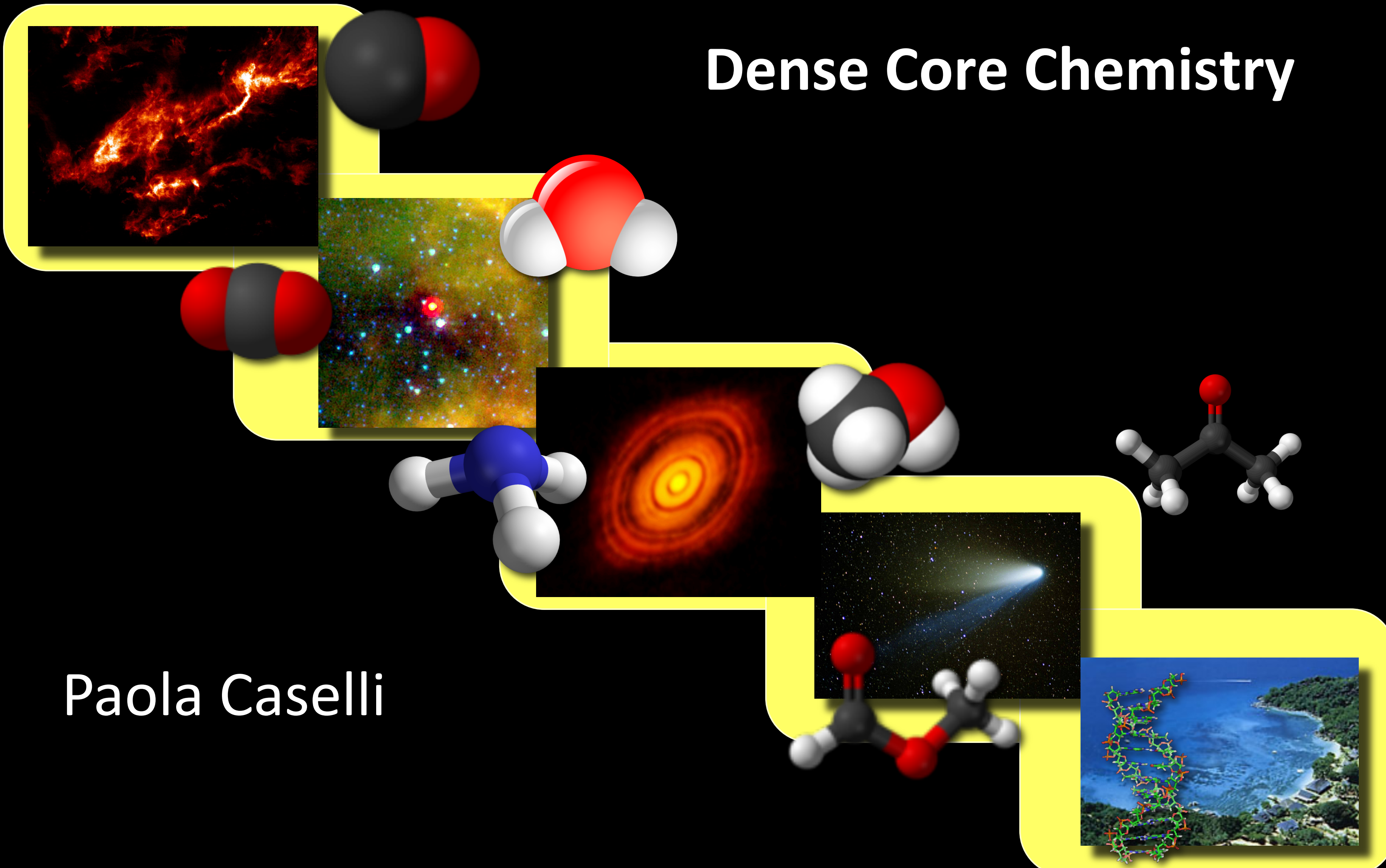
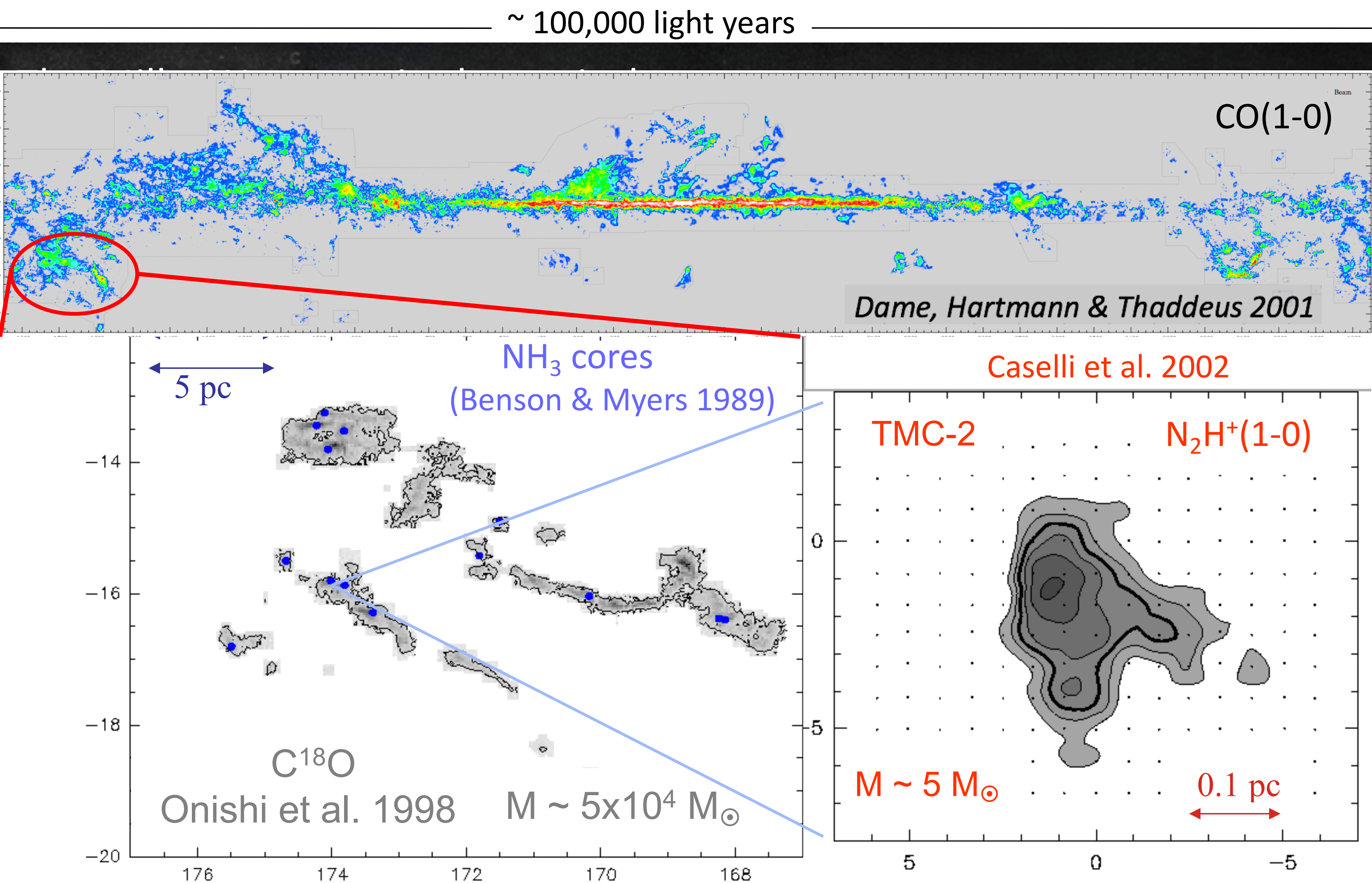
Center for Astrochemical Studies
Max-Planck-Institute for Extraterrestrial Physics

Dense Core Chemistry



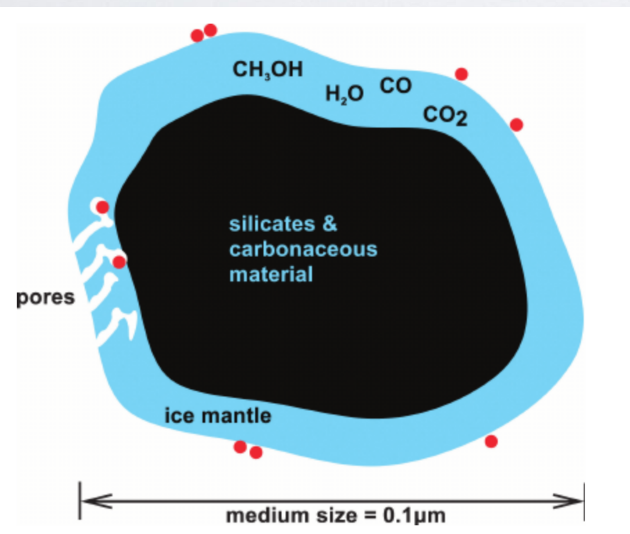
Paola Caselli

Molecular clouds and star formation

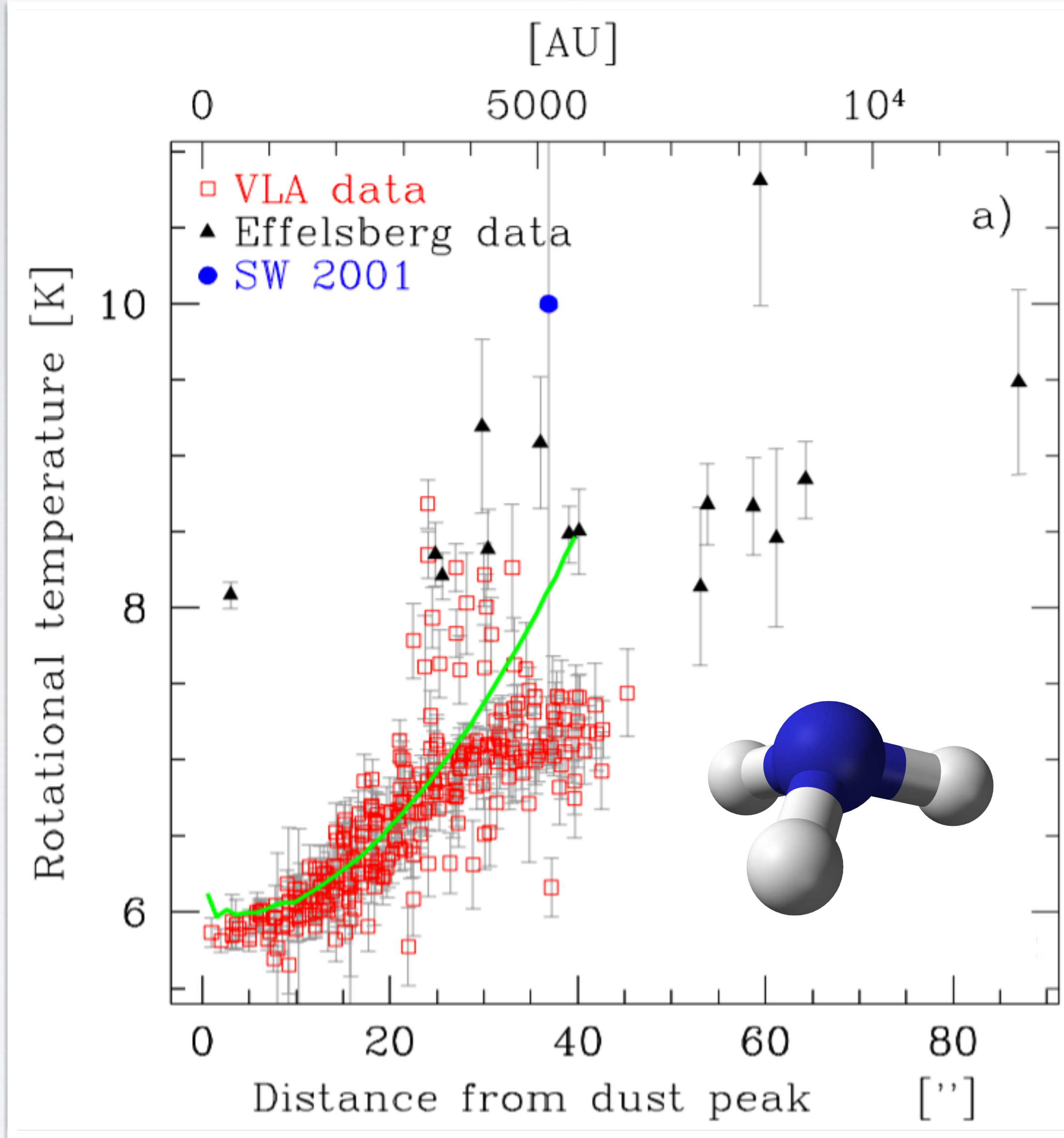


In pre-stellar cores, the gas temperature drops to ~6 K

→ **catastrophic freeze-out** (>90% CO in ice in the central 7000 AU, *Caselli+1999*) and **large D/H** (50(±20)%; *Crapsi+2007; Redaelli+2019*)



