



Electron-impact ionization of fluoromethanes – Review of experiments and binary-encounter models



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ARTICLE INFO

Article history:

Received 17 November 2013

Received in revised form

27 December 2013

Accepted 14 January 2014

Available online 25 January 2014

Keywords:

Ionization

Electron impact

Fluoromethanes

ABSTRACT

Experiments and recommended data on electron-impact ionization of methane and fluoromethanes (CH_3F , CH_2F_2 , CHF_3 , CF_4) are reviewed and compared with binary-encounter models (Gryziński's, Deutsch and Märk's, and Kim and Rudd's). A good agreement between recent experiments and the two latter classical-like models is shown. Kim and Rudd's model (calculated presently in the restricted Hartree-Fock 6-31**G orbital basis) predicts well total ionization cross sections for all five molecules considered. However, counting-ionization cross sections have to be extracted from experimental data to show this agreement. The additivity model of Deutsch and Märk performs equally well, once all molecular orbitals are taken into account. The maxima of total (counting) ionization cross sections calculated presently in Kim and Rudd's binary-encounter approximation correlate linearly with the molecular polarizability.

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1. Introduction

One hundred years from Born's formulation of the atomic model [1] the amount of experimental data on electron-atom scattering seems to be quite satisfactory, see for e.g. reviews by Märk and Dunn [2], Karwasz et al. [3], Lindsay and Mangan [4]. However, a more careful insight shows that some simple systematics are still missing, see for e.g. [5,6]. In the case of electron-impact ionization neither the total ionization cross section nor partitioning into specific ionic channels have been correlated to some other atomic or molecular features like electron affinity, ionization potential, polarizability. Numerical fitting of cross sections for particular processes like ionization for a vast choice of targets (e.g. Refs. [7–9]) and/or reviews of cross section sets for several possible processes but for selected targets only, like methane [10] or fluoromethanes [11,12] were undertaken, but no conclusive pictures have been obtained so far.

In the present work we perform an analysis of recent experimental data on fluoromethanes (and methane) and compare them with two binary-encounter models: Deutsch and Märk [13] and Kim and Rudd [14].

2. Deutsch–Märk and binary-encounter Bethe's models

As resumed by Margreiter et al. [15], Thomson [16] was the first to apply classical mechanics to derive a formula for the electron impact ionization cross section σ

$$\sigma = \sum_n 4\pi a_0^2 \xi_n \left(\frac{R}{I_n}\right)^2 \frac{t-1}{t}, \quad (1)$$

where n goes through atom subshells, ξ_n is the number of electrons on the n th subshell, I_n is the ionization energy of the n th subshell, t is the normalized kinetic energy of the incident electron $t = E/I_n$, R the Rydberg's constant and a_0 is the Bohr's radius. Thompson assumed that the velocities of the electron of the target atoms are small compared to the velocity of the incident electron.

Gryziński [17] included explicitly the continuous distribution of the velocities of the electrons in the target atom deriving the following expression for σ

$$\sigma = \sum_n 4\pi a_0^2 \xi_n \left(\frac{R}{I_n}\right)^2 \frac{1}{t} \left(\frac{t-1}{t+1}\right)^{3/2} \left\{ 1 + \frac{2}{3} \left(1 - \frac{1}{2t}\right) \ln[2.7 + (t-1)^{1/2}] \right\} \quad (2)$$

Deutsch and Märk [13] proposed a modification of Gryziński's formula, substituting Bohr's radius a_0 with radii r_n of the n th subshells and the factor 4 in Eq. (2) by weighting factors g_n obtained from

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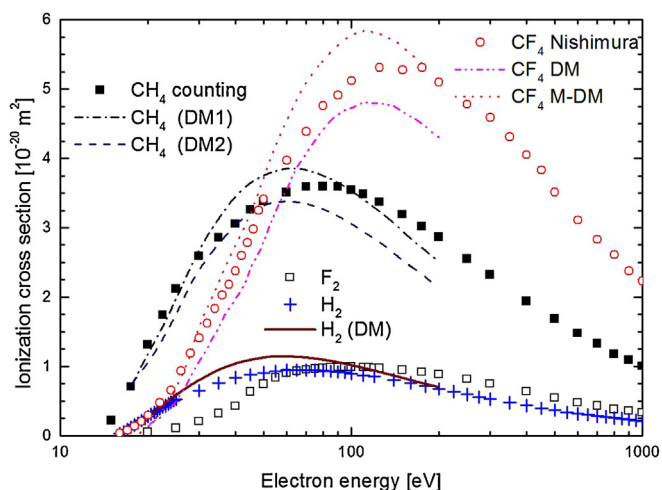


