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Multiple ionization of negative and positive ions, neutral atoms, and molecules under electron impact: data and databases

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Abstract

The present status of experimental cross section data for multiple ionization of neutral atoms/molecules and positive/negative ions under electron impact has been reviewed and some evaluated data are presented. (Int J Mass Spectrom 192 (1999) 75–85) © 1999 Elsevier Science B.V.

Keywords: Multiple ionization; Electron impact; Atom; Ion; Molecule; Databases

1. Introduction

Experimental investigations of multiple ionization of atoms (mostly rare gas and mercury atoms) by electron impact had begun in the early 1930s. Surprisingly, some of the cross sections are still in use as they have reasonable accuracies even by the present-day standards. A comprehensive survey of the data obtained before 1966 was summarized [1]. However, for measurements of the cross sections of the ionization of ions, where the effective target densities are extremely low compared with background neutral gas atoms/molecules in a collision region, a series of new techniques had to be developed in order to obtain reliable cross section data [2].

In addition to the basic interest in collision physics, multiple ionization of atoms and ions does play an important role in many fields of applications such as plasma physics, ion source developments, laser physics, and medical cancer treatments.

Most of the ionization cross section data including those for multiple ionization for both neutral atoms and positive and negative ions up to 1989 have been summarized in some articles [3–6]. General and basic theoretical aspects of multiple ionization processes have been described in [7]. Since then, through continuous efforts in both experiments and theories in order to obtain more detailed understanding of multiple ionization processes, a lot of single and multiple ionization cross section data are being accumulated for atoms and also for ions over a wide range of the charge state under electron impact.

Furthermore, with the advent of a new technique, namely an ion storage ring combined with an electron cooler, more detailed studies, in particular the resonance-like behavior of the cross sections due to the indirect ionization processes (see Sec. 2), are being

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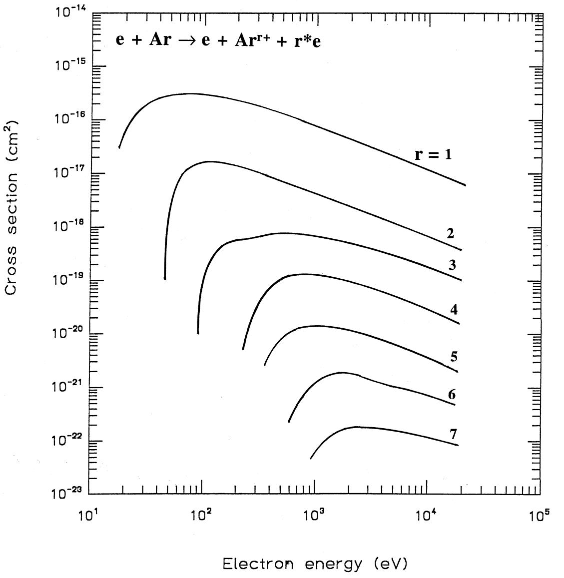

Fig. 1. Evaluated cross sections for the production of multiply charged A^{r+} ions up to $r = 7$ from neutral Ar atoms as a function of electron impact energy.

carried out [8]. The most recent compilation of ionization cross sections reported up to the mid-1998 has been published for atoms and ions under electron impact [9]. Fig. 1 shows the dependence of the evaluated cross sections [10] for the production of multiply charged A^{r+} ions from Ar atoms on the electron impact energy.

2. General features of multiple ionization by electron impact

Compared with the single ionization where the only direct ionization process plays a dominant role, multiple ionization processes are more complicated and, in addition to the direct ionization processes, so-called indirect ionization processes play a much more important role and often dominate over the direct ionization [11]. Some examples are give in the following.

(1) Direct process where r electrons are simultaneously removed under a single collision:

$$e + A^{q+} \rightarrow e + A^{(q+r)+} + r{*}e \tag{1}$$

where q is the initial charge state of the ion.

(2) Indirect processes: Typical indirect processes are as follows.

