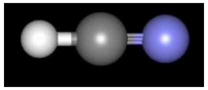

Astrochemistry
Lecture 3

Chemistry in the Early Universe

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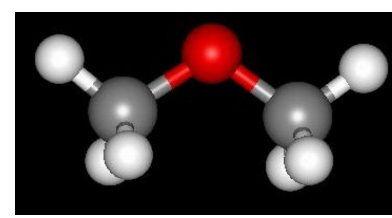
Leiden Observatory

May-June 2022

Literature:
Galli & Palla 2013, ARA&A (GP13)



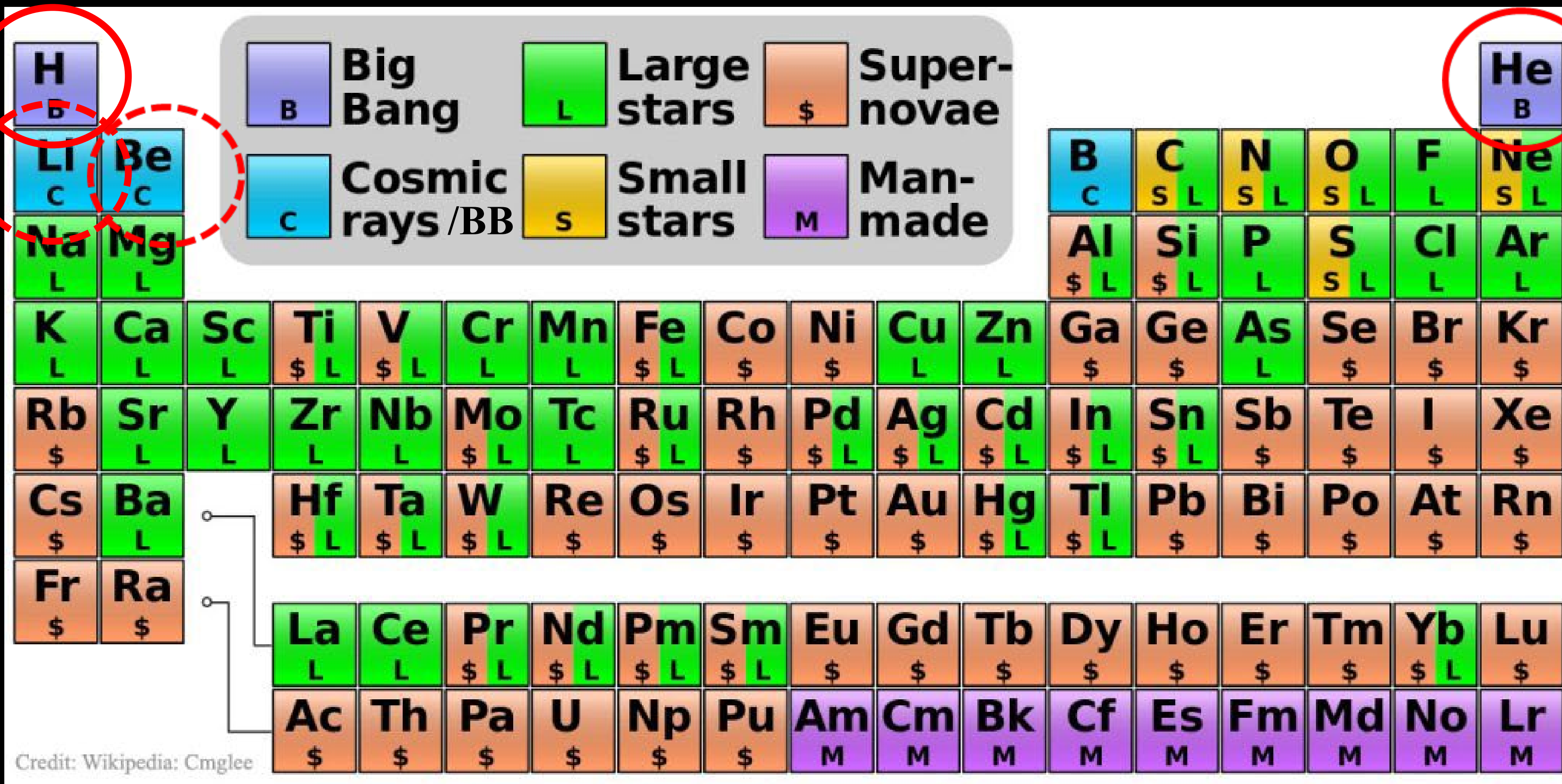
Outline

- Introduction to cosmology
- Chemistry in the early universe
- Model results
- Molecular cooling and cloud collapse
- Observations of molecules at $z<7$

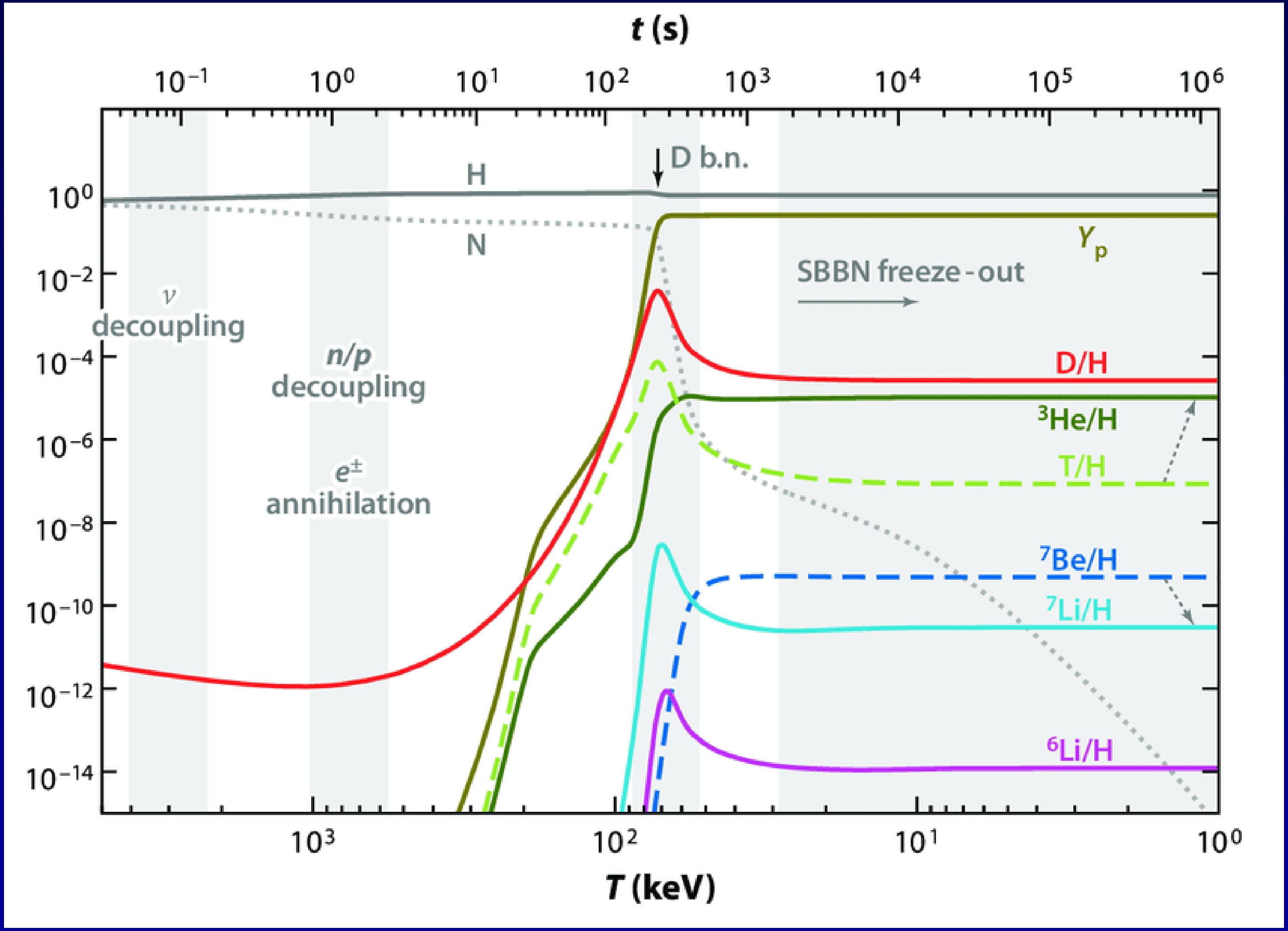
3.1 Introduction

- Chemistry in the early universe is interesting because
  - Chemistry is simple: only H, D, He, Li, ***no*** dust
  - First molecules may have had profound effects on the thermal properties of matter due to their cooling => collapse and fragmentation
  - Atoms and molecules observed in high-z galaxies can be used to probe physical conditions in interstellar and intergalactic medium
    - Note: the first molecules which formed around the era of recombination (z~1300) are not directly observable

Origin elements



Expansion: abundances 'frozen in' after first few minutes



wikipedia

3.2 Intro to cosmology

- Consider the ‘standard’ Big-Bang model (dd. 1990)

Era	**Time (s)**	***T* (K)**
Lepton	10^{-4}	10^{12}
Radiation-dominated	2	10^{10}
Matter-dominated	10^{11}-10^{12}	4000
Present	10^{18}	2.7 (CBR)

Cosmology (cont'd)

- Radiation temperature: $T_R \propto (1+z)$

- Density: $$n_b = \frac{\Omega_b \rho_{cr}}{\mu m_H}(1+z)^3$$

$$\rho_{cr} = \frac{3H_0^{\,2}}{8\pi G}$$

z=redshift

Ω_b=baryon mass density parameter

H_0=current expansion rate of universe in km s^{-1} Mpc^{-1}
'Hubble parameter'

- Note: cosmological parameters recently updated but basic conclusions unchanged

$$\boldsymbol{n_b \approx 2.2\mathrm{x}10^{-7}\,(1+z)^3 \quad \mathrm{cm}^{-3}}$$

Cosmology (cont'd)

- Composition of baryonic matter determined by nuclear processes in radiation-dominated or nuclear era

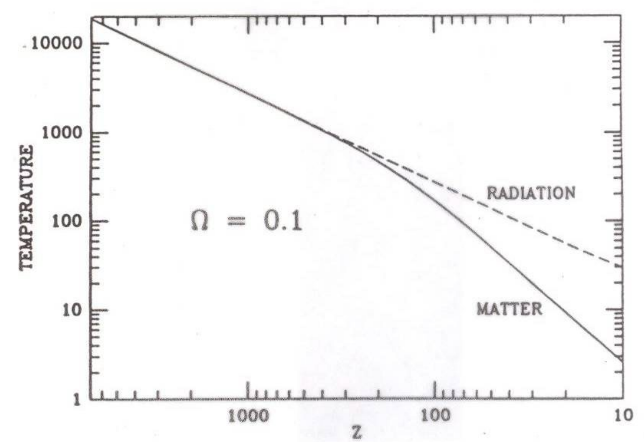
  H : D : ^{4}He : ^{3}He : ^{7}Li

  1 : 2.6×10^{-5} : 8×10^{-2} : 10^{-5} : 5×10^{-10}
- At end of nuclear era, all atoms fully ionized => all H in H^+, all He in He^{2+}, etc.
  - $H + h\nu \rightarrow H^+ + e$
  - $H^+ + e \rightarrow H + h\nu$ with rate k_{rec}
- Temperature of matter T_m is equal to T_R due to (elastic) Thompson scattering of photons with electrons
- Because $k_{rec} \propto T_m^{-0.61}$, recombination becomes more important as universe cools:
  - $f(H^+)=f(H)$ at z=1340 when $T_R=T_m$=3630 K (for old cosmology)

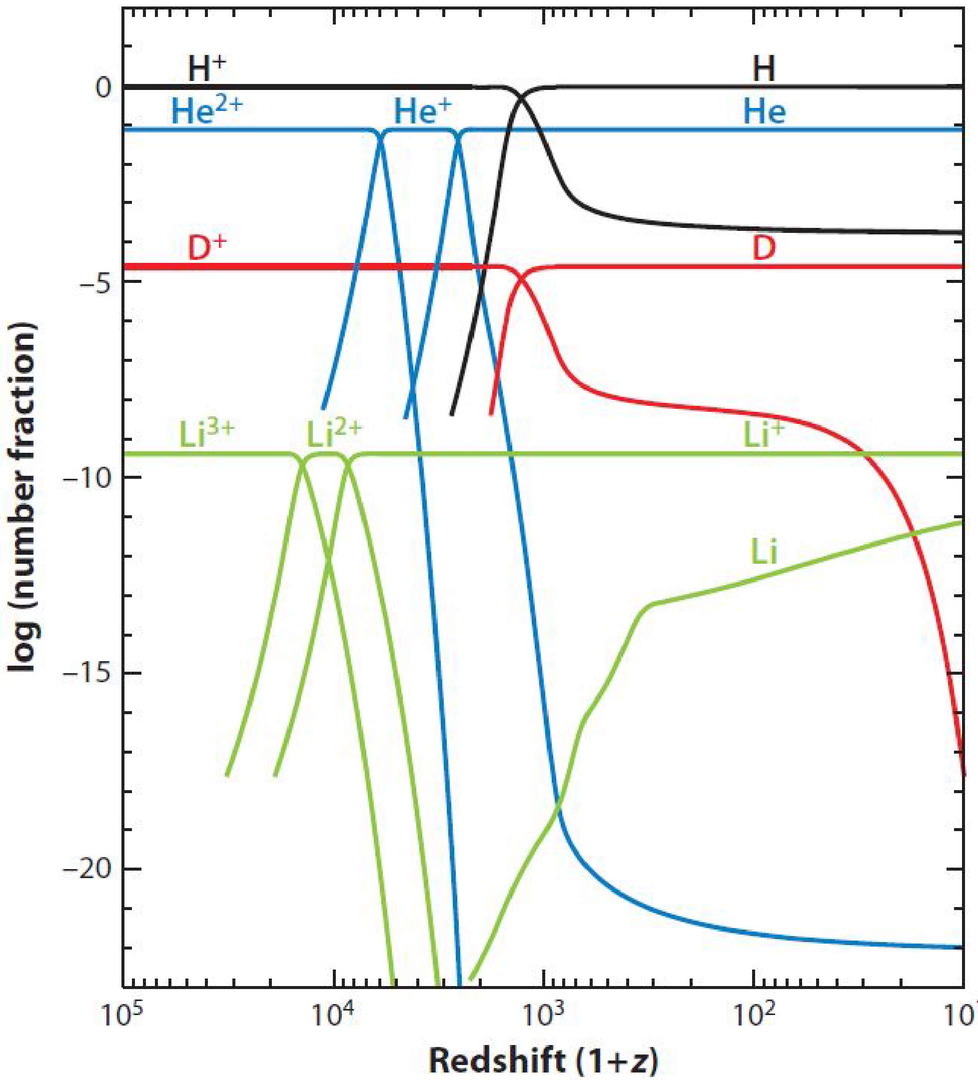
=> Universe becomes neutral: ***'Era of recombination'***

Cosmology (cont'd)

- Matter and radiation decouple at about the time of recombination => $T_m < T_R$
  - $T_R \propto (1+z)$
  - $T_m \propto (1+z)^2$
- Thermodynamic equilibrium no longer valid => need to consider detailed statistical equilibrium among microscopic processes
- As universe expands, density drops => recombination eventually ceases => asymptotic ionization fraction $n(e)/n_H \approx 3\times10^{-4}$



