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Plasma generated with gas mixtures at atmospheric pressure

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Objective and outline

- Objective:

  Results on the plasma characteristics generated with gas mixtures using emission spectroscopic techniques

- Outline:
  - Introduction
  - Spectral line shape and spectroscopy techniques: plasma parameters
  - Results:
    - **Ar-He and Ar-Ne**
    - **Ar-N_2**

Introduction

- Plasma is a reactive medium in which reactions that happen can be controlled as a function of the operational conditions used to generate the discharge
  - Pressure
  - Type and gas flow (mixtures)
  - Energy supplied (frequency and value)
  - Reactor design

Introduction

- Nowadays, in most technological applications of plasmas, the plasma gas is made up of gas mixtures

- The goal of gas mixtures is to induce reactions in which atoms, ions and molecules at excited levels of different elements are involved

Introduction

- Plasma at atmospheric pressure:
  - Collisional medium
  - Simple design since no pumping system is required
- Applications of plasmas with gas mixtures:
  - excitation source for elemental analysis
  - purification of noble gases
  - hydrogen production
  - sterilization of medical instruments

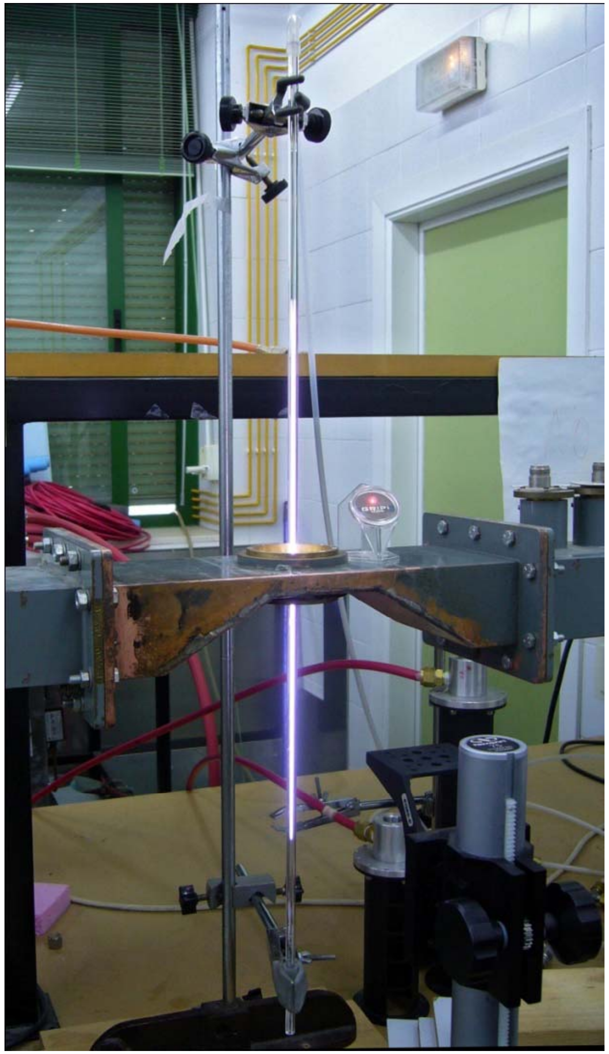
Introduction

- The maximum effectiveness of plasma applications:
  - densities of the plasma particles (n_e and n_p)
  - energy available in the discharge (T_e and T_{gas})

- Emission spectroscopic techniques based on the analysis of atomic spectral lines and molecular bands emitted by the plasma particles allow to know the processes that take place in the plasmas

Introduction

Surface wave discharge (SWD) is a special type of microwave discharges



Characteristics of SWDs:

- Dimensions higher than the wavelength of electromagnetic field
- The plasma extends outside the coupler device with the microwave power applied
- Plasma columns are equivalent, when they are measured from their ends

Properties for laboratory experiments:

- Frequency (MHz $\rightarrow$ GHz)
- Gases: Ar, Kr, Ne, Xe, He, N_2, O_2 …and mixtures gases
- Gas flow $<$ 500 ml / min
- No fluctuations or instabilities
- Good reproducibility

Spectral Line Shape …

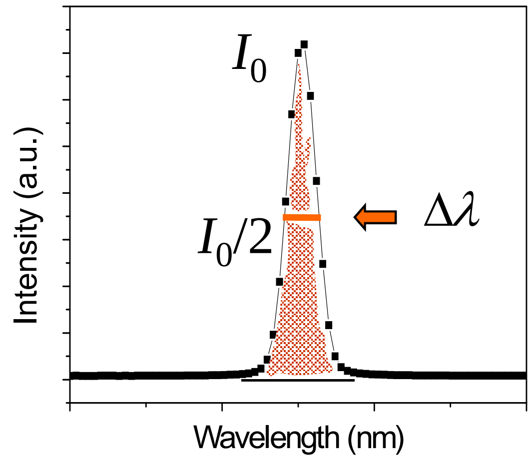
- Atomic lines: The profile shape depends on internal processes in the plasma

  The Area is related to the population of emitter atoms

  The Width is result of independent contribution of processes in the plasma

The main broadenings at high pressure

Instrumental, Doppler, Stark and van der Waals



FWHM $\Delta\lambda$

(*full width at half maximum*)

Instrumental $\Delta\lambda_I$

Doppler $\Delta\lambda_D = f(T_{gas})$

$$\Delta\lambda_G^2 = \sum_i (\Delta\lambda_{Gi})^2$$

Gaussian Profile

Stark $\Delta\lambda_S = f(n_e, T_e)$

van der Waals $\Delta\lambda_W = f(T_{gas})$

$$\Delta\lambda_L = \sum_i \Delta\lambda_{Li}$$

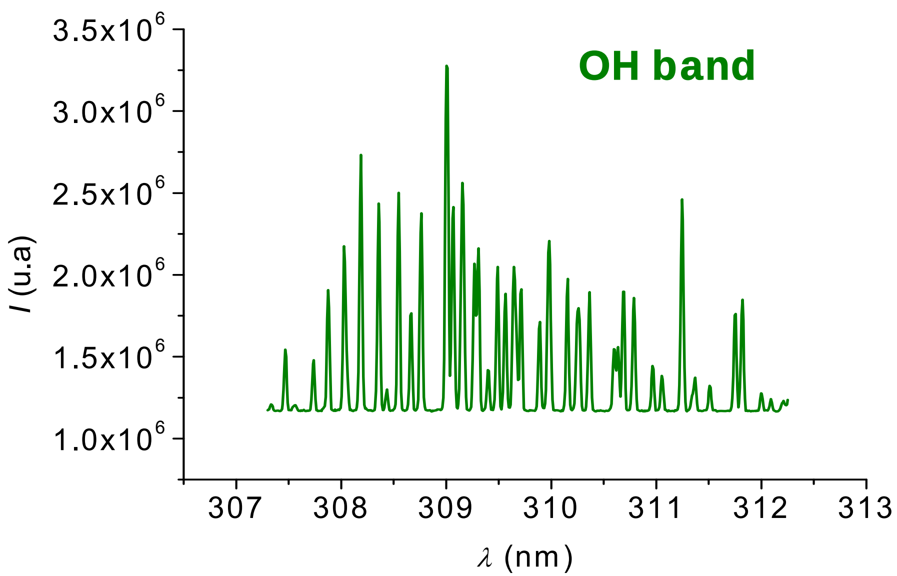
Lorentzian Profile

VOIGT Profile

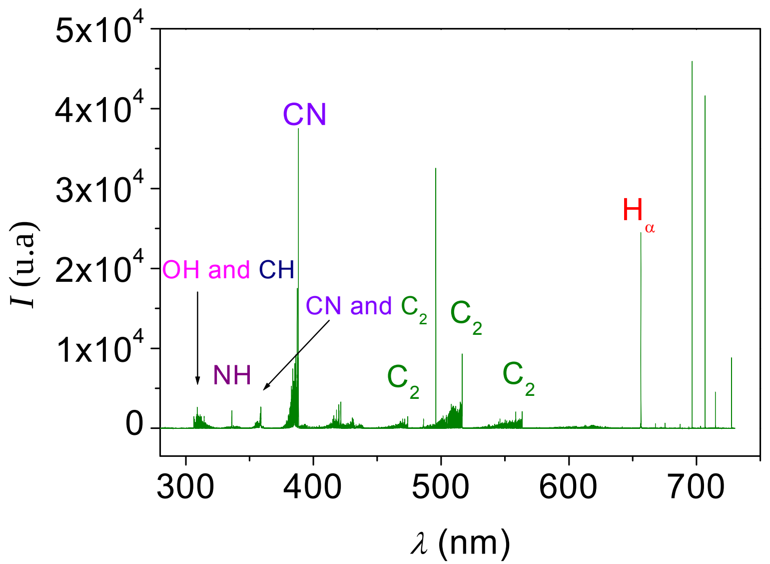
$\Delta\lambda_V$

Spectral Line Shape …

- Molecular bands: ro-vibrational spectra of molecular species in the plasma.
- These spectra give information on:
  - the energy obtained by these species from collisions with plasma particles (gas temperature, T_{gas})
  - Decomposition processes in the plasma



