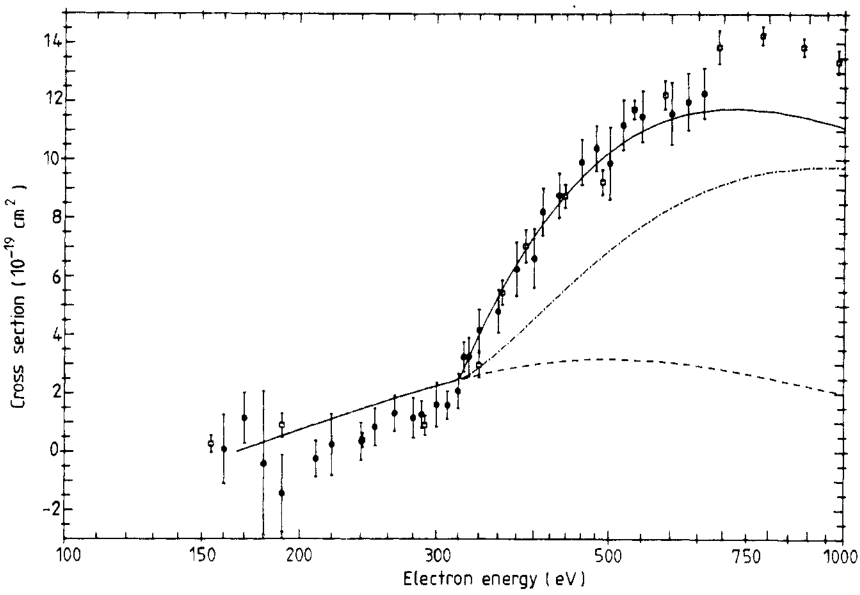

Figure 2. Electron impact double ionisation cross section $\sigma_{4,6}$ for Ar^{4+} ions: full circles, present measurement; open squares, measurement of the Oak Ridge group (Pindzola *et al* 1984); broken curve, direct double ionisation cross section calculated from semiclassical binary-encounter theory (equation (1)); chain curve, sum of direct double ionisation cross section (broken curve) and L-shell contribution $\sigma_{4,6}(L)$ from equation (2) with σ_{2s} and σ_{2p} calculated from binary-encounter theory (Gryzinski 1965) for single ionisation; full curve, sum of direct double ionisation cross section (broken curve) and L-shell contribution $\sigma_{4,6}(L)$ from equation (2) with σ_{2s} and σ_{2p} calculated from the Lotz formula.

The maximum of $\sigma_{q,q+2}(\mathrm{L})$ according to the Lotz formula is $1.36 \times 10^{-18}\ \mathrm{cm}^2$ for $q = 1$ at about 700 eV and $0.98 \times 10^{-18}\ \mathrm{cm}^2$ for $q = 4$ at about 850 eV. Thus, the L-shell contribution to double ionisation of Ar^{4+} is only about 30% less than that of Ar^{+}, the difference being attributed to the increased L-shell ionisation potentials. At the same time the cross section maximum for direct double ionisation decreases by more than one order of magnitude from $4.6 \times 10^{-18}\ \mathrm{cm}^2$ for Ar^{+} at 150 eV to roughly $3 \times 10^{-19}\ \mathrm{cm}^2$ for Ar^{4+} at about 500 eV. With increasing ion charge state it obviously becomes far less probable to ionise two electrons in a direct process than to eject one inner-shell electron with subsequent emission of a second electron (autoionisation or Auger ionisation). However, the L-shell contribution to the cross section $\sigma_{q,q+2}$ can be also expected to collapse when the Ar^{q+} ion charge state is increased from $q = 6$ to $q = 7$ since then there are no more M-shell electrons left to be ejected in an Auger process.

4. Conclusion

We have investigated double ionisation of Ar^{+} and Ar^{4+} ions. With the improved accuracy of our new experimental technique we are able to identify the L-shell contributions to the measured total cross sections. While the two-step process of L-shell ionisation–autoionisation nearly remains constant with increasing charge state of the Ar^{q+} ion, the direct double ionisation cross section decreases rapidly as the number of outer M-shell electrons decreases. As already observed in earlier experiments, indirect processes tend to become increasingly important for multiply charged ions.

References

Fraga S, Karwowski J and Saxena K M S 1976 *Handbook of Atomic Data* (Amsterdam: Elsevier) pp 465–73
Gryzinski M 1965 *Phys. Rev.* **138** A336–58
Lotz W 1968 *Z. Phys.* **216** 241–7
Moore C E 1970 *Atomic Energy Levels, NSRDS-NBS 34* (Washington, DC: US Govt Printing Office)
Müller A and Frodl R 1980 *Phys. Rev. Lett.* **44** 29–32
Müller A, Huber K, Tinschert K, Becker R and Salzborn E 1985 *J. Phys. B: At. Mol. Phys.* **18**
Pindzola M S, Griffin D C, Bottcher C, Crandall D H, Phaneuf R A and Gregory D C 1984 *Phys. Rev.* A **29** 1749–56