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Calculations of absolute electron-impact ionization cross sections for molecules of technological relevance using the DM formalism

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Abstract

The Deutsch-Märk (DM) formalism has been used to calculate absolute electron impact ionization cross sections for the technologically relevant molecules NO_2, BF_3, BCl_3, H*X* (*X* = F, Cl, Br, J), Br_2, J_2, WF_6, GeH_x (*x* = 1–4), TMS (tetramethylsilane), HMDSO (hexamethyldisiloxane), and TEOS (tetraethoxysilane). Our calculations are compared with experimental data, where available, and with calculated cross sections based on the Binary-Encounter-Bethe (BEB) method of Kim and Rudd. In some cases, comparisons are also made with predictions from the modified additivity rule (MAR). (Int J Mass Spectrom 206 (2001) 13–25) © 2001 Elsevier Science B.V.

Keywords: Electron-impact ionization; Cross-section calculations; Molecules

1. Introduction

Absolute cross sections for the electron impact ionization of molecules have been measured and calculated since the 1930s [1,2]. The ionization of a molecule induced by electron impact is a basic electron–molecule collision process. Electron-impact ionization processes are also important in many practical applications such as low-temperature processing plasmas; fusion-edge plasmas; gas discharges; planetary, stellar, and cometary atmospheres; radiation chemistry; mass spectrometry; and chemical analysis [2]. Considerable progress in the experimental determination of electron-impact ionization cross sections for atomic and molecular targets has been achieved in the past decade [2–6]. Rigorous quantum mechanical calculations of ionization cross sections for molecular targets are beyond the capability of current quantum-mechanical electron collision theory for essentially all molecules [7–9]. The need to incorporate molecular ionization cross sections in modeling codes for various applications (e.g., in fusion edge plasmas [10] and in plasma processing [11]) has stimulated the use of simplistic additivity rules to estimate molecular ionization cross sections. Many variants of the additivity rule, whose concept was first introduced by Ötvos and

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Stevenson [12], can be found in the literature [13,14], including the most recent variant, called MAR (modified additivity rule) [15,16]. Most of the early ones have, in general, limited predictive capabilities.

Recently, more rigorous methods that include quantum-mechanically calculated molecular structure information have emerged as alternative methods to calculate absolute electron-impact ionization cross sections for molecules in a comparatively straightforward fashion [17–29]. Among those, the Deutsch-Märk (DM) formalism [21–24] and the Binary-Encounter-Bethe (BEB) theory of Kim, Rudd, and coworkers [27–29] are perhaps the most widely used methods. Recently, Deutsch et al. [24] reviewed the application of the DM formalism to the calculation of ionization cross sections for 31 molecules and radicals. These authors compared their calculated results with available experimental data as well as with the results of the BEB theory and with predictions from several other methods to the extent that these methods had been applied to the list of 31 targets. In this article, we extend the application of the DM formalism to the technologically important molecules and radicals NO_2, BF_3, BCl_3, HX (X = F, Cl, Br, J), Br_2, J_2, WF_6, GeH_x (x = 1–4), TMS, HMDSO, and TEOS. Where available, we compare our calculated cross sections with experimental data and with the results of other cross-section calculations.

2. Theoretical background

A detailed discussion of the DM formalism can be found in the recent review of Deutsch et al. [24] to which we refer the reader for an in-depth discussion of the DM method. Briefly, the DM formula for the calculation of the absolute electron-impact ionization cross section σ of an atom has the form [17–20]

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

where $(r_{nl})^2$ is the radius of maximum radial density[1] of the atomic subshell characterized by the quantum numbers n and l (as listed in column 1 in the tables of Desclaux [30]), ξ_{nl} refers to the number of atomic electrons in the (n,l) subshell, and the g_{nl} are appropriately chosen weighting factors [24]. The function $f(U)$ describes the energy dependence of the ionization cross section where U is the reduced collision energy, $U = E/E_{nl}$. E denotes the energy of the incident electron and E_{nl} refers to the ionization energy in the (n,l) sub-shell. The function $f(U)$ has the explicit form

$$f(U) = d(1/U)[(U-1)/(U+1)]^a\{b + c[1 - (1/2U)]\ln[2.7 + (U-1)^{0.5}]\}, \qquad (2)$$

where the parameters a, b, c, and d have different values for s-, p-, d-, and f-electrons, as one might expect on the basis of the different angular shapes of atomic s-, p-, d-, and f-orbitals. Table 1 summarizes the values for the parameters a, b, c, and d for s-, p-, d-, and f-electrons.

