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## Cation Chemistry in Titan's Upper Atmosphere and its Influence on Tholin Formation

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### Abstract

Titan is Saturn's largest satellite. This object is unique in the solar system as it hosts a dense atmosphere [1] mainly made of molecular nitrogen  $N_2$  and methane  $CH_4$ , with a surface pressure of 1.5 bar. The nitrogen-rich atmosphere and the presence of liquid areas on the surface make it one of the most interesting nearby objects to understand the evolution of the primitive Earth before the emergence of life and to look for habitable environments in the solar system. The Cassini-Huygens Mission has been probing Titan since 2004. It has revealed an intense atmospheric photochemistry initiated by the photo-dissociation and ionization of  $N_2$  and  $CH_4$  [2]. Photochemistry on Titan leads to the formation of solid organic aerosols responsible for a smog permanently surrounding the moon [2,3]. In the upper atmosphere, Cassini detected signatures compatible with the presence of heavily charged molecules which are precursors for the solid core of the aerosols [4,5,6]. These observations indicate that ion chemistry has an important role for organic growth. However, the processes coupling ion chemistry and aerosol production are mostly still unknown. In this study, we investigate the cation chemistry, responsible for the organic growth that we observe in Titan's upper atmosphere, simulated using the PAMPRE plasma reactor [7]. Positive ions are investigated by *in situ* ion mass spectrometry in a dusty cold plasma, alongside neutral products additionally studied through infrared absorption spectroscopy and mass spectrometry.

### 1. Introduction

In Titan's upper atmosphere (Figure 1), Cassini's Ion and Neutral Mass Spectrometer (INMS) detected neutral and positive ion signatures [2]. Subsequently, the Cassini Plasma Spectrometer electron spectrometer (CAPS-ELS) unveiled the existence of negative ion-molecules well over the detection range of INMS ( $> 100 \text{ amu}$ ) consistent with the presence of heavy

molecules (over 10,000 Da. in mass) which are precursors for the solid core of the aerosols. This *in situ* observation unveiled for the first time the key role of heavy charged molecules (ions) initiated in the ionosphere. Thus, the ion chemistry in this organic mixture is thought to be anything but negligible. Furthermore, the gas-to-solid conversion at these high altitudes coexists in a fully coupled ionic and neutral chemistry. However, the processes coupling ion chemistry and aerosol production are at the moment mostly unknown. Experimental simulations as well as ground-based observations should help in constraining the wide population of cations.

The complexity of this material is already foreshadowed by the intricacies of the gas phase chemistry, acting as a precursor to the aerosol formation. Hence, the ion chemistry remains an open question for the characterization of the gas phase and chemical pathways leading to the formation of aerosols.

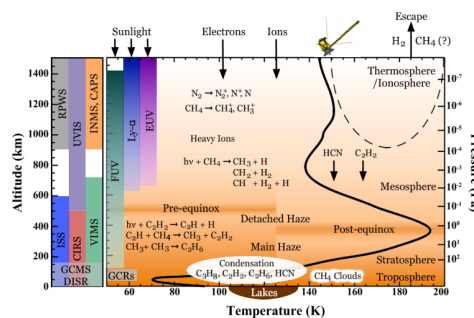


Figure 1: Titan temperature profile, the major chemical processes and approximate altitudinal coverage of the instrument suite onboard the Cassini spacecraft [8]. The coupled neutral-ion chemistry is initiated in the upper atmosphere ( $< 1,000 \text{ km}$ ).

## 2. Experimental Setup

We use the cold dusty plasma reactor PAMPRE [7] and Figure 2, in order to simulate Titan ionosphere conditions, at different initial  $CH_4$  conditions.

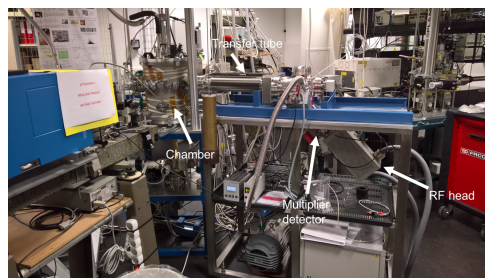


Figure 2: PAMPRE, with its ion mass spectrometer. The entrance aperture to the spectrometer measures ions within the chamber relatively close to the plasma, in order to avoid any contamination from the reactor walls.

We investigate the influence of initial  $CH_4$  concentrations and distance of measurements on the cation population detectable with this setup. Furthermore, we compare our results with Cassini-INMS data to constrain and characterize our cation chemistry. Moreover, we provide analysis for heavy cations ( $> 100 \text{ amu}$ ), outside of the INMS range.

## 3. Summary and Conclusions

With the coming end of the Cassini Mission, laboratory analyses of Titan simulations coupled with ground-based observations will be necessary in order to constrain our understanding of gas phase neutral, ion, and solid-state chemistry relevant to its atmosphere.

Our results show a strong dependency on the initial  $CH_4$  concentration. We also monitor the evolution of key ion-molecules such as  $HCNH^+$ ,  $CH_2NH_2^+$ ,  $C_3H_3^+$  and  $HC_3NH^+$  suspected of being significant in Titan's upper atmosphere and thus in aerosol formation.

## Acknowledgements

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