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Mass-resolved ion energy measurements at both electrodes of a 13.56 MHz plasma in CF₄

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The ion energy distributions (IEDs) at the electrodes in a capacitively coupled 13.56 MHz plasma in CF₄ have been measured mass resolved with a Balzers quadrupole in combination with a home-built energy analyzer. Mass-resolved determination offers the possibility to compare the IED of different ions achieved in the same sheath. The IEDs have been determined at both the largest and the smallest electrode. Apart from the IEDs of the CF₄ species, the IEDs of ionic species in plasmas in argon and nitrogen also were determined. Apart from the CF₄ species, CF₃⁺, CF₂⁺, CF⁺, and F⁺, CHF₃⁺ ions also are present in the CF₄ plasma due to residual water in the reactor. The CHF₃⁺ ions are not produced in the sheath and because we do not detect elastically scattered ions, the IEDs of these ions show the typical bimodal distribution for rf plasmas which corresponds to an IED of ions which have not collided in the sheath. From these IEDs we can obtain the sheath characteristics, such as the averaged sheath potential. From the IEDs of CF₄⁺ ions one can conclude that, in the sheath of the CF₄ plasma, a large number of chemical reactions takes place between the CF₄⁺ ions and the neutrals. © 1996 American Institute of Physics. [S0021-8979(96)00712-8]

I. INTRODUCTION

Radio-frequency (rf) plasmas are commonly used in industry for surface modification processes, e.g., for etching and deposition of semiconductor surfaces in the manufacturing of integrated circuits. These processes are caused by species which are produced in the low-pressure rf plasma and which are transported across the sheath, toward the substrate on the electrode surface. The bombardment of the surface by energetic ions is essential to achieve anisotropic etching results. The etching process usually takes place at the smallest powered electrode.

An important parameter in the process is the ion energy distribution (IED) at the electrode. The IED depends on parameters such as the ion density profile in the sheath, the mean kinetic electron energy, the cross sections for collisions taking place in the sheath, and thickness and voltage of the sheath. If in a low-pressure rf plasma the sheath may be regarded as collisionless the IED is saddle structured due to the time modulation of the sheath voltage drop. This has been shown experimentally as well as theoretically. The splitting of the saddle structure decreases with increasing excitation frequency of the plasma.

In the collisional case, where the mean free path of the ions is of the same order of magnitude as the sheath thickness, collisions in the sheath have a large influence on the IED. Charge exchange collisions between ions and neutrals cause extra peak structures in the IED at energies lower than the energy of the collisionless saddle structure. This also has been demonstrated both experimentally and theoretically. Elastic scattering of ions by neutrals does not cause any extra peak structures in the IED but results in a broadening.

In this article measurements of mass-resolved IEDs in a 13.56 MHz plasma in CF₄ are presented. The studied ion species are CF₃⁺, CF₂⁺, CF⁺, F⁺, and CHF₃⁺. The unexpected presence of CHF₃⁺ is attributed to a very small amount of residual water vapor in the reactor. The advantage of the presence of the CHF₃⁺ ions is that these ions hardly scatter inelastically. The influence of elastic scattering is known, so the IEDs of CHF₃⁺ give information on the sheath structure. From the IEDs of CF₃⁺, CF₂⁺, CF⁺, and F⁺, we may conclude in a first-order approach which ion–molecule reactions are important in the sheath.

II. EXPERIMENT

The experimental setup has been described elsewhere. The rf plasma is confined in a cylindrical cavity with an electrode area ratio of 3. The driven electrode is ac coupled to the power supply (see Fig. 1). The cavity has been used to measure the electron and negative ion densities by microwave techniques, and is created by extending the largest electrode around the plasma towards the smallest. Köhler et al. showed that the highest sheath voltage drop appears in front of the smallest electrode, irrespective whether this is the grounded or the driven one.

Because of practical reasons it is difficult to determine the IED at the driven electrode. The mass and energy selector would have to be electrically coupled to the time-dependent electrode potential. There would be severe interference between the rf fields of the plasma and the quadrupole. Therefore, we have measured the IEDs at the grounded electrode and have built two cavities with identical electrode geometries. One has a large and the other a small grounded electrode (see Fig. 2). For historical reasons the situation with the largest electrode grounded is called normal cavity. The other with the smallest electrode grounded is called inverse cavity. Since the potential difference over the electrodes is the same for both configurations when powered...
by the same excitation voltage $V_{rf}$, the plasma is identical in the normal and the inverse cavity.

