Complex molecules in Titan's upper atmosphere

Panayotis Lavvas
GSMA/CNRS

Roger V Yelle
LPL, University of Arizona

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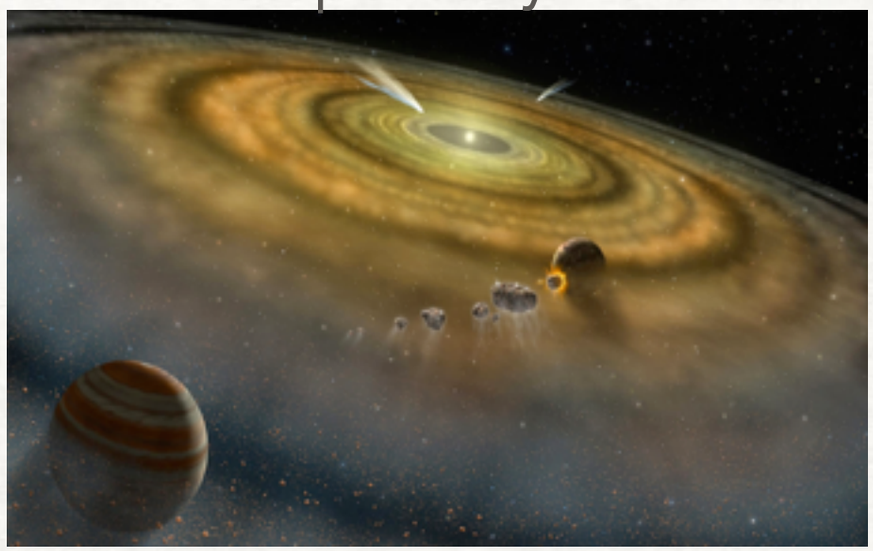
INTRODUCTION

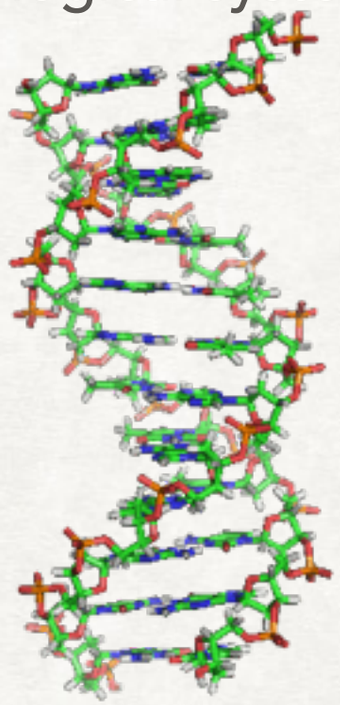
From ATOMS to MOLECULES to MACROMOLECULES …

Interstellar medium

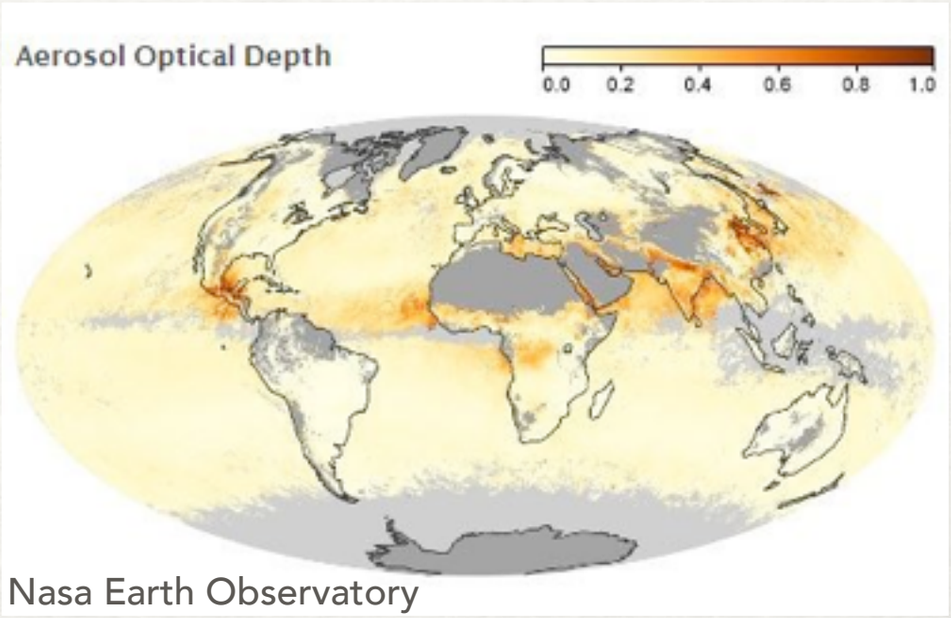
Protoplanetary Disks



Biological systems

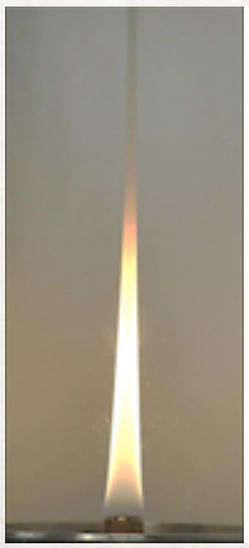


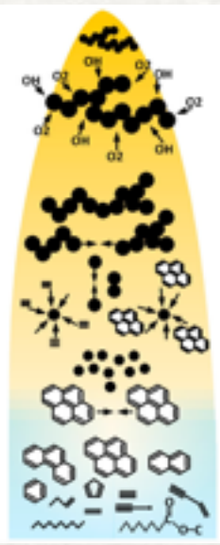
Global Climate

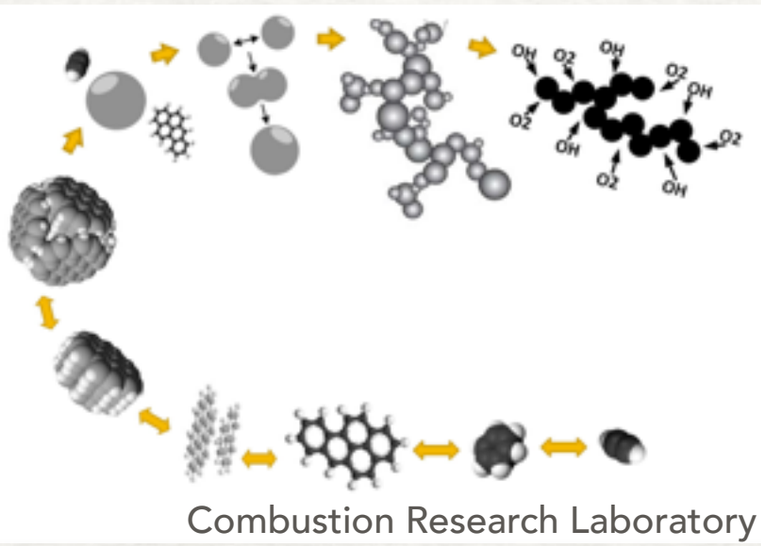


Nasa Earth Observatory

Combustion







Combustion Research Laboratory

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Interstellar medium

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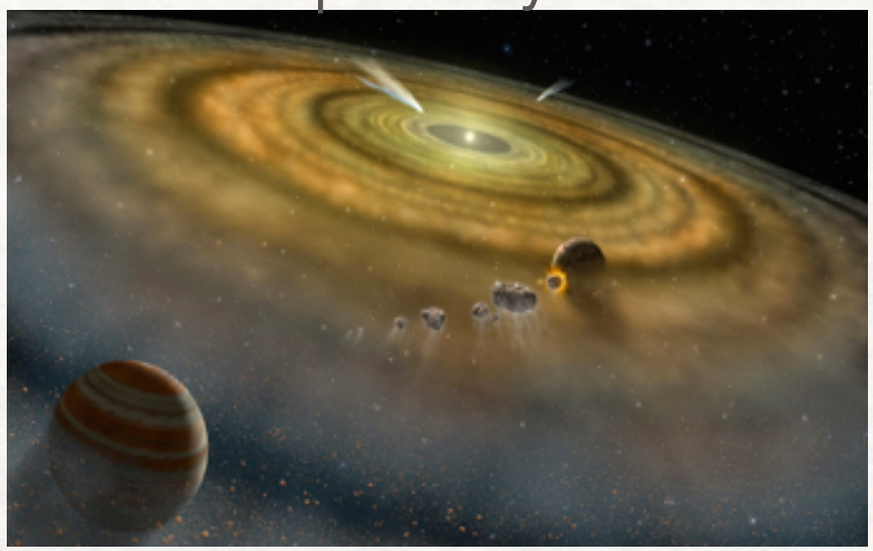

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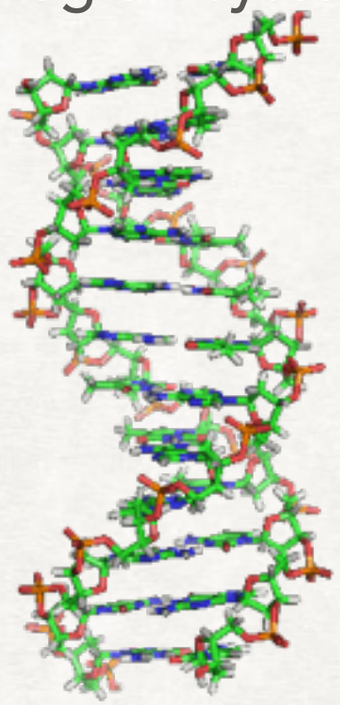

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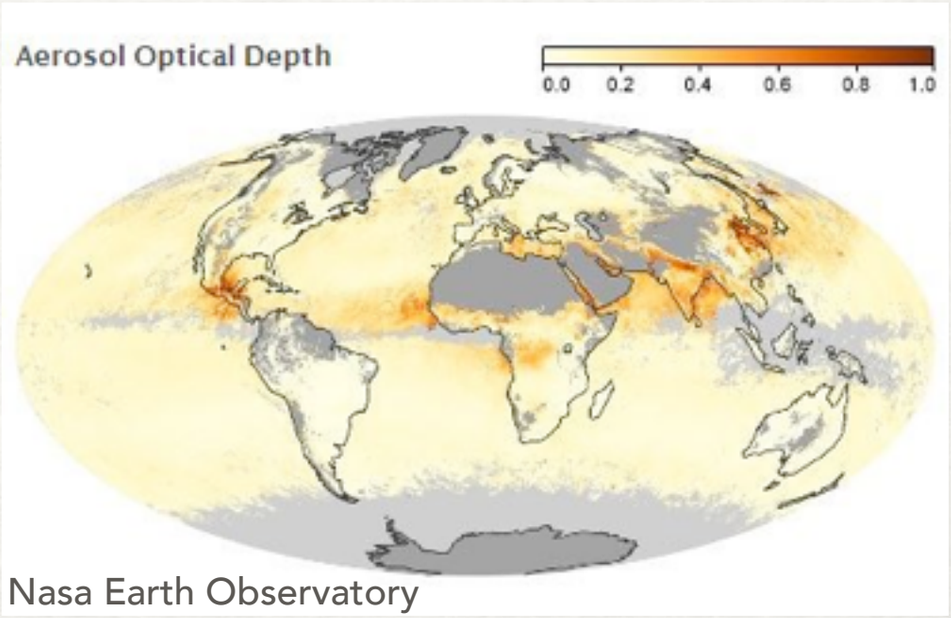

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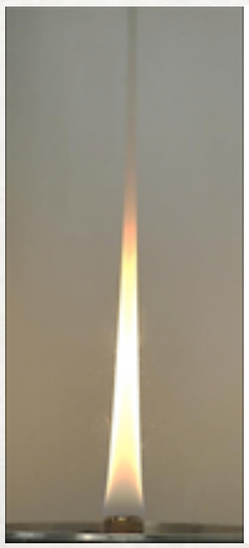

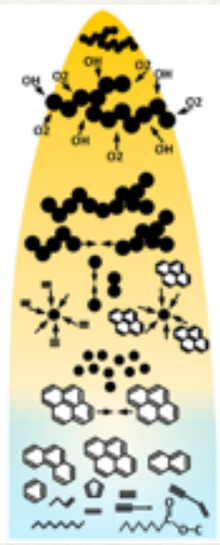

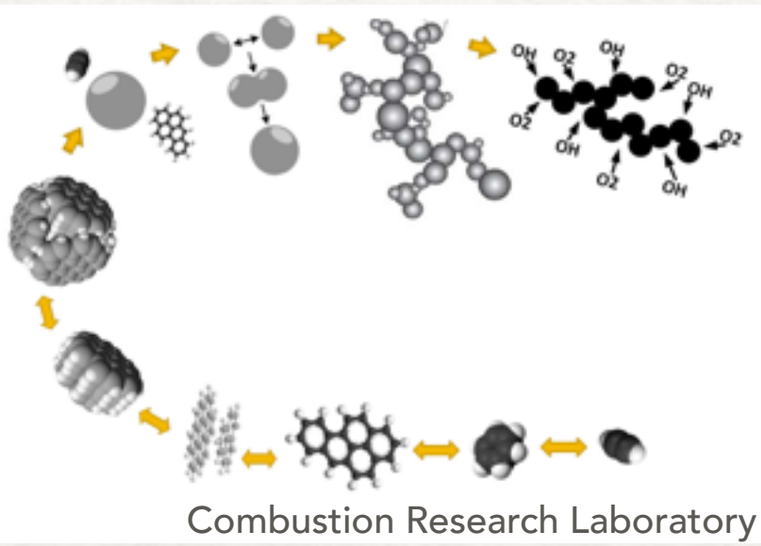

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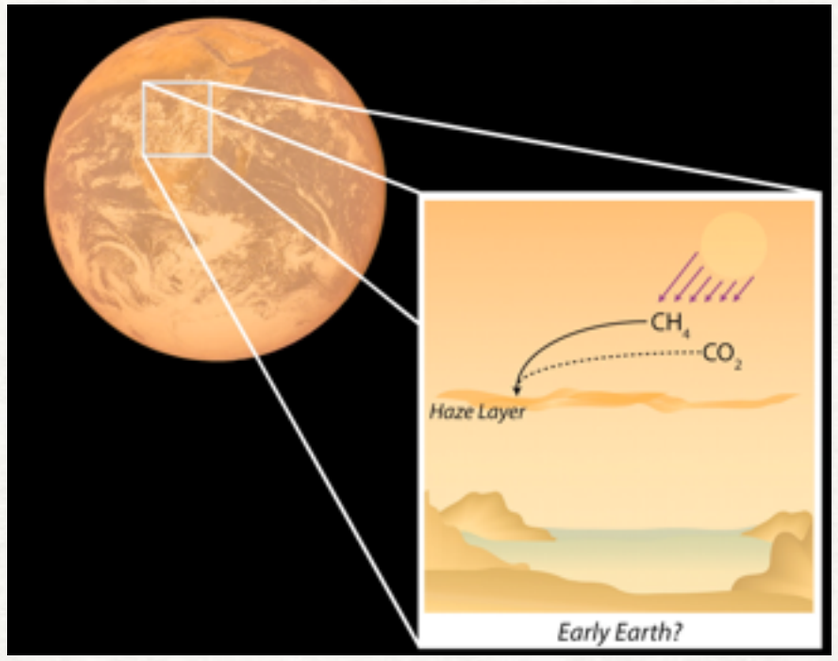
INTRODUCTION

