Photodetachment effect in a radio frequency plasma in CF₄

J. L. Jauberteau, G. J. Meeusen, M. Haverlag, G. M. W. Kroesen, and F. J. de Hoog
University of Technology, Department of Physics, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
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Experiments to study negative ion densities have been carried out using the photodetachment effect in a rf plasma in CF₄. Electrons are detached from the negative ions under the influence of the pulse of a Nd:YAG laser. The induced increase of the electron density is measured as a function of time using the shift of the resonance frequency of a microwave cavity containing the plasma. The negative ion density [F⁻] is found to be about \((4 \pm 1) \times 10^{15} \text{ m}^{-3}\), a factor 4 \pm 1 higher than the electron density.

Negative ions play a dominant role in the chemistry of (rf) plasmas in electronegative gases like CF₄. Calculations show that their concentration can be at least ten times as high as the electron density.\(^1\) However, experimental evidence is scarce. Usually the photodetachment effect is used.\(^2\) To detect the extra electrons produced by photodetachment, we have used the shift of the resonance frequency of a microwave cavity.

In our experiments a rf CF₄ plasma (frequency = 13.56 MHz) is produced in a modified parallel-plate reactor. The electrodes serve as walls of a cylindrical microwave cavity (Fig. 1). Through a hole in the wall of the cavity, 2 ns laser pulses from a Nd:YAG laser (355 nm) are shot into the plasma. The increase of the electron density gives rise to a shift of the resonance frequencies in the cavity.\(^3\) In our case the TM₀₁₀ mode at 3.0123 GHz is used.

The threshold wavelengths for vertical photodetachment of F⁻ and CF₃ are 359.8 and 440.1 nm, respectively. Thus, the used laser pulse can detach electrons from both F⁻ and CF₃ ions. According to Bisschops\(^4\) however, the CF₃ density is estimated to be from 1% to 10% of the F⁻ density. Therefore, the photodetachment effect detected is mainly attributed to F⁻ ions. To increase the effect, the inner surface of the cavity is made reflective. The laser pulse is "captured" in the cavity by multiple reflection.

To calculate the change in electron density \(\Delta n_e\) at the end of the laser pulse, we assume that diffusion and attachment have no effect during the time the laser pulse is present in the cavity. During the pulse, the local anion concentration \(N^-(r)\) in the irradiated volume can be written as

\[
\frac{dN^-(r,t)}{dt} = -D\sigma N^-(r,t),
\]

where \(\sigma\) is the cross section for photodetachment at the wavelength of the laser, \(D\) is the photon flux supposed constant during the pulse time, and \(t\) is the time from the start of the laser pulse. If the duration of the laser pulse is \(\zeta\), the total local increase of the electron density is

\[
\Delta n_e(r,\zeta) = N^-(r) \left[ 1 - \exp(-D\sigma \zeta) \right],
\]

which is valid within the irradiated volume only; here \(N^-(r)\) is the initial local anion concentration. Each time the light beam is reflected at the cavity wall, it is attenuated with the reflection coefficient \(R\) of the wall material. Adding all reflections \(t\), we get just after the laser pulse

\[
\Delta n_e(0) = \frac{N^-(r)}{V_T} \sum_{i=0}^{\infty} \int [1 - \exp(-D\sigma R\zeta)] dV_T,
\]

where \(\Delta n_e(0)\) is the total average increase of electron density when the pulse has lost its power, \(V_T\) is the irradiated volume between reflections \(i = 1\) and \(i\), \(V_T\) is the volume of the cavity, and \(D\sigma R\zeta\) is the initial photon flux. The sum will be called the effective volume so that

\[
V_{eff} = \sum_{i=0}^{\infty} \int [1 - \exp(-D\sigma R\zeta)] dV_T.
\]

Detaching all anions in this volume would give the same increase of electron density as in expression (3). In these expressions we considered only the average initial anion density \(N^-(r)\). In the calculations of the effective volume we take into account that an anion can only be detached once.

