Astronomical Complex Organic Molecules (ACOMs) in Sun-type star forming regions

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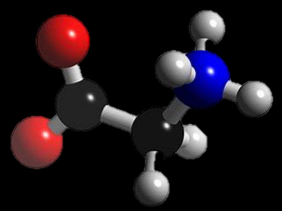
With billions thanks to:
N.Balucani, P.Caselli, C.Codella, F.Fontani, A.Jaber, C.Kahane, B.Lefloch, A. Lopez-Sepulcre, Y.Oka,L.Podio, A.Rimola, N.Sakai, V.Taquet, P.Ugliengo, C.Vastel, S.Viti, S.Yamamoto

Note: They are here at KITP Cold Universe

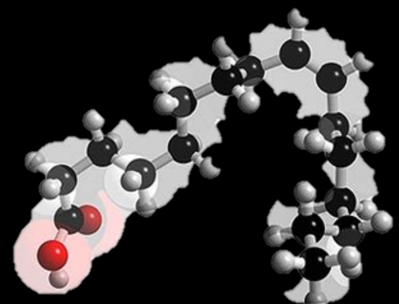
CONTEXT

1- Life on Earth & organic chemistry

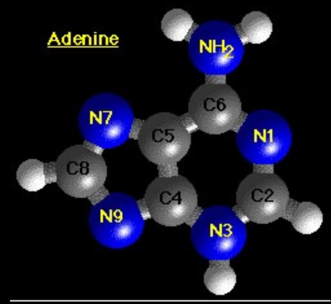
All living organisms, from microbes to men, are made up of the same basic components: amino acids, fatty acids, alcohols, and nitrogenous bases, etc. We are talking of about 50 small molecules of less than 100 atoms of **carbon**, with hydrogen, oxygen, nitrogen and other elements in smaller quantities.



GLYCINE



PALMITOLEIC ACID



LIFE ON EARTH IS BASED ON ORGANIC CHEMISTRY

CONTEXT
2- ISM largest detected molecules

It is not by chance that the longest molecules detected in the ISM are all carbon chains!

Actually, all molecules with more than 5 atoms contains C atoms.

6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	$c\text{-}C_6H_6$ *	$HC_{11}N$
$l\text{-}H_2C_4$	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	$n\text{-}C_3H_7CN$	C_{60} *
C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	$i\text{-}C_3H_7CN$ 2014	C_{70} *
CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$		
CH_3NC	CH_3CHO	C_6H_2	HC_7N				
CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CH_3SH	$c\text{-}C_2H_4O$	$l\text{-}HC_6H$ *	$CH_3C(O)NH_2$				
HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	C_8H^-				
HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
NH_2CHO		H_2NCH_2CN	CH_3CH_2SH (?)				
C_5N		CH_3CHNH					
$l\text{-}HC_4H$ *							
$l\text{-}HC_4N$							
$c\text{-}H_2C_3O$							
H_2CCNH (?)							
C_5N^-							
$HNCHCN$							

CONTEXT
3- Organic chemistry in space & life

C. De Duve,
1997 Nobel laureate

The building block of life form naturally in our Galaxy and, most likely, also elsewhere in the Cosmos.
The chemical seeds of life are universal.
("Singularities. Landmarks on the Pathways of life", Cambridge University Press 2005)

Life is an obligatory manifestation of matter, written into the fabric of the universe, and that there must be many sites of life, perhaps even intelligent life sometimes, in many parts of our Galaxy and in others.
(Phyl.Trans.RoyalSoc. 2011).

CONTEXT
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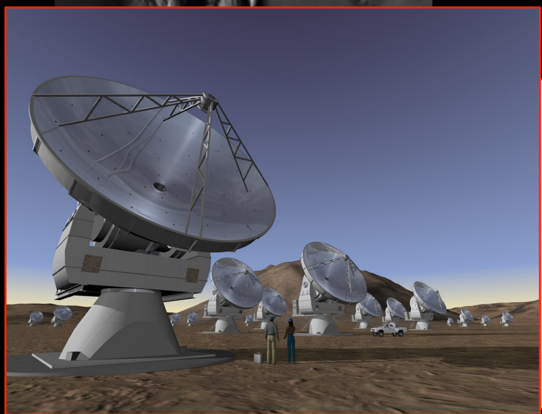
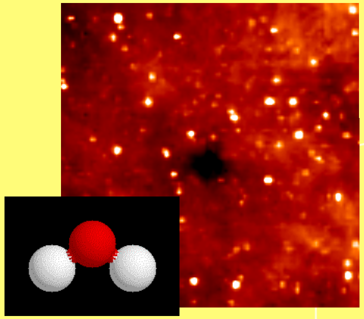


ASTRONOMER JOBS:

1. SEARCH FOR THE SEEDS
2. UNDERSTAND WHAT COMPLEXITY THEY CAN GROWTH TO IN SPACE

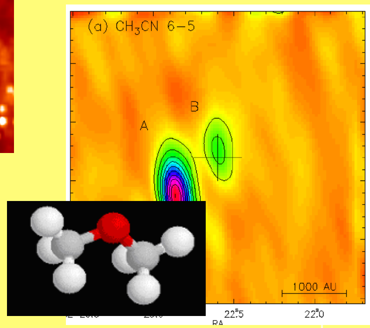
FROM A DIFFUSE CLOUD TO A PLANETARY SYSTEM
FROM ATOMS & SIMPLE MOLECULES TO LIFE

(adapted from Caselli & Ceccarelli 2012, A&ARev)



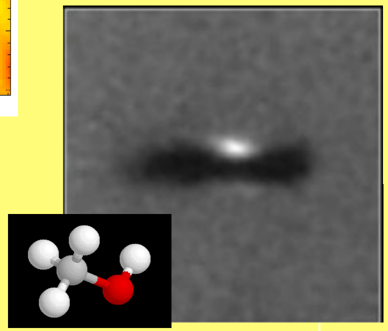
1- PRE-STELLAR PHASE: cold and dense gas

FORMATION OF SIMPLE/COMPLEX MOLECULES

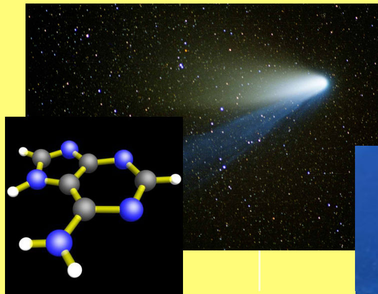


2- PROTOSTELLAR PHASE: collapsing, warm dense gas

SUBLIMATION/FORMATION OF COMPLEX MOLECULES



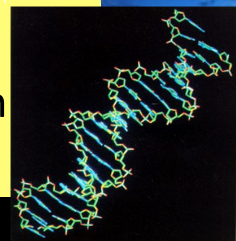
3- PROTOPLANETARY DISK PHASE:
cold and warm dense gas
SIMPLE & COMPLEX MOLECULES



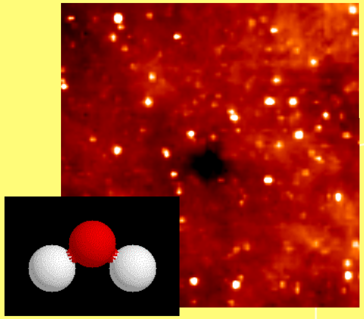
4- PLANETESIMAL FORMATION : grains agglomeration

STORAGE/REPROCESSING OF GRAIN MANTLE ICES

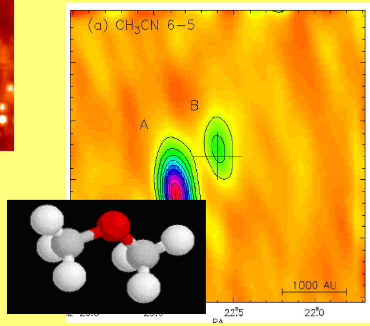
5- PLANET FORMATION AND THE “COMET/ASTEROID RAIN”:
planet migration, small bodies scattering; Earth oceans formation
CONSERVATION/DELIVERY OF OLD MOLECULES + LIFE?



FOCUS ON THE FIRST TWO PHASES, WHERE THE RULES OF THE GAME ARE SET



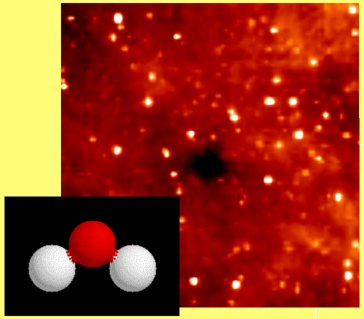
1- PRE-STELLAR PHASE: cold and dense gas
FORMATION OF SIMPLE/COMPLEX MOLECULES



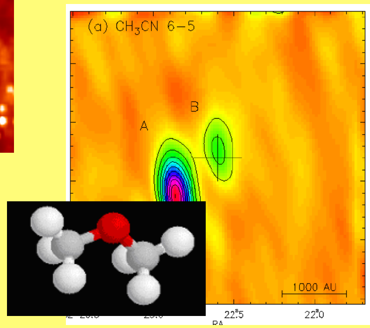
2- PROTOSTELLAR PHASE: collapsing, warm dense gas
SUBLIMATION/FORMATION OF COMPLEX MOLECULES

1- The same basic conditions applies to the other phases (mutata mutandis), but in these two phases processes are likely easier to characterize;
2- Once the processes at work are understood, we can extrapolate to molecules that we will never detect in the ISM;
3- In these phases, the “seeds” for the molecular complexity growth are planted.

