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LETTER TO THE EDITOR

Electron impact cross sections for multiple ionization of Ar: detector gain effects revealed

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Abstract. Partial cross sections were measured for the ionization $Ar+e\to Ar^{n+}+(n+1)e$ for $n=2$–5 as a function of electron energy (0–660 eV). Although recent investigations are in agreement with regard to the absolute cross sections for single ionization, large discrepancies still exist for multiple ionization. Our results support the measurements of Stephan *et al* and Wetzel *et al*, but disagree with other recent studies which invariably obtain larger cross sections. These discrepancies are attributable to the dependence of electron multiplier gain on ion impact energy and, therefore, ion charge. The cross sections presented here for Ar^{4+} and Ar^{5+} have not been previously measured.

The difficulty in measuring absolute cross sections for electron impact ionization is well documented (Märk 1985, Kieffer and Dunn 1966). Standard methods, based on commercial instruments, have proved inadequate. Deficiencies such as ion extraction and detection efficiencies that discriminate on the basis of mass-to-charge ratio m/z, adversely affect measurements of absolute cross sections. Variations in electron beam focusing and flux with energy distort the relative shape of cross section curves. Advances have been made to overcome these problems by implementing pulsed extraction, ion counting and internal standards to name a few. Generally good agreement is now obtained by different investigators for single ionization measurements of atoms. The cross sections for Ar^+ are considered reliable to within a few per cent.

We address a concern regarding measurements of multiple ionization cross sections. The most extensive and sophisticated measurements of partial ionization cross sections include those by Stephan *et al* (1980), Wetzel *et al* (1987) and Krishnakumar and Srivastava (1988) for the rare gases. The measurements of single ionization of the rare gases are in excellent agreement and stand as benchmark values. Ma *et al* (1991) have also measured partial ionization cross sections for Ar and obtain excellent agreement with the other results for Ar^+. Several other studies (Nagy *et al* 1980, Crowe *et al* 1972, Fletcher and Cowling 1973, Mathur and Badrinathan 1984) show general agreement for single ionization of Ar. The measured cross sections for multiple ionization, however, differ markedly among these studies. It is striking that the most recent measurements for Ar^{n+} seem to group into two sets of results such that the values of one group (Stephan *et al* 1980, Wetzel *et al* 1987) differ from the other group (Krishnakumar and Srivastava 1988, Ma *et al* 1991) by a margin that increases with ion charge.

In this letter, we show that the discrepancies in the reported cross sections for multiple ionization by electron impact are due to the dependence of electron multiplier gain on ion impact energy, which in turn depends on ion charge. This effect has long been known to distort measurements of relative intensities of ions of different charge when detecting current or charge at the detector anode (Fields *et al* 1977, Fox *et al* 1970, LaLau 1970, Burrous *et al* 1967). Pulse counting is used to alleviate this problem; however, we show that it is also vulnerable to discrimination effects because the pulse height distributions also vary with impact energy. We explore the extent of this problem for multiple ionization of Ar and reconcile previous discrepancies in terms of this detector gain effect.

Our experiment is based on a crossed electron-atomic beam, time-of-flight (TOF) mass spectrometer that has been described before (Syage 1988). Full details will be given elsewhere (Syage 1991). Briefly, a pulsed electron beam (50–500 ns) is crossed with an Ar beam (400 μs) in a field-free region. The ions are subsequently extracted by an electric field pulse (100 V, 4 μs) and accelerated (1500 V) toward an electron multiplier detector. The repetition rate is limited by the mechanics of the pulsed atomic beam valve to 50 Hz. (We now trigger the electron excitation/TOF mass detection sequence repetitively for the full duration of the gas pulse, thereby increasing the effective repetition rate to about 500 Hz.) Singly- and multiply-charged Ar ions are detected simultaneously by a TOF mass spectrometer. The relative intensities are normalized to the known cross sections for Ar^+ to obtain the cross sections for Ar^{n+} according to the expression

$$\sigma_M(E) = \frac{I_M}{I_R}\sigma_R(E)\kappa_{M,R}$$

where M and R refer to the measured ion Ar^{n+} and reference ion Ar^+, respectively. The present method overcomes many common discriminator effects such as the dependence of ion extraction efficiency on ion mass and velocity (Syage 1988, 1991). Effects that are independent of ion, such as the variation of electron flux with energy, cancel. Residual discrimination effects that differ for ions M and R are encompassed by $\kappa_{M,R}$ and include deflection efficiency and detector gain effects.

