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Application of the Modified Additivity Rule to the Calculation of Electron-Impact Ionization Cross Sections of Complex Molecules

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This paper describes the application of the modified additivity rule (MAR) to the calculation of total (counting) electron-impact ionization cross sections of complex molecules with sum formulas of the form A_xB_y, $A_xB_yC_z$, and $A_pB_sC_tD_u$. The MAR incorporates weighting factors for the contributions to the molecular ionization cross section from the ionization cross sections of the constituent atoms, which depend explicitly on the atomic radii and the effective number of atomic electrons except for a few special cases (hydrides where the other constituent atom has a radius smaller than the radius of the H atom and species where both constituent atoms have radii smaller than the radius of the H atom), where the weighting factors depend only on the atomic radii, i.e., on geometric effects. A comprehensive comparison of the predictions of the modified additivity rule with available experimental data and with other theoretical predictions is presented.

I. Introduction

Electron-impact ionization cross sections of molecules are important quantities in a variety of applications as diverse as low-temperature processing plasmas, fusion edge plasmas, gas discharges, planetary, stellar, and cometary atmospheres, radiation chemistry, mass spectrometry, and chemical analysis.[1] 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.[2,3] The need to incorporate molecular ionization cross sections in modeling codes for various applications (see e.g. in fusion edge plasmas[4] and in plasma processing[5]) 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 Stevenson,[6] can be found in the literature.[7,8] They all rely on the concept that the molecular ionization cross section is derived by adding in some fashion the ionization cross sections of the atomic constituents of the molecule with or without accounting for molecular bonding and/or weighting factors for the atomic cross sections. In addition to these rather simple approaches, there have been semiempirical and semiclassical approaches[9−12] including the DM formalism,[10,11] geometric approaches,[13,14] and the more rigorous Binary−Encounter Bethe (BEB) theory of Kim and collaborators[15−17] which combines the additivity concept with quantum mechanically calculated molecular quantities.

In a previous paper, Deutsch et al.[18] presented a comprehensive comparison of predicted molecular ionization cross sections using a modified additivity rule, which includes appropriately chosen weighting factors to account for molecular bonding, with available experimental data and, where available, with other calculations using the DM formalism,[10,11] the method of Khare and co-workers,[12] the approach of Bobeldijk et al.,[13] or the BEB method[16,17] for molecules with sum formulas of the form AB_n. The present paper reports the extension of the modified additivity rule to more complex molecules with sum formulas of the form A_xB_y, $A_xB_yC_z$, and $A_pB_sC_tD_u$. As was done before in the case of the molecules of the form AB_n, a comprehensive comparison with experimental data for selected molecules and with other available theoretical results is presented. Our approach is motivated by the need to provide a simple and easy-to-apply method for the calculation of a large number of molecular ionization cross sections, which relies on readily available information in the literature and thus avoids the necessity to carry out a large-scale quantum-mechanical calculation for each molecule. This is particular useful for applications where a large number of cross section data of reasonable accuracy are needed for modeling purposes.

II. Concept of the Modified Additivity Rule

The conventional additivity rule as introduced by Ötvos and Stevenson[6] and refined by Fitch and Sauter[7] and Deutsch and Schmidt[8] uses the concept that the molecular ionization cross section σ can be expressed in the form

$$\sigma = b + \sum_i n_i \sigma_i \tag{1}$$

where b is a constant, n_i is the number of atoms "i" in the molecule, and σ_i is the constant contribution of each atom "i" to the molecular ionization cross section. The additivity concept as represented by eq 1 is in principle not capable of reproducing the "inversion" of the molecular ionization cross sections which was first observed experimentally for the SiF_x ($x = 1-3$) free radicals[19−21] and discussed by Deutsch et al.[22] "Inversion" here refers to the fact that the total single ionization cross section

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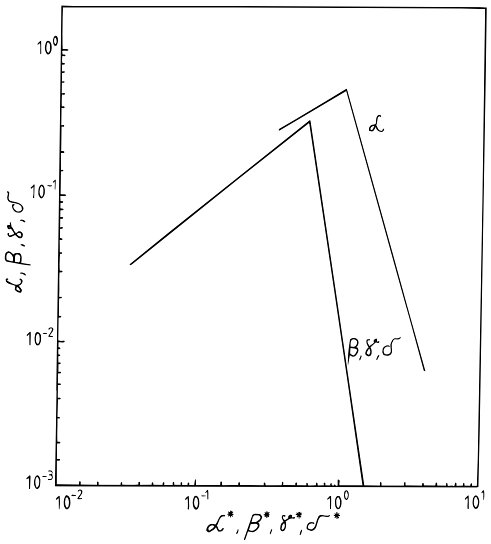

Figure 1. Functional dependence of the exponents α, β, γ, and δ on α*, β*, γ*, and δ* (see text for further details).

decreases with increasing number of atomic constituents in the molecule, i.e., $\sigma^+(SiF) > \sigma^+(SiF_2) > \sigma^+(SiF_3)$. The reason for this inversion comes from the fact that the contribution of the large Si ionization cross section to the molecular ionization cross section is increasingly screened by the surrounding F atoms, whose ionization cross section is much smaller, when going from SiF to SiF_2 to SiF_3 (see detailed discussion below).

