Production of N_2 Radiative States in N_2-H_2 Flowing D.C. Discharge

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Abstract. — Measurements of gas temperature, electric field and N_2 , second positive (2^{nd} pos.), N_2^+ , first negative (1^{st} neg.) band intensities have been performed in N_2-H_2 flowing D.C. discharge with H_2 less than 0.5%. The intensity variations of the N_2 , 2^{nd} pos. and N_2^+ , 1^{st} neg. bands when a few H_2 is added to N_2 are explained by the E/N reduced electric field (N neutral gas density) increase and by the N_2^+ density decrease, respectively.

Résumé. — La température du gaz, le champ électrique et les intensités des bandes de N_2 , deuxième système positif (2^{e} pos.) et de N_2^+ , premier système négatif (1^{er} neg.) ont été mesurés dans une décharge N_2-H_2 D.C. en écoulement avec moins de 0,5 % de H_2 . Les variations d'intensités des bandes de N_2 , 2^{e} pos. et N_2^+ , 1^{er} neg lorsqu'un peu de H_2 est ajouté à N_2 sont expliquées par un accroissement du champ électrique réduit E/N (N densité du gaz neutre) et par une diminution de la densité de N_2^+

1. Introduction

The surface treatment in post-discharge reactors is a recent established procedure [1], where the active species are produced in a flowing discharge and the sample is located downstream in a separated heated device. Experiments performed for nitriding steel pieces indicate that the substrate was very sensitive to oxidation residues. For this reason, small concentrations of H_2 are introduced into the N_2 discharge. This addition induced changes of the electrical and optical properties of nitrogen plasmas. For example, it has been shown that the addition of low H_2 concentrations induced an increased emission of the 2^{nd} pos. system of N_2 [2].

In a first time, in order to study how the population of the N_2 ($C^3\Pi_u$) state is influenced by a change in the reduced electric field, E/N , we have performed measurements of the 2^{nd} pos. system intensities in a flowing nitrogen discharge *versus* the gas velocity, correlated to the change of the gas temperature.

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Fig. 1. — Experimental set-up.

In the second time, we have studied the variation of the electric field at a constant discharge current and of the intensities of the 1st neg. and the 2nd pos systems when the H₂ percentage into N₂ was increased.

The electrical field and gas temperature are measured in order to establish correlations with the intensity measurements.

2. Experimental Set-Up and Experimental Procedure

The experimental arrangement is shown in Figure 1. A flowing d.c. discharge in pure N₂ is maintained between two identical Ni/Cr hollow electrodes, placed at 40 cm from each other, in a tube of 20 mm in diameter. The tube is connected to a forepump to maintain the proper pressure and flow rate. Pressure is measured at the end of the tube by a thermal gauge and the flows are regulated by MKS flowmeters. The following plasma parameters have been chosen: a constant current discharge $I = 50$ mA and three gas pressures with the corresponding flow rates: 1 torr – 120 sccm., 2 torr – 340 sccm and 3 torr – 600 sccm. The H₂ gas is introduced into N₂ at a flow rate less than 10 sccm that is a percentage less than 0.5%.

In pure nitrogen, the gas velocity was varied up to 6 m s⁻¹. In these conditions the residence time vary from 60 to 800 ms.

The optical emission of the discharge is detected perpendicularly to the axis of the discharge tube by a quartz optical fiber placed 10 cm from the cathode. It is connected to a Jobin-Yvon HR-320 spectrometer. The detector is a Hamamatsu photomultiplier R585. The spectral resolution of the system can reach 0.05 nm.

The electrical field was measured by two Langmuir probes on the axis of the positive column, 30 cm apart and by the increase of the positive column voltage with the discharge length.

Fig. 2. — Gas temperature *versus* the gas velocity ($I = 50$ mA).

Fig. 3. — I_2^+ — second positive intensity *versus* the gas velocity ($I = 50$ mA)

It was already shown that the gas temperature may be estimated from the rotational temperature of the N₂, 2nd pos. system [3]. The experimental rotational spectrum is compared to a computed one, calculated by using the experimental apparatus function.

Fig. 4. — $\frac{\Delta T}{T}$ — gas temperature variations (in %) *versus* the H_2 percent into N_2 ($I = 50$ mA)

Fig. 5. — $\frac{\Delta E}{E}$ — electric field variations (in %) *versus* the H_2 percent into N_2 ($I = 50$ mA).

