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Absolute ground-state nitrogen atom density in a N₂/CH₄ late afterglow: TALIF experiments and modeling studies

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Running Title: Absolute ground-state nitrogen atom density in a N₂/CH₄ late afterglow

Abstract

Following a first study on a late afterglow in flowing pure nitrogen post-discharge, we report new TALIF (Two-photon Absorption Laser-Induced Fluorescence) measurements of the absolute ground-state atomic nitrogen density N(⁴S) and investigate the influence of methane introduced downstream from the discharge by varying the CH₄ mixing ratio from 0 up to 50%. The N(⁴S) maximum density is about $2.2 \times 10^{15} \text{ cm}^{-3}$ in pure N₂ for a residence time of 22 ms and does not change significantly for methane mixing ratio up to ~ 15%, while above, a drastic decrease is observed. The influence of the residence time has been studied.

A kinetic model has been developed to determine the elementary processes responsible for the evolution of the N(⁴S) density in N₂/CH₄ late afterglow. This model shows the same decrease as the experimental results even though absolute density values are always larger by about a factor of 3. In the late afterglow three-body recombination dominates the loss of N(⁴S) atoms whatever the CH₄ mixing ratio. For high CH₄ mixing ratio, the destruction process through collisions with CH₃, H₂CN and NH becomes important and is responsible for the observed decrease of the N(⁴S) density.

1. Introduction

Reactive plasmas and post-discharges (afterglows) generated in pure N_2 and in $\text{N}_2\text{-CH}_4$ gas mixture are commonly used in surface treatments like nitriding and iron nitrocarburizing [1-3]. High pressure plasma experiments using spark [4] and corona discharges [5-6] and low pressure plasma experiments using glow [7-9], radiofrequency [10-11] or microwave discharges [12-13] have been employed to reproduce the complex organic chemistry occurring in Titan's atmosphere which is mainly composed of nitrogen with a few percents of methane. According to the authors [12-13], microwave discharge plasma experiments seem to be very promising for the simulation of the processes occurring in Titan's atmosphere. Fujii and Arai [12] have used CH_4 gas premixed with N_2 while Pintassilgo and Loureiro [13] presented a kinetic model for the afterglow of a pure N_2 flowing microwave discharge with 2 % CH_4 added in the post-discharge. The advantage of the latter method is given by the possibility to vary the time at which CH_4 is added in the afterglow. A large variety of species known to be present in the atmosphere of Titan were detected [13]. In the same publication, the results of a numerical simulation based on a self-consistent kinetic model are presented and discussed for discharge frequencies of 433, 915 and 2450 MHz, N_2 pressure ranging from 0.2 to 1 Torr and for CH_4 introduction times ranging from 10^{-5} to 10^{-3} s.

The present paper reports the results of a similar plasma study performed in the frame of a new program of Titan's laboratory simulations (SETUP, a French acronym for Experimental and Theoretical Simulation useful for Planetology) [14-16]. Using TALIF (Two-photon Absorption Laser-Induced Fluorescence) spectroscopy, we studied the influence of the amount of methane on the $\text{N} (^4\text{S})$ density and its variation as a function of both the discharge power and the residence time. Comparisons with numerical simulations are also presented using the same kinetic model mentioned above. Implications of this work on the development of our program of Titan's simulations conclude this paper.

2. Experimental arrangement

2.1. Plasma source

The apparatus generating the microwave plasma with its post-discharge shown in figure 1 is similar to the one presented elsewhere [17]. Briefly, the nitrogen microwave plasma discharge is obtained in a quartz tube through a surfatron device connected to a microwave generator at 2.45 GHz with a maximum output of 300 W. The quartz tube (8 mm external diameter, 6 mm internal diameter and 50 cm of length) is cooled by an air gas flow and connected to a post-discharge reactor of 20 cm in diameter. This chamber is evacuated to about 10^{-4} Pa by means of a turbo-molecular pump backed by a primary rotary pump. The N_2 (high purity 99.9998%) flow rate going through the discharge varies between 100 and 500 sccm (standard cm^3 per min). The N_2 gas pressure inside the post-discharge reactor is fixed at a value between 1 and 45 Torr in order to optimize the $N(^4S)$ atomic density [17]. Up to 23 Torr of CH_4 are injected perpendicularly to the nitrogen flow in the post-discharge reactor.

