Quantitative determination of density of ground state atomic oxygen from both TALIF and emission spectroscopy in hot air plasma generated by microwave resonant cavity

F. Marchal[1], M. Yousfi[1], N. Merbahi[1], G. Wattieaux[1], A. Piquemal[2]

[1]University of Toulouse, UPS, LAPLACE CNRS UMR 5213, 118 Route de Narbonne 31 062 Toulouse, FRANCE
[2]CEA, DAM, DIF, F-91297, Arpajon, France
Corresponding author's e-mail: yousfi@laplace.univ-tlse.fr

ABSTRACT

Two experimental methods have been used to quantify the atomic oxygen density of the hot air plasma generated by a microwave resonant cavity (2.45GHz). The first method is the standard two photon absorption laser induced fluorescence (TALIF) using xenon for calibration but applied for the first time in such post discharge hot air plasma with temperature up to about 4500K. The second method is a kind of actinometry based on the comparison of the emission lines in the visible range of specific atomic oxygen line (844nm) and xenon line (823nm) coming from the addition of a controlled low proportion of a chemically inert gas (1%Xe) in the air plasma.

1. INTRODUCTION

Many applications and understanding of plasma physics can be reached using the present hot air plasma generated by the microwave (MW) resonant cavity. In our case, the experimental characterization to obtain more particularly the density of atomic oxygen in such air plasma is needed for validation of a complex hydro-kinetics model involving kinetics, transport and plasma chemistry.

The studied hot air plasma is first generated inside a 2.45GHz MW resonant cavity with an input power of 1 kW before to be launched inside a cell of gas conditioning in order to be analysed under a post discharge regime. The inlet gas flow injected at 12 liter/min inside the MW cavity involves synthetic air with a small amount of H_2 to better detect OH(A-X) spectra for gas temperature estimation. 1%Xe is also injected to perform actinometry diagnostic. The determination of the density of the triplet atomic ground state oxygen (O^3P) is performed using a two-photon (2x225.65nm) absorption laser-induced fluorescence (TALIF) spectroscopy, along several radial and axial positions of the hot air plasma column inside the cell of gas conditioning at a fixed pressure of 600 mbar (see Fig. 1).

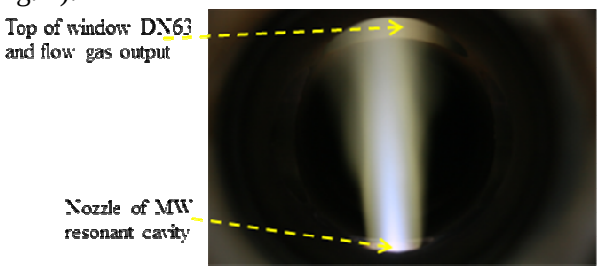

Fig. 1: Air plasma column inside the cell for P_{MW} = 1kW, Air gas flow=12 l/min and pressure=600 mbar taken from ref 1(nozzle: z=0mm and z=63mm for the top)

2. TALIF MEASUREMENTS

Fig. 2 displays the schematic diagram of experimental setup used for TALIF spectroscopy to measure the absolute density of atomic oxygen. A dye laser (Sirah Strech-Cobra) pumped by a Nd:YAG laser (Quanta Ray CGR 150, max pulse energy of 180 mJ) provided 7 ns pulse width with a repetition rate of 30 Hz. The spectral width of the laser radiation in the range between 435nm to 463nm, obtained using two 1800 grooves/mm gratings, amounts to 1.7 pm. The maximum pulse energy of the dye laser beam is about 20 mJ per pulse. The second harmonic of laser beam is generated by a nonlinear BBO crystal to obtain a wavelength range of 220 nm to 230 nm with a spectral width of 2 pm that allows us to excite the two-photon transition from the ground states of the triplet atomic oxygen $2p^4\ (3P)_{J\ =\ 0,1,2}$ to the excited states $3p\ (3P)_{J\ =\ 0,1,2}$ of atomic oxygen. The beam diameter is 2 mm and the pulse energy up to 0.2 mJ. The laser beam is focused at a given position of the plasma column using a MgF_2 lens with a focal length of 170 mm.

