Ion chemistry in N_2-H_2 and N_2-CH_4 plasmas
representative of Titan's ionosphere

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Abstract: Plasma discharges in N_2-H_2 and N_2-CH_4 lead to complex ion chemistry. In nature, such reactions happen in planetary ionospheres. In the case of Titan, even large organic aerosols result from this complex chemistry. Laboratory plasma discharges are an interesting way to study such a reactive environment. In this work, we study positive ions thanks to mass spectrometry and we focus on two strategies: 1- different gas compositions are studied, and 2- pulsed discharges are used to observe formation steps at short time scales.

Keywords: Ionosphere, N_2-H_2, N_2-CH_4, ion mass spectrometry, pulsed discharge, Titan

1. Introduction

Upper atmospheres of planets are partially ionized and can lead to complex ion chemistry. Terrestrial planets usually contain nitrogen in their atmospheres, while gaseous giants are mainly composed of hydrogen and helium. In any case, the most interesting ionospheres concerning chemistry are those of planets beyond the ice limit, starting with Jupiter. Indeed, they possess a non-negligible amount of methane, which reacts to form long carbon chains once ionized. When nitrogen is present, it is incorporated in the carbon chains and complex organic molecules are formed. In some cases, such an environment produces organic particles with diameters up to some tens to hundreds nanometres [1].

This work aims to experimentally study ionospheres with nitrogen and methane. Therefore, the experiment can simulate the ionosphere of Titan, Saturn's biggest moon (98.4% N_2, 1.4% CH_4, 0.2% H_2), but also partially those of Triton and Pluto (which have also a bit of CO) and certainly the ionospheres of many exoplanets. A mixture of nitrogen, hydrogen and/or methane at low pressure is ionized and ions formed are analysed.

2. Simulation of Titan's ionosphere

When excited, methane easily forms atomic or charged hydrogen. Consequently, N_2-CH_4 ion chemistry mixes reactions with nitrogen, hydrogen and carbon. To help understand the final result, ions are studied step by step, starting with pure N_2, then adding a few percent of hydrogen. The incorporation of methane is the final step.

In ionospheres, molecules are ionized by both UV solar irradiation and energetic particles coming from the environment of the planet. Here the global ionization is realized thanks to a plasma discharge with a similar energy spectrum [2].

Parameters such as pressure, gas composition and ionization power are varied one after the other. The objective is to characterize the effect of each of them to extrapolate as precisely as possible laboratory results to ionospheres.

3. Ion mass spectrometry in a CCP RF discharge

CCP RF discharges are particularly suited to study dusty plasmas, and this corresponds perfectly to our objective to simulate Titan's dusty ionosphere.

The reactor used is a stainless steel cylinder of 30cm in diameter and 40cm in height. The polarized electrode is 10cm in diameter and a grounded grid cage of 3.5cm in height and 10cm in diameter is used to confine the plasma. 55sccm of the chosen gas mixture is continuously injected in the chamber and maintains a pressure of 0.86mbar [2].

Positive ions are measured thanks to a quadrupole mass spectrometer (Hiden EQP series). The MS collecting head is positioned in front of a hole in the confining box.

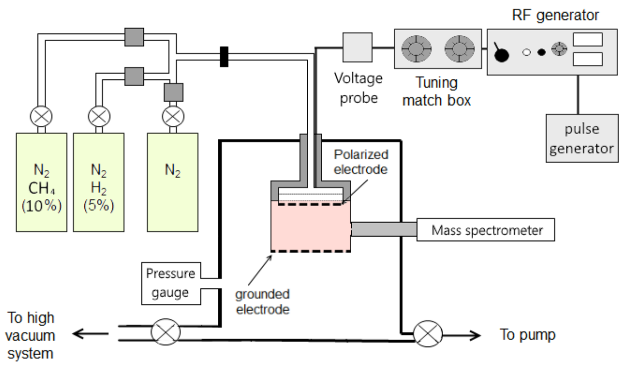

Fig. 1. Experimental setup

4. Ions in a N_2-H_2 plasma discharge

The first step is to understand how the addition of hydrogen modifies the ion populations of a N_2 plasma discharge. Results show a quick protonation of the major ion N_2^+ as soon as some hydrogen is injected. The formation of ammonia ions increases linearly with the amount of H_2 at least up to the addition of 5% of H_2 in N_2 (see Fig. 2.).

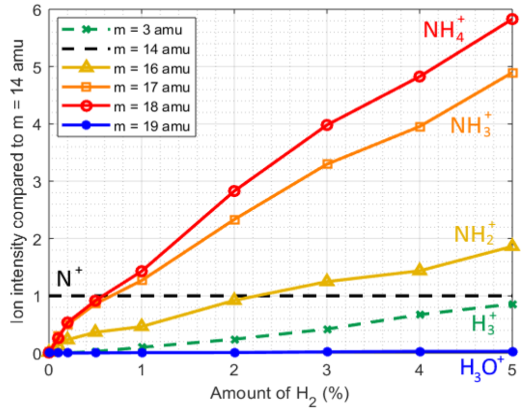

Fig. 2. Evolution of ammonia ions with H_2%.

