Life in a Cosmic Context, Sept 15-17, 2015, SISSA, Trieste

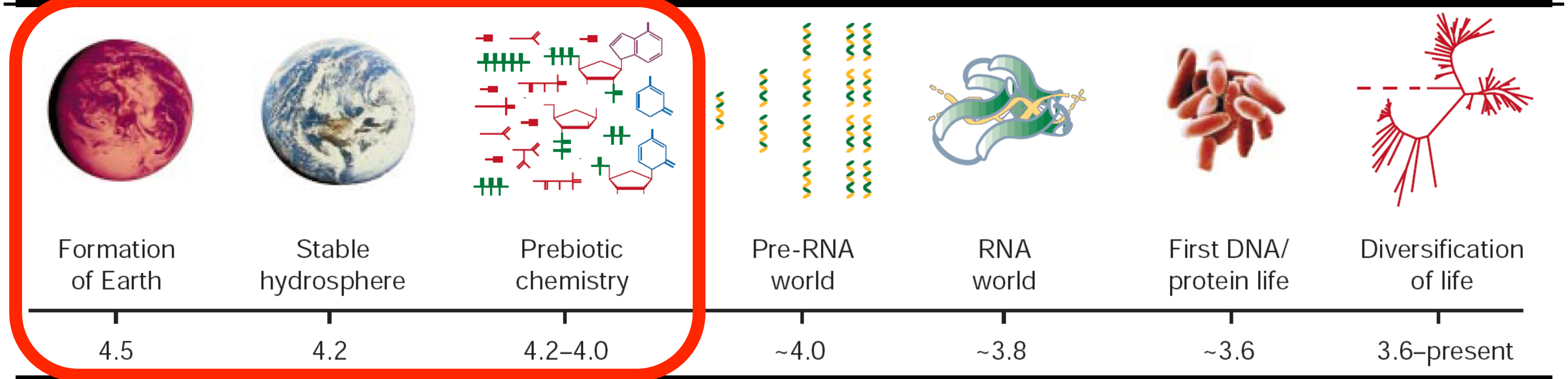
Gas-phase formation routes of simple prebiotic molecules in the interstellar medium

Nadia Balucani[1,2] & Cecilia Ceccarelli[2]

[1] DCBB, Università di Perugia, Perugia, Italy

[2] IPAG, Université Grenoble Alpes, France

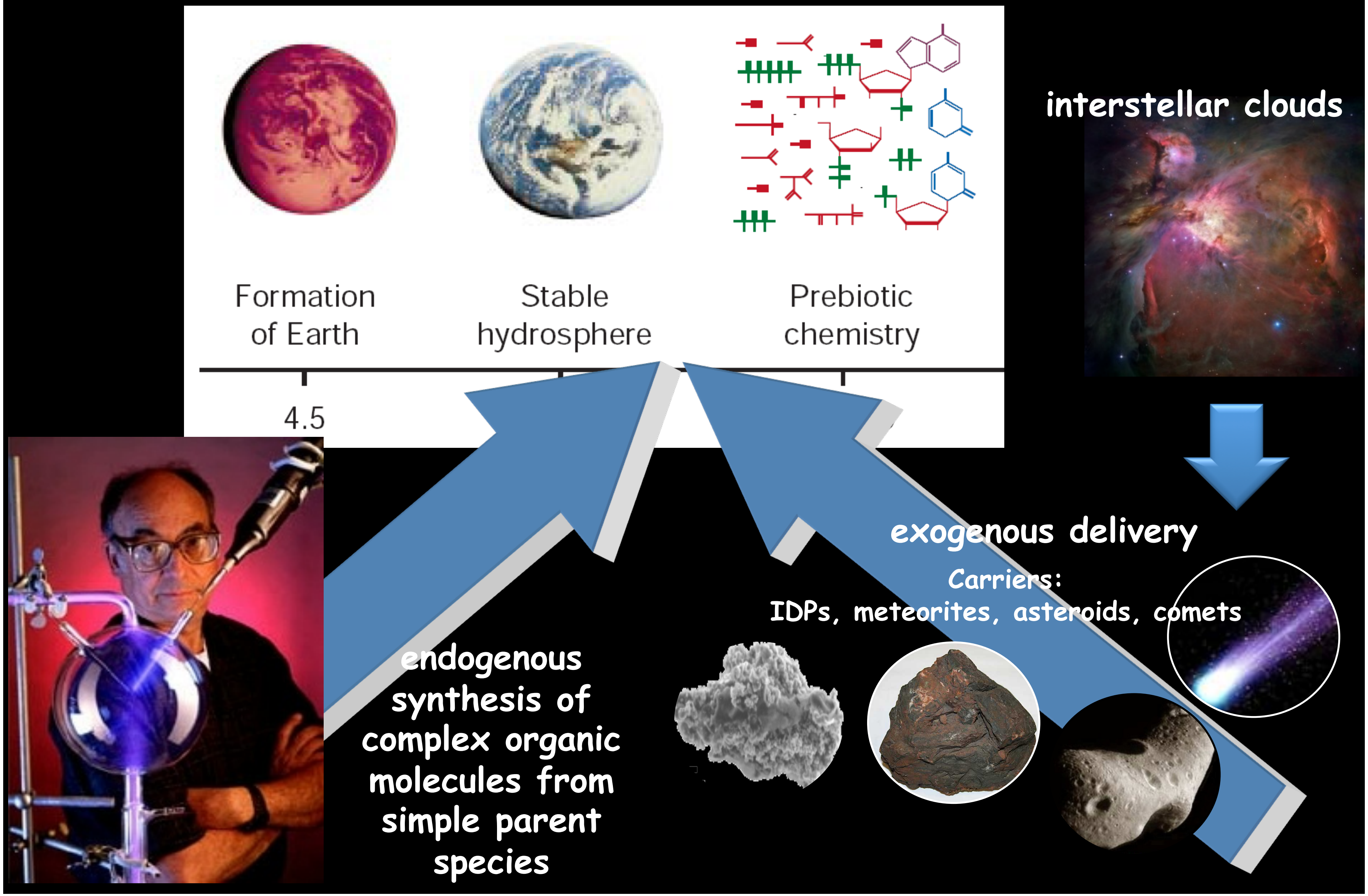
Basic steps in the origin of life



Gerald F. Joyce, Nature (2002)

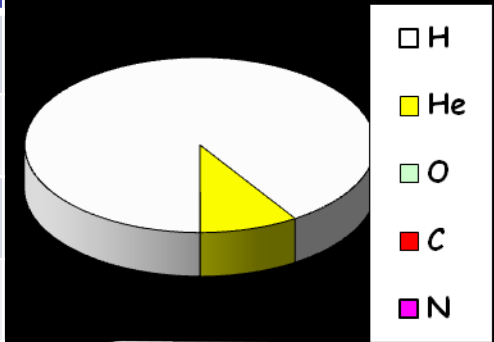
this contribution is focused on the chemical evolution which has taken place during the early steps along this sequence of events

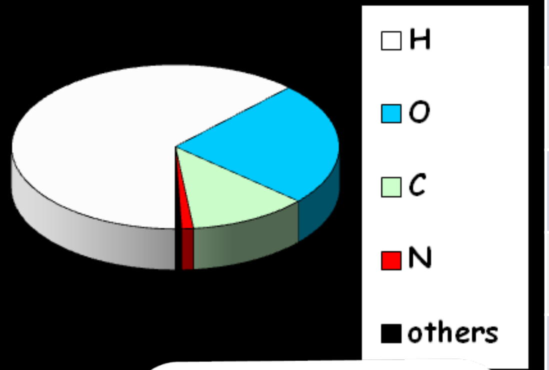
Very first steps in the origin of life: exogenous delivery or local formation of prebiotic molecules?



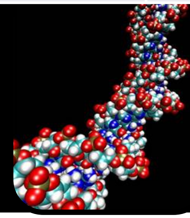
Chemical composition: Universe vs human body

element	mole fraction
H	0.91
He	0.09
O	2.7×10^{-4}
C	1.3×10^{-4}
N	7.3×10^{-5}
S	2.7×10^{-5}
Si	1.8×10^{-6}
Mg	9×10^{-7}
Fe	1.8×10^{-7}
others	$\sim 10^{-12}$





element	mole fraction
H	0.63
He	-
O	0.24
C	0.12
N	0.01
S	4×10^{-4}
Si	6×10^{-5}
Mg	7×10^{-5}
Fe	1.8×10^{-7}
others (Ca, P, Na, etc)	$\sim 6 \times 10^{-3}$



atomic species or simple molecules

Identified interstellar and circumstellar molecules/ions

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^+

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

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 HC_3N HC_2NC HCOOH CH_2NH H_2C_2O H_2NCN HNC_3 SiH_4
H_2COH^+ C_4H^- CNCHO $NCCNH^+$ SiH_3CN NH_3D^+ H_2NCO^+ CH_3O HNCNH

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

from www.astrochymist.org

7 atoms

C_6H CH_2CHCN CH_3C_2H HC_5N $HCOCH_3$ NH_2CH_3 c-C_2H_4O CH_2CHOH C_6H^-

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

Only 37 species do not contain carbon !!

