OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 3, March 2007, p. 137 - 142

New considerations on mechanisms involved in M-effect in electropositive-electronegative gas mixtures

G. MUSA, L. C. CIOBOTARU*
National Institute R&D for Laser, Plasma and Radiation Physics, PO Box MG 36, 077125, Bucharest, Romania

In some previously published papers we reported the possibility of obtaining nearly monochrome radiation spectra using A.C. /D.C. discharges in electronegative-electropositive gas mixtures at pressures bigger than 20 Torr. We called this effect the M-effect. In order to characterize the effect we introduced the M parameter defined as the ratio of the relative intensities of the radiation of two wavelengths of recorded spectra. One spectral line is called dominant line, having a spectacular growing at the addition of the electronegative gas and the other one is a common spectral line arbitrary chosen from the spectrum, which is considered the reference line. Using this parameter, various recorded spectra can be compared and thus, the M value can be considered a qualitative measure of the M-effect "intensity". The main mechanism proposed by us which determines the appearance of M-effect is a resonant three-body collision reaction. This type of reaction has one of the largest cross-section known, about 10^{-12} cm^2. According to the magnitude order of the defect energy reaction it can explain the appearance of one dominant spectral line, e.g. ($Ne+H_2$) gas mixture, or at least two dominant spectral lines, e.g. ($He+O_2/Cl_2$) or ($Ar+H_2$) gas mixtures.

(Received February 1, 2007; accepted February 14, 2007)

Keywords: M-effect, Three body reaction, Resonant polar recombination, Defect energy reaction

1. Introduction

The M-effect consists in the reduction (the monochromatisation) of the emission spectrum of an electronegative-electropositive gas mixture to one single intense line, like in ($Ne+H_2$) gas mixture or in at least two spectral lines like in ($He+O_2/Cl_2$) or ($Ar+H_2$) gas mixtures. This effect has been noticed in dielectric barrier discharge (DBD) - with its subtype PDP (Panel Discharge Plasma) - and in a D.C. discharge, at pressures higher than 20 Torr [1-10]. The devices used in both type of discharges have been described in detail in our previous scientific articles. In this paper we shall discuss only the results obtained in a PDP type discharge because the D.C discharge implies special conditions to obtain M-effect [8].

In order to characterize the "intensity" of this effect, we introduced the M parameter defined as the relative intensity ratio of the dominant (increased) single spectral line λ_1 and an arbitrary reference spectral line λ_2. For instance, for neon, the two lines are λ_1=585.3 nm and λ_2= 614.3 nm and the M parameter is defined like:

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

In the case of pure neon discharge, 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 24 was found. These results were obtained for a PDP in ($Ne+H_2$) gas mixture at pressures around 100 Torr.

2. Results and discussion

The emission spectrum of a discharge in pure neon is presented in Fig. 1 while in Fig. 2 is shown the spectrum of (Ne+1%Ar) + 40%H_2 Penning mixture gas discharge under identical experimental conditions [10].

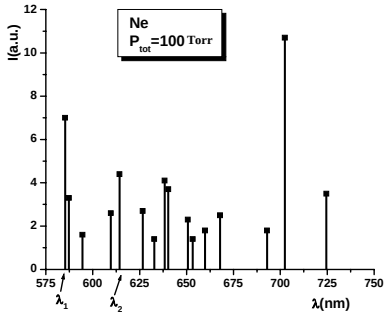

Fig. 1. Recorded spectrum of pure neon PDP discharge (λ_1=585.3 nm, λ_2=614.3 nm).

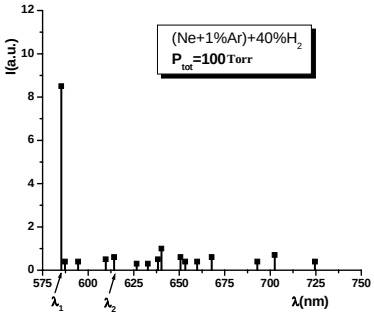

Fig. 2. Recorded spectrum of (Ne+1%Ar) + 40%H_2 gas mixture PDP discharge (λ_1=585.3 nm, λ_2=614.3 nm).

