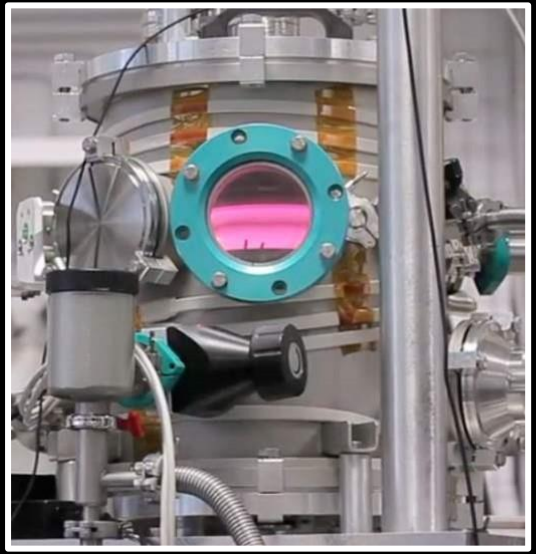
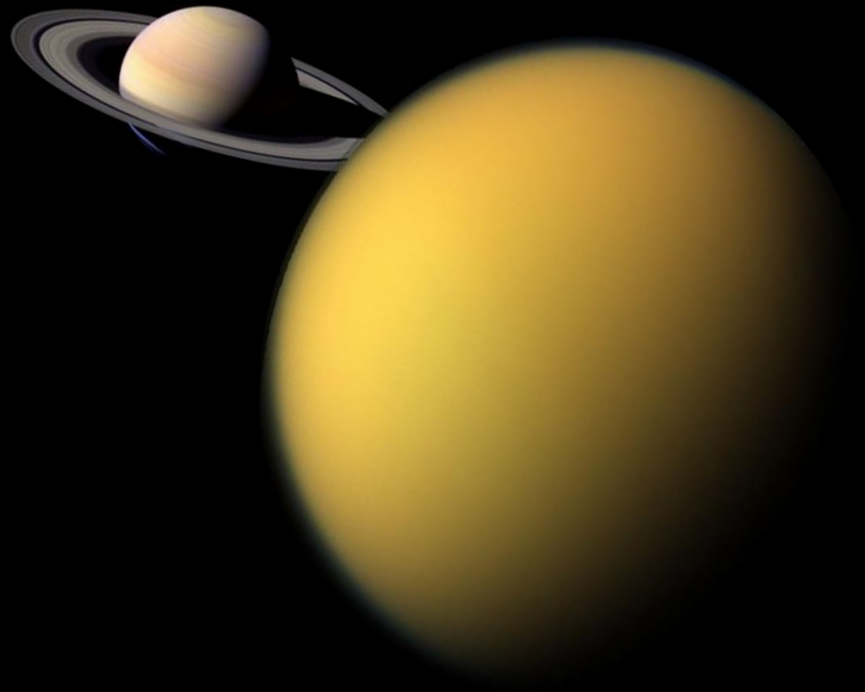
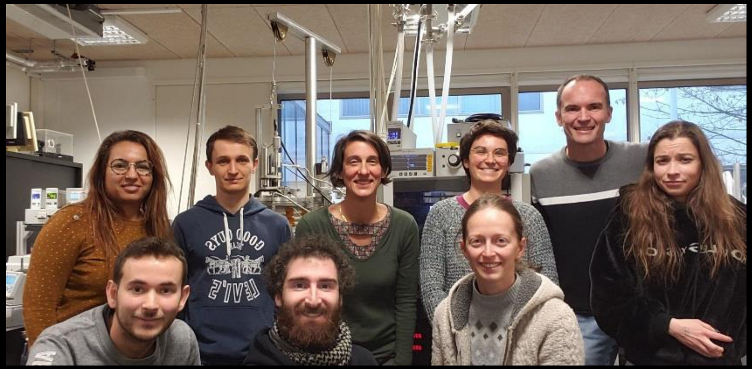
Simulating planetary atmospheres in the lab:
in depth investigation of chemical and microphysical processes in support to observations and models

Audrey CHATAIN

and the ATMOSIM team in LATMOS







since 1998 (28 years!)

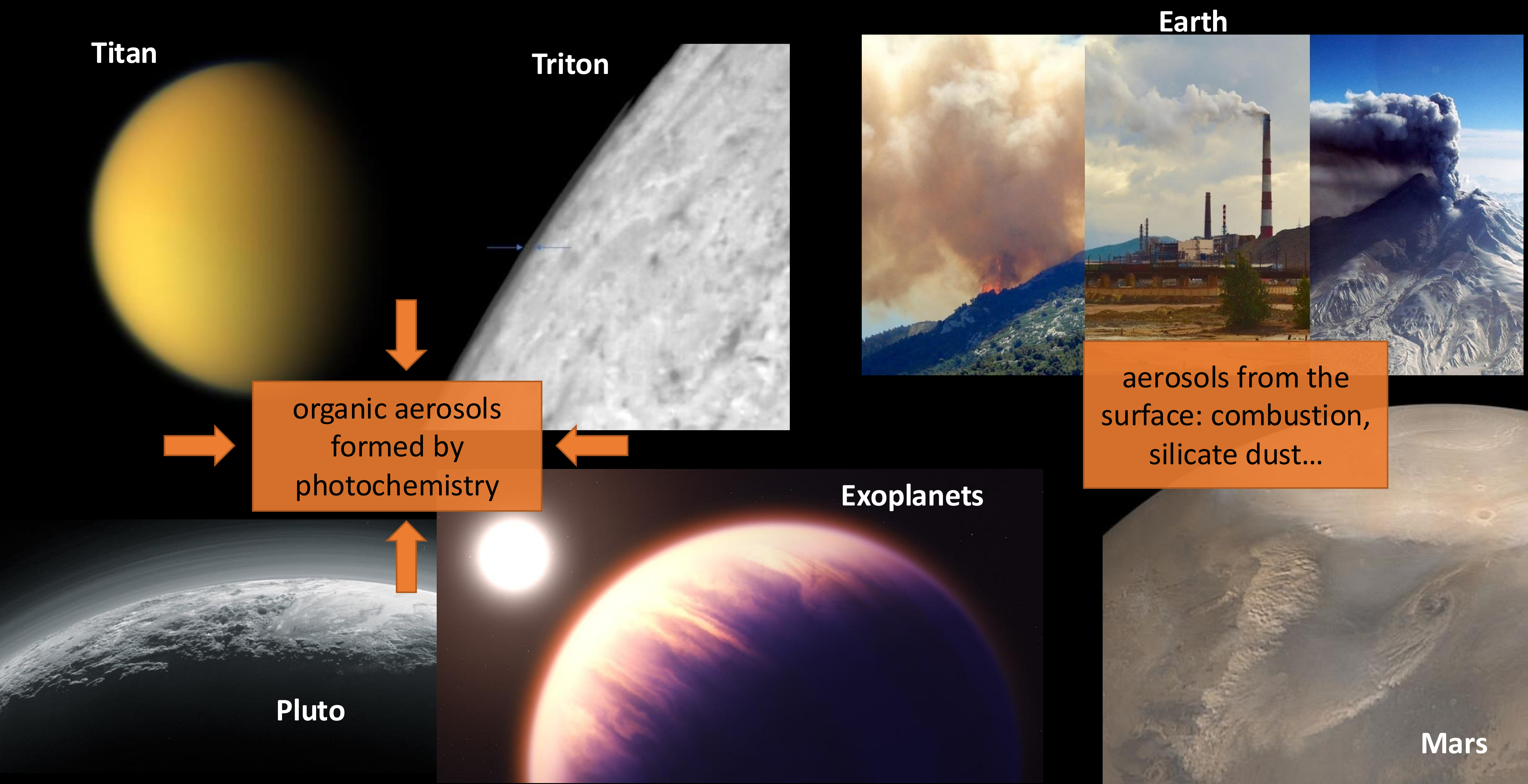
~50 researchers/engineers

15 PhD defended

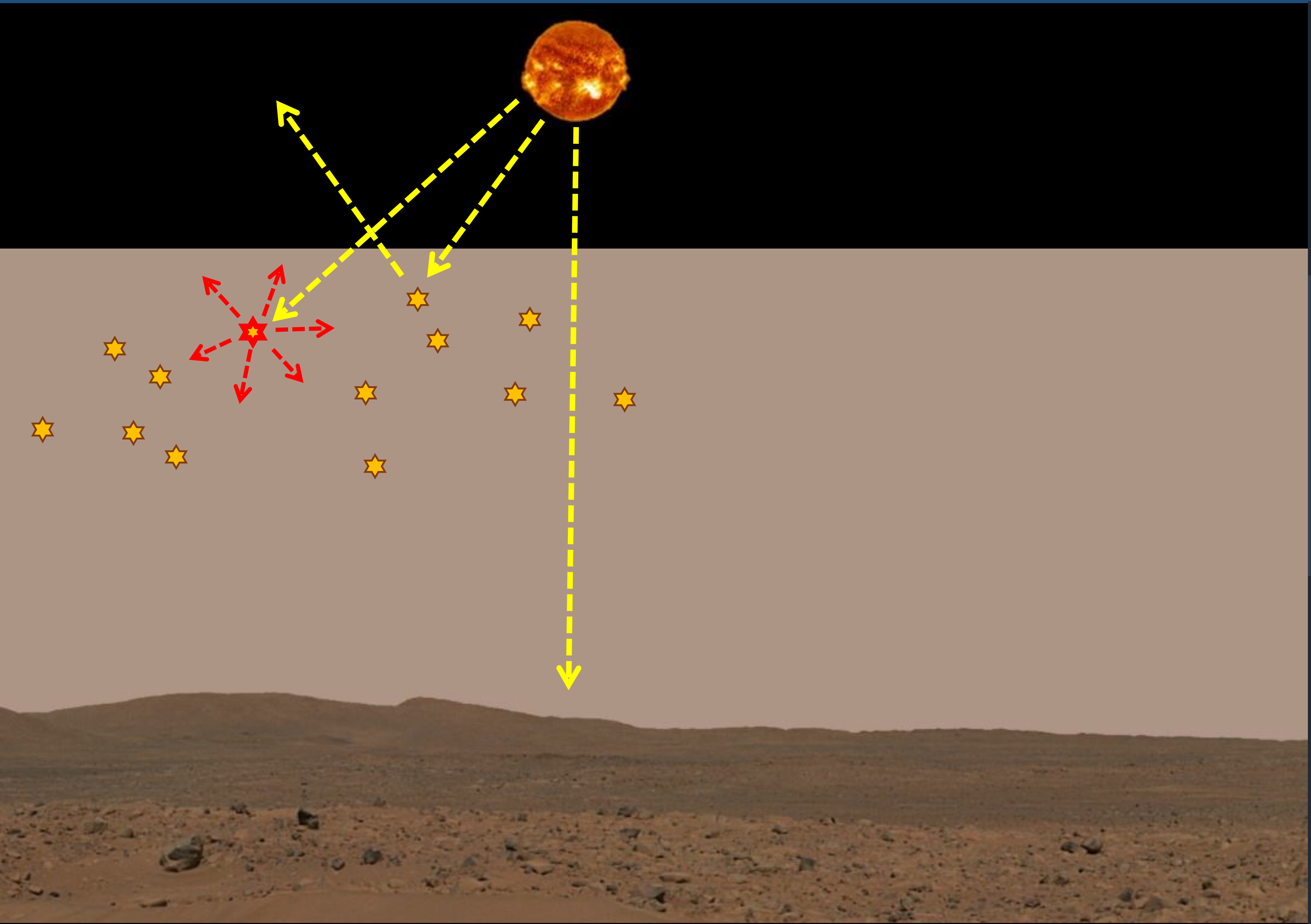
7 postdocs

MOTIVATION: AEROSOLS EVERYWHERE

(not including volatile condensation)



Issue 1: effect of aerosols on planetary climates



Important on all planets

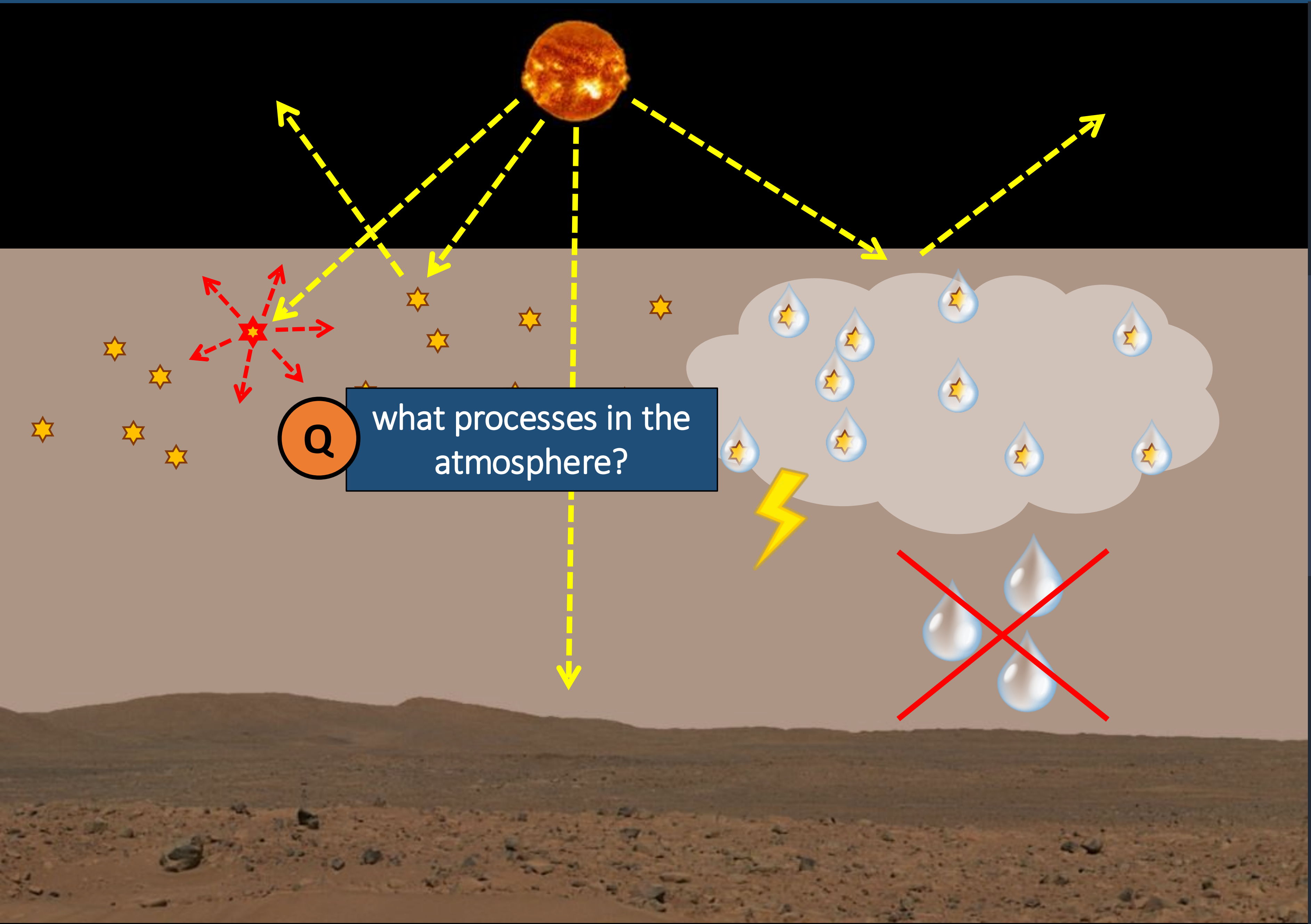
- Earth (pollution, climate)
- Mars (storms, CO_2 cycle)
- Titan (weather)
- …

Opposite effects

- radiative cooling
- heating in the atmosphere

[Ramanathan et al, 2001]

Issue 1: effect of aerosols on planetary climates



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- heating in the atmosphere
- hazes
- less precipitations
- charge effects

[Ramanathan et al, 2001]

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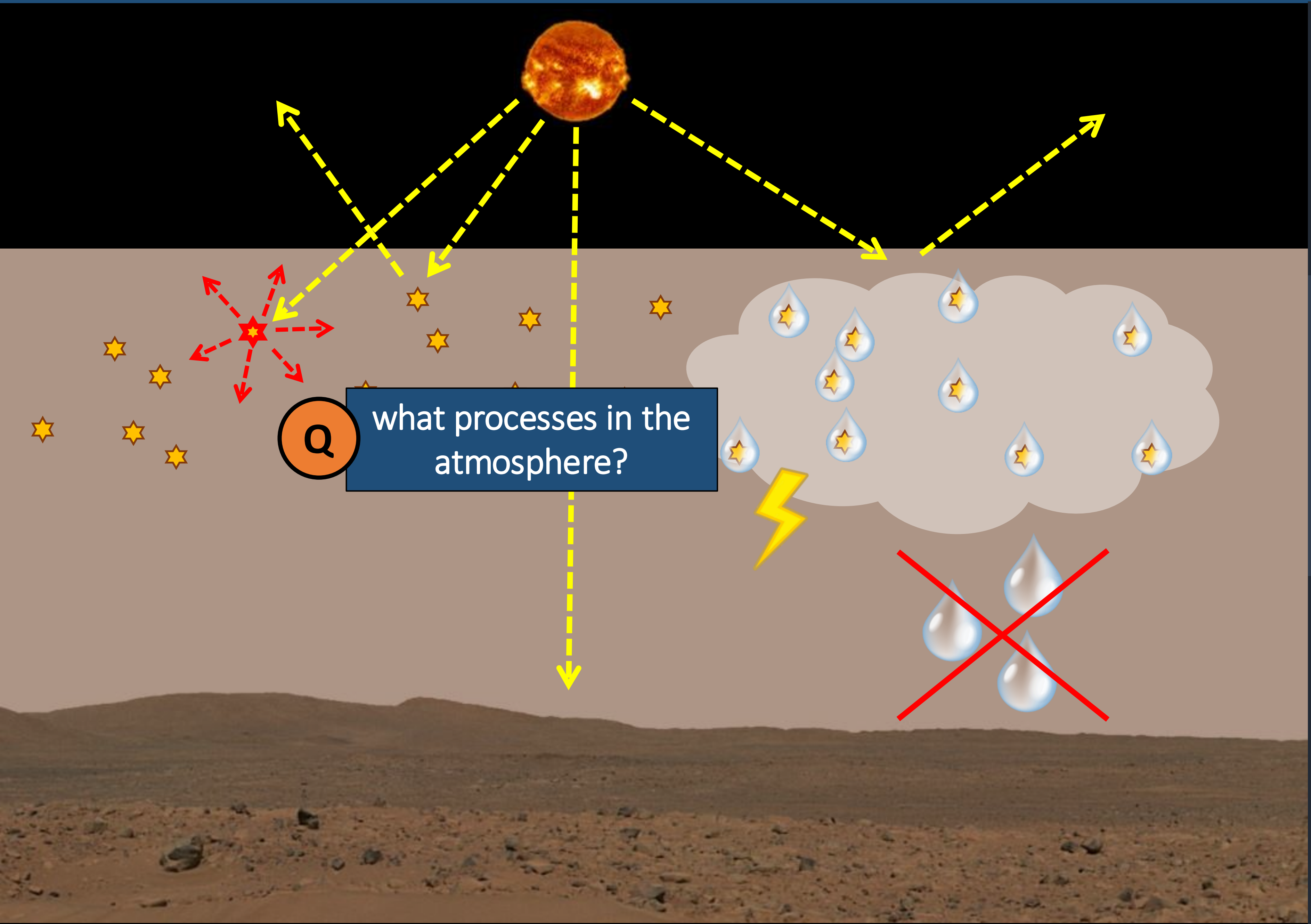

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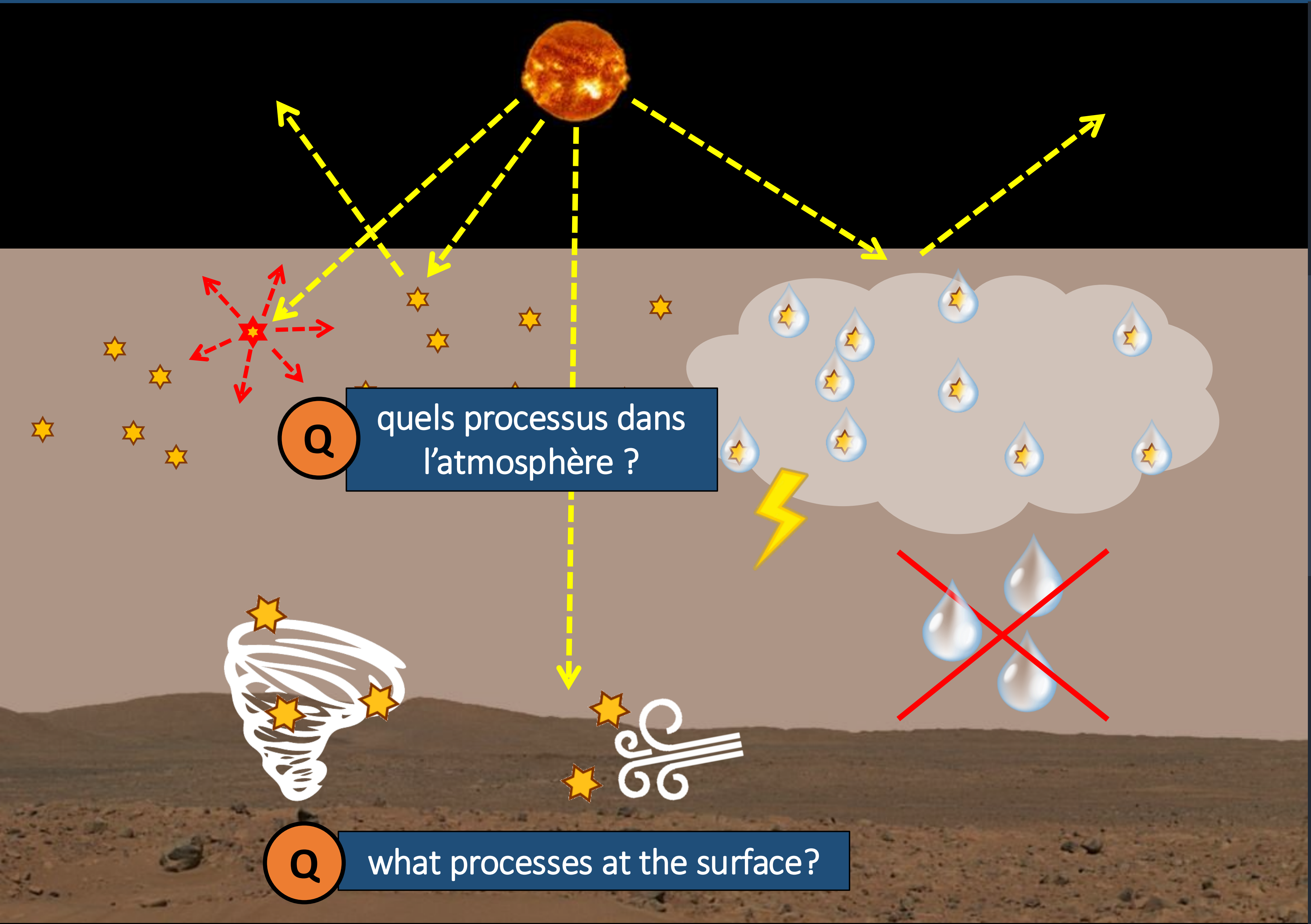
… dependant on the origin of the aerosols

- morphology
- chemical composition

Q

Issue 1: Effect of aerosols on planetary climates



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[Ramanathan et al, 2001]

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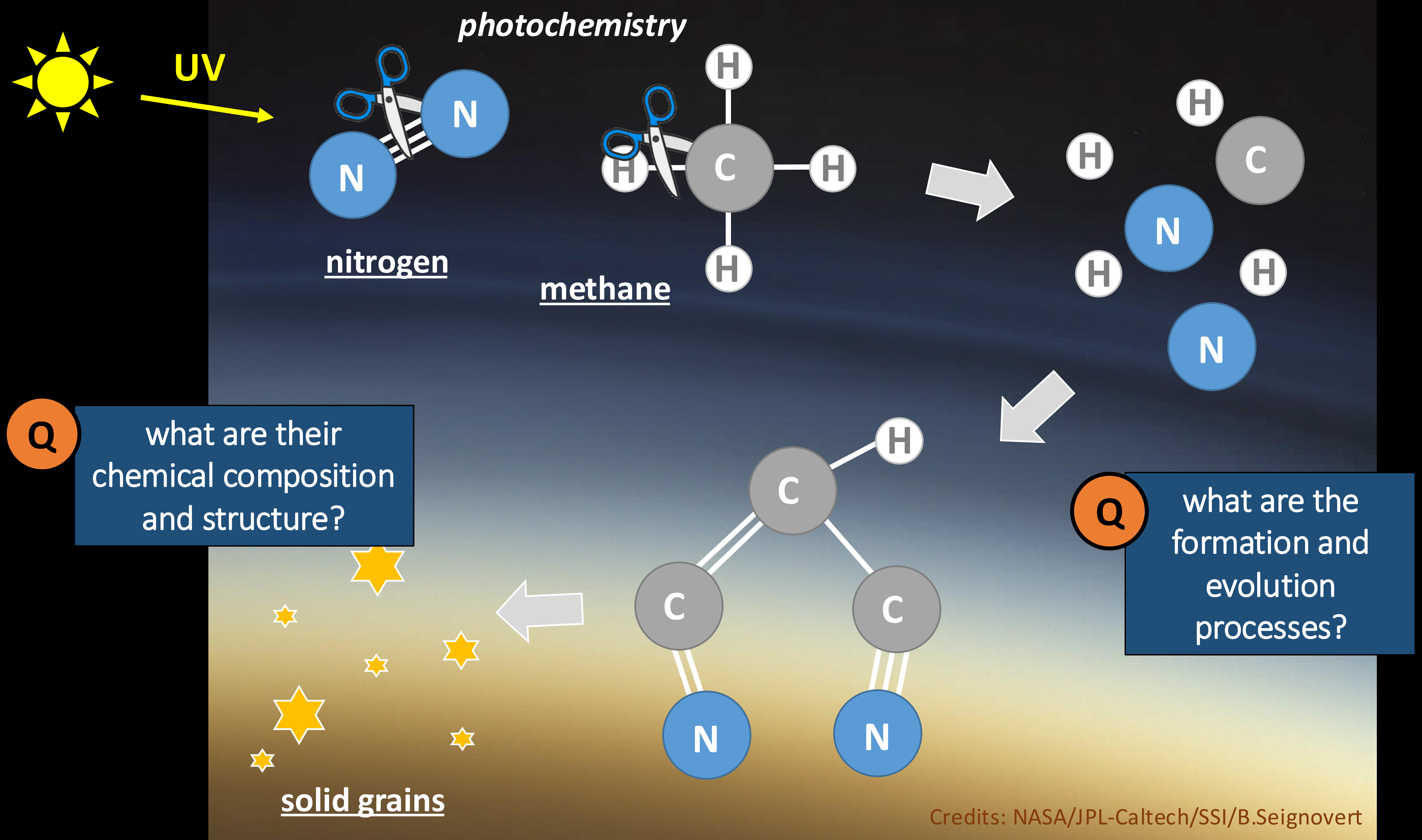
Q

ISSUE 2: PHOTOCHEMICAL AEROSOLS, PREBIOTIC MATERIAL?



