CF radical kinetics in the afterglow phase of pulsed CF$_4$ + H$_2$ RF plasmas

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Abstract: The Infrared Tunable Diode Laser Absorption Spectroscopy (IR-TDLAS) was applied to analyze the CF radical kinetics in the afterglow phase of pulsed CF$_4$ + H$_2$ capacitively coupled RF plasmas. Under selected conditions, chemical reactions in the reactor volume were found to be dominant in the afterglow kinetics of the CF radical, whereas the diffusion towards the chamber walls and the surface elimination (sticking) appeared to be of minor importance.

Keywords: CF radical, afterglow kinetics, CF$_4$ + H$_2$ RF plasma, IR-TDLAS.

1. Introduction

Wide application of complex plasmas, and in particular (pulsed) fluorocarbon radio-frequency (rf) discharges, in industry motivate fundamental investigations of them as model systems. Thus, experimental study on the kinetics of key reactive species helps to improve the knowledge on plasma chemical processes in these plasmas.

The CF molecule is a small radical which plays an important role in the kinetics of fluorocarbon plasmas. Recently, it has been investigated in various CF$_4$ or CF$_4$ + H$_2$ discharges (CCP, ICP or helicon), mainly by means of Laser-Induced Fluorescence (LIF) and broadband absorption spectroscopy in the UV spectral range, e.g. [1 – 4]. Besides, the Infrared Tunable Diode Laser Absorption Spectroscopy (IR-TDLAS) was applied to measure the absolute CF density in pulsed capacitively coupled CF$_4$ + H$_2$ rf plasmas [5].

In so called “stream mode” data acquisition approach, used for these measurements, the absolute CF concentration was calculated from measured absorption immediately after the CF absorption spectrum was taken. Therefore, the temporal resolution which could be achieved there was limited by the time that the analysis of one spectrum took, and was normally not better than 30 ms. That was sufficient to study relatively slow kinetics of CF$_2$ and C$_2$F$_4$ species also measured in [5], but too poor for investigations on the CF kinetics which has significantly lower time scales. The mentioned lack of the temporal resolution can be clearly seen in the example of the CF absolute number density trace measured within a plasma cycle in the “stream mode” (see figure 1).

Hence, another data acquisition approach called “burst mode” (see section 2) had to be applied in this work to provide much higher time resolved IR-TDLAS measurements on the CF radical kinetics in the afterglow phase of pulsed CF$_4$ + H$_2$ rf plasmas.

2. Experiment

The IR-TDLAS measurements were carried out in the cylindrical stainless steel reactor shown in figure 2, using the equipment and software described in [5, 6].

As follows from the theory of the linear absorption spectroscopy, the intensity $I(\nu)$ of the transmitted laser beam measured due to the absorption in a medium (e.g. the plasma gas phase) relates to the initial intensity $I_0(\nu)$ without absorption according to the well-known Lambert–Beer law:
\[ I(\nu) = I_0(\nu) \exp(-k(\nu)L) \]  

(1)

where \( L \) is the absorption path length and \( k(\nu) \) is the absorption coefficient depending on the wavenumber \( \nu \) of the radiation. On the other hand, the linestrength \( S \) is the proportional factor between the spectral integral over a single absorption line and the absolute number density \( n \) of the absorbing molecules [7]:

\[ \int \limits_{\text{line}} k(\nu) d\nu = S \cdot n \]  

(2)

Hence, if the strength of the measuring line is known, the absolute number density of the species can be easily calculated from the measured absorption, using equations (1) and (2).

The spectroscopic data, i.e. wavenumbers \( \nu \) and linestrengths \( S \), for all allowed vibrational-rotational transitions within both \( ^3\Pi_{3/2} \) and \( ^3\Pi_{1/2} \) ground electronic states of the CF radical have been calculated in [8] using molecular constants given in literature [9, 10]. Basing on these calculations, a relatively intensive \( ^3\Pi_{3/2} \, R(7.5) \) doublet at 1308.67 cm\(^{-1}\) was selected for the absolute CF absorption measurements in this work (see figure 3). Due to the \( \Delta \)-type doubling, this doublet is split into two absorption lines of the equal strengths \( S=2.34 \times 10^{-19} \) cm/molecule. However, it could not be experimentally resolved, since the gap between its two components is much narrower than their Doppler broadening. Therefore, this doublet was fitted with an effective Voigt profile of the double linestrength \( S=2(2.34 \times 10^{-19})=4.68 \times 10^{-19} \) cm/molecule.

