

# H ATOM DENSITY MEASUREMENTS IN A H<sub>2</sub> MICROWAVE DISCHARGE.

L. Tomasini, A. Rousseau, G. Gousset, P. Leprince

Laboratoire de Physique des Gaz et des Plasmas, Bat. 212, Université Paris-Sud,  
91405 ORSAY Cedex, France

We discuss the validity of optical emission spectroscopy (actinometry) as a valuable diagnostics for H atom density measurements in a non homogeneous microwave plasma column. A self consistent modeling of the discharge exhibits the strong influence of the first excited state of the H atoms on the whole discharge equilibrium, and particularly on the actinometric signal. Numerical calculations are used to determine experimental H atom density along the plasma column in a pulsed microwave discharge.

## Introduction.

The aim of actinometry is to deduce the unknown density [H] of a species (here H) from the ratio  $I(H)/I(Ar)$ . In this work,  $I(H)$  and  $I(Ar)$  correspond to the transitions  $H: n=3 \rightarrow n=2$  (656.3 nm) and  $Ar: 4p \rightarrow 4s$  (811,5 nm) respectively. This can be put:

$$[H]=f(I(H)/I(Ar))$$

Classical actinometry assumes a simple proportionality between [H] and the actinometric signal  $I(H)/I(Ar)$  [1]. Actually, the determination of  $f$  requires the knowledge of the electron distribution function as well as the various excitations/deexcitations processes of the excited states of both hydrogen and argon atoms.

For this, we have developed a modeling of the discharge, that couples self-consistently the electron kinetics, the positive ions kinetics ( $H^+$ ,  $H_2^+$ ,  $H_3^+$ ), the vibration kinetics of the ground state of  $H_2$  (14 levels) [2], the molecular kinetics (14 levels), and the atom kinetics. The discharge model, except the excited H atoms kinetics, is described in [3], so that we only recall the main points.

## Principle of the discharge modeling.

The radial transport and continuity equations for the charged particles are coupled to the atom and molecule kinetics. Input parameters are experimental data: discharge tube radius  $a$ , gas pressure  $p$ , electron density  $n_e$ , and gas temperature  $T_g$ . Moreover, the H

atom surface recombination probability  $\gamma$  is not wellknown and is considered as an adjustable parameter. The solution of the equations describing the discharge gives:

- the electric field required to sustain a steady state discharge,  $E_{\text{eff}}$  (termed effective field), that is compared to the experimental value.
- the concentration of the ions ( $H^+$ ,  $H_2^+$ ,  $H_3^+$ ,  $H^-$ ).
- the concentration of the excited levels of both H and  $H_2$ .

### Kinetics of the excited levels of the H atoms.

Under our experimental conditions, dissociation degree up to 65 % can be obtained, so that the excited states populations of the H atoms must be consistently calculated by the model. Excited states from  $n=2$  to  $n=5$  are taken into account. For  $n=2$ , the metastable state  $2s$  and the radiative state  $2p$  are separately considered. Processes taken into account in the rate balance equations are:

- electron impact excitation and superelastic deexcitation.



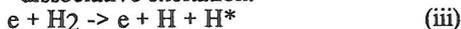
where  $H^*$  and  $H^{**}$  are two different states of the H atom (including the ground state).

- radiative decay.



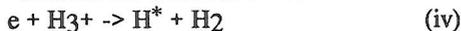
with  $A\Lambda$  being the transition frequency, where  $A$  is the spontaneous emission probability for the transition and  $\Lambda$  is the escape factor calculated as described in [4].

- dissociative excitation.

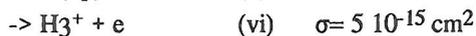


this reaction happens to be negligible for  $n \geq 3$ , under our discharge conditions since the atomic molar ratio  $X_H$  is always greater than 5% [5].

- electron-ion dissociative recombination



- Quenching of metastable H atoms by molecules [6].



This last reaction (vi) called associative ionisation has a considerable influence on the discharge equilibrium since it creates the molecular ion  $H_3^+$  from the H atom, as discussed below.

## Ion kinetics; influence of the associative ionisation on the discharge equilibrium and on the actinometric signal.

Three types of positive ions co-exist in H<sub>2</sub> discharges: H<sup>+</sup>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup>.

