Electron and ion swarm data of fluorinated gases used in plasma processing

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Abstract. This paper presents recent data (from 1999-to date) of the theoretical and experimental work that has been done on electron and ion interactions at energies between thermal and 200 eV on the flourinated gases CHF₃, CF₄, C₂F₄, C₂F₆ and c-C₄F₈, and their mixtures with Ar and N₂. These gases, used extensively in plasma processing, are currently the subject of intensive research. This review demonstrates that, in spite of the important progress gained in this line of research, many more measurements and refinements to the present theories are needed in order to obtain a complete picture of their interactions with electrons and ions and hence to have reliable and complete data sets with which a more realistic modeling of the gaseous discharges can be made.

1. Introduction

This paper presents and discusses recent data on the transport and ionization properties of electron and ions in the fluorinated gases CHF₃, CF₄, C₂F₄, C₂F₆ and c-C₄F₈, and their mixtures with Ar and N₂. These gases are widely used in plasma processes for the fabrication of semiconductors, among other applications.

There is an aim in this paper at presenting an overview of the recent work (1999-to date) on the measurement of cross sections relevant to electron and ion interactions in the above gases over the energy range from thermal to about 200 eV, and focused more specifically on the measurement and calculations of swarm coefficients that are useful both for plasma modeling, and also used for validating the many several sections involved in their calculation. The swarm coefficients to be discussed and presented in this paper are the electron drift velocity vₑ, the density-normalised longitudinal diffusion coefficients NDLₑ, respectively, the density-normalised electron impact ionisation and attachment coefficients α/N and η/N, respectively, as well as the density-normalised effective ionisation coefficient (α−η)/N. Wherever possible, ion transport and ion-molecule reactions will be dealt with, wherever possible, in the form of ion mobilities (drift velocities), diffusion coefficients and cross sections. It is also the aim of this paper to present the needs for future work, both experimental and theoretical, that would first of all lead to reliable, self consistent sets of cross sections and swarm data, since there are still discrepancies between cross section sets derived from particular measurements. On the other hand, it is important to insist on the importance of the study of electron detachment from negative ions and electron interactions with radicals.
2. Swarm coefficients and cross sections for electron-molecule interactions.

In this section we shall discuss the progress in the knowledge on the interactions of electrons and ions in fluorinated gases in terms of recent experimental and theoretical work. It has been chosen not to differentiate between theory and experiment since they are already interrelated.

2.1 CHF₃

CHF₃ has been regarded as a good substitute for CF₄ in plasma processes for semiconductor fabrication since CF₄ is a powerful greenhouse gas, while the residence time of CHF₃ in the earth’s atmosphere is 200 times less than that of CF₄ [1]. Thorough reviews on electron interactions with CHF₃ have been given recently by Christophorou et al [1,2]. These authors conclude their second review and update by strongly recommending more research regarding all elastic and inelastic scattering processes, cross sections and electron impact ionization and dissociation.

More recently, Fiegele et al [3] have studied the ionization behaviour close to the threshold for fragment ion production from CF₄, CHF₃ and two other hydrocarbons. In their experiment, they used a hemispherical electron monochromator with an energy resolution of ≈135 meV. The vibrationally cold target molecules were prepared in a supersonic expansion and the resulting ions were mass analysed using a quadrupole mass spectrometer. Their energy scale was calibrated from their experimental data on xenon. In order to obtain an absolute energy scale, their measured appearance energy (AE) of Xe⁺ was corrected according with the tabulated value of 12.129 87 eV [4]. Xenon was a sensible choice, since all of its higher excited ionic states are more than 1.3 eV above the AE for Xe⁺. Thus, such states would contribute negligibly to the cross section at the threshold. This study permitted Fiegele and co-workers to extend the usefulness of Wannier’s law for ionization in the threshold region

\[ \sigma(\varepsilon,\mu) \propto \varepsilon^{(2\mu-1)/4} \equiv \varepsilon^p \]  

with

\[ \mu(Z) = \frac{1}{2} \left[ \frac{(100Z-9)/(4Z-1)}{1/2} \right] \]  

where \( \varepsilon \) is the energy above the ionization energy and \( Z_e \) is the charge of the ion after ionization. The values of \( p \) and the measured appearance energies for the CHF₃ ionic fragments CF₃⁺, CF₂⁺, CF⁺, CHF₂⁺ and CHF⁺ are given in Table 3 of this paper [3].

In principle, Wannier’s threshold law is valid only for monoatomic systems, although Fiegele et al were able to extend it to CHF₃ and CF₄, among other molecules. In their experiment on CHF₃ they were able to observe CF₃⁺, CF₂⁺, CF⁺, CHF₂⁺ and CHF⁺. Also, it was found that the lifetime of the parent ion CHF₃⁺ was too short for observation in the millisecond time regime. One more finding of this research was the formation of C⁺ from CHF₃ by electron impact, which had not been reported in the literature before, either from electron impact or from photoionization experiments. Interestingly, it was found that the production of C⁺ is less energy demanding than that leading to CH⁺.

The availability of recent experimental data from swarm experiments and electron impact dissociation and ionization cross sections led Kushner and Zhang [5] to develop a working electron impact cross section set for CHF₃. These authors found that increased energy losses from dissociative electronic excitation processes were required to reproduce the experimental ionization coefficients, and also that the resulting cross sections for attachment were small, with some uncertainty in their magnitude at low energies.

