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Electron impact double ionisation of Ar^{q+} ions ($q = 1, 2, \ldots, 7$): two-electron processes compared with inner-shell contributions

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Abstract. Cross sections for electron impact double ionisation of Ar^{2+}, Ar^{3+}, Ar^{5+}, Ar^{6+} and Ar^{7+} ions have been measured for electron energies ranging from the threshold to 1000 eV. Earlier experiments on Ar^{+} and Ar^{4+} have thus been complemented at a comparable level of accuracy. The obtained data set permits analysis of trends in direct double ionisation and inner-shell ionisation, with subsequent Auger processes, to be made along the Ar isonuclear sequence.

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 multiple ionisation cross sections 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 one or more 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 the limited reproducibility of these early experiments it was not possible to identify the expected L-shell effect on the cross section $\sigma_{1,3}$ for double ionisation of Ar^{+}. After improving our experimental technique (Müller *et al* 1985a) we could make accurate cross section measurements on Ar^{+} ions which clearly showed the inner-shell contribution to $\sigma_{1,3}$, and the series of Ar^{q+} ions studied was extended to $q = 4$ (Müller *et al* 1985b). Our cross sections $\sigma_{4,6}$ for Ar^{4+} are in good agreement with the data published by Pindzola *et al* (1984).

The more recent data on Ar^{+} and Ar^{4+} allowed comparison of the relative contributions of multiple-electron processes to net double ionisation for two different charge states. The maximum of the direct part of $\sigma_{1,3}$ was found to be 46×10^{-19} cm^2 while that of $\sigma_{4,6}$ is only about 3×10^{-19} cm^2.

Direct multiple ionisation by electron impact is nearly unexplored and theoretical approaches have not been developed beyond the classical binary encounter approximation (BEA) of Gryziński (1965). There are no reliable predictions of cross sections for multi-electron processes contributing to multiple ionisation. On the other hand the available data on Ar^{q+} ions and a study by Howald *et al* (1986b) on Xe^{6+} show the importance of direct multiple ionisation of ions by electron impact.

In general, it is difficult to sort out different individual contributions to multiple ionisation of complex ions. The Ar isonuclear sequence, however, provides a relatively simple shell structure which easily allows one to discriminate between contributions from different shells. For electron energies below 1000 eV the K shell need not be considered. Ionisation or excitation of the L shell requires electron energies of several hundred eV so that multiple ionisation below the L-shell ionisation threshold can only be due to direct multi-electron processes in the M shell. Hence, we have complemented our earlier measurements of $\sigma_{1,3}$ and $\sigma_{4,6}$ (Müller *et al* 1985b) by experiments on Ar^{q+} ions in the remaining charge states up to $q=7$. Thus an almost complete set of multiple ionisation data has become available for an extended isonuclear sequence.

2. Experimental technique

The experiments were conducted using a new experimental set-up (Tinschert *et al* 1988). The experimental technique was the same as that described previously (Müller *et al* 1985a, c). In brief, multiply-charged ions were extracted from an electron cyclotron resonance (ECR) ion source (Mank *et al* 1986) and accelerated by 10 kV. Magnetically analysed beams of Ar^{q+} ions were passed through an electron gun which could be moved perpendicularly up and down across the ion beam covering a range from complete overlap to complete separation of both beams. The count rate of ionised ions analysed with a second magnet and the current of the parent ion beam was measured as a function of the electron gun position at a given electron energy and current. These measurements gave absolute cross sections without further measurements of background or beam overlap factors. The uncertainties of a single cross section measurement are due to counting statistics and systematic errors in the measured particle currents (5%), particle velocities (1%), detector efficiency (3%) and amplitude of electron gun displacement (1%). The total uncertainty is the quadrature sum of counting statistics on the signal at two standard deviations and systematic uncertainties in each of the measured parameters estimated at a comparable level of confidence.

3. Results and discussion

The new cross section data for electron impact double ionisation of Ar^{q+} ($q=2,3,5,6,7$) are listed in table 1 together with the total experimental uncertainties including the statistical error at two standard deviations.

