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Investigation of Monochromatization Light Effect at Molecular/Atomic Level in Electronegative-Electropositive Gas Mixtures Plasma

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***Abstract*—**In electronegative-electropositive gas mixtures plasma, at a total pressure varying in the range of ten to hundred Torr, the appearance of a quasi-mochromatization effect of the emitted radiation was reported. This radiation could be the result of the generating mechanisms at molecular level, which is the case of the excimer radiation but also at atomic level. Thus, in the last case, in (Ne+1%Ar/Xe+H_2) gas mixtures plasma in a dielectric barrier discharge, this effect, called M-effect, consists in the reduction of the discharge emission spectrum practice at one single, strong spectral line with λ = 585.3 nm. The present paper is concerned with the characteristics comparative investigation of the principal reaction mechanisms involved in the quasi-monochromatization effect existence in the case of the excimer radiation, respectively of the M-effect. Also, the paper points out the role of the metastable electronegative atoms in the appearance of the monochromatization – effect at atomic level.

***Keywords*—**Colombian forces, Direct Harpoon reaction, Monochromatization – effect, Resonant polar three-body reaction.

I. Introduction

EXCIMERS represent a class a molecules formed by the combination between a halogen and a rare gas, namely an electronegative-electropositive gas mixture. These molecules do not exist in the ground state which is highly unstable but only in their excited states. By a dissociating de-excitation process it can be generated UV excimer radiation which is a quasi-monochrome radiation. A molecular band is emitted at the transition from the upper excited molecular state to the lower level of the non-excited unstable molecule. The study was performed in a dielectric barrier discharge (DBD) having a plasmagen gas mixture formed by the rare gas (R_g), the halogen (X) and the buffer gases, which usually are chosen also as rare gases. The formation of the hetero-nuclear excimer molecules starts with the excitation and ionization processes of the rare gas atoms and molecular halogen by the high energy electrons collisions (e) produced in the DBD-glow phase [1] -[7]:

$$e + R_g \rightarrow 2e + R_g^+ \quad (1)$$

$$\rightarrow e + R_g^* \quad (2)$$

$$e + X_2 \rightarrow 2e + X + X^+ \quad (3)$$

$$\rightarrow 2e + X_2^+ \quad (4)$$

$$\rightarrow X + X^- \quad (5)$$

$$\rightarrow e + X_2^* \quad (6)$$

At low pressures, (0.5-5) Torr, the major reaction for the excimer formation is accepted to be the *reverse Harpoon – reaction* between the ground state rare gas atom and the excited states (^3P, ^1D) of the molecular halogen:

$$R_g + X_2^* \rightarrow R_g X^*(B) + X \quad (7)$$

This reaction is a two-body reaction and for this reason is very attractive one for explaining the formation of excimer molecules at low pressures.

At high pressure (10-760) Torr, the R_gX^* molecules excimer are generated either by the *direct Harpoon - reaction* or by the three-body ionic recombination reaction, depending on the work pressure range. Thus, at 10s Torr pressure the major reaction for the excimer formation is the *direct Harpoon reaction.* The excited states of the rare gas atoms are transferring an electron to the halogen molecule (or compounds containing halogen) and form electronically excited states of the excimer molecules:

$$R_g^* + X_2 \rightarrow R_g X^*(B) + X \quad (8)$$

At 100s Torr pressure the major process for the excimer formation is the ionic recombination reaction:

$$R_g^+ + X^- + M \rightarrow RgX^*(B) + M \quad (9)$$

The electronically excited excimer molecules $R_gX(B)$ decay radiatively to the molecular ground state in connection with the rapid excimer molecule dissociation attributed to the bound-free transitions:

$$R_g X^* \rightarrow R_g + X + h\nu \quad (10)$$

In contrast with the excimer radiation studies based on the fact that the excimer molecules exist only in excited states and in which appears the problem to find efficient channels reaction to form the excited molecules, in the frame of monochromatization effect study at atomic level the main problem consists in explaining the preferential population mechanism of the levels responsible for the dominant spectral lines emission. In fact, the so called"monochromatization – effect", (M-effect), consists in the reduction of the discharge emission spectrum practice at one single line, namely λ = 585.3 nm, in (Ne+Ar+H_2) or (Ne+Xe+H_2) gas mixtures. In the present experiments it was used a Dielectric Barrier Discharge (DBD), but the effect was observed also in DC discharge.

