Characterization of continuous vacuum ultraviolet lamps
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Implication on the study of methane photolysis at Lyman alpha (121.6 nm)

M.-C. GAZEAU[1], Y. BENILAN[1], ET. ES-SEBBAR[1,2], A. JOLLY[1], E. ARZOUMANIAN[1], N. FRAY[1] and H. COTTIN[1]

[1] LISA (*Laboratoire Interuniversitaire des Systèmes atmosphériques*), UMR CNRS 7583, Universités Paris-Est Créteil Val de Marne (UPEC) and Paris Denis Diderot,
CNRS-UMR 7583, IPSL, 61, avenue du Général de Gaulle, 94010 Créteil Cedex, France

[2] King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center (CCRC),Thuwal 23955-6900, Kingdom of Saudi Arabia

I. INTRODUCTION

Context: VUV Photons from gas discharges are efficient sources of electromagnetic radiation for photochemical studies in laboratory and simulations of planetary atmosphere. In such experiments, extensive investigation of the VUV emission as the function of the plasma parameters (photons flux and wavelength dependency) is required.

Objective: we want to increase the photon flux delivered by a H_2/He lamp at Lyman alpha (121.6 nm) by determining the accurate plasma parameters to be used. The effect of addition of rare gas (argon) on the monochromaticity of the lamp is also studied.

Approach: the emission spectrum of the lamp is recorded by a VUV spectrometer. Its photon flux is measured by chemical actinometry using CO_2 gas as an actinometer. The method is based on the temporal measurements of CO density issued from photo-dissociation of CO_2 at Lyman alpha using FTIR spectrometer. The temporal dependence of the CO density is determined by systematic comparison of experimental spectra with synthetic ones using spectroscopic parameters from the GEISA database [1].

II. EXPERIMENTAL

1. VUV source

VUV source
- The plasma is created in a quartz tube (i.d. 8 mm, e.d. 10 mm, length 20 cm) in which the flow of H_2 /He (/Ar) gas mixture is injected.
- The microwave excitation is coupled to the plasma through a McCarrol cavity (Opthos Instruments, Inc.) powered by a microwave generator (SAIREM-2.45 GHz-300W).
- Excited H atoms generated in the plasma are responsible for the VUV emission at Lyman alpha

2. Emission spectrum of the H_2/He(/Ar) microwave discharge lamp:

The lamp is connected to a VUV spectrometer in order to record its VUV emission spectrum (Fig. 1)

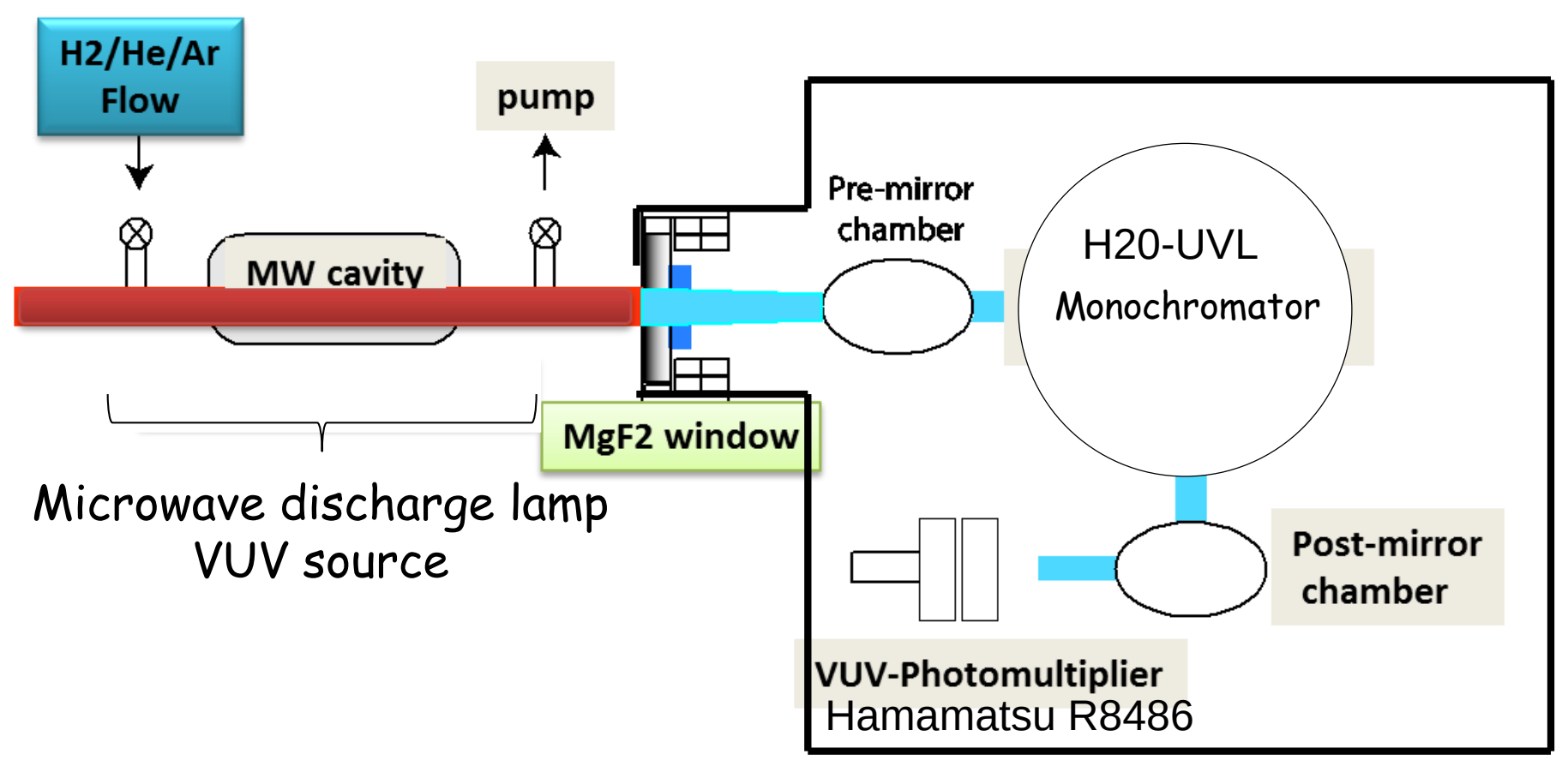

Fig. 1: The experimental arrangement of the microwave plasma source connected to a VUV spectrometer.

