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A crossed beam study of the multiple ionization of argon by electron impact

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Abstract. A pulsed crossed beam technique incorporating time-of-flight spectroscopy previously developed in this laboratory has now been applied to studies of the multiple ionization of argon by electron impact. Cross sections σ_n for the production of $n = 1$–5 times ionized argon have been determined for impact energies in the range from near threshold to 5300 eV. The measurements cover a wider energy range and extend to higher charge states n than most previous experiments. The results also provide valuable checks on the results of previous measurements which exhibit unexplained discrepancies. In the case of single ionization, our values of σ_t are compared with available theoretical predictions.

1. Introduction

In previous work in this laboratory (Shah *et al* 1987) we measured cross sections for electron impact ionization of atomic hydrogen using a specially developed pulsed crossed beam technique. These measurements were of considerably greater precision and covered a much wider energy range than the few previous investigations. The method, which has high sensitivity and utilizes time-of-flight spectroscopy for selective detection and single particle counting of the collision products, can also be applied with advantage to studies of both single and multiple ionization of stable gas targets. This was illustrated by our recent measurements of cross sections for single and double ionization of helium (Shah *et al* 1988) at impact energies ranging from near threshold to 10 keV. More recently (McCallion *et al* 1992) we have also used the same basic experimental approach to study multiple ionization of magnesium atoms.

In the present work we have applied our technique to studies of the electron impact ionization of argon. Cross sections σ_n for the formation of $n = 1$–5 times ionized argon have been determined at impact energies in the range 18–5300 eV. The measurements are a further demonstration of the effectiveness of our technique. While there have been a number of previous studies of multiple ionization of argon using different techniques, the present results cover a much wider energy range and extend to higher charge states n than most previous investigations. In addition, recent measurements by Tarnovsky and Becker (1991) and by Bonham and Bruce (1991) have highlighted the fact that at energies below 500 eV there are unexplained differences of up to about 30% in previously measured values of the double ionization cross sections and in the ratios $R = \sigma_2/\sigma_1$. The differences between electrons and other projectiles in the way in which R depends on impact velocity is also an area of considerable current interest for various targets (cf Charlton *et al* 1988).

There have been many previous measurements (cf McDaniel 1989) of total cross sections for ionization of argon $\sigma_t = \Sigma\, n\sigma_n$ based on studies of the total yield of slow

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ions from a carefully defined path length and gas density in beam-static-gas configurations. Of these, the data of Rapp and Englander-Golden (1965) which cover the energy range from near threshold to 1000 eV are now believed to be the most reliable with quoted uncertainties of ±7%. They paid special attention to systematic errors arising in particular from target density determination and the definition of collision path length. A mass spectrometric analysis of the slow ion products in the beam-static-gas approach of type carried out by Schram (1966) and by Nagy *et al* (1980) can provide separate cross sections σ_n; Schram (1966) only measured abundance ratios for Ar^{n+} formation up to $n = 7$. However, it is difficult to ensure that all product ions are extracted and recorded with equal efficiency. In a similar approach, Stephan *et al* (1980) have carried out a mass spectrometric analysis of the ions formed in a Nier-type electron impact ion source.

In a crossed beam experiment by Okudaira *et al* (1970), in which electrons intersect a thermal energy beam of argon, mass spectrometric analysis of the collision products provided abundance ratios for the formation of Ar^{n+} ions for up to $n = 5$. Both Krishnakumar and Srivastava (1988) and very recently Ma *et al* (1991) have employed crossed beam methods which have similar features to our own technique in measurements of σ_1, σ_2 and σ_3 up to 1000 eV and 500 eV respectively. Both these groups use a pulsed electron beam and pulsed electric field extraction of the product ions. In the measurements of Krishnakumar and Srivastava (1988) the product ions were analysed by a quadrupole mass spectrometer and counted by means of a channel electron multiplier. The measurements of Ma *et al* (1991) employed time-of-flight analysis and multichannel plate counting of the collision products. Both groups obtained cross sections by normalizing relative values to the total cross sections of Rapp and Englander-Golden (1965). Ma *et al* (1991) were also able to obtain absolute cross sections from measurements carried out with the vacuum system filled with argon gas.

