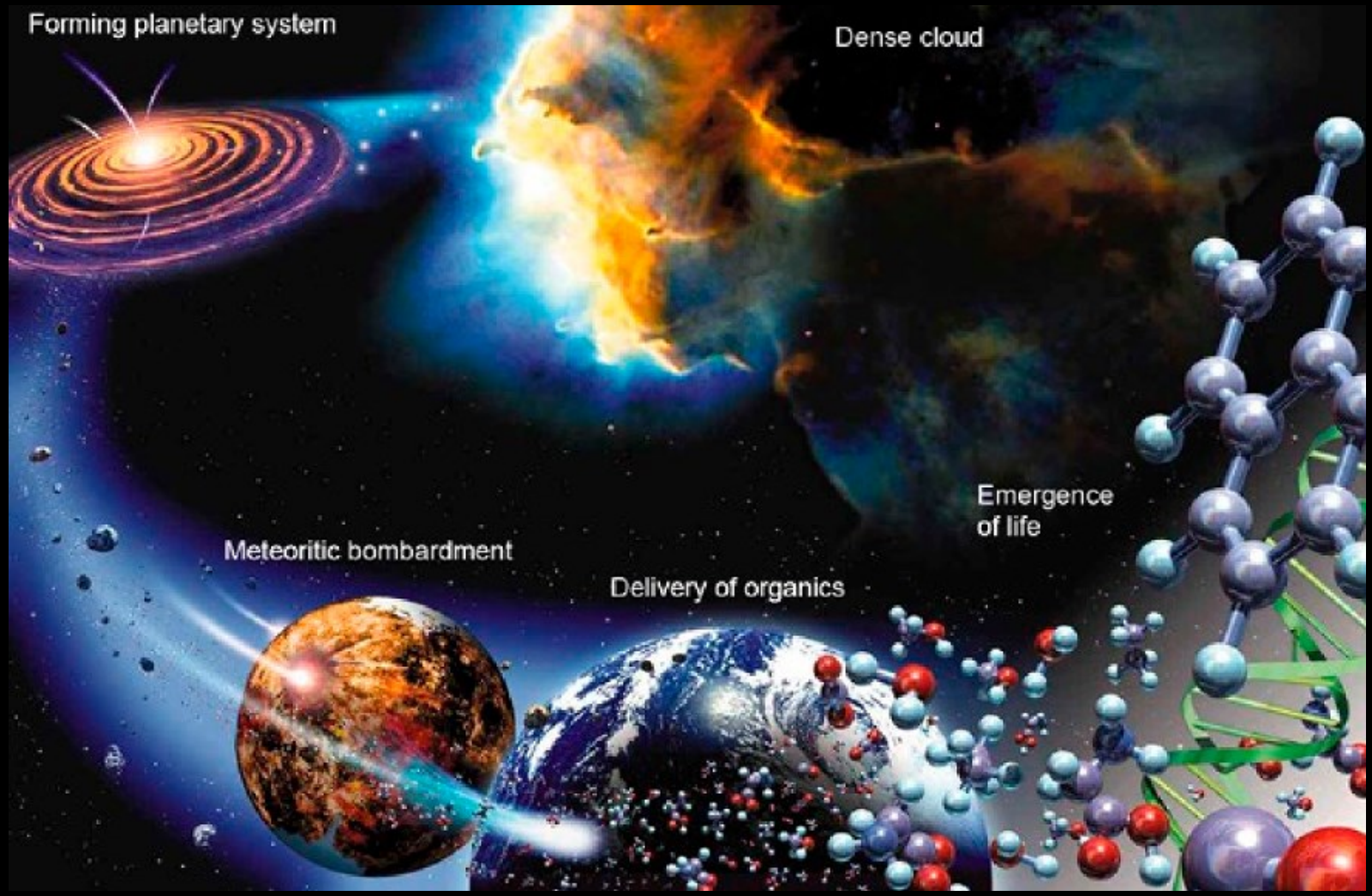
Master course: Astrochemistry I:

Lecture 6: Dark cloud chemistry

Reading list:

Bergin & Tafalla 2007, ARA&A

Herbst & van Dishoeck 2009, ARA&A



Dr. Helgi Rafn Hrodmarsson – UPEC – 2026-2027

Outline

- Introduction
- Observations
  - Gas-phase molecules
  - Ices
- Models
  - Gas-phase models
  - Gas-grain models
- Comparison with observations
  - TMC-1S vs other cores
  - Pre-stellar cores: L 1498, B 68, L 1544
- Conclusions

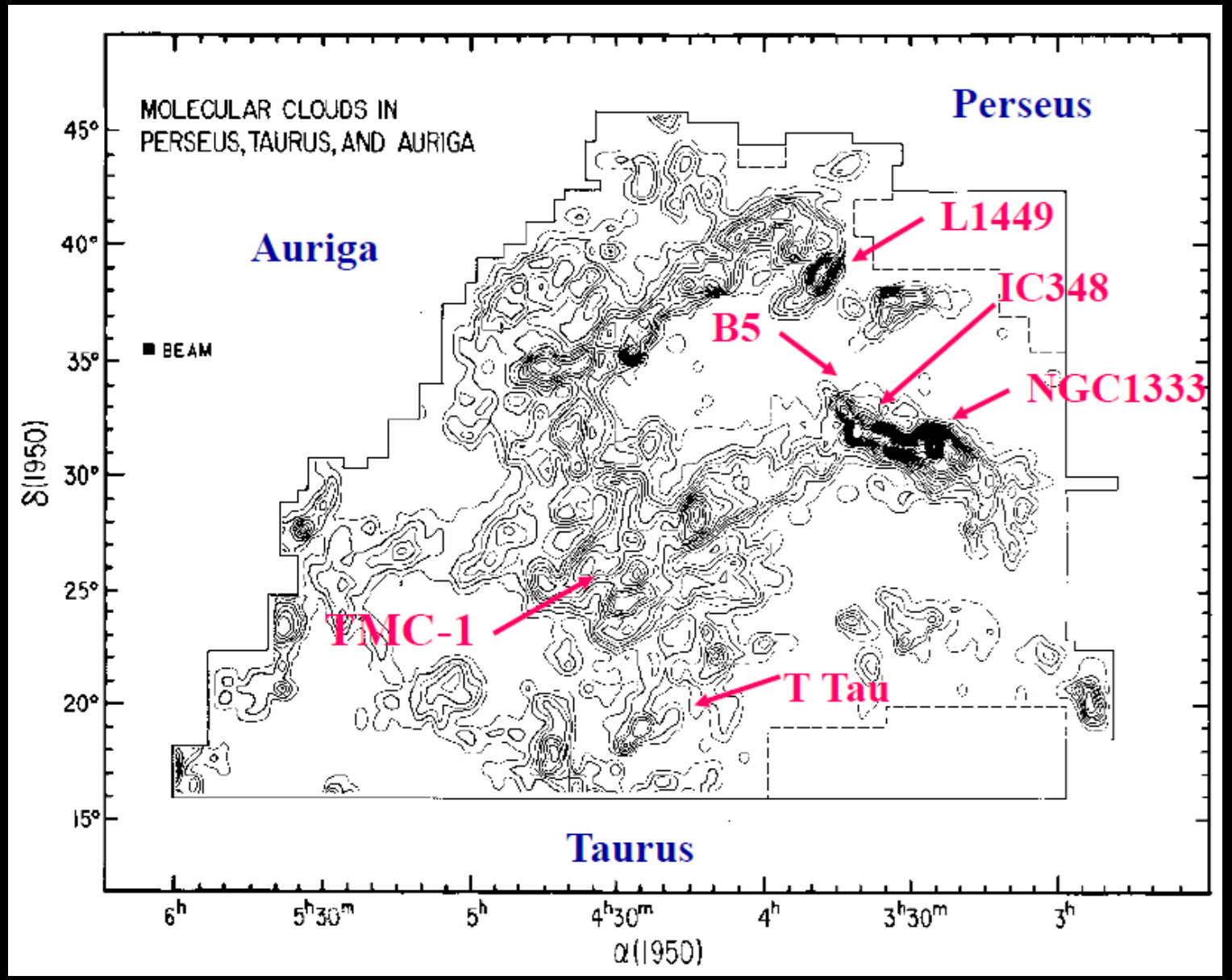
6.1 Introduction

- Basic dark cloud gas-phase ion-molecule chemistry developed by Herbst & Klemperer 1973, Watson 1976, Dalgarno & Black 1977, Prasad & Huntress 1980, Millar et al. 1991
- Early gas-phase models: no photoprocesses, no depth dependence, no grain-surface reactions (except H_2), comparison almost exclusively with TMC-1, where a growing number of molecules were detected
- Grain-surface chemistry gradually included by Allen & Robinson 1978, Tielens & Hagen 1982, d'Hendecourt et al. 1985, Herbst & Hasegawa 1993, ices observed since 1973
- What is the status of models and observations > 50 yrs later?

6.2 Observations

- Dark clouds have $T \approx 10$ K, $n_{\mathrm{H}} \approx 10^4$–$10^5$ cm^{-3} => strongest lines at mm wavelengths (low-J transitions)
- Intensively focused since 70's – 80's; searches for new molecules focus on TMC-1S
  - ~60 species found, including long carbon chains
  - Negative ions and more saturated chains
  - Recently: Many PAHs
- Some systematic studies on variations of abundances between clouds
- Focus on pre-stellar cores, e.g., B68 and L1544
  - Centrally concentrated structure, on the verge of collapse?
  - See summary in Bergin & Tafalla 2007

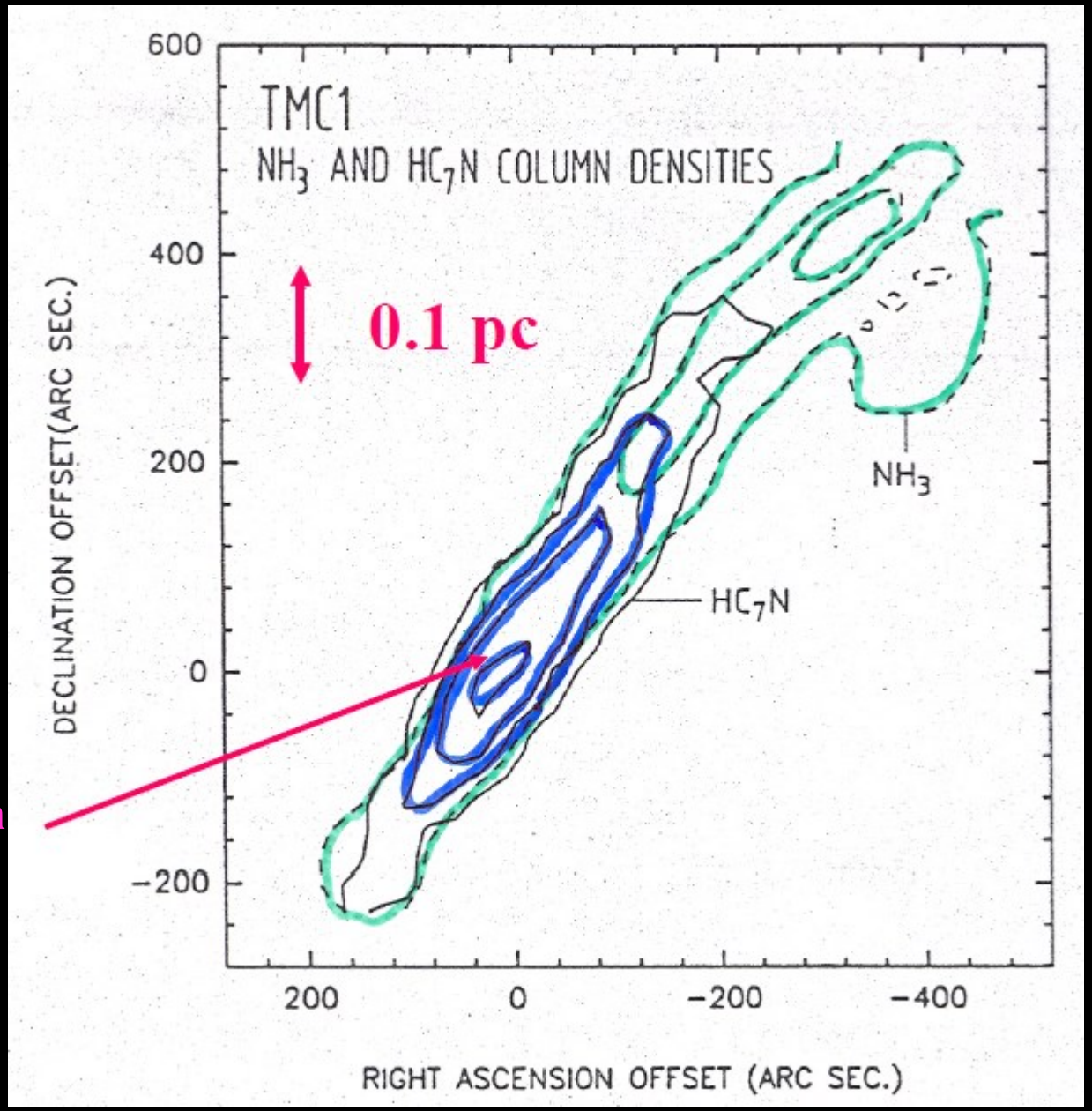
Taurus molecular cloud (TMC)



CO 1-0

Ungerechts & Thaddeus 1987

TMC 1: ‘home’ of long carbon chains



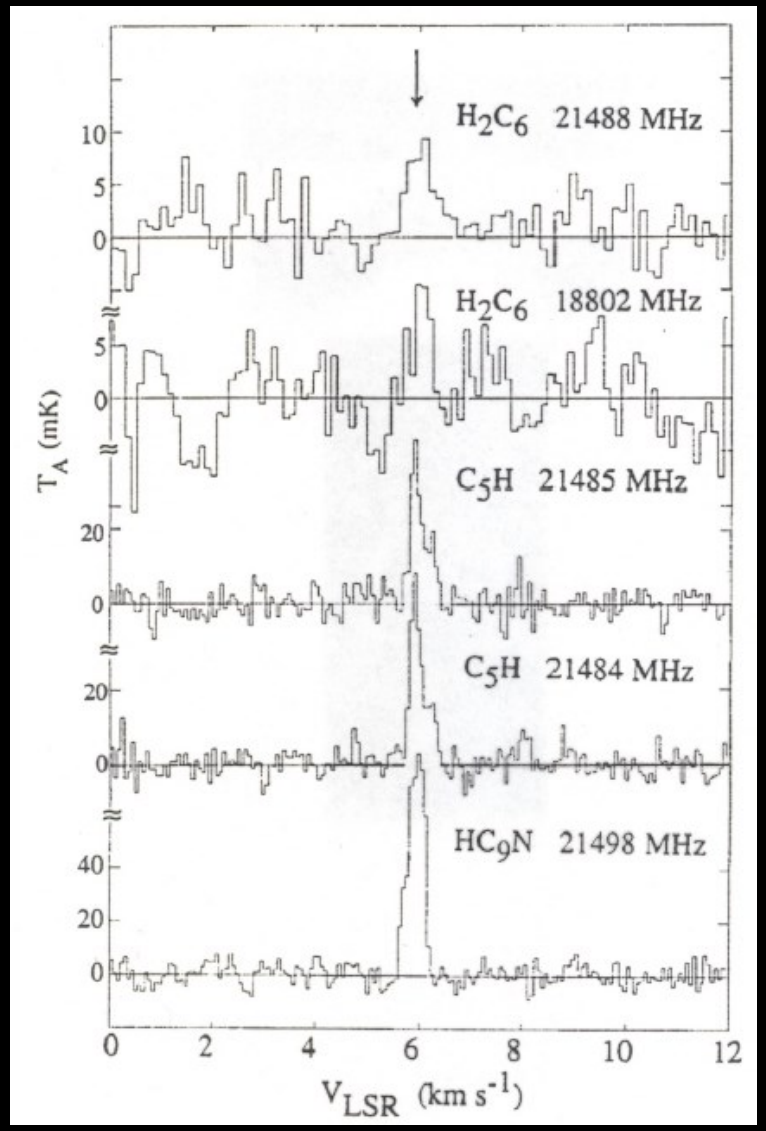
CO 1-0

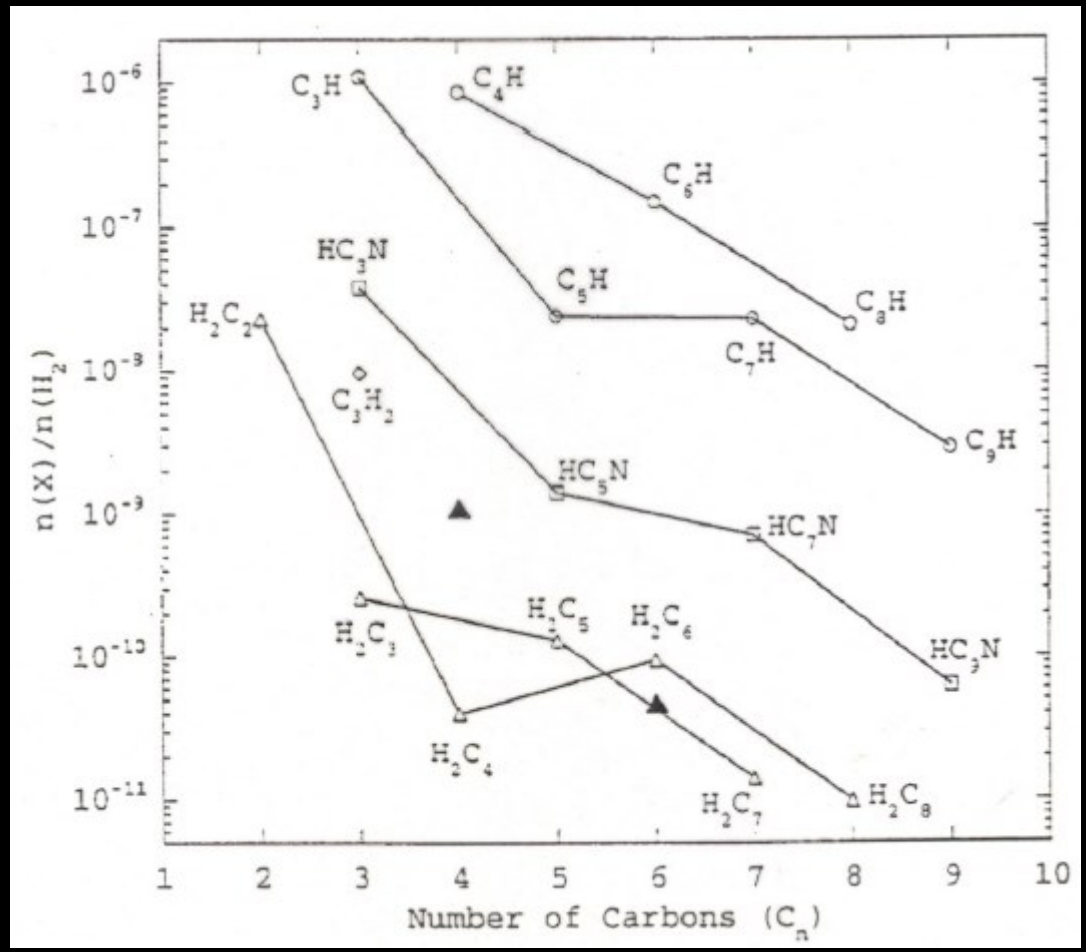
Note chemical differentiation NH_3 vs HC_7N