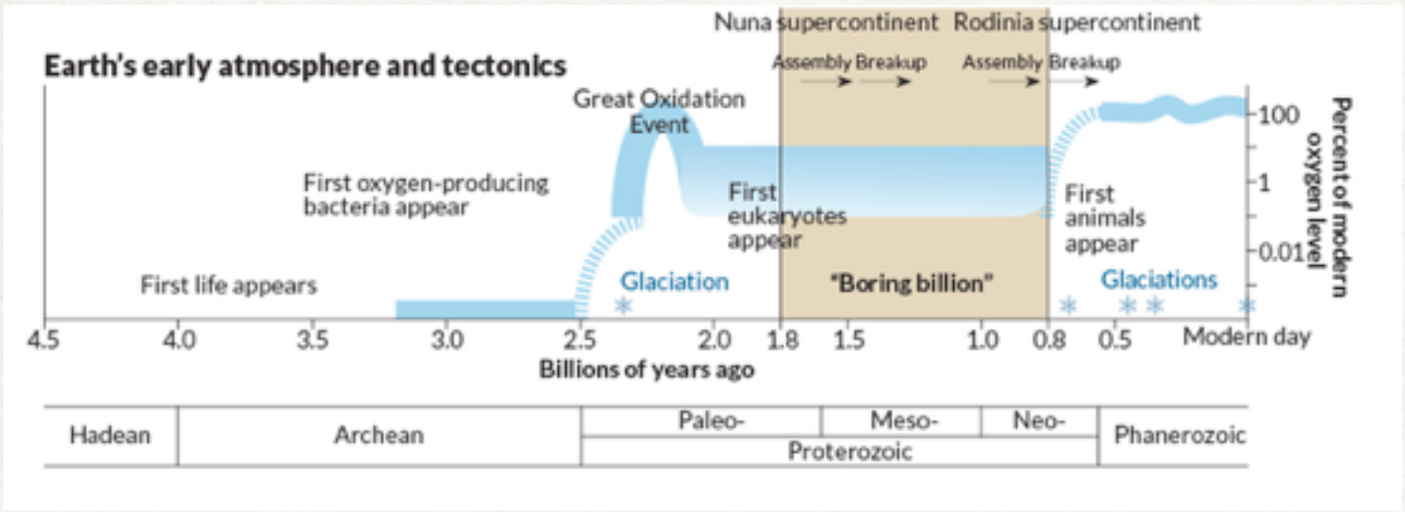
… to PHOTOCHEMICAL AEROSOLS in PLANETARY ATMOSPHERES

Trainer et al. 2005

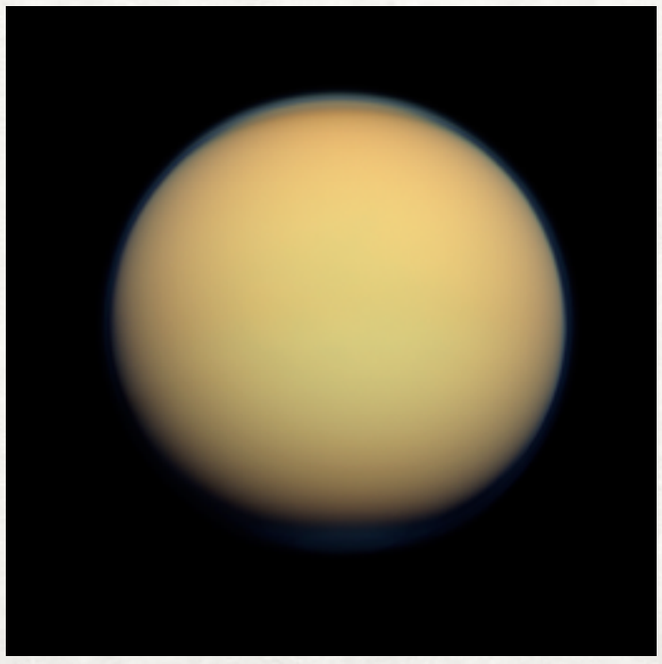


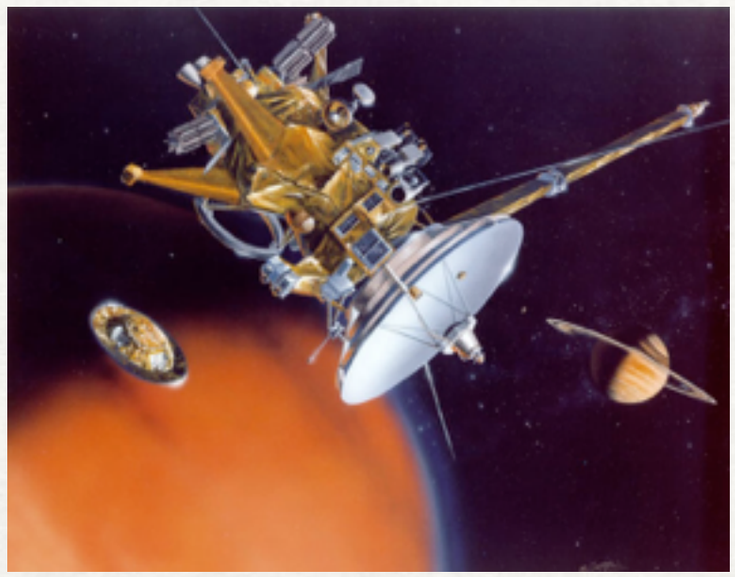
Earth's O_2 Level

Lyons et al. 2014



Titan

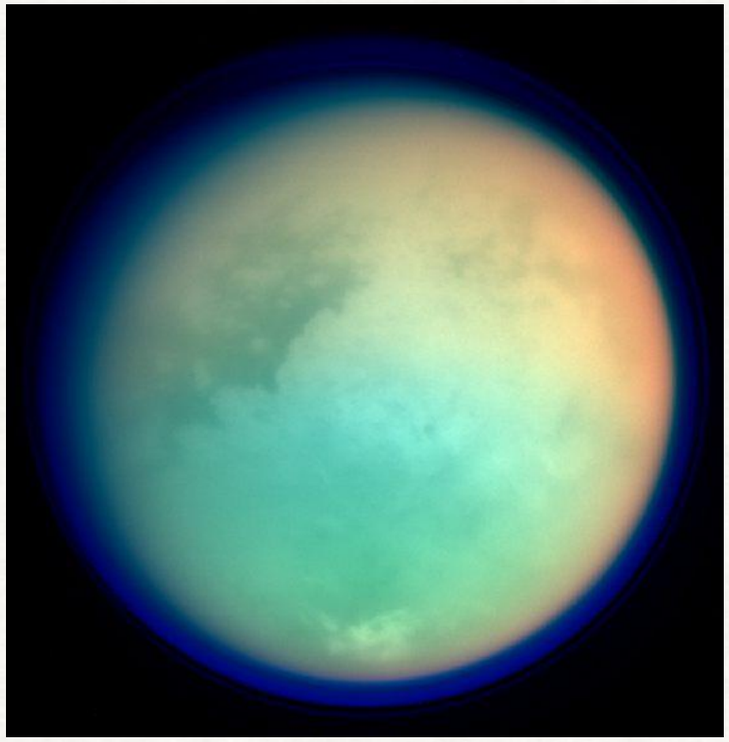




Cassini-Huygens

TITAN

Voyager 1 (1981)
Visible wavelengths



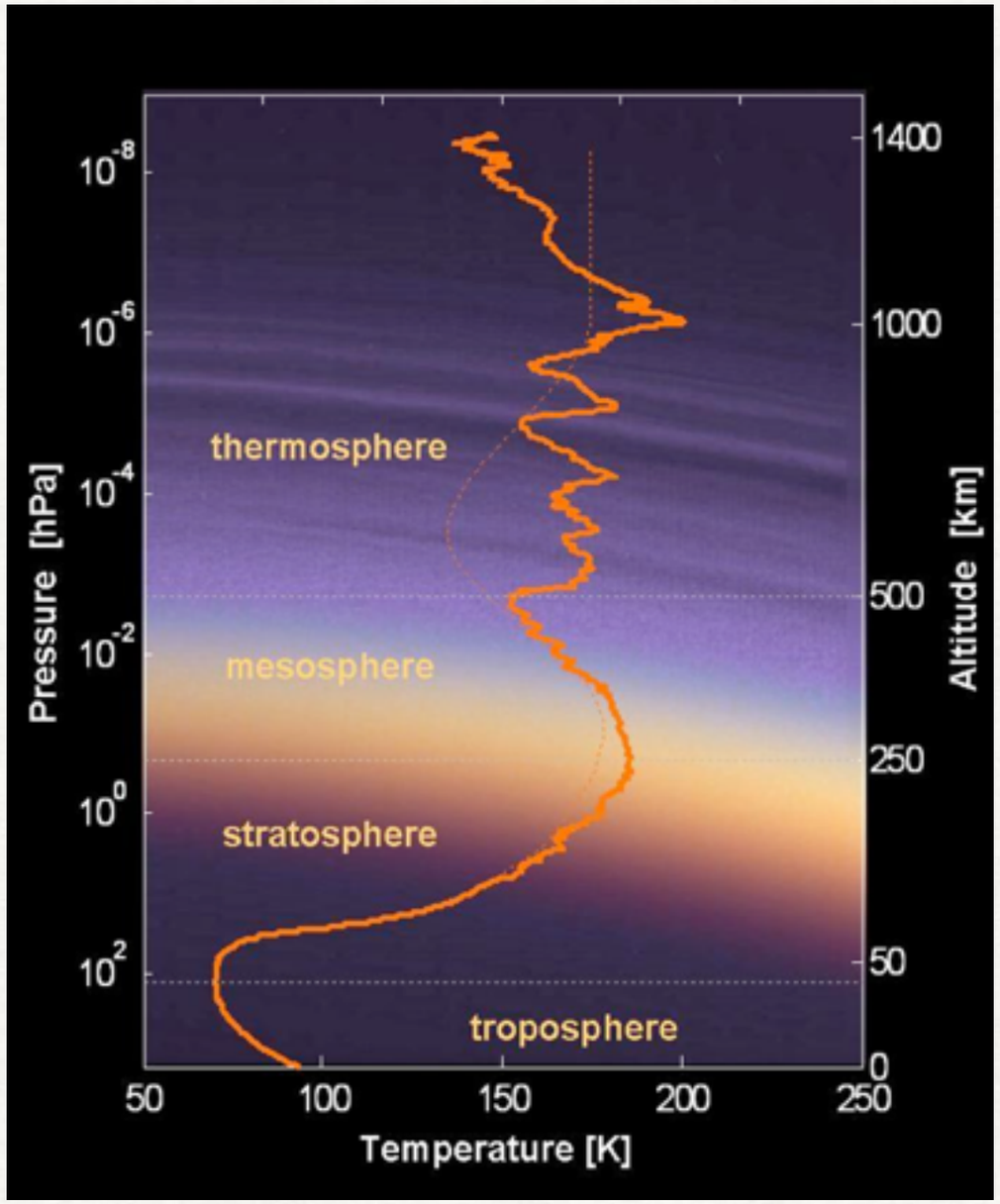
Cassini (2005)
Composite

	TITAN	EARTH
RADIUS:	2575 km	6371 km
COMPOSITION:	N_2 (95%), CH_4(5%)	N_2 (78%), O_2(21%), Ar(1%)
GRAVITY:	1.35 m/s^2	9.81 m/s^2
TEMPERATURE:	94 K	288 K
SURFACE PRESSURE:	1.5 atm	1 atm
ORBIT:	10 AU	1 AU

