Alix-surprise

N2(V-V) Mario Capitelli (> 1987)

THESE DE DOCTORAT D'ETAT
ès SCIENCES PHYSIQUES

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L'UNIVERSITE PIERRE ET MARIE CURIE
PARIS 6

pour obtenir le grade de

DOCTEUR ES SCIENCES

par

ALIX GICQUEL

ETUDE DES PROCESSUS CATALYTIQUES HETEROGENES DANS LES MILIEUX PLASMAS BASSE PRESSION HORS-EQUILIBRE

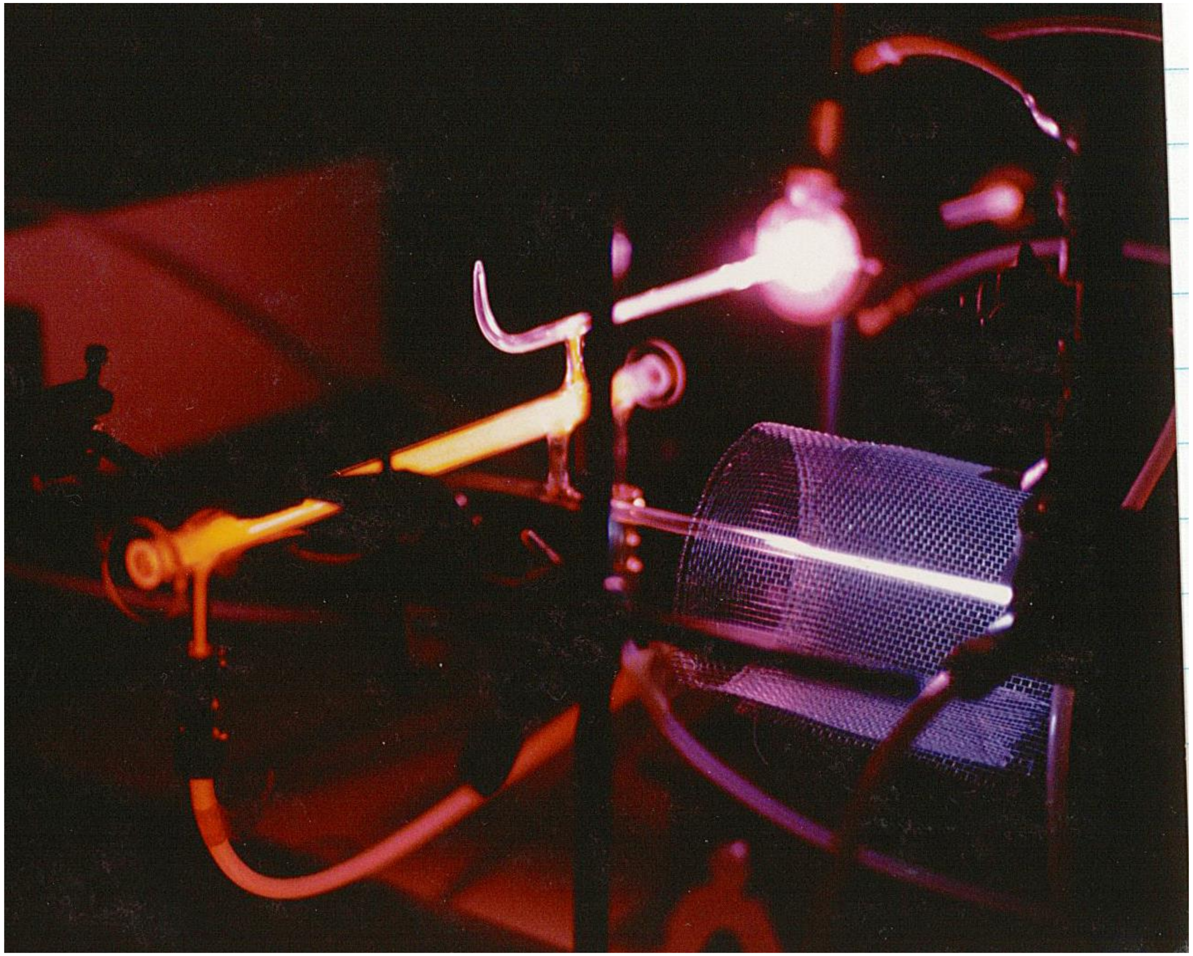
Soutenue le 1987, devant le jury composé de :

MM.	J. TALBOT	Président d'Honneur
	R. COLLONGUES	Président
	P. FAUCHAIS	Rapporteur
	A. RICARD	Rapporteur
	J. AMOUROUX	Rapporteur
	J. MILLET	Examinateur
	C. BOIZIAU	Examinateur
	D. RAPAKOULIAS	Examinateur
	F. CRAMAROSSA	Invité
	M. GOLDMAN	Invité