Karssemejer et al. 2012, PCCP

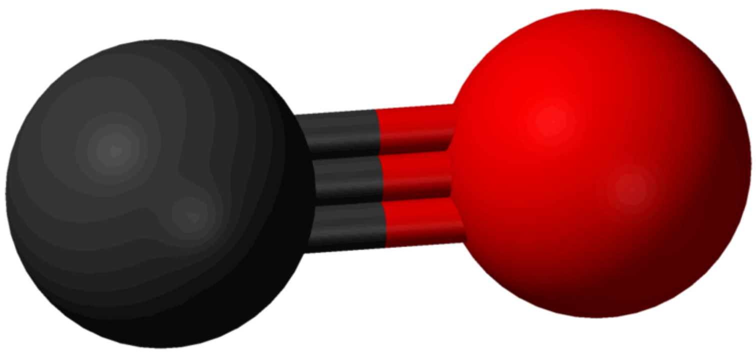


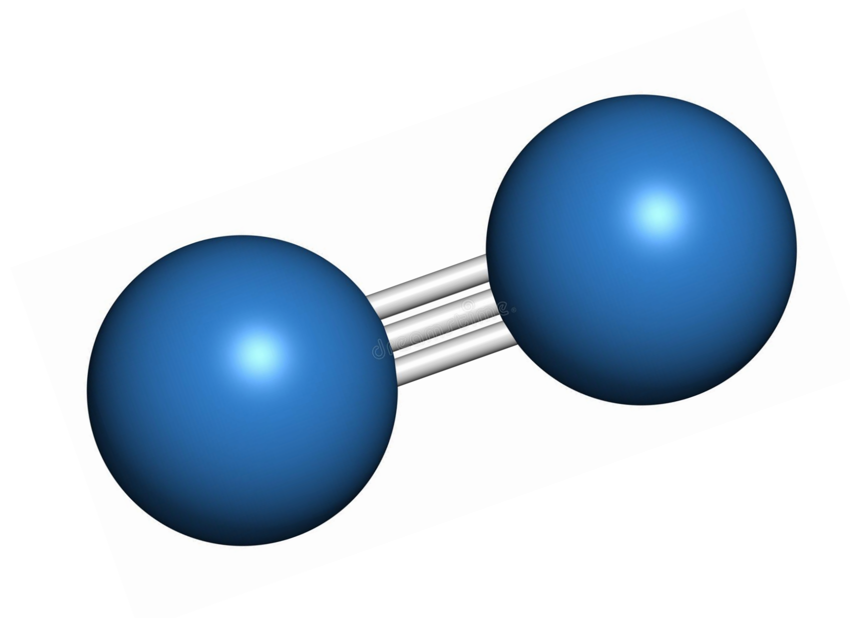
Crapsi, Caselli, Walmsley, Tafalla 2007

Outline

1. Carbon and nitrogen chemistry (CO and N_2)
2. Freeze-out
3. Deuterium fractionation
4. Complex Organic Molecules (COMs)

1. Carbon and nitrogen chemistry (CO and N_2)





The timescale to form CO

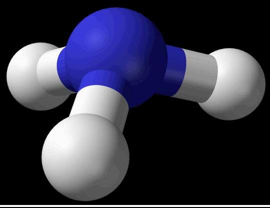
$H_2 + \text{c.r.} \rightarrow H_2^+ + e^- + \text{c.r.}$ $\qquad$ $H_2^+ + H_2 \rightarrow H_3^+ + H$

$$\boxed{C} \xrightarrow{H_3+} \boxed{CH+} \xrightarrow{H_2} \boxed{CH_2+} \xrightarrow{H_2} \boxed{CH_3+} \xrightarrow{O} HCO^+ \xrightarrow{e^-} CO$$

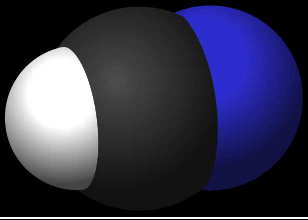
Assume: dark region where all H is in H_2 and all atoms more massive than He are in neutral atomic form.

The timescale on which almost all carbon becomes contained in CO ($n_O > n_C$) is at least equal to the timescale for one H_2 to be ionized for every C: $n_C/[\zeta\, n(H_2)] = 2\, n_C/[\zeta\, n_H]$.

For $\zeta = 3\times10^{-17}$ s^{-1} and $n_C/n_H = 10^{-4}$, the above expression gives a value of about 2×10^5 yr.



Nitrogen chemistry



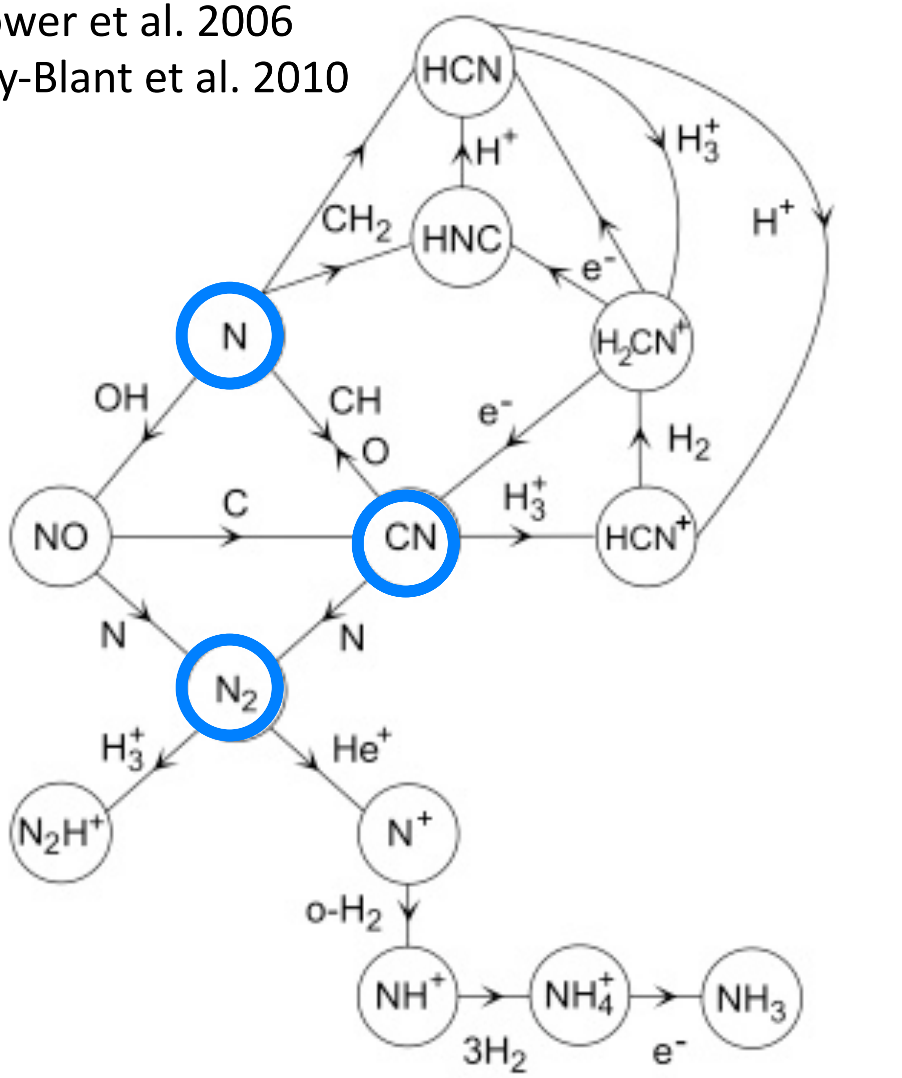
$$N + H_3^+ \not\rightarrow NH^+ + H_2$$

$$N + OH \rightarrow NO + H$$

$$N + CH \rightarrow CN + H$$

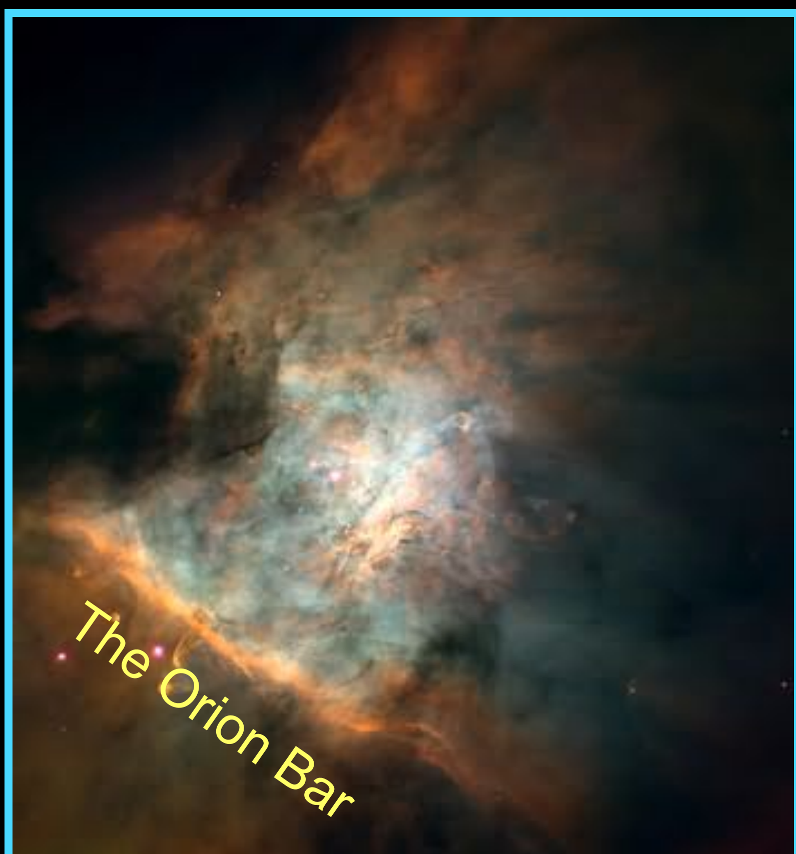
t_{N2} ~ 10^6 yr in UV-shielded clouds (about 5 times longer than t_{CO})

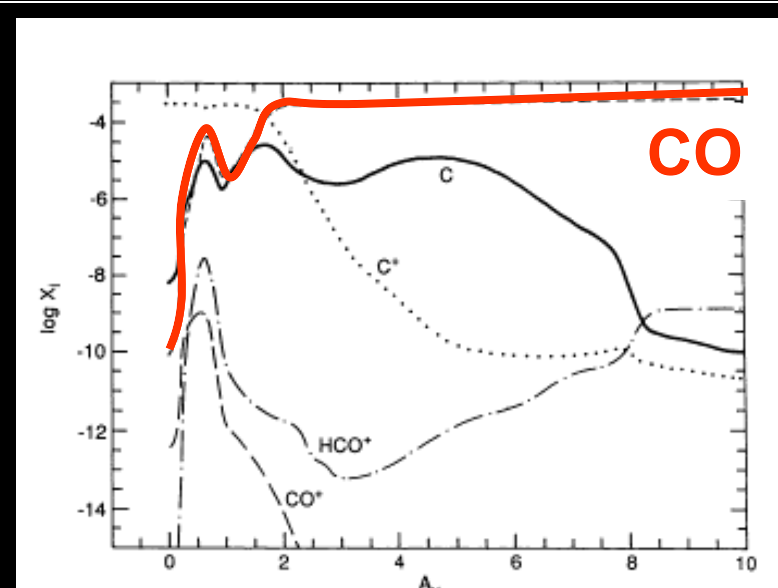
Flower et al. 2006
Hily-Blant et al. 2010