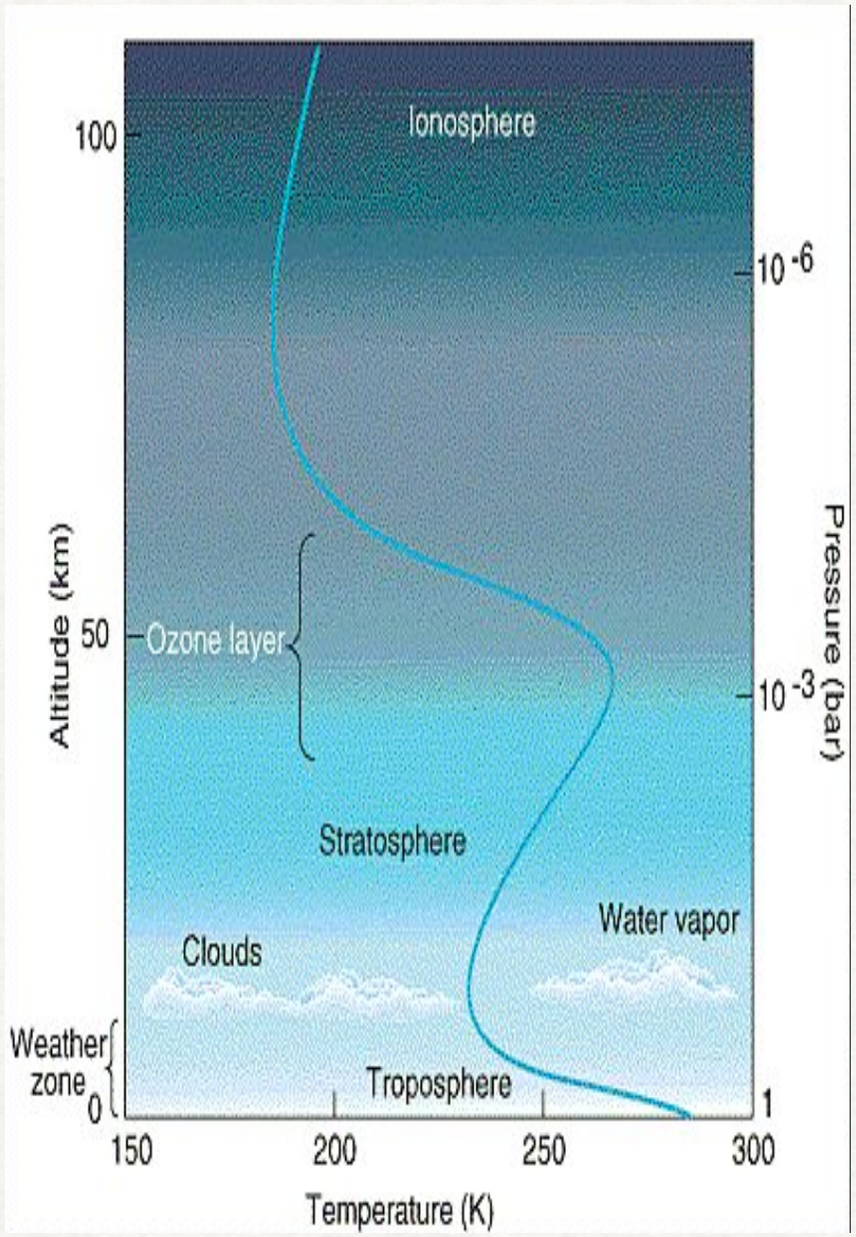
TITAN

THERMAL STRUCTURE

Titan

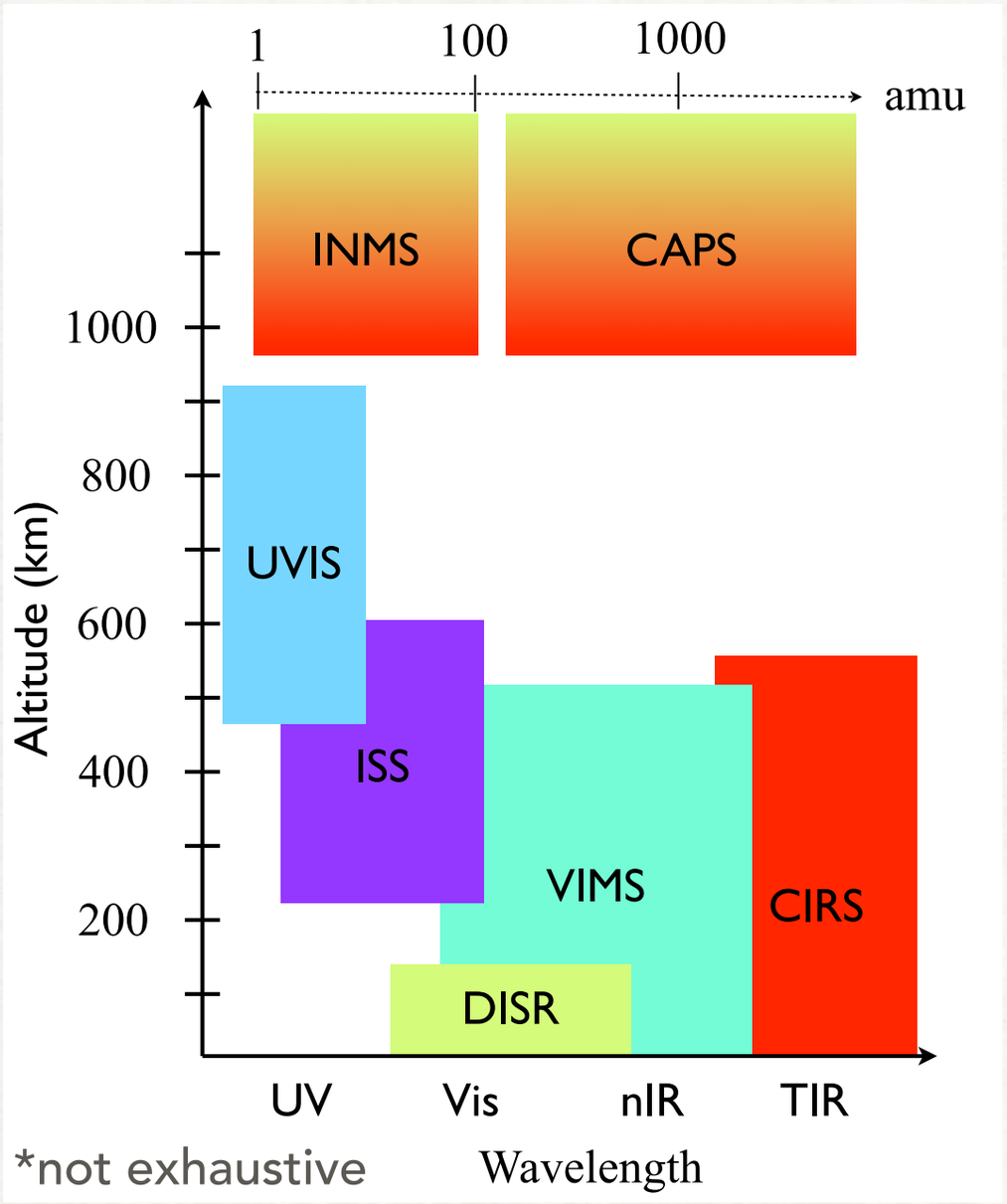


Earth



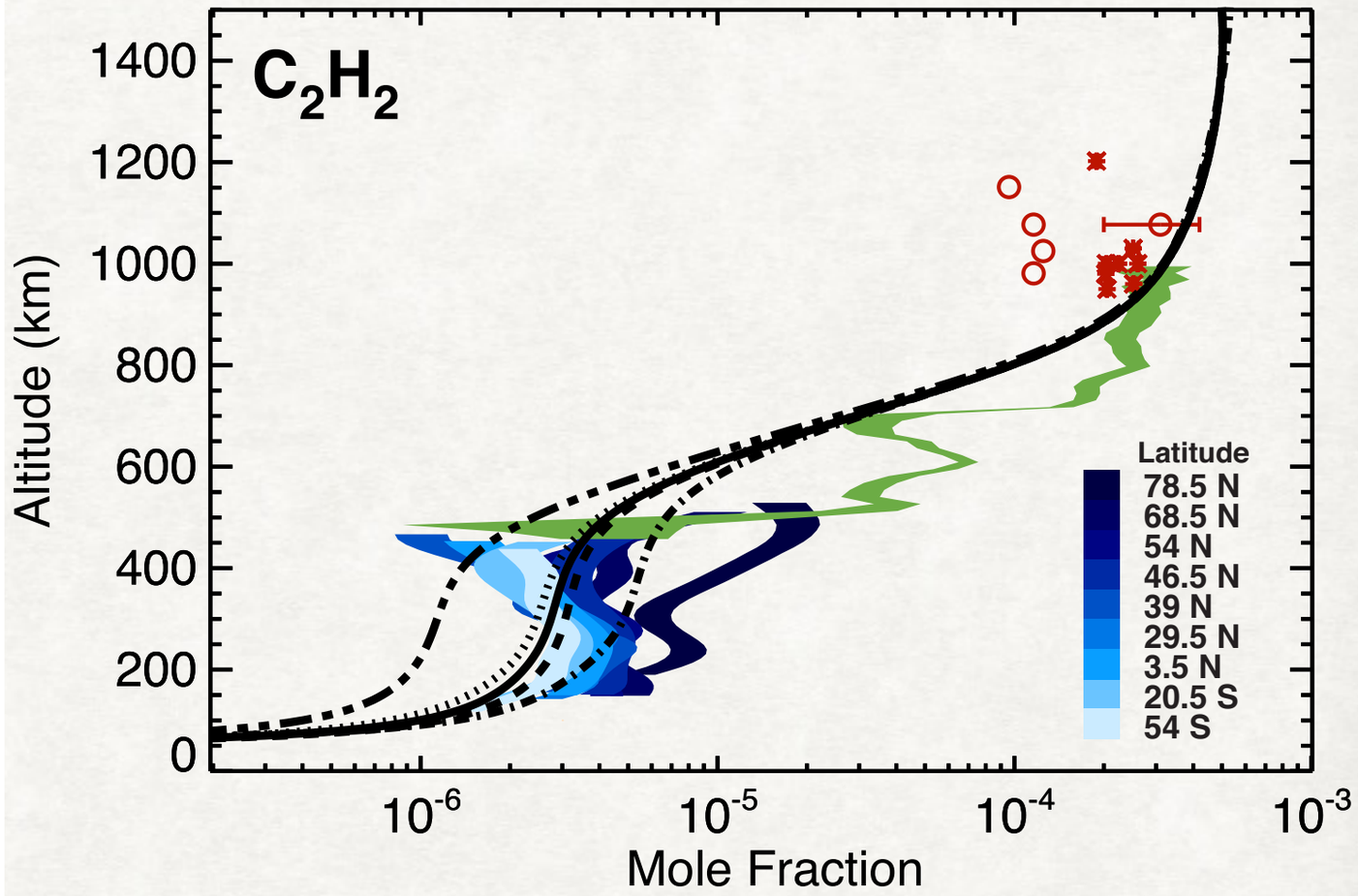
Cassini-Huygens

Cassini Instruments*



*not exhaustive

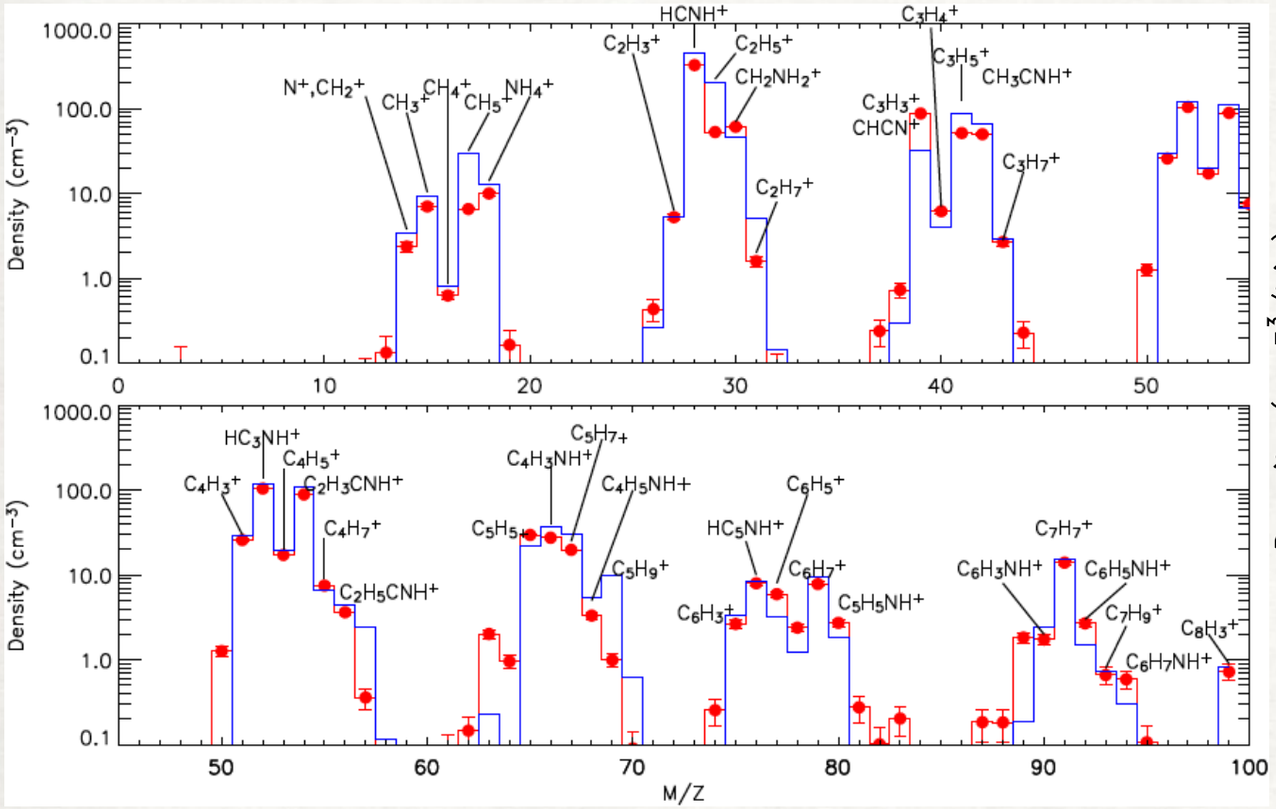
Vuitton et al. 2018



INMS (Yelle et al. 2006, Waite et al. 2007, Vuitton et al. 2008, …)
UVIS (Koskinen et al, 2011)
CIRS (Coustenis et al., 2007, Vinatier et al., 2011, Teanby et al., 2007, …)

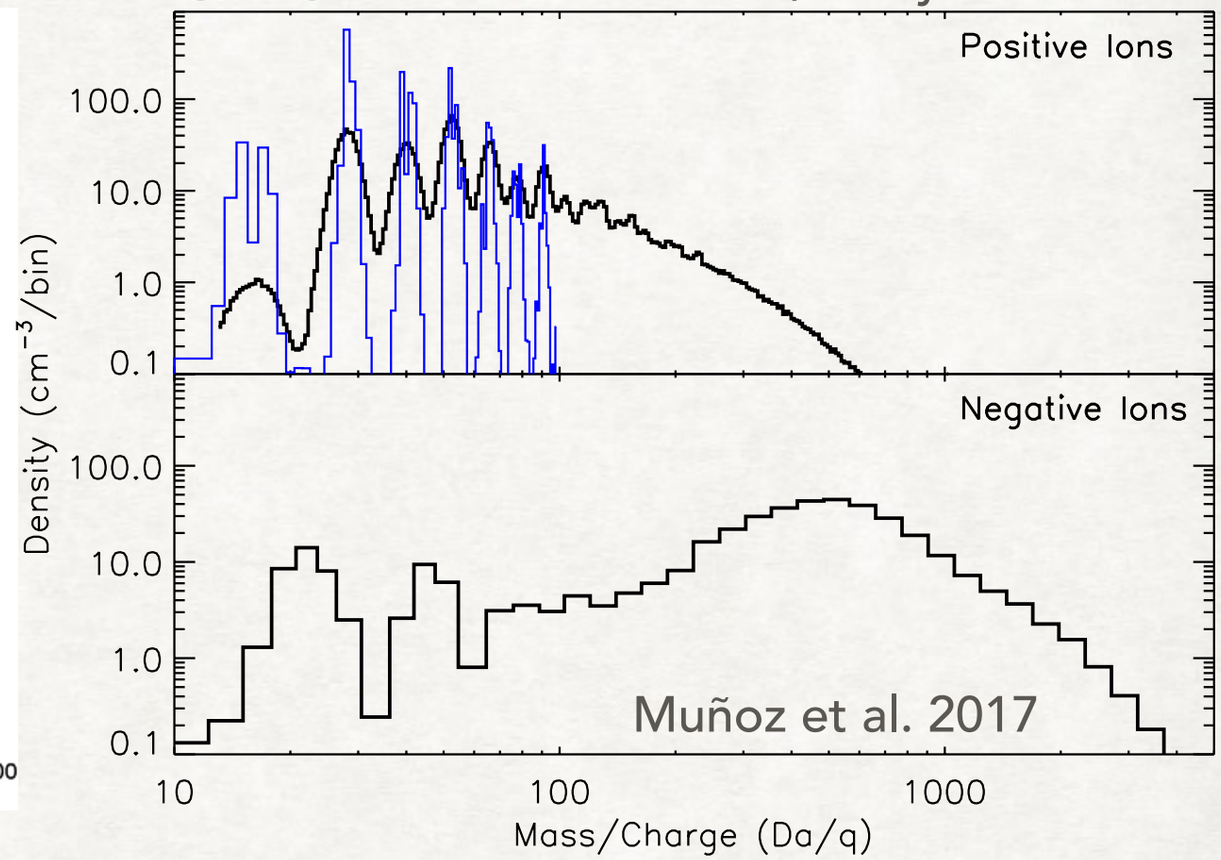
TITAN

Vuitton et al. 2007, 2008 INMS



CASSINI BREAKTHROUGH

CAPS Coates et al. 2007, Crary et al. 2009



A large number of new species identified for the first time in Titan's upper atmosphere with masses up to ~1000 Da.

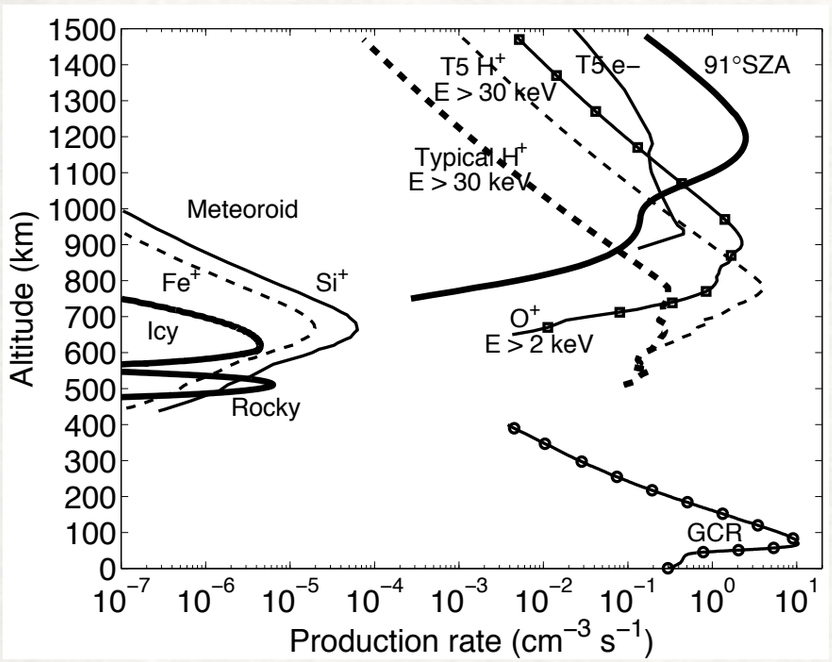
Aerosol formation takes place in the upper atmosphere!

Photochemistry (first steps)

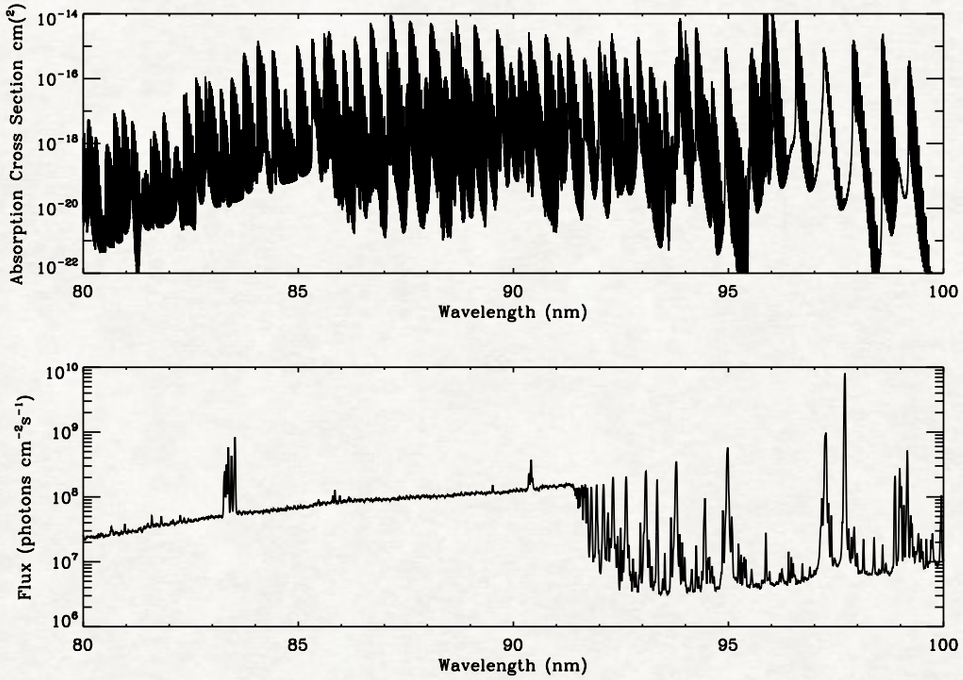
$CH_4 + h\nu >$ $CH_3 + H$
$CH_2 + H_2$
$CH_4^+ + e^-$
$CH_3^+ + H + e^-$
. . .