A fast crossed beam technique has been used by Wetzel *et al* (1987) and by Tarnovsky and Becker (1991) using essentially the same apparatus to obtain cross sections σ_n for $n = 1$–3 in the range from threshold to 200 eV. In this method a 3 keV beam of Ar atoms prepared by electron capture neutralization of Ar^+ in a gas target is crossed with an electron beam. The fast Ar^{n+} product ions are analysed by electrostatic deflection and counted with a channel electron multiplier while the Ar neutral atom beam intensity is recorded with a calibrated pyroelectric detector. The possible presence in the target atom beam of long lived excited atoms is a potential source of error in the fast crossed beam technique. However, Wetzel *et al* (1987) assessed this to be an insignificant problem in their measurements on argon.

Unlike most of the previous measurements, the ionization in our experiment takes place in the absence of both electric and magnetic fields thereby avoiding possible errors arising from distortion of primary electron beam trajectories. An 18-stage venetian blind type particle multiplier (EMI Type 9642/2B) is used as a product ion detector and this, together with the wide angle of acceptance of the extraction system (near 90°), ensured a high and uniform detection efficiency for all product ions.

2. Experimental approach

2.1. General description

A detailed description of the basic apparatus and measuring procedure has been given in our earlier papers (Shah *et al* 1987, 1988) and only the main features need be summarized here.

The electron gun was triggered by a pulse generator to provide electron pulses of 200 ns duration at 5×10^4 pulses/s. The electron beam intersected (at right angles) a beam of argon atoms effusing from a bunch of 1 mm diameter hypodermic needles packed into a 4 mm diameter tube. In the beam intersection region, which was located 10 mm from the tip of the needle assembly, the estimated Ar atom beam density was about 10^{11} atoms/cm^3. The intersection region was maintained at a base pressure of about 5×10^{-8} Torr throughout the measurements.

After the transit of each pulse of electrons through the argon beam, slow Ar^{n+} product ions were swept out of the beam intersection region by a pulsed electric field, of about 15 V cm^{-1} applied between two high transparency grids on either side of the beam intersection region, accelerated through the same potential difference of 5 kV and then recorded as individual counts by a particle multiplier. The extracted Ar^{n+} ions were identified and distinguished from background product ions by their different times of flight to the particle multiplier in accordance with their charge to mass ratios. As in our previous work, particular care was taken to ensure a high and equal extraction efficiency irrespective of either the primary electron beam energy or the charge state of the slow ions. A time-to-amplitude convector operated with start pulses from the extraction pulse generator and with stop pulses from the particle multiplier provided time-of-flight spectra on a multichannel analyser of the type shown in figure 1. In this case clearly resolved peaks corresponding to Ar^{n+} ions for $n=1$-5 can be seen for 1000 eV electrons in argon.

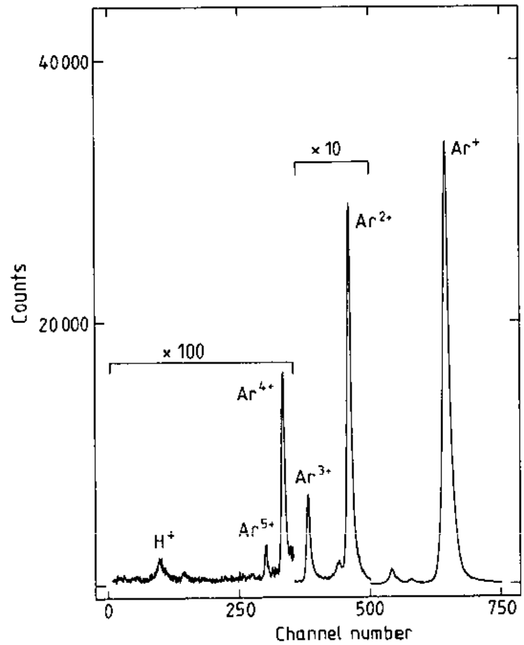

Figure 1. Time-of-flight spectrum showing Ar^+, Ar^{2+}, Ar^{3+}, Ar^{4+} and Ar^{5+} products of ionization obtained with 1000 eV electron impact.

2.2. *Electron beam system*

A pulsed electron beam of very small angular divergence and intensity equivalent to up to 10 nA in the continuous mode was derived from a seven-element electron gun of the type described previously (Shah *et al* 1987). The electron beam had a diameter of less than 2 mm in the beam intersection region while the diameter of the argon beam was 4 mm. As in our previous work, careful checks were made to ensure that the effective collision volume was insensitive to the position of the electron beam. The intensity of the electron beam was measured by means of a screened Faraday cup while an indication of the intensity of the argon beam was provided by an ionization gauge in the main vacuum chamber.