Long carbon chain peak

Olano et al. 1988

Detection of carbon chains in TMC-1S

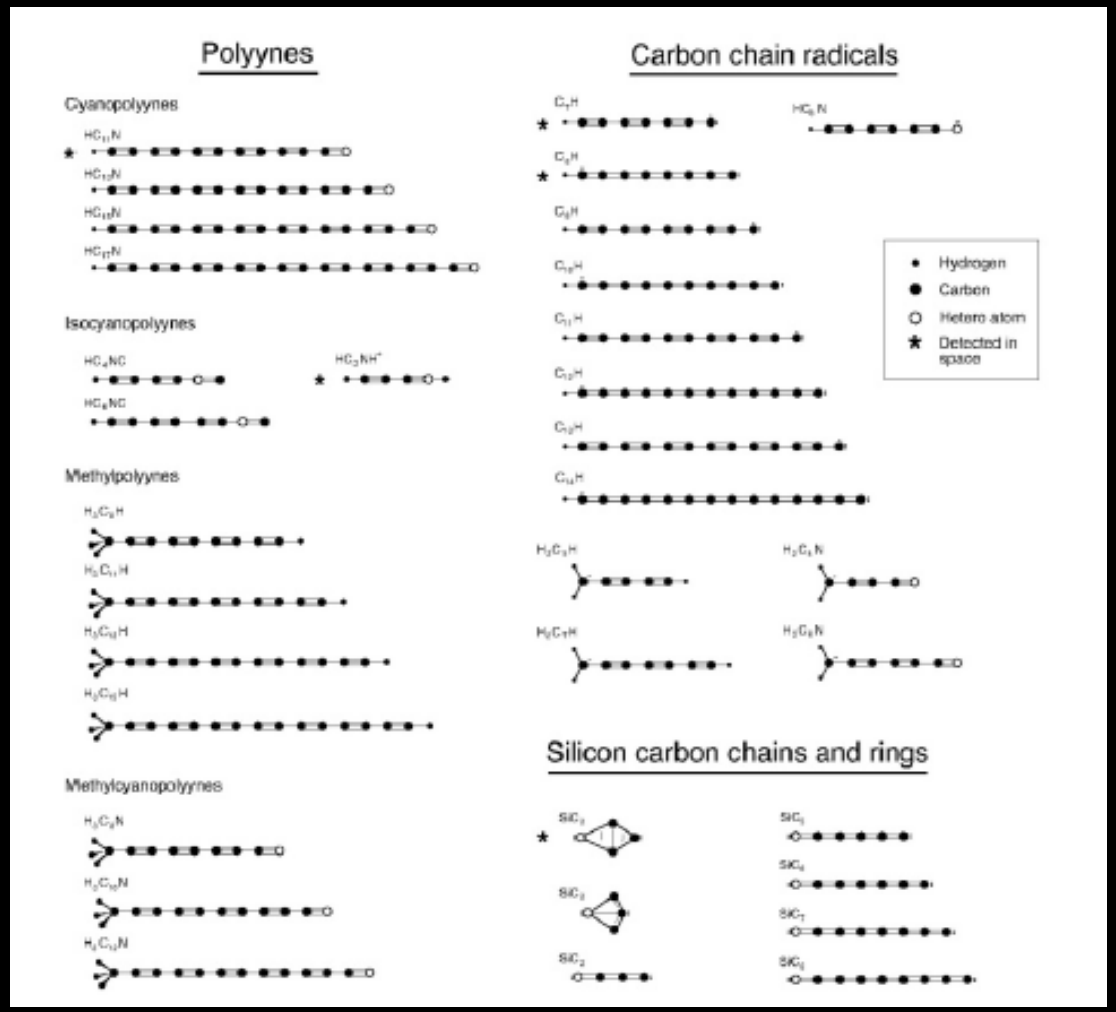


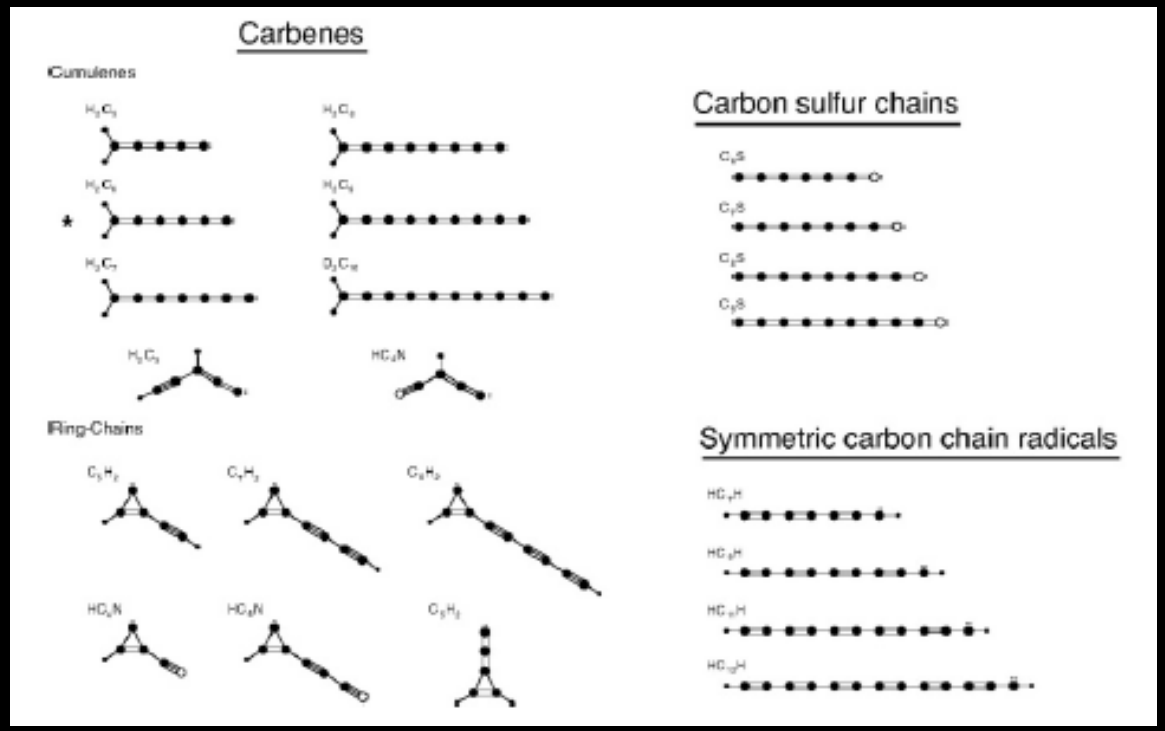


Note very narrow lines

Langer et al. 1997

Carbon chains in lab



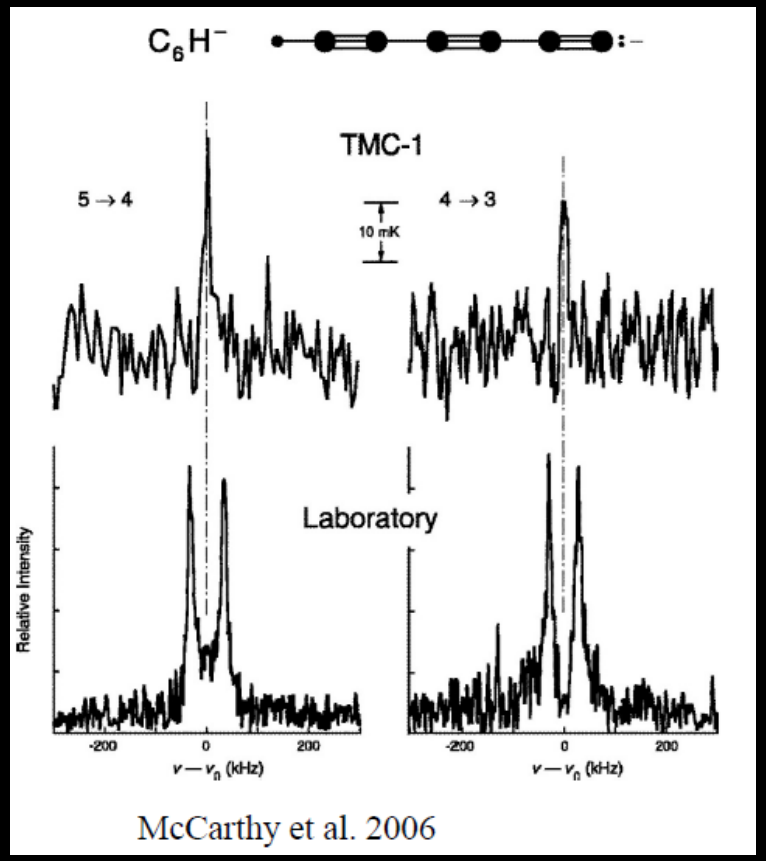


Many of these chains have not yet been observed in space

Thaddeus, McCarthy et al. 2000

Negative ions and saturated chains

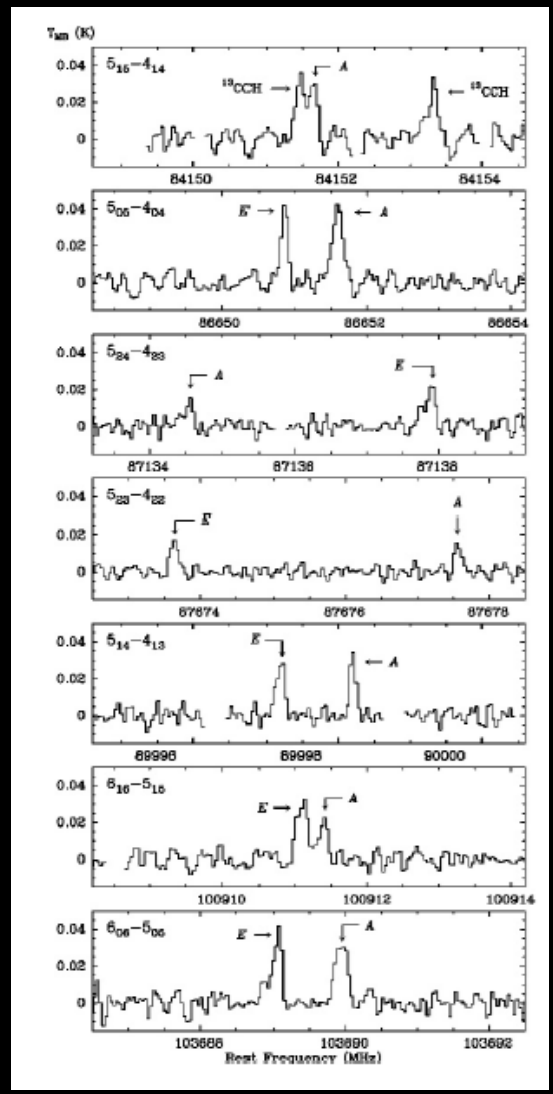
Negative ions



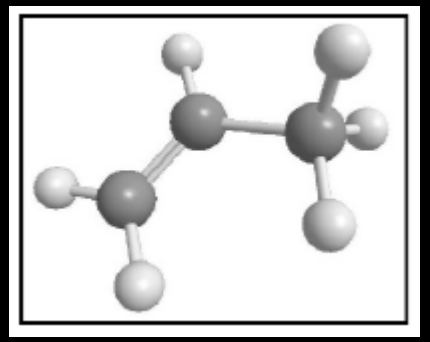
McCarthy et al. 2006

Electron attachment rate increases with size of chains => search for large species

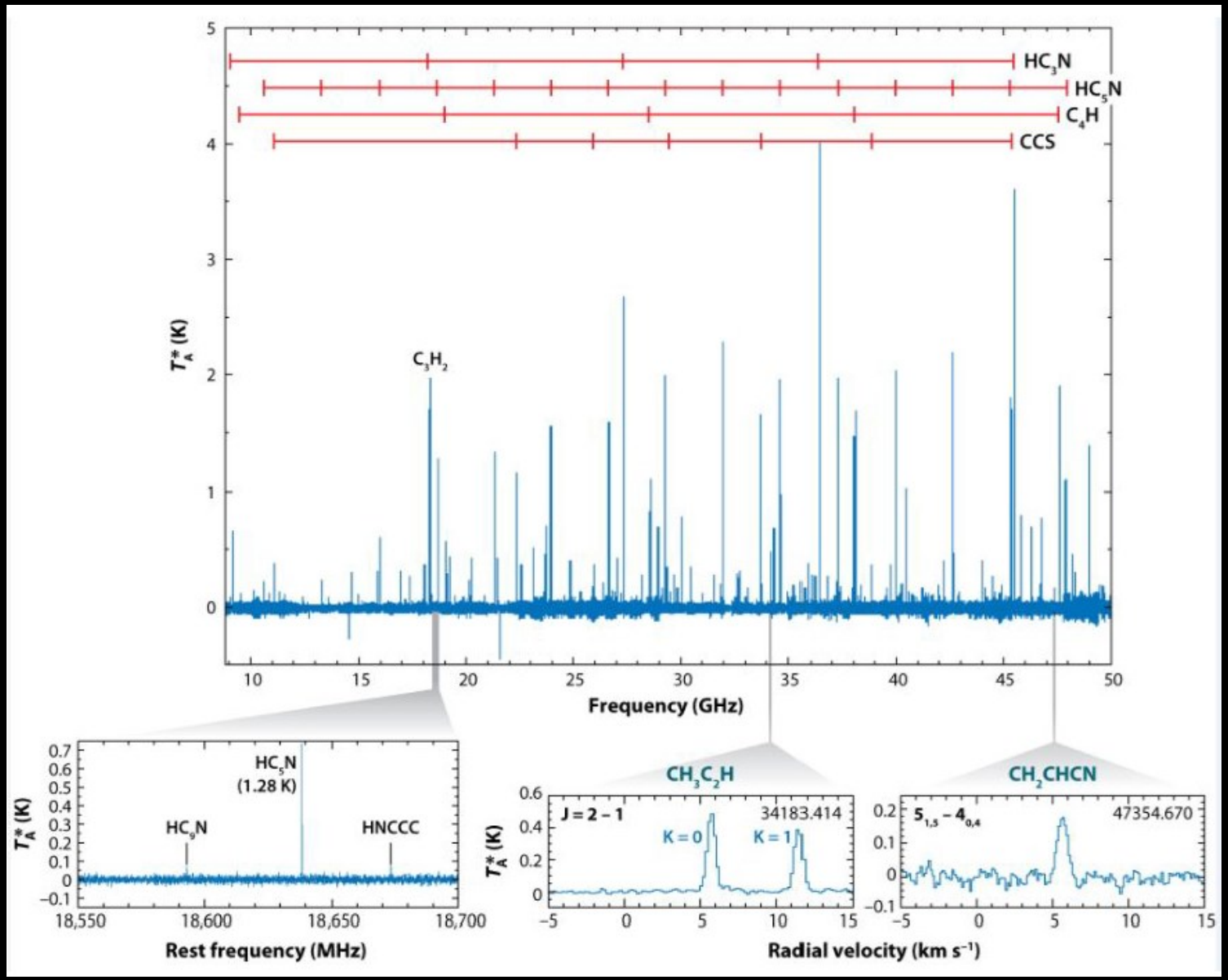
Propene in TMC-1



Marcelino et al. 2007



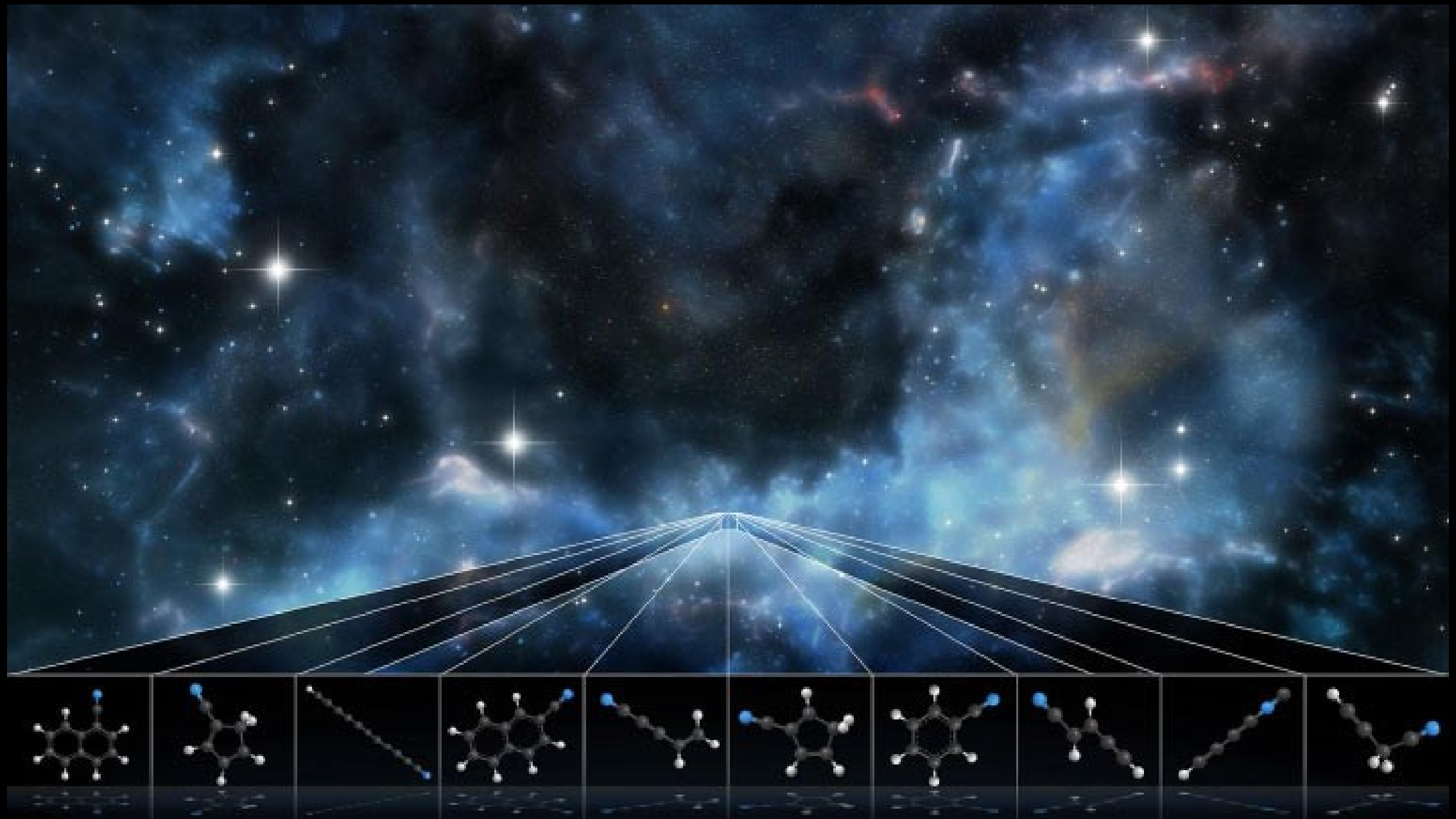
Nobeyama line survey TMC-1



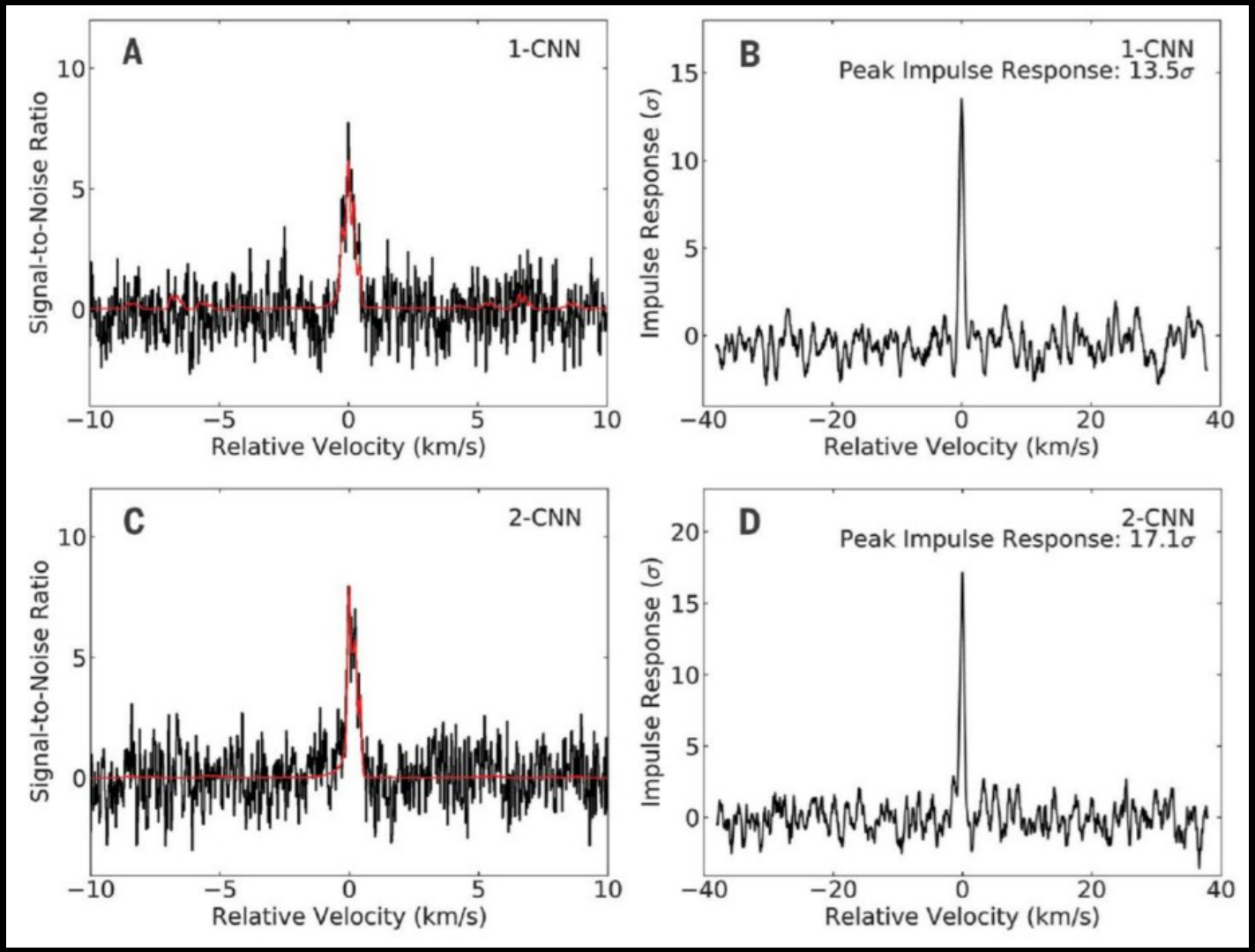
Kaifu et al. 2004

Spectrum dominated by carbon chain molecules

TMC-1 in the 2020‘s – PAH revolution



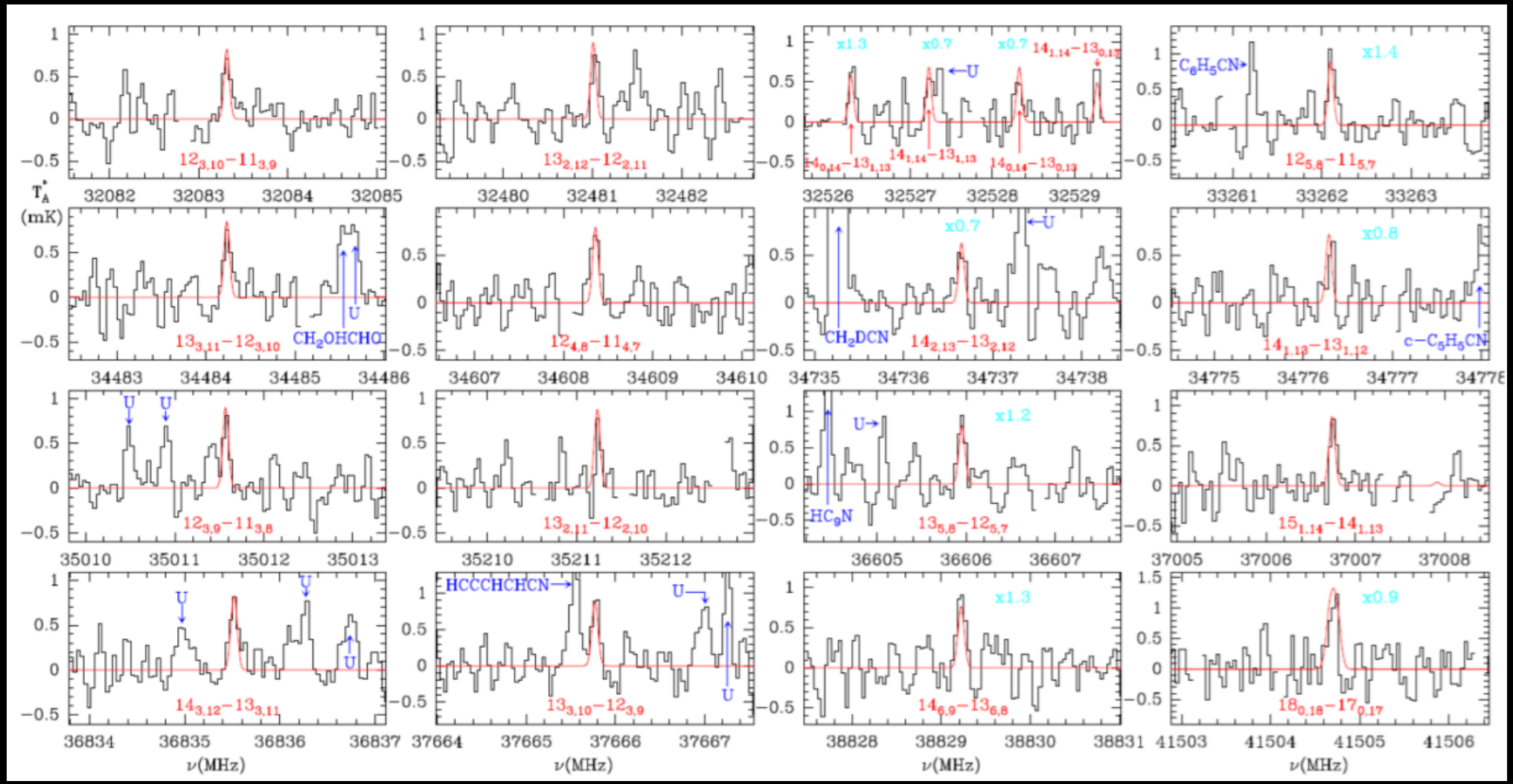
TMC-1 in the 2020‘s: GOTHAM survey



USA: Green Bank Observatory
Spectral stacking to increase S/N ratio

McGuire et al. 2021

TMC-1 in the 2020‘s: QUIJOTE survey



Spain: New heterodyne receiver technology - Yebes
Super high sensitivity – mK resolution

Cernicharo et al. 2021

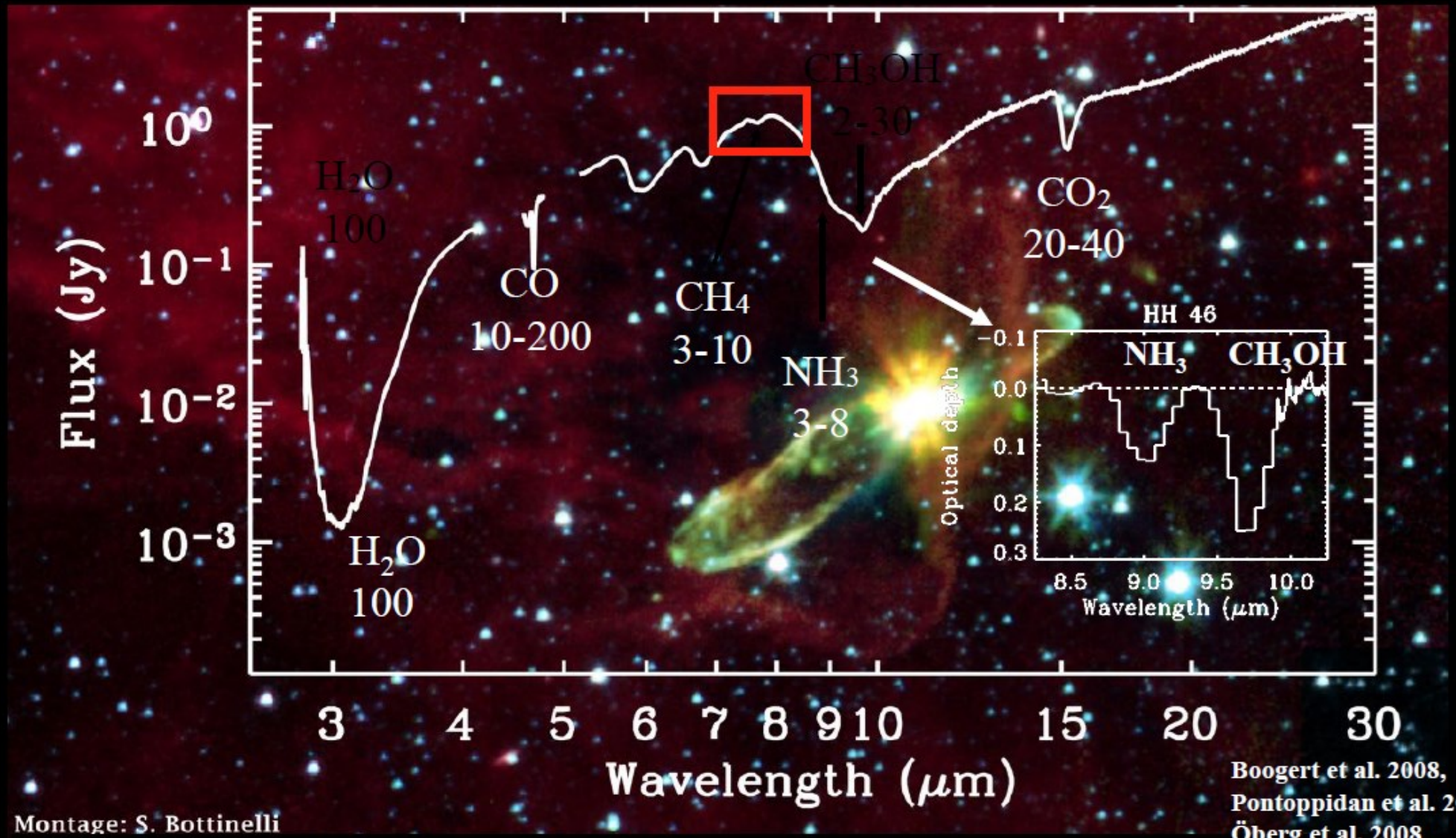
Observations of ices

- Observation of ices in absorption against background stars
- Ice mantles contain small molecules H_2O, CO, CO_2, but also more complex ones such as HCOOH, even under quiescent conditions
- In quiescent dark starless clouds, ices contain ~10–50% of heavy elements
- In the centers of pre-stellar cores with a central density concentration, up to 99% of the heavy elements may be frozen out

=> Ices are a significant component!

