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'CLEANING' MECHANISMS OF EMISSION SPECTRA FOR NEON/NITROGEN WITH HYDROGEN MIXTURES PLASMA

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Abstract. An interesting reduction phenomenon of the emission spectra appears at the addition of a certain amount of hydrogen in pure neon/nitrogen gas mixtures plasma. In plasma of hydrogen with neon gas mixture, the main reaction mechanism leading to this "cleaning effect" of the emission spectrum is the resonance ionic three - body reaction in which hydrogen plays a double role: that of the energy mediator in metastable atom state and the reaction partner as a negative ion. In the case of plasma formed by the mixture of nitrogen with hydrogen, the reaction mechanism is based on the ability of hydrogen to inhibit the dissociation process of the nitrogen molecule in the component atoms, resulting in a strong increase in the intensity of the Second Positive system of the nitrogen molecule at the expense of the other characteristic spectral system. The effect occurs in the first case in stationary discharges, both in alternating current and dc, at a total pressure of the gaseous mixture greater than 6 mbar while, in the second case, in a continuous flow dc discharge, at pressures below 6 mbar.

Key words: Cleaning effect, Hydrogen, Reaction mechanisms.

1. INTRODUCTION

In terms of this paper, by the "cleaning effect" of an emission spectrum is meant a simplification of it, in the sense that a significant number of spectral lines no longer occurs after the addition of a variable amount of hydrogen to the initial gas that forms the plasma, then pure neon and respectively, nitrogen.

In the first case, namely in a ($Ne+H_2$) gas mixture plasma, this effect of "cleaning" consists in an amazing reduction of neon emission spectrum, virtually at one single line λ=585.3 nm, of great intensity, the so called "yellow line" of the neon. In this type of gaseous mixture the effect is so strong that it is known in the scientific literature as the monochromatization - effect ("M-effect").

The M-effect has a marked addiction by the type of discharge, being more intensive in dielectric barrier discharge (DBD) with sub - millimeter gap and less strong for RF and dc discharges, in the latter case only appearing in the negative glow, no matter the other experimental parameters.

In the second case, the plasma of molecular nitrogen with very small amount (up to 0.1%) of added hydrogen or hydrogen – containing compounds, like methane, shows a modified molecular nitrogen emission spectrum with a Second Positive system very strong while the First Positive system significantly reduces its intensity. The experiment has been realized using a (N_2–CH_4) dc flowing discharge at values of total pressures less than 6 mbar.

2. EXPERIMENTAL SET-UP

The a.c. discharge device used in the present study represents an application of the dielectric barrier discharge, namely a plasma discharge panel, as shown in Fig. 1. The (Ne + 40% H_2) plasma discharge was produced between two parallel, linear aluminum electrodes with a thickness of 5 mm and a length of 200 mm – fig.1.

Both electrodes were covered with 20 □m glass layer acting as dielectric in discharge. The thin film conductors were obtained in vacuum, by deposition on two glass plates, applying a mask. According to the Paschen law, in regard with the sub - millimeter inter-electrodes distance (d=0.15 mm), the working pressures range can fluctuate between 40 and 400 mbar. The minimum breakdown voltage for a gas mixture total pressure up to 400 mbar is placed around 1 kV. The shape of voltage pulse was chosen rectangular. In DBD - type discharges, the common range of variation for the working frequencies is covered between 5÷100 kHz which was corresponding, for the total pressure of gas mixture in experiment of 133 mbar, to an optimum breakdown discharge frequency value of 8 kHz.

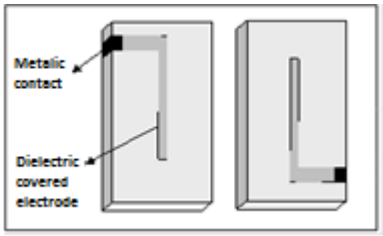

Fig. 1 - The experimental set-up of the (Ne+40%H_2) gas mixture plasma in DBD discharge.

Concerning the second type of gas mixture plasma, which has made the object of the present study, namely N_2+0.1%H_2 (CH_4), the characteristics of the experimental set-up is shown in Fig.2.

