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ASSESSED TOTAL AND PARTIAL IONIZATION CROSS SECTIONS FOR CF₄, C₂F₆, C₃F₈, CHF₃, CF₃I, *c*-C₄F₈, Cl₂, CCl₂F₂, BCl₃, SF₆, AND FRAGMENTS OF CF₄ AND SF₆

Loucas G. Christophorou* and James K. Olthoff**

1. INTRODUCTION

We have recently completed an updated review, synthesis, assessment, and discussion of low-energy electron interactions with the plasma processing gases CF₄, C₂F₆, C₃F₈, CHF₃, CF₃I, *c*-C₄F₈, Cl₂, CCl₂F₂, BCl₃, SF₆. This work, along with fundamental knowledge on electron-molecule collision processes, the definition of the various electron collision cross sections and rate coefficients, and the experimental and theoretical methods used for their determination have been described in Christophorou and Olthoff.¹ It has been shown in this reference, that reliable data on the electron transport, electron attachment, and electron-impact ionization coefficients generally exist for most of these molecules, except for electron transport in strongly electronegative gases. Also, reliable data exist on the collision cross sections for most of these molecules, but this knowledge depends on the collision process and the molecule under consideration. The cross sections and coefficients that have been recommended or suggested¹ were based on experimental measurements. This work¹ has shown that while a great deal of quantitative data have become available, especially recently, for the molecules under consideration, there is still a pressing need for quantitative measurements of the cross sections for electron-impact dissociation into neutral fragments, direct and indirect vibrational (and electronic) excitation, and electron interaction processes involving excited and transient (radical) species.

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Substantial amounts of new data have recently become available for these ten plasma processing gases, especially on their total and partial ionization cross sections. These have been reviewed, synthesized, assessed and discussed and have been shown to generally be more accurate than earlier measurements allowing better recommended cross sections.¹ In this paper we present total and partial ionization cross sections for CF₄ and SF₆ as examples of these data. We also present a comparison of experimental data and calculated results on the electron-impact ionization cross sections for the fragments of CF₄ and SF₆.

2. EXAMPLES OF RECENTLY RECOMMENDED TOTAL IONIZATION CROSS SECTIONS OF MOLECULES

Substantial amounts of new data have recently become available for these cross sections which have been reviewed, synthesized and discussed in Ref. 1. Examples of the recently recommended $\sigma_{it}(\epsilon)$ are shown in Figs. 1 and 2 for CF₄ and SF₆, respectively.

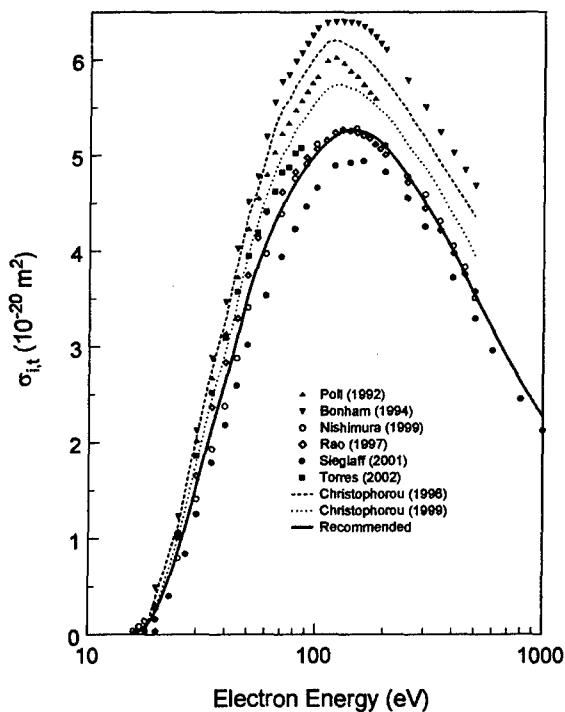


Figure 1. Total ionization cross section $\sigma_{it}(\epsilon)$ as a function of electron energy for CF₄. $\blacktriangle$, Ref. 2; $\blacktriangledown$, Refs. 3 and 4; $\circ$, Ref. 5; $\diamond$, Ref. 6; $\bullet$, Ref. 7; $\blacksquare$, Ref. 8; ---, Ref. 9; $\cdots$, Ref. 10; —, recommended, Ref. 1.

