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Calculated cross sections for the electron-impact ionization of excited argon atoms using the DM formalism

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Abstract

The semiclassical Deutsch-Märk (DM) formalism was used to calculate absolute cross sections for the electron-impact ionization of excited argon atoms from threshold to 1000 eV. Excited states of Ar where the outermost valence electron is excited to states with principal quantum numbers up to $n = 7$ and orbital angular momentum quantum numbers up to $l = 2$ have been considered. Systematic trends in the calculated cross section data are discussed.

Keywords: Electron ionization; Cross sections; Excited states; Rare gases

1. Introduction

Electrons interacting with atoms leading to the formation of positive ions are among the most fundamental processes in collision physics. Cross sections for the electron-impact ionization of atoms have been measured and calculated since the early days of collision physics [1] because of their basic importance and because of their relevance in practical applications such as gas discharges, plasmas, radiation chemistry, planetary atmospheres, and mass spectrometry. Considerable progress in the quantitative determination of ionization cross sections for atomic (and simple molecular) targets [2,3] has been made in the past decade. The ionization of rare gas atoms has been studied extensively, in particular the ionization of ground state rare gas atoms whose ionization cross sections are considered benchmark data [2]. Much less effort has been devoted to the ionization of atoms in excited states. Ionization cross sections have been measured for the metastable rare gas atoms He [4,5], Ne [6,7], and Ar [6] and several calculations using different approximations have been carried out for these targets [8–10] including an earlier calculation based on the semi-classical Deutsch-Märk (DM) formalism [11].

In this paper we report the results of the application of the DM formalism to the calculation of absolute electron-impact ionization cross sections for excited Ar atoms. Specifically, we consider 26 different excited states where the valence electron is excited to states characterized by principal quantum numbers up to $n = 7$ and orbital angular momentum quantum numbers up to $l = 2$. Excited rare gas atoms play an important role in the ionization balance in gas discharges and in low-temperature plasmas because of the importance of step-wise ionization processes (see e.g., [12]). It is interesting to note that Bogaerts et al. [13] have recently reported the development of an extensive collisional radiative model for argon atoms in a glow discharge [14]. Sixty-five effective argon atomic energy levels have been considered by these authors and one of the processes taken into account was electron-impact ionisation of atoms excited into these

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levels using however due to the lack of data a simple scaling formula.

Ar is also of special importance in magnetic confinement fusion [15] as a gaseous, non-retained species, introduced to provide strong radiative cooling at the plasma edge. In typical tokamak operating scenarios, there is substantial Ar gas puffing leading to relatively high concentrations in the plasma. It has become essential to characterize Ar fully through all ionization stages and diagnostics experiments to that end are currently scheduled [15]. A key part is the influx of Ar from the plasma periphery and recycling surfaces. Ar^+ line emissions in the visible (e.g., at 433.8 and 465.4 nm) are commonly used as a measure of Ar influx. Ar has also visible emissions at longer wavelengths (e.g., at 696.5 nm) which will be useful in upcoming experiments. These studies will provide linkage and fiducial in the dynamic ionization/transport/influx of Ar through two successive ionization stages. Emission modelling for Ar in the tokamak edge and divertor with electron densities of $1–5 \times 10^{19}\,\mathrm{m}^{-3}$ is in the generalized collisional-radiative regime. The theoretical effective emission coefficients and photon efficiencies used for analysis must include indirect processes via other excited states, including ionization losses. The effective ionization rates are markedly influenced by stepwise pathways and metastables must be distinguished. The present calculations will support these studies.

2. Theoretical background

The original concept of the DM formalism [16] has been modified and extended several times. The DM formula expresses the total single ionization cross section σ of an atom as

$$\sigma = \sum_{n,l} g_{nl} \pi r_{nl}^2 \xi_{nl} f(u) \tag{1}$$

where r_{nl} is the radius of maximum radial density of the atomic sub-shell characterized by quantum numbers n and l (as listed in column 1 in the tables of Desclaux [17]) and ξ_{nl} is the number of electrons in that sub-shell. The sum extends over all atomic sub-shells labelled by n and l. The factors g_{nl} are weighting factors which were originally determined from a fitting procedure [16,18] using reliable experimental cross section data for the rare gases and uranium. The energy dependence of the cross section is contained in the function $f(u)$ which is given by

$$f(u) = d\frac{1}{u}\left(\frac{u-1}{u+1}\right)^a \times \left\{b + c\left(1 - \frac{1}{2u}\right)\ln(2.7 + (u-1)^{1/2})\right\} \tag{2}$$

where $u = E/E_{nl}$. Here E refers to the incident energy of the electrons and E_{nl} is the ionization energy in the (n, l) sub-shell. The constants a, b, c, d have different values for s-, p-, d-, and f-electrons as one expects on the basis of the different angular shapes of atomic s-, p-, d-, and f-orbitals. Values of these constants as well as all other parameters relevant to the application of the DM formula can be found in the topical review by Deutsch et al. [19] to which we refer the reader for further details.

