

# Ion chemistry in exoplanetary atmospheres: a new probe for habitability?

Nathalie Carrasco

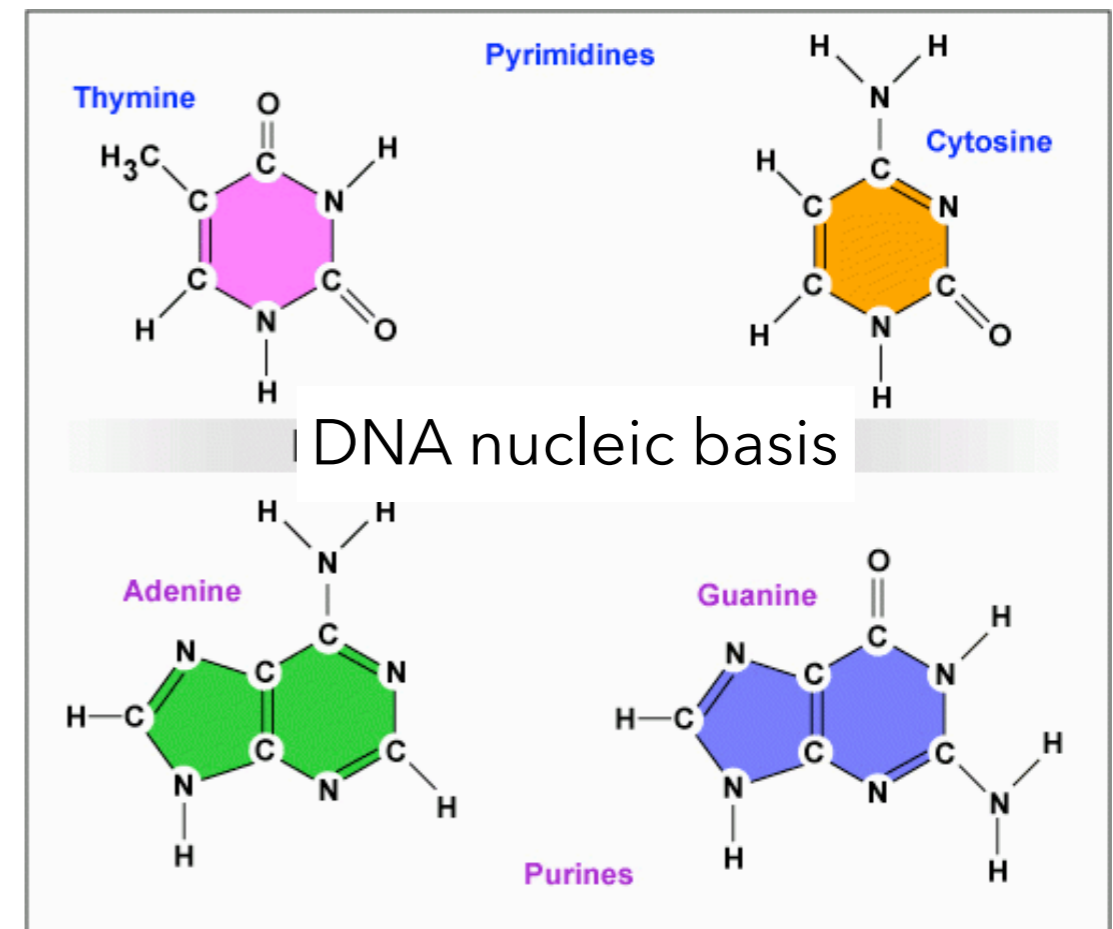
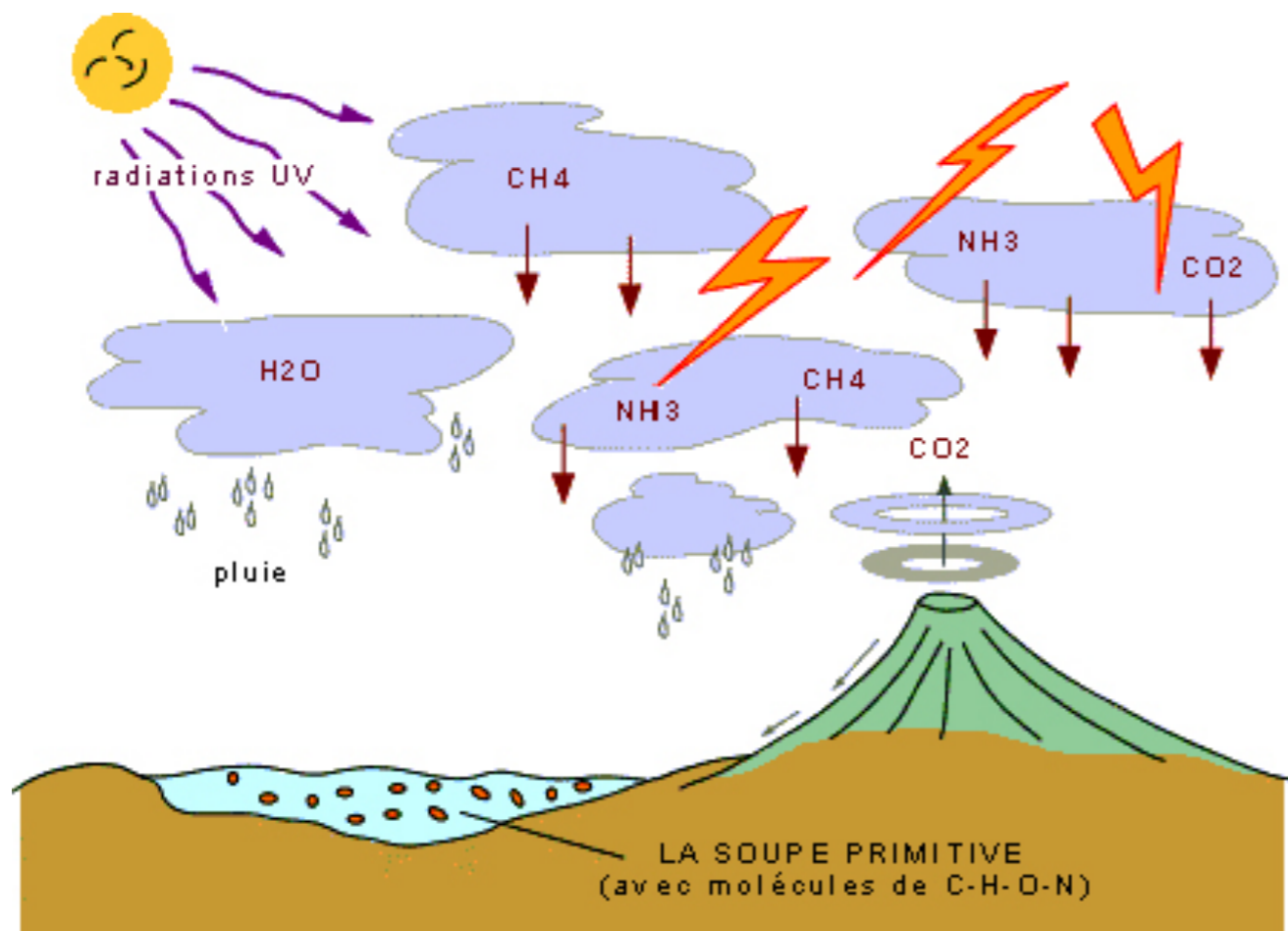
Thomas Drant, Jérémy Bourgalais, Audrey Chatain, David Dubois,  
Thomas Gautier, Ludovic Vettier





# How did atmospheric chemistry support the emergence of life on Earth?

## Prebiotic chemistry? Endogenous source of N- and O-rich organic molecules





# How did atmospheric chemistry support the emergence of life on Earth?

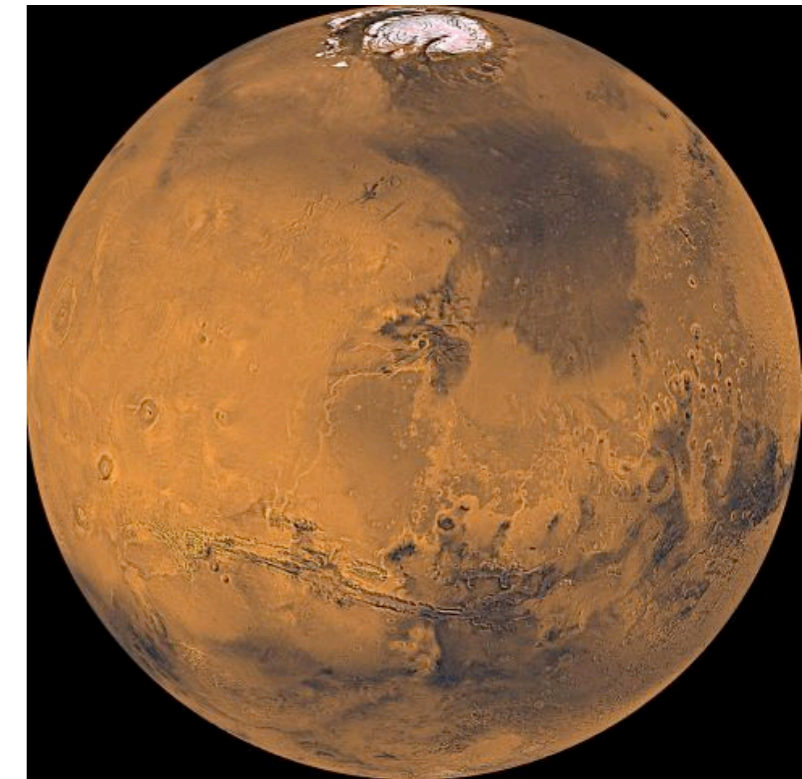
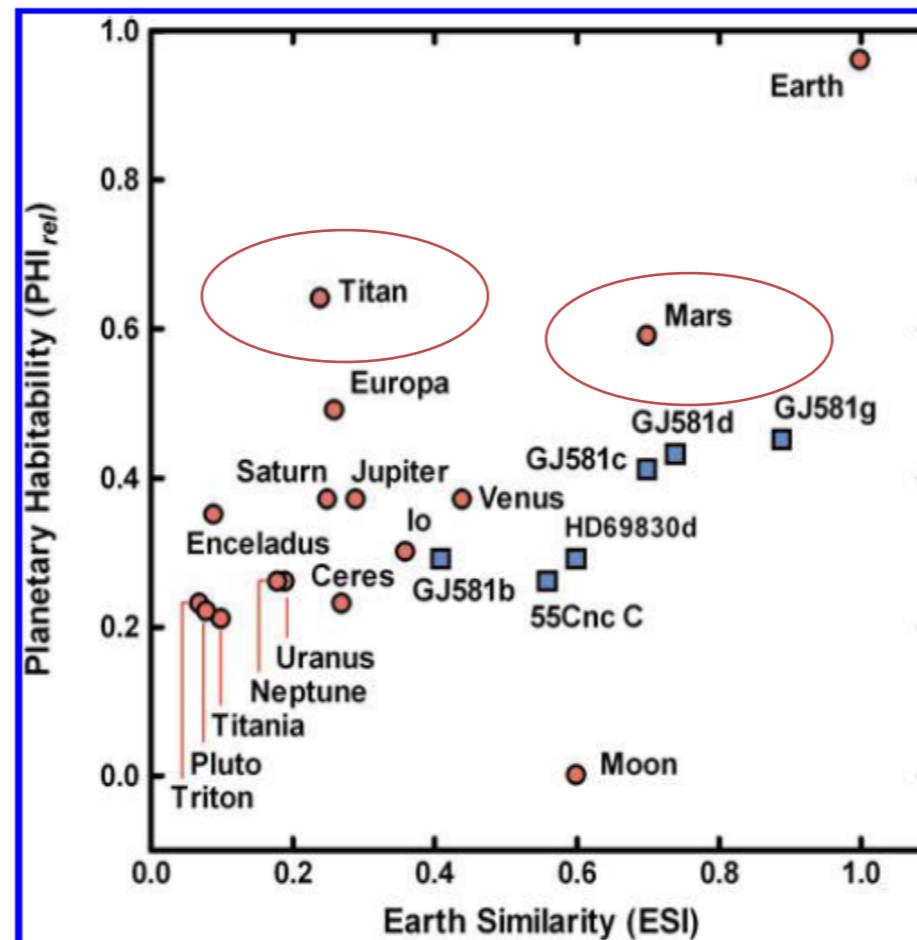
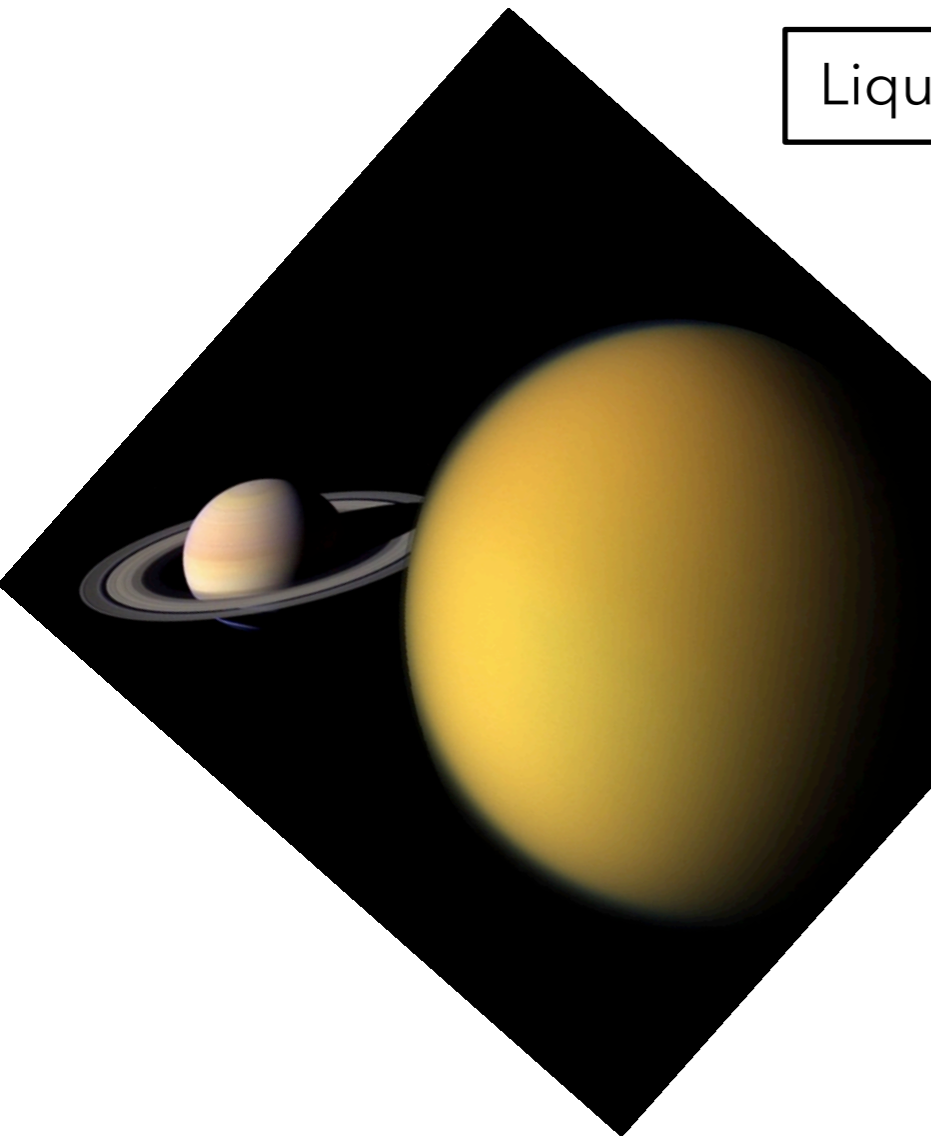
**No geological archives old enough on present Earth**  
→ **Investigation of other bodies in the solar system**