FOCUS ON THE FIRST TWO PHASES, WHERE THE RULES OF THE GAME ARE SET



1- PRE-STELLAR PHASE: cold and dense gas
FORMATION OF SIMPLE/COMPLEX MOLECULES



2- PROTOSTELLAR PHASE: collapsing, warm dense gas
SUBLIMATION/FORMATION OF COMPLEX MOLECULES

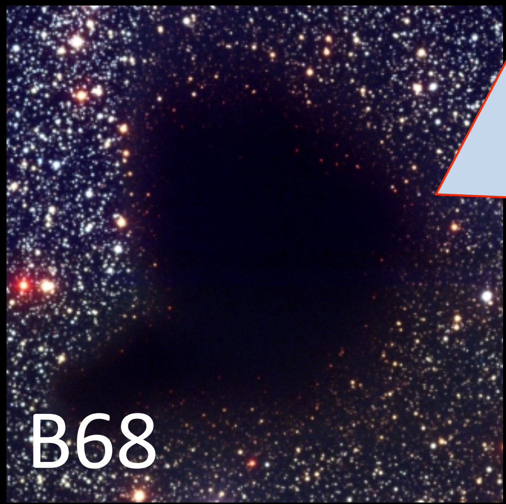
→ FOCUS ON ACOMs (Astronomical Complex Organic Molecules)

1. PRESTELLAR CORES (PSC)

BLACK SPOTS IN OPTICAL PICTURES

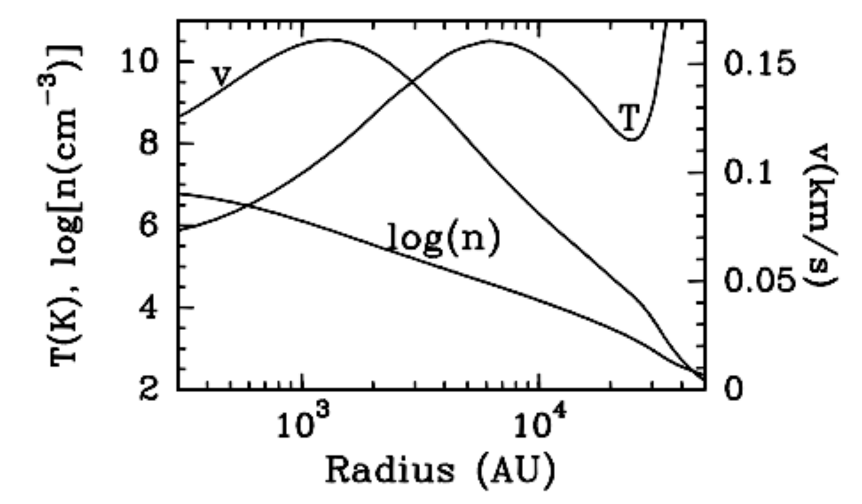
PSC are dense and cold condensations in molecular clouds:

PSC ARE THE SEEDS FROM WHICH STARS ARE BORN



PRE-STELLAR CORES in a nutshell

THE CENTERS OF PSC ARE COLD (≤10K) AND DENSE (≥10^5cm^{-3})



Caselli et al. 2012

MOLECULES, e.g. CO FREEZE OUT ONTO THE DUST GRAINS FORMING ICED MOLECULAR MANTLES

(reviews by Ceccarelli, Caselli, Herbst et al. 2005, PP5; Bergin & Tafalla 2006; Caselli & Ceccarelli 2012)

MANTLE COMPOSITION: H_2O, CO, CO_2, NH_3, CH_3OH

HYDROGENATON ON THE GRAIN SURFACES

→ LABORATORY EXPERIMENTS + **THEORY +** ASTROMODELS

Example of the methanol formation on the grain surfaces

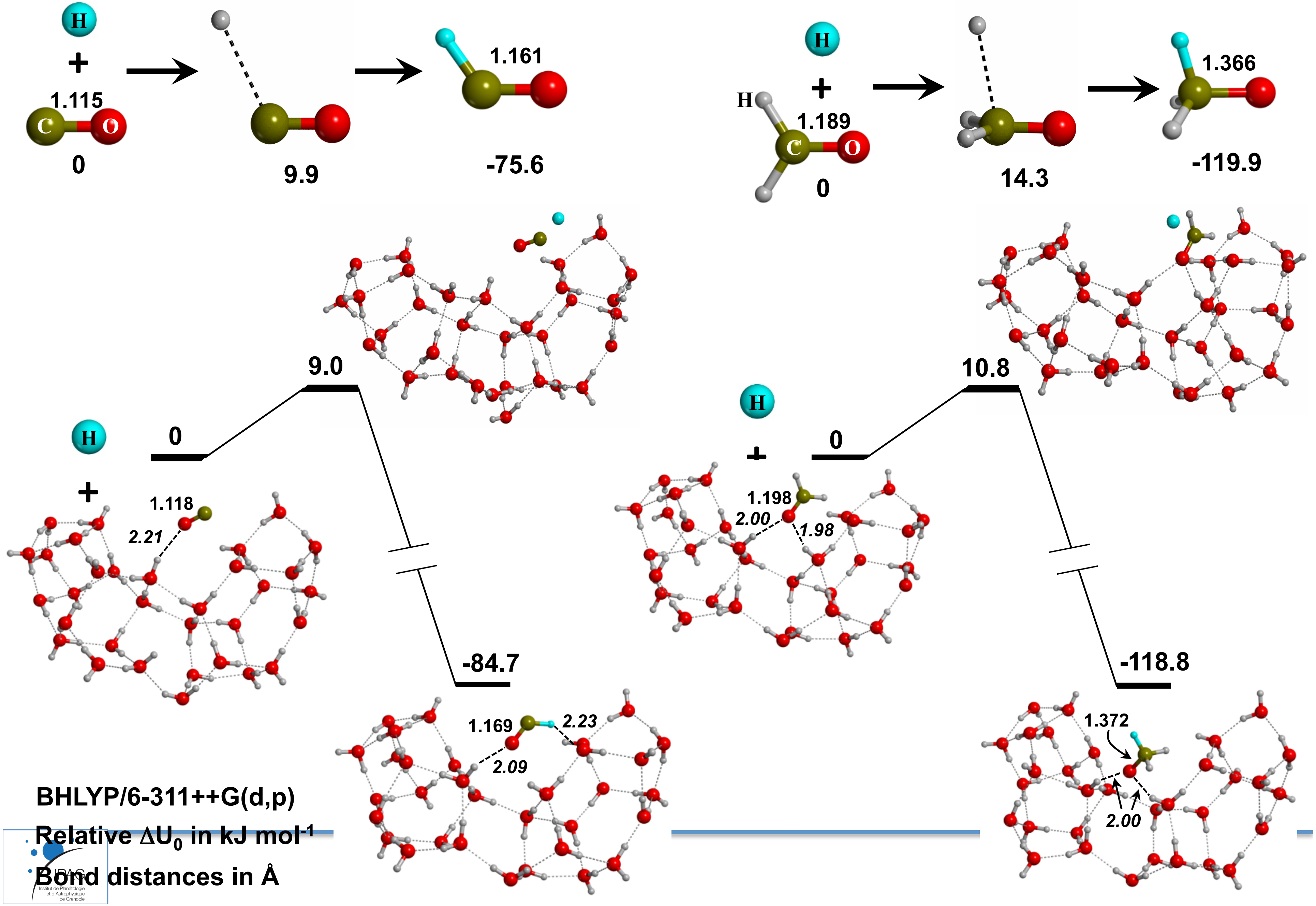
Rimola et al. 2014

HYDROGENATON ON THE GRAIN SURFACES

➔ LABORATORY EXPERIMENTS + **THEORY +** ASTROMODELS

Example of the methanol formation on the grain surfaces

Interstellar H_2CO and CH_3OH Formation



BHLYP/6-311++G(d,p)

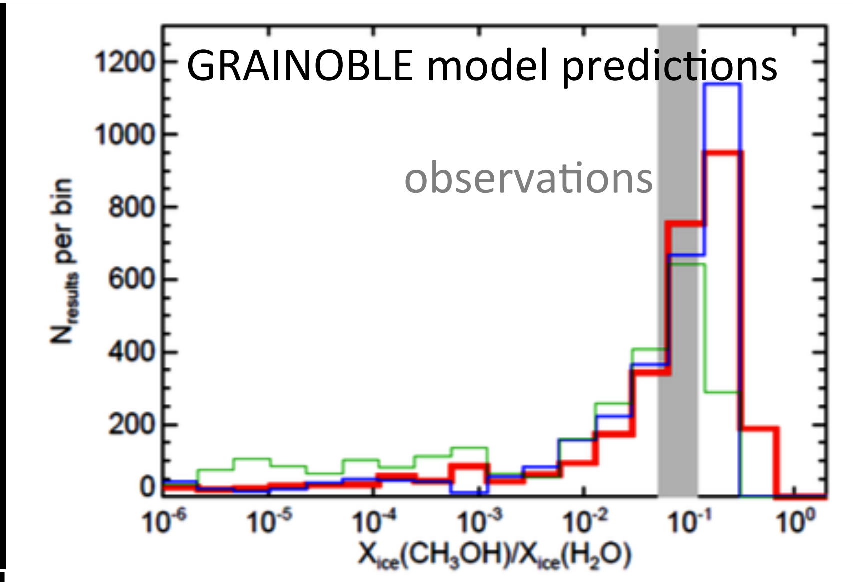
Relative ΔU_0 in kJ mol^{-1}

Bond distances in Å

HYDROGENATON ON THE GRAIN SURFACES

➔ LABORATORY EXPERIMENTS + **THEORY +** ASTROMODELS

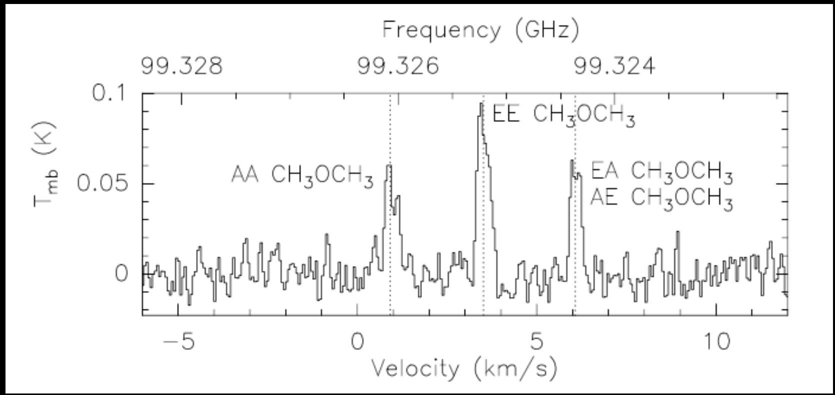
Example of the methanol formation on the grain surfaces