(orders of magnitude more abundant than carbon chains)

Recall: Ices around low-mass protostars

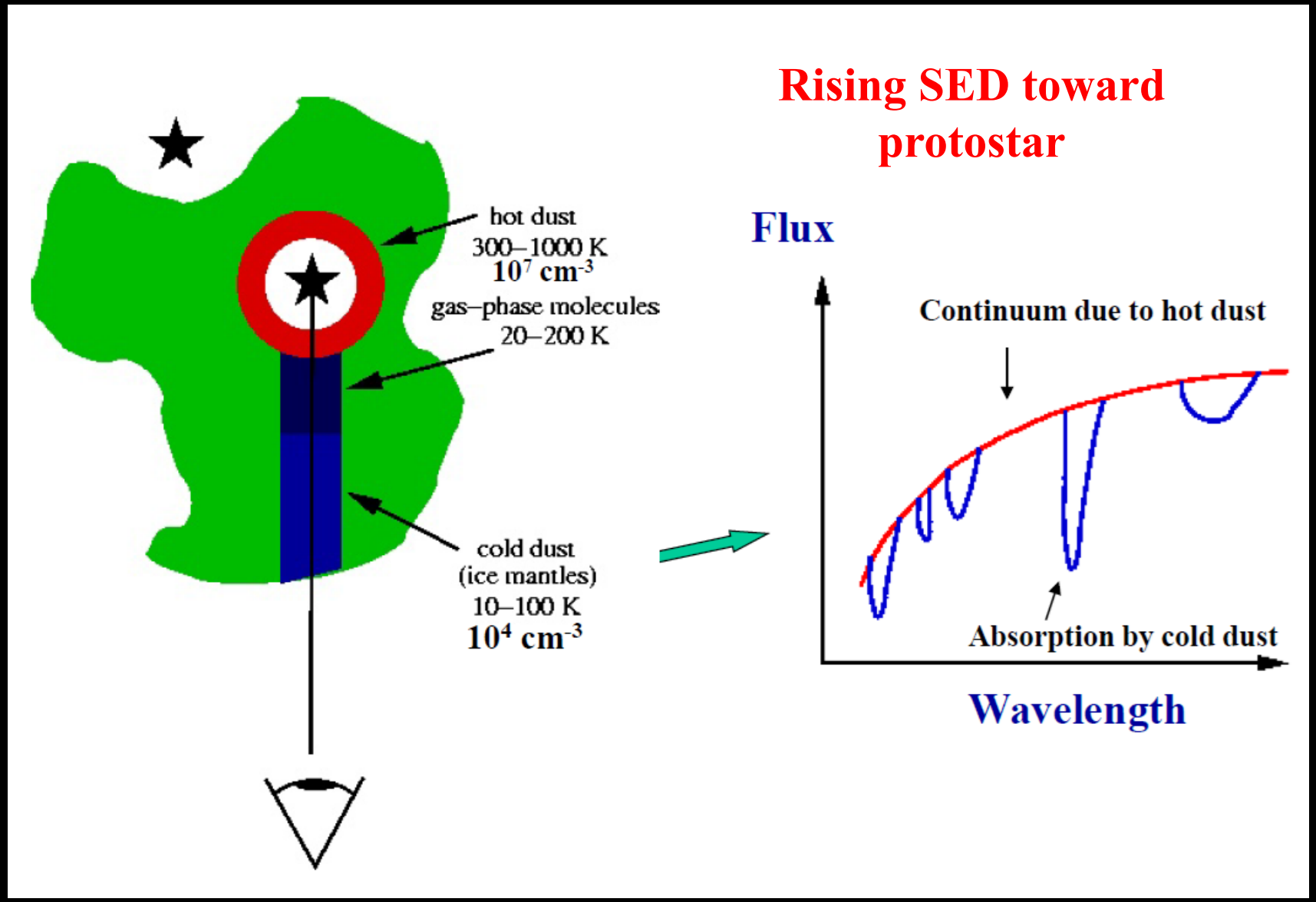


Montage: S. Bottinelli

- Variations seen in NH_3, CH_3OH and OCN^-

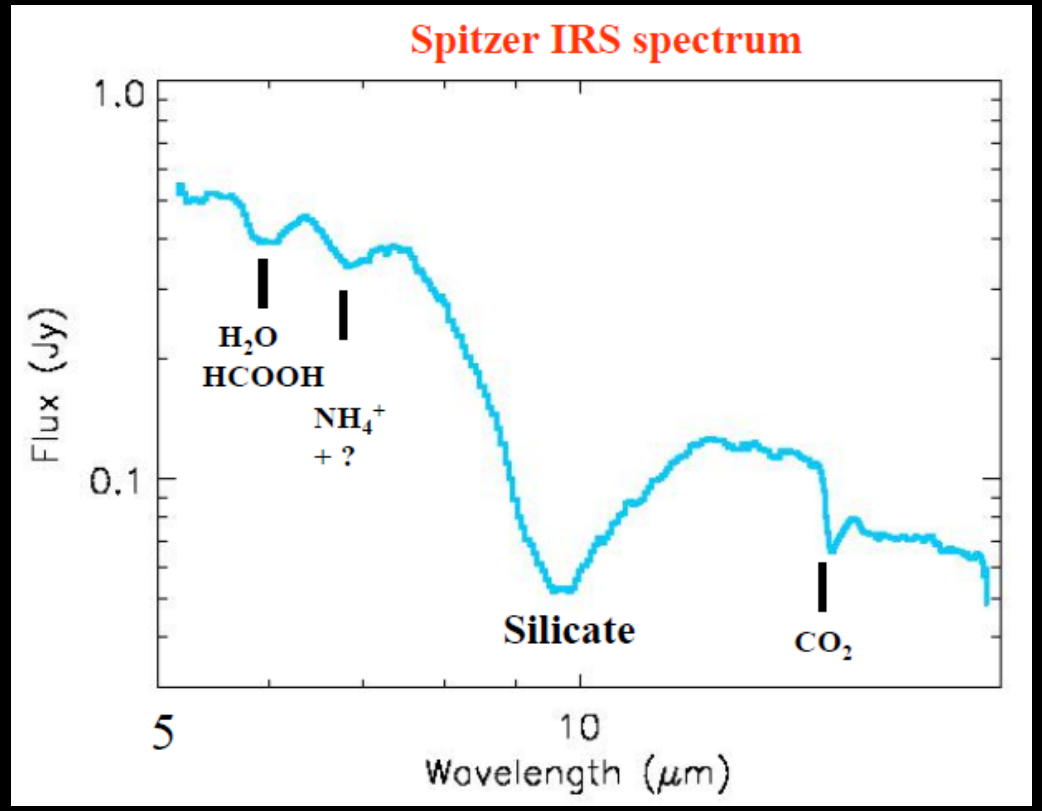
Boogert et al. 2008,
Pontoppidan et al. 2008,
Öberg et al. 2008
Bottinelli et al. 2010

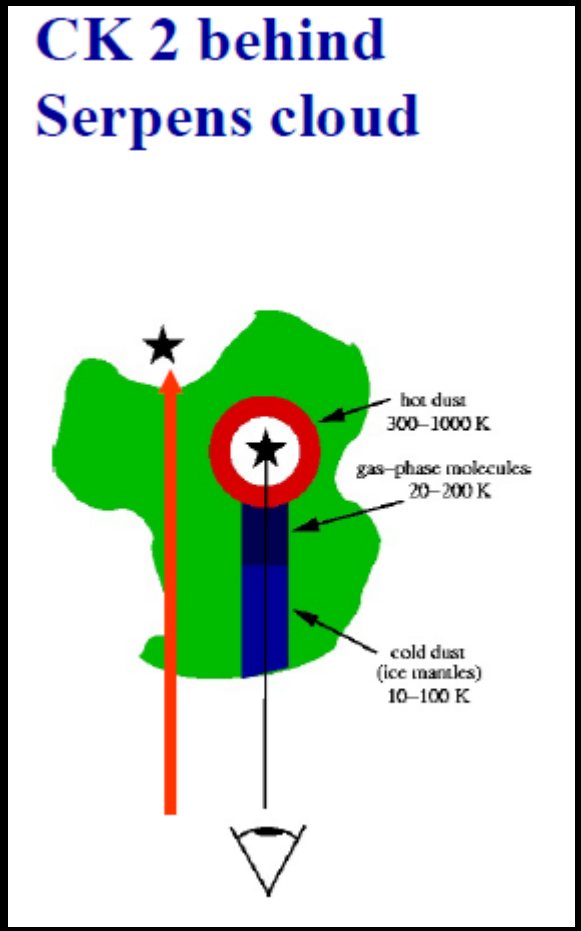
Lecture 1: IR absorption gas & solids



Vibrational transitions of gases *and* solids

Background sources: quiescent clouds

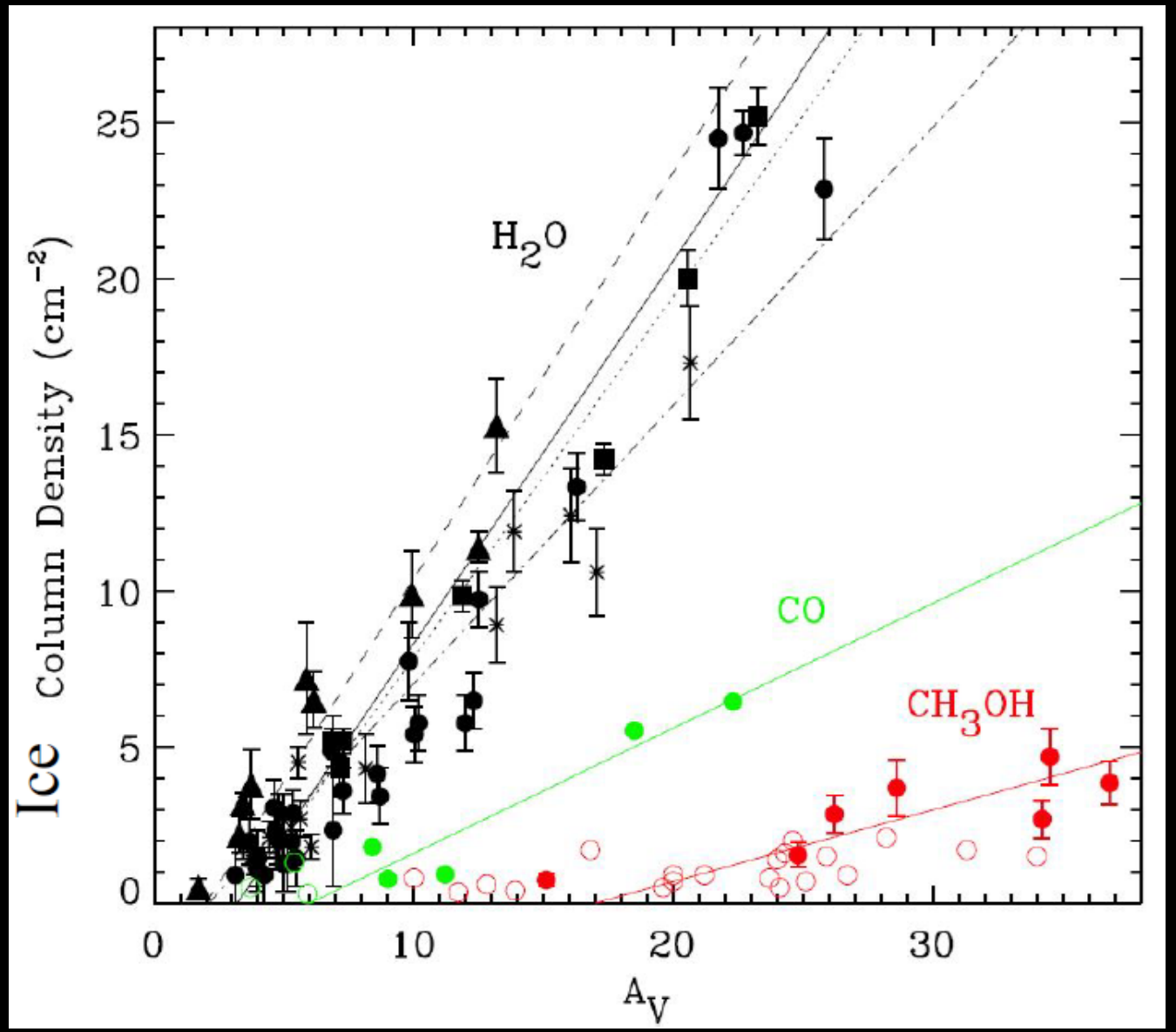




- Probe ice composition prior to star formation, unaffected by heating and radiation from star
- Features same as seen as for YSOs, including 6.0 and 6.8 μm bands => do not require heating
- ***Bulk of ices formed prior to star formation***

Knez et al. 2005
Bergin et al. 2005

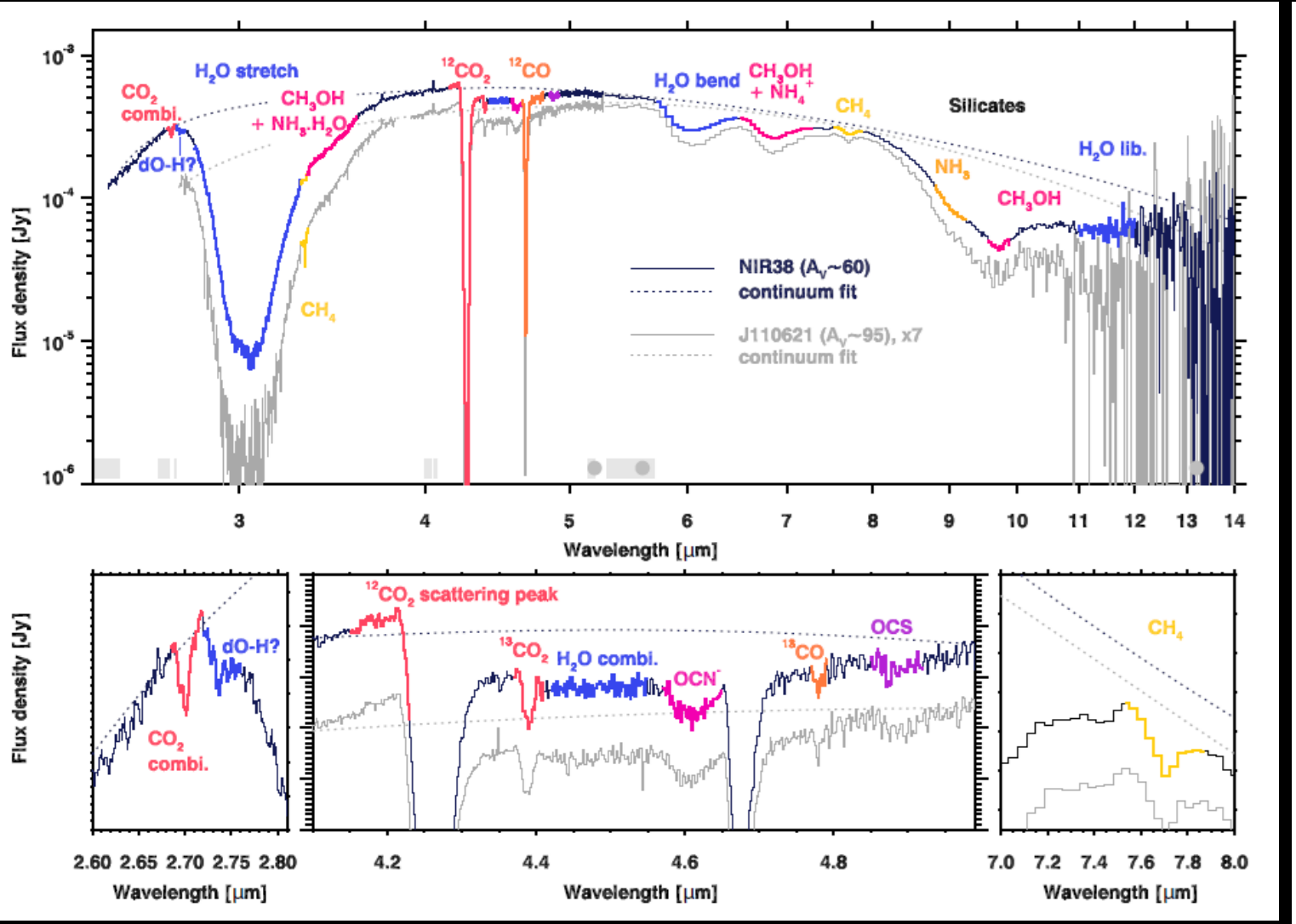
Ice formation threshold



Boogert et al. 2015

H_2O ice formation starts at $A_V \sim 3$ mag, CO and CH_3OH deeper into cloud

JWST sensitivity: isotopologues and sulfur



λ (μm)	ν (cm^{-1})	Species	Identification[a]	Detection NIR 38	Detection J110621
2.69	3708	CO_2	combination	✓	...
2.73	3664	H_2O	O–H dangling bond	✓	...
3.0	3330	H_2O	O–H stretch	✓	✓
3.24	3249	CH_3OH	O–H stretch	✓	✓
3.32	3012	CH_4	C–H stretch	✓	✓
3.47	2881	Ammonia hydrate	$NH_3 \cdot H_2O$	!	!
3.32–3.64	3012–2890	CH_3OH	C–H asym. str. + overt.	✓	✓
3.92	2548	H_2S	S–H	✗	...
4.07	2457	HDO	O–D str.	✗	✗
4.17–4.77	2400–2100	H_2O	combination	✓	✓
4.27	2340	$^{12}CO_2$	C–O str.	✓	✓
4.38	2280	$^{13}CO_2$	C–O str.	✓	✓
4.44	2252	CH_3CN	C–N str.	✗	✗
4.59	2175	OCN^-	C–N str.	✓	✓
4.67	2140	^{12}CO	C–O str.	✓	✓
4.76	2100	HCN	C≡N str.	✗	✗
4.78	2090	^{13}CO	C–O str.	✓	✓
4.90	2040	OCS	C–O str.	✓	✓
6.0	1666	H_2O	bending	✓	✓
6.85	1459	CH_3OH	CH_3 def.	✓	✓
6.85	1459	NH_4^+	N–H str.	✓	✓
6.9-7.5	1449-1333	Unidentified absorption	COMs functional groups?	✓	✓
7.24	1384	CH_3CH_2OH?	CH_3 def.	!	!
7.43	1362	CH_3CHO?	CH_3 def. + CH wag.	!	!
7.60	1318	SO_2	S–O str.	!	!
7.71	1300	CH_4	C–H str.	✓	✓
8.86	1131	CH_3OH	CH_3 rock	✓	✓
9.01	1110	NH_3	umbrella	✓	✓
9.74	1025	CH_3OH	C–O str.	✓	✓
9.80	1020	Silicate	Si–O str.	✓	✓
11.0	910	H_2O	libration wing	✓	✓

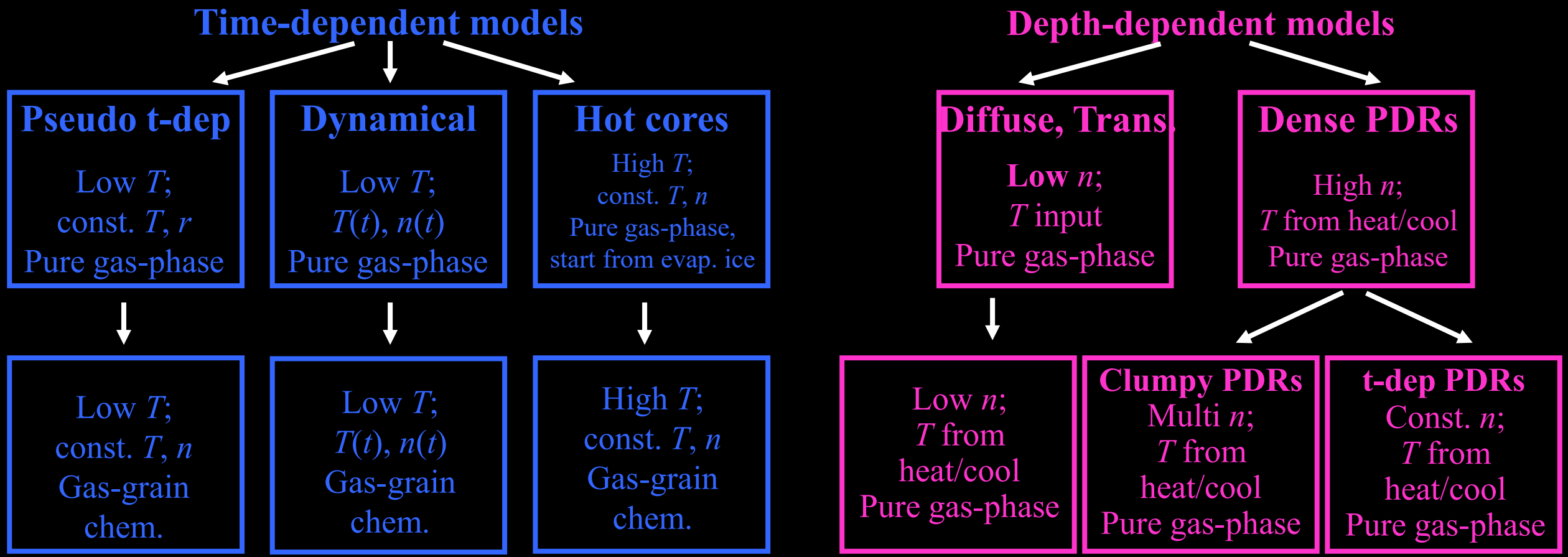
[a]Symbol legend: ✓- observed, ✗- not observed, ! - possibly observed, ... - insufficient data

- $^{13}CO_2$ and OCS detected in ice. Possibly COMs!
- Formation of complex molecules starts early in a water-rich environment

McClure et al. 2023

6.3 Models

Types of models



Lectures 6 & 7

Lecture 4

A. Pure gas-phase models

- See diffuse clouds for basic networks. More complex carbon-species formed by reactions with C^+, $C_2H_2^+$, C, for example:
  - $C^+ + CH_4 \rightarrow C_2H_3^+ + H,\ C_2H_2^+ + H_2$
  - $C^+ + C_2H_2 \rightarrow C_3H^+ + H$
  - $C + C_2H_2 \rightarrow C_3H + H$
  - $C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H,\ C_4H_2^+ + H_2$

- *Carbon insertion reactions*

Changes over the past decades

- Lectures 1 + 2 for details (fundamental process)
- Ion-polar molecule rate coefficients enhanced at low T
  - E.g., $C^+ + OH \rightarrow CO^+ + H$
- Dissociative recombination branching ratios
  - E.g., $H_3O^+ + e^- \rightarrow OH$ or H_2O
  - Larger molecules usually fragment (PAHs do not)
- Cosmic-ray induced photodissociation
- Photodissociation by external field at given A_V
- Rapid neutral-neutral reactions at low T
  - E.g., $CN + C_2H_2 \rightarrow$ products
- Inclusion of more complex molecules

Pure gas-phase models (continued)

- Most recent models contain nearly >5000 gas-phase reactions between ~450 species containing up to 13 atoms. Publicly available on web
- *UMIST code*
  - http://www.udfa.net
- Herbst/Wakelam (Bordeaux) Nahoon code
  - http://kida.astrophy.u-Bordeaux.fr/codes.html
- Most dark cloud models ignore depth dependence => solve chemical networks for given *T*, *n* at single position and assume:

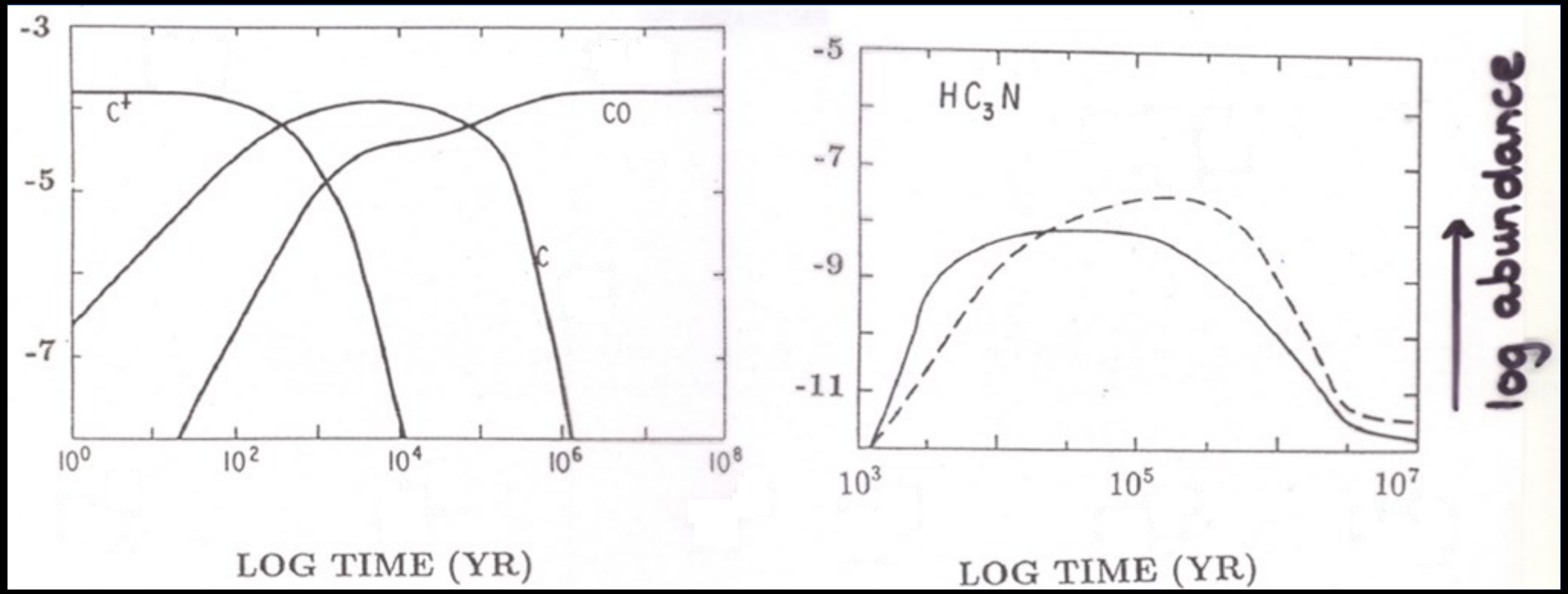
$$x(AB) = \frac{N(AB)}{N(H_2)} = \frac{n(AB)}{n(H_2)}$$

observed **calculated**

Pseudo time-dependent models

- Most species need ~10^5–10^6 yrs to reach chemical equilibrium => solve chemical network as function of ***time***, keeping ***n,T constant with time*** ($n_H = 2 \times 10^4$ cm^{-3}, $T = 10$ K)
- Need initial conditions; usual assumption is that H_2 is initially molecular; C, N, O, ... atomic => representative of diffuse molecular clouds.