The energy of the electron beam can be expressed as $E = V_f - d$ where V_f is the acceleration voltage applied to the midpoint of the V-shaped filament of the gun; d is a correction parameter which allows for filament misalignment and the effect of contact potentials. A value of $d = 0.8 \pm 0.1$ V was obtained by linear extrapolation of the apparent cross sections at low energy to the threshold value of 15.76 eV for the ionization of argon.

2.3. Cross section measurements and normalization

The Ar^{n+} yields were obtained at each particular impact energy from the average of several measurements of the area of the appropriate peak in the time-of-flight spectrum. Allowance could be made for any small contributions from the background gas by checking the time-of-flight spectrum in the absence of the argon.

Cross sections σ_n for the production of n times ionized argon can be expressed as

$$\sigma_n = S_n / k\mu \tag{1}$$

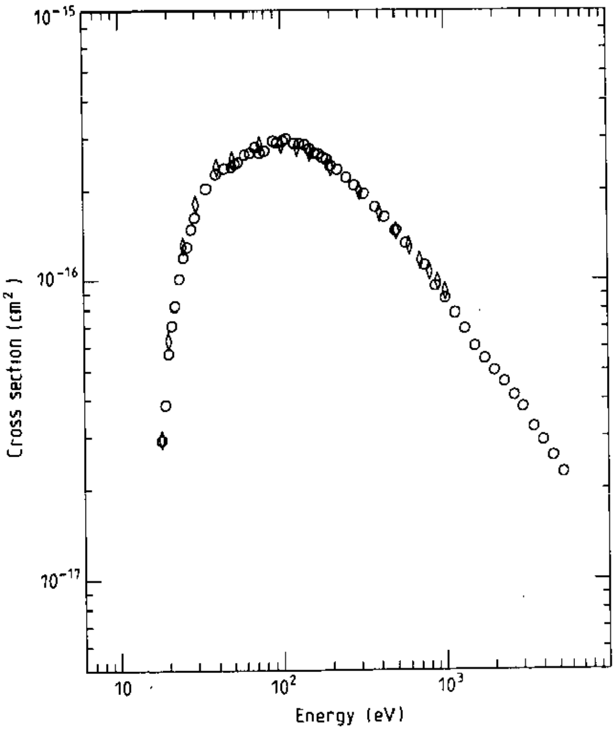

Figure 2. Total cross sections $\sigma_t = \Sigma_n n\sigma_n$ for ionization of argon by electron impact. ◇, Rapp and Englander-Golden (1965); ○, present results normalized to values of Rapp and Englander-Golden (1965).

Table 1. Cross sections σ_n for the formation of $n = 1$-5 times ionized argon by electron impact.