(a) One of the inner-shell electrons is first highly excited or ionized and then such an excited state or inner-shell vacancy state is stabilized through autoionization processes (EA):

$$e + A^{q+} \rightarrow e + A^{q+**} \rightarrow e + A^{(q+1)+*} + e \rightarrow \cdots \rightarrow e + A^{(q+r)+} + r{*}e \tag{2}$$

This cross section shows a relatively broad peak.

(b) The incident electron first excites one of the inner-shell electrons, losing most of its kinetic energy and, then, is resonantly captured into one of the highly excited states. The highly excited state is stabilized through autoionization processes [often called resonant excitation recombination–autoionization (RERA)]:

$$e + A^{q+} \rightarrow A^{(q-1)+***} \rightarrow A^{q+*} + e \rightarrow A^{(q+1)+*} + 2e \rightarrow \cdots \rightarrow A^{(q+r)+} + (r+1){*}e. \tag{3}$$

The cross section shows sharp resonance-like peaks at particular incident electron energies corresponding to the excited states of the target ion.

The contribution of the indirect ionization processes generally increases as the number of electrons in the ion increases. Such indirect ionization processes often enhance the ionization cross section by more than one order of magnitude over that for the direct ionization processes in a particular electron impact energy region. In fact, the indirect processes can clearly be seen even in total ionization cross sections. The cross section curve of the A^{3+} ion production from neutral Ar atom as seen in Fig. 1 has two broad peaks which can be easily understood as follows: the first peak at lower energy is due to the simultaneous ionization of three $3p$-shell electrons and the second peak at higher energy is due to the processes involving the inner-shell electrons, namely $2p$- or $2s$-shell electron ionization which follows the Auger electron emissions. As many closely spaced subshells can be involved in multiple ionization of heavier atoms/ions, such peaks tend to overlap and thus become indistinguishable, resulting in a broader

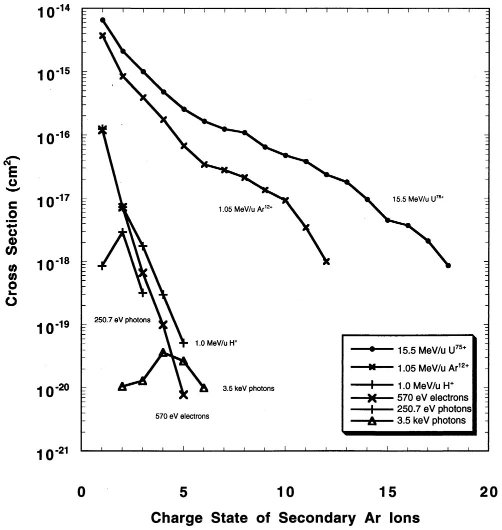

Fig. 2. Production cross sections of multiply charged Ar^{r+} ions under various particle impact on neutral Ar atoms as a function of the charge state of product ions. The incident particles include 15.5 MeV/u U^{75+} ions, 1.05 MeV/amu Ar^{12+} ions, 1.0 MeV/u H$^+$ ions, 570 eV electrons, 250.7 eV and 3.5 keV photons [12].

peak. It is clear that, in electron impact, the production cross section of multiply charged ions decreases drastically as the charge, r, of the ion defined in Eq. (1) increases (see Fig. 1). So far, a series of measurements of the cross section for multiple ionization of atoms and ions have also been performed under impact of different particles. The observed results show some common features and also significant difference among different incident particles. Typical examples of the observed multiple ionization cross section are shown in Fig. 2 for Ar atom targets under electron, proton, heavy ion and photon impact [12]. The multiple ionization cross sections under proton impact decrease very quickly with increasing the multiplicity, r, of the product ion, as in electron impact. But they are quite different from those under heavy particle impact where far more multiple ionization occurs due to the strong Coulomb interactions. Under the single impact of heavy particles such as a U^{75+} ion, all 18 electrons are ejected from the neutral Ar atom and bare Ar^{18+} ions are produced with significant cross section ($\sim 10^{-17}$ cm^2). There, in addition to the direct ionization processes, another important process, namely the capture of the inner-shell electrons into heavy projectile ions, significantly enhances the production of the secondary ions, in particular of multiply charged ions. It is noted in photon impact that the r dependence of the product ions shows a distinct photon energy dependence where the inner-shell electron ionization processes play an important role.

