SPECTROSCOPIC STUDY OF N_2-O_2 HIGH PRESSURE U.H.F. PLASMA

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1. INTRODUCTION

Nitric oxide synthesis has been performed by microwave discharges in N_2-O_2 gas mixtures. In this paper are given the results of a spectroscopic study of the plasma produced just in front of the U.H.F. antenna. From the spectra emitted by the plasma between 200 and 900 nm it has been possible to study the effect of O_2 on the emission of N_2^+, N_2, NO bands and OI spectral lines. The rotational structures of N_2 (λ = 380.5 nm) and NOγ (λ = 237 nm) has been recorded. Rotational temperatures have been deduced for N_2-O_2 plasmas in the pressure range 10-700 Torr for U.H.F. powers 80-400 watts.

An interpretation of these results is given where collisions of N_2^+ ions and vibrational excited $N_2(X,V)$ are taken into account.

2. EXPERIMENTAL SET-UP

The experimental device is shown in fig.1. The N_2-O_2 plasmas are produced in a quartz tube (diameter 10 mm) by means of a coaxial resonant cavity. This cavity has been constructed from the model of Dupret et al. [1]. U.H.F. power emitted by a magnetron enters the cavity via a coaxial antenna. The incident and reflected powers have been measured by means of a power meter. The nitrogen pressure is measured upstream of the cavity by means of a mercury manometer and the flow rate by a Brooks flowmeter.

For purpose of spectroscopic observation a rectangular hole (2 × 3.5 mm) was cut in the cavity.

The size of this hole is sufficiently small that it does not perturb the U.H.F. plasma. The spectroscopic analysis is achieved by a Jobin-Yvon HRS spectrometer : grating with 1.200 grooves/mm and blaze wavelength λ = 546 nm. With the slits aperture 0.2 mm commonly used, the resolution is $\delta\lambda$ = 0.25 nm. The spectral line intensities are detected by a RCA-C31 photomultiplier (spectral response 200 to 930 nm). The signal is amplified by a Keithley 414 S picoammeter.

Results are given for a constant gas velocity of 20 cm.sec^{-1} (flow rate 1 liter min^{-1}). When the gas pressure is increased the plasma size is more and more reduced. At high pressure (p > 100 Torr), the plasma is reduced to a small ball in front of the U.H.F. antenna. The spectroscopic observations have been performed on this plasma ball.

3. ROTATIONAL STRUCTURES OF NO AND N_2 SPECTRAL BANDS

Between 300 and 500 nm, the optical spectra is characterized by the emission of 2nd positive (N_2, $C^3\Pi_u \rightarrow B^3\Pi_g$), 1st negative ($N_2^+$, $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$) and NOγ bands (observed in 2nd order). Each vibrational band has a developped rotational structure that we have resolved for N_2(C,O-B,2) and NOγ(0,1) using an instrumental resolution $\delta\lambda$ = 0.05 nm. The second positive tail band is easy to analyze. It is essentially composed of R-branch with a small effect of P-branch. In the case of NOγ bands, six components overlap in a "rotational line" recorded by the spectrometer.

In the case of an homogeneous plasma, it is possible to deduce a rotational temperature from the rotational spectra if we assume a Boltzman distribution in the population of rotational levels. In the present experiments, the plasma appears less and less homogenous with increasing pressure. Nevertheless we attempted to determine a "mean rotational temperature" for $10 \leq p \leq 700$ Torr and U.H.F. powers $80 \leq W_T \leq 400$ watts.

The total intensity of N_2C(O-2) tail band can be written as :

$$I(K_R) = (\text{const})\left\{(S_R)\exp\left[-\frac{B'hc}{kT_R}(K_R+1)(K_R+2)\right] + (S_P)\exp\left[-\frac{B'hc}{kT_R}K_P(K_P-1)\right]\right\} \quad (1)$$

where K_R is the R-branch lower level of the transition. The correspondence with the rotational quantum number of the P-branch K_P is given by :

$$K_P = K_R + 16 \quad (2)$$

B' is the rotational constant, B'hc/k is equal to 2.61 (K^{-1}) and T_R is the rotational temperature.

