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THE SPECTRAL 'CLEANING' MECHANISMS OF EMISSION SPECTRA FOR NEON/NITROGEN WITH HYDROGEN MIXTURES PLASMA: A REVIEW

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Abstract. In this paper we review the interesting spectral 'cleaning' phenomenon that 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, namely 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 of the emission intensity of the second positive system of the nitrogen molecule at the expense of all others characteristic spectral systems. The effect occurs in the first case in stationary discharges, both in alternating current and in D.C., at a total pressure of the gaseous mixture greater than 10 mbar while, in the second case, in a continuous flow D.C. discharge, at pressures below 6 mbar.

Key words: cleaning effect, hydrogen, reaction mechanisms.

1. INTRODUCTION

In terms of this paper, the 'cleaning effect' of an emission spectrum means a clear 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, in this case, neon and respectively, nitrogen, see the previous works [1–16].

In the first case, namely in a ($Ne+H_2$) gas mixture plasma, this effect of "cleaning" consists in a significant reduction of neon emission spectrum, virtually at one single line $\lambda = 585.3$ 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-millimetric inter-electrode distance and less for RF and D.C. 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 aspect of the molecular nitrogen emission spectrum, in the sense that the second positive system becomes very strong while the first positive system significantly reduces its intensity. The experiment has been realized using a (N_2-CH_4) flowing D.C. discharge at total pressures values of gas mixture less than 6 mbar.

The aim of this review paper is to perform a comparative analysis of the role of molecular hydrogen added to the two types of plasma, nitrogen and neon, respectively. On this line, we have interpreted the results obtained in previous papers regarding the study of reaction mechanisms and elementary processes occurring in situ. These ones had led us to the observation of the appearance of a common effect consisting in the substantial reduction of numerous spectral lines/molecular bands in the neon and nitrogen emission spectra.

Nevertheless, an important distinction must be lastingly made between these two situations because in neon plasma these phenomena of reducing the spectral lines to the addition of some quantities of hydrogen

are produced by processes at atomic level, whereas in the case of nitrogen plasma all effects occur at molecular level.

2. EXPERIMENTAL SET-UP

The A.C. discharge device used in the present study is a flat tube, representing a direct application of the dielectric barrier discharge (DBD) type such as plasma discharge panel (PDP). This device was presented in detail in previous papers [7-16], so we will show here only a schematic diagram among with a short description of its main technical characteristics, see Fig. 1.

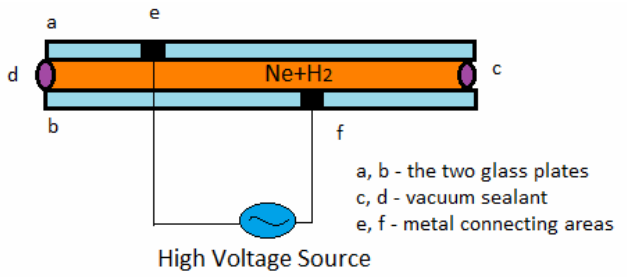

Fig. 1 – Lateral schematic representation of the PDP device.

Let us note that there are only two methods of generating non-equilibrium plasma at moderate to high pressures and room temperature, namely Corona and DBD-type discharges, the last ones called in the literature "silent discharges".

The DBDs are highly suited for chemical applications based on processes occurring in the plasma volume. These facilities are given by the combination of the property of having an intense excitement of the active species in the plasma volume, specific to the luminescence discharge (processes normally limited by the pressure increase) with the ability to work at high pressures, specific to the Corona discharge.

Dielectric barrier discharges take place in enclosures where at least one of the electrodes is dielectric coated. The insulation layer acts as a current limiter, stopping the transition to a Corona discharge. In fact, this limitation of the current pulse occurs due to the polarization of the electric charge on the dielectric, resulting in the appearance of a polarization voltage that opposes the voltage applied to the electrodes. For this reason, the discharge is extinguished, in the discharge chamber occurring phenomena specific to the post-glow regime (recombination, diffusion to the walls). The temporal duration of those two phases of glow and after-glow within a voltage pulse is determined by the magnitude of the polarization voltage. These phenomena manifest themselves at medium pressures (200÷400 mbar), the discharge keeping its luminous character (homogeneous and stable). From this succinct characterization of DBD is to be retained the possibility of obtaining active species with high energies at room temperature.