Time-dependent abundances



- Principal characteristic: $\mathbf{C^+ \rightarrow C \rightarrow CO}$
- Long carbon chains only abundant at early times (~10^5 yr) when atomic carbon is still abundant

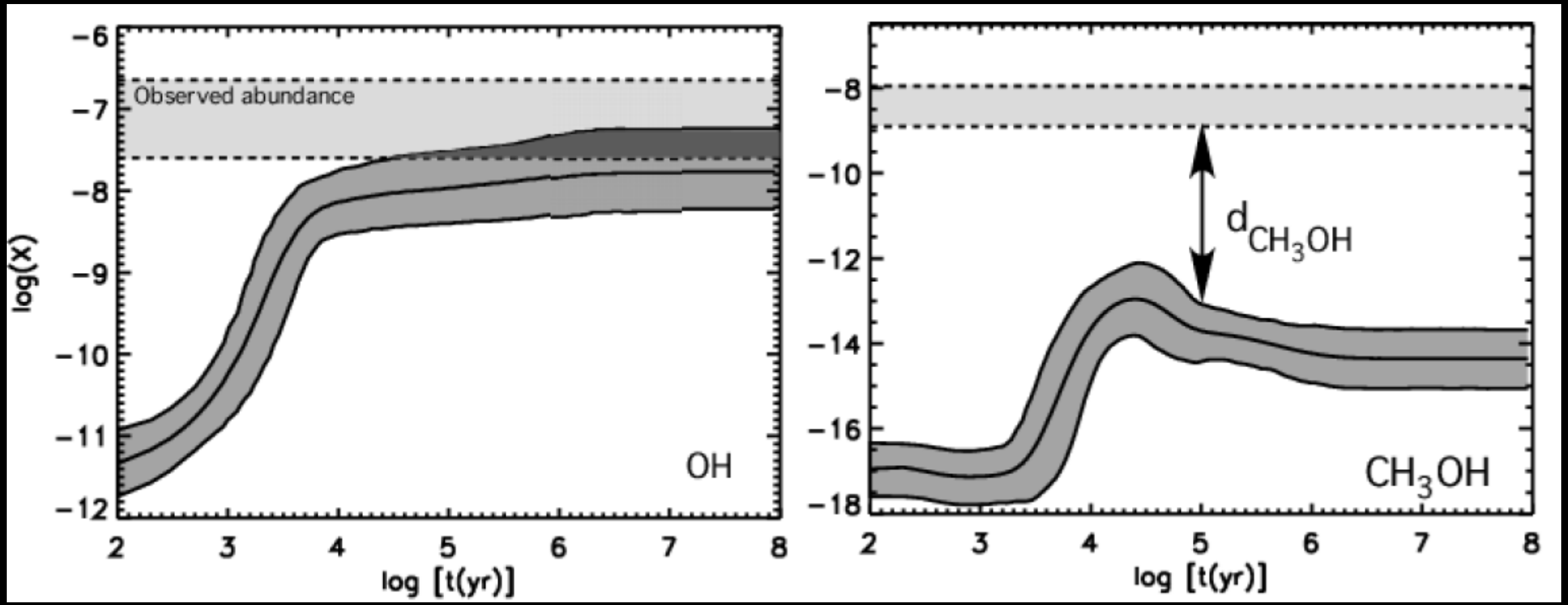
Successes in ion-molecule chemistry

- Abundances of protonated ions
  - HCO^+, N_2H^+, $HOCO^+$, $HCNH^+$, HC_3NH^+, ...
  - H_3^+ detected (Geballe & Oka 1996)
- Abundances of metastable species
  - HNC/HCN; l-C_3H/c-C_3H, ...
- Abundances of anions
- Isotopic fractionation at low *T*
  - $^{12}CO/^{13}CO$ due to $^{13}C^+ + {}^{12}CO \leftrightarrow {}^{13}CO + C^+$
    - Reaction toward ^{13}CO at low *T* because of lower zero-point vibrational energy
  - DCO^+/HCO^+, DCN/HCN, ... (see 6.4)
- Abundances of unsaturated molecules
  - Many neutrals and large (*n*>4 atoms) ions cannot react with H_2 because reactions are endothermic => networks naturally predict that molecules are hydrogen poor, in spite of overabundance of H_2 by factor 10^4

Problems

- Different steady-state models can differ by up to order of magnitude or more in abundances, even for small species
- Comparison with observed abundances in TMC-1S shows ‘good’ agreement (better than factor of 10 for 80% of species) but only at early times $t \approx 10^5$ yr: why such a young age?
- Oxygen chemistry: models predict all O in O_2, but observations give very low limits
- Bistability
- More recently: PAHs very underabundant

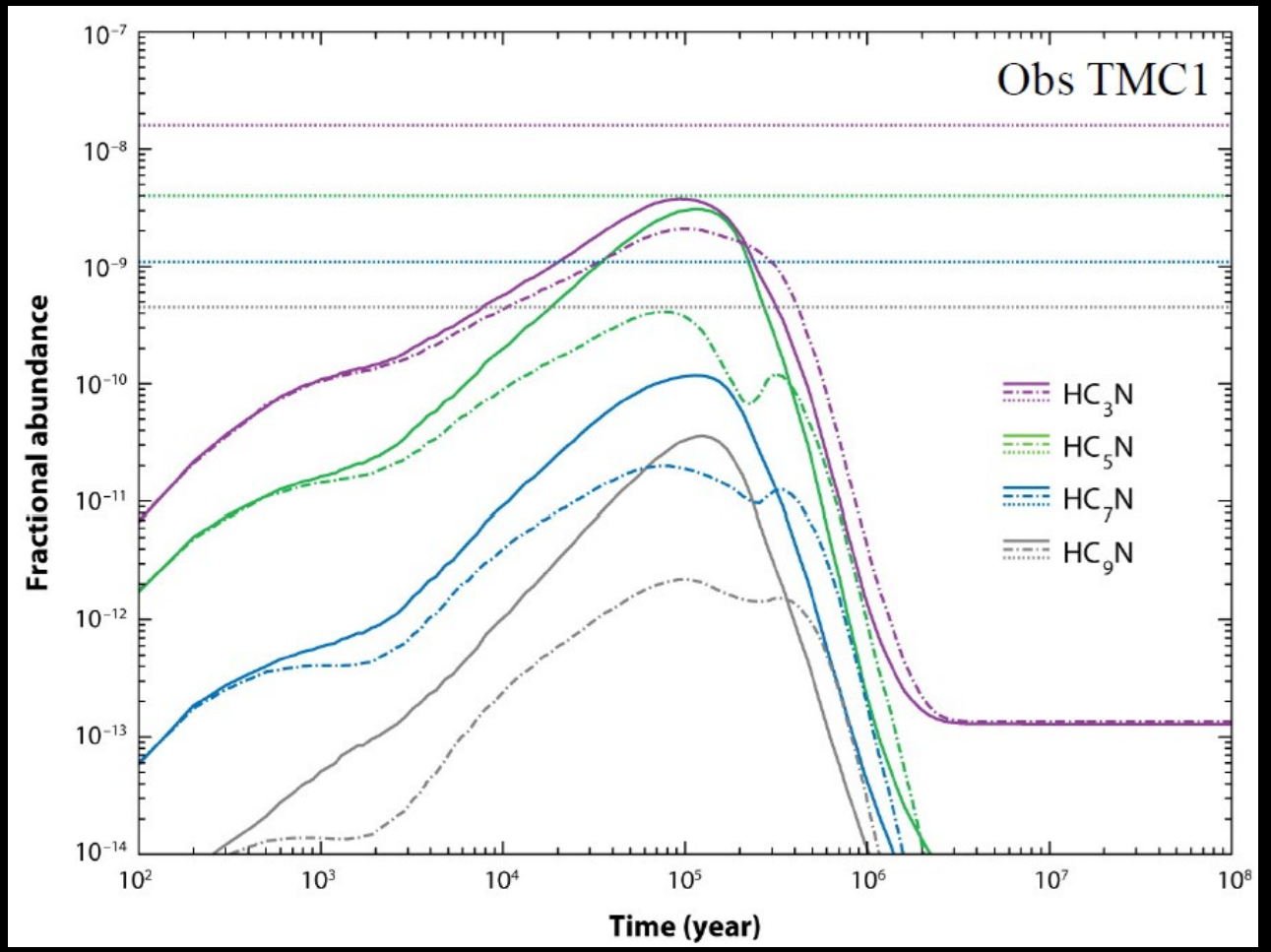
Sensitivity analysis



- Dark grey area account for uncertainties in all reaction rates
- Right panel shows that underabundance of CH_3OH in models cannot be due to uncertainties in relevant rate coefficients

Wakelam et al. 2006, 2009, 2010

Making long carbon chains

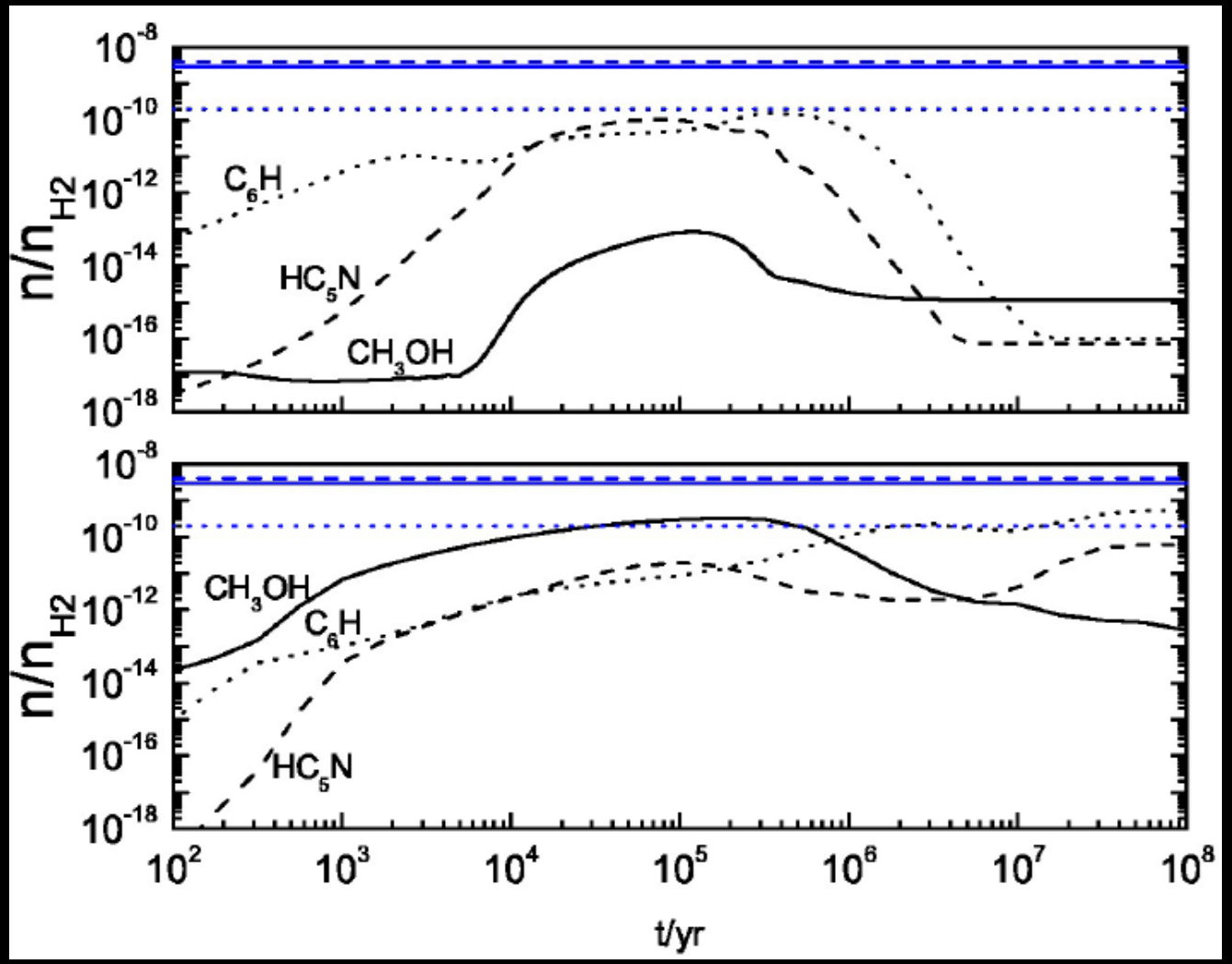


T = 10 K
n_H = 2 x 10^4 cm^{-3}
C/O = 0.4

Herbst & van Dishoeck 2009

- Full lines: with anion; dashed line: without anions → anions help!
- However, carbon chains still underproduced even at peak abundances

Making methanol in cold clouds



Blue = observed

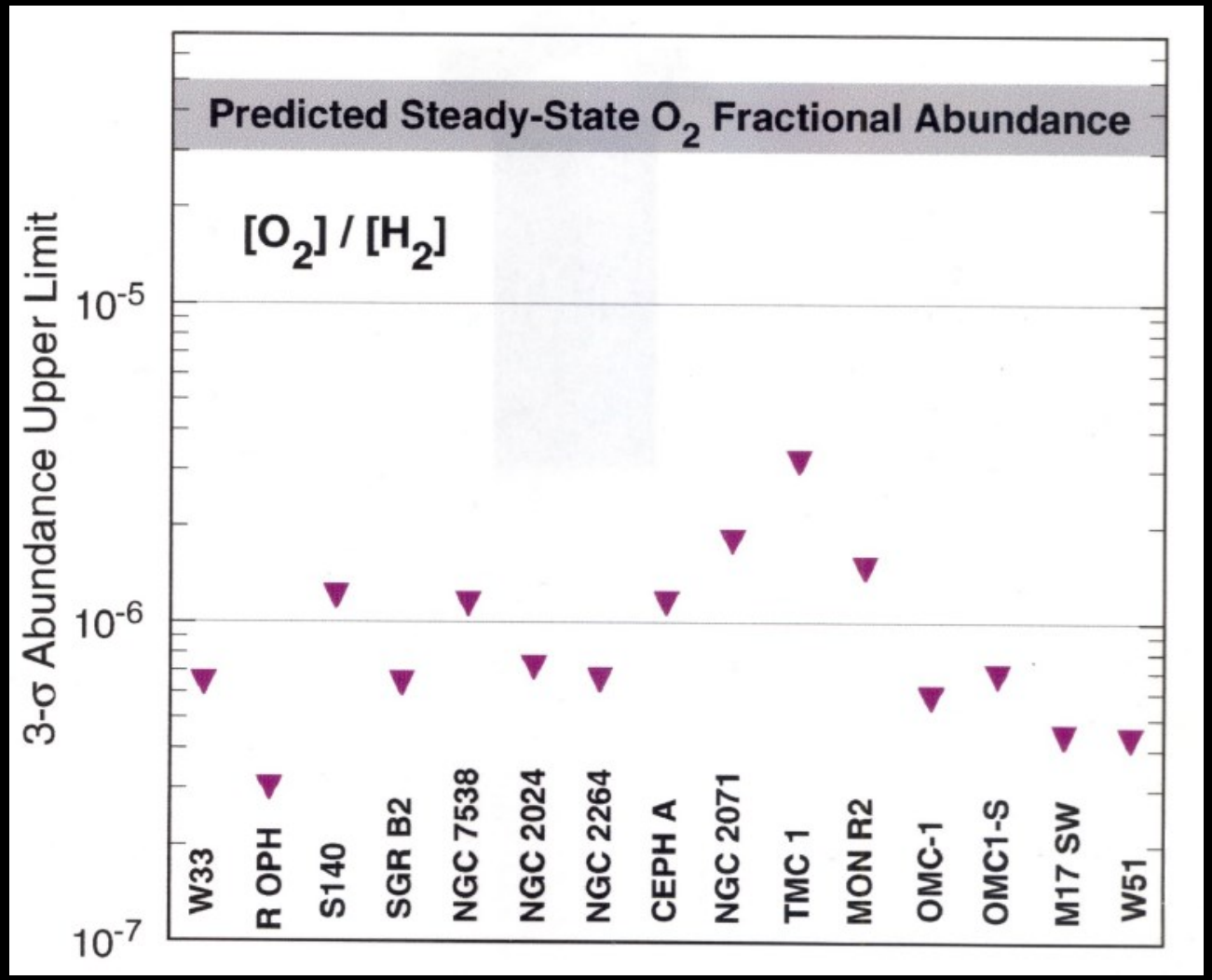
Without grain-surface chemistry

With grain-surface chemistry

Herbst & van Dishoeck 2009

- Observed (low) abundance of CH_3OH in dark clouds can only be approached with grain-surface chemistry included

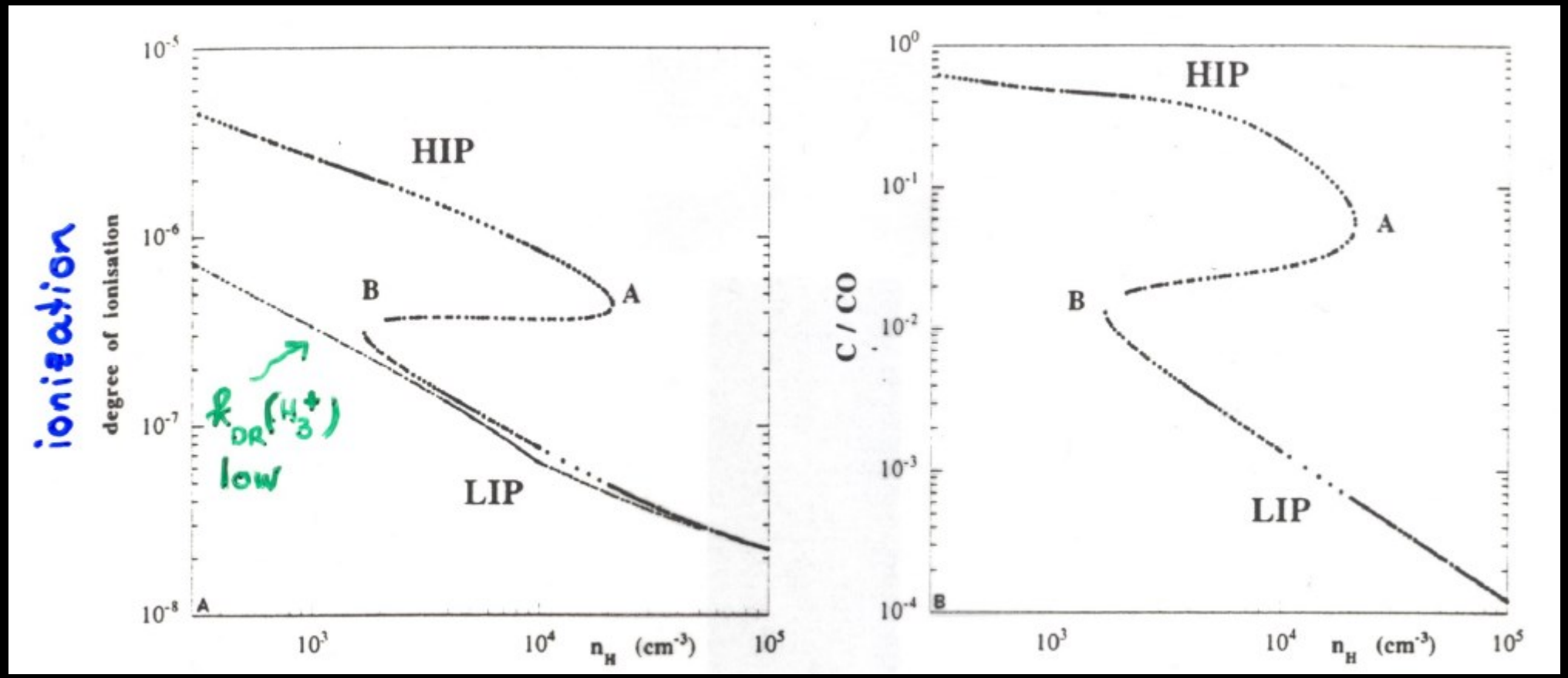
Limits on O_2



Goldsmith et al. 2000, 2010: SWAS, Herschel

- Models produce factor 100 more O_2 than observed
- Solution lies in freeze-out of O on grains (Bergin et al. 2000)

Bistability



Le Bourlot et al. 1995

- Different initial conditions can lead to different results
- Can depend on specific rate coefficient (e.g., H_3^+ DR)
- Inclusion of gas-grain chemistry often removes bistable solution (only Low Ionization Phase retained)

Beyond pseudo time-dependent models

- Dynamical models: n, T vary with time
  - *modern* collapse models, e.g., Visser et al. 2009
- Depth-dependent models:
  - PDR models (see Lecture 4, but with $I_{UV} < 1$)
    - e.g., Lee et al. 1996, Hollenbach et al. 2009
  - Photodissociation makes it more difficult to build up large molecules such as observed in TMC-1S
- Dynamical mixing models: parcels of gas cycle from dense → diffuse → dense gas
  - Increase C and complex molecules inside dense cloud
    - Boland & de Jong 1982, Chièze et al. 1991, Xie et al. 1995, Willacy et al. 2002

B. Gas-grain models

- At $n_H \geq 10^4$ cm^{-3}, collisions between gas-phase molecules and grains are sufficiently rapid (~10^5 yr) that gas-grain interactions must play a role
  - $t_{depl} \approx 2 \times 10^9 / y_S n_H$ yr with y_S = sticking coefficient ≈ 1 at 10 K
- Distinguish:
- **Passive accretion:** molecules condense on grain
  - No reactions, no return to gas
    - Iglesias 1977, Millar & Nejad 1985
- **Active accretion:** reactions on surface form other species
  - No return to gas
    - Tielens & Hagen 1982; Brown & Charnley 1990, Bergin & Langer 1997
- **Gas-grain chemistry:** atoms and molecules condense and react on surface
  - Return to gas
    - D'Hendecourt et al. 1985, Herbst & Hasegawa 1993, Shalabiea & Greenberg 1994, Aikawa et al. 2005, 2008, Garrod & Herbst 2008, *Garrod et al. 2022* ***(state-of-the-art)***

Gas-grain chemistry (from Lecture 2)

- Only diffusive mechanisms considered
- Typical ‘day in the life’ on the surface of a grain in a dense cloud
  - A few molecules or atoms land on the icy surface
  - All species except He stick with $y_S = 1$
  - If sufficiently light, the particle can migrate (diffuse) over the surface by tunneling or thermal hopping
  - Migrating species: H, O, C, N
  - Perhaps: CH*, CH_2*, NH, OH, NH_2, CH_3
  - Reactions may occur if activation barriers for diffusion and reaction are sufficiently low

*CH and CH_2 on surfaces may be very important for many COMs (Garrod et al. 2022)

Relevant time scales

- See Sect. 2.3 for formulae for adsorption (= residence) and migration (= thermal hopping, diffusion) times
- Tunneling only important for H, H_2
- Limiting activation barriers of reactions T_d = 10 K (rough estimates)
- H $\leq$ 3500 K
- H_2 $\leq$ 4500 K
- O, C, N $\leq$ 450 K

Typical time scales (10 K)

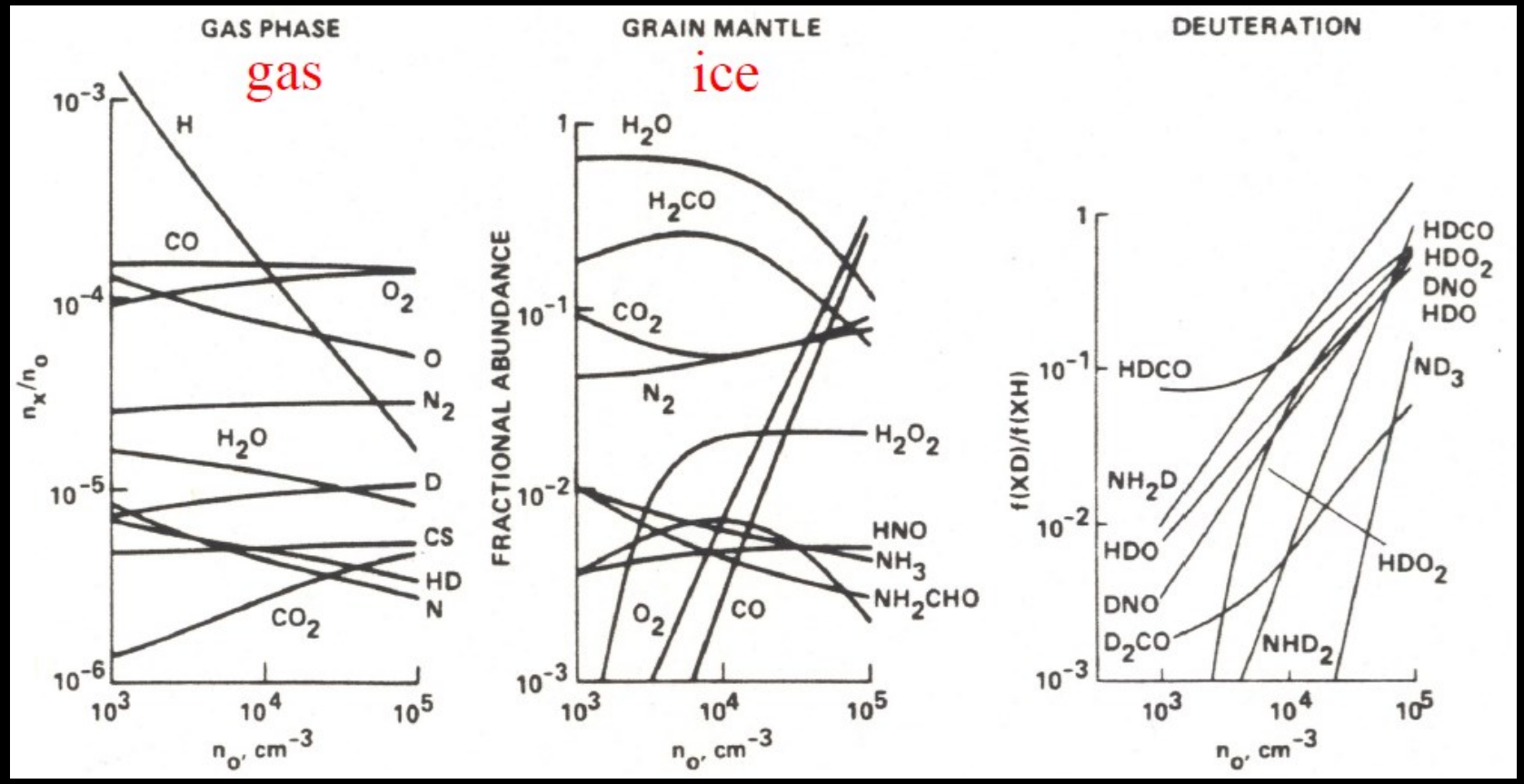
Species	E_D (K)	t_{des} (s)	t_{hop} (s)	t_{acc} (s)
H	350	500	10^{-12}	7×10^{12}
H_2	450	10^{7}	4×10^{-12}	5×10^{12}
C	800	10^{22}	10^{-2}	2×10^{12}
CH_4	2600	-	-	1×10^{12}

1×10^{12} s ~ 10^{5} – 10^{6} yrs

Grain mantle composition

- **Low density**
  - Large gas-phase H abundance => hydrogenation: H_2O, CH_4, NH_3, ...
- **High density**
  - Large gas-phase O abundance => oxidation: O_2, CO, CO_2