A year later, Morgan et al [6] published a computed set of cross sections for elastic electron scattering and electron-impact excitation of CHF₃ using the Schwinger multichannel method [7,8]. They also made use of systematic procedures for adjusting all cross sections to obtain consistency with known swarm parameters. These authors discussed the differences between their calculations and
those of Kushner and Zhang and ascribe the differences to (a) the use of different partial ionization cross section measurements having very different energy dependencies near threshold, (b) the use of a total scattering cross section instead of a momentum-transfer cross section below 10 eV, together with the use of a coarse ab initio momentum-transfer cross section above 10 eV, and (c) the simple scaling, by a large factor, of measured dissociation cross sections. As a result of the above, Morgan et al were of the opinion that, regarding items (b) and (c), their own ab initio momentum-transfer and dissociation cross sections produce a better starting point for the swarm calculations and, ultimately, for a better outcome.

An additional, very useful result of this work was the possibility of calculating two vibrational, four ionization and one dissociation rate coefficients \( k \) for electron collisions with CHF\(_3\) over the electron temperature \( (T_e) \) range from 0 to 15 eV by means of the equation

\[
k(T_e) = \alpha T_e^{\beta} \exp[-\gamma/T_e] \tag{3}
\]

with \( k(T_e) \) in units of cm\(^3\) s\(^{-1}\). The coefficients \( \alpha, \beta \) and \( \gamma \) are given in Ref. [6].

Covering a wide range of electron impact energies over the range 0.1 to 10 keV, a set of calculated total and differential elastic cross sections for CHF\(_3\) have been published by Manero et al [9].

Varella et al [10] have measured and calculated differential elastic cross sections, as well as calculated integral cross sections for elastic electron collisions with CH\(_3\)F, CH\(_2\)F\(_2\), CHF\(_3\), and CF\(_4\). Again, the calculated cross sections were obtained with the Schwinger multichannel method, and a Born-closure procedure was used to improve the differential cross sections for polar systems. Polarization effects were found to be relevant even for systems with moderately large permanent dipole moments, such as CH\(_3\)F and CHF\(_3\). In general, the agreement between theory and experiment was found to be good. These authors state that, with the exception of CF\(_4\), all fluoromethanes possess considerable permanent dipole moments, and their consequences on how elaborate calculations should be in order to reproduce the experimental data. Their electron impact energy range of study was restricted to less than 15 eV, where polarization is by far more computationally demanding by inclusion of a longer-range \( (1/r^2) \) interaction. Indeed, they state that three main factors determining the behaviour of the low-energy electron-scattering cross sections are (a) fluorination effects, (b) dipole moment magnitudes, and (c) polarization effects.

Voloshin et al [11], based on previous collision cross sections sets, modified some of the vibrational excitation cross sections for CHF\(_3\) in order to produce a good fit to measured drift velocities and ionization coefficients in CHF\(_3\)-Ar mixtures, using a Monte Carlo method to calculate the swarm parameters in both pure CHF\(_3\) and in CHF\(_3\)-Ar mixtures. Using the cross sections of Kushner et al [5] and of Morgan et al [6], Voloshin and his co-workers used a two-term approximation to the solution of Boltzmann equation, and concluded that such cross sections were unable to reproduce the experimental drift velocities in CHF\(_3\)-Ar. However, it is well known that the two-term approximation could be inappropriate when, for example, one of the mixture constituents is of electronegative character, such as CHF\(_3\), in this case. On the other hand, following a further adjustment to previous cross section sets, their calculated electron drift velocities and ionization coefficients, derived from a Monte Carlo calculation were found in much better agreement with the experimental ones. It is believed that a real and fair comparison between previous cross sections and Voloshin’s adjusted ones would have been valid should the same Monte Carlo method be used with all of the cross section sets.

The pulsed Townsend technique has been used by Hernández-Ávila et al [12] to measure the electron drift velocity, the density-normalized effective ionization coefficient \( (\alpha-\eta)/N \) (\( \alpha \) and \( \eta \) are the ionization and attachment coefficients, respectively), the density-normalized longitudinal diffusion coefficient \( N_D \), and the ratio between the longitudinal diffusion coefficient and the electron mobility \( D_e/K \), in CHF\(_3\) and its mixtures with Ar and N\(_2\), over a wide range of the density-normalized electric field strength \( E/N \), from 0.2 to 400 Td (1 Td = 10\(^{-17}\) V cm\(^2\)). The CHF\(_3\) content in the mixtures was varied between 1% and 50%.
Regions of negative differential conductivity (NDC) appear in the plots of the electron drift velocity as a function of $E/N$ (see Figs. 1 and 2). This effect is more pronounced for the CHF$_3$–Ar mixtures than for the CHF$_3$–N$_2$ ones, since it results from the presence of a deep Ramsauer–Townsend minimum in the momentum transfer cross section for Ar, which is absent in N$_2$. For the CHF$_3$–N$_2$ case, a shallow region of NDC is observed, and it is due to several inelastic collision processes between the electrons and the buffer gas, and also to the steep fall of the scattering cross sections for CHF$_3$ at low electron energies.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** The electron drift velocity in CHF$_3$–Ar [12]  
**Figure 2.** The electron drift velocity in CHF$_3$–N$_2$ [12]

