

Metastable CF and CF₂ molecules in CF₄ inductively-coupled plasmas

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Abstract

The radicals CF and CF₂, which are important intermediates in fluorocarbon plasma chemistry, both have low-lying metastable levels (⁴CF at 3.54 eV and ³CF₂ at 2.46 eV). Recent calculations (Rozum *et al* 2006 *J. Phys. Chem. Ref. Data* in press) indicate that electron-impact excitation of the

ground-state radicals into these states could be fast. A recent study of inductively-coupled plasmas (ICP) in low-pressure CF₄ (Booth *et al* 2005 *Plasma Sources Sci. Technol.* **14** 273) indicated the presence of a fast electron-impact induced loss process for ground-state CF and CF₂ molecules, which could be attributed to this process. In the current study ⁴CF and ³CF₂ were detected in the afterglow of ICP in pure CF₄ at pressures between 3 and 33 mTorr, from their weak forbidden optical emission back to their respective ground-states. From the lifetimes of these optical emission signals, determined as a function of gas pressure, the quenching coefficients at the chamber walls and the metastable destruction rates by gas-phase processes (giving unknown products) were estimated. Another prominent and long-lived feature of the afterglow is strong emission from the d state of C₂ molecules: the emitting C₂ molecules may be produced by chemiluminescent reactions or by excitation transfer from ³CF₂.

1. Introduction

Plasma discharges in fluorocarbon gases are widely used in the microelectronics industry for the etching of nanometre-scale features in thin SiO₂ films. They can also be used to modify the surface of polymers or to deposit fluorocarbon polymer films, which may be of use as low dielectric-constant insulators in integrated circuits. Free radicals, including CF and CF₂, play key roles in these deposition and etching processes. There have been a number of studies on the kinetics of these species in capacitively-coupled [3–5] and inductively-coupled plasmas (ICP) [6, 7]. In particular Abada *et al* [2, 8–10] have used laser-induced fluorescence (LIF) to determine the space and time resolved densities of these species in ICP in pure CF₄. Their results showed hollow CF and CF₂ ground-state density profiles, indicating the presence of a rapid gas-phase destruction process of these species and significant production of the ground-state radicals at the reactor top and bottom surfaces. The LIF technique also allowed the gas temperature to be measured and showed high gas temperatures

and temperature gradients in this system [9]. These must be taken into account when calculating diffusive transport [2]. Other groups have seen similar phenomena in ICP [6, 7], electron-cyclotron resonance (ECR) [11] and helicon [12, 13] reactors.

The gas-phase loss rates necessary to explain the observed hollow CF_x profiles are many hundreds per second, but the mechanism has not been convincingly identified so far. However, recent theoretical work on electron interactions with CF and CF₂ [1] has indicated that electron-impact excitation into low-lying metastable levels may be very rapid: if this is the case, the observations may be explained simply as excitation into metastable states, followed by diffusion to the reactor walls where these species are quenched back to their ground-states.

The metastable ³B₁ state of CF₂, which lies at 2.46 eV above the ground-state, was first observed as a product of the chemiluminescent reaction of oxygen atoms with tetrafluoroethylene [14], leading to a broad-band but structured emission back to the ground-state in the spectral region of 470–720 nm. Triplet CF₂ has subsequently been observed

as a product of the spin-forbidden excitation transfer from N₂ ($A^3\Sigma_u^+$) to ground-state CF₂ [15], but has not, to our knowledge, been previously observed as a product of direct electron-impact excitation of ground-state CF₂. Relatively little is known about the reactivity of $^3\text{CF}_2$: two molecules can undergo triplet–triplet annihilation [14] to form one ground-state CF₂ molecule and one A^1A_1 state CF₂ molecule (which relaxes rapidly to the ground-state by emission of a photon). Measurements have been made of the rates of reaction of $^3\text{CF}_2$ with O atoms [16], with O₂ molecules [17], with NO and H₂ [18] and with hydrocarbons [19], and the rate of collisional deactivation by He atoms has been estimated [16].

Although several theoretical studies [20–22] predicted the existence of a metastable quartet state of CF, only Grieman *et al* [23] have reported an experimental observation. In a dc flowing afterglow in He/CF₄ at 760 mTorr they observed the spin-forbidden emission from ^4CF to the ground-state at 350 nm, putting the state at 3.54 eV above the ground-state. Nothing is known of the reactivity of this species.