2.2. Optical system and $N(^4S)$ atom detection and quantification

Among the optical diagnostics that can be used to determine $N(^4S)$ density in afterglow, the Two-photon Absorption Laser-Induced Fluorescence (TALIF) spectroscopy is very effective. This technique allows measuring the $N(^4S)$ absolute density when completed by krypton calibration measurements [17-20]. TALIF can also provide temporal and spatial resolution [21]. Details of the apparatus to generate the UV photons needed for the TALIF measurements have been described elsewhere [17]. A Q-switched Nd:YAG laser (repetition rate=10 Hz, pulse-width duration=8 ns) with second harmonic generation at 532 nm is used to pump a dye laser system of RhB/Rh101 mixture in ethanol. The output which maximum of efficiency is observed at 615 nm is doubled and tripled using (KDP) and (BBO) crystals generating UV photons at 206.7 and 204.3 nm with a maximum energy of 4 mJ. Those wavelengths permit two photons

excitation of nitrogen ($\text{N } (2p^3 \text{ } ^4S_{3/2}) \rightarrow \text{N } (3p \text{ } ^4S_{3/2})$) and krypton ($\text{Kr } (4p^6 \text{ } ^1S_0) \rightarrow \text{Kr } (5p' \text{ } [3/2]_2)$). The fluorescence signals are observed between 742 and 746 nm and at 826.3 nm respectively corresponding to $\text{N } (3p \text{ } ^4S_{3/2}) \rightarrow \text{N } (3s \text{ } ^4P_{1/2,3/2,5/2})$ and $\text{Kr } (5p' \text{ } [3/2]_2) \rightarrow \text{Kr } (5s' \text{ } [1/2]_1)$. The photons are imaged perpendicularly to the laser beam by a lens system to the interferential filter placed in front of a photomultiplier tube detector. The time-resolved fluorescence signal is averaged and recorded by means of an acquisition system. In our study, we assume that the ground state of both species (N and Kr) at low UV energy is unchanged. Also, the photo-ionization processes by the absorption of a third photon as well as the amplified stimulated emission are negligible [22]. In these conditions, the absolute nitrogen atom density n_N can be determined from the ratio of the integrated fluorescence signal (S) from N (4S) atom to that of Kr ($4p^6 \text{ } ^1S_0$) at a known gas density n_{Kr} [17-20]:

$$n_N \propto n_{Kr}(S_N / S_{Kr}) \quad (1)$$

In our investigation, the calibration procedure has been performed in pure Kr with a density of $8.3 \times 10^{16} \text{ cm}^{-3}$. The lifetimes of the Kr and N species and their quenching coefficients (Kr with Kr and N with N_2 and CH_4) are taken from Niemi et al. [18].

3. Experimental results

TALIF measurements have been carried out as a function of the energy of the pulse laser in various experimental conditions (figure 2): (a) with pure N_2 (b) 2% CH_4/N_2 and (c) with pure Kr for the calibration procedure. At low laser energy, the slope of the linear fit in log-log plot is (2.0 ± 0.1) , in agreement with a two-photon absorption process. Saturation is observed at higher energy, above 150, 210 and 65 μJ respectively for measurements (a), (b) and (c). In order to avoid any saturation, all nitrogen and Kr measurements have been carried out respectively at 120 and 40 μJ .

The measurements of N (4S) density as a function of the microwave discharge power are presented in figure 3 for different percentages of methane: (2%, 10% and 20%). Results obtained in pure N_2 are also

displayed for comparison. All curves show the N (⁴S) density increasing with the microwave power and reaching a plateau above 90 W. We have therefore chosen in the following measurements a discharge power of 100 W in order to optimize the nitrogen density value. Note that the maximum density in pure N₂ reaches $2.2 \times 10^{15} \text{ cm}^{-3}$ and the addition of methane lowers this value down to $0.9 \times 10^{15} \text{ cm}^{-3}$ for a methane mixing ratio of 20%.

Figure 4 shows the measured absolute N (⁴S) density obtained at fixed discharge power (100 W) as a function of the methane mixing ratio for different flow rate (sccm)/pressure (Torr): 500/22, 200/16 and 100/12 (i.e. corresponding to residence times of 22, 41 and 61 ms respectively). As already described in [17], the N (⁴S) density decreases with the increasing residence time. The addition of CH₄ in the late afterglow induces no significant effect on the N (⁴S) atomic density up to about 15% confirming and extending the results obtained by Pintassilgo et al [3] for a CH₄ proportion less than 1% in N₂. For larger methane mixing ratio (above 15%), a rapid decrease of the N (⁴S) atomic density is observed. To understand this behavior, the kinetic model presented in [3, 13] is adapted for our experimental conditions as described in the following paragraph.