The longitudinal diffusion coefficients for electrons in pure CHF$_3$ and the CHF$_3$–Ar mixtures for 1%, 5% and 20% CHF$_3$ are shown plotted in Fig. 3 as a function of $E/N$, together with the corresponding values for Ar and CHF$_3$. Other values of $NDL$ for both mixtures can be found in Ref. [12]. The mixture curves display well-defined regions with maxima followed by minima that are indicative of strong inelastic collision processes, which are in turn responsible for the NDC behaviour noticed in the plots of the drift velocities in figures 1 and 2. Note also that the maxima in $NDL$ shift towards higher $E/N$ values as the content of CHF$_3$ in the mixture is increased. It is also interesting to note that, past the minima, the $NDL$ curves tend asymptotically towards attaining a trend lying between the Ar and the CHF$_3$ curves, depending upon the concentration ratio. A fairly similar behaviour, although not so strong, is observed in the $NDL$ curves for the CHF$_3$–N$_2$ mixtures displayed in figure 4.

![Figure 3](image3.png)  ![Figure 4](image4.png)

**Figure 3.** Density-normalized longitudinal diffusion coefficients of electrons in CHF$_3$–Ar [12]  
**Figure 4.** Density-normalized longitudinal diffusion coefficients of electrons in CHF$_3$–N$_2$ [12]

The ionisation coefficients in the mixtures of CHF$_3$ with Ar and N$_2$ are shown in Figs. 4 and 5, for several gas mixture ratios, respectively. In both cases, the attaching character in both mixtures was
found to be very small. An interesting feature of the CHF\textsubscript{3}-N\textsubscript{2} mixture is that, for $E/N < 80$ Td and CHF\textsubscript{3} concentrations of less than 20\%, the values of ($\alpha - \eta$)/$N$ are higher than those expected due to only electron impact. One possible mechanism that would be invoked to explain this observation is that of Penning ionization of CHF\textsubscript{3} due to highly excited N\textsubscript{2} molecules. Even though the ionization potential of CHF\textsubscript{3} is not so well established \cite{1}, the lowest threshold energies for the appearance of positive ions by electron impact lie in the range 14–15.2 eV for the process

$$\text{CHF}_3 + e^{-} \rightarrow \text{CF}_3^+ + \text{H}. \quad (4)$$

The closest excited states of N\textsubscript{2} that could be involved in the Penning ionization process may be either $y^1\Pi_g$ or $x^1\Sigma_u^+$, lying at about 14.2 eV. On the other hand, this effect is not seen in the curve for ($\alpha - \eta$)/$N$ for CHF\textsubscript{3}-Ar in Fig. 5, since the appearance potential of CHF\textsubscript{3} is nearly 3.2 eV higher than that of the Ar metastables ($\approx 11$ eV). Moreover, the disappearance of this effect for CHF\textsubscript{3} concentrations greater than 50\%, and for $E/N > 120$ Td for the CHF\textsubscript{3}-N\textsubscript{2} mixture can be explained in terms of the overwhelming effect of electron impact ionization over that of Penning ionization, since the latter effect is only apparent for $E/N$ values closer to or lower than the electron impact ionization threshold.

Peko et al \cite{13} have measured the collision-induced dissociation for CF\textsubscript{3}\textsuperscript{+} on CHF\textsubscript{3}, the dissociative charge transfer for CF\textsubscript{3}\textsuperscript{+} and F\textsuperscript{+} on CHF\textsubscript{3}, and the electron detachment from F\textsuperscript{-} on CHF\textsubscript{3}, for collision energies in the range 20-240 eV.

The dissociative charge-transfer cross sections are plotted in Fig. 7 as a function of the relative collision energy for F\textsuperscript{+} on CHF\textsubscript{3}. Interestingly, the highest yield was found for the product ion CF\textsuperscript{+}, even though this is an endothermic channel ($\sim 3.4$ eV), in contrast with its competing thermoneutral channel yielding CF\textsubscript{2}\textsuperscript{+}, turning out to be smaller by a factor of three over the entire energy range studied. Moreover, the competing channels for dissociative charge transfer yielding either CF\textsubscript{3}\textsuperscript{+} or CHF\textsubscript{2}\textsuperscript{+} are exothermic, and have very small cross sections. Peko et al are of the opinion that more insight is needed in order to understand these reactions.

Peko et al could also measure the dissociative charge-transfer cross sections for CF\textsubscript{3}\textsuperscript{+} in CHF\textsubscript{3}, and are shown here in Fig. 8, where the most abundant product ions were found to be CHF\textsubscript{2}\textsuperscript{+} and CF\textsuperscript{+}. The cross section for producing CF\textsubscript{3}\textsuperscript{+} from the dissociation of CHF\textsubscript{3} into CF\textsubscript{3} + F, with an endothermicity of -6.2 eV, was found to be smaller than the other two leading to CHF\textsubscript{2}\textsuperscript{+} and CF\textsuperscript{+}, even though these have higher endothermicities of -7.8 and -11.9 eV, respectively. Note also that the summed cross section is also considerably less than that for the F\textsuperscript{+} projectile (Fig. 7), and increases sharply as a function of collision energy.