Energy (eV)	σ_1 (10^{-16} cm^2)	σ_2 (10^{-17} cm^2)	σ_3 (10^{-19} cm^2)	σ_4 (10^{-20} cm^2)	σ_5 (10^{-20} cm^2)
18.0	0.294±0.020				
19.0	0.384±0.015				
20.0	0.575±0.007				
21.0	0.715±0.016				
22.0	0.828±0.023				
23.5	1.02±0.03				
25.0	1.20±0.04				
26.5	1.30±0.03				
28.0	1.49±0.03				
29.5	1.64±0.03				
34.5	2.05±0.04				
39.5	2.29±0.04				
44.5	2.39±0.05				
49.3	2.40±0.06	0.136±0.020			
52.0	2.41±0.06	0.280±0.029			
54.5	2.40±0.04	0.480±0.030			
57.5	2.37±0.06	0.719±0.043			
60.0	2.46±0.05	0.965±0.064			
65.0	2.44±0.04	1.27±0.09			
70.0	2.49±0.16	1.61±0.09			
75.0	2.36±0.05	1.63±0.08			
80.0	2.39±0.04	1.69±0.09			
90.0	2.55±0.07	1.99±0.11			
95.0	2.53±0.08	1.97±0.12			
103	2.53±0.06	2.05±0.08	1.28±0.51		
108	2.57±0.05	2.10±0.12	2.00±1.20		
120	2.48±0.05	2.04±0.10	3.76±1.31		
130	2.47±0.07	2.03±0.12	4.77±0.95		
140	2.44±0.06	2.04±0.11	6.48±1.10		
150	2.37±0.05	1.96±0.14	6.05±0.91		
160	2.30±0.05	1.87±0.11	6.41±0.96		
170	2.29±0.05	1.78±0.09	7.23±1.16		
180	2.23±0.06	1.75±0.08	6.95±0.76		
190	2.20±0.03	1.69±0.10	6.58±1.12		
200	2.10±0.07	1.58±0.11	7.11±1.07		
220	2.05±0.06	1.52±0.08	6.62±0.80		
250	1.94±0.04	1.35±0.06	6.84±0.96		
280	1.83±0.04	1.25±0.08	5.80±0.87		
320	1.72±0.04	1.15±0.05	6.84±0.82		
375	1.56±0.03	0.99±0.07	7.43±0.90		
430	1.45±0.04	0.875±0.044	8.10±0.57	9.0±4.1	
500	1.31±0.02	0.781±0.039	8.73±0.70	14.3±2.8	
570	1.19±0.05	0.680±0.075	9.12±0.73	14.0±4.5	
650	1.07±0.02	0.601±0.033	8.53±1.02	15.3±5.0	
750	0.983±0.021	0.550±0.031	8.74±0.73	17.9±2.5	0.91±0.68
870	0.845±0.023	0.445±0.026	7.77±0.76	16.8±2.9	1.7±1.2
1000	0.758±0.016	0.423±0.022	8.40±0.50	19.0±3.0	2.1±0.8
1150	0.687±0.015	0.368±0.018	7.40±0.52	19.3±3.1	2.7±0.8
1320	0.614±0.027	0.311±0.018	7.03±0.77	18.1±2.4	2.9±0.9
1520	0.533±0.009	0.284±0.015	6.37±0.41	13.9±2.6	2.7±1.1
1750	0.481±0.011	0.261±0.021	6.14±0.57	12.7±1.7	1.5±0.7
2000	0.440±0.009	0.236±0.016	5.37±0.38	11.7±1.6	1.9±0.4
2300	0.401±0.006	0.218±0.016	5.34±0.38	11.5±1.4	1.6±0.8

Table 1. (continued)

Energy (eV)	σ_1 (10^{-16} cm^2)	σ_2 (10^{-17} cm^2)	σ_3 (10^{-19} cm^2)	σ_4 (10^{-20} cm^2)	σ_5 (10^{-20} cm^2)
2650	0.363 ± 0.009	0.197 ± 0.015	4.85 ± 0.49	10.0 ± 1.3	1.9 ± 0.5
3000	0.331 ± 0.007	0.176 ± 0.011	4.28 ± 0.39	10.0 ± 1.2	1.3 ± 0.4
3500	0.283 ± 0.006	0.148 ± 0.011	3.97 ± 0.48	8.7 ± 1.3	1.5 ± 0.4
4000	0.254 ± 0.005	0.140 ± 0.010	3.67 ± 0.37	7.3 ± 0.8	1.0 ± 0.3
4600	0.225 ± 0.005	0.122 ± 0.008	3.49 ± 0.39	6.8 ± 0.9	0.8 ± 0.3
5300	0.197 ± 0.005	0.112 ± 0.005	3.06 ± 0.31	5.9 ± 0.8	0.7 ± 0.3

where S_n is the Ar^{n+} yield per unit electron beam intensity and μ is the effective target thickness of the atoms, a quantity related to the pressure recorded in the crossed beam vacuum chamber. The constant k is the overall detection efficiency of the argon ions. The ratios of S_n/S_1 for $n > 1$ were found to become constant when the potential difference through which the ions were accelerated to the particle multiplier was increased to values in the range 3–5 kV with the pulse discriminator level set at 50 mV. This confirmed our previous observation (Shah and Gilbody 1985) that the detection efficiency was equal for different charge states of the slow ions when accelerated through a potential difference of 5 kV.

In order to determine individual cross sections σ_n, the product $k\mu$ in equation (1) was determined by normalizing our relative values of the total cross section $\sigma_t = \Sigma_n n\sigma_n$ to the absolute values measured by Rapp and Englander-Golden (1965) in the range from near threshold to 1000 eV. Figure 2 shows the excellent overall agreement in the energy dependence of the two sets of data.

