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Application of the DM formalism to the calculation of electron-impact ionization cross sections of alkali atoms

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Abstract

On the basis of the results of recent calculations of K-shell ionization cross sections (removal of a 1s electron) for 11 atoms [Deutsch et al., Int. J. Mass Spectrom. 177 (1998) 47] using the semiclassical DM formalism, we revisited our earlier calculations of electron-impact ionization cross sections of the alkali atoms Li, Na, K, Rb, and Cs whose ionization at low energies is also dominated by the removal of the lone ns electron (n= 2–6 for Li–Cs). We investigated the effect of (1) a slightly revised energy dependence in the low-energy region similar to the one developed for the K-shell ionization cross sections, and (2) a slightly revised set of empirically determined weighting factors on the overall cross section shape. A detailed comparison with available experimental data and with other calculated cross sections reveals that the revised cross section shape yields better agreement with experiment and with other calculations. Moreover, in accordance with predictions from Vallance and Harland [Int. J. Mass. Spectrom. Ion Processes 171 (1997) 173], we find a linear relationship between the presently calculated maximum cross section value σ_{max} and the polarizability volume α. This can be viewed as an independent justification of the reliability of the DM calculation for the alkali ionization cross sections and in particular for the use of the revised parameters. (Int J Mass Spectrom 185/186/187 (1999) 319–326) © 1999 Elsevier Science B.V.

Keywords: Electron impact ionization; Cross sections; Theoretical calculation; Alkali atoms

1. Introduction

In 1987, Deutsch and Märk [1] introduced a semiclassical method (DM formalism) for the calculation of total single electron-impact ionization cross sections of atoms. The DM formalism is based on a combination of the binary encounter approximation and the Born–Bethe approximation. It consists of a simple analytical expression that contains only basic known atomic properties and appropriately chosen weighting factors to account for the different contributions of the various atomic subshells to the total single ionization cross section. In a subsequent publication, Margreiter et al. [2] used the DM formalism to calculate total single electron-impact ionization cross sections for 45 atoms for which experimental cross section data were available and compared their calculations with experiment and with other calculations. In many cases, Margreiter et al. [2] found good

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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agreement between the DM calculations and the measured cross sections.

The notable exceptions were the alkali atoms Li, Na, K, Rb, and Cs. Even though these atoms are of a remarkably simple structure, being quasi-one-electron atoms with a single electron in the ns subshell (n = 2–6 for Li, Na, K, Rb, and Cs), there are significant discrepancies in the reported measured alkali ionization cross sections even for Na, which has been studied more than any other alkali atom [3–8]. Rigorous quantum mechanical calculations have also been carried out for Na [9, 10] that are, however, in less than satisfactory agreement with each other and with some of the experimental data, particularly at low impact energies. By contrast, the measured electron-impact ionization cross sections for the rare gases are known from experiment to within ± 5%, and these cross section values are also supported by theoretical calculations.

A recent study, in which the DM formalism was applied to the K-shell ionization of 11 atoms [11], revealed the need to revise the energy dependence of the calculated DM cross section in the low-energy region, in cases where the ionization proceeds solely via the removal of a single 1s electron. Since the ionization of the alkali atoms in the low-energy region (up to about ten times the ionization energy) is dominated by a similar process, viz. the removal of the lone outer ns electron, a revised energy dependence in the low-energy region of the DM ionization cross section of the alkali atoms similar to the energy dependence of the K-shell ionization cross sections was thought to lead to an improved agreement with experimental cross section data. The revised energy dependence of the s electrons and a slight revision of the g_{ns} weighting factors introduced in the course of the present study (see discussion below) led to a shift of the maximum in the ionization cross section curve towards lower impact energies without changing the peak cross section value significantly. A detailed discussion of the revised calculated DM ionization cross sections for the alkali atoms Li, Na, K, Rb, and Cs is presented in this article and a comparison is made with available experimental data and other calculated cross sections. This comparison with available experimental data and with other calculated cross sections reveals that the revised cross section shape yields better agreement with experiment and with other calculations. We also included atomic hydrogen in our present study as a benchmark target that is also affected by the revised weighting factors of the s electrons and where accurate recent measurements and calculations are available for comparison.