The modified additivity rule introduced by Deutsch et al.[18] attempted to account for the effects of molecular bonding by introducing empirically determined weighting factors that depend on the atomic orbital radii and the electron occupation numbers of the various atomic orbitals. A detailed comparison with existing molecular ionization cross section data for molecules of the form AB_n suggested the following explicit form of the total single ionization cross section $\sigma^+(AB_n)$ of such a molecule

$$\sigma^+(AB_n) = f_A(r_A,r_B,\xi_A,\xi_B)\, \sigma^+(A) + f_B(r_A,r_B,\xi_A,\xi_B) n\, \sigma^+(B) \quad (2)$$

Here r_A, r_B and ξ_A, ξ_B refer to respectively the radii and the effective number of electrons of the atoms "A" and "B", and $\sigma^+(X)$ denotes the total single electron-impact ionization cross section of the atoms X. The weighting factors f_A and f_B are given by

$$f_A(r_A,r_B,\xi_A,\xi_B) = [(\pi r_A^{\,2})/(\pi r_B^{\,2})]^{\alpha}[\xi_A/(\xi_A + n\xi_B)] \quad (3a)$$

$$f_B(r_A,r_B,\xi_A,\xi_B) = [(n\pi r_B^{\,2})/(\pi r_A^{\,2})]^{\beta}[n\xi_B/(\xi_A + n\xi_B)] \quad (3b)$$

The exponents α and β are explicitly dependent on r_A, r_B, ξ_A, and ξ_B. Specifically, we have

$$\alpha = g_1(\alpha^*) \quad \text{and} \quad \beta = g_2(\beta^*) \quad (4)$$

where the functions g_1 and g_2 are shown in Figure 1 and the arguments are given by

$$\alpha^* = [(r_A/r_B)\xi_A/(\xi_A + \xi_B)] \quad \text{and} \quad \beta^* = [(r_B/r_A)\xi_B/(\xi_A + \xi_B)] \quad (5)$$

The two curves in Figure 1 were obtained empirically from a fitting procedure using a few benchmark cross sections (see Deutsch et al.[18] for further details).

For the previously mentioned case of the SiF_x ($x = 1-3$) radicals, for which an "inversion" of the ionization cross section had been observed experimentally,[19-21] the calculation of the ionization cross sections using the modified additivity rule yields the following result (we also included a calculation for the stable SiF_4 molecule and measured cross sections for S and F, see ref 18)

$$\sigma^+(Si) = 1.00\sigma^+(Si) + 0.00\sigma^+(F)$$
$$(\sigma^+(Si) \text{ at 70 eV: } 5.9 \times 10^{-16}\ \text{cm}^2)$$

$$\sigma^+(F) = 0.00\sigma^+(Si) + 1.00\sigma^+(F)$$
$$(\sigma^+(F) \text{ at 70 eV: } 0.9 \times 10^{-16}\ \text{cm}^2)$$

$$\sigma^+(SiF) = 0.88\sigma^+(Si) + 0.46\sigma^+(F)$$
$$(\sigma^+(SiF) \text{ at 70 eV: } 5.6 \times 10^{-16}\ \text{cm}^2)$$

$$\sigma^+(SiF_2) = 0.54\sigma^+(Si) + 1.24\sigma^+(F)$$
$$(\sigma^+(SiF_2) \text{ at 70 eV: } 4.3 \times 10^{-16}\ \text{cm}^2)$$

$$\sigma^+(SiF_3) = 0.39\sigma^+(Si) + 2.13\sigma^+(F)$$
$$(\sigma^+(SiF_3) \text{ at 70 eV: } 4.2 \times 10^{-16}\ \text{cm}^2)$$

$$\sigma^+(SiF_4) = 0.31\sigma^+(Si) + 3.10\sigma^+(F)$$
$$(\sigma^+(SiF_4) \text{ at 70 eV: } 4.6 \times 10^{-16}\ \text{cm}^2)$$

In these calculations we used the tabulated values for the atomic radii,[18,23] 3.81×10^{-11} m for fluorine and 11.53×10^{-11} m for silicon, and values for the effective numbers of electrons of 7 (F) and 4 (Si). These numbers, in turn, determine the arguments α* and β*, and Figure 1 is then used to extract the exponents α and β for each target. It is apparent that the contribution to the molecular ionization cross section from Si is decreasing as one goes from SiF to SiF_3 due to the screening of Si by the increasing number of F atoms, whereas the contribution due to F is increasing as the number of constituent F atoms increases. However, since the absolute atomic ionization cross section of Si is much larger than that of F, the decreasing Si contribution to the molecular ionization cross section when going from SiF to SiF_3 is not fully compensated by the increasing contribution from the F cross section. As a result, the molecular ionization cross section decreases from SiF to SiF_3, which is what was observed experimentally by Freund and co-workers.[19-21] It is only for the SiF_4 molecule that the inversion in the ionization cross sections is partially reversed, i.e., $\sigma^+(SiF_4) > \sigma^+(SiF_3)$, $\sigma^+(SiF_2)$. This is due to the fact that the addition of a fourth F atom to SiF_3 contributes little to the further screening of the Si atom.

