Eur. Phys. J. D **12**, 283–287 (2000)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences

Calculation of absolute electron-impact ionization cross-sections of dimers and trimers

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Received 6 December 1999 and Received in final form 10 April 2000

Abstract. We report calculations of the electron-impact ionization cross-sections of selected dimers (homonuclear diatomic molecules) and trimers (homonuclear triatomic molecules) using a method which relies only on macroscopic quantities in conjunction with a "defect concept". The empirically determined defect describes the deviation of the cluster (dimer, trimer) cross-sections from a simple linear dependence on the cluster size. We compare the calculated cross-sections to experimental data for the dimers S_2 and F_2 and the trimer O_3 and we present predictions for the ionization cross-sections of Br_2, I_2, C_2 and C_3 for which no experimental data are available. Lastly, we extend the method to the calculation of ionization cross-sections for the fullerenes C_{60} and C_{70}.

PACS. 34.50.Gb Electronics excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.) – 34.80.Dp Atomic excitation and ionization by electron impact

1 Introduction

Electron collisions with molecules leading to ionization are among the most fundamental processes in collision physics. Cross-sections for electron-impact ionization of molecules have been measured and calculated since the early days of collision physics [1] because of their basic importance in the kinetics and dynamics of collisions and because of their relevance in many practical applications such as gas discharges, plasmas, radiation chemistry, planetary upper atmospheres and mass spectrometry. Since the last comprehensive review of electron-impact ionization processes [2], considerable progress in the quantitative determination of cross-sections for molecular targets has been achieved both experimentally and theoretically, particularly in the past decade [3]. On the theoretical side, rigorous, fully quantum mechanical calculations are still beyond current capabilities. Among the more rigorous (*i.e.* partially quantum mechanical) methods that have been used successfully in the calculation of molecular ionization cross-section, three approaches have achieved a certain prominence, the method of Khare and co-workers [4,5], the Binary-Encounter-Dipole (BED) and Binary-Encounter-Bethe (BEB) methods of Kim and Rudd [6–8], and the Deutsch-Märk (DM) formalism [9–12]. These theoretical approaches are microscopic in nature in the sense that they are based on considerations involving individual molecular orbitals and individual electrons. A recent topical review [12] presented a comprehensive comparison between calculated ionization cross-sections using the DM formalism (as well as, where available, the BED/BEB methods and the method of Khare and co-workers) and measured data for more than 30 molecules and free radicals. With very few exceptions, good to satisfactory agreement between the measured and the calculated cross-sections (and among the various calculated cross-sections) was found.

Recently, the DM formalism was also applied to calculations of ionization cross-sections for small silver clusters, Ag_n ($n = 2–7$) [13]. In this work, Deutsch *et al.* [13] also used an alternate approach to the microscopic DM formalism. This alternate approach utilized a modified additivity rule which included a "defect concept" to account for the fact that a cluster X_n consisting of n atoms X is different from a simple collection of n atoms X (nX). Using this defect concept, the ionization cross-section [14] of a cluster X_n, $\sigma(X_n)$, is expressed in terms of the ionization cross-section of the constituent atom X, $\sigma(X)$, in the well-known manner (see [13] and references therein to earlier work) as

$$\sigma(X_n) = n^a \sigma(X) \tag{1}$$

where the exponent "a" is smaller than unity. The difference between $a = 1.00$ and the actual value of the exponent "a" is a measure of the deviation of equation (1) from a simple, straightforward additivity rule. Equation (1) has

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been used by other authors prior to the work of Deutsch *et al.* [13] (see references in their paper [13] to earlier work). We note that for large clusters on the basis of geometrical considerations a value of $a = 2/3$ has been proposed [15]. The same formula was later derived by Deutsch *et al.* [16] using a simplified version of the DM approach [9–12] in calculations of ionization cross-sections for H_2 and CO_2 clusters in the size range of several 100 to approximately 100 000. These authors replaced the atomic radius of the outermost shell of the target by the radius of the cluster and used an empirically determined factor of $a = 0.84$ [16], somewhat larger than the lower limit of 2/3, which corresponds to some kind of hard sphere packing. In the course of their cross-section calculations for the Ag_n ($n = 2-7$) clusters, Deutsch *et al.* [13] found a value of $a = 0.9$, which is close to the empirically determined value of 0.84 for H_2 and CO_2 clusters.