Fig. 1. Different applications of Deutsch–Märk model for molecules: H₂ DM model [15]; for CH₄ “DM1” and “DM2” models from [15] using two alternative Mulliken populations of molecular orbitals and orbitals radii; for CF₄ “DM” from [15] and “modified DM” from [24]. Experiments: CF₄, Nishimura et al. [42] and CH₄ presently suggested total counting cross sections, see Fig. 3. Lower symbols are experimental recommended [4] total gross cross sections of H₂ and F₂.

empirical data for electron scattering on noble gases [18,19]

$$\sigma = \sum_n g_n \pi r_n \xi_n \frac{1}{t} \left(\frac{t-1}{t+1} \right)^{3/2} \left\{ 1 + \frac{2}{3} \left(1 - \frac{1}{2t} \right) \ln [2.7 + (t-1)^{1/2}] \right\} \quad (3)$$

This so called Deutsch–Märk (DM) approach was extended [15] to molecular ionization assuming an additivity rule, i.e. that the molecular cross section (i.e. σ_{AB}) is a sum of the cross sections of constituent atoms (σ_A and σ_B) with appropriate weighting factors ζ_A and ζ_B .

$$\sigma_{AB} = \zeta_A \sigma_A + \zeta_B \sigma_B \quad (4)$$

The outer electrons (i.e. those from the molecular orbitals) bring the main contribution to the ionization cross section. In order to include the details of the molecular structure into the additivity rule Eq. (4), the weighting factors ζ_n are made equal to the partial contributions of the constituent atoms (i.e. A and B) to the specific molecular orbitals. Let us recall again that radii r_n in Eq. (3) and in consequence in Eq. (4) are taken from quantum mechanical calculations for constituent atoms and the factors g_n from the semiempirical analysis [18,19]. For example, for H₂ the weighting factor is $g_H = 3$, $r_H = a_0$ (and $\zeta_H = 2$) [15]. A comparison between DM results from Ref. [15] and presently recommended experimental values for H₂, CH₄ and CF₄ are shown in Fig. 1. The DM model for CH₄ predicts the maximum of the total cross section within the existing spread for recent experimental data. For CF₄ the agreement of the DM model with recent experiments is also quite good.

For the DM additivity model for molecules, the knowledge of partial occupancies of molecular orbitals by electrons from constituent atoms (Mulliken populations) is needed. Further, the molecular cross sections depend on the ionization energies of the constituent atoms. Obviously, this is an indirect way to account for the structure of the molecule. The DM model predicts reasonably well the magnitude of total ionization cross sections, in particular in the region between the threshold and the maxima of the cross section, i.e. in the range which is most important for practical applications of plasmas.

The DM model was also successfully applied to multiple ionization [20] and inner-shell ionization of atoms [21]. A more refined analysis of the weighting factors ζ_i in formula (5), based on a broad experimental base was incorporated into a modified DM model

[22–24]. The modified DM model predicts quite well amplitudes of the total ionization cross sections in molecules, see Fig. 1 for CF₄.

Neither Gryziński’s nor Deutsch and Märk’s model takes into account explicitly the velocities of the electrons in the different orbitals and their binding energies (i.e. the real ionization energies of the molecule). A further step in the semiempirical understanding of the electron-impact ionization was done by Kim [25] and Rudd [26] who proposed new formulae not only for total but also for differential cross sections (vs. angle, vs. collision energy and vs. energy-loss). Subsequently, using Mott’s [27] approximation for low and Bethe’s [28] approximation for high-energy collisions, Kim and Rudd [14,29] proposed the following approximation for total ionization cross sections

$$\sigma = \sum_n 4\pi a_0^2 \xi_n \left(\frac{R}{I_n} \right)^2 \frac{1}{t + u_n + 1} \left\{ 1 - \frac{1}{t} + \frac{\ln t}{2} \left(1 - \frac{1}{t^2} \right) - \frac{\ln t}{t + 1} \right\} \quad (5)$$

where u_n is a normalized kinetic energy of an electron on the n th orbital, $u_n = U_n/I_n$. As this model includes the binary-encounter and Bethe’s ideas it is commonly called BEB.