A special case arises for hydrides where the second atom has a mean radius of the valence electron that is smaller than the radius of the H atom, e.g., H_2O, OH, and HF, and in cases where the radii of both atoms are smaller than the radius of the H atom (NO, N_2O, and NO_2). The ionization cross section for these molecules is determined by geometric effects alone which is accomplished by setting the factors containing the ratios of the electron numbers equal to one, which leads to

$$\sigma^+(AB_n) = [(\pi r_A^{\,2})/(n\pi r_B^{\,2})]^{\alpha}\sigma^+(A) + [(n\pi r_B^{\,2})/(\pi r_A^{\,2})]^{\beta} n\sigma^+(B) \quad (6)$$

where the exponents α and β are now also determined solely by the ratios of the atomic radii; i.e., the factors containing the effective electron numbers is set equal to unity. This is shown in the following example of NH_x ($x = 1-3$):

$$\sigma^+(\mathrm{NH}) = 0.99\sigma^+(\mathrm{N}) + 1.00\sigma^+(\mathrm{H})$$

$$\sigma^+(\mathrm{NH_2}) = 0.70\sigma^+(\mathrm{N}) + 2.00\sigma^+(\mathrm{F})$$

$$\sigma^+(\mathrm{NH_3}) = 0.57\sigma^+(\mathrm{N}) + 3.00\sigma^+(\mathrm{F})$$

The H atom contributes with its full atomic ionization cross section to the molecular ionization cross section, whereas the contribution of the N atom is reduced by a factor $(1/x)^\alpha$.

The above-described modified additivity rule can be extended to the calculation of electron-impact ionization cross sections for molecules with a sum formula of the form A_xB_y, $A_xB_yC_z$, and $A_pB_sC_tD_u$. The corresponding expressions are in their simplest form (factors of π which cancel have been omitted for simplicity):

$$\sigma^+(A_xB_y) = [(r_A^2)/(r_B^2)]^\alpha[x\xi_A/(x\xi_A + y\xi_B)]x\sigma^+(A) + [(yr_B^2)/(xr_A^2)]^\beta[y\xi_B/(x\xi_A + y\xi_A)]y\sigma^+(B) \quad (7a)$$

$$\sigma^+(A_xB_yC_z) = [(y + z)/x]^\alpha[(r_A^2)/(r_B^2 + r_C^2)]^\alpha[x\xi_A/(y\xi_B + z\xi_C)]x\sigma^+(A) + [(x + z)/y]^\beta[(r_B^2)/(r_A^2 + r_C^2)]^\beta[y\xi_B/(x\xi_A + z\xi_C)]y\sigma^+(B) + [(x + y)/z]^\gamma[(r_C^2)/(r_A^2 + r_B^2)]^\gamma[z\xi_C/(x\xi_A + y\xi_B)]z\sigma^+(C) \quad (7b)$$

$$\sigma^+(A_pB_sC_tD_u) = [(s + t + u)/p]^\alpha[(r_A^2)/(r_B^2 + r_C^2 + r_D^2)]^\alpha[p\xi_A/(s\xi_B + t\xi_C + u\xi_D)]p\sigma^+(A) + [(p + t + u)/s]^\beta[(r_B^2)/(r_A^2 + r_C^2 + r_D^2)]^\beta[s\xi_B/(p\xi_A + t\xi_C + u\xi_D)]s\sigma^+(B) + [(p + s + u)/t]^\gamma[(r_C^2)/(r_A^2 + r_B^2 + r_D^2)]^\gamma[t\xi_C/(p\xi_A + s\xi_B + u\xi_D)]t\sigma^+(C) + [(p + s + t)/u]^\delta[(r_D^2)/(r_A^2 + r_B^2 + r_C^2)]^\delta[u\xi_D/(p\xi_A + s\xi_B + t\xi_C)]u\sigma^+(D) \quad (7c)$$

The exponents α and β for the molecules A_xB_y are determined in a fashion similar to the case of the molecules AB_n. We also note that eq 7a becomes identical to eq 2 for the case $x = 1$ (and $y = n$). The exponents α, β, and γ for the molecules $A_xB_yC_z$ are obtained from Figure 1 using the functions

$$\alpha = g_1(\alpha^*), \quad \beta = g_2(\beta^*), \quad \gamma = g_2(\gamma^*) \quad (8)$$

where the exponents α^*, β^*, and γ^* are given by

$$\alpha^* = [(r_A/(r_B + r_C)][\xi_A/(\xi_B + \xi_C)] \quad (9a)$$

$$\beta^* = [(r_B/(r_A + r_C)][\xi_B/(\xi_A + \xi_C)] \quad (9b)$$

$$\gamma^* = [(r_C/(r_A + r_B)][\xi_C/(\xi_A + \xi_B)] \quad (9c)$$

The exponents α, β, γ, and δ for the molecules $A_pB_sC_tD_u$ are obtained from Figure 1 using the functions

$$\alpha = g_1(\alpha^*), \quad \beta = g_2(\beta^*), \quad \gamma = g_2(\gamma^*), \quad \delta = g_2(\delta^*) \quad (10)$$

where the arguments are given by

$$\alpha^* = r_A/(r_B + r_C + r_D)\xi_A/(\xi_B + \xi_C + \xi_D) \quad (11a)$$

$$\beta^* = r_B/(r_A + r_C + r_D)\xi_B/(\xi_A + \xi_C + \xi_D) \quad (11b)$$

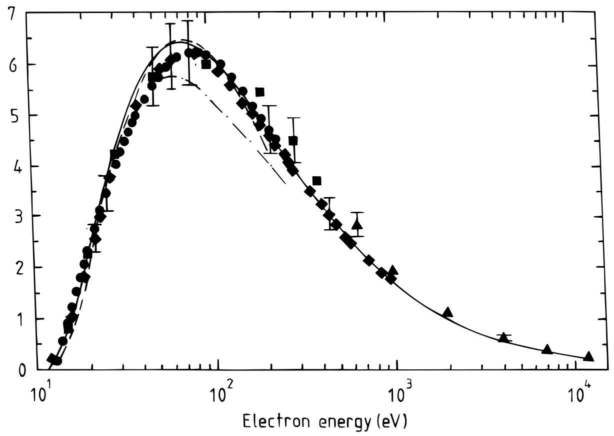

Figure 2. Electron impact ionization cross section of C_2H_6 as a function of electron energy. The data points are from refs 25 (triangles, ▲), 26 (squares, ■), 27 (circles, ●), and 28 (diamonds, ◆); the solid line represents the BEB calculation of Kim and co-workers,[16] the dashed line represents the DM calculation,[9] and the dash-dot line is the present MAR result.

