Mon. Not. R. astr. Soc. (1983) **203**, 1269–1280

Electron impact ionization of complex ions*

Alan Burgess and Marita C. Chidichimo *Department of Applied Mathematics and Theoretical Physics, Silver Street, Cambridge CB3 9EW*

Received 1982 October 30; in original form 1982 August 23

Summary. The simple procedure suggested by Burgess *et al.* to allow for inner-shell excitation and auto-ionization has been used with an empirical formula of similar form to that of Lotz and compared with a wide range of crossed-beam experimental data for ions of charge $z \geqslant 2$. The resulting simple general formula for the total ionization cross-section, and the corresponding rate coefficient, represents the experimental data to within ± 23 per cent rms deviation. The formula is consistent with the earlier formulae of Seaton (valid only near threshold) and of Lotz, but gives a significantly smaller rms deviation through the consistent inclusion of auto-ionization effects. For simple ions, comparisons with much more elaborate quantal calculations are satisfactory. Comparisons are also made with the simplified ECIP formula.

For more complex ions, any accurate quantal calculation would require consideration of the effects of strong coupling between final states. Some allowance for these effects is included in our procedure, and agreement with experiments for these complex ions is reasonably good.

1 Introduction

Collision cross-sections for electron impact ionization of highly charged ions are essential to the analysis of astrophysical and laboratory plasmas. A very wide range of elements and stages of ionization may be involved. Accurate *ab initio* calculations are very difficult because of the infinite number of strongly coupled final states, and direct laboratory measurements, for example by the crossed-beam method, are also difficult as the cross-sections become very small when the ion charge becomes large. Hence the need for semi-empirical formulae to fit to, and extend, what experimental and theoretical data are available.

For plasmas near to ionization balance, cross-sections mainly near to threshold are required and the formula due to Seaton (1964) has been widely used. However, for rapidly evolving non-equilibrium plasmas, cross-sections well above threshold may be required and formulae such as Lotz (1968) may then be more appropriate.

The excitation of auto-ionizing states can, in some cases, strongly affect the ionization cross-section. As they stand, neither of the above formulae take this into account. However,

* We would like to dedicate this paper to Professor M. J. Seaton FRS in honour of his sixtieth birthday.

for ions of not too high a charge, a simple procedure to allow for auto-ionization effects in such formulae was suggested in Burgess *et al.* (1977) and subsequent detailed quantal calculations for N^{+2} (Chidichimo 1982) have confirmed this procedure.

Since the 1977 review (Burgess *et al.*), further crossed-beam experimental data, covering a wider range of ion charge, have become available. A reassessment, taking into account both the new data and the auto-ionization effects, is therefore timely. In this paper we assess the data for ions of initial charge number $+z$, with $z \geqslant 2$; for these ions there is a relatively small scatter, and we find we can represent all the data to within ±23 per cent rms deviation. We also reassess the simple ECIP formula (Burgess 1964; Burgess & Summers 1976) and show how our results relate to recent Born approximation (Moores, Golden & Sampson 1980; Sampson & Golden 1981; Sampson 1982) and distorted-wave (Griffin, Bottcher & Pindzola 1982) calculations.

2 The semi-empirical formula

To show (and analyse) clearly the experimental results, we express them relative to a simple functional form which follows the dominant form of variation of the cross-section at all energies. Thus, for incident electron energy E we write the ionization cross-section as

$$Q(E) = C \sum_j \zeta_j (I_H/I_j)^2 (I_j/E) \ln (E/I_j)\, W(E/I_j) \qquad (\pi a_0^2), \tag{1}$$

where the summation is over shells (or subshells) j of the initial ion, ζ_j is the effective number of electrons in j, I_j is the effective ionization energy of j (this may differ from the true ionization energy because of auto-ionization effects), and $I_H = 13.6058$ eV. The function $W(E/I_j)$ represents approximately the deviation from linear behaviour in the threshold neighbourhood (Wannier 1953; Peterkop & Liepinski 1981), and is given by

$$W(E/I_j) = \begin{cases} 0 & (E \leqslant I_j) \\ [\ln (E/I_j)]^{\beta I_j/E} & (E > I_j) \end{cases} \tag{2}$$

where

$$\beta = \frac{1}{4} \{[(100z + 91)/(4z + 3)]^{1/2} - 5\}. \tag{3}$$

It has a significant effect only for small z and E very near threshold.

For any given experimental $Q(E)$ (once the ζ_j and I_j have been assigned), equation (1) defines the value of C as a function of E. Thus C is finite and slowly varying for all E and it shows more clearly the variation of the experimental results than Q itself, especially in the near threshold region where Q is small and rapidly varying. For assessing the data and for taking evenly weighted means over ions and energy ranges, plots of C are therefore much more useful than the usual Q plots.

3 Assignment of ζ_j and I_j

(a) If there are no significant contributions to Q arising from excitation of auto-ionizing states, ζ_j is the actual number of electrons in j, and I_j is the true ionization energy of j.

(b) To take into account auto-ionization contributions, we use the procedure and categorization of ions defined in Burgess *et al.* (1977, pp. 277–8). Thus, if the lowest configuration obtainable by excitation of an inner-shell electron lies well above the outer-shell

ionization threshold, we have case (i); if it is well below, the case is (ii). In the earlier paper, all the inner-shell excitations clearly separated into cases (i) or (ii): no intermediate cases arose. With the new data, there are now some intermediate cases (Ti^{+3}, Zr^{+3}, Hf^{+3}) and we designate them as case (iii).

