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Monochromatization effect kinetic model for Penning gas mixtures emission mechanisms

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Abstract

The monochromatization effect (M-effect), which consists in the reduction of an electronegative-electropositive gas mixtures discharge emission spectrum to only a few or a single line, was largely explained in our previous published papers together with their generation mechanisms, namely the polar ion-ion recombination and the energy resonance condition. This paper presents a kinetic model for the M-effect based on the radiative and collisional processes which appear between $1s_2$, $1s_3$, $1s_4$ and $1s_5$ Paschen levels, in Penning gas mixtures, where this effect was observed to be the most powerful.

Key Words: Monochromatization-effect, kinetic model, collisional processes

PACS: 52.20.- j Elementary processes in plasma.

1. Introduction

In contrast to excimer radiation studies based on the fact that excimer molecules exist only in excited states, and in which appears the problem to find efficient reaction channels to form the excited molecules, in the frame of monochromatization effect study the main problem consists in explaining the preferential population mechanism of the levels responsible for the dominant spectral lines emission. The so-called "Monochromatization effect" consists in the reduction of the discharge emission spectrum to one single line, namely $\lambda = 585.3$ nm, in Ne + Ar + H_2 or Ne + Xe + H_2 gas mixtures. In the present work, we used a Dielectric Barrier Discharge (DBD), [1–4]; the effect was also observed in AC/RF discharges.

Figures 1(a) and 1(b) show the emission spectrum of a Plasma Discharge Panel (PDP) in pure neon and, respectively, the emission spectrum in a Ne + 1%Ar + 40% H_2 gas mixture. The emission spectrum is observed to be nearly monochromatic when (for a Penning-type mixture) hydrogen is added to half partial pressure of the gas mixture. The red color of the discharge turned into a yellow monochromatic color, while the whole spectrum was reduced to a single spectral line.

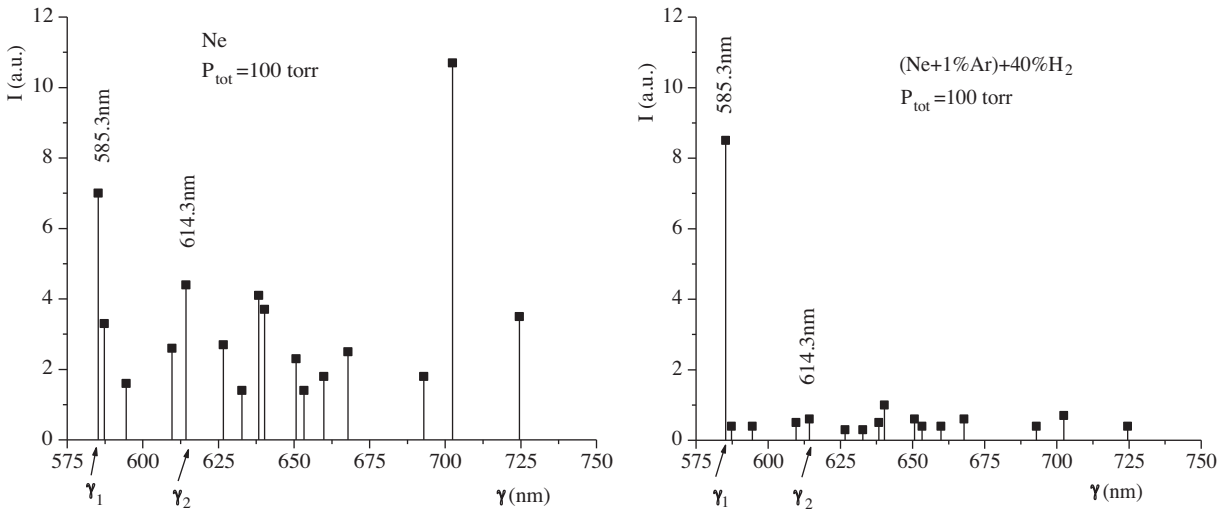

Figure 1. Emission spectra of PDP discharges in **(a)** pure Neon gas and **(b)** gas mixture (Ne+1%Ar) + 40%H_2.