In BEB both ionization energies of electrons on n th orbital (i.e. their binding energies) as well as their average kinetic energies have to be evaluated from quantum mechanical codes for molecular structures. As a consequence, the BEB results depend to some extent on the molecular orbital basis sets chosen. The BEB model was successfully applied to light atoms (He), (Ne), molecules (H₂, H₂O), ions (Li⁺⁺) [14], metals [30] and targets like N₂, O₂, CO, CO₂, NH₃, C₃H₈, but rarely to CH₄ [31].

The DM and BEB models of fluoromethanes (CH₃F, CH₂F₂, CHF₃ and CF₄) were extensively discussed by Torres et al. [32]. In particular they exploited the original DM approach with the additivity rule [15] and with the modified DM additivity rule [23] calculating Mulliken’s molecular-orbital populations and weighting factors for atomic electrons (g_n) directly from quantum-mechanic numerical codes (GAUSSIAN 98W). Torres et al. [32] concluded for all the four gases considered that the D-M model with Hartree-Fock STO-3G tends to overestimate total ionization cross sections while with other molecular bases considered (HF/6-311G, HF/6-311**G, MP2/6-311G, MP4/6-311G, CC/6-311G, CISD/6-311G) the results differ in almost undistinguishable way (within 1%) and tend to underestimate slightly the experiments, see their Fig. 3 in [32].

In the BEB model the influence of the molecular basis chosen is similarly insignificant (with differences within 2%), apart from the HF/STO-3G basis which overestimates the experiments [32]. In present work we calculated BEB cross sections using restricted Hartree-Fock 6-31**G orbital basis set for the entire series, CH₄, CH₃F, CH₂F₂, CHF₃, CF₄ and compared them with experimental data in Figs. 3–5.

3. Discussion of experimental data

3.1. Methane

Methane is one of the most extensively studied molecular targets – it is important for global warming balance, for tokamak edge plasmas [5] and for hydrogen production via electric-discharge pyrolysis [33]. The BEB model was applied to CH₄ by Kim and collaborators, [34] and [31], using vertical (14.25 eV) and adiabatic (12.6 eV) ionization potentials, respectively. Obviously, the use of lower ionization potential rises the total cross section, bringing the maximum to about $4.3 \times 10^{-20} \text{ m}^2$, i.e. above the highest experimental data [35,36] and shifting the maximum toward lower energies.

The results of different measurements of total ionization cross sections of CH₄ are shown in Fig. 2. At 100 eV the different data

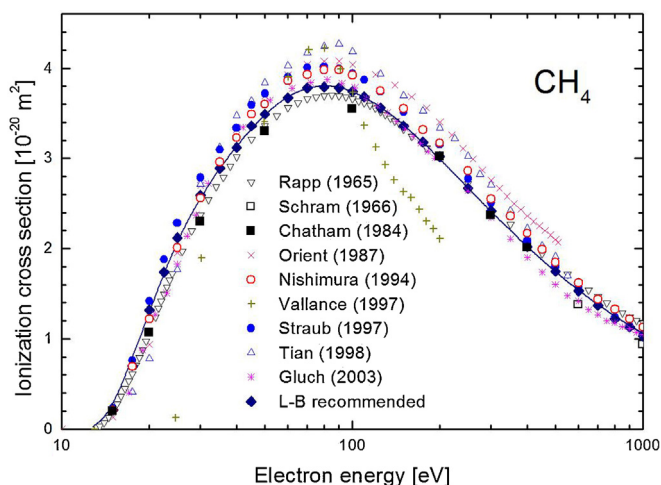


Fig. 2. Review of experimental gross ionization cross sections for CH_4 . Rapp and Englander-Golden [37], Schram et al. [79], Chatham et al. [80], Orient and Srivastava [35], Nishimura and Tawara [39], Vallance et al. [61], Straub et al. [40], Tian and Vidal [36], the data of Gluch et al. [41] have been re-normalized to the measurements of Rapp and Englander-Golden [37]. “L-B” with line drawn as eye-guide stands for recommended values of Ref. [4].