Fig. 3. The unresolved \(^3\Pi_{3/2} \, R(7.5) \) CF doublet and N\(_2\)O reference lines measured at 1308.67 cm\(^{-1}\).

The main idea of the applied “burst mode” approach was to collect the raw absorption spectra during a few hundreds of milliseconds in the early afterglow phase and analyze (fit) them afterwards. Therefore, the possible temporal resolution was only limited by the duration of one scan over a single spectrum and was as small as 940 \( \mu \)s. However, the noise level in a single spectrum was relatively high in comparison with the total intensity of the measured CF lines, which complicated the fitting procedure to the extent of a fit crash. In order to solve this problem, an absorption line of the N\(_2\)O at 1308.72 cm\(^{-1}\) was measured simultaneously and served as a reference line for the “double species” fit. Therefore, the proper spectral position for putting the CF fit profile resulted from the known difference between the wavenumbers of the considered lines.

The “burst mode” sampling of the absorption spectra was always triggered on the switching the plasma off. Thus, the high time resolved absolute density traces were obtained for the CF radical in the early afterglow phase. Finally, these measurements were repeated and averaged, typically, over 50 plasma pulse cycles.

3. Results and discussion

Basing on the CF absorption spectra measured in the “burst mode” during the afterglow phase, the time resolved CF absolute density traces were calculated. An example of one such trace measured under pressure of 4 Pa in the afterglow is shown in figure 4 in both linear and logarithmic scale. This CF decay curve was fitted with a first order kinetics, i.e. with an exponential function \( \sim \exp(-t/\tau) \), and an effective life time \( \tau \) of the CF radical in the afterglow phase was obtained as a free parameter of the fit.

Generally, the effective CF decay time \( \tau \) is determined by the following loss processes:

(i) diffusion towards the reactor wall and surface reactions on it,

(ii) chemical reactions with other species in the gas phase, and

(iii) gas exchange which takes place in the plasma reactor under considered gas flow conditions.

Thus, the total decay time may be represented by an equation of the form:

\[ \tau^{-1} = (\tau_{\text{wall}})^{-1} + (\tau_{\text{volume}})^{-1} + (\tau_{\text{gas exchange}})^{-1} \]  

(3)

The losses due to the gas exchange can be neglected, since the mean residence time for species in the chamber was estimated to be more than two orders of magnitude larger than typical time constants \( \tau \) observed for the CF decay.

Obviously, the volume loss rate is proportional to the total pressure \( p \): \( \tau_{\text{volume}}^{-1} \sim p \). On the other hand, in the case of cylindrical geometry, the \( \tau_{\text{wall}} \) term in (3) can be estimated from the following formula [11]:

\[ \tau_{\text{wall}} = \frac{p}{D} \left[ \frac{\pi}{h} \right]^2 + \left[ \frac{2.4}{R} \right]^2 \right] \frac{R h (2 - \beta)}{(R + h)(\nu) \beta} \]  

(4)
where $R$ and $h$ are the radius and height of the cylindrical reactor, respectively, $\beta$ is the surface reaction (sticking) coefficient, $u_0$ – the mean thermal velocity and $D$ – the CF diffusion coefficient assumed to be of 1.7 m$^2$ Pa s$^{-1}$ [1]. Hence, the total decay time $\tau$ depends on the total pressure $p$ as follows:

$$\frac{1}{\tau} = \frac{1}{A \cdot p + B} + C \cdot p$$  \hspace{1cm} (5)

($A$, $B$, $C$ – some constants).

In order to verify the dependence (5), the high time resolved plasma density traces were measured in the afterglow under various total pressures $p$, whereas other plasma conditions (rf power, flows of the feed gases and pulsing regime) were kept constant. The total loss rates $\langle \tau \rangle^{-1}$ found from these measurements are shown in figure 5. The uncertainty of the estimated $\tau$ values was typically of ± 2 ms, resulting in higher $\langle \tau \rangle^{-1}$ errors for shorter $\tau$. Unfortunately, the total pressure range had to be limited by ~ 30 Pa, since the CF decays obtained at higher pressures were too fast and noisy to be properly fitted with an exponential function. On the other hand, by the completely open butterfly-valve between the chamber and the rotary pump, a total pressure was settled at 3 Pa under selected gas flow conditions. Therefore, total pressures lower than 3 Pa could not be realized.