The dependency of M parameter on the wavelengths of the radiation emitted and on the percentage of electronegative gas added at the Ne are shown in the Fig. 3 and Fig. 4. As it can be observed, the maximum of the function M = f (λ) appears at λ_1=585.3 nm and the maximum for M=f (p% H_2) is reached for p=40%H_2 [6].

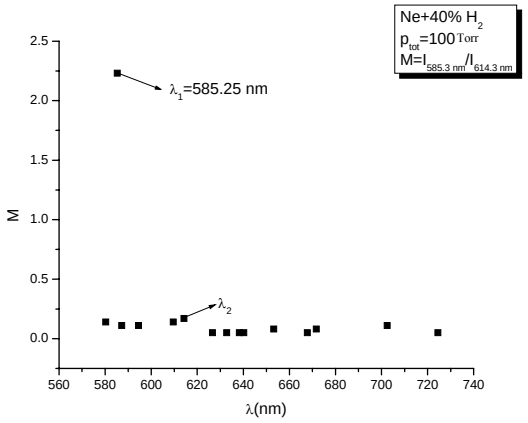

Fig. 3. Variation of M=f(λ) in a PDP (Ne+H_2) gas mixture (λ_1=585.3 nm; λ_2=614.3 nm).

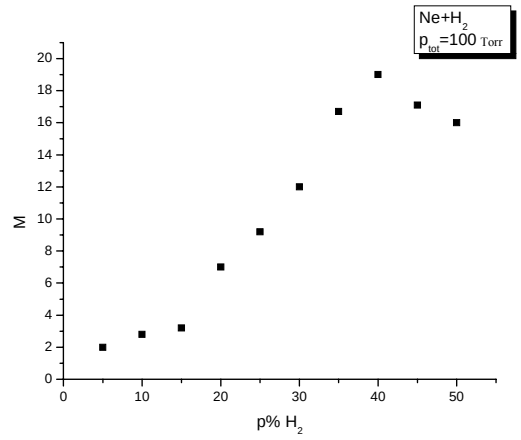

Fig. 4. Variation of M=f(p% H_2) in a PDP (Ne+H_2) gas mixture (p=40%H_2).

There are some gas mixtures, e.g. (He+O_2/Cl_2) and (Ar+H_2) [7-9] in which the number of dominant lines is more than one, like in the previously gas mixture (Ne+H_2). The correspondent spectra for each gas mixture mentioned before and the dependencies of M parameter on the wavelengths of the radiation emitted and on the percentage of the electronegative added gas (H_2, O_2, Cl_2) to the electropositive gases (Ar, He) are shown in the Figs. 5 – 16.

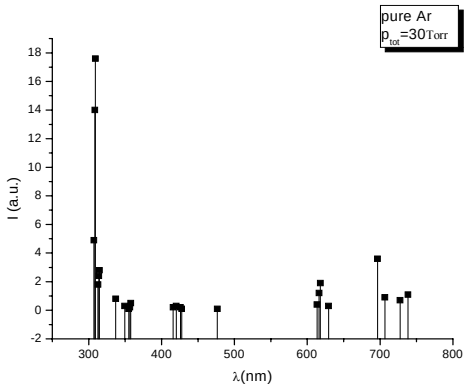

Fig. 5. The emission spectrum of a PDP type discharge in pure argon.

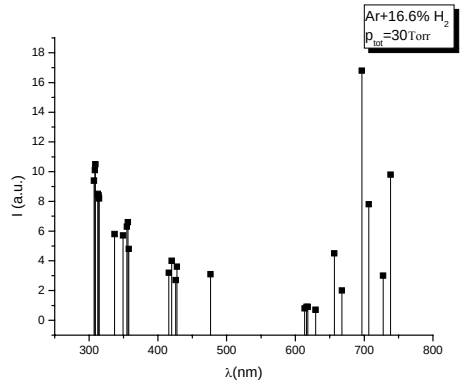

Fig. 6. The emission spectrum of a PDP type discharge in (Ar+16.6 %H_2) gas mixture (λ_1=696.5 nm; λ_2=616.3 nm).