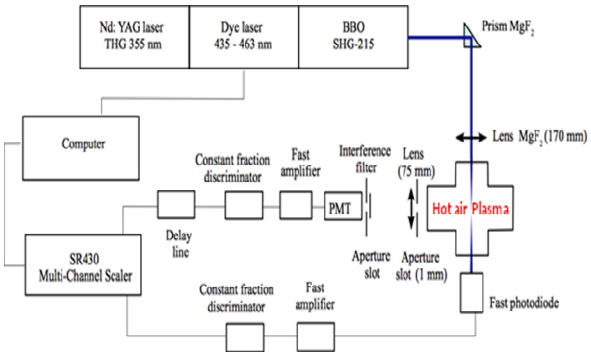

Fig. 2. View on the scheme of the TALIF experimental setup

The TALIF fluorescence is detected perpendicularly to the incident laser beam. The laser focus is imaged onto the photocathode of a photomultiplier (PMT HamamatsuH7421-50) working in a single photon counting mode, by using BK7 lens with the ratio f/D=3.0 (i.e. 75 mm focal length over 25 mm diameter). The size of the image is limited by a diaphragm placed in the focal plane in front of the photomultiplier. A second diaphragm (1 mm diameter) is placed between the lens and the cell in order to reduce the flux of fluorescence. The anode pulses delivered by the PMT are delayed via a delay line and then processed via a constant fraction discriminator (CFD). The number of photons is stored in a multi-channel Stanford Research SR-430 analyser set having 16 384 channels and 5ns resolution. For each laser pulse, the SR 430 is monitored by fast photodiode.

Fig. 3 shows the usual two-photon excitation schemes showing the fluorescence of O (844.9nm) and Xe (834.9nm) used for calibration.

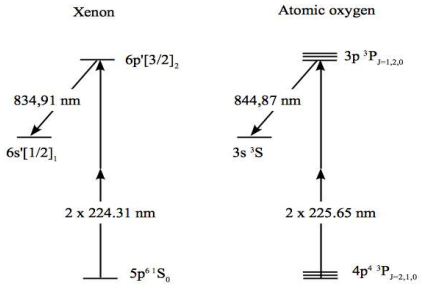

Fig. 3. Two-photon excitation schemes of atomic oxygen and xenon related to the determination of absolute atomic ground state densities using xenon as a reference for TALIF calibration.

Fig. 4 displays the integrated and normalized to one laser pulse TALIF signal of atomic oxygen measured versus the square laser pulse energy. This signal corresponds to a given position of the air plasma column (z=12mm along the axis column shown in Fig. 1). TALIF signal is unsaturated until the laser pulse energy reaches 100 μJ. This means, that at these low energies, the TALIF measurements are carried out without any saturation and photo-ionization effects.

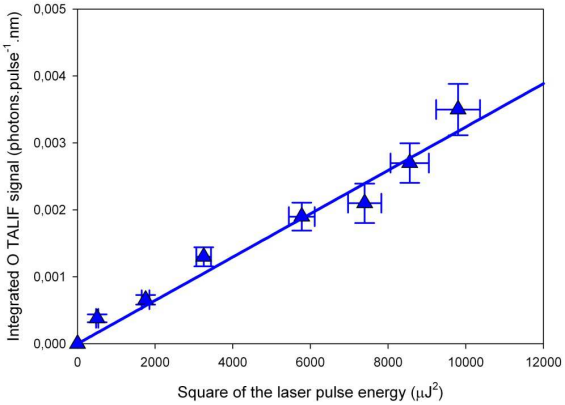

Fig. 4. Integrated O TALIF signal versus the square of the laser pulse energy at 600 mbar, Air flow= 11.64 L/min, H_2 flow= 0.36 L/min, P_{MW} = 1 kW

In order to determine the calibration factors, Fig 5 displays the variation of Xe TALIF signal which is integrated and normalized in the same way as oxygen TALIF signal. The laser pulse energy was tuned low enough, below 70 μJ, to avoid xenon ionization by one photon absorption of the two-photon excited state Xe 6p'$[3/2]_2$. Beyond this energy limit, the xenon TALIF signal seems to be slightly saturated.

