Università degli Studi “Aldo Moro” di Bari
Chemistry Department

INAF – Istituto Nazionale di Astrofisica
Osservatorio di Arcetri

Primordial H_2 formation in the early Universe

15th October 2014

Carla Maria Coppola

OUTLINE:

1. **early Universe: the “standard” chemistry**

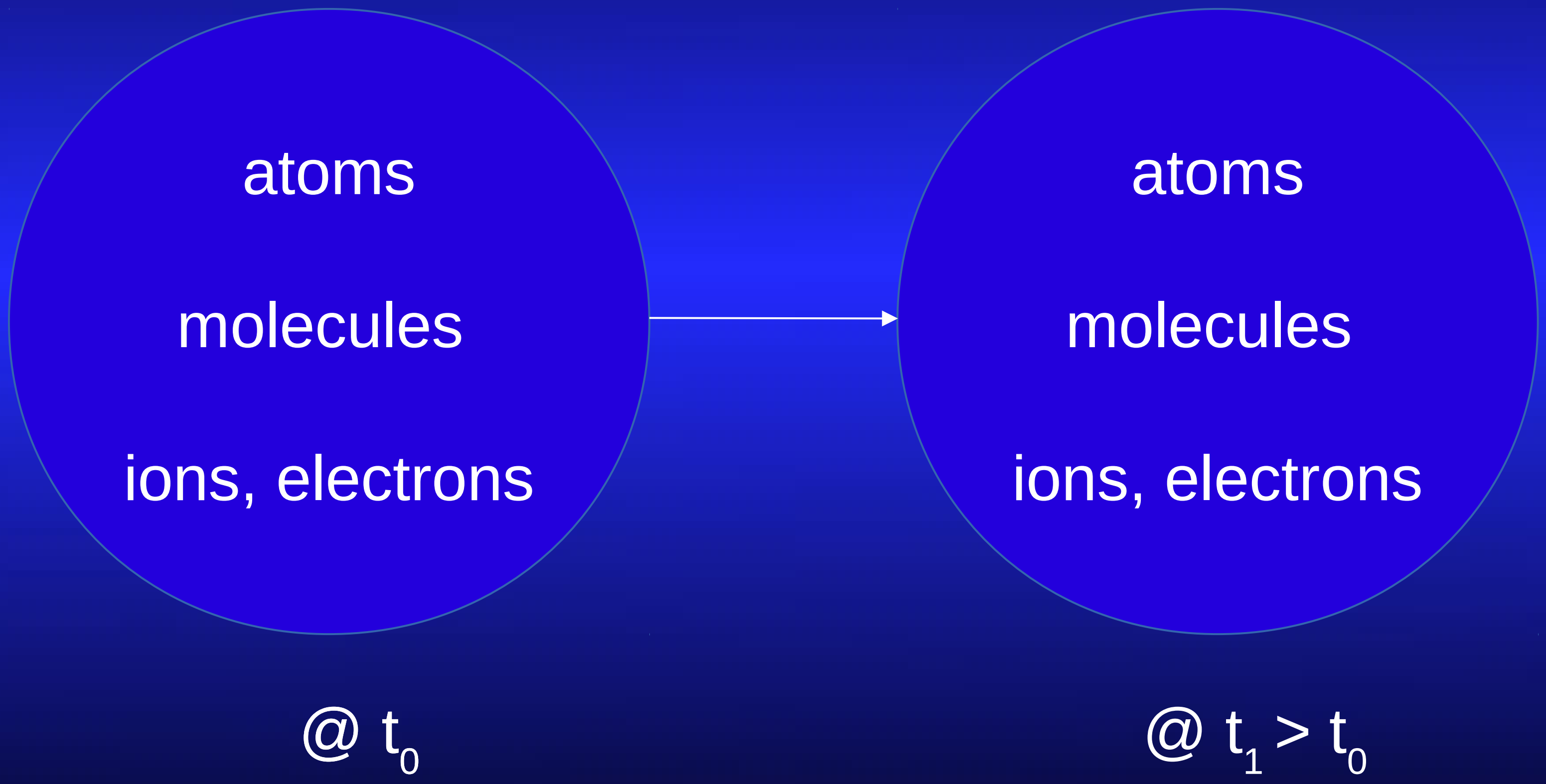
2. **non-equilibrium distributions**

- molecular internal states resolution:
  - vibration;
- **spectral distortions:**
  - primordial atomic recombination;
  - molecular processes;
  - dark matter annihilation

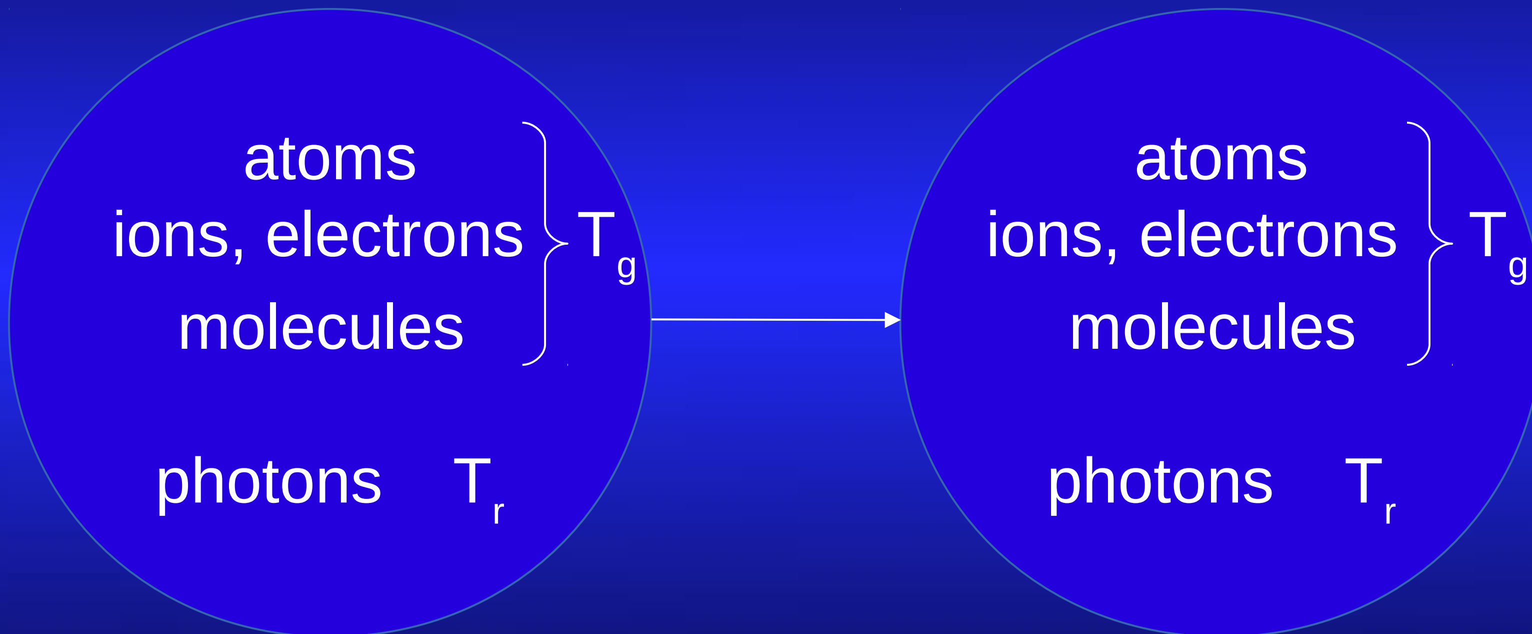
3. **“modified” chemistry**

4. **chemistry in pre-galactic shocks**

CHEMICAL KINETICS: DEFINITIONS AND EQS (I)



CHEMICAL KINETICS: DEFINITIONS AND EQS (II)



@ t_0 @ $t_1 > t_0$

KINETIC MODEL: ODEs SYSTEM (III)

$$\frac{dn_i}{dt} = k_{form}(T)\, n_j n_k - k_{dest}(T)\, n_i + \ldots$$

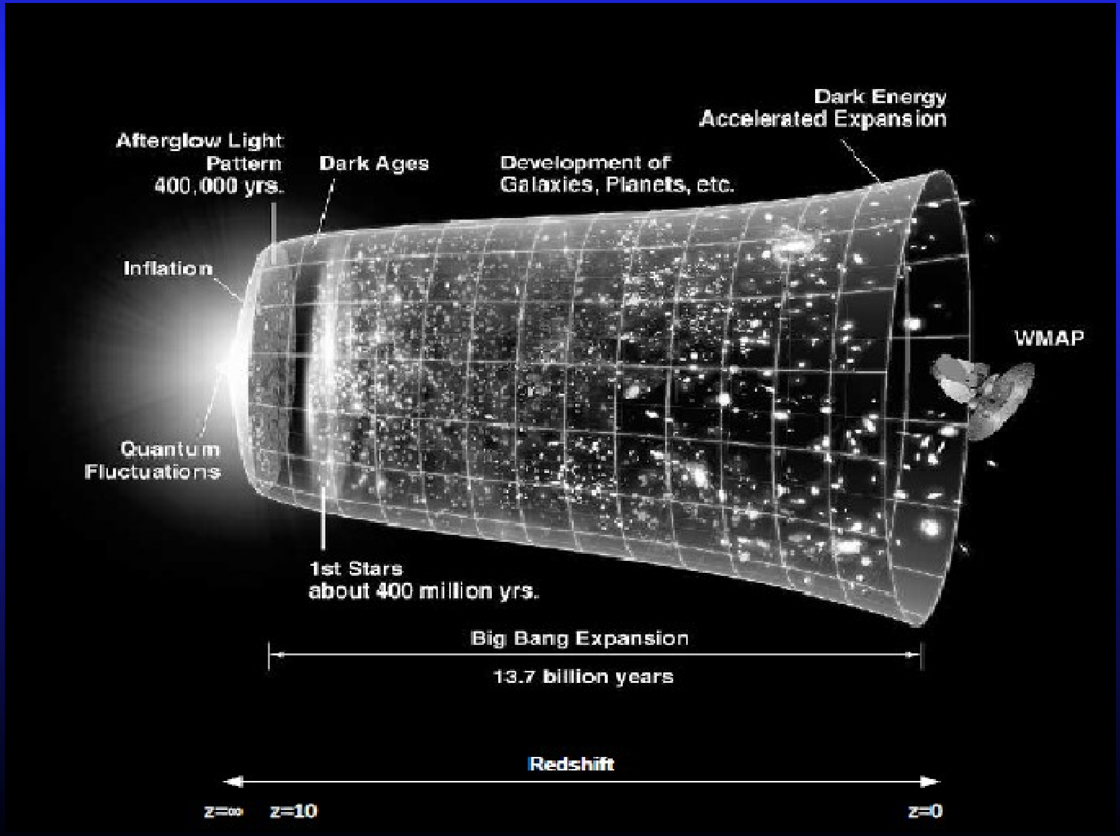
- initial conditions $n_i(t_0)$
- reaction rates $k(T)$

DENSITIES AND TEMPERATURE RANGES: THE ISM

Warm ionized medium (densities ~ 0.3 cm^{-3} - T ~ 10000 - 8000 K)
Warm neutral medium (densities ~ 0.3 cm^{-3} - T ~ 8000 K)
Cold neutral medium (densities ~ 30 cm^{-3} - T ~ 50 K)
Molecular clouds (densities > 100 cm^{-3}- T > 10 K)

DENSITIES AND TEMPERATURE RANGES: PRIMORDIAL UNIVERSE CHEMISTRY

Densities ~ 10^5- 10^{-7} cm^{-3}
T ~ 30000 K – 0.003 K



$$\frac{dn_i}{dt} = k_{form} n_j n_k - k_{dest} n_i + \ldots$$

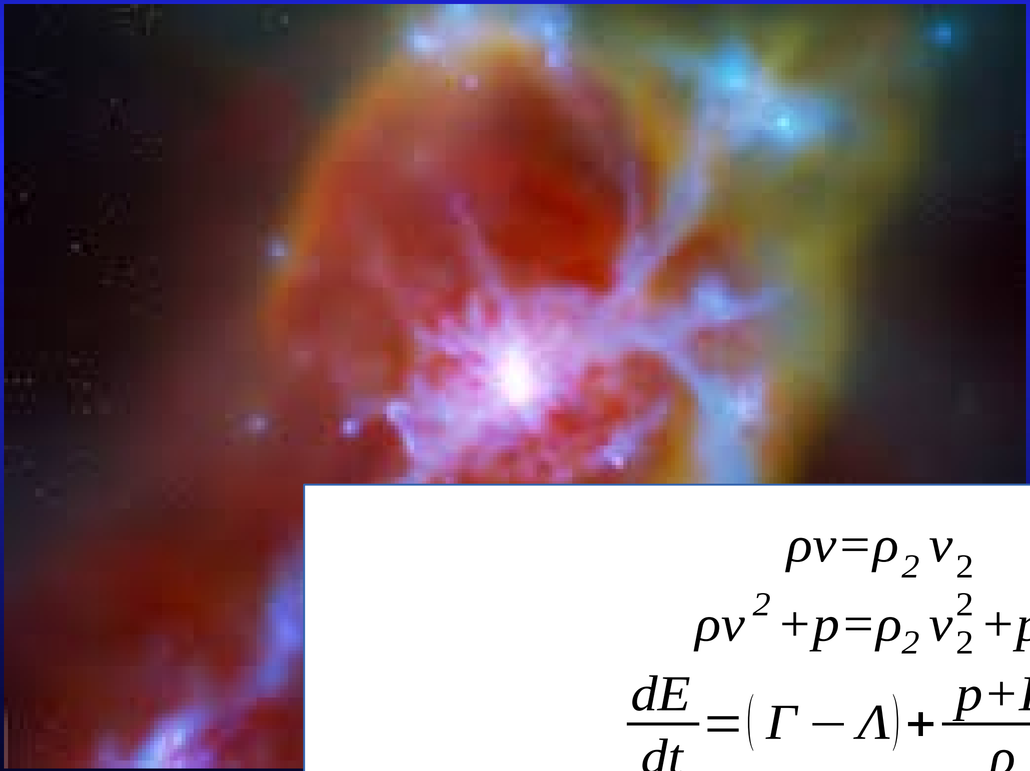
$$\frac{dn_i}{dz} = \frac{dt}{dz} \frac{dn_i}{dt}$$