In an open configuration the plasma potential is constant due to the very large electrode surface ratio. Since in our geometry the surface ratio is only 3, the plasma potential is $V_{rf}$ modulated. This effect is larger for the inverse cavity. A quadrupole mass spectrometer (Balzers QMG311) in combination with a cylindrical mirror energy analyzer is implemented in the grounded electrode. It is situated in a differentially pumped chamber (see Fig. 1). The pressure in this chamber is kept lower than $10^{-6}$ Torr. In the center of the grounded electrode a small molybdenum plate (diameter 2.5 cm) is mounted with an orifice of 40 $\mu$m. Molybdenum is used so no charging of the plate occurs. The pressure in the quadrupole chamber is sufficiently low in order to generate that no modification of the IED take place when ions pass the orifice. Behind the orifice the ions are focused by an ion lens into a beam parallel to the quadrupole axis. The voltages, geometry, and the position of the ion optics have been designed using the computer program SIMION. After mass selection, the ions are energy selected in the cylindrical mirror analyzer. The analyzer has an exit slit of 1 mm, which results in an energy resolution of 1 eV. The resolution of the quadrupole is $0.1 \mu$. The selected ions are detected by a channeltron. After amplification the pulses are counted by a counter card in an IBM-compatible PC.

Both the resolution and the transmission of the quadrupole and energy selector depend on the kinetic energy of the ions. In order to obtain a constant resolution and transmission during a measurement, ions are accelerated or decelerated by the ion lens before entering the quadrupole, so all ions which are detected have the same kinetic energy when passing the mass and energy selectors. Therefore, the reference (=axis) potential of the total system, including the ion lens, is changed during an energy scan (see Fig. 3), whereas the local electric fields in the quadrupole and energy selector remain the same. The kinetic energy of the ions when passing the analyzing system $E_{\text{pass}}$ can be chosen between 5 and 30 eV.

As a consequence of the geometry and the voltage of the ion lens it is only possible to detect ions which hit the electrode surface with a velocity directed nearly perpendicularly to the surface (within an angle of 4° with the normal). It is known that for low-pressure plasmas in which the ion mean free path is larger than the sheath thickness, the sheath is nearly collisionless. Because the ions are accelerated perpendicularly to the electrode, the angular distribution is narrow. In this case all the ions that pass the orifice will be within the acceptance angle of 4° and the measured IED corresponds to the real IED.

For the high-pressure case, where the mean free path of the ions is less than the sheath thickness, collisions in the sheath become important. This is the case for pressures higher than $5–10$ mTorr. Due to the collisions the angular distribution becomes broader. Ions that do not pass the orifice within the 4° acceptance angle will not be detected and the measured IED may not correspond to the real IED. This
effect has to be taken into account for the interpretation of the IEDs.

III. THE EFFECT OF COLLISIONS

Charge exchange collisions between a fast ion and a thermal neutral generates a thermal ion and a fast neutral. The newly created ions start with thermal energy \( \approx 0 \) and are accelerated perpendicularly toward the electrode. Due to this effect the ions, which reach the electrode, always hit the electrode surface perpendicularly. Consequently, all these ions pass the ion lens and are analyzed by the spectrometer. Due to the fact that the newly created ions have zero starting energy, these ions generate IED features at lower energies than the primary saddle structure. In an argon plasma, symmetric \( ^{-} \) resonant \( ^{-} \) charge exchange takes place between an \( \text{Ar}^{+} \) ion and an \( \text{Ar} \) neutral,

\[
\text{Ar}^{+} + \text{Ar} \rightarrow \text{Ar} + \text{Ar}^{+}. \tag{1}
\]

The IED of \( \text{Ar}^{+} \) ions measured at the largest electrode in a 40 mTorr plasma in argon is shown in Fig. 4. The peaks of the primary saddle structure are at 42 and 54 eV. The other features are induced by charge exchange. Symmetric charge exchange for atomic ions has a large cross section \( \approx 10^{-16} \) cm\(^2\) on the order of \( \approx 10^{-16} \) cm\(^2\).

The cross section of asymmetric charge exchange between two nonidentical species,

\[
A^{+} + B \rightarrow A + B^{+} \tag{2}
\]

is of the order \( 10^{-17} \) cm\(^2\).

Also elastic collisions occur frequently in the sheath. The cross section of these collisions is in the order of \( 5-40\times 10^{-16} \) cm\(^2\).\(^21\) In this case the energy of the ion is distributed among the colliding particles. The energy and the direction of the ion will change. Consequently, the ion angular distribution becomes broader\(^2\) and most of the ions that are scattered do not hit the electrode within the 4° acceptance angle of the spectrometer.

There is always some residual water vapor in the reactor which is responsible for the formation of hydrogen-containing ions such as \( \text{ArH}^{+} \).\(^2\) Due to the fact they have no unpaired electron, the \( \text{ArH}^{+} \) ions are quite stable. Because of the low density of the \( \text{H}_2\text{O} \) molecules, the hydrogen-containing ions hardly have any influence on the space charge in the plasma and the sheath. \( \text{ArH}^{+} \) ions can collide in the sheath with an argon atom and then dissociate or scatter elastically. In the first case, the \( \text{ArH}^{+} \) ion is destroyed and cannot be detected anymore. In the latter case, the direction of the ions is changed and the angular distribution at which the scattered ions hit the electrode is broadened.