Figure 5 shows also the best fit of the obtained total loss rates $\langle \tau \rangle^{-1}$ by use of the equation (5). The contribution of the wall losses $\langle \tau_{\text{wall}} \rangle^{-1}$ was fitted according to (4) and is shown in figure 5 separately. As a parameter of the fit, the sticking coefficient $\beta$ was found to be of about 0.02, which correlates with low values for the CF sticking on the fluorocarbon thin films known from literature. Indeed, the addition of H$_2$ to the CF$_4$ process gas leads to a change of the fluorocarbon radicals known from literature. Indeed, the channel (II.) of the CF radical with F$_2$ molecule seems to be not decisive, since, in presence of hydrogen in plasma, the most of free fluorine would be normally bound into a chemically stable HF molecule. Therefore, the channel (I.), i.e. the CF consumption by the reaction with CF$_3$ radicals, might be responsible for the main loss of the CF radical in the gas phase.

Thus, as clearly seen in figure 5, the CF radical losses in the afterglow took place mainly in the gas phase, due to volume reactions with other species. According to [1], the following reactions may be considered as possible loss channels here:

I.  $\text{CF} + \text{CF}_3 \rightarrow \text{CF}_2 + \text{CF}_2$  
II.  $\text{CF} + \text{F}_2 \rightarrow \text{CF}_2 + \text{F}$  
III. $\text{CF} + \text{F} + \text{M} \rightarrow \text{CF}_2 + \text{M}$  
IV.  $\text{CF} + \text{F}_2 + \text{M} \rightarrow \text{CF}_3 + \text{M}$  
V.  $\text{CF} + \text{CF}_x + \text{M} \rightarrow \text{C}_2\text{F}_{x+1} + \text{M}$

The last three reactions (III–V) appear to be of minor importance, since a third collision partner M in the gas phase is required (unless the reactor wall acts as M). However, under considered low pressure conditions, the three-body collisions are very unlikely. Also the second reaction (II.) of the CF radical with F$_2$ molecule seems to be not decisive, since, in presence of hydrogen in plasma, the most of free fluorine would be normally bound into a chemically stable HF molecule. Therefore, the channel (I.), i.e. the CF consumption by the reaction with CF$_3$ radicals, might be responsible for the main loss of the CF radical in the gas phase.

Besides, there are two further channels of the CF
volume losses, due to reactions with molecules of the precursor gases:

VI. \( \text{CF} + \text{CF}_4 \rightarrow \text{products} \)
VII. \( \text{CF} + \text{H}_2 \rightarrow \text{products} \)

These reactions were proposed and their rate constants \( k \leq 1.0 \cdot 10^{-14} \, \text{cm}^3/\text{molecule s} \) were estimated in [13]. Although the upper limit of the rate constants \( k \) is quite low, the reactions (VI.–VII.) might actually contribute to the CF consumption, since new CF\(_4\) and H\(_2\) molecules were continuously fed into the chamber volume. The CF losses due to the suggested reaction channels (I.), (VI.) and (VII.) can be better specified and compared only after the complement measurements on the CF\(_3\), CF\(_4\) and H\(_2\) absolute density in the afterglow phase.

4. Conclusions

Absolute number density traces of the CF radical in the afterglow of CF\(_4\) + H\(_2\) cc-rf plasmas have been measured under various pressures with a high temporal resolution of 940 \( \mu s \). From the fit of the measured CF decays, the effective live times \( \tau \) were obtained and analyzed. Under selected conditions, chemical reactions in the reactor volume were found to be the dominant loss channels in the afterglow kinetics of the CF radical, whereas the diffusion towards the chamber walls and following surface reactions (sticking) seemed to be of minor importance.

In order to decide, whether CF\(_3\) radical or molecules of the precursor gases was the most effective reaction partner for the CF consumption, further measurements on their absolute number density in the afterglow phase are necessary.

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References