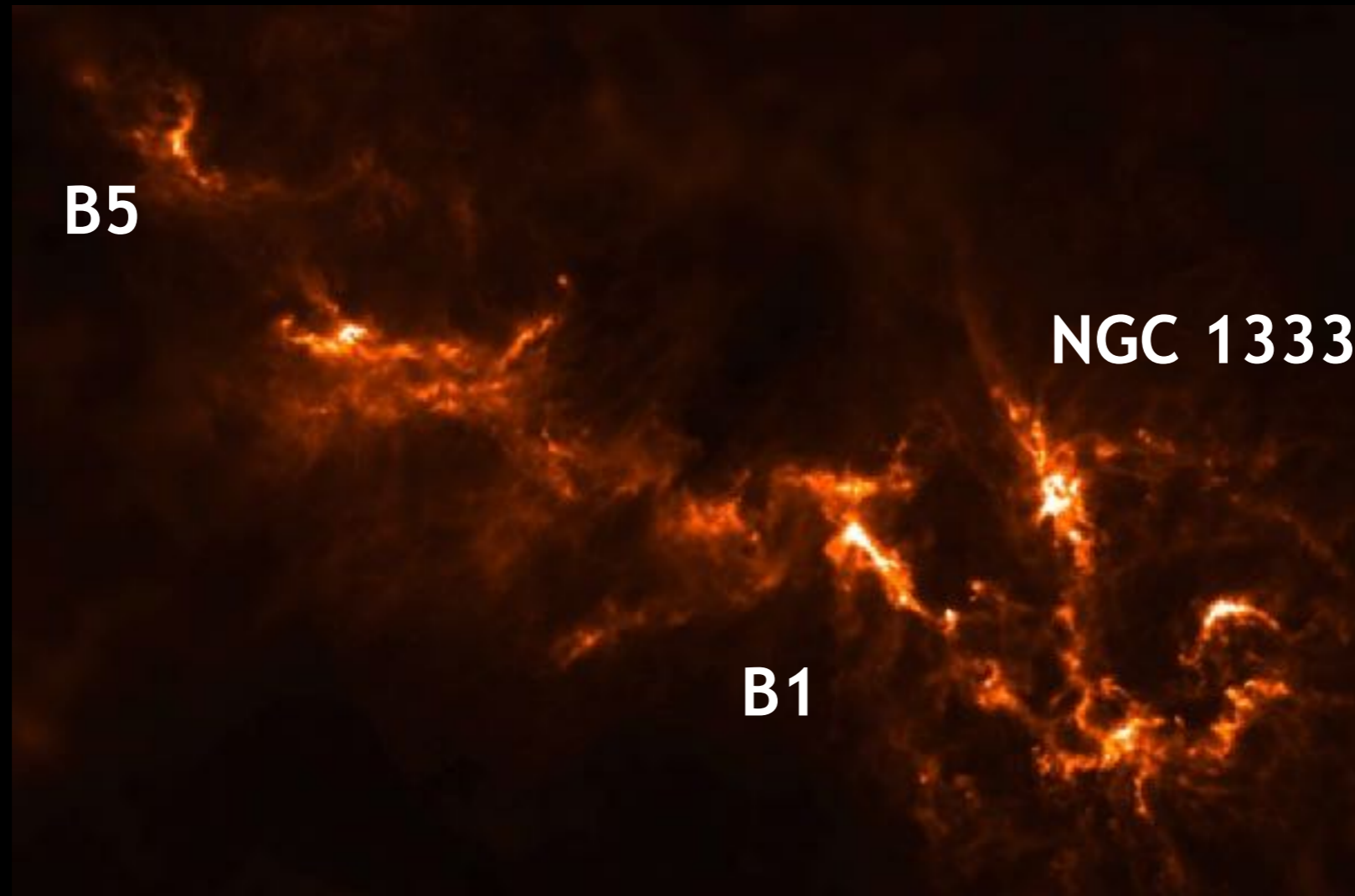


# Cold gaseous methanol and non-thermal desorption processes



Perseus molecular cloud as observed with the *Herschel* Space Observatory (Gould Belt Survey, PI: P. André)

**Vianney Taquet**

INAF - Osservatorio Astrofisico di Arcetri  
Marie Sklodowska-Curie AstroFlt2 fellow

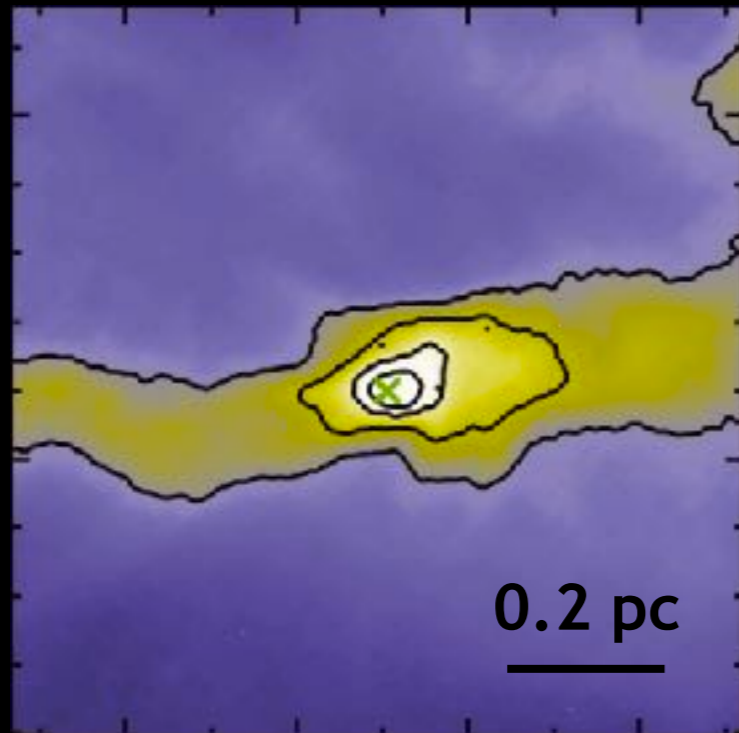


# Cold COMs in prestellar cores

First detections of several saturated O-bearing complex organic molecules in nearby prestellar cores: L1689B and L1544

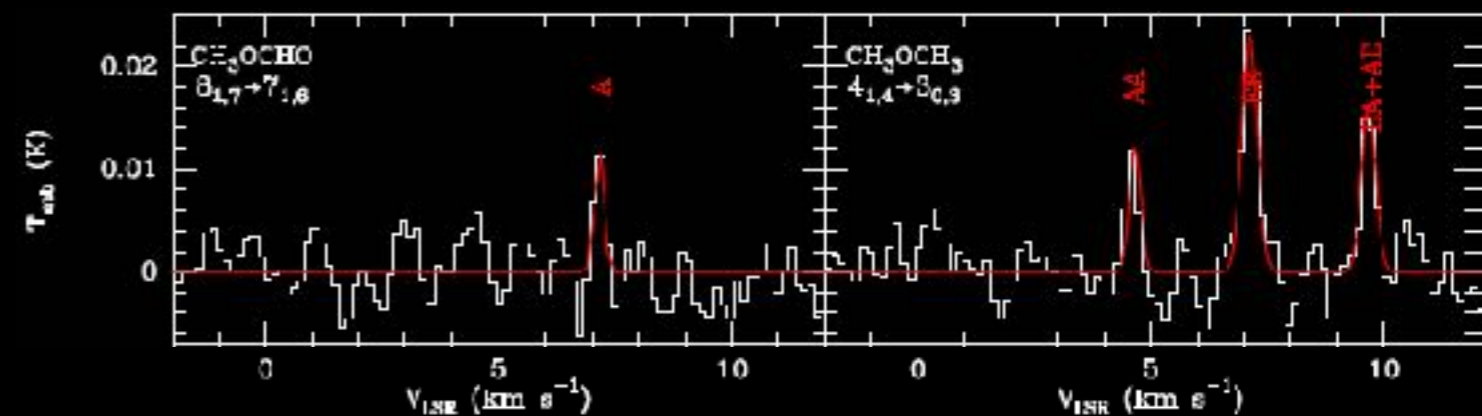
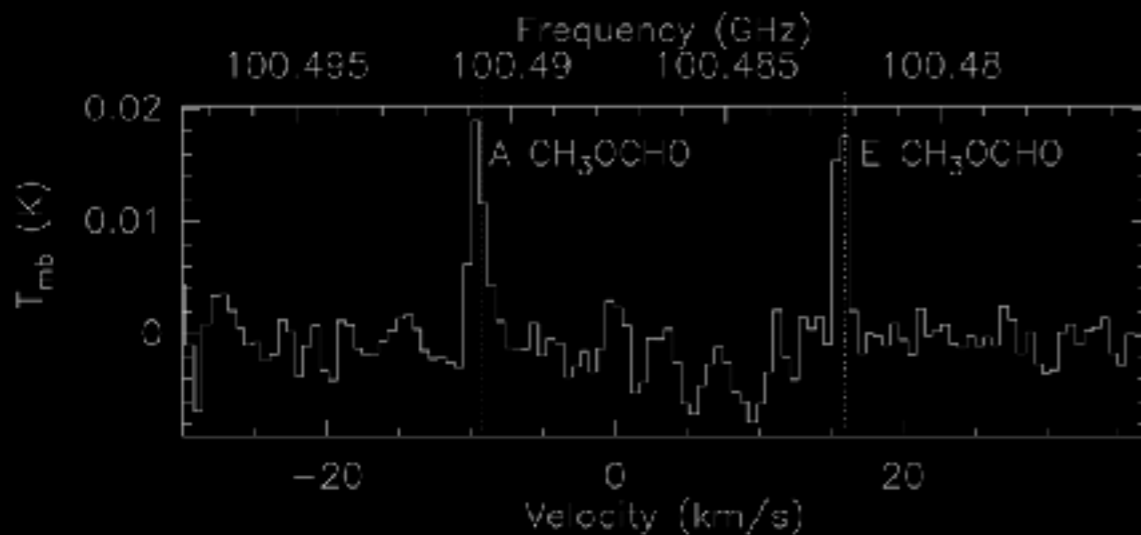
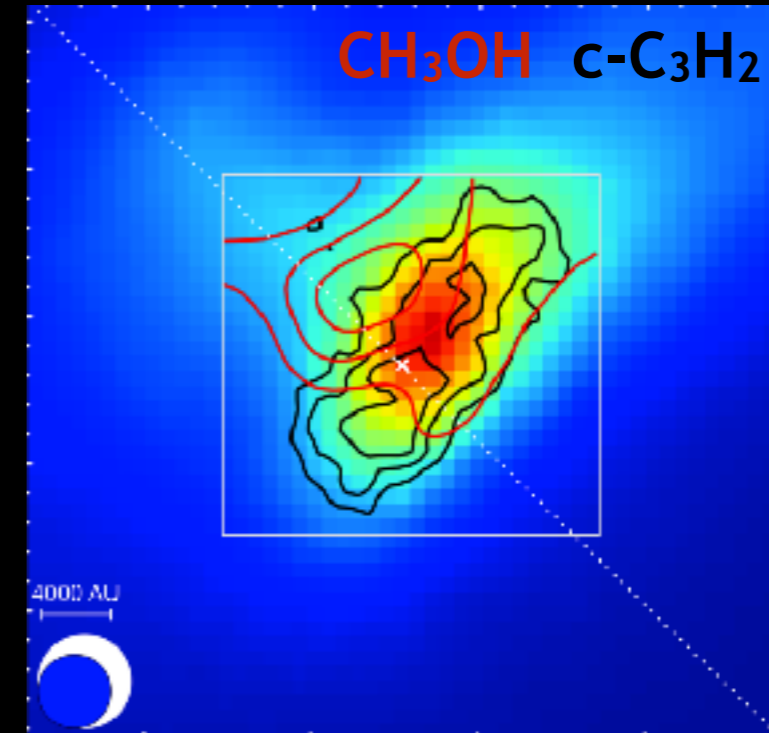
**L1689B**