2. Experimental

The plasma reactor has been described previously [9]. Briefly, it is an ICP in a 15 cm radius, 5.3 cm high Al cylinder, with an alumina window at the top. Pure CF₄ gas was flowed through the reactor at 25 sccm, the pressure being regulated with a throttle valve in front of the turbo-molecular pump. The plasma is excited with a 4-turn flat pancake coil placed on the alumina window, powered at 13.56 MHz via an impedance matching network. The RF power (typically 250 W) could be turned on or off in less than 5 μs .

Light from the plasma was collected via a fused silica window at the reactor side and focused onto the entrance slit of a 30 cm monochromator, equipped with 1200 and 2400 l mm^{-1} gratings. The light was detected and analysed using an intensified CCD camera. The intensifier was triggered at different set delays after the extinction of the RF power and integrated over periods varying between 50 to 200 μs . The signal was accumulated for many trigger cycles to improve the signal to noise ratio.

3. Results and discussion

3.1. CF₂ metastables

A part of the emission spectrum (in the 540–590 nm spectral region) observed in the afterglow of a 3.5 mTorr CF₄ discharge at 250 W RF power is shown in figure 1, for various time delays. The signal was integrated for 0.2 ms after the trigger in each case. After the first 0.2 ms three emission bands can be seen clearly at 540.5 nm, 560.6 nm and 582.3 nm, corresponding to emission from $^3\text{CF}_2 \tilde{a}(0, 0, 0)$ to the ground-state $\tilde{X}(0, v_2', 0)$, with $v_2' = 2, 3$ and 4, respectively [14]. At the beginning of the afterglow the $^3\text{CF}_2$ emission spectrum is partially masked by intense structured emission that can be attributed to C₂ Swann band emission (d-a (2,3), (1,2) and (0,1) bands at 554.1 nm, 558.58 nm and 563.55 nm, respectively [24]). The stronger (0,0) band at 516 nm was also clearly observed in other experiments (not shown). There is some evidence of hot bands, particularly a strong band at 589 nm which decays

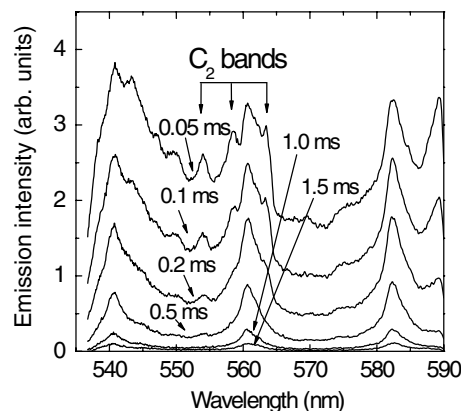


Figure 1. Optical emission in the afterglow of a 3.5 mTorr CF₄ discharge at 250 W RF.

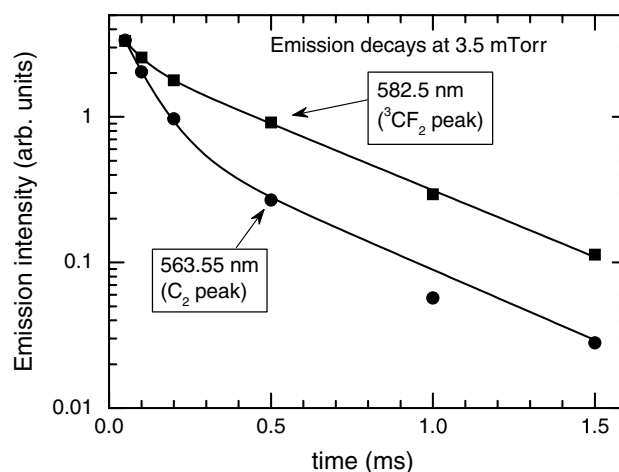


Figure 2. Decay rates of $^3\text{CF}_2$ and C₂ emission at 4 mTorr.

rapidly, which is possibly due to the (0,1,0)–(0,5,0) transition of $^3\text{CF}_2$.

The decays of the emission at a $^3\text{CF}_2$ peak (582.5 nm) and at a C₂ peak (563.55 nm, d-a (0,1)) are shown in figure 2. Both data sets were fitted to a sum of two exponential decays, using the same lifetimes, τ_1 and τ_2 , in each case but varying the relative intensities of the two contributions, c_1 and c_2 :

$$I = c_1 \exp(-t/\tau_1) + c_2 \exp(-t/\tau_2). \quad (1)$$

The decay at 582.5 nm ($^3\text{CF}_2$ peak) contains only a small contribution from the rapid component, and we therefore attribute the slower decay time of $\tau_1 \approx 0.52$ ms to $^3\text{CF}_2$. The emission at 563.55 nm (a C₂ peak) contains a much larger fast-decaying component ($\tau_2 \approx 0.11$ ms) superimposed on the slower decay of the underlying $^3\text{CF}_2$ signal. We therefore equate $\tau_2 \approx 0.11$ ms with the C₂ emitting state lifetime.