3. Photon Flux of the H_2/He(/Ar) microwave discharge lamp (Chemical Actinometry):

The lamp is connected to a multi-reflexion white cell containing CO_2 (Fig. 2).

The CO issued from CO_2 photolysis is monitored by a Fourier Transform Infrared Spectrometer. A spectroscopic model is used to deduce the CO column density [2] (Fig. 3).

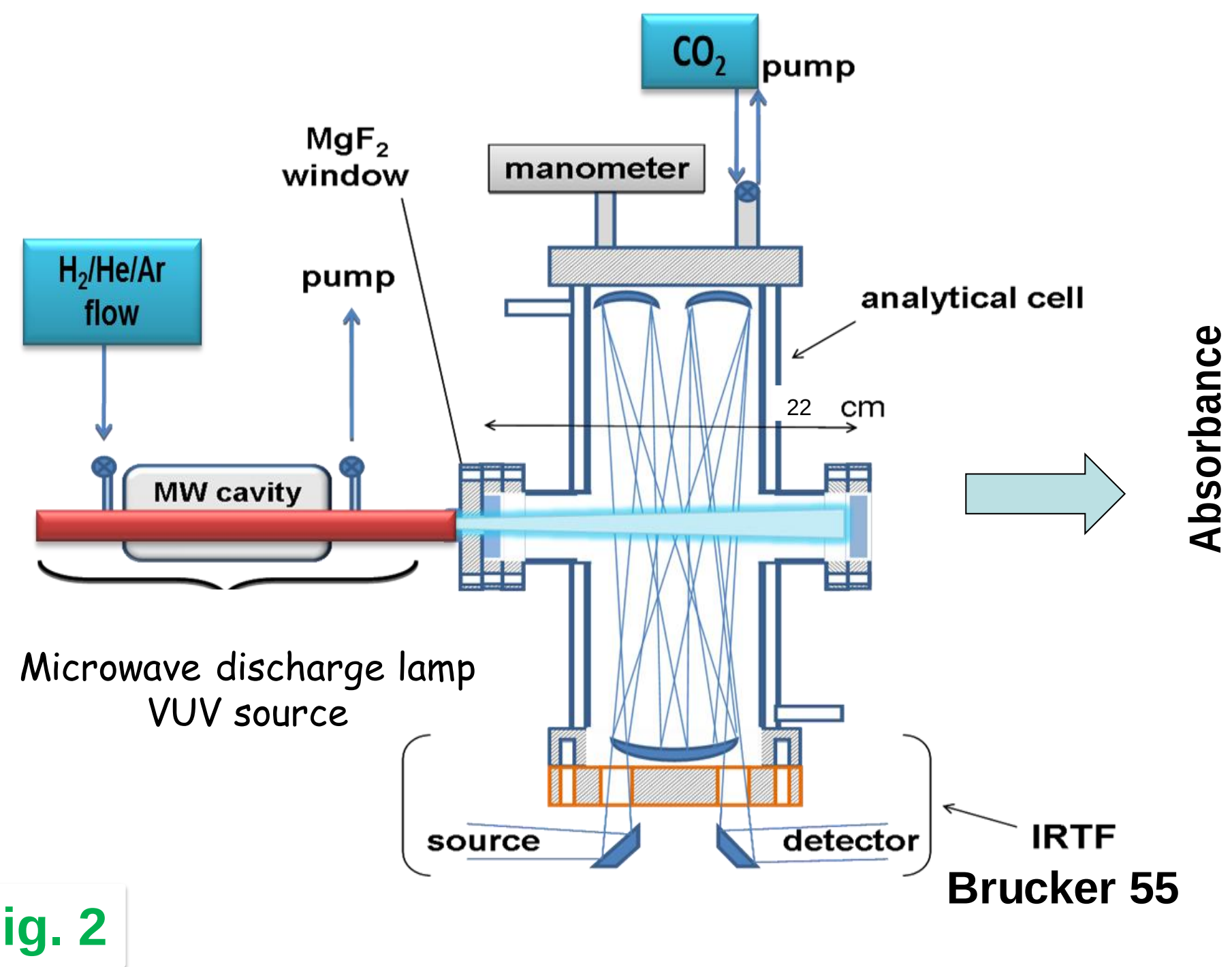

Fig. 2

SETUP to study the photolysis of CO_2 by a microwave discharge lamp.

