Complex Organic Molecules in space: where do we find them and how can we make them?

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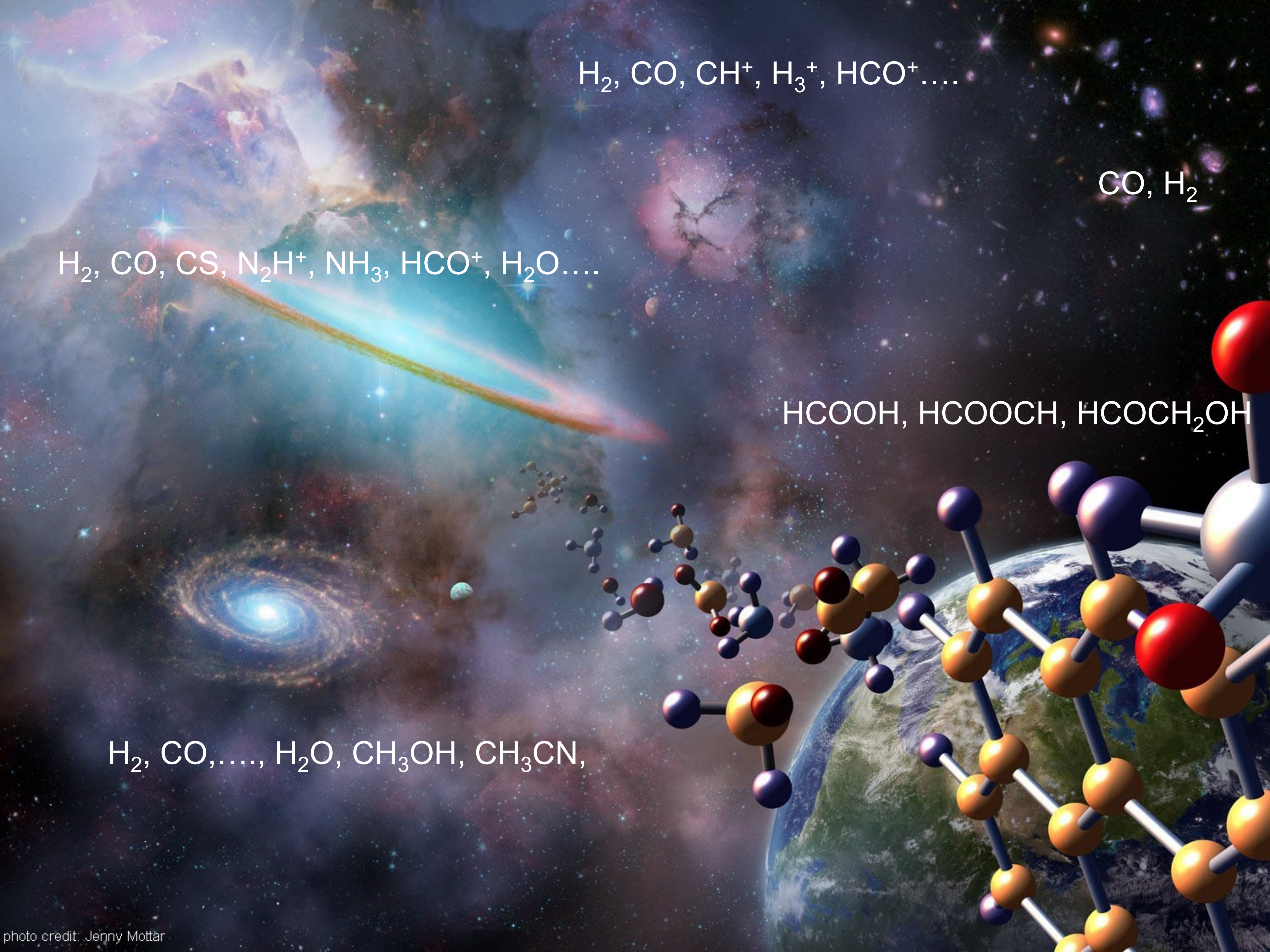


H_2, CO, CH^+, H_3^+, HCO^+….

CO, H_2

H_2, CO, CS, N_2H^+, NH_3, HCO^+, H_2O….

HCOOH, HCOOCH, $HCOCH_2OH$

H_2, CO,…., H_2O, CH_3OH, CH_3CN,

photo credit: Jenny Mottar

Complex Organic Molecules (COMs):

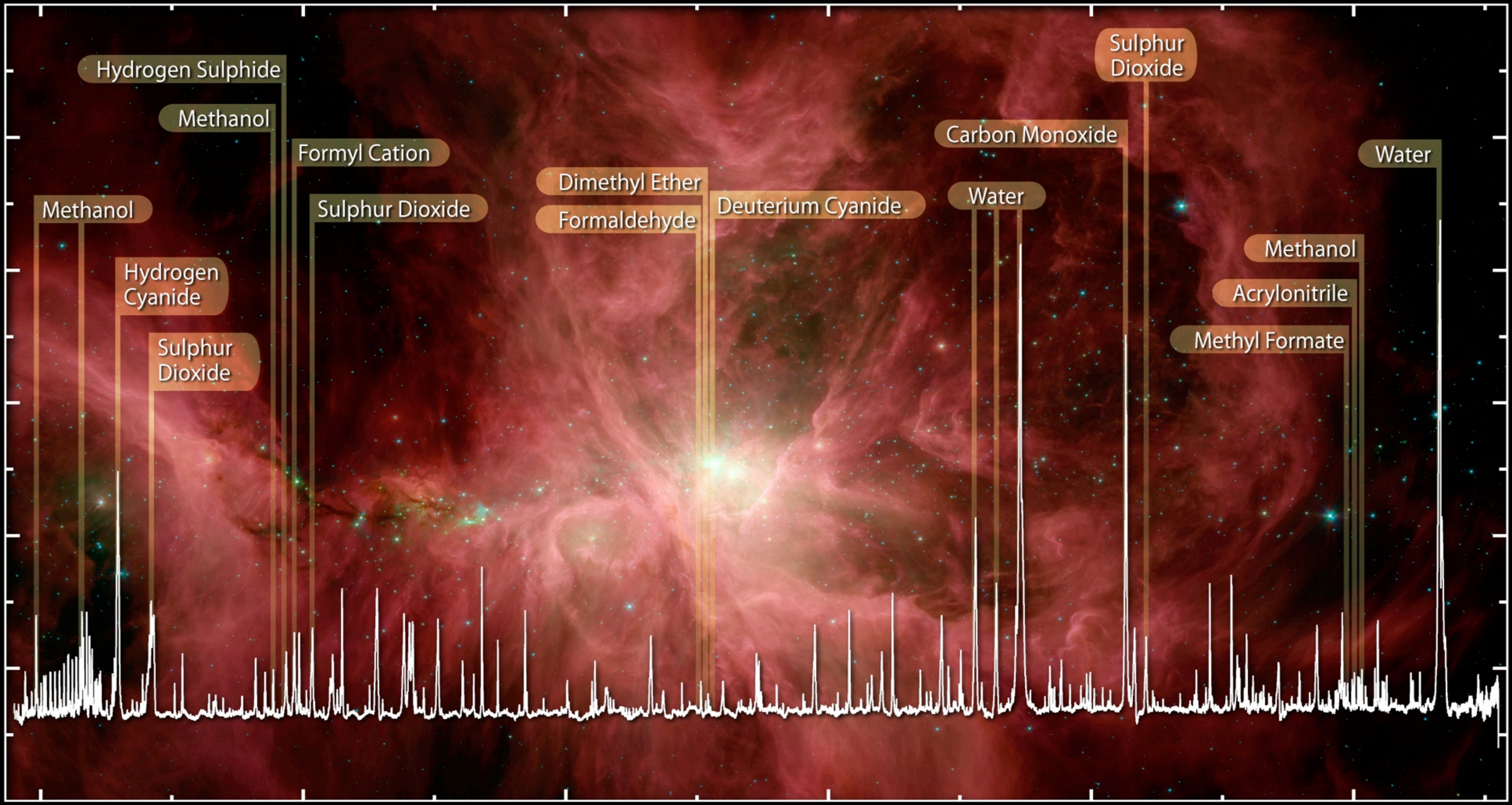
- They contain carbon
- ≥ 6 atoms
- Unsaturated (e.g. C_nH, HC_nN..)
- Saturated (e.g. CH_3OCH_3)

Reviews: Herbst & van Dishoeck 2009; Caselli & Ceccarelli 2012

We find COMs in:

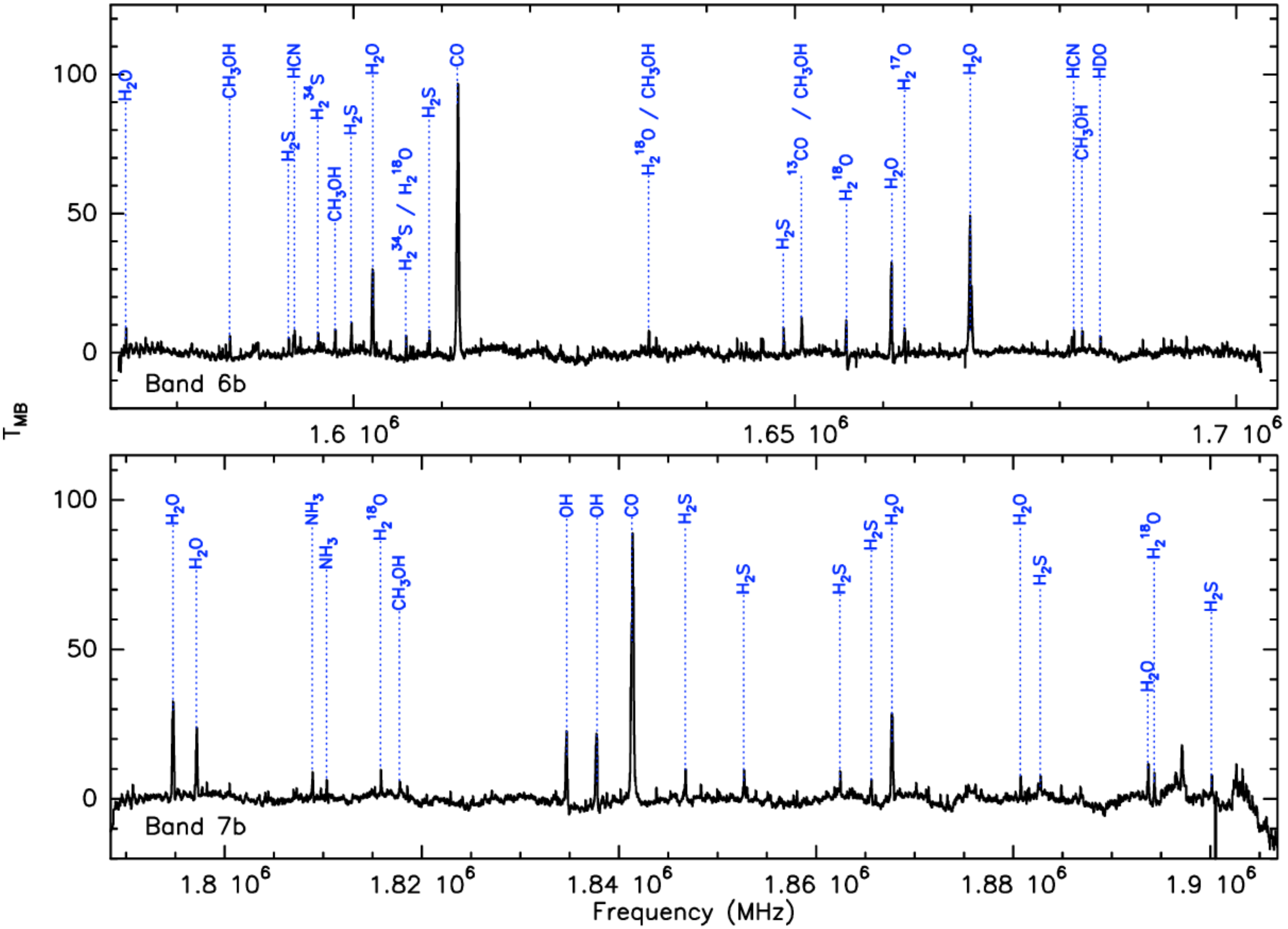
- **Hot cores and corinos: gas around high and low mass stars, left over from the star (and planet?) formation process**
- Circumstellar envelopes
- **Cold dark clouds**
- Stellar outflows/shocked regions
- Nearby starburst galaxies

