

MEASUREMENTS OF N ATOM AND N₂(A) MOLECULE DENSITIES IN THE FLOWING AFTERGLOW OF A DINITROGEN MICROWAVE PLASMA

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Measurements of N atom concentration by means of NO chemical titration and spectroscopic measurements of emission intensity of several bands of N₂ spectrum [N₂(B,11 ----> A, 7), N₂(B,2 ----> A,0), N₂(C,0 ----> B,2) and N₂⁺(B,0 ----> X,0)] have been carried out for several pressures along the post-discharge. N₂(A,v) density has been obtained from emission intensities and kinetics of the excited species N₂(B,11) and N₂(C,0)

1) Introduction

Nitrogen flowing post-discharges are widely used for numerous applications as surface treatments or chemical synthesis and we used the afterglow of nitrogen microwave (2450 MHz) plasmas for steel nitriding [1] or methane conversion [2]. To improve such applications, it is necessary to know temperature and chemical composition of the medium. Species with high lifetime such as nitrogen atom N and excited metastable species N₂(A,v) or N₂(X,v) are responsible of chemical reactions with an added gas or solid surfaces. In another work, we have measured rotational and vibrational temperatures in the N₂/CH₄ flowing discharge [3]. Here, we report N atom density measurements along the reactor by means of NO chemical titration and also N₂(B,11), N₂(B,2), N₂(C,0), N₂⁺(B,0) and N₂(A) density calculations. In the far afterglow, N₂(B,11) is mainly produced by N atom recombination; so knowing N concentration, it is possible to derive the N₂(B,11) concentration, written [N₂(B,11)]. Intensity ratio $I_{(X)}/I_{(B,11)}$, and calibration of the spectroscopic set-up allow to compute the X density, [X], from the ratios [X]/[N₂(B,11)] where X is for N₂(B,2), N₂(C,0) and N₂⁺(B,0). The N₂(A,v) density is derived from that of N₂(C,0).

2) Experimental set-up

The experimental set-up is shown in figure 1. The plasma is produced in a silica tube (12 mm o.d.; 10 mm i.d.) crossing a cylindrical resonant cavity connected to a microwave generator (Raytek, 2.45 GHz, adjustable power up to 2 kW). The gas pressure and the gas flow rate are measured by means of a baratron gauge (MKS, 122A) and a mass flowmeter (Alfagaz, RDM 280).

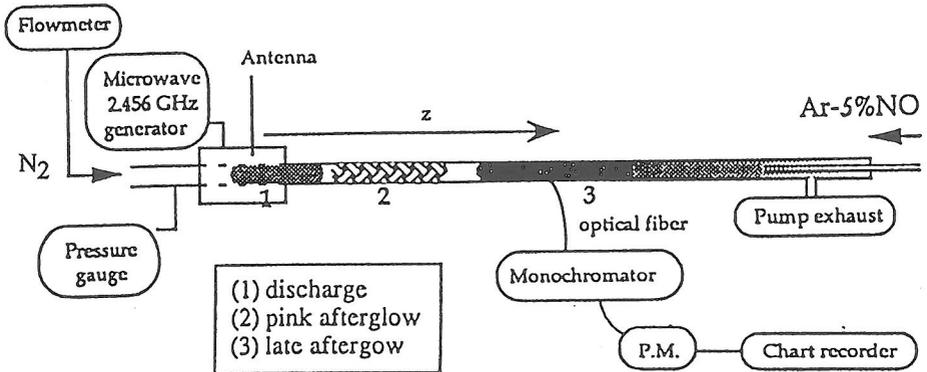


Fig. 1: Experimental set-up.

The N atom density is measured by chemical titration with nitrogen monoxide. NO is introduced in the post-discharge by means of a pipe tube (o.d. 4 mm) which can move along the discharge tube. An Ar-5% NO gas mixture is used, the titration being unperturbed by the Ar gas. A good mixing between N atoms and NO is ensured by ending the pipe tube with three small slots of about 1 mm width.

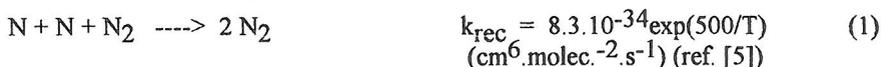
Optical emission of the following bands is analyzed by means of a monochromator (Jobin-Yvon, HRS1, 1220 lines/mm) and a photomultiplier (Hamamatsu, R928): 580.4 nm (B,11 \rightarrow A,7), 380.5 nm (C,0 \rightarrow B,2) and 775.3 nm (B,2 \rightarrow A,0) and also 391.4 nm (B,0 \rightarrow X,0) of N_2^+ .

