Photochemical Pathways: Monomers to Polymers

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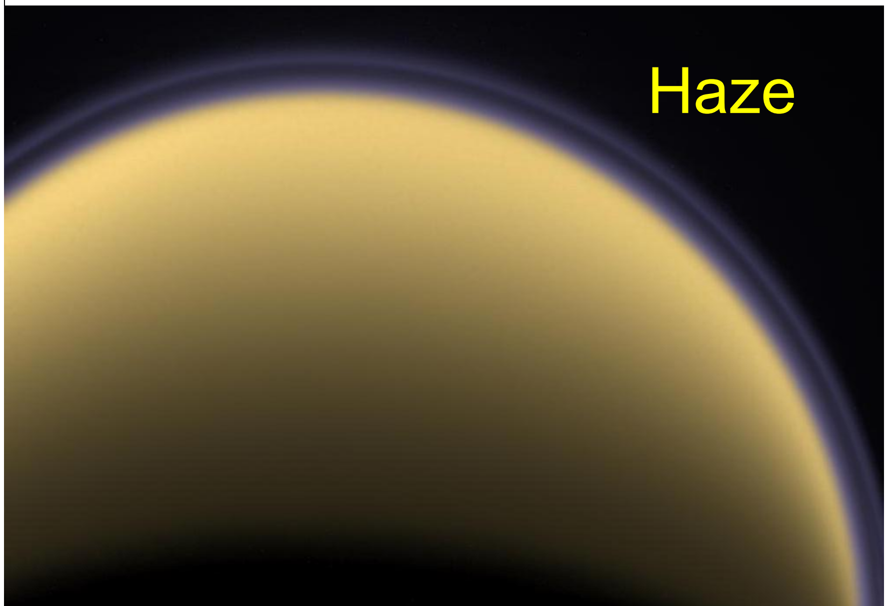
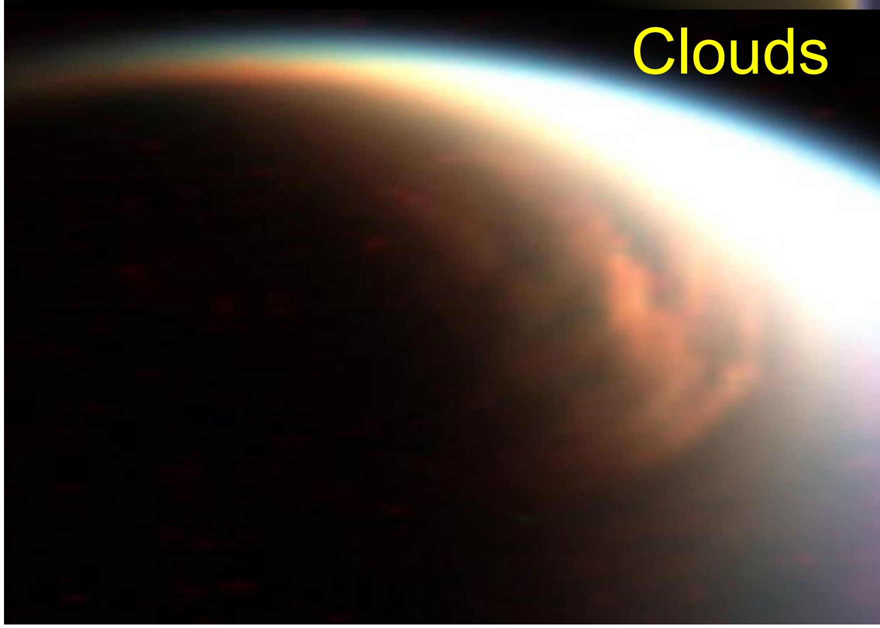
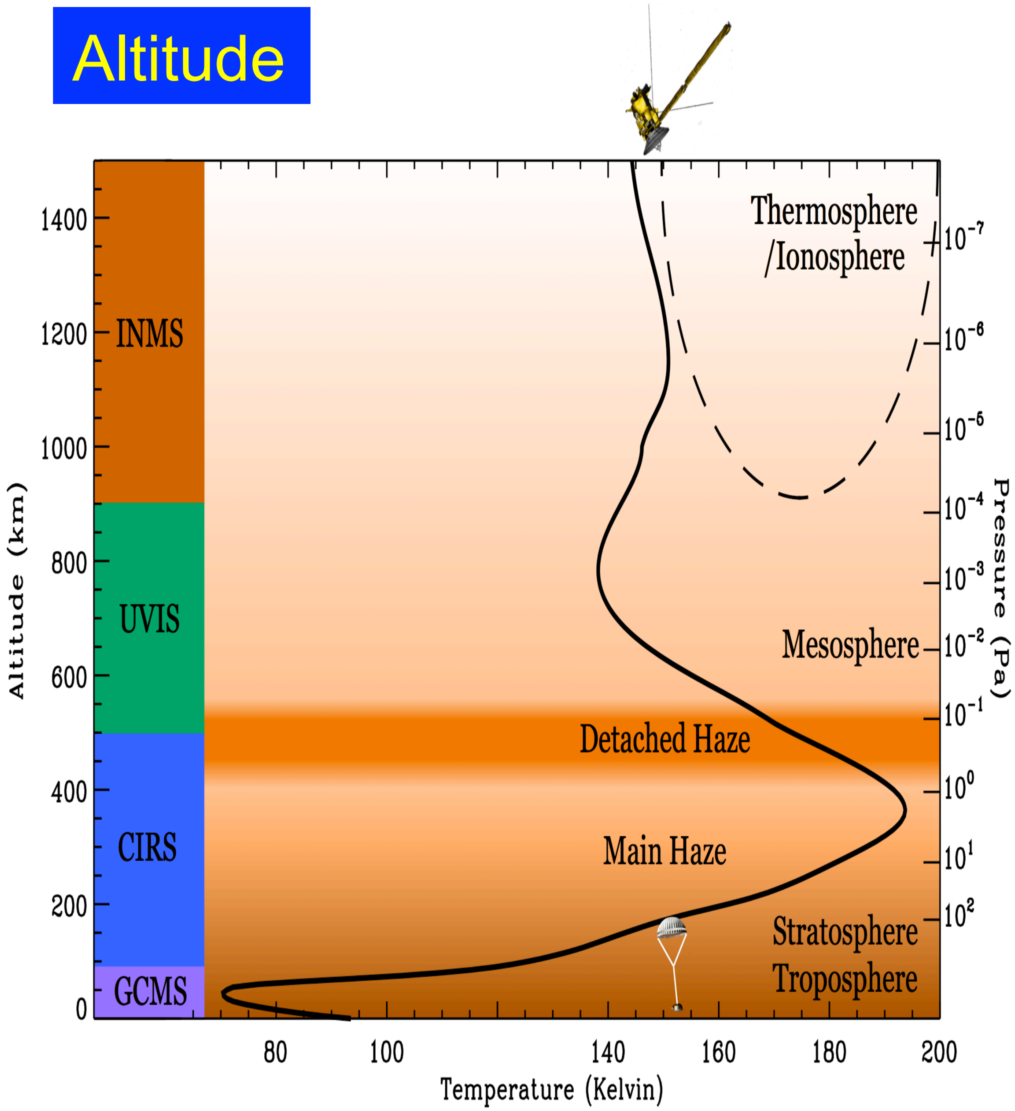
Titan - Atmosphere