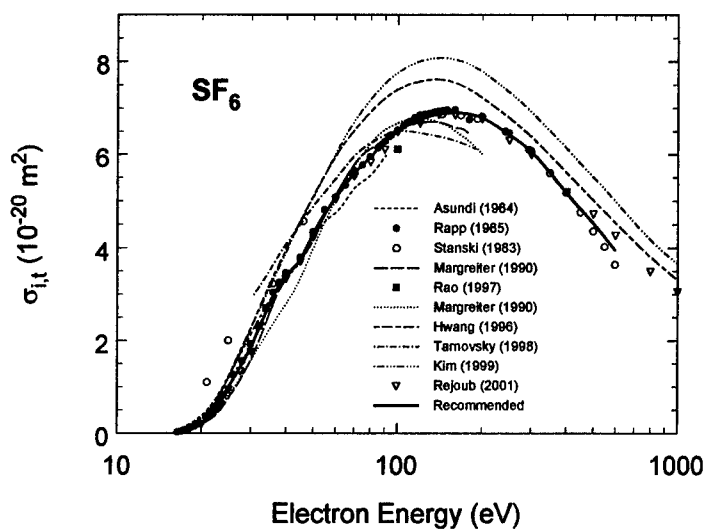


Figure 2. Total ionization cross section $\sigma_{i,t}(\epsilon)$ as a function of electron energy for SF_6 , ---, Ref. 11; •, Ref. 12; ○, Ref. 13; —, Ref. 14; ■, Ref. 15; ▽, Ref. 16; ..., Ref. 17; - - -, Ref. 18; _ . _ , Ref. 19; _ ... _ , Ref. 20; —, recommended.

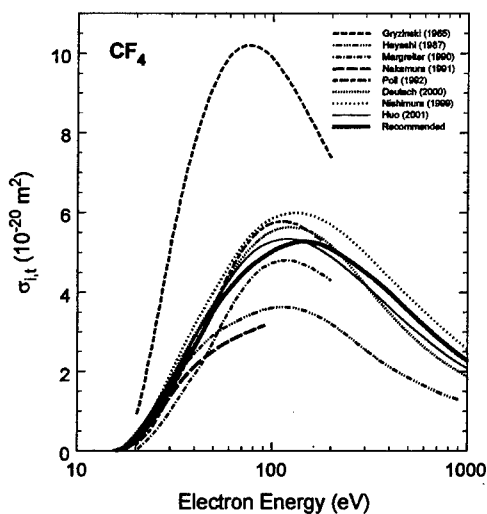


Figure 3. Comparison of the recommended $\sigma_{i,t}(\epsilon)$ for CF_4 with the results of various calculations. —, from Fig. 1; ---, Ref. 21; - - -, Ref. 2; - . - , Ref. 22; - ... - Ref. 23; —, Ref. 24 ... , Ref. 5; ..., Ref. 25; _ . _ , Ref. 26.

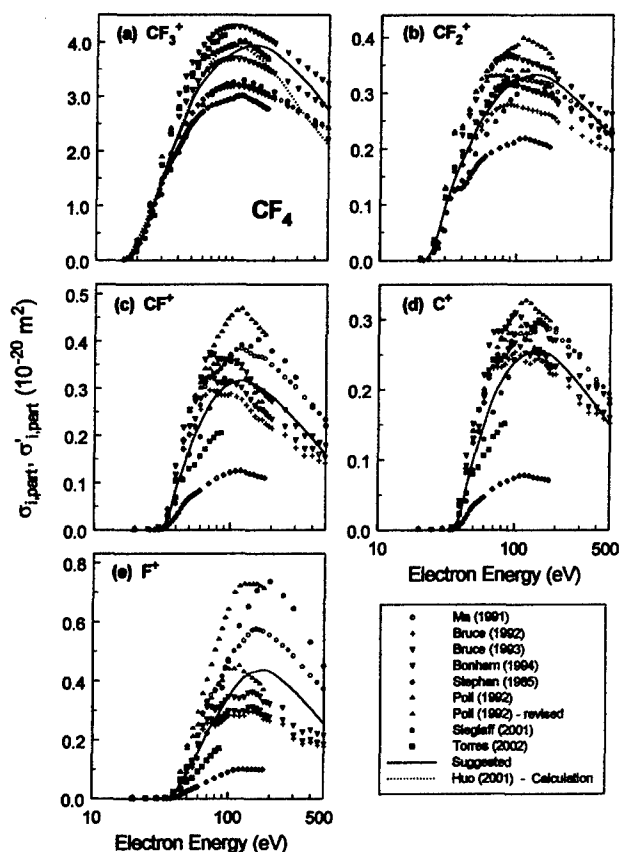


Figure 4. Partial ionization cross section for (a) CF_3^+ , (b) CF_2^+ , (c) CF^+ , (d) C^+ , and (e) F^+ by electron impact on CF_4 . $\circ$, Ref. 27; $+$, Ref. 28; ∇ , Ref. 4; ∇ , Ref. 3; $\diamond$, Ref. 29; Δ , $\blacktriangle$ Refs. 2 and 1; $\bullet$ Ref. 7; $\blacksquare$, Ref. 8; —, suggested. Also shown (. . .) is a calculation of the cross section for CF_3^+ production by electron impact on CF_4 (Ref. 30).