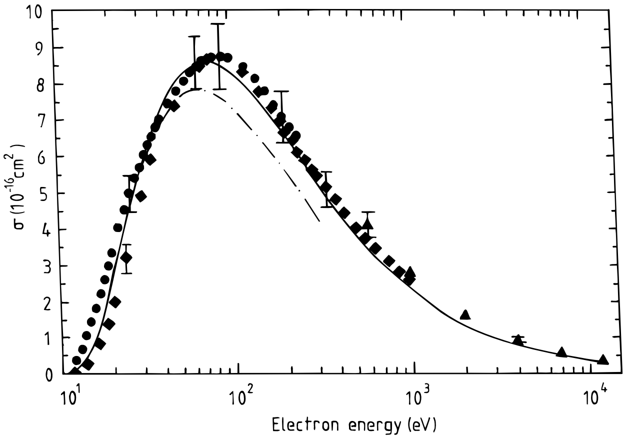

Figure 3. Electron impact ionization cross section of C_3H_8 as a function of electron energy. The data points are from refs 25 (triangles, ▲), 27 (circles, ●), and 29 (diamonds, ◆); the solid line represents the BEB calculation of Kim and co-workers,[16] and the dash-dot line is the present MAR result.

$$\gamma^* = r_C/(r_A + r_B + r_D)\xi_C/(\xi_A + \xi_B + \xi_D) \quad (11c)$$

$$\delta^* = r_D/(r_A + r_B + r_C)\xi_D/(\xi_A + \xi_B + \xi_C) \quad (11d)$$

We note that the factors containing the effective electron numbers in the expression for α^* and β^* are set equal to unity for the molecules A_xB_y similar to the case of the molecules AB_n, if one or both atoms have mean radii of their valence electrons that are smaller than the radius of the H atom. In the case of the molecules $A_xB_yC_z$ and $A_pB_sC_tD_u$ the same applies, if the radii of the atoms are smaller than or equal to the radius of the H atom.

III. Results and Discussion

In this section we compare the results of our calculation using the modified additivity rule of eqs 7a–7c with available experimental data and with various other calculations, primarily the DM formalism[9–11] and the BEB results of Kim and co-workers.[15–17,24] We note that the agreement between calculated and measured cross sections also depends crucially on the reliability of the atomic ionization cross sections that are used in the calculations. In most cases, the level of accuracy of the atomic ionization cross sections is in the range 15–30% (see e.g. ref 9).

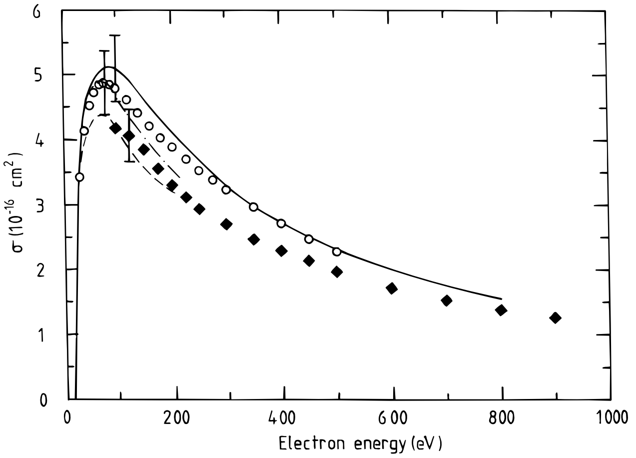

Figure 4. Electron impact ionization cross section of C_2H_2 as a function of electron energy. The data points are from refs 30 (open circles, ○), 31 (solid line), and 32 (diamonds, ◆); the dashed line represents the DM calculation,[9] and the dash-dot line is the present MAR result.

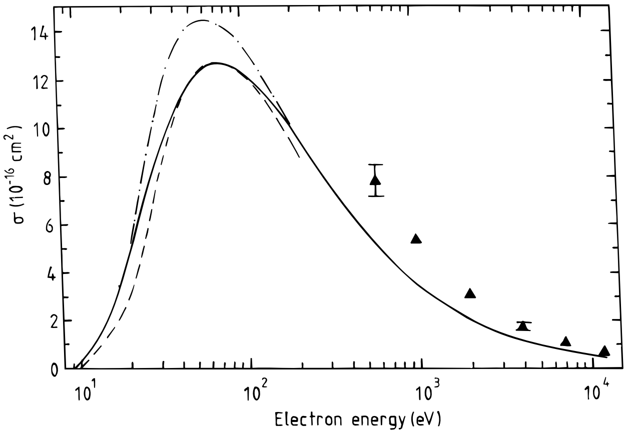

Figure 5. Electron impact ionization cross section of C_6H_6 as a function of electron energy. The data points are from ref 25 (triangles, ▲); the solid line represents the BEB calculation of Kim and co-workers,[16] the dashed line is the DM calculation,[9] and the dash-dot line is the present MAR result.