The discharge was ignited in a Pyrex tube with a 22 mm inner diameter and a 24 mm outer diameter, between two side-armed identical hollow Ni-Cr cylinder electrodes of 10 mm diameter, spaced at 400 mm distance. The first electrode, in the direction of gas flow, was the anode. Spectral purity gases (99.98 %) were used. Gas flows were regulated and measured by MKS mass flow-meters with a measurement scale of maximum 1500 sccm for nitrogen and 10 sccm for methane, and the pressure was measured at the end of the discharge tube. The tube was connected to a fore-pump in order to maintain the right pressure and flow rate during the experiment. Spectral data were obtained within the glow zone, and they were recorded by means of a classic spectral analysis system consisting of: a Varian -Techtronic spectrophotometer (S) equipped with a grating of 1200 grooves/mm, a 5 mm wide slit and 300÷860 nm measurement range, a Hamamatsu R 585 (PM) Photomultiplier, a quartz optical fibre (OF) and a recorder (R). The spectral resolution of the system was 0.05 nm. Alternatively, it was used an Optical Multichannel Analyzer (OMA) of 220÷900 nm spectral range and a resolution of 1.5 nm. The integration time could be varied in the 200÷1000 ms range, depending on the brightness of the emitted radiation.

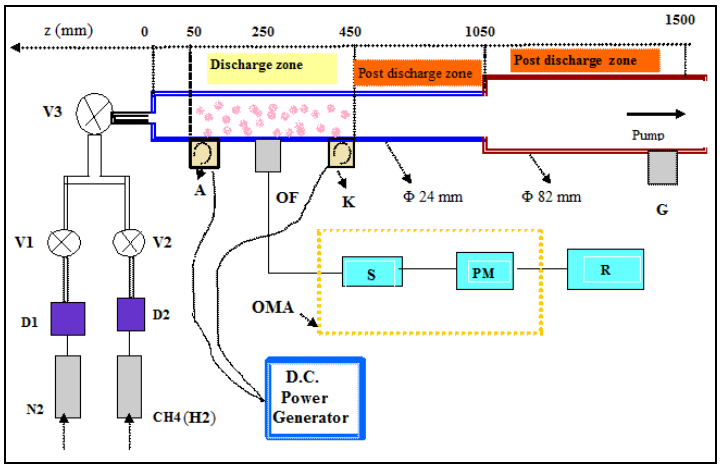

Fig. 2 - Experimental set-up of the nitrogen/hydrogen gas mixture plasma in d.c. flowing discharge (D1, D2 – flow meters; V1, V2, V3 – valves; S - spectrophotometer; PM – photomultiplier; R- recorder; OF – optical fiber; G- thermal gauge, A - anode, K- cathode, OMA- Optical Multichannel Analyzer).

3. RESULTS AND DISCUSSION

The basic mechanism which generates the M- effect in ($Ne+H_2$) gas mixture plasma was identified as being the polar resonant three body reaction [1]:

$$Ne^+ + H^- + H^*(n=2) \rightarrow (Ne^+H^-) + H^*(n=2) \rightarrow Ne^*(2p_1) + H^*(n=3) + H(n=1) + \Delta E \quad (1)$$

The notations in the equation (1) are the following: P and N, the symbols for the atoms of the electropositive and electronegative gas respectively, P^+, the symbol for the positive ion, N^-, the symbol for the negative ion, N^{met}, the symbol for the metastable electronegative atom, $(N^{met})^*$, the symbol for the metastable electro-negative atom in a state of higher energy than the previous, P^* the symbol for the electropositive excited atom and ΔE is the usual symbol for the energy defect of reaction, which in this case must be nearly zero.

The neon atom excited on $2p_1$ energy level (n=2, using the Paschen notation – Fig.3) decays radiatively on $1s_2$ energy level via reaction (2), leading to the emission of the dominant yellow spectral line [2]-[3]:

$$Ne^*(2p_1) \rightarrow Ne^*(1s_2) + h\upsilon \quad (2)$$

where υ is the frequency corresponding to λ=585.3 nm.

