Pressure dependence of the nitrogen atom recombination probability in late afterglows

B Rouffet, F Gaboriau, J.-P. Sarrette

► To cite this version:

B Rouffet, F Gaboriau, J.-P. Sarrette. Pressure dependence of the nitrogen atom recombination probability in late afterglows. *Journal of Physics D: Applied Physics*, 2010, 43 (18), pp.185203. 10.1088/0022-3727/43/18/185203 . hal-00569594

HAL Id: hal-00569594

<https://hal.science/hal-00569594>

Submitted on 25 Feb 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Pressure dependence of the nitrogen atom recombination probability in late afterglows

B Rouffet³, F Gaboriau^{1,2} and J P Sarrette^{1,2,4}

¹ Université de Toulouse, UPS, INPT ; LAPLACE (Laboratoire Plasma et Conversion d'Energie) ; 118 route de Narbonne, F-31062, Toulouse cedex 9, France

² CNRS ; LAPLACE, F-31062, Toulouse cedex 9, France

³ Laboratoire d'Electronique des Gaz et des Plasmas, Université de Pau et des Pays de l'Adour, F-64000, Pau, France

⁴ Author to whom any correspondence should be addressed

E-mail : jean-philippe.sarrette@laplace.univ-tlse.fr

Abstract. Atomic nitrogen recombination probabilities (γ_N) are presented for different materials. They were obtained in late afterglow conditions through a comparison between local measurements of the nitrogen atom density with TALIF (Two-photon Absorption Laser Induced Fluorescence) and atomic concentration profiles calculations at the vicinity of substrates. A comparison is also made between a spatially resolved technique (TALIF) and a non-spatially resolved one (based on optical emission spectroscopy) for the measurement of the N-atom concentration. For each of the studied materials, an inverse pressure dependence of γ_N was observed, while the obtained data were found to be in good agreement with previously published values, derived from surface temperature measurements.

Keywords : Afterglow, Atomic recombination, Nitrogen atoms, TALIF.

PACS : 52.70.Kz – Optical measurements; 82.33.Xj – Plasma reactions

1. Introduction

In flowing nitrogen afterglows at reduced pressure, large amounts of nitrogen atoms are created in the discharge or in the short-lived (pink) afterglow during collisions of nitrogen molecules with electrons, vibrationnally excited nitrogen molecules and metastable states [1-2].

As the atomic recombination process is highly exothermic, the excess energy transported by the atoms must be transferred either to a third body (if reaction takes place in the gas phase) or to a surface (if recombination occurs at the wall). At low pressure (typically below 2.5 kPa), the probability for a 3-body collision tends to be lower than the wall recombination probability γ , ratio between the number of atoms effectively recombining at the surface over the number of atom / wall collisions. As both probabilities are low, nitrogen atoms can be transported over large distances allowing separating the production zone to the treatment zone where milder processing conditions can be reached. Treatment reactors usually run far away from the discharge, in the Lewis-Rayleigh afterglow (also called nitrogen late afterglow, NLA), characterized by a visible emission in the yellow part of the spectrum, associated with the recombination of the nitrogen atoms in the gas phase. Such low-pressure flowing nitrogen afterglows systems are of particular interest in numerous applications such as nitridation [3-4], material processing [5] or bacteriological decontamination [6-7].

Surface recombination was extensively studied in the past but the methods used were either based on non-local N-atom concentration measurements (NO titration [8-9], mass spectrometry [10], first

positive intensity temporal decay [11-13]) or based on indirect data such as the electrical temporal behaviour of successive discharges [14-15] or the wall temperature increase due to the heat deposited during heterogeneous recombination [16-18]. This can explain the large discrepancies in the γ values published in the literature and the lack of knowing of γ variations with the operating parameters (pressure, gas temperature, wall temperature), even for the most commonly used materials.

This paper presents a method for obtaining the atomic nitrogen recombination probabilities (γ_N) on different materials. It is based on the comparison between direct local measurements of the nitrogen atom density by the TALIF (Two-photon Absorption Laser Induced Fluorescence) technique and calculations of atomic density profiles at the vicinity of the substrates submitted to the NLA flow.