Ar plasma



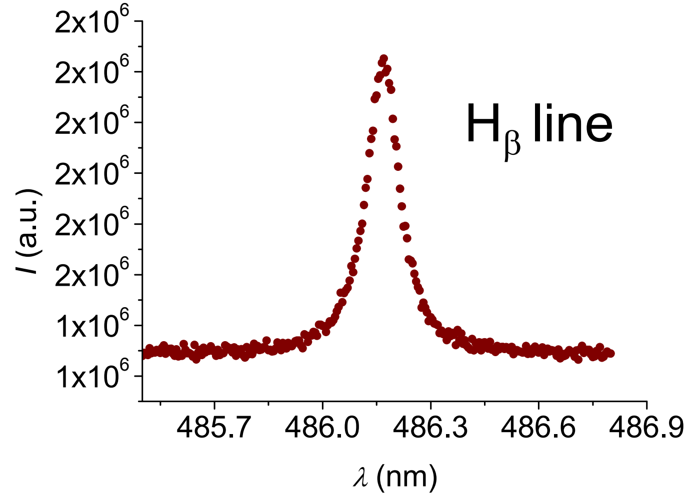
CH_3-CH_2OH decomposition

Spectral Line Shape …

The characteristics of the optical device:

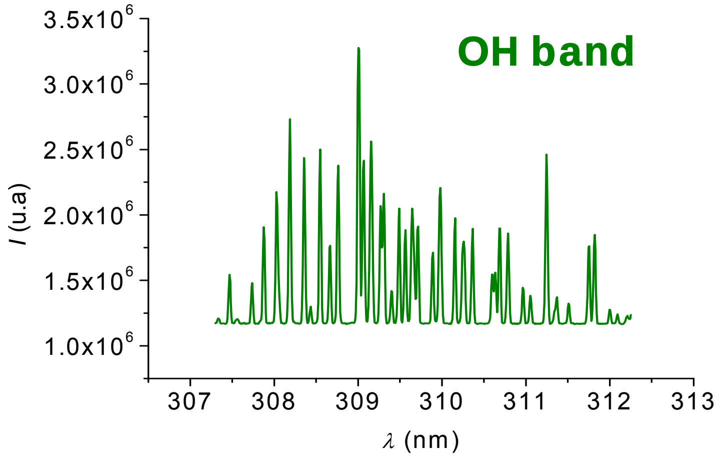
a) atomic lines:

- small instrumental broadening
- low noise signal
- possibility to choose the number of points for the profile



b) molecular bands:

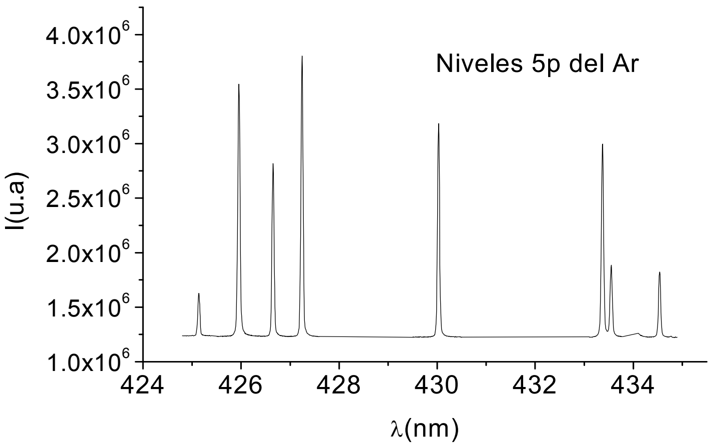
- high resolution
- low noise signal

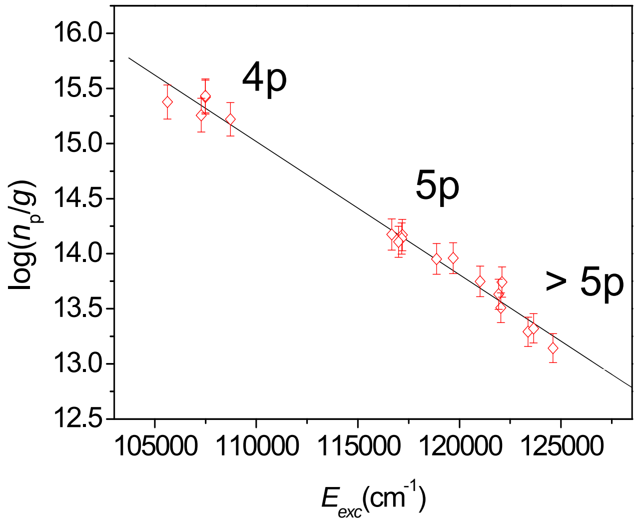


Spectral Line Shape …

- Excitation temperature (T_{exc}) is the energy set in motion in the excitation processes in the plasma

Boltzmann-plot method: log ($I\lambda/gA$) versus E_{exc}





$$\log\left(\frac{I\lambda}{gA}\right) = mE_{exc} + C$$

$$\boxed{m = -\frac{0.625}{T_{exc}}}$$

Ar plasma: 4000-7000 K

Ne plasma: 9000-10000 K

Spectral Line Shape …

- Gas temperature (T_{gas}) is related to the energy of the heavy plasma particles

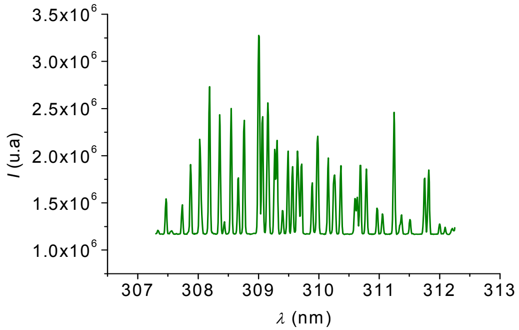
a) van der Waals broadening of plasma atomic lines

Deconvolution of the profile $\nearrow \boxed{\Delta\lambda_G}$ $\searrow \boxed{\Delta\lambda_L}$

$$\boxed{\Delta\lambda_L = \Delta\lambda_S + \Delta\lambda_W} \quad \nearrow \boxed{\Delta\lambda_S} \quad \searrow \boxed{\Delta\lambda_W}$$

$$\boxed{\Delta\lambda_W \approx 8.18\times10^{-5}\,\lambda^2\left(\alpha\langle R^2\rangle\right)^{2/5}\left(\frac{T_{gas}}{\mu}\right)^{3/10} N}$$

b) ro-vibrational spectra of molecular species: OH, N_2^+…, assuming that these species are in equilibrium with the plasma gas atoms



$$\boxed{\log\left(\frac{I\lambda}{A}\right) = mE_{j'} + C} \qquad m = -\frac{0.625}{T_{rot}} \quad \Rightarrow \quad \boxed{T_{rot} \approx T_{gas}}$$

Spectral Line Shape …

- Electron density (n_e) is one of the most important plasma parameters because the electrons control the processes of ionization and excitation that take place in the discharges

Stark broadening of the spectral lines is often used as a technique for the n_e diagnosis

a) Stark broadening of the Balmer lines: H_α, H_β and H_γ (taking into account the ion dynamics)

Plasma $n_e \geq 10^{15}$-10^{16} cm^{-3} $\quad \Delta\lambda_L \approx \Delta\lambda_S$

Plasma $n_e < 10^{15}$ cm^{-3} $\quad \Delta\lambda_L = \Delta\lambda_S + \Delta\lambda_W$

b) Stark broadening of neutral atomic lines

Plasmas: Ar-He

J. Muñoz and M.D. Calzada
J.Phys.D: Appl. Phys. 42 (2008)

J. Muñoz, M.S. Dimitrijević, C. Yubero and M.D. Calzada
Spectrochim. Acta B 64 (2009)

J. Muñoz and M.D. Calzada
Spectrochim. Acta B 65 (2010)

Plasmas: Ar-He

- Reason:

  Several mechanisms are proposed for the excitation-ionization of elements in which the metastables are involved (Penning excitation and ionization)

  He metastable: energy ≈ 19.8 eV

  Ar metastable: energy ≈ 11.5 eV

- High power (> 1kW) is necessary to create and maintain He plasma togheter the use of a cooling system