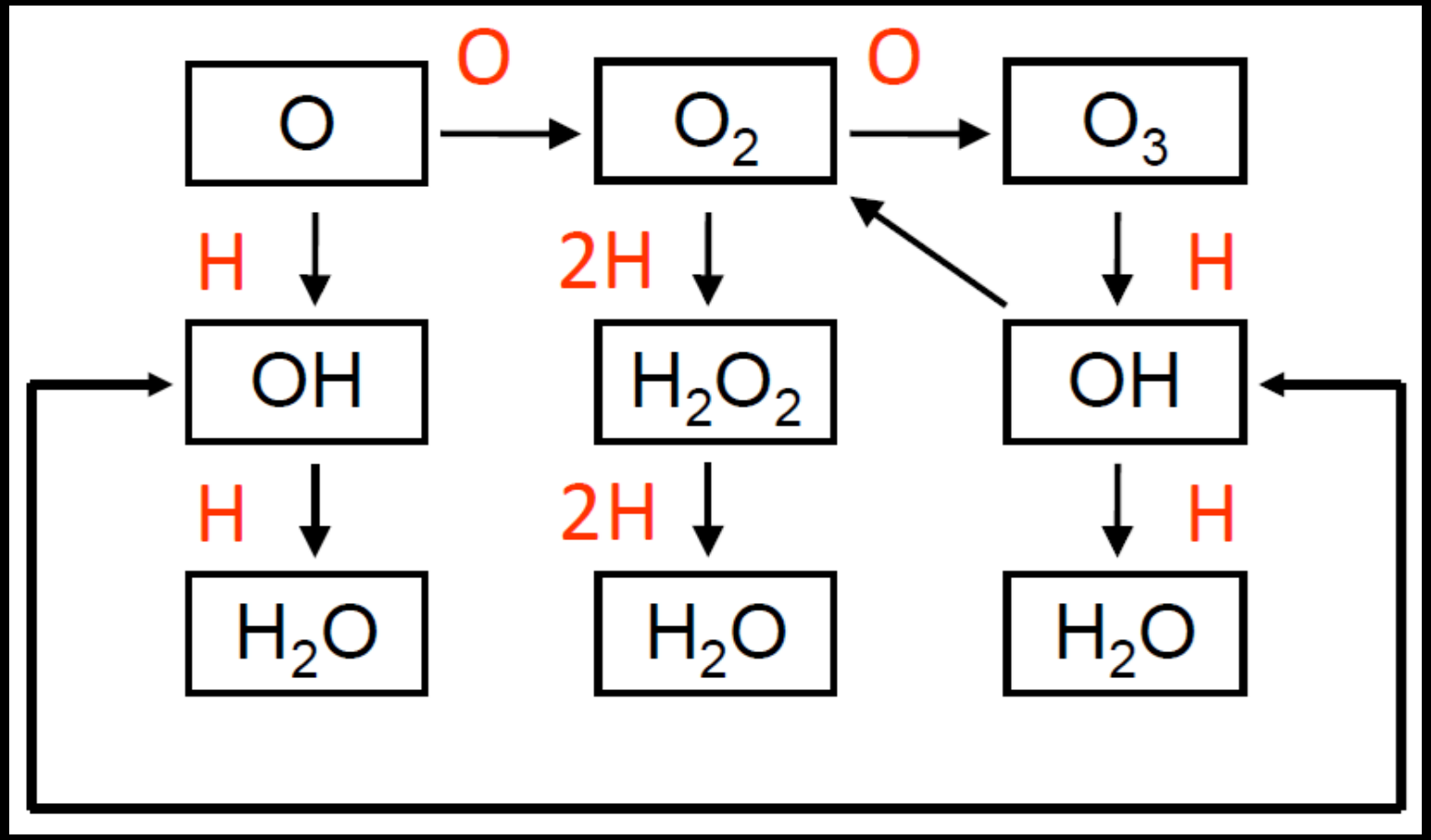
Grain mantle composition



- Note change from H_2O dominated to CO dominated ice at high densities
- O_2 too high in these models

Tielens 1989

Grain surface chemistry

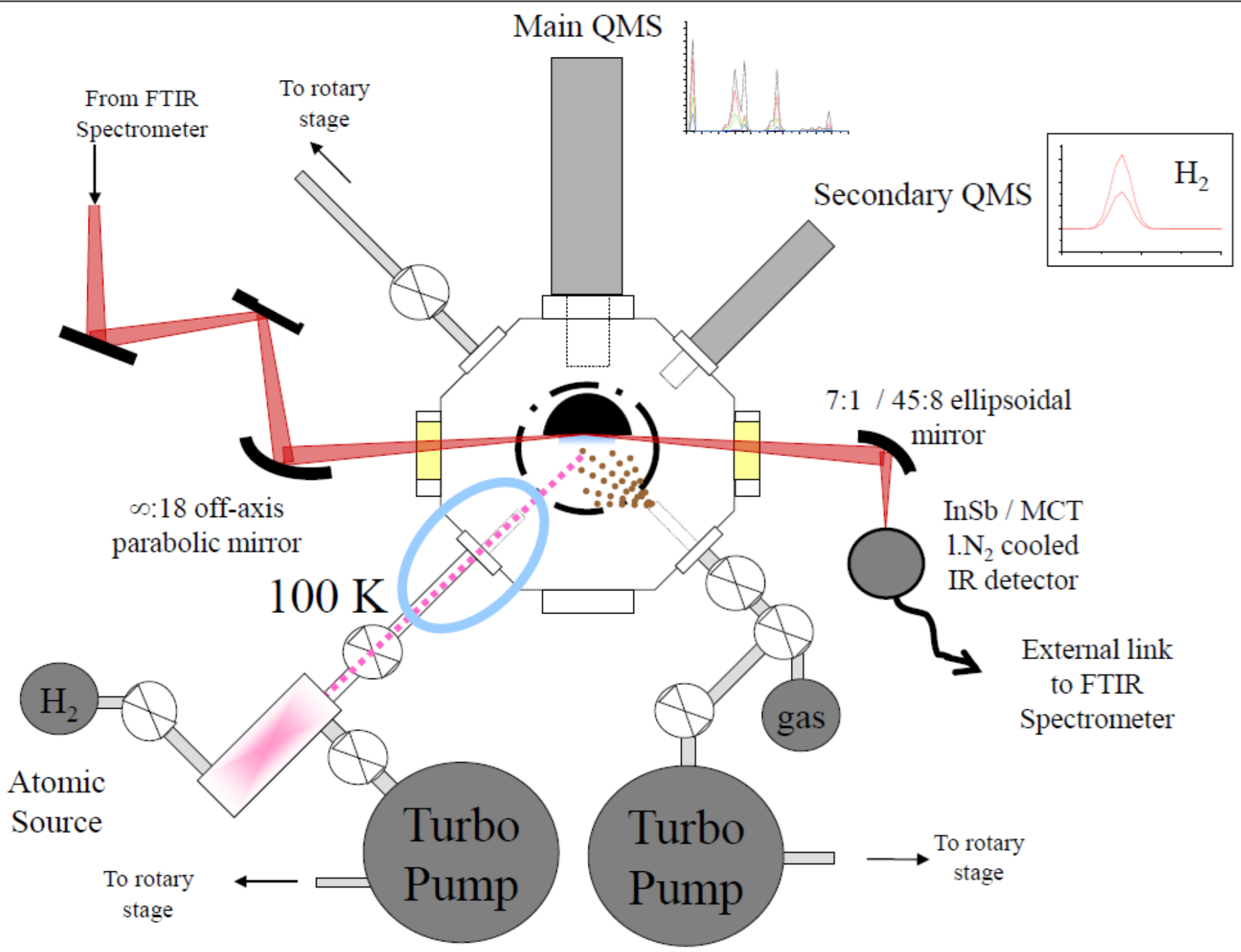


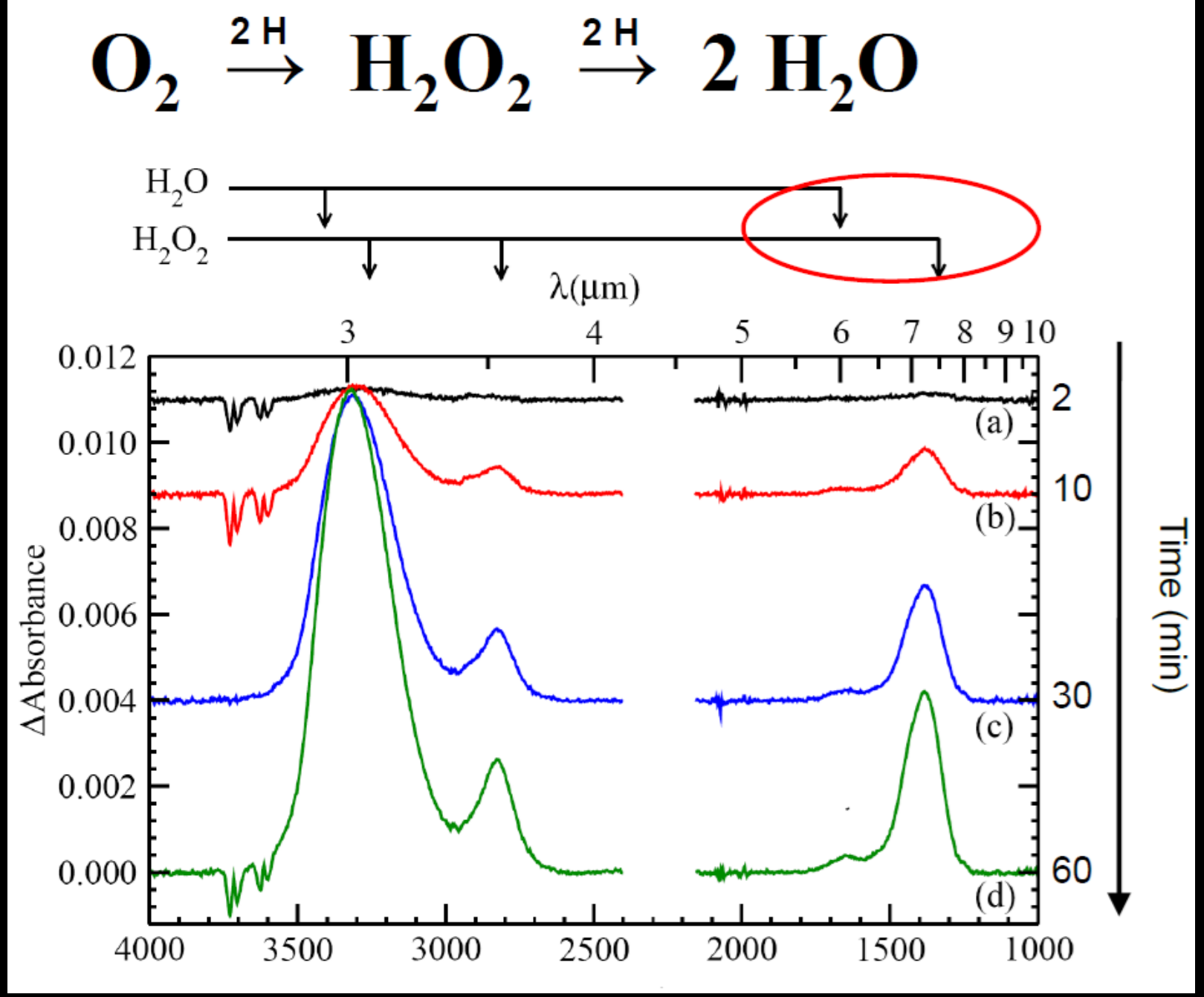
Tielens & Hagen 1982

- Postulated 45 years ago, these reactions have since been tested in the laboratory in the past ~15 years

Experimental simulation

- Condensation of ice (CO, O_2, N_2, …) in UHV chamber
- Bombardment by cooled atomic beam (H, O) produced in microwave or DC discharge
- Analysis of products by Reflection Absorption InfraRed Spectroscopy (RAIRS) and Mass Spectrometry
- Few groups around the world capable of these experiments, some in Ile-de-France

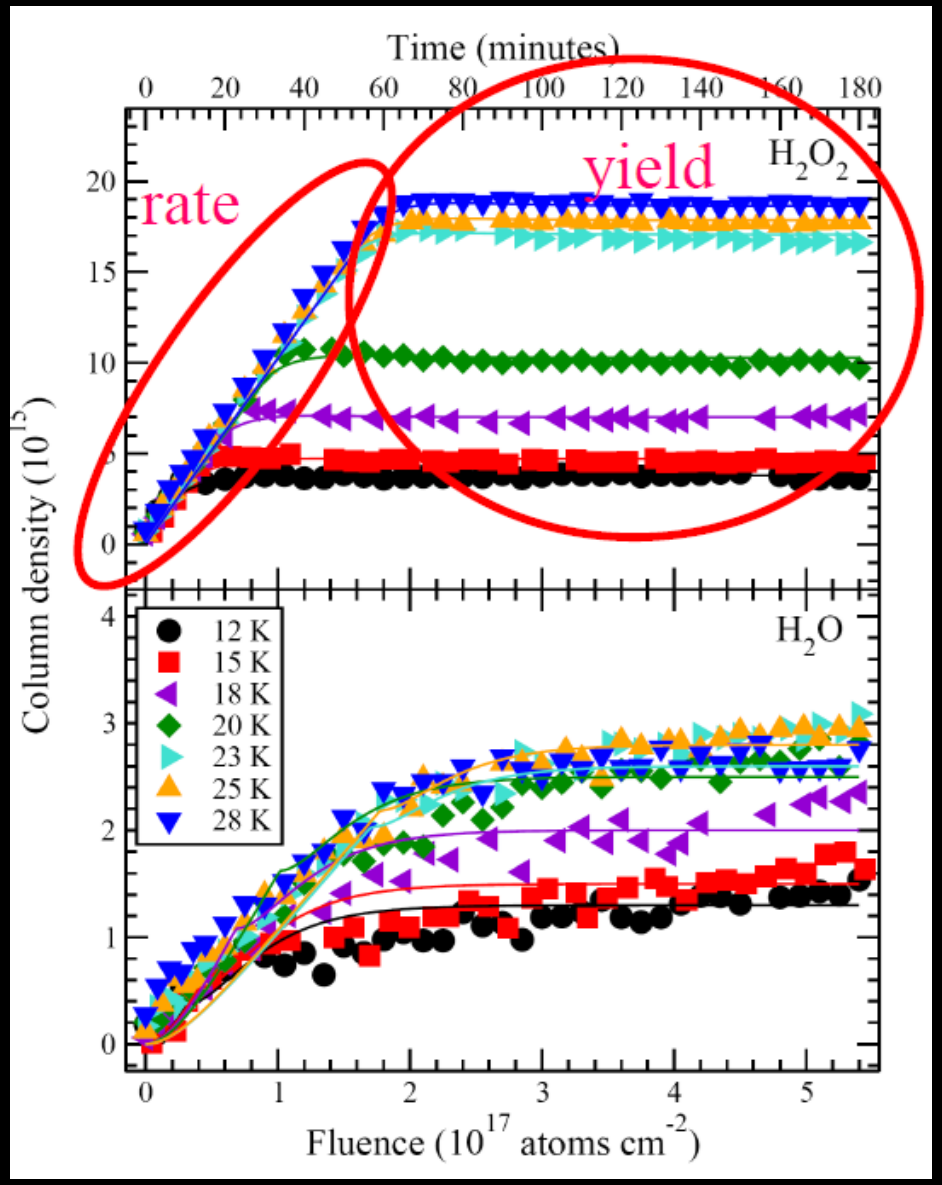

Main QMS
From FTIR Spectrometer
To rotary stage
Secondary QMS
H_2
7:1 / 45:8 ellipsoidal mirror
∞:18 off-axis parabolic mirror
100 K
InSb / MCT
l.N_2 cooled
IR detector
External link to FTIR Spectrometer
H_2
gas
Atomic Source
Turbo Pump
Turbo Pump
To rotary stage
To rotary stage



Ioppolo et al. 2008

- *Both H_2O_2 and H_2O indeed formed at low T!*

Reaction yields at low T



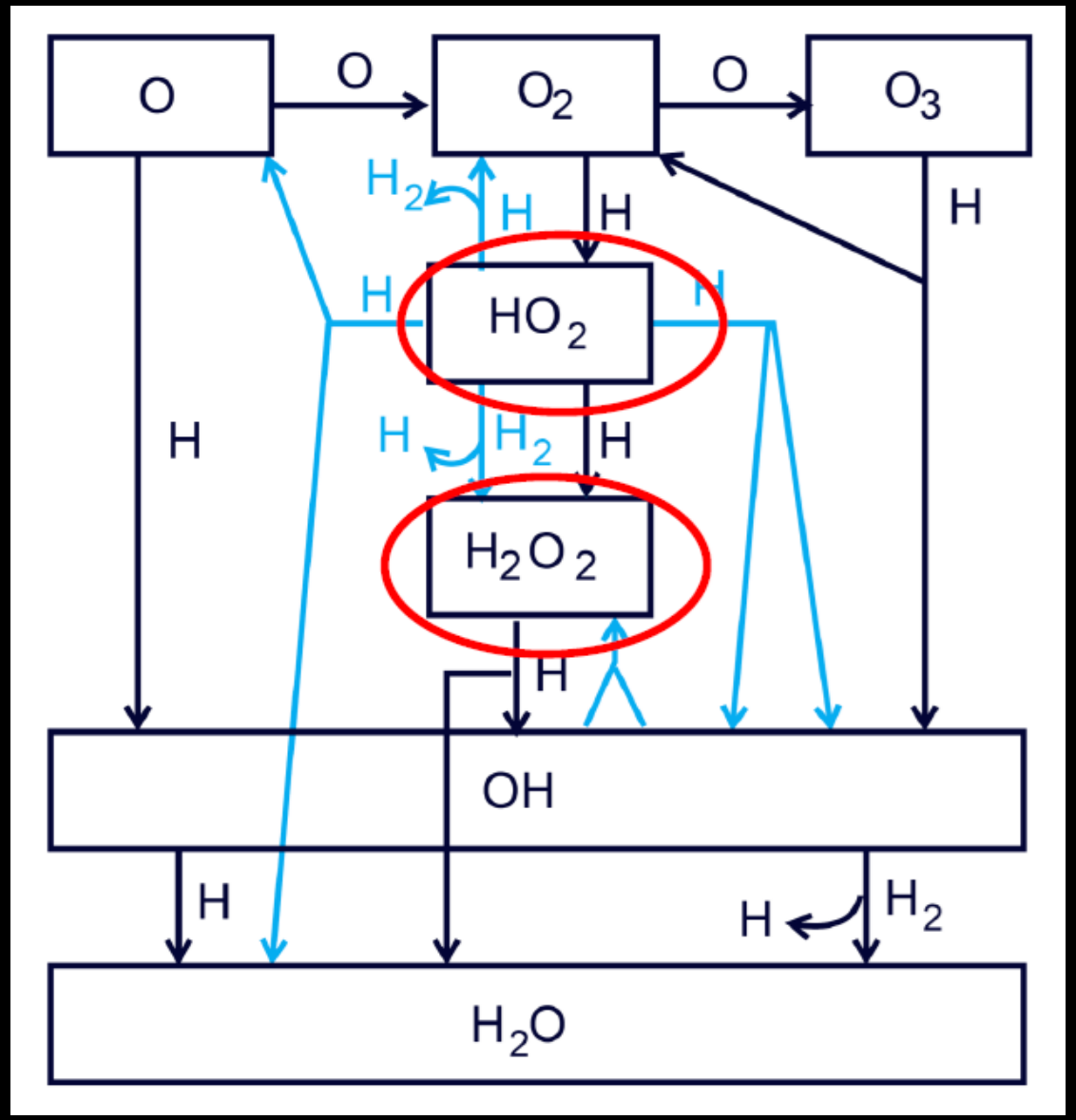
- Rate of reaction is temperature independent
- Yield increases with temperature
- More efficient than estimated

=> Formation path can be quantified and included in chemical models

Starts in clouds with A_V > 3 mag

Based on
Cuppen et al. 2010

How to make water in space?



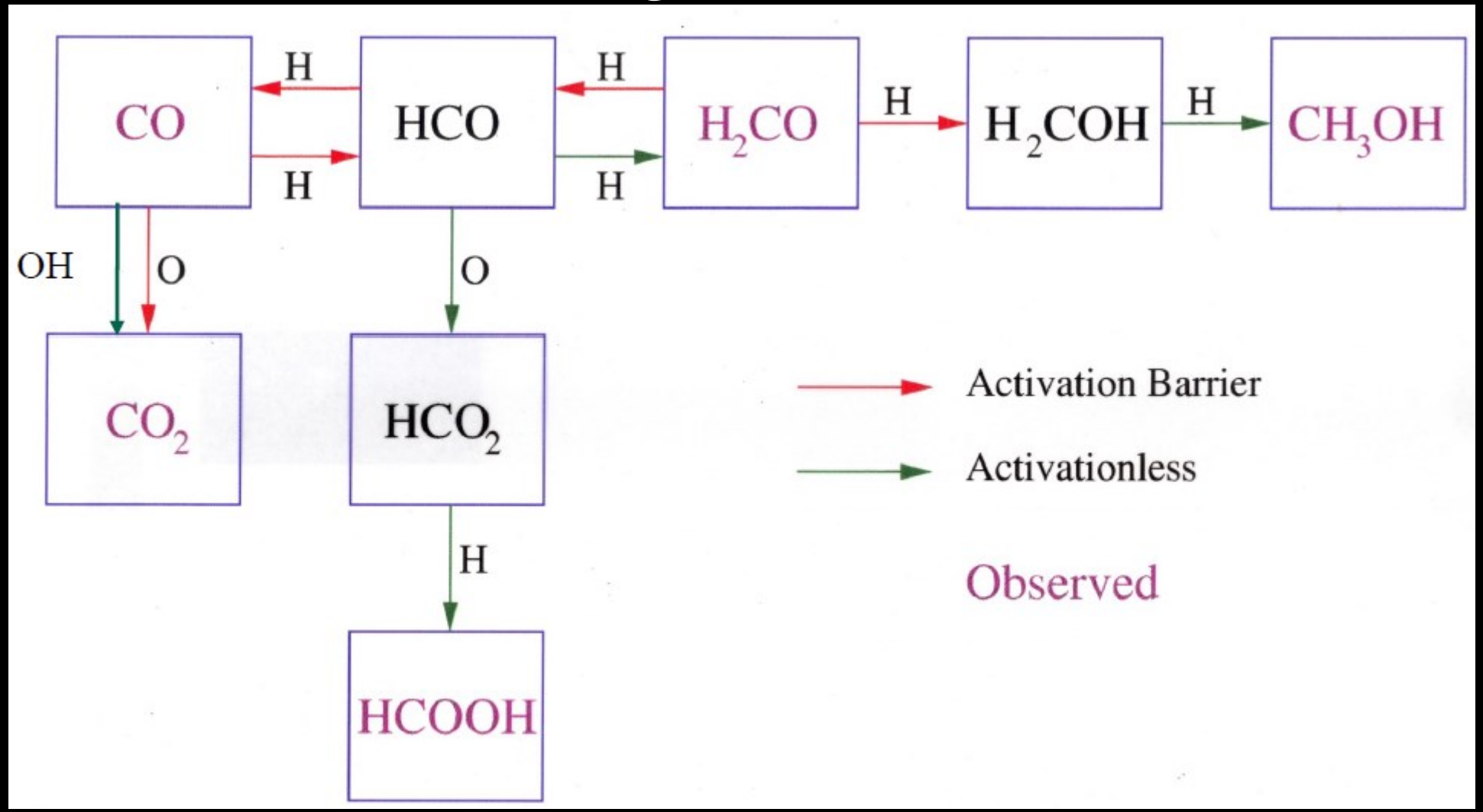
Detected in 2011 and 2012
Bergman, Parise et al.

Tielens & Hagen 1982

Ioppolo et al. 2008, 2010
Cuppen et al. 2010
Watanabe+
Dulieu+

Detailed laboratory experiments reveal multiple routes at 10 K

Example: CH_3OH and HCOOH

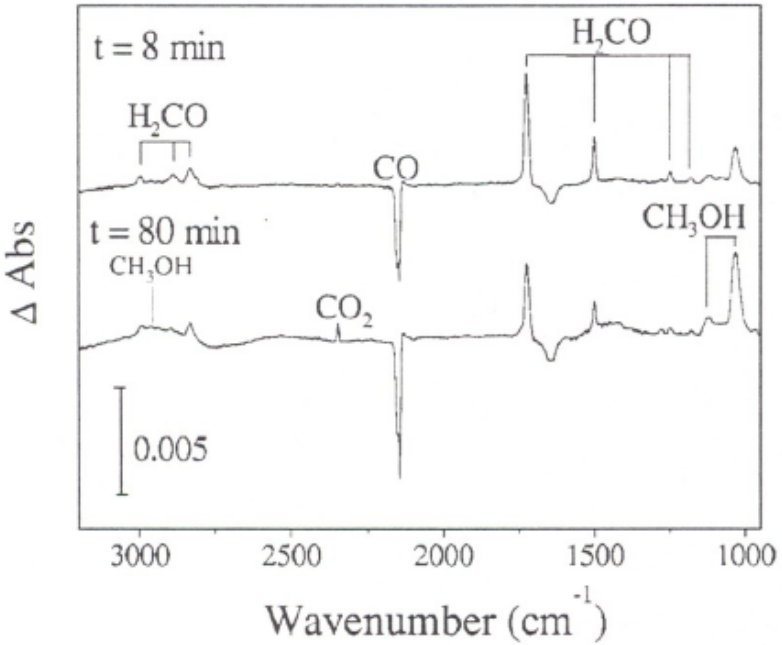


CH_3O observed by Cernicharo et al. 2012
CH_2OH still undetected (Chitarra et al. 2020) – and still elusive in 2026

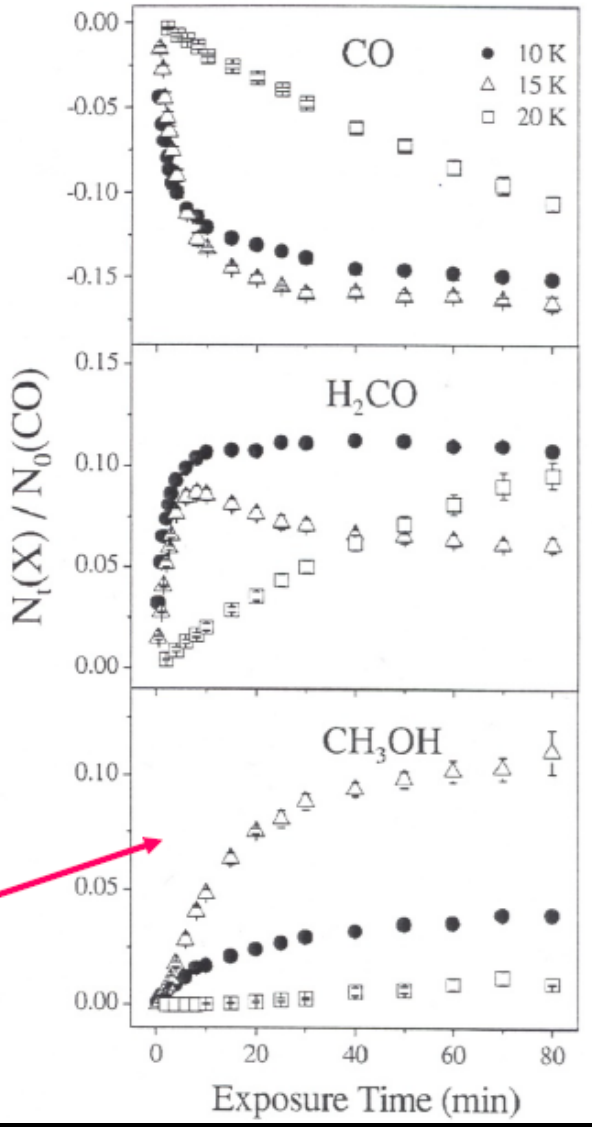
See also
Watanabe et al. 2005
Fuchs et al. 2009
Ioppolo et al. 2011a,b

CH_3OH experiment

IR spectroscopy to monitor products



time



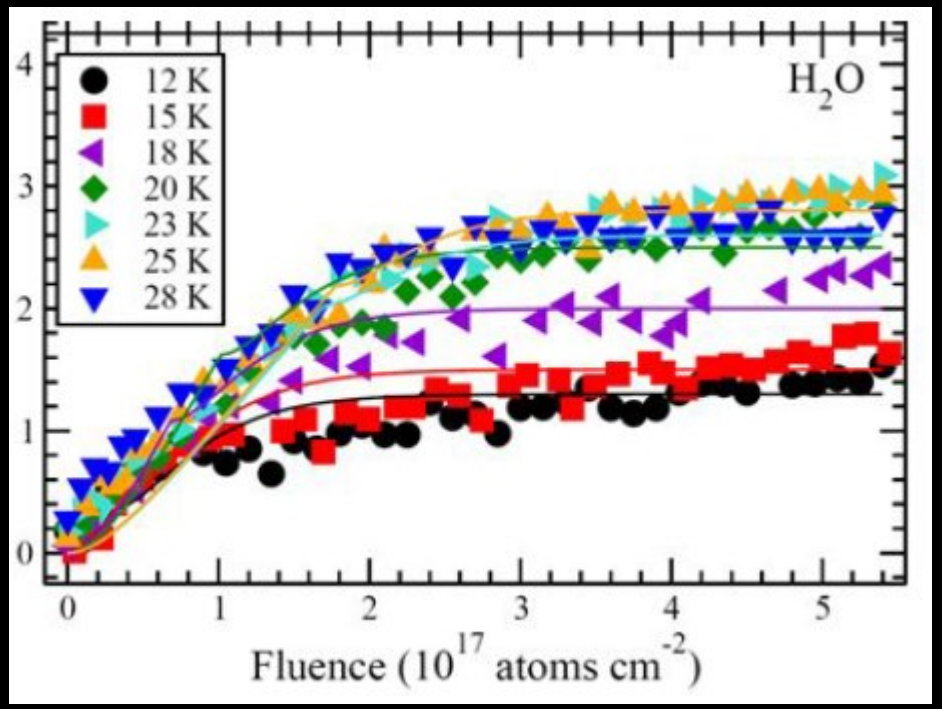
Max. CH_3OH yield at 15 K

Higher T => less sticking of H

Watanabe et al. 2003
Fuchs et al. 2009

CH_3OH can be formed at temperatures as low as 10 K!