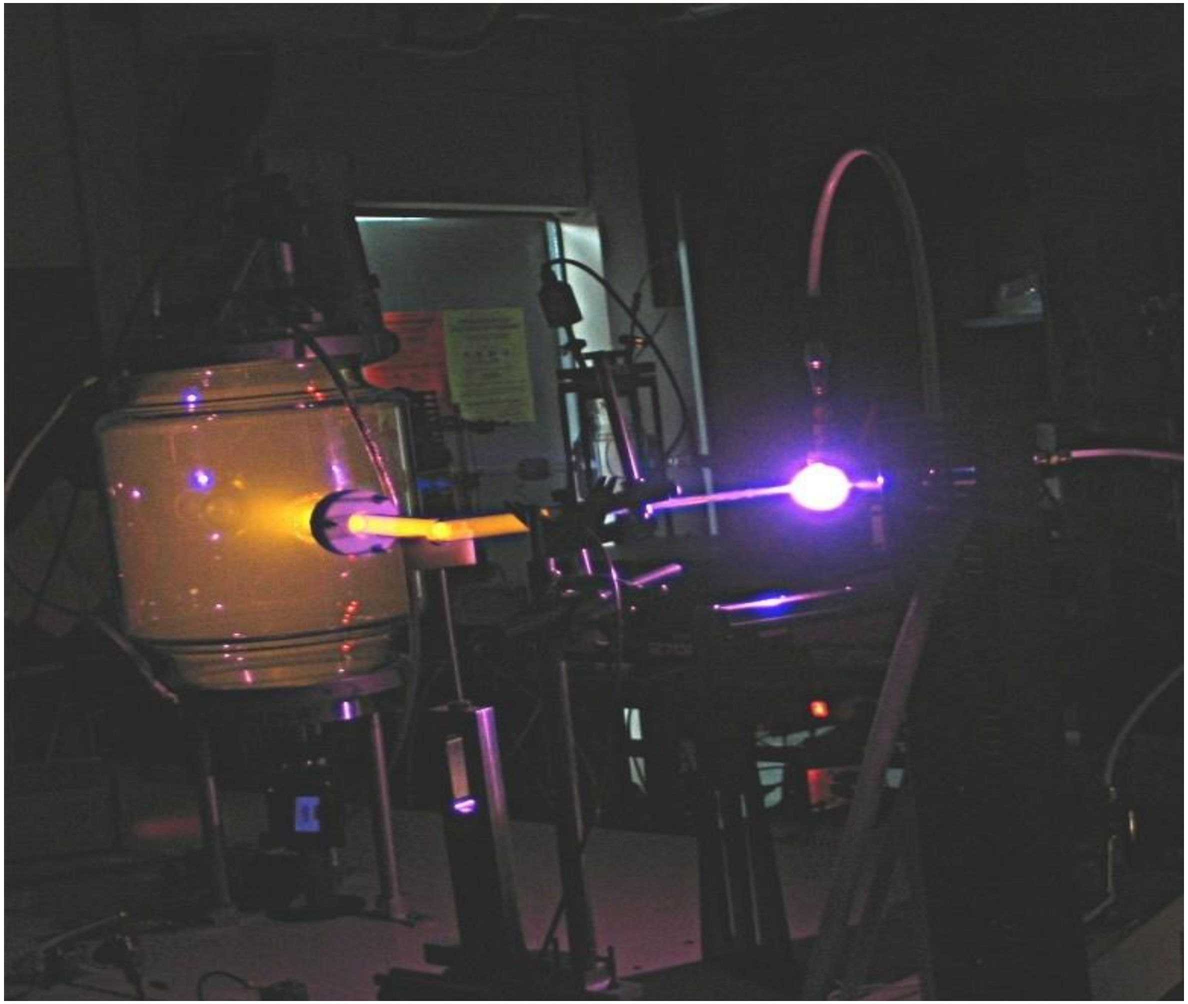
Alix-surprise

Montréal (90th) -Michel Moisan(>75)

Double Ar-N2 and Ar-H2-CH4 microwave afterglows



Microwave flowing afterglow in Laplace-Toulouse



Main kinetics reactions in the early afterglow : N-atom density

1 - In late afterglow , $N + N + N_2 \rightarrow N_2(B,11) \rightarrow N_2(A,7) + h\nu(580nm)$

- $I^m(580) = c(580)\, hc/580\, A_{580}\, [B,11]$ with $[B,11] = [N]^2 [N_2]\, k_a / (\nu_r^{B,11} + [N_2]\, k_{N2}(B,11))$

As : $\nu_r^{B,11} < [N_2]\, k_{N2}(B,11)$ at p> 4 Torr , it comes :

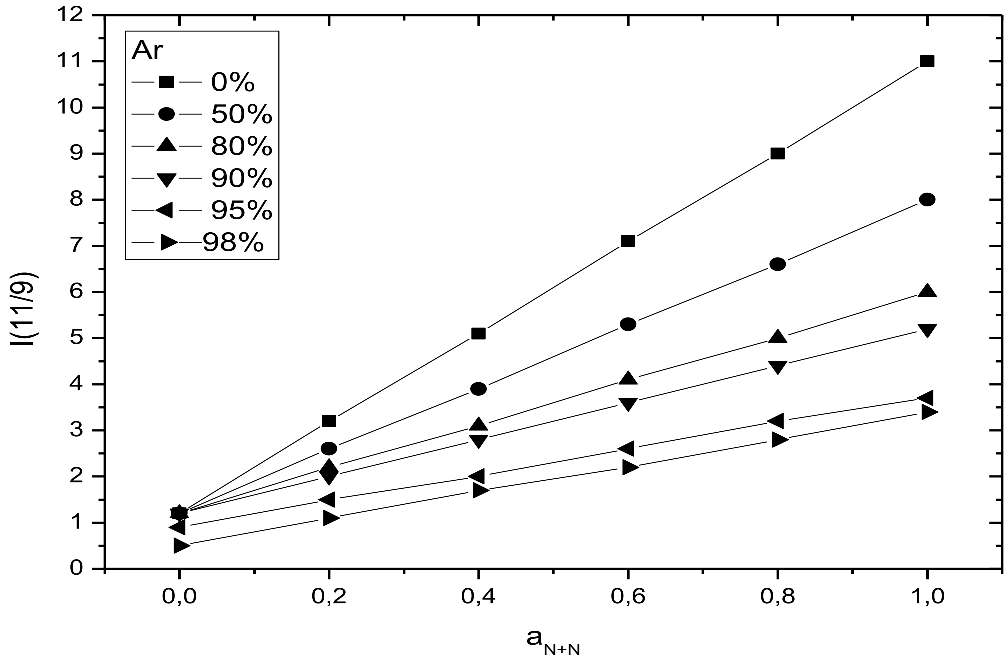
$I^m_{580} = c(580)\, hc/580\, A_{580}\, k_a\, [N]^2 / k_{N2}(B,11) = k_1 [N]^2$

Calibration of N-atom density by NO titration

2 - In early afterglow , part a_{N+N} of N+N recombination in I^m_{580}
determined from I(11)/I(9) intensity as deduced from calculated R(B,v'') :

$a_{N+N}\, I^m_{580} = k_1 [N]^2$

N-atom titration by NO by introducing Ar-2%NO before the 5 litre reactor : $a_{N+N} = 1 \rightarrow k_1$



Titration of N – atoms by NO

Case of pure N_2 afterglow

Introducing NO (Ar – 2% NO) in the N_2 post-discharge :

$N + NO_{ext} \rightarrow N_2 + O$

At low Q(NO_{ext}) , it remains N – atoms :

$N + O + N_2 \rightarrow NO\ (B) + N_2$

$NO\ (B) \rightarrow NO\ (A) + h\nu$ (NO_β, 320 nm)

At high Q(NO_{ext}), only O atoms from N atoms :

$O + NO_{ext} + N_2 \rightarrow NO_2^* + N_2$

$NO_2^* \rightarrow NO_2 + h\nu$ (continum, 550 nm)