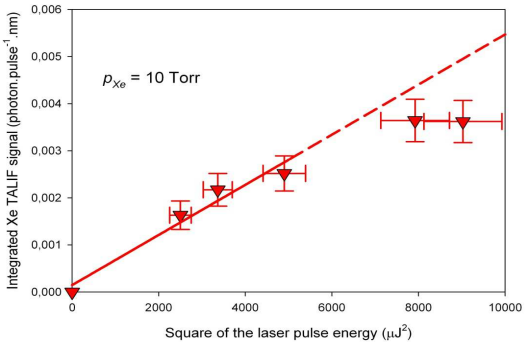

Fig. 5. Integrated Xe TALIF signal versus the square of the laser pulse energy.

The unknown density of atomic oxygen n_O is then derived from the known xenon gas density n_{Xe} and the ratio S_0/S_{Xe} of normalized TALIF signals measured for xenon and oxygen in the plasma column. At 600 mbar and z=12 mm from the nozzle in the axis of the plasma column, the absolute density of background level of atomic oxygen is determined from the following relation [1,2]:

$$n_O = \frac{T_{Xe}\eta_{Xe}}{T_O\eta_O}\frac{a(Xe)\sigma_{Xe}^{(2)}}{a(O)\sigma_O^{(2)}}\left(\frac{\lambda_L(Xe)}{\lambda_L(O)}\right)^2 n_{Xe}\frac{S_O}{S_{Xe}} = 0.62\times n_{Xe}$$

$$= (2.05\pm 0.52)\times 10^{+17}\,\mathrm{cm}^{-3}$$

Noting that the detection sensitivity of the photomultiplier (η_O or η_{Xe}) is nearly equal for

both fluorescence wavelengths at 834.9 nm (λ_L(Xe) for xenon) and 844.9 nm (λ_L(O) for oxygen). The transmission of the interferential filters are respectively T_{Xe}=63% and T_O=81% (taken from data sheet calibration curves). According to the literature [2], the optical branching ratio for the atomic oxygen transition 3p $^3P_J \rightarrow$ 3s ^3S is unity ($a(O)$ =1) and $a(Xe)$=0.733 for xenon transition 6p'$[3/2]_2 \rightarrow$ 6s'[3/2] while the two-photon excitation cross section ratio is $\sigma^{(2)}_{Xe}/\sigma^{(2)}_{O}$ = 1.9±0.4. [2].

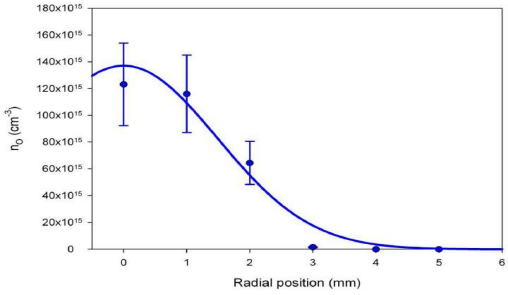

Fig. 6. Absolute atomic oxygen density in the microwave plasma column versus radial position at z=17 mm from the nozzle of resonant cavity: pressure= 600 mbar, Air flow= 11.64 L/min, H_2 flow= O.36 L/min, P_{MW} = 1 kW

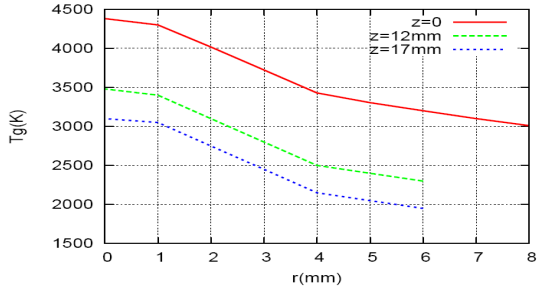

Fig. 7. Measured gas temperature along the radial direction of the air plasma column for 3 axial positions (z=0 near the nozzle of resonant cavity, z=12 mm and z=17 mm) in the case of P_{MW}=1 kW, Pressure=600 mbar, inlet gas composition=Air+2%H_2, and Gas flow=12 l/min.