Argon has a $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$ electron configuration in its ground state, which is a $^1S_0$ state. The lower lying excited states of Ar result from the promotion of one of the six (3p)-electrons into higher orbitals such as 4s, 4p, 3d, etc. In order to apply the DM formula to the calculation of ionization cross sections of excited Ar atoms, we need to know the values of the two parameters r_{nl} and E_{nl} for the higher-lying (n, l) sub-shells. The values for E_{nl} were obtained from the well-known energy level diagram of the Ar atom [20]. The radii r_{nl} for Ar were obtained from numerical Hartree–Fock calculations [21]. We calculated them (a) for the $[\mathrm{Ne}](3s)^2(3p)^5$ configuration (corresponding to the situation where one 3p electron of Ar is promoted to one of the higher-lying orbitals) and (b) for the $[\mathrm{Ne}](3s)^2(3p)^6 = [\mathrm{Ar}]$ configuration (meaning that another electron occupies one of the higher-lying orbitals of Ar). The differences between the calculated radii (and also for the energies of the orbitals above 3p) were quite small and we used the wave function from (a) for our cross section calculations. Table 1 summarizes the values for r_{nl} and E_{nl} used in the present calculation up to values of $n = 7$ and $l = 2$. Furthermore, the application of the DM formalism requires knowledge of the weighting factors g_{nl} for the higher-lying (n, l) sub-shells. As these weighting factors were determined from a fitting procedure using experimentally determined reliable cross section data and such data are only available for values of the orbital angular momentum quantum number l up to $l = 2$ (d-electrons), the lack of reliable weighting factors g_{nl} for higher l-values limits the present calculations to electron configurations where the outermost valence electron is

Table 1
Values of the radii r_{nl} and energies E_{nl} for outermost Ar valence electron

Quantum numbers (n, l) of valence electron	Value of r_{nl} (same for both configurations) (m)	Value of E_{nl} (eV)
4s, 4s′	2.49×10^{-10}	4.21, 4.04
5s, 5s′	6.35×10^{-10}	1.69, 1.52
6s, 6s′	1.26×10^{-9}	0.92, 0.75
7s, 7s′	2.08×10^{-9}	0.58, 0.40
4p, 4p′	3.40×10^{-10}	2.67, 2.38
5p, 5p′	8.15×10^{-10}	1.24, 1.05
6p, 6p′	1.52×10^{-9}	0.73, 0.55
7p, 7p′	2.35×10^{-9}	0.49, 0.31
3d, 3d′	4.36×10^{-10}	1.76, 1.51
4d, 4d′	1.05×10^{-9}	0.99, 0.79
5d, 5d′	1.84×10^{-9}	0.62, 0.44
6d, 6d′	2.84×10^{-9}	0.42, 0.25
7d, 7d′	3.89×10^{-9}	0.32, 0.13

In the case of the radii, we used the same value for both the primed and unprimed configuration. In the case of the energy values, we used energies averaged over all fine structure components of each (n, l) and (n, l') configuration.

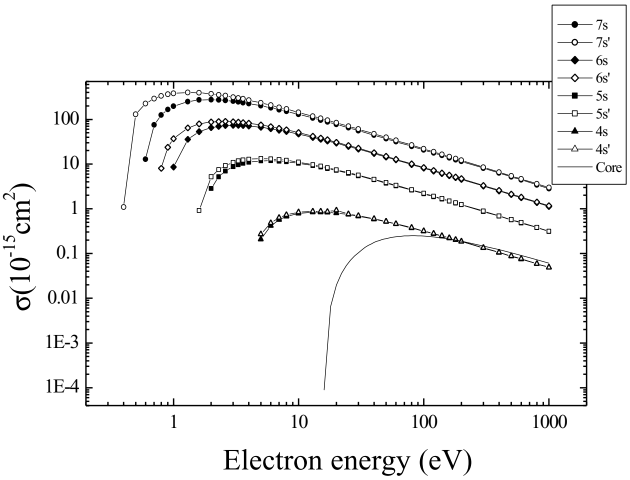

Fig. 1. Calculated electron-impact ionization cross section of excited Ar atoms with ... $(3p)^5ns$ and ... $(3p)^5ns'$ ($n = 4$–7) electron configurations as a function of electron-impact energy up to 1000 eV using the DM formalism. The various curves are labelled and represent the contribution to the ionization cross section arising from the removal of the electron from the designated (*nl*) sub-shell. Also shown as full line is the contribution to the ionization cross section arising from the core electrons (see text for details).