Case (i) leads to jumps in the cross-section but at energies well above threshold, where the outer-shell contribution is substantial. We can thus, to a reasonable approximation, take the inner-shell contributions into account by setting I_j equal to the excitation energy of the lowest auto-ionizing state reachable by the ξ_j inner-shell electrons involved.

Case (ii) inner-shell excitations lead to a large number of small jumps in the cross-section, and we set those I_j equal to the outer-shell ionization energy as discussed in Burgess *et al.* (1977). The accuracy of this procedure has been checked by detailed distorted-wave calculations for N^{+2} (Chidichimo 1982).

Case (iii) inner-shell excitations lead to substantial jumps in the cross-section near to threshold where the outer-shell contribution is small. Thus, in this energy region, the total cross-section depends critically on the detailed positions and types of the inner-shell excited states and it is not obvious how to apply any simple semi-empirical formula. We therefore defer consideration of these cases to a later section (Section 8).

Table 1. Details and parameters for ions used in crossed-beam experiments.

Ion		Contributing shell	$\{\xi_j\}$	$\{I_j\}$ eV	$\bar{C}$	Reference
B^{+3}	(a)	$1s^2$	2	259.4	2.34 ± 19%	1
C^{+4}	(a)	$1s^2$	2	392.1	2.28 ± 32%	1
N^{+5}	(a)	$1s^2$	2	552.1	3.28 ± 11%	1
C^{+3}	(b)	$1s^2 2s$	2(i), 1	300, 64.5	1.82 ± 7%	2
N^{+4}	(b)	$1s^2 2s$	2(i), 1	420, 97.9	2.38 ± 5%	2
O^{+5}	(b)	$1s^2 2s$	2(i), 1	530, 138.1	2.61 ± 10%	2
C^{+2}	(b)	$2s^2$	2	47.9	2.56 ± 10%	3
N^{+3}	(b)	$2s^2$	2	77.5	2.44 ± 12%	1
O^{+4}	(b)	$1s^2 2s^2$	2(i), 2	550, 113.9	2.87 ± 3%	1
N^{+2}	(b)	$2s^2 2p$	2(ii) + 1	47.4	2.18 ± 3%	4
O^{+3}	(b)	$2s^2 2p$	2(ii) + 1	77.4	2.25 ± 5%	1
O^{+2}	(b)	$2s^2 2p^2$	2(ii) + 2	54.9	2.36 ± 5%	5
Mg^{+2}	(b)	$2s^2 2p^6$	2(i), 6	105.1, 80.1	1.71 ± 22%	6
Al^{+2}	(b)	$2p^6 3s$	6(i), 1	80.0, 28.4	1.23 ± 8%	7
Si^{+3}	(b)	$2p^6 3s$	6(i), 1	112.0, 45.1	1.92 ± 16%	7
Ar^{+}	(b)★	$3s^2 3p^5$	2(i), 5	30.6, 27.6	1.86 ± 11%	8
Ar^{+2}	(b)	$3s^2 3p^4$	2(i), 4	44.5, 40.7	2.40 ± 20%	9
Ar^{+3}	(b)	$2s^2 2p^6 3s^2 3p^3$	2(i) + 6(i), 2(ii) + 3	250.0, 59.8	2.11 ± 12%	9
Ar^{+4}	(b)	$2s^2 2p^6 3s^2 3p^2$	2(i) + 6(i), 2(ii) + 2	250.0, 75.0	2.40 ± 15%	1,9†
Ar^{+5}	(b)	$2s^2 2p^6 3s^2 3p$	2(i) + 6(i), 2(ii) + 1	250.0, 91.0	2.72 ± 14%	9

★For Ar^{+}, the lowest state ($3s\,3p^6$) obtainable by excitation of an inner shell $3s$ electron, lies reasonably well below the outer-shell ionization threshold indicating case (ii). However, the higher ones are all above the threshold (starting with $3s\,3p^8 3d$ at about 3 eV above the threshold) so that the auto-ionizing states are [unusually for case (ii)] not closely spaced near to the outer-shell threshold. Thus it is probably more accurate to treat this as case (i).

† The two experiments are in good agreement and we adopt the mean of the two sets of results.

References

1. Crandall, Phaneuf & Gregory (1979)
2. Crandall *et al.* (1979)
3. Woodruff *et al.* (1978)
4. Aitken, Harrison & Runder (1971)
5. Aitken & Harrison (1971)
6. Peart, Martin & Dolder (1969)
7. Crandall *et al.* (1982)
8. Woodruff, Hublet & Harrison (1978)
9. Müller *et al.* (1980)