2. Experimental set-up

For the M-effect study a plasma-panel discharge device (display-type) was employed. 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 was covered with a vacuum deposited 1 micrometer thin Al-film linear electrode (see Figure 2). The length and the width of the electrodes were 190 mm and 4 mm, respectively. The electrical connections to the electrodes were on a perpendicular line to the end of each one. The glass surfaces with electrodes were covered with a uniform dielectric layer having a thickness of 18–20 micrometers, except for the surfaces marked on the Figure 2 with black color. These surfaces are a connector-type used to include the device in an electrical circuit in order to generate radiation. The glass plates are vacuums tight assembled with 1mm discharge space. The linear electrodes were mounted face to face. Polished quartz windows were used in order to record the emitted UV radiation. The discharge was ignited and maintained using a square wave A.C. voltage with a frequency in the range of 10 kHz up to 100 kHz and an applied voltage peak-to-peak value of 1 kV. The discharge device was connected to a vacuum pumping unit and can be filled with various gas mixtures at the established pressures. During the measurements, the discharge device was connected to the pumping unit. The total pressure values of the gas mixture were in the range of 10–45 Torr. In order to record the emission spectra, an Optical Multichannel Analyzer (OMA), spectral range between 200–900 nm and 0.5 nm resolution, was used. The integration time was chosen in the range of 0.5–3.5 s. High spectral purity noble gases were used in the experiments.

3. Results and discussion

In order to characterize the "quality" of this effect, it was 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, these two spectral lines were chosen as $\lambda_1 = 585.3$ nm, respectively $\lambda_2 = 614.3$ nm.

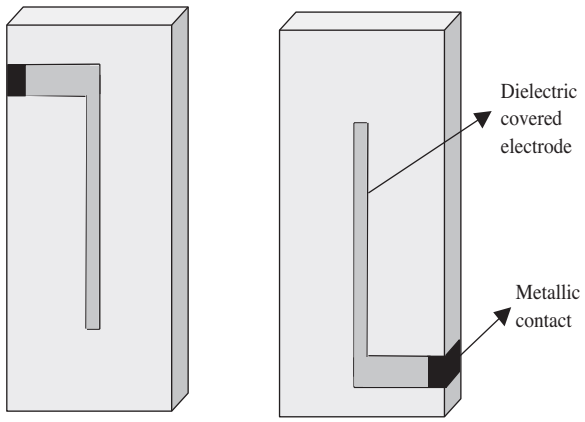

Figure 2. Deposited thin film electrodes - face view on glass plates.

The M parameter so defined is:

$$M = \frac{I_{\lambda_1=585.3\,nm}}{I_{\lambda_2=614.3\,nm}} \tag{1}$$

In case of the pure neon discharges, the value of the M parameter was on order of a few units, whereas at 40% hydrogen content in the neon-hydrogen gas mixture, a value as high as 40 units was found. These results were obtained for a dielectric barrier discharge in (Ne + H_2) mixture at total pressure values around 100 Torr. Table 1 shows some data proving the generality of the effect for other types of electronegative-electropositive gas mixtures, besides neon + hydrogen, in a dielectric barrier discharge [5–10]. Recently, it has been reported the appearance of more dominant spectral lines in AC plasmas of one negative and two/three electropositive gases special mixtures [11–13].

Table 1. Characteristic data concerning the monochromatization effect in different types of electronegative-electropositive gas mixtures and different types of discharges.

Discharge type		Gas mixture type	The M-effect existence	Dominant spectral lines, λ_1 (nm)	Reference spectral lines λ_2 (nm)	h	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
*	-	Ar+Cl_2	*	515.8	312.8	4	25	-
*	-	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
*	-	He+H_2	-	-	-	-	-	-
*	-	He+Cl_2	*	335.4	706.7	14	25	More dominant spectral lines
*	-	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	-	-	-	-	-	-

For hydrogen fractions greater than 50%, the absolute intensity of the neon spectral lines decreased, inclusive the yellow line $\lambda_1 = 585.3$ nm, due to the energy loss of the electrons situated on the hydrogen molecular roto-vibrational levels, with the consequence of the electronic temperature decrease.

