KINETIC STUDY OF N-N RECOMBINATION IN A N_2-H_2 POST DISCHARGE

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ABSTRACT

A Nitrogen Plasma is produced in a quartz tube by means of a HF structure. Hydrogen gas has been introduced in the post discharge. The perturbation of 1st positive afterglow has been studied, when the hydrogen flow is increasing.

1. INTRODUCTION

The purpose of the present work is to study the influence of molécular hydrogen on the recombination of nitrogen atoms, by means of spectroscopic methods.

2. EXPERIMENTAL

The experimental arrangement is represented in fig 1. A nitrogen plasma is produced in a quartz tube by means of a H.F.(27 Mhz) structure. The highly excited plasma inside the H.F. structure is followed by an intense flowing afterglow. This afterglow, due to the recombination of nitrogen atoms is characterised by the emission of the first positive system of N_2. At a sufficiently great distance from the structure, the effect of nitrogen atoms prevails : In pure nitrogen, the vibrationnal structure of the emission spectra is typical and the intensities depend on the atomic density only.

Discharge parameters are the following : Pressure 10-100 Torr, flow rates 1-3 liter m^{-1} and electrical power 200-400 Watts. The rate of atomic nitrogen was previously mesured (1), between 1 to 10 % according to pressure.

3. INTERPRETATION OF EXPERIMENTAL DATA

a/ Afterglow in pure active nitrogen

For the studied pressures, diffusion processes can be neglected. The fluorescence is due to the recombination reaction

$$N + N + N_2 \longrightarrow N_2^* + N_2$$

According to previous workers (2, 3) the direct three body recombination of nitrogen into $N_2(A^3\ \Sigma\ u^+)$ is followed by collision induced crossing into $N_2(B^3\ \Pi g)$ state. At sufficiently high pressures, destruction of B state is essentially due to the Quenching by $N_2(X)$ molecules. These mechanisms don't take into account the influence of atomic nitrogen as thirth body for recombination, or as Quencher. The final result can be written

$$I_{(\lambda)} = C_{(\lambda)} |N_2^*| = \frac{C_{(\lambda)} |N|^2 k_N^{N2} |N_2|}{k_Q^{N2} |N_2|}$$

where $C_{(\lambda)}$ depend on λ.

k_N^{N2} and k_Q^{N2} are respectively the recombinaition coefficient (and the Quenching coefficient of the B state)

b/ Afterglow in an active nitrogen - hydrogen mixture.

The hydrogen is introduced by the capillary tube (fig 1). The spectroscopic observation is made at such a distance l from the injection point, that the mixture is homogeneous. Downstream partial pressures of hydrogen P_{H2} and nitrogen P_{N2} are related to the flow rates Q_{H2} and Q_{N2} by the relation.

$$\frac{P_{H_2}}{P_{N_2}} = \frac{Q_{H_2}}{Q_{N_2}} = Y \text{ and } P_{H_2} + P_{N_2} = P_T$$

Upstream, nitrogen pressure is P_T.

To the observation point and if l is sufficiently small flow conservation can be written

$$\frac{|N|_Y}{|N|_{Y=0}} = \frac{1}{|1+Y|} \quad \text{for given } P_T \text{ and } Q_{N2}$$

In order to express the intensity of the fluorescence spectra we have to take into account the two following processes

$$N + N + H_2 \xrightarrow{k_N^{H2}} N_2^* + H_2$$

$$N_2^* + H_2 \xrightarrow{k_Q^{H_2}} \text{products}$$

$$\text{if} \qquad R_Y(\lambda) = \frac{I_Y(\lambda)}{I_{Y=0}(\lambda)} |1 + Y|^2$$

One obtains

$$R_Y = \frac{1 + Y \dfrac{k_N^{H_2}}{k_N^{N_2}}}{1 + Y \dfrac{k_Q^{H_2}}{k_Q^{N_2}}}$$

The experimental study of R_Y versus Y can give informations on the behaviour of hydrogen. Here, destruction of atomic nitrogen by molecular hydrogen is not considered; Previous workers indicate that this mechanism is a very improbable one (4).

RESULTS :

Studies were performed for different total pressures between 40 and 70 Torrs. The vibrationnal intensities distribution depends on Y only.

The total intensities (normalised as indicated before) which is, of course, proportionnal to the B state population is reported on fig 2. The intensity reaches a minimum for Y ∿ 0,20. There is no simple explanation for this result. With an additionnal gase as argon or helium such a curve is not observed. Influence of a chemical compound is not excluded.