Table 1
Parameters a, b, c, and d for the energy-dependent function $f(U)$ in Eq. (2) for s-, p-, d-, and f-electrons

	a	b	c	d
s-electrons	1.06	0.23	1	1.1
p-electrons	2	1	1	1
d-electrons	3/2	3	2/3	1
f-electrons	3/2	1	2/3	1

In the case of molecular targets, it was found advantageous [24] to reduce the molecular ionization cross-section calculation to the atomic cross-section formula of Eq. (1). This requires an atomic orbital population (Mulliken) analysis [31] or an equivalent method that expresses the molecular orbitals in terms of the atomic orbitals of the constituent atoms. As the atoms in the investigated molecules range from H to W, different basis sets and quantum chemical methods were used to calculate geometries, atomic orbital coefficients, and ionization energies. For NO_2, the geometry was obtained from DFT calculations with B3LYP functional [32] and the aug-cc-pVDZ basis set [33], while the populations were calculated with the Hartree-Fock method and the MKSBJ effective core potential and basis set [34,35]. The ionization

[1] Note that in most of the previous publications relating to the DM formalism the quantity $(r_{nl})^2$ was erroneously referred to as the mean square radius of the (n,l) subshell.

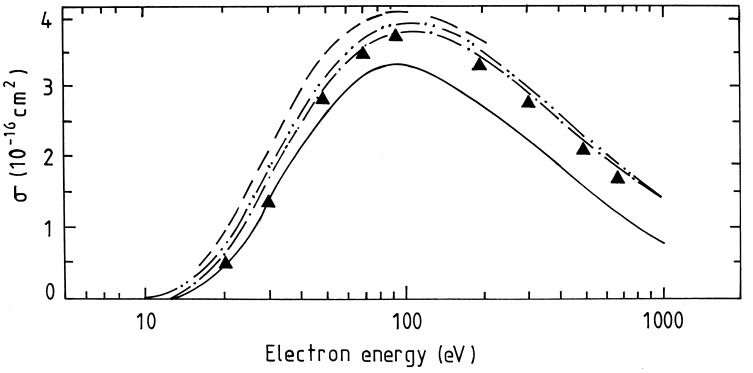

Fig. 1. Electron-impact ionization cross section of NO_2 from threshold to 1000 eV. The measured data of Lukic et al. [40] (designated by filled triangles) are compared to calculated cross sections based on the Deutsch-Märk formalism (solid line), the modified additivity rule approach (dashed line) [15,16], and two variants of the Binary-Encounter-Bethe method [41] (dash-dot-dash line using the vertical ionization energy and dash-dot-dot-dash line using the adiabatic ionization energy).

energies were calculated via Hartree-Fock with the aug-cc-pVGZ basis set [36]. For BF_3 and BCl_3, geometries and ionization energies were derived from MP2 calculations with the aug-cc-pVQZ basis set and the populations were derived by Hartree-Fock calculations with the MKSBJ basis set. For the molecules HF, HCl, HBr, HJ, Br_2, I_2, GeH_x, and WF_6 all properties were calculated via the MP2 method and the SDD basis set [37,38]. For the three compounds containing Si, geometries and ionization energies were obtained from Hartree-Fock calculations with MIDI-X basis set [39] and the atomic populations from Hartree-Fock calculations with the MKSBJ basis set.

3. Results and discussion

The calculations presented in this article involve target molecules and free radicals that are of relevance in various technological applications. Particular attention in the selection of the targets was given to species of importance as feed-gas constituents and by-products in plasma-assisted materials processing and/or remediation applications.

3.1. The molecule NO_2

The interest in the NO_2 molecule stems from the importance of NO_x compounds in the remediation of the exhaust gas emitted by combustion engines. Furthermore, NO_2 was the only compound in the N_2O, NO, NO_2 sequence for which no reliable experimental total ionization cross-section data had been measured (see, e.g., ref. [15]) until the very recent work of Lukic et al. [40]. The measured total electron-impact ionization data of these authors are compared in Fig. 1 to calculated cross sections using the DM formalism[2], the MAR [15,16], and two variants of the BEB formalism [41]. The experimental data are best represented by the BEB calculations that are in excellent agreement with the data for all energies above ~30 eV. The low-energy data (threshold to 30 eV) agree best with the DM cross section. However, the DM calculation yields an overall cross-section curve that lies below the data for energies >30 eV. The MAR cross section exceeds the measured data by ~10%–12% at all impact energies.

3.2. Halogen-containing compounds (BF_3, BCl_3, HX (X = F, Cl, Br, J), Br_2, J_2, WF_6)

The halogen-containing molecules listed above have gained prominence in a variety of plasma-

[2] We note that all parameters except for the atomic orbital populations that are required for the DM calculation can be found in Ref. 24. The atomic orbital populations for all species for which DM ionization cross sections were calculated as part of this publication may be obtained upon request (e-mail to: *michael.probst@uibk.ac.at*).