2. Experiment

2.1. Flowing afterglow system

A cylindrical Pyrex reactor ($\phi = 160$ mm, $h = 300$ mm, figure 1) was filled with pure nitrogen at controlled mass flow rate in the range ($Q_{N_2} = 0.1$ -3.0 slm). The vacuum in the chamber was obtained through a primary pump (Edwards two stage rotary vane pump $30 \text{ m}^3 \text{ h}^{-1}$) and the pressure was regulated by a valve allowing modifying the diameter of the pumping orifice.

The discharge was created with a microwave surfatron generator working at a frequency of 2450 MHz for an injected power P_{MW} adjustable between 50 and 300 W.

The length L of the discharge tube (quartz, $\phi_i = 5$ mm) can also be modulated between 20 and 60 cm in order to reach different afterglow conditions [19]. All the results presented in the present paper were obtained with $L = 450$ mm and for pressures higher than 0.67 kPa, providing full NLA conditions.

The connection between the discharge tube and the reactor is realized through an injector (quartz, $\phi_i = 15$ mm, $l = 92$ mm) ensuring a correct mixing between the afterglow flow and the Ar/2%NO injection during NO titration.

Figure 1 : Schematic diagram of the flowing afterglow and of the fluorescence detection system used for TALIF measurements. A : location of the spectroscopic measurements (NO titration and I_{580nm}). The embedded figure shows the modified injection system used for TALIF measurements at the reactor inlet, the distance L being conserved between both configurations.

The top of the reactor is a removable window which allows the installation of plates (10 cm x 10 cm, $t = 5$ mm) of different materials on four Pyrex supports.

2.2. Measurement of the nitrogen atoms concentration

NO titration, optical emission spectroscopy and TALIF were used to measure the N-atom density at the reactor inlet (A point, figure 1) while the atomic concentration profiles in the empty reactor and close to the plates were only obtained with the TALIF technique. For the TALIF measurements at the reactor inlet, the afterglow injection system was modified as is shown embedded in figure 1, the distance between the surfatron and the measurement point being kept constant (54 cm).

2.2.1. Spectroscopic methods. The two spectroscopic methods mentioned below allow obtaining the absolute (NO titration) and relative (I_{11-7}^{580nm}) nitrogen atoms concentrations. Both are non-local since the intensity emitted by the afterglow is collected in a cone corresponding to the solid angle of aperture of the optical fiber.

2.2.1.a. NO titration. With this method, described in details by Ricard *et al.* [20], an Ar-2%NO gas mixture is added to the NLA flow in the injector (figure 1). For low nitric oxide flow rates ($[NO] < [N]$), oxygen atoms are produced by reaction (1):

The produced O-atoms react with the remaining nitrogen atoms to create the excited $NO(B^2\Pi)$ state (reaction (2)), giving rise to the violet emission of the NO_β system (reaction (3)):

When the nitric oxide flow rate exceeds the nitrogen atom flow rate ($[NO] > [N]$), all the nitrogen atoms of the afterglow have been eliminated from the flow and reaction (2) cannot occur. The oxygen atoms then react with the remaining nitric oxide (reaction (4)) to produce the $NO_2(A)$ excited state, emitting the NO_2 continuum (green emission, reaction (5)):

The atomic nitrogen density is obtained at the extinction point, where no emission is observed, corresponding to equal added NO and N flow rates (figure 2).

Figure 2 : Dependence of the NO(B) and NO₂* intensities measured at point A with the Ar-2%NO flow rate added to the afterglow ($Q_{N_2} = 0.5$ slm, $p = 2.67$ kPa).

2.2.1.b. Nitrogen first positive emission intensity. The NLA emission is dominated by the $N_2(B, v'=11) \rightarrow N_2(A, v''=7)$ band of the first positive system at 580 nm [21], correlated to the 3-body recombination process (reaction (6), with the rate constant $k_{vol} = 3.0 \cdot 10^8 \exp(500/T) \text{ m}^6 \text{ kmole}^{-2} \text{ s}^{-1}$ taken from Krivonosova [22]) :

As the $N_2(B, v'=11)$ state can desexcite either radiatively to the A state with a global frequency ν_{rad}^{11} or collisionally by quenching with the nitrogen molecules (k_q^{11}), the emitted intensity can be written :

$$I_{11-7}^{580nm} \propto [N_2(B, v'=11)] \propto \frac{k_{vol}[N]^2[N_2]}{\nu_{rad}^{11} + k_q^{11}[N_2]} \quad (7).$$