Once again, for the interpretation of the measured IEDs one has to take into account that only those ions are detected which strike the electrode within the 4° acceptance angle of the spectrometer. In the case of elastic scattering, we distinguish three groups of \( \text{ArH}^{+} \) ions that fulfill this condition. The first one consists of ions which do not collide in the sheath. The electric field in the sheath is perpendicular to the electrode, so the ions are accelerated perpendicularly to the electrode. These ions are responsible for the primary saddle structure. The second group consists of ions which lose nearly all their energy during their last collision before they hit the electrode. They behave identically to ions formed by charge exchange collisions and also cause low-energy features in the IEDs. In the case of \( \text{ArH}^{+} \) ions scattered elastically by argon atoms, only head-on collisions satisfy this condition due to the small mass difference between the two species. The energy of the ions in this case is less than the energy related to the saddle structure. The third group consists of ions that, after two or more collisions, are directed perpendicularly to the electrode by coincidence. The energy of the ions in this case is randomly distributed and no peaks are present. The probability that ions end up in the last two

![Fig. 4](image4.png)

**FIG. 4.** The IED of \( \text{Ar}^{+} \) ions incident on the grounded electrode in the normal cavity. The pressure is 40 mTorr and the power injected in the plasma is 40 W. The peaks of the primary saddle structure are at 42 and 54 eV.

![Fig. 5](image5.png)

**FIG. 5.** (a) Measurement and (b) simulation of the IED of \( \text{ArH}^{+} \) ions incident on the grounded electrode in an argon plasma in the normal cavity. The pressure is 40 mTorr and the rf power injected in the plasma is 50 W. The solid line in (b) represents the full angular distribution, whereas the dashed line represents only the detectable 2°×4° cone.
groups is small and we may conclude that the measured IEDs of ArH$^+$ ions mainly consist of ions which have not collided in the sheath. The measured ArH$^+$ IEDs show a well-pronounced saddle and may therefore be interpreted as being collisionless and therefore serve as a very illustrative "probe" of the determination of the energy range of the primary saddle structure.\textsuperscript{7,8}

The effect of the collisions in the sheath has also been demonstrated by simulations. The local and time-dependent electric field in the sheath used in the simulations to calculate the ion trajectories and the ion energy is calculated from solutions of particle-in-cell (PIC) simulations\textsuperscript{24,25} and is proved to be close to selfconsistency.\textsuperscript{8} Trajectories of 150 000 ions entering the sheath at 200 different phases were calculated. The thickness of the space-charge region is varying in time. The maximum sheath thickness is 1.56 mm and the mean free path is 0.8 mm. The collisions are randomly chosen and are treated as hard sphere elastic scattering where the collision angle in the mass centered system is randomly distributed and the total energy and momentum are conserved.

The measured IED of ArH$^+$ ions at the largest electrode in a 40 mTorr plasma in argon is shown in Fig. 5(a). The rf power is 50 W. The IED clearly shows the saddle structure whereas small features are noticed at lower energy. These are generated by the elastically scattered ions which bombard the electrode within an angle of 4°. The agreement with the measurement is obvious.

IV. RESULTS AND DISCUSSION

A. Introduction

Janes\textsuperscript{27} and others already pointed out that the ion dynamics in the sheath of a CF$_4$ plasma is far more complex than in the case of Ar or N$_2$. The number of ion species is larger, as is the number of different ion–molecule reactions. This is also a consequence of the abundance of radical species.

In a CF$_4$ plasma the following positive ions are present: CF$_3^+$, CF$_2^+$, CF$^+$, F$^+$, C$^+$, and at higher pressures also C$_2$F$_5^+$ ions are detected. The presence of CHF$_3$ molecules in the plasma has been shown by Haverlag\textsuperscript{16} using IR techniques. As a result, CHF$_2^+$ ions are created in the plasma. Negative ions are also present. These ions, mainly F$^-$, are trapped in the glow. The density and the temperature of these ions determine the Bohm velocity of the positive ions entering the sheath, but they have no further influence on the dynamics of the positive ions in the sheath. The Bohm velocity in electronegative gases is smaller than in a plasma without negative ions.\textsuperscript{8} The consequence of this is that the positive ion density decreases more rapidly toward the electrode than in a plasma without negative ions. Subsequently the sheath thickness is larger than in a plasma without negative ions.

Experimentally determined IEDs of CF$_3^+$, CF$_2^+$, CF$^+$, F$^+$, and CHF$_2^+$ ions are presented both for the normal and the inverse cavity case. These results show large differences be-
between the IEDs of the different species. From these results conclusions about the sheath behavior and the ion kinetics in the sheath are derived. It is shown that ions are produced in the sheath. Because of the low electron density in the sheath, these new ions must be formed by ion–molecule reactions.