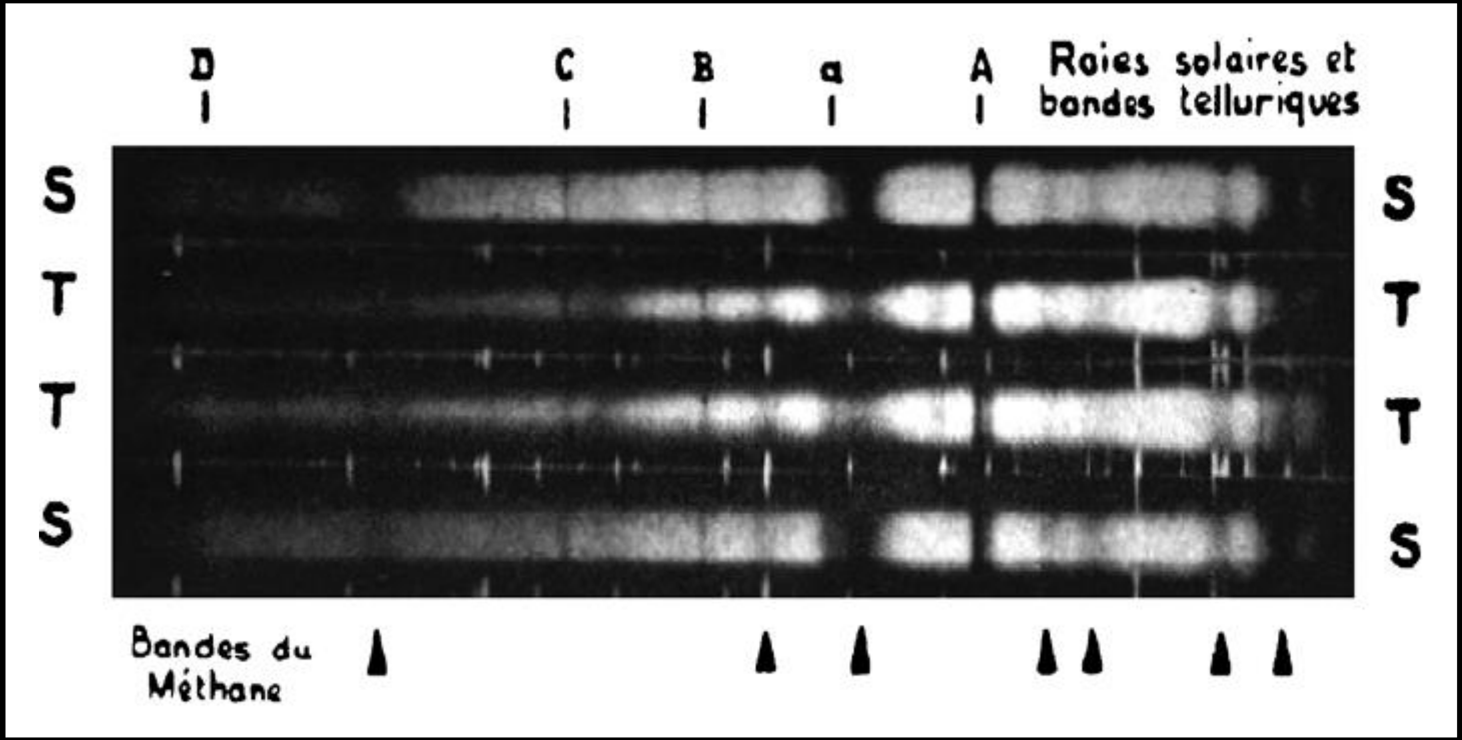
Beginning of the lab experiments: the mystery of Titan's atmosphere

- **methane (CH_4) detection** with a 2m telescope and a prism spectrograph [Kuiper, 1944]

- **di-hydrogene (H_2) detection**
=> what source?? [Trafton, 1972]

- **UV absorption**
=> from micron-size particles? [Barker & Trafton, 1973]

- **hydrocarbons detection** in the IR: C_2H_2, C_2H_4 and C_2H_6 [Gillett, 1975]

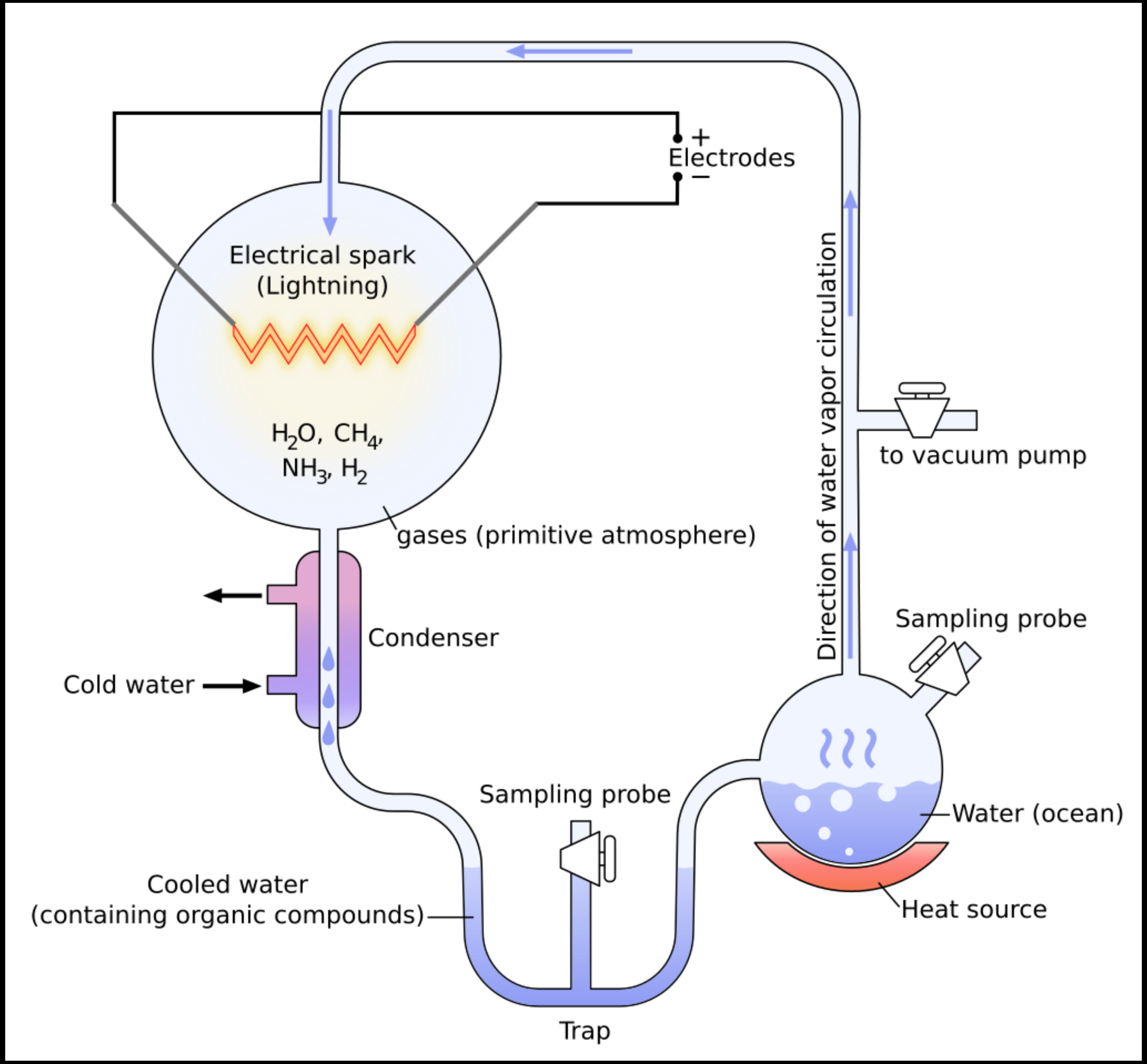


Spectra of Saturne (S) and Titan (T) by Kuiper, at the MacDonald observatory (1944).

Beginning of the lab experiments: the mystery of Titan's atmosphere

- **Miller-Urey experiment** (1953): the atmosphere of Early Earth could have formed amino acids

© Peter Sawyer/Smithsonian Institution



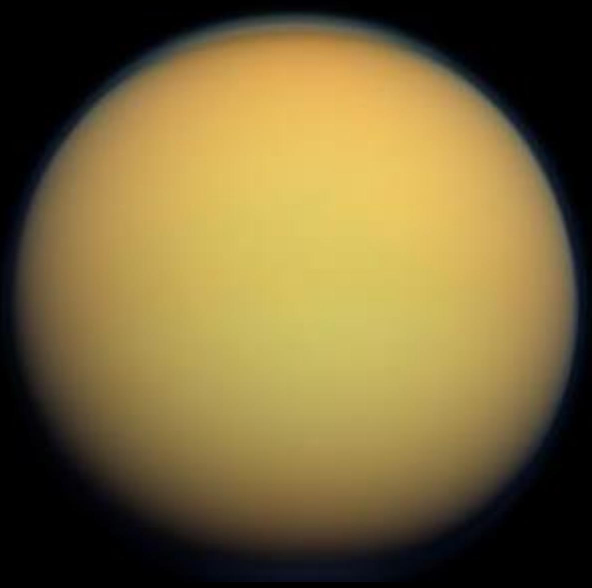
© wikimedia:YassineMrabet

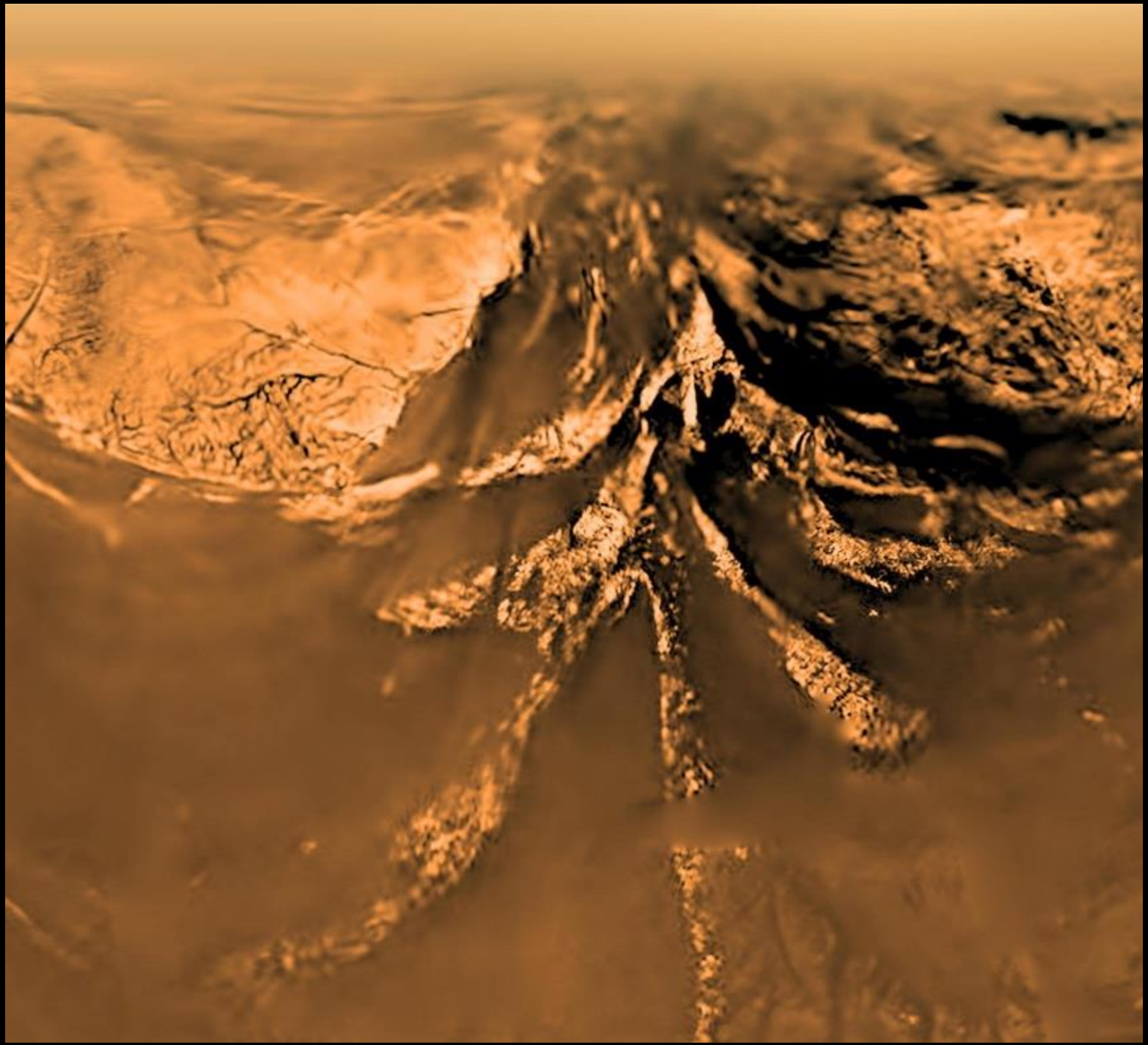
- **similar experiments adapted to Titan** from 1971

  ⇒ Production of complex organic molecules and orange grains (*tholins*)!

  ⇒ Voyager 1 is deviated to visit Titan!

Target n°1: Titan, photochemical aerosol factory



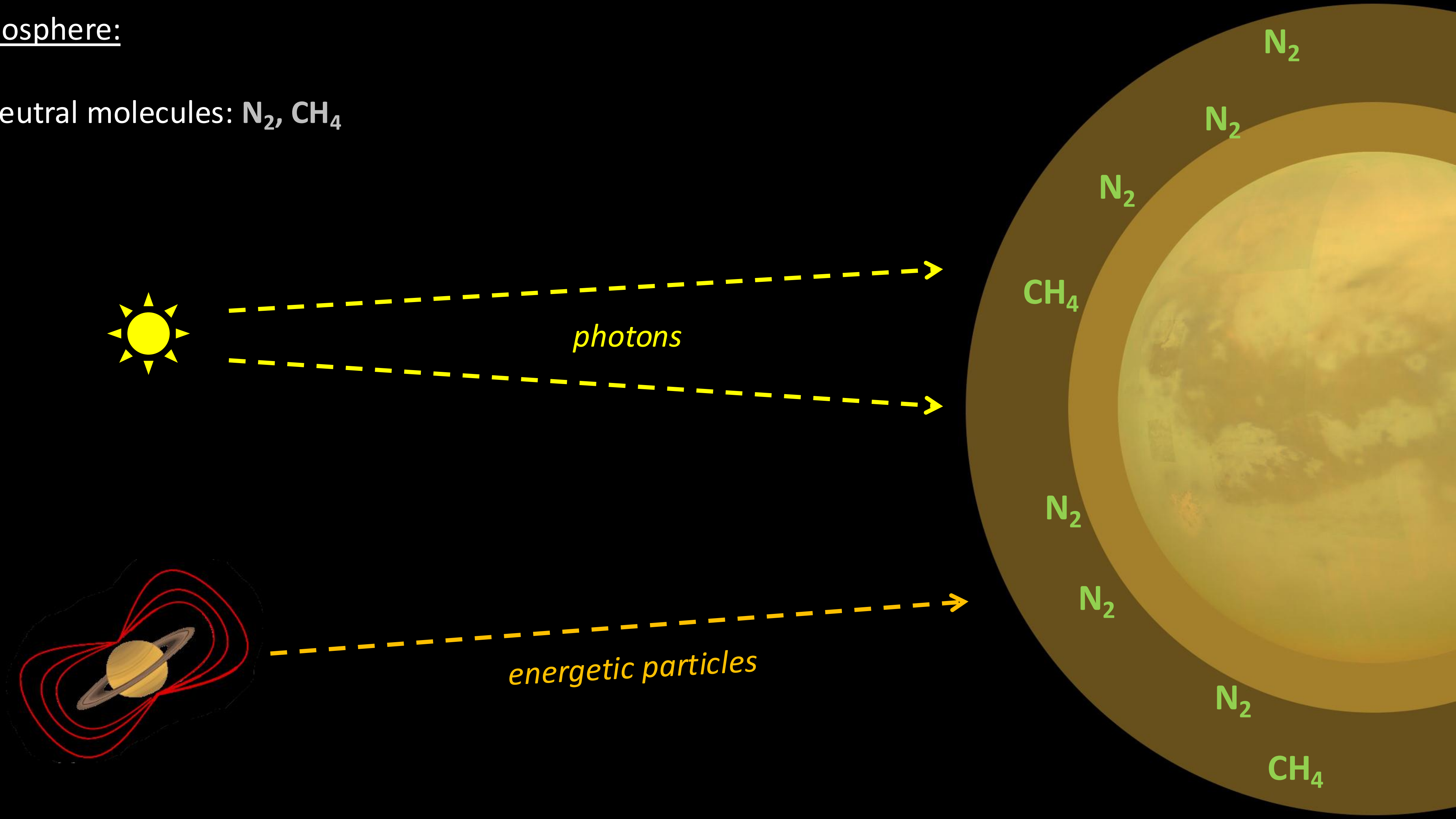


Crédits : NASA-ESA

Photochemical aerosols: how does it work?

Species in the ionosphere:

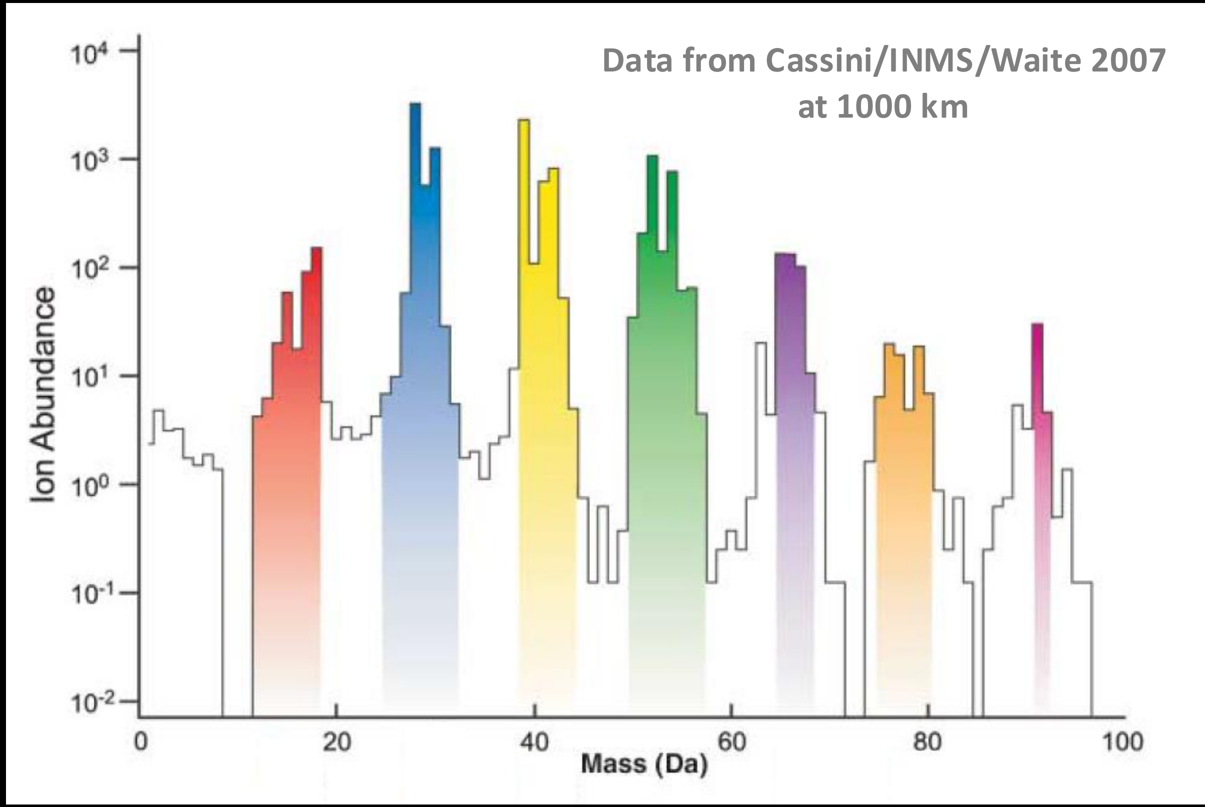
- neutral molecules: N_2, CH_4

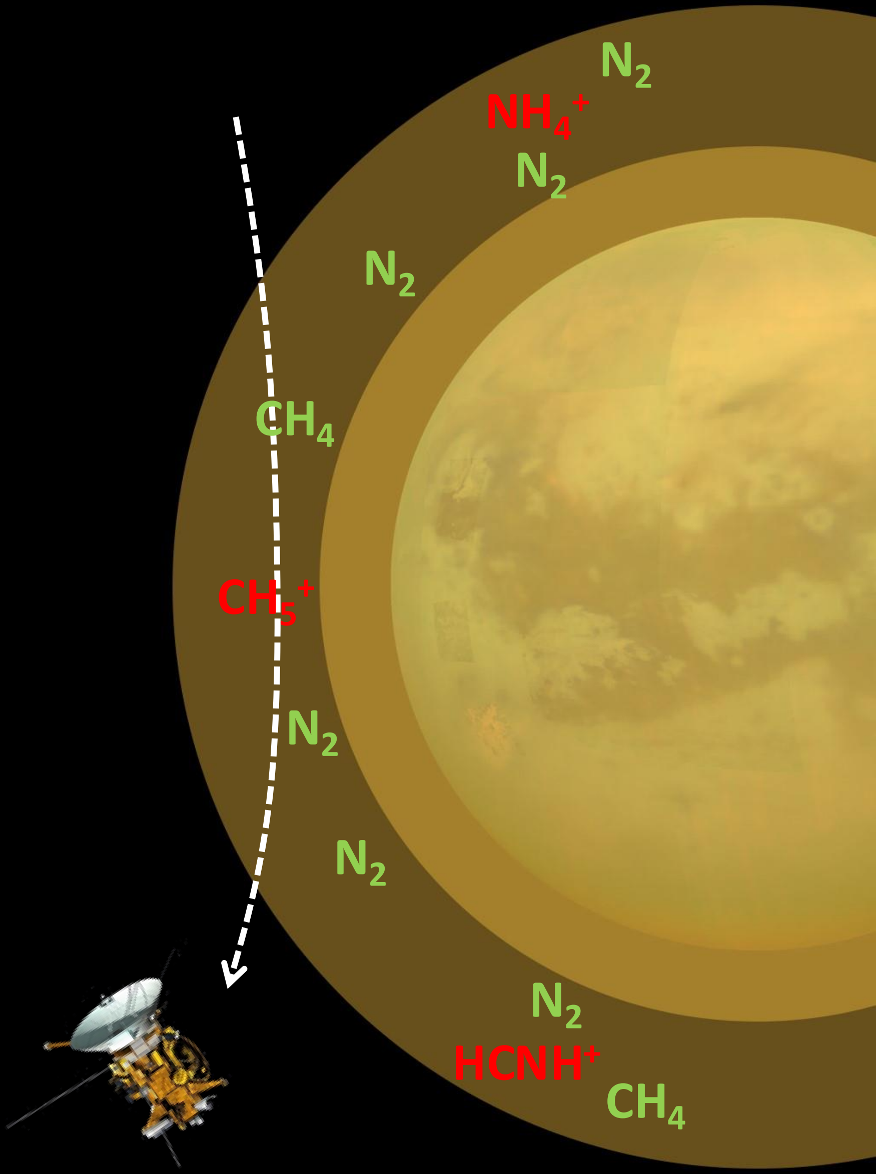


PHOTOCHEMICAL AEROSOLS: HOW DOES IT WORK?