With the values $\nu_{rad}^{11} = 1.7 \cdot 10^5 \text{ s}^{-1}$ and $k_q^{11} = 5 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, taken from Gordiets [23], it appears that the evolution of the N-atom concentration can be followed monitoring I_{11-7}^{580nm} for pressures higher than 133 Pa ($k_q^{11}[N_2] \gg \nu_{rad}^{11}$) :

$$[N] \propto (I_{11-7}^{580nm})^{0.5} \quad (8).$$

2.2.2. TALIF

Laser-induced fluorescence is based on the forced transition from a low energy state E_1 of a given species (atom or molecule) to a radiative higher energy state E_2 with a laser tuned to the wavelength equal to the energy difference between the two states ($\Delta E_{exc} = E_2 - E_1 = h \nu_{laser}$). The fluorescence signal is emitted during the radiative desexcitation of the E_2 state to a third state of lowest energy E_3 ($\Delta E_{flu} = E_2 - E_3 = h \nu_{flu}$) [24].

The duration of the laser pulse (8 ns) being much shorter than the lifetime of the excited state E_2 , the mechanisms of population and depopulation of this state can be temporally separated, allowing the

determination of the concentrations of the excited state E_2 and of the initial state E_1 , often identified with the ground state of the chemical species.

The intensity of the fluorescence signal, directly proportional to the density of the ground state, is usually observed in an optical axis different from the incident laser beam.

Unlike classical spectroscopic methods only providing information on the population of the radiative states, LIF methods give access to the ground states densities. They also have the advantage of high temporal and spatial resolutions, the laser energy being deposited in a controllable defined volume.

However, when the excitation threshold (energy of the first radiative state) is large (greater than 6 eV), which is the case for most of the light atoms (H, N, O), the excitation wavelength of the laser requires the use of VUV photons ($\lambda < 200$ nm), more complex to use (absorbed by the air, they require to be transported in a nitrogen atmosphere). It is then preferable to use the TALIF technique, associated with a 2-photon excitation scheme (figure 3), whose wavelengths are greater than 200 nm [25].

Figure 3 : Energy levels of the two-photon excitation and fluorescence mechanisms of atomic nitrogen and krypton.

In the laser system used in this work, the second harmonic of a Nd-YAG laser (532 nm) was used to pump a dye laser (619 nm). This output frequency was tripled by two non-linear crystals (BBO and KDP) to obtain the excitation wavelength at 206.65 nm. The laser beam (of pulse energy about 50 μ J) was then focused into the afterglow reactor, equipped with 8 Brewster angle windows at different heights to allow the passage of the laser beam without reflection. The fluorescence signal was collected perpendicularly to the laser beam, passed through a narrow band filter (to avoid interferences with the natural radiation of the afterglow) and focused by two lenses on the entrance slit of a HAMAMATSU (R 928) PMT, before amplification and averaging (figure 1).

Figure 4 : Axial and radial evolutions of the fluorescence signal.

In the direction perpendicular to the laser beam, the size of the excitation volume is about the size of the beam ($\cong 1$ mm). As the radial and axial evolutions of the fluorescence signal are similar (figure 4), one can infer that the axial extension of the excitation volume is also about 1 mm. This spatial resolution is sufficient enough to obtain a precise mapping of the atomic concentrations, even near the walls, where density profiles are more pronounced. The uncertainty on TALIF measurements is mainly due to fluctuations of the laser energy, corresponding to an uncertainty lower than 15% on the N-atoms relative density.

By introducing krypton (without flow) into the afterglow reactor at a controlled pressure P_{Kr} and at a fixed temperature T , it is possible to deduce the absolute concentration of the nitrogen atoms from the fluorescence ratio of the two species [26] :

$$[N] = \frac{K_{826.3nm}^{Kr}}{K_{745nm}^N} \cdot \frac{a_{23}^{Kr}}{a_{23}^N} \cdot \frac{\sigma_{Kr}^{(2)}}{\sigma_N^{(2)}} \cdot \left(\frac{\nu_N E_N}{\nu_{Kr} E_{Kr}} \right)^2 \cdot \frac{I_{826.3nm}^{Kr}}{I_{745nm}^N} \cdot \frac{P_{Kr}}{k_B T} \quad (9)$$

where I is the intensity of the fluorescence signal, ν is the laser excitation frequency, E is the deposited laser energy, σ is the two-photon absorption cross section, a_{23} is the optical branching ratio and K is the detection sensitivity.