Deflector plates are used to compensate for the velocity of the atomic beam, which is perpendicular to the field that accelerates the ions toward the detector. The deflection efficiency is easily optimized to a value that is within 1% for all Ar^{n+} ions (Syage 1991). The energy dependent cross sections are measured by scanning the electron energy E (in 2 eV increments) and recording the detector anode charge by gated integration over the TOF duration for each ion. This current measurement has very high sensitivity, but does not establish the absolute scale because of the detector gain dependence on ion charge. The energy-dependent curves are scaled by relative intensities measured by pulse counting at several energies. By using these procedures $\kappa_{M,R} = 1$ in these studies.

An important point of this letter concerns how detector m/z discrimination effects perturb measurements of cross sections for multiple ionization, even when using pulse counting detection. Figure 1 shows the measured pulse height distributions (PHD) for detection of Ar^+, Ar^{2+}, and Ar^{4+} using a dual microchannel plate detector (MCP) (18 mm diameter, 50 Ω anode, operated at 1 kV per plate). The anode pulses were amplified and a bandwidth limiter (50 MHz) was used to eliminate ringing that can cause spurious counts at low discriminator levels. The ions are accelerated toward the MCP by a 1.55 kV potential. The front surface of the MCP is biased at −2.2 kV. The ion impact energies are, therefore, given by $n \times (1.55+2.2)$ keV. The relative MCP gain for Ar^{n+} detection in figure 2(a) was determined by comparing the intensity ratios for Ar^{n+}/Ar^+ measured by anode current versus pulse counting. An independent

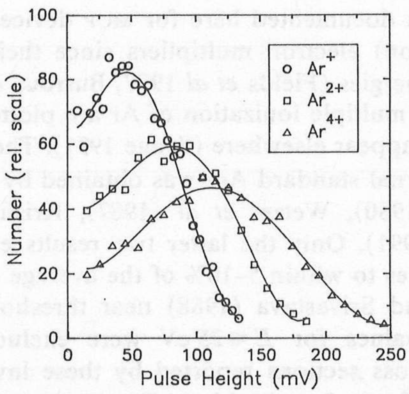

Figure 1. Pulse height distributions for detection of Ar^+, Ar^{2+} and Ar^{4+} produced by 470 eV excitation. Counts were measured over 5 mV channels. Curves are drawn through points for clarity. Each set of data has been normalized to the same total number of counts. Pulse heights include preamplification and filtering.

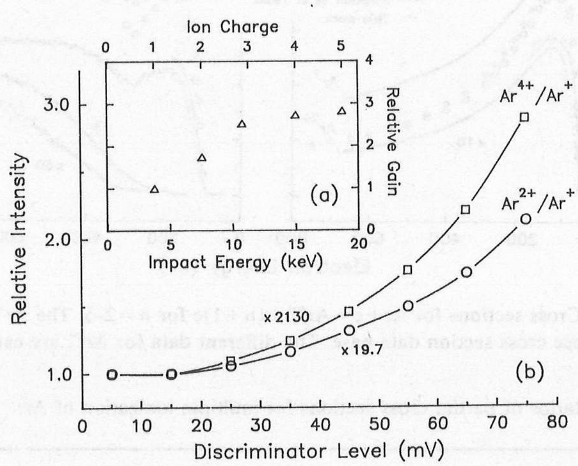

Figure 2. (a) Detector gain as a function of ion impact energy and corresponding ion charge. (b) Ratio of ion counts for Ar^{2+}/Ar^+ and Ar^{4+}/Ar^+ as a function of discriminator level. Electron energy was 470 eV.

determination was also made based on the PHD mean pulse heights. The onset to saturation in the gain versus impact energy curve in figure 2(a) occurs at about 10 keV. Similar measurements for Kr^{n+} and Xe^{n+} indicate that the onset to gain saturation occurs at higher impact energy with increasing mass (Syage 1991).

