INAUGURAL WORKSHOP ON NUCLEAR ASTROCHEMISTRY
26 FEBRUARY 2024 – 01 MARCH 2024, ECT*, VILLA TAMBOSI, VILLAZZANO(TN)

Molecular complexity in space, from the interstellar medium to planetary atmospheres

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Let me introduce myself: I am a chemist (not a biochemist) and I study the chemistry of rarefied gases

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… I am interested in astrochemistry, cosmochemistry, prebiotic chemistry and astrobiology

ALMA

FAUST

PRIN – 2020

BEYOND-2p

Astrochemistry beyond the Second Period Elements

ASI MIGLIORA (prebiotic chemistry) + PRIN PNRR ThermOPoly (degradation of space-technology polymers by thermospheric oxygen) just started

Dawn of Organic Chemistry

erc

ACO

EU H2020 Innovative Training Network

Astro-Chemical Origins

Genesis-SKA

Italian Project of Astrobiology

LIFE in SPACE – Origin, Presence, Persistence of life in Space: from molecules to extremophiles

NOEMA

SOLIS

Seeds Of Life In Space

Let me introduce myself: I am a chemist (not a biochemist) and I study the chemistry of rarefied gases

there are no test tubes in my lab

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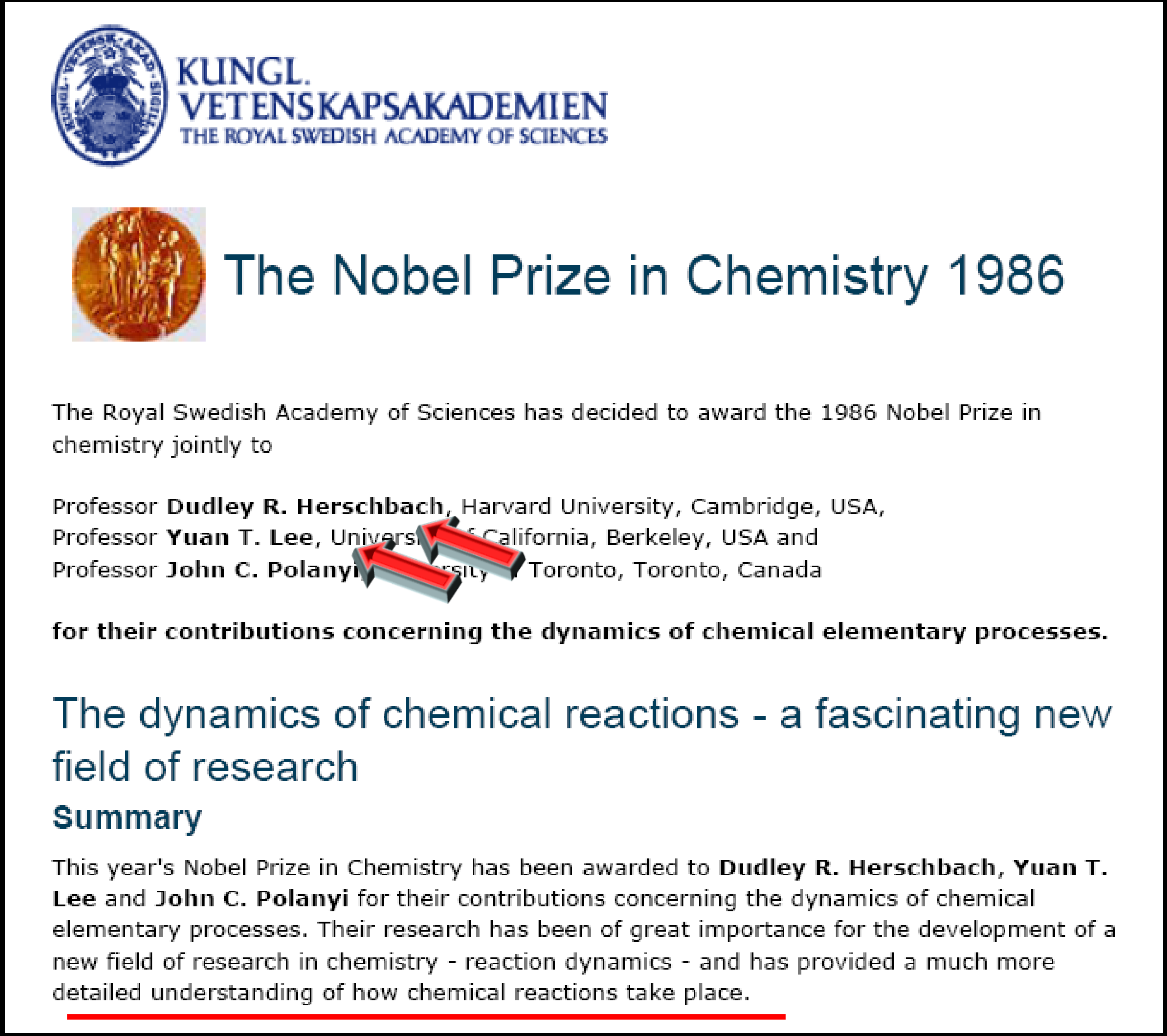
You are seeing a crossed molecular beam apparatus to study reactive bimolecular collisions

The CMB technique: an experimental technique born to address fundamental issues that (by chance) nicely reproduce the low number density conditions of the interstellar medium or upper planetary atmospheres



KUNGL.
VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

The Nobel Prize in Chemistry 1986

The Royal Swedish Academy of Sciences has decided to award the 1986 Nobel Prize in chemistry jointly to

Professor **Dudley R. Herschbach**, Harvard University, Cambridge, USA,
Professor **Yuan T. Lee**, University of California, Berkeley, USA and
Professor **John C. Polanyi**, University of Toronto, Toronto, Canada

for their contributions concerning the dynamics of chemical elementary processes.

The dynamics of chemical reactions - a fascinating new field of research

Summary

This year's Nobel Prize in Chemistry has been awarded to **Dudley R. Herschbach, Yuan T. Lee** and **John C. Polanyi** for their contributions concerning the dynamics of chemical elementary processes. Their research has been of great importance for the development of a new field of research in chemistry - reaction dynamics - and has provided a much more detailed understanding of how chemical reactions take place.

During my master thesis: we studied what we could study

now: we study what we want to study

Molecular complexity in space

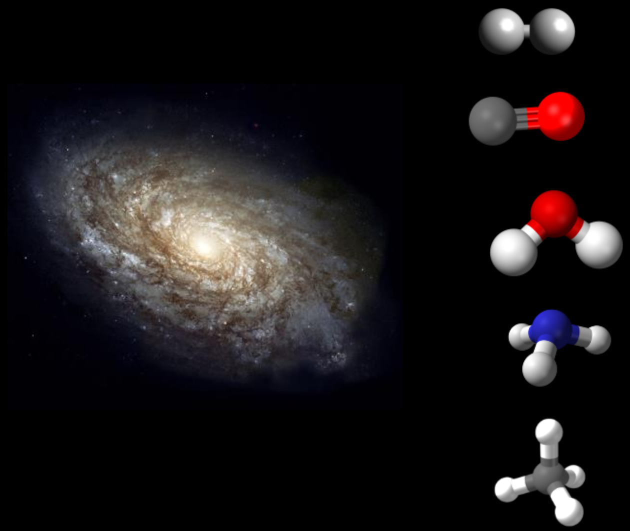
Why do we care to begin with?

Where do we find it?

How does it work?

For a chemist, the most interesting challenge is to understand how living matter originated from inanimate matter

most common molecules in the Galaxy



Increase in complexity: how does the increase in molecular complexity occur?

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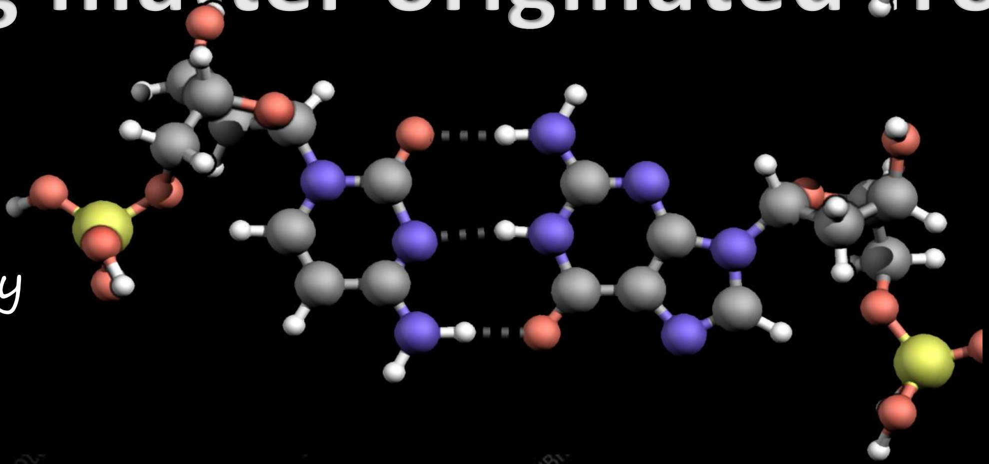

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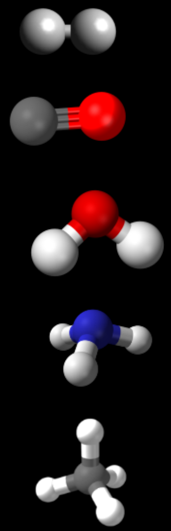
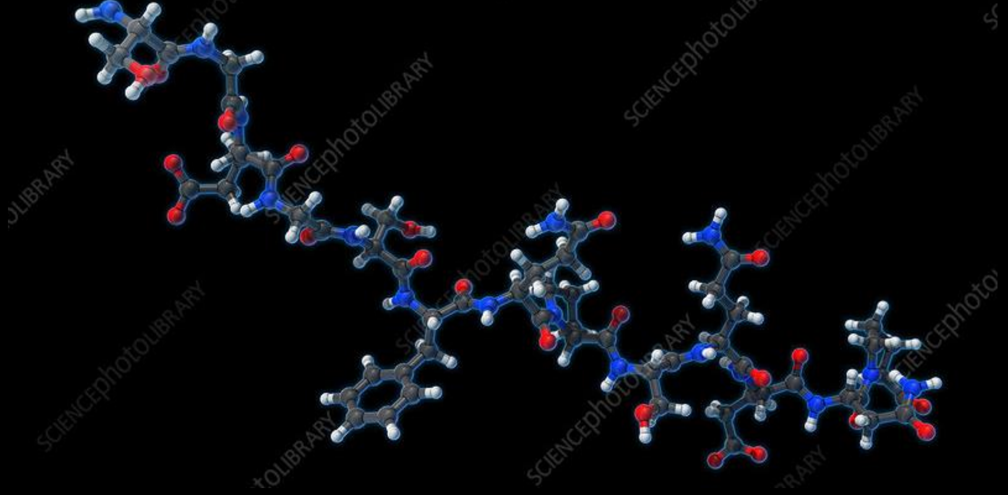
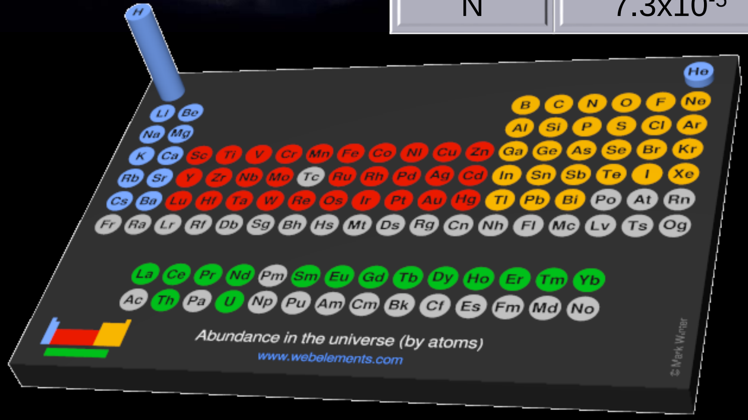




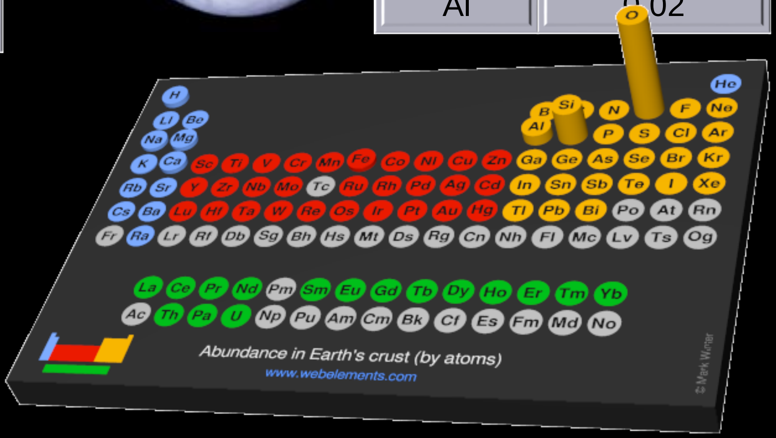
Increase in complexity: how does the increase in molecular complexity occur?

Chemical composition: Universe vs human body

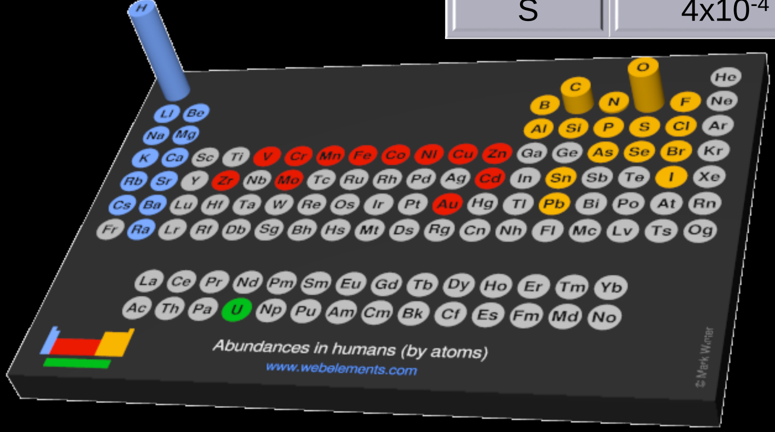
element	molar fraction
H	0.91
He	0.09
O	2.7×10^{-4}
C	1.3×10^{-4}
N	7.3×10^{-5}



element	molar fraction
O	0.48
Mg	0.16
Si	0.15
Fe	0.15
Al	0.02



element	molar fraction
H	0.63
O	0.24
C	0.12
N	0.01
S	4×10^{-4}



Chemical composition: Universe vs human body

are we aliens?

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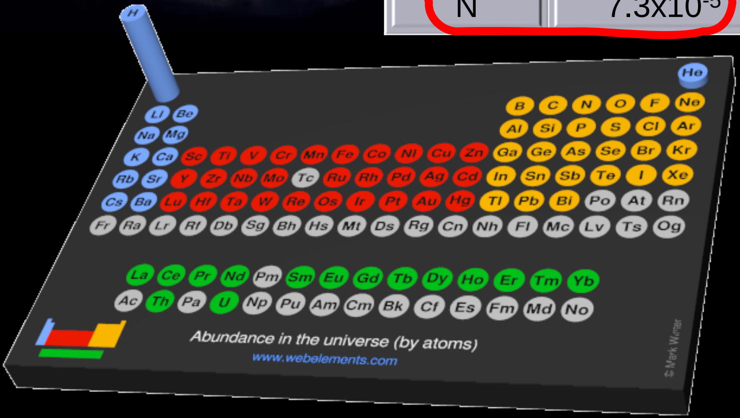

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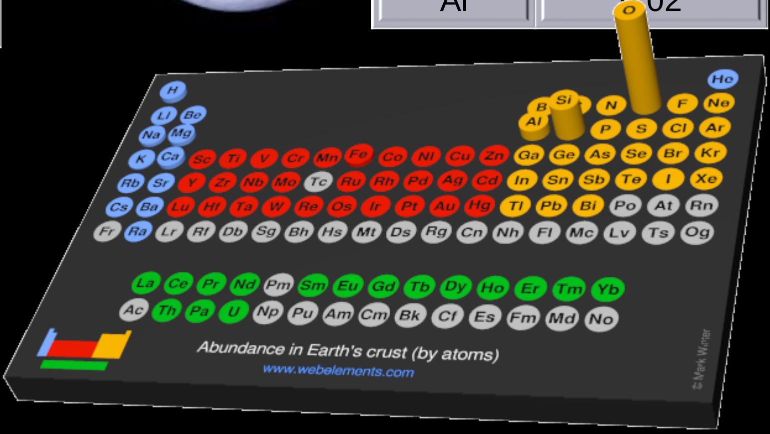

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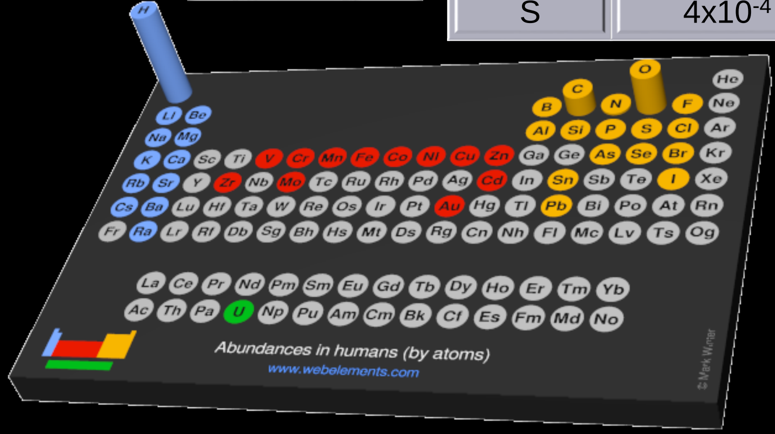
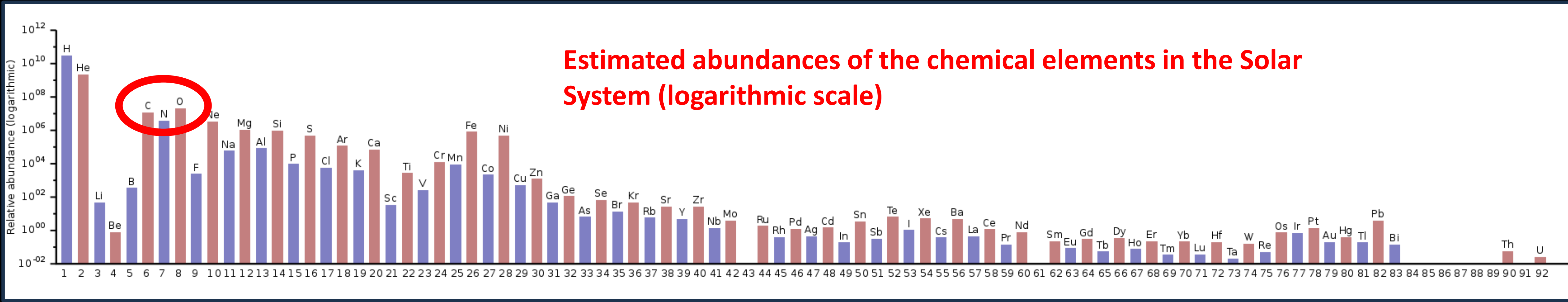
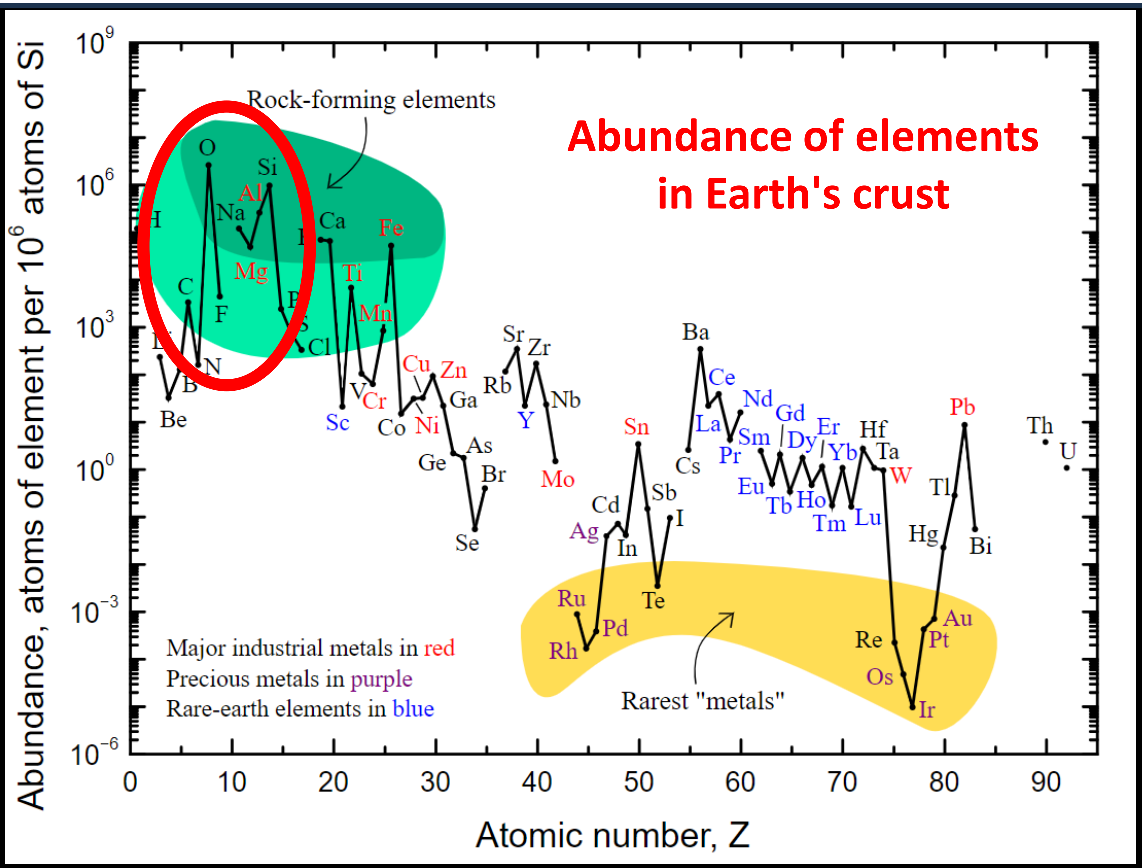




Estimated abundances of the chemical elements in the Solar System (logarithmic scale)

A little amount of carbon and mostly in the wrong form (CO_2 or carbonates)

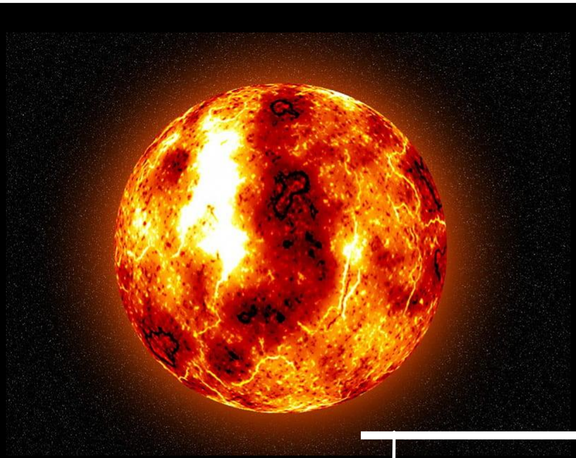
Carbon is present in oxidized forms while life requires reduced carbon



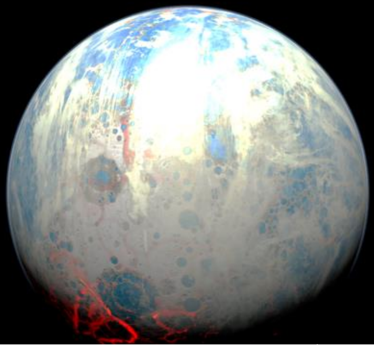
Abundance of elements in Earth's crust

Internal rocky planets are depleted of volatile species AND of carbon

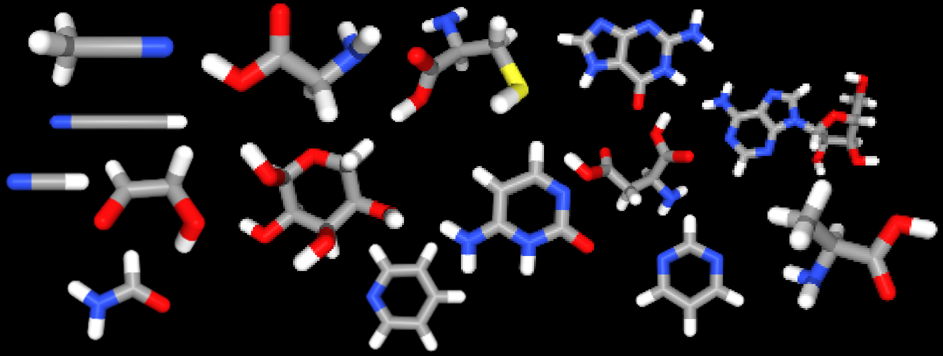
Basic steps in the origin of life



4.5 billion years ago:
Formation of the
Solar System and
planet Earth



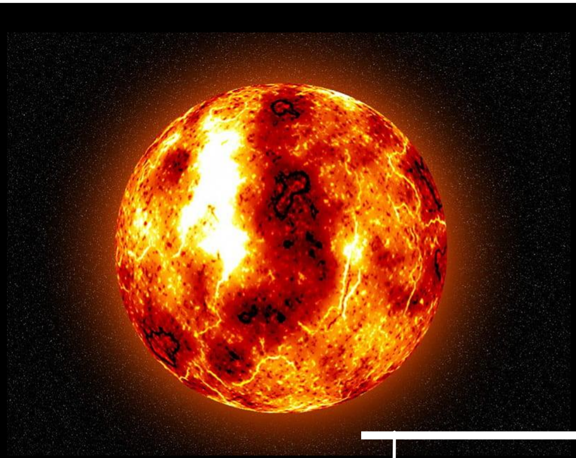
4.2 billion years ago:
Stable hydrosphere

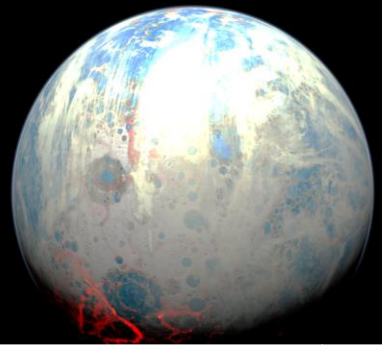


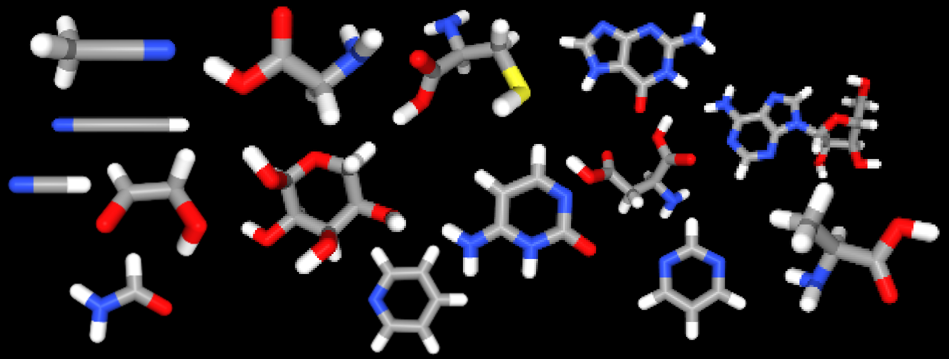
4.2–4.0 billion years ago:
Prebiotic chemistry

Adapted from G. F. Joyce, Nature (2002)

Basic steps in the origin of life







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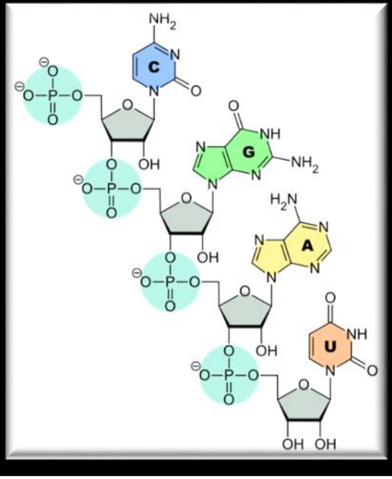
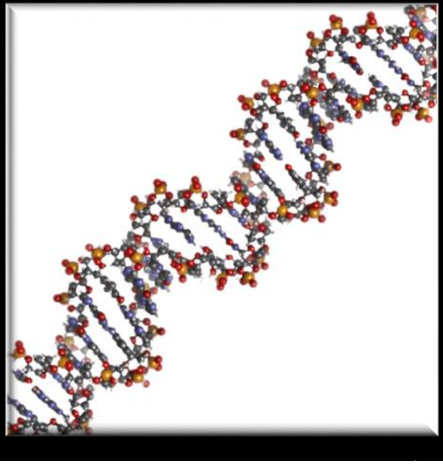
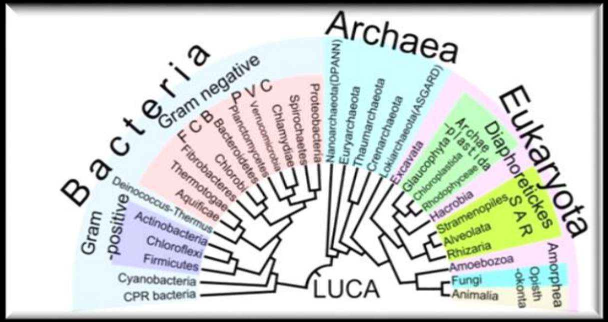






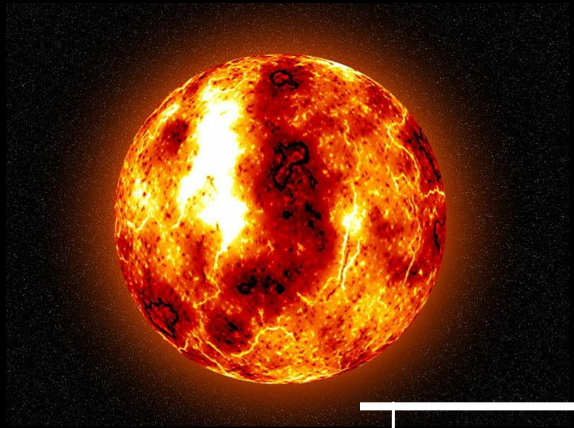
ca. 4 billion years ago:
Pre-RNA and RNA world

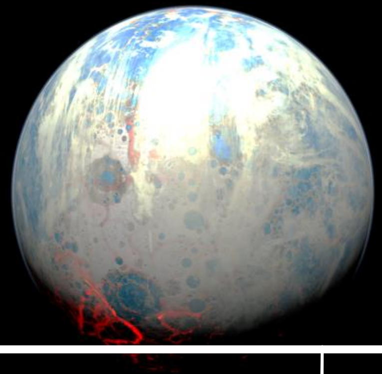
ca. 3.6 billion years ago:
First DNA /protein life

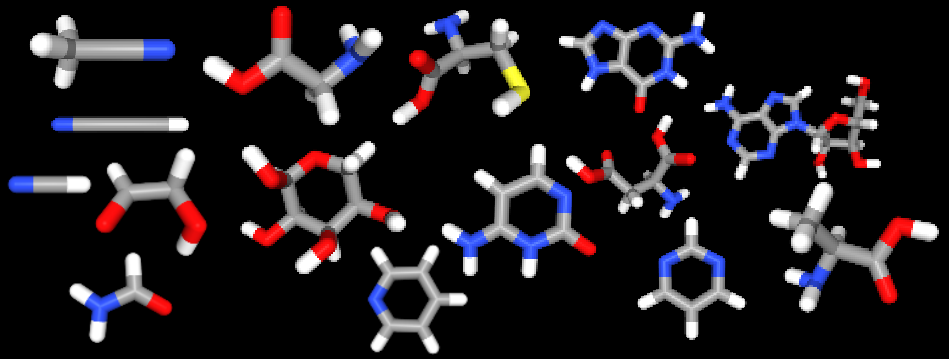
3.6 billion years ago – now:
Diversification of life

Adapted from G. F. Joyce, Nature (2002)

Basic steps in the origin of life







4.5 billion years ago:
Formation of the
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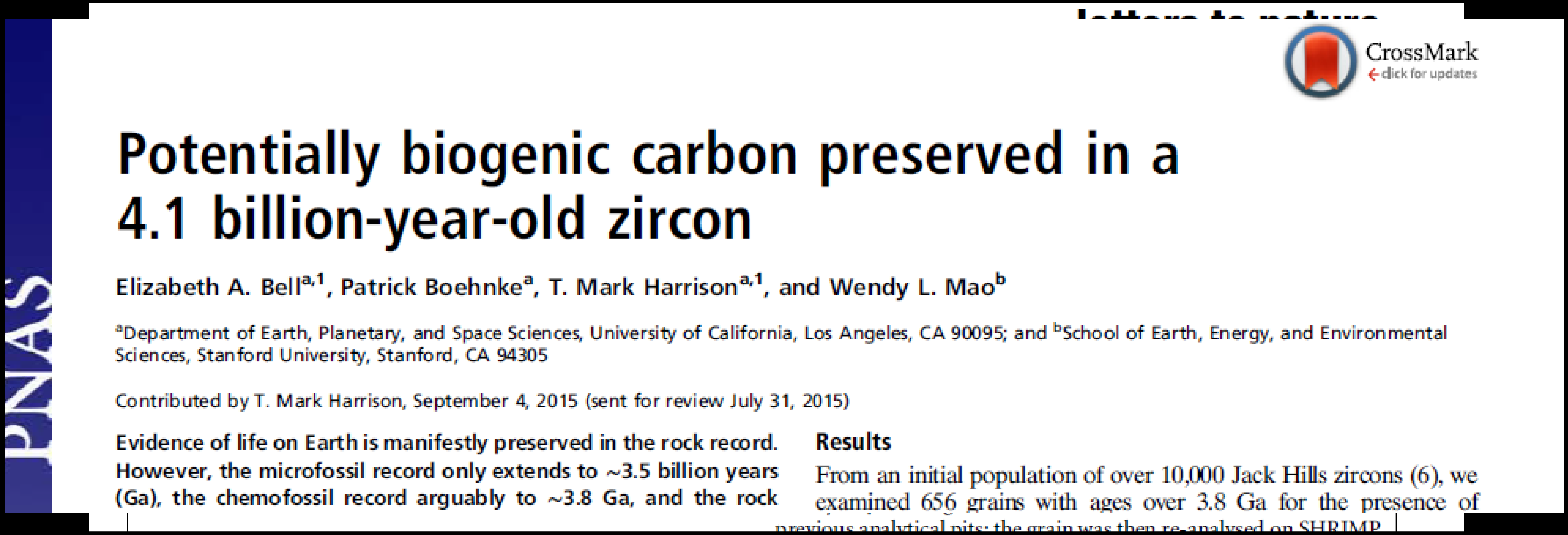
4.4

4.2 billion years ago:
Stable hydrosphere

before 4.1

4.2–4.0 billion years ago:
Prebiotic chemistry

THE FIRST STEPS HAVE PROBABLY BEEN FASTER THAN WHAT WE HAVE THOUGHT



Potentially biogenic carbon preserved in a 4.1 billion-year-old zircon

Elizabeth A. Bell[a,1], Patrick Boehnke[a], T. Mark Harrison[a,1], and Wendy L. Mao[b]

[a]Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, CA 90095; and [b]School of Earth, Energy, and Environmental Sciences, Stanford University, Stanford, CA 94305

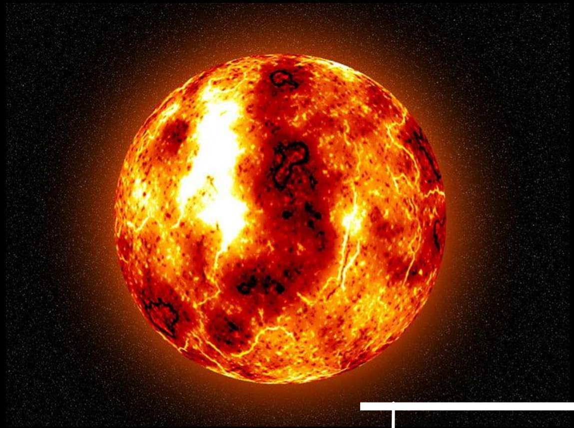
Contributed by T. Mark Harrison, September 4, 2015 (sent for review July 31, 2015)

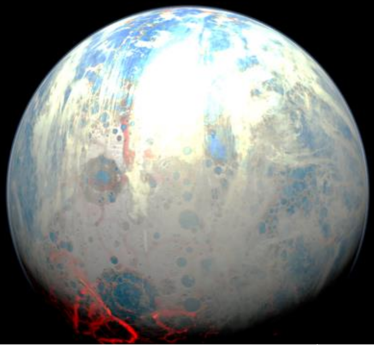
Evidence of life on Earth is manifestly preserved in the rock record. However, the microfossil record only extends to ~3.5 billion years (Ga), the chemofossil record arguably to ~3.8 Ga, and the rock

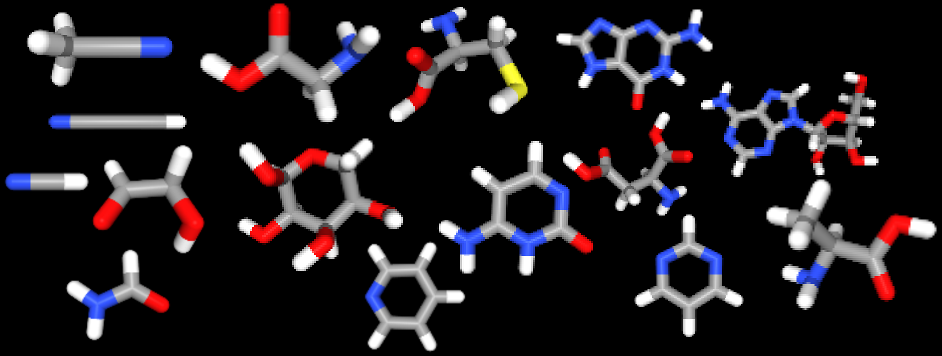
Results

From an initial population of over 10,000 Jack Hills zircons (6), we examined 656 grains with ages over 3.8 Ga for the presence of

Basic steps in the origin of life







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4.2 billion years ago:
Stable hydrosphere

before 4.1

4.2–4.0 billion years ago:
Prebiotic chemistry

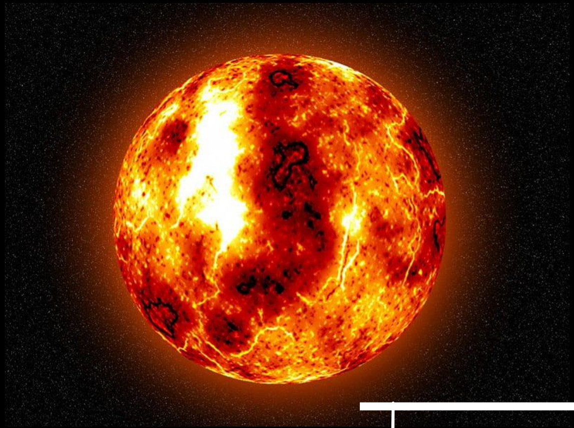
= organic chemistry

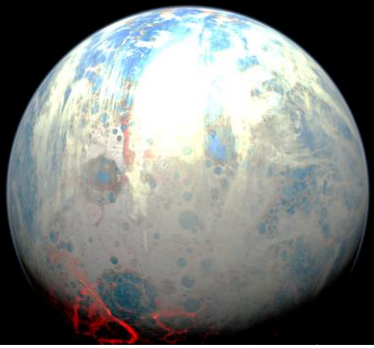
Nowadays, after billions of years of active photosynthesis that converted CO_2 into biochemicals, the total mass of living entities is only of the order of 5.5×10^{14} kg to be compared with 1.35×10^{21} kg of (surface) water. How could two aminoacids, randomly formed by sporadic favorable processes, meet each other and form a peptide bond in such an unfavorable scenario?

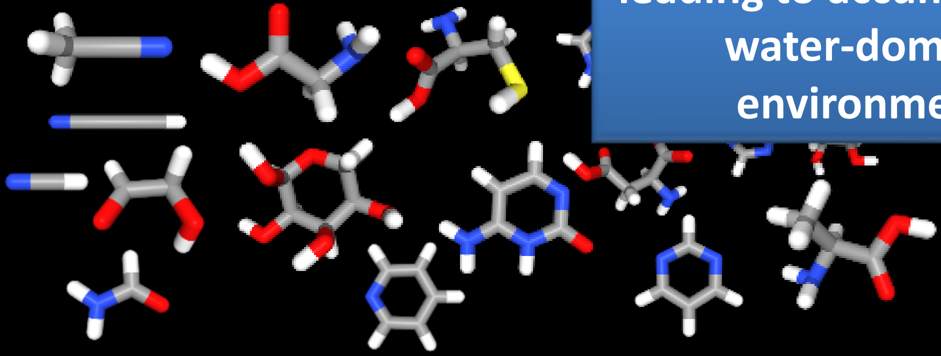
massive organic synthesis leading to accumulation in a water-dominated environment???

Basic steps in the origin of life

massive organic synthesis leading to accumulation in a water-dominated environment???







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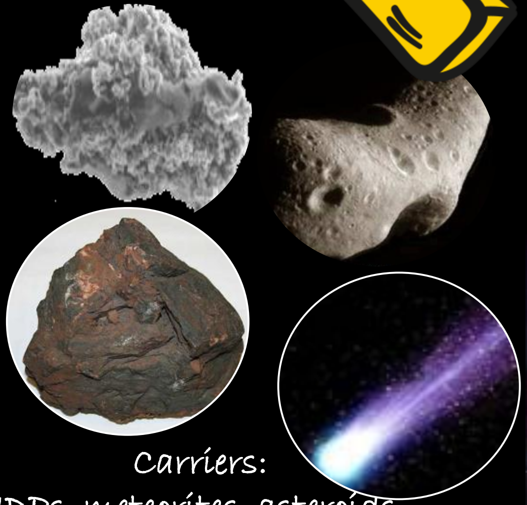
4.2-4.0 ears ago:
Prebic mistry

endogenous
synthesis of complex
organic molecules
from simple parent
species

exogenous
delivery

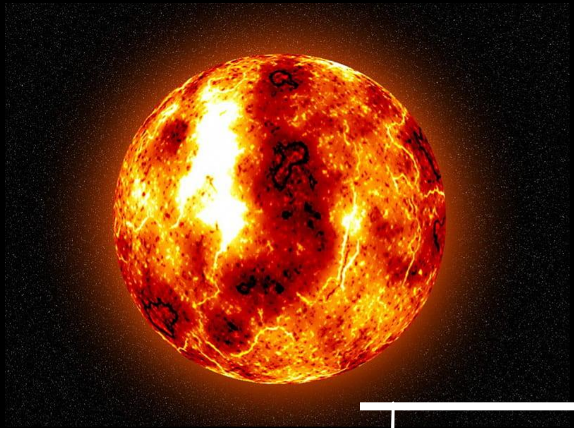


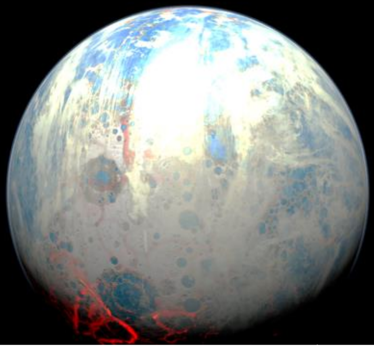
Carriers:
IDPs, meteorites, asteroids,
comets

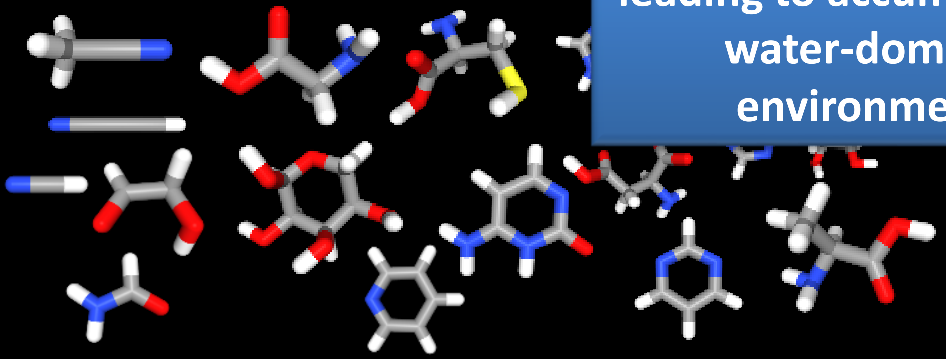
Star-forming
regions in the
interstellar
medium

Basic steps in the origin of life

massive organic synthesis leading to accumulation in a water-dominated environment???







