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First Ion Insights during Titan's Ionosphere Relevant Gas Mixture EUV Irradiation

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Abstract

In titan's ionosphere, the chemical growth in the atmosphere is believed to occur through the chemical coupling of radicals and reactive charged species but the complexity of the chemistry is far from being understood. Here we present a series of EUV Titan's atmosphere simulation experiments. We irradiated at 73.6nm different gas mixtures ($N_2/CH_4 \& He/CH_4$) in a photochemical reactor. Our work is focused for the first time on photochemical ionic products.

1. Introduction

The arrival of the Cassini-Huygens spacecraft led to the discovery of an unexpected efficient organic chemistry, including very heavy ionic species [1,2] in the Titan's thermosphere. It showed that large condensable molecules are formed in the upper region of the moon where the flux of photons partly initiate chemical reactions. The photochemistry of CH₄ is one of the dominant chemical processes, but the large amount of N₂ is believed to significantly change the subsequent chemistry. As a matter of fact, the instruments onboard to the Cassini spacecraft showed that nitrogen participates in the chemistry and Titan's aerosols contain significant amounts of nitrogen [3,4]. In addition, Titan's atmosphere simulation experiments [5-7] have also demonstrated that the presence of nitrogen increases the molecular complexity. However, even if the chemical growth in the atmosphere is believed to occur through the chemical coupling of radicals and reactive charged species (ionic species and electrons) the complexity of the chemistry is far from being understood. Indeed, the current photochemical models [8] reasonably explain the formation of small carbon/nitrogen bearing molecules, but fail at giving accurate processes for the formation of heavy C and/or N-based species observed (>4 carbon and/or nitrogen atoms). It is mainly due to the complexity of reaction pathways and the limited set of available data (branching ratios and coefficient rates) for chemical reactions.

2. Experimental Approach

Numerous laboratory studies investigated the gas phase products in the atmosphere of Titan through irradiation of N₂/CH₄ mixtures by using a variety of energy sources (e.g., laser induced plasma, electrical discharge, UV lamps or synchrotron). However, those sources, despite synchrotron beamline, allow to work only above 110nm. Indeed, it requires EUV wavelengths (<110 nm) in order to address the effect of photoionisation of nitrogen as it might plays a key role in the upper part of the atmosphere of Titan regarding the ionization cross section at these wavelengths and the abundance of the molecule. There is only one EUV synherotron radiation study on N₂/CH₄ gas mixture [7,9,10]. They have shown that the presence of the dominant nitrogen species in the gas mixture (ca. 95%) enhances the formation of unsaturated hydrocarbons (e.g., benzene, toluene) at wavelength below 80nm. The production is believed to initially come from a dissociative charge-transfer reaction between N_2^+ and methane, leading to the formation of unsaturated complex hydrocarbons through production of $C_2H_5^+$ with subsequent dissociative recombination. However, they were not able to look at ions to validate this mechanism assumption.

Our work aims at corroborating the major role, highlighted by Imanaka *et al.*, played by the photoionization of nitrogen in the formation of complex organic molecules by monitoring simultaneously neutral and ion EUV photoproducts.

3. Results

Accordingly, here we present a series of EUV Titan's atmosphere simulation experiments. We irradiated at 73.6nm different gas mixtures ($N_2/CH_4 \& He/CH_4$) in

the APSIS (Atmospheric Photochemistry SImulated by Synchrotron) reactor recently developed in the LATMOS laboratory [11]. The wavelength is obtained by using a surfatron-type discharge with a neon gas flow in the mbar pressure range coupled to the photochemical APSIS reactor. This experimental setup designed to carry research on planetary atmospheres allow *in situ* mass spectrometry analysis of the neutral and ionic species produced in the APSIS reactor.

The first experiment analysis for the photolysis of only methane seems to confirm the assumption of Imanaka *et al.* with CH_5^+ and $C_2H_5^+$ as the main ion species. However, in the case of a coupled N₂/CH₄ system, CH_3^+ is not the main contributor for the growth of the unsaturated species. The formation seems to be driven by nitrogen species such as N₂⁺, HCNH⁺ and NH₄⁺. As shown in Figure 1 illustrating a mass spectrum of the positive ions detected in the photochemical reactor obtained from a N₂/CH₄ gas mixture irradiated 73.6nm. We also notice an efficient ion production up to m/z 150.



Figure 1: Positive ions mass spectrum obtained from a N_2/CH_4 gas mixture irradiated 73.6nm

This work constraints the detailed chemical mechanisms by bringing for the first time information about ionic and neutral species formed in nitrogen-dominated atmospheres by EUV irradiation. This work is important to reduce the sources of uncertainty and/or bias in the model predictions of Titan's ionosphere.

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