Electron detachment cross sections of Peko et al for F\textsuperscript{-} in CHF\textsubscript{3}, are reproduced here in Fig. 9 as a function of the relative collision energy. Starting from the electron affinity of F\textsuperscript{-}, these increase rapidly.
with collision energy. Thus, in connection with the etching processes in a CHF₃ discharge, electron detachment of F in CHF₃ may be a significant contributor to the population of neutral fluorine.

![Graph](image1)

**Figure 7.** Dissociative charge-transfer cross sections for F⁺ + CHF₃ as a function of the relative energy of collision. The summed cross section contains the contribution of other minor ionic fragments [13].

![Graph](image2)

**Figure 8.** Dissociative charge-transfer cross sections for CF₃⁺ + CHF₃ as a function of the relative energy of collision. The summed cross section contains the contribution of other minor ionic fragments [13].

![Graph](image3)

**Figure 9.** Electron detachment cross section for collision of F⁻ with CHF₃ as a function of the relative energy [13].

The only ion-molecule reaction study under swarm conditions that we know of in CHF₃ is that of Basurto et al [14] who used a double mass spectrometer-drift tube to measure the relative abundance of ions resulting from the collision of CHF₂⁻ and CF₃⁻ in Ar at pressures in the range 25-100 mTorr.
These measurements are of relevance since CHF₃ is diluted in Ar normally in plasma reactors. The results of such measurements are plotted in Fig. 10 for the collision system CHF₂⁺-Ar. In this case, C⁺ is the most abundant ion for E/N<70 Td, although this situation reverses in favour of the formation of Ar⁺ formation for E/N>200 Td, which becomes 100% efficient for E/N>400 Td. This finding is quite consistent with the measurement of Wang et al. [15] for a rf plasma in a 50:50 mixture of CHF₃ and Ar at 5 mTorr, where the Ar⁺ signal was found to be about ten times higher than that of CHF₂⁺.

![Figure 10](image_url)

**Figure 10.** Abundance of C⁺ (closed symbols) and Ar⁺ (open symbols) resulting from injecting CHF₂⁺ into Ar as a function of E/N. Ar pressures of 100 mTorr (circles), 50mTorr (triangles) and 25mTorr (squares) [14].

The mobilities of and of CHF₂⁺ in CHF₃ are shown plotted in Fig. 11 as a function of E/N [14]. The mobility curve displays a trend towards a constant value at low E/N which, on purely qualitative grounds, results from the predominance of the attractive part of the interaction potential over its repulsive counterpart. Comparison of the average reduced mobility at low E/N of the these ions with the so-called polarization limit formula [16,17] or Langevin’s equation for the zero-field reduced mobility

$$K_{00} = 13.56 \left( \alpha_d \mu_r \right)^{1/2}$$

where αₐ is the dipole polarizability of the neutral in Å³, and μᵣ is the reduced mass of the ion-neutral system. For CHF₂⁺ drifting in CHF₃, one obtains a calculated value of K₀₀=1.33 cm² V⁻¹ s⁻¹, which is 2.4 times larger than that measured of 0.53±0.01 cm² V⁻¹ s⁻¹. The strong discrepancy between these two values may due to the highly polar character of CHF₃ in contrast with that of CF₄ (see below) since, as expressed by Fiegele et al [3], CHF₃ itself is very similar to CF₄ and can be obtained after the substitution of one fluorine atom by hydrogen, thereby changing the point symmetry group and leading to a more polar molecule.

2.2 **CF₄**

As with CHF₃, the work on electron interactions has been revised up to 1999 by Christophorou et al [2,18]. Since then, there has been some progress in the refinement of cross sections and swarm coefficients.
Fiegele et al [3] studied the behaviour of dissociative ionization of CF$_4$ near the threshold. Both Wannier’s coefficient $\rho$, used for the calculation of the cross sections by means of Eq. (1) and the corresponding appearance energies were determined for C$^+$, CF$^+$, CF$_2^+$ and CF$_3^+$. Fairly good agreement was found with previously tabulated values for the appearance energies, with the exception of CF$^+$. Among many interesting features of this research, the appearance energy for CF$_3^+$ from photoionization studies [19] turns out to be 0.8 eV smaller than that of obtained from this electron impact study; this difference is ascribed to the fact that photoionization and electron impact studies are not directly comparable, since the transition complex arising from the interactions is different. In other words, photoionization takes place from a neutral molecule, while electron impact ionization proceeds from the decay of a short-lived, highly excited anion under the ejection of two electrons.

Torres et al [20] have studied the electron-impact dissociative ionization of CF$_4$ by electron bombardment (up to 100 eV) to a supersonic beam of CF$_4$ neutrals in a time-of-flight mass spectrometer. They report the partial (absolute) ionization cross sections of the nascent ions CF$_2^+$, CF$_2^{2+}$, CF$_3^+$, CF$_3^{2+}$, CF$^+$, C$^+$, and F$^+$. Their study allowed the determination of the kinetic energy distributions of the nascent ions, and of their appearance potentials. In turn, this would provide an improved means of identification of the molecular dissociative channels. Even though their partial ionization cross sections are not always in agreement with the previously measured or calculated ones, their total ionization cross section is in good agreement with the recommended values of Christophorou and Olthoff [18] and with the and the calculations of Torres et al [21].

