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

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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 hydrokinetics 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 H₂ 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 (O³P) 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 P₀₀ = 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 Strec-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 2p⁴ (3P) ⁴S = 0,1,2 to the excited states 3p (3P) ⁴S = 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 MgF₂ lens with a focal length of 170 mm.
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. 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. 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]. Beyond this energy limit, the xenon TALIF signal seems to be slightly saturated.

The unknown density of atomic oxygen \( n_O \) is then derived from the known xenon gas density \( n_{Xe} \) and the ratio \( S_O/S_{Xe} \) 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]:

\[
n_O = \frac{T_{Xe} n_{Xe} \sigma(Xe) \sigma(O) \lambda(Xe)}{T_O n_O \sigma(O) \lambda(O)} n_{Xe} \frac{S_O}{S_{Xe}} = 0.62 \times n_{Xe}
\]

\[
= (2.05\pm0.52) \times 10^{17} \text{cm}^{-3}
\]

Noting that the detection sensitivity of the photomultiplier (\( \eta_O \) or \( \eta_{Xe} \)) is nearly equal for
both fluorescence wavelengths at 834.9 nm (\(\lambda_{L}(\text{Xe})\) for xenon) and 844.9 nm (\(\lambda_{L}(\text{O})\) for oxygen). The transmission of the interferential filters are respectively \(T_{\text{Xe}}=63\%\) and \(T_{\text{O}}=81\%\) (taken from data sheet calibration curves). According to the literature [2], the optical branching ratio for the atomic oxygen transition \(3p\ P_{2} \rightarrow 3s\ S\) is unity (\(a(O)=1\)) and \(a(\text{Xe})=0.733\) for xenon transition \(6p'[3/2] \rightarrow 6s'[3/2]\) while the two-photon excitation cross section ratio is \(\sigma^{(2)}_{\text{Xe}}/\sigma^{(2)}_{\text{O}} = 1.9\pm 0.4\). [2].

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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= 0.36 L/min, \(P_{\text{MW}}\) = 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 \(P_{\text{MW}}\)=1 kW, Pressure=600 mbar, inlet gas composition=Air+2%H\(_2\), and Gas flow=12 l/min.

If we consider the two atomic transitions O(844nm) and Xe(823nm) that are the closest in the wavelength range therefore the density of atomic oxygen \(n_{\text{O}}\) can be proportional to the density of atomic xenon \(n_{\text{Xe}}\) 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 \(T_{\text{ex}}\) for excitation temperature.

The proportionality relation is then [3]:

\[
\frac{n_{\text{O}}}{n_{\text{Xe}}} \propto \frac{I_{\text{O}}}{I_{\text{Xe}}} \frac{\lambda_{\text{O}} Z_{\text{O}} A_{\text{O}} g_{\text{O}} \gamma_{\text{O}}}{\lambda_{\text{Xe}} Z_{\text{Xe}} A_{\text{Xe}} g_{\text{Xe}} \gamma_{\text{Xe}}} \exp\left(\frac{E_{\text{O}}-E_{\text{Xe}}}{k_{B}T_{\text{ex}}}\right)
\]

\(I_{\text{O}}\) and \(I_{\text{Xe}}\) 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.). \(A_{\text{O}}\) and \(A_{\text{Xe}}\) are the corresponding probability of radiative transitions, \(Z_{\text{O}}\) and \(Z_{\text{Xe}}\) the partition function, \(g_{\text{O}}\) and \(g_{\text{Xe}}\) the degeneracy of the upper level, \(\gamma_{\text{O}}\) and \(\gamma_{\text{Xe}}\) the quenching rate of the upper level and \(E_{\text{O}}\) and \(E_{\text{Xe}}\) the excitation energy of the upper level of the considered transition line.

\(I_{\text{O}}\) and \(I_{\text{Xe}}\) come from measurements (see e.g. Fig. 8a and 8b) while the various atomic data are taken from literature and \(T_{\text{ex}}\) is estimated from UV optical emission spectroscopy as following.

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).
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 \( \{T_v, T_{ex}\} \). 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) \( v=1,v'=1 \)
-338.3 nm 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 \( T_{ex} \) as shown in Fig 9.

For the position of air plasma column considered in Fig 9 where gas temperature \( T_g=4200K \) (Fig.7), the best fit between measured and calculated spectra leads to the following estimation: \( 11000K \leq T_{ex} \leq 13000K \) and \( T_v \approx 8000K \).

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 \( T_g=3500K \) (Fig 7) is: \( 9000K \leq T_{ex} \leq 10000K \) and \( T_v \approx 9000K \).

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 \( z=12mm \).

\[
T_{ex}=10000K \quad n_O/n_{Xe}=18 \Rightarrow n_O=2.25x10^{17} \text{ cm}^{-3}
\]
\[
T_{ex}=12000K \quad n_O/n_{Xe}=16.1 \Rightarrow n_O=1.66x10^{17} \text{ cm}^{-3}
\]
\[
T_{ex}=13000K \quad n_O/n_{Xe}=14.8 \Rightarrow n_O=1.52x10^{17} \text{ cm}^{-3}
\]

Table 1: Ratio of \( n_O/n_{Xe} \) for the estimated range of \( T_{ex} \) for \( z=0 \) mm in the axis of air plasma column (for \( T_g=4200K \), gas density=1.03 x10^{17} \text{ cm}^{-3} \) and initial \( O_2 \) proportion=2.00x10^{17} \text{ cm}^{-3} \)

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

\[
T_g=9000K \quad n_O/n_{Xe}=18 \Rightarrow n_O=2.25x10^{17} \text{ cm}^{-3}
\]
\[
T_g=9500K \quad n_O/n_{Xe}=16 \Rightarrow n_O=2.09x10^{17} \text{ cm}^{-3}
\]
\[
T_g=10000K \quad n_O/n_{Xe}=15 \Rightarrow n_O=1.87x10^{17} \text{ cm}^{-3}
\]

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

We have 3 main remarks:
- for \( z=12mm \), there is a very good agreement with TALIF measurement (2.05 x10^{17} \text{ 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 \( T_{ex} \) 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.

**REFERENCES**