## HABITABILITY

Liquid Water

Organic chemistry

Energy source

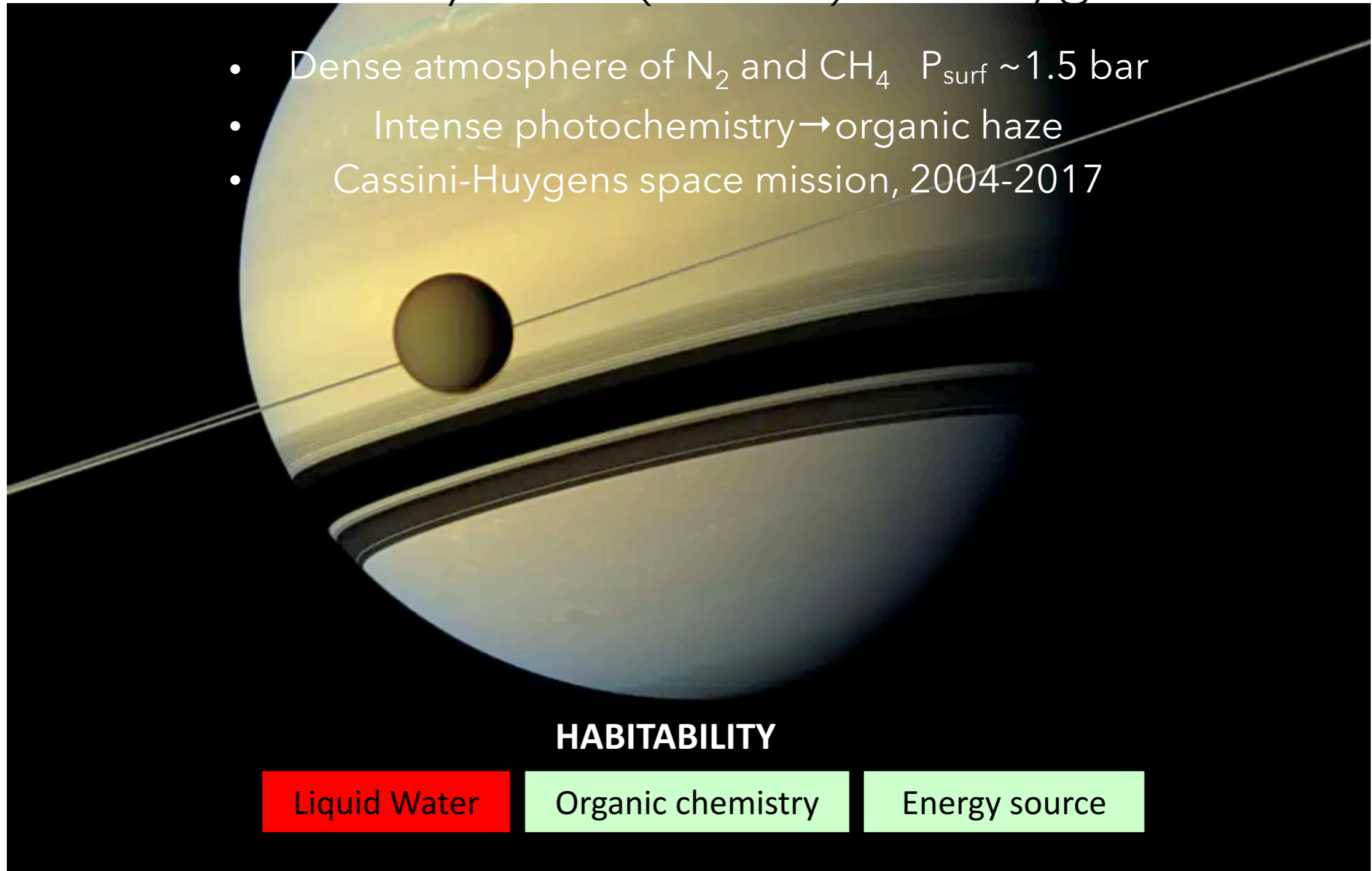


Credits: NASA-JPL

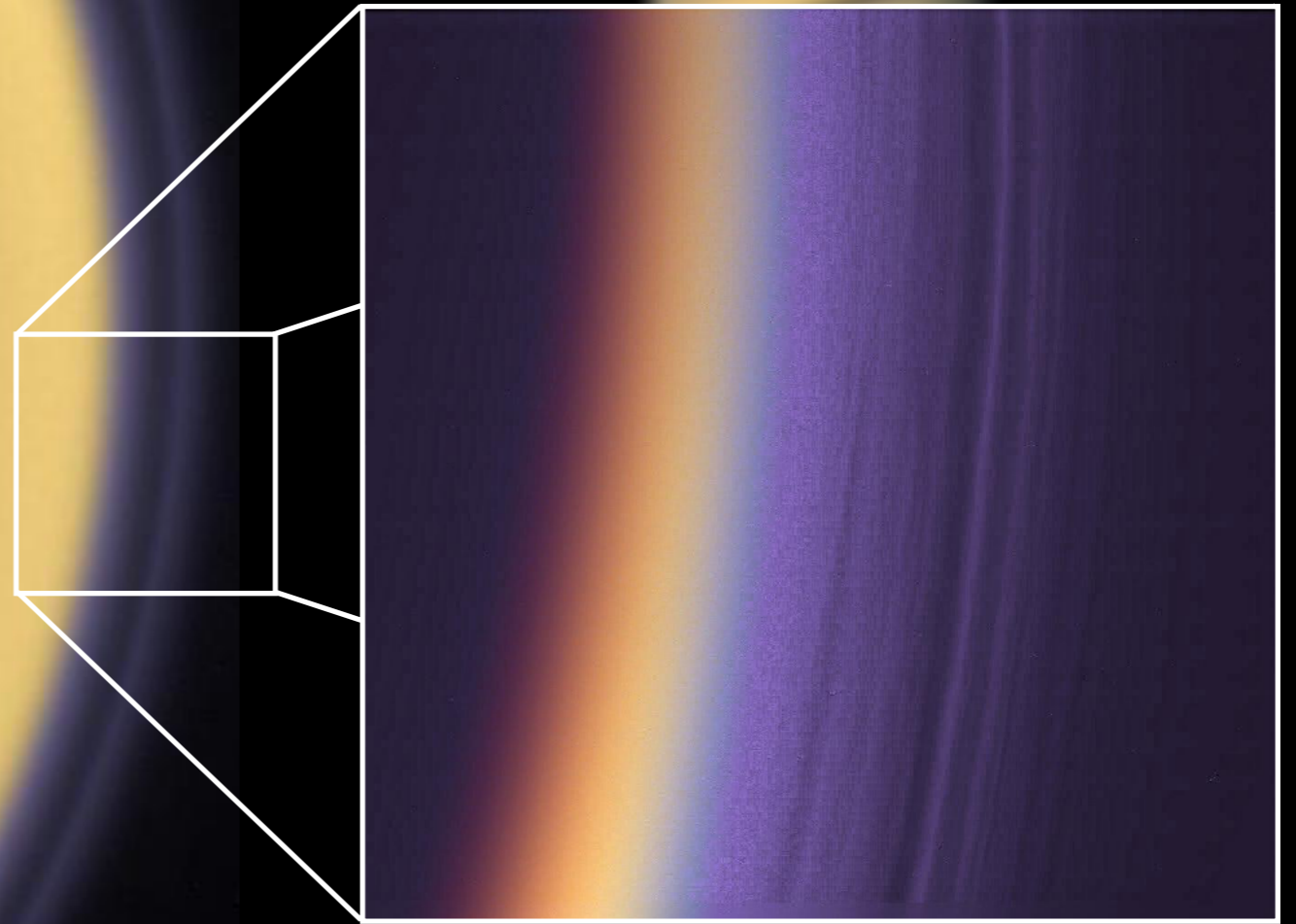


# Titan: a unique place to observe prebiotic chemistry with (almost) no oxygen

- Dense atmosphere of  $N_2$  and  $CH_4$   $P_{surf} \sim 1.5$  bar
- Intense photochemistry  $\rightarrow$  organic haze
- Cassini-Huygens space mission, 2004-2017

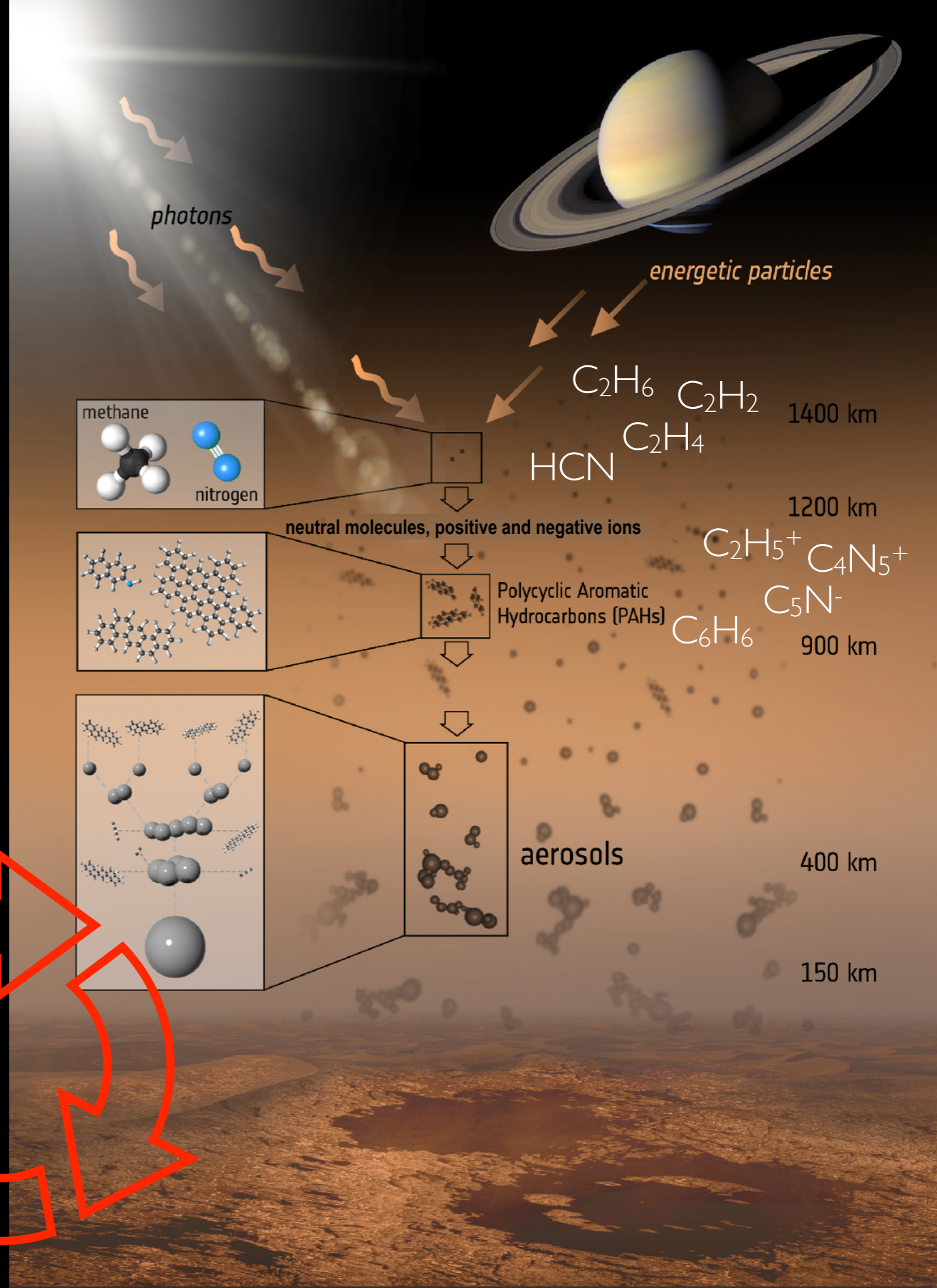
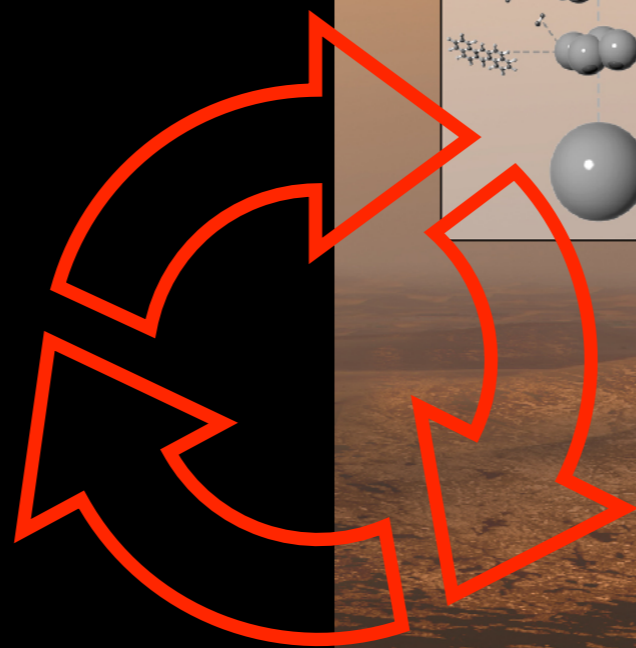


