

THE MONOCHROMATISATION EFFECT OF RADIATION IN AC/DC MULTIPLE GAS MIXTURES DISCHARGES AND THE COMPARISON WITH THE EXCIMER RADIATION GENERATION MECHANISMS

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Abstract. The monochromatisation-effect (M-effect) consists in the decrease of the emission spectra of an electronegative-electropositive gas mixtures discharge to only few intense spectral lines or even only one line, as in the case of Ne-H₂ gas mixture. In previous papers published it has been reported the study results related to the M-effect appearance in other different gas mixtures, both in AC and DC discharges. The present paper informs about the registered spectra obtained, the optimum values of the electronegative percentages corresponding to the maximum values of the M-parameter, and the main mechanisms reactions responsible by the appearance of the M-effect by comparison with the generation mechanisms of excimer radiation.

Key words: monochromatisation, gas mixtures, AC discharges, excimers.

1. THE MONOCHROMATISATION -EFFECT OF RADIATION

1.1. THE DEFINITION OF M-EFFECT

1.1.1. The M-effect in Ne+H₂ gas mixture

In a number of previously published papers we reported that, on hydrogen addition to neon, reduction of neon emission spectra to practically one line was observed. The wavelength of this line was $\lambda_1=585.3$ nm and corresponds to the $2p_1-1s_2$ transition in the Paschen notation [1-3]. Due to the fact that the spectra obtained had practically one line, this phenomenon was called by us the “Monochromatisation-effect” (M-effect).

In order to characterize the “quality” of this effect, we introduced the M parameter defined as the relative intensity ratio of the increased single line, called dominant spectral line, and an arbitrary reference spectral line. For neon, the two lines are $\lambda_1=585.3$ nm, respectively $\lambda_2=614.3$ nm, the M parameter so defined is:

$$M = \frac{I_{\lambda_1=585.3\text{nm}}}{I_{\lambda_2=614.3\text{nm}}}. \quad (1)$$

In the case of pure neon discharges, the value of the M parameter is of the order of a few units, whereas at 40% hydrogen content in the neon-hydrogen gas mixture, a value as high as 40 was found. These results were obtained for a dielectric barrier discharge in (Ne+H₂) mixture at pressures around 100 Torr. The chosen geometry for the discharge was a PDP-type one (Plasma Discharge Panel), a subtype of the dielectric barrier discharge.

The emission spectrum of a discharge in pure neon is presented in Fig. 1; in Fig. 2, the spectrum of (Ne + 40%H₂) mixture discharge under identical experimental conditions is shown.

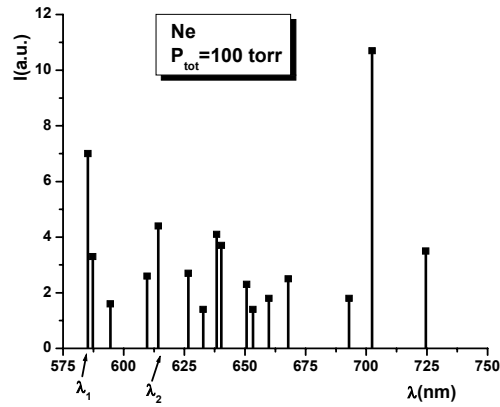


Fig. 1 – Emission spectrum of pure neon PDP discharge ($\lambda_1=585.3\text{nm}$, $\lambda_2=614.3\text{nm}$).

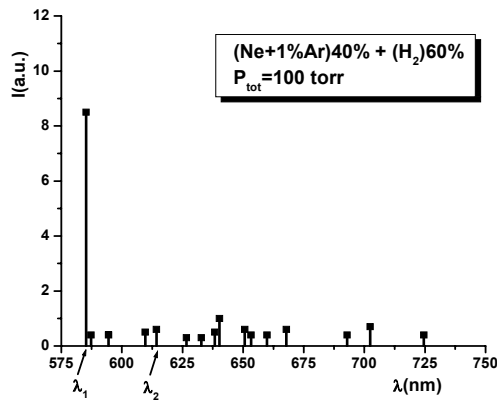


Fig. 2 – Emission spectrum of (Ne+1%Ar) 40% + (H₂)60% gas mixture PDP discharge ($\lambda_1=585.3\text{nm}$, $\lambda_2=614.3\text{nm}$).

1.1.2. Main conditions for M-effect appearance

The M-effect can be observed both in AC and DC discharges [4]. It can be concluded that two processes are responsible for the appearance of this effect:

1. ion-ion recombination, a process with very high cross-section;
2. resonant three- body collision reaction of heavy particles (with nearly zero energy defect);

As it was observed in various types of discharges and also in various electronegative-electropositive gas mixtures, the M-effect is considered to have a general character. A number of experimental conditions are necessary in order to obtain the M-effect, namely:

- electronegative-electropositive gas mixture;
- low gas temperature and elevated pressure of the gas mixture in order to increase the heavy particles cross-section triple collision reaction (so-called *thermolecular reactions*);
- 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.

