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Measurements of negative ion densities in 13.56-MHz rf plasmas of CF₄, C₂F₆, CHF₃, and C₃F₈ using microwave resonance and the photodetachment effect

M. Haverlag, A. Kono, D. Passchier, G. M. W. Kroesen, W. J. Goedheer, and F. J. de Hoog

Eindhoven University of Technology, Department of Physics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The high-power density of a frequency quadrupled pulsed Nd-YAG laser has been used to photodetach electrons from negative ions in rf plasmas generated within a microwave cavity. Negative ion densities have been determined by measuring the frequency shift of the resonance transmission, the shift being caused by the photoelectrons created by irradiating the plasma with the laser pulse. By measurement of the shape of the resonance curve as a function of time and of microwave frequency, and consecutive fitting of a parabola to the top of the resonance curve, the negative ion density has been determined as a function of gas pressure, rf power, and position in the plasma. Measurements were performed in plasmas of CF₄, C₂F₆, CHF₃, and C₃F₈. The results indicate that the negative ion densities are about one order of magnitude larger than the electron density, which is in good agreement with a fluid model calculation. The pressure and power dependence of the electron density and of the negative ion density gives insight in the relation between the electron temperature and the macroscopic plasma parameters. Measurements as a function of the laser wavelength, using a pulsed dye laser, show that in CF₄ the negative ions mainly consist of F⁻, whereas in C₂F₆ significant densities of other negative ions may occur.

I. INTRODUCTION

rf plasmas in halogen-containing electronegative gases are widely used for dry etching of semiconductor materials in submicron technology. The etching characteristics of these plasmas are determined predominantly by the reaction kinetics and the transport of particles in the plasma. It is well established that neutral radicals play an important role in the etching process since these particles, once adsorbed to the surface, can act as etching or passivating species. The production of these neutral particles is determined largely by the electron density, ion densities (both positive and negative), and the electron temperature. Positive ions, bombarding the substrate exert a large influence on the etching profile, the selectivity, and the degree of damaging of the surface during the process. The positive ion energy distribution at the surface is directly related to the sheath potential between the glow and the electrodes. The presence of large quantities of negative ions in the plasma can have a large influence on the sheath potential, the positive ion densities, and the electron temperature in the plasma.

Therefore, any attempt to model such a halogen-containing plasma should include the negative ion density as a parameter. In order to check rf plasma models in halogen-containing gases it is necessary to obtain experimental data on both neutral species, e.g., reaction products and radicals, and charged particles.

This paper is concerned with the experimental determination of the negative ion density in 13.56-MHz rf plasmas of fluorocarbon gases (CF₄, C₂F₆, C₃F₈, and C₂F₆) generated in a quasi-parallel electrode system at pressures between 30 and 250 mTorr and power densities from zero up to 0.25 W/cm².

For the observation of positive ions in an rf discharge both probe methods and mass spectrometry of effusing ions have been used. With the first technique the compensation of the rf component in the probe current and effects due to the presence of negative ions makes the analysis difficult, whereas with the latter it is very difficult to translate measured ion currents to ion densities in the plasma.

To obtain results for negative ions is an even more difficult task. The reason for this is that negative ions are trapped in the glow region of the plasma as a result of the potential difference between the glow and the electrodes. This potential difference is induced by the fact that the mobility of the electrons is much larger than the mobility of the ions. This makes it difficult to measure negative ion densities in situ without disturbing the plasma severely. As an example, measurements using mass spectrometry can only be done in the afterglow of the plasma. At the time the ions are detected, the composition of the plasma is totally different from the undisturbed situation. Hence, it is difficult to obtain quantitative results.