Peko et al [22] have measured the absolute cross section in CF$_4$ for collision energies between 20 and 200 eV. The reactions investigated dealt with the collision-induced dissociation and dissociative electron transfer reactions for CF$_3^+$ and F$^+$ colliding with CF$_4$, and the electron detachment of F$^-$ colliding with CF$_4$. These authors payed special attention to the production of CF$_2^{2+}$ from the interaction of F$^+$ with CF$_4$, with cross sections in the range 2-6 x10$^{-16}$ cm$^2$, which in turn means another efficient process for the conversion of F$^-$ from F$^+$. Electron detachment, beginning at the electron affinity of F$^-$~3.4 eV, increases rapidly with energy. For F$^-$ impact energies in the range 25-75 eV, a fairly high cross section in the range 12-18 x10$^{-16}$ cm$^2$ is measured, thereby indicating, again, that electron detachment of F$^-$ may be a significant contributor to the population of chemically active fluorine, an important radical in plasma etching processes.

The mobility of CF$_3^+$ in CF$_4$ has been measured by Basurto et al [14], and is shown in Fig. 11. The measured low-field mobility of this ion is 0.96 cm$^2$V$^{-1}$s$^{-1}$, and it was found in good agreement with that measured for the CF$3^-$ ion in CF$_4$ by Dutton et al of 0.99 cm$^2$V$^{-1}$s$^{-1}$ [23]. The mobility curve of
CF$_3^+$ in CF$_4$ shows a well defined maximum for 200<$E/N<$300 Td, then followed by a decrease, due to the predominance of the repulsive part of the interaction potential. The calculated value for the mobility of CF$_3^+$ in CF$_4$ by means of Eq. (5) is 1.11 cm$^2$ V$^{-1}$ s$^{-1}$, which is 15% higher than that measured. A deviation like this is expected, since Langevin's equation was formulated for monoatomic systems at vanishingly low temperatures.

Also shown in Fig. 11 is the mobility of C$^+$ in Ar. The fragment ion abundance described in Fig. 12 below indicates that substantial amounts of C$^+$ are formed over the $E/N$ range 30-200 Td. A comparison of the measured low-field reduced mobility of C$^+$ in Ar ($K_00=3.40\pm0.08$ cm$^2$V$^{-1}$s$^{-1}$) with its calculated value of 3.48 cm$^2$V$^{-1}$s$^{-1}$, shows a surprisingly small difference of only 2.5%.

Figure 12 shows a measurement of the abundance of the secondary ions resulting from the injection of CF$_3^+$ in Ar at pressures between 25 and 100 mTorr. For $E/N<100$ Td, C$^+$ is the predominant ion, followed by smaller amounts of CF$^+$ and Ar$^+$. This situation reverses for $E/N>150$ Td, where the production of Ar$^+$ takes over, and reaches a relative abundance of nearly 70% at $E/N\approx400$ Td.

Also of interest for plasma modelling are the measurements of Basurto et al [14] on the fast reaction between Ar$^+$ and CF$_4$ leading to the formation of substantial amounts of CF$_3^+$, as is shown in Fig. 13, where the share of other resulting fragment ions is comparatively small. A possible mechanism leading to the formation of CF$_3^+$ may be the dissociative charge transfer reaction

$$\text{Ar}^+ + \text{CF}_4 \rightarrow \text{CF}_3^+ + \text{F} + \text{Ar}$$

(6)

The beam study of Fisher et al [24] supports this assumption. These authors determined a cross section of 2x10$^{-14}$ cm$^2$ at Ar$^+$ energies of 0.02 eV that decreases monotonically down to 3x10$^{-15}$ cm$^2$ at 2 eV, and then remains fairly constant up to their measurement limit of 50 eV. Moreover, it was also found that the reaction cross section was essentially equivalent to the total cross section over this range, thereby indicating that it occurred practically with 100% efficiency at all kinetic energies up to 50 eV. In the absence of any published mobility data of Ar$^+$ in CF$_4$, Basurto et al used Eq. (5) to estimate that -order of magnitude- the Ar$^+$ energies in their experiment ranged between 0.02 and 2 eV, thereby confirming that their abundance measurements were due to a reaction operating with an efficiency close to 100%, in agreement with Jarvis et al [25] who found this reaction to proceed...
with 100% efficiency at 300 K. Finally, in coincidence with these latter authors, Basurto et al found no trace of the CF$_4^+$ species, since this is a predissociative state leading to CF$_3^+$ + F.