If the $^3\text{CF}_2$ decay is principally due to quenching at the reactor walls, the quenching probability, β , can be estimated from the observed decay rate. The relationship between the decay rate due to diffusion and quenching at the walls, k_{wall} , and the surface destruction probability is given by Chantry [25]:

$$\frac{1}{k_{\text{wall}}} = \frac{L(2 - \beta)}{\bar{v}\beta} + \frac{1}{D} \left(\frac{L}{\pi} \right)^2, \quad (2)$$

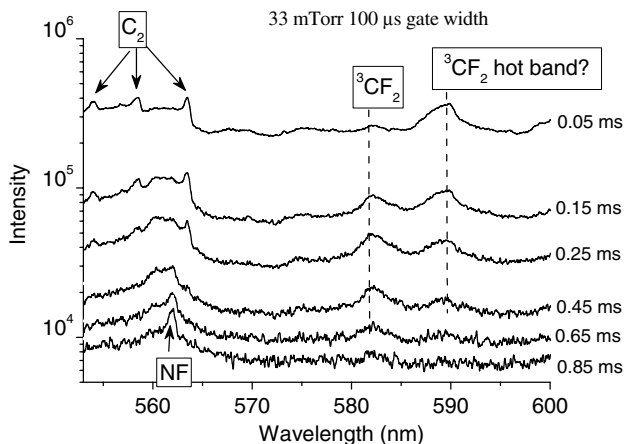


Figure 3. Optical emission in the afterglow of a 33 mTorr CF_4 discharge at 250 W RF.

where L is the reactor height (5.3 cm) and \bar{v} is the mean kinetic velocity ($4.4 \times 10^4 \text{ cm s}^{-1}$, assuming an average gas temperature of 450 K [9]), and D is the diffusion coefficient. At this low pressure diffusion will be fast and the second term can be ignored. This gives a value of $\beta_{^3\text{CF}_2} \approx 0.4$.

The observed 0.11 ms lifetime of the C_2 emission, which is much longer than the radiative lifetime of the emitting d state (170 ns), indicates that excited d-state C_2 continues to be produced in the afterglow, possibly by chemiluminescent reactions as observed in high-pressure CO discharges [26–28]. Alternatively, the excitation transfer reaction



is very close to resonant and could therefore be a source of excited C_2 molecules.

Emission spectra taken at the higher pressure of 33 mTorr are shown in figure 3 (log scale, spectral region 555–600 nm, with 100 μs integration time). Here the C_2 Swan band emission is very strong compared with the $^3\text{CF}_2$ emission: the only $^3\text{CF}_2$ band that is clearly observable is the transition to $\tilde{X}(0,4,0)$, at 582.3 nm. A sharp and long-lived band at 562.2 nm can be attributed to the b-X(0,1) band emission from metastable NF radicals [29], present due to a small amount of air leaking into the system (the much stronger (0,0) band at 528.8 nm was also observed in other experiments).

It is possible that in this case the $^3\text{CF}_2$ is highly vibrationally excited, and the apparent continuum is due to hot band emission. In particular, the band at 589 nm is again observed and is much stronger.

The $^3\text{CF}_2 \tilde{a}(0,0,0) \rightarrow \tilde{X}(0,4,0)$ emission at 582.3 nm decays non-exponentially, initially very fast but slowing down (figure 4). The decay was fitted with equation (1), giving time constants of about 0.06 and 0.35 ms. These loss rates are much faster than those observed at 3.5 mTorr. Under these higher pressure conditions diffusion to the walls will be slower (despite the higher gas temperature of 800 K cooling to 600 K in the first 0.5 ms of the afterglow [9]). Using equation (2) with $D(\text{cm}^2 \text{ s}^{-1}) = 65 \cdot (T/300)^{3/2} \text{ p(Torr)}^{-1}$ [30] and the value of $\beta_{^3\text{CF}_2}$ obtained above gives $k_{\text{wall}} = 1400 \text{ s}^{-1}$ at 800 K and 1100 s^{-1} at 600 K. Therefore this fast decay of $^3\text{CF}_2$ must be caused by a fast gas-phase process. Considering the