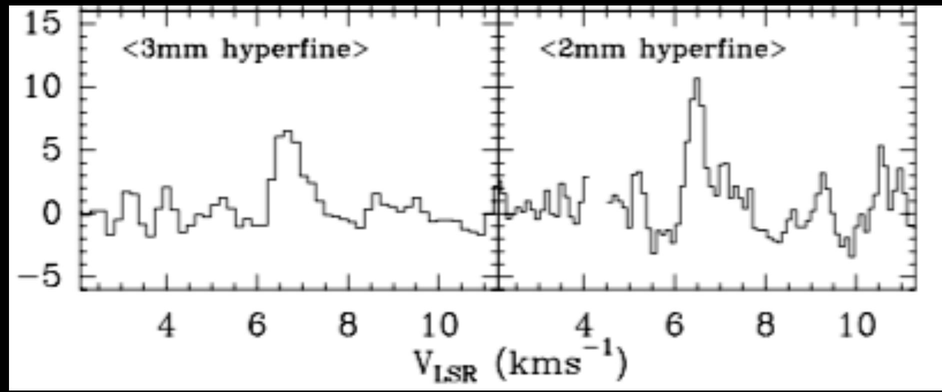
Rimola et al. 2014

2012-2014: DISCOVERY OF ACOMs in PSCs

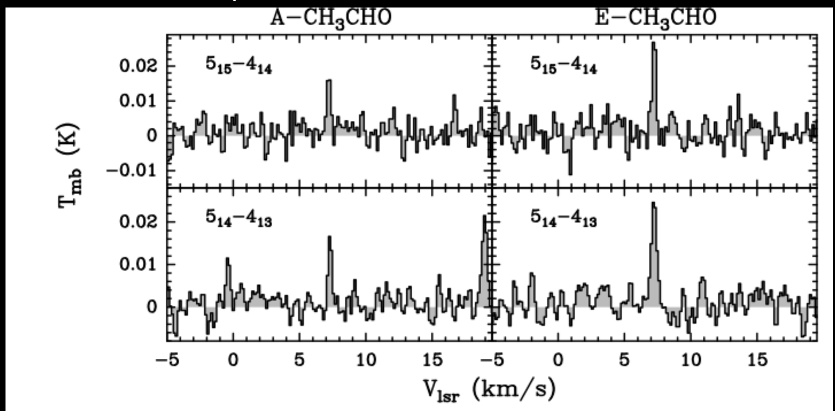
Dimethyl ether & methyl formate in L1689B; Bacmann et al. 2012

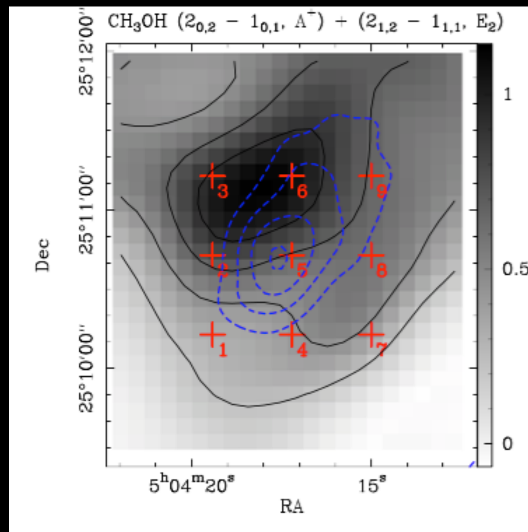


Methoxy in B1-b; Cernicharo et al. 2012



Acetaldehyde in L1544; Vastel et al. 2014





Methanol in L1544; Bizzocchi et al. 2014

3. WHAT IS THE ACOMs ABUNDANCE?

SPECIES	ABUNDANCE (wrt H_2)		
	L1544	**L1689B***	**B1-b***
CH_3OH	$\approx 6x10^{-9}$		$\approx 3x10^{-9}$
CH_3CHO	$\approx 1x10^{-10}$	$\approx 10^{-10}$	
HCOOH	$\approx 1x10^{-10}$		
H_2CCO	$\approx 1x10^{-9}$	$\approx 10^{-10}$	
CH_3CCH	$\approx 5x10^{-9}$		
CH_3OCH_3	$\leq 2x10^{-10}$	$\approx 10^{-10}$	$\approx 1x10^{-11}$
$HCOOCH_3$	$\leq 2x10^{-9}$	$\approx 10^{-10}$	$\approx 1x10^{-11}$
CH_3O	$\leq 2x10^{-10}$		$\approx 2x10^{-12}$

*Note: the abundances are computed assuming that the emission arises from the whole core

3. WHAT IS THE ACOMs ABUNDANCE?

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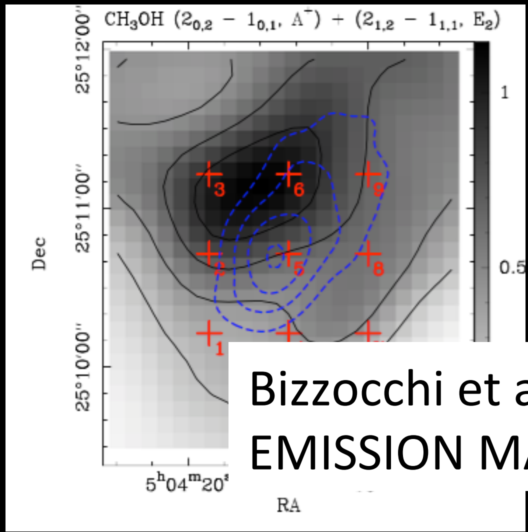
CH_3OH	≈$6x10^{-9}$		≈$3x10^{-9}$
CH_3CHO	≈$1x10^{-10}$	≈10^{-10}	
HCOOH	≈$1x10^{-10}$	[illegible]	
H_2CCO	[illegible]	≈10^{-10}	
CH_3CCH	[illegible]	[illegible]	
CH_3OCH_3	≤[illegible]	≈10^{-10}	≈$1x10^{-11}$
$HCOOCH_3$	[illegible]	≈10^{-10}	≈$1x10^{-11}$

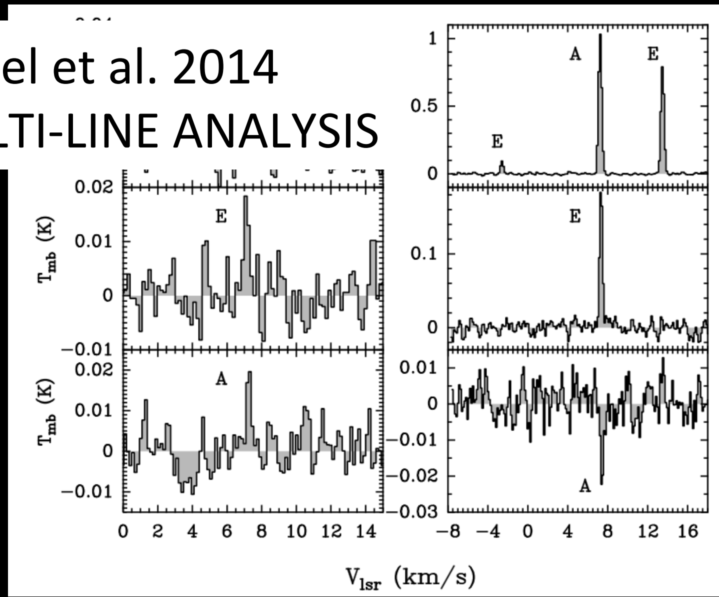
→ PROBLEM

1) HOW THOSE LARGER MOLECULES ARE FORMED??? (no tunnel effet! No diffusion of heavy elements at 10K!)
2) WHY ARE THEY IN THE GAS PHASE???

1. WHERE DOES THE ACOMs EMISSION COME FROM?
ANALYSIS OF METHANOL IN L1544



Bizzocchi et al. 2014
EMISSION MAP

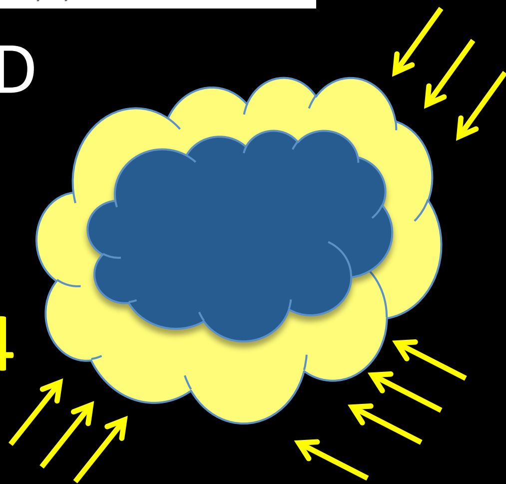


Vastel et al. 2014
MULTI-LINE ANALYSIS

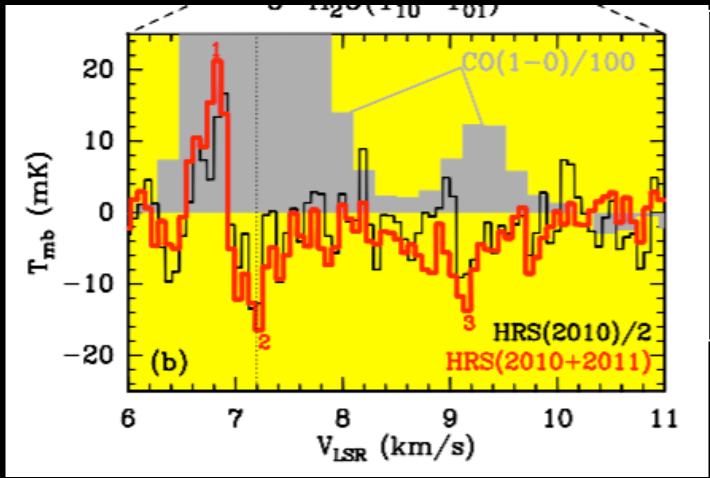
METHANOL EMISSION FROM AN EXTENDED (>30'') REGION WHERE $n_H \approx 3 \times 10^4 cm^{-3}$ and T≈10K

➔ FROM THE BORDER OF THE L1544

CONDENSATION



2. WHY ARE ACOMs IN THE GAS PHASE?



WATER IS ABUNDANT (≈10^{-6}) AT THE BORDER OF THE L1544 CONDENSATION

→ PHOTODESORBED BY THE IS FUV PHOTONS FROM THE ICE MANTLES?