![Figure 13. Abundance of C$^+$ (closed symbols) and Ar$^+$ (open symbols) resulting from injecting CHF$_2^+$ into Ar as a function of E/N. The ion abundance measurements correspond to Ar pressures of 100 mTorr (circles), 50mTorr (triangles), and 25mTorr (squares) [14].](image)

### 2.3 C$_2$F$_4$

Tetrafluoroethylene, C$_2$F$_4$, is mostly used in the fabrication of semiconductors via plasma processes. C$_2$F$_4$ is formed as a dissociation fragment of c-C$_4$F$_8$ [26]. C$_2$F$_4$ is also attractive for plasma etching since it dissociates readily into the fragments CF$_2$ and CF$_2^+$. In contrast to plasma etching gases such as CF$_4$, C$_2$F$_6$, C$_3$F$_8$, CHF$_3$, and c-C$_4$F$_8$, all of them having a high global warming potential, that of C$_2$F$_4$ is considered to be negligible because of its high reactivity with OH radicals, with a global and yearly averaged atmospheric lifetime of the molecule of 1.9 days [26]. It has also been pointed out that C$_2$F$_4$ cannot play a significant role in the depletion of the ozone layer [27].

The recent review of Rozum et al [28] presents a thorough compilation of data on integral elastic electron scattering cross sections, electron impact ionization cross sections, and momentum transfer cross section over the energy range from 0.01 to 100 eV, including the only experimental data on the total cross sections for C$_2$F$_4$ available in the recent paper of Szmytkowski et al. [29]. The only calculated total ionization cross section from Joshipura [30] is also discussed in this paper. The authors conclude that the data base for C$_2$F$_4$ is far from satisfactory and that considerable effort, both experimental and theoretical, is required for a better modeling of C$_2$F$_4$ plasmas. On the other hand, these authors present a wealth of data regarding the integral elastic scattering and excitation to the first excited state cross sections, momentum transfer cross sections for excitation to other dissociative states, and an estimated dissociative attachment cross section for the CF, CF$_2$, and CF$_3$ radicals. These calculations are believed to be very important for plasma modeling, since comparatively little is known on the influence of radicals in the discharge.

Goyette et al [31] performed a series of measurements on electron transport, ionization, and attachment in C$_2$F$_4$ and its mixtures with Ar. In addition to electron impact ionization, their measured effective ionization coefficients in C$_2$F$_4$-Ar mixtures indicate a contribution from Penning ionization in dilute C$_2$F$_4$-Ar mixtures at E/N values close to the limiting one, where $\alpha = \eta$. The rate constant for
electron attachment to C\textsubscript{2}F\textsubscript{4}, as well as the product of the longitudinal electron diffusion coefficient and the gas number density \(N D_L\) in the mixtures of C\textsubscript{2}F\textsubscript{4} with Ar as functions of \(E/N\) are also reported.

The values of the electron drift velocity in C\textsubscript{2}F\textsubscript{4} from Goyette et al. [31] are shown in Fig. 13 as a function of \(E/N\). The electron drift velocity in the C\textsubscript{2}F\textsubscript{4}-Ar mixtures showed interesting regions of negative differential conductivity, and the values of \(E/N\) at which the drift velocity exhibits a local maximum, \((E/N)_{\text{max}}\), varied linearly with the share of C\textsubscript{2}F\textsubscript{4} in Ar [31].

Measurements of the effective ionization coefficient in C\textsubscript{2}F\textsubscript{4} by Goyette et al. are shown in Fig. 14 as a function of \(E/N\). From these data, the limiting field strength for C\textsubscript{2}F\textsubscript{4} is \(E/N\)\textsubscript{lim}= 130 Td. It was found that C\textsubscript{2}F\textsubscript{4} is only slightly electronegative, and that even its lowest values may be due to a strongly attaching impurity. As a matter of fact, the study of Illenberger et al. [32] revealed a variety of negative ions produced over the electron energy range between 1-15 eV, of which F\textsuperscript{-} was the dominant ion.

Yoshida et al. [33] measured the electron drift velocities, longitudinal diffusion coefficients, and ionization coefficients in C\textsubscript{2}F\textsubscript{4}. Using these data and the results of \textit{ab initio} calculations of the elastic, momentum-transfer, and neutral-excitation cross sections, along with measurements of the partial ionization cross sections, these authors constructed a self-consistent set of electron impact cross sections for C\textsubscript{2}F\textsubscript{4}. Their swarm analysis consists of solutions to Boltzmann’s equation for electrons in C\textsubscript{2}F\textsubscript{4} for \(E/N<500\) Td and direct Monte Carlo simulation of electron transport for 500 Td<\(E/N<2000\) Td. The two-term spherical harmonic solution to Boltzmann’s equation was found to fail for \(E/N>500\) Td. Monte Carlo simulations for high values of \(E/N\) were used instead.

Using the steady-state Townsend (SST) method to measure the ionization coefficients in C\textsubscript{2}F\textsubscript{4}, the values of Yoshida et al. and those of Goyette et al. [31] were found in good agreement in the overlap range. On the other hand, Yoshida et al. were able to extend their measurements up to \(E/N=2\) kTd. They also measured the electron drift velocity with a drift tube of standard design and used the concept of the so called mean arrival time drift velocity to explain the difference between their measurements and those of Goyette et al. [31], who used the pulsed Townsend method (PTM).
appears to be some confusion in defining these velocities since, what is indeed different from these two experiments is the means of detecting the electron swarm, by measuring (a) the flux (SST) or (b) the displacement current (PTM); in both cases, the measured quantity is equally affected by ionization growth or decay, if any. What it does affect a measurement, be it SST or PTM, is the duration of either the electron pulse (SST) or the photoelectron pulse from the cathode (PTM). Then it would have been of much help that Yoshida et al would have stated the duration of their electron pulse in order to compare it with the mean transit time of the electrons. Fig. 4 in their paper shows a large discrepancy between their measurements and their own calculations, reaching up to about 60% difference at \( E/N = 2 \) kTd.