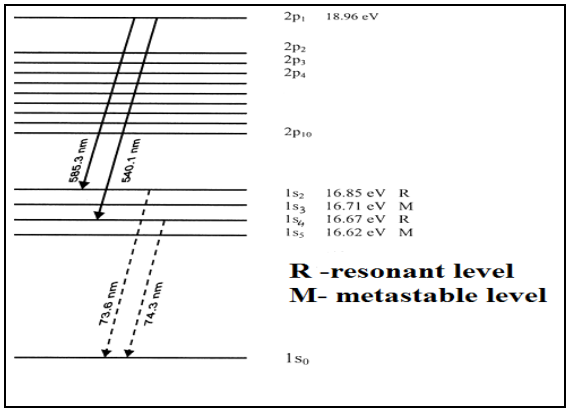

Fig. 3 - Simplified Paschen energy diagram of neon.

The principal reactions, in which are involved the hydrogen atoms, are the following [1], [4]:

$$e + H_2 \rightarrow e + H_2^* \rightarrow H^- + H^* \quad (3)$$

$$H^- + Ne^+ \rightarrow Ne^*(2p_1) + H \quad (4)$$

$$H^- + Ne^+ + M \rightarrow Ne^*(2p_1) + H + M \quad (5)$$

$$Ne^*(1s_i) + H_2 \rightarrow H_2^+ + Ne + e; \text{ (Penning reaction)} \quad (6)$$

where M is the notation for the third body which appears in the reaction.

From these reactions we can cut off the effect of the hydrogen addition on the reduction of neon emission spectrum.

So, the hydrogen is involved in the feeding of the upper level $2\ p_1$ which decays to the $1s_2$ level through the agency of the three-body resonant reaction (5), in the same time having a contribution to the depletion of the lower level $1s_2$ through Penning collision, as indicated in reaction (6). It results that hydrogen influences in two opposite ways the "cleaning" mechanism of the neon emission spectrum, which denotes its versatile character [5], [8-11].

The two spectra obtained based on OES measurements accomplished in pure neon and, respectively (Ne+40%H_2) plasma are shown in figures 1 and 2.

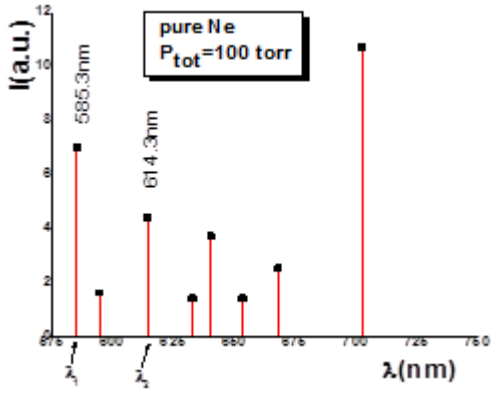

Fig. 4 ─ Emission spectrum of DBD discharge in pure Neon.

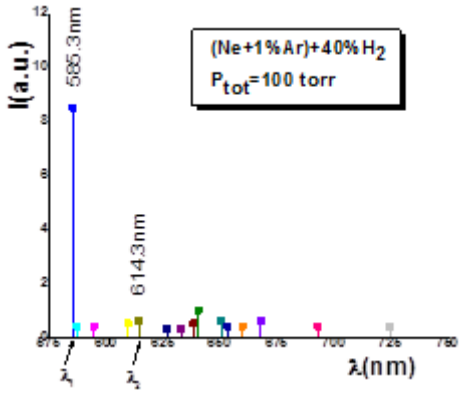

Fig. 5 ─ The emission spectrum of DBD discharge in (Ne+40%H_2) gas mixture.

On addition of up to 0.1% hydrogen (methane) to pure nitrogen, a remarkable change in spectral lines intensities of the two molecular nitrogen principal spectral systems was observed, namely the (1^+) spectral system intensity had a significant decrease whereas the (2^+) spectral system intensity equally increases – figures 6 and 7**.**

Molecular nitrogen has one of the densest spectra of any diatomic molecule. Numerous bands systems corresponding to electronic transitions of N_2 appear within the spectral region from 49 to 8500 nm. The whole visible region and part of the near ultraviolet (down to about 280 nm) and the near infrared regions are dominated by the very strong $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ First and $C^3\Pi_u \rightarrow B^3\Pi_g$ Second Positive systems [(1^+) and, respectively (2^+)], and only on special excitation conditions these systems could be sufficiently suppressed in order to allow observations of weaker spectral systems of molecular nitrogen [6].