Molecules with Sum Formulas of the Form A_xB_y. Figure 2 and Figure 3 show a comparison of our MAR calculations with available experimental data and with the BEB calculation for the two hydrocarbon molecules C_2H_6 and C_3H_8. In the case of C_2H_6, where we also show the results of the DM formalism, there is good agreement between the four available experimental data sets[25−28] and between the experimental data and the three calculations for impact energies up to about 70 eV. For higher impact energies, the MAR calculation lies systematically below the experimental data, whereas the BEB and DM calculations describe the cross section very well for higher impact energies as well. A similar situation is found for C_3H_8 (Figure 3) where the three available experimental data sets[25,27,29] agree well with each other and with the BEB calculations over the entire energy range up to 10 keV, whereas the MAR calculation describes the experimental data very well up to about 60 eV, but declines more rapidly than the measured data and the BEB calculations for higher impact energies. No DM calculations are available for C_3H_8.

Figure 4 shows three sets of experimental ionization cross section data[30−32] for C_2H_2 in comparison with the MAR and the DM calculations. There is good agreement between the three experimental data sets within their combined error margins, and there is also satisfactory agreement between the measured and calculated cross sections. It would appear that the DM calculation favors the experimental data of Tate and Smith,[29] whereas the MAR calculation is closer to the data of Gaudin and Hagemann,[31] but the differences are less than 20%.

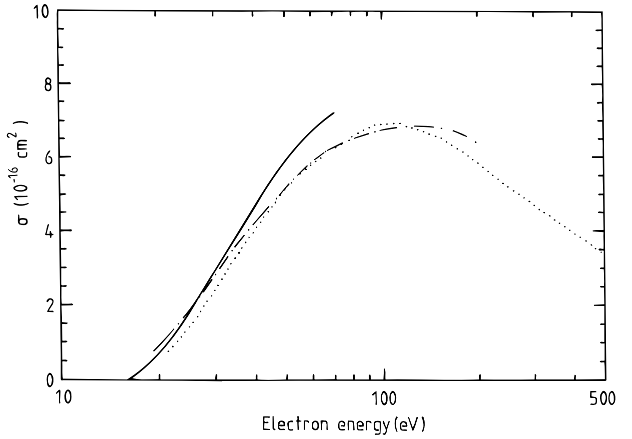

Figure 6. Electron impact ionization cross section of C_2F_6 as a function of electron energy. The solid line represents the "recommended" cross section of Olthoff and Christophorou,[33] the dots represents the BEB calculation of Kim and co-workers (as quoted in ref 33), and the dash-dot line is the present MAR result.

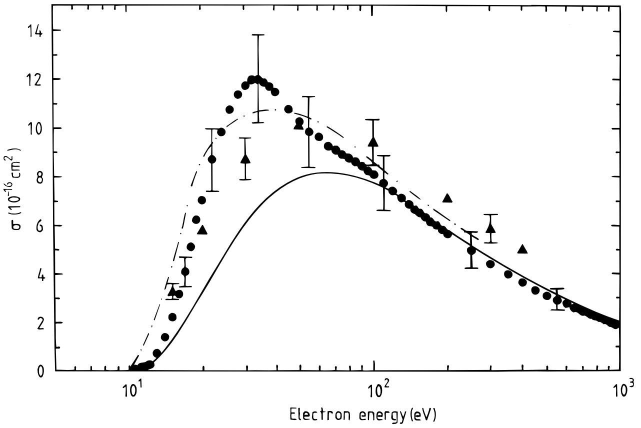

Figure 7. Electron impact ionization cross section of Si_2H_6 as a function of electron energy. The experimental data points are from Krishnakumar and Srivastava[34] (circles, ●) and Chatham et al.[26] (triangles, ▲), the solid line represents the BEB calculation of Kim and co-workers,[24] and the dash-dot line is the present MAR result.

There is only a single set of experimental ionization cross sections for the C_6H_6 molecule,[25] which is limited to impact energies higher than 500 eV. The BEB model, the DM formalism, and the MAR predict a cross section that lies below the measured data in that energy range (see Figure 5). The calculations yield similar cross sections with the MAR calculation predicting a maximum cross section that is about 15% higher than the maximum cross section from the BEB and the DM calculations.

C_2F_6 is an important molecule for plasma processing applications using fluorocarbon plasmas. Figure 6 shows our MAR calculation in comparison with the BEB calculation and with the "recommended" experimental data set of Olthoff and Christophorou[33] which these authors derived from a critical evaluation of all available experimental cross section data for C_2F_6. The two calculations agree very well with each other, and both calculated cross sections lie somewhat below the "recommended" cross section of Olthoff and Christophorou[33] for energies above about 30 eV.

