

Molecular complexity in Orion-KL:

IRAM and ALMA observations of O-bearing molecules

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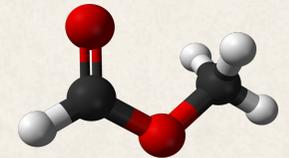


Molecular complexity

❖ Chemical complexity: hydrocarbons -> + functional groups

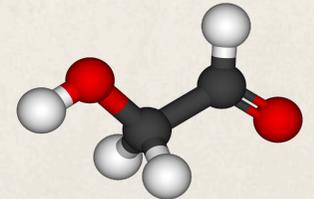
- ❖ Even if continuous progress in the sensitivity of millimeter wave telescopes have led to an increase in the number of species detected in the interstellar medium, complex molecules have long been detected in the interstellar medium and the first detections date back to the 1970s.

Methanol (1970), Ethanol (1975), Dimethylether (1974), Methanethiol (1979), Cyanomethane (1971), Formaldehyde (1969), Acetaldehyde (1973), Formic acid (1975), Methylformate (1975), Formamide (1971), Methylamine (1974) and more recently: Acetone (1987), Acetic acid (1997)



- ❖ Chemical complexity has increased with the detection of molecules with more than one functional group.

Glycolaldehyde (Hollis et al., 2000), Ethylene glycol (Hollis et al., 2002), Amino acetonitrile (Belloche et al., 2008), Cyanoformaldehyde (Remijan et al., 2008), Cyanomethanimine (Zaleski et al., 2013).



➔ Molecular complexity race: what is the limit to complexity in space?

with a goal: prebiotic molecules

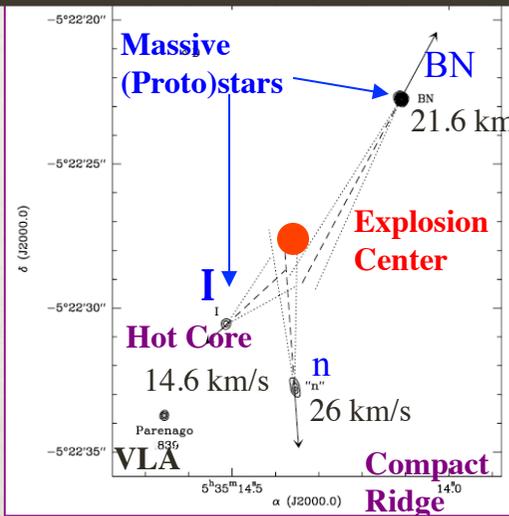
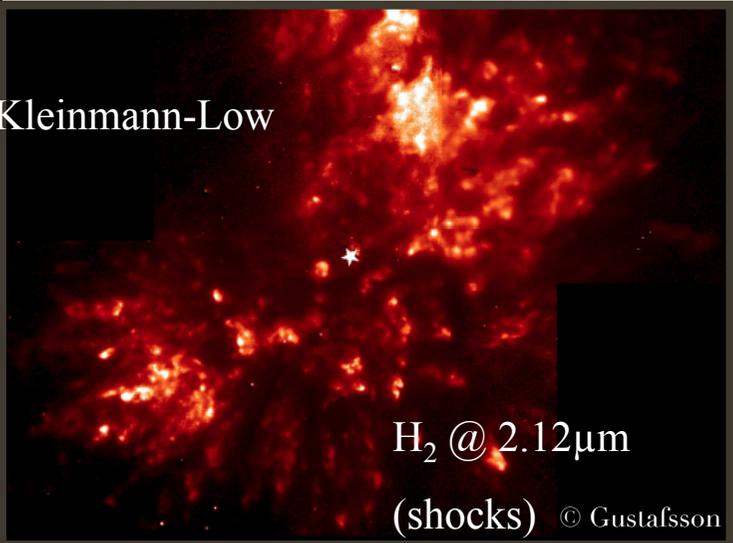
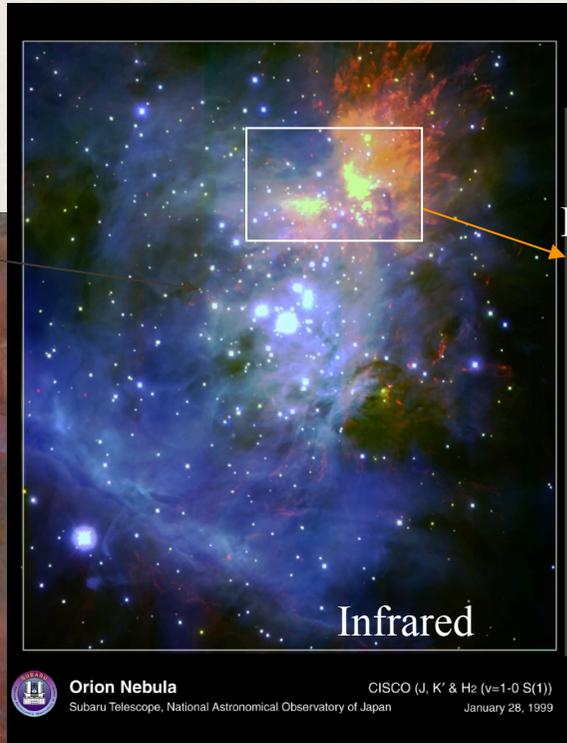
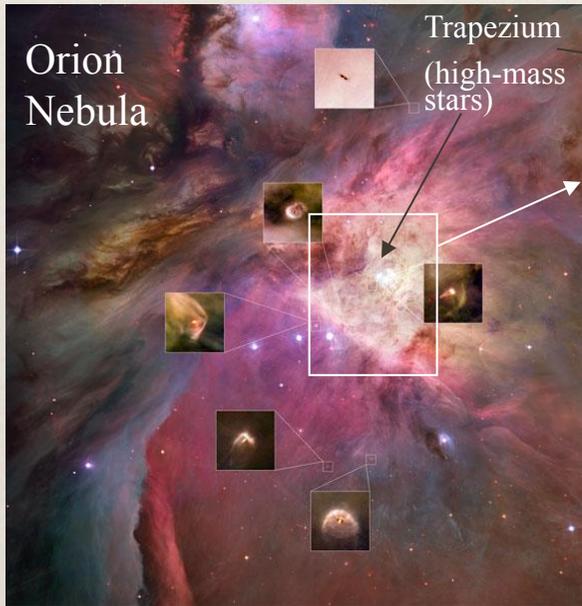
Do some molecules in comets come from the ISM?

- ❖ Competition between Orion-KL and SgrB2(N)

The Orion Kleimann-Low nebula

A stellar encounter 500-1000 yr ago!

