Temperature diagnostics in a high-pressure hydrogen microwave plasma torch I: experimental characterization

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Abstract. We present preliminary results of an experimental study of a hydrogen plasma flame produced using a microwave axial injection torch (torche à injection axiale or TIA). This device usually runs in argon or helium at atmospheric pressure providing a stable discharge at high HF power levels and a two-temperature plasma. In the current work, hydrogen plasma is launched in a helium filled chamber to prevent hydrogen-air explosive reactions. Seven spectroscopic hydrogen lines have been detected in the visible spectrum (the Balmer series of hydrogen). Using a Boltzmann-plot representation it is shown that the plasma is far from equilibrium, but the electron temperature still can be obtained from a modified plot via a $p_x$-correction, which shows that the lower energy levels of Balmer series of the hydrogen system is ruled by the excitation-saturation balance (ESB).

1. Introduction

The Axial Injection Torch or TIA (torche à injection axiale [1]) is a device designed for the production of plasmas by microwaves at atmospheric pressure, generally using gases such as argon or helium, in open air or inside a reactor chamber. For applications of chemical purpose in reactive plasmas, $O_2$ and $N_2$ are also used [2]. Usually a plasma of two well-differentiated temperatures is obtained (2-T plasma), one for the electrons and another, lower one, for the heavy particles. That is due to the step wise structure of energy transfer from the microwaves to the plasma: the free electrons receive the energy from the microwaves, transfer part of their energy to the heavy particles (atoms, ions and molecules) whereas the latter are cooled to the environment. Therefore, the electrons will attain a higher temperature than that of the gas temperature (atoms, ions and molecules) and the plasma is not in a local thermodynamic equilibrium (LTE).

As a new challenge, we have attempted to generate a hydrogen discharge using the TIA device. In the construction of the discharge set-up, it is necessary to take very rigorous precautions when working with hydrogen gas because it can react in an explosive way when it comes into contact with the oxygen of the air.

The line spectrum of the hydrogen in the visible range is dominated by the Balmer series that corresponds to transitions from highly excited levels to the second electronic level. If one is interested in knowing the degree of equilibrium departure in the discharge and it is possible to measure the
intensity of different spectroscopic lines, a first step is the study of the population excited states. In that way, deviations from the equilibrium values given by the Saha-Boltzmann equation can be established. In the above equation the equilibrium value \( n^s(p) \) of the excited state with effective principal quantum number \( p \) is expressed as a function of the electron density \( n_e \), the ion density \( n_i = n^+ \), the ionization potential of the level \( I_p \), and the ionization temperature \( T_{ion} \). If the plasma is in equilibrium, the ionization temperature \( T_{ion} \) is the same as the electron temperature \( T_e \) and the \( T \)-value can be obtained experimentally from a logarithmic representation of the populations as a function of the ionization potential.

But a priori it can be expected that the atomic state distribution function will deviate from the equation given above. The reason is that the plasma is small in size whereas the diffusion of hydrogen atoms is a fast process. This outward diffusion of electron-ion pairs will pull the electron density downwards. Therefore the recombination process will be unimportant and the Saha balance of ionization and three-particle recombination will be disturbed severely. As a consequence the ground state of the hydrogen system will be overpopulated and this overpopulation will propagate through the system. This overpopulation is usually expressed by the \( b \) parameter defined as

\[
b(p) = \frac{n(p)}{n^s(p)}. \quad (2)
\]

It was found for several systems that under several conditions \( \delta b(p) = b(p) - I \) obeys a power law such that \( b(p) - I \propto p^x \) with \( x \) somewhere between 5 and 6 [3, 4]. It is evident that in case \( b(p)>>1 \) we can write

\[
\frac{n(p)}{n^s(p)} \propto p^{-x}. \quad (3)
\]

In previous works carried out in our groups [5], though for middle-pressure argon discharges, this relationship was found experimentally and a procedure was established to find the value of the exponent \( x \) and the Boltzmann exponent in \( \exp(I_p/kT_e) \). This modified Saha-Boltzmann representation will be used for the current plasma conditions as well.