Fig. 1 and Fig. 2 show the emission spectrum of a dielectric barrier discharge in pure Neon gas respectively, the emission spectrum in a (Ne +1%Ar+*40% H_2*) Penning gas mixture . It

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has been observed an emission spectrum nearly monochromatic since when, at the Penning-type mixture, was added hydrogen with a maximum half partial pressure as against the total pressure of the gas mixture (after this value of hydrogen pressure the effect diminished drastically). The red color of the discharge turned into a yellow monochromatic one, while the whole spectrum practice was reduced at a single, strong spectral line with $\lambda_1 = 585.3$ nm.

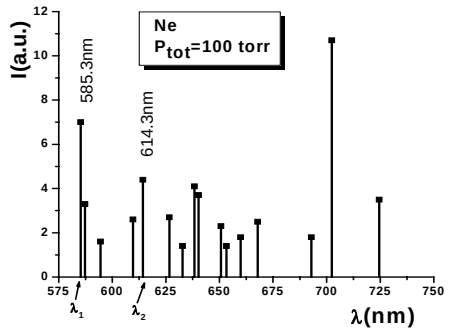

Fig. 1 Emission spectrum of dielectric barrier discharge in pure Neon gas

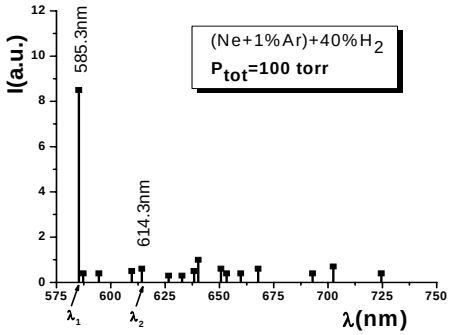

Fig. 2 Emission spectrum of dielectric barrier discharge in *(Ne+1%Ar) + 40%H_2* gas mixture

As it was assumed in our previous papers [8]-[11], the monochromatization-effect of light at atomic level is the result of the *resonant polar three-body collision reaction* of ionized and excited atoms. Besides the main requirement to have positive-negative ions, it is also necessary to have accomplished other experimental conditions as: low gas temperature and elevated pressure of the gas mixture in order to increase the heavy particles triple collision reaction cross-section (the *thermolecular reactions*) and high density of the negative ions. Low electric field in the plasma and high electron densities can both increase the density of negative ions, conditions accomplished in the after-glow phase of the dielectric barrier discharge for the AC discharges and in the negative light region for the DC discharges.

The general form of the reaction, in case of the M-effect, is the following:

$$P^+ + N^- + N^{met} \rightarrow (P^+N^-) + N^{met} \rightarrow P^*(s_i) + N^{ground\ state} + (N^{met})^* + \Delta E\ ,\ (\Delta E \approx 0) \quad (11)$$

where the notation s_i represents the selective populated level.

The used notations are the following: P and N are symbols of the atoms of electropositive and respectively the electronegative gases in the mixture, P^+ is the symbol for the positive ion, N^- is the symbol of the negative ion, N^{met} is the symbol for the metastable negative atom, $(N^{met})^*$ is the symbol of the excited electronegative atom standing in a upper state energy, P^+ is the electropositive atom in an excited state and ΔE is the notation for the energy defect of reaction.

The first reaction is followed by the radiative de-excitation reaction of the electropositive atom:

$$P^* \rightarrow P + hc/\lambda_1 \quad (12)$$

where λ_1 is the dominant line producing the monochromatization effect, and then followed by the reaction:

$$(N^{met})^* \rightarrow N^{met} + hc/\lambda. \quad (13)$$

This reaction is very important in the economy of the process because it indicates the way in which the number of the electronegative metastable atoms is remaining constant.

II. Experimental Set-Up

The AC discharge was a dielectric barrier discharge in electronegative-electropositive gas mixtures produced between two thin, parallel and linear aluminum electrodes of 5 mm width and 200 mm length. Both electrodes were covered with 20μm glass dielectric layer. The distance between the electrodes (i.e. discharge space) was d≤1 mm. The thin film conductors were obtained in vacuum, by deposition on two glass plates, through the agency of an applied mask. The electrical supply was an AC $1kV_{pk-pk}$ square wave voltage with an optimum of frequency in the range of 10-50 kHz – Fig. 3 [8].