Recombination of main atoms



GP13

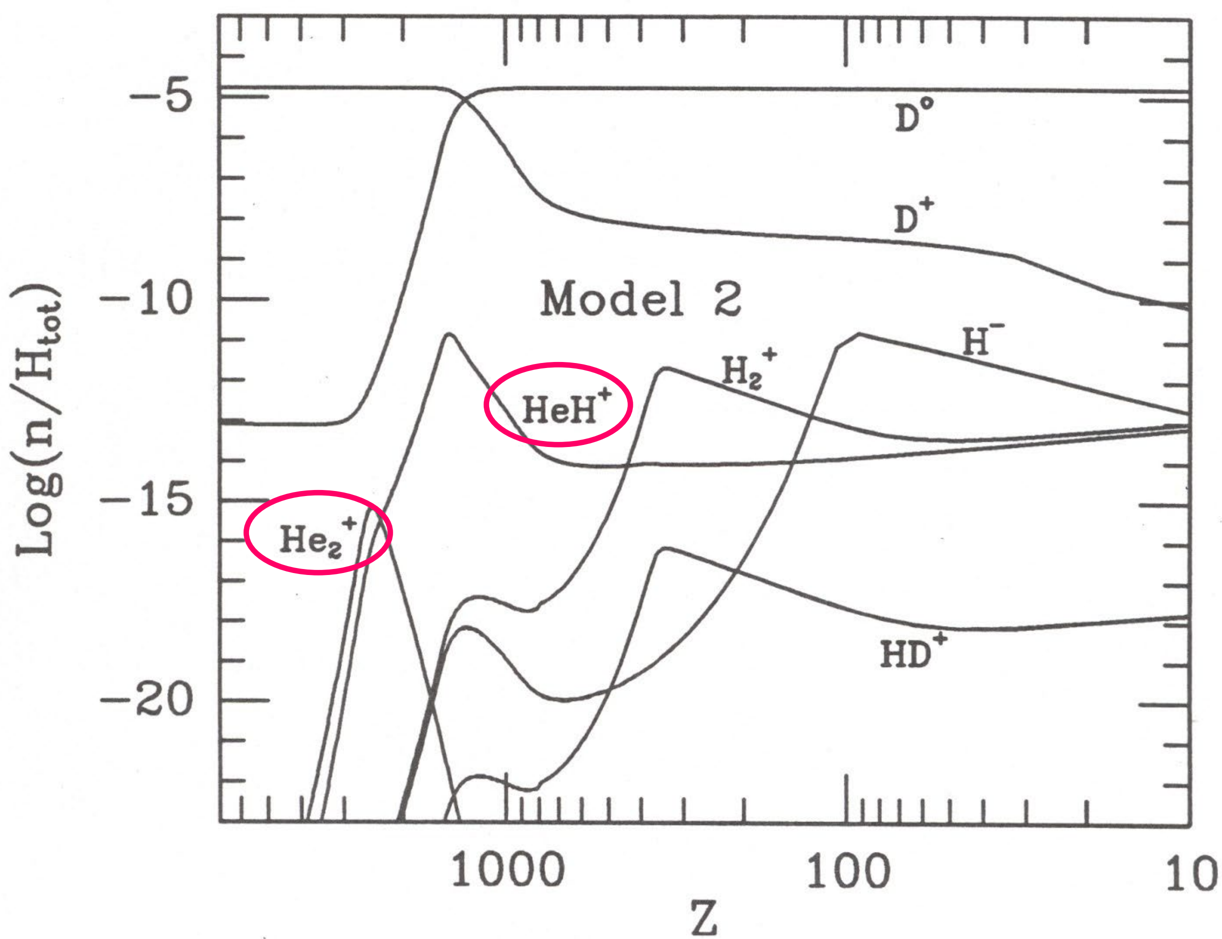
- Atoms sequentially recombine with z
- D^+ does not reach a constant plateau due to $D^+ + H \rightarrow D + H^+$ -43K

3.3 Chemistry

a. He chemistry

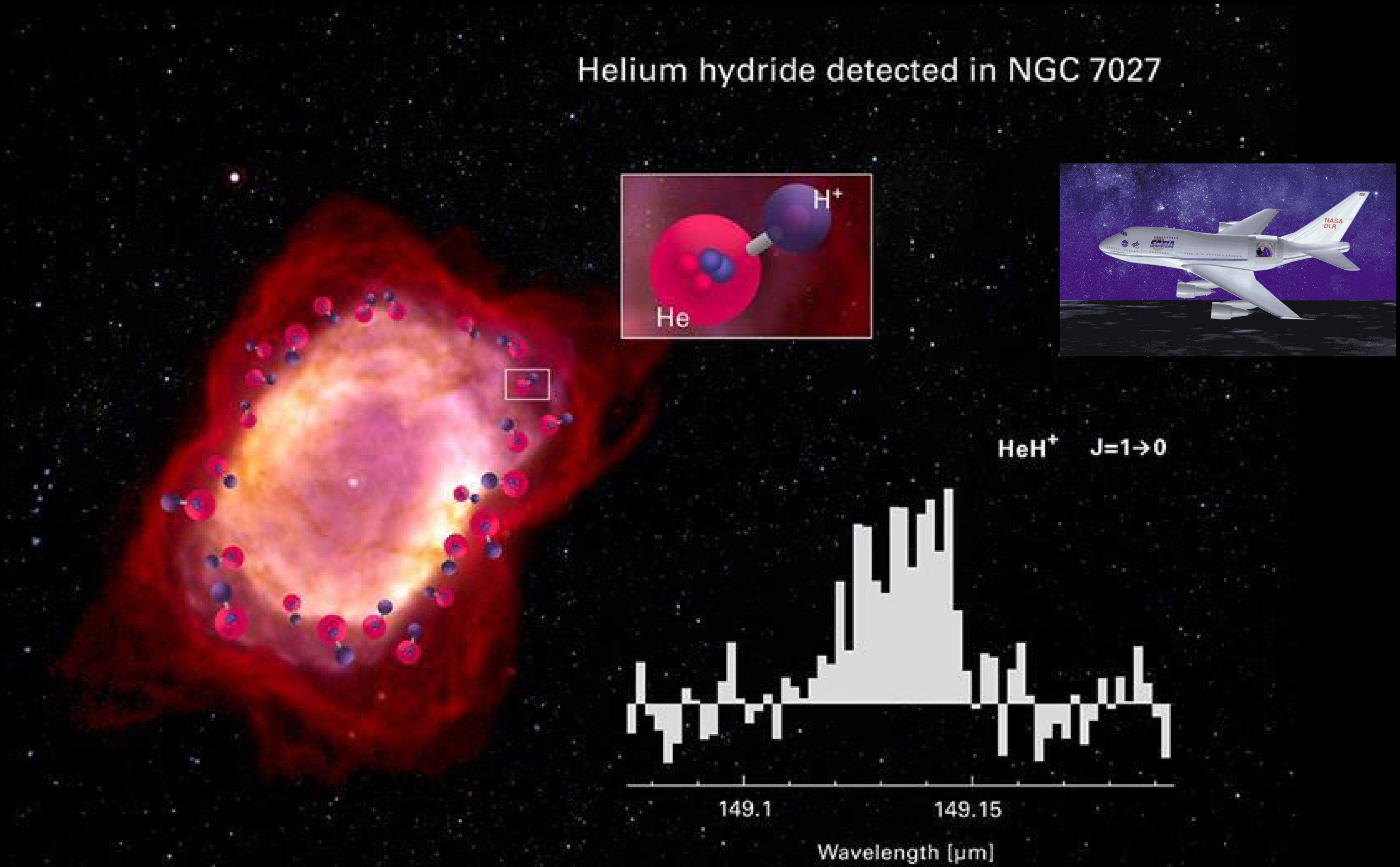
- He-bearing molecules form first, because He^{2+} recombines earlier than H^+
  - $He^{2+} + e \rightarrow He^+ + h\nu$
  - $He^+ + e \rightarrow He + h\nu$
- The first molecules in the universe were He_2^+ and HeH^+, formed by radiative association
  - $He^+ + He \rightarrow He_2^+ + h\nu$
  - $He + H^+ \rightarrow HeH^+ + h\nu$

First molecules in universe: He_2^+ and HeH^+



Latter 1989

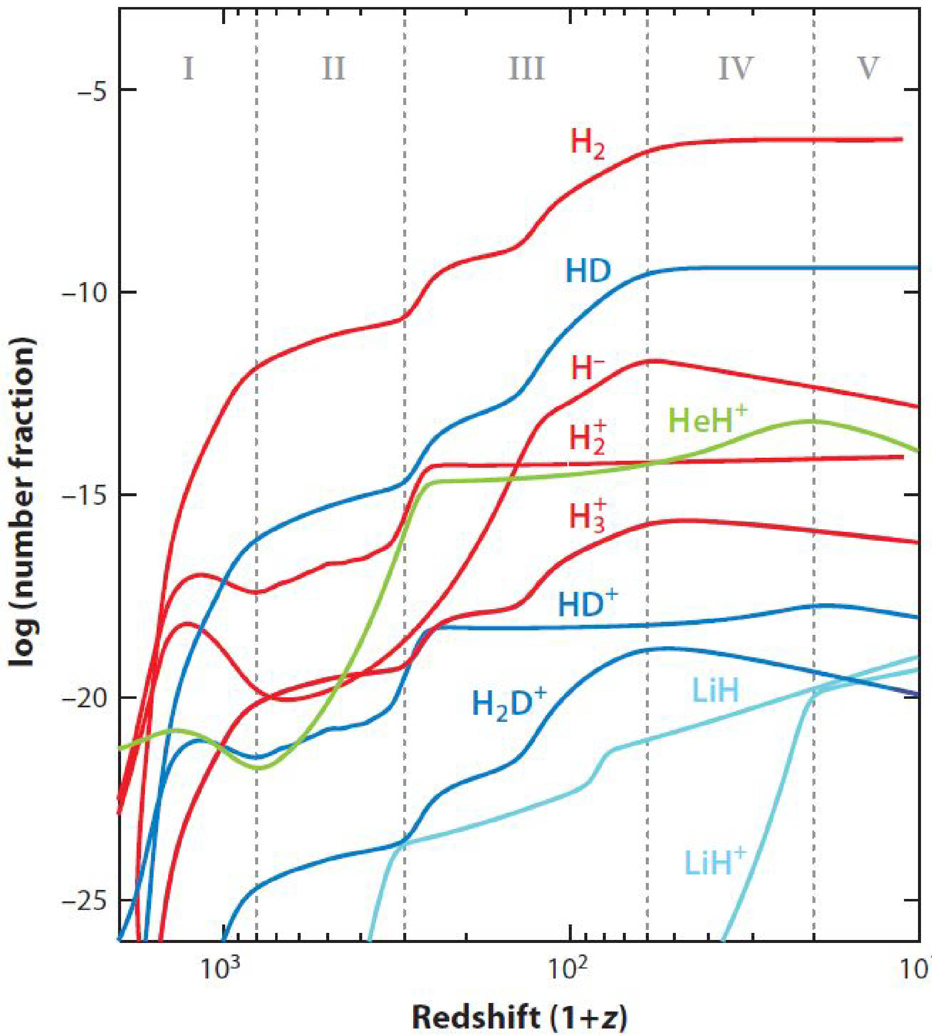
HeH^+ detection in planetary nebula



Not primordial HeH^+, but proves that chemistry is correct

Güsten et al. 2019, SOFIA

Formation of molecules



GP13

b. H chemistry

- Hydrogen chemistry in early universe is very different from that in the current era due to the absence of dust => H_2 must be formed by slow gas-phase reactions
- Direct formation by radiative association $H + H \rightarrow H_2 + h\nu$ is much too slow since H_2 does not have a dipole moment => consider other routes

H^+ route

- H_2 formation:
  - $H + H^+ \rightarrow H_2^+ + h\nu$
  - $H_2^+ + H \rightarrow H_2 + H^+$
- H_2^+ can be destroyed by photodissociation and dissociative recombination
  - $H_2^+ + h\nu \rightarrow H + H^+$
  - $H_2^+ + e \rightarrow H + H$

=> Formation of H_2 only becomes effective when T_R<4000 K and photodissociation of H_2^+ ceases

H^- route

- At later times (z~100), H_2 can be formed through H^-
  - $H + e \rightarrow H^- + h\nu$
  - $H^- + H \rightarrow H_2 + e$
- H^- is destroyed by photodetachment
  - $H^- + h\nu \rightarrow H + e$

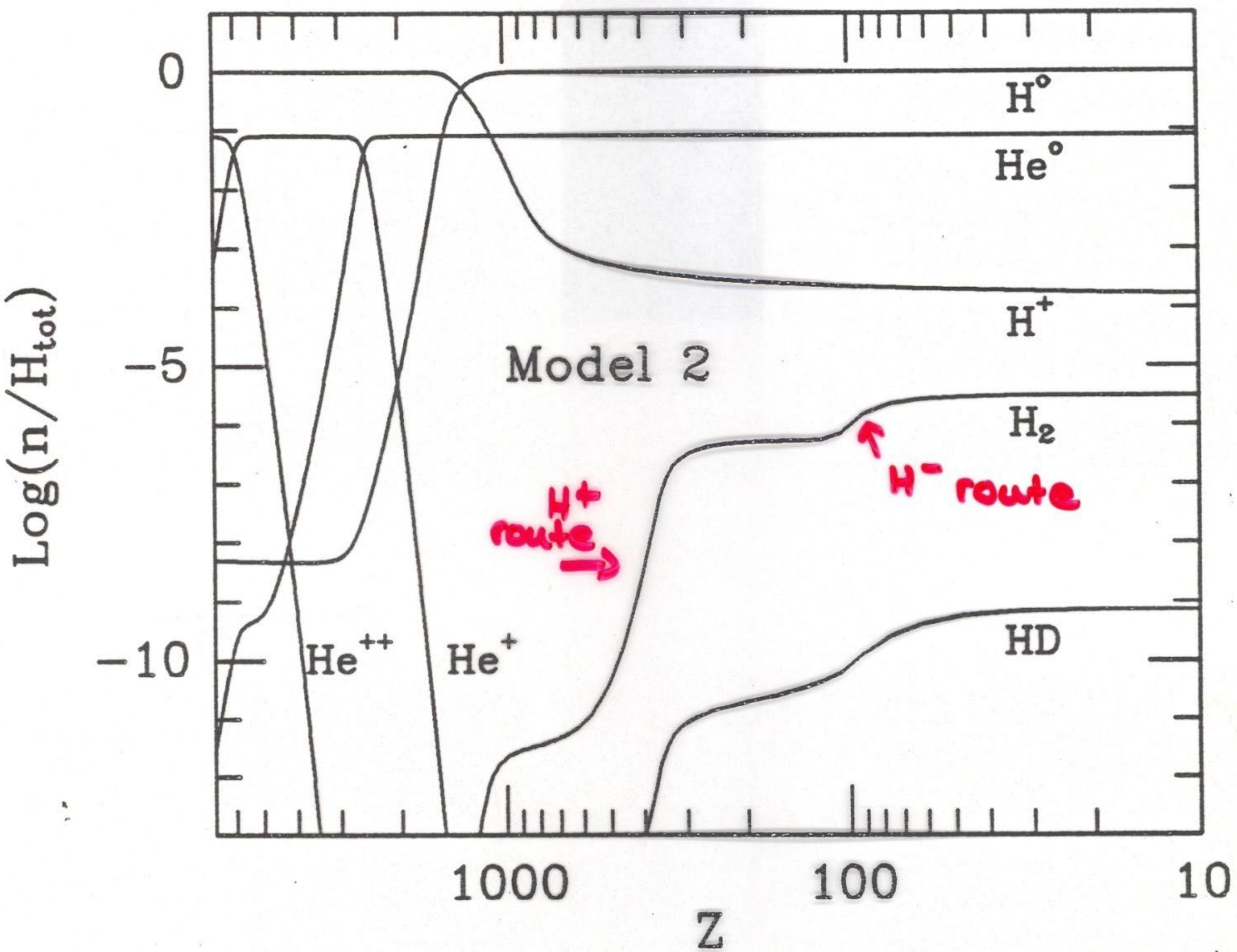
  with threshold of 0.75 eV => need $T_R <$ 1000 K before route becomes effective