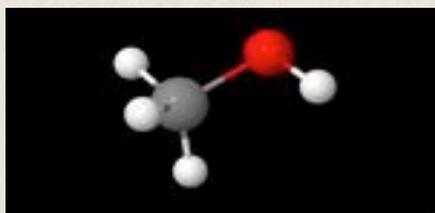
A *high-mass star* forming region
414 pc from the Sun
(Menten et al. 2007)



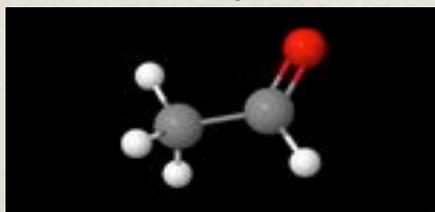
- Shock waves
- Unique conditions for the study of interstellar chemistry: *recent desorption (< 1000 yr)* of molecules from the icy mantles of interstellar grains

Main molecules under study

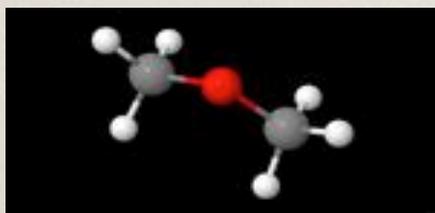
- Small organic molecules



Methanol CH_3OH



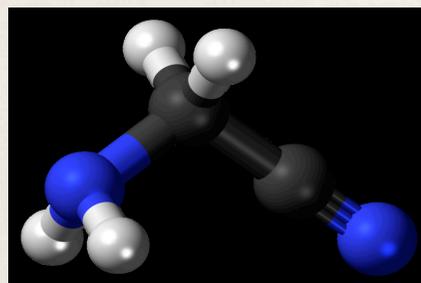
Acetaldehyde CH_3CHO



Dimethyl ether CH_3OCH_3

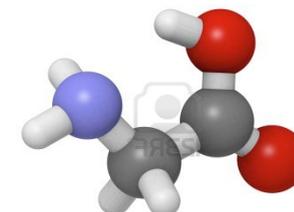


Methyl formate HCOOCH_3



Aminoacetonitrile $\text{NH}_2\text{CH}_2\text{CN}$

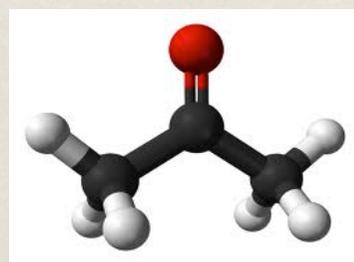
H_2O (liq.)



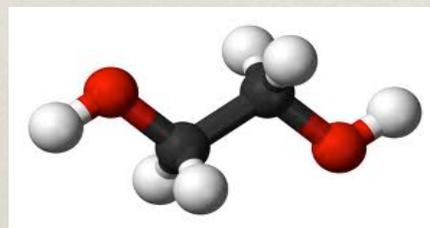
Glycine $\text{NH}_2\text{CH}_2\text{COOH}$
(amino acid)

- Search for molecules of interest for prebiotic chemistry: upper limits in Orion KL

- Glycolaldehyde, CH_2OHCHO , a pre-sugar
 - Aminoacetonitrile, $\text{NH}_2\text{CH}_2\text{CN}$, a glycine precursor
 - Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$, itself
- have been searched for but only upper limits have been obtained in Orion-KL (e.g. Favre et al 2011)

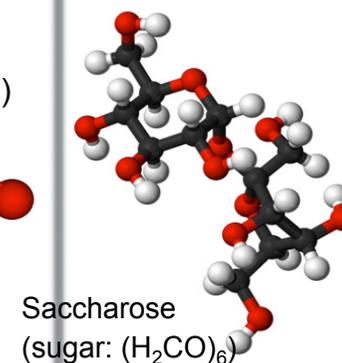
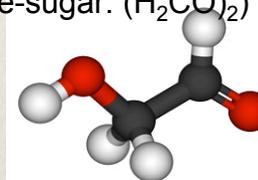


Acetone CH_3COCH_3



Ethylene glycol $\text{CH}_2\text{OHCH}_2\text{OH}$

Glycolaldehyde
 CH_2OHCHO
(pre-sugar: $(\text{H}_2\text{CO})_2$)