5. Ions in a N_2-CH_4 plasma discharge

The addition of methane to N_2 discharges leads to the formation of new ions not seen in N_2-H_2 (see Fig. 3.), and grouped as clusters with the same number of heavy atoms (C or N). Indeed, ionized CH_4 reacts easily to form carbon chains of various lengths and lead to the organic synthesis of complex $C_xN_yH_z^+$ ions, such as CH_3^+, $C_2H_3^+$, HCN^+, $HCNH^+$, $C_3H_4^+$… Spectra in N_2-CH_4 are similar to mass spectra taken on Titan's ionosphere [3] and this reinforces the validity of our experimental simulation.

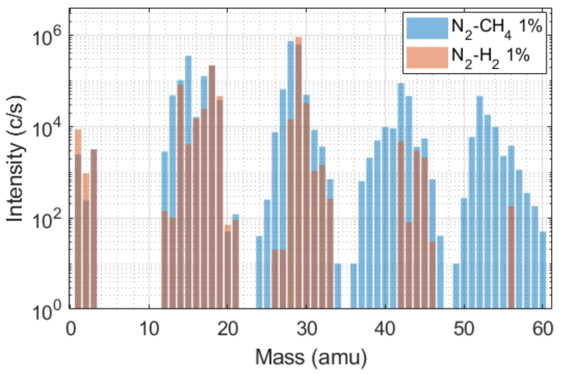

Fig. 3. Ions in N_2-H_2 and N_2-CH_4 gas mixtures

6. Formation steps of ions in a N_2-CH_4 plasma discharge

Studies in the two previous parts are done at steady states for ions formation. However, a lot of information on ion chemistry can be learned when studying the first microseconds of the discharge. The RF generator is pulsed at 1kHz with an asymmetrical rectangle signal and the plasma is ignited during various durations down to 20µs. Ions are collected during the last 20µs of the plasma duration (see Fig. 4.).

With discharges of 20µs, the main peak is at 28amu whereas with 30µs plasmas, 29amu is dominant. Later, the peak at 28amu grows again. This can give indications on the successive time scales of ions formation and we can compare with the model described in [4].

28amu can correspond to N_2^+ and $HCNH^+$ while the 29amu peak can be due to N_2H^+ or $C_2H_5^+$. N_2^+ is needed to form other ions so it seems N_2^+ is the major ion during the first 20µs. Besides, N_2^+ is a primary ion, formed by direct electronic impact. $C_2H_5^+$ is formed from N_2^+ and CH_3^+. As CH_3^+ (15amu) does not appear yet in the spectra, N_2H^+ could be the one seen at 29amu.

Besides, we also observe that peaks at masses higher than 30amu start to appear after 30µs of plasma. Carbon chain growth starts progressively after this time scale.

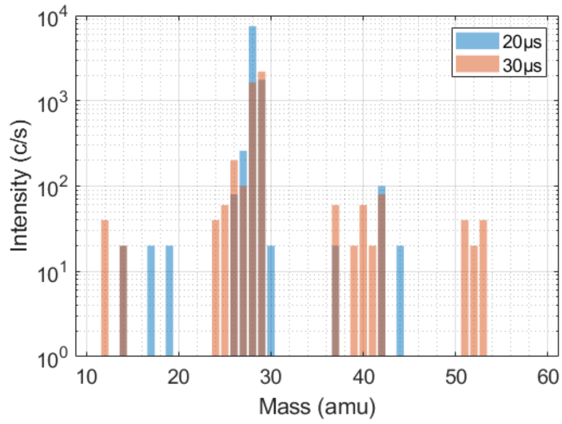

Fig. 4. First ions formed in the discharge (N_2-CH_4 1%)

7. Conclusion and perspectives

Planetary ionospheres often lead to complex ion chemistry which is difficult to study from space. Our project here to simulate such chemical reactions in the laboratory gives us the opportunity to study in detail the different steps of formation of complex ions.

The successive study of N_2, N_2-H_2 and N_2-CH_4 gas mixtures enables to study separately the influence of H_2 and CH_4. Hydrogen tends to protonate ions and form ammonia ions, whereas methane leads to long carbon chain growth. Our objective is to compare our results with kinetic models. This work is currently on going on N_2-H_2 discharges, following a previous study in pure N_2 [5].

To get more details on the formation steps of ions, we recently started to study pulsed plasma discharges. Spectra gain in complexity after 30µs, with a changing major peak and ions at higher masses. Further experiments are scheduled with a pulsed discharge to explore new parameters such as pressure and gas composition.

8. Acknowledgements

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

AC acknowledges ENS Paris-Saclay Doctoral Program.

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