The other systems in this region include the $A^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ First negative and $A^2\Pi_u \rightarrow X^2\Sigma_g^+$ Meinel - systems of ionized nitrogen, but part of the $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ Vegard – Kaplan system and some other peculiar systems are also observed.
The rest of the near ultraviolet region (from 280 to 200 nm) does not contain any other intense spectral structure.

Yet, part of the Vegard - Kaplan system, the $D^3\Sigma_u^+ \rightarrow B^3\Pi_g$ Forth Positive system, and a series of different singlet systems are also observed, but not under present experimental conditions.

In this case, the active species identified in the discharge zone were the radiative species N_2 (B) and N_2 (C), which emit the nitrogen spectral systems (1^+) and respectively (2^+).

By the decomposition of methane molecule one obtains molecular hydrogen:

$$CH_4 + N_2 \rightarrow 2\ H_2 + CN_x \quad (7)$$

The main mechanism of creating the N_2 (B) species in the discharge zone is represented by the so - called "*pooling reaction":*

$$N_2(A) + N_2(A) \rightarrow N_2(B) + N_2(X) \quad (8)$$

with the reaction rate $k_3 = 1.1 \times 10^{-9}$ cm^3 s^{-1}.

This process is followed by the *radiative transition* process*:*

$$N_2(B^3\Pi_g, v') \rightarrow N_2(A^3\Sigma_u^+, v) + h\nu\ (1^+) \quad (9)$$

with an emission probability of $A_4 = 2.4 \times 10^5$.

The N_2 (C) active species population were created via two consecutive reactions:

- the *electronic excitation* of the nitrogen molecular energy ground-state:

$$e + N_2(X_1\Sigma_g^+) \rightarrow N_2(C^3\Pi_u) + e \quad (10)$$

with the reaction rate $k = 7.5 \times 10^{-12}$ cm^{3}s^{-1},

- the *radiative transition*:

$$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu\ (2^+) \quad (11)$$

with the radiative life time $\tau = (45.4 \pm 4.0 \div 1.5 \pm 0.5) \times 10^{-9}$s for pressures varying in the range of ($10^{-4} \div 1.0132 \times 10^3$) mbar.

A significant decrease of N_2 (B) active species population, due to the quenching mechanisms, was observed while the N_2 (C) active species population have a spectacular increase. The atomic nitrogen concentration was also strongly reduced in the presence of hydrogen.

In the main, the explanation of this behavior is due to the fact that the presence of pure hydrogen or compounds containing hydrogen, even in very small quantities, produces a strong de-activation of the vibrational higher energy levels via *vibration-translation* energy transfer reactions between molecular nitrogen and molecular hydrogen, a process which becomes dominant for the high values of vibration numbers ($v \geq 45$), as it follows:

$$H_2 + N_2(X, v) \rightarrow H_2 + N_2(X, v\text{-}1). \quad (12)$$

The effect of this reaction is a strong diminution of the dissociation rate of the molecular nitrogen at addition of increasing amounts of hydrogen which results in a decrease of nitrogen atoms concentration and a considerable reduction of the intensity of the first spectral positive system of molecular nitrogen [7].

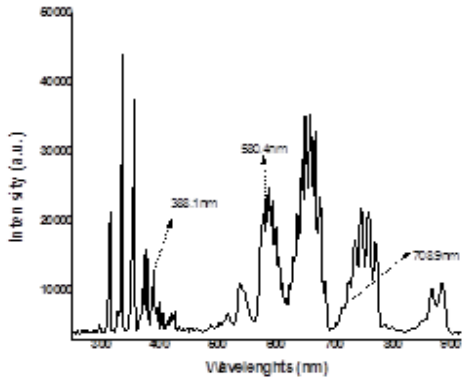

Fig. 6 - Emission spectrum of pure molecular nitrogen plasma in d.c. flowing discharge (p=4 mbar, I=50 mA).