show a spread of about 20% what makes the comparison with BEB models difficult. Some validation of experimental techniques used in different measurements is needed. Rapp and Englander-Golden [37] normalized their data to own measurements of H_2 ; Tian and Vidal [36] normalized their data to Ar^+ measurements by Straub et al. [38]. Nishimura and Tawara [39] measured absolute cross sections; their data almost coincide with those by Straub et al. [40]. Lindsay and Morgan [4] compared different experiments including that from their laboratory [40] and produced a set of recommended values; this set differs by -9% at 100 eV and by -2% at 1000 eV from the experiment by Straub et al. [40].

Gluch et al. [41] normalized the sum of their partial cross sections to the total value of Rapp and Englander-Golden [37]. In Fig. 2 we have re-normalized the data of Gluch et al. by a factor of πa_0^2 to the original value of Rapp and Englander-Golden at 100 eV. The most recent data [39–41] and the recommended values [4] agree

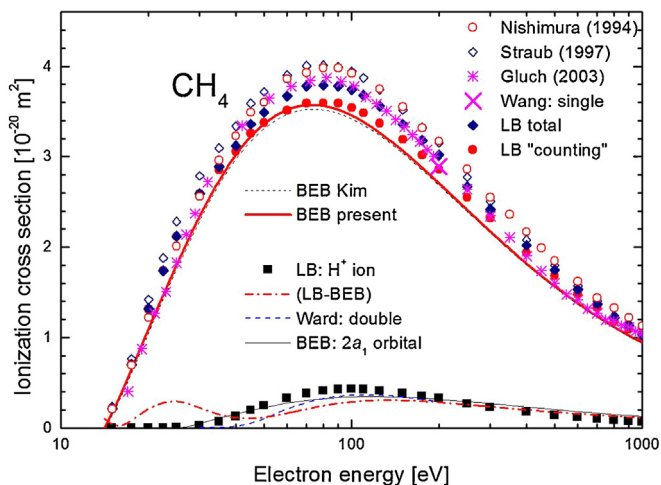


Fig. 3. Search for total counting ionization cross sections for CH_4 . Experiment and “LB total”, see Fig. 2. “Wang” single ionization [50]. “LB counting” has been obtained from recommended gross total “LB total” [4] by subtracting half of the H^+ yield (“LB: H^+ ion” [4]), see text for the discussion. BEB Kim [34] “Ward: double” is the sum of H^+ , CH^+ , C^+ , H_2^+ , CH_3^+ , CH_2^+ yields coming from double ionization processes. “BEB $2a_1$ ” is present calculation for ionization from the $2a_1$ molecular orbital.

within 10%, see Fig. 3. The present BEB model remains lower than these experiments.

The usual explanation [42] of this difference is that BEB models include also the dissociation into neutrals. This, in turn disagrees with the very basis of the classical models, Eq. (1)–(5): their kinematics assume an electron leaving the molecule. Measurements of dissociation into neutrals exist for only few molecules. Winters [43] measured the total yield of dissociated fragments (ions + neutrals) by adsorption on titanium getter obtaining a cross section of about $4.0 \times 10^{-20} \text{ m}^2$ at the maximum at 80 eV, comparable to the maximum in the gross ionization cross section. At 80 eV the parent ionization (i.e. into CH_4^+) is $1.55 \times 10^{-20} \text{ m}^2$ [4] so BEB would underestimate the sum of the ionization and dissociation-into-neutrals cross sections.

The difference between present BEB calculations and experiments can be explained in terms of multiple ionization, and more precisely in terms of multiple counting ions coming from the same ionization event. Methods in which the total charge is measured give so-called gross total cross section. This quantity differs from the counting ionization cross sections as multiply charged ions are counted with weights of their charge. For argon at 100 eV the $\text{Ar}^{2+}/\text{Ar}^+$ ratio amounts to 6.6%, see [3]. In molecules, dissociative ionization is a competing channel to multiple ionization. Generally the double ionization in molecules is low: in CF_4 at 180 eV the summed contribution from CF_2^{2+} and CF_3^{2+} is about 1–2% of the total gross ionization cross section [44,45].

