## **Exoplanetary Atmospheres and Habitability**

Observatoire de Nice

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# N-rich prebiotic chemistry in the atmosphere of Titan



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## Why looking at Titan ?

|        | Earth   | Titan   |
|--------|---------|---------|
| Radius | 6378 km | 2575 km |
| Tsurf  | 288 K   | 93 K    |
|        |         |         |
|        |         |         |

Titan as an exoplanet and Habitability: Physical and chemical conditions favoring extremes forms of life, not necessarily those known on Earth



## 1- A dense atmosphere



|             | Earth                | Titan                   |
|-------------|----------------------|-------------------------|
| Psurf       | 10 <sup>5</sup> Pa   | 1.5 ×10 <sup>5</sup> Pa |
| Atmospheric | N <sub>2</sub> 78 %, | N <sub>2</sub> 98 %,    |
| composition | O <sub>2</sub> 21 %  | CH <sub>4</sub> 2 %     |

Protects the surface from harsh UV irradiations



## 2- Organic molecules



## 3- Liquid area



Storms and methane rain

(Copyright NASA)



## The Cassini-Huygens mission: 2004-2017

• Data for probing Titan's atmosphere





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Ionosphere:
 In situ instruments / MS
 neutrals, cations, anions, e-

Stratosphere:
 Remote sensor / IR
 Neutrals, aerosols



## Stratosphere: IR spectroscopy



HCN: abundant molecule @ppm



## Stratosphere: IR spectroscopy

#### Unsuspected reactivity of nitriles: Missing consumption process



- Stronger polar enrichment of nitriles than hydrocarbons for a similar photochemical lifetime
- Steeper HCN profile
  observed than predicted

Teanby et al. 2010 Vinatier at al. 2007

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## Ionosphere: chemical involvement of N<sub>2</sub>

- Photodissociation and ionization of N<sub>2</sub>
  - N<sub>2</sub>\*, N(<sup>4</sup>S), N(<sup>2</sup>D), N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, N<sub>2</sub><sup>++</sup>, N<sup>++</sup>

Dutuit et al. 2013, APJ Sup ser.

- Reactions with hydrocarbons:  $CH_4 - C_3H_8$ 





## Ionosphere: unexpected organic growth



- INMS: Neu & Ion<sup>+</sup>
- CAPS-IBS : Ion+
- « Ion chemistry » models hardly explain ion growth
   Highest abundances =
  - N-containing ions

Waite et al 2007 Vuitton et al. 2008 Carrasco et al. 2007 LATM

## Ionosphere: main ion HCNH<sup>+</sup>





4

S

## Ionosphere: protonated imines



### $N(^{2}D)+CH_{4}\rightarrow CH_{2}=NH + H$ highly polymerizable



 $\rightarrow$ key towards aerosols ?



## Ionosphere: where aerosol are initiated

- Mass transfer from positive ions to negatively charged particles
  - Correlation between CAPS IBS and CAPS ELS spectra



## Stratosphere: IR spectroscopy

Aerosols signature FIR-MIR



## A future mission to Titan after Cassini ?

- What cannot be answered with the present instruments onboard Cassini
  - Identification of the large molecules in the atmosphere
    - N content ?
    - Nucleation precursors

 $\rightarrow$ Mass resolution improvement in the upper atmosphere  $\rightarrow$ In situ analysis of the aerosols in the stratosphere



## Meanwhile : experimental simulation

#### Plasma: dissociation and dissociative ionization of N<sub>2</sub> and CH<sub>4</sub> by electronic impact







## Aerosol collection and analysis

 10 hrs ≈ 100 mg of Titan's organic aerosol analogues





## High resolution mass spectrometry

070626\_lot2MeOH #3-225\_RT: 0,06-6,54\_AV: 223\_NL: 6,25E5\_





#### Complex composition, but well structured spectra → polymeric structure

Pernot et al. Anal. Chem 2010.



## High resolution mass spectrometry



## **Molecular identification**

- Nitrogen-rich prebiotic matterial
  Derivatization + GC-MS analysis
  - + comparison to a standard





## Nitrogen efficient for chemical growth

- Comparison of the aerosol productions with and without N<sub>2</sub>
- CH<sub>4</sub> diluted either in N<sub>2</sub> or in He (90-10%)

|   | With N <sub>2</sub> | With He |
|---|---------------------|---------|
| Aerosol<br>production rate<br>mg.hr <sup>-1</sup> | 6.1                 | 1.0     |



## Pyr-GCMS analysis of analogues



## Conclusion

- Titan is an accessible model of exoplanet with a high habitability interest
- Nitrogen is found to be essential for chemical growth
- The accessibility and the numerous Cassini data enabled to validate global experimental simulation to study upper atmospere system

→ Plasma experiments provide a pertinent and powerful tool to explore the reactivity of exoplanet upper atmospheres.