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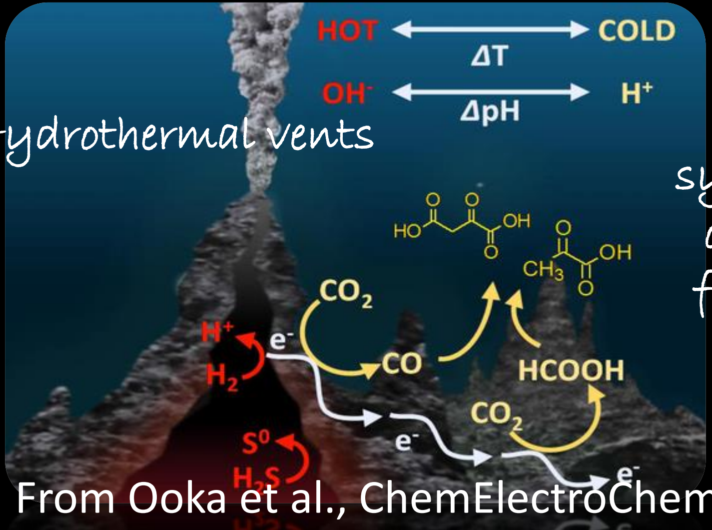
Prebic mistry

Hydrothermal vents



From Ooka et al., ChemElectroChem 2019

endogenous
synthesis of complex
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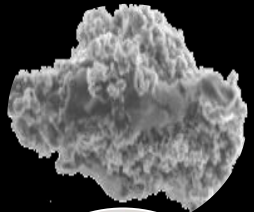

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Star-forming
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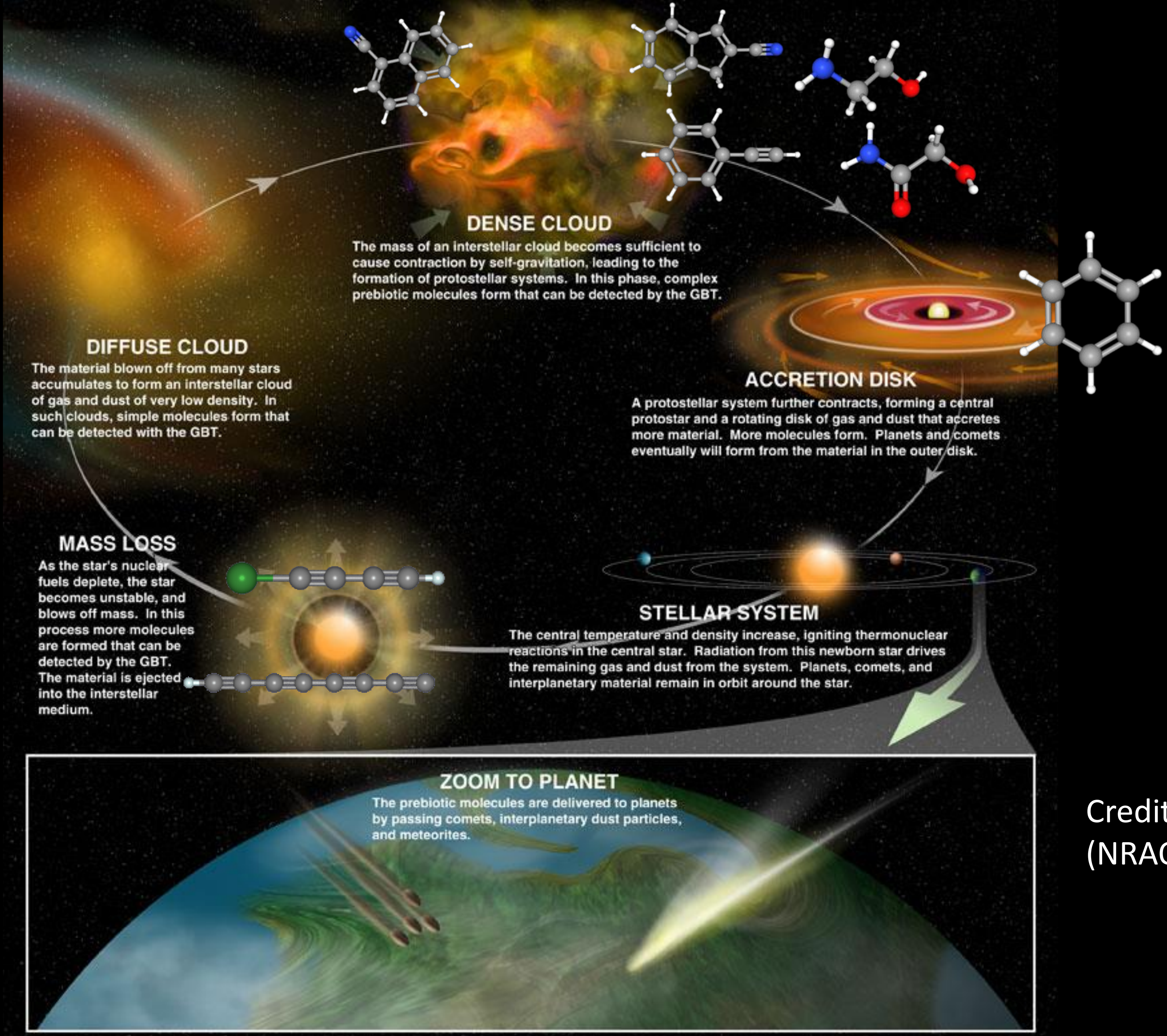


DENSE CLOUD

The mass of an interstellar cloud becomes sufficient to cause contraction by self-gravitation, leading to the formation of protostellar systems. In this phase, complex prebiotic molecules form that can be detected by the GBT.

ACCRETION DISK

A protostellar system further contracts, forming a central protostar and a rotating disk of gas and dust that accretes more material. More molecules form. Planets and comets eventually will form from the material in the outer disk.

STELLAR SYSTEM

The central temperature and density increase, igniting thermonuclear reactions in the central star. Radiation from this newborn star drives the remaining gas and dust from the system. Planets, comets, and interplanetary material remain in orbit around the star.

MASS LOSS

As the star's nuclear fuels deplete, the star becomes unstable, and blows off mass. In this process more molecules are formed that can be detected by the GBT. The material is ejected into the interstellar medium.

DIFFUSE CLOUD

The material blown off from many stars accumulates to form an interstellar cloud of gas and dust of very low density. In such clouds, simple molecules form that can be detected with the GBT.

ZOOM TO PLANET

The prebiotic molecules are delivered to planets by passing comets, interplanetary dust particles, and meteorites.

prebiotic molecules could be a legacy of ISM chemistry

Credit: Bill Saxton
(NRAO/AUI/NSF)

Prebiotic molecules in space (according to my own definition):

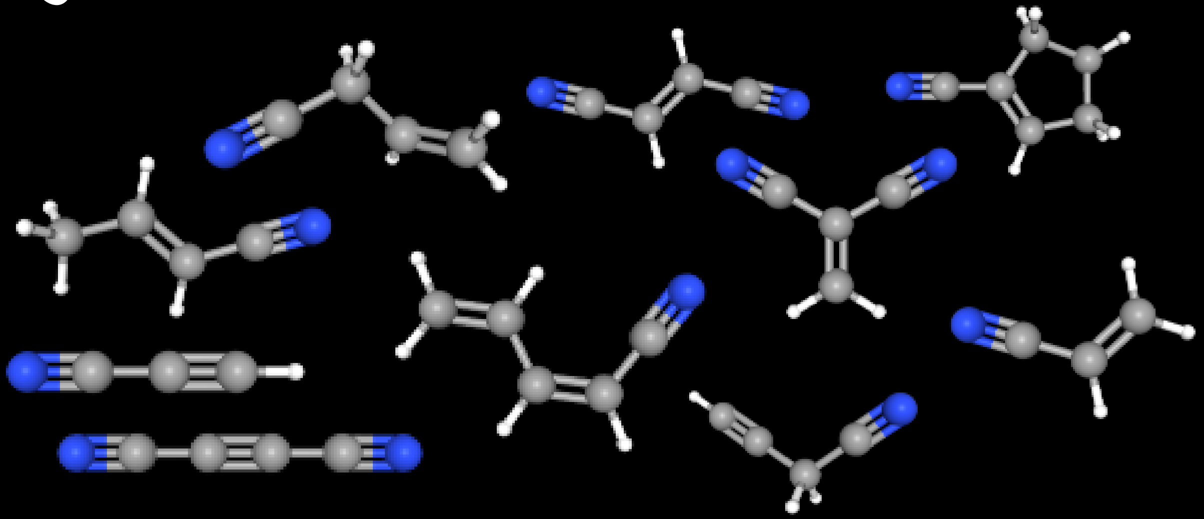
simple enough to be formed in abiotic processes, but containing the functional groups of biological molecules (or their precursors) AND having the capability to evolve in more complex species

Prebiotic molecules in space (according to my own definition):

simple enough to be formed in abiotic processes, but containing the functional groups of biological molecules (or their precursors) AND having the capability to evolve in more complex species

have they been observed in the interstellar medium?

e.g. unsaturated nitriles



Why them? In the presence of liquid water they easily hydrolyze forming amino acids

Identified interstellar and circumstellar species

2 atoms

AlF AlCl C_2 CH CH^+ CN CO CO^+ CP CS CSi HCl H_2 KCl NH NO NS NaCl OH PN SO SO^+ SiN SiO SiS HF SH FeO S_2 CF^+ O_2 PO SH^+
AlO ArH^+ NO^+ TiO HCl^+ NS^+ CrO

from www.astrochymist.org

3 atoms

C_3 C_2H C_2O C_2S CH_2 HCN HCO HCO^+ HCS^+ HOC^+ H_2O H_2S HNC HNO MgCN MgNC N_2H^+ N_2O NaCN OCS SO_2 c-SiC_2 CO_2 NH_2 H_3^+
AlNC FeCN KCN SiNC HCP CCP SiCSi CCN TiO_2 HO_2 HCS S_2H

4 atoms

c-C_3H l-C_3H C_3N C_3O C_3S C_2H_2 CH_2D^+ HCCN $HCNH^+$ HNCO HNCS $HOCO^+$ H_2CO H_2CN H_2CS H_3O^+ NH_3 SiC_3 C_3N^- PH_3 HCNO HOCN
HCCO NCCP MgCCH HMgNC l-C_3H^+ H_2O_2

5 atoms

C_5 C_4H C_4Si l-C_3H_2 c-C_3H_2 CH_2CN CH_4 HCCCN HC_2NC HCOOH CH_2NH H_2C_2O H_2NCN HNC_3 SiH_4 H_2COH^+ C_4H^- CNCHO $NCCNH^+$
NH_3D^+ H_2NCO^+ CH_3O HNCNH CH_3Cl

+ PAHs family

6 atoms

C_5H C_5O C_2H_4 CH_3CN CH_3NC CH_3OH CH_3SH HC_3NH^+ HC_2CHO $HCONH_2$ l-H_2C_4 C_5N HC_4N c-H_2C_3O CH_2CNH C_5N^- C_5S CNCHNH
SiH_3CN

ca. 300 molecules
Less than 40 species do not contain carbon !!

7 atoms

C_6H CH_2CHCN CH_3C_2H HC_5N $HCOCH_3$ NH_2CH_3 c-C_2H_4O

8 atoms

CH_3C_3N $HCOOCH_3$ CH_3COOH C_7H H_2C_6 CH_2OHCHO CH_2CHCHO C_2H_6 CH_2CCHCN NH_2CH_2CN $(NH_2)_2CO$ CH_3CHNH CH_3SiH_3

9 atoms

CH_3C_4H CH_3CH_2CN $(CH_3)_2O$ CH_3CH_2OH HC_7N C_8H CH_3CONH_2 C_8H^- CH_2CHCH_3 CH_3CH_2SH CH_3NHCHO HC_7O CH_2CHCH_2CN
H2CCHC3N H2CCCHCCH H2CCCHCCH

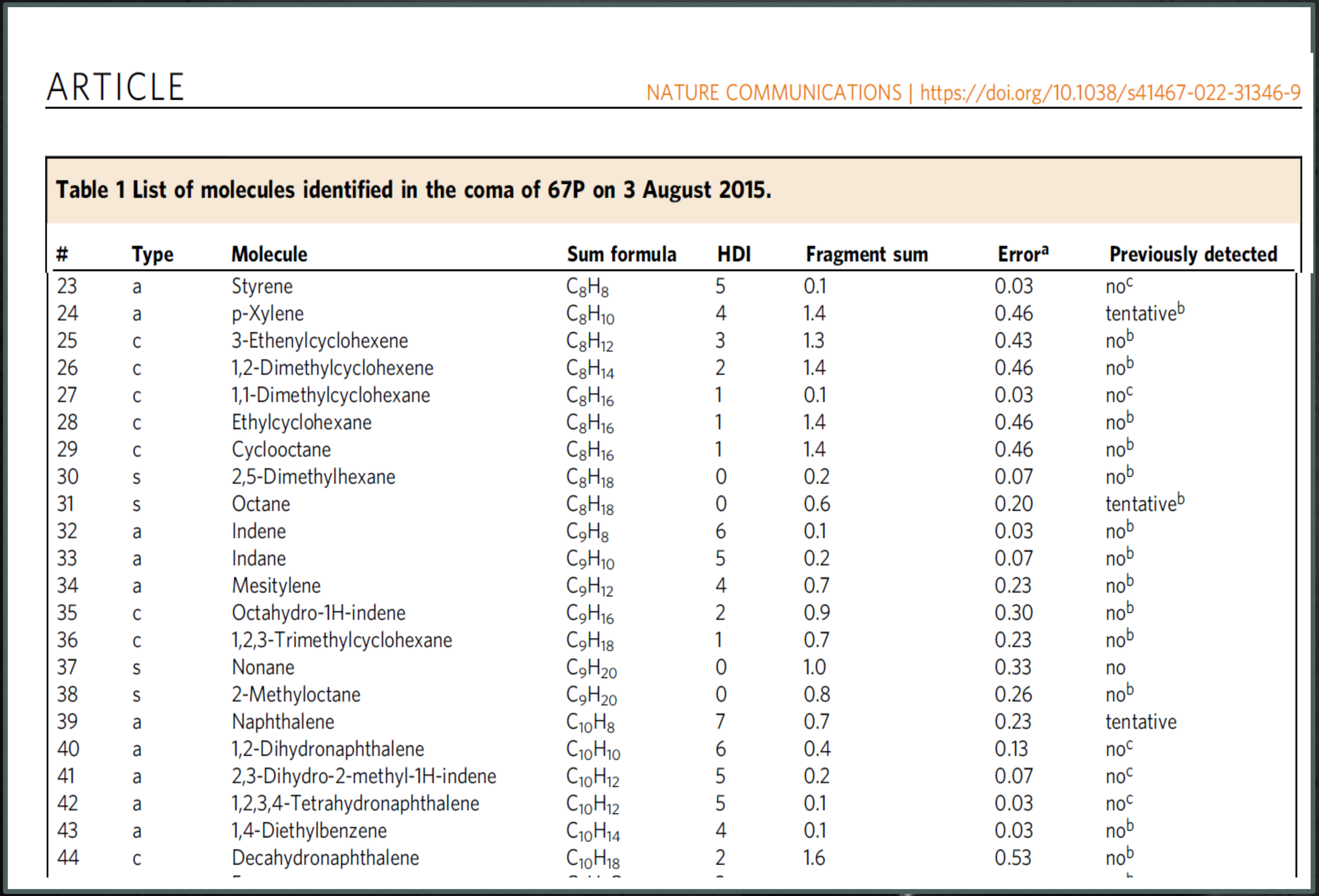
10 atoms

CH_3C_5N $(CH_3)_2CO$ NH_2CH_2COOH CH_3CH_2CHO CH_2OHCH_2OH CH_3OCH_2OH HC_7NH^+ $CH_3CHCHCN$ $CH_3C(CN)CH_2$ CH_2CHCH_2CN

≥ 11 atoms

HC_9N CH_3C_6H C_6H_6 $HC_{11}N$ $CO(CH_2OH)_2$ $HCOOC_2H_5$ CH_3COOCH_3 $CH_3CH(O)CH_2$ C_3H_7CN $C_{14}H_{10}^+$ $HOCH_2CH_2NH_2$ H_2CCCHC_4H
CH_3C_7N c-C_5H_5CN C_6H_5CN $C_{10}H_7CN$ C_9H_7CN C_5H_5CCH c-$C_5H_4CCH_2$ C_{60} C_{60}^+

Molecules/ions detected in comets

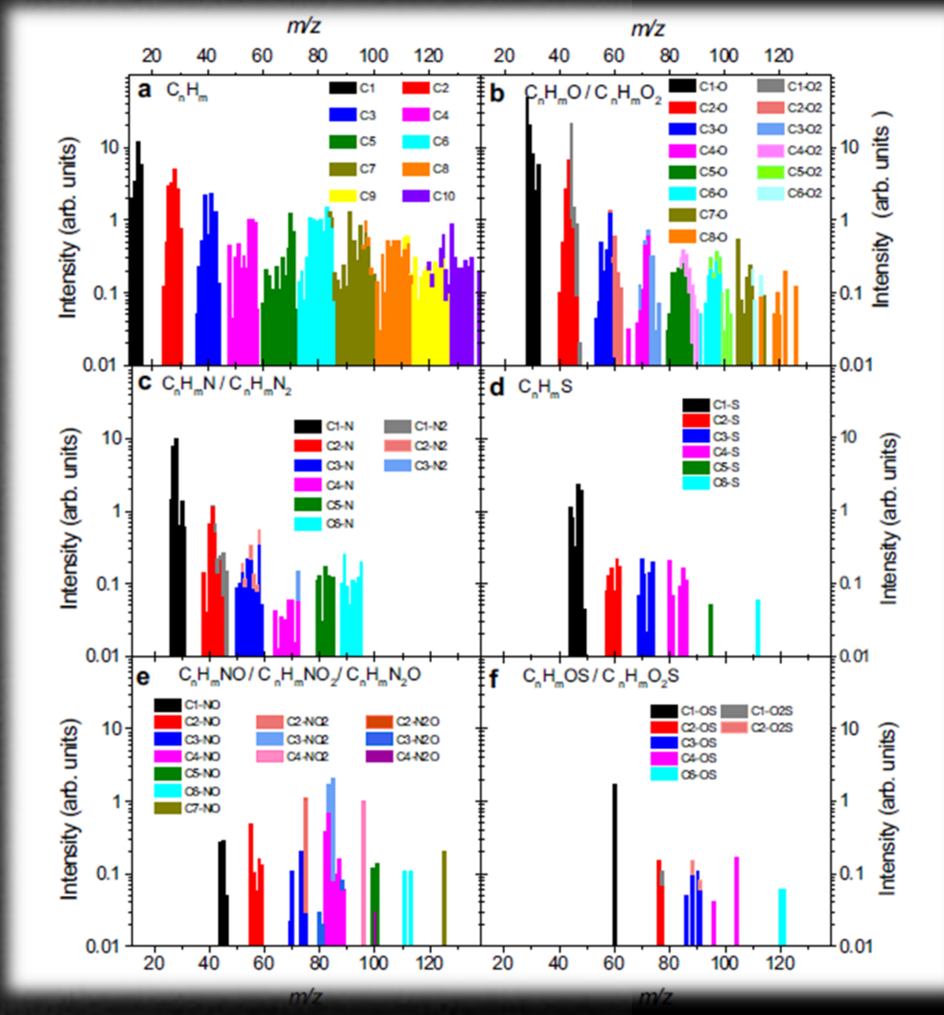


ARTICLE

NATURE COMMUNICATIONS | https://doi.org/10.1038/s41467-022-31346-9

Table 1 List of molecules identified in the coma of 67P on 3 August 2015.

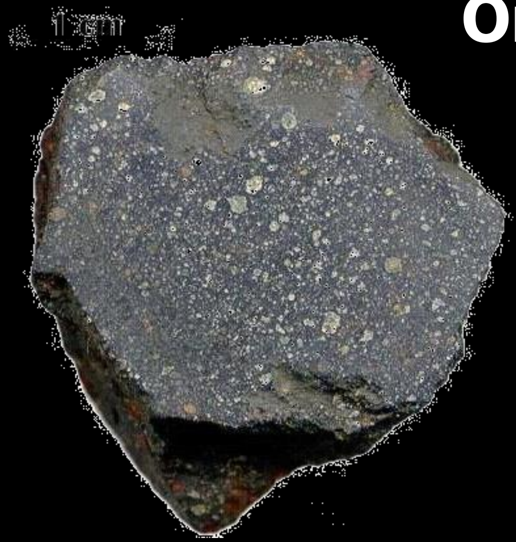
#	Type	Molecule	Sum formula	HDI	Fragment sum	Error[a]	Previously detected
23	a	Styrene	C_8H_8	5	0.1	0.03	no[c]
24	a	p-Xylene	C_8H_{10}	4	1.4	0.46	tentative[b]
25	c	3-Ethenylcyclohexene	C_8H_{12}	3	1.3	0.43	no[b]
26	c	1,2-Dimethylcyclohexene	C_8H_{14}	2	1.4	0.46	no[b]
27	c	1,1-Dimethylcyclohexane	C_8H_{16}	1	0.1	0.03	no[c]
28	c	Ethylcyclohexane	C_8H_{16}	1	1.4	0.46	no[b]
29	c	Cyclooctane	C_8H_{16}	1	1.4	0.46	no[b]
30	s	2,5-Dimethylhexane	C_8H_{18}	0	0.2	0.07	no[b]
31	s	Octane	C_8H_{18}	0	0.6	0.20	tentative[b]
32	a	Indene	C_9H_8	6	0.1	0.03	no[b]
33	a	Indane	C_9H_{10}	5	0.2	0.07	no[b]
34	a	Mesitylene	C_9H_{12}	4	0.7	0.23	no[b]
35	c	Octahydro-1H-indene	C_9H_{16}	2	0.9	0.30	no[b]
36	c	1,2,3-Trimethylcyclohexane	C_9H_{18}	1	0.7	0.23	no[b]
37	s	Nonane	C_9H_{20}	0	1.0	0.33	no
38	s	2-Methyloctane	C_9H_{20}	0	0.8	0.26	no[b]
39	a	Naphthalene	$C_{10}H_8$	7	0.7	0.23	tentative
40	a	1,2-Dihydronaphthalene	$C_{10}H_{10}$	6	0.4	0.13	no[c]
41	a	2,3-Dihydro-2-methyl-1H-indene	$C_{10}H_{12}$	5	0.2	0.07	no[c]
42	a	1,2,3,4-Tetrahydronaphthalene	$C_{10}H_{12}$	5	0.1	0.03	no[c]
43	a	1,4-Diethylbenzene	$C_{10}H_{14}$	4	0.1	0.03	no[b]
44	c	Decahydronaphthalene	$C_{10}H_{18}$	2	1.6	0.53	no[b]



Comet 67P/C-G on 7 July 2015. Image credits: ESA/Rosetta/NAVCAM.

Hanni et al.
NATURE COMMUNICATIONS |
https://doi.org/10.1038/s41467-022-31346-9

Organic molecules & meteorites



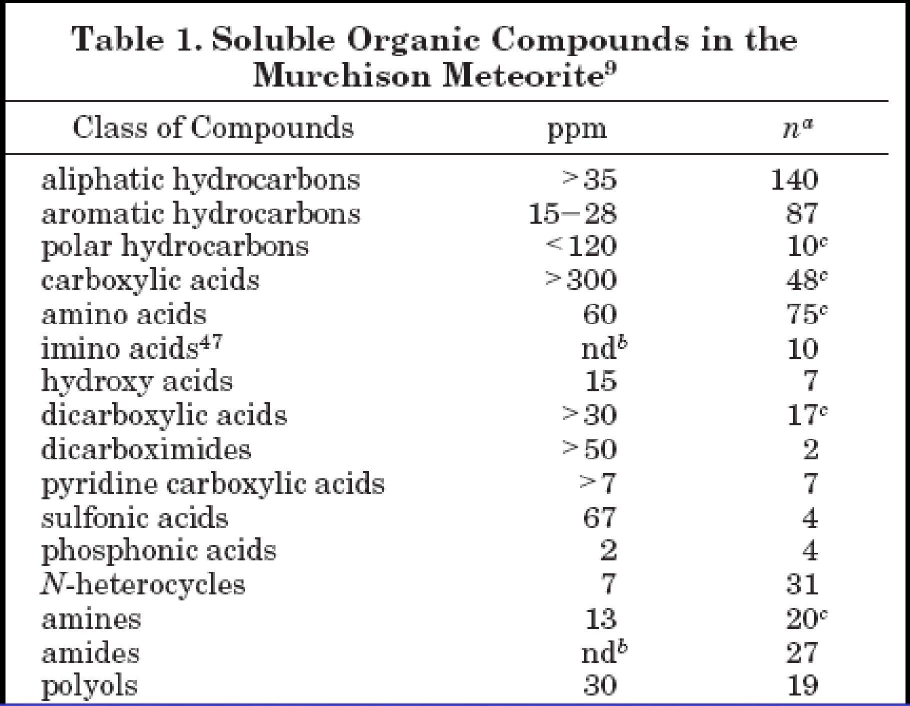
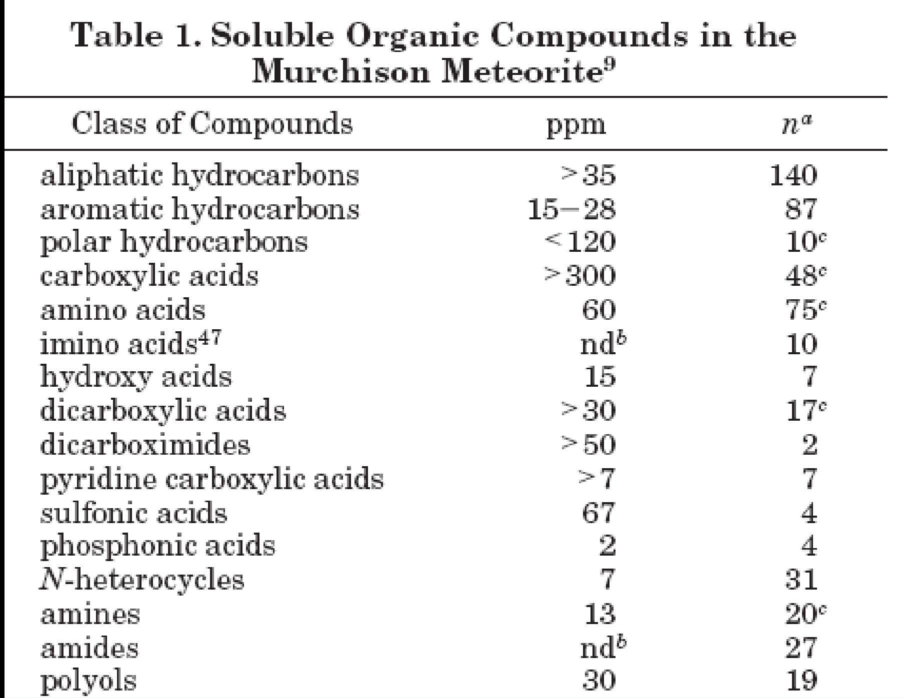


Table 1. Soluble Organic Compounds in the Murchison Meteorite[9]

Class of Compounds	ppm	n[a]
aliphatic hydrocarbons	>35	140
aromatic hydrocarbons	15–28	87
polar hydrocarbons	<120	10[c]
carboxylic acids	>300	48[c]
amino acids	60	75[c]
imino acids[47]	nd[b]	10
hydroxy acids	15	7
dicarboxylic acids	>30	17[c]
dicarboximides	>50	2
pyridine carboxylic acids	>7	7
sulfonic acids	67	4
phosphonic acids	2	4
N-heterocycles	7	31
amines	13	20[c]
amides	nd[b]	27
polyols	30	19

From Pizzarello, Acc. Chem. Res. 2006

Organic molecules & meteorites



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imino acids[47]	nd^b	10
hydroxy acids	15	7
dicarboxylic acids	>30	17^c
dicarboximides	>50	2
pyridine carboxylic acids	>7	7
sulfonic acids	67	4
phosphonic acids	2	4
N-heterocycles	7	31
amines	13	20^c
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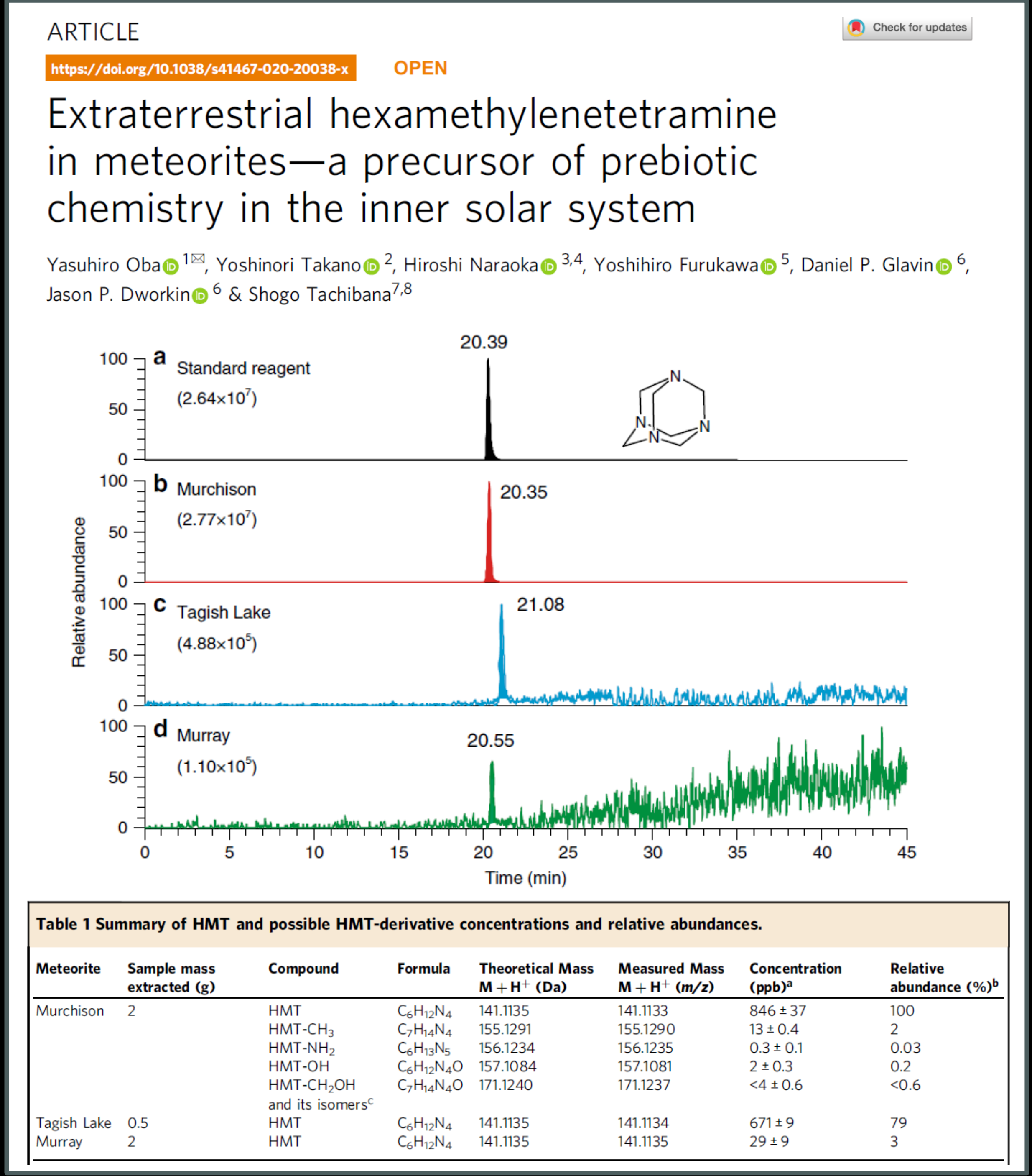


ARTICLE

https://doi.org/10.1038/s41467-020-20038-x

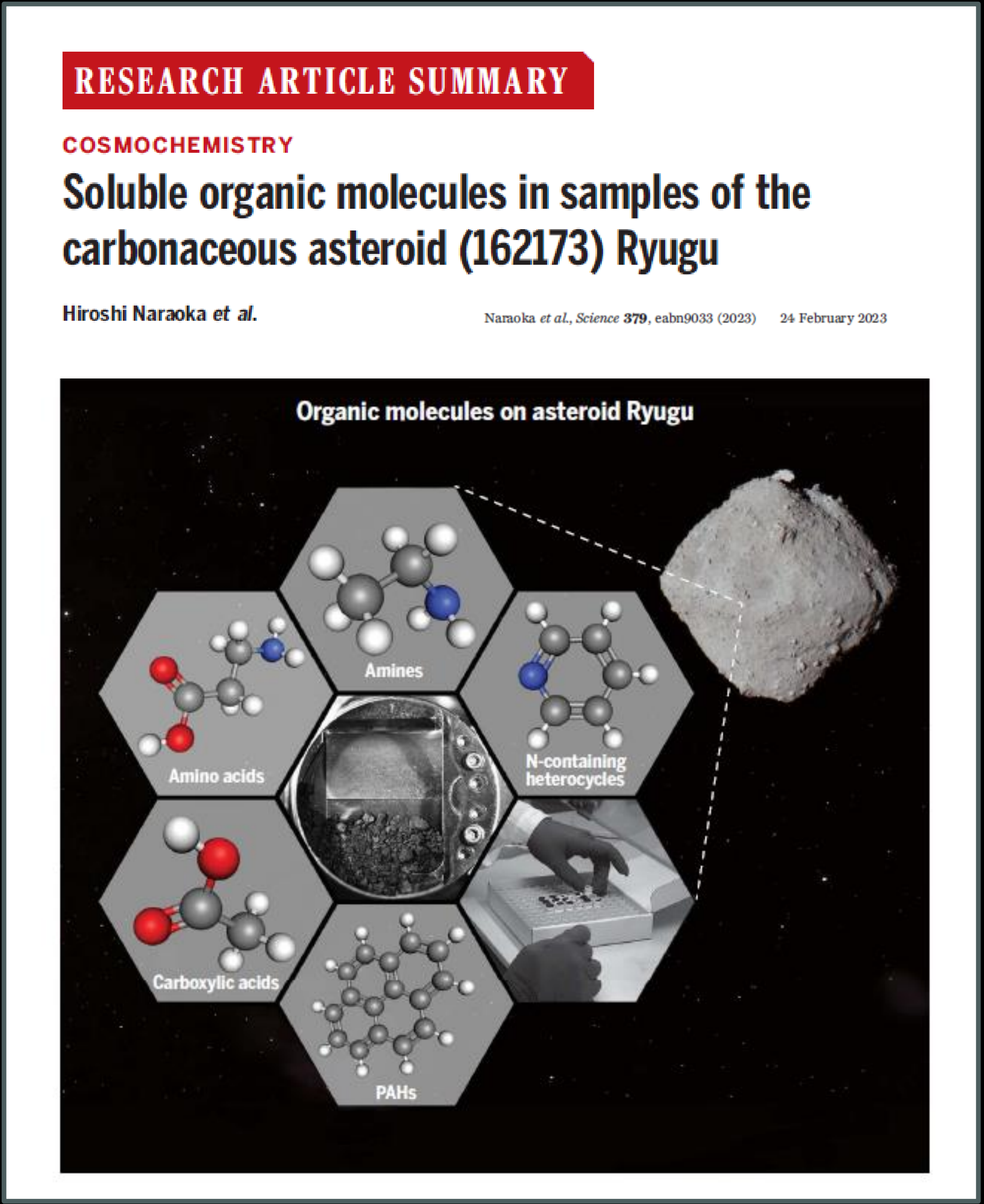
OPEN

Extraterrestrial hexamethylenetetramine in meteorites—a precursor of prebiotic chemistry in the inner solar system

Yasuhiro Oba [1✉], Yoshinori Takano [2], Hiroshi Naraoka [3,4], Yoshihiro Furukawa [5], Daniel P. Glavin [6], Jason P. Dworkin [6] & Shogo Tachibana [7,8]

Table 1 Summary of HMT and possible HMT-derivative concentrations and relative abundances.

Meteorite	Sample mass extracted (g)	Compound	Formula	Theoretical Mass $M+H^+$ (Da)	Measured Mass $M+H^+$ (m/z)	Concentration (ppb)^a	Relative abundance (%)^b
Murchison	2	HMT	$C_6H_{12}N_4$	141.1135	141.1133	846 ± 37	100
		HMT-CH_3	$C_7H_{14}N_4$	155.1291	155.1290	13 ± 0.4	2
		HMT-NH_2	$C_6H_{13}N_5$	156.1234	156.1235	0.3 ± 0.1	0.03
		HMT-OH	$C_6H_{12}N_4O$	157.1084	157.1081	2 ± 0.3	0.2
		HMT-CH_2OH and its isomers^c	$C_7H_{14}N_4O$	171.1240	171.1237	<4 ± 0.6	<0.6
Tagish Lake	0.5	HMT	$C_6H_{12}N_4$	141.1135	141.1134	671 ± 9	79
Murray	2	HMT	$C_6H_{12}N_4$	141.1135	141.1135	29 ± 9	3



RESEARCH ARTICLE SUMMARY

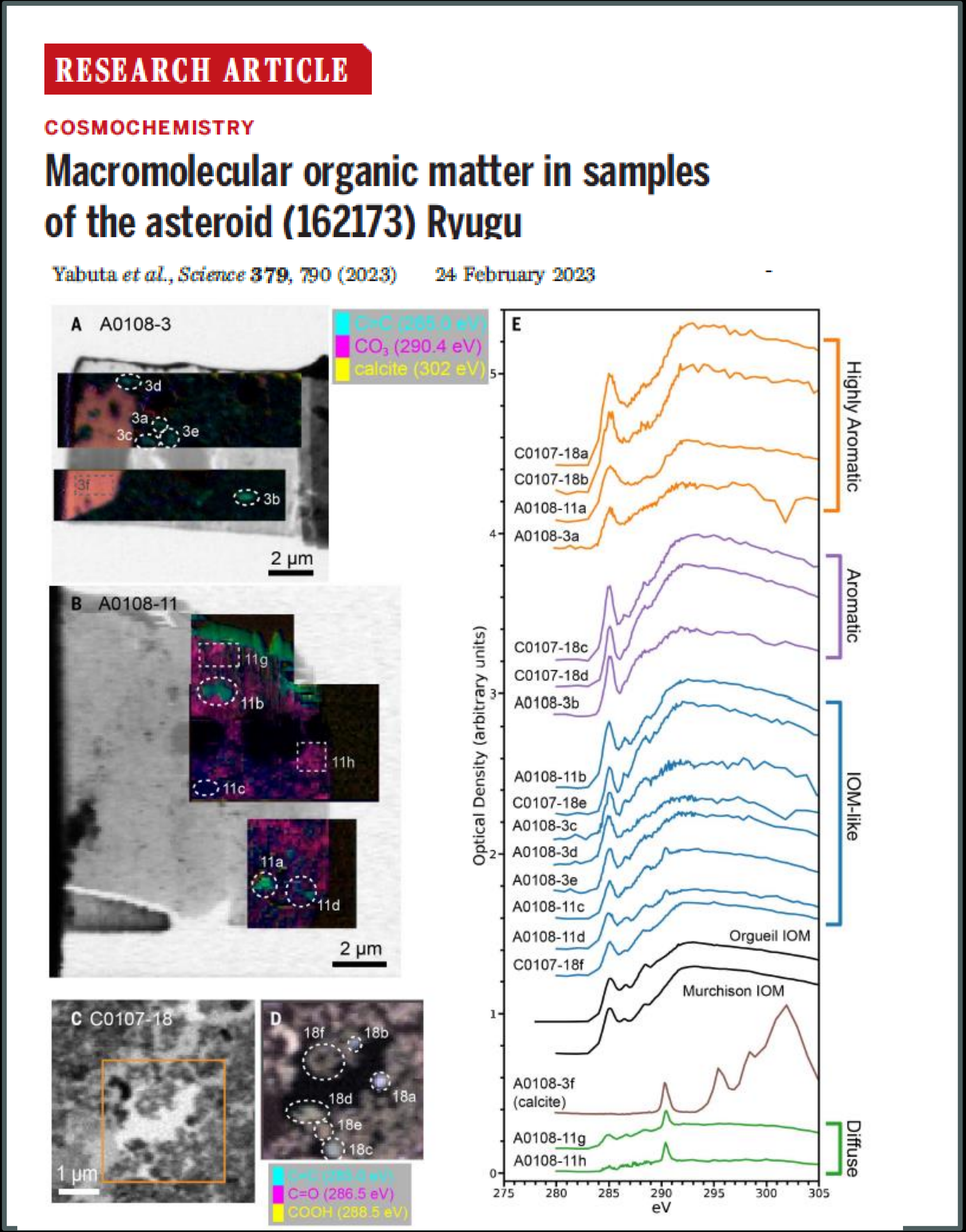
COSMOCHEMISTRY

Soluble organic molecules in samples of the carbonaceous asteroid (162173) Ryugu

Hiroshi Naraoka *et al.*

Naraoka *et al.*, *Science* **379**, eabn9033 (2023) 24 February 2023

Organic molecules on asteroid Ryugu

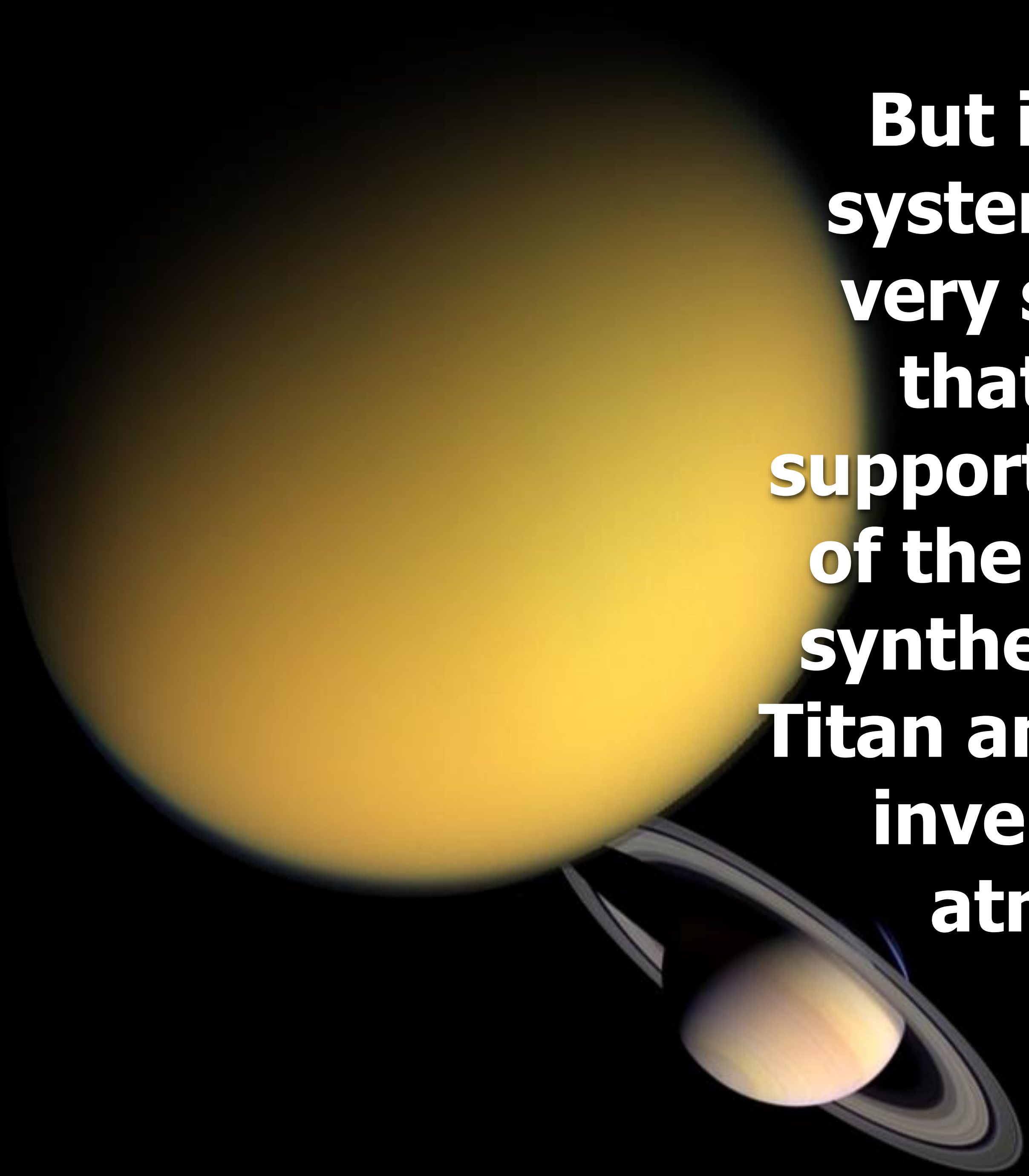


RESEARCH ARTICLE

COSMOCHEMISTRY

Macromolecular organic matter in samples of the asteroid (162173) Ryugu

Yabuta *et al.*, *Science* **379**, 790 (2023) 24 February 2023



But in our solar system, there is a very special case that seems to support a new vision of the endogenous synthesis scenario: Titan and the organic inventory of its atmosphere

Global chemical scheme

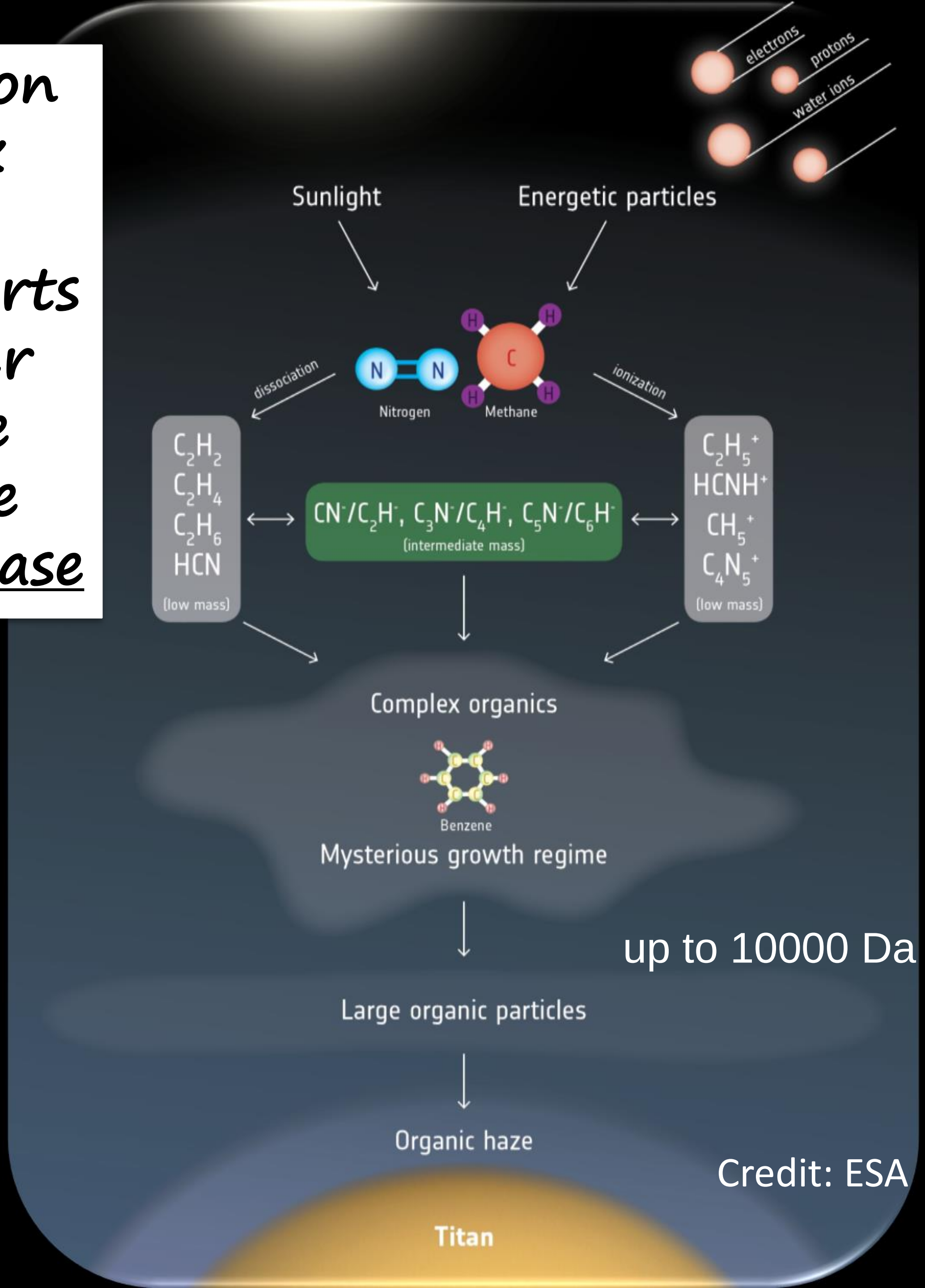
N_2 ca. 98%; CH_4 ca. 2%

EUV and energetic particles induce the formation of active forms of nitrogen ($N^{\cdot}$, N_2^*, N^+, N_2^+)

UV photons induce dissociation and ionization of methane

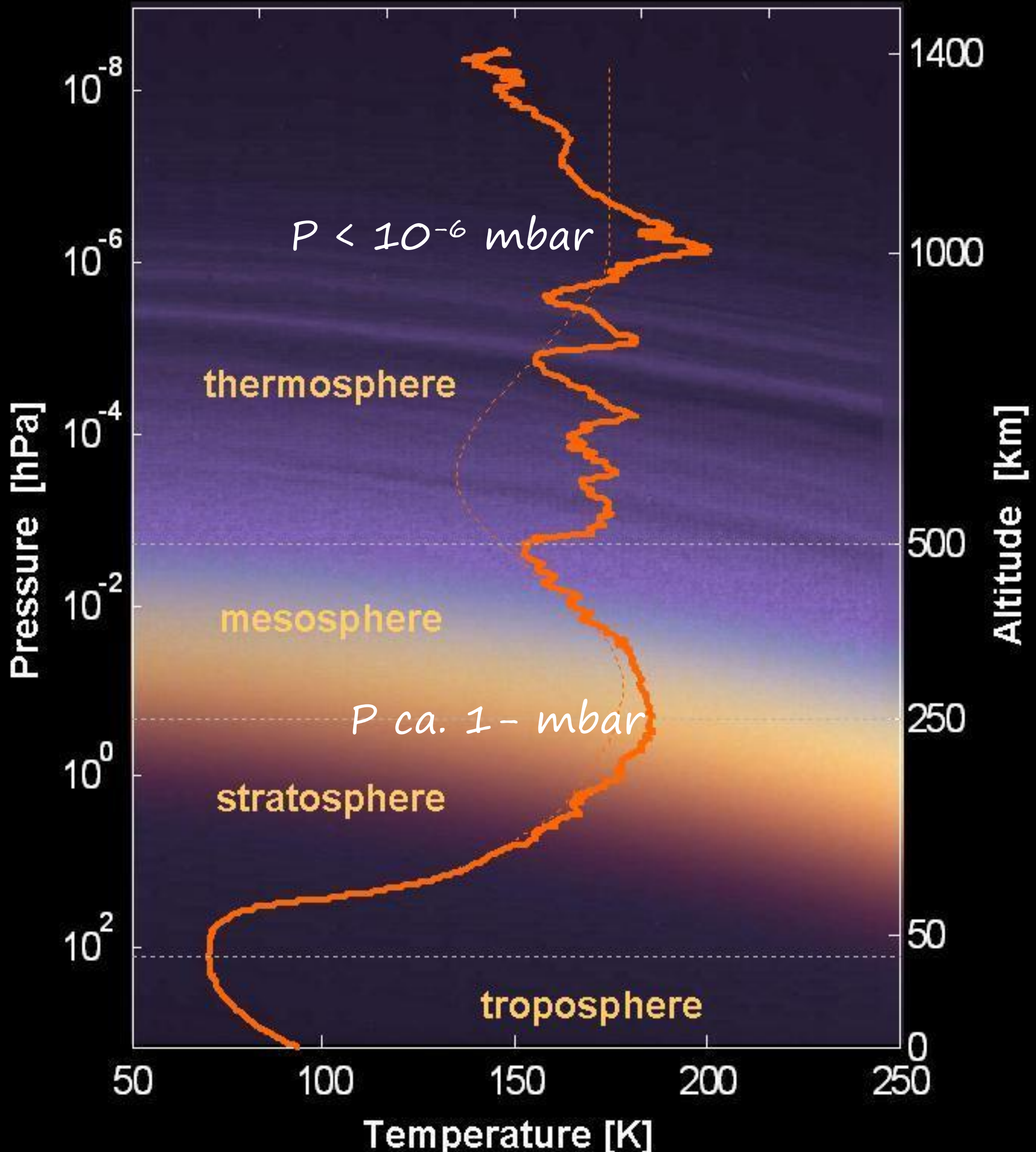
A very active chemistry begins, leading up to organic macromolecules and their ions.