The Honl-London factors S_R, S_P are given by Herzberg [2] :

$$S_R = \frac{K_R(K_R+2)}{K_R+1} \quad \text{and} \quad S_P = \frac{(K_R+15)(K_R+17)}{K_R+16} \quad (3)$$

Results for a N_2-5 % O_2 mixture at 10 Torr is shown in figure 2 for varying U.H.F. powers. The curves of figure 2 are calculated from relation (1) by normalizing $I(K_R = 16) = 10$.

In a similar but more complicated way, intensities of several groups of NOγ(O-1) rotational lines have been calculated versus T_R. In figure 3 are given calculated curves for two rotational lines intensities ratios r_1 = I,236.4 nm/I,229.7 nm and r_2 = I,236.4 nm/I,231.3 nm which allow a determination of T_R in the range $T_R < 4\times10^3$°K. Mean values of rotational temperatures are shown in figure 4 for pressure 10-700 Torr and powers 80-400 watts.

The lower value $T = (1.5\text{-}2)\times10^3$ K obtained at 10 Torr, 80 watts is equally found in standart glow discharges. The main error is occuring when measuring the height of the recorded rotational lines. Indeed we have to eliminate the feet of adjacent lines.

Considering the results reported in figure 4, the mean rotational temperature $T_R = 3.5(\pm0.5)\times10^3$ K is found to be nearly constant for p > 25 Torr and W = 300-400 watts.

In this pressure range, the exchanges between rotation and translation are very quick processes and we can conclude that this mean

value is close to the kinetic temperature of the plasma both near the U.H.F. antenna.

It is important to have a nearly constant rotational temperature when variations of spectral bands intensities have to be measured in function of the discharge parameters : pressure, O_2/N_2 ratio. In this case, the ratio of band head and total intensities remains a constant value.

4. IONIC AND NEUTRAL BANDS OF MOLECULAR NITROGEN FOR $[O_2]/[N_2] < 0.1$

The N_2^+, 1st negative is strongly emitted in pure nitrogen plasma at p > 100 Torr and U.H.F. powers W_T > 200 watts. On the contrary, the N_2, 2nd positive decreases sharply when the pressure increases from 10 to 100 Torr and at p > 100 Torr only the 1st negative emits. The band heads intensities of N_2^+, λ = 391.4 nm and N_2, λ = 380.5 nm, λ = 315.9 nm have been measured with a spectral resolution $\delta\lambda$ = 0.25 nm.

The ionic band is the more intense of the 1st negative and the neutral bands have been chosen as being unperturbed by rotational tails of adjacent bands. For pressure p > 100 Torr, the N_2, λ = 380.5 nm has been eliminated, being perturbed by the rotational structure of N_2^+, λ = 391.4 nm. The strong 2nd positive N_2, λ = 337.1 nm has also been eliminated being perturbed by the NH impurity emission at λ = 337 and 336 nm.

When O_2 is added to pure N_2 plasma, the neutral bands intensities are not perciptibly varying unlike the ionic bands whose intensities are quickly decreasing with the O_2 concentration. With a view to eliminate the variation of plasma dimensions with varying pressure, the true intensities ratio $r_v = I(N_2^+, \lambda$=391.4 nm)/$I(N_2, \lambda$=315.9 nm) (r_v is corrected for the detector spectral response) has been considered. Variations of r_v with pressure are given in figure 5 for pure N_2, N_2-5 % O_2 and N_2-10 % O_2 at W_T = 300 watts. For N_2-20 % O_2, r_v has not been determined since the ionic bands have disappeared from the spectra. We verify that the N_2^+ emissions are very sensitive to the O_2 presence at p > 50 Torr.

5. EMISSION OF N_2, NOγ AND OI IN N_2-O_2 MIXTURES

For $[O_2]/[N_2] > 0.1$, the spectral lines and bands emitted by O, N_2 and NO are observed. In figure 6 are reported the intensities of OI 777.3 nm and N_2, $C^3\Pi_u(0,2)$, NOγ (0,1) band heads versus the N_2 percentage in N_2-O_2 mixtures at 150 Torr, 300 W_T. These experimental conditions have been chosen as being the more efficient for the nitric oxydes synthesis operations. The NOγ and N_2, C(0-2) are increasing with the ratio of N_2 while OI 777.3 nm is decreasing. There is a plateau for $[N_2]/[N_2]+[O_2] > 80$ %, except for NOγ which is decreasing beyond 90 %.