2. Experimental setup

The plasma is created with the help of a TIA by 2.45 GHz microwave energy at HF powers of 600 and 1000 W. The plasma is produced in a hydrogen flow at atmospheric pressure expanding in a helium environment in order to prevent explosions. The procedure to create the hydrogen plasma is very complicated and laborious and required many attempts until a suitable parameter setting was found. The necessary precautions for the use of hydrogen imply additional difficulties for handling the experimental device. In short, the procedure finally optimized to get the stable hydrogen discharge is: i) to create an inert atmosphere with a high flow of circulating helium (about 15 l/min) inside the discharge chamber; ii) to produce an argon plasma (flow of 2 l/min) at high microwave power (1 KW); iii) to introduce hydrogen in the argon discharge by slowly increasing the hydrogen flux and in the same time decreasing the argon flux in a very precise, controlled way; iv) finally, when there is no more argon in the discharge a pure hydrogen plasma can be maintained at a flow of 9 l/min.

A plasma flame of 2 millimeters in diameter and a few centimeters long was produced expanding in the surrounding helium atmosphere occupying the discharge chamber. Only spectroscopic lines of hydrogen were observed. Neither helium nor other species could be observed (at the starting, when the hydrogen plasma is launched, some molecular rotational bands and other lines are observed, but they disappear after a few minutes). The main difference between this hydrogen plasma flame and the usual
argon or helium plasma flames launched by a TIA in previous works is the heating of its components and particularly of the TIA’s tip. In the hydrogen plasma this can be due to the relatively high temperature of heavy particles (neutral and ions) that is responsible for the heating of the physical structure of devices producing microwave discharges, once the existence of microwave energy mismatches was minimized. As a consequence, the device could not be used for long periods of time.

For the spectroscopic diagnostics of this discharge, a standard optical arrangement is used to increase the image size and to focus the light emitted by the brightest zone of the plasma flame into the entrance slit of a THR 1000 (Jobin-Yvon) monochromator. At its exit slit side, a double optical detection system is mounted, which are chosen by means of a rotating mirror, and we can select between the two detection branches: a) an iCCD (intensified Coupled Charge Device, FlameStar II, LaVision); b) a phototube (Hamamatsu). Both detectors work in the visible region. As a main peculiarity, a Dové prism is used to rotate the image 90° (see Figure 2). In this way, the light collected in the radial direction by the focusing lens comes from different zones inside the plasma at a fixed axial position $z$ (see Figure 1). So, the diagnostics presented here is representative (or apparent) for this $z$ position in the plasma and not for any specific radial point. This position is measured from the beginning of the discharge ($z = 0$ at the tip of the TIA’s nozzle, as appears in Figure 2). Our measurements are made at $z = 1$ mm and the phototube arrangements were used.

![Diagram of the experimental setup](image)

**Figure 1**

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**Table 1**

| COMPONENTS       | DESCRIPTION                              |
|------------------|------------------------------------------|
| Microwave generator | SAIREM GMP 12 KE/T                        |
| Monochromator    | THR-1000 (Jobin-Yvon) 1200 grooves/mm    |
| Photomultiplier  | Hamamatsu R636                           |
| TIA              | Axial Injection Torch (torche à injection axiale) |
| Flowmeter        | Vacuum General – DynaMass                |
3. Results
From the Balmer series, the first six lines were observed with enough clarity (H\(\alpha\), H\(\beta\), H\(\gamma\), H\(\delta\), H\(\epsilon\), H\(\zeta\)). The seventh line of this series was observed as well, but not always with good resolution. Therefore, we present here results of the measurement for the 1000 W case. From the experimental spectral lines, the integrated intensity (area) \(I_{\text{exp}}\) is calculated after eliminating the different background signals at each part of the spectrum and after calibrating the response of the experimental setup as a function of wavelength. Using these intensities, we obtained the experimental (relative) populations corresponding to the departure level \(p\)

\[
\frac{n(p)}{g_p} \propto \frac{I_{\text{exp}} \cdot \lambda}{g_p \cdot A_{pq}},
\]

where we have also used the degeneration of the departure level \(g_p\), the transition probabilities \(A_{pq}\) and the wavelength of the lines \(\lambda\) (Table 2). In the following figures we used the energy of the transition \((E_{pq})\) instead of the energy of the departure level \((E_p)\) since \(E_{pq} = E_p - E_q\) and \(E_q\) is constant for all the transitions.