Figures 1(a)–(d) display the measured cross sections $\sigma_{2,4}$, $\sigma_{3,5}$, $\sigma_{5,7}$, $\sigma_{6,8}$ as functions of the electron energy. Statistical uncertainties are indicated when exceeding the size of the symbols. The data for double ionisation of Ar^{2+} and Ar^{3+} suggest the presence of two contributions:

(i) direct double ionisation; i.e. removal of two electrons from the M shell in a direct process

$$e+Ar^{2+}(2p^6 3s^2 3p^4)\rightarrow Ar^{4+}(2p^6 3s^2 3p^2)+3e \tag{1}$$

and

Table 1. Electron impact double ionisation cross sections $\sigma_{q,q+2}$ ($q = 2, 3, 5, 6, 7$) for Ar^{q+} ions. Estimated total uncertainties are given including the statistical error at a confidence level of two standard deviations.

Electron energy (eV)	Cross section (10^{-19} cm^2)	Electron energy (eV)	Cross section (10^{-19} cm^2)	Electron energy (eV)	Cross section (10^{-19} cm^2)
$\sigma_{2,4}$: $Ar^{2+} \rightarrow Ar^{4+}$					
95.0	−0.02 ± 0.13	230.0	8.09 ± 0.64	450.0	15.7 ± 1.2
100.0	0.06 ± 0.15	245.0	8.26 ± 0.66	470.0	16.2 ± 1.3
102.0	0.39 ± 0.13	260.0	8.45 ± 0.67	495.0	16.0 ± 1.3
105.1	0.72 ± 0.10	270.0	8.76 ± 0.69	520.0	16.5 ± 1.3
110.0	1.77 ± 0.21	280.0	9.18 ± 0.72	545.0	16.8 ± 1.3
115.0	2.60 ± 0.26	290.0	9.99 ± 0.79	570.0	16.7 ± 1.3
120.0	3.60 ± 0.31	300.0	10.7 ± 0.8	600.0	16.8 ± 1.3
125.2	4.33 ± 0.37	310.0	11.2 ± 0.9	630.0	17.0 ± 1.3
132.1	5.14 ± 0.42	320.0	12.0 ± 0.9	660.0	17.1 ± 1.3
140.0	5.94 ± 0.48	330.0	12.7 ± 1.0	690.0	17.2 ± 1.3
150.0	6.66 ± 0.54	340.0	13.2 ± 1.0	730.0	17.3 ± 1.4
160.0	7.34 ± 0.60	350.0	13.6 ± 1.1	770.0	17.2 ± 1.3
170.0	7.59 ± 0.62	365.0	14.2 ± 1.1	810.0	17.1 ± 1.3
180.0	7.92 ± 0.64	380.0	14.7 ± 1.2	850.0	17.0 ± 1.3
190.1	7.99 ± 0.64	395.0	15.0 ± 1.2	900.0	16.7 ± 1.3
200.0	8.00 ± 0.65	410.0	15.3 ± 1.2	950.0	16.8 ± 1.3
215.0	8.20 ± 0.65	430.0	16.0 ± 1.3	1000.0	16.4 ± 1.3
$\sigma_{3,5}$: $Ar^{3+} \rightarrow Ar^{5+}$					