The intensities ratios of NOγ (0-1) over OI and NOγ (0-1) over N_2, C(0-2) are increasing with the N_2 ratio reaching a maximum for ratios between 80 and 90 % of N_2. All the spectral emissions are increasing with U.H.F. power. Intensities are multiplied by a factor between 6 and 8 when the U.H.F. power is increased from 130 to 400 watts (air mixture at 200 Torr). The flow rate has not marked effect as no variation of intensity has been observed for flows ranging between 0.5 to 4 liters min^{-1}. (air mixture at 150 Torr).

The effect of N_2-O_2 pressure is shown in figure 7 for mixtures N_2-(10-20 % O_2) at 300 watts. If the OI and N_2, C intensities are

decreasing sharply when the N_2-O_2 pressure is rising, the NOγ band decreases more slowly. Variations of the ratio $I_\gamma(0\text{-}1)/I_{01}$ versus pressure is shown in fig.8. A similar variation is observed for $I_\gamma(0\text{-}1)/I_{N_2,C}(0\text{-}2)$. At high pressures, the NOγ bands are the most excited in the spectra.

6. DISCUSSION ON THE 1st NEGATIVE N_2^+ EMISSION

The predominant ionic emission in pure N_2 at p > 100 Torr, W_T > 200 watts can be explained by the following reaction :

$$N_2^+(X) + N_2(X,v) \xrightarrow{k^+} N_2^+(B) + N_2 \qquad (4)$$

where $N_2(X,v)$ are vibrational excited molecules.

The rate coefficient k^+ is given by [4] :

$$k^+ = (2\pm0.5)\times10^{-10} \exp(-\frac{810}{T}) \text{ in cm}^3 \text{ sec}^{-1}$$

for gas pressure 0.7-4 Torr and temperature 350-700 K. In the present condition p > 100 Torr, T = 3500 K, we calculate $k^+ = (1\text{-}2)\times10^{-10}$ cm^3 sec^{-1}. The rate coefficient k^+ is high but the $N_2(X,v)$ molecules must be excited to vibrational states v > 12 since the threshold for the excitation $N_2^+(X\rightarrow B)$ is 3.1 eV. From previous studies [5] in pure N_2, it has been concluded that a vibrational temperature $\theta_1 = 10^4$ K can be reached. Besides we have determined the $N_2^+(B)$ vibrational temperature by measuring the band heads intensities of the following 1st negative lines : λ = 391.4 nm (v'=0-v"=0), λ = 427.8 nm (v'=0)v"=1), λ = 423.6 nm (v'=1-v"=2), λ = 470.9 nm (v'=0-v"=3), λ = 465.2 nm (v'=1-v"=3) and λ = 460 nm (v'=2-v"=4). The measured intensities $I_m(v',v")$ are related to the upper level population $[B,v']$ by the relation :

$$I_m(v',v") = C(\lambda)[B,v'] \frac{p(v',v")}{\lambda^3(v',v")} \qquad (5)$$

where the band strengths p(v',v") have been calculated by Lewis [6]. The spectral response C(λ) of the entire detection system is determined by comparison with the brightness of a tungsten lamp.

The vibrational distribution $N_2^+(B,v')$ is shown in figure 9 for v' = 0, 1 and 2 by normalizing $[B,0] = 1$. The full lines are the Boltzman distribution calculated for $T_{v'}^+ = 4 - 15 \times 10^3$ K.

$$\left[[B,v']/[B,0] = \exp - \left[\frac{\Delta E(0,v')}{kT_{v'}^+}\right]\right] .$$

The experimental results are inside the two distributions corresponding to the apparent temperatures $T_{v'}^+ = 6$ and 10×10^3 K. At 700 Torr, the results are independent of the transmitted power between 150 and 300 watts. With $\theta_1 = 6\text{-}10\ 10^3$ K, we can calculate the $N_2(X,v)$ distribution f(v) using the Gordiets equation [7] :

$$f(v<v_1) = f(0)\exp\left[-v\{\frac{E_1}{\theta_1} - (v-1)\frac{\Delta E}{T_g}\}\right]$$
$$f(0) = 1 - \exp(-E_1/\theta_1) \qquad (6)$$

where $v_1 = \frac{\theta_1}{1.24\times10^{-2}T_g}$, E_1 = 3400 K and ΔE = 21.15 K.