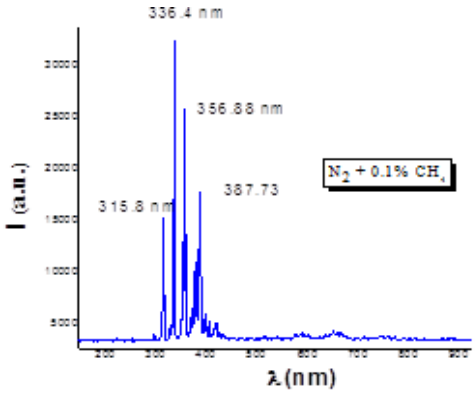

Fig. 7- Emission spectrum of (nitrogen+0.1% methane) gas mixture plasma in d.c. flowing discharge (p=4 mbar, I=50 mA).

4. CONCLUSIONS

In this paper there were presented two types of plasma discharges with different characteristics: an alternating current discharge into a mixture of neon and hydrogen, at pressures of about 140 mbar and a flowing discharge in continuous current in nitrogen and hydrogen mixture, at pressures up to 5 mbar.

The common element in the two types of discharges presented in this paper is the hydrogen. It has a decisive role in the mechanisms that lead to a "cleaning effect "of the plasma emission spectrum obtained under different pressures and electrical power conditions.

However, in both cases, the quenching mechanisms of certain energy levels of neon, respectively nitrogen occur by involving the high vibrational levels of the hydrogen molecule, as it happens with the Penning reaction in neon and hydrogen plasma as well as in the reactions that take place in plasma of nitrogen and hydrogen. In the molecular hydrogen spectrum there is a great variety of electronic levels, each one with its superimposed vibrational and rotational structures.

As we have mentioned before, the molecular nitrogen has one of the richest spectra of any diatomic molecule. This means that the great number of energy levels that characterizes both molecules of hydrogen and nitrogen spectra facilitates the energetic transfers between them, by non - radiative de-excitation processes.

As to the role of hydrogen mediator in the production of the M-effect, it should be noted that, as a third partner in the resonant three-body reaction, it acts in its atomic state (metastable level), in which the surplus energy of the reaction is taken up.

Future studies can elucidate the area of energy levels involved in these energy shifts in the studied collision processes.

REFERENCES

1. G.Musa, A.Popescu, A. Baltog, C.P. Lungu, *Monocchromatization of the radiation of discharges in multiple gas mixtures*, Romanian Reports in Physics, **45**, 287-341 (1993).
2. G. H. Dieke, *The Molecular Spectrum of Hydrogen and Its Isotopes*, Journal of Molecular Spectroscopy, **2**, 494-517 (1958).

3. L. Ciobotaru, P. Chiru, C.C. Neacsu, G. Musa, *PDP type barrier discharge ultraviolet radiation source*, Journal of Optoelectronics and Advanced Materials, **6**, 321-324 (2004).
4. L.C. Ciobotaru, *Monochromatisation effect - AC/DC discharges comparative behavior*, Romanian Reports in Physics, **62**, 134-141 (2010).
5. I. Gruia, L.C. Ciobotaru, *Monochromatization and polarization of neon spectral lines in constant/variable magnetic field*, Romanian Reports in Physics, **69**, 409 (2017).
6. Alf Lofthus and P.H. Krupenie, *The Spectrum of Molecular Nitrogen*, J. Phys. Chem. Ref. Data, **6**, no. 1 (1977).
7. L.C. Ciobotaru, D.S. Popa, *Wall material interaction with the active species in a nitrogen-methane D.C. flowing discharge*, Vacuum, **110**, 183-189 (2014).
8. C. Gavrila, I. Gruia, C. Lungu, *Determining the radial distribution of the emission coefficient from a plasma source*, Optoelectronics and Advanced Materials – Rapid Communications, **3**, 835–838 (2009).
9. L.C. Ciobotaru, I. Gruia, *Study of Paschen condition in the frame of monochromatization – effect of visible light*, Romanian Journal of Physics, **61**, 1339–1353 (2016).
10. L.C. Ciobotaru, I. Gruia, *Quasi-monochrome light polarization study in binary electropositive-electronegative gas mixture*, Romanian Journal of Physics, **61**, 657–665 (2016).
11. C. Gavrila, I. Gruia, A.E. Sandu, *Correlation analysis of the polarization degree for the gas mixture H_2-Kr*, Romanian Journal of Physics, **61**, 638–647 (2016).