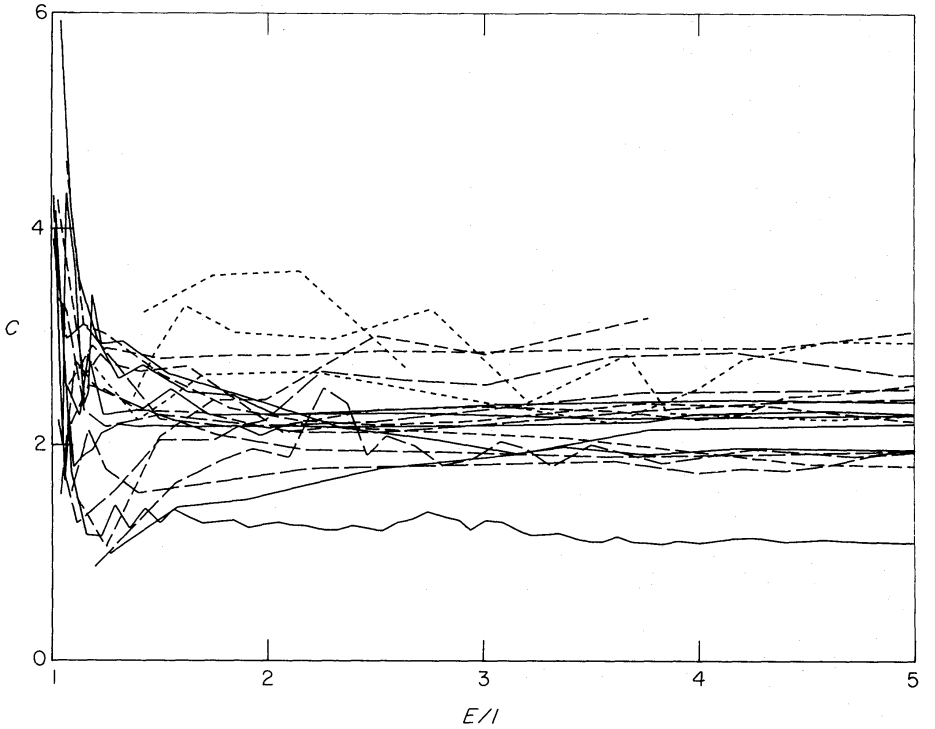

Figure 1. Parameter C for ions of charge $z \geqslant 2$, plotted against incident electron energy in threshold units. —— $z = 2$; – – $z = 3$; - - - $z = 4$; ----- $z = 5$.

In Table 1 we list the ions considered and indicate whether auto-ionization contributes or not [(b) or (a)]. The ordered sets of values of ζ_j and I_j adopted for each ion are also given. For inner-shell electrons, following each contribution to ζ_j, we give the case [(i) or (ii)].

4 Analysis of experimental results

Using the experimental results for Q and the ζ_j, I_j values specified in Table 1, the values of C as a function of energy can be obtained, for each particular ion, from equation (1). The results* for all ions with $z \geqslant 2$ are shown in Fig. 1, where C is plotted as a function of E/I, with I equal to the outer-shell I_j. It is seen that for any particular ion the values of C (as E/I varies) are constant to quite a good approximation. Just near to threshold there is more scatter in the C values due to the larger experimental errors, but there is no systematic variation in C. Thus, the simple functional form (1) gives a remarkably good representation of the data if used with a value of C averaged over E/I for each ion. The mean value $\bar{C}$ and the rms deviation are shown for each ion in Table 1. The means were evaluated over the range $1.2 \leqslant E/I \leqslant 5$ to avoid the large experimental errors just near threshold. The average of the rms deviations shown in Table 1 is ±12 per cent.

The average rms deviation for ions having case (ii) inner-shell electrons is ±9 per cent. It is interesting to compare this with the mean rms deviation of ±27 per cent obtained for these ions if auto-ionization contributions are neglected [i.e. if they are treated as in Section 3(a)]. Thus, including auto-ionization as described in Burgess *et al.* (1977) gives a significant improvement to the fit.

If we now average the $\bar{C}$ values over all the ions with $z \geqslant 2$, we obtain a mean and rms deviation of $\bar{\bar{C}} = 2.30 \pm 19$ per cent. Thus, if equation (1) with $C = \bar{\bar{C}}$ is used as a 'general

*Detailed tabulated values for these ions, and for ions of lower charge, will be given elsewhere.

formula' for ionization of ions with $2 \leqslant z \leqslant 5$, then about 12 per cent deviation as E/I is varied, and about ±19 per cent deviation from ion to ion, should be expected. The combined effect of these two deviations (i.e. the rms deviation as both E/I and the ion change) is ±23 per cent.

It is interesting that this mean value of 2.30 lies very close to the value 2.2 adopted by Seaton (1964) in his semi-empirical formula valid near threshold. We also note that if auto-ionization contributions are neglected [i.e. all ions are treated as in Section 3(a)] we obtain a mean value of 2.70 for $\bar{\bar{C}}$, and this compares closely with the value 2.77 which was adopted by Lotz (1968) with a formula nearly the same as (1) and a procedure which neglected auto-ionization. However, for case (ii) ions, such a procedure leads to much greater deviations as E/I varies, as noted above.

5 The results for argon ions

The extremely simple formula proposed by Müller *et al.* (1980) for Ar^{+z} ($1 \leqslant z \leqslant 5$) deserves special attention. In spite of it making no explicit allowance for the varying number of outer-shell electrons or for inner-shell ionization and excitation to auto-ionizing states, it gives a good fit to their experimental data. However, the threshold energies that they use in their formula are extrapolated from their experimental results and are consistently lower than the accurate ionization energies derived from spectroscopic data. This suggests some inaccuracy in their electron energy scale. Since substantially different results are obtained if accurate ionization energies are used, the good fit may be partly fortuitous and a formula of their type is probably of limited use for ions of other species.

In Fig. 2 we show the values of C obtained using equation (1) with the data of Müller *et al.* (1980) and ζ_j, I_j as in Table 1. It is seen that the formula and procedure represents the data well. With $C = 2.3$ the overall rms deviation from the data is ~ 20 per cent.