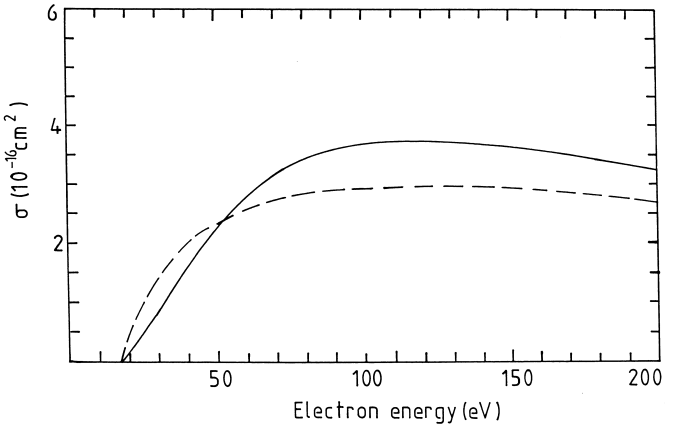

Fig. 2. Calculated BF_3 ionization cross sections using the Deutsch-Märk formalism (solid line) and the modified additivity rule, shown as the dashed line from threshold to 200 eV.

assisted etching applications of, among other materials, Si, SiO_2, and silicides as well as in thin-film deposition processes.

3.2.1. BF_3, BCl_3

These boron-containing molecules are frequently used as sources of fluorine and chlorine atoms and ions in etching plasmas. No experimental ionization cross-section data are available for BF_3, and only one ionization cross-section measurement has been reported for BCl_3 [43]. Fig. 2 shows the result of the present DM calculation for the ionization cross section of BF_3 from threshold to 200 eV in comparison with a prediction for the same cross sections from the MAR [16]. Both curves are in fair agreement (to within 25% or better) in this energy range. In the case of BCl_3 (Fig. 3), we show a comparison of the DM cross section and the MAR cross section, which are in good agreement (better than 20%) in the energy range from threshold to 200 eV with the result of a BEB calculation [42] and with the experimental data of Jiao et al. [43], which cover only the energy range from threshold to 60 eV. The three calculated cross sections are in reasonable agreement with each other. The experimental data appear to agree best with the MAR calculation, although the overall agreement of the measured data with all three calculated cross-section curves is satisfactory in the limited energy range covered by the experiment of Jiao et al. [43].

3.2.2. HF, HCl, HBr, HJ

Even though only HCl and HBr are commonly used in plasma-processing applications, we calculated DM cross sections for all four halogen-hydrides (Fig. 4). As in the case of $B\pm3$ and BCl_3 the MAR cross sections (not shown in Fig. 4) are in good agreement with the DM cross sections. To the best of our knowledge, there are no experimental ionization cross-section data for these molecules in the literature. The maximum cross-section values range from $\sim 6.5 \times 10^{-16}$ cm^2 (HJ) to $\sim 1.2 \times 10^{-16}$ cm^2 (HF), with HBr and HCl having essentially the same maximum cross-section values. This ordering in the maximum cross-section values for the halogen-hydrides reflects the ordering in the maximum ionization cross-section values of the atomic halogens, which span the range from 6×10^{-16} cm^2 (J) to $\sim 1 \times 10^{-16}$ cm^2 (F) [44].

3.2.3. Br_2, J_2

Our main motivation to carry out DM calculations for the ionization of the dimers Br_2 and J_2, for which no experimental data have been reported in the literature, was the fact that we had already used a

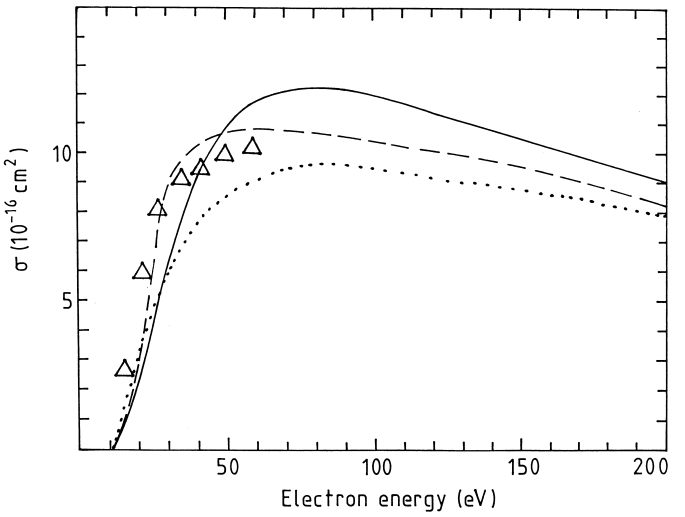

Fig. 3. Calculated BCl_3 ionization using the Deutsch-Märk formalism (solid line) and the modified additivity rule (dashed line) from threshold to 200 eV. Also shown are the experimental data of Jiao et al. [43] (designated by open triangles) and the Binary-Encounter-Bethe calculation of Kim [42] (dotted line).

different defect concept to calculate ionization cross sections for these two molecules [45] and that we wanted to compare the results of these earlier calculations with the results of the DM formalism. As can be seen in Fig. 5, the agreement between the calculated cross sections based on the DM approach and the defect concept is excellent for both molecules, except perhaps for a slight difference in the energy shape. The DM cross section peaks at a somewhat higher electron energy.

