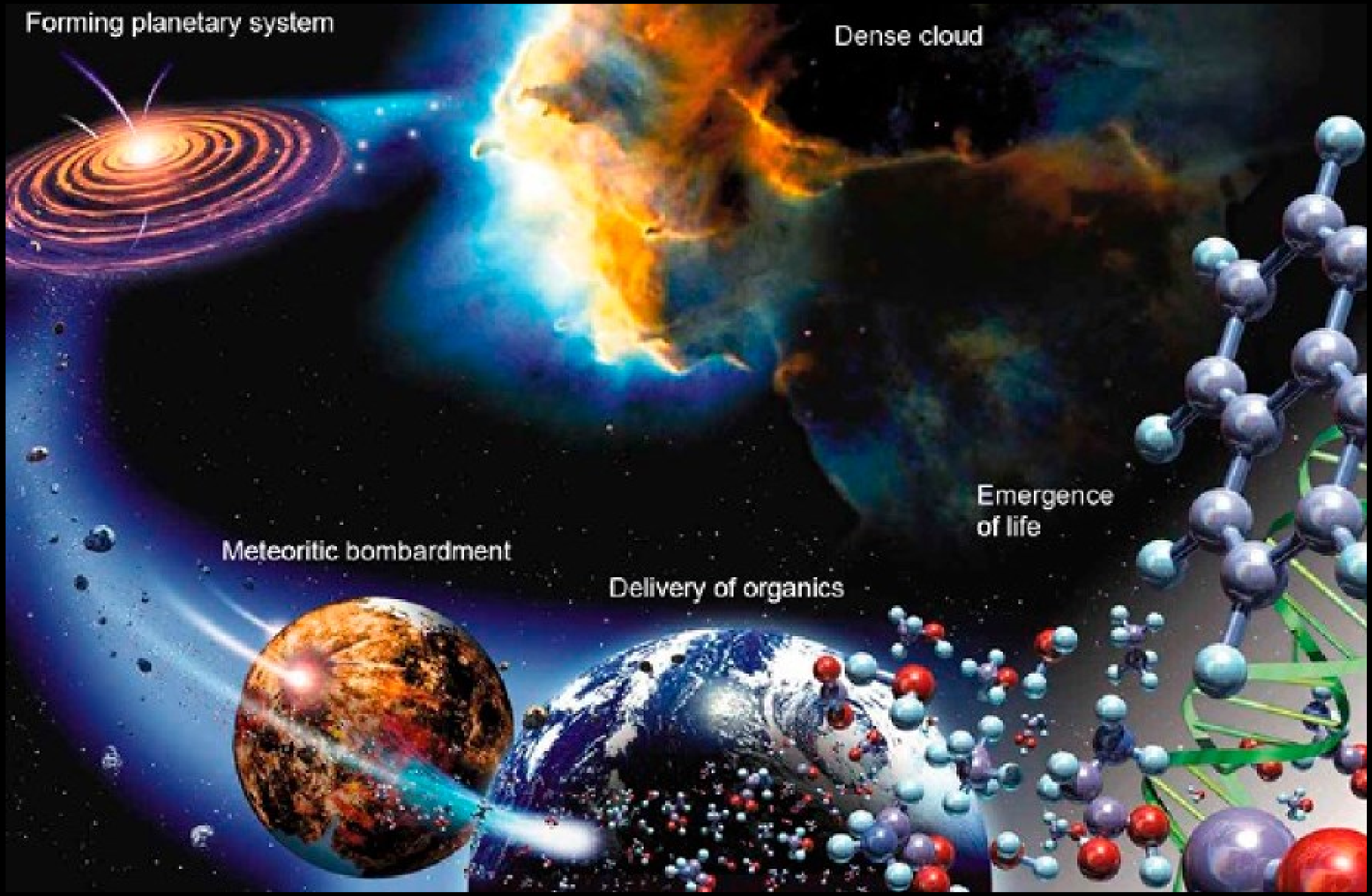
Master course: Astrochemistry I:

Lecture 3: Early Universe chemistry

Reading list:

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

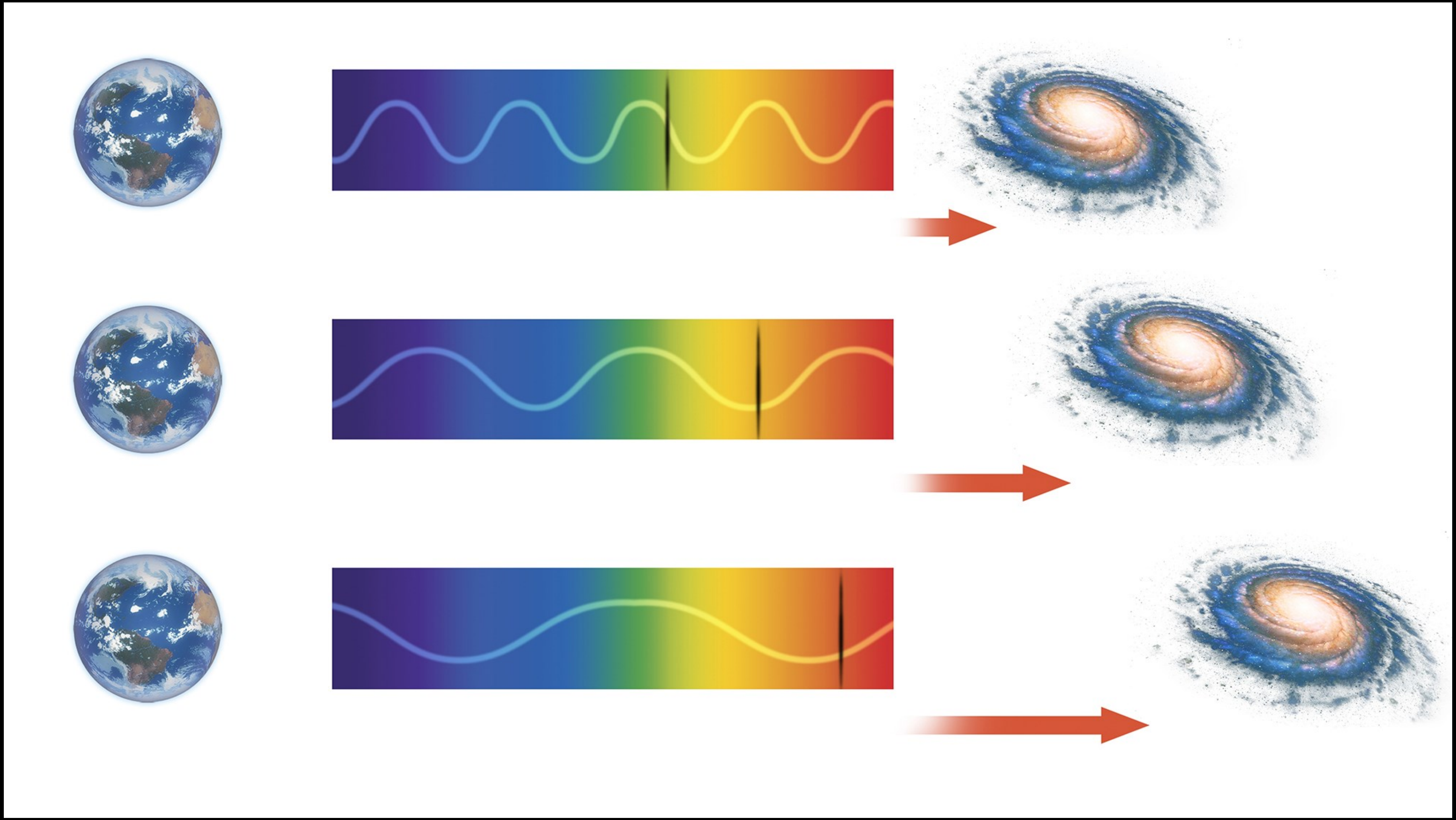


Dr. Helgi Rafn Hrodmarsson – UPEC – 2026-2027

Outline

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

3.0 Pre-Introduction – redshift (z)



3.0 Pre-Introduction – redshift (z)

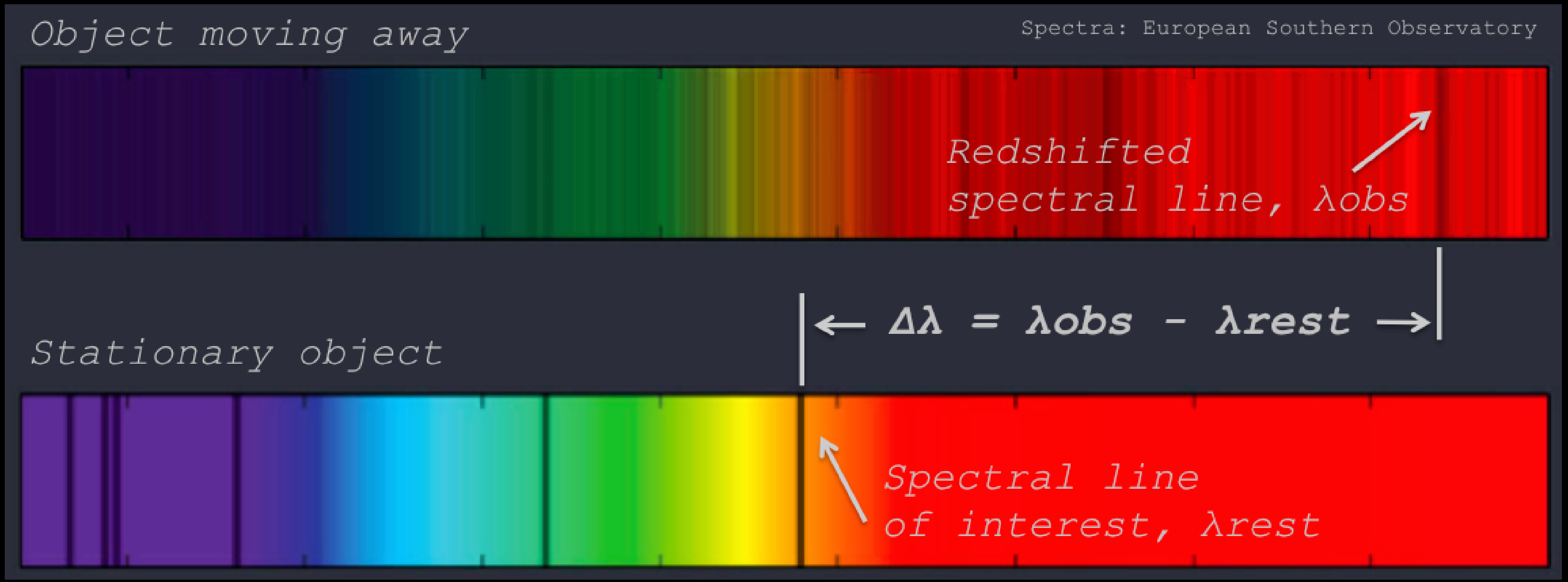
- Redshift (z) definition:

Also slides 68-69 in Lecture 1

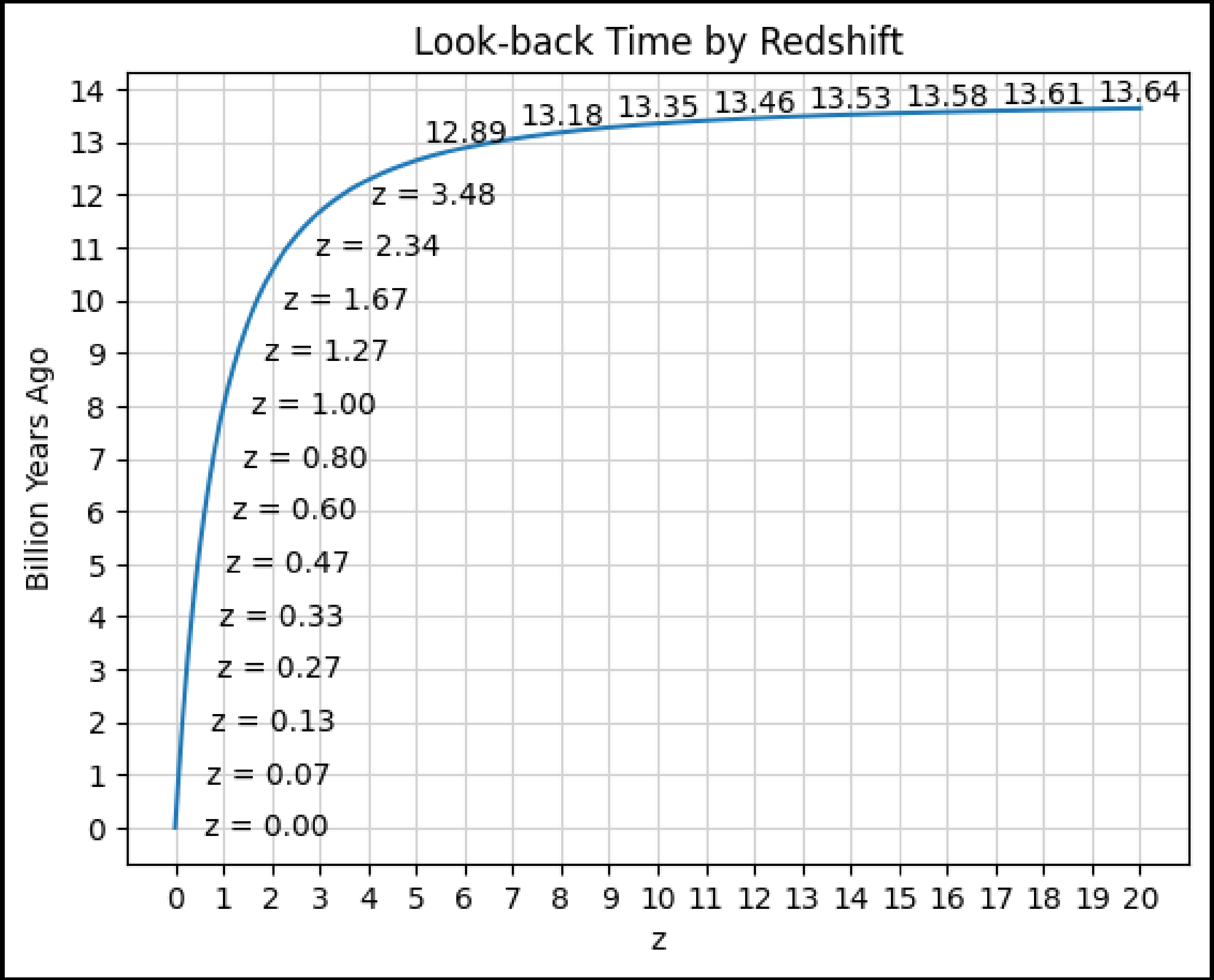
$$z = \frac{\lambda_{observed} - \lambda_{rest}}{\lambda_{rest}} = \frac{\Delta\lambda}{\lambda_{rest}}$$

$$1 + z = \frac{1}{\sqrt{1 - v^2/c^2}}$$

- Larger redshift = object further away = older



3.0 Pre-Introduction – redshift (z)



3.1 Introduction

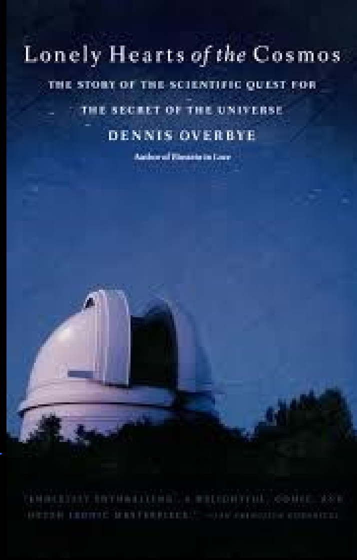
- Chemistry in the early universe is interesting because
  - Chemistry is simple: only H, D, He, Li, ***no dust***
  - First molecules may have had profound effects on the thermal properties of matter due to their cooling => collapse and fragmentation
  - Atoms and molecules observed in high-z galaxies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

3.2 Intro to cosmology

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)

- Consider the ‘standard’ Big-Bang model dated 1990

Cosmology (continued)



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

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

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

z = redshift
Ω_b = baryon mass density parameters
H_0 = current expansion rate of universe in km s^{-1} Mpc^{-1} 'Hubble parameter'

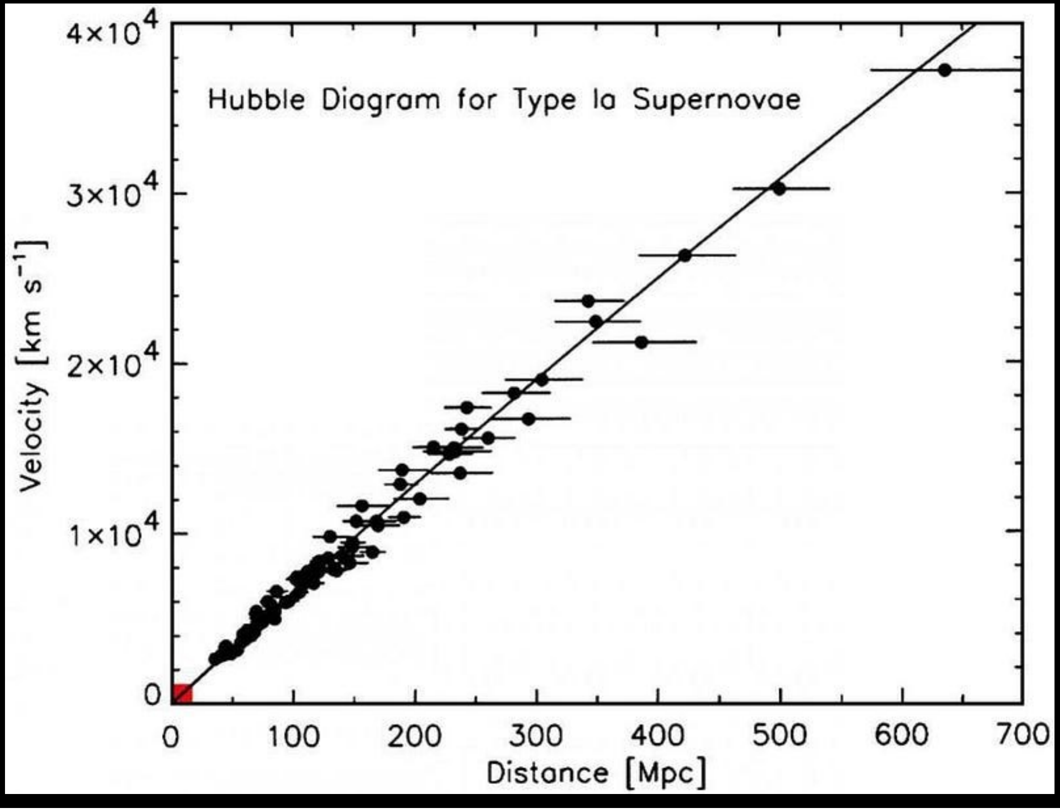
- Note: cosmological parameters recently updated but basic conclusions unchanged

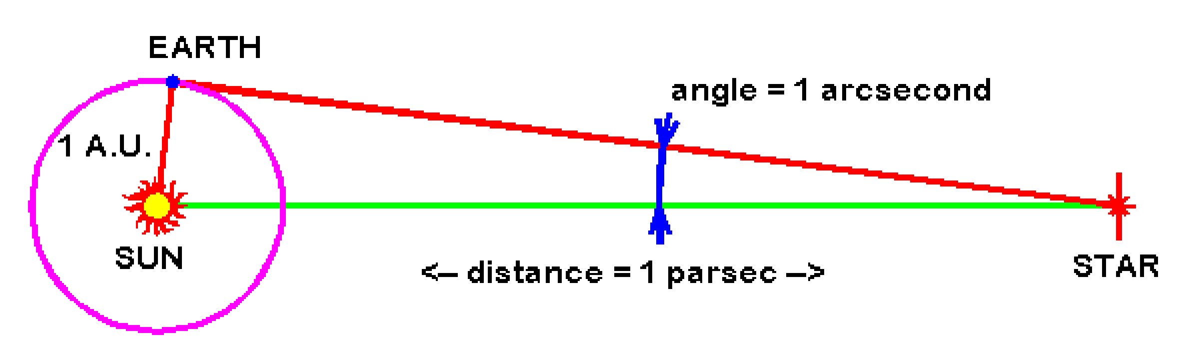
$$n_b \approx 2.2 \times 10^{-7}\,(1+z)^3\ cm^{-3}$$

Small exercise – Age of the Universe

- Given H_0 = 73 km/s/Mpc
- pc = 31 x 10^{12} km

- Find the "Hubble time" ($1/H_0 = t_H$)
- "Age of the Universe"