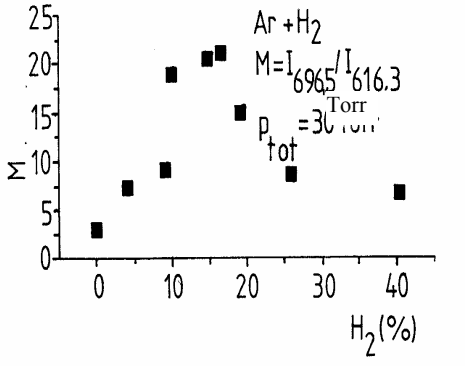

Fig. 7. Dependence of the M parameter value on the percentage of added H_2 for a PDP type discharge in (Ar+H_2) gas mixture (λ_1=696.5 nm).

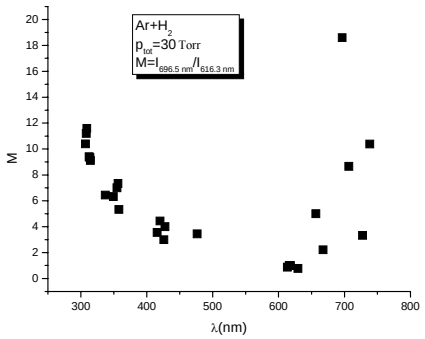

Fig. 8. Dependence of the M parameter value on the wavelengths λ for a PDP type discharge in (Ar+H_2) gas mixture (p=16.6% H_2).

The total pressure of (Ar+H_2) gas mixture was 30 torr. The maximum of the function M = f(λ) appears for λ_1=696.5 nm and the maximum of function M=f (p% H_2) is reached for p=16.6% H_2.

As it can be observed in Figs. 9 and 10, the dominant lines in a PDP type discharge in (Ar+H_2) gas mixture are more than one, respectively λ_1=696.5 nm (the reference line λ_2=616.3 nm), namely λ= 656.4 nm/ 667.9 nm/ 706.7 nm/ 727.4 nm and 738.4 nm, the M-effect being very clearly emphasized (the M parameter values have over 20 units for λ=738.4 nm and 12 units for λ=696.5 nm [9]).

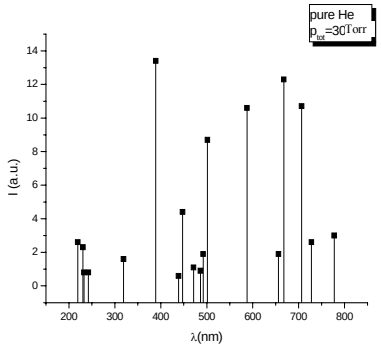

Fig. 9. The emission spectrum of a PDP type discharge in pure helium.

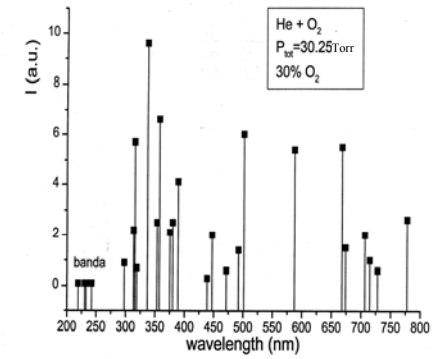

Fig. 10. The emission spectrum of a PDP type discharge in (He + 30 % O_2) gas mixture (λ_1 = 335.4 nm; λ_2=501.6 nm).

