PRECISION
Strategic Research Cluster

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

J. Conway, G.S. Gogna, C. Gaman, M. M. Turner and S. Daniels

Introduction:

- In this work we use Two-photon Absorption Laser Induced Fluorescence (TALIF) to investigate atomic oxygen density [O] in an atmospheric pressure plasma jet which uses air as the gas source for the plasma. The RF power deposited into the plasma is varied by changing the voltage in the system power supply and the resulting atomic oxygen density is measured. The TALIF system is calibrated using photolysis to generate a known number density of atomic oxygen and measuring the resulting TALIF signal. Calibration typically involves using Xe gas to generate TALIF signals as it uses similar excitation and fluorescence wavelengths to the atomic oxygen TALIF scheme. However, Xe is an expensive gas to work with particularly if flowing it through an atmospheric plasma so in this work we use photolysis of atmospheric O_2 content to generate our calibration TALIF signal.

Photolysis:

- A laser is used to dissociate O_2 molecules producing a known atomic oxygen population. The laser pulse also interacts with these O atoms over the course of the pulse causing two-photon excitation. The resulting TALIF signal is recorded. The amount of [O] produced depends on the wavelength, photon fluence and molecular O_2 density $[O_2]$ the laser beam interacts with. The dissociation energy of O_2 is 5.17 eV so once the photon energy of the laser exceeds this value [O] will be generated.

- Single laser shot: λ = 225.6 nm (E_{photon} = 5.5 eV) Δt_{Laser} = 8 ns
  - → 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 ($\sim 10^{-13}$ - 10^{-14} s)
  - → Laser then excites these O atoms via 2-photon absorption → TALIF signal

- Photolysis [O] density:

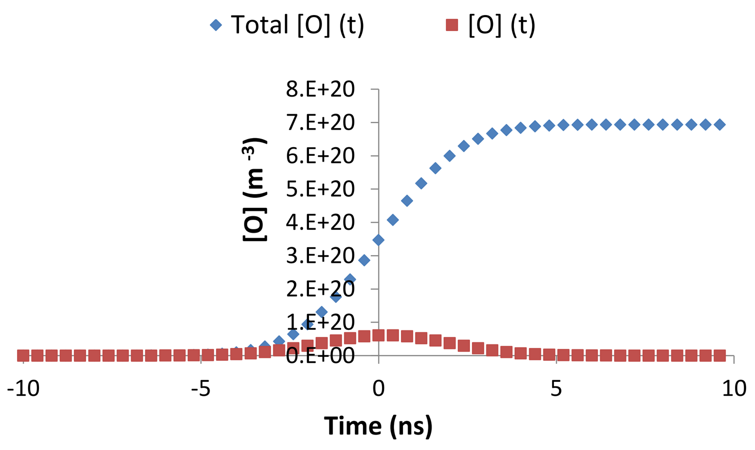
$$[O] = 2 \times [O_2](1 - \exp(-\sigma\phi))$$

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

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

- Laser pulse energy E_{pulse}: 1.2 mJ
- Laser Frequency f: 1.33×10^{15} Hz.
- Focal spot area A: 6.03×10^{-9} m^2.

As the resulting atomic oxygen density is a function of the laser energy, [O] will vary over the course of the laser pulse. The laser pulse has a Gaussian temporal behaviour so the resulting [O] generated will also vary in a Gaussian manner. Using atmospheric oxygen as our calibrating gas (atm. Pressure = 1.013×10^5 Pa, temperature = 300 K, humidity 0.45) the overall atomic oxygen density value at the end of laser pulse $[O]_{Cal}$ is 7.08×10^{19} m^{-3}.