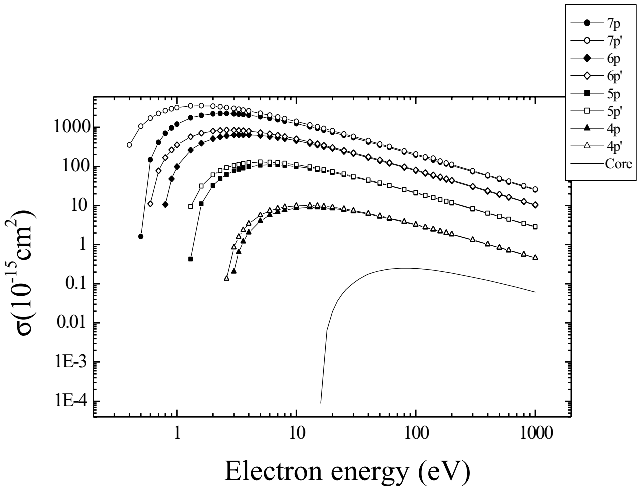

Fig. 2. Calculated electron-impact ionization cross section of excited Ar atoms with ... $(3p)^5np$ and ... $(3p)^5np'$ ($n = 4$–7) electron configurations as a function of electron-impact energy up to 1000 eV using the DM formalism. The various curves are labelled and represent the contribution to the ionization cross section arising from the removal of the electron from the designated (*nl*) sub-shell. Also shown as full line is the contribution to the ionization cross section arising from the core electrons (see text for details).

in higher-lying s-, p-, and d-orbitals. Lastly, in the context of the present calculations, we do not distinguish between metastable and radiating excited states of a single (*nl*) state.

All excited Ar electron configurations are of the form "core+*nl*", where the core is of the form $(1s)^2(2s)^2(2p)^6(3s)^2$ $(3p)^5$. Since the DM formalism calculates the ionization cross section as the sum of the partial cross sections for the removal of an electron from a particular (*nl*) orbital summed over all (*nl*) configurations (Eq. (1)), it is illustrative to calculate separately the contribution to the total ionization cross section arising from the removal of an electron from the core and from the (*nl*) valence electron. The contribution due to the core electrons (designated by a full line in Figs. 1–3), which is common to all configurations treated here, peaks at around 80 eV with a maximum value of 2.5×10^{-16} cm^2 and is in good accordance with our previous results [11] where we used the radii given by Desclaux [17] which are in very good agreement with the present calculations, i.e., for the 1s-orbital 2.969×10^{-11} m versus 2.939×10^{-11} m, for the 2s-orbital 1.784×10^{-11} m versus 1.800×10^{-11} m, for the 3s-orbital 6.233×10^{-11} m versus 6.2835×10^{-11} m, for the 2p-orbital 1.4930×10^{-11} m versus 1.4925×10^{-11} m and the for 3p-orbital 6.8856×10^{-11} m versus 6.6887×10^{-11} m, respectively.

3. Results and discussion

We present the results of our calculations in three figures. Fig. 1 summarizes the calculated ionization cross sections for excited Ar atoms with the electron configurations ... $(3p)^5ns$ and ... $(3p)^5ns'$ ($n = 4$–7). Here, the unprimed configurations correspond to those states whose $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$ core has a total angular momentum of 3/2, whereas the primed configurations denote the states whose core has a total angular momentum of 1/2. We note that the curves in Figs. 1–3 represented by the connected symbols denote the contribution to the ionization cross section attributable to the removal of the outermost