1.2. THE EXPERIMENTAL SET-UP

1.2.1. The experimental set-up for the PDP (AC)-type discharge

The experimental set-up [5] for the AC discharge consists in two float glass plates with a thickness of 5 mm and the surface size of (300 × 50) mm are used to build the discharge device. Each glass plate is covered with a vacuum deposited 1 micrometer thin Al-film linear electrode. The length and the width of the electrodes are 190 mm and 4 mm respectively. The electrical connections to the electrodes are on a perpendicular line to the end of each one. The glass surfaces with electrodes are covered with a uniform glass dielectric layer having a thickness of 18–20 micrometers, except for the surfaces marked with black color. These surfaces are used to include the device in an electrical circuitry in order to generate radiation. The glass plates are vacuum tight assembled, the discharge space being $d \leq 1\text{mm}$. The linear electrodes are mounted face to face. Polished quartz windows are used to record the emitted UV radiation (if there is the case).

The discharge is ignited and is maintained using a square wave AC-voltage with a frequency in the range of 10 kHz up to 100 kHz and a peak-to-peak value of the applied voltage of 1 kV. The discharge device is connected to a vacuum pumping unit and can be filled with various gas mixtures at the established pressures. During the measurements, the discharge device remained connected to the pumping unit. A grating spectrometer (1200 traces/mm) has been used to record the spectra of the emitted radiation, or in others cases, an Optical Multichannel Analyzer (OMA).

1.2.2. The experimental set-up for DC discharge

The experimental set-up [5] used for measurements in DC discharge consists in a discharge tube from 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 discharge out of the inter-electrodes space. The distance between the two electrodes was 8 mm. The discharge tube was connected to the vacuum pumping unit and can be filled with various gas mixtures at the established pressures. An OMA recorded the spectra of the emitted light. The electrical ignition voltage was in the range of 1.2 kV to 2.0 kV.

1.3. RESULTS AND DISCUSSION

1.3.1. The emission spectra for the AC-discharge

In a previous revue-paper [6] it was studied minutely the appearance conditions of the M-effect in Ne+(Ar)+H₂ gas mixtures, in which the M-effect was found to be very intense. Still there are others types of electronegative-electropositive gas mixtures in which the M-effect appears. First of all, it will be presented the (Ar/Xe/He+O₂/H₂/Cl₂) emission spectra and then the main reaction mechanisms wich explain the appearance of the M-effect.

The total pressure of the gas mixtures for a PDP-type discharge-(AC) discharge-was comprised in the range of (30-200) Torr and was specified directly on Figs. 3–12. The intensity of the emitted radiation is given in arbitrary units (a.u.).