Fig. 6 displays the radial variation of atomic oxygen density at a given position (z=17mm) of the plasma column. The shape of atomic oxygen density with a maximum on the plasma axis is followed by a decrease along the radial direction. This is coherent with the gas temperature behaviour [1] measured from the comparison between measured OH(A-X) spectra and the calculated ones using LIFBASE software. Indeed, as displayed in Fig 7, the gas temperature for the same axial position z=17mm is maximal on the axis (3500K) and decreases down to about 2000K for a radial position close to 5mm.

3. OES FOR MEASUREMENT OF ABSOLUTE ATOMIC OXYGEN DENSITY

A low amount of xenon is added to the air plasma without any visible change on the thermal and chemical properties of the air plasma column. For instance, there is no change on the oxygen atomic line (844nm) spectrum (Fig. 8a) with and without the addition of 1%Xe while the atomic line of Xe (823nm) is detected as expected only when xenon is added (Fig 8b).

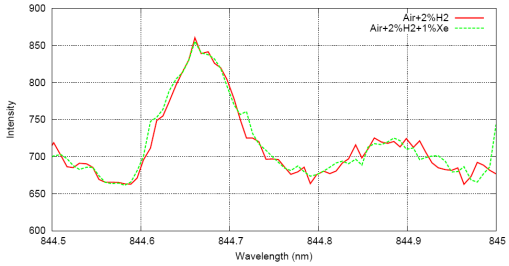

Fig. 8a : Atomic line of oxygen for 844 nm transition with and without the addition of 1%Xe for the position z=0mm on the axis of MW air plasma column

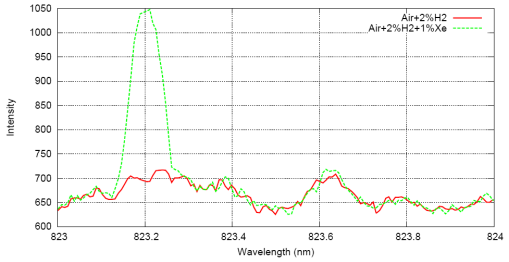

Fig. 8b : Atomic line of xenon for 823 nm transition with and without the addition of 1%Xe for the position z=0mm on the axis of MW air plasma column

If we consider the two atomic transitions O(844nm) and Xe(823nm) that are the closest in the wavelegnth range therefore the density of atomic oxygen n_O can be proportional to the density of atomic xenon n_{Xe} in the cases where:
-these transitions are dominant for the de-excitation of their respective upper level,
-the population of the excited level of each atom is described by a Boltzmann distribution having T_{ex} for excitation temperature.
The proportionality relation is then [3]:

$$\frac{n_O}{n_{Xe}} \propto \frac{I_O}{I_{Xe}} \frac{\lambda_O}{\lambda_{Xe}} \frac{Z_O}{Z_{Xe}} \frac{A_{Xe}}{A_O} \frac{g_{Xe}}{g_O} \frac{\gamma_{Xe}}{\gamma_O} \exp\left(\frac{E_O - E_{Xe}}{k_B T_{ex}}\right)$$

I_O and I_{Xe} are the intensities of emission spectra measured under the same spectroscopic conditions (slit of spectrophotometer, exposure time, distance between the fiber and the plasma, etc.). A_O and A_{Xe} are the corresponding probability of radiative transitions, Z_O and Z_{Xe} the partition function, g_O and g_{Xe} the degeneracy of the upper level, γ_O and γ_{Xe} the quenching rate of the upper level and E_O and E_{xe} the excitation energy of the upper level of the considered transition line.
I_O and I_{Xe} come from measurements (see e.g. Fig. 8a and 8b) while the various atomic data are taken from literature and *Tex* is estimated from UV optical emission spectroscopy as following.

It is noteworthy that the intensities of NH(A-X) spectrum for the different head bands are strongly dependent on the couple of vibration and excitation temperatures {Tv, Tex}. The wavelengths of these head bands are for the vibrational quanta v,v' [4]:
-336 nm for emission NH(A-X) v=0,v'=0
-337 nm for emission NH(A-X) v=1,v'=1
-338.3nm for emission NH(A-X) v=2,v'=2
Then the comparison between the calculated (using SpecAir software) and the measured NH(A-X) spectra can give the estimation of more particularly *Tex* as shown in Fig 9.