From lab experiments to model parameters



Ioppolo et al. 2008

?

ADSORPTION ENERGIES (K)

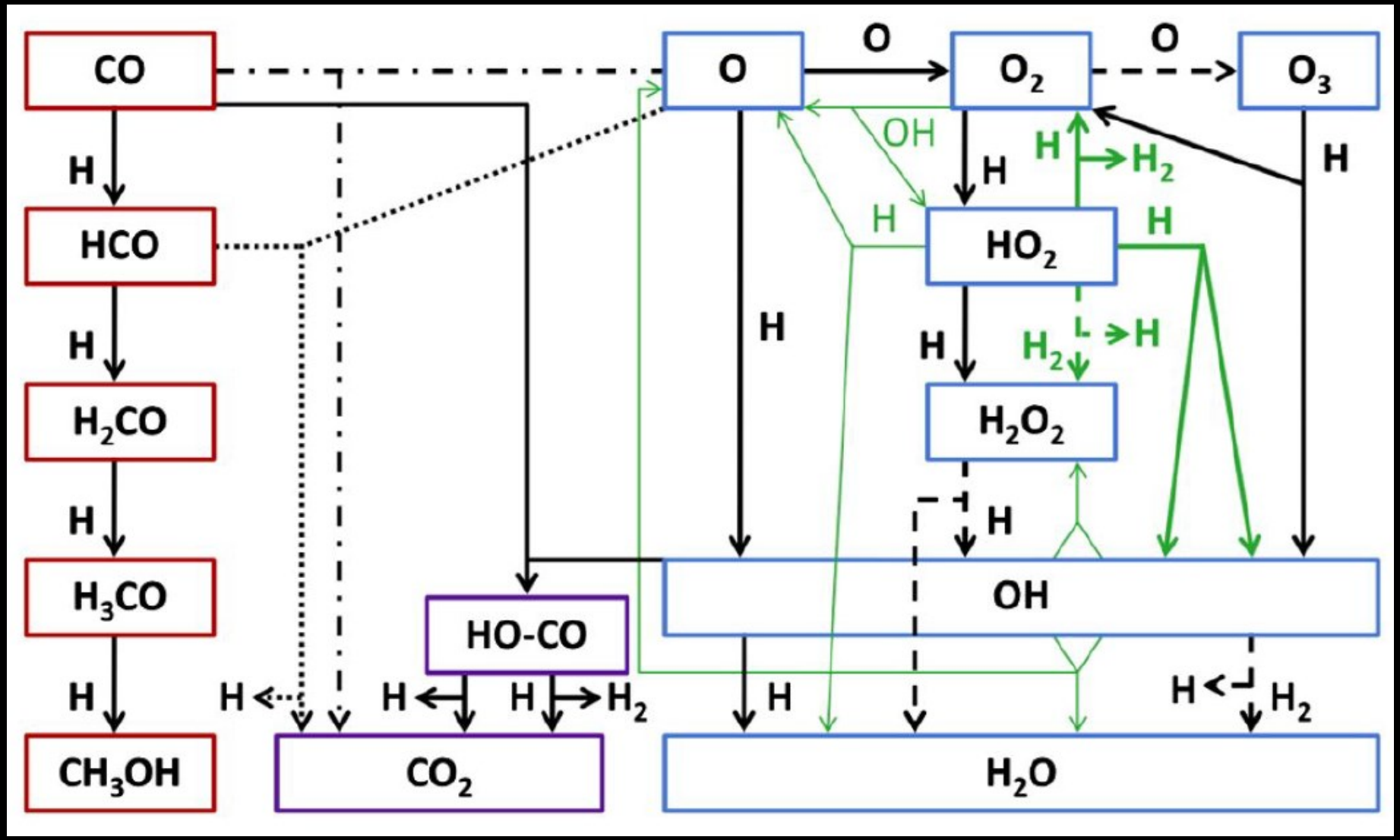
Species	Model A[a]	Model B[b]
CO	1210	960
N_2	1210	750
CO_2	2500	2690
H_2O	1860	4820
HCN	1760	4280
SO_2	3070	3460
C_2H_2	1610	2490
NH_3	1110	3080
CH_4	1360	1120

Aikawa et al. 2001, Cuppen et al. 2009, Lamberts et al. 2013

- Lab provides rates as function of H or UV fluence or some other parameter over timescales of hours
- Astronomical applications involve timescales of $>10^5$ yr
- Models need barriers for desorption, diffusion, etc.

Q: how to translate lab data to model parameters?

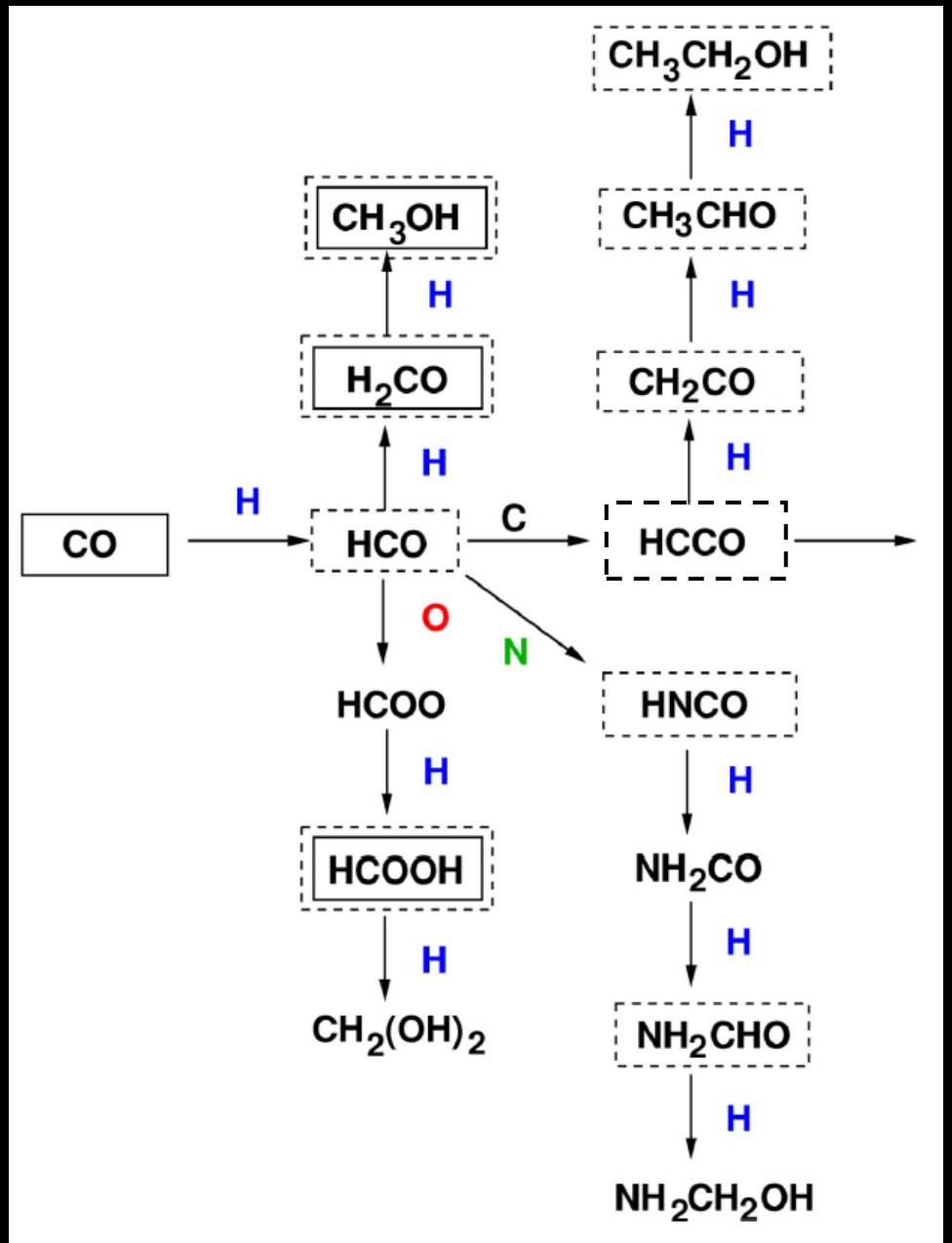
Summary: making H_2O, CO_2, and CH_3OH ice



Solid: no or small barrier, thin, inefficient
Dashed: large barrier; dotted: not measured

Fuchs et al. 2009
Cuppen et al. 2010
Ioppolo et al. 2011

Forming complex molecules on grains starting from CO

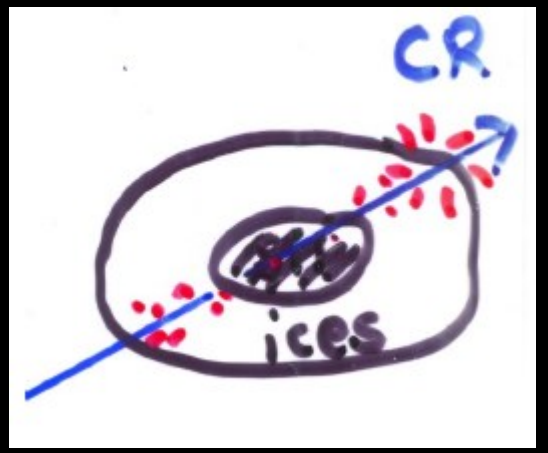


Dashed: detected in gas
Solid: detected as ice

Tielens & Charnley 1997
Bisschop et al. 2007

Desorption mechanisms

- Thermal evaporation
  - Only significant if $T_d \geq 20$ K
  - Depends on type of surface (silicate, ices, …)
  - 'Non-polar' species (N_2, CO, O_2, …) evaporate at much lower temperatures than 'polar' (hydrogen-bonding) species (H_2O, CH_3OH, …)
- Cosmic-ray spot heating
  - $t_{CR} \approx 4 \times 10^6$-$10^7$ yr



Ivlev et al. 2015

Desorption mechanisms continued

- Photodesorption
  - Shown by lab experiments and calculations to be more efficient than before; probably dominates desorption of CO and H_2O in cold cores
- Explosive desorption
  - Exothermic reactions between stored radicals at $T_d \approx 27$ K (seen in laboratory experiments)
  - Cosmic-ray induced: $t_{exp\text{-CR}} \approx 4 \times 10^5$ yr
  - Grain-grain collisions at v $\geq$ 0.1 km/s: $t_{exp\text{-gg}} \approx 2 \times 10^9 / n_H$ yr

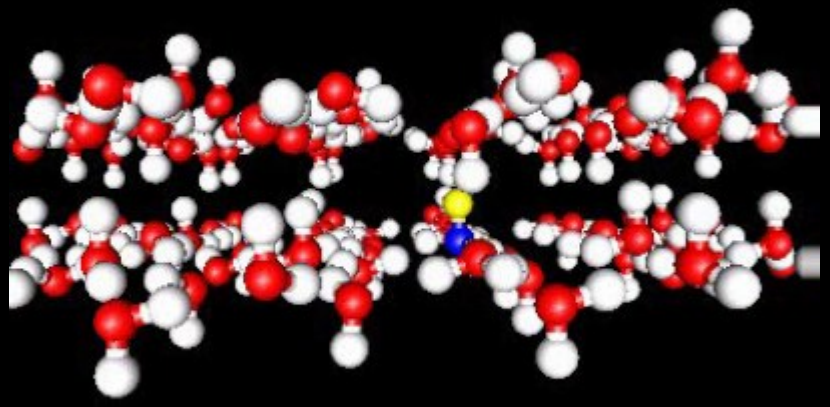
Desorption mechanisms continued

- Grain-grain collisions in turbulent boundary layers
  - See also Lecture 5 on ice mantle sputtering by shocks
- Heating by energy liberated by reactions (chemical desorption)
  - Efficient locally or for very small grains (~100 Å)
  - Often adopted as a last resort; new experiments

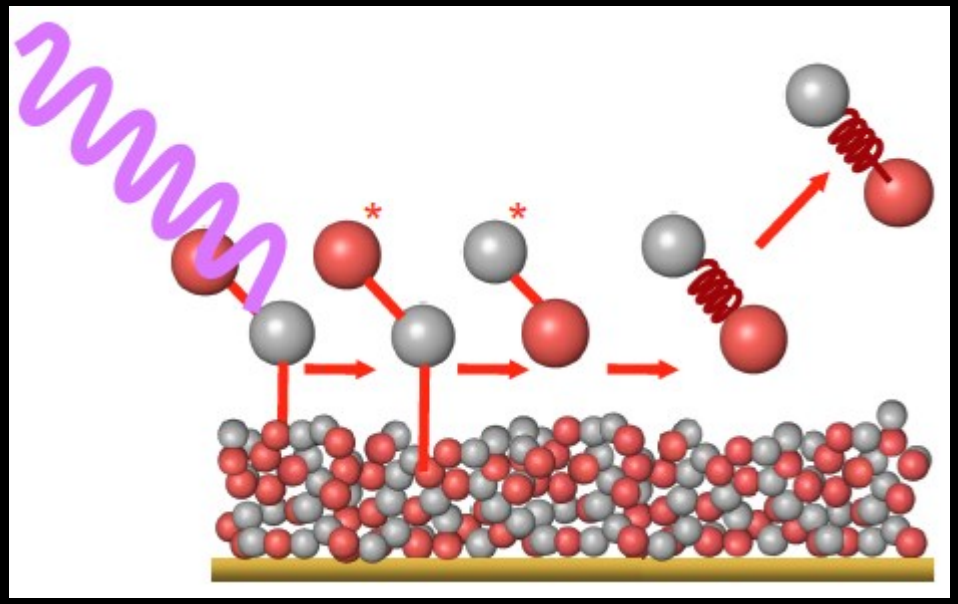
All mechanisms are efficient for CO, N_2, O_2 ice, but not for H_2O ice

Getting molecules off the grains at low T: photodesorption

Typical efficiencies of 10^{-3} per incident photon



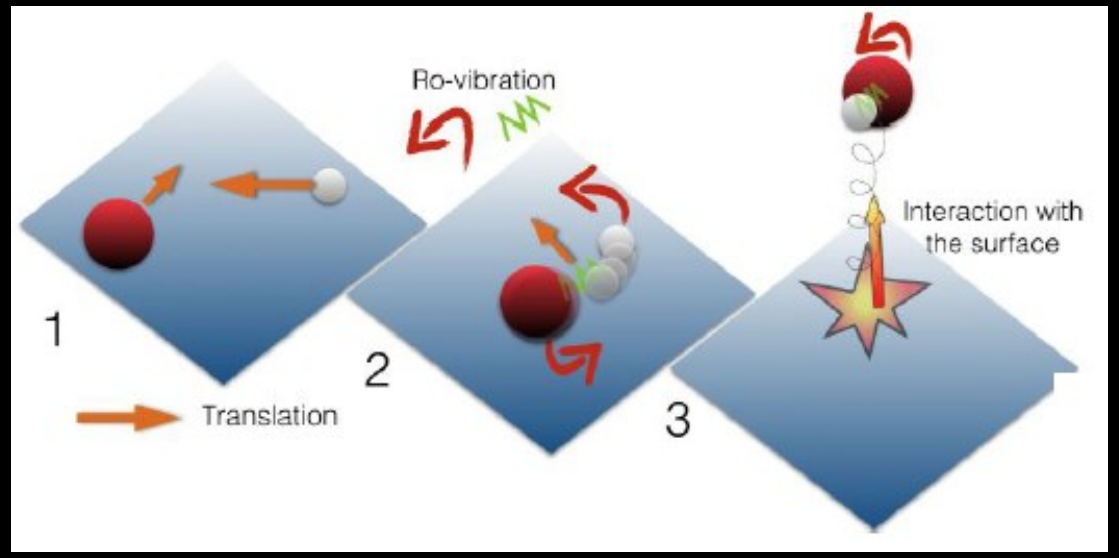
Direct vs kick-out mechanism

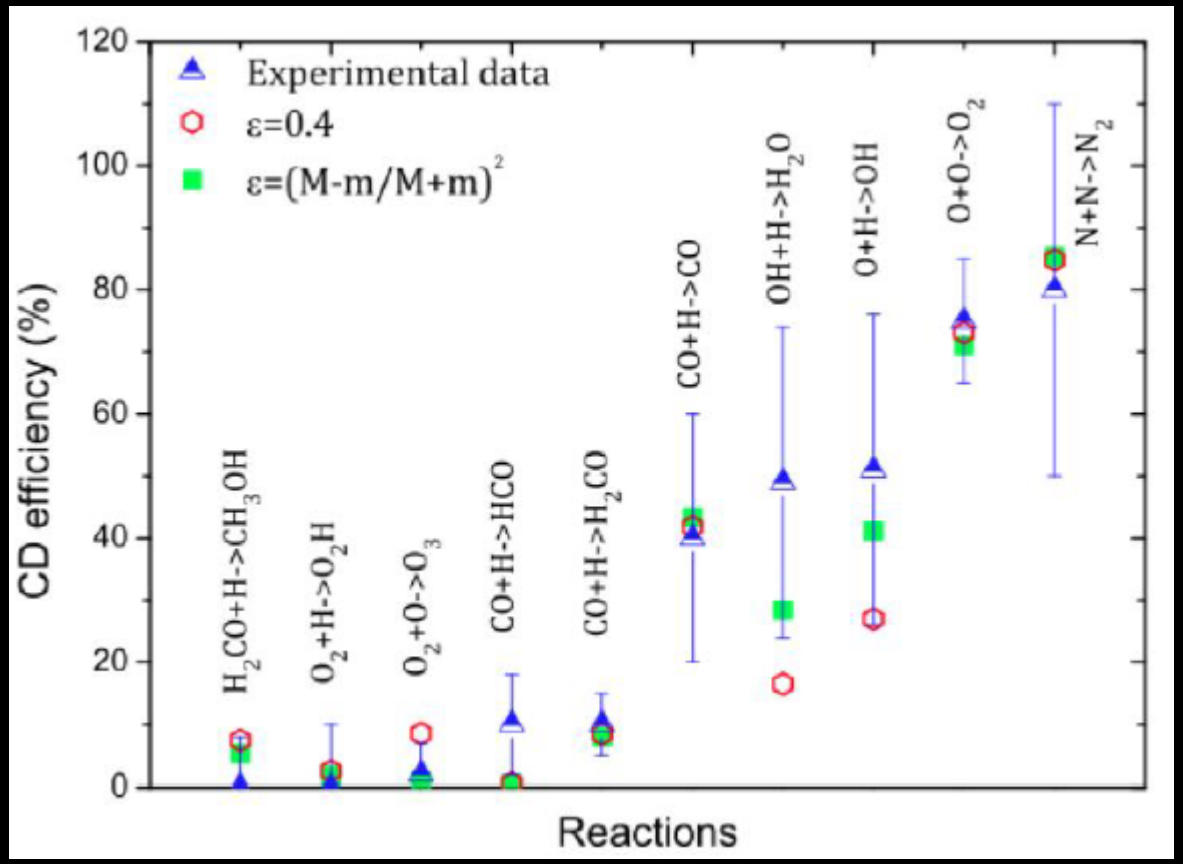


Öberg et al. 2007, 2009

Chemical desorption

Desorption efficiencies range from < 1% to > 50%, with large uncertainties





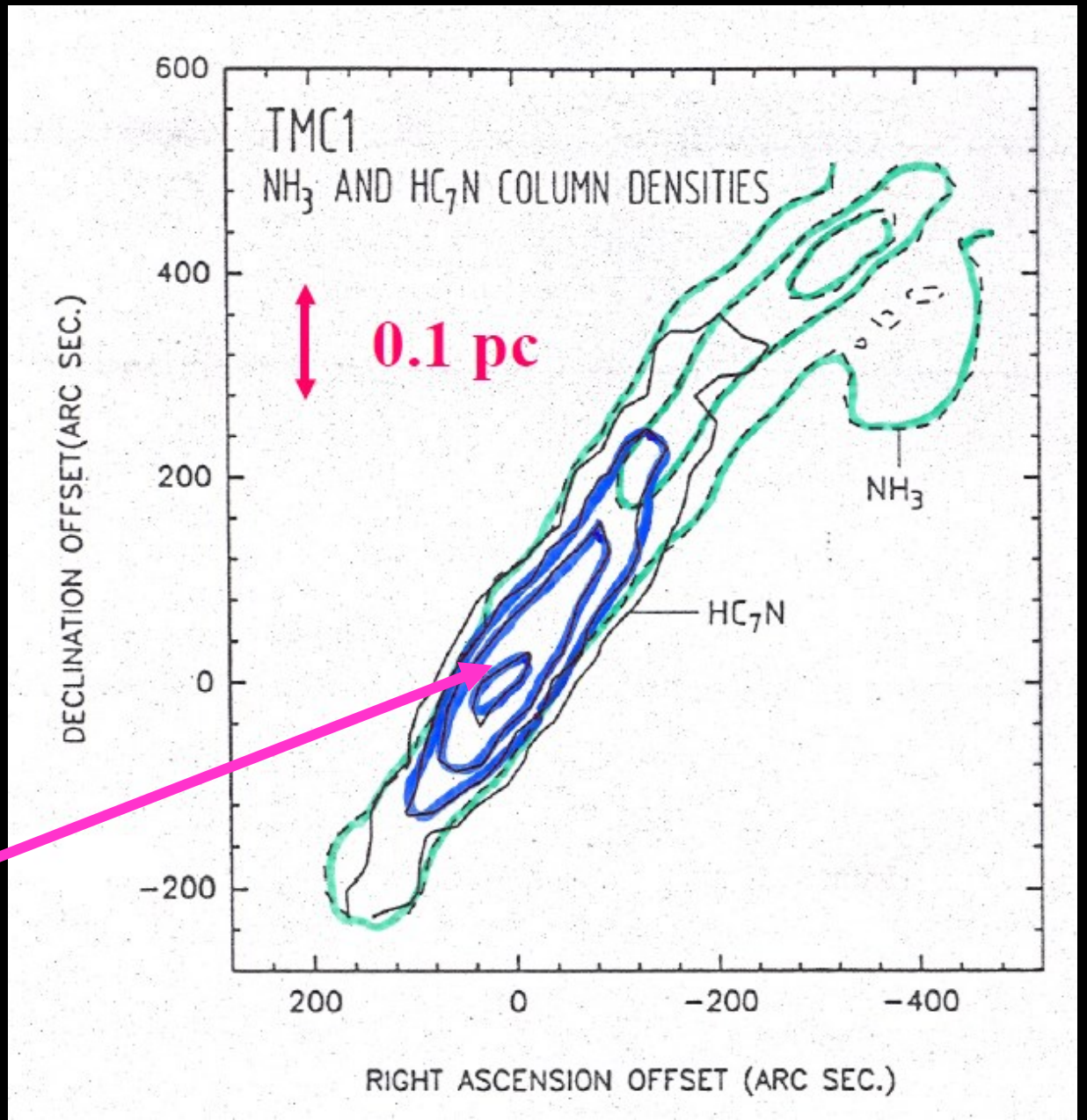
Depend sensitively on surface (e.g., silicate vs ice)

Minissale et al. 2016

16.4 Comparison with observations

- Most effort has focused on TMC-1S, where large abundances of carbon-bearing molecules are found => indication of early-time chemistry?
  - ~10^5 yr since diffuse cloud stage
- Systematic surveys of characteristic molecules in a large sample of dark cores show a good correlation among carbon chains ('early time indicators'), but not with NH_3 or N_2H^+ ('late time indicators') => **C_2S/NH_3** or **C_2S/N_2H^+** as indicator of cloud evolution