Most detections are in hot cores, and hot corinos: T = 100-300 K, n_H = 10^6 – 10^7 cm^{-3}
Some of the detected COMs tightly linked to biological processes

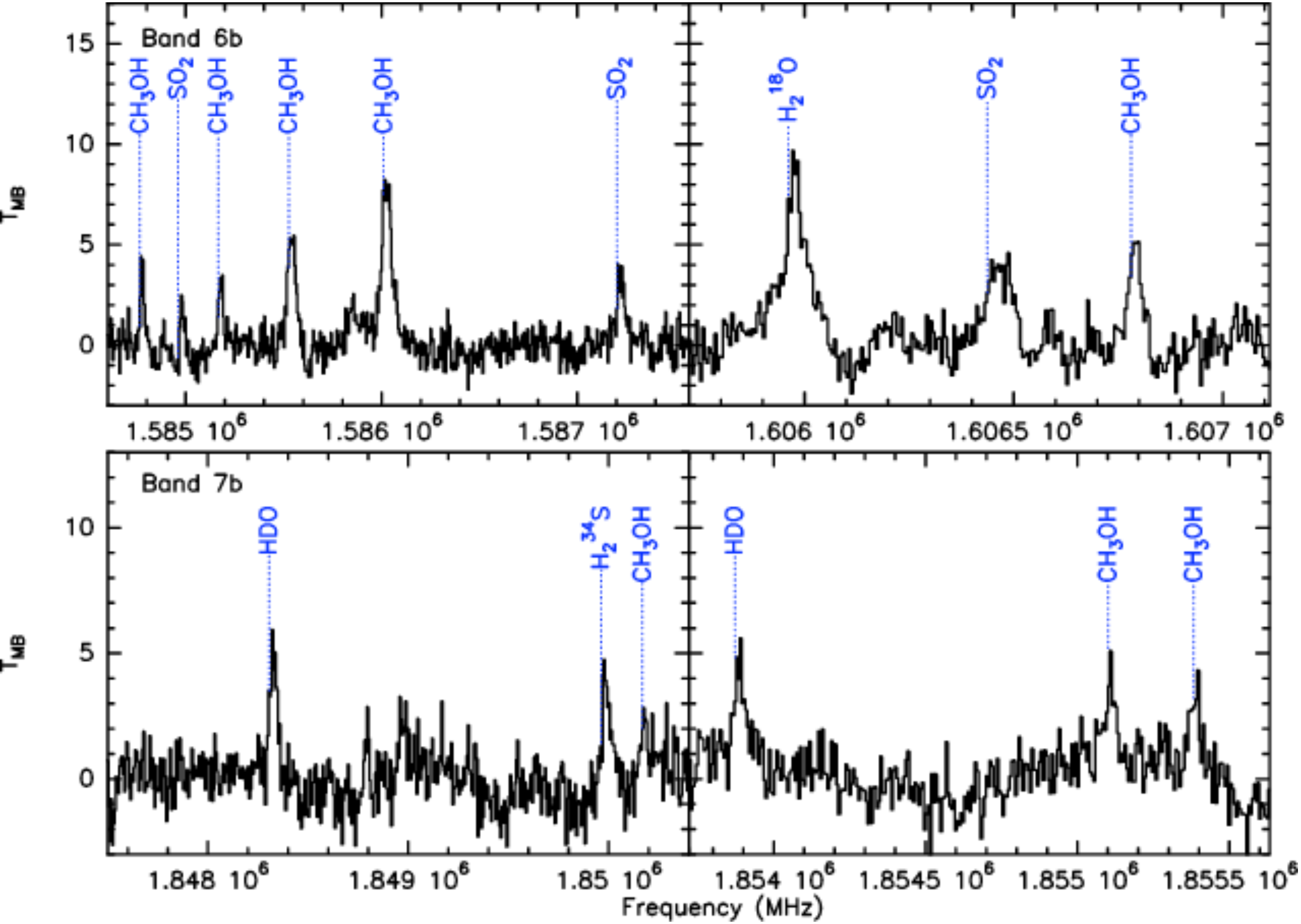


HIFI Spectrum of Water and Organics in the Orion Nebula

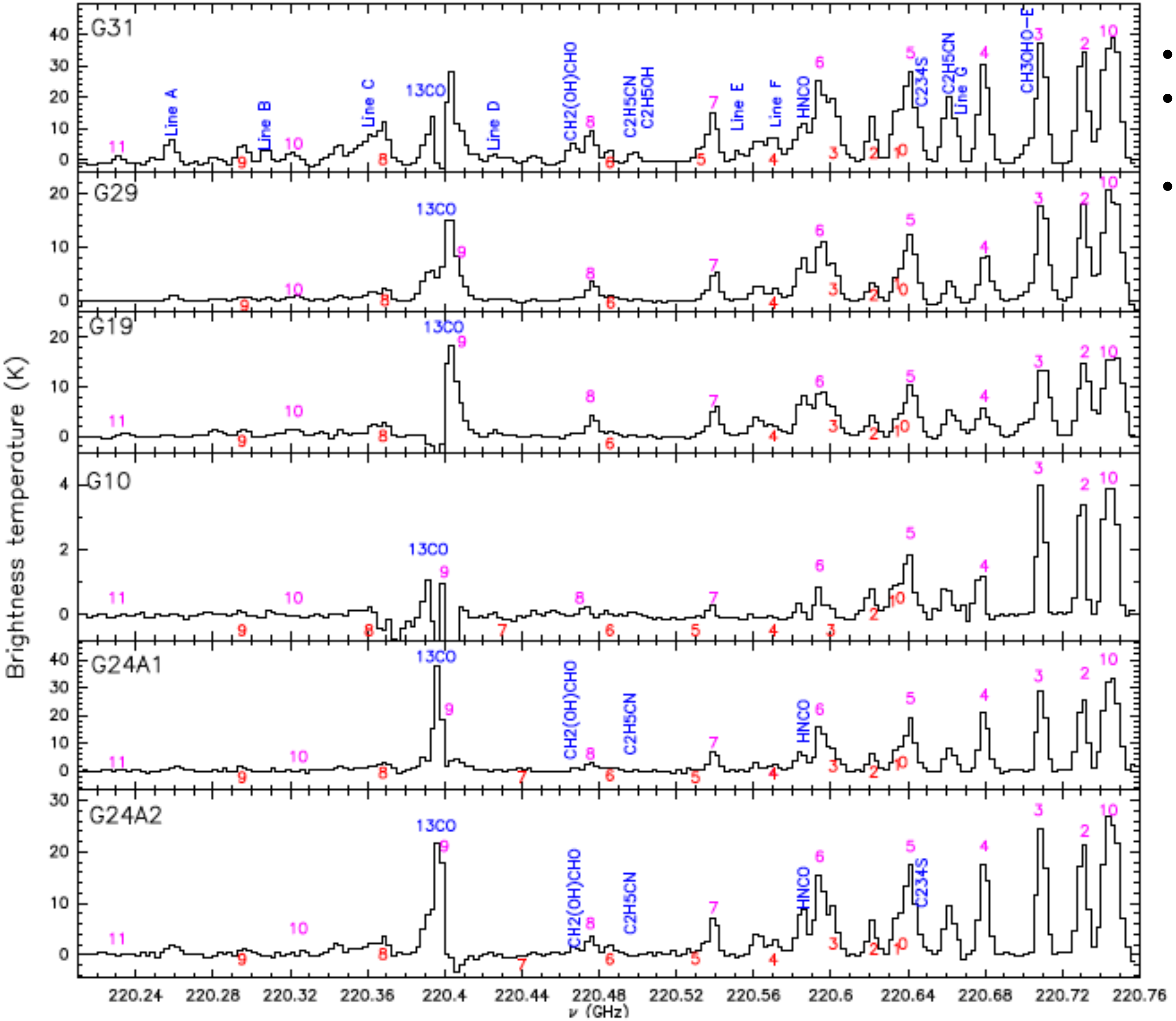
Massive star forming regions: the big problem of line confusion in the submm/far IR



Crockett et al. (2010)



If one zooms in…..



Line confusion due to:

- Richness of the spectrum
- Blending (due to large linewidths)
- Uncertainties in the lab rest frequencies as well as in the observations

↓

This leads to only tentative detections in most cases (e.g. glycolaldehyde @ 220.4 GHz may be acetone instead!)