Volume of the multireflextion white cell : V_{cell}= 2600 cm^3

Optical pathlength = 500 cm

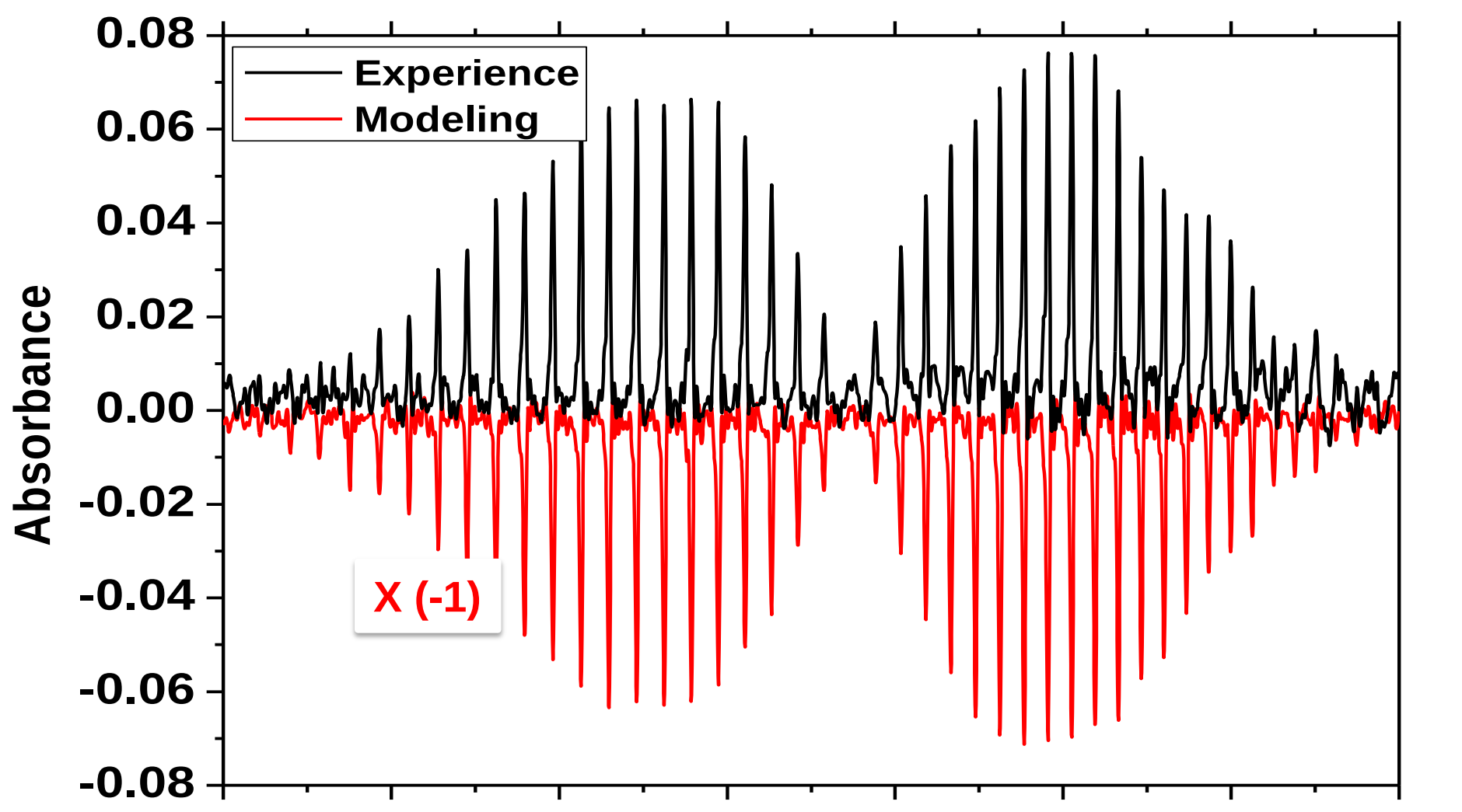

Fig. 3

CO production from CO_2 photolysis monitored in the ~ 2040-2240 cm^{-1} range (spectral resolution: 0.5 cm^{-1}). Comparison between experiment and theoretical data.

The total number of Lyman alpha photons entering the cell per second, $\Phi_{121.6}$, is calculated from the determination of the CO production rate (d[CO]/dt) (Fig. 4) using equation 1:

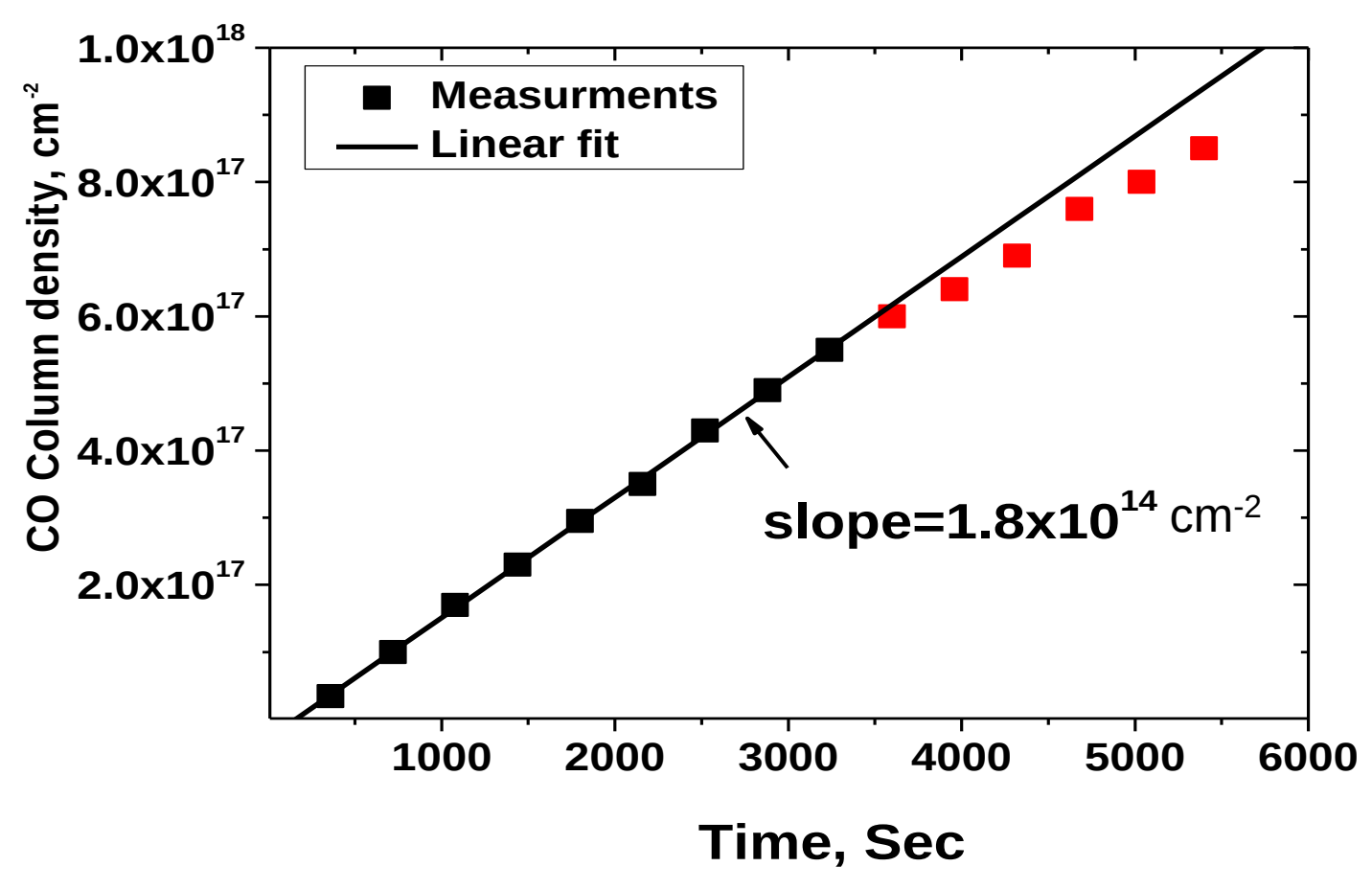

Fig. 4: CO column density as the function of the irradiation time.