The terminology "defect concept" for equation (1) becomes apparent when it is re-written in the form

$$\sigma(X_n) = n^{1-\Delta}\sigma(X) \tag{2}$$

where the quantity Δ is called the "defect" since it describes the deviation from the strict proportionality of the cluster cross-section with the cluster size n.

In this paper we report the results of the application of the defect concept to the calculation of ionization cross-sections of selected dimers (homonuclear diatomic molecules) and trimers (homonuclear triatomic molecules), where a comparison with experimental ionization cross-section data is possible. We also applied our formalism to predict ionization cross-sections for several dimers and trimers, where no experimental data are available at present. Lastly, we extended the method to the calculation of ionization cross-sections of the fullerenes C_{60} and C_{70}.

2 Theoretical background

The application of the defect concept of equation (2) requires the determination of the defect Δ as a function of the nuclear charge Z or the atomic mass number A of the constituent atom X. The simplest "clusters" are the dimers (or homonuclear diatomic molecules). Reliable experimentally determined ionization cross-section data are available for the simple diatomic gases H_2, N_2, and O_2 (see the recent paper by Straub *et al.* [17] and references therein to earlier publications) and in these cases one also finds reliable ionization cross-sections for the constituent atoms H, N, and O [18,19]. From equation (2) one can then extract values for the defect Δ for these three cases. The three values are shown in Figure 1 plotted *vs.* the nuclear charge Z of the respective constituent atom. The three data points fall on a straight line. If one extrapolates this straight line to higher values of Z, the line intersects the Z-axis at around $Z = 16$ (corresponding to sulfur, S). This means that for dimers consisting of atoms heavier than sulfur, the defect Δ becomes negative and, as a consequence, the dimer ionization cross-section exceeds twice the ionization cross-section of the constituent atom. This is obviously unrealistic. It is, therefore, important to extend the plot of Δ *vs.* Z to larger values of Z using additional benchmarks at higher values of Z. We derived a value of Δ from the previously obtained value of the exponent "a" in equation (1) for Ag_2 clusters [13] and a Δ value extracted from the recommended ionization cross-section of Cl_2 from Christophorou and Olthoff [20] as additional benchmarks at $Z = 47$ and $Z = 17$, respectively. The Δ values for Cl and Ag are essentially identical. This determines the horizontal line in Figure 1 from Cl to Ag which we feel confident to extrapolate to higher values of Z as well. The straight line in the low-Z region and the horizontal line in the intermediate-Z and high-Z range are then connected smoothly as indicated in Figure 1. The Δ curve in Figure 1 allows one to calculate ionization cross-sections for any dimer ($n = 2$) on the basis of equation (2) provided the respective atomic ionization cross-section is known either from experiment or from calculations.

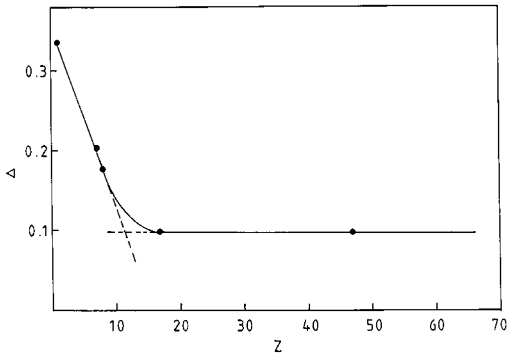


Fig. 1. Defect Δ plotted *vs.* the nuclear charge Z. The straight line in the low-Z regime and the horizontal line in the intermediate-Z and high-Z regime have been connected smoothly (see text for further details).

It is interesting to compare the present method with a geometric approach to the calculation of electron-impact ionization cross-sections proposed by Bobeldijk *et al.* [21]. The cross-section expression given by these authors can be expressed in the form

$$\sigma(X_2)/\sigma(X) = C(Z) \tag{3a}$$

where $C(Z)$ is a coefficient that varies as a function of Z. Likewise, the equation (1) as well as equation (2) can be expressed in the case of dimers in a similar fashion as

$$\sigma(X_2)/\sigma(X) = C^*(Z). \tag{3b}$$

Both coefficients $C(Z)$ and $C^*(Z)$ are constant for $Z > 17$ and have essentially the same value (to within 8%) in that range. For low values of Z, $Z < 17$, the two coefficients behave slightly differently as a function of Z, but their difference never exceeds 15%.

