LIF investigations of O and NO products in air like RF plasma jet

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Abstract Laser induced fluorescence by one (LIF) and two photon (TALIF) excitation has been employed to characterize NO, O species in the expanded stream of N₂-O₂ air like low pressure plasma jet. The gas, excited in a coaxial RF capacitive discharge at pressure P₁, expands through a de Laval nozzle into a vessel at P₂=0.25 Torr at expansion ratio P₁/P₂ of about 35. The multiple expansion–compression waves of the jet are traced by laser induced fluorescence of NO and O dissociation products expanding through the nozzle. The quantitative O and NO densities, obtained by in-situ calibration of TALIF and LIF signals are discussed.

1. Introduction
Air like plasma jet expansions as sources of supersonic flows for laboratory experiments on the interaction with material targets used in thermal protection systems of the space shuttle for Earth atmosphere re-entry are still involving aerospace laboratories [1]. Aerospace testing facilities based on plasma jet, employ high enthalpy high Mach number supersonic flows (as an example several tens of MJ/Kg and Mach higher than 7) produced by arc discharge at high pressure (0.1-1 bar). Such huge devices and their operating condition are very complex from the point of view of microscopic, atomic and molecular, diagnostics [2]. On the other hand expanded flows through a supersonic nozzle are intrinsically non-equilibrium flows whatever is the discharge condition [3], this making diagnostics of non equilibrium systems very important [4]. In this context advanced laser diagnostics can be tested on non equilibrium features of small wind tunnel installation and then applied confidently to more hostile expanded flows plasma jet facilities. Here we consider low enthalpy air like plasma jets produced by a capacitively coupled low pressure (~10 Torr) radio-frequency discharge [3]. Such an installation, plasma jet and diagnostics, has been used in previous studies to characterize gas/plasma expansions fed by N₂/O₂/NO gas based mixtures [5-9]. Here we focus our attention on NO and O product species by measuring their axial and radial profiles by calibrated laser induced fluorescence by one (LIF) and two photons (TALIF) as well as on the behavior of some electronic state emissions of N₂ and NO by Optical emission spectroscopy (OES) with the aim to get insights on the presence of some energy carriers in the expanded flow.

2. Experimental
2.1 RF plasma jet installation
The RF plasma jet installation has been described in details in [5]. It is based on a discharge reactor (plasma source) ending with a stainless steel de Laval nozzle. Gas expanding through the nozzle in a low pressure chamber is pumped by root pump. The sketch of the discharge chamber is shown in figure 1. Essentially the discharge is located at the bottom of a stainless steel cylinder (length L= 500 mm and internal diameter d=40 mm) whose jacket is cooled by tap water. The plasma source is a capacitively coupled discharge with a co-axial RF electrode configuration driven under continuous and pulsed regime. The throat diameter of the nozzle is 4 mm while the convergent/divergent section lengths are respectively Lₐ =15 mm and Lₐ = 10 mm. The discharge region of plasma source is not accessible for diagnostics so the expansion region is investigated by a spectroscopic setup supporting computer controlled movements of both target and discharge holders.

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2.2 Spectroscopic measurements

An air like plasma jet has been investigated by a spectroscopy setup based on OES and LIF, not shown here, and described in detail in [5].

The plume investigated looks like that in the snapshot of figure 2 that refers to the condition in which the discharge reactor is fed at pressure $P_{1}^\text{OFF} = 7.1 \text{ Torr}$ with $\text{N}_2$/$\text{O}_2$ mixture ($\Phi_{\text{N}_2} = 780 \text{ sccm}$ and $\Phi_{\text{O}_2} = 220 \text{ sccm}$, i.e. mass flow rate $M_{\Phi}(\text{N}_2$–$\text{O}_2) = 2.09 \times 10^{-4} \text{ Kg/s}$) that expands into vessel kept at $P_{2}^\text{OFF} = 0.25 \text{ Torr}$. The nominal power delivered to the reactor is $W_0 = 215 \text{ watt}$. When the plasma is activated, $P_{1}^\text{ON}$ rises at 8.72 Torr while $P_{2}$ does not vary ($P_{2}^\text{ON} = P_{2}^\text{OFF}$). Under present experimental condition the Mach number is about 3, and the jet enthalpy about 1 MJ/Kg.

3. Results and discussion

3.1 NO Laser Induced Fluorescence

The detection of NO by laser induced Fluorescence has been done by exciting the (0,0) band of $\text{NO}_2$ ($A^{2}\Sigma_u^+ - X^{2}\Pi$) system and detecting fluorescence of (0,2) band. The laser has been tuned close to $\lambda_{\text{exc}} = 226.287 \text{ nm}$ (vacuum) with the excitation of $^6P_{3/2} + Q_1$ band head of $^2\Sigma^{-} - ^2\Pi_{1/2}$ sub band where the signal is very high and less sensitive to temperature variation. UV excitation photons are produced by third Harmonic generation of dye laser pumped by second harmonic of Nd-YAG laser. The laser line width is large to overlap several $J$ lines of various sub-band of $J$ manifold. LIF calibration has been operated in-situ by flowing a mixture of $\text{N}_2 + 0.3\% \text{ NO}$ in the vessel at 1 Torr.

