

Changes of the nitrogen 2-nd positive system due to small methane addition

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The influence of small quantities of methane on the behavior of the nitrogen radiative species $N_2(C)$ has been studied by emission spectroscopy in a $N_2 - CH_4$ d.c. flowing discharge. Second positive nitrogen system, especially the 0-0 transition with $\lambda = 337.1$ nm, was investigated for methane proportion varying in the range 0.00 – 0.1 %. A sensitive increase (up to 6 times) of the band intensities of the second positive system has been found when the methane concentration raised. This is explained in correlation with the increase of the E/N reduced electric field, due to a lower ionization threshold in a $N_2 - CH_4$ mixture.

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1. Introduction

In a previous paper [1], strong changes in the $N_2(C)$ population were reported to appear in a nitrogen d.c. flowing discharge when small amounts of hydrogen are added. Increases of the $N_2(C)$ population up to 10 times were recorded for $N_2 - x H_2$ gas mixtures, with x ranging between 0.1 - 0.5%. The explanation is that the presence of a few hydrogen reduces the ionization process in nitrogen [2] and consequently the electric field in the discharge must increase to maintain a constant current.

We investigate in this paper the possibility that a similar situation may occur in a $N_2 - CH_4$ mixture, by taking into account that hydrogen appears in the discharge by methane decomposition under discharge conditions.

2. Experimental device

A schematic view of the experimental set up is presented in Fig. 1. The discharge is produced in a Pyrex tube with 22 mm inside diameter and 26 outside diameter, between two identical side Ni/Cr electrodes, spaced at 40 cm. The first electrode in the sense of flowing is the anode. Gases of spectral purity are supplied from metal tanks. Gas flows are regulated and measured by mass flowmeters and pressure is measured by a thermal gauge. Spectral data from the discharge are recorded by means of an optical system consisting of: optical fiber, OMA (Optical Channel Analyzer) and computer. The spectral range of the system is situated in the range 200 – 900 nm and the optical resolution is 1.5 nm.

The influence of small quantities of methane on the behavior of the nitrogen radiative species $N_2(C)$ has been studied by emission spectroscopy in a $N_2 - CH_4$ d.c. flowing discharge. The second positive nitrogen system was monitored. This system is emitted during the radiative decay of the $N_2(C)$ species, as a consequence of the reactions

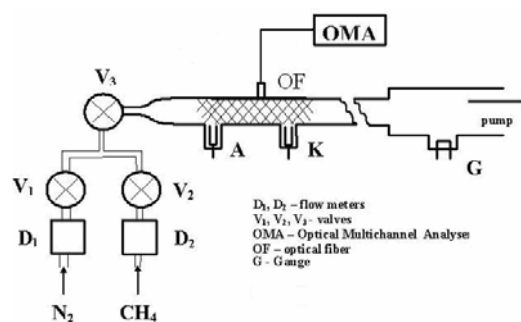
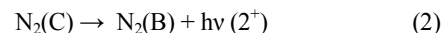
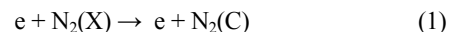


Fig. 1. Experimental device.



where $N_2(X)$ is the ground state nitrogen molecule, $N_2(C)$ and $N_2(B)$ are vibrational excited states of the nitrogen molecule. As resulted from the reaction (2), the intensity of the second positive system is proportional to the $N_2(C)$ population density, so being a convenient indicator of any modification in the density of this population occurring in the discharge.

The experimental conditions for the $N_2 - CH_4$ flowing discharge were:

- Pressure : 100 – 500 Pa
- Nitrogen flow rate : 600 – 1000 sccm
- Methane ratio to nitrogen : 0 – 0.1 %
- D.C. intensity : 50 – 100 mA

3. Results and interpretation

The modification of the second positive nitrogen system produced by the addition of small quantities of methane has been studied by emission spectroscopy in a N_2

– CH₄ d.c. flowing discharge. Spectra for pure nitrogen and N₂ – 0.1 % CH₄ are comparatively presented in Fig. 2 and 3.

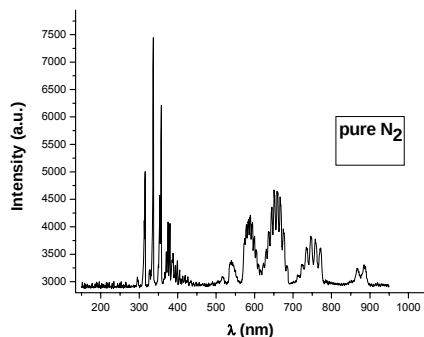


Fig. 2. Recorded spectrum for pure nitrogen

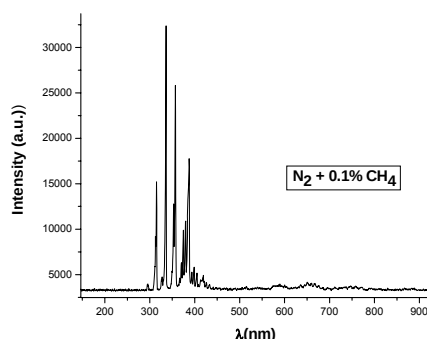


Fig. 3. Recorded spectrum for a N₂ – 0.1 % CH₄ mixture.

The second positive nitrogen system, especially the 0-0 transition with $\lambda = 337.1$ nm, was investigated for methane proportion varying in the range 0.00 – 0.1 % where a sensitive increase (up to 6 times) of the band intensities of the second positive system has been found when the methane concentration raised, as shown in Fig. 4.

This phenomenon is similar with the one observed earlier in a N₂ – H₂ mixture [1]. It can be explained considering the resulted hydrogen from methane dissociation in the electrical discharge. As pointed out in [3], the main plasma chemical reactions, which produce hydrogen are:

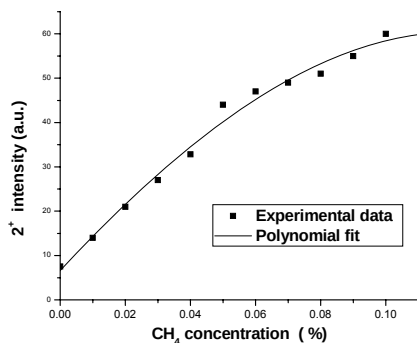
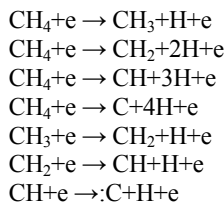
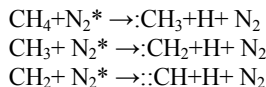


Fig. 4. Intensity of the 2-th positive system versus methane concentration.

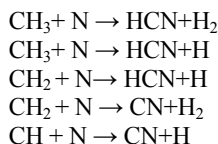
Dissociation by electron collisions



Dissociation by excited molecular nitrogen collisions



Reactions of radicals with atomic nitrogen



The resulting hydrogen atoms are responsible for the changes in the N₂ population density by a change in ionization from a stepwise process which reduces the ionization threshold in pure N₂ to a direct process in N₂ – H₂ mixtures [3]. Also, a reduction of ionization by associative processes is relevant. As a consequence, the electrical field in the discharge must increase, in order to maintain a constant discharge current. A larger electric field produces more N₂(C) species, according to the reactions (1) and this explains the experimental results illustrated in Fig. 4.

4. Conclusions

Significant increase of the N₂(C) population was found in N₂ – CH₄ mixtures for very low methane concentrations (up to 0.1%). This is explained by the influence on the ionization process in the discharge of the resulted hydrogen from methane decomposition. Similar results are expected from nitrogen mixtures with other hydrogen containing gases.

References

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