Gottscho and Gaebel introduced an alternate method to detect negative ions by applying photons to transform the negative ions by photon detachment into electrons and neutrals and subsequently detect the increase of the electron density. Although this is still an indirect method, it is possible to detect negative ions this way. In our setup we...
use a microwave cavity\textsuperscript{14} to detect the released electrons. In this way quantitative measurements can be done relatively easily. Some preliminary results of this method have already been reported.\textsuperscript{15,16} In this paper an enhanced method is described that offers a higher sensitivity and accuracy. Experimental results will be given for rf plasmas of CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, CHF\textsubscript{3}, and C\textsubscript{3}F\textsubscript{8} as a function of several macroscopic plasma parameters and as a function of the position in the plasma. In Sec. II the basic features of the method are described. In Sec. III the experimental setup that has been used for the experiments and some details of the data analysis are described. In Sec. IV the results of some test experiments and of negative ion density measurements in a number of fluorocarbon gases are given. In Sec. V a numerical simulation based on a fluid model is presented and some results of this simulation are given. In Sec. VI the experimental and numerical results are discussed and compared.

\section{II. METHOD}

Microwave cavity resonance spectroscopy is a very sensitive method (the detection limit is \( \approx 2 \times 10^{11} \text{ m}^{-3} \)) to determine electron densities \textit{in situ} and nonintrusive. Results obtained in capacitively coupled rf plasmas of several fluorocarbons have been reported previously.\textsuperscript{14} However, this method only detects charged particles that have a mobility high enough to follow the microwave field. Therefore, for practical frequencies around a few GHz, only electrons are detected by this method. In order to use it for the determination of negative ion densities, the negative ions can be transformed into electrons and neutrals using a laser-induced photodetachment reaction. In practice this means that a short laser pulse is fired through the plasma. A number of electrons is then released by the photodetachment effect. After this, both the electron density and the negative ion density decay to the original equilibrium values. If the electron density is monitored as a function of time, a jump in the electron density is observed shortly after the laser is fired. This density jump depends on the fraction of the negative ions which is eliminated by photodetachment. If all negative ions in the irradiated volume are detached, the effect saturates. This saturation was checked by performing the experiment as a function of the laser power.\textsuperscript{16} In saturation the height of the jump can be easily related to the average number of negative ions within the volume of the laser beam. In a previous paper,\textsuperscript{16} two ways to operate the experiment have been discussed. In the first method the laser pulse travels only once through the plasma. This method offers an easy interpretation of the results. In the second method the laser beam reflects several times inside the (cylindrically shaped) cavity, and therefore this method offers a higher signal level. However, in the latter case the interpretation is more difficult. For the experiments described in this paper the single pass method has been applied.

The electron density in the cavity can be inferred from the change of the resonance frequency with respect to the resonance frequency of the empty cavity as given by\textsuperscript{14}

\begin{equation}
\frac{f'}{f_0} = \frac{\int \int \int \frac{n_e(r) e^2}{m_e \omega_0^2} [1 + (\frac{\nu_m^2}{\omega^2})] \frac{E^2}{r} \, d^3r}{\int \int \int \frac{E^2}{r} \, d^3r},
\end{equation}

where \( f \) is the frequency shift caused by the electrons, \( f_0 \) is the resonance frequency of the empty cavity, \( e \) is the elementary charge, \( \omega \) the angular frequency of the microwaves, \( \nu_m \) the electron collision frequency, and \( E \) the microwave electric field distribution in the cavity. For the microwave field distribution we used the TM\textsubscript{020} mode in all experiments. The integrations are to be performed over the entire volume of the cavity. For the extra electrons produced by the photodetachment process the same expression applies. However, since the extra electrons are only produced in the irradiated volume, in the numerator the integration only runs over that volume. The laser beam axis lies along a cavity diameter. Therefore, if we assume that the extra electron density \( \Delta n_e \) is constant over the volume of the laser beam, the expression for the frequency shift, just after the laser pulse, caused by the extra electrons reduces to

\begin{equation}
\frac{\Delta n_e}{n_e} = \frac{\left( \frac{\Delta n_e e^2}{m_e \omega_0^2} \right) \cdot O / \left( 1 + \left( \frac{\nu_m^2}{\omega^2} \right) \right) \int \int \int \frac{E^2}{r} \, d^3r}{f_0}.
\end{equation}

where \( O \) is the area of the laser beam and \( R \) is the inner radius of the cavity. From this expression \( \Delta n_e \) can be calculated if the frequency shift \( f' \) is already known. This can be achieved by measuring some data points before the laser is fired. Provided that the photodetachment effect is completely in saturation, \( \Delta n_e \) is directly the negative ion density in the volume of the laser beam. If the negative ion density is not constant over the volume of the laser beam, a small correction of about 10–20\% must be performed.\textsuperscript{14} Because we have no information on the spatial dependence of the negative ion density in the radial direction of the cavity, no such correction was performed. Since the method only releases electrons in the irradiated volume, it is possible to get spatially resolved negative ion densities in the axial direction of the cavity by varying the position of the laser beam.