Caselli et al. 2012; Quinard et al. 2015

a) IS METHANOL PHOTODESORBED FROM THE ICES ?

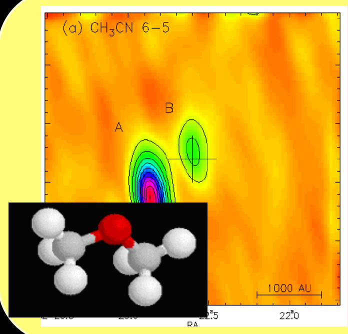
experiments (Minissale et al. 2016) suggest <1% (when photodesorbed methanol is broken in parts…)

b) IS IT FORMED IN THE GAS FROM OTHER PHOTODESORBED SPECIES?

no known reactions

Vastel et al. 2014

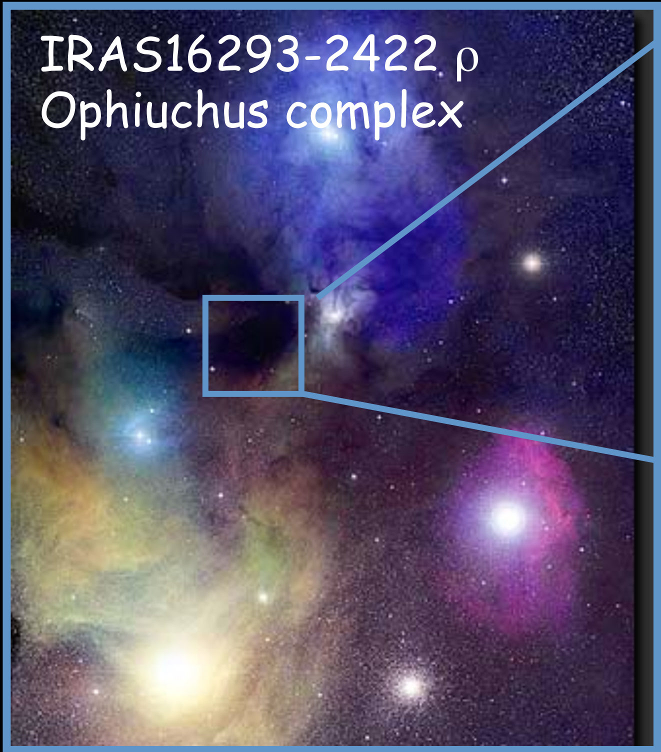
CLASS 0 PROTOSTARS AND HOT CORINOS:

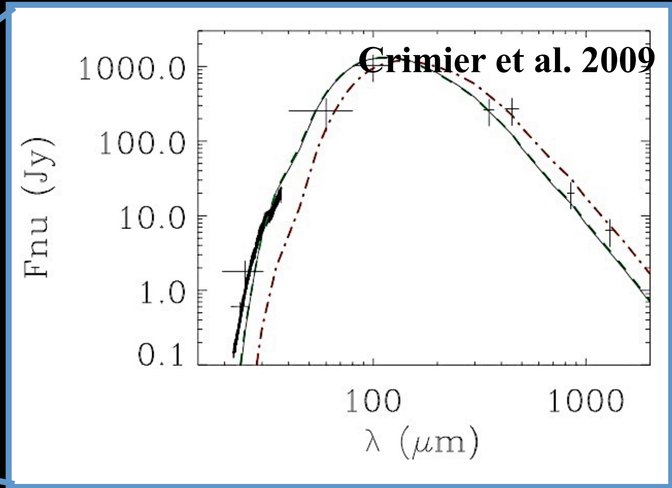


2- PROTOSTELLAR PHASE: collapsing, warm dense gas

FORMATION OF COMPLEX MOLECULES

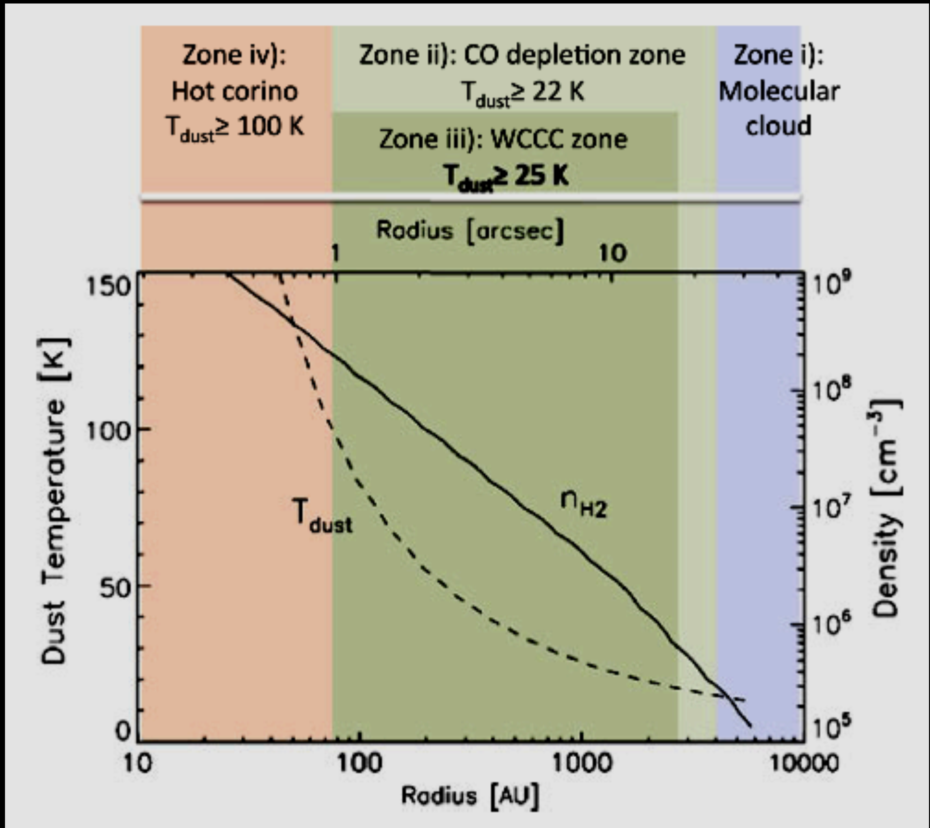
CLASS 0 PROTOSTARS AND HOT CORINOS: the retail shops of ACOMS





CLASS 0 ARE COLD (<30K) SOURCES OF FEW M_O, EMITTING MOSTLY IN THE mm/submm

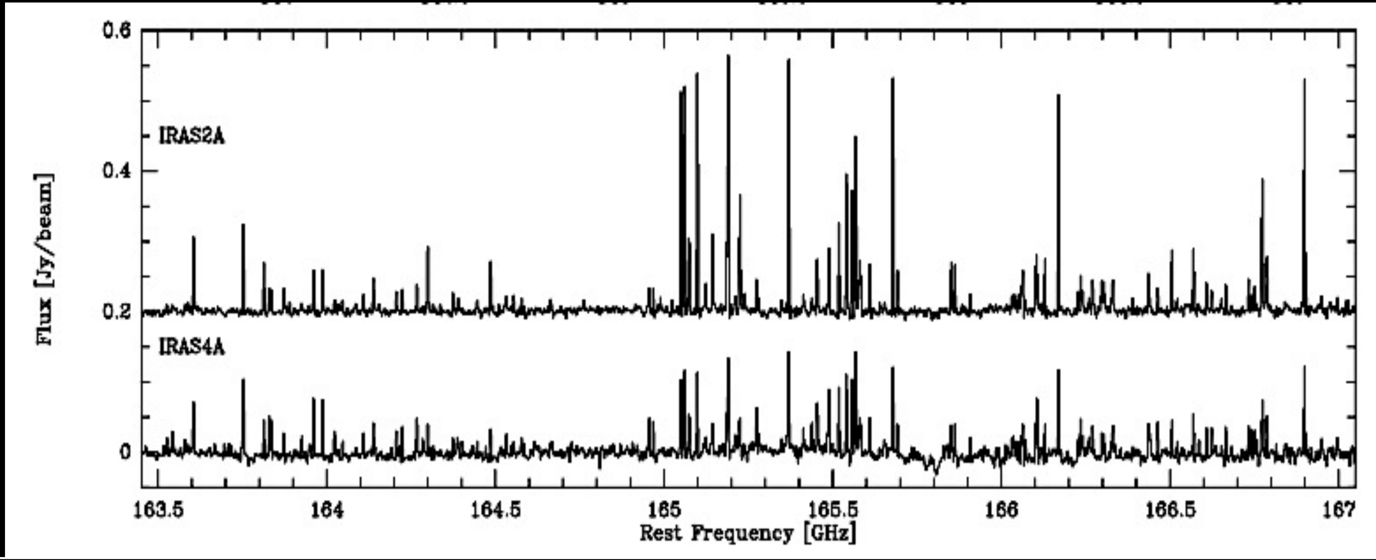
CLASS 0 PROTOSTARS AND HOT CORINOS: the retail shops of ACOMS



Caselli & Ceccarelli 2012

HOT CORINO: HOT (>100K) AND DENSE (10^7cm^{-3}) GAS
CHEMISTRY DOMINATED BY THE SUBLIMATION OF THE GRAIN MANTLES => THE PREVIOUS OBJECT HISTORY