B. IEDs at the largest electrode

In Figs. 6, 7, 8, 9, and 10, the measured IEDs of CF$_3$+, CF$_2$+, CF+, F+, and CHF$_2$+ ions are presented for several plasma conditions in the normal cavity case. The power indicated in the figures means the power injected in the plasma. During these measurements $E_{\text{pass}}$ was 20 eV.

The behavior of CHF$_2$+ ions is quite similar to ArH$^+$ ions in an argon plasma: The most probable reactions of CHF$_2$+ ions are elastic scattering or an ion–molecule reaction with a CF$_4$ neutral. In the latter case the ion will be destroyed and cannot contribute to the IED any longer. Once again we remark that the measured spectrum only includes the ions which have hit the electrode surface within an angle of 4°. Because of the mass difference between the CHF$_2$+ ion and the CF$_4$ neutral, the ion will never lose all of its energy when it collides elastically. This means that the measured IED will mainly represent ions which did not collide in the sheath. No elastic scattering features as are occurring in the case of ArH$^+$ are to be expected.

At high pressures the saddle structure is still well recognizable, although the structure is less pronounced than at low pressures (see Fig. 10). At high pressures most of the CHF$_2$+ ions are scattered and are not detected. The IEDs of CHF$_2$+ ions determined in 5 W plasmas for several pressures do not show a saddle structure but one single peak. This is caused by the fact that at such low power densities the plasma potential is roughly equal to the floating potential. Consequently, the modulation depth of the voltage across the sheath is small: 30%–50%. At higher powers the modulation depth can be as large as 90%–100%; then the saddle structure appears again.

The density of the CF$_3$+ ions is expected to be the highest of all the observed ions. When we analyze the IED of the CF$_3$+ ions (Fig. 6), we can recognize the primary saddle structure in the low-pressure case (~20 and 40 mTorr), whereas this structure vanishes at higher pressures (~160 mTorr). In the low-pressure case the IEDs show some small features at energies lower than the saddle structure. These features cannot be generated by elastic scattering because the elastically scattered CF$_3$+ ions do not contribute to the measured IED; therefore, the features must be generated by CF$_3$+ ions which are created in the sheath. Furthermore, for the newly created ions to arrive at the electrode within the acceptance angle of 4° it is required that they have a starting energy close to 0 eV.

When we consider the IED of CF$_2$+ ions in Fig. 7, we can only recognize the primary saddle structure at 20 mTorr. At higher pressures this structure vanishes. This means that the CF$_2$+ ions which start from the glow are either scattered elastically or destroyed by chemical reactions. Apparently, in contrast to CF$_3$+ ions, the probability for CF$_2$+ ions to cross the sheath without any collision is very small. The cross section for elastic scattering of CF$_3$+ ions and CF$_2$+ ions with CF$_4$ neutrals will be of the same order. This cannot explain

![Figure 7](http://jap.aip.org/abstract/jap/79/156801/1)
the different behavior. This means that the CF$_2^+$ ions have a relatively large chance to be destroyed in the sheath by ion–molecule reactions. This is in agreement with the fact that they have one unpaired electron, while ions such as CF$_3^+$, CF$_4^+$, and CHF$_2^+$ only have paired electrons. Therefore, the CF$_2^+$ ions are more reactive. The feature in the IEDs of the CF$_2^+$ ions at energies smaller than the primary saddle must be generated by production of CF$_2^+$ ions in the sheath. The pro-

FIG. 8. The IED of CF$_2^+$ ions incident on the grounded electrode in the normal cavity for several pressure and rf power conditions: (a) 20 mTorr; (b) 40 mTorr; (c) 80 mTorr; and (d) 160 mTorr.

FIG. 9. The IED of F$^+$ ions incident on the grounded electrode in the normal cavity for several pressure and rf power conditions: (a) 20 mTorr; (b) 40 mTorr; (c) 80 mTorr; and (d) 160 mTorr.
duction rate is relatively large in order to compensate the rather high loss rate, which is responsible for the vanishing of the primary saddle.

The IEDs of CF$_3^+$ ions (see Fig. 8) are similar to those of CF$_3^-$: The primary saddle structure can be recognized up to about 80 mTorr. The strong increase of low-energy ions at higher pressures can again only be explained by production of forwardly directed ions in the sheath. The smaller number of features is due to the smaller mass of the CF$_3^+$ ions with respect to the mass of the CF$_3^-$ ions, which results in a shorter sheath transit time. The fact that, except for the primary saddle, there are no peak structures may also be the consequence of a possible excess energy after the formation of CF$_3^-$ ions.