Ar-He could be considered as an alternative to pure He plasma

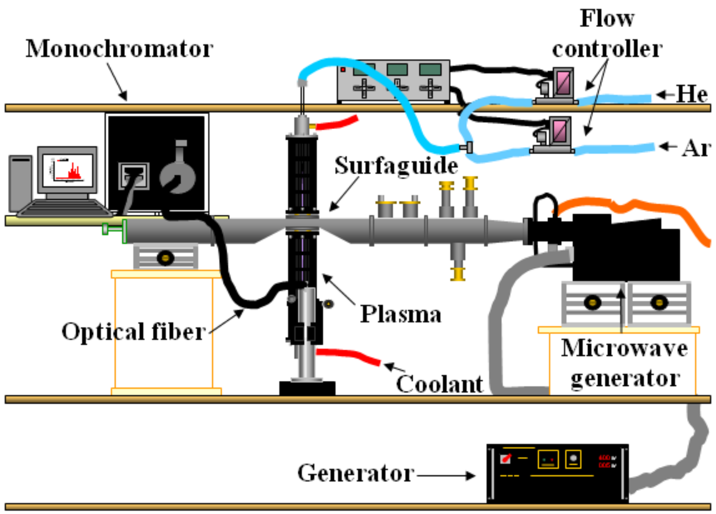
Plasmas generated with Ar-He

o <u>Experimental system</u>:

- Power: 75 – 800 W (at 2.45 GHz, surfaguide coupler device)
- Cooling system: dielectric liquid (α-Tetradecene) or air
- Ar-He mixtures up to 60% of He (total flow 0.5 slm)
- Jobin-Yvon monochromator (1m focal length and 2400 lines/mm)
    - photomultiplier R928P and shymphony CCD

o <u>Plasma parameters:</u>

- Linear power density, $\overline{L}$
- Electron density, n_e
- Populations of excited levels
- Excitation and ionization kinetics
- Plasma radial contraction

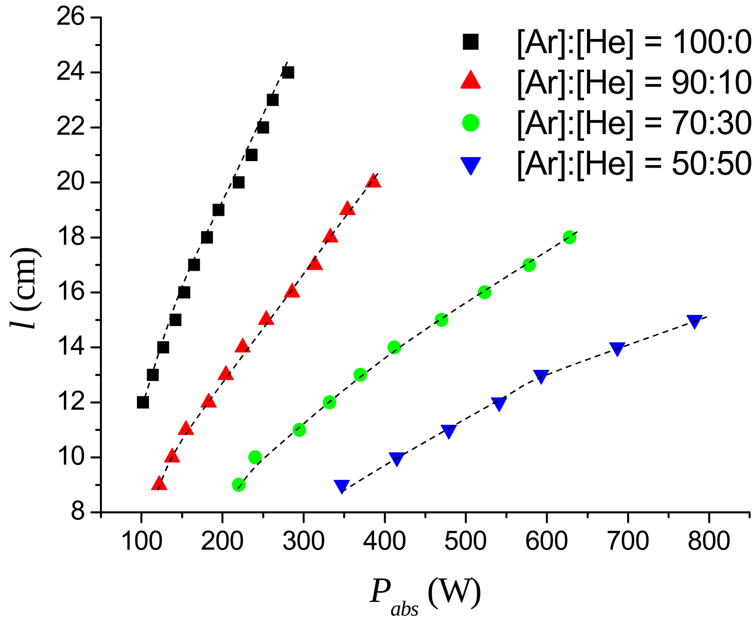


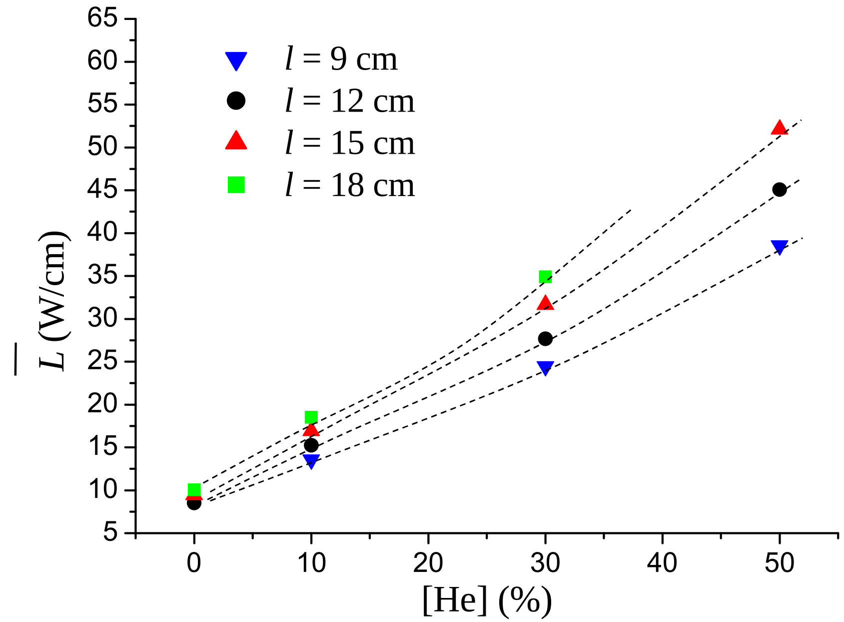
Plasmas generated with Ar-He

- **Linear power density (L)** is defined as the power absorbed per plasma unit length
  (related to the energy available in the plasma)
- Experimentally L can be measured by:

$$\bar{L} = \frac{P_{abs}}{l}$$

$P_{abs} \equiv$ absorbed power
$l \equiv$ plasma length

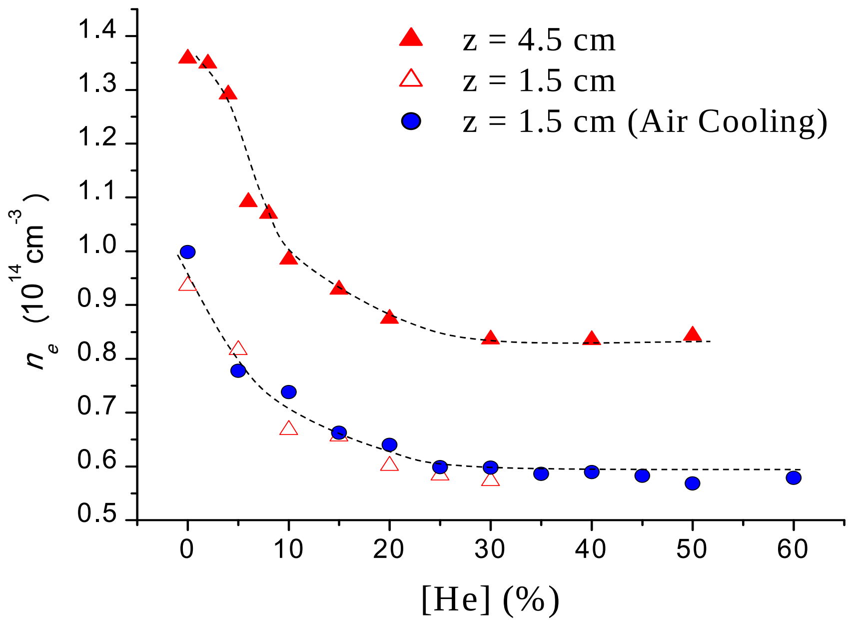


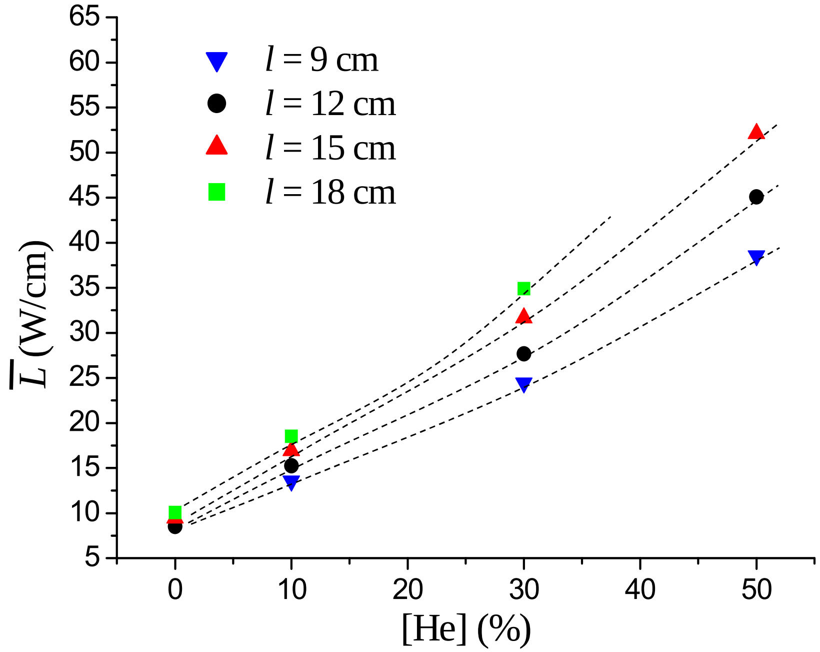


Plasmas generated with Ar-He

- **Electron density, n_e:**

  Stark broadening of H_β is used: its profile was ascribed to the Stark effect



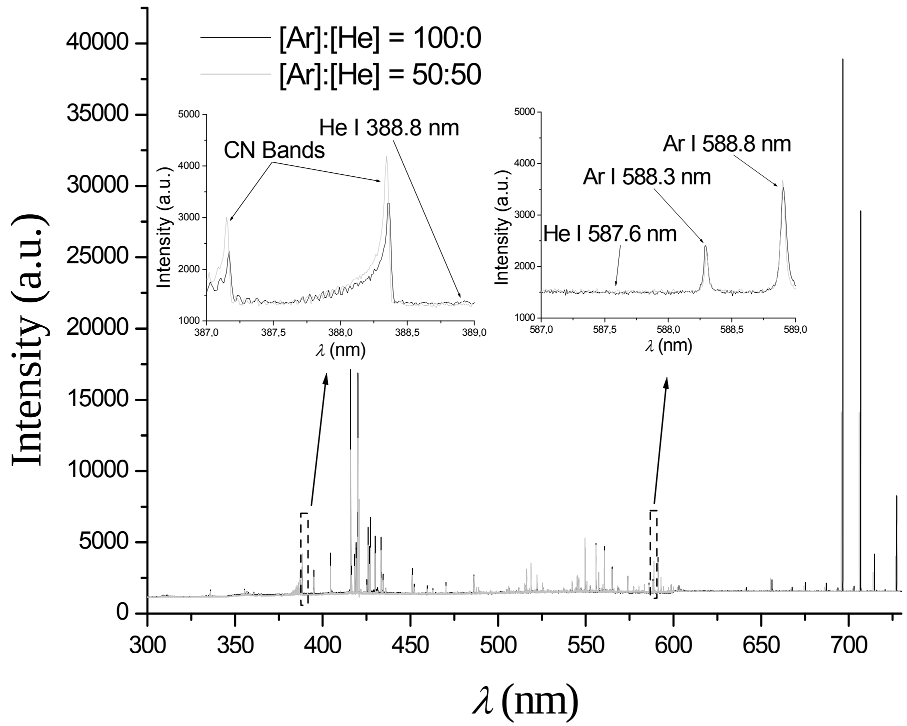


In plasmas of pure Ar: the higher the $\overline{L}$ value, the higher the n_e value

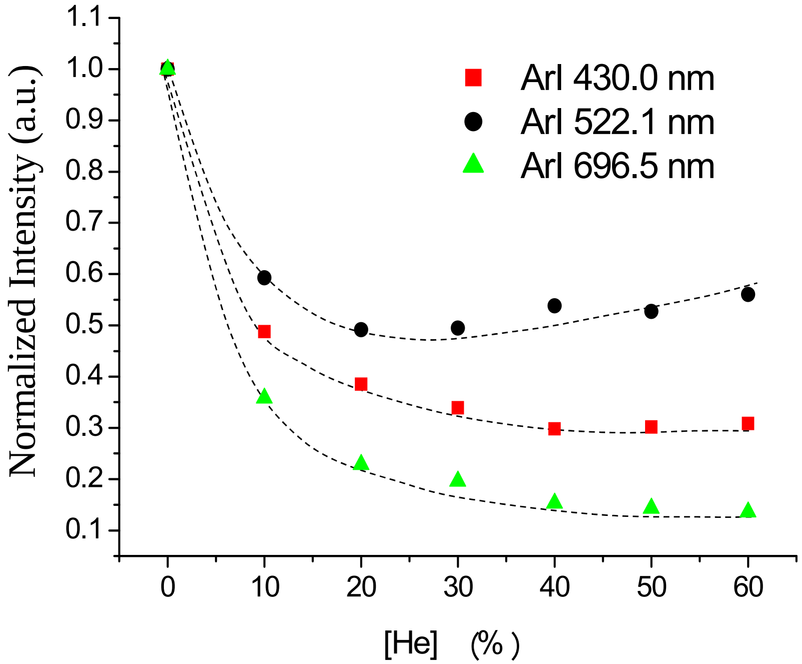
In plasmas Ar-He: the increase in energy is not used in ionization processes

Plasmas generated with Ar-He

- **Population of excited levels, n_p:**
  - The intensity of a spectral line is proportional to the population density of the upper levels to the associated transition
  - Variations in the intensity of the lines are related to the processes that take place in the discharge



Hel and ArII are not observed



Group 1: 696.5 nm, E_{exc} < 13.5 eV

Group 2: 430.0 nm, 14 eV < E_{exc} < 15 eV

Group 3: 522.1 nm, E_{exc} > 15 eV

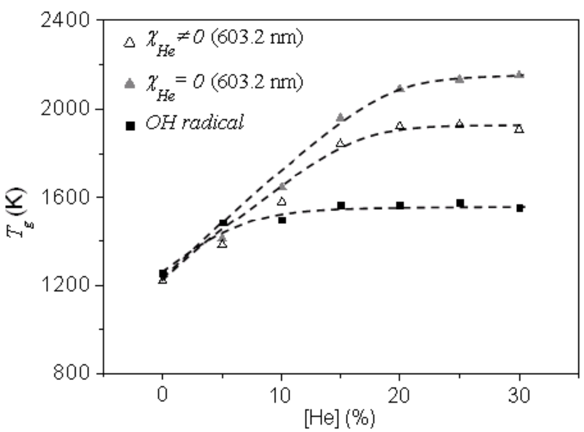
Plasmas generated with Ar-He

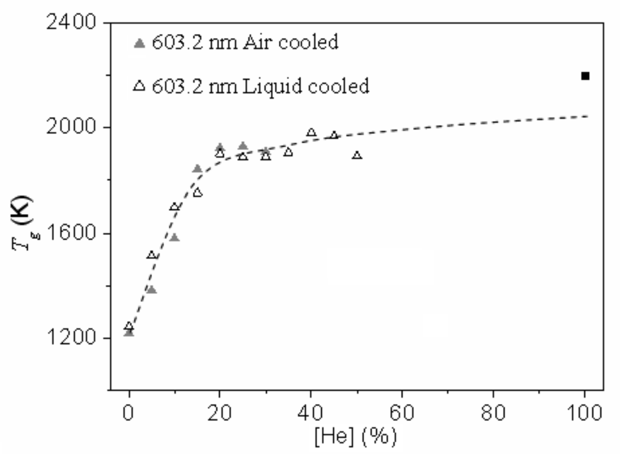
- In plasmas generated by using an Ar-He mixture, the van der Waals of spectral lines is provoked by the collisions with Ar and He atoms

$$w_W = 8.18\times10^{-26}\lambda^2\left(<\overline{R}^2>\right)^{2/5}\left(T_g\right)^{3/10}\left[\left(\alpha_{Ar}\right)^{2/5}\left(\frac{1}{\mu_{Ar-Ar}}\right)^{3/10}N_{Ar}+\left(\alpha_{He}\right)^{2/5}\left(\frac{1}{\mu_{Ar-He}}\right)^{3/10}N_{He}\right]$$

χ_{Ar} and χ_{He} the volumen fraction in per cent

$$w_W(603.2\text{nm}) = \chi_{Ar}\frac{4.217}{T_g^{0.7}} + \chi_{He}\frac{3.019}{T_g^{0.7}}$$



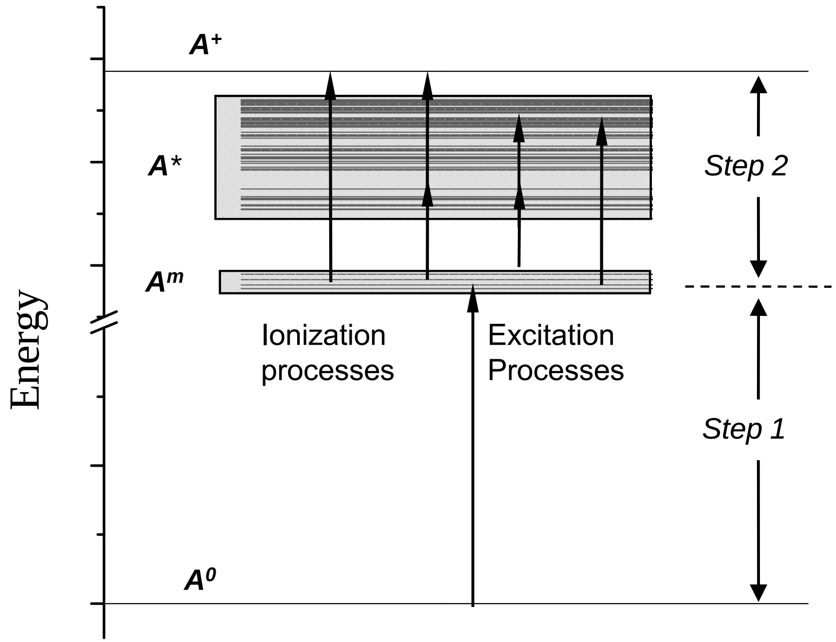


- Gas temperature values from OH radical have only a small variation when more than 5% He is in the mixture and from this percentage the temperature remains constant