2003: DISCOVERY OF ACOMs IN HOT CORINOS



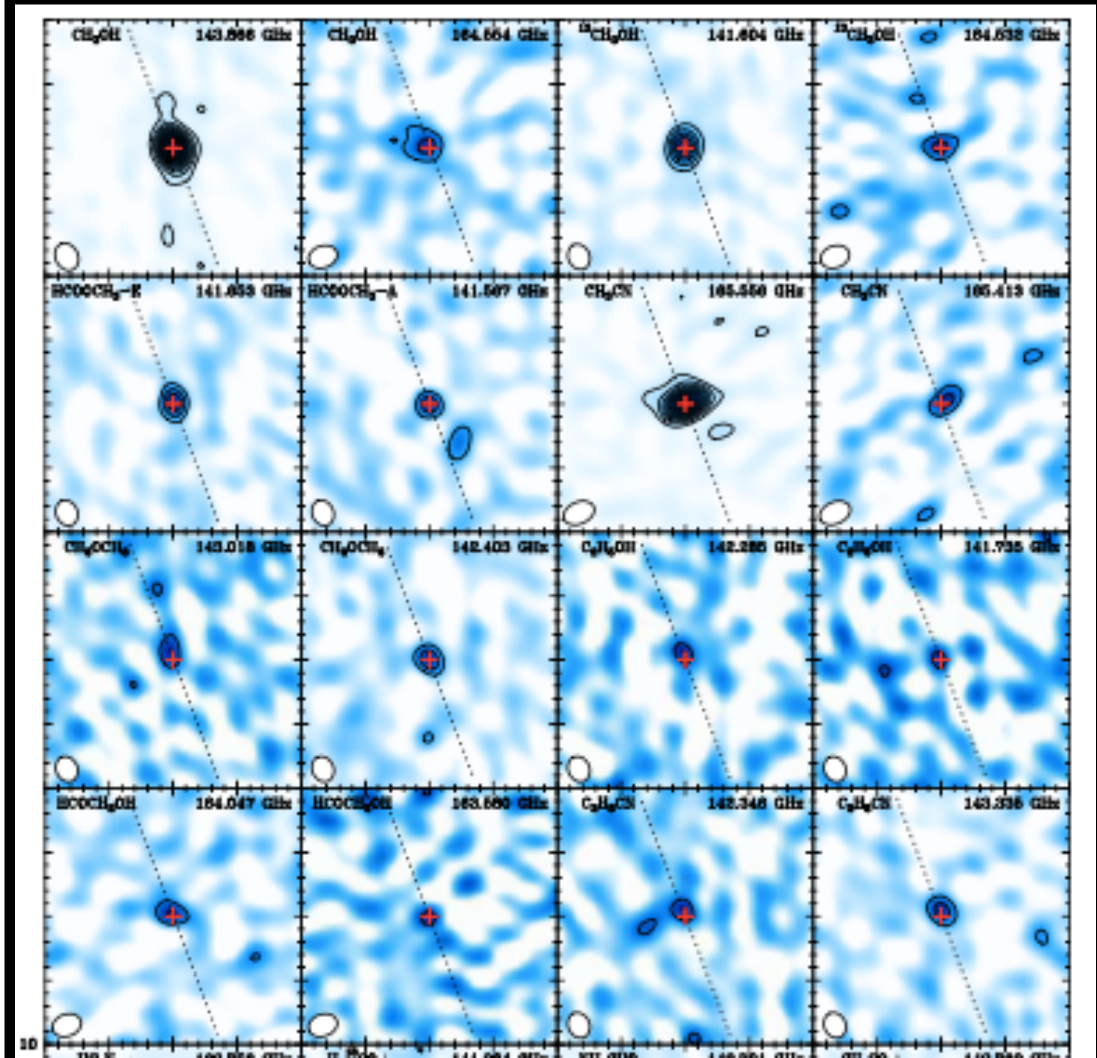
Taquet et al. 2015

DETECTED ACOMs: METHYL FORMATE, DIMETHYL ETHER, FORMIC ACID, METHYL CYANIDE, ETHYL CYANIDE, GLYCOLALDEHYDE, FORMAMIDE

(Cazaux et al. 2003, Bottinelli et al. 2004, 2006; Jorgensen et al. 2012; Kahane et al. 2013; Coutens et al. 2015; Taquet et al. 2015…)

=> BUT NOTE: ONLY 5 HOT CORINOS KNOWN SO FAR <=

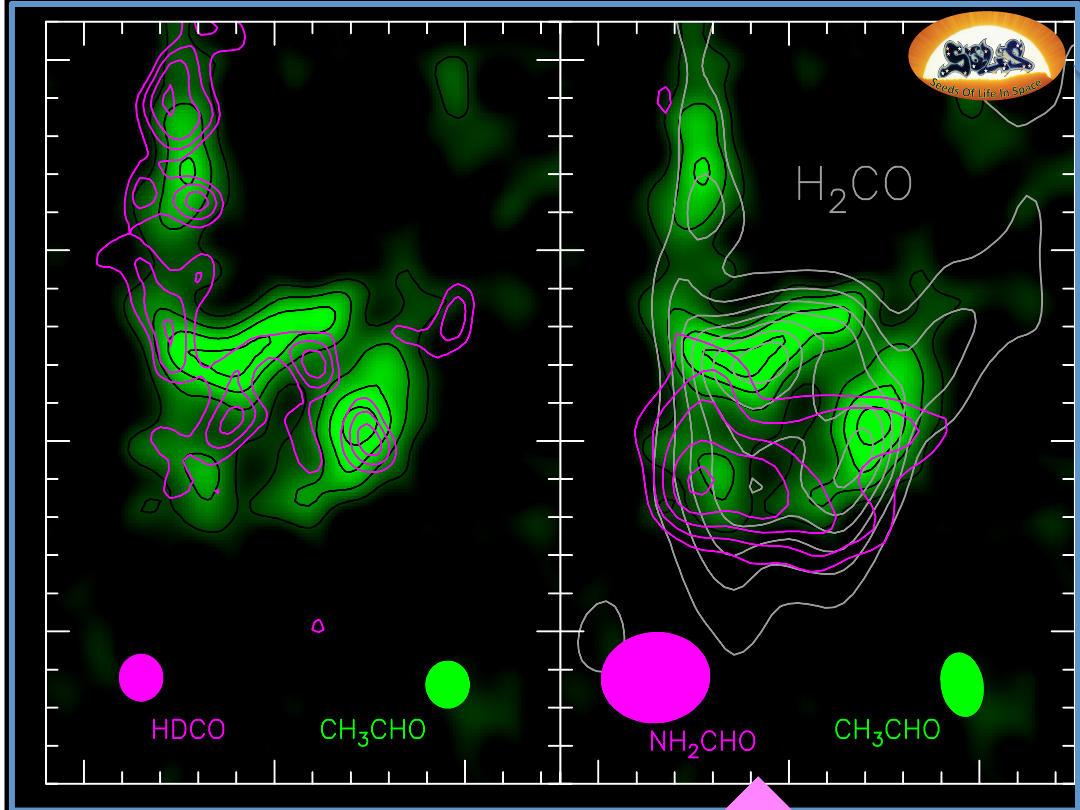
WHERE DOES THE ACOMs EMISSION COME FROM?



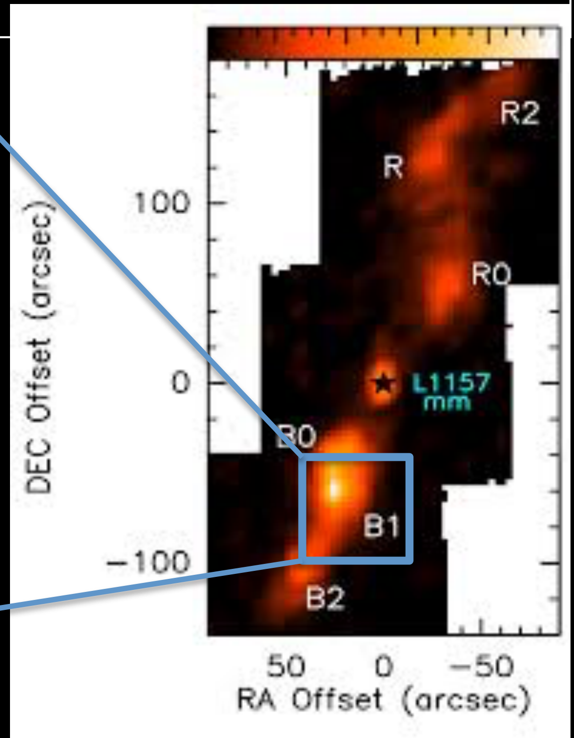
Taquet et al. 2015

DEFINITIVELY FROM THE SMALL (≤ 100AU) HOT CORINO REGION

WHERE DOES THE ACOMs EMISSION COME FROM?