The variations of PHD in figure 1 are a direct result of the MCP gain dependence on ion impact energy and can lead to systematic error in measuring relative intensities by pulse counting. This is illustrated in figure 2(b) for the relative counts measured for the ratios Ar^{2+}/Ar^+ and Ar^{4+}/Ar^+ as a function of discriminator level. The correct ratio, representing the ratio of cross sections $\sigma_{Ar^{n+}}/\sigma_{Ar^+}$, is obtained only at very low discriminator levels where the counting efficiency is the same for both ions. As discriminator levels are increased, the count rate for Ar^+ falls off more rapidly than for Ar^{n+} causing a distortion in the measure of relative intensity that overstates the cross section for multiple ionization. The severity of this distortion increases with ion charge. The problem of gain effects documented here for MCP devices may be less serious for channeltron (or spiratron) electron multipliers since their gain curves typically saturate at lower impact energies (Fields *et al* 1977, Burrous *et al* 1967).

The measured cross sections for multiple ionization of Ar are plotted in figure 3. A comprehensive table of data will appear elsewhere (Syage 1991). The reference set of cross sections $\sigma_R(E)$ for the internal standard Ar^+ was obtained by averaging the measurements of Stephan *et al* (1980), Wetzel *et al* (1987), Krishnakumar and Srivastava (1988) and Ma *et al* (1991). Only the latter two results extend beyond 200 eV. Each set of σ_{Ar^+} values agrees to within 5–10% of the average except for the measurements of Krishnakumar and Srivastava (1988) near threshold, which are significantly lower; hence, their values for $E \leqslant 25$ eV were excluded from the average. The multiple ionization cross sections reported by these investigators are compared to the present results in figure 3 and table 1. Two noteworthy trends are

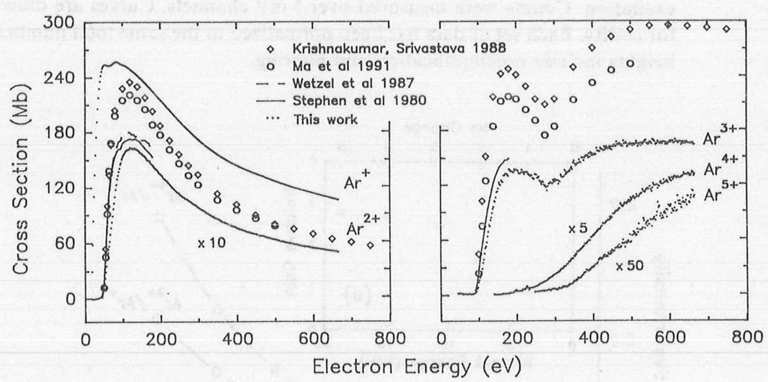

Figure 3. Cross sections for $Ar + e \rightarrow Ar^{n+} + (n+1)e$ for $n = 2$–5. The Ar^+ points represent the reference cross section data base. The different data for Ar^{2+} are each scaled by ×10.

Table 1. Ratios of partial cross sections for multiple ionization of Ar.