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

10 atoms

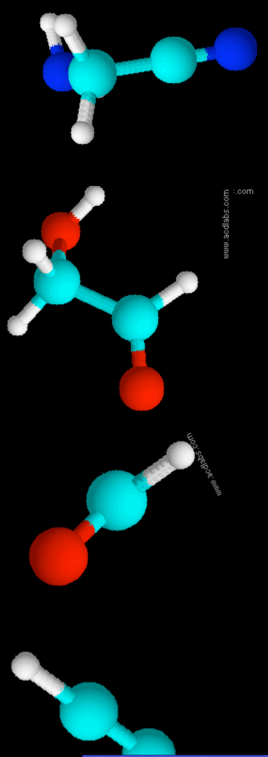
CH_3C_5N $(CH_3)_2CO$ NH_2CH_2COOH CH_3CH_2CHO CH_2OHCH_2OH

+ PAHs family

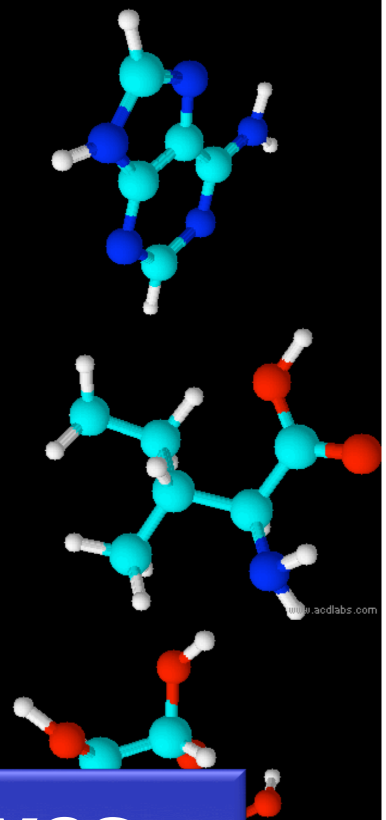
≥ 11 atoms

HC_9N CH_3C_6H C_6H_6 $HC_{11}N$ $CO(CH_2OH)_2$ $HCOOC_2H_5$ CH_3COOCH_3 C_3H_7CN $C_{14}H_{10}^+$ C_{60} C_{60}^+

Simple organic molecules: are they the link between matter in the Universe and matter in living entities?

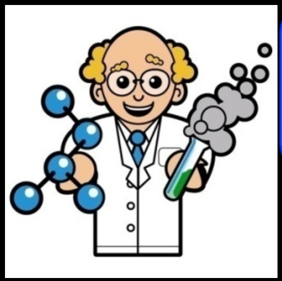


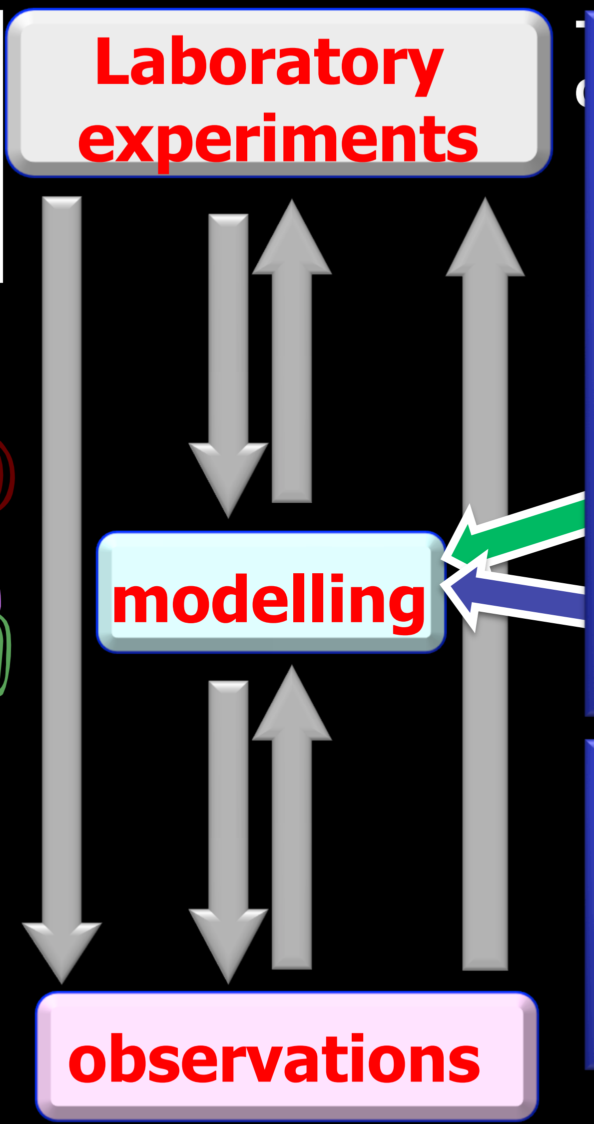
gas-phase molecules	potential precursor of
with C-N bonds (e.g. HCN, CH_3CN, C_2N_2, HCCCN, CH_2NH, C_2H_3CN)	**aminoacids & nucleic bases**
with C-O bonds (e.g. H_2CO, CH_3OH, CH_3COH, CH_3CHO, $(CH_2OH)_2$,CH_2OHCHO)	**sugars & aminoacids**
with C-C multiple bonds (e.g. from C_2H_2 up to	**long carbon chain molecules, PAHs**



If we agree that the answer is yes, we need to face another question: how were they formed to begin with?

The chemistry of the interstellar medium: a multidisciplinary approach





Hundreds or thousands of elementary reactions including:

- dissociation, excitation & ionization processes
- neutral-neutral reactions
- ion-molecule reactions
- heterogeneous processes

a large fraction of these processes need to be characterized in lab experiments yet taken from Eric Herbst 2006 (Interstellar Clouds) when he started considering grain chemistry for the formation of more complex molecules:

GAS-PHASE MODEL NETWORKS

4,400 reactions; 10-20% "studied";
450 species through 13 atoms in size

in 9 years this percentage has not changed much;
more recent models: 8000 reactions involving also negative ions

elements: H, He, N, O, C, S, Si, Fe, Na

elemental abundances: "low metal"

photodestruction: external, internal (via

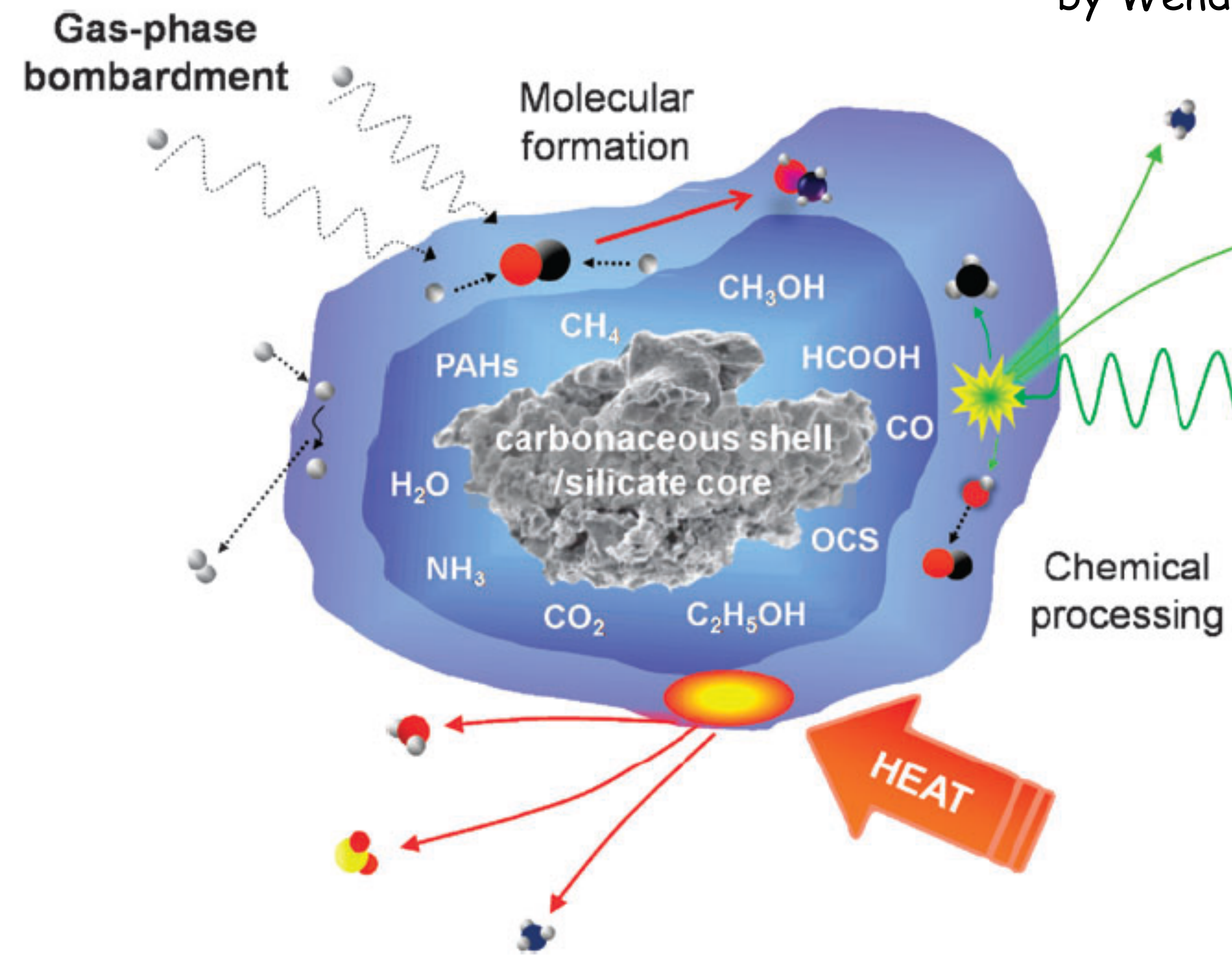
Successes for quiescent cores:

(1) Reproduces 80% of abundances including ions, radicals, isomers

(2) Predicts strong deuterium fractionation

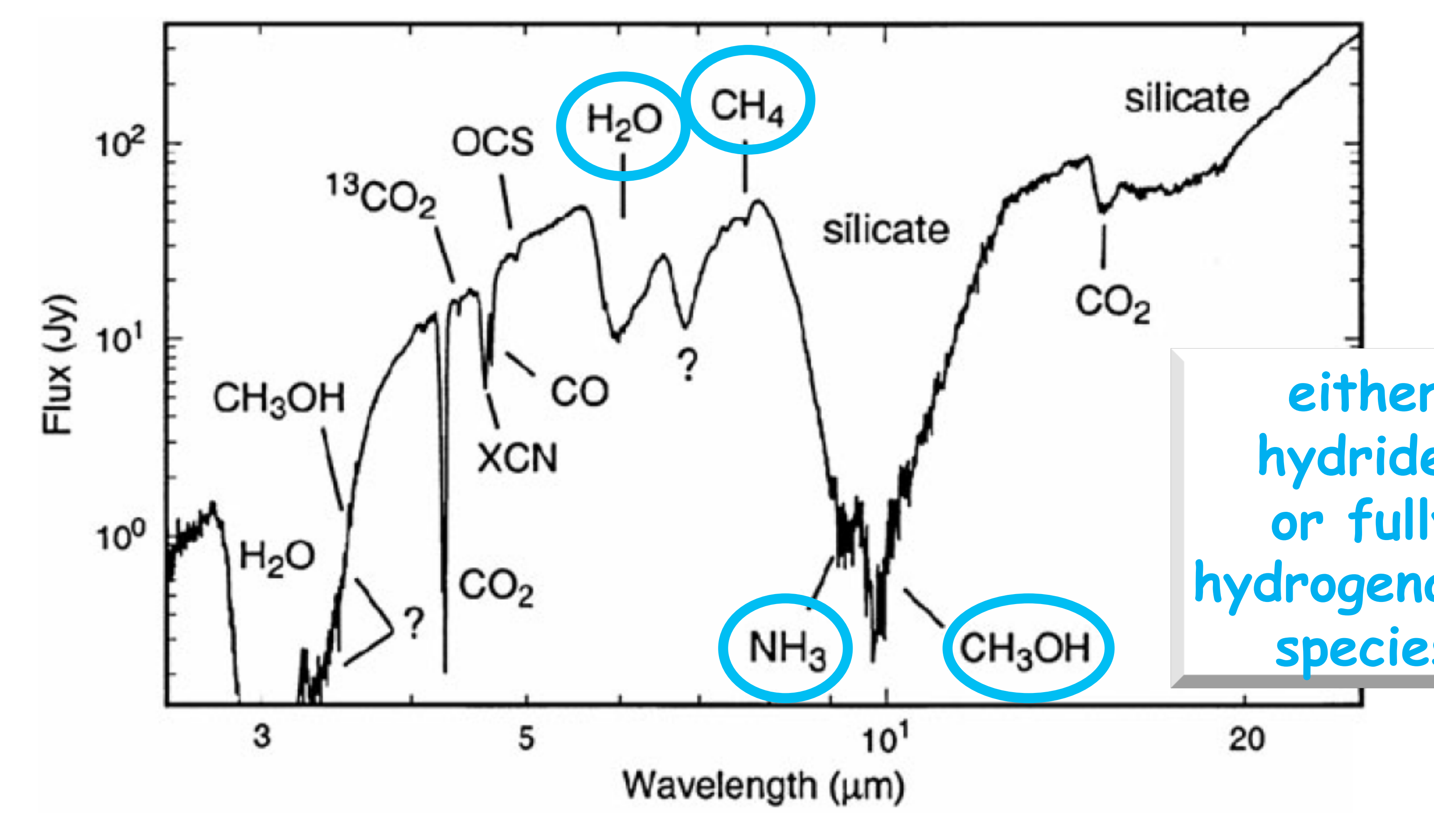
Dust particles and icy mantles: preferential sites to induce chemical reactivity?

by Wendy Brown (PCCP 2014)



Problems:
- mobility of frozen species at 10 K;
- desorption mechanisms

The ISM ice composition



either hydrides or fully hydrogenated species

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

Degrees of saturation: in the ISM there are completely saturated (e.g. CH_4, CH_3NH_2, CH_3OH), partially saturated (e.g. $CH_3CH=CH_2$, $CH_2=NH$, H_2CO) and strongly unsaturated molecules (e.g. C_2H_2 and cyanopolyynes, HCN, PAHs) in the presence of abundant hydrogen atoms/molecules

Different formation routes?

fully hydrogenated species: ice induced processes	unsaturated species: gas phase processes

Garrod & Herbst, A&A 2006: ice induced chemistry responsible for the formation of most complex organic molecules (missing gas phase routes of formation)

… missing gas phase routes of formation …

Is that true?

many **gas-phase routes have actually been overlooked** and not considered in the astrochemical models, while **their inclusion** with the **parameters determined in laboratory experiments** or **via accurate theoretical calculations** **could be decisive in reproducing the observed abundances of complex molecules**

Following the observation of relatively complex molecules also in very cold interstellar objects (no mobility, no easy desorption), in Grenoble we have started a systematic search for new formation routes in the gas phase by:

Following the observation of relatively complex molecules also in very cold interstellar objects (no mobility, no easy desorption), in Grenoble we have started a systematic search for new formation routes in the gas phase by:

1) extensively searching the literature for previously overlooked bimolecular reactions in the gas phase;

2) making use of recent experimental results where the reactions of interest have been investigated under the appropriate experimental conditions (low T and P)

3) guiding theoretical chemists in the choice of reactions for which laboratory experiments are extremely difficult (if not impossible)

4) testing the new formation routes in astrochemical models

1) extensively searching the literature for previously overlooked bimolecular reactions in the gas phase

methyl formate formation:
unsolved puzzle
⇓
grain surface chemistry invoked

1) extensively searching the literature for previously overlooked bimolecular reactions in the gas phase

gas phase reactions leading from dimethylether to methyl formate

$$Cl/F + CH_3OCH_3 \rightarrow CH_3OCH_2 + HCl/HF$$

$$O + CH_3OCH_2 \rightarrow HCOOCH_3 + OH$$

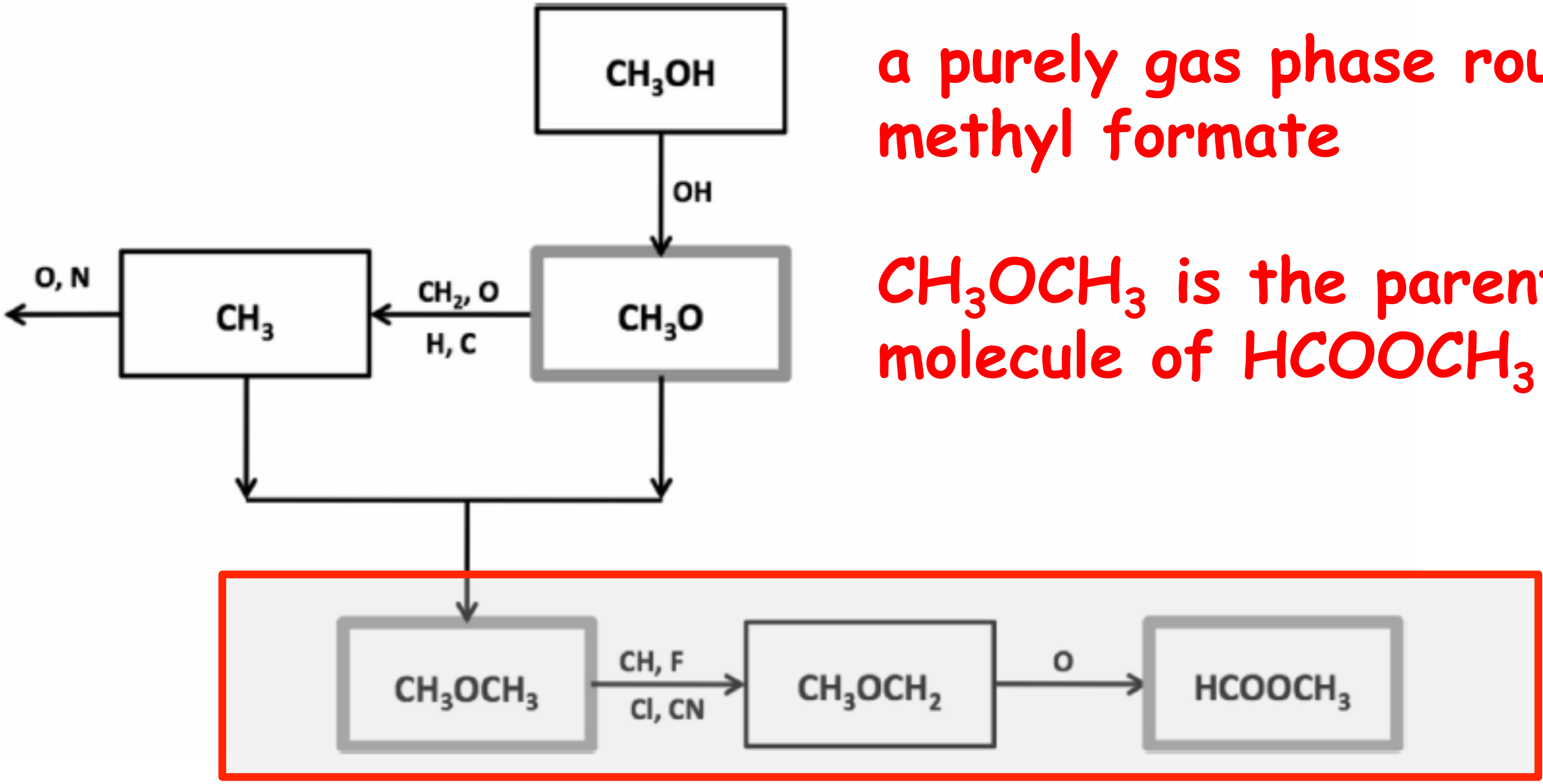
Experimental studies: 1) Wallington T. J., Skewes L. M., Siegel W. O., Wu C.-H., Japar S. M., 1988, Int. J. Chem. Kinetics, 20, 867; 2) Hoyermann K., Nacke F., 1996, Symp. Int. Combust. Proc. Vol. 26, Elsevier, Amsterdam, p. 505