Our measured cross sections σ_n for $n = 1$–5 are given in table 1. The uncertainties associated with each individual cross section are assessed at the 67% confidence level and reflect the degree of reproducibility of the measured values in terms of the various experimental parameters and statistical fluctuations. An additional estimated uncertainty of ±8% in the absolute values of σ_n is associated with our normalization procedure.

3. Results and discussion

Figure 3 shows our measured cross sections σ_1 and σ_2 for single and double ionization. We also include results of some of the previous experimental measurements mentioned in section 1. Plots of the fractional deviation of these results from the present measurements are also shown to facilitate comparison. The discrepancies between these different results can be seen to be largest in the case of σ_2 although agreement in most cases is generally within the maximum combined experimental uncertainty. For example, we note that at 120 eV the cross section σ_2 obtained recently by Ma *et al* (1991) is 1.08 times our value while that obtained by both Wetzel *et al* (1987) and Tarnovsky and Becker (1991) is 0.88 times our value. The double peak structure in σ_1 clearly observable in the present data and some but not all previous measurements has been ascribed by Crowe *et al* (1972) to an autoionization process involving the 3d and 4p levels of argon. There is no evidence of structure in the corresponding cross section curve for σ_2.

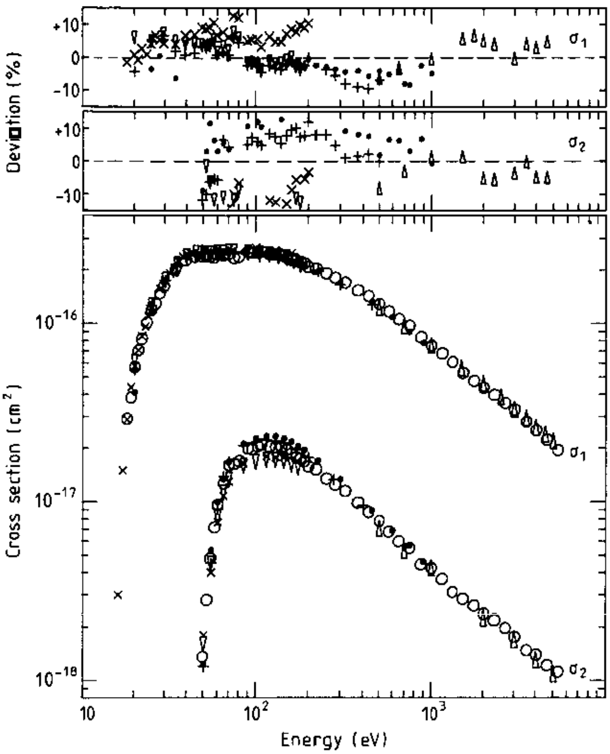

Figure 3. Cross sections σ_1 and σ_2 for single and double ionization of argon by electron impact. ○, present data; ×, Wetzel *et al* (1987) (note that these values are in very close agreement with those of Tarnovsky and Becker (1991) which are not shown separately); △, Nagy *et al* (1980); ▽, Stephan *et al* (1980); •, Krishnakumar and Srivastava (1988); +, Ma *et al* (1991). The upper plots show the fractional deviation of previous measured values of σ_1 and σ_2 from the present values.

In figure 4 we show our measured ratios $R = \sigma_2/\sigma_1$ of cross sections for double to single ionization together with the results of a number of previous measurements. These include recent measurements by Charlton *et al* (1989) using a scattering chamber technique and a single measurement at 40 MeV due to Müller *et al* (1988). The discrepancies between the values from different experiments can be seen to be greatest in the region where R attains a peak value. The energy dependence of R is very similar to that observed for a helium target (cf Shah *et al* 1988) in that, at high impact energies, R approaches an energy invariant value which the results of Müller *et al* (1988) at 40 MeV indicate is about 0.063 for argon and 2.6×10^{-3} for helium. The case of helium has been considered in terms of the simple shake model (cf McGuire 1982) in which, at high velocities, double ionization follows single ionization through final state rearrangement. The ratio R at high velocities is then expected to be independent of both the velocity and the properties of the projectile. However, at low and intermediate velocities, the large observed differences between the observed values of R for different projectiles are still the subject of further theoretical investigations (cf Charlton *et al* 1989). The present values of R shown in figure 4 do differ from the results of some of the previous experiments but, in most cases, agreement is within the maximum combined uncertainties. However, the values of R obtained by Krishnakumar and