In the present experiment, the discharge device is made of two perfectly flat glass sheets with a thickness of 5 mm and an area of (300×50) mm^2, known as plasma discharge panel (PDP). Each glass plate is vacuum coated with a thin aluminium layer of 1 μm thickness forming a linear electrode. The length and thickness of the electrodes are 190 mm and 4 mm, respectively. The electrical connections of the electrodes are made on a perpendicular line on the surface they were deposited. Electrode glass surfaces are coated with a uniform dielectric layer having a thickness of 18-20 μm, barring the surface marked in black on the figure. These marked surfaces are used to include the discharge device in a power supply circuit equipped with a limitation resistance of 10 kΩ. The glass plates are tightly assembled, the discharge space being of maximum 1 mm, then filled with a ($Ne+40\%H_2$) gas mixture. The linear electrodes are placed face to face. Two polished quartz windows are mounted at the ends of the discharge tube in order to allow the recording of the emitted radiation, including the UV spectral lines.

According to the Paschen law, in regard with the sub-millimetre inter-electrodes distance, 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,

corresponding to the total pressure of gas mixture in experiment of 133 mbar and an optimum breakdown discharge frequency value varying between 8 and 10 kHz.

Concerning the second type of gas mixture plasma used in experiment, namely [$N_2+0.1\%H_2$ (CH_4)], the schematic diagram was also presented very thoroughly in previous works [3-6]. We shortly reiterate the description of the discharge tube construction and the main technical features, as follows: the discharge took place in a Pyrex tube, having the geometrical dimensions of 22 mm inner diameter and, respectively 24 mm outer diameter, between two side-armed identical hollow cylinder electrodes, made from an alloy of chromium-nickel, with 10 mm diameter. The inter-electrodes space was about 400 mm, measured in straight line. In the geometry of the discharge tube concerning the direction of the gas flow, firstly was placed the anode. Obviously, in experiment were used spectral purity gases (99.98%), because the impurities represent important centres of quenching. Gases flows were controlled and measured using mass flow-meters of MKS-type, with a range of measurement up to 1500 sccm (here sccm represents the acronym for Standard Cubic Centimetre per Minute) for nitrogen and, respectively 10 sccm for hydrogen/methane (or other hydrogen compounds).

All the measurements of pressure were made at the end of the tube, namely in the post discharge zone. In order to keep both the right pressure and flow rate during the experiment, the discharge tube was connected to a preliminary vacuum pump (the total pressure of the gas mixture must not exceed 6 mbar). Spectral data were obtained within the glow and after-glow discharge zones, and were recorded by means of a classic spectral analysis chain consisting of Varian-Techtronic spectrophotometer, equipped with a grating of 1200 grooves/mm, a 5 mm wide slit and $300\div860$ nm measurement range, Hamamatsu R 585 Photomultiplier, quartz optical fibre and recorder-system. The spectral resolution of the system was 0.05 nm. Alternatively, during the experiment, it was used an Optical Multichannel Analyzer (OMA) of $220\div900$ nm spectral range and a resolution of 1.5 nm. The integration time could be varied during the experiments in the $200\div1000$ ms range, depending on the brightness of the emitted radiation. The characteristics of the D.C. power supply were 5 kV / 0.2 A.

Other experimental conditions in discharge were established as follows: the total pressure of the gas mixture in the range of $130\div400$ Pa, the nitrogen flow rate in the range of $600\div1000$ sccm, the electrical power between $300\div360$ W and the value of the discharge D.C. intensity chosen in the range $50\div100$ mA, which was kept constant during all the measurements.

3. RESULTS AND DISCUSSION

The basic mechanism that generates the M-effect in electronegative-electropositive gas mixture was established to be the polar resonant three-body reaction with the following general form [7,8,17]:

$$P^+ + N^- + N^{\text{met}} \rightarrow (P^+N^-) + N^{\text{met}} \rightarrow P^* + N^{\text{ground state}} + (N^{\text{met}})^* + \Delta E \qquad (\Delta E \approx 0), \tag{1}$$

which, in the particular case of the ($Ne+H_2$) gas mixture plasma, becomes:

$$Ne^+ + H^- + H^*(n=2) \rightarrow (Ne^+H^-) + H^*(n=2) \rightarrow Ne^*(2p_1) + H^*(n=3) + H(n=1) + \Delta E. \tag{1*}$$

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, $(N^{\text{met}})^*$, the symbol for the metastable electronegative atom in a state of higher energy than the previous one, 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, see Fig.2) decays radiatively on $1s_2$ energy level via reaction (2), leading to the emission of the dominant yellow spectral line:

$$Ne^*(2p_1) \rightarrow Ne^*(1s_2) + h\upsilon, \tag{2}$$

where υ is the frequency corresponding to $\lambda=585.3$ nm.