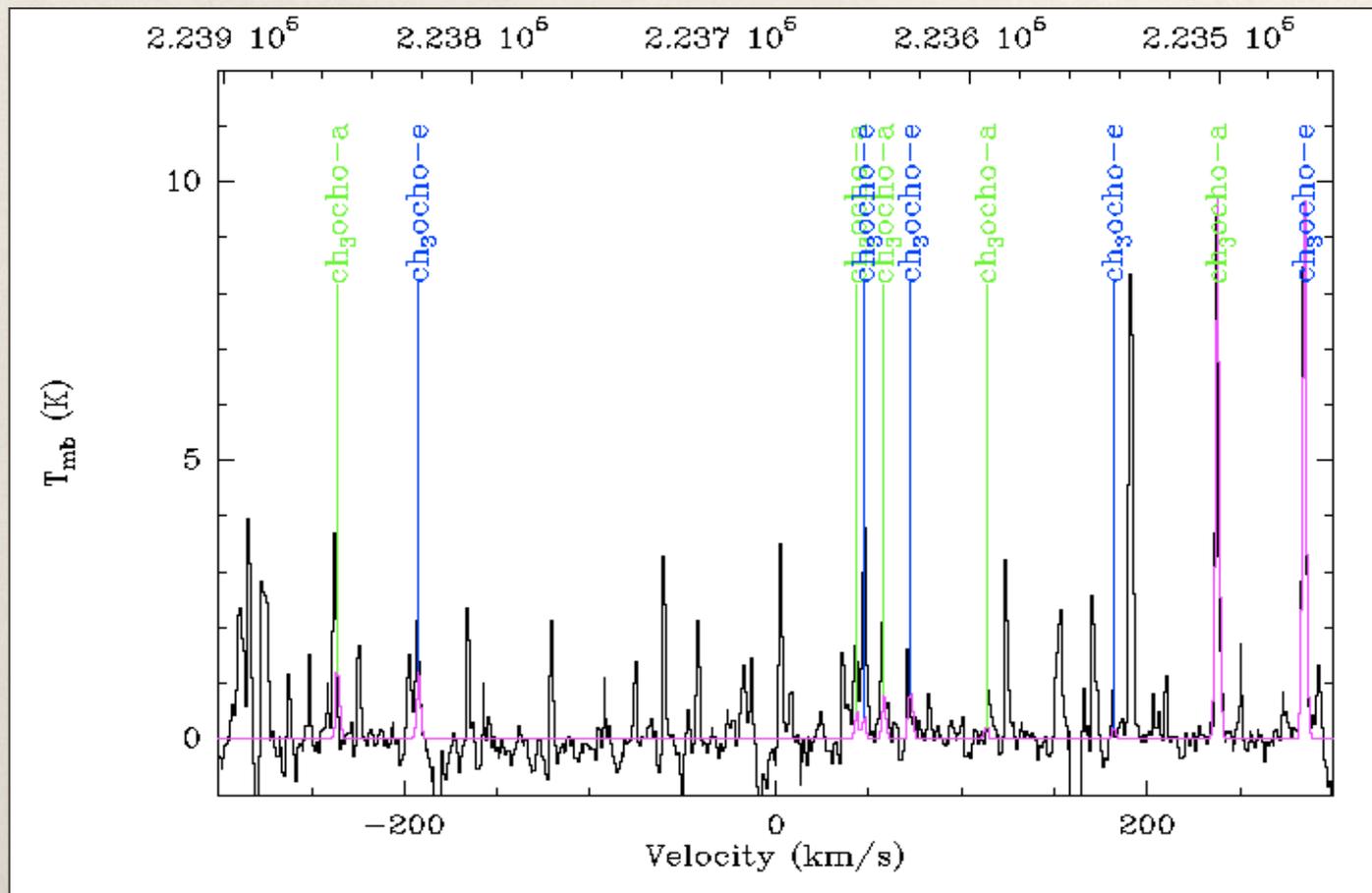


Saccharose
(sugar: $(\text{H}_2\text{CO})_6$)

Detection of a molecule

✧ Main criteria to detect a molecule

- rest frequencies known with a high degree of accuracy
- the central velocity and line width must agree for all detected transitions
- consistency of the relative intensities of the different transitions
- all transitions with intensity predictions leading to detectable signal levels must be present



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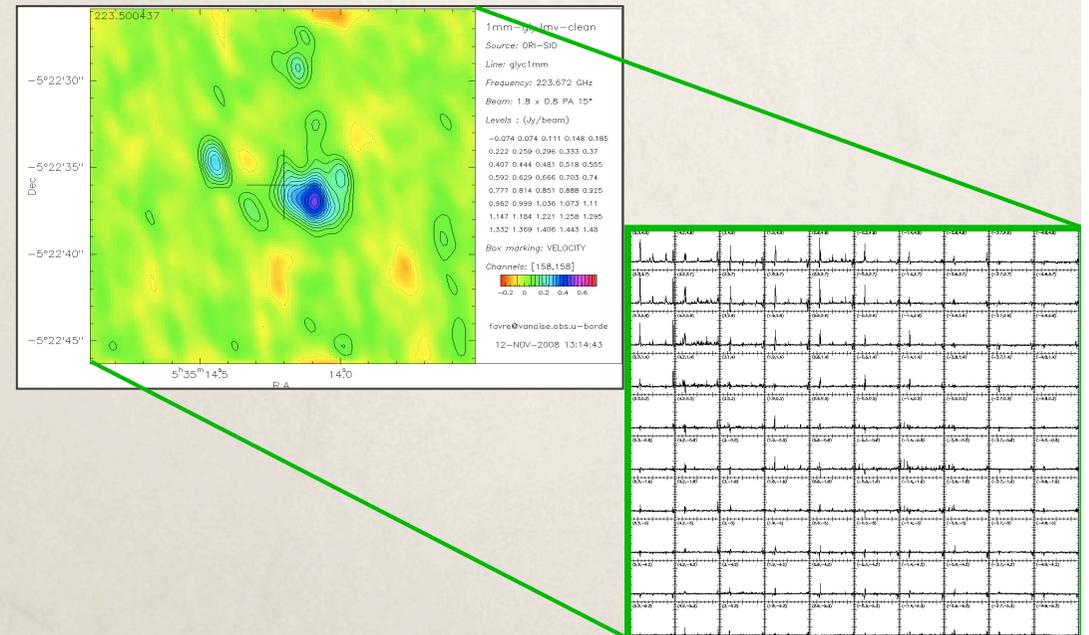
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✧ Problems: confusion, weakness of the lines

Need for good spectroscopic data

Need for large bandwidth (to have enough good lines)

High spatial resolution observations improve fighting the confusion problem (different molecules usually have different spatial distributions)



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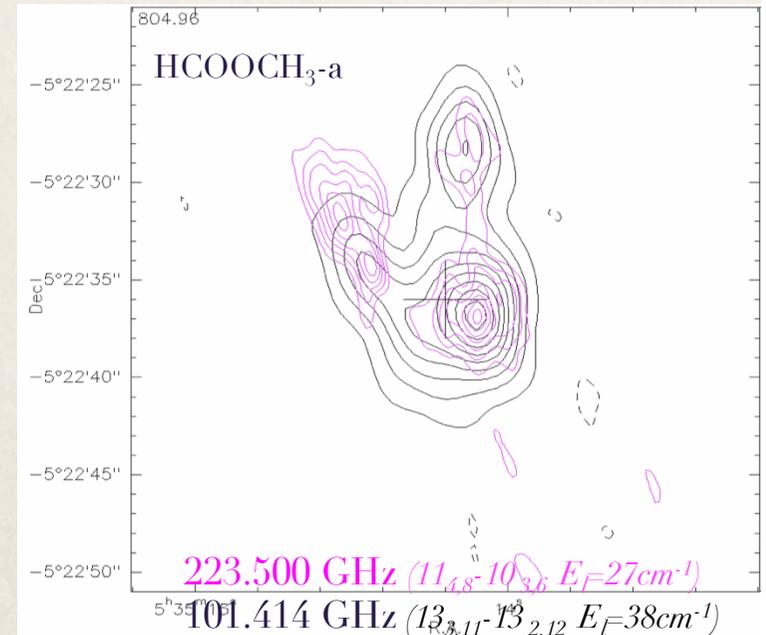
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- ✧ **Solution:** line surveys with broad bandwidth + maps (coherent spatial distribution, i.e. same distribution for transitions of similar energies)



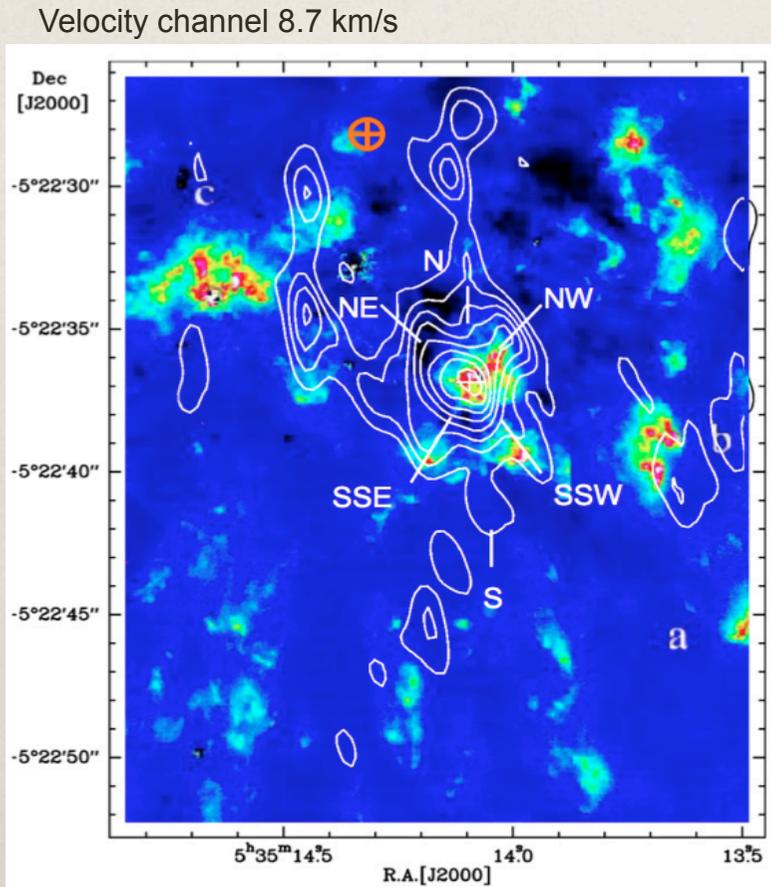
➔ **ALMA:** high sensitivity and broad frequency range + spatial resolution to image the relevant physical and chemical scales