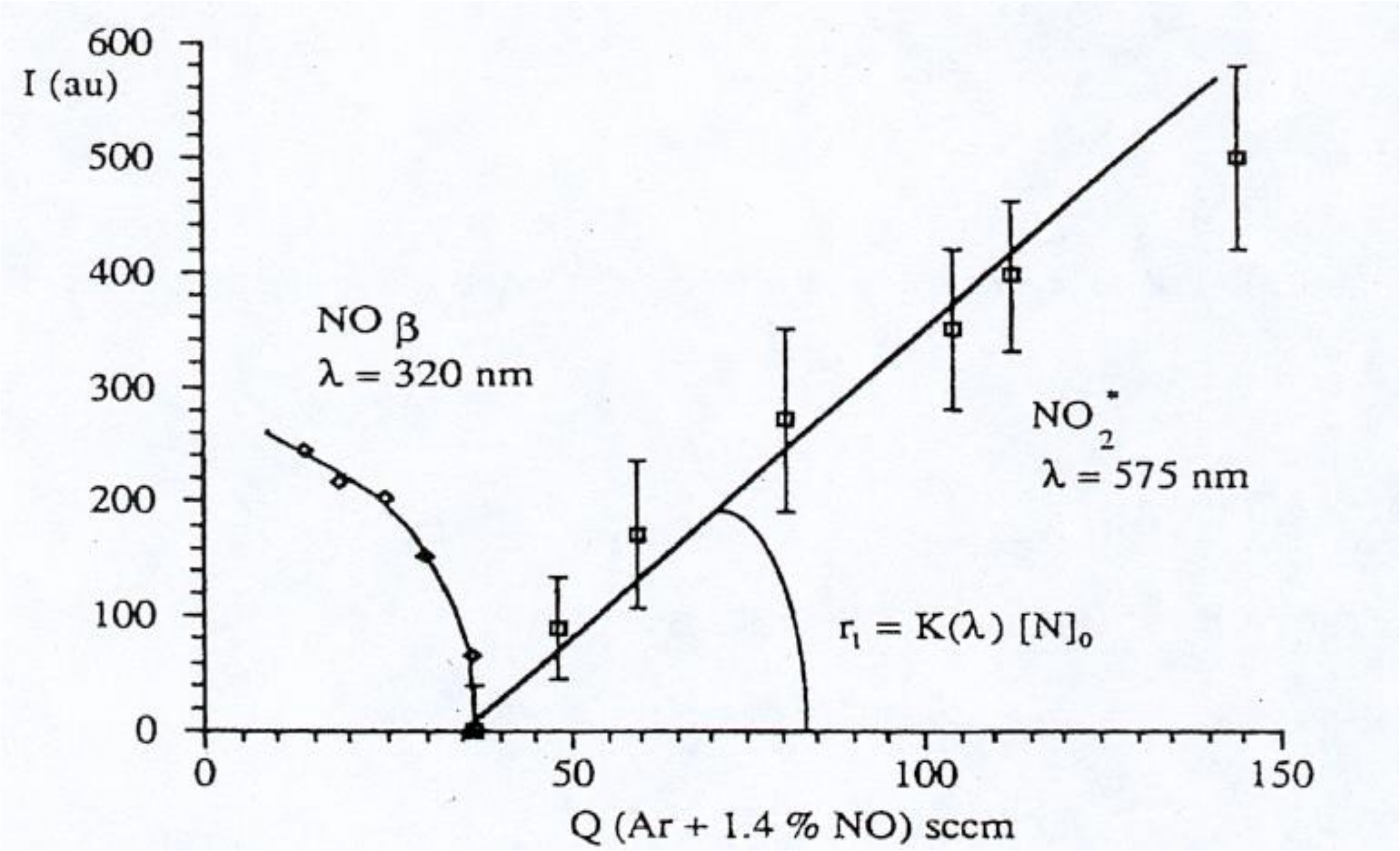
Afterglow extinction : Q(NO_{ext}) = Q(N)

$[N] / [N_2] = Q(N) / Q(N_2)$

Titration of N –atoms in Ar-4%N_2 post-discharge : [N] = 7 10^{13} cm-3

Conditions 2.3 Torr , 0.5 slm , 130 Watt

(T.Czerwiec et al. J.Phys III 6 (1996) 1205)



Alix surprise
Line ratio intensity (90th)

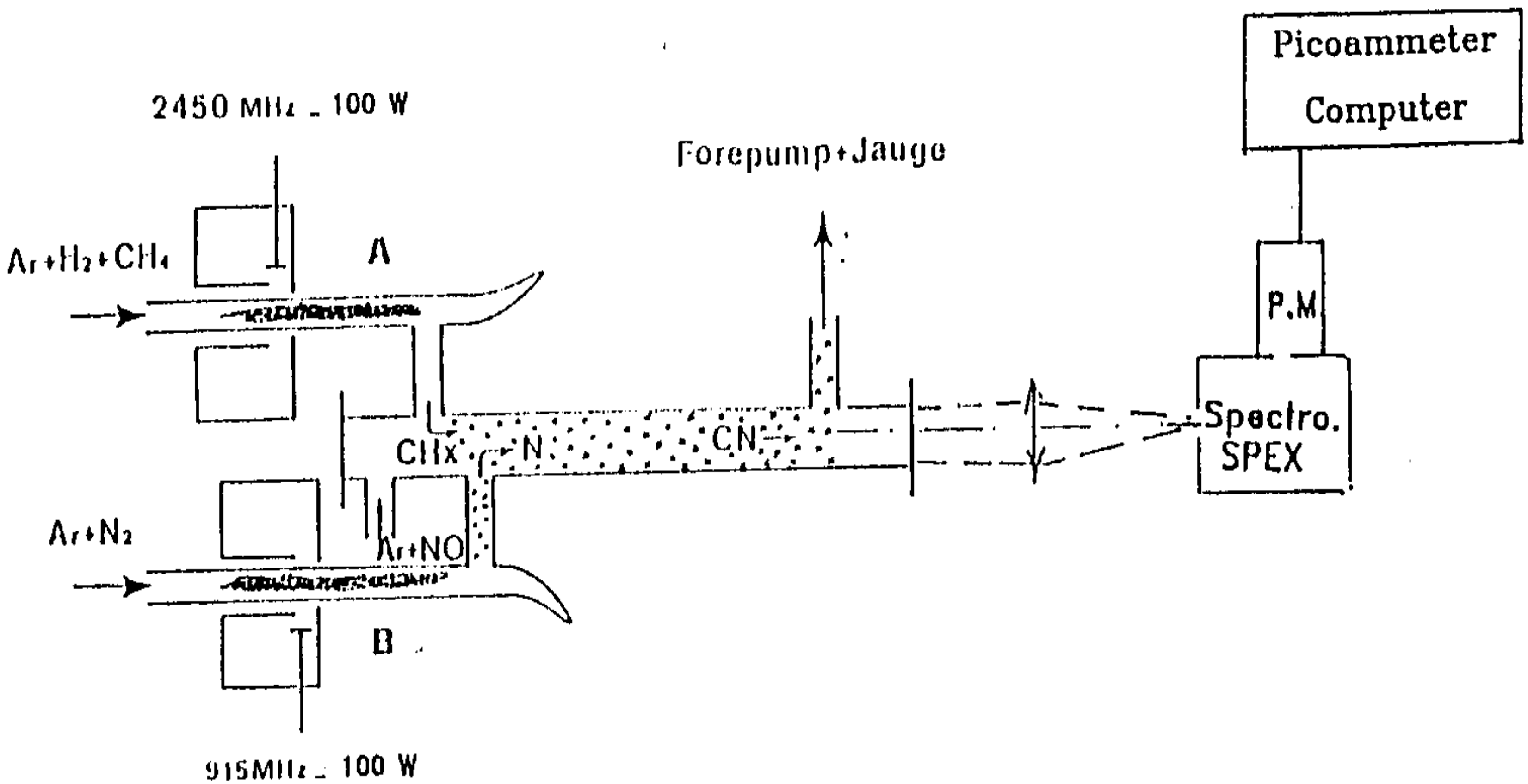
ASI- Workshop Microwave Discharges
Vimeiro (Portugal 1992)