2. Theoretical concept

The DM formalism expresses the atomic ionization cross section σ as a sum over the various atomic subshells [1,2]

$$\sigma = \sum_{nl} g_{nl}\pi(r_{nl})^2\xi_{nl}f_{k(1)}(U) \quad (1)$$

where $(r_{nl})^2$ is the mean square radius of the atomic nl subshell, ξ_{nl} refers to the effective number of electrons in the nl subshell, and g_{nl} are weighting factors (see [1] and [2] for further details). The energy dependence of the ionization cross section (for nonrelativistic energies) is given by the function $f_{k(1)}(U)$. Here U refers to the reduced impact energy, $U = E/E_{nl}$, where E is the energy of the incident electron and E_{nl} refers to the binding energy of the nl electrons. The function $f_{k(1)}(U)$ has the form

$$f_{k(1)}(U) = \mathrm{d}\,(1/U)[(U-1)/(U+1)]^{\mathrm{a}}\{\mathrm{b} + \mathrm{c}[1 - (2U)^{-1}]\ln[2.7 + (U-1)^{1/2}]\} \quad (2)$$

where the parameters a, b, c, and 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. As discussed in the context of the calculations of the K-shell ionization cross sections, the optimized values for s electrons are a = 1.06, b = 0.23, c = 1.00, and d = 1.1. For p, d, and f electrons, the values of the parameters a, b, and c are the same as given in the article by Margreiter et al. [2], and the parameter d is equal to 1.

The empirically determined weighting factors g_{nl} (see [1] and [2] for details) also had to be revised (in some cases up to 30%) for the s electrons as compared

Table 1
Revised and previously reported [2] values of the reduced weighting factors g_{ns} E_{ns} in units of eV for H, Li, Na, K, Rb, and Cs

Element and valence electron	g_{ns} E_{ns} previous value	g_{ns} E_{ns} revised value
H (1*s*)	50.00	38.20
Li (2*s*)	12.00	12.00
Na (3*s*)	14.00	9.80
K (4*s*)	10.00	7.40
Rb (5*s*)	7.50	6.35
Cs (6*s*)	6.00	5.40

to the values reported previously by Margreiter et al. [2]. This change in the g_{nl} parameters was not only triggered by the much better agreement between the calculated values and the recent experiments (see below), but also by accompanying studies on the cross sections of small molecules thereby updating and improving our previous calculations on molecular ionization cross sections. Table 1 shows the revised values of the reduced weighting factors g_{ns} E_{ns} in comparison with the previous values. We note that all other weighting factors g_{nl} remain unchanged. Fig. 1 shows the reduced weighting factors g_{ns} E_{ns} as a function of the ionization energy E_{ns} for H and the five alkali atoms Li, Na, K, Rb, and Cs in a semilog plot. It is interesting to point out that the reduced weighting factors follow essentially a straight line. We also note that the present reduced weighting factors g_{ns} E_{ns} for 1s electrons decrease monotonically with n in a similar fashion as the $(1s)^2$ values given in [2], i.e. the anomaly for the 3s electron now being removed in the ns series.

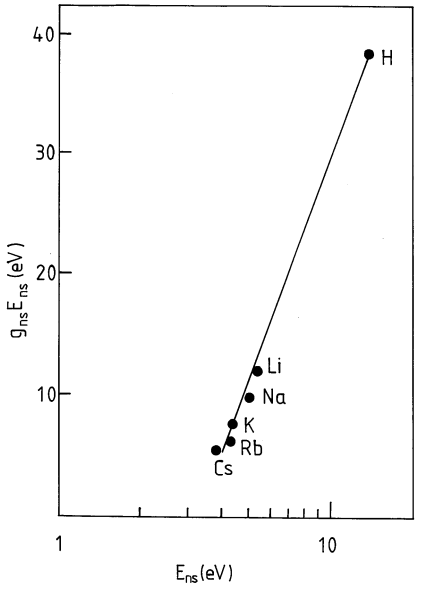

Fig. 1. Revised reduced weighting factors g_{ns} E_{ns} vs. ionization energy E_{ns} for H, Li, Na, K, Rb, and Cs on a semilog scale.

3. Results and discussion

As a first test of our revised DM formalism for the removal of ns electrons, we revisited the ionization of atomic hydrogen where the ionization is described by the removal of the single 1s electron. Fig. 2 shows the the revised DM calculation (dash-dot line) in comparison with the BED calculation of Kim and Rudd [12] and with the experimental data of Shah et al. [13]. There is excellent agreement between the two calculations and between the calculated and measured cross sections.