Plasmas generated with Ar-He

- **Excitation and ionization kinetics: Atmospheric pressure**

  - Kinetics is controlled by collisions with e^-
  - Step-wise processes : the first excited level (metastable) is the departure level for them

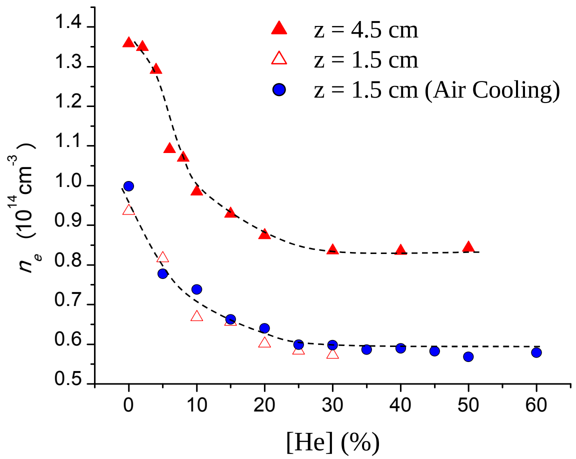


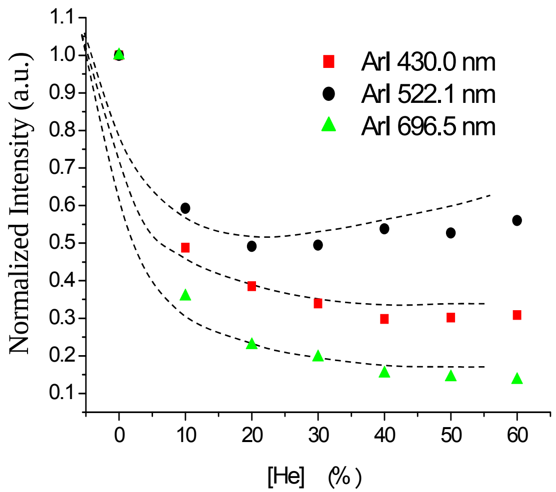
$$A + e^-(f) \rightarrow A^m + e^- \Rightarrow \text{Step 1}$$

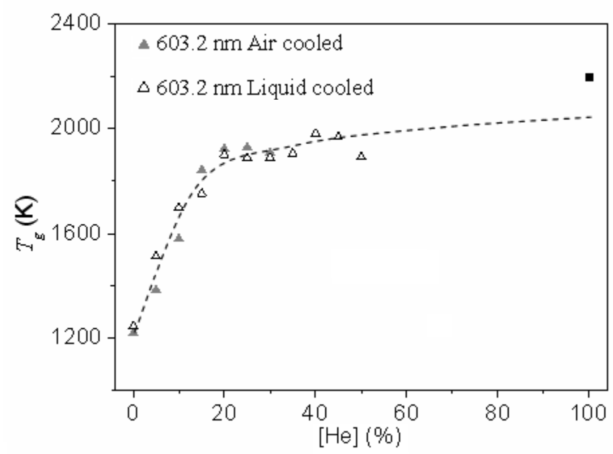
$$A^m + e^- \rightarrow A^* + e^- \Rightarrow \text{Step 2 (excitation)}$$

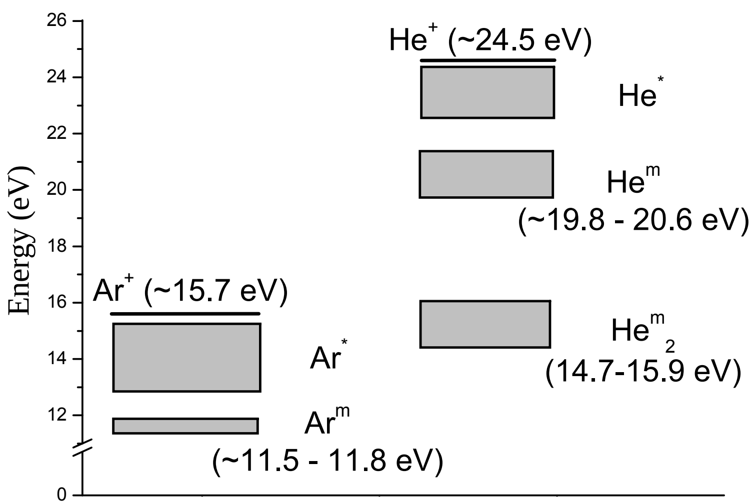
$$A^m + e^- \rightarrow A^+ + e^- \Rightarrow \text{Step 2 (ionization)}$$

Plasmas generated with Ar-He









Ar-He plasma:

1) He < 20-30%: same behaviour for n_e and I (a.u.) ⇒ Ar atoms populated by e$^-$ collisions

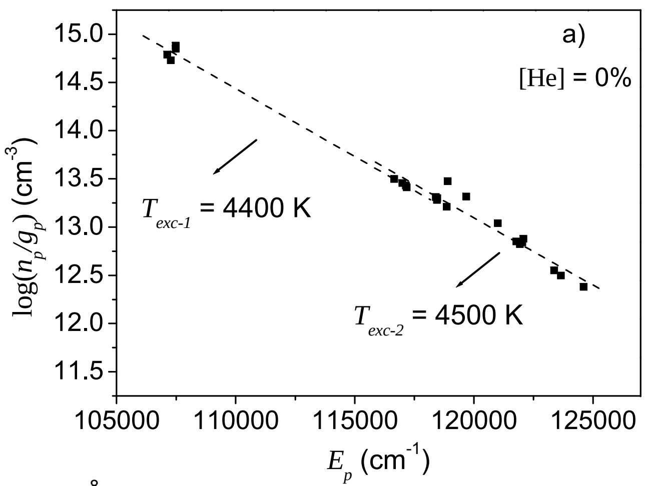
2) He > 30%: different behaviour depending on the level

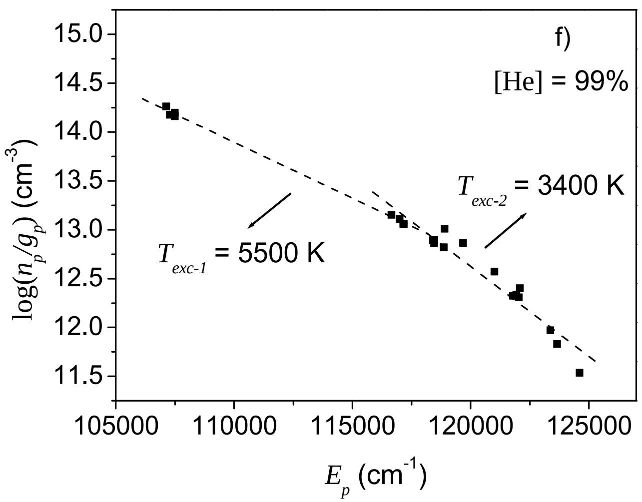
   - Groups 1 and 2 (E_{exc} < 15 eV) ⇒ e$^-$ collisions
   - Group 3 (E_{exc} > 15 eV) ⇒ e$^-$ collisions and He_2^m

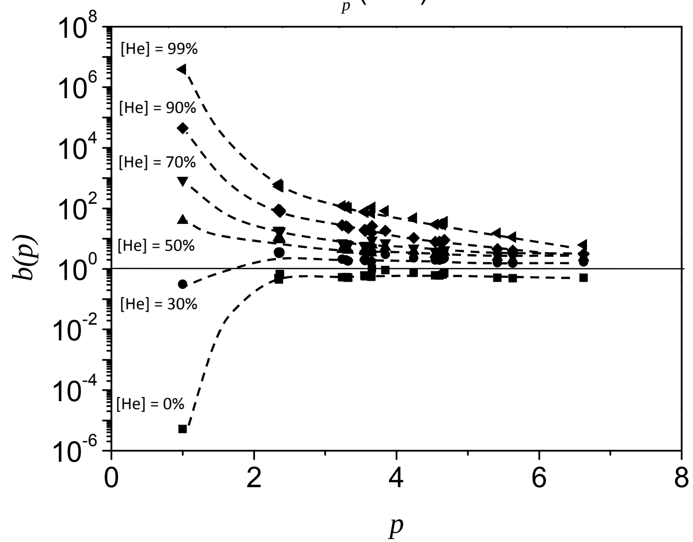
3) [He] ↑ ⇒ ionization of Ar atoms ↑ and direct ionization by He^m ⇒ n_e constant from He 30%

