Measurements of ground state atomic nitrogen in high-pressure NRP discharges using fs-TALIF

C. Dumitrache , A. Gallant, G. D. Stancu and C. O. Laux

[1]*Laboratoire EM2C, CNRS, CentraleSupélec, Université Paris-Saclay, 91190 Gif-sur-Yvette, France*

Abstract: Measurements of ground state atomic nitrogen inside of a nanosecond repetitively pulsed (NRP) discharge operating at pressures between 0.1-5 bar were performed using a femtosecond two-photon absorption laser induced fluorescence (fs-TALIF) technique. The main goal of this research work is to develop a quench-free diagnostic technique which would allow measurements at high-pressure conditions (up to 10 bars).

Keywords: fs-TALIF, nanosecond discharges, spectroscopy, REMPI, quenching

1. Introduction

Efficient production of large amounts of nitrogen atoms is of importance for many industrial applications such as the enhancement of nitridation processes[1], the synthesis of novel nanomaterials[2] or biomedical treatment[3,4]. Moreover, it is also important to understand the high-pressure kinetic pathways that lead to atomic nitrogen production in plasma-assisted combustion in order to evaluate the plasma influence on NOx generation[5,6]. Despite the growing interest, measurements of the ground-state atomic nitrogen are challenging to perform because the excitation photon energy lies in the VUV range (λ =100-120 nm) which is not readily accessible by direct absorption spectroscopy. The present contribution is geared toward measurements of the ground-state population of atomic nitrogen in a nanosecond repetitive pulsed (NRP) discharge at pressures above 1 bar using fs-TALIF as a diagnostic tool.

It has been shown in the past that ns-TALIF is a reliable technique for measurements below several tens of millibars[7]. Above this pressure, de-excitation by collisional quenching becomes the major loss mechanism with a sub-nanosecond time scale [8]. Therefore, the main challenge of this study is to develop a "quenching-free" diagnostic technique in the pressure range of interest (p=1-10 bar) using a femtosecond laser as the excitation source.

2. Theory & Modelling

In a typical N-atom fs-TALIF experiment, a two-photon absorption scheme ($\lambda = 2 \times 206.6$ nm) is used to probe the ground state population of atomic nitrogen ($2p^3\ ^4S$) inside the discharge. The scheme involves the excitation of the 3p $^4S_{3/2}$ level with the subsequent fluorescence collection taking place from the radiative decay to the 3s ^4P triplet state around 745 nm. The main processes taking place during fs-TALIF are presented schematically in Fig. 1 below and include: two-photon absorption, $W_{1,2}^{(2\nu)}$, collisional and radiative decay (presented in Fig. 1 as a single term: $T_{i,j} = Q_{i,j} + A_{i,j}$), photo-ionization, $W_{2,3}^{(i)}$, and stimulated emission, $W_{2,1}^{(2\nu)}$.

A 3-level rate model based on the energy level diagram presented above is implemented in order to understand the influence of quenching on the measured signals.

The model includes the following rate equations:

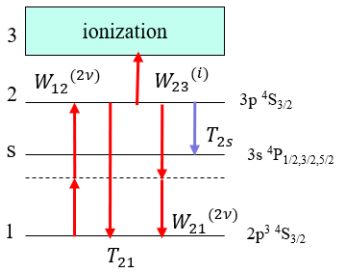

Figure 1: Energy level diagram for N-atom TALIF

$$\frac{dN_1}{dt} = -N_2 W_{12}^{(2\nu)} + N_1 W_{21}^{(2\nu)}$$

$$\frac{dN_2}{dt} = N_1 W_{12}^{(2\nu)} - N_2\left(W_{21}^{(2\nu)} + W_{23}^{(i)} + A_{2s} + Q_{2s}\right) \quad (1)$$

$$\frac{dN_3}{dt} = N_2 W_{23}^{(i)}$$

where the number of photons fluorescing at time t is given by:

$$n_{fl}(t) = \int_0^t A_{2s}\, N_2(t')dt \quad (2)$$

Using Eqs. (1)-(2), one can obtain the time evolution of the fluorescence signal as a function of laser intensity.