The atomic ion H<sup>+</sup> is created through the reaction:  $e + H^* \rightarrow e + e + H^+$

The molecular ion H<sub>2</sub><sup>+</sup> is created through the reaction:  $e + H_2 \rightarrow e + e + H_2^+$

The molecular ion H<sub>3</sub><sup>+</sup> is created either by the reaction:  $H_2^+ + H_2 \rightarrow H_3^+ + H$

either by associative ionisation (vi).

If associative ionisation is not considered, calculations show that H<sup>+</sup> increases with atomic molar ratio X<sub>H</sub>, and so does the calculated effective electric field (due to the weak mass of H<sup>+</sup>), what contradicts experimental results. In the opposite, when associative ionisation (vi) is taken into account, H<sub>3</sub><sup>+</sup> is always the dominating ion, even for high X<sub>H</sub>, due to the very large cross section of (vi). In this case, the experimental and calculated effective fields become in good agreement.

H atoms are created in the plasma bulk, (mainly by electron impact dissociation of the molecules, and partly through the ion kinetics) and are lost by wall recombination with the probability  $\gamma$  (calculations show that volume recombination is negligible under our pressure and temperature conditions).  $\gamma$  is a variable input parameter. Figure (1) presents the influence of  $\gamma$  on the H atom molar ratio X<sub>H</sub> for typical experimental conditions ( $n_e = 2 \cdot 10^{12} \text{cm}^{-3}$ ,  $T_g = 1500 \text{ K}$ ,  $p = 1 \text{ torr}$ ).

Figure (2) presents the calculated reduced effective electric field  $E_{\text{eff}}/N$  as a function of [H], for  $n_e = 2 \cdot 10^{12} \text{cm}^{-3}$ ,  $T_g = 1500 \text{ K}$  and  $p = 1 \text{ torr}$ .

Figure (3) presents the calculated actinometric signal as a function of [H]. The curve is not linear at all except for low dissociation degree where classical relative actinometry remains still valid. For high dissociation degree, the excited states of H (especially the  $n=2$  state) play a key role in the non linearity of the actinometric signal with respect to the H atom density. Such a result can be applied to the determination of the H atom density axial profile in a pulsed hydrogen plasma column.

### Application to experiment.

The experimental set up is extensively described in [5,7]. The microwave plasma is created in a quartz tube (inner diameter  $2a = 8 \text{ mm}$ ), via a surfaguide; the gas pressure is  $p = 133 \text{ Pa}$ , the gas flow rate is equal to  $5 \text{ sccm}$ , 10 % argon is added. The pulsed power is  $P_{\text{max}} = 750 \text{ W}$ , the pulse duration  $t = 10 \text{ ms}$ , and the periode of the cycle is  $50 \text{ ms}$ . A minimum power  $P_{\text{min}} = 250 \text{ W}$  is applied between two pulses in order that the plasma switches on. Time resolved electron density measurements are performed using microwave interferometry. A Boxcar averager opens a gate  $1 \text{ ms}$  before the end of the

pulse, when the plasma column has reached a steady state. At the same time, the ratio  $I(H)$  and  $I(Ar)$  are recorded with a digital oscilloscope. Temperature measurements are described in [8].

The plasma column is sustained by a surface wave so that the electron density decreases from the surfaguide to the end of the plasma. For a given axial position, values of the electron density and of the gas temperature are experimentally determined, and then used as input parameters of the model. With the recombination  $\gamma$  varying as a parameter, one can deduce the H atom density by comparing the calculated and the experimental values of  $I(H)/I(Ar)$ . Figure (4) presents the axial profile of the experimental ratio  $I(H)/I(Ar)$  with the H atom density deduced.

The main point is that from  $z=3,5$  cm to  $z=17,5$  cm from the surfaguide,  $I(H)/I(Ar)$  is multiplied by about 5, when  $[H]$  is only multiplied by less than 2! This is an example of the errors that classical actinometry can lead to when using a simple proportionality function for high H atom molar ratio.

## Conclusion

Optical emission spectroscopy is powerfull and easy to implement diagnostic. However, the relation between the actinometric signal and the H atom density is no longer proportionnal as soon as the H atom density exceeds few tenths. This seems to be mainly caused by the complex kinetics of excited states of H and especially by the  $n=2$  state, whose ratio  $H(n=2)/n_e$  can be as high as 1, mainly because of the radiation trapping.