PRODUCTION OF ACTIVE SPECIES IN FLOWING MICROWAVE DISCHARGES FOR IRON SURFACE TREATMENT AND DIAMOND FILM DEPOSITION

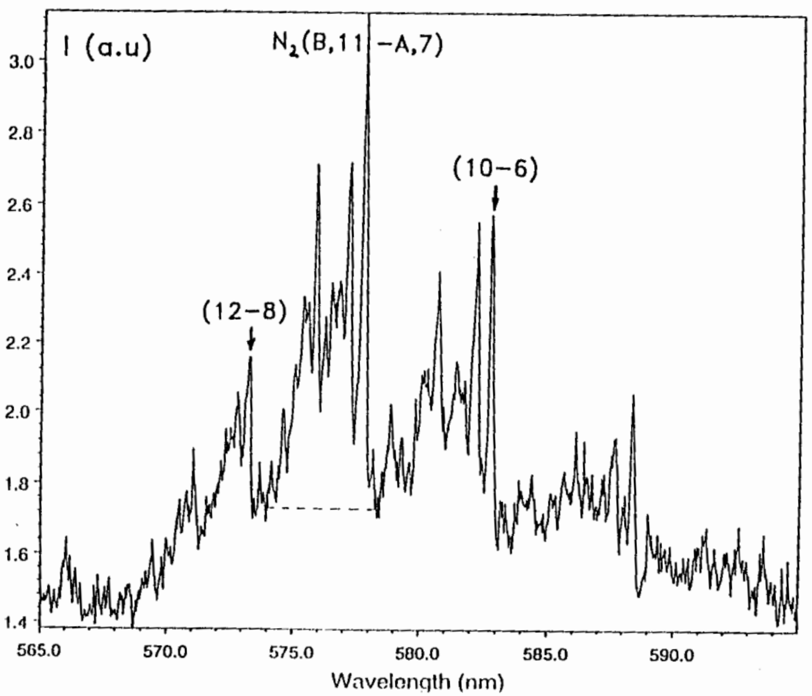
A. Ricard [1], A. Gicquel [2], H. Malvos [3], H. Michel [3],
S. Bordeleau [4] and J. Hubert [4]

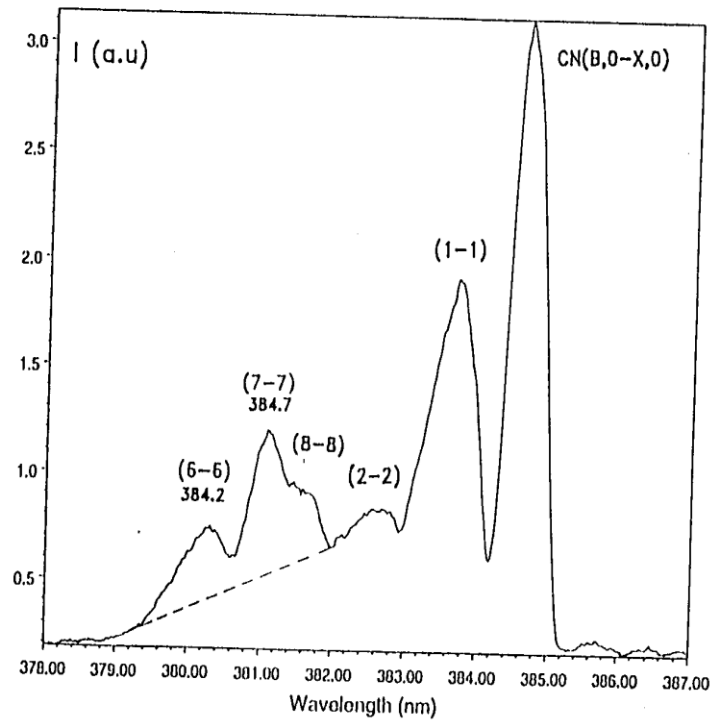
[1] L.P.G.P. - C.N.R.S. - Bâtiment 212 - Université Paris-Sud 91405 Orsay
[2] L.I.M.H.P.- C.N.R.S.- Université Paris-Nord - 93430 Villetaneuse
[3] L.S.G.M. - C.N.R.S. - École des Mines - 54042 Nancy
[4] Chimie, Université de Montréal, C.P. 6128, Montréal, H3C 3J7, Canada

Alix surprise
Line ratio intensity (90th)



Alix surprise
Line ratio intensity (90th)





Line ratio intensity method

$$\mathbf{a_{N+N} \,.\, I_{580} = k_1 [N]^2} \qquad (1)$$

with $k_1 = \frac{c(580)}{580} A_{N_2(A,7)}^{N_2(B,11)} \frac{k_b[N_2]}{(\nu_{N_2(B,11)}^{R} + [N_2] k_{N_2(B,11)}^{Q})}$

$C + N + N_2 \rightarrow CN(B,7) + N_2$ (a)

with $k_a = 9\ 10^{-33}\ cm^6 s^{-1}$ [10].

$$\mathbf{I_{385} = k_2\ [C][N]} \qquad (2)$$

with $k_2 = \frac{c(385)}{385} A_{CN(X,7)}^{CN(B,7)} \frac{k_a[N_2]}{(\nu_{CN(B,7)}^{R} + [N_2] k_{CN(B,7)}^{Q})}$

$$\mathbf{a_{N+N} \cdot \frac{I_{580}}{I_{385}} = \frac{k_1}{k_2} \frac{[N]}{[C]}}$$

Alix surprise
Line ratio intensity (90th)

Table 2. Intensity ratio $I^t_{CN} / I^t_{N_2}$, k-values, nitrogen and carbon atom densities in the post-discharge of a%Ar–b%H_2–1.3%CH_4 and Ar–16%N_2 discharges.

Gas composition a%Ar, b%H_2					
a%, %b	100, 0	75, 25	50, 50	25, 75	0, 100
$I^t_{CN} / I^t_{N_2}$	14.5-19.3	9.1	8	7.9	7-7.5
k (10^{-4})	1.11	0.93	0.86	0.78	0.72
[N] (10^{15} cm^{-3})	1.35	1.1	1.1	1	1
[C] (10^{12} cm^{-3})	2.1-2.9	0.9	0.8	0.6-0.7	0.6

Pressure : 25 Torr, Flow rate = 0.68 $SL.min^{-1}$

Alix surprise
Line ratio intensity (90th)

constant N-atom density with x= 0-2,5%

Table 3. Nitrogen and carbon atom densities in the post-discharge of (Plasma-A) : H_2–x%O_2–1.3%CH_4 and (Plasma-B): Ar–16%N_2 discharges.

x% (O_2) (%)	0	0.25	0.63	1.25	2.5
[N] (10^{15} cm^{-3})			1.1		
[C] (10^{11} cm^{-3})	3.9	4.1	4.5	3.3	1.6

Pressure : 23 Torr, Flow rate = 0.68 SL.min^{-1}

Alix surprise
diamond films (1990th)

Silicon (100) substrates, whose surface was initially roughened with diamond powder, were introduced inside the discharge tube of plasma (A) (Fig. 1). Treatments of 2 h of the samples were performed in H_2–x%O_2–1.3%CH_4 plasmas at 80 Watts, 25 Torr and 0.08 $SL.min^{-1}$. The surface temperature of the silicon substrate was estimated by optical pyrometry to be 1500 K. In the absence of oxygen (x = 0%), no diamond crystals were observed by optical microscopy. However with x = 0.25% and 0.65% O_2, well defined diamond crystals were detected by Raman spectrometry. The Raman spectrum exhibits the characteristic diamond peak at 1333 cm^{-1} as shown in Figure 6.