Titan



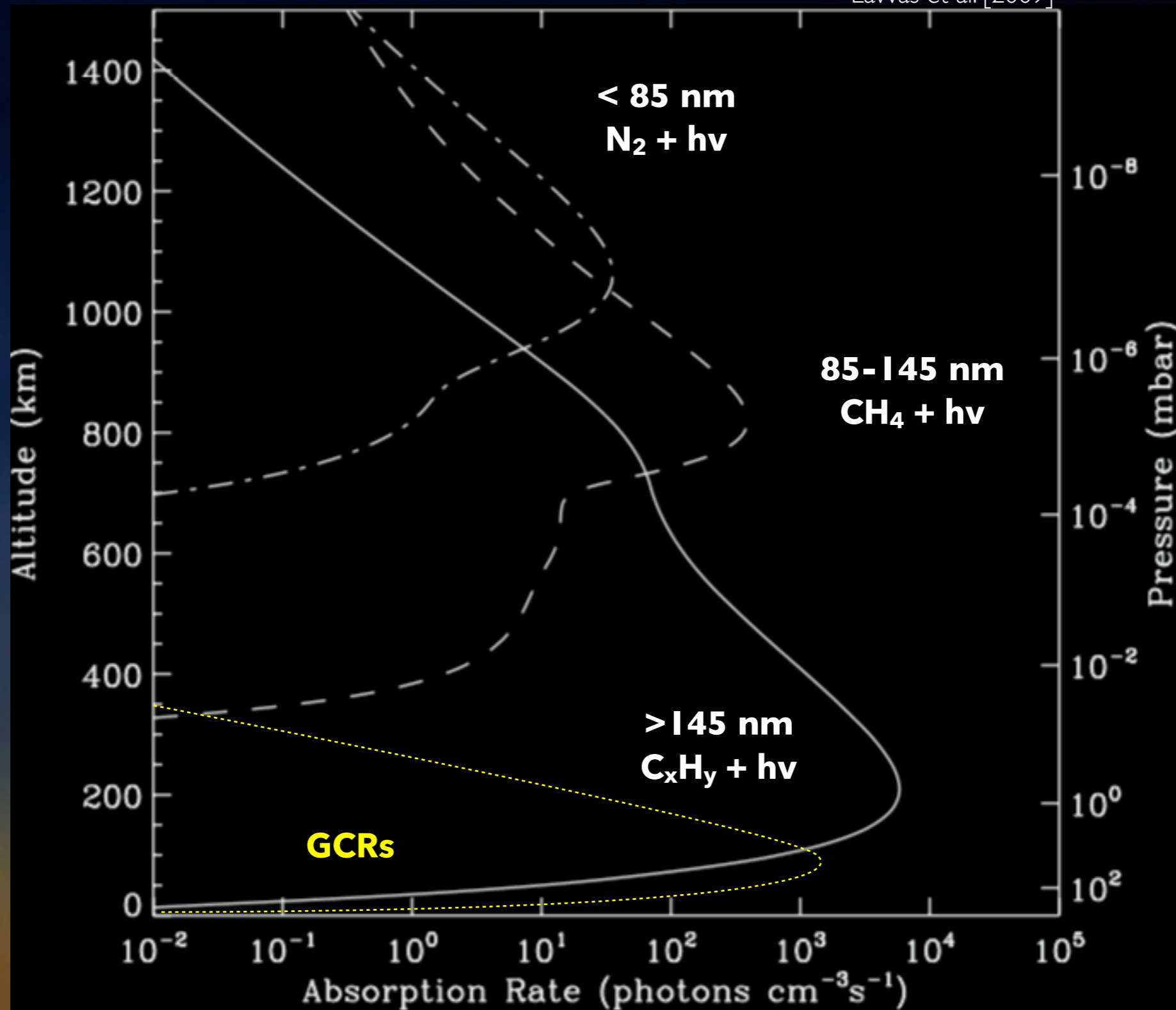
# Titan

Lifetime :  
 $T_{CH_4} = 10-100 \text{ Myr}$



# Titan

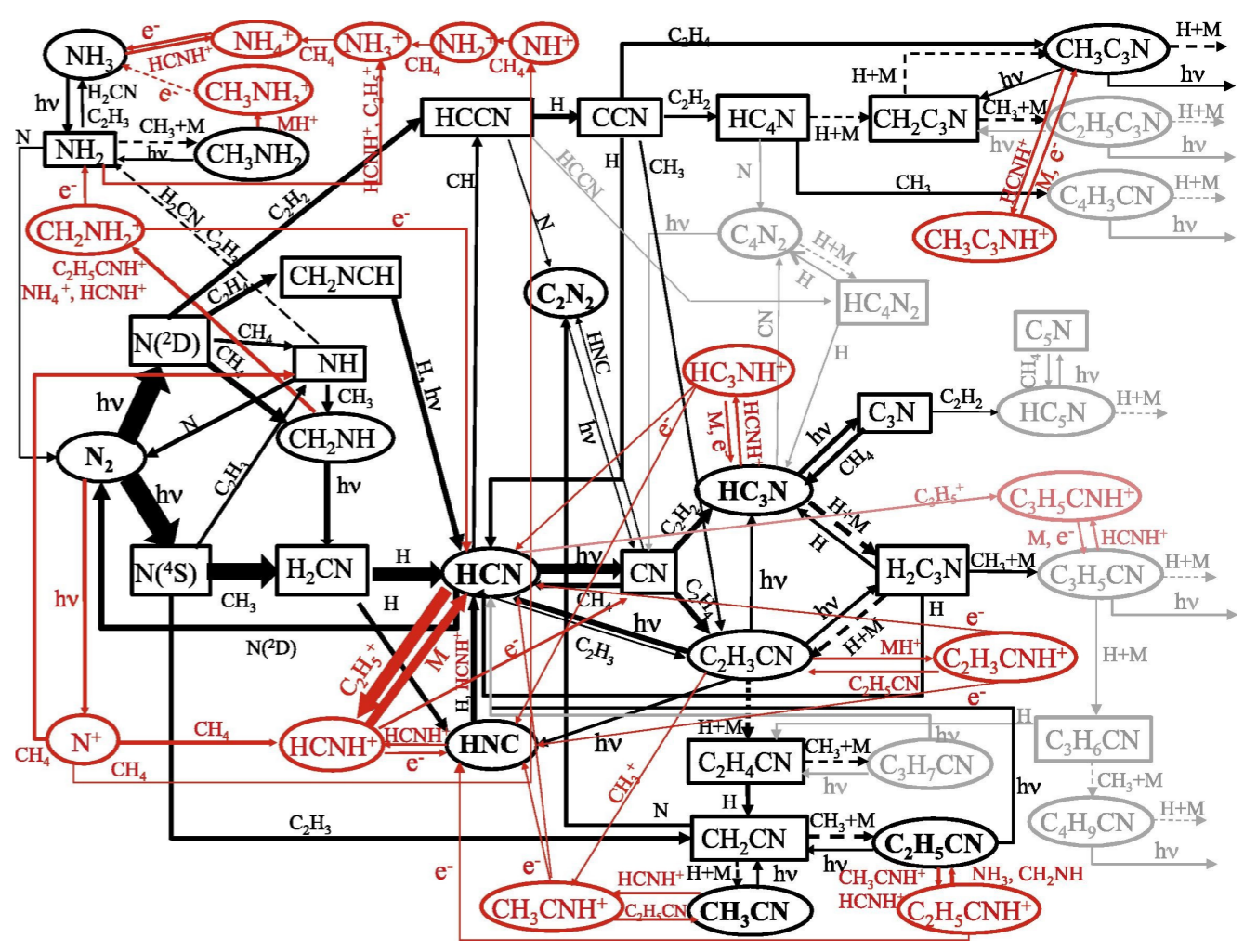
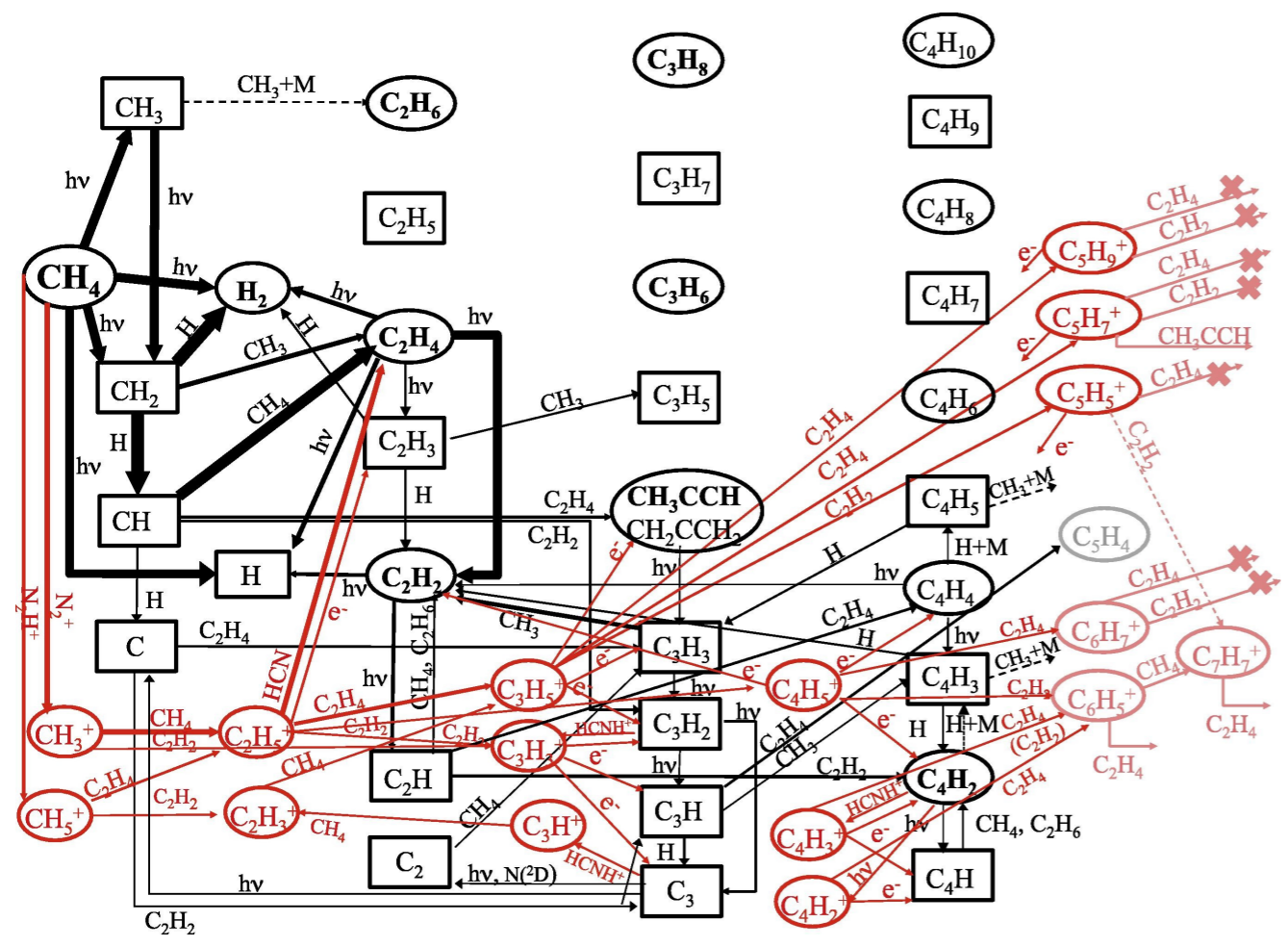
Lavvas et al. [2009]





# Titan

Dobrijevic et al. [2016]