The primary saddle structure in the IEDs of F$^+$ ions (see Fig. 9) is recognizable at low pressures (20 and 40 mTorr), while also one very sharp peak can be distinguished up to 160 mTorr. This peak may be produced by ions created in the sheath by ion–molecule reactions or resonant charge exchange reactions. From investigations of Haverlag it is known that the density of F neutrals is about five times as high as the CF$_3$ neutral density. One should take into account that the F$^+$ ions cannot disappear by dissociation reactions as CF$_n^+$ ions can.

Several ion–molecule reactions can appear in the CF$_3$ sheath. From the measured IEDs we may conclude what reactions are dominant. This is discussed in Sec. IV E.

C. IEDs at the smallest electrode

In Figs. 11–13, the IEDs of CF$_3^+$, CF$_2^+$, and CF$^+$ ions are presented as measured in the inverse cavity case in a CF$_4$ plasma of 5, 14.5, and 72 mTorr, respectively. During these measurements $E_{\text{pass}}$ was 33 eV. This is higher than the $E_{\text{pass}}$ used in the normal cavity in order to increase the transmission of the spectrometer.

The saddle structure in the IED of CF$_3^+$ ions is only recognizable at low pressures, up to about 15 mTorr. At higher pressures the saddle vanishes due to the small probability of the ions to cross the sheath without any collision.

The IEDs of CF$_3^+$ ions do not show any specific features and they look similar for the whole pressure range. The saddle structure has already vanished at pressures as low as 5 mTorr, which corresponds to the results obtained in the normal cavity: The loss rate of CF$_2^+$ in the sheath is high compared to other ion species. The average energy of the whole

![Figure 10](image1.png)

**FIG. 10.** The IED of CHF$_2^+$ ions incident on the grounded electrode in the normal cavity for several pressure and rf power conditions: (a) 20 mTorr; (b) 40 mTorr; (c) 80 mTorr; and (d) 160 mTorr.

![Figure 11](image2.png)

**FIG. 11.** The IED of CF$_3^+$ (solid line), CF$_2^+$ (dashed line), and CF$^+$ ions (dotted line) incident on the grounded electrode in the inverse cavity. The pressure is 5 mTorr and the rf power injected in the plasma is 85 W.
IED decreases with increasing pressure, which is due to the increasing number of collisions in the sheath.

The IEDs of CF$_r^+$ ions also look similar for the whole pressure range. The maximum always occurs at about 100 eV. Just like in the CF$_2$ case, the saddle structure has already vanished at 5 mTorr. Hardly any ion can reach the electrode without a collision, and the loss rate in the sheath is higher than the production rate.

In conclusion, the IEDs measured in the inverse cavity show the same features as those measured in the normal cavity; however, the effects induced by collisions in the sheath are enhanced because of the larger sheath thickness.

D. Remarks

When we compare the IED of the normal and of the inverse cavity, we can distinguish a difference in the intensity of the measured distributions. This is partly due to different adjustments of the spectrometer. The main reason, however, of the intensity difference is the number of collisions in the sheath. In the inverse cavity the sheath is thicker due to a higher sheath voltage. Consequently the number of collisions in the sheath increases and the number of ions which do not collide in the sheath (and hit the electrode within the acceptance angle of 4°) decreases.

From the IEDs in which the primary saddle structure can be recognized, the splitting energy difference $\Delta E$ can be derived. The splitting energy difference appears to be inversely proportional to $\sqrt{m_i}$ as shown in Fig. 14 for a plasma in air. This empirical relation is also valid in pure CF$_4$, Ar, and N$_2$ plasmas.

In Fig. 15 the splitting energy difference $\Delta E$ of the saddle structure of the IED of CHF$_2^+$ ions is given as function of the averaged energy of the primary saddle structure $E_{\text{sad}}$. $\Delta E$ increases more than linearly with $E_{\text{sad}}$. Based on theoretical investigations, from the increasing ratio between $\Delta E$ and $E_{\text{sad}}$ we may conclude that the transit time of the ions decreases with increasing $E_{\text{sad}}$ and, subsequently, that the sheath becomes thinner with increasing $E_{\text{sad}}$. To generate a thinner sheath at higher sheath voltages, the ion density at the sheath–presheath edge has to increase with increasing $E_{\text{sad}}$.

When we consider $\Delta E$ in CF$_4$ plasmas for different pressure conditions at a certain $E_{\text{sad}}$, we see that $\Delta E$ is the largest at the lowest pressures. From this we may conclude that the sheath thickness is the smallest at the lowest pressures: The splitting is larger when the transit time is smaller. The smaller sheath thickness at lower pressures is a consequence of a higher density of the positive ions. Investigations of Haverlag confirm the decrease of the density of the positive ions with increasing pressure. This behavior is in contrast with an argon plasma, where $\Delta E$ increases with the pressure.
at a certain $E_{\text{sad}}$. The ion density has to increase with pressure,\(^8\) which is also observed experimentally by Haverlag.\(^{16}\)