Calcutt et al. 2014

Glycolaldehyde	CH_2OHCHO	SgrB2, YSOs
Acetic acid	CH_3COOH	SgrB2, YSOs
Methyl formate	$HCOOCH_3$	SgrB2, YSOs, CC
Formamide	CH_3NO	SgrB2, YSOs
Amino acetonitrile	H_2NCH_2CN	SgrB2
iso-Propyl Cyanide	C_4H_7N	SgrB2
Acetone	$(CH_3)_2CO$	SgrB2, Orion KL
Acetaldehyde	CH_3CHO	SgrB2, evolved stars
Ethyl Formate	C_2H_5OCHO	SgrB2, Orion KL
Methoxy	CH_3O	CC
Triacarbon monoxide	C_3O	CC?
cyanamide	NH_2CN	SgrB2, Extragal
Dymethyl ether	CH_3OCH_3	Orion
Propanal	CH_3CH_2CHO	SgrB2
Propene	CH_3CHCH_2	CC
Glycolic acid	$HOCH_2COOH$	SgrB2
Ethyl alcohol	CH_3CH_2OH	Not yet detected
Formic acid	$HCOOH$	SgrB2, CC, YSO
Hydroxylamine	NH_2OH	not yet detected
glycine	H_2NCH_2COOH	not yet detected
ketenimine	CH_2CNH	SgrB2

YSO: young stellar objects
CC: cold core

IMPORTANCE OF COMs

- Their detection is a confirmation of the high density cores where stars form
- COMs are now known to be present in cold gas in pre-stellar cores e.g. propylene (Marcelino et al. 2007)
- Some believe that formation of aminoacids may have occurred in the ISM and comets (e.g. Glavin et al. 2006; Elsila et al. 2009)

A more comprehensive list can be found in Herbst & van Dishoeck 2009

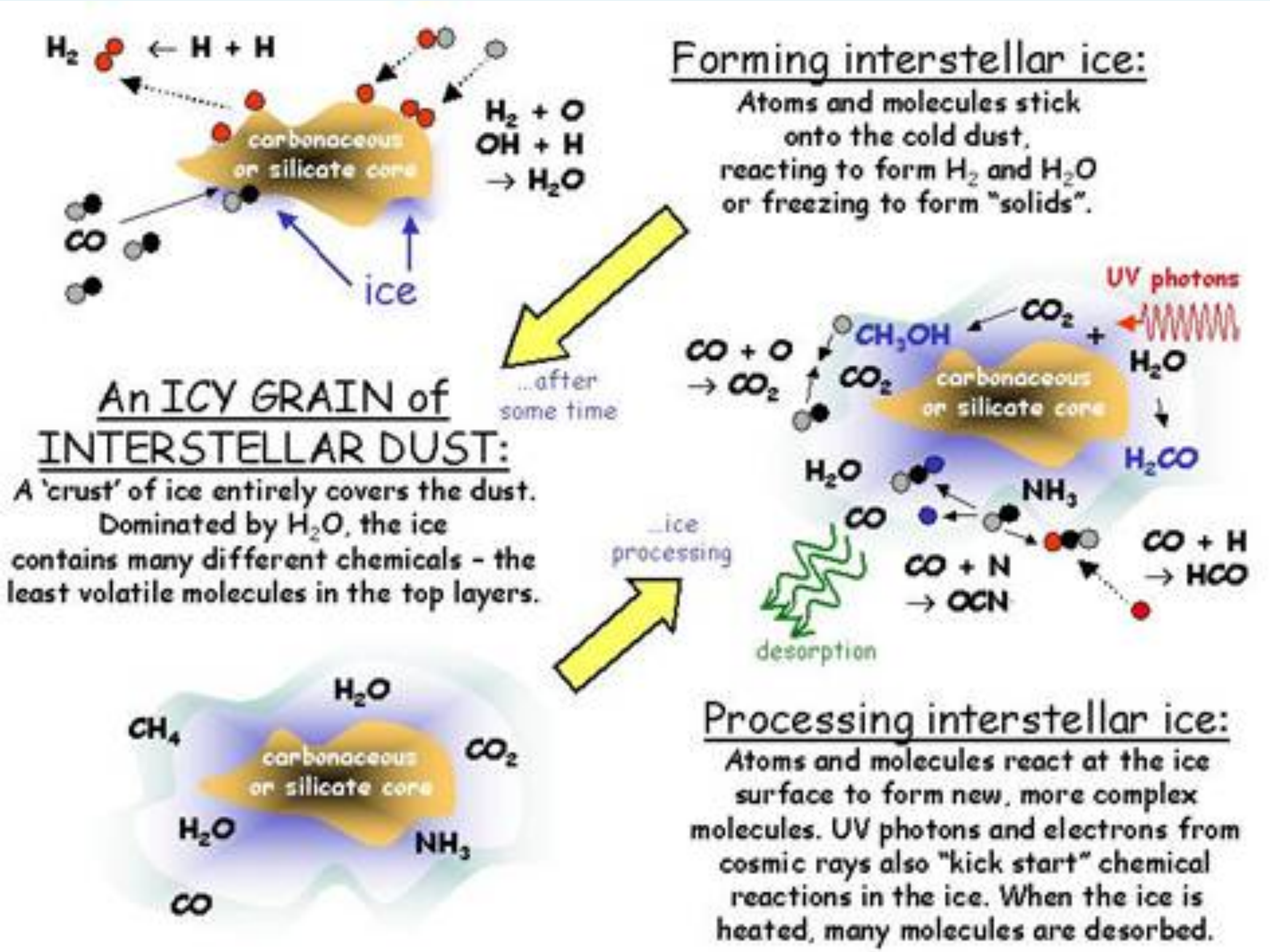
How do these COMs form?

- Possibly on the surface of dust grains by:
    - hydrogenation
    - radical-radical reactions (only efficient at T>30 K?)

- However, gas-phase and surface reactions well-characterized experimentally only for a few COMs (e.g. CH_3OH, methyl formate)

- **Surprising detection of COMs in cold objects (T<10 K)**

- Molecules can be formed on the surface of the dust **(this is how H_2 form):**



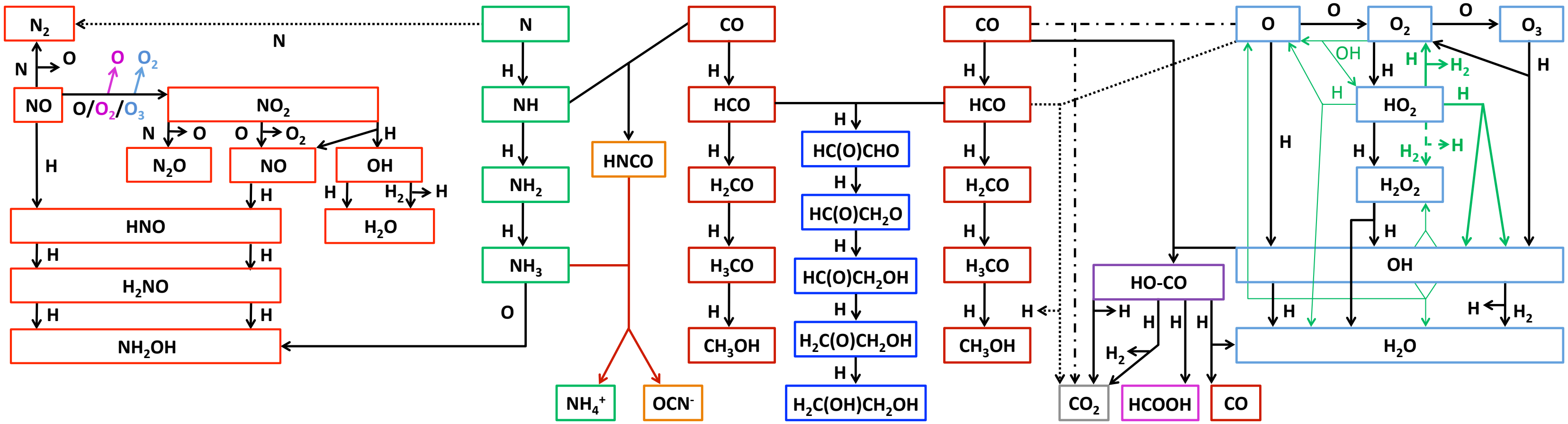
Forming interstellar ice:
Atoms and molecules stick onto the cold dust, reacting to form H_2 and H_2O or freezing to form "solids".

An ICY GRAIN of INTERSTELLAR DUST:
A 'crust' of ice entirely covers the dust. Dominated by H_2O, the ice contains many different chemicals - the least volatile molecules in the top layers.

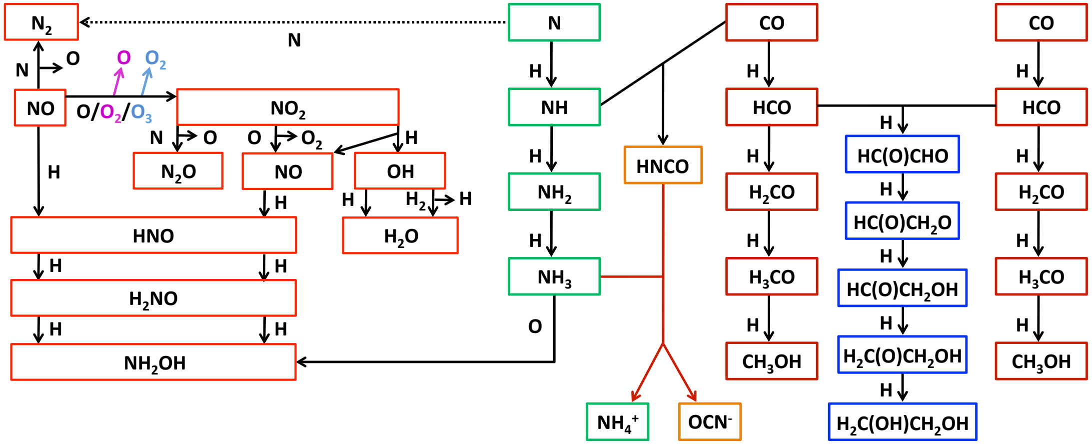
Processing interstellar ice:
Atoms and molecules react at the ice surface to form new, more complex molecules. UV photons and electrons from cosmic rays also "kick start" chemical reactions in the ice. When the ice is heated, many molecules are desorbed.

Fraser et al. 01

Scheme from Linnartz et al. 2015



Hydrogen very abundant; T = 10 K; $n_H = 10^4\text{-}10^7\ cm^{-3}$



Energetic processes can affect the formation/ destruction of COMs on grains

Experiments show formation of COMs by secondary UV photons or via cosmic-ray bombardment

however

UV radiation field used in experiments >> UV field from secondary UV γs in dark cloud cores

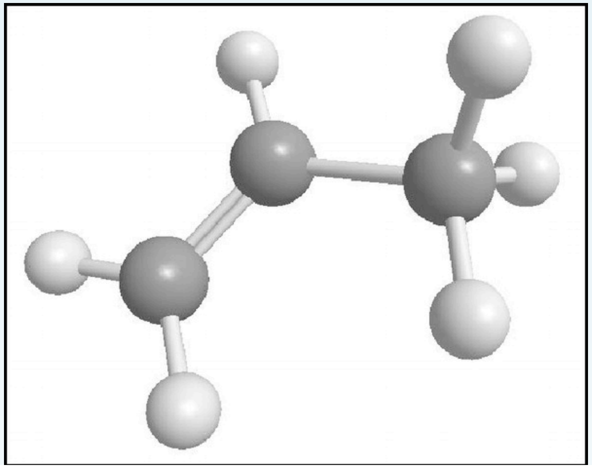
Experiments available for only few species (CH_3OH, $HCOOCH_3$).

Variable Ice Mixtures (some without H_2O!)

….**moreover, from the dust grains, these large molecules would need to sublimate**…

Discovery of Interstellar Propylene or Propene (CH_2CHCH_3 or C_3H_6)

Found in TMC-1 (T~ 10K, $n_H \sim 10^{4-5}$ cm^{-3}) where ***no*** ice sublimation has occurred, but not in Orion (T ~ 300 K, $n_H \sim 10^{6-7} cm^{-3}$) where ***all*** the ices are sublimated!