The formation of complex organic molecules starts in the upper part of the atmosphere <u>in the gas phase</u>



up to 10000 Da

Credit: ESA



Complex molecules already seen at 1000 km

Thermosphere 500-1400 km

a detached haze layer at an altitude of 500 km is 150–200 km higher than that observed by Voyager

Mesosphere 250-500 km

Stratosphere 50-250 km

Troposphere 0-50 km

haze layers in Pluto’s atmosphere

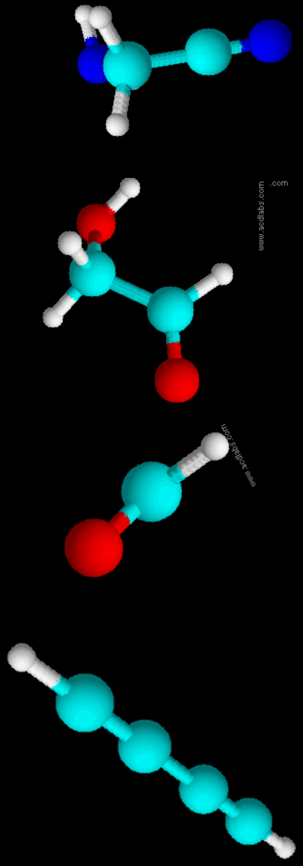
200 km of altitude
P of a few microbars

Image Credit: NASA

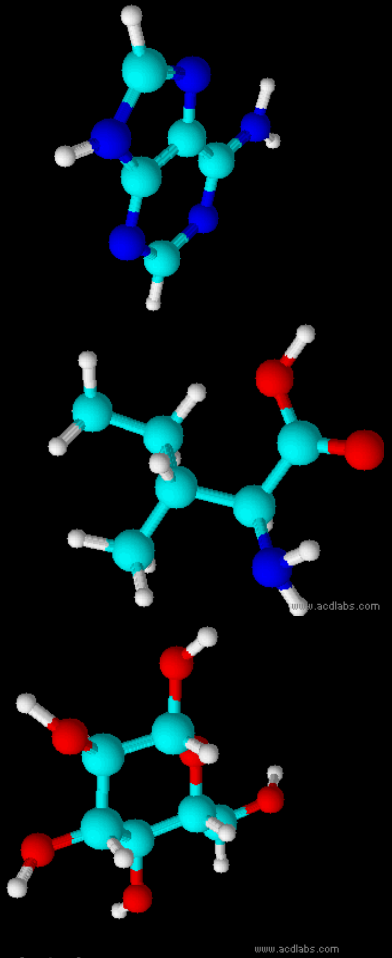
- either in star forming regions or in planetary atmospheres, gas phase chemistry can account for the formation of simple prebiotc molecules or even macromolecules

- simple prebiotic molecules can further evolve/react, possibly leading to the accumulation of organic molecules/macromolecules that allegedly preceded life

Prebiotic (simple organic) molecules: are they the link between matter in the Universe and matter in living entities?



gas-phase molecules	potential precursor of
with C-N bonds (e.g. HCN, CH_3CN, C_2N_2, $HCCCN$, CH_2NH, C_2H_3CN)	aminoacids & nucleic bases
with C-O bonds (e.g. H_2CO, CH_3COH, CH_3COOH, $(CH_2OH)_2$, CH_2OHCHO)	sugars & aminoacids
with C-C multiple bonds (e.g. from C_2H_2 up to polyynes)	long carbon chain molecules, PAHs

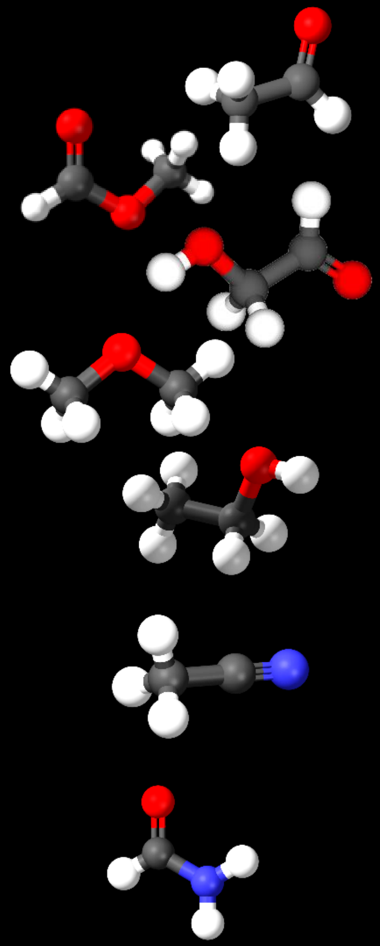


+ many others which might be present/synthesized in the gas-phase
e.g. H_2O, NH_3, NH_2CH_2CN, $HCOCN$, CH_3CONH_2, $HCONH_2$, CH_3SH etc.

# of interstellar molecules > 300 (see CDMS or JPL catalogues)

~45% of them are organic molecules with at least 6 atoms (Interstellar Complex Organic Molecules) and have some prebiotic potential

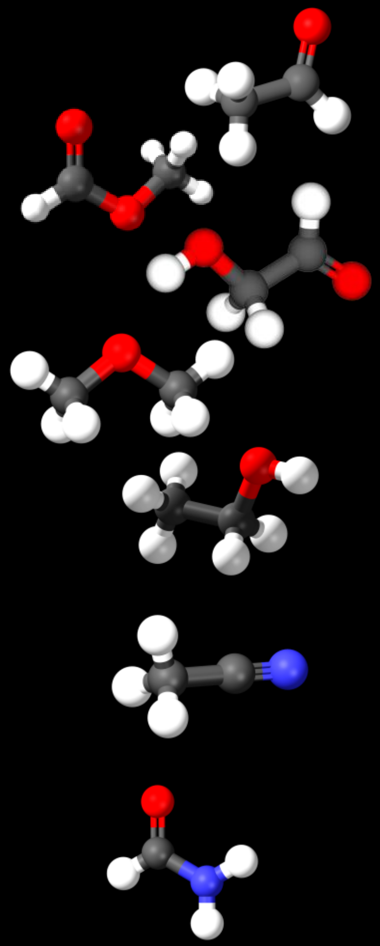
observed in the gas-phase, their origin is debated

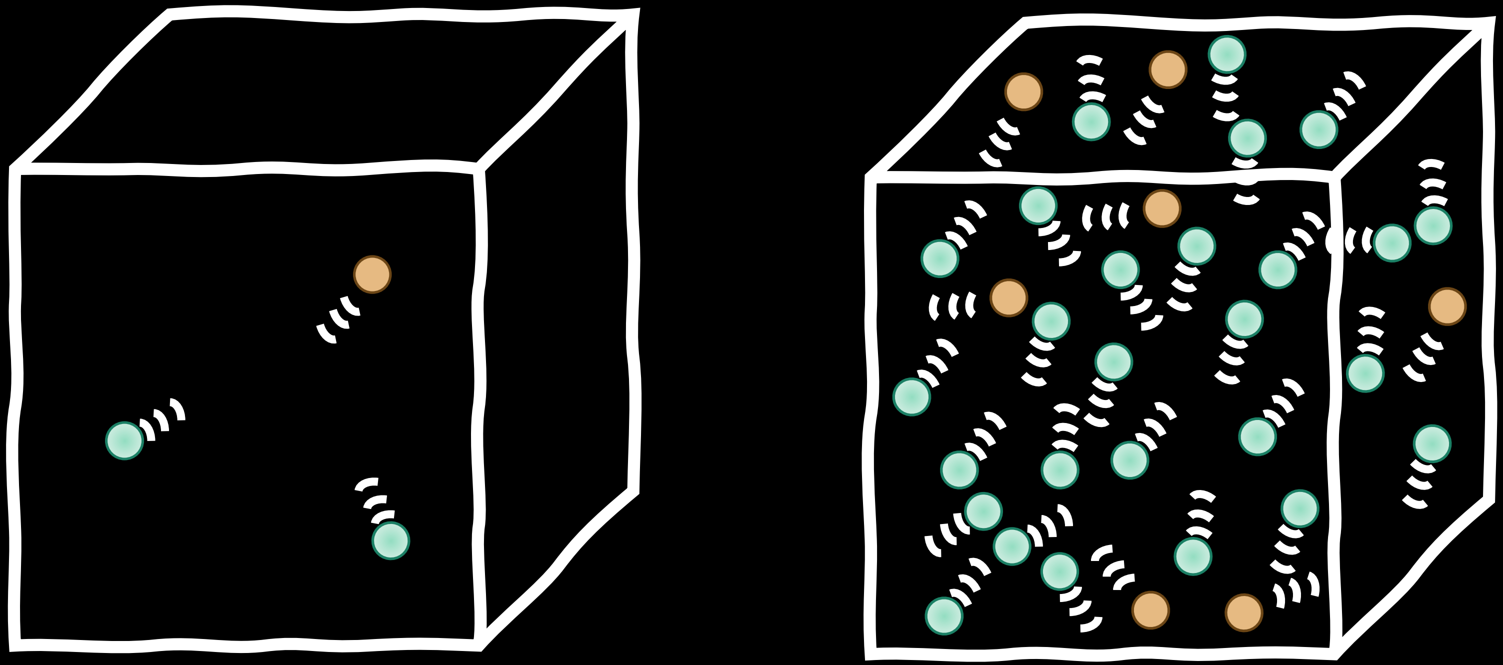


How are they formed under the harsh environments of the interstellar medium?

How are they formed under the harsh environments of the interstellar medium?

❶ Low number density (as low as 10^4 cm^{-3})

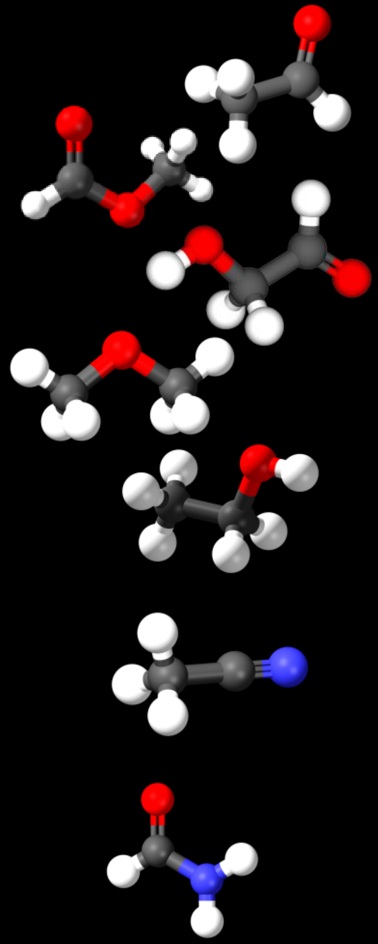


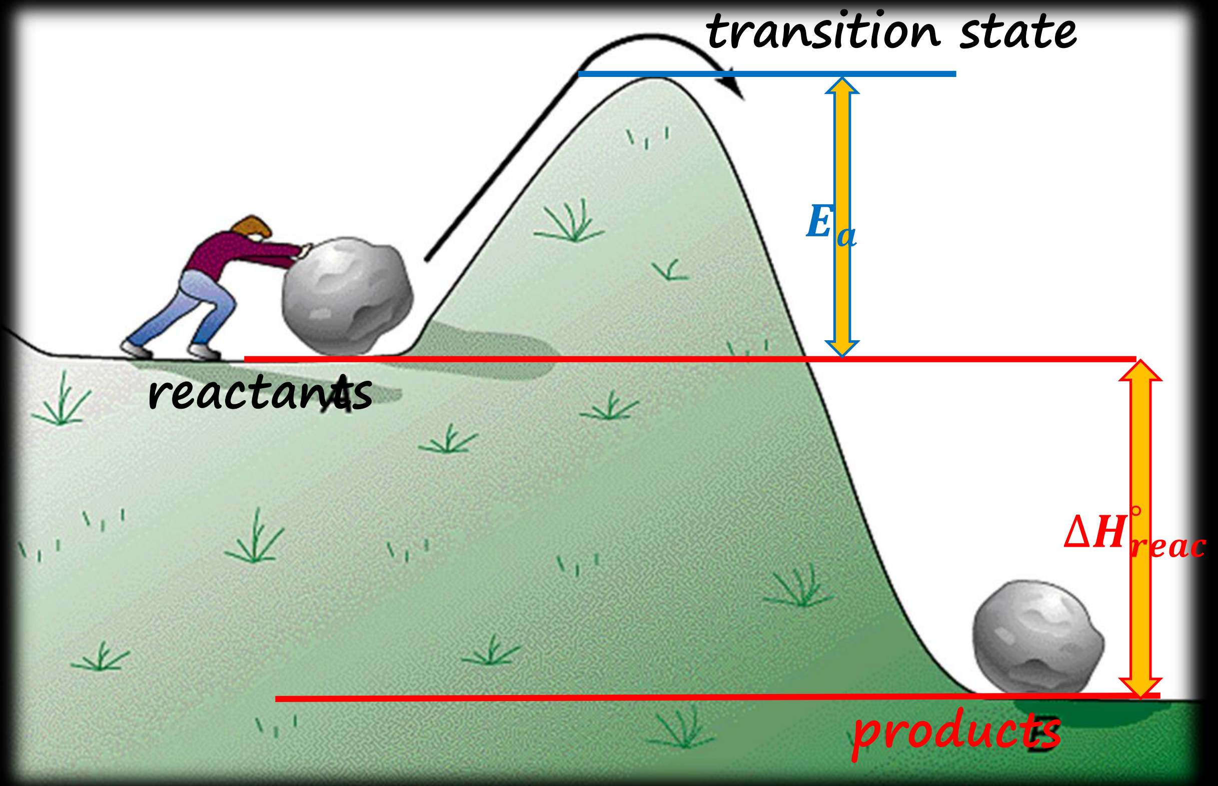


- Chemistry needs molecular encounters
- In those conditions, no 3-body collisions

How are they formed under the harsh environments of the interstellar medium?

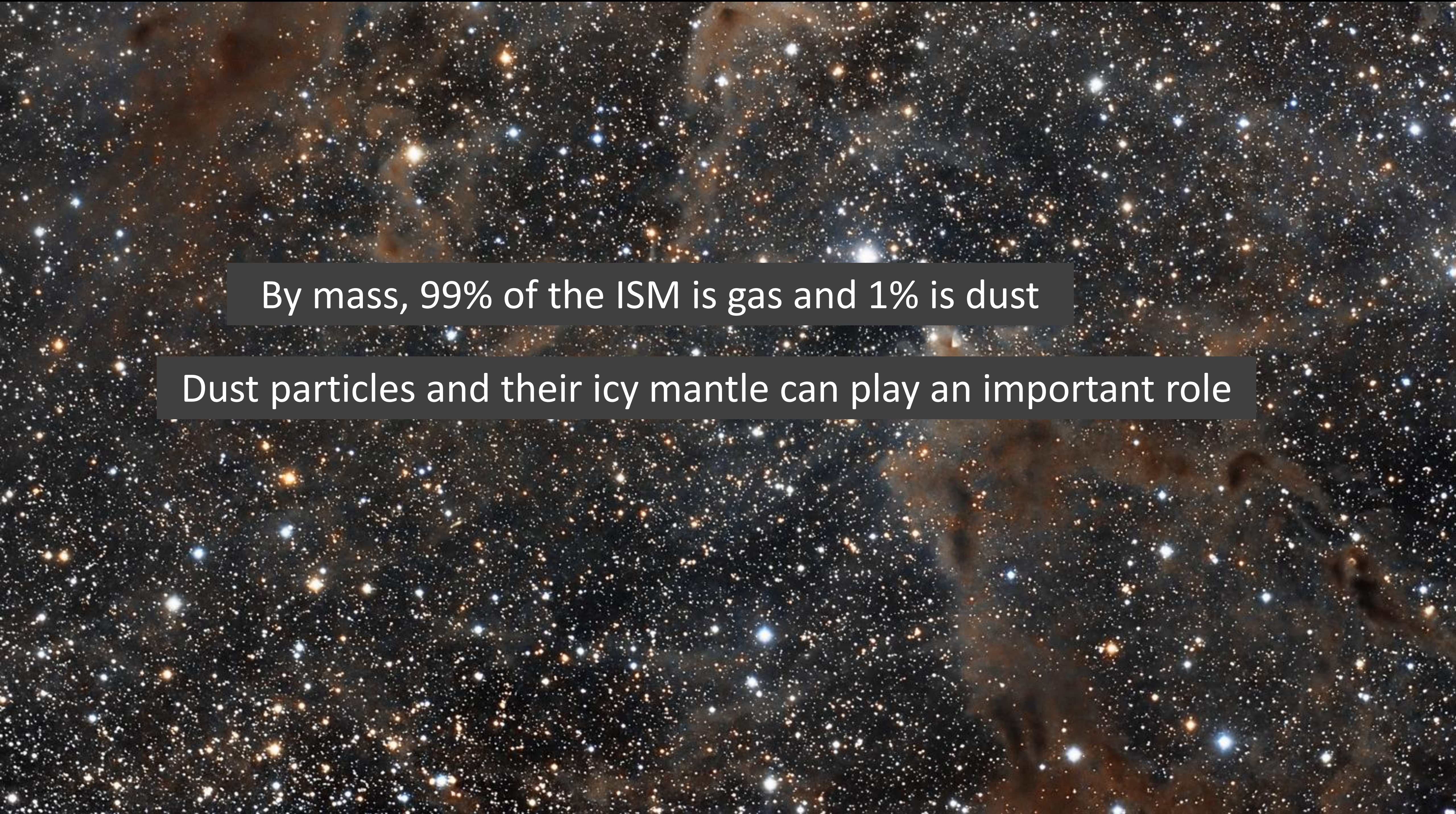
❷ Low temperature (as low as 10 K)





Relevant reactions must involve transient species (ions, radicals)

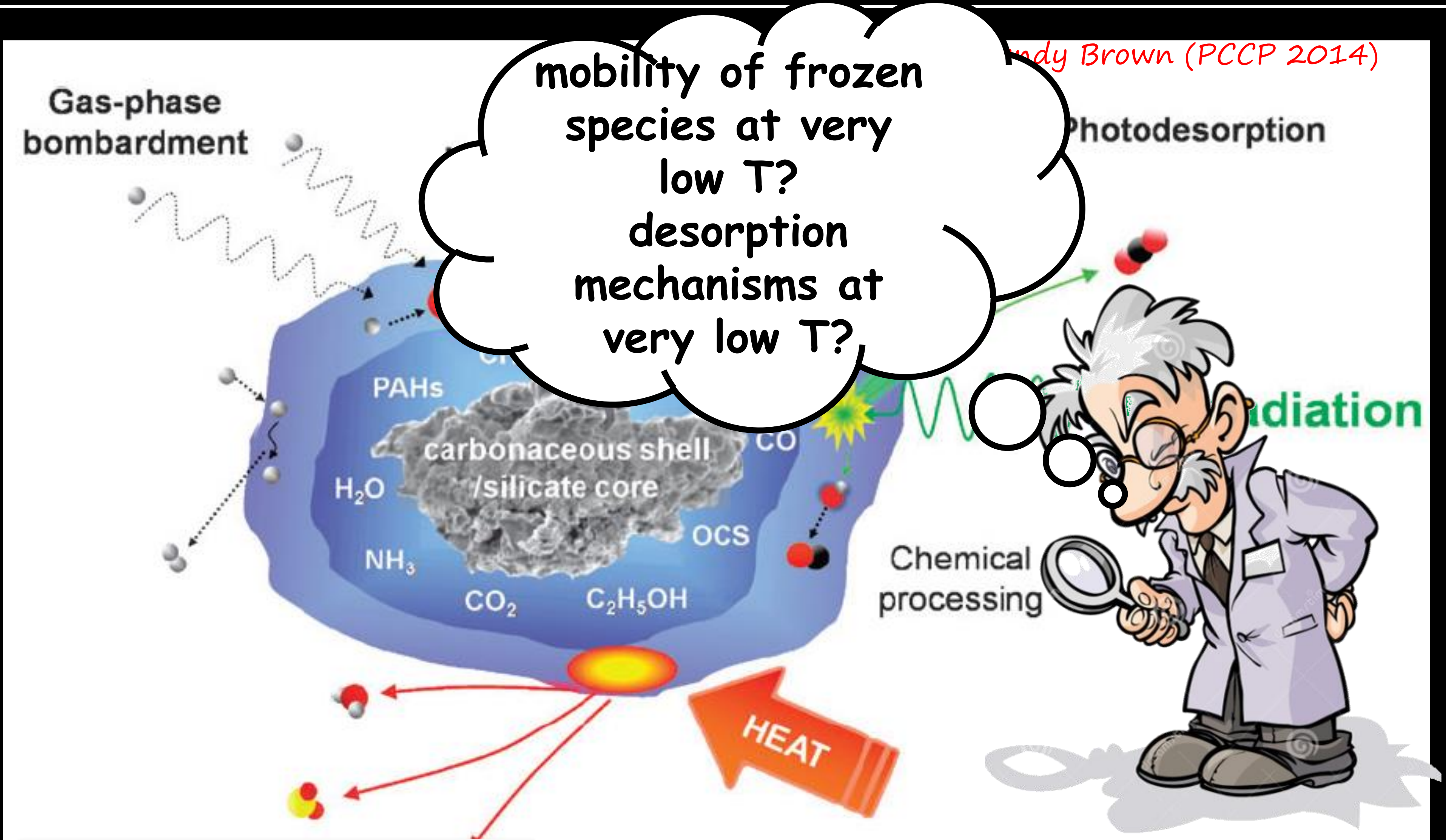
Chemistry needs energy to promote reactivity
also for exothermic reaction



By mass, 99% of the ISM is gas and 1% is dust

Dust particles and their icy mantle can play an important role

Dust particles and icy mantles: preferential sites to induce chemical reactivity?



ndy Brown (PCCP 2014)

mobility of frozen species at very low T?
desorption mechanisms at very low T?

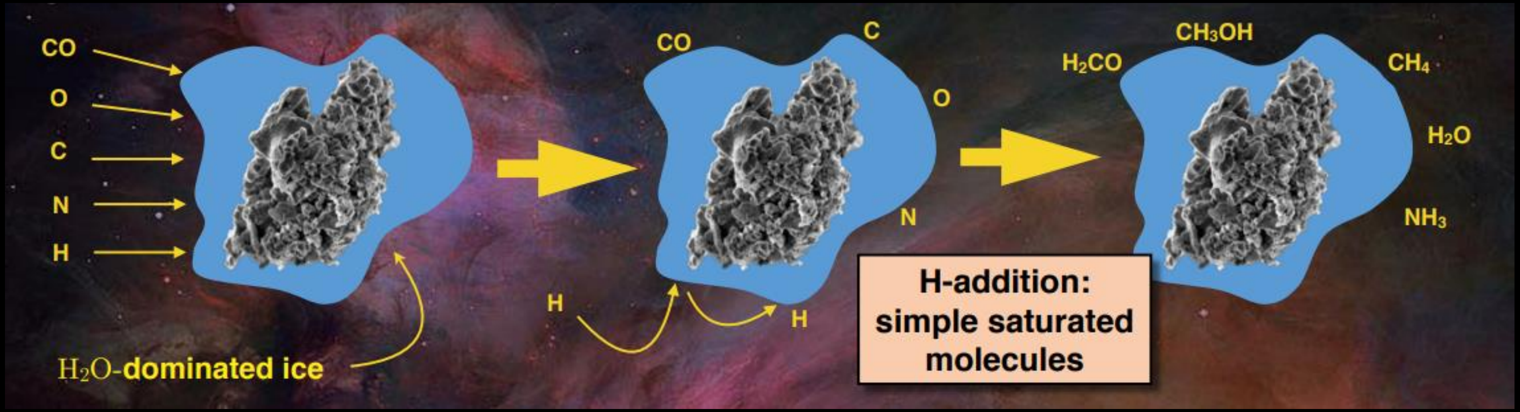
- perfect third body
- “concentrator”

Perugia e l'Università degli Studi in lutto, addio allo scienziato Giulio Alberti: la ricerca la sua grande passione

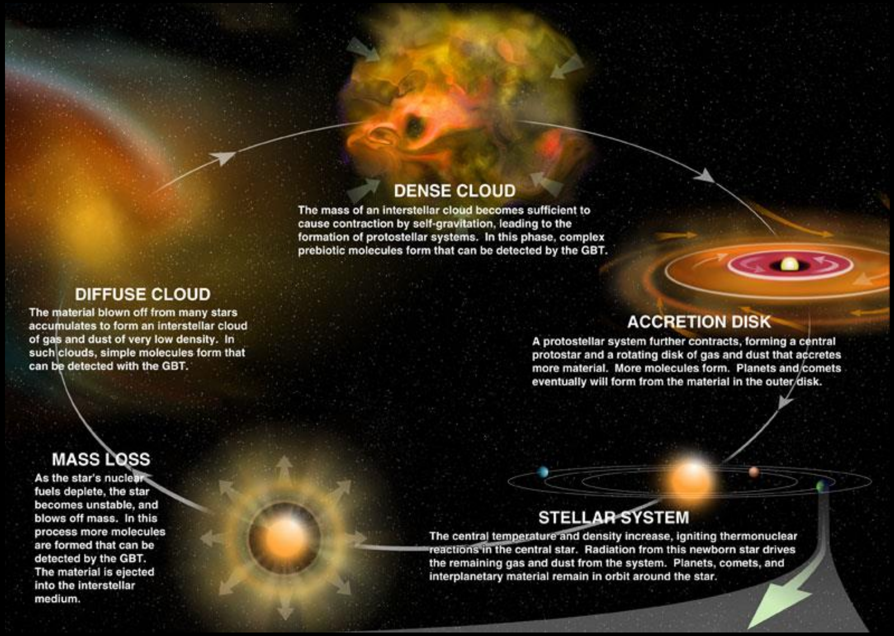
My solid-state chemistry professor, a luminary in his field, told us in the first lecture of his course

“solid-state chemistry does not exist”.

Dense cloud (very low T)



consensus



DENSE CLOUD

The mass of an interstellar cloud becomes sufficient to cause contraction by self-gravitation, leading to the formation of protostellar systems. In this phase, complex prebiotic molecules form that can be detected by the GBT.

DIFFUSE CLOUD

The material blown off from many stars accumulates to form an interstellar cloud of gas and dust of very low density. In such clouds, simple molecules form that can be detected with the GBT.

ACCRETION DISK

A protostellar system further contracts, forming a central protostar and a rotating disk of gas and dust that accretes more material. More molecules form. Planets and comets eventually will form from the material in the outer disk.

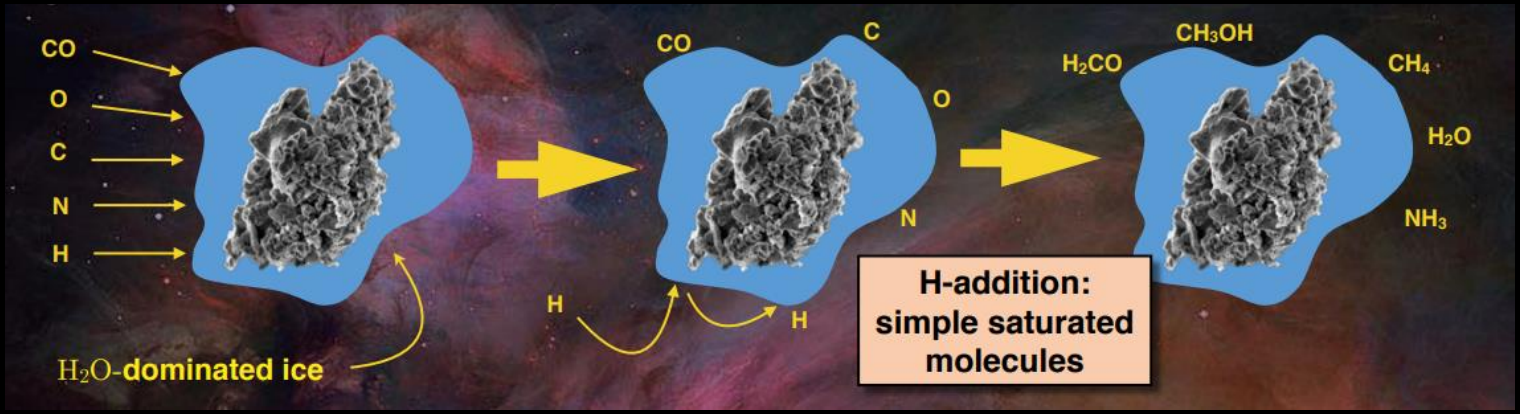
MASS LOSS

As the star's nuclear fuels deplete, the star becomes unstable, and blows off mass. In this process more molecules are formed that can be detected by the GBT. The material is ejected into the interstellar medium.

STELLAR SYSTEM

The central temperature and density increase, igniting thermonuclear reactions in the central star. Radiation from this newborn star drives the remaining gas and dust from the system. Planets, comets, and interplanetary material remain in orbit around the star.

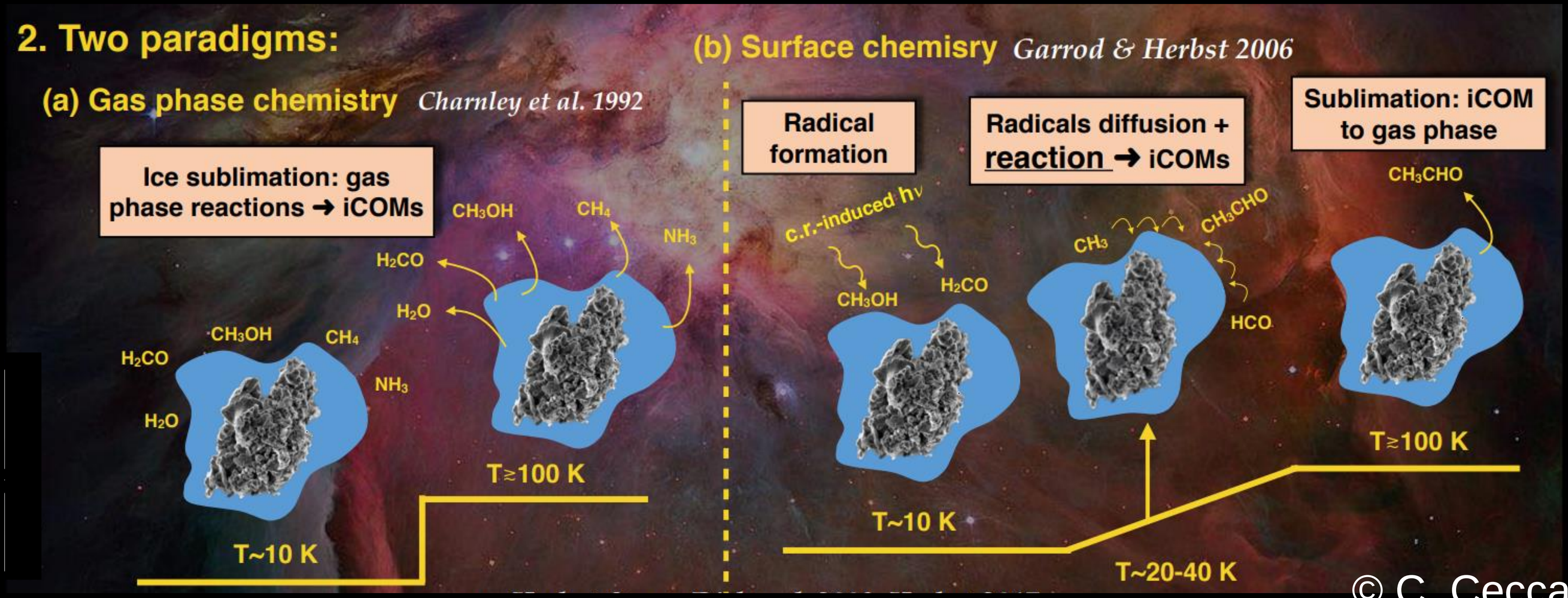
Dense cloud (very low T)



H-addition: simple saturated molecules

consensus

Protostellar phase



2. Two paradigms:

(a) Gas phase chemistry *Charnley et al. 1992*

Ice sublimation: gas phase reactions ➜ iCOMs

(b) Surface chemisry *Garrod & Herbst 2006*

Radical formation

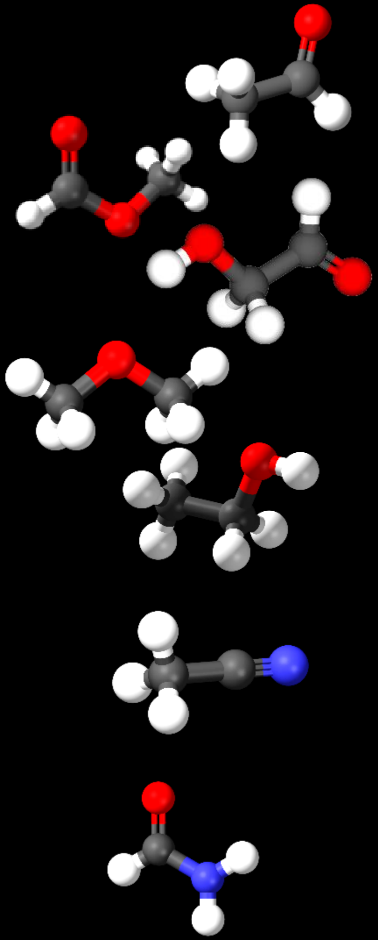
Radicals diffusion + reaction ➜ iCOMs

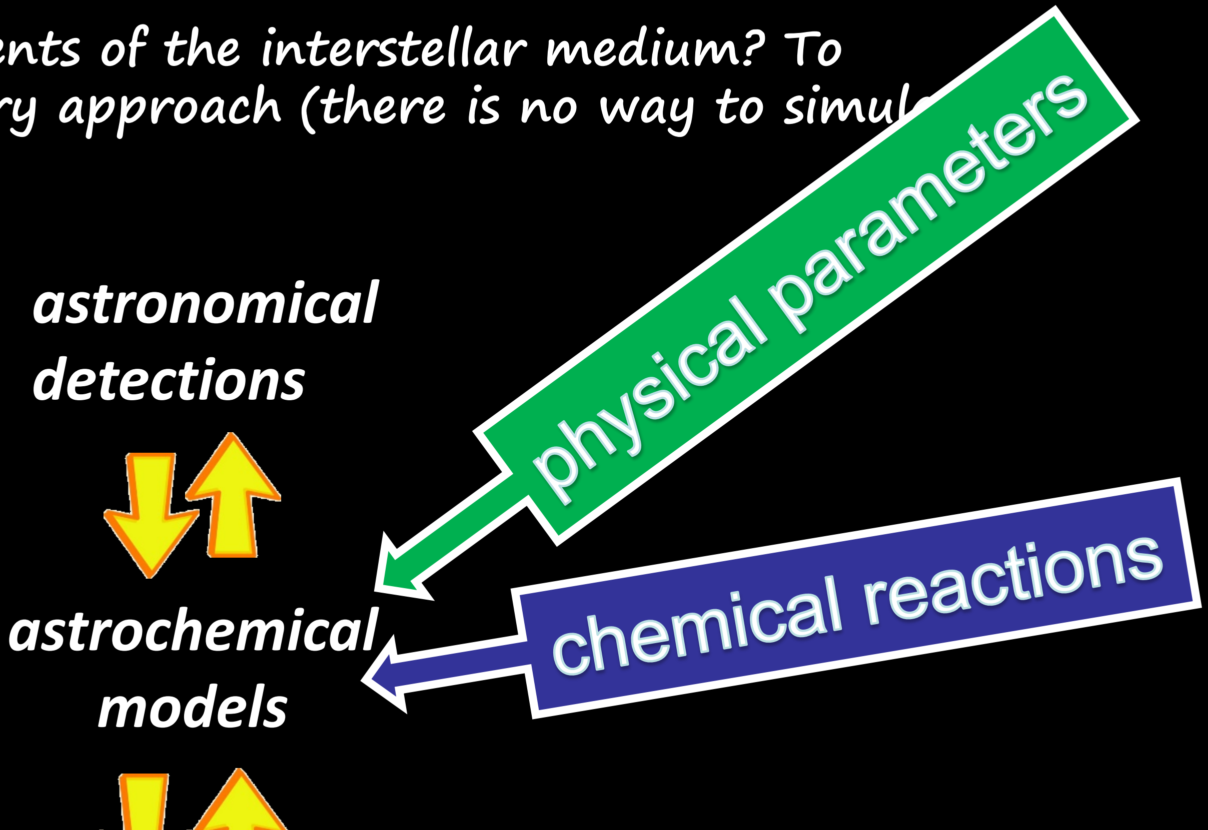
Sublimation: iCOM to gas phase

hotly debated

© C. Ceccarelli (IPAG)

How are they formed under the harsh environments of the interstellar medium? To answer this question we rely on a multidisciplinary approach (there is no way to simul this chemistry in one single experiment)





astronomical detections

astrochemical models

physical parameters

chemical reactions

exp

quan

ca. 8000 elementary reactions including:

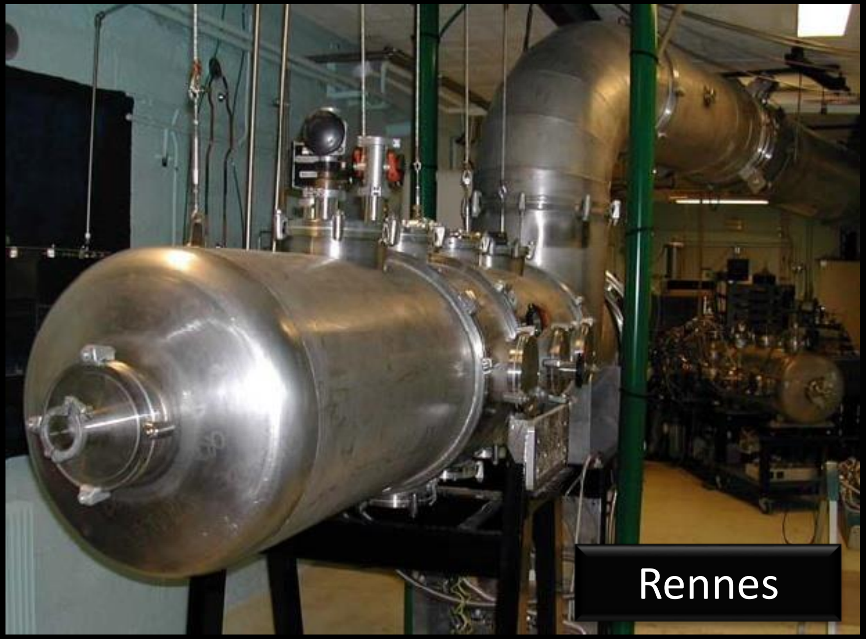
- dissociation, excitation & ionization processes
- neutral-neutral reactions
- ion-molecule reactions
- heterogeneous processes (1% dust)

Only a small percentage has been characterized in lab experiments yet

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

we have three pillars

❶ CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) technique



credit: S. Le Picard

low T, as low as those of interest in the ISM

Fantastic experimental technique that has twice revolutionised our common sense in astrochemistry: at the beginning of the 90's by proving that neutral-neutral reactions can be very fast at the low T of cold interstellar objects and now showing significant non-Arrehnius behavior for some reactions

BUT it does not provide a single-collision environment

What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

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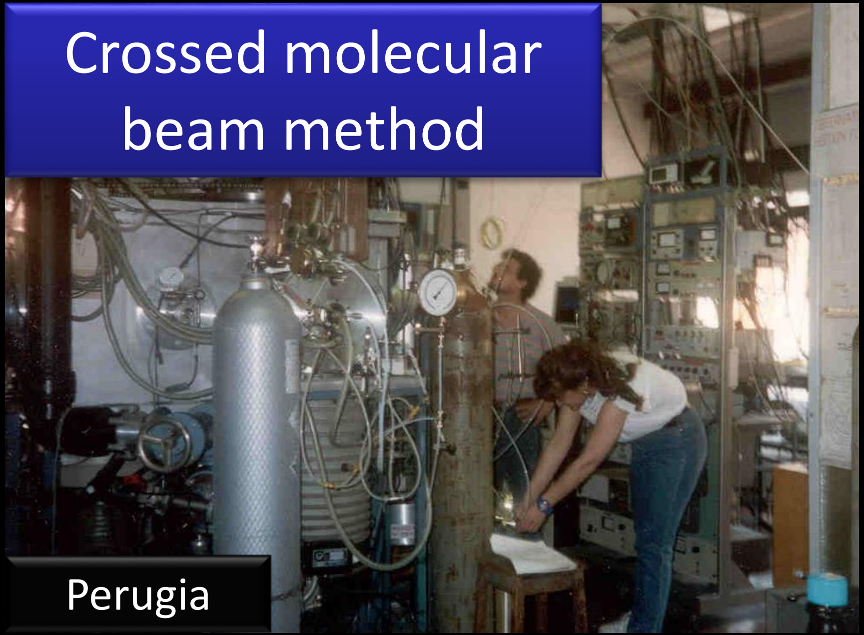
❷ *collision free experiments (molecular beam experiments)*