From the measurements the relation between the maximum sheath voltage ($V_{\text{rf}}+V_{\text{dc}}$) and $E_{\text{sad}}$ can be determined. In Fig. 16 this relation is shown for $\text{CE}_2^+$ ions ($\text{CF}_4$ plasma, pressures of 5 and 20 mTorr). In the case where the sheath voltage modulation is purely sinusoidal, so purely capacitive, $E_{\text{sad}}$ has to equal $\frac{1}{2}\varepsilon(V_{\text{rf}}+V_{\text{dc}})$. The measurements show that $E_{\text{sad}}$ is less than $\frac{1}{2}\varepsilon(V_{\text{rf}}+V_{\text{dc}})$, so we may conclude that the sheath voltage modulation is not sinusoidal at high rf voltages. The deviation from a sinusoidal sheath voltage modulation is larger for low-pressure plasmas in $\text{CF}_4$ where the ion density is higher and the sheath thickness smaller. This conclusion is in agreement with the sheath in argon plasmas where the ion density is the largest for high-pressure plasmas. Consequently, the deviation from a sinusoidal voltage modulation is the largest.\(^8\)

### E. Sheath kinetics

To explain the IEDs of the ion species which are present in the sheath of a $\text{CF}_4$ plasma, ion–molecule reactions have to be taken into account. The most important reactions are discussed in this subsection.

Exact data on cross sections of reactions in which $\text{CF}_4^+$ ion species are involved are not available. Therefore, we use the reaction enthalpy as a probe for the reaction rate; as a first estimation in terms of tendencies toward equilibrium, a consideration of the enthalpies can be very useful.

Ions may be produced by ionization of neutrals which collide with electrons or with energetic ions. In the sheath, the contribution of electron impact may be neglected. This is supported by measurements of the IED of the $\text{N}^+$ and $\text{N}_2^+$ ions in a $\text{N}_2$ plasma. Ionization of N and $\text{N}_2$ species by electron impact would generate characteristic features in the IEDs of the $\text{N}^+$ and $\text{N}_2^+$ ions since these newly formed ions start with thermal energy and are accelerated to the electrode surface. From the absence of these features (see Fig. 17) we may conclude that the contribution of electron impact to the newly formed ions in the sheath may be neglected. We extend this conclusion to the $\text{CF}_4$ plasmas, even though the kinetics are more complex than in the $\text{N}_2$ plasma.

A neutral atom or molecule can only be ionized by an ion if the energy is a few keV. These energies cannot be obtained in the sheath of a rf plasma. Therefore, ionization of neutrals by highly energetic ions cannot occur in the sheath.

The ions which are present in the plasma can collide with a $\text{CF}_4$ molecule and a fluorine atom transfer reaction may take place (disproportionation reactions). The following reactions can be distinguished. For an endothermic reaction the enthalpy difference\(^{28,29}\) is added on the left-hand side. For an exothermic reaction the reaction enthalpy\(^{28,29}\) is added on the right-hand side.

\[
\begin{align*}
\text{CF}_3^+ + \text{CF}_4 & \rightarrow \text{CF}_4^+ + \text{CF}_3, \\
\text{CF}_2^+ + \text{CF}_4 & \rightarrow \text{CF}_4^+ + \text{CF}_3 + 0.52 \text{ eV}, \\
\text{CF}^+ + \text{CF}_4 & \rightarrow \text{CF}_4^+ + \text{CF}_3 + 0.30 \text{ eV}, \\
\text{C}^+ + \text{CF}_4 & \rightarrow \text{CF}_4^+ + \text{CF} + 1.78 \text{ eV}, \\
\text{F}^+ + \text{CF}_4 & \rightarrow \text{CF}_4^+ + \text{F}_2 + 4.29 \text{ eV}.
\end{align*}
\]

In reaction (3) a $\text{CF}_4^+$ ion is formed. This ion, however, directly decomposes into $\text{CF}_4^+$ and $\text{F}$.\(^{28}\) The exothermic reactions sometimes occur spontaneously. The endothermic reactions may occur when the energy difference is supplied by the accelerated ion in the sheath.

Also charge exchange reactions may occur in the sheath. The cross sections of charge exchange reactions between two identical species (symmetric charge exchange) are quite large ($\approx 10^{-18} \text{ m}^2$). The cross sections of charge exchange reactions between not-identical species (asymmetric charge
exchange) is in general smaller than for symmetric charge exchange ($\approx 10^{-21}$ m$^3$). This is mainly the consequence of the energy difference $\delta E$ between the ionization levels of the involved ions. In the case of resonant (i.e., $\delta E=0$) asymmetric charge exchange the cross section can be of the same order of magnitude as for symmetric charge exchange reactions.