Bacmann et al. (2012)

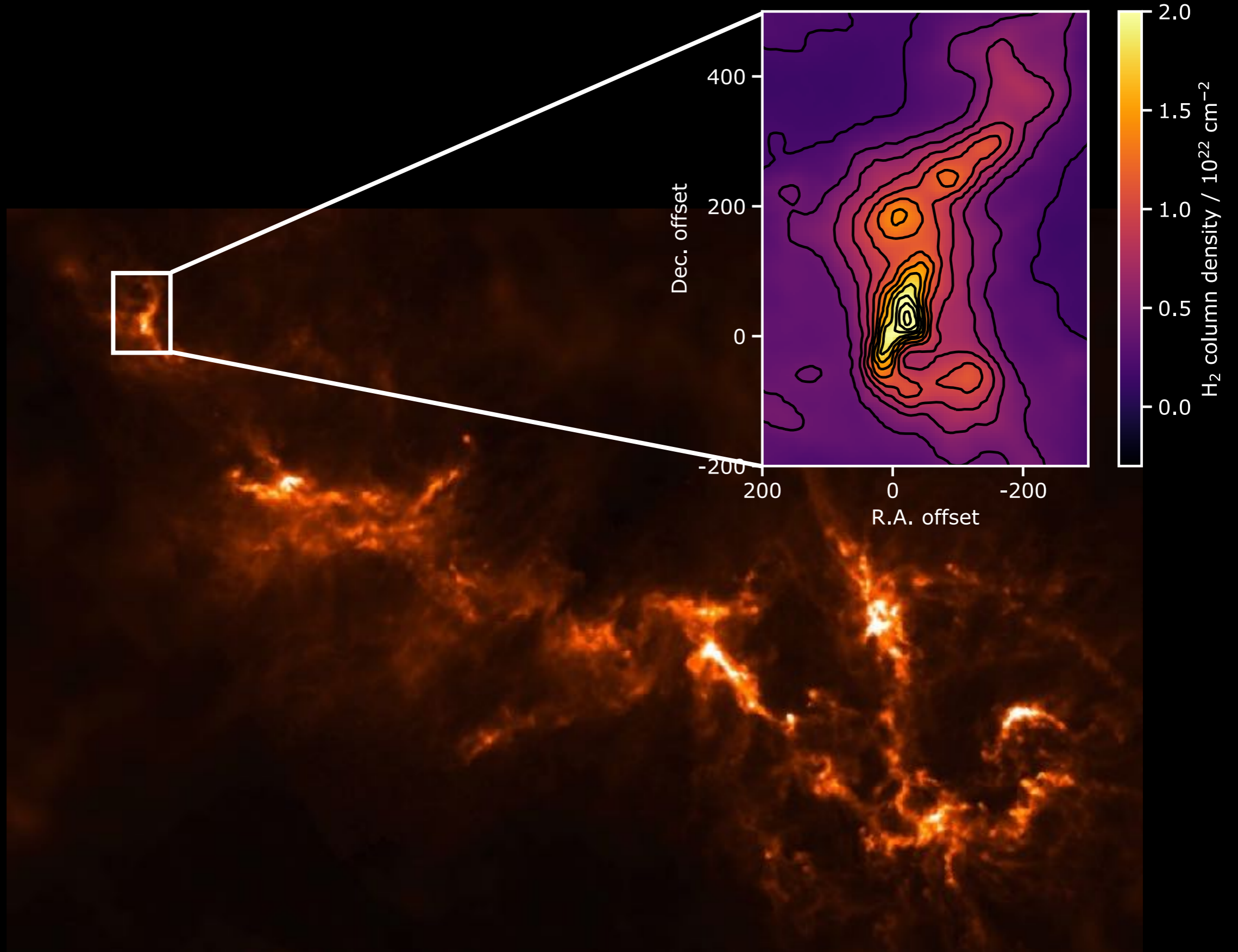


**L1544**

Vastel et al. (2014), Jimenez-Serra et al. (2016)



# The Barnard 5 molecular cloud

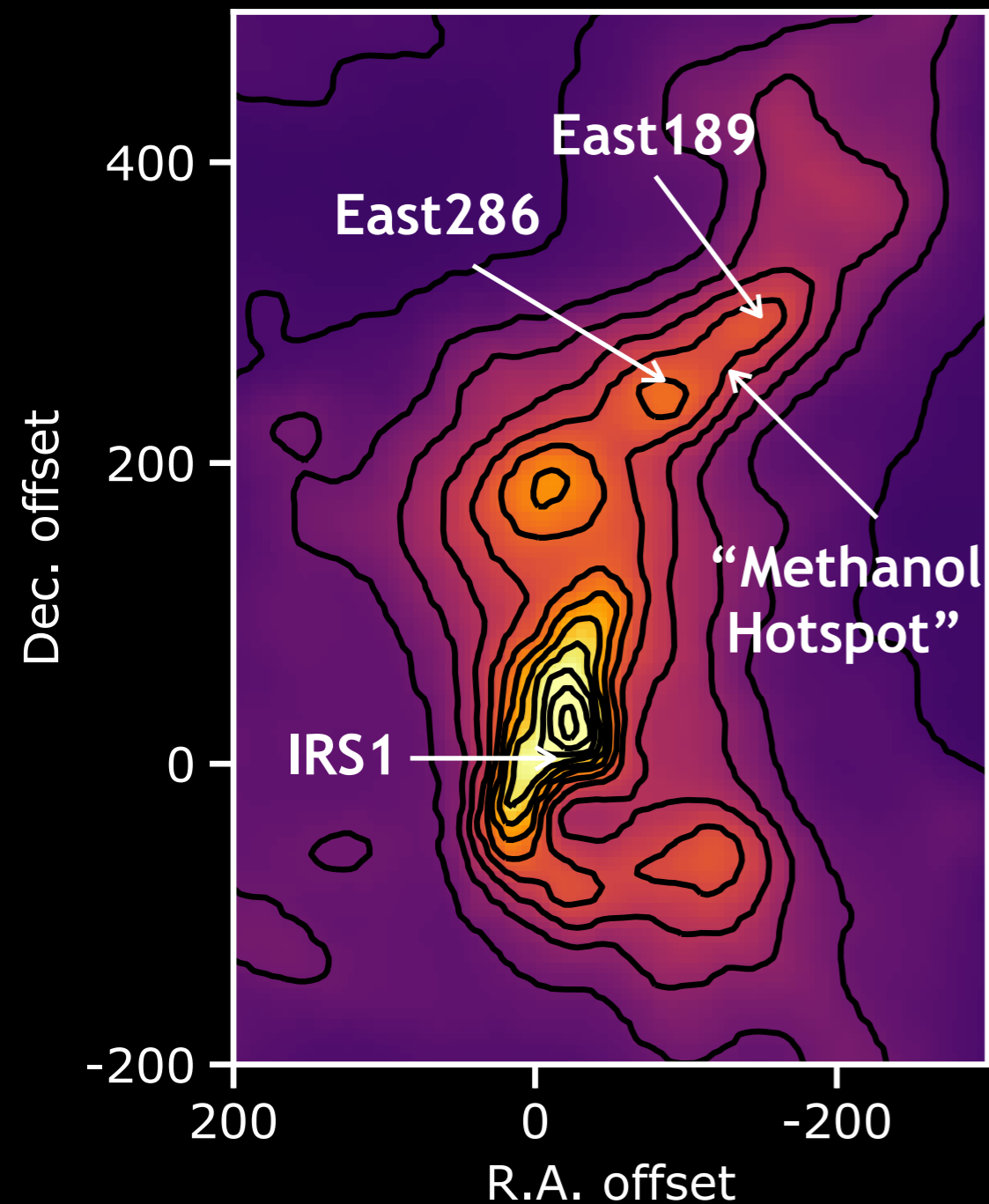


# The “methanol hotspot” in Barnard 5

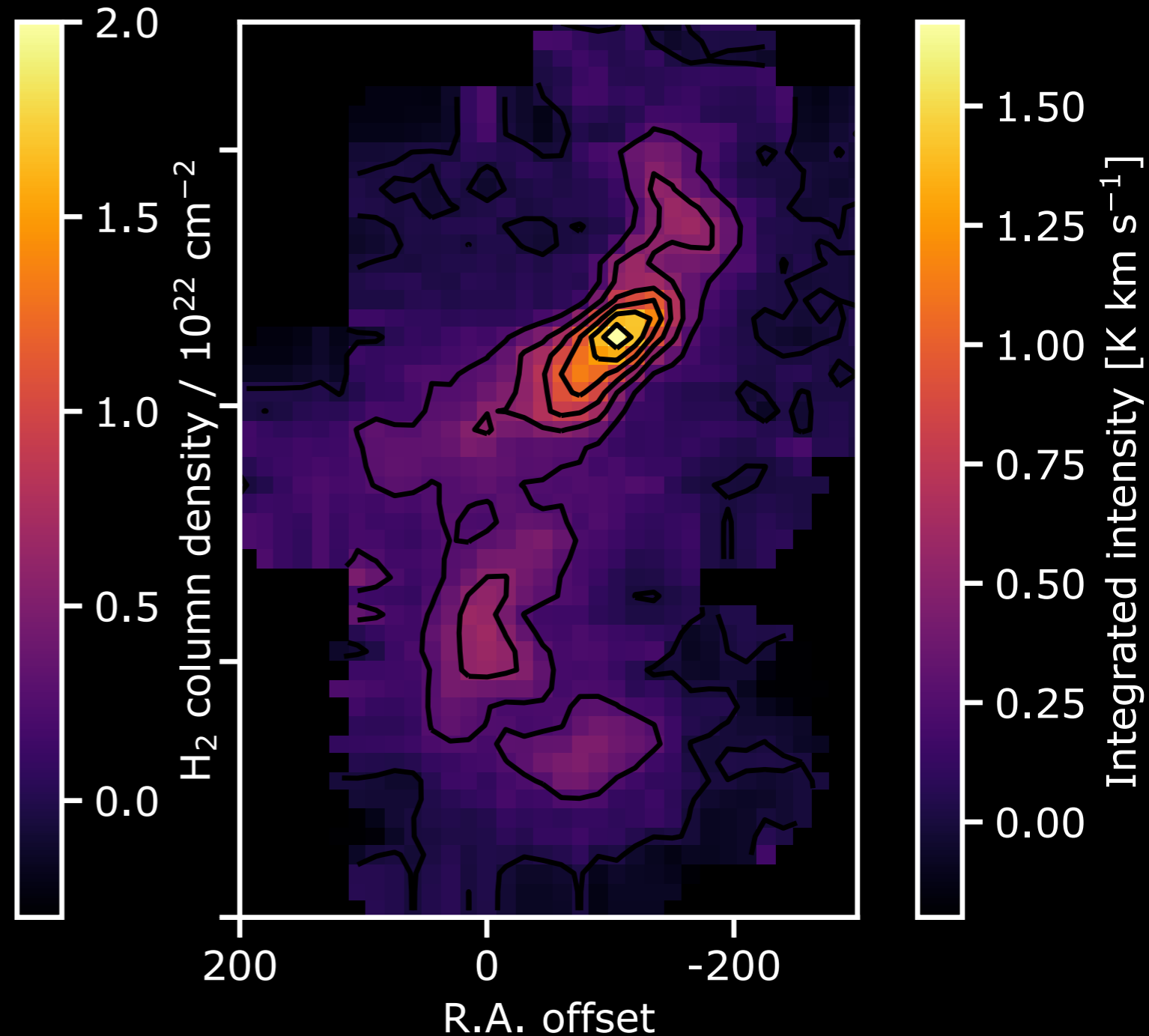
Detection of a “Methanol Hotspot” in the Barnard 5 Molecular Cloud, also showing water emission, located between two cold dense cores