For $T_g = 3.5\times10^3$ K, $\theta_1 = 10^4$ K, we calculate f(0) = 0.3 and $f(v=12) = 10^{-2}$. For $T_g = 3.5\times10^3$ K, $\theta_1 = 6\ 10^3$ K, f(0) = 0.4 and $f(v=12) = 10^{-3}$.

Vibrational population $N_1(X,v>12) \sim 10^{15}-10^{16}$ cm^{-3} can be found for N_2 pressure over 100 Torr.

Furthermore, we have tried to evaluate the electrons densities by means of the Stark H_β profiles in N_2-0.3 % H_2 discharges. The H_β line broadening is less than 0.05 nm. Following the results of ref. [7], we can conclude that $n_e < 5\times10^{14}$ cm^{-3}. Consequently, the $N_2(X,v)$ are the most populated active species producing the 1st negative emission by reaction (4). The N_2^+ ions are prompty destroyed by the following reactions :

$$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+ \qquad (7)$$

$$N_2^+ + O \xrightarrow{k_2} NO^+ + N \qquad (8)$$

with k_1 = 1 and $k_2 = 2.5\times10^{-10}$ cm^3 sec^{-1} [9].

Vibrational molecules $N_2(X,v)$ can also be destroyed by O_2 and therefore, the excitation of N_2^+, B following reaction (4) is playing a minor part. Consequently, the 1st negative emission is quenched by the O_2 molecules. A direct quenching of N_2^+ (B,v=0) can be ruled out since it has be found that the rate coefficients for this process in N_2 and O_2 are in the same order of magnitude [10].

7. CONCLUSION

This spectroscopic study of N_2-O_2 U.H.F. plasmas has allowed to determine a local kinetic temperature T = 3.5(±0.5)×10^3 K just in front of the coaxial antenna for gas pressure p > 50 Torr and transmitted powers 300-400 watts.

The vibrational temperature is higher being between 6 to 10×10^3 K. Consequently, vibrational excited molecules $N_2(X,v)$ are the most populated active species. The pure N_2 emission which is characterized by the N_2^+, 1st negative in the range p > 100 Torr and W_T > 200 watts can be due to the heavy particules collisions $N_2^+ + N_2(X,v)$. In presence of a small proportion of O_2, the N_2^+ ions are efficiently destroyed and the 1st negative emission vanishes.

The variations of spectral intensities with the discharge parameters $[N_2]/[N_2]+[O_2]$ and total pressure have shown that a maximum of NOγ bands are obtained for N_2-(10-20 % O_2) mixtures. The NOγ/OI and NOγ/N_2,C intensities ratios are increasing functions of N_2-O_2 pressure.

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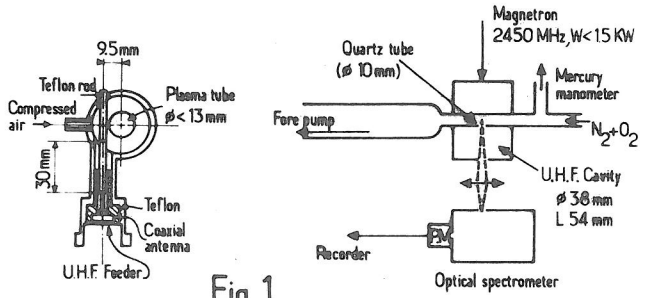

Fig.1.

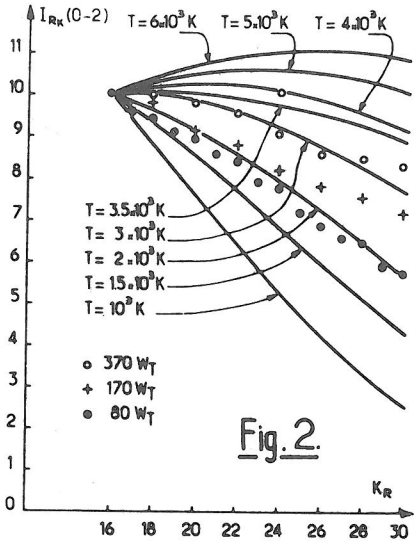

Fig.2.