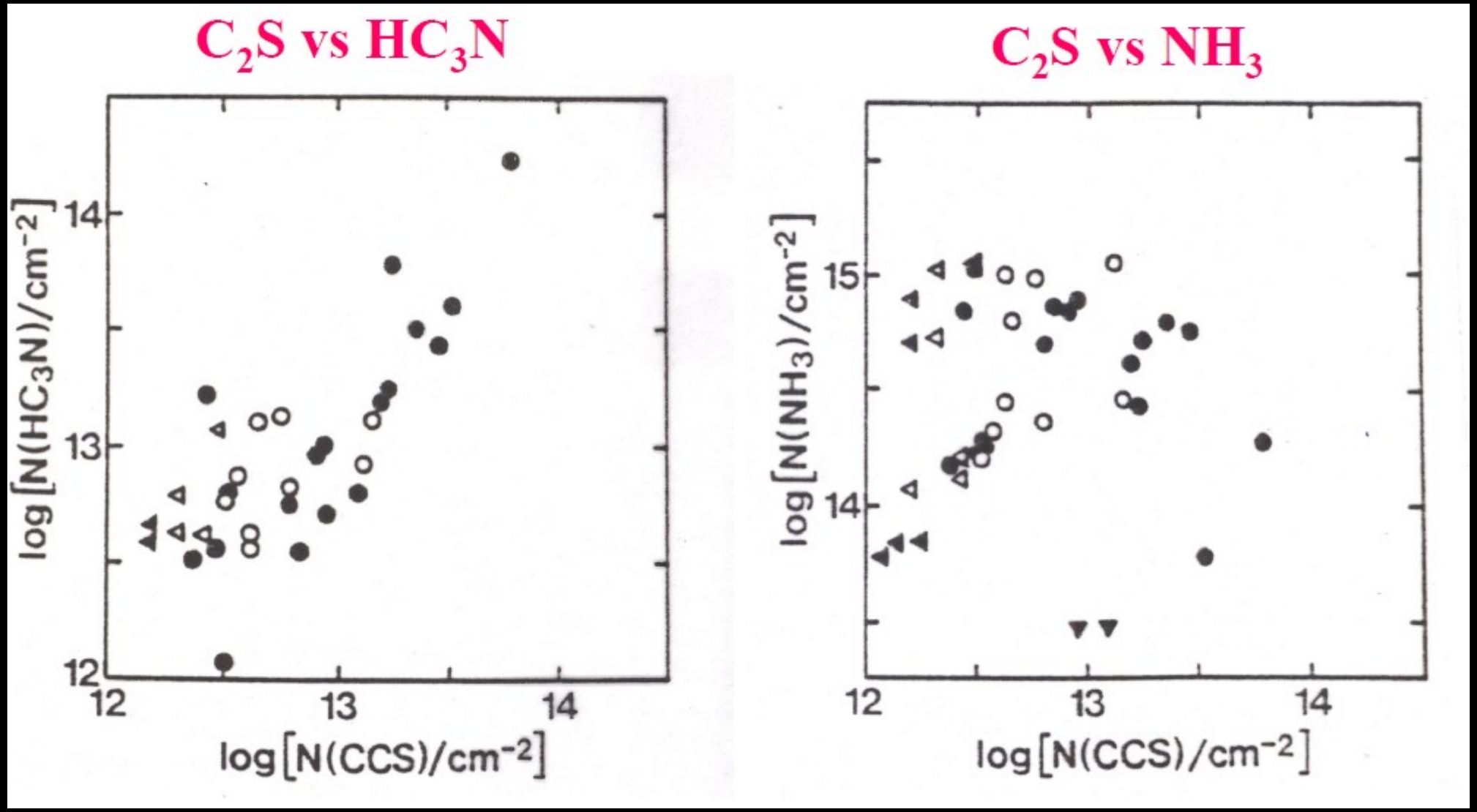
Chemical gradient in TMC-1



Long carbon chain peak

Olano et al. 1988

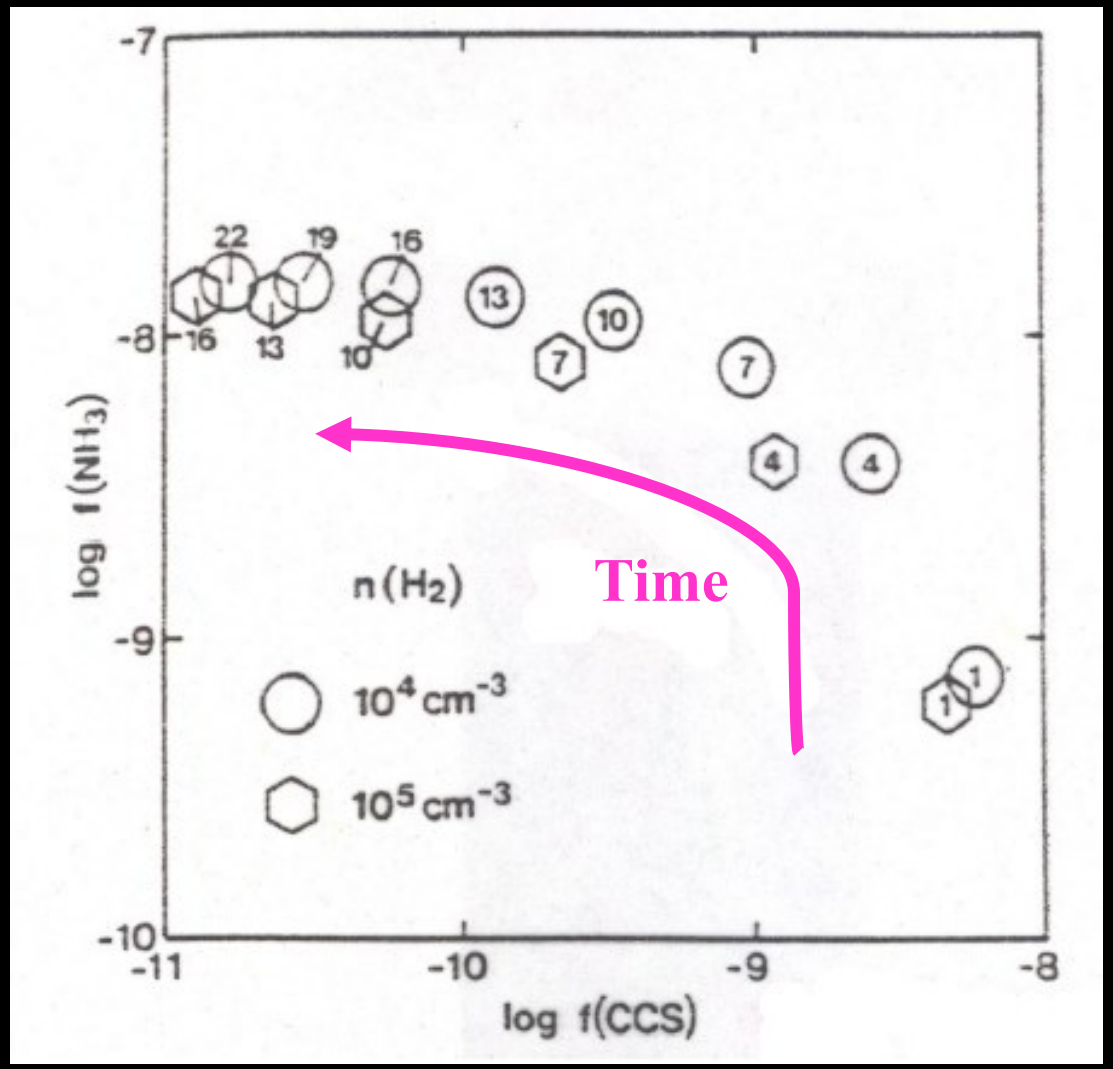
Carbon chain surveys



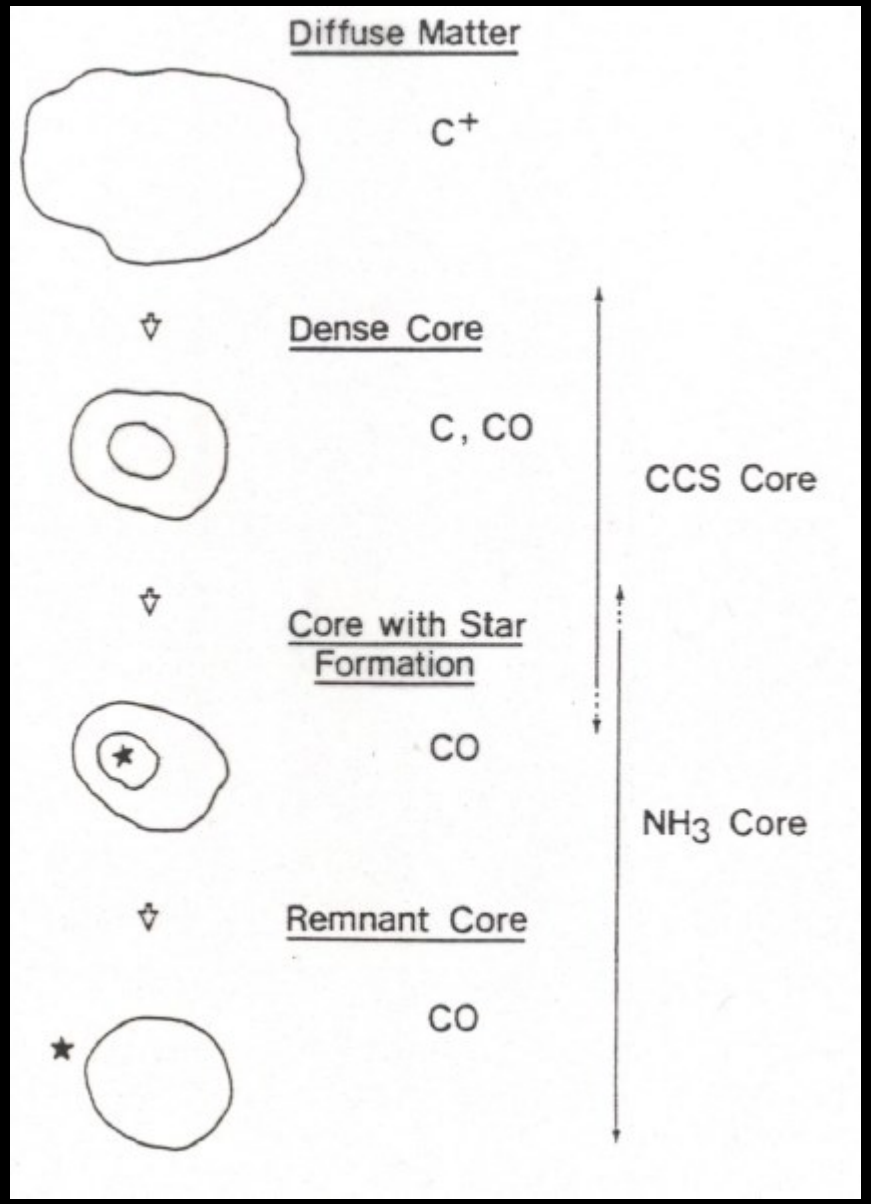
- Open symbols: cores with stars
- Closed symbols: cores without stars

Suzuki et al. 1992
Taurus cores

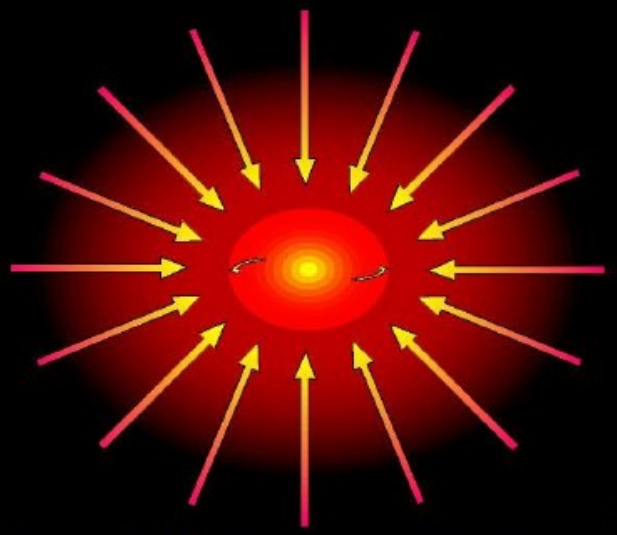
C_2S vs NH_3 evolution



Suzuki et al. 1992
Confirmed by Hirota et al. 2009,
Sakai et al. 2010 for other clouds

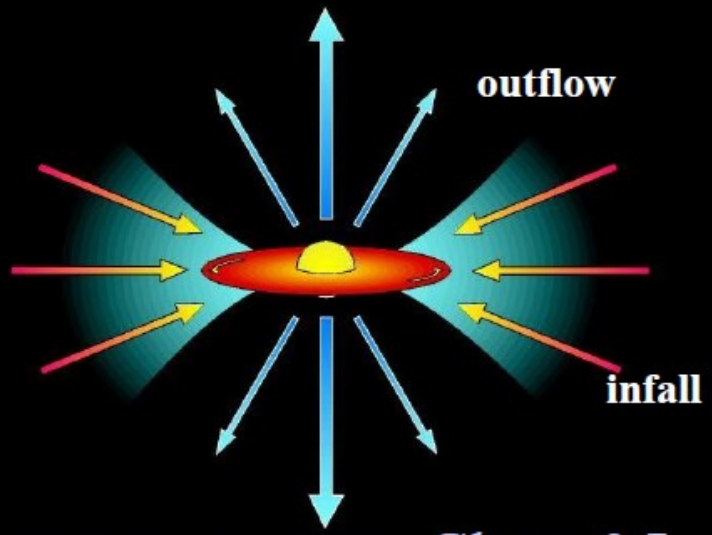


Scenario for star- and planet formation



Pre-stellar cores

Factor 1000 smaller

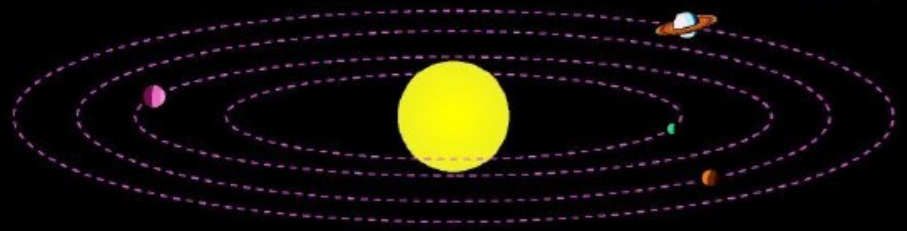


Class 0,I

Cloud collapse t=0

Class II

Rotating disk $t=10^5$ yr



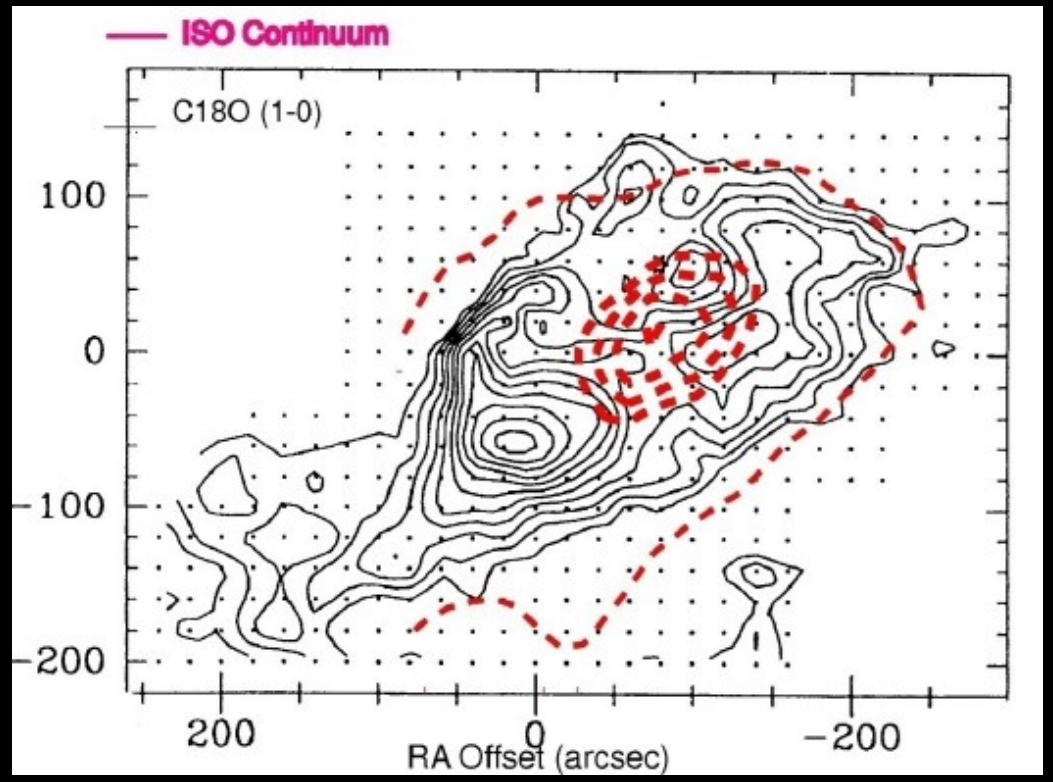
Formation planets $t=10^7$ yr

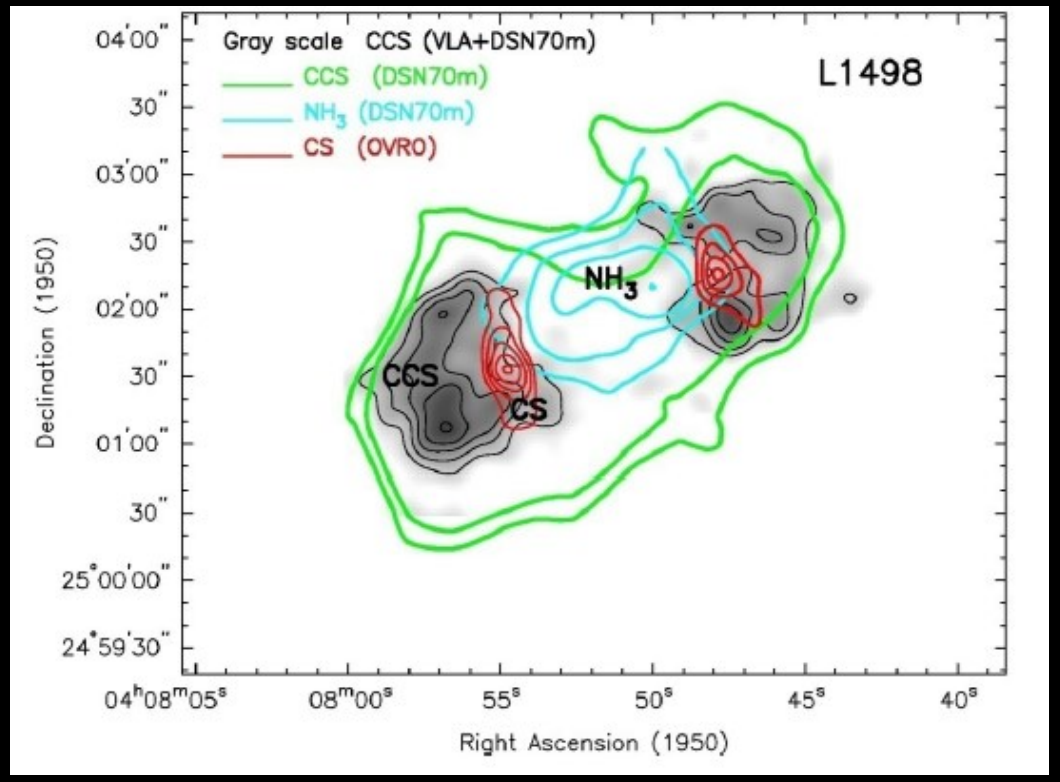
Solar system $t>10^8$ yr

Pre-stellar cores: L 1498

- So far considered dense starless cores
- L 1498 has centrally concentrated density structure and is likely on the verge of collapse to form a star
- High-resolution images show differentiated structure
  - C_2S: traces clumpy, atomic C-rich outer part
  - NH_3: peaks in inner high-density core
  - $C^{18}O$: avoids densest part => depletion
  - Extremely high deuterium fractionation: $DCO^+/HCO^+ \approx 0.1$

L 1498 images





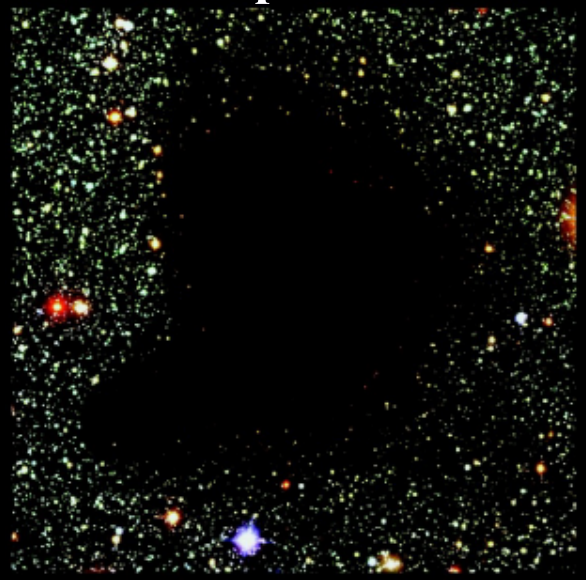
$C^{18}O$ avoids central part

CCS in outer part core
NH_3 in center

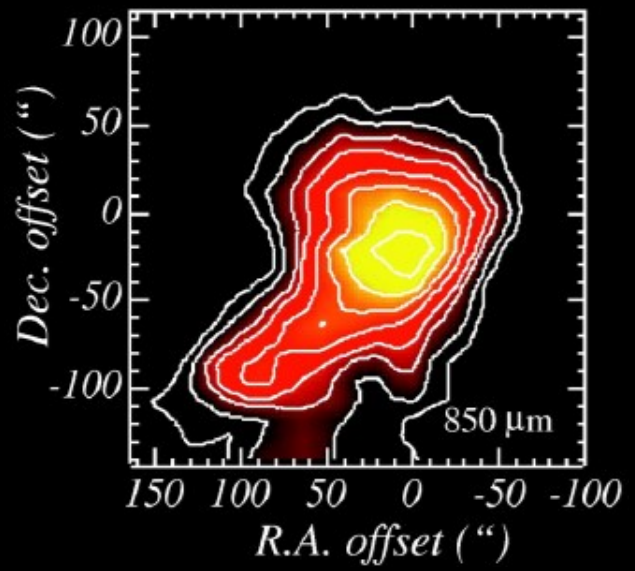
Willacy 1998

Freeze-out in B 68

Optical

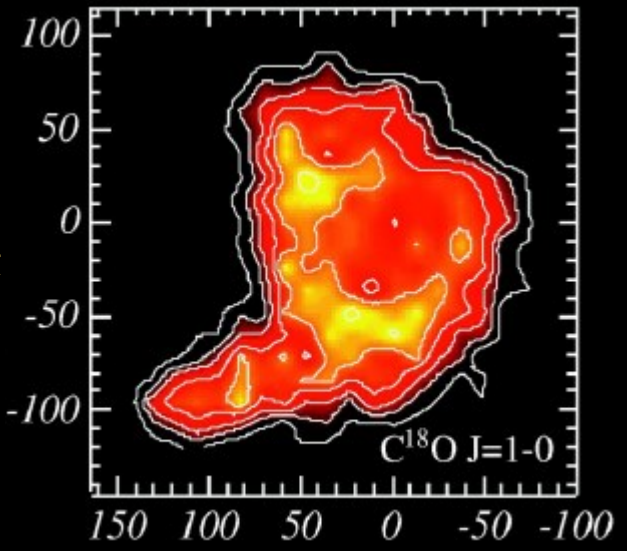


Submm continuum => cold dust

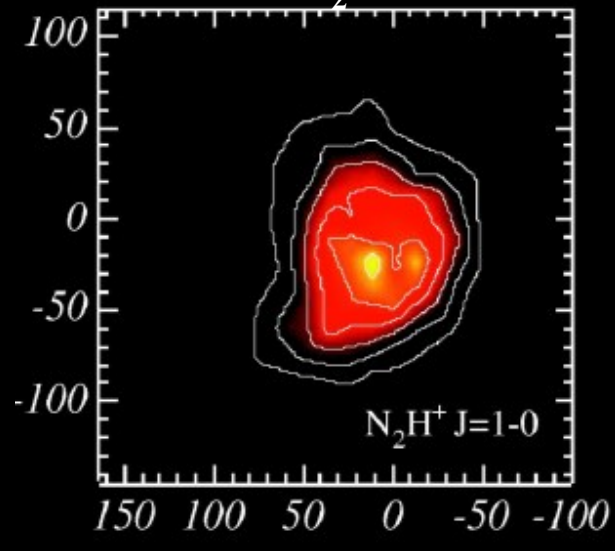


More than 90% of all molecules except most volatile species frozen out on $T \sim 10$ K grains