The added helium influence to the Ne + 1%Xe or Ne + 1%Ar gas mixtures had a diminution effect of the neon yellow spectral line intensity and not, as it would has expected, an increase effect. In this case, the monochromatization parameter value, namely $M(\lambda_1, \lambda_2)$, had a significant decrease, under the unit value, especially at low pressures. At higher pressures (above 100 Torr) the influence of the helium addition on the M value was negligible. In Figure 3 is presented the neon energy levels simplified structure in Paschen notation.

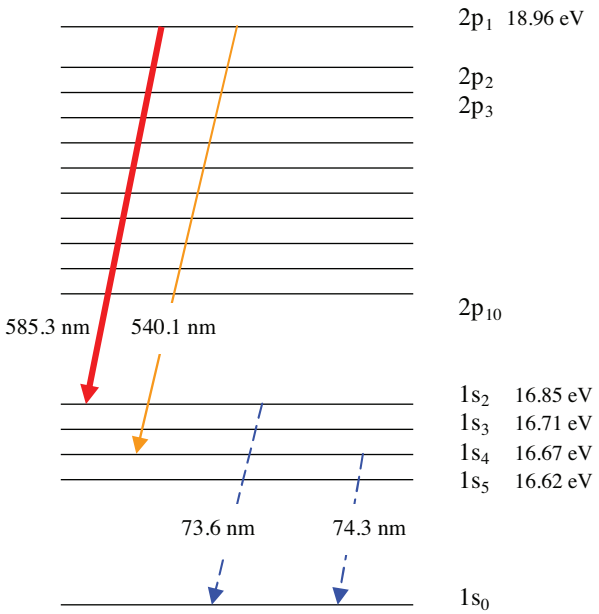

Figure 3. Neon Paschen energy levels for the M-effect.

As it can be observed, the spectral line $\lambda_1 = 585.3$ nm proceeds from the transition $2p_1 \rightarrow 1s_2$. Therefore, the most of the neon excited atoms, in the frame of monochromatization-effect, must be on $2p_1$ energy level because the emitted radiation intensity is directly proportional to the population of the initial level.

A second permitted transition starting on this level is $2p_1 \rightarrow 1s_4$ with the wavelength of the emitted radiation $\lambda = 540.1$ nm. Still, this spectral line is not a dominant one because the emission probability is about one hundred time weaker than for the first transition. The levels $1s_2$ and $1s_4$ are resonant levels for neon atom and their theoretical life-time are $\tau_{s_2} = 2 \times 10^{-8}$ s, respectively $\tau_{s_4} = 1.5 \times 10^{-9}$ s. The excited atoms standing on these levels return to the fundamental energy level by radiative de-excitation or collisional processes.

The wavelengths of the resonance radiation are $\lambda = 73.6$ nm and respectively $\lambda = 74.4$ nm, corresponding to the two transitions, namely $1s_2 \rightarrow 1s_0$, respectively $1s_4 \rightarrow 1s_0$ (where s_0 is the notation for the fundamental energy level). Under a few Torr total pressure values, due to the resonance radiation trapping phenomenon, the real life-time of the excited neon atoms standing on the resonance energy level becomes comparable with the life-time on the metastable energy levels. Theoretically, the life-time of the atoms on the metastable levels is about one second, but in real discharge conditions, the life-time is significantly reduced, being of about 10^{-3}

s order. The radiative and collisional processes which appear between $1s_2$, $1s_3$, $1s_4$ and $1s_5$ levels could be described by the following equations:

$$Ne^*(1s_i) + e \rightarrow Ne^{**}(2p_m) + e \qquad i = 1, \ldots, 4; m = 1, \ldots, 10; \tag{2}$$

$$Ne^{**}(2p_m) \rightarrow Ne^*(1s_j) + h\nu; \qquad j = 1, \ldots, 4; m = 1, \ldots, 10; \tag{3}$$

$$Ne^*(1s_i) + Ne \rightarrow Ne^*(1s_j) + Ne; \qquad i, j = 1, \ldots, 4, i \neq j; \tag{4}$$

$$Ne^*(1s_i) + M \rightarrow Ne^*(1s_j) + M; \qquad i, j = 1, \ldots, 4; i \neq j. \tag{5}$$

The notation Ne^{**} denotes neon atoms standing at higher excited levels.