Species in the ionosphere:

- neutral molecules: N_2, CH_4
- positive ions: $C_xH_yN_z^+$





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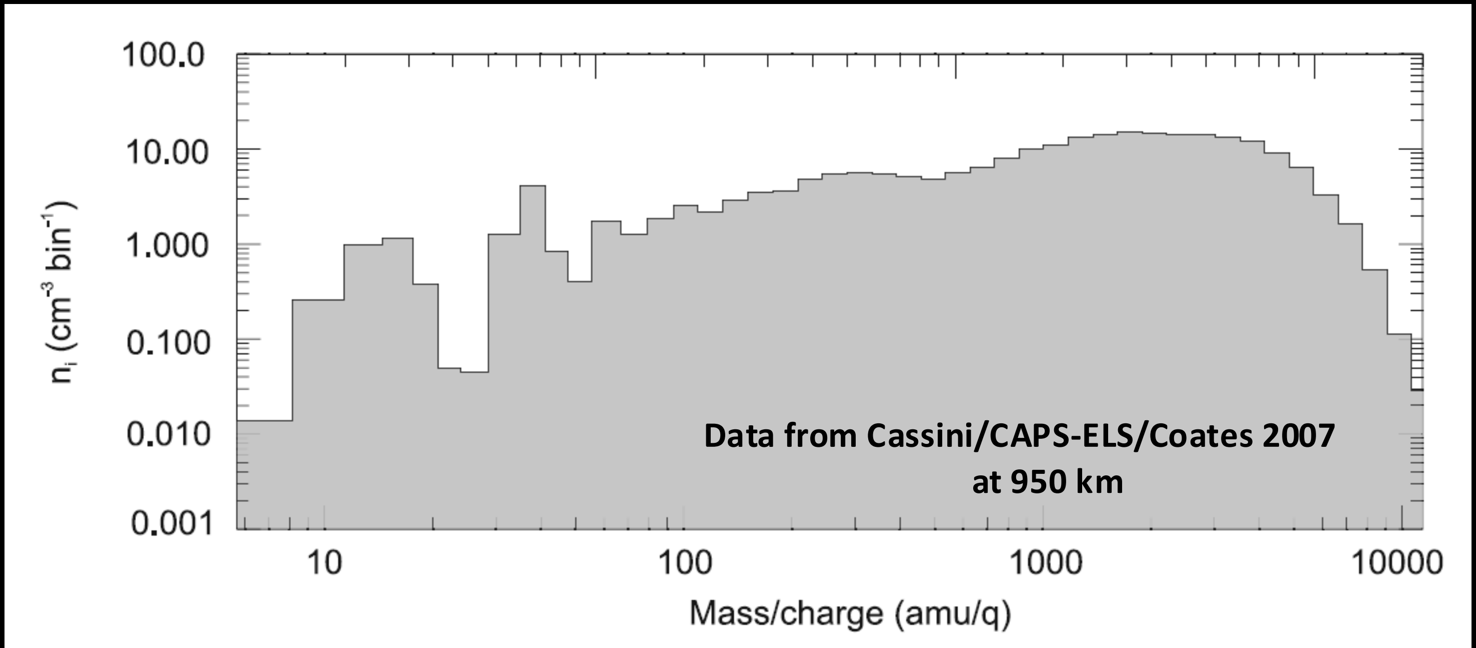
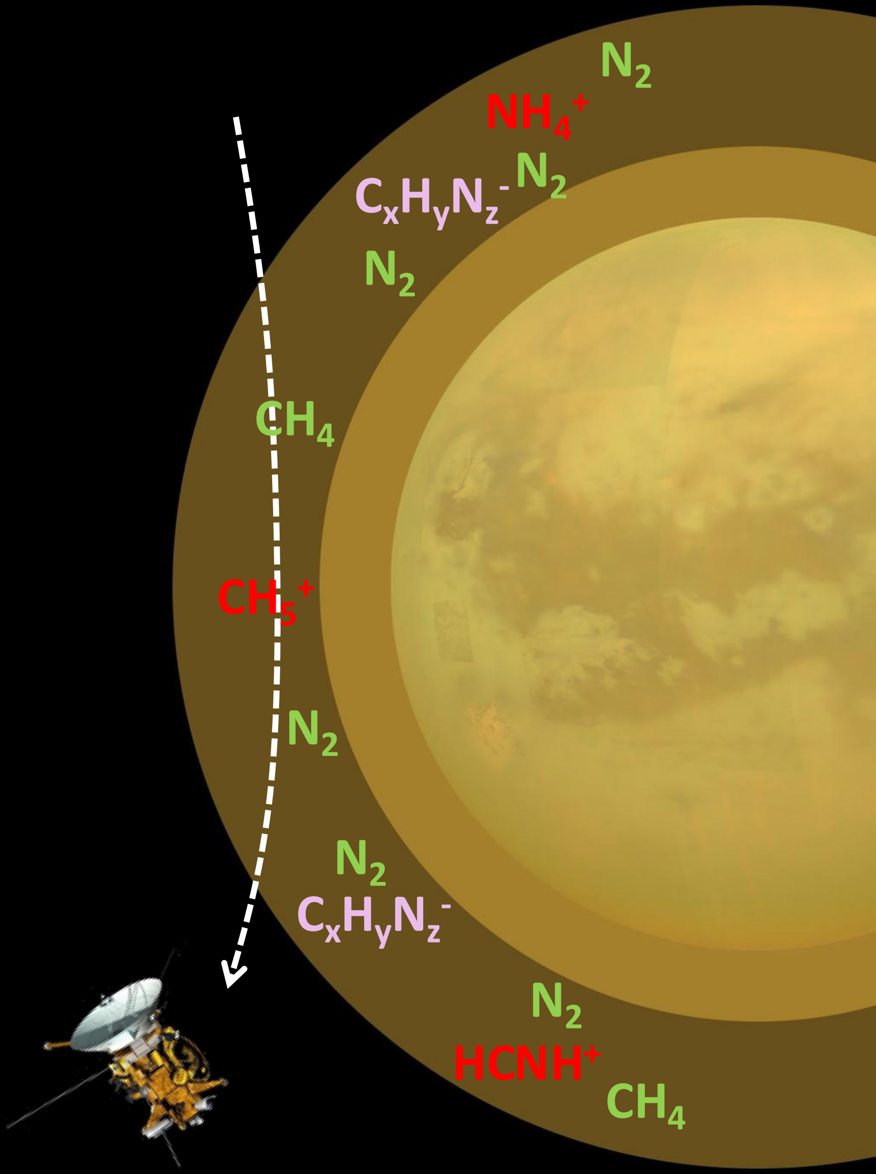
- negative ions: some with >1000 atoms!!!

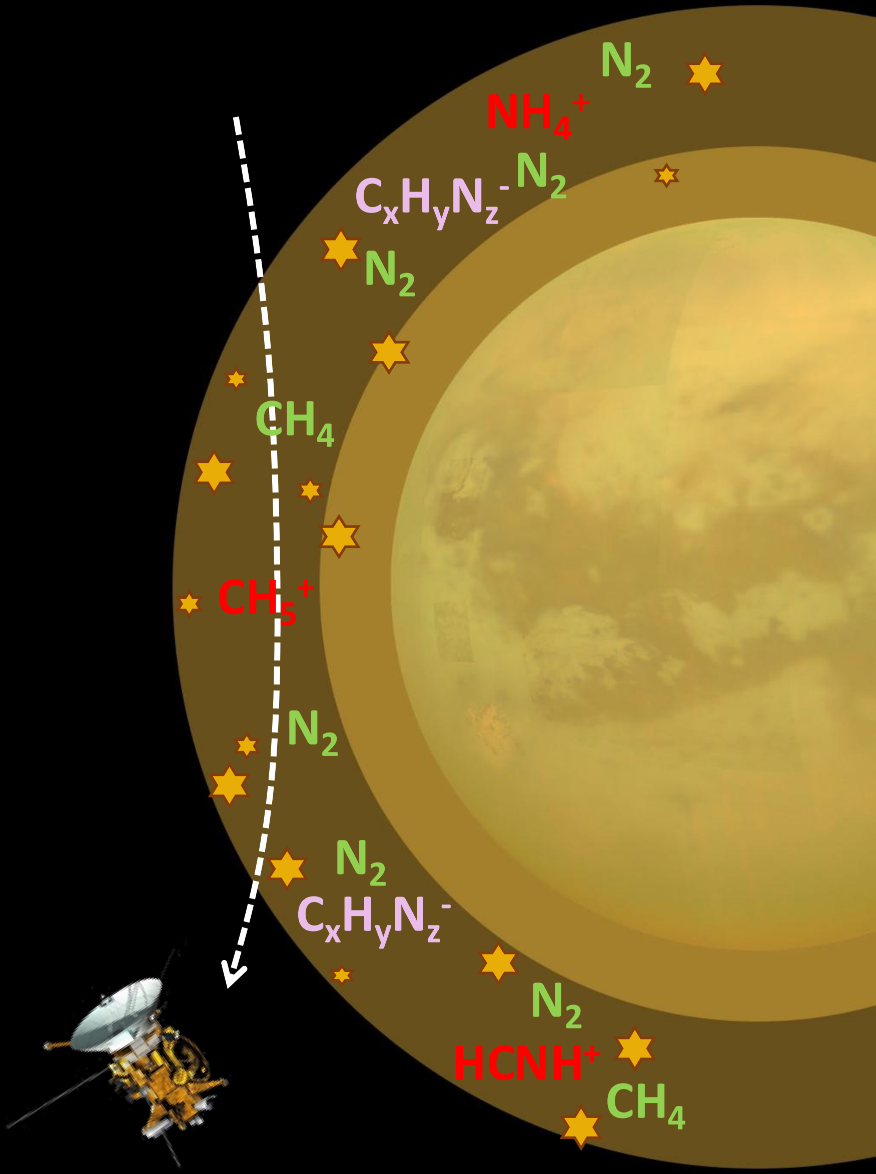




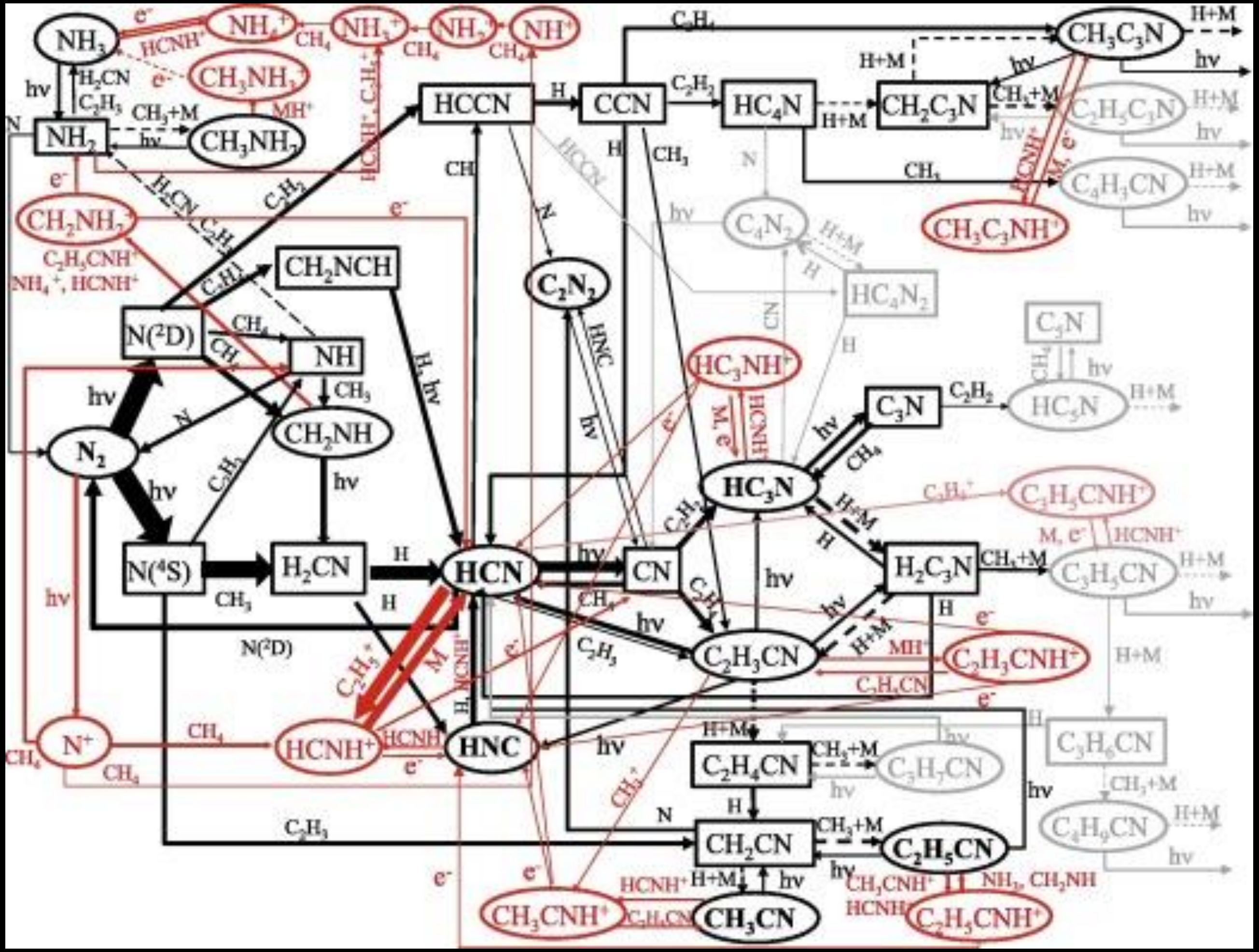
PHOTOCHEMICAL AEROSOLS: HOW DOES IT WORK?

Species in the ionosphere:

- neutral molecules: **N_2, CH_4**
- positive ions: $C_xH_yN_z^+$
- negative ions: some with >1000 atoms!!!
- organic dust: 1-10 nm



Photochemical aerosols: difficult theory



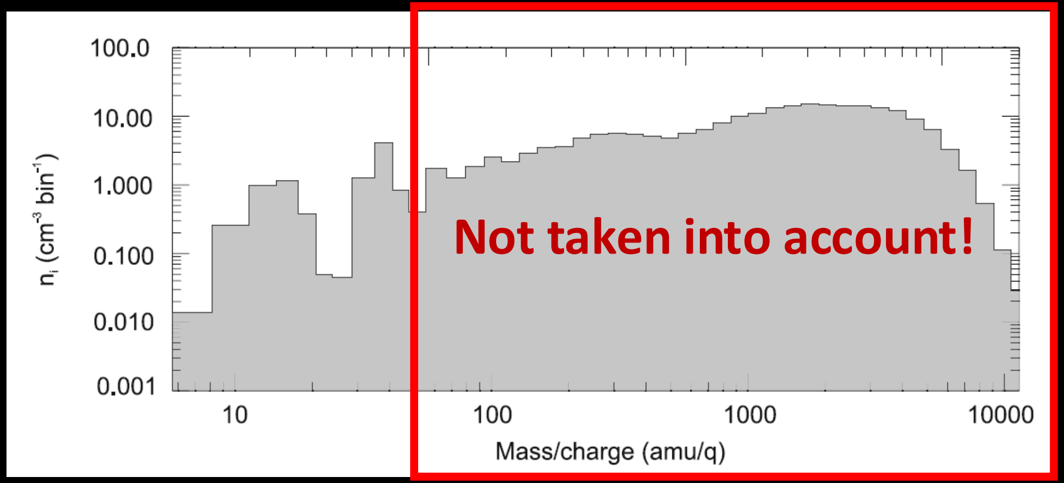
Theorical photochemical models:

→ all species

→ all reactions and their coefficients

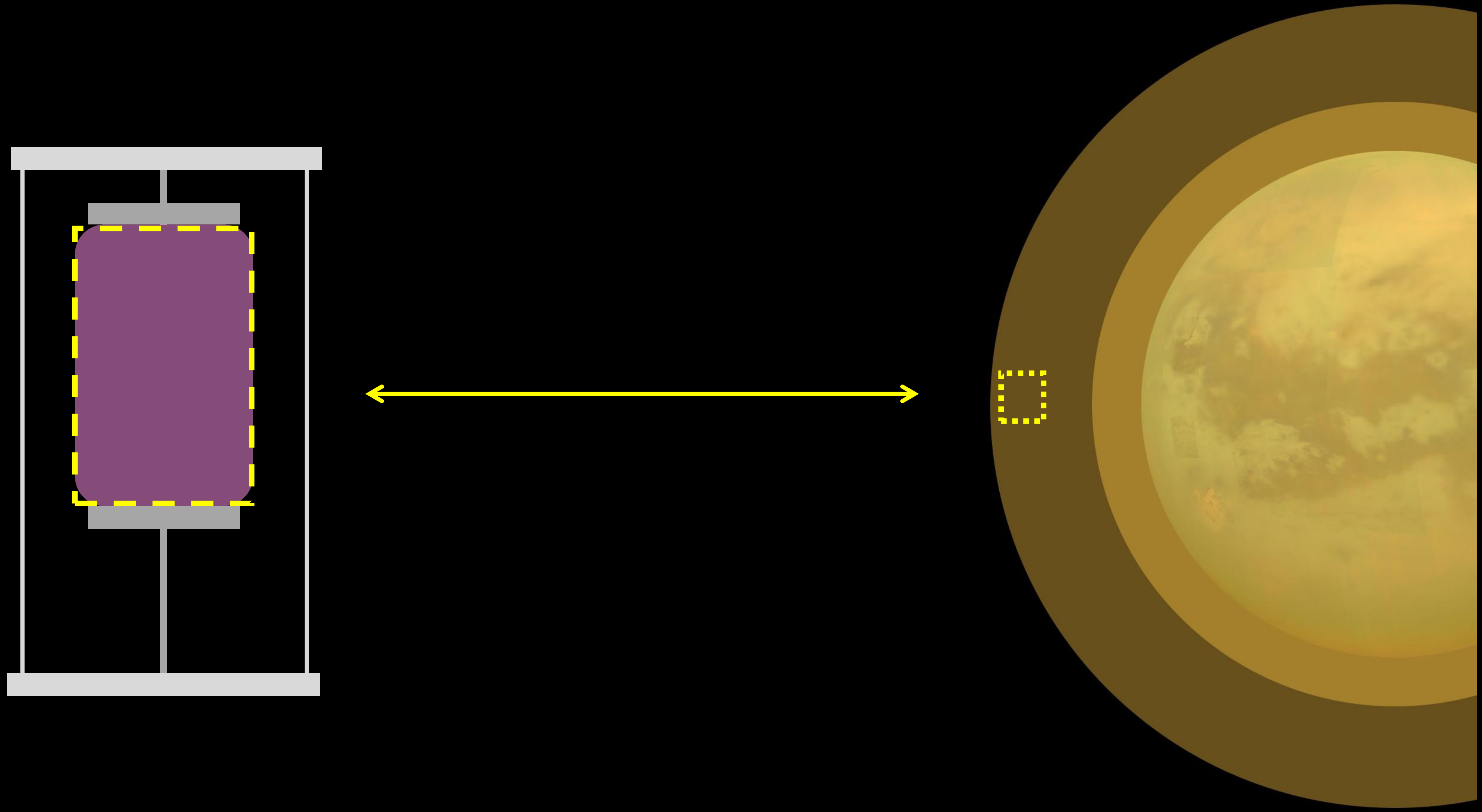
⇒ Hundreds of pages of equations

⇒ Limited to 74u…



Vuitton et al, Icarus (2019)
Dobrijevic et al, Icarus (2016)

Study the formation of aerosols in the lab



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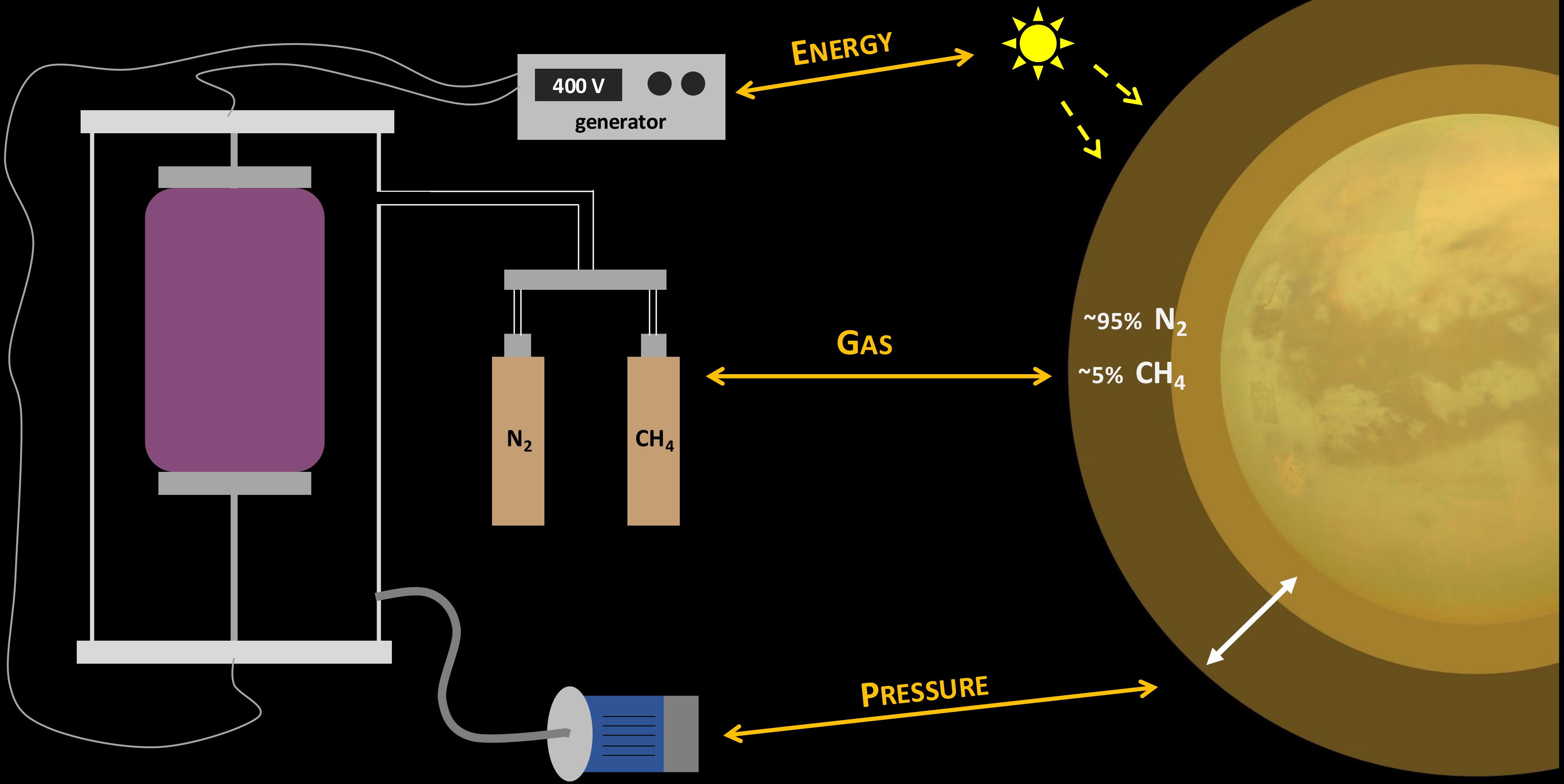
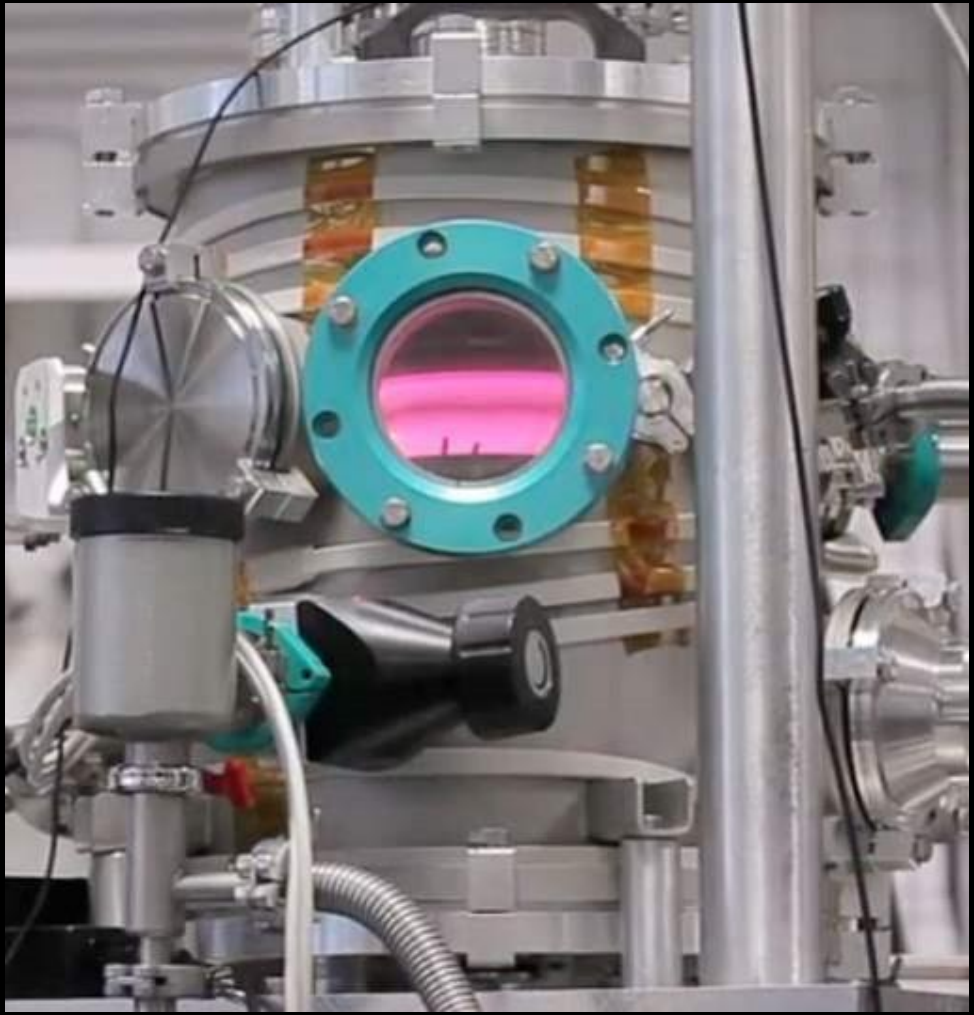
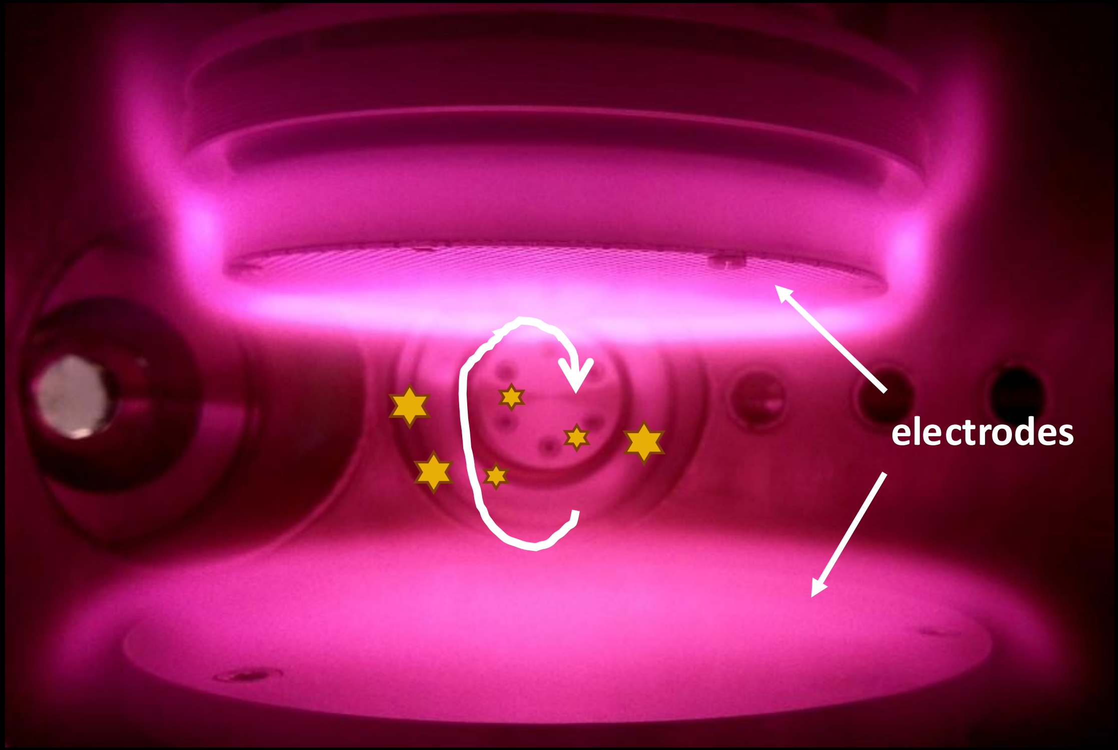