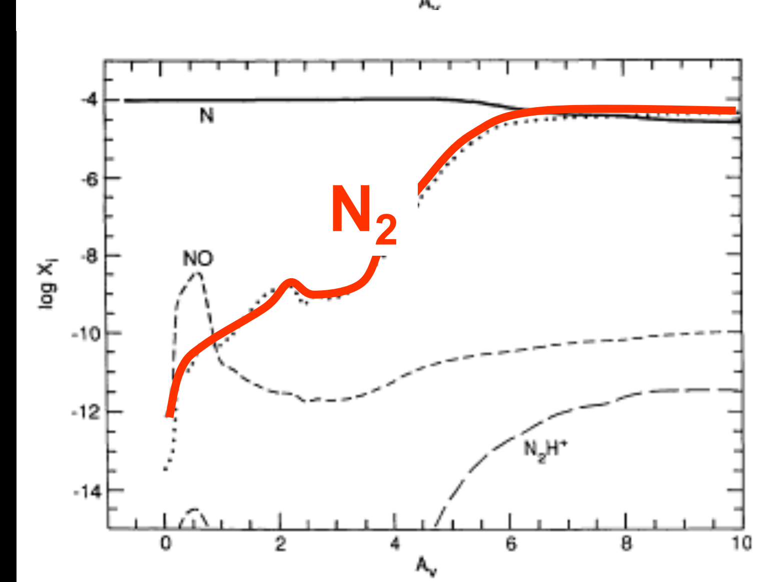


$\mathcal{N}_2$ vs. CO

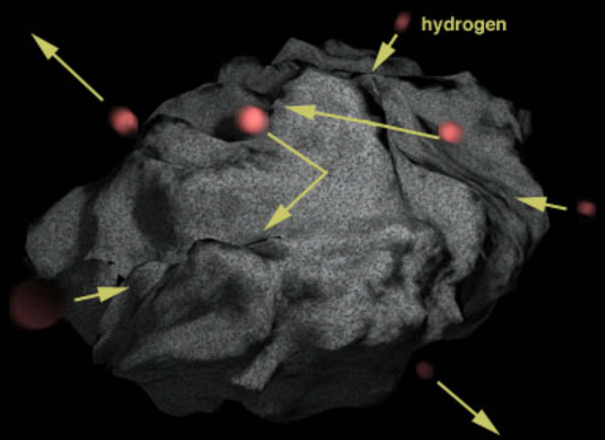
Chemistry in Photodissociation Regions (PDRs)
Sternberg & Dalgarno 1995

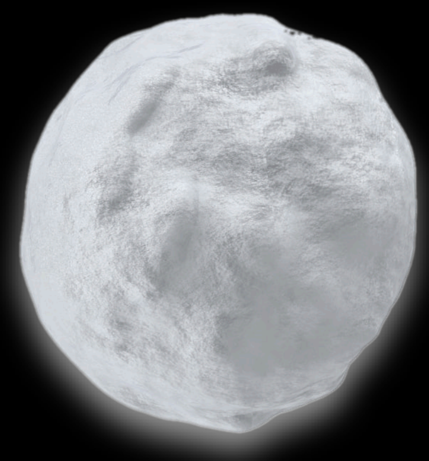




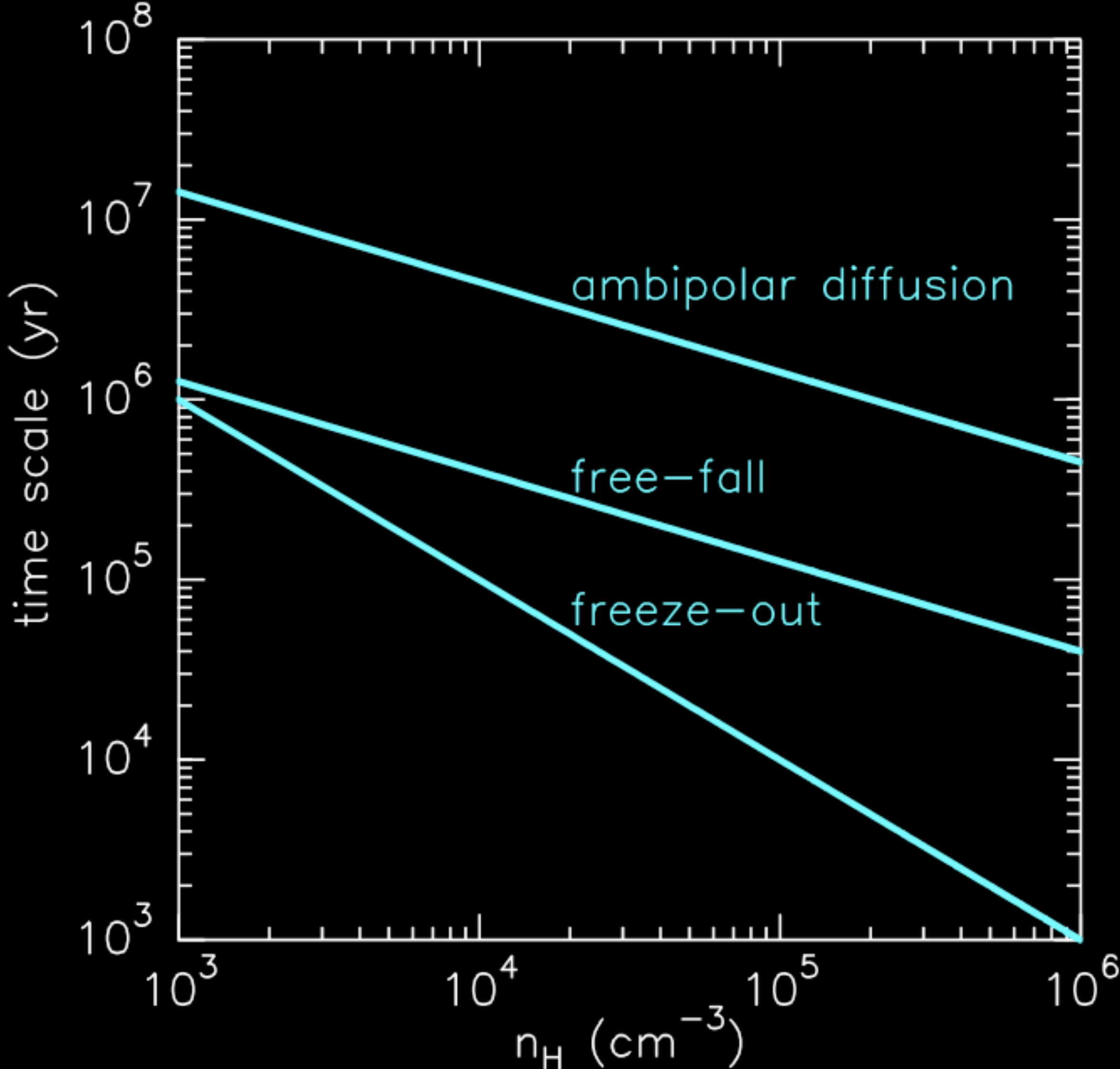


2. Freeze-out





Dynamical and freeze-out timescales



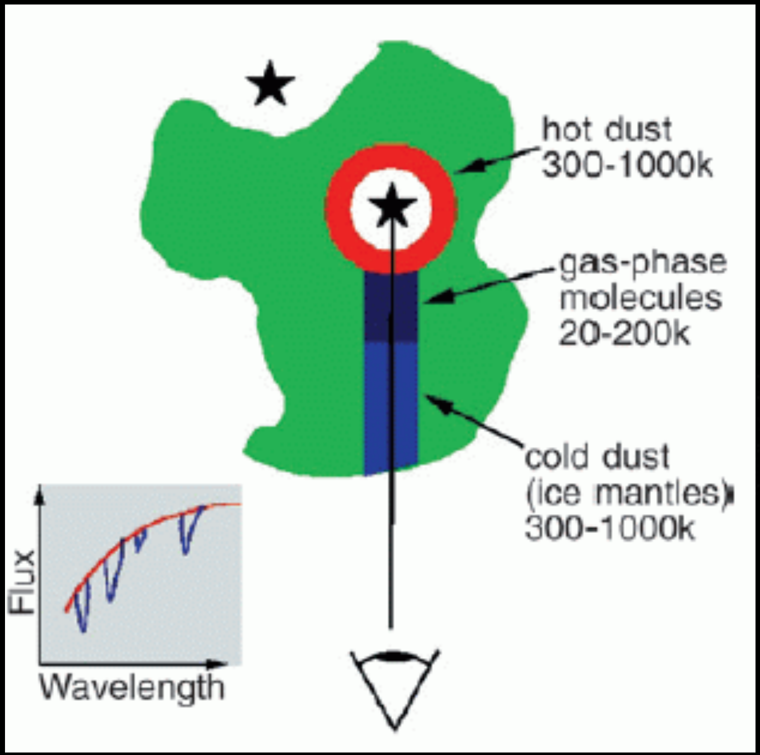
$$t_{ambipolar} \approx 2.5 \times 10^{13}\, x(e)\ \text{yr}$$
$$\approx 4.5 \times 10^{8} / \sqrt{n_H}\ \text{yr}$$

$$t_{free-fall} = \sqrt{\frac{3\pi}{32G\rho}}$$
$$\approx 4 \times 10^{7} / \sqrt{n_H}\ \text{yr}$$

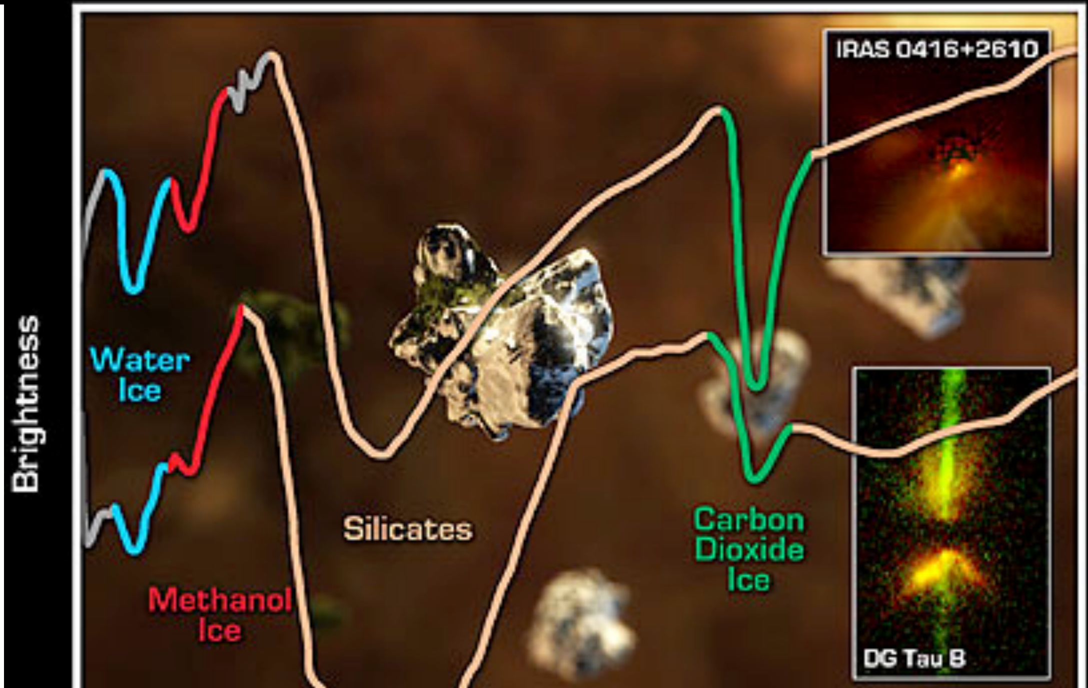
$$t_{freeze-out} = \frac{1}{\alpha n_d \pi a_d^2 \mathrm{v}_t}$$
$$\approx 10^{9} / n_H\ \text{yr}$$

Walmsley 1991; Bergin&Tafalla (2007)

Evidence of icy mantles: absorption features



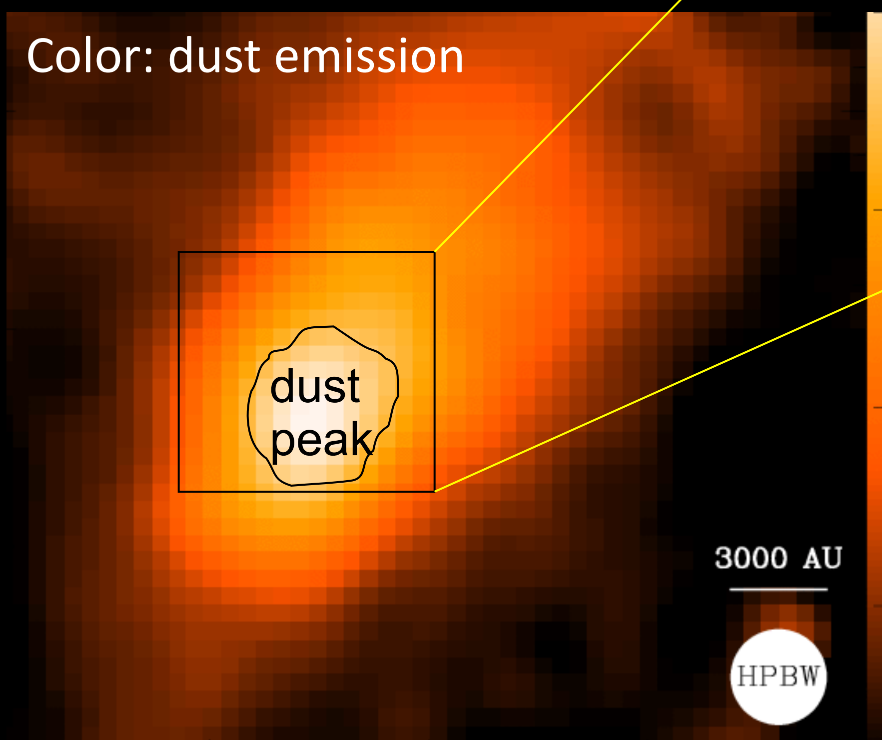
from van Dishoeck et al. 2003

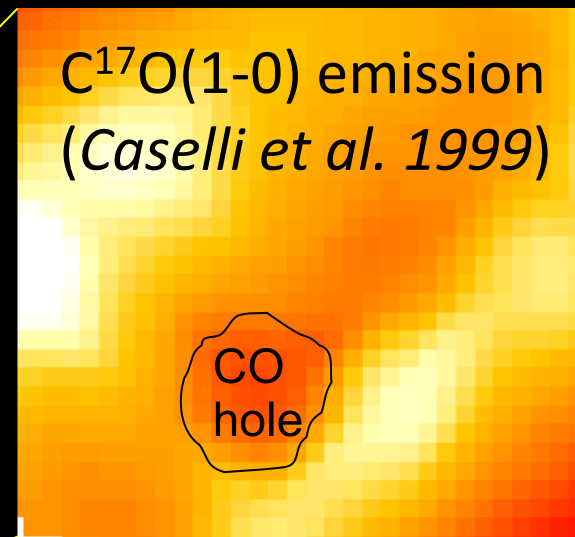


Pontoppidan+2007; Chiar+2011; Boogert+2015

Evidence of freeze-out: CO "holes"