$$n(z) = \Omega_b n_{cr} (1+z)^3$$

DENSITIES AND TEMPERATURE RANGES: PRIMORDIAL STAR FORMATION/ MOLECULAR CLOUDS COLLAPSE

Densities ~ 1- 10^{23} cm^{-3}

T ~ 100,000 K – few K



$$\rho v = \rho_2 v_2$$

$$\rho v^2 + p = \rho_2 v_2^2 + p_2$$

$$\frac{dE}{dt} = (\Gamma - \Lambda) + \frac{p+E}{\rho}\frac{d\rho}{dt}$$

$$E = \frac{\sum p_i}{\gamma_i - 1}; \quad p_i = n_i KT; \quad \frac{1}{n}\frac{dn}{dt} = -\frac{1}{T}\frac{dT}{dt}$$

mass
momentum
energy
} conservation

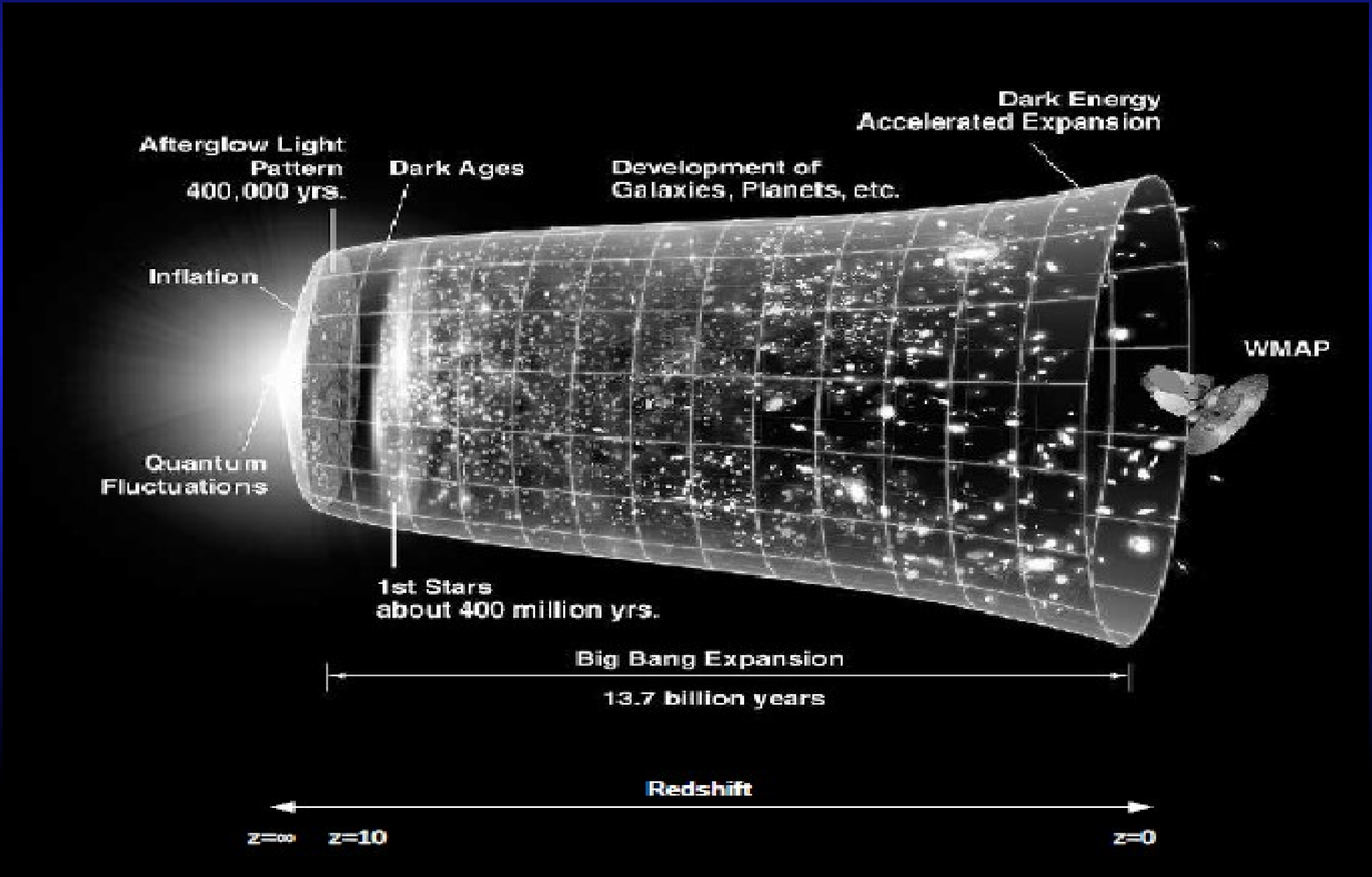
DIFFERENT ASTROPHYSICAL APPLICATIONS...

SAME PROBLEM:

WIDE RANGES OF TEMPERATURES AND DENSITIES...

SEARCH FOR CHEMICAL DATA

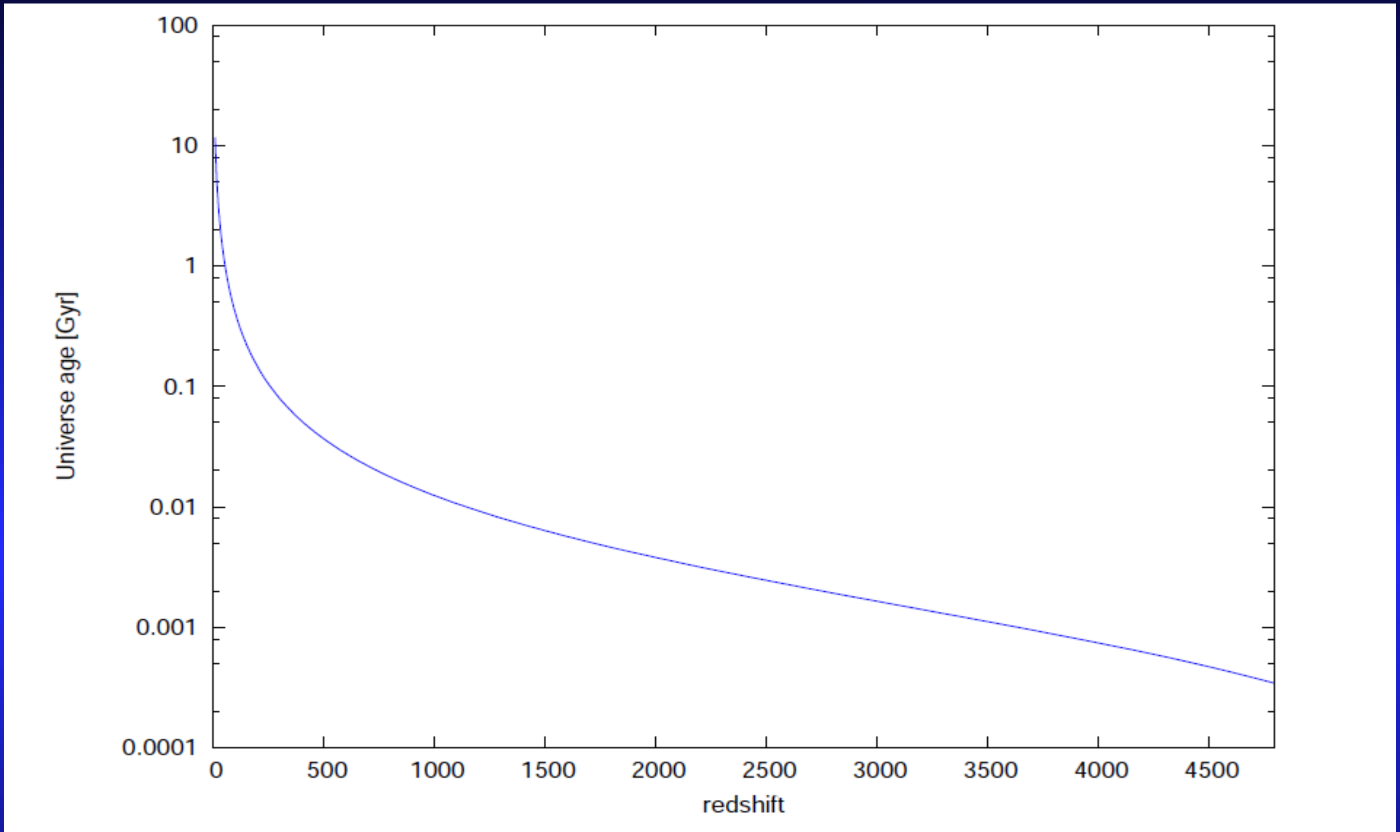
UNIVERSE HISTORY...



KINETIC MODELS: CHEMICAL SPECIES

H^+	D^+		HD^+	
H	D		HD	
H^-	D^-		H_3^+	H_2D^+
He^{++}	He^+	He	HeH^+	
Li	Li^+	Li^-	LiH	LiH^+
e^-	γ		H_2^+	H_2

SOME COSMOLOGY DEFINITIONS...



COSMIC TIME vs REDSHIFT

$$1 + z = \frac{a(t_0)}{a(t)} \equiv \frac{a_0}{a(t)}$$

$$\frac{dt}{dz} = -\frac{1}{(1+z)H(z)}$$

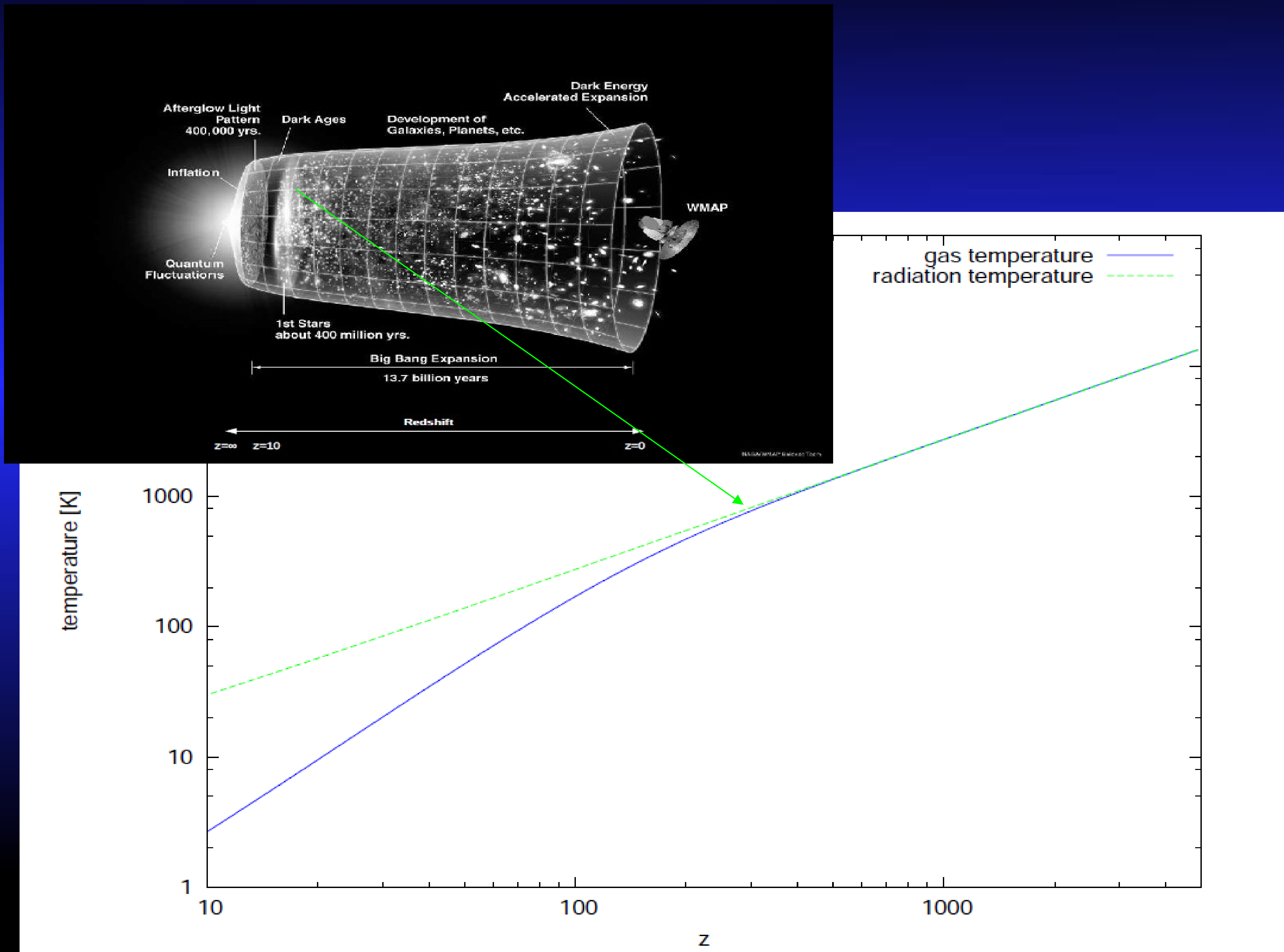
$$H(z) = H_0\sqrt{\Omega_r(1+z)^4 + \Omega_m(1+z)^3 + \Omega_K(1+z)^2 + \Omega_\Lambda}$$