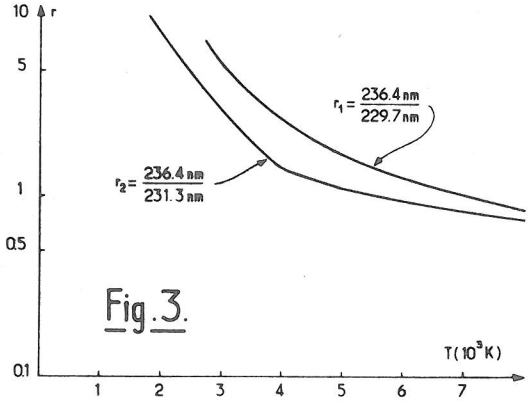
10
r
5
1
0.5
0.1
$r_1 = \frac{236.4\,nm}{229.7\,nm}$
$r_2 = \frac{236.4\,nm}{231.3\,nm}$
T(10^3K)
1
2
3
4
5
6
7

Fig.3.

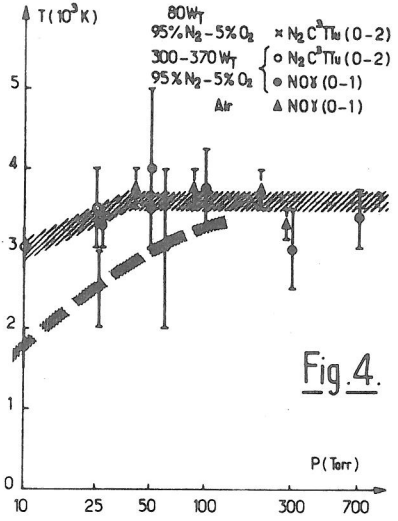
T(10^3K)
80W$_T$
95%N$_2$-5%O$_2$
300-370W$_T$
95%N$_2$-5%O$_2$
Air
× N$_2$ C^{3}Πu (0-2)
○ N$_2$ C^{3}Πu (0-2)
● NOγ (0-1)
▲ NOγ (0-1)
5
4
3
2
1
0
P(Torr)
10
25
50
100
300
700

Fig.4.

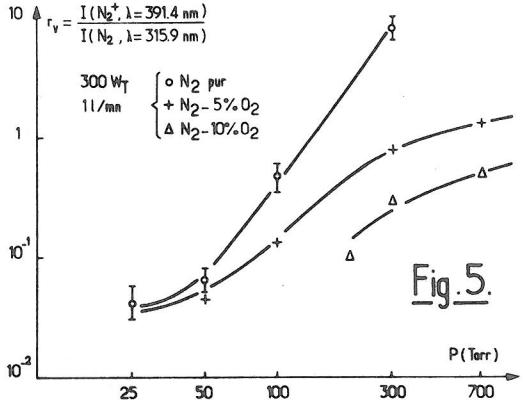
10
1
10^{-1}
10^{-2}
$r_v = \frac{I(N_2^+, \lambda = 391.4\ nm)}{I(N_2, \lambda = 315.9\ nm)}$
300 W
1 l/mn
o N_2 pur
+ N_2 - 5% O_2
Δ N_2 - 10% O_2
P (Torr)
25
50
100
300
700

Fig. 5.

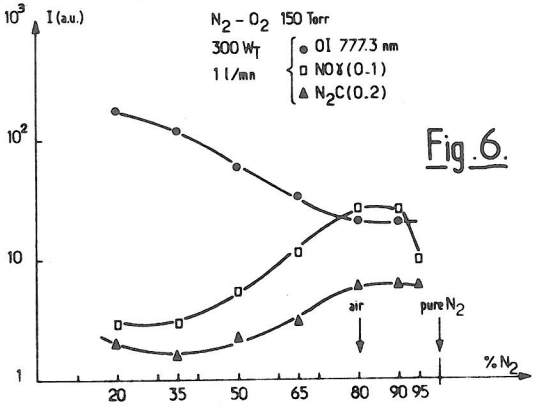
10^3
10^2
10
1
I (a.u.)
$N_2 - O_2$ 150 Torr
300 W
1 l/mn
● OI 777.3 nm
□ NOγ (0.1)
▲ N_2C (0.2)
air
pure N_2
% N_2
20
35
50
65
80
90
95

Fig. 6.