H_2 chemistry

- Both H^+ and H^- routes are catalytic, since H^+ and e returned
- H_2 destroyed by
  - $H_2 + H^+ \rightarrow H_2^+ + H$
  - $H_2 + e \rightarrow H + H^-$
- Net result: $\boldsymbol{f(H_2) = n(H_2)/n_H \approx 10^{-6}}$ as $z \rightarrow 0$

Small molecular fraction in early universe

H_2 formation by H^+ and H^- routes

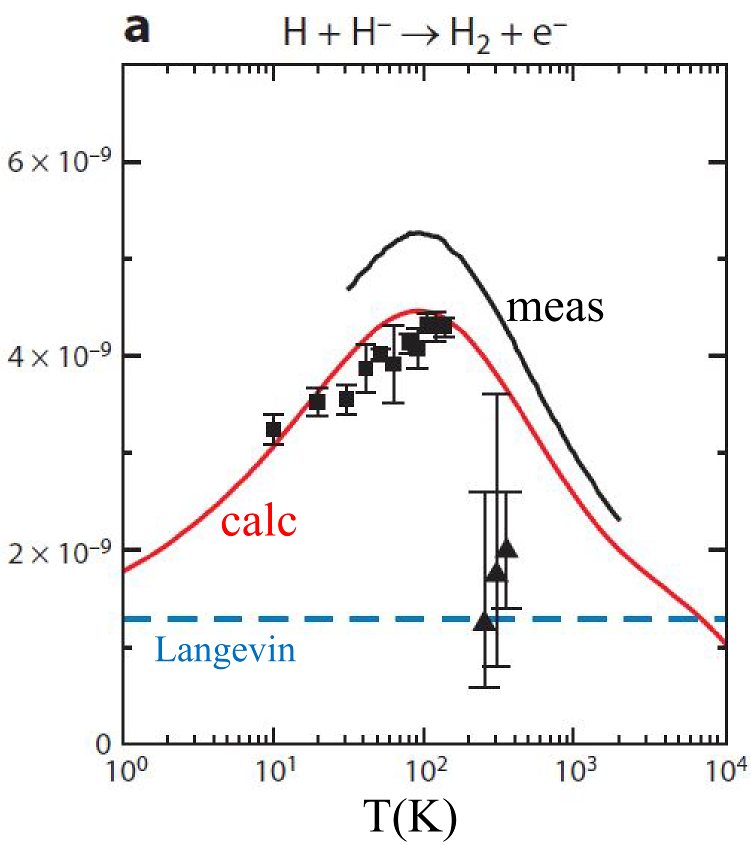


Latter 1989

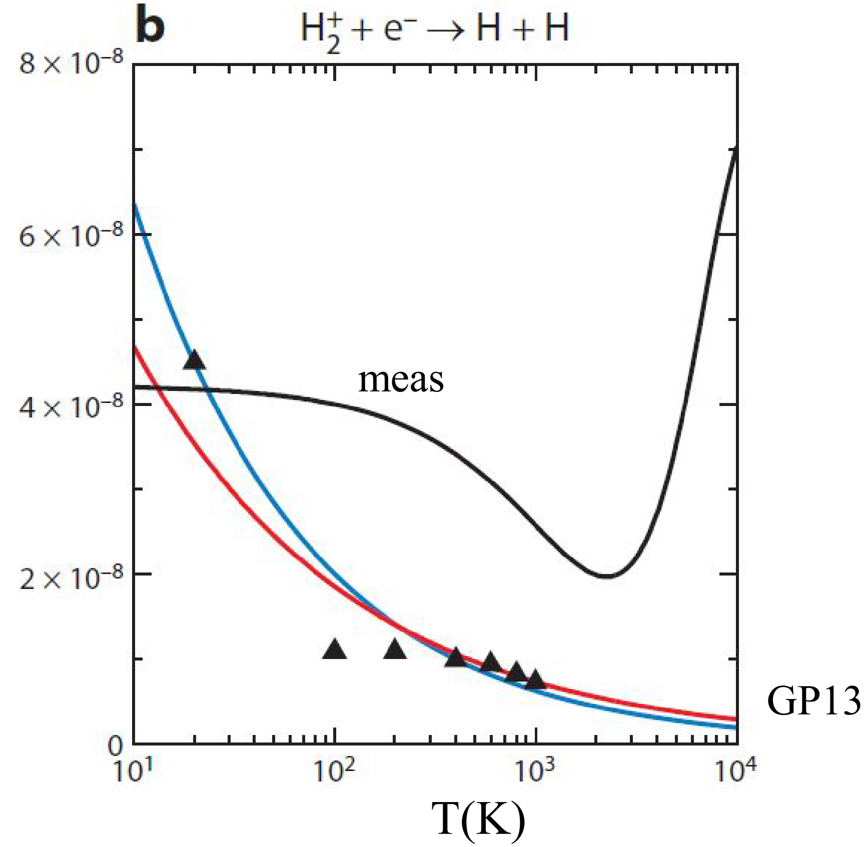
Recent developments

- CMB field has non-thermal contribution from absorption and emission in H Lyman bands
  - Affects H^- photodetachment
- H_2^+ is vibrationally excited
  - Enhanced photodissociation rate for v>0
- Laboratory experiments on some critical reaction rate coefficients

Recent lab experiments important rate coefficients

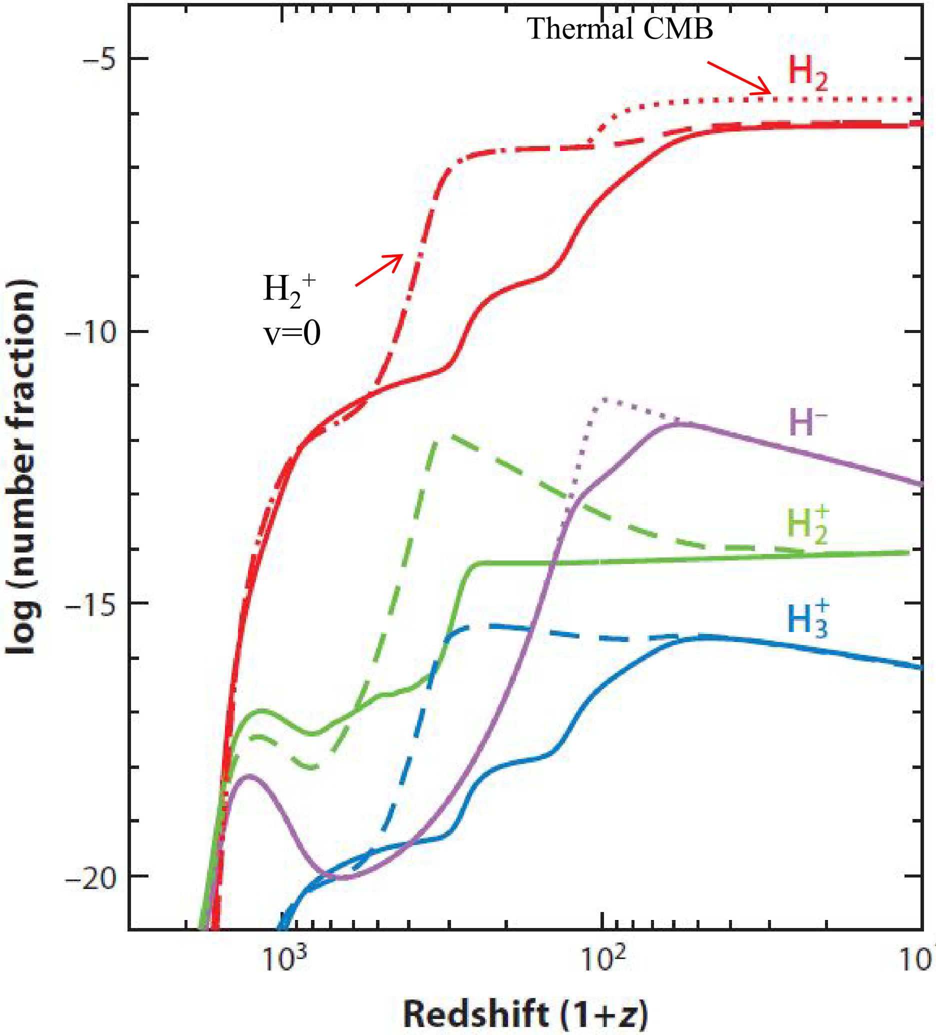


Gerlich et al. 2012, Bruhns et al. 2010



Schneider et al. 1994, Coppola et al. 2011

Hydrogen chemistry



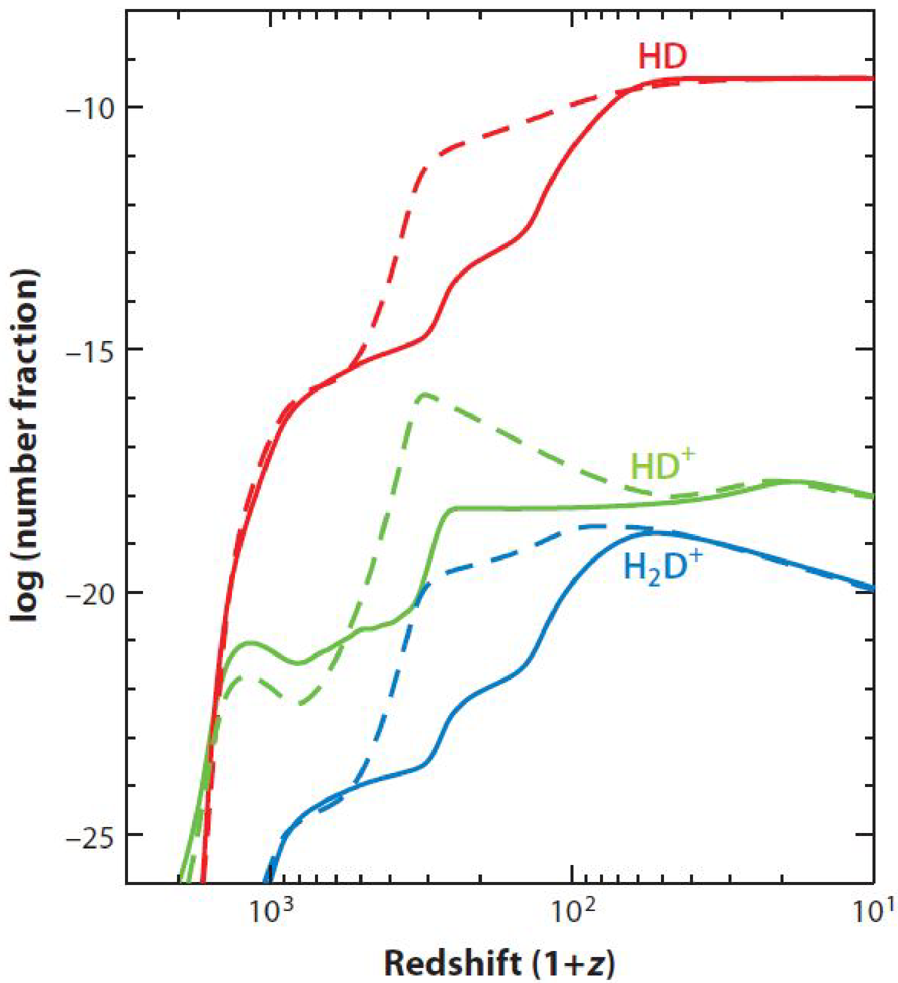
Full: all processes included
Dashed: neglect H_2^+ (v>0)
Dotted: neglect non-thermal CMB photons

GP 13

c. D chemistry

- Formation of HD is dominated by
  - $H^+ + D \rightarrow H + D^+$
  - $D^+ + H_2 \rightarrow HD + H^+$
- The molecule is also formed by
  - $H + D \rightarrow HD + h\nu$
  - $H^+ + D \rightarrow HD^+ + h\nu$
  - $H + D^+ \rightarrow HD^+ + h\nu$
  - $HD^+ + H \rightarrow HD + H^+$
- HD is destroyed by similar processes as H_2
  => $\boldsymbol{f(\mathrm{HD}) \approx 10^{-10} - 10^{-9}}$

Deuterium chemistry



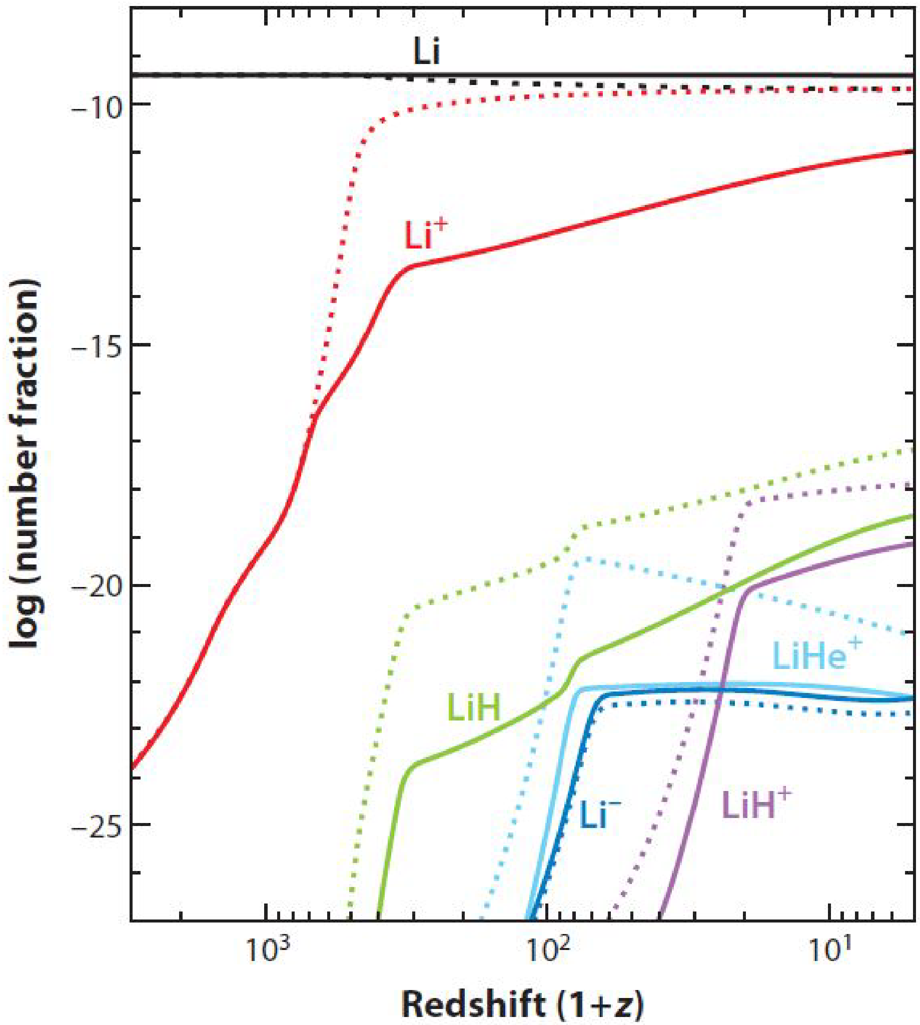
Dashed: neglect H_2^+ (v>0)