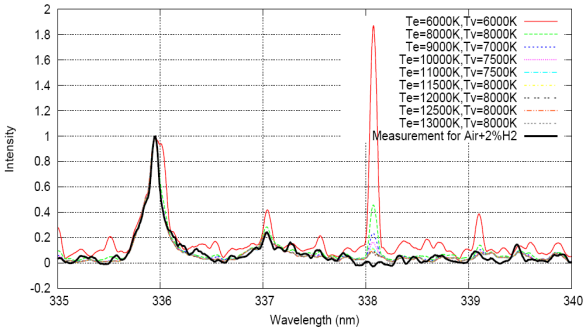

Fig. 9 : Measured NH(A-X) for the position z=0mm on the axis of MW air plasma column. Comparison with calculated NH(A-X) spectra using several couples of {Tv, Tex}

For the position of air plasma column considered in Fig 9 where gas temperature Tg=4200K (Fig.7), the best fit between measured and calculated spectra leads to the following estimation: 11000K ≤ Tex ≤ 13000K and Tv ≈ 8000K.
The same comparison between measured and calculated NH(A-X) spectra are done for a second position of the plasma column (z=12mm) already considered for TALIF measurements (section 2). The best fit for this position where Tg=3500K (Fig 7) is: 9000K ≤Tex ≤ 10000K and Tv ≈ 9000K
Using previous proportionality relation between n_O and n_{Xe}, the density of atomic oxygen is given in Table 1 for z=0mm and in Table 2 for z=12mm.

Tex=11000K n_O/n_{Xe} =17.9 =>n_O= 1.84x10^{17} cm^{-3}
Tex=12000K n_O/n_{Xe} =16.1 =>n_O=1.66x10^{17} cm^{-3}
Tex=13000 K n_O/n_{Xe} =14.8 =>n_O=1.52x10^{17} cm^{-3}

Table 1: Ratio of n_O/n_{Xe} for the estimated range of Tex for z=0 mm in the axis of air plasma column (for Tg=4200K, gas density= 1.03 x10^{18} cm^{-3} and initial O_2 proportion=2.007x10^{17} cm^{-3})

As the Xe density is known at the considered position from the knowledge of gas temperature Tg at 600 mbar (n_{Xe} =1.03x10^{16} cm^{-3} for 4200K and 1.24x10^{16} cm^{-3} for 3500K), the density of oxygen is then obtained from the ratio n_O/n_{Xe}.

Tex=9000 K n_O/n_{Xe} =18 =>n_O = 2.25x10^{17} cm^{-3}
Tex=9500 K n_O/n_{Xe} =16 =>n_O = 2.09x10^{17} cm^{-3}
Tex=10000 K n_O/n_{Xe} =15=> n_O = 1.87x10^{17} cm^{-3}

Table 2: Ratio of n_O/n_{Xe} for the estimated range of Tex for z=12 mm in the axis of air plasma column (for Tg=3500K, gas density=1.24x10^{18} cm^{-3} and initial O_2 proportion=2.41x10^{17} cm^{-3})

We have 3 main remarks:
- for z=12mm, there is a very good agreement with TALIF measurement (2.05 x10^{17} cm^{-3}) given in section 2,
-for z=12mm, the dissociation degree of molecular oxygen is between 77% and 93% depending on Tex value,
-for z=0mm (position not accessible to TALIF due to the geometric configuration of the gas conditioning cell), the dissociation degree of molecular oxygen is between 75% and 90%.

CONCLUSION

A good agreement between the two methods (TALIF and OES) used for measurement of absolute density of atomic oxygen is emphasized in the case of hot air plasma column generated by a MW resonant cavity.
In the range of gas temperature, 2500 K to 4200K estimated from OH(A-X), and for the estimated excitation temperature *Tex* using NH(A-X) spectra, the dissociation degree of molecular oxygen obtained from the present measurements shows an underestimated dissociation in comparison of the case where local thermodynamic equilibrium is assumed.
This means that in such air flow plasma column (behaving as a post-discharge), there is neither thermal nor chemical equilibrium. This is certainly due to the not yet achieved relaxation of the long-living excited species which will be analysed in details in future studies.

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