In Fig. 3 the recommended $\sigma_{i,t}(\epsilon)$ of CF_4 is compared with the results of various calculations. The results of the semiempirical (additivity-rule-based) calculations^{5,25,26} are in reasonable agreement with experimental data, especially the results of the simple-Binary-Encounter-Dipole (sBED) model of Huo.²⁶

3. PARTIAL IONIZATION CROSS SECTIONS FOR CF_4 AND SF_6

In Figs. 4 and 5 are shown the partial ionization cross sections, $\sigma_{i,\text{part}}(\epsilon)$, for the formation of various ions by electron impact on CF_4 and SF_6 respectively. Although there is agreement among the measurements of various groups, the partial ionization cross sections for light fragments still seem to be uncertain due to ion discrimination problems.

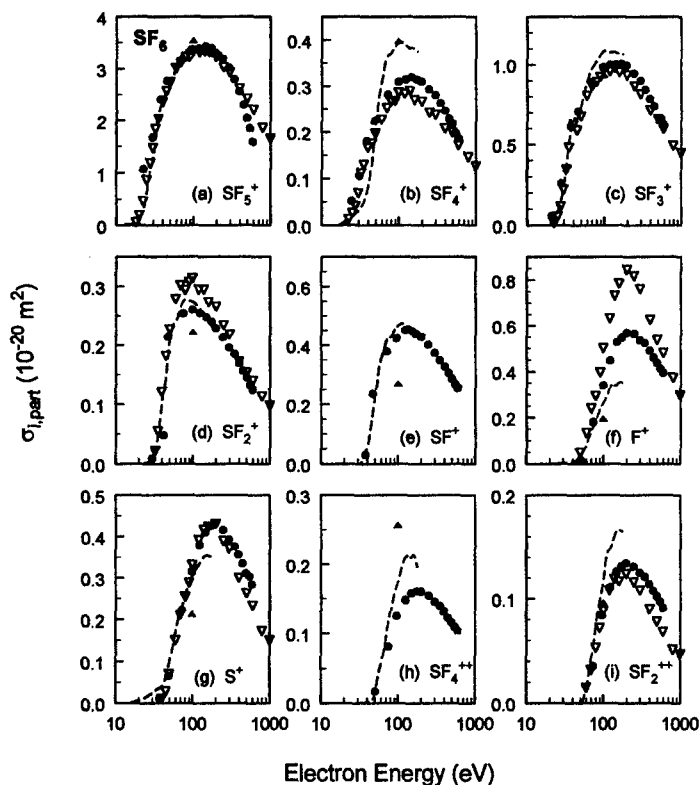


Figure 5. Partial ionization cross sections, $\sigma_{i,\text{part}}(\epsilon)$, as a function of electron energy for SF_6 . •, Ref. 13; ---, Ref. 14; ▲, Ref. 15, ▽, Ref. 16.

4. TOTAL IONIZATION CROSS SECTIONS FOR RADICALS OF CF_4 AND SF_6

There are limited data on the partial and total ionization cross sections of radicals. In Fig. 6 are shown the available data on electron-impact ionization of fragments of CF_4 . The data on the total ionization cross sections of the three radicals from CF_4 were obtained by summing up the partial ionization cross sections shown in the figure. They are in reasonable agreement with the results of semiempirical calculations.^{25,31} This agreement is gratifying because it shows that these semiempirical calculations can be employed to provide values of the total ionization cross sections of radicals and reactive species, which are normally difficult to study experimentally.

Limited data are available for the ionization cross sections of SF_6 radicals. These are compared with the results of semiempirical calculations in Fig. 7.