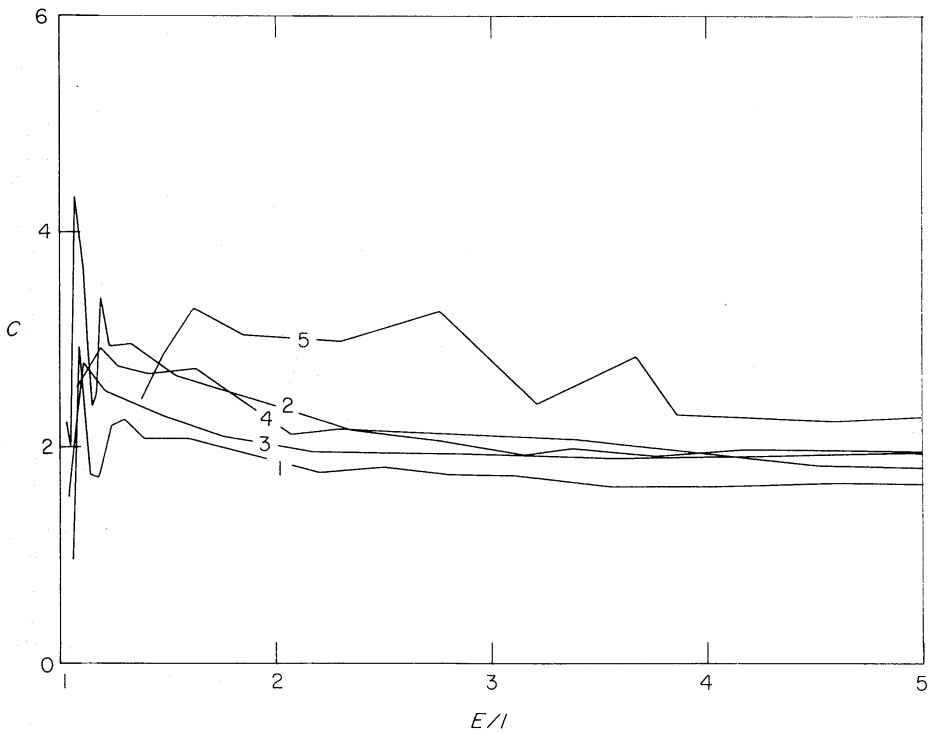

Figure 2. Parameter C for Ar^{+z} ions plotted against incident electron energy in threshold units. The curves are labelled by the values of z.

6 Highly charged ions

In the above analysis, we have assumed that all states produced by inner-shell excitation, that can auto-ionize, do in fact auto-ionize. They may, however, radiate instead. This causes a reduction in the total ionization cross-section. For the experimental ions considered in this paper ($2 \leqslant z \leqslant 5$), the effect is not important. However, for large values of z, the radiative rates increase rapidly so that procedure 3(a) should then be adopted. Preliminary estimates indicate that the effect becomes appreciable for $z > 10$.

Thus, for highly charged ions, neglecting the radiative effects may be regarded as giving an upper bound Q_U for the cross-section, while procedure 3(a) gives a lower bound Q_L. The way in which Q varies between these two bounds depends on z, E/I and the type of configuration. It may also depend on the effect of perturbing fields and particles on the ion. For example, in crossed-beam experiments, if the inner-shell excited ion does radiate instead of auto-ionizing, it may be left in a highly excited state which is then easily ionized by the large electric and magnetic fields acting on the ion. This therefore counteracts the radiative effects. For an ion in a plasma, secondary collisions may play a similar role.

The results in Section 4 show that averaging over $1.2 \leqslant E/I \leqslant 5$ and over ions with the configurations specified in Table 1 gives a mean value of $Q_L/Q_U \simeq 0.84$. However, some cases will have a much wider range of variation than this. For example, a limiting case is a $2s^2 2p$ or a $3s^2 3p$ ion of large z; for this, $Q_L/Q_U \simeq \frac{1}{3}$ when $E/I \simeq 1$. Further work is in progress.

7 Coulomb–Born approximation results

Sampson & Golden (1981) and Moores *et al.* (1980) have calculated the Coulomb–Born Exchange (CBE) cross-sections for ionization from the *nl* subshell of hydrogenic ions in the limit $z \to \infty$. Using their results in equation (1) (with $\{\zeta_j\} = \{1\}$; $\{I_H/I_j\} = \{n^2/z^2\}$ and taking

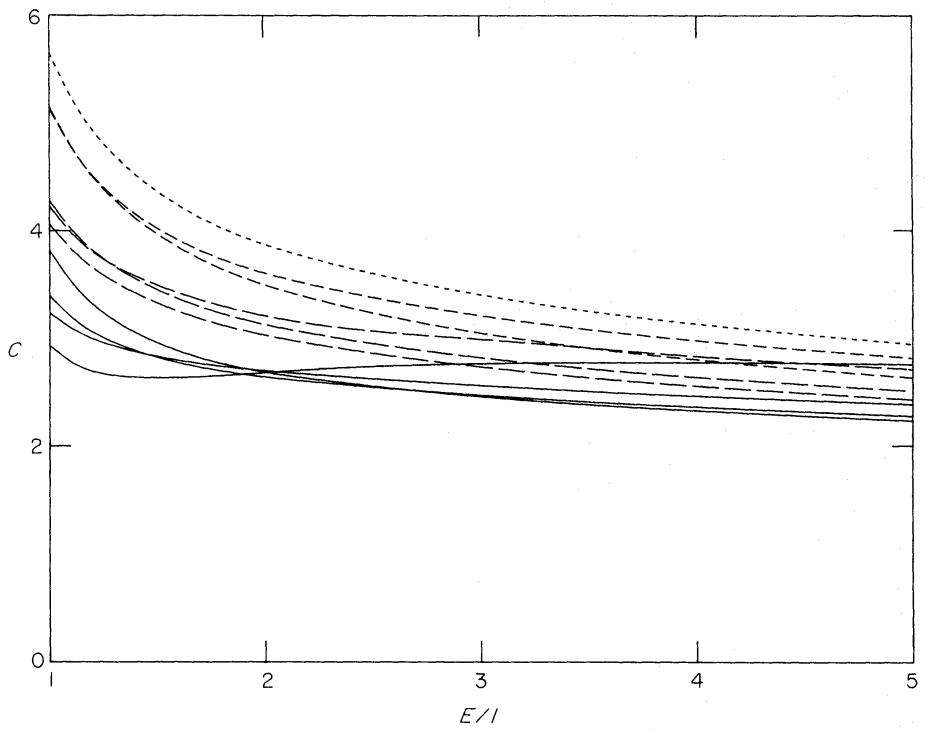

Figure 3. Parameter C for CBE $z = \infty$ hydrogenic *nl* orbitals, against incident electron energy in threshold units. Successive curves, reading upwards at $E/I = 1.0$, correspond to: $1s$, $2s$, $3s$, $4s$, $4p$, $2p$, $3p$, $4d$, $3d$, $4f$.