The method described above only yields reliable results for densities up to about \( 5 \times 10^{16} \text{ m}^{-3} \) for the TM\textsubscript{020} mode as has been evaluated by Persson.\textsuperscript{17} The densities observed in our experiments are all below this limit.

\section{III. EXPERIMENT}

Large parts of the experimental setup have already been described elsewhere.\textsuperscript{14–16} Therefore only a brief description will be given of the features which are specific for these experiments. A schematic view of the experiment is given in Fig. 1.

The capacitively coupled rf plasma is produced within a cylindrically shaped microwave cavity. Part of the cavity wall is rf powered (using a matching network) and the rest

\begin{align}
\rho &= \frac{1}{\varepsilon_0} \int\int\int \frac{\epsilon_0 E^2}{r} \, d^3r, \\
\sigma &= \frac{1}{\varepsilon_0} \int\int\int \frac{\epsilon_0 E^2}{r} \, d^3r, \\
\text{where} \quad \epsilon_0 &= \frac{f}{1 + (\frac{\nu_m^2}{\omega^2})} \\
\text{and} \quad \sigma &= \frac{\epsilon_0 E^2}{r} \, d^3r.
\end{align}
FIG. 1. Schematic view of the experimental setup. The rf plasma is produced within the microwave cavity. The laser beam is fired through two slits in the wall of the cavity. The transmitted microwave signal is measured as a function of time using a digitizing oscilloscope.

is grounded. The rf voltages over the electrodes were measured using an rf voltage probe.

A frequency quadrupled Spectra Physics DCR-11 Nd:YAG laser at 266 nm with a 2-ns pulse length and 10-Hz repetition frequency is used for all negative ion density measurements. The laser beam enters the vacuum system through quartz windows. The microwave cavity has two slits to allow the laser beam to pass through the plasma. After exiting the vacuum system the beam is dumped. All wavelengths of the laser (1ω, 2ω, and 4ω) are directed coaxially, but only the 4ω beam produces any photodetachment effect in the gases investigated.16 After passing the vacuum system the beam is separated from the 1ω and 2ω beams by a Pellin–Broca prism. The intensity is calibrated with a laser power meter. To avoid scattering of the laser beam at the walls of the cavity, the beam diameter was kept smaller than the width of the slits of the cavity using a diaphragm. For wavelength-dependent measurements the 2ω beam of the Nd-YAG laser was used to pump a Spectra Physics PDL-3 dye laser. For the latter an LDS 750 dye was used around 720 nm. The output of the dye laser was again frequency doubled to obtain wavelengths around 360 nm.

The microwave signal is generated by a Gigatronics model 605 synthesized generator and coupled in and out of the cavity by two small antennas which are positioned outside the glow region of the plasma to avoid disturbance of the plasma.