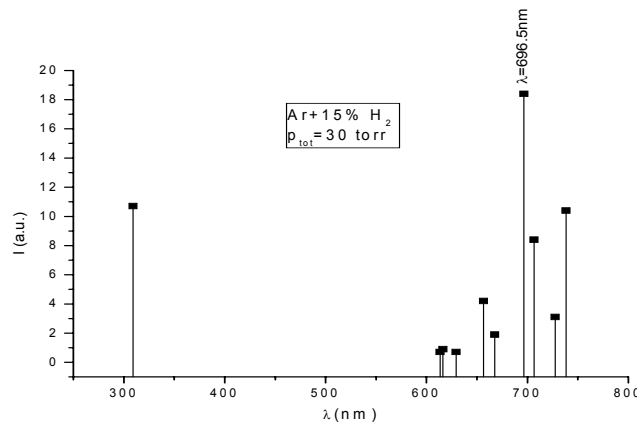
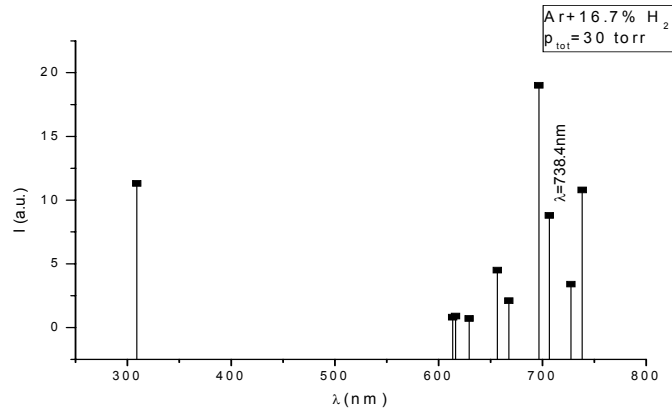
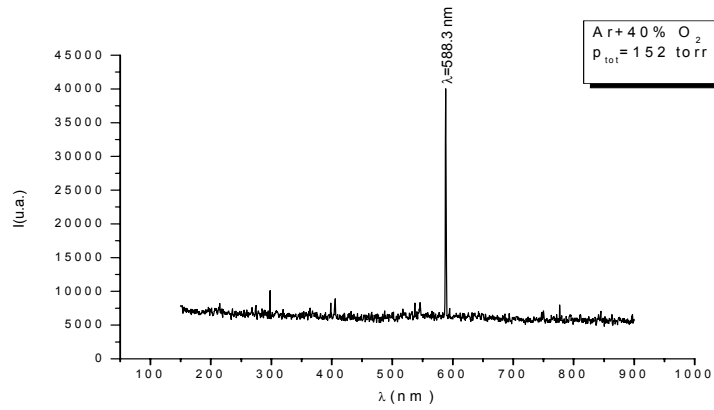
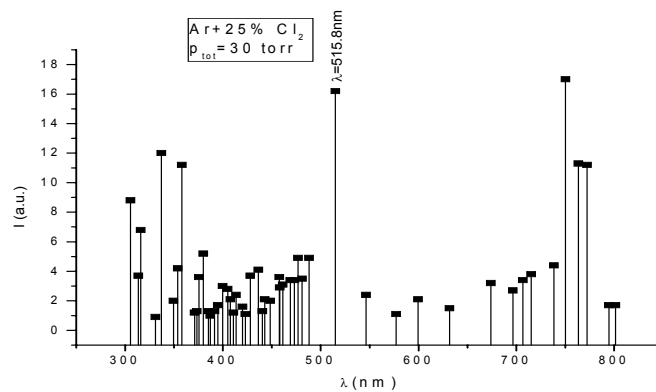
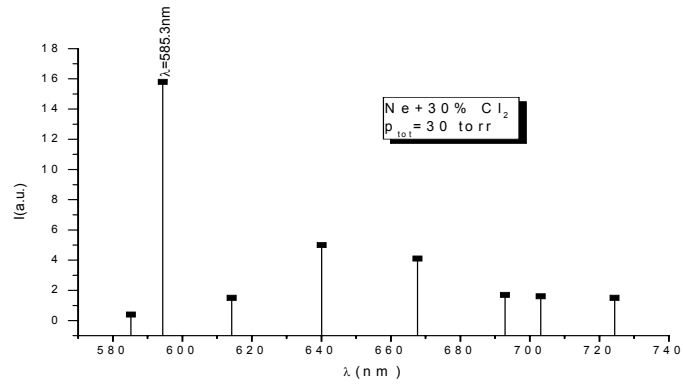
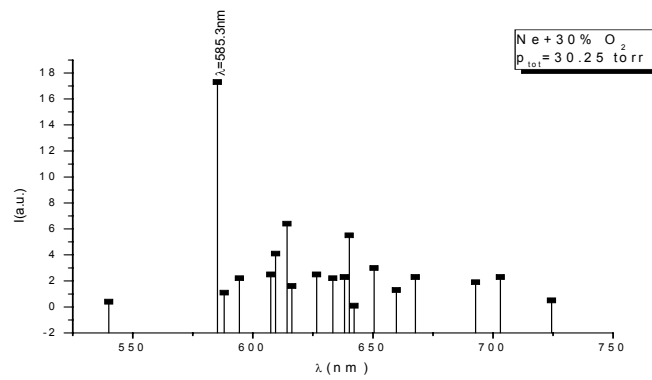
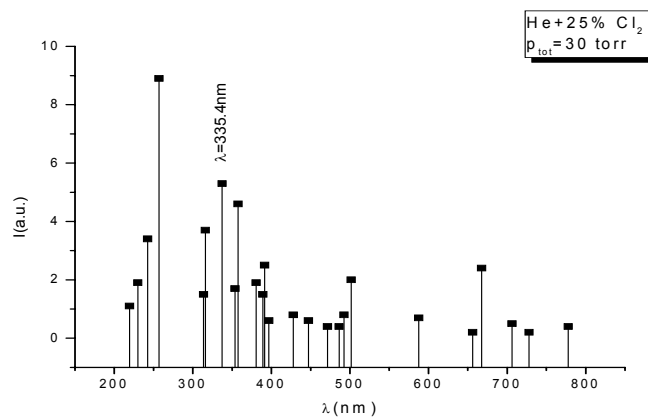
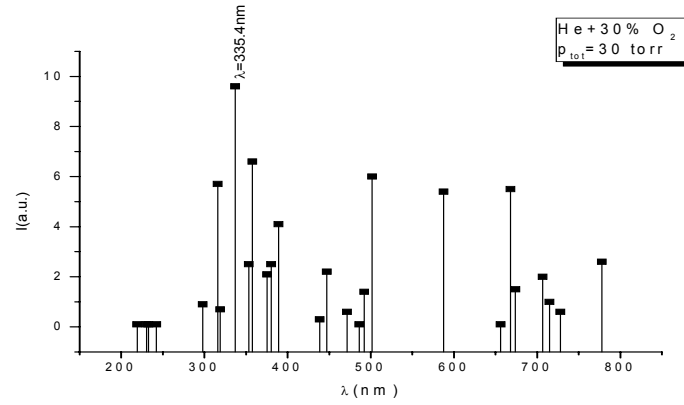
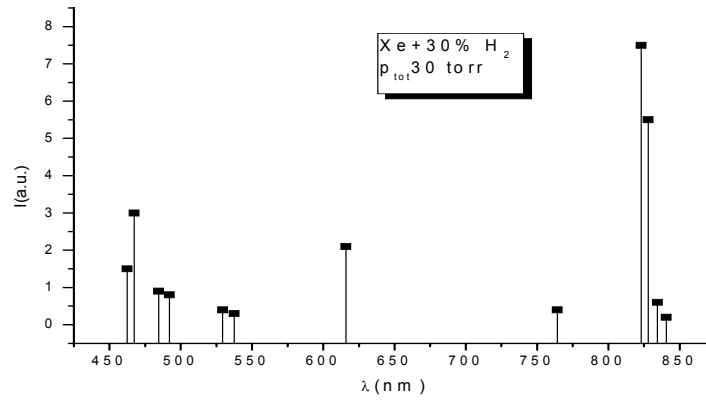
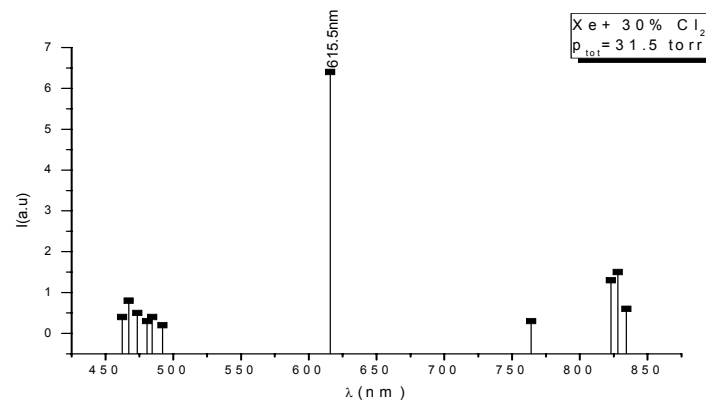