GP13

d. Li chemistry

- Lithium chemistry started at $z \approx 450$ when
  - $Li^+ + e \rightarrow Li + h\nu$
  - $Li^+ + H^- \rightarrow Li + H$
- **LiH⁺** chemistry
  - $Li^+ + H \rightarrow LiH^+ + h\nu$ formation
  - $LiH^+ + e \rightarrow Li + H$ destruction
  - $LiH^+ + h\nu \rightarrow Li^+ + H$
- **LiH** chemistry
  - $Li + H \rightarrow LiH + h\nu$ formation
  - $Li + H^- \rightarrow LiH + e$
  - $Li^- + H \rightarrow LiH + e$
  - $LiH + h\nu \rightarrow Li + H$ destruction
  - $LiH + H \rightarrow Li + H_2$

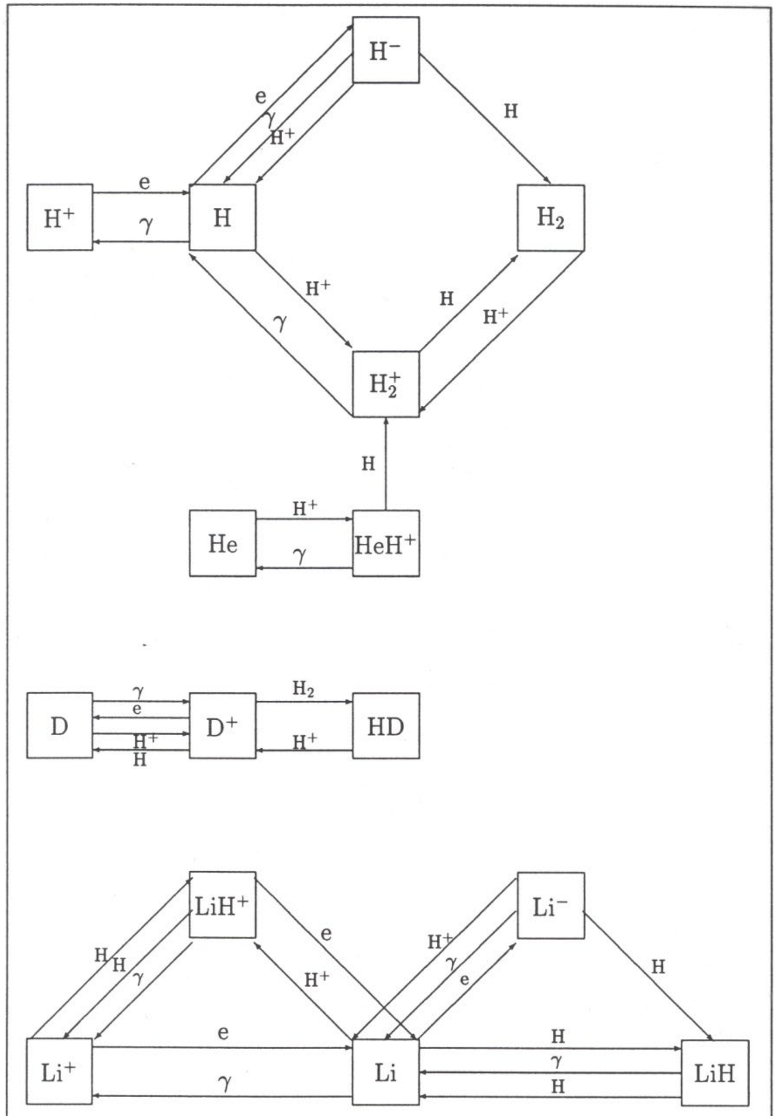
Lithium chemistry



Dotted: neglect non-thermal CMB photons

GP13

Summary principle processes

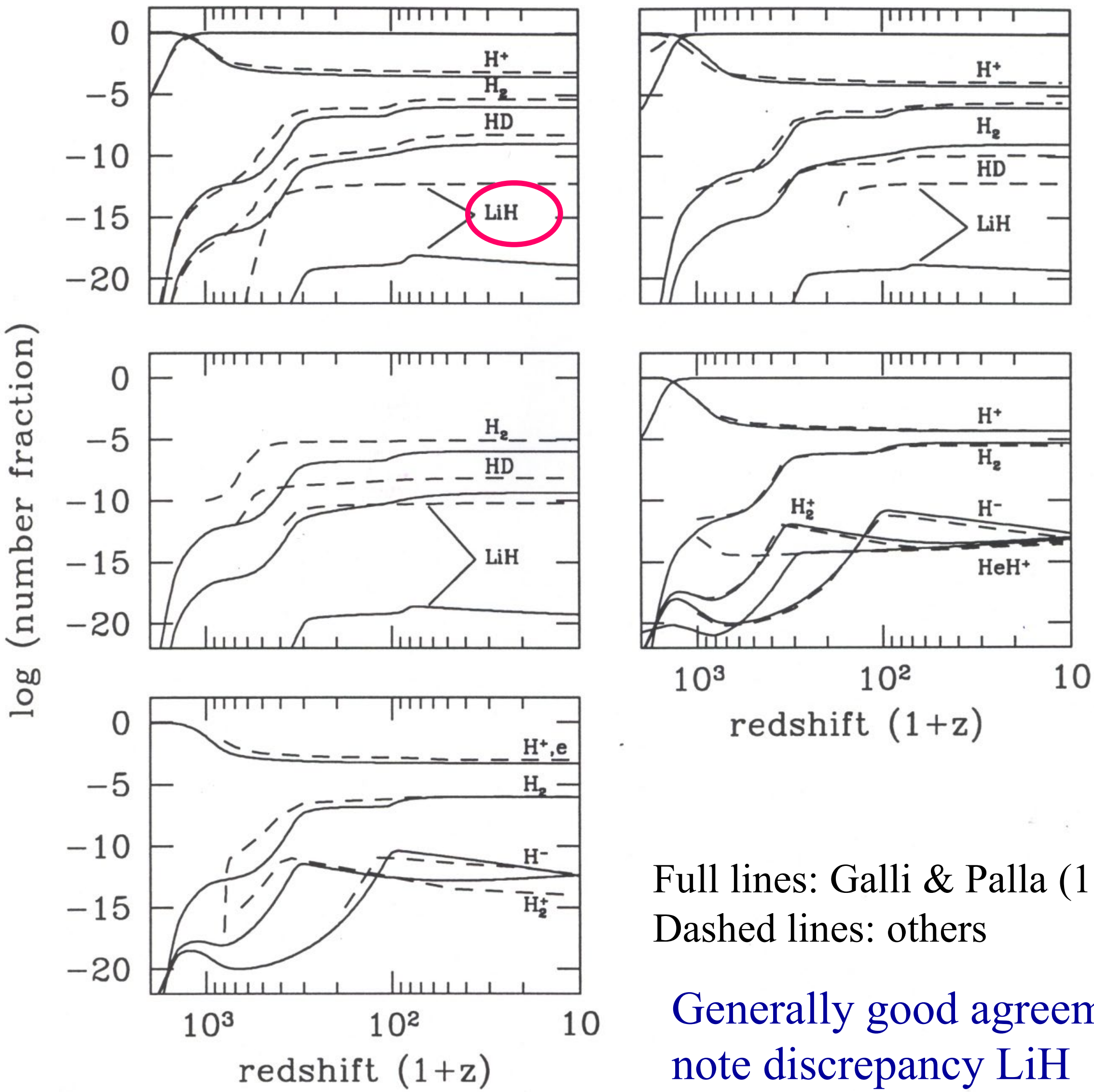


Galli & Palla 1998

3.4 Comparison models

- Models of early universe chemistry have been developed by various groups
  - Lepp & Shull (1984), Dalgarno & Lepp (1987), Latter (1989), Black (1990), …., Stancil et al. (1996, 1998), Galli & Palla (1998)
  - Summary in Galli & Palla (2013)
- General trends are similar, but some discrepancies found, especially for LiH
  - $f(H_2) \approx 10^{-6}$
  - $f(HD) \approx 10^{-10}$-10^{-9}
  - $f(HeH^+) \approx 10^{-13} - 10^{-12}$
  - $f(LiH^+) \approx 10^{-18} - 10^{-17}$
  - $f(LiH) \approx 10^{-20} - 10^{-16}$
- Differences can be due to
  - Different networks (some reactions not taken into account)
  - New values for rate coefficients
  - Different cosmology

Comparison models



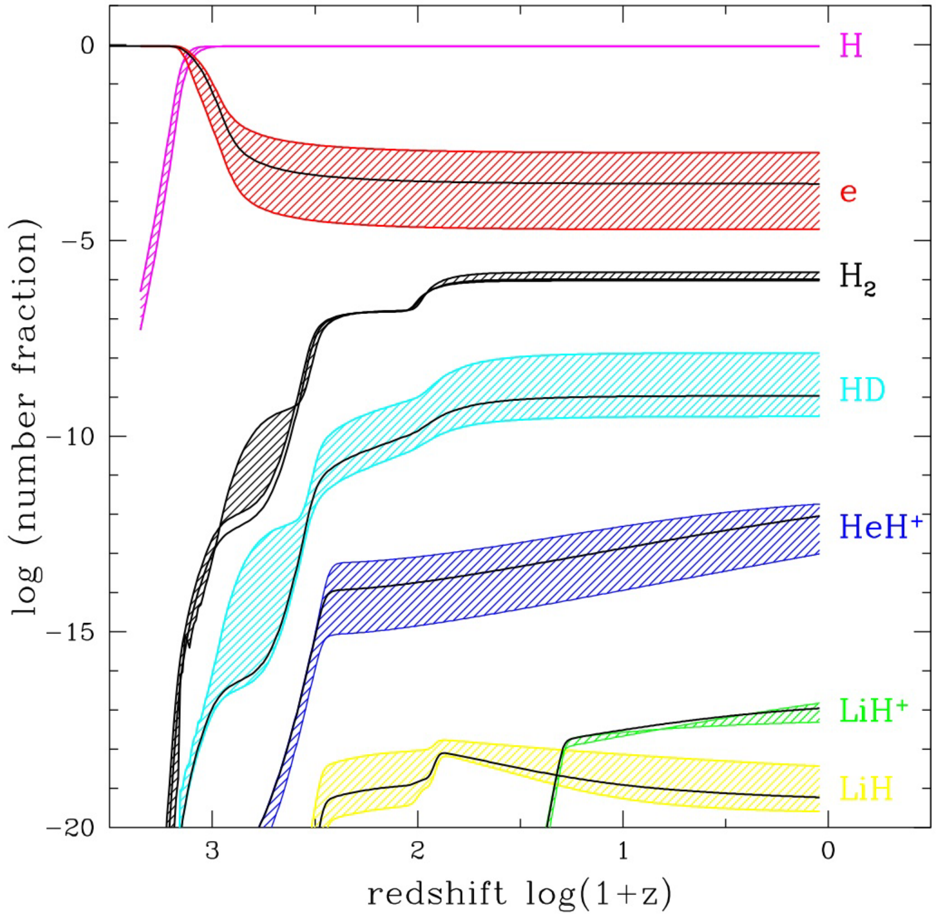
GP98 vs Black

Full lines: Galli & Palla (1998)
Dashed lines: others

Generally good agreement but note discrepancy LiH

Galli & Palla 1998

Sensitivity to cosmological parameters



GP98

- Hatched area covers range of variation of Ω_0=0.1-1, $h=H_0/100$=0.3-1 and η_{10}=baryon/photon=1-10
- Cosmological parameters now well determined so no longer an issue

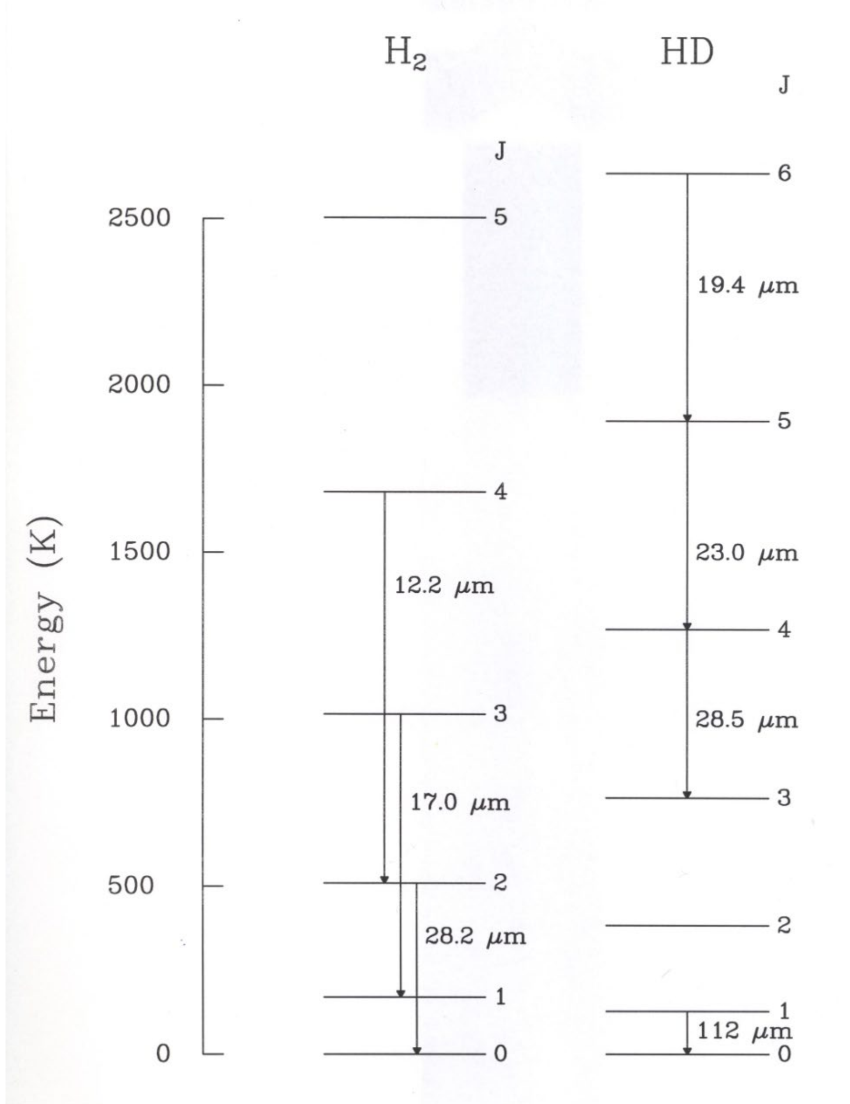
3.5 Molecular cooling and cloud collapse

- Cooling of universe is dominated by adiabatic expansion globally. Cooling by lines of atomic species, e.g.
  - $H(1s) + H \rightarrow H(2p) + H$
  - $H(2p) \rightarrow H(1s) + h\nu$ Lyman α