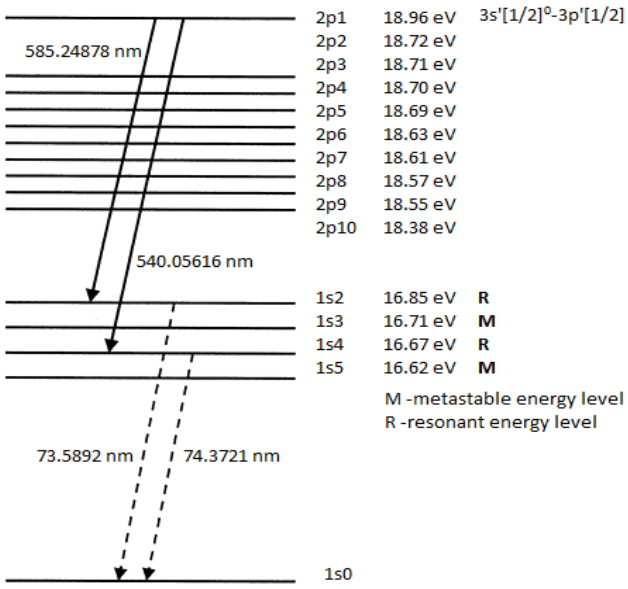

Fig. 2 – Simplified Paschen energy diagram of neon (adapted from N.A. Kaptov, *"Electrical phenomena in gases and vacuum"*, Ed. Tehnica, Bucharest, 1955).

The other principal reactions, in which is involved the hydrogen, except for Eq. (2), are the following:

$$e + H_2 \rightarrow e + H_2^* \rightarrow H^- + H^*, \tag{3}$$

$$H^- + Ne^+ \rightarrow Ne^*(2p_1) + H, \tag{4}$$

$$H^- + Ne^+ + M \rightarrow Ne^*(2p_1) + H + M, \tag{5}$$

where M is the notation for the third body that participates in the reaction, and

$$Ne^*(1s_i) + H_2 \rightarrow H_2^+(v=6) + Ne + e \ \ (\textit{the Penning-type reaction}); \ \ i = 1 \div 4. \tag{6}$$

We take $k(s_i) = (0.6 \div 1.4) \times 10^{-10}$ cm^3/s [18].

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 $2p_1$, which afterwards decays to the $1s_2$ level, via the three-body resonant reaction (5), at the same time having a contribution to the depletion of the lower level $1s_2$ through Penning-type collisions, as indicated in reaction (6).

It is interesting to observe that the two reactions underlying the occurrence of the M-effect, namely the preferential population of the $2p_1$ level and the depopulation of the level $1s_2$, in order to achieve the $(2p_1 - 1s_2)$ transition resulting in the M-effect, are both resonant.

So, from a large number of experimental measurements, it was established that the polar three-body reaction in Eq. (1) has a significant probability of realization when the energy defect values vary in the range of $[\pm 1$ eV].

At the same time, for the reaction from Eq. (6), the energy defect is only 0.05 eV, because the energy of neon resonance level $1s_2$ is 16.85 eV and the energy of hydrogen molecular ion on the vibration level $v = 6$ is 16.8 eV [19-20].

Even the depletion of the $1s_2$ level represents a very important process in obtaining the M-effect, inclusive for lasing (or LASER effect), we have to consider the following aspects:

– the lifetime of $Ne(1s_2)$ is 1.5 ns while for $Ne(2p_2)$ is 14.4 ns, that is, ten times bigger;

– the neon excited atoms $Ne^*(1s_i)$, $i = 1 \div 4$, are precursors of excited neon atoms $Ne^{**}(2p_m)$, $m = 1 \div 10$, obtained by electronic coupling reactions of the form: $Ne^*(1s_i) + e \rightarrow Ne^{**}(2p_m) + e$; $i = 1 \div 4$, $m = 1 \div 10$.