Plasmas generated with Ar-He

Boltzmann-plots of ArI system for different He concentrations







- [He] ↑, $b(p)$ values change in a similar way than the observed one in Boltzmann-plots
- The atoms with the high ionization energy control the excitation mechanisms in the plasma

Plasmas generated with Ar-He

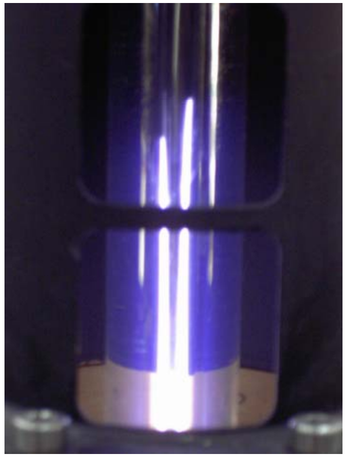
- **Radial contraction** appears for plasmas at pressure higher than 10 Torr and depends on the T_{gas} radial distribution

$\Downarrow$

T_{gas} radial gradient depends on the gas thermal conductivity:

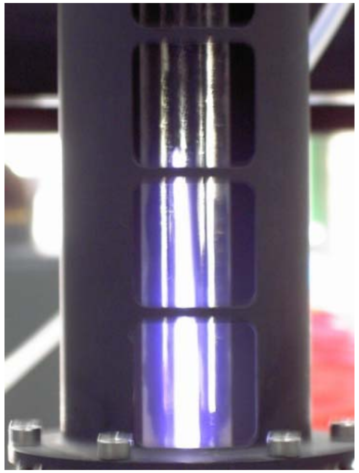
[He] $\uparrow \Rightarrow \kappa \uparrow \Rightarrow$ radial contraction disappears

k (10^{-2} W/mK)	Ar	He
κ (300 K)	1.17	20.6
κ (2000 K)	6.45	82-103



He 0%

He 10%

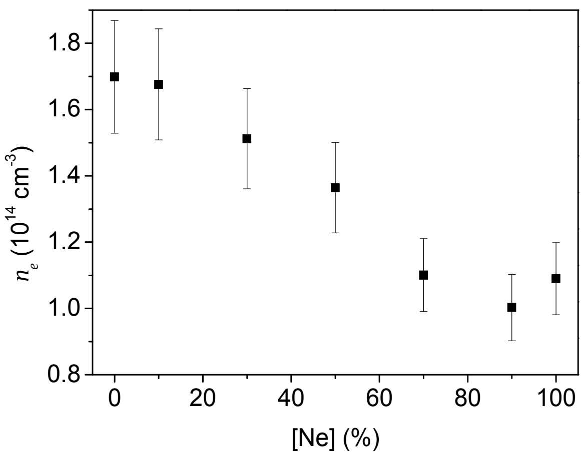


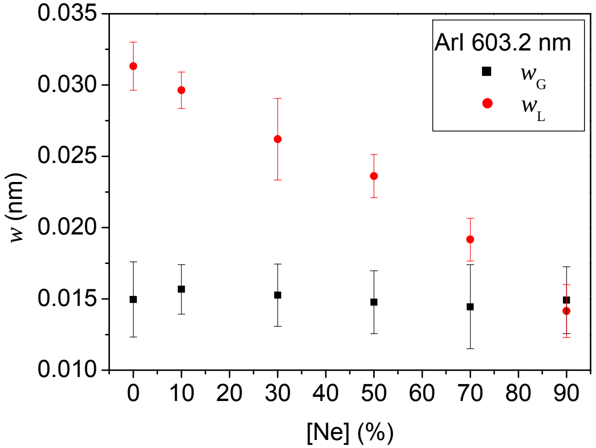
He 20%

Plasmas: Ar-Ne

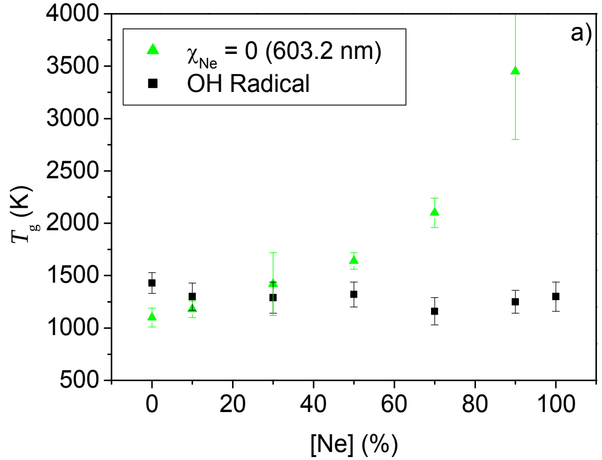
J. Muñoz, M.S. Dimitrijević and M.D. Calzada
Spectrochim. Acta B (submitted)

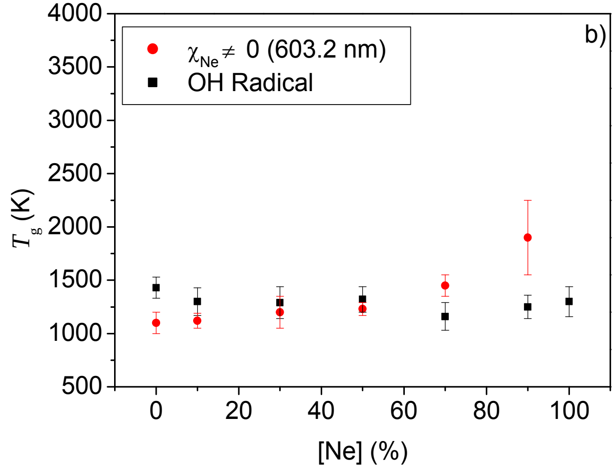
Plasmas generated with Ar-Ne





Gas temperature: $$w_W\left(603.2\ \mathrm{nm}\right)=\chi_{Ar}\frac{4.217}{T_g^{0.7}}+\chi_{Ne}\frac{2.683}{T_g^{0.7}}$$





The results are in agreement with those obtained for Ar-He mixtures

Plasmas: Ar-N_2

J. Muñoz, J. Bravo and M.D. Calzada

The Open Spectros. J. vol.3 (2009)

Plasmas generated with Ar-N_2

- **Reason:**
  Nitrogen (N_2) as a gas in a mixture induces modifications on the surface of metals (Steel), textile fibers and food conservation

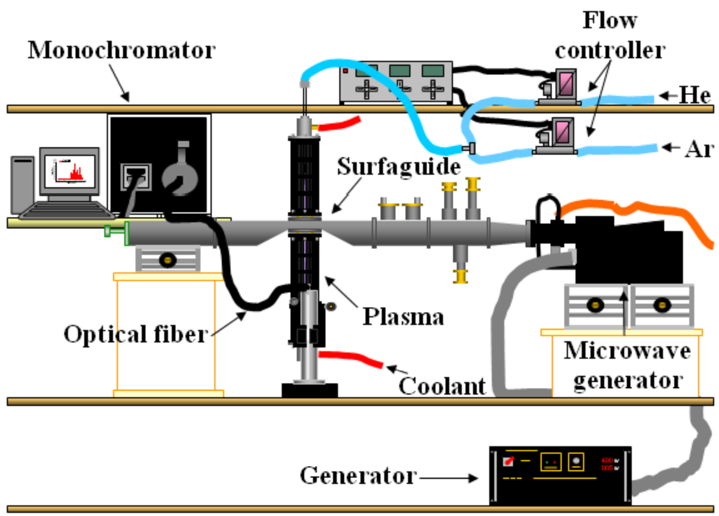
- Pure N_2 plasma needs high power ($\approx$ 1 kW) to be generated together with a cooling system

- Ar-N_2 plasma can be generated with 400 W

Plasmas generated with Ar-N_2

- <u>Experimental system</u>:
  - Power: 100 – 400 W (surfaguide as energy coupler device)
  - Ar-N_2 mixtures up to 10% of N_2 (total flow 2 slm)
  - Jobin-Yvon monochromator (1m focal length and 2400 lines/mm)
    - photomultiplier R928P and shymphony CCD