110.0	−0.40 ± 0.23	280.0	2.43 ± 0.21	500.0	12.5 ± 1.0
120.0	0.06 ± 0.17	290.0	3.12 ± 0.25	520.0	12.8 ± 1.0
140.0	0.25 ± 0.13	300.0	3.76 ± 0.30	545.0	13.1 ± 1.0
150.0	0.47 ± 0.12	310.0	4.80 ± 0.41	570.0	13.5 ± 1.1
160.0	0.78 ± 0.12	320.0	5.97 ± 0.48	600.0	13.9 ± 1.1
170.0	0.82 ± 0.14	330.0	6.71 ± 0.54	630.0	14.0 ± 1.1
180.0	1.04 ± 0.15	340.0	7.34 ± 0.59	660.0	14.3 ± 1.1
190.0	1.19 ± 0.15	350.0	7.90 ± 0.63	690.0	14.5 ± 1.1
200.0	1.46 ± 0.15	365.0	8.99 ± 0.71	730.0	14.7 ± 1.2
210.0	1.50 ± 0.15	380.0	9.47 ± 0.75	770.0	14.7 ± 1.2
220.0	1.69 ± 0.17	395.0	10.2 ± 0.8	810.0	14.8 ± 1.2
230.0	1.63 ± 0.16	410.0	10.7 ± 0.8	850.0	14.9 ± 1.2
240.0	1.81 ± 0.18	430.0	11.1 ± 0.9	900.0	14.9 ± 1.2
250.0	1.87 ± 0.21	450.0	11.2 ± 0.9	950.0	14.9 ± 1.2
260.0	2.21 ± 0.20	470.0	11.9 ± 0.9	1000.0	14.7 ± 1.2
270.0	2.25 ± 0.20	495.0	12.2 ± 1.0		
$\sigma_{5,7}$: $Ar^{5+} \rightarrow Ar^{7+}$					
250.0	0.27 ± 0.24	445.0	5.03 ± 0.41	625.0	9.02 ± 0.73
300.0	0.28 ± 0.17	450.0	5.05 ± 0.44	650.0	9.22 ± 0.75
330.0	0.41 ± 0.14	465.0	5.81 ± 0.47	675.0	9.63 ± 0.77
350.0	1.06 ± 0.17	475.0	5.38 ± 0.45	700.0	9.54 ± 0.76
360.0	1.68 ± 0.18	485.0	6.35 ± 0.51	730.0	9.57 ± 0.76
370.0	2.08 ± 0.21	500.0	6.23 ± 0.54	760.0	9.78 ± 0.78
387.0	2.88 ± 0.29	520.0	7.14 ± 0.59	790.0	10.2 ± 0.8
400.0	3.32 ± 0.31	540.0	7.45 ± 0.62	825.0	10.0 ± 0.8
410.0	4.14 ± 0.34	560.0	7.84 ± 0.65	860.0	10.0 ± 0.8
415.0	3.95 ± 0.34	580.0	8.58 ± 0.69	900.0	10.5 ± 0.8
435.0	4.67 ± 0.40	600.0	8.87 ± 0.71	950.0	10.4 ± 0.8
$\sigma_{6,8}$: $Ar^{6+} \rightarrow Ar^{8+}$					
370.0	0.31 ± 0.20	500.0	4.29 ± 0.44	800.0	7.21 ± 0.64
385.0	0.89 ± 0.19	550.0	5.27 ± 0.47	850.0	7.77 ± 0.71
400.0	1.27 ± 0.37	600.0	5.89 ± 0.53	900.0	7.36 ± 0.67
415.0	2.09 ± 0.24	650.0	6.42 ± 0.55	950.0	7.75 ± 0.65
430.0	2.67 ± 0.27	700.0	6.61 ± 0.59	1000.0	7.63 ± 0.65
460.0	3.33 ± 0.33	750.0	7.38 ± 0.62		
$\sigma_{7,9}$: $Ar^{7+} \rightarrow Ar^{9+}$					
750.0	0.77 ± 0.12	900.0	1.06 ± 0.26		