Theoretical study of O + CH_3OCH_2: Song X., Hou H., Wang B., 2005, Phys. Chem. Chem. Phys., 7, 3980

Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY
MNRAS 449, L16–L20 (2015) doi:10.1093/mnrasl/slv009

Formation of complex organic molecules in cold objects: the role of gas-phase reactions

Nadia Balucani,[1,2,3] Cecilia Ceccarelli[2,3★] and Vianney Taquet[4]

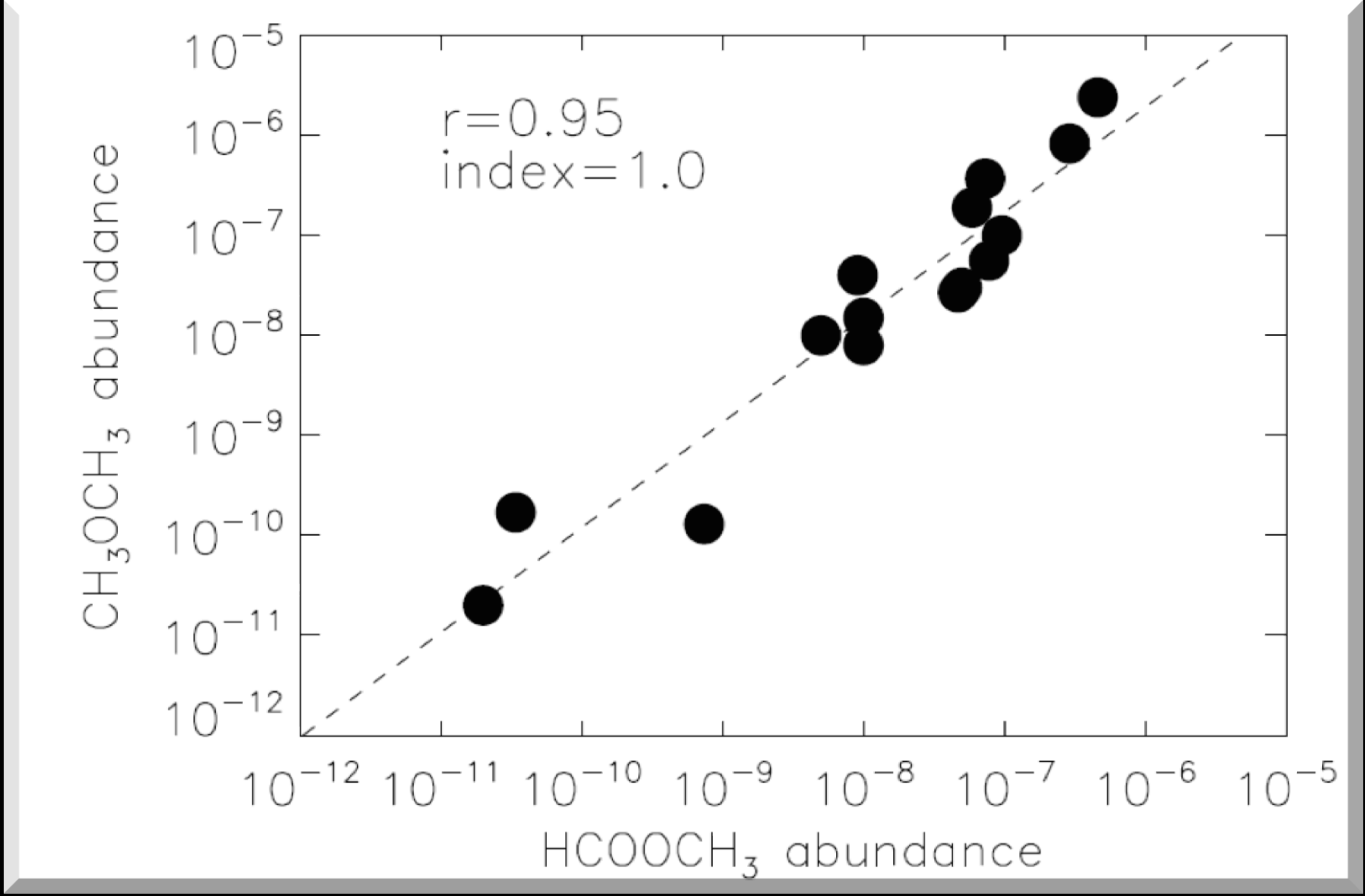


a purely gas phase route to methyl formate

CH_3OCH_3 is the parent molecule of $HCOOCH_3$

Abundance of dimethyl ether as a function of the abundance of methyl formate in different ISM sources

r = correlation coefficient + power-law index



Jaber, Ceccarelli, Kahane, Caux
ApJ 2014, 791:29

2) making use of recent experimental results where the reactions of interest have been investigated under the appropriate experimental conditions (low T and P)

$$OH + CH_3OH \rightarrow CH_3O \,/\, CH_2OH + H_2O$$

$$k\,(300\ K) = 9 \times 10^{-13}\ cm^3\ molec^{-1}\ s^{-1}$$

$$E_a = \begin{array}{l} 3\ kJ/mol\ (CH_2OH+H_2O) \\ 15\ kJ/mol\ (CH_3O+H_2O) \end{array}$$