Table 1
Experimental data for ionization (electron detachment) of negative ions by electron impact

	Final charge	
Ion	Single ionization	Double ionization
H$^-$	H^0	H$^+$
B$^-$	B^0	B$^+$
C$^-$	C^0	C$^+$
O$^-$	O^0	O$^+$
F$^-$	F^0	F$^+$

3. Present status of experimental multiple ionization cross section data

Some detailed investigations have been performed on the multiple ionization of atoms and ions. The following gives a short summary of the present situation of the experimental investigations.

3.1. Negative ions

The ionization (electron detachment) experiments involving negative ions under electron impact are quite limited so far, as summarized [13] in Table 1. Only a few determinations of the ionization cross sections of negative ions have been reported. Some evaluated ionization cross sections have been given in a recent paper [14]. An interesting feature of the single electron-detachment cross section of H$^-$ and O$^-$ ions can be noted in Fig. 3 where the cross section is shown as a function of the reduced electron impact energy, namely the electron impact energy divided by the electron ionization energy: (1) The maximum cross section is roughly a factor of 6–10 small, compared with the scaled cross section taking into

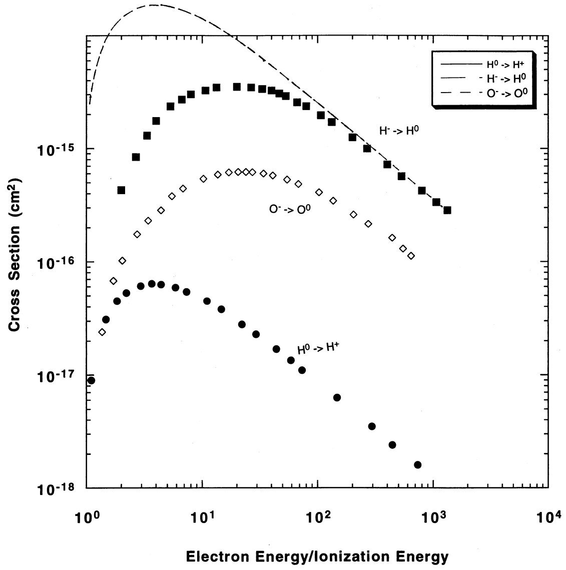

Fig. 3. Comparison of the evaluated cross sections of single ionization among negative ions and neutral atoms under electron impact. Their energy dependence for negative ions is clearly different from that for neutral atoms. The dotted curve at the top is scaled with the inverse square of the binding energy between negative hydrogen ions and neutral hydrogen atoms [thus, those for negative hydrogen ions are multiplied by $(13.6/0.75)^2 = 329$, compared with those for neutral hydrogen atoms].

account the ionization energy of the weakly bound outermost-shell electron in the negative ion, (2) the reduced energy, where the cross section becomes maximum, is a factor of 6–7 higher, compared with that for the neutral atom, and (3) the peak is much broader, compared with that for the ionization of neutral atom. These features can be understood qualitatively and also quantitatively due to the strong deflection of the weakly bound electron due to the incident electron, thus reducing the ionization probabilities at low energy impact [15,16]. This is supported by the fact that the cross sections at higher impact energies (more than a few 100 times the ionization energy) are roughly in an agreement with those empirically expected from the inverse square of the ionization energy. The detailed theoretical consideration on this problem has been recently given [17,18].

So far, the double ionization cross sections of some negative ions such as H^-, C^-, O^-, and F^- ions have

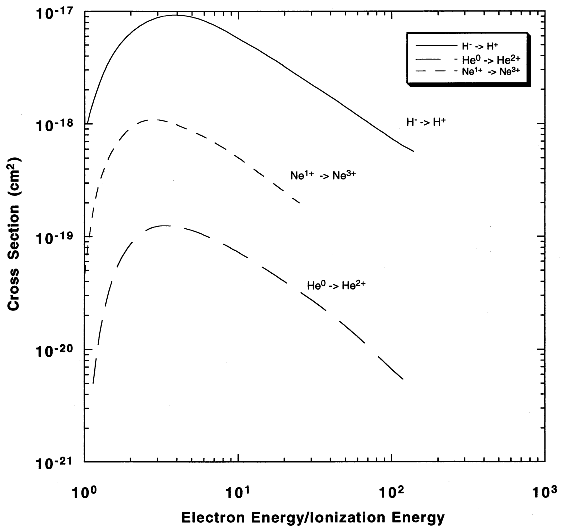

Fig. 4. Comparison of the evaluated cross sections of double electron ionization among negative ions, neutral atoms and positive ions under electron impact. Note that the electron impact energy seems to be similar among these three particle species.