Duration of an electronic collision is about 3×10^{-9} s at a pressure of 1 Torr, for a plasma panel discharge. Consequently, for a gas pressure of 10–100 Torr the time between two consecutive electronic collisions was about 3×10^{-11}–3×10^{-10} s, which is a much smaller life-time than that of excited neon atoms on the resonance/metastable energy levels. At the same time, a neon atom excited to the $1s_i$ energy level will suffer in its life time a great number of collisions with neutral atoms.

For neon atoms standing on metastable energy levels, their real life-time is shorter than 10^{-3} s due to the Penning-type collisions. These reactions, which produce a quick quenching of the neon excited atoms on metastable/resonant levels, are the following:

$$Ne^*(1s_i) + Ar \rightarrow Ar^+ + Ne + e \tag{6}$$

$$Ne^*(1s_i) + Xe \rightarrow Xe^+ + Ne + e \tag{7}$$

$$Ne^*(1s_i) + H_2 \rightarrow H_2^+(v \neq 0) + e \tag{8}$$

$$i = 2, 3, 4, 5, \ldots.$$

The diminution population process on the $1s_2$ level, due to the existence of the $2p_1 \rightarrow 1s_2$ transition (which generated the $\lambda = 585.3$ nm spectral line) was initially considered to be the main agent of the population inversion in neon-pulsed lasers. The monochromatization effect is implying, too, in the case of electric discharges in (neon + argon/xenon + hydrogen) gas mixtures, the existence of a selective mechanism in order to populate the $2p_1$ neon energy level. Consequently, together with the diminution of the emitting transition of the $\lambda = 585.3$ nm spectral line due to the Penning reactions, it can be assumed the existence of a simultaneous feeding process of the high energy level $2p_1$. This process is considered to be the polar ion-ion recombination reaction, namely the recombination between negative hydrogen ions and positive neon ions. A very important role in the process is the effect the addition of hydrogen has on the neon + argon/xenon gas mixture. The temporal evolution of a PDP spectral emission points out the hydrogen role in generation of the monochromatization-effect.

Figures 4(a) and 4(b) show the relative luminescence intensity diagrams for neon + xenon and, respectively, for neon + xenon + hydrogen gas mixtures, for a plasma panel discharge. In the first case it can be observed a single peak, which is clearly outlined compared to the second case, where an additional peak appears at the $\lambda = 585.3$ nm neon spectral line. The large maximum of the emitted quasi-monochrome radiation that appeared in Figure 4(b) corresponds to the shape of a post-luminescent plasma temporal evolution diagram.

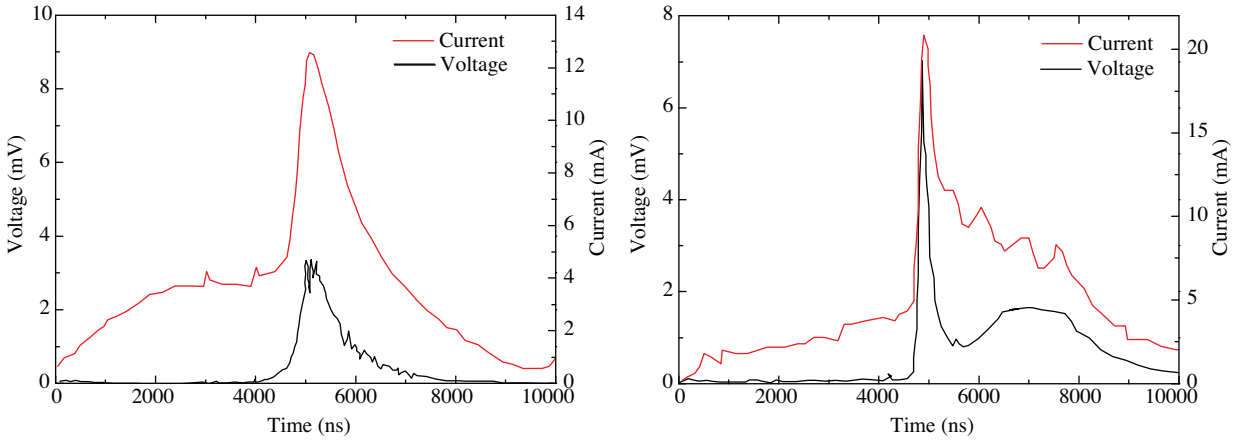

Figure 4. (a and b): The luminiscent relative intensity diagrams in (neon+xenon) and respectively in (neon+xenon+hidrogen gas mixtures for a plasma panel discharge.