the limit $z \to \infty$), the corresponding values of C may be calculated. The values of C obtained, for all nl from $1s$ to $5f$ are shown in Fig. 3.

It is interesting to compare these values with those obtained from the crossed-beam experiments. For ions with $z \geqslant 2$, there are experiments only for $l = 0$ and 1, and the CBE results agree quite well with the experimental values of C. However, for larger values of l, the near-threshold CBE results show a trend to significantly higher values. On the other hand, for energies well above threshold, C lies close to the mean value 2.3 in all cases.

By employing z-scaling methods, the CBE $z = \infty$ results have been used to estimate ionization cross-sections for highly charged complex ions. In particular, Sampson (1982) has used them to get cross-sections and rate coefficients for a range of Na-like ions. These ions constitute a particularly testing case for our method since, although they have to be treated as case (i), the inner-shell contributions are very large and start at an energy not all that well above threshold. In Fig. 4 we compare the scaled CBE results (Sampson 1982) with our results for the ionization cross-section of Fe^{+15}, where we have used $C = 2.30$, $\{\zeta_j\} = \{2, 6, 1\}$ and $\{I_j\} = \{820, 709, 489.3\}$ eV in equation (1).

It is also interesting to compare the ionization rate coefficients (see Section 10) produced by the two methods. In Table 2 we give values of $\{I_j\}$, to be used in equation (6), for all the ions treated in Sampson (1982). The values of I_j for the $2s$ shell were estimated using a Slater-type model potential (Burgess, in preparation), so that some of the values of I_j differ slightly from those adopted by Sampson (1982), but not by enough to affect significantly the comparisons with the results in Sampson (1982). (See also the worked example in Section 10.) In Table 3 we compare our rate coefficients with those of Sampson (1982) for the selection of ions Ar^{+7}, Fe^{+15}, Mo^{+31}. The agreement, for this testing case, is good, certainly well within the range of variation to be expected from either of the methods. It is also clear that the neglect of radiative effects (Section 6) in our present results does not have a very large overall effect, even for Mo^{+31}.

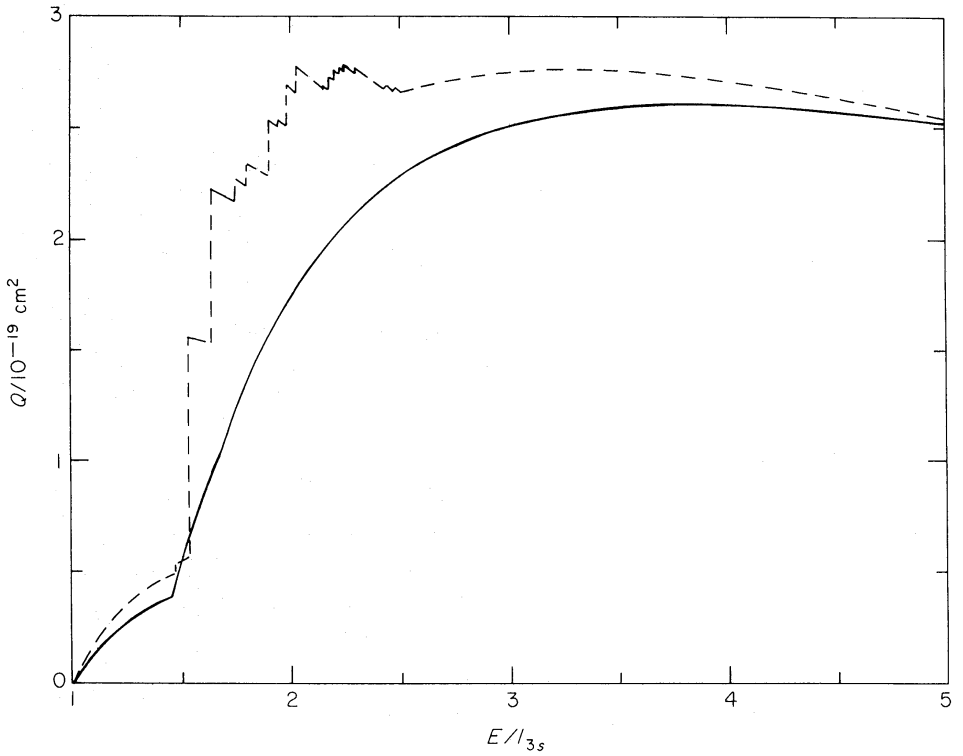

Figure 4. Total ionization cross-section Q (in units 10^{-19} cm^2) for Fe^{+15}, against incident electron energy in threshold units ($I_{3s} = 489.3$ eV). – – – – Sampson (1982); —— present results.

Table 2. Energies $\{I_j\}$ for Na-like ions.