$$d[CO]/dt = \Phi_{121.6}.\eta.\beta \quad \text{Eq. 1.}$$

η is the quantum yield of CO production from CO_2 photolysis at 121.6 nm assumed equal unity.
β_{CO2} is the fraction of the absorbed flux by CO_2 which is given by the Beer-Lambert law $\beta_{CO2} = 1 - \exp(-(\sigma_{CO2}.l.p)$ where $\sigma = 1.61\ atm^{-1}cm^{-1}$ is the absorption cross section of CO_2 with value at 121.6 nm taken from [3], l=22 cm is the length of the cell and p is the gas pressure of CO_2 (4 Torr).

$d[CO]/dt = slope \times V_{cell}/\text{Optical pathlength}$
$= 9.36\ 10^{14}\ s^{-1}$

Using Eq. 1., the flux of photons delivered from the H_2/He discharge lamp is $5.5{\times}10^{15}\ s^{-1}$.

III. RESULTS

1. VUV spectrum of H_2/He microwave discharge lamp, influence of the plasma parameters:

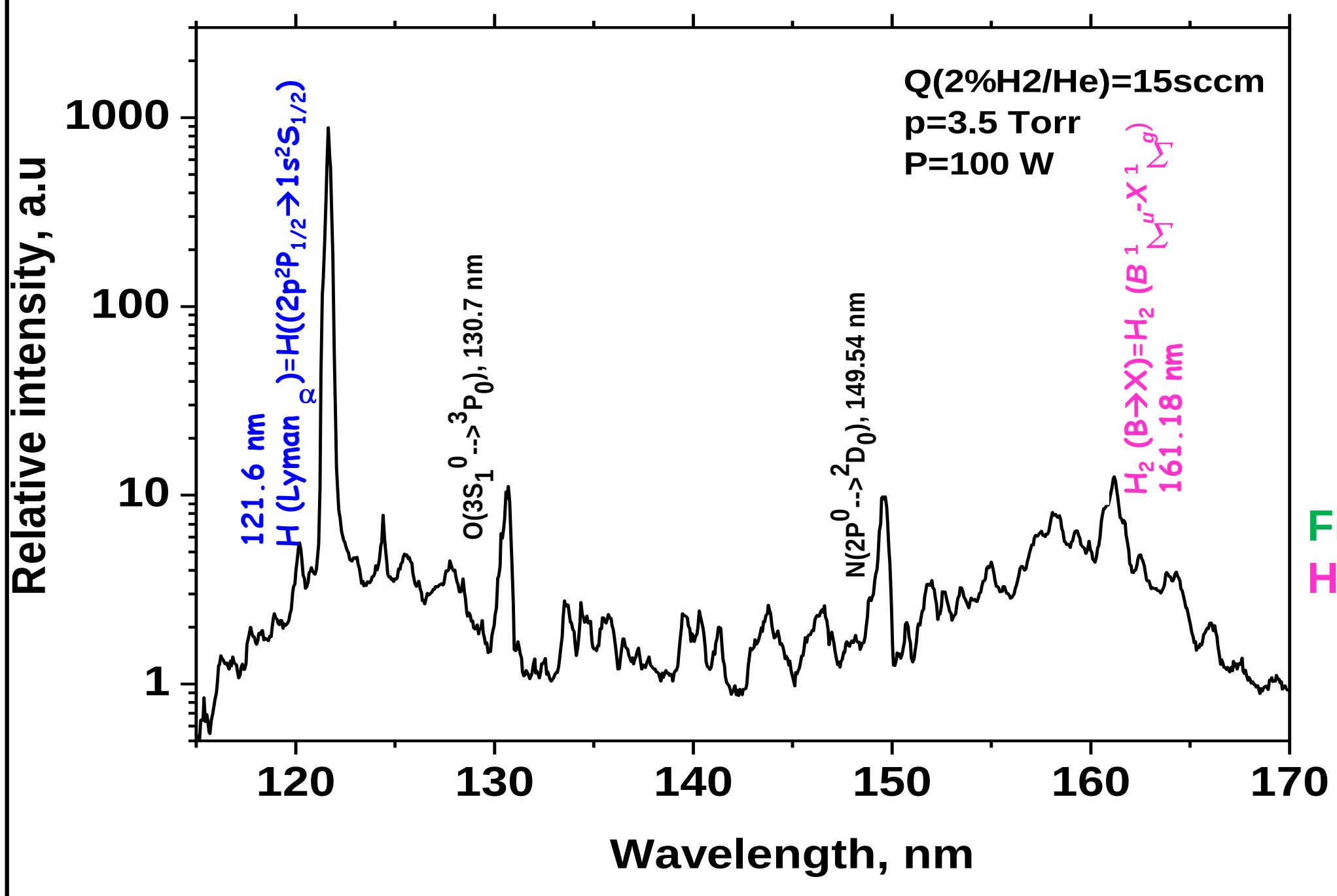

Fig. 5: A typical VUV spectrum between 115 and 170 nm.
The main features emission are identified.
Experimental conditions:
2%H_2/He, p=3.5 Torr, flow rate=15 sccm and P=100 W.

