Lecture 2: "Chemistry from Big Bang till Present"

Outline

1. Chemistry in the early Universe
2. Chemistry in molecular clouds
3. Chemistry in protoplanetary disks

The Universe is expanding

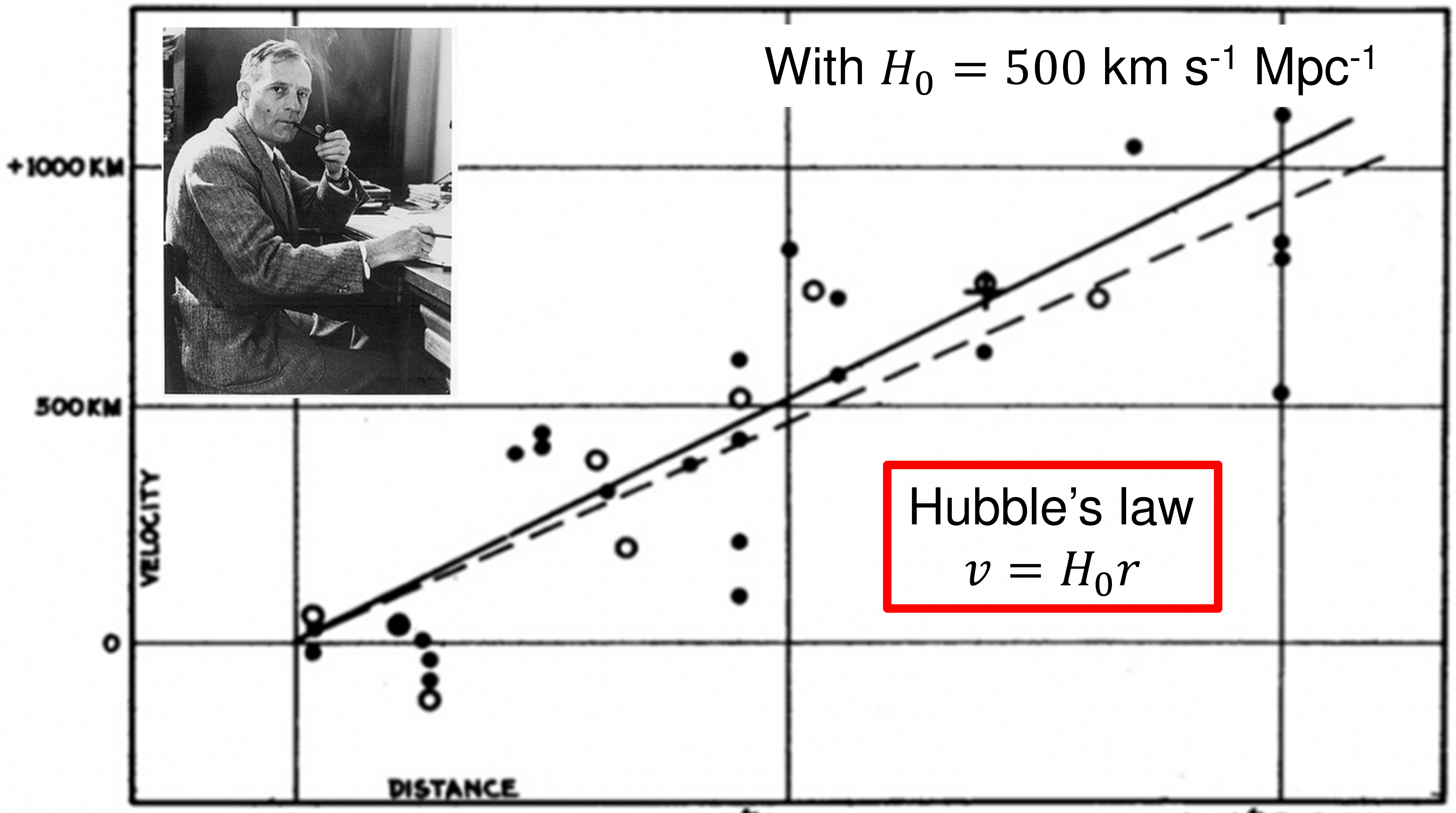


FIGURE 1
Velocity-Distance Relation among Extra-Galactic Nebulae.

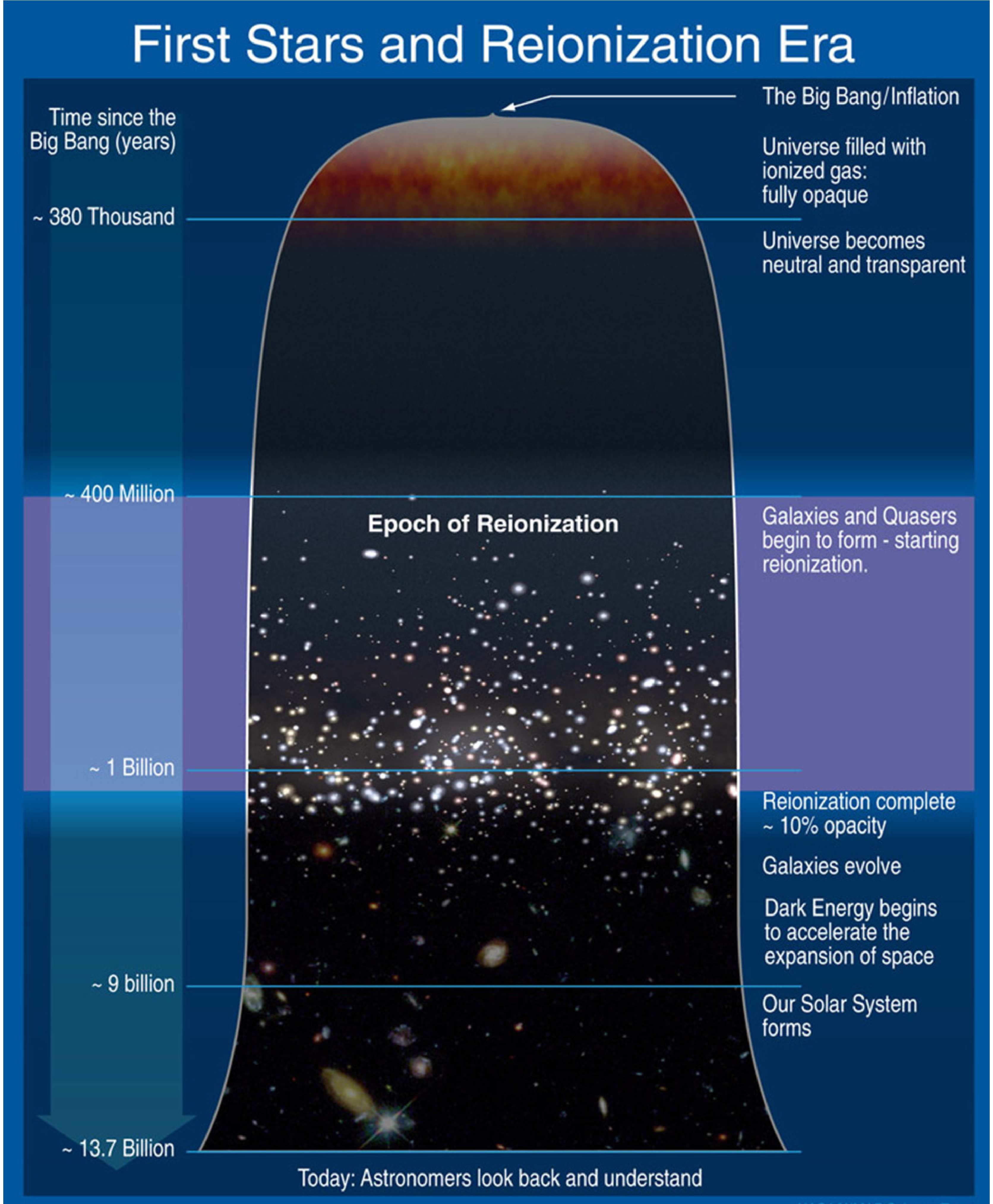
Edwin Hubble, PNAS, vol. 15 no. 3, pp.168-173 (1929)

- Distance from brightness and variability of Cepheid stars
- Velocity from a measured Doppler shift: $z = \lambda_{obs} / \lambda_{emit} - 1 \approx V / c$
- Modern value: $H_0 = 69.32 \pm 0.80$ km s^{-1} Mpc^{-1} $\Rightarrow t \approx 1/H_0 \sim 13.77$ Gyr

T

10,000 K

30 K



Recombination

First molecules

First stars and galaxies

Solar system is born

The Universe after Big Bang

Epoch	Time, s	T_R, K	n_H, cm^{-3}
Baryons and leptons: e^-, p^+, n	$10^{-11} – 2$	$>10^{12}$	–
Radiation-dominated	2	10^{10}	–
Matter-dominated	$10^{11} – 10^{12}$	4,000	500
Present	10^{18}	2.73	$2\ 10^{-7}$

Standard Cosmological Model

- Composition at the beginning of the matter-dominated era:

  H : D : ^{4}He : ^{3}He : ^{7}Li

  1 : 4 10^{-5} : 8 10^{-2} : 10^{-5} : 2 10^{-10}

(1) $H + h\nu \rightarrow H^+ + e^-$, rate ~ radiation field

(2) $H^+ + e \rightarrow H$, rate ~ $T^{-0.61}$

- As Universe expands and cools, recombination occurs:

  $n(H^+) = n(H)$ at $z = 1340$, $T_R = 3630$ K

- No thermodynamical equilibrium

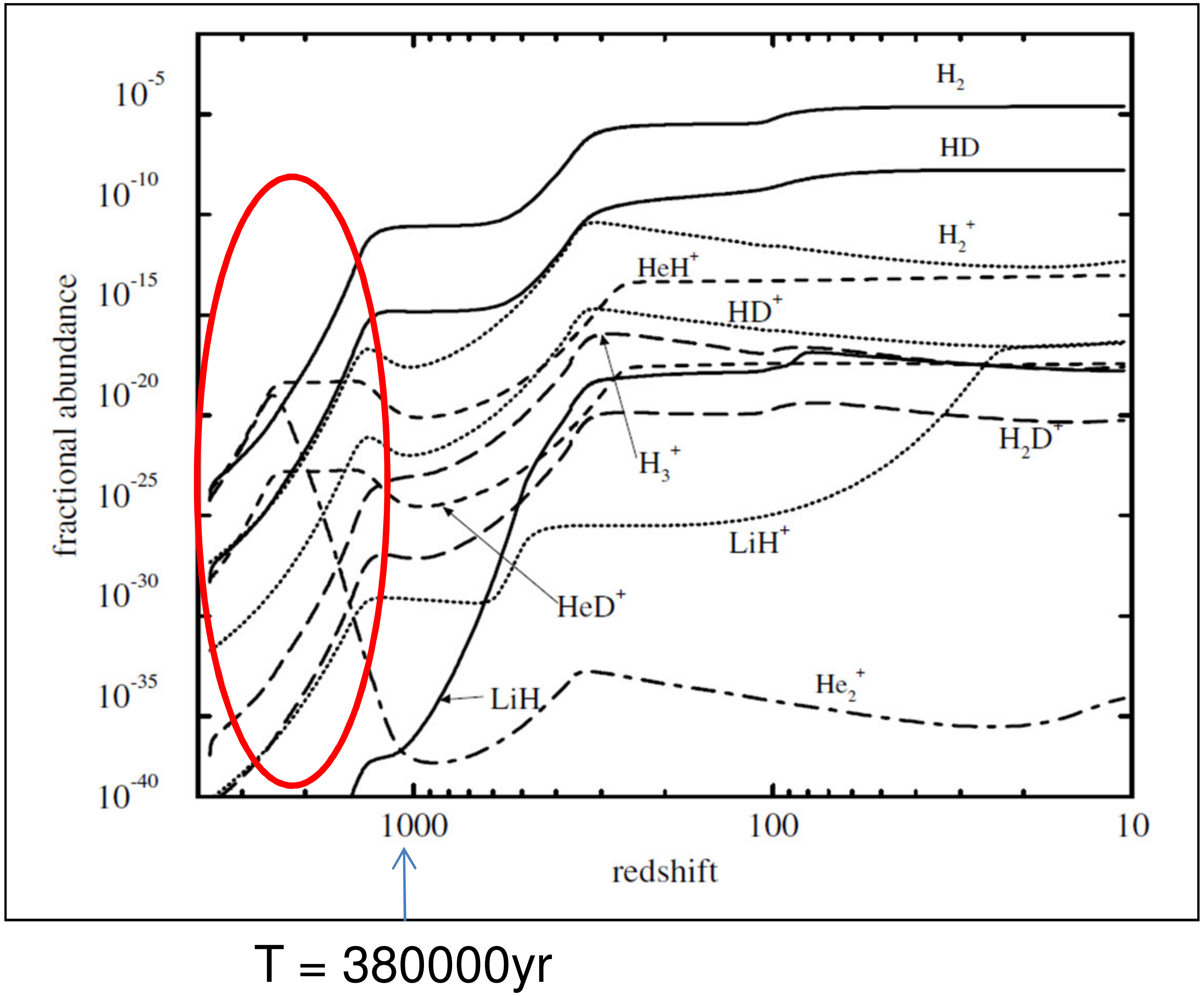
First neutral atoms

Ionization potentials [in eV]

	1st	2nd	3rd
H	13.6		
He	**24.6**	54.4	
Li	5.4	75.6	122.5

- First: $He^+ + e^- \Rightarrow He + h\nu$
- Second: $H^+ + e^- \Rightarrow H + h\nu$

First Molecules



Lepp, Stancil, Dalgarno,
J. Phys. B., At. Mol. Opt. Phys 35 (2002)

$He^+ + He \rightarrow He_2^+ + h\nu$ (RA)

$He + H^+ \rightarrow HeH^+ + h\nu$ (RA)

Destroyed by photodissociation and dissociative recombination with e^-

Chemistry of H

- H_2 forms via gas-phase reactions

- Formation by radiative association is too slow:

$$H + H \nrightarrow H_2 + h\nu$$

(H_2 does not have a dipole moment => difficult to get rid of excess of energy via radiation of photons)

Formation of H_2 from HeH^+

First, H_2 formed via ion-molecule reactions with HeH^+:

$He + H^+ \rightarrow HeH^+ + h\nu$

$HeH^+ + H \rightarrow H_2^+ + He$

$H_2^+ + H \rightarrow H_2 + H^+$

(here He and H are catalysts!)