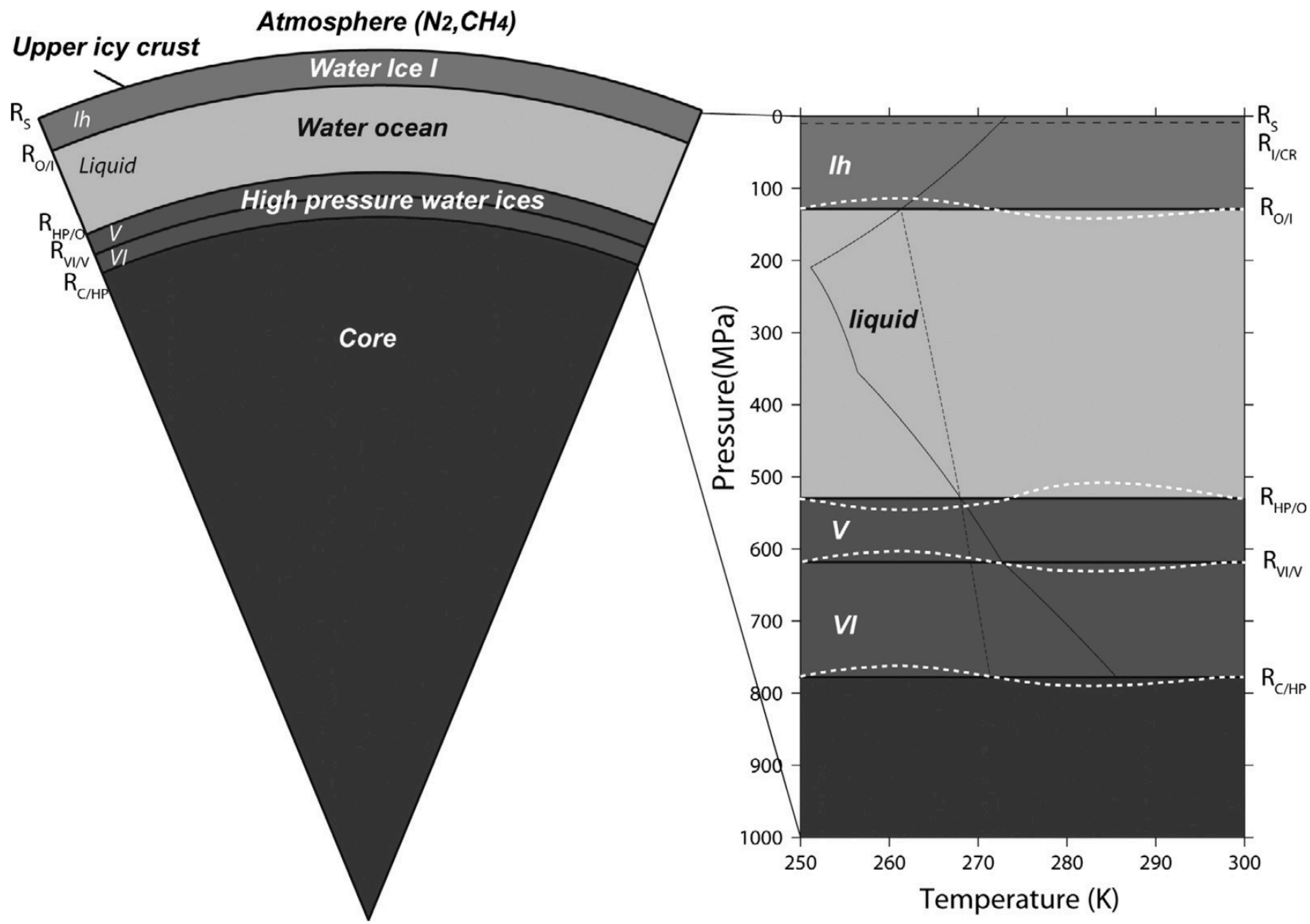


Altitude



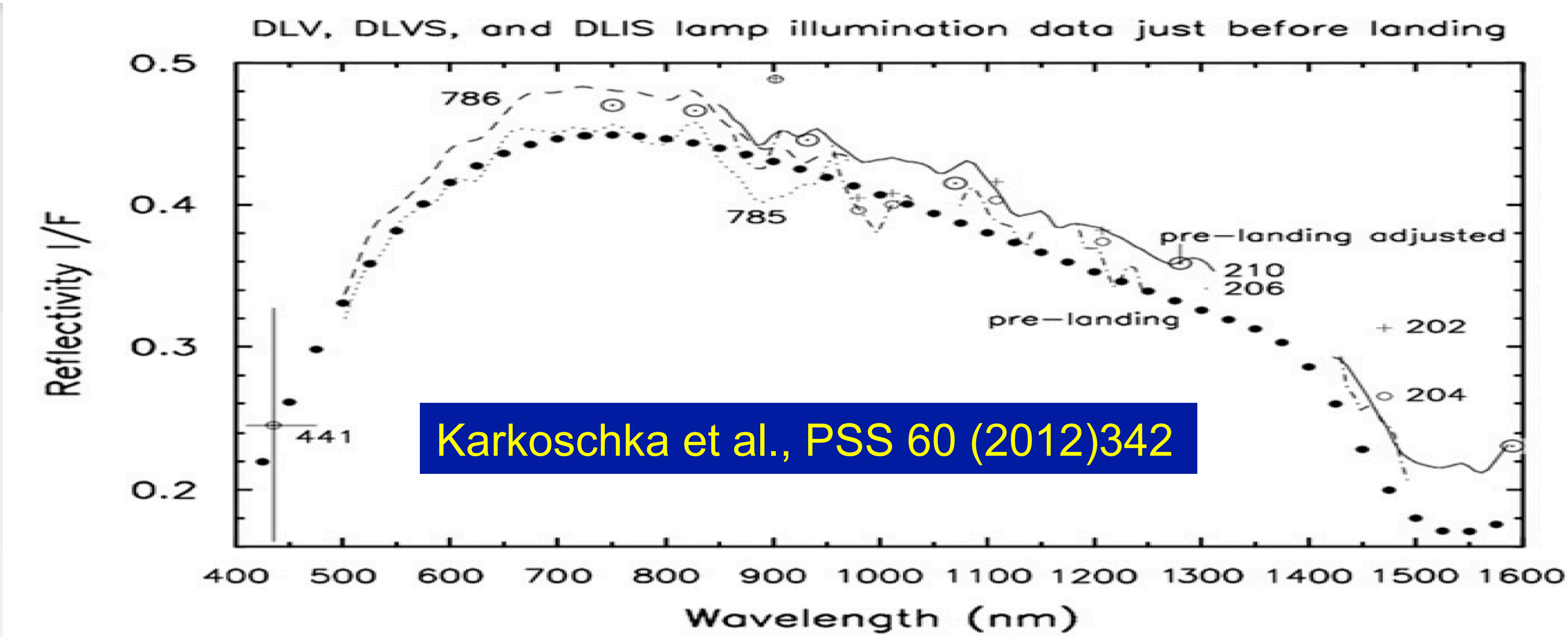
Titan's Interior Water Oceans

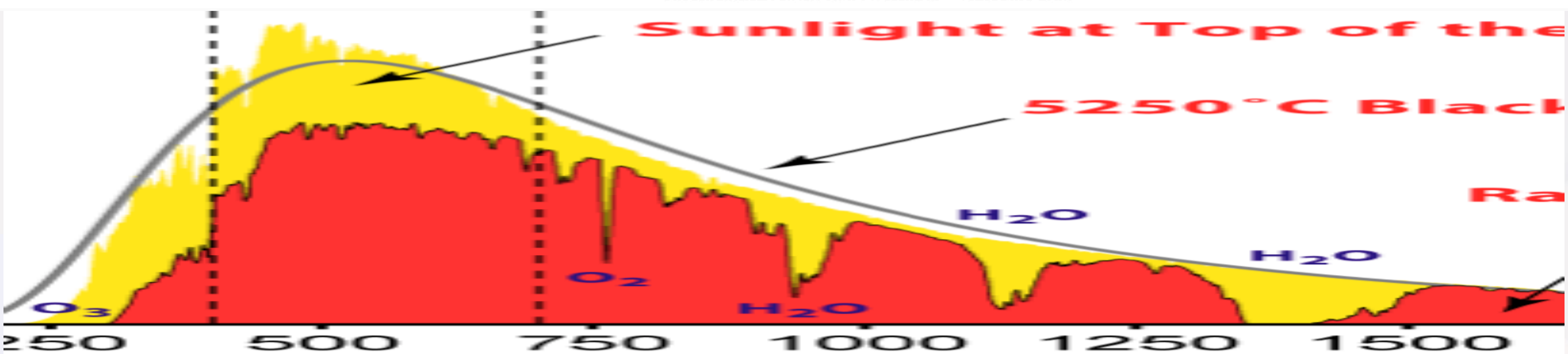
A. Lefevre et al. / Icarus 237 (2014) 16–28



Earth-Like Photochemistry on Titan?

Maximum Wavelength on Titan shifted to 700 nm





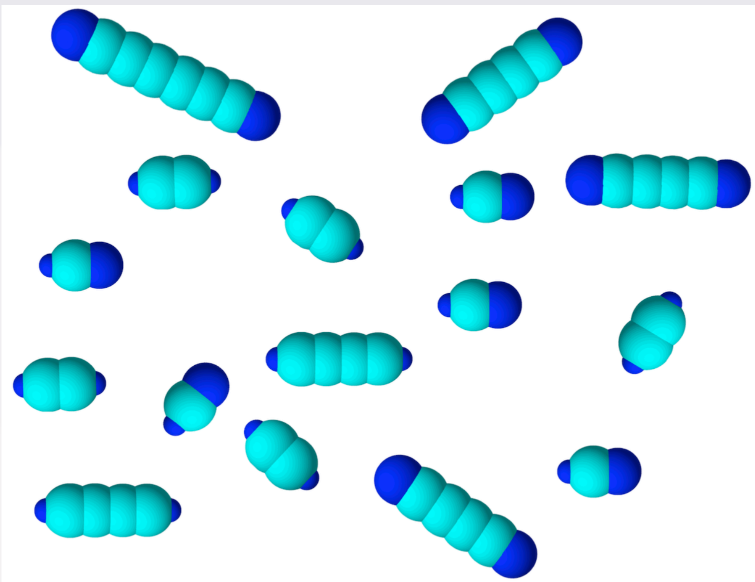
Habitability is the Potential, not the Proof for Life

Habitability is the Potential for an Environment to Harbor Life IF it were to exist there.

Let's first understand the Physical, Chemical, and Geological conditions of a Body before talking about its Habitability!

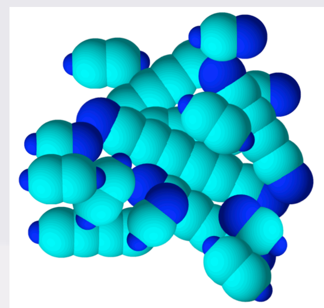
Is Titan's atmosphere photochemically more active than thought before?

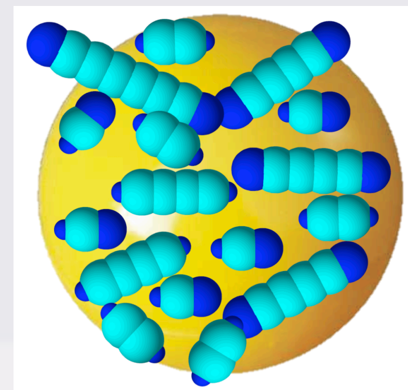
Condensation of small and medium molecules



Gas-phase

Condensed Ices





Condensed on Aerosols

Photochemistry in Lakes on the Surface

Gudipati et al., Nature Communications 4(2013)1648

Dipole Moment

The Molecules of Titan

Couturier-Tamburelli, Piétri, Gudipati; A&A 578, A111 (2015)

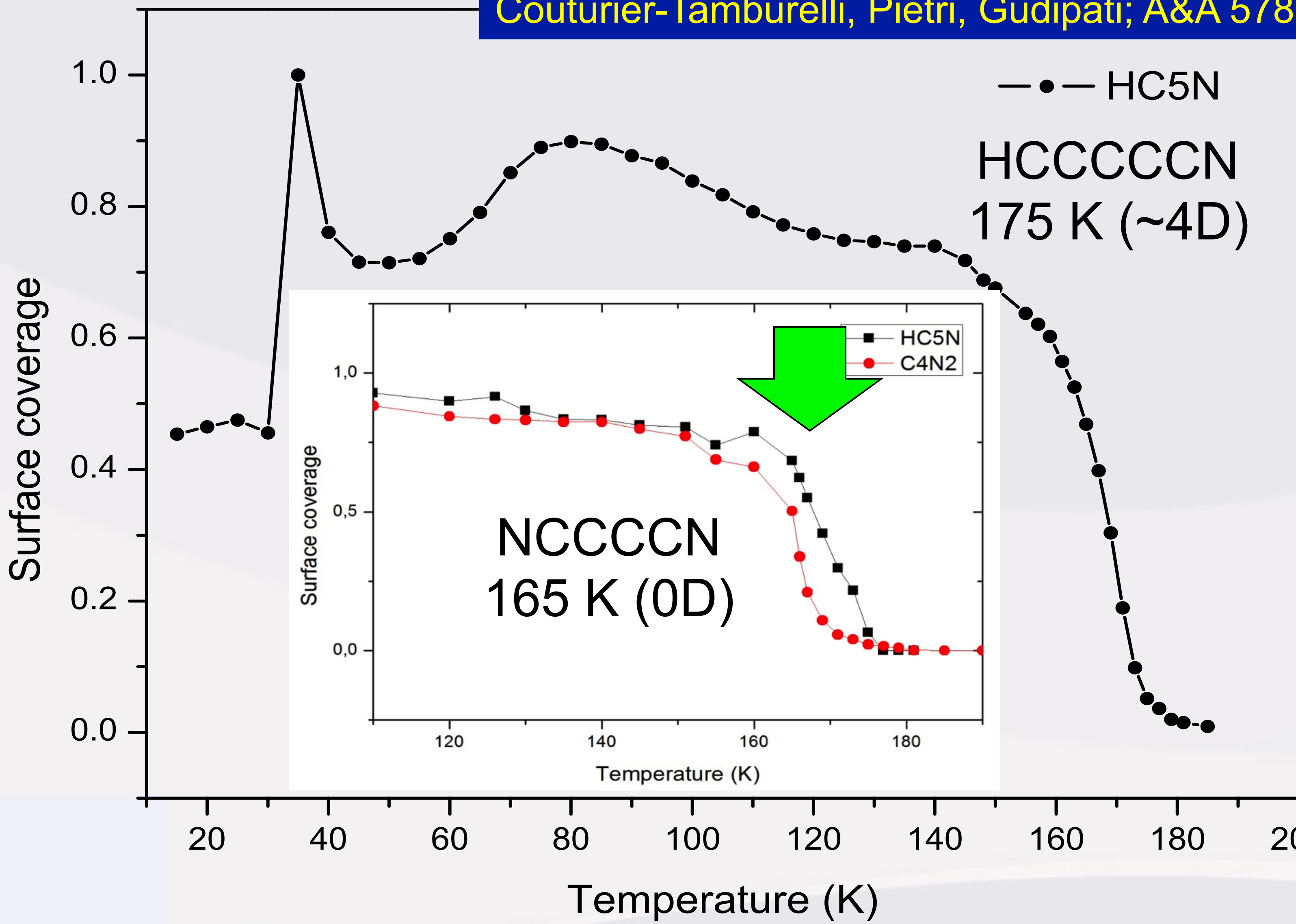
Molecule	$S_0 - S_1$ (first excited singlet state) threshold	$S_0 - T_1$ (first excited triplet state) threshold	S_0 (ground -state) dipole moment
	Wavelength (nm)	Wavelength (nm)	(Debye)
Acetylene (C_2H_2)	237[a], 231[*]	346[a], 295[*]	0
Diacetylene (C_4H_2)	286[b], 301[c], 298[*]	387[e], 385[*]	0
Triacetylene (C_6H_2)	355[c], 348[*],	450[*]	0
Hydrogen Cyanide (HCN)	~155[f]	~225[f]	3.02[d], 2.7[*]
Cyanoacetylene (HC_3N)	260[a], 267[b], 269[*]	341[*]	3.73[d], 3.33[*]
Cyanodiacetylene (HC_5N)	353[b], 329[*]	421[*]	4.33[g], 3.9[*]
Cyanotriacetylene (HC_7N)	371[*]	477[*]	4.3[*]
Cyanogen (C_2N_2)	300[b], 355[c], 272[*]	350[*]	0
Dicyanoacetylene (C_4N_2)	280[b], 350[*]	390[*]	0
Dicyanodiacetylene (C_6N_2)	407[*]	551[*]	0