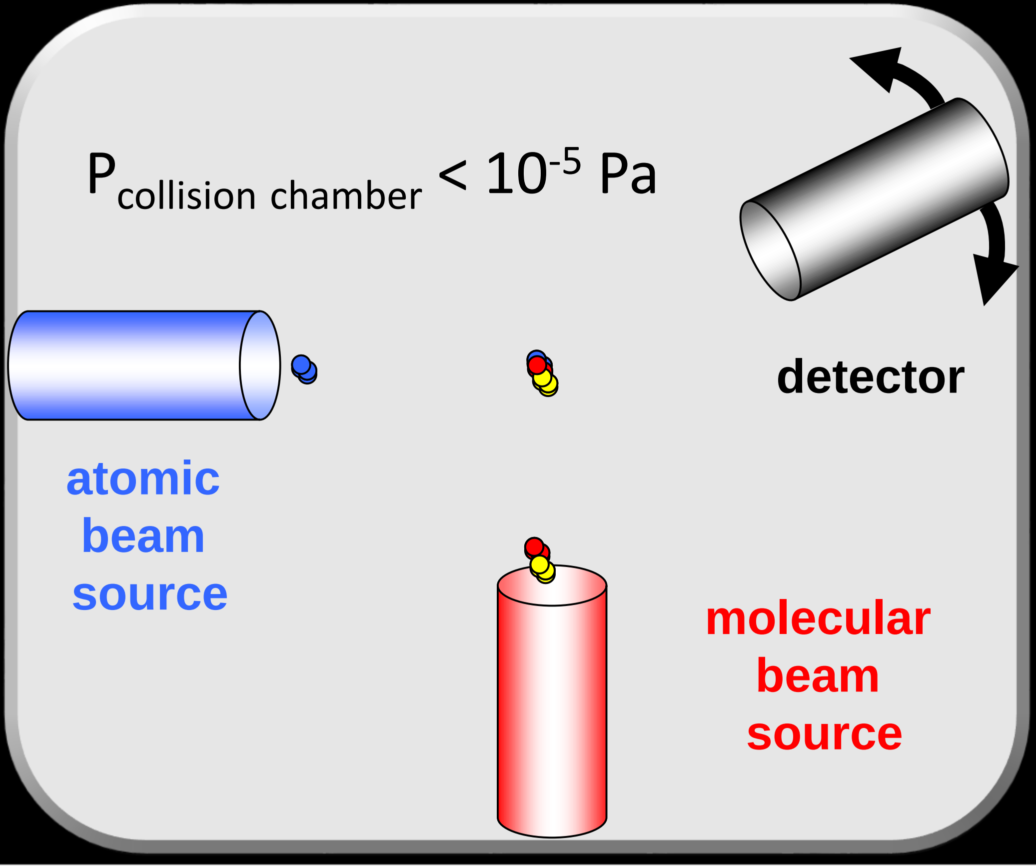
Crossed molecular beam method



Perugia

very low pressure (reactions under single collision conditions)

The crossed molecular beam method: an experimental technique to study bimolecular reactions under single collision conditions



the colliding species are prepared by expanding the gases into two distinct molecular beams which cross each other at a specific angle and collision energy

➲ *the species of each beam are made to collide only with the molecules of the other beam at the collision center; the formed products fly undisturbed towards the detector*

👍

- *because of the large mean free path, the products do not undergo secondary or wall collisions before arriving at the detector chamber*
- *this allows us to observe the consequences of (many) identical well-defined single molecular collisions*

Crossed beam apparatus with "universal" mass spectrometric detection and time-of-flight analysis

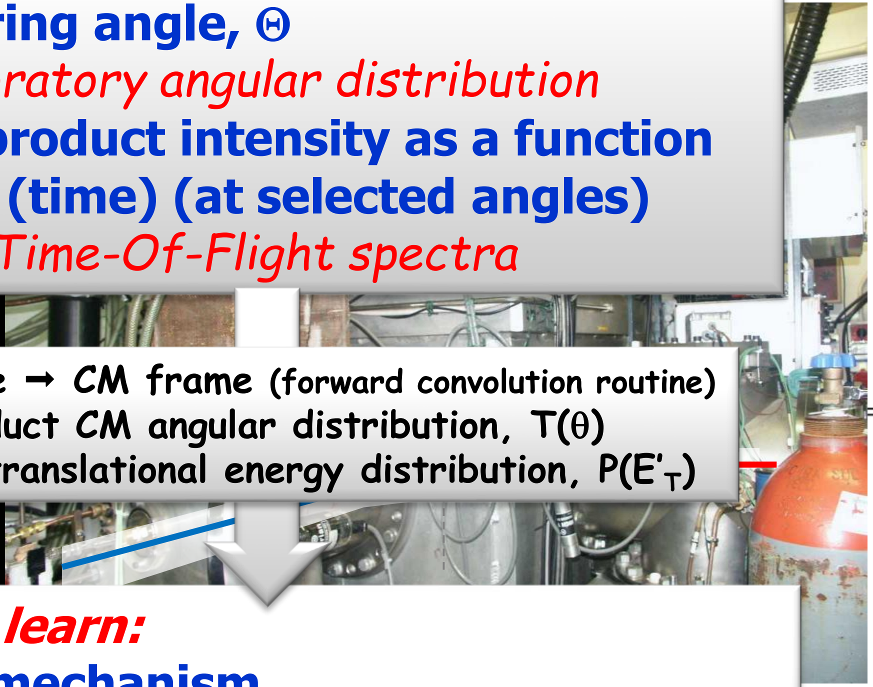
What we measure:

- $N(\Theta)$ product intensity as a function of the scattering angle, Θ

  laboratory angular distribution

- $N(\Theta,v)$ product intensity as a function of velocity (time) (at selected angles)

  Time-Of-Flight spectra



LAB frame → CM frame (forward convolution routine)
product CM angular distribution, $T(\theta)$
product translational energy distribution, $P(E'_T)$

What we learn:

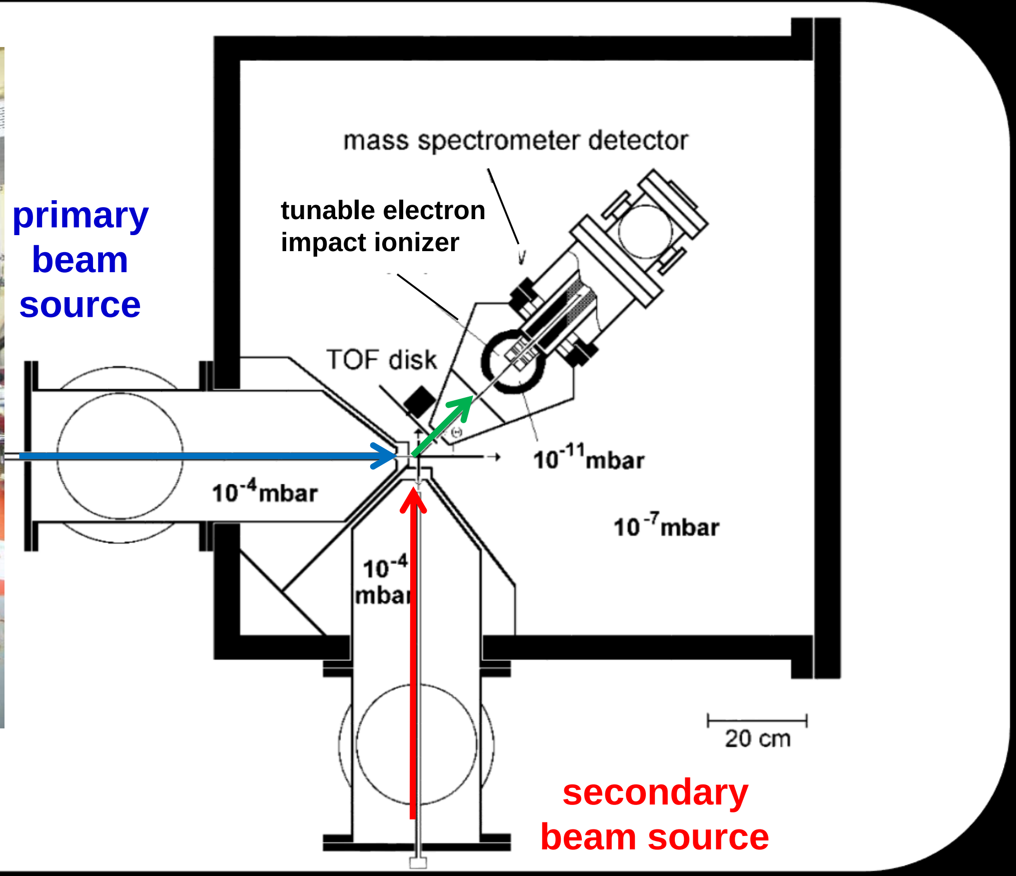
- reaction mechanism
- energy release

↓

potential energy surface (PES)

- primary products & branching ratios

PERUGIA



- continuous beams
- crossing angle: 45°, 90°, 135°

Neutral-neutral reactions of astrophysical relevance investigated in Perugia with the crossed molecular beam method:

- O + C_2H_2, C_2H_4, CH_2CCH_2, CH_3CCH, CH_3CHCH_2, H_2S, C_6H_6, C_5H_5N, $C_6H_5CH_3$, C_2H_3CN, HCCCN
- OH + H_2, CO, C_2H_4
- O + CH_3, C_3H_5

- CN + C_2H_2, CH_3CCH, C_2H_4, C_2H_3CN, H
- $N(^2D)$ + H_2, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, CH_2CCH_2, CH_3CCH C_2H_3CN, HCCCN, C_6H_6, C_5H_5N, $C_6H_5CH_3$

- C + C_2H_2, C_2H_4, CH_3CCH
- $C_2(X^1\Sigma_g^+, a^3\Pi_u)$ + C_2H_2
- C_6H_5 + O_2, 1,3-butadiene
- $C(^1D)$ + CH_4
- $S(^1D)$ + C_2H_2, C_2H_4, CH_4

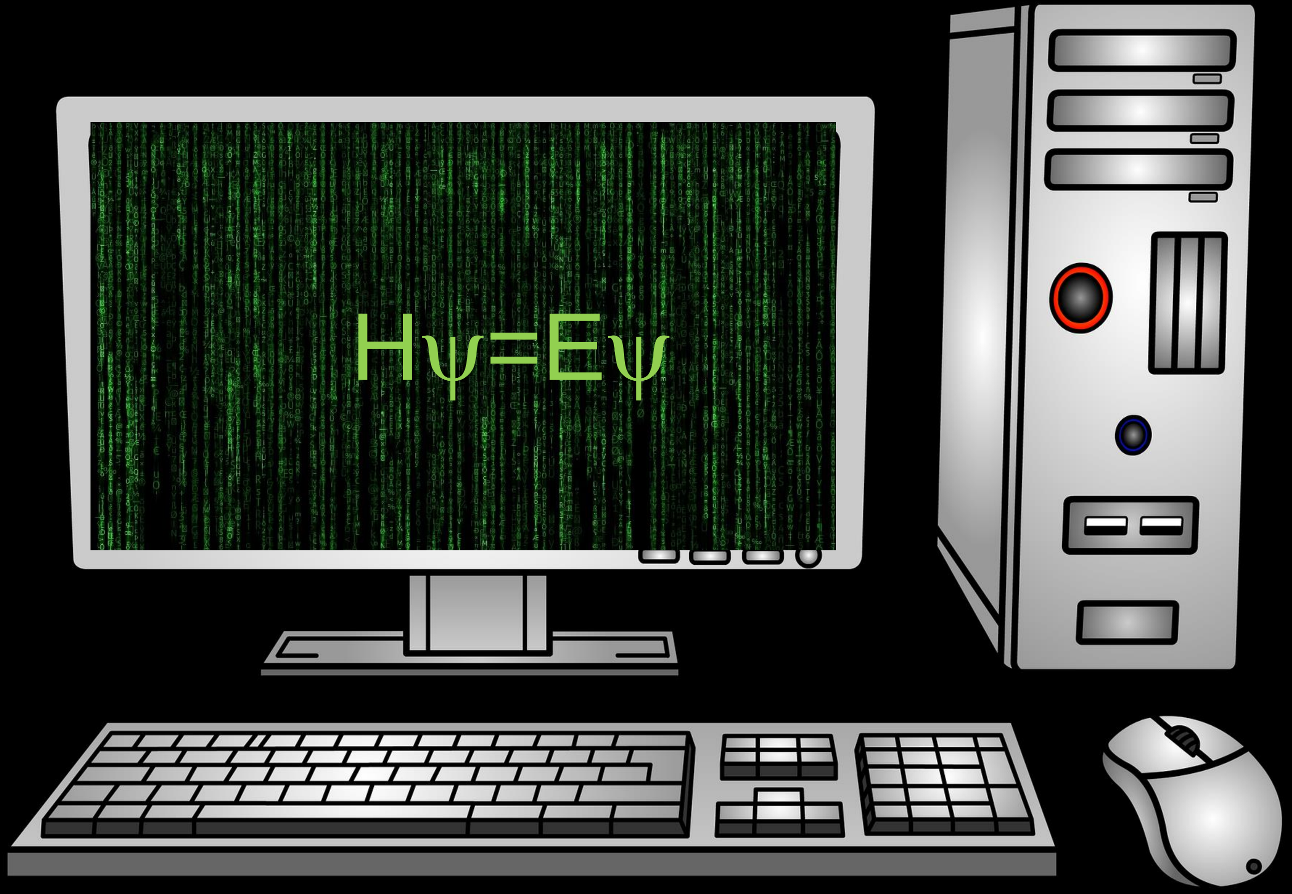
+ the huge amount of work by Ralf Kaiser (Univ Hawaii)

This approach nicely reproduces the low-density conditions of interstellar objects, but NOT their low temperatures

What is the status of our knowledge of gas phase reactions?
In particular, bimolecular reactions...

we have three pillars

❸ *quantum chemistry calculations*



Potential energy surface:

- DFT calculations
- CCSD(T) calculations
- CASPT2 calculations

Gaussian, Molpro

kinetics calculations:

- RRKM
- capture theory
- modified Lennard-Jones capture theory

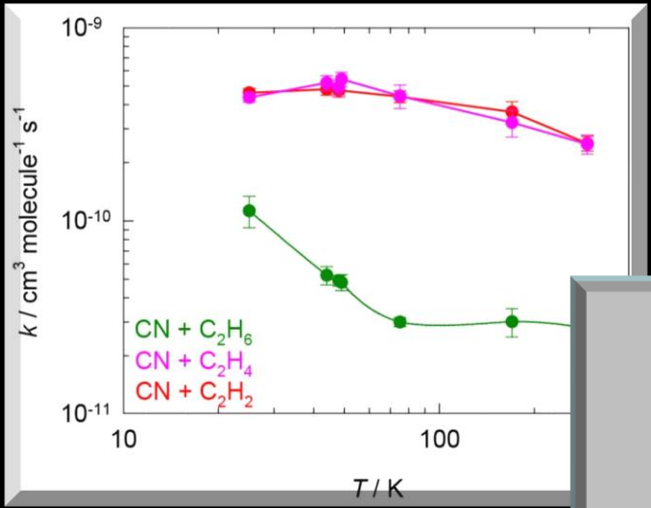
What is the status of our knowledge of gas phase reactions? In particular, bimolecular reactions…

we have three pillars

❸ *quantum chemistry calculations*

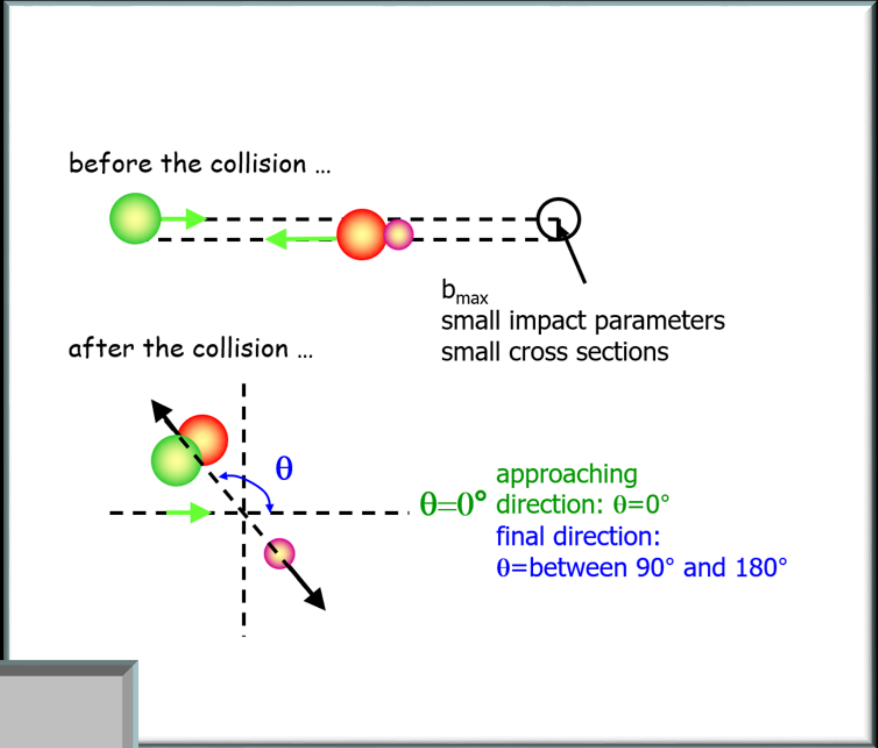
a) There are no versatile experimental techniques achieving both low T and P: a theoretical description of the reactive process via electronic structure calculations of the relevant potential energy surface + kinetics calculations can provide the rate coefficients under the conditions of interest; the comparison with available experimental data tests the accuracy of the calculations

Rate coefficients at low T (CRESU)

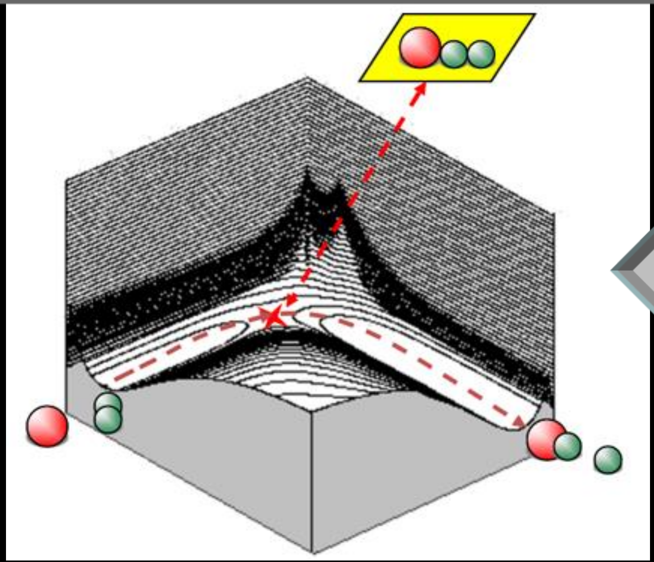


Calculate anything you need

Reaction mechanism + product branching ratios (crossed molecular beam experiments)



Accurate potential energy surface



What is the status of our knowledge of gas phase reactions?
In particular, bimolecular reactions…

we have three pillars

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a) There are no versatile experimental techniques achieving both low T and P: a theoretical description of the reactive process via electronic structure calculations of the relevant potential energy surface + kinetics calculations can provide the rate coefficients under the conditions of interest; the comparison with available experimental data tests the accuracy of the calculations ✓

b) There are no experimental data at all: a theoretical description of the reactive process via electronic structure calculations of the relevant potential energy surface + kinetics calculations can provide an educated guess of the reaction rate coefficients

⚠ CAUTION

I will now illustrate a couple of case studies of systems that has been characterized in my group with a theoretical approach only and with a combined experimental and theoretical approach (one is related to the interstellar medium and one is related to Titan)

before that, a caveat: usually, we expect that by increasing the complexity of the reactants, we will also have an increase in the complexity of the products
- this is not necessarily true

by increasing the complexity of the reactants,
we expect more complex products

$$NH + CH_3 \rightarrow CH_2{=}NH + H$$

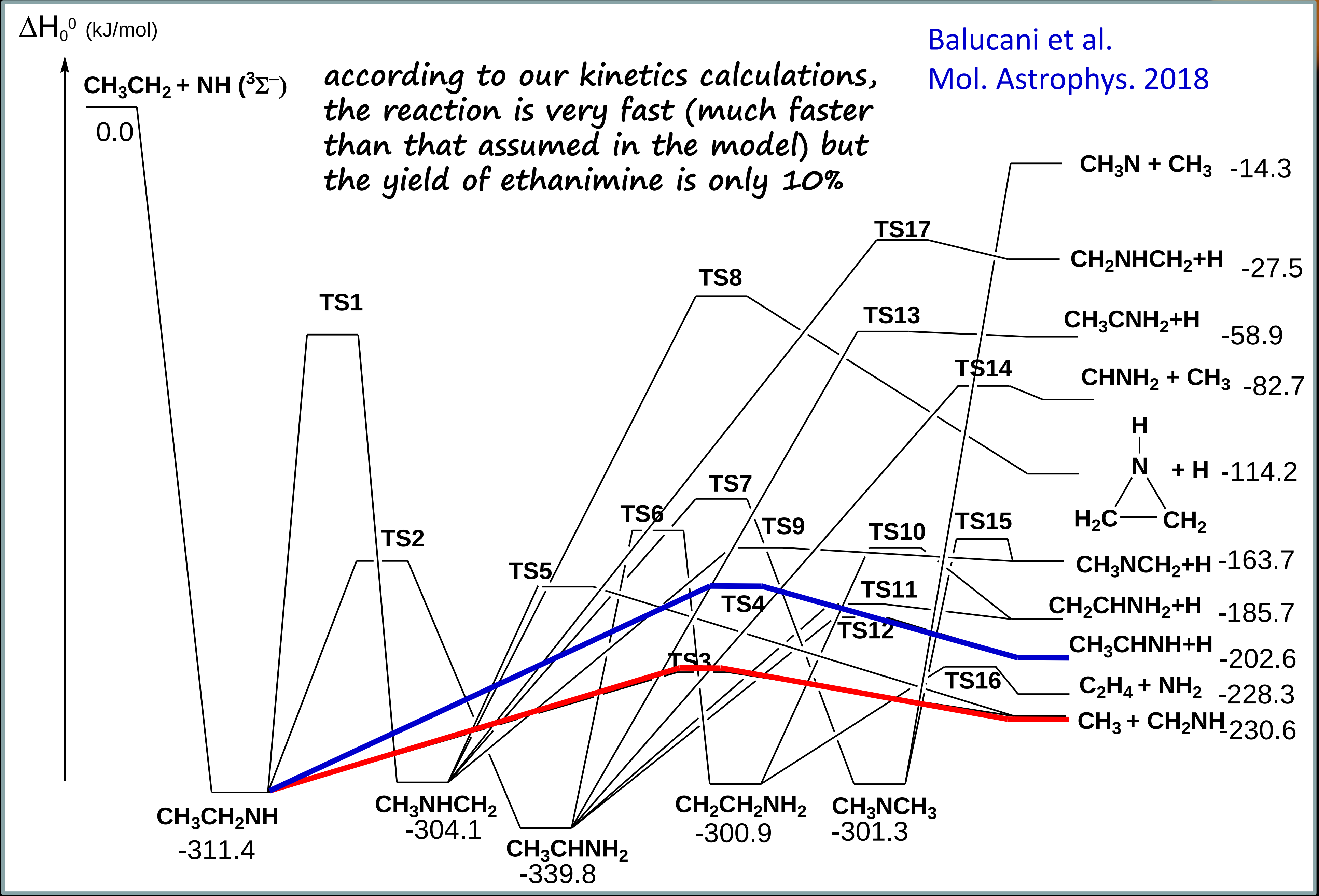
widely investigated system

by increasing the complexity of the reactants,
we expect more complex products

$$NH + C_2H_5 \rightarrow CH_3CH{=}NH + H$$

suggested by Quan et al. (ApJ 2016)

The reaction NH + C_2H_5

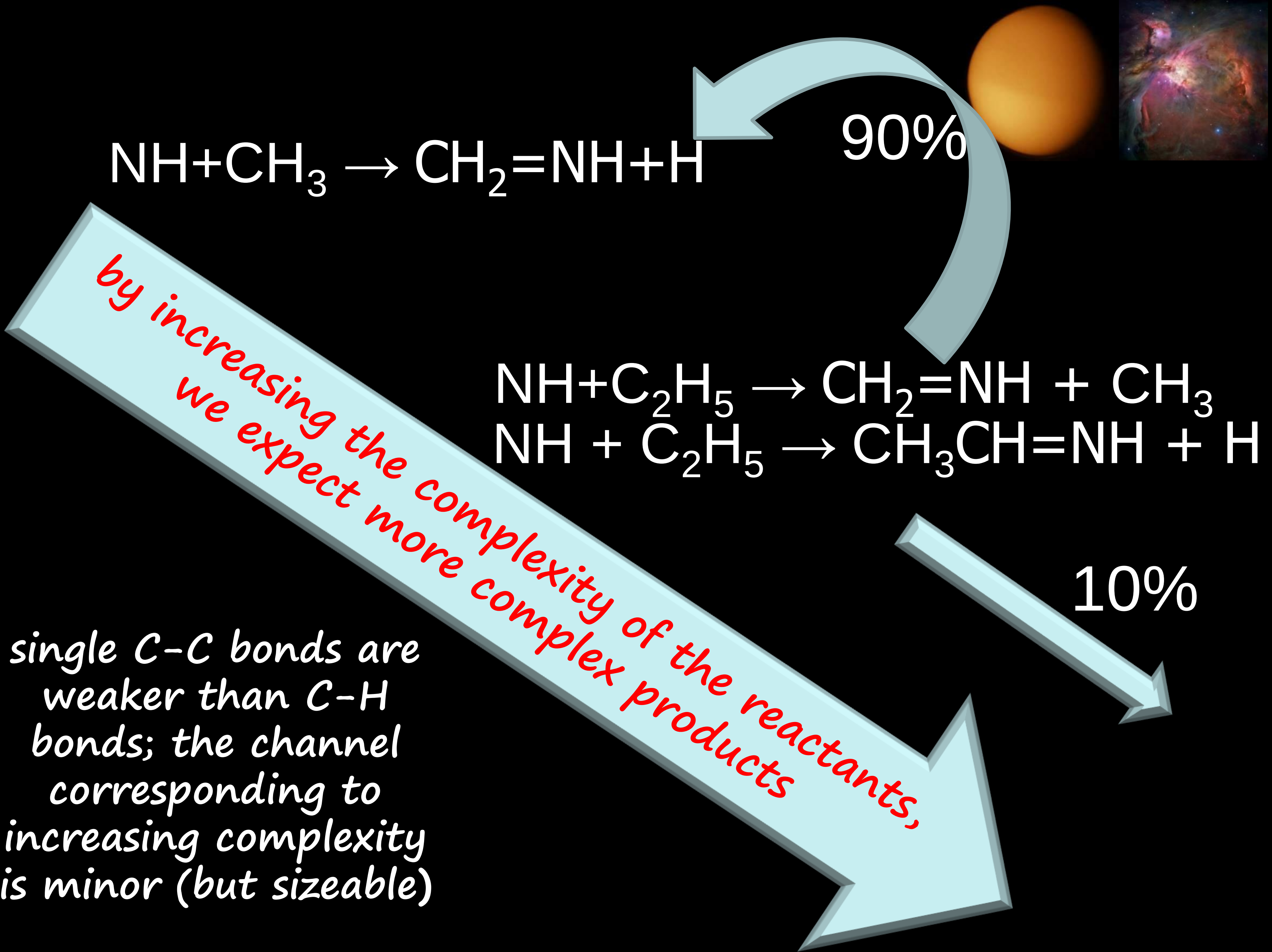


according to our kinetics calculations, the reaction is very fast (much faster than that assumed in the model) but the yield of ethanimine is only 10%

Balucani et al.
Mol. Astrophys. 2018

This because sigma C–C bond are weaker than other sigma bonds (in particular C–H) and, therefore, easier to break.

No surprise that most of the interstellar complex organic molecules do have multiple C–C bonds.



$NH + CH_3 \rightarrow CH_2{=}NH + H$

90%

$NH + C_2H_5 \rightarrow CH_2{=}NH + CH_3$

$NH + C_2H_5 \rightarrow CH_3CH{=}NH + H$

10%

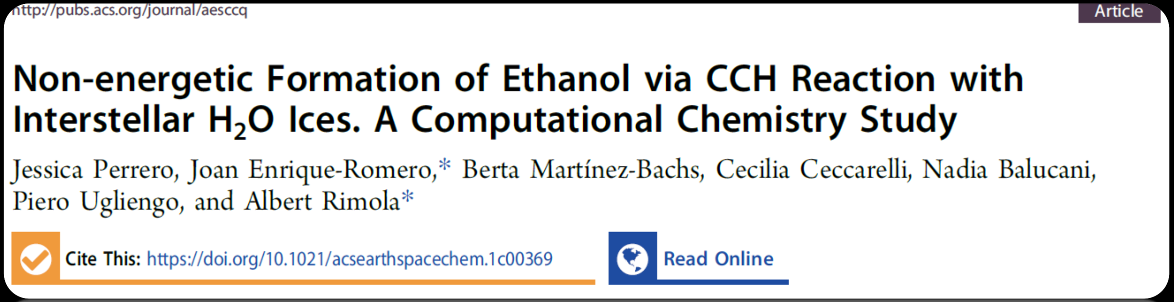
by increasing the complexity of the reactants, we expect more complex products

single C–C bonds are weaker than C–H bonds; the channel corresponding to increasing complexity is minor (but sizeable)

The formation of glycolaldehyde from ethanol

an astrochemical connection among interstellar CH_3CH_2OH and HCOOH, CH_3COOH, CH_2OHCHO

Ethanol in easily formed on the water ice of dust grains by the direct reaction of the C_2H radicals with the water molecules of ice



http://pubs.acs.org/journal/aesccq

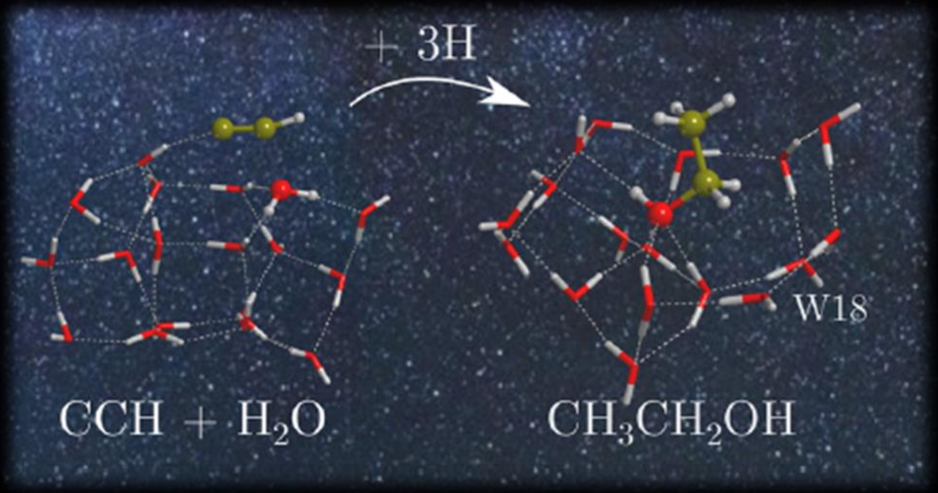
Article

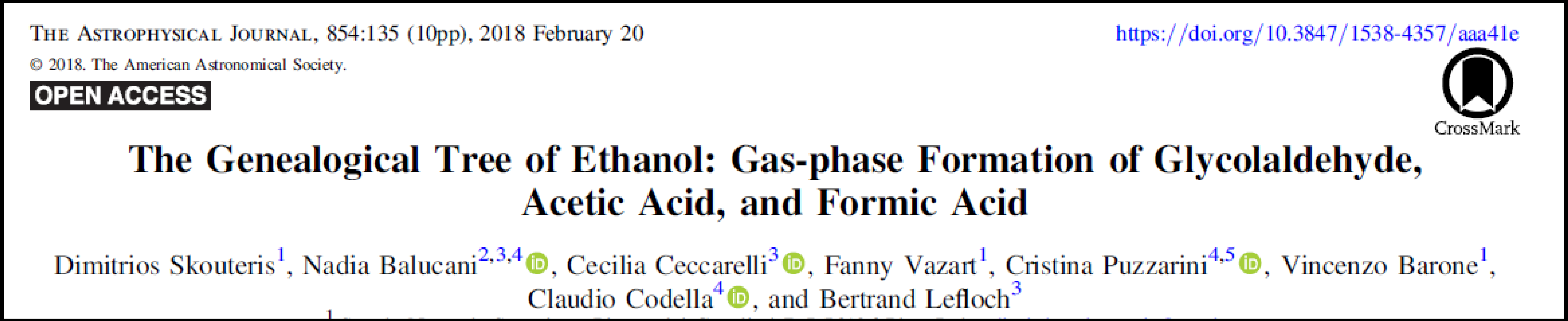
Non-energetic Formation of Ethanol via CCH Reaction with Interstellar H_2O Ices. A Computational Chemistry Study

Jessica Perrero, Joan Enrique-Romero,* Berta Martínez-Bachs, Cecilia Ceccarelli, Nadia Balucani, Piero Ugliengo, and Albert Rimola*

Cite This: https://doi.org/10.1021/acsearthspacechem.1c00369

Read Online

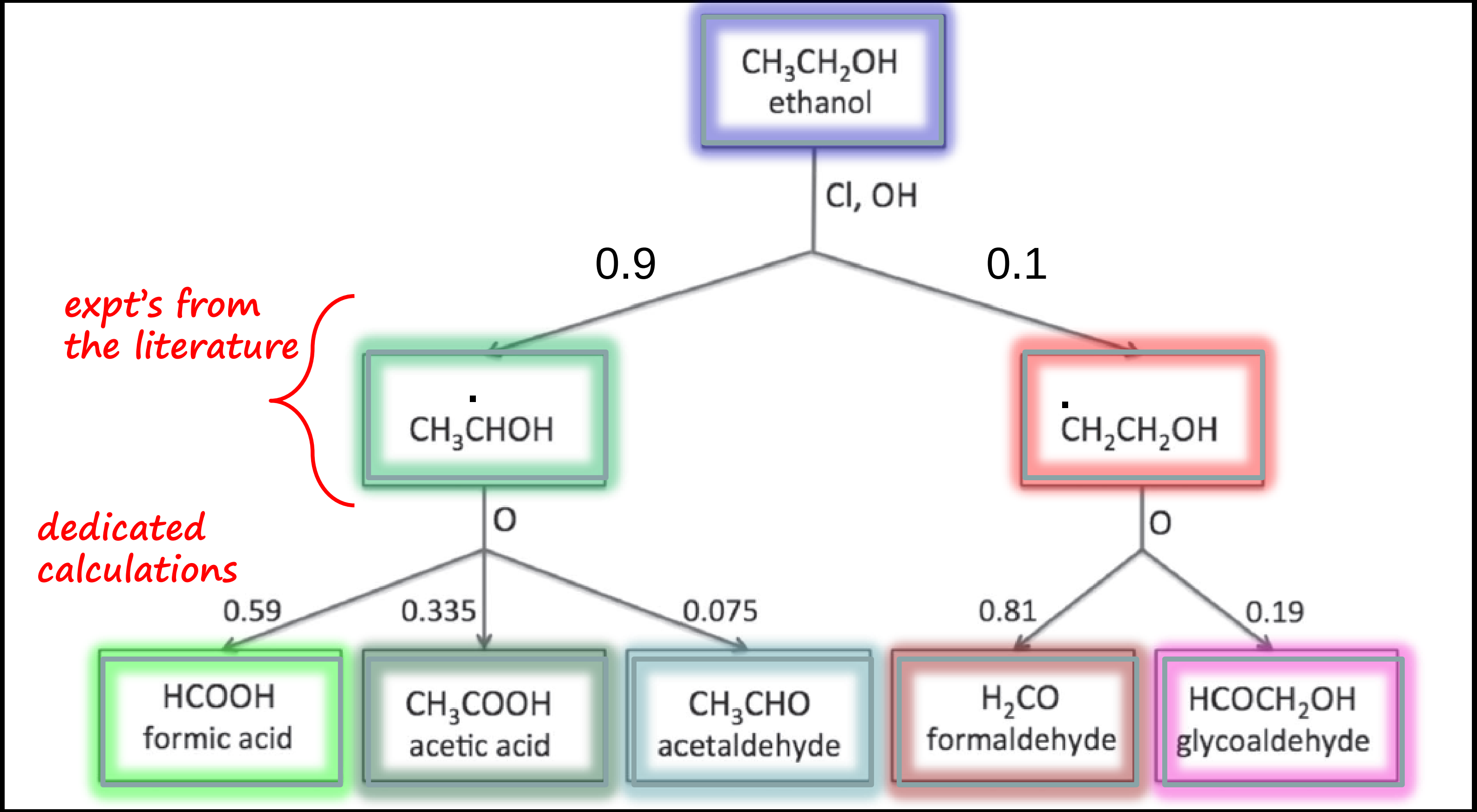




The Astrophysical Journal, 854:135 (10pp), 2018 February 20
https://doi.org/10.3847/1538-4357/aaa41e

The Genealogical Tree of Ethanol: Gas-phase Formation of Glycolaldehyde, Acetic Acid, and Formic Acid

Dimitrios Skouteris[1], Nadia Balucani[2,3,4], Cecilia Ceccarelli[3], Fanny Vazart[1], Cristina Puzzarini[4,5], Vincenzo Barone[1], Claudio Codella[4], and Bertrand Lefloch[3]



CH_3CH_2OH
ethanol

Cl, OH

0.9 0.1

expt's from the literature

$CH_3\dot{C}HOH$

$\dot{C}H_2CH_2OH$

O

dedicated calculations

0.59 0.335 0.075

0.81 0.19

$HCOOH$
formic acid

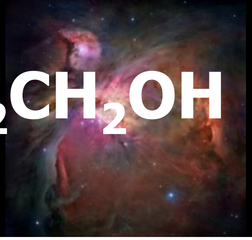
CH_3COOH
acetic acid

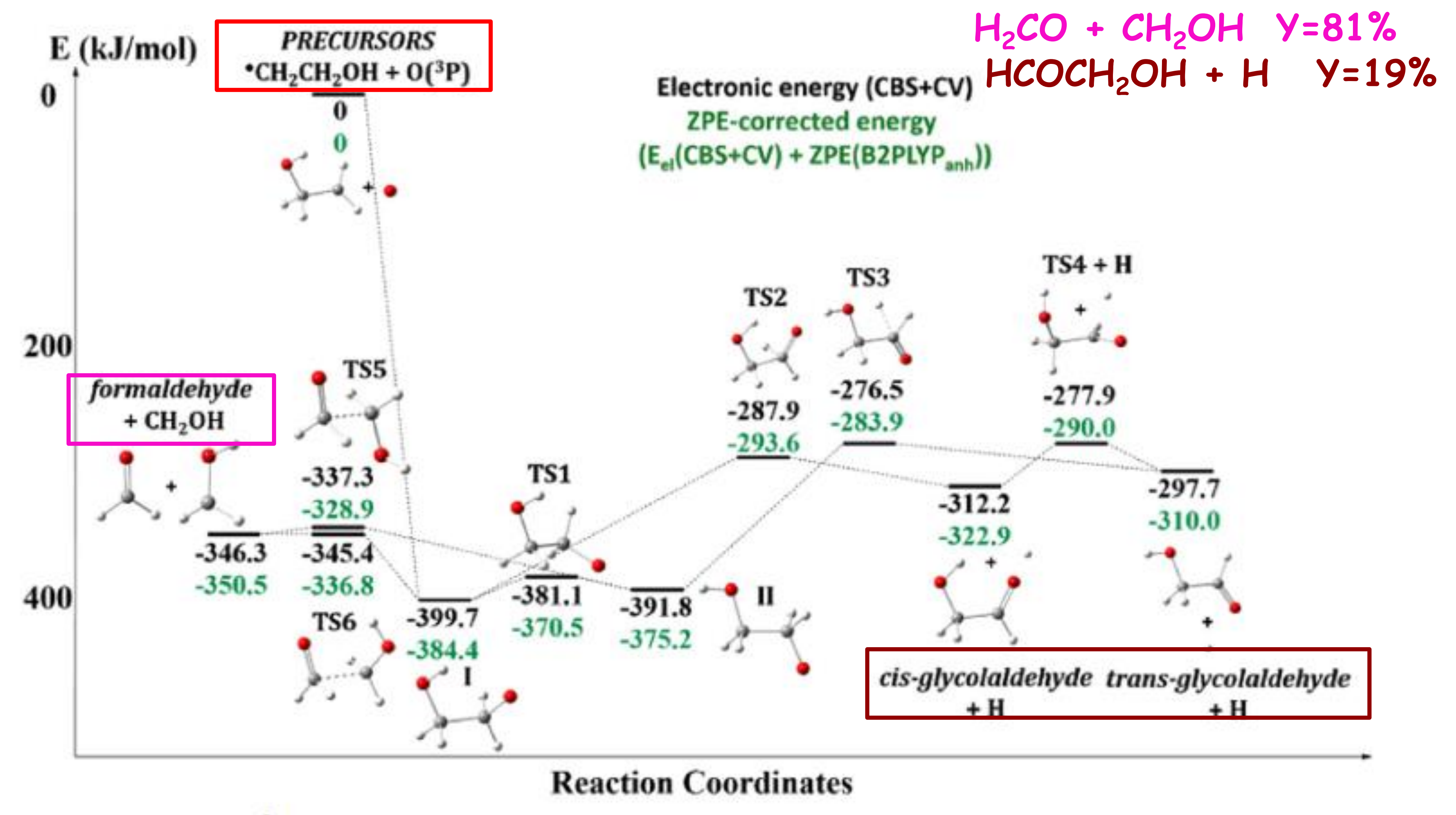
CH_3CHO
acetaldehyde

H_2CO
formaldehyde

$HCOCH_2OH$
glycoaldehyde

The potential energy surface for the reaction $O+CH_2CH_2OH$



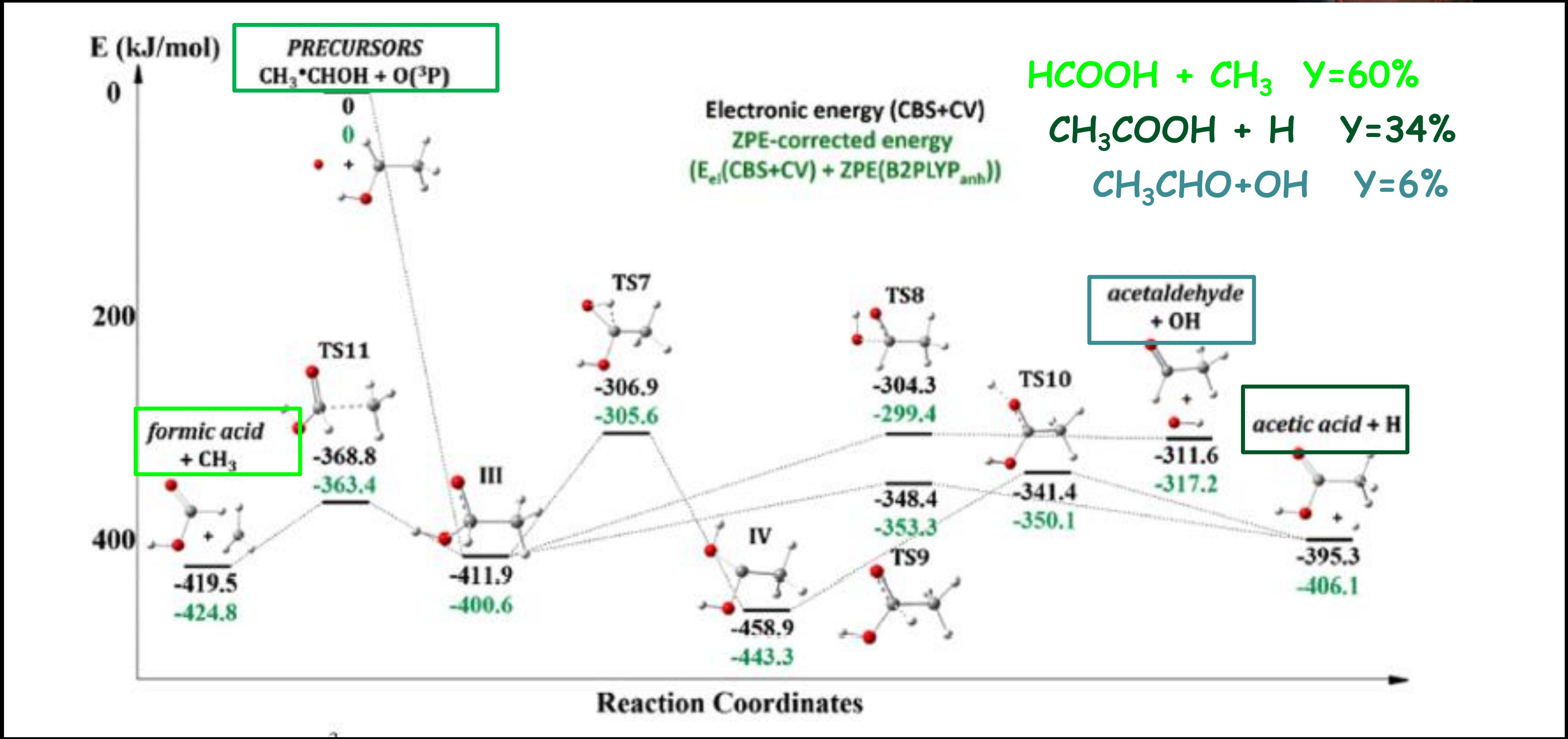


$H_2CO + CH_2OH$ Y=81%

$HCOCH_2OH + H$ Y=19%

Skouteris et al. ApJ 2018, 854, 135

The potential energy surface for the reaction $O+CH_3CHOH$



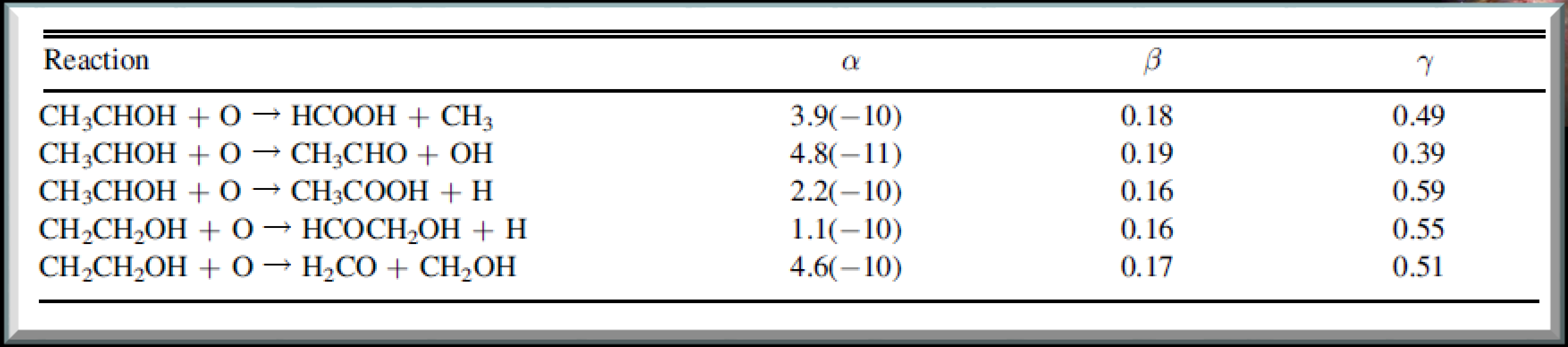
$HCOOH + CH_3$ Y=60%

$CH_3COOH + H$ Y=34%

$CH_3CHO+OH$ Y=6%

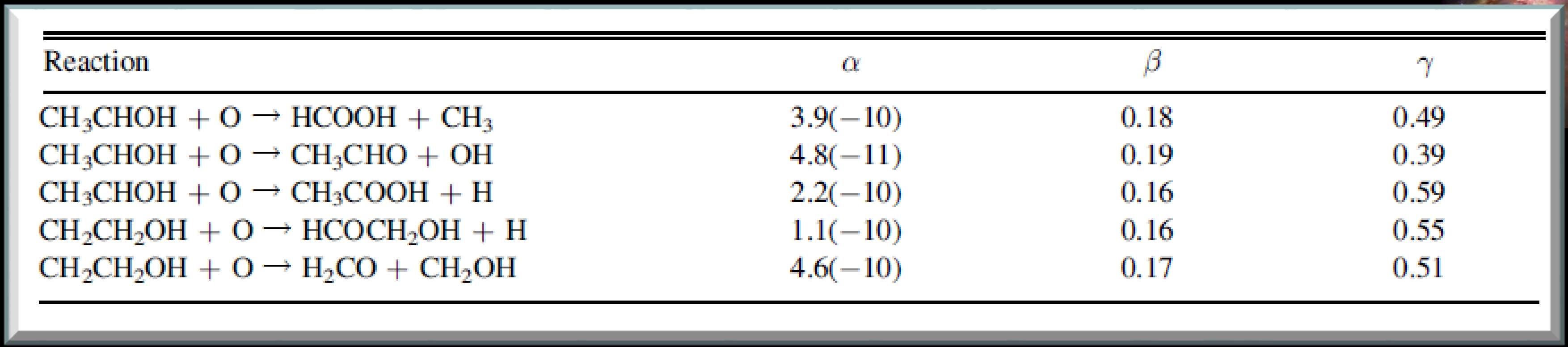
Skouteris et al. ApJ 2018, 854, 135

Kinetics calculations (Capture Theory + RRKM)



