Interaction of complex organic matter with N_2-H_2 plasma,
to understand Titan's ionospheric dusty plasma

A. Chatain[1,2], N. Carrasco[1], T. Gautier[1], L. Vettier[1], N. Ruscassier[3] and O. Guaitella[2]

[1]LATMOS/IPSL, UVSQ Université Paris-Saclay, Sorbonne Université, CNRS, 78280 Guyancourt, France
[2]LPP, École polytechnique, Sorbonne Université, université Paris-sud, CNRS, 91128 Palaiseau, France
[3]LGPM, Centrale-Supélec, Université Paris-Saclay, CNRS, 91190 Gif-sur-Yvette, France

Abstract: Titan's ionosphere is a dusty plasma mixing N_2-CH_4-H_2 plasma species and organic aerosols with diameters of about 100nm. Here we experimentally study the interaction between aerosols and plasma species. Analogues of Titan's aerosols are exposed to a N_2-H_2 DC plasma discharge partially representative of the ionosphere. A multi-instrumental analysis with electron microscopy, *in situ* infrared spectroscopy and mass spectrometry monitors the evolution of the aerosols and the gas phase.

Keywords: dusty plasma, laboratory simulation, organics, N_2-H_2, IR spectroscopy, Titan

1. Introduction

Titan, Saturn's biggest moon, has an unexpectedly thick and complex atmosphere. One of its main mysteries is the presence of an orange haze of organic aerosols created in the ionosphere [1]. The Cassini mission gathered only few data on these aerosols, and we still do not know their formation process and composition. However, aerosols govern atmospheric and surface processes on Titan. Therefore, it is fundamental to learn more about them, to understand Titan and design the next missions to go there.

To get clues, laboratory experiments try to mimic as close as possible the processes leading to the formation of aerosols in Titan's ionosphere [2,3]. Here, our interest is focused on the interaction between plasma species and small aerosols already formed in the ionosphere. We experimentally produce analogues of Titan's aerosols (named "tholins"), and we expose them to a N_2-H_2 plasma.

2. Plasma setup to mimic Titan's ionospheric processes

Titan's aerosols are complex organic grains formed in the ionosphere. To mimic this phenomenon, a dusty plasma in nitrogen with 5% of methane is ignited in a CCP RF discharge. Orange highly nitrogenous grains of a few 100nm are formed in the reactor and collected [2,3]. Grains are then pressed either with KBr grains or on thin metallic gratings to obtain rigid pellets of few hundreds of micrometres in depth.

On Titan these grains stay several weeks in the upper atmosphere, ionized by solar photons and energetic particles from Saturn. To understand the interactions between the organic grains and the plasma species, collected tholins are positioned at the centre of a 2 cm inner diameter glass tube in which a DC plasma discharge is ignited. The positive column of a glow discharge at few millibars is known to be quite homogeneous, which makes it a good tool for studying its interaction with tholins surface. In this range of pressure, most of radicals (N and H atoms) will recombine on surfaces and the sheath is already collisional enough to consider that ion bombardment remains similar for all working parameters used.

Titan's upper atmosphere is mainly composed of N_2 (98.4%), CH_4 (1.4%) and H_2 (0.2%). We know ionized methane leads to carbon chain growth [3]. However, here we want to study how nitrogen and hydrogen plasma species evolve the organic grains. Therefore, a mixture of N_2 and H_2 is continuously injected in the reactor.

To get clues on the effects of different parameters, pressure (0.5 to 4mbar), hydrogen content (up to 5%) and plasma current (10 to 60mA) are varied one by one. Such a study is fundamental to know in what extent results can be extrapolated to Titan's conditions, where ionization depends on the insolation and where hydrogen content and pressure vary with the altitude.

3. Multi-instrumental analysis

A first idea of the evolution of the sample's surface is given by an Environment Scanning Electron Microscope (E-SEM, model Quanta 200 from FEI). The samples are analysed before and after exposure.

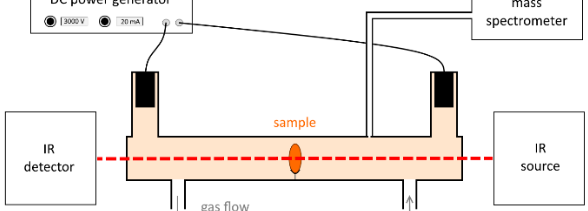

Fig. 1. Experimental setup

IR spectroscopy is also performed in transmission through the samples (FTIR V70 by Bruker). This diagnosis is done *in situ*, during the exposure of the sample to the plasma discharge. Therefore, it gives the time evolution of tholins chemical structure which signature is given by IR absorption spectrum.

In order to understand plasma/surface interaction mechanism both surface modification and gas phase species have to be characterized in the same system since the surface influences the plasma as much as the plasma is affecting the surface. Therefore, the gas phase is analysed by mass spectrometry (Hiden EQP series). Neutral species and positive ions formed in the plasma or by interaction with the organic matter are collected and identified by the spectrometer.

4. Erosion of the sample

Both SEM and IR spectroscopy measurements attest a strong loss of organic particles. The evolution of absorption in time can be fitted by three exponentials with strongly different timescales: ~1min, ~20min and ~20h (see Fig. 2.).

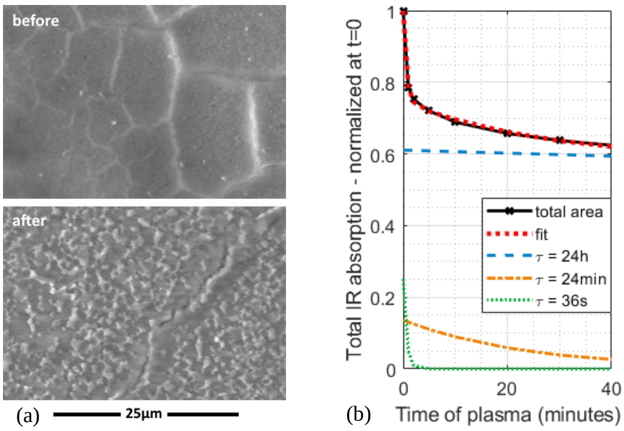

Fig. 2. Sample erosion as seen by (a) electron microscopy and (b) IR spectroscopy

These are attributed to different erosion processes at different locations in the sample: the surface of grains, the inside of grains and the grains more protected in the middle of the sample (see Fig. 3.).

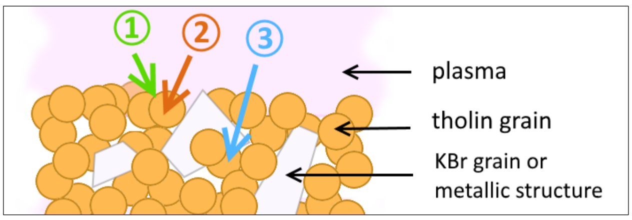

Fig. 3. Interpretation of the erosion steps of a pellet

5. Chemical evolution of the organic material

IR spectra acquired along the exposure to plasma witness the evolution of the chemical structure of tholins. Among them, the study of aliphatic C-H and amines shows that these chemical bonds are differently affected by the plasma. C≡N bonds are also strongly modified (see Fig. 4.): isonitriles ① disappear and new unsaturated nitriles ② appear.

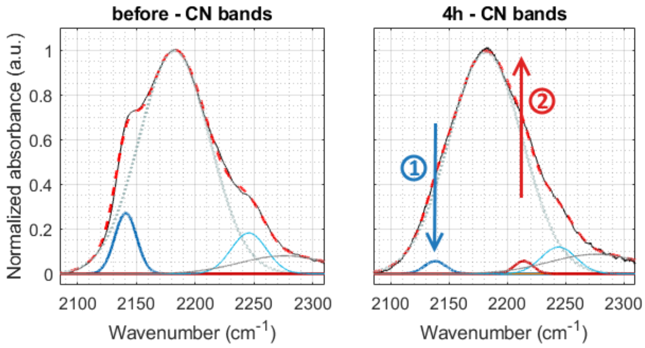

Fig. 4. Chemical evolution of the nitrile bands as seen by IR spectroscopy

6. Evolution of the gas phase

Mass spectrometry measurements on neutral species show that the production of ammonia in the reactor is diminished by the presence of tholins. Besides, new molecules are created at masses such as 27, 41 or 52amu. They can correspond respectively to the formation of HCN, acetonitrile (C_2H_3N) and C_4H_4.

A lot of new positive ions are also created during the interaction of tholins with plasma. We can guess the formation of various $C_xH_yN_z$ species on Fig. 5.

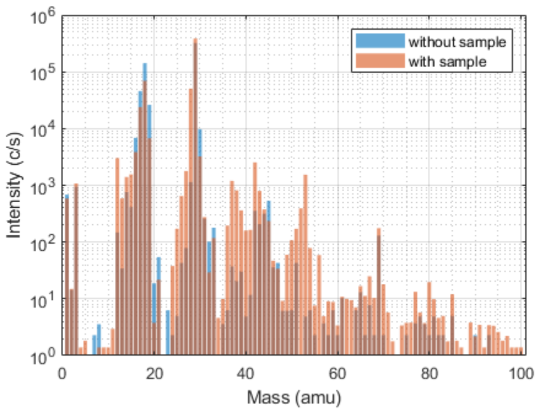

Fig. 5. Mass spectra of positive ions in the reactor without and with tholins.

7. Conclusion and perspectives

MEB and IR spectroscopy show that plasma environment modifies strongly the organic sample. On Titan, N_2 and H_2 plasma species should make the aerosols evolve similarly in the ionosphere. This evolution is in parallel with the carbon chain formation initiated by the presence of methane [3].

While matter loss is seen on the sample, new particles appear in the gas phase. Both neutral species and positive ions are formed from the interaction of N_2-H_2 plasma with tholins. The next step will be to link the apparition of new species to the chemical evolution of tholins seen by IR.

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.

9. References

[1] H. Waite, Science, **316**, 870 (2007).

[2] C. Szopa, Planetary and Space Science, **54**, 394-404 (2006).

[3] E. Sciamma-O'Brien, Icarus, **209**, 704-714 (2010).