We have also pointed out the influence of the  $n=2$  state on the discharge equilibrium via the associative ionisation.

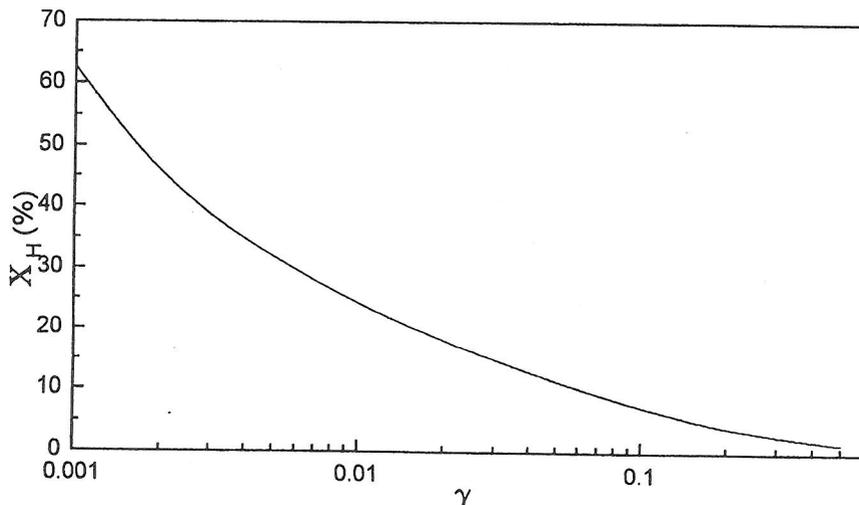


Figure 1: Calculated molar ratio  $X_H$  as a function of  $\gamma$  ( $p=1\text{torr}$ ,  $n_e=2 \cdot 10^{12} \text{ cm}^{-3}$ ,  $T_g=1500\text{K}$ )

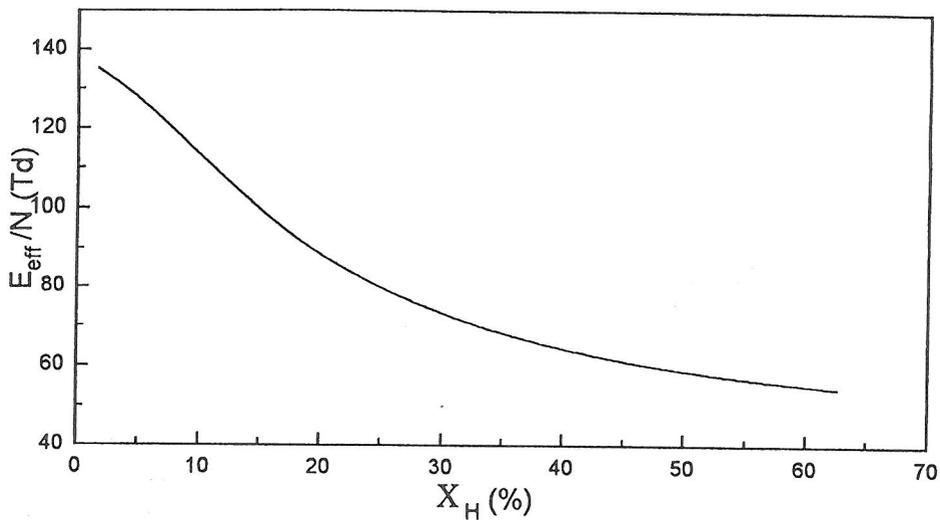


Figure 2: Calculated  $E_{\text{eff}}/N$  as a function of  $X_H$  ( $p=1\text{torr}$ ,  $n_e=2 \cdot 10^{12} \text{ cm}^{-3}$ ,  $T_g=1500\text{K}$ )