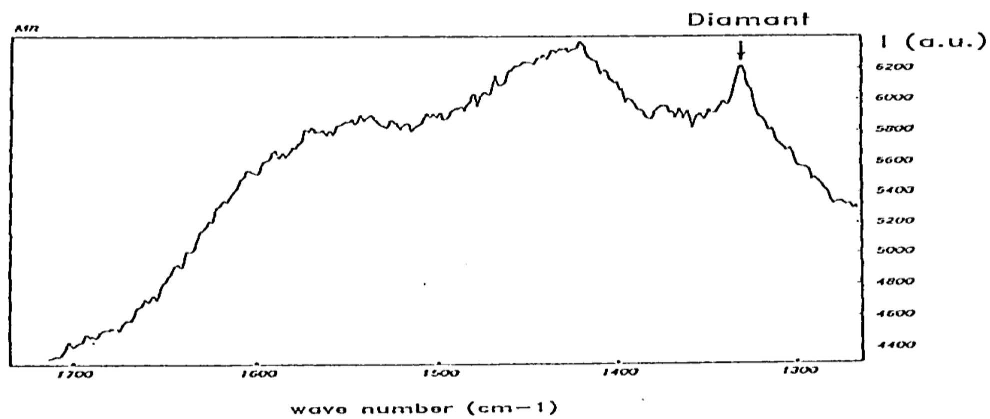
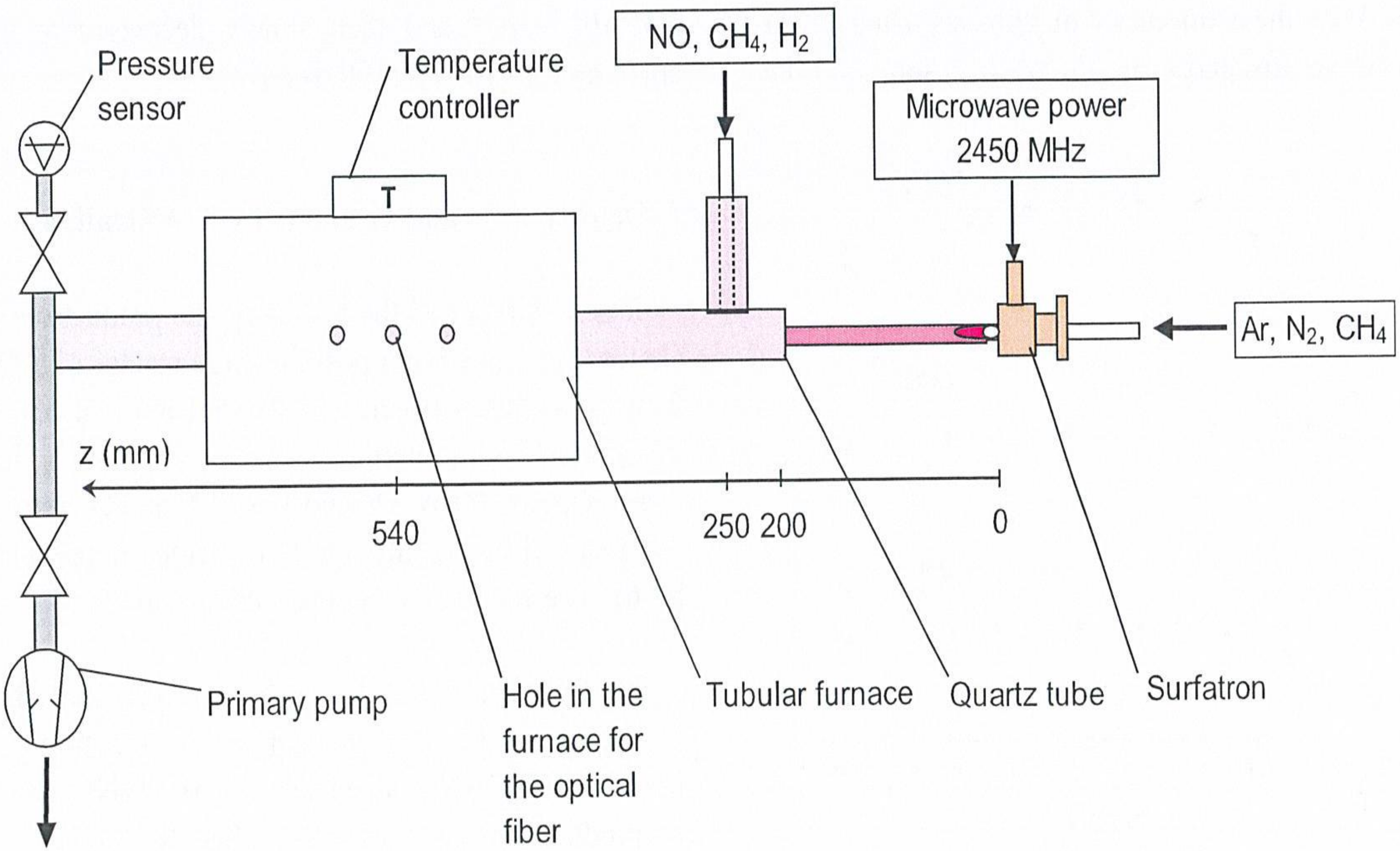


Figure 6. Raman spectrum of diamond film deposited on a silicon (100) substrate inside a (A) H_2–0.25%O_2–1.3%CH_4 microwave discharge at 80 Watts and 25 Torr.

The obtained diamond peak is however weak in intensity and a broad continuum is observed between 1400 and 1600 cm^{-1}. This continuum can be related to an amorphous compound such as polyacetylene.[9]

The experimental set up used was not intended for diamond film deposition and was certainly not optimum. The discharge tube diameter is too small (internal diameter of 4 mm) and therefore the plasma produces an important etching of the fused silica tube walls. However, it is was interesting to find that the gas mixtures, the operating pressure and the power density of the microwave discharge could produce some diamond film deposition.

Afterglow in Ar-N2-CH4
Nancy-Toulouse (2000 th)



. 3. Postdischarge reactor (quartz tube of dia. 2.6 cm, length 60 cm) for iron nitrocarburizing inside an external furnace. Titration by NO at the beginning of postdischarge tube.