Electron-impact ionization cross sections for Li have been measured by McFarland and Kinney [3], Zapesochnyi and Aleksakhin [5], and Jalin et al. [14]. The various data sets are shown in Fig. 3 in comparison with the revised DM calculation and with the theoretical results of McGuire [9] and the Born approximation of McDowell et al. [15]. Our calculations follow the experimental data of Zapesochnyi and Aleksakhin [5] from threshold to about 15 eV very closely. At higher impact energies our calculation exceeds the data reported by these authors and eventually, for energies above 100 eV, the DM cross section follows the experimental data of McFarland and Kinney [3], who did not report any cross sections for energies below 100 eV. The data of Jalin et al. [14], which are also limited to impact energies above 100 eV, are significantly smaller than our calculations as are the theoretical results of McGuire [9] and McDowell et al. [15].

Fig. 4 shows the revised DM calculations for the ionization of Na in comparison with the experimental data of McFarland and Kinney [3], McFarland [4],

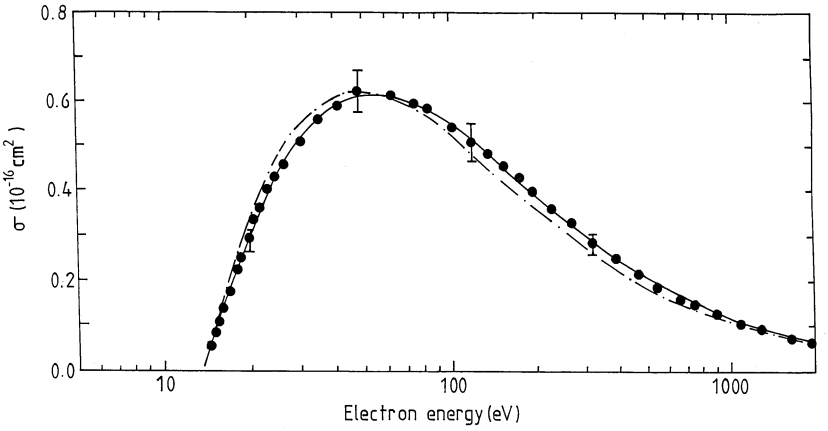

Fig. 2. Electron-impact ionization cross section of H as a function of energy. The experimental data are from Shah et al. [13]; the solid line is the BED calculation of Kim and Rudd [12], and the dash-dot line is the revised DM calculation.

Zapesochnyi and Aleksakhin [5], Johnston and Burrow [6], and Fujii and Srivastava [7] from threshold to 1 keV. As can be seen, there is excellent agreement between our calculations and the data of Johnston and Burrow [6]. Fig. 5 shows the low-energy region of the Na ionization cross section from threshold to 30 eV in more detail. Here we show the DM calculation in comparison with the experimental data of [3] and [6], with the recent low-energy ionization cross section data of Tan et al. [8], and with the calculations of McGuire [9] and Bray [10]. Our calculation follows the experimental data of Johnston and Burrow [6] and of Tan et al. [8], which agree very well with each

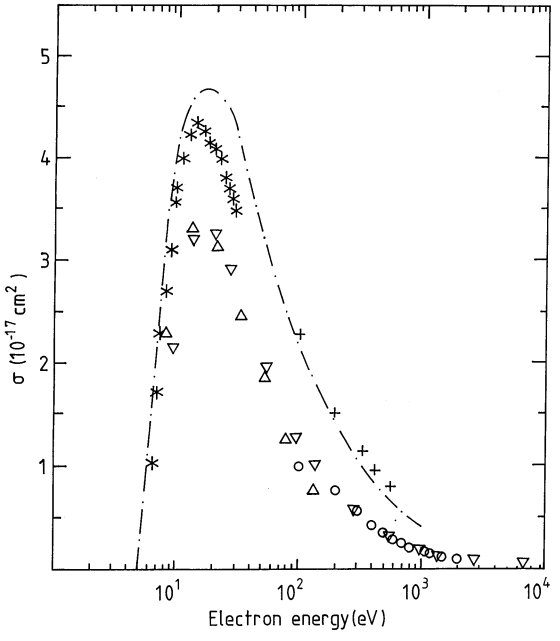

Fig. 3. Electron-impact ionization cross section of Li as a function of energy. The experimental data are from [3] (+), [5] (*), and [14] (○); the triangles denote the Born approximation of McDowell et al. [15]; the inverted triangles refer to the calculated cross sections of McGuire [9], and the revised DM calculation is shown as the dash-dot line.