For this reason, the percentage value of hydrogen in the gaseous mixture cannot be greater than the value of 50, in which case there is no longer the M-effect.

It results that hydrogen entails in two opposite ways the "cleaning" mechanism of the neon emission spectrum and, at the intersection of these two processes, appears the monochromatization effect of visible light.

Note that, although energetic active species such as excited atoms and neon ions appear in the glow phase, negative hydrogen ions are formed only in the after-glow region where the necessary conditions are met (low or zero electric field, low energy and high electron density). That is why the M-effect also appears in the DBD after-glow phase.

The two spectra obtained based on Optical Emission Spectroscopy (OES) measurements accomplished in pure neon and respectively in ($Ne+40\%H_2$) plasma, at a total gas mixture pressure of 100 torr (133 mbar), are shown in Figs. 3 and 4.

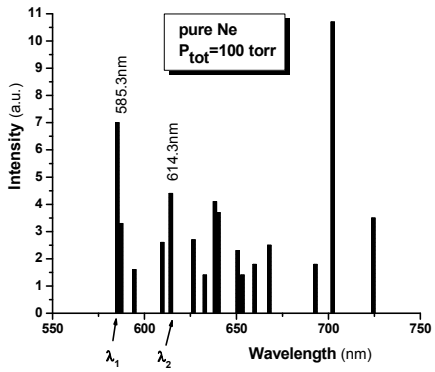

Fig. 3 – The emission spectrum of pure neon plasma in a DBD (adapted from Ref. [16]).

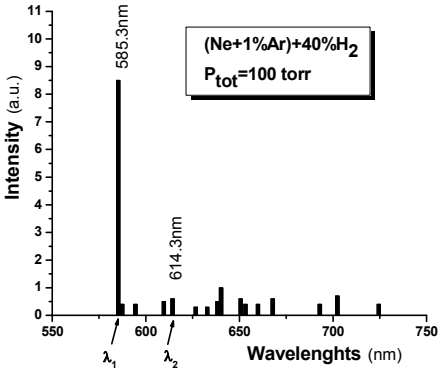

Fig. 4 – The emission spectrum of (Ne+40%H2) gas mixture plasma in a DBD (adapted from Ref. [16]).

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 increases – see Figures 5 and 6.

Molecular nitrogen has one of the densest spectra of any diatomic molecule [21]. Numerous molecular 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.

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 particular case, the active species identified in the discharge zone were the radiative species $N_2(B)$ and $N_2(C)$ that emit the nitrogen spectral systems (1^+) and respectively (2^+), whose generating mechanisms are briefly presented below:

a) The production of $N_2(B)$ species. By the decomposition of the methane molecule, one obtains the molecular hydrogen:

$$CH_4 + N_2 \rightarrow 2\,H_2 + (CN)_x,\ x = 1,2 \tag{7}$$

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

$$N_2(A) + N_2(A) \rightarrow N_2(B) + N_2(X) \tag{8}$$

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

This process is followed by the radiative transition process:

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

with an emission probability of $A_4 = 2.4\times10^5$.

b) The production of $N_2(C)$ species. The $N_2(C)$ active species population and their radiation were created via two consecutive reactions, listed below:

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

$$e + N_2(X_1\Sigma_g^+) \rightarrow N_2(C^3\Pi_u) + e \tag{10}$$

with the reaction rate $k = 7.5\times10^{-12}$ cm^3 s^{-1}

– the radiative transition:

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

with the radiative life time $\tau = (45.4\pm4.0 \div 1.5\pm0.5)\times10^{-9}$ s for pressures varying in the range of $(10^4 \div 1.0132\times10^3)$ mbar.