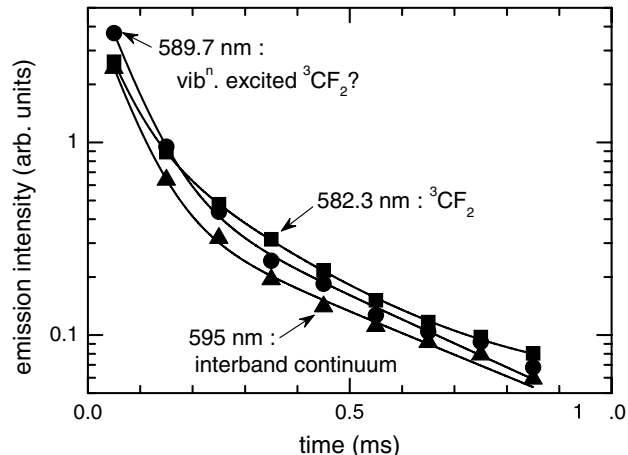


Figure 4. Decays of the optical emission at various wavelengths for the same conditions as figure 3.

period after 0.5 ms, a gas-phase loss rate of about 2000 s^{-1} is necessary in addition to the diffusive loss (1100 s^{-1}) to explain the observed loss rate of 3000 s^{-1} .

Now let us consider the possible mechanisms for gas-phase destruction of $^3\text{CF}_2$. The rate of quenching of $^3\text{CF}_2$ to $^1\text{CF}_2$ by CF_4 has not been measured, but by comparison with the rates measured in similar gases (C_3H_4 , C_3F_6 , C_3H_8 and iso- C_4H_8) [19] we can estimate a value of around $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This would lead to a first order $^3\text{CF}_2$ removal rate of about 100 s^{-1} in 33 mTorr CF_4 at 600 K, which is negligible compared with the rates observed here. A process that could be very rapid is chemical quenching with atomic fluorine:



We can estimate the rate of this reaction from the analogous quenching reaction of NO [18], which has a rate constant of about $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 500 K. An F atom density of $1 \times 10^{14} \text{ cm}^{-3}$ (a mole fraction of 20%) would be adequate to explain the observed $^3\text{CF}_2$ decay.

The very fast initial decay is more difficult to explain. Possibly the apparent continuum emission which decays very rapidly is not from $^3\text{CF}_2$ but is in fact from another (unidentified) short-lived emitter, possibly a product of electron–ion recombination. Alternatively it could be a rapid process with a significant activation energy which is therefore fast at 800 K but much slower at 600 K.

The production rate of $^3\text{CF}_2$ by electron-impact on ground-state CF_2 can be estimated from the cross-sections given by Rozum *et al* [1] (threshold 2.5 eV, peak value $1 \times 10^{-20} \text{ m}^2$ at 6 eV), assuming [9] a Maxwellian electron energy distribution at 3 eV and an electron density of $4 \times 10^{10} \text{ cm}^{-3}$, giving an excitation rate of 245 s^{-1} . The reverse (super-elastic) electron-scattering process should have a comparable cross-section (but weighted by the ratio of the electronic degeneracies of the states, favouring excitation). However, we observe loss rates far in excess of this rate due to surface and gas-phase chemical processes, so that this process can be neglected, and the population of $^3\text{CF}_2$ will not be in equilibrium with the electron temperature.

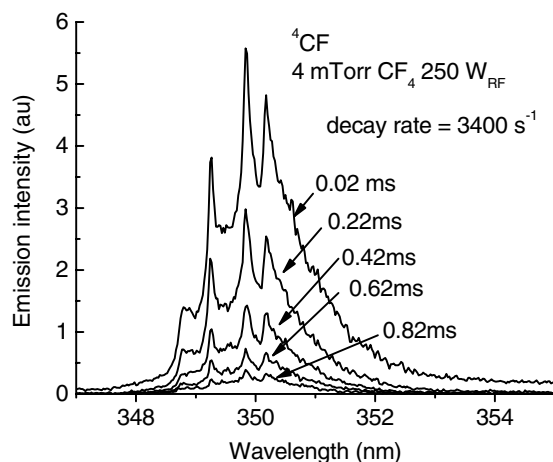


Figure 5. ⁴CF emission in a 4 mTorr CF₄ plasma.

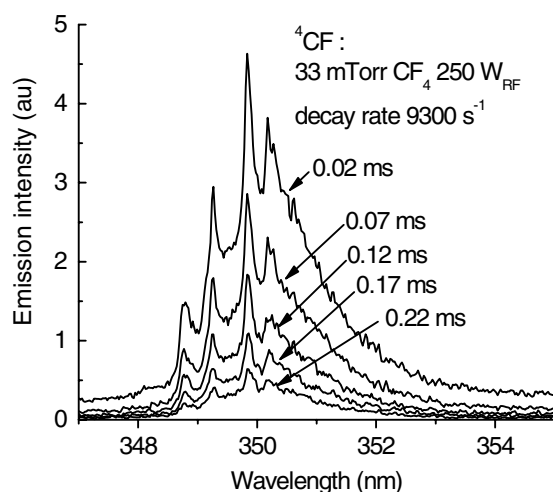


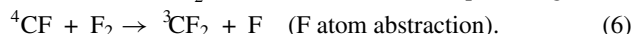
Figure 6. ⁴CF emission in a 33 mTorr CF₄ plasma.