The experimental data permitted explanation of the monochromatization effect in (neon + argon + hydrogen gas) mixtures, for a plasma-display discharge at moderate to high pressures. This effect is considered to be based on the recombination between the neon positive ions and hydrogen negative ions, namely on the polar recombination process. The principal reactions are:

$$e + H_2 \rightarrow e + H_2^* \rightarrow H^- + H^* \tag{9}$$

$$H^- + Ne^+ \rightarrow Ne^*(2p_1) + H \tag{10}$$

$$H^- + Ne^+ + M \rightarrow Ne^*(2p_1) + H + M \tag{11}$$

$$Ne^*(2p_1) \rightarrow Ne^*(1s_2) + h\nu(\lambda = 585.3nm), \tag{12}$$

where M is the notation for the third body involved in the reaction. This is an extension of the resonant character of a two body reaction in the frame of Zenner theory [14–17]. The experimental studies performed using the variable wavelength laser absorption method, where the lower level of the neon atom was $1s_i$ (i = 2, 3, 4, 5...), indicated a significant decrease of the excited density atoms on these levels after the addition of hydrogen. Consequently, this means that the addition of hydrogen induced population of the upper excited levels of the neon atoms, namely $2p_1$; but, at the same time, this produced the depopulation of the neon metastable atoms. It is more convenient to have a low power density in plasma and low electrons energy, because the attachment energy of an electron at the hydrogen atom is only of 0.75 eV. In this way, it can be obtained in plasma a high density of hydrogen negative ions. Due to the Coulomb attraction force between the neon positive ion and hydrogen negative ion, the cross- section reaction is very large, around 8×10^{-12} cm^2, and decreases proportionally with gas temperature.

At total moderate-to-high gas mixture pressures, the polar recombination reaction becomes a three-body process.

In addition, note that the highest negative ion density was reached in the after-glow plasma zone.

As already pointed out, the $1s_5$ level is a metastable state with a life time of about 1 second, while $1s_3$ is a quasi-metastable level. The generation mechanisms of the neon quasi-monochrome radiation with $\lambda = 585.3$ nm are performed at moderate to high pressure (approximately 100 mbar), and for this reason the collisions

frequency between the heavy particles is rather high. These Penning-type collisions were taking place between the neutral and the excited neon atoms standing on the $1s_i$ levels, which are energetically very close. Finally, these collisions were producing small changes in the energy levels of the neutral neon atoms, accordingly to the following equation [10, 18]:

$$Ne^*(1s_i) + Ne \rightarrow Ne^*(1s_j) + Ne \pm \Delta E, \tag{13}$$

where ΔE represents the energy change between the different $(i \neq j)$ neon energy levels.

These collisions have led to the appearance of a collisional coupling between levels which were responsible of the life-time decrease of the excited neon atoms. Actually, it can be considered that $1s_2$ level is directly coupled with the neon metastable $1s_5$, being dependent of its population.

Based on these considerations, it can be assumed a simplified kinetic model of the monochromatization effect, which permitted the explanation of the collisional coupling between $2p_1$ and $1s_5$ neon excited levels.