Dipole Moment

Accessible with solar UV-VIS

Polar Molecules Ice and Clouds first in Titan's Atmosphere

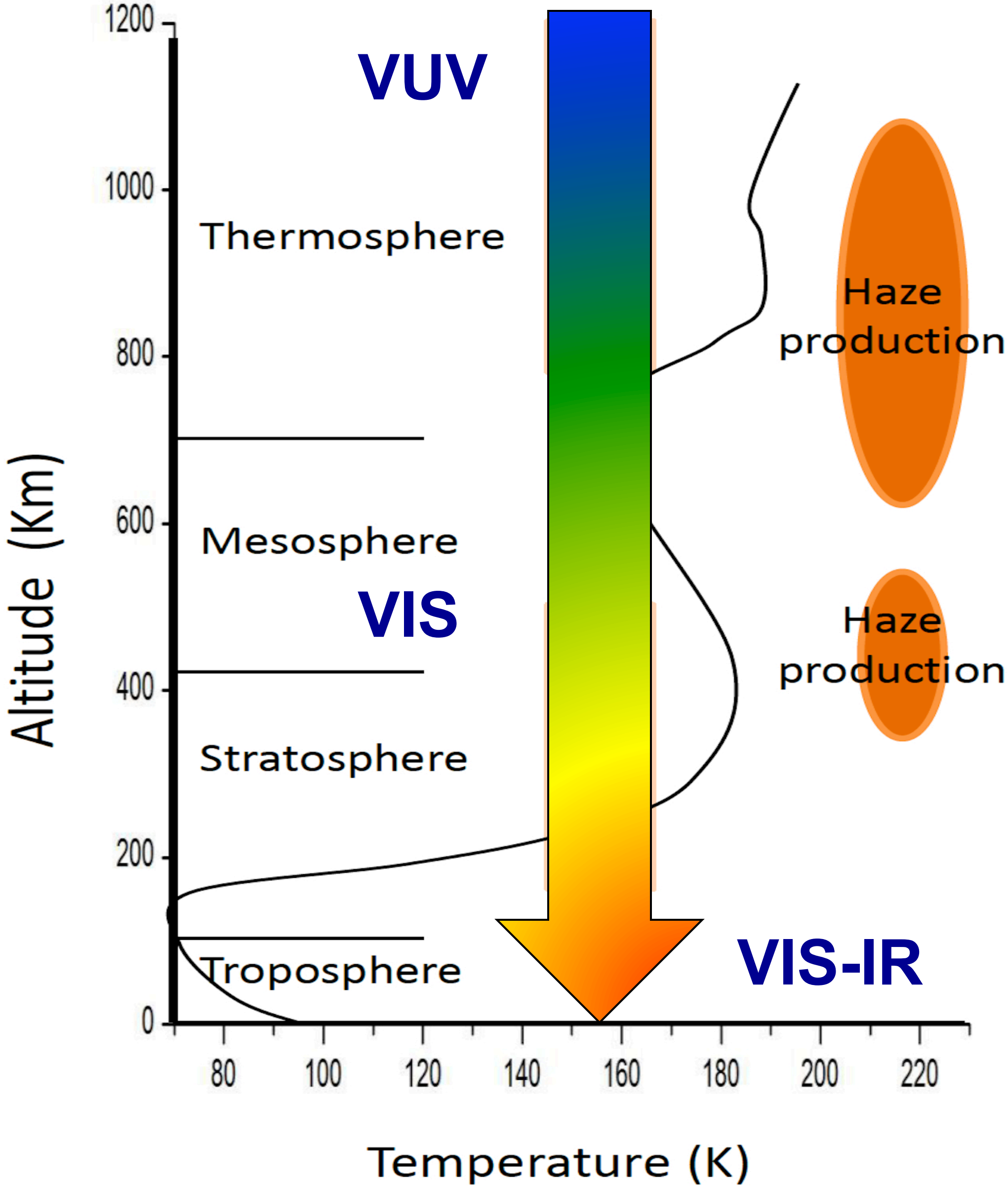
Couturier-Tamburelli, Piétri, Gudipati; A&A 578, A111 (2015)

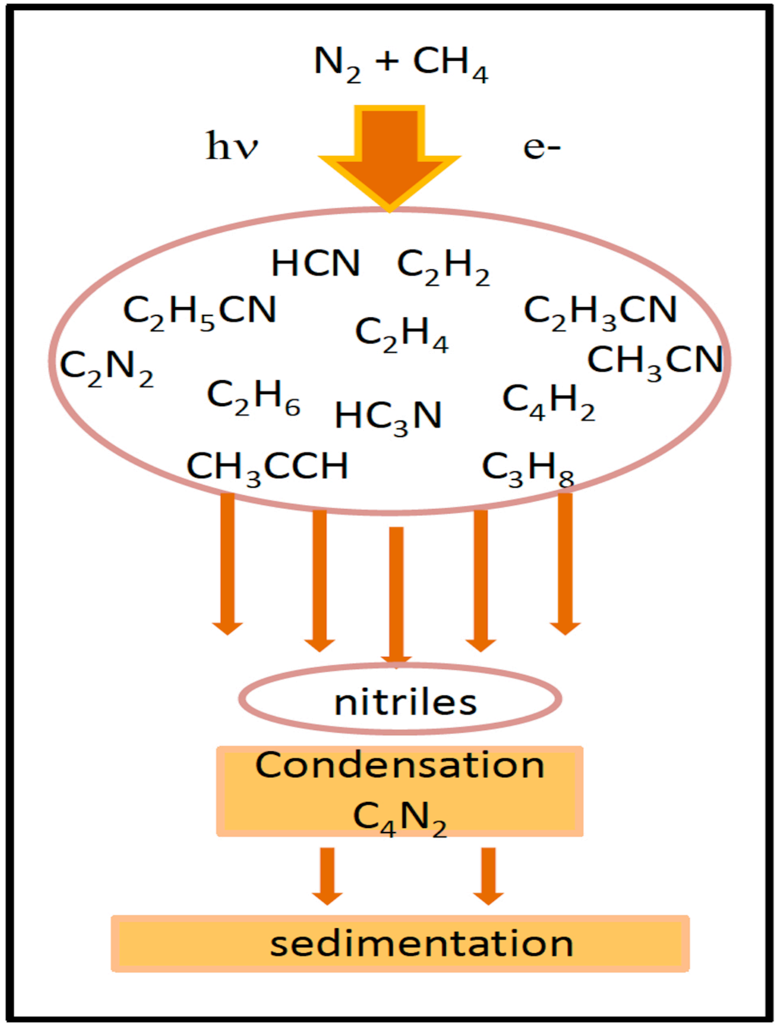


Similar molecular weight

Titan – Altitude vs. Photochemistry

Couturier-Tamburelli, Piétri, Gudipati; A&A 578, A111 (2015)





Production of Organic Solid Through Photochemistry

Titan's Condensed Aerosol Chemistry

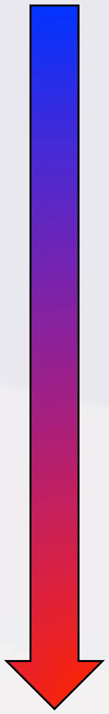
Couturier-Tamburelli, Piétri, Gudipati; A&A 578, A111 (2015)

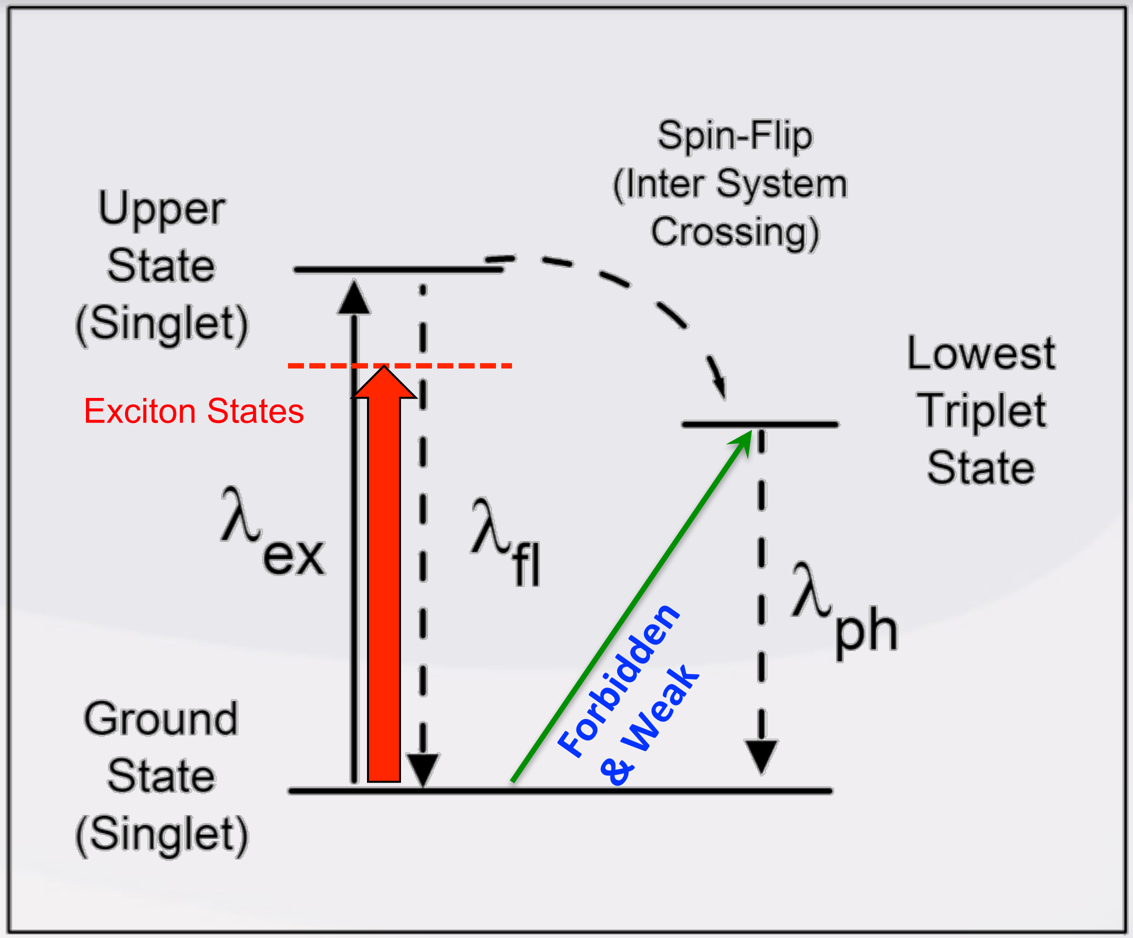
Theoretical Background

In the Condensed Phase

- Weak transitions become stronger
- Exciton interactions lead to new electronic states with lower excitation energy (longer wavelength)

Increasing Wavelength

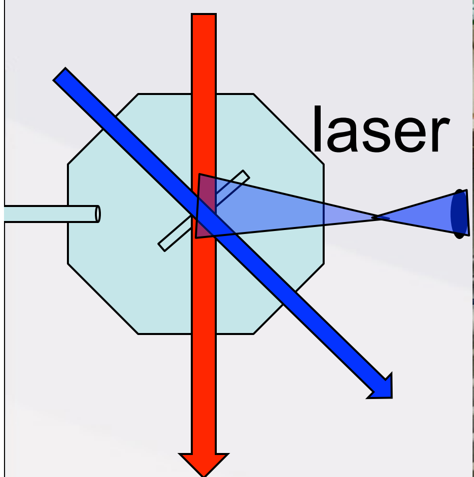


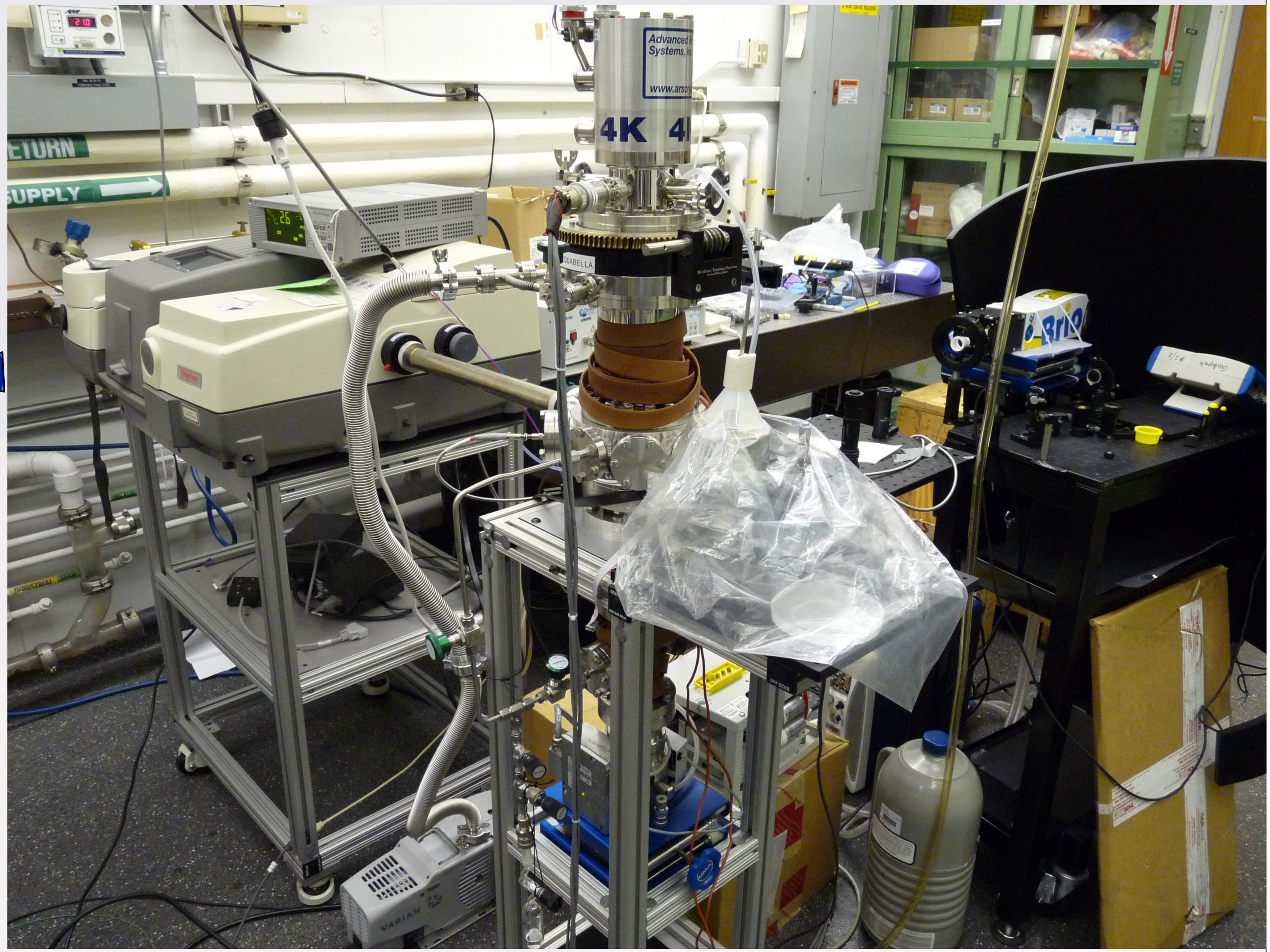


Condensed-phase photochemistry can occur at longer wavelengths than in the gas-phase