WF_6

Tungsten hexafluoride is used as a constituent in low-temperature plasmas for the plasma-assisted deposition of tungsten. WF_6 is also a volatile by-product

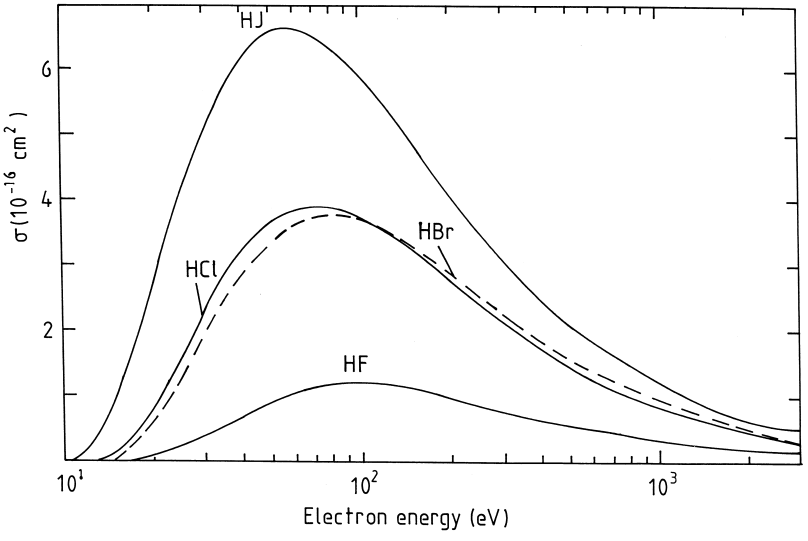

Fig. 4. Electron-impact ionization cross section of the HF, HCl, HBr, and HJ molecules calculated using the Deutsch-Märk formalism.

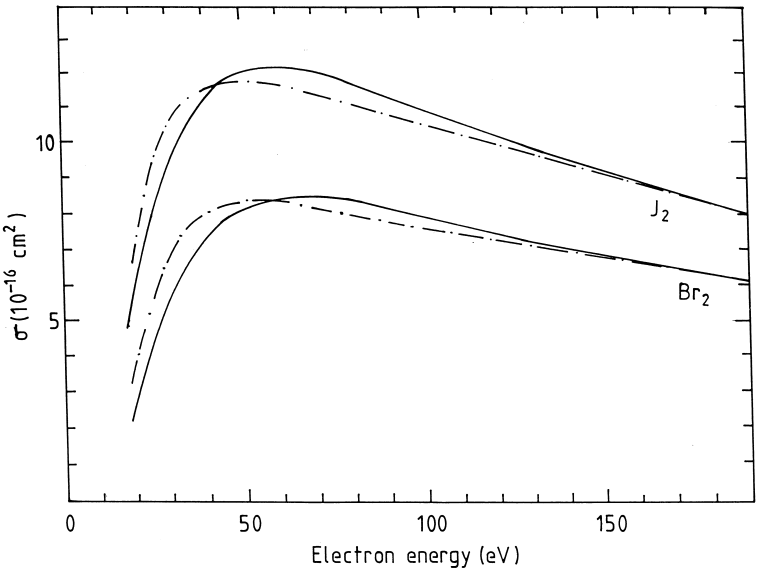

Fig. 5. Electron-impact ionization cross section of Br_2 and J_2 from threshold to 200 eV. The Deutsch-Märk cross sections (solid lines) are compared to the predictions from a defect concept [45], shown as the dash-dot lines.

of tungsten etching with F-bearing molecules. There has only been one experimental determination of partial WF_6 ionization cross sections from which the authors obtained an estimate of the total WF_6 ionization cross section [46]. The experimental data of Basner et al. [46] shown in Fig. 6 as filled circles are compared with the DM cross section (solid line), two variants of the BEB method [47] (short dashed line, small dots), and two variants of the MAR (long dashed line, dash–double dot line). It is noteworthy