Preliminary results of time-dependent measurements of the transmitted microwave signal at a fixed microwave frequency15,16 showed that a considerable increase of the electron density is observed after firing the laser beam through the plasma. However, for a correct interpretation of the data as described in the previous chapter, it is necessary to know the resonance curve as a function of time to be able to calculate the extra shift caused by the photodetachment process. Presently, this is done by measuring the microwave signal as a function of time using a HP 54111D digitizing oscilloscope. The oscilloscope is controlled by an IBM PC/AT using an IEEE-488 connection. The microwave generator frequency is also controlled in this way. The time-dependent signal was measured for a large number of microwave frequencies. Several shots (typ. 20) were averaged. In this way a matrix is obtained of the transmitted microwave signal as a function of time and of microwave frequency. Although the measurements are taken in the time direction, the analysis is performed in the microwave frequency direction, searching the maximum in the resonance curve at a given time. In a three-dimensional plot of this matrix the shift in the resonance curve can be easily recognized (see Fig. 2). The resonance frequency at each temporal point was calculated from the measurement data by fitting a second-order polynomial to the top of the curve using a least-squares procedure. As a result of the automation and of the fitting procedure, it is now possible to detect negative ion densities of less than 10^{14} m^{-3}, an improvement of about a factor of 10 as compared to a measurement at a fixed microwave frequency.15,16 A typical example of the change in the electron density as a function of time is given in Fig. 3. The response time τ of the measurement is determined by the quality factor Q of the cavity: \( τ = Q/πf \). For a quantitative evaluation of wave generator frequency is also controlled in this way.

FIG. 2. Three-dimensional plot of the microwave signal versus time and microwave frequency. The resonance curve is shifted as a result of the release of extra electrons by the photodetachment process. After the shot the electron density decays to its original equilibrium value.

FIG. 3. Amount of extra electrons produced by the photodetachment process as a function of time. It can be clearly seen that the decay contains at least two time constants. The initial jump in the electron density can be directly related to the negative ion density.

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boundary, indicating that the particles that produce the electrons are the time constant of the decay after the laser pulse. In most cases the standard quality factor $Q$ (2300) corresponding to a time constant of about 240 ns sufficed. In $C_2F_6$ and $C_3F_8$ plasmas the quality factor of the cavity had to be decreased, by repositioning the microwave antennas, to $Q \approx 500$ and a response time of about 53 ns.

Experiments on the time dependence of negative ion densities in the afterglow of the plasma have been done by using a time delay circuit and by gating of the rf generator.

IV. EXPERIMENTAL RESULTS

A. Attribution of the photoinduced production of electrons to photodetachment

First of all we need to be sure that the measured effect can indeed be attributed exclusively to photodetachment of negative ions. Possible other processes for photoinduced production of extra electrons are photoelectric effects and photoionization from metastable levels.

To exclude these other photon-induced effects, first of all some test experiments have been performed in argon. To investigate possible wall effects, an experiment was performed in an Ar-filled cavity without rf power applied. No detectable signal was found in this way. Therefore photoelectric effects are negligible. Next an experiment was performed with an Ar plasma at several rf powers and pressures. In contrast to plasmas containing fluorocarbons no detectable signal was found, despite the fact that metastables will certainly be present in argon plasmas. For instance the $4s[1/2]$ metastable level of Ar is situated at 11.72 eV, which is close enough to the ionization level at 15.76 eV to be ionized by the 266-nm photons in the 4w laser beam. The fact that no signal is found suggests that metastables do not significantly contribute to the observed phenomenon.

Secondly, the axial profile of the extra electron density was determined using a 1-mm diaphragm to restrict the laser beam. The results are depicted in Fig. 4. The extra electron density is observed to drop sharply in the sheath region of the plasma. This can be understood only when the extra electrons are generated either by a neutral species that has a very short lifetime, or by a species that is strongly confined in the glow region of the plasma. Concerning the first possibility, any neutral species which has a density high enough to release a detectable amount of photoelectrons should have a long lifetime, and such a neutral species would live long enough to diffuse into the sheath region. Therefore the species will have to be charged. As the glow is charged positively, only negative ions are trapped in the glow. The measured signal must therefore result from the photodetachment of negative ions.

Thirdly, a measurement was performed in the afterglow of a CF$_4$ plasma at 110 mTorr. The evolution of the electron density was measured as a function of the time between plasma switch-off and the start of the laser pulse. The time dependence was measured with (a) the beam going through the glow region and with (b) the beam going through the sheath region of the plasma. The results are depicted in Fig. 5. It shows that in the glow region the density of the extra electrons decreases with the time gap between plasma switch-off and the laser pulse. In the sheath region however we see temporally a small increase in the extra electron density after about 50 ps. This behavior can be expected from negative ions: in the first tens of $\mu$s the negative ion density in the sheath decreases due to ion-ion recombination and collisional detachment. Then the confining sheath potential vanishes. As a result, negative ions from the glow region start to diffuse out towards the electrodes and they reach the irradiated volume about 50 $\mu$s after plasma switch-off, giving rise to a temporary increase in the negative ion density at that position.