This expression can be used if no change is made in the acquisition system between calibration and measurement and under the condition that the two-photon excitation schemes of the two species are similar (figure 3). For nitrogen and krypton, coefficients a_{23} and σ were taken from Niemi [26].

2.2.3. Model

For typical operating conditions ($p > 0.67$ kPa, $T = 300$ K, $Q_{N_2} = 0.5$ -1.0 slm), the Knudsen number of the afterglow flow is much less than unity and the Reynolds number is about 250. Continuity equations can then be used to simulate the behaviour of the nitrogen flow. Steady state laminar transport equations (for momentum, heat and mass fractions) closed by the ideal gas law were solved in the actual 3D geometry taking into account the eventual presence of the sample plates, using the Fluent software, as exposed in detail in a previously published paper [17].

At the reactor entrance, the boundary condition for the concentration of the nitrogen atoms was deduced from the $(I_{11-7}^{580nm})^{0.5}$ measurements normalized with TALIF at 0.67 kPa (see below).

In such conditions, the conservation equation of the nitrogen atoms can be written as :

$$\nabla \cdot (\rho \vec{u} m_N - D_{N/N_2} \rho \vec{\nabla} m_N) = S_N . \quad (10)$$

Here, ρ and $\vec{u}$ are the gas density (in kg m^{-3}) and the gas velocity (in m s^{-1}), m_N and D_{N/N_2} are respectively the mass fraction (adimensional) and the diffusion coefficient (in $\text{m}^2 \text{s}^{-1}$) of the N atoms in molecular nitrogen while S_N is the source term (in $\text{kg m}^{-3} \text{s}^{-1}$) for the atomic species due to chemical reactions.

D_{N/N_2} was here derived from the classical kinetic theory of gases [27], considering a Lennard-Jones (12-6) interaction potential between the two colliding species.

In full NLA conditions, S_N is reduced to the atomic nitrogen losses due to recombination mechanisms in the gas phase (reaction 6) and at the walls, assuming a first order reaction:

The corresponding rate coefficient (in s^{-1}) was obtained using the expression:

$$K_{\text{surf}} = \gamma_{\text{N/wall}} v_{\text{th}} \left(\frac{\text{Surf}}{4 \cdot \text{Vol}} \right), \quad (12)$$

where $\gamma_{\text{N/wall}}$ is the N-atom recombination probability on the wall, v_{th} is the mean thermal velocity of the atoms and Surf and Vol are respectively the surface on which the atoms can recombine and the volume of the reactor. Relation (12), established by Chantry [28] for an ideal diffusion limited flow is yet valid for the studied afterglow flow as the diffusion limit is greater than the radius of the reactor, the whole spatial distribution of the nitrogen atoms being modified when considering wall recombination on the reactor walls or on the plates.

In the results presented below, the $\gamma_{\text{N/wall}}$ value was used as a parameter in the model, allowing fitting the calculated N-atom density spatial repartition with the measured profiles.

3. Results and discussion

3.1. N-atom concentration in the empty reactor

Figure 5 shows the evolution with pressure of the absolute N atom density obtained at the reactor inlet by TALIF and NO titration. Densities deduced from equation (8) and normalized with the TALIF concentration at 0.67 kPa are also given. All measurements show an increase of the N-atom density with pressure, following the variation already obtained in the discharge by actinometry [18].

Figure 5 : Absolute N-atom concentrations measured at the reactor inlet by TALIF and NO titration for $Q_{\text{N}_2} = 0.5$ slm and $P_{\text{MW}} = 100$ W. Densities obtained from $(I_{11-7}^{580\text{nm}})^{0.5}$ and normalized with the TALIF value at 0.67 kPa are also shown for comparison.

While the evolutions given by TALIF and deduced from $(I_{11-7}^{580\text{nm}})^{0.5}$ are in good agreement, values given by the NO titration technique are somewhat greater. This overestimation can be explained by mixing problems between the titration gas flow and the afterglow flow.