Fig. 3 – Emission spectrum of a PDP-type discharge in Ar+15% H₂.

Fig. 4 – Emission spectrum of a PDP-type discharge in Ar+16.7% H₂.Fig. 5 – Emission spectrum of a PDP-type discharge in Ar+40%O₂.Fig. 6 – Emission spectrum of a PDP-type discharge in Ar+25% Cl₂.

Fig. 7 – Emission spectrum of a PDP-type discharge in Ne+30%Cl₂.Fig. 8 – Emission spectrum of a PDP-type discharge in Ne+30%O₂.Fig. 9 – Emission spectrum of a PDP-type discharge in He+25%Cl₂.

Fig. 10 – Emission spectrum of a PDP-type discharge in He+30%O₂.Fig. 11 – Emission spectrum of a PDP-type discharge in Xe+30%H₂.Fig. 12 – Emission spectrum of a PDP-type discharge in Xe+25%Cl₂.

1.3.2. The emission spectra for the DC discharge

The experimental conditions in which are registered the emission spectra are the following: the range of work pressures was (30-300) Torr. In this range the ignition voltage rises nearly linear up to the approximate value of 1.3 kV for a total pressure of the gas mixture of 300 Torr. The limitation electrical resistance value was 10 k Ω . The spectra were registered using an OMA device, with following characteristics: spectral range (200-900) nm, resolution 1.5 nm, integration time (50-1000) ms. The total pressure of the gas mixtures and the percentage of electronegative gas were specified directly on Figs. 13–18.

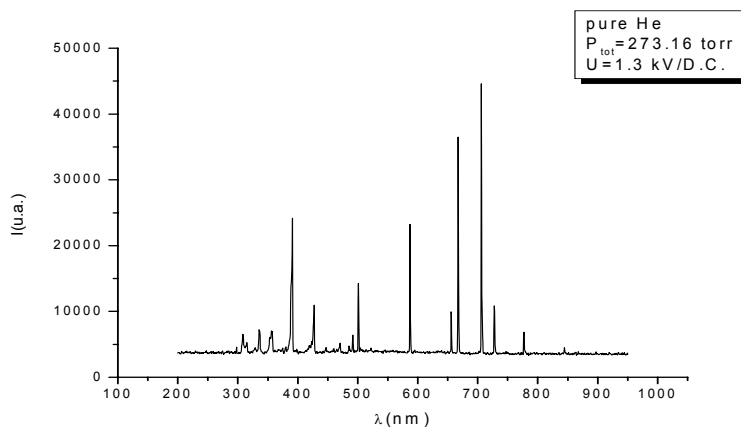


Fig. 13 – Emission spectrum of *pure helium* in a DC discharge.

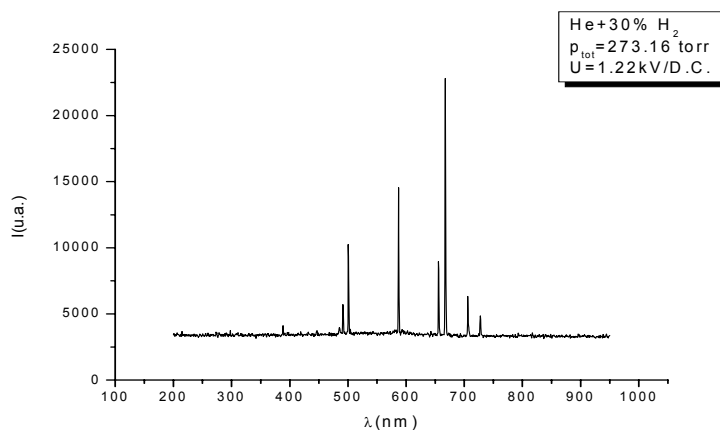


Fig.14 – Emission spectrum of a DC discharge in (He+30%H₂) gas mixture.