We consider the following symmetric (resonant) charge exchange reactions:

$$\begin{align*}
\text{CF}_3^+ + \text{CF}_3 & \rightarrow \text{CF}_3 + \text{CF}_3^+ , \\
\text{CF}_2^+ + \text{CF}_2 & \rightarrow \text{CF}_2 + \text{CF}_2^+ , \\
\text{CF}^+ + \text{CF} & \rightarrow \text{CF} + \text{CF}^+ , \\
\text{F}^+ + \text{F} & \rightarrow \text{F} + \text{F}^+ .
\end{align*}$$

Asymmetric charge exchange reactions will mainly take place between an ion and a CF$_4$ neutral. We distinguish the following asymmetric charge exchange densities:

$$\begin{align*}
\text{CF}_3^+ + \text{CF}_4 & \rightarrow 6.2 \text{ eV} \rightarrow \text{CF}_3 + \text{CF}_4^+ , \\
\text{CF}_2^+ + \text{CF}_4 & \rightarrow \text{CF}_2 + \text{CF}_4^+ , \\
\text{CF}^+ + \text{CF}_4 & \rightarrow 6.3 \text{ eV} \rightarrow \text{CF} + \text{CF}_4^+ , \\
\text{F}^+ + \text{CF}_4 & \rightarrow 2.7 \text{ eV} \rightarrow \text{F} + \text{CF}_4^+ .
\end{align*}$$

The energy difference for reaction (13) is unknown.

The probability that the reactions (3)–(15) occur in the sheath depends on the cross sections and on the densities of the neutrals. The densities of the CF$_3$, CF$_2$, and CF neutrals are of the order $10^{18}$–$10^{19}$ m$^{-3}$. The density of the F radicals is of the order of $2.5 \times 10^{19}$ m$^{-3}$. The densities of all these species are much lower than the CF$_4$ neutral density ($1.6 \times 10^{20}$–$5.3 \times 10^{21}$ m$^{-3}$); however, due to the larger cross sections for resonant charge exchange, the reaction rates of both types of charge exchange will be comparable.

The next ion–molecule reactions which we discuss are dissociation reactions of CF$_n$ ions by a collision with a neutral, most of the times a CF$_4$ molecule. We distinguish the following reactions:

$$\begin{align*}
\text{CF}_4 + \text{CF}_3^+ & \rightarrow 3.77 \text{ eV} \rightarrow \text{CF}_4 + \text{CF}_3^+ + \text{F} , \\
\text{CF}_4 + \text{CF}_3^+ & \rightarrow 8.08 \text{ eV} \rightarrow \text{CF}_4 + \text{CF}_3^+ + \text{2F} , \\
\text{CF}_4 + \text{CF}_3^+ & \rightarrow 13.7 \text{ eV} \rightarrow \text{CF}_4 + \text{CF}_3^+ + \text{3F} , \\
\text{CF}_4 + \text{CF}_3^+ & \rightarrow 5.31 \text{ eV} \rightarrow \text{CF}_4 + \text{CF}_3^+ + \text{F} , \\
\text{CF}_4 + \text{CF}_3^+ & \rightarrow 10.9 \text{ eV} \rightarrow \text{CF}_4 + \text{CF}_3^+ + \text{2F} , \\
\text{CF}_4 + \text{CF}_3^+ & \rightarrow 5.59 \text{ eV} \rightarrow \text{CF}_4 + \text{CF}_3^+ + \text{F} .
\end{align*}$$

From the measured IEDs we may conclude which of the reactions (3)–(21) take place in the sheath. The density of F radicals is higher than of CF$_2$, whereas the CF$_2$ density is higher than the CF$_3$ density.

In the previous subsection, from the vanishing of the saddle structure at low pressures we have concluded that there must be an inelastic reaction with a large cross section by which CF$_3$ ions are lost. This may be reaction (4), an exothermic disproportionation reaction. Due to the high density of the CF$_4$ molecules, the probability that this reaction takes place will be large. The reaction rate can be estimated as follows. At 40 mTorr nearly the whole saddle structure has vanished. The CF$_3$ density in this case is $2.6 \times 10^{21}$ m$^{-3}$. 95% of the CF$_2$ ions will be destroyed when the mean free path is $\frac{1}{2}$ of the sheath thickness. The sheath thickness will be of the order of 2 mm, so the mean free path is 0.7 mm. This gives a cross section of $5 \times 10^{-19}$ m$^2$, which is quite reasonable. The charge exchange reactions (9) and (13) also lead to a loss of CF$_2$ ions but their contribution to the total loss will be much smaller than that of reaction (4). At 40 mTorr the mean free path for resonant charge exchange [reaction (9)] is about 12 cm. The mean free path for asymmetric charge exchange [reaction (13)] is about 40 cm. Reactions (3) and (5) are endothermic and their cross section will be small. This can explain why the primary saddle in the IEDs of CF$_3^+$ and CF$_2^+$ ions does not vanish. When the cross section is a factor of 10 smaller, the mean free path is a factor of 10 larger. This means that only 3% of the ions will be destroyed by collision.