been reported and recently summarized [12,19,20]. It is interesting to note that there is no such reduction of the double ionization cross sections of negative ions. A comparison shows that the dependence of the cross sections for the double ionization on the electron impact energy is practically the same for negative and positive ions as well as for neutral atoms (see Fig. 4). Unfortunately, no observation has been reported for higher multiple ionization removing more than two electrons from negative ion under electron impact.

3.2. Positive ions

In order to obtain reliable cross sections for the ionization of ions, the so-called crossed-beams method [2] is indispensable, but requires various new and advanced instruments and techniques. Technically, this method has been well developed. Yet only a few groups are working on this issue using such techniques. Table 2 summarizes the present situation for the ionization of ions with various charge states. Some evaluated cross section data for the single ionization of the singly charged ions have been given recently [21].

Table 2
Experimental work for ionization of positive ions by electron impact; the numbers show the entry for experiments performed so far

		Initial charge state																											
Element	Total	−1	+0	+1	+2	+3	+4	+5	+6	+7	+8	+9	+10	+11	+12	+13	+14	+15	+16	+17	+18	+19	+20	+21	+22	+23	+24	+25	+26
H	12	4	8																										
He	52	—	43	9																									
Li	21	—	9	10	2																								
Be	2	—	—	2	—	—																							
B	6	—	1	1	2	2	—																						
C	38	1	2	9	9	10	3	4																					
N	54	—	4	12	9	11	11	5	2																				
O	54	2	9	11	8	4	8	10	1	1																			
F	7	1	1	1	1	—	—	3	—	—	—																		
Ne	97	—	59	13	4	8	1	1	2	4	1	4																	
Na	20	—	7	11	1	—	—	—	—	—	—	—	—																
Mg	31	—	13	11	6	—	—	—	—	—	—	—	—	—															
Al	29	—	4	4	9	4	1	1	1	1	1	—	—	—	—														
Si	8	—	2	1	1	4	—	—	—	—	—	—	—	—	—	—													
P	8	—	2	1	—	—	5	—	—	—	—	—	—	—	—	—	—												
S	14	—	6	3	1	—	4	—	—	—	—	—	—	—	—	—	—	—											
Cl	9	—	2	2	1	—	—	4	—	—	—	—	—	—	—	—	—	—	—										
Ar	154	—	79	12	10	12	7	5	6	8	5	—	1	1	1	—	3	1	1	1									
K	20	—	7	10	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—								
Ca	19	—	9	6	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—							
Sc	26	—	—	—	1	6	6	3	3	3	3	1	—	—	—	—	—	—	—	—	—	—	—						
Ti	10	—	1	1	2	3	—	1	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—					
V	4	—	—	—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—				
Cr	9	—	2	1	—	—	—	—	1	1	1	—	1	—	—	1	—	—	—	—	—	—	—	—	—	—			
Mn	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Fe	123	—	4	6	6	6	5	5	5	4	8	7	3	4	3	4	1	—	—	—	—	—	—	—	—	—	—	—	
Ni	33	—	1	2	1	3	1	2	2	2	2	1	2	2	3	2	2	1	2	2	—	—	—	—	—	—	—	—	—
Cu	13	—	9	—	2	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zn	6	—	3	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ga	12	—	9	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ge	4	—	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
As	3	—	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Se	4	—	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Br	3	—	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kr	85	—	55	6	8	6	4	1	—	1	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rb	14	—	5	9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sr	9	—	6	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zr	3	—	1	—	—	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mo	13	—	1	1	—	—	1	6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ru	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pd	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ag	10	—	9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cd	3	—	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
In	11	—	9	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sn	4	—	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sb	9	—	3	2	1	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Te	5	—	5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
I	5	—	3	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Xe	88	—	54	9	8	5	5	1	4	—	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cs	14	—	7	7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ba	26	—	13	10	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