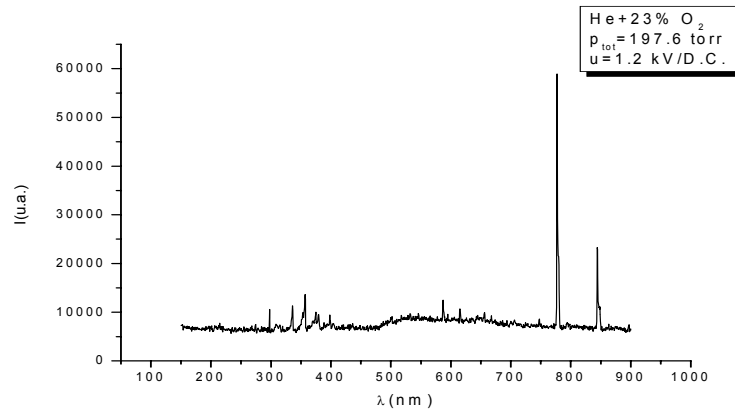


Fig. 15 – Emission spectrum of a DC discharge in (He+23%O₂) gas mixture.

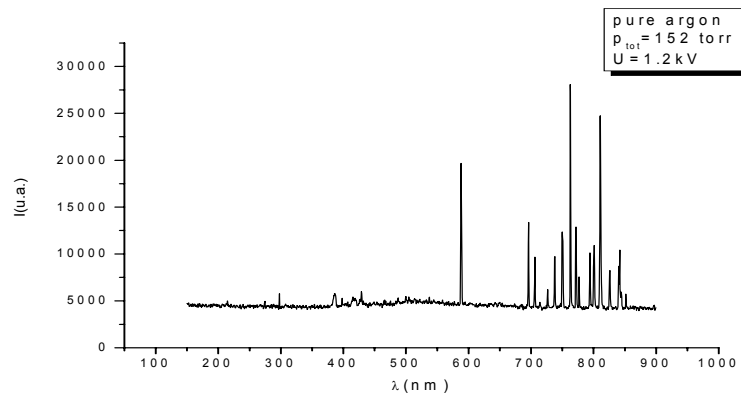


Fig. 16 – Emission spectrum of *pure argon* in a DC discharge.

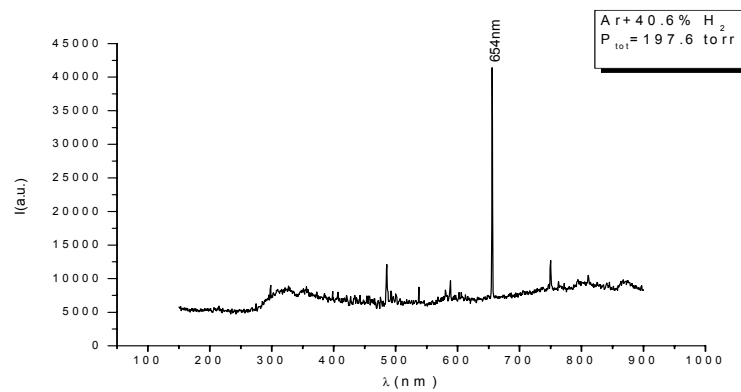


Fig. 17 – Emission spectrum of a DC discharge in (Ar+40.6%H₂) gas mixture.

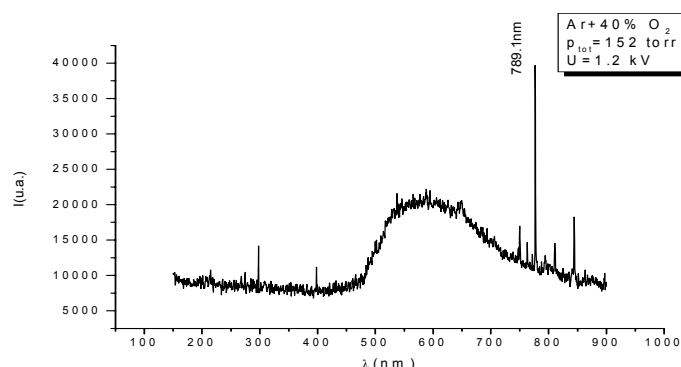


Fig. 18 – Emission spectrum of a DC discharge in (Ar+40%O₂) gas mixture.

The registered spectra were analysed using those spectral lines whose relative intensities presented a special behavior against the rest of considered lines spectrum.