4. Model

4.1. Description

The calculations are based on self-consistent solutions of the homogeneous electron Boltzmann equation coupled to a system of rate balance equations for the most important neutrals and charged species produced inside the pure nitrogen microwave discharge. The end of the discharge occurs when electron density reaches the critical value of $3.74 \times 10^{11} \text{ cm}^{-3}$ (calculated at 2.45 GHz and for a quartz tube) [3, 23]. The concentrations of the various active species determined at this moment are used as initial conditions for the modelling of the post discharge. The evolution of the system in the early afterglow is calculated by considering the relaxation of the same system of master balance equations. The introduction of methane into the post-discharge at 25 cm downstream from the end of the discharge (see figure 1) can then be

modeled by solving a system of time-varying kinetic rate-balance equations for different species produced in a N_2 - CH_4 gas mixture. The model for the active discharge region takes into account the vibrationally excited states of molecular nitrogen ($N_2(X^1\Sigma_g^+, v)$), the electronically excited states of molecular nitrogen ($N_2(A)$, $N_2(B)$, $N_2(C)$, $N_2(a')$, $N_2(a)$, and $N_2(w)$), both ground and excited states of atomic nitrogen ($N(^4S)$, $N(^2D)$, and $N(^2P)$) and the N_2^+ and N_4^+ ions. In addition to those species, the master equations used to describe the mixture in the post-discharge region consider the CH_4 fragments together with species produced by reactions with N_2 (see references [8] and [13] for further details). The model also includes surface reactions, in particular the wall recombination probability for the nitrogen atoms which is equal to 2.1×10^{-4} (referred below in table 2 as d6) as determined in our recent publication [17].

4.2. Results and discussion

Model results are presented in figure 4 and compared to experimental ones. They are systematically a factor of 3 larger than the experimental data. This can be due to the fact that the flow rates are so important that stationary conditions are not reached at the end of the discharge. Consequently, the absolute $N(^4S)$ density is critically dependent on the initial conditions taken at the beginning of the afterglow. In contrast, the experimental and theoretical curves show a very similar behaviour towards the increasing methane mixing ratio.

Reaction name	Processes
p1	$N(^2P) + N_2(X^1\Sigma_g^+, v=0) \rightarrow N(^4S) + N_2$
p2	$N_2(X^1\Sigma_g^+, 10 < v < 25) + N_2(X^1\Sigma_g^+, 10 < v < 25) \rightarrow 2 N(^4S) + N_2(X^1\Sigma_g^+, v=0)$
p3	$N(^2P) + N(^4S) \rightarrow 2 N(^4S)$
p4	$N(^2P) + N_2(X^1\Sigma_g^+, v \geq 10) \rightarrow N(^4S) + N_2(A^3\Sigma_u^+)$
p5	$N_2(A^3\Sigma_u^+) + N_2(X^1\Sigma_g^+, 15 \leq v \leq 19) \rightarrow 2 N(^4S) + N_2$

Table 1. Main populating mechanisms of $N(^4S)$ atoms under the conditions of the present work

Reaction name	Processes
d1	$N(^4S) + N(^4S) + N_2 \rightarrow N_2 + N_2 (B)$
d2	$N(^4S) + N_2 (A^3\Sigma_u^+) \rightarrow N_2 (X^1\Sigma_g^+, 6 \leq v \leq 9) + N(^2P)$
d3	$N(^4S) + CH_3 \rightarrow H_2CN + H$
d4	$N(^4S) + H_2CN \rightarrow HCN + NH$
d5	$N(^4S) + NH \rightarrow N_2 (X^1\Sigma_g^+, v=0) + H$
d6	$N(^4S) + wall \rightarrow \frac{1}{2} N_2 (X^1\Sigma_g^+, v=0)$

Table 2. Main depopulating mechanisms of N (⁴S) atoms in the conditions of the present work