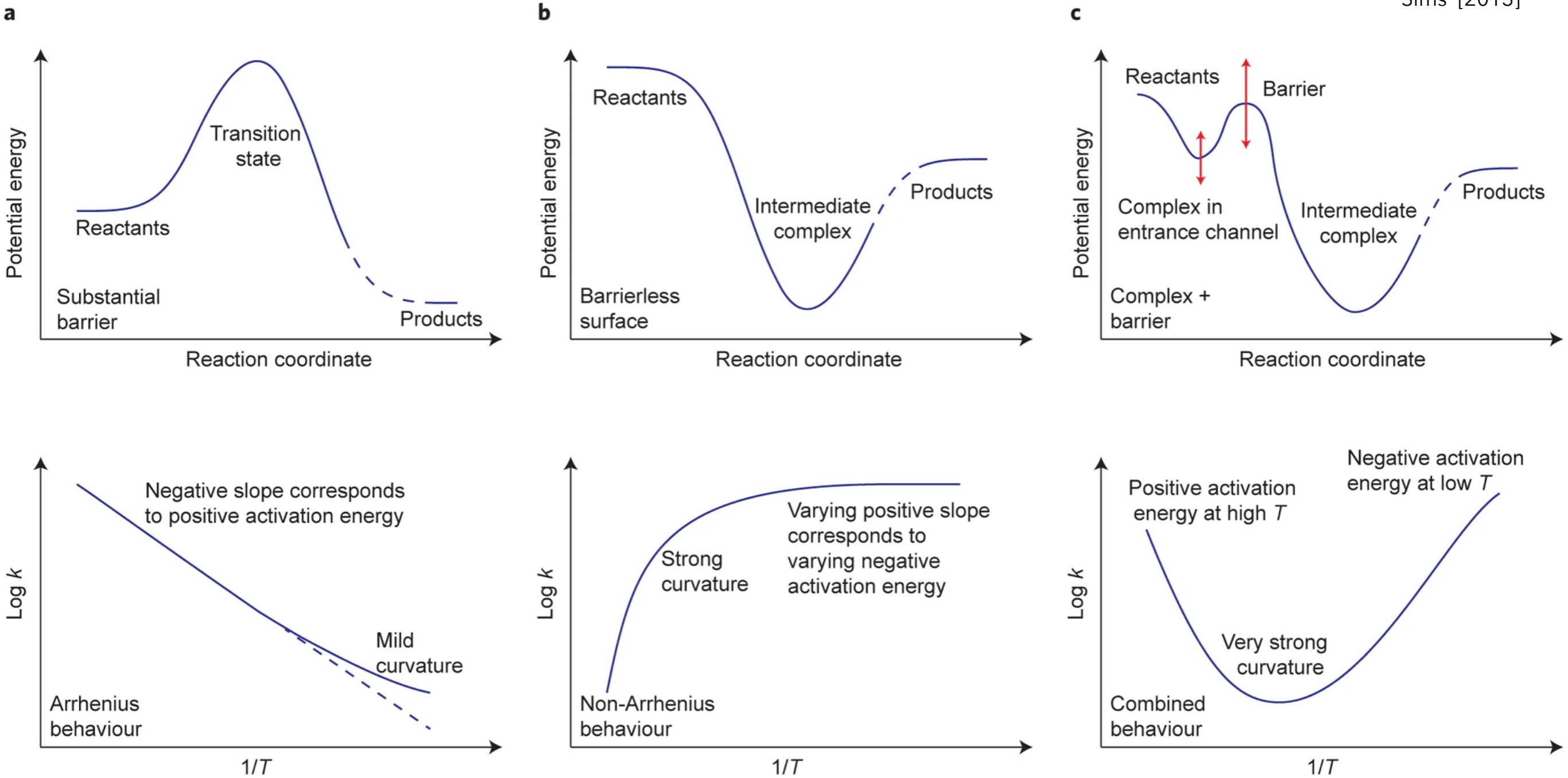






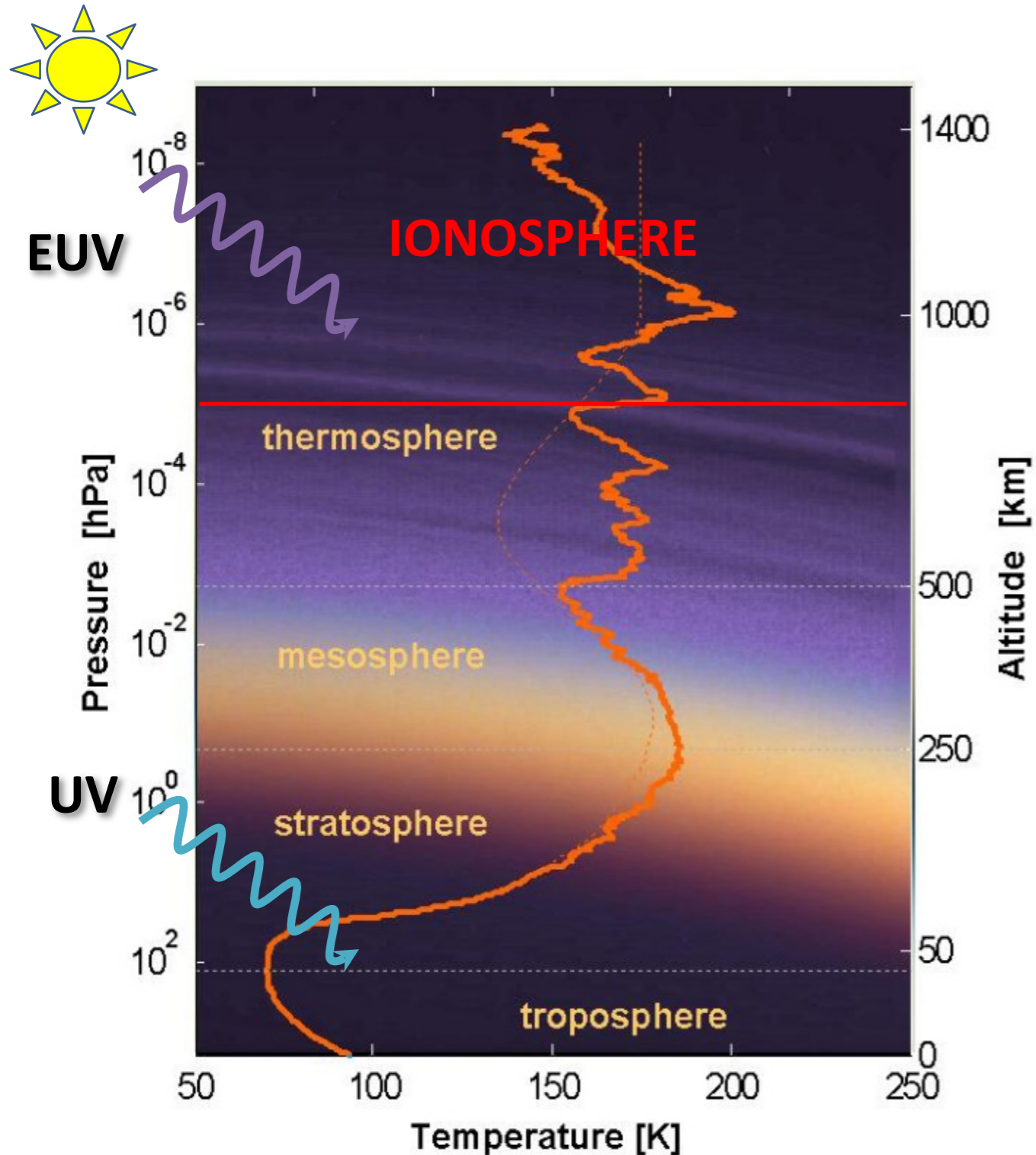
# Low-temperature chemistry

Sims [2013]





# Most striking result from Cassini space mission: Large N-rich ions (up to 10,000 amu)



- Solid organic aerosols
- High prebiotic interest (amino-acids)

**Ionosphere: a new source of  
prebiotic molecules**

**Specificity: Extreme-UV photons  
trigger  $N_2$  reactivity**



# Building extreme-UV laboratory experiments to simulate Titan's ionospheric chemistry

Groups:

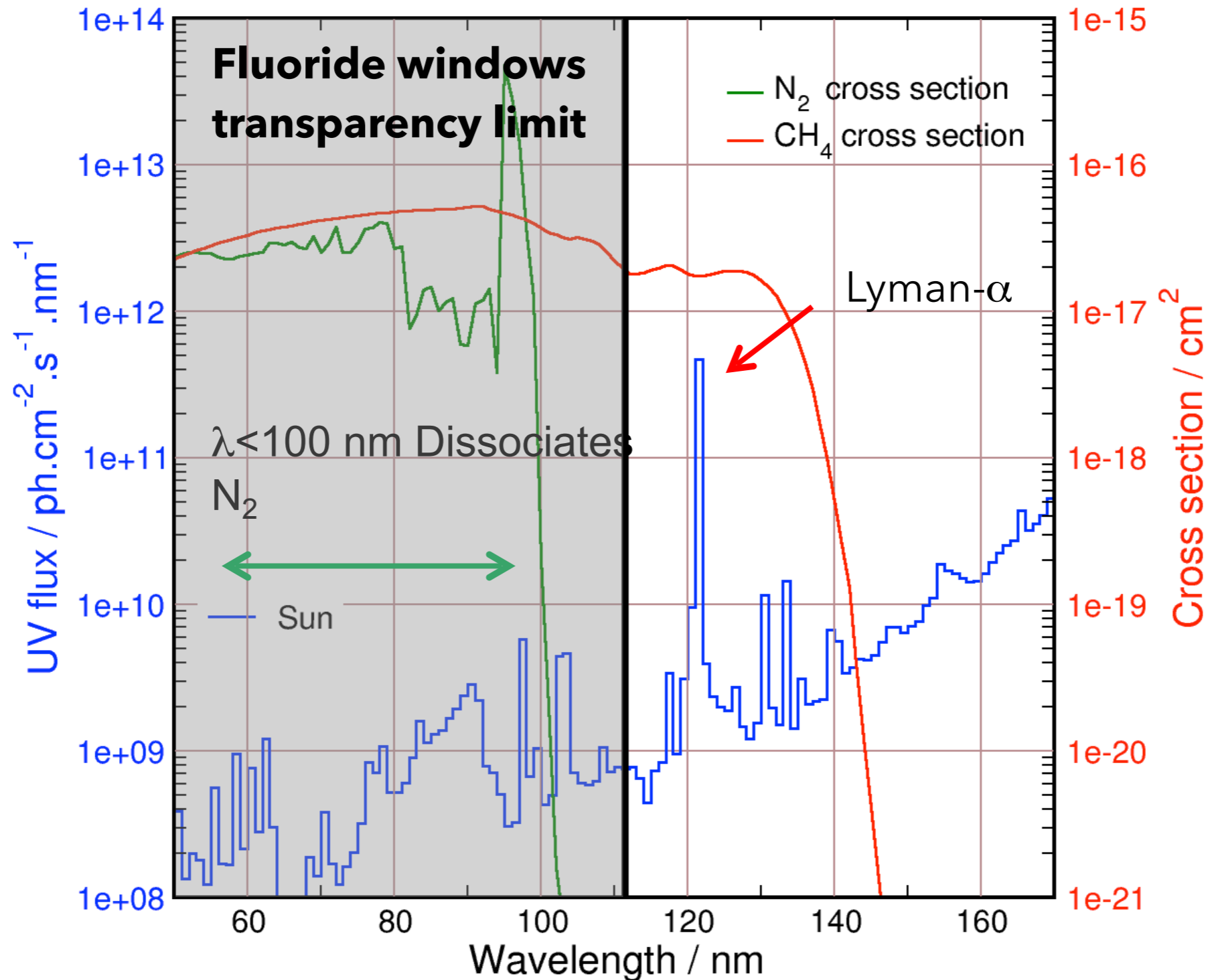
Imanaka and Smith, University of Arizona

Hörst and col., John Hopkins University

Carrasco and col., Université Versailles Saint Quentin

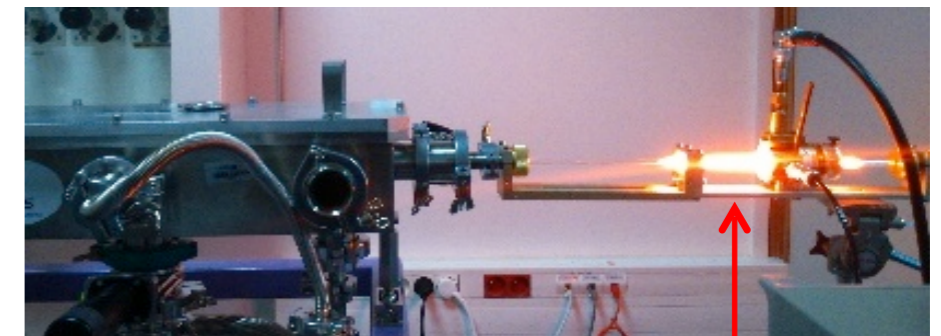
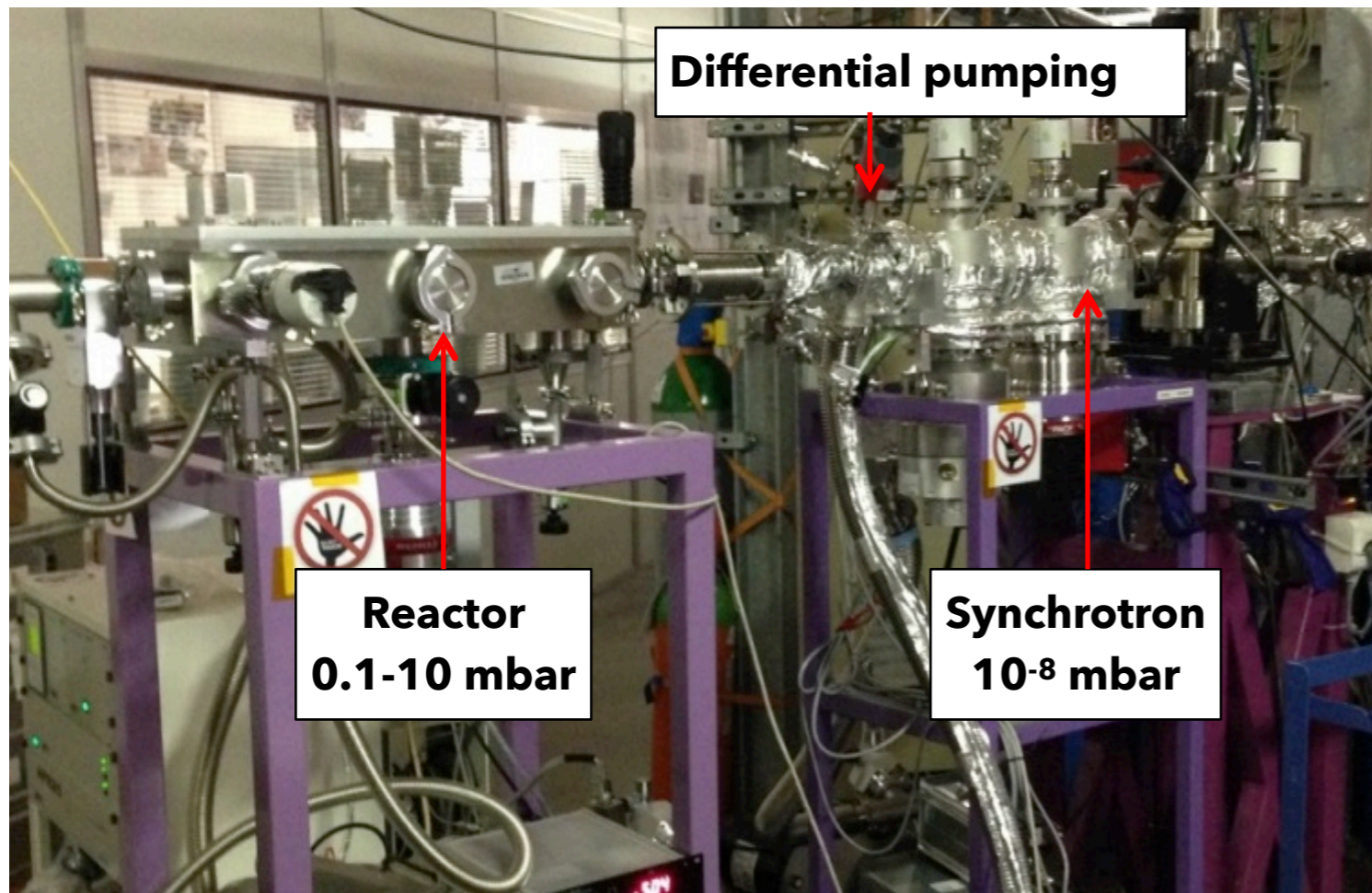