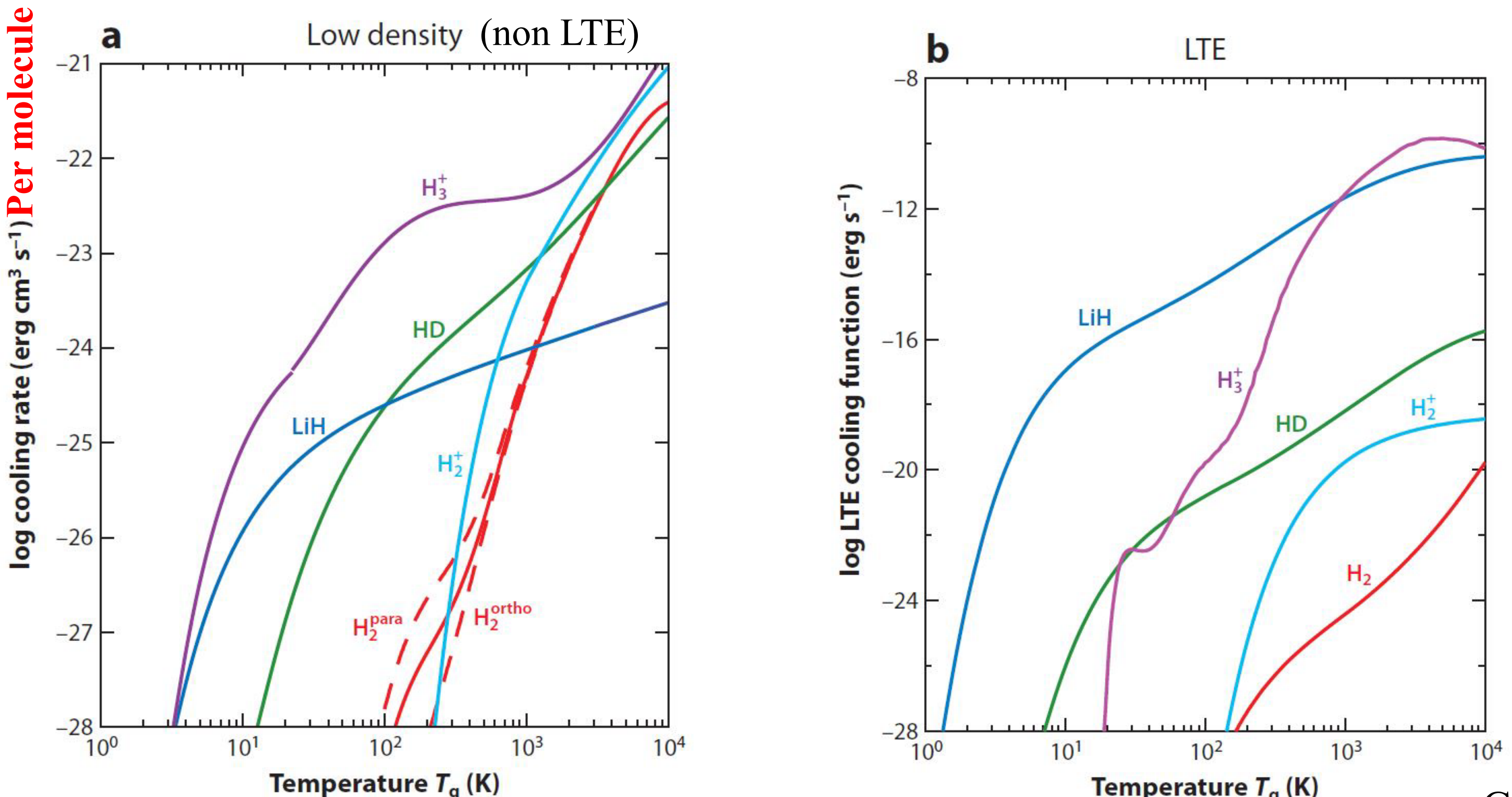
  is ineffective at $T_m < 10^4$ K

- Molecules H_2, HD and LiH are more important coolants at low temperatures due to their rotational lines
  - **H_2**: J=2 at ~500 K $J=2 \rightarrow 0$
  - **HD**: J=1 at ~100 K $J=1 \rightarrow 0$
  - **LiH**: J=1 at ~30 K $J=1 \rightarrow 0$

H_2 and HD energy levels



Cooling rate per molecule



GP13

- Need to multiply by abundance molecule to get overall cooling rate

Cloud collapse

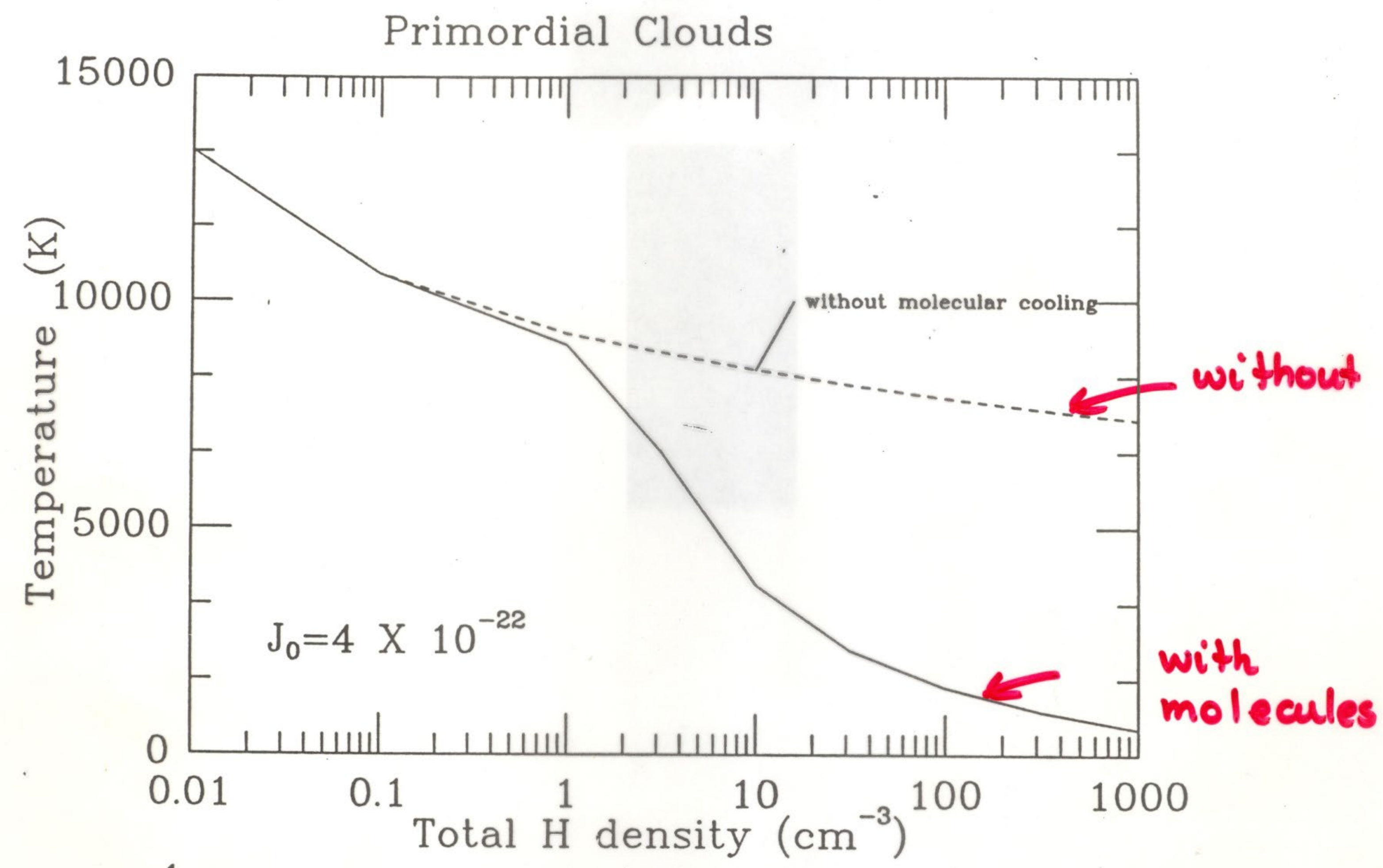
- Ability of cloud to collapse is given by Jeans' mass

$$M_J \approx 60 T_m^{3/2} n_H^{-1/2} \quad M_\odot$$

which is the smallest mass for which gravitational contraction can overcome thermal gas pressure

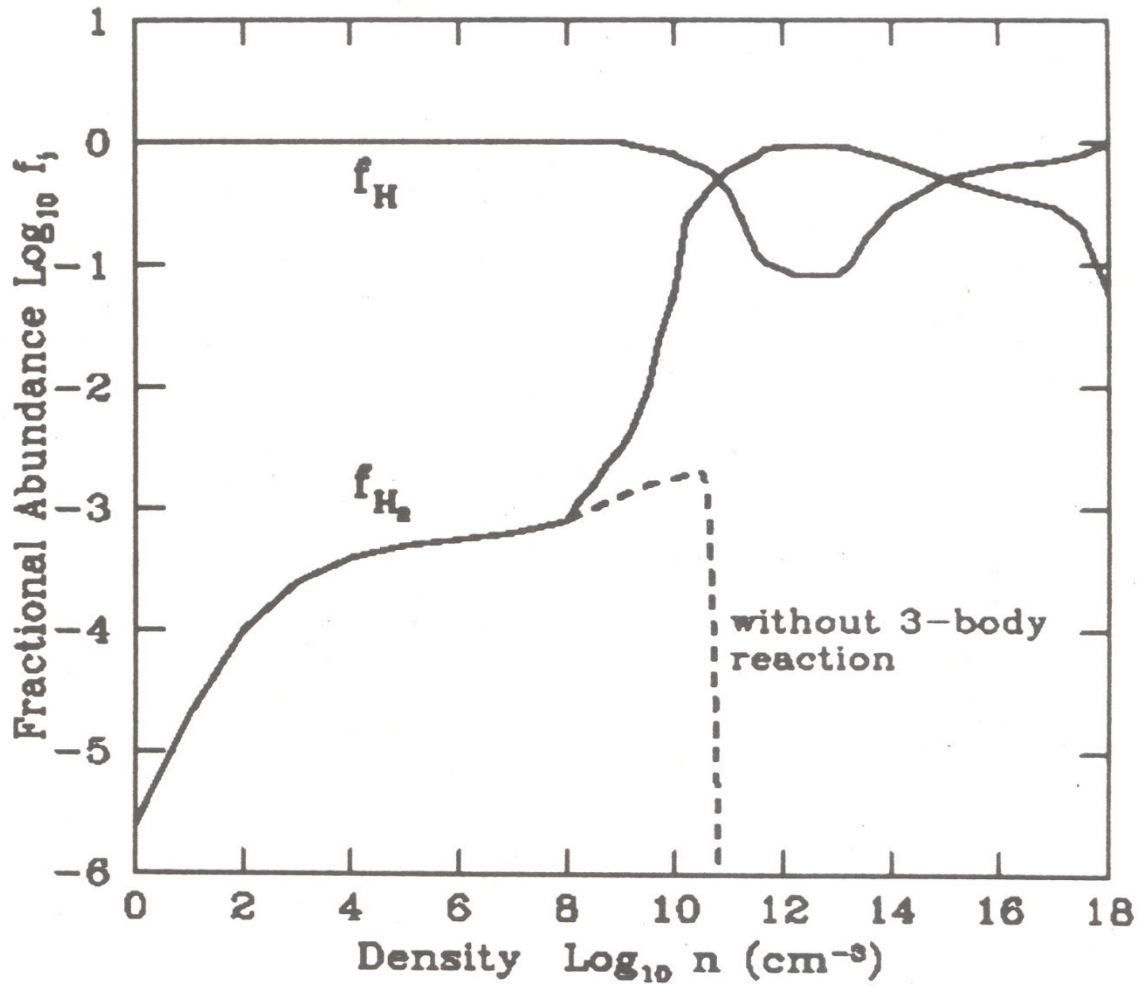
  - Ex: $M_J = 9\times10^5\ M_\odot$ at $z=1300$; $10^4\ M_\odot$ at $z=10$
- Additional cooling due to molecules lowers T_m and thus M_J, permitting fragmentation and contraction to occur on smaller scales (down to $< 1\ M_\odot$)
- As density in condensations increases due to collapse, H_2 formation can be enhanced by 3-body processes
  - $\mathbf{H + H + H \rightarrow H_2 + H}$ $\quad n_\mathrm{H} \geq 10^9\ \mathrm{cm}^{-3}$

Effect of molecular cooling



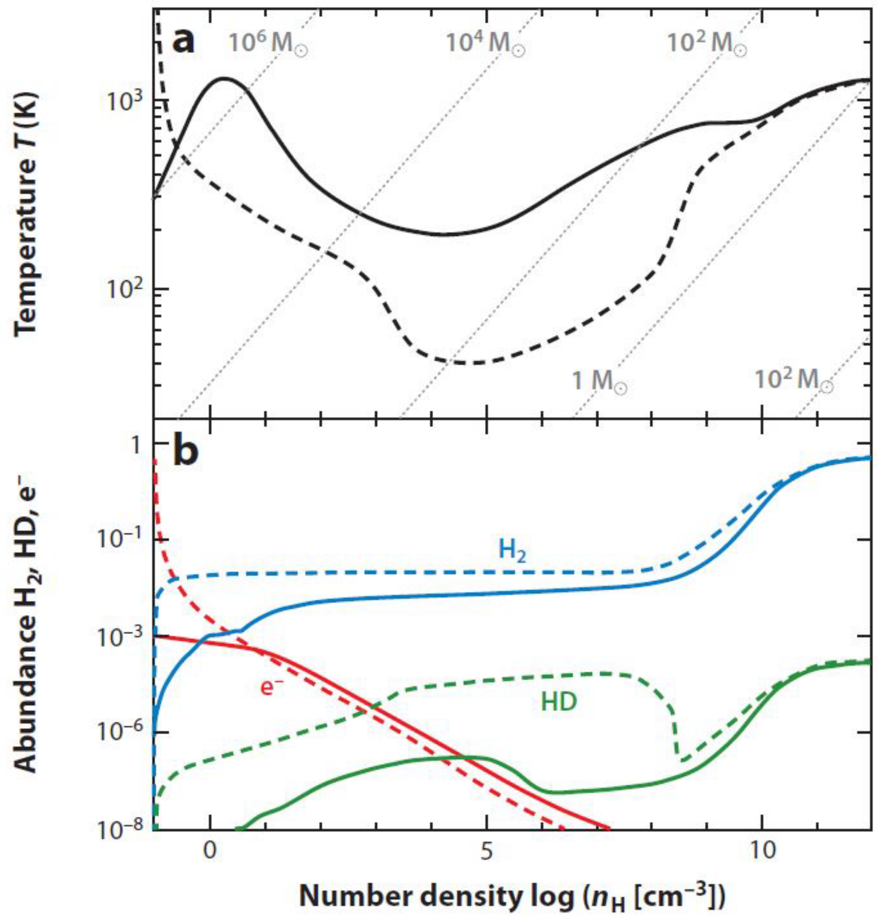
Latter 1989

Importance of 3-body H_2 formation



Palla et al. 1983

Collapsing primordial cloud



GP13

Figure 6

(*a*) Thermal and (*b*) chemical evolution of collapsing primordial gas clouds. The solid lines show collapse in a predominantly neutral minihalo, whereas the dashed lines display the evolution of gas that is preionized and cooled from high temperatures. Lines of constant Jeans mass are shown as dotted lines in panel *a*. Courtesy of K. Omukai.