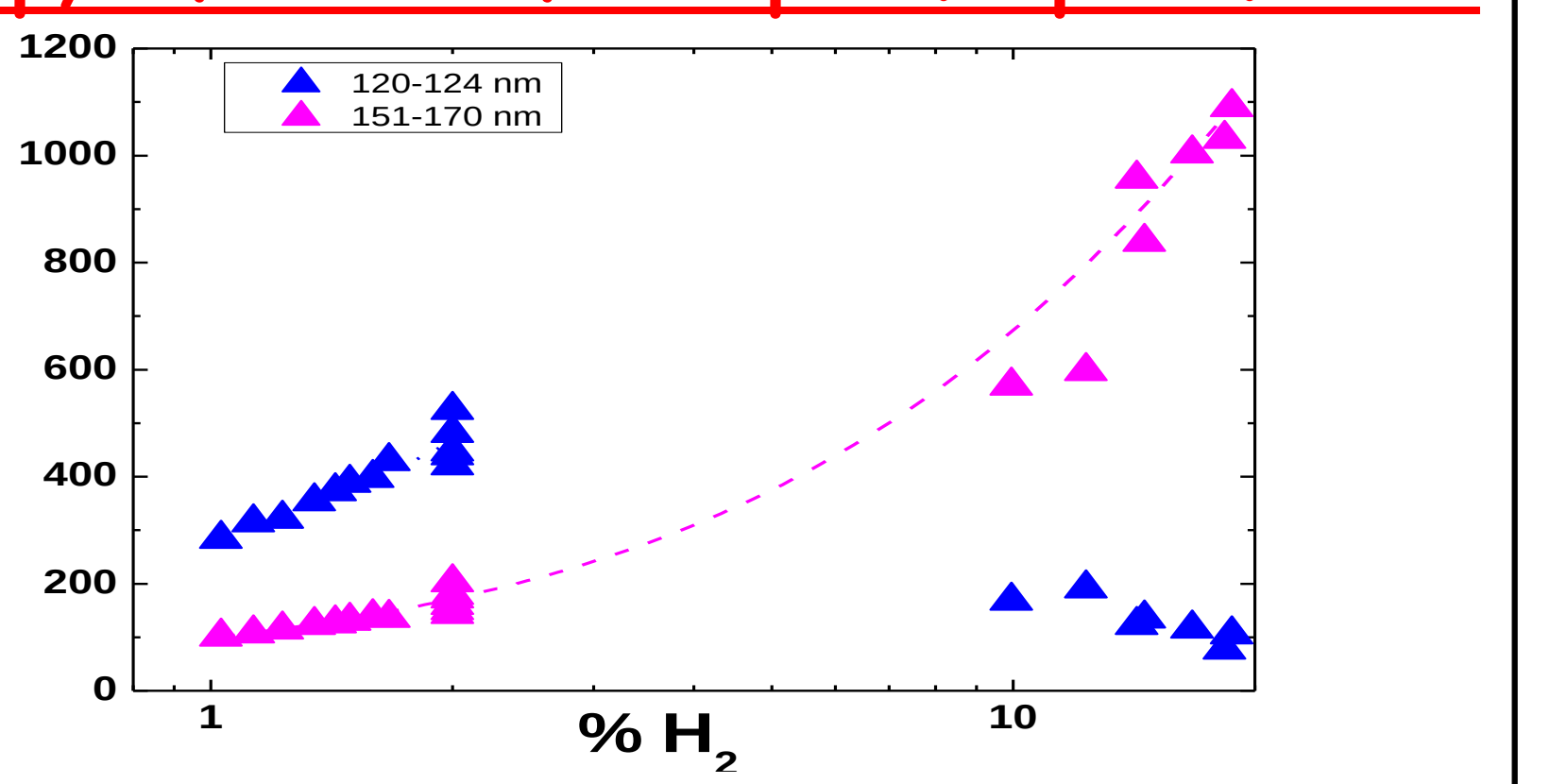

Fig. 6: Dependence of integrated line of H (Lyman α) and H_2 (B→X) with the % H_2 in He. p= 3.5 Torr and P=100 W.

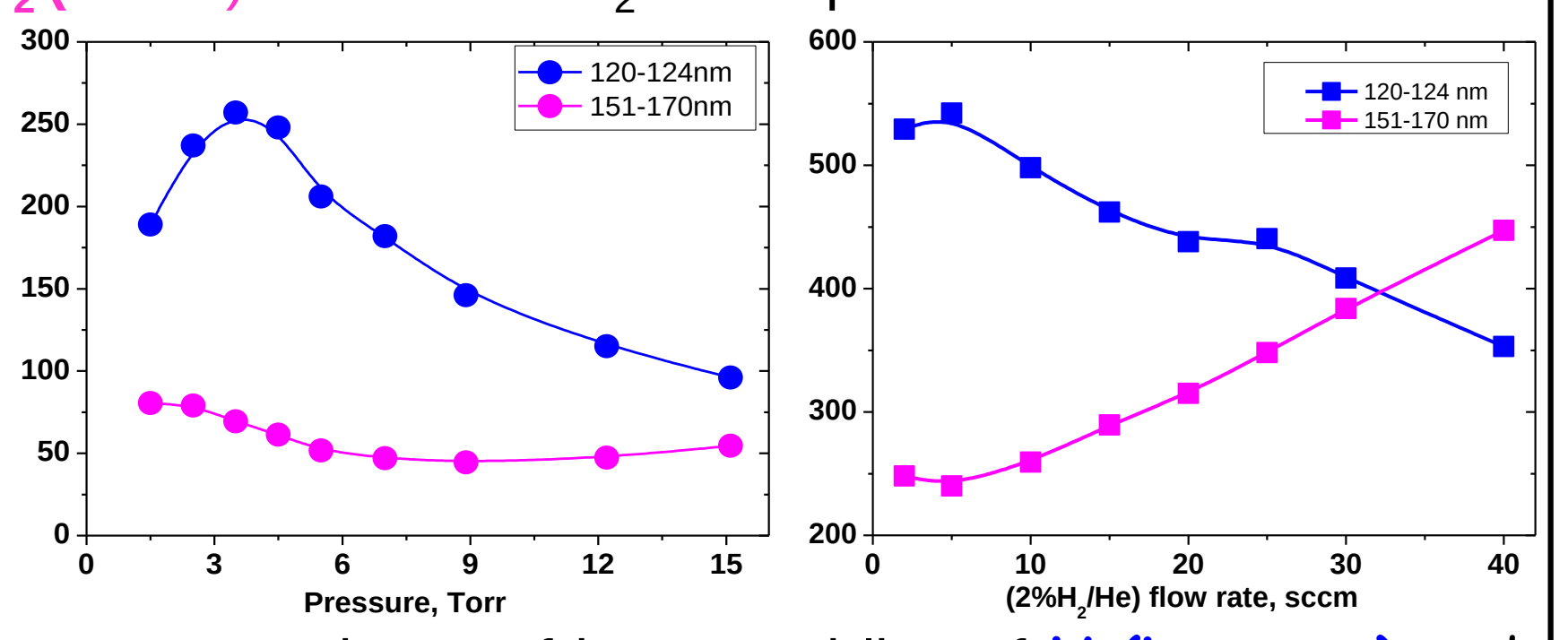

Fig. 7: Dependence of integrated line of H (Lyman α) and H_2 (B→X) with the gas pressure (left panel) and flow rate (right panel). 2% H_2/He and P=100 W.