Afterglow in Ar-N2-CH4
Nancy-Toulouse (2000 th)

Production of N, H, O, and C atoms in flowing microwave discharges

A. Ricard, C. Jaoul, F. Gaboriau N. Gherardi S. Villeger

(Surface & Coatings Technology 188–189 (2004) 287– 293)

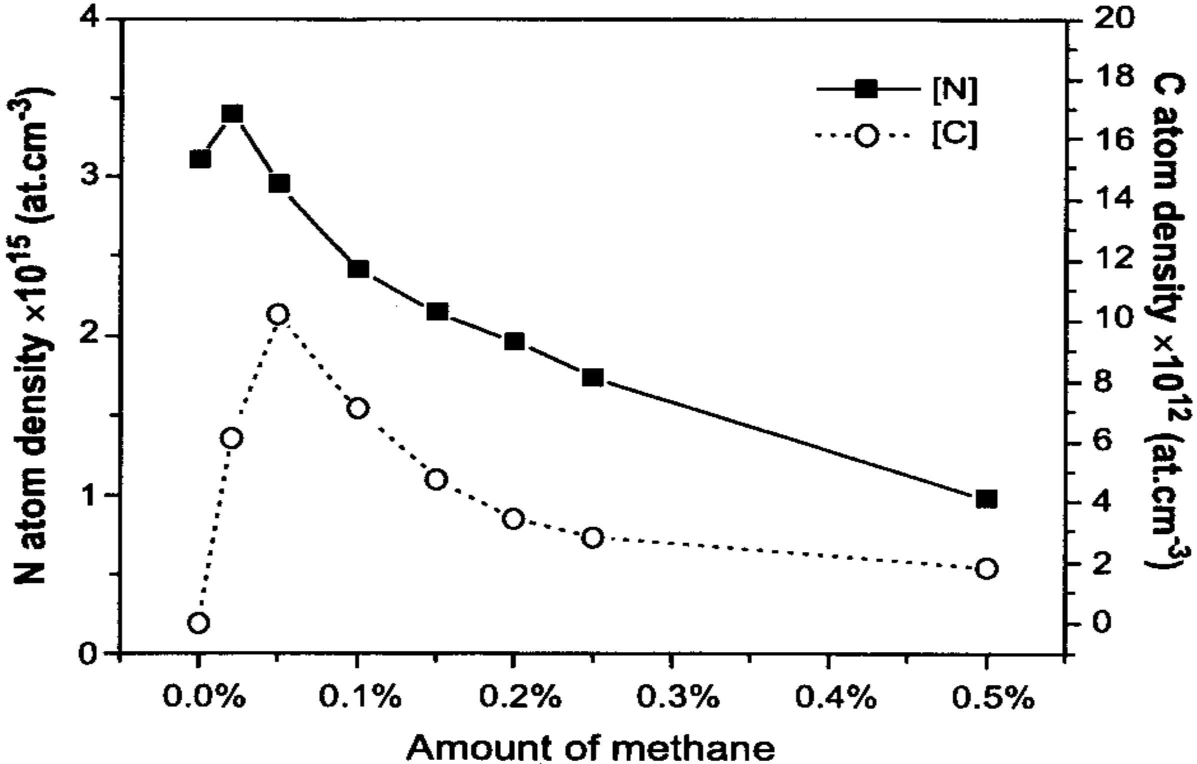


Fig. 8. Density of N and C atoms versus CH_4 percentage into N_2, at 150 W, 2.6×10^3 Pa (20 Torr), and 1 slm.

Afterglow in Ar-N2-CH4
Nancy-Toulouse (2000 th)

- **Production of N, H, O, and C atoms in flowing microwave discharges**

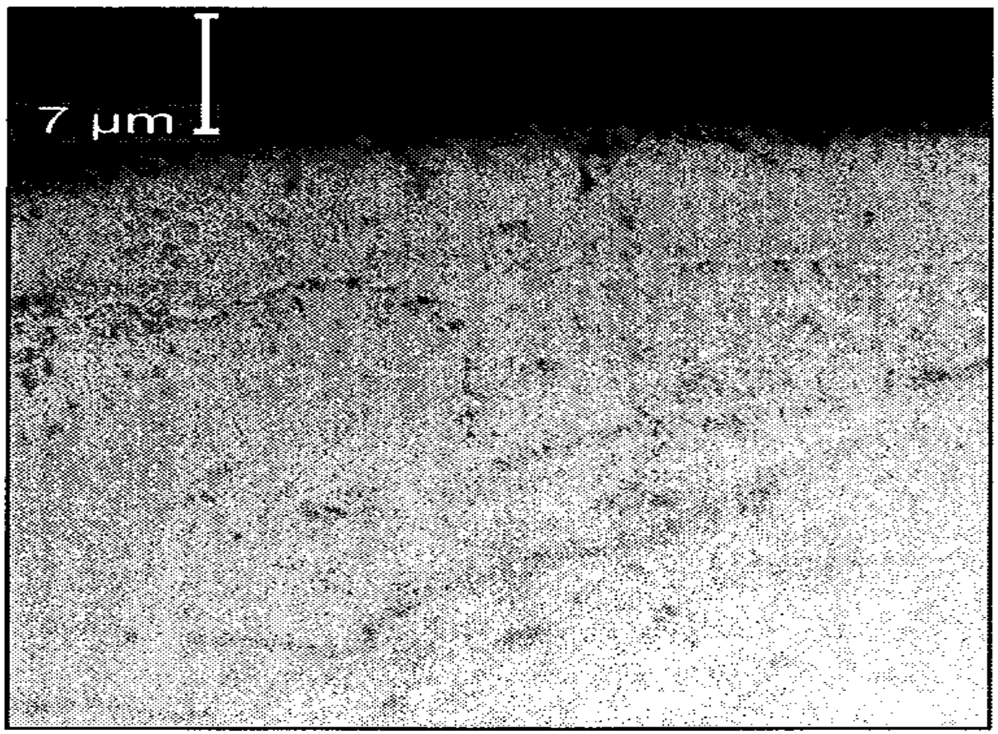
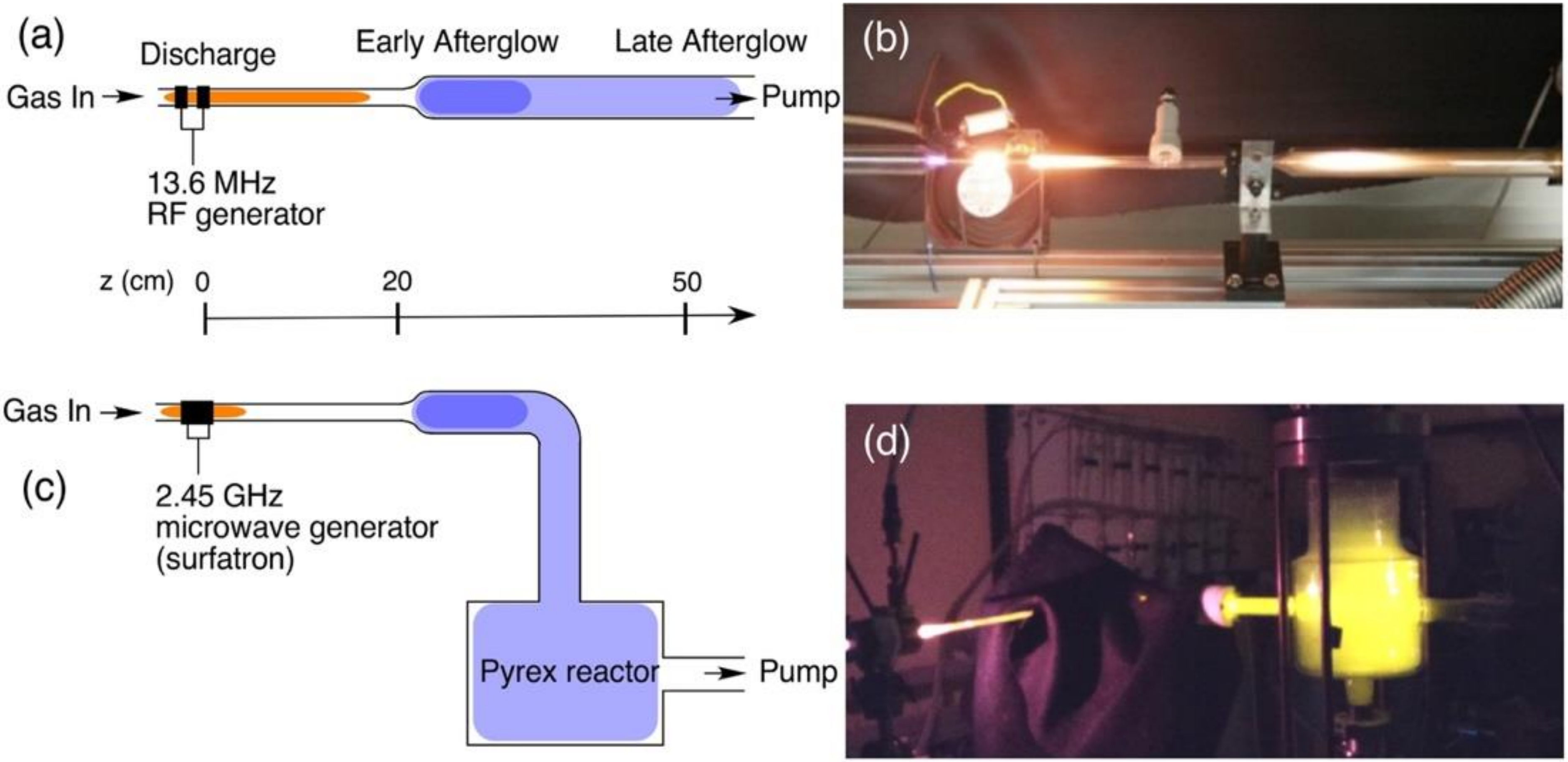