Nitric oxide is a potentially dangerous gas. For safety, it is mixed in low proportion (2%) with an inert gas, argon. For nitrogen dissociation rates less than 1%, as the ones obtained in the NLA with our operating conditions, the Ar/2%NO flow necessary to obtain the extinction point is less than the half

of the afterglow flow. The NO titration method assumes a perfect mixture between the NO flow and the afterglow flow, but this condition is not always fulfilled, as illustrated by the three pictures of figure 6 obtained for a 1 slm nitrogen flow rate and an operating pressure of 0.67 kPa (the afterglow is flowing from right to left and the titration gas is injected by the small tube at the top). Three flow regimes can clearly be identified looking at the grey zone (green in the electronic colour version, corresponding to the $\text{NO}_2(\text{A})$ emission, reaction (5)). For low Ar-2% NO flow rates (0.1 slm, picture a), the NO flow does not penetrate the afterglow, it even seems to flow upstream. For intermediate flow rates (0.2 slm, picture b), a part of the NO flow is penetrating the afterglow while another part is sheathing it. The mixture is incomplete and one must inject more NO than necessary to obtain the extinction point, conducing to an overestimation of the N-atom density. For higher Ar-2% NO flow rates (0.3 slm, picture c), the mixing is correct and complete, the extinction can be obtained downstream the NO injection.

To validate the model, concentration profiles were first calculated in the empty afterglow reactor (without plates) and compared with the N-atom densities measured by TALIF in the four observation windows (Table 1 and figure 7).

Figure 6 : Photographs of the mixing zone between the (Ar-2% NO) gas flow arriving from the top and the afterglow, flowing from the right to the left of the pictures. ($Q_{\text{N}_2} = 1$ slm, $p = 0.67$ kPa).

a) Q (Ar-2% NO) = 0.1 slm : poor mixing; b) Q (Ar-2% NO) = 0.2 slm : uncomplete mixing; c) Q (Ar-2% NO) = 0.3 slm : correct mixing.

Table 1 : Absolute [N]-atom concentrations measured and calculated (assuming no recombination on the Pyrex walls of the reactor) at the reactor inlet and at the intersection between the afterglow axis and the reactor axis. $Q_{\text{N}_2} = 0.5$ slm, $P_{\text{MW}} = 100$ W.

p (kPa)	0.67	1.33	2.00	2.67	3.33	4.00
$[N]_{\text{inlet}}^{\text{TALIF}} (10^{14} \text{ cm}^{-3})$	10.0	14.3	16.3	17.6	17.9	17.8
$[N]_{\text{centre}}^{\text{TALIF}} (10^{14} \text{ cm}^{-3})$	5.2	6.9	6.9	6.2	5.7	5.3
$[N]_{\text{centre}}^{\text{calc}} (10^{14} \text{ cm}^{-3})$ with $\gamma_{\text{N/Pyrex}} = 0$	5.5	6.5	6.5	6.1	5.2	4.6

In the pressure range studied, a maximum of the N-atom density is observed in the reactor around 2.0 kPa contrarily to what was found at the reactor inlet (figure 5). Atomic losses are important in the reactor (around or higher than 50%), due to the increase of the residence time, as the flow velocity decreases (for example, for $Q_{\text{N}_2} = 1.0$ slm and $p = 0.67$ kPa, the maximum velocity is higher than 50 m s^{-1} at the inlet and less than 2 m s^{-1} in most of the reactor). Above 2.0 kPa, the decrease in the N-atom density is related to the rapid increase of the gas phase recombination processes (reaction 6).

Absolute experimental and calculated atomic concentrations are in good agreement. It is also shown that calculated axial density profiles are weakly influenced by the chosen value of the recombination

probability on the Pyrex walls of the reactor. As TALIF measurements were performed far from the walls, they cannot be used to obtain accurate values of the recombination probability of the nitrogen atoms on the Pyrex walls of the reactor. It can only be concluded that the $\gamma_{N/Pyrex}$ value is low, probably ranging between 10^{-4} and 10^{-5} , in agreement with values obtained by different authors in similar NLA conditions [9-10].

Figure 7 : Comparison between the TALIF measurements of the [N]-atom density and the calculated profiles along the reactor axis for different $\gamma_{N/Pyrex}$ values ($Q_{N_2} = 0.5$ slm, $p = 4.0$ kPa, $P_{MW} = 100$ W).

Data are normalized at the C point, located at the intersection between the afterglow axis and the reactor axis.