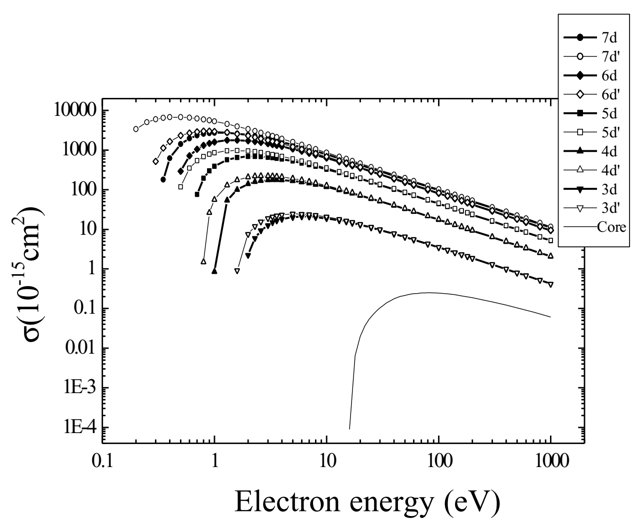

Fig. 3. Calculated electron-impact ionization cross section of excited Ar atoms with ... $(3p)^5nd$ and ... $(3p)^5nd'$ ($n = 3$–7) electron configurations as a function of electron-impact energy up to 1000 eV using the DM formalism. The various curves are labelled and represent the contribution to the ionization cross section arising from the removal of the electron from the designated (*nl*) sub-shell. Also shown as full line is the contribution to the ionization cross section arising from the core electrons (see text for details).

valence electron ("valence contribution"). Also shown as the solid line is the contribution to the ionization cross section arising from the core electrons ("core contribution", see above). For each electron configuration, the total single ionization cross section is thus given as the sum of the "core contribution" and the respective "valence contribution". It is apparent that the "core contribution" is appreciable only for $n = 4$ (4s, 4s′). The cross section maxima increase with increasing principal quantum number n. The increase per unit change in n is somewhat less than an order of magnitude from 8×10^{-16} cm^2 for $n = 4$ to 4×10^{-13} cm^2 for $n = 7$. As one would expect the cross section maxima and the thresholds of the cross section curves shift to lower energy as n increases. In all cases, the cross section curve corresponding to the primed state lies slightly above the cross section curve for the unprimed state and has a slightly lower ionization energy. This is to be expected as the unprimed configurations lie energetically slightly below the primed configuration and have a slightly higher ionization energy. The difference in the absolute ionization cross section values between any two curves corresponding to the primed and unprimed configuration, respectively, is generally very small and becomes noticeable only for the larger values of n and there only in the low-energy region.

In the case of the calculations for the 4s and 4s′ configurations we can compare the present results with our earlier calculation [11] for the 4s′ configuration. As we used an estimated value of the radius $r_{4s'}$ in our earlier calculation which was about 2% smaller than the value used here and the cross section depends on $(r_{nl})^2$, the present cross section is about 4% larger for the 4s′ configuration than our previously reported cross section. We also note that the only experimental data available for the ionization of excited Ar atoms are those of Dixon et al. [6] for the ... $(3p)^5 4s'$ metastable state which have only appeared in Conference Proceedings. As discussed in detail in [11] these data agree reasonably well with our calculated cross section below 20 eV, but lie below our calculation at higher energies.

Fig. 2 shows the calculated cross sections for the ... $(3p)^5 n$p and ... $(3p)^5 n$p′ (n = 4–7) configurations. The trends that were found before in the case of the ns and ns′ configurations are also observed here. The difference between the two cross sections corresponding to the primed and unprimed configuration for a given value of n is somewhat larger than before. The "core contribution" as before is appreciable only for $n = 4$ (4p, 4p′). The maximum values of the cross sections which range from about 9×10^{-15} cm^2 ($n = 4$) to 2×10^{-12} cm^2 ($n = 7$) are roughly one order of magnitude larger than those for the ns and ns′ configurations. As one goes to the ... $(3p)^5 n$d and ... $(3p)^5 n$d′ (n = 4–7) configurations, the previously observed trends are even more pronounced. The difference between the cross sections for the primed and unprimed configurations is now quite noticeable and reaches a factor of 3 for $n = 7$ and the "core contribution is negligible for all values of n". The maximum cross section values are even larger ranging from 1×10^{-13} cm^2 ($n = 4$) to 6×10^{-12} cm^2 ($n = 7$). In the case of the d-orbitals, we also included calculations for the 3d and 3d′ configurations which yielded maximum cross section values around 2×10^{-14} cm^2.

If one looks at the l-dependence of the calculated cross sections for a given value of the principle quantum number n, the following trends are apparent: (1) the position of the cross section maximum shifts towards lower impact energies as l increases and (2) the maximum cross section increases roughly by one order of magnitude as one goes from $l = 0$ to $l = 1$ to $l = 2$.

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