H_2 and H_2^+ are rapidly destroyed by background radiation

Formation of H_2 from H^+

Later, formation H_2 involves RA & ion-molecule reaction:

$H + H^+ \rightarrow H_2^+ + h\nu$

$H_2^+ + H \rightarrow H_2 + H^+$

H_2^+ is destroyed by photodissociation and DR:

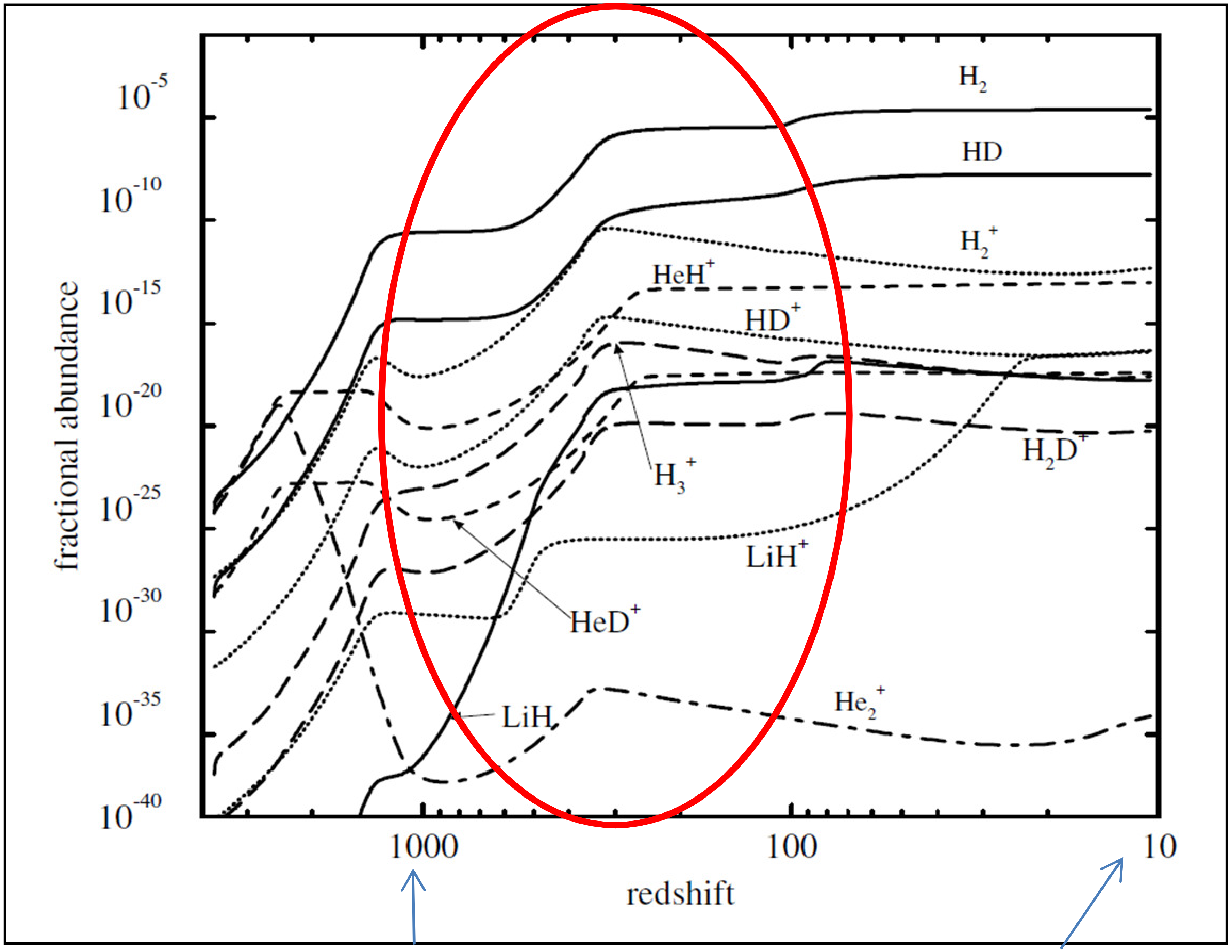
$H_2^+ + h\nu \rightarrow H + H^+$

$H_2^+ + e \rightarrow H + H$

Photodissociation of H_2^+ is efficient when $T_R > 4000$ K =>

no much of H_2 at $z > 1000$

Formation of H_2 from H^+



T = 380000yr

t = 480 x10^6 yr

Formation of H_2 from H^-

At z ~ 100, H_2 can be formed through H^-:

$H + e \rightarrow H^- + h\nu$ (radiative attachment)

$H^- + H \rightarrow H_2 + e$ (associative detachment)

H^- is destroyed by photodetachment reaction:

$H^- + h\nu \rightarrow H + e^-$ (barrier is 0.75 eV) => slow when $T_R < 1000$ K

Destruction of H_2

H_2 is destroyed by ion-molecule reactions with H^+ and collisional dissociation:

$H_2 + H^+ \rightarrow H_2^+ + H$

$H_2 + e^- \rightarrow H + H^-$

Small molecular fraction in the early Universe: $X(H_2) \sim 10^{-6}$

Chemistry of D

Formation of HD:

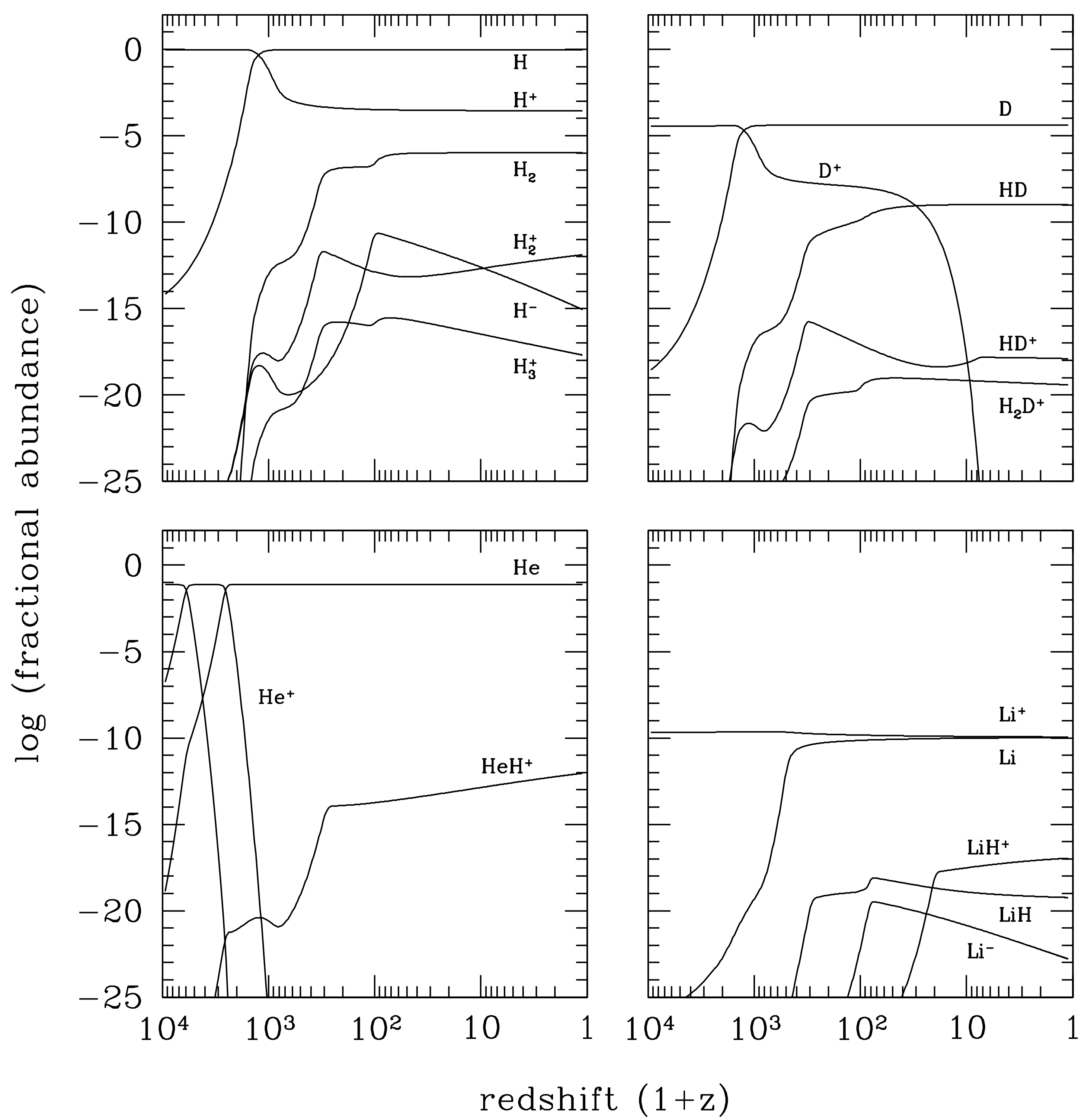
$H^+ + D \rightarrow H + D^+$

$D^+ + H_2 \rightarrow HD + H^+$

HD is destroyed as H_2

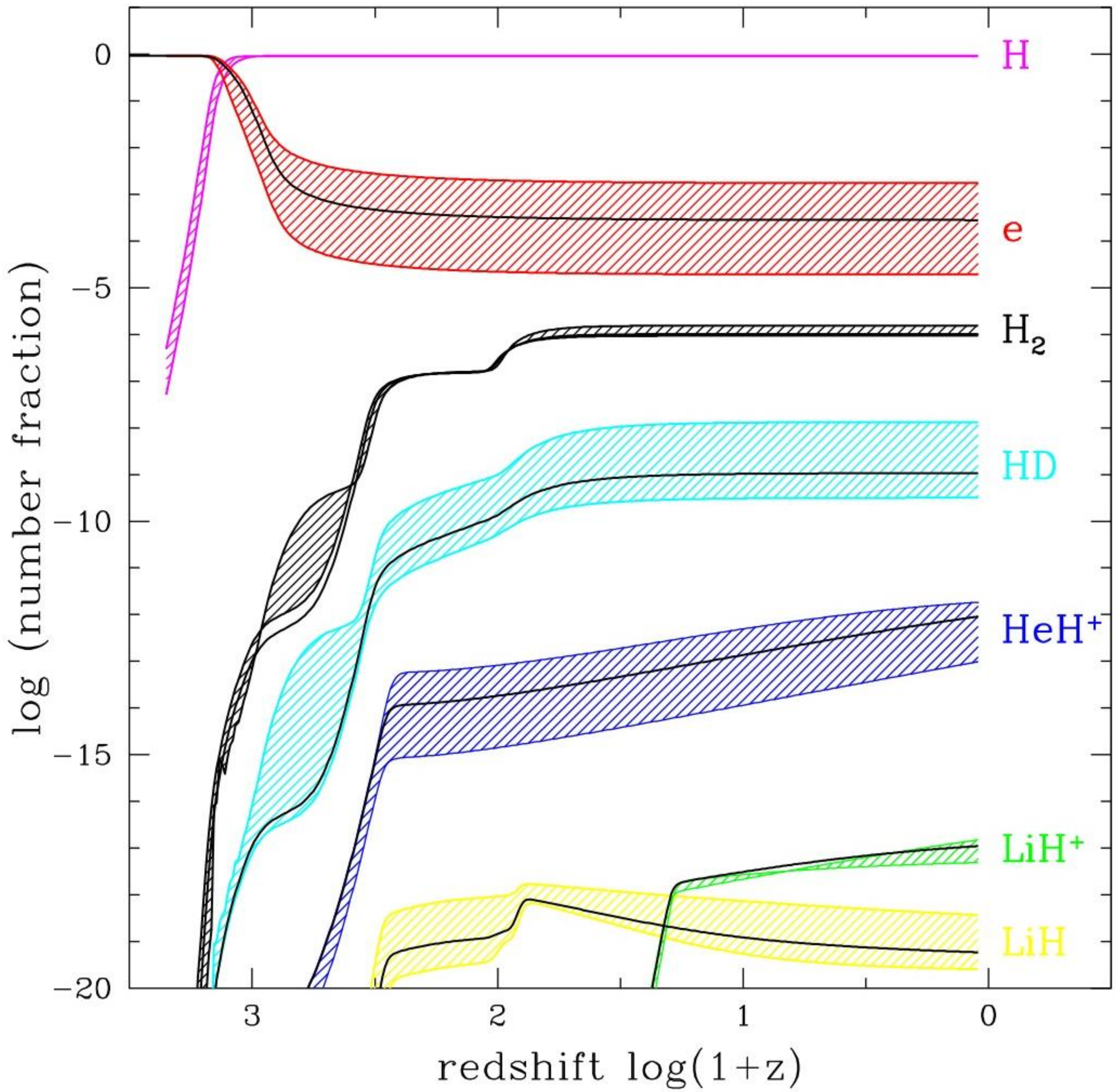
=> $X(HD) \sim (D/H) * X(H_2) \sim 10^{-10} – 10^{-9}$