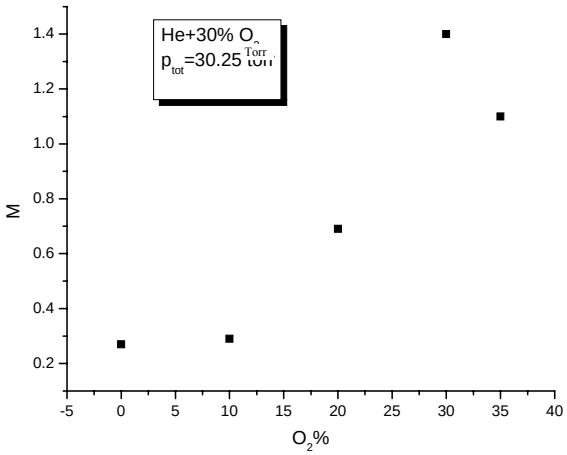

Fig. 11. Dependence of the M parameter value on the percentage of added O_2 for a PDP type discharge in (He+O_2) gas mixture (λ_1=335.4 nm; λ_2=501.6 nm).

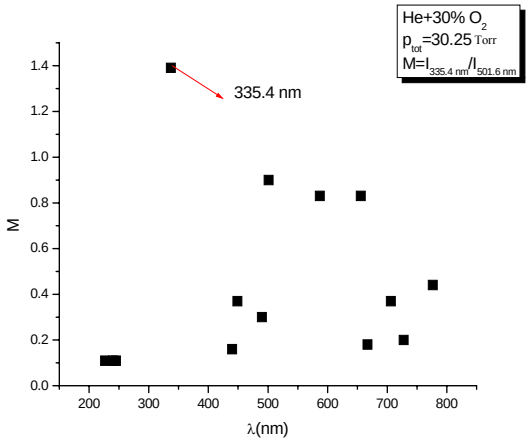

Fig. 12. Dependence of the M parameter value on the wavelengths λ for for a PDP type discharge in (He+O_2) gas mixture (p=30% O_2).

Also, in (He+Cl_2/O_2) gas mixtures, it can be observed too the appearance of more than one dominant spectral line, namely λ=257.7 nm and 335.4 nm [7]. We can choose for analyse any of these spectral lines. In the (He+O_2) gas mixture, it has been considered the dominant spectral line λ_1=335.4 nm and the reference spectral line λ_2=501.6 nm at a total pressure of 30.25 Torr and in (He+Cl_2) gas mixture the dominant spectral line was λ_1= 257.7 nm and the reference spectral line λ_2= 501.6 nm at a total pressure of 30 Torr.

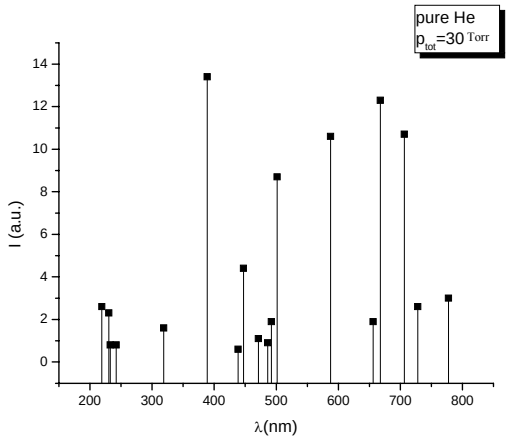

Fig. 13. The emission spectrum of a PDP type discharge in pure helium.

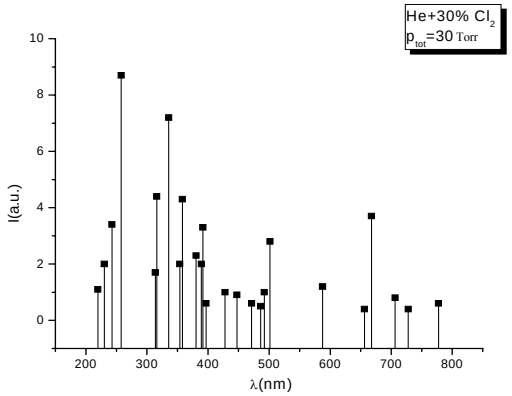

Fig. 14. The emission spectrum of a PDP type discharge in (He+30%Cl_2) gas mixture (λ_1=257.7 nm; λ_2=501.6 nm).