However, in molecules considered in this paper, particularly in CH_4 and CF_4 careful attention must be paid to discriminate for double ion counts, like $(\text{CH}_2^+ + \text{H}^+)$ etc. For methane several recent experimental papers [46–48] showed that the dication CH_4^{2+} in its ground and excited states dissociates immediately and decays into two ionized fragments. In particular, using the coincidence technique, Ward et al. [46] have reported cross sections for formation of pairs of dissociated ions and attributed them to a specific precursor (monocation, dication, trication); their data are relative to the CH_4^+ yield. This technique was already used by Lindsay et al. [49], who reported cross sections for production of $(\text{CH}_2^+ + \text{H}^+)$, $(\text{CH}^+ + \text{H}^+)$, $(\text{C}^+ + \text{H}^+)$ ion pairs but their results are probably underestimated, compare with [46]. In total, at 200 eV as much as 58% of the gross ionization cross section comes from dissociative ionization (i.e. from other channels than formation of the CH_4^+ ion) [4]; obviously in part of these events the second fragment can be a neutral.

Already Wang and Vidal [50] noticed a relatively high amount of multiple countings of ions coming from dissociative channels that contributes to the gross total cross section. They evaluated the cross section for the double ionization at 200 eV as $0.23 \times 10^{-20} \text{ m}^2$ (vs. $2.89 \times 10^{-20} \text{ m}^2$ for single ionization). Wang and Vidal [50] estimated roughly that the H^+ ion is formed in about half of the dissociative ionization events. According to Ward et al. [46], at 200 eV as much as 52% of H^+ ions result from a double ionization (and 1.6% from triple ionization). The absolute value for the H^+ overall yield at 200 eV is $0.328 \times 10^{-20} \text{ m}^2$ according to the recommended values in [4] and $0.30 \times 10^{-20} \text{ m}^2$ for the summed-up yield of single, double and triple ionization channels reported by Ward et al. [46] (and normalization them to the CH_4^+ yield from [4]). The sum of all cross sections for appearance of ion pairs reaches a maximum of $0.37 \times 10^{-20} \text{ m}^2$ at 100 eV [46].

For all these experimental evidences it is reasonable to assume that the counting cross section (i.e. with the exclusion of double counting ion pairs) of CH_4 can be roughly evaluated by subtracting half of the cross section for the formation of H^+ ion [4] from the gross total cross section [4]. We did so in Fig. 3 – we consider full points on this figure as semi-empirically suggested values for the total counting ionization cross section in CH_4 . Now the BEB model coincides

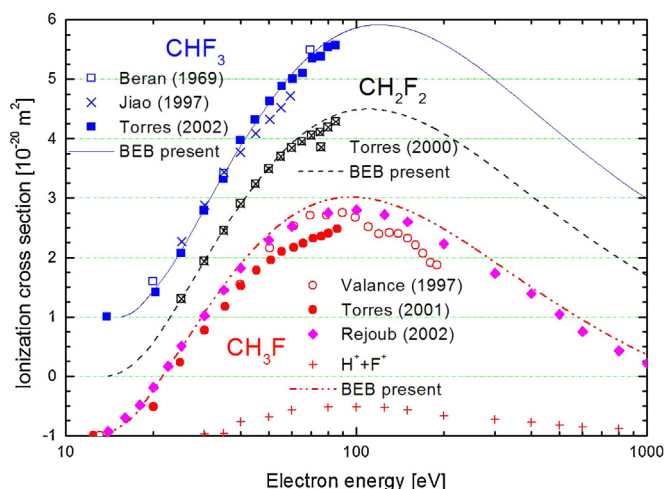


Fig. 4. Ionization cross sections in fluoromethanes. CH_3F (shifted by -1): gross total Vallance et al. [61], Torres et al. [32], Rejoub et al. [58,4]; $\text{H}^+ + \text{F}^+$ yield from [32]. CH_2F_2 : Torres et al. [57]. CHF_3 (shifted by $+1$): Beran and Hevan [60], Jiao et al. [59], Torres et al. [45]. BEB is present RHF 6-31**G calculation.

in the 40–1000 eV range with the experiment within the combined uncertainty of the experimental and evaluation procedures.