The extension of the defect concept to trimers and higher clusters is straightforward. If one assumes that the exponent "a" in equation (1) remains unchanged, if one goes from the dimer X_2 to the trimer X_3 to the cluster X_n, the defect Δ is also independent of the cluster size.

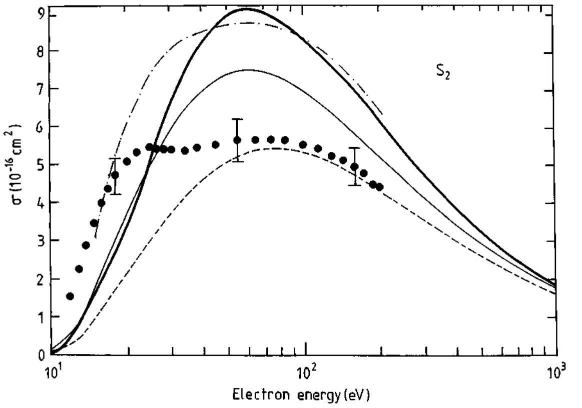


Fig. 2. Electron-impact ionization cross-section of S_2. The filled circles are the measured cross-section data of Freund *et al.* [22], the dash-dot line is the present calculation, the thick solid line is the DM calculation [12], the thin solid line is the "original" BEB calculation of Kim *et al.* [8], and the dashed line is a "reduced" BEB calculation (see Ref. [8] for details).

The assumption of a constant value "a" and consequently a constant value "Δ" means that the "packing density" of the cluster remains the same as the cluster size increases. This notion was supported by our findings for the large H_2 and CO_2 clusters [16] and also by the results for the small Ag_n ($n = 2-7$) clusters [13].

3 Results and discussion

We first use the defect concept outlined above to calculate ionization cross-section for the dimer S_2 for which experimental ionization cross-section data have been reported by Freund *et al.* [22]. Figure 2 shows the experimental data in comparison with the present calculation (dash-dot line), with a DM calculation [12] (thick solid line), and with two variants of the BEB method [8], the original BEB calculation (thin solid line) and a "reduced" variant (dashed line). It is obvious that the original BEB calculation, the DM calculation, and the present calculation lie significantly above the experimental data for all but the lowest impact energies with the BEB cross-section being somewhat lower than the other two calculations, particularly in the region of the cross-section maximum. Moreover, none of the three calculations reproduces the unusual energy dependence displayed in the experimental data. This leads one to believe that the experimental data may have been affected by some kind of systematic error which was unknown to the authors. This notion is supported by the observation that the measured S_2 cross-sections of Freund *et al.* [22] are only marginally larger than the atomic S cross-sections measured by the same authors [23]. The fact that the "reduced" BEB calculation agrees with the experimental data in the regime above about 100 eV is not surprising, since the main purpose of the "reduced" BEB calculation was to improve the agreement between experimental data and the BEB calculation at higher impact energies (see Ref. [8] for details).

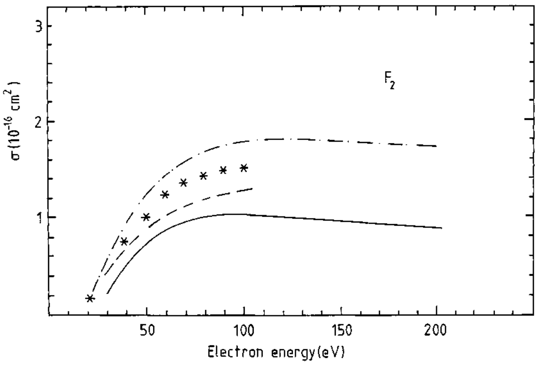


Fig. 3. Electron-impact ionization cross-section of F_2. Three sets of experimental data (Ref. [24], stars (∗); Ref. [25], dashed line; Ref. [26], solid line) are compared with the present calculation (dash-dot line).