Recent developments

- Couple chemistry and cooling with hydrodynamical simulations of cosmological evolution, e.g., in Cold Dark Matter models, overdense regions with $M \approx 10^5 - 10^7\ M_\odot$ are found at $100 < z < 10$. Can baryonic matter collapse to form the first stars?
- Critical H_2 fraction:

$$f_{H_2} \approx 2 \times 10^{-4} \left(\frac{h\Omega_b}{0.03} \right)^{-1} z_{100}{}^{-3/2} \left(1 + \frac{10 T_3{}^{7/2}}{60 + T_3{}^4} \right) e^{512/T}$$

$\approx 5 \times 10^{-4}$ 'rule of thumb'

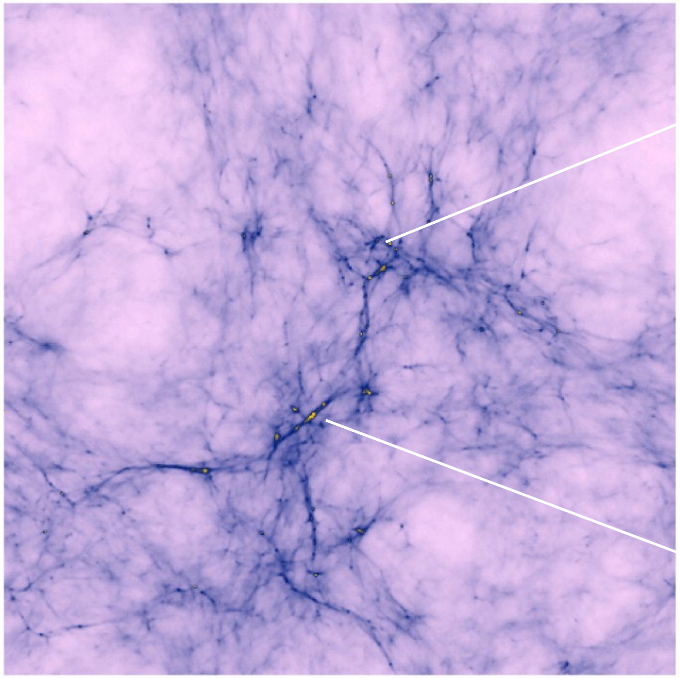
$\Rightarrow$determine minimum mass for collapse as function of z

- Work by Tegmark et al. (1997), Abel et al. (1997), Bromm et al. (2002), Yoshida et al. (2003), and now many more ….

End of dark ages and onset of star formation if $t_{\mathrm{cool}} << t_{\mathrm{Hubble}} \rightarrow$

The role of H_2 and HD within first structures

Projected gas distribution at z = 17



Yoshida et al 2003

Mini-halos $M \sim 10^6\ \mathrm{M_{sun}}$ $z = 20 - 30$

$T_{\mathrm{vir}} << 10^4$ K H_2 cooling

$$\mathrm{H} + e^- \rightarrow \mathrm{H}^- + h\nu$$
$$\mathrm{H}^- + \mathrm{H} \rightarrow \mathrm{H}_2 + e^-$$

positive feedback from X-rays, shocks, relic HII regions …

negative feedback from UV background

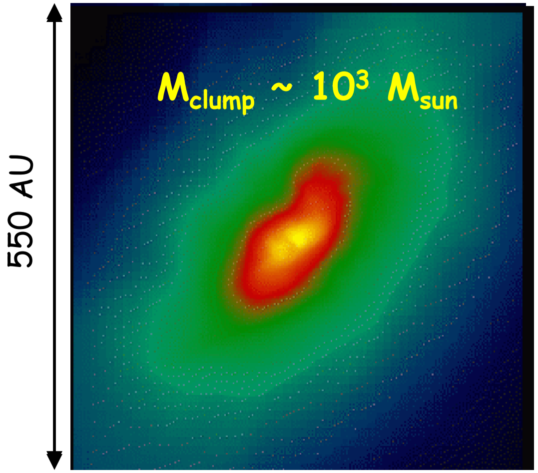
Dwarfs $M \sim 10^8\ \mathrm{M_{sun}}$ $z = 10\text{-}20$

$T_{\mathrm{vir}} \geq 10^4$ K H cooling (Lyα)

PopIII star formation in mini-halos

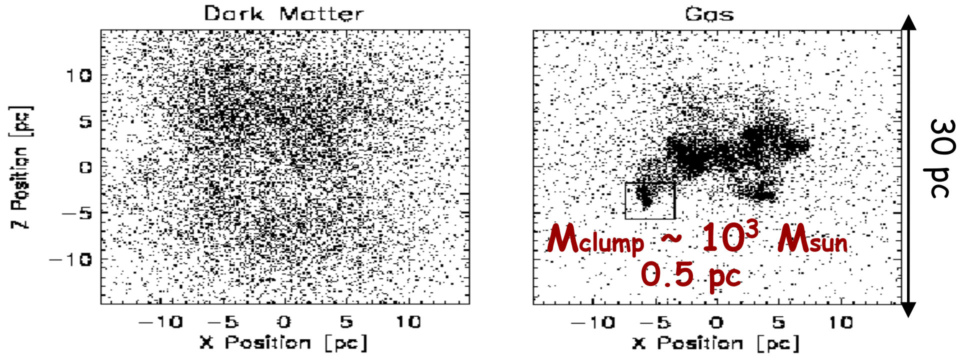
3D simulations: from cosmological initial conditions to molecular clouds

Adaptive Mesh Refinement



Abel, Bryan & Norman (2000-2002)

Smooth Particle Hydrodynamics



Bromm, Coppi & Larson (2000-2002)

Convergence toward a regime with $T_{cr} \sim 200$ K and $n_{cr} \sim 10^4$ cm^{-3} ← H_2 properties

Fragmentation into protostellar clouds with

$$M_{clump} \geq M_{jeans}(n_{cr}, T_{cr}) = 700\ M_{sun}(n/n_{cr})^{-1/2}(T/T_{cr})^{3/2}$$

Final stellar mass 30 M_{sun} < M_* < 150 M_{sun}

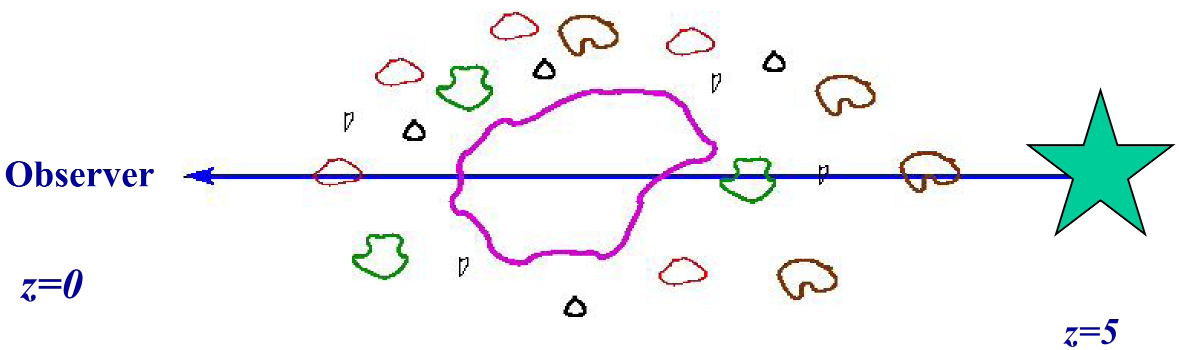
? Radiative feedback during accretion ?

3.6 Observations of molecules at $z<7$

- Molecules at high redshifts $z<7$ can be observed in optical and mm spectra of quasars, and through submm emission of CO and other molecules from starburst galaxies

a. Quasar absorption lines

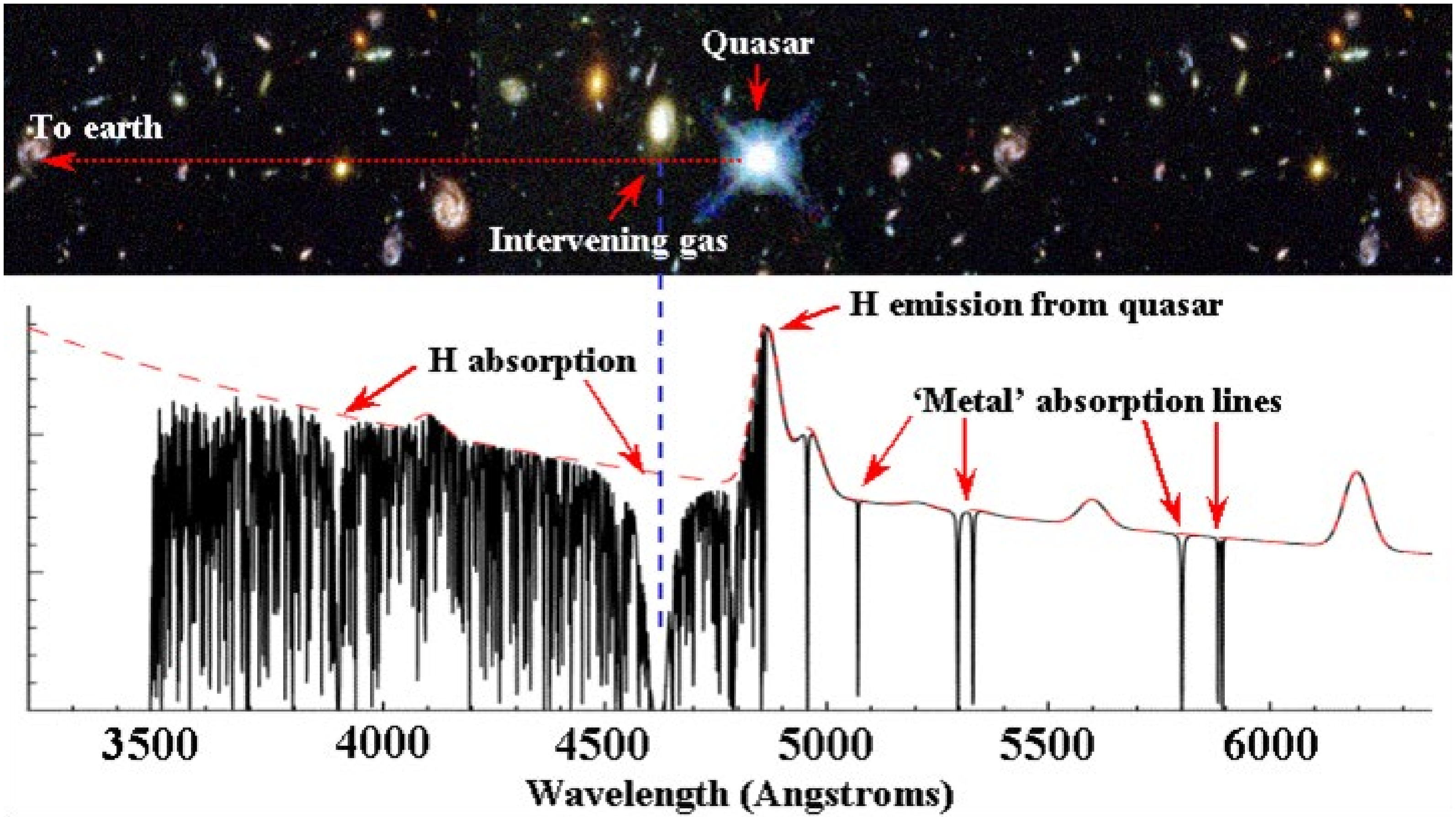
- QSO shines through intergalactic medium



- Radiation encounters many clouds / structures containing H between z=5 and z=0 $\Rightarrow$ strong absorption by each cloud at $\lambda_{obs}=(1+z)\lambda_{rest}$
- Dominant line: **H 1s $\rightarrow$2p** Lyman α

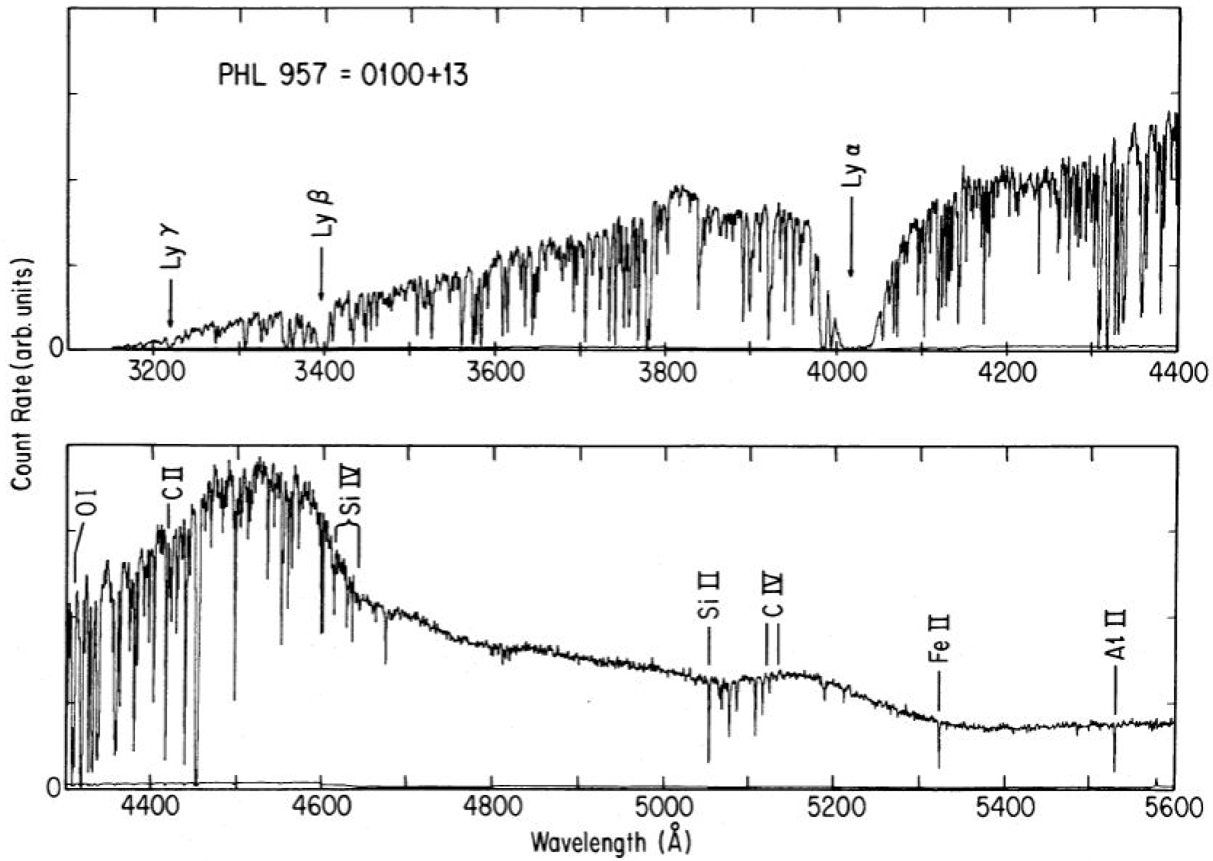
$\Rightarrow$ **'Lyman-α forest'**

Quasar absorption line forest



Quasar PHL 957 at z=2.7

Lyman α forest



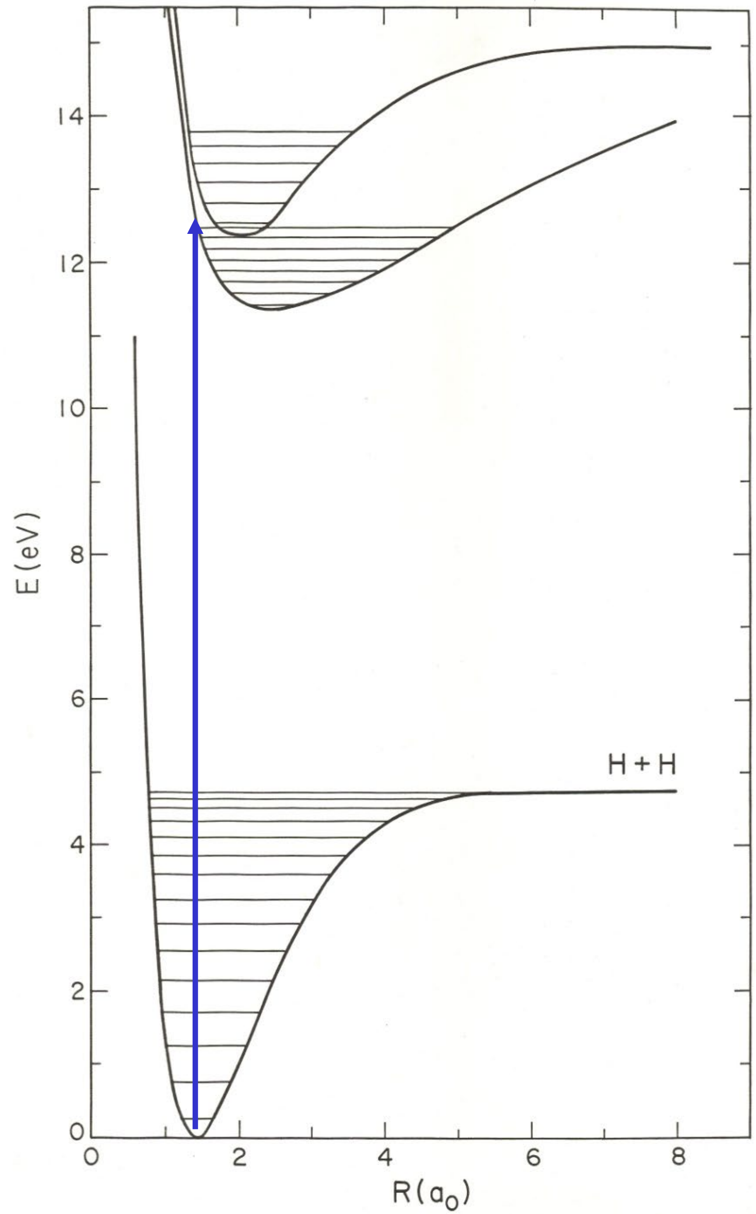
Black 1990

Note damped Ly-α system at z=2.3 and corresponding 'metal' lines longward of Ly α