Summary: evolution of chemical species in the early Universe



Galli, Palla (1998), A&A, 335, 403

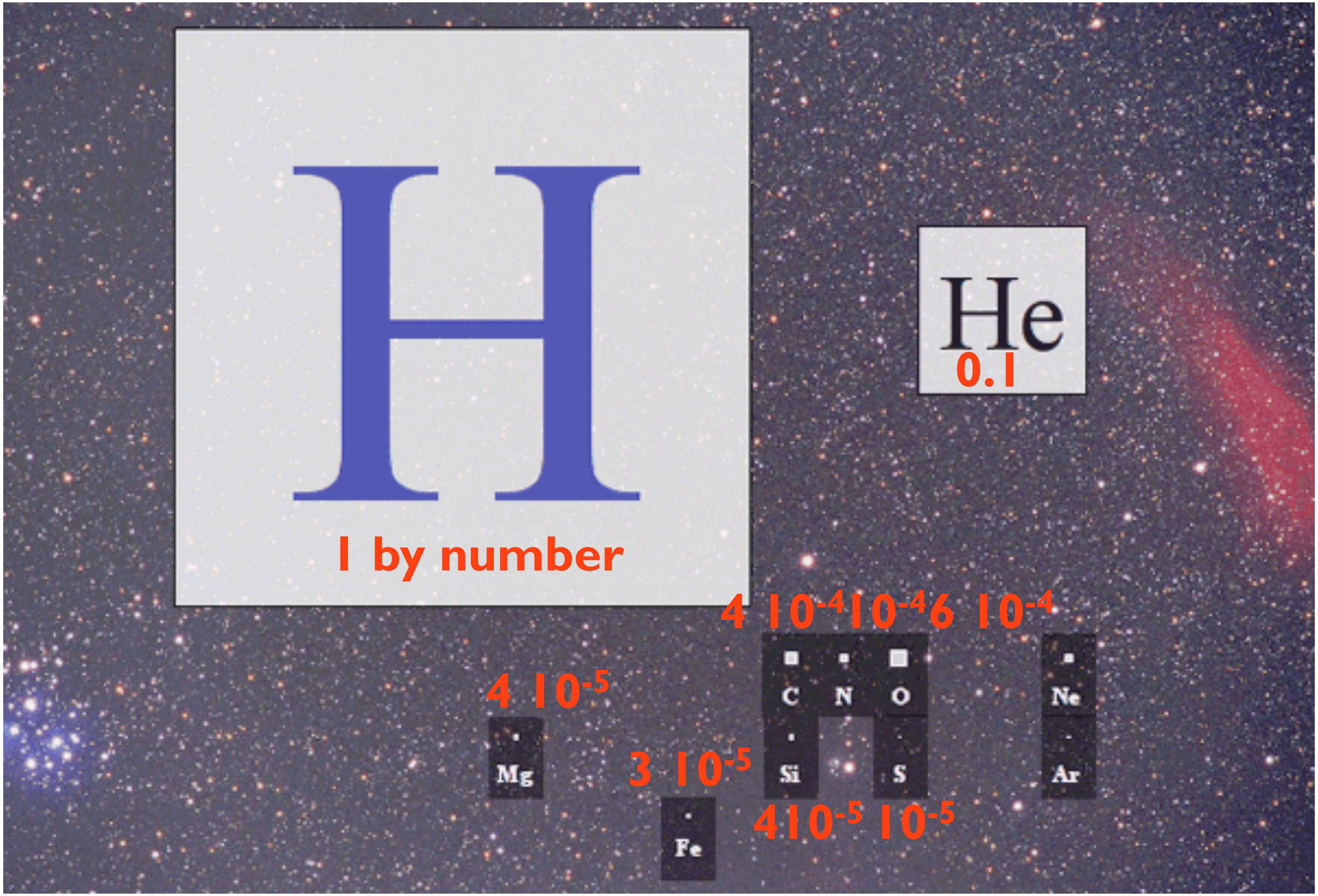
Sensetivity to cosmological parameters



E. van Dishoeck, "Master course in Astrochemistry" (2011)

"Chemistry in molecular clouds and protoplanetary disks"

Astronomer's periodic table



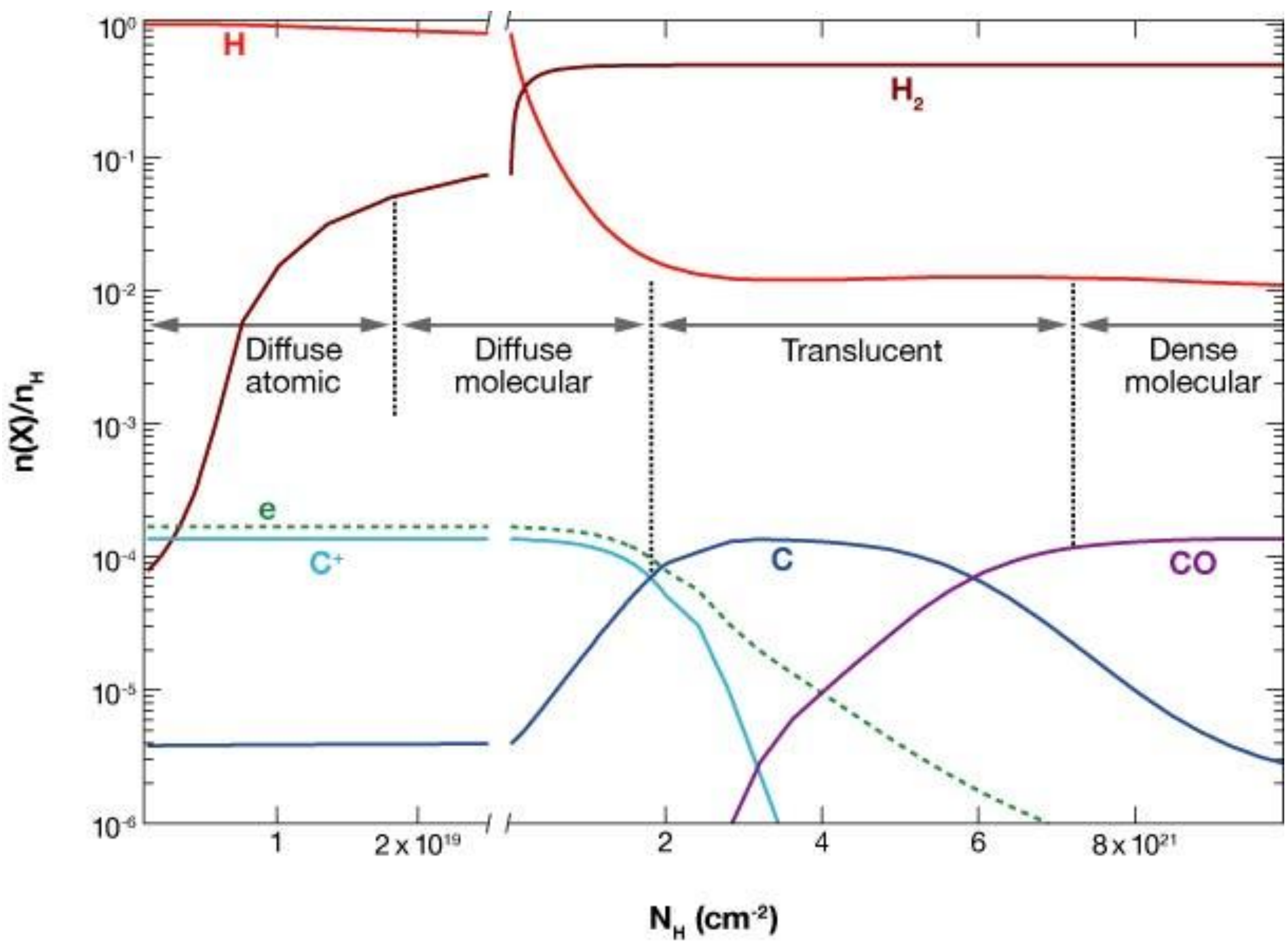
- 99% gas, 1% dust (by mass), depletion of refractory elements

McCall (2001)

Key factors in interstellar chemistry

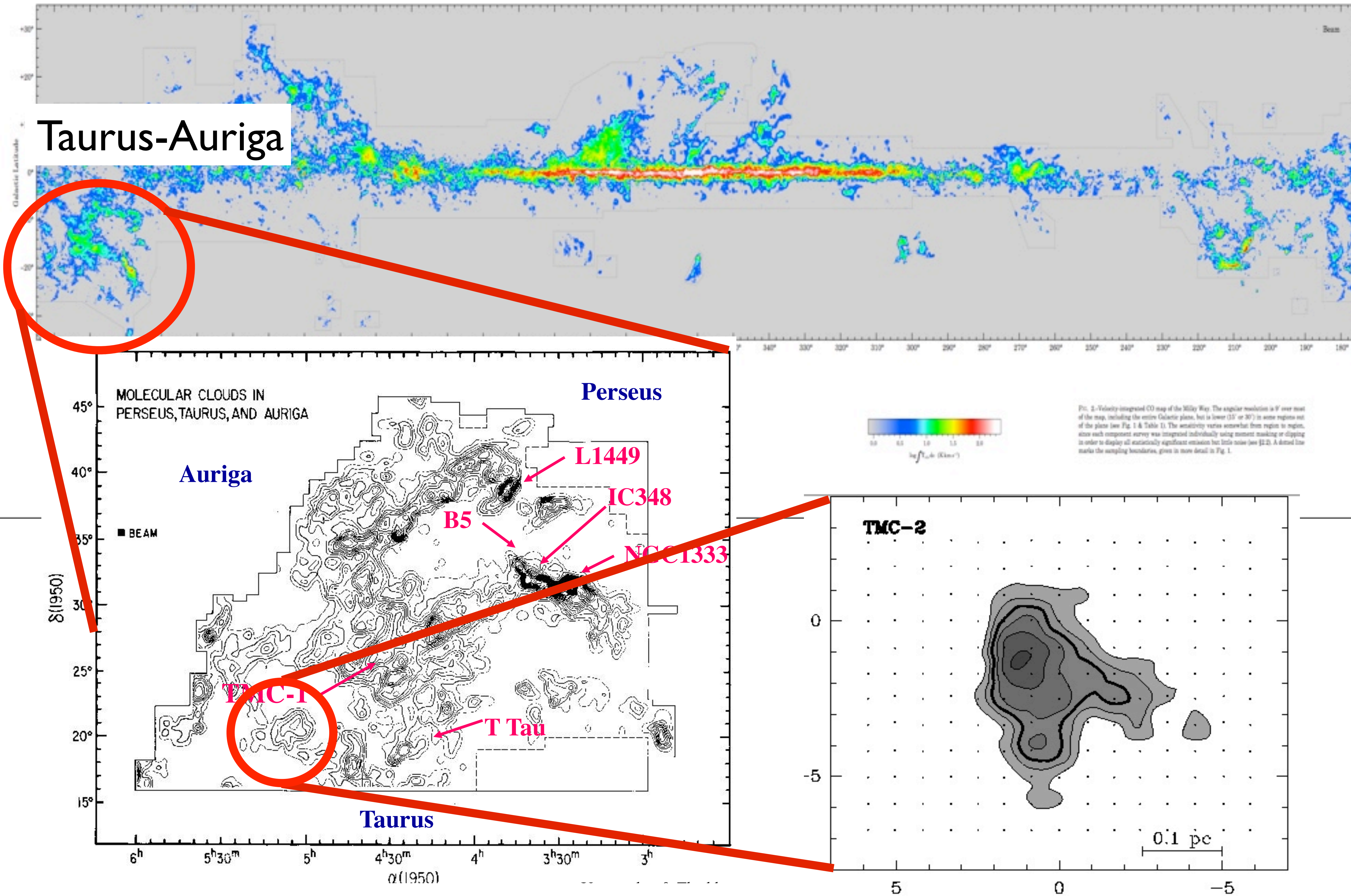
- Heavily H-dominated: X(C, O, N) < 10^{-4}
- Solar composition: C/O ~ 0.46
- In dark, dense regions:
  - Almost all C is locked in CO
  - 1/2 of O is in CO, another 1/2 of O is in H_2O
  - Almost all N is locked in N_2
- In UV-irradiated regions: C^+, S^+, O, N, H
- At T < 100 K ice mantles start to grow
- Cosmic ray ionization

Types of molecular clouds



- Diffuse clouds: T_{kin}~100 K, n ~100 cm^{-3}
- Translucent: T_{kin}~50–100 K, n ~10^2–10^3 cm^{-3}
- Dark dense clouds: T_{kin}~10–100 K, n ~10^4–10^8 cm^{-3}

CO (1-0) survey of Milky Way



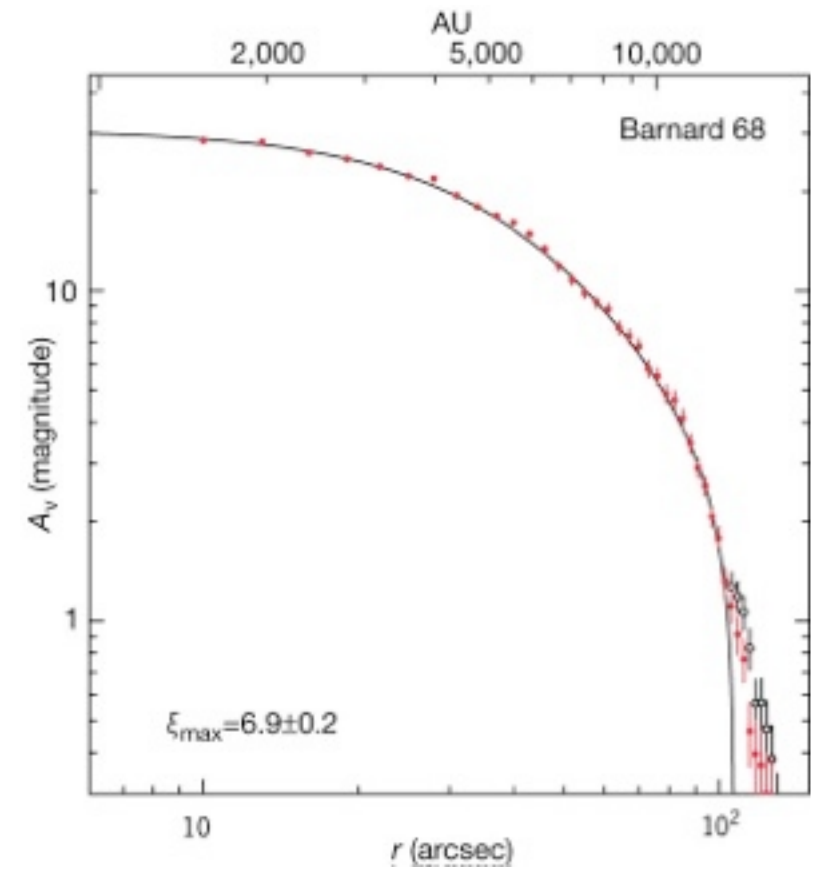
Prestellar cores

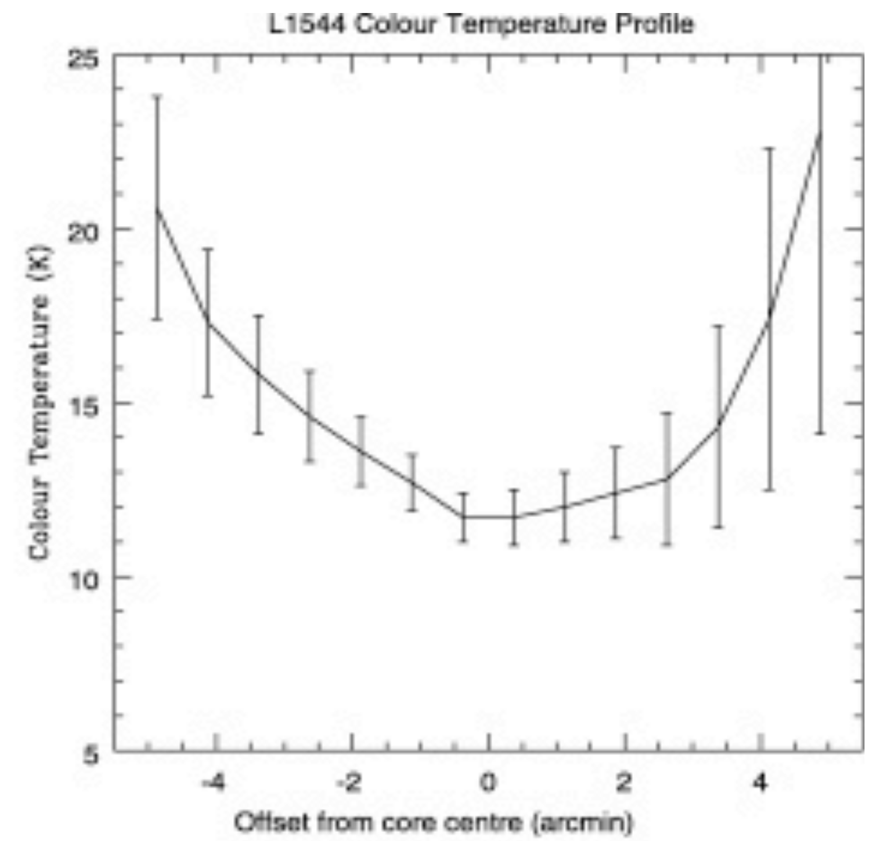
Visible

Infrared

- Typical mass ~10 – 10^3 M_{sun}, size < 1 pc, n >10^4 cm^{-3}, T ~10 K
- Dynamically "quiet", t ~ 1 – 10 Myr
- No protostars inside