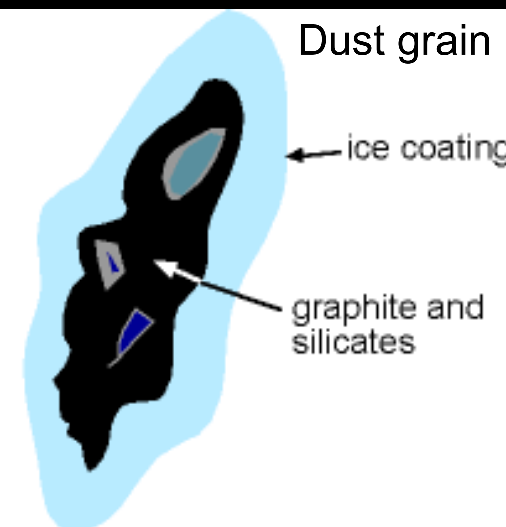
"Catastrophic" CO freeze-out within the central 7000 au



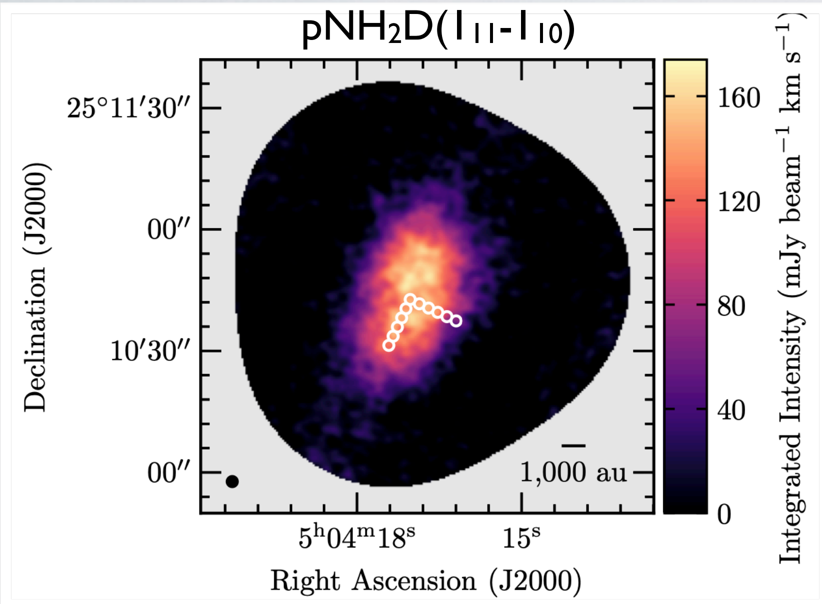


90% of CO molecules are frozen onto dust grains

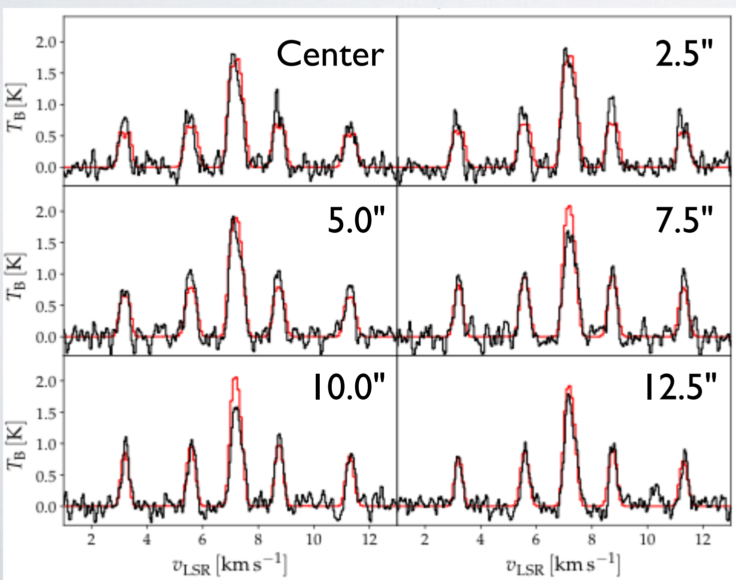
Molecules freeze out onto dust grains in the center of pre-stellar cores

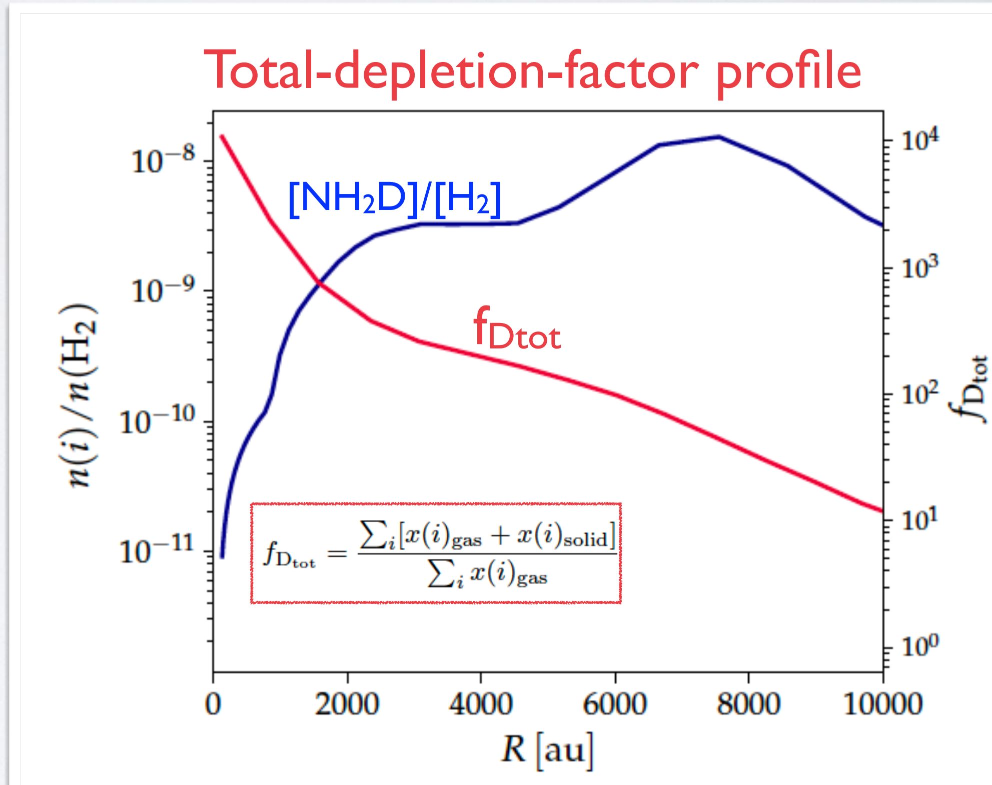


In the central 2000 au, 99.99% of all species heavier than He are frozen onto dust grains



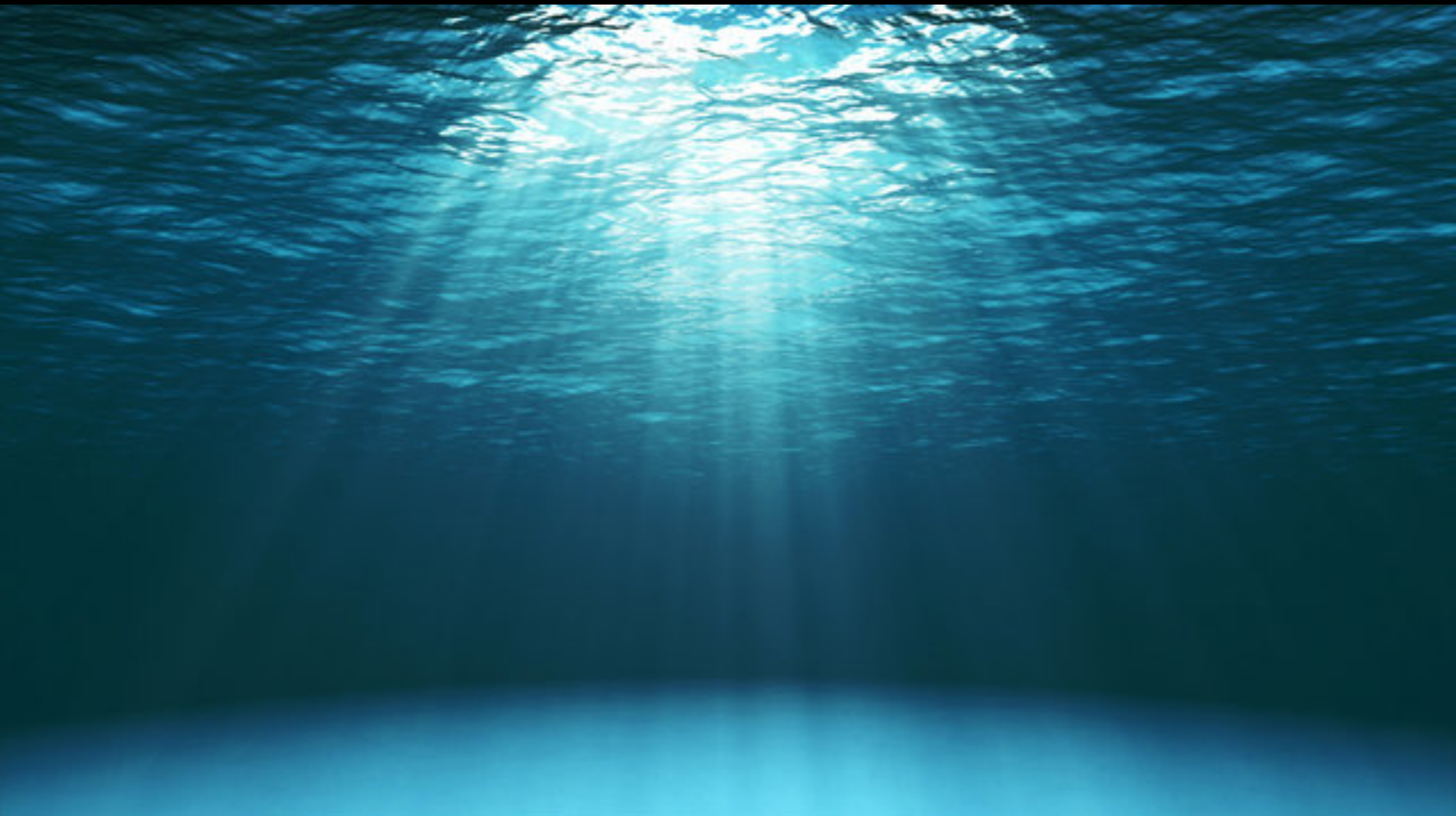
L1544 **ALMA**-Band 3 observations + comparison with gas-grain chemical/RT model: *NH_2D abundance sharply drops in the central 2000 au.*



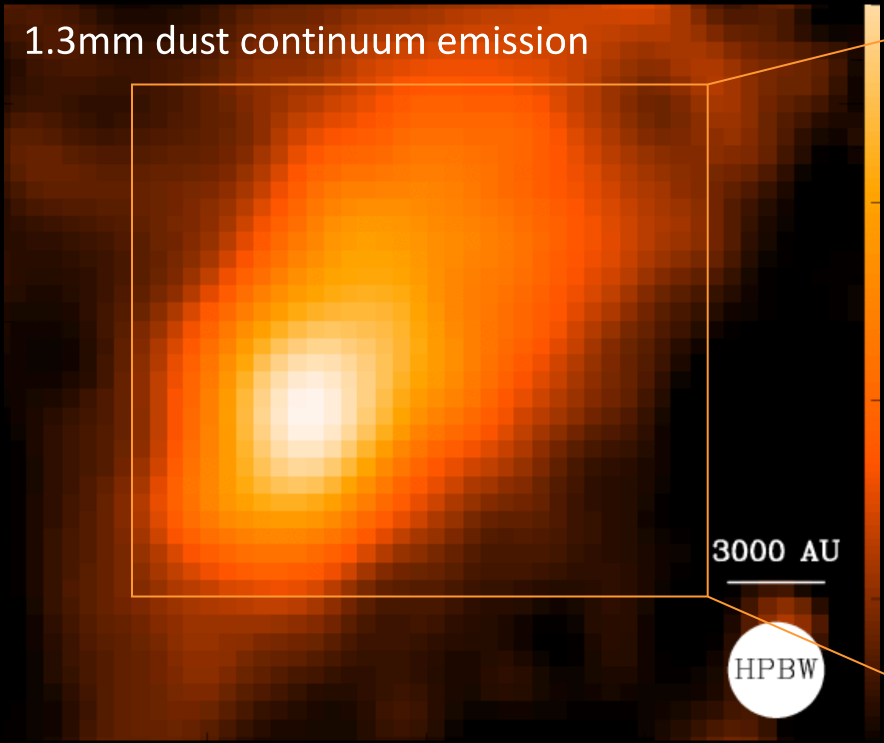


Caselli, Pineda, Sipilä+2022 (+Pineda+2022)

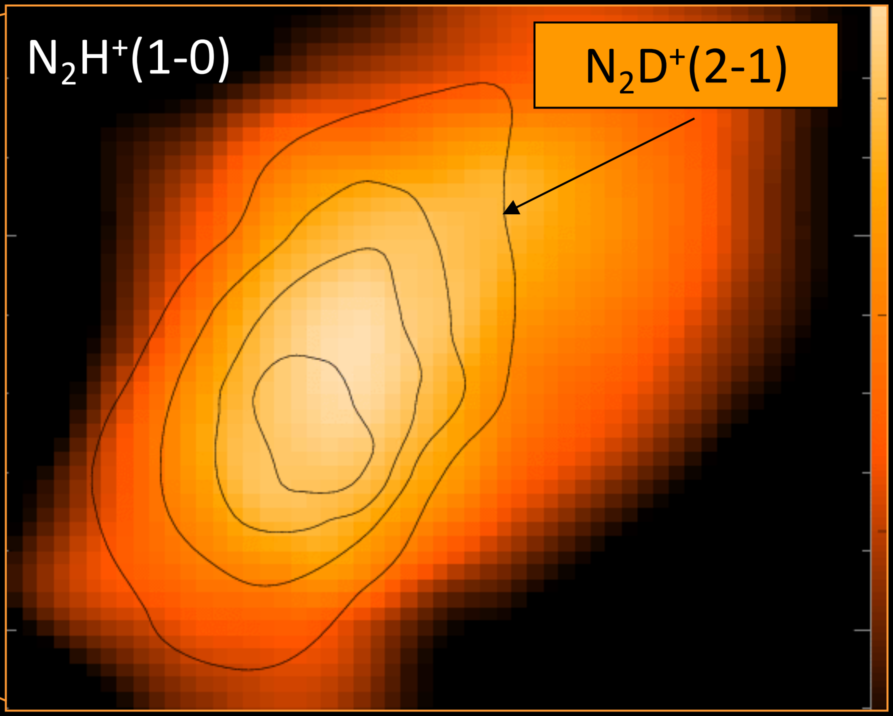
3. Deuterium Fractionation



Freeze-out and Deuterium fractionation



Dust emission in the pre-stellar core L1544 (Ward-Thompson et al. 1999)

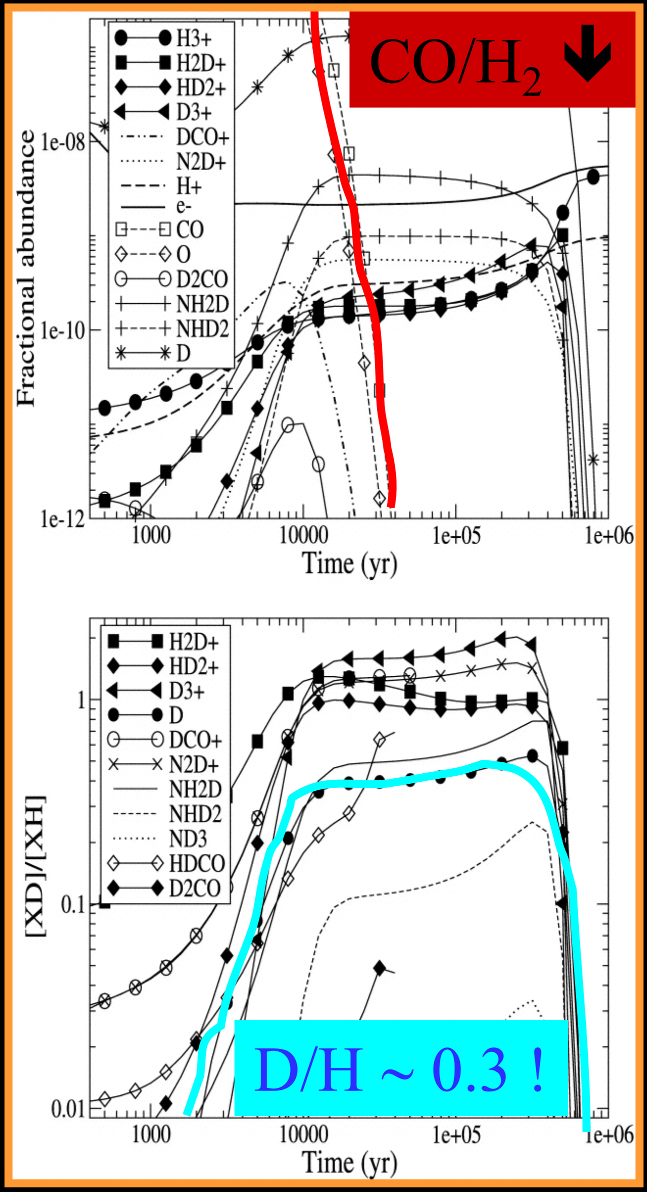


D-fraction increases towards the core center to ~ 0.3 (*Caselli+2002; Crapsi+2004, 2005; Redaelli+2019*)

$$H_3^+ + HD \Rightarrow H_2D^+ + H_2 + 230\ K$$

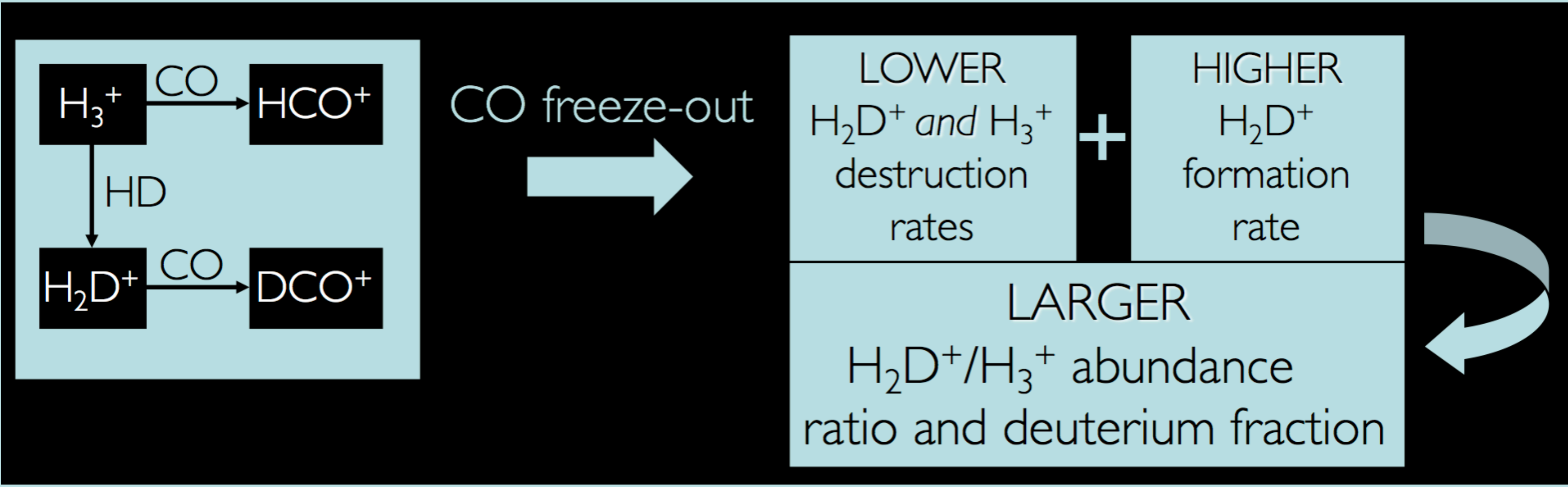
$$H_2D^+ + \begin{cases} N_2 \rightarrow N_2D^+ + H_2 \\ CO \rightarrow DCO^+ + H_2 \end{cases}$$

Roberts, Millar & Herbst 2003 →



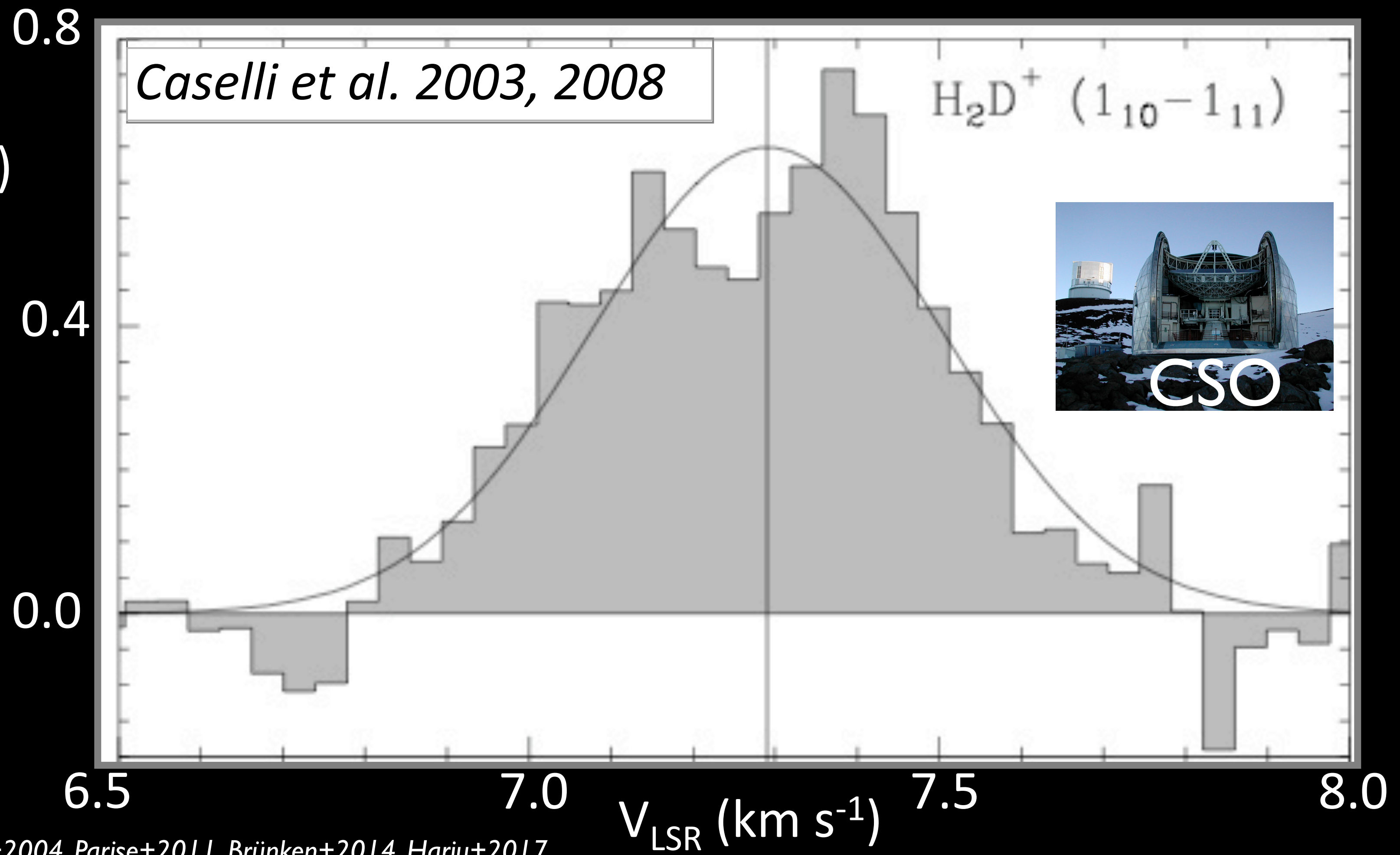
$$H_3^+ + HD \Rightarrow H_2D^+ + H_2 + 230\ K\ (at\ T < 30\ K)$$

H_2D^+ / H_3^+ (and D/H) increases if the abundance of gas phase neutral species decreases (Dalgarno & Lepp 1984).

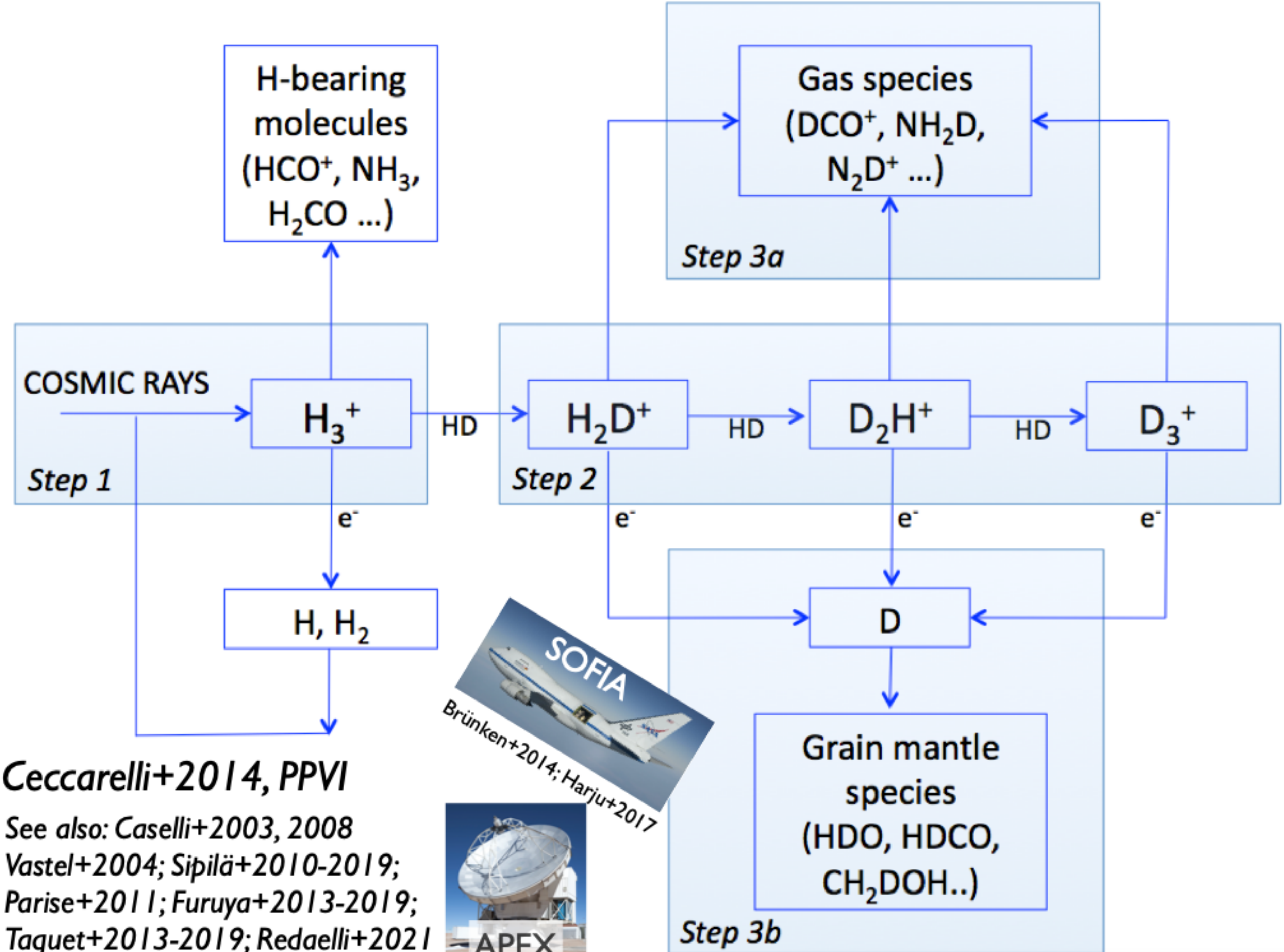


Surprisingly strong ortho-H_2D^+ in pre-stellar cores

- Led to strong revision of astrochemical models (e.g. Roberts et al. 2003)
- Triggered new laboratory work (e.g. Hugo et al. 2009)



See also Vastel+2004, Parise+2011, Brünken+2014, Harju+2017

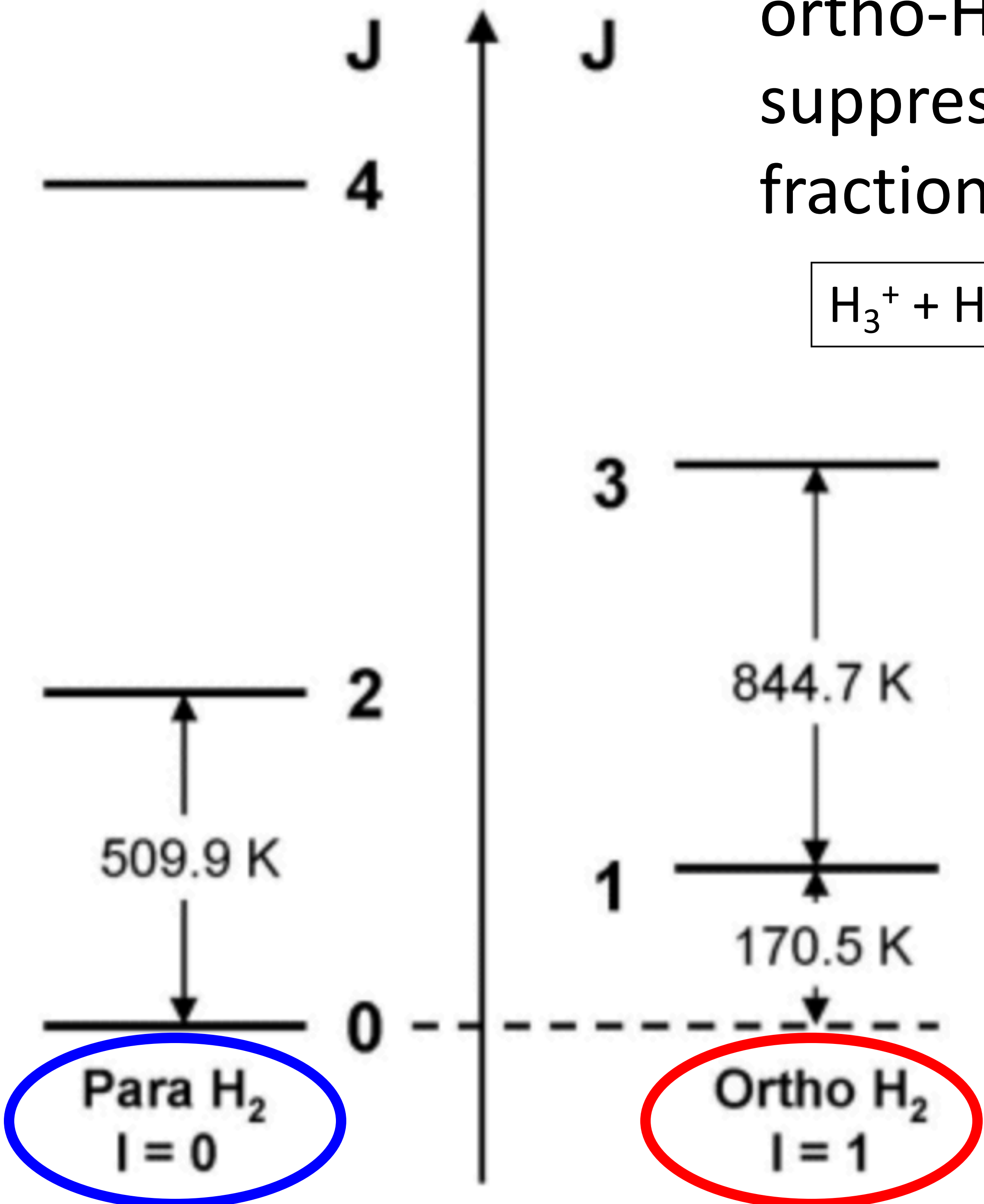


Ceccarelli+2014, PPVI

See also: Caselli+2003, 2008 Vastel+2004; Sipilä+2010-2019; Parise+2011; Furuya+2013-2019; Taquet+2013-2019; Redaelli+2021

ortho-H_2 can slow down / suppress the deuterium fractionation

$$H_3^+ + HD \longleftrightarrow H_2D^+ + H_2 \; + 230\ K$$



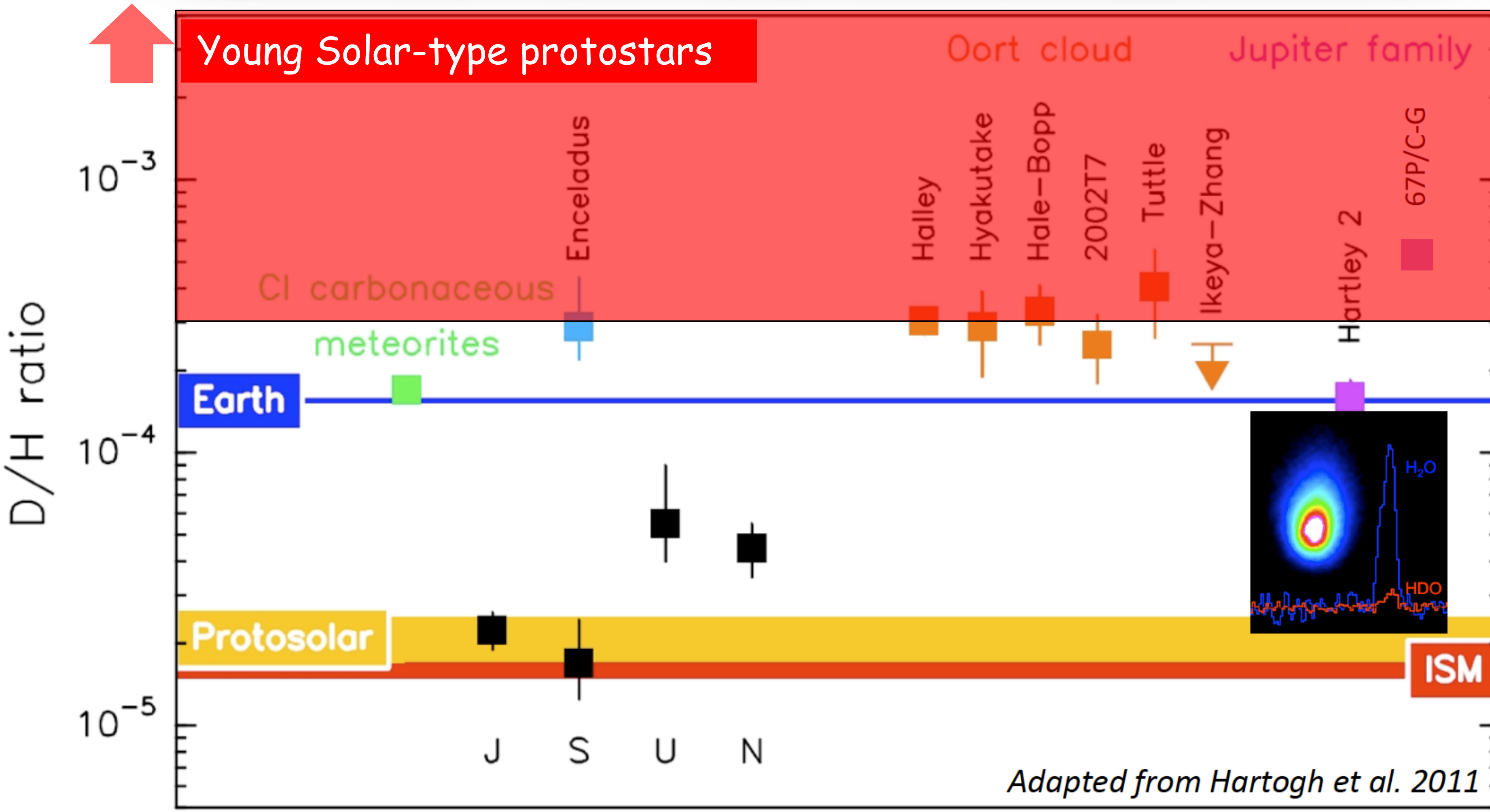
$H_3^+ + HD \rightarrow H_2D^+ + p\text{-}H_2$