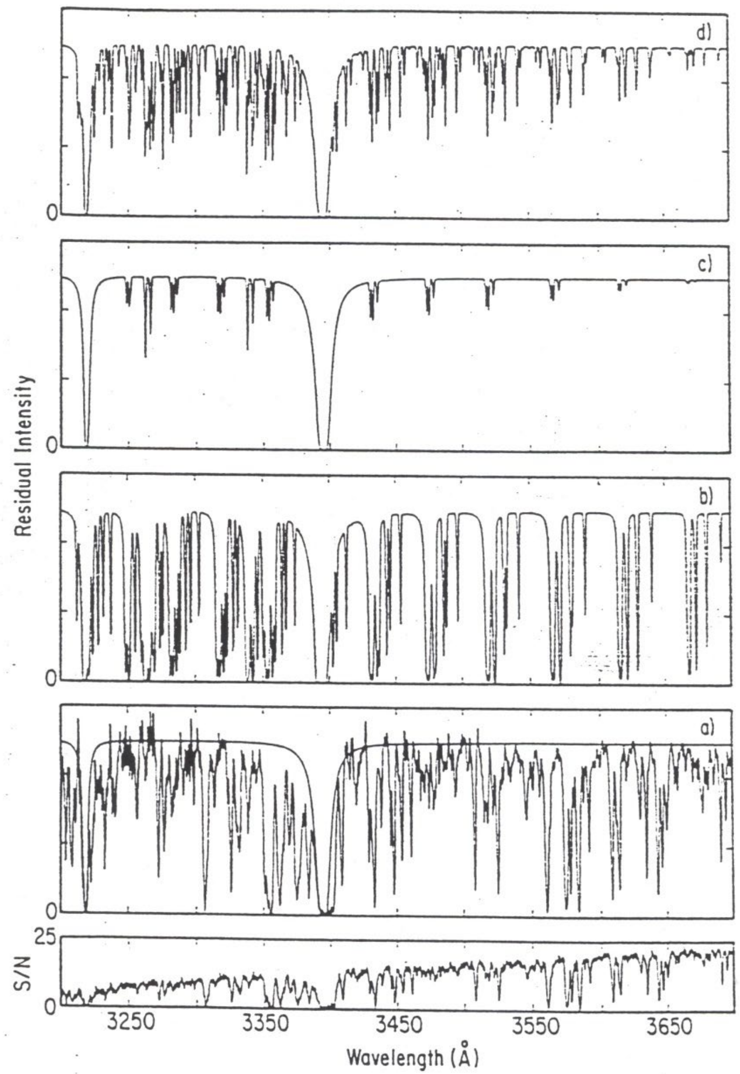
H_2 searches

- Searches for H_2 in QSO spectra problematic since H_2 only has strong transitions at $\lambda_{rest} \approx 900$-1100 Å, i.e., the same region where H Ly α at other redshifts absorbs ⇒ need to search for H_2 lines in Ly-α forest
- Careful modeling of H_2 in systems with damped (saturated) Ly-α H profiles (⇒N(H)>10^{21} cm^{-2}) has resulted in detection of H_2 in a few systems
- Fraction of H_2 generally low⇒ H_2 efficiently destroyed by UV at high z?
- Abundances of C, O, N, … often factor of 10-100 lower than solar

H_2 absorptions



Search for H_2 toward PHL 957



Synthetic H+ H_2 spectra
N=10^{16} cm^{-2}
T_{ex}=1000 K

N=10^{15} cm^{-2}
T_{ex}=100 K

N=6×10^{19} cm^{-2}
T_{ex}=100 K

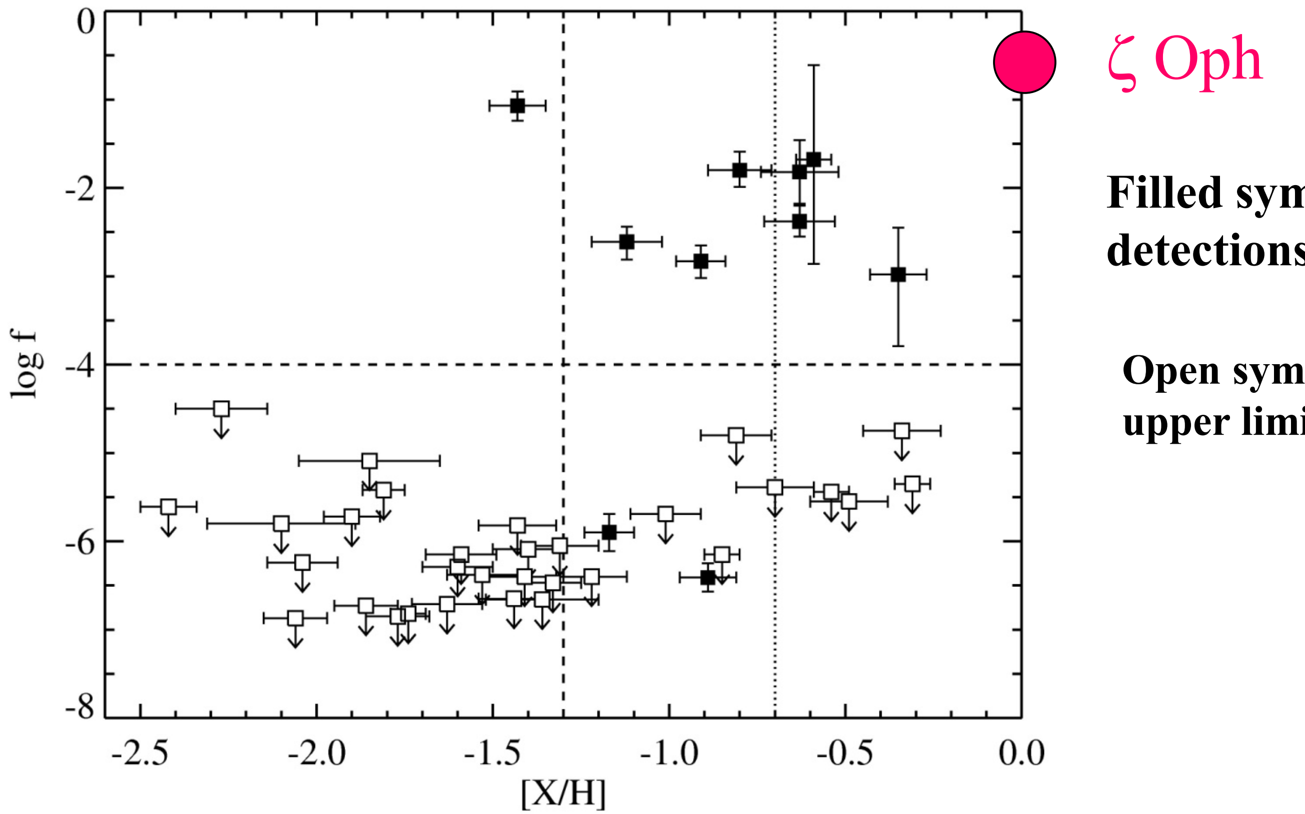
Obs + H fit

Obs

Black et al. 1987

- Note ***anti***-coincidences => No H_2 detection with $f(H_2)\leq5\times10^{-6}$

Recent H_2 searches



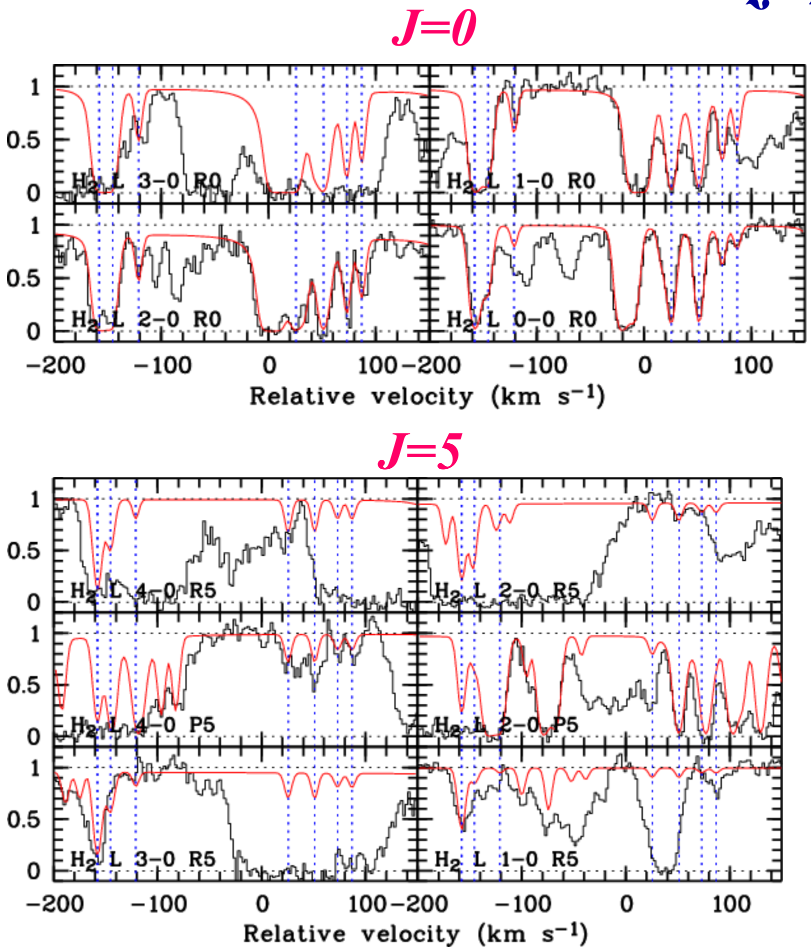
Filled symbols: detections

Open symbols: upper limits

- Search for H_2 in damped Ly-α systems with $z>1.8$
- Trend to have more H_2 with higher metallicity
- H_2 fraction generally low $f<10^{-4}$-10^{-6}

H_2 detection toward Q2348-011

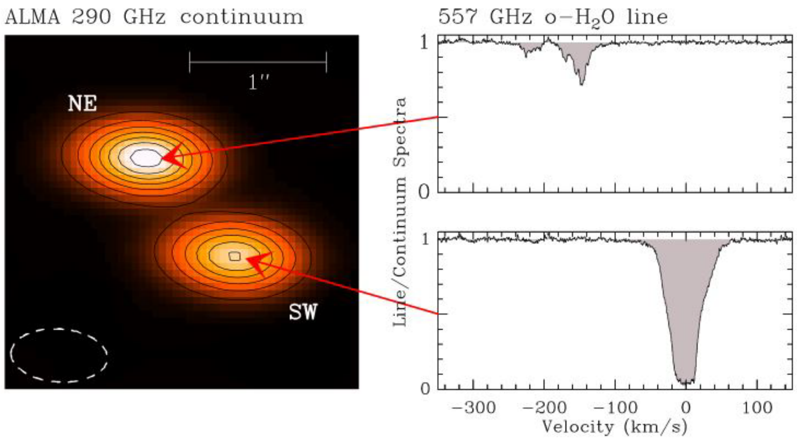
***z*=2.426**



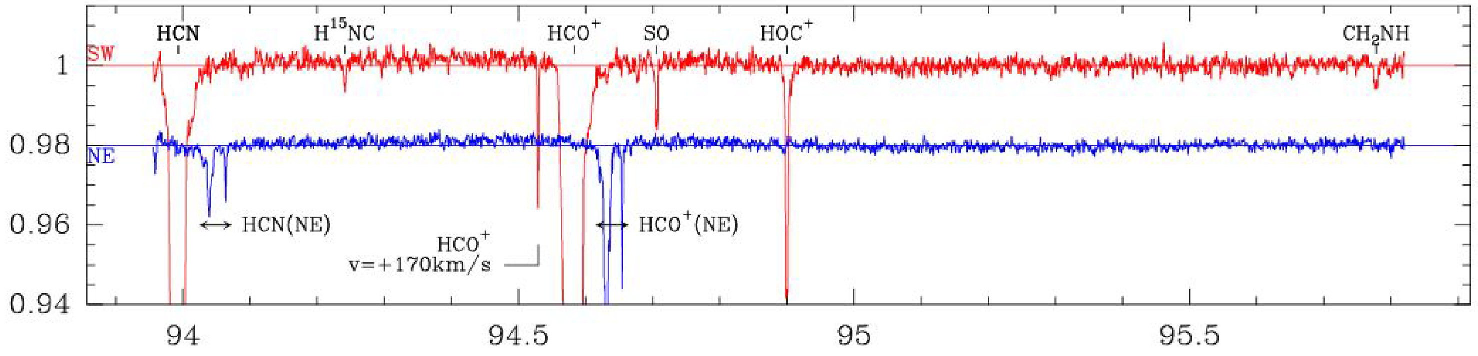
Noterdaeme et al. 2007
Petitjean et al.2008