General scheme: physics





- Heating: CR and UV
- Cooling: dust and molecular lines (C, CO, OH)
- Cold center, warmer outer shell
- Density profile: a quasy steady state?
- Rotation, infall, turbulence

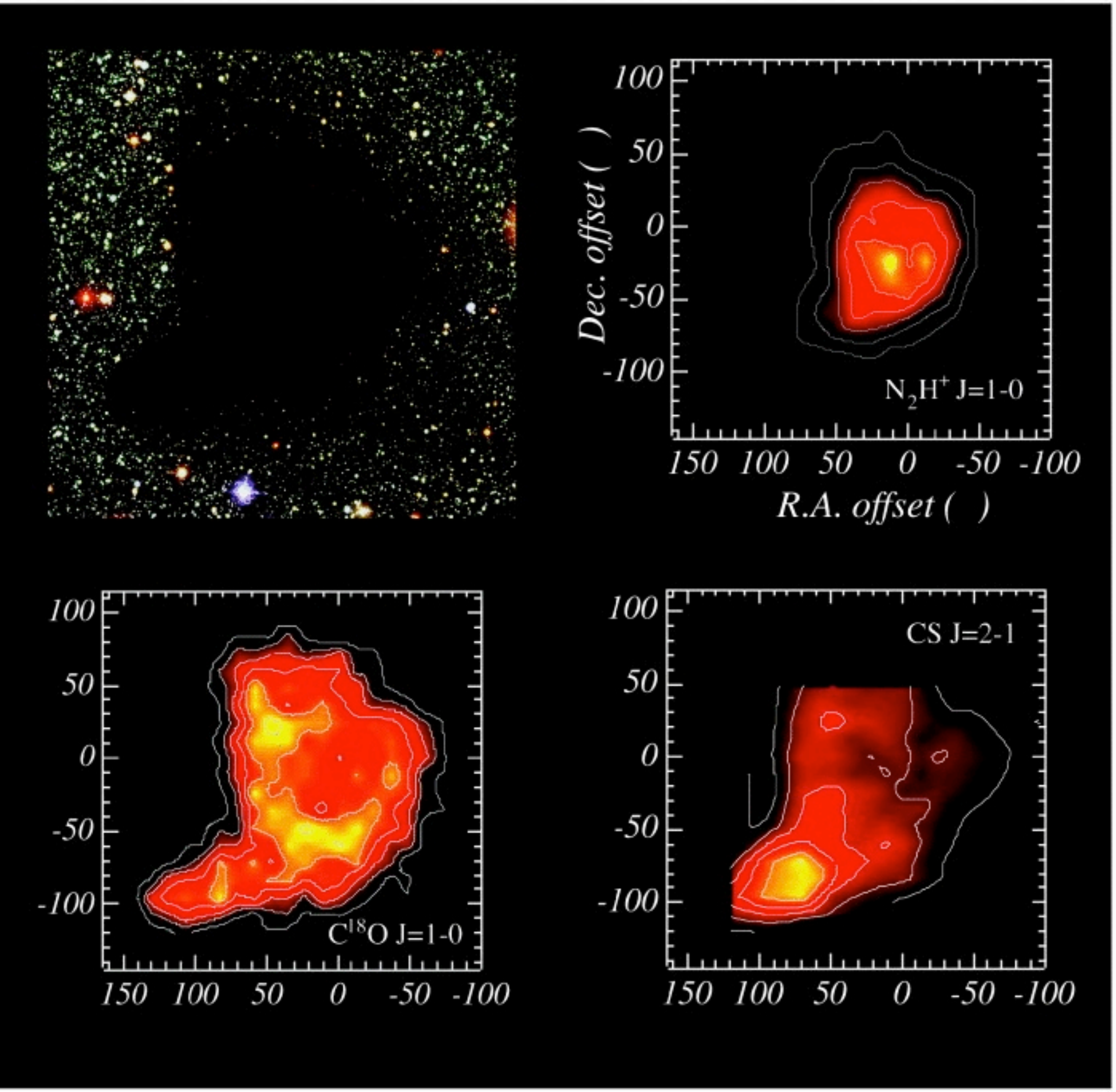
Alves et al. 2001

Molecules in dense clouds

- >1970's, "classical" source: TMC-1S or TMC-1CP
- Formation of ices: CO, CCS, CS, ...
- Non-depletion of N_2H^+ and NH_3
- Carbon chains
- Negative ions
- Deuterated species
- Simple organics: HCOOH, CH_3OH, ...

Pause

Barnard 68 cloud



- CO frozen in the center (at T < 20 K)
- There, N_2 and H_2 exist:

$H_2 + CRP \rightarrow H_2^+ + e^-$

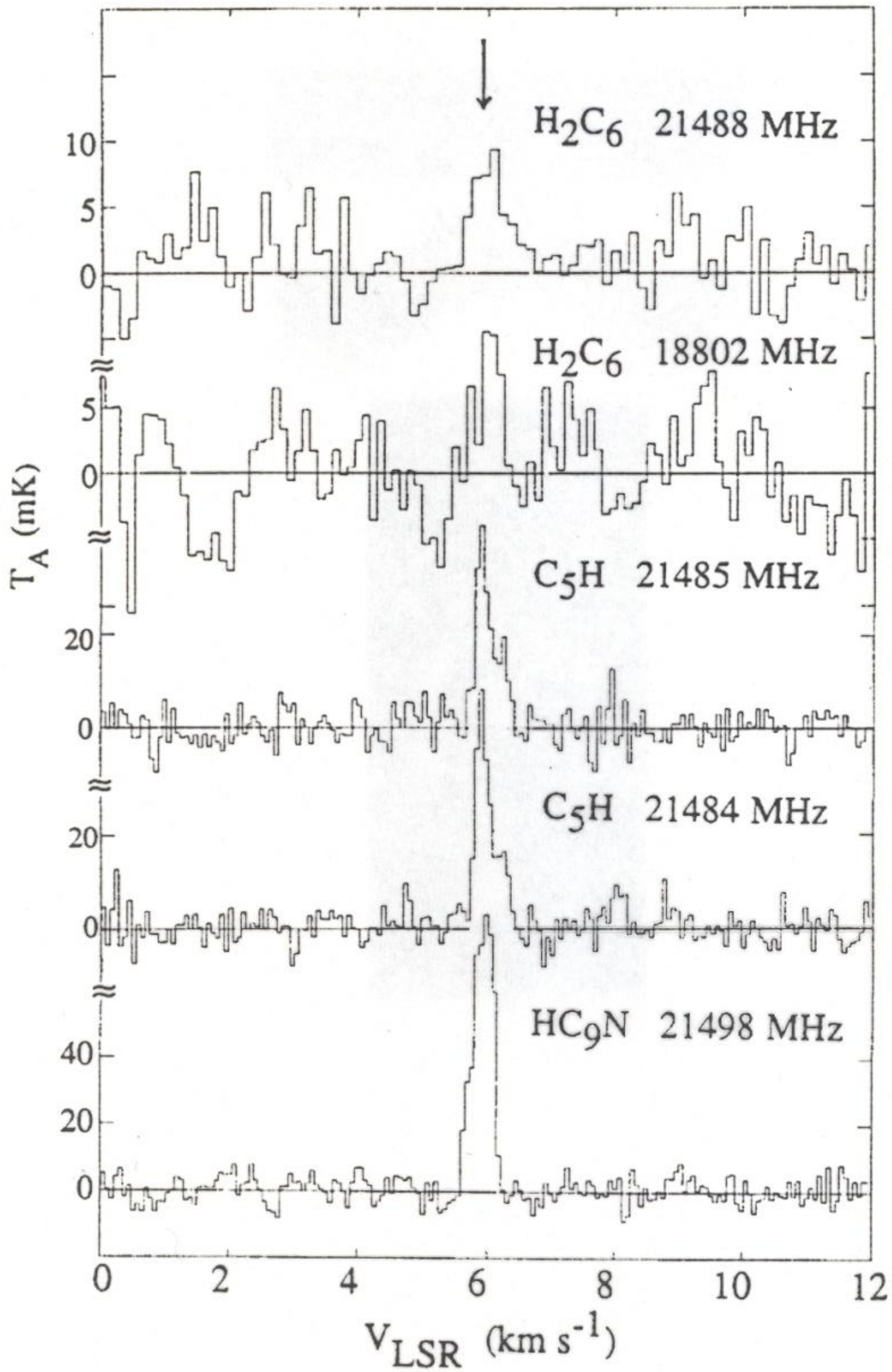
$H_2 + H_2^+ \rightarrow H_3^+ + H$

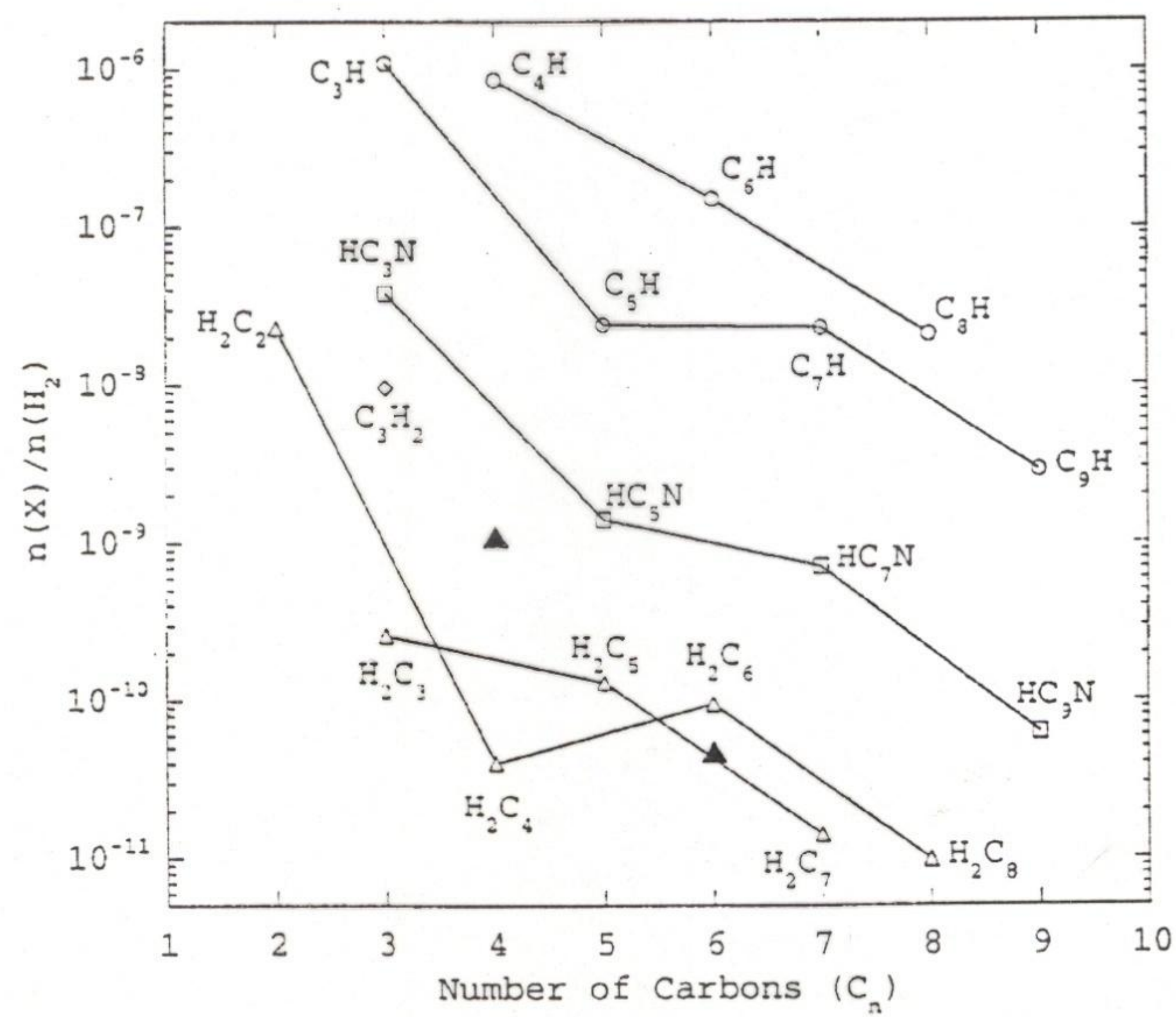
$H_3^+ + H \rightarrow N_2H^+ + H_2$

- When CO is not frozen:

$N_2H^+ + CO \rightarrow HCO^+ + N_2$

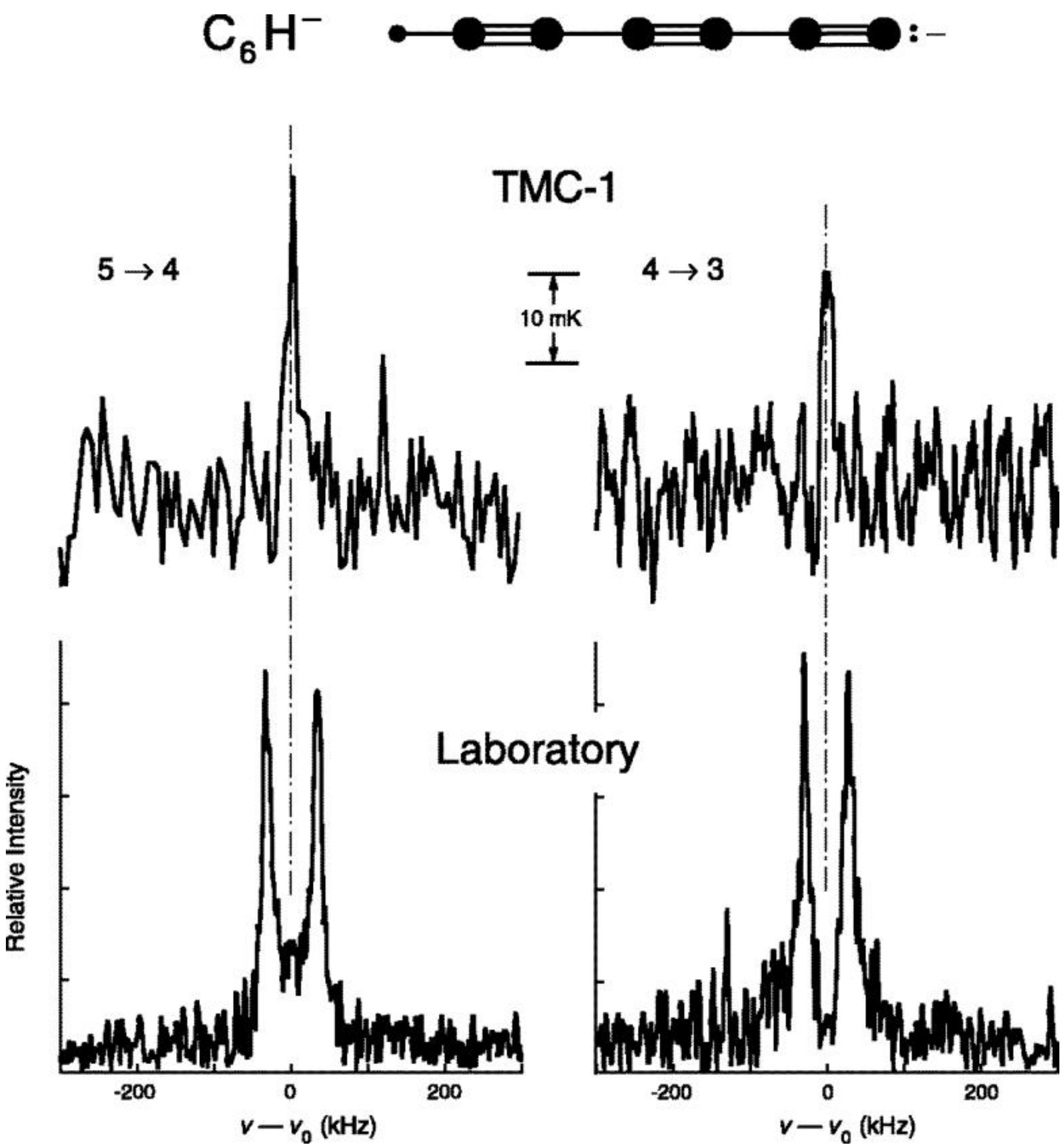
Long carbon chains in TMC-1





Langer et al. 1997

Negative ions in TMC-1



McCarthy et al. 2006

$C_6H + e^- \Rightarrow C_6H^- + h\nu$

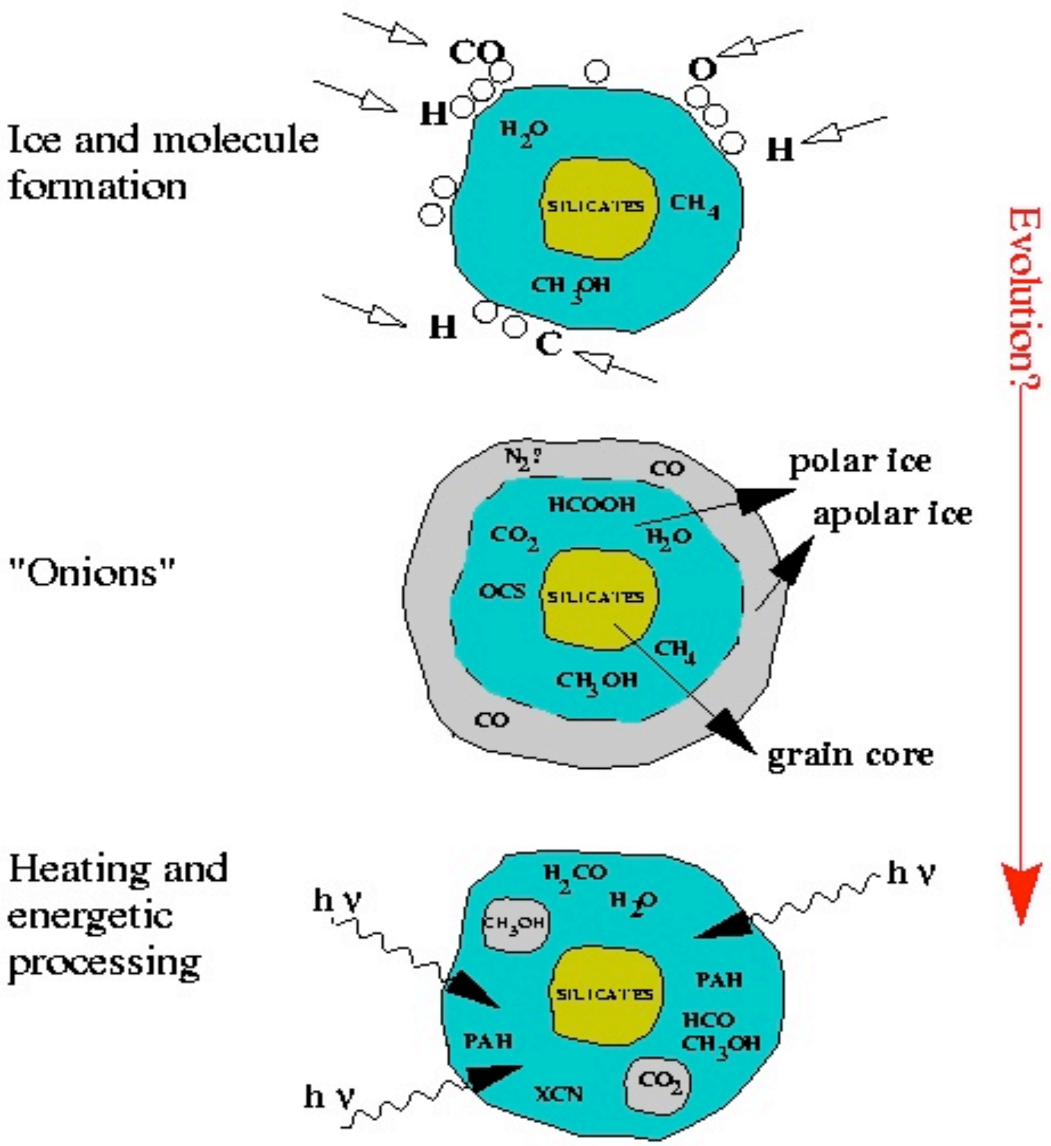
$k \approx <10^{-7}\ cm^3s^{-1}$

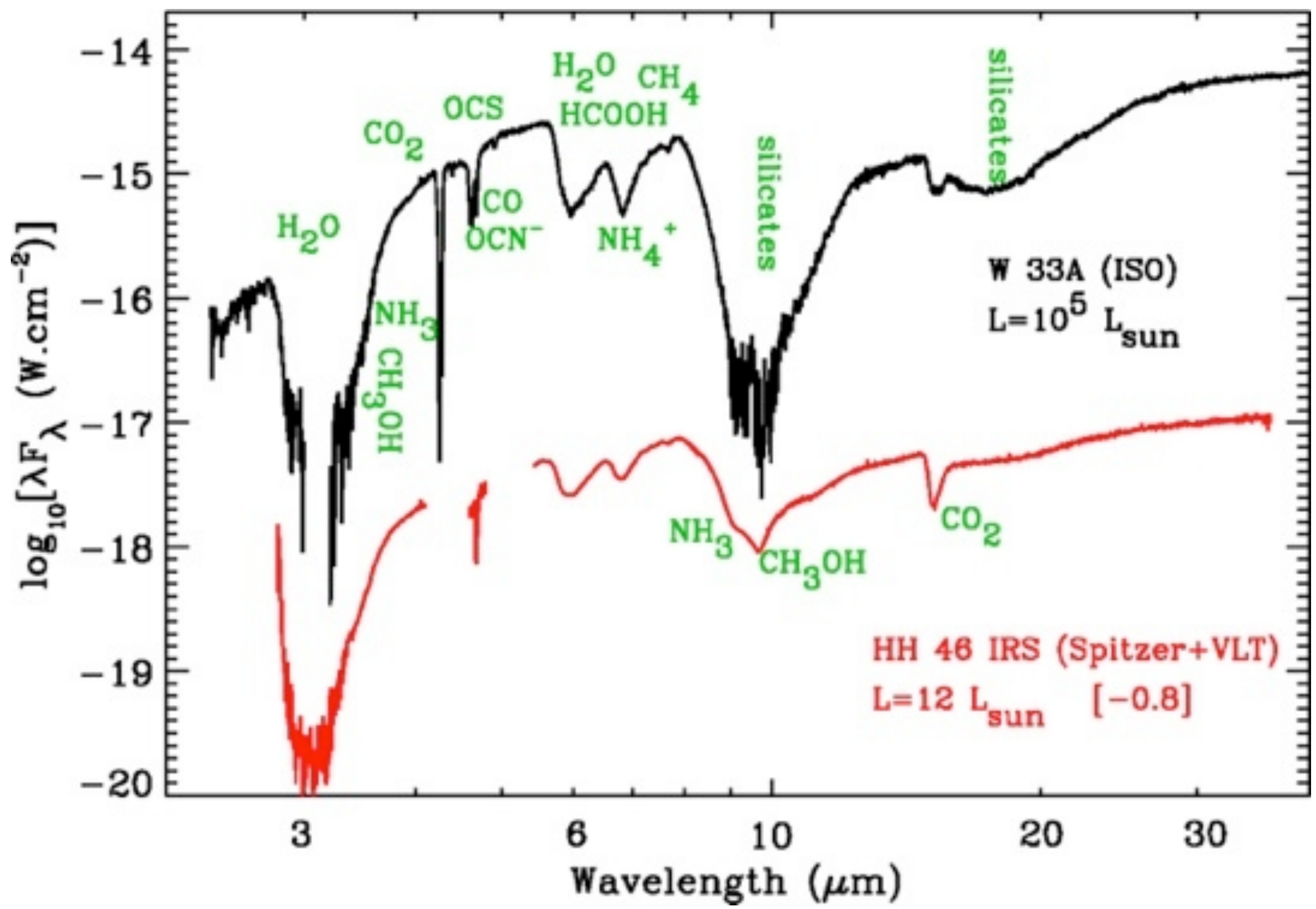
Effective for molecules with large e- affinities

<10% of anion/neutral (predicted by Herbst 1981)

Discovered in clouds with predicted abundances (McCarthy et al. 2006, Bruencken et al. 2007)

Ices in dense clouds





- Dominated by H_2O, CO, CO_2,
- Complex ices: HCOOH, CH_3OH,
- ~10–50% of heavy elements are in ices
- Up to 99% of the heavy elements may be frozen out

Oxygen chemistry

I.P. of O > 13.6 eV ⇒ oxygen mostly neutral

Ionization provided by cosmic rays:

$H_2 \Rightarrow H^+, H_2^+, H_3^+$ (rapid)

$H^+ + O \rightarrow H + O^+$ (+227 K)

$O^+ + H_2 \rightarrow OH^+ + H$

$H_3^+ + O \rightarrow OH^+ + H_2$

Once OH^+ formed, rapid ion-molecule reactions lead to OH, H_2O and O

$OH + O \rightarrow O_2 + H$

Carbon chemistry

I.P. of C < 13.6 eV ⇒ carbon mostly C^+

Initial reactions:

$C^+ + H_2 \not\rightarrow CH^+ + H$: endothermic by 0.4 eV

$C^+ + H_2 \rightarrow CH_2^+ + h\nu$ (RA, works at low T)

or $C + H_3^+ \rightarrow CH^+ + H_2$

CH^+ or CH_2^+ react with $H_2 \Rightarrow CH_3^+, CH_5^+$

Dissociative recombination leads to CH, CH_2, CH_3, CH_4

$C^+ + CH_n \Rightarrow$ carbon chains

Nitrogen chemistry

I.P. N > 13.6 eV ⇒ nitrogen mostly neutral

Nitrogen chemistry:

$N + H_3^+ \rightarrow NH_2^+ + H$ does not occur

$N^+ + H_2 \rightarrow NH^+ + H$ (barrier of ~100 K)