In order to explain the observed evolution of the N (⁴S) density as a function of the methane mixing ratio in the range 0 - 50%, we have identified the contribution of the main reactions of production (table 1) and loss (table 2) of this specie. Figure 5 (a) presents the relative contribution of the different N (⁴S) production processes calculated for a residence time of 22 ms (corresponding to a flow rate of 500sccm and pressure of 22 Torr) as a function of the methane mixing ratio. The production of N (⁴S) atoms is mainly due to collisions between metastable N (²P) and N₂ (X ¹Σ_g⁺,v) (reaction p1), and the reaction between two molecules N₂ (X ¹Σ_g⁺,10<v<25) (reaction p2). The latter process becomes the major pathway above 15% of methane while p1 decreases and becomes less important. In comparison to p1 and p2, the contributions of the other reactions (p3, p4 and p5) are always negligible. The decrease of p1 results essentially from the fact that N₂ (A ³Σ_u⁺) is strongly quenched by methane during the afterglow through reactions N₂ (A ³Σ_u⁺) + CH₄ -> N₂ (X ¹Σ_g⁺,v) + CH₃+H and -> N₂ (X ¹Σ_g⁺,v) + CH₂+H₂. Hence, as the amount of methane introduced into the post-discharge increases, the population of N₂ (A ³Σ_u⁺) decreases. This also leads to a decrease of the concentration of N (²P) since this species is mostly produced via the reaction N(⁴S) + N₂ (A ³Σ_u⁺) -> N₂ (X ¹Σ_g⁺, 6≤v≤9) + N (²P) (designated by d2 in table 2).

Figure 5 (b) presents the relative contribution of N (⁴S) loss processes as a function of the methane mixing ratio for the same residence time and pressure than the previous figure. We can observe that the three body recombination (reaction d1) is predominant but decreases slowly when CH₄ is added. The collisions of N (⁴S) with N₂ (A ³Σ_u⁺) (reaction d2) is the second most important pathway and also decreases when the

CH₄ mixing ratio increases. Three other depopulating processes, reactions d3, d4 and d5, correspond to collisions of N (⁴S) with CH₃, H₂CN and NH which are produced by the dissociation of CH₄ reacting with metastable N₂ (A ³ Σ_u⁺) and N (²D) atoms (see [3] for details). Note that the contribution of the two processes d4 and d5 to the loss of N (⁴S) atoms is similar. As the percentage of methane increases, the relative contribution of these three processes becomes more important.

While d5 restores N (⁴S), the reaction d3 followed by d4 leads to the production of HCN which definitively traps nitrogen. Therefore the concentration of nitrogen atoms decreases for high CH₄ mixing ratios as shown in figure 4.

Performed for longer residence times (i.e. 41 and 61 ms, corresponding to pressures of 16 and 12 Torr), similar contributions of the N (⁴S) production and loss are obtained except for the loss through wall surface recombination (reaction d6). Indeed, the loss of nitrogen atoms at the reactor's surface becomes significant for longer residence time, as a result lower pressure working conditions. Figure 6 shows that the value of the contribution of d6 reaches 12% for a residence time of 61 ms compared to 1% for 22 ms (figure 5). This result is consistent with the variation of the maximum of N (⁴S) density as a function of the residence time (figure 4).

In spite of the qualitative agreement between experiment and modeling, the calculated densities for nitrogen atoms in the afterglow are in general larger than the measured ones. This can be due to several causes. First, the present simulations assume homogeneous discharge and afterglow regions. This hypothesis seems reasonable in the case of the microwave plasma where the tube has an inner diameter of 6 mm. But, in the afterglow region the experimental measurements were performed in a reactor that has a 200 mm inner diameter. Under these conditions, the heavy species may present radial profiles, which are not taken into account by the present model. Secondly, we have considered constant values of the gas temperature in the discharge (~1000 K) and post-discharge (300 K) regions. Thus, we have not taken into account temperature gradient at the end of the discharge. This simplification affects the rate coefficients associated with vibration–vibration (V-V) and vibration–translation (V-T) processes, which play an

important role in the temporal evolution of the vibrational distribution function (VDF), which in turn affect the populating and depopulating mechanisms of nitrogen atoms in the afterglow.

5. Conclusion

The present studies have been performed in the frame of the development of Titan simulation programs called SETUP (a French acronym for Experimental and Theoretical Simulation useful for Planetology). Titan's atmospheric neutral chemistry is driven by electrons from Saturn's magnetosphere and solar UV photons. Until now, the simulations involved only one energy source, i.e. electrons or photons (see recent works [24] and [25] respectively). Thus, a dedicated device has been developed using plasma discharge to dissociate N_2 and photons for CH_4 photolysis (continuous Lyman α or pulsed 248 nm irradiations) [16].