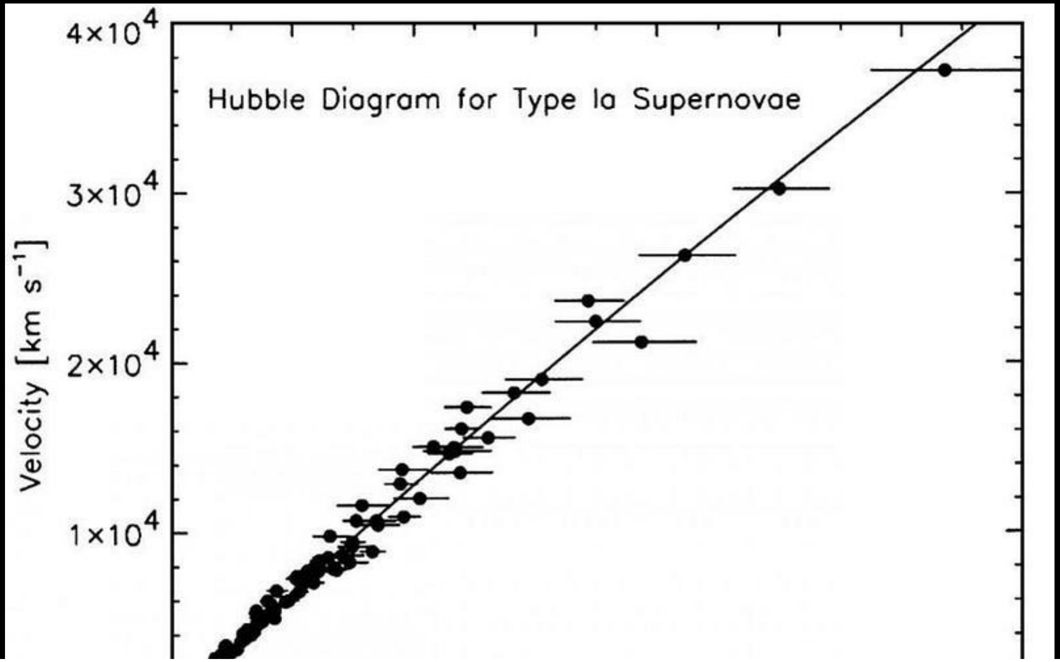
Small exercise – Age of the Universe

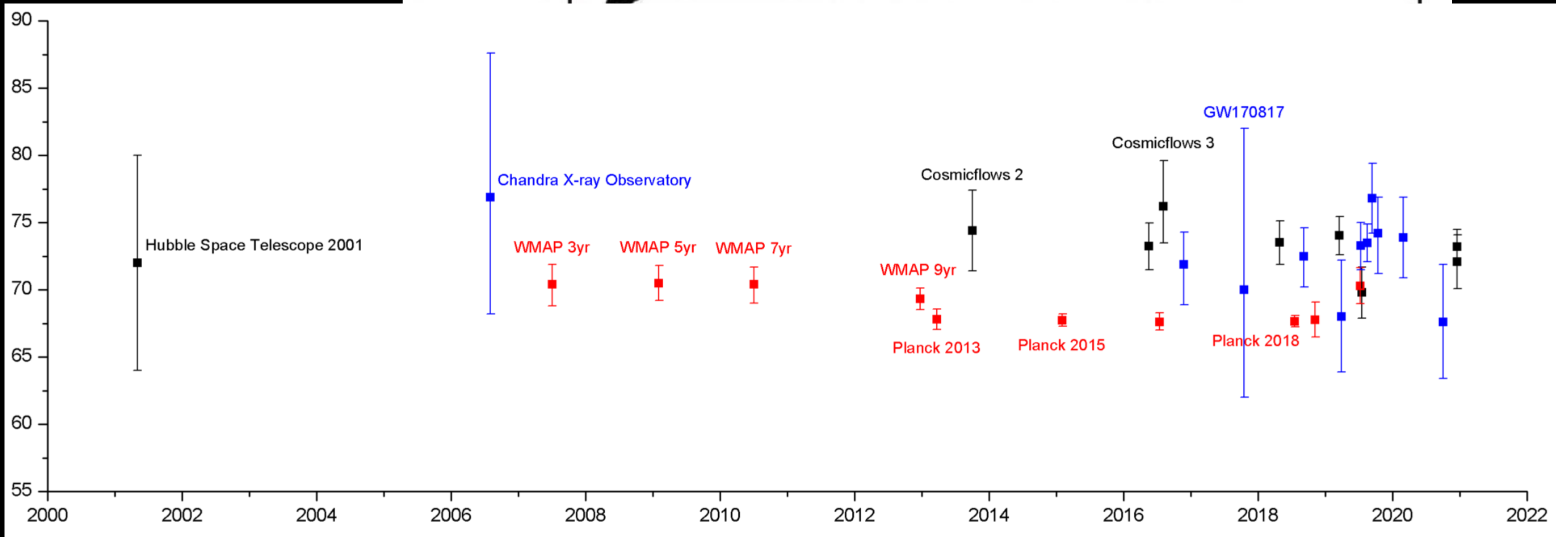
- Given $H_0 = 73$ km/s/Mpc
- pc = 31 x 10^{12} km

- Find the "Hubble time" ($1/H_0 = t_H$)
- "Age of the Universe"

- $t_H \approx 13.5$ billion years

- H_0 reevaluated regularly





Cosmology (continued)

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

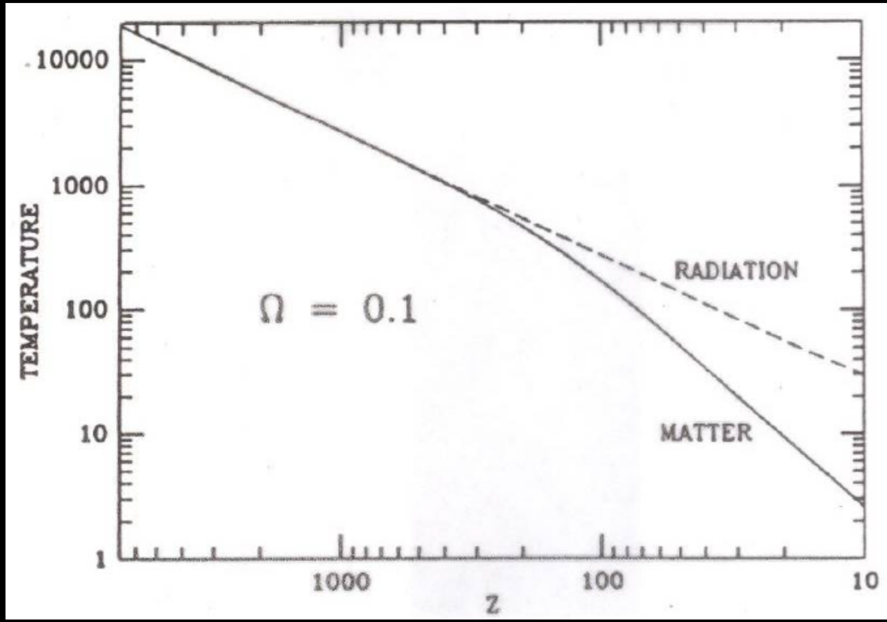
  H : D : ^{4}He : ^{3}He : ^{7}Li

  $1 : 2.6\times10^{-5} : 8 \times 10^{-2} : 10^{-5} : 5 \times 10^{-10}$
- At end of nuclear era, all atoms fully ionized => all H in H^+, all He in He^{2+}, etc.
  - $H + h\nu \rightarrow H^+ + e^-$
  - $H^+ + e^- \rightarrow H + h\nu$
- 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)

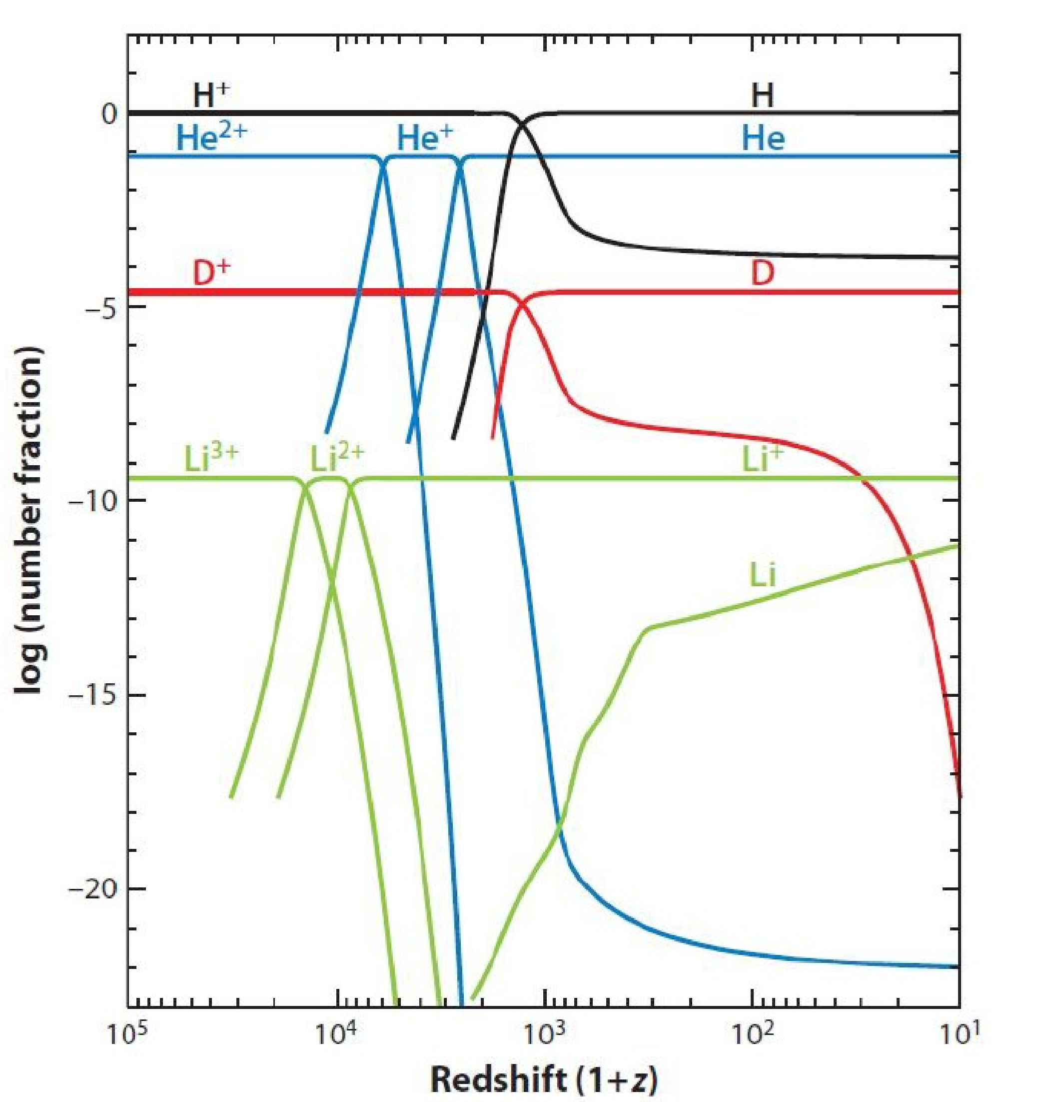
- => Universe becomes neutral: ***'Era of recombination'***

Cosmology (continued)

- 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

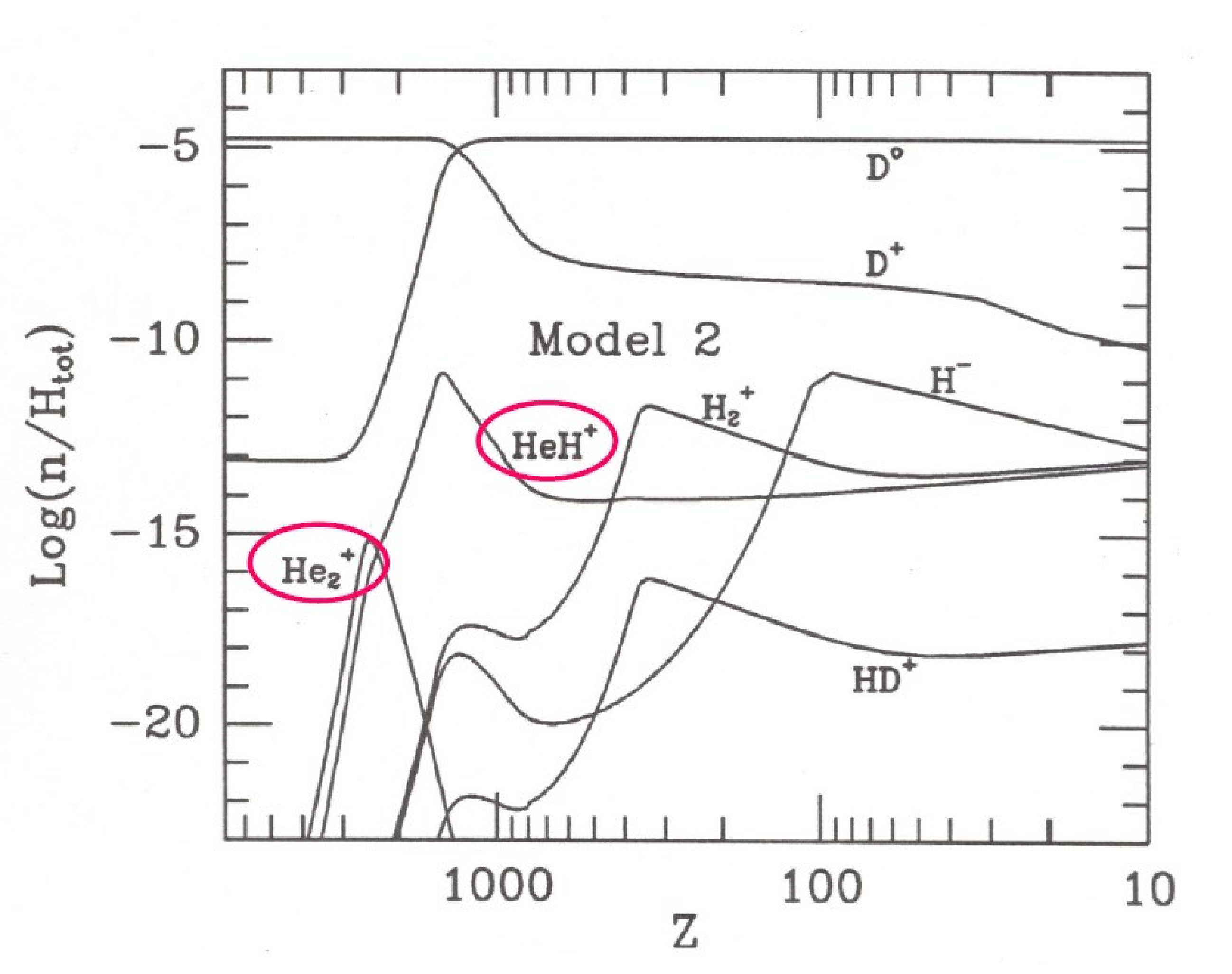
- Atoms sequentially recombine with z
- D^+ does not reach constant plateau due to $D^+ + H \rightarrow D + H^+$ (ΔH = -3.7 meV or 43 K)

3.3 Chemistry

a. He chemistry

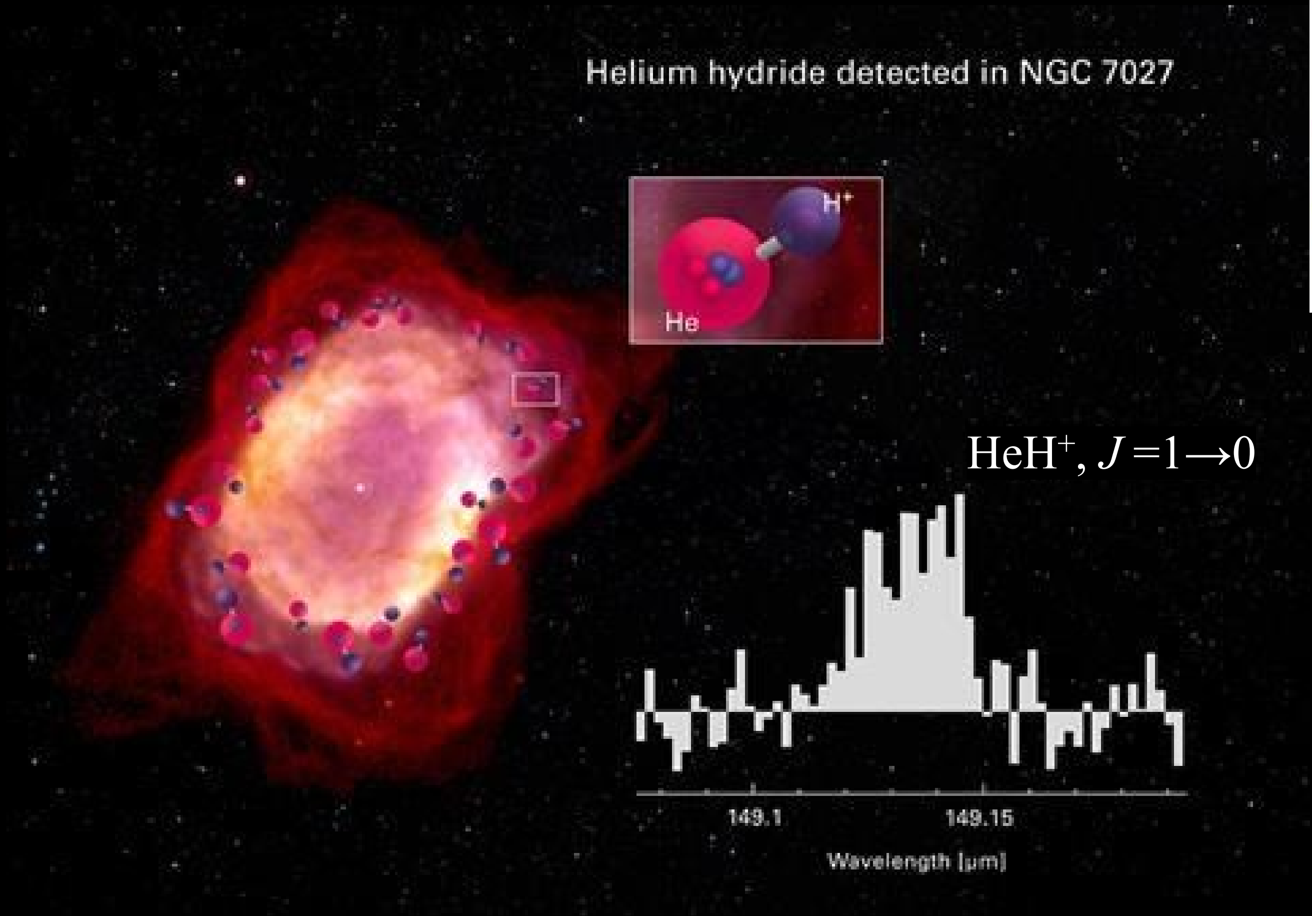
- He-bearing molecules form first, because He^{2+} recombines earlier than H^+
  - $He^{2+} + e^- \rightarrow He^+ + h\nu$
  - $He^+ + e^- \rightarrow He + h\nu$
- The first molecules in the universe were He_2^+ and HeH^+, formed by radiative association
  - $He^+ + He \rightarrow He_2^+ + h\nu$
  -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