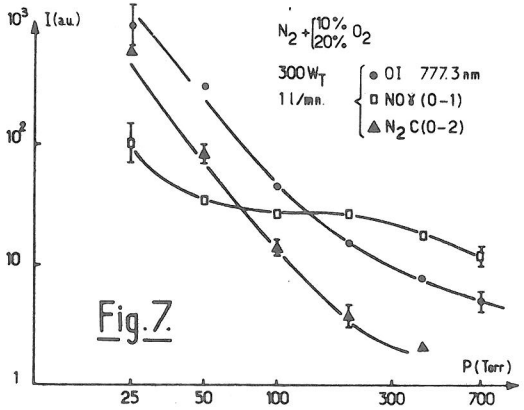
10^3 I(a.u.)
10^2
10
1
N_2 + {10% 20% O_2
300 W_T
1 l/mn.
● OI 777.3 nm
□ NO γ (0-1)
▲ N_2 C(0-2)
P(Torr)
25
50
100
300
700

Fig.7.

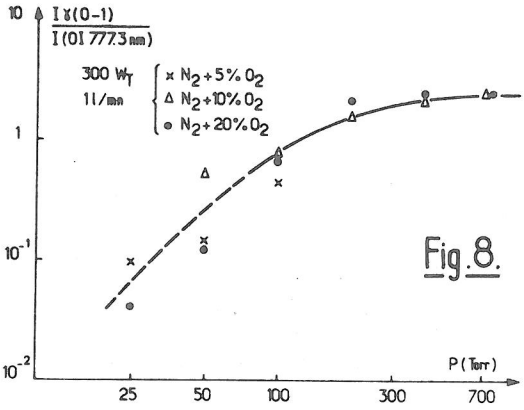
10
1
10^{-1}
10^{-2}
I γ(0-1) / I(OI 777.3 nm)
300 W_T
1 l/mn
× N_2+5% O_2
Δ N_2+10% O_2
● N_2+20% O_2
P(Torr)
25
50
100
300
700

Fig.8.

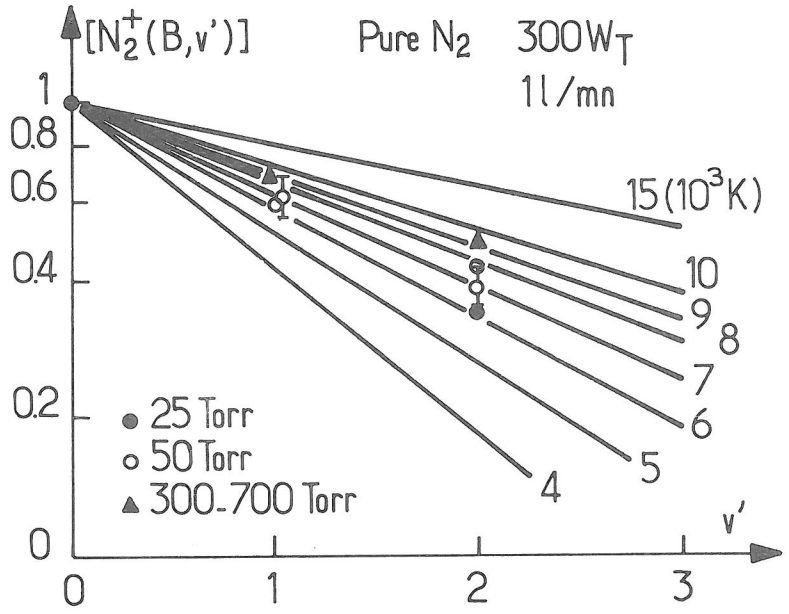
[N2+(B,v')]
Pure N2 300WT
1l/mn
1
0.8
0.6
0.4
0.2
0
15(10^3K)
10
9
8
7
6
5
4
25 Torr
50 Torr
300-700 Torr
v'
0
1
2
3

Fig.9