Chemical and spectroscopic measurements have been carried out along the discharge tube from the end of the discharge to about 300 mm downstream. The experimental conditions are the following ones: flowrate, 1 L(STP).mn⁻¹; pressure, 12.5 to 100 mbar; absorbed microwave power, 180 W.

3) Results

N atom density: figure 2 shows N atom density versus the post-discharge time for several pressures. In another work presented in the present conference [4], we have shown that NO titration is not reliable in the pink afterglow where NO reacts not only with nitrogen atoms but also with excited dinitrogen molecules; this fact leads to a overestimate of N density in this part of the post-discharge. It appears, as shown in Fig.2, that N density decays nearly independently of pressure. Hence, N decay is mainly due to recombination on the tube wall (reaction 2) and not due to homogeneous

recombination (reaction 1) which is nearly negligible before heterogeneous recombination in our experimental conditions:



The [N] decay is expressed from reactions 1 and 2 by the following equation:

$$d[N]/dt = - 2 \cdot k_{\text{rec}}[N]^2[N_2] - k_w[N] \quad (a)$$

This kinetic law corresponds to two parallel reactions of the first and second order. Integration of this equation is expressed as it follows:

$$1/[N]_t = (1/[N]_{t=0}) \cdot \exp(k_w t) + [N_2](2 \cdot k_{\text{rec}}/k_w) (\exp(k_w t) - 1) \quad (b)$$

From equation (b), it has been determined a value of k_w equal to $17(\pm 4) \text{ s}^{-1}$ at 350 K. A value of k_{rec} ($3.1 \cdot 10^{-33} \text{ cm}^6 \cdot \text{molec.}^{-2} \cdot \text{s}^{-1}$) has been also obtained but with a poor precision. From k_w , we have calculated the recombination coefficient γ by the relation $k_w = \gamma \langle v \rangle / 2r$ (where r is the discharge tube radius and $\langle v \rangle$ the particle mean velocity); the value obtained is $2.5(+0.6) \cdot 10^{-4}$ (350 K). This value is in good agreement with the published data $\gamma = 2 \cdot 10^{-4}$ [6].

Emission intensities along the flowing discharge and post-discharge: emission intensity of the N_2 1st positive, N_2 2nd positive and N_2^+ 1st negative band systems (580.4, 775.3, 380.5 and 391.4 nm) have been monitored versus distance from the discharge for several pressures (12.5, 18, 25, 32 and 40 mbar). The pink afterglow was clearly observed for pressures lower than 40 mbar but whatever the pressure this axial emission intensity showed a maximum for all bands (Fig. 3 and 4 for $P = 12.5$ and 32 mbar). This maximum is shifted downstream when the pressure decreases. At 12.5 mbar, it appears a second maximum (Fig. 3). The 1st negative band system decreases more rapidly with pressure than the other bands. It is interesting to notice that, in the late afterglow, the $I_{580.4}$ axial distribution does not follow the same behavior as that the $I_{775.3}$ one (Fig. 4).

N_2 (B,11) density: it is known that, in the late afterglow, the first positive emission is produced by the following reaction:



with a strong enhancement of $N_2(B,11)$ which is the signature of N atom recombination. The $N_2(B,11)$ decrease is mainly due to quenching by N_2 , (radiation decay is low before quenching):



Hence, it is deduced the following steady-state density of $N_2(B,11)$:

$$[N_2(B,11)] = k_{\text{rec}} [N]^2 / 2k_Q \quad (c)$$

From equation (c) and N concentration (measured by NO titration), it is possible to compute $N_2(B,11)$ concentration. Then, after calibration of the spectral response of the optical spectrometer, the $N_2(C,0)$, $N_2(B,2)$ and $N_2^+(B,0)$ densities are deduced from that of $[N_2(B,11)]$ by measuring $I_{380.5} / I_{580.4}$, $I_{775.3} / I_{580.4}$ and $I_{391.4} / I_{580.4}$ band head intensity ratios. The values obtained are mean values along the diameter of the discharge tube.

Table I shows the maximum values of $N_2(B,11)$, $N_2(C,0)$, $N_2(B,2)$ and $N_2^+(B,0)$ concentrations for several pressures. It appears that $[N_2(C,0)]$ is several orders of magnitude lower than $[N_2(B,11)]$. Also is reported in table I, the $N_2(A,v)$ density presently calculated (see below, part 4).