By “special behavior” it gets on a fast increase of the intensity of spectral line chosen as dominant (or, if there is the case, a limited number of spectral lines), function of electronegative gas percentage added to the electropositive gas. These dominant spectral lines can be used to distinguish, in the considered gas mixtures, the appearance of the M-effect. The experimental data presented in Figs. (3–18) are synthesized in the Table 1. The table contains the following synthetic data: the type of gas mixture, the type of discharge (AC or DC), the appearance (or not-appearance) of the M-effect, the dominant spectral lines, respectively the reference spectral lines for each type of gas mixture used, the maximum parameter M value accordingly to the optimum value of the electronegative gas percentage added. For this optimum value the emitted radiation intensity is maximum.

We can also notice that in a PDP-type discharge, in some gas mixtures, namely (Ar+H₂) ($\lambda = 654.0$ nm, 667.9 nm, 696.5nm/ 706.7nm/ 727.4nm/ 738.4nm) and He+O₂/Cl₂. ($\lambda = 266.3$ nm/265.2nm/264.4nm/335.4nm/351.2nm), the M-effect shows clearly the appearance of more than one dominant spectral line (the spectral lines from the brackets). The aspect of spectrum indicates a shift to the IR-region in the case of (Ar+H₂) and to the UV-region in the case of (He+O₂/Cl₂).

Table 1

Discharge type		Gas mixtures type	The appearance of M-effect	Dominant spectral lines λ_1 (nm)	Reference spectral lines λ_2 (nm)	M-parameter value (adimensional)	The optimum percentage value of electronegative gas (%)	Note
AC (PDP)	DC							
*	-	Ar+H ₂	*	696.5 738.4	616.3 616.3	18.5 7.4	15 16.7	More dominant spectral lines Spectrum shift to the IR region
*	-	Ar+Cl ₂	*	515.8	312.8	4	25	-

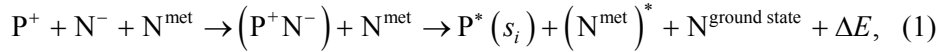
Table 1 (continued)

*	-	Ar+O ₂	*	588.3	762.1	5	40	-
*	-	Ne+O ₂	*	585.3	594.4	8	30	-
*	-	Ne+H ₂	*	585.3	614.3	17	40	-
*	-	Ne+Cl ₂	*	585.3	614.3	10	30	-
*	-	He+O ₂	*	335.4	706.7	7.5	25	More dominant spectral lines Spectrum shift to the UV region
*	-	He+H ₂	-	-	-	-	-	-
*	-	He+Cl ₂	*	335.4	706.7	14	25	More dominant spectral lines Spectrum shift to the UV region
*	-	Xe+Cl ₂	*	615.5	462.8	19.5	25	-
*	-	Xe+H ₂	-	-	-	-	-	-
-	*	Ar+H ₂	*	654.0	596.4	4.7	40	-
-	*	Ar+O ₂	*	789.1	596.4	2.3	40	-
-	*	He+O ₂	*	781.6	501.4	8.8	23	-
-	*	He+ H ₂	-	-	-	-	-	-

1.3.3. Discussions

As we have already noticed, in our previously [7-9] papers which refer at the M-effect, the main mechanism responsible of the appearance of M-effect in electropositive-electronegative gas mixtures is the *resonant polar three body reaction*. This is the only type of reaction which can explain the strong selectivity of the process that finally leads to the preferential population of an energetic level (in some cases more levels).

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



where 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, $(N^{\text{met}})^*$ is the symbol of the excited electronegative atom standing in a upper state energy that the metastable level, P^+ is the electropositive atom in an excited state and ΔE is the notation for energy defect of reaction.

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



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



2. THE EXCIMER RADIATION

2.1. THE GENERATION MECHANISMS

Excimers represent a class of molecules formed by the combination between a halogen and a rare gas. These molecules do not exist in the ground state which is unstable but only in an excited state. 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-xenon (R_g), the halogen (X)-iodine/chlorine and the buffer gases – neon/argon.

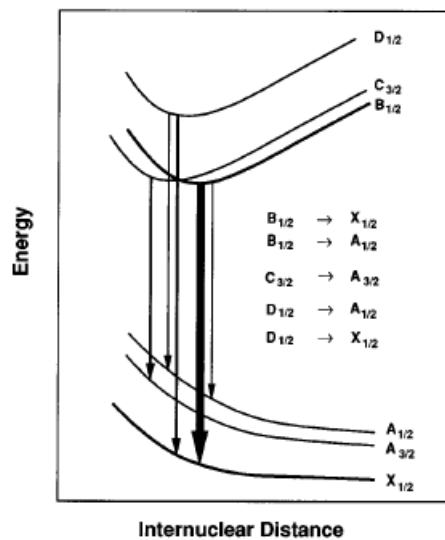


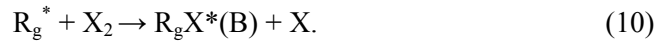
Fig. 19 – Potential energy diagram of excimer molecule.

