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► **To cite this version:**

Jérémy Bourgalais, Nathalie Carrasco, Pascal Pernot. Gas-Phase Positive Ion Insights during Laboratory EUV Irradiation of Titan's Relevant Gas Mixtures. EPSC-DPS Joint Meeting 2019, Sep 2019, Geneva, Switzerland. pp.EPSC-DPS2019-1337-1. insu-02196260

**HAL Id: insu-02196260**

**<https://insu.hal.science/insu-02196260>**

Submitted on 27 Jul 2019

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# Gas-Phase Positive Ion Insights during Laboratory EUV Irradiation of Titan's Relevant Gas Mixtures

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## Abstract

In the atmosphere of Saturn's moon Titan, the chemical growth is believed to occur through an efficient chemical coupling between radicals and reactive charged species. However, the role of positively charged particles in haze formation chemistry is far from being understood. Here, we present a mass spectrometry investigation with a relatively low pressure interface to chemically characterize the positive ions formed in the pre-haze formation phase starting from the EUV photolysis of  $N_2/CH_4$  gas mixtures.

## 1. Introduction

Thanks to the discoveries of the Cassini-Huygens mission, it is assumed that the haze formation in Titan's atmosphere is initiated in the ionosphere, mainly by energetic solar photon dissociating  $N_2$  and  $CH_4$ , the main components.[1, 2, 3, 4, 5] Heavy ions have been detected including cations up to  $m/z$  99 by the Cassini Ion and Neutral Mass Spectrometer (INMS) at both even and odd masses suggesting positively charged C- and N-bearing species.[6, 7] However, even if they are thought as a key step in haze formation their formation is far from being understood.[2, 4]

In order to better understand Titan's haze formation, numerous laboratory experiments investigated the gas phase products in the atmosphere of Titan through irradiation of  $N_2/CH_4$  mixtures using various energy sources (e.g., plasma discharge, electron beam, photon flux) to simulate the molecular growth occurring in Titan's upper atmosphere.[8] However, commonly used light sources allow to work only above 110nm (Far UltraViolet) which is the dominant energy in the low atmosphere and do not provide sufficient energy to ionize or dissociate  $N_2$ , essential to understand observed N-incorporation into gas-phase products. It requires EUV wavelengths (<110 nm) to address the effect of photoionisation of  $N_2$  in the upper atmosphere

of Titan. There is only two EUV studies on  $N_2/CH_4$  gas mixtures using synchrotron radiation [9, 10] in which they showed that  $N_2^+$  enhances the formation of unsaturated hydrocarbons at wavelength below 80nm. Thus, ion chemistry is a potential pathway for nitrogen incorporation even if there is still a lack of data characterizing ion composition in Titan's atmosphere simulation experiments.

Thus, our work aims at corroborating the major role, played by the photoionization of nitrogen in the formation of complex organic molecules by monitoring ion EUV photoproducts.

## 2. Experimental Method

Accordingly, here we present the chemical composition of cations produced in the APSIS (Atmospheric Photochemistry SIMulated by Synchrotron) reactor during the irradiation at 73.6nm of a methane in nitrogen gas mixture using an EUV source.[11] The light source used a neon gas flow discharge in the mbar pressure range coupled windowless to the photochemical APSIS reactor. In situ mass spectra were taken with a relatively low pressure interface to determine the chemical composition of ions.

## 3. Results

Figure 1 illustrates mass spectra of cations measured in the APSIS reactor during irradiation at 73.6nm for different pressures, ranging from  $10^{-2}$  to 1mbar. Main ion species already observed in previous EUV experiments are detected such as  $CH_5^+$  and  $C_2H_5^+$  along with an efficient ion production up to  $m/z$  140 at 1mbar. Preliminary analysis allows to believe that the production comes initially from a dissociative charge-transfer reaction between ionized molecular nitrogen and methane leading to the formation of unsaturated hydrocarbons through subsequent dissociative recombination.

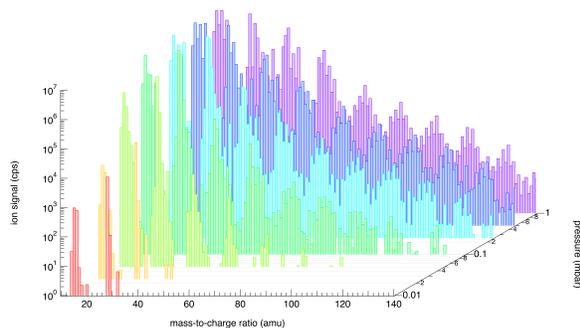


Figure 1: Positive ion mass spectra obtained from  $\text{N}_2/\text{CH}_4$  gas mixtures irradiated 73.6nm at different pressures, ranging from  $10^{-2}$  to 1mbar.

This work will allow to constrain the detailed chemical kinetic model by bringing informations about ionic species formed in N-dominated atmospheres. This is important to reduce the sources of uncertainty and/or bias in the model predictions of Titan's ionosphere.

## Acknowledgements

This research is supported by the ERC Starting Grant PRIMCHEM, grant agreement n°636829.

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