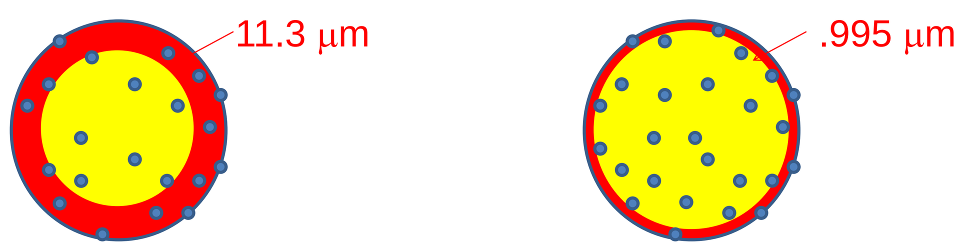
- The atomic O produced by photolysis are "hot".

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

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

- Δt_{Laser} = 8 nm ⇒ O_{hot} atoms travel ~ 11.3 μm while laser on so ~ 45 % of O_{hot} potentially lost from the focal zone over the duration of the laser pulse.

However due to the **small mean free path** at **atmospheric pressures** (~ 66 nm) the root mean square diffusion distance $x_{RMS} = \sqrt{4Dt}$ = 9.95×10^{-7} m so only ~ 4.5 % of the atomic O leave the focal zone over the duration of the laser pulse.



O atoms in the red zone can potentially leave the laser focal zone and so will not contribute to the TALIF signal recorded

- The hot oxygen atoms produced during photolysis will 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

Two-photon Absorption Laser Induced Fluorescence (TALIF):

- When a laser of appropriate wavelength interacts with a fixed atomic density n_O the photon density produced due to TALIF is given by the expression:

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

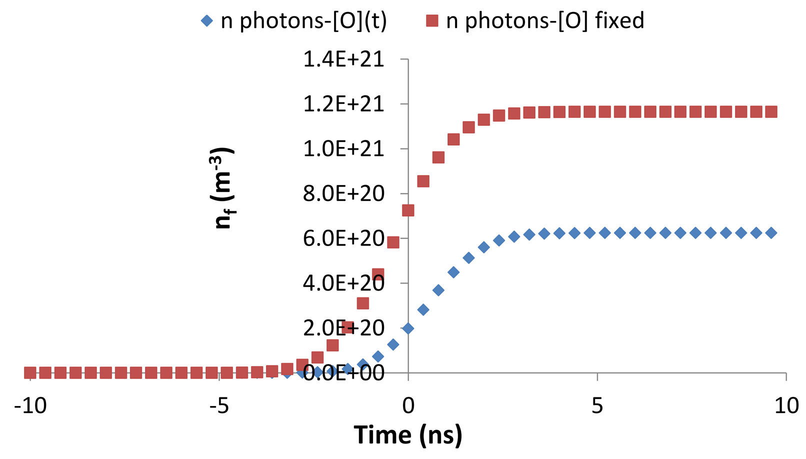
where A_{ij} is the transition rate of the upper level for the fluorescence wavelength, A is the total transition rate from the upper level, Q is the quenching coefficient of the upper level, f is the laser frequency, $\sigma^{(2)}$ is the two-photon absorption cross section, $G^{(2)}$ is the photon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

- In this work the oxygen density generated by the laser is a function of time (i.e. n_O(t)) so the above expression is modified to take account of this giving:

$$n_{f2} = \frac{A_{ij}}{A+Q}\frac{\sigma^{(2)}}{(hf)^2}G^{(2)}g(\omega)\int_0^\infty n_O(t) I_0{}^2 dt$$

If we take the ratio of the photon densities we get: $\frac{n_{f2}}{n_f} = \frac{\int_0^\infty n_O(t) I_0{}^2 dt}{n_O \int_0^\infty I_0{}^2 dt}$ = 0.5358

The fluorescence signal is reduced to 53.6 % due to the fact that [O] varies over the course of the laser pulse. Using this correction factor we can relate the TALIF signal S_{Cal} to the atomic oxygen density $[O]_{Cal}$ produced by photolysis and so calibrate the system.



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

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.