We note that the addition of very small amounts of hydrogen or compounds containing hydrogen in the plasma of pure nitrogen inhibits practically the formation of the excited species of neutral and ionic molecular nitrogen, including the production of nitrogen atoms, less the active species $N_2(C)$ that presents a multiplication up to 6 times [1–3]. These processes lead to the significant decrease of intensities for the spectral molecular systems 1 plus, 1 minus and the atomic spectral lines of nitrogen, at the same time with the strong intensification of the 2 plus spectral system emission. The explanation of this phenomenon consists in the fact that the existence of molecular hydrogen in pure nitrogen plasma causes the extinction of $N_2(A)$ metastable species by the following excitation energy transfer reaction:

$$N_2(A) + H_2(CH_4) \rightarrow N_2(X) + H_2(CH_4) \tag{12}$$

with reaction rate $k_{(CH4)} = 1\times10^{-14}$ cm^3 s^{-1}.

So, a significant decrease of $N_2(B)$ active species population, due to the quenching mechanisms of the $N_2(A)$ metastable species, can be observed from Eq. (8); on the contrary, the $N_2(C)$ active species population has a spectacular increase. This behaviour is due to the decrease of associative ionization reaction rate in pure nitrogen plasma mixed with very small hydrogen amounts, a fact that implies an increase in the reduced electric field in order to maintain a constant discharge current value. Consequently, the degree of excitation of molecular nitrogen on the vibrational level (C) increases very much, as active species produced directly by electronic colliding processes.

The atomic nitrogen concentration was also strongly reduced in the presence of hydrogen. The explanation of this behaviour is due to the fact that the presence of pure molecular hydrogen or compounds containing hydrogen in the original nitrogen plasma, even in a very small quantity, 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 that becomes dominant for the high values of vibration energy numbers ($\nu \geq 45$):

$$H_2 + N_2(X, \nu) \rightarrow H_2 + N_2(X, \nu-1). \tag{13}$$

The effect of this reaction is a strong diminution of the dissociation rate of the molecular nitrogen, as presented bellow in Eq. (14), which results in a decrease of nitrogen atoms concentration and a considerable reduction of the intensity of the nitrogen atomic spectral lines:

$$N_2(X, \nu) + N_2(X, \nu = 45) \rightarrow N_2(X, \nu-1) + N + N. \tag{14}$$

These processes are also related to the exceptional chemical stability of nitrogen, which can be diminished by increasing the temperature. Thus, nitrogen forms a bi-atomic molecule, between nitrogen atoms being a distance of approximately 0.1 nm. A particular aspect is the difficulty of "breaking" the nitrogen molecule, even at high temperatures, the dissociation energy having a very high value of about 9.78 eV.

In plasma similar to that of the experiments overviewed in this paper, that is, at low pressure and high electrical power dissipated in discharge, the dissociation process generates nitrogen atoms in fundamental energy state, which then evolve into molecules in a state of unstable energy that pass then in stable energetic condition. This situation may explain the occurrence of de-excitation process presented in Eq. (13).

Another interesting link to the processes presented in this article can be made with relatively recent studies (performed in the last decade) about the phenomenon of interference occurring in the ionization of bi-atomic molecules, especially the hydrogen and nitrogen molecules. This phenomenon is due to the bi-centric character of the respective molecules. Thus, when ionizing the hydrogen molecule through the impact of rapid projectiles, as the electrons of great velocity, there is a phenomenon of superposition of the waves associated with the electron scattered on the two nuclei that cause oscillations in the ratio of the effective cross sections $\sigma(H_2)/\sigma(2H)$, depending on the electron velocity emitted by ionization [22]. As we have shown, the positive molecular hydrogen ion plays an essential role in the Penning reaction, eq. (6), underlying the occurrence of the M-effect. As for the molecular nitrogen ion, it emits the *1-minus* spectral system, also inhibited by the addition of hydrogen, process that has not been discussed in this article, but which can be included in a future study to be published elsewhere.

The results presented here are also very interesting because the conditions in the high terrestrial atmosphere from the polar zones are very similar to those described in the experiment, both the hydrogen and nitrogen, known as the most abundant element in the terrestrial atmosphere, being present in their ionized and excited energy states.

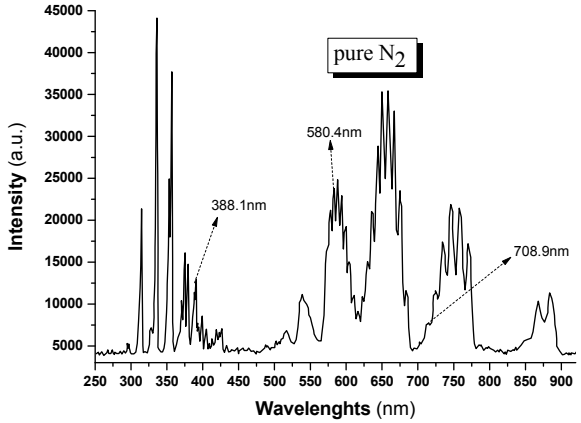

Fig. 5 – Emission spectrum of pure molecular nitrogen plasma in D.C. flowing discharge (p=4 mbar, I=50 mA) – adapted from Ref. [5].