The formation of the excimer molecules starts with the excitation and ionization of the rare gas atoms and molecular halogen by high energy electrons collisions produced in glow-DBD phase:





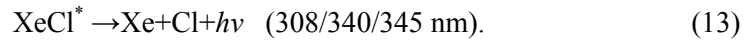
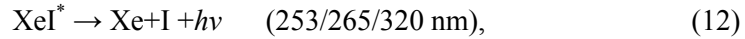
At moderate to high pressures one of the major reaction for excimer formation is the *Harpoon reaction*. The excited states of the rare gas atoms are transferring an electron to the halogen molecule (or compounds containing halogen) and form electronically excited states of the excimer molecules:



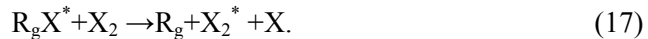
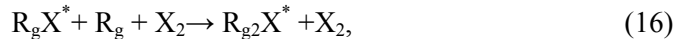
The second major reaction for excimer formation is the *ionic recombination*:



The excited excimer molecules $XeI(B)$ decay radiatively to the molecular ground state.



The mechanisms of excimer generation compete with the quenching mechanisms:



From the equations (13) and (14) can be pointed the formation of the $R_{g2}X^*$ trimer.

2.2. EXPERIMENTAL SET-UP

The experimental set-up used for the study of the excimer radiation was a classical, coaxial discharge device [10], composed of two concentric quartz tubes, outer and inner metallic electrodes, both made by steel, an external RF high voltage generator (up to 20kV), and a heating system of the iodine pure crystals. The

discharge was of a DBD-type and it was matched using a sinusoidal voltage value of 4 ± 0.5 kV, the frequency range between 20–400 kHz. The high voltage was applied on the inner electrode, while the outer UV mesh transparent electrode was grounded. In order to record the emission spectra an OMA (Optical Multichannel Analyzer), spectral range between 200–900 nm, and 1.5 nm resolution, was used. The integration time was in the range of 0.5–1 ms.

2.3. RESULTS AND DISCUSSION

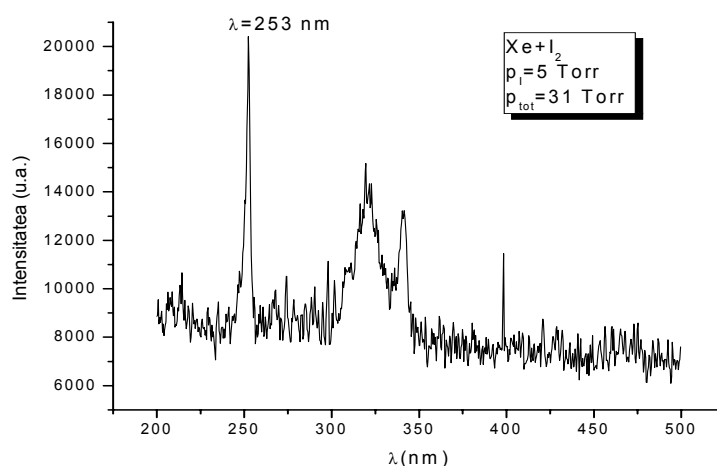


Fig. 20 – Emission spectra of (Xe+ I₂) gas mixture in a DB discharge.

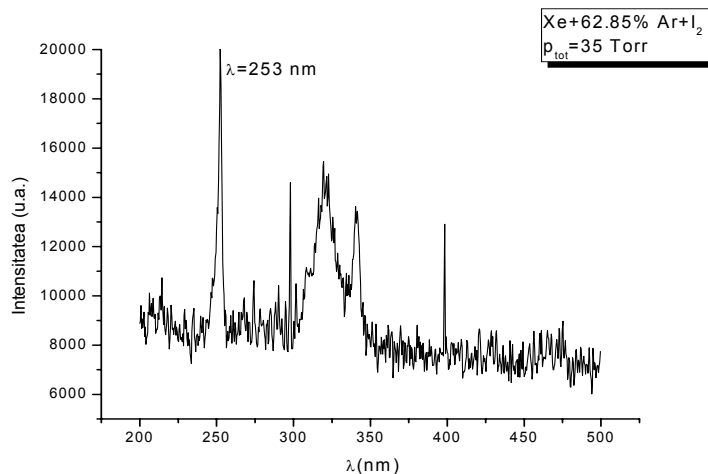


Fig. 21 – Emission spectra of (Xe+ 62.85%Ar+I₂) gas mixture in a DB discharge.

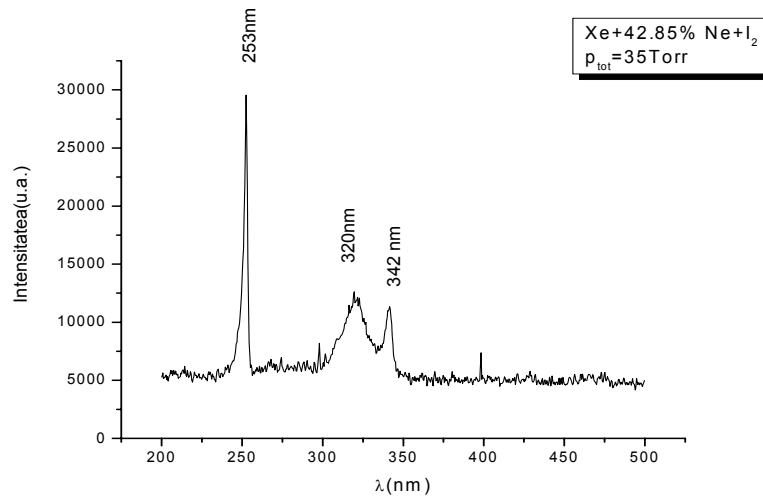


Fig. 22 – Emission spectrum of (Xe+42.85%Ne+I₂) gas mixture in a DB discharge.