Finally, the dependence of the extra electron density on the wavelength of the light pulse was determined with a constant laser pulse energy. Since the intensity of the dye laser is smaller than that of the Nd-YAG laser alone, the
This time dependence shows some interesting features. In constant of 1.1 ps is observed for about 2 ps. Then the parts. In the-first... be detached at wavelengths up to 465 nm.

The conclusion of these tests is that the detected extra electrons produced by the laser pulse are coming from negative ions in the laser beam volume.

**B. Time dependence of the extra electron density**

The density of the extra electrons in the plasma has been measured as a function of time after the laser pulse. This time dependence shows some interesting features. In Fig. 3 an example is shown of the time dependence of the extra electron density in a CF₄ plasma at 100 mTorr and 20-W rf power. The decay can roughly be divided into two parts. In the first part a relatively fast decay with a time constant of 1.1 μs is observed for about 2 μs. Then the decay slows down. The curve becomes exponential with a time constant of about 18 ps.

In the second part of the decay we assume that the extra electrons have the same temperature and the same spatial distribution as the rest of the electrons. However, the total number of electrons is higher than before the laser pulse and will therefore still tend to return to the original value. Since the number of extra electrons is small compared to the total number of electrons already present in the plasma, it is reasonable to assume that the change in $T_e$ will also be small. We can therefore linearize the response of $T_e$ and accordingly, $G$ to the density perturbation. This can explain the observed exponential decay of the extra electron density to the original equilibrium value. If the decay rate of the second part of the decay is plotted as a function of the pressure, we obtain an approximately linear line (increasing decay rate with increasing pressure). However, an attempt to correlate the slope of such a plot with the attachment rate constant, as was done in an earlier paper, is invalidated because the extra electron density decays not by attachment (and axial diffusion) only, but by the imbalance between generation (ionization) and loss (attachment and diffusion).

**C. Dependence of the negative ion density on macroscopicplasma parameters**

Densities of electrons and negative ions were determined as a function of pressure and rf power in plasmas of CF₄, CHF₃, C₂F₆, and C₃F₈. The results of these measurements are depicted in Figs. 7–14 together with the ratio of the negative ion density and the electron density. 10 at a power of 10 W. The conclusion of these tests is that the detected negative ions are coming from negative ions in the laser beam volume.

The fast decay rate of the first part of the curve in Fig. 3 may be understood as follows: the extra electrons are produced with an energy ($\approx 1$ eV) which is lower than the average electron energy and their spatial distribution is concentrated initially in the central region of the discharge where the laser beam is fired. This fact and the fact that the same rf power (or even less, since the matching network will be detuned as a result of the changed impedance of the plasma) is now dissipated by more electrons means that the electron temperature $T_e$ in the central region will become slightly lower than before the laser pulse. This will favor attachment with respect to ionization, resulting in a decrease of the net generation rate $G$ of the electrons. Due to the concentration of the extra electrons in the central region this imbalance will persist until the extra electrons are diffused to the sheath boundary, where they may be heated more efficiently than in the glow region. By using an effective ambipolar diffusion constant based on Ref. 22 an estimate can be made of the time required for the extra electron distribution to spread out in the axial direction; the results give a correct magnitude of the duration of the first part of the decay.

An effect which only apparently increases the extra electron decay rate is diffusion in the lateral direction; this brings electrons to the region where the microwave field is weak, resulting in a decrease of the detected frequency shift. An estimated time scale for this effect to occur is however several times longer than the duration of the fast part of the decay. The latter effect is therefore probably mixed up with the second part of the decay.