The intensity of the H (Lyman α) emission line is optimized within plasma conditions (P=100W): ~ 2-5% H_2 in He, p = 3.5 Torr, flow rate ~ 5-10 sccm)

2. H(Lyman α)/H_2(B →X) emission, effect of the addition of Ar in the H_2/He mixture:

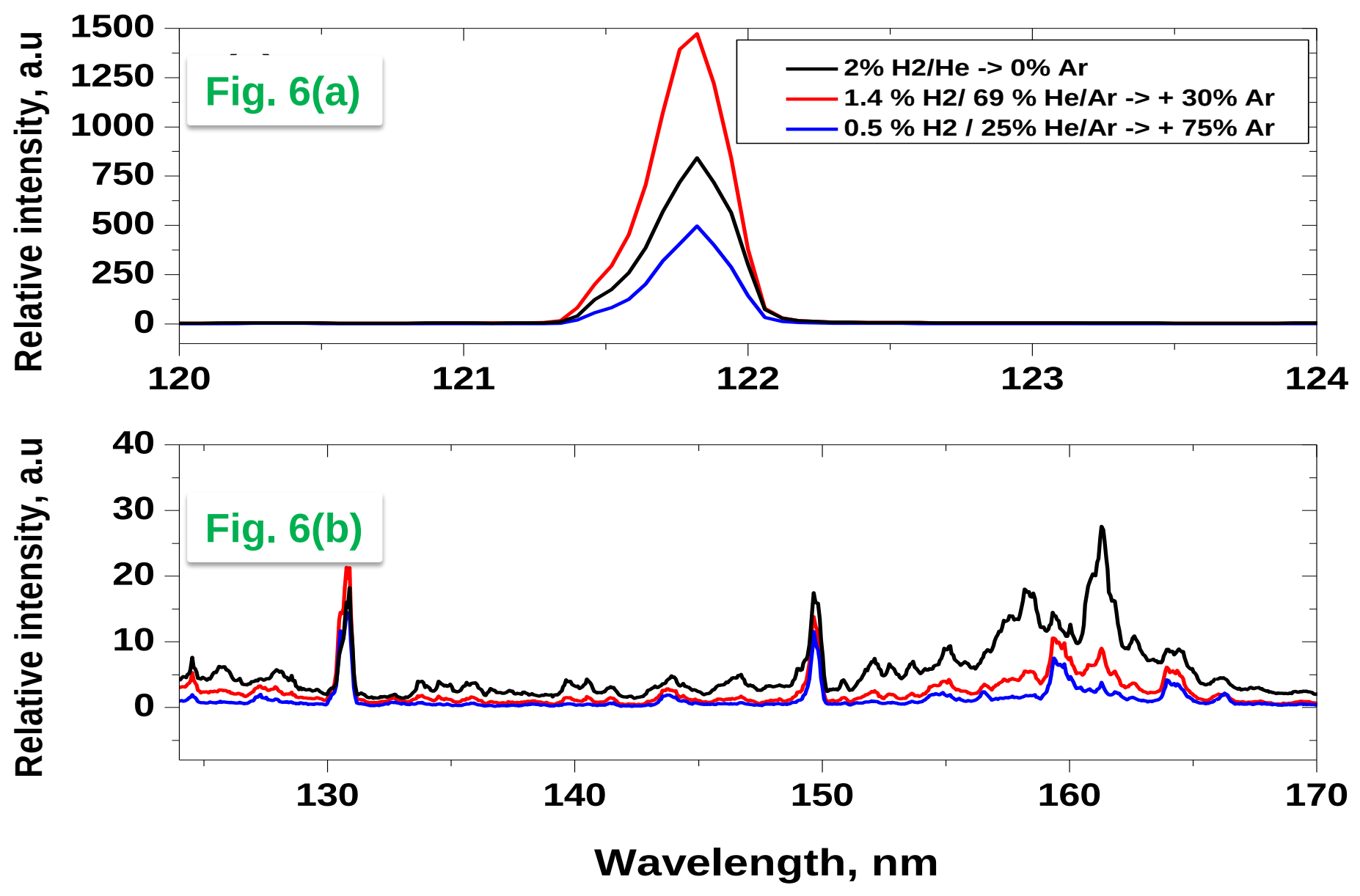

Fig. 6: VUV line emission in the range (a) 120-124 nm and (b) 124-170 nm as a function of the Ar addition in H_2/He.