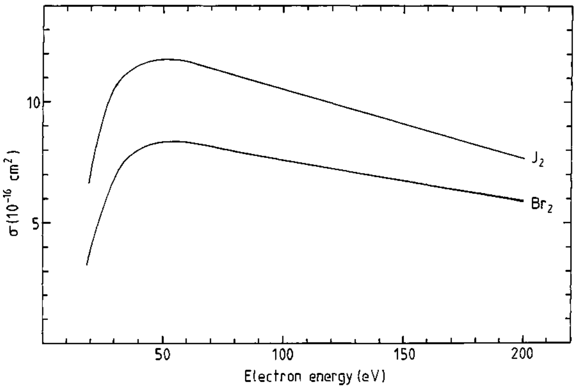


Fig. 4. Calculated electron impact ionization cross-sections for Br_2 and I_2. The two curves represent the results of the present calculations. No experimental data are available for comparison in either case.

Fluorine, F_2, is the only other diatomic homonuclear molecule (dimer) for which experimentally determined ionization cross-section are available [24–26]. These data are shown in Figure 3 in comparison with the present calculation. All three experimental data sets are below the calculated cross-section. However, the experimental data of Center and Mandel [24] are consistent with our calculation in view of the 20% error margin of their data. Figure 4 shows our calculated ionization cross-sections for the other two halogens Br_2 and I_2. To the best of our knowledge, there are no experimental data available for these two molecular gases for a comparison.

Ozone, O_3, is the only trimer for which experimental ionization cross-section data are available. Figure 5 shows two experimental data sets for O_3, the absolute cross-sections measured by Siegel [27] and the relative cross-section measurement of Newson *et al.* [28] which these authors normalized to the absolute cross-section of Siegel. Also shown in Figure 5 are the results of the present calculation, the result of a DM calculation [12] and a calculated BEB cross-section [8]. All three calculated cross-sections overestimate the experimental data, particularly in the region of the cross-section maximum. We note that

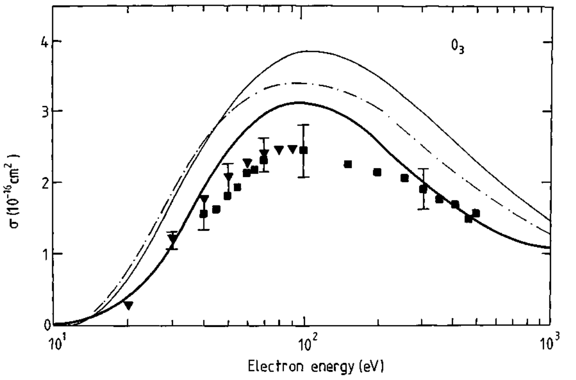


Fig. 5. Electron-impact ionization cross-section of O_3. The experimental data points from reference [27] (filled squares) are normalized to the absolute measurements of reference [28] (filled inverted triangles). The dash-dot line line represents the present calculation, the thin solid line is the result of a DM calculation [12], and the thick solid line denotes the BEB calculation [8].

the O_3 experimental cross-section data are essentially of the same magnitude as the O_2 experimental cross-section data which casts some doubt on the reliability of the experimental data.

It is also interesting to use the present method to calculate ionization cross-sections for the carbon dimer (C_2) and trimer (C_3). Experiments aimed at measuring the ionization cross-sections of these clusters are currently underway [29]. Figures 6a and 6b show the results for C_2 and C_3, respectively. In both cases, the present calculation is compared to a DM calculation [12] using two different sets of atomic wave functions in the Mulliken representation of the respective cluster (see Ref. [12] for details). It is apparent that in both cases the present calculations are in very good agreement with the prediction from the microscopic DM formalism.