STUDY THE FORMATION OF AEROSOLS IN THE LAB

Plasma experiment PAMPRE (at LATMOS) :



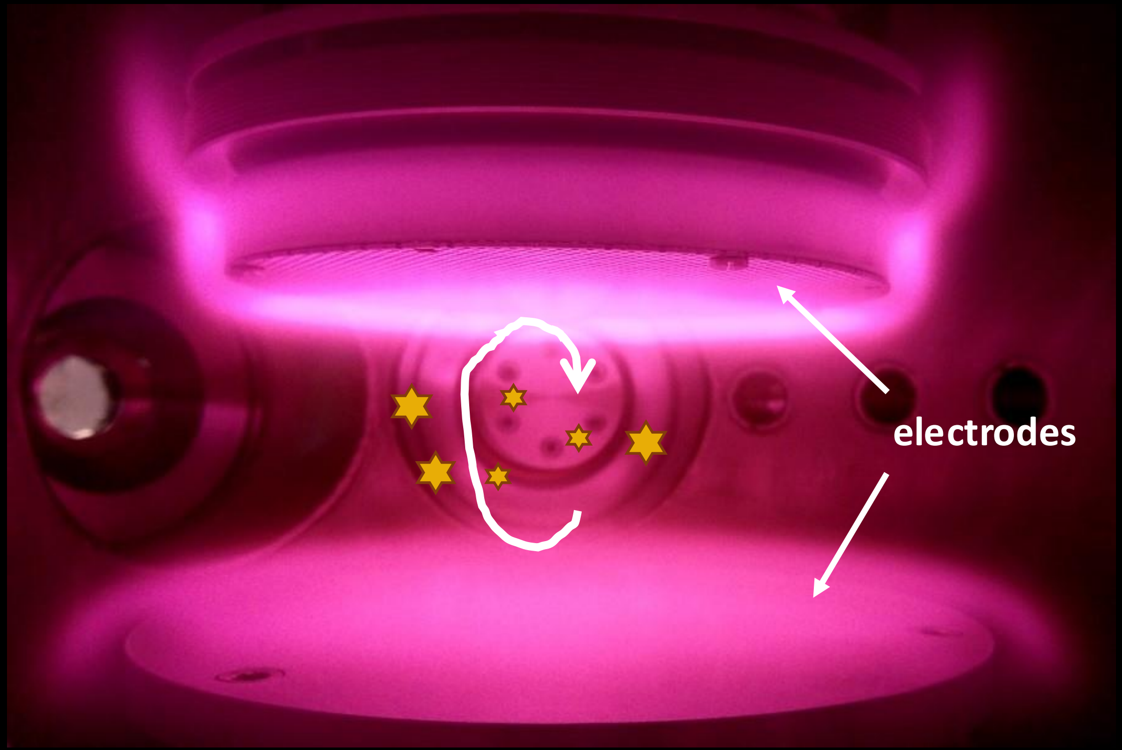
[Szopa, Cernogora et al, 2007]



PAMPRE: Production d'Aérosols en Microgravité par Plasma REactifs

STUDY THE FORMATION OF AEROSOLS IN THE LAB

video



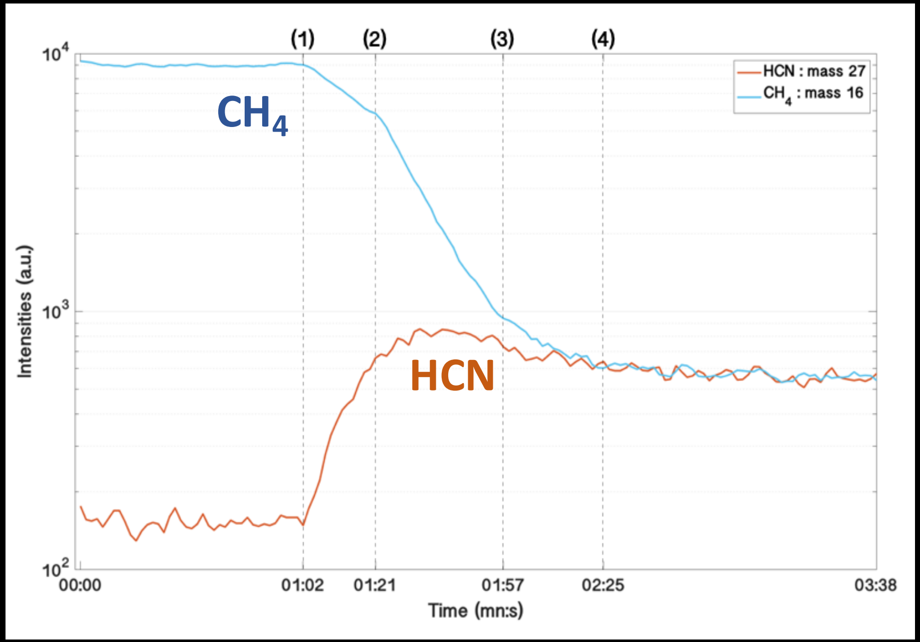
PAMPRE: Production d'Aérosols en Microgravité par Plasma REactifs

STUDY THE FORMATION OF AEROSOLS IN THE LAB

Plasma experiment PAMPRE (at LATMOS) :

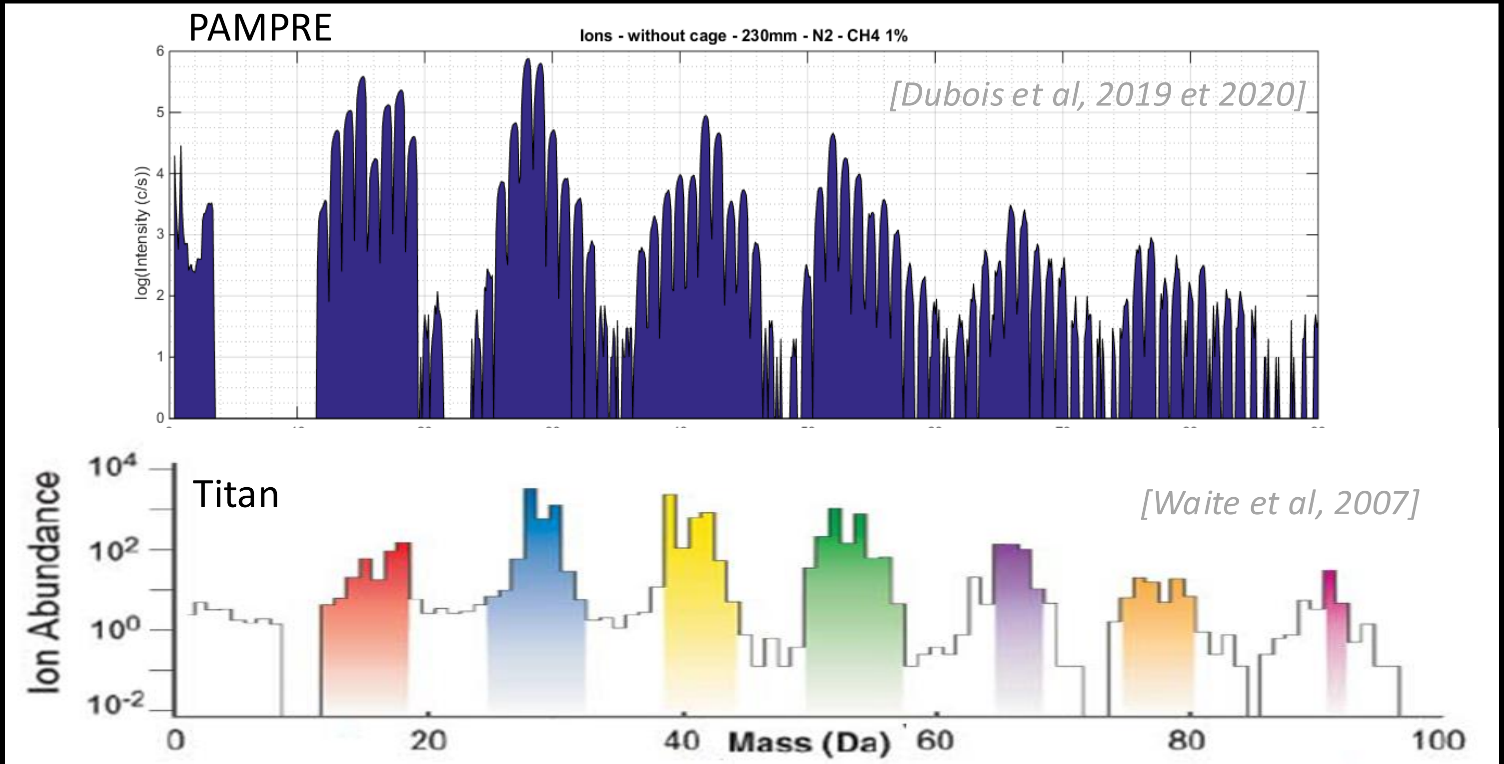
Mass spectrometry for the gas phase
=> to understand the processes

When the plasma is started: consumption of methane and production of new compounds:



[Perrin et al, 2021]

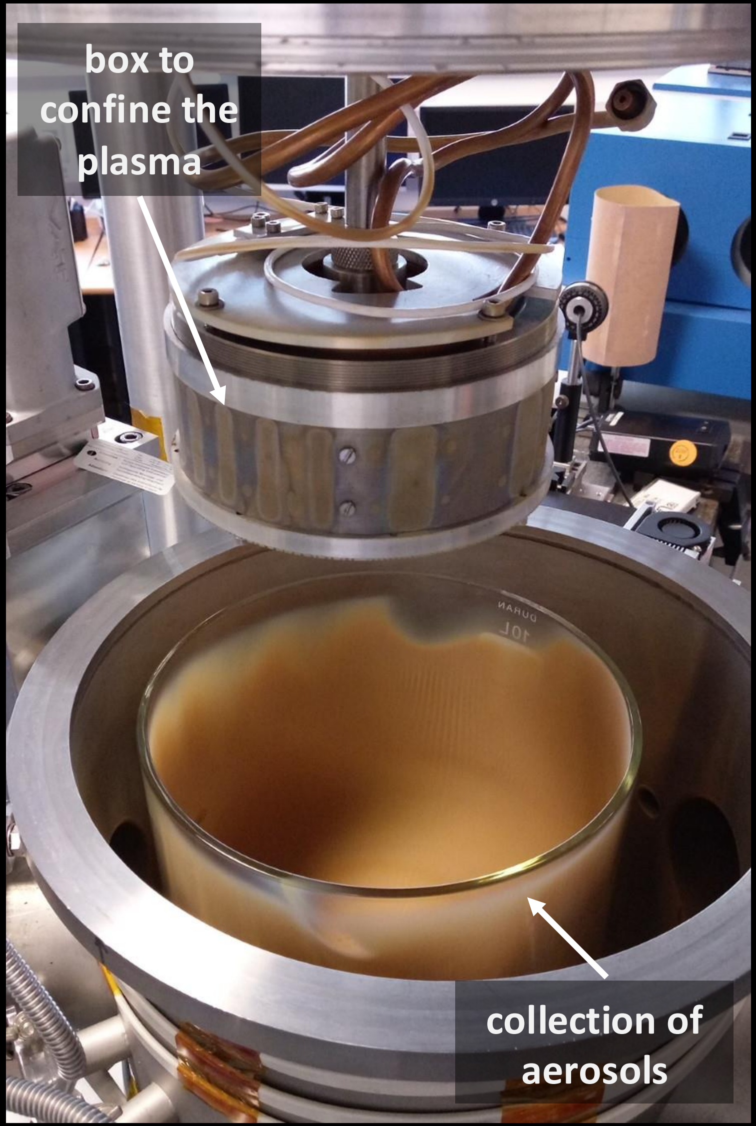
Positive ions obtained:



Other possible analyses of the gas phase: IR, visible and UV spectroscopy; cold trap and GC-MS…

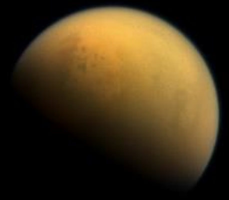
STUDY THE FORMATION OF AEROSOLS IN THE LAB

Plasma experiment PAMPRE (at LATMOS) :



A plasma discharge in N_2-CH_4 leads to the formation of organic dust, called *tholins*.

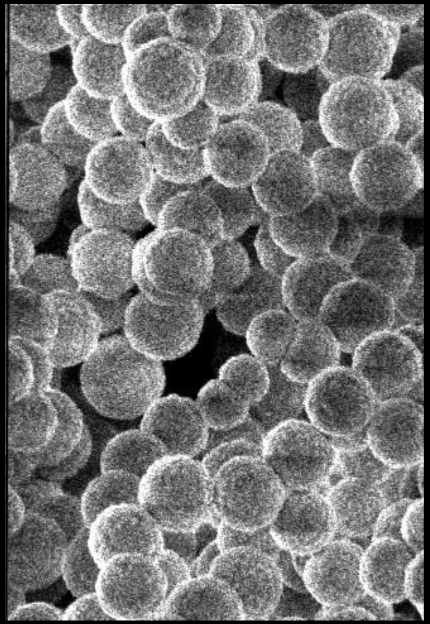
1% CH_4 **10% CH_4**

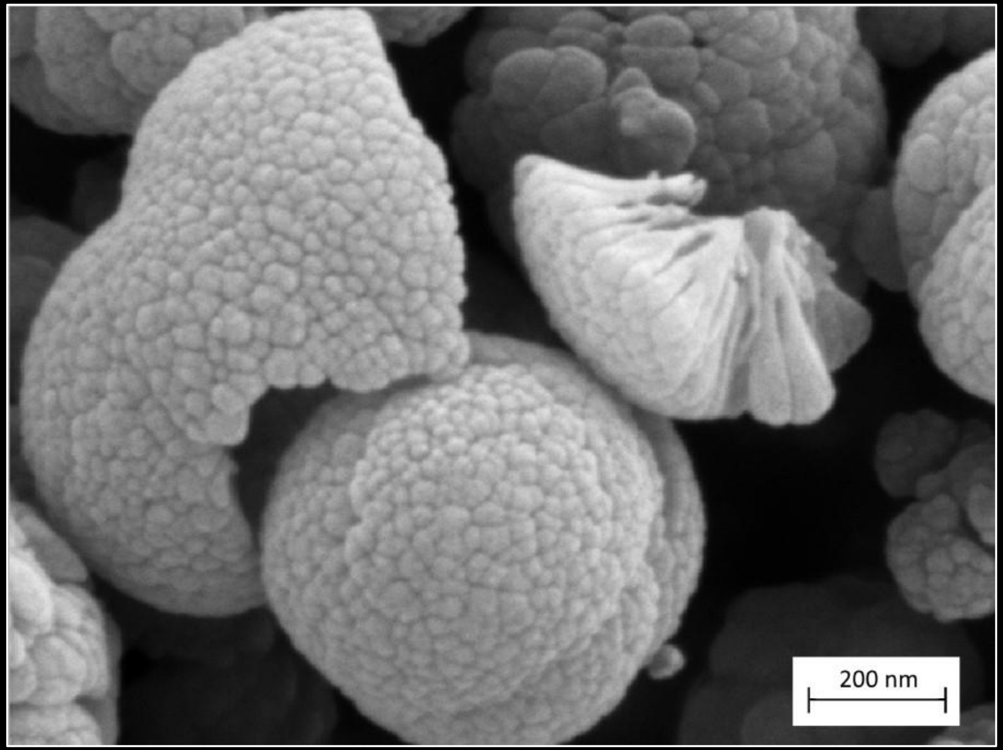


=> collected to be analyzed *ex situ*

AEROSOL PROPERTIES: CAULIFLOWER SPHERES

- Spheres from 200 nm to a few µm
- Size that depends on the exposure time
- Possibly agglomerates
- Radial growth





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LGPM GÉNIE DES PROCÉDÉS ET MATÉRIAUX
CentraleSupélec

AEROSOL PROPERTIES: WHAT CHEMICAL COMPOSITION?

- A lot of nitrogen incorporated!

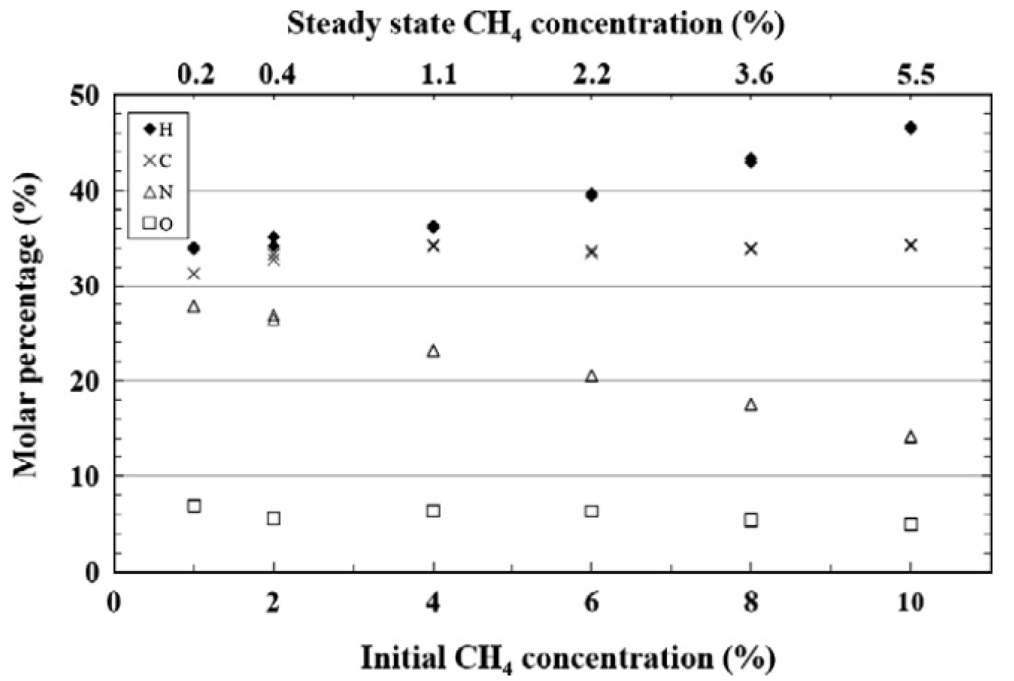


Fig. 6a. Elemental composition of tholins as a function of initial (bottom horizontal axis) and steady state (top horizontal axis) CH_4 concentrations, for p = 0.9 mbar: H, black diamonds; C, crosses; N, triangles; O, squares.

1% CH_4

10% CH_4

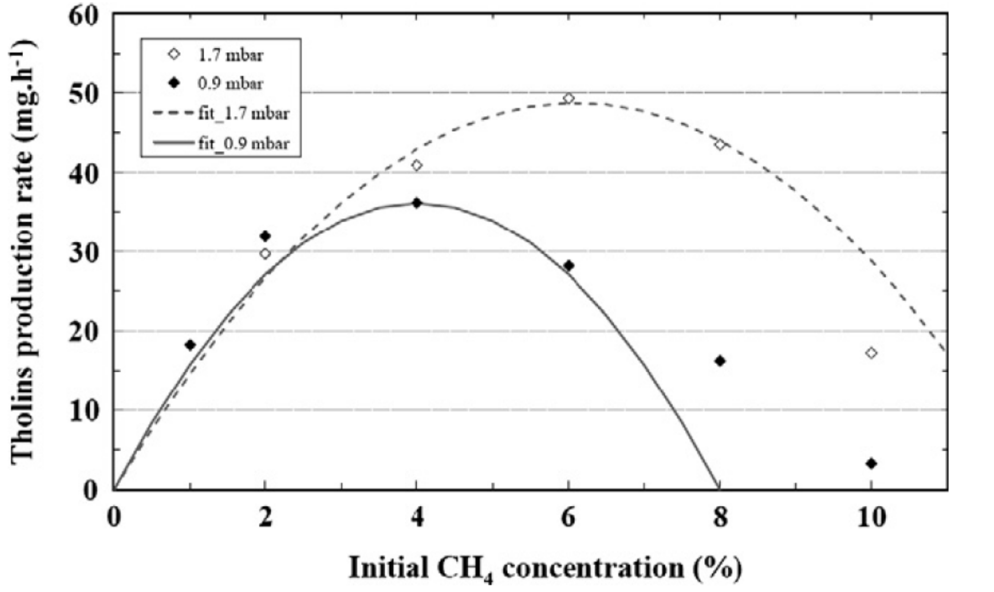
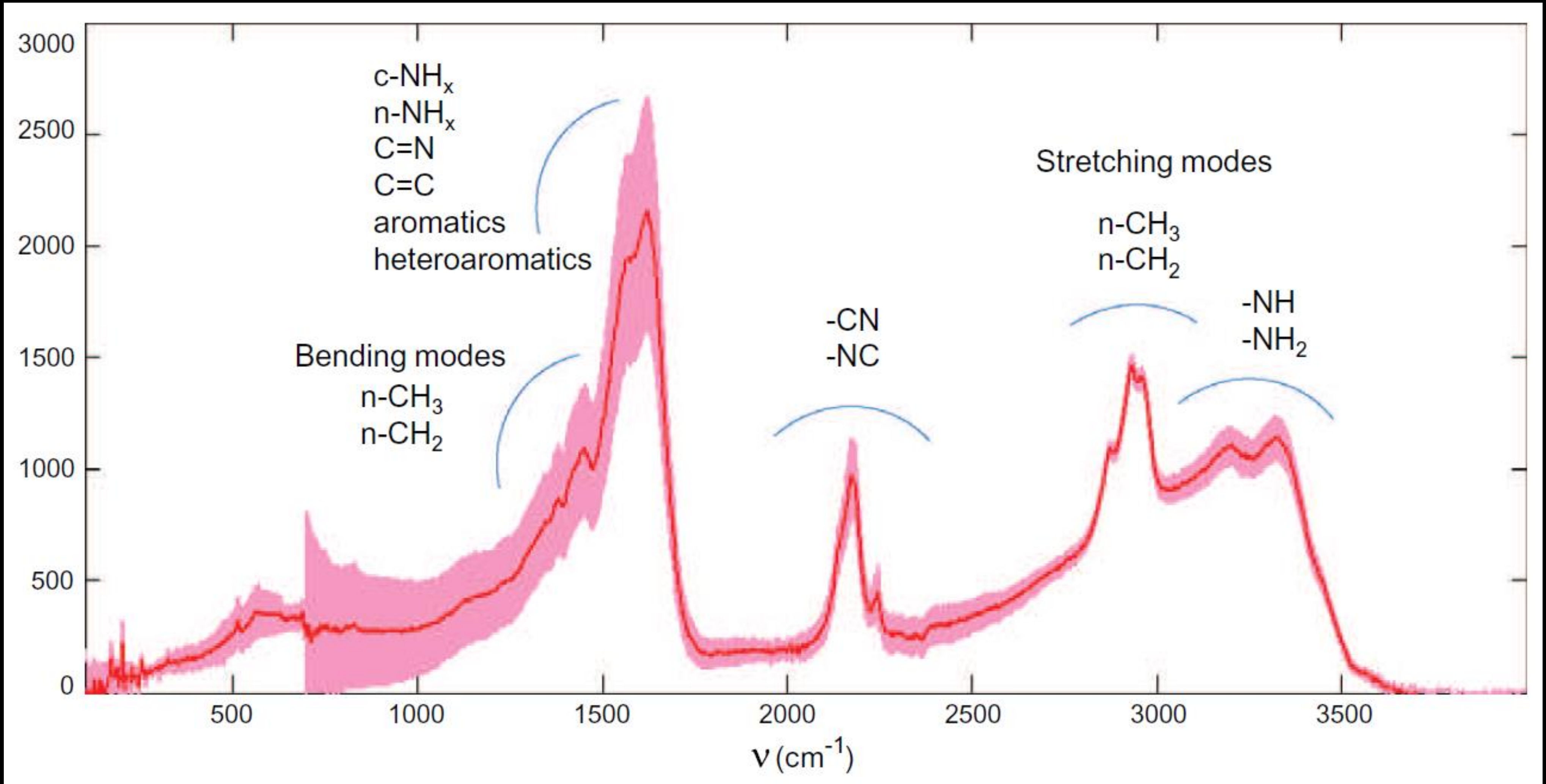


Fig. 5. Tholin production rate as a function of initial CH_4 concentration, for p = 0.9 mbar (black diamonds) and p = 1.7 mbar (white diamonds).