Reaction	α	β	γ
$CH_3CHOH + O \rightarrow HCOOH + CH_3$	3.9(−10)	0.18	0.49
$CH_3CHOH + O \rightarrow CH_3CHO + OH$	4.8(−11)	0.19	0.39
$CH_3CHOH + O \rightarrow CH_3COOH + H$	2.2(−10)	0.16	0.59
$CH_2CH_2OH + O \rightarrow HCOCH_2OH + H$	1.1(−10)	0.16	0.55
$CH_2CH_2OH + O \rightarrow H_2CO + CH_2OH$	4.6(−10)	0.17	0.51

Kinetics calculations (Capture Theory + RRKM)



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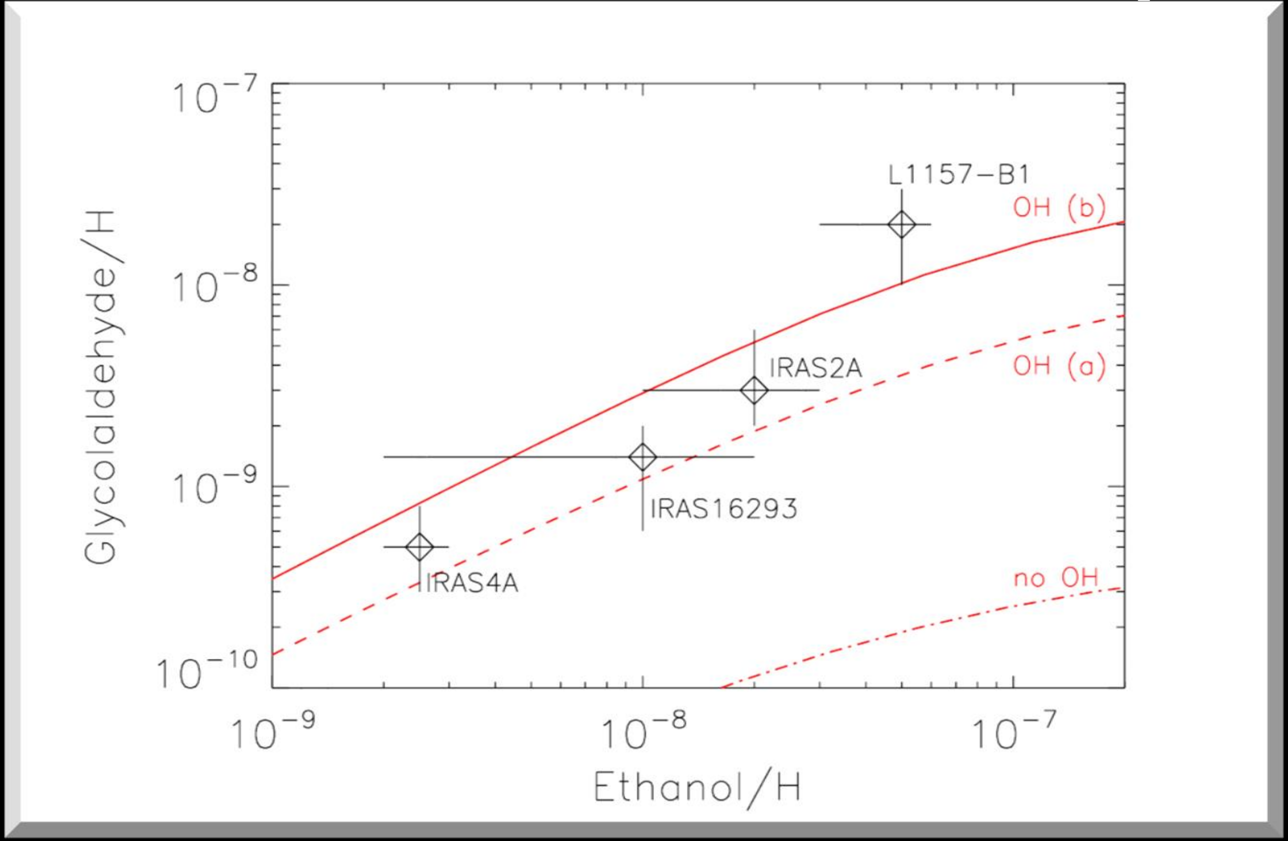
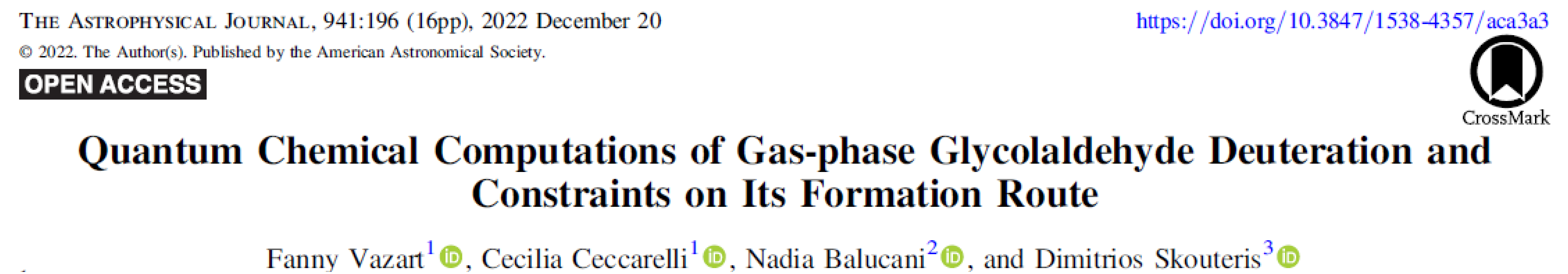
$CH_2CH_2OH + O \rightarrow H_2CO + CH_2OH$	4.6(−10)	0.17	0.51

The astrochemical model (Nahoon + revised KIDA database)



The abundance of glycolaldehyde plotted against the abundance of ethanol for four different astrochemical objects follows closely the theoretical predictions based on our model (the three red curves correspond to different branching ratios of the ethanol radicals on hydrogen abstraction by the OH radical).

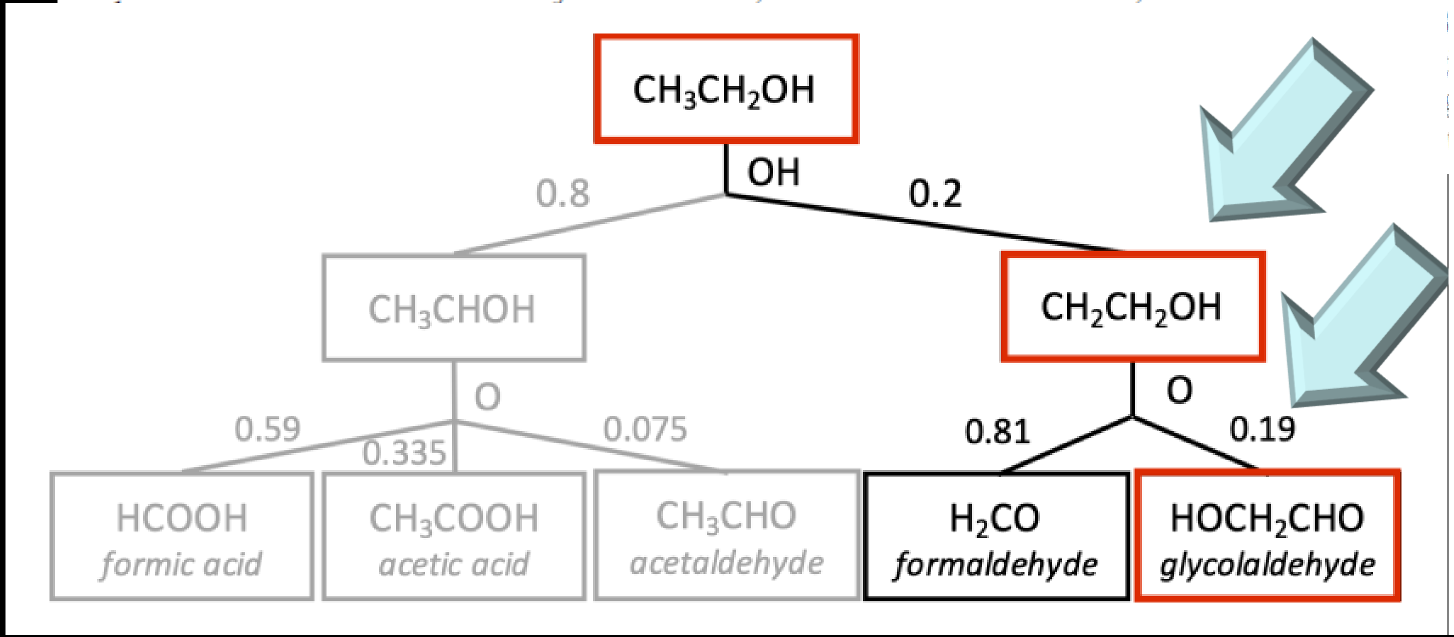
glycolaldehyde if formed by the ethanol tree scheme: a further confirmation by the study of its deuteration degree

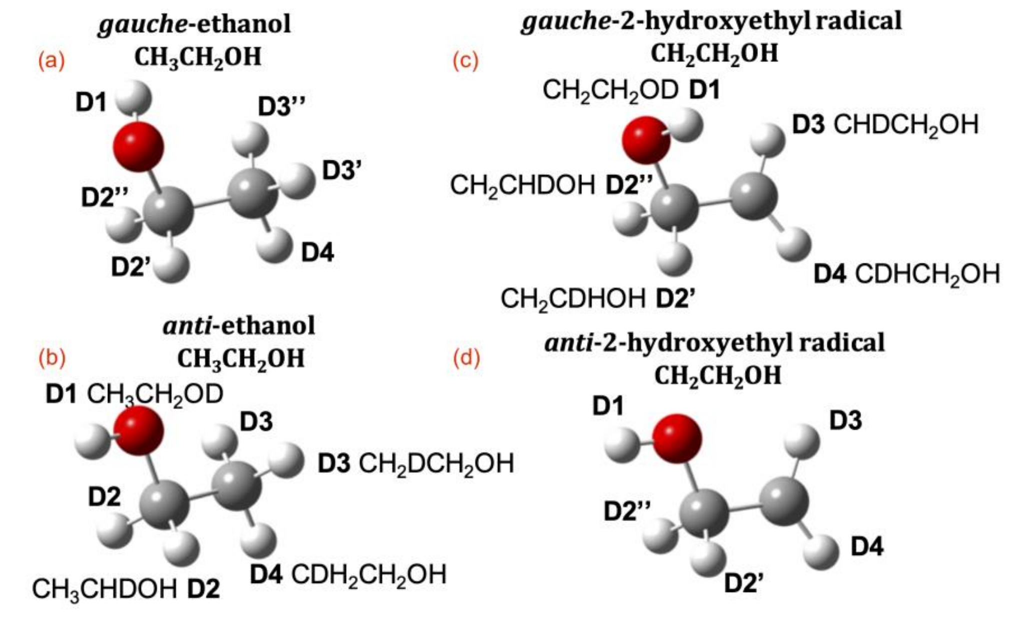


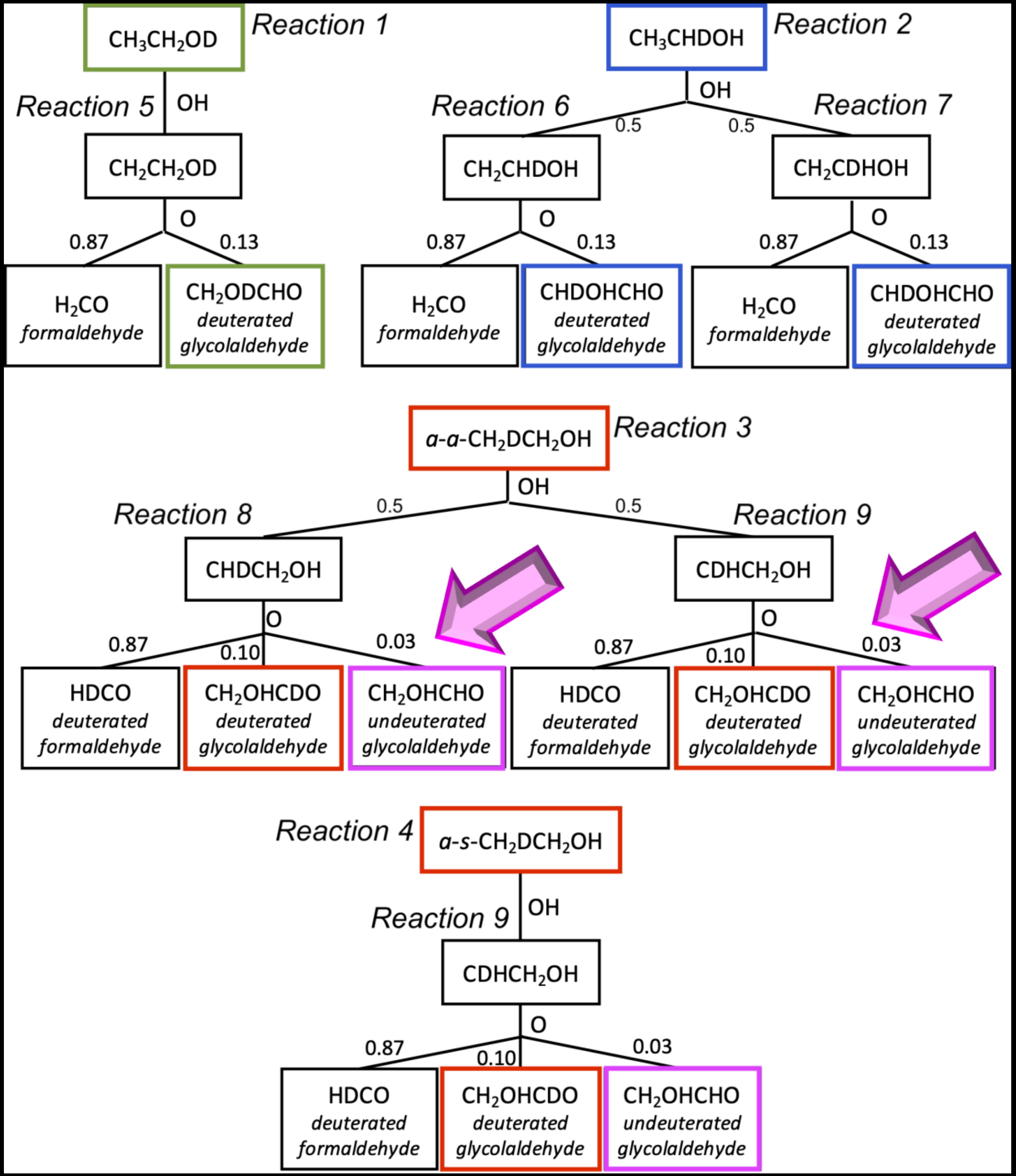
THE ASTROPHYSICAL JOURNAL, 941:196 (16pp), 2022 December 20 https://doi.org/10.3847/1538-4357/aca3a3

Quantum Chemical Computations of Gas-phase Glycolaldehyde Deuteration and Constraints on Its Formation Route

Fanny Vazart[1], Cecilia Ceccarelli[1], Nadia Balucani[2], and Dimitrios Skouteris[3]







Reaction 1

CH_3CH_2OD

Reaction 5

OH

CH_2CH_2OD

O

0.87 0.13

H_2CO *formaldehyde*

CH_2ODCHO *deuterated glycolaldehyde*

Reaction 2

CH_3CHDOH

OH

Reaction 6 0.5

Reaction 7 0.5

CH_2CHDOH

O

0.87 0.13

H_2CO *formaldehyde*

$CHDOHCHO$ *deuterated glycolaldehyde*

CH_2CDHOH

O

0.87 0.13

H_2CO *formaldehyde*

$CHDOHCHO$ *deuterated glycolaldehyde*

Reaction 3

a-a-CH_2DCH_2OH

OH

Reaction 8 0.5

Reaction 9 0.5

$CHDCH_2OH$

O

0.87 0.10 0.03

HDCO *deuterated formaldehyde*

CH_2OHCDO *deuterated glycolaldehyde*

CH_2OHCHO *undeuterated glycolaldehyde*

$CDHCH_2OH$

O

0.87 0.10 0.03

HDCO *deuterated formaldehyde*

CH_2OHCDO *deuterated glycolaldehyde*

CH_2OHCHO *undeuterated glycolaldehyde*

Reaction 4

a-s-CH_2DCH_2OH

Reaction 9

OH

$CDHCH_2OH$

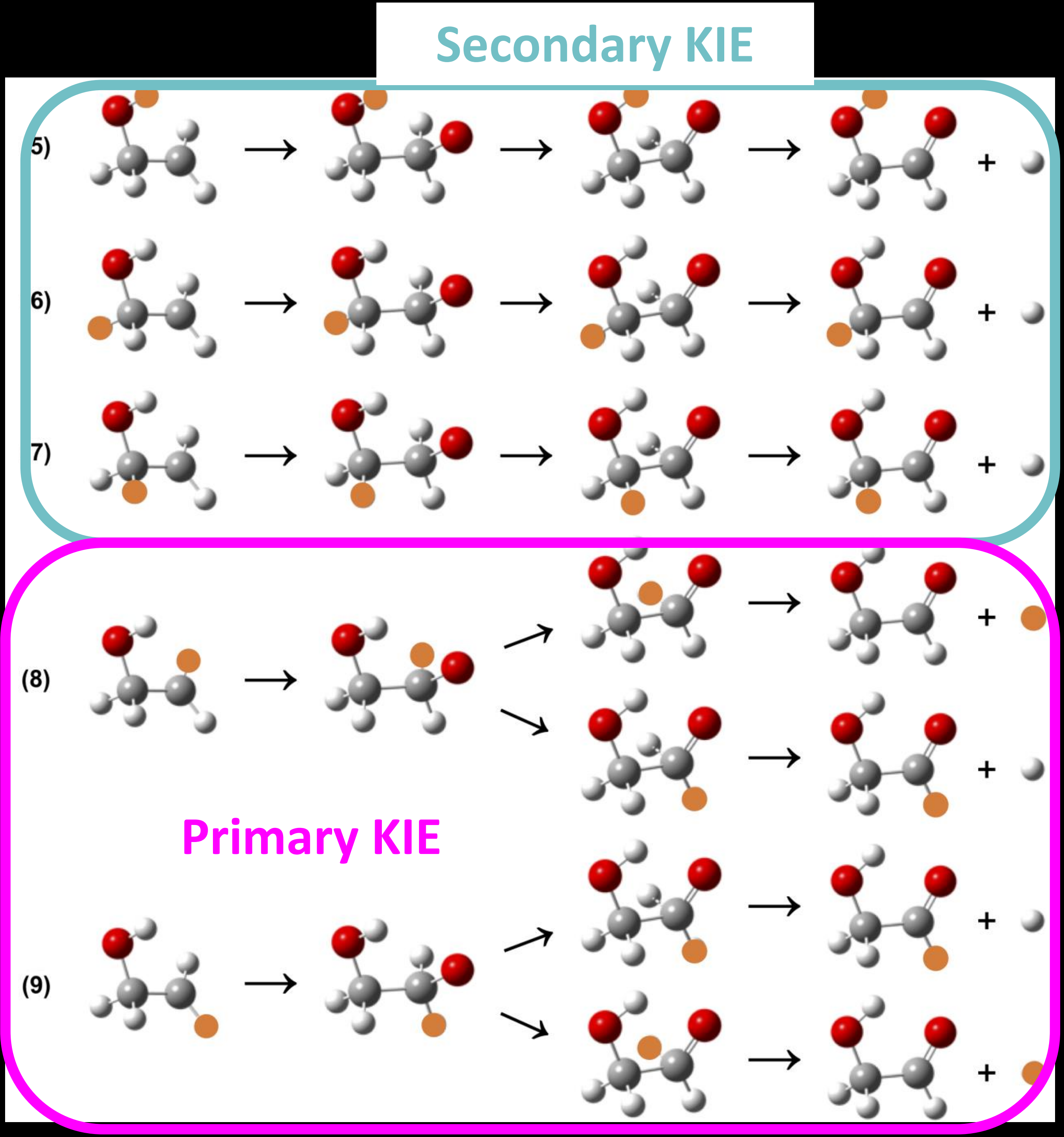
O

0.87 0.10 0.03

HDCO *deuterated formaldehyde*

CH_2OHCDO *deuterated glycolaldehyde*

CH_2OHCHO *undeuterated glycolaldehyde*



FORMATION OF DEUTERATED GLYCOLALDEHYDE

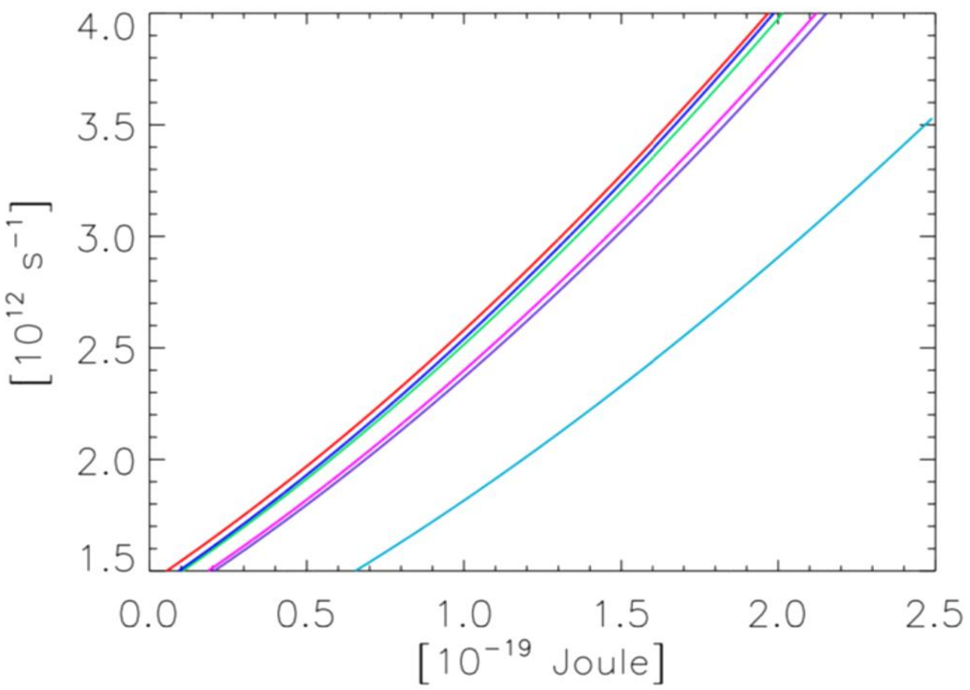
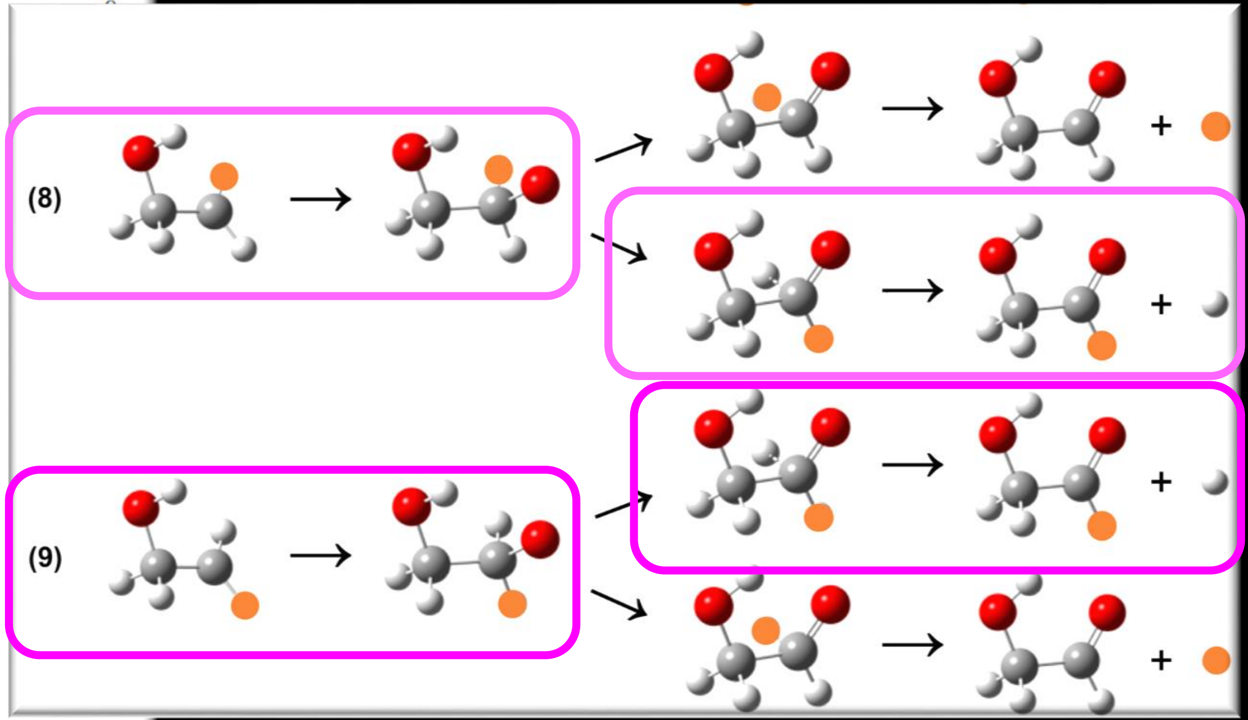
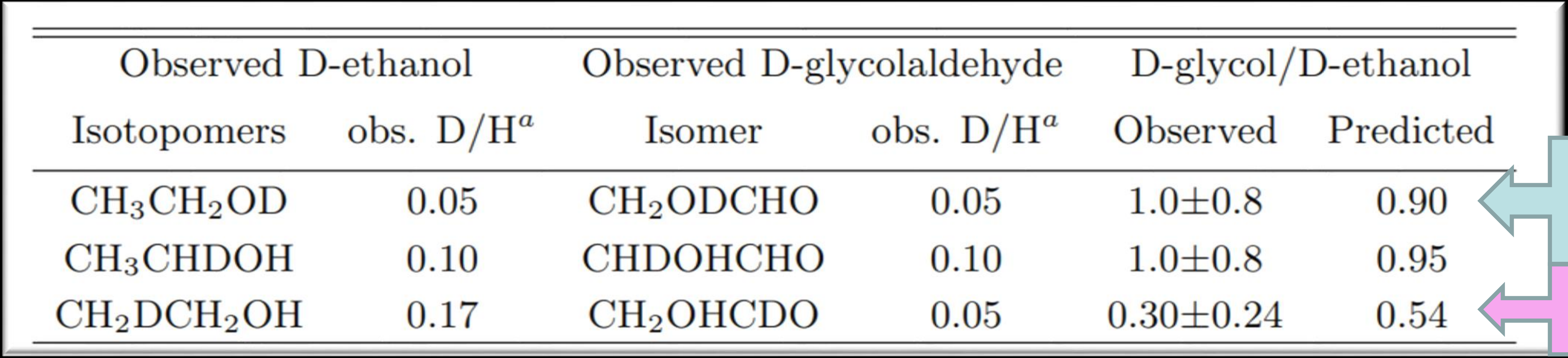


Figure 5. Unimolecular rate coefficients from RI1 to *cis*-glycoaldehyde via TS2. Red: all-protium reaction. Green: CH_2ODCHO from reaction 5. Blue: CHDOHCHO from reaction 6. Magenta: CHDOHCHO from reaction 7. Light blue: CH_2OHCDO from reaction 8a. Purple: CH_2OHCDO from reaction 9a.

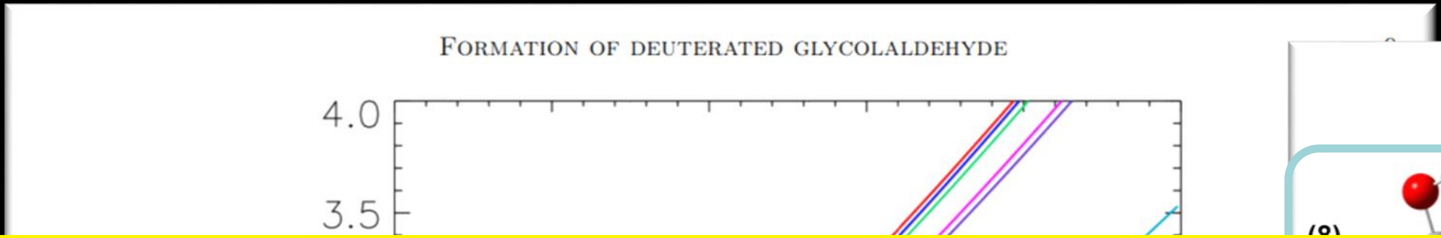


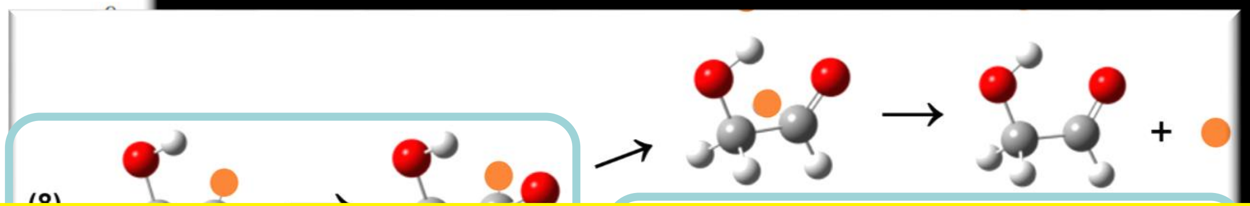


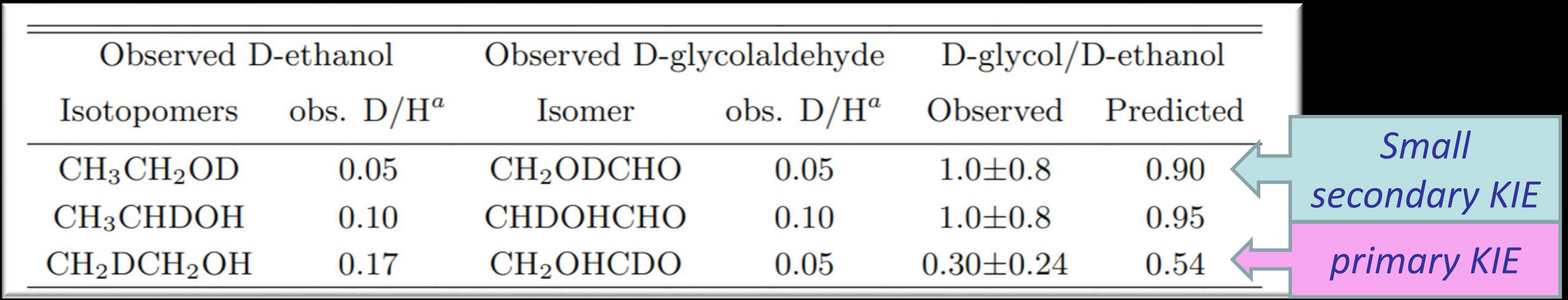
Observed D-ethanol		Observed D-glycolaldehyde		D-glycol/D-ethanol	
Isotopomers	obs. D/H^a	Isomer	obs. D/H^a	Observed	Predicted
CH_3CH_2OD	0.05	CH_2ODCHO	0.05	1.0±0.8	0.90
CH_3CHDOH	0.10	CHDOHCHO	0.10	1.0±0.8	0.95
CH_2DCH_2OH	0.17	CH_2OHCDO	0.05	0.30±0.24	0.54

Small secondary KIE

primary KIE


FORMATION OF DEUTERATED GLYCOLALDEHYDE





Observed D-ethanol		Observed D-glycolaldehyde		D-glycol/D-ethanol	
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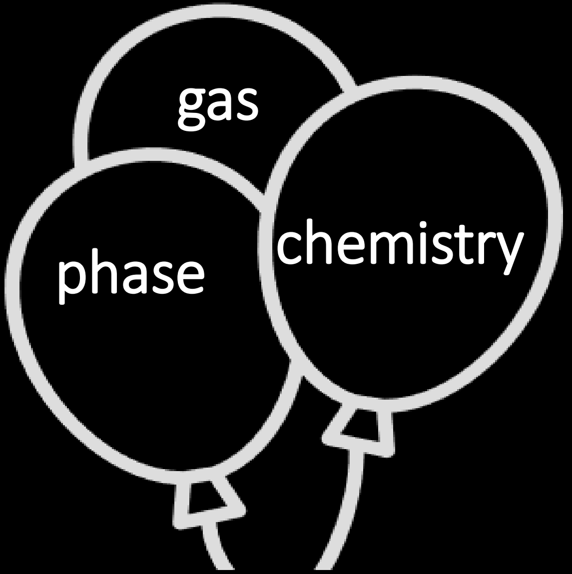
CH_2DCH_2OH	0.17	CH_2OHCDO	0.05	0.30±0.24	0.54

Small secondary KIE

primary KIE

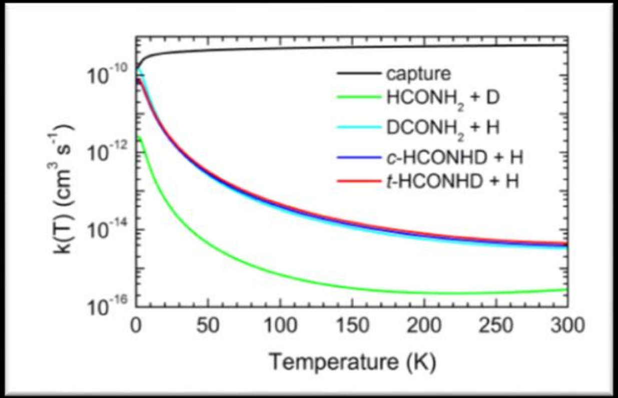
We have tested three case systems



$NH_2 + H_2CO$

formamide

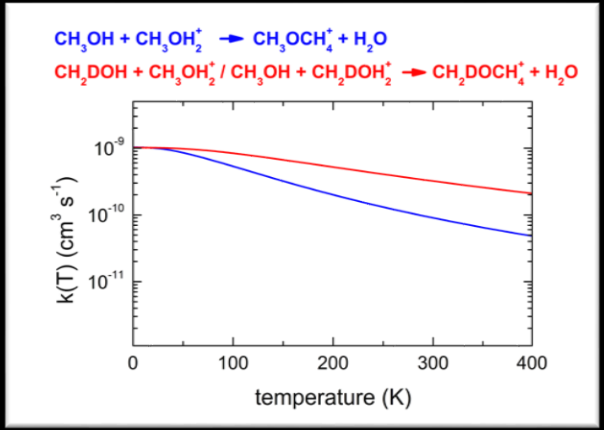
Skouteris et al. MNRAS 2017



$CH_3OH + CH_3OH_2^+$

dimethyl ether

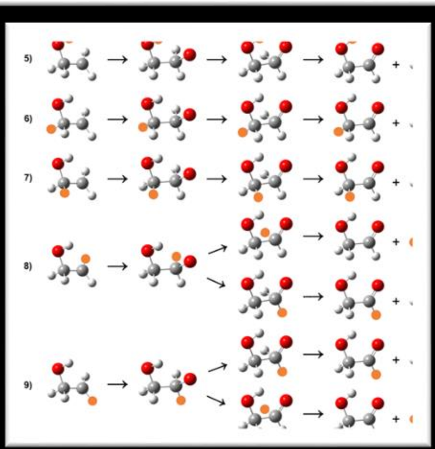
Pannacci et al., in preparation



$O + CH_2CH_2OH$

glycolaldehyde

Vazart et al. ApJ 2022

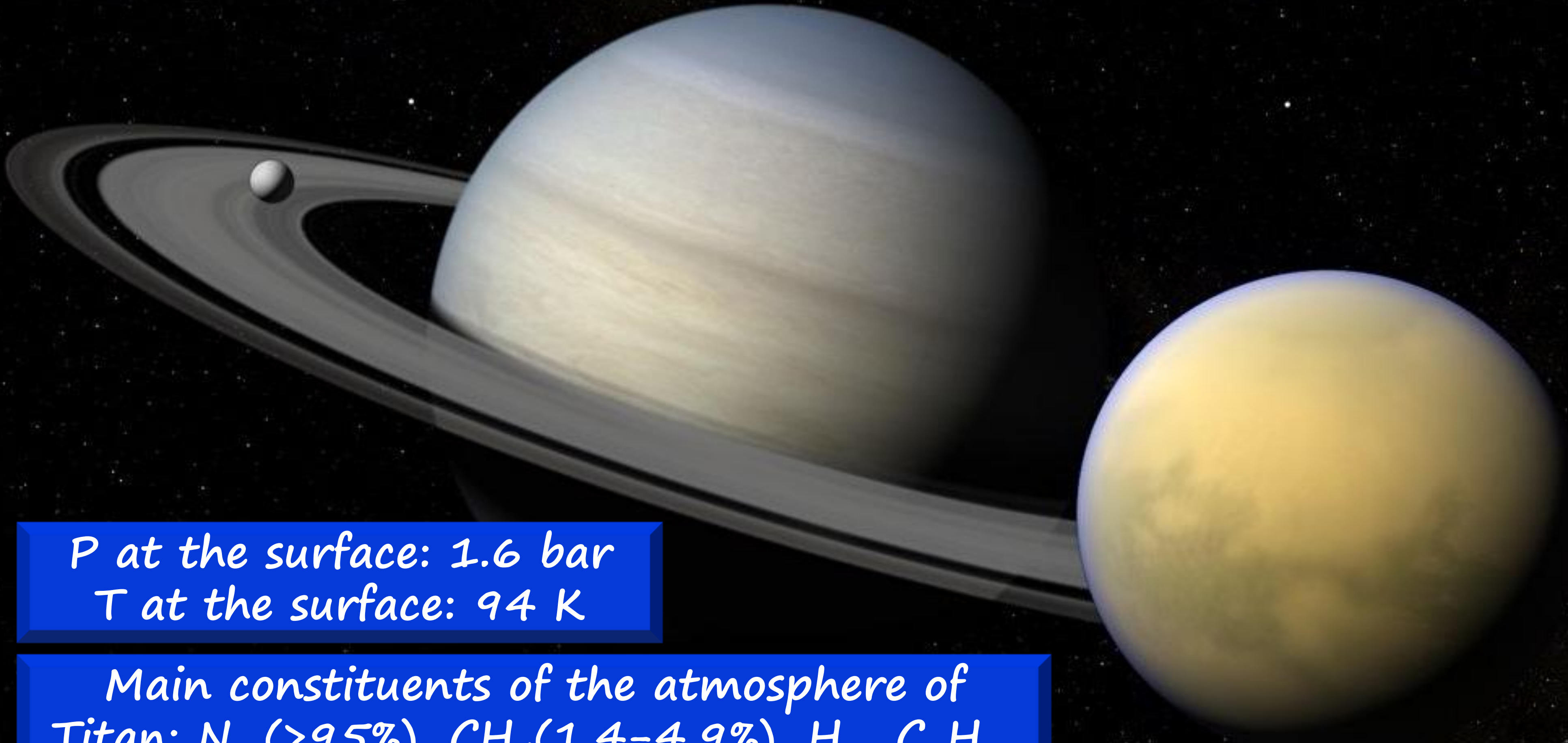


We are now working on a fourth case

$O + CH_3OCH_2$

methyl formate

The atmospheric chemistry of Titan, the massive moon of Saturn



P at the surface: 1.6 bar
T at the surface: 94 K

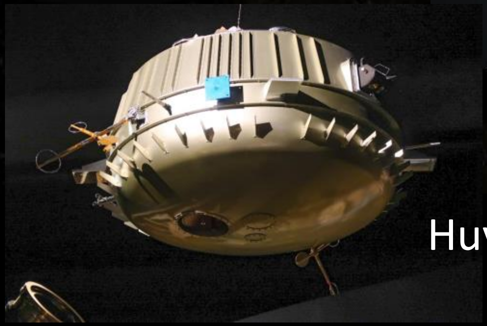
Main constituents of the atmosphere of Titan: N_2 (>95%), CH_4(1.4–4.9%), H_2, C_2H_6, C_2H_2, C_2H_4, HCN, HCCCN, C_2N_2, …

defined by Carl Sagan “a laboratory for prebiological organic chemistry” on a planetary scale

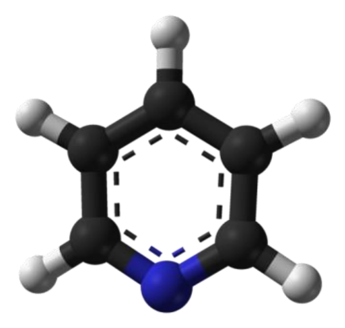
Sagan et al. Acc. Chem. Res. 1992

Voyager

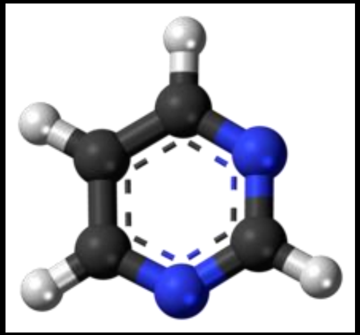
Cassini



Huygens

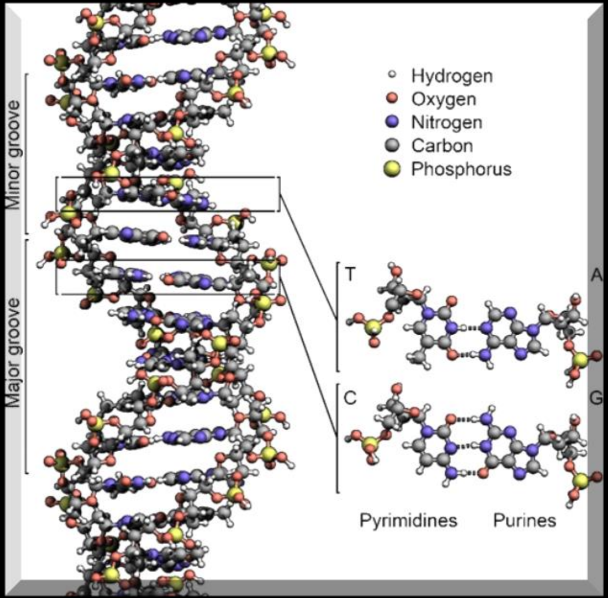


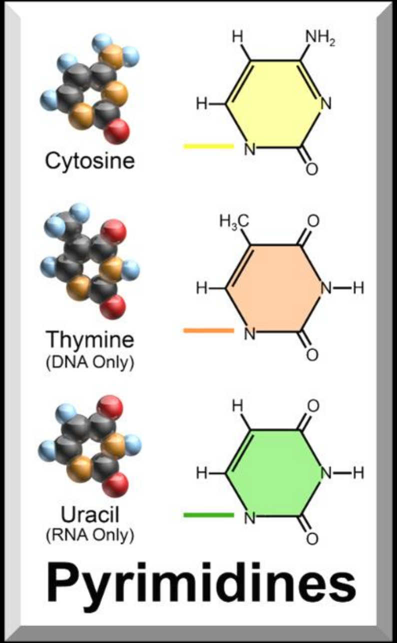
is it possible to synthesize pyridine and pyrimidine under the conditions of the upper atmosphere of Titan?