Fig. 9. Micrograph of iron surface after a treatment by a N_2–0.05%CH4 gas mixture at 823K during 2 h, at 150 W, 4.2×10^3 Pa (32 Torr), and 1 slm; $\varepsilon+\gamma'$ layer of 5–6 μm and α layer inside; 1%C in the $\varepsilon+\gamma'$ layer.

Afterglows Ajou-Toulouse (2010-17)



Afterglow in Ar-N2-CH4
Ajou-Toulouse

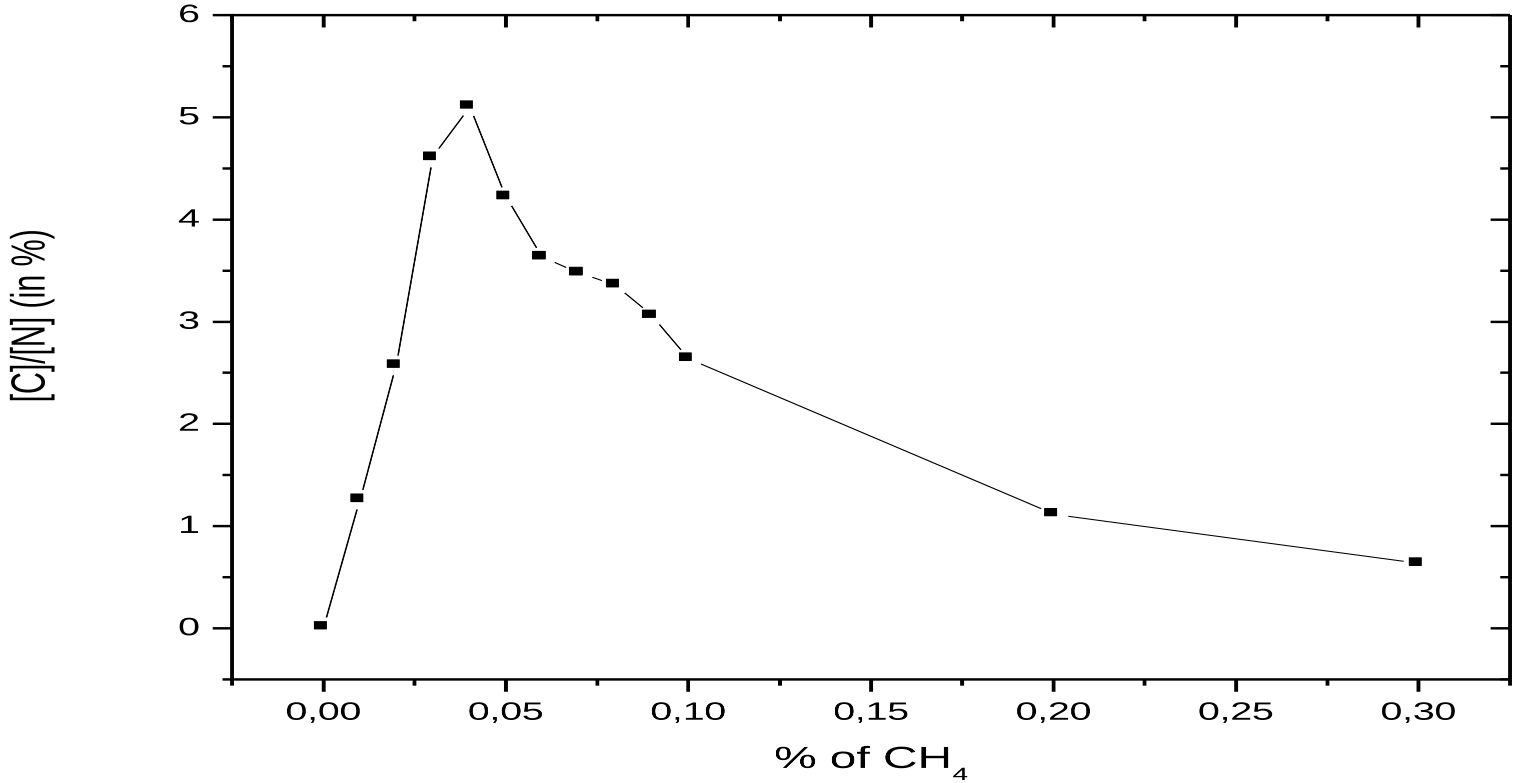


Figure 3. *Variation of the [C]/[N] density ratio for HF afterglows at p = 13 Torr, z = 50 cm, Q = 0.5 slpm and* P_{HF} *= 100 W.*

Afterglow in Ar-N2-CH4

Ajou-Toulouse

b)