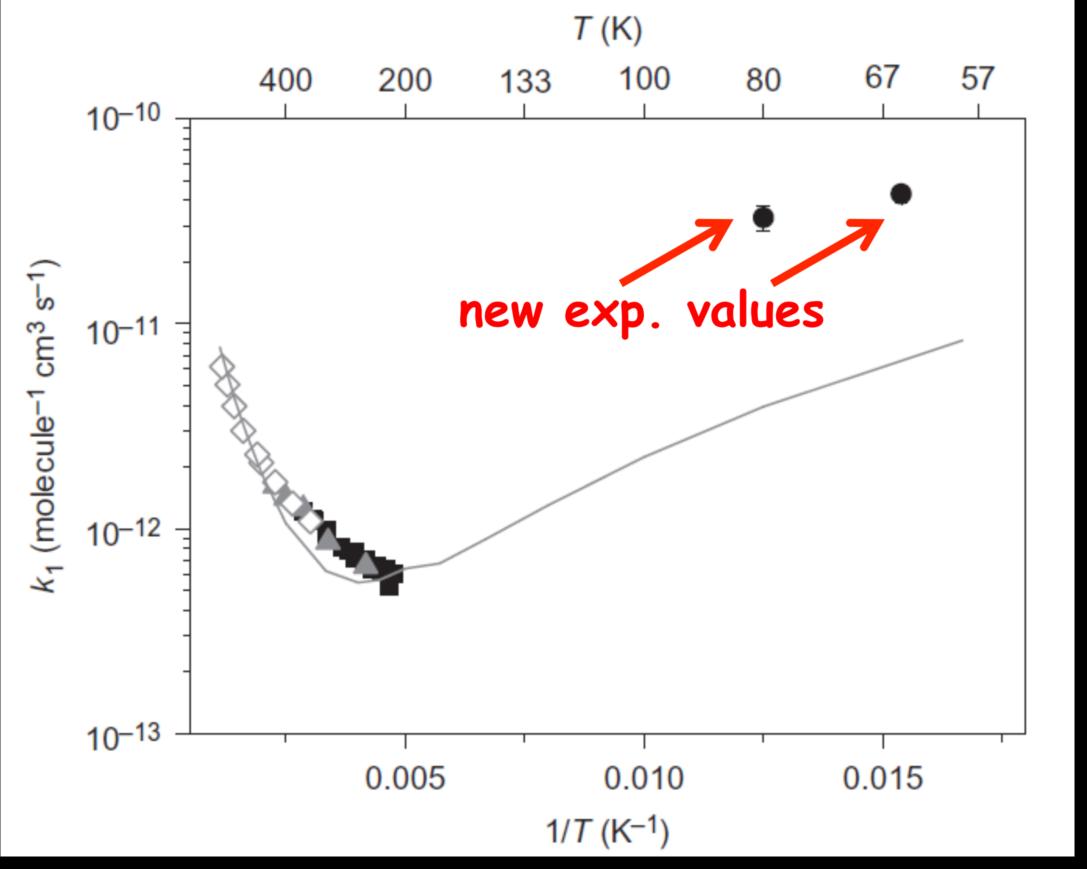
nature chemistry

ARTICLES

PUBLISHED ONLINE: 30 JUNE 2013 | DOI: 10.1038/NCHEM.1692

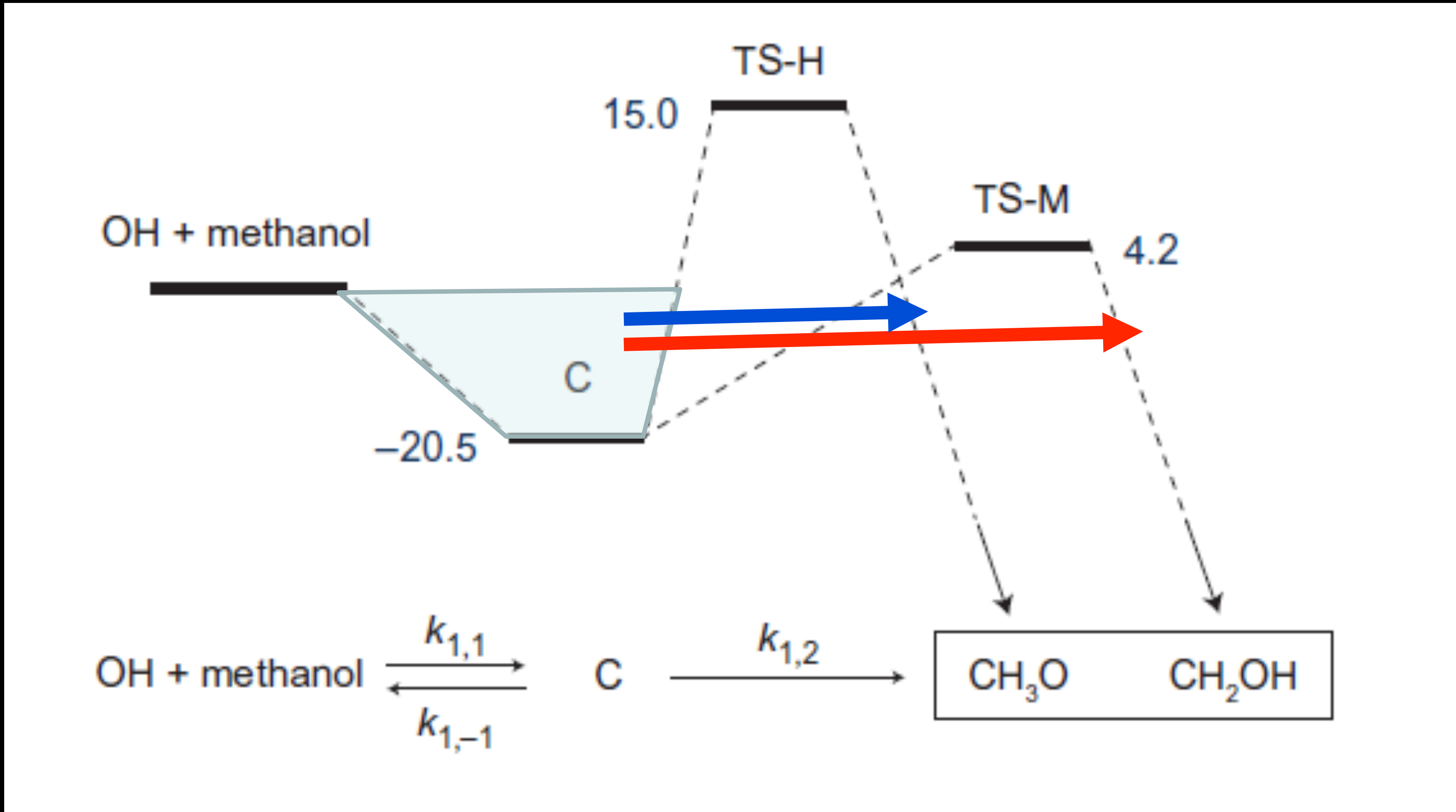
Accelerated chemistry in the reaction between the hydroxyl radical and methanol at interstellar temperatures facilitated by tunnelling

Robin J. Shannon[1], Mark A. Blitz[1,2], Andrew Goddard[1] and Dwayne E. Heard[1,2]*



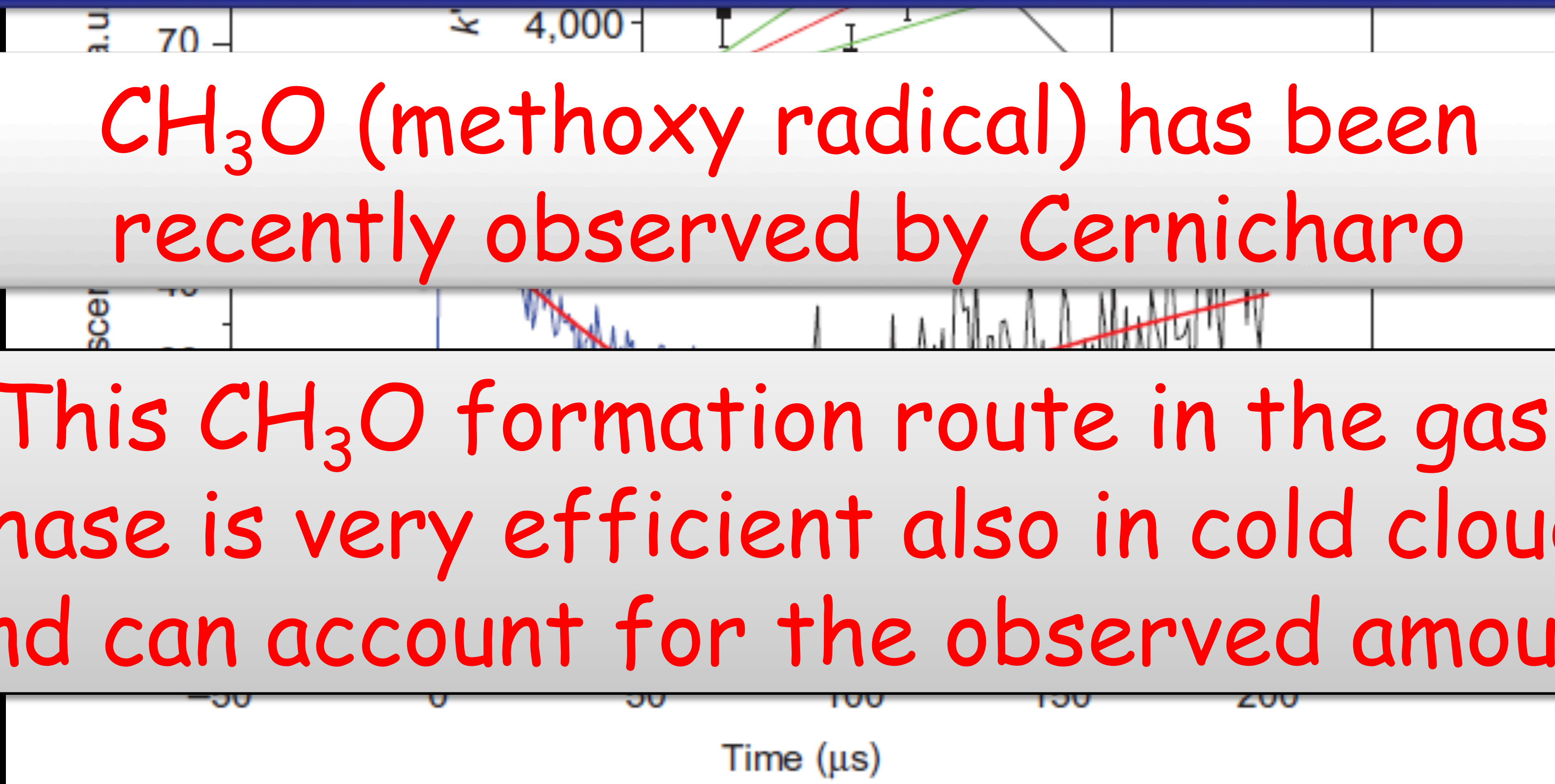
Despite the presence of an entrance barrier, the rate coefficient at 63 K was found to be larger than that at 200 K.