➔ **Time consuming:** need to develop new analysis tools and new methods

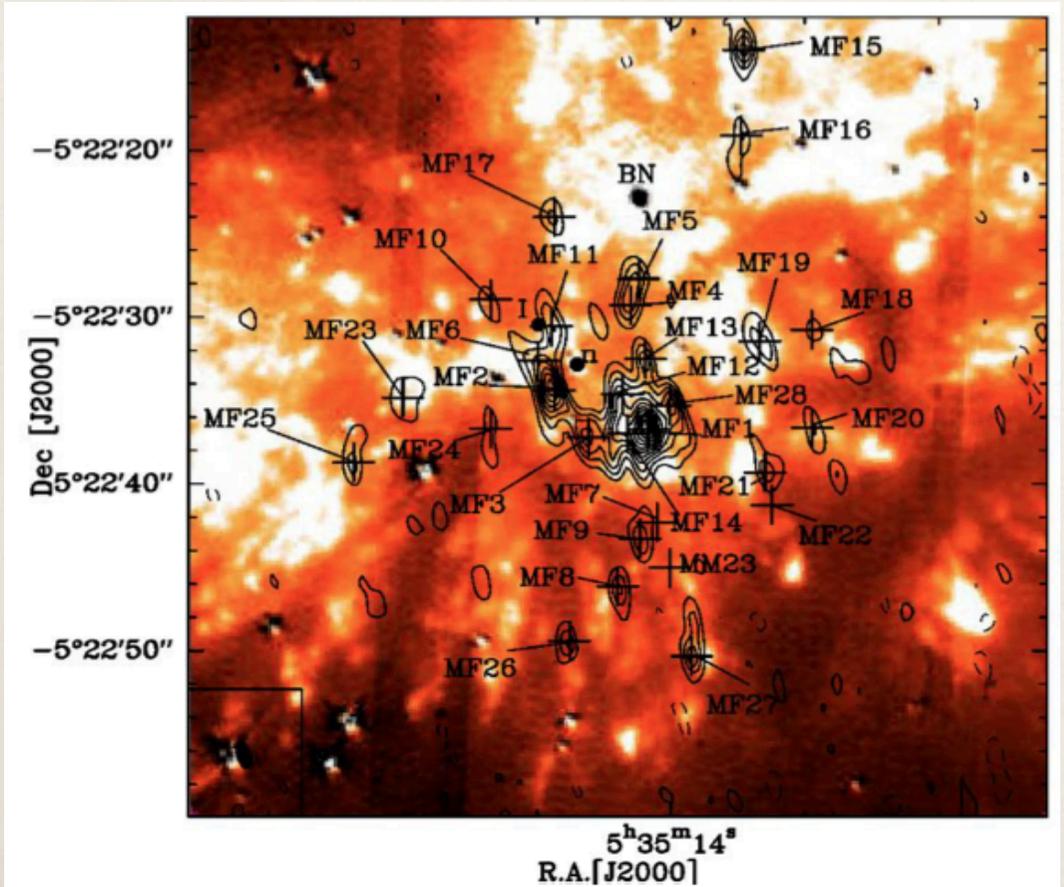
Methyl formate HCOOCH_3 : a link with shocks?

The study of HCOOCH_3 has shown some spatial association between this molecule and the peaks of the $2.12 \mu\text{m}$ excited H_2 emission, which traces shocks.

Contours: HCOOCH_3



H_2 2.2 μm Map- Lacombe et al. 2004



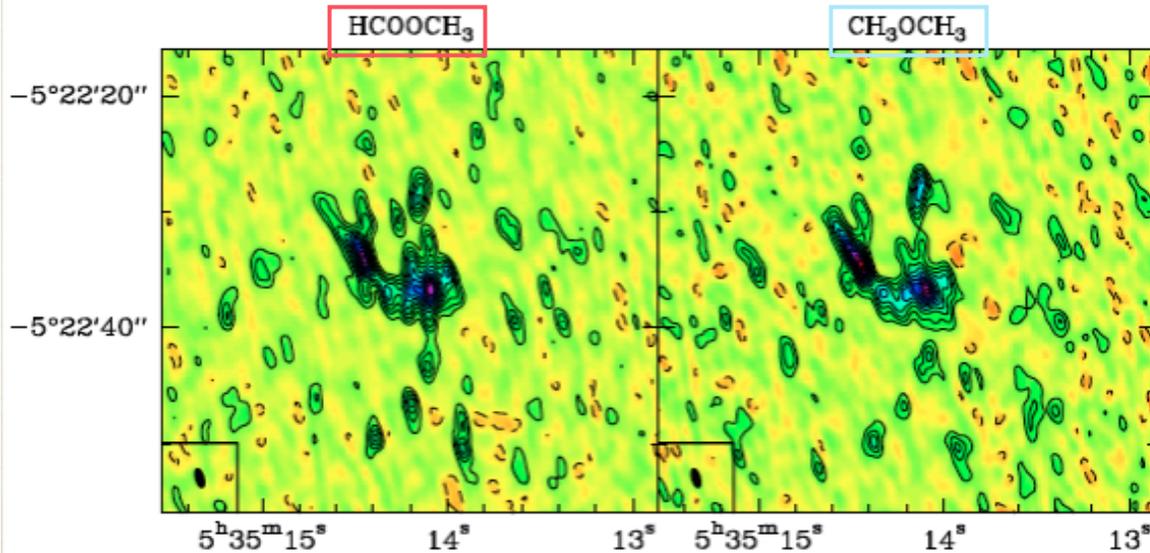
Contours: IRAM Plateau de Bure observations

H_2 2.2 μm Map - Subaru Telescope

Background images: shocked gas

Favre et al. 2011

Methyl formate vs Dimethyl ether



Spatial distribution (spatial resolution 1.8"x0.8" ~ 500 AU)

Striking correlation of the spatial distribution of methyl formate and dimethyl ether on a small scale.