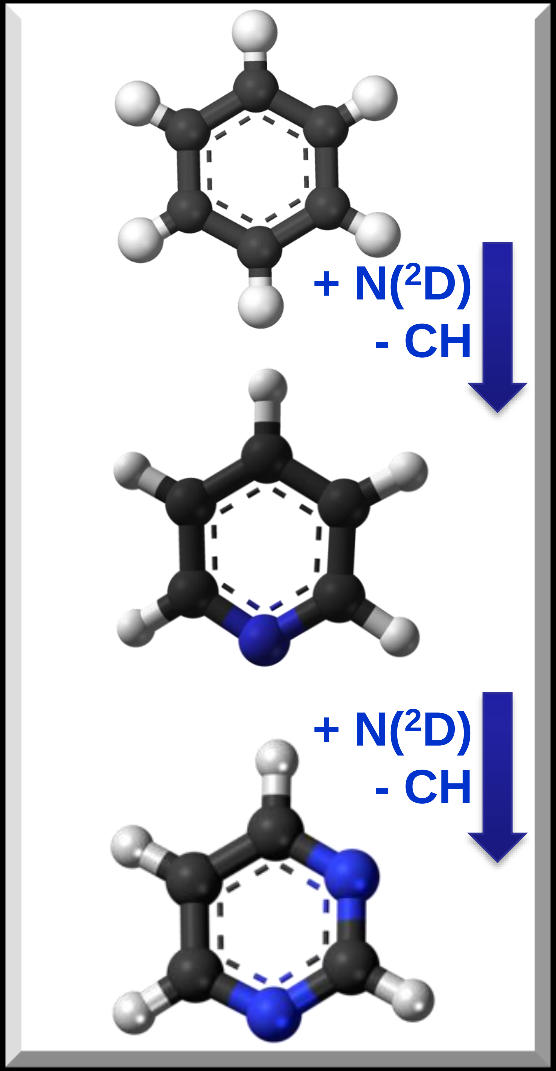


possible detection of pyridine (m/z=80) by the Ion Neutral Mass Spectometer onboard Cassini

Implications for prebiotic chemistry



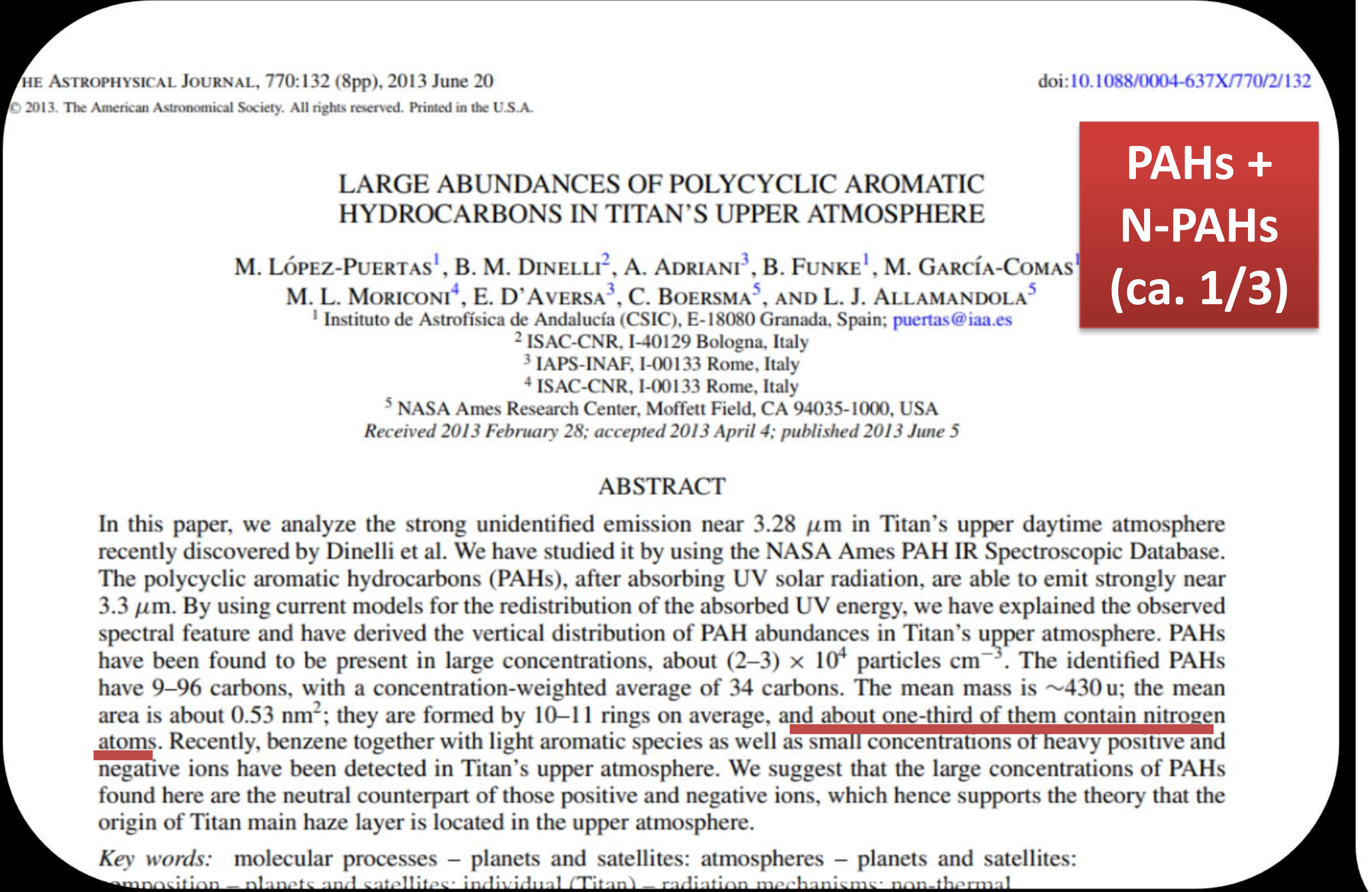




A theoretical characterization of both reactions indicates that they can occur under the conditions of the upper atmosphere of Titan, being exothermic and without barriers above the energy of the reactants asymptote (Rosi et al. 2018)

But those specific reaction channels are in competition with other channels – we need to run experiments to establish the product yield (branching ratios)

emission near 3.28 μm in Titan's upper daytime atmosphere



HE ASTROPHYSICAL JOURNAL, 770:132 (8pp), 2013 June 20 doi:10.1088/0004-637X/770/2/132

LARGE ABUNDANCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN TITAN'S UPPER ATMOSPHERE

M. López-Puertas[1], B. M. Dinelli[2], A. Adriani[3], B. Funke[1], M. García-Comas[1],
M. L. Moriconi[4], E. D'Aversa[3], C. Boersma[5], and L. J. Allamandola[5]
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Received 2013 February 28; accepted 2013 April 4; published 2013 June 5

PAHs + N-PAHs (ca. 1/3)

ABSTRACT

In this paper, we analyze the strong unidentified emission near 3.28 μm in Titan's upper daytime atmosphere recently discovered by Dinelli et al. We have studied it by using the NASA Ames PAH IR Spectroscopic Database. The polycyclic aromatic hydrocarbons (PAHs), after absorbing UV solar radiation, are able to emit strongly near 3.3 μm. By using current models for the redistribution of the absorbed UV energy, we have explained the observed spectral feature and have derived the vertical distribution of PAH abundances in Titan's upper atmosphere. PAHs have been found to be present in large concentrations, about (2–3) $\times 10^4$ particles cm^{-3}. The identified PAHs have 9–96 carbons, with a concentration-weighted average of 34 carbons. The mean mass is ~430 u; the mean area is about 0.53 nm^2; they are formed by 10–11 rings on average, and about one-third of them contain nitrogen atoms. Recently, benzene together with light aromatic species as well as small concentrations of heavy positive and negative ions have been detected in Titan's upper atmosphere. We suggest that the large concentrations of PAHs found here are the neutral counterpart of those positive and negative ions, which hence supports the theory that the origin of Titan main haze layer is located in the upper atmosphere.

Key words: molecular processes – planets and satellites: atmospheres – planets and satellites: omposition – planets and satellites: individual (Titan) – radiation mechanisms: non-thermal

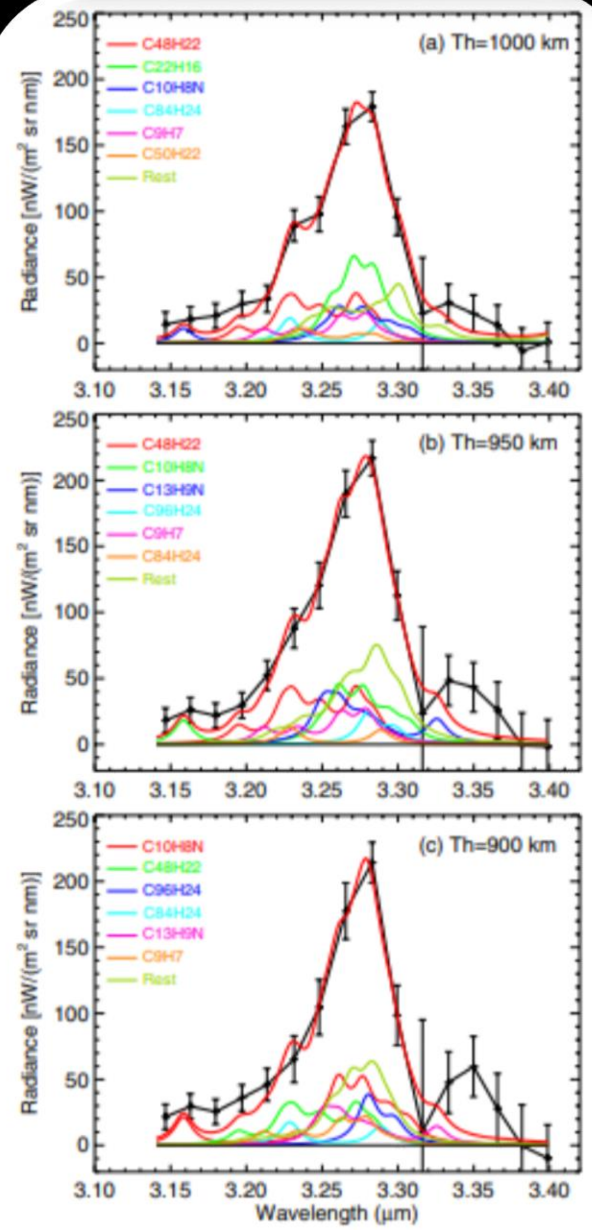
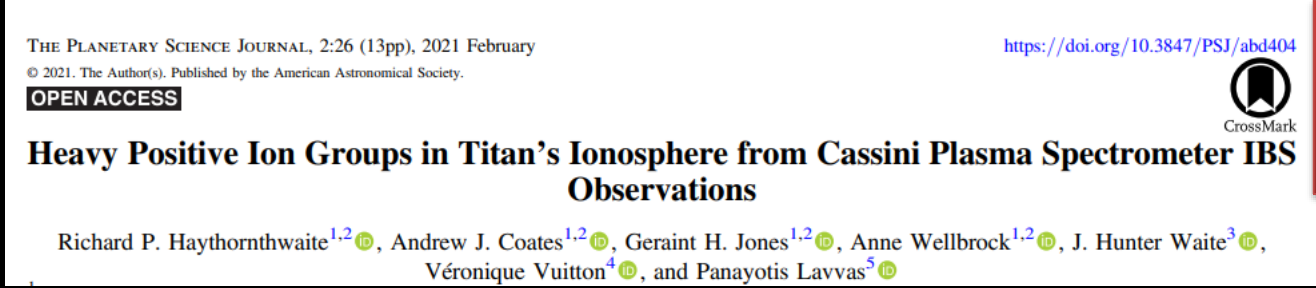


Figure 4. Spectral fit of the VIMS "unidentified" emission spectra with the neutral PAH species in the NASA Ames PAH IR Spectroscopic Database. We used the VIMS measurements listed in Table 1. Measured VIMS spectra and noise errors (black) and the fitted contributing PAHs (individuals in colored thin lines and total in thick red) for tangent heights of 1000 km, 950 km, and 900 km. color version of this figure is available in the online journal.)



The Planetary Science Journal, 2:26 (13pp), 2021 February https://doi.org/10.3847/PSJ/abd404

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OPEN ACCESS

Heavy Positive Ion Groups in Titan's Ionosphere from Cassini Plasma Spectrometer IBS Observations

Richard P. Haythornthwaite[1,2], Andrew J. Coates[1,2], Geraint H. Jones[1,2], Anne Wellbrock[1,2], J. Hunter Waite[3], Véronique Vuitton[4], and Panayotis Lavvas[5]

PAHs & PANHs in Titan

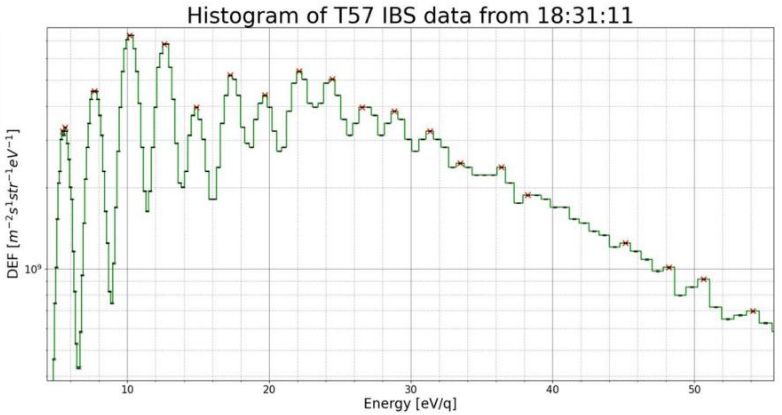
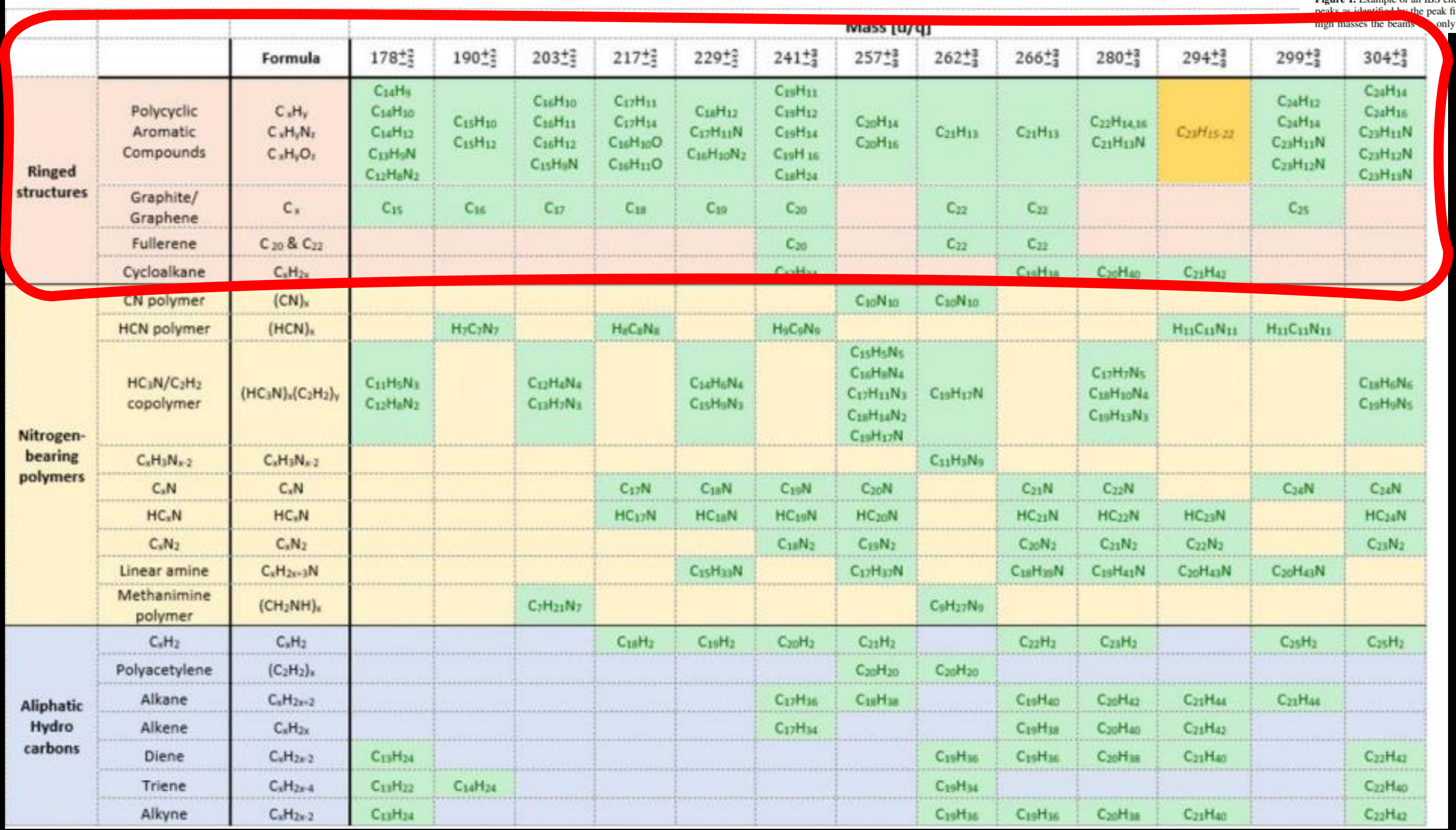


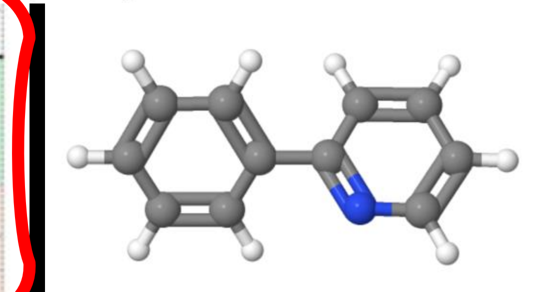
Figure 1. Example of an IBS energy spectra during the T57 flyby. The error bars shown represent the uncertainty due to Poisson counting error. Red x's indicate the peaks as identified by the peak finding algorithm. Due to the logarithmic energy scale, at low energies the ion beams can be seen over a number of bins, while at the high masses the beams [illegible] only be seen in a single bin.

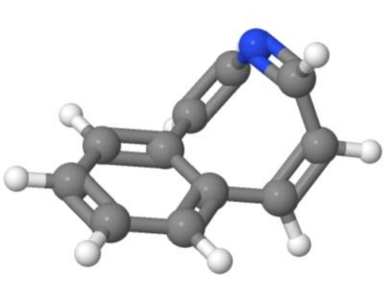
The Planetary Science Journal, 2:26 (13pp), 2021 February

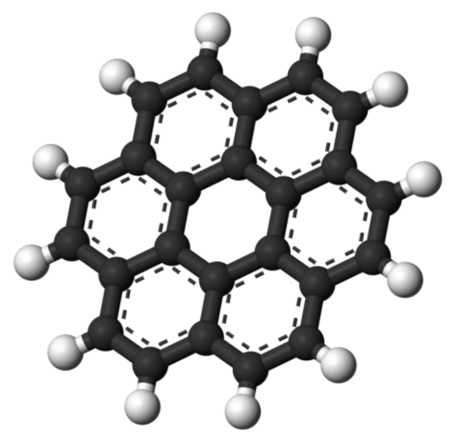
Haytho



			Mass [u/q]												
		Formula	178^{+3}_{-3}	190^{+3}_{-3}	203^{+3}_{-3}	217^{+3}_{-3}	229^{+3}_{-3}	241^{+3}_{-3}	257^{+3}_{-3}	262^{+3}_{-3}	266^{+3}_{-3}	280^{+3}_{-3}	294^{+3}_{-3}	299^{+3}_{-3}	304^{+3}_{-3}
Ringed structures	Polycyclic Aromatic Compounds	C_xH_y $C_xH_yN_z$ $C_xH_yO_z$	$C_{14}H_9$ $C_{14}H_{10}$ $C_{14}H_{12}$ $C_{13}H_9N$ $C_{12}H_8N_2$	$C_{15}H_{10}$ $C_{15}H_{12}$	$C_{16}H_{10}$ $C_{16}H_{11}$ $C_{16}H_{12}$ $C_{15}H_9N$	$C_{17}H_{11}$ $C_{17}H_{14}$ $C_{16}H_{10}O$ $C_{16}H_{11}O$	$C_{18}H_{12}$ $C_{17}H_{11}N$ $C_{16}H_{10}N_2$	$C_{19}H_{11}$ $C_{19}H_{12}$ $C_{19}H_{14}$ $C_{19}H_{16}$ $C_{18}H_{24}$	$C_{20}H_{14}$ $C_{20}H_{16}$	$C_{21}H_{13}$	$C_{21}H_{13}$	$C_{22}H_{14,16}$ $C_{21}H_{13}N$	$C_{23}H_{15\text{-}22}$	$C_{24}H_{12}$ $C_{24}H_{14}$ $C_{23}H_{11}N$ $C_{23}H_{12}N$	$C_{24}H_{14}$ $C_{24}H_{16}$ $C_{23}H_{11}N$ $C_{23}H_{12}N$ $C_{23}H_{13}N$
	Graphite/ Graphene	C_x	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}		C_{22}	C_{22}			C_{25}	
	Fullerene	C_{20} & C_{22}						C_{20}		C_{22}	C_{22}				
	Cycloalkane	C_xH_{2x}						$C_{17}H_{34}$			$C_{19}H_{38}$	$C_{20}H_{40}$	$C_{21}H_{42}$		
Nitrogen-bearing polymers	CN polymer	$(CN)_x$							$C_{10}N_{10}$	$C_{10}N_{10}$					
	HCN polymer	$(HCN)_x$		$H_7C_7N_7$		$H_8C_8N_8$		$H_9C_9N_9$					$H_{11}C_{11}N_{11}$	$H_{11}C_{11}N_{11}$	
	HC_3N/C_2H_2 copolymer	$(HC_3N)_x(C_2H_2)_y$	$C_{11}H_5N_3$ $C_{12}H_8N_2$		$C_{12}H_4N_4$ $C_{13}H_7N_3$		$C_{14}H_6N_4$ $C_{15}H_9N_3$		$C_{15}H_5N_5$ $C_{16}H_8N_4$ $C_{17}H_{11}N_3$ $C_{18}H_{14}N_2$ $C_{19}H_{17}N$	$C_{19}H_{17}N$		$C_{17}H_7N_5$ $C_{18}H_{10}N_4$ $C_{19}H_{13}N_3$			$C_{18}H_6N_6$ $C_{19}H_9N_5$
	$C_xH_3N_{x\text{-}2}$	$C_xH_3N_{x\text{-}2}$								$C_{11}H_3N_9$					
	C_xN	C_xN				$C_{17}N$	$C_{18}N$	$C_{19}N$	$C_{20}N$		$C_{21}N$	$C_{22}N$		$C_{24}N$	$C_{24}N$
	HC_xN	HC_xN				$HC_{17}N$	$HC_{18}N$	$HC_{19}N$	$HC_{20}N$		$HC_{21}N$	$HC_{22}N$	$HC_{23}N$		$HC_{24}N$
	C_xN_2	C_xN_2						$C_{18}N_2$	$C_{19}N_2$		$C_{20}N_2$	$C_{21}N_2$	$C_{22}N_2$		$C_{23}N_2$
	Linear amine	$C_xH_{2x+3}N$					$C_{15}H_{33}N$		$C_{17}H_{37}N$		$C_{18}H_{39}N$	$C_{19}H_{41}N$	$C_{20}H_{43}N$	$C_{20}H_{43}N$	
	Methanimine polymer	$(CH_2NH)_x$			$C_7H_{21}N_7$					$C_9H_{27}N_9$					
Aliphatic Hydro carbons	C_xH_2	C_xH_2				$C_{18}H_2$	$C_{19}H_2$	$C_{20}H_2$	$C_{21}H_2$		$C_{22}H_2$	$C_{23}H_2$		$C_{25}H_2$	$C_{25}H_2$
	Polyacetylene	$(C_2H_2)_x$							$C_{20}H_{20}$	$C_{20}H_{20}$					
	Alkane	C_xH_{2x+2}						$C_{17}H_{36}$	$C_{18}H_{38}$		$C_{19}H_{40}$	$C_{20}H_{42}$	$C_{21}H_{44}$	$C_{21}H_{44}$	
	Alkene	C_xH_{2x}						$C_{17}H_{34}$			$C_{19}H_{38}$	$C_{20}H_{40}$	$C_{21}H_{42}$		
	Diene	$C_xH_{2x\text{-}2}$	$C_{13}H_{24}$							$C_{19}H_{36}$	$C_{19}H_{36}$	$C_{20}H_{38}$	$C_{21}H_{40}$		$C_{22}H_{42}$
	Triene	$C_xH_{2x\text{-}4}$	$C_{13}H_{22}$	$C_{14}H_{24}$						$C_{19}H_{34}$					$C_{22}H_{40}$
	Alkyne	$C_xH_{2x\text{-}2}$	$C_{13}H_{24}$							$C_{19}H_{36}$	$C_{19}H_{36}$	$C_{20}H_{38}$	$C_{21}H_{40}$		$C_{22}H_{42}$





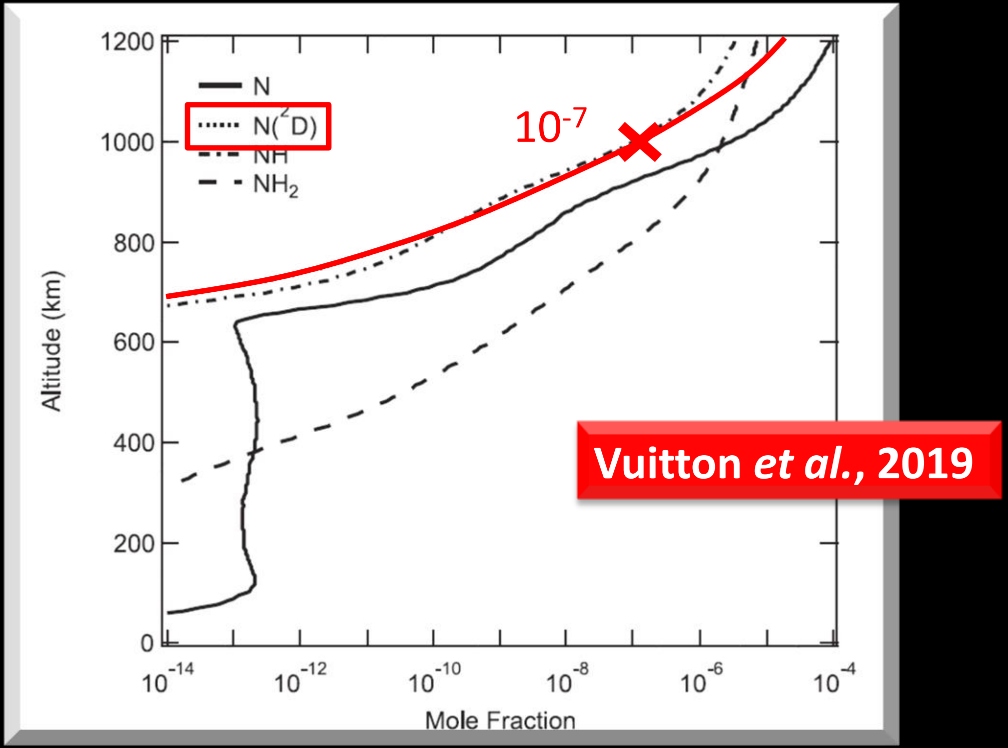


Cassini Plasma Spectrometer
-
Ion Beam Spectrometer

Nitrogen fixation in the atmosphere of Titan

Atomic nitrogen in the excited ^2D state is metastable with a very long radiative lifetime (~ 48 h) and a very high energy content (230 kJ/mol). In the upper atmosphere ot Titan EUV & electron impact induced dissociation, dissociative ionization and N_2^+ dissociative recombination produce $N(^4S)$ and $N(^2D)$ states in similar amounts.

mole fractions as a function of the altitude



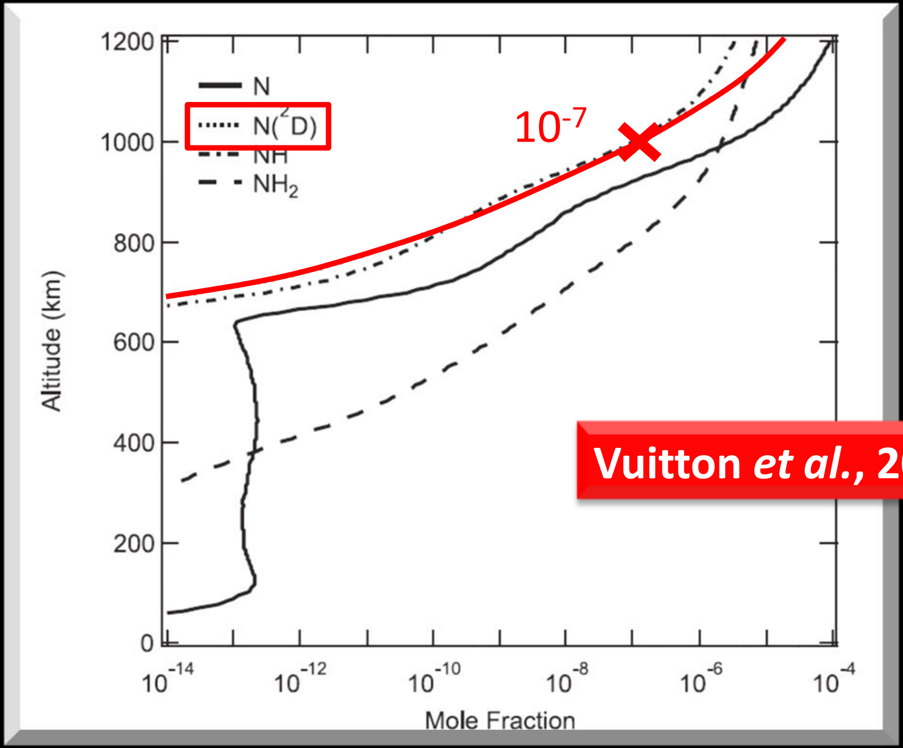
Vuitton *et al.*, 2019

In our laboratory,
we have already investigated
the reactions of $N(^2D)$ with
the aliphatic hydrocarbons
abundant in Titan,
e.g., CH_4, C_2H_6,
C_2H_4, C_2H_2, C_3H_4, HC_3N

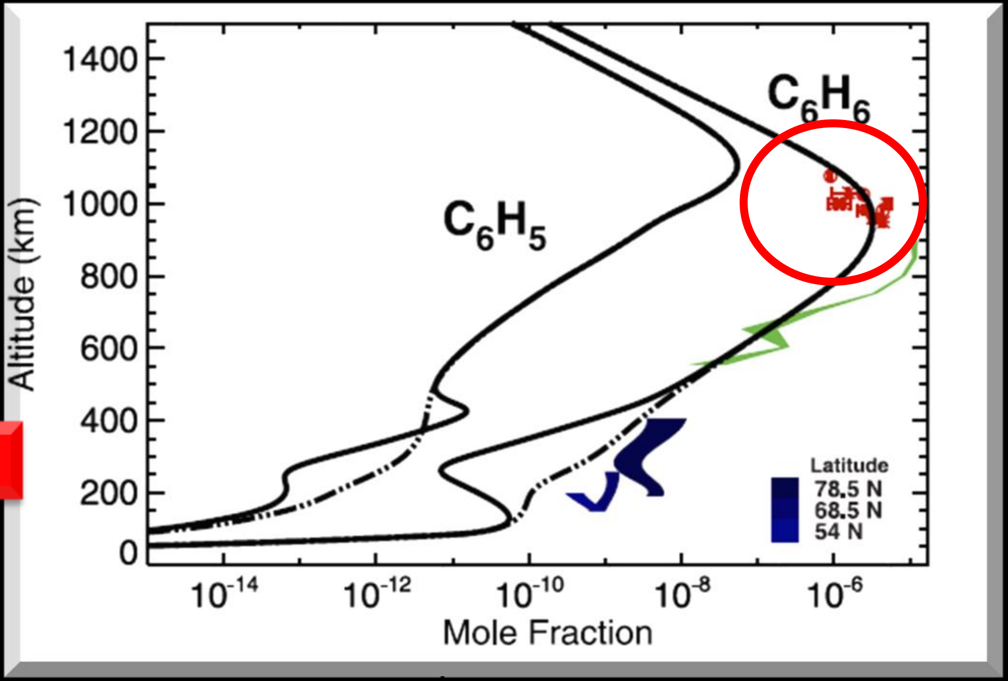
Nitrogen fixation in the atmosphere of Titan

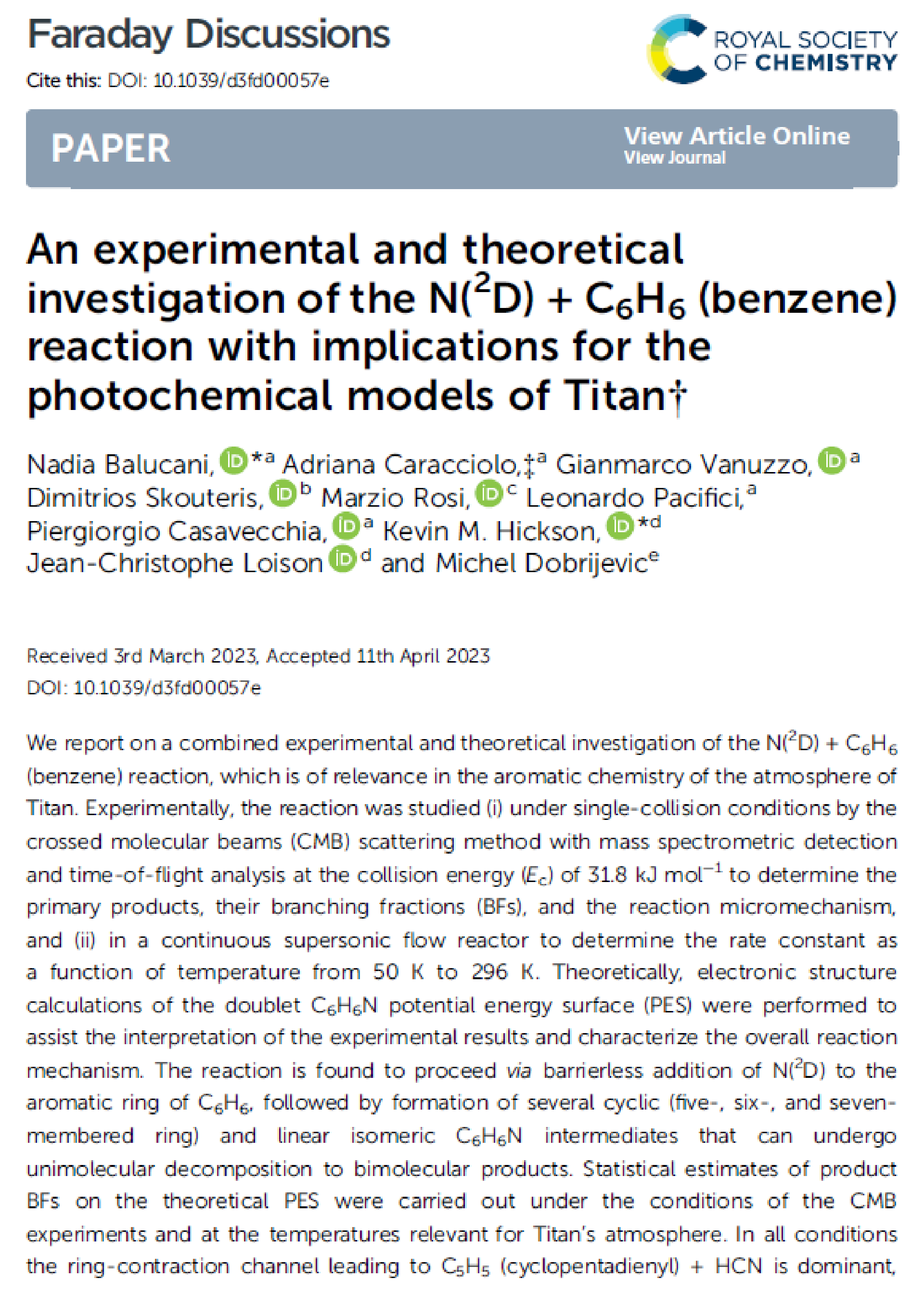
Atomic nitrogen in the excited ^2D state is metastable with a very long radiative lifetime (~ 48 h) and a very high energy content (230 kJ/mol). In the upper atmosphere ot Titan EUV & electron impact induced dissociation, dissociative ionization and N_2^+ dissociative recombination produce $N(^4S)$ and $N(^2D)$ states in similar amounts.

mole fractions as a function of the altitude



Vuitton *et al.*, 2019





Faraday Discussions

ROYAL SOCIETY OF CHEMISTRY

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PAPER

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An experimental and theoretical investigation of the N(^{2}D) + C_6H_6 (benzene) reaction with implications for the photochemical models of Titan†

Nadia Balucani, *[a] Adriana Caracciolo,‡[a] Gianmarco Vanuzzo, [a] Dimitrios Skouteris, [b] Marzio Rosi, [c] Leonardo Pacifici,[a] Piergiorgio Casavecchia, [a] Kevin M. Hickson, *[d] Jean-Christophe Loison [d] and Michel Dobrijevic[e]

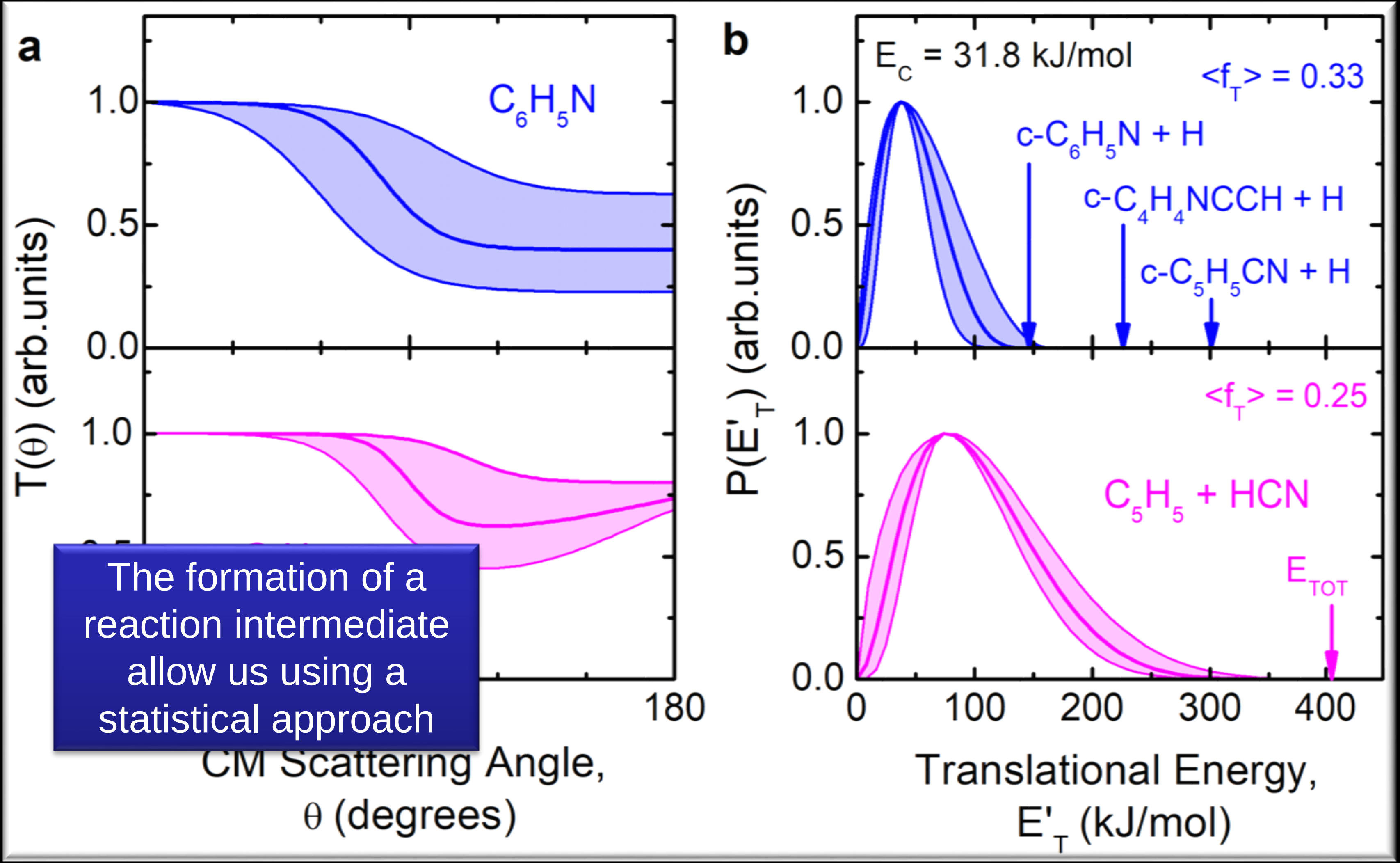
Received 3rd March 2023, Accepted 11th April 2023
DOI: 10.1039/d3fd00057e

We report on a combined experimental and theoretical investigation of the N(^{2}D) + C_6H_6 (benzene) reaction, which is of relevance in the aromatic chemistry of the atmosphere of Titan. Experimentally, the reaction was studied (i) under single-collision conditions by the crossed molecular beams (CMB) scattering method with mass spectrometric detection and time-of-flight analysis at the collision energy (E_c) of 31.8 kJ mol^{-1} to determine the primary products, their branching fractions (BFs), and the reaction micromechanism, and (ii) in a continuous supersonic flow reactor to determine the rate constant as a function of temperature from 50 K to 296 K. Theoretically, electronic structure calculations of the doublet C_6H_6N potential energy surface (PES) were performed to assist the interpretation of the experimental results and characterize the overall reaction mechanism. The reaction is found to proceed *via* barrierless addition of N(^{2}D) to the aromatic ring of C_6H_6, followed by formation of several cyclic (five-, six-, and seven-membered ring) and linear isomeric C_6H_6N intermediates that can undergo unimolecular decomposition to bimolecular products. Statistical estimates of product BFs on the theoretical PES were carried out under the conditions of the CMB experiments and at the temperatures relevant for Titan's atmosphere. In all conditions the ring-contraction channel leading to C_5H_5 (cyclopentadienyl) + HCN is dominant,

- *Crossed beam experiment (Perugia, product yields)*
- *CRESU experiments (Bordeaux, global rate coefficient)*
- *quantum chemistry and kinetics calculations (Perugia)*
- *photochemical model simulation for Titan (Bordeaux)*

N(^{2}D) + C_6H_6

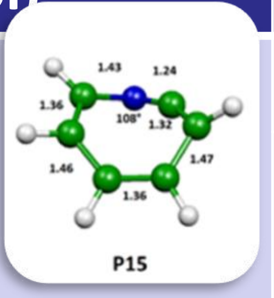
Best-fit center-of-mass functions



The formation of a reaction intermediate allow us using a statistical approach

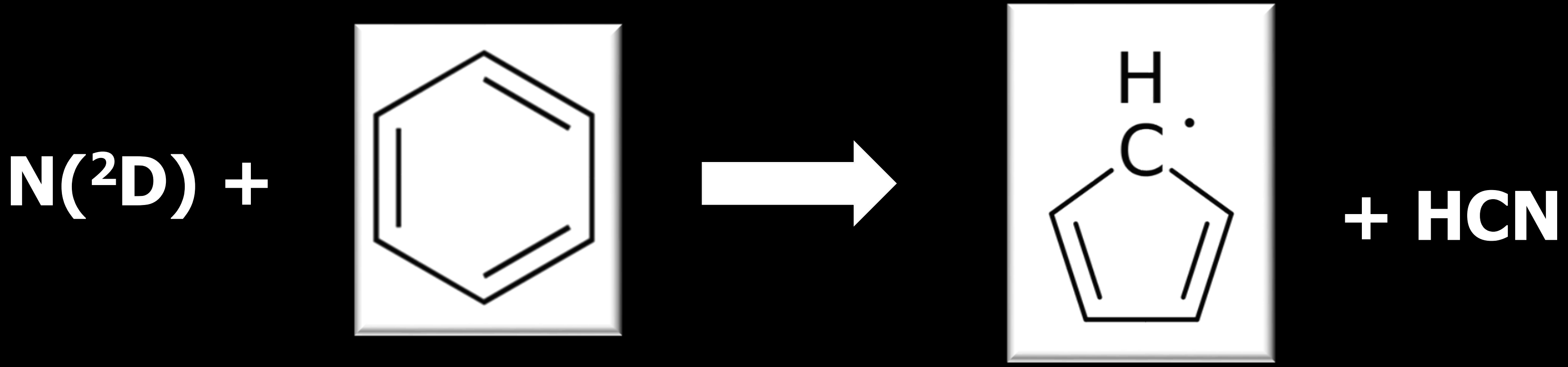
the dominant channel is a ring-contraction reaction with the formation of the coproduct HCN

Experimental BR
H-displacement channel: 0.05 ± 0.03
Ring-contraction channel: 0.95 ± 0.15

Primary products	Experimental branching ratio (E_c=31.8 kJ/mol)	RRKM branching ratio
C_6H_5N + H	0.05 ± 0.03  P15	7-atom ring: 0.12 H-displacement with contraction of the ring: 0.02
C_5H_5 + HCN or C_4H_4N + C_2H_2	0.95 ± 0.15	C_5H_5 + HCN: 0.79 C_4H_4N + C_2H_2: 0.04