Figure 8 : [N]-atom density profiles calculated on the reactor axis between the plate and the C point for different values of $\gamma_{N/plate}$. ($Q_{N_2} = 0.5$ slm, $p_{N_2} = 2.67$ kPa and $\gamma_{N/Pyrex} = 10^{-5}$)

3.2. N-atom concentration with the plates

When a plate of a given material is introduced in the reactor, the spatial distribution of the [N]-atoms is modified. Figure 8 gives the absolute atomic concentration profiles calculated on the axis of the reactor between the plate and the C point for various $\gamma_{N/plate}$ values.

The diameter of the TALIF windows (20 mm) allows measuring the density profiles on the first 15 mm above the plates, where density variations are the most pronounced. $\gamma_{N/plate}$ were thus obtained by adjusting the calculated profiles with the measured ones (normalized at the distance $d = 15$ mm above the plate, figure 9). Considering the normalized calculated profiles shown in figure 10, this method presents an excellent sensitivity for materials having recombination probabilities between 10^{-3} and 10^{-5} .

Figure 9 : Normalized [N]-atom density profiles measured by TALIF on the reactor axis at the vicinity of a brass plate for different pressures. ($Q_{N_2} = 1.0$ slm and $\gamma_{N/Pyrex} = 10^{-5}$)

Figure 10 : Comparison between the normalized [N]-atom profiles calculated close to the brass plate with different $\gamma_{N/brass}$ values and the TALIF measurements. ($Q_{N_2} = 1.0$ slm, $p_{N_2} = 2.67$ kPa and $\gamma_{N/Pyrex} = 10^{-5}$)

3.3. Pressure dependence of γ_N recombination probabilities

Figure 11 shows the variation of γ_N with pressure for the four materials studied (Pyrex, alumina, aluminium and brass). Since the N-atom density in the reactor is presenting a maximum when the pressure increases, it is demonstrated that γ_N depends on pressure and not on the flux of atoms at the surface.

Figure 11 : Evolution with pressure of the N-atom recombination probabilities γ_N obtained using TALIF profiles for Pyrex, aluminium, brass and alumina. Values previously obtained from surface temperature measurements [17] are indicated.

The obtained inverse pressure dependence is similar to the one previously deduced from measurements of the surface temperature of materials submitted to the afterglow flow [17]. It is also consistent with the heterogeneous recombination theory [16, 23] and the results of Cartry [29] and Guerra [30] showing that both Eley-Rideal and Langmuir-Hinshelwood mechanisms contribute to surface recombination for pressures around 0.13 kPa. When the pressure increases, the number of collisions between the gas phase species and the surface increases, preventing the physisorbed atoms to diffuse at the surface to reach chemisorptions sites. The behaviour observed in figure 11 can therefore be interpreted as the decrease of the influence upon wall recombination of Langmuir-Hinshelwood processes. The asymptotic limit is reached when the pressure independent Eley-Rideal processes remain the only ones to contribute to surface recombination.

The agreement between the γ_N values given independently by TALIF profiles and surface temperatures is good for brass and alumina and acceptable for aluminum. Table 2 compares the γ_N values here determined with typical literature values (no data was found for brass).

Table 2 : Nitrogen atoms heterogeneous recombination probabilities of the literature.

Material	Reference	p (kPa)	γ_N	This work
Alumina	[2]	0.19-0.48	$1.6 \cdot 10^{-3}$	$> 3.5 \cdot 10^{-4}$
Aluminium	[6]	0.67	$1.0 \cdot 10^{-3}$	$5.5 \cdot 10^{-4}$
Quartz	[12]	0.4-4.67	$5 \cdot 10^{-4}$ - $7 \cdot 10^{-6}$	$8 \cdot 10^{-5}$ - $2 \cdot 10^{-5}$
Quartz	[3]	1.50	$2.1 \cdot 10^{-5}$	$3 \cdot 10^{-5}$
Silica	[4]	0.03	$2.0 \cdot 10^{-4}$	$> 8 \cdot 10^{-5}$
Pyrex	[1]	0.08-0.56	$3.2 \cdot 10^{-6}$	$> 8 \cdot 10^{-5}$
Pyrex	[13]	0.4	$1.0 \cdot 10^{-5}$	$> 8 \cdot 10^{-5}$

5. Conclusions

Local (TALIF) and non-local (NO titration, I_{11-7}^{580nm}) methods were used to determine the N-atom concentration at the inlet of a flowing afterglow reactor. While similar results were obtained with TALIF and I_{11-7}^{580nm} , NO titration was shown to overestimate the N-atom density, due to incomplete mixing between the titration gas and the afterglow flow.