3. Experimental Results

3.1. PURE N_2 DISCHARGE

Gas Temperature. — The dependence of the gas temperature on the gas velocity if reproduced in Figure 2. The temperature is decreasing when the gas velocity is increasing and this effect

Fig. 6. — I_2^+ — second positive intensity *versus* the H₂ percent into N₂ ($I = 50$ mA).

Fig. 7. — I_1^- — first negative intensity *versus* the H₂ percent into N₂ ($I = 50$ mA).

is a little more pronounced at lower gas pressure. As a result, the neutral molecule density is growing with the gas velocity.

Field Measurements. — The electric field, E , of the positive column was found to increase up to 10% with the gas velocity. The reduced electric field (E/N) can then be determined by using the following equation:

$$\frac{E}{N} = \frac{EkT}{p} \quad (1)$$

with E , the electric field, N , the gas density, p , the pressure and T , the temperature.

Optical Emission Measurements. — The intensity of the N_2 2nd pos. system for N_2 (C, $v = 0 \rightarrow B$, $v = 0$), $\lambda = 337.1$ nm, is reproduced in Figure 3 as a function of the gas velocity for $p = 1$ and 2 torr and $I = 50$ mA. It can be observed a noticeable intensity decrease as the gas velocity is growing.

3.2. N_2 - H_2 DISCHARGE

Gas Temperature. — The variation of the gas temperature as a function of the H_2 percentage is reproduced in Figure 4. A weak increase, up to $\Delta T/T = 10\%$, is observed as $[H_2]/[N_2]$ grows up to 0.5%.

Field measurements. — The $\Delta E/E$ variation as a function of H_2 percentage into N_2 is reported in Figure 5. It is observed a strong increase of $\Delta E/E$ up to 35% when H_2/N_2 varies from 0 to 0.5%.

Optical Emission Measurements. — Variations of the N_2 2nd pos. system intensity *versus* the H_2/N_2 percentage are reproduced in Figure 6. A sensitive increase is observed as H_2/N_2 is between 0 and 0.1%. This increase is more pronounced at higher pressure and saturates for H_2/N_2 larger than 0.1%.

The N_2^+ 1st neg. intensity *versus* the H_2 percentage is reproduced in Figure 7. Clearly, the N_2^+ intensity strongly decreases as a few H_2 is introduced into N_2 and this effect is more sensitive at high pressure.

4. Discussion

4.1. PURE N_2 DISCHARGE. — The 2nd pos. bands are emitted from the $N_2(C^3\Pi_u)$ state. The density of this state is determined by the following reaction:

The quenching of the $N_2(C)$ state can be neglected at the present working gas pressure ($p = 1-3$ torr). Therefore, the steady state of $N_2(C)$ density is given by the following equation:

$$[N_2(C)] = \frac{k_e n_e [N_2(X)]}{A} \quad (3)$$

where k_e is the electronic excitation coefficient for the $N_2(C)$ state, n_e is the electron density, $[N_2(X)]$ is the ground state density and A is the radiative emission probability.

In the present experimental conditions, the gas pressure variation is less than 10% along the discharge tube. So, it is deduced from equation 1 that E/N varies approximately like the gas temperature. This temperature decreases with the gas velocity (Fig. 2). Then the k_e rate which is related to E/N must also decrease with the gas velocity. This fact can explain the decrease of N_2 2nd pos. intensity as observed in Figure 3.

4.2. N₂-H₂ DISCHARGE. — The strong increase in electric field, at constant discharge current, as a few H₂ is introduced into N₂ has recently been explained [4] by a change in ionization from a stepwise process which reduces the ionization threshold in pure N₂ to a direct process in N₂-H₂ mixture. Also, a reduction of ionization by associative processes is relevant. Then, the electric field must increase to maintain a constant discharge current, thus explaining the N₂ 2nd pos. system increases as observed in Figure 6.

The decrease of the N₂⁺, 1st neg. as observed in Figure 7 could be explained in part by the following charge transfer reaction:

which is very efficient [5] and also by the reduction of associative ionization from N₂ metastable states. These processes could reduce the N₂⁺(B) excitation by electron collisions as follows:

5. Concluding Remarks

Diagnostics of N₂ radiative states and discharge electric fields have been performed in N₂-H₂ D.C. positive columns. It has been found a sensitive increase in the discharge electric field of about 35% by adding 0.5% H₂ into N₂. As a consequence, the N₂ second positive bands increase in intensity. Conversely, the N₂⁺ first negative bands decrease as a result in part of the efficient charge transfer: N₂⁺ + H₂ → N₂H⁺ + H and of the decrease of associative ionization reactions, for another part. The gas temperature has also been determined from the rotational structure of the N₂, 2nd pos. bands.

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