None of the gas phase routes seems to lead to enough propylene

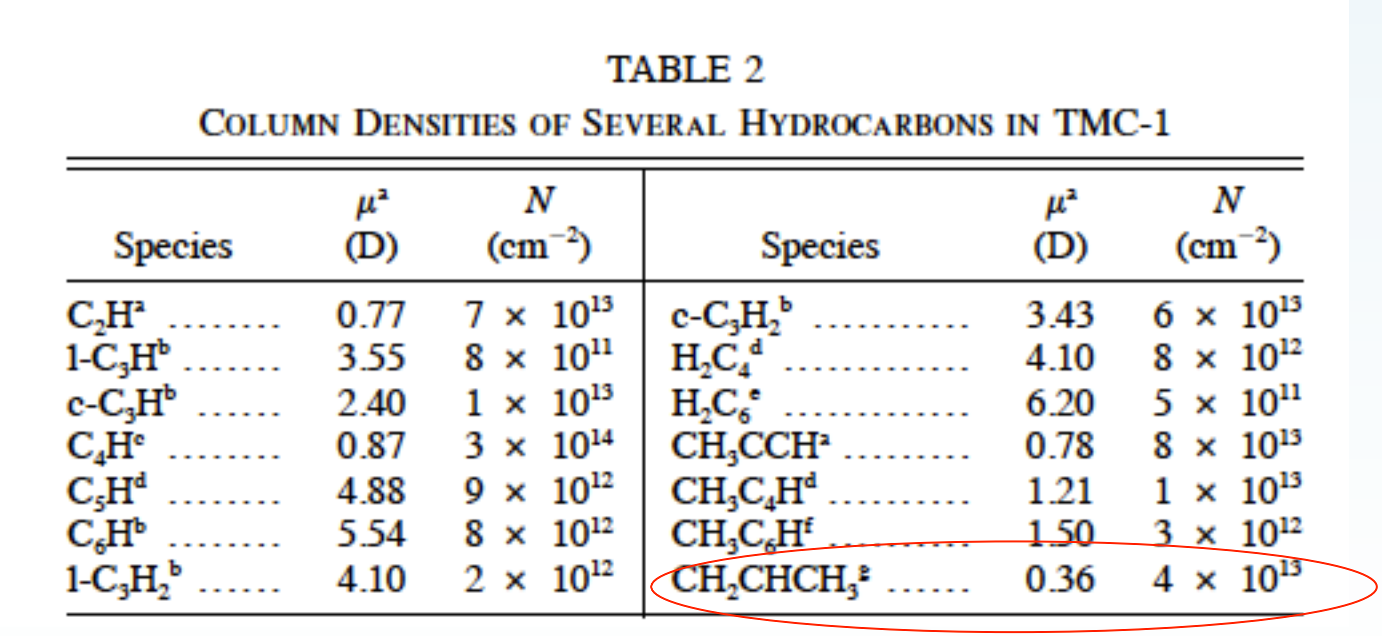


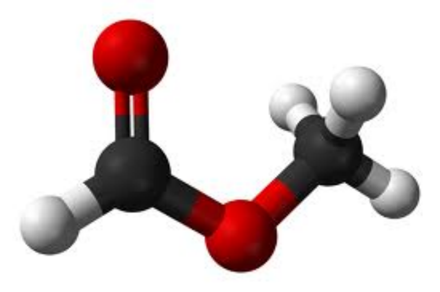
TABLE 2

COLUMN DENSITIES OF SEVERAL HYDROCARBONS IN TMC-1

Species	μ[a] (D)	N (cm^{-2})	Species	μ[a] (D)	N (cm^{-2})
C_2H[a]	0.77	7×10^{13}	c-C_3H_2[b]	3.43	6×10^{13}
1-C_3H[b]	3.55	8×10^{11}	H_2C_4[d]	4.10	8×10^{12}
c-C_3H[b]	2.40	1×10^{13}	H_2C_6[e]	6.20	5×10^{11}
C_4H[c]	0.87	3×10^{14}	CH_3CCH[a]	0.78	8×10^{13}
C_5H[d]	4.88	9×10^{12}	CH_3C_4H[d]	1.21	1×10^{13}
C_6H[b]	5.54	8×10^{12}	CH_3C_6H[f]	1.50	3×10^{12}
1-C_3H_2[b]	4.10	2×10^{12}	CH_2CHCH_3[g]	0.36	4×10^{13}

Marcelino et al. (2007)

Methyl formate ($HCOOCH_3$): abundant in both cold and hot cores

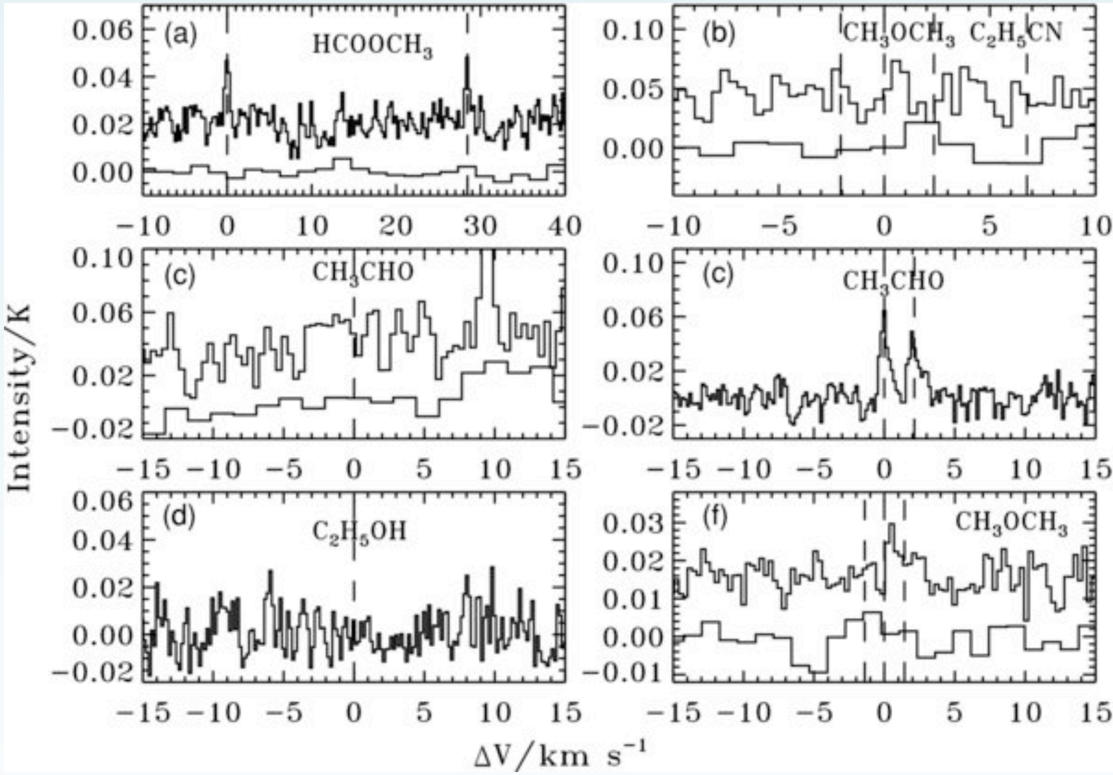


- Simpler example of an ester
- Derived from formic acid (HCOOH)
- Detected in several environments in space
- Its formation mechanism(s) is debated: in gas phase, on grains during cold phase, or on grains during warm up phase?

If on grains, how can it sublimate back to the gas phase in cold cores? E.g. B1-b source

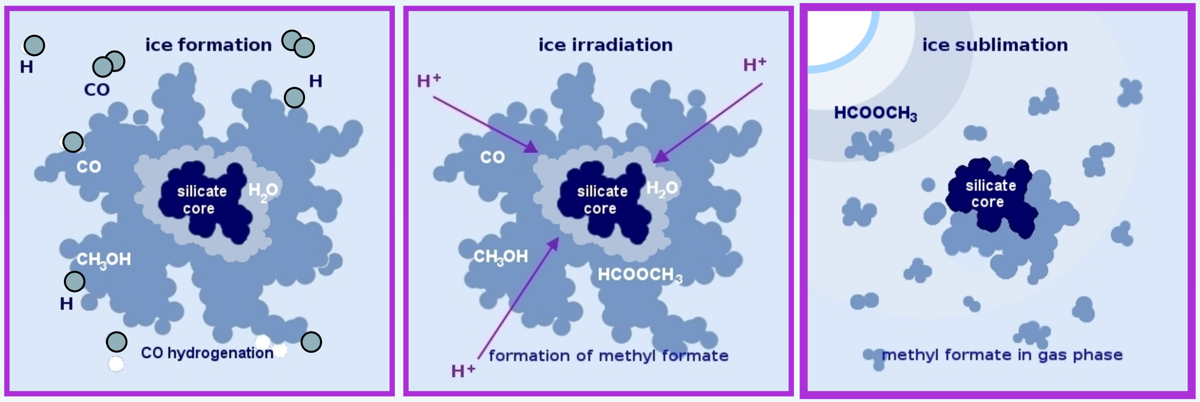
- Cold methyl formate detected toward the quiescent CH_3OH peak

- Oberg et al. (2010) explains this by a combination of UV/ c.r. processing on grains followed by non thermal desorption



Oberg et al. 2010

Occhiogrosso et al (2011) based on Modica and Palumbo (2010) estimated the feasibility of the processing+non thermal desorption route