The results allow the following remarks:

i. The axial profile at the distance $y = 10 \text{ cm}$ from nozzle (see figure 3) evidences a clear sequence of expansion-compression waves that are almost fully relaxed. Numerical simulations of $\text{O}_2$/NO cold expansion through this nozzle in [6] showed that at such a distance from nozzle exit a subsonic flow region is reached.
The radial profiles carried out by radial scans between x=1 cm and x=-2.5 cm evidence a centreline minimum at y-positions corresponding to expansion waves and a centreline maximum at y-positions corresponding to compression waves. The figure 4 shows one of such profiles measured at y= 2 cm (first compression wave). The radial hill, whose width is about ±0.5 cm, grows on a noisy broad baseline that declines for x>1.8 cm. The radial scan at y=10 cm on contrary does not evidence significant structures within the scattering (±15%) of data and NO centerline density at y=10 cm is pretty close to the value at x= -1 cm y= 2 cm. This fact would indicate a quite broad distribution of NO in the jet.

ii. Considering the background NO density, $[\text{NO}]_b \approx 1.5 \times 10^{12} \text{ cm}^{-3}$, measured at x=-2.4 cm, y=2 cm, representative of NO density in the background region (where $T_{\text{gas}} \approx 300 \text{ K}$, $P= 0.27 \text{ Torr}$, $N_{(N_2-O_2)} \approx 9.5 \times 10^{15} \text{ cm}^{-3}$), its fraction in $N_2$-$O_2$ mixture would be about 0.014%.

3.2 O-atoms Two Photon Laser Induced Fluorescence (TALIF)

TALIF measurement of O($^3P$) atoms and the in-situ calibration in plasma jet are described in details in [5, 6]. The two photon excitation-detection scheme is:

$$\text{O}(2p^3P_2) + 2h\nu_L \rightarrow \text{O}(3p^3P_2) \rightarrow \text{O}(3s^3S_1)+ h\nu_E$$

Where excitation is done at $\lambda_L = 225.58 \text{ nm}$ and detection at $\lambda_E = 844.6 \text{ nm}$. UV excitation photons are produced with the same laser configuration used for LIF measurements of NO. Detection is done by red-extended photomultiplier. The axial and radial profiles of O density, obtained upon TALIF calibration carried out as described in [6], shown in figures 5 and 6 offer the following insights:

i. The axial profile of O-atoms evidences the same expansion-compression structures of NO.

ii. The radial scan at various distance y from the nozzle instead reveals a different distribution of atoms in the jet section. A saddle profile with clear double maximum at $x \approx \pm 0.4 \text{ cm}$ is seen in the expansion region and single maximum in the compression wave region. The background is clearly reached at y= 0 cm x= -2 cm: $[\text{O}]_b \approx 3 \times 10^{12} \text{ cm}^{-3}$. Instead at y= 10 cm, x= -2.5 cm laser beam crosses the jet border: $[\text{O}]_b \approx 7 \times 10^{12} \text{ cm}^{-3}$.

iii. The fraction of O-atoms in the background gas, $[\text{O}]_b / N_{(N_2-O_2)}$, is about 0.03-0.07 % depending on the uncertainty of background values.

3.3 Optical Emission spectroscopy

Optical Emission Spectroscopy (OES) from plasma plume has been carried out trough a monochromator SPEX 500 using both Photomultiplier and ICCD detectors. The spectral window is set on the band head and the entrance slit of the monochromator is typically 0.2 x 1 mm$^2$. The recording of photomultiplier signal is by photon counter under computer control.

Figures 7 and 8 report the axial scan of the emission intensity of NO ($A^2\Sigma_u^+ -X^2\Pi$) (0.2) band of $\gamma$ system and of $N_2$ ($C^3\Pi_u -B^3\Pi_g$) (0.2) band of Second Positive system (SPS) respectively.
Figure 7. Axial scan of NO emission

Figure 8. Axial scan of N$_2$(SPS) emission

The expansion traced by such species shows a significant dynamic range difference. While NO$_\gamma$ shows clearly the structure of multiple expansion-compression waves, the decline of N$_2$(SPS) by four order of magnitude at 4 cm from nozzle masks them significantly. The positions of maxima and minima coincide with those seen by NO and O species in the ground state. Excited species like N$_2^*(C^3\Pi_u$ at the excitation threshold $E_{th}$ ~ 11 eV) and NO$^*(A^2\Sigma^+\nu$ at $E_{th}$ ~ 5.5 eV) give insights on the electrons and N$_2(A^3\Sigma_u^+)$ metastable precursors [3] as well as on nitrogen and oxygen collision processes. In air like mixture it is known that the density of N$_2(A^3\Sigma_u^+)$ is rather low [10] because of strong quenching by N, O, and O$_2$. The analysis of the vibrational distribution of N$_2(C^3\Pi_u)$ state confirms that in the plume even at long distance from nozzle (figure 8) N$_2$ electronic excitation occurs by electron impact from ground state. The excitation of NO$_\gamma$, that typically is by N$_2(A^3\Sigma_u^+)$ energy transfer [11], consequently has to occur by N+O+M recombination excitation.

4. Concluding remarks

The study has evidenced a plasma jet rich of structures observable both by Laser induce fluorescence and Optical Emission Spectroscopy investigations. Apart of the density measurements of NO and O, relevant species of air like plasma jet, by LIF and TALIF, the combined used of LIF and OES diagnostics has been seen useful to get insights on the active species in the jet. In the present RF plasma jet the presence of energetic electrons, likely sustained by plasma potential in the plume, has to be considered non negligible even at distance from nozzle as far as 4 cm. In the core of jet there is a significant density of O and NO products while in the background their fraction, about 0.05% and 0.014% respectively, is relatively low. The composition of gas in the background, due to recirculation of gas from bottom of chamber should represent a lower limit of jet gas composition if deactivation and recombination processes in the jet and in the background are negligible.

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