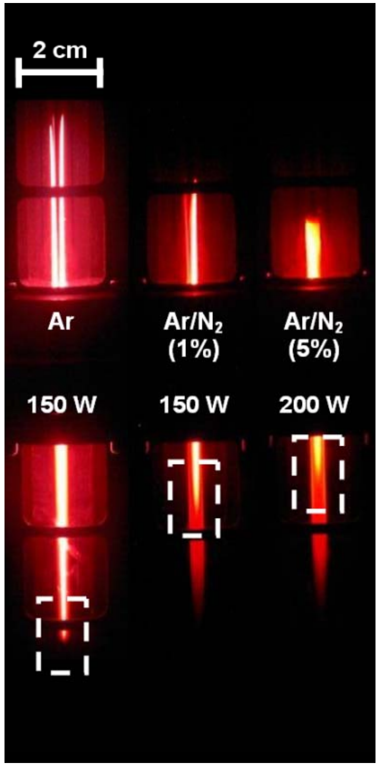
- <u>Plasma parameters:</u>
  - Discharge morphology
  - Linear power density, $\bar{L}$
  - Emitted spectra

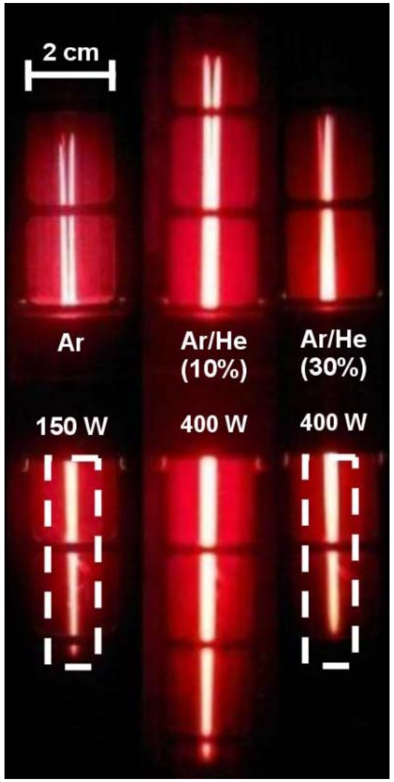


Plasmas generated with $Ar\text{-}N_2$

o Discharge morphology

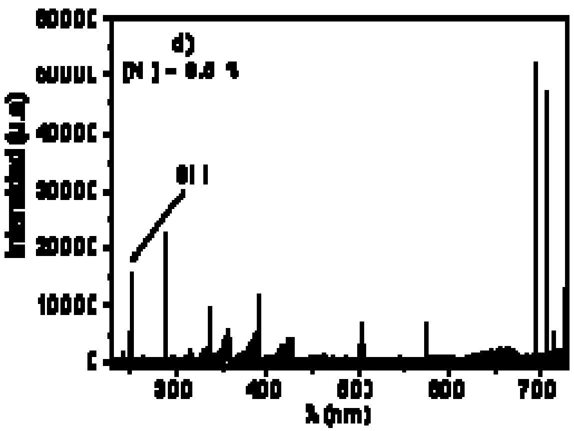
• $Ar\text{-}N_2$ plasma presents changes in the external morphology regarding a pure Ar plasma

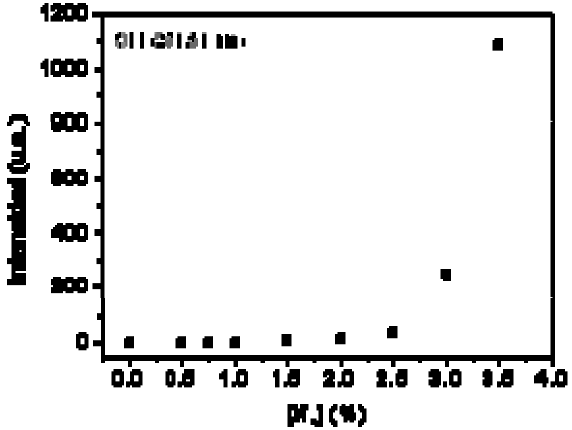




Changes:

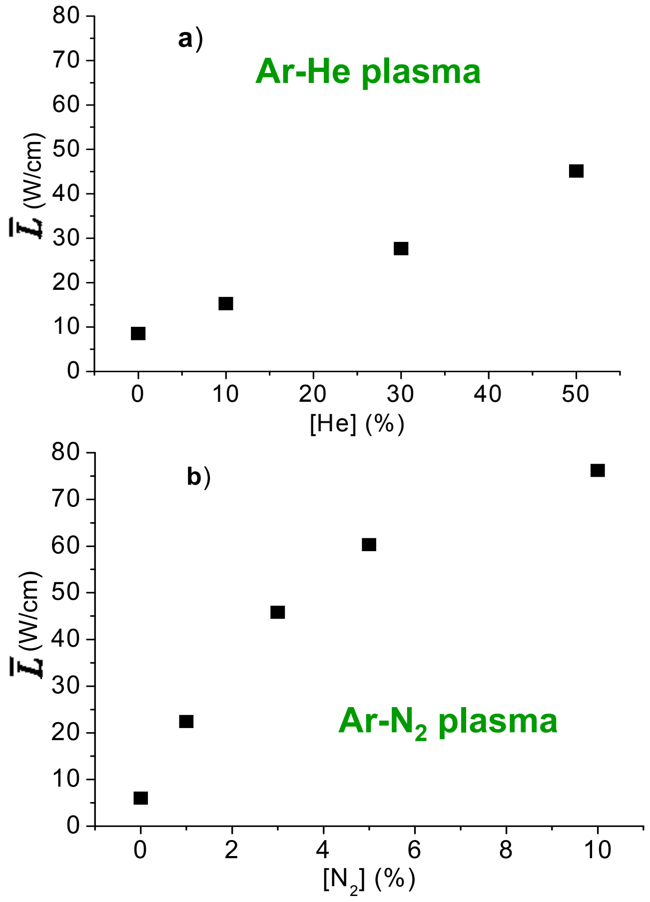
- Shortening of the discharge
- Discharge filamentation disappears and plasma extends towards the tube walls)
- Two areas can be well distinguished:
  - plasma: electrons and active species
  - post-discharge: neutral active species





Plasmas generated with Ar-N_2

o Linear power density $\overline{L}$



$$\overline{L} = \frac{P_{abs}}{l}$$

$P_{abs} \equiv$ absorbed power
$l \equiv$ plasma length

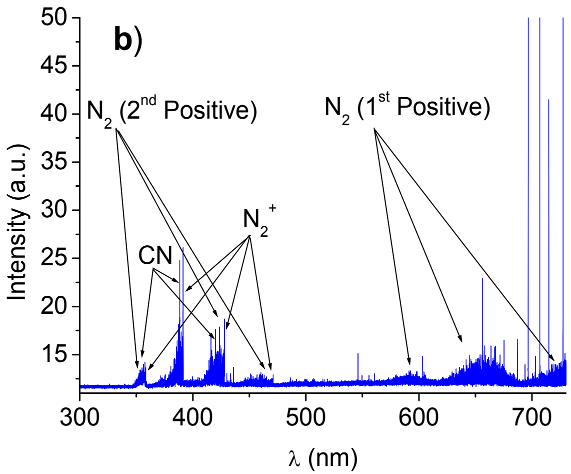
- The N_2 percentage in the plasma gas induces an increase of $\overline{L}$

- The $\overline{L}$ increase is more significant when N_2 is added to plasma gas in comparison to the Ar-He case

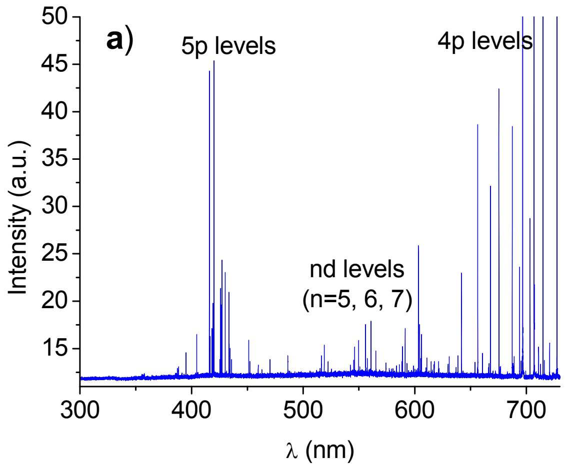
Plasmas generated with Ar-N_2

o Emitted spectra: comparison with Ar-He plasmas

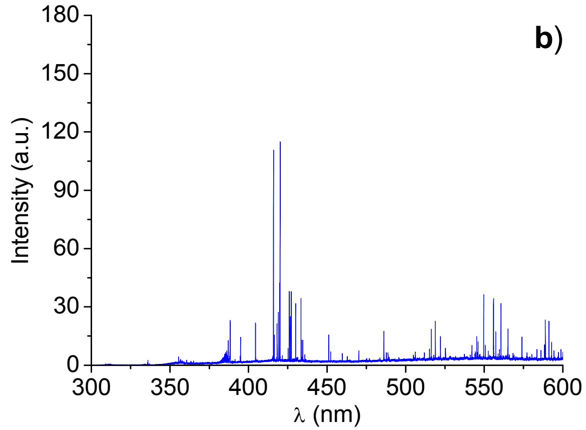
- N_2 at low percentage leads to the apparition of new molecular species
- In Ar-He mixtures only a decrease of Ar line intensities is observed