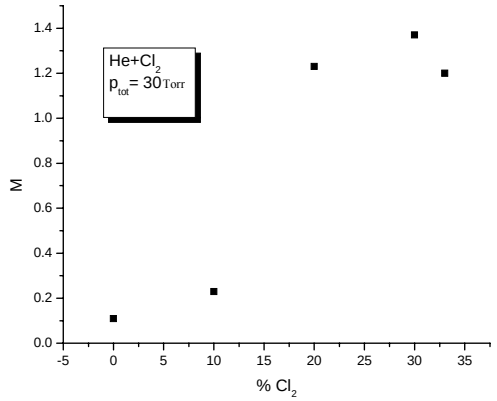

Fig. 15. Dependence of the M parameter value on the percentage of added Cl_2 for a PDP type discharge in (He+Cl_2) gas mixture (λ_1=257.7 nm; λ_2=501.6 nm).

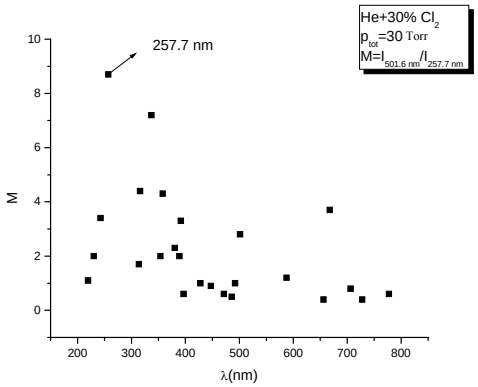

Fig. 16. Dependence of the M parameter value on the wavelengths λ for a PDP type discharge in (He+Cl_2) gas mixture (p=30% Cl_2).

As it can be observed from the Figs. 11-16, the maximum of the function M = f (λ) appears for λ_1=335.4 nm and the maximum for M=f (p%O_2) is reached for p=30%O_2 in the case of (He+O_2) gas mixture, respectively for λ_1=257.7 nm and p=30%Cl_2, in the case of (He+Cl_2) gas mixture.

3. Discussion

As we have already noticed, in our previously papers which refer at the M-effect, the main mechanism responsible for the appearance of M-effect in electropositive-electronegative gas mixtures is the *resonant polar three body reaction [5]*. This is the only type of reaction which can explain the strong selectivity process that finally leads to the preferential population of an energetic level (in some cases more than one). Even the Landau–Zenner theory [11,12] shows that only the *polar two-body reaction* can have a resonant character. There are experimental arguments that many of the reactions of this type does not succeed. Thus, there are cases in which the energetic balance of reaction is met, but the reaction does not take place, like in (Ne+O_2) gas mixture, and cases in which even the defect of energy reaction is close to zero, and the reaction does not occur. The three-body reaction has not a high rate of production because the collision probability of three particles is considerably smaller that in the case of the two body reaction but his great advantage consists in his very large cross section, one of the highest known (around $10^{-12}cm^2$) due to the electrostatic forces between the charged particles involved in reaction.

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

$$P^+ + N^- + N^{met} \rightarrow P^* + N^{ground\ state} + (N^{met})^* + \Delta E \quad (1)$$

where the 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 that the metastable level, P^+ is the electropositive atom in an excited state and ΔE is the reaction energy defect.

The first reaction is followed by the radiative disexcitation reaction:

$$P^* \rightarrow P + hc/\lambda_1 \quad (2)$$

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

$$N^{met*} \rightarrow N^{met} + hc/\lambda \quad (3)$$

For this wavelength it was chosen the first three most probable transitions from the metastable levels of the electronegative atom to the upper levels (from the published tabulated data).

As a result of many experimental determinations in electropositive-electronegative gas mixtures, the fulfillment condition for the reaction (1) is considered accomplished for a calculated value of the defect energy reaction in the range (-4 ÷ +4) eV. The possibility that a resonant reaction can take place at a value of the defect energy reaction even of this order of magnitude was confirmed by others authors in their studies related to the Starck effect [13,14].