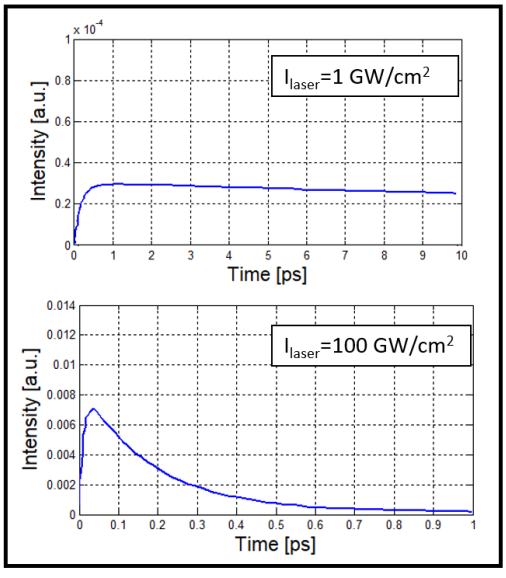

Figure 2: Time evolution of TALIF signal for I_{laser}=1GW/cm^2 (top) and I_{laser}=100GW/cm^2 (bottom)

The results shown in Fig. 2 for a pressure of 1 bar, suggest that, at low laser fluence (1 GW/cm^2), the fluorescence signal decays over a few tens of picosecond (see Fig. 2-top) following an exponential relation that depends of the Einstein coefficient for spontaneous emission and the collisional quenching rate:

$$N_2(t) = N_2(\tau)exp[-(A_{2s} + Q_{2s})t] \qquad (3)$$

This rate of decay predicted by the model renders impossible the measurement of quenching using a PMT and suggests that a quench-free diagnostic is desirable in high-pressure discharges. Interestingly, as the laser fluence is further increased (100 GW/cm^2), the fluorescence signal decays much faster (see Fig. 2-bottom) due to the presence of photo-ionization which acts to decrease the population of the excited state 3p $^4S_{3/2.}$ If the laser fluence is increased to the point in which the rate of depopulation of the excited state by 2+1 REMPI becomes much stronger than the rate of quenching, the fluorescence decays almost completely by the end of the laser pulse and the measurement becomes unaffected by quenching. A similar result was also indicated by Stancu for oxygen TALIF [9] using the density matrix approach which includes Rabi oscillations and Stark shifts. We should mention that the rate equation approach used here is precise only at low laser intensities. However, figure 2 captures qualitatively the significant reduction of the fluorescence time for the high intensity case. This result suggests that for $p > 1$ bar it is more convenient to operate in the saturated regime.

3. Experimental Setup

The optical layout used for the fs-TALIF experiment is presented in Fig. 1 below and will be only succinctly described here. A more detailed description of the femtosecond laser system used is given in one of our previous work[10]. The femtosecond laser pulses are produced by a Ti:Sapphire laser system (Spectra Physics Solstice ACE) which operates in the wavelength range λ = 780-830 nm. In its current configuration, the Solstice Ace system provides 100 fs pulses with an average pulse power ~7 Watts at a repetition rate of 1 kHz. The output beam of the Ti:Sapphire laser (λ = 828 nm) is frequency-quadrupled to reach the TALIF wavelength using a third harmonic stage (Spectra Physcs TP-1A-THG) followed by a fourth harmonic stage (Spectra Physics TP-1A-FHG). The fourth harmonic is selected at the laser exit using a pair of dichroic mirrors and a prism before being sent inside of the reactor using an f=100 mm lens. Finally, the fluorescence signal is collected using an f/2.8 lens and imaged onto a spectrometer (Acton SP-500i) that is operated with a 250 µm entrance slit.

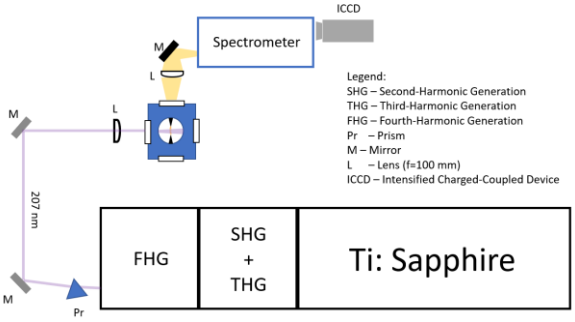

Figure 3: Optical Layout used for fs-TALIF experiments

The NRP discharges are produced with a FID FPG20-30MKS50 high-voltage pulse generator. The generator can deliver pulses of up to 20 kV, with a pulse length tunable between 10-50 ns at a maximum repetition rate of 30 kHz. The maximum current attained in NRP discharges is about 50 A giving a typical pulse energy absorbed into the gas of about 10 mJ.