In this paper, we have studied the evolution of absolute N (4S) density in late afterglow N_2 microwave discharge when different methane mixing ratios are introduced. Experimental and theoretical results agree showing that the N (4S) density does not vary significantly up to $\sim 15\%$ of methane mixing ratio before decreasing drastically. The remaining discrepancy between model and experiments concerns the absolute density can be explained by the uncertainty on the initial conditions to be considered in the model. In spite of this disagreement, the synergy between modelling simulations and the experiments allows to explain the diminution of N (4S) density with increasing CH_4 mixing ratio. The present results confirm experimentally and extend the conclusions that were obtained in previous theoretical studies [3, 13]: methane reacts with metastable energetic nitrogen species when introduced in the N_2 post discharge zone, and a complex chemistry leading mainly to HCN is initiated. Owing to this new study, we are now aware that, especially when introduced with a high mixing ratio, the methane dissociation through the flowing plasma plays a role in the production of numerous compounds suspected to be also produced during its photo-dissociation. Thus, we will be able to disentangle the relative contribution of both mechanisms when the SETUP simulations (including photolysis) will be carried out.

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Figures

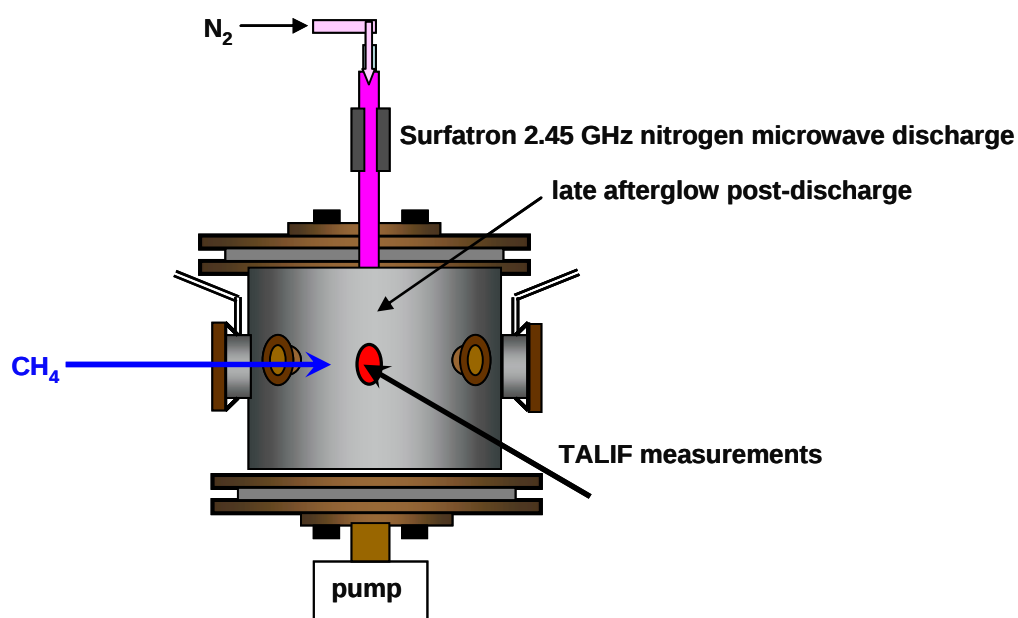


Figure 1. Experimental set up for the investigation of the microwave flowing post-discharge afterglow by TALIF spectroscopy.