 Sciamma-O'Brien et al, *Icarus* (2010)

AEROSOL PROPERTIES: WHAT CHEMICAL STRUCTURE?

- A lot of nitrogen incorporated!



 Gautier et al, *Icarus* (2012)

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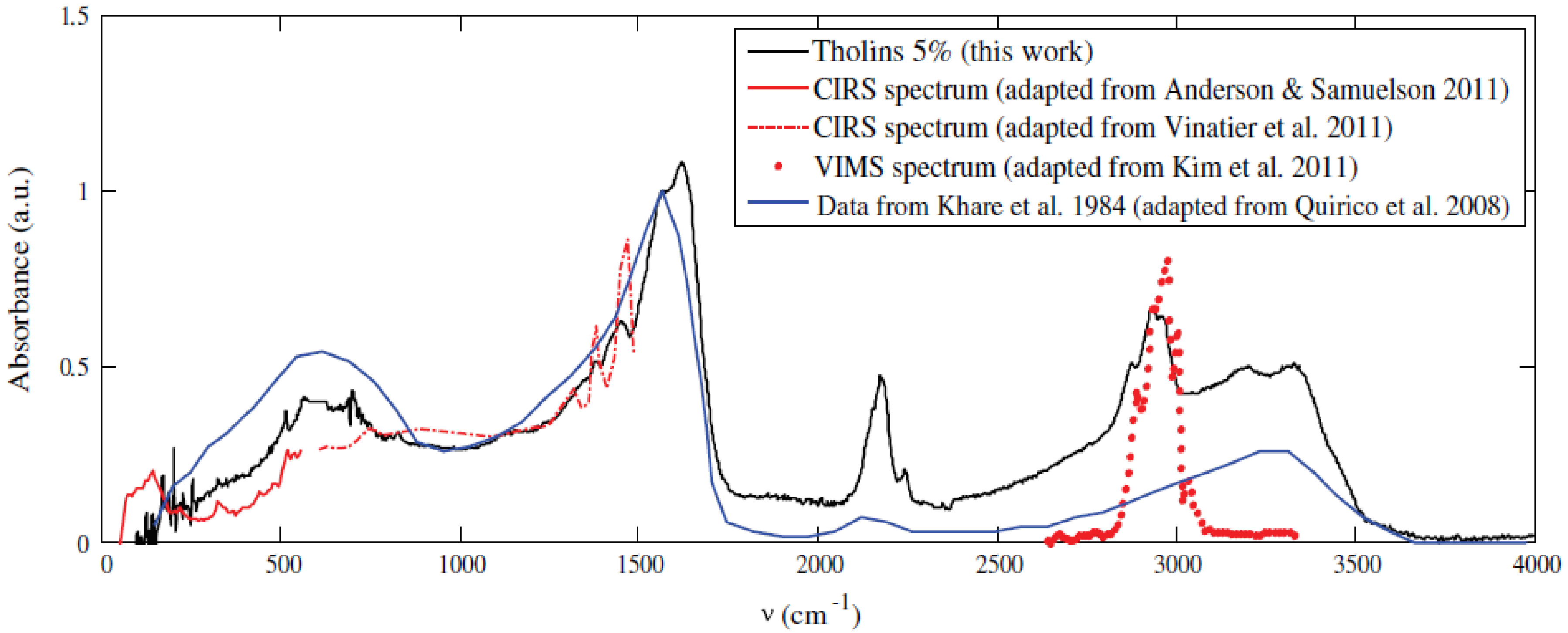


Fig. 4. Absorbance spectrum from far-IR to mid-IR of PAMPRE tholin made with 5% of CH_4 (black curve) compared to Quirico et al. (2008) tholin spectra (extracted from Khare et al. (1984) tholin, blue), Cassini-CIRS observations (red line, from Anderson and Samuelson (2011) and Vinatier et al. (2011) and Cassini-VIMS spectra (red dots, from Kim et al. (2011)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

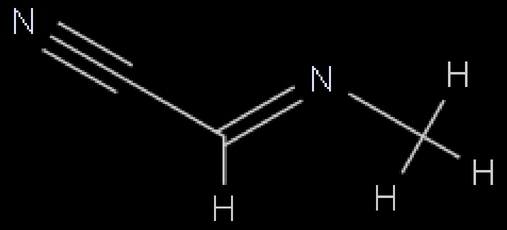
 Gautier et al, *Icarus* (2012)

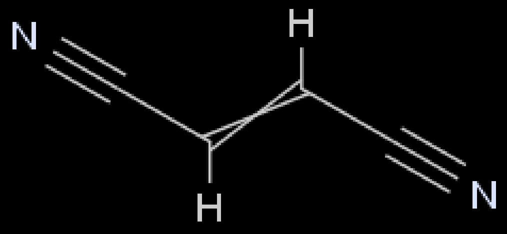
AEROSOL PROPERTIES: POLYMERIC STRUCTURE

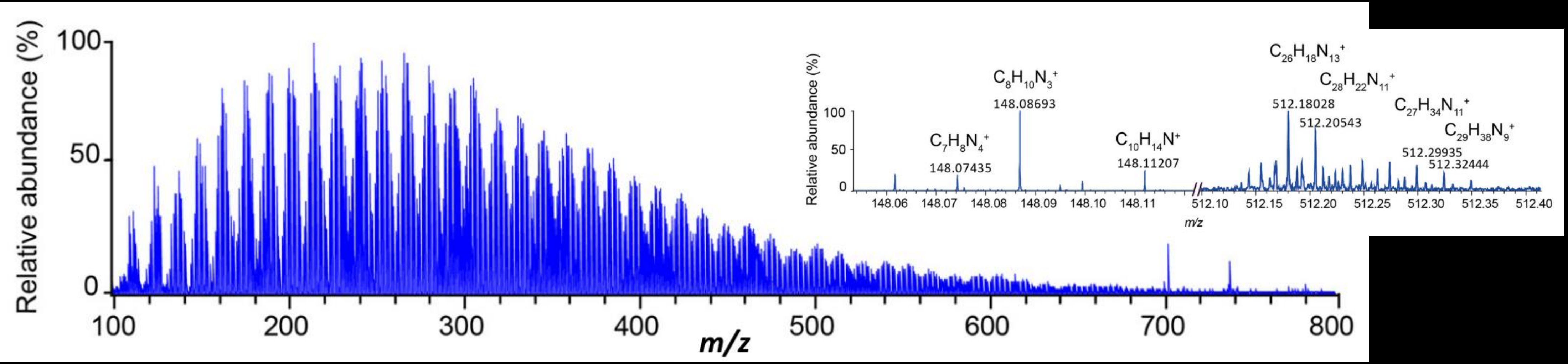
Very high resolution mass spectrometry:

⇒ Softly fragment tholins and find the exact mass (and formula) of the fragments

⇒ Detection of amino acids…

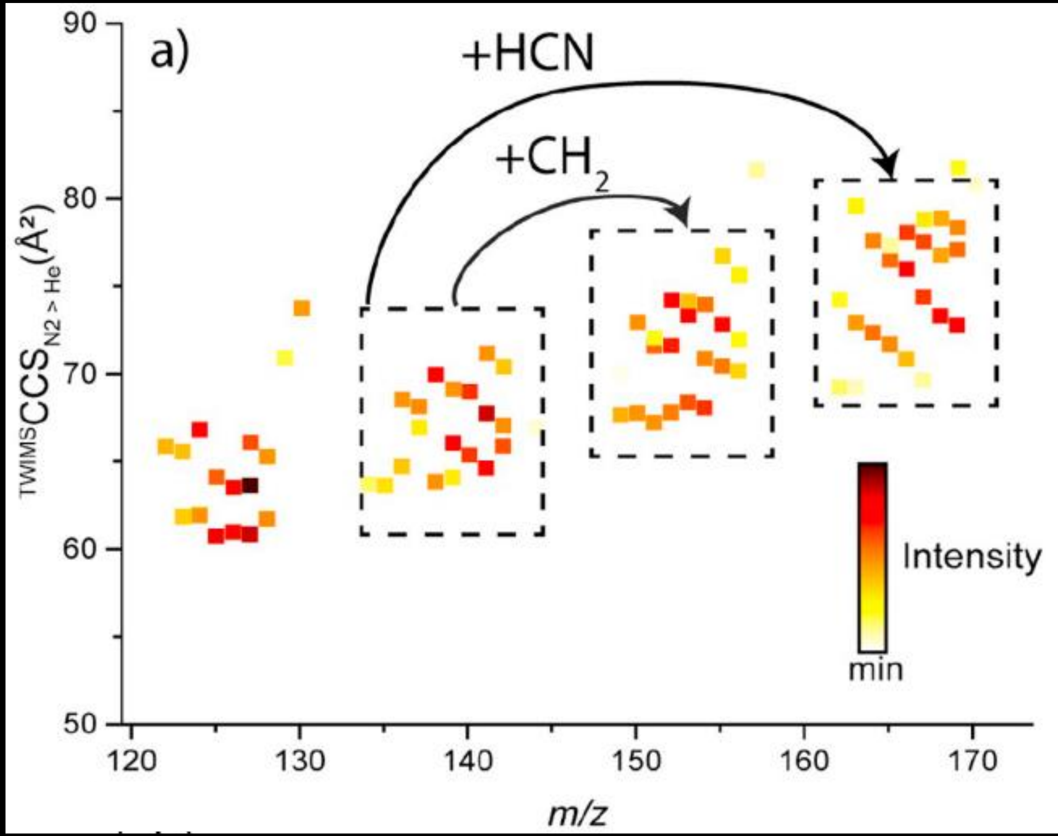






Maillard et al. (EPSL - 2018)

Polyrmeric structure?



Islands of a few aromatic rings linked by aliphatic bonds (C-H) :

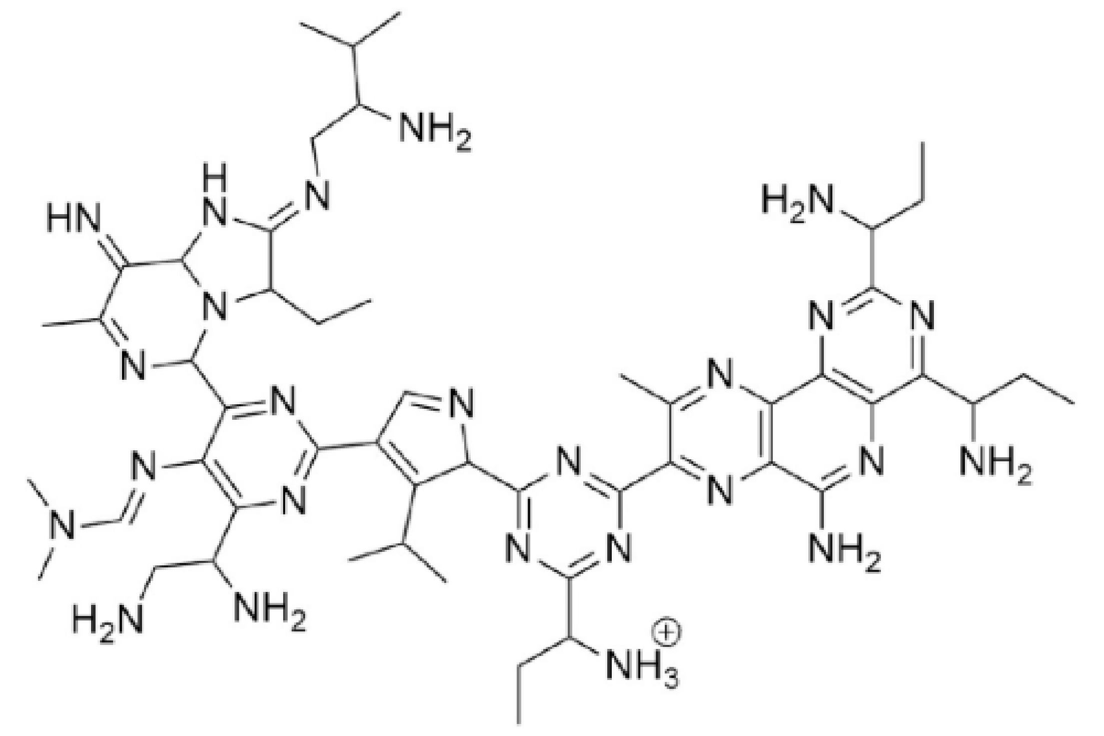


Fig. 5. Growing path possibility of families containing triazine and pyrazole cores. As example here, a compound with raw formula $C_{52}H_{78}N_{25}$ note: This structure by itself was not detected directly in the laboratory tholins but represents a general idea of molecules that could be embedded in them.

[Maillard et al, 2020]

Aerosol properties: nitrogen-containing cycles and aromatics

Structure of small tholin fragments at the atomic force microscope (AFM):

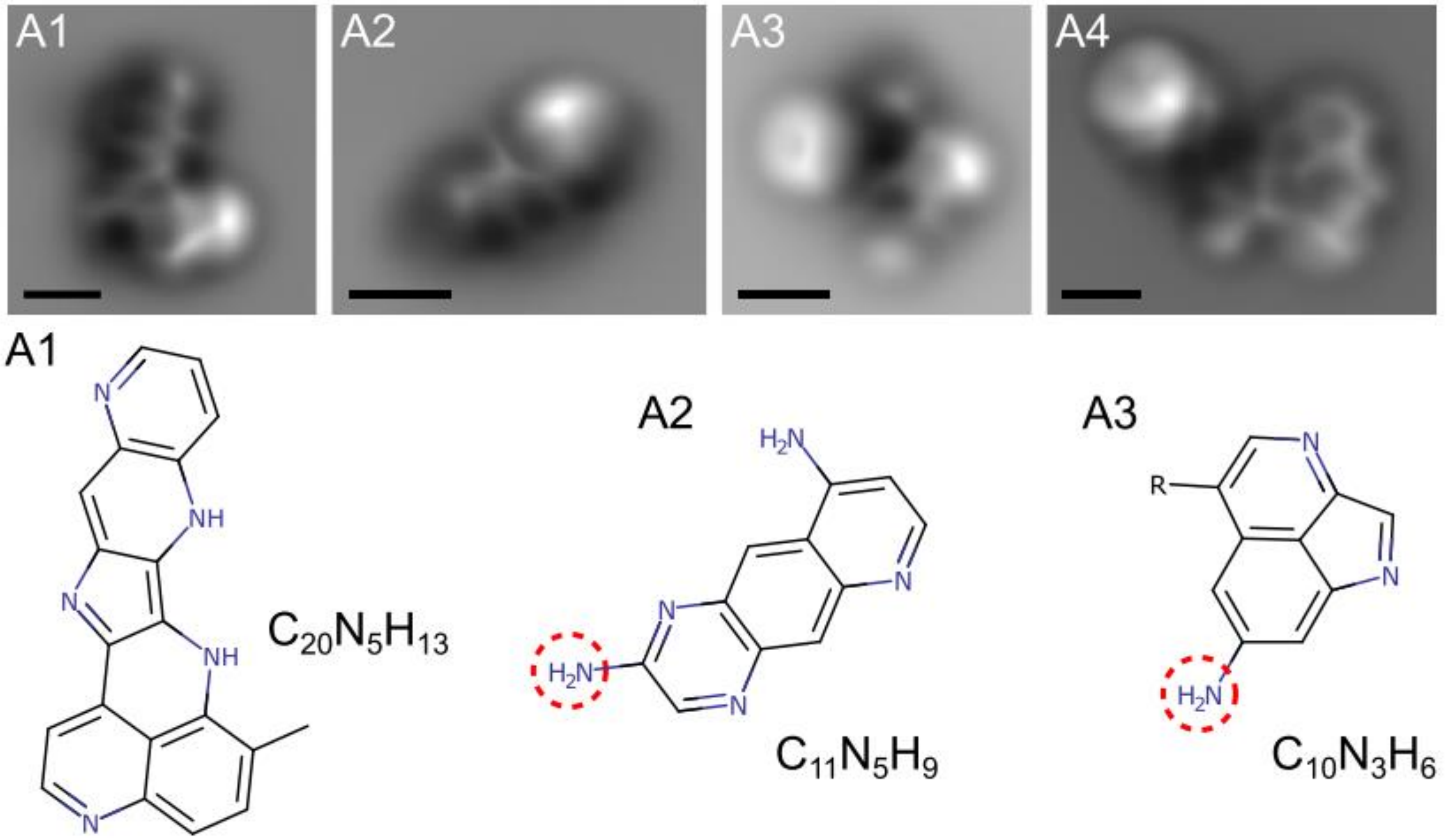
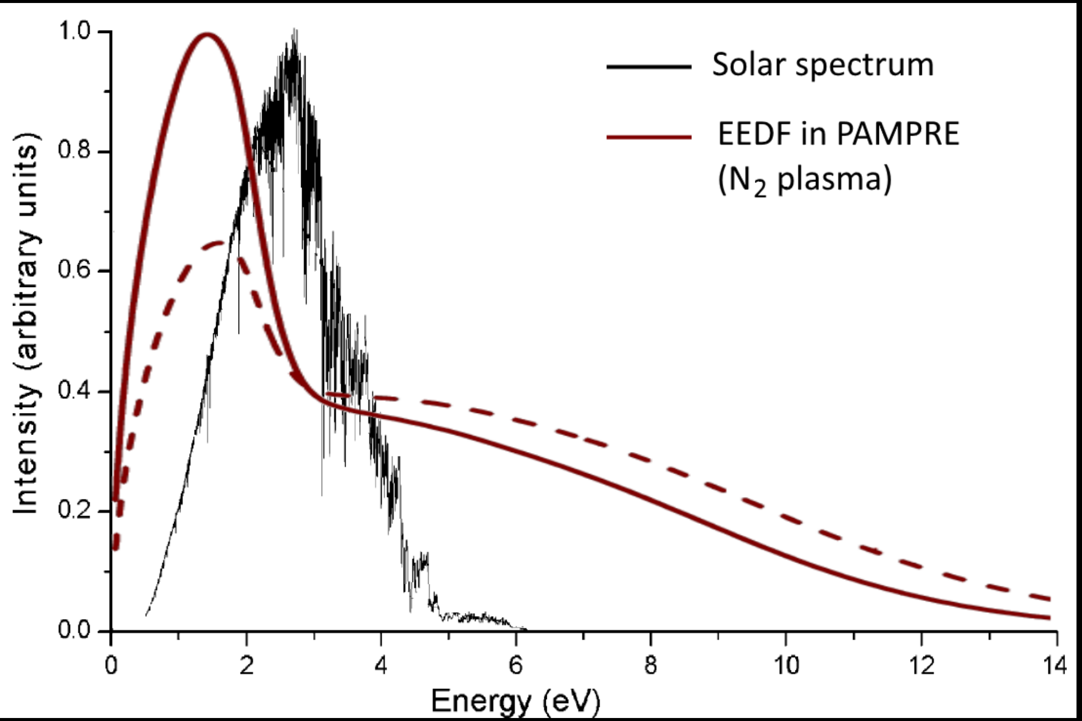


Figure 1. High-resolution AFM images and assigned structures of tholins from the common fraction. All scale bars are 5 Ångström. Red dashed circles indicate uncertain moieties. A possible alternative assignment for the uncertain -NH_2 group in A2, A3 is a -CN group. Additional data obtained on the same molecules is presented in Figure A4 in the Appendix.

[Schulz et al, 2021]

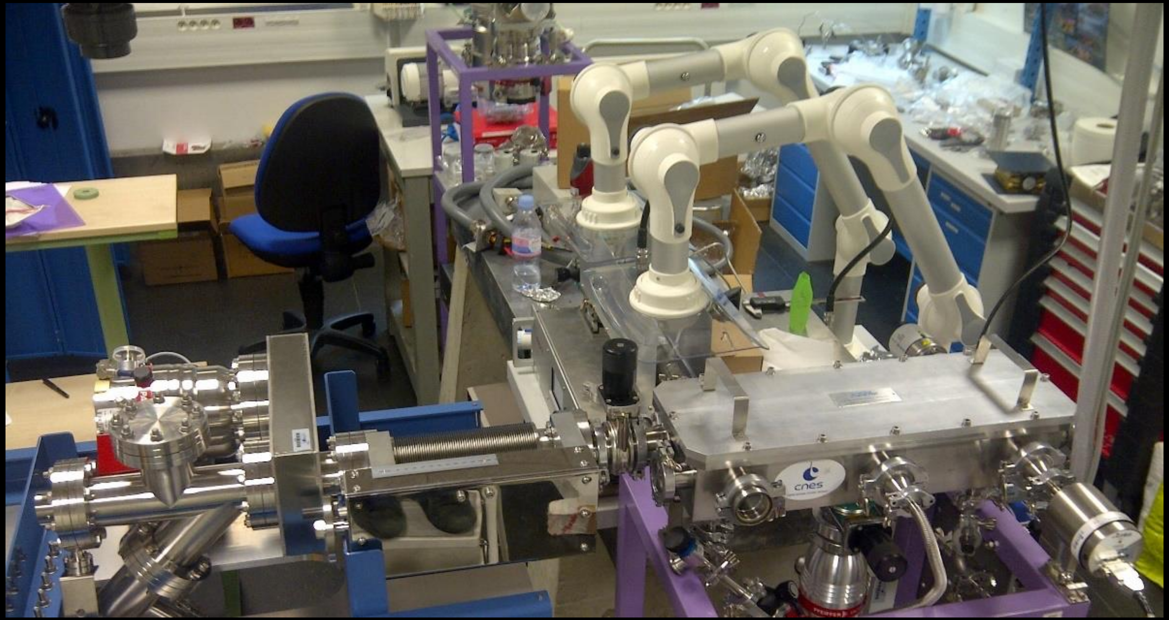
ENERGY DISTRIBUTION: STUDY OF CHEMICAL REACTIONS STEP BY STEP

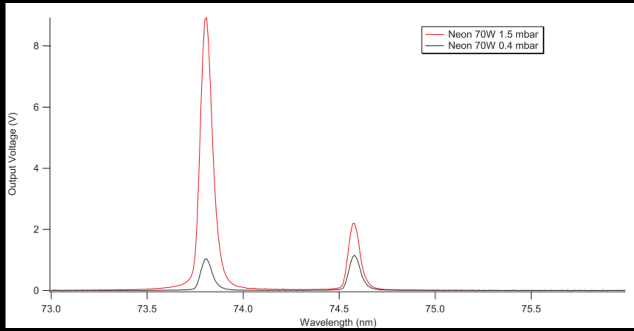
Case of PAMPRE: electrons created by 2 electrodes
large energetic distribution
=> complete chemistry



Comparison of the solar spectrum to the modelled Electron Energy Distribution Function (EEDF) of a pure N_2 discharge in PAMPRE at 1 mbar (solid line) and 0.5 mbar (dashed line). From Alves et al. (2012) and Szopa et al. (2006).