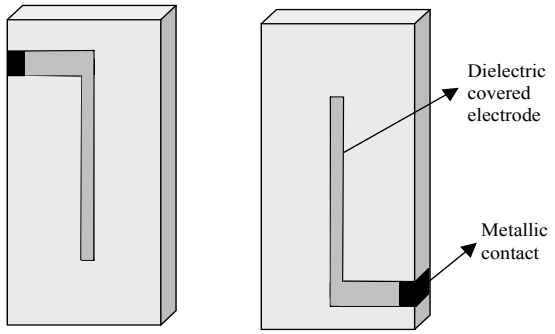

Fig. 3 View of the deposited thin film electrodes on glass plates

The experimental set-up used for measurements in DC discharge consists in a discharge tube of 30 mm diameter Pyrex glass having a central part of quartz, in order to allow the passage of the UV radiation. The length of this part was of 80 mm and the total length of the tube 160 mm. The two electrodes are made of Φ 1.5 mm tungsten rod. The top of the electrodes (1-2 mm) is sharp while the rest is covered with glass in order to limit the discharges out of the inter-electrodes space. The distance between the two electrodes was of 8 mm [9]. The experimental discharge devices can be pumped down and then filled with various gas mixtures. The optical emission spectra of the discharges were registered using an OMA (Optical Analyzer Multichannel), spectral range 200-900 nm and the resolution of 1.5 nm – Fig. 4.

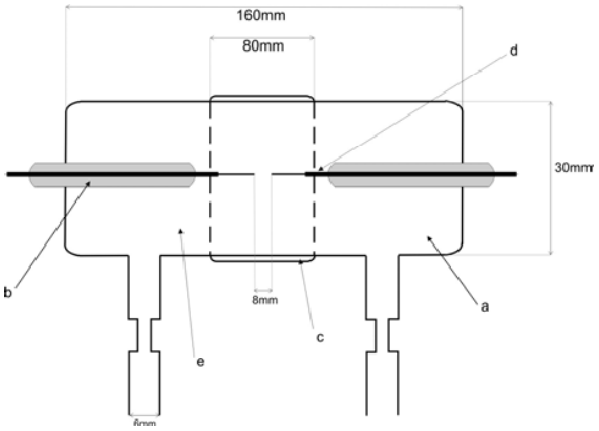

Fig. 4 The experimental set-up for DC discharge (*a.* Pyrex – glass discharge tube, *b.* glass cover, *c.* wolfram electrodes Φ 1.5 mm, *d.* Pyrex- glass capillary tubes Φ 6.0 mm)

III. Results and Discussion

The *Harpoon reactions* are a type of chemical reactions between two substances, one of them prone to form a cation, in our case the rare gas, and the other one prone to form an anion, generally a halogen. The main feature of these reactions type is the fact that they have *steric factors* greater than unity, and by consequence they take place faster than predicted by collision theory. The colliding particles have greater cross sections than the pure geometrical ones due to the fact that, when the particles involved in collision are close enough, an electron "jumps" from one of the particles to the other forming an anion and a cation, between, subsequently, it will appear the Colombian attraction force.

Marking with R_{max} the largest distance at which the electronic charge transfer can occur on energetic ground states, the *Harpoon reactions* can be energetic characterized by the following equation:

$$\frac{-e^2}{R_{\max}} + \Delta E_0 = 0 \tag{14}$$

Where

$$\Delta E_0 = V_p - V_a \tag{15}$$

In relation (15), V_p is the ionization potential of the rare gas and V_a is the electron affinity of the halogen. The reaction (14) represents a minimal energetic condition in order to permit the appearance of an excited molecule formed by the rare-gas and the halogen, being a reaction with an energetic threshold. The kinetic energy gained in the high energy electrons collisions produced in the DBD glow - phase must be large enough in order to permit the necessary proximity which allows the electron "jumping" between the two colliding particles. The rest of the colliding particles kinetic energy could be used for the electronic - vibrational excitation of the excimer molecule, including the metastable and the resonant states. The de-excitation process takes place in two steps: first, the excited states decay to vibrationally excited excimer states and in the next step the highly–excited states molecules submit vibrational relaxation with subsequent radiative dissociation or decay radiatively directly on the molecular ground state followed by the rapid dissociation of the excimer molecule due to its high instability.

Unlike this mechanism reaction which leads to the formation of the excited states of a molecule which does not exist in his ground state, the monochromatization of light at atomic level, which was called in our previous published papers *M-effect*, is a phenomenon based on the reaction of the positive atomic ion of the rare gas and the negative atomic ion of an electronegative gas (the halogens, the oxygen and especially the hydrogen). This reaction is based on the existence of a third particle, in a convenient energetic state, namely the metastable atoms of the electronegative gas. Only if this condition is accomplished, the reaction becomes resonant. A detailed explanation of the kinetics reaction in the most representative case for the M-effect, namely in neon-hydrogen gas mixtures, was presented in our previous papers [12].