First molecules in the universe: He^{2+} and HeH^+



Latter 1989

HeH^+ detection in planetary nebula

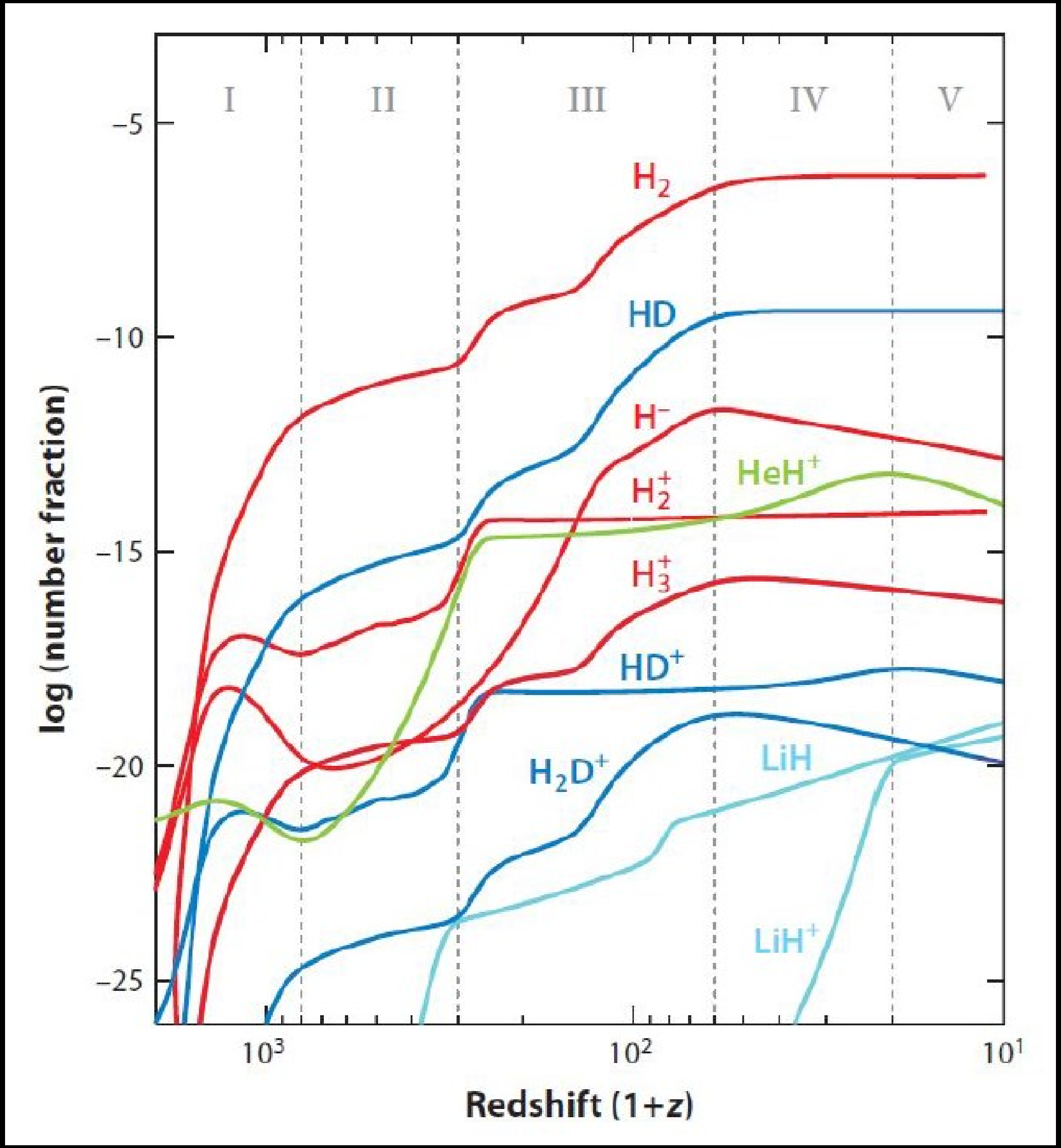


Not primordial HeH^+

But proves that chemistry is correct

Güsten et al. 2019, SOFIA

Formation of molecules



GP13

Chemistry (continued)

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 reaction
- 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
  - $H^- + h\nu \rightarrow H + e^-$

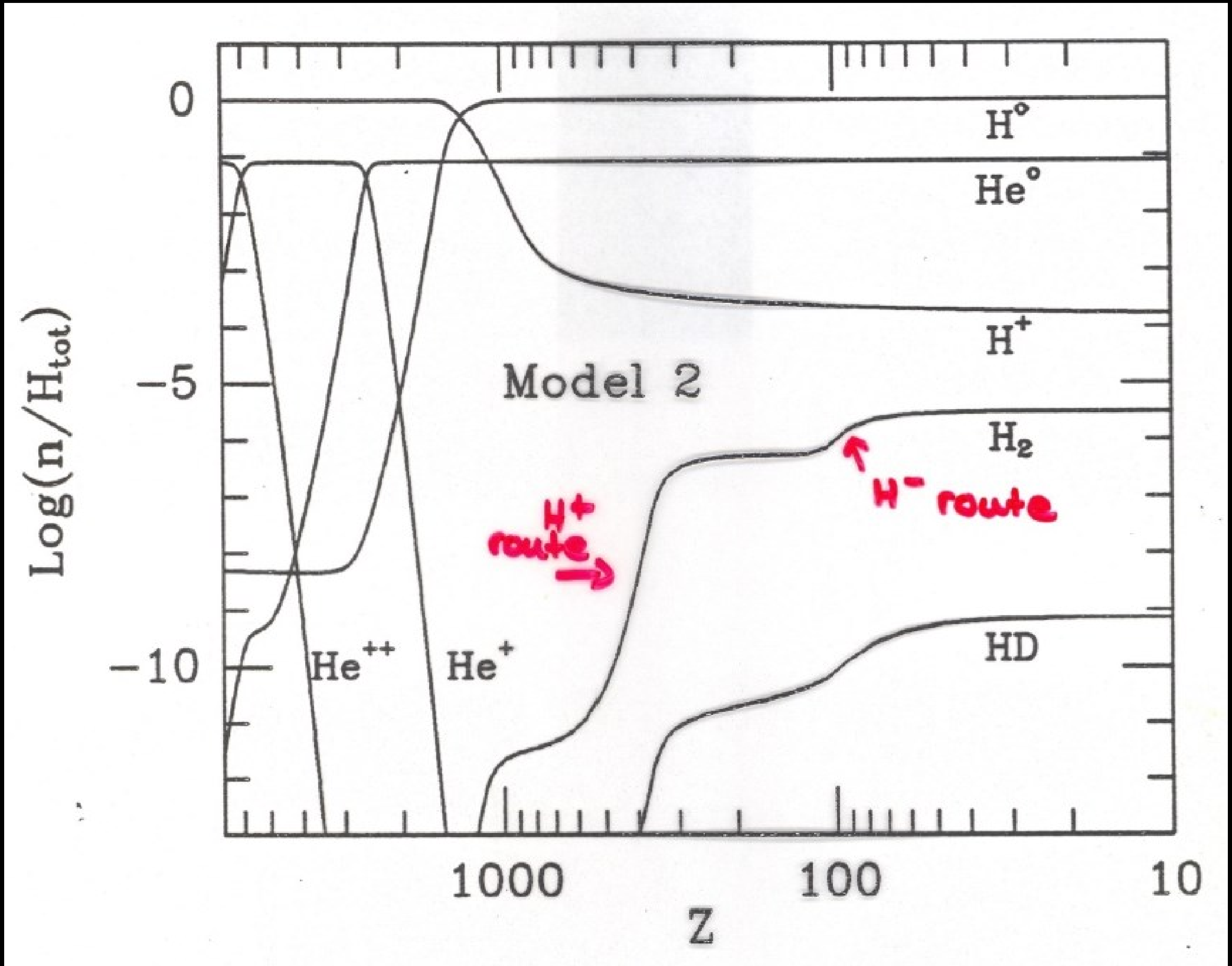
with threshold of 0.75 eV => need $T_R < 1000$ K before route becomes effective

H_2 Chemistry

- Both H^+ and H^- routes re-catalytic, since H^+ and e^- are returned
- H_2 destroyed by
  - $H_2 + H^+ \rightarrow H_2^+ + H$
  - $H_2 + e^- \rightarrow H + H^-$
- Net result: $\boldsymbol{f(\mathrm{H}_2) = n(\mathrm{H}_2)/n_\mathrm{H} \approx 10^{-6}}$ as $z \rightarrow 0$

Small molecular fraction in early universe

H_2 formation by H^+ and H^- routes

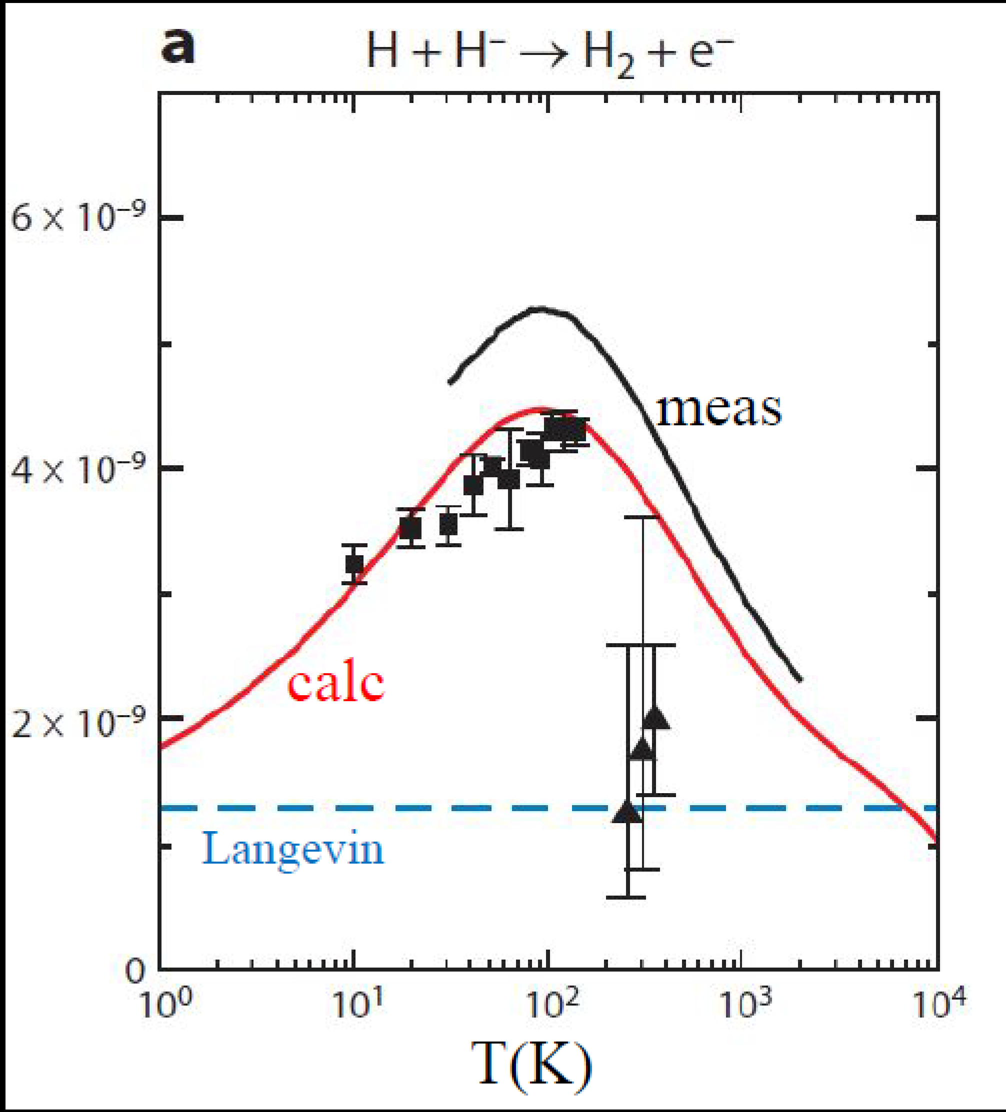


Latter 1989

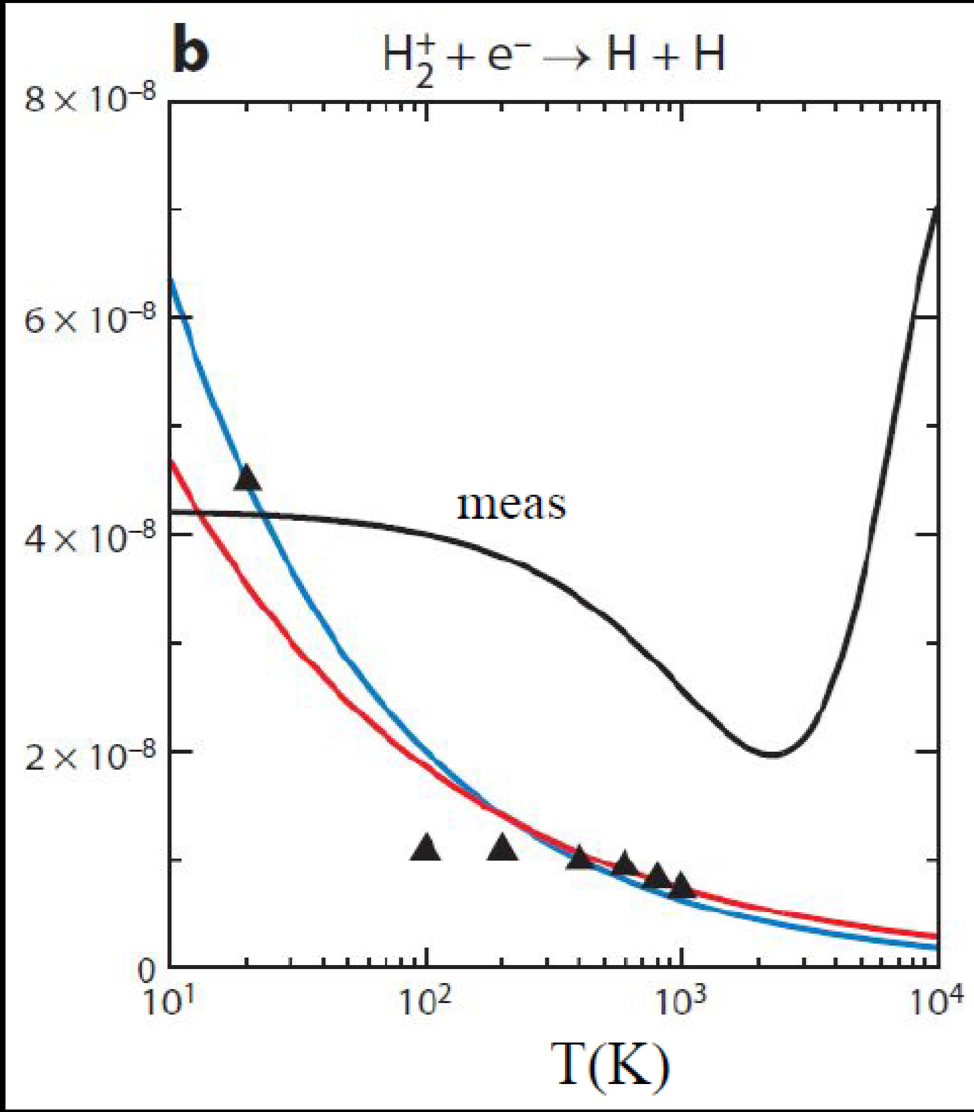
Later developments

- CMB field has non-thermal contributions 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 coefficient

Lab measurements – important rate coefficients



Gerlich et al. (2012), Bruhns et al. (2010)

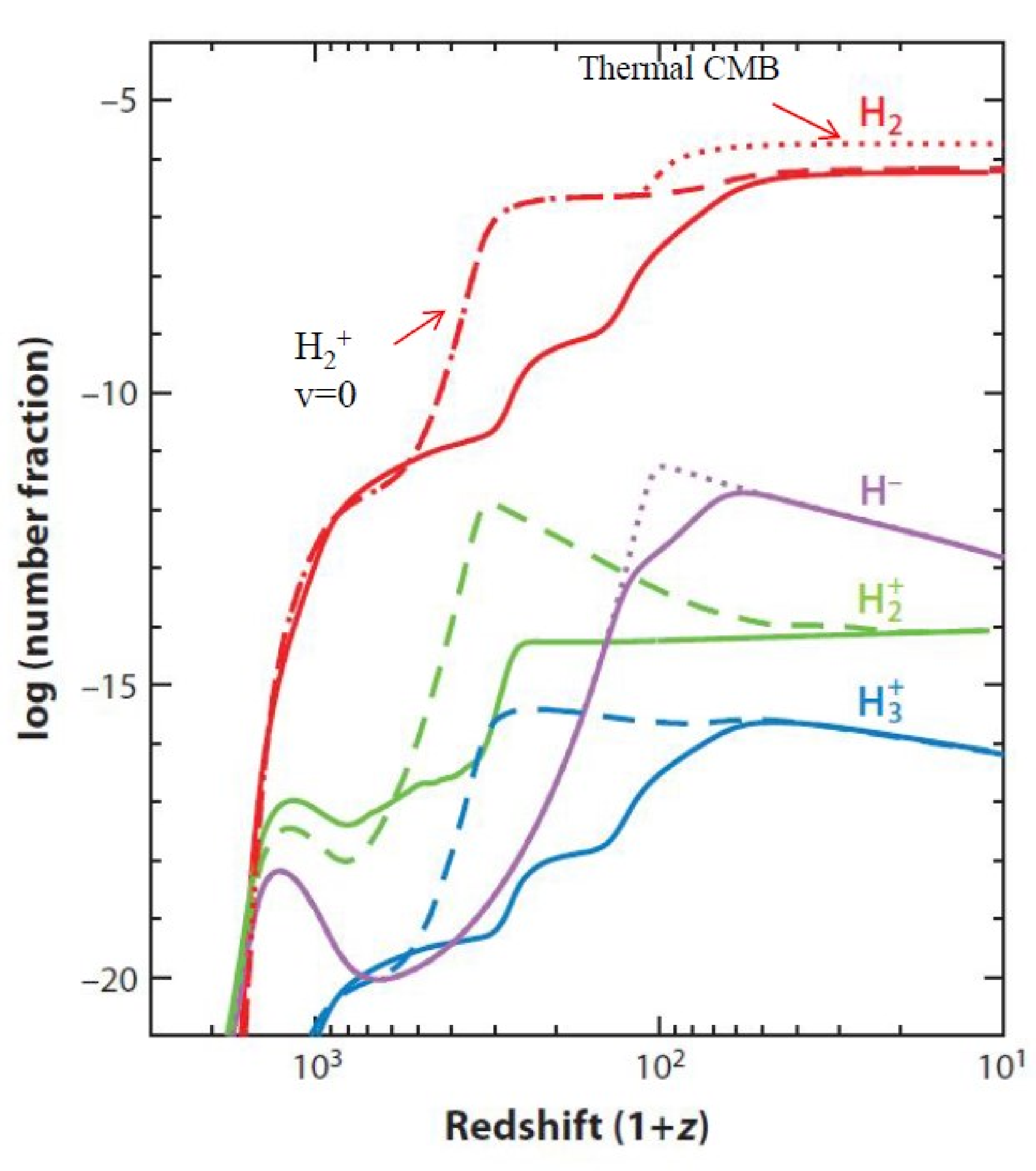


Schneider et al. (1994), Coppola et al. (2011)

GP13

Hydrogen chemistry

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



GP13

Chemistry (continued)

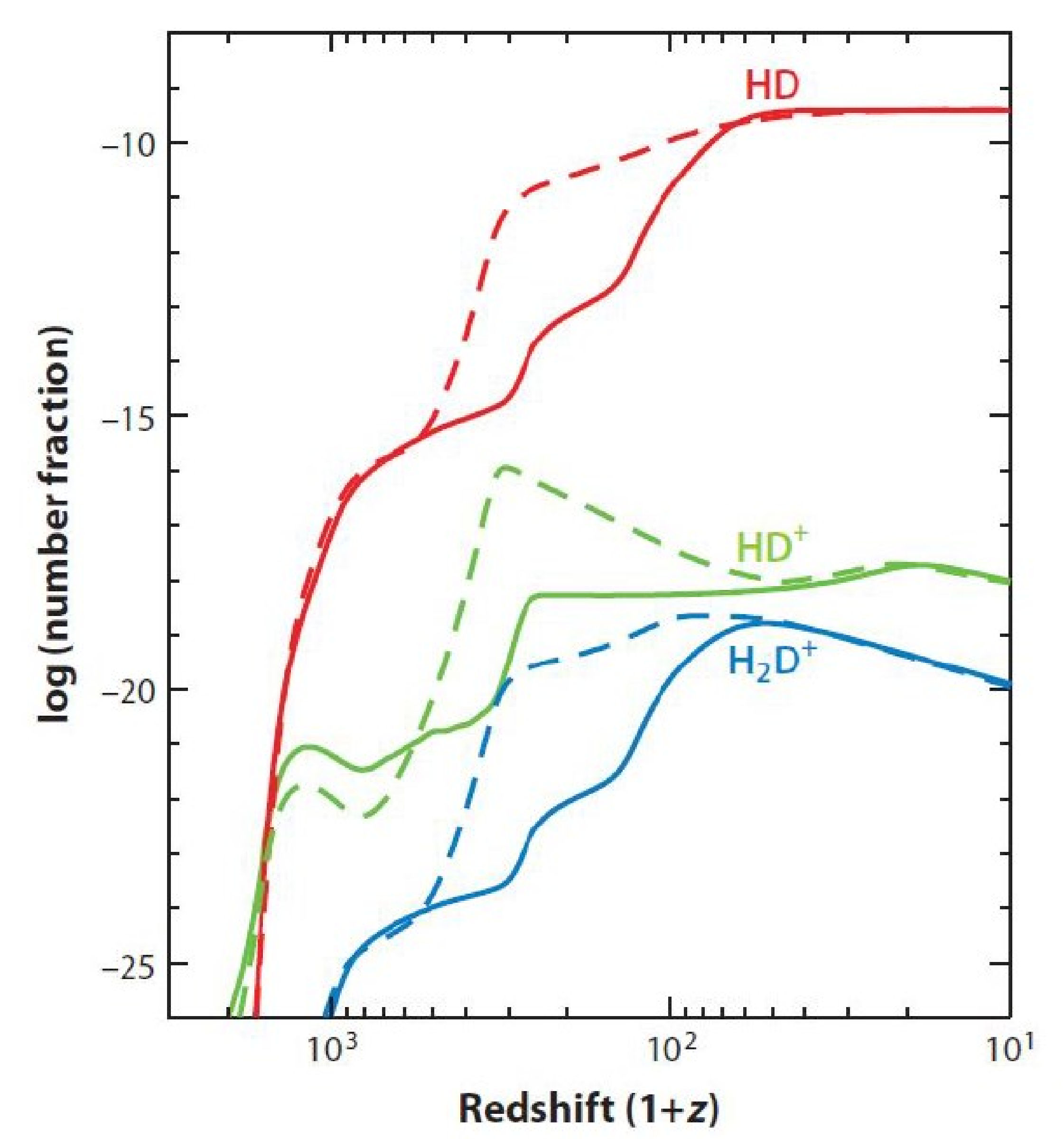
c. D chemistry

- 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

  => $f(\mathrm{HD}) \approx 10^{-10}$–$10^{-9}$

Deuterium chemistry

Dashed: neglect H_2^+ ($v > 0$)