A Boltzmann-plot is then constructed and represented in a semi-log plot (Figure 3). For both values of the HF powers, the plasma was found not to be in LTE, because a straight line corresponding to Equation 1 could not be found. Yet, in the double log representation of the populations vs. the principal quantum number, the situation is clearly different (Figure 4).

| Balmer series | \(\lambda\) (nm) | \(E_{pq}\) (eV) | \(g_p\) | \(A_{pq}\) \(\times 10^8\) s\(^{-1}\) | Transition |
|---------------|----------------|----------------|--------|----------------------------|------------|
| \(H_\alpha\)  | 656.28         | 1.8892         | 18     | 0.441000                   | 3p \(\rightarrow\) 2s |
| \(H_\beta\)   | 486.13         | 2.5504         | 32     | 0.084190                   | 4p \(\rightarrow\) 2s |
| \(H_\gamma\)  | 434.05         | 2.8564         | 50     | 0.025300                   | 5p \(\rightarrow\) 2s |
| \(H_\delta\)  | 410.18         | 3.0227         | 72     | 0.009732                   | 6p \(\rightarrow\) 2s |
| \(H_\epsilon\)| 397.01         | 3.1230         | 98     | 0.004389                   | 7p \(\rightarrow\) 2s |
| \(H_{8,2}\)   | 388.90         | 3.1880         | 128    | 0.002215                   | 8p \(\rightarrow\) 2s |
| \(H_{9,2}\)   | 383.54         | 3.2326         | 162    | 0.001216                   | 9p \(\rightarrow\) 2s |

Table 2
The populations corresponding to each Balmer transition are linearly distributed in this new representation with the exception of the first line in the series, \( H_\alpha \). The reason could be that such line suffers from self-absorption. Indeed, for \( H_\alpha \), self-absorption could be really important for but it is expected to be much less relevant for the rest of the Balmer lines. In the case of working with a small amount of hydrogen in the discharge as we did in the past [4], it is possible to consider the plasma as optically thin for the Balmer lines. But now for the case of pure hydrogen plasma, self-absorption of the \( H_\alpha \) line becomes important due to the relative high concentration of the \( 3p \) atomic level of the hydrogen that is responsible of the transition. Excluding \( H_\alpha \), a linear fit can be obtained, resulting slopes that are near to the theoretical value of the \( p^{-1} \) law: we obtain \( 5.6 \pm 0.1 \) for 600 W and \( 5.8 \pm 0.1 \) for 1000 W. So, we can assume that the plasma is very close to the excitation-saturation balance. And using this experimental value for the exponent, we can correct the experimental populations to obtain the equilibrium ones (equation 3), i.e., the populations of the excited levels in a theoretical LTE.
As a consequence, we have a modified Boltzmann-plot and it is possible to obtain the electron temperature $T_e$ by using Equation 1. The results approximately are $9600 \pm 400$ K for 600 W, and $10000 \pm 400$ K for 1000 W respectively. The main contribution to this error comes from the linear fits in which the dispersion in the line intensity measurements (i.e., the area of the peaks) is included.

4. Conclusions
The hydrogen plasma produced by the TIA is a very hard experiment, but it can be very useful. Under our experimental conditions, the results show that the hydrogen plasma is not in the local thermodynamic equilibrium. In Fujimoto and Van der Mullen theories for the excitation-saturation balance, the overpopulation of excited states depends on the effective quantum number $p$ (for the hydrogen equal to the principal quantum number $n$) obeying the $p^x$ law. We have found for these exponent values around 5.5-5.9, very close to 6. So, the TIA hydrogen plasma can be considered to be ruled by the excitation-saturation balance (ESB) and the Boltzmann-plot can be modified so that the underlying equilibrium values of the populations are obtained. From this the value of the electron temperature can be deduced. Values of around one electron-volt (10000 K) were found, which are in a good agreement with what we can expect according to other studies in TIA produced plasmas.

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