Deviations from Arrhenius behavior are quite common. In some cases they are associated to the tunnelling effect…



According to master equation calculations explicitly considering the tunnelling effects, at temperatures lower than 200 K the lifetime of the van der Waals complex is very long and tunnelling towards CH_3O+H becomes the dominant channel (99%)

Not only is the reaction several orders of magnitude faster than suggested by room temperature experiments,
but the dominant products are CH_3O+H and not CH_2OH+H



CH_3O (methoxy radical) has been recently observed by Cernicharo

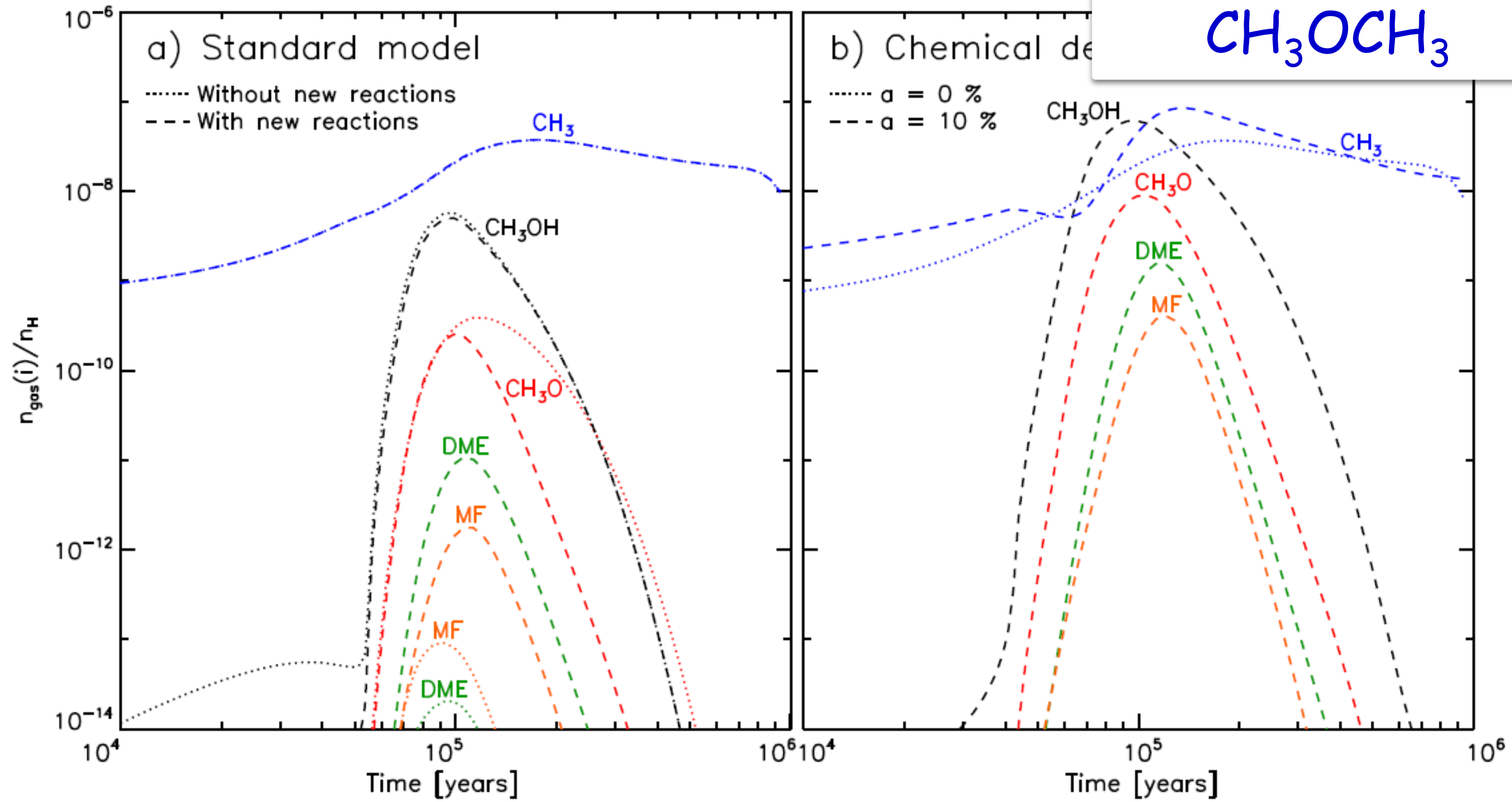
This CH_3O formation route in the gas-phase is very efficient also in cold clouds and can account for the observed amount

Monthly Notices
of the
ROYAL ASTRONOMICAL SOCIETY
MNRAS 449, L16–L20 (2015) doi:10.1093/mnra

Formation of complex organic molecules in cold objects: the role of gas-phase reactions

Nadia Balucani,[1,2,3] Cecilia Ceccarelli[2,3]★ and Vianney Taquet[4]

The conversion of CH_3OH to CH_3O is pivotal to achieve the formation of CH_3OCH_3



3) guiding theoretical chemists in the choice of reactions for which laboratory experiments are difficult (if not impossible)

formamide formation in the gas phase

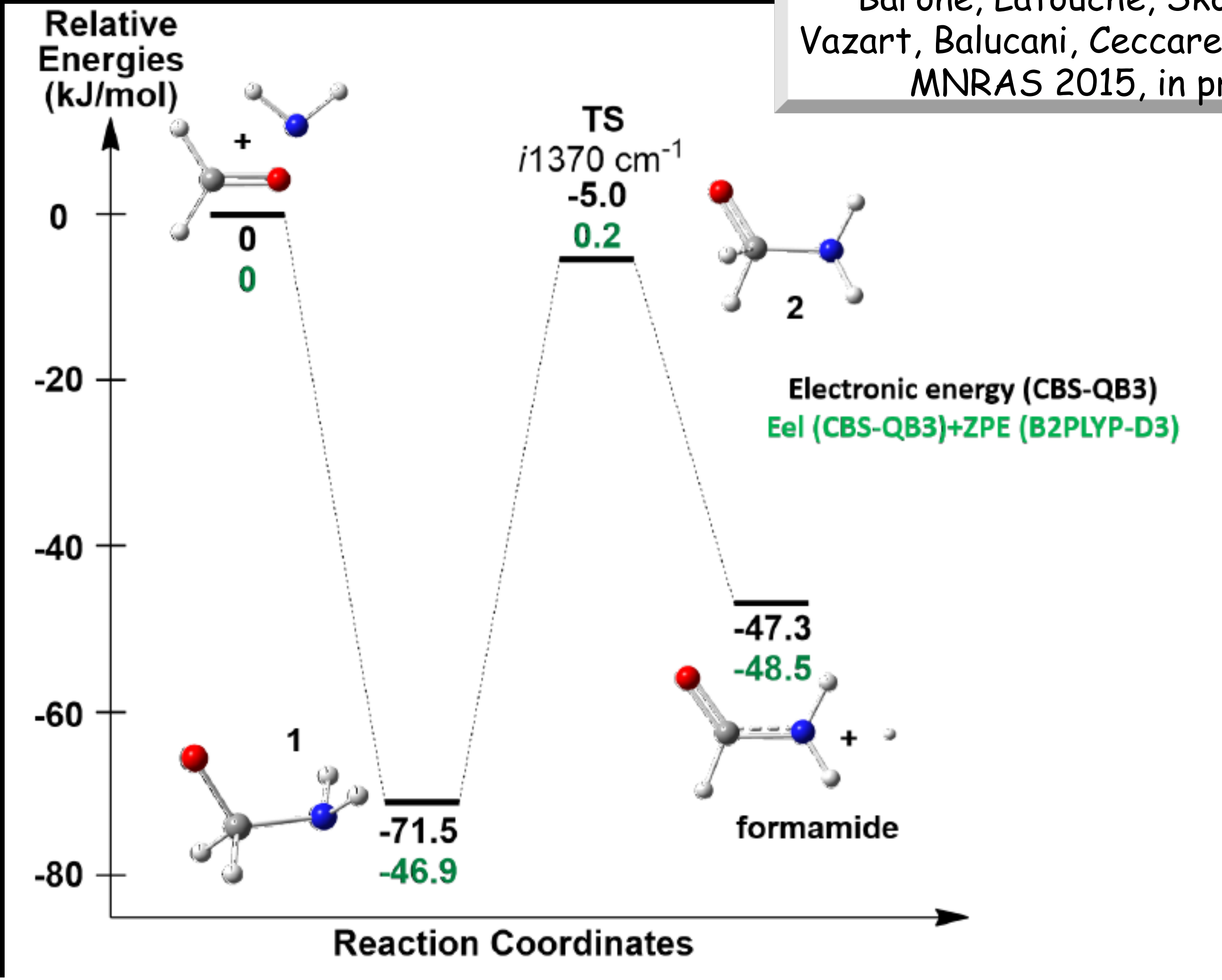
$$NH_2 + H_2CO \rightarrow HCONH_2 + H$$