$N_2 + h\nu >$ $N + N(^2D)$
$N + N^+ + e^-$
$N_2^+ + e^-$
. . .

Galand et al. 2014



Lavvas et al. 2011



Models
Strobel et al. 1978
Yung et al. 1984
Toublanc et al. 1995
Lara et al. 1996
Lebonnois et al. 2001
Wilson & Atreya 2004
Vuitton et al. 2007/8
Horst et al. 2008
Lavvas et al. 2008a,b
Krasnopolsky 2009/12
Yelle et al. 2010
Mandt et al. 2012
Vuitton et al. 2012
Loison et al. 2015
Vuitton et al. 2018
+++

100s - 1000s of reactions

Immense efforts from experimental & theoretical investigations

Cassini observations show that solar input has the dominant role in the upper atmosphere

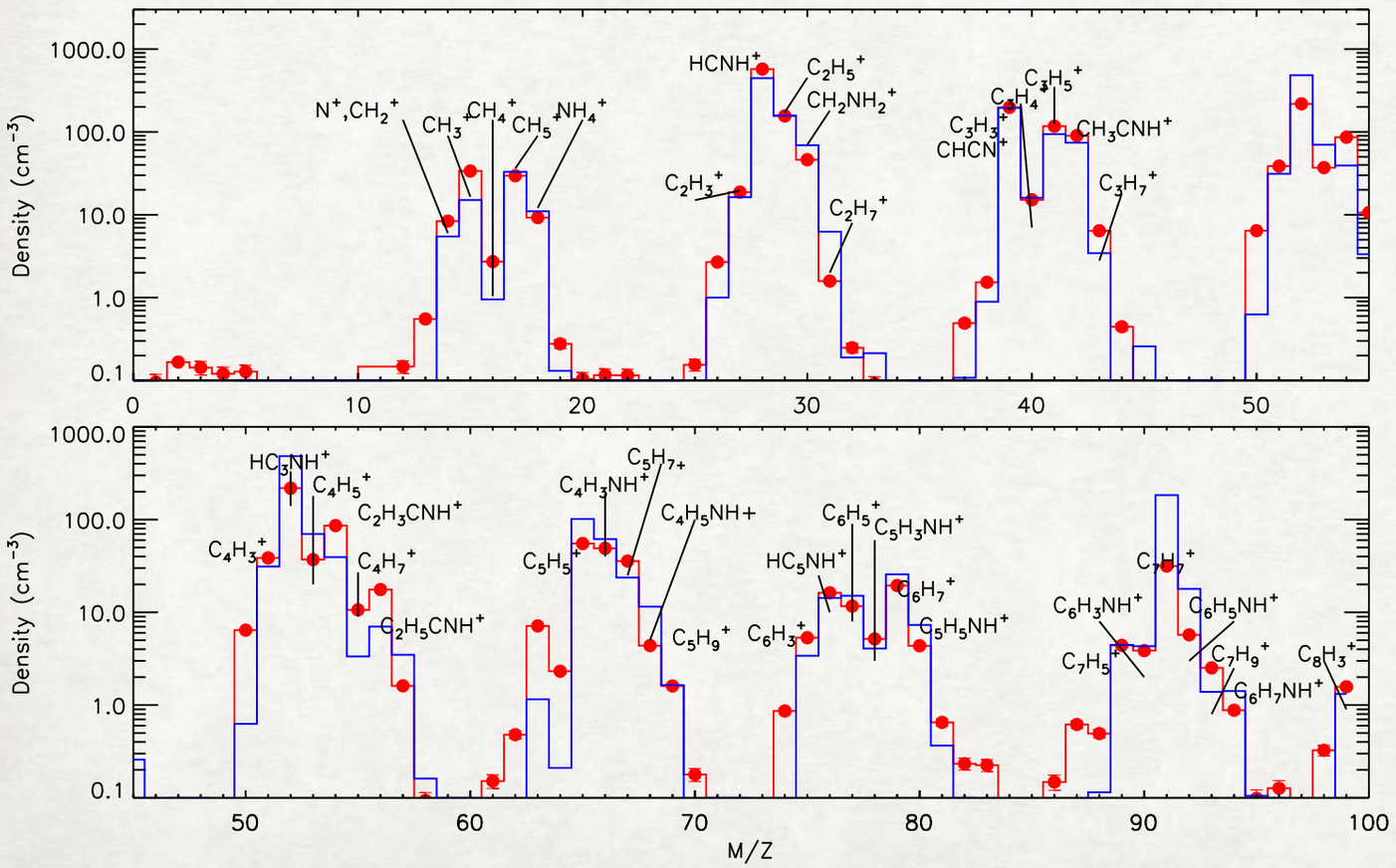
Ion Neutral Chemistry

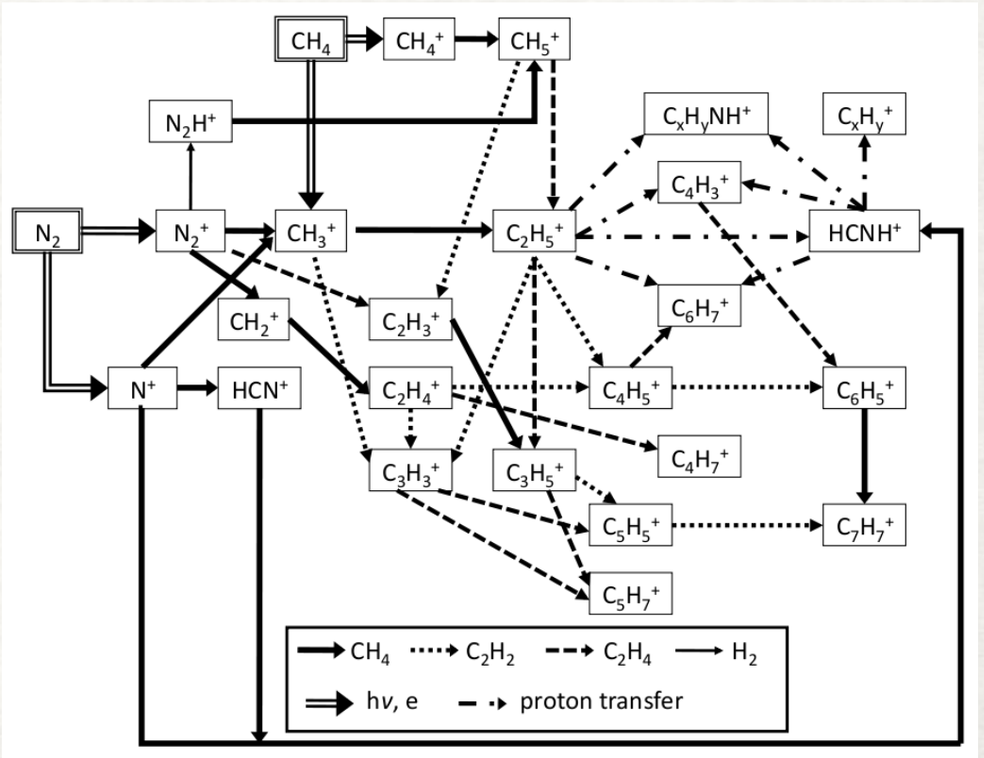
Positive Ions

Vuitton et al. 2018, Icarus

Positive ions	
(Dissociative) photoionization	$AB + h\nu \rightarrow AB^+(A^+ + B) + e^-$
(Dissociative) electron ionization	$AB + e_S^- \rightarrow AB^+(A^+ + B) + 2e^-$
Bimolecular reactions	$A^+ + BC \rightarrow AB^+ + C$
Termolecular association	$A^+ + B + M \rightarrow AB^+ + M$
Radiative association	$A^+ + B \rightarrow AB^+ + h\nu$
Dissociative recombination	$AB^+ + e_T^- \rightarrow A + B$
Radiative recombination	$A^+ + e_T^- \rightarrow A + h\nu$

Charge transfer from species with low proton (hydrocarbons) affinity to species with higher proton affinity (nitrogen bearing species).





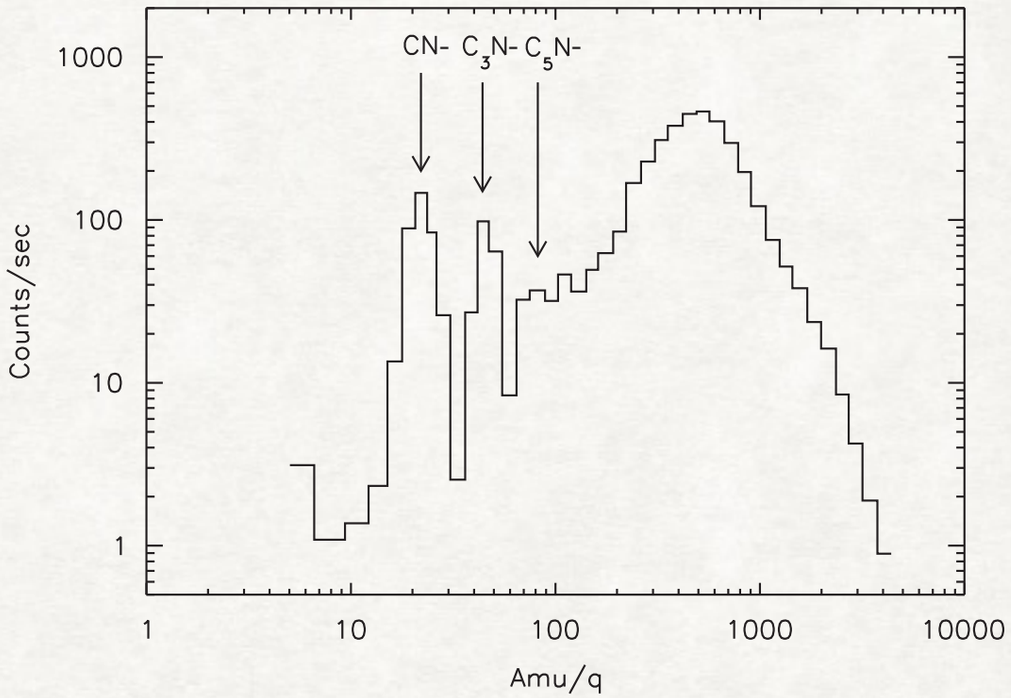
Ion Neutral Chemistry

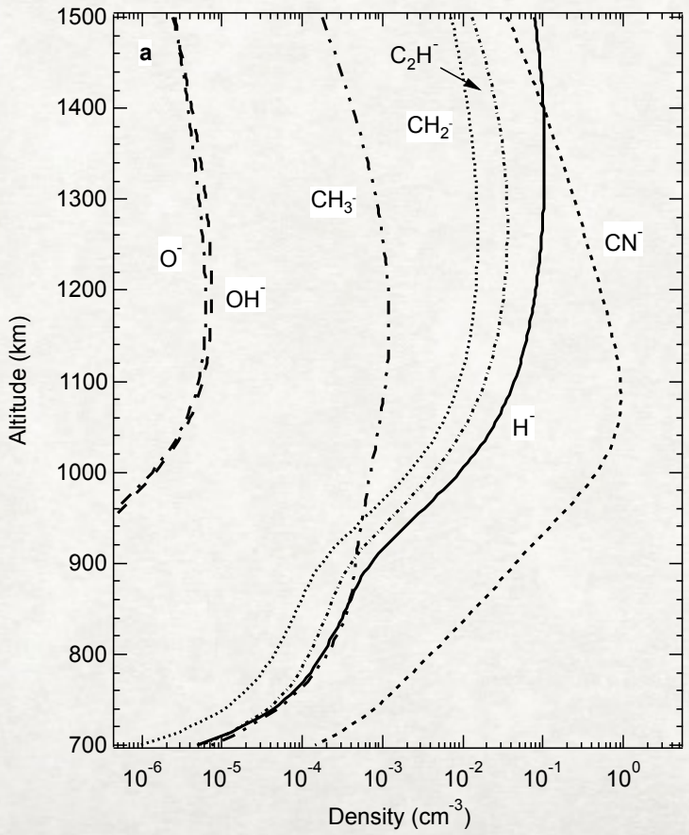
Negative Ions

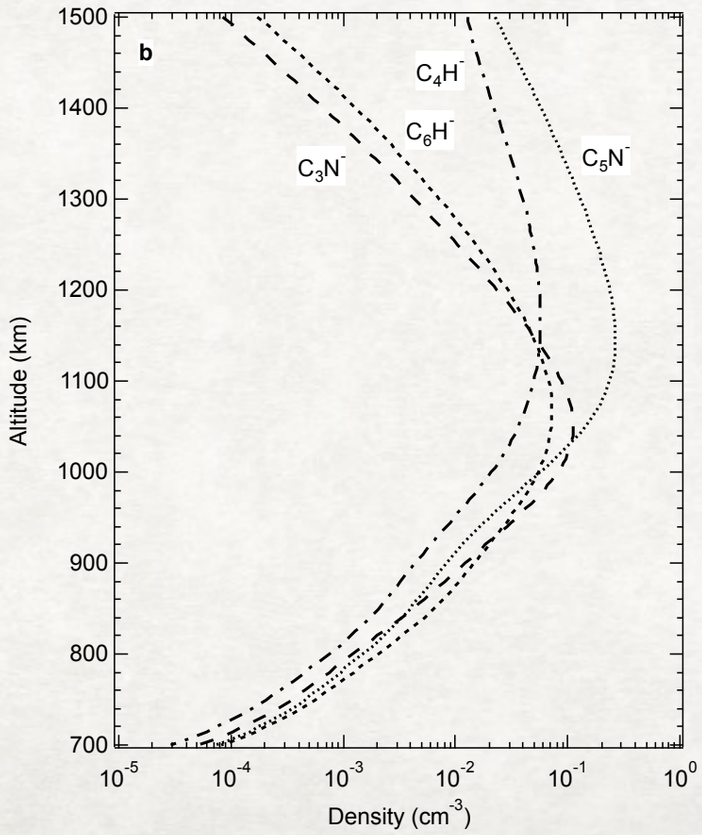
Negative ions	
Ion-pair formation	$AB + h\nu \rightarrow A^- + B^+$
Dissociative attachment	$AB + e_S^- \rightarrow A^- + B$
Radiative attachment	$A + e_T^- \rightarrow A^- + h\nu$
Bimolecular reactions	$A^- + BC \rightarrow AB^- + C$
Photodetachment	$A^- + h\nu \rightarrow A + e^-$
Ion recombination	$A^- + BC^+ \rightarrow AB + C$
Associative detachment	$A^- + B \rightarrow AB + e^-$

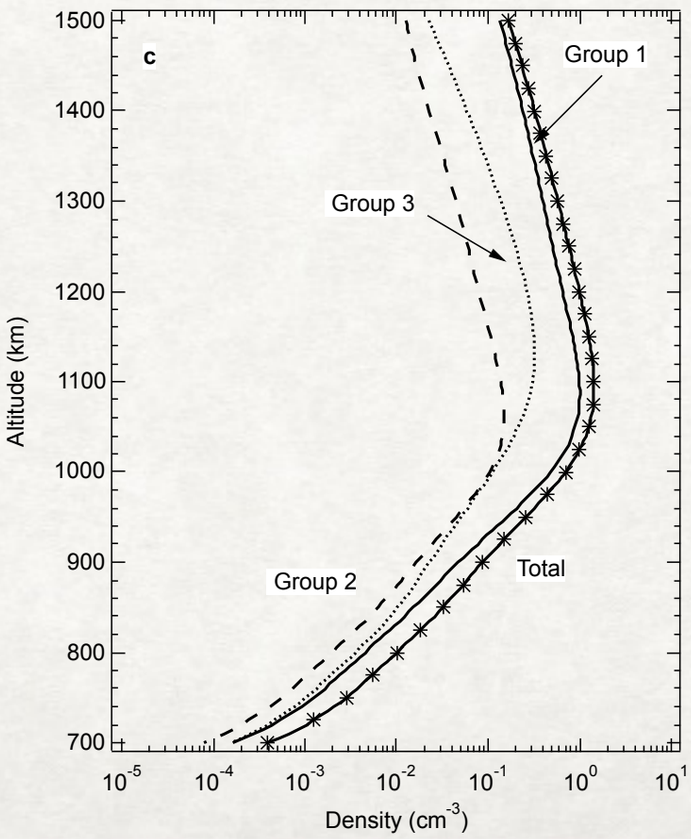
Mass group	Mass range (u)	Negative ions
1	12-30	H^-, CH_2^-, CH_3^-, C_2H^-, CN^-, O^-, OH^-
2	30-55	C_4H^-, C_3N^-
3	55-95	C_6H^-, C_5N^-