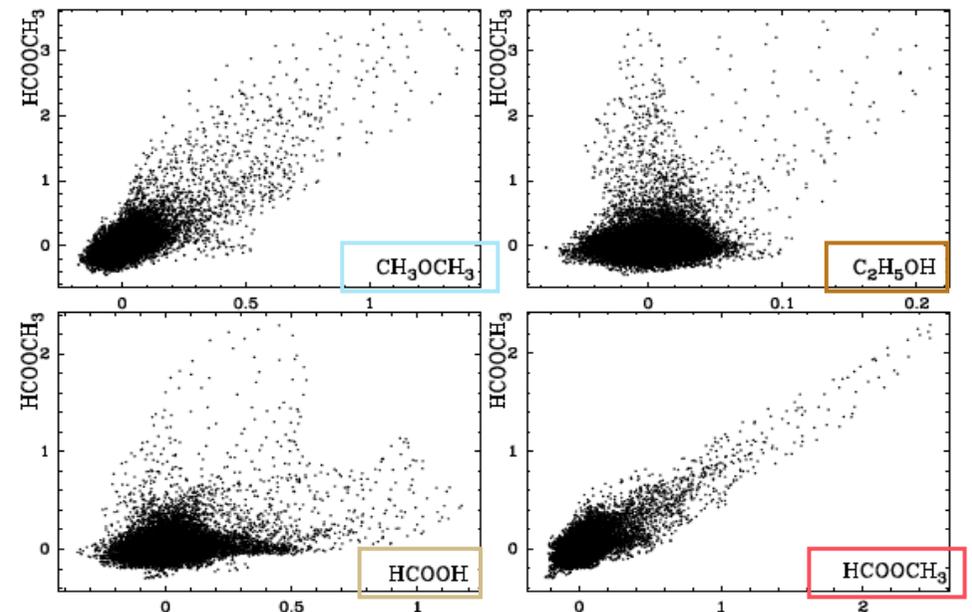
A common precursor is the simplest explanation.

Brouillet et al. 2013

Left: map of methyl formate at 223.534 GHz, $E_u=305$ K

Right: map of dimethyl ether at 223.41 GHz, $E_u=330$ K

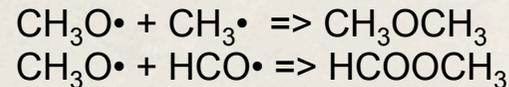
Pixel to pixel correlations



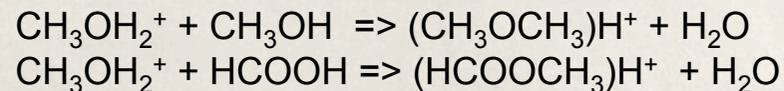
Similarity of dimethyl ether CH_3OCH_3 and methyl formate HCOOCH_3 spatial distributions: a common precursor ?

Two main models have been proposed to form these species:

- ✧ **If the formation occurs on grains** (Bisschop et al 2007, Oberg et al 2010), the common precursor would be the $\text{CH}_3\text{O}\cdot$ radical:



- ✧ **If the formation takes place in the gas phase**, protonated methanol CH_3OH_2^+ would be the common precursor (Neill et al 2010) of the related protonated species



An electronic dissociative recombination of the latter would complete the process. The presence of protonated methanol is linked to methanol injection into the gas phase from icy grain mantles.

Another reaction, producing HCOOCH_3 from H_2CO has been considered (Blake et al 1988), but suffers from a too high energy barrier ($128 \text{ kJ}\cdot\text{mol}^{-1} \sim 15000 \text{ K} \sim 1.2 \text{ eV}$; Horn et al. 2004).

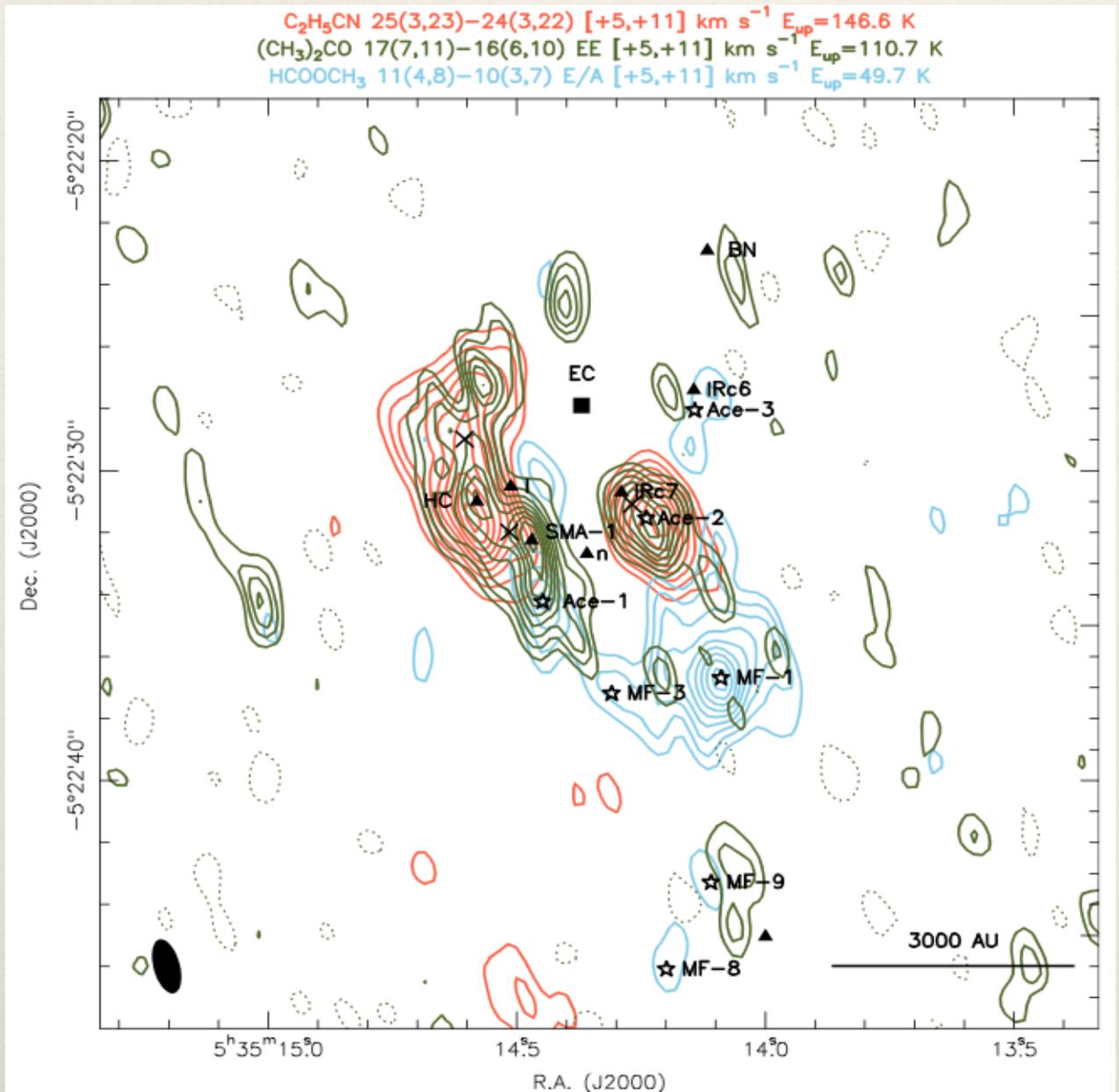
Could the supplement of (kinetic) energy in the shock help overcome this barrier ?