4. Results

In a typical ns-TALIF experiment the time integrated fluorescence signal is proportional to the square of the laser intensity if the laser intensity is low enough (the unsaturated regime). However, a much lower dependency on laser intensity was observed experimentally for fs-TALIF in atomic nitrogen over a range of laser fluences between 1-4 TW/cm^2 (see Fig. 4). The reported $I^{0.98}$ dependence is indicative of additional loss channels such as 2+1 REMPI and (possibly) stimulated emission.

To complement these observations, significant emission from free/free transitions (or bremsstrahlung emission) has also been observed experimentally with the spectrometer after the plasma background has been subtracted. This gives a further indication that photoionization induced by the laser is indeed present in fs-TALIF. It should be noted that a laser pulse duration of 100 fs with a focused spot size of ~100 μm yields a laser peak intensity on the order of ~1 TW/cm^2. This is much higher than the typical intensities required to achieve 2+1 REMPI even with nanosecond laser pulses [11]. In order to perform N-atom TALIF measurements in the quench-free regime at elevated pressure one has to operate in conditions of high laser fluence which means that photoionization and stimulated emission need to be carefully considered.

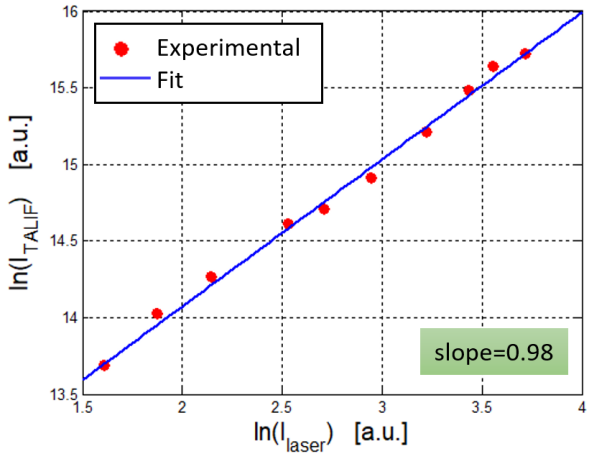

Figure 4: Fluorescence signal as a function of laser intensity for atomic nitrogen. This x-axis corresponds to a range of fluences I_{laser}=1-4GW/cm^2 (100 fs pulse, w_0=50 µm)

The atomic nitrogen fluorescence signal decay after the discharge is shown at various pressures (p=0.1-2 bar) in Fig. 5 below. The signal is initially stronger as the pressure increases. This is because there is more molecular nitrogen available to be dissociated in the discharge. However, the signal decays faster with time at higher pressure due to the faster three-body recombination of atomic nitrogen to form in particular N_2(B)[12–14]. An interesting finding is that the TALIF signal stays relatively constant between 10-60 µs (and even longer at low pressures). Over this range of time delays, the recombination is counter-balanced by the increase in ground state population through collisional de-excitation of atomic nitrogen excited states (N(^{2}P), N(^{2}D) and N(^{4}D),in particular) [12,15]

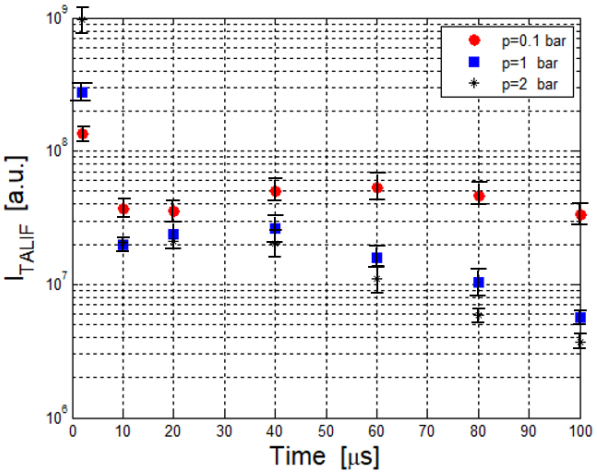

Figure 5: Atomic nitrogen TALIF signal evolution in time for various pressures inside of an NRP discharge (V_{disch}=15 kV)

The highest pressure in which fs-TALIF signal was collected so far corresponds to 5 bar and was limited by the window thickness on the reactor and the ability to supply the voltage required to generate breakdown at higher pressures. As shown from Fig. 6, all three transitions of the triplet are still visible at 5 bars and the signal-to-noise level is still reasonably high at 5 bars (SNR_{742nm}=6.7, SNR_{744nm}=14,SNR_{746nm}=31.4) indicating that it is possible to further increase the pressure once the chamber is adapted for higher pressure operation and the pulse voltage is augmented.