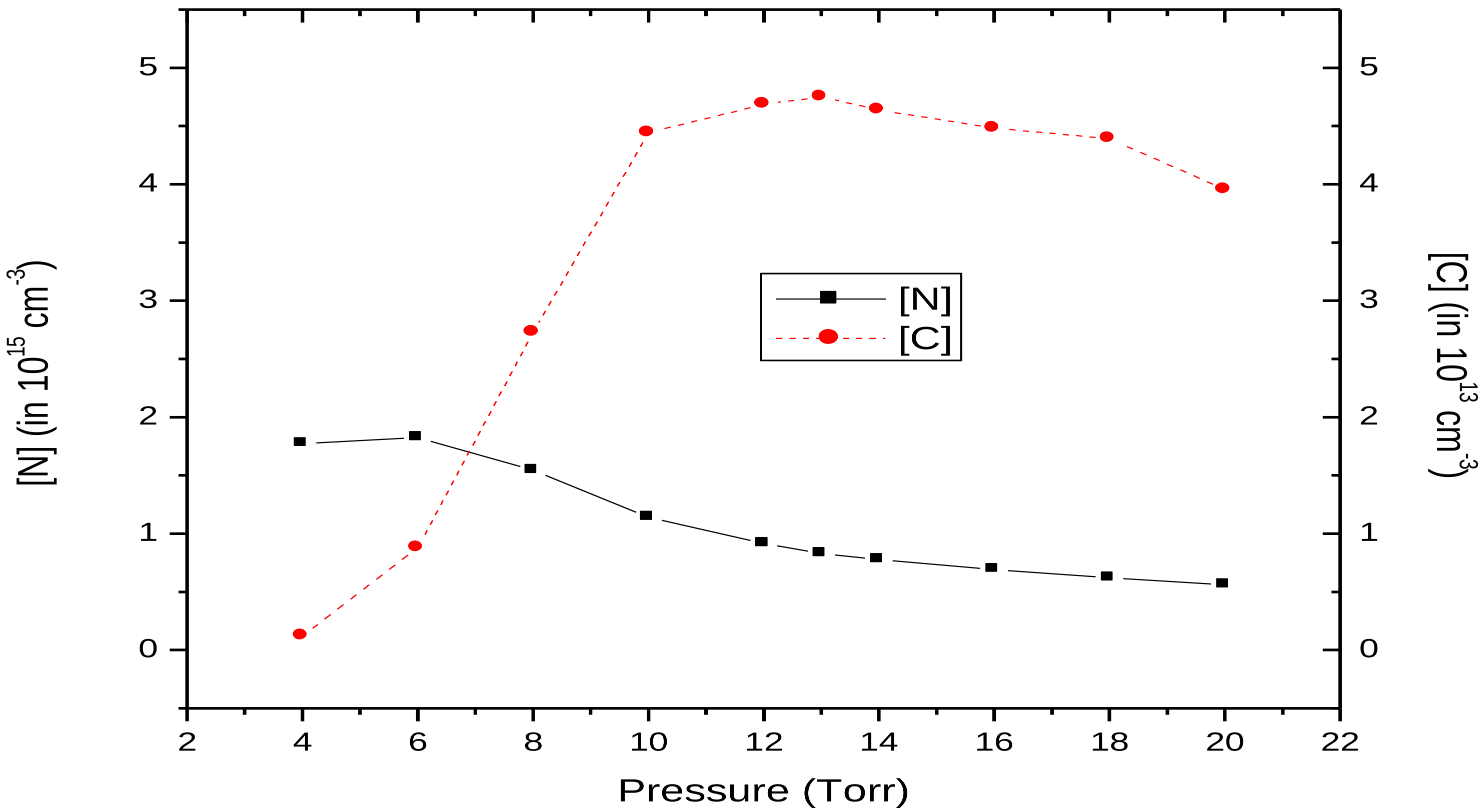
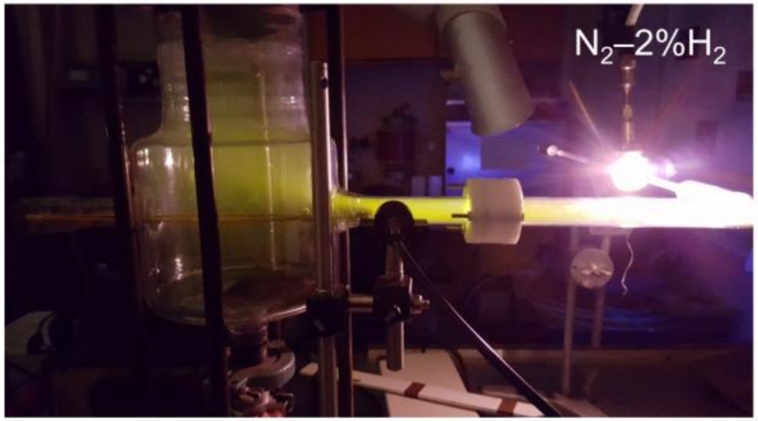


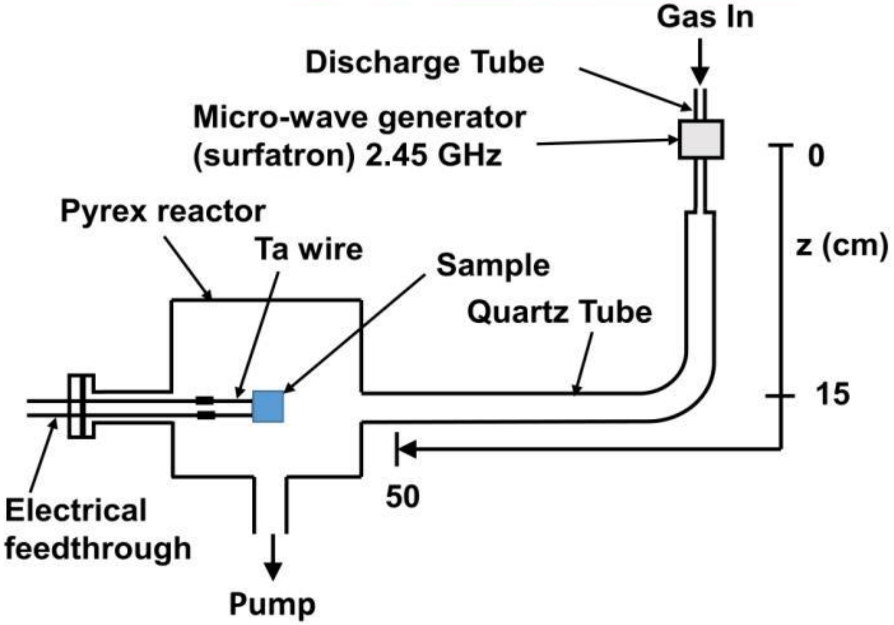
Figure 4. *[C] and [N] densities measured at z = 50 cm for the N_2 / 0.04% CH_4 versus pressure. (Q = 0.5 slpm and P_{HF} = 100 W)*

Afterglow in N2-H2
Ajou-Toulouse

Enhanced nitriding of anatase TiO2 films by the addition of H2 in the N2 microwave plasmas

Yunfei Wang, Andre Ricard, Jean-Philippe Sarrette, Ansoon Kim, Seol Ryu and Yu Kwon Kim





Afterglow in N2-H2

Ajou-Toulouse

XPS : Ns at 396 eV substitutional (bulk) – Ni at 400 eV interstitial (surface)

reduction : 2H +TiO2 →H2O↗ + TiO2 (-O) **substitution : N + TiO2 → TiO2 (+N)**