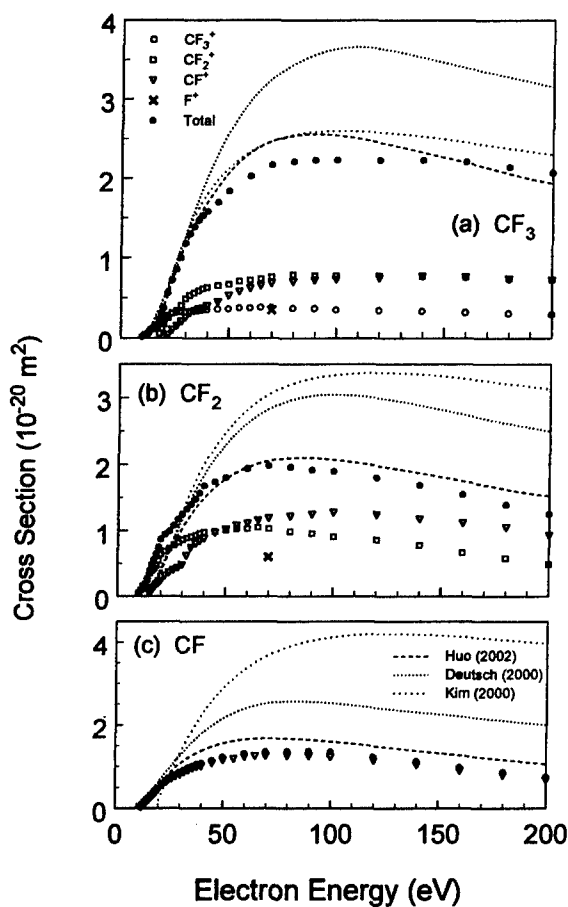


Figure 6. Electron-impact ionization cross section for the fragments (a) CF_3 , (b) CF_2 , and (c) CF : $\bullet$, total ionization cross section (Ref. 31); $\circ$, CF_3^+ (Refs. 32, 33); $\square$, CF_2^+ (Refs. 32, 33); ∇ , CF^+ (Refs. 32, 33); $\times$, F^+ (Ref. 32). Also shown are calculated total ionization cross sections for each fragment; ---, Ref. 31; ..., Ref. 25; . . ., Ref. 34.

5. CONCLUSIONS

Based on our comprehensive work¹ on fundamental electron interactions with plasma processing gases, we can conclude that:

- While much progress has been made in our understanding of low-energy electron-molecule interaction processes and reasonable progress has been made in our effort to build up a sound database on such processes, **much is still needed.**

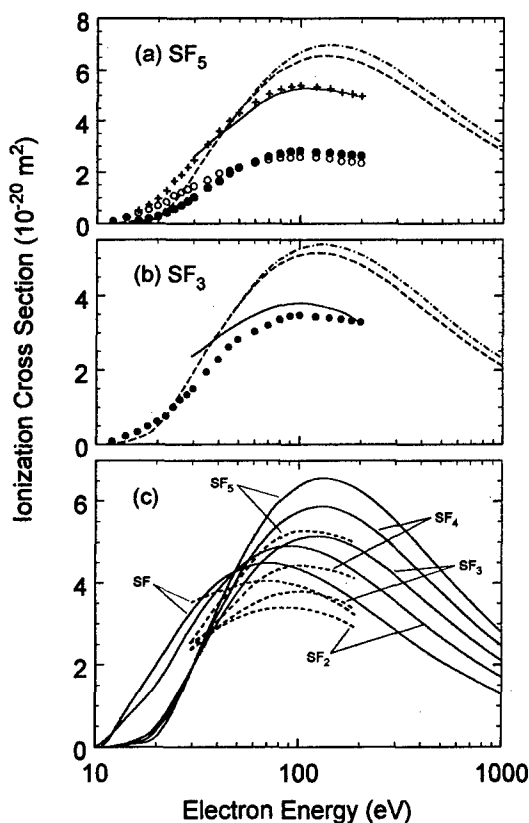


Figure 7. Electron-impact ionization of SF_6 radicals: (a) Cross section for SF_5^+ and SF_4^+ by electron impact on SF_5 . Measurements (Ref. 19): $\circ$, SF_5^+ ; $\bullet$, SF_4^+ ; $+$, sum. Calculations of the total single ionization cross section of SF_5 : —, Ref. 19 - - -, — · —, Ref. 35. (b) Cross section for SF_3^+ by electron impact on SF_3 : $\bullet$, measurements (Ref. 19); Calculations, —, Ref. 19, - - -, — · —, Ref. 35. (c) Calculated electron-impact total single ionization cross sections for the radicals SF_5 , SF_4 , SF_3 , SF_2 , and SF : - - -, Ref. 19, —, Ref. 35 (see Ref. 1)

- The fundamental generality of low-energy electron-molecule interactions, their generic significance to modern technology, and their basic role in life sciences, stresses the **need for further coordinated and quantitative studies in this area.**

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