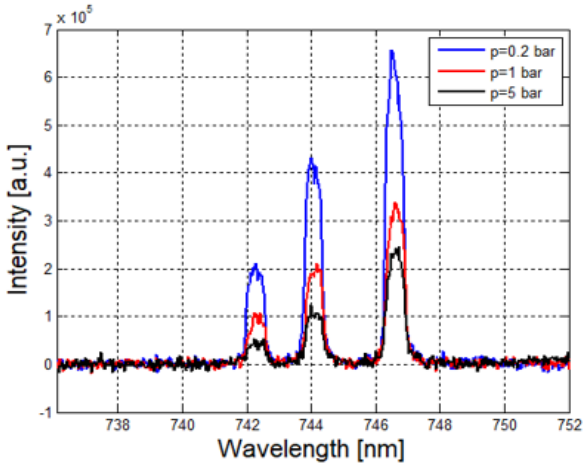

Figure 6: Fluorescence signal for atomic nitrogen at three different pressures (V_{disch}=15 kV).

5. Conclusions

In this study, we demonstrate the ability to perform measurements of the ground state atomic nitrogen ($2p^3\ ^4S$) generated by dissociation of N_2 in an NRP discharge us fs-TALIF. The main finding is that fluorescence signal can be successfully collected for pressures as high as 5 bars with the ability to extend the range further in the future. It is reported here that the fluorescence signal is affected by saturation due to the high laser fluence of the femtosecond laser system (I_{laser} ~ 1 TW/cm^2). Numerical modeling predicts this result and suggests that a quench-free diagnostic can be obtained as long as the rate of photo-ionization is much higher than collisional quenching de-excitation.

Future work will further develop the fs-TALIF technique presented in order to provide quantitative information by using an atomic nitrogen calibration cell as a calibration source. Moreover, the technique will be expanded to provide temporally resolved 2-D spatial mappings of the atomic nitrogen inside the NRP discharge at pressures up to 10 bar.

6. Acknowledgements

This research was funded by French National Research Agency, ANR, Project ASPEN ANR-16-CE30-0004 and IdF-SESAME, project DIAGPLAS .

7. References

[1] Cho C, Kinemuchi Y, Suematsu H, Jiang W and

Yatsui K, *Japanese* J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap. **42** 1763–5 (2003)
[2] Pai D Z, Ostrikov K K, Kumar S, Lacoste D A, Levchenko I and Laux C O, *Sci. Rep.* **3** 1–7 (2013)
[3] Noli F, Pichon L and Öztürk O, Metall. Mater. Trans. A Phys. Metall. Mater. Sci. **49** 1383–96 (2018)
[4] Liu R, Li X, Hu X and Dong H, Surf. Coatings Technol. **232** 906–11 (2013)
[5] Uddi M, Jiang N, Adamovich I V. and Lempert W R, J. Phys. D. Appl. Phys. **42** (2009)
[6] Sun W and Ju Y, *J. Plasma Fusion Res.* **89** 208–19 (2013)
[7] Dobele H F, Mosbach T, Niemi K and Schulz-Von Der Gathen V, Plasma Sources Sci. Technol. **14** (2005)
[8] Agrup S, Ossler F and Aldén M, Appl. Phys. B Lasers Opt. **61** 479–87 (1995)
[9] Stancu G D, Spectroscopy and Spectroscopic: measurement techniques for aerospace flows ed D Giordano and Y Babou (Von Karman Institute) (2014)
[10] Dumitrache C, Gallant A, Stancu G D and Laux C O, AIAA 2019-1507 (2019)
[11] Dumitrache C, Butte C, Eickelberg A and Yalin A P, AIAA 2018-1431 (2018)
[12] Popov N A, Plasma Phys. Reports **39** 420–4 (2013)
[13] Levaton J, Amorim J, Souza a R, Franco D and Ricard A., J. Phys. D. Appl. Phys. **35** 689–99 (2002)
[14] Amorim J, IEEE Trans. Plasma Sci. **33** 368–9 (2005)
[15] Volynets A V, Lopaev D V, Chukalovsky A A, Mankelevich Y and Popov N A, Artic. J. Phys. D Appl. Phys. **51** 364002 (2018)