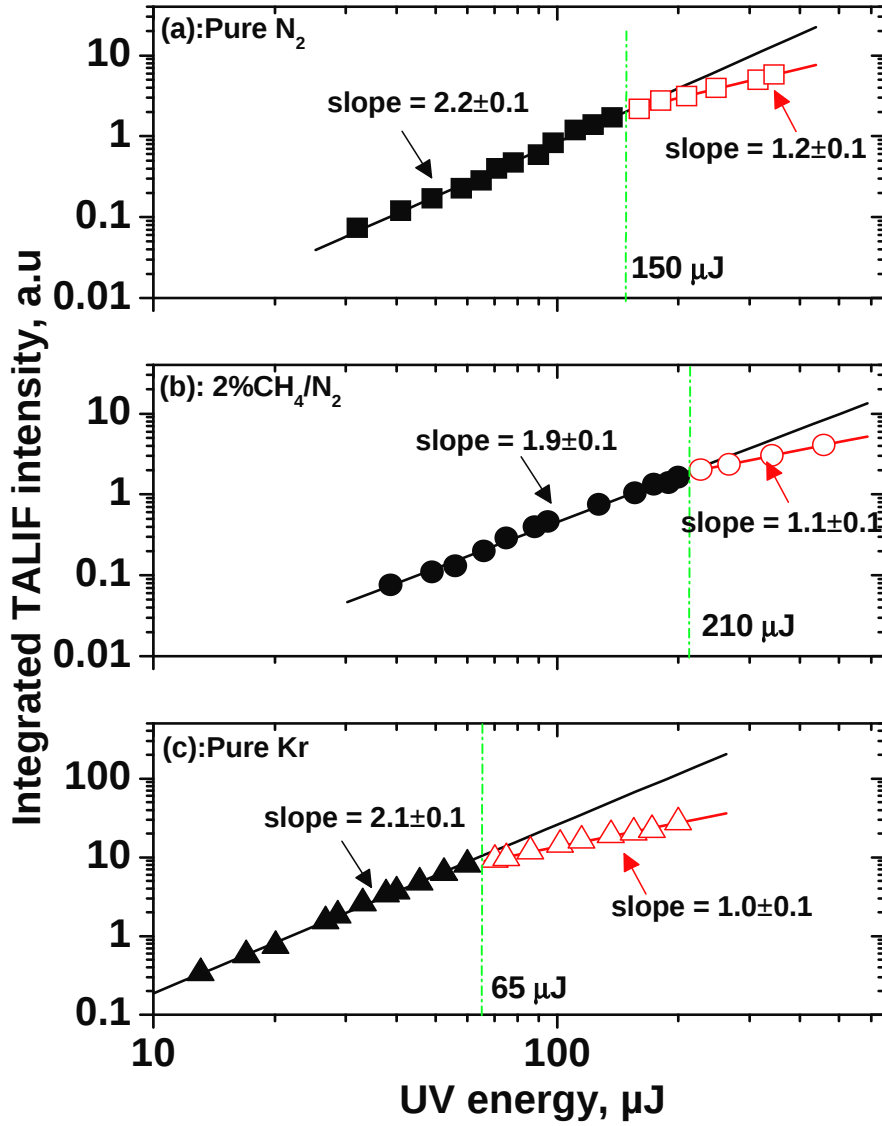


Figure 2. log-log plot of $\text{N}(^4\text{S})$ -TALIF in: (a) in pure N_2 , (b) 2% CH_4/N_2 and $\text{Kr}(^1\text{S}_0)$ -TALIF in (c) pure Kr. TALIF measurements in pure N_2 and N_2/CH_4 mixtures have performed for a discharge power of 100 W and a gas pressure of 22 Torr. TALIF calibration with krypton has been made without discharge for a gas pressure of 2.3 Torr.

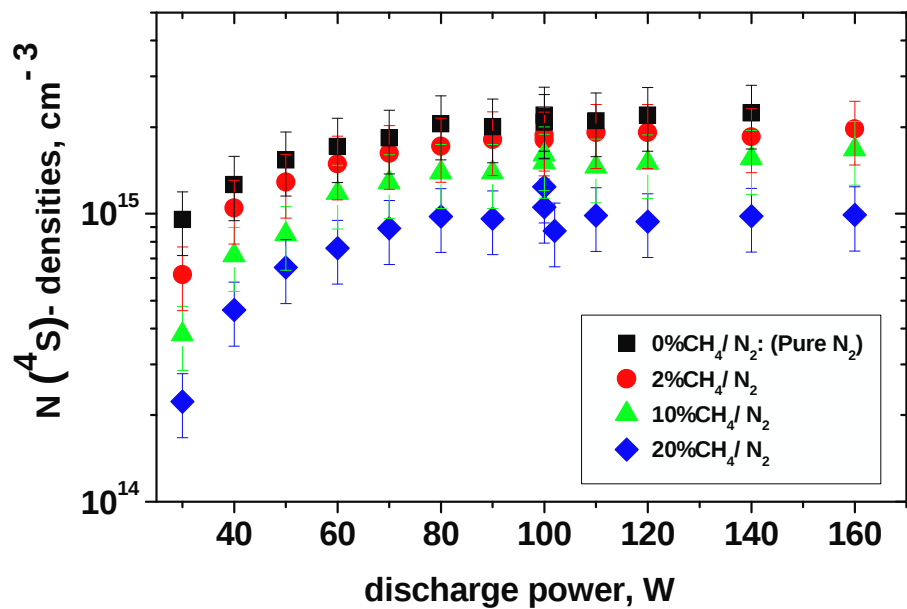


Figure 3. Absolute densities of $N(^4S)$ atoms in N_2/CH_4 mixture as a function of the microwave discharge power for N_2 gas flow rate=500 sccm and pressure=22 Torr (residence time=22ms) and for percentages of CH_4 added in late afterglow of 2% (dots), 10 % (triangles) and 20% (diamonds). The $N(^4S)$ density measured in pure N_2 is also shown for comparison (squares).

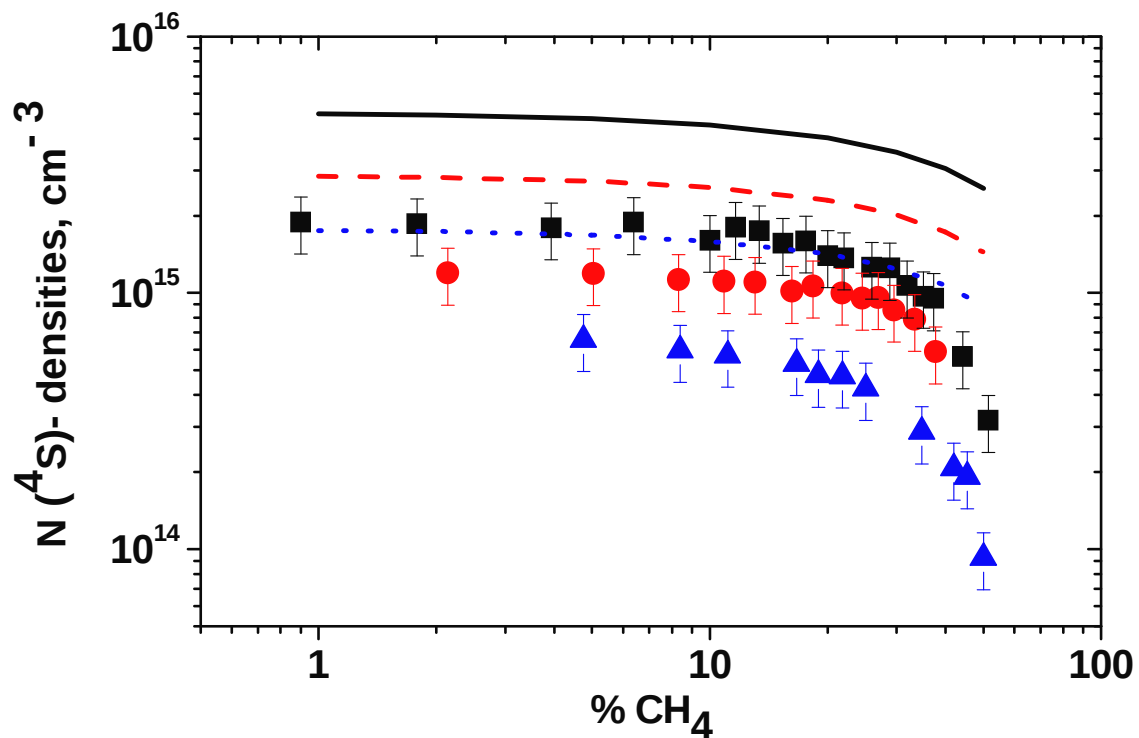


Figure 4. Measured (symbols) and theoretical (lines) reporting the absolute densities of N (⁴S) atoms in N₂/CH₄ mixture as a function of the CH₄ mixing ratio injected in the late afterglow for different flow rate (sccm)/pressure (Torr) of 500/22, 200/16 and 100/12 corresponding to residence times of 22 ms (■, black line), 41 ms (●, red dashes line) and 61 ms (▲, blue dotted line), respectively. The microwave discharge power is 100 W.