RRKM: Small dependence of BR on the available energy

the dominant channel is a ring-contraction reaction

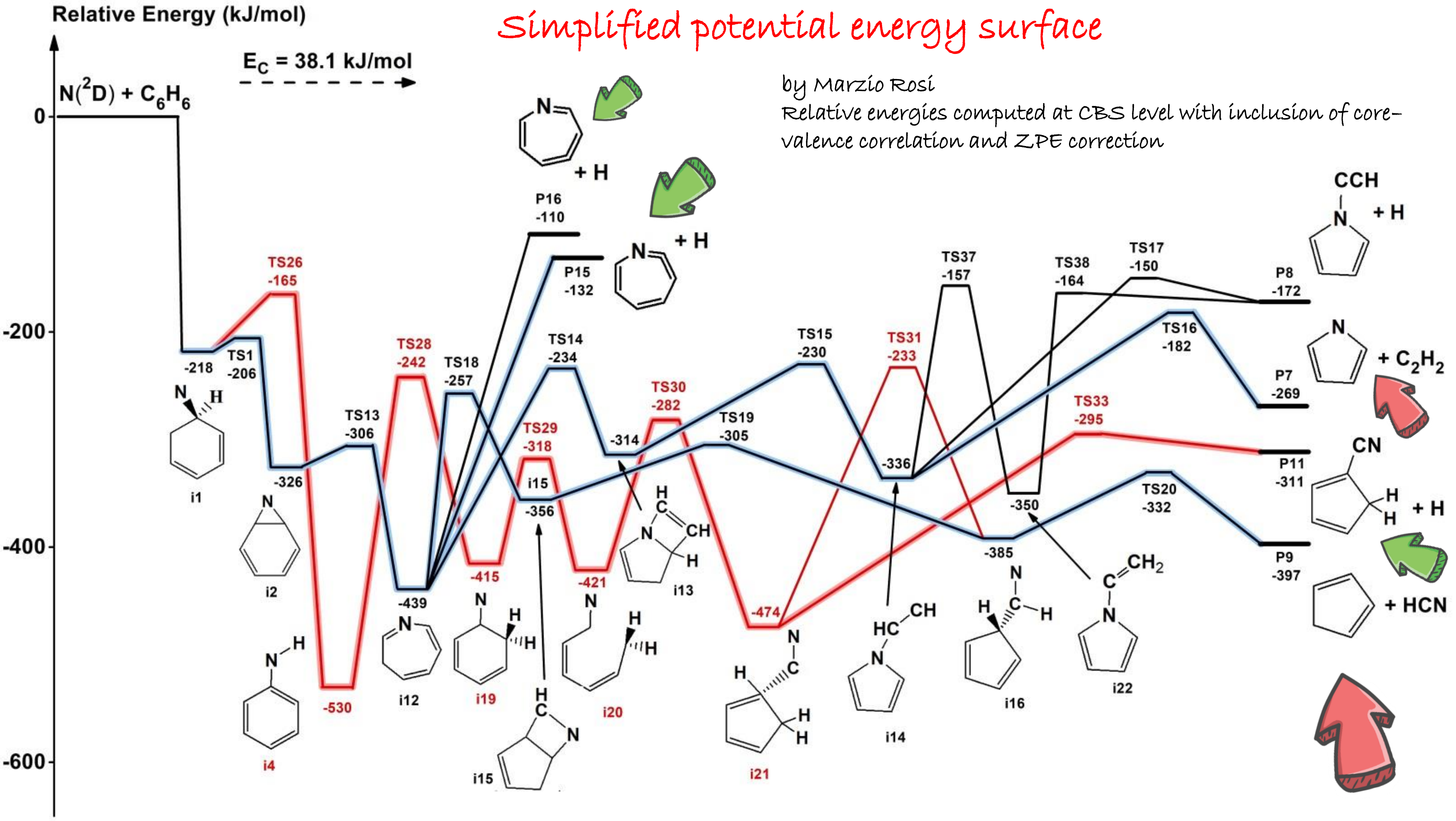


$N(^2D)$ + **+ HCN**

Simplified potential energy surface

by Marzio Rosi

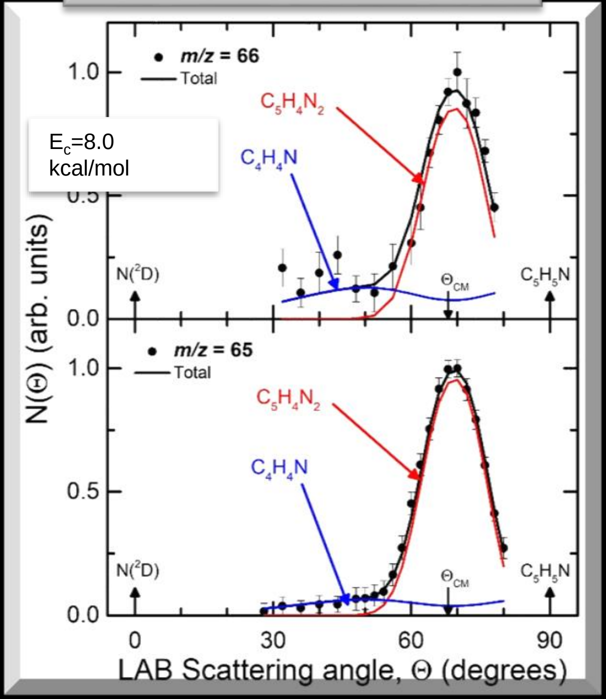
Relative energies computed at CBS level with inclusion of core-valence correlation and ZPE correction



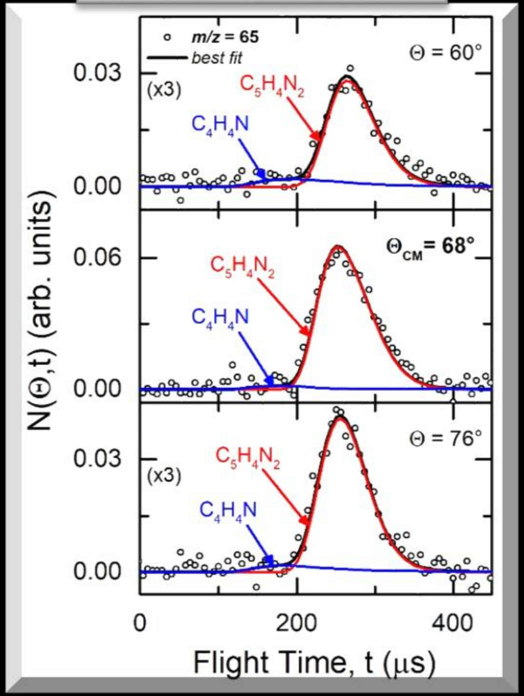
N(^{2}D) + C_5H_5N, the second step: from pyridine to pyrimidine

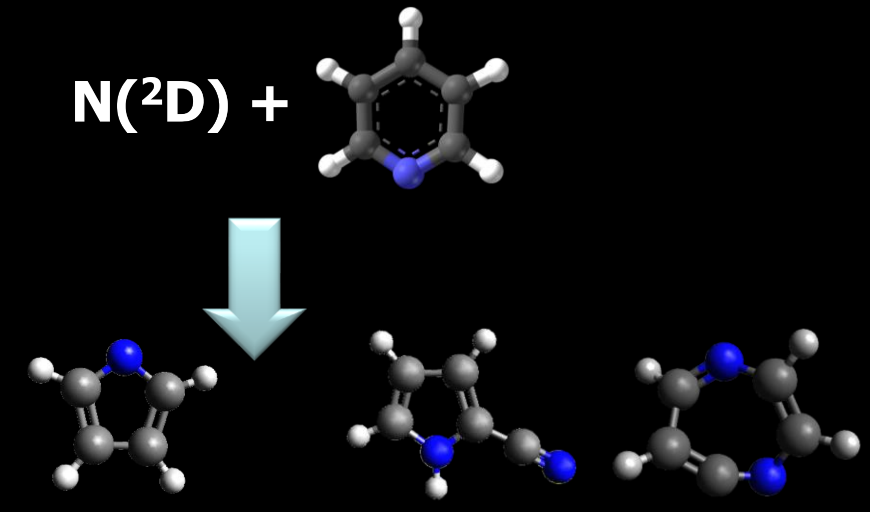
It does not work either: also in this case, the dominant channel is a ring contraction reaction

Laboratory angular distributions



Time-of-flight spectra



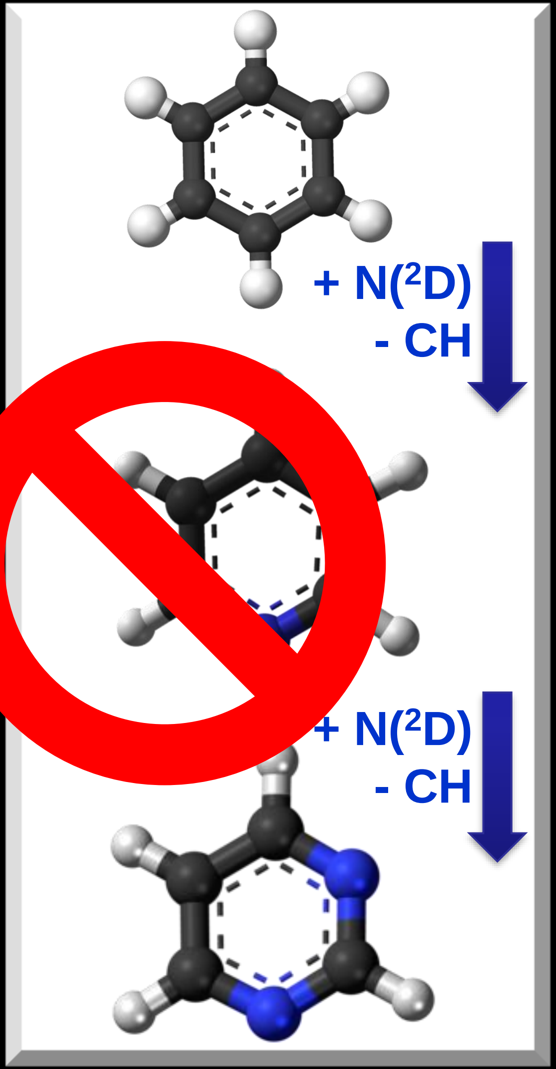


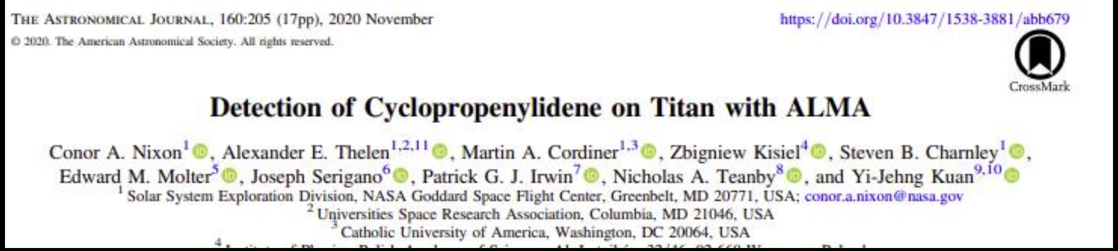
N(^{2}D) +

+ HCN
ca. 60%

+ H
40%

Pyridine and pyrimidine have been searched for with ALMA and not found




THE ASTRONOMICAL JOURNAL, 160:205 (17pp), 2020 November
https://doi.org/10.3847/1538-3881/abb679

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CrossMark

Detection of Cyclopropenylidene on Titan with ALMA

Conor A. Nixon[1], Alexander E. Thelen[1,2,11], Martin A. Cordiner[1,3], Zbigniew Kisiel[4], Steven B. Charnley[1], Edward M. Molter[5], Joseph Serigano[6], Patrick G. J. Irwin[7], Nicholas A. Teanby[8], and Yi-Jehng Kuan[9,10]

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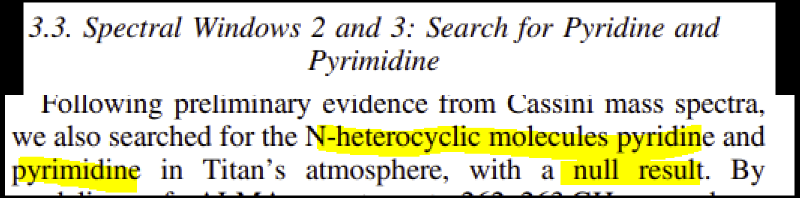
[2] Universities Space Research Association, Columbia, MD 21046, USA
[3] Catholic University of America, Washington, DC 20064, USA


3.3. Spectral Windows 2 and 3: Search for Pyridine and Pyrimidine

Following preliminary evidence from Cassini mass spectra, we also searched for the N-heterocyclic molecules pyridine and pyrimidine in Titan's atmosphere, with a null result. By

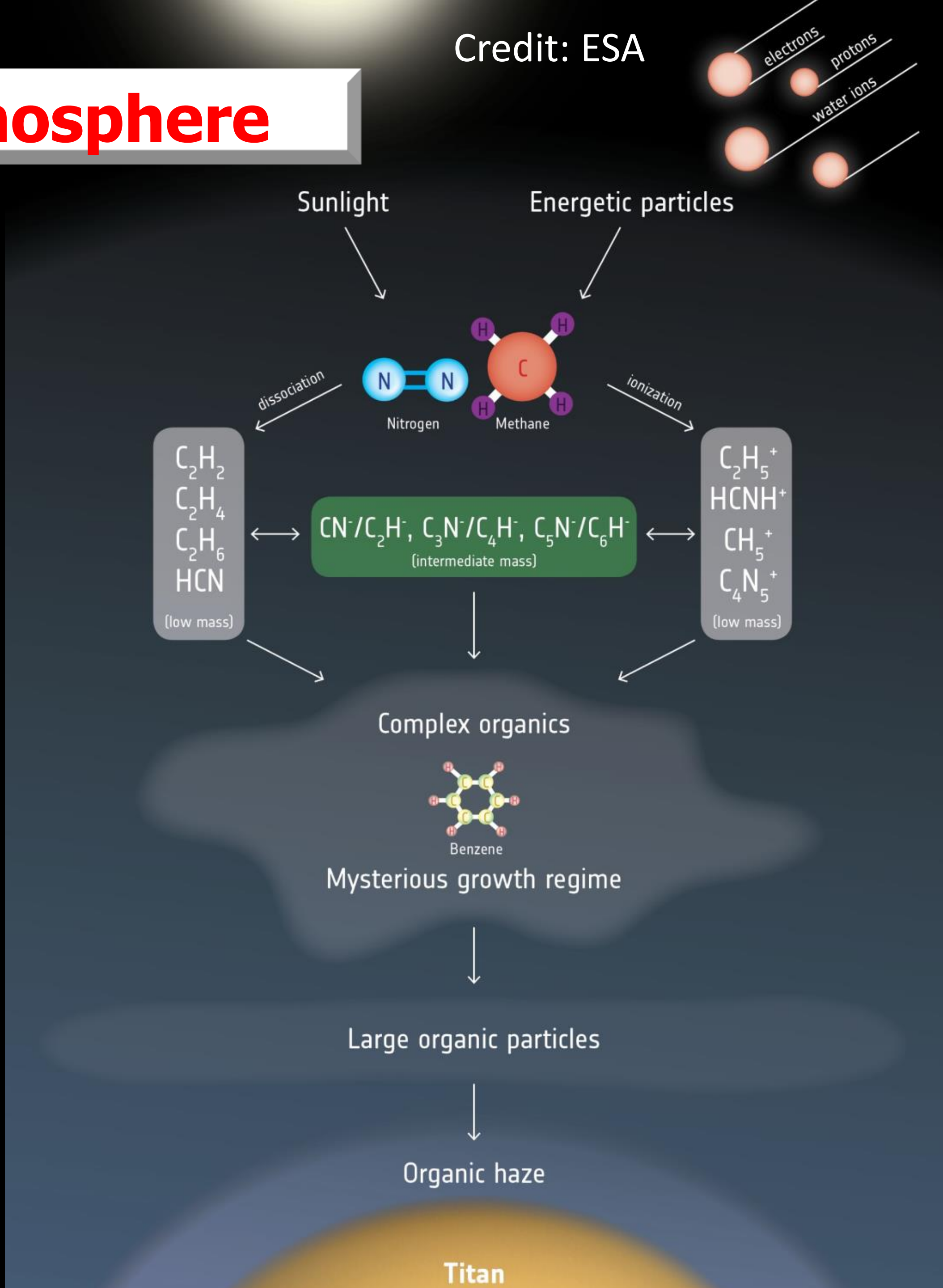
Global chemical scheme of upper atmosphere

EUV photons and energetic particles (electrons, protons from the magnetosphere of Saturn) induce the formation of active forms of nitrogen ($N^\bullet$, N^*, N_2^*, N^+, N_2^+)

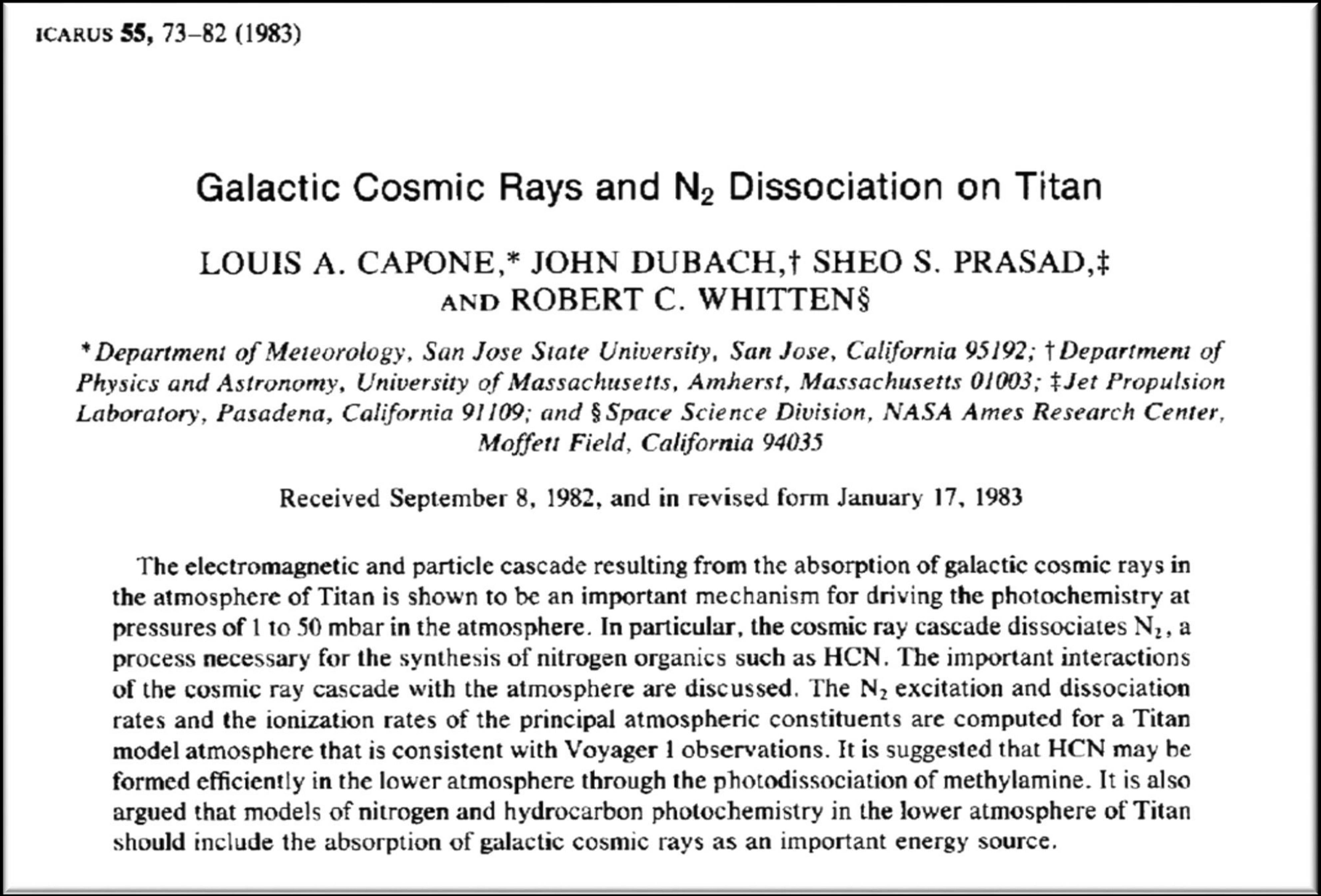
VUV photons and energetic particles induce dissociation and ionization of methane

A very active chemistry begins, leading up to N-bearing macro-molecules and their ions.

Also galactic cosmic rays induce similar processes but at much lower altitude



Credit: ESA



ICARUS **55,** 73–82 (1983)

Galactic Cosmic Rays and N_2 Dissociation on Titan

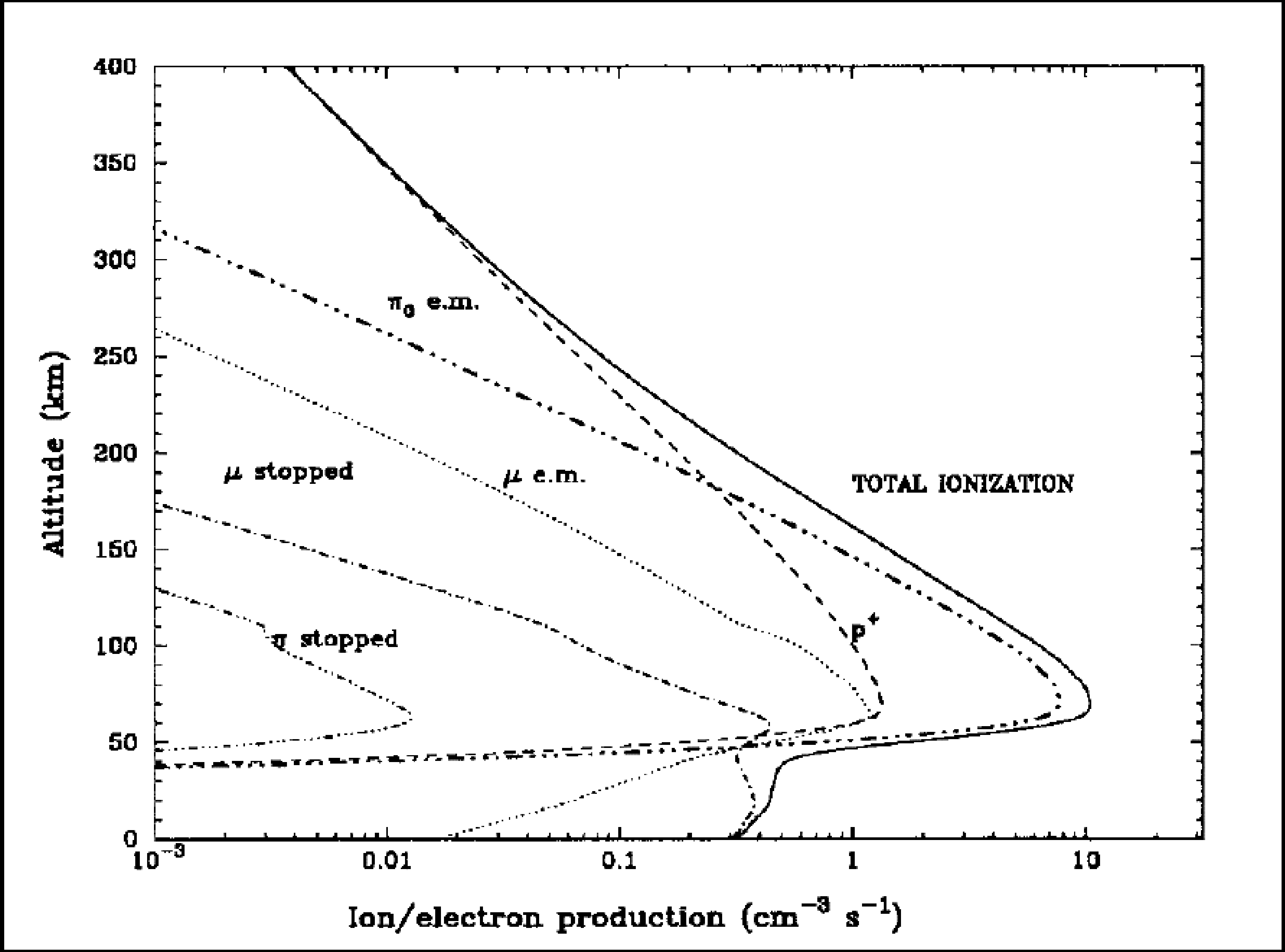
LOUIS A. CAPONE,* JOHN DUBACH,† SHEO S. PRASAD,‡
AND ROBERT C. WHITTEN§

**Department of Meteorology, San Jose State University, San Jose, California 95192; †Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts 01003; ‡Jet Propulsion Laboratory, Pasadena, California 91109; and §Space Science Division, NASA Ames Research Center, Moffett Field, California 94035*

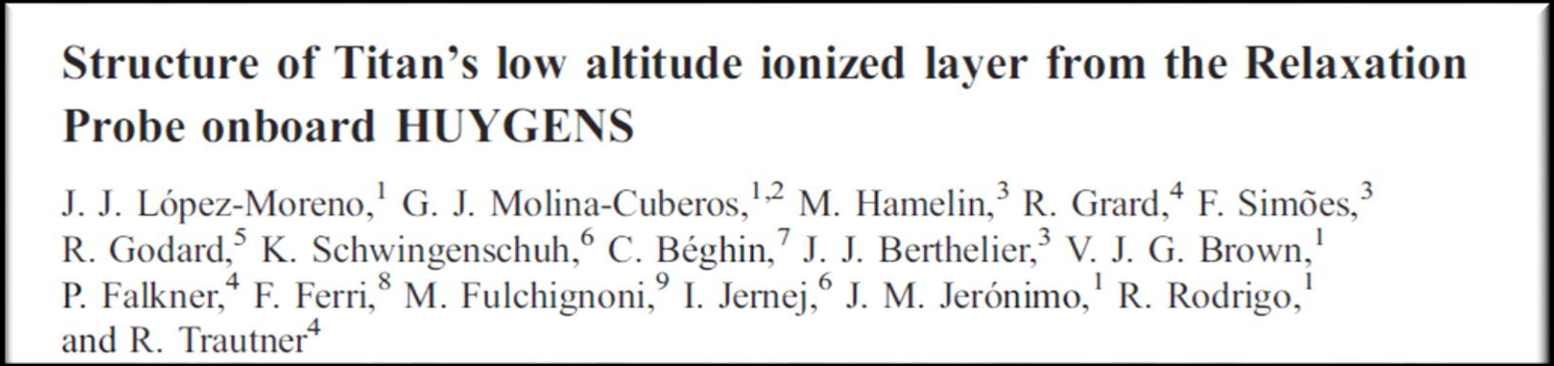
Received September 8, 1982, and in revised form January 17, 1983

The electromagnetic and particle cascade resulting from the absorption of galactic cosmic rays in the atmosphere of Titan is shown to be an important mechanism for driving the photochemistry at pressures of 1 to 50 mbar in the atmosphere. In particular, the cosmic ray cascade dissociates N_2, a process necessary for the synthesis of nitrogen organics such as HCN. The important interactions of the cosmic ray cascade with the atmosphere are discussed. The N_2 excitation and dissociation rates and the ionization rates of the principal atmospheric constituents are computed for a Titan model atmosphere that is consistent with Voyager 1 observations. It is suggested that HCN may be formed efficiently in the lower atmosphere through the photodissociation of methylamine. It is also argued that models of nitrogen and hydrocarbon photochemistry in the lower atmosphere of Titan should include the absorption of galactic cosmic rays as an important energy source.

Molina-Cuberos et al. Planetary and Space Science 1999



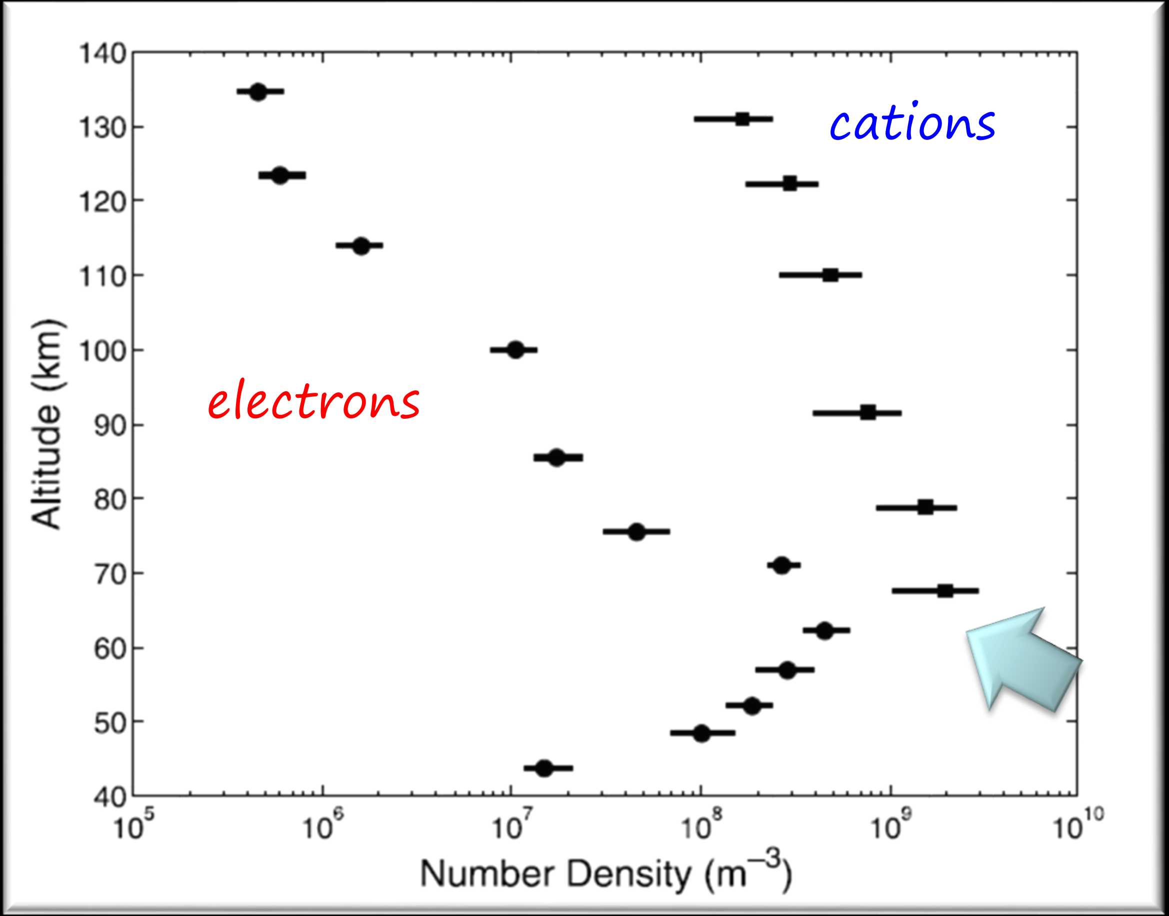
cosmic rays ionization in Titan's atmosphere:
- total ionization;
- electrostatic stopping of protons;
- electrostatic stopping of charged pions;
- electrostatic stopping of muons;
- (thicker line) electromagnetic shower due to π_0;
- electromagnetic shower due to muons



Structure of Titan's low altitude ionized layer from the Relaxation Probe onboard HUYGENS

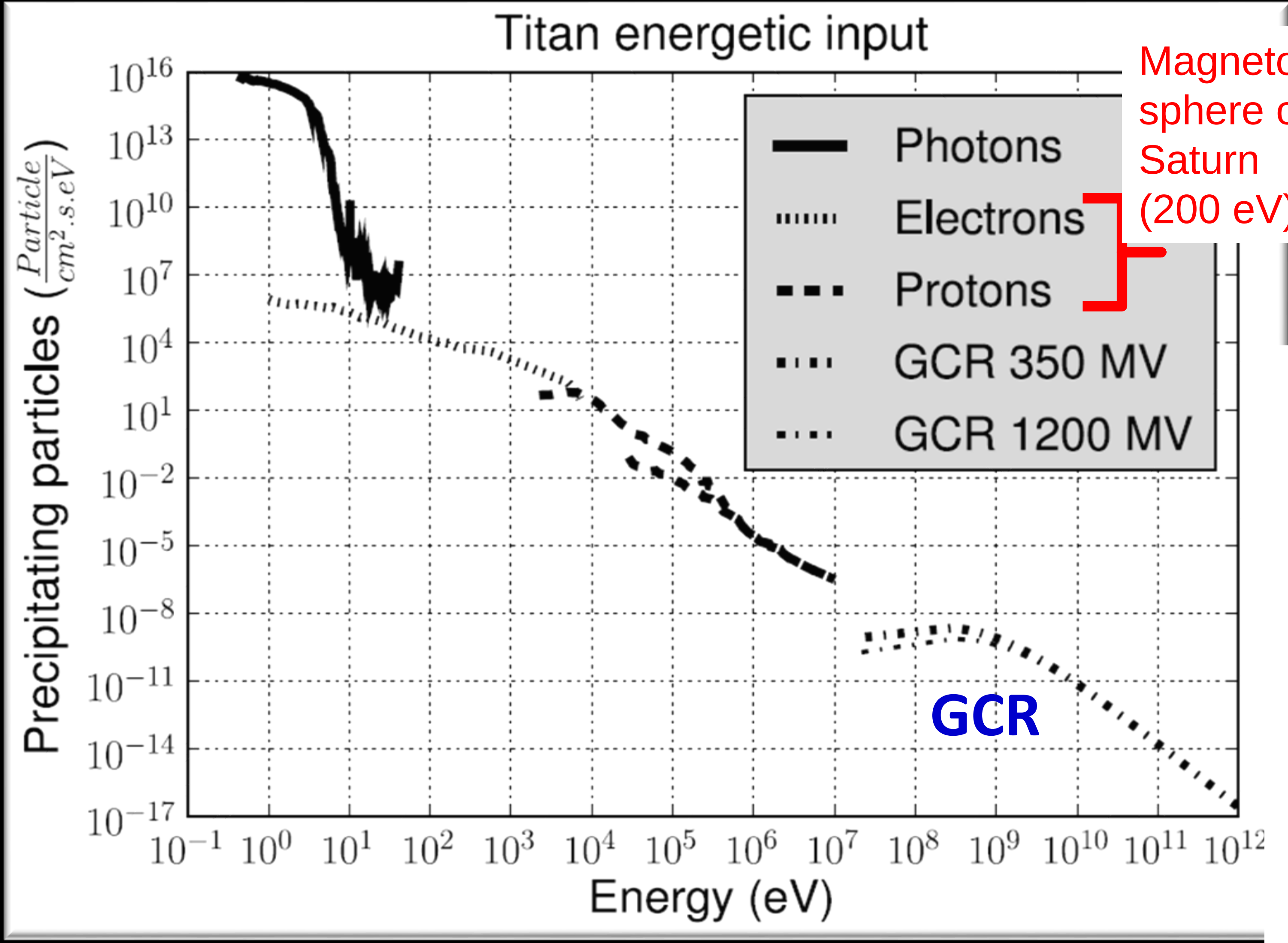
J. J. López-Moreno,[1] G. J. Molina-Cuberos,[1,2] M. Hamelin,[3] R. Grard,[4] F. Simões,[3] R. Godard,[5] K. Schwingenschuh,[6] C. Béghin,[7] J. J. Berthelier,[3] V. J. G. Brown,[1] P. Falkner,[4] F. Ferri,[8] M. Fulchignoni,[9] I. Jernej,[6] J. M. Jerónimo,[1] R. Rodrigo,[1] and R. Trautner[4]

GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L2210
doi:10.1029/2008GL035338,
2008

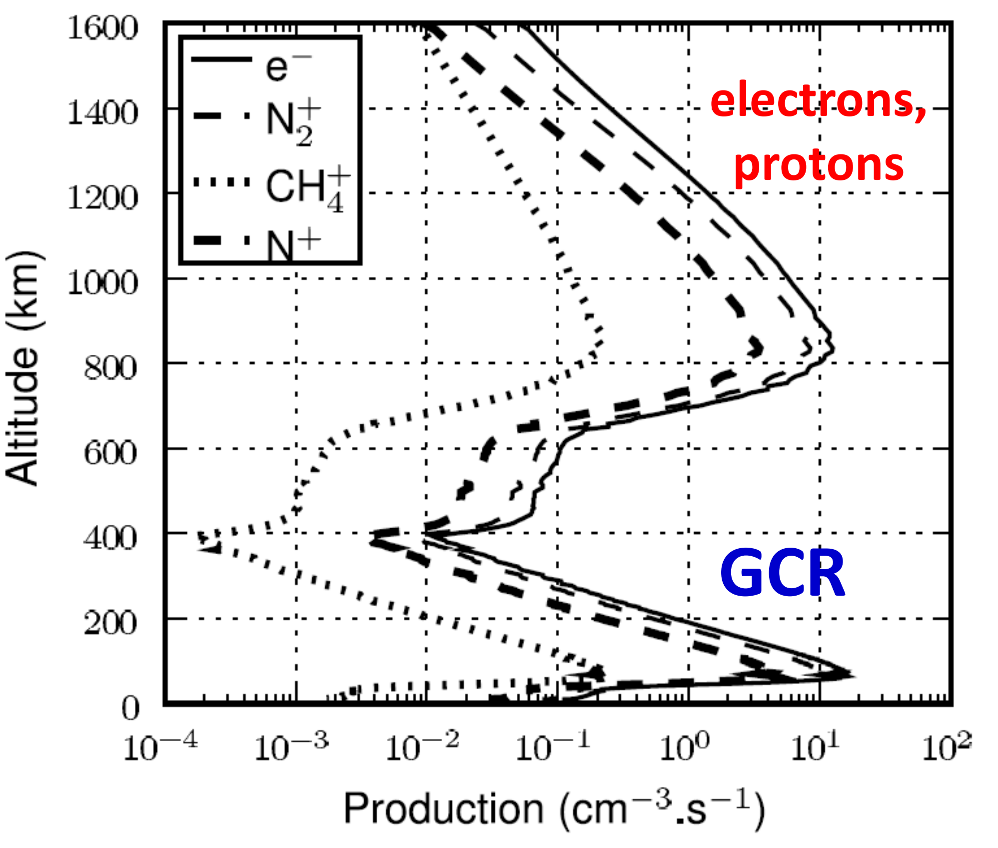


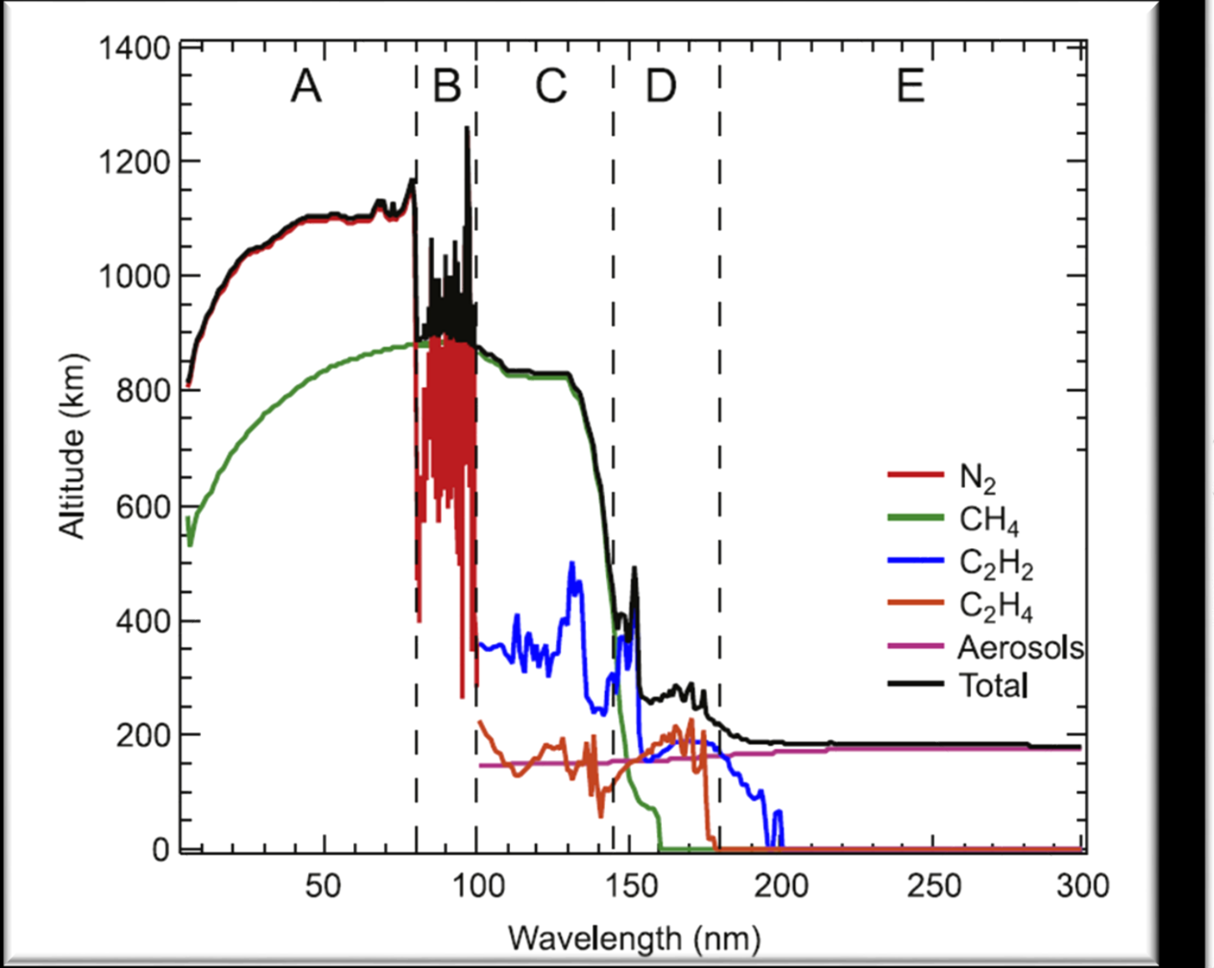
The Permitivity Wave and Altimetry system (Huygens) detected a hidden ionosphere much below the main ionosphere. Theoretical models predicted a low altitude ionosphere produced by cosmic rays that, contrary to magnetospheric particles and UV photons, are able to penetrate down in the atmosphere.