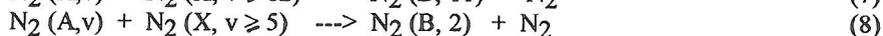
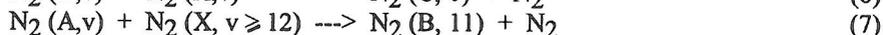
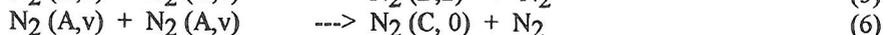
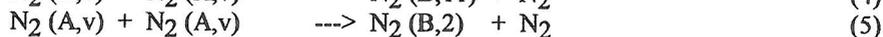
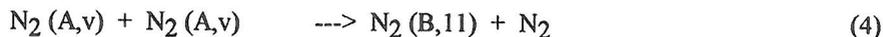
Pressure (mbar)	$[N_2(B,11)]$ (cm-3)	$[N_2(C,0)]$ (cm-3)	$[N_2(B,2)]$ (cm-3)	$[N_2^+(B,0)]$ (cm-3)	$[N_2(A,v)]$ (cm-3)
12.5	$10.5 \cdot 10^9$	$6.2 \cdot 10^7$	$15.7 \cdot 10^{+10}$	$4.3 \cdot 10^8$	$7.8 \cdot 10^{+12}$
18	$4.1 \cdot 10^9$	$3.6 \cdot 10^7$	$6.4 \cdot 10^{+10}$	$2.1 \cdot 10^8$	$6.0 \cdot 10^{+12}$
25	$1.4 \cdot 10^9$	$1.5 \cdot 10^7$	$2.2 \cdot 10^{+10}$	$0.9 \cdot 10^8$	$4.0 \cdot 10^{+12}$
32	$0.8 \cdot 10^9$	$0.9 \cdot 10^7$	$1.2 \cdot 10^{+10}$	$0.5 \cdot 10^8$	$3.1 \cdot 10^{+12}$
40	$0.3 \cdot 10^9$	$0.4 \cdot 10^7$	$0.4 \cdot 10^{+10}$	$0.1 \cdot 10^8$	$2.1 \cdot 10^{+12}$

Table I

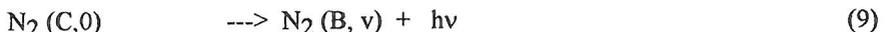
4) Discussion - $N_2(A,v)$ density

Several reactions can lead to the first and second positive systems in the post-discharge of a dinitrogen plasma. These reactions are surveyed and taking into account the rate constants found in the literature, a mechanism is proposed to explain the results obtained in our experimental conditions.

Piper [8] and Hayes and Oskam [9] have shown that $N_2(B,v)$ and $N_2(C,v)$ can be produced by energy pooling of $2 N_2(A,v)$ according to reactions (4), (5) and (6) and they have measured the corresponding rate constants. By taking into account that reactions (4) and (5) rate constants are 1 order of magnitude lower than that of reaction (6), it cannot be explain that $N_2(B,v)$ density is about 3 orders of magnitude higher than $N_2(C)$ one. Reaction (7) proposed by Piper [10] can explain this discrepancy when $N_2(X,v>5)$ concentration is higher than $N_2(A,v)$ concentration. Piper [10] assumes that the rate constants of reactions (7) and (8) are of the same order of magnitude but higher vibrational levels of $N_2(B)$ are obtained from higher vibrational levels of $N_2(X)$. Moreover reaction (1') also leads to $N_2(B,11)$.



Decay of these excited species is mainly by radiation and quenching (reactions (3), (9), (10) and (11)). Radiation decay of $N_2(B,v)$ is negligible before quenching and for the pressures used here, quenching rate is of the same order of magnitude than decay rate by radiation for $N_2(C,0)$.



So applying a quasi-stationary state, reactions (1') to (11) give the following equations for $[N_2(B,11)]$, $[N_2(C,0)]$ and $[N_2(B,2)]$:

$$[N_2(B,11)] = (k_7[N_2(A,v)][N_2(X,12)] + (k_{rec}/2)[N]^2[N_2]) / k_Q[N_2] \quad (d)$$

$$[N_2(B,2)] = k_8[N_2(A,v)][N_2(X,5)] / k_{10}[N_2] \quad (e)$$

$$[N_2(C,0)] = k_6[N_2(A,v)]^2 / (k_{11}[N_2] + k_9) \quad (f)$$

k_9 , k_{10} and k_{11} can be found in references [11], [7] and [12].