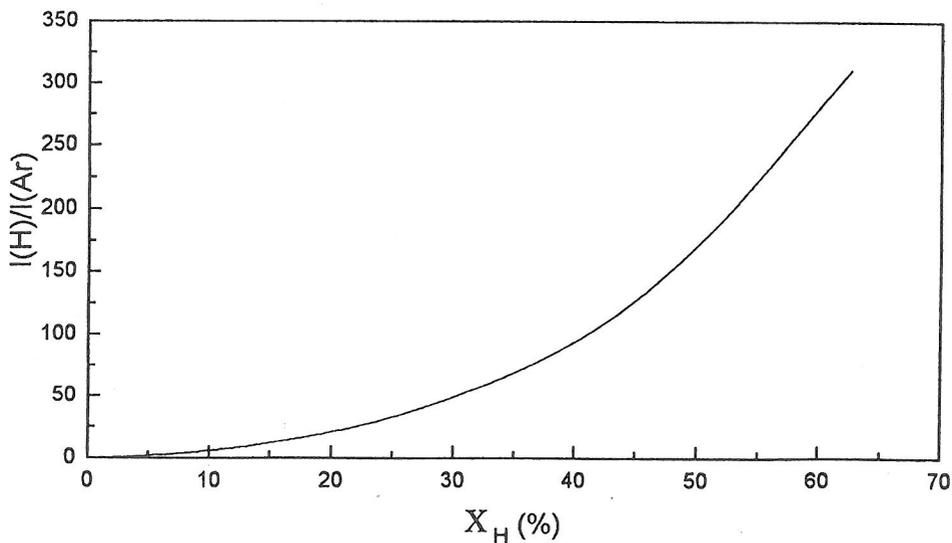


Figure 3: Calculated  $I(\text{H})/I(\text{Ar})$  as a function of  $X_H$  ( $p=1\text{torr}$ ,  $n_e=2 \cdot 10^{12} \text{ cm}^{-3}$ ,  $T_g=1500\text{K}$ )

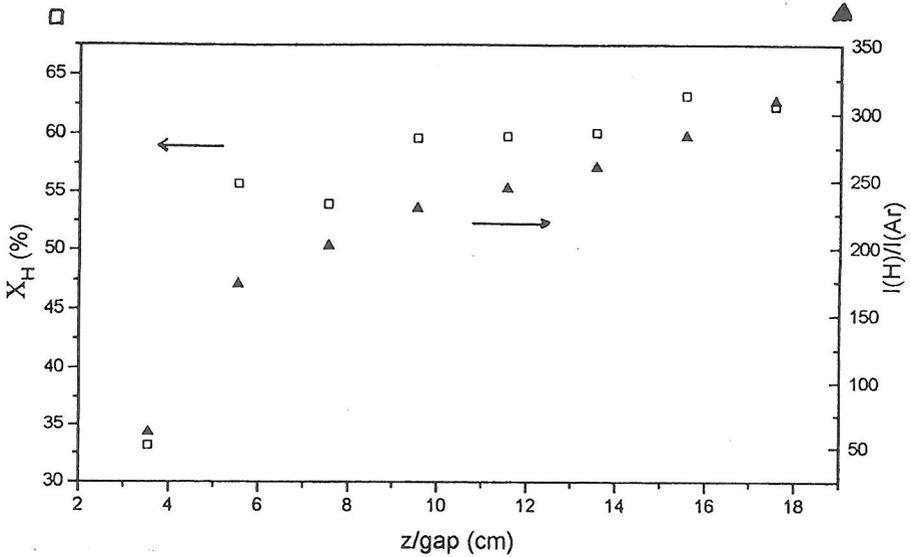


Figure 4: Experimental  $I(H)/I(Ar)$  and  $X_H$  along the plasma column ( $P_{max}=750W$ ,  $p=1Torr$ )

## References.

- /1/ J.W. Coburn and M. Chen, *J. Appl. Phys.* 51 (1980) 3134
- /2/ J. Loureiro and C.M. Ferreira, *J. Phys. D: Appl. Phys.* 22 (1989) 1680
- /3/ G. Gousset, J. Bretagne, P. Leprince and A. Rousseau XI ICPIG Bochum 19-24 sept. (1993) 379
- /4/ L.L. Alves, G. Gousset, C.M. Ferreira, *J. Phys. D: Appl. Phys.* 25 (1992) 1713
- /5/ A. Rousseau, G. Granier, G. Gousset and P. Leprince *J. Phys. D: Appl. Phys.* 27 (1994) 1412
- /6/ M. Glass-Maujean *Phys. Rev. Lett.* 62 (1989) 144
- /7/ A. Rousseau, L. Tomasini, G. Gousset, C. Boisse-Laporte and P. Leprince *J. Phys. D: Appl. Phys.* 27 (1994) 2439
- /8/ L. Tomasini, A. Rousseau, G. Gousset, P. Leprince. ISPC (1995).