Ar-N_2 plasma (1% N_2)



Pure Ar plasma



Ar-He plasma (30% He)

$$\mathrm{Ar}\left({}^3\mathrm{P}_0, {}^3\mathrm{P}_2\right) + \mathrm{N}_2\left(\mathrm{X}^2\Sigma_g^+\right) \rightarrow \mathrm{Ar}^0 + \mathrm{N}_2\left(\mathrm{C}^3\Pi_u\right)$$

$$\mathrm{Ar}^+ + \mathrm{N}_2\left(\mathrm{X}^2\Sigma_g^+\right) \rightarrow \mathrm{Ar}^0 + \mathrm{N}_2^+\left(\mathrm{X}^2\Sigma_g^+\right)$$

$$N_2\left(A^3\Sigma_u^+\right) + e^- \rightarrow N_2^+\left(X^2\Sigma_g^+\right) + e^- + e^-$$

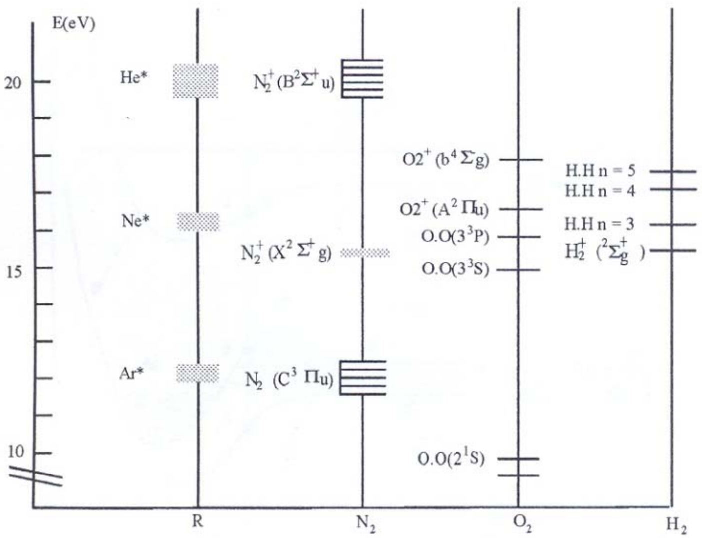
$$N_2\left(B^3\Pi_g\right) + e^- \rightarrow N_2^+\left(X^2\Sigma_g^+\right) + e^- + e^-$$

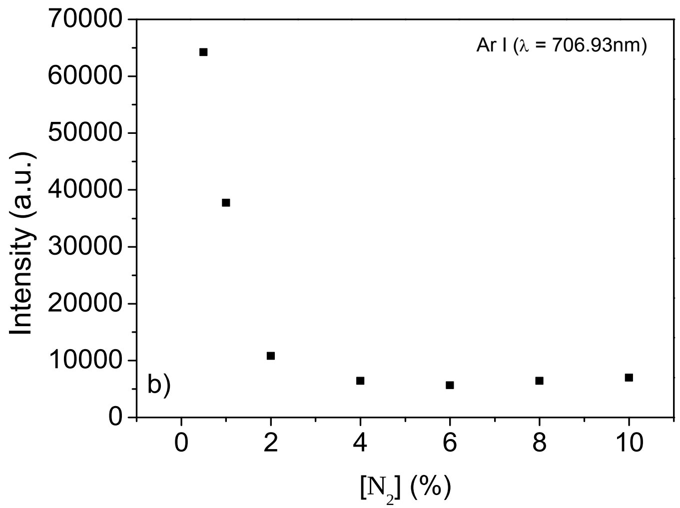
$$N_2\left(C^3\Pi_u\right) + e^- \rightarrow N_2^+\left(X^2\Sigma_g^+\right) + e^- + e^-$$

$$N_2^+\left(X^2\Sigma_g^+\right) + e^- \rightarrow N_2^+\left(B^2\Sigma_u^+\right) + e^-$$

Plasmas generated with Ar-N_2

o Intensities of ArI lines in Ar-N_2 plasmas



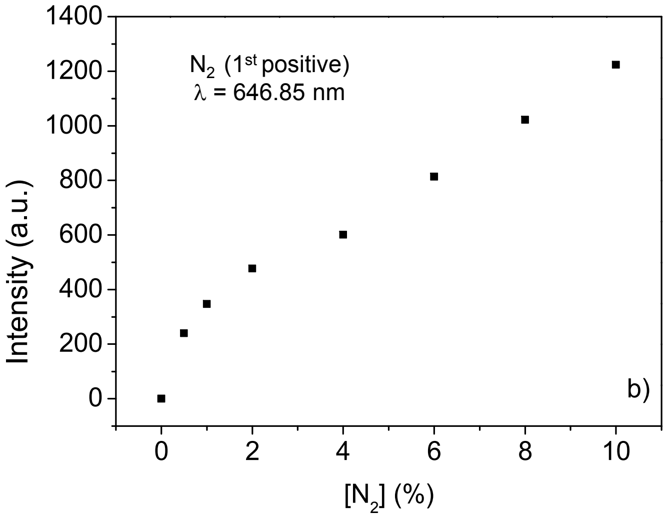


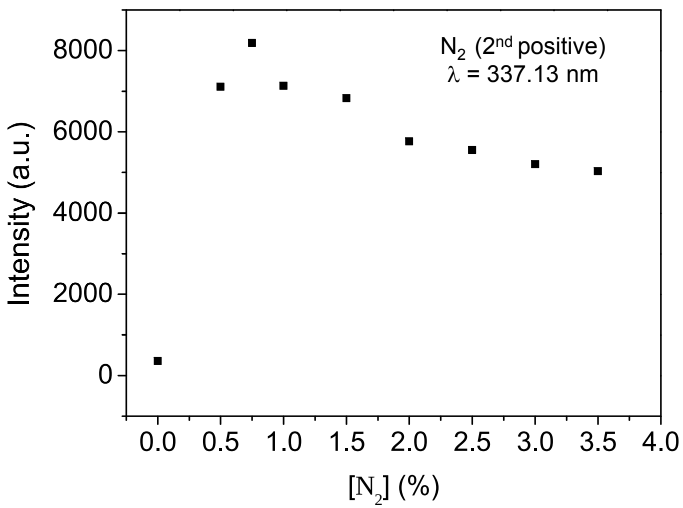
● Excitation Penning: $Ar^m + N_2 \rightarrow Ar + N_2^*$

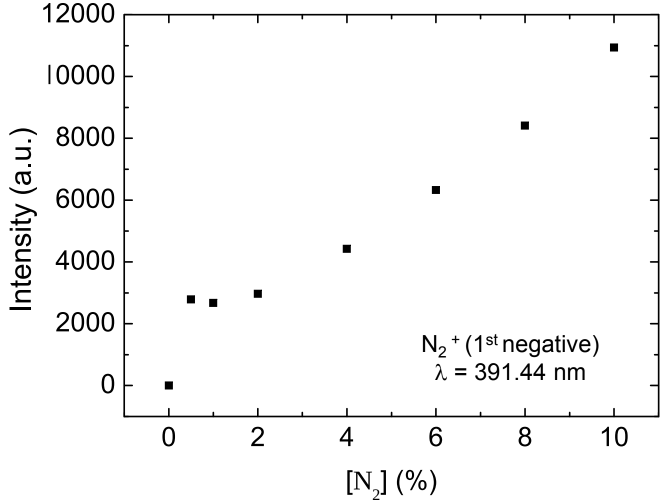
● Decrease of the Ar I line intensities indicates a decrease in the number of metastable Ar atoms

Plasmas generated with Ar-N_2

- Nitrogen molecular bands







1st Positive System

$$N_2\left(B^3\Pi_g\right) \rightarrow N_2\left(A^3\Sigma_u\right)$$

2nd Positive System

$$N_2\left(C^3\Pi_u\right) \rightarrow N_2\left(B^3\Pi_g\right)$$

1st Negative System

$$N_2^+\left(B^2\Sigma_u^+\right) \rightarrow N_2^+\left(X\,^2\Sigma_g^+\right)$$

Plasma generated with gas mixtures at atmospheric pressure

Conclusions:

- **Plasmas generated with gas mixtures of Ar-He, Ar-Ne and Ar-N_2 can be considered as an alternative to pure He, Ne and N_2 plasmas**

- **Theoretical modelisation of these discharges has to be carried out in order to understand their internal kinetics**

Thank you for your attention

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