Vuitton et al. 2009







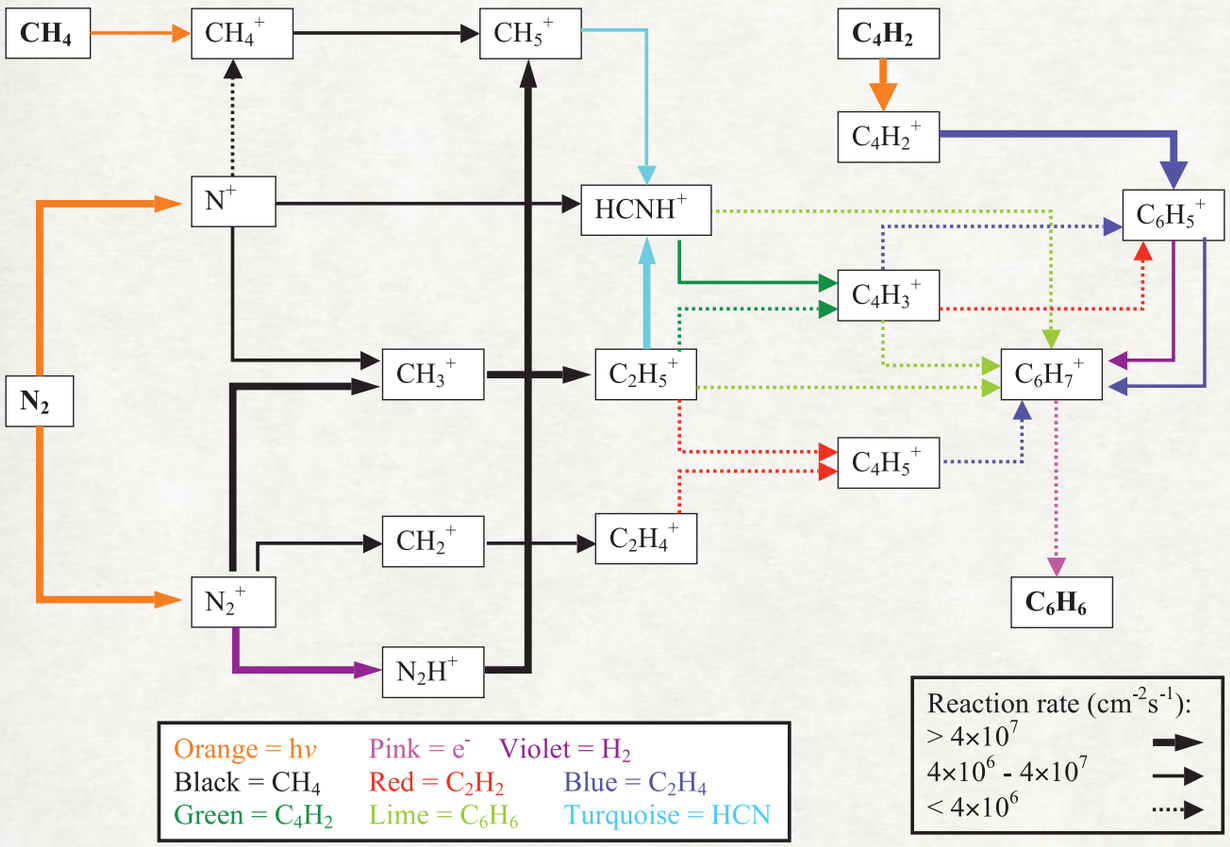


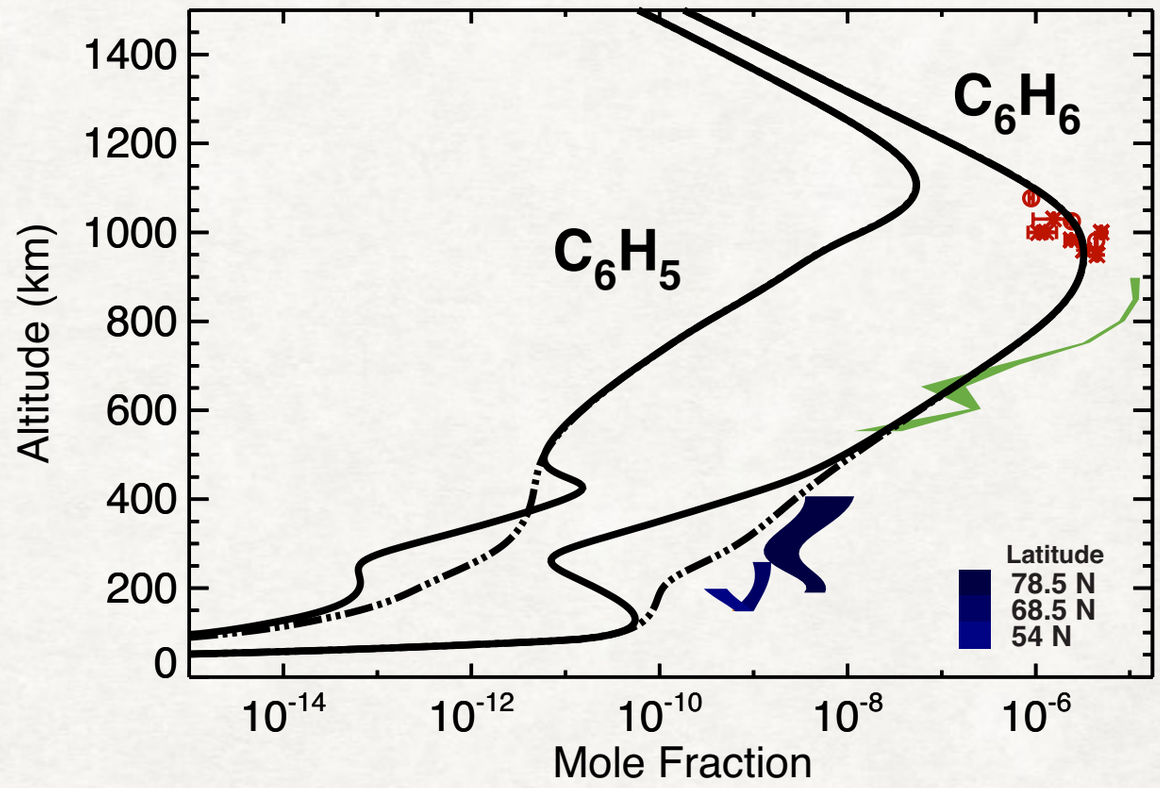
Ion Neutral Chemistry

Neutrals

Formation of benzene from ion-neutral chemistry

Vuitton et al. 2008





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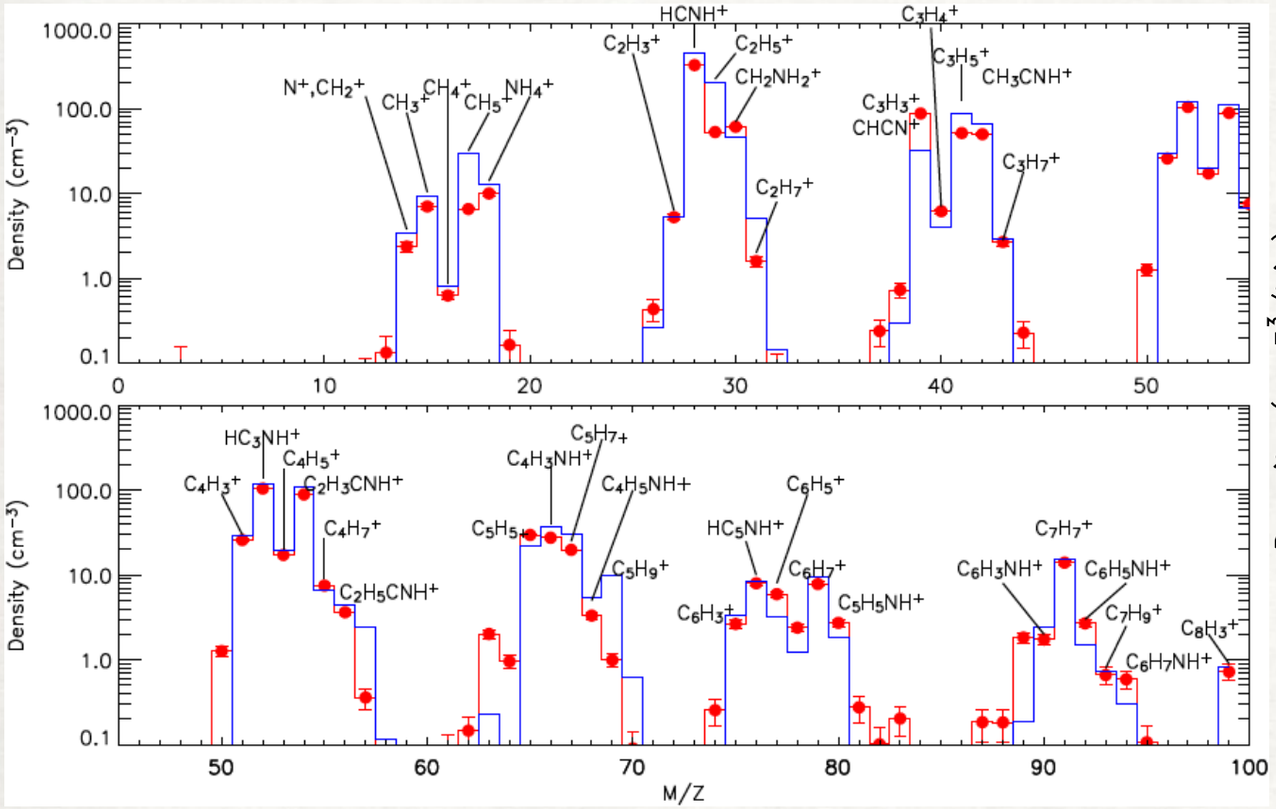
Vuitton et al. 2007, 2008 INMS



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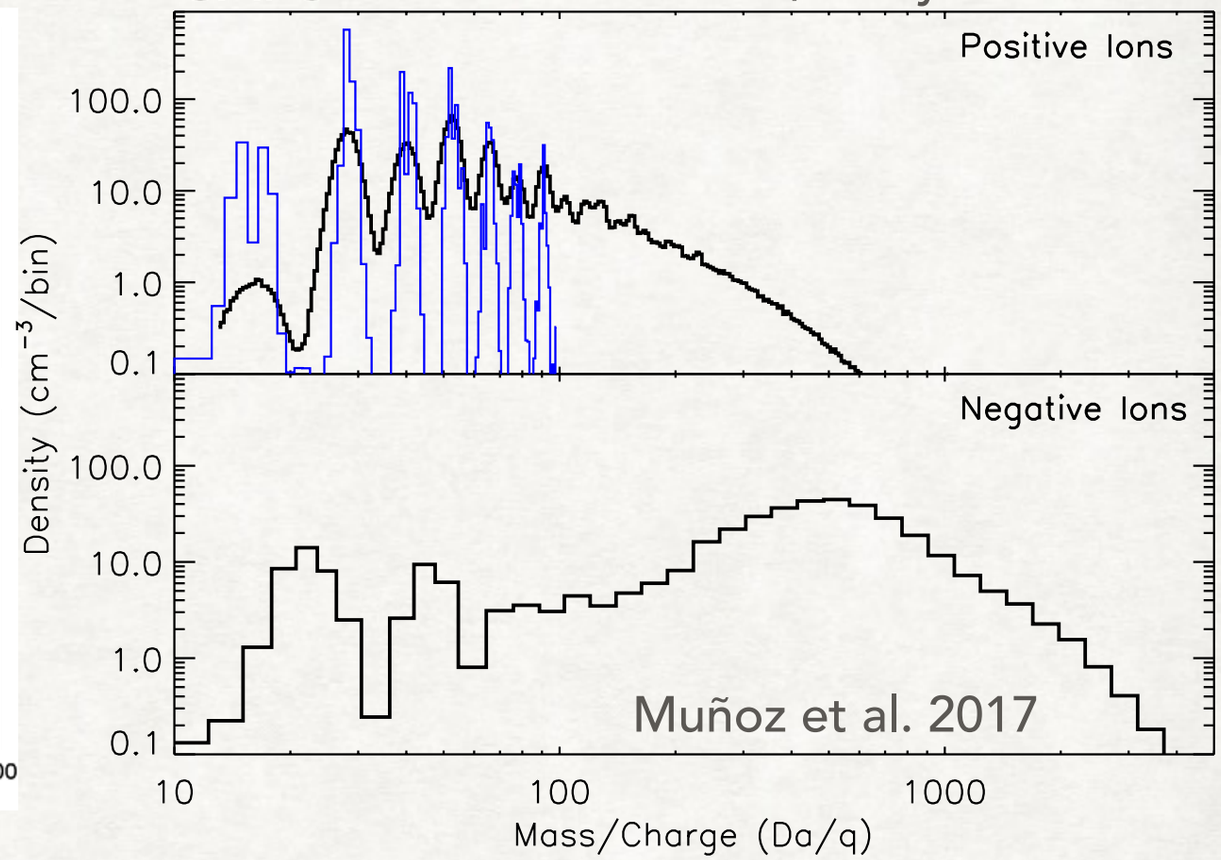

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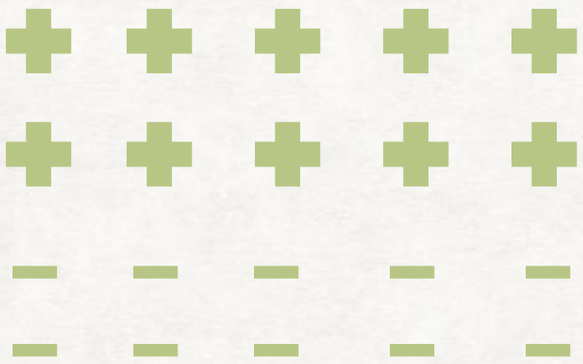
MOLECULAR GROWTH

Photochemical products



Positive ions

electrons

Macromolecules from ion chemistry

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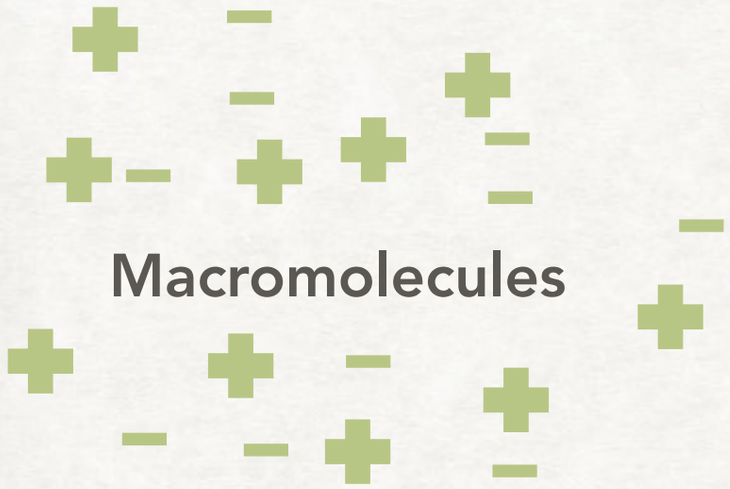
MOLECULAR GROWTH