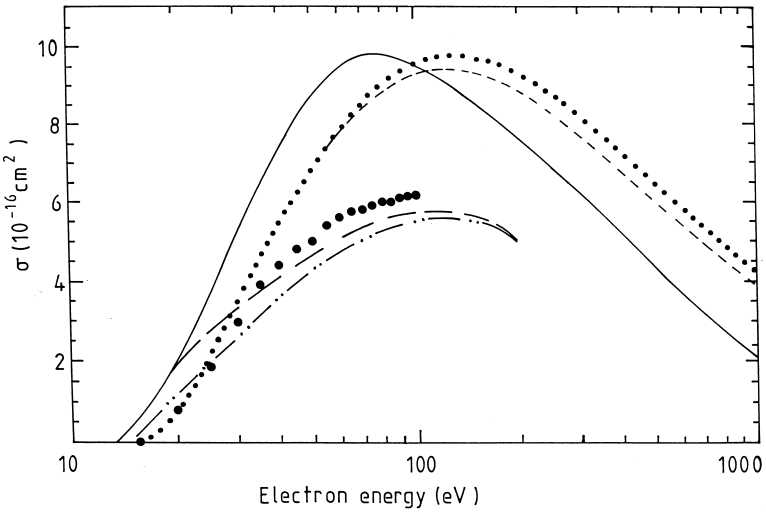

Fig. 6. Electron-impact ionization cross section of WF_6. The experimental data of Basner et al. [46] (designated by filled large circles) are compared with the Deutsch-Märk cross section (solid line), two variants of the Binary-Encounter-Bethe calculation [47] (short dashed line and small dots), and two variants of the modified additivity rule method (long dashed line and dash-double dot line).

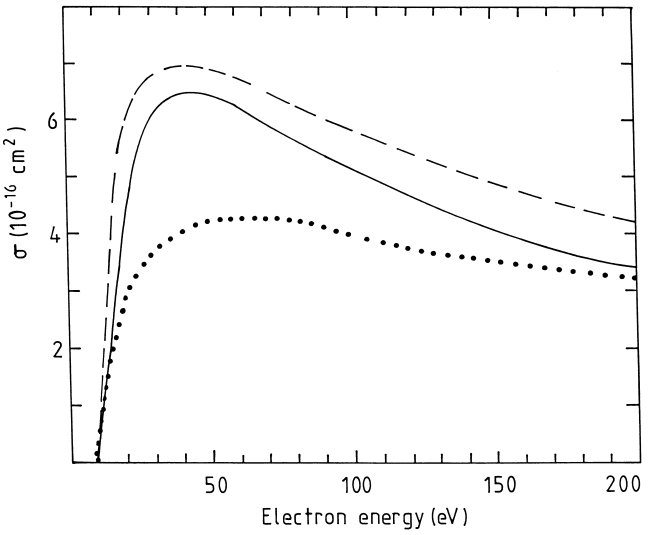

Fig. 7. Electron-impact ionization cross section of GeH. The calculated Deutsch-Märk cross section (solid line) is compared to calculations using the modified additivity rule concept (dashed line) and the Binary-Encounter-Bethe formalism (small filled circles) of Ali et al. [50]. Note the rather small BEB cross section (in comparison to the DM and MAR values) despite the fact that the BEB cross section has been increased by two correction procedures in [50].

that both BEB calculations and the DM formalism predict essentially identical maximum cross-section values, albeit at somewhat different electron energies. Both methods yield cross sections that exceed the measured data by >50%. The two variants of the MAR are based on two different values of the effective number of electrons contributing to the ionization cross section (see ref. [16] for details). The lower curve is based on six effective electrons [16] (the four (5d) electrons plus the two (6s) electrons), whereas the upper curve also includes the six (5p) electrons and the two (5s) electrons, for a total of 14 effective electrons. Surprisingly, the MAR calculations, which do not include any quantum-mechanically calculated molecular structure information, appear to provide the best description of the experimental data. However, it should be noted that the total cross section of Basner et al. [46], which was obtained as the sum of all measured partial ionization cross sections, should be considered as a lower limit of the total WF_6 cross section. It is not clear to what extent these authors accounted for the complete extraction and detection of all energetic fragment ions in their experiment [48].

3.3. The GeH_x (x = 1–4) compounds

Germanium hydride, GeH_4, is used as a feed-gas in low-temperature plasmas for semiconductor processing. The GeH_x (x = 1–3) radicals are readily formed in plasmas containing GeH_4 in the feed-gas mixture. The ionization properties of all four GeH_x (x = 1–4) compounds are important quantities in any effort to understand and model the plasma chemical processes in GeH_4-containing low-temperature plasmas. Unfortunately, there appears to be only a single measured ionization cross-section data point in the literature, a measurement for GeH_4 at 100 eV by Perrin et al. [49]. No data are available for any of the GeH_x (x = 1–3) free radicals. This is a rather unsatisfactory data situation for these technologically important species. Figs. 7–10 summarize the calculated ionization cross sections for the four GeH_x compounds. In all cases, the calculated DM cross section exceeds the BEB cross section [50] by margins ranging from 40% to 100% near the maximum of the ionization cross section. This discrepancy between the DM cross sections and the BEB cross sections is rather puzzling