Ion		$\{I_j\}$ eV	
Ar^{+7}	310	243	143.5
Ca^{+9}	420	336	211.3
Ti^{+11}	540	446	291.5
Cr^{+13}	670	569	384.2
Fe^{+15}	820	709	489.3
Ni^{+17}	990	863	607.0
Zn^{+19}	1170	1033	738
Ge^{+21}	1370	1222	881
Kr^{+25}	1810	1644	1206
Mo^{+31}	2600	2400	1792

Table 3. Ionization rate coefficients in units of 10^{-12} cm^3 s^{-1}.

	Ar^{+7}		Fe^{+15}		Mo^{+31}	
kT/I_{3s}	Equation (6)	Sampson (1982)	Equation (6)	Sampson (1982)	Equation (6)	Sampson (1982)
0.2	3.93(0)*	4.89(0)	7.90(−1)	1.14(0)	1.47(−1)	2.22(−1)
0.4	8.13(1)	1.17(2)	1.94(1)	2.78(1)	3.69(0)	4.78(0)
0.6	2.65(2)	3.95(2)	6.37(1)	8.57(1)	1.18(1)	1.37(1)
0.8	5.05(2)	7.44(2)	1.19(2)	1.52(2)	2.14(1)	2.33(1)
1.0	7.59(2)	1.09(3)	1.75(2)	2.15(2)	3.10(1)	3.22(1)
1.2	1.00(3)	1.42(3)	2.28(2)	2.71(2)	3.98(1)	4.00(1)
1.4	1.23(3)	1.70(3)	2.76(2)	3.20(2)	4.76(1)	4.68(1)
1.8	1.63(3)	2.18(3)	3.57(2)	3.98(2)	6.06(1)	5.76(1)
2.2	1.96(3)	2.54(3)	4.20(2)	4.57(2)	7.07(1)	6.56(1)
2.6	2.22(3)	2.82(3)	4.71(2)	5.02(2)	7.87(1)	7.17(1)
3.0	2.44(3)	3.04(3)	5.11(2)	5.37(2)	8.50(1)	7.64(1)

*The integer in brackets denotes the power of 10 by which the number preceding it should be multiplied.

8 Case (iii) ions

We consider here data for Ti^{+3}, Zr^{+3} and Hf^{+3} (Falk *et al.* 1981). These intermediate case ions are not easily treatable theoretically and special physical effects (concerned with final-state interactions) must be considered before they can be related to any semi-empirical formula, so they were not used in Section 4 to establish the mean value of C to employ in equation (1).

For energies of the inner-shell excited states, we use the calculated values of Griffin *et al.* (1982). These authors also give ionization cross-sections calculated using the distorted-wave approximation. However, these calculations suffer from three important defects:

(α) Only dipole-allowed transitions were taken into account. For near-threshold ionization, such transitions often contribute less than half the total cross-section.

(β) Weak coupling between initial and final states was assumed and exchange was neglected. This can lead to substantial over-estimation of the cross-section.

(γ) Interactions between final states of the ion + colliding electron system were neglected. This effect would be very difficult to include in any detailed quantal treatment but it is likely to be important for near-threshold ionization and does not appear to have been discussed previously in the literature. We discuss it further below.

In spite of the fact that (α) counteracts (β) to some extent, the calculations of Griffin *et al.* (1982) are roughly 2.5 times greater than the experimental values. This indicates that

strong coupling between initial and final states (β) is very important and hence that strong coupling between final states (which are energetically close) (γ) is also likely to be important for these ions.

In order to discuss the effect of final-state interactions we consider the case of Ti^{+3} (initial configuration $3s^2 3p^6 3d$). The lowest inner-shell excited configuration, $3s^2 3p^5 3d^2$, has 45 states $^{2S+1}L_J$, of which only six are above the outer-shell ionization threshold (43.25 eV). Neglecting radiative and perturbing field effects (see Section 6), the processes we need to consider in calculating the reactance matrix are

$$\mathrm{Ti}^{+3}(3p^6 3d) + e(E_1, l_1) \underset{\mathrm{A}}{\rightarrow} \mathrm{Ti}^{+3}(3p^5 3d^2\, {}^{2S+1}L_J) + e(E_2, l_2) \underset{\mathrm{C}}{\rightarrow} \mathrm{Ti}^{+4}(3p^6) + e(E_3, l_3) + e(E_2, l_2)$$

$$\downarrow\uparrow \mathrm{B}$$

$$\mathrm{Ti}^{+3}(3p^5 3d^2\, {}^{2S'+1}L'_{J'}) + e(E'_2, l'_2) \underset{\mathrm{D}}{\rightarrow} \mathrm{Ti}^{+4}(3p^6) + e(E'_3, l'_3) + e(E'_2, l'_2)$$

where $(E_1, l_1), (E_2, l_2), (E_3, l_3), (E'_2, l'_2)$ and (E'_3, l'_3) denote the energies and angular momentum quantum numbers of the continuum electrons.

If final-state interactions (B) are neglected, then only primary excitations (A) to the six states $^{2S+1}L_J$ that are above 43.25 eV can lead to ionization (C). But, if final-state interactions (B) are taken into account, primary excitations (A) to any of the 45 states $^{2S+1}L_J$ may in general lead to ionization (C) or (D), (provided only that the incident energy E_1 is sufficient to excite one of the states $^{2S+1}L_J$ that can auto-ionize).

In the limit of very strong coupling between the $^{2S+1}L_J$ states, one might expect the relative probability for ionization to be given by

$$\sum_J{}' (2J+1) \Big/ \sum_J (2J+1) \tag{4}$$

where Σ ranges over the states that can be excited and Σ' ranges over the states that can be excited and can auto-ionize. However, the relative probability for auto-ionization may be appreciably greater than this since the coupling to the continuum may greatly increase the

Table 4. Details and parameters for case (iii) ions.