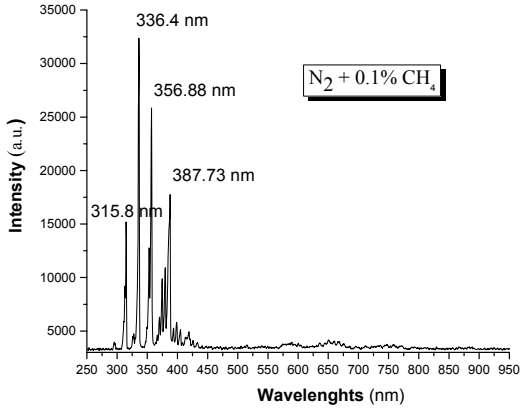

Fig. 6 – Emission spectrum of (nitrogen + 0.1% methane) gas mixture plasma in D.C. flowing discharge (p=4 mbar, I=50 mA) – adapted from Ref. [5].

4. CONCLUSIONS

In this paper we have reviewed the results obtained for 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 6 mbar.

These discharges have as a common element, namely the presence of the molecular hydrogen. It has a key role in the mechanisms that lead to a "cleaning effect" of the plasma emission spectrum obtained under different pressures and electric parameters. As observed, on the basis of numerous experimental measurements, the molecular hydrogen causes strong enhancement of the line $\lambda = 585.3$ nm in all combinations with noble gases, the most marked effect appearing when was mixed with neon. This is due not only to its very important role in realizing the depopulation of the lower level of the transition on which the radiative emission is produced, but also as an important agent of the process of population inversion. In the first case, hydrogen is involved in the Penning reaction as a positive molecular ion while, in the second case, acts in the polar three-body reaction like a negative atomic ion. Therefore, although it shows many similarities with the LASER effect, the M-effect is essentially distinguished by the population mechanism of the higher energy level of radiative transition, which is extremely selective due to its resonant character.

In nitrogen/hydrogen plasma, the pressure of the mixture being smaller by two orders of magnitude than in the case of neon/hydrogen, the hydrogen acts only in its excited states. However, the effect is

amazing: it succeeds in inhibiting the emergence of all major molecular systems of nitrogen (namely *1-plus*, *2-plus* and *1-minus*), including the atomic spectral lines.

In the molecular hydrogen spectrum there is a great variety of electronic levels, each one with its superimposed vibrational and rotational structures. An interesting aspect is related to the spatial distribution of the energy levels of rotation that, at the hydrogen molecule, are very distant due to its small mass. As we have mentioned before, the molecular nitrogen has one of the richest spectra of any diatomic molecules.

This means that the existence of a great number of energy levels, which equally characterizes hydrogen and nitrogen molecular spectra, facilitates the energetic transfers between them by non-radiative de-excitation processes. Upcoming studies must be performed in order to elucidate the area of energy levels involved in these energy shifts in the studied collision processes.