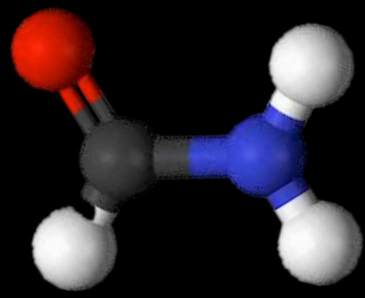
SOMETIMES IN SHOCK SITES



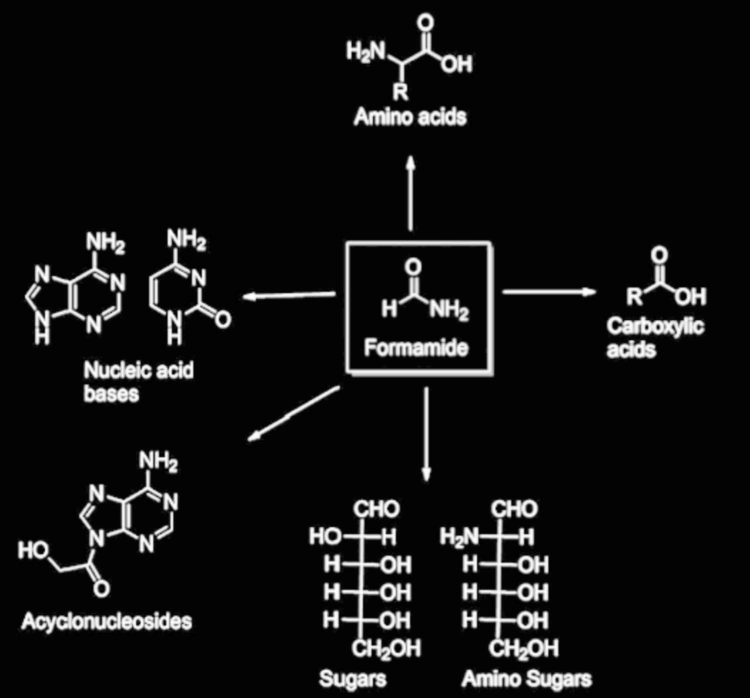
H_2CO, HDCO: Fontani et al. 2015
CH_3CHO: Codella et al. 2015
NH_2CHO: Codella et al. 2016

FORMAMIDE (NH_2CHO)

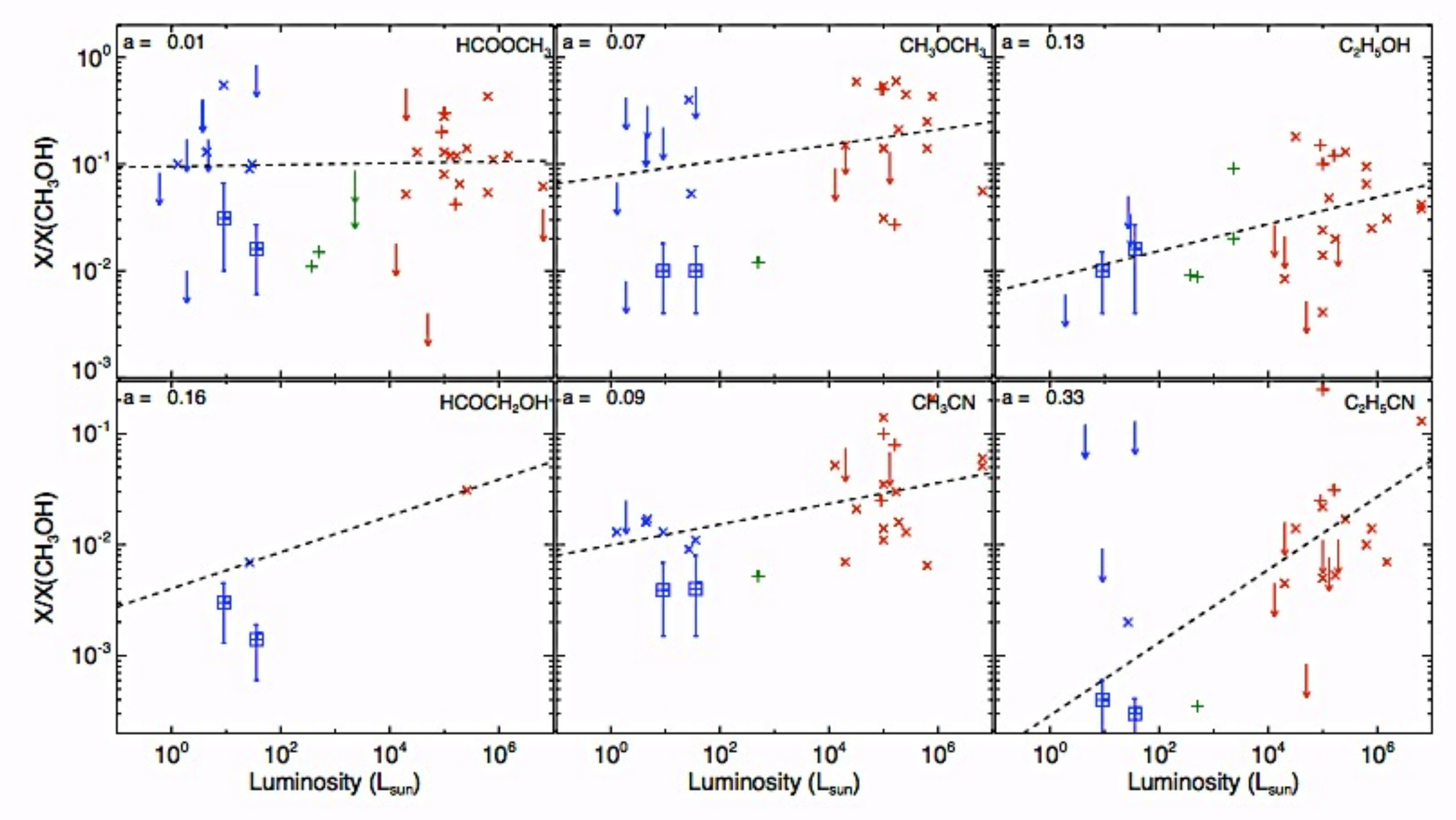
FORMAMIDE (NH_2CHO)
A KEY TO LIFE?



Formamide (NH_2CHO) may have been the starting point for the prebiotic synthesis of both **metabolic and genetic** species (Saladino et al. 2012).



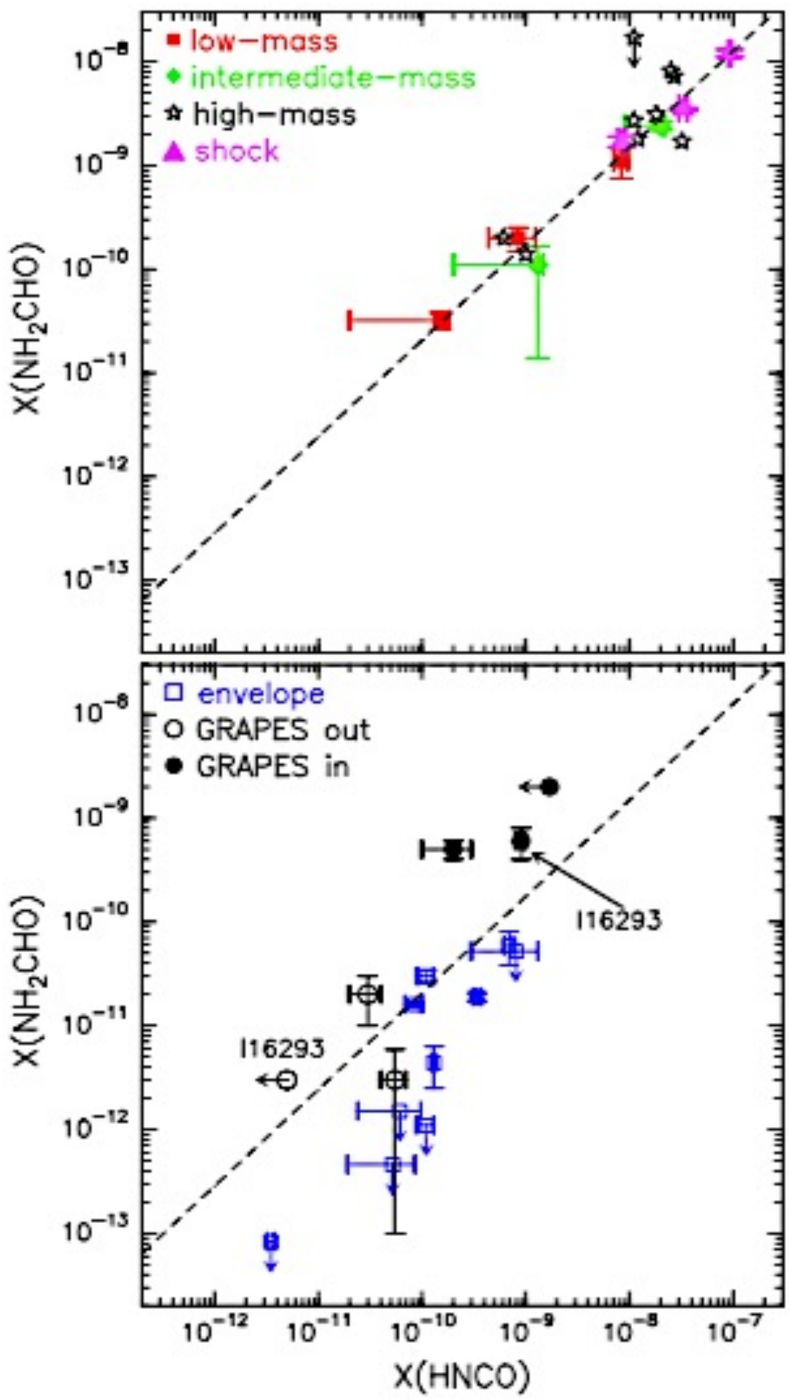
WHAT IS THE ACOMs ABUNDANCE?