To validate further our estimate, in Fig. 3 we show: (i) the difference between the L-B recommended [4] gross total ionization cross section and the present BEB results, (ii) the H^+ ion yield according to the L-B review [4], (iii) the sum of H^+ , CH^+ , C^+ , H_2^+ , CH_2^+ , CH_3^+ yields coming from double ionization processes (table II from Wards et al. [46]) normalized presently to the recommended CH_4^+ yield [4]. These three sets show a similar range of amplitudes.

The difference between the recommended gross and present BEB cross section remains unexplained only around 30 eV, i.e. where dissociations into neutrals (CH_2 and CH_3 signals) reach their maxima [51]. However, we are not able to judge on the amplitude of possible contribution to the gross ionization cross section coming from possible dissociation into a neutral + ionized fragment via an excitation to some higher electronic states. Existing experiments [51–53] are fragmentary and disagree with theories [54]. Additionally, the BEB model with the vertical ionization potential probably underestimates cross sections in the near-threshold region, see the BEB calculation with the adiabatic potential [31]. Experimental checks [55,56] of the energy dependences in this region are therefore precious.

3.2. Fluoromethanes (CH_3F , CH_2F_2 , CHF_3)

Torres et al. [32,45,57] performed recently a series of measurements of partial and total ionization cross sections up to 85 eV with a declared uncertainty less than 10%. Morgan and Lindsay [4] gave recommended cross sections for CH_3F coinciding with the measurements of Rejoub et al. [58]. For all three mixed fluoromethanes, CH_3F , CH_2F_2 and CHF_3 the agreement between the present BEB model and recent experiments [25,45,57–60] is very good, see Fig. 4. For CH_3F we show also the sum of H^+ and F^+ ion production [57], with a maximum of $0.4 \times 10^{-20} \text{ m}^2$, but it does not mean necessarily that these ions come from double ionization events.

3.3. Tetrafluoromethane (CF_4)

Tetrafluoromethane is the gas most commonly used for plasma etching in semiconductor industries [62], therefore numerous experiments have been performed, starting from the determination of the dissociation (ionization plus neutral-dissociation) cross

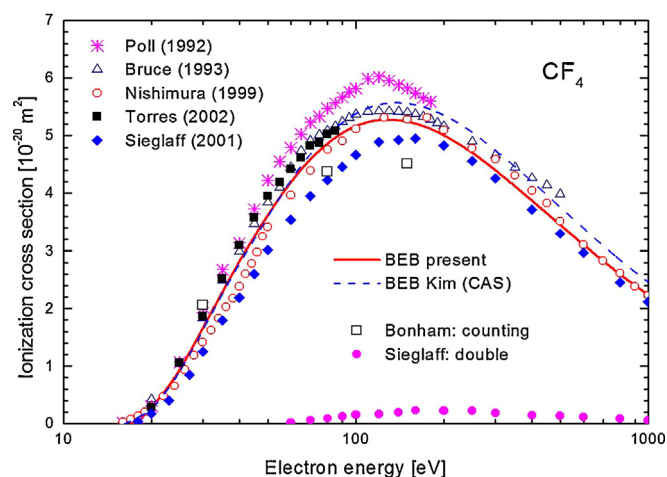


Fig. 5. Ionization cross sections in CF_4 . Experimental gross total: Poll et al. [24], Bruce and Bonham [64], Nishimura et al. [42], Torres et al. [45], Sieglaff et al. [65,4]; Bonham counting [70]; Sieglaff double ($\text{CF}_3^+ + \text{F}^+$ and $\text{CF}_2^+ + \text{F}^+$) from [65]; BEB Kim is complete-active-space calculation; BEB present is RHF 6-31**G calculation.

section of $5.5 \times 10^{-20} \text{ m}^2$ at its maximum [63]. All ionization events in CF_4 lead to the dissociation of the molecule, with the CF_3^+ ion predominant ($3.3 \times 10^{-20} \text{ m}^2$ at its maximum [4]). Some early experiments suffered from incomplete collection of light fragment ions but newer results [24,42,45,64] form a congruent dataset, agreeing within $\pm 15\%$, see Fig. 5. Out of several recent experimental data, the results from Innsbruck laboratory [24] that account for the correction of ion trajectories in the ion source form the highest set, give a maximum of $6.0 \times 10^{-20} \text{ m}^2$ at 120 eV while the result of Nishimura et al. [42] is $5.3 \times 10^{-20} \text{ m}^2$ at 125–175 eV. The coincidence measurements by Sieglaff et al. [65] done in absolute way with $\pm 5\%$ uncertainty gave at maximum a lower value, $4.95 \times 10^{-20} \text{ m}^2$.