CO



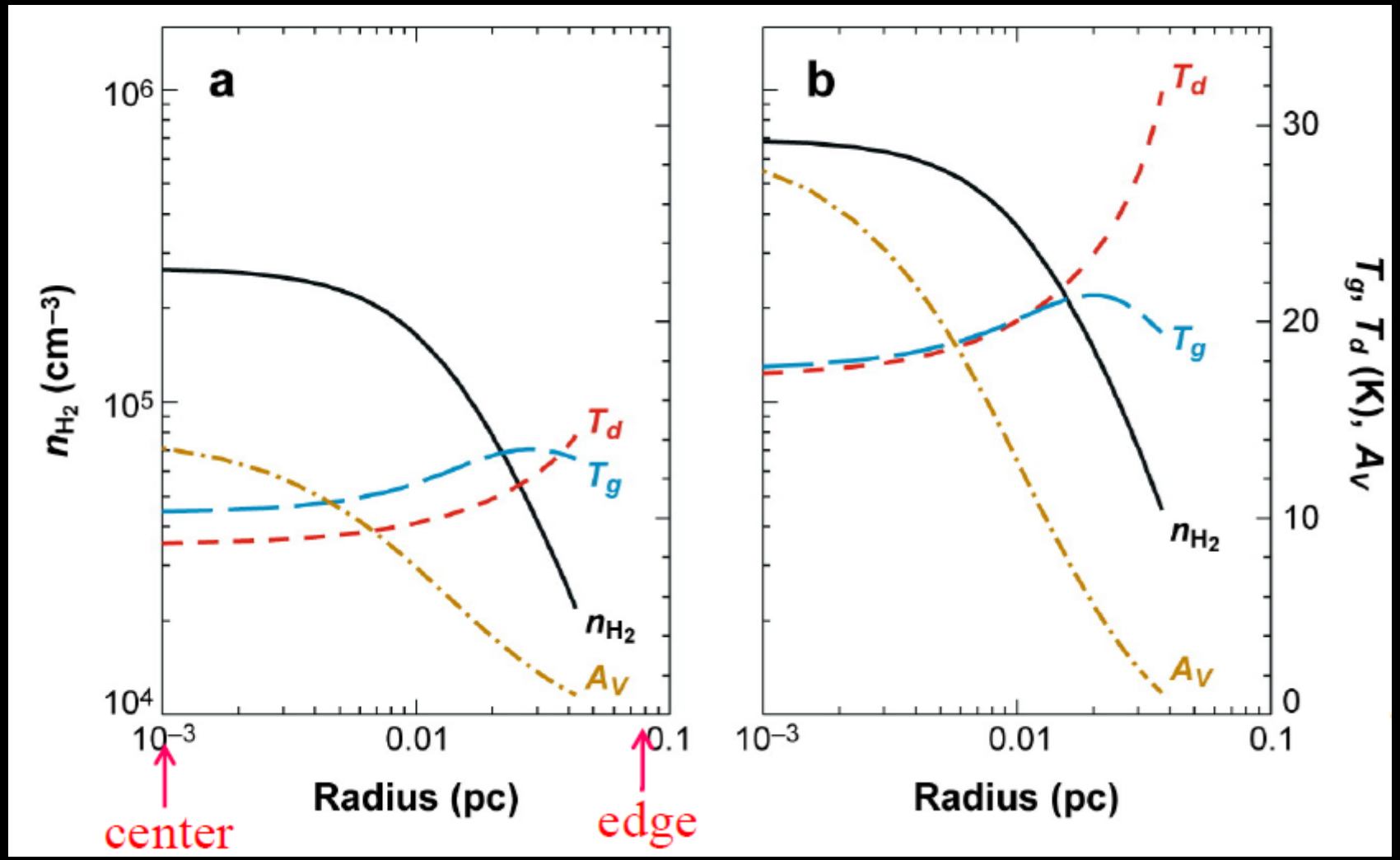
N_2H^+



$C^{18}O$ avoids densest, coldest part of core

Bergin et al. 2002
Caselli et al. 2002

Physical structure pre-stellar cores

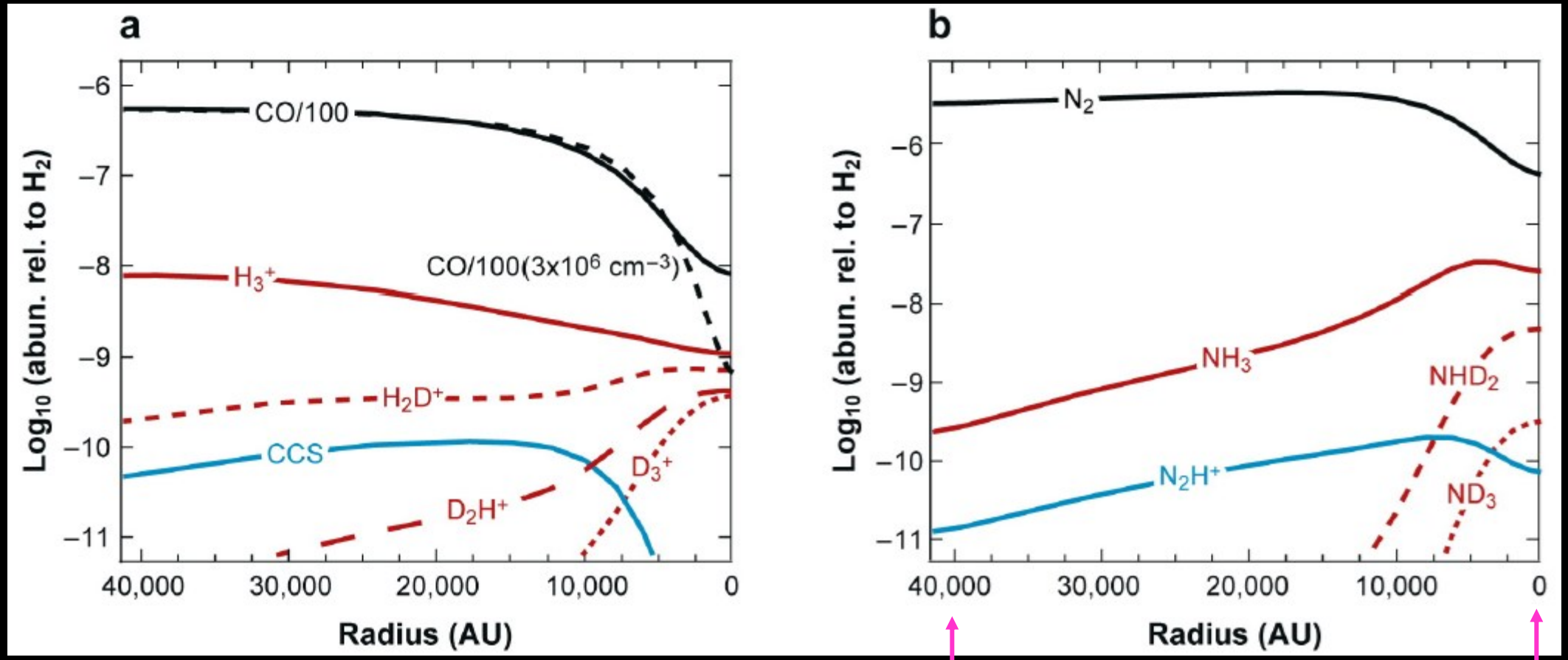


Galli et al. 2002

Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96

-Left: M = 1 $M_\odot$, I_{UV} = 1 x ISRF
-Right: M = 1.6 $M_\odot$, I_{UV} = 10 x ISRF

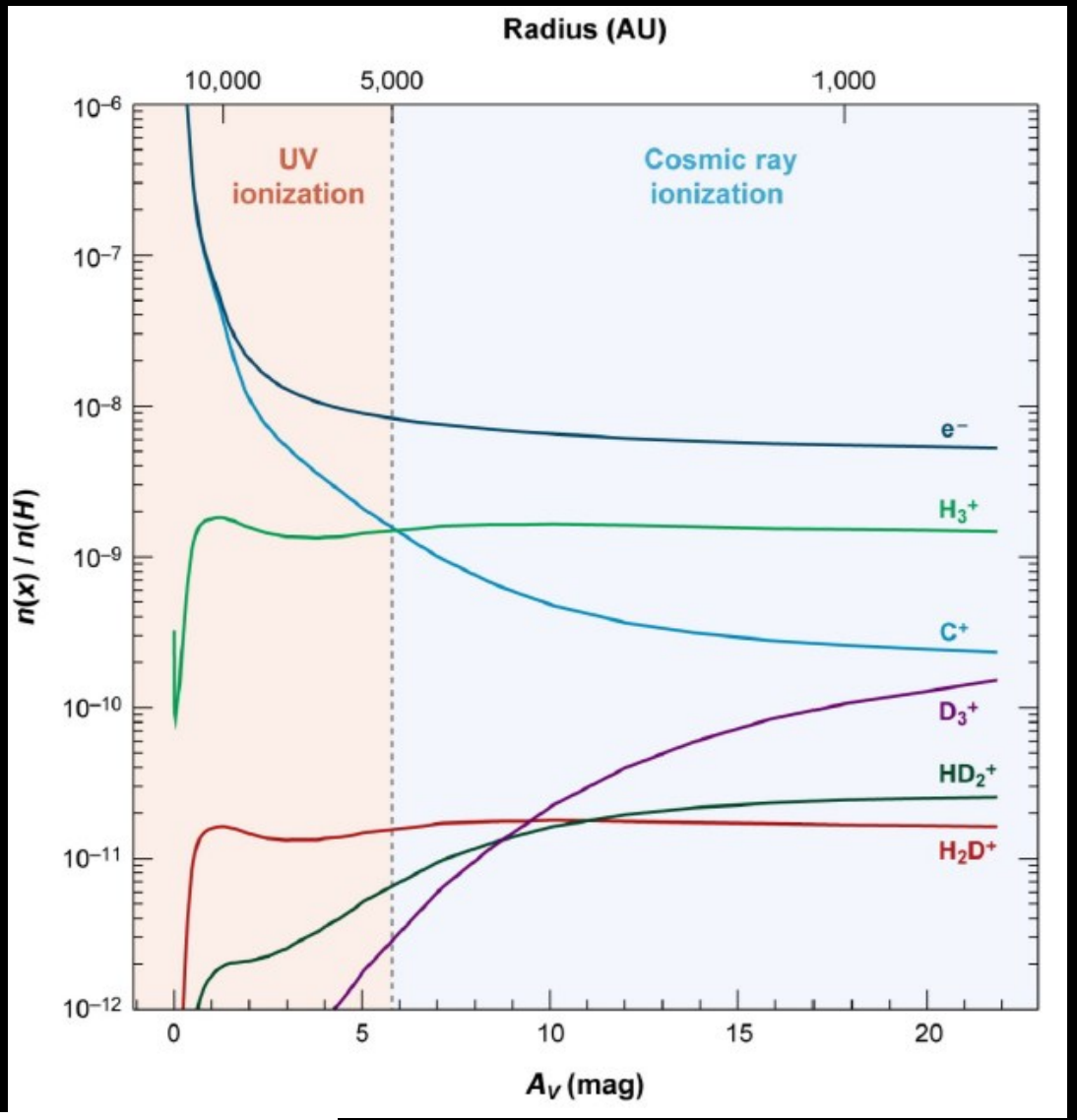
Chemical structure pre-stellar cores



Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96

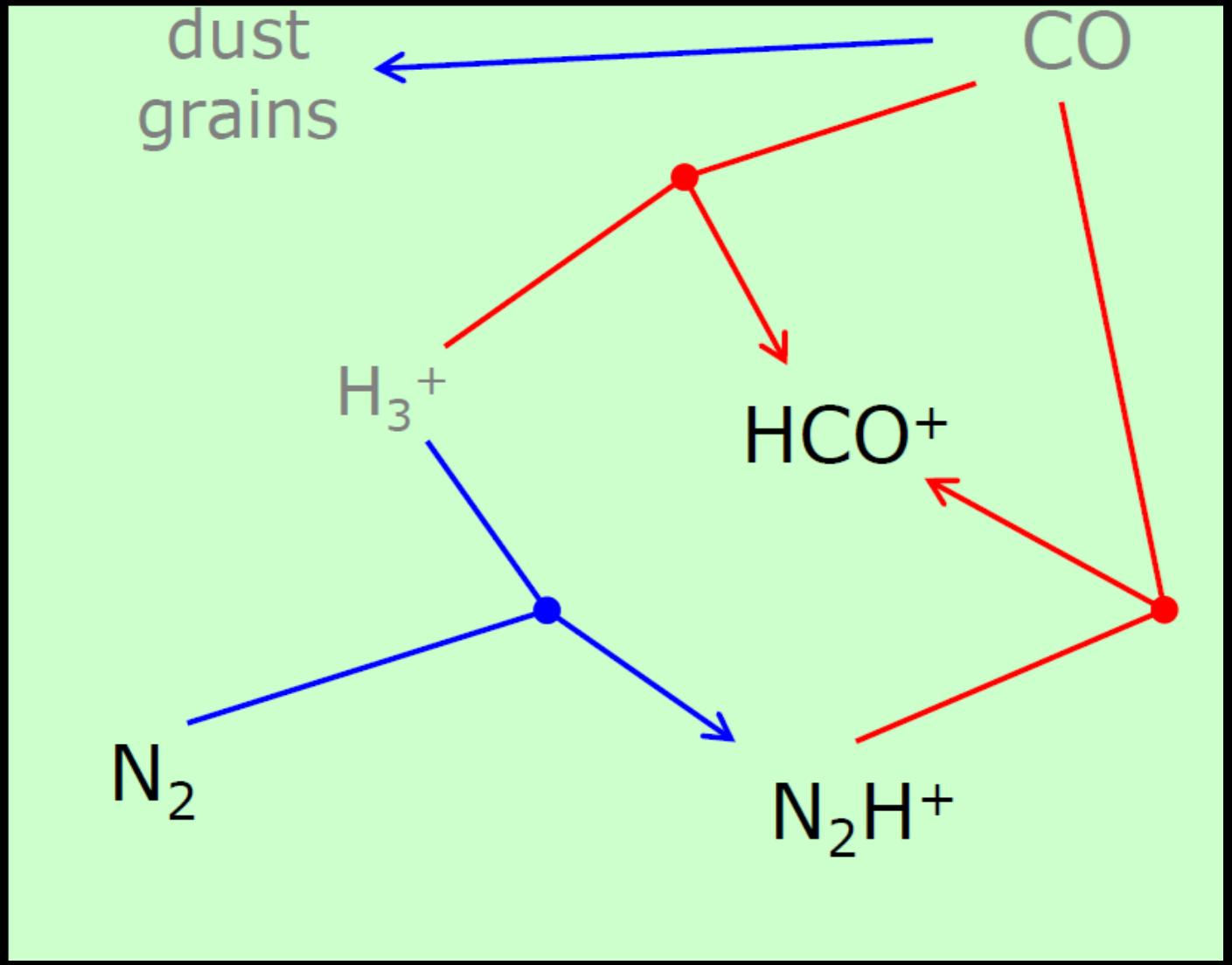
Note: CO freeze-out and increase of deuteration and nitrogen molecules in center

Ionization and deuterium fractionation



Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96

Chemical effects of CO depletion



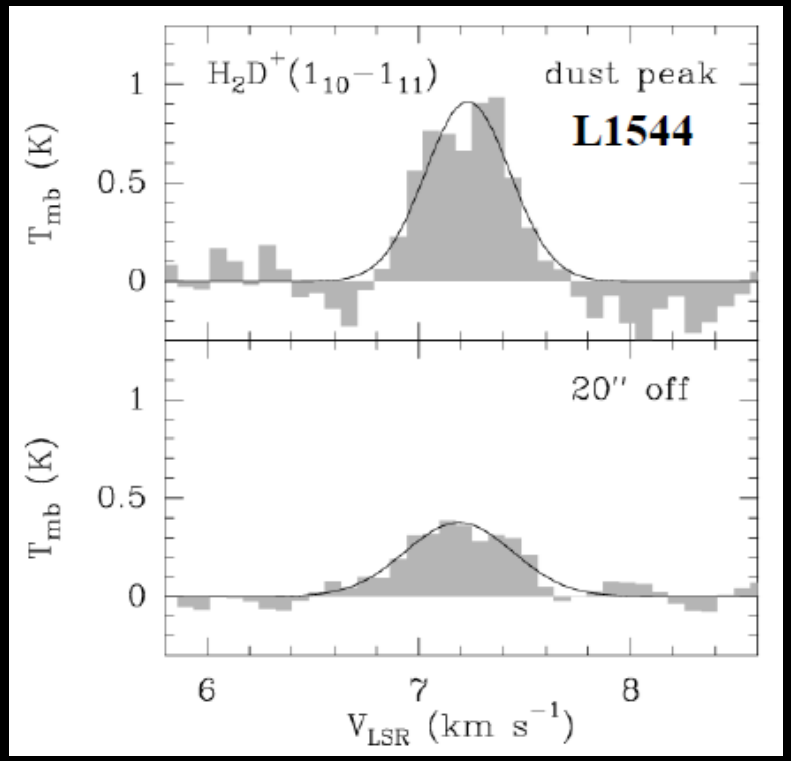
Jørgensen et al. 2004

N_2H^+ enhanced when CO, the main destroyer of N_2H^+, is frozen out:

$$N_2H^+ + CO \rightarrow HCO^+ + H_2$$

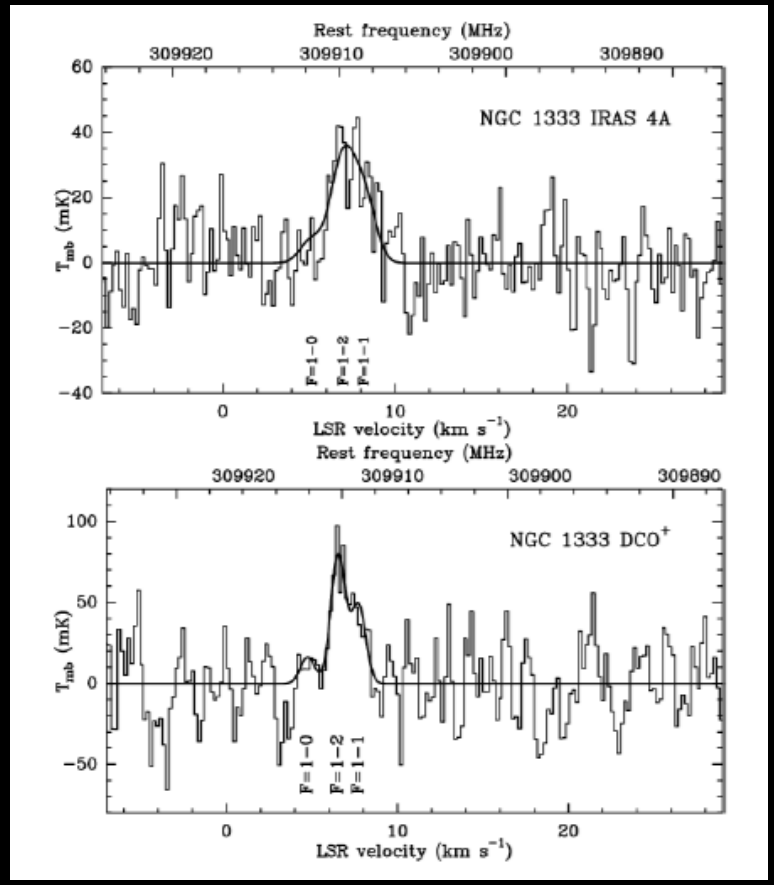
Extreme deuteration: tracer of freeze-out

Strong H_2D^+ in pre-stellar cores



Caselli et al. 2003

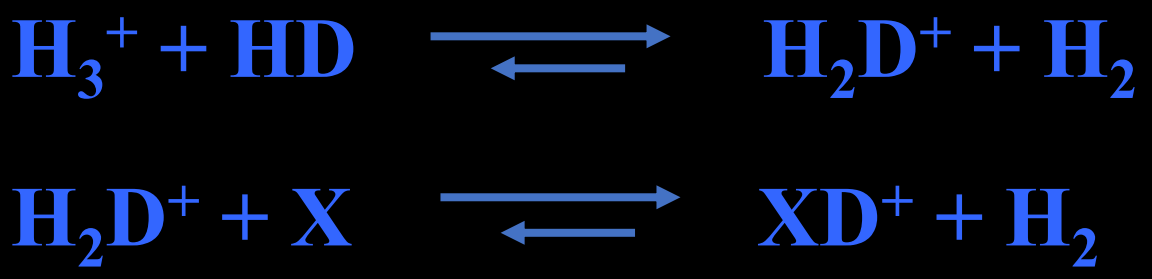
Triply deuterated ammonia: ND_3



Lis et al. 2002
van der Tak et al. 2002

Note detections of H_2D^+, D_2H^+, and ND_3!

Origin of strong deuteration

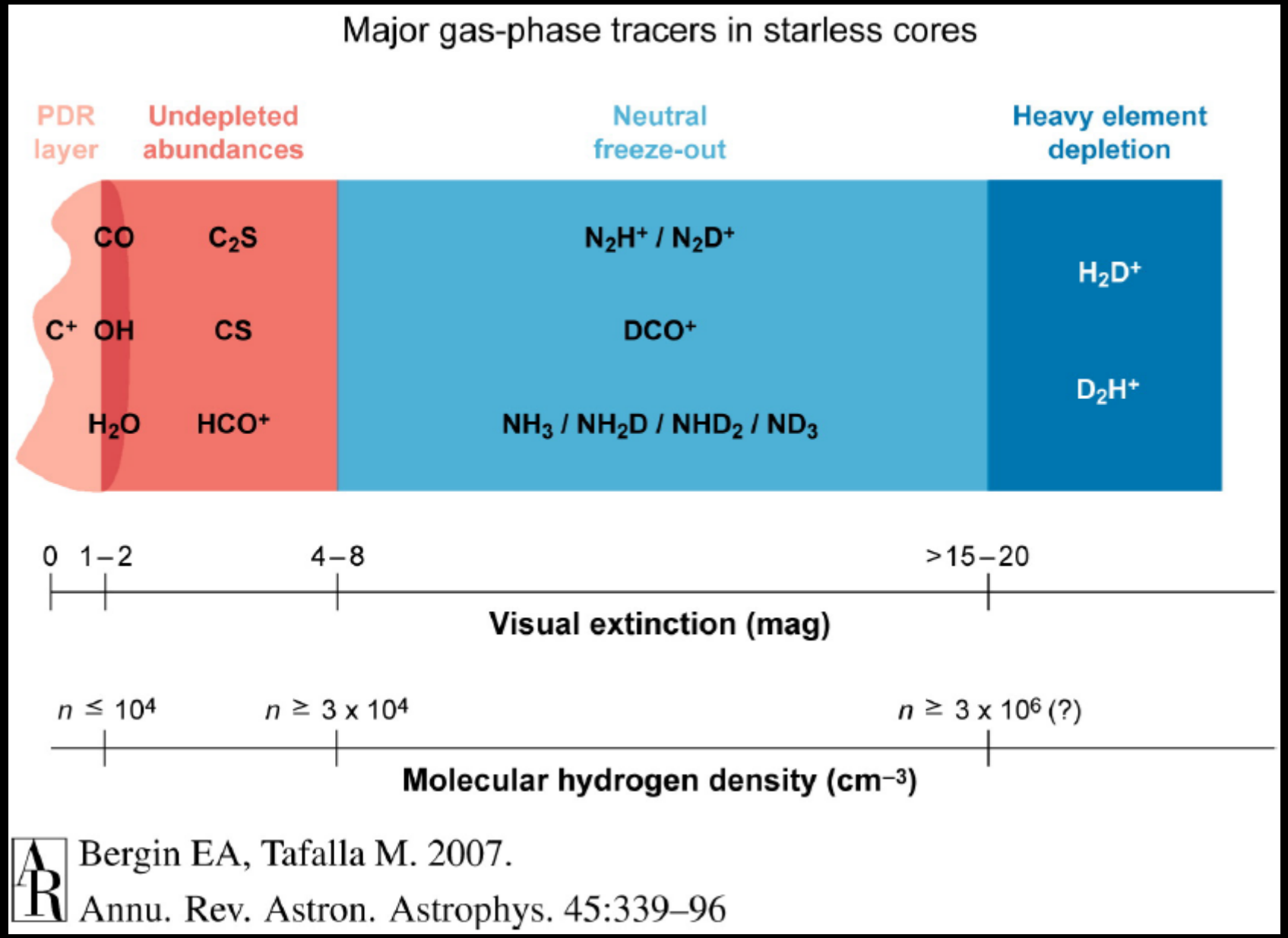


- Reactions more rapid in forward direction at low *T* (exoergic by 230 K due to difference in zero-point vibrational energy – proper calculation required considering *o*/*p* states)
- H_3^+ and H_2D^+ greatly enhanced when their main destroyer, CO, is frozen out on grains

6.5 Summary

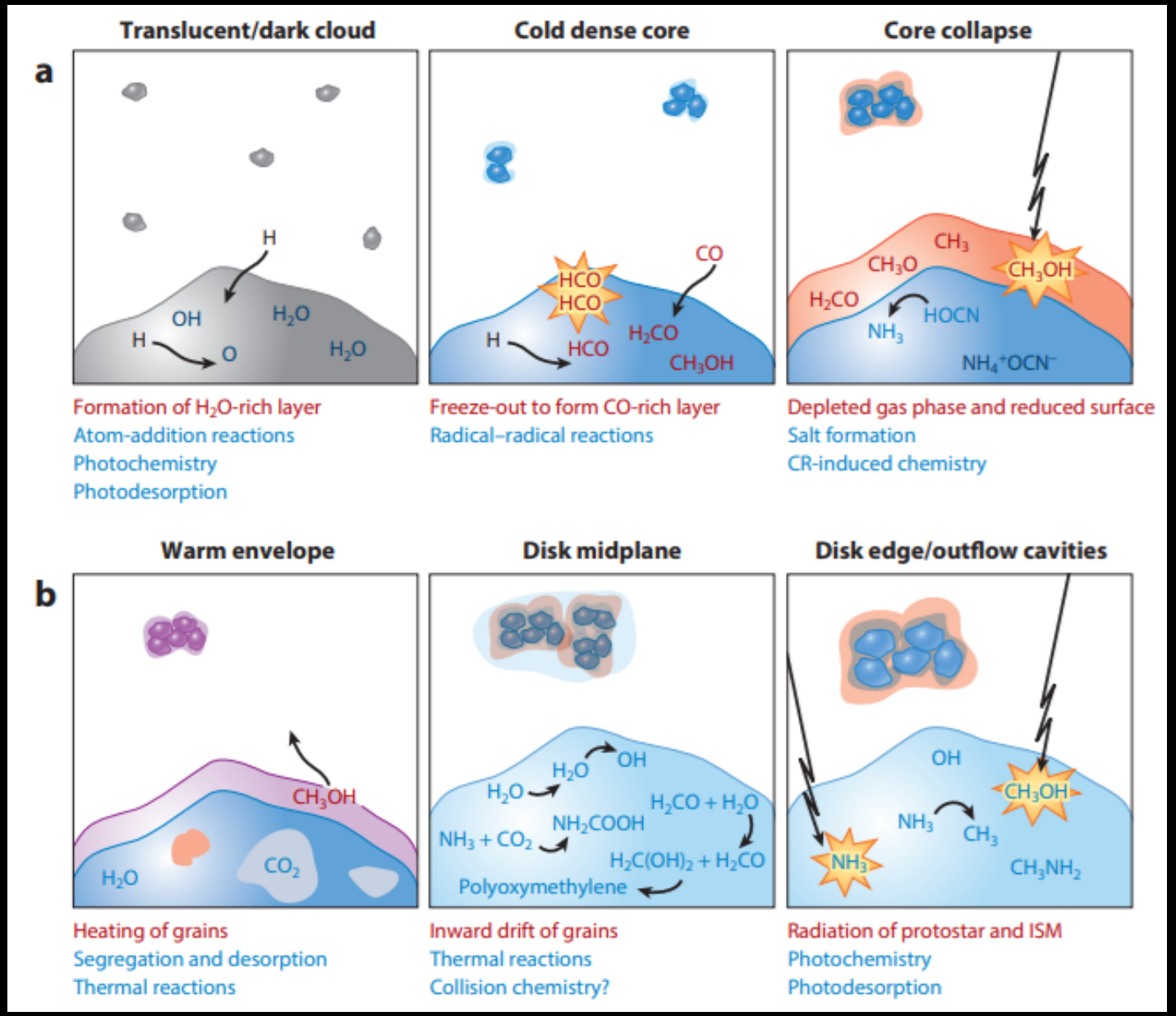
- Some starless cores have high abundances of carbon chain molecules
  - Indicative of a ‘young’ gas-phase chemistry where fresh atomic carbon has recently (within ~10^5 yr) been added
- Centrally concentrated pre-stellar cores show significant freeze-out in center, leading to high deuterium fractionation. Nitrogen-bearing molecules less affected by freeze-out.
- Chemical models must include gas-grain chemistry

Summary structure



Bergin EA, Tafalla M. 2007.
Annu. Rev. Astron. Astrophys. 45:339–96

Outlook – star formation



Annual Review of Astronomy and Astrophysics

Laboratory and Computational Studies of Interstellar Ices

Herma M. Cuppen,[1] H. Linnartz,[2] and S. Ioppolo[3]

[1]Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands; email: h.cuppen@science.ru.nl

[2]Laboratory for Astrophysics, Leiden Observatory, Leiden University, Leiden, The Netherlands

[3]Center for Interstellar Catalysis, Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark