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Experimental and theoretical studies on nitrogen plasma and methane photolysis

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Abstract

We present some studies that have been performed in the frame of the development of a new Titan laboratory simulations program called SETUP (a French acronym for Experimental and Theoretical Simulation useful for Planetology).
Methane is, together with molecular nitrogen, the main precursor of Titan's atmospheric chemistry. High energy electrons from Saturn's magnetosphere and solar UV photons drive the chemical evolution of the atmosphere. SETUP simulations will implement a pure N_2 flowing microwave plasma discharge in order to generate N atoms while CH_4, added in the late afterglow of the nitrogen post-discharge, will be photolysed by UV photons to produce CH_3, CH_2 and CH photo-fragments. In situ analysis of the interaction zone simulating Titan's neutral chemistry will be performed by laser-based spectroscopy techniques. Indeed, the detection and the quantification of the stable species as well as the short life intermediates will allow determining precisely the implied chemistry, and consequently, refining its description in theoretical models.
The late afterglow of the nitrogen plasma discharge in various experimental conditions has been studied by TALIF spectroscopy. The density of the generated nitrogen atoms $N(^4S)$ involved in the reaction zone has been determined as the function of the amount of added methane. A kinetic model has been developed in parallel to determine the elementary processes responsible for the evolution of the $N(^4S)$ density in the late afterglow.
Secondly, methane photolysis at 121.6 and 248 nm have been studied and compared. Again, an approach combining experiments and modelling has been used in order to get information of the chemical mechanisms involved in both cases.
The implications of the results obtained either in the plasma or the photochemical studies on the SETUP laboratory simulation program will be discussed.

1. Introduction

Until now, Titan's atmosphere simulations involved only one energy source, i.e. electrons or photons. In order to improve the representativeness of simulation experiments toward Titan's conditions, a dedicated device has been developed in our laboratory (figure 1). Plasma discharge will be used to dissociate N_2 while photolysis of CH_4 will be conducted by continuous Lyman α or pulsed 248 nm irradiations

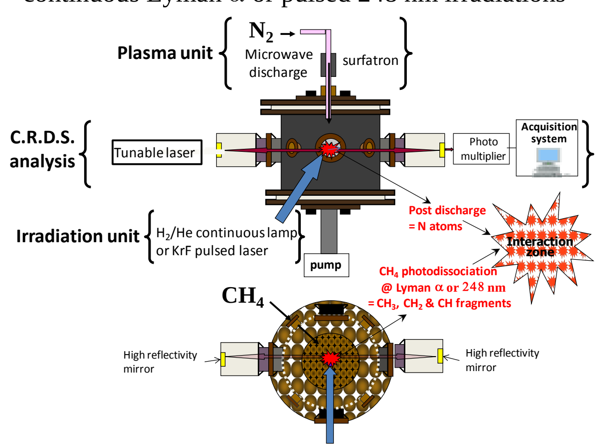

Figure 1: Experimental device

2. Plasma studies

In our Titan's simulation experiments device, thanks to a surfatron, a microwave flowing post-discharge is created in a tube directly connected to the reactor. Nitrogen atoms in the ground state, $N(^4S)$, are generated and flow into the interaction zone. The quantification of the produced nitrogen atoms is performed by the TALIF (Two photons Absorption Laser Induced Fluorescence) technique.
First, we have studied a flowing pure nitrogen post-discharge. We have shown that the control of different parameters (i.e. the microwave discharge power, the nitrogen pressure range and flow rate)

allows adjusting the N(^{4}S) density in the reactive zone [1].
Secondly, we have investigated experimentally and theoretically the influence of methane introduced downstream from the discharge [2].

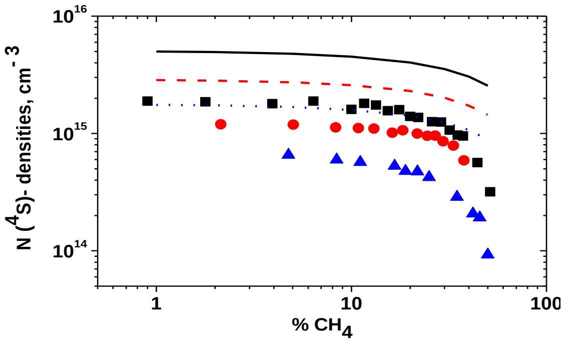

Figure 2: Measured (symbols) and theoretical (lines) absolute densities of N (^{4}S) atoms in N_2/CH_4 mixture as a function of the CH_4 mixing ratio injected in the late afterglow for different flow rate (sccm)/pressure (Torr) of 500/22(■, black line), 200/16 (●, red dashes line) and 100/12 (▲, blue dotted line).

The results obtained by both approaches (figure 2) agree showing that the N(^{4}S) density does not vary significantly up to ~ 15% of methane mixing ratio before decreasing drastically. This evolution has been explained thanks to the theoretical examination of the contribution of the reactions of production of N(^{4}S) in the late afterglow [2]. For high CH_4 mixing ratio, the destruction process through collisions with CH_3, H_2CN and NH becomes important and is responsible for the observed decrease of the N (^{4}S) density.

3. Photochemical studies

In Titan's atmosphere, photolysis of methane mainly involves Lyman-α photons (121.6 nm). Classical H_2 photochemical lamps can deliver such UV photons. Unfortunately, these continuous sources are not suitable for high-speed kinetic studies. Therefore, in our simulation experiments, the use of a pulsed laser (KrF Excimer delivering photons at 248 nm) has also been considered to photodissociate methane. A comparative methane photolysis study at 121.6 and 248 nm - involving one or two photons respectively - have thus been performed. IR analysis of the stable products formed after irradiation of CH_4 at both wavelengths has shown that photolysis at 121.6 and 248 nm are energetically equivalent. However, thanks to an approach combining irradiation experiments and photochemical modelling, we have shown that chemistry is different depending on the wavelength. Indeed, at 248 nm, CH_4 is more likely photoionised through a three-photon absorption process than photodissociated following two-photon absorption.

4. Summary and Conclusions

Owing to our new plasma study, we are now aware that, especially when introduced with a high mixing ratio, the CH_4 dissociation through the flowing plasma plays a role in the production of numerous compounds suspected to be also produced during its photo-dissociation [2]. Thus, we will be able to disentangle the relative contribution of both mechanisms when the SETUP simulations (including photolysis) will be carried out.

The results of our photochemical study indicate that photolysis at 248 nm is not suitable to study Titan's neutral chemistry. A VUV pulsed source will be developed to provide a full description of the chemical processes through time resolved analysis of the system. In the meantime, a photochemical lamp will be used to photodissociate CH_4. This will not allow us to probe the reactive intermediates and no information could be retrieved on fast kinetic processes. Yet it will still be possible to study the kinetic evolution of the stable products.

Acknowledgements

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