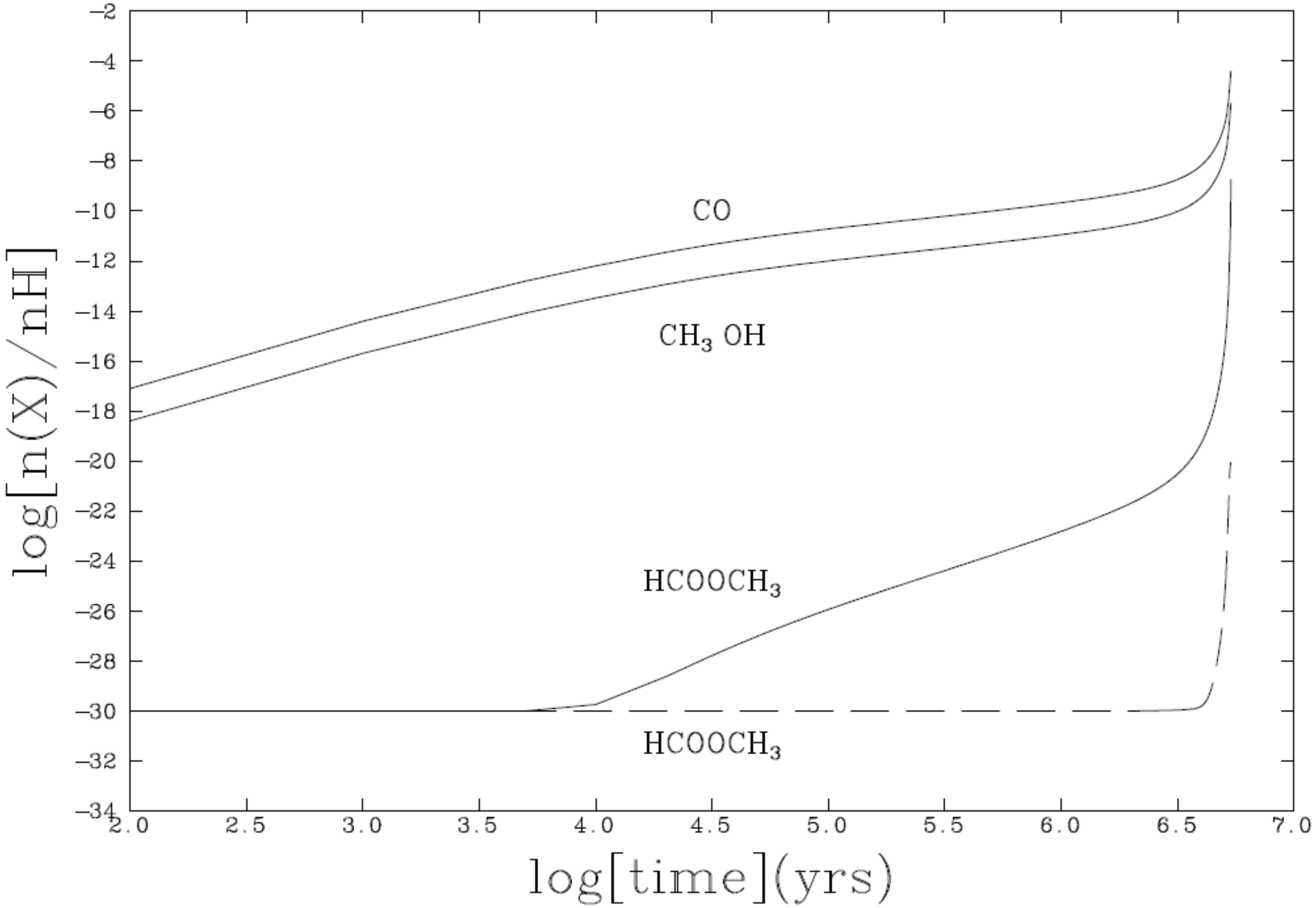
→ reproduce the gas-phase observed abundances in dark clouds but on the ices! UV or cosmic rays do not seem to be enough to sublimate the ices.

Modica & Palumbo 2010

$$CO + CH_3OH \xrightarrow{C.R.} HCOOCH_3$$

$$R = \sigma_{ISM} \times F_{ISM} = 6.2 \times 10^{-18}\ s^{-1}$$

CO, CH_3OH, $HCOOCH_3$ in the solid phase

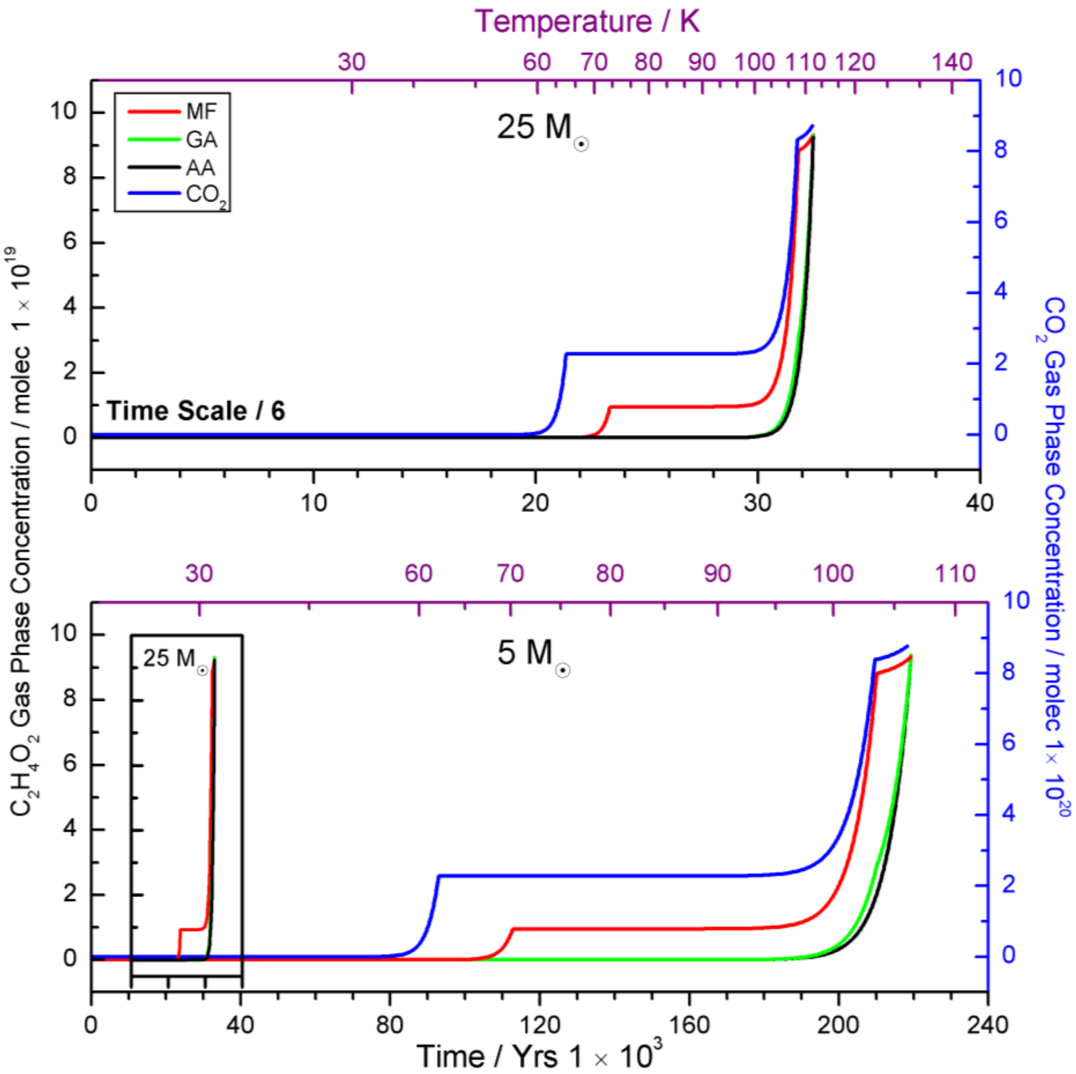


Occhiogrosso et al. 2011

Burke et al’s (2015) TPD studies: rescuing surface grains paths?

Temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) studies of glycolaldehyde, methyl formate and acetic acid adsorbed at 20 K:

- **Glycolaldehyde and acetic acid form hydrogen bonded structures → larger multilayer desorption energies**
- **Methyl formate → monolayer, bilayer and multilayer growth**
- **Acetic acid has the strongest interactions with itself and with water; methyl formate has the weakest interactions. Glycolaldehyde is intermediate between the two.**



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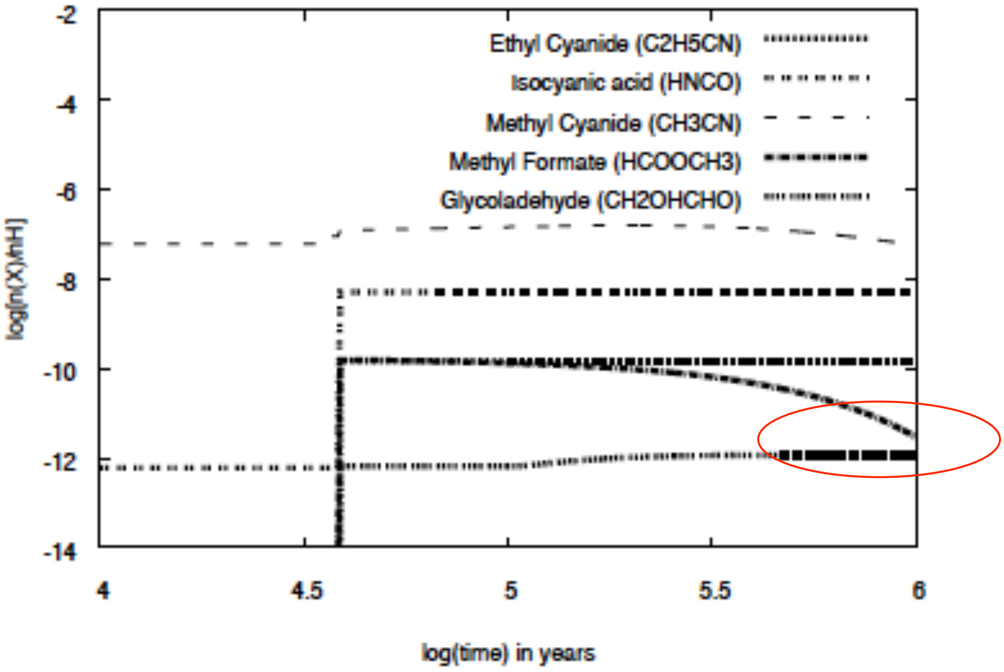
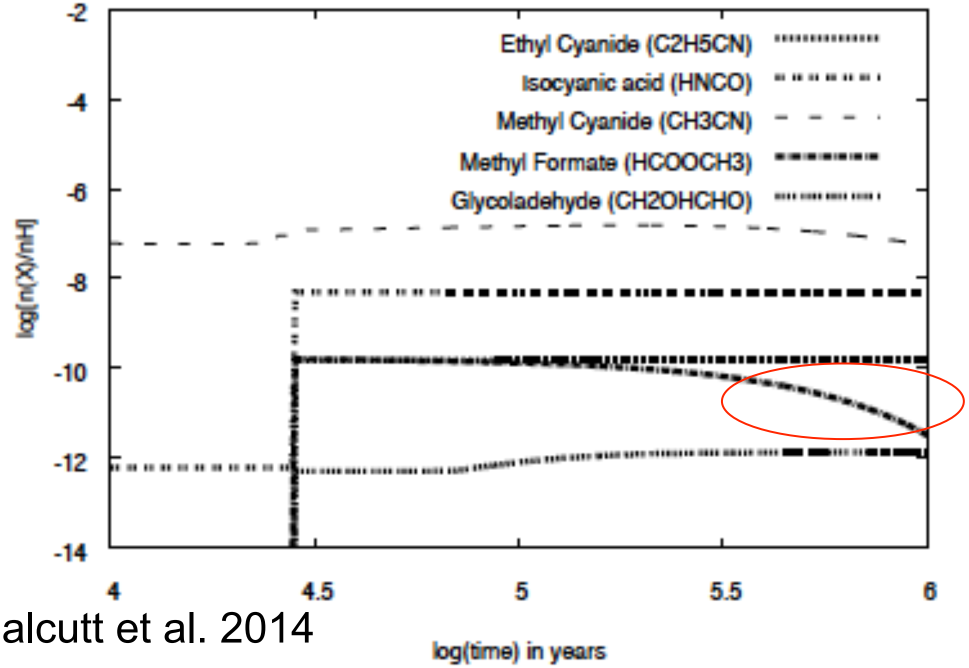
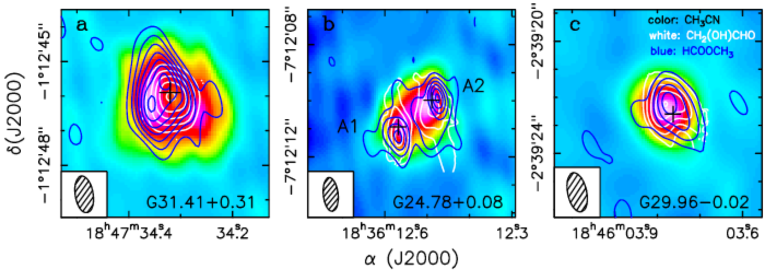
Could this explain why methyl formate only one of these three isomers tohave been observed in cold cores?