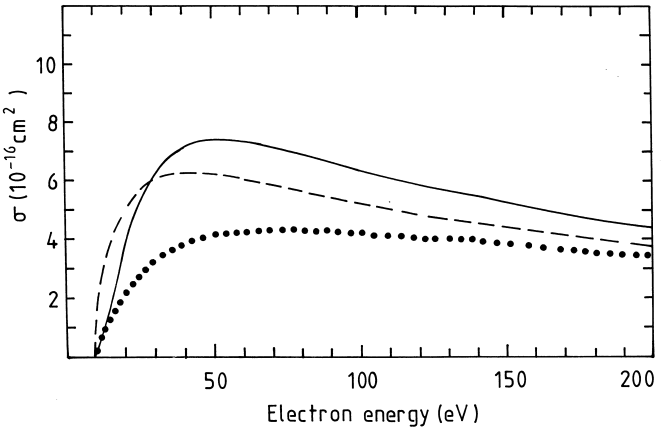

Fig. 8. Electron-impact ionization cross section of GeH_2. The calculated Deutsch-Märk cross section (solid line) is compared to calculations using the modified additivity rule concept (dashed line) and the Binary-Encounter-Bethe formalism (small filled circles) of Ali et al. [50].

in view of the generally good agreement (to within 20% or better) that was found for most of the 31 molecules and radicals discussed in the recent review of Deutsch et al. [24]. We have no obvious explanation for this discrepancy. We also included in Figs. 7–10 the corresponding MAR cross sections. We find that the MAR cross section for GeH exceeds the BEB cross section by a factor of two and is very close to the cross section determined experimentally by Freund et al. [51] for Ge ($\sim 7.5 \times 10^{-16}$ cm^2). This discrepancy decreases systematically as one goes from GeH to GeH_2 to GeH_3 to GeH_4, where the MAR cross section is comparable in magnitude to the BEB cross section but exhibits a somewhat different energy dependence.

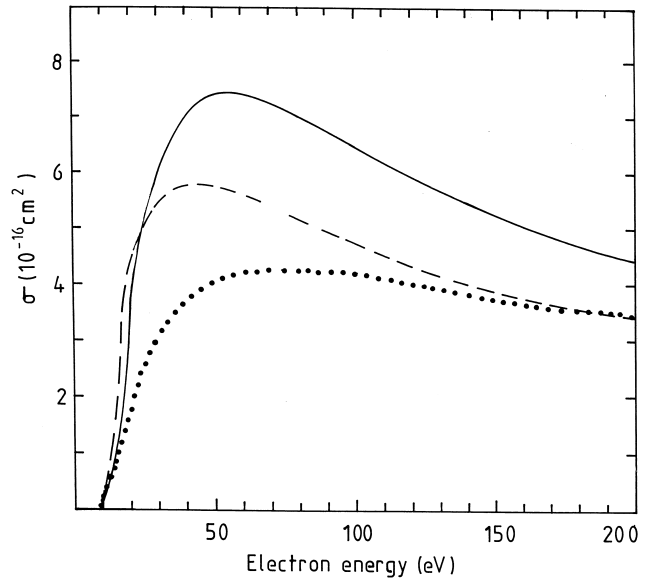

Fig. 9. Electron-impact ionization cross section of GeH_3. The calculated Deutsch-Märk cross section (solid line) is compared to calculations using the modified additivity rule concept (dashed line) and the Binary-Encounter-Bethe formalism (small filled circles) of Ali et al. [50].

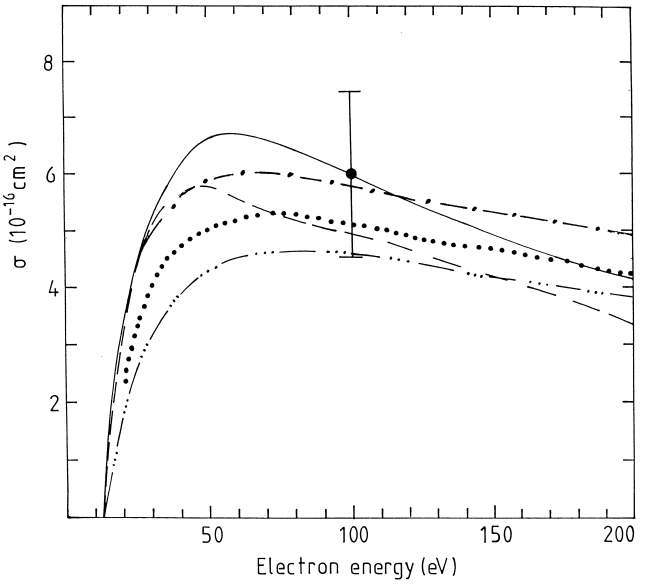

Fig. 10. Electron impact ionization cross section of GeH_4. The calculated Deutsch-Märk cross section (solid line) is compared to calculations using the modified additivity rule concept (dashed line) and two variants of the Binary-Encounter-Bethe formalism (small filled circles and dash–triple dot line designaling calculations by Ali et al. [50] using the adiabalic and vertical ionization energy, respectively). Also shown is the single data point from ref [49] (designated by a large filled circle) with its 25% error margin and recent results by Szmytkowski and Ptasinska-Denga [52] designated by a dash-dot line.