Acétone (CH₃)₂CO

The distribution of N-bearing (e.g. C₂H₅CN) and O-bearing (e.g. HCOOCH₃) molecules is clearly different in Orion BN/KL.

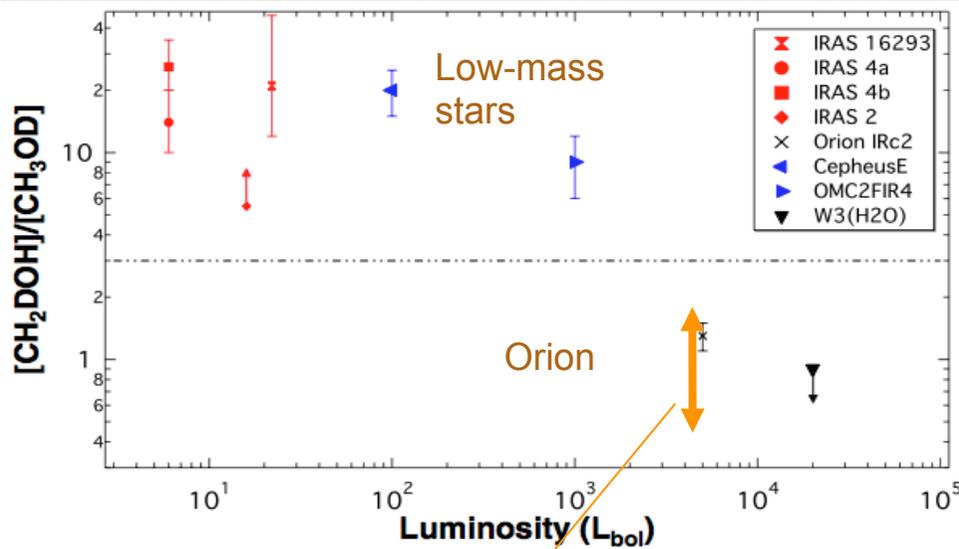
However **acetone**, (CH₃)₂CO, which is an O-bearing molecule, has a **very different distribution from those of large O-bearing molecules**. It is even similar to that of **N-bearing molecules** like C₂H₅CN and NH₃.

This suggests that the formation and/or destruction of acetone may involve ammonia or large N-bearing molecules in a shocked gas environment.



Deuterated methanol: CH₃OD vs CH₂DOH Sublimation of ancient ices?

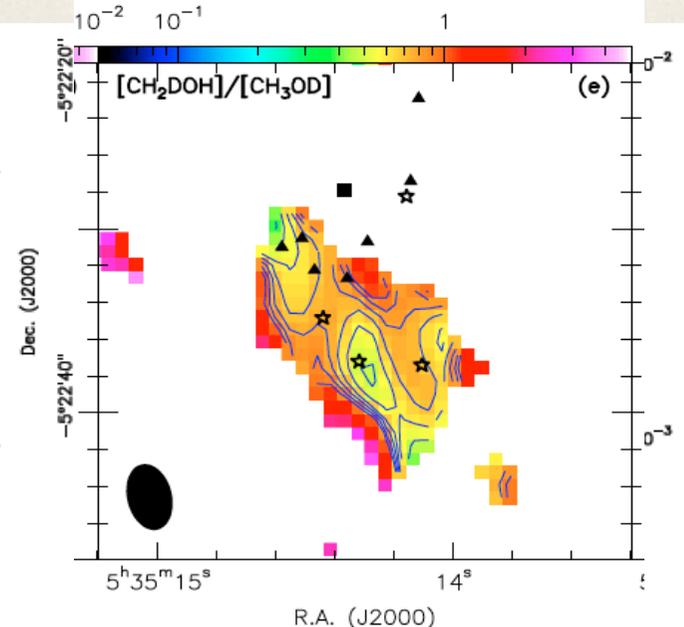
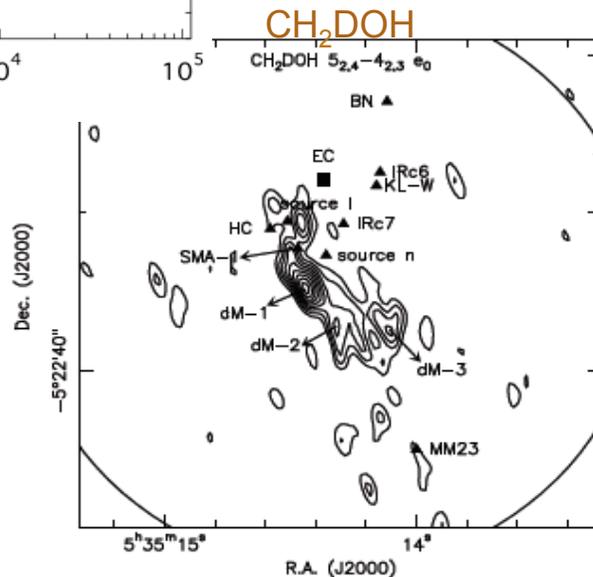
The study of deuterated methanol has shown that the ratio CH₂DOH/CH₃OD is relatively constant in Orion KL. This contrasts with the present variety of physical conditions in the region, and **suggests that deuterated methanol formed in ice mantles at a time the interstellar matter in the region was more homogeneous.**



The value we find (<1 on average) confirms the strong difference between Orion KL and the surroundings of low-mass protostars (e.g. IRAS16293) found by Rataczack et al 2011.