REFERENCES

1. S.D. POPA, *Vibrational distributions in a flowing nitrogen glow discharge,* Journal of Phys D: Appl. Phys., **29**, *2*, pp. 411–416, 1996.
2. S.D. POPA, L. HOCHARD, A. RICARD, *Production of N_2 radiative states in N_2-H_2 flowing D.C. discharge*, Journal de Physique III (France), **7**, pp. 1331–1337, 1997.
3. S.D. POPA, P. CHIRU, L. CIOBOTARU, *Modification of the nitrogen spectrum in a N_2-H_2 flowing dc discharge*, Journal Phys D – Appl. Phys., **31**, pp. L53–L55, 1998.
4. S.D. POPA, L. CIOBOTARU, *Changes of the nitrogen 2-nd positive system due to small methane addition,* Journal of Optoelectronics and Advanced Materials, **9**, *9*, pp. 2935–2936, 2007.
5. L.C. CIOBOTARU, D.S. POPA, *Wall material interaction with the active species in a nitrogen-methane D.C. flowing discharge*, Vacuum, **110**, pp. 183–189, 2014.
6. L.C. CIOBOTARU, I. GRUIA, *Study of the carbon atoms production in methanol/ethanol-nitrogen flowing post-discharge plasma*, Romanian Journal of Physics, **60**, *9-10*, pp. 1536–1549, 2015.
7. G. MUSA, A. POPESCU, A. BALTOG, C.P. LUNGU, *M-effect, monochromatization of the radiation of discharges in multiple gas mixtures* (paper review), Romanian Reports in Physics, **45**, p. 287, 1993.
8. C.C. SURDU-BOB, G. MUSA, *The kinetics of monochromatization of plasma light emission,* Journal of Physics D: Applied Physics, **41**, p. 172004, 2008.
9. L. CIOBOTARU, P. CHIRU, C.C. NEACSU, G. MUSA, *PDP type barrier discharge ultraviolet radiation source,* Journal of Optoelectronics and Advanced Materials, **6**, *1*, pp. 321–324, 2004.
10. L.C. CIOBOTARU, *Monochromatization effect – AC/DC discharges comparative behavior*, Romanian Reports in Physics, **62**, *1*, pp. 134–141, 2010.
11. L.C. CIOBOTARU, *Comparative investigation of monochromatization light effect at molecular/atomic level in electronegative-electropositive gas mixtures plasma*, Optoelectronics and Advanced Materials, Rapid Communications, **6**, 5-6, pp. 668–672, 2012.
12. L.C. CIOBOTARU, *Considerations on the Penning reactions role for the monochromatization – Effect in noble gases-hydrogen mixture*, Optoelectronics and Advanced Materials, Rapid Communications, **5**, *3*, pp. 327–329, 2011.
13. G. MUSA, L.C. CIOBOTARU, B. IONUT, *The M-effect in A.C./D.C. discharges in $He+O_2/Cl_2$ gas mixtures,* Journal of Optoelectronics and Advanced Materials, **8**, *3*, pp. 1292–1297, 2006.
14. G. MUSA, L.C. CIOBOTARU, *Tentative explanation of selective population of the $2p_1$ level of neon atoms in the case of M-effect in neon + hydrogen and neon + oxygen gas mixtures*, Journal of Optoelectronics and Advanced Materials, **6**, *4*, pp. 1339–1344, 2004.
15. L.C. CIOBOTARU, I. GRUIA, *Study of Paschen condition within the frame of monochromatization – effect of light*, Romanian Journal of Physics, **61**, *7-8*, pp. 1339–1353, 2016.
16. G. MUSA, C.L. CIOBOTARU, P. CHIRU, A. BALTOG, *The M-effect in argon-hydrogen gas mixtures*, Journal of Optoelectronics and Advanced Materials, **6**, pp. 459–464, 2004.
17. L.C. CIOBOTARU, I. GRUIA, *Main factors affecting the appearance of M-effect in variable magnetic field*, Vacuum, **167**, pp. 500–508, 2019.
18. M.A. LIEBERMAN, A.J. LICHTENBERG, *Principles of plasma discharges and materials processing,* John Wiley & Sons, N.Y., 1994.
19. G.H. DIEKE, *The molecular spectrum of hydrogen and its isotopes,* Journal of Molecular Spectroscopy, **2**, pp. 494–517, 1958.
20. A.V. PHELPS, *Diffusion, de-excitation, and three-body collision coefficients for excited neon atoms*, Phys. Rev. A, **114**, p. 1011, 1959.
21. ALF LOFTHUS, P.H. KRUPENIE, *The spectrum of molecular nitrogen*, J. Phys. Chem. Ref. Data, **6**, *1*, 1997.
22. N. STOLTERFOHT, B. SULIK, L. GULYÁS, B. SKOGVALL, J.Y. CHESNEL, F. FRÉMONT, D. HENNECART, A. CASSIMI, L. ADOUI, S. HOSSAIN, J.A. TANIS, *Interference effects in electron emission from H_2 by 68-MeV/u Kr^{33+} impact: Dependence on the emission angle*, Phys. Rev. A, **67**, 3, p. 030702, 2003.

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