The single measured data point for GeH_4 at 100 eV [49] falls exactly on the calculated DM cross section for this molecule. However, this agreement must be viewed as coincidental, particularly in view of the 25% error margin of the experiment, which renders this data point essentially consistent with all calculations. Nevertheless, it is interesting to note that recent results reported by Szmytkowski and Ptasinska-Denga [52] confirm this data point and the somewhat larger cross sections obtained by the DM method as compared to the BEB values. The results by Szmytkowski and Ptasinska-Denga [52] are based on a comparison of total electron scattering cross sections with total electron-impact ionization cross sections for various perfluorinated molecules and a simple regression formula deduced from this. Clearly, there is a need for experimental data for the four GeH_x compounds and perhaps a renewed effort aimed at elucidating the possible reason(s) for the serious discrepancy between the DM cross sections and the BEB cross sections for this family of species.

3.4. The silicon-organic compounds TMS, HMDSO, and TEOS

Organic silicon-containing molecules such as TMS (tetramethylsilane), HMDSO (hexamethyldisiloxane), and TEOS (tetraethoxysilane) are frequently used as constituents of feed-gases used in plasma chemical applications such as plasma-assisted thin-film deposition. A slight, often minimal, variation of the discharge conditions of a deposition plasma containing Si–organic compounds can have a profound impact on the properties of the deposited films [6].

3.4.1. TMS

Strictly speaking, this molecule with the sum formula $Si(CH_3)_4$ is not an organic molecule. It is derived from silane, SiH_4, by replacing the four H atoms with four methyl (CH_3) groups. TMS is the only molecule in this group for which ionization cross sections have been measured by more than one group [53,54] in the past 5 years. However, the two data sets

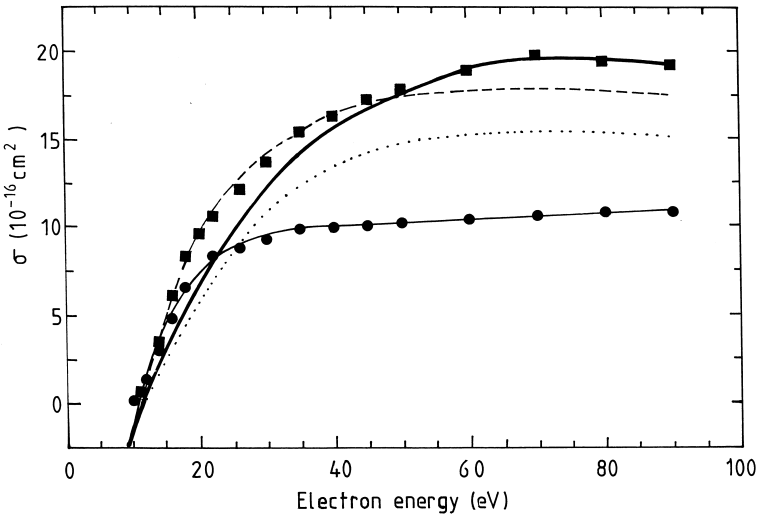

Fig. 11. Electron-impact ionization cross section of tetramethylsilane. The calculated Deutsch-Märk cross section (solid line) is compared with a modified additivity rule calculation (dashed line), a Binary-Encounter-Bethe calculation (small filled dots), and the experimental data of Basner et al. [54] (filled squares) and McGinnes et al. [53] (filled circles connected by thin line).

differ by almost a factor of two in terms of the maximum value of the ionization cross section, and there are also discrepancies in the measured energy dependence in the two data sets. Fig. 11 shows the two experimental data sets in comparison with calculated cross sections on the basis of the DM approach, the BEB theory [50], and the MAR method [16]. All three calculated cross sections clearly favor the measured cross section of Basner et al. [54] in terms of the absolute cross-section value and the energy dependence, even though there are some minor discrepancies in the energy dependence predicted by the various calculations and between the calculated cross sections and the cross-section shape reported by Basner et al. [54].

3.4.2. HMDSO

The ionization properties of this molecule with a sum formula $Si_2O(CH_3)_6$ and a structure $(CH_3)_3$-Si–O–Si–$(CH_3)_3$ have been studied extensively by Basner et al. [55]. There are also earlier data in the literature [56] that lie considerably below the more recent data of Basner et al. [55]. We carried out both a DM calculation and a MAR calculation, and it can be seen from Fig. 12 that both calculated cross sections are in fair agreement with the measured data of Basner et al. [55], with the MAR calculation yielding the better agreement. However, the discrepancy of 20% in the maximum cross-section value between the DM calculation and the measured data is not serious in view of the complex structure of this molecule.