Photochemical products

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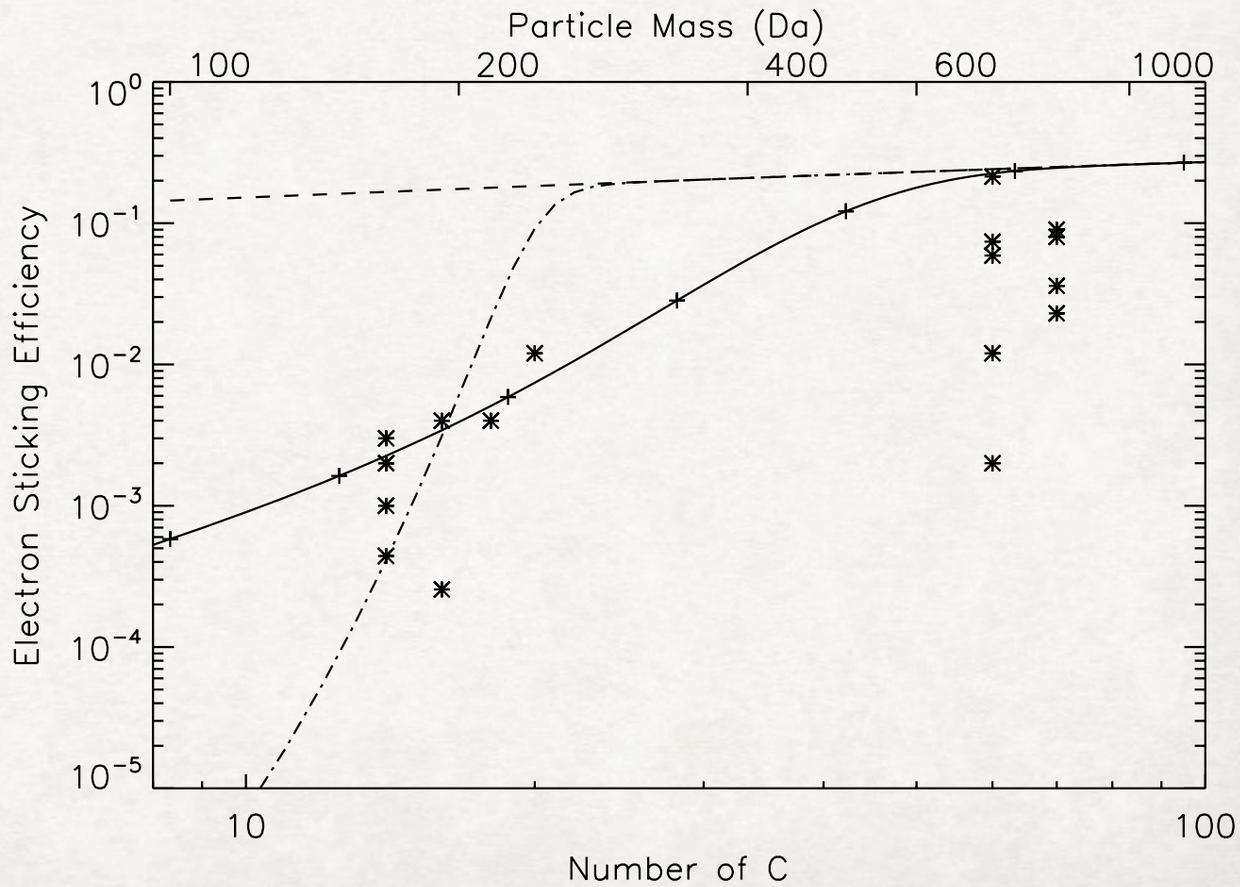
MOLECULAR GROWTH

electrons attach
on macromolecules



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MOLECULAR GROWTH

- Charged macromolecules attract positive ions

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MOLECULAR GROWTH

Macromolecules

Recombination leads to
mass transfer to macromolecules

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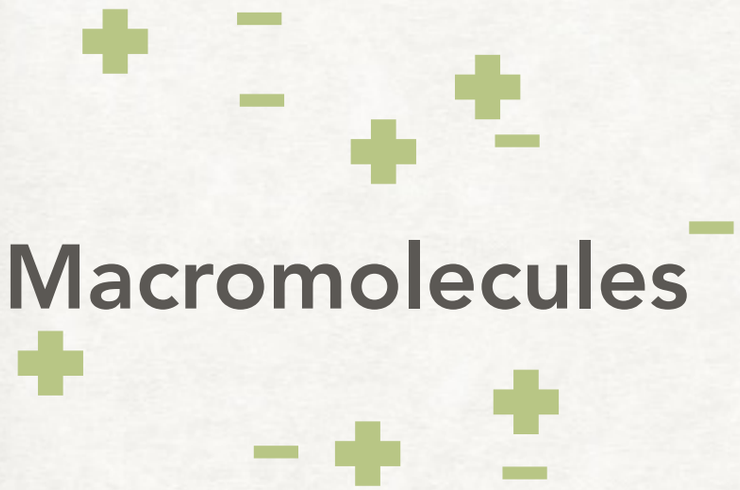
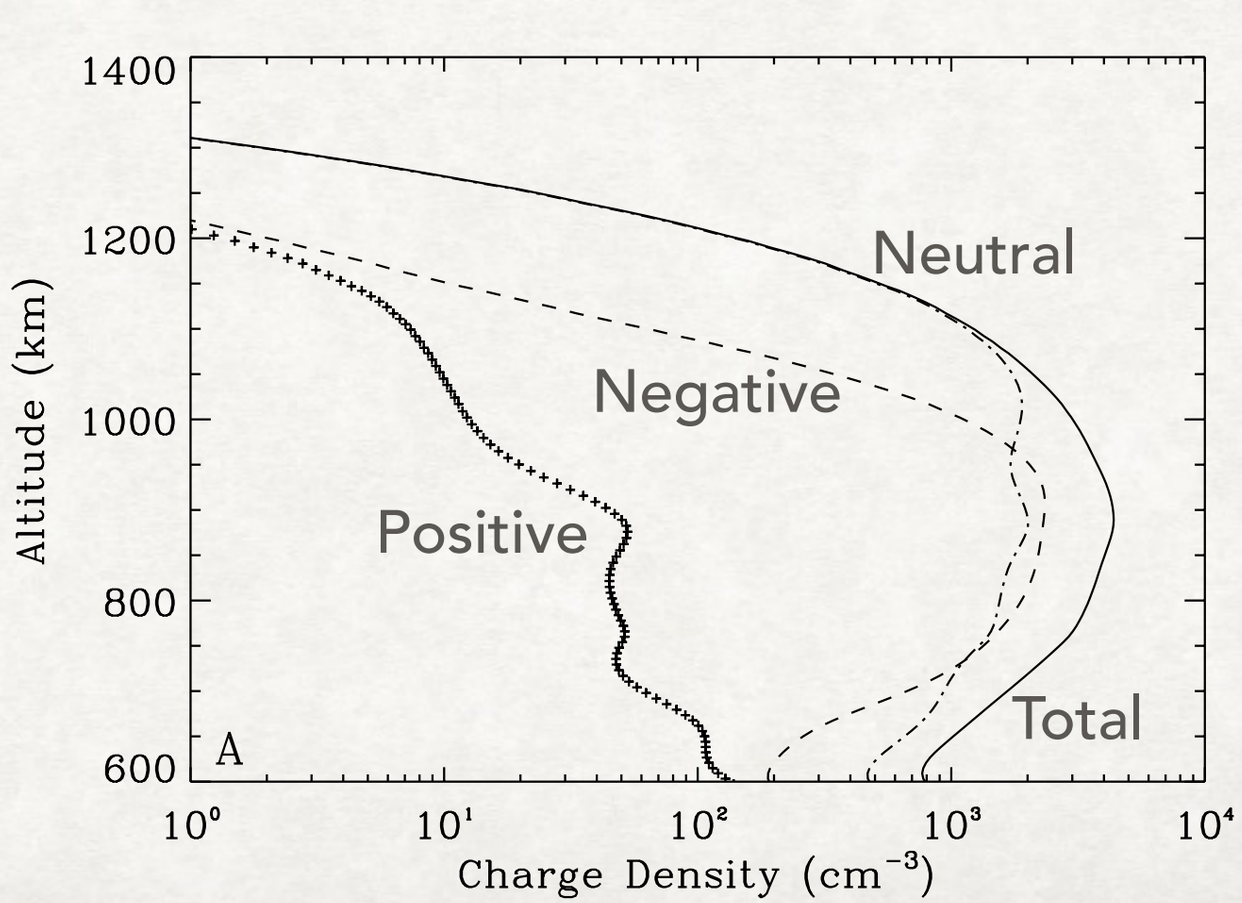
MOLECULAR GROWTH



Macromolecules

Recombination leads to
mass transfer to macromolecules

Charge balance based
on collisions with ion/electrons
& photoelectric effect



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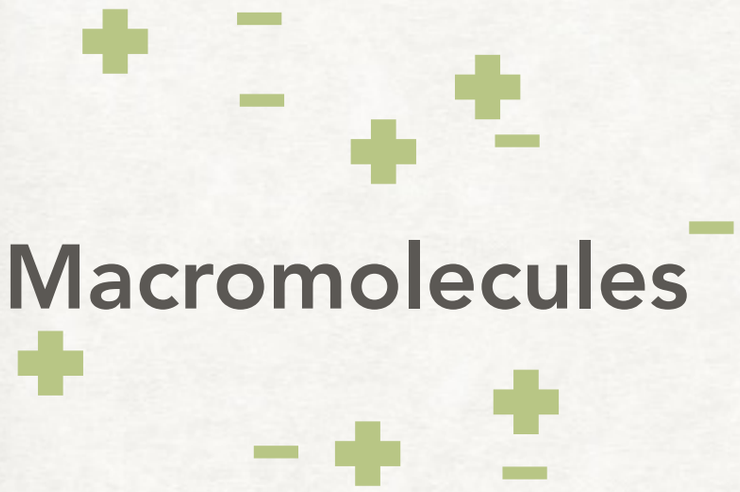
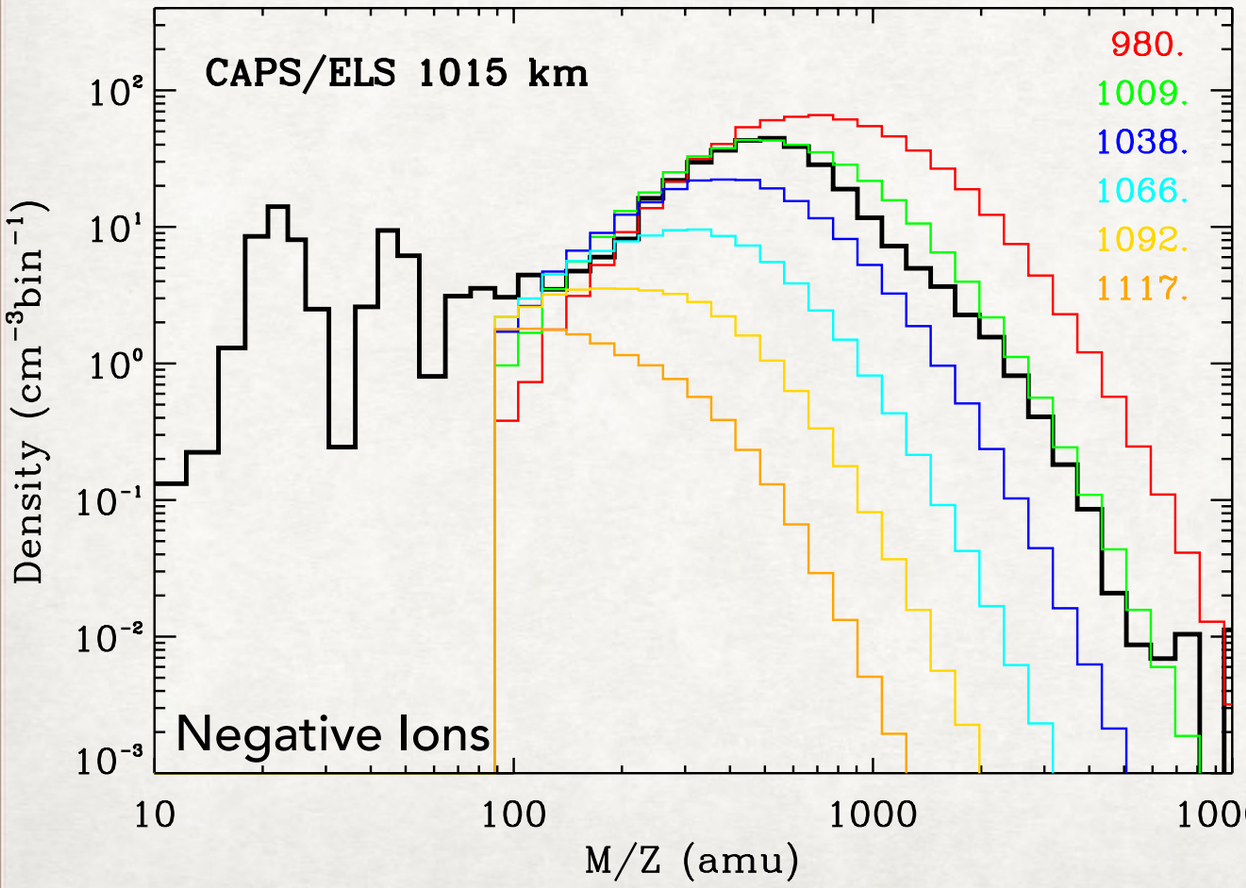
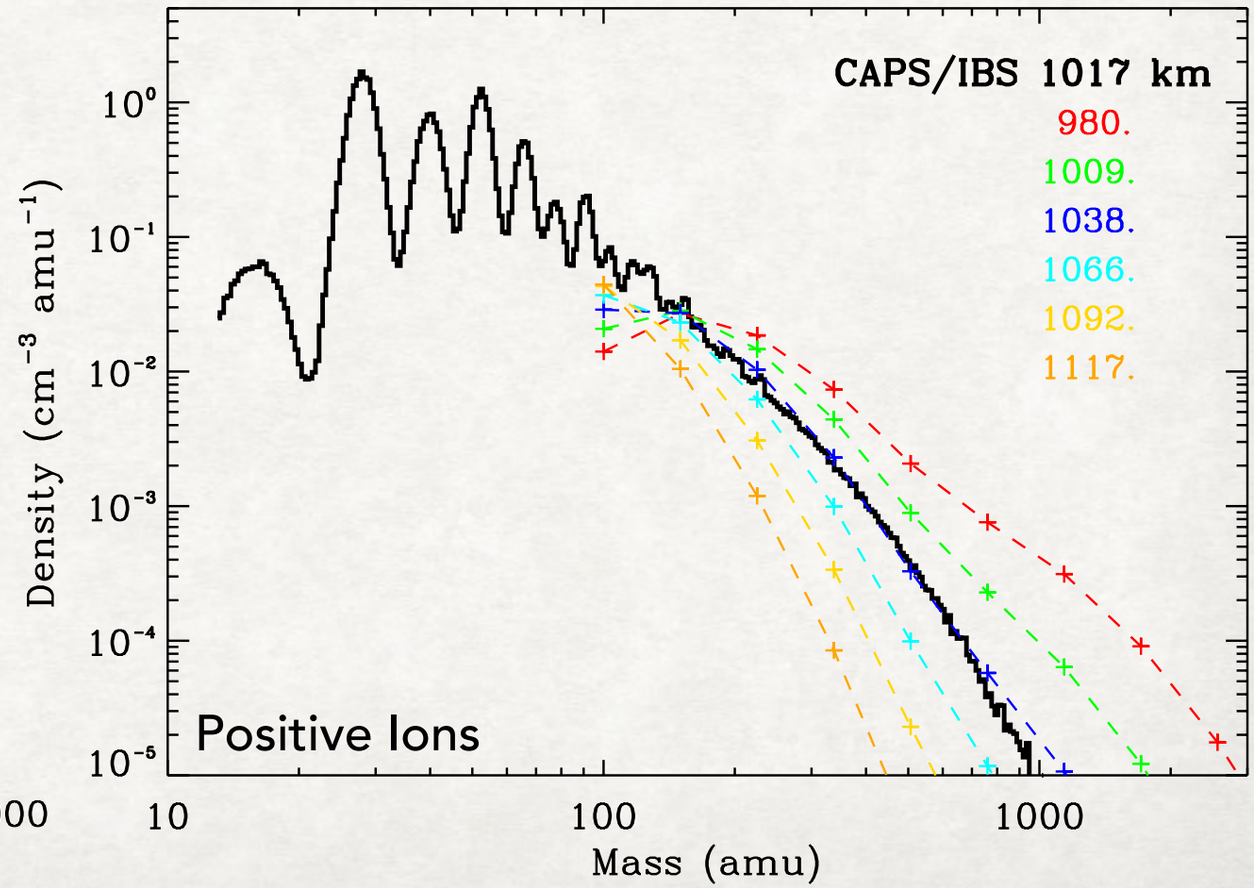


