PRECISION
Strategic Research Cluster

Two-photon absorption laser-induced fluorescence measurement of atomic Oxygen density in an atmospheric pressure air plasma jet

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Introduction:

- Two-photon Absorption Laser Induced Fluorescence (TALIF) is used to investigate atomic oxygen density [O] in an air Atmospheric Pressure Plasma Jet (APPJ). The RF power into the plasma is varied for a fixed air flow, and the resulting [O] measured. In-situ calibration of the TALIF system is achieved using photolysis of O_2. As O is the probe species during calibration and [O] measurement, any laser induced high intensity saturation effects will be identical during both. As a consequence, laser intensity can be increased outside the TALIF quadratic laser power region without affecting calibration reliability. Higher laser intensity also helps overcome weak TALIF signals often encountered at atmospheric pressure due to collisional quenching. O_2 photo-dissociation and two-photon excitation of the resulting [O] are both achieved within the same laser pulse. Photolysis generates an [O] which is spatially non-uniform and time varying, so spatial and temporal correction factors are required to allow valid comparison with [O] in a plasma. Knowledge of the laser pulse intensity $I_0(t)$, and wavelength allows correction factors to be found using a rate equation model. [O] was found to increase with RF power in the APPJ system.

Photolysis:

- A laser is used to dissociate O_2 molecules (E_{Diss}:5.17 eV) producing a known atomic oxygen density $[O]_{Cal}$
- <u>Single laser shot</u>: $\lambda = 225.6$ nm ($E_{photon} = 5.5$ eV) : Δt_{Laser}: 8 ns : Laser pulse shape $I_0(t)$: Gaussian
  - → Single photon absorption in the Herzberg continuum of O_2 ($\sigma = 3.21 \times 10^{-24}$ cm^2 at 225.6 nm)
  - → Photo-dissociation of $O_2 \rightarrow 2\,O(^3P)$ atoms. Fast process (~10^{-13} - 10^{-14} s)
  - → Laser then excites these O atoms via 2-photon absorption → TALIF signal
- Photolysis atomic oxygen density $[O]_P$:

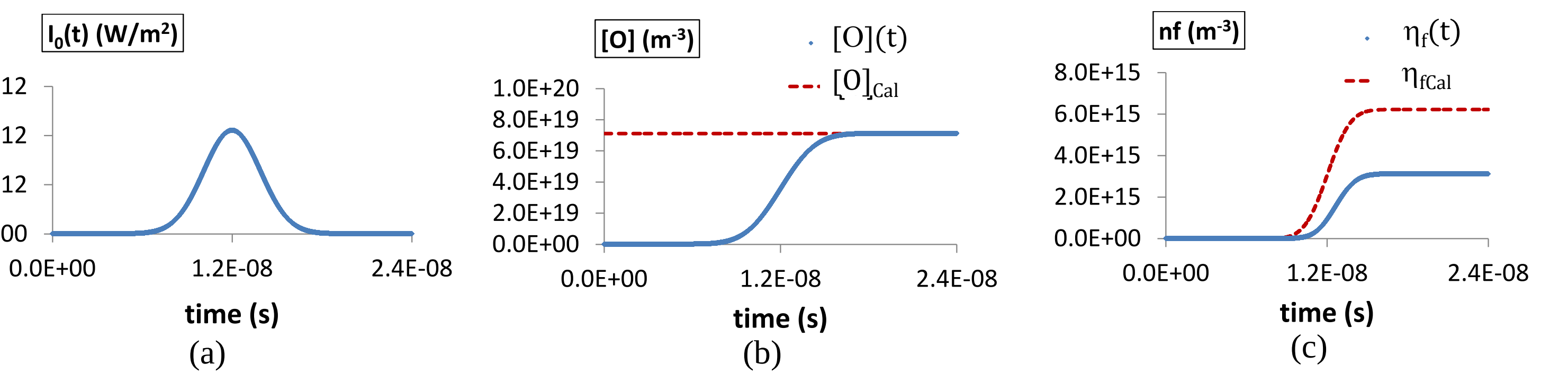
$$[O]_P = 2 \times [O_2](1 - \exp(-\sigma\phi))$$

where σ: Photo-dissociation cross section at λ_{Laser}
ϕ: Photon fluence.

$$\phi = \frac{E_{pulse}}{hfA}$$

where E_{pulse}: laser pulse energy:1.2 mJ, *f*: laser frequency: 1.33×10^{15} Hz, *A*: focal area: 6.03×10^{-9} m^2.