(continued)

Table 2 *(continued)*

		Initial charge state																											
Element	Total	−1	+0	+1	+2	+3	+4	+5	+6	+7	+8	+9	+10	+11	+12	+13	+14	+15	+16	+17	+18	+19	+20	+21	+22	+23	+24	+25	+26
La	5	—	—	1	3	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hf	2	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ta	2	—	—	1	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
W	4	—	3	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Au	3	—	2	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hg	14	—	10	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tl	4	—	3	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pb	11	—	11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Bi	8	—	3	2	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
U	10	—	5	—	—	—	—	—	—	—	—	—	2	—	1	1	—	—	1	—	—	—	—	—	—	—	—	—	—

Another important issue in ion target experiments is how to produce multiply charged target ions, particularly in specific electronic states, with sufficient intensities. The present-day powerful ion sources such as electron cyclotron resonance (ECR) ion source can provide ions required for measurements of the ionization cross sections. Unfortunately, the ions produced in ECR ion source often include the excited and metastable state ions with significant intensities. As the cross sections for the excited state ion are usually much larger than those for the ground state ion, the contribution of even a tiny fraction of the excited ion species can be seen clearly in the observed results where the ionization cross sections start to increase before the threshold for ionization.

Recently, a limited number of metastable-state-free ion beam experiments are under way using storage rings where multiply charged target ions are stored for a while, thus cooled down, and collide with a high density cooling electron beam [8].

3.3. Neutral atoms

A number of experimental studies have been performed for neutral atom targets as the basic experimental setup is relatively simple, though there are a lot of problems when the absolute cross sections are being determined. Table 3 shows a list of experimental studies for neutral atoms performed so far [22].

3.4. Neutral molecules

So far, no reliable ionization cross sections have been reported even for the double ionization of molecules, except for a few scattered data. This is because most of the final channels of the doubly charged molecular ions are in the metastable states (whose lifetimes are not well established yet except for a few ions) and tend to dissociate into atomic ions through a so-called Coulomb explosion which provides relatively large kinetic energies. This complicates complete collection of the multiply charged, atomic ions formed in dissociation of multiply charged molecular ions. If the ion collection field is too strong, the incident electron beam is deflected away from its original path before interacting with the target. Therefore, except for those for the production of the singly charged parent molecular ions, the cross sections for any dissociative product ions are found to be largely scattered and even the observed dependence on the electron impact energy is often significantly different among experiments [23–25]. Careful measurements of singly charged molecular ions dissociated from hydrocarbon molecules have been reported recently [26].

Multiply charged atomic ions, for example up to bare N^{7+} ions from N_2 molecule targets, have been observed in experiments under high energy, heavy ion impact [27]. In this experiment, the kinetic energy of N^{7+} ions have been observed to be equal to the expected Coulomb explosion energy of completely

Table 3
Experimental work for ionization of neutral atoms by electron impact; the numbers show the entry for experiments performed so far