From the abundance of low-energy features in the IED of CF$_4^+$, we have concluded that there must be a reaction by which CF$_2$ ions are produced in the sheath. As shown above, the reaction rates of charge exchange reactions is small. That this reaction is not a dominant production process is confirmed by the fact that no specific charge exchange peaks in the IEDs of the CF$_2$ ions can be observed. Therefore, the dissociation of CF$_3$ ions [reaction (16)] is the most probable production process of CF$_2$ ions in the sheath.

CF$_3$ ions are involved in several reactions. The cross section of resonant charge exchange [reaction (8)] is quite large, but due to the low CF$_3$ radical density the reaction rate is small (mean free path $\approx 25$ cm). Due to the small cross sections, asymmetric charge exchange [reaction (12)] does not have a high rate, either. Therefore, probably CF$_3$ ions are mainly produced in the sheath by the fluorine atom transfer reaction (3) where CF$_4$ decomposes into CF$_3^+$ and a F radical. The mean free path of this reaction is of the order of 4 mm. The IED of CF$_3^+$ ions shows some secondary peak structures, although less pronounced than expected for charge exchange. In the IED of CF$_3^+$ more peak structures can be distinguished than for CF$_2$ due to the longer transit time of the CF$_3$ ions (larger mass).

In the CF$_3^+$ case, similar reactions are responsible for the production and loss as for CF$_2^+$. The difference is that reaction (5) is now slightly endothermic. The consequence is that the ratio between loss and production reactions is different from CF$_2^+$. Therefore, in the IED of CF$_3^+$ the primary saddle structures can be recognized up to higher pressures than for CF$_2^+$.

F$^+$ ions are destroyed by the ion transfer reaction. This reaction is exothermic and due to the large CF$_4$ density the probability for this reaction to occur in the sheath will be quite large. The IEDs of F$^+$ ions show large peaks, which suggests that resonant charge exchange [reaction (11)] occurs in the sheath. This seems to be quite likely because the F radical density is about five times higher than the CF$_3$ and CF$_2$ densities. Furthermore, the cross section for resonant charge exchange is large.
TABLE I. Dominant production and elimination reactions in the sheath of a 
CF₄ plasma.

<table>
<thead>
<tr>
<th>Species</th>
<th>Production reaction</th>
<th>Elimination reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₂⁻</td>
<td>disproportion with CF₄ (3)</td>
<td>dissociation into CF₃⁻ (16)</td>
</tr>
<tr>
<td>CF₃⁻</td>
<td>dissociation of CF₂⁻ (16)</td>
<td>disproportion with CF₄ (4)</td>
</tr>
<tr>
<td>CF₄⁺</td>
<td>disproportion of CF₃⁻ (17)</td>
<td>disproportion with CF₅ (5)</td>
</tr>
<tr>
<td>F⁺</td>
<td>resonant charge exchange with F (11)</td>
<td>disproportion with CF₆ (7)</td>
</tr>
</tbody>
</table>

V. CONCLUSIONS
The sheath in a CF₄ plasma is far more complex than in an argon or nitrogen plasma. This is due to the number of ion species and to the large variety of ion–molecule reactions.

From the IEDs of the ion species one may conclude which reactions are dominant for the production and loss of the different species in the sheath. These reactions are listed in Table I.

Because most of the elastically scattered ions are not detected, and because there are no reactions by which CHF₂⁻ ions can be produced in the sheath, the IEDs of the CHF₂⁻ ions mainly represent the ions which have not collided in the sheath. Therefore the IEDs of CHF₂⁻ ions may be interpreted as collisionless and can be used to analyze the general sheath behavior.

25 The simulations have been performed with the particle-in-cell simulation program of C. K. Birdsall in the internal report VDF/NG 92-02, Department of Physics, Eindhoven University of Technology, 1992.
32 The simulations have been performed with the particle-in-cell simulation program of C. K. Birdsall and A. Langdon [see, e.g., *Plasma Physics Via Computer Simulations* (McGraw–Hill, New York)]. The results are described by J. van Breda in the internal report VDF/NG 92-02, Department of Physics, Eindhoven University of Technology, 1992.
38 The simulations have been performed with the particle-in-cell simulation program of C. K. Birdsall and A. Langdon [see, e.g., *Plasma Physics Via Computer Simulations* (McGraw–Hill, New York)]. The results are described by J. van Breda in the internal report VDF/NG 92-02, Department of Physics, Eindhoven University of Technology, 1992.
44 The simulations have been performed with the particle-in-cell simulation program of C. K. Birdsall and A. Langdon [see, e.g., *Plasma Physics Via Computer Simulations* (McGraw–Hill, New York)]. The results are described by J. van Breda in the internal report VDF/NG 92-02, Department of Physics, Eindhoven University of Technology, 1992.