The values of R_Y for all vibrationnal transitions, and for increasing values of Y are shown in fig 3 ; It is seen that, in presence of hydrogen, recombination prevails high vibrationnal levels, and Quenching is more efficient for the first levels.

Coumpounds which may be produced are condensed in the liquid nitrogen traps. Hydrazine were characterised. But obtained quantities were very small and no quantitative dosing possible. No NH_3 could be detected. Hydrazine sharing in the two traps were very different according to the pressure. For small pressure (high velocities) hydrazine is produced only in the second trap. Inverse phenomena was observed for high pressures. The mechanism of hydrazine production probably involves unstable chemical species, which could not be identified.

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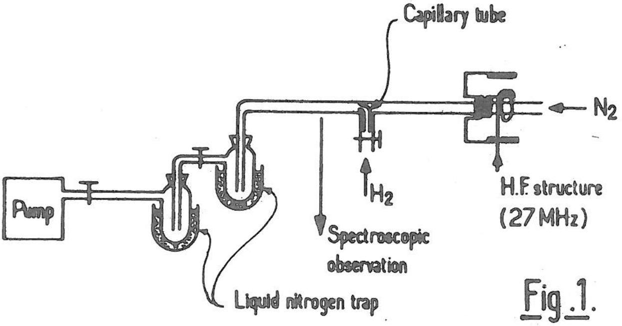
Capillary tube
N2
Pump
H2
H.F. structure
(27 MHz)
Spectroscopic observation
Liquid nitrogen trap

Fig. 1.

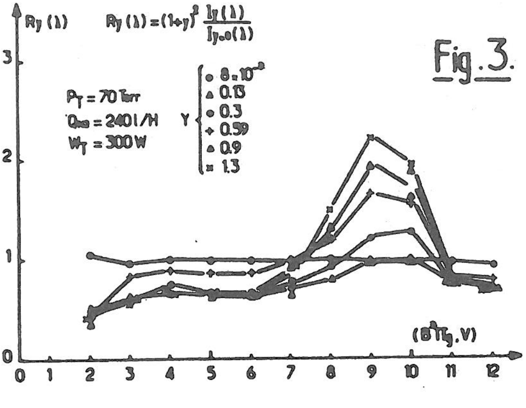
Rγ (λ)
Rγ (λ) = (1+γ)² Iγ(λ) / Iγ=0(λ)
PT = 70 Torr
QN2 = 240 l/H
WT = 300 W
γ
● 8.10⁻²
▲ 0.13
● 0.3
+ 0.59
▲ 0.9
× 1.3
(B³Πg, v)
0
1
2
3
0
1
2
3
4
5
6
7
8
9
10
11
12

Fig. 3.

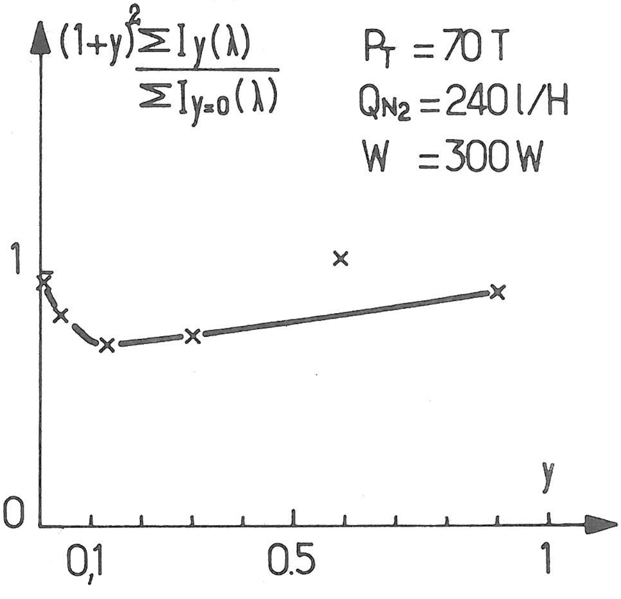
$(1+y)^2 \frac{\Sigma I_y(\lambda)}{\Sigma I_{y=0}(\lambda)}$
$P_T = 70$ T
$Q_{N_2} = 240$ l/H
W = 300 W
1
0
y
0,1
0.5
1

Fig. 2