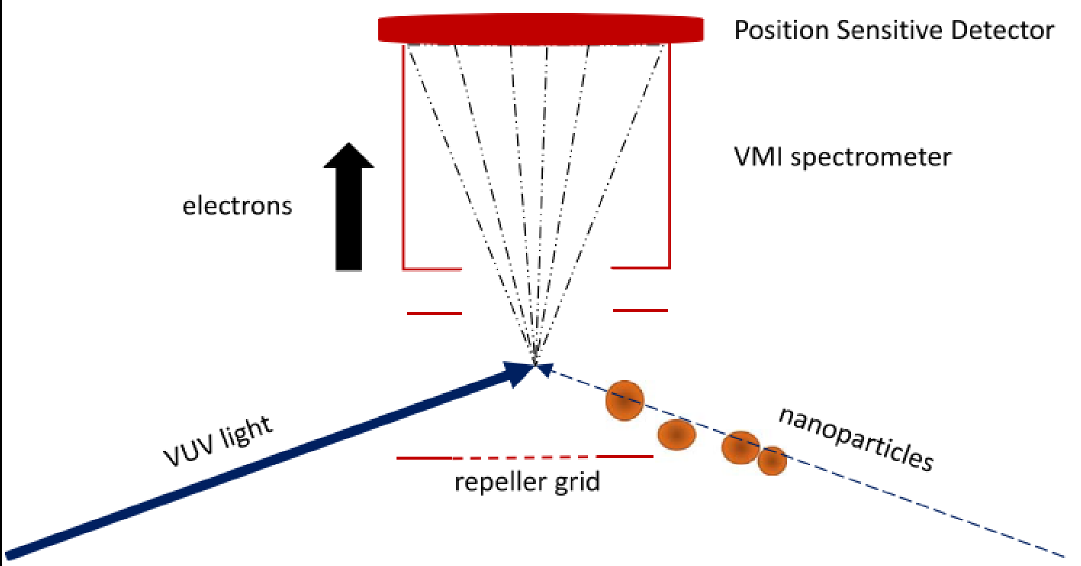
Other type of experiment: exposure to a VUV lamp
very precise wavelengths
=> selective chemistry





- Tigrine et al, *Icarus* (2016)
- Bourgalais et al, *JGR* (2019)

INTERACTION AEROSOLS-UV? PHOTO-IONISATION



Can aerosols be a source of secondary electrons by interaction with solar UV photons?
(experiments at Soleil synchrotron)

- Tigrine et al, *ApJ* (2018)

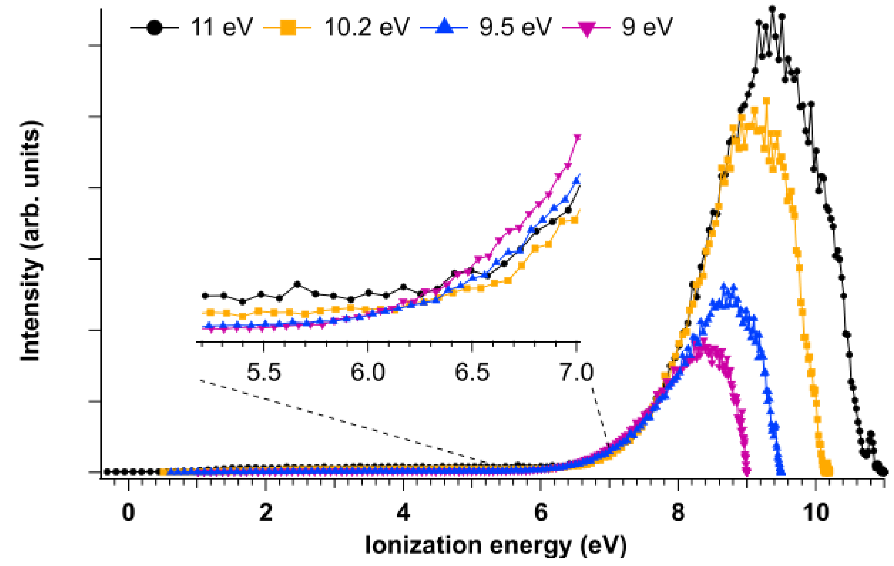


Figure 6. Photoelectron spectra of tholins aerosols recorded at different photon energies (11, 10.2, 9.5, and 9 eV). The area of the curves has been normalized to the total cross sections derived in Section 3.3. The inset shows a zoom of the ionization onset.

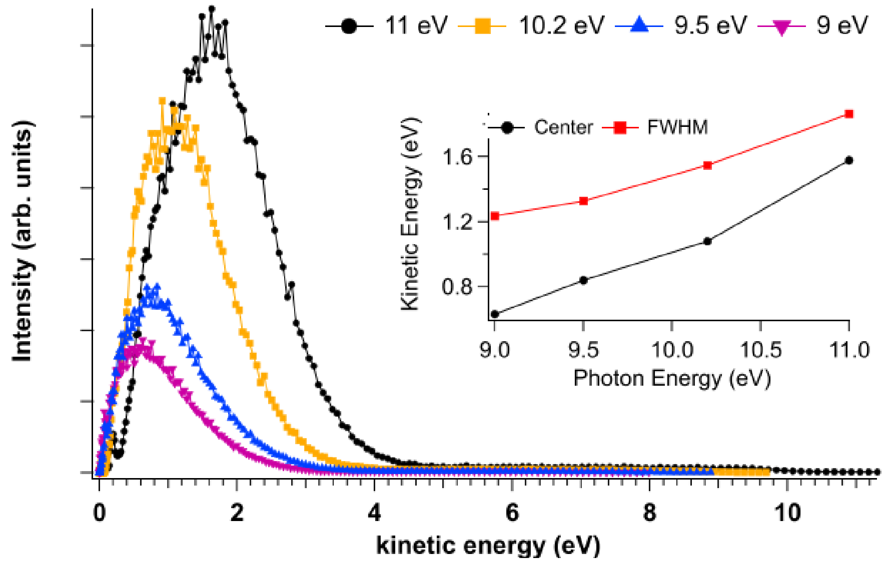
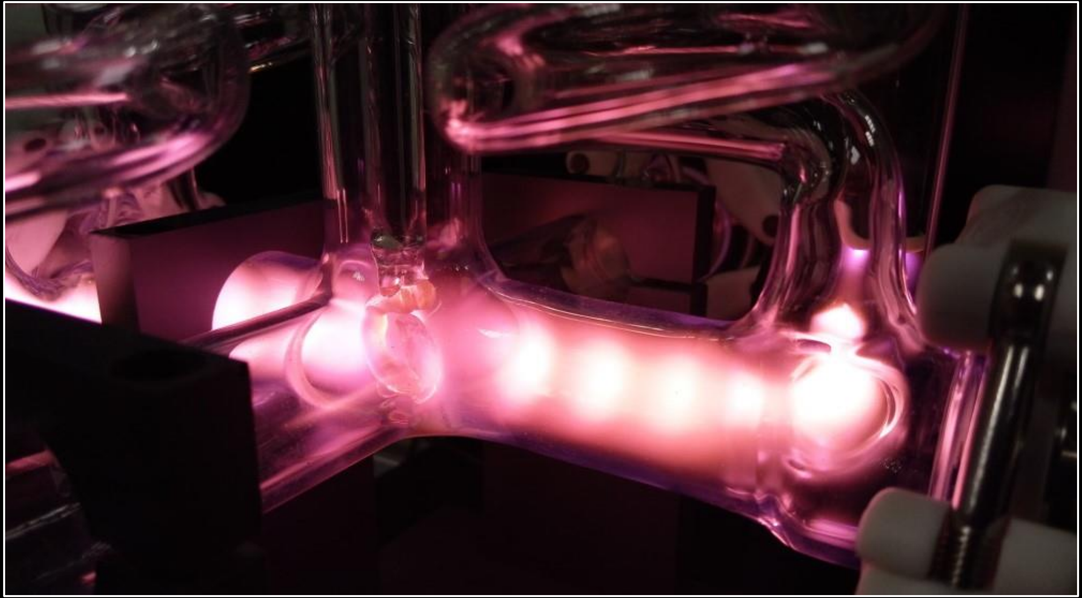
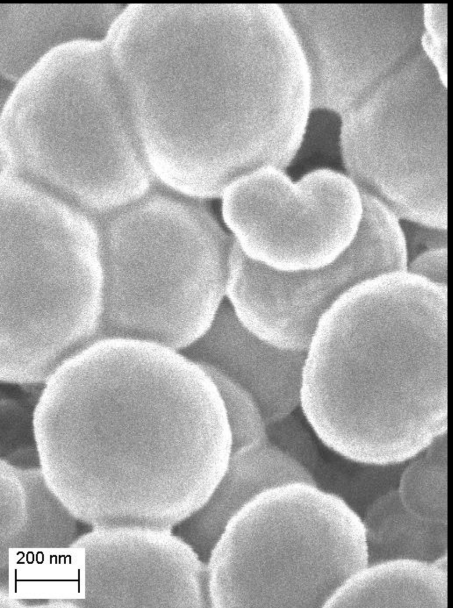


Figure 7. Kinetic energy distributions of the electrons coming from the photoionization of tholins at different photon energies. The area of the curves has been normalized to the total cross sections derived in Section 3.3. The inset shows the evolution of the position of the most probable kinetic energy (center) and FWHM as a function of the photon energy.

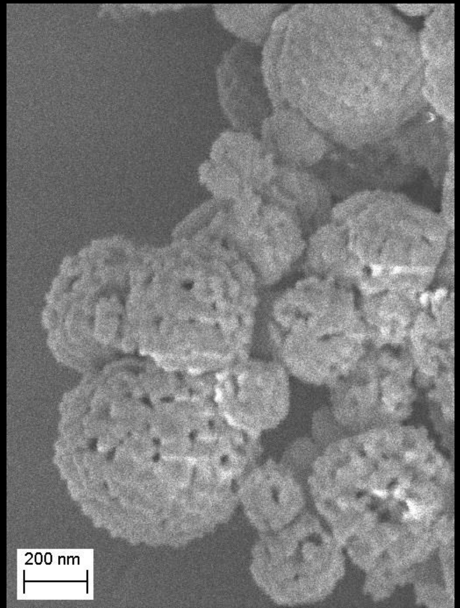
AEROSOL INTERACTION WITH N_2-H_2 PLASMA SPECIES

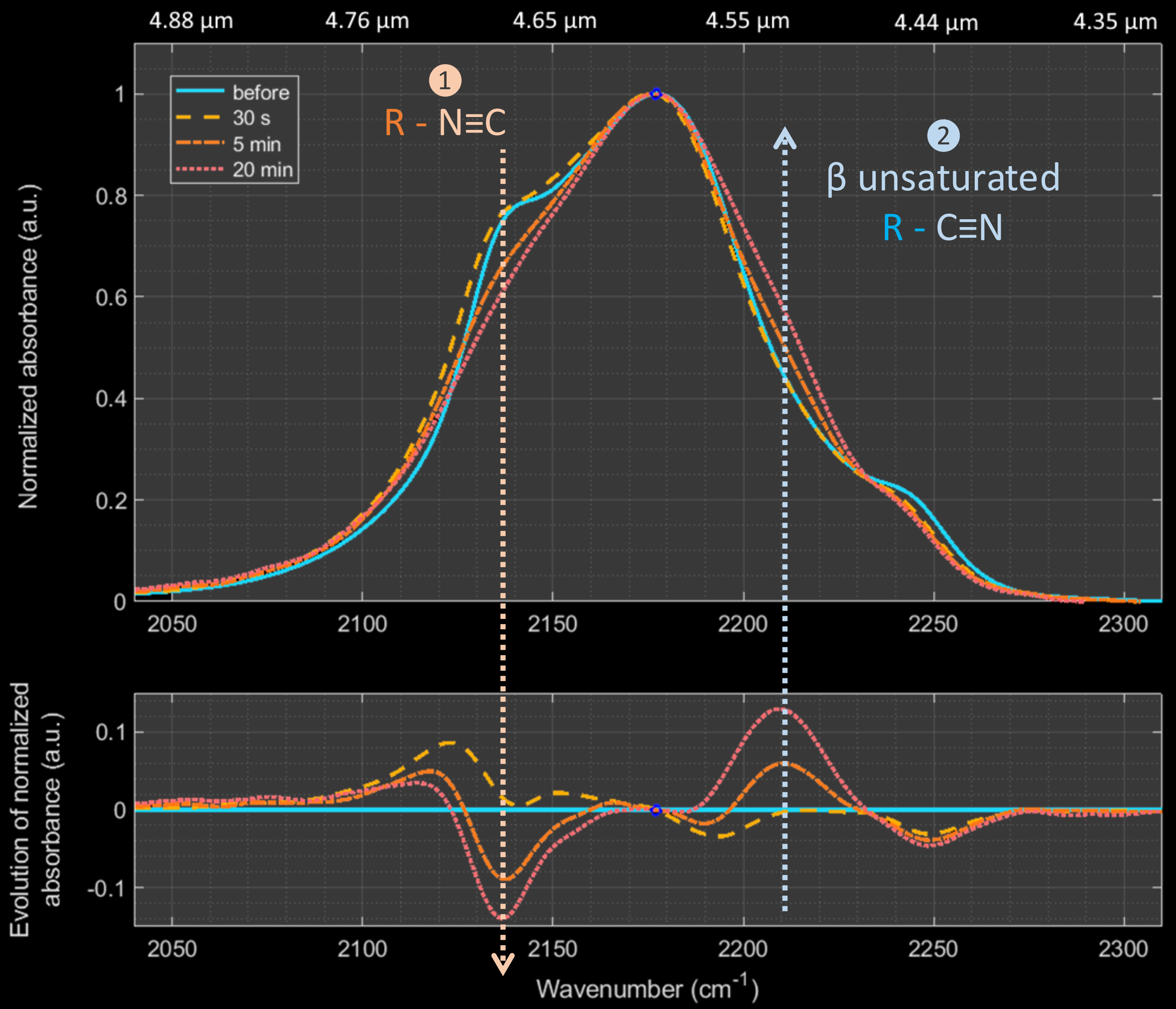
Chatain et al (2020b), *Icarus*





plasma (N_2-H_2)

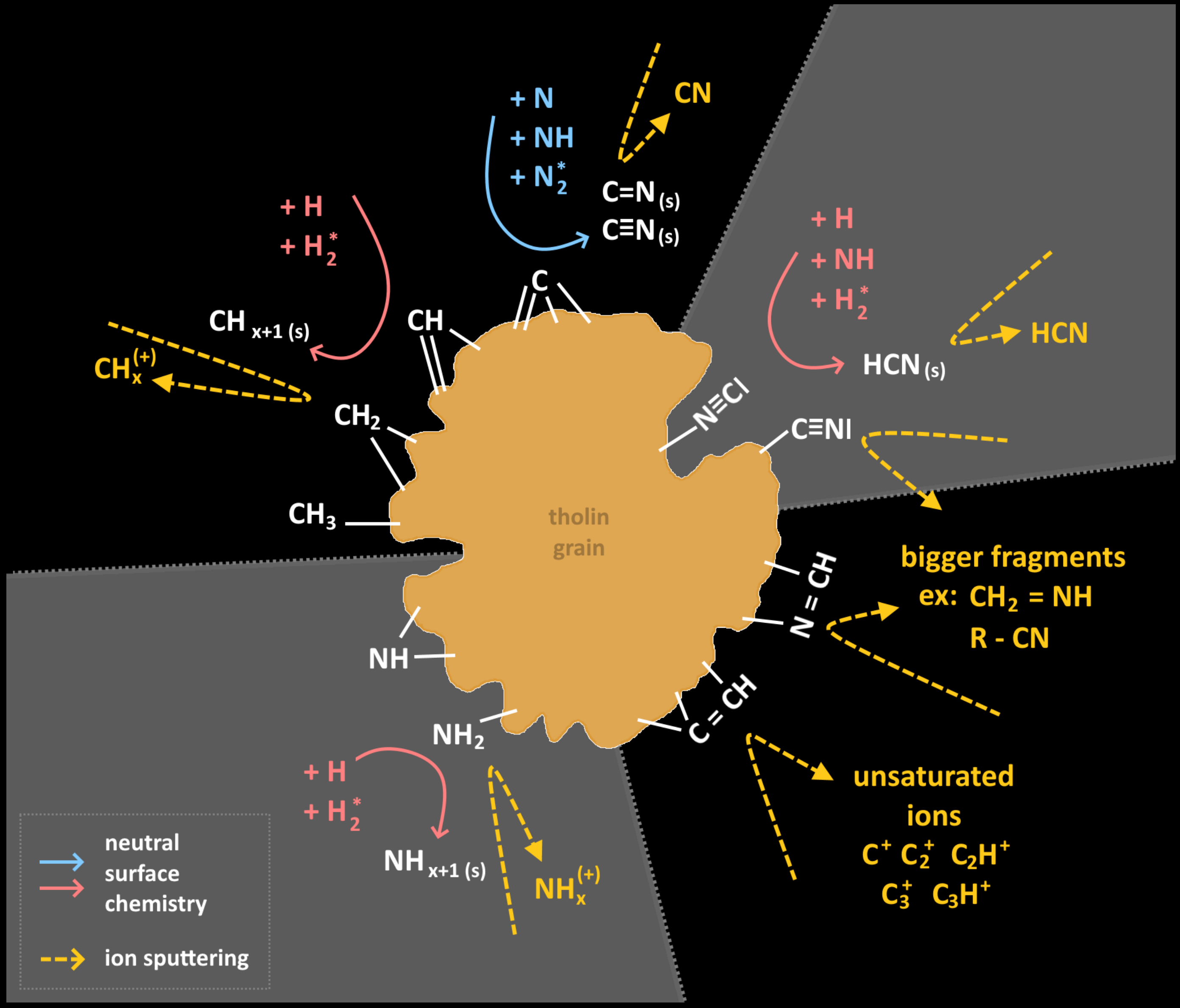




PROCESSES AT THE SURFACE OF GRAINS IN THE IONOSPHERE?

Chatain et al (2023)

Combination of solid IR results and gas phase mass spectrometry



Two complementary processes:

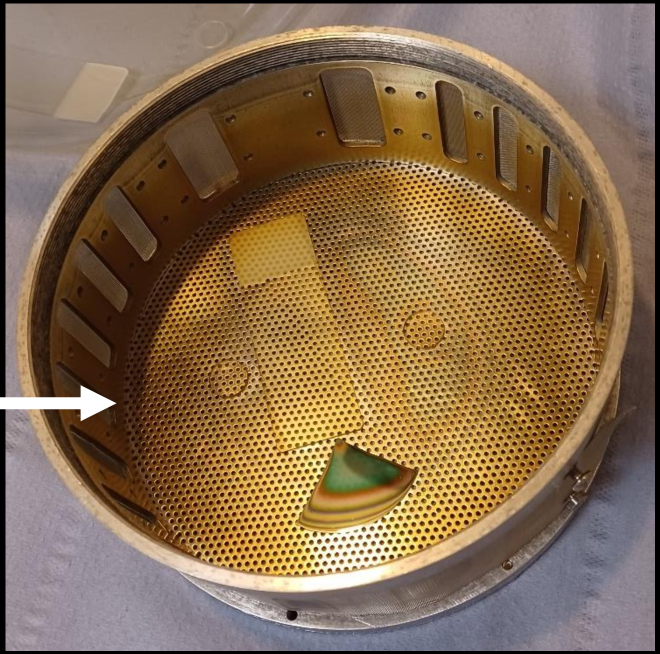
1. neutral surface chemistry (with radicals)
2. ion sputtering: removal of small particles

secondary ion + HCN source ?

Van Laer et al, *PSST* (2013): (C:H) films interaction with N_2-H_2 plasma in microelectronics.

suggested processes

Effect of the exposure time: films vs aerosols



Advantages of films:

- homogeneous: useful for many measurements like optical constants
- form even in difficul conditions

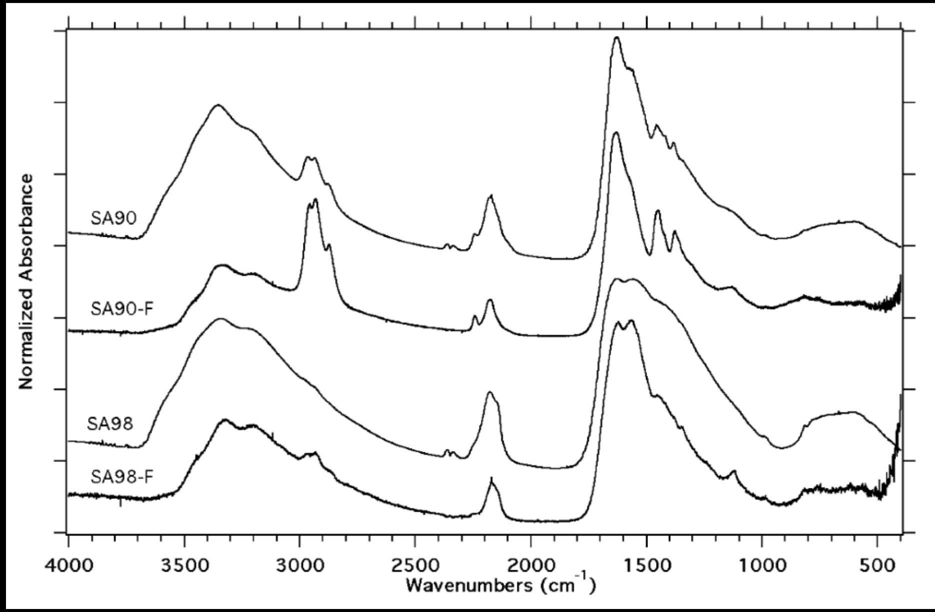
BUT:

their properties are different from aerosols…

Table 2
Elemental analysis of both thin films and grains. Thin films N/C ratios are determined here from XPS data at a 150 nm depth; and thin films H/C ratios are taken from Cs–M$^+$ molecular ions from SIMS analysis. The grains elemental analysis has been made in (Sciamma-O'Brien et al., 2010; Fleury et al., 2014).

Samples (%)	Thin films		Grains	
	N/C (XPS)	H/C (SIMS)	N/C	H/C
1	0.4	~0.1	0.9	1.1
2	0.3	~0.1	0.8	1.1
5	0.2	~0.1	0.6	1.2
10	0.1	~0.1	0.4	1.4

- Carrasco et al, *PSS* (2016)



- Quirico et al, *Icarus* (2008)

SEDIMENTATION OF AEROSOLS THROUGH THE ATMOSPHERE

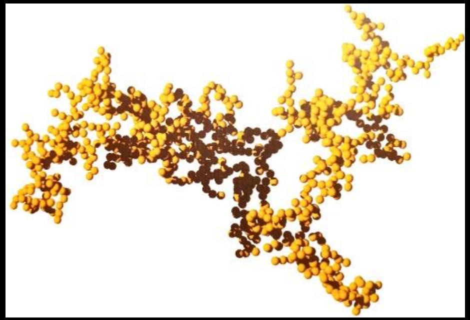
Les aerosols descend towards the surface:

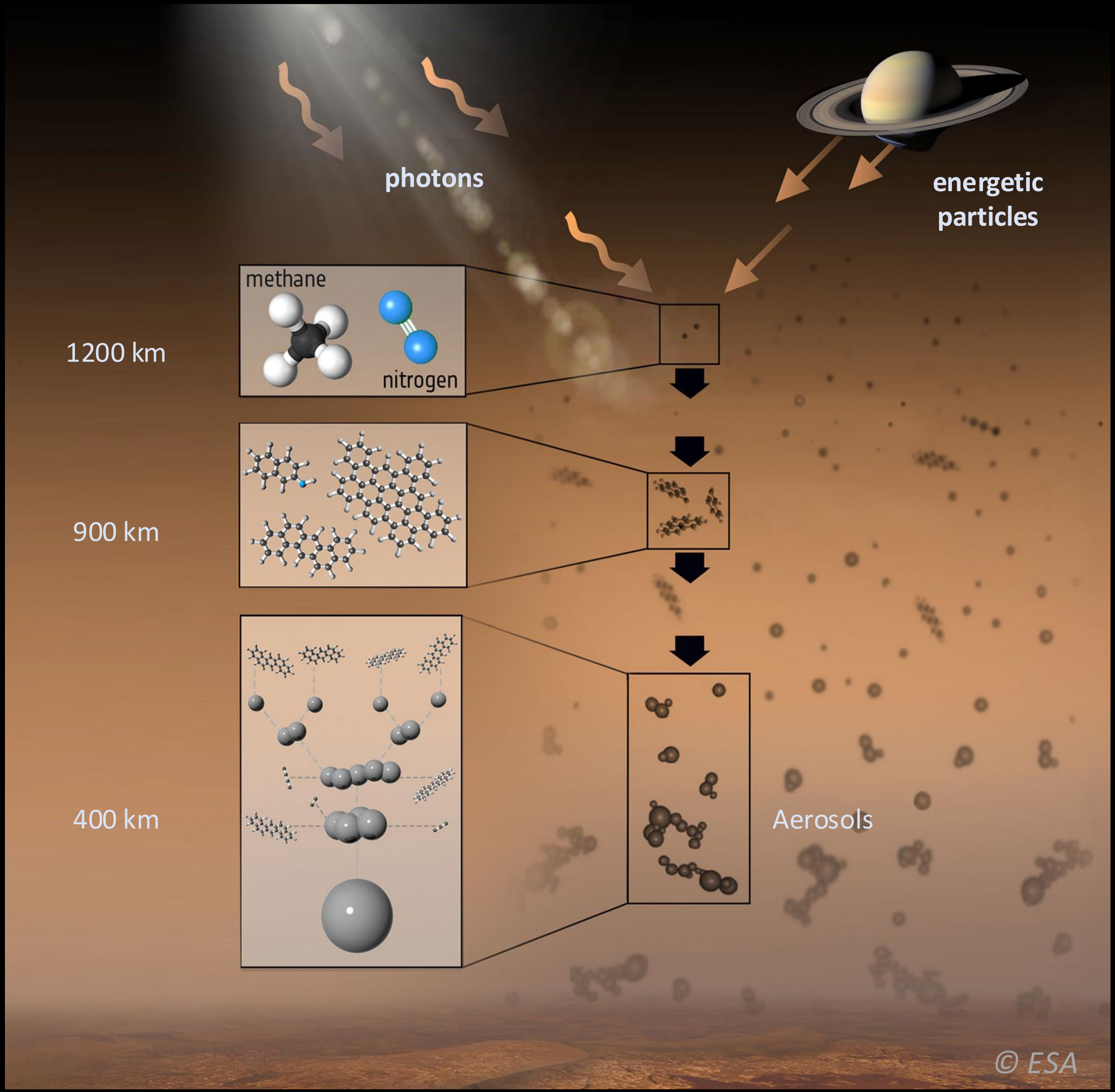
-formation of agregates (~4000 monomers for a total size of ~5 µm)

-growth by condensation of volatile species

-chemical evolution (radiations?)