Figure 5 shows the neon energy levels and the different reaction channels responsible for the monochromatization effect. The reaction channels are proposed to be the following:

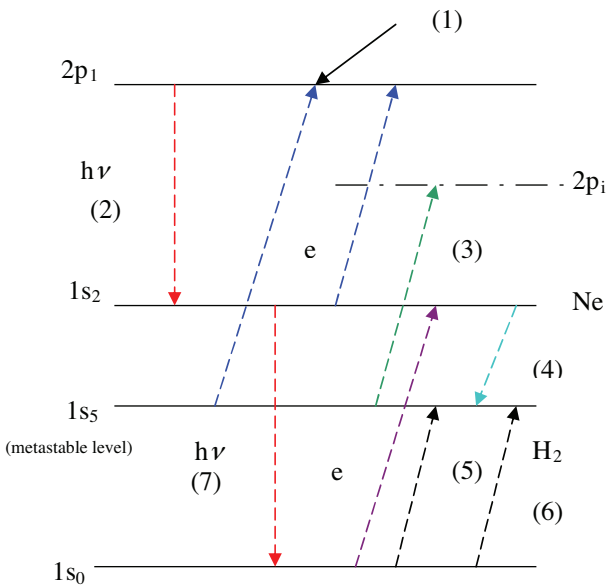

Figure 5. The principal reaction channels in the simplified kinetic model of the monochromatization effect and the neon energy levels of interest.

- *Channel 1*: the population of $2p_1$ level due to $(Ne^+ + H^-)$ recombination process;
- *Channel 2*: the $2p_1$ level radiative de-excited process on $1s_2$ level;
- *Channel 3*: the $2p_i$ (inclusive $2p_1$) levels population by electronic collisions starting from $1s_j$ levels;
- *Channel 4*: $1s_i$ levels collisional coupling and the transition $1s_2 \rightarrow 1s_5$ (metastable level) due to the collisions with neon neutral atoms;
- *Channel 5*: the population of $1s_i$ levels by electronic collisions starting from

$1s_0$ fundamental energy level;

- *Channel 6*: the de-excitation of $(1s_5)$ metastable level of neon excited atoms due to the Penning collisions with hydrogen atoms;
- *Channel 7*: the radiative de-excitation process of the $1s_2$ level.

Population of the Ne^* $(2p_1)$ excited level was generated by an ion-ion recombination process and as a result it was directly proportional to $[Ne^+] \times [H^-]$ concentrations, level which was radiative de-excited on the $1s_2$ level. Following this, because of the collisional coupling, the neon excited atoms reached the metastable state Ne^* $(1s_5)$. The population of this metastable level was determined by the collisional excitation process with the electronic gas, which was in equilibrium with the process of de-excitation produced by Penning collisions with metastable states.

Taking into account the weak contribution of the electronic gas, because the monochromatization effect was maximum in the after-glow, one can obtain the following expression for the concentrations of Ne^* $(2p_1)$ and Ne^* $(1s_5)$ levels, which were the ones that really control the process:

$$Ne(1s_5) = \frac{f_1 - f_2}{k_1 H_2 - k_2 \frac{Ne}{H_2} \times Ne\langle 2p_1 \rangle}, \tag{14}$$

where k_1 and k_2 are the reaction constant values, f_1 is the population rate by electronic collisions of the metastable level $1s_5$ and f_2 is the depopulation rate of this level by the excitation process on upper energetic levels.

4. Conclusion

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

- electronegative-electropositive gas mixture;
- low gas temperature and elevated pressure of the gas mixture;
- 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.

It can be concluded that two main processes are responsible for the appearance of the monochromatization 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).

To sum-up, the principal radiative transitions involved in the appearance of the M-effect in Ne+H_2+Ar/Xe gas mixtures are: $2p_1 \rightarrow 1s_2$ (dominant spectral line 585.3 nm), $2p_1 \rightarrow 1s_4$ (540.1 nm), $1s_2 \rightarrow 1s_0$ (73.6 nm resonance spectral line), $1s_4 \rightarrow 1s_0$ (74.4 nm resonance spectral line), the radiative processes between $2p_m \rightarrow 1s_i$ ($i = 2, 3, 4$; $m = 1,\ldots, 10$) and the non-radiative transitions produced by collisions: $1s_j \rightarrow 2p_i$ ($i, j = 1,\ldots, 4$, $i \neq j$), (electronic collisions), $1s_2 \rightarrow 1s_5$ (collisions with neon neutral atoms), $1s_0 \rightarrow 1s_i$ (electronic collisions), and $1s_5 \rightarrow 1s_0$ (Penning collisions).

A very important role is considered to have the collisional coupling between the neon energy levels which finally permits to vary the energy reaction defect in order to fulfill the resonance energy condition.

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