Can the models reproduce methyl formate if Tdust > Tsublimation?





Calcutt et al. 2014



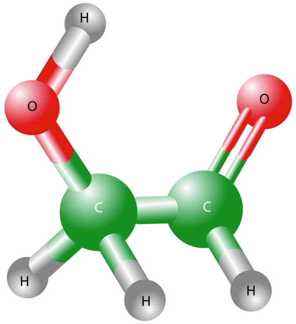
UCL_CHEM Models:

- ~10^{16} cm^{-2}
- An increase in gas density from 10^7 to 10^8 cm^{-3} only a factor of few in abundances
- **Methyl formate seems to decrease with time!**

↓

Is there a way to maintain methyl formate in the gas phase?

Other COMs in warm regions: Glycolaldehyde (CH_2OHCHO)



- Simplest of the monosaccharide sugars
- Now detected in **several** star and planet forming regions
- *There are no experimentally known route for its formation and destruction*
- Several gas-phase and solid-phase route of formation have been proposed
- But its parent species are also difficult to 'maintain'

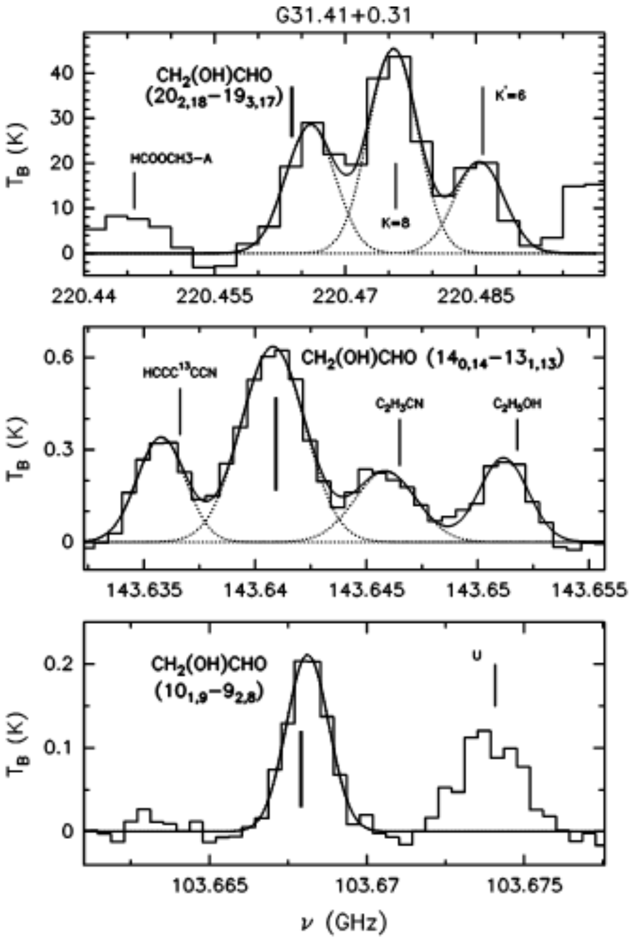


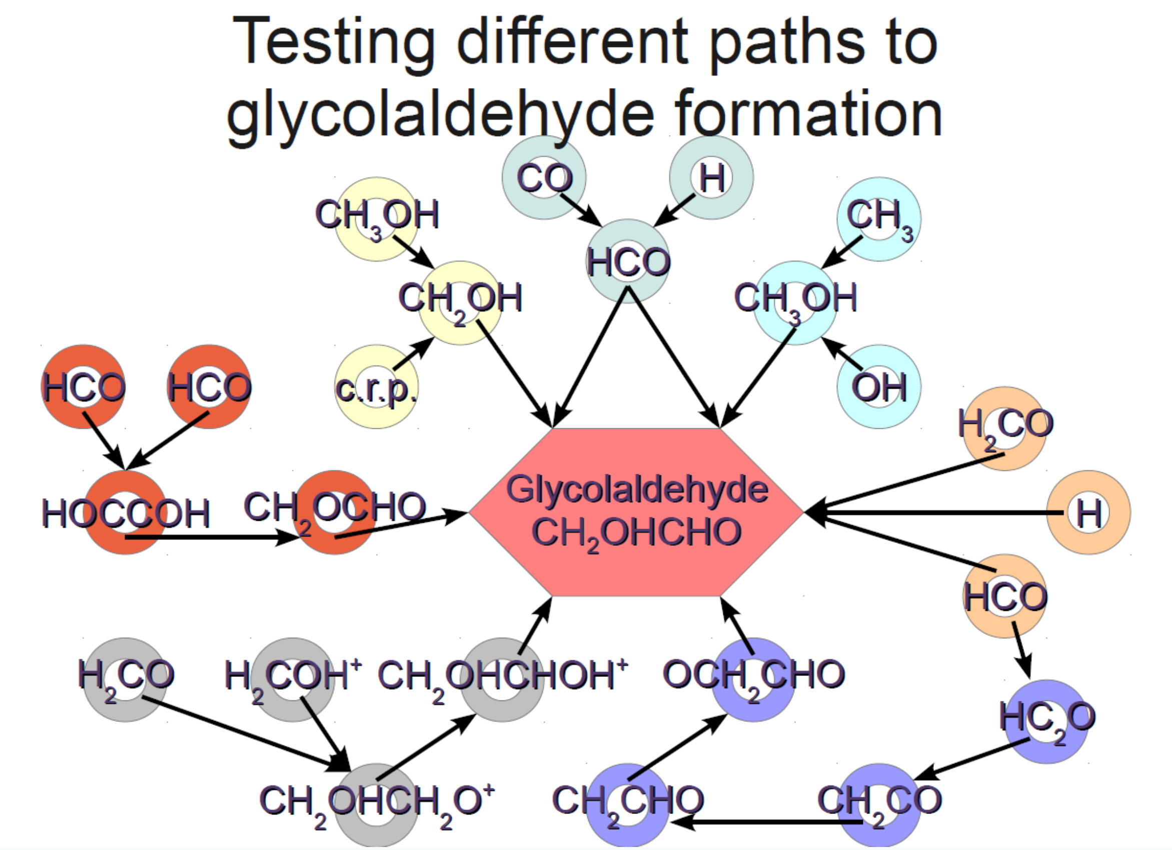
Figure 1. Beam-averaged spectra in T_B scale of the CH_2OHCHO $(20_{2,18}-19_{3,17})$, $(14_{0,14}-13_{1,13})$, and $(10_{1,9}-9_{2,8})$ at 220463.87, 143640.94, and

Beltran et al. 2011

Suggestions for gas-phase reactions:

- Gas-phase radical reactions of HCO with methanol and/or formaldehyde: too slow
- H_2CO dimerization via mediation by H_3^+:
  - requires very high energy for the initiation step and co-existence of large abundances of H_3^+ and H_2CO
  - However, during high mass star formation the latter is unlikely to occur →
    - During the quiescent phase (collapse) T = 10K, H_3^+ is abundant but H_2CO will not have formed yet
    - During the 'hot' phase (after the star is born), H_2CO is abundant but no H_3^+ will survive/form

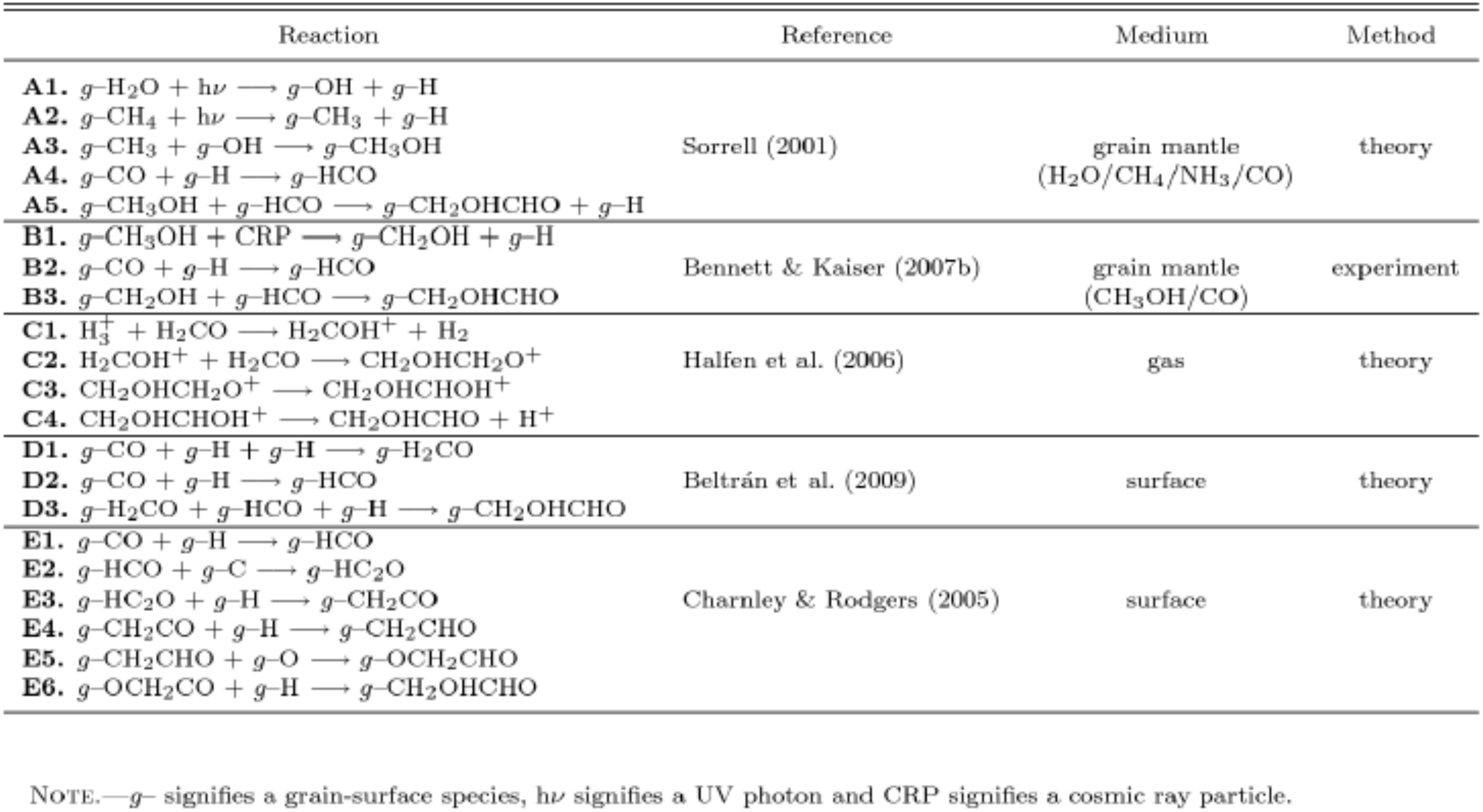
Glycolaldehyde formation on the dust grains:



No knowledge of rate coefficients → Statistical investigation of likelihood of **each reaction**

Woods et al. 2012, 2013

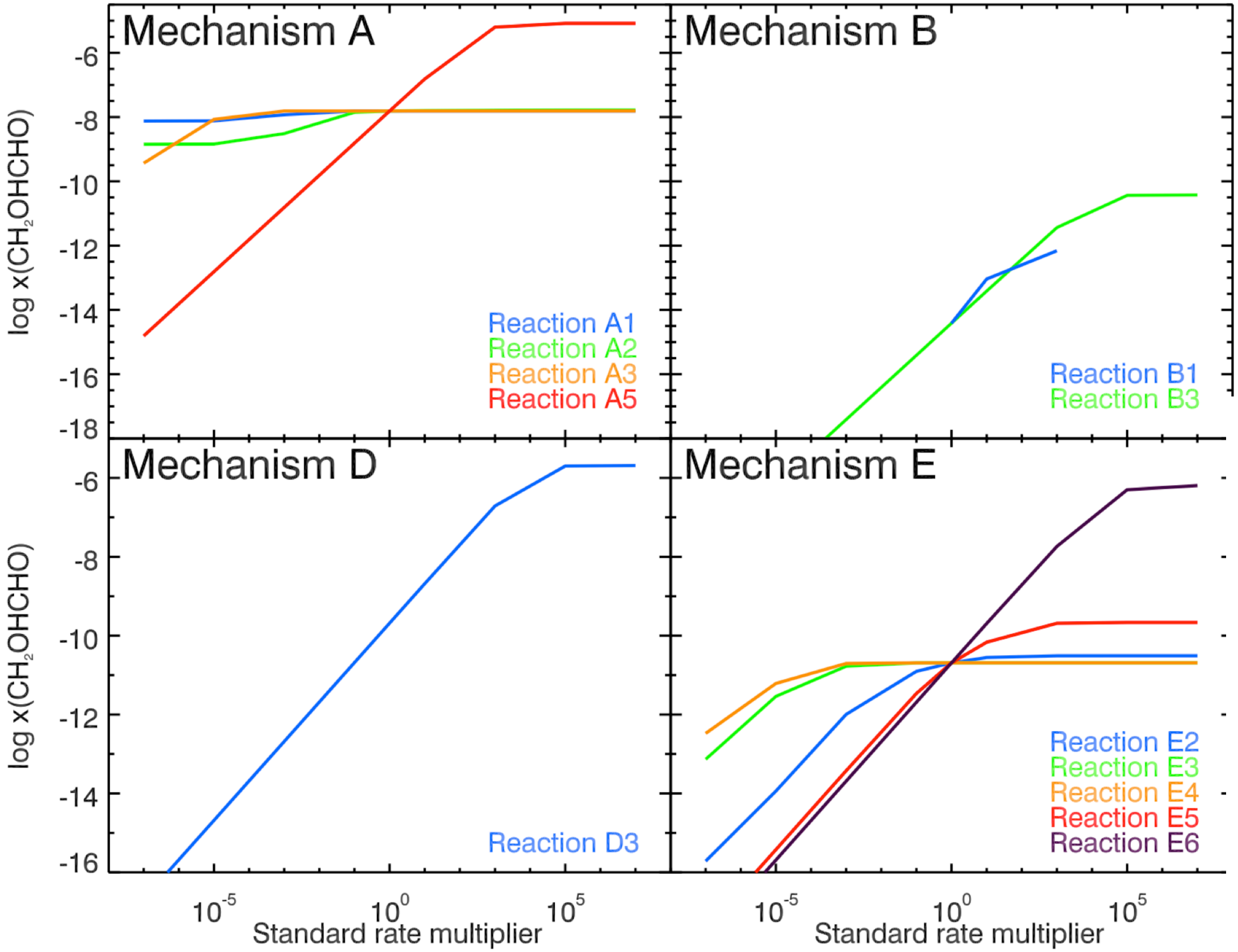
An investigation of glycolaldehyde formation at low temperatures → 400 models



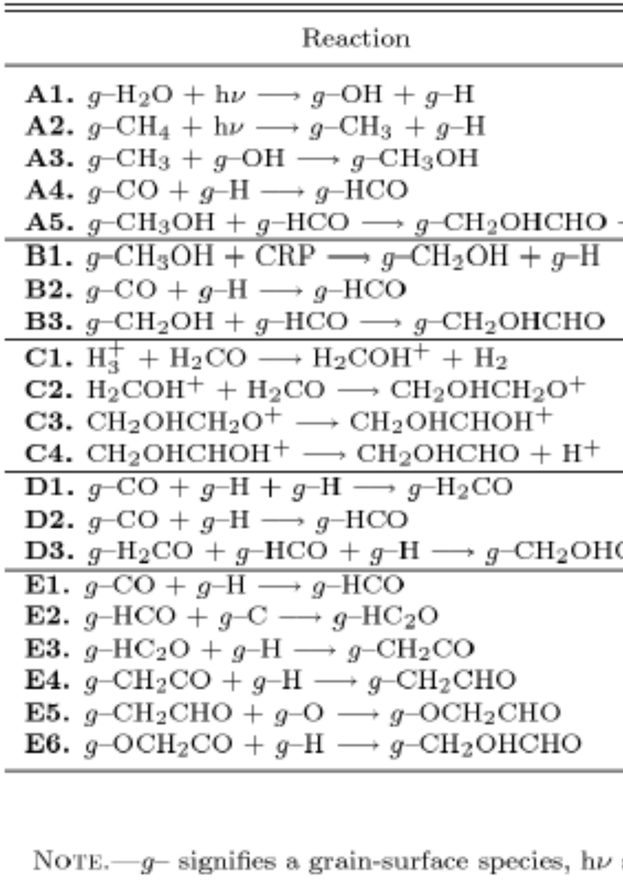
Reaction	Reference	Medium	Method
A1. $g\text{–}\mathrm{H_2O} + h\nu \longrightarrow g\text{–}\mathrm{OH} + g\text{–}\mathrm{H}$	Sorrell (2001)	grain mantle ($\mathrm{H_2O/CH_4/NH_3/CO}$)	theory
A2. $g\text{–}\mathrm{CH_4} + h\nu \longrightarrow g\text{–}\mathrm{CH_3} + g\text{–}\mathrm{H}$			
A3. $g\text{–}\mathrm{CH_3} + g\text{–}\mathrm{OH} \longrightarrow g\text{–}\mathrm{CH_3OH}$			
A4. $g\text{–}\mathrm{CO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{HCO}$			
A5. $g\text{–}\mathrm{CH_3OH} + g\text{–}\mathrm{HCO} \longrightarrow g\text{–}\mathrm{CH_2OHCHO} + g\text{–}\mathrm{H}$			
B1. $g\text{–}\mathrm{CH_3OH} + \mathrm{CRP} \longrightarrow g\text{–}\mathrm{CH_2OH} + g\text{–}\mathrm{H}$	Bennett & Kaiser (2007b)	grain mantle ($\mathrm{CH_3OH/CO}$)	experiment
B2. $g\text{–}\mathrm{CO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{HCO}$			
B3. $g\text{–}\mathrm{CH_2OH} + g\text{–}\mathrm{HCO} \longrightarrow g\text{–}\mathrm{CH_2OHCHO}$			
C1. $\mathrm{H_3^+} + \mathrm{H_2CO} \longrightarrow \mathrm{H_2COH^+} + \mathrm{H_2}$	Halfen et al. (2006)	gas	theory
C2. $\mathrm{H_2COH^+} + \mathrm{H_2CO} \longrightarrow \mathrm{CH_2OHCH_2O^+}$			
C3. $\mathrm{CH_2OHCH_2O^+} \longrightarrow \mathrm{CH_2OHCHOH^+}$			
C4. $\mathrm{CH_2OHCHOH^+} \longrightarrow \mathrm{CH_2OHCHO} + \mathrm{H^+}$			
D1. $g\text{–}\mathrm{CO} + g\text{–}\mathrm{H} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{H_2CO}$	Beltrán et al. (2009)	surface	theory
D2. $g\text{–}\mathrm{CO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{HCO}$			
D3. $g\text{–}\mathrm{H_2CO} + g\text{–}\mathrm{HCO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{CH_2OHCHO}$			
E1. $g\text{–}\mathrm{CO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{HCO}$	Charnley & Rodgers (2005)	surface	theory
E2. $g\text{–}\mathrm{HCO} + g\text{–}\mathrm{C} \longrightarrow g\text{–}\mathrm{HC_2O}$			
E3. $g\text{–}\mathrm{HC_2O} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{CH_2CO}$			
E4. $g\text{–}\mathrm{CH_2CO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{CH_2CHO}$			
E5. $g\text{–}\mathrm{CH_2CHO} + g\text{–}\mathrm{O} \longrightarrow g\text{–}\mathrm{OCH_2CHO}$			
E6. $g\text{–}\mathrm{OCH_2CO} + g\text{–}\mathrm{H} \longrightarrow g\text{–}\mathrm{CH_2OHCHO}$			

NOTE.—g– signifies a grain-surface species, hν signifies a UV photon and CRP signifies a cosmic ray particle.