# N<sub>2</sub> photochemistry in closed cells impossible in the lab



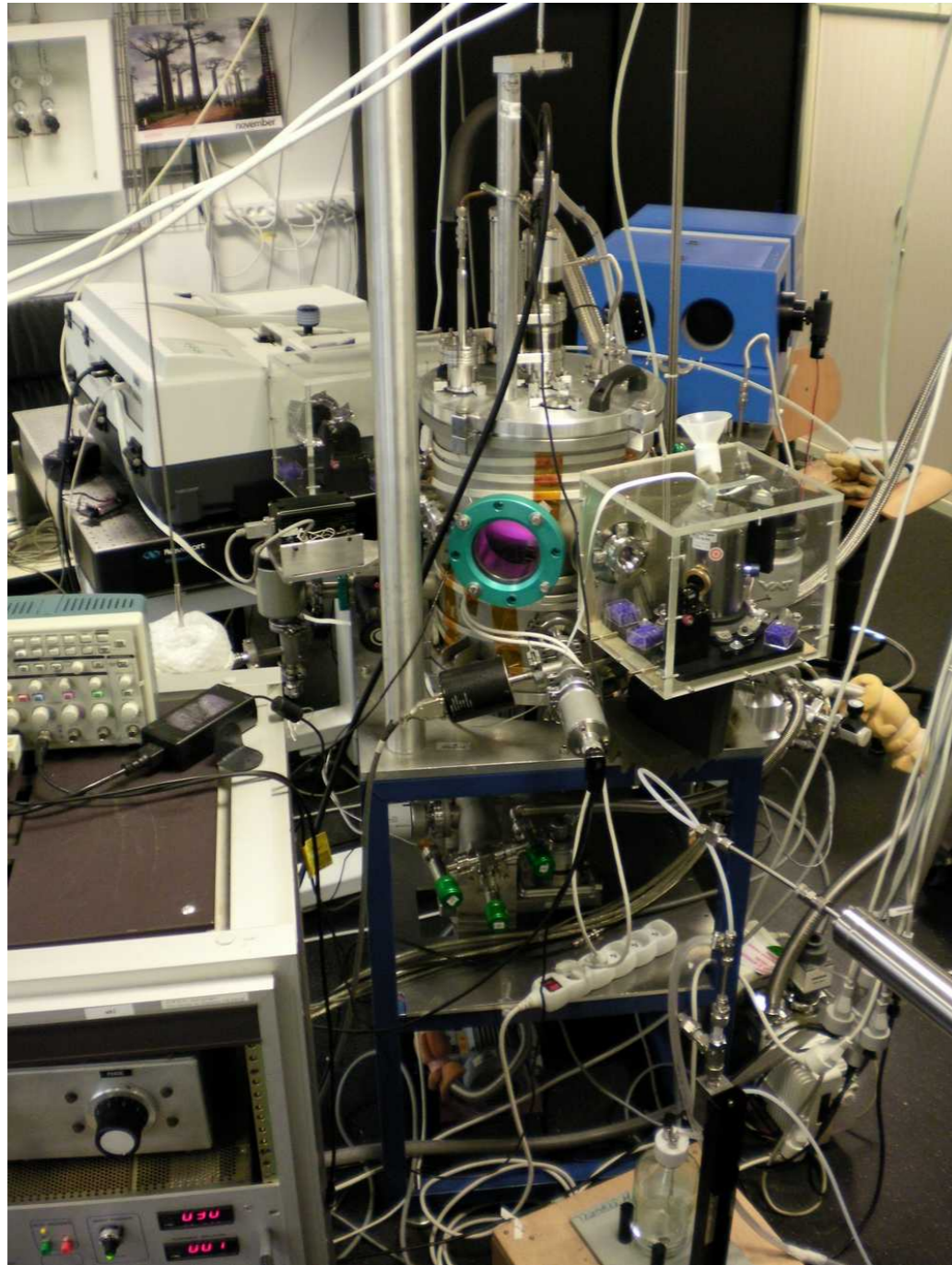


# EUV photochemical reactors

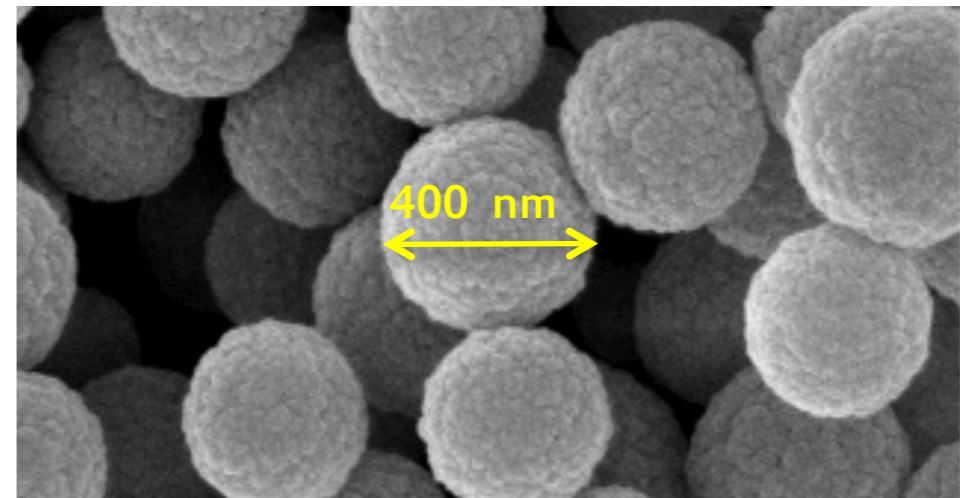




# Dusty plasma experiment



- Optimized for haze production



Hadamcik et al. [2009]

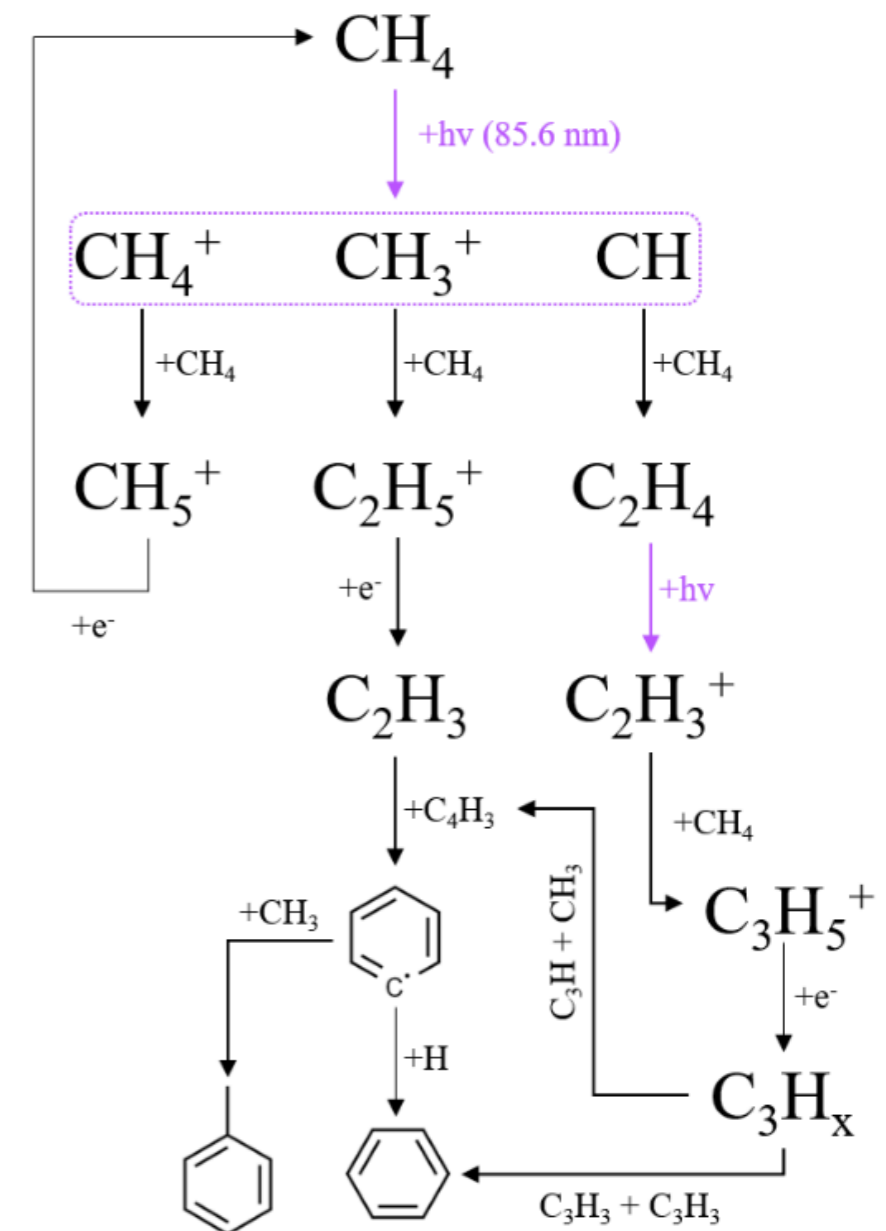
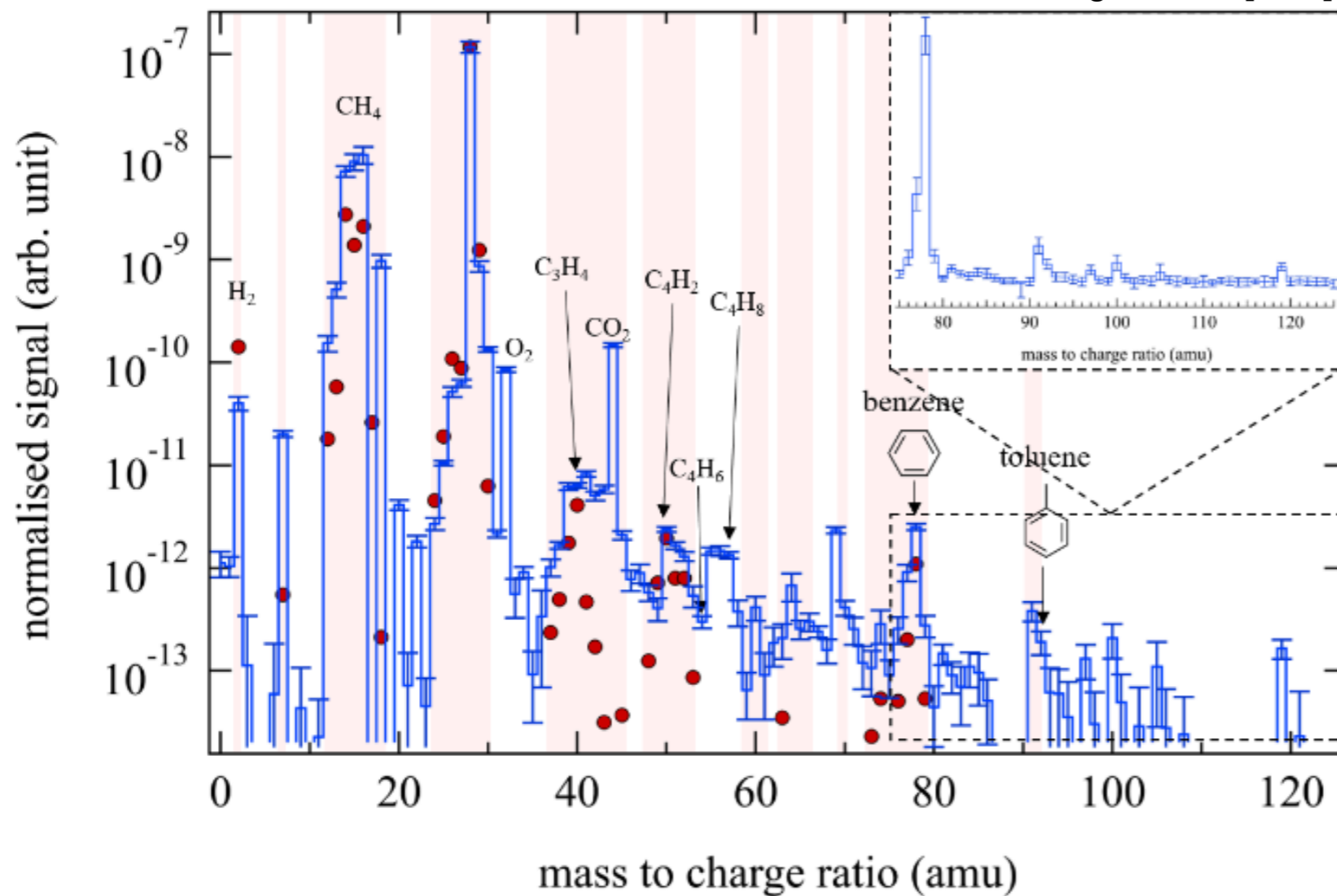
- Radicals and ions from electronic impact