It can be distinguished three different cases, according to the magnitude order of the reaction energy defect, namely:

a.) $\Delta E \leq \pm 10^{-2}$ eV

In this case only one single dominant spectral line appears in the spectrum, the rest of the spectral lines have very low intensities by comparison with this one (Table 1). The spectrum has that spectacular, distinctive aspect of monochromatisation. We called this case the *M-effect of zero order* which is specific for a PDP type discharge in $(Ne+H_2)$ gas mixture. We can verify this assumption by calculating ΔE, in this particular case, for different spectral lines of Ne (the kinetic energy was neglected) [15].

Table 1. $(Ne+40\%H_2)$.

λ_1 (nm)	P^+(eV)	N^-(eV)	N^{met}(eV)	P^*(eV)	N^{met*}(eV)	ΔE(eV)	M_{Ne} (a.u.)	M_{Ne+H2} (u.a.)	μ
540.0	21.57	0.75	10.2	18.96	12.09	-0.03	0.01	2.41	24.0
585.2	21.75	0.75	10.2	18.96	12.09	-0.03	3.15	70.24	22.3
607.4	21.75	0.75	10.2	18.71	12.09	+0.22	0.54	1.66	3.0
614.3	21.75	0.75	10.2	18.63	12.09	+0.3	0.33	0.33	1.0
626.7	21.75	0.75	10.2	18.69	12.09	0.24	0.62	0.59	0.9

The μ parameter is defined as the ratio of the M parameter value in electropositive-electronegative gas mixture to the M parameter value in electropositive gas.

We consider that the spectral lines for which the μ parameter values are grater than unity are the result of the M-effect appearance. It can be observed that, for these spectral lines, the values of μ parameter are very small reported to those for the dominant lines λ= 585.2 nm (540.0 nm). These two spectral lines have almost the same μ parameter values because they are resulting from the transitions, in the Paschen notation for Ne spectrum, ($2p_1$-$1s_2$) respectively ($2p_1$-$1s_4$), both having the same initial energy level (the selectively populated level).

b.) $\Delta E \leq \pm 10^{-1}$ eV

In this case, which appears in $(Ar+H_2)$ and $(He+Cl_2/O_2)$, it can be observed the existence of more than one dominant, very intensive spectral line, as we have mentioned before. We called this case the *M-effect of order one.* The possibility that the three-body reaction could be accomplished, even the reaction energy defect is great, was experimentally established in the case of M-effect, but the increase of the dominant spectral lines number is due to the structure of the Ar and He spectra. Thus, the Ar spectrum of the excited energetic levels in Paschen notation is formed by 4- s lines ($1s_2$-$1s_5$) and 10 p- lines ($2p_1$-$2p_{10}$), whereas for the He the spectrum is even more complicated due to its specific structure of energetic levels (orto and para helium). For this reason, the number of combinations of the permitted transitions between these levels is greater than in the case of Ne spectrum consisting of a single s-line ($1s_2$) and 10-p lines, which finally leads to the appearance of more dominant spectral lines (with respect to the transitions rules for dielectric dipole).

Table 2. $(Ar+16.6\%H_2)$.

λ_1 (nm)	P^+(eV)	N^-(eV)	N^{met}(eV)	P^*(eV)	N^{met*}(eV)	ΔE(eV)	M_{Ar} (a.u.)	M_{Ar+H2} (u.a.)	μ
621.2	15.76	0.75	10.2	15.17	12.09	-2.05	0.7	0.5	0.7
696.5	15.76	0.75	10.2	13.33	12.09	-0.21	1.4	20	14.2
738.4	15.76	0.75	10.2	13.30	12.09	+0.18	0.57	12	21.0

c.) $\Delta E \geq 1$ eV

In this case, the M-effect does not appear, like in ($Ne+SF_6$) or in ($He/Xe+H_2$) gas mixtures, because the energetic condition to have an energy defect reaction close to zero is not accomplished. There are not energetic levels between could take place permitted transitions in order to obtain dominant lines. We have presented in the Table 3 some calculations for ($Xe+H_2$) gas mixture at a total pressure of 100 Torr.

Table 3. ($Xe+42\%H_2$).