- Using atmospheric oxygen, $[O]_P$ has a value of is 7.12×10^{19} m^{-3}. **(= calibration density $[O]_{Cal}$)**
- This atomic oxygen density is not constant over pulse - Grows to $[O]_{Cal}$ in 8 ns → **[O](t)**
  (note: ∫[O](t) over pulse = $[O]_{Cal}$)
- The laser pulse interacts with [O](t) producing a TALIF signal which is recorded.
  - This TALIF signal is smaller than signal would get from a fixed oxygen density $[O]_{Cal}$
- Comparing the TALIF photon density $\eta_f(t)$ produced by [O](t) to η_f from fixed oxygen density $[O]_{Cal}$,, a correction factor R_t can be found



(a) (b) (c)

Figure 1. Plot of (a) $I_0(t)$, the laser Intensity vs time (b) [O](t) and $[O]_{Cal}$ produced by photolysis (c) TALIF photon density $\eta_f(t)$ and η_{Cal} over the duration of the laser pulse

Photolysis generated [O] - problems:

(i) <u>**Fly-out**</u>

- The atomic O produced by photolysis are "hot".

$E_{O(hot)} = E_{photon(225.6\,nm)} - E_{dissociation} = 5.5 - 5.17 = 0.33$ eV

⇒ O fragments have velocities of up to 1411 m/s and may leave the laser focal zone before two-photon absorption occurs.

The **small mean free path** at **atmospheric pressures** (~ 66 nm) means the root mean square diffusion distance travelled, $x_{RMS} = \sqrt{4Dt} = 9.95 \times 10^{-7}$ m

⇒ ~ <u>**99.5 % of the atomic O remain inside the focal zone**</u> over the duration of the laser pulse.

(ii) <u>**Quenching**</u>

- The hot oxygen atoms produced during photolysis will also experience enhanced quenching due to their high velocities when compared with O atoms produced in the plasma. This affects the quenching factor *Q* which will affect the branching ratio $a_{ij} = A_{ij}/(A + Q)$ for the excited state of these "hot" O atoms.

$$Q = \Sigma k_Q n_Q$$
$$= [(0.78)k_Q(N_2) + (0.209)\,k_Q(O_2) + (0.009)\,k_Q(Ar)] \times \frac{P_{atm}}{kT}$$

O	O_2	N_2	Ar	a_{ik}
k_Q values @ 300 K (cm^{3}s^{-1})	9.40E-10	5.90E-10	1.40E-11	0.00179
k_Q values Corrected for hot O	1.72E-09	1.05E-09	2.65E-11	0.000996

Table 1: Quenching factors and branching ratio for plasma generated O atoms at 300 K and for Hot O produced by photolysis

(iii) <u>**Boltzmann correction**</u>

- Atomic O has a triplet ground state $^3P_{2,1,0}$
- Only the lower J = 2 level probed by laser ⇒ Need J= 1, 0 populations to get total O ground state population
- Applying Boltzmann equation for a gas temperature of 291 K find J = 2 level accounts for 74.7 % of the total ground state population.

(iv) <u>**Spatial Correction**</u>

- Laser beam is focussed ⇒ laser intensity varies across the focal zone ⇒ photolysis [O] also varies
- However, $[O]_{Plasma}$ is constant over the focal zone.
- A comparison of η_f for both situations found the photon densities to be almost identical. R_Z = 1.06