- both NH_2 and H_2CO are abundant species in cold clouds

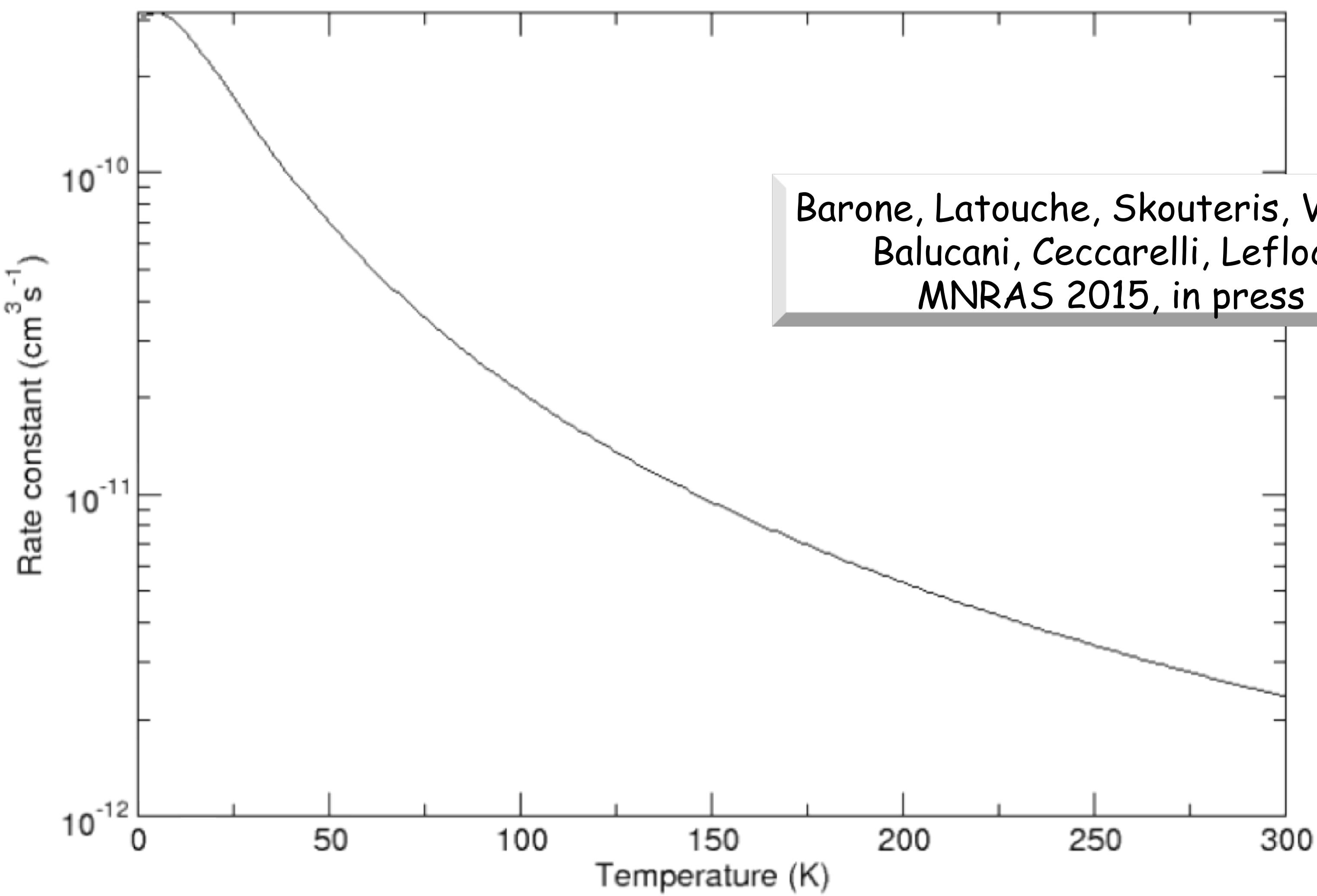
- previously disregarded because the similar reaction $OH + H_2CO$ is slow and characterized by a significant energy barrier

3) guiding theoretical chemists in the choice of reactions for which laboratory experiments are difficult (if not impossible)

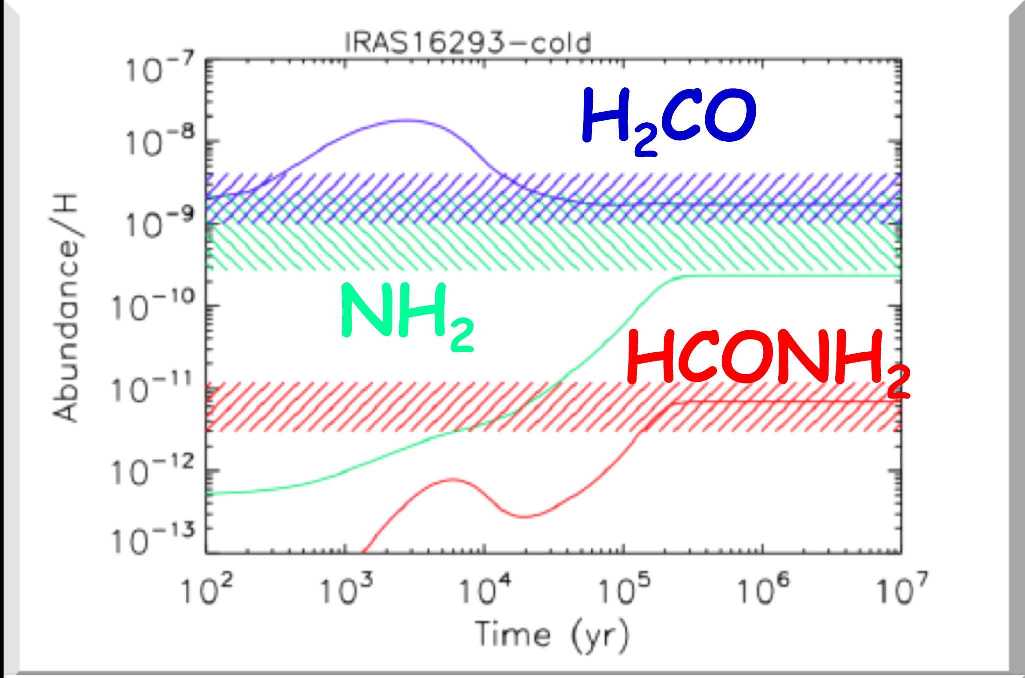
Barone, Latouche, Skouteris, Vazart, Balucani, Ceccarelli, Lefloch MNRAS 2015, in press

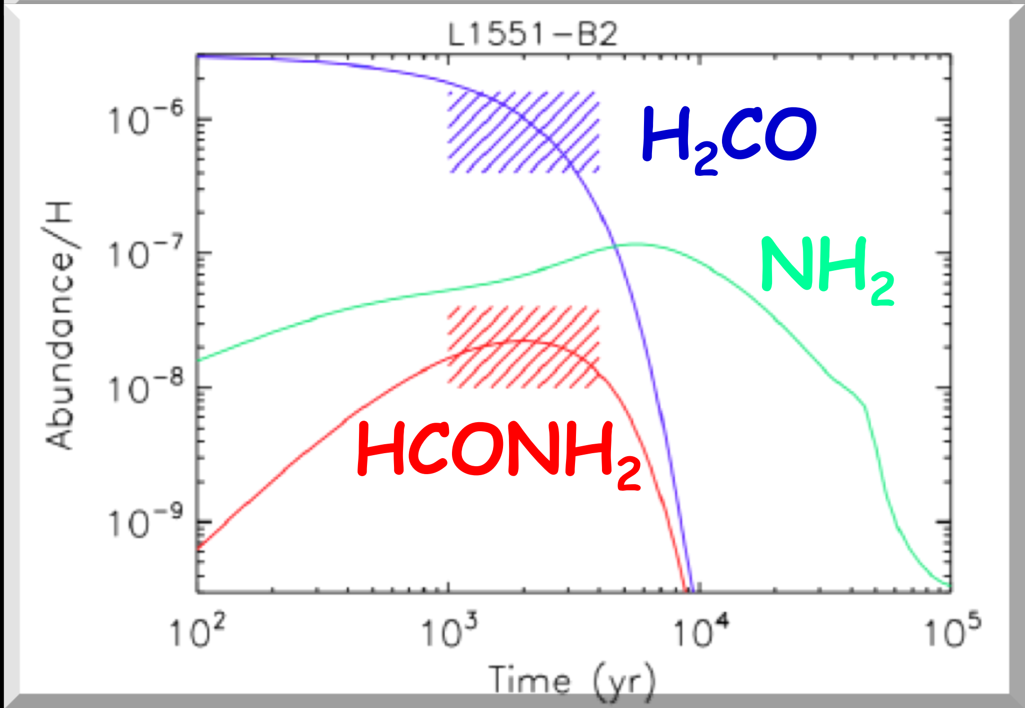


Rate coefficient as a function of T (10-300 K): $\alpha = 2.6\times10^{-12}$ cm^3 s^{-1}, β = -2.1, γ = 26.9



Barone, Latouche, Skouteris, Vazart, Balucani, Ceccarelli, Lefloch
MNRAS 2015, in press





the proposed mechanism can well reproduce the abundances of formamide observed in two very different interstellar objects: the cold envelope of the Sun-like protostar IRAS16293-2422 and the molecular shock L1151-B2

there is no need to invoke grain-surface chemistry to explain the presence of formamide provided that its precursors, NH_2 and H_2CO, are available in the gas-phase

Barone, Latouche, Skouteris, Vazart, Balucani, Ceccarelli, Lefloch
MNRAS 2015, in press