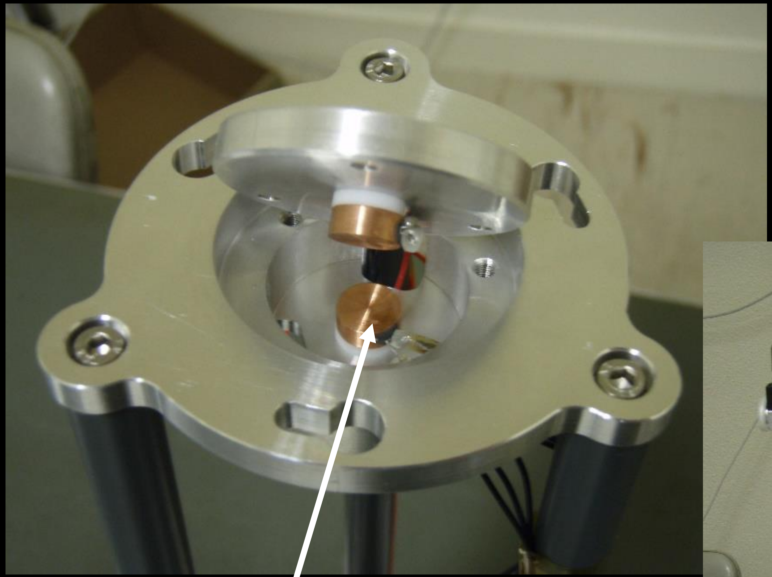
-physical and chemical evolution once at the surface (wind, rain…)





Dielectric properties of tholins?

Measurement of the dielectric permittivity:
→ /!\ temperature dependance
→ to interpret Huygens data (permittivity probe) & Cassini (radar)



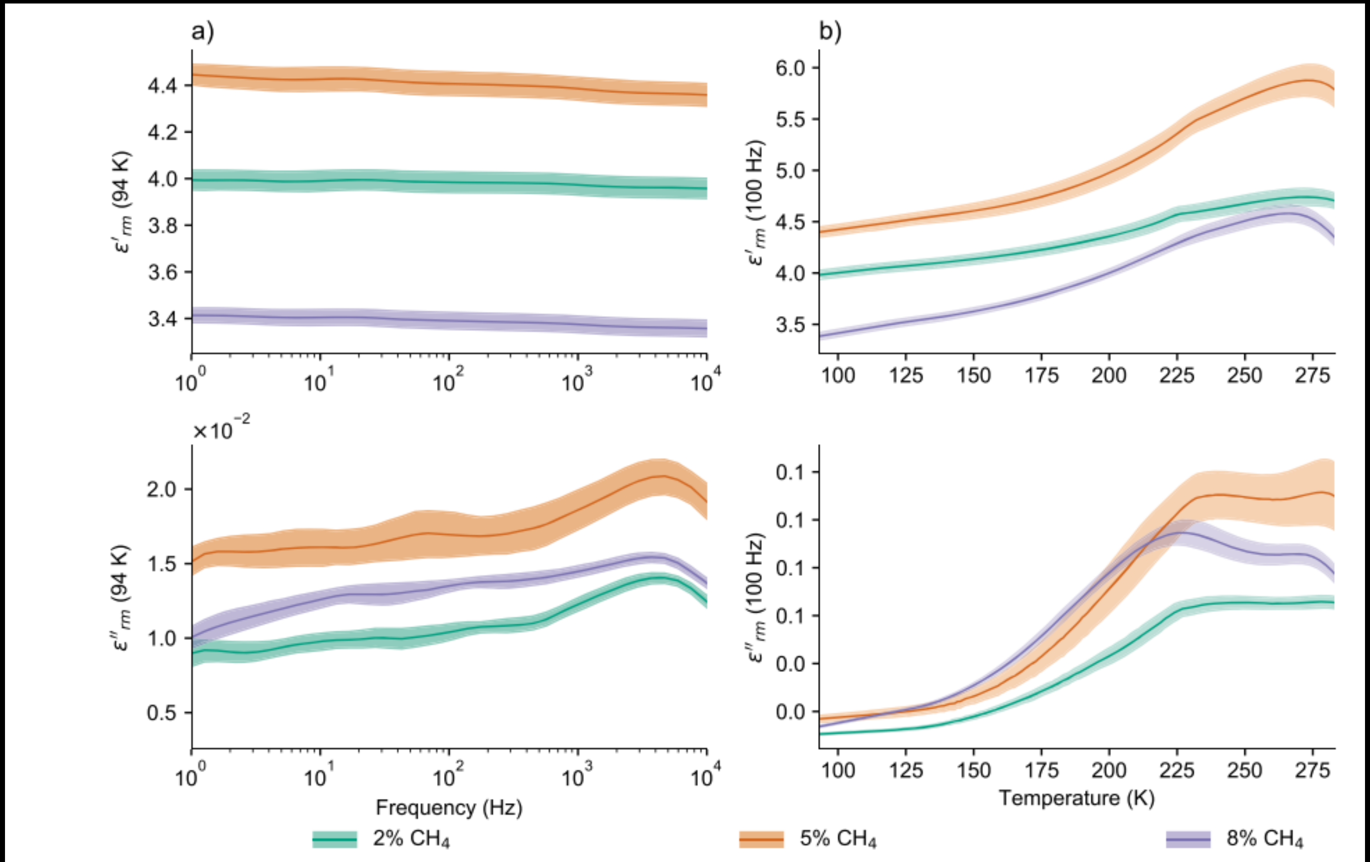
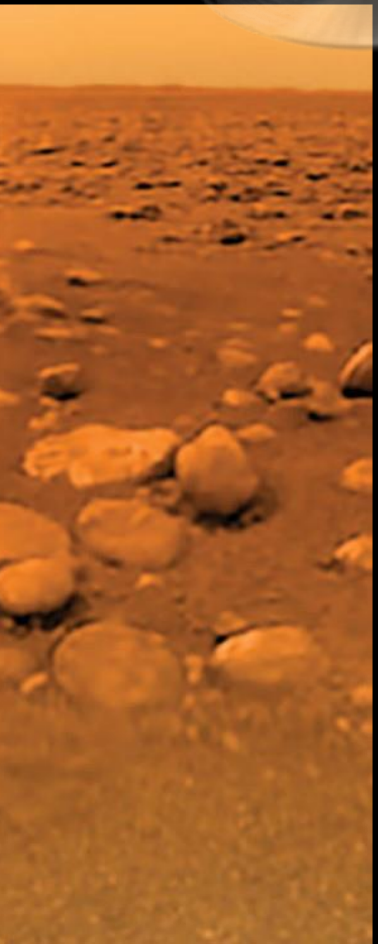
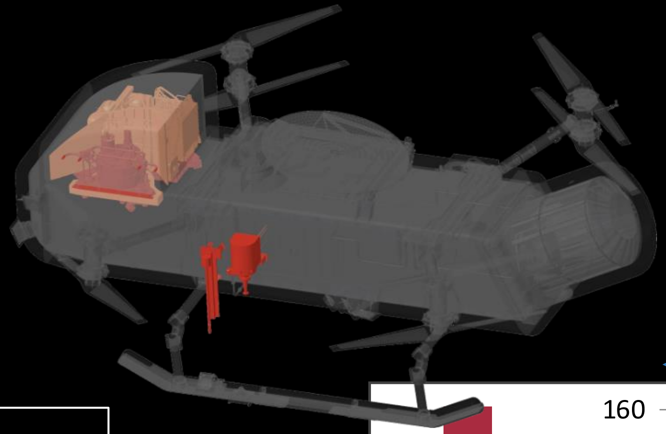


Figure 4. Frequency (at a temperature of 94 K, column a) and temperature (at a frequency of 100 Hz, column b) dependence and of the real and imaginary parts of the complex permittivity of bulk tholins obtained for three gas mixture compositions.

Lethuillier et al, *JGR Planets* (2018)

PREPARATION FOR DRAGONFLY

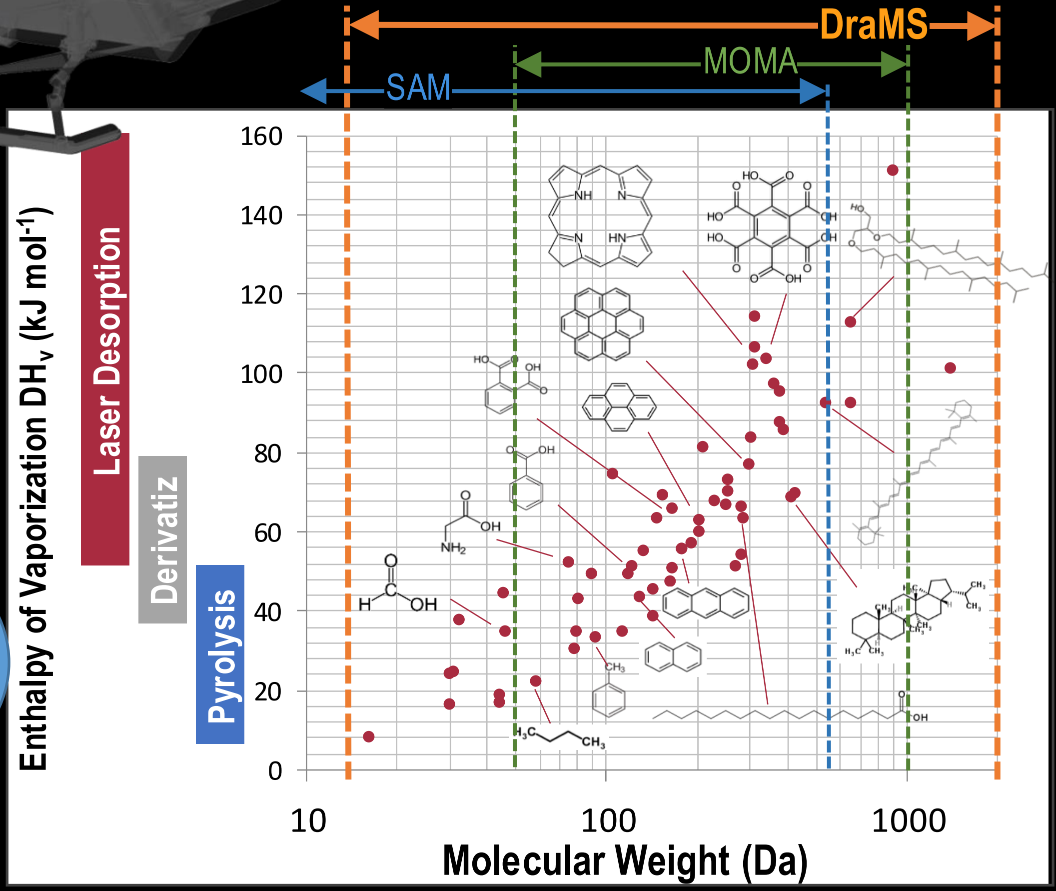




DraMS: chemical analysis of surface samples

DraMS: mass spectrometer

DrACO: drill



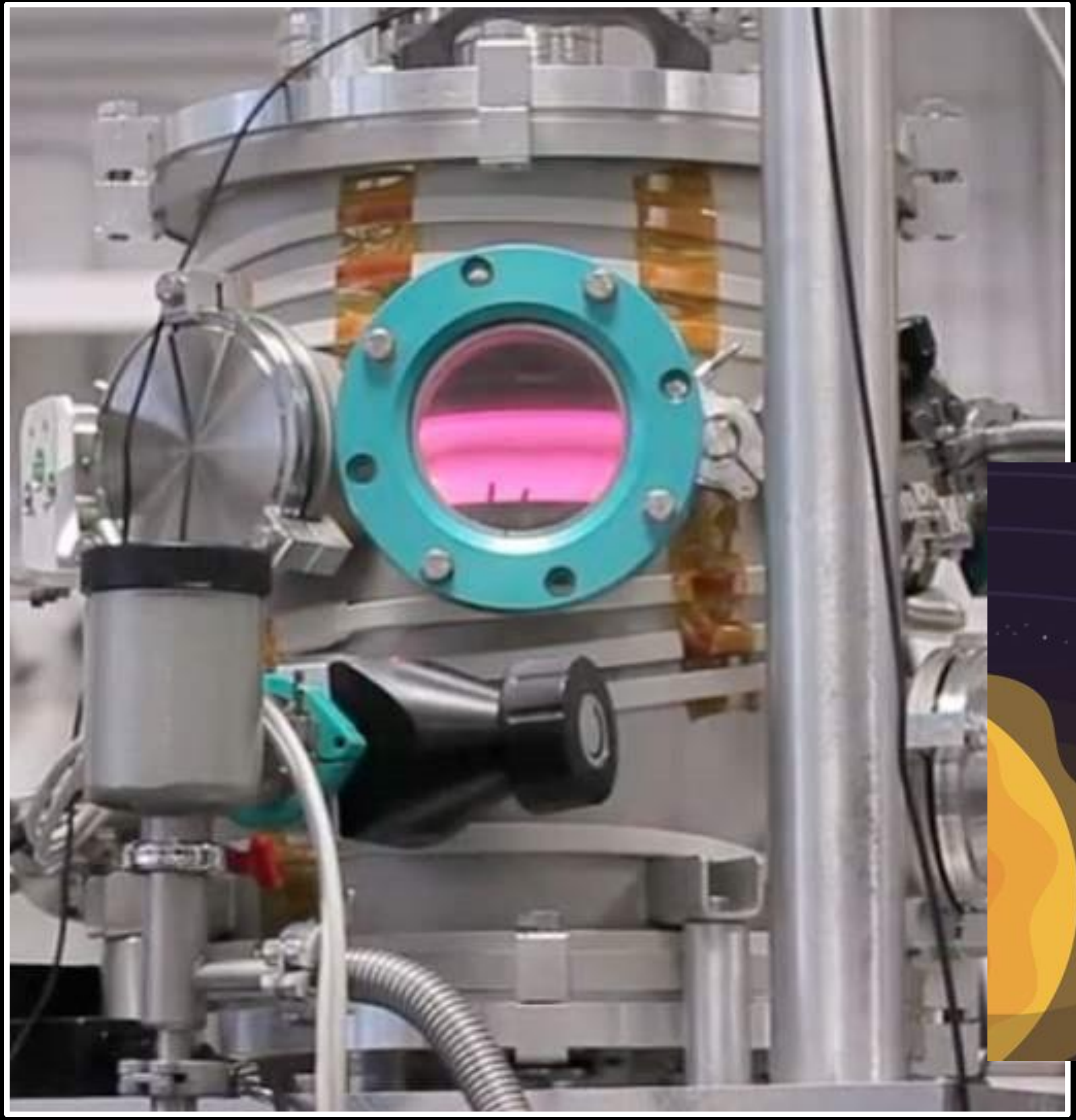
(Trainer et al., 2017)

Questions:

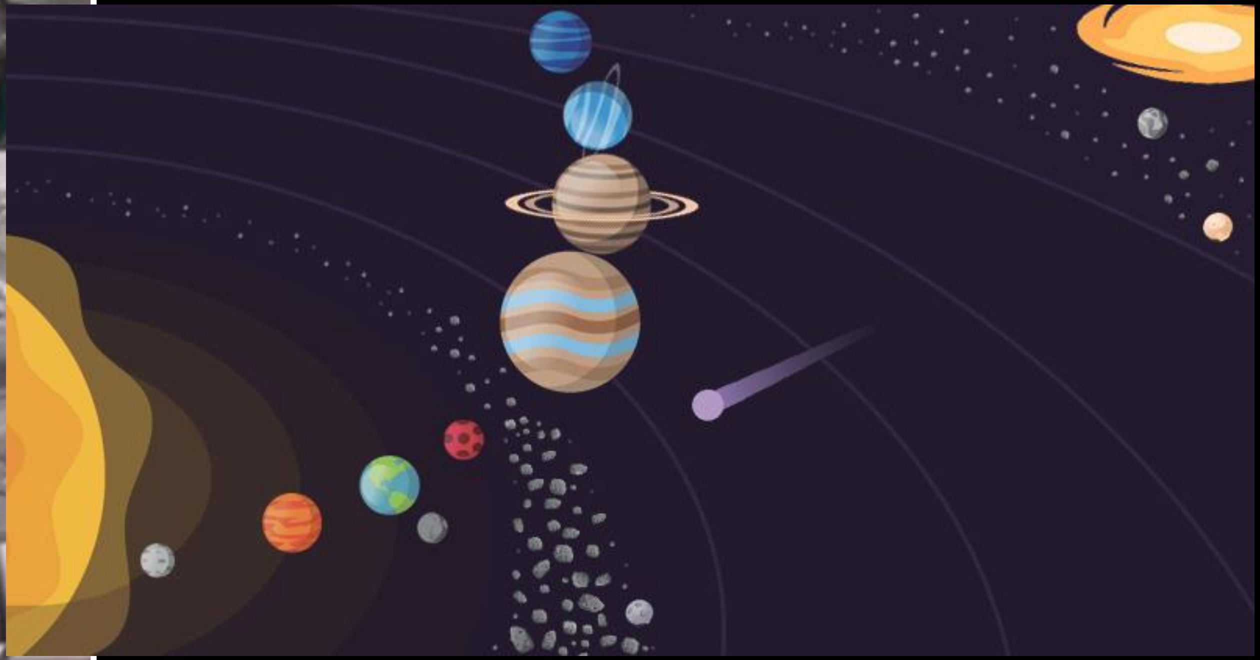
- **surface composition?**
- geological processes?

Tholins from the lab: a first idea of what we could get!

Partly developed in LATMOS!

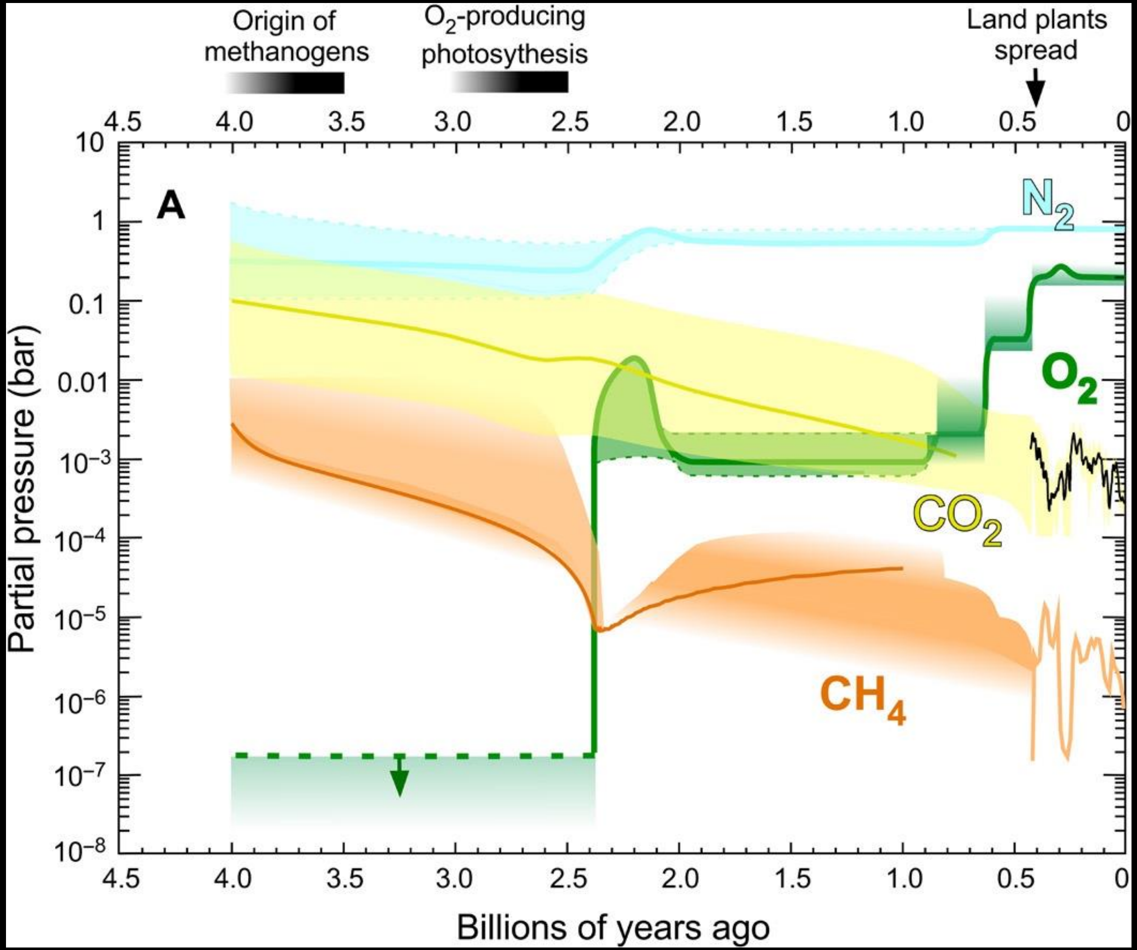


PAMPRE can simulate the ionospheric chemistry of all atmospheres!



Early Earth

Before life: $N_2 + CO_2 + CH_4$



Catling & Zahnle 2020

EARLY EARTH

Before life: $N_2 + CO_2 + CH_4$

CO_2 limits the formation of aerosols
If $CH_4/CO_2 < 0.2$: nearly nothing

Postdoc Felicia Haase 2025+

PLUTO

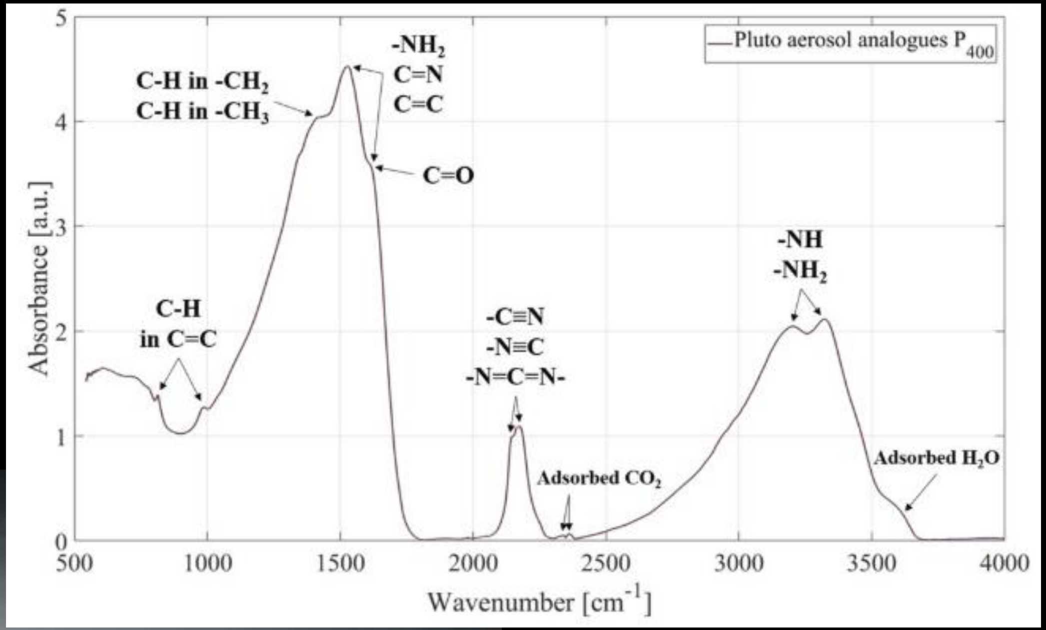
Photochemical hazes observed by New Horizon

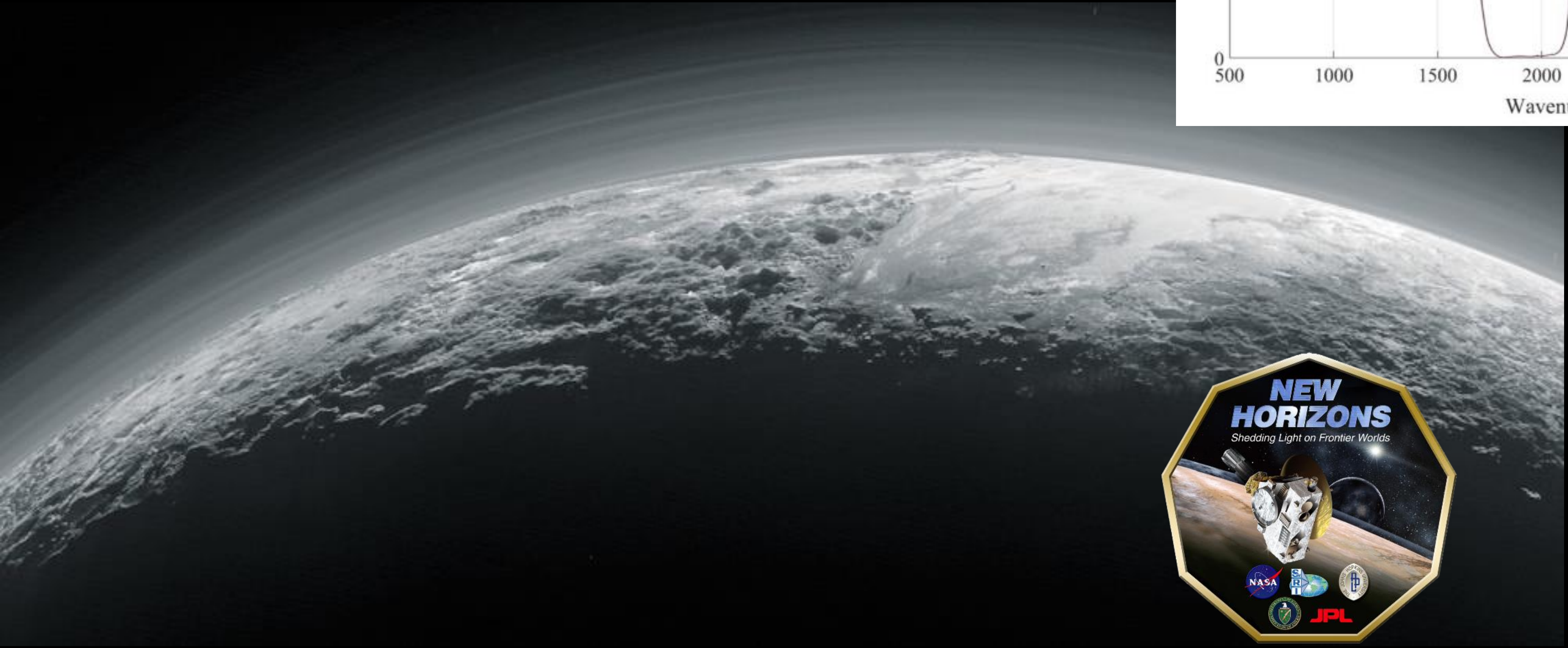
$N_2 + CH_4 + CO$

$\Rightarrow$ form aerosols! (but less efficient)

$\Rightarrow$ incorporation of oxygen into the aerosols

PhD Lora Jovanovic 2021



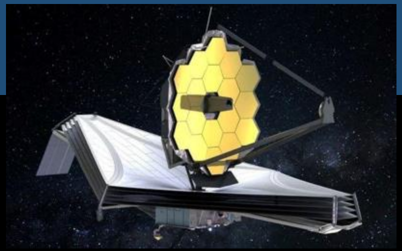


Similar process on Triton?