Lastly, we used the value of the exponent "a" of 0.786 on the basis of a value for Δ of 0.214 for the C_2 dimer to calculate the ionization cross-sections of the fullerenes C_{60} and C_{70} according to equation (1) and we obtain the following relations

$$\sigma(C_{60}) = (60)^{0.786}\sigma(C) = 25\sigma(C) \tag{4a}$$

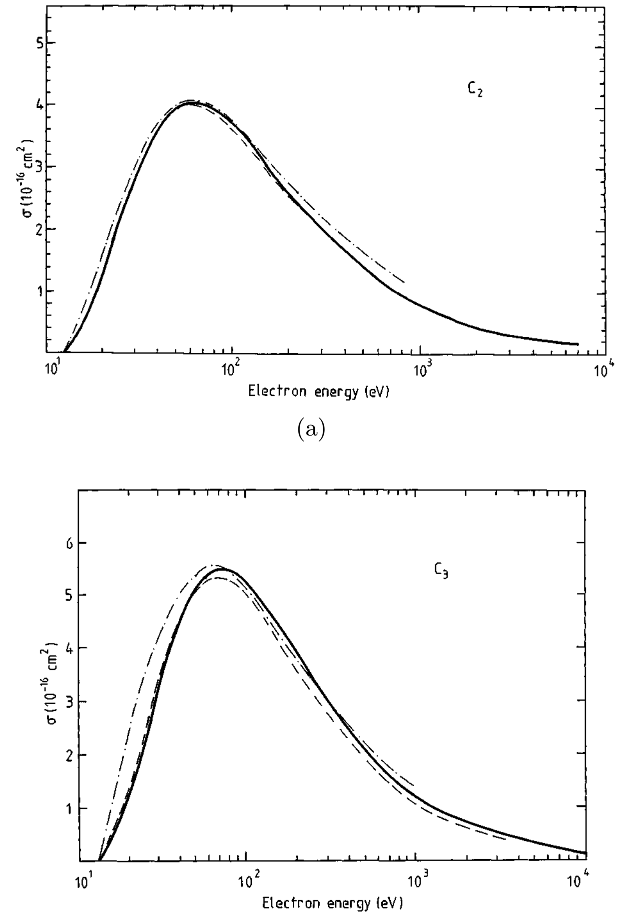
and

$$\sigma(C_{70}) = (70)^{0.786}\sigma(C) = 28\sigma(C) \tag{4b}$$

which leads to a ratio

$$\sigma(C_{60})/\sigma(C_{70}) = 1.12. \tag{5}$$

This value is in good agreement with the experimentally determined ratio of 1.27 in view of the 20% error margin in the experimentally determined ratio [30]. Equations (4a, 4b) result in calculated maximum ionization cross-section values for C_{60} and C_{70} of respectively 58×10^{-20} m^2 and 66×10^{-20} m^2 on the basis of the known (maximum) ionization cross-section for atomic carbon [11]. Two observations are quite noteworthy: (1) these values are in reasonably fair agreement with the experimental cross-sections determined by Matt *et al.* [28] which have been confirmed independently by two other measurements [31,32] (see also [33]) and (2) these cross-sections are only about 50% of the C_{60} and C_{70} cross-sections that resulted from the application of the DM formalism [34] (102×10^{-20} m^2 for C_{60}). We note again here that the DM formalism is based on a microscopic treatment of all electrons of all 60 carbon atoms. Moreover, the microscopic DM formalism treats all 60 C atoms equally.



(a)

(b)

Fig. 6. (a) Electron-impact ionization cross-section of C_2. The solid line and the dashed line denote two variants of the DM calculation [12] using different atomic C basis sets in the Mulliken representation of the dimer and the dash-dot line represents the present calculation. (b) Same as (a) for C_3.

Harland and co-workers [35,36] developed a method which allows the calculation of the maximum ionization cross-section of a molecule using the polarizability of the molecule (which is also a microscopic quantity in the sense that it is determined by the all molecular electrons). For all dimers considered here, the present calculation and the method of Harland and co-workers [34,35] yield maximum ionization cross-section values that agree with each other to within 10%. If one applies the method of Harland and co-workers [35,36] to C_{60}, on the other hand, one finds a maximum ionization cross-section of about (117×10^{-20} m^2), which is comparable to the DM result (102×10^{-20} m^2) and almost exactly twice as big as the present result.

We would like to note, however, that the satisfactory agreement between the experimentally determined fullerene ionization cross-sections and those calculated on the basis of the present macroscopic defect concept should not be overemphasized, since our model assumes a cluster structure for C_{60} and C_{70} which is very different from their actual structure.

This work has been carried out within the Association EURATOM-ÖAW and was partially supported by the FWF, BWFV Wien, Austria. One of us (KB) acknowledges partial support by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

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