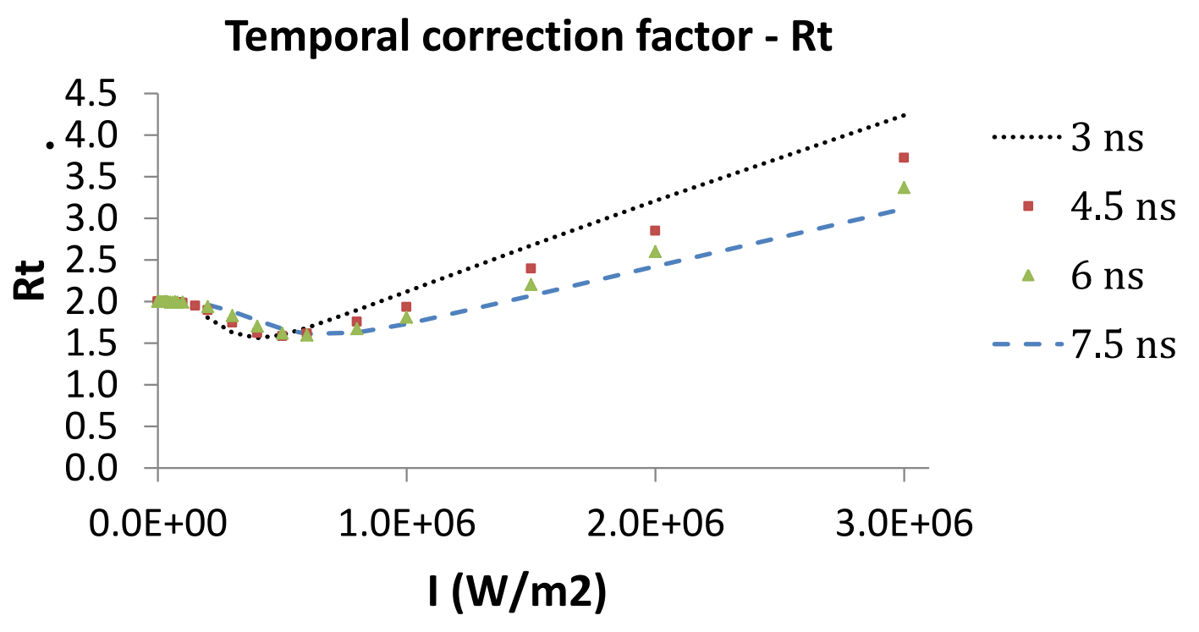
Two-photon Absorption Laser Induced Fluorescence (TALIF):

- When a laser of appropriate wavelength interacts with atomic oxygen density *[O]*, the photon density η_f produced by TALIF is given by:

$$n_f = \frac{A_{ij}}{A+Q}\frac{\sigma^{(2)}}{(hf)^2}G^{(2)}g(\omega)[O]\int_0^\infty {I_0}^2(t)dt$$

where A_{ij}: transition rate from upper level for $\lambda_{fluorescence}$, *A:* total transition rate from upper level, *Q:* quenching coefficient of upper level, *f:* laser frequency, $\sigma^{(2)}$: two-photon absorption cross section, $G^{(2)}$: photon statistic factor, $g(\omega)$: normalized line profile, $I_O(t)$: laser intensity.

- A rate model was developed that included, REMPI, ground state depletion and TALISE allowing η_f to be calculated for various laser intensities and pulse widths, including when saturation occurs.
- Photolysis can be turned on or off in the model → can find η_f for $[O]_{Cal}$ or [O](t).
- Taking the ratio $R_t = \frac{n_f(t)}{n_{Cal}}$ allows photolysis TALIF signal for a known $[O]_{Cal}$ be corrected for time varying [O] to allow comparison to TALIF signal from fixed atomic densities ⇒ calibrating the system.



R_t was calculated for a range of laser intensities and pulse widths and plotted in figure 2.
For our experiment: R_t = 1.97