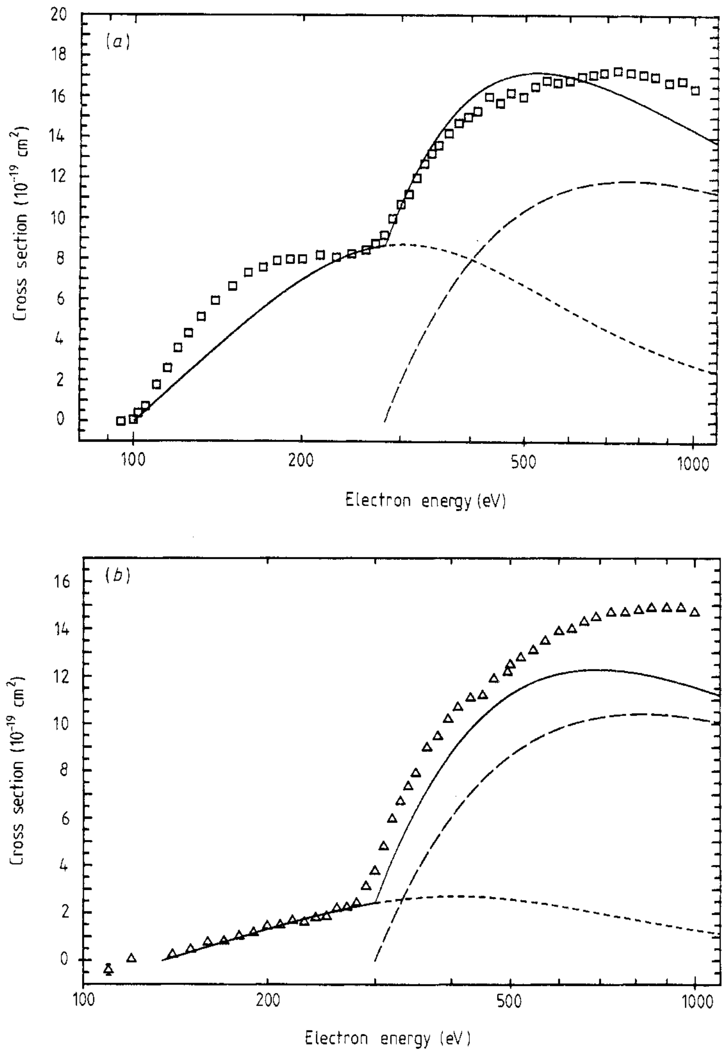

Figure 1. Measured cross sections for electron impact double ionisation of: (*a*) Ar^{2+}, (*b*) Ar^{3+}, (*c*) Ar^{5+} and (*d*) Ar^{6+}. Statistical uncertainties are shown where they exceed the size of the symbols. The short broken curves represent calculations following the work of Gryziński (1965) which had to be multiplied by the factors of 0.12 and 0.19 for Ar^{2+} and Ar^{3+}, respectively, in order to obtain some degree of agreement with the experiment. The long broken curves show the inner-shell contributions to the measured cross section calculated by using the Lotz formula (1968) for L-vacancy production and the branching ratios for subsequent autoionisation processes as known for neutral Ar (Müller and Frodl 1980). Ionisation potentials of L-shell electrons were obtained from tables compiled by Zschornack *et al* (1986).

(ii) inner-shell ionisation–autoionisation; i.e. removal of one electron from the L shell and a subsequent Auger process such as

$$\begin{aligned} e + Ar^{2+}(2p^6 3s^2 3p^4) &\rightarrow Ar^{3+}(2p^5 3s^2 3p^4) + 2e \\ &\rightarrow Ar(2p^6 3s^2 3p^2) + e. \end{aligned} \tag{2}$$