Woods et al. 2012, 2013



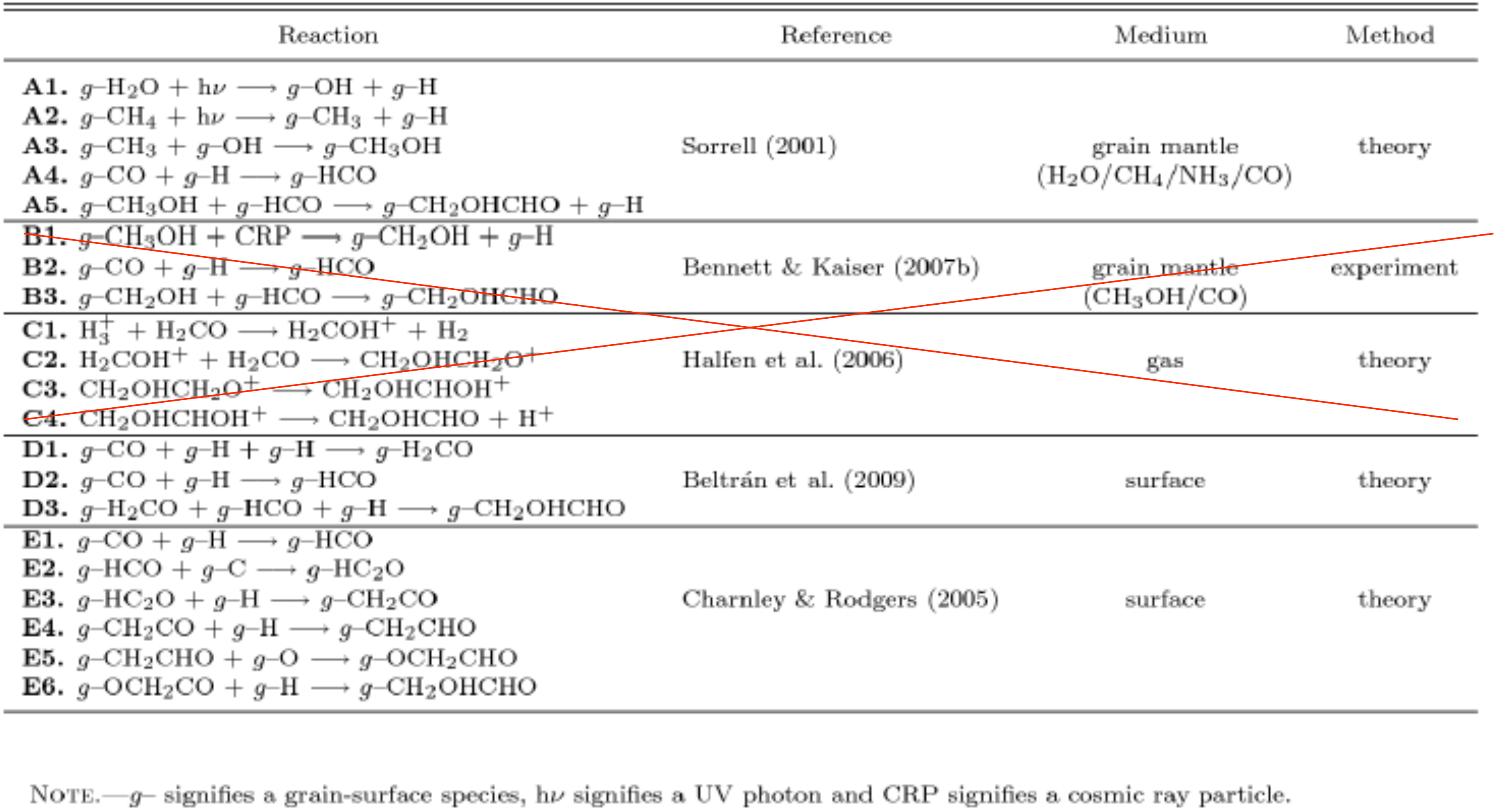
Production of glycolaldehyde via different mechanisms (labelled A, B, D and E) for a gas density of 10^6 cm^{-3}.



	Reaction
A1.	g–H_2O + h$\nu \longrightarrow g$–$OH + g$–H
A2.	g–CH_4 + h$\nu \longrightarrow g$–$CH_3 + g$–H
A3.	g–$CH_3 + g$–$OH \longrightarrow g$–CH_3OH
A4.	g–$CO + g$–$H \longrightarrow g$–HCO
A5.	g–$CH_3OH + g$–$HCO \longrightarrow g$–CH_2OHCHO
B1.	g–CH_3OH + CRP $\longrightarrow g$–$CH_2OH + g$–H
B2.	g–$CO + g$–$H \longrightarrow g$–HCO
B3.	g–$CH_2OH + g$–$HCO \longrightarrow g$–CH_2OHCHO
C1.	$H_3^+ + H_2CO \longrightarrow H_2COH^+ + H_2$
C2.	$H_2COH^+ + H_2CO \longrightarrow CH_2OHCH_2O^+$
C3.	$CH_2OHCH_2O^+ \longrightarrow CH_2OHCHOH^+$
C4.	$CH_2OHCHOH^+ \longrightarrow CH_2OHCHO + H^+$
D1.	g–$CO + g$–$H + g$–$H \longrightarrow g$–H_2CO
D2.	g–$CO + g$–$H \longrightarrow g$–HCO
D3.	g–$H_2CO + g$–$HCO + g$–$H \longrightarrow g$–CH_2OH
E1.	g–$CO + g$–$H \longrightarrow g$–HCO
E2.	g–$HCO + g$–$C \longrightarrow g$–HC_2O
E3.	g–$HC_2O + g$–$H \longrightarrow g$–CH_2CO
E4.	g–$CH_2CO + g$–$H \longrightarrow g$–CH_2CHO
E5.	g–$CH_2CHO + g$–$O \longrightarrow g$–OCH_2CHO
E6.	g–$OCH_2CO + g$–$H \longrightarrow g$–CH_2OHCHO

NOTE.—g– signifies a grain-surface species, hν

Upper limits from each mechanism



Reaction	Reference	Medium	Method
A1. $g\text{–H}_2\text{O} + h\nu \longrightarrow g\text{–OH} + g\text{–H}$	Sorrell (2001)	grain mantle $(\text{H}_2\text{O}/\text{CH}_4/\text{NH}_3/\text{CO})$	theory
A2. $g\text{–CH}_4 + h\nu \longrightarrow g\text{–CH}_3 + g\text{–H}$			
A3. $g\text{–CH}_3 + g\text{–OH} \longrightarrow g\text{–CH}_3\text{OH}$			
A4. $g\text{–CO} + g\text{–H} \longrightarrow g\text{–HCO}$			
A5. $g\text{–CH}_3\text{OH} + g\text{–HCO} \longrightarrow g\text{–CH}_2\text{OHCHO} + g\text{–H}$			
~~**B1.** $g\text{–CH}_3\text{OH} + \text{CRP} \longrightarrow g\text{–CH}_2\text{OH} + g\text{–H}$~~	~~Bennett & Kaiser (2007b)~~	~~grain mantle~~ ~~$(\text{CH}_3\text{OH}/\text{CO})$~~	~~experiment~~
~~**B2.** $g\text{–CO} + g\text{–H} \longrightarrow g\text{–HCO}$~~			
~~**B3.** $g\text{–CH}_2\text{OH} + g\text{–HCO} \longrightarrow g\text{–CH}_2\text{OHCHO}$~~			
~~**C1.** $\text{H}_3^+ + \text{H}_2\text{CO} \longrightarrow \text{H}_2\text{COH}^+ + \text{H}_2$~~	~~Halfen et al. (2006)~~	~~gas~~	~~theory~~
~~**C2.** $\text{H}_2\text{COH}^+ + \text{H}_2\text{CO} \longrightarrow \text{CH}_2\text{OHCH}_2\text{O}^+$~~			
~~**C3.** $\text{CH}_2\text{OHCH}_2\text{O}^+ \longrightarrow \text{CH}_2\text{OHCHOH}^+$~~			
~~**C4.** $\text{CH}_2\text{OHCHOH}^+ \longrightarrow \text{CH}_2\text{OHCHO} + \text{H}^+$~~			
D1. $g\text{–CO} + g\text{–H} + g\text{–H} \longrightarrow g\text{–H}_2\text{CO}$	Beltrán et al. (2009)	surface	theory
D2. $g\text{–CO} + g\text{–H} \longrightarrow g\text{–HCO}$			
D3. $g\text{–H}_2\text{CO} + g\text{–HCO} + g\text{–H} \longrightarrow g\text{–CH}_2\text{OHCHO}$			
E1. $g\text{–CO} + g\text{–H} \longrightarrow g\text{–HCO}$	Charnley & Rodgers (2005)	surface	theory
E2. $g\text{–HCO} + g\text{–C} \longrightarrow g\text{–HC}_2\text{O}$			
E3. $g\text{–HC}_2\text{O} + g\text{–H} \longrightarrow g\text{–CH}_2\text{CO}$			
E4. $g\text{–CH}_2\text{CO} + g\text{–H} \longrightarrow g\text{–CH}_2\text{CHO}$			
E5. $g\text{–CH}_2\text{CHO} + g\text{–O} \longrightarrow g\text{–OCH}_2\text{CHO}$			
E6. $g\text{–OCH}_2\text{CO} + g\text{–H} \longrightarrow g\text{–CH}_2\text{OHCHO}$			

NOTE.—g– signifies a grain-surface species, $h\nu$ signifies a UV photon and CRP signifies a cosmic ray particle.

Gas-phase alternatives for COM formation

1. ‘Rapid Radical Association’ (RRA): 3-body gas-phase reactions between radicals in warm high density gas: an environment that exist for a very short period of time, following the sudden and total sublimation of grain ice mantles driven by catastrophic recombination of trapped hydrogen atoms, and other radicals, in the ice (Rawlings et al. 2103).

2. ‘Overlooked’ gas phase reactions: an example is the formation of methyl formate via dimethyl ether (Balucani et al. 2015)

…AND MORE COMBINATIONS

3. Surface reactions followed by explosive desorption via cosmic rays impacts on grains? (Reboussin et al 14; Ivlev15)

4. Tunneling effects on heavy atoms? (e.g. O; Minissale+14)

Data Needs for COMs:

1. Collisional coefficients

Because we are often not in LTE environments and/or we do not know the temperature of the gas → need collisional coefficients to solve the radiative transfer equations and obtain best gas density and temperature

BUT:

a. **For none of the COMs a full set of collisional coefficients is available, apart from methyl formate and only within a certain range of temperatures (Faure et al. 2014)**
b. Collisional coefficients are important for some COMs with transitions with small dipole strengths (Beltran et al. 2009)
c. For SKA the need for collisional coefficients is even more important as it has been shown that a lower frequencies NLTE effects are more important (Faure et al. 2014)

2. **Rest Frequencies**

Catalogues disagree in some rest frequencies!

E.g

- Glycolaldehyde: some low J transitions within Band 3 and 4 of ALMA disagreement up to 0.3 MHz.
- Acetic Acid: only one source of frequencies (LOVAS) with errors > 0.1 MHz

3. **Partition functions**

E.g

- For Acetic Acid SPLATALOGUE does not report any partition function (now estimated/calculated by several groups (eg Calcutt et al. 2015))
- For methyl formate: SPLATALOGUE/JPL has two contributions for the partition functions which seem to differ by over an order of magnitude at high (300K) temperatures.

Summary on Complex Organic Molecules:

- Large (≥ 6 atoms) molecules are common place in the interstellar medium
- Formation is not necessarily due to warm temperatures and/or high densities
- While several possible mechanisms are viable when gas temperatures > sublimation temperatures, more ‘extravagant’ mechanisms have to be invoked for high abundances at low temperatures
- **Large survey programs with both single dish telescopes and interferometers are being made/planned → COM inventory**