The present BEB model agrees well with the recent experiments [42,45,64] and coincides with the BEB calculation done in slightly higher molecular orbital basis, RHF 6-311+G(d) [42], see Fig. 5. Kim and collaborators [42] tried to evaluate the effect of multiple ionization performing BEB calculations with the use of a complete-active-space wave functions set (CAS, in Fig. 5). Such a model overestimates the gross ionization measurements [42,45,64], see Fig. 5.

Whilst all ionization processes in CF_4 lead to the dissociation of the molecule, the data of Sieglaff et al. [64] show that the double ionization ($\text{CF}_2^+ + \text{F}^+$ and $\text{CF}^+ + \text{F}^+$) is lower than for CH_4 and reaches a maximum of $0.23 \times 10^{-20} \text{ m}^2$ at 200 eV, see Fig. 5. This can be explained by the high electronegativity of fluorine and its components what makes the formation of two positive ions less probable in CF_4 than in CH_4 (i.e. the second fragment in the dissociative ionization of CF_4 should predominantly be a neutral). This is also indirectly confirmed by studies of dissociation into neutrals [52,63]. The cross section of the formation of an F atom in ionizing and neutral-dissociation events is about $7 \times 10^{-20} \text{ m}^2$ at its maximum [52] compared to $0.74 \times 10^{-20} \text{ m}^2$ for the formation of the F^+ ion [4].

Note, however, that the distinction between gross and counting ionization cross sections of CF_4 is far less decisive than for CH_4 . A whole series of re-measurements and re-analysis coming from several groups [24,44,66–70] testifies this.

4. Toward systematics of total ionization cross sections

Present analysis of experimental uncertainties and corrections bring credibility to the systematic tendencies observed both in BEB

Table 1

Linear dependence of the maximum cross sections σ_{\max} [10^{-20} m²] in present BEB model vs. molecular dipole polarizability α [10^{-30} m³], experimental values from Ref. [73].

Molecule	α [$\times 10^{-30}$ m ³]	σ_{\max} [$\times 10^{-20}$ m ²]	σ_{\max}/α
CH ₄	2.593	3.571	1.377
CH ₃ F	2.97	4.02	1.354
CH ₂ F ₂	3.27 ^a	4.5	1.376
CHF ₃	3.57	4.92	1.378
CF ₄	3.838	5.273	1.374

^a Value interpolated between CH₃F and CHF₃.

(present and [32]) and in DM [42] estimates of ionization cross sections. In particular, we repute that the BEB model with 6-31**G molecular orbital basis reproduces the total counting ionization cross sections for the whole series CH₄ – CF₄ within 5% accuracy. In this series the maximum of the cross section rises from 3.57×10^{-20} m² for CH₄ to 5.27×10^{-20} m² for CF₄. The position of the cross section maximum rises in a similar manner, from 75 eV in CH₄ to 140 eV in CF₄. This rather reflects the increase in energy depth of orbital levels than the changes in threshold values, 14.13, 13.63, 14.01, 15.47 and 17.08 eV for CH₄, CH₃F, CH₂F₂, CHF₃ and CF₄, respectively.

In several works systematic dependences of ionization cross sections were examined. Harland et al. [71] studied the correlation of atomic and molecular maximum ionization cross sections σ_{\max} on the dipole polarizability α , checking both $\sigma_{\max} \propto \alpha$ and $\sigma_{\max} \propto \sqrt{\alpha}$ proportionalities. Kim and collaborators [42] postulated for fluorocarbons CF₄, C₂F₆, C₃F₈ a $\sigma_{\max} \propto \sqrt{\alpha Z}$ dependence with Z being the total number of electrons in the target. A similar dependence on the polarizability in the range of 50–100 eV and the application of the additivity rule was also noticed for total-scattering cross sections [72].