		$\sigma(M^{n+})/\sigma(M^{m+})$				
M (*n*, *m*)	*E* (eV)	This work	SHM[a]	WBHF[b]	KS[c]	MSB[d]
Ar (2, 1)	50	0.00462	0.0064	0.0069	0.00497	0.0048
	100	0.0606	0.068	0.0651	0.0904	0.0870
	150	0.0659	0.071	0.0673	0.0966	0.0909
	200	0.0626		0.0660	0.0895	0.0843
	300	0.0569			0.0786	0.0745
Ar (3, 1)	100	0.00017	0.0003		0.00057	0.0003
	150	0.00157	0.0019		0.00335	0.0029
	180	0.00203	0.0023		0.00380	0.0033
	300	0.00243			0.00419	0.0037
	400	0.00351			0.00627	0.0057
	500	0.00432			0.00771	0.0069
	600	0.00487			0.00901	

[a] Stephan *et al* (1980).
[b] Wetzel *et al* (1987).
[c] Krishnakumar and Srivastava (1988).
[d] Ma *et al* (1991).

apparent: (i) our results are in excellent agreement with Stephan *et al* (1980) and Wetzel *et al* (1987); and (ii) the discrepancy between these results and those of Krishnakumar and Srivastava (1988) and Ma *et al* (1991) increases with ion charge. We refer to these two groupings of results as group I and group II, respectively, and interpret the differences in terms of the detector gain effects described above.

Stephan *et al* (1980) employed a Faraday cup and electrometer to measure total charge reaching the detector. This device, unlike an electron multiplier, is free of discrimination effects that depend on ion impact energy. Wetzel *et al* (1987) used a MCP and pulse counting to measure ion intensities. They tested the gain characteristics of their detector to arrive at operating conditions that ensure maximum counting efficiency for all ions (Wiza 1979). These two studies, for which gain effects are either absent or avoided, are in agreement with the present results. This gives us confidence in the absolute values of the cross sections reported here and in group I.

The multiple ionization cross sections reported by group II are important because they extend to much higher energy than previously measured. The energy-dependent shapes of these curves are in good agreement with the group I results; however, the magnitudes are much larger. It is difficult to judge whether the group II results suffer from detector gain effects because sufficient experimental detail is not provided. Krishnakumar and Srivastava (1988) employ pulse counting but the detector used is not mentioned; we assume an electron multiplier from their earlier work (Orient and Srivastava 1983). The experiment by Ma *et al* (1991) suffered from noise which prevented them from using low discriminator levels. They ruled out detector effects on the basis of relative intensities $I_{Ar^+}/I_{Ar^{2+}}$ that did not vary with ion impact energy ranging from 2–4/4–8 keV. However, this ratio is not expected to vary as long as the increase in gain for these ions is linear, which is the case for our detector up to 10 keV impact energy (figure 2(*a*)). That the discrepancy in the measured cross sections in group II relative to group I increases with n is consistent with a detector gain effect. This trend is also apparent in the partial cross section measurements by Krishnakumar and Srivastava (1988) for Kr^{n+} ($n=1$–4) and Xe^{n+} ($n=1$–5). Their values for $n=4$ are about twice that measured by Stephan *et al* (1980) and Stephan and Mark (1984) and in our laboratory (Syage 1991).

Finally, we comment on the much higher intensity ratios measured for multiply-charged to singly-charged rare gas ions by Van der Wiel *et al* (1969) and El Sherbini *et al* (1970) compared with Nagy *et al* (1980) and Schram *et al* (1966a, b) in experiments that focused on high energy (>500 eV) excitation. For Ar, the discrepancy ranges from a factor of 1.7 for $n=2$ to a factor of 4 for $n=5$. These factors scale closely to the relative gain that we have measured (figure 2(*a*)), which suggests that an electron multiplier discrimination effect may explain the larger set of values in this group of studies.

To summarize, this work presents absolute cross sections for multiple ionization of Ar by electron impact. Cross sections for Ar^{4+} and Ar^{5+}, to our knowledge, have not been previously reported over the energy range studied here. Literature values for Ar^{2+} and Ar^{3+} show large discrepancies that we attribute to a detector gain effect that adversely affects pulse counting measurements. Because the pulse height distributions depend on gain which varies with ion charge, the counting efficiencies for each ion will likewise vary unless saturated pulse conditions and minimal discriminator levels are employed.

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