Figure 7 shows the two available data sets for Si_2H_6 from Krishnakumar and Srivastava[34] and Chatham et al.,[26] which are

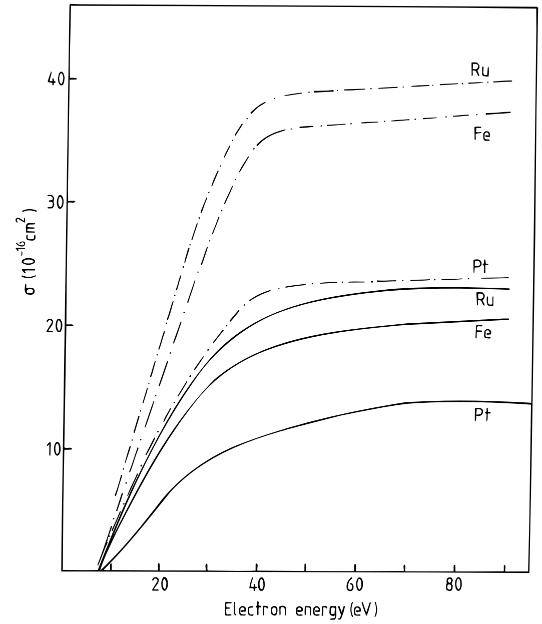

Figure 8. Electron impact ionization cross section of the three metal−organic compounds $(C_5H_5)-Pt-(CH_3)_3$, $(CH_3C_5H_4)_2-Ru$, and $(CH_3C_5H_4)_2-Fe$ as a function of electron energy. The experimental data are from Basner et al.[35] (solid lines), and the dash-dot lines are the present MAR results. Each curve is labeled by the metal atom of the compound.

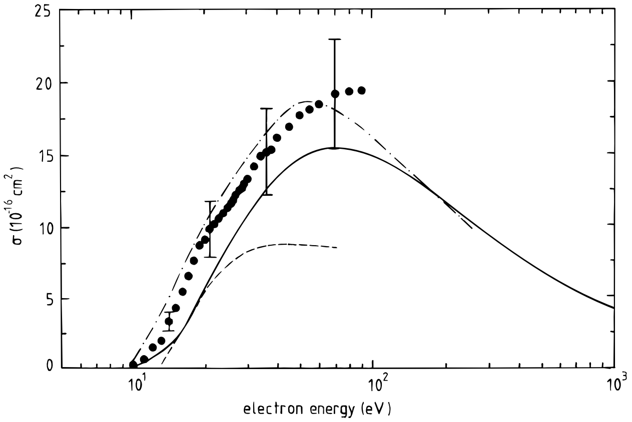

Figure 9. Electron impact ionization cross section of TMS as a function of electron energy. The data points are from refs 36 (circles, ●) and 37 (dashed line); the solid line represents the BEB calculation of Kim and co-workers,[24] and the dash-dot line is the present MAR result.

in reasonable agreement with each other (except near the peak in the cross section), in comparison with our calculation and with the BEB calculation.[24] Our MAR calculation agrees well with the experimental data over the entire range of impact energies, in particular with the data of Krishnakumar and Srivastava,[34] whereas the BEB calculation predicts a cross section that lies significantly below the experimental data up to about 100 eV.

Molecules with Sum Formulas of the Form $A_xB_yC_z$. Figure 8 compares the MAR calculation with available experimental data for three metal−organic compounds that are used as precursors in chemical vapor deposition applications, $(C_5H_5)-Pt-(CH_3)_3$, $(CH_3C_5H_4)_2-Ru$, and $(CH_3C_5H_4)_2-Fe$. The experimental data are those of Basner et al.[35] Two observations are noteworthy: (i) the MAR calculations yields cross section data that are systematically higher than the experimental values; (ii) the factor by which the calculations exceed the experimental data is about 1.75 for all three targets, which means that the calculation reproduces the experimentally determined ordering of the cross sections for these three very complex compounds.

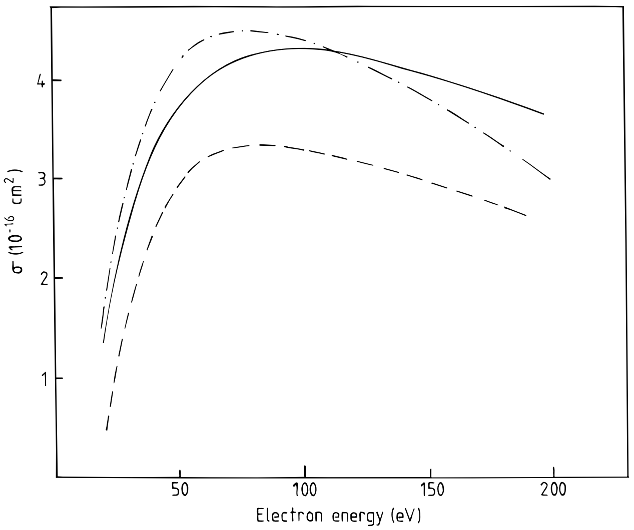

Figure 10. Electron impact ionization cross section of methanol, CH_3-OH, as a function of electron energy. The solid line represents the experimental data of Djuric et al.,[38] the dashed line is the DM calculation,[9] and the dash-dot line is the present MAR result.

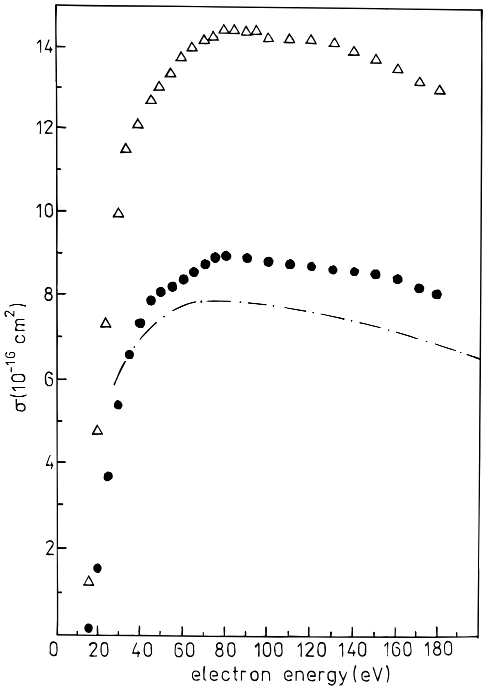

Figure 11. Electron impact ionization cross section of CCl_2F_2 as a function of electron energy. The data points are refs 39 (triangles, △) and 40 (circles, ●), and the dash-dot line is the present MAR result.