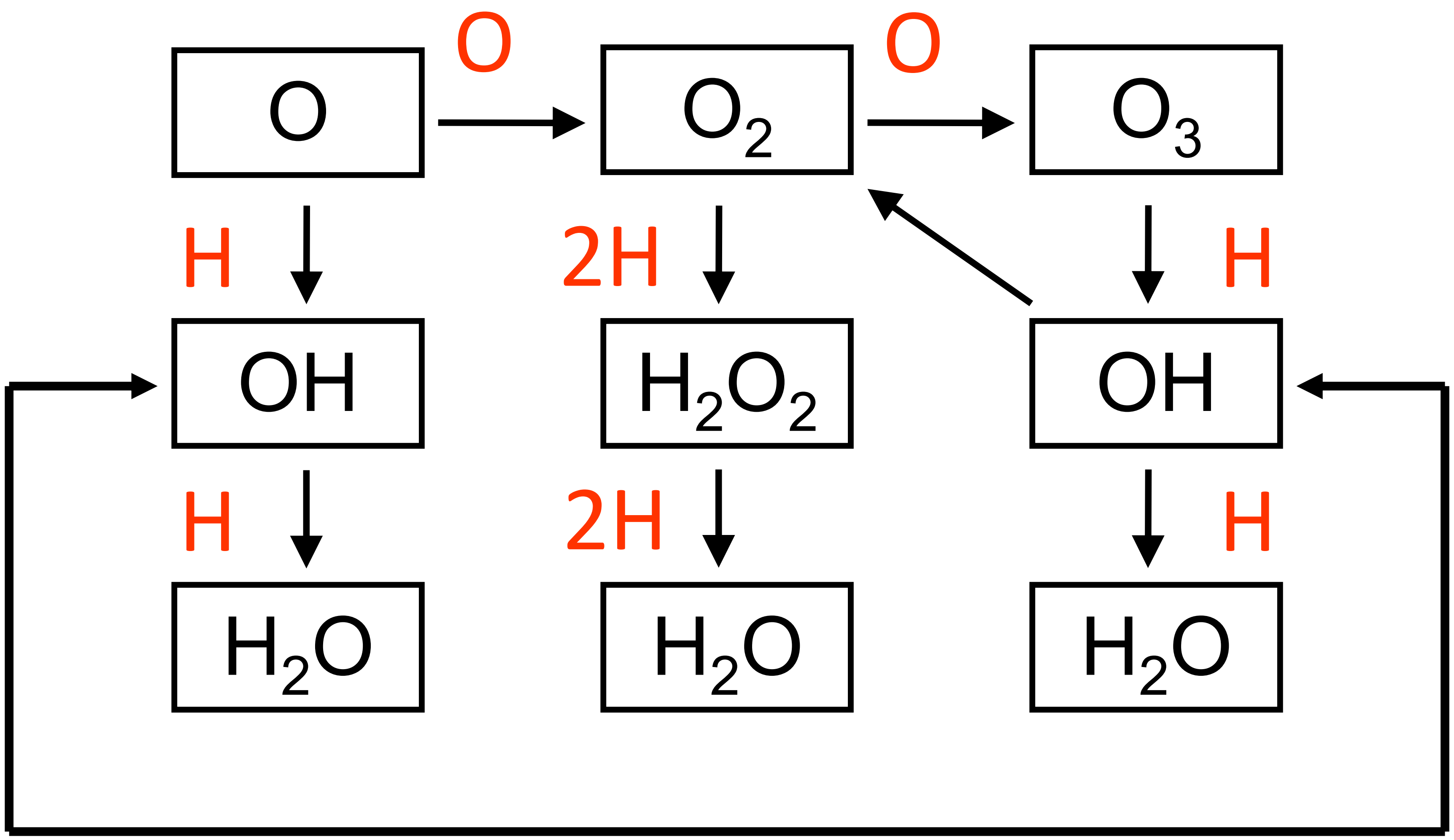
Starts with neutral-neutral chemistry linked to carbon:

$CH, C_2 + N \rightarrow CN + H, C$

$CH_3^+ + N \rightarrow H_2CN^+ + H$

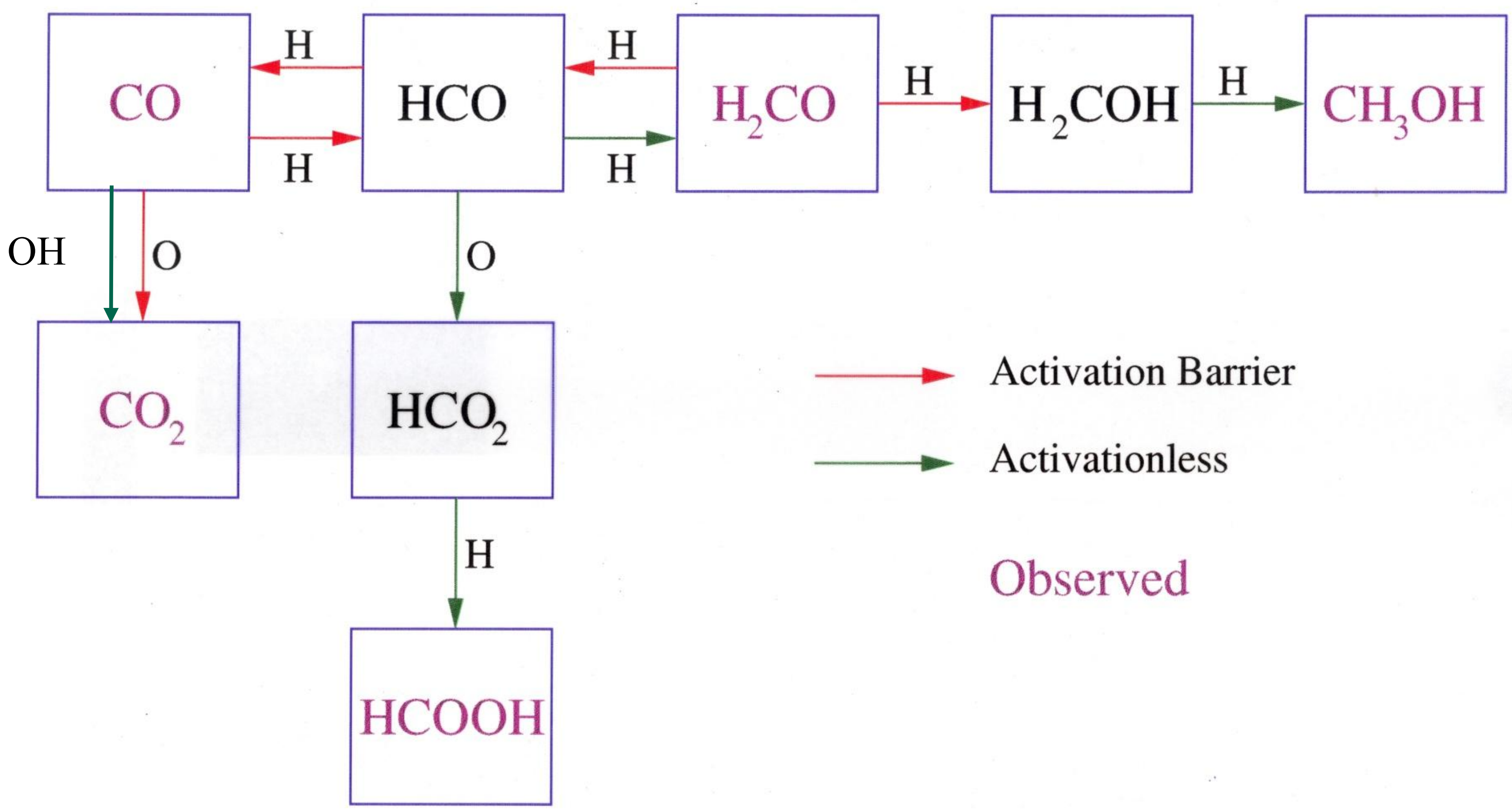
$H_2CN^+ + e \rightarrow HCN$ or $HNC + H$ or $CN + H_2$

Surface chemistry: O

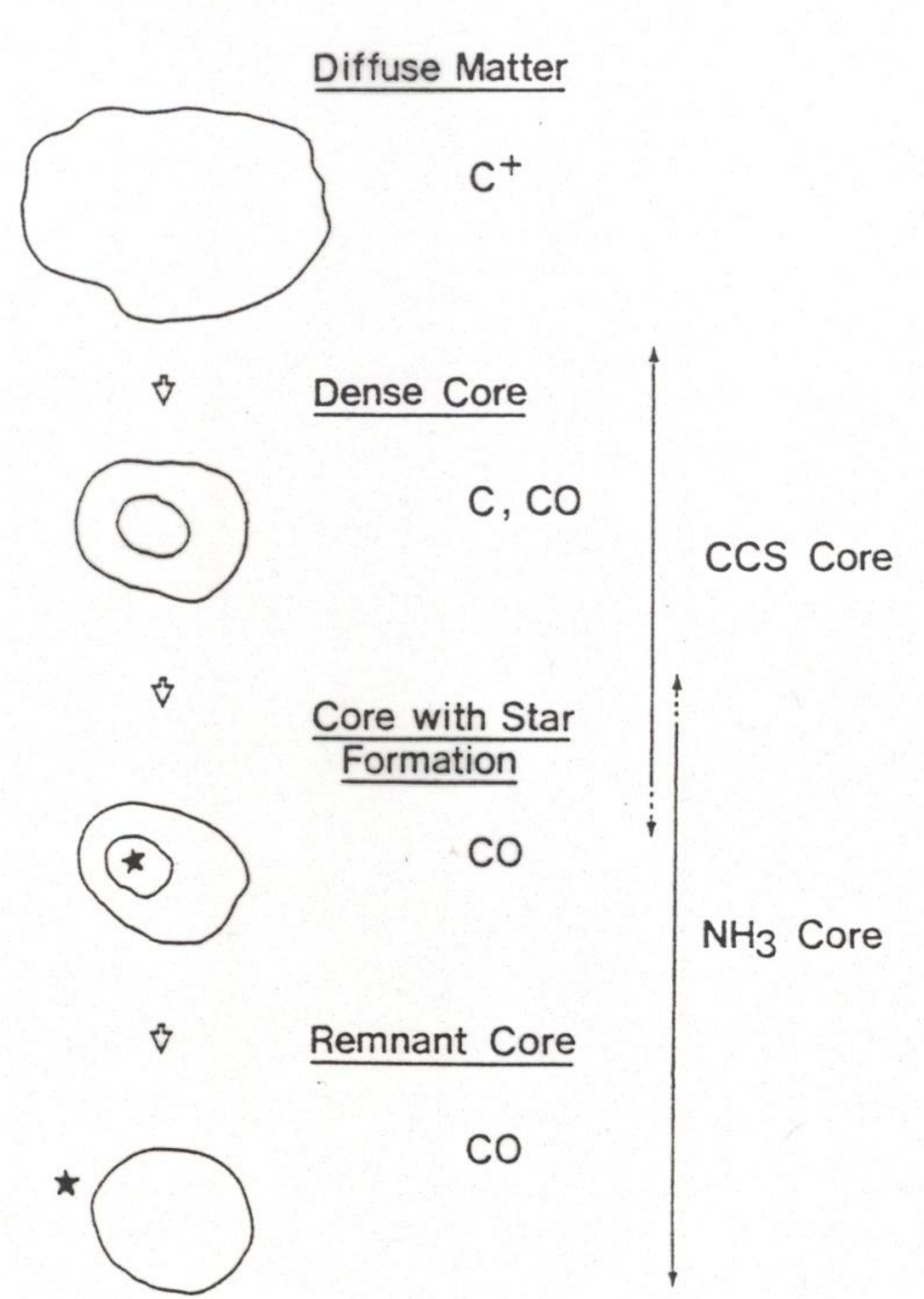


Tielens & Hagen 1982

Surface chemistry: CO



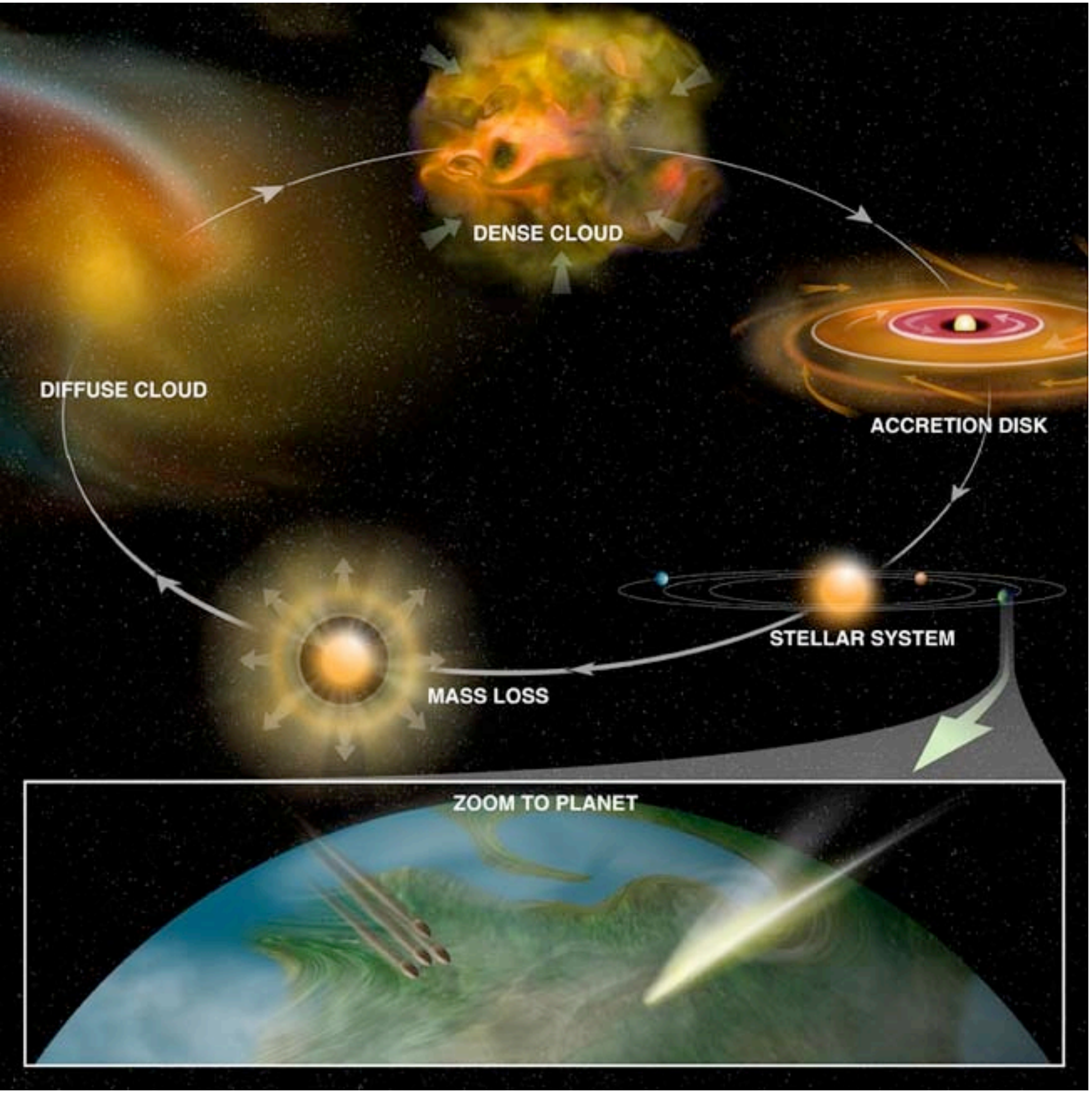
General scheme: chemistry



- Dense core: C^+ is converted to C and CO
- Early times: CCS and HC_nN are abundant
- Late times: N_2H^+, H_2D^+, NH_3, CO is absent in the center
- CCS traces outer shell, NH_3 traces central region