Figure 2: R_t vs laser intensity at different laser pulse widths

$$[O] = \chi\frac{S_O}{R_t R_Z S_{Cal}}[O]_{Cal}$$

Where

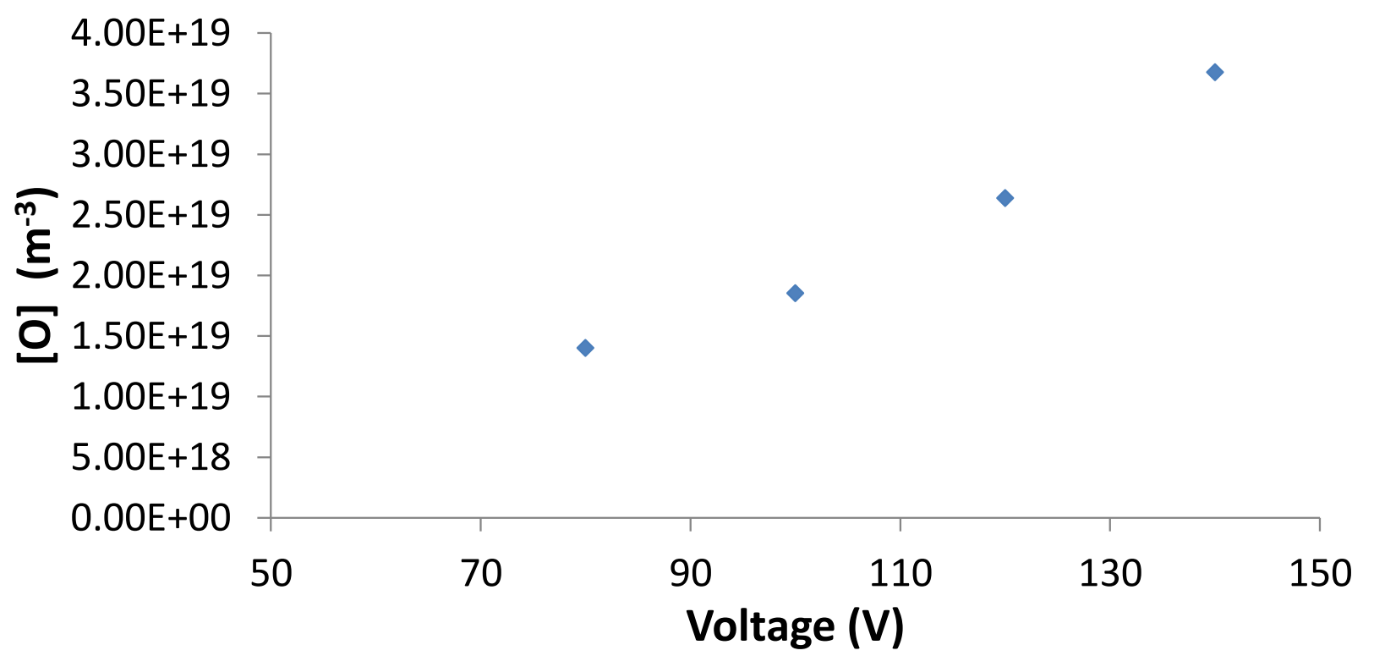
$$\chi = \frac{\cancel{T}_O}{\cancel{T}_O}\frac{\cancel{\eta}_O}{\cancel{\eta}_O}\frac{\cancel{\sigma}_O}{\cancel{\sigma}_O}\frac{\overset{.5563}{\cancel{a}_{21}{}^O}}{\cancel{a}_{21}{}^O}\left(\frac{\cancel{\chi}_O}{\cancel{\chi}_O}\right)^2 = 0.5563$$

S_O : TALIF signal integrated w.r.t. time and wavelength,
T: Transmission of optics,
η: Quantum efficiency of the detector,
a_{ij}: Branching ratio.
σ: Two-photon absorption cross section.

- Experimental set up identical for experiment and calibration ⇒ simple to implement.
- Both laser and fluorescence wavelengths are the same ⇒ most of the constants in χ cancel.
- The <u>*branching ratios a_{ij} are different*</u> due the difference in quenching coefficients.

Results:

- Plasma jet air flow turned on and the TALIF signal due to photolysis in the air flow recorded.
- The APPJ turned on, the RF power supply voltage increased from 80 V – 140 & TALIF signals recorded at each voltage.
- The air flow TALIF signal was subtracted from Plasma-On signal to get TALIF signal due to O produced by the plasma jet.
- The [O] number density was calculated using the photolysis calibration approach:



Discussion: -

- Atomic oxygen density is measured in an air atmospheric pressure plasma jet using TALIF
- A photolysis based scheme using O_2 in air is used to calibrate the system in-situ.
- Use of a single laser pulse to photo-dissociate the atmospheric O_2, and generate a corresponding TALIF signal to be used for calibration purposes.
- Account of the temporal & spatial variation in the [O] density generated by photolysis allows correction factors to be determined using a rate model equation.
- These correction factors allow valid comparison of photolysis TALIF signals to TALIF signals from static [O] populations such as in a plasma.
- The hot species produced by photolysis can lead to (i) enhanced quenching (ii) loss of species from the laser focal zone so need to take both of these effects into account.
- The results are plotted and show that [O] increases by a factor of ~ 3 as increase the voltage from 80 V – 140 V on the plasma jet system used.

<u>**Reference:**</u> "Two-photon absorption laser induced fluorescence measurement of atomic oxygen density in an atmospheric pressure air plasma jet". J Conway, GS Gogna, C Gaman, MM Turner & S Daniels. Plasma Sources Sci. Technol. **25** (2016) 045023

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