2.4 \( \text{C}_2\text{F}_6 \)

The two reviews of Christophorou and Olthoff on electron interactions in \( \text{C}_2\text{F}_6 \) [2,34] cover the research performed on this gas up to 1999. Recent swarm data have been published [35] on electron drift velocities, longitudinal diffusion, and effective ionization coefficients in \( \text{C}_2\text{F}_6 \) and its mixtures with \( \text{N}_2 \) and \( \text{Ar} \) over a wide range of \( E/N \) from 0.1 to 500 Td.

The recent electron drift velocities in \( \text{C}_2\text{F}_6 \) [35] are displayed in Fig. 16 as a function of \( E/N \), together with those for \( \text{C}_2\text{F}_6\text{-Ar} \). The measurements of Hunter \textit{et al} [36], not shown in this figure for the sake of clarity, were found in very good agreement in the overlap range 6–400 Td. It interesting to note that both research groups used the same pulsed Townsend method. Strong disagreement was found with previous data of Naidu and Prasad [37] who used a drift tube, and with the calculations of Hayashi and Niwa [38] for \( E/N > 130 \) Td. Thus, the electron drift velocity values of Hunter \textit{et al} have been confirmed, while the range of measurement has been extended up to \( E/N = 500 \) Td.

It is worth noting that the \( \text{C}_2\text{F}_6\text{-Ar} \) drift velocity curves bear very pronounced regions of negative differential conductivity (NDC) [39] at the lower \( E/N \) end. The electron drift velocity for the \( \text{C}_2\text{F}_6\text{-N}_2 \) mixtures is shown in Fig. 17 for \( \text{C}_2\text{F}_6 \) concentrations between 0.5% and 20%. Again, a comparison with the data of Hunter \textit{et al} [36] show an excellent agreement with our values for \( E/N > 20 \) Td for the
mixtures containing 0.5%, 2% and 10% C2F6. It is interesting to note that even though neither C2F6 nor N2 bear a Ramsauer–Townsend minimum in their momentum transfer cross-sections, the electron drift velocity curves do display a NDC region. This effect has been explained in detail thoroughly before [40,41].

The density-normalized diffusion coefficients for electrons \( N D_L \) for C2F6 and some values for the C2F6–Ar mixtures studied in Ref. [35] are shown plotted in Fig. 18. Other values of \( N D_L \) for C2F6-Ar and C2F6-N2 are given in this paper. The \( N D_L \) curve for pure C2F6 shows a deep minimum between \( E/N = 40-50 \) Td, which is due to the same process responsible for the NDC region in the electron drift velocity curve. For the mixtures, we observe a consistent shift of this minimum towards lower \( E/N \) values as the C2F6 content in the mixtures decreases in the C2F6–Ar mixtures. Furthermore, the 1% and 5% C2F6 mixtures display two well-defined maxima, which are not apparent in the 10% mixture. A similar behaviour is observed for the C2F6-N2 mixture, although in this case the three sets of curves merge into a single one for \( E/N > 50 \) Td. No other \( N D_L \) values for these mixtures are known to be available in the literature.

\[
\begin{array}{c|c|c|c|c}
\% C2F6 & 1 & 5 & 10 & 100 \\
\hline
E/N (Td) & 0.1 & 1 & 10 & 100 \\
NDL \left(10^{22} \text{cm}^{-1}\text{s}^{-1}\right) & 1 & 5 & 10 & 100 \\
\end{array}
\]

The recent measurement of the effective ionization coefficient \( (\alpha - \eta)/N \) in pure C2F6 [35] is shown in Fig. 19, together with that for the C2F6-Ar mixtures. Previous work on the measurement of \( (\alpha - \eta)/N \) for C2F6 has been revised in Ref. [34] where a curve for this parameter was suggested. Strong disagreement with these suggested values those of Ref. [35] has been found. In the same Ref. [35], more measurements of \( (\alpha - \eta)/N \) for the mixtures of C2F6 with Ar and N2 are also given.

The shape of the \( (\alpha - \eta)/N \) curves indicates that attachment proceeds dissociatively. In this respect, previous electron beam studies on the formation of negative ions by electron impact in C2F6 state that the two main fragment anions are formed from a negative ion resonance in the range 2–7 eV. These processes are [42,43]

\[
\begin{align*}
\text{C}_2\text{F}_6^- & \rightarrow \text{F}^- + \text{C}_2\text{F}_5 \\
\rightarrow & \text{CF}_5^- + \text{CF}_3
\end{align*}
\]
with relative yields of 10:3.5, respectively, and peaking at about 4 eV.