3.2. CF metastables

Figure 5 shows the optical emission in the 350 nm region from the afterglow of a 4 mTorr discharge in CF₄ at 250 W. This spectrum can clearly be identified as the (0,0) band of the a–X transition as assigned by Grieman *et al* [23]. The same band-heads are observed, although the shape of the bands is somewhat different due to the higher gas temperature (about 550 K [9]) in this case. The (1,0) band was also clearly observed at 367 nm. Under these conditions the emission decayed exponentially at a rate of 3400 s⁻¹. Grieman *et al* made a theoretical estimate of the a-state fluorescence lifetime of 14 ms, whereas they observed a lifetime of about 2 ms (which may, however, have been shortened by collisional quenching). If we consider therefore that radiative decay and gas-phase collision processes are negligible at this low pressure, the quenching probability at the walls can be estimated from equation (2) to give a quenching probability at the reactor walls of $\beta_{4\text{CF}} \approx 0.5$.

Figure 6 shows the ⁴CF emission spectra observed at the higher pressure of 33 mTorr. The spectra are very similar to those at 4 mTorr, although a close examination shows that this spectrum is slightly broader and has different relative band-head intensities due to the higher gas temperature (of the order

of 800 K [9]). The emission intensity (cps extrapolated to the start of afterglow) is about twice as high and decays much faster, at a rate of 9300 s⁻¹, indicating the presence of a very fast gas-phase process destroying ⁴CF (if surface processes dominated the loss then the decay rate would be expected to decrease with gas pressure). Two gas-phase processes can be proposed for this rapid ⁴CF destruction:



Both these reactions are strongly exothermic (3.54 eV and 4.8 eV, respectively, for (5) and (6)) and are expected to be very fast [31], with rate constants approaching the gas-kinetic limit of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. Although reaction (6) involves a closed-shell reactant, the activation energies for atom-transfer reactions decrease with exo-thermicity, and one would expect it to be quasi-barrierless. For comparison, the analogous reaction of ground-state CF [32], which is much less exothermic (1.25 eV), has a rate constant of 4 × 10⁻¹² cm³ molecule⁻¹ s⁻¹.

With these reaction rates a combined density of ([F] + [F₂]) ≈ 10¹⁴ cm⁻³ would account for the observed ⁴CF decay rate: these densities are reasonable, representing about 20% of the total gas density. If reaction (6) is important it will contribute to ³CF₂ formation, making the ³CF₂ lifetime at least as long as that of ⁴CF. However, this is not inconsistent with the observations (³CF₂ lifetime 0.35 ms, ⁴CF lifetime 0.11 ms at 33 mTorr).

The excess energy of reaction in both the cases will be distributed between kinetic energy and internal (vibrational) energy of the products (the vibrationally-excited intermediate ³CF₂* in reaction (5) will dissociate rapidly before losing any energy in collisions). Previous measurements of CF and CF₂ UV absorption spectra in fluorocarbon plasmas [33, 34] have indeed indicated the presence of vibrational excitation.

The rate of electron-impact excitation of ground-state CF into the quartet level can be estimated from the cross-sections given by Rozum *et al* [1] (peak value 0.9 × 10⁻²⁰ m² at 6.5 eV), assuming [9] a Maxwellian electron energy distribution at 3 eV and an electron density of 4 × 10¹⁰ cm⁻³, giving an excitation rate of $k_{\text{ex}} = 139 \text{ s}^{-1}$. Taking a ground-state CF density of the order of 1 × 10¹³ cm⁻³ at 33 mTorr [2] and an effective quartet state destruction rate of $k_{\text{loss}} \approx 10^4 \text{ s}^{-1}$, we estimate the quartet state density to be of the order of $k_{\text{ex}} \cdot [{}^2\text{CF}] / k_{\text{loss}} \approx 10^{11} \text{ cm}^{-3}$.

4. Conclusions

The metastable molecules ⁴CF and ³CF₂ have been detected in a low-pressure ICP in CF₄. Electron-impact excitation of ground-state molecules is expected to be fast and accounts for the presence of these species. At the lowest pressures these species are lost by quenching at the reactor walls, with probabilities of about 0.5 and 0.4, respectively. At higher pressures fast gas-phase chemical quenching appears to become important.

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