Revisited Kinetics of the Short Lived Afterglow of a nitrogen microwave discharge

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1. Introduction

Nitrogen discharges and afterglows at pressures of a few hundreds of Pascal have been very extensively studied in the past two decades. However, most of the experimental works are based on emission spectroscopy and so far no overall description of the plasma together with the kinetics of the neutral species has been reported. Modeling the discharge itself is now routinely achieved through numerical codes [1] but analysis of the afterglow is much more complicated. Indeed, due to the absence of energetic electrons, the kinetics of the afterglow is mainly dominated by neutral energy-carrier species like vibrationally excited ground state molecules, N atoms and metastable molecules. In particular, the case of the well-known Short Lived Afterglow (SLA) of a µ-wave discharge, also called the Pink afterglow, is of primary interest. The most intriguing peculiarity of the SLA, that is expected to be free from the µ-wave field that sustains the discharge, is the appearance of a very bright molecular emission after the dark space that follows the discharge zone.

In an effort to obtain a better understanding of the neutral-neutral reactions responsible for the formation of the SLA, several diagnostic techniques have been implemented in the same flow tube to probe the axial dependence of the density of neutral species N(^4S) and N_2(Å^3Σ_u^+) but also of the electrons resulting from ionisation processes in the afterglow. The absolute ground state nitrogen atom N(^4S) density is determined by means of an original calibration method based on Two-photon Absorption Laser Induced Fluorescence (TALIF) spectroscopy [2]. The Intra-Cavity Laser Absorption Spectroscopy (ICLAS) [3] was shown as a powerful approach to directly determine the N_2(Å^3Σ_u^+) absolute density and also the gas temperature, with a very high sensitivity [4]. Additionally, a first determination of the absolute electron density by microwave interferometry was completed. Supported by the set of data obtained under the same experimental conditions, a simple kinetic model is proposed and discussed to account for the observed behaviors of the different species density.

2. Experimental

The Pyrex discharge tube (l=1.70 m, φ=3.8 cm) is basically the same that described in [4]. N atoms and N_2(Å^3Σ_u^+) metastable molecules are generated in flowing nitrogen ("U" grade, Air Liquide) by a microwave discharge resonant cavity at 433 MHz. The gas pressure, measured by a Pirani gauge, is 440 Pa while the flow rate is 1.5 slm. This results in a flow velocity, before the discharge zone, of 5 m/s. The microwave power supplied to the µ-wave cavity is 300 W and the reflected power is negligible. The flow tube is extended by two arm-tubes at right angle which are closed at both ends with Brewster angle windows (total length of the arm-tubes: l=42 cm, φ=2 cm). This tube has been either inserted inside the ICLAS system (see Fig. 1) or adapted to detect the fluorescence induced by two-photon (207 nm)
laser radiation in the same region [2]. The TALIF signal was calibrated through the fluorescence yield of krypton. The space resolution is obtained by translating the microwave cavity. Measurements were performed from 4 cm from the centre of the discharge zone (region where the power is transmitted to the plasma) to about 50 cm (late afterglow).

3. Results

- **Gas temperature**: Gas temperature is deduced from the Boltzmann distribution of populations in rotational levels of the $N_2(A^3\Sigma_u^+; v=0)$ metastable state. This rotational temperature, $T_r$, is about 950 K in the end of the discharge zone ($z=4$ cm), drops quickly to about 550 K at the minimum of the emission intensity in the SAL ($z \sim 12$ cm) and then decays slowly to reach room temperature in the late afterglow ($z \geq 50$ cm). Translational temperatures, measured from the Doppler width of the isolated rotational lines, are in quite good agreement with $T_r$ values [5]. The Doppler temperature of N atoms, deduced from TALIF measurements, suffers from a large uncertainty in the early afterglow ($z \leq 10$ cm) and seems to show a radial temperature gradient close to the discharge zone.

- **N atoms density**: As shown in Fig. 2, N density slowly increases from the discharge zone and reaches a plateau of about $3 \times 10^{21}$ m$^{-3}$ at long distances, following almost a $1/T_g$ law as a result of the gas flux conservation. This clearly points out that in the afterglow of our system the flux of N atoms is conserved and suggests that both creation and lost mechanisms of N are of little importance [2].

- **$N_2(A^3\Sigma_u^+)$ density**: The space-dependent density of $N_2(A^3\Sigma_u^+; v=0)$ metastable molecules, is shown in Fig. 2. Density of $N_2(A^3\Sigma_u^+)$ molecules is about $5 \times 10^{17}$ m$^{-3}$ in the end of the discharge zone ($z=4$ cm) and then continuously decays by almost two orders of magnitude to reach a minimum at $z=12$ cm before monotonically increasing to a secondary maximum of $5 \times 10^{16}$ m$^{-3}$ around $z=19$ cm. It then slowly decays to the longer distances. This density essentially follows the same trend as the emission intensity from $N_2(B^3\Pi_g)$ state, also shown in Fig. 2 [5]. It is clearly seen that for $z>12$ cm these molecules are locally formed in the SLA and not carried to this region by the gas flow. Production of $N_2(A^3\Sigma_u^+)$ molecules
from the three body N atom volume recombination, as well as by collisional processes involving high vibrational levels of the ground state N₂(X,v) molecules have been analyzed. We propose a strong coupling of the N₂(A³Σ_u⁺) state with the N₂(X,v≥8) molecules through N(²P) metastable atoms following reactions [5]:

\[
\begin{align*}
N₂(A³Σ_u⁺) + N(4S) &→ N₂(X¹Σ_g⁺,v) + N(²P) \quad (1) \\
N(²P) + N₂(X¹Σ_g⁺,v≥8) &→ N₂(A³Σ_u⁺) + N(4S) \quad (2)
\end{align*}
\]

Acting together, this pair of reactions recycles N₂(A³Σ_u⁺) molecules and results in an effective quenching rate of N₂(A³Σ_u⁺) molecules much slower than if only reaction (1) was considered. The initial decay of the density in the early afterglow (z<10 cm) can perfectly be explained by these reactions. The rising edge of the SLA for z>12 cm is attributed mainly to the enhancement of the production rate of the excited nitrogen molecules by three body atom-atom recombination. This results from the increase of the N atom and gas densities, due to the temperature drop, and also the enhancement of the three body recombination coefficient with decaying temperature. A partial contribution from N₂(X¹Σ_g⁺,v≥25) molecules is also possible. The final decay of N₂(A³Σ_u⁺) molecules, for z>20 cm, is probably due to the depletion of N₂(X¹Σ_g⁺,v≥8) molecules that reduces the contribution of reaction (2) and consequently increases the effective quenching rate of the N₂(A³Σ_u⁺) molecules.

![Image](image-url)

**Electron density**: The space dependence of the electron density, measured by microwave interferometry, is almost similar to that of the excited molecules and shows also a pronounced minimum at z=12 cm and reaches a maximum of 6 x 10^{15} m⁻³ around z=19 cm. Possible processes for this local ionisation, in the absence of any electric field, could be binary collisions of electronically excited molecules, and/or of vibrationally excited ground state molecules in the v''≥30 levels.

**Fig. 2** – Axial variation of N₂(A³Σ_u⁺; 0) and N (⁴S) densities in the SLA of a 440 Pa, nitrogen µ-wave discharge. Note different scales. Is also shown the emission intensity of the 1⁰ positive band.

**References:**