Two experimental data sets are available for tetramethylsilane (TMS), $Si(CH_3)_4$, the data of Basner et al.[36] and the data of McGinnis et al.[37] Both the BEB calculation of Kim and co-workers[24] and the present MAR calculation support the experimental data of Basner et al.,[36] which exceed the data of McGinnis et al.[37] by about a factor of 2 at all impact energies as shown in Figure 9.

Figure 10 shows our MAR calculation for methanol, CH_3-OH, in comparison with the experimental data of Djuric et al.[38] and with a DM calculation.[9] The DM calculation yields a cross section that lies systematically below the experimental data and the MAR cross section by about 30%. It is interesting to note, however, that the cross section shape predicted by the DM

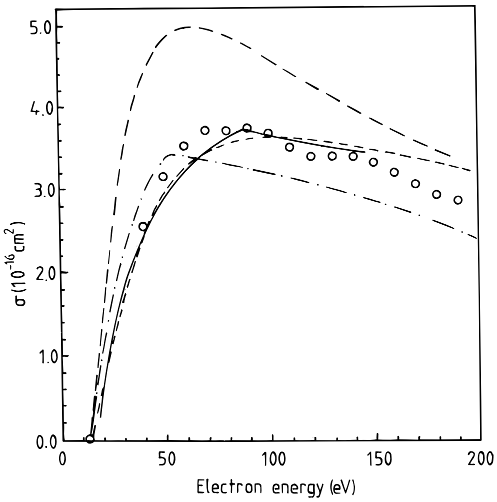

Figure 12. Electron impact ionization cross section of CH_3F as a function of electron energy. The data points are from Vallance et al.,[41] the solid line is the calculation of Harland and Vallance,[42] the short dashed line is a BEB calculation (as reported in refs 41 and 42), the long dashed line is a DM calculation carried out by Harland and co-workers,[41,42] and the dash-dot line is the present MAR result.

calculation is in better agreement with the experimental data than the calculated MAR cross section, which, on the other hand, is in better agreement with the experimental data in terms of the maximum cross section value.

There are two data sets in the literature for the electron impact ionization of the etching gas CCl_2F_2 which show a significant disagreement in terms of the absolute cross section value.[39,40] Figure 11 shows the two data sets in comparison with the present MAR calculation. It is apparent that the MAR calculation supports the lower cross section values of Leiter et al.[40]

Recently, Vallance et al.[41] measured ionization cross sections for three CH_3X compounds ($X = F$, Cl, Br). Figure 12 shows the experimental data for CH_3F which are compared with the present MAR calculation, a BEB calculation (as reported in refs 41 and 42), a DM calculation carried out by Harland and co-workers,[41.42] and a model proposed by Harland and Vallance.[42] All calculations except for the DM calculation agree with each other reasonably well, and they are also in good agreement with the experimental data. In the case of CH_3Cl (Figure 13), the experimental data are best represented by the calculation of Harland and Vallance[42] and by the DM formalism for energies up to about 70 eV, whereas the other two calculations (MAR and BEB) appear to underestimate the data in that energy region by respectively 15% and 30%. For higher energies, however, the MAR and BEB calculations describe the experimental data better than the predictions of Harland and Vallance[42] and the DM calculation.[41,42] A very similar situation is found for CH_3Br (Figure 14), where the MAR and BEB calculations underestimate the measured cross section near the maximum by respectively 12% and 30% but are found to agree with the measured data quite well for energies above about 120 eV. The DM calculation tends to overestimate the experimental data slightly for all energies. No calculations based on the model of Harland and Vallance[42] have been carried out for this molecule.

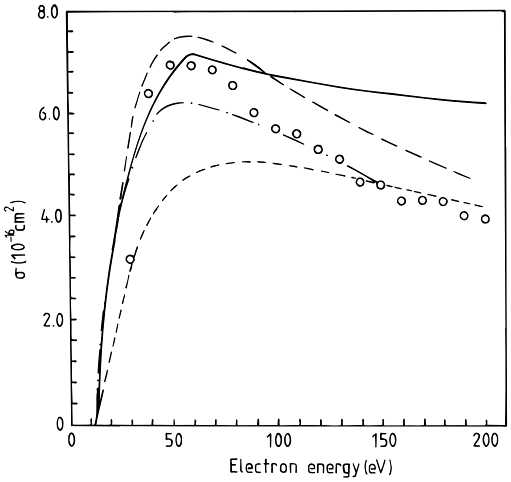

Figure 13. Electron impact ionization cross section of CH_3Cl as a function of electron energy. The data points are from Valance et al.,[41] the solid line is the calculation of Harland and Vallance,[42] the short dashed line is a BEB calculation (as reported in refs 41 and 42), the long dashed line is a DM calculation by Harland and co-workers,[41,42] and the dash-dot line is the present MAR result.