GP13

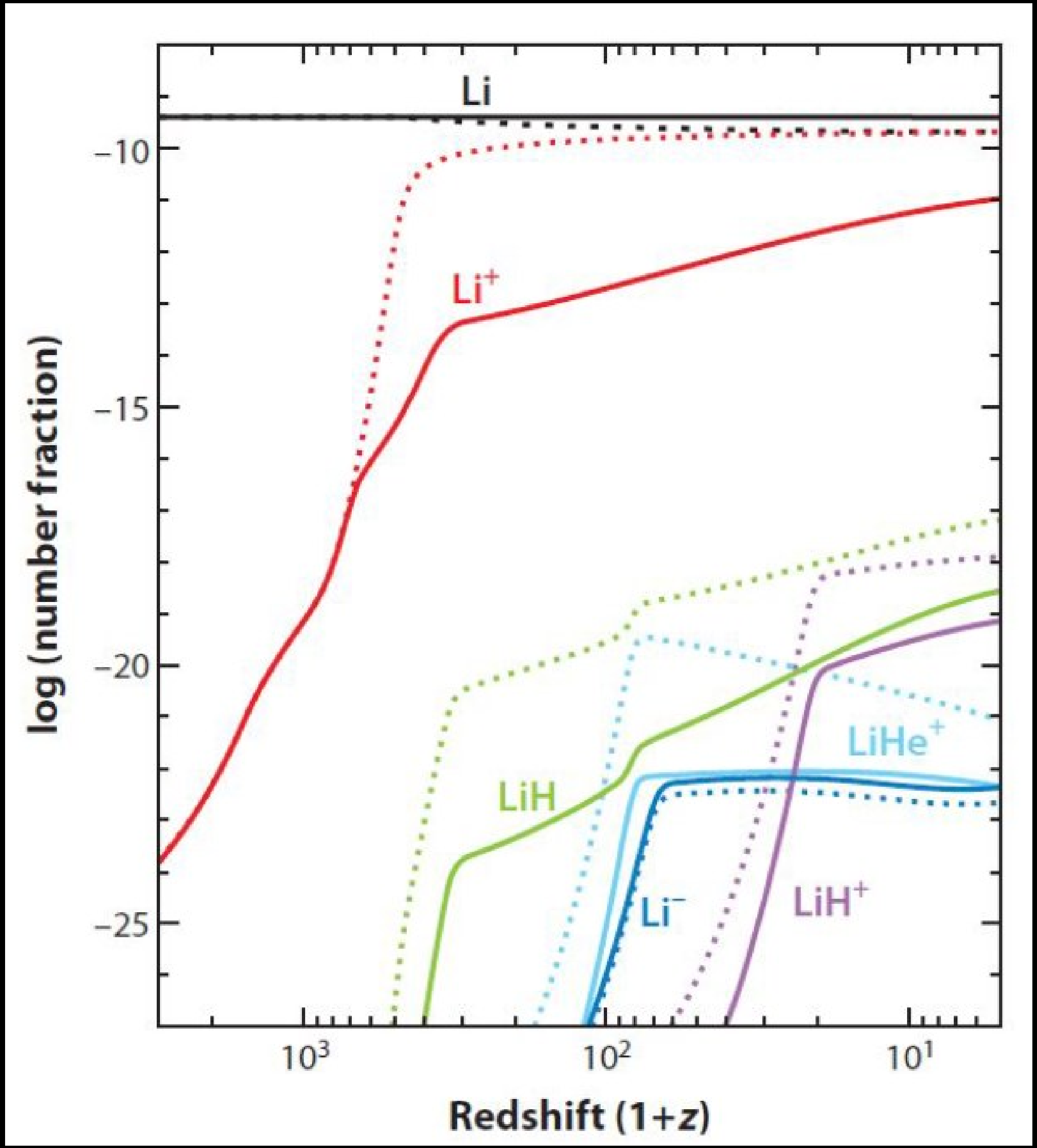
Chemistry (continued)

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
  - $LiH + H \rightarrow Li + H_2$

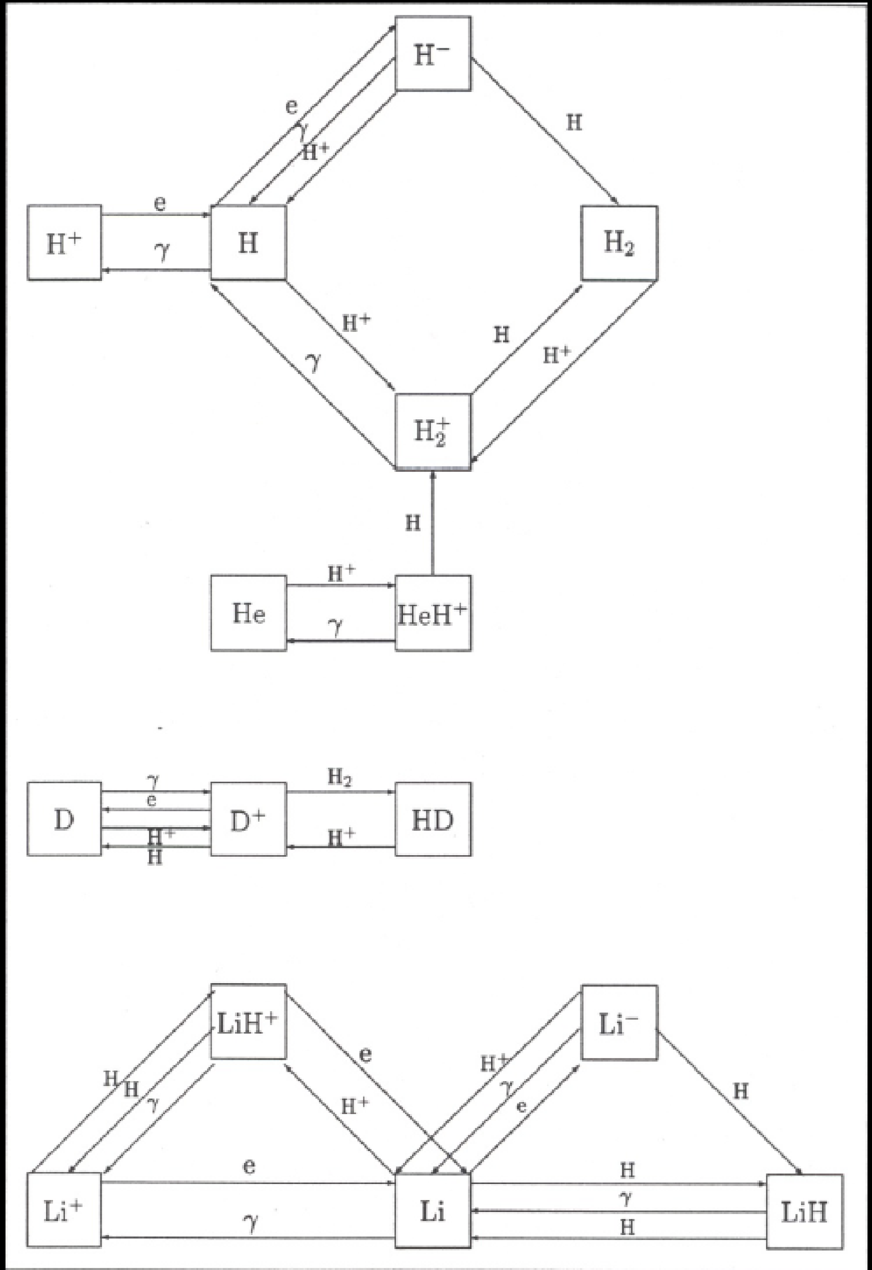
Lithium chemistry

Dotted: neglect non-thermal CMB photons



GP13

Summary of principle processes

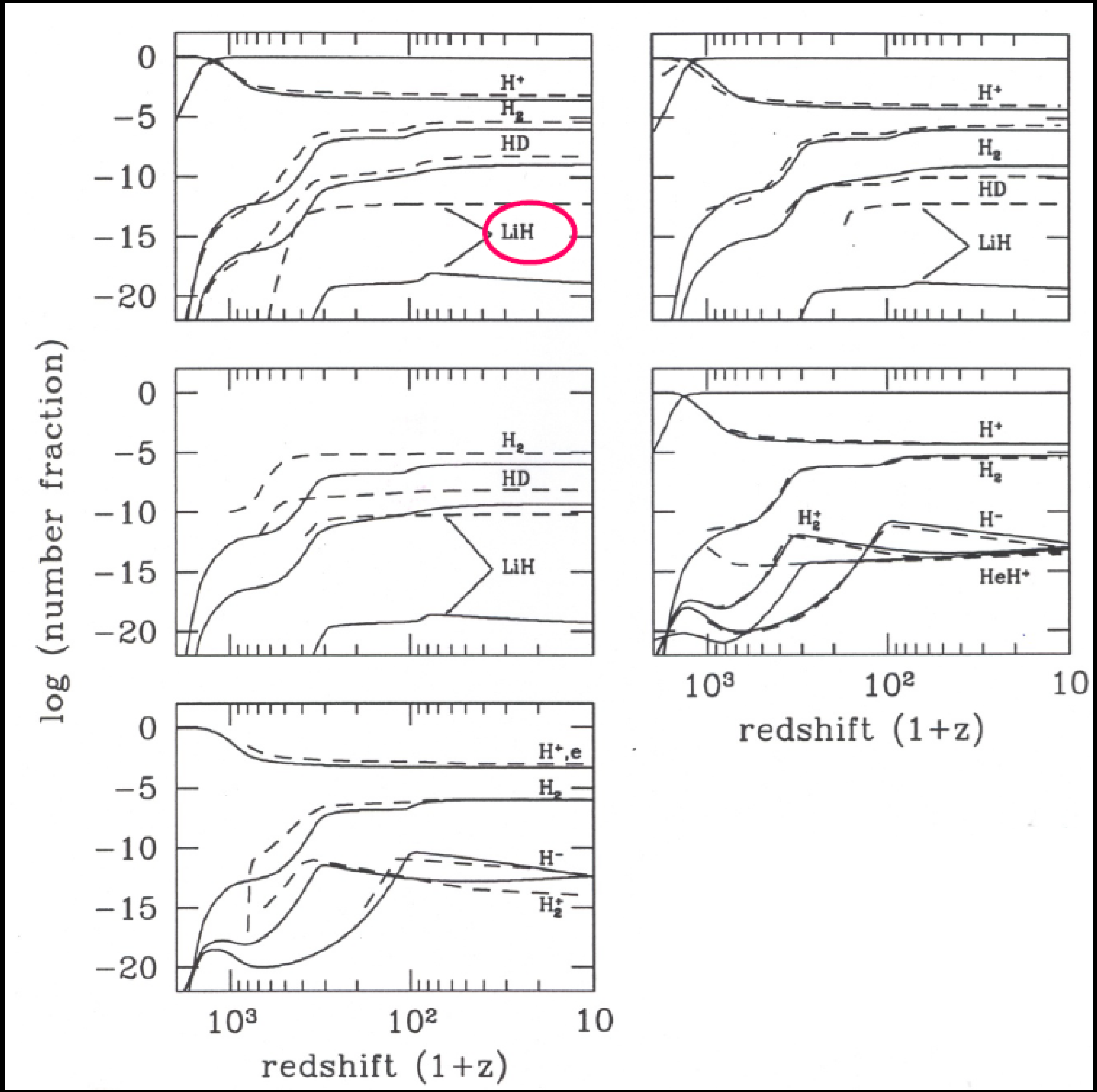


Galli & Palla 1998

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



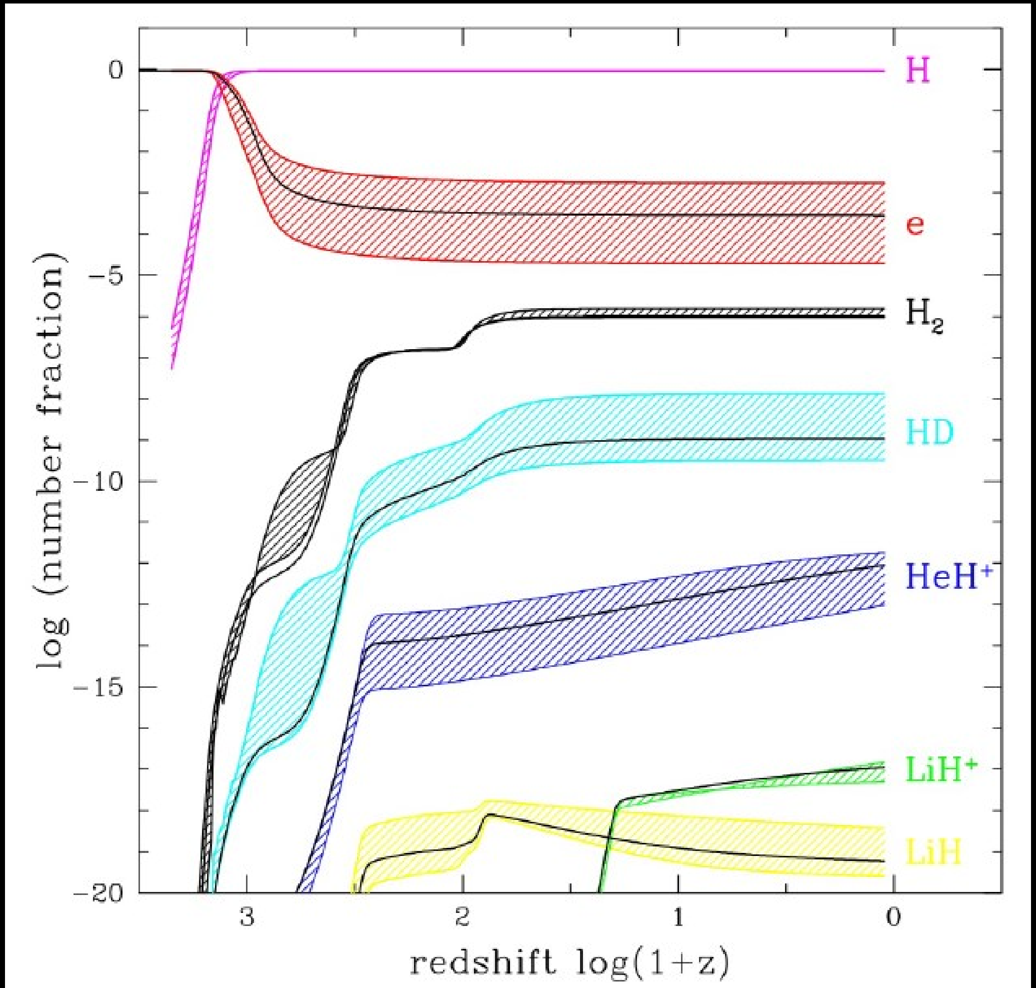
GP98 vs Black

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

Note discrepancy LiH

Galli & Palla (1998)

Sensitivity to cosmological parameters



GP98

- Shaded area covers range of variation of $\Omega_0 = 0.1–1$, $h = H_0/100 = 0.3–1$ and η_{10} = baryon/photon = 1–10
- Cosmological parameters now well determined so no longer an issue

3.5 Molecular cooling and cloud collapse

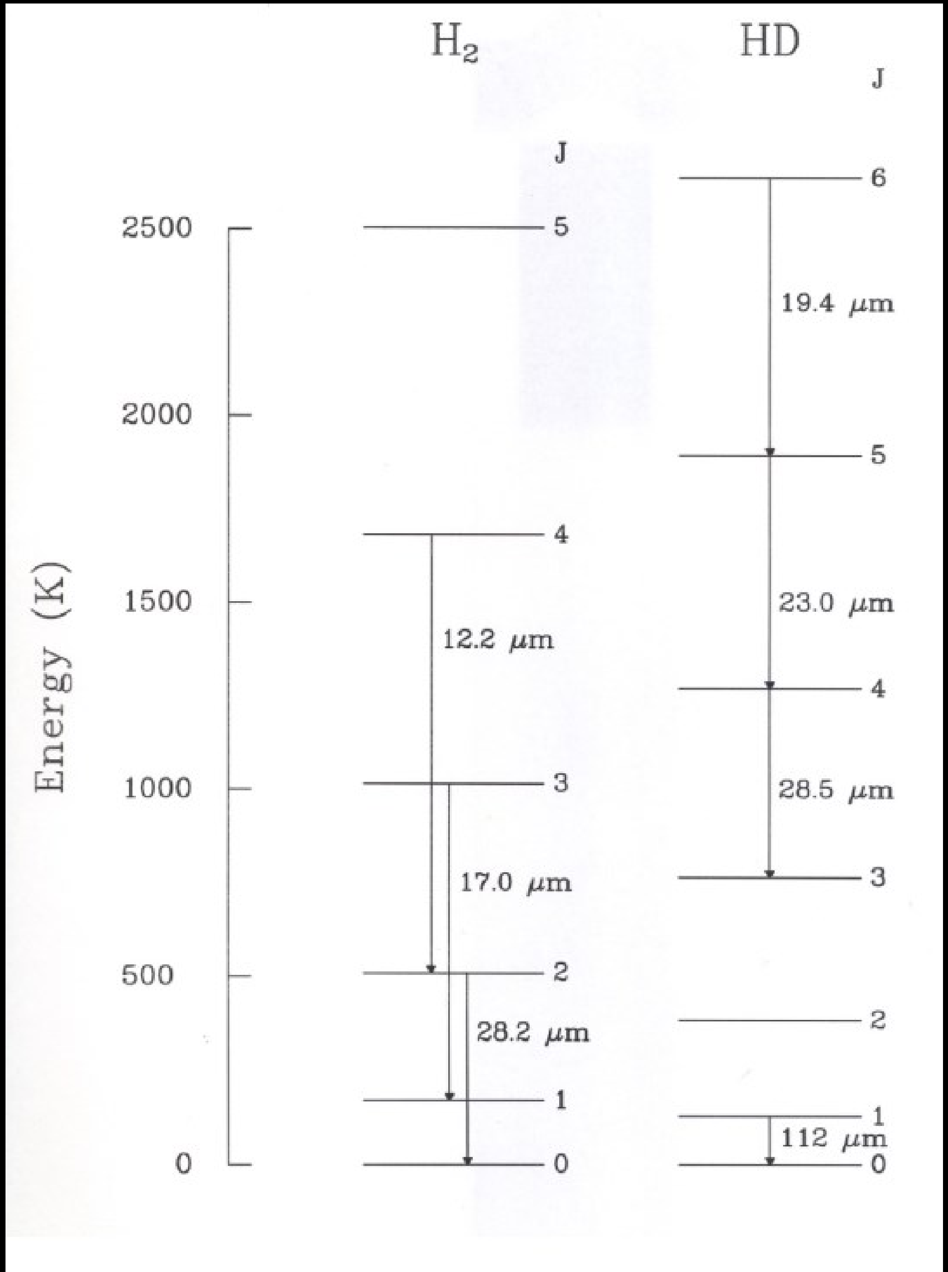
- Cooling universe is dominated by adiabatic expansion globally. Cooling by lines of atomic species, e.g.

  - H(1s) + H $\rightarrow$ H(2p) + H
  - H(2p) $\rightarrow$ H(1s) + $h\nu$ Lyman α

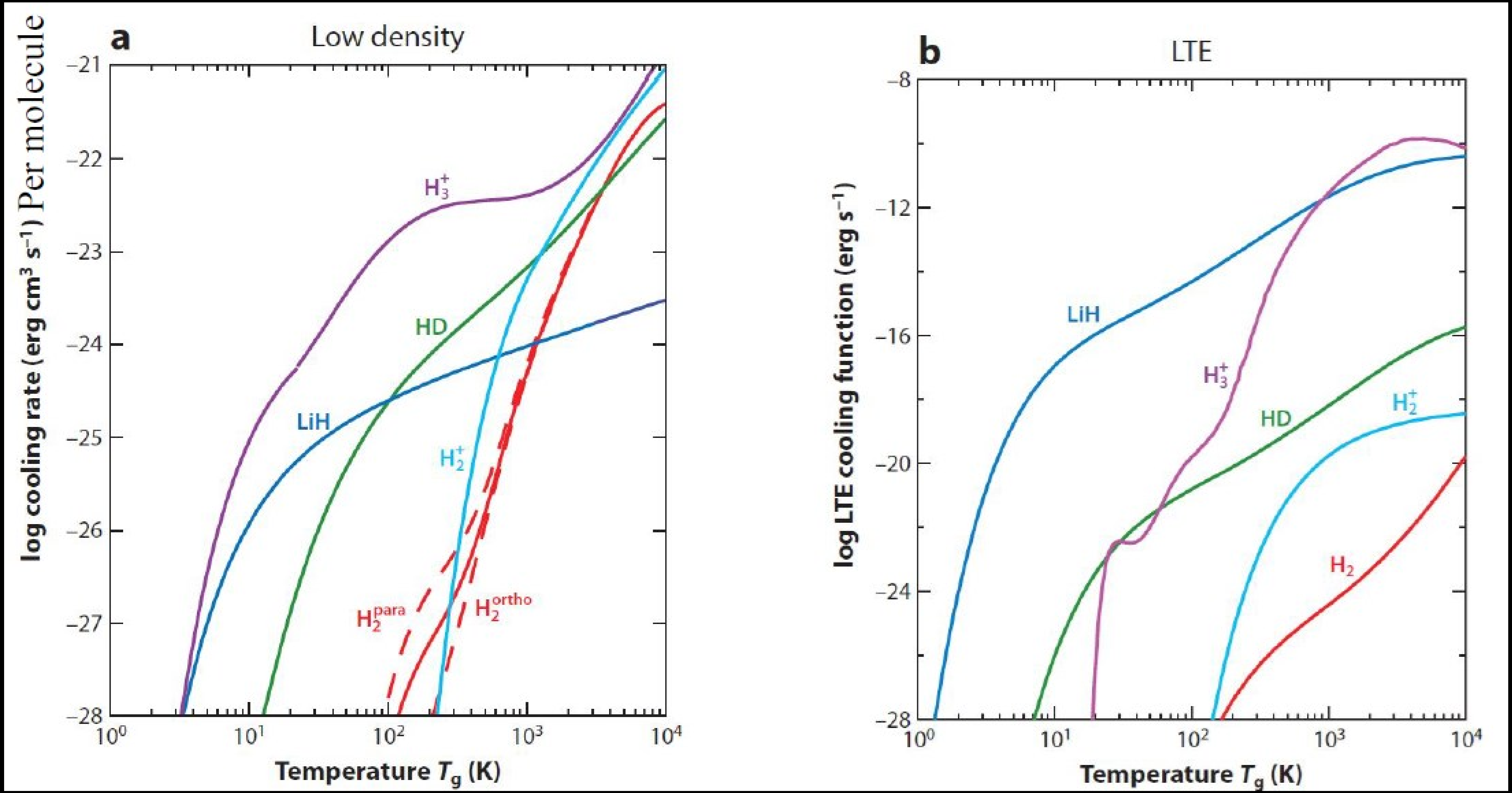
  is ineffective at $T_m < 10^4$ K

- 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 molecule abundance to get overall cooling rate.

Cloud collapse

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

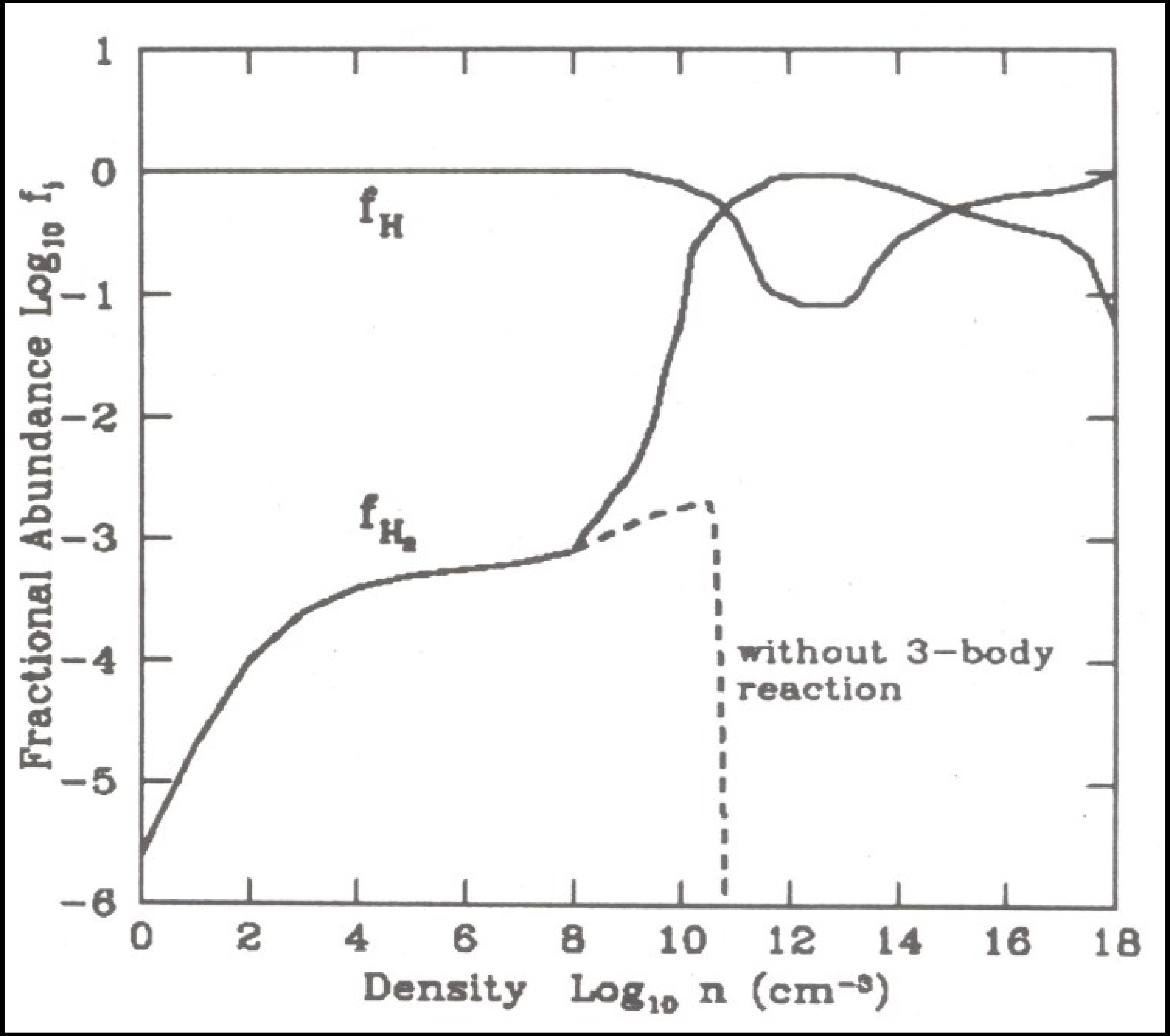
$$M_J \approx 60\, T_m^{3/2}\, n_H^{-1/2}\; M_\odot$$

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 $z = 10$

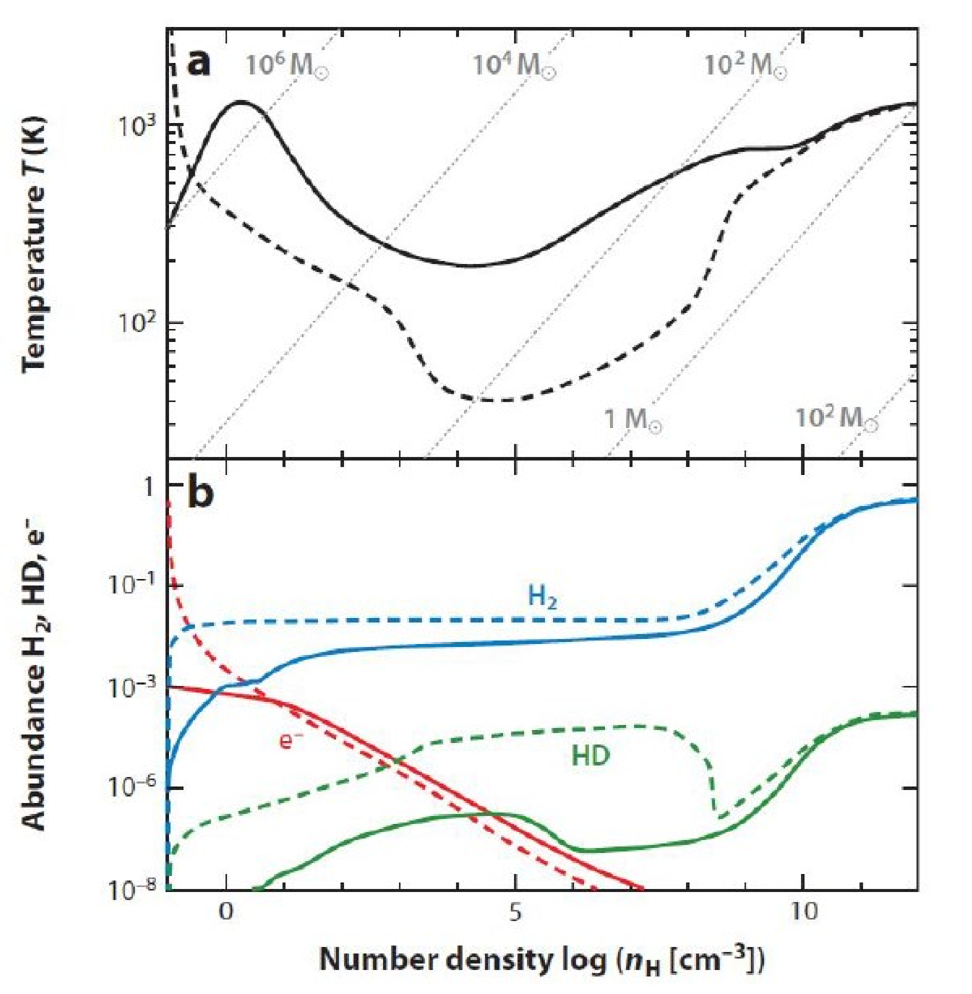
- Additional cooling due to molecules lowers T_m and thus M_J
  - Permits fragmentation and contraction to occur on smaller scales (down to $< 1\, M_\odot$)
- As density in condensations increases due to collapse, H_2 formation can be enhanced by 3-body processes
  - $\mathrm{H + H + H \rightarrow H_2 + H}$ $\quad n_H \geq 10^9\ \mathrm{cm}^{-3}$

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.

Later 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:

$$f_{H_2} \approx 2.2 \times 10^{-7} \left(\frac{h\Omega_b}{0.03}\right)^{-1} z_{100}^{-\frac{3}{2}} \left(1 + \frac{10T_3^{\frac{7}{2}}}{60 + T_3^4}\right) e^{\frac{512}{T}} \approx 5 \times 10^{-4}$$

‘rule of thumb’

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

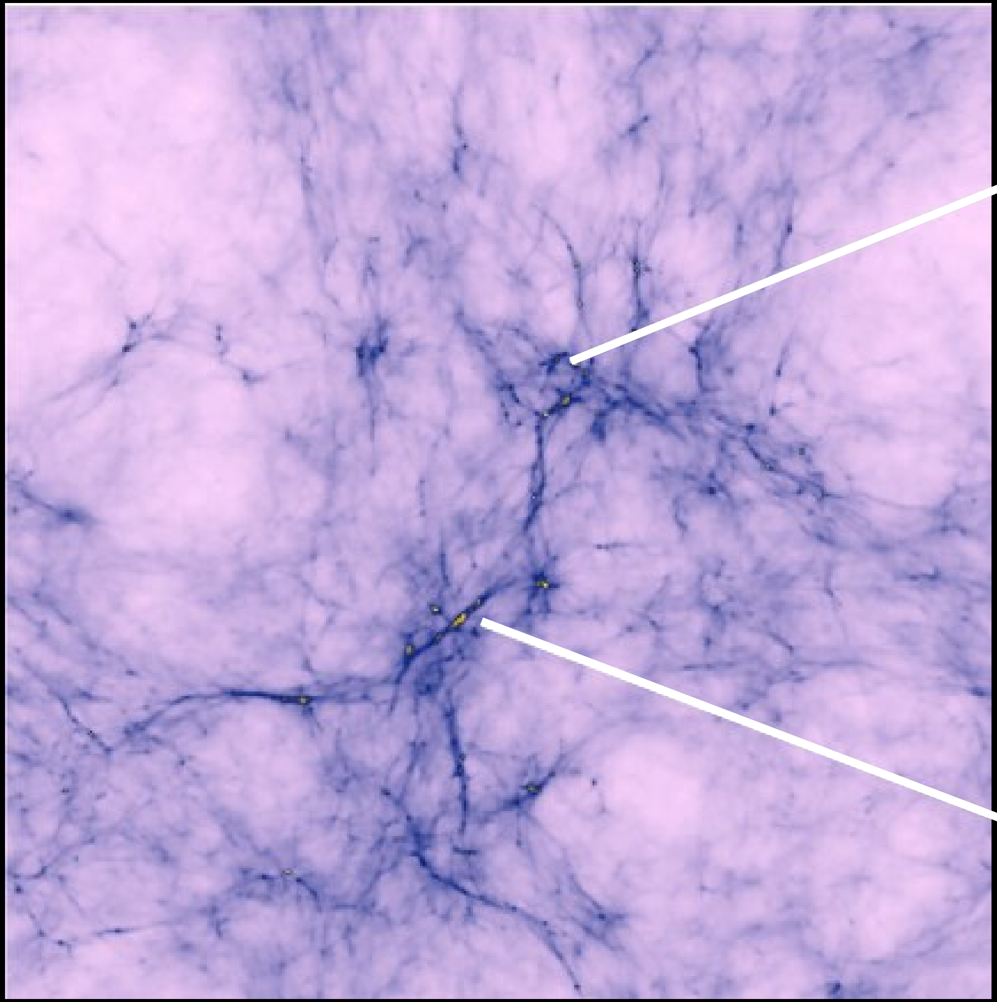
- Work by Tegmark et al. (1997), Abel et al. (1997), Bromm et al. (2002), Yoshida et al. (2003), and many more

End of dark ages and onset of star formation if

$t_{\text{cool}} \ll t_{\text{Hubble}}$

=>The role of H_2 and HD within first structures

Projected gas distribution at z = 17



Yoshida et al. 2002

<u>Mini-halos</u> $M \sim 10^6\, M_\odot$ $z = 20 – 30$

$T_{\text{vir}} \ll 10^4$ K H_2 cooling

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

Positive feedback from X-rays, shocks, relic H II regions ...

Negative feedback from UV background

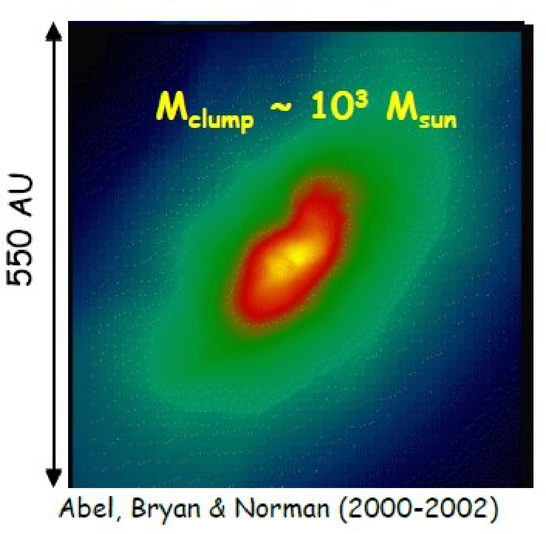
<u>Dwarfs</u> $M \sim 10^8\, M_\odot$ $z = 10 – 20$

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

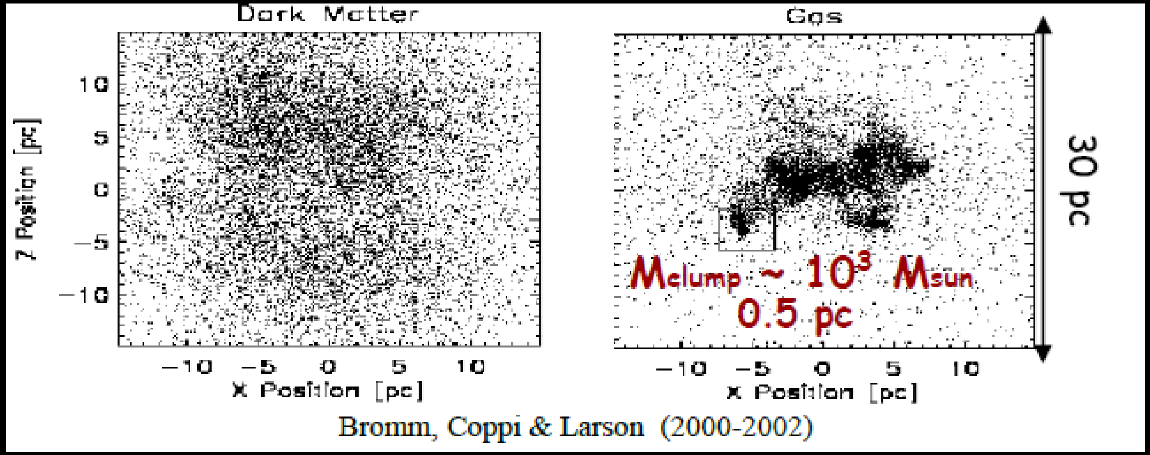
Pop III star formation in mini-halos

- 3D simulations: from cosmological initial conditions to molecular clouds

Adaptive Mesh Refinement



Smooth Particle Hydrodynamics



Convergence toward a regime with T_{cr} ~ 200 K and n_{cr} ~ 10^4 cm^{-3} <= H_2 properties

Fragmentation into protostellar clouds with

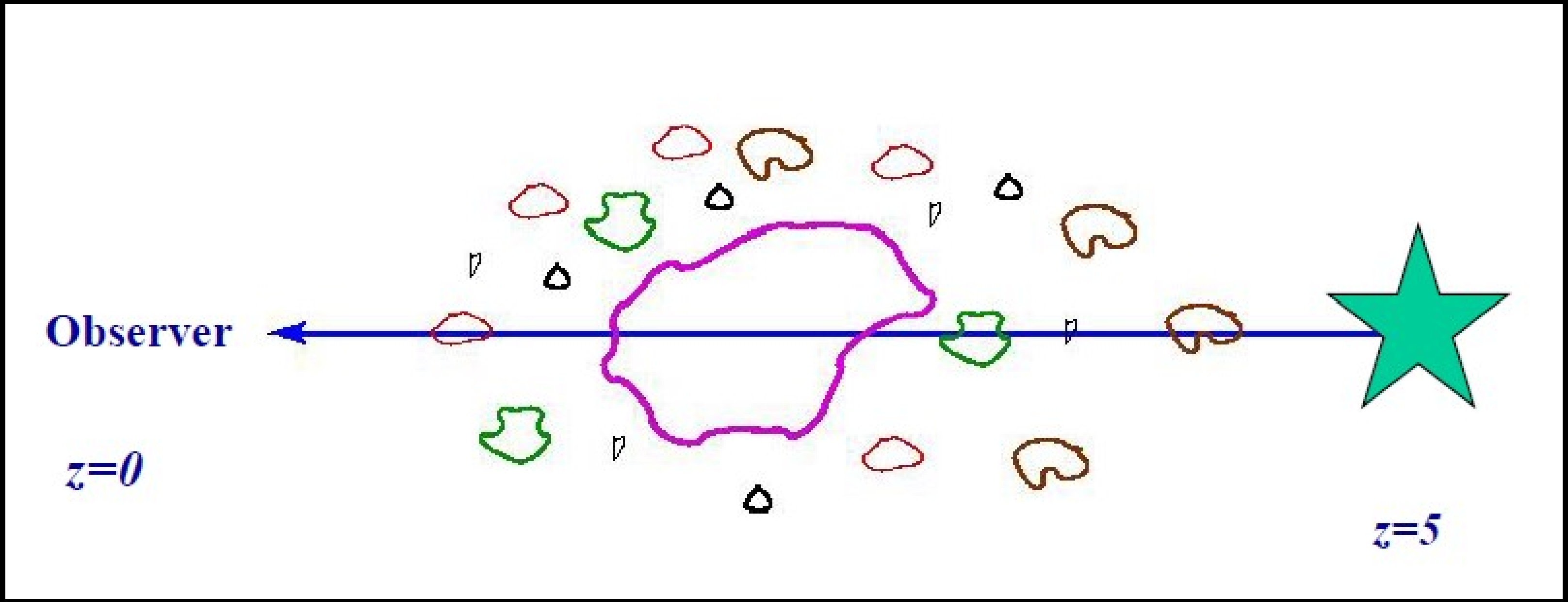
$$M_{clump} \geq M_{jeans}(n_{cr}, T_{cr}) = 700\ M_\odot\ (n/n_{cr})^{-1/2}\ (T/T_{cr})^{3/2}$$

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 sub-mm emission of CO and other molecules from starburst galaxies

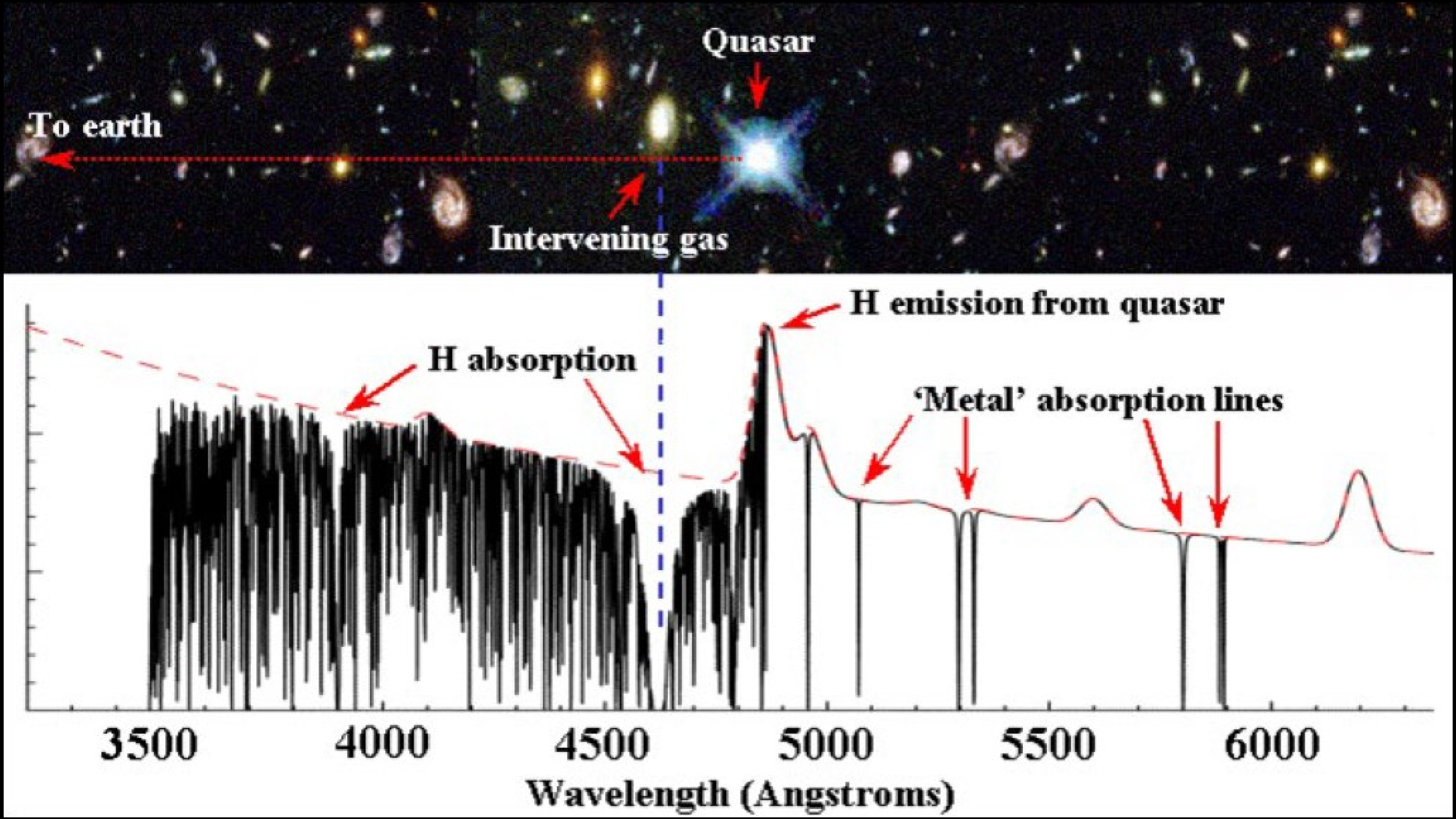
a. Quasar absorption lines

- Quasi-stellar object (QSO) shines through intergalactic medium



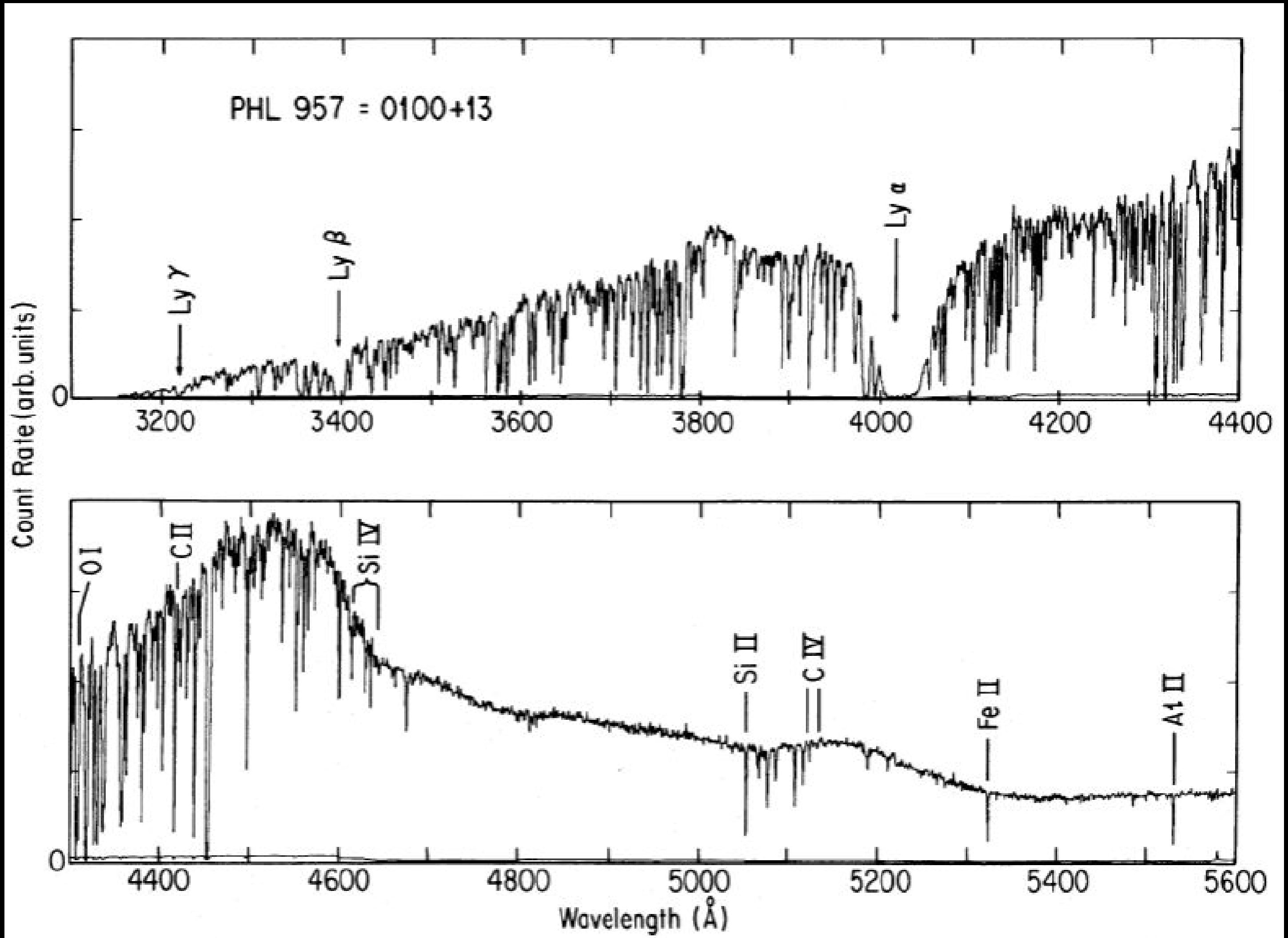
- Radiation encounters many clouds / structures containing H between z = 5 and z = 0 => strong absorption by each cloud a $\lambda_{obs} = (1 + z)\lambda_{rest}$
- Dominant line: **H 1s → 2p** Lyman α
- => **'Lyman-α forest'**

Quasar absorption line forest



Quasar PHL 957 at *z* = 2.7

Lyman α forest



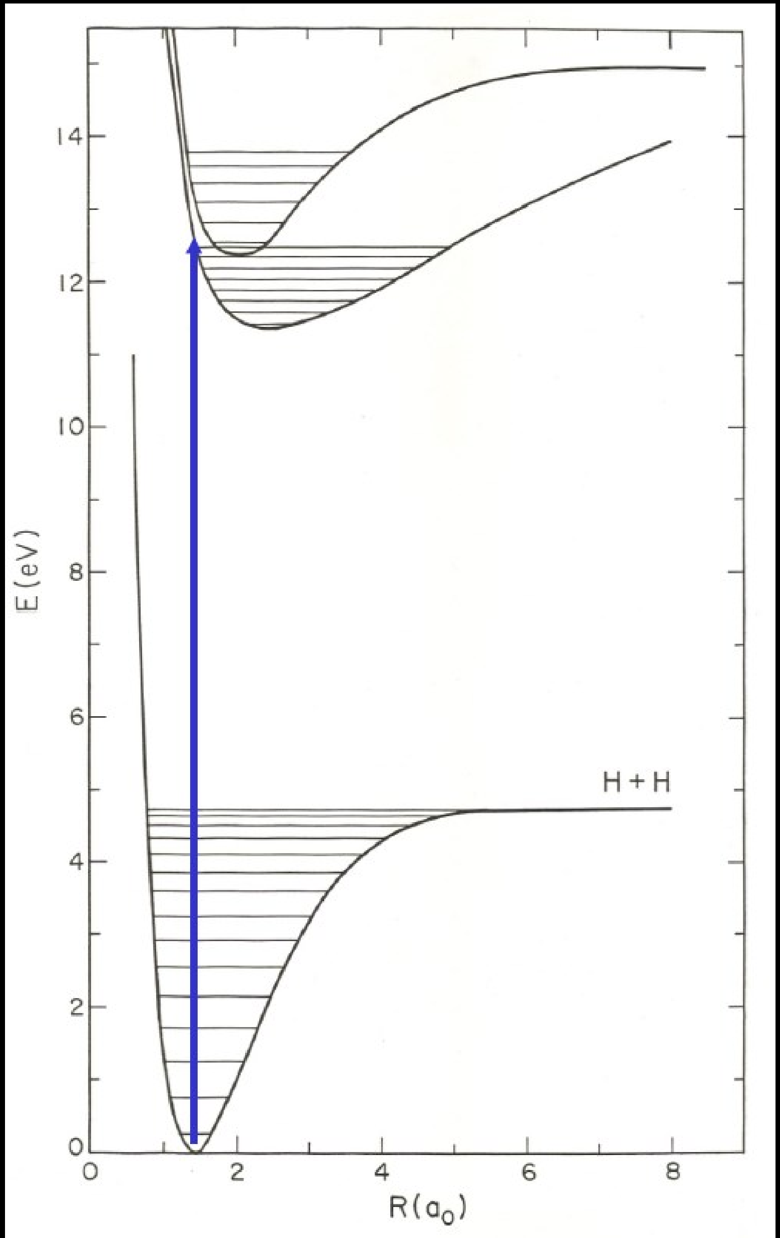
Black 1990

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

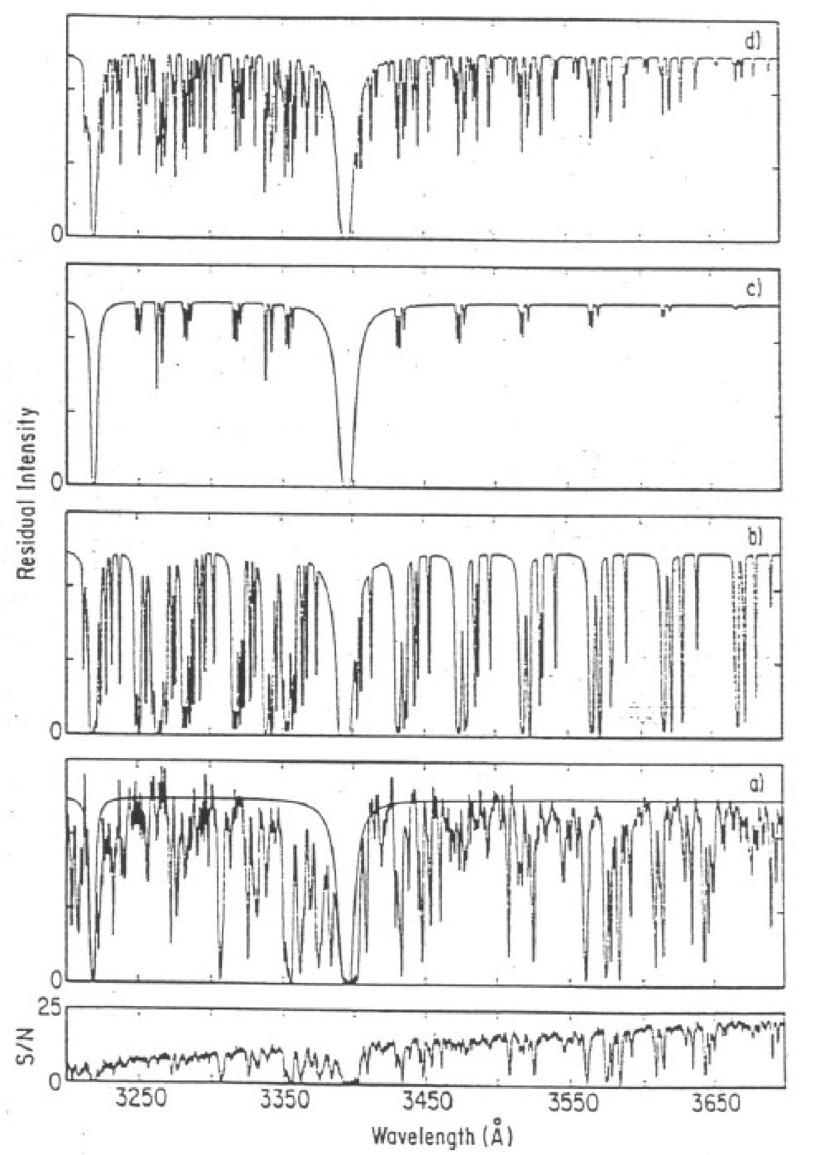
H_2 searches

- 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 (=> $N(\mathrm{H}) > 10^{21}$ 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 a 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

$N = 6 \times 10^{19}$ cm^{-2}
T_{ex} = 100 K

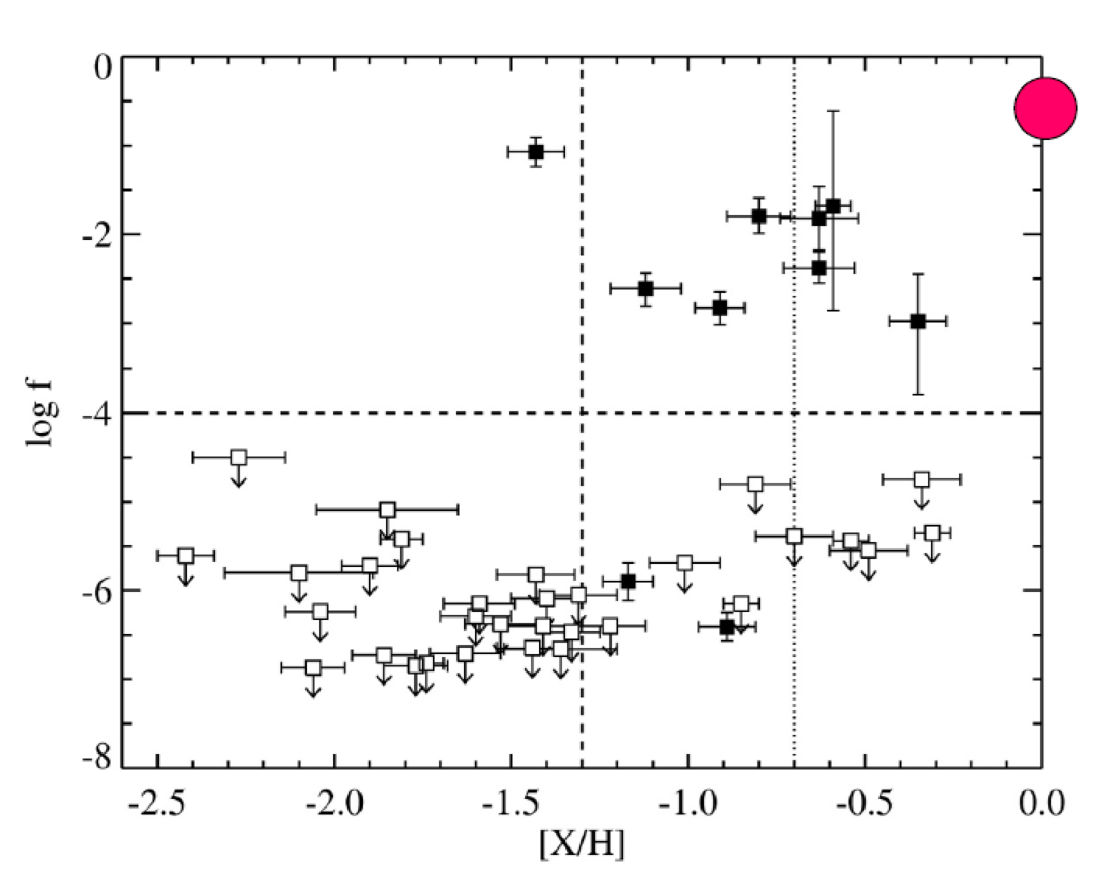
Obs + H fit

Obs

Black et al. (1987)

Note ***anti***-coincidences => No H_2 detection with $f(H_2) \leq 5 \times 10^{-6}$

H_2 searches



ζ Oph

Filled symbols: detections

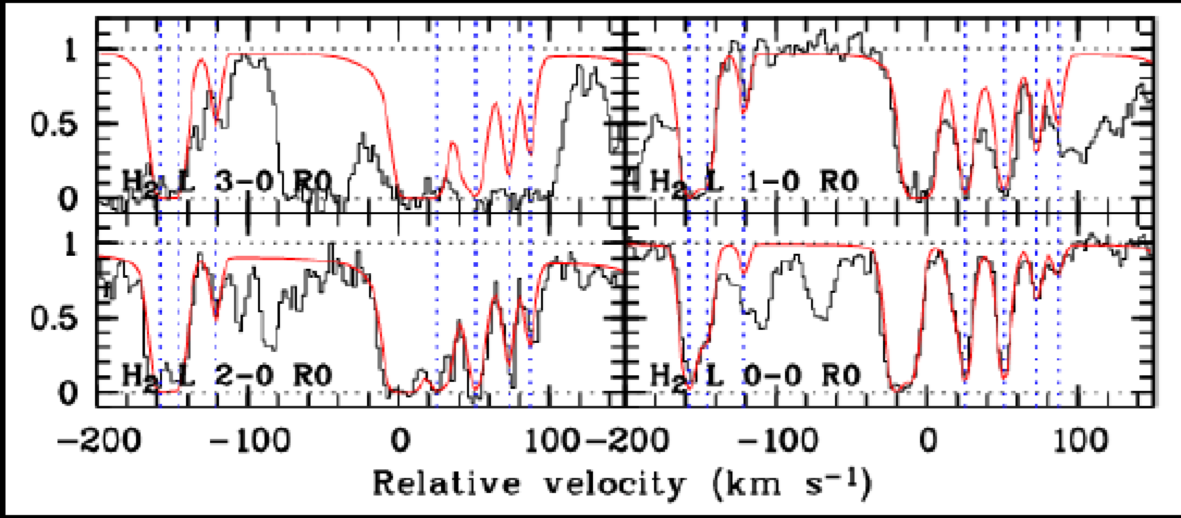
Open symbols: upper limits

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

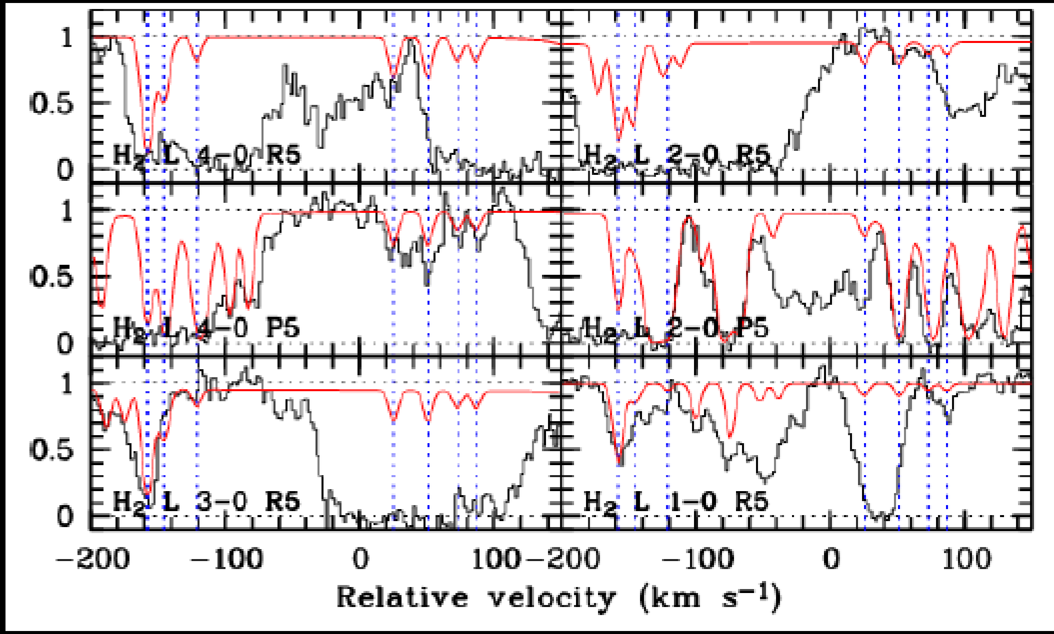
H_2 detection toward Q2348-011

$z = 2.426$

$J = 0$



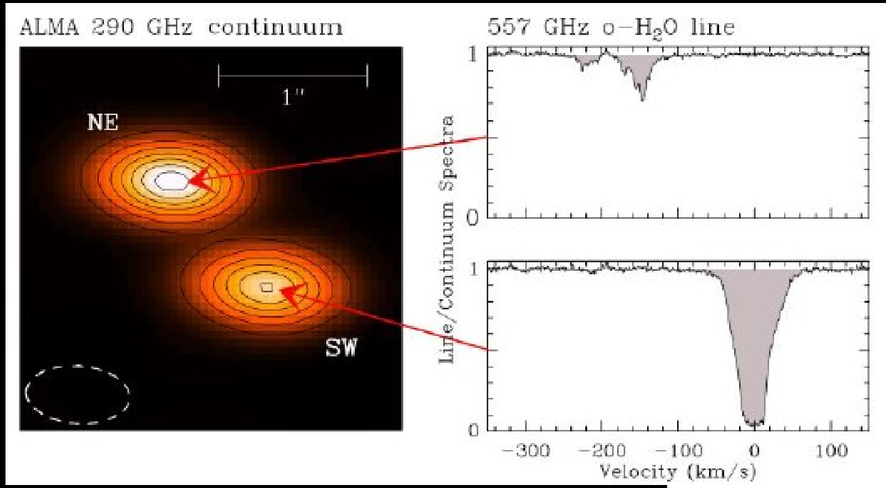
$J = 5$



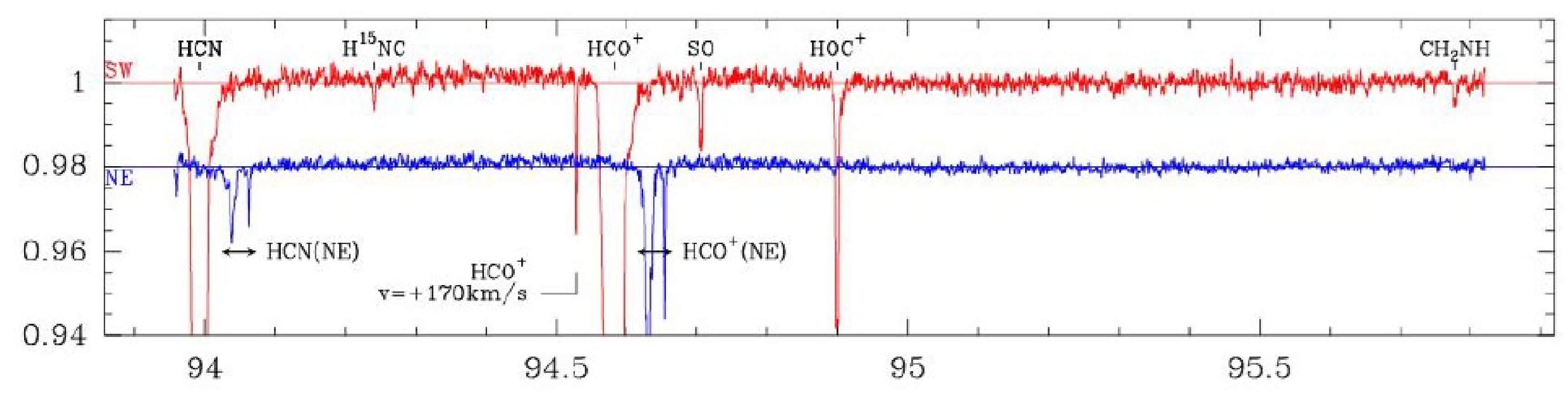
Noterdaeme et al. 2007
Petitjean et al. 2008

- Molecular fraction $f = 1.7 \times 10^{-2}$
- Lines out of $J = 0$–5 detected => $T > 130$ K, $n \sim 100$–200 cm^{-3}

b. QSO absorption at mm



PKS1830-211 $z = 0.89$
ALMA



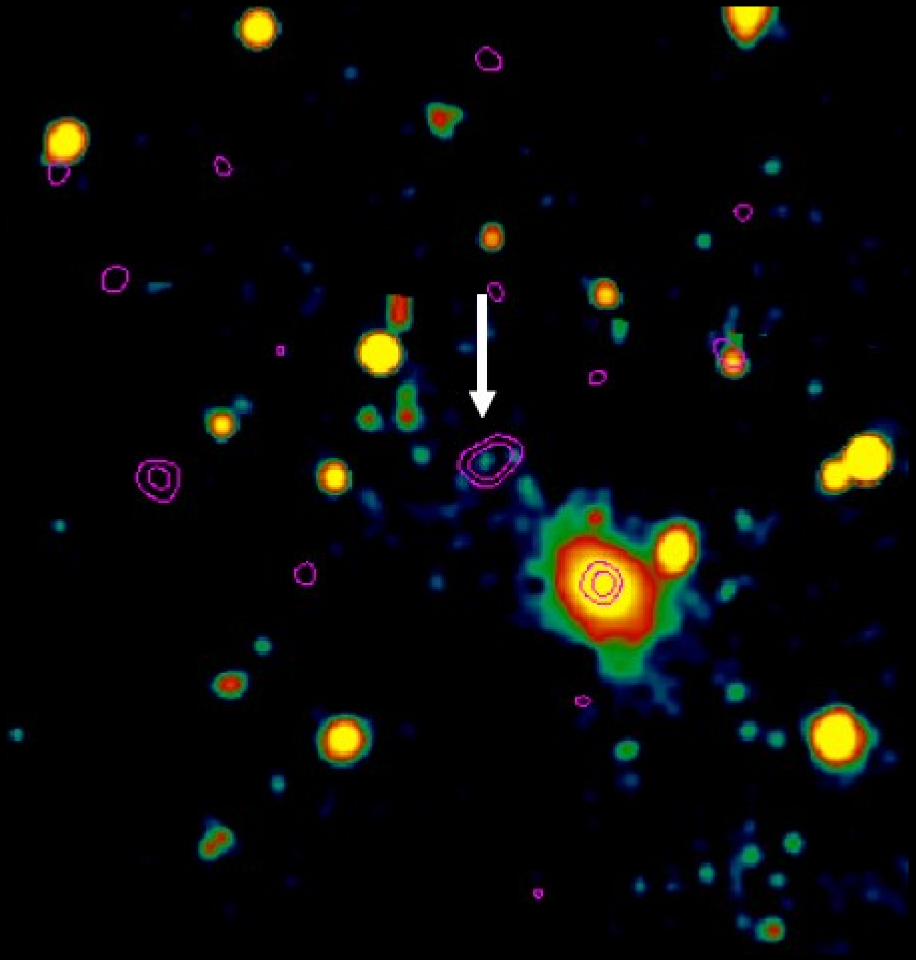
- Observe molecules at high z in mm, up to $z \sim 3$
- Detections of CO, HCO^+ , HCN, CS, …
- Even detection of minor species such as CF^+

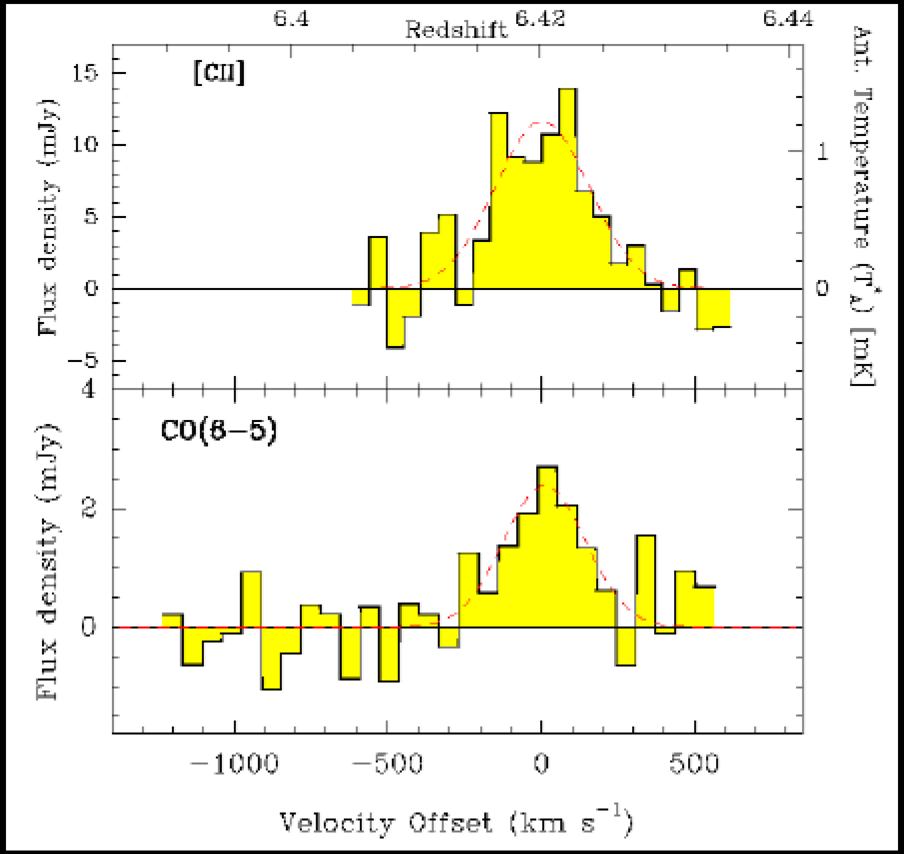
Muller et al. 2014
Combes, Wiklind & Nakai 1997

c. Sub-mm emission lines

- Recent detections of CO $J = 3 \rightarrow 2$, $4 \rightarrow 3$, $5 \rightarrow 4$, ..., $7 \rightarrow 6$, 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 100x more molecular gas than Milky Way => enormous reservoir of matieral for forming stars
- Elemental abundances close to solar => stars formed very fast => ***'burst'***

Molecules at high redshift: z = 6.4!



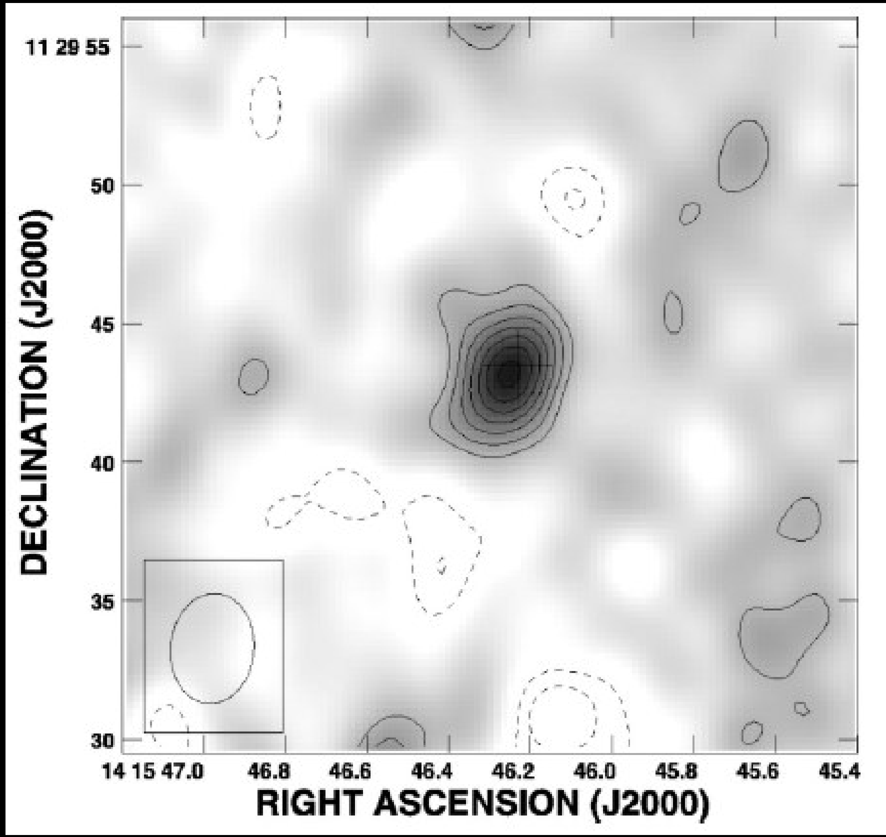


**Walter et al. 2003,
Maiolino et al. 2005**

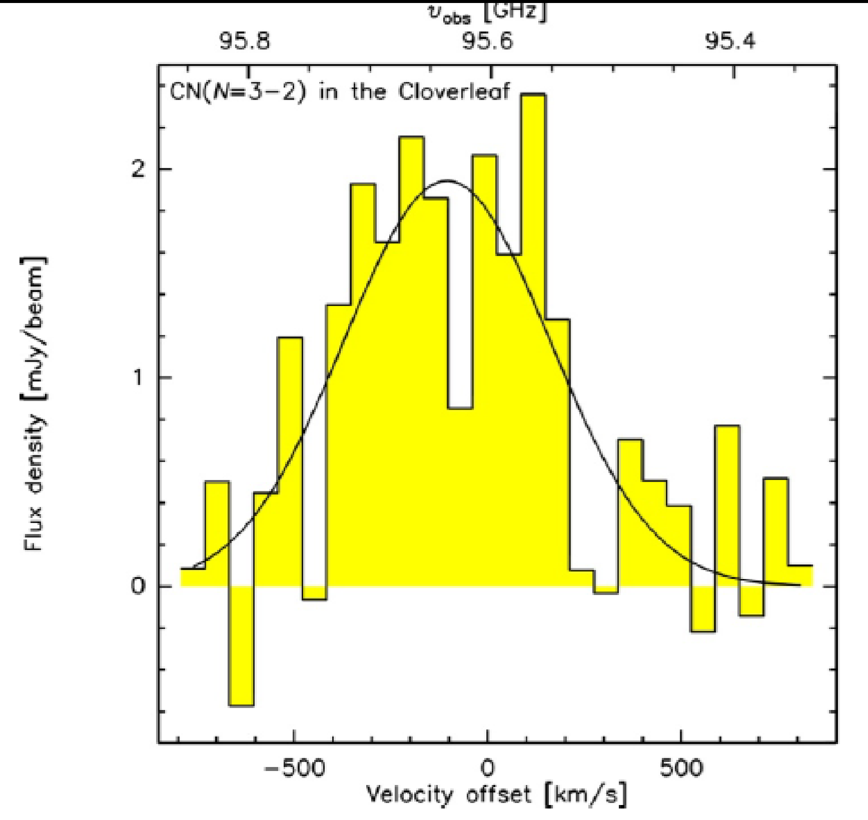
CO and [C II] in quasar SDSS J1148+5251 at $z = 6.4$

HCO$^+$, CN at high z

HCO$^+$



CN

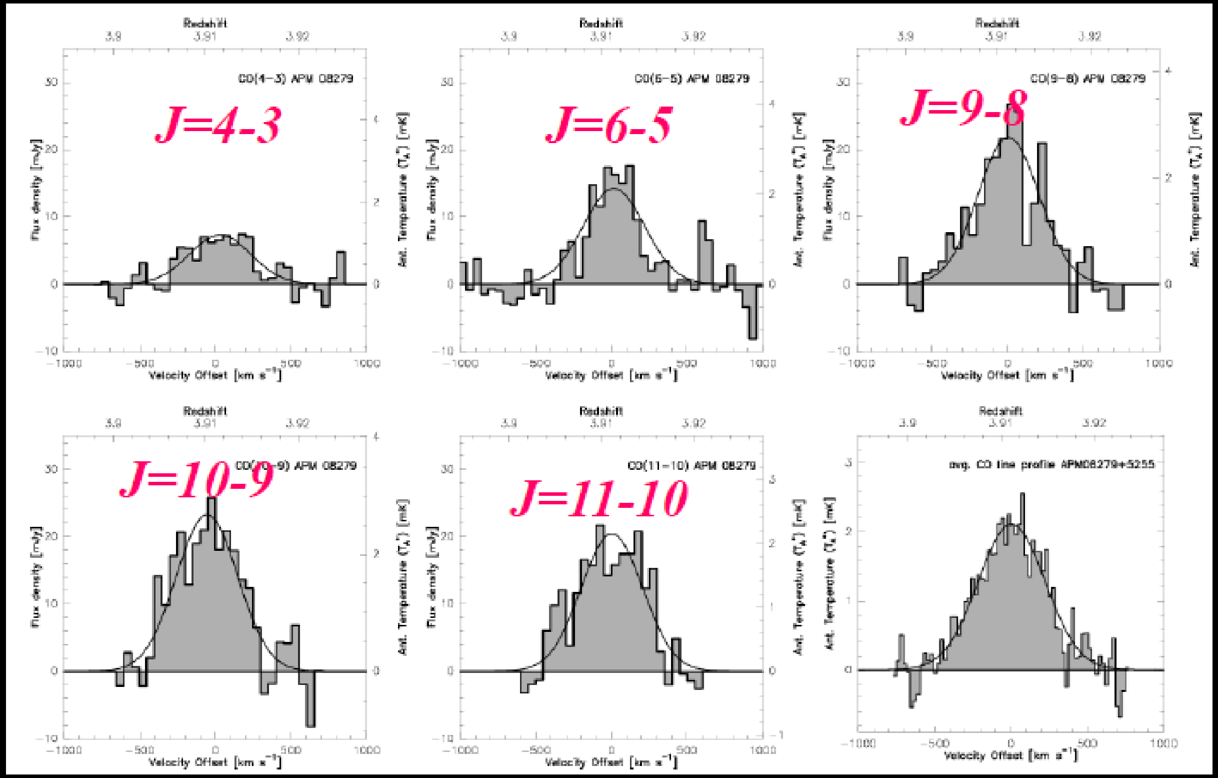


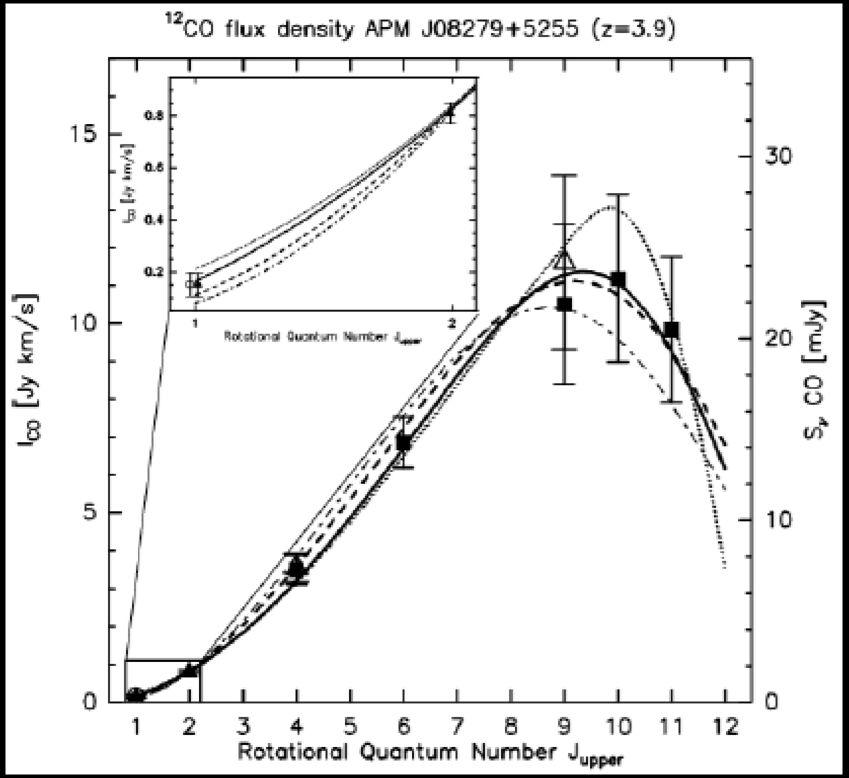
Riechers et al. 2007a,b

- 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 excitations

CO excitation at high *z*

APM 0827+5255 *z* = 3.9

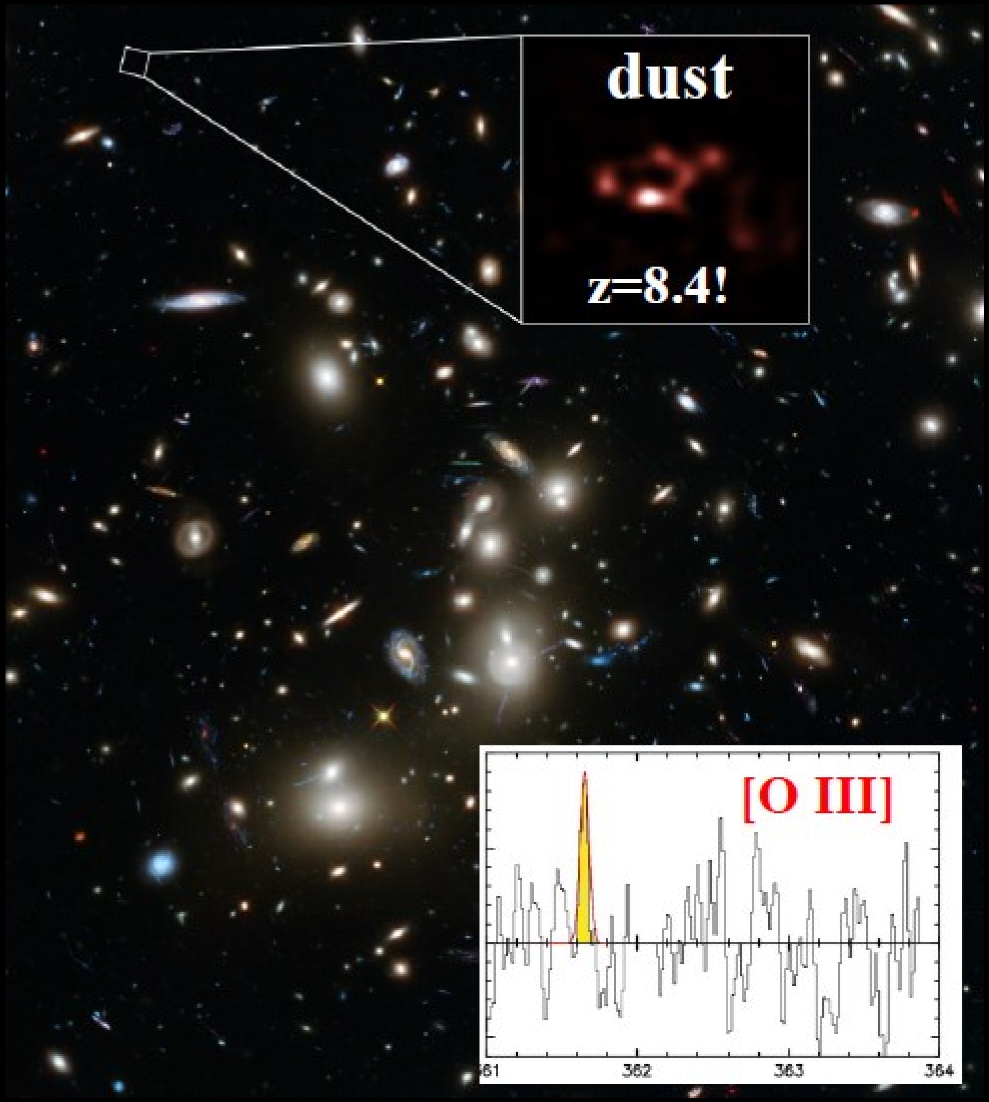




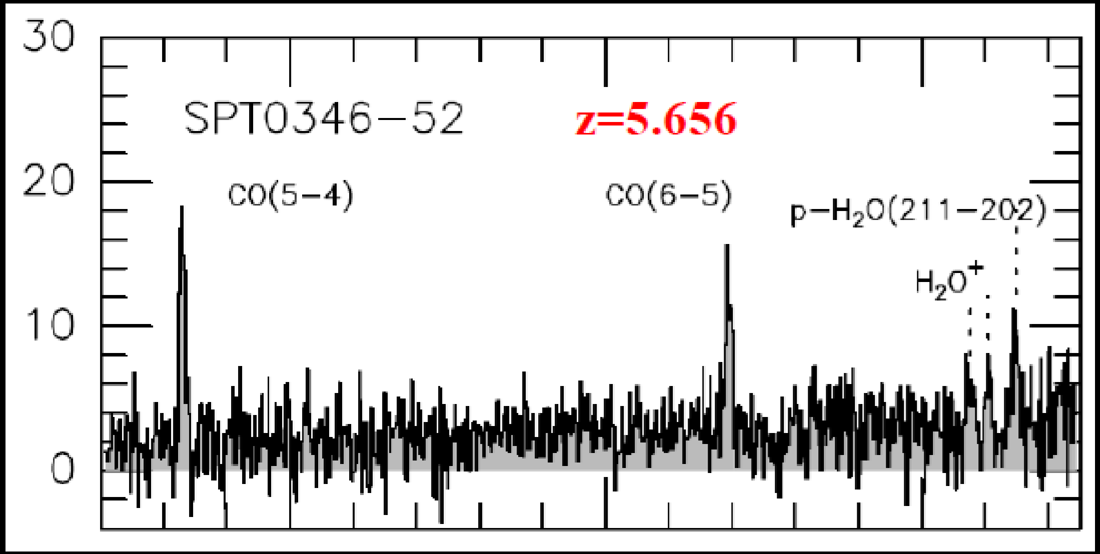
- CO 4-3 up to 11-10 detected at $z = 3.9$
- Excitation best fit by two components:
- Cold: $T \sim 65$ K, $n = 10^5$ cm^{-3}
- Warm: $T \sim 220$ K, $n = 10^4$ cm^{-3}

Weiss et al. 2007

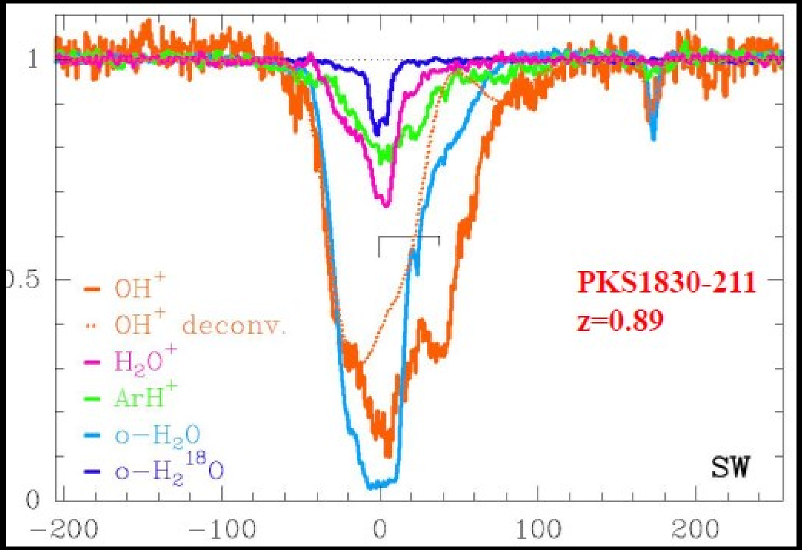
Highest redshift galaxies with ALMA



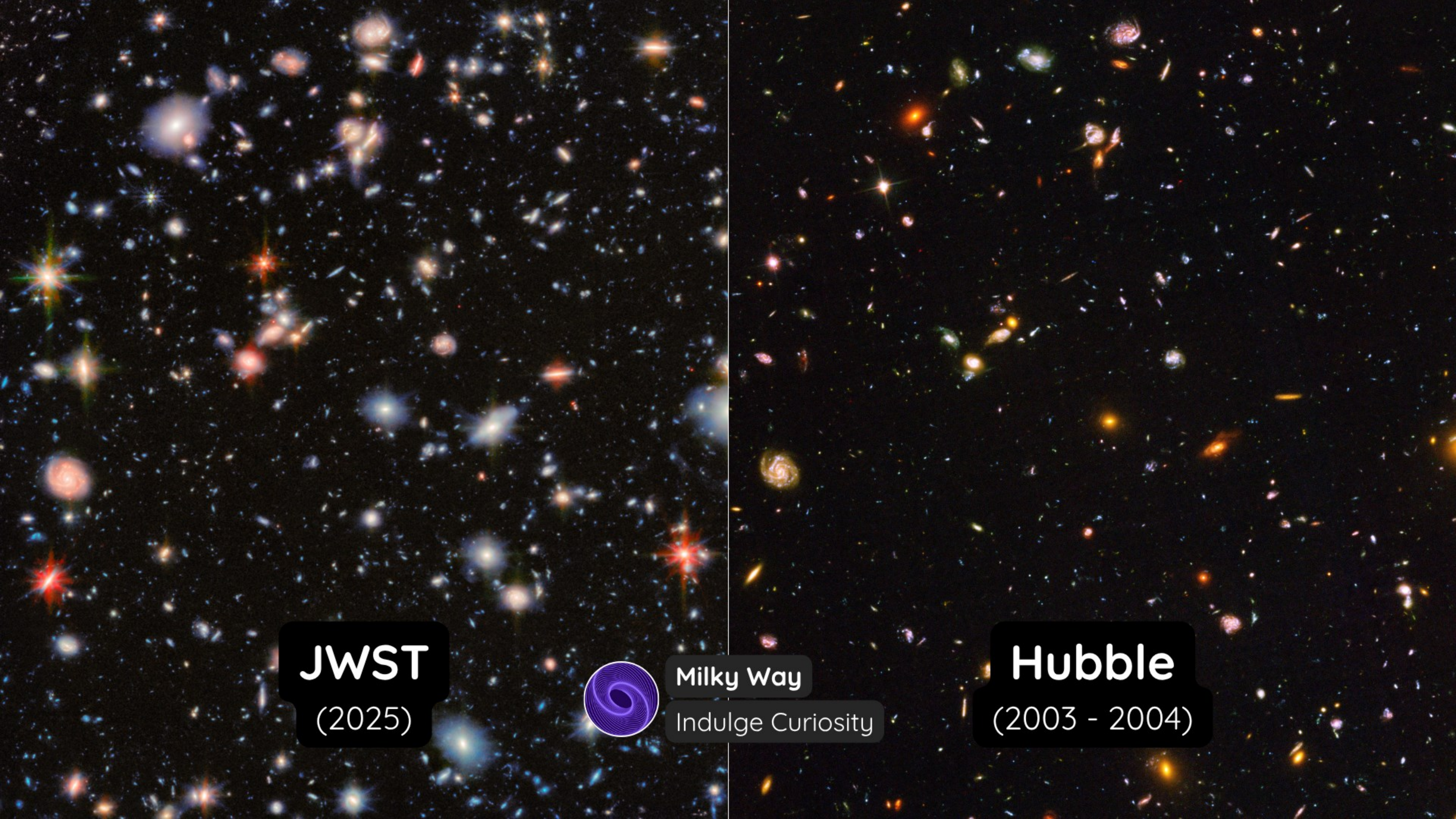
Laporte et al. 2017



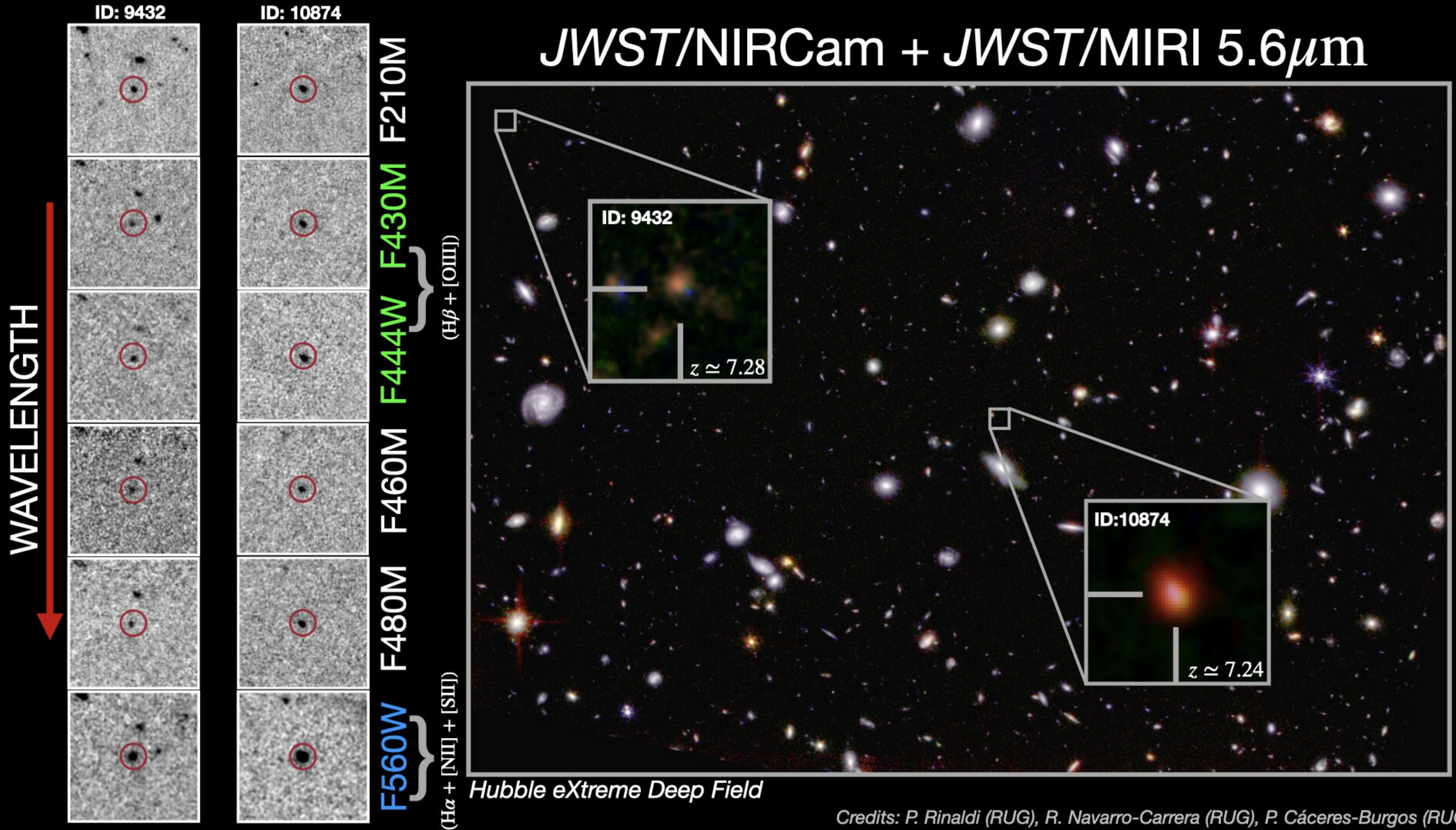
Weiss et al. 2013



Muller et al. 2016


JWST
(2025)
Milky Way
Indulge Curiosity
Hubble
(2003 - 2004)

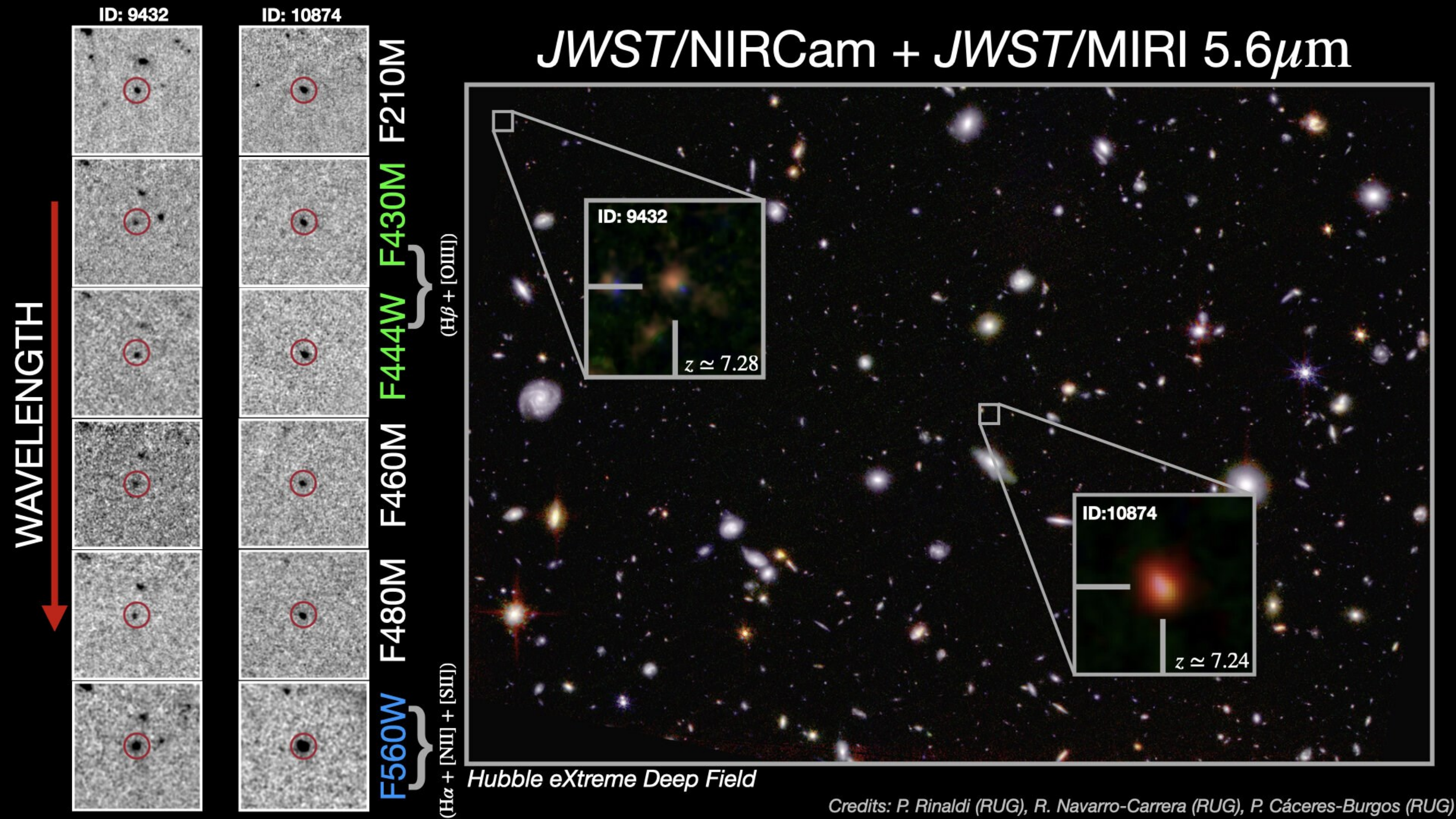
JWST – H(α) detection during epoch of reionization



Credits: P. Rinaldi (RUG), R. Navarro-Carrera (RUG), P. Cáceres-Burgos (RUG)

JWST – H(α) detection during epoch of reionization

- ***Review of redshift calculations:***
- If H(α) is found at 656 nm (red light), where is it expected in a z = 8 galaxy?



Summary Lecture 3

- ‘Simple’ chemistry in the early Universe
    - No dust, no ice, only gas phase reactions
- Chemistry (reactions) commence during era of recombination
    - Ion-molecule reactions
    - H, D, He, Li chemical networks
- Molecule cooling leads to cloud collapse and star formation
- Cooling due to atomic excitation is ineffective below 10000 K
- Molecules now observed at high redshifts (early Universe chemistry)