3.4.3. TEOS

The only ionization cross section data for TEOS with a sum formula $SiO_4C_8H_{20}$ and a structure Si(O-CH_2-$CH_3)_4$ have been reported by Basner et al. [6]. The data that are shown in Fig. 13 are in good agreement with the DM cross section and in fair agreement with the MAR cross section. It appears that the measured cross section has not yet reached its maximum value at 100 eV, which is the highest energy for which measured data are available. Further experiments involving this molecule are desirable.

4. Summary

We applied the Deutsch-Märk (DM) formalism in a series of calculations of absolute electron impact

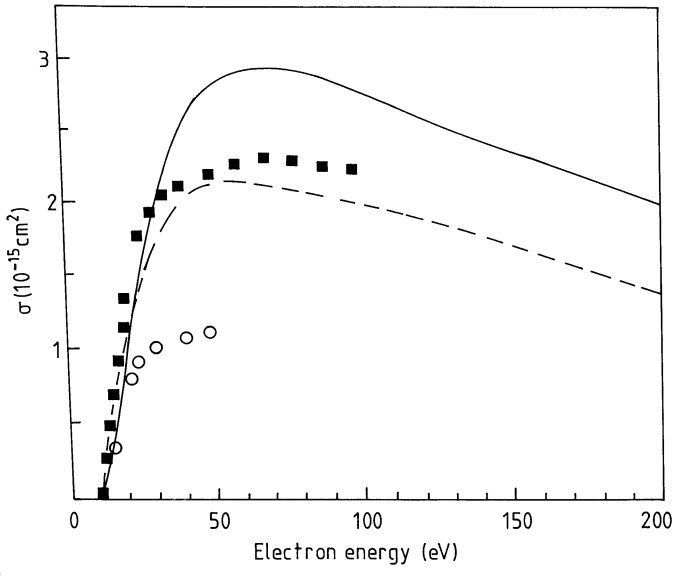

Fig. 12. Electron impact ionization cross section of hexamethyldisiloxane. The calculated Deutsch-Märk cross section (solid line) is compared with a modified additivity rule calculation (dashed line) and with the experimental data of Basner et al. [55] (filled squares) and the data of Seefeldt et al. [56] (open circles).

ionization cross sections for the technologically relevant molecules NO_2, BF_3, BCl_3, H*X* (*X* = F, Cl, Br, J), Br_2, J_2, WF_6, GeH_x (*x* = 1–4), TMS, HMDSO, and TEOS. Our calculations were compared with experimental data, where available (NO_2, BCl_3, WF_6, GeH_4, TMS, HMDSO, and TEOS), and with calcu-

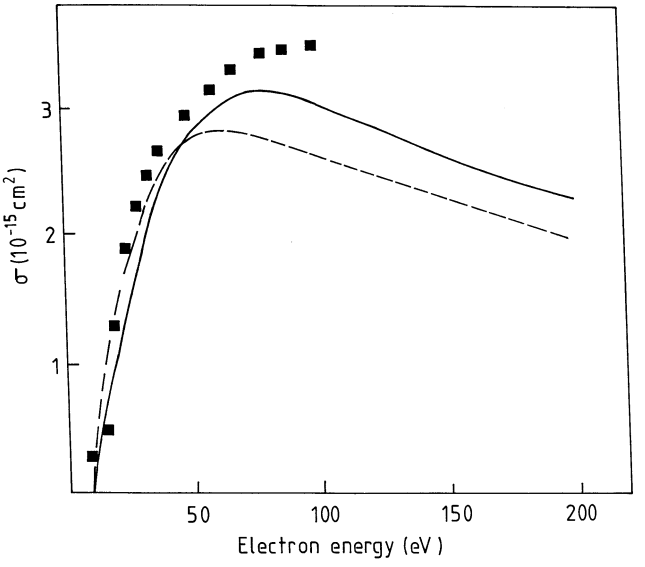

Fig. 13. Electron impact ionization cross section of tetraethoxysilane. The calculated Deutsch-Märk cross section (solid line) is compared with a modified additivity rule calculation (dashed line), and with the experimental data of Basner et al. [6] (filled squares).

lated cross sections based on the Binary-Encounter-Bethe (BEB) method. In some cases, comparisons were also made with predictions from the modified additivity rule (MAR). The agreement between the calculated DM cross sections and the available experimental data is generally good to satisfactory except in the case of WF_6, where the available data represent perhaps only a lower limit of the total ionization cross section. The agreement between the DM cross sections and the BEB cross sections is also generally quite good except for the four GeH_x ($x = 1$–4) compounds.

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