Macromolecules

Recombination leads to
mass transfer to macromolecules

Lavvas et al. 2013





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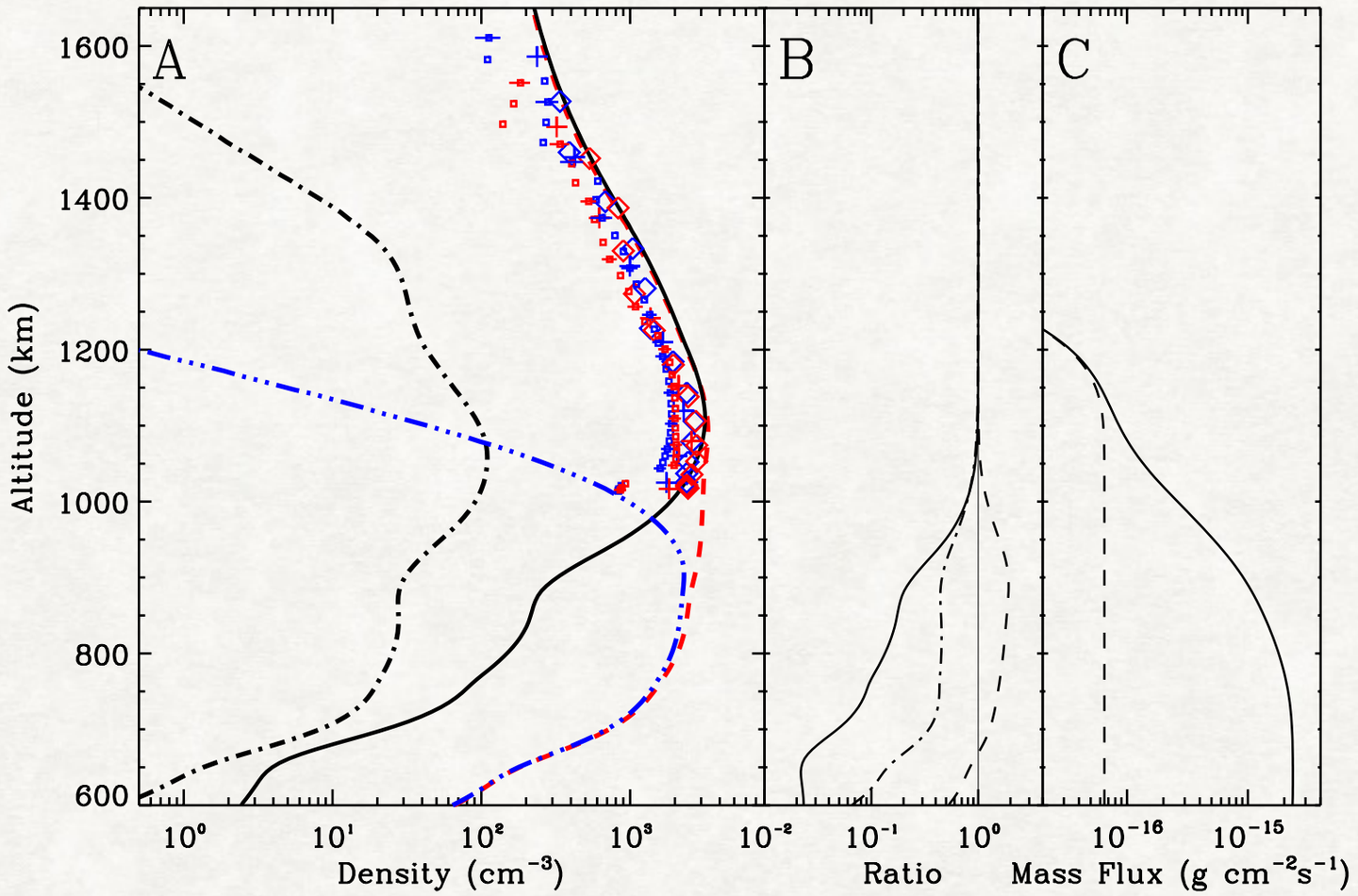

Aerosol Mass flux from DISR observations : ~3×10^{-14} g $cm^{-2}s^{-1}$ (Lavvas et al. 2010)

Ion chemistry drives a rapid formation of aerosol embryos
but is not sufficient to explain the total mass flux of aerosols observed.

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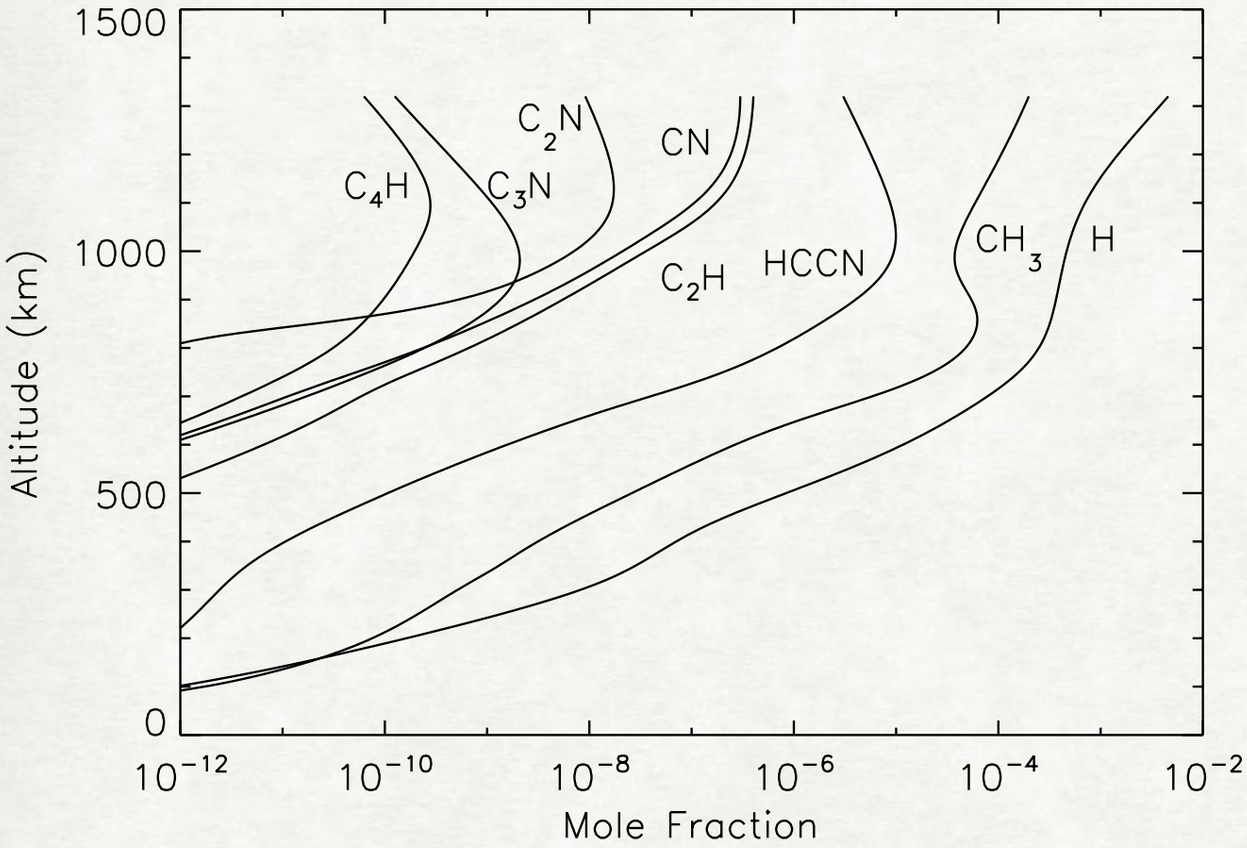
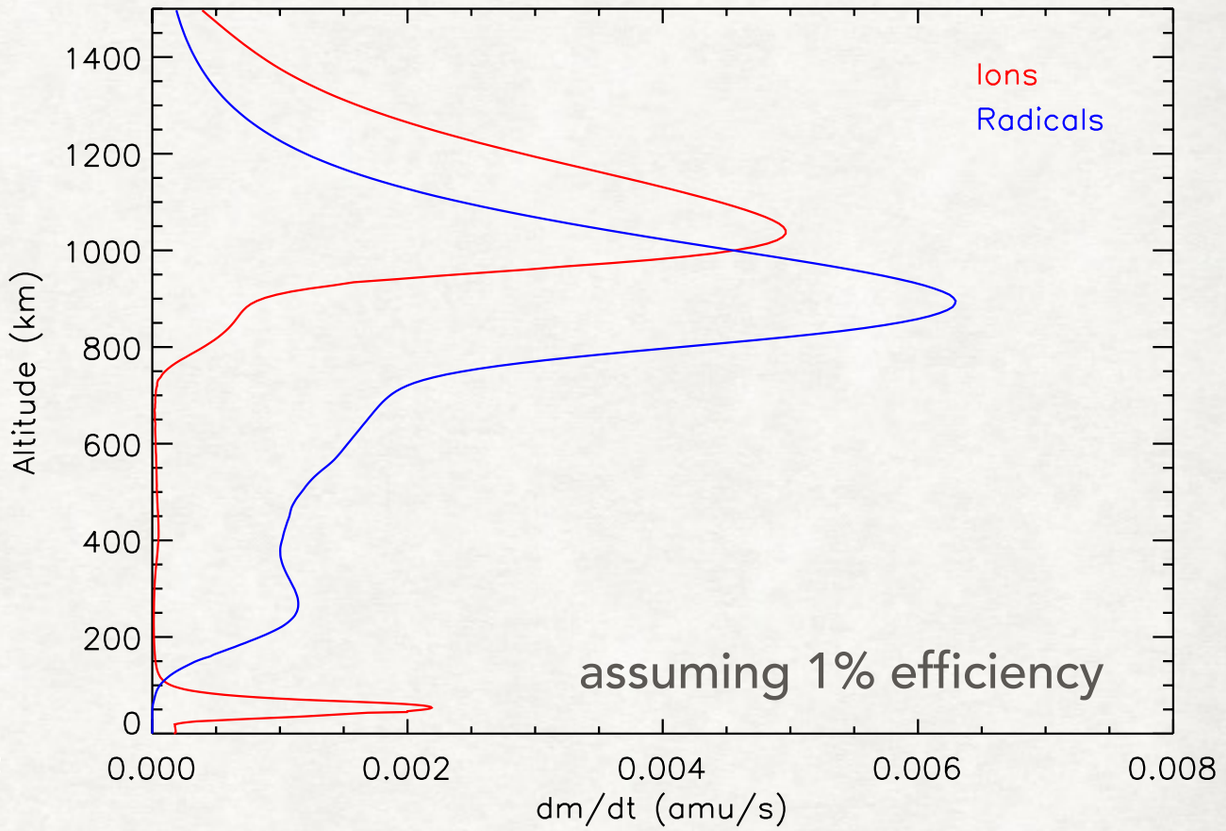
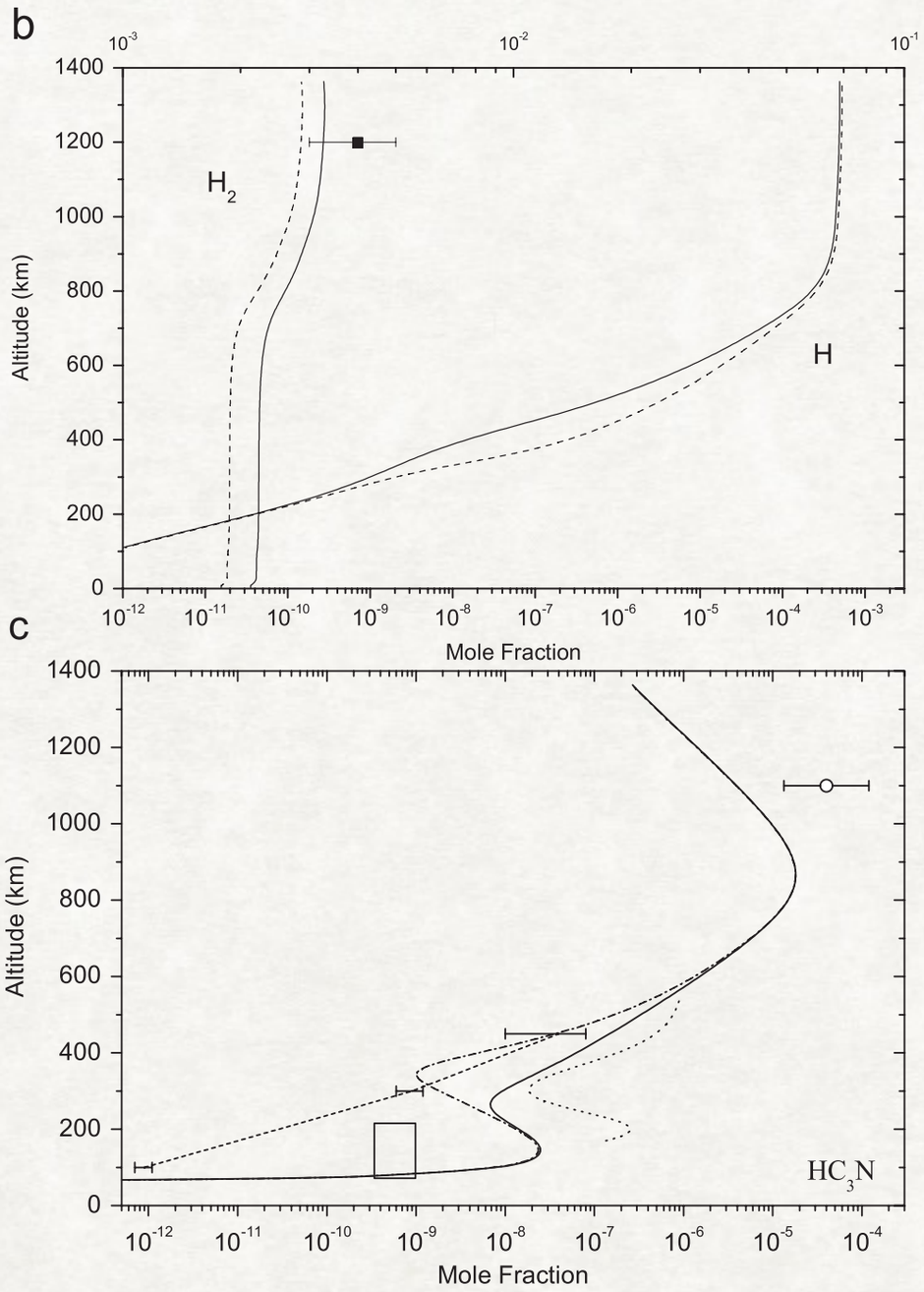
HETEROGENEOUS CHEMISTRY



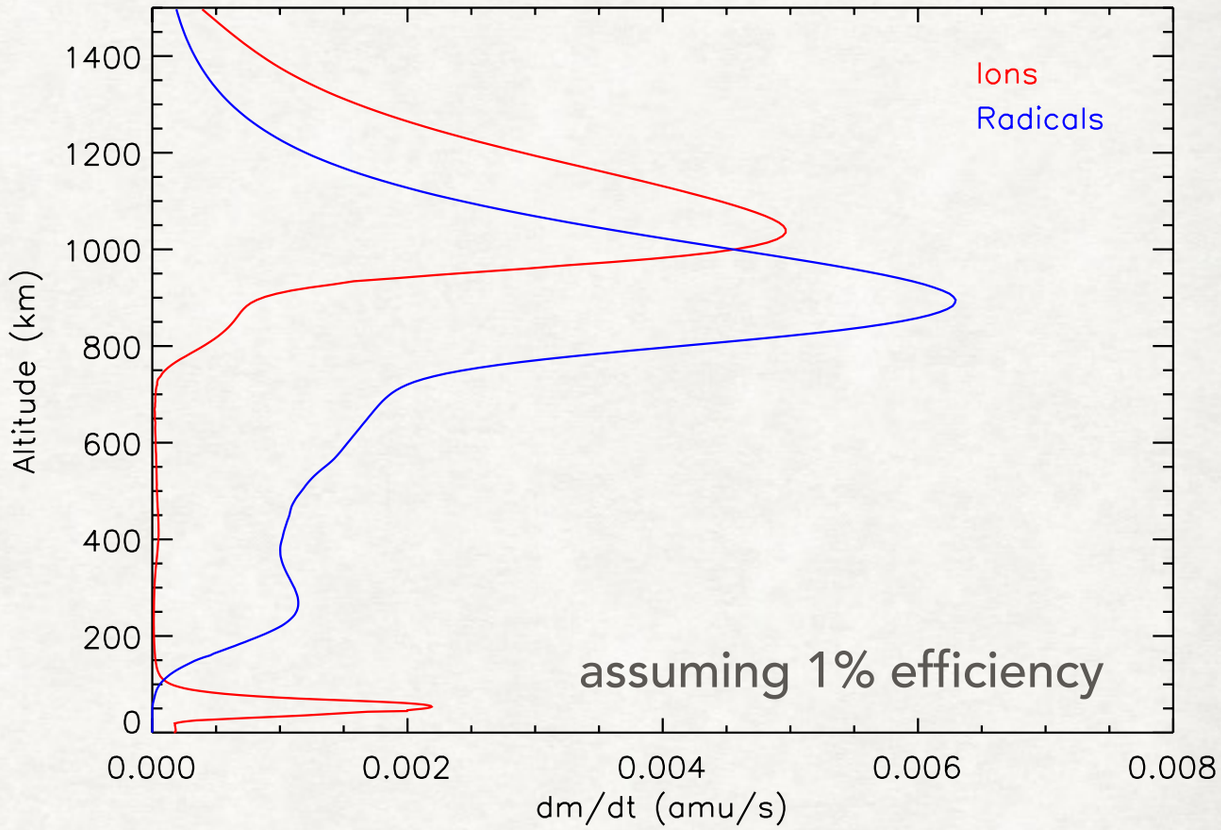


Heterogeneous reactions with neutral components can provide a further addition to the aerosol mass flux as well as affect the gaseous abundances.