# Positive ions: pathways to aromatics

**EUV photolysis at 85.6 nm: CH<sub>4</sub> ionized, N<sub>2</sub> dissociated**

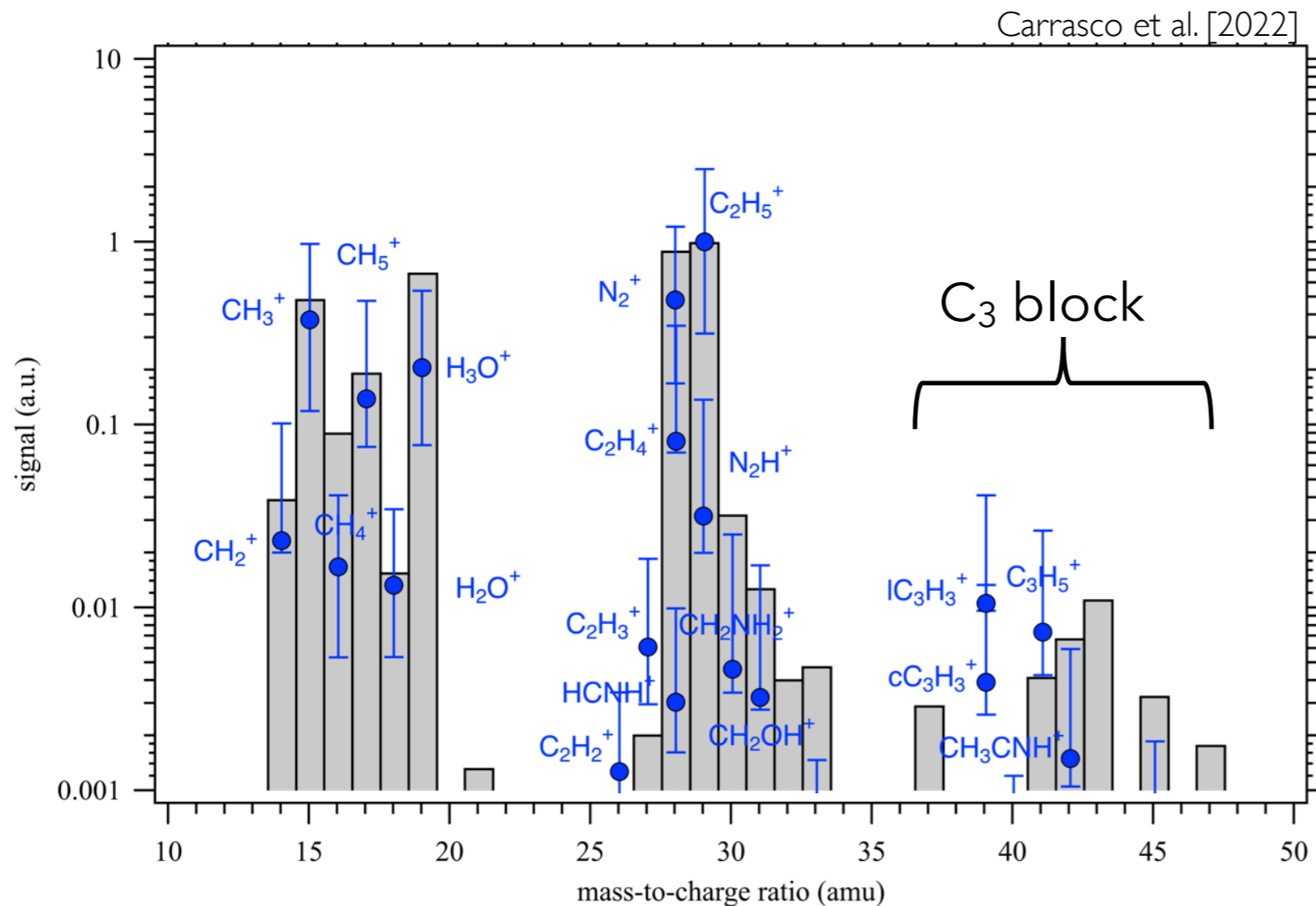
Bourgalais, et al. [2021]





# Positive ions investigation

## 1/ Limited predictions for ions with more than 3 heavy atoms



Comparison of the  
experimental  
measurements with 0D  
chemical model  
predictions

→ Limitation with our  
current knowledge on  
C<sub>3</sub> ions

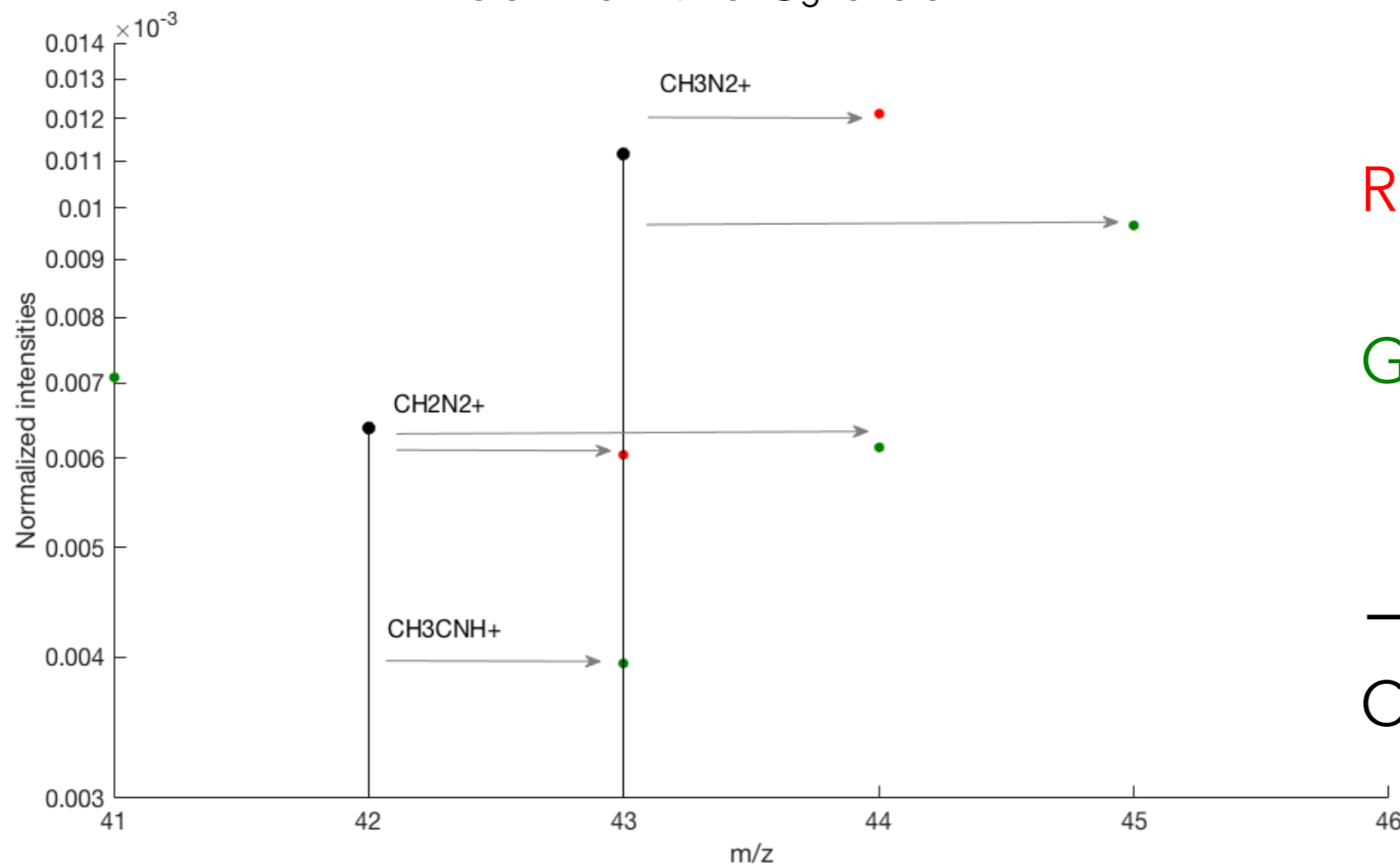




# Positive ions investigation

## 2/ Isotopic labelling: diazo cations identification

Zoom on the C<sub>3</sub> block



Red: <sup>13</sup>C labelling

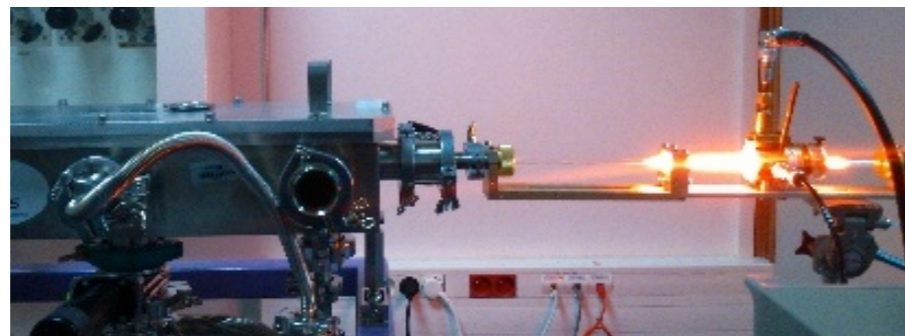
Green: <sup>15</sup>N labelling

→ Reveal the formation of  
CH<sub>2</sub>N<sub>2</sub><sup>+</sup> and CH<sub>3</sub>N<sub>2</sub><sup>+</sup>

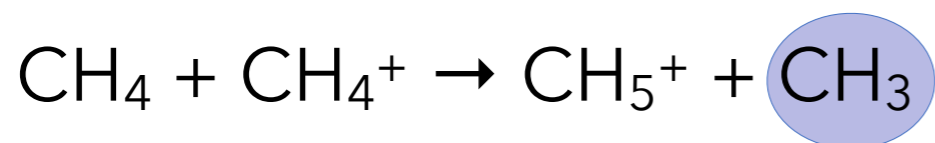
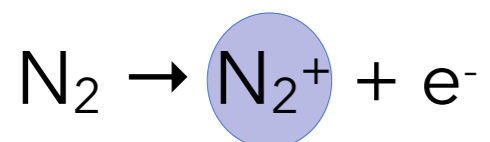


## Positive ions investigation

### 3/ Process explaining their formation: $\text{N}_2^+ + \text{CH}_3$



**EUV Lamp  
@73.6 nm**



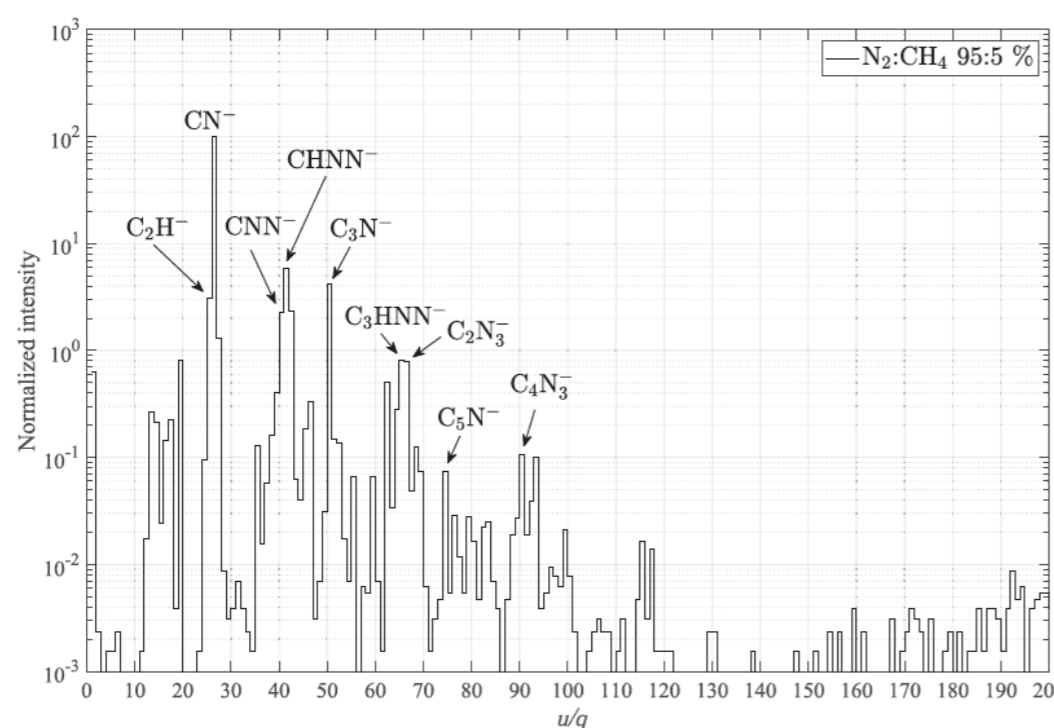
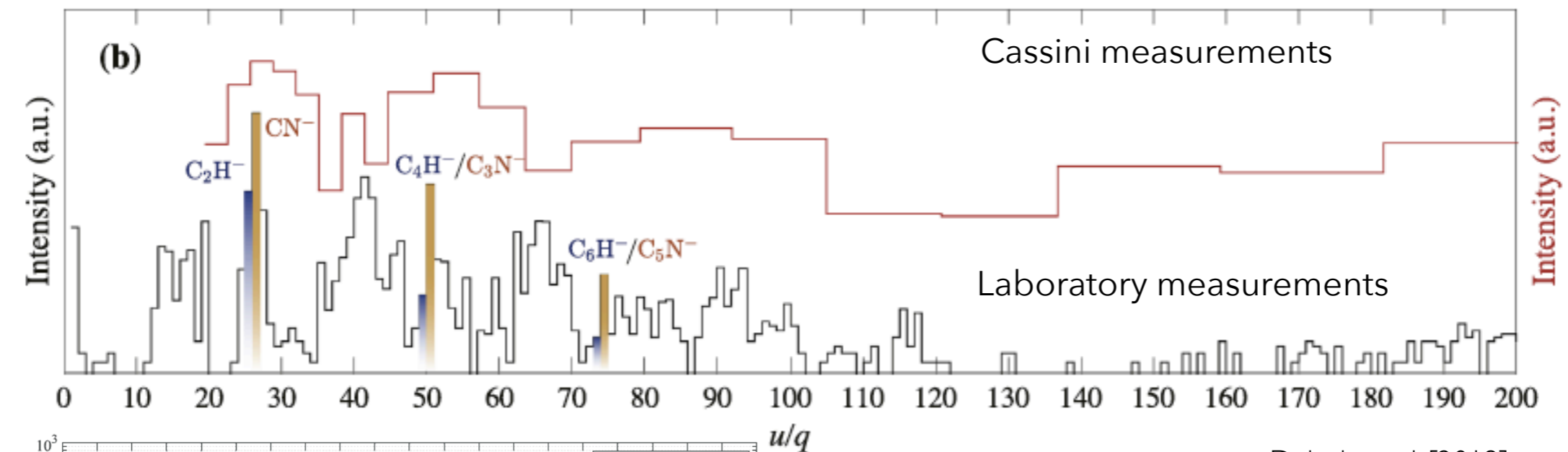
- Abundant reactive species produced by primary processes
- Not yet studied :  $\text{N}_2^+ + \text{CH}_3$   
→ Theoretical study calculations