The Titan Organic Aerosol Synthesis/Spectroscopy and chemisTry (TOAST) Lab @JPL

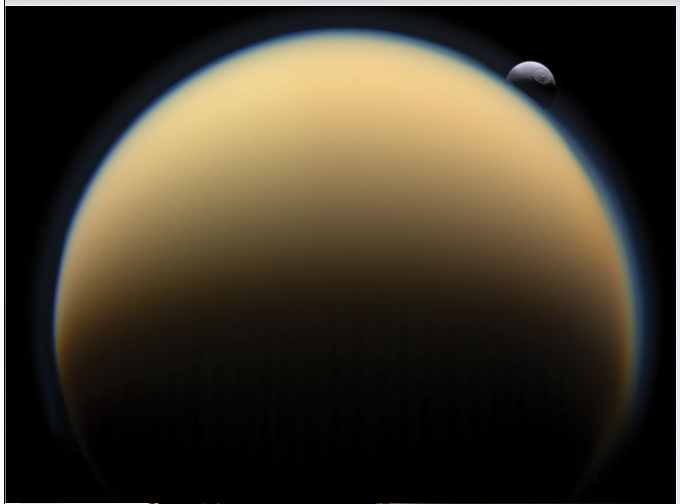
Spectroscopy and Photochemistry Setup

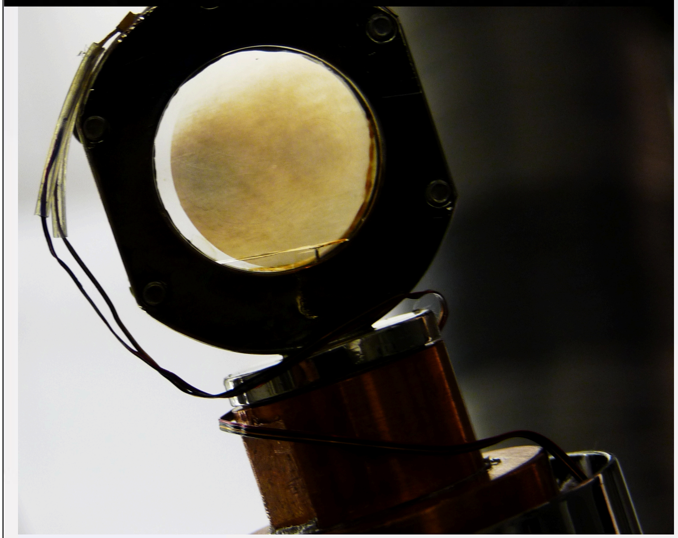




Longer Wavelength Photopolymerization

Gudipati et al., Nature Communications 4(2013)1648

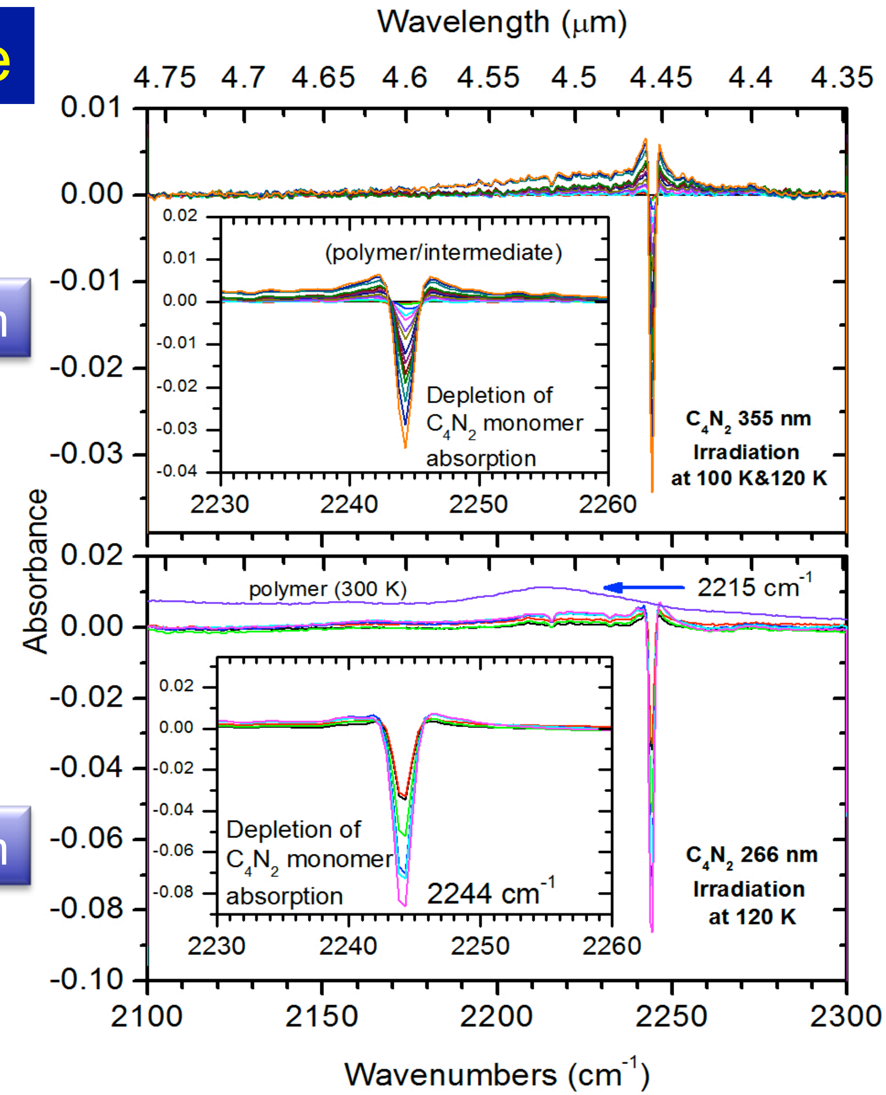




C_4N_2 Ice

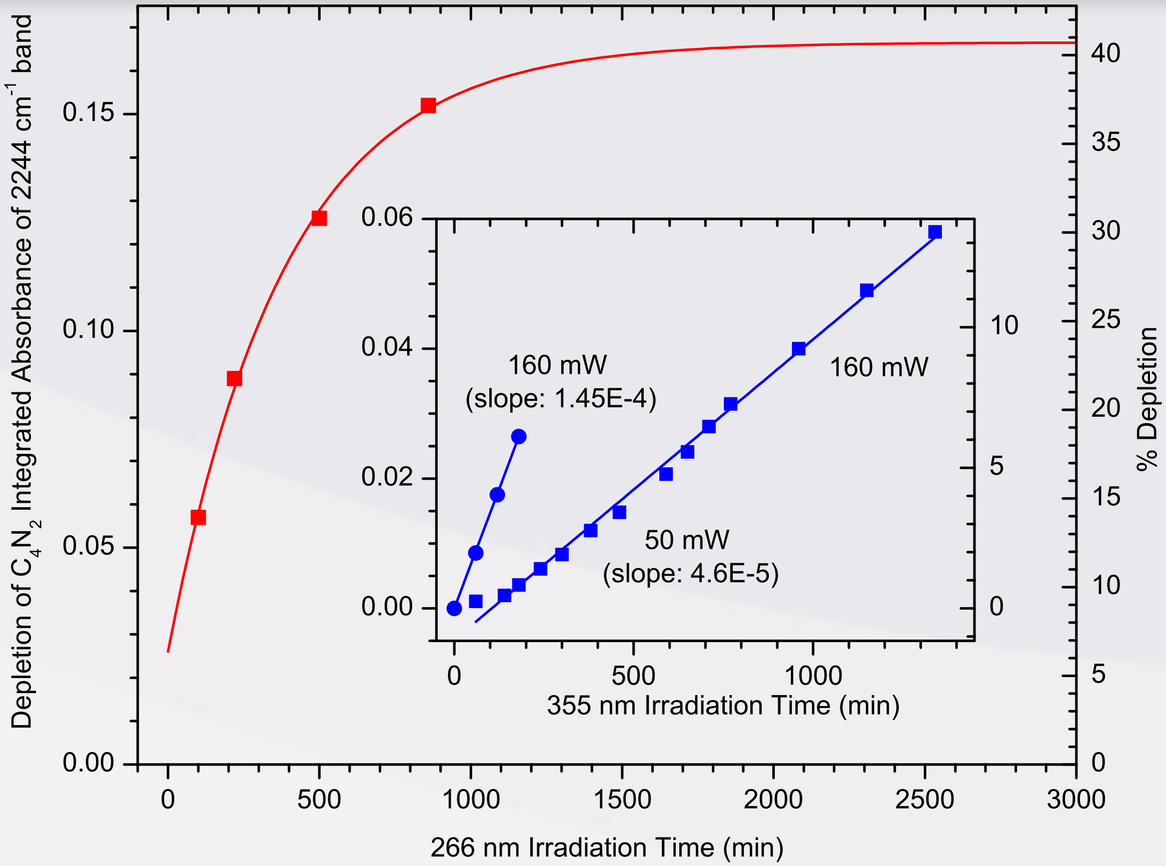
355 nm

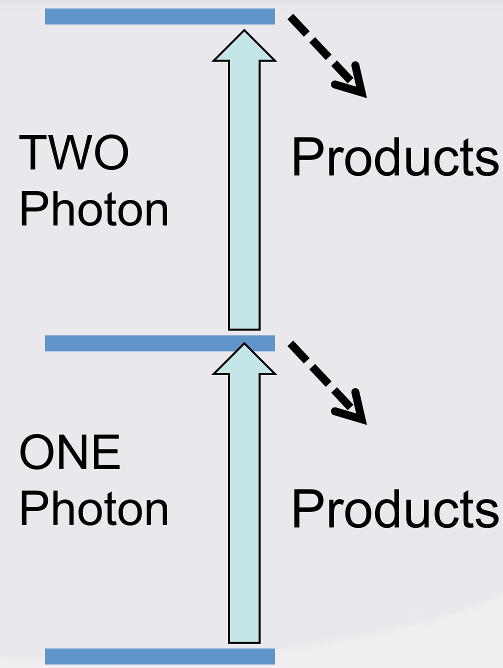
266 nm



Dicyanoacetylene (C_4N_2) – detected in Titan's Atmosphere by Anderson & Samuelson

Photochemistry: A one-photon process (Titan's Conditions)