For instance, the polar three-body resonant reaction (11) in case of a DBD in neon- hydrogen, helium-oxygen and argon-hydrogen gas mixtures can be written as following:

$$Ne^+ + H^- + H^*(n=2) \rightarrow (Ne^+H^-) + H^*(n=2) \rightarrow Ne^*(2p_1) + H^*(n=3) + H(n=1) \pm \Delta E \tag{16}$$

$$He^+(24.5eV) + O^-(1.46eV) + O^{met}(9.146\ eV/9.521eV) \rightarrow He^* + O^{met*}(10.74eV) + O(0\ eV) \tag{17}$$

$$Ar^+(15.76eV) + H^-(0.75eV) + H^{met}(10.2eV) \rightarrow Ar^* + H^{met*}(12.09eV) + H(0\ eV) \tag{18}$$

In these reactions, namely in (16), (17) and (18), the colliding particles are already ionized and the existence of the electronegative metastable atoms, which take the excess of energy, prevents the formation of a *molecular* compound. For pressures above the value of 10 Torr, the appearance of the trapping phenomenon of the resonance radiation allows the formation of electronegative quasi-metastable atoms standing in n = 2 level energy with a life-time comparable with the one of the metastable energetic states. For instance, as it can be observed in (16), the intermediary state of this reaction, namely the formation of a three-particles compound, corresponds to the binding of the negative-positive ions close by the excited hydrogen atom on the resonance level $2p^2\,P^0_{3/2}$ (n=2).

The cross-section of the resonant polar reaction three-body collision reaction is affected by the attraction electric forces between the colliding particles, by the increase of the total pressure of the gas mixture and by the plasma ionization degree in contrast to the excimer radiation emission which can appear inclusively at low pressures (up to a few Torr) because the particles involved in reaction are only in excited states.

For the gas mixtures in which the electronegative gas has a great electronic affinity, for instance the chlorine atoms, the generation reaction for the M-effect could be binary in the sense of the Landau-Zener theory [13]-[14]. The existence of a third body it is no longer necessary because the reaction is resonant, the excess of energy being compensated by the

existence of the kinetic energy gained in the Colombian forces field. The M-effect has a general, distinct character proved by his appearance not only in binary but also in multiple electronegative-electropositive gas mixtures, in DC or in AC discharges, as it is shown in Figs 5 to 9 [15]-[16].

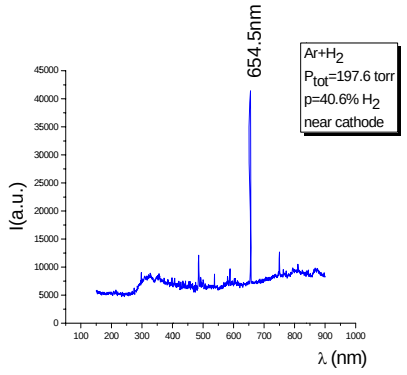

Fig. 5 Emission spectrum of a DC discharge *in (Ar+40.6 % H_2)* at p_{tot}=197 Torr (near cathode)

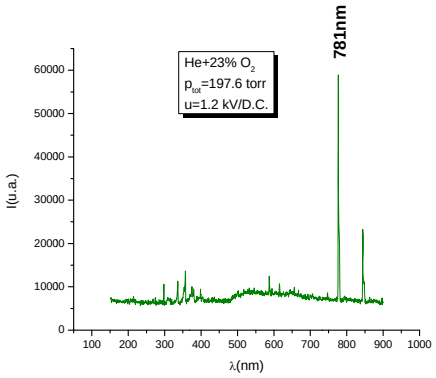

Fig. 6 Emission spectrum of a DC discharge *in (He+23 % O_2)* at p_{tot}=197 Torr

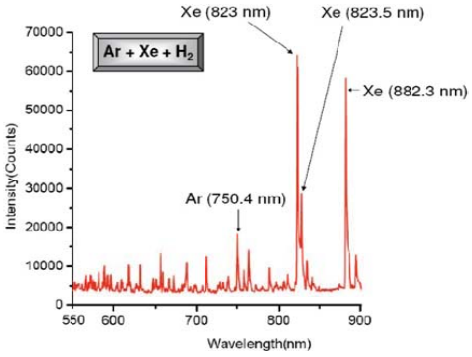

Fig. 7 Emission lines of the M-effect in *Ar-Xe-H_2* mixture dielectric barrier discharge (pH_2 = 35%) at 50 Torr total pressure