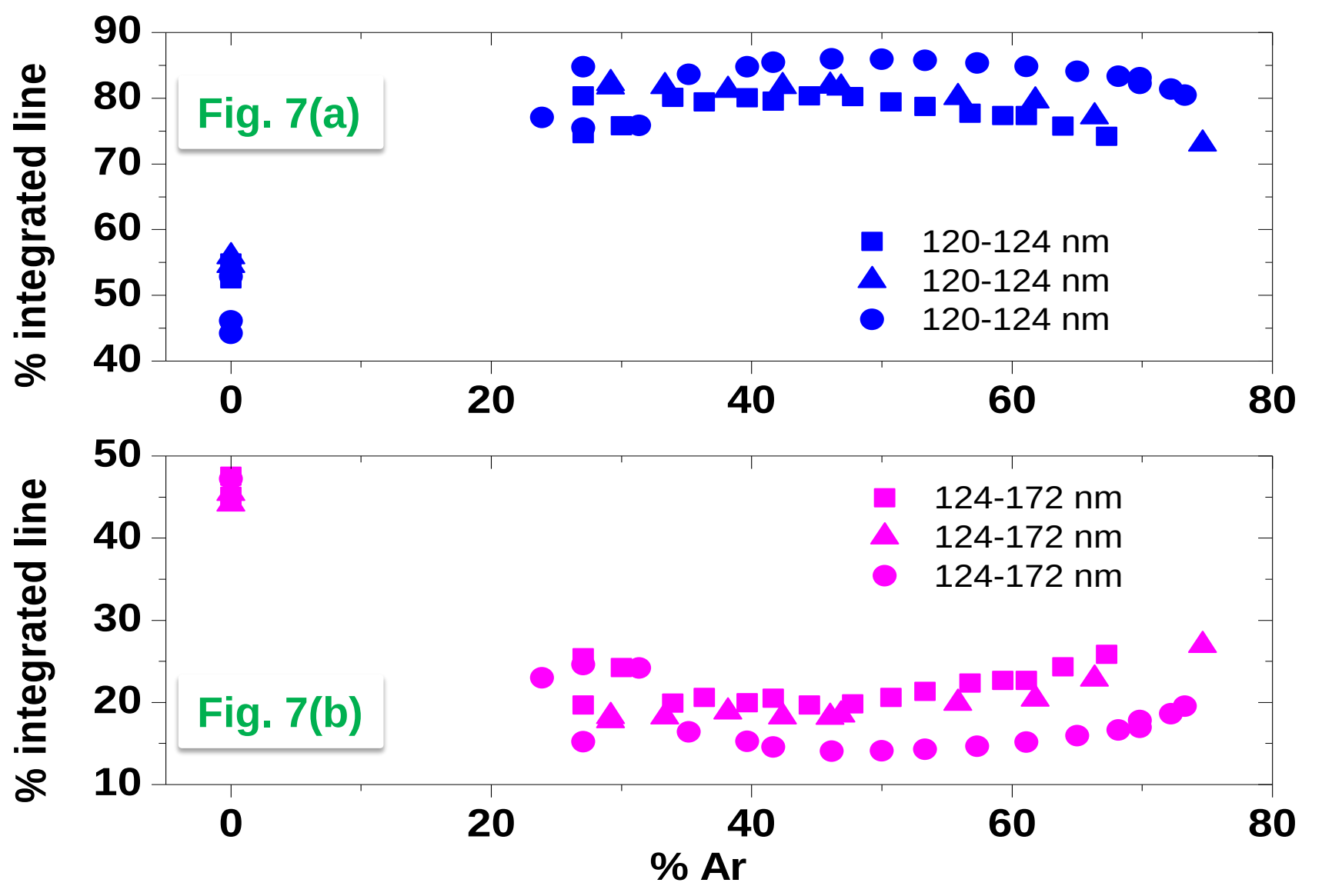

Fig. 7: integrated line intensity of (a) H (Lα) and (b) H_2(B →X) *as a function of %Ar added in H_2/He.*
(Three series of measurements in the same plasma conditions)

The addition of Ar in the H_2/He gas mixture induces a maximum increase of the H (Lyman α) line intensity of 80% relative to the total emission flux.

Indeed, H atoms in the excited state are generated through energy transfer collisions between $Ar(^3P_2)$ metastable and H_2: $Ar(^3P_2) + H_2 \rightarrow Ar + H + H$ and $Ar(^3P_2) + H_2 \rightarrow ArH^* + H$; In parallel, $Ar^+ + H_2 \rightarrow ArH^+ + H$
Therefore, H (Lyman α) emission is enhanced through:
$Ar(^3P_2) + H \rightarrow ArH^* \rightarrow ArH^* + H\ (n=2)$
$H\ (n=2) \rightarrow H\ (n=1) + (\text{Lyman } \alpha = 121.6\ nm)$
For high Ar amount added, the H (Lyman α) intensity drops and the $H_2(B \rightarrow X)$ intensity increases due to quenching of $Ar(^3P_2)$ metastable by H_2.

3. Photon Flux at Lyman alpha (121.6 nm)

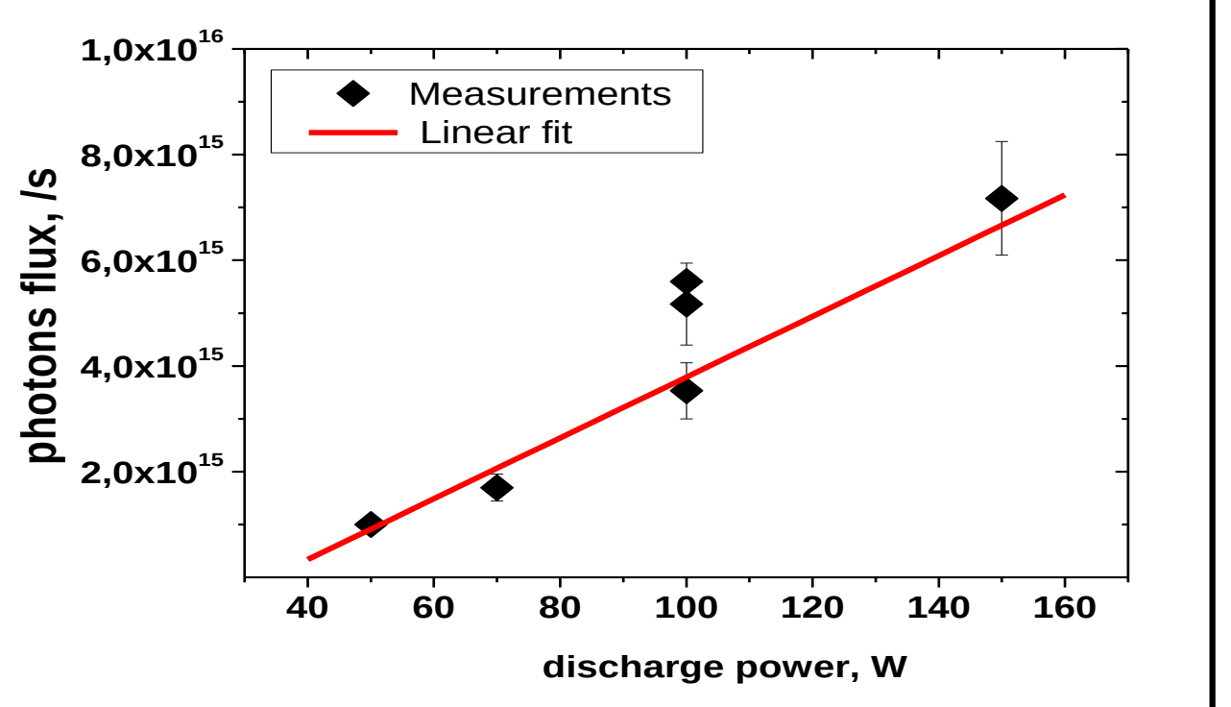

Fig. 8: Dependence of the photon flux on the discharge power.
The experimental conditions are: flow rate=15 sccm, 2% H_2/He+30%Ar, p=3.5 Torr.
The photon flux was determined through Eq. 1.