$H_3^+ + HD \leftarrow H_2D^+ + o\text{-}H_2$

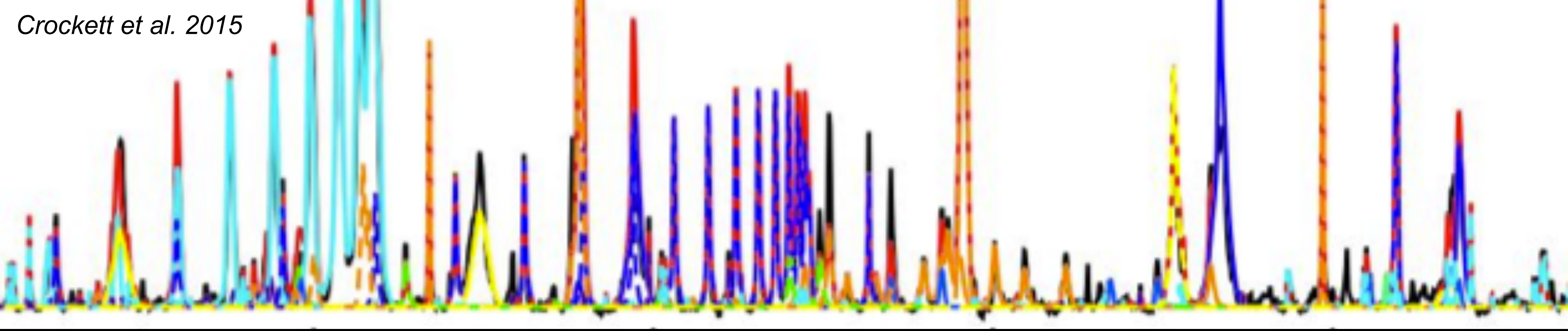
Pagani et al. 1992
Gerlich et al. 2002
Hugo et al. 2009
Sipilä et al. 2013
Kong et al. 2015

HDO/H_2O in our Solar System

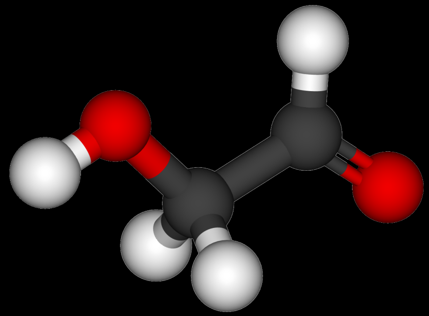
(high D/H ratios in Earth's oceans, comets, carbonaceous chondrites)

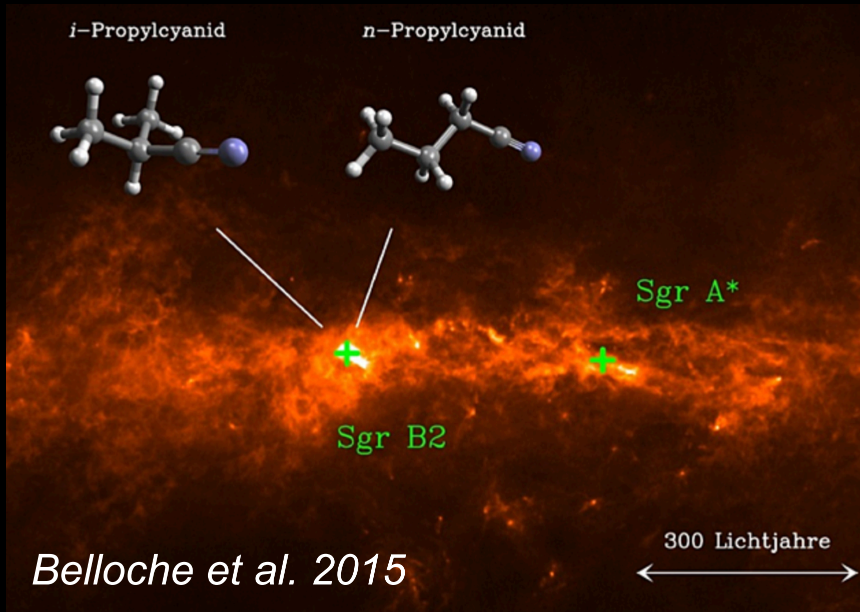


HDO/H_2O in our Solar System requires ice production during the cold phase (Cleeves+2014) ⇒ pre-stellar core chemistry is important !



4. Complex* Organic Molecules (COMs)





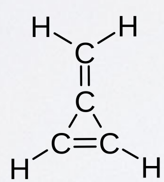
* ≥ 6 atoms in size *(Herbst & van Dishoeck 2009)*

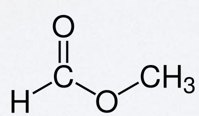
COMs form at the edge of the "catastrophic" CO freeze-out zone

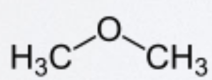
(see theory work by Vasyunin+2017)

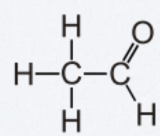
See also:

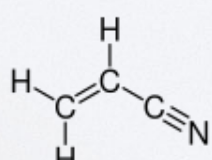
Marcelino+2007
Öberg+2010
Bacmann+2013
Bizzocchi+2014
Vastel+2014
Bacmann&Faure 2016
Jiménez-Serra+2016, 2021
Spezzano+2016, 2017, 2020
Scibelli & Shirley 2020
Ambrose+2021
Punanova+2022

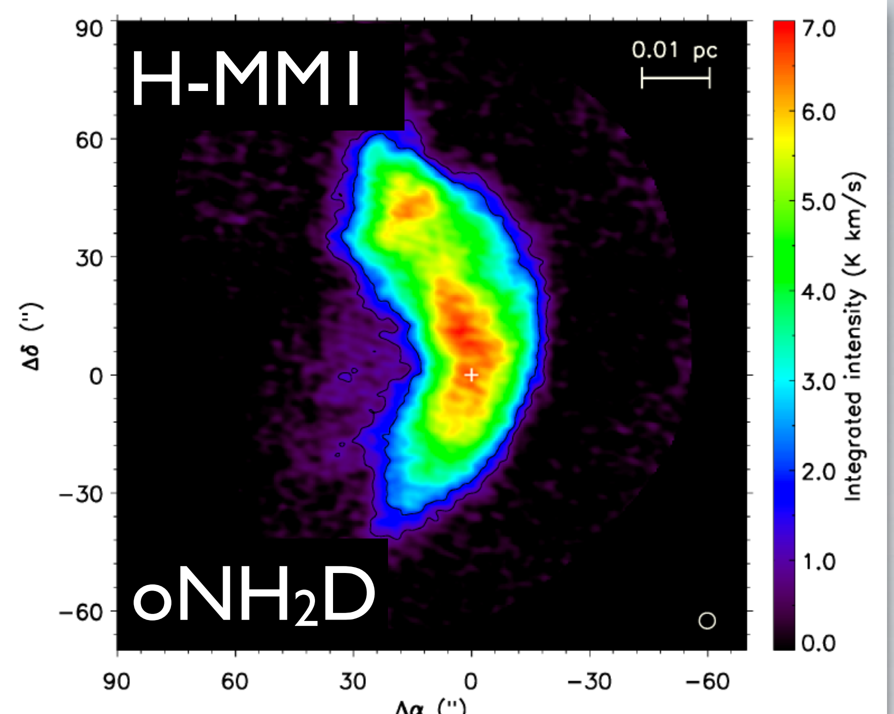


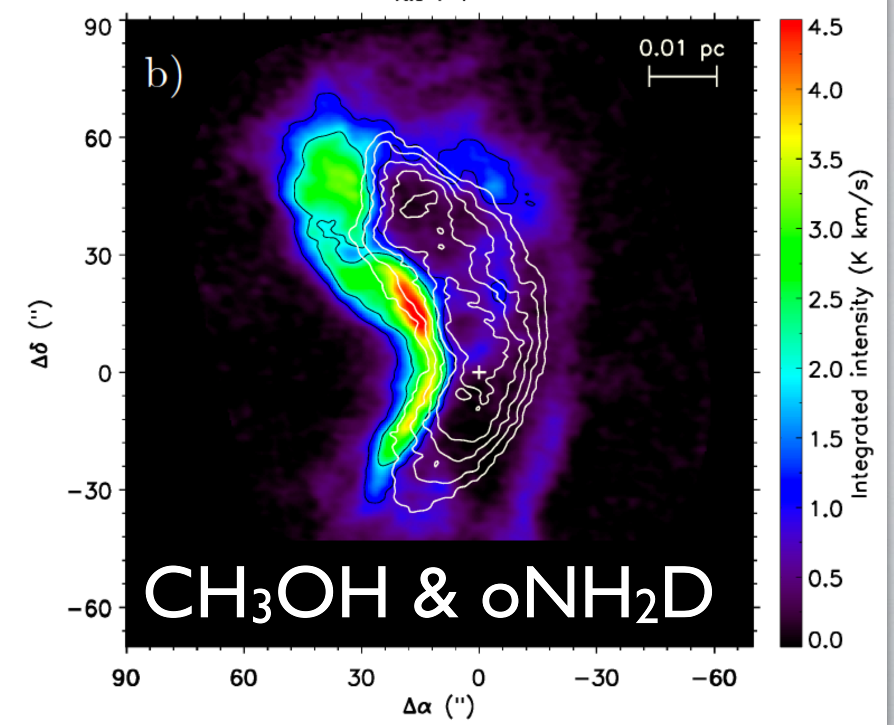








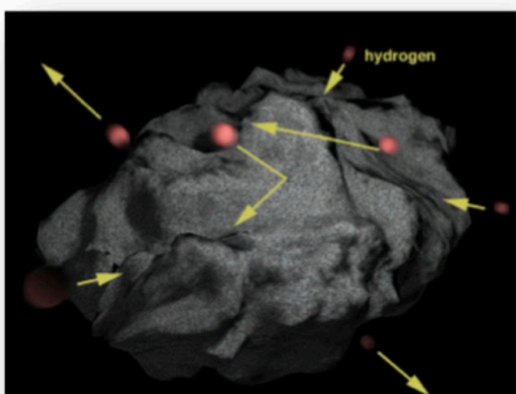




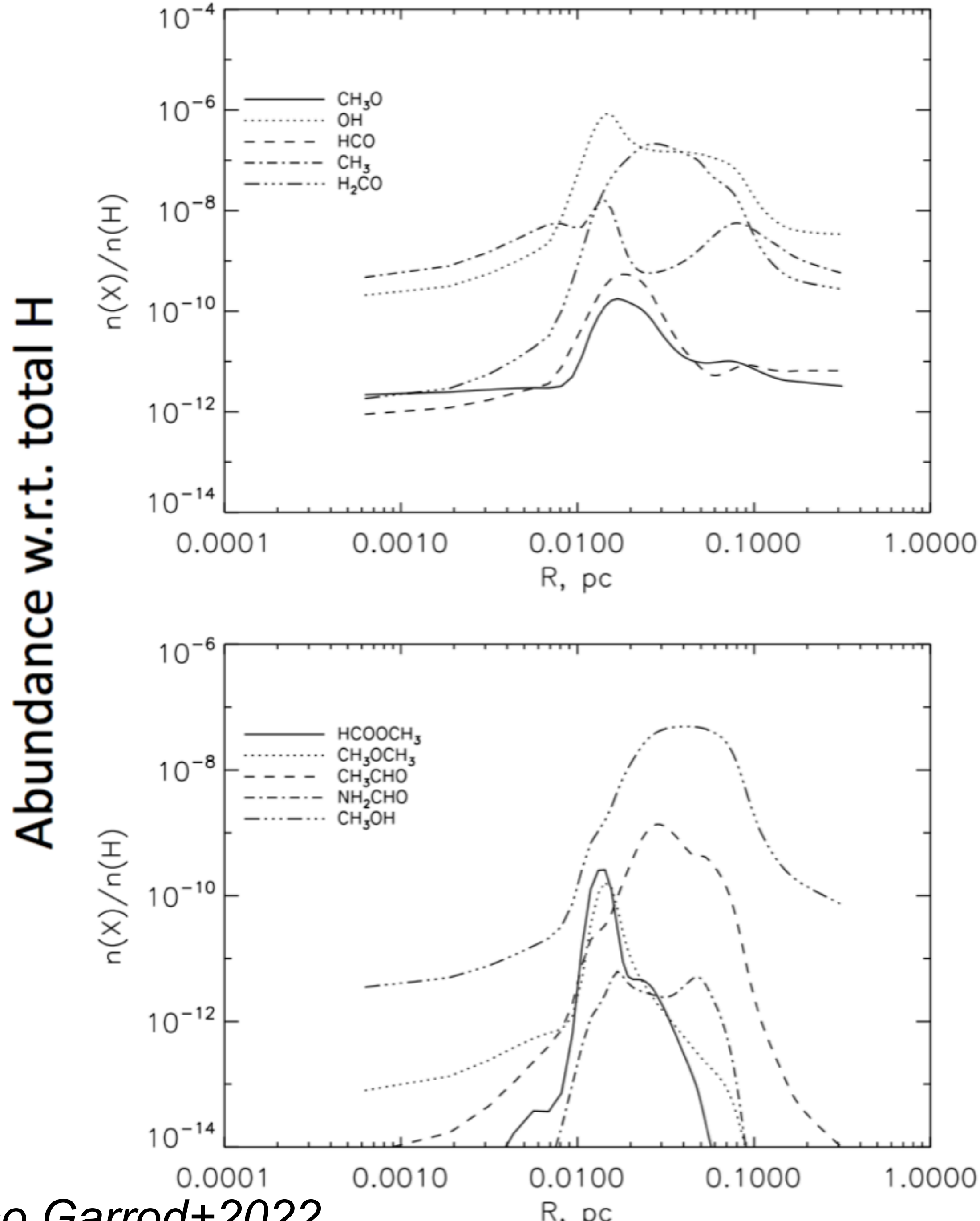
Gas + grain chemistry in L1544

- physical structure
- gas-grain chemistry
- reactive desorption
- photodesorption
- neutral-neutral reactions