	Final charge state														
Element	+1	+2	+3	+4	+5	+6	+7	+8	+9	+10	+11	+12	+13	+14	+15
H	8														
He	26	8													
Li	6	1	—												
Be	2	—	—	—											
B	1	—	—	—	—										
C	2	—	—	—	—	—									
N	3	—	—	—	—	—	—								
O	7	3	—	—	—	—	—	—							
F	1	—	—	—	—	—	—	—	—						
Ne	20	14	14	5	2	—	—	—	—	—					
Na	3	1	—	—	—	—	—	—	—	—	—				
Mg	6	3	1	1	—	—	—	—	—	—	—	—			
Al	2	—	—	—	—	—	—	—	—	—	—	—	—		
Si	1	1	—	—	—	—	—	—	—	—	—	—	—	—	
P	1	1	—	—	—	—	—	—	—	—	—	—	—	—	—
S	2	2	1	1	—	—	—	—	—	—	—	—	—	—	—
Cl	1	1	—	—	—	—	—	—	—	—	—	—	—	—	—
Ar	22	20	14	9	7	4	1	—	—	—	—	—	—	—	—
K	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—
Sc	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ti	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
V	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cr	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mn	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Fe	3	1	—	—	—	—	—	—	—	—	—	—	—	—	—
Co	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ni	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cu	2	2	1	1	1	—	—	—	—	—	—	—	—	—	—
Zn	2	—		—	—	—	—	—	—	—	—	—	—	—	—
Ga	4	4	3	1	—	—	—	—	—	—	—	—	—	—	—
Ge	2	1	1	—	—	—	—	—	—	—	—	—	—	—	—
As	1	1	1	—	—	—	—	—	—	—	—	—	—	—	—
Se	2	1	1	—	—	—	—	—	—	—	—	—	—	—	—
Br	1	1	1	—	—	—	—	—	—	—	—	—	—	—	—
Kr	12	10	8	6	4	4	2	2	1	—	—	—	—	—	—
Rb	1	6	1	1	1	—	—	—	—	—	—	—	—	—	—
Sr	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—
Y	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Zr	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nb	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mo	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tc	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ru	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rh	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pd	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ag	3	2	1	—	—	—	—	—	—	—	—	—	—	—	—
Cd	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
In	3	3	2	—	—	—	—	—	—	—	—	—	—	—	—
Sn	2	1	1	—	—	—	—	—	—	—	—	—	—	—	—
Sb	1	1	1	—	—	—	—	—	—	—	—	—	—	—	—
Te	2	1	1	—	—	—	—	—	—	—	—	—	—	—	—

(continued)

Table 3 *(continued)*

	Final charge state														
Element	+1	+2	+3	+4	+5	+6	+7	+8	+9	+10	+11	+12	+13	+14	+15
I	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Xe	10	9	9	5	5	3	1	1	1	1	1	1	1	—	—
Cs	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ba	4	2	1	1	—	—	—	—	—	—	—	—	—	—	—
La	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ce	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pr	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nd	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pm	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sm	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Eu	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Gd	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tb	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dy	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ho	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Er	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tm	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Yb	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Lu	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hf	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ta	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
W	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Re	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Os	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ir	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pt	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Au	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hg	2	1	1	1	1	—	—	—	—	—	—	—	—	—	—
Tl	2	1	—	—	—	—	—	—	—	—	—	—	—	—	—
Pb	3	3	2	—	—	—	—	—	—	—	—	—	—	—	—
Bi	1	1	1	—	—	—	—	—	—	—	—	—	—	—	—
Po	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
At	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Rn	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ac	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Th	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pa	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
U	1	1	1	1	—	—	—	—	—	—	—	—	—	—	—

stripped N_2^{14+} ions, suggesting that all 14 electrons in N_2 molecules are ejected under a single collision. In another case, I^{17+} ions having the kinetic energy as high as 1 keV have been observed due to the dissociation of multiply charged molecular ions, I_2^{35+} or I_2^{36+} [28]. However, no absolute cross sections for the production of such multiply charged ions have been determined yet. Important experimental and theoretical features of multiply charged molecular ions have been described in detail [29].

4. Semiempirical formulas

Empirical formulas are useful in applications. Therefore, various formulas have been proposed for estimating the cross sections for the single ionization of atoms and ions [7] as well as molecules [30,31] with some success. However, multiple ionization processes are quite complicated, as mentioned before, and thus only a few empirical formulas have been proposed for multiple ionization cross sections for

Table 4
Fitting parameters for multiple ionization, a and b, in Eq. (4)

n	a	b
2	14.0	1.08
3	6.30	1.20
4	0.50	1.73
5	0.140	1.85
6	0.049	1.96
7	0.021	2.00
8	0.0096	2.00
9	0.0049	2.00
10	0.0027	2.00

atoms and ions under electron impact. All of them do take into account only the direct ionization processes, though they are, in a number of cases, known to be dominated with those from the indirect ionization processes, particularly near the threshold energy region (see previous discussion). The contribution of the inner-shell electron ionization/excitation processes in the production of multiply charged ions is difficult to express in any unified forms as their cross sections strongly depend upon the electronic configurations of the ion. Thus, most of the empirical formulas proposed so far are only partly successful in describing multiple ionization cross sections at relatively high impact energies of electrons where the indirect processes cease to play a role.