(Wirström et al. 2014)

H<sub>2</sub> column density



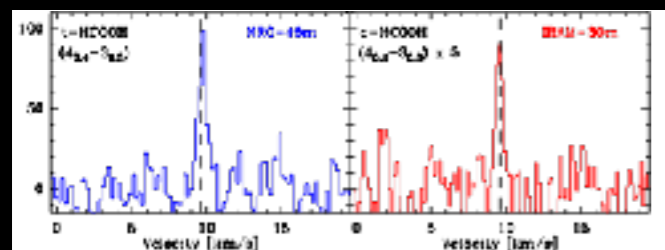
CH<sub>3</sub>OH @ 96.741 GHz



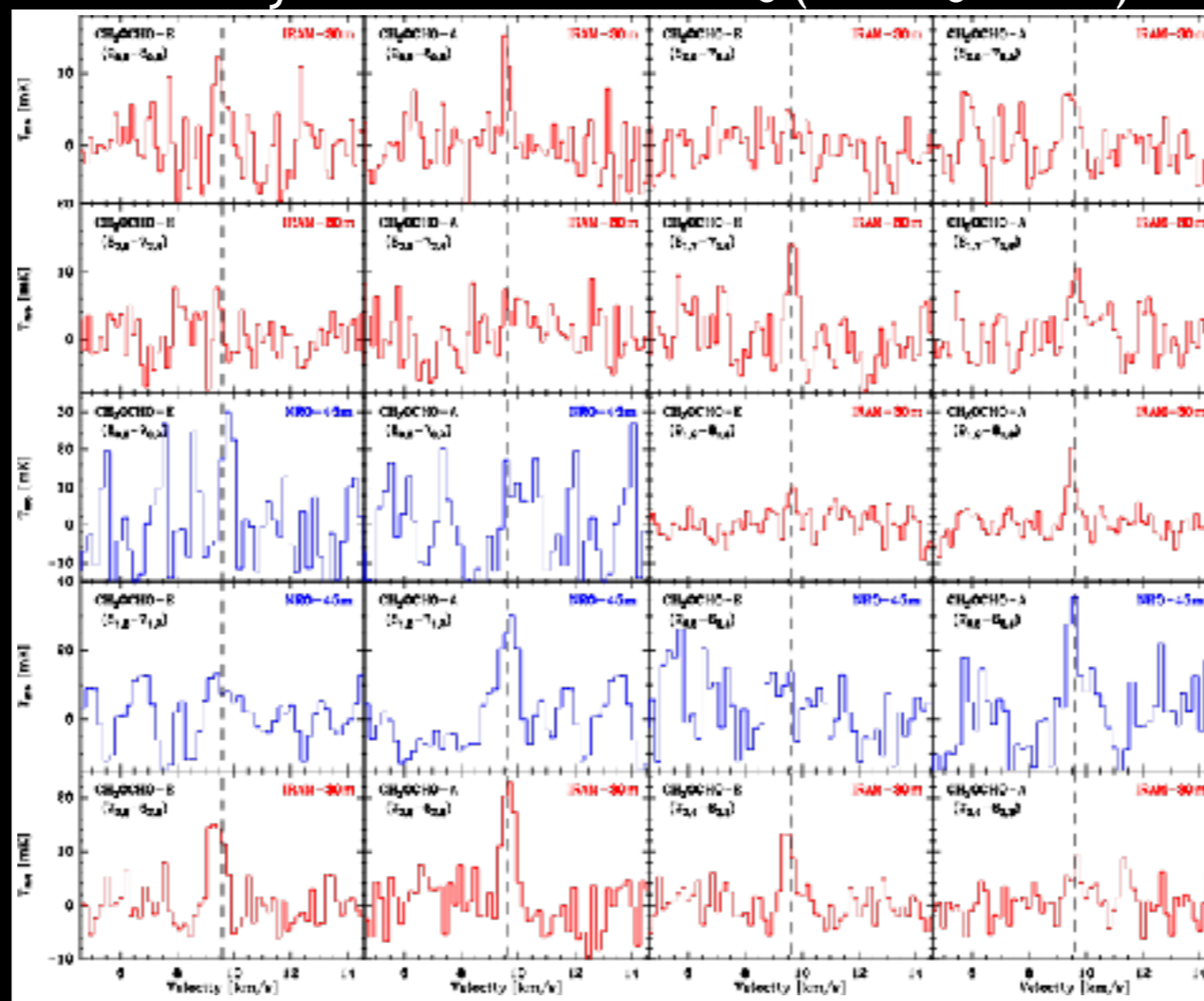
# Detection of COMs in Barnard 5

Detection of several O-bearing COMs with the IRAM 30m, NRO 45m, and OSO 20m towards the methanol hotspot

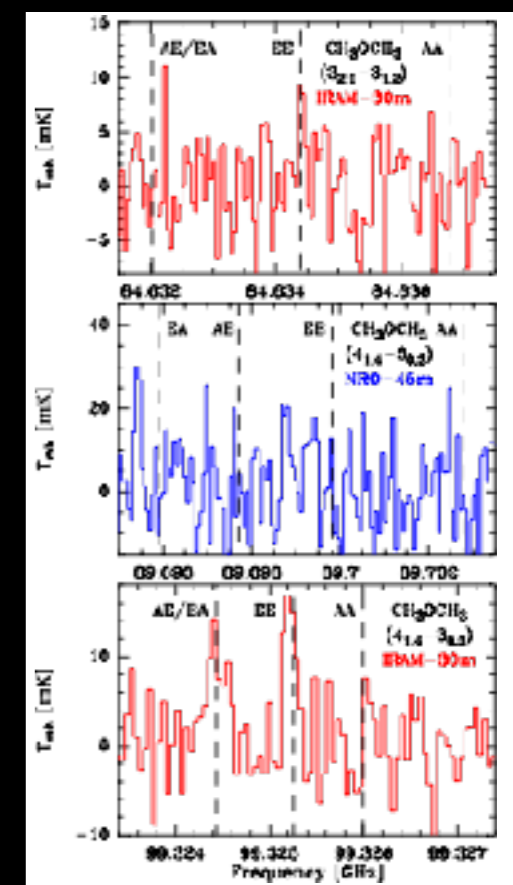
Formic acid HCOOH



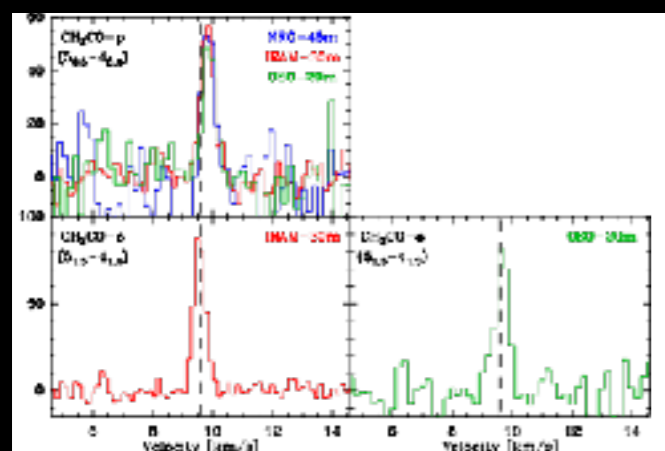
Methyl formate HCOOCH<sub>3</sub> (or CH<sub>3</sub>OCHO)



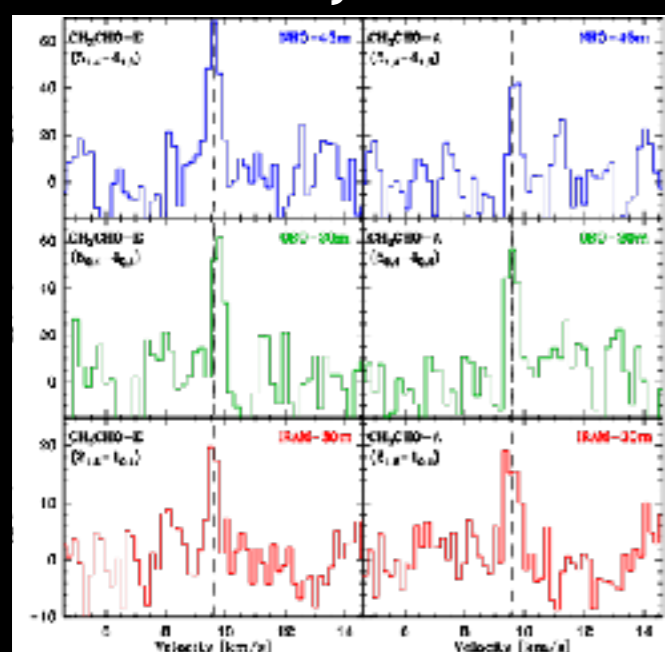
Tentative detection of dimethyl ether CH<sub>3</sub>OCH<sub>3</sub>



Ketene CH<sub>2</sub>CO

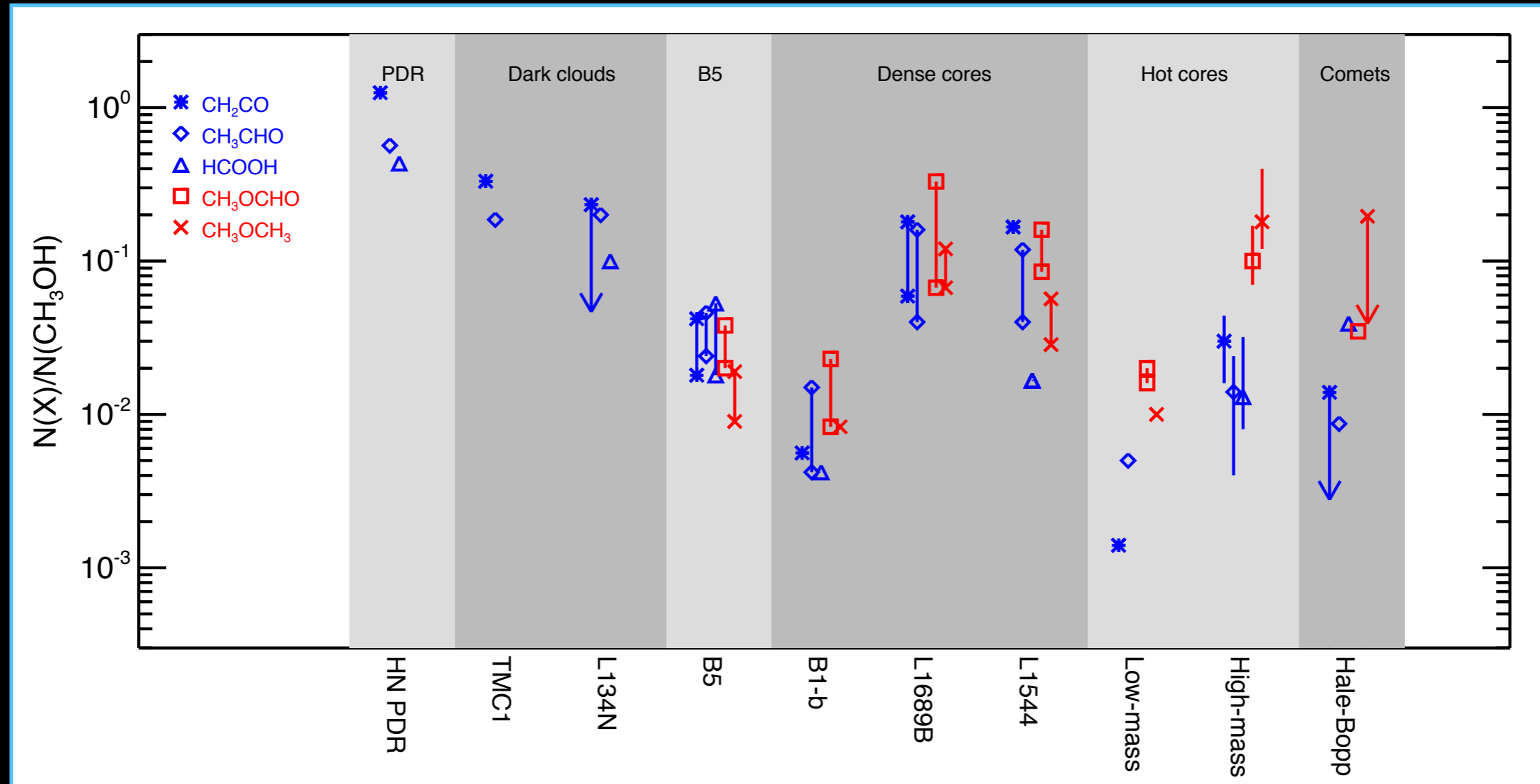


Acetaldehyde CH<sub>3</sub>CHO



# Abundances of COMs with evolutionary stage

Abundances of “cold” COMs decrease with respect to “warm” species with the evolutionary stage

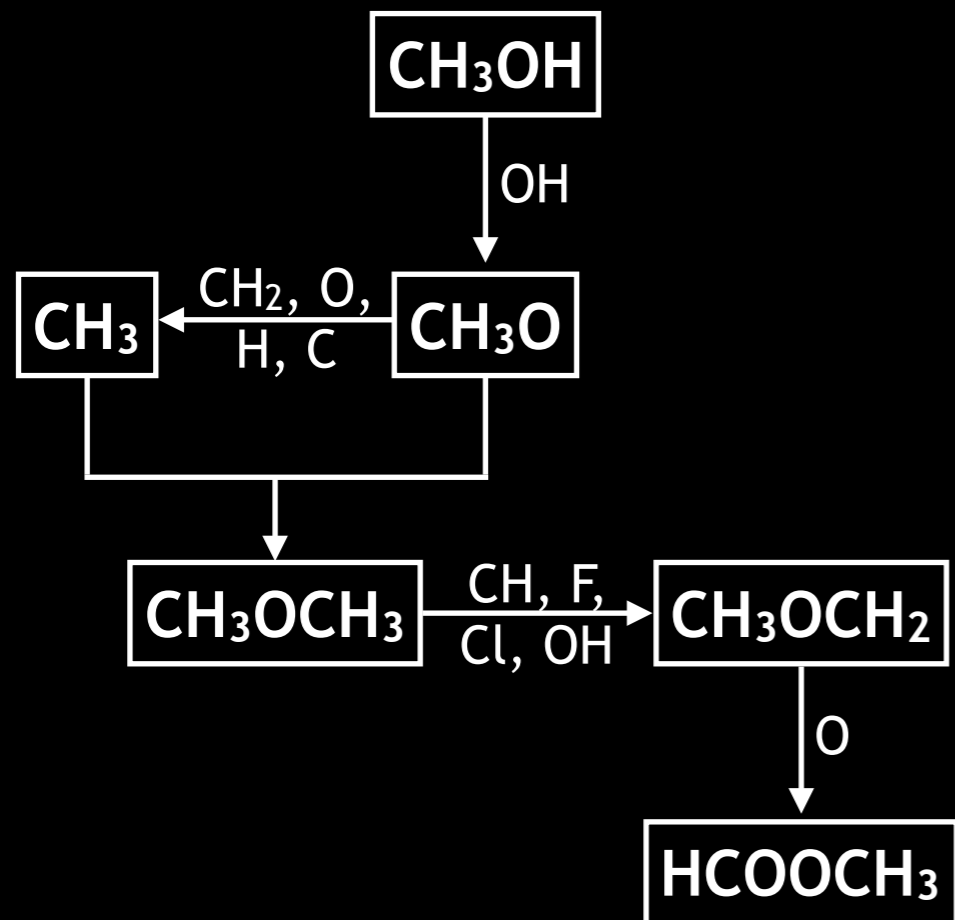


“Warm” species would be mainly produced after the “cold” species (i.e. during the protostar stage) or “cold” species are destroyed

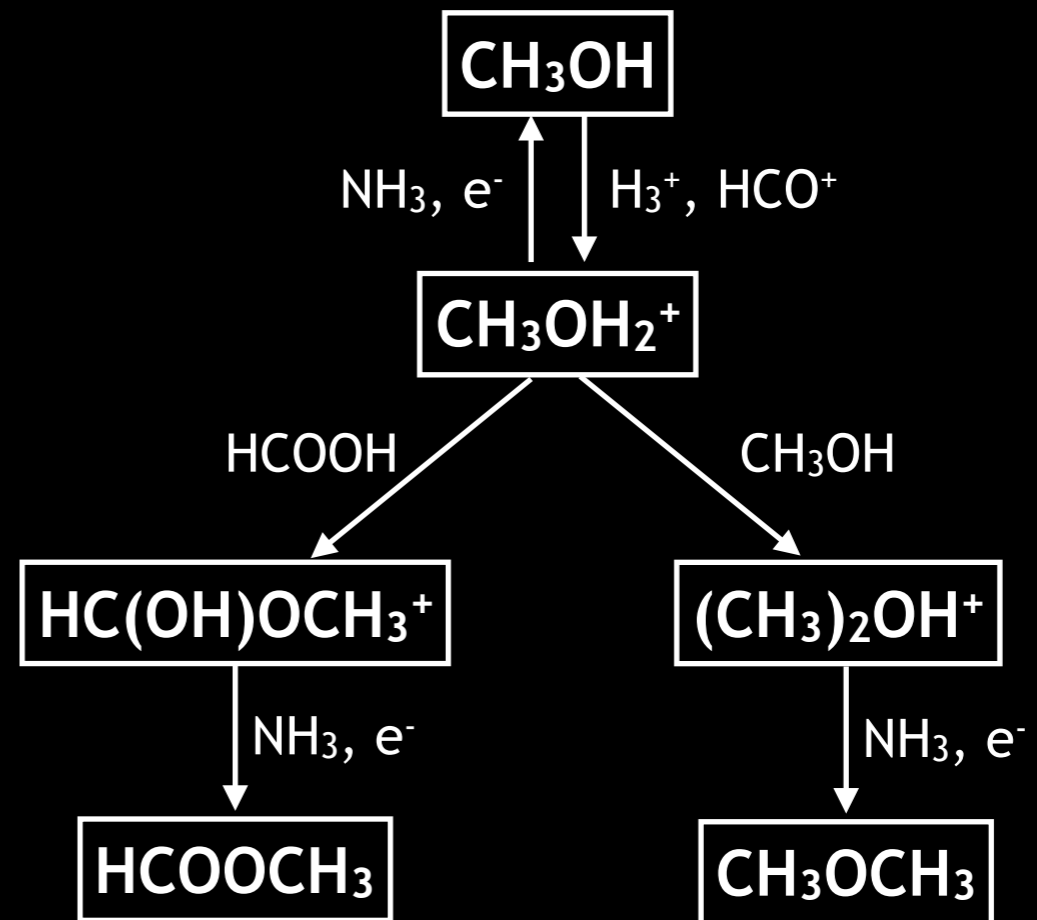
# Formation of cold COMs in the gas phase

Gas phase formation pathways proposed to explain the detection of cold COMs are based on the presence of gaseous methanol

## Neutral-neutral chemistry



## Ion-neutral chemistry



Vasyunin & Herbst 2013, Balucani et al. 2015, Charnley et al. (1992), Rodgers & Charnley (2001), Vasyunin et al. (2017), Taquet et al. (2016)

How to produce methanol in the cold gas phase ?

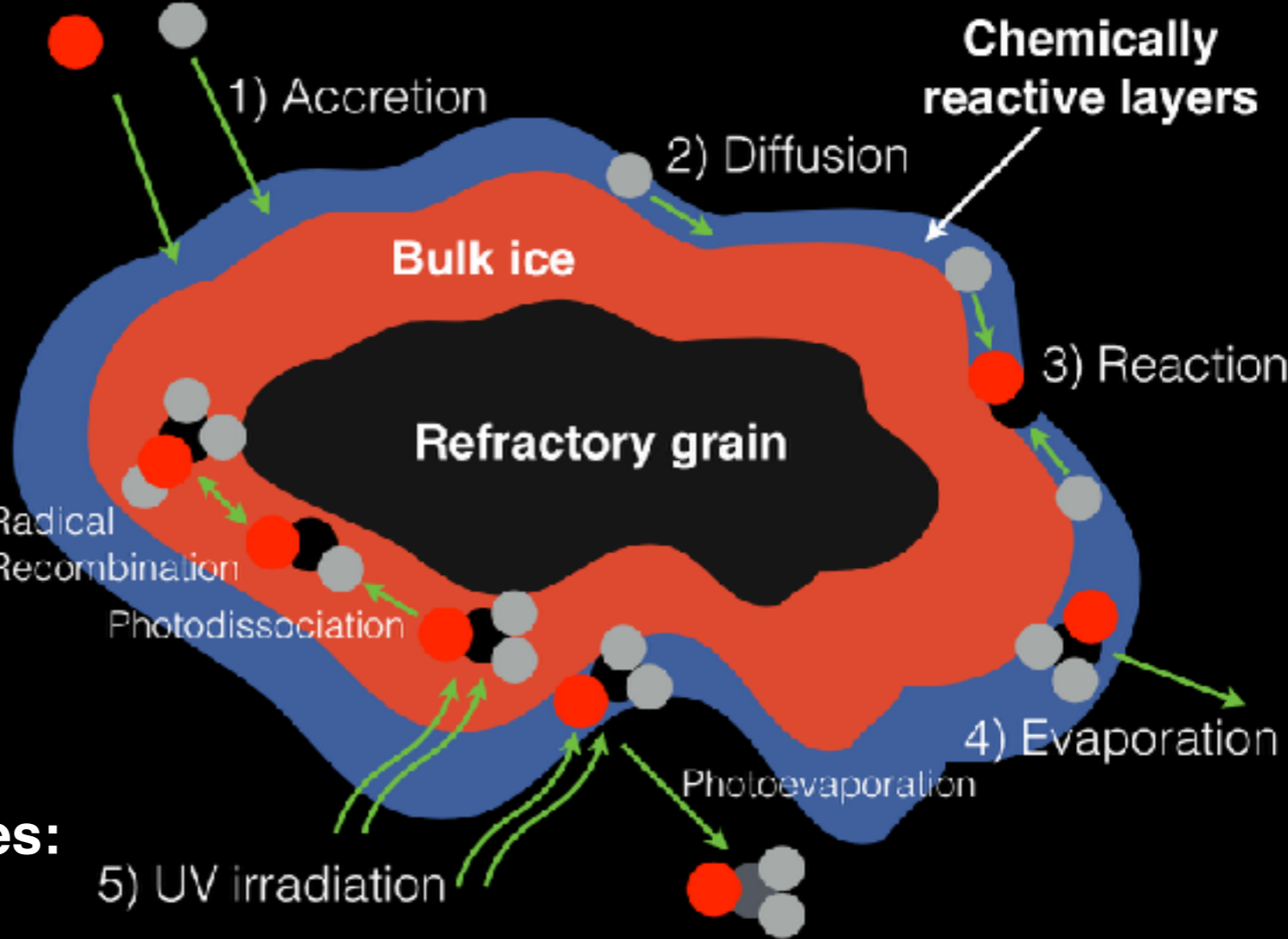
$$X(\text{CH}_3\text{OH}) \sim 10^{-9} - 10^{-8}$$

# Modelling the chemical processes in the ISM

## Gas phase chemistry

Dissociation, ionisation, ion-neutral, neutral-neutral reactions (KIDA, or UMIST chemical databases)

## Gas-grain processes



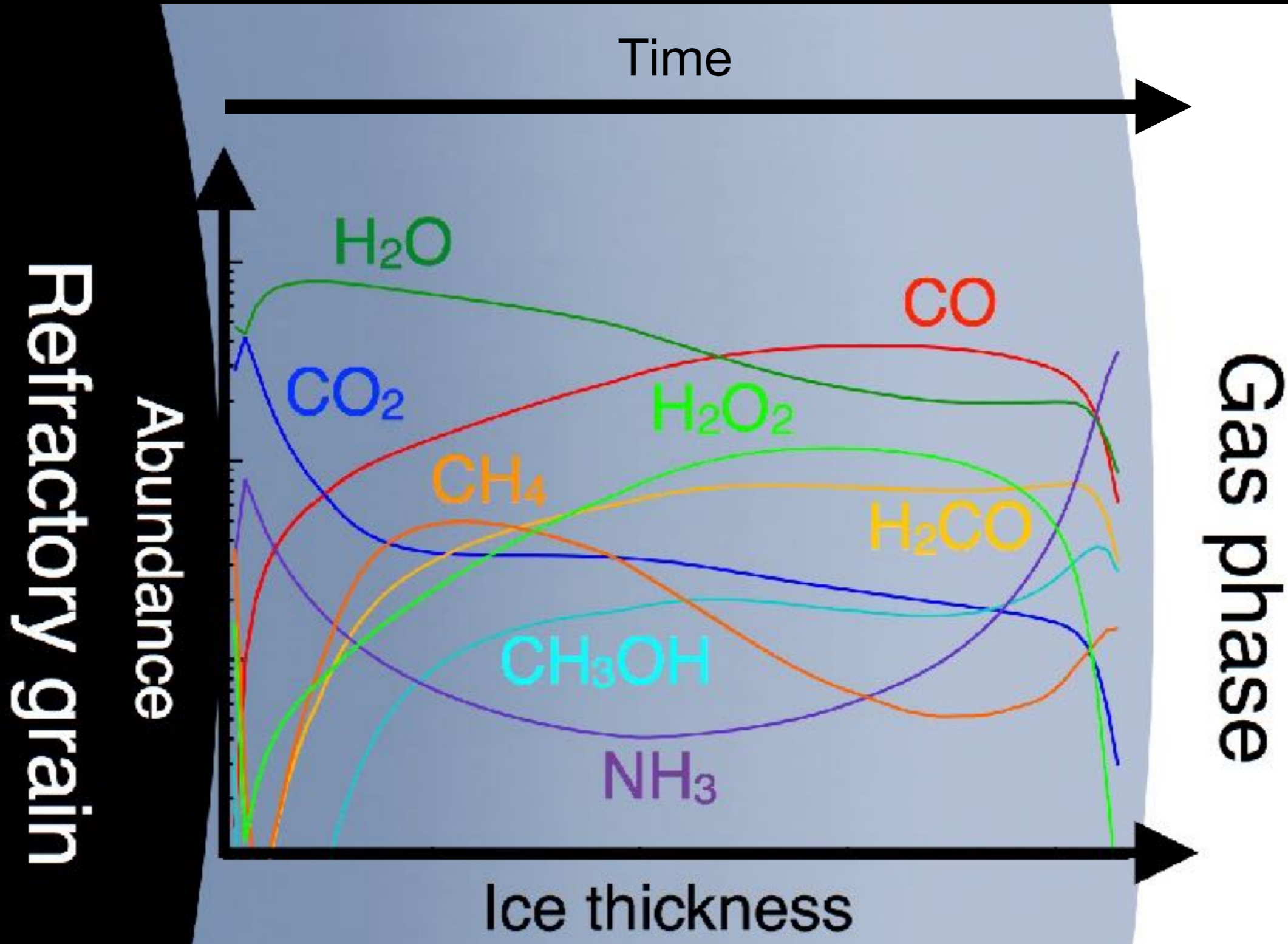
## Non-thermal desorption processes:

- 1) CR-induced grain heating
- 2) Photolysis
- 3) CR ice sputtering
- 4) Chemical desorption
- 5) Explosive desorption



# Ice structure predicted by macroscopic models

**Multiphase models** predict the **chemical heterogeneity of ices** induced by the evolution of gas phase abundances physical conditions in dark clouds



Taquet et al. (2014), see also Charnley & Rodgers (2009), Vasyunin & Herbst (2013), Furuya et al. (2016)

# Gas phase formation of methanol

Methanol in the gas phase can be formed by the radiative association reaction:

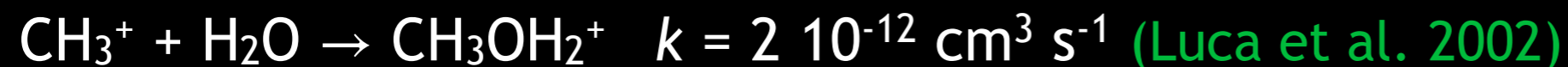


Followed by electronic recombination

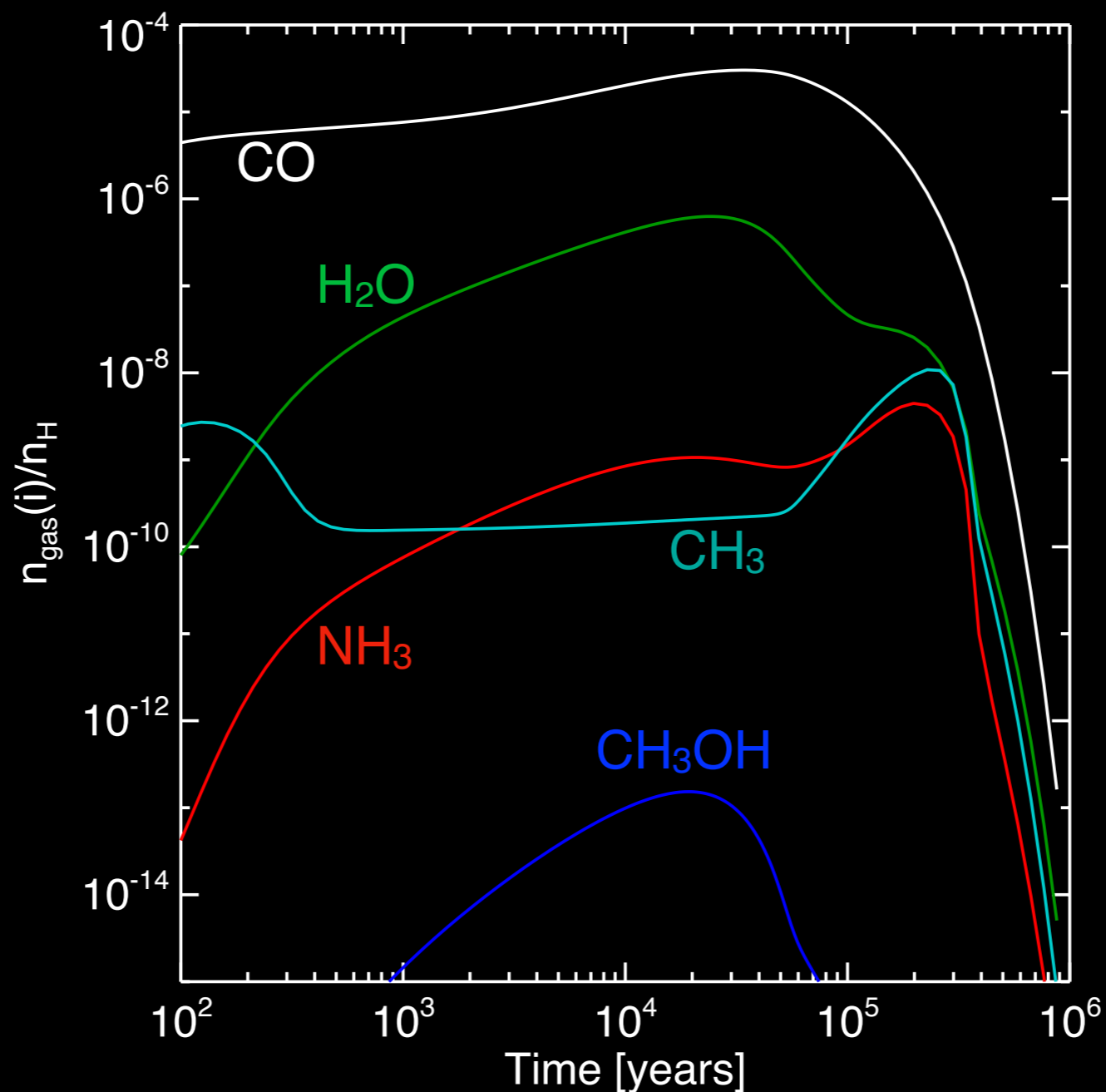


# Gas phase formation of methanol

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Followed by electronic recombination



$n_{\text{H}} = 10^5 \text{ cm}^{-3}$   
 $T_{\text{d}} = T_{\text{g}} = 10 \text{ K}$   
 $A_{\text{V}} = 20 \text{ mag}$   
 $\zeta = 10^{-17} \text{ s}^{-1}$

# Desorption by CR-induced grain heating

Cosmic-ray particles with energies between 20-70 MeV / nucleon deposit:  
about 0.4 MeV on 0.2  $\mu\text{m}$  grains  $\rightarrow$  grain heating from 10 to 70 K (Léger et al. 1985)

$$k_{\text{CR}}(i) = f(70 \text{ K}) k_{\text{ev}}(70 \text{ K}, i) \text{ (Hasegawa et al. 1993)}$$

$f(70 \text{ K})$ : fraction of time spent at 70 K =  $3.2 \cdot 10^{-19}$

= grain cooling time / time interval between two heating events =  $10^{-5} \text{ s} / 3.2 \cdot 10^{13} \text{ s}$

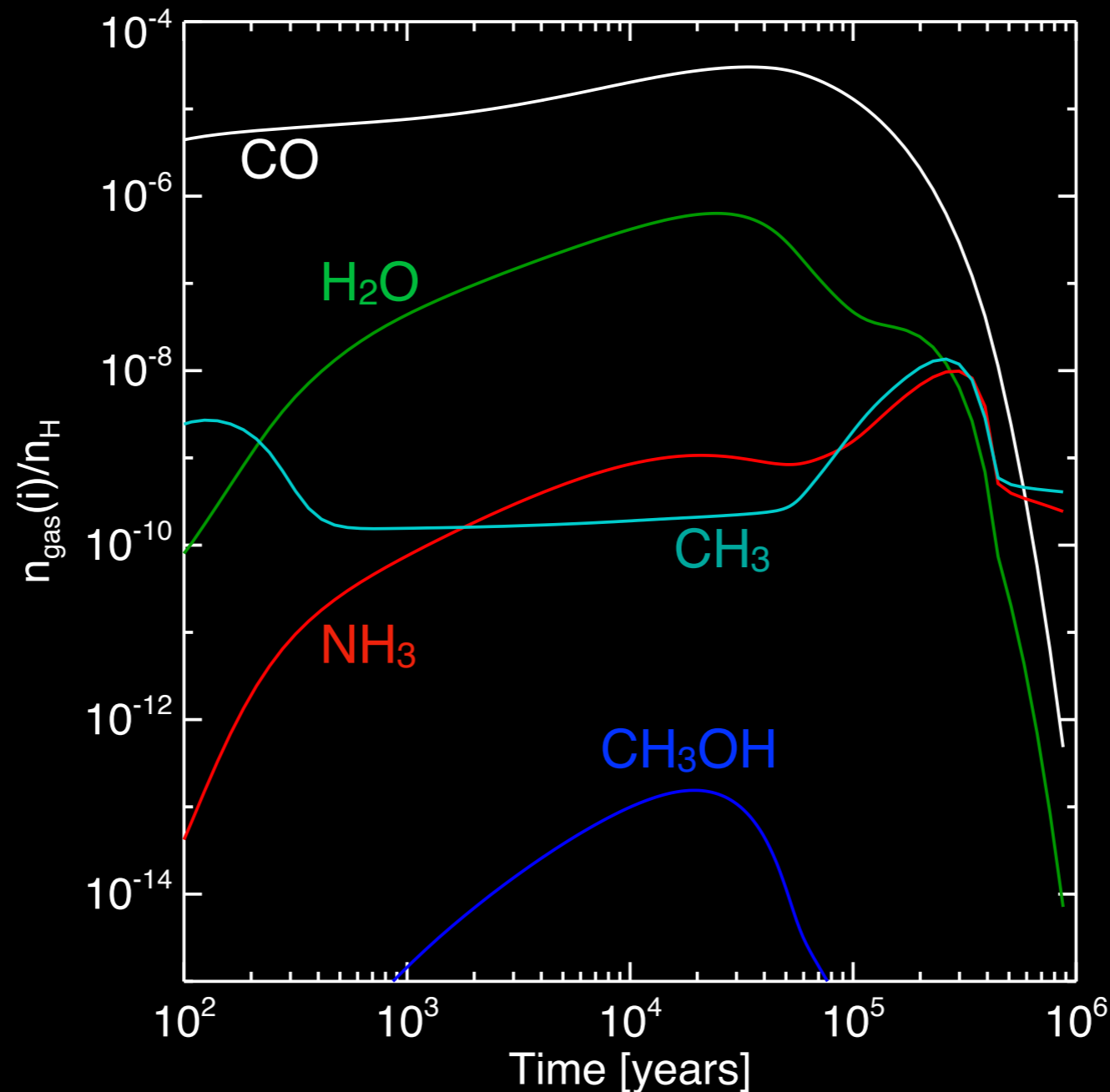
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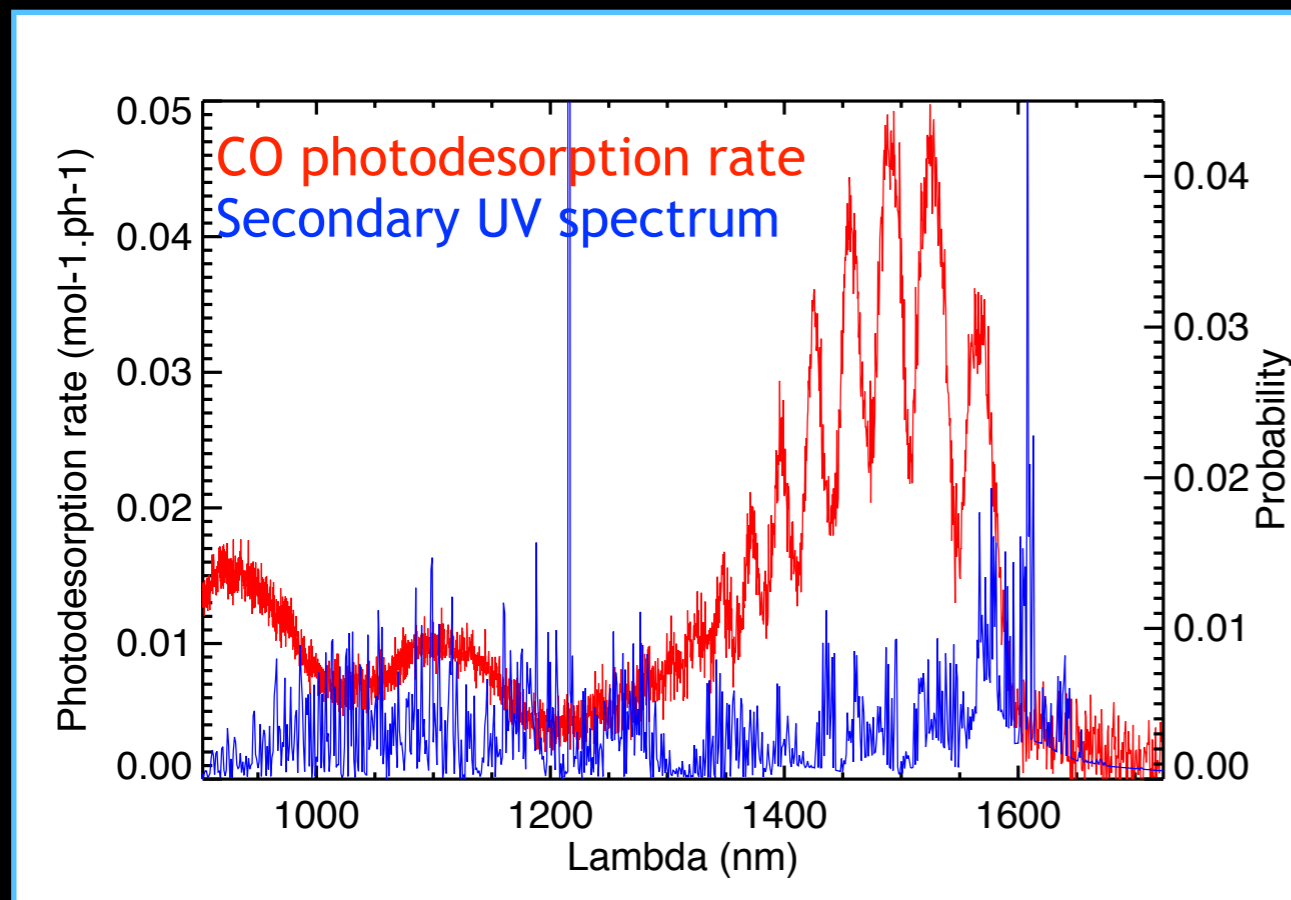
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# Desorption by UV photolysis

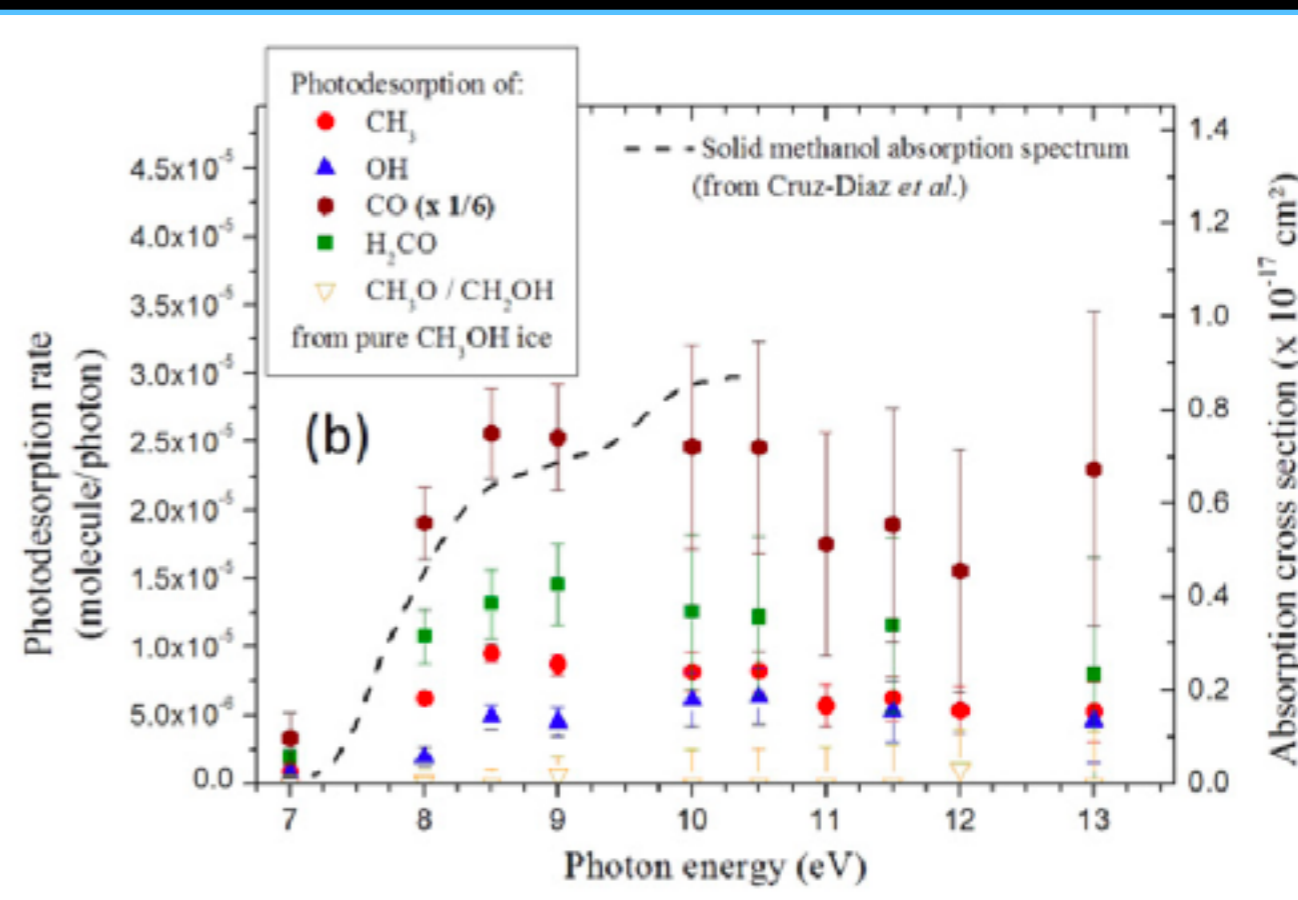
Flux of UV photons ( $\approx 10^4$  photons  $\text{cm}^{-2} \text{s}^{-1}$ ) produced by the relaxation of  $\text{H}_2$  excited by secondary electrons formed through ionisation of  $\text{H}_2$  by CRs (Prasad & Tarafdar 1983, Sternbeg et al. 1987, Shen et al. 2004)

→ Need for wavelength-dependent studies of UV photolysis of ices

Pure CO ice



Pure CH<sub>3</sub>OH ice



Yield(CO photodesorp.)  $\sim 10^{-2}$  mol photon $^{-1}$  Yield(CH<sub>3</sub>OH photodesorp.)  $\sim 10^{-5}$  mol photon $^{-1}$

Fayolle et al. (2011)

Bertin et al. (2015)

See also Cruz-Diaz et al. (2016)

# Desorption by UV photolysis

Incorporation of measured or computed absorption cross sections and photo-dissociation / photo-evaporation yields

$$k_{UV}(i) = (F_{UV,ext} Y_{UV,ext}(i) + F_{UV,CR} Y_{UV,CR}(i)) \sigma_d / N_s$$

(Andersson & van Dishoeck 2008, Fayolle et al. 2011, Bertin et al. 2013, 2015, etc)

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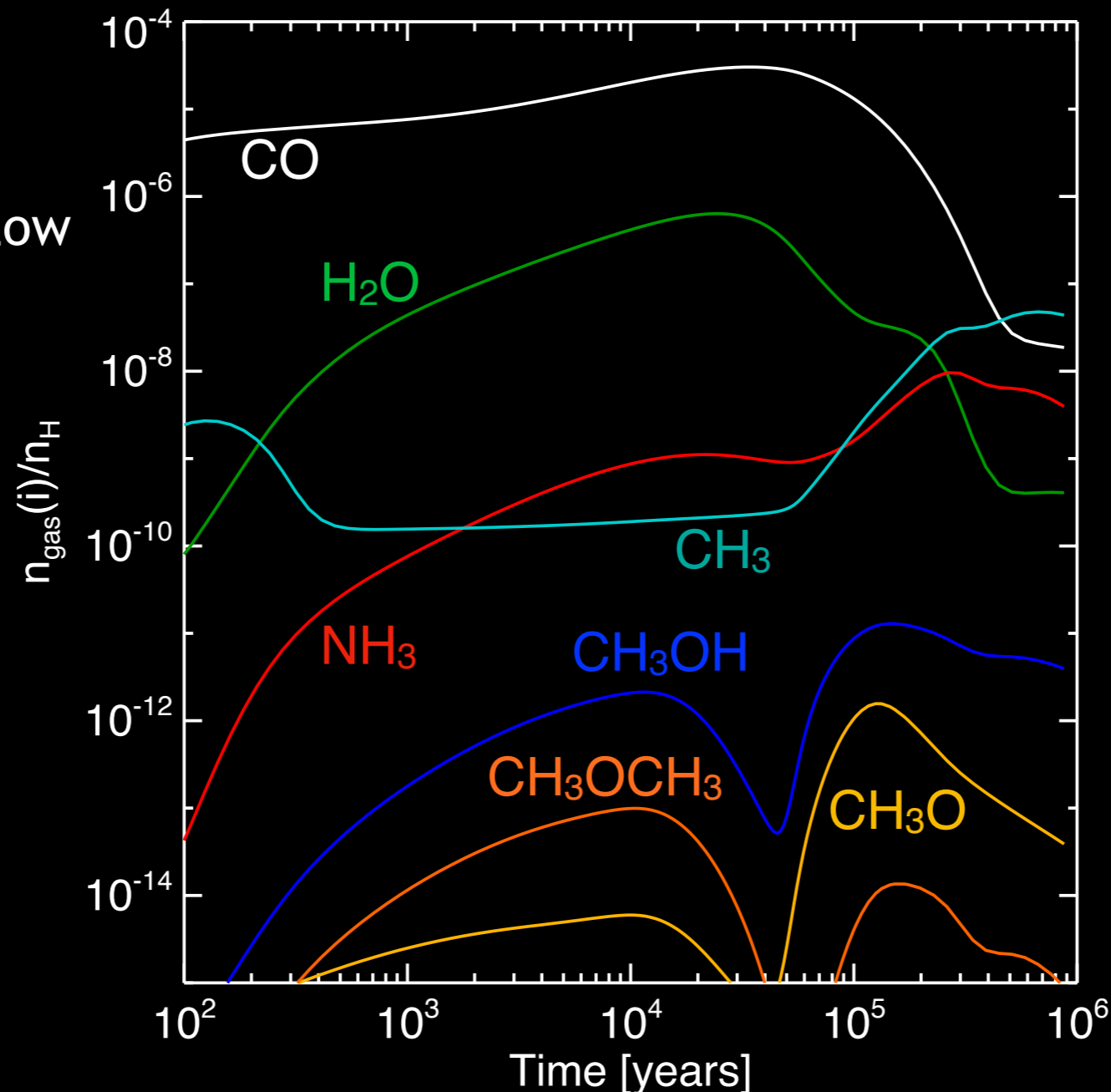
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(Andersson & van Dishoeck 2008, Fayolle et al. 2011, Bertin et al. 2013, 2015, etc)

## 2 CH<sub>3</sub>OH peaks:

- 1) CH<sub>3</sub>+O triggered by low CH<sub>3</sub> binding energy
- 2) CO hydrogenation

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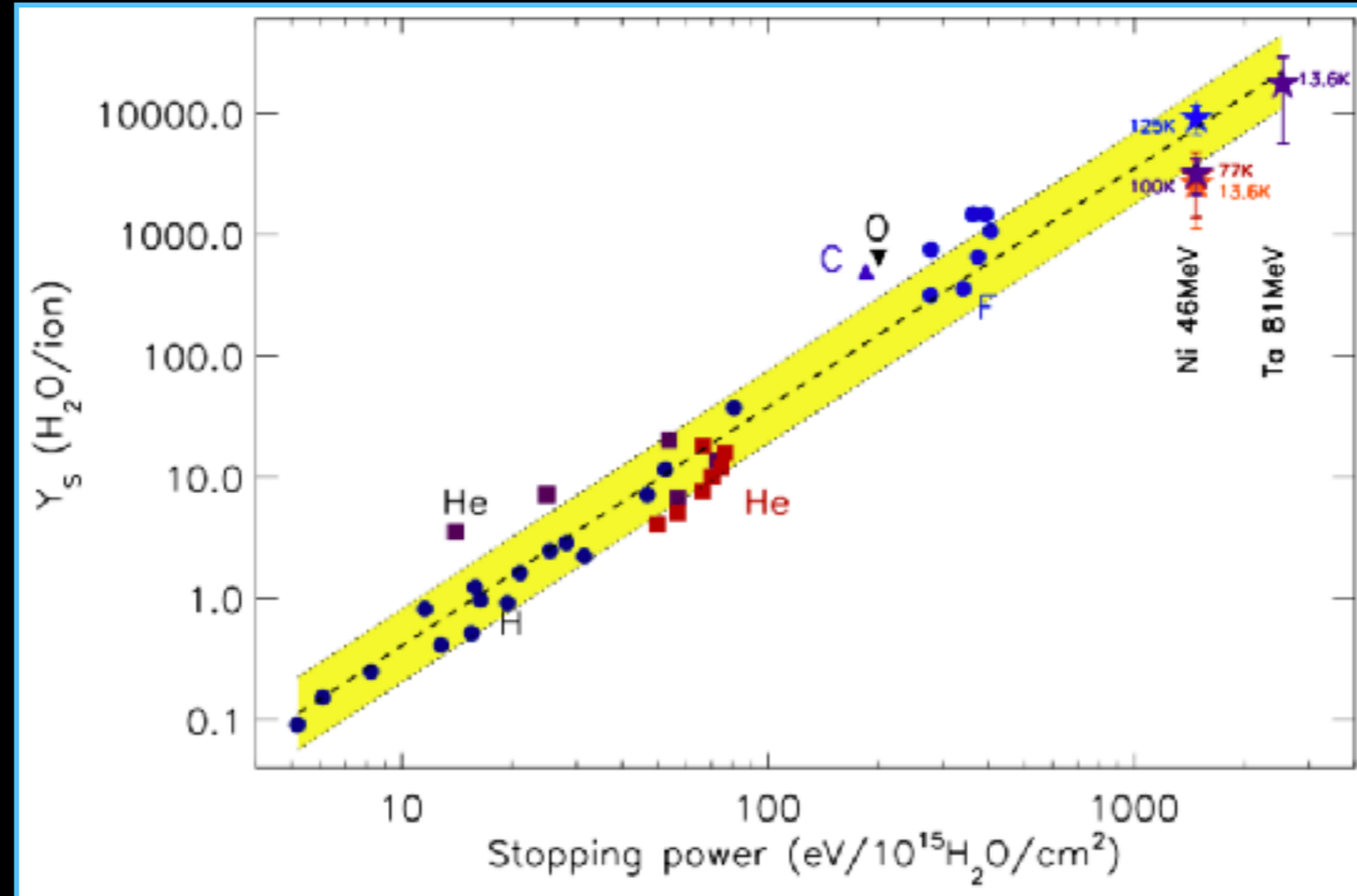




# Ice sputtering by cosmic rays

In addition to crystallisation, cosmic-rays can sputter interstellar ices as shown by laboratory experiments

(Brown et al. 1984, Dartois et al. 2015)



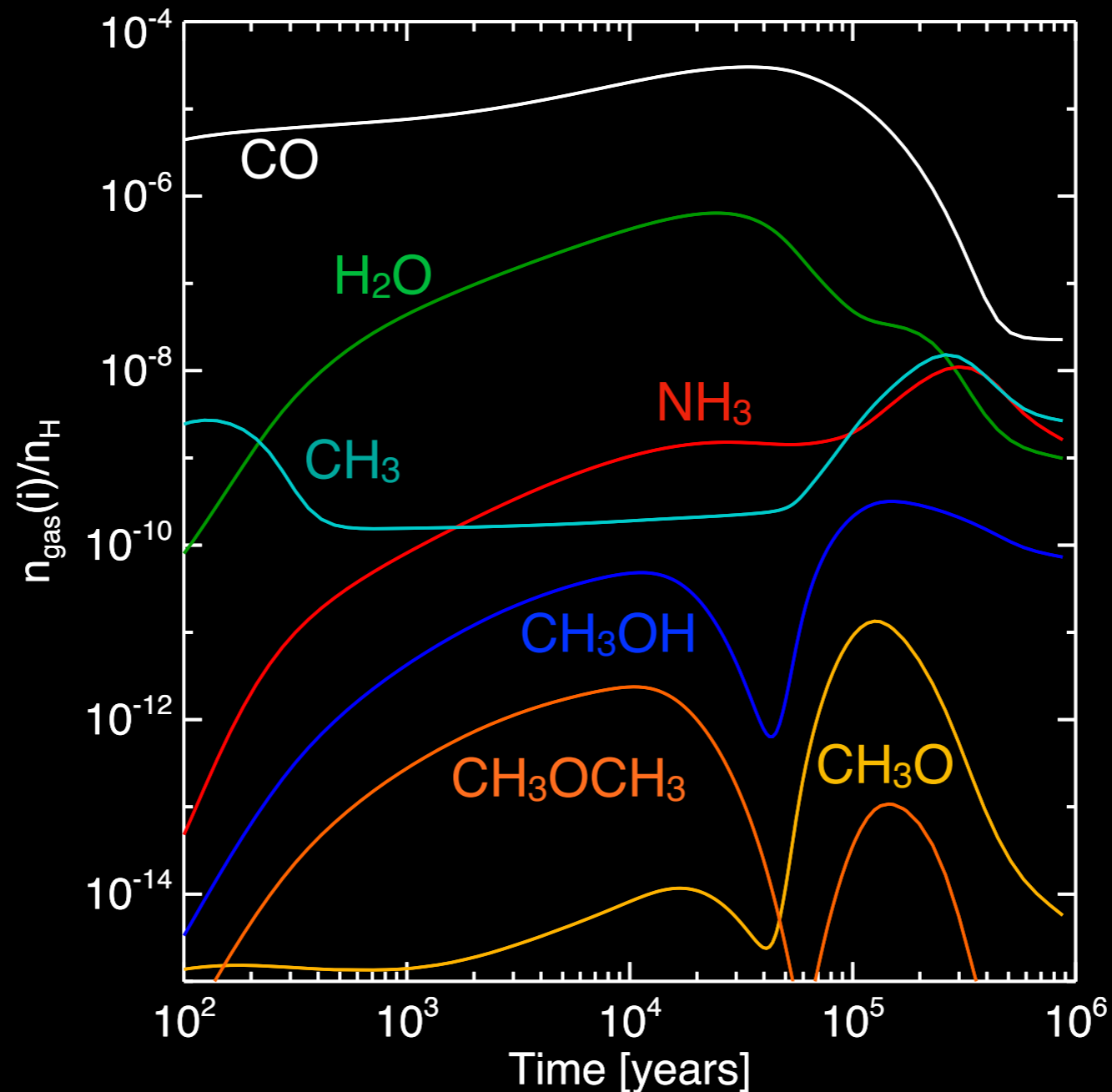
	GCR		
$E_0$ (MeV)	200	400	600
$\zeta(\text{s}^{-1})^a$	$3.34(-16)$	$5.89(-17)$	$2.12(-17)$
$\eta^{\text{GCR}}(\text{H}_2\text{O}/\text{cm}^2/\text{s})^b$	$27.0^{+26}_{-13}$	$8.3^{+8.2}_{-4.1}$	$4.1^{+4.1}_{-2.1}$

$Y \sim 10^{-3}$  (vs  $\sim 10^{-5}$  for UV photodesorption of  $\text{CH}_3\text{OH}$ )

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# Chemical desorption

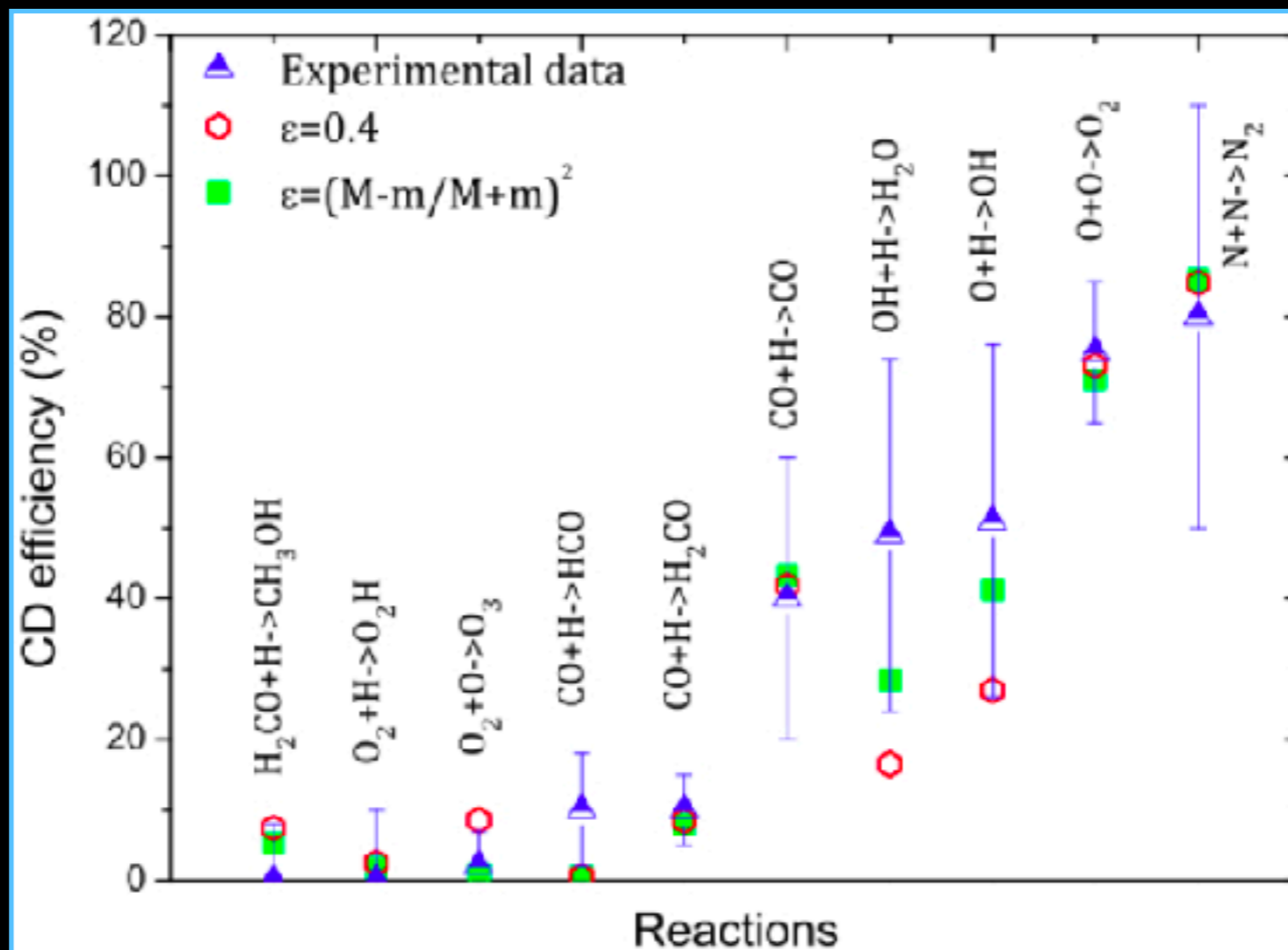
Energy released by exothermic surface reaction can break binding energy of product through the so-called “chemical desorption” process

Efficiency of product ejected in the gas estimated to be ~ 1 - 2 % (Garrod et al. 2007)

Experiments show that this fraction depends on product, reaction, and substrate:

$$CD = e^{-\frac{E_{\text{binding}}}{\epsilon \Delta H_R / N}}$$

Minissale & Dulieu (2014), Minissale et al. (2016)

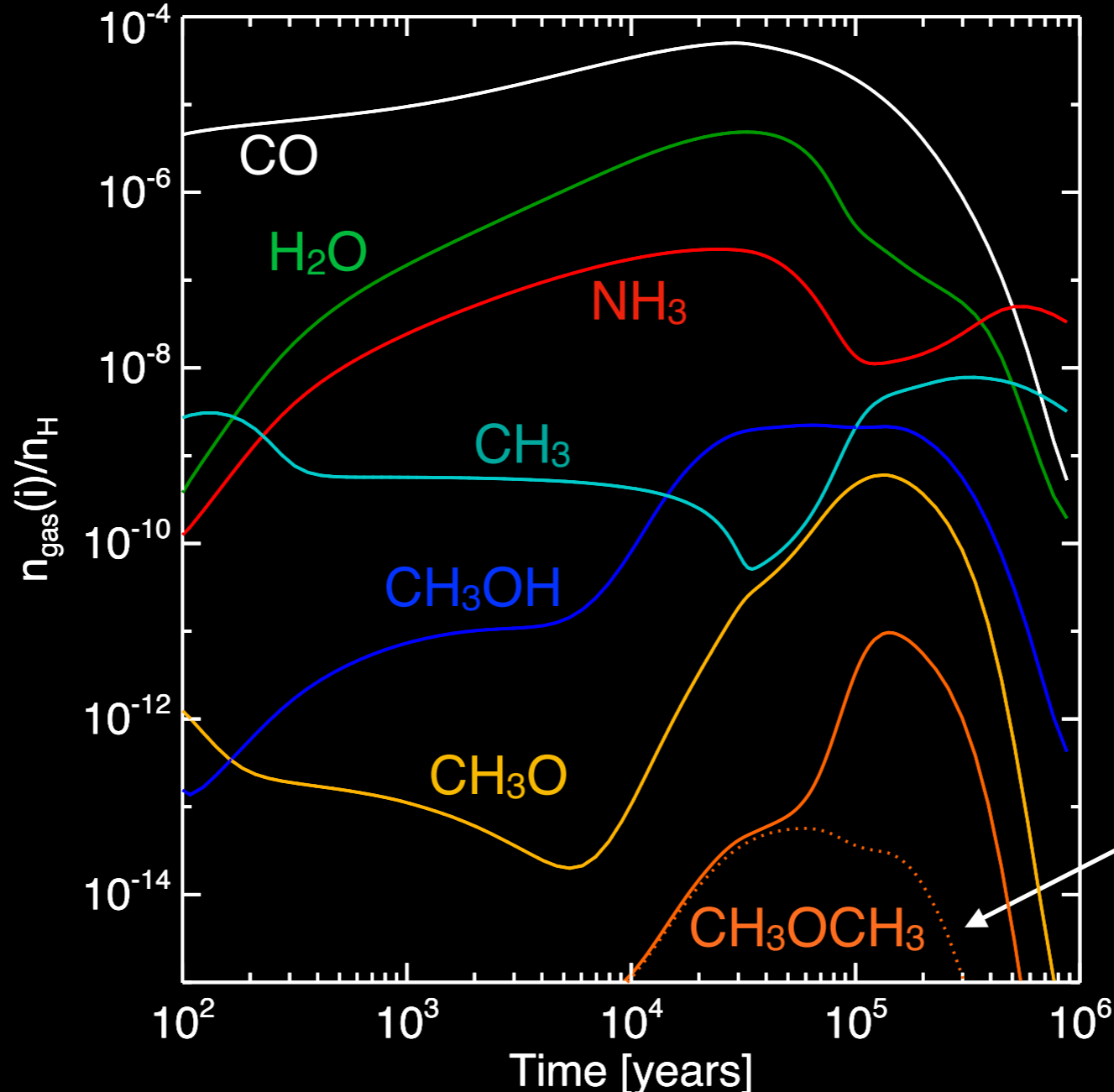


See  
A. Vasyunin's talk

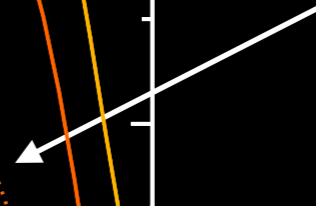
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Without  $CH_3O+CH_3$  reaction



# Conclusions

Several desorption processes have been proposed during the last four decades to explain the detection of volatile (CO, CH<sub>3</sub>OH) species in cold gas:

- Efficiency of all processes highly depends on substrate, and specific species
- Chemical desorption on bare or CO surfaces seems to be the most efficient way to explain the abundance of CH<sub>3</sub>OH in dark clouds

Cold neutral-neutral gas phase chemistry can explain the presence of COMs in cold dense clouds with abundances of a few percents / CH<sub>3</sub>OH

Can this neutral-neutral chemistry important around protostars ?