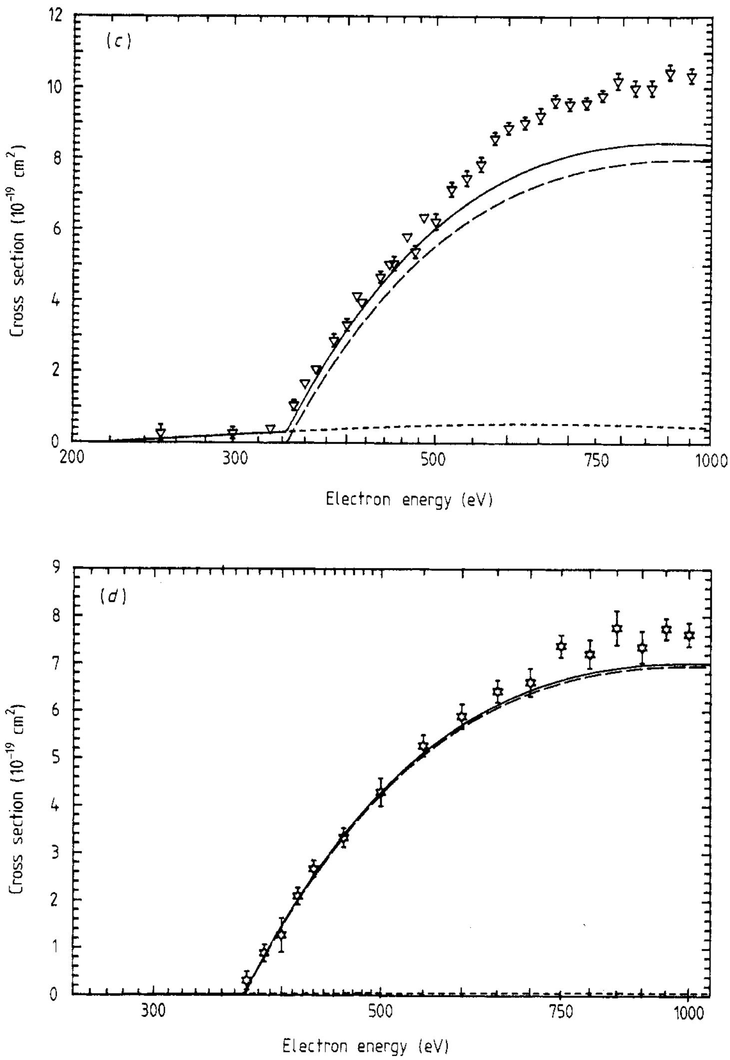

Figure 1. (continued)

The threshold for process (i) is given by the sum of ionisation potentials for the two most loosely bound electrons while process (ii) has its onset at the threshold of the inner-shell ionisation process which is roughly 300 eV for the present ions.

There is no available general theory based on quantum physics for process (i). Gryziński (1965) has used a classical binary encounter approach (BEA) to provide a prescription for estimating cross sections for direct double ionisation. The BEA results had to be multiplied by factors 0.12 and 0.19 for Ar^{2+} and Ar^{3+} ions, respectively, in order to obtain some degree of agreement with our experimental data. The normalised results are shown by the short broken curves in figure 1.

The long broken curves represent the indirect contributions to the cross section and were calculated using the approach of Müller and Frodl (1980) assuming charge-state independence of the branching ratios for the single Auger and the single Auger with shake-up processes subsequent to ionisation of the 2p and 2s subshells. The cross sections for ionisation of the L subshells were calculated from the semiempirical Lotz formula (Lotz 1968). The full curves give the sum of the short broken and long broken curves and should provide an estimate of the observed double ionisation cross sections. From the figures it is apparent that the inner-shell contributions are reproduced reasonably well both in shape and size by the simple approach used (Lotz formula plus branching). The direct double ionisation, however, is not properly describe by the BEA calculations.

For demonstration of cross section dependences on the ion charge state, we show our measured cross sections $\sigma_{q,q+2}$ ($q=1,2,\ldots,7$) in figure 2, which includes data published previously (Müller *et al* 1985b) for double ionisation of Ar^{q+} ions ($q=1,4$). For Ar^{+}, process (i) has a sizable cross section which exceeds the L-shell contribution by a factor of three while, for Ar^{5+}, process (i) is insignificant compared with the inner-shell ionisation contribution, which is only slightly decreased. For Ar^{7+} the inner-shell contribution should be completely gone provided the parent ion beam is in its ground state. The L-shell ionisation

$$e+Ar^{7+}(2p^{6}3s)\rightarrow Ar^{8+}(2p^{5}3s) \tag{3}$$

does not lead to an autoionising state and hence the observed cross section drops by about one order of magnitude between $q=6$ and $q=7$.