From Gronoff et al. A&A 2009

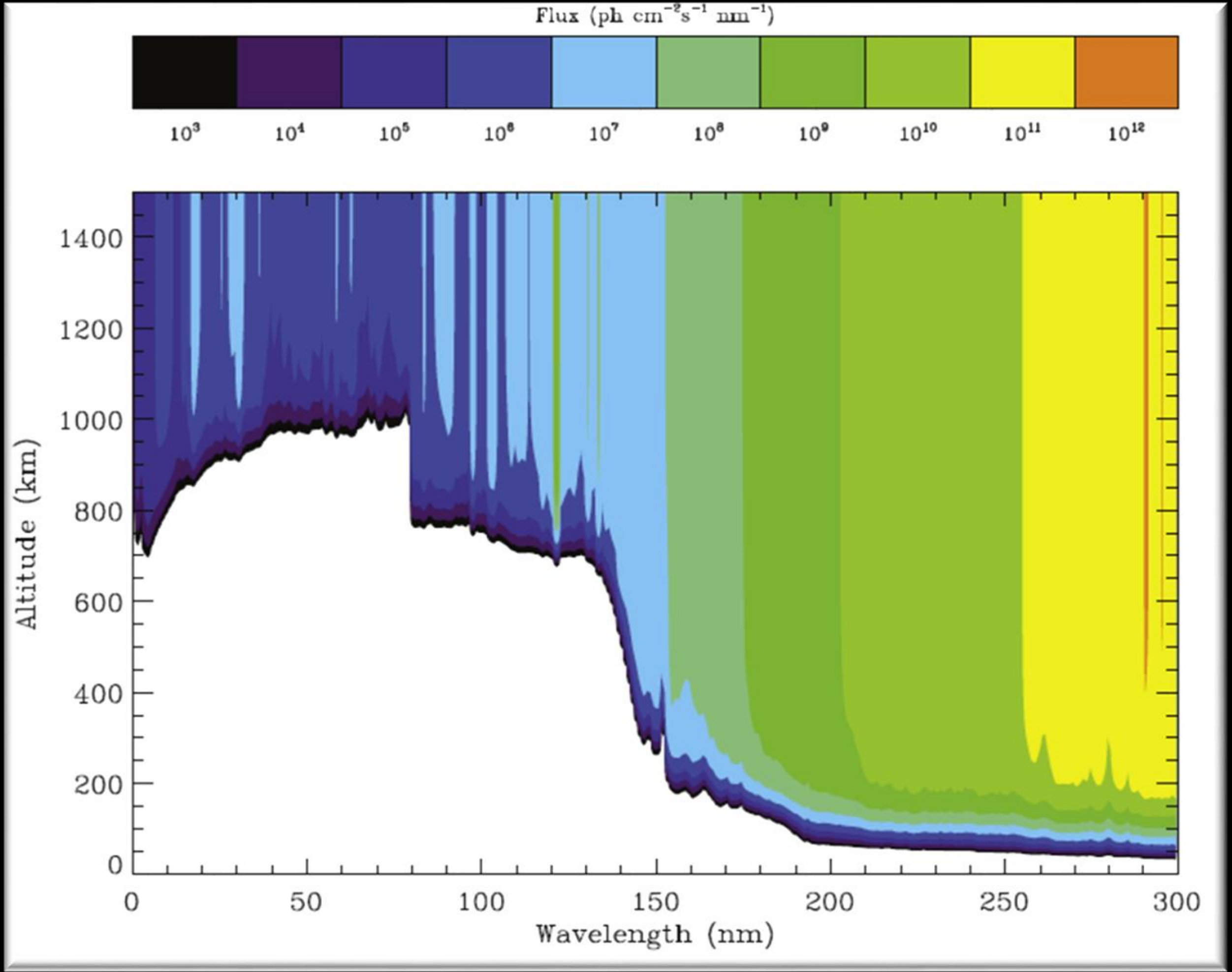


Total ionization computed for the nightside T5 flyby conditions





Photon penetration altitude as a function of wavelength



Photon flux versus altitude and wavelength

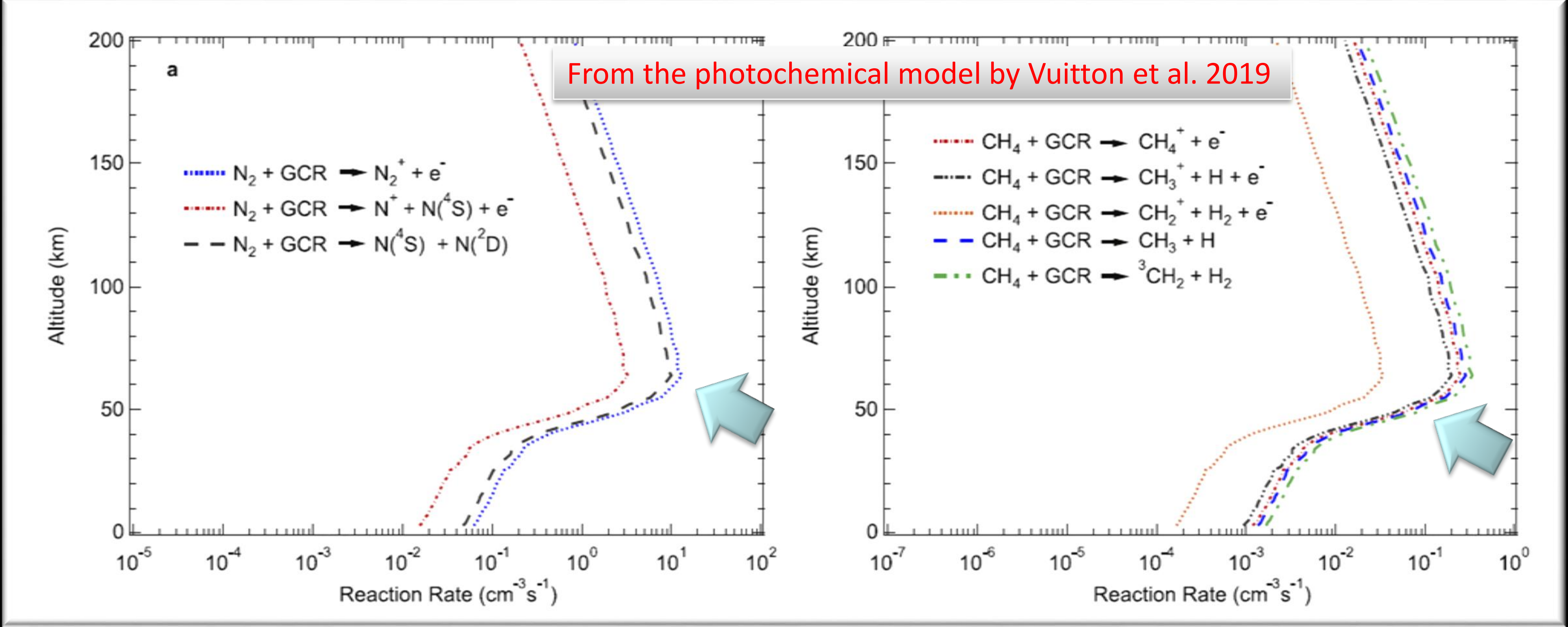
From the photochemical model by Vuitton et al. 2019

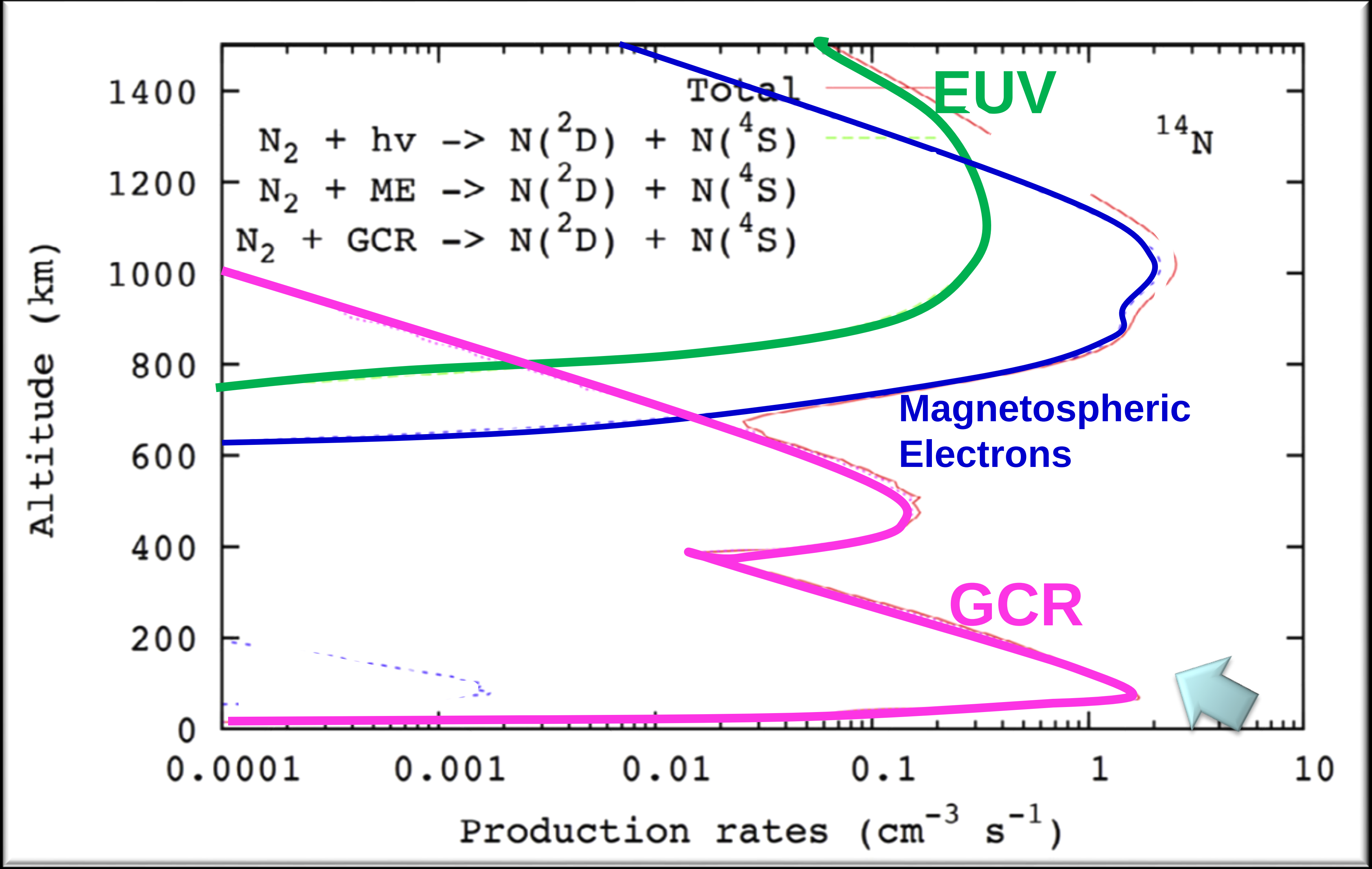
GCR produce also neutral transient species

$N_2 + GCR \rightarrow N(^4S)/N(^2D) + N^+ + e^-$ 12%

$N_2^+ + e^-$ 53%

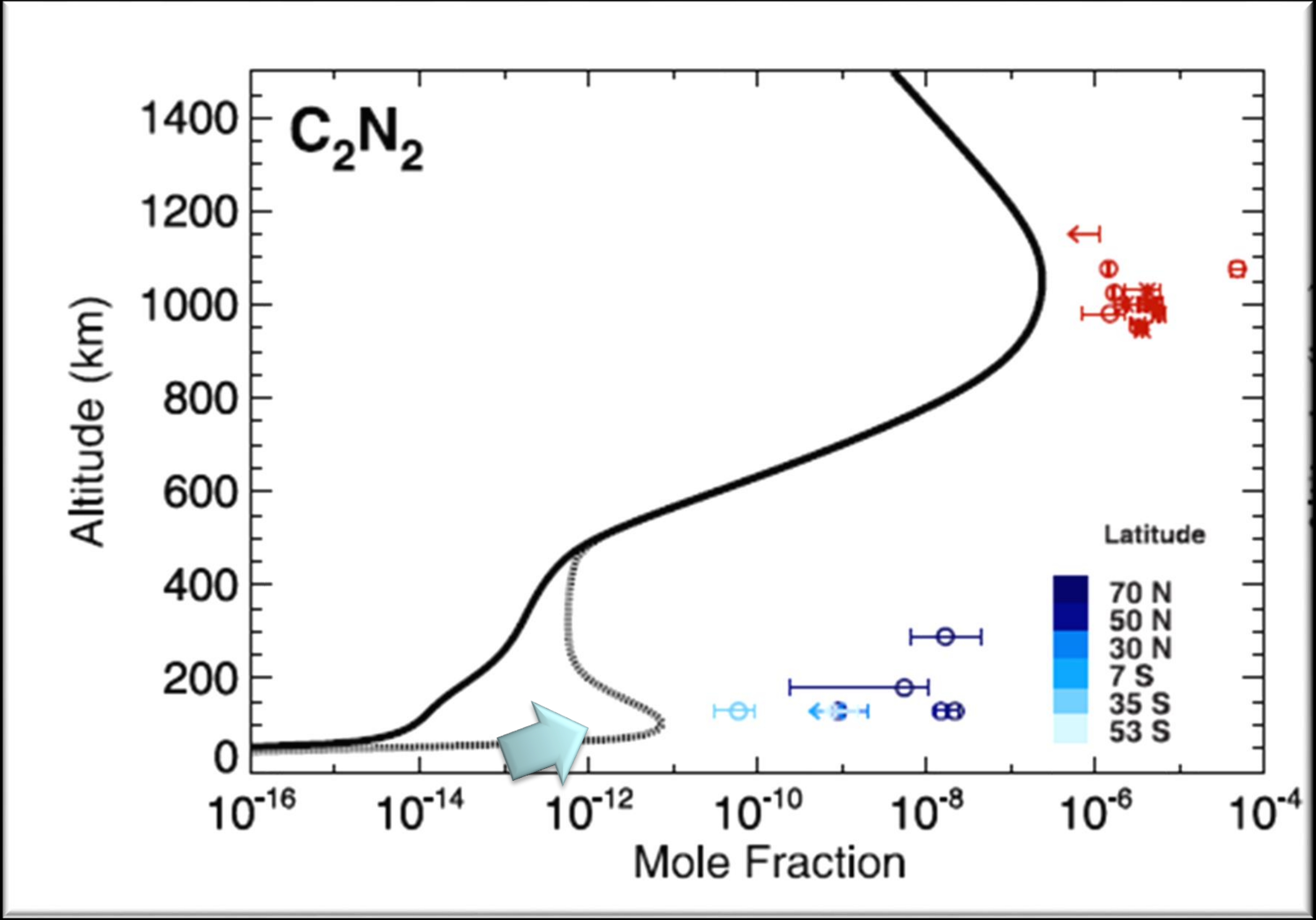
$N(^4S) + N(^2D)$ 35%


From the photochemical model by Vuitton et al. 2019

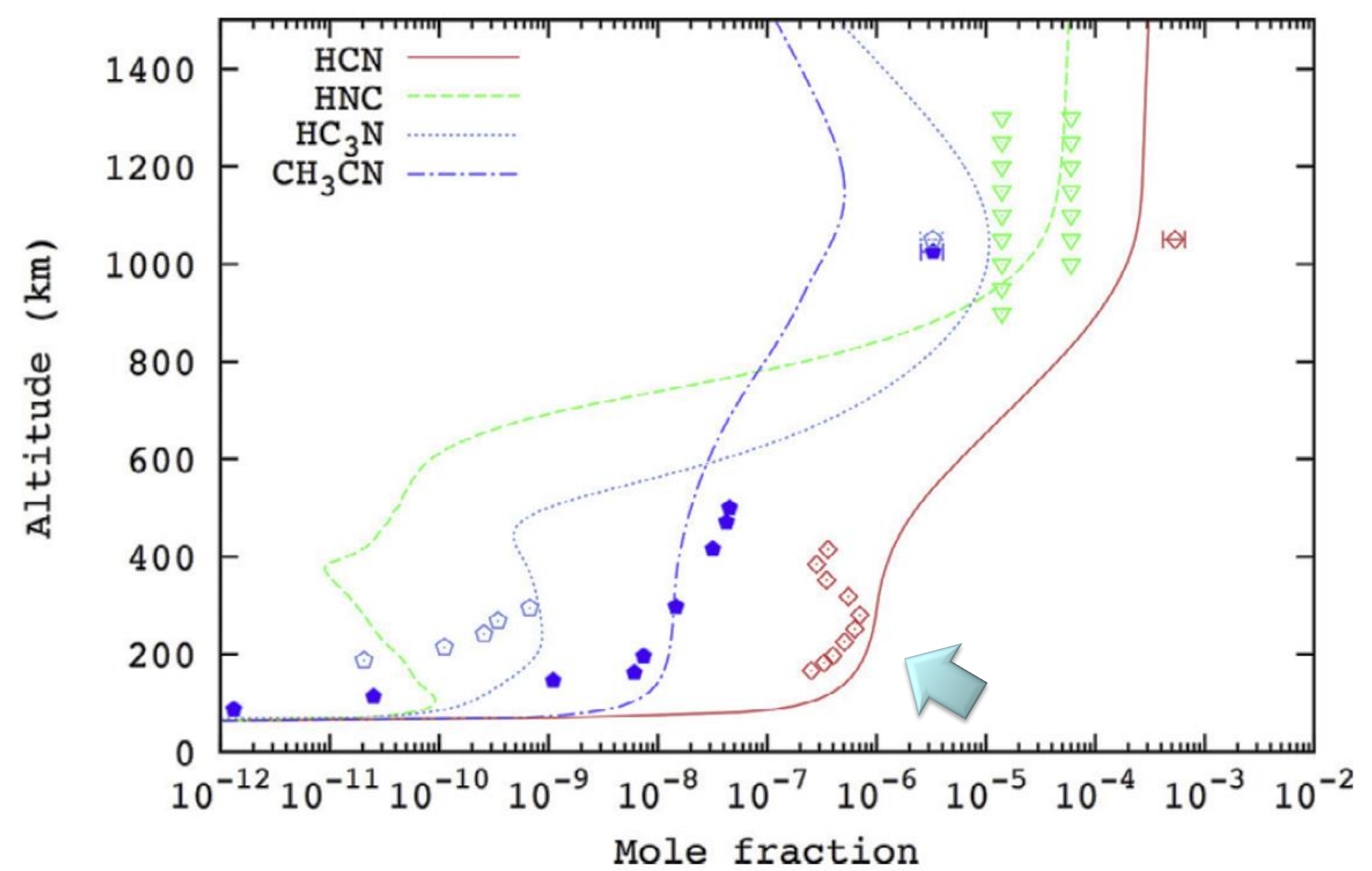


Dobrijevic
& Loison
Icarus 2018

Cyanogen

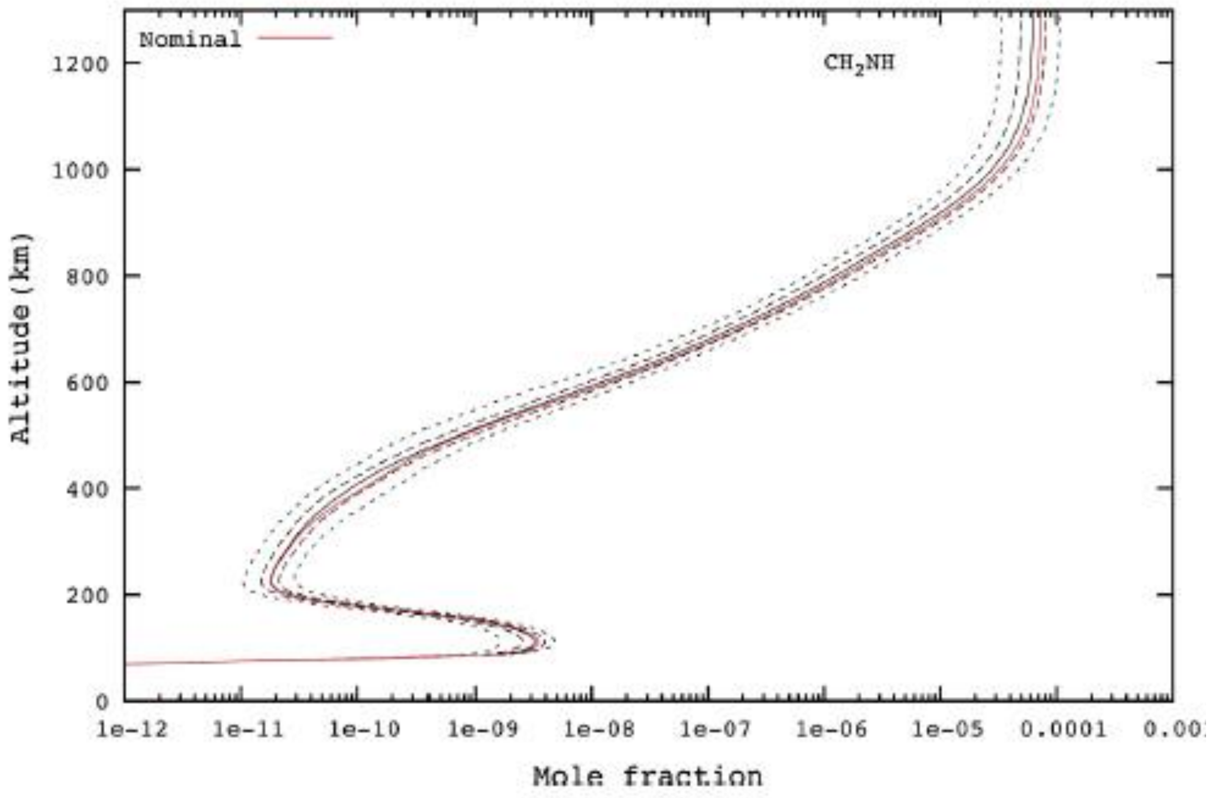


Vuitton et al. 2019

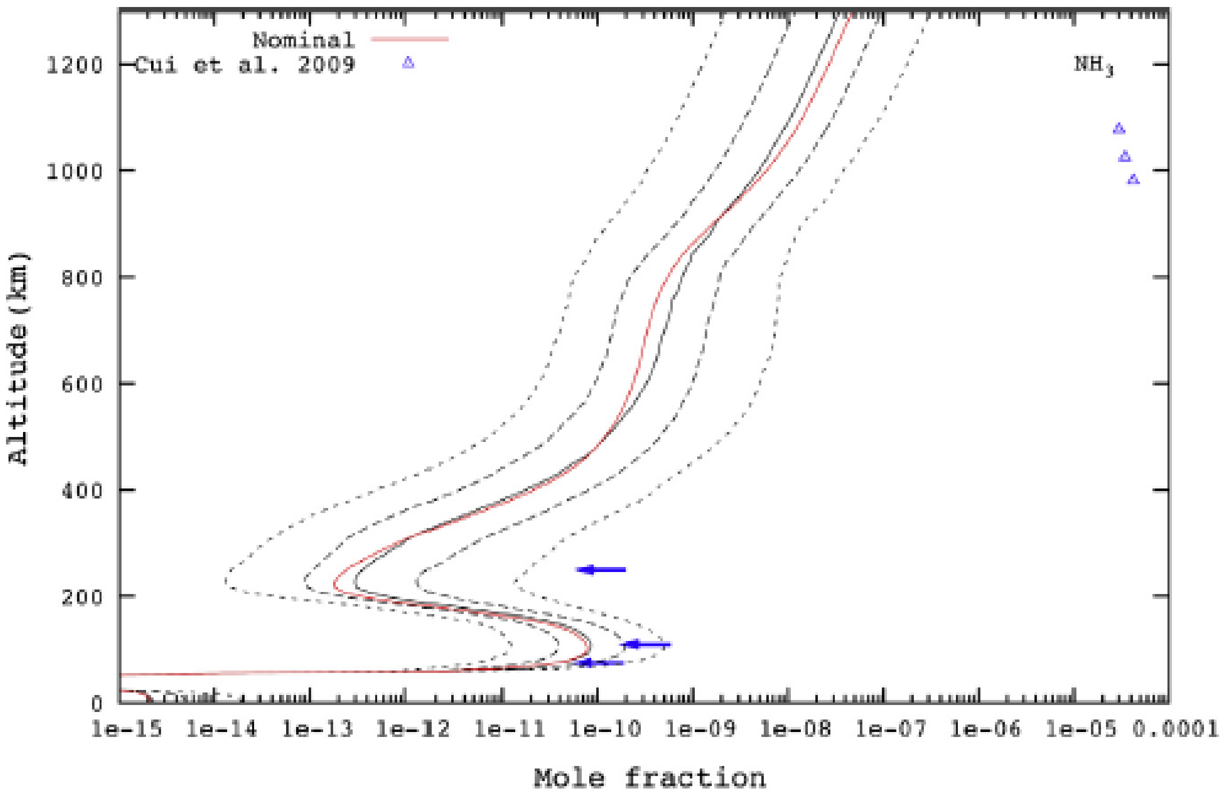


Dobrijevic
& Loison
Icarus 2018

methanimine



ammonia



Loison et al

Icarus 2015

Gas-phase chemistry and molecular complexity in space: how far do they go?

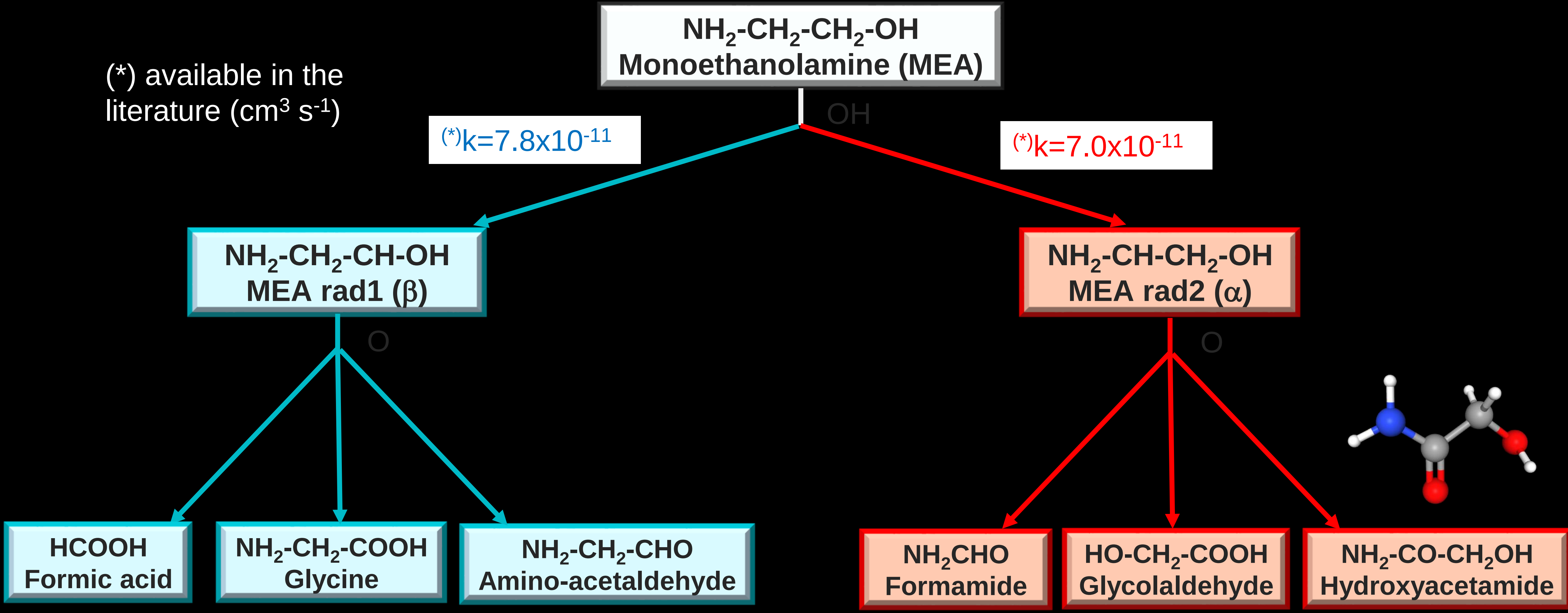
Discovery in space of ethanolamine, the simplest phospholipid head group

Víctor M. Rivilla[a,b,1], Izaskun Jiménez-Serra[a], Jesús Martín-Pintado[a], Carlos Briones[a], Lucas F. Rodríguez-Almeida[a], Fernando Rico-Villas[a], Belén Tercero[c], Shaoshan Zeng[d], Laura Colzi[a,b], Pablo de Vicente[c], Sergio Martín[e,f], and Miguel A. Requena-Torres[g,h]

[a]Centro de Astrobiología, Consejo Superior de Investigaciones Científicas–Instituto Nacional de Técnica Aeroespacial "Esteban Terradas", 28850 Madrid, Spain; [b]Osservatorio Astrofisico di Arcetri, Istituto Nazionale de Astrofisica, 50125 Florence, Italy; [c]Observatorio Astronómico Nacional, Instituto Geográfico Nacional, 28014 Madrid, Spain; [d]Star and Planet Formation Laboratory, Cluster for Pioneering Research, RIKEN, Wako 351-0198, Japan; [e]ALMA Department of Science, European Southern Observatory, Santiago 763-0355, Chile; [f]Department of Science Operations, Joint Atacama Large Millimeter/Submillimeter Array Observatory, Santiago 763-0355, Chile; [g]Department of Astronomy, University of Maryland, College Park, MD 20742; and [h]Department of Physics, Astronomy and Geosciences, Towson University, Towson, MD 21252

the genealogical tree of monoethanolamine

(*) available in the literature ($cm^3\ s^{-1}$)



NH_2-CH_2-CH_2-OH
Monoethanolamine (MEA)

OH

$^{(*)}k=7.8\times10^{-11}$

$^{(*)}k=7.0\times10^{-11}$

NH_2-CH_2-CH-OH
MEA rad1 (β)

NH_2-CH-CH_2-OH
MEA rad2 (α)

O

O

HCOOH
Formic acid

NH_2-CH_2-COOH
Glycine

NH_2-CH_2-CHO
Amino-acetaldehyde

NH_2CHO
Formamide

HO-CH_2-COOH
Glycolaldehyde

NH_2-CO-CH_2OH
Hydroxyacetamide

THE ASTROPHYSICAL JOURNAL LETTERS, 953:L20 (11pp), 2023 August 20 https://doi.org/10.3847/2041-8213/ace977

First Glycine Isomer Detected in the Interstellar Medium: Glycolamide ($NH_2C(O)CH_2OH$)

Víctor M. Rivilla[1], Miguel Sanz-Novo[1,2,3], Izaskun Jiménez-Serra[1], Jesús Martín-Pintado[1], Laura Colzi[1], Shaoshan Zeng[4], Andrés Megías[1], Álvaro López-Gallifa[1], Antonio Martínez-Henares[1], Sarah Massalkhi[1], Belén Tercero[5], Pablo de Vicente[6], Sergio Martín[7,8], David San Andrés[1], Miguel A. Requena-Torres[9,10], and José Luis Alonso[2]

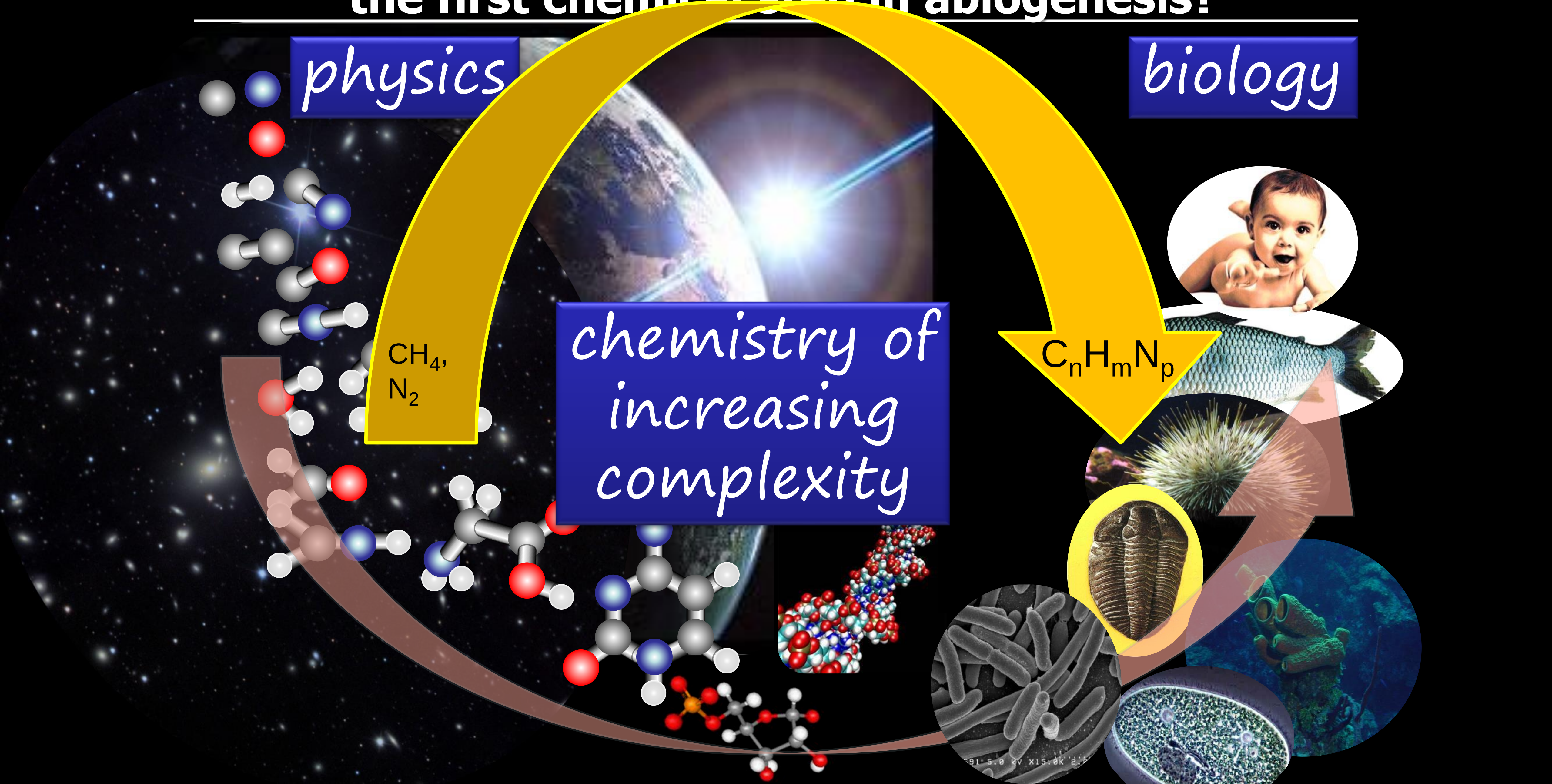
[1] Centro de Astrobiología (CAB), INTA-CSIC, Carretera de Ajalvir km 4, Torrejón de Ardoz, E-28850 Madrid, Spain; vrivilla@cab.inta-csic.es

Gas-phase chemistry and molecular complexity in space: how far do they go?

They can go far, but it is not as easy as we might imagine. In the interstellar medium, complex molecules are much less abundant than simple ones (as observed) because of the competition among reaction channels (including those going back to simpler molecules).

In planetary atmospheres with a significant abundance of hydrocarbons, gas phase chemistry can generate also macromolecules

Gas-phase prebiotic chemistry: the first chemical step in abiogenesis?



physics

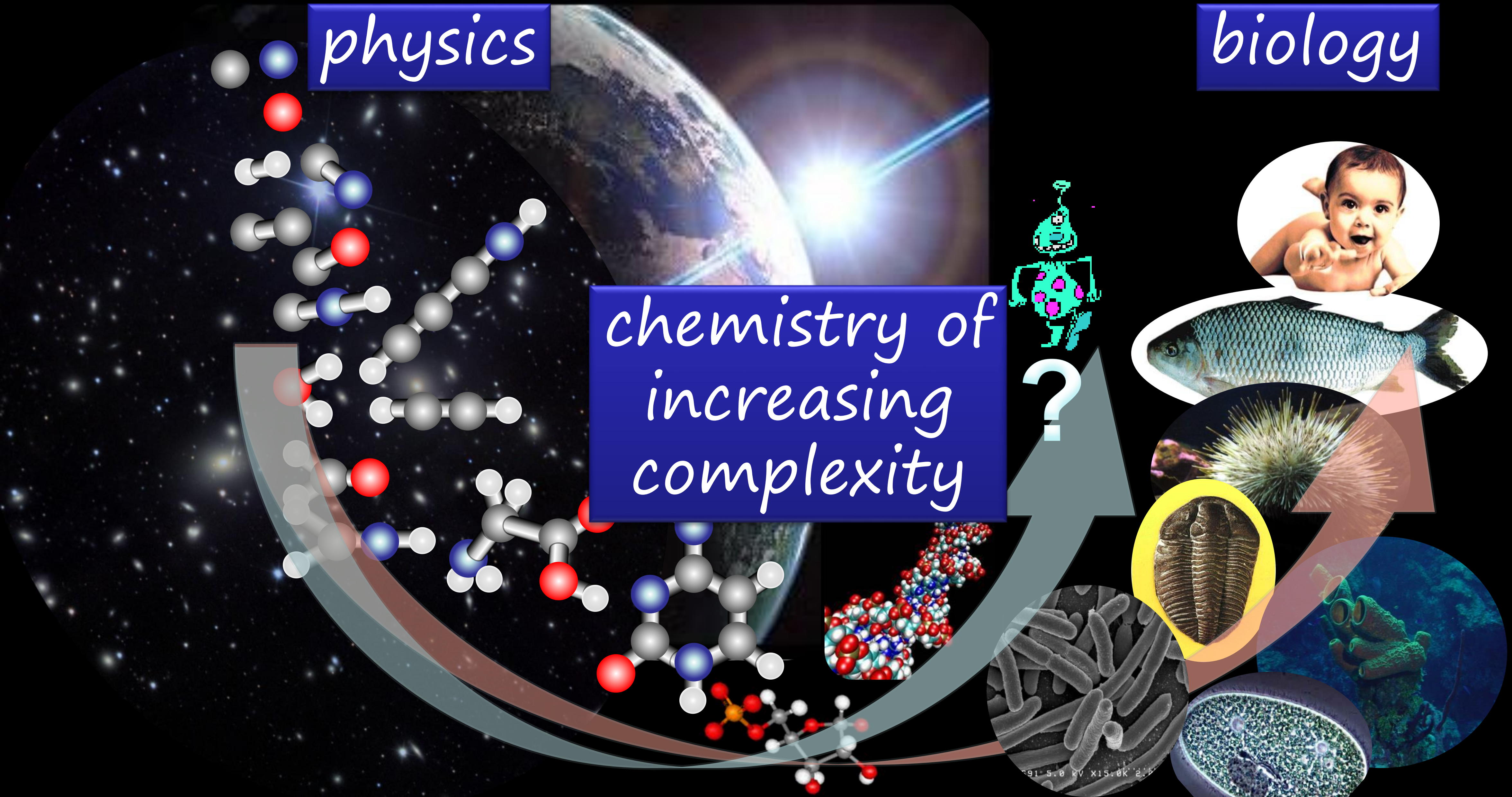
biology

chemistry of increasing complexity

CH_4, N_2

$C_nH_mN_p$

Gas-phase prebiotic chemistry: the first chemical step in abiogenesis?



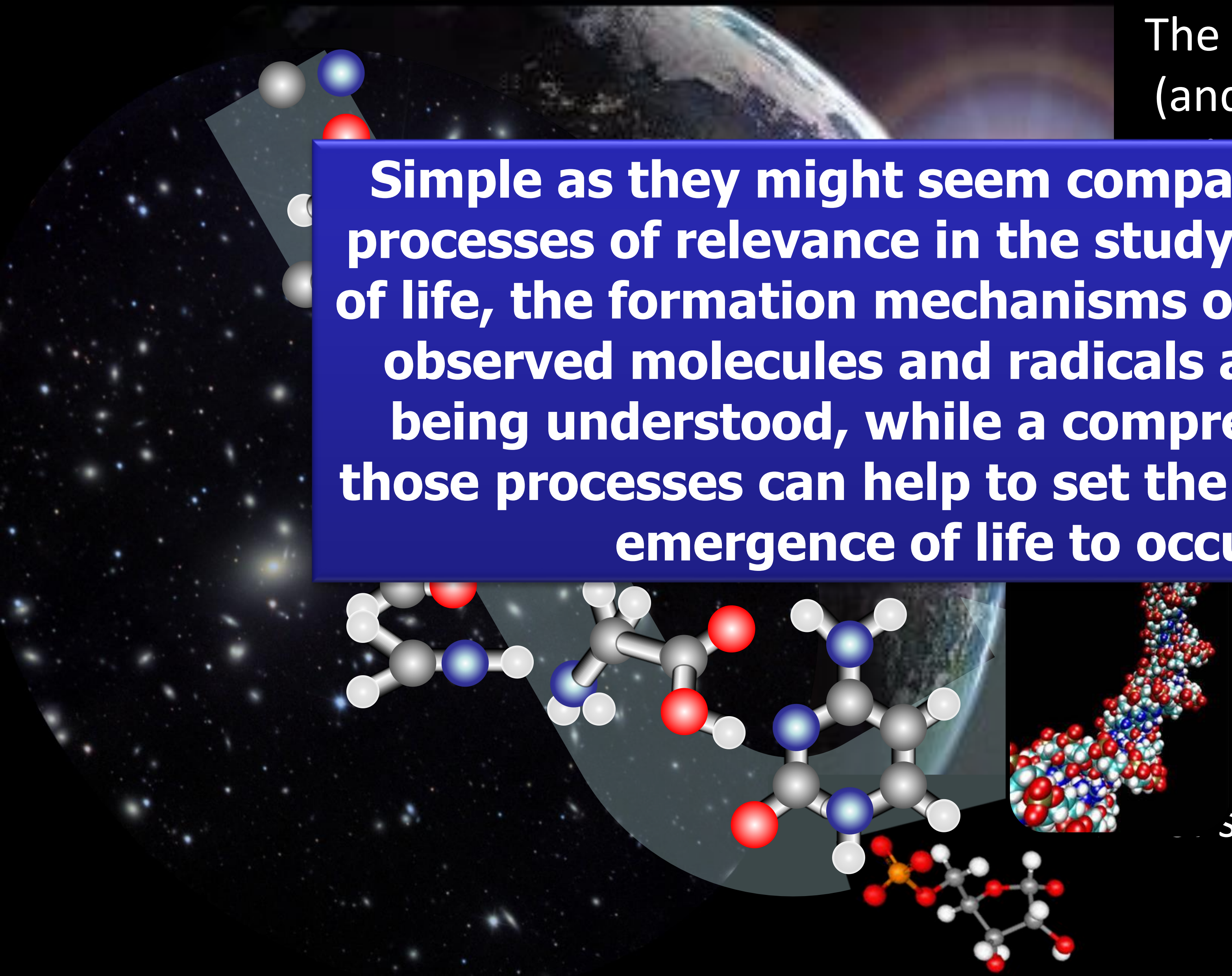
physics

chemistry of increasing complexity

?

biology

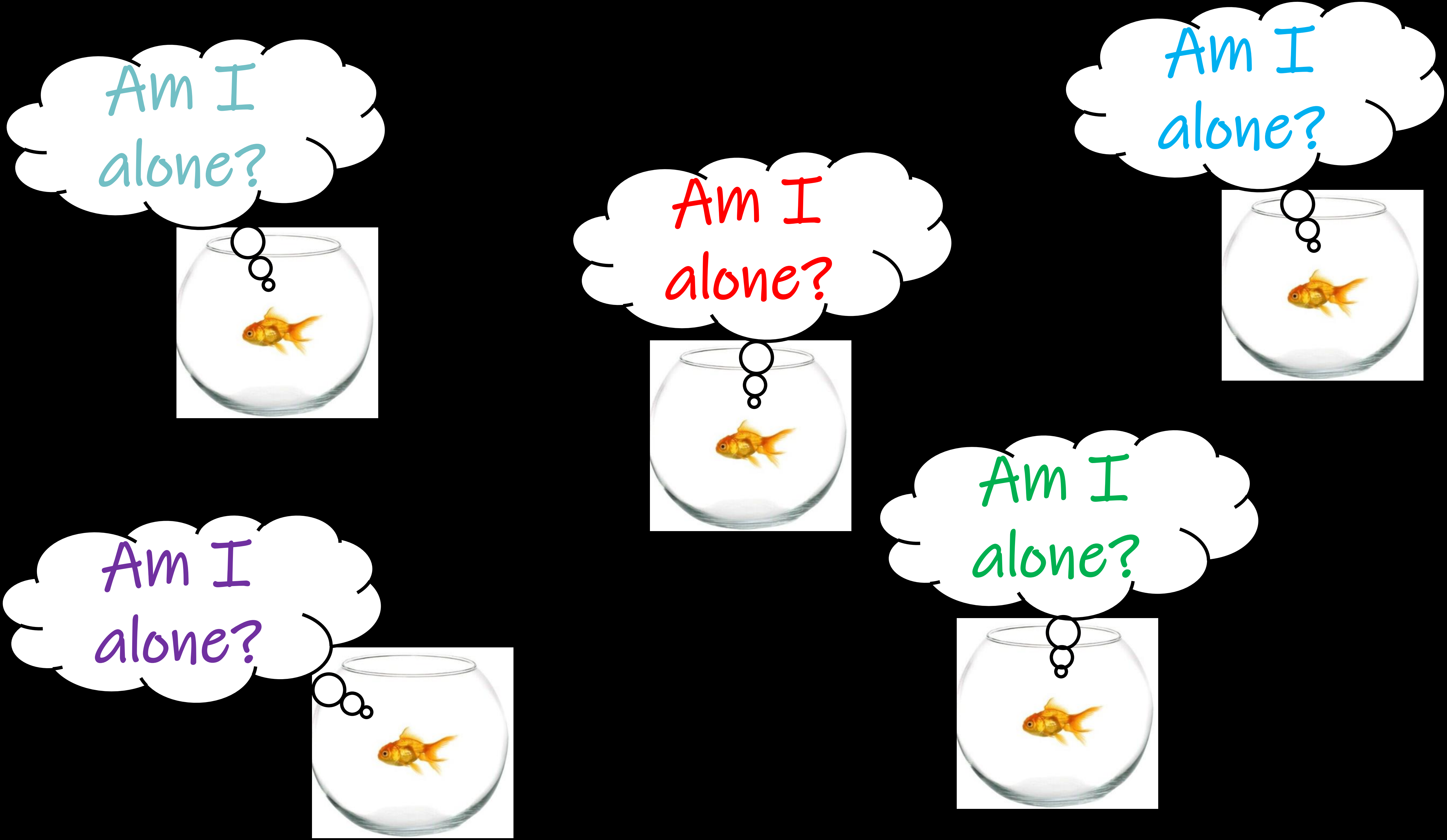
Gas-phase prebiotic chemistry: the first chemical step in abiogenesis?



The aggregation of H, O, N, C
(and other elements) atoms
the
ical
urring
e, as
e
e than
s in the
chemical environments
nterstellar clouds and by
ne gas-phase chemical
ution of the atmospheres
several solar objects like
Titan.

Simple as they might seem compared to other processes of relevance in the study of the origin of life, the formation mechanisms of many of the observed molecules and radicals are far from being understood, while a comprehension of those processes can help to set the stage for the emergence of life to occur.


Am I alone?


Am I alone?
Am I alone?
Am I alone?
Am I alone?
Am I alone?

Other Postdocs: Demian Marchione (ASI Project), Vanessa Murray

Gianmarco Vanuzzo
(postdoc)

Adriana Caracciolo
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Complutense
Luis Banares’ group)

Piero
Luca
Casavecchia
Mancini

Marzio Rosi

Dimitris

Skouteris

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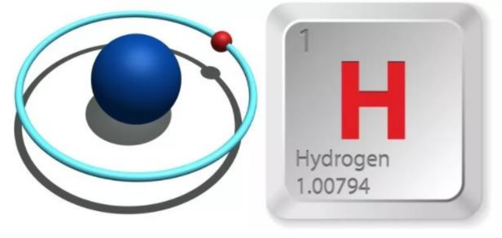
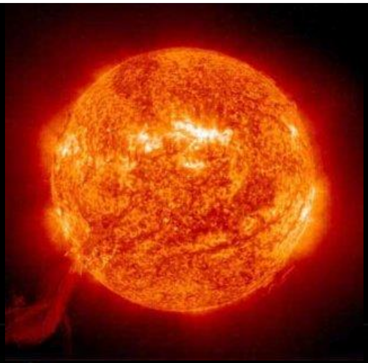
Andrea Giustini

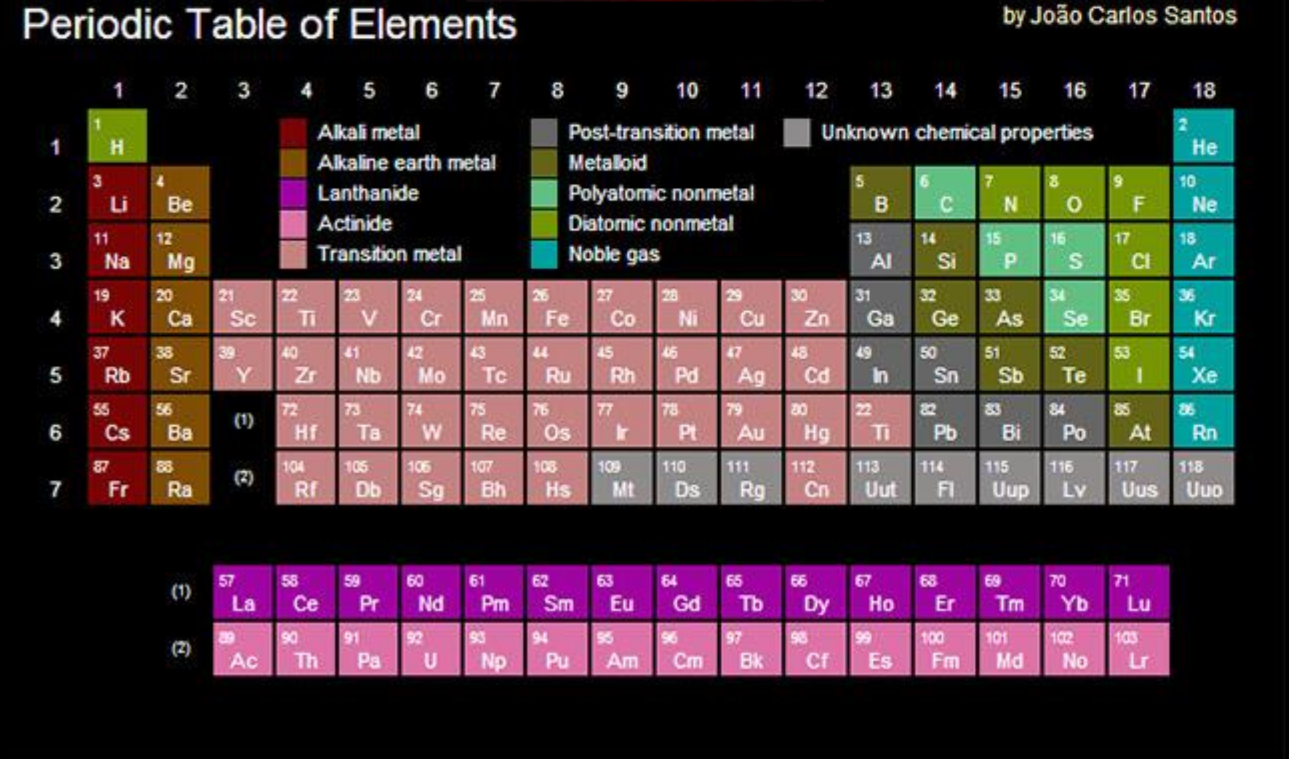
Massimiliano Aschi
(Univ. L’Aquila)

Cecilia Ceccarelli
(IPAG)

Nuclear astrophysics







Periodic Table of Elements

by João Carlos Santos

- Alkali metal
- Alkaline earth metal
- Lanthanide
- Actinide
- Transition metal
- Post-transition metal
- Metalloid
- Polyatomic nonmetal
- Diatomic nonmetal
- Noble gas
- Unknown chemical properties

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	(1)	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	22 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	(2)	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		(1)	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		(2)	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

it provides us with the ingredients for the recipe of life

for your attention