(Shannon+2008; Balucani+2015; Barone+2015; Skouteris+2017)

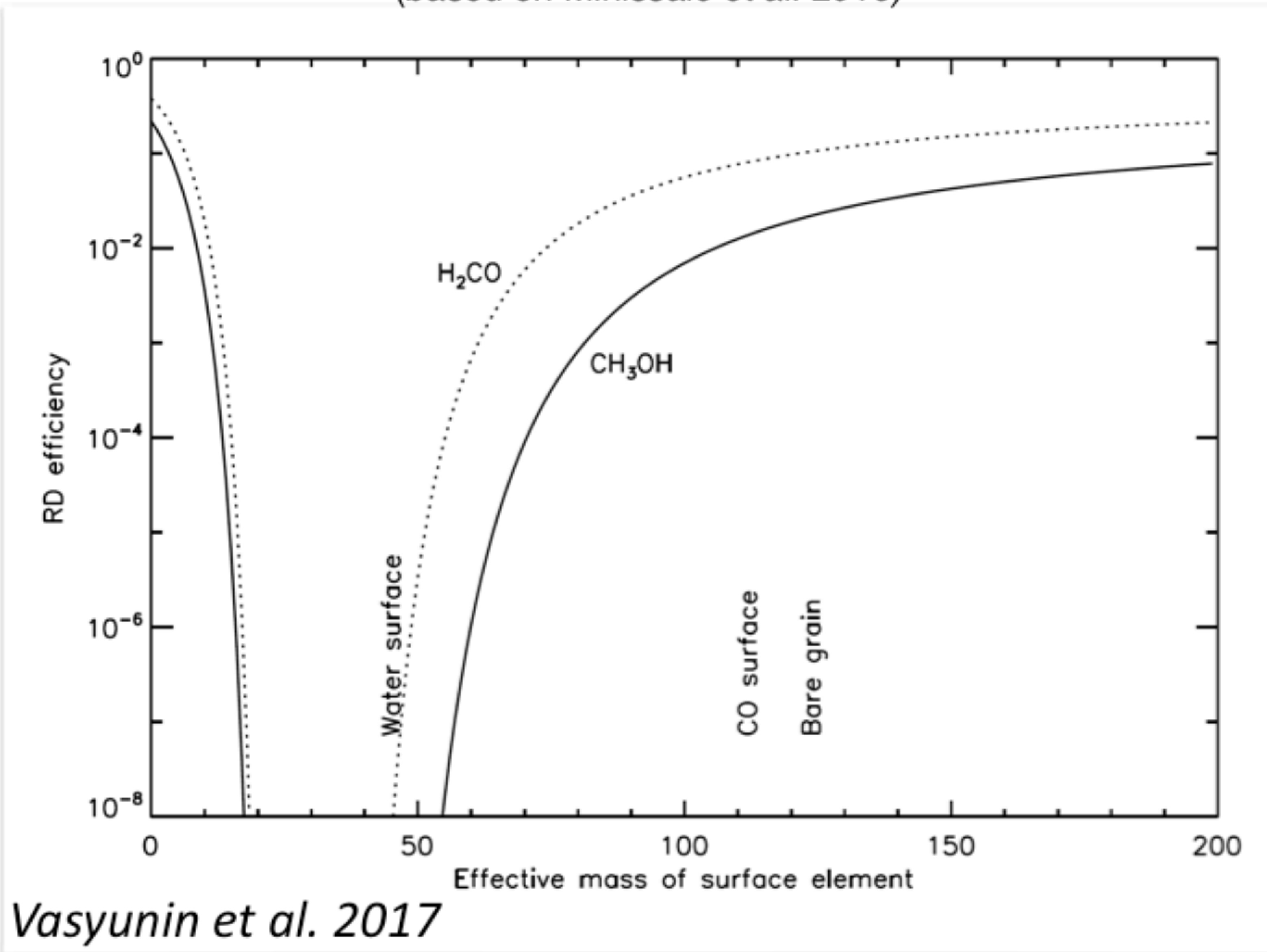


Vasyunin et al. 2017



see also Garrod+2022

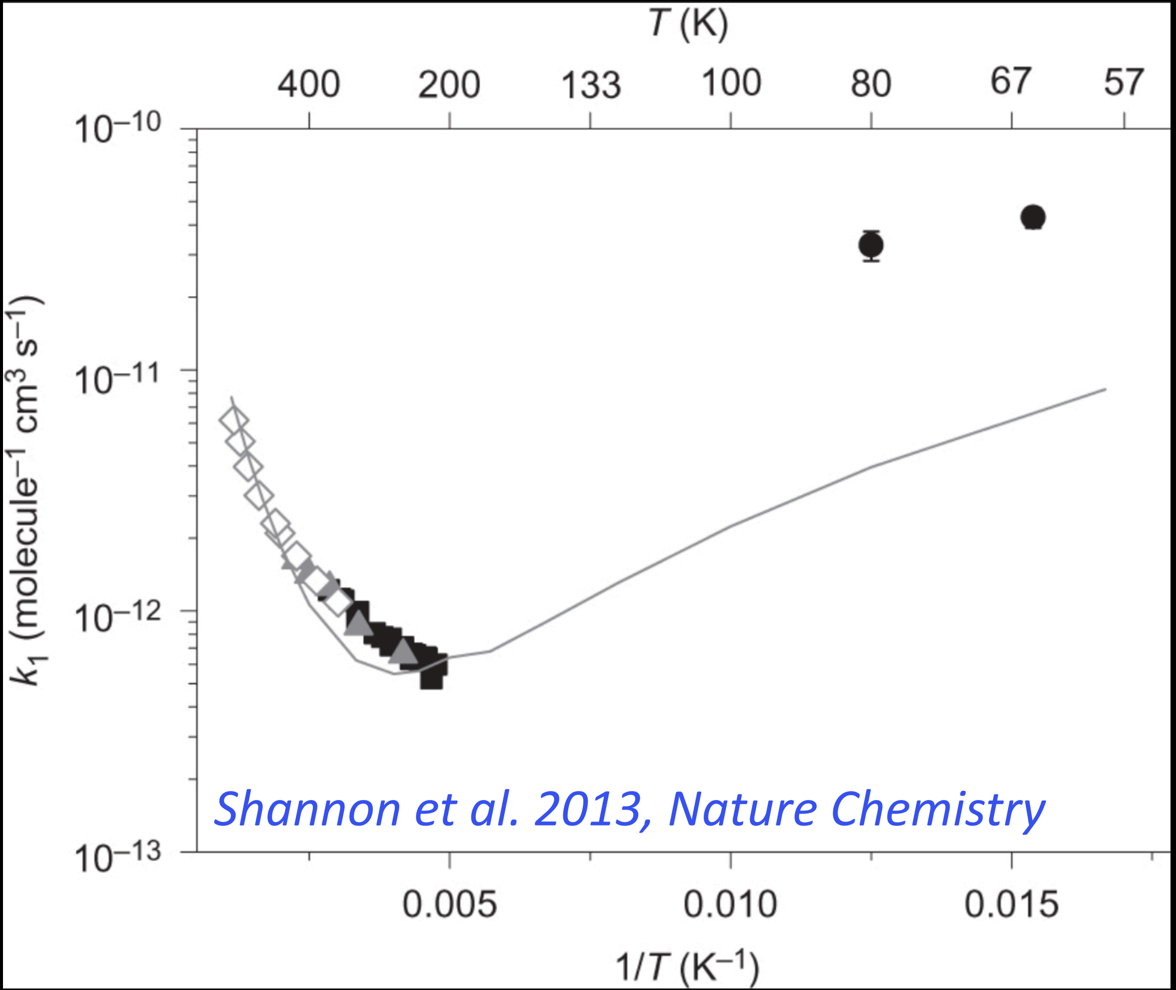
Reactive desorption efficiency of CH_3OH and H_2CO in surface reactions $H + HCO \rightarrow H_2CO$ and $H + H_3CO \rightarrow CH_3OH$, vs. the effective mass of the surface element (based on *Minissale et al. 2016)*



Neutral-Neutral reactions

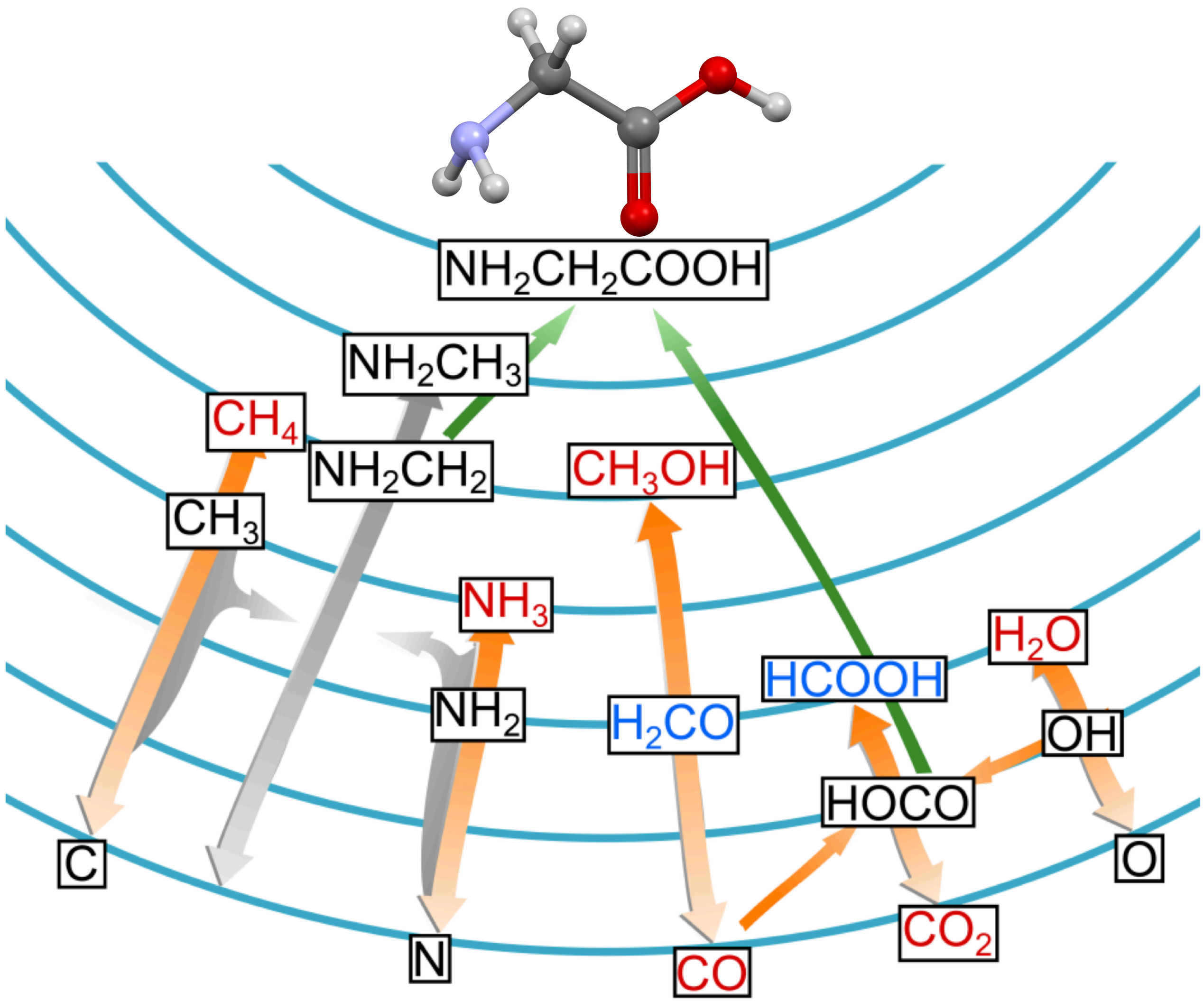
$$OH + CH_3OH \rightarrow CH_3O + H_2O$$

Accelerated chemistry at low interstellar temperatures, facilitated by tunneling.



Shannon et al. 2013, Nature Chemistry

Formation of glycine in a water-rich ice at low T



Laboratory experiment: *Ioppolo+2021, Nature Astronomy*

see also Krasnokutski+2022, Nature Astronomy