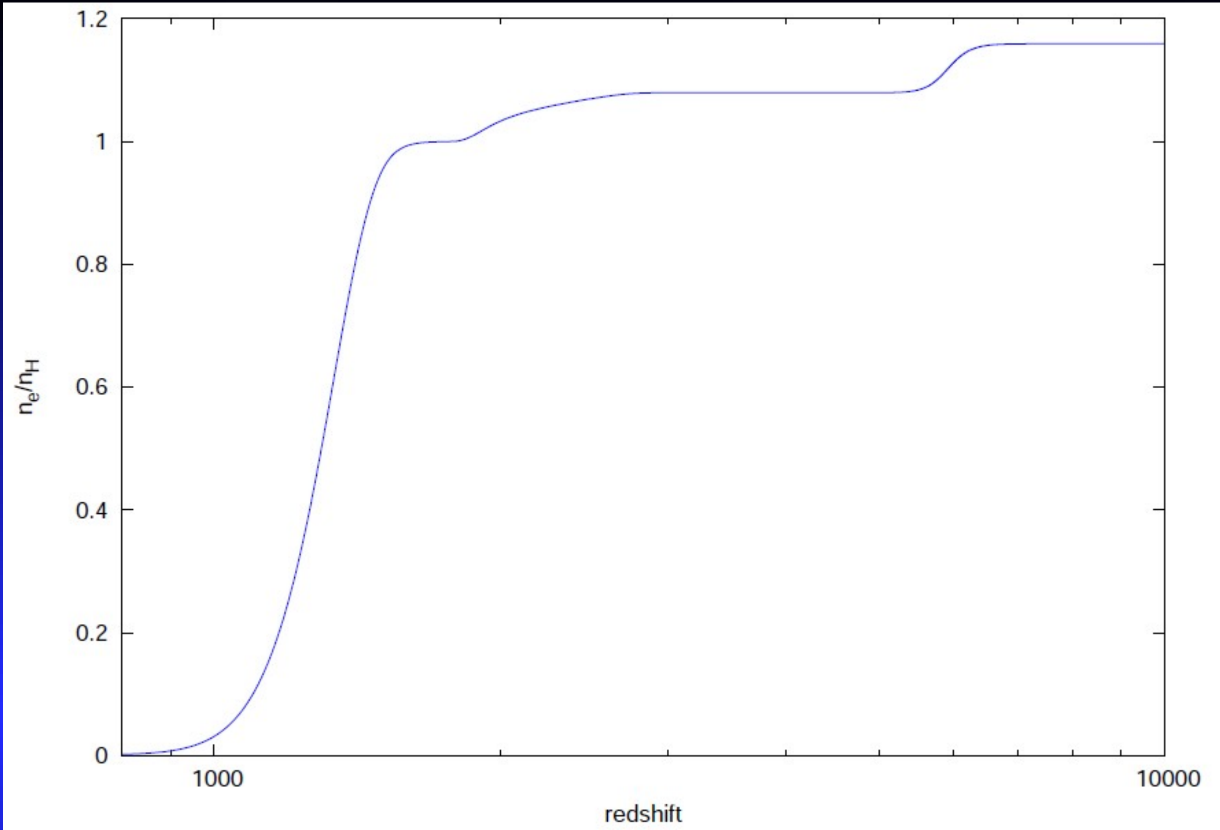
KINETIC MODELS IN PRIMORDIAL UNIVERSE CHEMISTRY: A BRIEF OVERVIEW...

- '60s: studies on elementary processes useful
  in molecular hydrogen formation in the early Universe
  (Saslaw & Zipoy (1967), Peebles & Dicke (1968))

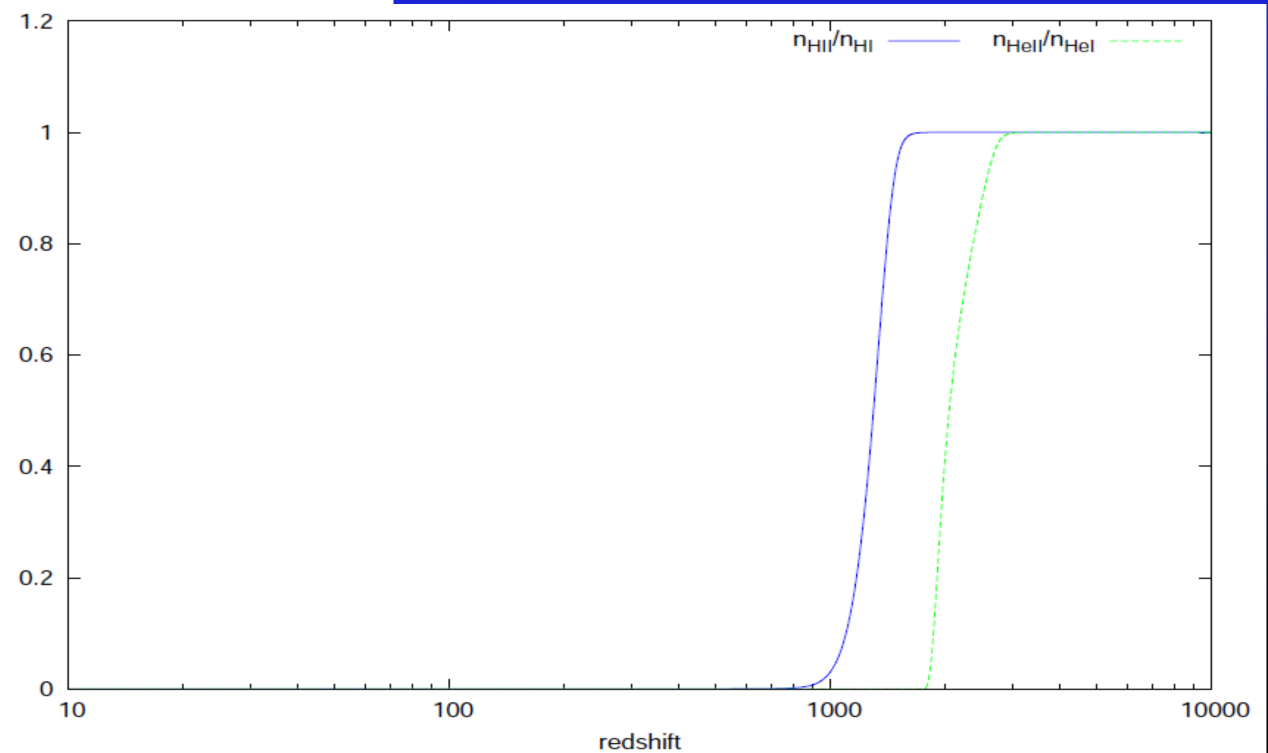
- Chemical kinetics in the early Universe:
  Dalgarno & Lepp (1987)
  Black (1990)
  Shapiro (1992)
  Puy et al. (1993,1996)
  Dalgarno & Fox (1994)
  Lepp, Stancil & Dalgarno (1996), Lepp & Stancil (1998)
  Bougleux & Galli (1997)
  Galli & Palla (1998, 2002)
  Schleicher et al. (2008)

RADIATION AND MATTER TEMPERATURES

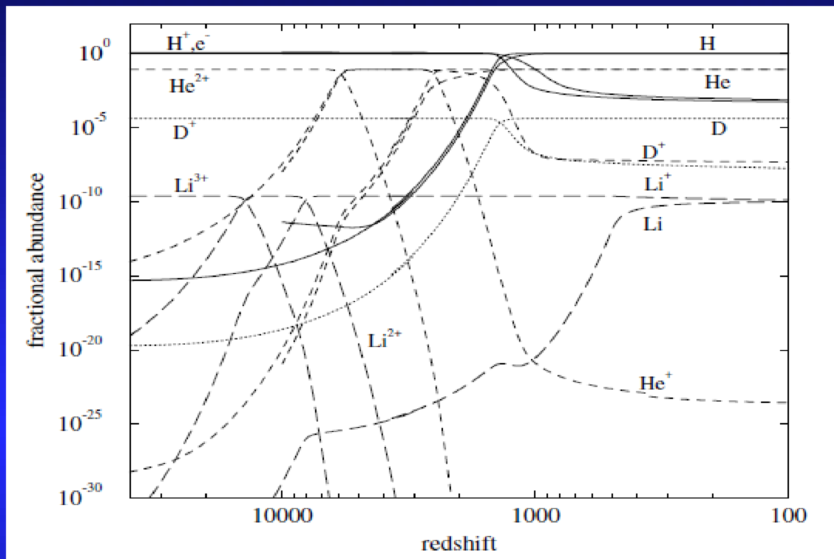




IONIZATION FRACTION & IONIZATION POTENTIALS



KINETIC MODEL: FRACTIONAL ABUNDANCES



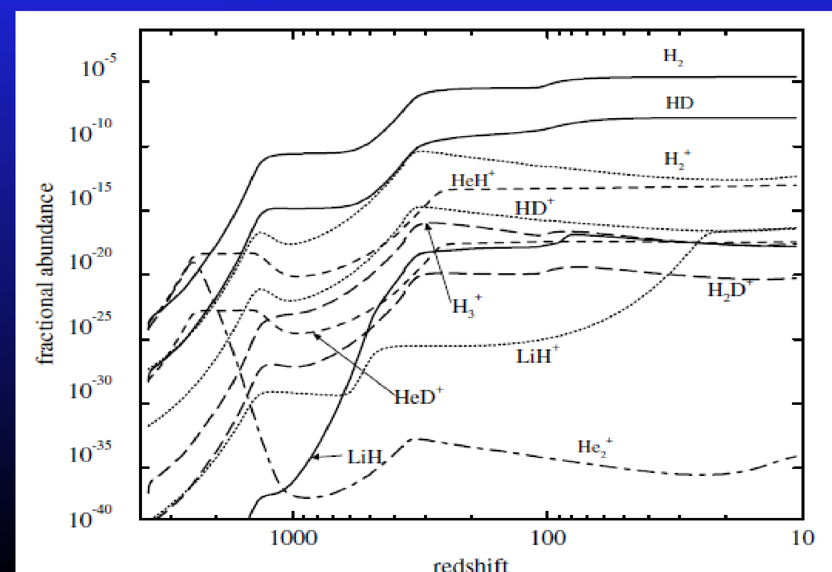
$$\frac{dn_i}{dt} = k_{form} n_j n_k - k_{dest} n_i + \ldots$$

$$\frac{dn_i}{dz} = \frac{dt}{dz}\frac{dn_i}{dt}$$

$$n(z) = \Omega_{\mathrm{b}} n_{\mathrm{cr}} (1+z)^3$$

Lepp, Stancil &Dalgarno,

2002, J. Phys. B: At. Mol. Opt. Phys. **35**, R57–R80



KINETIC MODEL: CHEMICAL PROCESSES

Chemical process	Rate coefficient [MKS]
1] $\mathrm{H} + \mathrm{e}^- \longrightarrow \mathrm{H}^- + h\nu$	$1.4 \times 10^{-24} T_m^{0.928} e^{-T_m/16200}$
2] $\mathrm{H}^- + \mathrm{e}^- \longrightarrow \mathrm{H} + 2\mathrm{e}^-$	fit from reference
3] $\mathrm{H}^- + \mathrm{H} \longrightarrow 2\mathrm{H} + \mathrm{e}^-$	fit from reference
4] $\mathrm{H}^- + \mathrm{H}^+ \longrightarrow 2\mathrm{H}$	$1.40 \times 10{-}13 \left(\frac{\mathrm{T_m}}{300}\right)^{-0.487} e^{T_m/29300}$
5] $\mathrm{H}^- + h\nu \longrightarrow \mathrm{H} + \mathrm{e}^-$	$0.01 \mathrm{T_r}^{2.13} e^{\mathrm{T_m}/29300}$
6] $\mathrm{D}^- + h\nu \longrightarrow \mathrm{D} + \mathrm{e}^-$	estimated by rc 5
7] $\mathrm{HD}^+ + h\nu \longrightarrow \mathrm{D} + \mathrm{H}^+$	$\frac{1}{2} 1.63 \times 10^7 e^{-32400/\mathrm{T_r}}$
8] $\mathrm{HD}^+ + h\nu \longrightarrow \mathrm{D}^+ + \mathrm{H}$	$\frac{1}{2} 1.63 \times 10^7 e^{-32400/\mathrm{T_r}}$
9] $\mathrm{HD}^+ + h\nu \longrightarrow \mathrm{H}^+ + \mathrm{D}^+ + \mathrm{e}^-$	$9.0 \times 10^1 \mathrm{T_r}^{1.48} e^{-335000/\mathrm{T_r}}$
10] $\mathrm{HD} + h\nu \longrightarrow \mathrm{HD}^+ + \mathrm{e}^-$	$2.9 \times 10^2 \mathrm{T_r}^{1.56} e^{-178500/\mathrm{T_r}}$
11] $\mathrm{D} + \mathrm{H}^+ \longrightarrow \mathrm{D}^+ + \mathrm{H}$	$2.0 \times 10^{-16} \mathrm{T_m}^{0.402} e^{-37.1/\mathrm{T_m}} - 3.31 \times 10^{-23} \mathrm{T_m}^{1.48}$
12] $\mathrm{D}^+ + \mathrm{H} \longrightarrow \mathrm{D} + \mathrm{H}^+$	$2.06 \times 10^{-16} \mathrm{T_m}^{0.396} e^{-33.0/\mathrm{T_m}} + 2.03 \times 10^{-15} \mathrm{T_m}^{-0.332}$
13] $\mathrm{D} + \mathrm{H} \longrightarrow \mathrm{HD} + h\nu$	see reference in Schleicher et al [11]
14] $\mathrm{HD}^+ + \mathrm{H} \longrightarrow \mathrm{HD} + \mathrm{H}^+$	6.4×10^{-16}
15] $\mathrm{D} + \mathrm{H}^+ \longrightarrow \mathrm{HD}^+ + h\nu$	$dex(-19.38 - 1.523 \log_{10}(\mathrm{T_m}) + 1.118 \log_{10}^2(\mathrm{T_m}) - 0.1269 \log_{10}^3(\mathrm{T_m}))$
16] $\mathrm{D}^+ + \mathrm{H} \longrightarrow \mathrm{HD}^+ + h\nu$	$dex(-19.38 - 1.523 \log_{10}(\mathrm{T_m}) + 1.118 \log_{10}^2(\mathrm{T_m}) - 0.1269 \log_{10}^3(\mathrm{T_m}))$
17] $\mathrm{HD}^+ + \mathrm{e}^- \longrightarrow \mathrm{D} + \mathrm{H}$	$7.2 \times 10^{-14} \mathrm{T_m}^{-0.5}$
18] $\mathrm{D}^+ + \mathrm{e}^- \longrightarrow \mathrm{D}^- + h\nu$	$3.0 \times 10^{-22} \left(\frac{\mathrm{T_m}}{300}\right)^{0.95} e^{-\mathrm{T_m}/9320}$
19] $\mathrm{D}^+ + \mathrm{D}^- \longrightarrow 2\mathrm{D}$	$1.96 \times 10^{-13} \left(\frac{\mathrm{T_m}}{300}\right)^{-0.487} e^{\mathrm{T_m}/29300}$
20] $\mathrm{H}^+ + \mathrm{D}^- \longrightarrow \mathrm{D} + \mathrm{H}$	$1.61 \times 10^{-13} \left(\frac{\mathrm{T_m}}{300}\right)^{-0.487} e^{\mathrm{T_m}/29300}$
21] $\mathrm{H}^- + \mathrm{D} \longrightarrow \mathrm{H} + \mathrm{D}^-$	$6.4 \times 10^{-15} \left(\frac{\mathrm{T_m}}{300}\right)^{0.41}$
22] $\mathrm{D}^- + \mathrm{H} \longrightarrow \mathrm{D} + \mathrm{H}^-$	$6.4 \times 10^{-15} \left(\frac{\mathrm{T_m}}{300}\right)^{0.41}$
23] $\mathrm{D}^- + \mathrm{H} \longrightarrow \mathrm{HD} + \mathrm{e}^-$	$1.5 \times 10^{-15} \left(\frac{\mathrm{T_m}}{300}\right)^{0.1}$
24] $\mathrm{D} + \mathrm{H}^- \longrightarrow \mathrm{HD} + \mathrm{e}^-$	rc 22
25] $\mathrm{H}^- + \mathrm{D}^+ \longrightarrow \mathrm{D}$	[illegible]
26] $\mathrm{He} + \mathrm{H}^+ \longrightarrow \mathrm{He}$	
27] $\mathrm{He}^+ + \mathrm{H} \longrightarrow \mathrm{He}$	
28] $\mathrm{He} + \mathrm{H}^+ \longrightarrow \mathrm{He}$ radiative association	
29] $\mathrm{He} + \mathrm{H}^+ + h\nu -$ stimulated radiative	
30] $\mathrm{He}^+ + \mathrm{H} \longrightarrow \mathrm{He}$	
31] $\mathrm{He}^+ + \mathrm{e}^- \longrightarrow \mathrm{H}$	
32] $\mathrm{HeH}^+ h\nu \longrightarrow \mathrm{He}$	
33] $\mathrm{HeH}^+ h\nu \longrightarrow \mathrm{He}$	

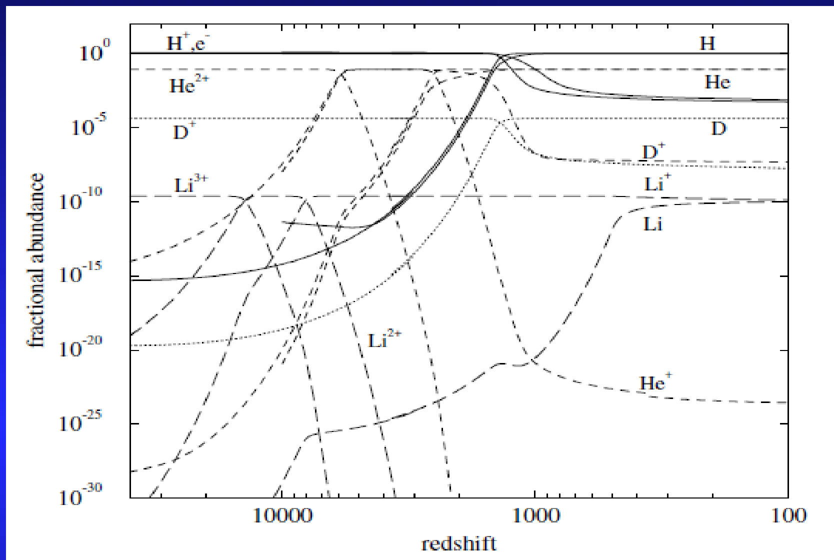
A&A 490, 521–535 (2008)
DOI: 10.1051/0004-6361:200809861

Astronomy & Astrophysics

Effects of primordial chemistry on the cosmic microwave background

D. R. G. Schleicher[1], D. Galli[2], F. Palla[2], M. Camenzind[3], R. S. Klessen[1], M. Bartelmann[1], and S. C. O. Glover[4]

KINETIC MODEL: FRACTIONAL ABUNDANCES



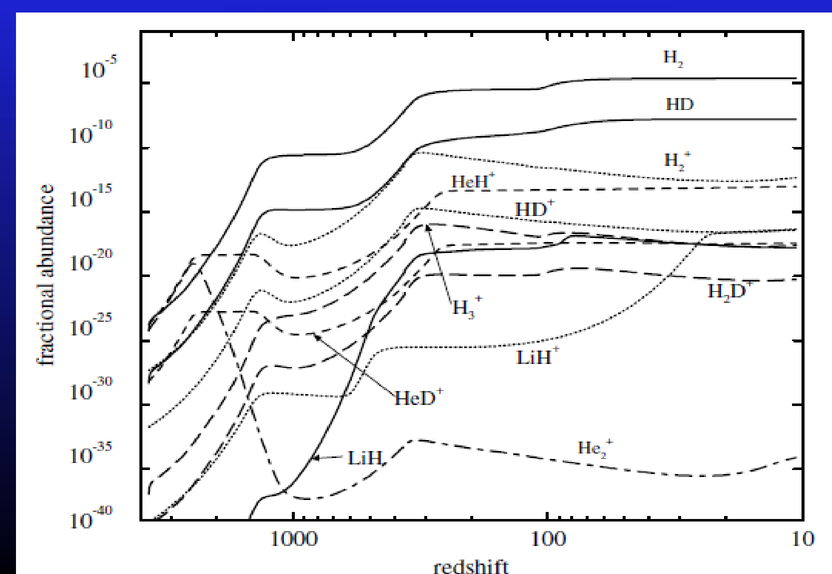
$$\frac{dn_i}{dt} = k_{form} n_j n_k - k_{dest} n_i + \ldots$$

$$\frac{dn_i}{dz} = \frac{dt}{dz}\frac{dn_i}{dt}$$

$$n(z) = \Omega_b n_{cr}(1+z)^3$$

Lepp, Stancil &Dalgarno,

2002, J. Phys. B: At. Mol. Opt. Phys. **35**, R57–R80



KINETIC MODEL: CHEMICAL PROCESSES

MASSIVE PARTICLES

SCATTERING

PHOTONIC PROCESSES

$$k(T) = \left(\frac{2}{k_B T}\right)^{3/2} \frac{1}{\sqrt{\mu\pi}} \int_0^\infty dE \; E \; e^{-\frac{E}{k_B T}} \sigma(E)$$

$$n_b = 1.123 \times 10 \cdot (1 - Y_p)\Omega_b h^2 (1+z)^3 \quad [m^{-3}]$$

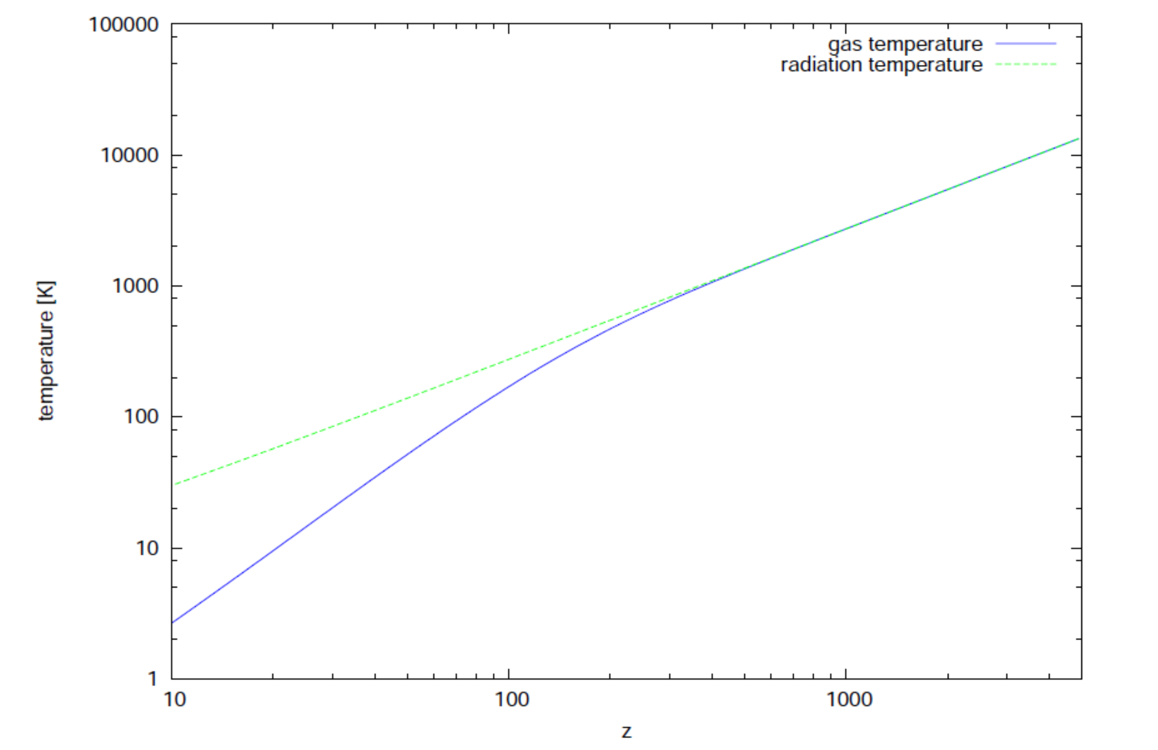
$$k_{rad}(\mathrm{T_{rad}}) = 4\pi \int_0^\infty \frac{\sigma(\nu)}{h\nu} J_\nu(\mathrm{T_{rad}}) d\nu$$

$$J_\nu(\mathrm{T_{rad}}) = \frac{2h\nu^3}{c^2} \frac{1}{\mathrm{e}^{\mathrm{h}\nu/\mathrm{kT_{rad}}} - 1}$$

KINETIC MODEL: MATTER AND RADIATION TEMPERATURE

$$\frac{dT_m}{dt} = -2H(t)T_m + \frac{8\sigma_t a T_r^4 (T_r - T_m) x_e}{3 m_e c} + (\Gamma - \Lambda)_{\mathrm{mol}}$$

$$T_r = 2.7(1+z)$$



RECFAST

Wong et al.

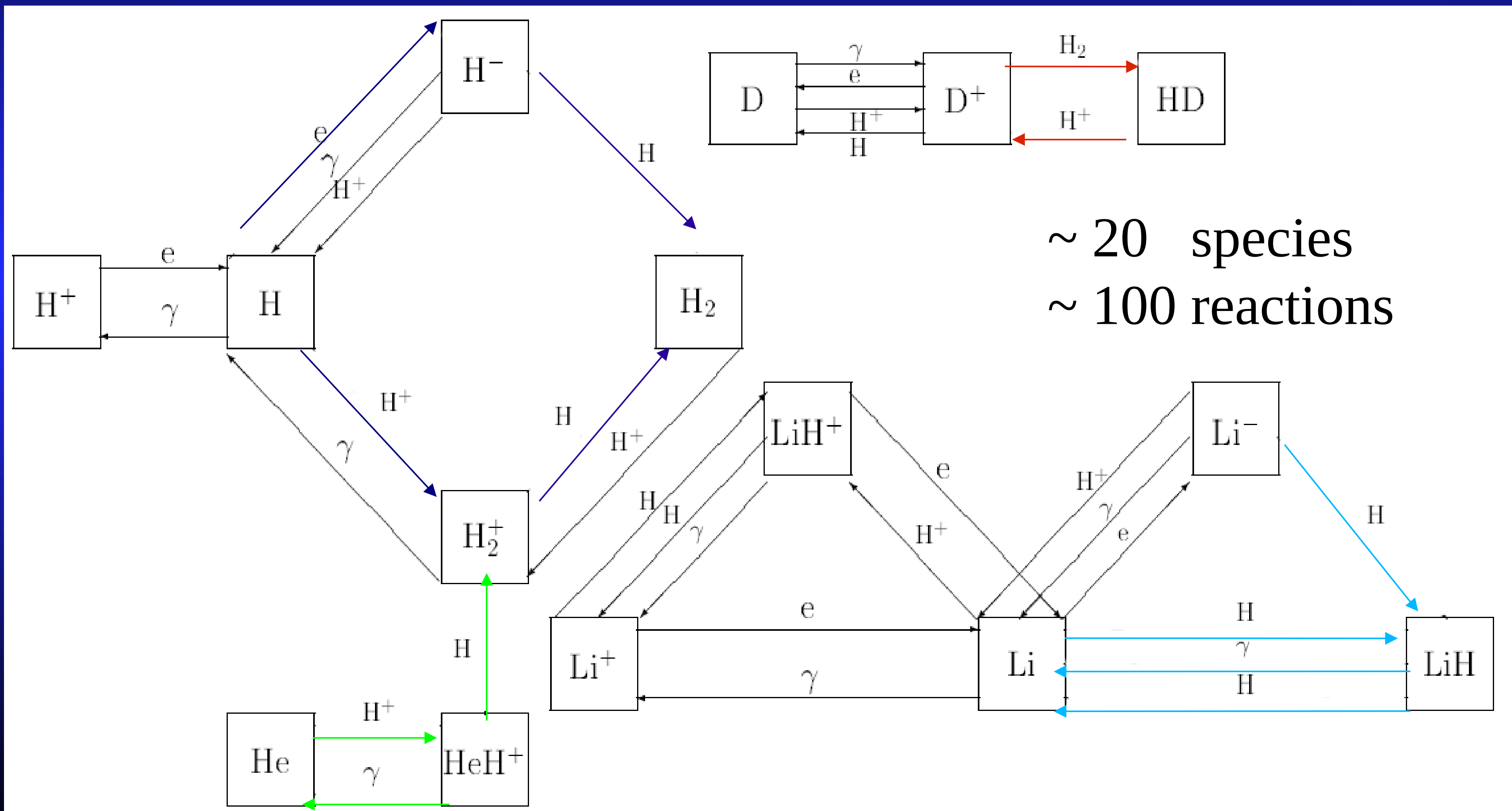
2008, MNRAS, **386**, 1023-1028

CosmoRec

Rubiño Martín et al.

2010, MNRAS, **403**, 439-452

KINETIC MODEL: CHEMICAL PROCESSES



Galli & Palla, 1998, A&A, **335**, 403–420

BEYOND THE “STANDARD” KINETICS...

Non-equilibrium effects:

- state-to-state kinetics → Maxwell-Boltzmann's distributions

?

- CMB photons → Planck's distributions

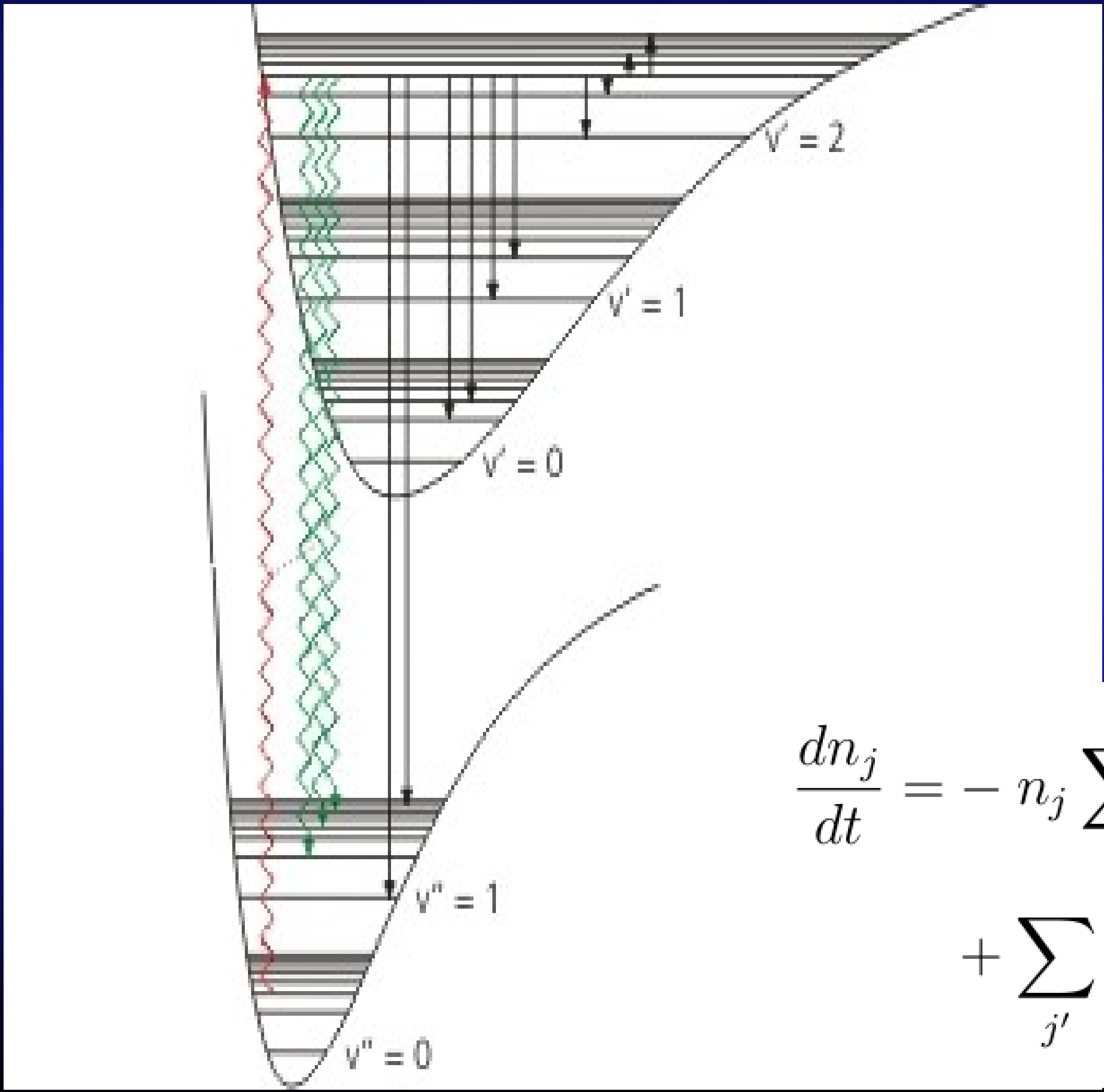
BEYOND THE “STANDARD” KINETICS...

- non-equilibrium distributions:
  - molecular vibration
  - distortion photons
    - atomic
    - molecular

    “origin”

- “chemical feedback on the chemistry”

STATE-TO-STATE APPROACH

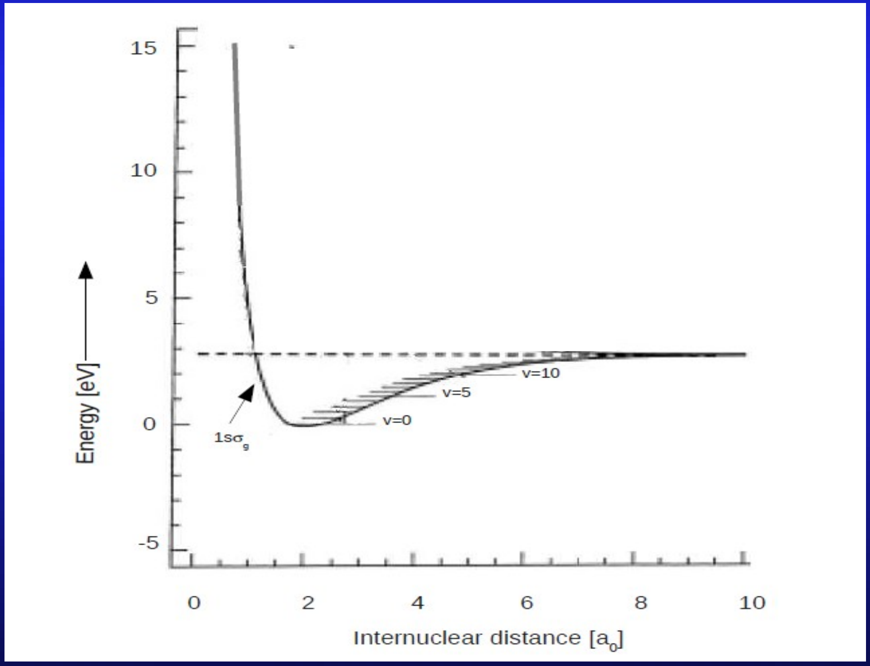


- Electronic
- Vibrational
- Rotational

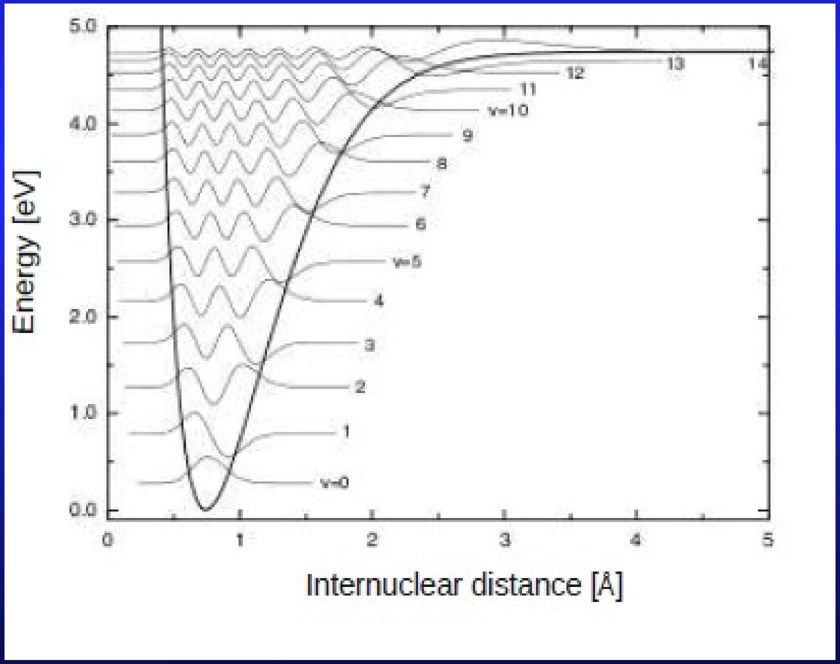
$$\frac{dn_j}{dt} = -n_j \sum_{j'} (R_{jj'} + P_{jj'} + C_{jj'} n_{j'}) + $$
$$+ \sum_{j'} R_{jj'} n_{j'} + \sum_{j'} \sum_{j''} \mathbf{C}_j^{j'j''} n_{j'} n_{j''}$$

KINETIC MODEL: CHEMICAL SPECIES

H_2^+ → 18 levels



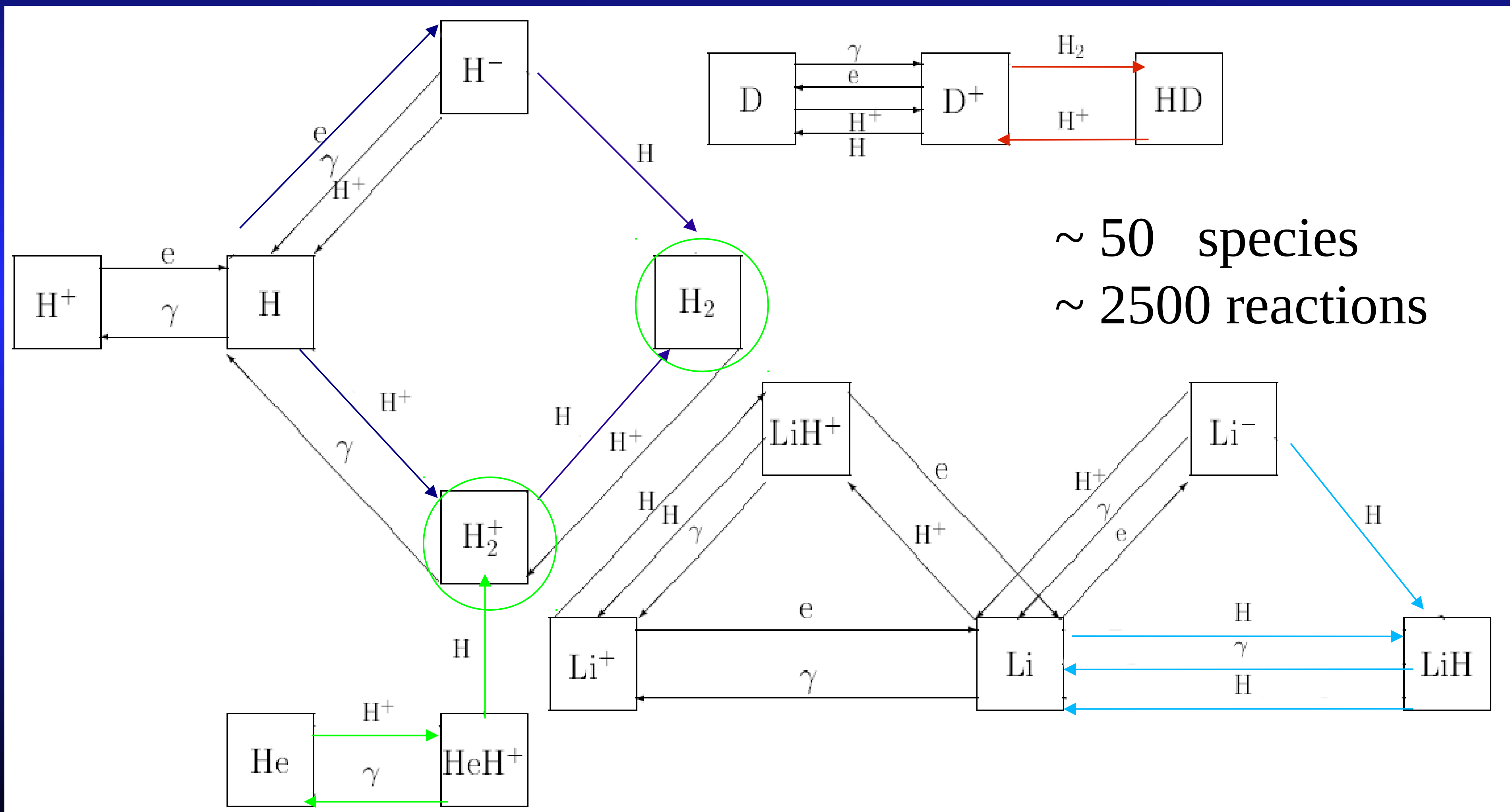
H_2 → 15 levels



KINETIC MODEL: CHEMICAL PROCESSES

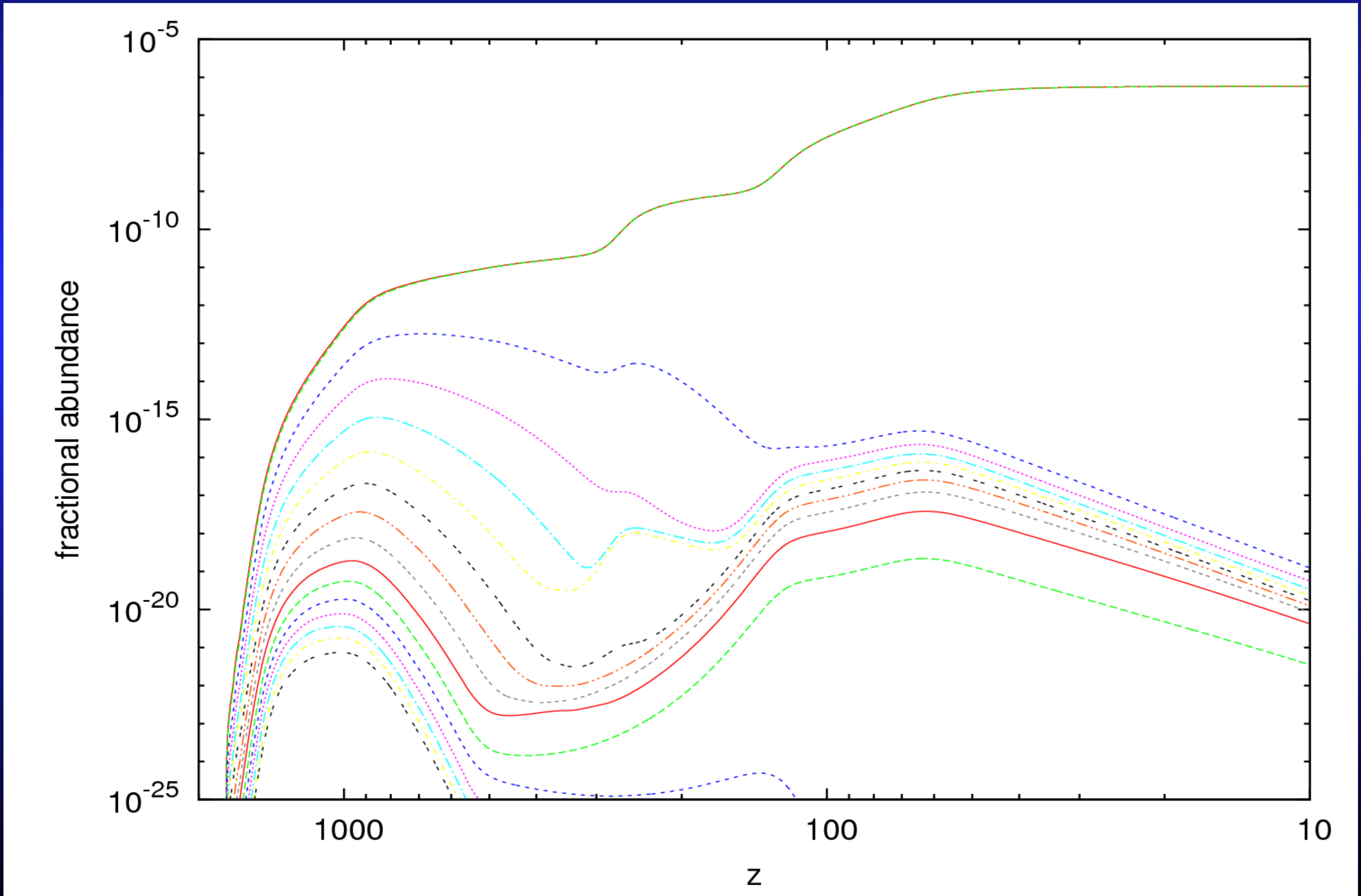
1] $H + H_2(v) \longrightarrow H + H_2(v)$
2] $H + H^- \longrightarrow H_2(v) + e^-$
3] $H + H^+ \longrightarrow H_2^+(v) + h\nu$
4] $H_2^+(v) + H \longrightarrow H_2(v') + H^+$
5] $H_2(v) + H \longrightarrow H_2^+(v') + H^+$
6] $H + H_2^+(v) \longrightarrow H + H_2^+(v)$
7] $H^+ + H_2(v) \longrightarrow H^+ + H_2(v)$
8] $H_2^+(v) + H \longrightarrow H + H + H^+$
9] $H_2(v) + H^+ \longrightarrow H + H + H^+$
10] $H_2(v) + h\nu \longrightarrow H_2^+(v') + e^-$
11] $H_2^+(v) + h\nu \longrightarrow H + H^+$
12] $H_2(v) + h\nu \longrightarrow H + H$
13] $H_2^+(v) + e^- \longrightarrow H + H$
14] $H_2(v) + e^- \longrightarrow H + H^-$
15] $H_2(v) + e^- \longrightarrow H_2(v) + e^- + h\nu$
16] $H_2(v) \longrightarrow H_2(v') + h\nu$
17] $H_2^+(v) \longrightarrow H_2^+(v') + h\nu$
18] $H + H_2(v) \longrightarrow H + H + H$
19] $HeH^+ + H \longrightarrow H_2^+(v) + He$

KINETIC MODEL: STATE-TO-STATE KINETICS



Galli & Palla, 1998, A&A, **335**, 403–420

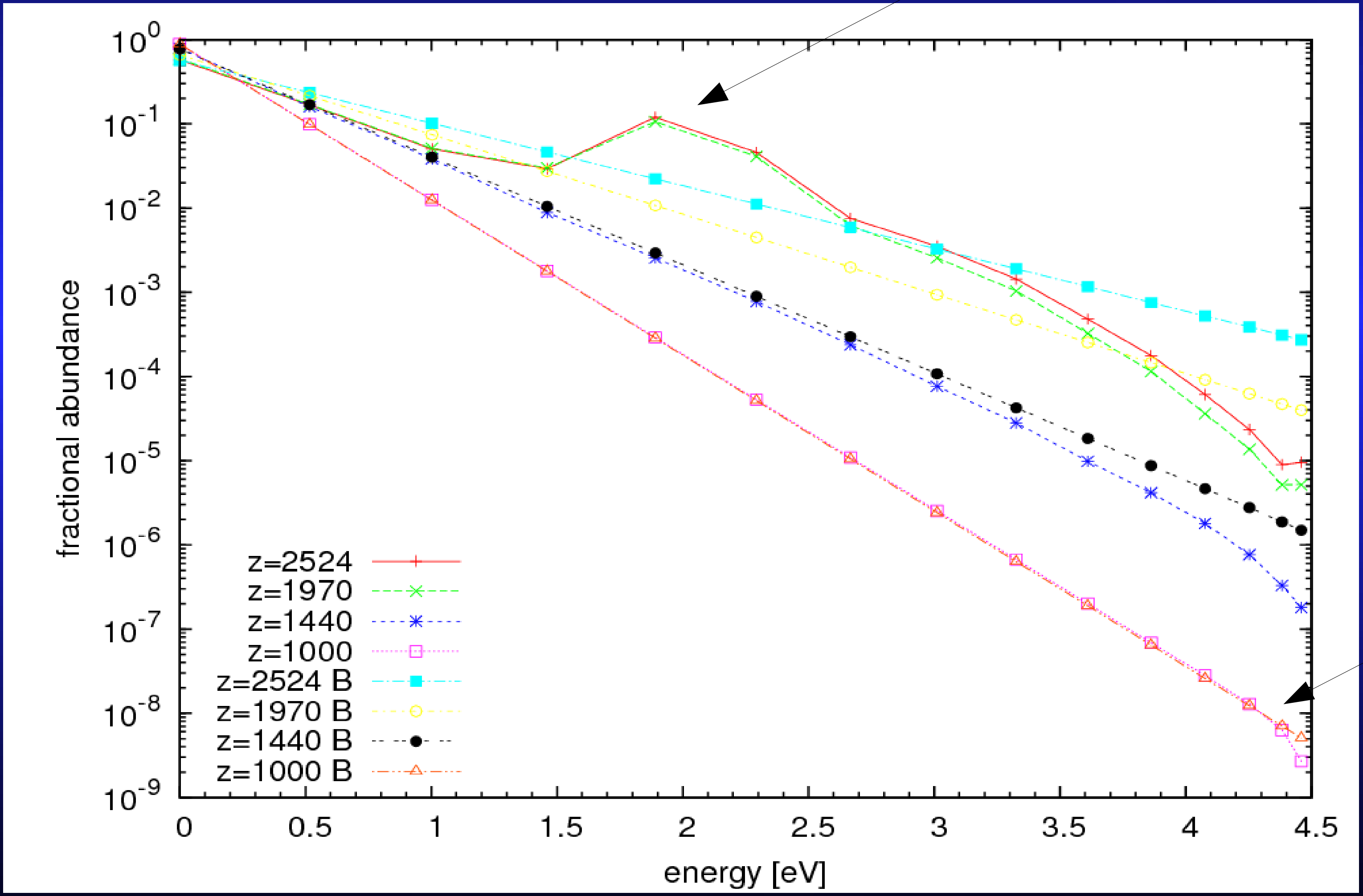
RESULTS: VDF H_2 (I)



Coppola, Longo, Capitelli, Palla, Galli, 2011, ApJS, **193**, 7-18

RESULTS: VDF H_2 (II)

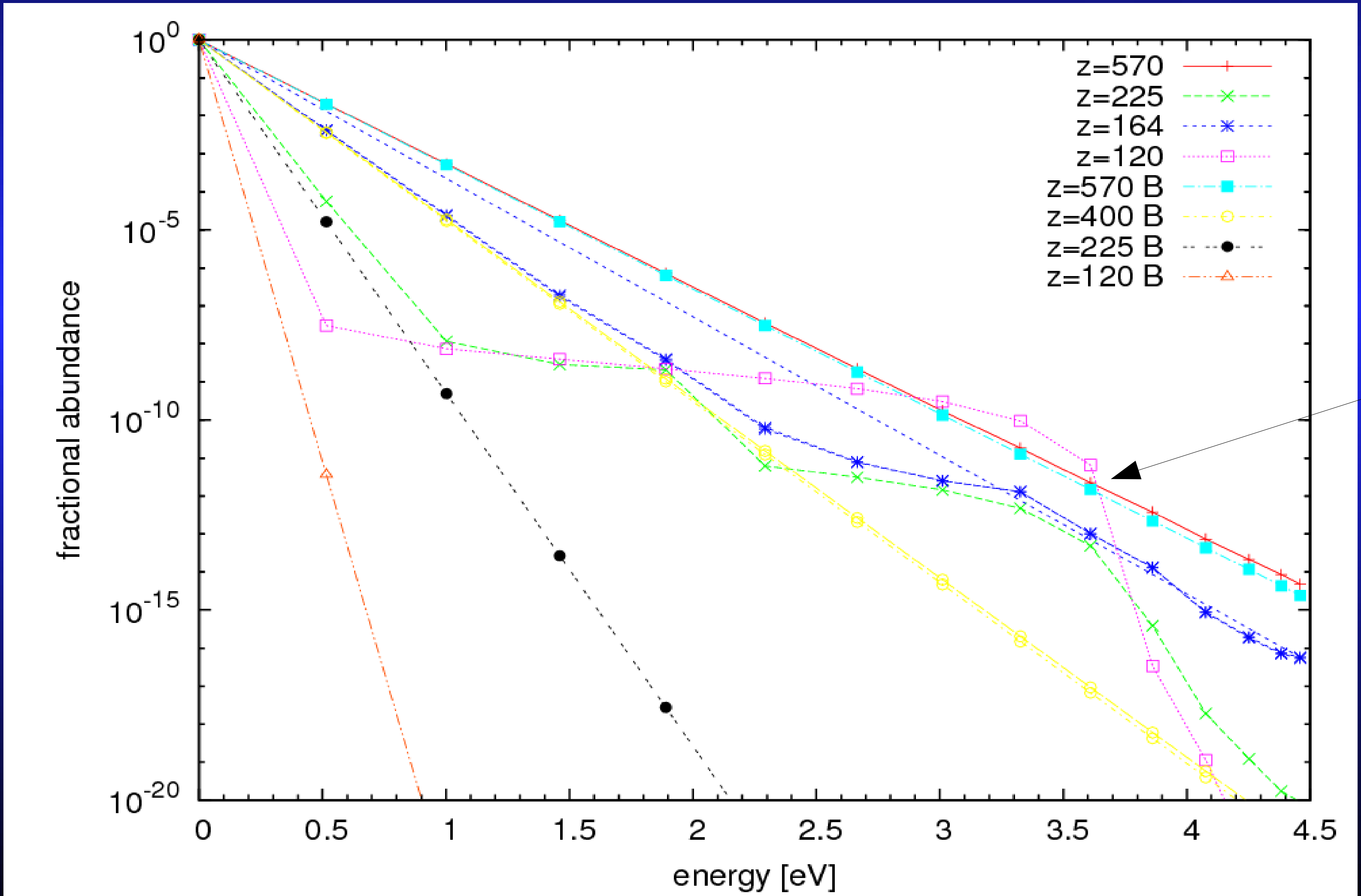
H_2^+ channel



Equilibrium!!!

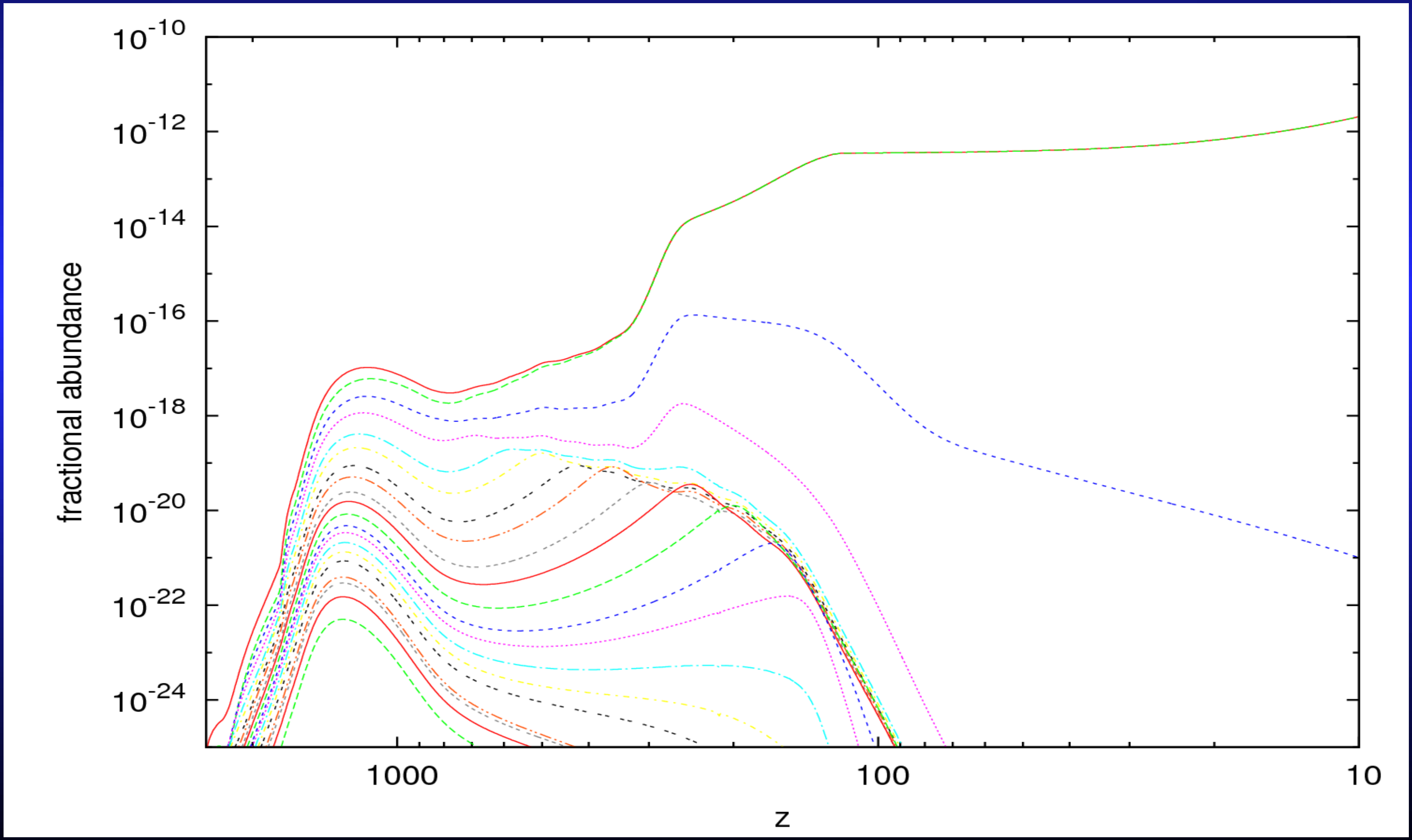
Coppola, Longo, Capitelli, Palla, Galli, 2011, ApJS, **193**, 7-18

RESULTS: VDF H_2 (III)

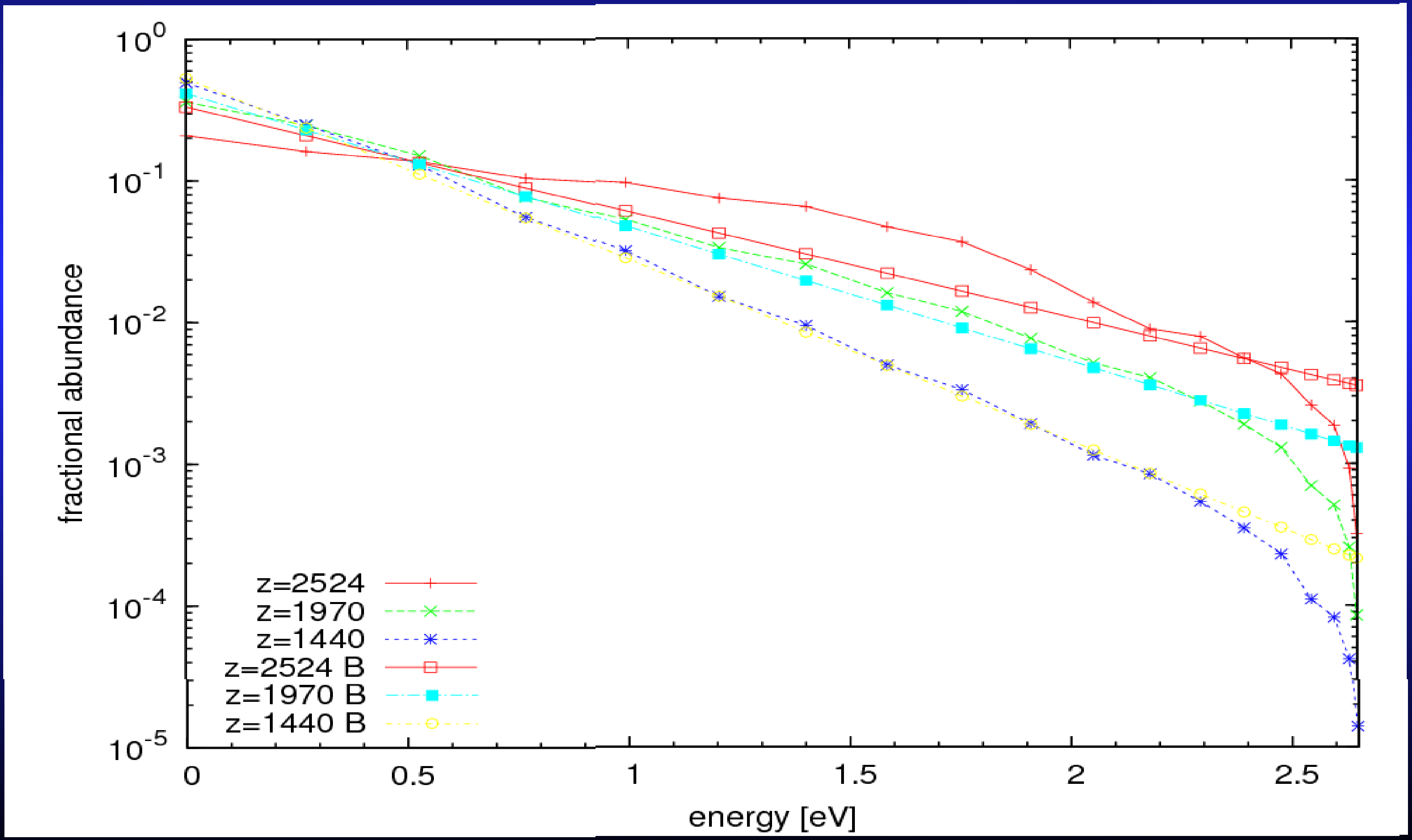


Coppola, Longo, Capitelli, Palla, Galli, 2011, ApJS, **193**, 7-18

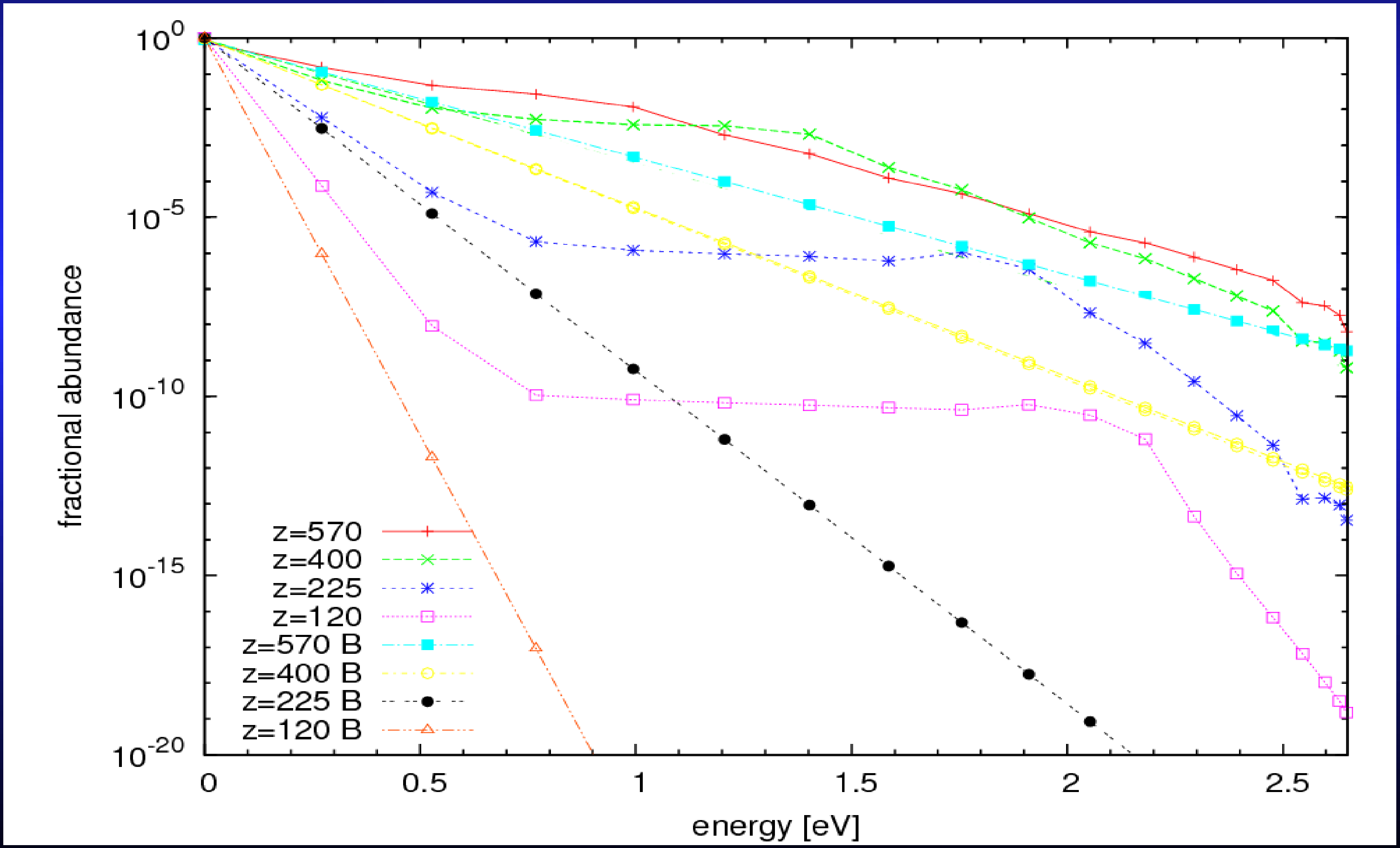
RESULTS: VDF H_2^+ (I)