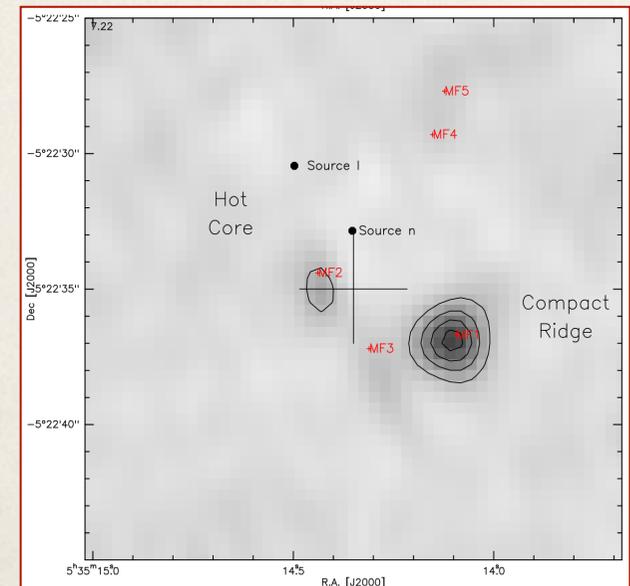
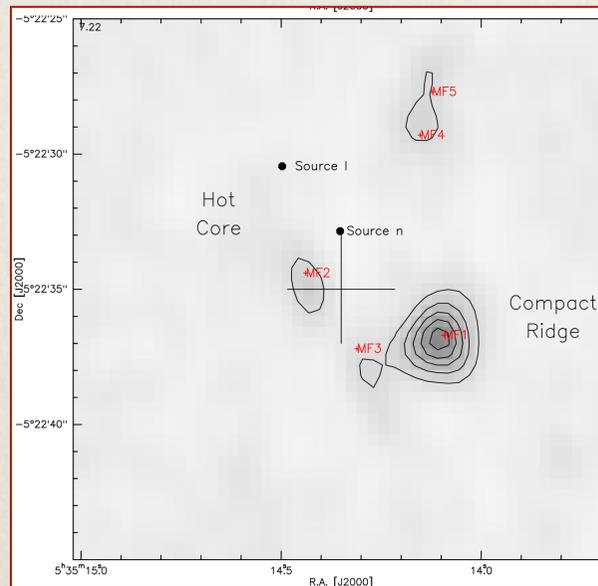
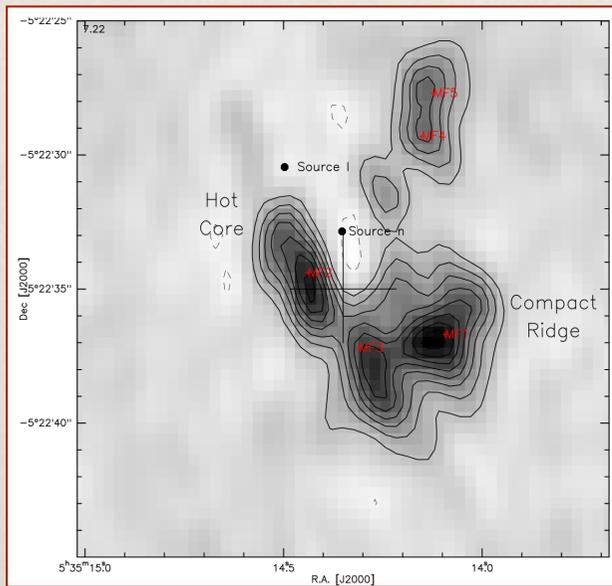
A simple model would give a statistical ratio of 3.

Range of values of CH₂DOH/CH₃OD in our map.



$^{12}\text{C}/^{13}\text{C}$ Methyl Formate

The analysis gives a $^{12}\text{C}/^{13}\text{C}$ isotopic ratio in methyl formate of 68.4 ± 10.1 toward the Compact Ridge and 71.4 ± 7.8 toward the Hot Core SW. For both ^{13}C -methyl formate isotopologues, it is close to the well-known $^{12}\text{C}/^{13}\text{C}$ ratio of the simple species CO and also of CH_3OH .



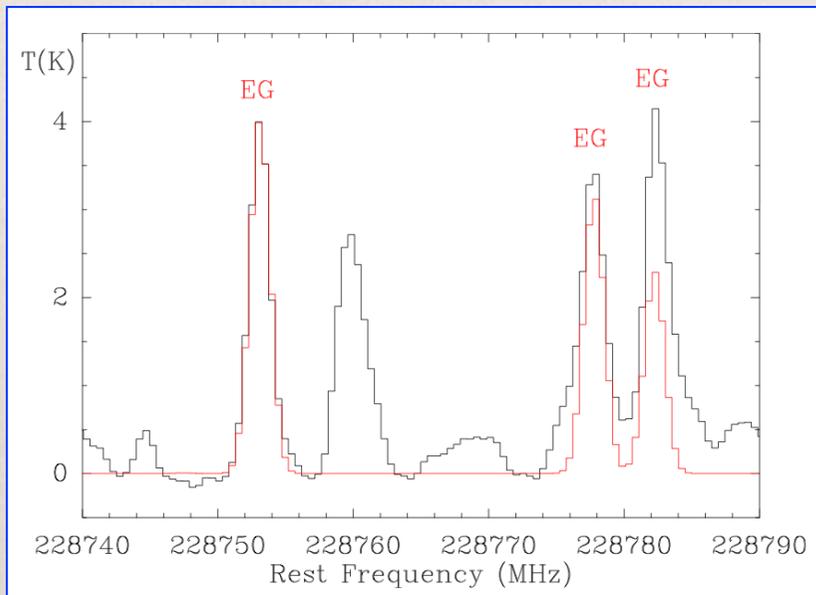
Emission channel maps at 7.22 km/s observed with ALMA.

The $^{12}\text{C}/^{13}\text{C}$ ratio derived from both ^{13}C -methyl formate isotopologues suggests that grain surface chemistry is at work in the Compact Ridge and Hot Core and that complex molecules are released from ice mantles.

Ethylene glycol: comparison with comets

We have detected ethylene glycol in Orion KL and the identification was possible thanks to the ALMA data:

- **high spatial resolution** observations improve considerably fighting the confusion problem as different molecules usually exhibit different spatial distributions.
- **a large frequency range** is necessary because many individual transitions (tens of lines) are required to securely identify large organic molecules (33 GHz for these ALMA data).



Part of the ALMA spectrum (in black) towards the ethylene glycol peak. The synthetic spectrum of ethylene glycol (EG) is overlaid in red. The parameters used for the synthetic spectrum are:

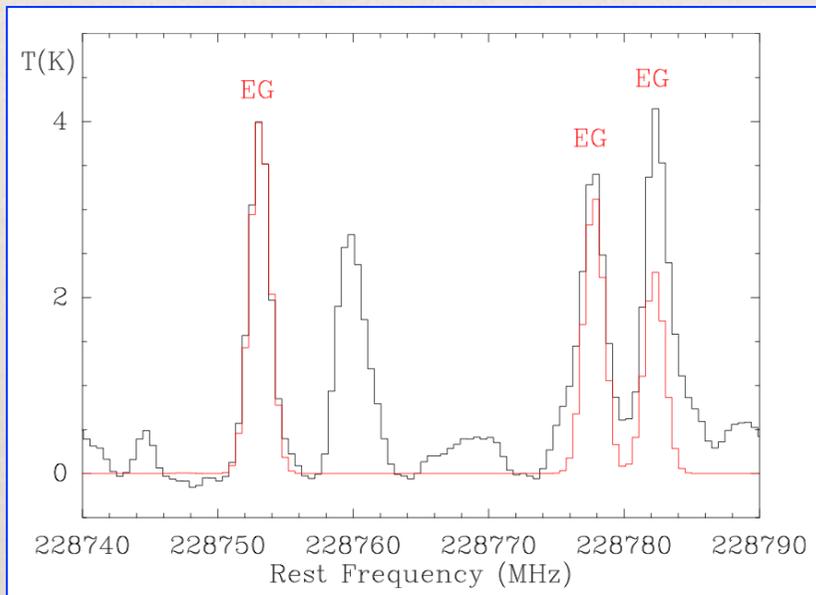
$$v_{LSR} = 7.6 \text{ km/s}, \Delta v_{1/2} = 2.3 \text{ km/s}, T = 145 \text{ K},$$

$N_{\text{HOCH}_2\text{CH}_2\text{OH}} = 4.6 \cdot 10^{15} \text{ cm}^{-2}$. Only the line on the left is devoid of confusion.

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Despite a good first order correlation between chemical abundances in comets and hot cores, complex oxygenated species do show differences:

- **Ethylene glycol**: difficult to detect in the interstellar medium but rather abundant with respect to other O-bearing species in Hale-Bopp.
- **Glycolaldehyde** shows similar abundances as Ethylene glycol in Sgr B2, while it has not yet been detected in Orion-KL and only a five times lower limit has been obtained in Hale-Bopp.
- **Ethanol**, an abundant species in the interstellar medium, is not yet detected in comets.

These molecules appear thus as key species in the comparison of interstellar and cometary ices, and the subsequent discussion on the formation of cometary matter.

Molecule	Column density ^a (cm ⁻²)		Abundance (%H ₂ O)
	Orion-KL	Sgr B2	Hale-Bopp
(CH ₂ OH) ₂	4.6 · 10 ¹⁵	2.3 · 10 ¹⁵	0.25
CH ₃ OH	4.2 · 10 ¹⁸	5.6 · 10 ¹⁸	2.4
CH ₃ CH ₂ OH	2.5 · 10 ¹⁶	2.1 · 10 ¹⁶	≤0.1
CH ₂ OHCHO	≤3.5 · 10 ¹⁴	1.8 · 10 ¹⁵	≤0.04

Comparison of the column densities of ethylene glycol and related molecules in Orion KL, Sgr B2 and comets.

Tentative detection of *trans* Ethyl Methyl Ether t-CH₃CH₂OCH₃

Comparison of the distribution of species containing the functional groups **formate**, **ether** and **alcohol** with both the **methyl** and **ethyl** groups (ALMA data).

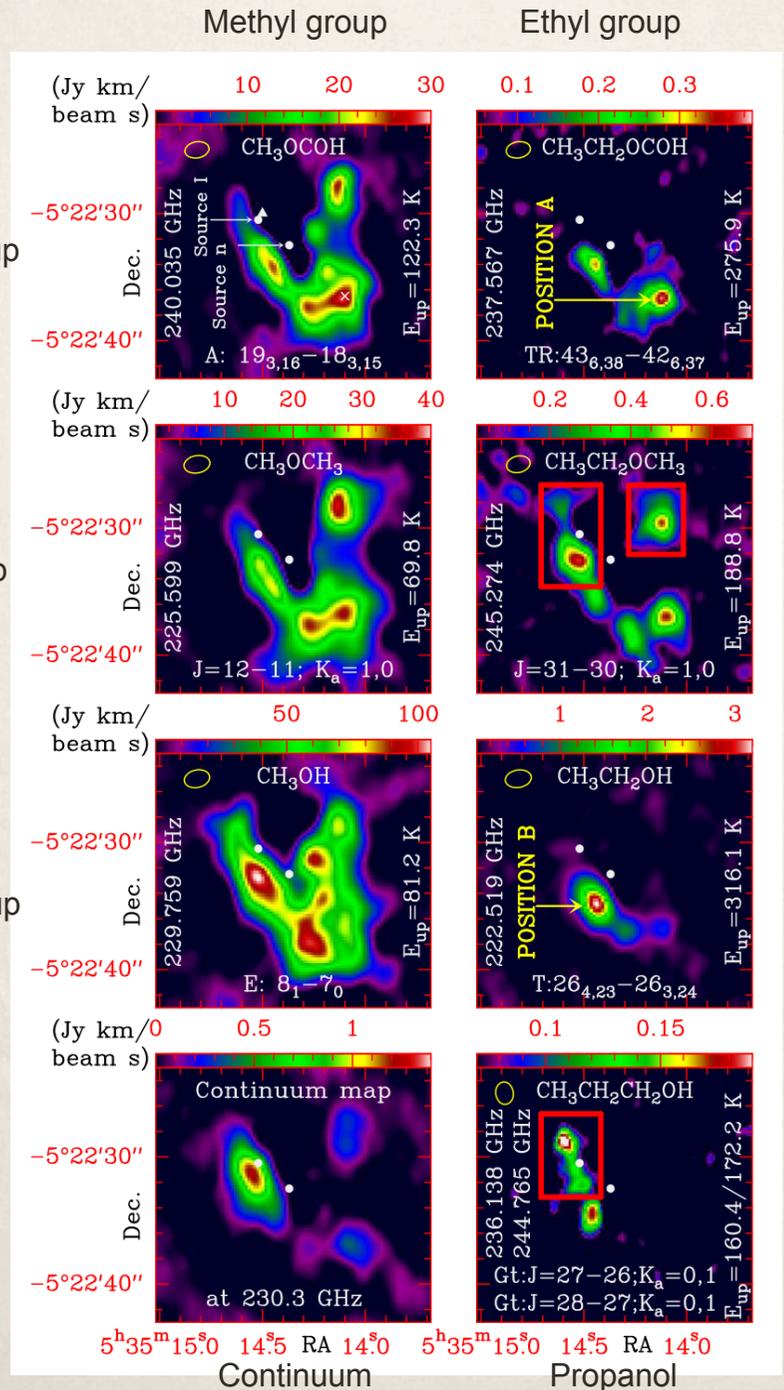
Emission that probably arises from blended species in these maps is confined inside red rectangles.

Comparing the methyl and ethyl species, we note a reduced spatial distribution of the three ethyl species with respect to their methyl counterpart.

Formate group

Ether group

Alcohol group





Conclusion

- ✧ The Orion-KL region is one of the two richest interstellar molecular sources, with SgrB2, known in our Galaxy. A better knowledge of the physical and chemical conditions in this region will help us to constrain the molecular formation pathways and to investigate the limit of molecular complexity in the interstellar medium.
- ✧ Importance of a large bandwidth to detect the complex molecules.



Thankyou for your attention!