Note that in equations (d) and (e), reactions (4) and (5) have been neglected before reactions (7) and (8). Relations (d) and (e) explain that $I_{580.4}$ decreases more slowly than $I_{775.3}$ due to $N_2(B,11)$ formation by N atom recombination in the late afterglow. Production of $N_2(B,v)$ by energy exchange takes place mainly in the pink afterglow. Relation (f) allows to compute $N_2(A)$ density shown in table I. The values obtained for $N_2(A)$ are in good agreement with those measured by Augustyniak and Borysov [13] and Bosan et al. [14].

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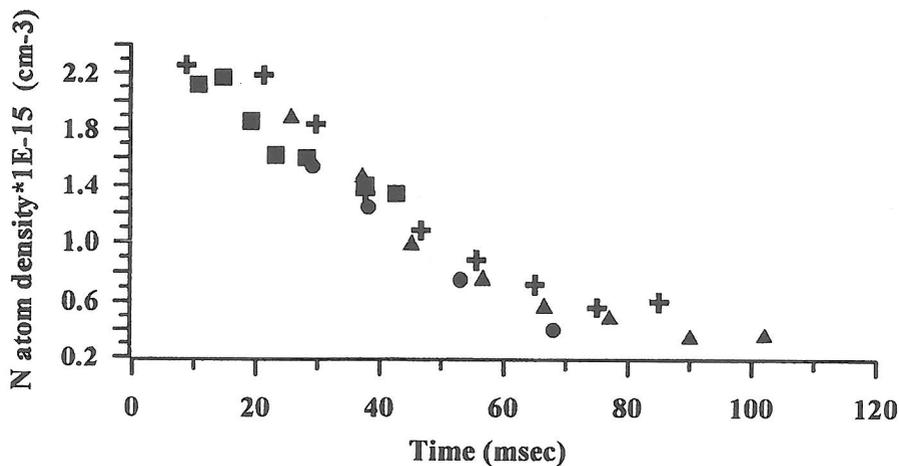


Fig. 2: N atom density versus post-discharge time for several gas pressures: ● = 90; ▲ = 60; + = 50; ■ = 25 mbar.

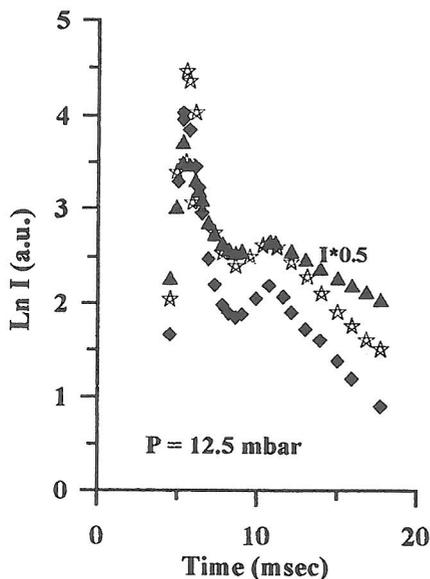


Fig. 3: Emission intensities versus time. ▲ = 391.4 nm ($N_2^+ B, 0$); ◆ = 380.5 nm ($N_2 C, 0$); ☆ = 580.4 nm ($N_2 B, 11$).

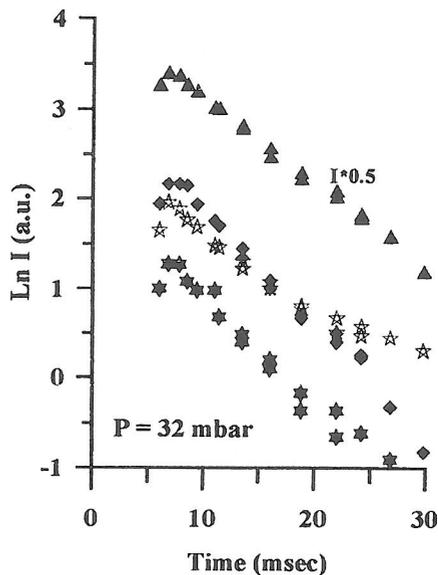


Fig. 4: Emission intensities versus time. ▲ = 391.4 nm; ◆ = 380.5 nm; ☆ = 580.4 nm; * = 775.3 nm ($N_2 B, 2$).