Where

$$\chi = \frac{T_O}{T_O}\frac{\eta_O}{\eta_O}\ \frac{\sigma_O}{\sigma_O}\ \frac{a_{21}{}^O}{a_{21}{}^O}\left(\frac{\lambda_O}{\lambda_O}\right)^2 = 0.5563$$

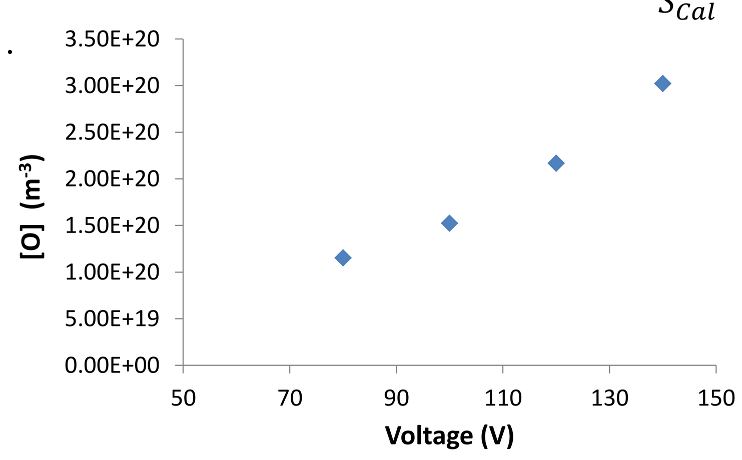
(.5563)

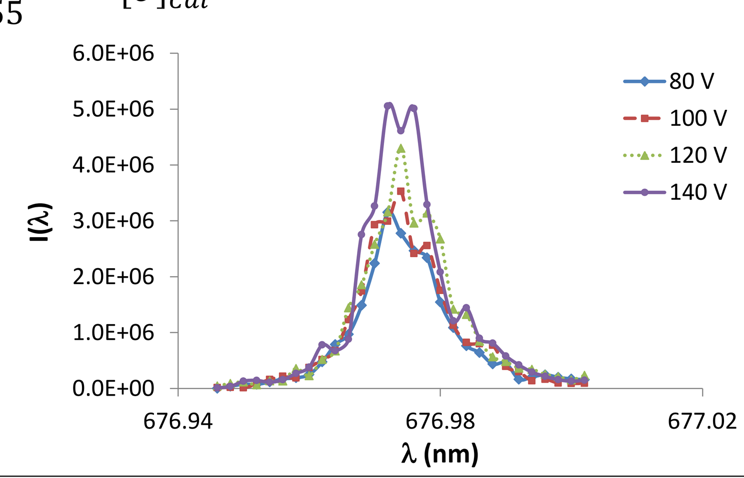
- As experimental set up (i.e. Laser, optics, cross section, detector efficiency etc.) identical for both the experimental and calibration stages using atomic O, this approach is much simpler than using Xe.
- As the fluorescence wavelength is the same for both the calibrated and measured species most of the constants in the ratio above cancel out.
- The branching ratios a_{ij} need to take account of the fact that the photolysis O is hotter than the O produced in the plasma so the quenching coefficients need to be corrected for this giving a branching ratio quotient of 0.5563.

Results:

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

$$[O] = \frac{S_O}{S_{Cal}}\frac{(0.5358)(0.5563)}{0.955}[O]_{Cal}$$





Discussion: -

- Atomic oxygen density is measured in an air atmospheric pressure plasma jet using TALIF
- Typically use Xe to calibrate the system but this is expensive.
- A photolysis scheme using O_2 in air is used to calibrate the system instead.
- By taking account of the temporal dynamics of the [O] density generated over the course of a laser pulse the same laser pulse can be used to both photo-dissociate the atmospheric O_2 and also to generate a TALIF signal that can be used for calibration purposes if know the local air pressure and temperature.
- 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.

Acknowledgement : *"This material is based upon works supported by the Science Foundation Ireland under Grant No.08/SRC/I1411."*