TALIF density profiles were also measured in the reactor and at the vicinity of surfaces of different materials, allowing deducing nitrogen atoms wall recombination probabilities. The determined γ_N values are in correct agreement with the data available in literature and show an inverse pressure dependence, as previously obtained using the heat transferred to the surface during wall recombination.

References

- [1] Guerra V, Sá P A and Loureiro J 2004 *Eur. Phys. J. Appl. Phys.* **28** 125
- [2] Levaton J, Amorim J, Souza A R, Franco D and Ricard A 2002 *J. Phys. D: Appl. Phys.* **35** 689
- [3] Oseguera J, Castillo F, Gomez A and Fraguela A 2006 *Thin Solid Films* **515** 1197
- [4] Belmonte T, Jaoul C and Borges J N 2004 *Surf. Coat. Technol.* **188-189** 201
- [5] Canal C, Molina R, Erra P and Ricard A 2006 *Eur. Phys. J. Appl. Phys.* **36** 35
- [6] Cousty S, Villeger S, Sarrette J P, Ricard A and Sixou M 2006 *Eur. Phys. J. Appl. Phys.* **34** 143
- [7] Villeger S, Sarrette J P, Rouffet B, Cousty S and Ricard A 2008 *Eur. Phys. J. Appl. Phys.* **42** 25
- [8] Vorob'ev V P, Kovtun V V and Kudryavtsev N N 1989 *Kinetics and Catalysis* **30** 1155
- [9] Belmonte T, Lefèvre L, Czerwiec T, Michel H and Ricard A 1999 *Thin Solid Films* **341** 27
- [10] Yamashita T 1979 *J. Chem. Phys.* **70** 4248
- [11] Young R A 1961 *J. Chem. Phys.* **34** 1292
- [12] Brennen W and E C Shane 1971 *J. Phys. Chem.* **75** 1552
- [13] Hays G N, Tracy C J and Oskam H J 1974 *J. Chem. Phys.* **60** 2027
- [14] Marković V Lj, Petrović Z Lj and Pejović M M 1994 *J. Chem. Phys.* **100** 8514
- [15] Pejović M M, Risti G S, Milosavljević S and Pejović M M 2002 *J. Phys. D: Appl. Phys.* **35** 2536
- [16] Kim Y C and Boudart M 1991 *Langmuir* **7** 2999
- [17] Sarrette J P, Rouffet B and Ricard A 2006 *Plasma Process. Polym.* **3** 120
- [18] Gaboriau F, Cvelbar U, Mozetic M, Erradi A and Rouffet B 2009 *J. Phys. D: Appl. Phys.* **42** 055204
- [19] Boudam M K, Saoudi B, Moisan M and Ricard A 2007 *J. Phys. D: Appl. Phys.* **40** 1694
- [20] Ricard A, Moisan M and Moreau S 2001 *J. Phys. D: Appl. Phys.* **34** 1203
- [21] Noxon J F 1962 *J. Chem. Phys.* **36** 926
- [22] Krivonosova O E, Losev S A, Nalivaiko V P, Mukoseev Y K and Shatalov O P 1991 *Reviews of Plasma Chemistry* vol 1, ed B M Smirnov (New York: Consultants Bureau) p 9
- [23] Gordiets B and Ricard A, 1993 *Plasma Sources Sci. Technol.* **2** 158
- [24] Amorim J, Baravian G and Jolly J 2000 *J. Phys. D: Appl. Phys.* **33** R51
- [25] Bischel W K, Perry B E and Crosley D R 1981 *Chem. Phys. Lett.* **82** 85
- [26] Niemi K, Schulz-von der Gathen V and Döbele H F 2001 *J. Phys. D: Appl. Phys.* **34** 2330
- [27] Hirschfelder J O, Curtiss F E and Bird R B 1954 *Molecular Theory of Gases and Liquids* New York: Wiley
- [28] Chantry P J 1987 *J. Appl. Phys.* **62** 1141
- [29] Cartry G, Magne L and Cernogora G 2000 *J. Phys. D: Appl. Phys.* **33** 1303
- [30] Guerra V and Loureiro J 2004 *Plasma Sources Sci. Technol.* **13** 85