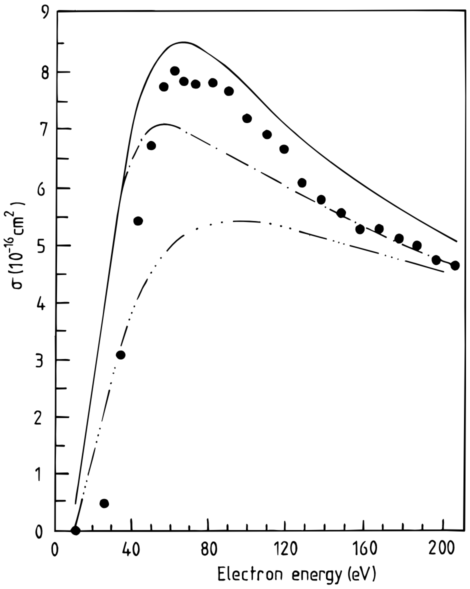

Figure 14. Electron impact ionization cross section of CH_3Br as a function of electron energy. The data points are from Vallance et al.[41] The solid line is DM calculation carried out by Harland and co-workers.[41,42] The two dash-dot lines are respectively a BEB calculation (as reported in refs 41 and 42, - ··· -) and the present MAR result (- · -).

Molecules with Sum Formulas of the Form $A_pB_sC_tD_u$. Figure 15 and Figure 16 show the comparison of the only available data sets[43,44] for the two Si−organic molecules HMDSO, $(CH_3)_3{-}Si{-}O{-}Si{-}(CH_3)_3$, and TEOS, $Si(O{-}CH_2{-}CH_3)_4$, with the MAR calculations. While there is very good agreement between calculated and measured cross sections for HMDSO (Figure 15), the agreement is less satisfactory for TEOS (Figure 16), where the measured cross section exceeds the calculation for energies above about 50 eV by as much as 30% and appears to peak at a higher energy. A possible reason for this discrepancy could be a significant contribution from ion pair formation processes to the measured cross section at higher impact energies. Ion pair formation, however, is a process that is not included in the MAR model.

Last, we would like to point out that the MAR has been applied to various other molecules with sum formulas of the form A_xB_y and $A_xB_yC_z$ which are not discussed here in detail and for which experimental data are available. In all cases, the level of agreement with experiment was found to be comparable to that of those molecules discussed here. We are not aware of any other experimental ionization cross section data for complex molecules of the form $A_pB_sC_tD_u$.

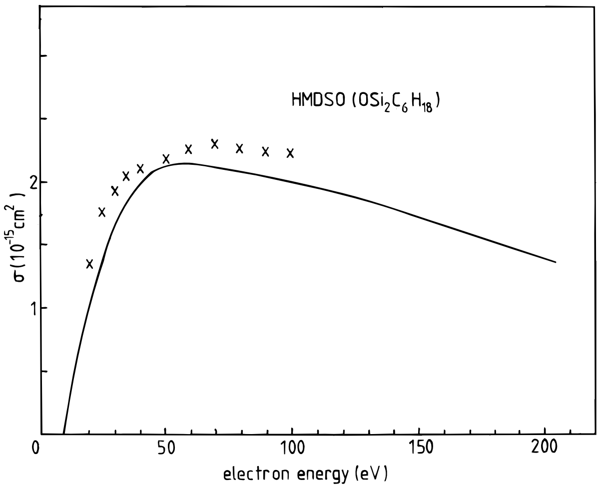

Figure 15. Electron impact ionization cross section of HMDSO as a function of electron energy. The data points are from Basner et al.,[43] and the solid line is the present MAR result.

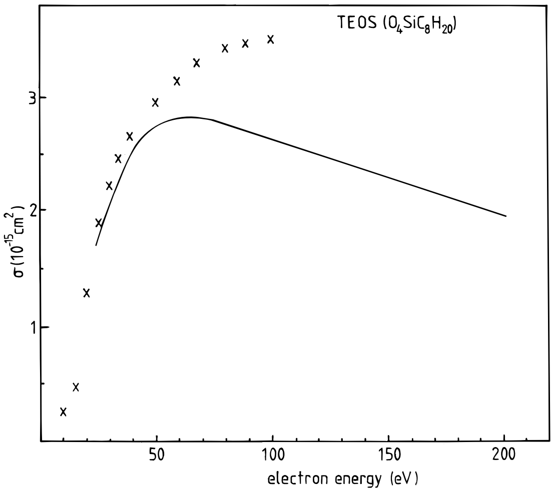

Figure 16. Electron impact ionization cross section of TEOS as a function of electron energy. The data points are from Basner et al.,[44] and the solid line is the present MAR result.

IV. Conclusions

We have extended the concept of the modified additivity rule (MAR), which was developed for the calculation of electron-impact total (single) ionization cross sections of molecular targets of the form AB_n (see ref 18), to more complex molecules of the form A_xB_y, $A_xB_yC_z$, and $A_pB_sC_tD_u$. A comprehensive comparison of the predictions of the MAR with available experimental data and with the predictions of other theoretical methods shows reasonable to good agreement with experiment and with other calculations for most molecules. In general, where more than one calculation is available, the MAR prediction achieves a level of agreement with experiment that is comparable to the DM formalism and to the more rigorous and more complex BEB method.[15−17] It is difficult to assess the predictive capability of MAR calculations for targets where no experimental results are available, because of the empirical nature of the MAR approach. However, on the basis of the comprehensive comparison with molecules for which data exist, we feel confident that the MAR can predict total single ionization cross sections to better than 20% for simple diatomic and triatomic molecules and to better than 50% for very complex (organic) molecules.

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