A CONSIDERABLE FRACTION (few %) OF GASEOUS CARBON (Taquet et al. 2015; see also Jaber et al. 2014 and Oberg et al. 2014)

CORRELATIONS AMONG ACOMs ABUNDANCES

HELP TO INDIVIDUATE
MOTHER/DAUGHTER OR SISTER SPECIES
➔ THEIR FORMATION MECHANISM

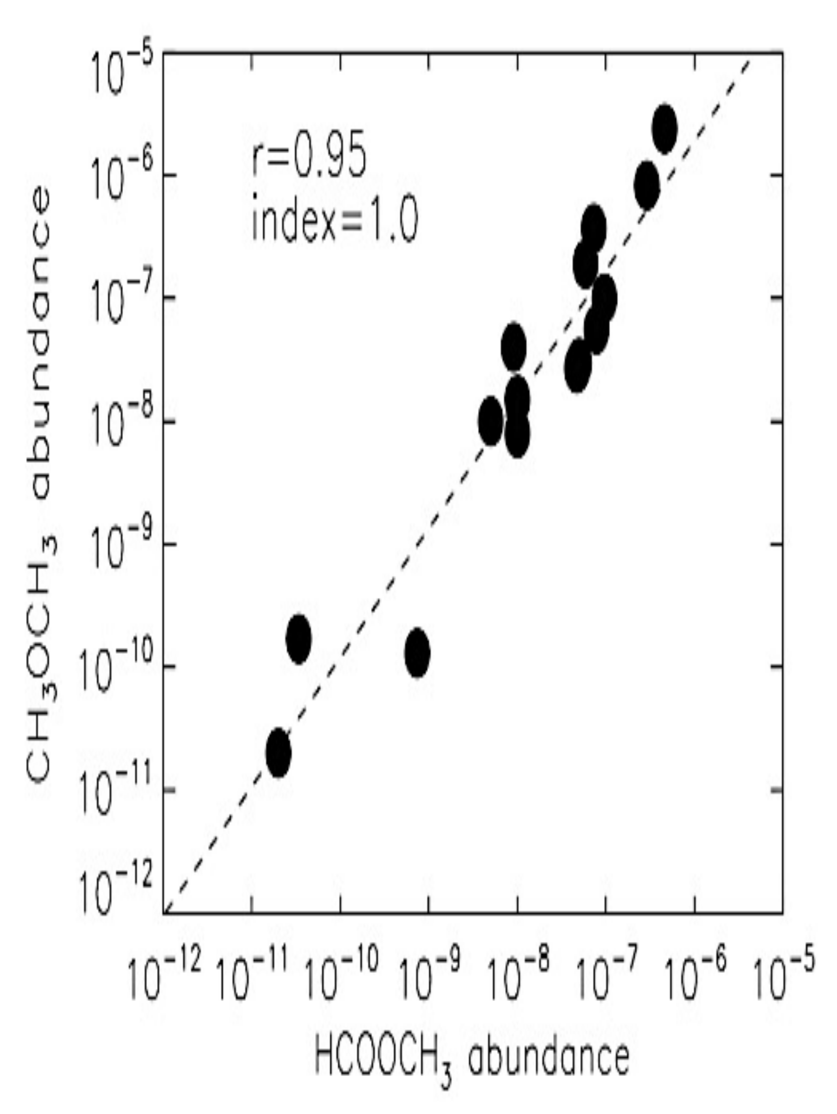


Lopez-Sepulcre et al. 2015

FORMAMIDE
vs
ISOCYANIC ACID

LABORATORY EXPERIMENTS RULE OUT HYDROGENATION OF HCNO → NH_2CHO (Noble et al. 2015)

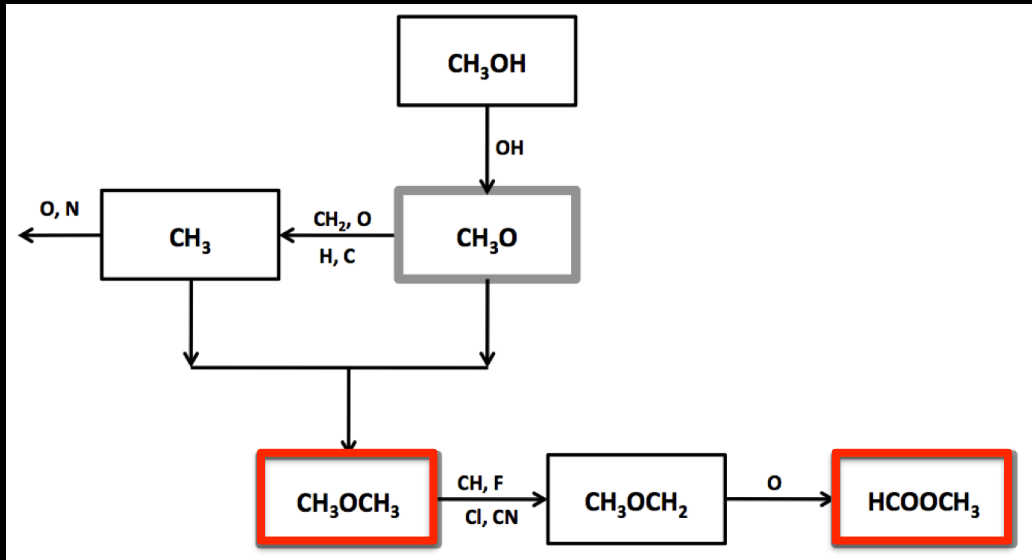
- POSSIBLE GAS PHASE ROUTE $NH_2 + H_2CO$ → NH_2CHO (Barone et al. 2015)



Jaber et al. 2014

METHYL FORMATE
vs
DIMETHYL ETHER

PROPOSED GAS PHASE ROUTE (Balucani et al. 2015)



IN SUMMARY

ACOMs ARE PRESENT IN ENVIRONMENTS WITH TEMPERATURES RANGING FROM 10K TO >100K

HOW ARE ACOMs FORMED?

(and how are they injected into the gas phase?)

HOW ARE ACOMs FORMED?

IN VOGUE UNTIL 2003/5	IN VOGUE UNTIL 2012/3
GAS PHASE reactions in the gas phase, often started by the injection of hydrogenated molecules formed on the grain surfaces	**GRAIN SURFACES** reactions on the grain surfaces between radicals during the warm-up of the dust; radicals are formed in the cold phase

Gas phase:

<u>Step 1</u>	<u>Step 2</u>	<u>Step 3</u>
H_2CO CH_3OH NH_3	ice sublimation	$HCOCH_2OH$ CH_3OCH_3 NH_2CHO

10 K → 100 K

Grain surfaces:

<u>Step 1</u>	<u>Step 2</u>	<u>Step 3</u>
H_2CO CH_3OH NH_3	$HCOCH_2OH$ CH_3OCH_3 NH_2CHO	ice sublimation

10 K → 100 K

TEMPERATURE

IN BOTH SCHEMES MOLECULES ARE THERMALLY DESORBED FROM GRAIN MANTLES at 100K

THE GRAIN SURFACES THEORY

➔ SEVERAL LABORATORY EXPERIMENTS SHOW THE FORMATION OF ACOMs IN FUV ILLUMINATED ICES

QUESTION: ARE THEY APPLICABLE TO THE ISM CONDITIONS?

CRITICAL ASSUMPTIONS IN THE ISM MODELS:

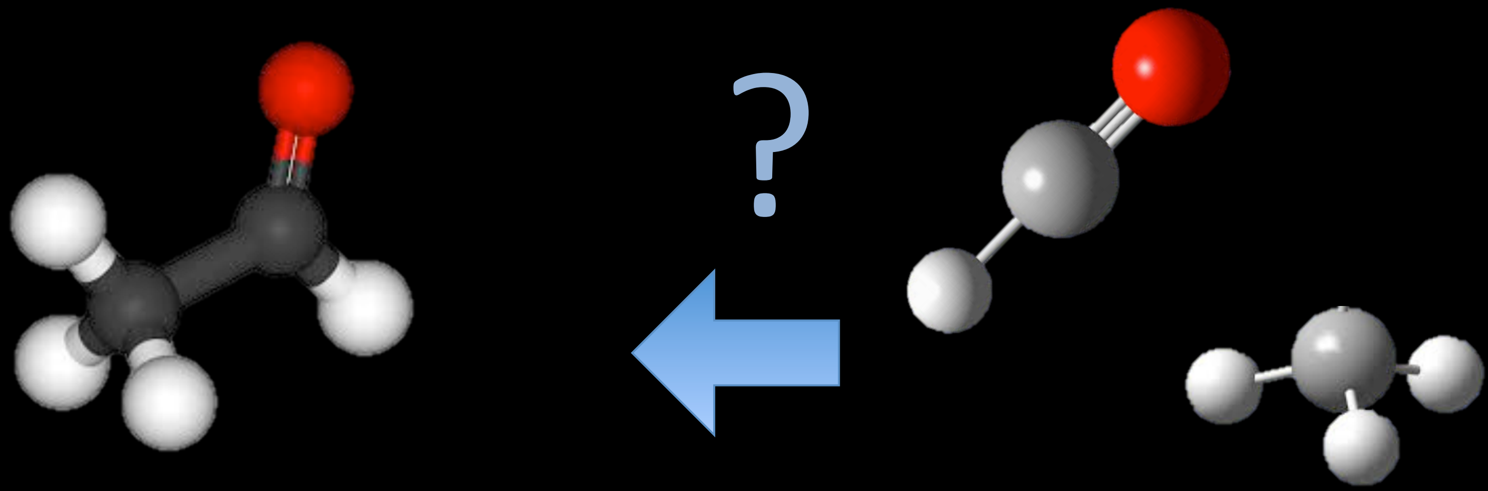
- ⇒ FUV CREATE RADICALS TRAPPED IN THE ICES (current models assume gas-phase production rates)
- ⇒ AT T_{dust}>30K RADICALS HAVE ENOUGH ENERGY TO MOVE AROUND

  ACOMs ARE DETECTED ALSO IN COLD 10K REGIONS
- ⇒ RADICALS COMBINE AND FORM ACOMs

  IS THIS TRUE?