Combining the well-known Bethe-Born theory with some reliable experimental data, a relatively simple empirical, analytical formula with only two fitting parameters has recently been proposed for estimating the multiple ionization cross sections of atoms and ions [32,33]. This empirical formula is expressed for the cross sections of multiple ionization ejecting r electrons as follows:

$$\sigma_r = (aN^{\mathrm{b}}/I_r^2)^*(u/u+1)^{\mathrm{c}}{}^*\ln(u+1)/(u+1) \cdot (10^{-18}\ \mathrm{cm}^2) \quad (4)$$

where a and b are given in Table 4, N the total number of electrons in the target, I_r the minimal ionization energy (in Rydberg units = 13.6 eV) required to remove r outermost-shell electrons, $u = (E/I_r) - 1$, E being the electron impact energy and c is the constant which is empirically determined to be 1.0 for neutral atoms and 0.75 for ions. It is interesting to note that, for multiple ionization with a relatively large number of electrons to be removed, the parameter b asymptotically approaches 2, instead of unity, indicating that there is a strong correlation among electrons. For $r > 10$, the following asymptotic form for the constant a can be used [32,33]:

$$a \approx 1350r^{-5.7}. \quad (5)$$

This formula has been found to reproduce the observed data up to 13 times ionization from neutral atoms within a factor of 2. As this formula does not take into account the indirect ionization processes, the agreement is not so good near the maximum of the cross section where the excitation or ionization processes followed by autoionization become dominant.

The second, semiclassical formula, first developed for the single ionization of neutral atoms by electron impact [34], has been extended for the production of multiply charged ions up to bare ions from neutral Ne and Si atoms [35]. It is interesting to note that this empirical formula provides the cross sections for the production of bare ions under a single electron collision on neutral atoms which are very small, down to 10^{-30} cm^2 (for Si^{14+} ion production from neutral Si atoms) at the maximum, compared with those of 10^{-16} cm^2 observed for the single ionization (production of Si^{+} ion from neutral Si atoms). It is note worthy that, roughly speaking, the multiple ionization cross sections decrease by one order of magnitude when the number of electrons to be ejected increases by unity. A similar extension has recently been made to the cross sections of multiply charged ions up to bare ions for Be, B, C, and O atoms. For details, refer to an article in this special issue [36]. So far, the agreement among this empirical formula and experiments seems to be reasonably good up to $r = 5$, but this prediction has to be confirmed experimentally for higher charge states.

The third formula composes of functions of the electron impact energy dependence, which are empirically fitted to the experimental data, in combination with statistical consideration [37]. General agreement