- Molecular fraction f=1.7×10^{-2}
- Lines out of J=0-5 detected ⇒ T>130 K, n~100-200 cm^{-3}

b. QSO absorption at mm



PKS1830-211 z=0.89
ALMA



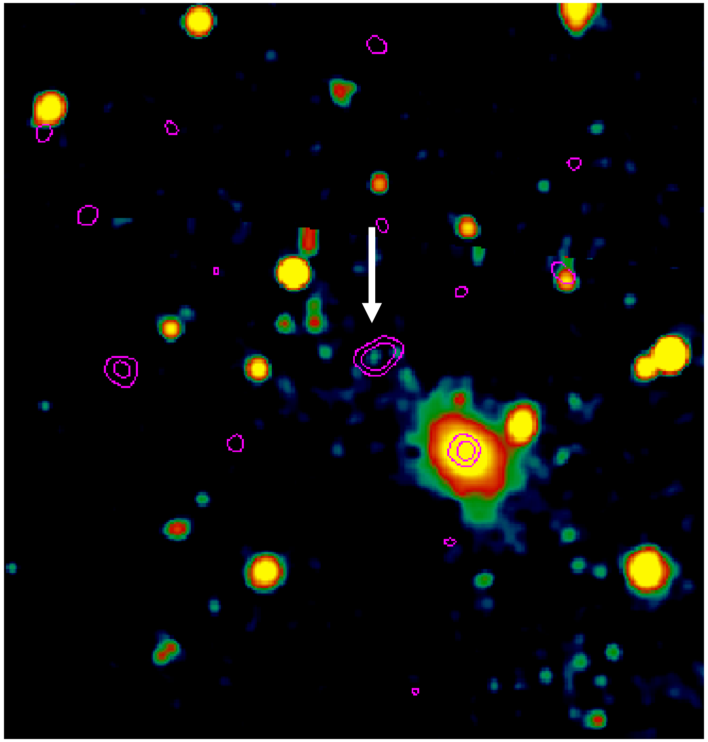
Muller et al. 2014
Combes, Wiklind & Nakai 1997

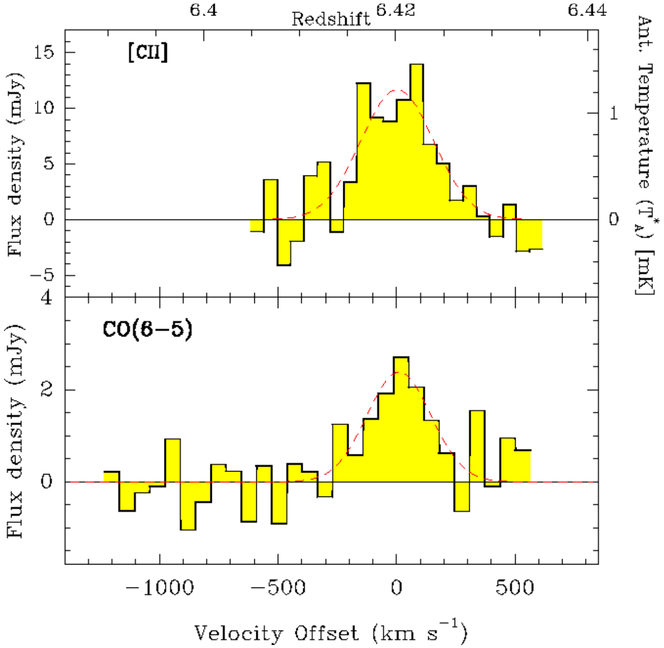
- Observe molecules at high z in mm, up to z~3
- Detection of CO, HCO$^+$, HCN, CS, ….
- Even detection of minor species such as CF$^+$

c. Submm emission lines

- Recent detections of CO J=3 →2, 4 →3, 5 →4, …, 7 →6 in starburst galaxies and active galactic nuclei at z=2-7
- Strong dust continuum emission up to z=7 observed as well
- [C I], [C II], HCN, HCO^+ detected in a few systems
- Starburst galaxies have 100× more molecular gas than Milky Way ⇒ enormous reservoir of material for forming stars
- Elemental abundances close to solar ⇒ stars formed very fast ⇒ ***'burst'***

Molecules at high redshift: z=6.4!



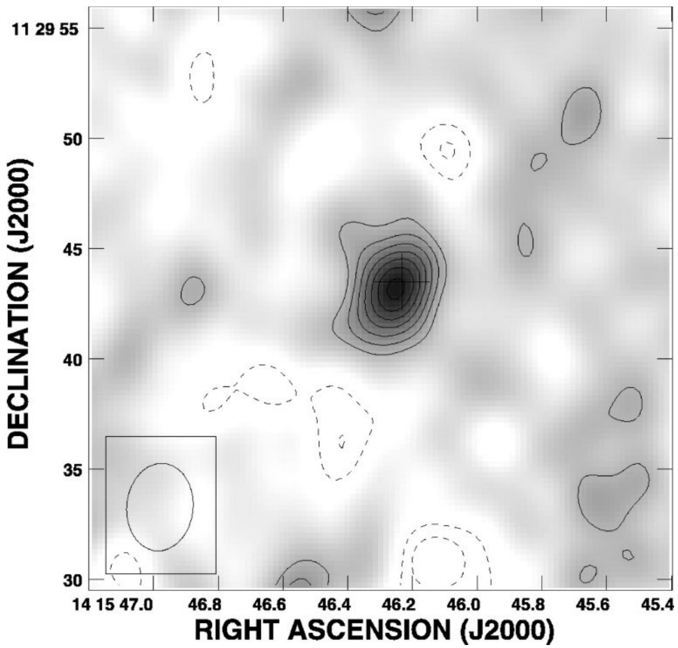


CO and [C II] in quasar SDSS J1148+5251 at z=6.4

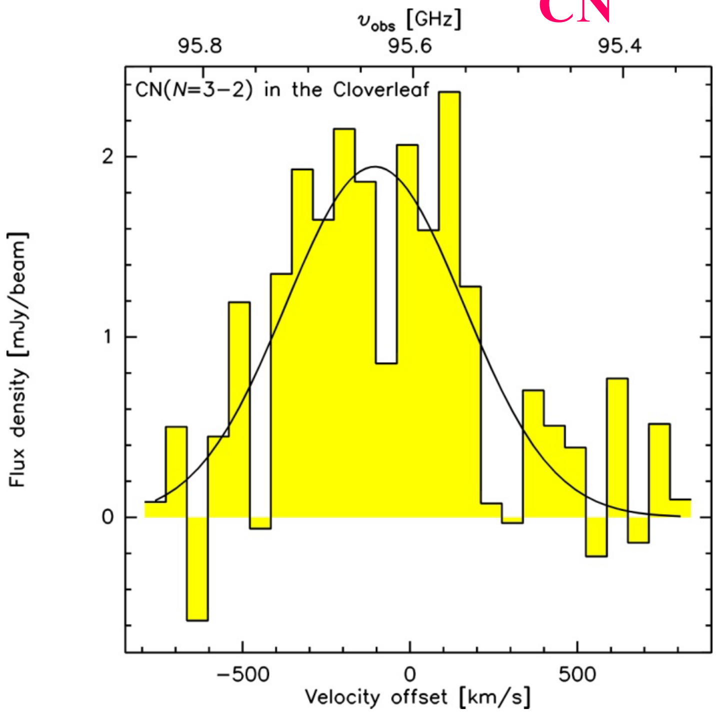
Walter et al. 2003, Maiolino et al. 2005

HCO^+, CN at high z

HCO^+



CN

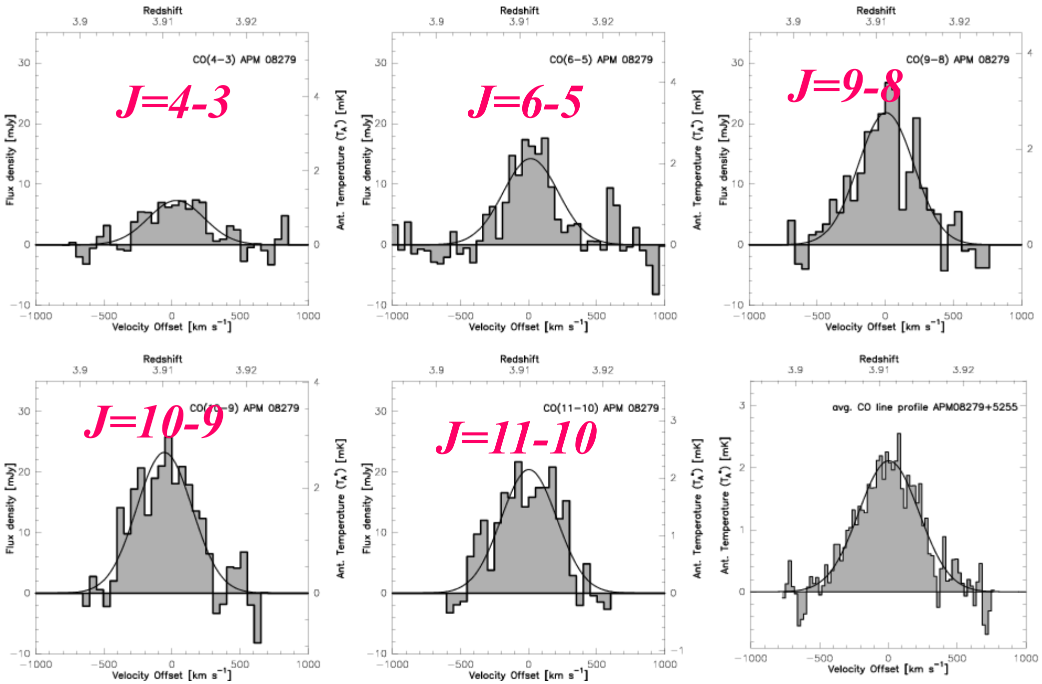


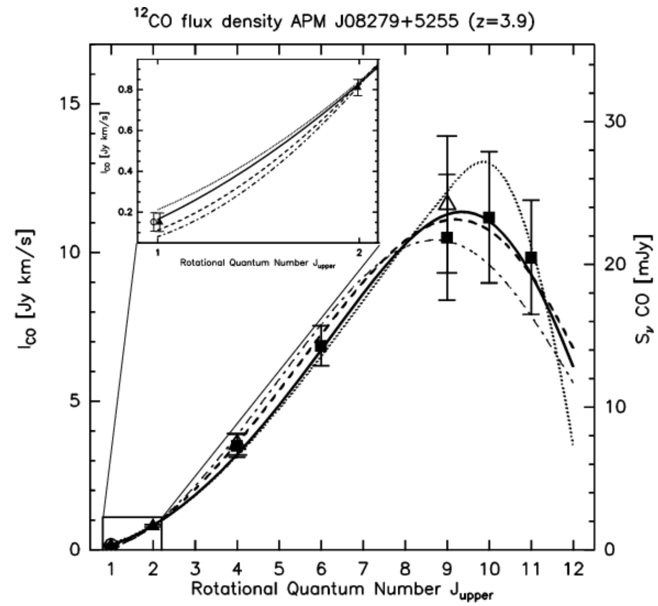
Riechers et al. 2007a,b

- Detection of HCO^+ and CN toward Clover Leaf quasar at z=2.56 (lensed system => signal enhanced)
- Both lines require high densities 10^5-10^6 cm^{-3} for excitation

CO excitation at high z

APM 0827+5255 z=3.9

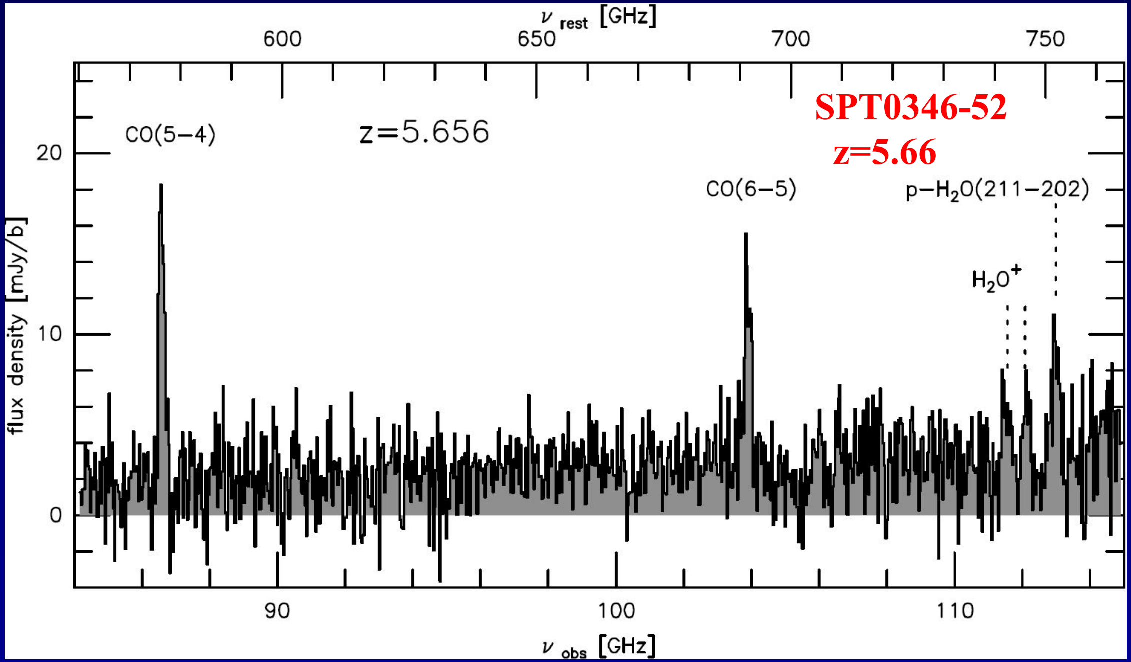




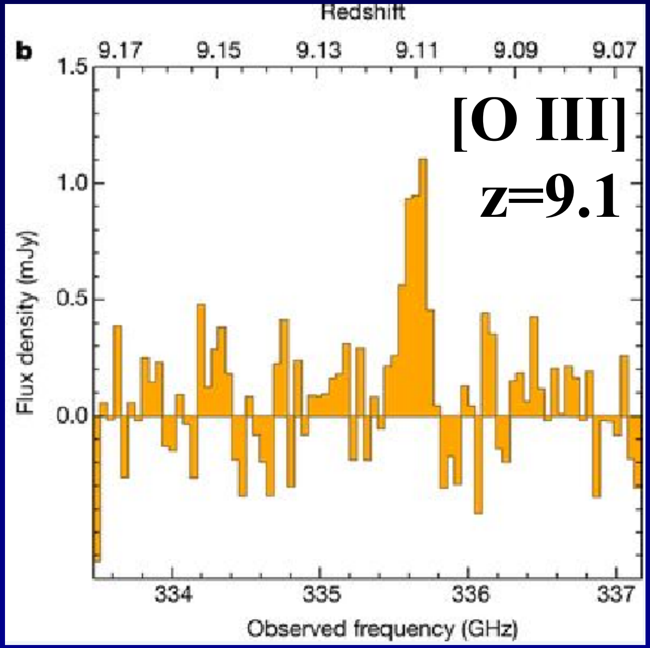
Weiss et al. 2007

- CO 4-3 up to 11-10 detected at z=3.9
- Excitation best fit by two components:
  - Cold: T~65 K, n=10^5 cm^{-3}
  - Warm: T~220 K, n=10^4 cm^{-3}

ALMA: Water, CO in high-z galaxies



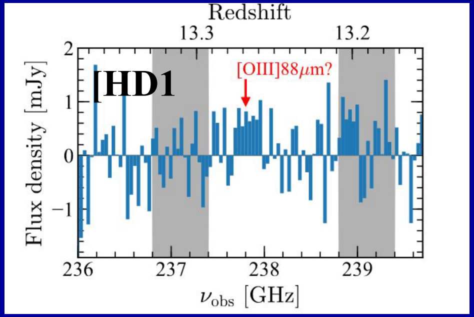
Weiss et al. 2013



Hashimoto et al. 2018

- [O III] 88 μm at z=9.1
  (and perhaps at z=13.2)
- H_2O and H_2O^+ at z=5.7

Harikane et al. 2022



Summary Lecture 3

- Write down your own summary points here