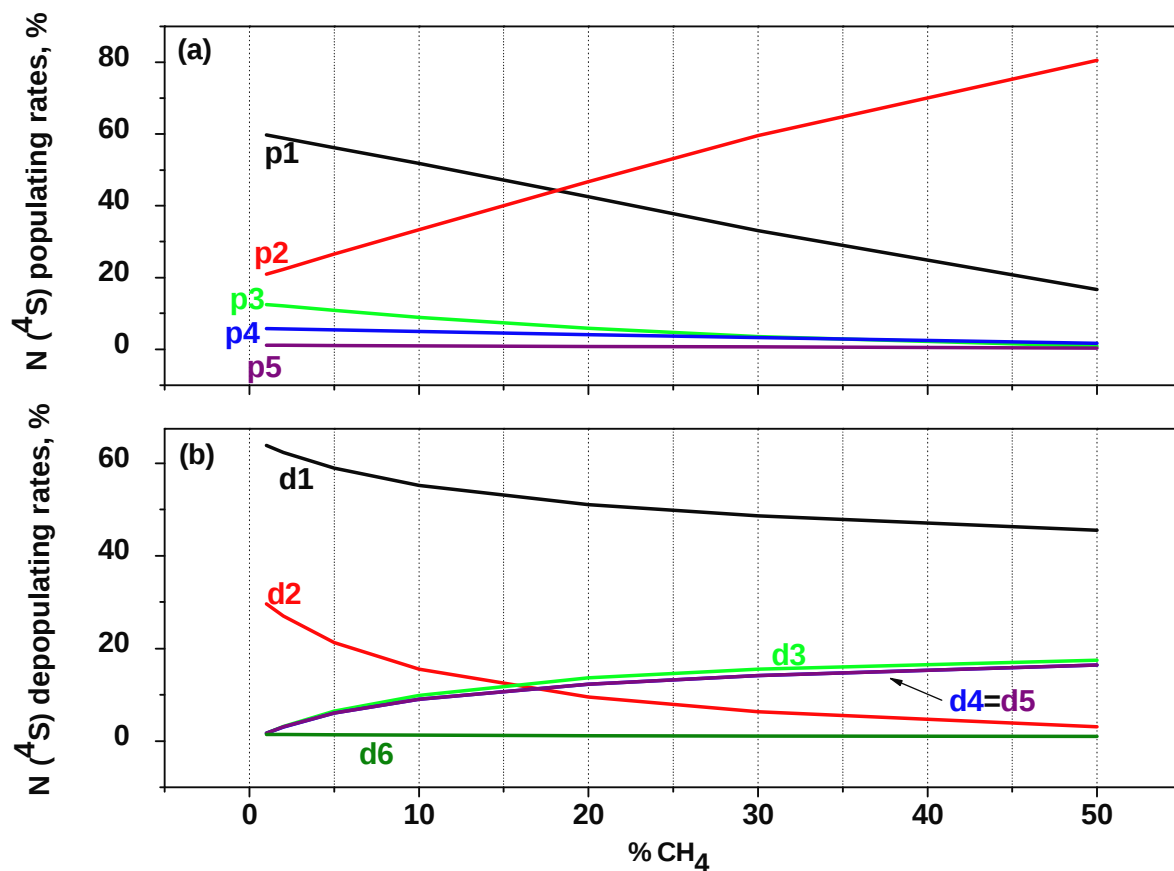


Figure 5. Calculated relative contribution of the rate leading to the (a) production and (b) loss of $\text{N}(^4\text{S})$ atoms as a function of the CH_4 mixing ratio as listed in tables 1 and 2, respectively. The calculation is performed in the same conditions such as results of figure 4 in the case of 22ms of afterglow time.

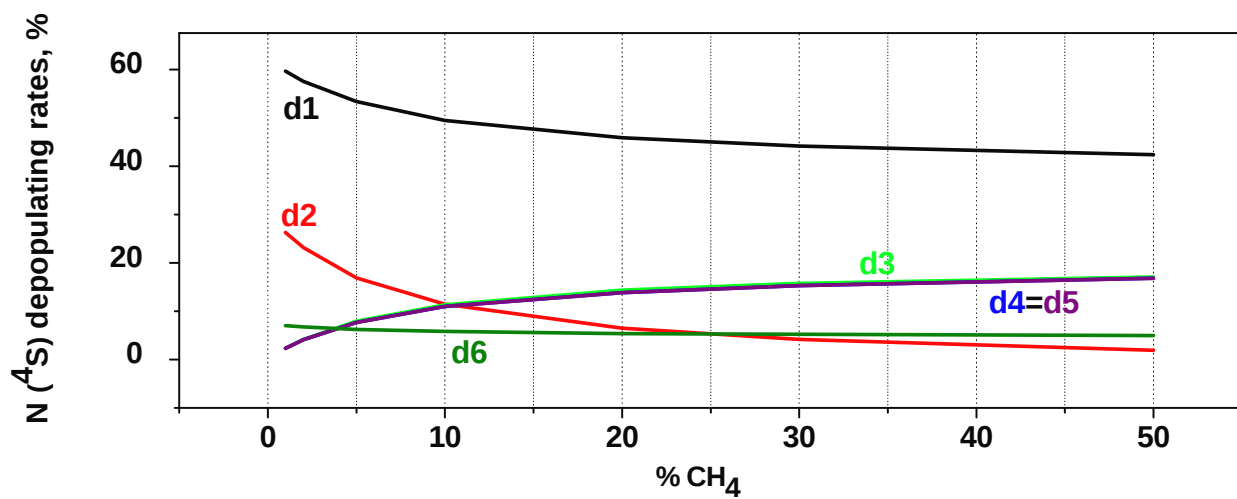


Figure 6. Calculated relative contribution of the rate leading to the loss of N (4S) atoms as a function of the CH₄ mixing ratio as listed in table 2. The calculation is performed in the same conditions such as results of figure 4 in the case of 61 ms of afterglow time.