Ion	Contributing shell	$\{\xi_j\}$	$\{I_j\}$ eV	$\bar{C}$
Sc^{+2}	$3p^6 3d$	6(ii) + 1	24.15	
Ti^{+3}	$3s^2 3p^6 3d$	2(i), 6(ii) + 1	64.0, 43.25	3.34 ± 8%
V^{+3}	$3p^6 3d^2$	6(ii) + 2	46.7	
Cr^{+2}	$3p^6 3d^3$	6(ii) + 3	49.1	
Mn^{+4}	$3p^6 3d^3$	6(ii) + 3	72.4	
Mn^{+3}	$3p^6 3d^4$	6(ii) + 4	51.2	
Fe^{+4}	$3p^6 3d^4$	6(ii) + 4	75.0	
Fe^{+3}	$3p^6 3d^5$	6(ii) + 5	54.8	
Co^{+4}	$3p^6 3d^5$	6(ii) + 5	79.5	
Ni^{+4}	$3p^6 3d^6$	6(ii) + 6	75.5	
Cu^{+4}	$3p^6 3d^7$	6(ii) + 7	79.9	
Zn^{+4}	$3p^6 3d^8$	6(ii) + 8	82.5	
Ga^{+4}	$3p^6 3d^9$	6(ii) + 9	85★	
Y^{+2}	$4p^6 4d$	6(ii) + 1	20.51	
Zr^{+3}	$4s^2 4p^6 4d$	2(i), 6(ii) + 1	56.0, 34.33	5.53 ± 14%
La^{+2}	$5p^6 5d$	6(ii) + 1	19.17	
Hf^{+3}	$5p^6 4f^{14} 5d$	14(i), 6(ii) + 1	36, 33.3	1.69 ± 16%

★Read from Griffen *et al.* (1982) plot.

effective statistical weight of the states that can auto-ionize. To allow properly for this effect, detailed calculations of the collision times and auto-ionization lifetimes would be required. In the absence of such calculations we make the simplifying assumption that the ratio (4) is equal to 1.

The assignments for $\{\xi_j\}$ and $\{I_j\}$ which we then make are as shown in Table 4, where we also give values for other case (iii) ions whose energy levels have been calculated by Griffin *et al.* (1982). The experimental results for Ti^{+3}, Zr^{+3} and Hf^{+3} (Falk *et al.* 1981) may then be used to obtain values for $\bar{C}$ as described in Section 4. The values of $\bar{C}$ are given in Table 4 and the cross-sections obtained using these values in equation (1) are compared with experiment in Fig. 5. The good agreement in curve shape and the reasonable agreement between the $\bar{C}$ values (*cf.* $\bar{\bar{C}} = 2.3$) for these difficult ions give some reassurance that the assumptions made above may have some validity.

For the other case (iii) ions given in Table 4, it is likely that (in lieu of experimental data) using $\bar{\bar{C}} = 2.3$ in equation (1) would give ionization cross-sections correct to a factor ~ 2 or 3, which is probably rather more accurate than a first-order distorted-wave calculation could be expected to be for these ions.

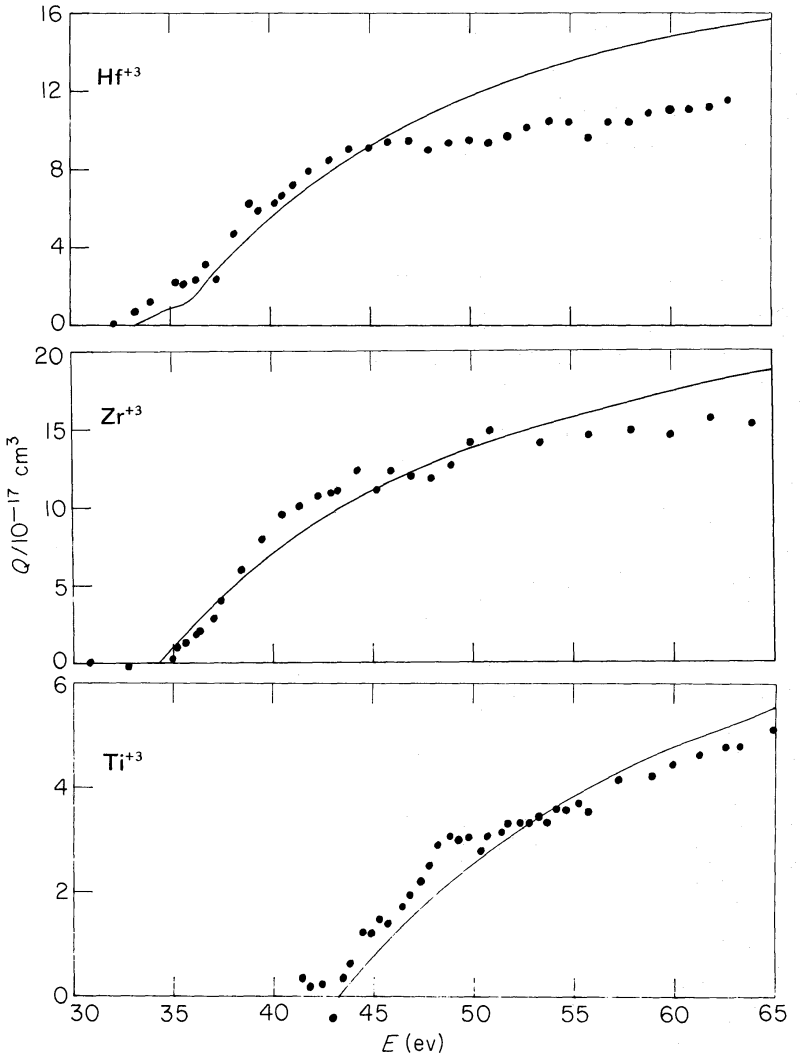

Figure 5. Total ionization cross-section Q (in units 10^{-17} cm^2) for Ti^{+3}, Zr^{+3} and Hf^{+3}, against incident electron energy in eV. —— Present results; • Experiment (Falk *et al.* 1981).