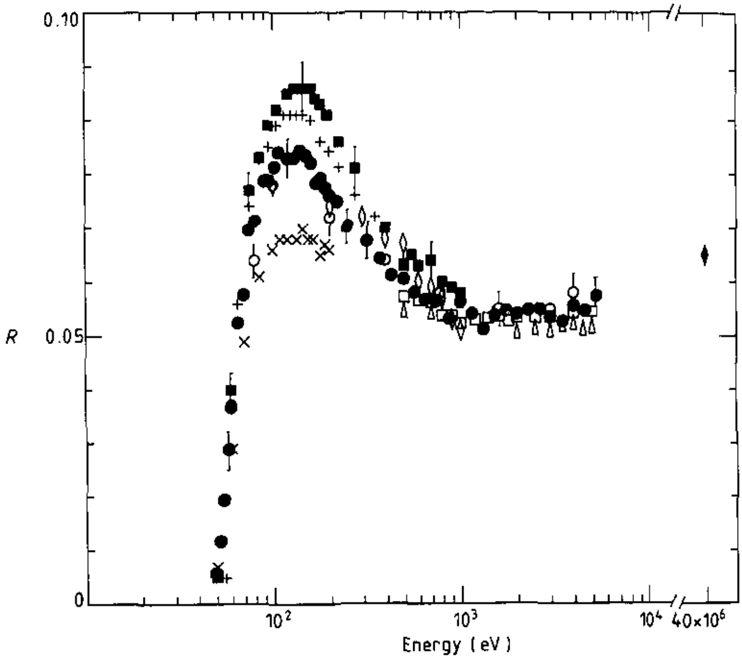

Figure 4. Ratio $R = \sigma_2/\sigma_1$ of cross sections for double to single ionization of argon. ●, present results including representative statistical uncertainties; ○, Charlton *et al* (1989) including representative statistical uncertainties; □, Schram (1966); △, Nagy *et al* (1980); ◇, Okudaira *et al* (1970); ■, Krishnakumar and Srivastava (1988); ×, Wetzel *et al* (1987); +, Ma *et al* (1991); ◆, Muller *et al* (1983) obtained at 40 MeV.

Srivastava (1988) can be seen to be up to 1.2 times larger than the present values in the region where R attains a maximum value. The high energy trend of our results can be seen to be consistent with the single value of R obtained at 40 MeV by Müller *et al* (1988).

In figure 5 we show our measured cross sections σ_3, σ_4 and σ_5 together with some of the previous experimental measurements. For the previous beam-static-gas measurements we note that our values of σ_3 are up to about 1.3 larger than those of Nagy *et al* (1980) and our respective values of σ_3, σ_4 and σ_5 are up to 1.2, 1.3 and 1.4 times larger than those of Schram (1966). In the latter case cross sections were derived from their measured abundance ratios by normalizing to our values of σ_t. The pronounced structure evident in the curve for σ_3 is believed (cf Okudaira *et al* 1970) to arise from an Auger cascade mechanism $A^{+}_{L_1} \to A^{2+}_{L_{2,3}M_1} \to A^{3+3}_{M_1M_2M_{2,3}}$ following ejection of an electron from the L shell by electron impact in the range 245–287 eV. There is no clear evidence of similar processes in the curves for σ_4 and σ_5.

Theoretical estimates of cross sections for ionization of argon are available only in the case of σ_1. In figure 6 the present values of σ_1 are compared with a number of calculated values. All the calculations can be seen to provide overestimates of the cross section at energies in the region of and beyond the cross section peak values. The values calculated by Peach (1971) using the Ochkur approximation can be seen to be in reasonable agreement with experiment only at low impact energies below the cross section peak. Cross sections based on the distorted wave approximation by Younger