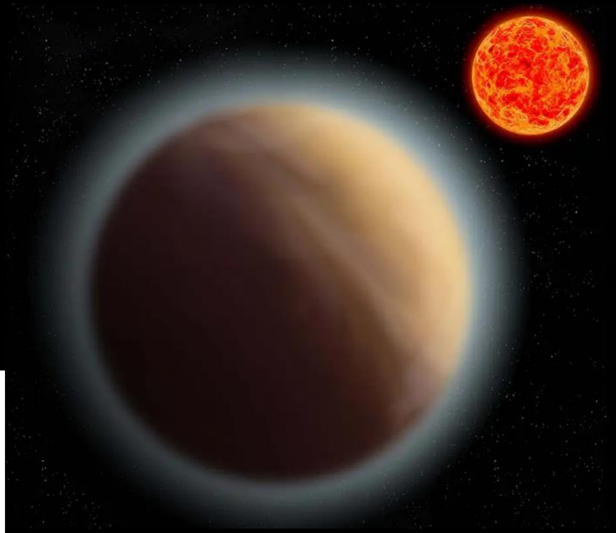
OPTICAL PROPERTIES OF AEROSOLS

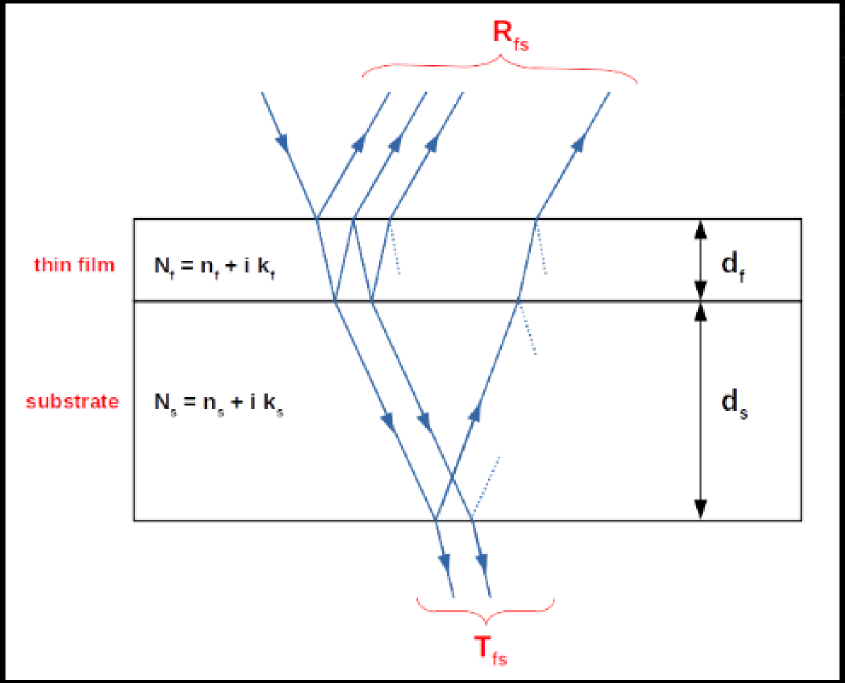
Thomas Drant
postdoc

Atmospheric chemistry of rocky exoplanets



*Spectrophoto-
metry vs
ellipsometry*





Smaller
absorption
in this
study

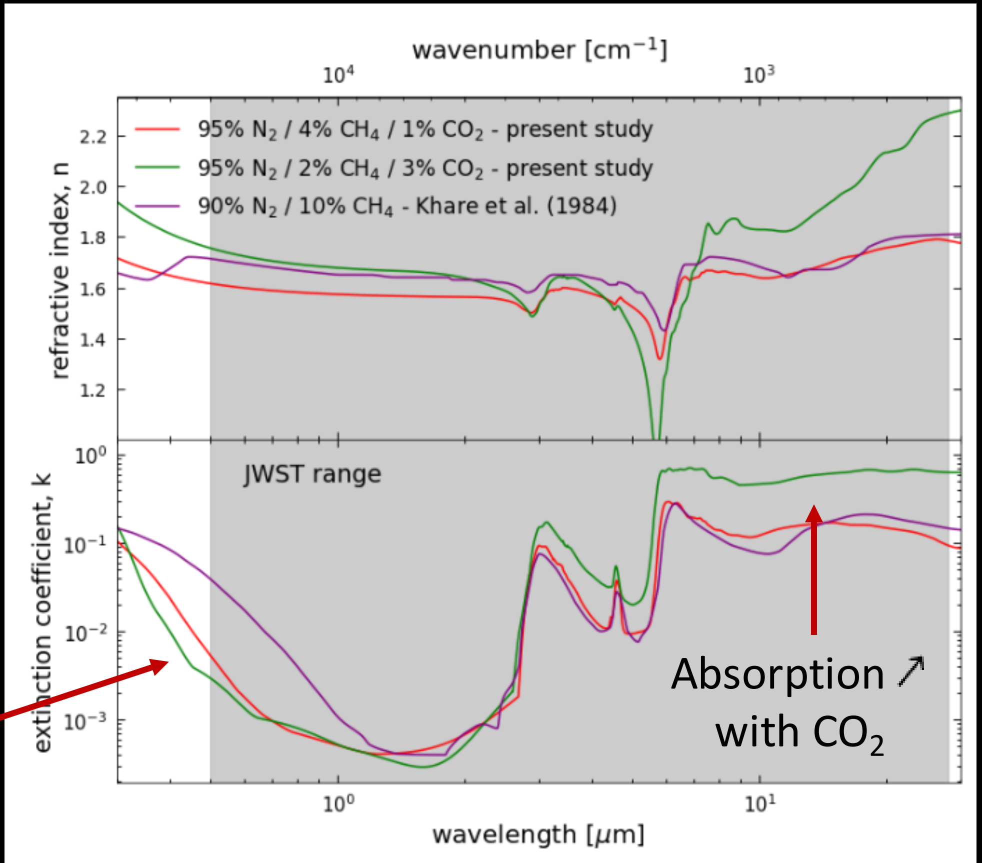
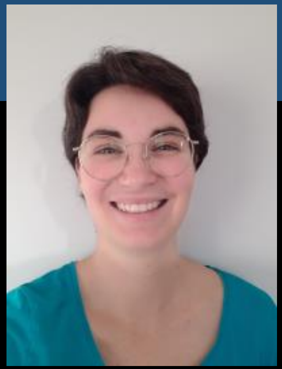


Fig. 12. Optical constants (n and k) measured from 0.3 to 30 μm on two exoplanet haze analogs. The analogs are produced from a 95% N_2 gas mixture with different CO_2 to CH_4 ratios (see Table 1). The seminal data of Khare et al. (1984) for Titan haze analogs is shown in comparison.

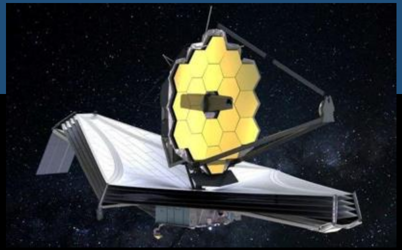
Drant et al 2024 (A&A)

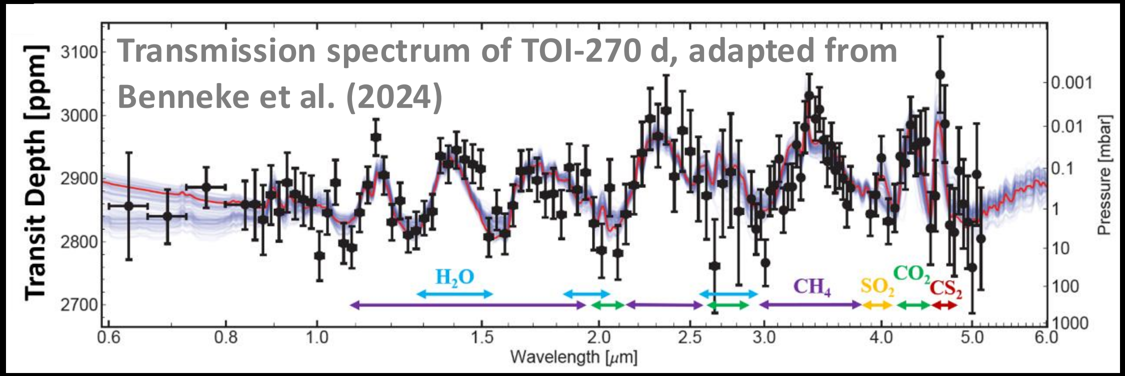
OXYDIZED ORGANIC COMPOUNDS AS CONDENSATES?



Ori Sohier
PhD 3rd year

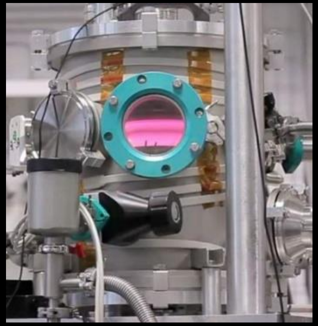
Atmospheric chemistry of temperate exoplanets « mini-Neptunes »





Dominated by H_2, some % CH_4 and CO_2

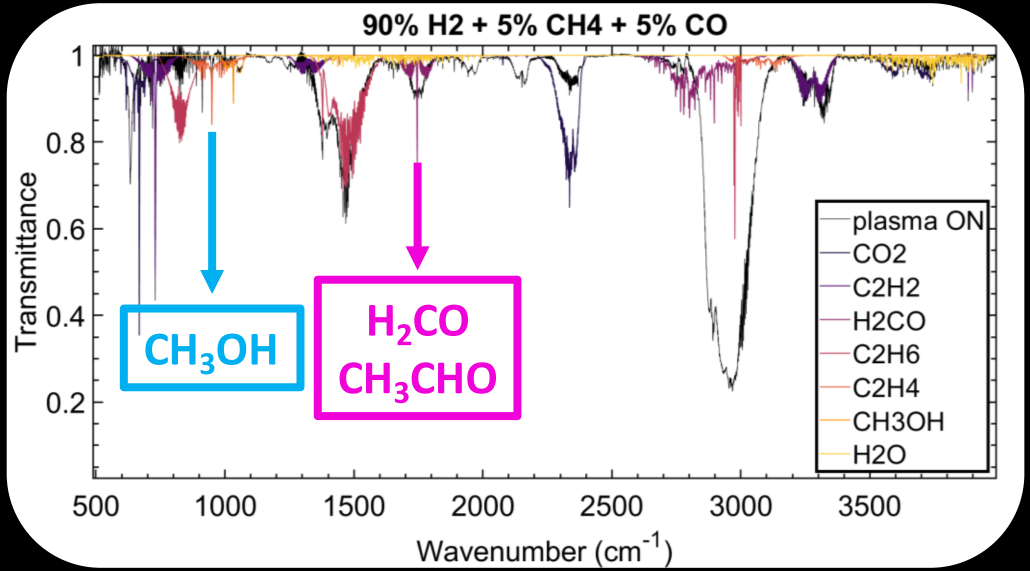
➢ *No formation of aerosols observed*



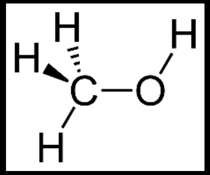
Study of the gas phase

➢ *Complex organic growth*

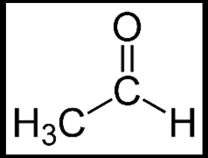
➢ *Production of oxidized organic molecules = potential condensates?*



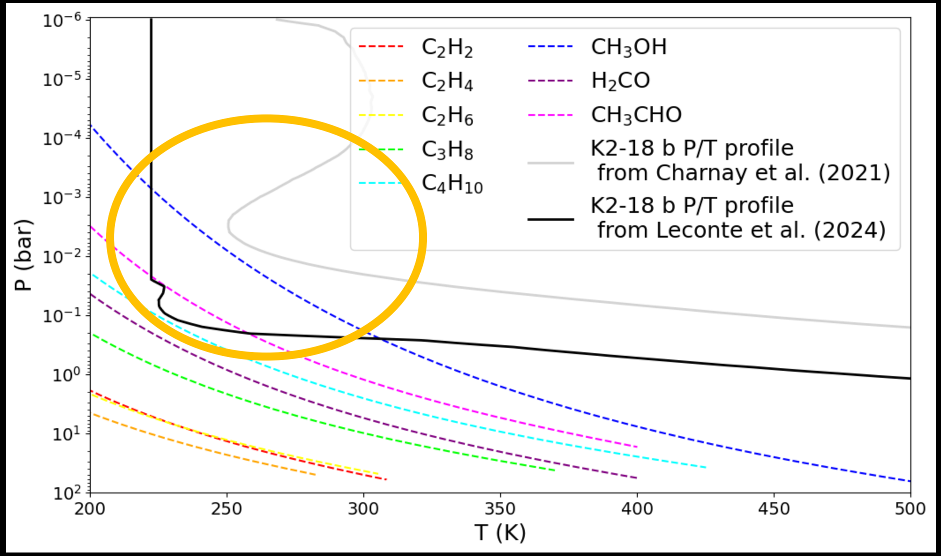
IR spectra



Methanol



Acetaldehyde

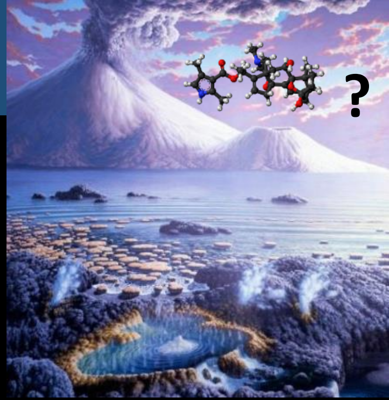


Condensation profiles of the main photochemical compounds observed, superimposed on the estimated P/T profile of K2-18 b

EFFECT OF SULFUR ON PHOTOCHEMICAL AEROSOLS

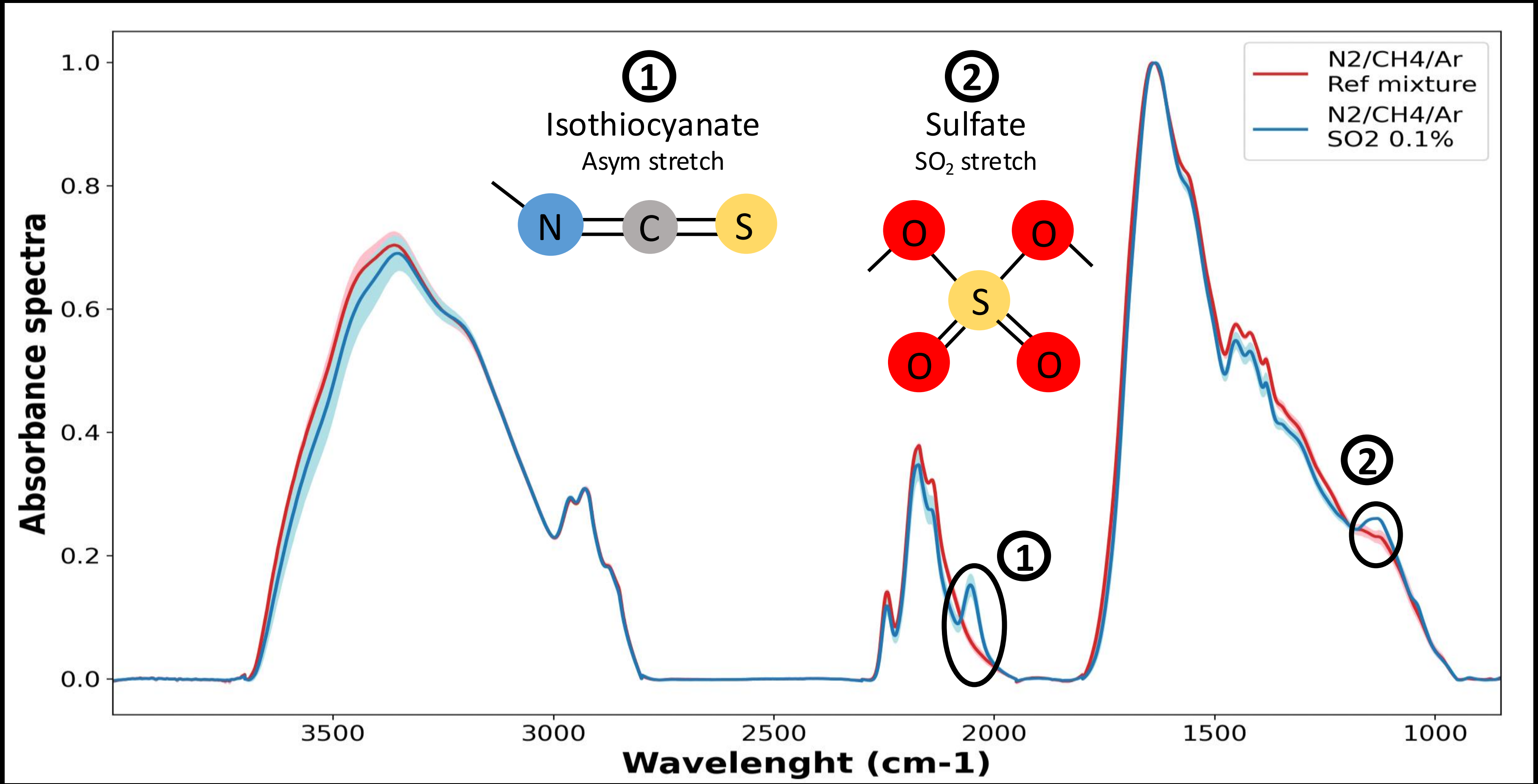
Louis Maratrat
postdoc

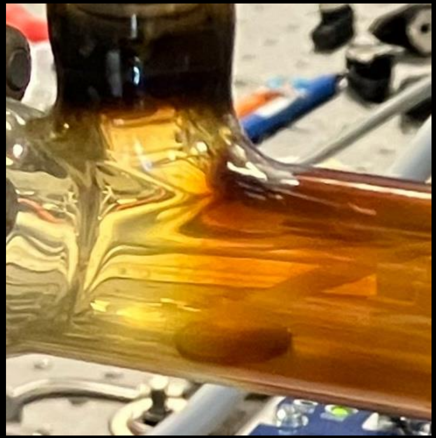
Contribution of volcanism and sulfur chemistry to the prebiotic chemistry and habitability



Coupling the sulfur and carbon chemistry: a source of organics for the Early Earth and elsewhere?

Comparison between organic and organo-sulfur aerosols in the IR



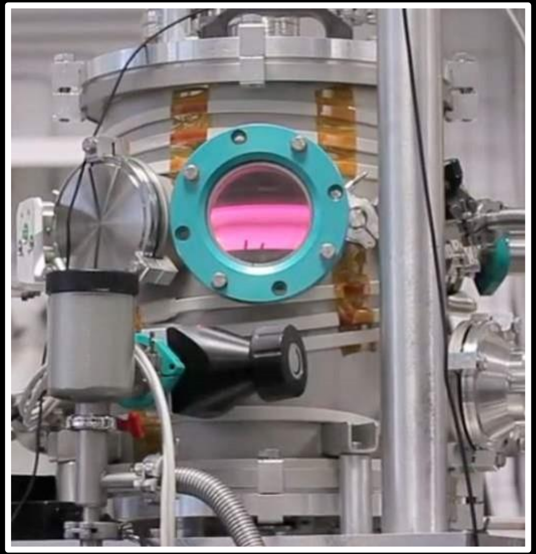


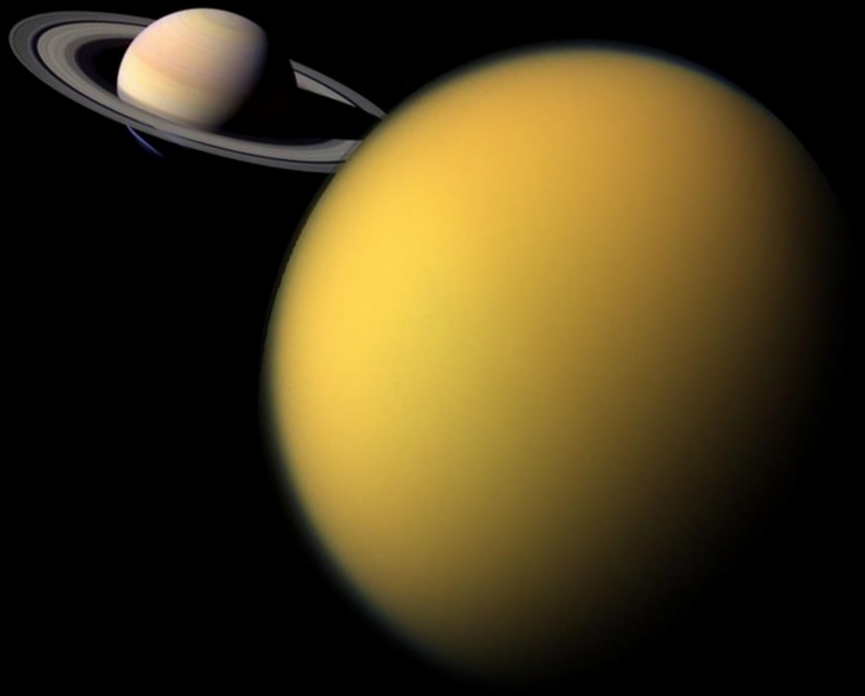
Experimental production of organo-sulfur aerosols
$N_2/CH_4/$**SO_2**
$N_2/CH_4/$**H_2S**

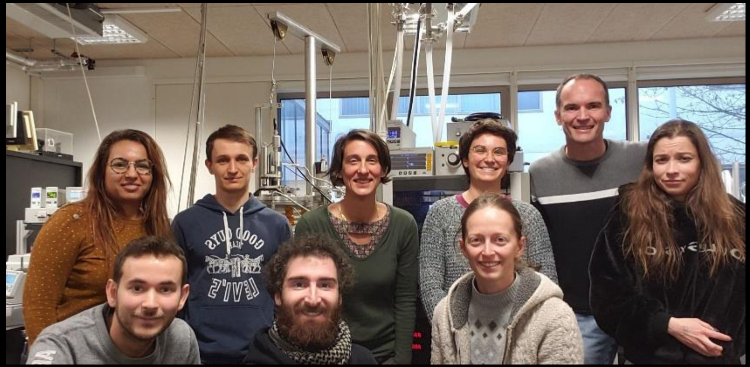
Simulating planetary atmospheres in the lab:
in depth investigation of chemical and microphysical processes in support to observations and models

Audrey CHATAIN

and the ATMOSIM team in LATMOS







since 1998 (28 years!)

~50 researchers/engineers

15 PhD defended

7 postdocs