TITAN



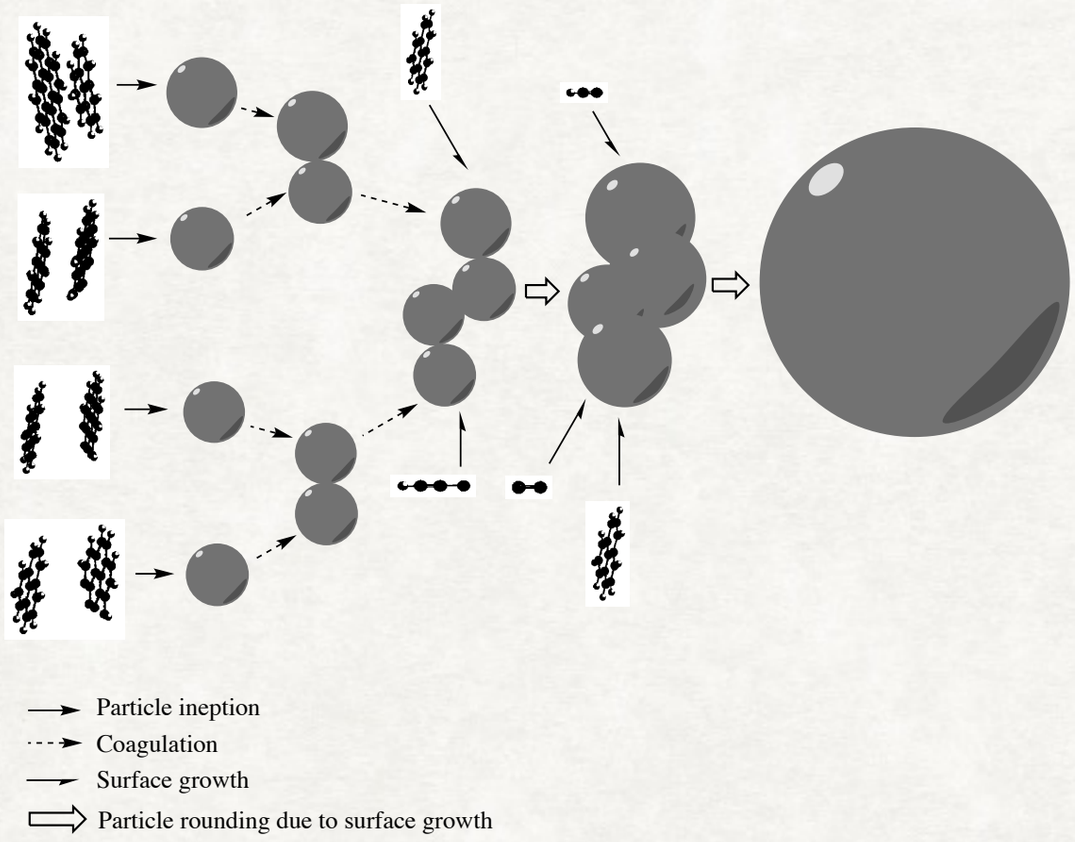
HETEROGENEOUS CHEMISTRY



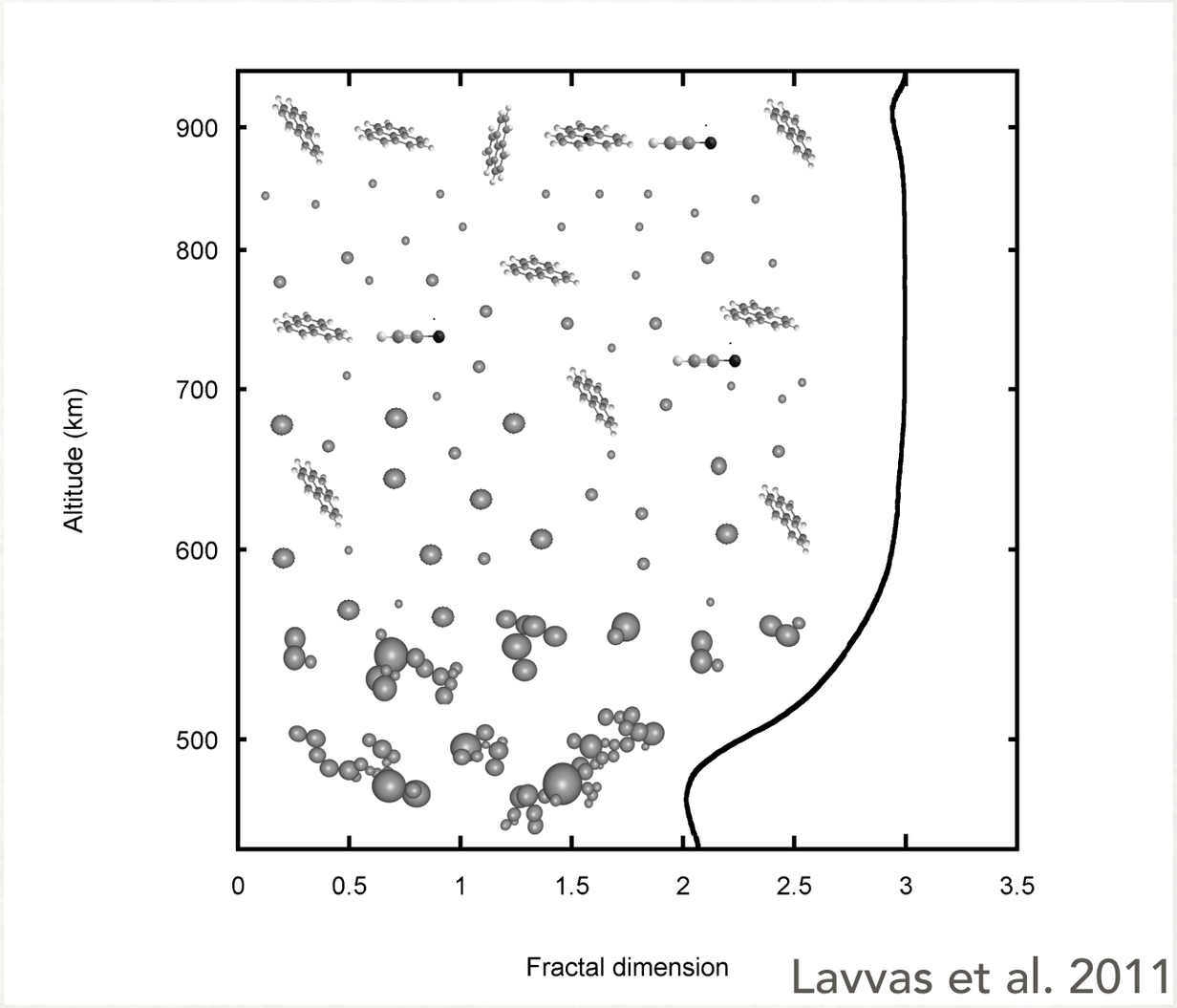
Lavvas et al. 2008
Sekine et al. 2008

Heterogeneous reactions with neutral components can provide a further addition to the aerosol mass flux as well as affect the gaseous abundances.

TITAN



HETEROGENEOUS CHEMISTRY



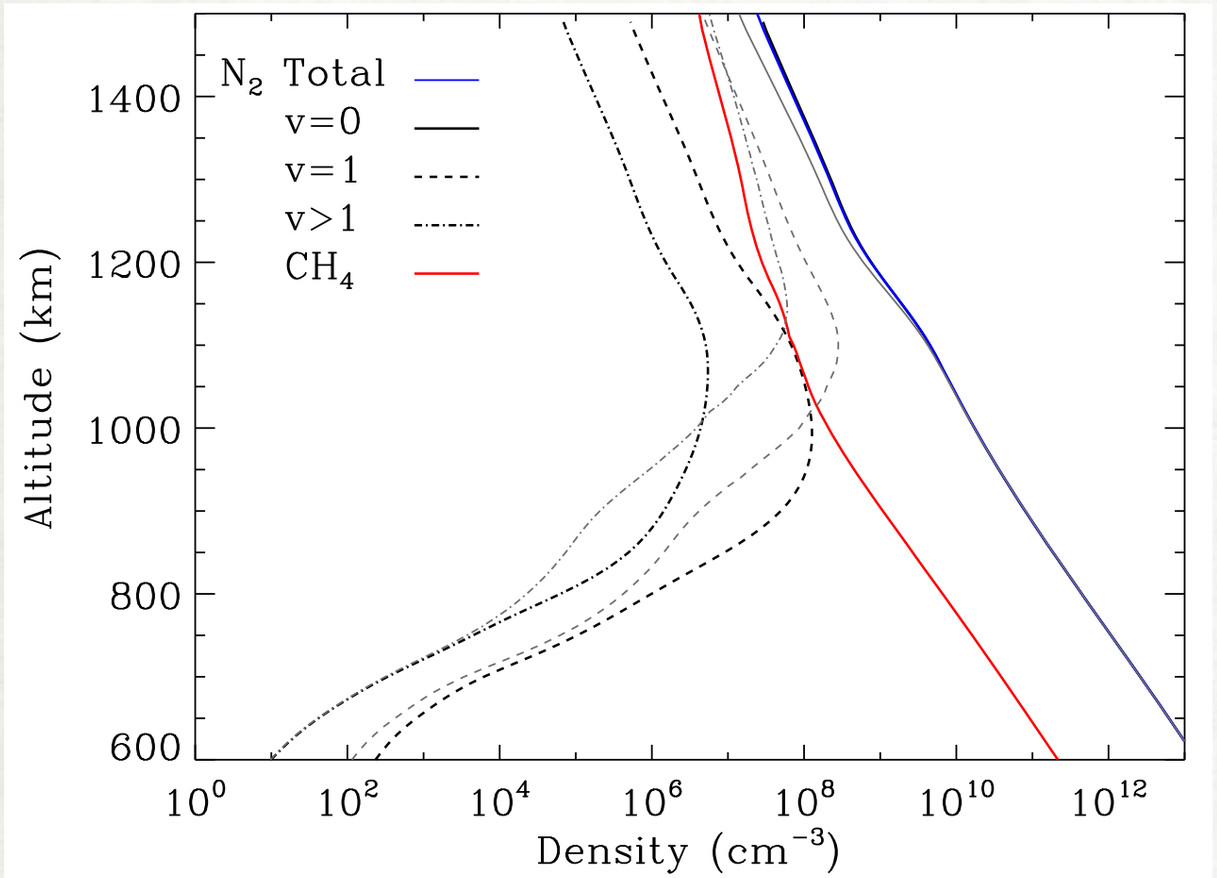
Lavvas et al. 2011

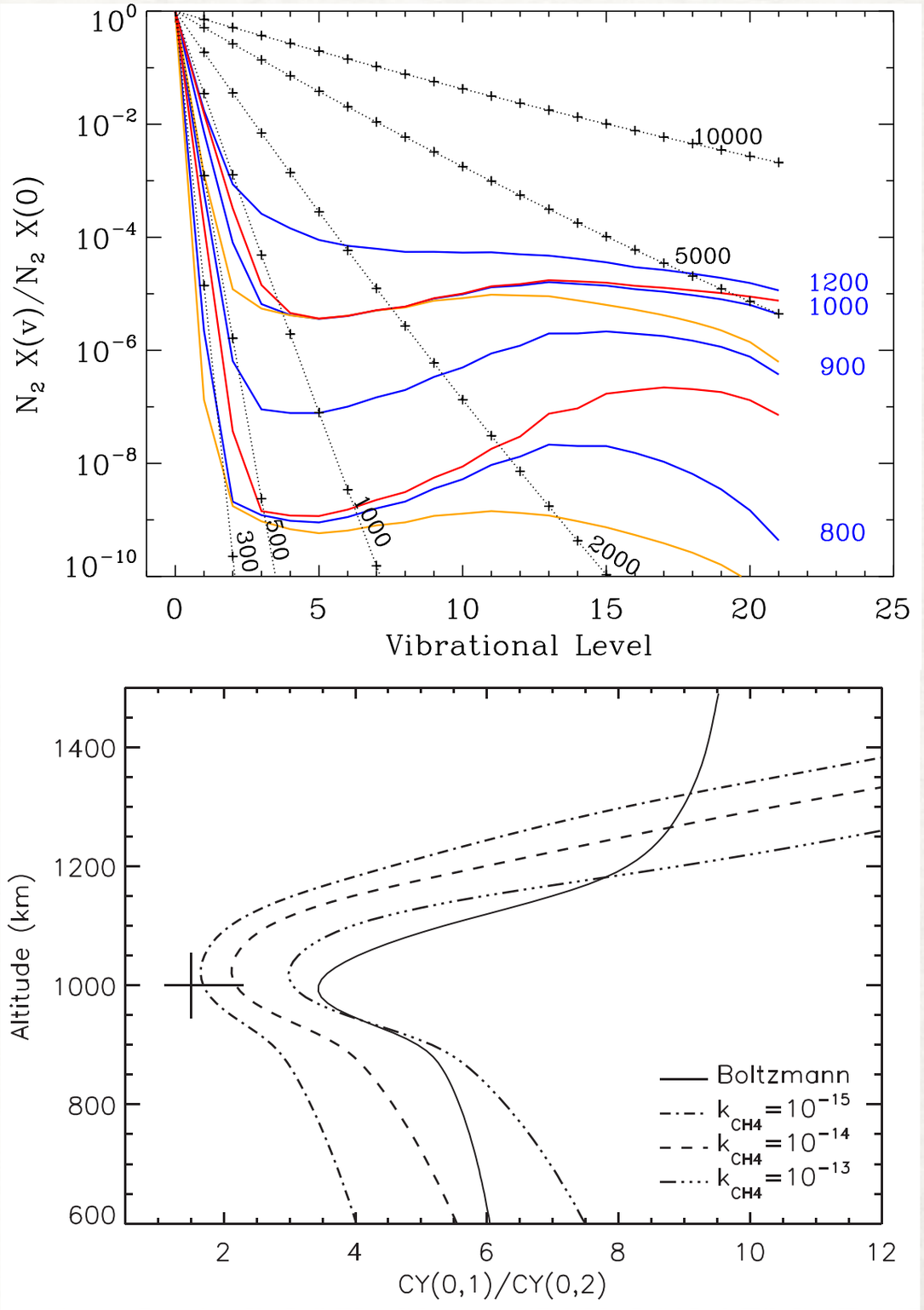
Heterogeneous reactions affect the particle shape and the transition from spheres to aggregates

Need new input from laboratory studies

Hot N_2

Lavvas et al. 2015





Chemical implications unknown

Conclusions

Titan’s atmosphere is the most complex organic laboratory in our Solar system

Ion-Neutral chemistry has a fundamental role in the formation of complex molecules and eventually to the birth of the photochemical aerosols in Titan’s atmosphere

Neutral chemistry generates the most abundant photochemical products and drives that growth of the photochemical aerosols through heterogeneous reactions

Titan, through Cassini-Huygens, has provided valuable lessons on complex chemistry and photochemical aerosol formation and evolution that help us understand other environments (Pluto, Giant Planets, Exoplanets)