λ_1 (nm)	P^+(eV)	N^-(eV)	N^{met}(eV)	P^*(eV)	N^{met*}(eV)	ΔE(eV)	M_{Xe} (a.u.)	M_{Xe+H2} (u.a.)	μ
462.4	12.13	0.75	10.21	0.99	12.09	-1.50	1	1	1
467.1	12.13	0.75	10.21	0.99	12.09	-1.48	0.4	0.2	0.6
823.2	12.13	0.75	10.21	0.99	12.09	-0.33	3.8	2.4	0.6
828.0	12.13	0.75	10.21	0.99	12.09	-0.44	7.4	1.6	0.6

4. Conclusions

The main mechanism which determines the appearance of the M effect in electronegative–electropositive gas mixtures was identified to be the resonant polar three-body reaction, despite of the fact that the Landau-Zenner theory assumes that only a two-body reaction can accomplish the energetic resonant condition. This specific character is due the fact that the monochromatisation effect (the M-effect) appears only at medium to high pressures (over 20 Torr) which implies the existence of a third particle, able to take over the excess energy of the reaction. In this particular case, this particle is the electronegative metastable atom being in a convenient energy state.

We have summarized the main gas mixtures in which appear more dominant lines, e.g. ($Ar+H_2$) and ($He+O_2/Cl_2$) and the optimum percentages of added electronegative gases for some dominant lines chosen from the spectrum of the Ar and He. Of course, this analysis could be made for others dominant lines too, related to the value of the wavelength spectral line needed.

The appearance of one very intense single spectral line or more dominant spectral lines shifted to the IR or UV spectral region was related to the magnitude order of the energy reaction defect, according to the spectra of the excited energy levels of the electropositive gases between which could take place the permitted transitions.

References

[1] G. Musa, L. Nastase, M. Tache, Contrib. to Plasma Physics **21**, 59-66 (1981).
[2] G. Musa, A. Popescu, A. Baltog, I. Mustata, Journal of Physics, D-Applied Physics **18**, 2119 (1985).
[3] G. Musa, A. Baltog, G. Bajeu, C. P. Lungu, E. Raiciu, I. Borcoman, A. Ricard, The European Pysical Journal, Applied Phyisics **4**, 165-169 (1998).
[4] A. Baltog, E. Raiciu, G. Musa, Contribution to Plasma Physics **40**(5-6), 537-544 (2000).
[5] G. Musa, A. Baltog, Contribution to Plasma Physics, **43**, 216-223 (2003).
[6] G. Musa, L. C. Ciobotaru, J. Optoelectron. Adv. Mater. 6(4), 1339-1344 (2004).
[7] G. Musa, L. C. Ciobotaru, Barbu Ionut, J. Optoelectron. Adv. Mater. **8**(3), 1292-1297 (2006).
[8] L. C. Ciobotaru, P. Chiru, C.Neacsu, G. Musa, J. Optoelectron. Adv. Mater. **6**(1), 321-324 (2004).
[9] G. Musa, L. C. Ciobotaru, P. Chiru, A. Baltog, J. Optoelectron. Adv. Mater. **6**(2), 459-464 (2004).
[10] G. Musa, A. Popescu, A. Baltog, C. P. Lungu, Roum. Reports in Physics, **45**, (1993) - (review paper).
[11] L. Landau, Phys. Z. Sowjet, **46**, 1932.
[12] C. Zener, Proc. Roy. Soc. A, **137**, 696 (1932).
[13] H. Tewoujek, W. Janos, W. Jelenski, Journal of Technical Physics, vol. **40**, p 271-274, Warsawa, 1999.
[14] H. Tewoujek, W. Janos, W. Jelenski, Plasma 95, Second National Symposium, Research and and Applications of Plasma, Warsaw, June 1995, Vol.1, Contributed Papers.
[15] C. Surdu-Bob, G. Musa, P. Chiru, O. Branza, J. Optoelectron. Adv. Mater. **7**(5), 2391 (2005).

*Corresponding author: catalinaciobotaru@yahoo.com