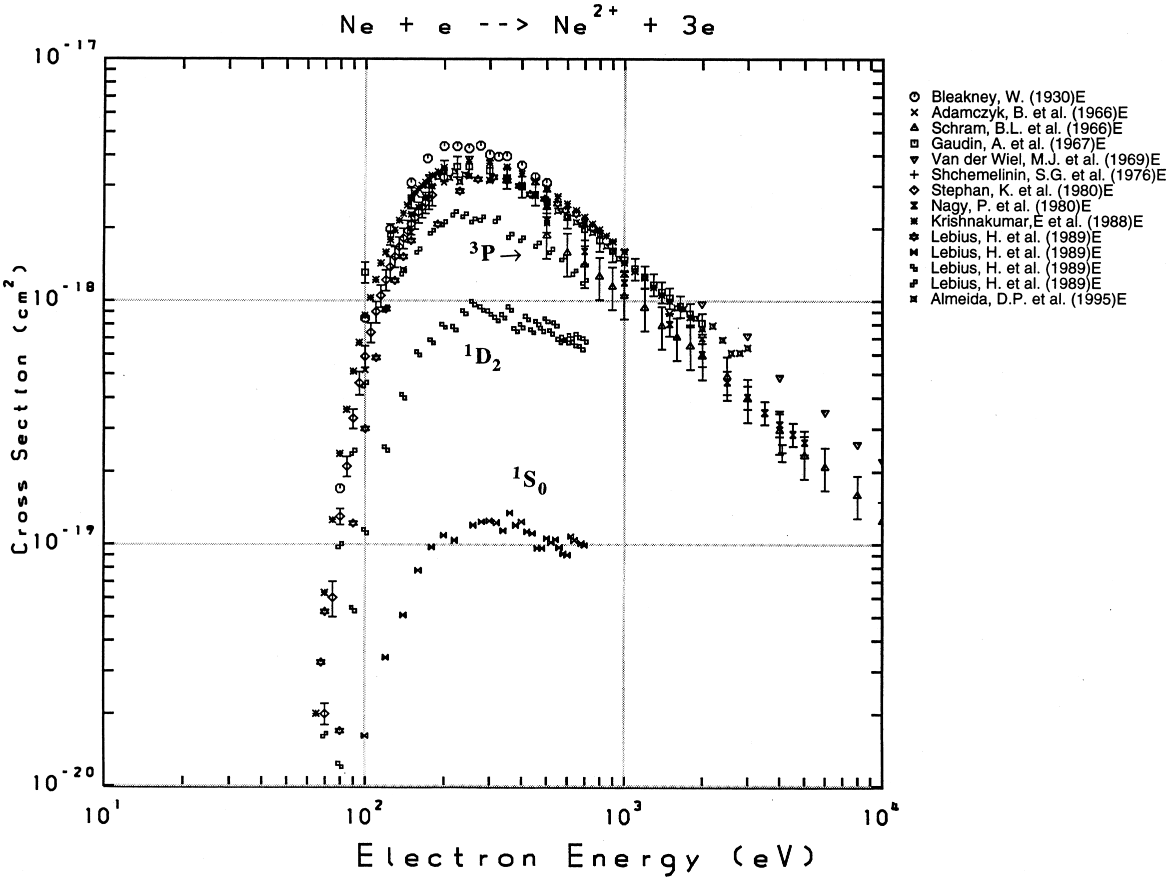

Fig. 5. An example of the plotted double ionization (Ne^{2+}) cross sections for Ne atoms as a function of the electron impact energy taken from NIFS database on the WWW. Note that, in addition to total double ionization cross sections, some state-specified double ionization cross sections are shown.

has been observed for neutral Kr ionization up to $r = 8$.

5. Databases

It is important to have convenient databases that are electronically accessible. In fact, such databases are under development in several parts of the world. One of them is our database at the National Institute for Fusion Science which is accessible (free of charge but requiring an ID) via WWW at http://dbshino.nifs.ac.jp, where the ID is provided upon request and at http://amdata.nifs.ac.jp, where numerical data and plotted curves as well as bibliographic data relevant not only to ionization processes but also to excitation and recombination processes by electron impact are available. Also, limited cross sections for ionization and electron transfer processes under heavy particle impact, sputtering of solids by ions, and backscattering of ions from solids can be obtained. One of several examples seen on the WWW is shown in Fig. 5, where the cross section data for the double ionization of Ne atoms are plotted as a function of the electron impact energy. Note that most data clustered at the top area correspond to total ionization of two electrons from the outermost 2*p* shell, resulting in the production of the doubly charged, unspecified-state Ne^{2+} ions, and data points just below refer to the production of ^3P state Ne^{2+} ions. Furthermore, the data points in the middle area refer to the production of Ne^{2+} ions in the $^1D_2$ state and those at the bottom refer to those for $^1S_0$ state Ne^{2+} ions.

The Atomic Data Unit of the International Atomic Energy Agency (IAEA, Vienna, Austria) also offers its databases for ionization data (and also many others) via the WWW at http//iaea/org.at. Another extensive database at Oak Ridge National Laboratory (Tennessee, USA) is accessible at http//ornl.gov. A comprehensive list of the atomic and molecular data Web sites can be obtained at http//plasma-gate.weizmann.ac.il.

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