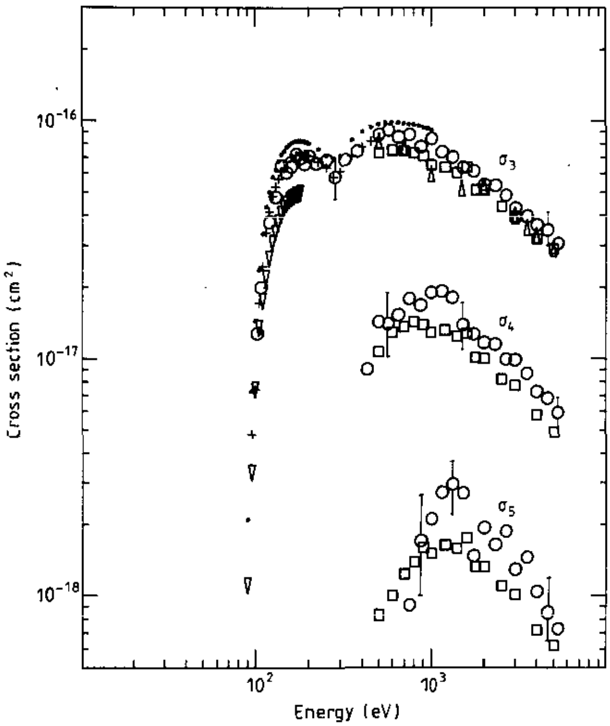

Figure 5. Cross sections σ_3, σ_4 and σ_5 for Ar^{3+}, Ar^{4+} and Ar^{5+} production in collisions of electrons with argon. ○, present results; ▽, Stephan *et al* (1980); △, Nagy *et al* (1980); □, Schram (1966) (derived form measured abundance ratios); ×, Wetzel *et al* (1987); +, Ma *et al* (1991); •, Krishnakumar and Srivastava (1988).

(1982) are about 1.6 times larger than experiment in the cross section peak region. Values based on the generalized oscillator strength approximation (McGuire 1971), although larger, can be seen to be approaching the experimental values at energies beyond the cross section peak. The most recent calculations by Bartschat and Burke (1988) using the *R*-matrix approach, exhibit the best overall agreement with experiment at intermediate energies; in the cross section peak region these values are about 1.4 times our observed cross sections.

In conclusion, we believe that the present measurements provide a useful extension of the results of previous measurements in terms of the relatively wide energy range and charge states *n* considered. Some discrepancies with previous results have been noted and some of these exceed the maximum combined experimental uncertainties. There is no simple explanation of these discrepancies, although Bonham and Bruce (1991) are now trying to identify some of the main potential sources of error in different experimental approaches.

Note added in proof. Since this paper was submitted Syage (1991) has reported data for $n = 2$–5 up to 660 eV. He suggests that some of the discrepancies in previous data based on single particle counting are attributable to variations in the dependence of electron multiplier gain on the final energy of the product ions. However, full account for this possibility was taken in the present work.

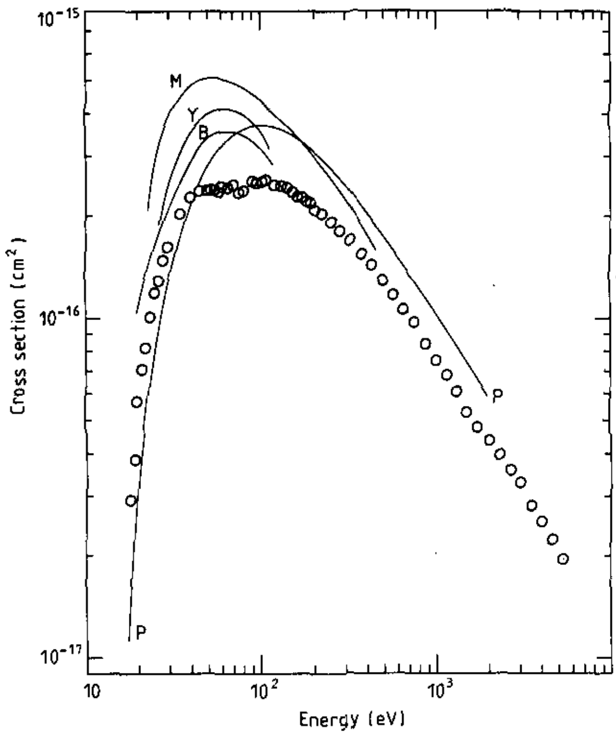

Figure 6. Comparison of present cross sections σ_1 for single ionization of argon by electrons with theoretical predictions. ○, present results; P, Peach (1971), Ochkur approximation; M, McGuire (1971), generalized oscillator strength approximation; Y, Younger (1982), distorted wave approximation; B, Bartschat and Burke (1988), *R*-matrix method.

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