Summary

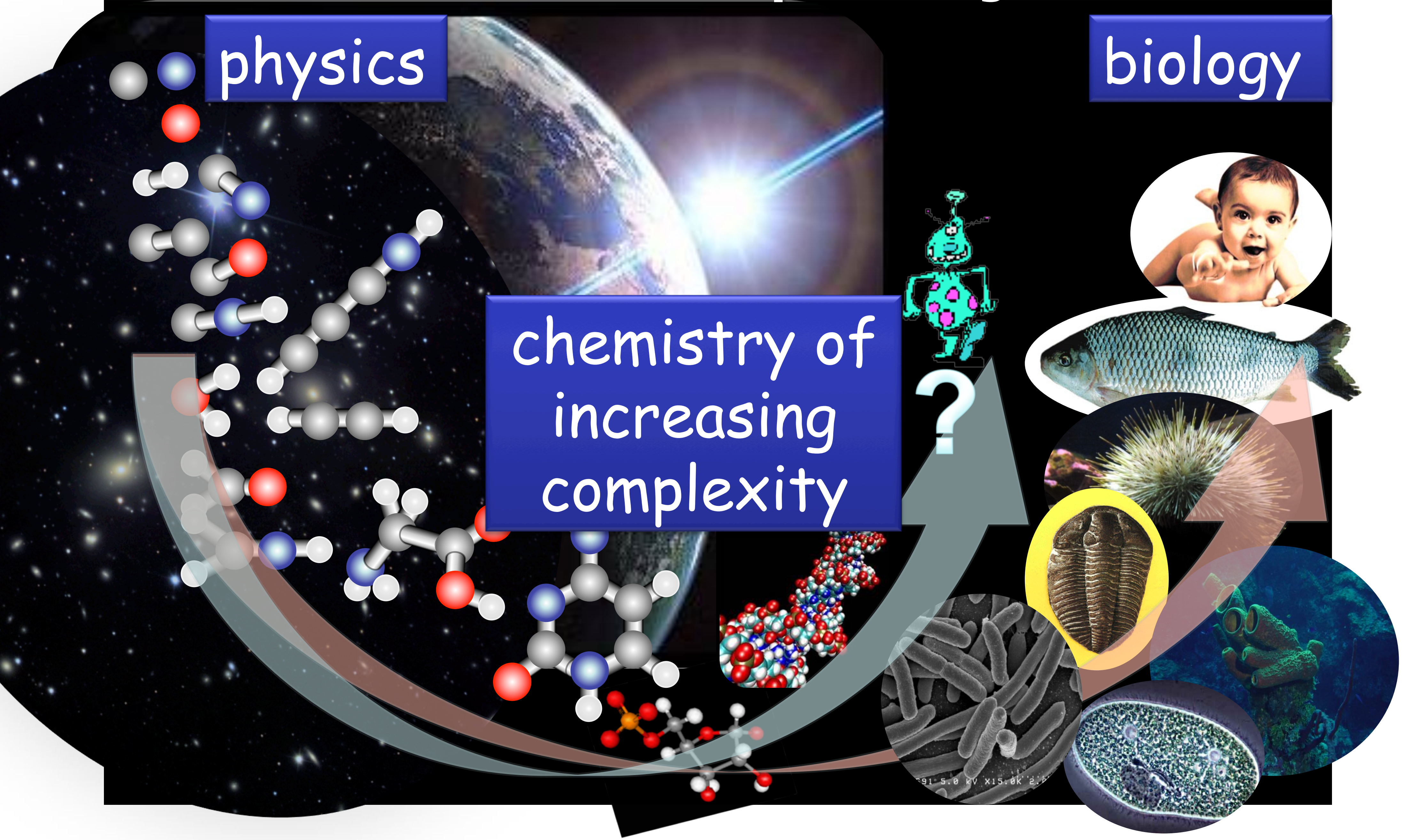
1) Gas phase reactions are major actors in the formation of relatively complex organic molecules in the cold objects of the interstellar medium (methoxy radical, dimethylether, methyl formate, formamide)

This challenges the exclusive role of grain surface chemistry and favours a combined grain-gas chemistry

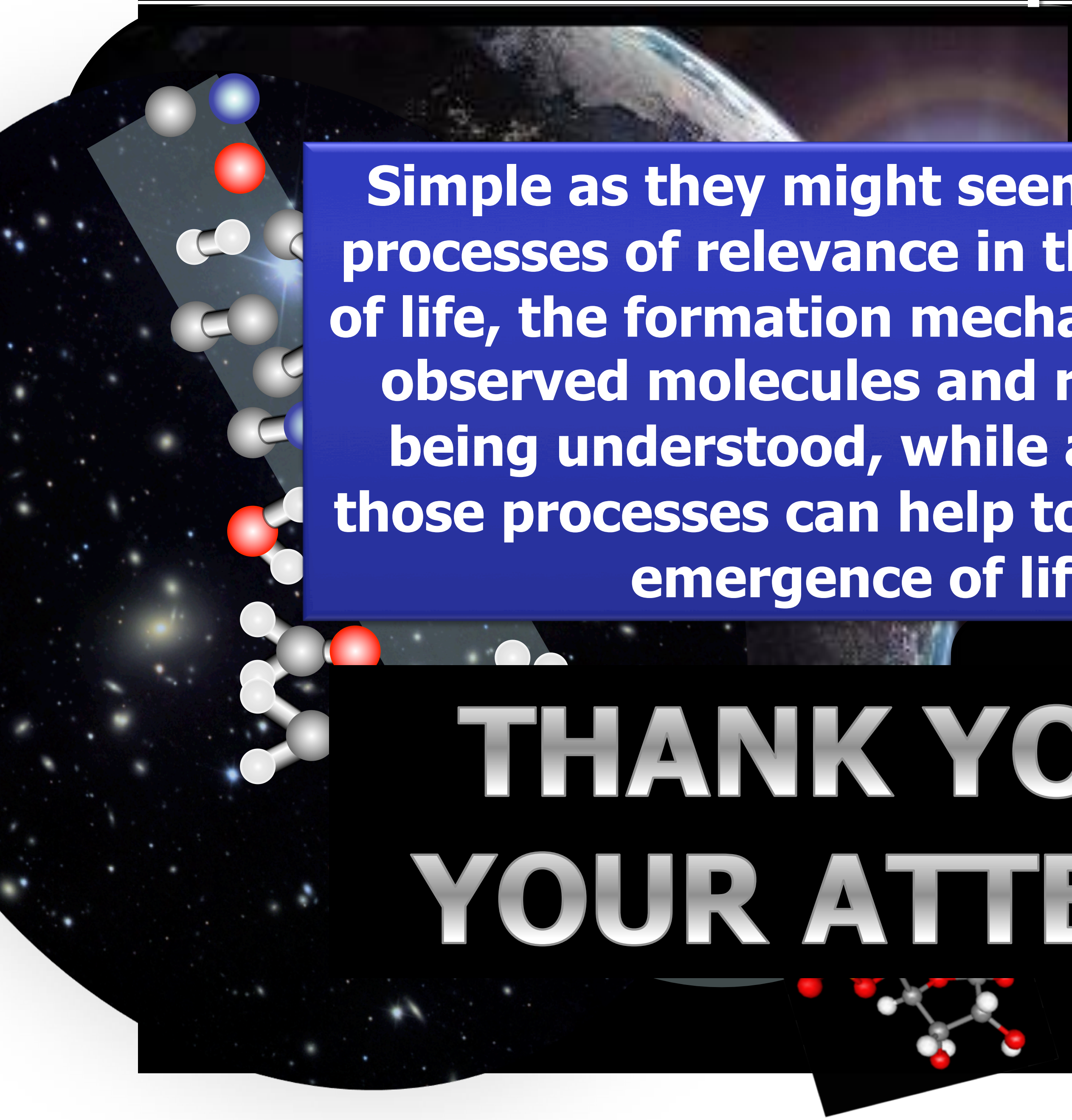
2) Hydrogenation of simple molecules (CO, C_2, HCN ➲ CH_3OH, C_2H_6, CH_3NH_2) is still the realm of grain surface chemistry, but molecular complexity can be achieved also in gas phase reactions leading to or involving unsaturated species

3) More work in progress. Other examples: cyanomethanimine formation or methanimine dimerization (see the oral contributions by Fanny Vazart and Marzio Rosi)

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



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



The aggregation of H, O, N, C (and other elements) atoms

ng

n

ies in the harsh chemical

tellar

phase

the

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.

THANK YOU FOR YOUR ATTENTION

The 50 molecules/ions detected in comets

CH CH^+ NH CH_4 NH_2 NH_3 OH OH^+ H_2O
H_2O^+ NH_4^+ HDO C_2 $^{12}C^{13}C$ ^{13}CN C_2H_2 CN CN^+
HCN HNC CO CO^+ DCN $H^{13}CN$ N_2^+ HCO
HCO^+ CH_3CH_3 H_2CO CH_3OH HS^+ H_2S H_2S^+
C_3 CH_3CN HNCO $HNCO^-$ CH_3CHO CO_2 CO_2^+
CS NH_2CHO H_2CS HCOOH NS HC_3N
$HCOOCH_3$ OCS S_2 SO_2

from www.astrochymist.org

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