One Photon Yields = k1*(laser flux)
Two Photon Yields = k2*(laser flux)^2

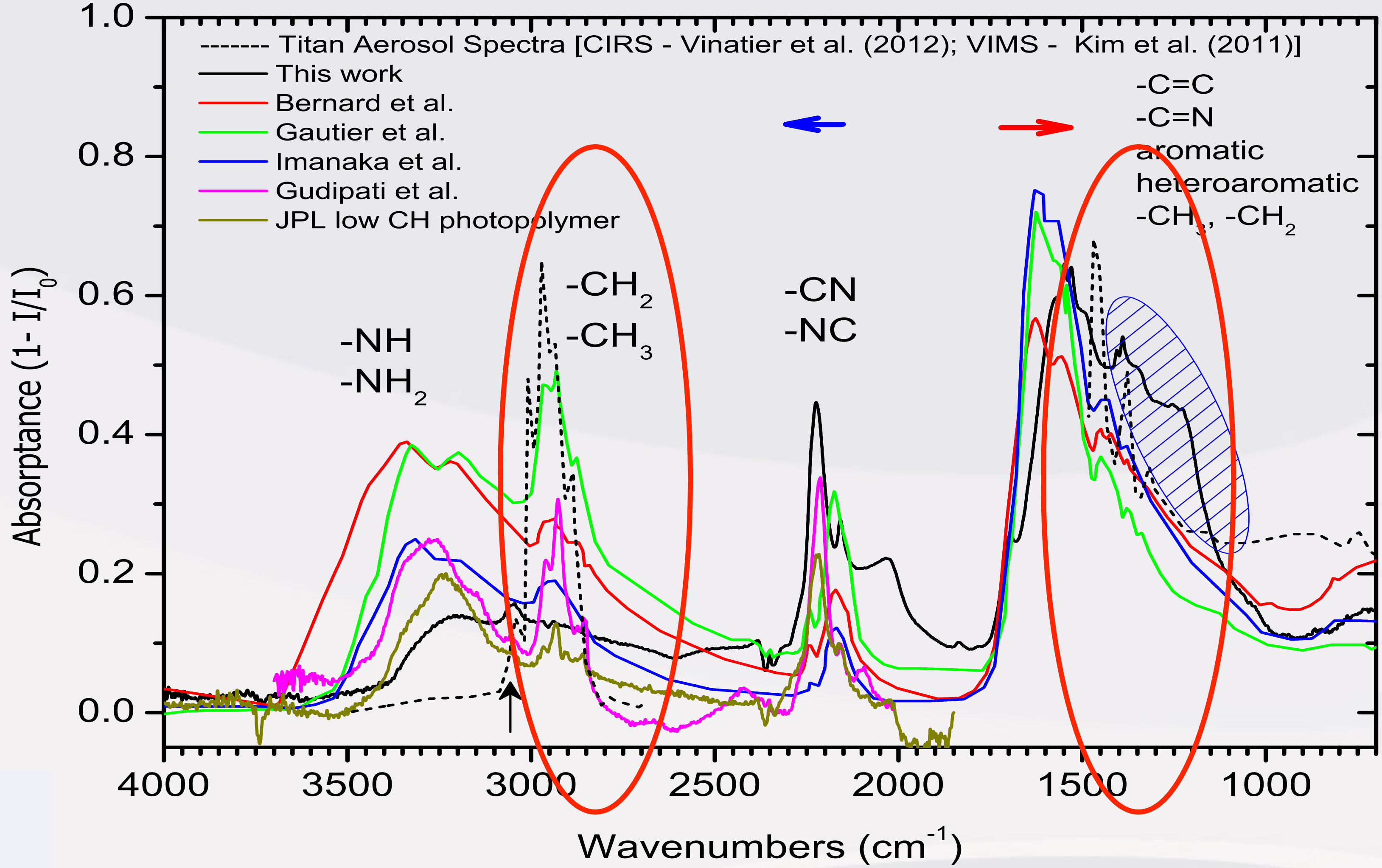
160/50 = 3.2 (1-photon)

(160/50)^2 = 10.24 (2-photons)

1.45E-4/4.6E-5 = 3.15 (observed)

Comparison with Cassini CIRS/VIMS Data

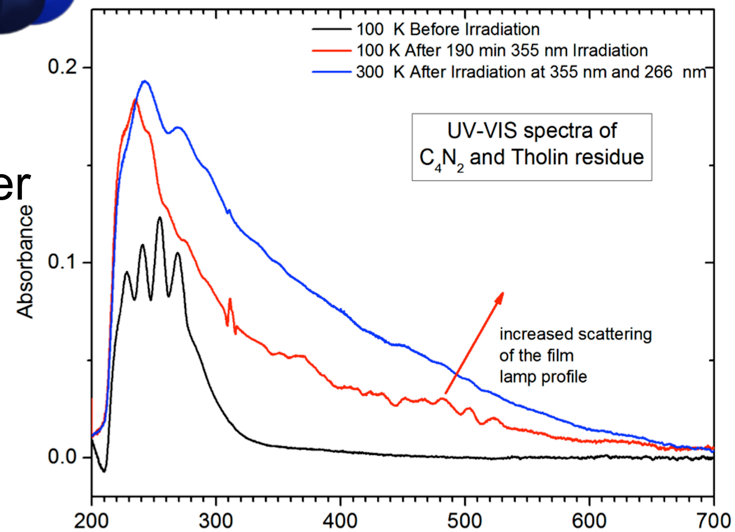
VIMS: Ratio of NH/CH at 2.8 to 3.5 microns (3500 – 2800 cm^{-1}) is very small indicating depleted NH in the condensates of Titan's stratosphere.
Could this be due to dominant hydrocarbon ices compared to aerosols or upper atmosphere photochemistry?

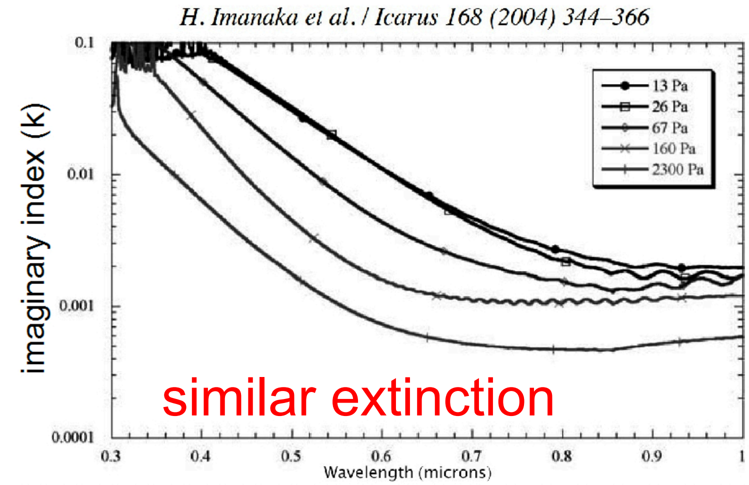


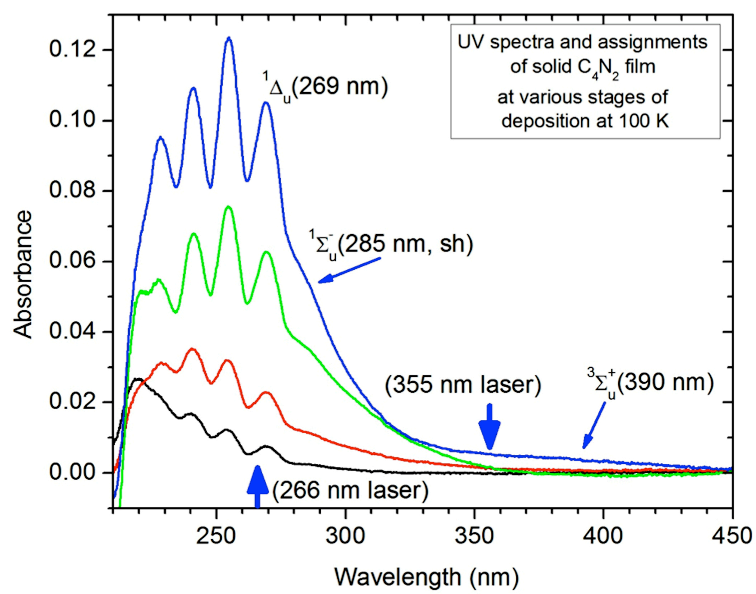
Coutier-Tamburelli, Gudipati et al., Icarus 234 (2014) 81–90

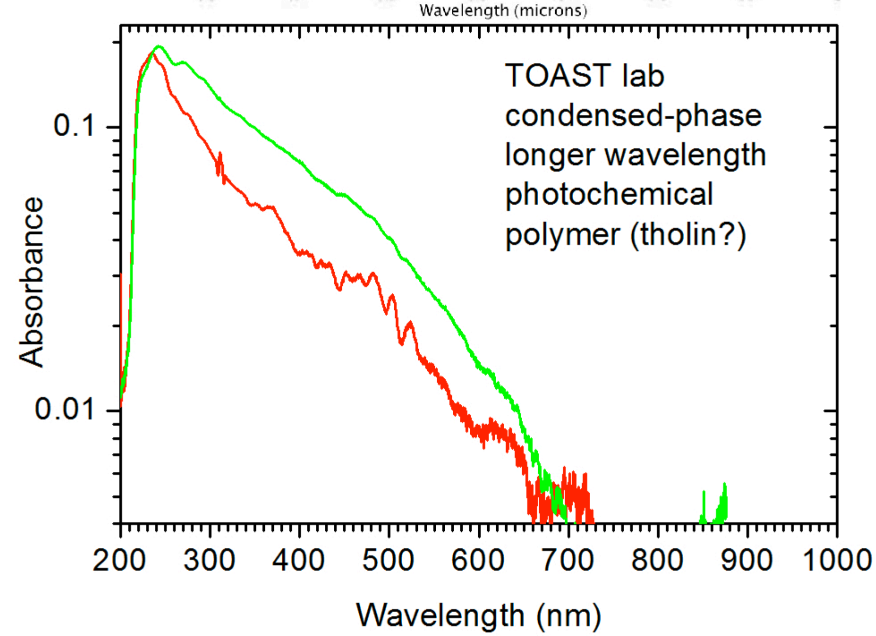
Expected UV-VIS Absorption of Ice, Haze, and Surface on Titan

C_4N_2
Monomer









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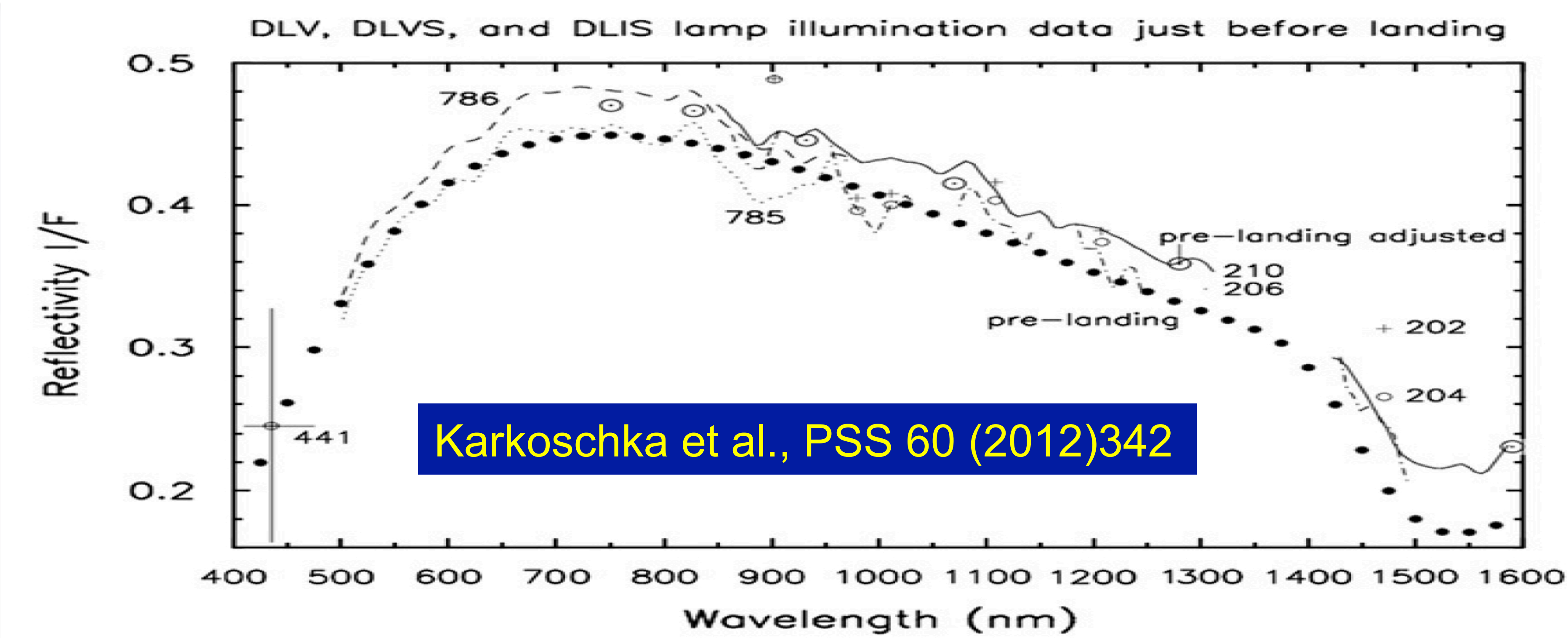
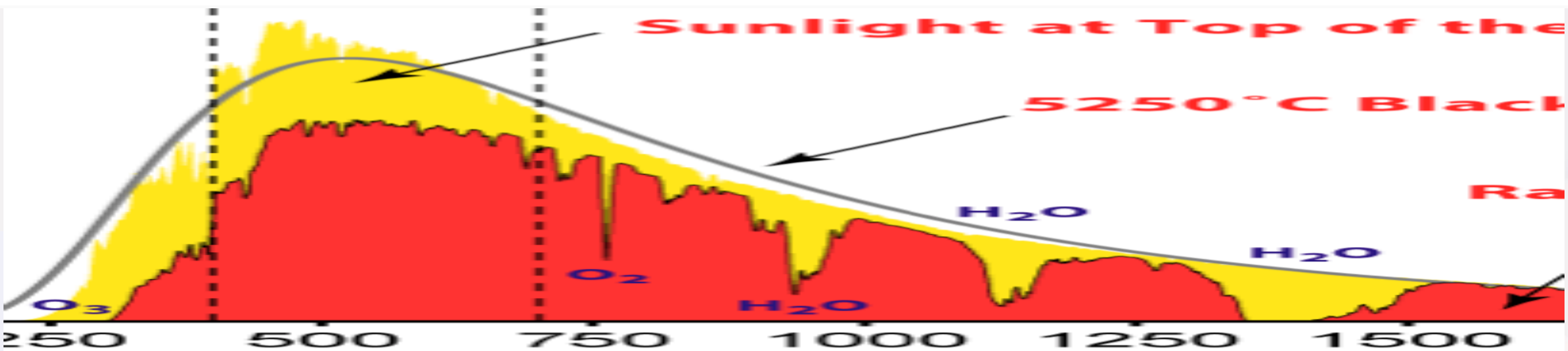


Karkoschka et al., PSS 60 (2012)342



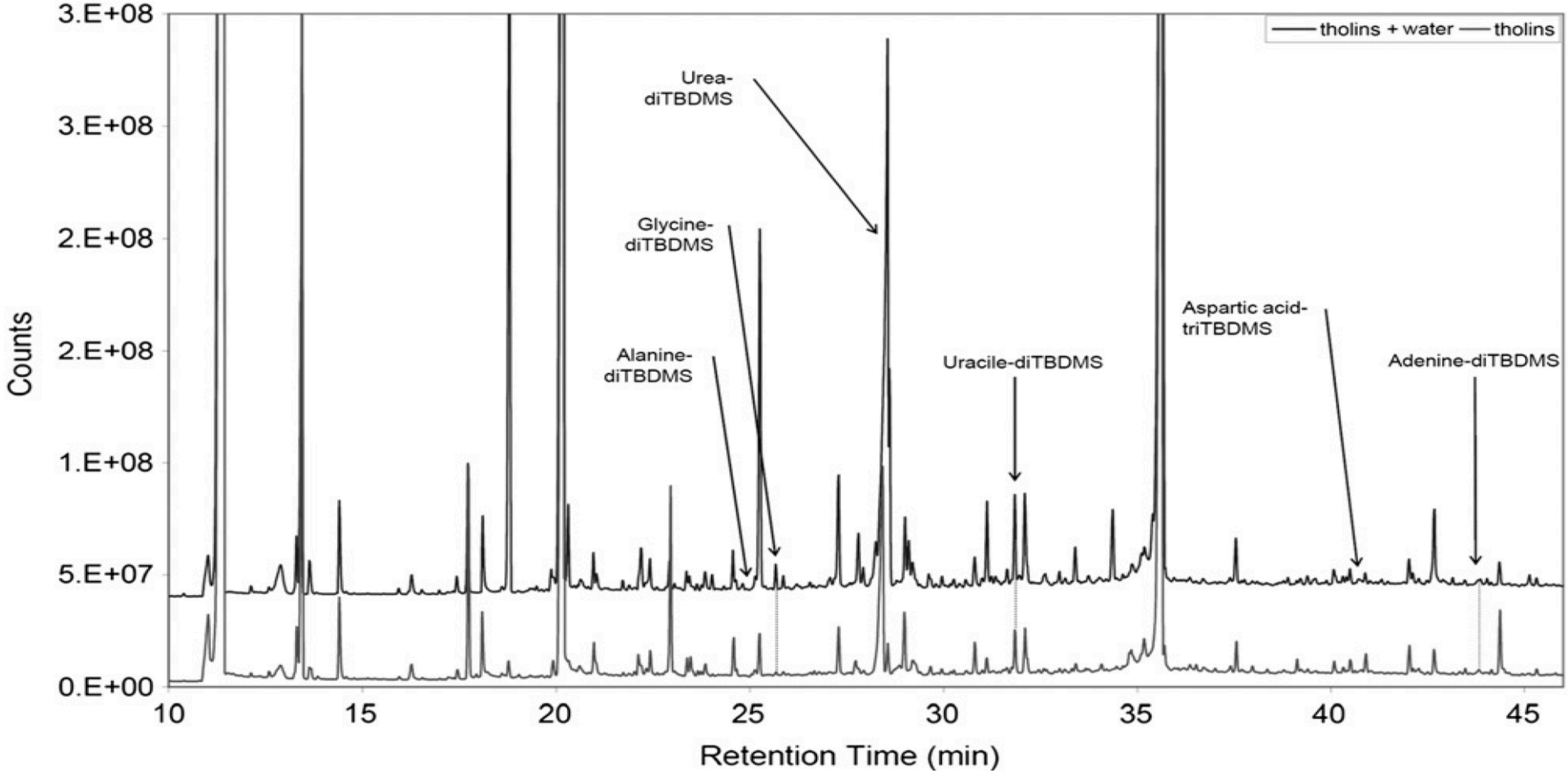
Organic Polymer (Nitrogen containing) When meets with H_2O Gives Biomolecules (Essential for Life?)

Production of Prebiotic Molecules from Analogs of Titan's Complex Organics

Titan's atmosphere is depleted of oxygen (and water)
Surface may have water-ice in contact with organic liquid and solid
Subsurface is expected to have large reservoirs of water

O. Poch et al. / Planetary and Space Science 61 (2012) 114–123

Formation of Amino Acids and Nucleobases



Production of Prebiotic Molecules from Analogs of Titan's Complex Organics

Formation of Nucleobases

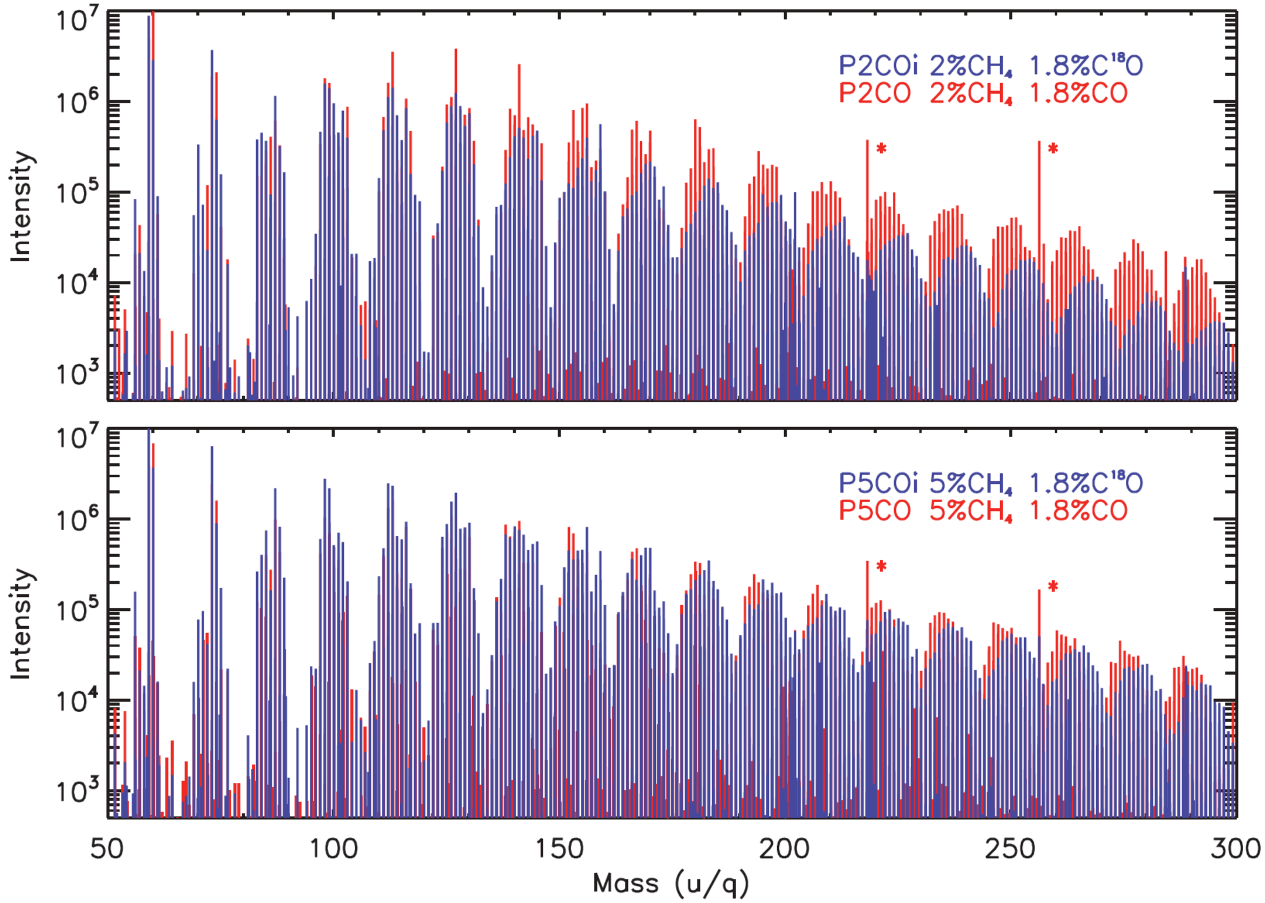


FIG. 1. Orbitrap positive ion mass spectra of P2CO (top, red), P2COi (top, blue), P5CO (bottom, red), and P5COi (bottom, blue) from 50 to 300 u/q. Asterisks indicate known contaminants. Plotted spectra are an average of 200 spectra with a mass resolution of 10^5. The observed mass shift in the isotopic samples results from the incorporation of ^{18}O, which has been confirmed through assignment of the peaks.

Hörst et al., ASTROBIOLOGY 12(2012)809

Production of Prebiotic Molecules from Analogs of Titan's Complex Organics

Formation of Amino Acids and Nucleobases

Hörst et al., ASTROBIOLOGY 12(2012)809

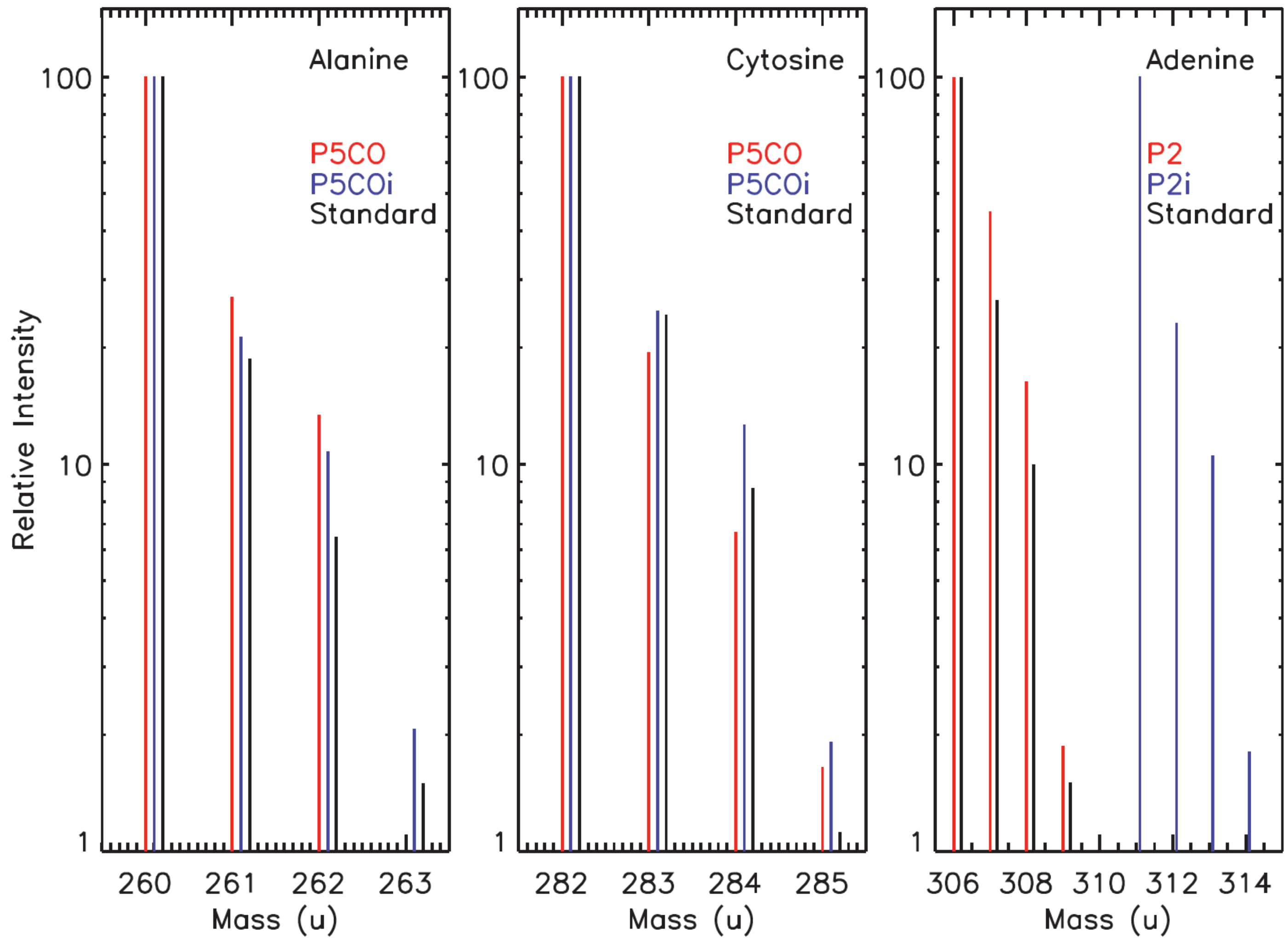
Table 1. Summary of Observed Prebiotic Molecules

				P2CO	*P2COi*	*P5CO*	*P5COi*
			$\%N_2$	96.2	96.2	93.2	93.2
			$\%CH_4$	2	2	5	5
			%CO	1.8	1.8 $C^{18}O$	1.8	1.8 $C^{18}O$
Name	*Mass*	*Formula*	*Fig.*				
Nucleotide base							
cytosine	111	$C_4H_5N_3O$	2	OT	OT	OT/GC-MS	OT
uracil	112	$C_4H_4N_2O_2$		OT	OT	OT/GC-MS	OT
thymine	126	$C_5H_6N_2O_2$		OT	OT	OT/GC-MS	OT
adenine[a]	135	$C_5H_5N_5$	2	OT		OT/GC-MS	
guanine	151	$C_5H_5N_5O$		OT		OT/GC-MS	
Biological amino acid							
glycine	75	$C_2H_5NO_2$		OT		OT/GC-MS	
alanine	89	$C_3H_7NO_2$		OT		OT/GC-MS	
serine	105	$C_3H_7NO_3$		OT		OT	
proline	115	$C_5H_9NO_2$		OT		OT	
valine	117	$C_5H_{11}NO_2$		OT		OT	
threonine	119	$C_4H_9NO_3$		OT			
isoleucine/ leucine[b]	131	$C_6H_{13}NO_2$		OT		OT	
asparagine	132	$C_4H_8N_2O_3$		OT		OT	
glutamine	146	$C_5H_{10}N_2O_3$		OT		OT	
lysine	146	$C_6H_{14}N_2O_2$		OT		OT	
histidine	155	$C_6H_9N_3O_2$	2	OT		OT	OT
phenylalanine	165	$C_9H_{11}NO_2$		OT		OT	
arginine	174	$C_6H_{14}N_4O_2$		OT		OT	

Production of Prebiotic Molecules from Analogs of Titan's Complex Organics

Formation of Amino Acids and Nucleobases

Hörst et al., ASTROBIOLOGY 12 (2012)809



Production of Prebiotic Molecules from Analogs of Titan's Complex Organics

Formation of Long-Chain Primary Amines

M.L. Cable et al. / Earth and Planetary Science Letters 403 (2014) 99–107 103

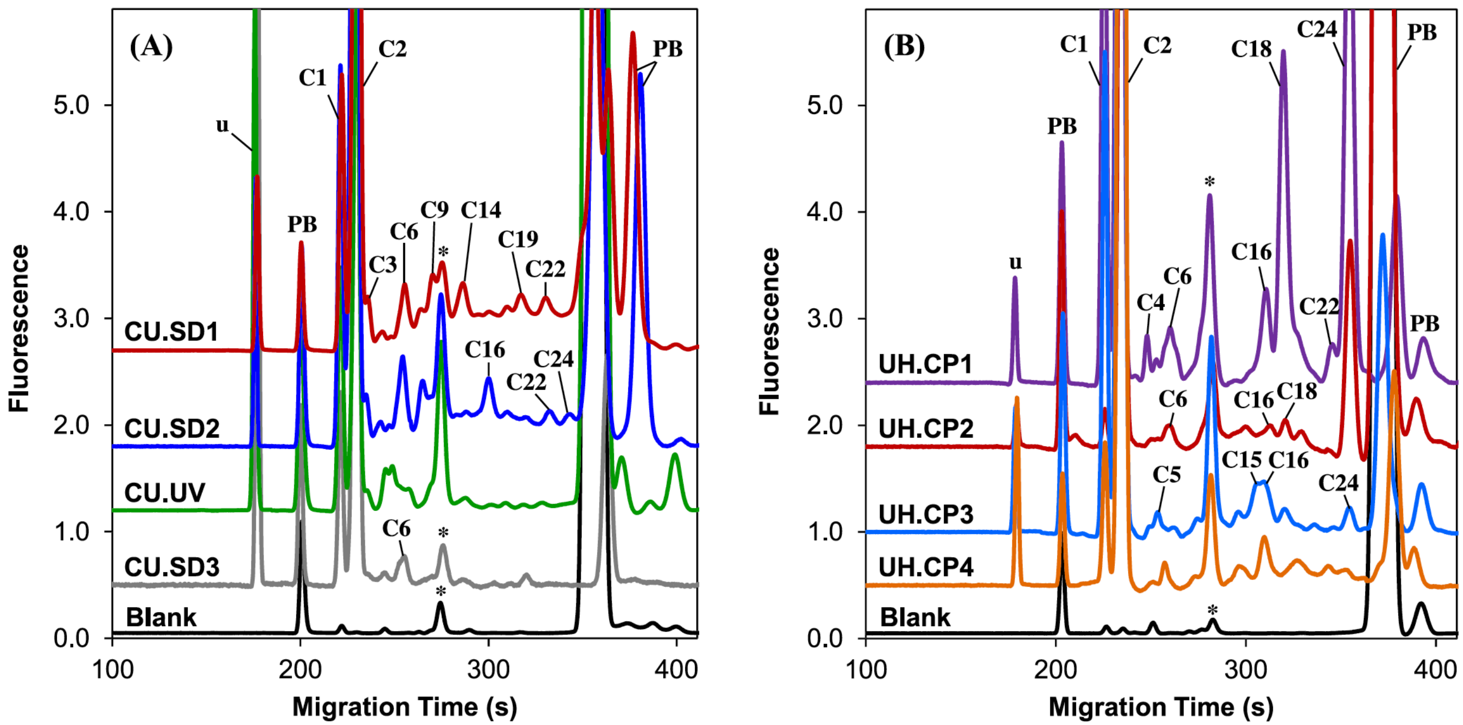


Fig. 3. Nonaqueous separations of 1 mg/mL labeled tholins, with significant primary amine products noted. (A) Tholin samples generated at the University of Colorado at Boulder. (B) Tholins produced at the University of Houston. All samples were labeled at 50 mg/mL with 5 mM Pacific Blue in 25 mM diisopropylethylamine in ethanol. Separations were performed in 100 mM tetrabutylammonium acetate and 1.05 M acetic acid in ethanol. Blank is a 1:1 mix of ethanol/DMSO exposed to identical conditions during extraction, labeling and separation. The peak marked 'u' is present in all tholins and is at present unidentified. The starred contamination peak (∗) is present in all blanks and controls.

Titan is not a sleeping Giant anymore

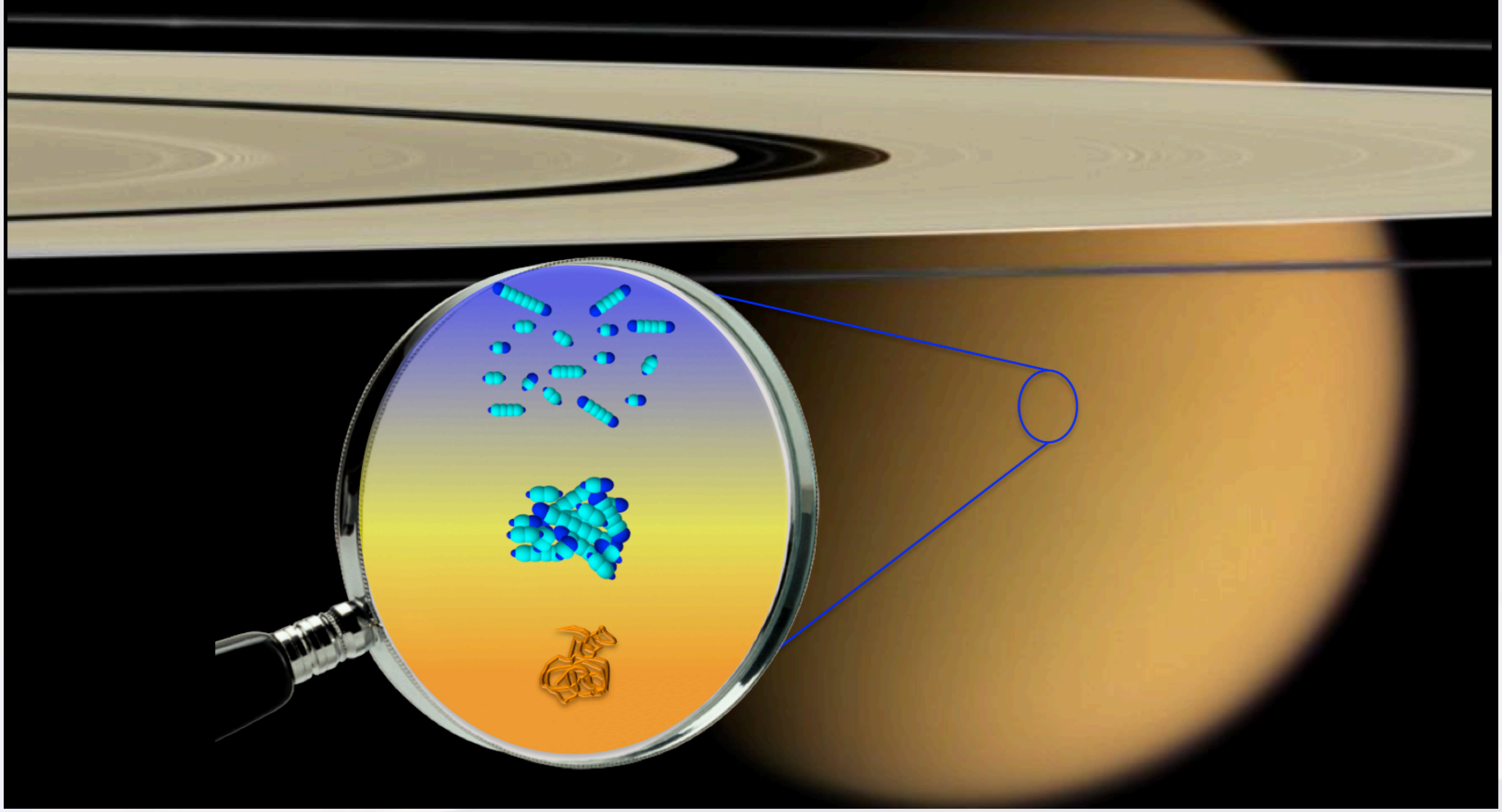
- Titan's atmosphere and surface is photochemically active though a couple of orders slower than on Earth.
- **In the presence of water-ice, photochemistry could lead to the formation of prebiotic molecules (amino acids and nucleobases) on Titan's surface and transported to subsurface water oceans that could be Habitable.**

Solar Photons and Titan's Atmosphere

Lower the Altitude – longer the Wavelength of Solar Photons

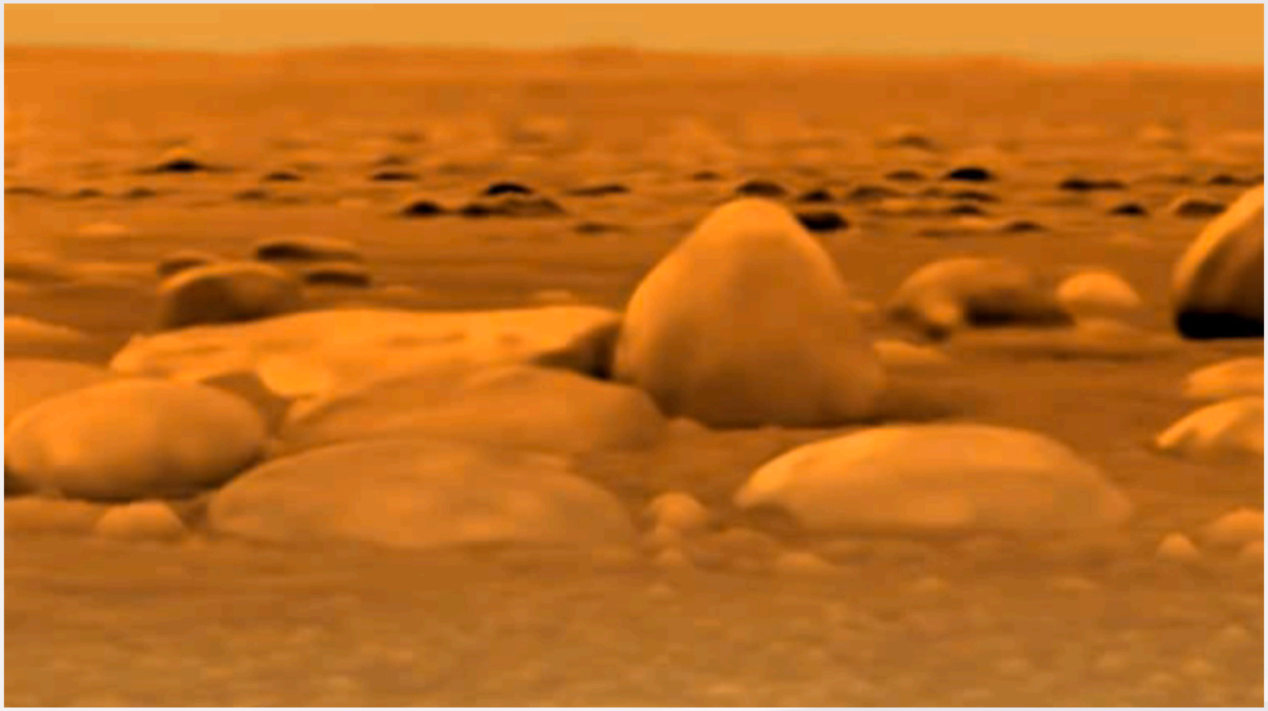
Murthy Gudipati; January 26 2013

Molecules on Titan are capable of harvesting solar photons throughout its atmosphere and on the surface to form complex organics capable of supporting life



Titan Subsurface Oceans: Habitable?

If this Titan's surface boulder were to be water-ice coated with organic solid and exposed to >350 nm solar photons, then building blocks of life would be formed here and transported into the interior water oceans – a habitable environment.



Cosmic Rays vs. Solar Photons

Cosmic Rays are NON-Selective with respect to the species interacting. They interact with highest abundant species: N_2, CH_4, C_2H_6 etc. in Titan's atmosphere.

Longer-wavelength photons ARE selective. They do not interact with the abundant species if there is no absorption of these photons. They can interact with less abundant aerosols and ices more effectively.

Gronoff et al., A&A 529, A143 (2011)

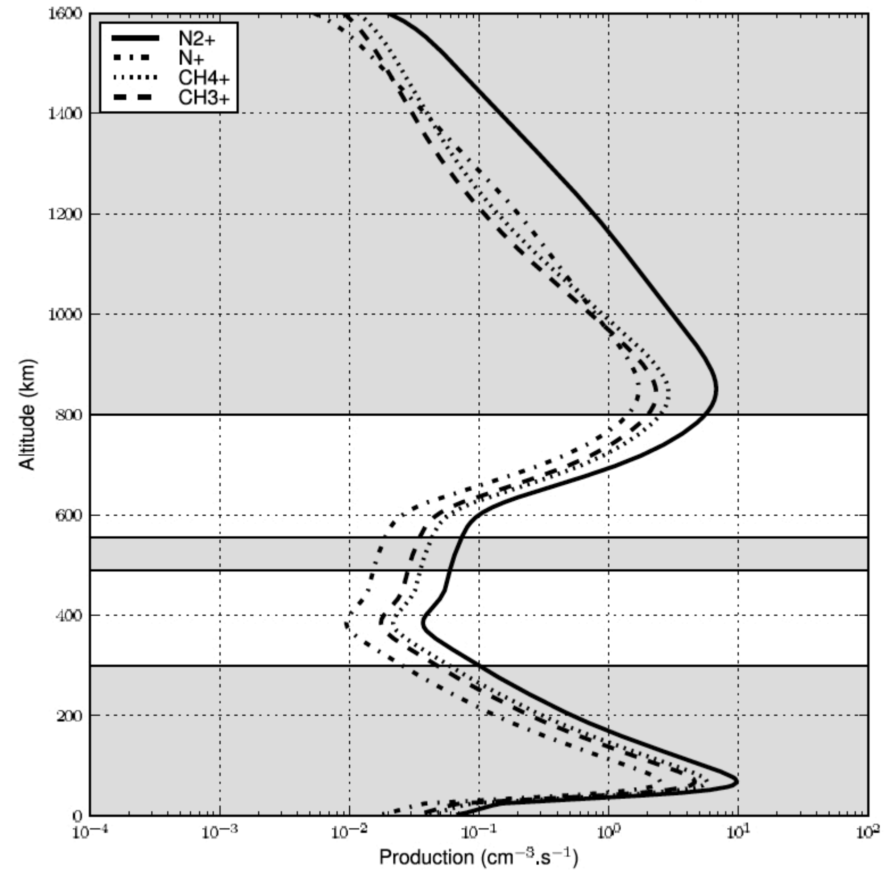


Fig. 6. Updated full ionization profile for the nightside, high precipitation conditions, and low solar activity (Φ_{Earth} = 450 MV, Fig. 18 in Paper I). The parts highlighted in gray are the haze layers, including the thermosphere.

Photons vs. Cosmic Rays in Titan's Lower Atmosphere

Solar photons reaching Titan:
~10^{15} photons cm^{-2} s^{-1} (~200 nm to 650 nm)

If 10% of these photons make it to the main haze layer (temperature <100 K), and cause condensed-phase photochemistry at 10^{-4} efficiency, then we will have:

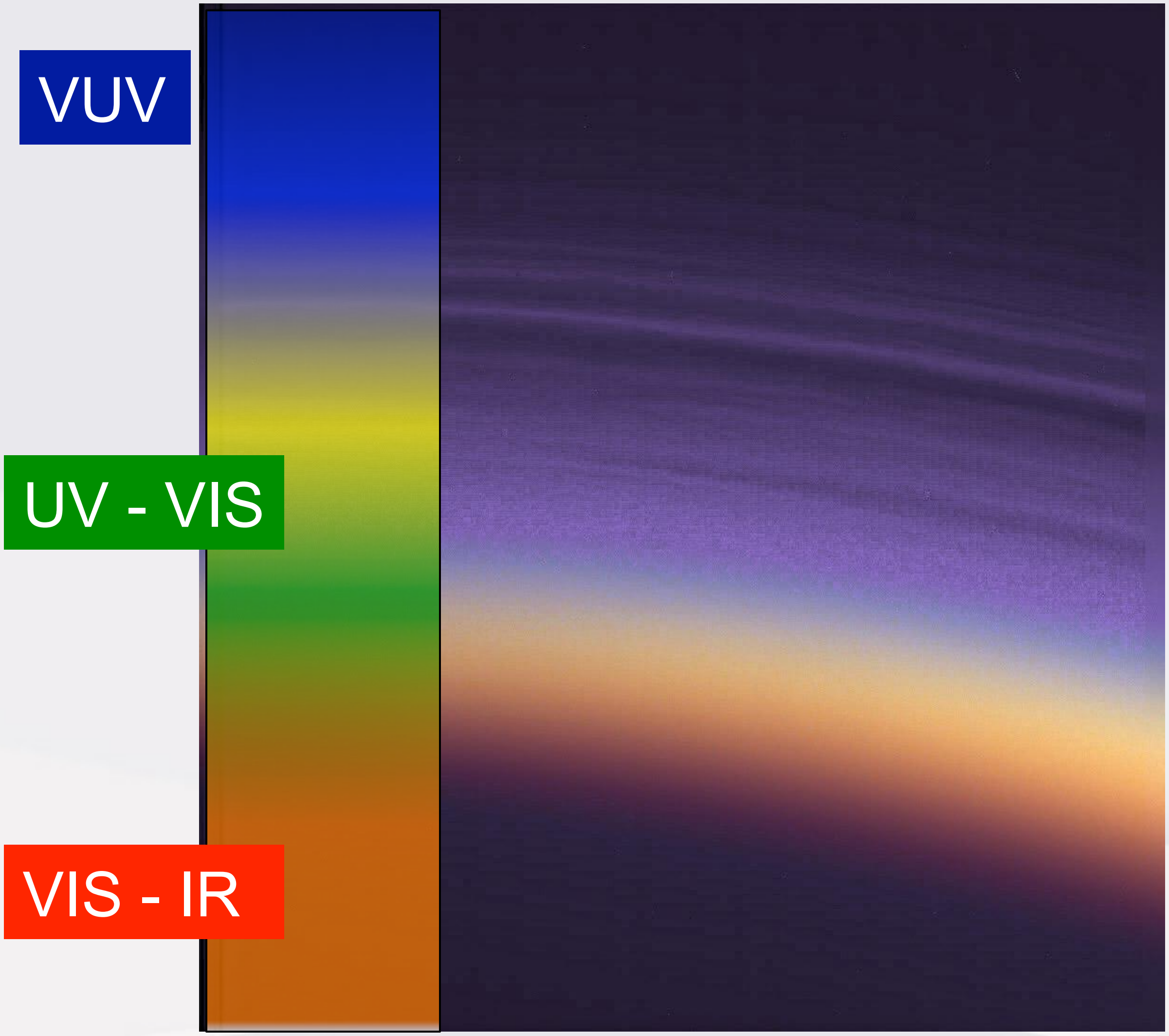
10^{15} X 10^{-1} X 10^{-4} = 10^{10} photochemical events cm^{-2} s^{-1}.

Compared to a maximum of 10^{1} ionization events cm^{-3} s^{-1} caused by cosmic rays. Maximum effective aerosol/ice ionization below 500 km: 10 X 10^{-2} X 500 X10^{4} = 5 X 10^{5} events cm^{-2} s^{-1}

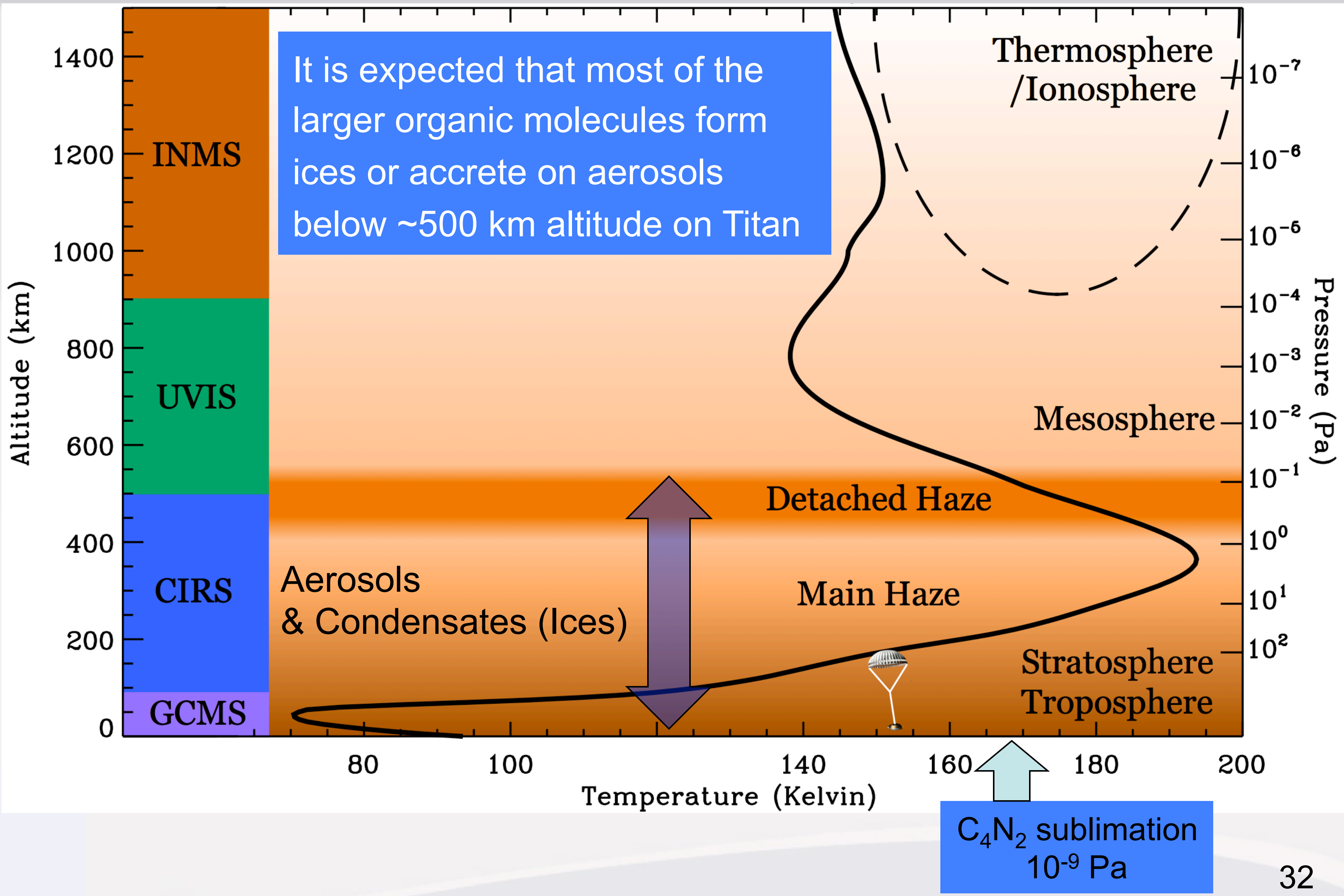
Clearly, photochemical processes in the condensed Titan aerosols and ices dominate the evolution of Titan's atmospheric molecules.

Titan's Atmosphere and Aerosol Chemistry

Can UV-VIS-NIR light that penetrates through into the lower atmosphere and on to the surface; induce chemistry in Titan's condensed aerosol, ices and solid surface?



Titan's atmosphere as we know now – thanks to Cassini-Huygens



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