In the second part of the decay we assume that the extra electrons have the same temperature and the same spatial distribution as the rest of the electrons. However, the total number of electrons is higher than before the laser pulse and will therefore still tend to return to the original value. Since the number of extra electrons is small compared to the total number of electrons already present in the plasma, it is reasonable to assume that the change in $T_e$ will also be small. We can therefore linearize the response of $T_e$ and accordingly, $G$ to the density perturbation. This can explain the observed exponential decay of the extra electron density to the original equilibrium value. If the decay rate of the second part of the decay is plotted as a function of the pressure, we obtain an approximately linear line (increasing decay rate with increasing pressure). However, an attempt to correlate the slope of such a plot with the attachment rate constant, as was done in an earlier paper, is invalidated because the extra electron density decays not by attachment (and axial diffusion) only, but by the imbalance between generation (ionization) and loss (attachment and diffusion).
FIG. 7. Electron and negative ion density, and the ratio of the two as a function of pressure in a CF₄ plasma. The rf power was held constant at 20 W. It shows that the major negatively charged particles in the plasma are negative ions.

ratio is found for CHF₃. In C₂F₆ and C₃F₈ even higher values are found, up to 35. Therefore negative ions are the major negatively charged particles in the plasma. The pressure dependencies of N⁻/nₑ follow the same trend for all gases, i.e., a slow increase with pressure. The dependence of the ratio on the rf power shows some differences between the gases without hydrogen on one hand and CHF₃ on the other.

V. NUMERICAL MODEL

In all gases the ratio of the negative ion density and the electron density is much larger than unity and it is a function of the macroscopic plasma parameters. We want to analyze the background of this phenomenon.

Therefore, we have used a fluid model of the plasma in which the continuity equations for all charged particles, together with Poisson's equation are solved numerically in one dimension. This approach is based on a paper by Boeuf²¹ and the basic equations can be found in that arti-

FIG. 8. Electron and negative ion density, and the ratio of the two as a function of rf power in a CF₄ plasma. The gas pressure was 120 mTorr. Especially at low power levels the ratio becomes large.

cle. The calculation is performed for the case of CF₄. For this gas sufficient data is available on transport coefficients.²³⁻²⁷ These data were not yet used in the model of Boeuf²¹ where some ad hoc assumptions were done for the transport coefficients. We have inserted these experimental data into the model, taking the mobilities and diffusion coefficients for the positive and negative ions (D⁻, D⁺, µ⁻, and µ⁺) from Ref. 23, the electron mobility µₑ as a function of the reduced electric field E/N from Ref. 24 and the diffusion/mobility ratio for the electrons Dₑ/µₑ as a function of E/N from Refs. 25-27. The major positive ion was assumed to be CF₄⁺ and the mobility for this ion was taken equal to the mobility of CF₄⁺ (from Ref. 18). The major negative ion was taken to be F⁻. The rate coefficients for dissociative attachment and ionization kₓ and kᵢ as a function of E/N were taken from Refs. 23 and 28. In contrast to Boeuf²¹ we calculated the drift velocity vₑ of the electrons directly from the value of
FIG. 11. Electron and negative ion density, and the ratio of the two as a function of pressure in a C$_2$F$_6$ plasma. The rf power was kept constant at 30 W. The relative behavior is similar to that of CF$_4$, but the ratio is about four times larger than in the case of CF$_4$.

E/N. Simulations of the charged particle kinetics were performed until all densities and the electric fields were a periodic function of time. The reduced electric field $E/N$ in the center of the cavity and the ratio of the negative ion density with respect to the electron density given by the simulations as a function of pressure and rf power have been depicted in Figs. 15 and 16. Since the model is in principle only valid for higher pressures, where the assumption of "local equilibrium" is justified, the calculation has only been performed at pressures above 200 mTorr and we will only compare the trends. Some interesting conclusions can be drawn from the simulation. It yields that the reduced electric field $E/N$ tends to decrease as a function of pressure and increases with rf power. This means that the electron temperature $T_e$ must also decrease with pressure and increase with rf power since $T_e$ is monotonously increasing function of $E/N$. Furthermore the simulation yields that the ratio $N^-/n_e$ increases as a function of pressure and decreases with rf power, in agreement with the experiment. The values of $N^-/n_e$ agree with the experimental values within a factor of 2.