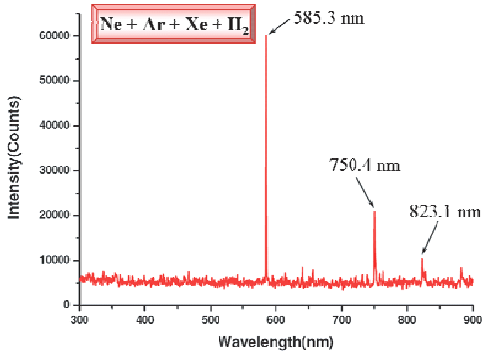

Fig. 8 Emission lines of the M-effect in *Ne-Ar-Xe-H_2* mixture dielectric barrier discharge with 50% H_2 at 80 Torr total pressure

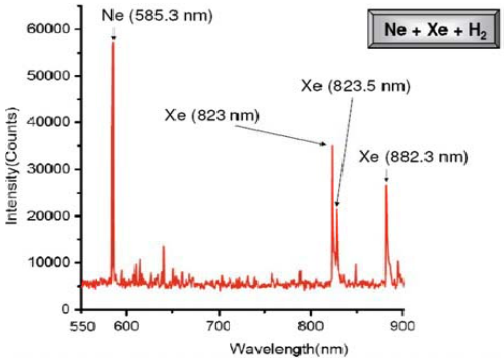

Fig. 9 Emission lines of the M-effect in (*Xe-Ne-H_2*) mixture dielectric barrier discharge (pH_2 = 35%) at 80 Torr total pressure

As it can be observed in the Harpoon- reactions - as in (7) and (8) - one of the colliding particles is in a excited state, fact which permits, after the appearance of the positive, respectively negative ions trough the agency of the electron "jumping", to form molecules of rare-gas and halogen in vibrationally excited states. These are the unique energetic states in which this type of molecules can exist for a short time (nanoseconds order). For the excimer radiation emission the non-existence of a trapping radiation, due to the high instability of the ground state excimers molecule, represents a great advantage of the process energetic efficiency.

Also, it is interesting to notice that the addition of other rare gases (buffer-gases) in the excimer mixtures has a certain influence on the excimer emission intensity, producing either an enhancement or a diminution of this one.

The explanations of this behavior are multiple. Generally, when the buffer-gases atoms replace the atoms of the rare gas from the initial excimer mixture in collisions processes, the intensity of the excimer radiation diminishes. In other cases, the high excited atoms of the buffer-gases could transfer their energy to the atoms of the rare gas from the excimer mixture, via Penning reactions, fact which leads to an increase of the excimer radiation, [1], [17].

In case of M-effect, the addition of rare-gases at the primary mixtures has no influence of the emission radiation, [15], [16]; only the addition of hydrogen (generally, of the electronegative gas) produces a dramatic change in structure

of the emission spectrum as it can be observed in fig. 1comparative with the fig.2.

The explanation consists in fact that the principal generation mechanism of the M-effect, the polar three-body resonant reaction, depends upon the existence of the metastable electronegative gas atoms in the proximity of the rare gas atoms.

IV. Conclusion

The generation of the excimer radiation and also of the M-effect appearance is mainly based on the reaction between the positive and negative ions, reaction with a very large cross-section due to the favorable factor represented by the existence of attraction Colombian forces between colliding particles.

In both cases, in the intermediate stage of the reaction, appear compounds formed by two particles, in the case of the excimer molecule (positive or negative ions in excited states), respectively three particles (positive and negative ions plus electronegative metastable atoms), in the case of the M-effect. The existence of the electronegative metastable atom in convenient energetic state permits the fulfillment of the energetic condition for the three-body reaction, ($\Delta E \approx 0$).

The M-effect appears only at gas mixtures total pressures above the value of 10 Torr because is based exclusively on the positive-negative ions existence while the excimer radiation could appears at Torr units order low pressures, due to the fact that its precursors are the excited atoms of rare gas and halogen, formed at lower energies in plasma.

In the end, it can be concluded that, although there are many similarities in the generating mode of the two processes, the M-effect proved to have a general character, representing a new physical effect.

Acknowledgment

This paper represents the result of many useful discussions in the past with Prof. Geavit Musa, the discoverer of the M-effect and also its principal promoter in the scientific community.

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