Suzuki et al. 1992

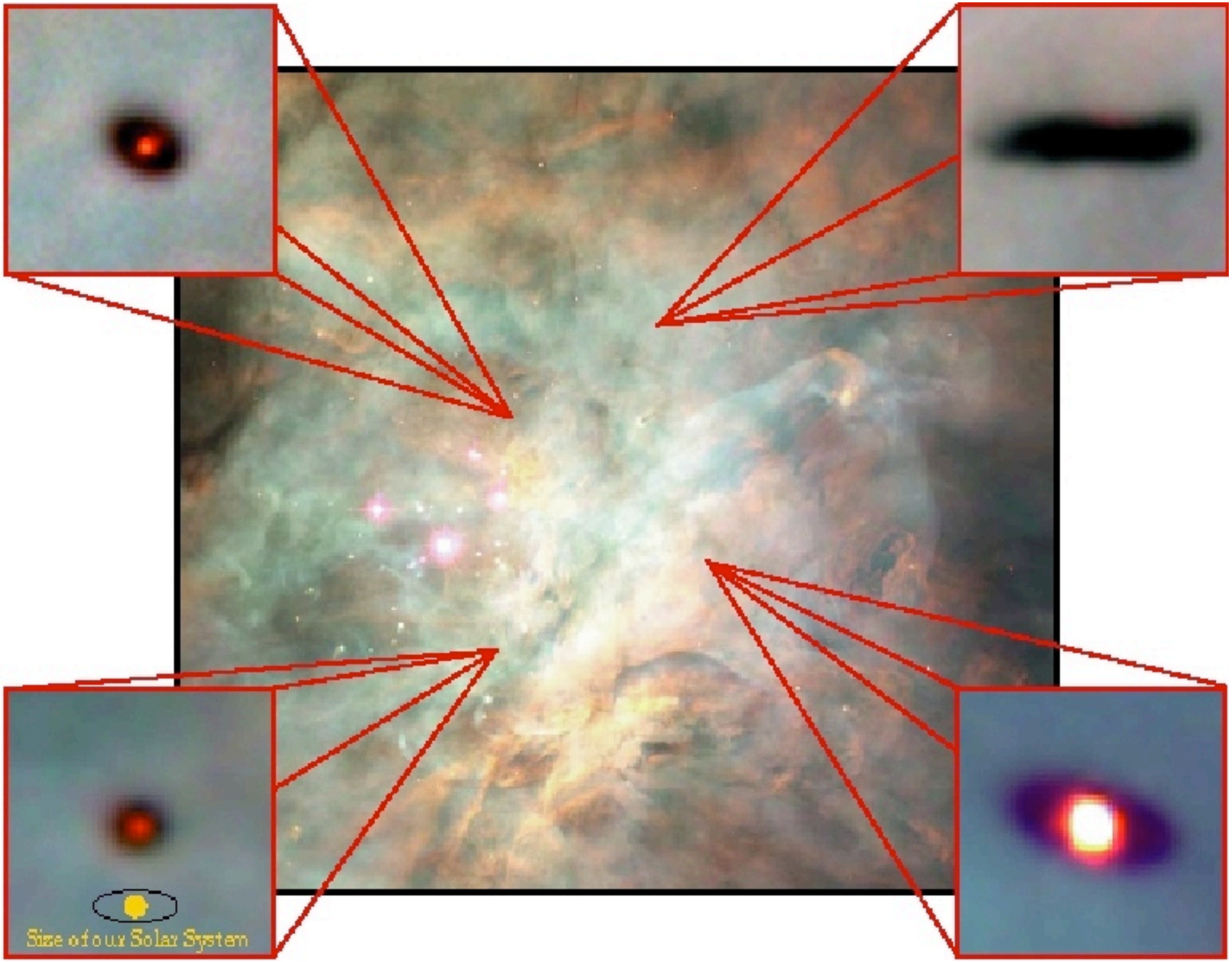
"Chemistry in protoplanetary disks"



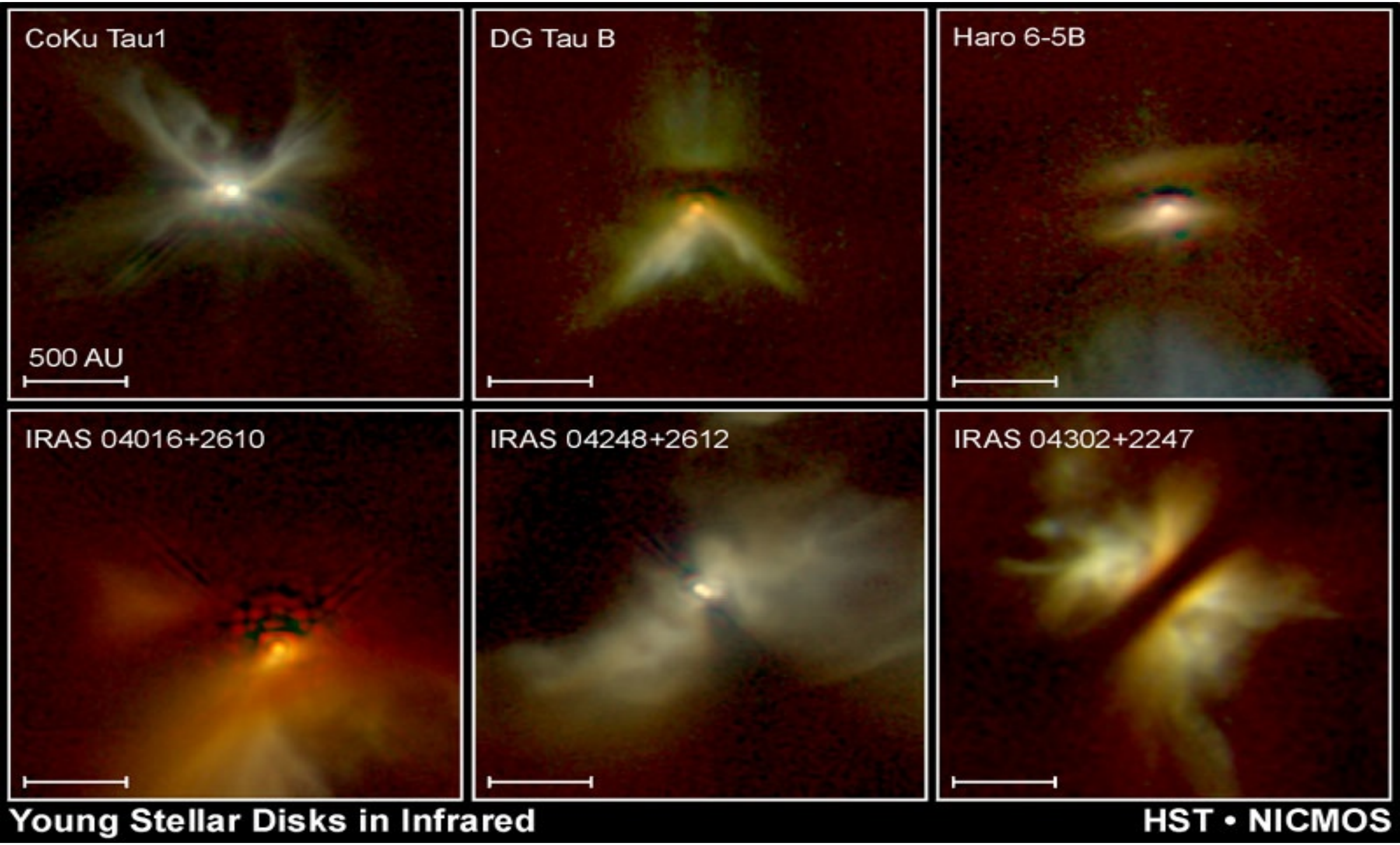
- Planet formation
- Comets and asteroids
- Primordial chemistry
- Organic molecules

Credit: Bill Saxton, NRAO/AUI/NSF

Protoplanetary disks in Orion: optics, Hubble

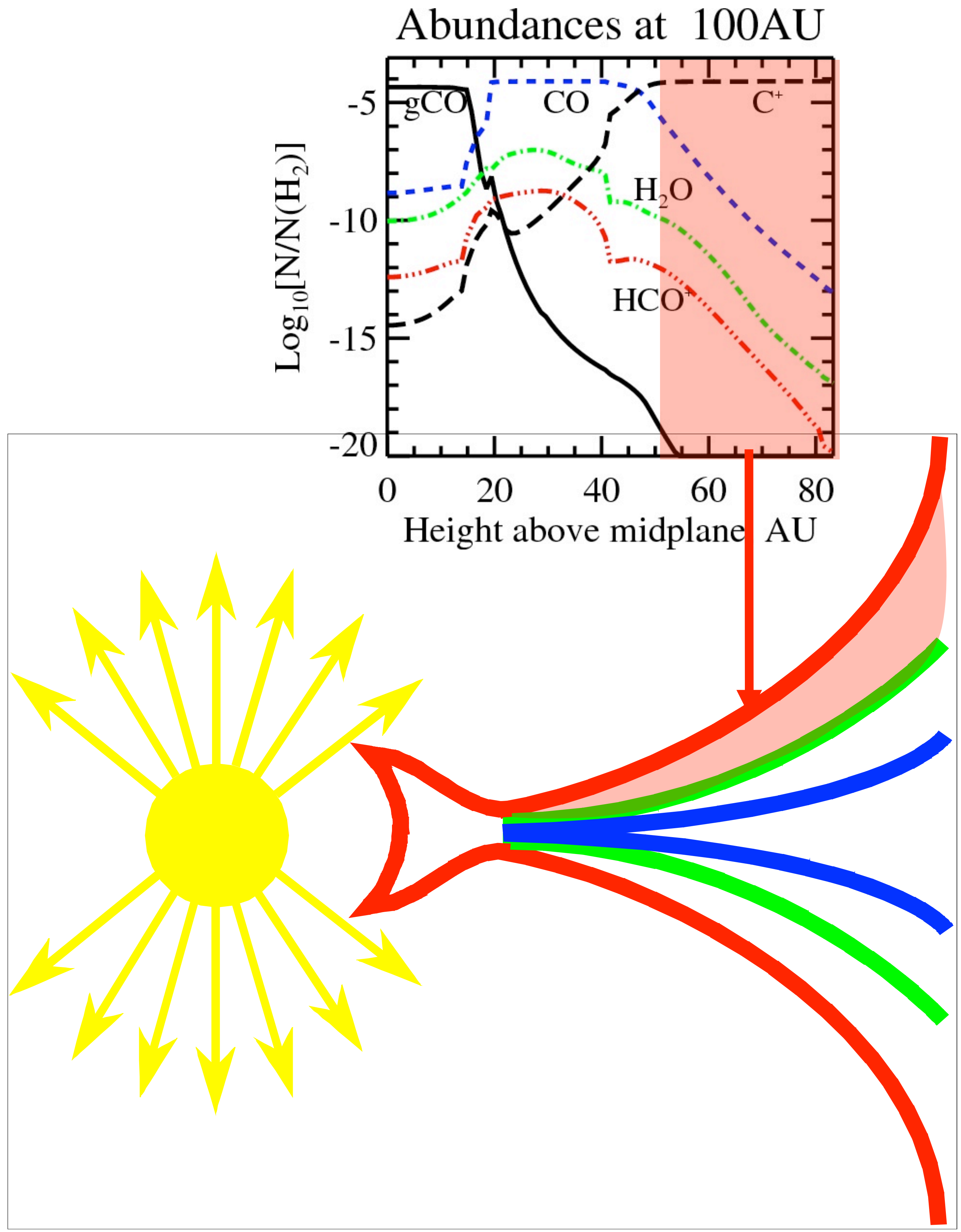


Young protoplanetary disks in Taurus



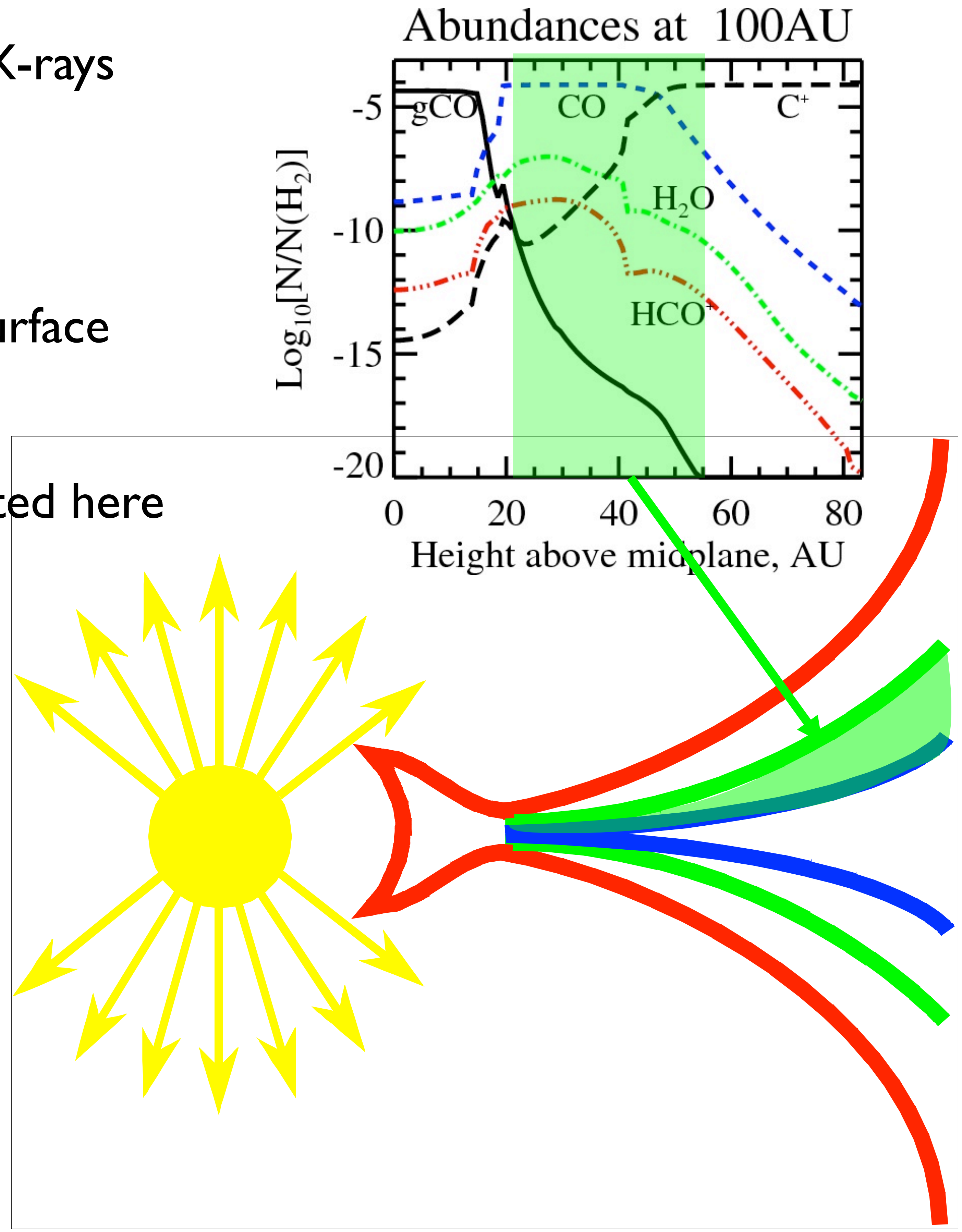
Zone of ions and radicals (atmosphere)