VI. DISCUSSION

To compare the experimental results with the results of the simulation, we will make an effort to deduce from the experimental densities of electrons and negative ions how the reduced electric field (which can be related to the electron temperature) behaves as a function of pressure. For this it is helpful to solve the negative ion balance equation. Since the negative ions can not escape from the plasma, only volume processes need to be considered. For simplicity, the rate coefficients and electron densities are taken as appropriate averages over the discharge volume. Taking dissociative attachment, recombination and collisional detachment with neutral radicals into account we arrive at

$$k_a[CF_4] \cdot n_e = k_r[N^+ \cdot N^-] + k_d[CF_4] \cdot N^-.$$ (3)
FIG. 15. Ratio of the negative ion density and the electron density, and the reduced field \( E/N \) in the centre of the volume as a function of pressure resulting from a fluid model calculation, and the reduced effective field as derived from the experimental value of the attachment rate. It indicates that the electron temperature decreases with pressure.

In this expression, \( N^+ \) and \( N^- \) are the densities of positive and negative ions respectively, \( k_r \) is the rate coefficient for ion-ion recombination, and \( k_d \) is the rate coefficient for collisional detachment with neutrals (in this case mostly CF\(_2\) and CF\(_3\) radicals). Taking realistic values for \( k_r \left( 5.5 \times 10^{-13} \text{ m}^3 \text{ s}^{-1} \right) \), taken from after glow data\(^{25} \), \( k_d \left( 5 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} \right) \), taken from Ref. 2, \([\text{CF}_4]\) (around \( 10^{19} \text{ m}^{-3} \)), see Refs. 30 and 31), and the concentrations of the negative ions, it follows that the detachment term can have the same order of magnitude as the recombination term. Therefore both terms must be taken into account. Using charge quasi-neutrality it follows that

\[
k_d = \frac{N^- (N^- + n_e) \cdot k_r + N^- \cdot [\text{CF}_4] \cdot k_d}{n_e [\text{CF}_4]}.
\]

Inserting the measurement data into this expression, we can obtain a set of values for \( k_d \) as a function of pressure and rf power. Since the dependence of \( k_d \) on \( E/N \) is known,\(^{24} \) we can derive the corresponding values of \( E/N \). The results for the pressure dependence of \( E/N \) have been depicted in Fig. 15. Despite the fact that there is some discrepancy between experiment and theory (probably due to the fact that the assumption of “local equilibrium” in the fluid model is not correct at the pressure range and rf frequency concerned), both the experimental results and the simulation yield that \( E/N \) decreases with pressure. The value of \( E/N \) in the glow found in the simulation implies that \( k_d \) is smaller than the ionization rate coefficient \( k_i \) in the glow. This implies that in most of the volume attachment is faster than ionization and that the ionization must therefore mainly take place at the sheath boundary as has already been indicated by the numerical work of Boeuf.\(^{21} \)

The interpretation in the case of the other gases may be somewhat different because in these gases CF\(_2\)-radical densities may be so high (as a result of the higher C/F ratio and/or the presence of H atoms) that the negative ion loss is mainly due to collisional detachment.

VII. CONCLUSIONS

It has been shown that the microwave cavity method in combination with the photodetachment effect can be effectively used for the determination of densities of negative ions in rf plasmas of CF\(_4\), CHF\(_3\), C\(_2\)F\(_6\) and C\(_2\)F\(_8\) at 13.56 MHz. In CF\(_4\) the negative ions consist almost only of F\(^-\), whereas in C\(_2\)F\(_6\) significant densities of other negative ions may be present. Densities of negative ions have been determined as a function of gas pressure and rf power. The results indicate that, depending on the gas and on the plasma parameters, negative ion densities are a factor 4–35 higher than the electron density in the plasma, which has been measured by the same method. The behavior of the ratio of the densities of electrons and negative ions indicates that the electron temperature increases with the rf power and decreases with pressure. Furthermore it is concluded that the loss of negative ions by collisional detachment with neutral radicals plays, next to ion-recombination, an important role.

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