Maxima of the BEB total ionization cross sections σ_{\max} vs. the dipole polarizabilities [73] of the five molecules considered are resumed in Table 1. The σ_{\max} rises proportionally to the dipole polarizability of the target with the proportionality coefficient $1.37(\pm 0.01)$, $\sigma_{\max} = 1.37\alpha$, if σ_{\max} is expressed in 10^{-20} m² and α in 10^{-30} m³. The correlation of the linear fit is 0.999.

This rather simple dependence deserves some comments. All four classical-like formulae considered here indicate that the number of electrons on molecular orbitals determines the amplitude of the ionization cross section. On the other hand, the molecular polarizability can be considered as a sum of polarizabilities from separate molecular bonds. Secondly, from classical electrodynamics, the polarizability is the measure of the deformation of the electronic cloud in the external electric field. From quantum mechanical point of view, the polarizability is the measure for the sum of all virtual excitations of the target: electronic [74] and vibrational [75]. Again, the vibrational excitations reflect properties of the molecular bonds; for electronic excitations the sum of oscillator strengths is equal to the number of valence electrons even if the detailed electronic-excitation spectra of molecules can be quite complex [76]. Therefore, presently observed interdependence of the ionization cross section and the polarizability can reflect the same, somewhat synthetic molecular feature: the number of valence electrons convoluted with their binding (and kinetic) energies.

We are aware that these arguments are not conclusive so further analysis are needed. Note also that for sake of comparisons on an equal basis we used polarizabilities from the same type of optical measurements [73]. Theories, including the present HF method, tend to underestimate the molecular polarizabilities, even if the general trend for the series of molecules is preserved. The quality of calculation depends much on the choice of the molecular orbital basis, compare for e.g. [77,78].

5. Conclusions

Binary-encounter models [13,14,17] prove to be quite successful in predicting ionization cross sections. What becomes clear from the case of methane, these are rather experimental single-ionization (i.e. counting) cross sections that agree with Kim and Rudd's [14] BEB model. Out of numerous experiments only few allow to estimate the single-ionization cross section which is the output of the binary-encounter models.

For methane, Ward et al. [46] showed that at 200 eV more H⁺ ions come from the double ionization process than from the single ones. Subtracting the estimate for the double ionization from the recommended [4] gross ionization one leads to an almost perfect agreement with the present BEB model (6-31**G orbitals and the vertical ionization energy of 14.128 eV).

More uncertainty exists on such a distinction for CF₄ and other fluoromethanes. Quantum chemistry calculations of the energetics of specific dissociation channels – into neutrals, into neutrals and ions, and into ion pairs, are important in this context [32].

From experimental side, single coincidence [46] and kinetic-energy release measurements [41] are important for understanding possible ionization channels. Such a knowledge is essential for projecting and diagnosis of plasma processes in many technical applications.

Deutsch and Märk's model [13,15,24] underestimates the position of the ionization maximum but this should be rather attributed to the simplified applications of the method, where only the lowest ionization thresholds are considered, as in Fig. 1. As shown by Torres et al. [32] who incorporated a more complete set of quantum levels, including inner orbitals, into their calculation, the agreement of the DM model with experiments is not worse than for BEB.

An extension of the BEB model to double and dissociative ionization would be desirable. Already Gryziński [17] showed two possible mechanism of double ionization: the direct process, i.e. the second ionization by the (scattered) incoming electron, and the recoil process, i.e. ionization by the (leaving) secondary electron. It is not to be excluded that the information on the dissociative ionization can be already extracted from the standard BEB calculation. In Fig. 3 we compare the experimental H⁺ yield [4] with the ionization from the 2a₁ molecular orbital in the present BEB model: the two curves seem to coincide.

Present calculations do not take into account the possibility of ionizing transitions coming from higher vibrational states. In other words, we assume that the vibrational temperature of the target molecules is $T=0$. As already noticed by Kim and collaborators, the vibrational structure of the electronic levels would modify the ionization cross sections in the near-to-threshold region. Further calculations would be needed to explore this question in detail.

Acknowledgments

A part of this work has been done in Quantum Optics Center (COK), UMK Toruń. Numerical calculations in the GAUSSIAN code have been performed at the Academic Computer Center in Gdańsk (TASK). We thank dr A. Karbowski for the preparatory work on the analytical fits for CH₄ cross sections. GK thanks for the hospitality at NFRI, Gunsan.

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