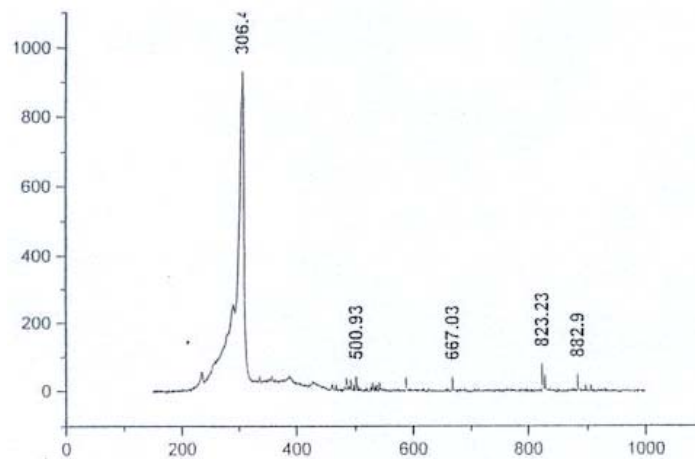


Fig. 23 – Emission spectrum of (Xe+86.2%Ne+Cl₂) gas mixture in a DB discharge.

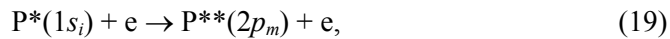
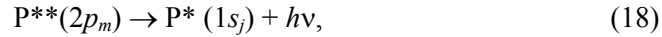
3. COMPARAISON BETWEEN MONOCHROMATISATION-EFFECT AND EXCIMER RADIATION MECHANISMS OF GENERATION

As it can be observed from the presented data, both phenomena, namely the M-effect and the excimer radiation generation, are characterized by the appearance of a quasi-monochrome radiation.

Nevertheless, while M-effect represents the consequence of the de-excitation at atomic level, the excimer radiation mechanisms take place at molecular level.

As we have noticed, the principal mechanism of feeding the selective populated level s_i is the polar recombination reaction (1), with (nearly) zero energy defect reaction.

In the DB discharge-phase, the high energy electrons produce the excitation of the electropositive atoms on different energy levels, process followed by the reactions:



where “ s ” and “ p ” are the atomic energetic levels in the Paschen notation. We have noticed by P^{**} the electropositive atom which stands on upper energy levels. The reactions (19-21) produce a diminution of the population of the s_i level. In some experiments, we have used Penning gaseous mixtures. In this case, a supplementary decrease of the s_i level population could appear by the Penning-type collisions.

From the energetic point of view the most important condition is that the polar reaction has a resonant character [11-14]. This condition can be accomplished when collisional coupling between the s -levels appear. In this way it could be possible to obtain a sharp adjustment of the electropositive atoms energy, in order to fit the energetic condition (1). Also, an important role is played by the metastables levels of the electropositive atoms that stand on the third body involved in reaction and which, by their longer life-time, increase the possibility of the polar recombination reaction achievement [15]. As it can be observed, all the processes which are concerning the monochromatisation effect are of atomic type.

The excimer molecules are formed by the excitation into atomic or ionic states, (including the metastable $3P^2$ and the resonant $3P^1$ states) by electron collisions in the discharge-phase of the DB – equations (4)–(9). These processes are the same as in the case of the M-effect but, in contrast with that, are followed by the formation of the excimer molecules which can exist only in their excited states-equations (10)–(11).

The $3P^2$ and the $3P^1$ states decay *via* three-body collisions to highly vibrational excited states ($v > 20$). This process is followed first by a vibrational relaxation on levels with $v \approx 0$, and then by a radiative dezexcitation on the ground state connected with the rapid dissociation of the excimer molecule. During this process is emitted the excimer radiation as a result of the bound-free transitions. This radiation has a continuum character (like in the case of xenon dimmer). As it can be observed from Fig. 19 a radiative process of dezexcitation could appear also between the excited excimer states A, B, C and D or from these excited states directly on the ground state X according to the electric dipole transitions rules. The most intense transition, $B \rightarrow X$, is a molecular transition centered to the principal spectral line which is characteristic for each excimer-type.

4. CONCLUSIONS

Both phenomena, the monochromatisation-effect and the excimer radiation are generating a quasi-monochrome radiation but the mechanisms responsible are not the same. Thus, while the M-effect is the result of the atomic processes, based on the resonant ionic recombination, the excimer radiation is emitted by the deexcitation of the excimer molecule on his highly unstable ground state.

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