4. CH_4 Photolysis at Lyman alpha (121.6 nm)

Methane photolysis at Lyman alpha is studied in the frame of a program dedicated to simulations of Titan's atmosphere [2]. Irradiations have been performed using a microwave He/H_2 (98/2) discharge lamp. The chemical evolution of the gas mixture resulting from the irradiations is monitored by FTIR. The determination of the chemical mechanism involved requires the comparison with a dedicated 0D kinetic model in which photolysis rates are fundamental parameters. Their values depend on the emission spectrum of the source.

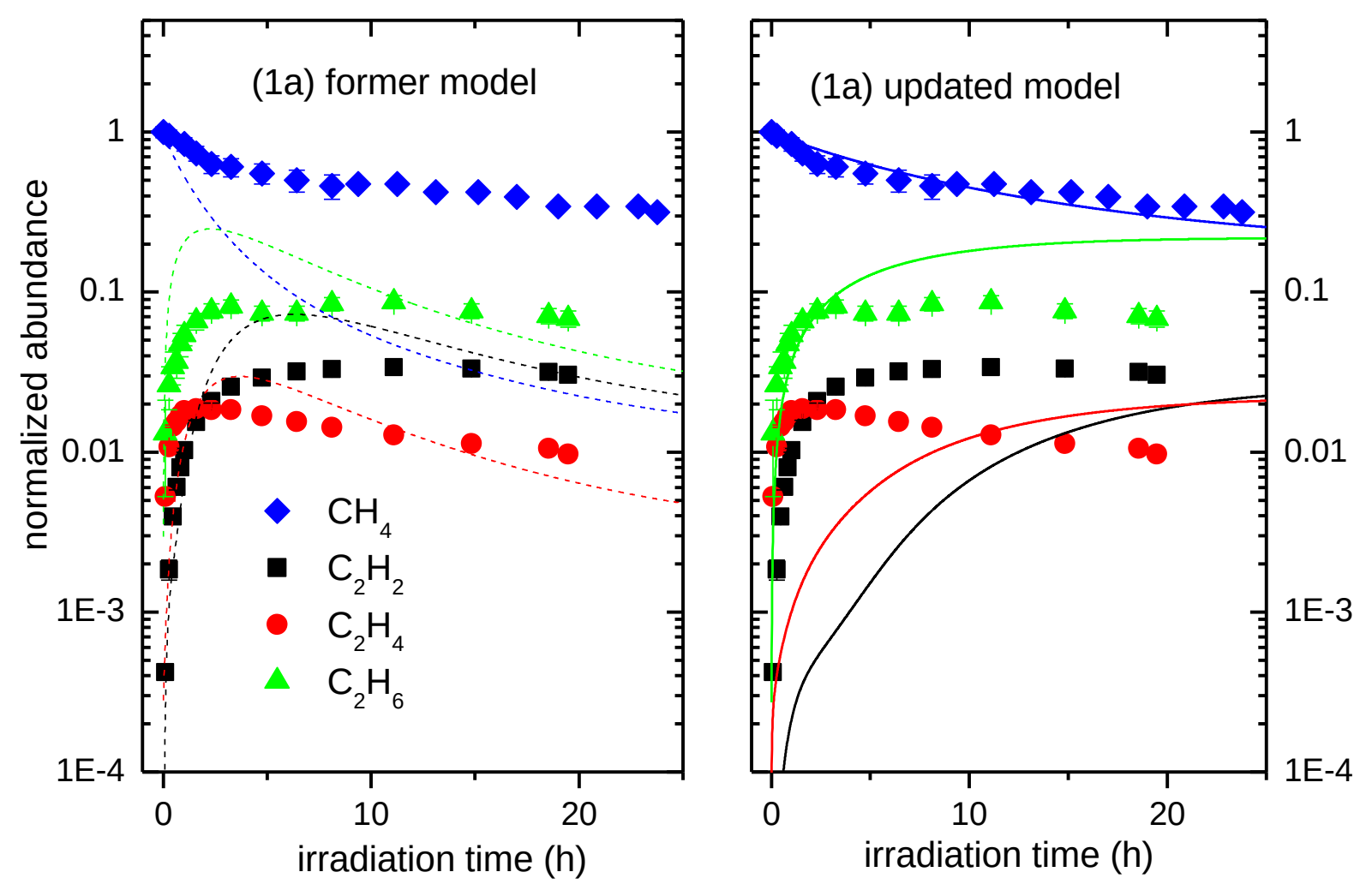

Fig. 9: Comparison between experimental abundances and calculated abundances obtained with the former model (left panel), and the improved model (right panel).

In a former model [2], the comparison of experimental and theoretical results was not entirely satisfactory since the destruction of methane was overestimated by the model as well as the production of ethane.

Recently, the fact that lamp is not monochromatic at Lyman α, as shown above, has been taken into account.
In the updated model, new values for the photon flux, $\Phi_{120-180}$ and the photolysis rates, $J^{A}_{120-180}$, have been used since CO_2 as well as CH_4 and C2 compounds absorb in the emission domain of the lamp (120-180 nm) :

$$d[CO]/dt = \int_{120}^{180} \Phi_\lambda.\eta.\beta\, d\lambda \qquad \Phi_{120-180} = \int_{120}^{180} \Phi_\lambda\, d\lambda$$

and $J^{CH4}_{120-180} = \int_{120}^{180} (\sigma^{CH4}_\lambda.\eta^{CH4}_\lambda.\Phi_\lambda / S)\, d\lambda$ S: irradiated surface (cm^2)

This improvement allows a better agreement between experimental and theoretical data concerning CH_4 and C_2H_6. Reliable comparison can only be achieved when the irradiation source is well characterised in terms of flux and wavelength dependency.

Acknowledgment

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