2.5 \textit{c-C}_4\textit{F}_8

Octafluorocyclobutane, \textit{c-C}_4\textit{F}_8, is used in plasma processing because of its selectivity to SiO$_2$, and also due to its relatively low global warming potential in comparison to that of SF$_6$. Interesting work has been done since the recent review of Christophorou and Olthoff [44]. Font et al [45] have developed a numerical model for a \textit{c-C}_4\textit{F}_8 discharge. For such purpose, a set of cross sections was assembled for electron collisions with \textit{c-C}_4\textit{F}_8 based on a combination of \textit{ab initio} calculations, beam measurements, and swarm coefficients based on electron transport. A full set of collision cross sections was proposed for the electron interaction processes of momentum transfer, vibrational excitation, attachment leading to the formation of \textit{C}_4\textit{F}_8\textsuperscript{-} and \textit{F}_-, dissociation and ionization leading to \textit{C}_2\textit{F}_4\textsuperscript{+}, \textit{C}_3\textit{F}_5\textsuperscript{+}, \textit{CF}_3\textsuperscript{+}, and \textit{CF}_2\textsuperscript{+}. In addition, Font et al were able to compute the rate coefficients for electron collisions with \textit{c-C}_4\textit{F}_8, \textit{C}_2\textit{F}_4, \textit{CF}_3, \textit{CF}_2, and \textit{CF} and fit them to the Arrhenius form given by Eq. (3).

Attachment processes are particularly important, since these are sometimes reflected in the measured electron drift velocities, shown in Fig. 20 [46]. At energies between 0.01 eV to about 2 eV, \textit{C}_4\textit{F}_8\textsuperscript{-} is formed; and above about 2 eV, dissociative attachment predominate, leading to the formation of \textit{F}_-. The lifetime of \textit{C}_4\textit{F}_8\textsuperscript{-} against autodetachment ranges between 10-500 $\mu$s [44], where the lifetime of the complex may depend upon the kinetic energy of the attaching electron. In this context, the measured drift velocity of de Urquijo and Basurto [46] was found to be pressure dependent over the range 300$<E/N<$600 Td. This is shown in Fig. 20. Moreover, for fixed $E/N$, the drift velocity decreases with an increase in pressure. The measurements of Wen and Wetzer [47], who used the same pulsed Townsend method, were found to be only slightly lower than those of Ref. [46]. The calculations of Font et al [45] are in good agreement with the measurements reported in Ref. [46] at 0.6 torr. The experiment in Ref. [46] permitted the measurement of the electron drift velocity over the low $E/N$ region from 12-43 Td. No other measurements or calculations are available for comparison.

The measurements of the effective ionization coefficient from Ref. [45], shown here in Fig. 21, also report a pressure dependent effect, similar to that of their measured drift velocities. Thus, if excited \textit{C}_4\textit{F}_8\textsuperscript{−} autodetaches during the electron transit, then the decrease of $(\alpha−\eta)/N$ with increasing pressure suggests that the negative ion would stabilize by collision at higher pressures, whereas at lower pressures a fraction of the ions would autodetach before stabilization and therefore contribute to current growth, thereby increasing the apparent value of $(\alpha−\eta)/N$. The calculations of Font et al [45] are in very good agreement with the measurements of Ref. [46]. It is clear from Fig. 21 that the steady-state measurements of Naidu et al [48] disagree strongly from those derived from time-resolved measurements.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure20.png}
\caption{The drift velocity of electrons in \textit{c-C}_4\textit{F}_8 [46].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure21.png}
\caption{The density-normalized effective ionization coefficient in \textit{c-C}_4\textit{F}_8 [46].}
\end{figure}
Recently, Yamaji and Nakamura [49] have determined a cross section set for c-C4F8 by resorting to their previously measured electron drift velocities, longitudinal diffusion coefficients and effective ionization coefficients in 0.468% and 4.910% c-C4F8/Ar. Some of the existing cross sections were modified, especially those of vibrational excitation and elastic momentum transfer. Their measured drift velocity and longitudinal diffusion coefficients in pure c-C4F8 were used to determine the adequate elastic momentum transfer cross section that fitted the data satisfactorily. Their calculated electron transport coefficients were derived using the Monte Carlo simulation method.

3. Conclusions
An overview of recent research on the electron and ion interaction with the fluorinated gases CHF3, CF4, C2F4, C2F6 and c-C4F8, and their mixtures with Ar and N2. It appears that much progress has been gained in some of the swarm and beam measurements, and that many of the relevant cross sections have been revised and attempts have been made to derive self-consistent sets of data. In spite of these efforts, there are still many other issues pending as regards the reproducibility of the measured swarm coefficients in gas mixtures of these gases with Ar or N2, for example, from particular cross section sets. Thus, it would be desirable that new cross section sets be also tested for these gaseous mixtures in order to have a more reliable and versatile set of cross sections.

As regards ion interactions, much more is still left to be done in the field of the measurement of ionic mobilities and reaction coefficients. More reliable data on positive and negative ion transport is needed, and also on ion-molecule reactions, either from beam experiments or from swarm methods, and this in turn will stimulate the calculation of the relevant cross sections. For instance, the importance of the ion-molecule reaction studies of Peko et al [13,22] should be stressed, since it deals with the interaction of positive and negative ions with CHF3 and CF4 in order to assess the importance of F ions and radicals in plasma etching processes. Additionally, electron detachment from negative ions is an important issue that needs attention, mostly from the point of view of swarm experiments. Thus, 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 are strongly needed. Besides, the search for gases with lesser global warming potentials is remains a serious challenge.

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