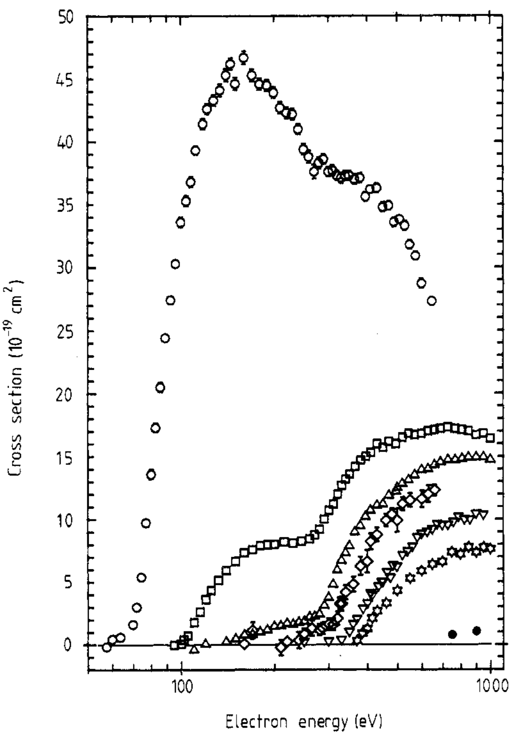

Figure 2. Measured cross sections $\sigma_{q,q+2}$ for double ionisation of Ar^{q+} ions in charge states $q=1,2,\ldots,7$. In addition to the present data, the figure includes previous measurements (Müller *et al* 1985b). The symbols are: ○, $\sigma_{1,3}$; □, $\sigma_{2,4}$; △, $\sigma_{3,5}$; ◇, $\sigma_{4,6}$; ▽, $\sigma_{5,7}$; ☆, $\sigma_{6,8}$; ●, $\sigma_{7,9}$. Statistical uncertainties are shown where they exceed the size of the symbols.

Looking at the rapid decrease of the direct contribution (process (i)) to $\sigma_{q,q+2}$ when q is increased, the observed cross section $\sigma_{7,9}$ is still not extremely low (about 1×10^{-19} cm^2 at 900 eV). It is well known from earlier experiments (Howald *et al* 1986a) that ECR ion sources produce Na-like ions in metastable autoionising quartet and doublet states with configurations ($2p^5 3s3p$). For Ar^{7+} ions in these states a single L-shell ionisation process could again produce net double ionisation via

$$\begin{aligned} e + Ar^{7+}(2p^5 3s3p)^{**} &\rightarrow Ar^{8+}(2p^4 3s3p)^{**} + 2e \\ &\rightarrow Ar^{9+}(2p^5) + e. \end{aligned} \tag{4}$$

If we assume that the observed cross section $\sigma_{7,9}$ arises solely from such a metastable fraction m in the parent ion beam then the calculation using the Lotz formula with the same branching ratios as before would result in an upper limit of roughly 15% for m. This fraction decreases when the cross section for direct double ionisation is non-zero. A definitive answer to the question of a possible metastable content in the parent Ar^{7+} ion beam might be possible by searching for the onset of $\sigma_{7,9}$. In our experiments, however, we did not obtain sufficient Ar^{7+} ion current to do measurements below the ground-state double ionisation threshold at 565.9 eV.

4. Conclusion

We have complemented earlier measurements on electron impact double ionisation of Ar^{q+} ions, such that cross sections $\sigma_{q,q+2}$ are now available for all charge states q between 1 and 7. The experiments show that the ionisation-autoionisation process involving the L shell can be described fairly well by constant branching ratios for Auger and radiative de-excitation processes independent of the ion charge state. Between $q=1$ and $q=6$ the maximum absolute contribution from indirect L-shell ionisation-autoionisation decreases only from about 1.5×10^{-18} cm^2 to 7.3×10^{-19} cm^2 which can be explained by the increasing binding energy of the L-shell electrons. Along the same sequence of ion charge states the maximum contribution from direct double ionisation decreases by about two orders of magnitude as seen from the measured cross sections and their comparison with the BEA calculations. This decrease is faster than would be expected from a simple $(8-q)(8-q-1)$ dependence based only on the number of electrons in the M shell available for direct double ionisation.

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