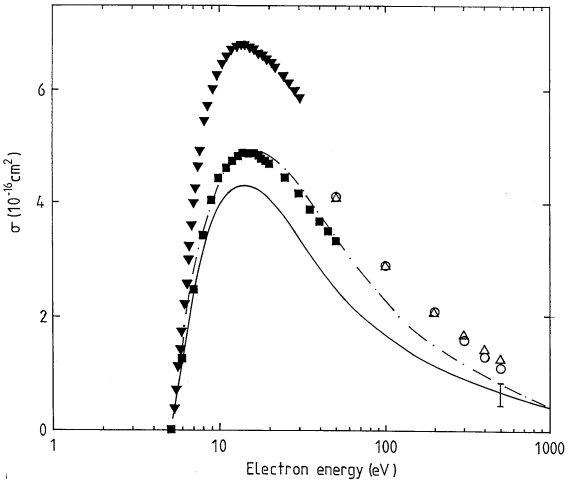

Fig. 4. Electron-impact ionization cross section of Na as a function of energy. The experimental data are from [3] (△), [4] (○), [5] (▼), [6] (■), and [7] (solid line), and the revised DM calculation is shown as the dash-dot line.

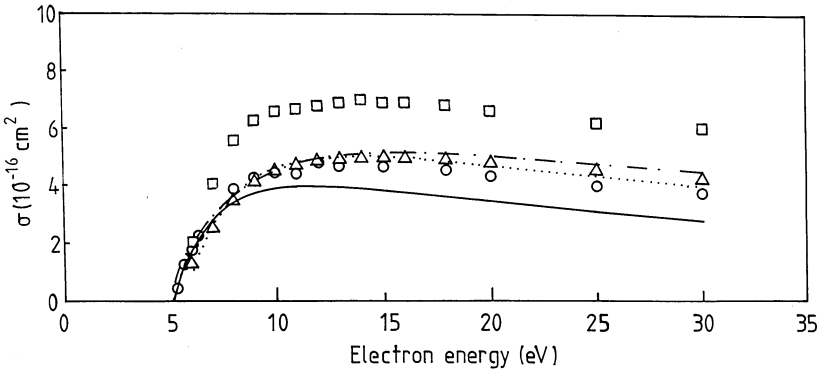

Fig. 5. Electron-impact ionization cross section of Na as a function of energy in the low-energy region. The experimental data are from [5] (□), [6] (△), and [8] (○); the solid line denotes the calculation of Bray [10]; the dotted line refers to the calculation of McGuire [9], and the revised DM calculation is shown as the dash-dot line.

other. Moreover, very closely within the stated uncertainties of these two experiments and our calculated cross section is the calculation of McGuire [9]. It would seem that the experimental data of [3] are too high and that the calculated cross section of Bray [10] declines too rapidly as a function of impact energy.

There are four data sets of electron-impact ionization cross sections for K in the literature to the best of our knowledge [3, 5, 16, 17]. Fig. 6 shows the four data sets in comparison with the revised DM calculation for electron energies from threshold to 600 eV. As can be seen, the data of McFarland and Kinney [3], which are limited to energies above 50 eV, are in good agreement with our DM calculation in the region of higher energies. The low-energy data of [5] and [17] are also in reasonably good agreement with the DM calculation in the energy region from threshold to 30 eV with the exception of the pronounced peak in