RADICAL S COMBINATION INTO ACOMs

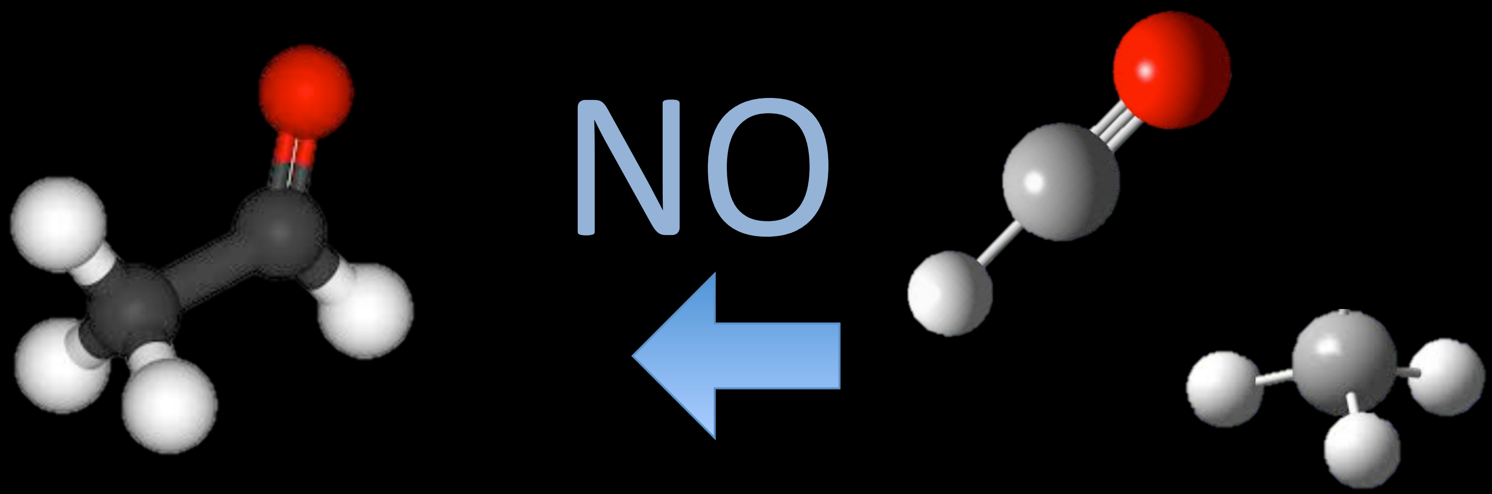
EXAMPLE OF ACETALDEHYDE



➔ LABORATORY EXPERIMENTS + **THEORY**
ARE NECESSARY TO UNDERSTAND WHAT HAPPENS

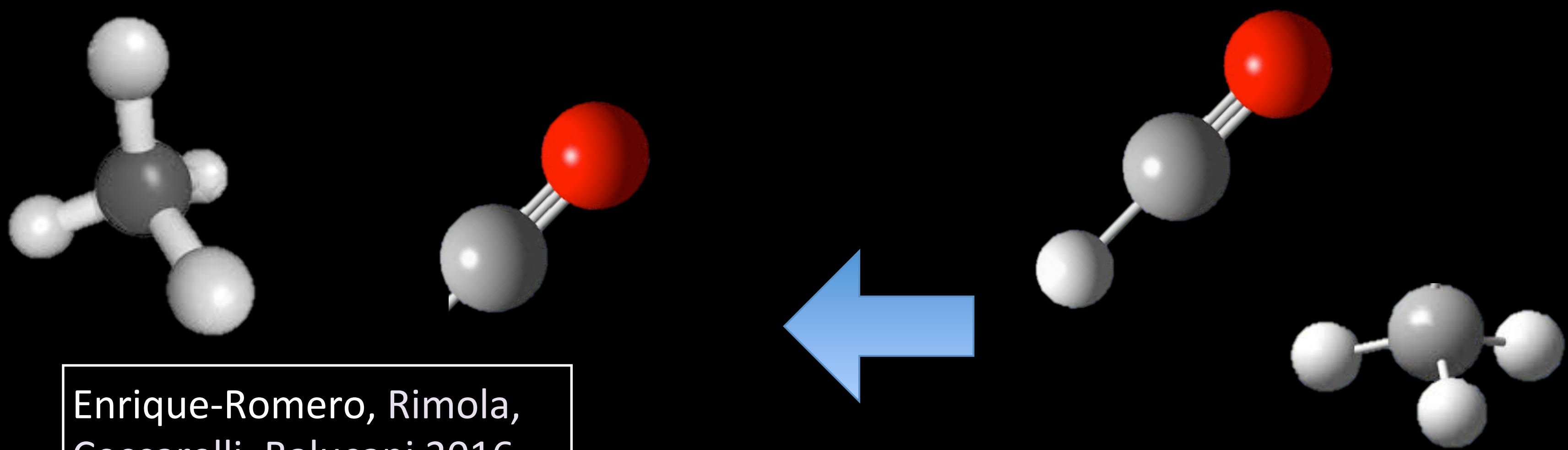
RADICAL S COMBINATION INTO ACOMs

EXAMPLE OF ACETALDEHYDE



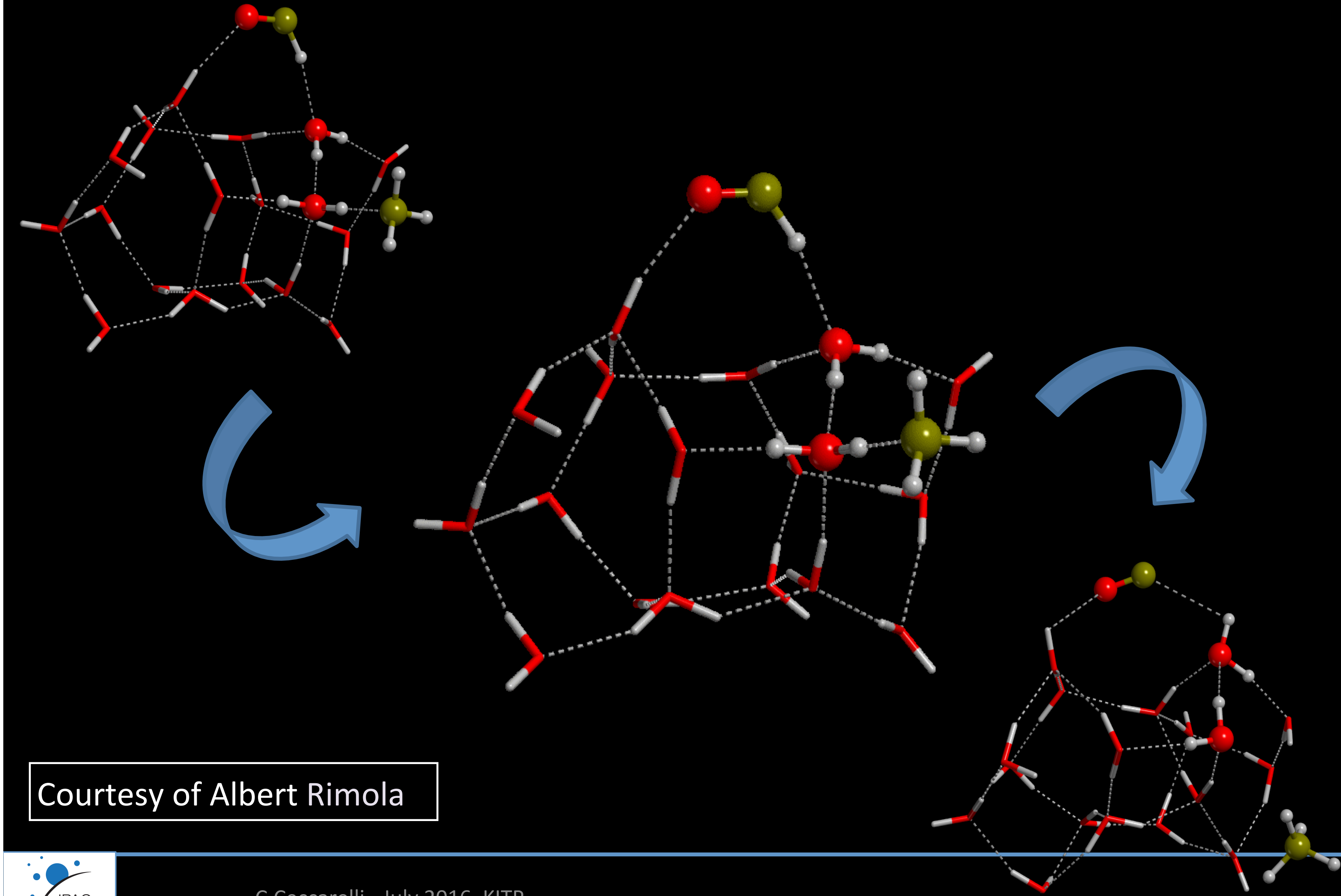
RADICAL S COMBINATION INTO ACOMs

EXAMPLE OF ACETALDEHYDE



Enrique-Romero, Rimola, Ceccarelli, Balucani 2016

Acetaldehyde Formation. CH_3 + HCO reaction on grain surfaces



Courtesy of Albert Rimola

THE GAS PHASE THEORY

HYPOTHESIS/ASSUMPTIONS:

1. AT T_{dust}≤20K, FROZEN O/CO/N/C ARE HYDROGENATED => SIMPLE MOLECULES FORMATION: H_2O, H_2CO, CH_3OH, NH_3, CH_4…
2. (A FRACTION OF) THESE ICED MOLECULES SUBLIMATE, REACT IN THE GAS AND FORM ACOMs

IS IT TRUE? ..IN SOME CASES YES…

(BUT MUCH REMAINS TO BE DONE)

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Institut de Planétologie et d'Astrophysique de Grenoble

THE ROLE OF GAS PHASE REACTIONS IN THE ACOMs FORMATION, EVEN AT ≈10K

ACOMs ARE CERTAINLY THE RESULTS OF THE COMBINATION OF GAS PHASE AND SURFACE CHEMISTRY:

THE QUESTION IS:

WHO PLAYS WHEN?

SUMMARY

- ACOMs ARE PRESENT IN ENVIRONMENTS WITH TEMPERATURES RANGING FROM 10K TO >100K
- ACOMs ARE SURELY THE RESULT OF A COMBINED SURFACE + GAS PHASE CHEMISTRY
- VERY LIKELY, THE GAS PHASE CHEMISTRY ROLE HAS BEEN OVERLOOKED, THOUGH, AND NEEDS TO BE BETTER UNDERSTOOD
- OBSERVATIONS + THEORY + EXERIMENTS + MODELING ARE ABSOLUTELY NECESSARY TO UNDERSTAND WHAT'S GOING ON

Take home message: ACOMs are easily synthetized in the ISM

WHAT NEXT (on our side) ?

Seeds Of Life In Space

IRAM NOEMA LARGE PROGRAM
(interferometer): ACOMs
PI: C.Ceccarelli & P.Caselli