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► **To cite this version:**

Audrey Chatain, Nathalie Carrasco, Olivier Guaitella, Maryse Napoleoni, Ludovic Vettier, et al.. Experimental study of ammonia formation in Titan's ionosphere. European Planetary Science Congress 2018, Sep 2018, Berlin, Germany. EPSC Abstracts. insu-02940713

**HAL Id: insu-02940713**

**<https://insu.hal.science/insu-02940713v1>**

Submitted on 16 Sep 2020

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# Experimental study of ammonia formation in Titan's ionosphere

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## Abstract

Ammonia is an interesting molecule suspected to be formed in Titan ionosphere and leading to further complex chemistry. Here we experimentally study one of the two ways of formation of ammonia in the ionosphere: the catalysis on surfaces in a  $N_2$ - $H_2$  plasma. We vary plasma conditions in a CCP RF discharge and follow the ammonia formation thanks to IR and mass spectrometries. We show the strong effect of pressure,  $H_2$  percentage, plasma power and metallic surfaces.

## 1. Introduction

Titan's ionosphere is the place of complex gas chemistry. The interaction of the major species  $N_2$ ,  $CH_4$  and  $H_2$  with the surrounding plasma leads to the formation of new molecules. Here we study the formation of ammonia, which has a great role for further chemical reactions [1]. However, data of the Cassini-Huygens mission are complex to interpret concerning ammonia. Neutral mass spectrometry at low masses is blurred by molecule splitting and the explanation of the detection of the ion  $NH_4^+$  is still under debate [2].

In such cases laboratory simulation can be useful to get clues on the chemistry going on. Ammonia has been detected in experiments simulating Titan's ionosphere [3]. Two different chemical paths have been spotted to form ammonia: with carbon chemistry in the gas phase or without carbon but using surfaces, which can be nanograins or walls. As a first step here we simplify the system to study only the influence of surfaces. A radiofrequency Capacitively Coupled Plasma (CCP RF) discharge is ignited in a  $N_2$ - $H_2$  mixture simulating Titan's ionosphere without carbon. The evolution of the system is diagnosed with infrared absorption spectroscopy, neutral and positive ion mass spectrometry. We looked at the influence of pressure,  $H_2$  percentage and power.

## 2. Experimental device

### 2.1 Plasma reactor - PAMPRE

A cylindrical stainless steel chamber is used to reproduce Titan atmospheric conditions [3]. It is 40cm high and 30cm in diameter. A  $N_2$ - $H_2$  gas mixture with 0 to 5% of  $H_2$  is injected in the chamber at up to 55sccm, varying the pressure up to 1mbar.

The CCP RF discharge is confined in a smaller cylindrical box of 13.6cm in diameter, inside the chamber. We studied cases with electrodes RF potential tuned up to 460V in peak to peak amplitude.

### 2.2 IR spectrometry

Ammonia formed in the chamber is quantified by IR absorption spectroscopy with a Nicolet 6700 Fischer FTIR spectrometer. The measurement is directly done during the discharge, and the absorption length is the diameter of the chamber. An accumulation of 5000 scans is needed to obtain a reasonably high signal to noise ratio at  $2cm^{-1}$  resolution, which takes 2 to 3 hours.

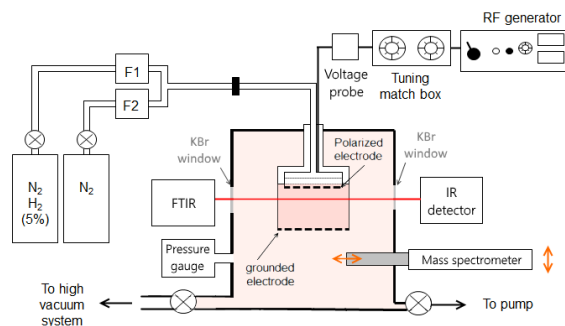


Figure 1: plasma reactor and diagnoses

## 2.3 Mass spectrometry

In order to better characterize the evolution of ammonia concentration along time and space, we use a mass spectrometer of Hiden EQP series. It is calibrated thanks to IR measurements.

The spectrometer is also used to detect positive ions. For this measurement, the collector head is put in contact with the internal box, in which we drilled a hole to let ions out to the spectrometer without disturbing the ground configuration.

## 3. Results

### 3.1 Influence of H<sub>2</sub> percentage

All measurements agree on the strong role of H<sub>2</sub> amount on the formation of ammonia and its ions.

First IR results show a linear dependence of ammonia formation with the H<sub>2</sub> amount in the gas phase. It reaches about  $3 \cdot 10^{13} \text{ cm}^{-3}$  for 5% of H<sub>2</sub> in N<sub>2</sub> at 0.92mbar.

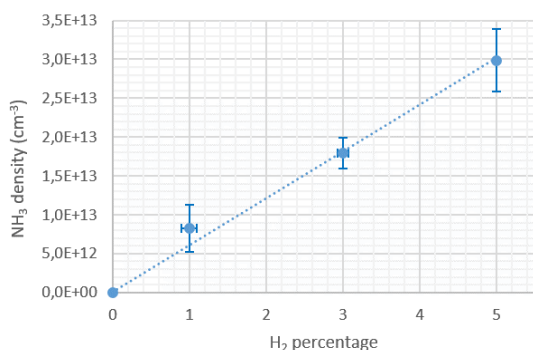


Figure 2: Quantification of ammonia with IR absorption spectrometry at 0.92mbar and 30W.

### 3.2 Sensitivity to plasma parameters

With the mass spectrometer, we show that ammonia formation is strongly sensitive to plasma parameters. The ammonia to nitrogen ratio increases by about 40% when we increase the peak-to-peak RF voltage of 100V for 0.92mbar of N<sub>2</sub>-H<sub>2</sub> at 5%. It doubles when the pressure drops from 0.92mbar to 0.36mbar. When the central box is removed, the quantity of ammonia is divided by two.

## 3.3 Positive ions

Positive ion populations change quickly as soon as some hydrogen is added into the reactor. N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, N<sub>3</sub><sup>+</sup> and N<sub>4</sub><sup>+</sup> here in pure N<sub>2</sub> decrease and are replaced by N<sub>2</sub>H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub><sup>+</sup>, H<sub>3</sub><sup>+</sup>...

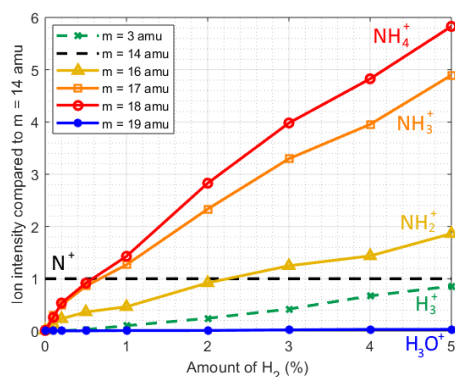


Figure 3: Relative ion intensities as function of H<sub>2</sub> percentage at 0.91mbar and 30W

## 4. Perspectives

Here we studied the formation of ammonia on the planar metallic surfaces of the reactor. The next step to understand ammonia formation on Titan will be to add methane in the gas mixture to quantify the chemical path using carbon to form ammonia. The formation of aerosols inside the chamber will also complex the study, giving new surfaces to create ammonia according to the first chemical path.

## Acknowledgements

NC acknowledges the financial support of the European Research Council (ERC Starting Grant PRIMCHEM, Grant agreement no. 636829).

AC is grateful to the doctoral program of ENS Paris-Saclay for its financial support.

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