9 ECIP results

The exchange classical impact parameter method has been discussed in Burgess *et al.* (1977, see particularly p. 277). It is important to repeat that, in its usual simplified form, the method was not primarily intended to give the most accurate ground-state ionization cross-sections. Nevertheless, that is the form that has most often been adopted, so it may be of some interest to compare that form of ECIP with the present experimental data.

For the data of the previous review (Burgess *et al.* 1977) the averaged ratio ECIP/experiment was 1.06 (± 58 per cent). As elsewhere in this paper we give the rms deviation from the mean; in the previous review the standard deviation was given. For the present data, averaging over all the ions (except the singly charged case Ar^+) listed in Table 1 and including auto-ionization, we obtain a mean ECIP/experiment = 0.70 (±44 per cent). The main reason for this lower value is that the present data refer mainly to multiply charged ions ($z \geqslant 2$) whereas the earlier data were mainly for singly charged ions.

In general, ECIP (for ground-state ions) tends to be in quite good agreement with experiment for ions of low charge ($z < 2$) and for hydrogenic and helium-like ions. However, for other ions ECIP/experiment is on average $\simeq 0.6$.

10 Ionization rate coefficient

For ionization by thermalized electrons, the rate coefficient is

$$q = \int v Q(E)\, f(v)\, dv \tag{5}$$

where $f(v)$ is the Maxwell velocity distribution. The presence of the Wannier factor $W(E)$ in (1) prevents a simple analytic result for this. However, to a good approximation we have

$$q = 2.1715 \times 10^{-8}\, C \sum_j \zeta_j\, (I_H/I_j)^{3/2}\, (I_j/kT)^{1/2}\, E_1\, (I_j/kT)\, w \quad (\mathrm{cm^3\ s^{-1}}) \tag{6}$$

where $E_1(x)$ is the first exponential integral (see, e.g. Abramowitz & Stegun 1970, sections 5.1.53, 54) and

$$w = [\ln(1 + kT/I_j)]^{\beta/(1 + kT/I_j)} \tag{7}$$

with β given by equation (3). The factor w has a significant effect only for ions of low charge and for very small values of kT/I_j. Values of ζ_j, I_j and mean experimental values ($\bar{C}$) of C are given in Tables 1, 2 and 4.

For cases in which experimental data are not available, equation (6) may be used as a 'general formula' with the overall mean C value ($\bar{\bar{C}} = 2.3$), and with ζ_j, I_j assigned as described in Section 3 or 8. The inner-shell excitation energies, that are required in order first to decide whether the ion is case (i), (ii) or (iii) and then [if it is case (i)] to decide the values of I_j for the inner shells, may not always be readily available. However, in many cases they may be estimated quite simply and to sufficient accuracy for present purposes, by judicious use of energy level data for other related transitions.To illustrate the methods involved we consider a worked example:

$Fe^{+15}\ 2s^2 2p^6 3s$.

Energy level data are tabulated in Reader & Sugar (1975). We have Fe XVII $2s^2 2p^6$ – Fe XVI $2s^2 2p^6 3s$ = 3 946 150 cm^{-1}, so that I_{3s} = 489.3 eV directly. Similarly, Fe XVI $2s^2 2p^5 3s^2$ – $2s^2 2p^6 3s$ = 5 718 000 cm^{-1} so that I_{2p} = 709 eV [and we clearly have case (i)]. Unfortunately,

Fe XVI $2s2p^63s^2 - 2s^22p^63s$ has not been observed. However, we note that Fe XVIII $2s2p^6 - 2s^22p^5 = 1\,064\,610$ cm^{-1}, so that (assuming Fe XVIII $2s2p^6 - 2s^22p^5 \simeq$ Fe XVI $2s2p^63s^2 - 2s^22p^53s^2$), we have Fe XVI $2s2p^63s^2 - 2s^22p^63s = (2s2p^63s^2 - 2s^22p^53s^2) + (2s^22p^53s^2 - 2s^22p^63s) \simeq 5\,718\,000 + 1\,064\,610$ cm^{-1}, giving $I_{2s} \simeq 841$ eV. Similarly, if Fe XVI $2s^22p^53s^2 - 2s^22p^63s$ had not been observed, it could have been estimated roughly from Fe XVII $2s^22p^53s - 2s^22p^6 = 5\,852\,700$ cm^{-1}, giving $I_{2p} \simeq 726$ eV.

These simple rough estimates of I_{2s} and I_{2p} lead to rate coefficients which agree to within 7 per cent with those obtained from the more accurate energies adopted in Section 7.

11 Conclusions

The procedure suggested in Burgess *et al.* (1977) for allowing for inner-shell excitation and auto-ionization when used with an empirical formula of simple functional form similar to that of Lotz has been shown to be capable of representing a wide range of crossed-beam experimental data to a good accuracy. For complex ions having many, possibly strongly coupled, final states, the resulting general formula is probably at least as good as currently practicable *ab initio* quantal calculations. Further work is required on the effects of coupling between decaying and non-decaying final states.

Acknowledgment

This work was supported in part by an SERC grant.

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