The resonance frequency \(\omega_r\) of an empty cavity will increase with \(\Delta \omega(t)\) if free electrons are present in the cavity. From this shift we can calculate the average electron density \(\langle n_e(t) \rangle\) defined as the space average of the electron density \(n_e(r,t)\) weighted with the square of the electrical microwave field distribution\(^9,10\):

\[
\frac{\Delta \omega(t)}{\omega_r} = \frac{\langle n_e(t) \rangle}{\left[ 2m_e\epsilon_0(a^2 + v_e^2)/\epsilon^2 \right]},
\]

where \(\epsilon\) is the elementary charge, \(m_e\) is the electron mass, \(\epsilon_0\) is the dielectric constant, \(\omega_r\) is the microwave frequency, and \(v_e\) is the electron-neutral collision frequency, assuming that \(v_e\) is constant\(^1\) and \(\Delta \omega \ll \omega_r\). The plasma-containing cavity has resonance frequency \(\omega_0\) which is larger than the reso-

![FIG. 1. Schematic view of the experimental setup. The rf plasma between two parallel electrodes is surrounded by a microwave cavity. The Nd:YAG laser is fired into the cavity and the pulses are captured by the reflecting inner wall. The microwave field is induced and detected by two wire loops.](image-url)
nance frequency of the empty cavity $\omega_e$. When a laser pulse is shot, the detached electrons cause the resonance frequency to increase from $\omega_0$ to $\omega_\text{max}$ at the end of the pulse. After the pulse it decreases back to $\omega_0$ in about $10 \mu s$ due to attachment and diffusion. Using Eq. (5) we obtain

$$\langle n_e(t) \rangle / \langle n_e(0) \rangle = [\omega(t) - \omega_e] / [\omega_0 - \omega_e],$$

(6)

where $\langle n_e(0) \rangle$ is the undisturbed average electron density.

In order to investigate the time-resolved shifting of the resonance frequencies, a microwave signal from an oscillator is fed to the plasma through a metal loop in the wall of the cavity (Fig. 1). With a similar loop connected to a memory scope the response of the plasma and the cavity to the microwave signal is detected. If the microwave generator is tuned to a frequency $\tilde{\omega}$ ($\omega_0 < \tilde{\omega} < \omega_\text{max}$) somewhere between the undisturbed and the maximum frequency, the detected signal will go through a maximum (at a time $t$) when the (shifting) resonance frequency of the cavity equals $\tilde{\omega}$. Repeated measurements at increasing frequencies $\tilde{\omega}$ produce data points $t(\langle n_e \rangle)$. Inversion now yields the electron density $\langle n_e(t) \rangle$.

After the pulse, diffusion and attachment decrease the electron density. The decay which is observed is found to follow:

$$\langle \Delta n_e(t) \rangle = \langle \Delta n_e(0) \rangle \exp(-t/t_e).$$

(7)

The electron loss time $t_e$ depends on the attachment rate constants and diffusion lengths. Using Eqs. (4) and (7) and taking the cross section $\sigma$ from Vacqué et al.,\textsuperscript{11} we can estimate the $F^+$ concentration and the electron loss time $t_e$ by studying the evolution of $\langle \Delta n_e(t) \rangle$ versus time.

To check the exponential dependence of the increase of the electron density on the photon density as expressed in Eq. (4), in Fig. 2 the measured electron density increase $\Delta n_e$ is plotted versus $V_{\text{eff}}$. Since the reflection coefficient of the cavity wall is 0.92, a summation over 100 reflections appears more than adequate. Taking into account the volume fractions, the negative ion density $N_{\text{tot}}^-$ can be calculated using Eqs. (3), (5), and (7). Under our experimental conditions

![FIG. 2. Electron density increase $\Delta n_e$ plotted vs $V_{\text{eff}}$. The points are generated by changing the photon flux $D_\text{p}$.](image)

[power = 13.3 Pa, rf power = 15 W, and CF$_4$ flow = 15 scc/min], we find $N_{\text{tot}}^- = (4 \pm 1) \times 10^{15}$ m$^{-3}$, a factor $4 \pm 1$ higher than the electron density. The inaccuracy arises mainly from the cross section data, which show a relative inaccuracy (at this wavelength) of 30%.

The exponential decay of the electron density after the pulse due to attachment and diffusion [Eq. (7)] is confirmed in Figs. 3(a) and 3(b), which contain a linear and a logarithmic plot of the extra electron density as a function of time. From these graphs the electron loss time $t_e$ can be deduced. For our conditions we find that $t_e = 3.2 \mu s$.

![FIG. 3. (a) Linear and (b) logarithmic plot of the electron density increase $\Delta n_e$.](image)

![FIG. 4. Average negative ion density $N_{\text{tot}}^-$ and $\langle n_e(0) \rangle$ as a function of discharge pressure.](image)
In Fig. 4 the negative ion density is shown as a function of discharge pressure. The pressure at which the negative ion density approaches its saturation value roughly agrees with the pressure for which a maximum in the electron density is found.9

To conclude, by combining resonant microwave spectroscopy with laser-induced photodetachment, a very reasonable estimation can be found for the F− concentration in rf plasmas in CF₄.

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