**Conclusion: abundant ions in Titan ionospheric conditions,  
between  $10^{-2}$  and  $10^{-4} \times \text{HCNH}^+$**



# Negative ions identification

## Better performances of lab instruments, Diazo anions



Dubois et al. [2019]

- Identification of negative ions not yet predicted by models
- Consistent with positive ions
- N incorporation in organic molecules



# Search for Earth-analogs outside the solar system

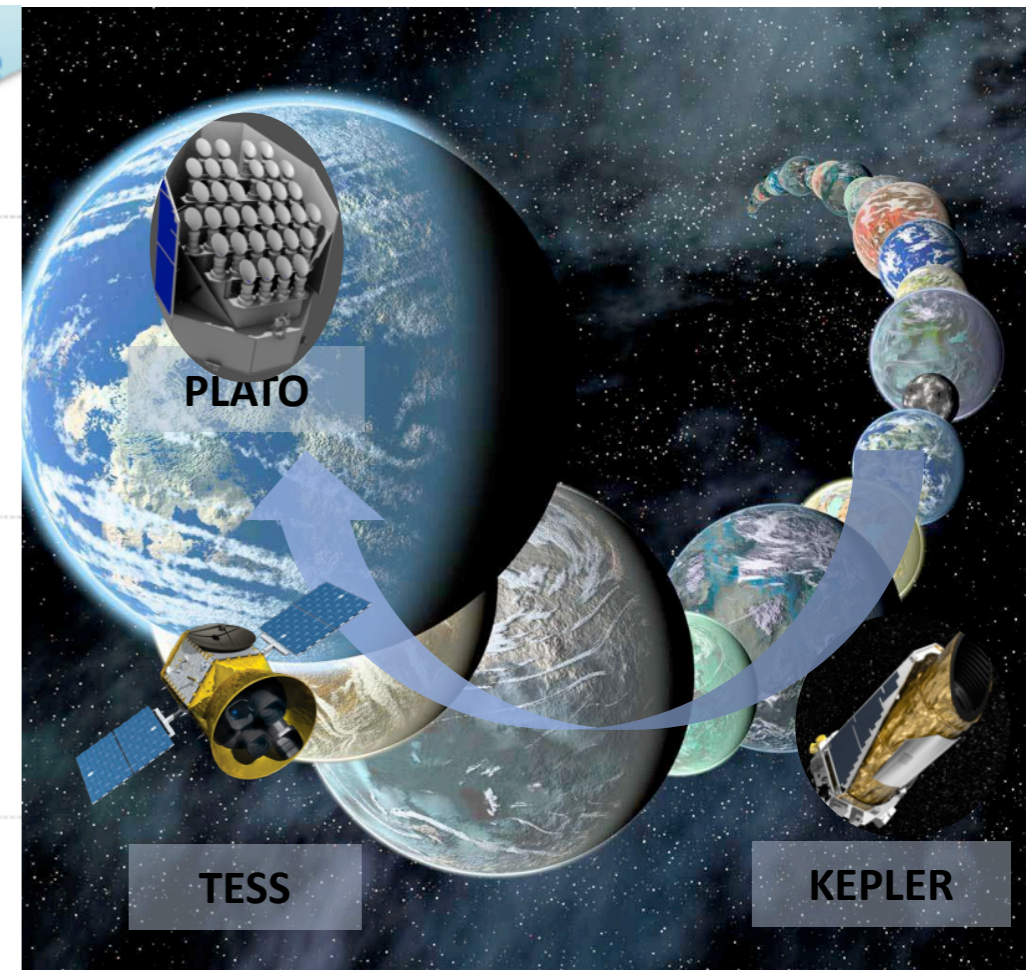
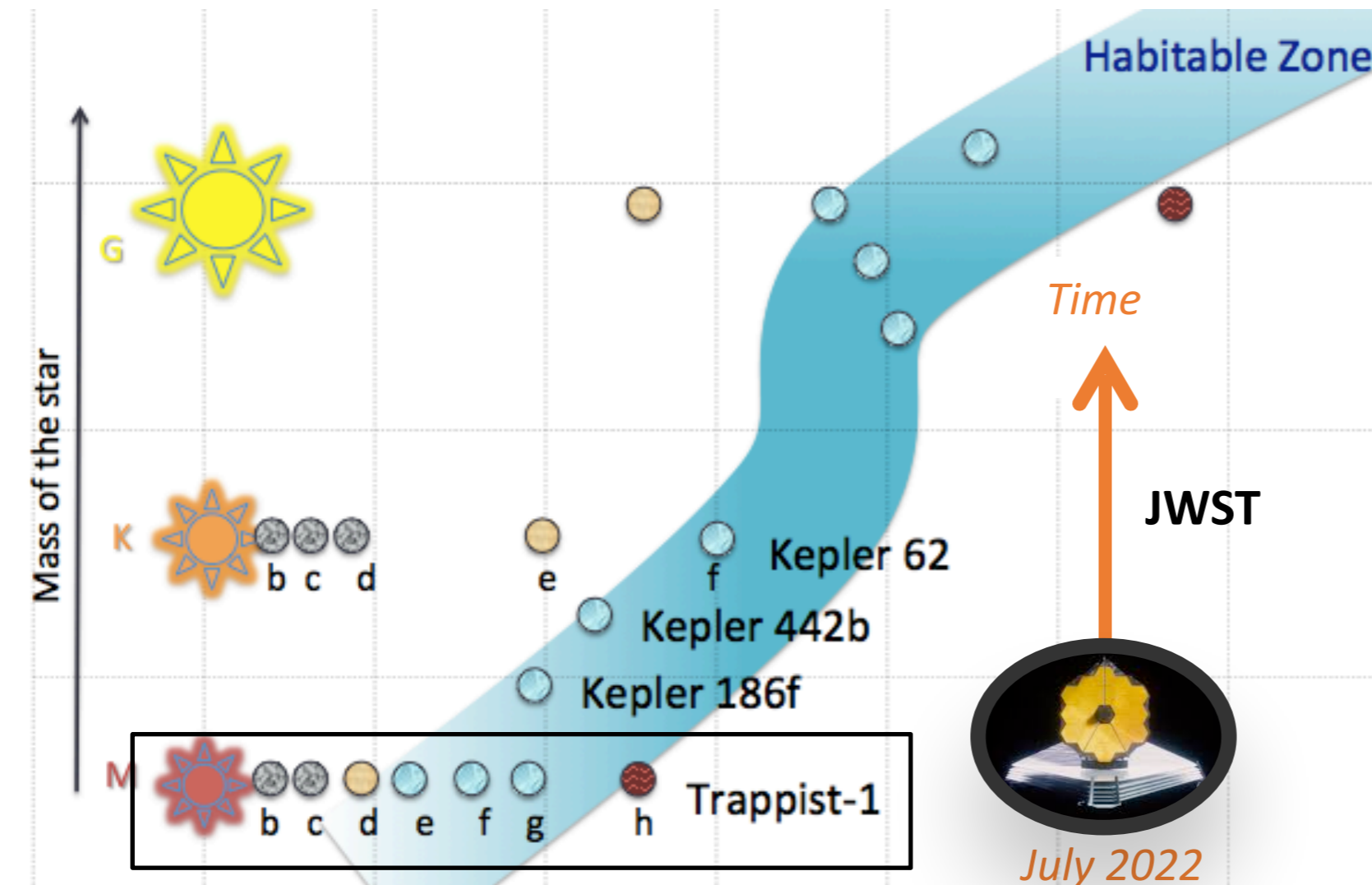
## Humid conditions : the Habitable Zone (HZ)

### HABITABILITY

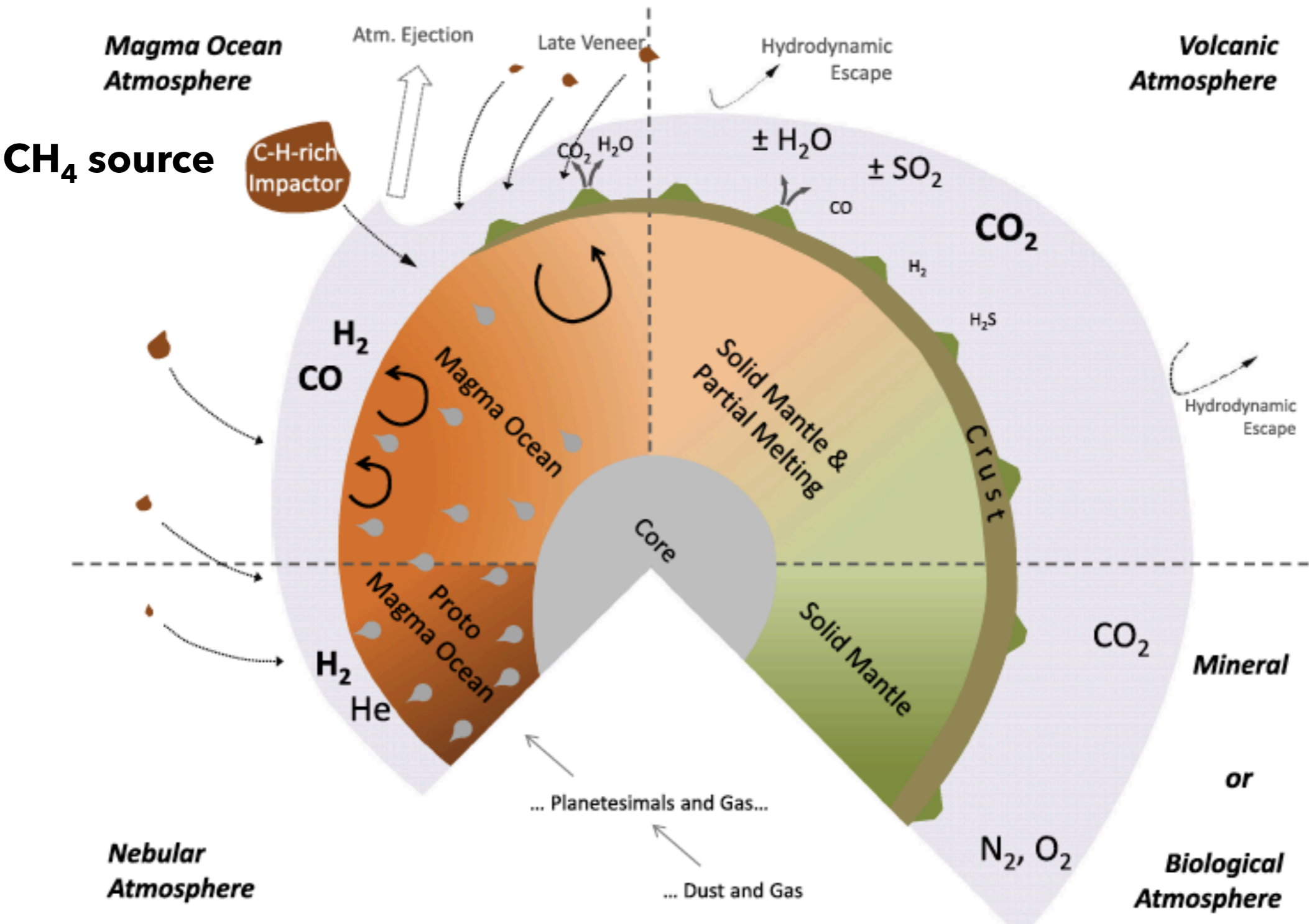
Liquid Water

Organic chemistry

Energy source



Adapted from Nasa/JPL-Caltech



Gaillard and Scaillet [2014]



## Large range of possible atmospheric compositions: CO<sub>2</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, etc

Schaefer and Fegley [2010]

**Table 1**

Major gas compositions of impact generated atmospheres from chondritic planetesimals at 1500 K and 100 bars.

Gas (vol.%)	<i>CI</i>	<i>CM</i>	<i>CV</i>	<i>H</i>	<i>L</i>	<i>LL</i>	<i>EH</i>	<i>EL</i>
H <sub>2</sub>	4.36	2.72	0.24	<b>48.49</b>	<b>42.99</b>	<b>42.97</b>	<b>43.83</b>	14.87
H <sub>2</sub> O	<b>69.47</b>	<b>73.38</b>	17.72	18.61	17.43	23.59	16.82	5.71
CH <sub>4</sub>	$2 \times 10^{-7}$	$2 \times 10^{-8}$	$8 \times 10^{-11}$	0.74	0.66	0.39	0.71	0.17
CO <sub>2</sub>	19.39	18.66	<b>70.54</b>	3.98	5.08	5.51	4.66	9.91
CO	3.15	1.79	2.45	26.87	32.51	26.06	31.47	<b>67.00</b>
N <sub>2</sub>	0.82	0.57	0.01	0.37	0.33	0.29	1.31	1.85
NH <sub>3</sub>	$5 \times 10^{-6}$	$2 \times 10^{-6}$	$8 \times 10^{-9}$	0.01	0.01	$9 \times 10^{-5}$	0.02	$5 \times 10^{-5}$
H <sub>2</sub> S	2.47	2.32	0.56	0.59	0.61	0.74	0.53	0.18
SO <sub>2</sub>	0.08	0.35	7.41	$1 \times 10^{-8}$	$1 \times 10^{-8}$	$3 \times 10^{-8}$	$1 \times 10^{-8}$	$1 \times 10^{-8}$
Other <sup>a</sup>	0.25	0.17	1.02	0.33	0.35	0.41	0.64	0.29
Total	99.99	99.96	99.95	99.99	99.97	99.96	99.99	99.98

<sup>a</sup> Other includes gases of the rock-forming elements Cl, F, K, Na, P, and S. See text.