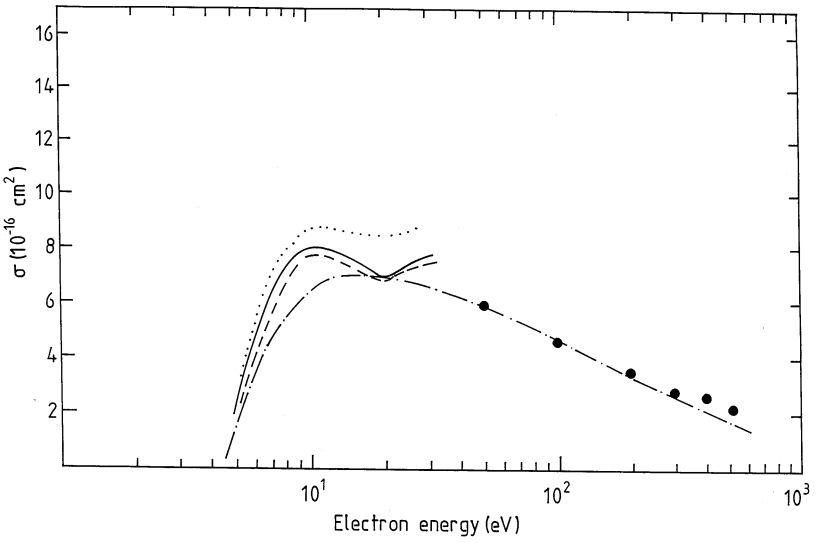

Fig. 6. Electron-impact ionization cross section of K as a function of energy. The experimental data are from [3] (filled circles), [5] (dashed line), [16] (dotted line), and [17] (solid line), and the revised DM calculation is shown as the dash-dot line.

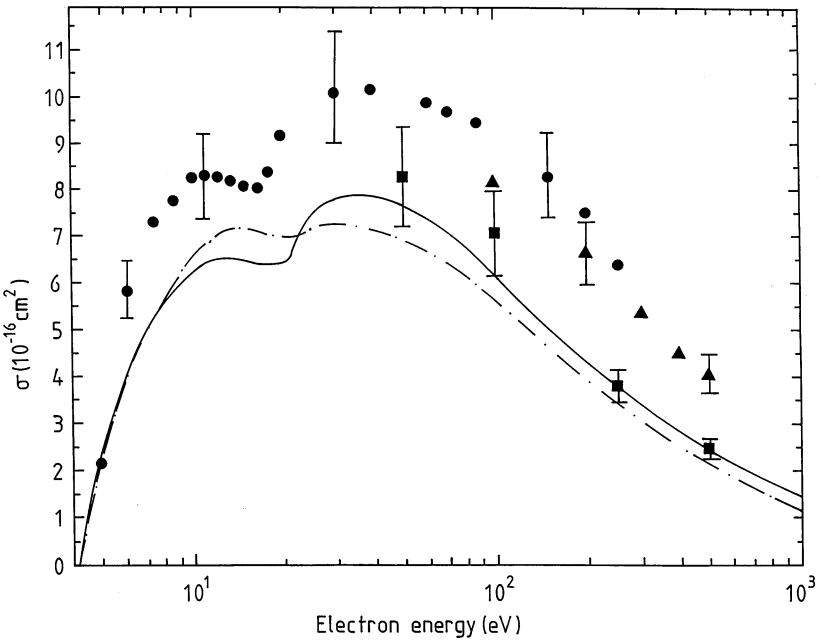

Fig. 7. Electron-impact ionization cross section of Rb as a function of energy. The experimental data are from [3] (■), [19] (●), and [20] (▲); the solid line denotes the BED calculation of Kim et al. [18], and the revised DM calculation is shown as the dash-dot line.

the measured cross section that is most likely due to autoionization and, thus, cannot be described by the DM formalism. The data of [16] lie consistently above all other data sets.

Fig. 7 shows the revised DM calculation for the ionization of Rb in comparison with the BED calculation of Kim et al. [18] and the experimental data of McFarland and Kinney [3], Nygaard and Hahn [19], and Schappe et al. [20]. There is very good agreement between the two calculations in shape and absolute magnitude of the cross section. The contributions to the ionization cross section arising from the different channels (removal of the 5s electron with a threshold of 4.18 eV and removal of a core electron starting at about 20 eV) are clearly apparent in the cross sections. We note that the BED calculation also includes a contribution from the autoionizing excitation of the 4p electrons that is not included in our DM formalism. The cross section values reported recently by Schappe et al. [20], which were obtained from a novel experimental technique using trapped Rb atoms, are unfortunately limited to four data points at energies above 50 eV. These four data points agree reasonably well with both calculations. The experimental data of McFarland and Kinney [3] and Nygaard and Hahn [19] are significantly higher than the calculated cross sections. It is noteworthy, however, that the cross section shape reported by Nygaard and Hahn is very close to the calculated cross section shapes.

Fig. 8 shows the experimental data for the electron-impact ionization cross section of Cs in the low-energy region measured by four groups [5, 16, 17, 21] in comparison with the revised DM calculation. The pronounced structure in the measured cross sections around 15 eV is due to autoionization and is, therefore, not expected to be reproduced by the DM calculation. The DM cross section agrees best in terms of the absolute cross section value with the experimental data of Zapesochnyi and Aleksakhin [5] and Nygaard [17]. McFarland and Kinney [5] also measured the electron-impact ionization cross section of Cs, but only for impact energies from 30 eV to 500 eV. Their data are in good agreement with the DM calculation in this energy regime.