- Intense UV and X-rays
- Low densities
- High temperatures
- High ionization degree
- Limited gas-phase chemistry



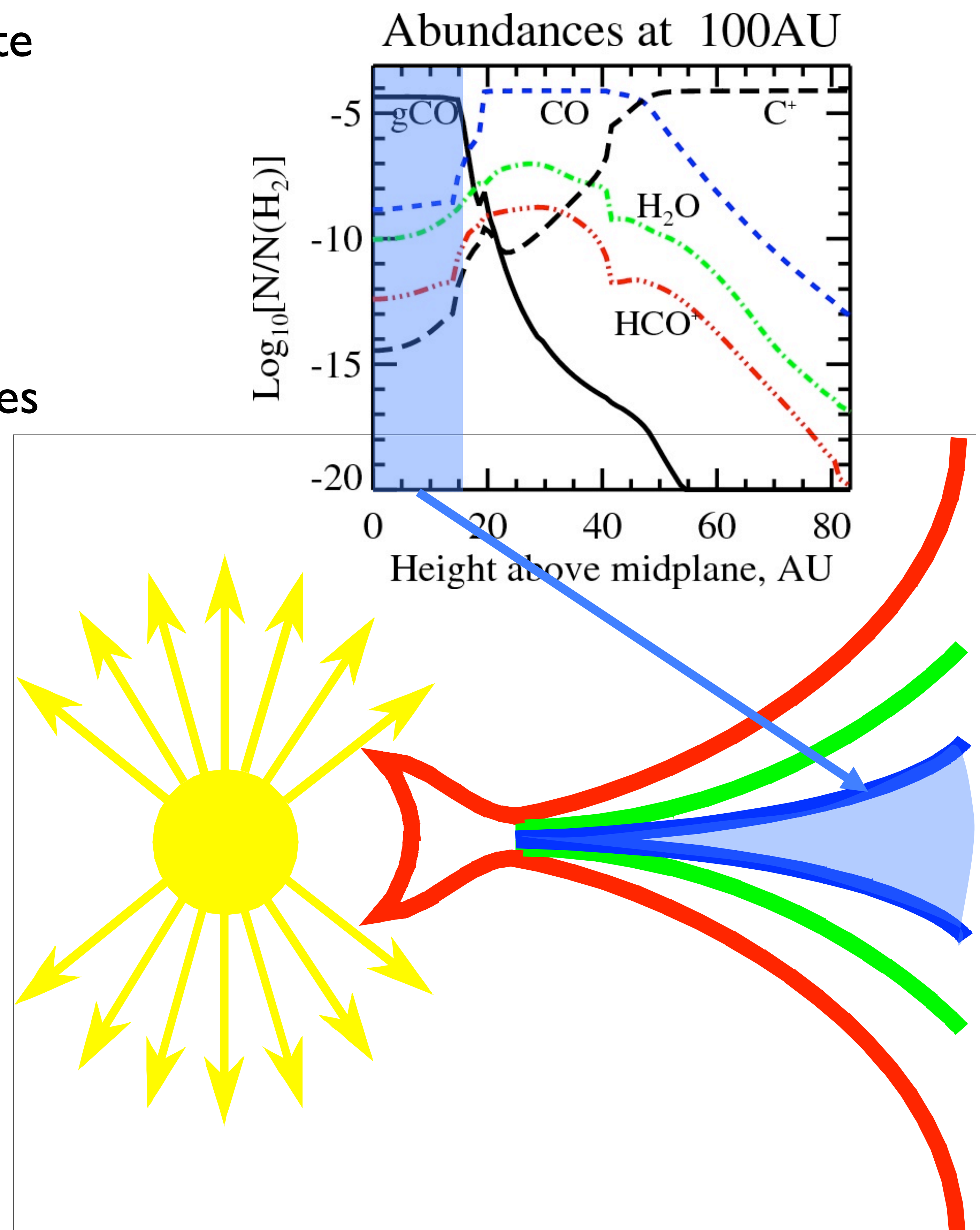
Zone of molecules (intermediate layer)

- Partly shielded from UV and X-rays
- Moderate densities
- Moderate temperatures
- Oasis of rich chemistry: gas-surface cycling, photoprocessing of ices
- Most molecular lines are excited here



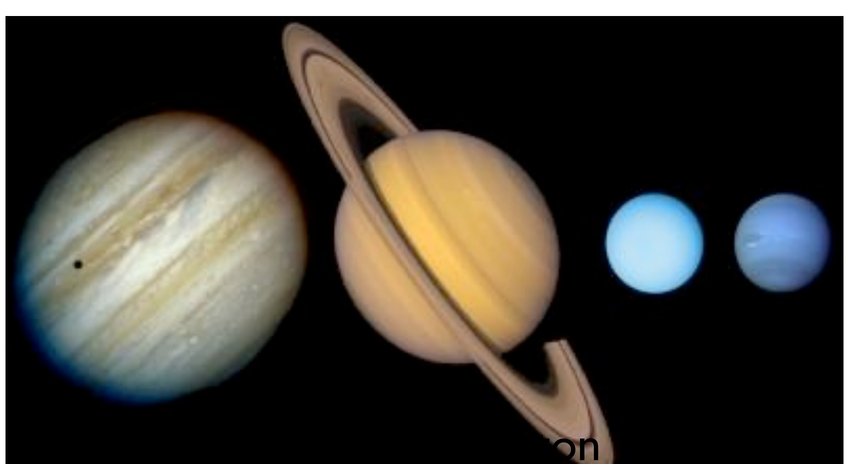
Zone of ices (midplane)

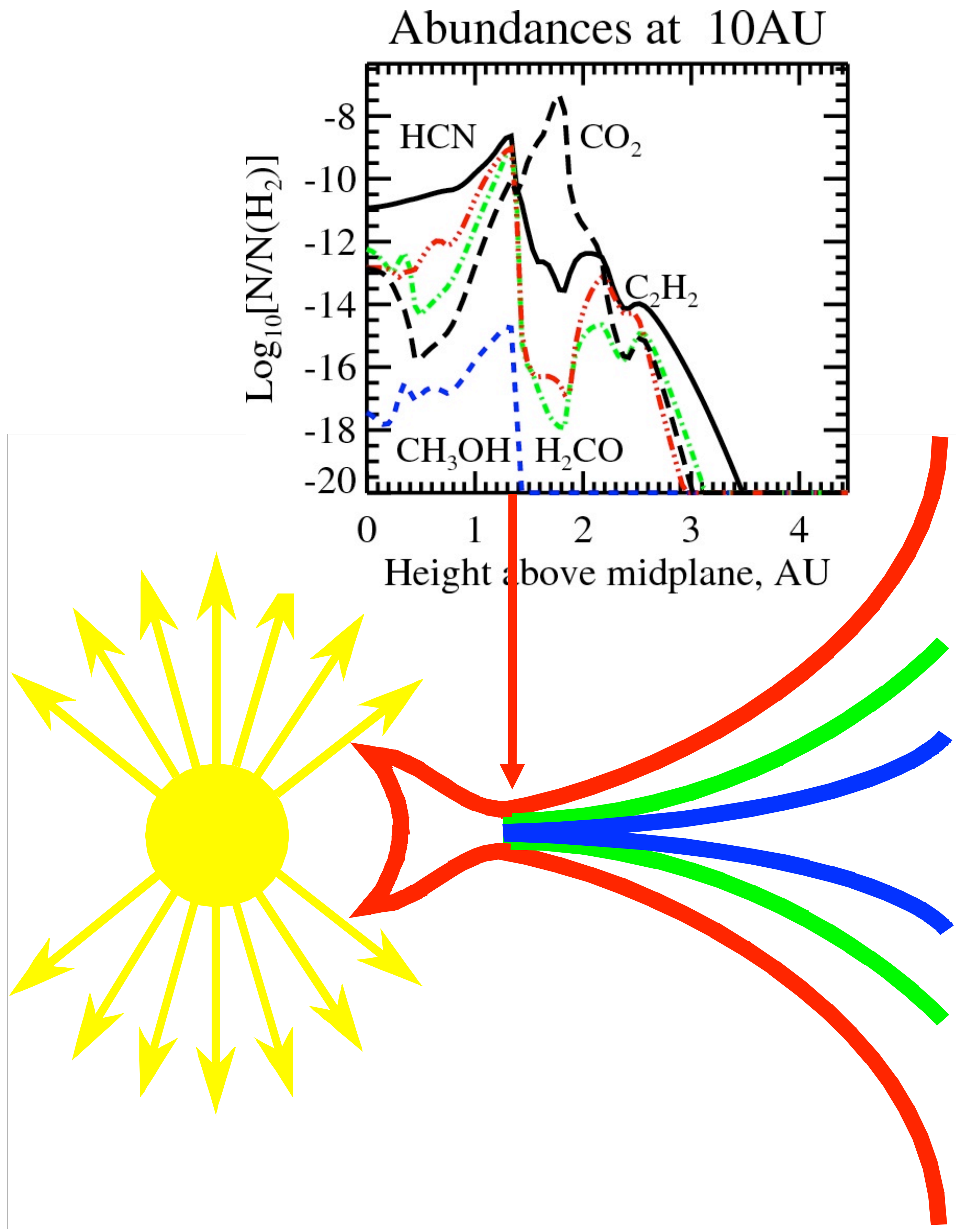
- Only cosmic rays can penetrate
- High densities
- Low temperatures
- Molecules are frozen out
- Rich chemistry on dust surfaces



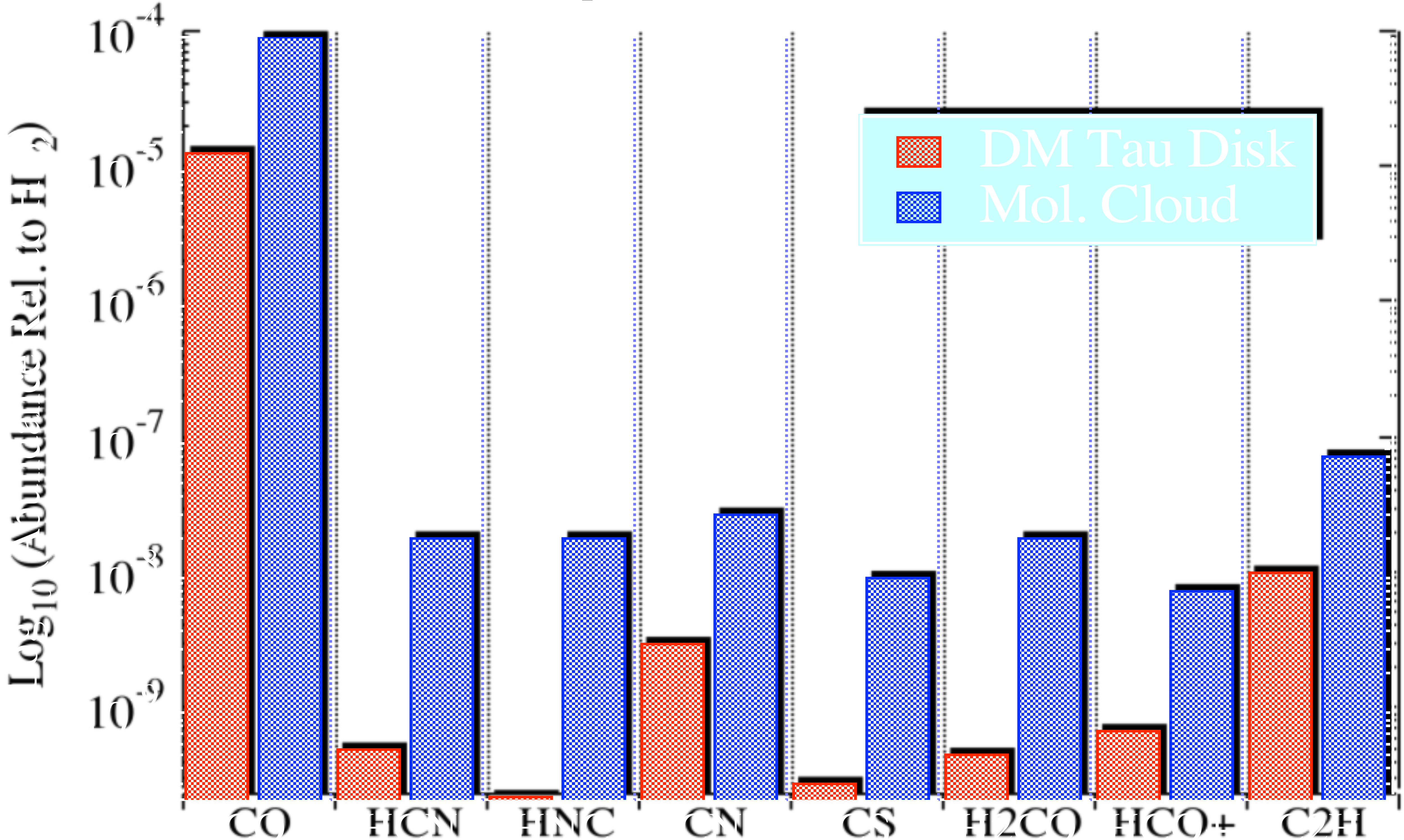
Inner, planet-forming zone

- High n, T
- Reactions with barriers
- 3-body collisions
- X-ray-driven processes
- No freeze-out
- Fast grain evolution





Chemical composition: disks vs clouds



- Strong depletion of gas-phase molecules
- Freeze-out & UV dissociation

Observations vs predictions: DM Tau

Species	Observed column density, cm^{-2}	Modeled column density, cm^{-2}
CO	3.0 (17)	3.0 (17)
HCO^+	1.7 (13)	8 (12)
H_2CO	1-2 (13)	6.2 (12)
N_2H^+	4 (11)	3.4 (11)
CS	4 (12)	8.1 (10)
CN	4 (13)	1.4 (13)
HCN	8 (12)	1.2 (13)
HNC	3 (12)	1.0 (13)
CCH	3 (13)	1.1 (13)
Agreement		7/8

- Agreement with molecules in outer disk
- Agreement with cometary ices (inner Solar nebula)

Takeaway message

- Layered chemical structure
- Depletion of gaseous molecules: UV + freeze-out
- Large observational & modeling programs
- Models qualitatively agree with observations
- Different chemistry in Herbig Ae and T Tauri disks?