Available online at www.sciencedirect.com
ScienceDirect
International Journal of Mass Spectrometry 271 (2008) 58–62
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Calculated absolute cross-sections for the electron-impact ionization of atoms with atomic numbers between 20 and 56 using the Deutsch-Märk (DM) formalism

H. Deutsch [a], K. Becker [b,c,*], T.D. Märk [d,1]

[a] *Institut für Physik, Ernst Moritz Arndt Universität Greifswald, Felix-Hausdorff Str. 6, D-17487 Greifswald, Germany*
[b] *Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030, USA*
[c] *Center for Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, USA*
[d] *Institut für Ionenphysik, Leopold Franzens Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria*

Received 5 July 2007; accepted 3 October 2007
Available online 7 October 2007

Abstract

We report results of the calculation of electron-impact ionization cross-sections for atoms with atomic numbers Z in the intermediate range of Z-values ($20 < Z < 56$) using the DM formalism. For atoms with Z-values in this range (which contains many atoms of practical importance), there are some experimentally determined ionization cross-sections, but there has only been a single systematic theoretical study from 30 years ago, which was based on the Born approximation. The Born approximation tends to yield cross-sections which show an "overestimation" in the energy regime of the cross-section maximum compared to experimental data. The DM approach, on the other hand, has adequately reproduced the region of the cross-section maximum for many low-Z atoms as well as for the heavier rare gases. In the present case of atoms with Z-values from 20 to 56, the DM calculation typically shows a cross-section maximum lower than that predicted from the Born approximation by 25–50%, except for Xe, Ni, Cd, and Pd. The Born approximation and the DM formalism yield cross-sections that converge at higher impact energies.

Keywords: Electron-impact ionization; Cross-section calculations

1. Introduction

The ionization of an atom by electron impact is one of the most basic electron-driven processes both in terms of its importance in fundamental collision physics and from an application-motivated viewpoint in environments such as discharges and plasmas, planetary and cometary atmospheres, mass spectrometry, and chemical analysis. The removal of an electron from a neutral atom as the consequence of the impact of another electron is the simplest electron collision process resulting in the formation of three charged particles, the incident and ejected electrons (which are indistinguishable) and a positive ion. The complexity of the interactions of the three charged particles in the exit channel of this collision process renders a rigorous quantum mechanical description impossible even for the simplest target, atomic hydrogen. Reliable ionization cross-sections for a broad range of atoms are also important for the calculation of ionization cross-sections of molecules, which relies on a molecular population analysis, in which the molecular orbitals are expressed as linear combinations of the respective atomic orbitals (see e.g. [1,2],). For atoms with atomic numbers Z below about 20 (hydrogen through calcium), there is a broad data base of experimentally determined as well as calculated electron-impact ionization cross-sections (data exist for H, He, Li, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ar, K, and Ca) and the level of agreement is generally quite good (better than 20%). DM calculations have been carried out for all atoms for which experimentally determined ionization cross-sections are available [3,4]. In the regime of atoms with high Z-values, there are only a few measurements and/or calculations of ionization cross-sections of heavy atoms, i.e., atoms with Z

* Corresponding author. Present Address: Polytechnic University, 6 MetroTech Center, Brooklyn, NY 11201, USA. Tel.: +1 718 260 3608; fax: +1 718 260 3755.
E-mail address: kbecker@poly.edu (K. Becker).
[1] Dept. Plasmaphysics, Univerzita Komenskeho, Mlynska dolina, 842 48 Bratislava 4, Slovak Republic.

1387-3806/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2007.10.001

above 56 (barium) (data exist for Hg, Pb, Bi, and U and there has also been a single set of measurements for some of the lanthanides). For atoms with Z-values between about 20 and 56, a range which contains many atoms of practical importance such as Ti, V, Fe, Ni, Cu, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Ag, In, Sn, Sb, Te, I, Xe, Cs, Ba, there are some experimentally determined ionization cross-sections, but there has only been a single systematic theoretical study by McGuire [5–7]. In his approach, McGuire used the generalized oscillator strength formulation of the Born approximation. As is well known, this approach tends to reproduce reliable cross-sections at higher impact energies (energies about 20 times the ionization threshold). Thus, the calculations of McGuire may serve as a test for other theoretical approaches as well as experiments at higher impact energies, where the Born–Bethe cross-section is valid. It is also known (and stated explicitly by McGuire) that this approach tends to overestimate the cross-section in the region of low energies (i.e., for energies below about five times the ionization threshold).

In this paper, we report results of the calculation of electron-impact ionization cross-sections for atoms in the intermediate range of Z-values ($20 < Z < 56$) using the DM formalism, which does not show the "overestimation" of the cross-section in the low-energy regime. The calculation of McGuire and the DM calculations are expected to converge at higher impact energies. In the case of Mo and W, a comparison will also be made with the BEB calculation of Kim and co-workers [8,9]. For Cr, we also compare the DM calculation to more recent calculations of Bartschat and collaborators [10] and in the case of Zn, a comparison is made with the calculated cross-section of Omidvar et al. [11]. To the extent possible, a comparison with available experimental data will be made. In this context, McGuire already pointed out that his calculation showed significant discrepancies with experimental data for Xe ($Z = 54$), which he attributed to the presence of configuration interactions that are not described in his approach.

2. Theoretical background

The Deutsch-Märk (DM) formula [3,4] to calculate the ionization cross-section of an atom A (in its electronic ground state) is based on a quantum mechanical description of the atom in terms of its (nl) sub-shells labeled by the principal quantum number n and the orbital angular quantum number l. Each (nl) sub-shell is characterized by the binding energy of an electron in this sub-shell (E_{nl}), its quantum mechanically calculated radius (r_{nl}) or more precisely the radius of maximum radial density (as listed in column 1 in the tables of Desclaux [12]) and the number of electrons in this sub-shell (ξ_{nl}). The DM formalism calculates the total single ionization cross-section σ of an atom (i.e., the cross-section for the removal of one electron from the atom) by separately evaluating the partial cross-sections σ_{nl} for removing an atomic electron from a particular (nl) sub-shell and by summing over all sub-shells:

$$\sigma = \sum_{n,1} \sigma_{nl} \tag{1}$$

Each partial cross-section σ_{nl} is calculated as a function of the so-called reduced energy $U = E/E_{nl}$ where E is the energy of the incident electron and has the explicit form:

$$\sigma_{nl}(U) = \pi r_{nl}^2 g_{nl} \xi_{nl} f_{nl}(U) \tag{2}$$

The factor g_{nl} is a weighting factor or ionization factor and can be viewed as a measure for the likelihood to remove an electron from that particular sub-shell. The g_{nl} factors for the various sub-shells were determined semi-empirically from a fitting procedure using a set of reliable experimental ionization cross-section data such as those for the rare gases and a few other selected atoms [3,4]. The energy dependence of the partial ionization cross-sections is given by the function $f_{nl}(U)$, which is different for different (nl) sub-shells as one would expect because of the different shapes of different orbitals (s, p, d, f, etc.):

$$f_{nl}(U) = b_{nl}^{(q)}(U) \left[\ln \frac{(c_{nl} U)}{U} \right] \tag{3}$$

with the energy-dependent function $b_{nl}^{(q)}(U)$ has the explicit form:

$$b_{nl}^{(q)} = \frac{A_1 - A_2}{1 + (U/A_3)^p} + A_2 \tag{4}$$

In the case of the DM formalism, the explicit form of the various functions $f_{nl}(U)$ were also determined from a fitting procedure using a set of reliable cross-section shapes. All functions $f_{nl}(U)$ must converge in the limit of high-impact energy to the Born–Bethe cross-section shape given by $\ln(U)/U$.

The DM formalism represents a concept that can easily be extended to other targets such as atoms in excited states, atomic (positive and negative) ions, molecules, molecular (positive and negative) ions, and clusters. In the case of molecules and molecular ions, quantum mechanical population analyses are required that express the molecular orbitals in terms of the atomic orbitals of the constituent atoms.

3. Results and discussion

We present here the results of our calculation for 12 atoms (Fe, Xe, Ti, Cr, Ni, Zn, Sr, Zr, Cd, Pd, Mo, and W) which we compare with the corresponding calculations reported by McGuire [6]. In the case of Mo and W, we also present a comparison with the BEB calculation of Kim and co-workers [8,9].

We begin with the two atoms Fe ($Z = 26$) and Xe ($Z = 54$), for which we also compare the calculated cross-sections with experimental data. In the case of Fe (Fig. 1), the DM cross-section and the calculation of McGuire show the expected behavior, good agreement at very low energies (below 20 eV) a roughly 15% overestimation of the McGuire data near the cross-section maximum and good agreement at higher impact energies above about 60 eV. The two experimental data sets do not agree very well with one another. The data reported by Freund [13] show non-zero cross-section values below the first ionization threshold of the Fe atom in its electronic ground state. This may indicate that their cross-section contains contributions from the ionization of

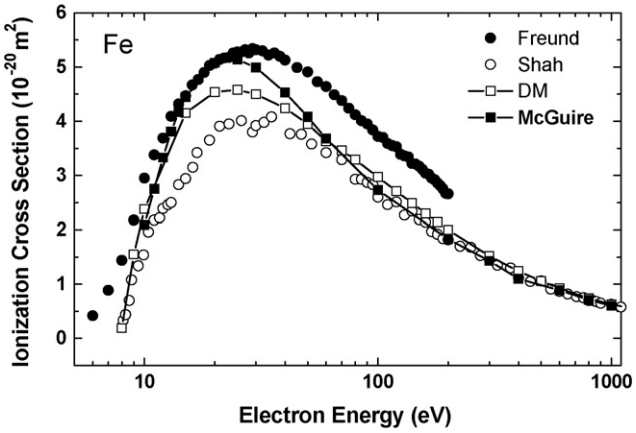

Fig. 1. Electron-impact ionization cross-section of Fe as a function of electron energy. The calculated DM cross-section (open squares) is compared with the calculated cross-section of McGuire [6] (solid squares) and the experimental data of Freund and co-workers [13] (solid circles) and Shah et al. [14] (open squares).

metastable Fe, a notion that is supported by the fact that their data lie above the experimental data of Shah et al. [14] and also above the calculated cross-sections for essentially all impact energies. Fig. 2 shows the measured Xe ionization cross-section [15], which is in excellent agreement with the present calculation for all energies. We note that there have been numerous experimental determinations of the Xe ionization cross-section. Those experimental data that are considered most reliable (see e.g., discussion in [15]) agree with one another to within 8% both in absolute value and cross-section shape. The calculation of McGuire [6] exceeds the other two curves by as much as a factor of 3 in the region of the cross-section maximum and lies consistently significantly above the other two curves. McGuire attributes the discrepancy to the fact that his calculation neglects configuration interaction effects in the target atom.

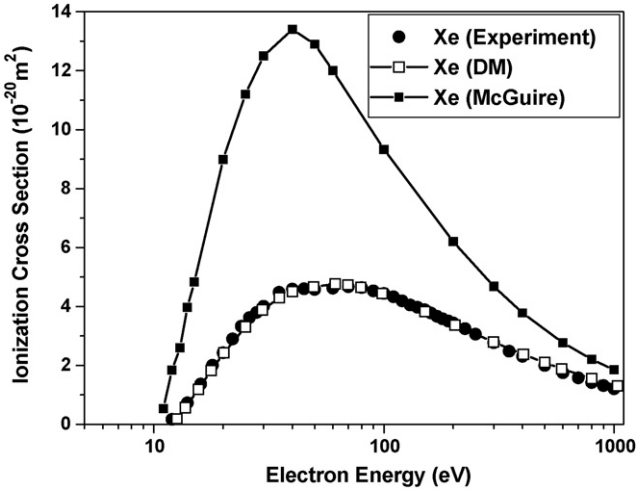

Fig. 2. Electron-impact ionization cross-section of Xe as a function of electron energy. The calculated DM cross-section (open squares) is compared with the calculated cross-section of McGuire [6] (solid squares) and the experimental data of Shah et al. [15] (solid squares).

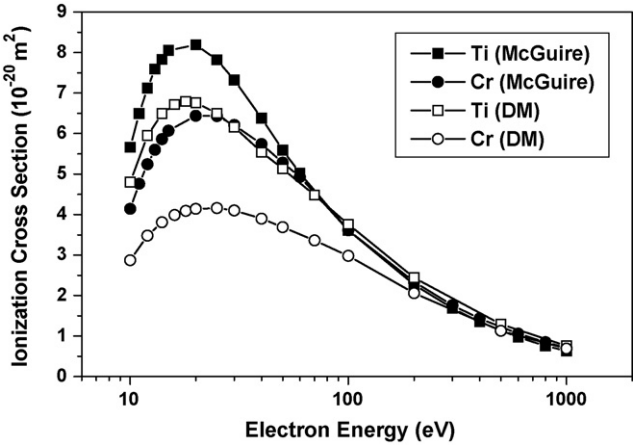

Fig. 3. Electron-impact ionization cross-section of Ti and Cr as a function of electron energy. The calculated DM cross-sections (open squares for Ti, open circles for Cr) are compared with the calculated cross-section of McGuire [6] (solid squares for Ti, solid circles for Cr).

Fig. 3 shows a comparison of the present calculation with the Born calculation of McGuire for Ti ($Z=22$) and Cr ($Z=24$). In both cases, the Born calculation lies above the DM cross-section in region of the cross-section maximum, by as much as 30% in the case of Ti and about 50% for Cr. We note that an R-matrix calculation by Reid et al. [10] for Cr revealed an energy dependence that is different from both curves shown in Fig. 3 in the low-energy region and a maximum that exceeds even the Born maximum, but agrees with both calculations shown here at higher impact energies. In the case of Ni ($Z=28$) shown in Fig. 4, both the Born and the DM calculation yield cross-section values that are very similar to one another (no overestimation of the Born cross-section). There is a slight discrepancy in the cross-section shapes, which is somewhat exaggerated by the logarithmic energy scale.

Fig. 5 shows the results for Zn ($Z=30$), Sr ($Z=38$), and Zr ($Z=40$). In all cases, the two calculations show a similar and expected behavior, an overestimation of the Born calculation in the region of the cross-section maximum and good agree-

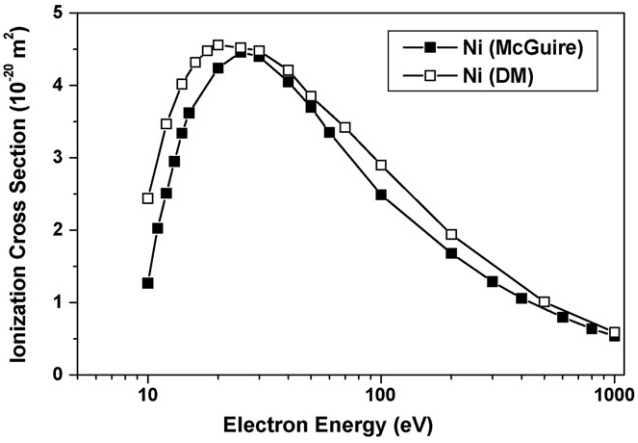

Fig. 4. Electron-impact ionization cross-section of Ni as a function of electron energy. The calculated DM cross-section (open squares) is compared with the calculated cross-section of McGuire [6] (solid squares).

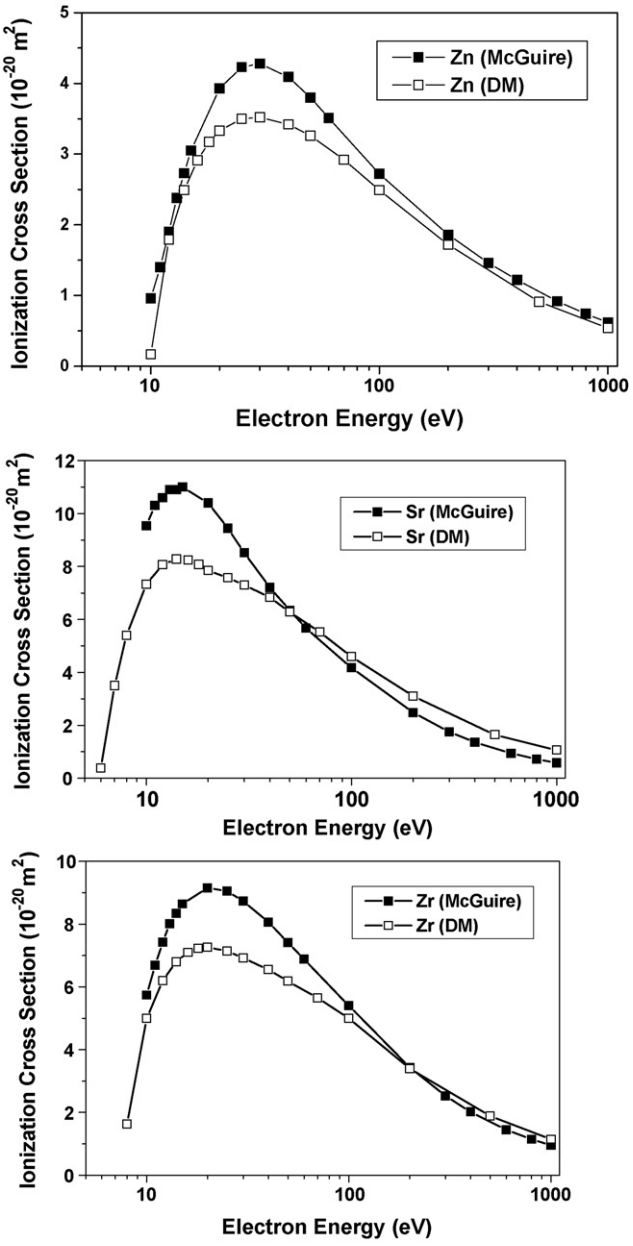

Fig. 5. Electron-impact ionization cross-section of Zn (top diagram), Sr (center diagram), and Zr (bottom diagram) as a function of electron energy. The calculated DM cross-sections (open squares) are compared with the calculated cross-section of McGuire [6] (solid squares).

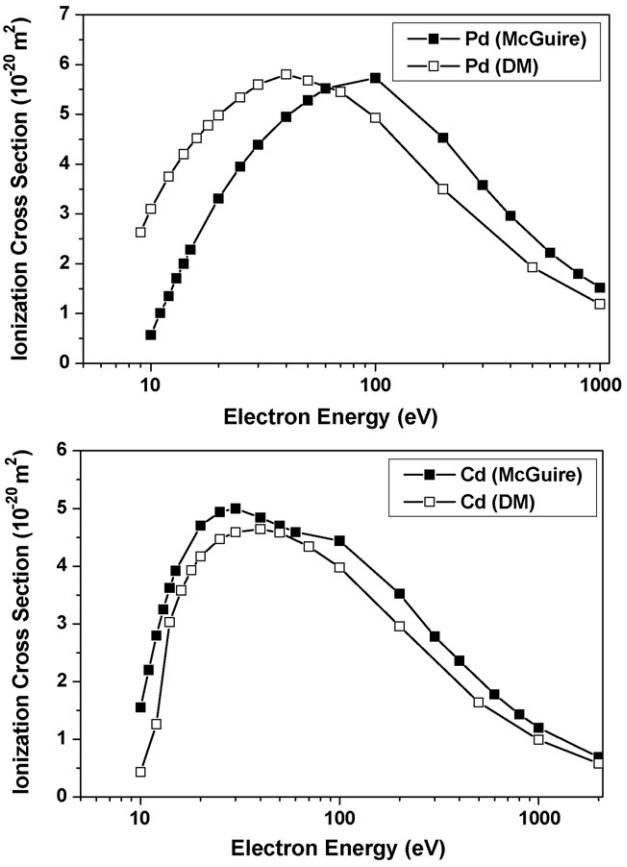

Fig. 6. Electron-impact ionization cross-section of Pd (top diagram) and Cd (bottom diagram) as a function of electron energy. The calculated DM cross-sections (open squares) are compared with the calculated cross-section of McGuire [6] (solid squares).

ment at higher impact energies. The overestimation is in the range of 25–30% in all three cases. In the case of Zn, Omidvar et al. [11] performed a quantum mechanical calculation, which yielded cross-section values which lie above the DM calculation in the region of the cross-section maximum (maximum value of 4.2×10^{-20} m^2 around 30 eV) and above both curves shown in Fig. 5 at higher impact energies. Likewise, an experimentally determined Zn ionization cross-section [16] lies above all calculated cross-sections with a maximum value of slightly above 5×10^{20} m^2.

The results for Pd ($Z = 46$) and Cd ($Z = 48$) are shown in Fig. 6. In both cases, the calculation of McGuire yielded unusual cross-section shapes which differ significantly from the typical Born cross-section shape and from the DM cross-section shapes. In the case of Pd, the cross-section of McGuire reaches its maximum at a higher impact energy (100 eV) compared to the DM cross-section (around 40 eV), while both calculation yield very similar values for the cross-section maxima. The cross-section of McGuire also shows an unusually sharp bent at this energy, before merging into the expected high-energy shape. The Cd cross-section also show very similar maximum values of the cross-section, but again McGuire reports an unusual cross-section shape with a distinct "bump" in the energy dependence around 100 eV.

Fig. 7 shows the results for Mo ($Z = 42$) and W ($Z = 74$) for which we compare our calculations with those of McGuire [6,7] and the BEB calculation of Kim and co-workers [8,9]. In the case of Mo, the BEB calculation lies above the other two calculations and also reaches its maximum value at a somewhat higher impact energy. All three curves converge at higher impact energies around 500 eV. The situation is slightly different in the case of W. While the ordering of the cross-section maxima $\sigma_{BEB} > \sigma_{McGuire} > \sigma_{DM}$ is similar to what as observed for Mo, the DM cross-section shape is somewhat different from the other two shapes. The DM cross-section peaks at 30 eV compared to 50 eV for the other two curves and the level of agreement between the three curves in the high-energy region is also not as good as in

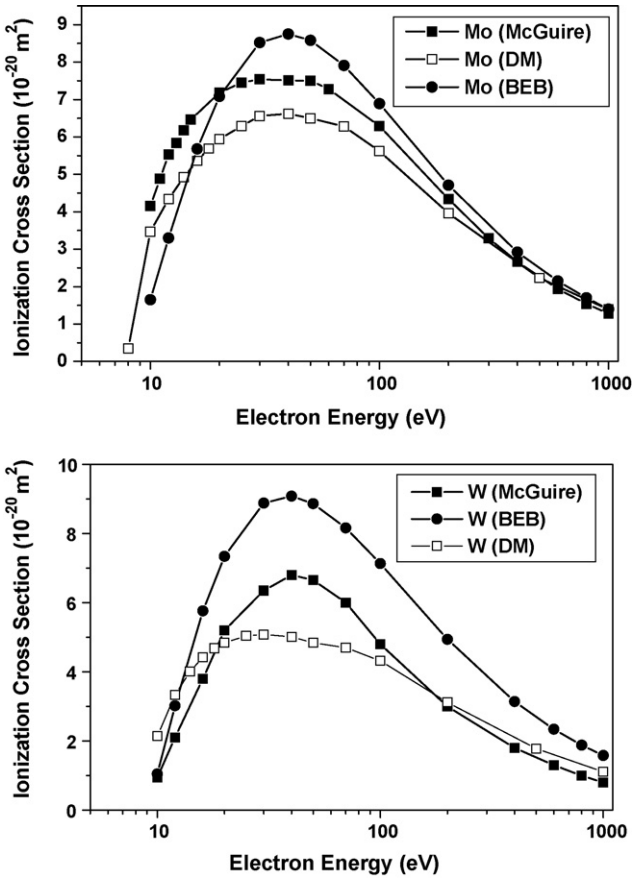

Fig. 7. Electron-impact ionization cross-section of Mo (top diagram) and W (bottom diagram) as a function of electron energy. The calculated DM cross-sections (open squares) are compared with the calculated cross-section of McGuire [6] (solid squares) and the BEB cross-sections of Kim and co-workers [8,9] (solid circles).

the Mo case. We note in this context that the Lotz formula [17] for the W cross-sections also yields a cross-section maximum at around 30 eV, but the absolute value of 9.5×10^{-20} m^2 exceeds even the maximum value of the BEB cross-section.

4. Conclusions

We calculated electron-impact ionization cross-sections for atoms in the intermediate range of Z-values ($20 < Z < 56$) using the DM formalism. Our results do not show the "overestimation" of the cross-section in the low-energy regime, which is typical of the Born approximation that was used in an earlier systematic theoretical treatment of atoms in this range of Z-values by McGuire [5–7]. The overestimation of the Born cross-sections ranges typically from 25% to 50%. Exceptions are Xe on one hand, where the overestimation is almost a factor of 3 and the atoms Ni, Pd, and Cd, where the calculation of McGuire and the DM approach yield comparable cross-section maxima, but different cross-section shapes. The calculation of McGuire and the DM calculations were found to converge at higher impact energies as expected.

Acknowledgments

This work has been carried out within the Association EURATOM-ÖAW. The content of the publication is the sole responsibility of its publishers and it does not necessarily represent the views of the EU Commission or its services. It was partially supported by the FWF, Wien, Austria. KB acknowledges partial financial support from the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, U.S. Department of Energy and from the US National Aeronautical and Space Administration (NASA).

References

[1] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833;
R. Tang, J. Callaway, J. Chem. Phys. 84 (1986) 6858.
[2] H. Deutsch, K. Becker, S. Matt, T.D. Märk, Int. J. Mass Spectrom. 197 (2000) 37.
[3] H. Deutsch, P. Scheier, K. Becker, T.D. Märk, Int. J. Mass Spectrom. 233 (2004) 13, and references therein to earlier work.
[4] H. Deutsch, P. Scheier, S. Matt-Leubner, K. Becker, T.D. Märk, Int. J. Mass Spectrom. 243 (2005) 215;
H. Deutsch, P. Scheier, S. Matt-Leubner, K. Becker, T.D. Märk, Erratum Int. J. Mass Spectrom. 246 (2005) 113.
[5] E.J. McGuire, Phys. Rev. A 3 (1971) 267.
[6] E.J. McGuire, Phys. Rev. A 16 (1977) 62.
[7] E.J. McGuire, Phys. Rev. A 20 (1979) 445.
[8] D.-H. Kwon, Y.-J. Rhee, Y.-K. Kim, Int. J. Mass Spectrom. 245 (2005) 26.
[9] D.-H. Kwon, Y.-J. Rhee, Y.-K. Kim, Int. J. Mass Spectrom. 252 (2005) 213.
[10] R.G.H. Reid, K. Bartschat, P.G. Burke, J. Phys. B 25 (1992) 3175.
[11] K. Omidvar, H.L. Kyle, E.C. Sullivan, Phys. Rev. A 5 (1972) 1174.
[12] J.P. Desclaux, Atom. Data Nucl. Data Tables 12 (1973) 325.
[13] T.R. Hayes, R.C. Wetzel, R.S. Freund, Phys. Rev. A 35 (1987) 578.
[14] M.B. Shah, P. McCallion, K. Okumo, H.B. Gilbody, J. Phys. B 26 (1993) 2393.
[15] R. Rejoub, B.G. Lindsay, R.F. Stebbings, Phys. Rev. A 65 (2002) 042713.
[16] R.F. Potti, J. Chem. Phys. 44 (1966) 916.
[17] W. Lotz, Z. Phys. 232 (1970) 101.