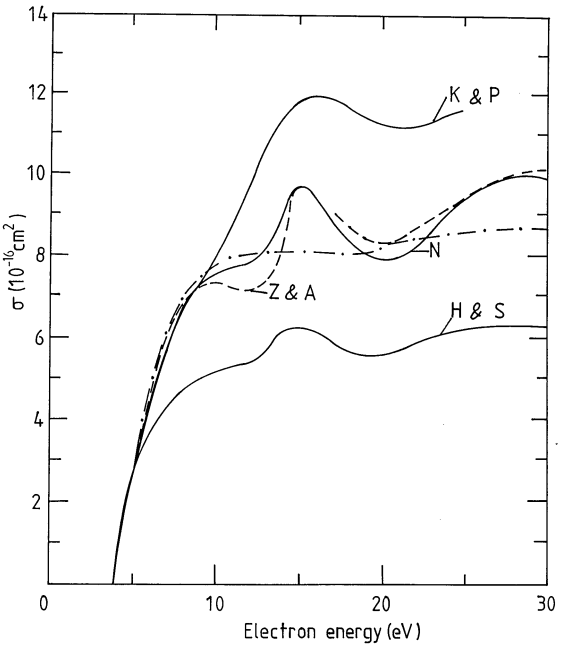

Fig. 8. Electron-impact ionization cross section of Cs as a function of energy in the low-energy region. The experimental data are from [5] (labeled Z&A, dashed line), [16] (labeled K&P), [17] (labeled N), [21] (labeled H&S), and the revised DM calculation is shown as the dash-dot line.

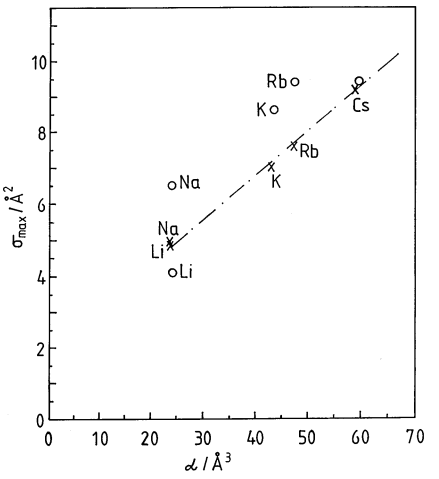

Fig. 9. Maximum electron-impact ionization cross section σ_{max} vs. polarizability volume α for the alkali atoms. The crosses connected by the dash-dot line represent the cross section values from the revised DM calculation; the open circles were taken from [22].

Recently, Harland and Vallance [22] demonstrated that a strong correlation exists between the maximum value of the electron-impact ionization cross section and the square root of the ratio of the atomic polarizability volumes to the ionization energies. They argued that the relationship between the maximum cross section value σ_{max} and the polarizability volume α should follow a straight line within a given group of elements (e.g. alkalis, earth alkalis, main group elements, and transition metals). Their analysis was readily verified for the main group elements and the transition metals; the linear relationship between σ_{max} and α did not seem to hold for the alkali atoms and the earth alkali atoms when they used the published measured ionization cross section data for these elements. If we use the σ_{max} values for the alkalis derived from the present DM calculations and plot them against α (see Fig. 9), we readily verify the linear relationship as predicted by Harland and Vallance [22]. This, in turn, can be viewed as an independent justification of the reliability of the DM calculation for the alkali ionization cross sections.

4. Conclusions

We revisited the application of the semiclassical DM formalism to the calculation of electron-impact ionization cross sections of the alkali atoms Li, Na, K, Rb, and Cs. This was motivated by the results of recent DM calculations of atomic K-shell ionization cross sections for 11 elements [11] which suggested that the description of the removal of s electrons requires (1) a slightly modified energy dependence of the cross section in the low energy region, and (2) slightly modified weighting factors. The result of this modification is a slight shift in the peak position of the cross section towards lower impact energies without changing the absolute value of the cross section significantly. A detailed comparison with available cross section data for the ionization of the alkali atoms reveals that the revised DM calculations lead to an improved agreement with measured and other calculated ionization cross sections.

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