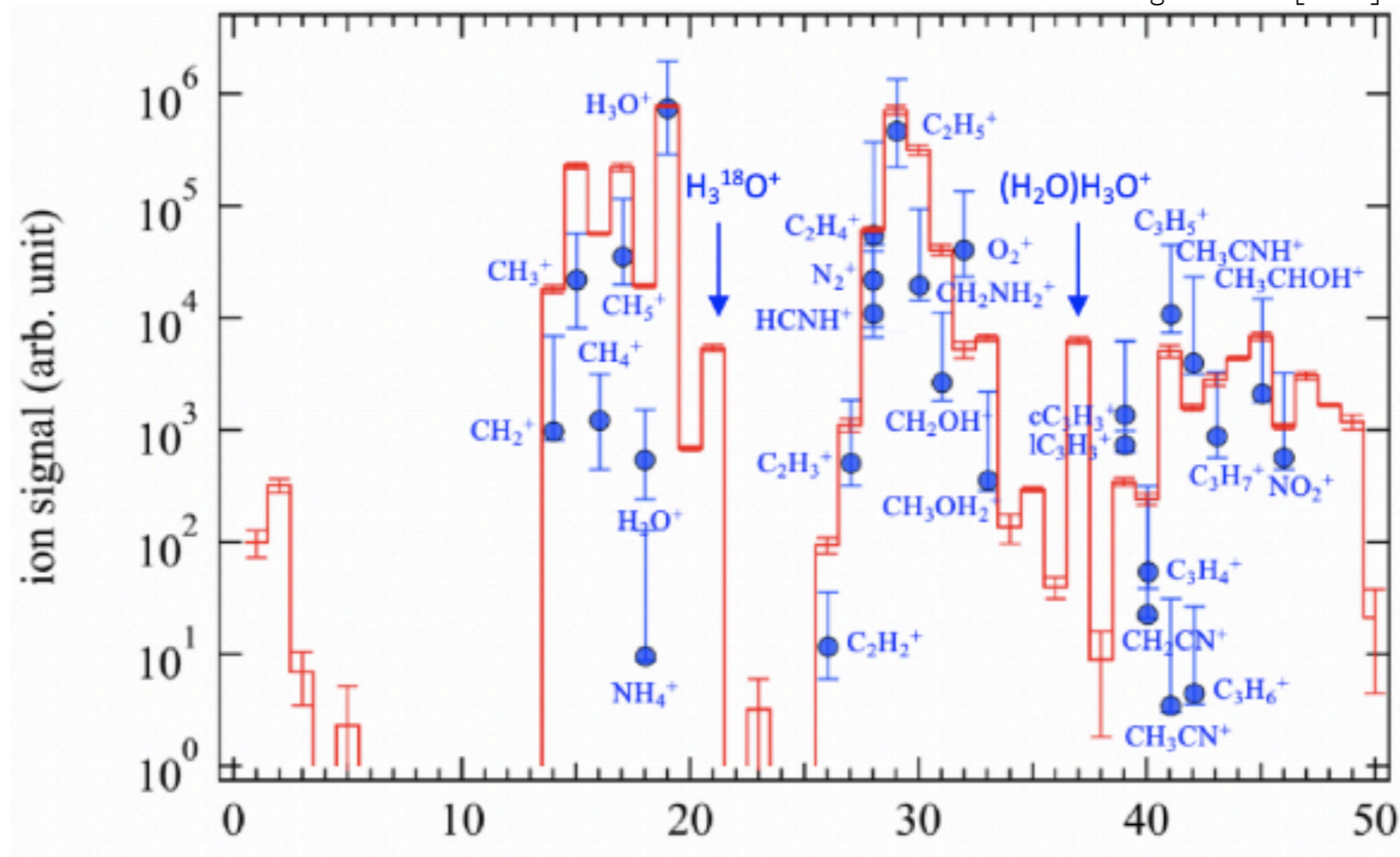
- Experimental method
  - Specific cases, along with JWST future detections
  - Parametric approach
    - E.g. : varying the C/O ratio, at a given N<sub>2</sub> concentration



# Ion chemistry: Titan in the Habitable Zone

## Efficient oxygen incorporation in $\text{N}_2$ -dominated atmospheres ( $\text{N}_2/\text{CH}_4 + \xi \text{H}_2\text{O}$ )

Bourgalais et al. [2021]

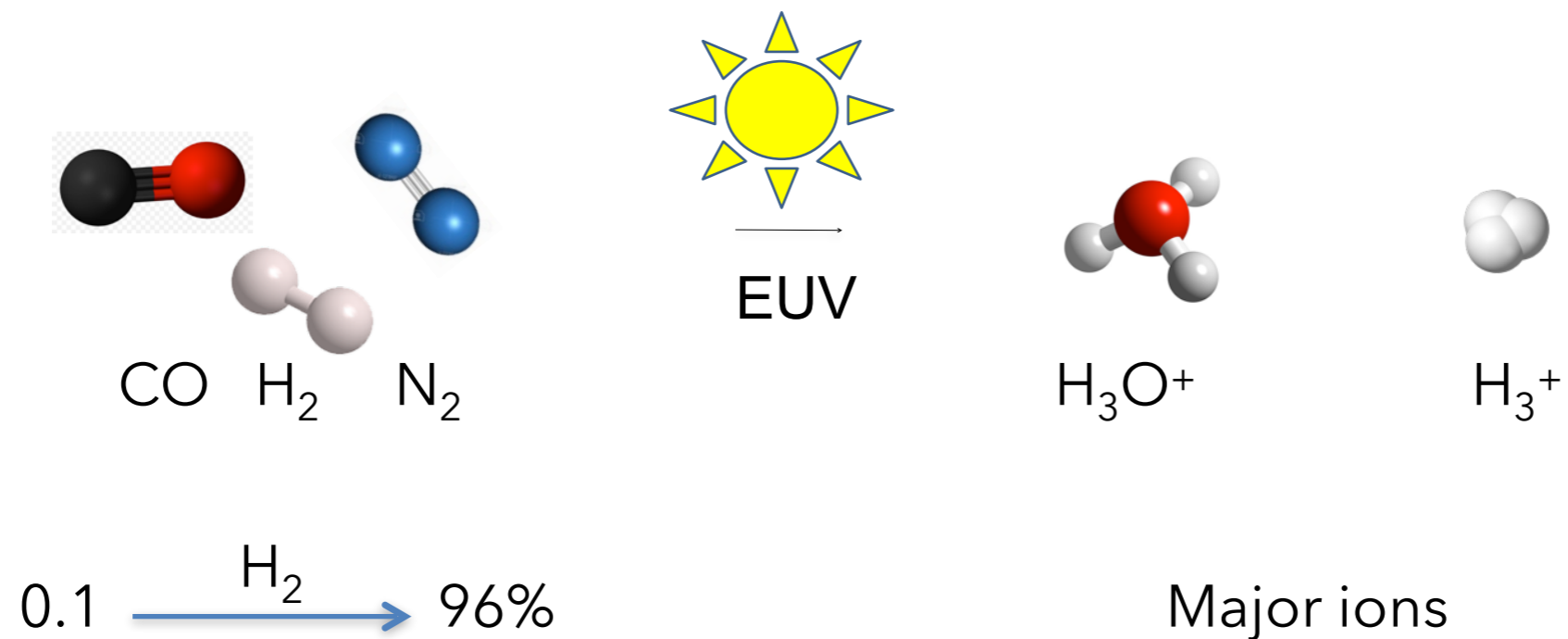




# Detectability of ions with JWST and ARIEL?

## Ionospheric signature above the cloud deck?

Bourgalais et al. [2020]

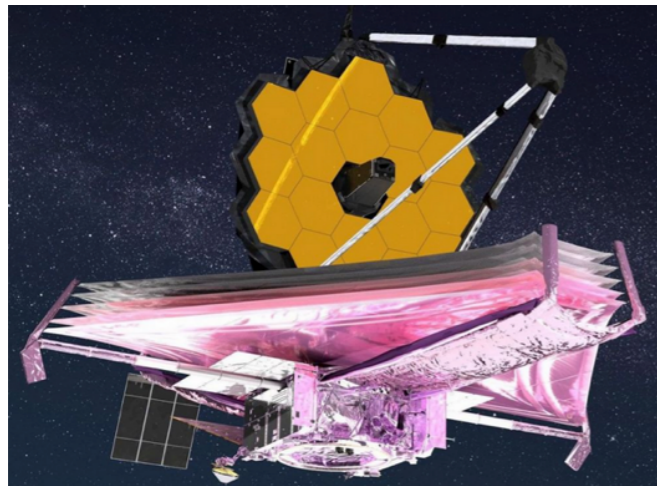






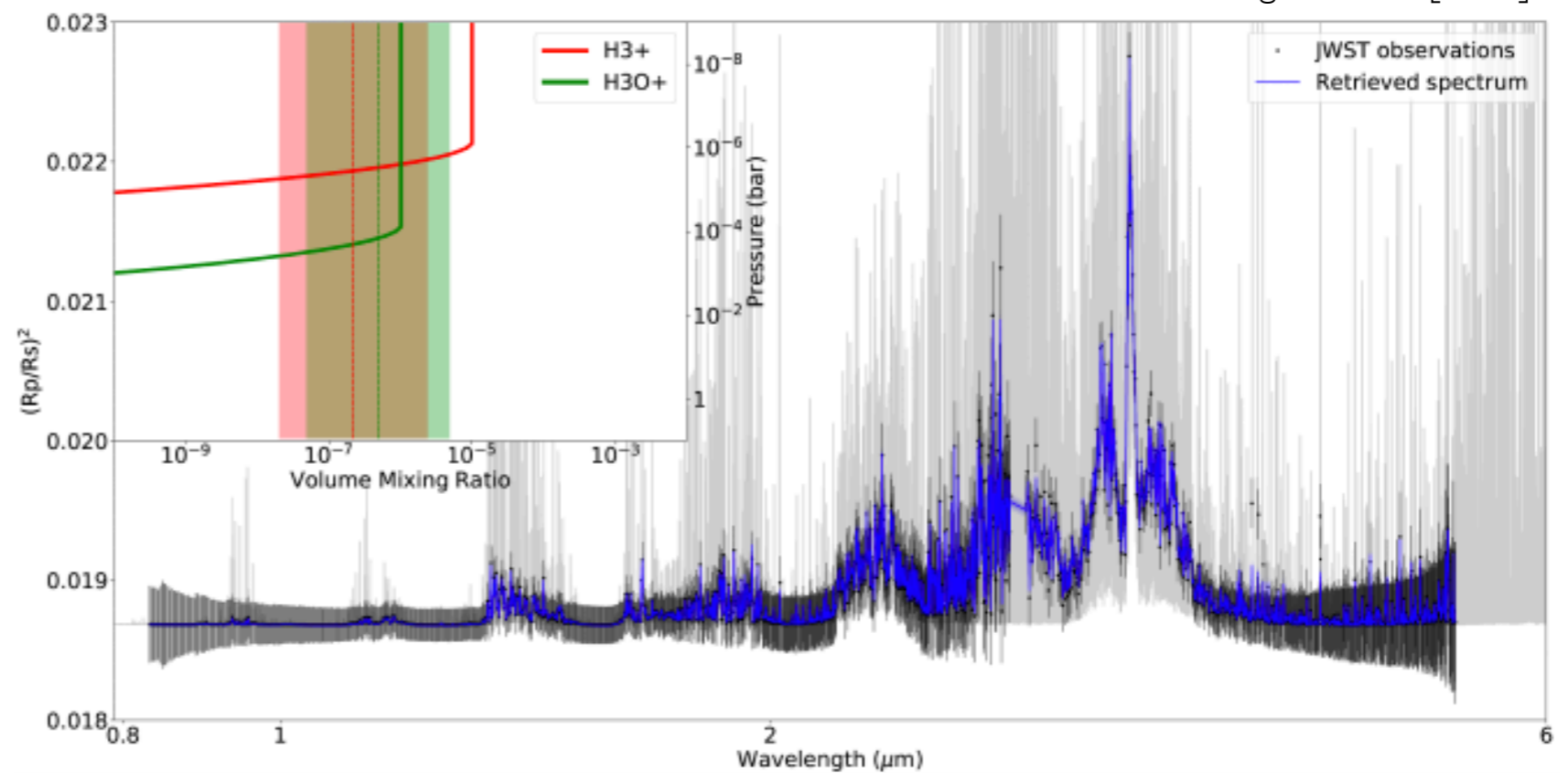
# Detectability of ions with JWST and ARIEL?

## Ionospheric signature above the cloud deck?



Nasa GSFC/CIL/Adriana Manrique Gutierrez

Bourgalais et al. [2020]



Retrieved spectra for simulations  
of a GJ1214b-like planet with  $\text{H}_3\text{O}^+$  and  $\text{H}_3^+$  ions.



# Detectability of ions with JWST and ARIEL?

## Ionospheric signature above the cloud deck?

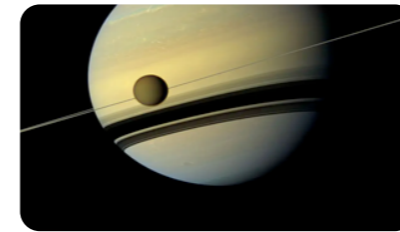
Bourgalais et al. [2020]

Detectable with ARIEL and JWST	$\text{H}_3\text{O}^+$	$\text{H}_3^+$
Volatile-Rich Super-Earths	✓	✓
Rocky Super-Earths	✓	✗

Possibility to distinguish  $\text{H}_2$ -rich and  $\text{H}_2$ -poor atmospheres  
from their main ions signatures



# Primitive Chemistry in upper planetary atmospheres



@NASA

Activate  $N_2$  chemistry

Chemical growth with ions

Detectable ion signatures