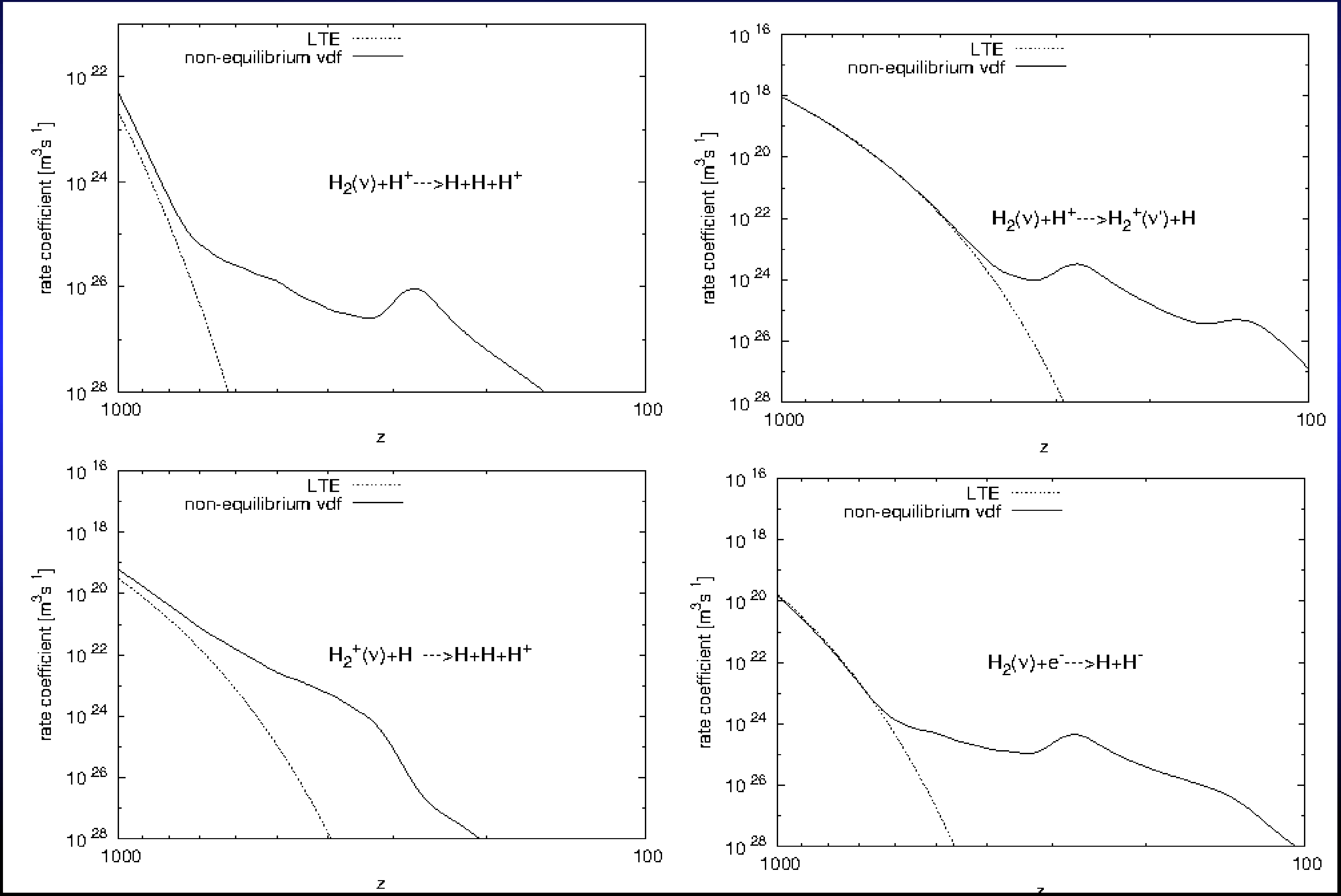
RESULTS: VDF H_2^+ (II)



RESULTS: VDF H_2^+ (III)

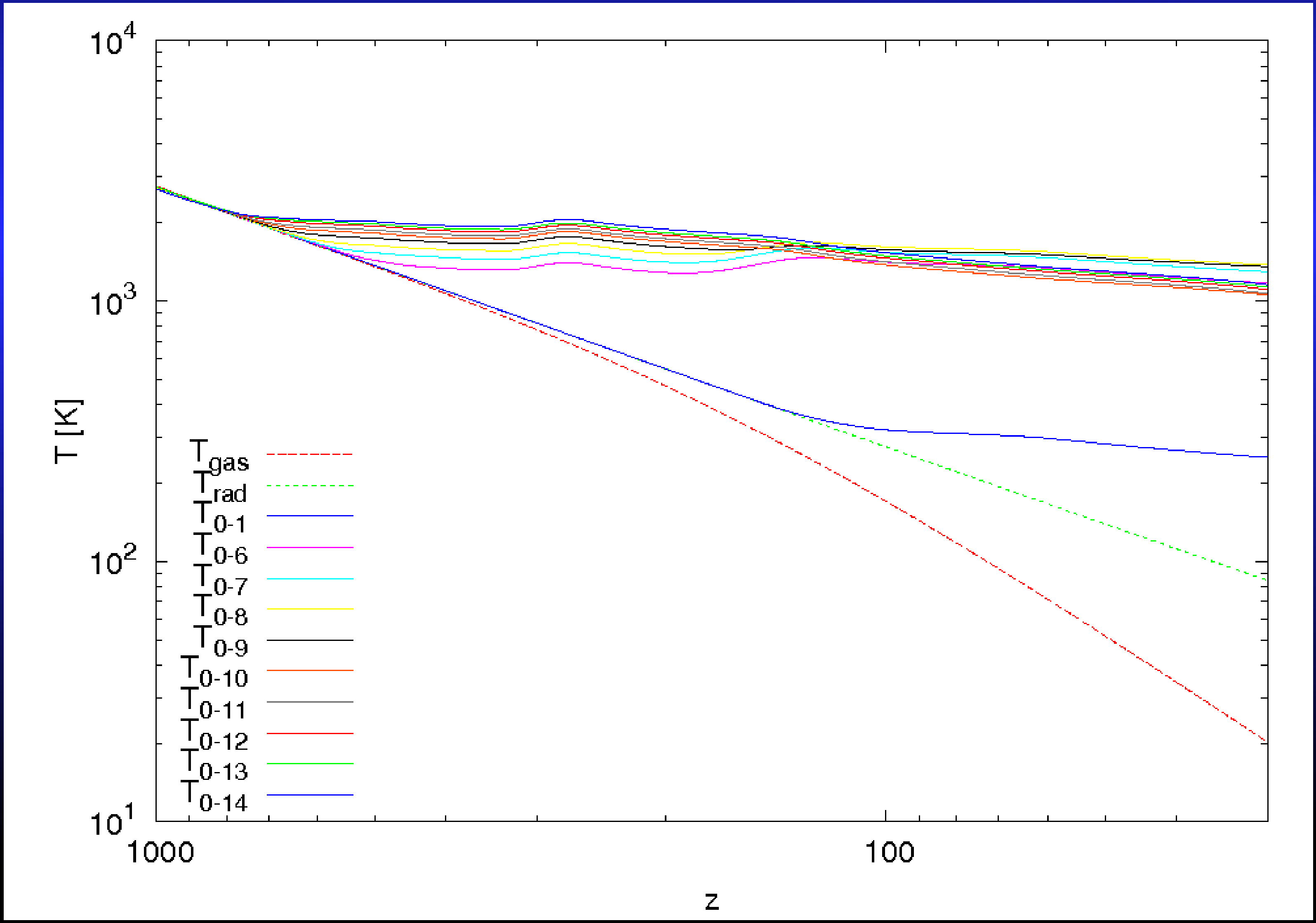


" MODIFIED" RATE COEFFICIENTS



EXCITATION TEMPERATURES

$$T_{0-v} = \frac{E_v - E_0}{k_B \ln(n_0/n_v)}$$



BEYOND THE “STANDARD” KINETICS...

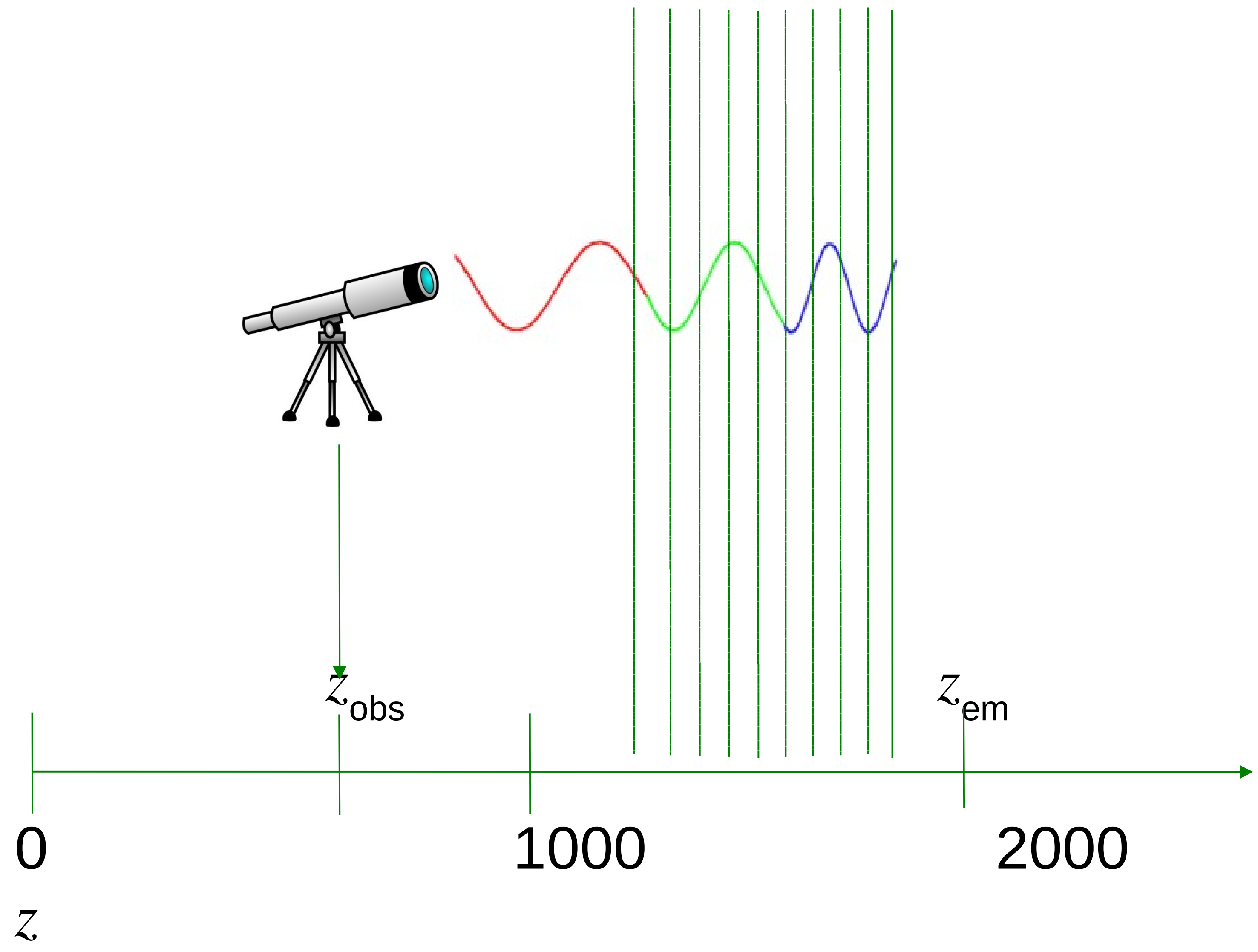
Non-equilibrium effects:

- state-to-state kinetics → Maxwell-Boltzmann's distributions

?

- CMB photons → Planck's distribution

SPECTRAL DISTORTIONS



SPECTRAL DISTORTIONS

$$j_{\nu_{ij}}(z) = h\nu_{ij}\Delta R_{ij}(z)\phi(\nu(z))$$

$$\Delta R_{ij}(\nu) = A_{ij}N_i \frac{e^{h\nu_{ij}/kT_r}}{e^{h\nu_{ij}/kT_r}-1}\left[1-\frac{N_j}{N_i}e^{-h\nu_{ij}/kT_r}\right]$$

$$I_{ij}^{z_{obs}}(\nu) = \frac{c}{4\pi}\int_{z_{em}}^{z_{obs}} \frac{j_{\nu_{ij}}(z)}{(1+z)^3}(1+z_{obs})^3\left|\frac{dt}{dz}\right| dz$$

$$I_{ij}^{z_{obs}}(\nu) = \frac{ch}{4\pi}\frac{\Delta R_{ij}(z_{em})}{H(z_{em})}\frac{(1+z_{obs})^3}{(1+z_{em})^3}$$

SPECTRAL DISTORTIONS

$$\frac{1}{c}\frac{\mathrm{d}J_\nu}{\mathrm{d}z} = \frac{\kappa_\nu J_\nu - j_\nu}{H_0(1+z)^2\sqrt{1+\Omega_0 z}} + \frac{3J_\nu}{c(1+z)}$$

$$\kappa_\nu = \frac{c^2}{8\pi\nu^2} n_1 A_{\mathrm{ul}} \frac{g_{\mathrm{u}}}{g_{\mathrm{l}}}\left(1 - \frac{g_{\mathrm{l}} n_{\mathrm{u}}}{g_{\mathrm{u}} n_{\mathrm{l}}}\right)\phi(\nu - \nu_{\mathrm{ul}})$$

$$j_\nu = \frac{h\nu}{4\pi} n_{\mathrm{u}} A_{\mathrm{ul}} \phi(\nu - \nu_{\mathrm{ul}})$$

$$\left.\frac{\Delta J_\nu}{J_\nu}\right|_{z=0} = [R(z_{\mathrm{i}}) - 1][1 - \mathrm{e}^{-\tau(z_{\mathrm{i}})}]$$

$$R(z_{\mathrm{i}}) = \left[\frac{g_{\mathrm{u}} n_{\mathrm{l}}(z_{\mathrm{i}})}{g_{\mathrm{l}} n_{\mathrm{u}}(z_{\mathrm{i}})} - 1\right]^{-1}\left\{\exp\left[\frac{h\nu_{\mathrm{ul}}}{kT_{\mathrm{r}}(z_{\mathrm{i}})}\right] - 1\right\}$$

Bougleux, E. & Galli, D. **1997**
MNRAS, **288**, 638-648

SPECTRAL DISTORTIONS

- matter/antimatter annihilation
- decaying particles
- interaction with matter

....

- primordial atomic recombination ($z \sim 1100$)

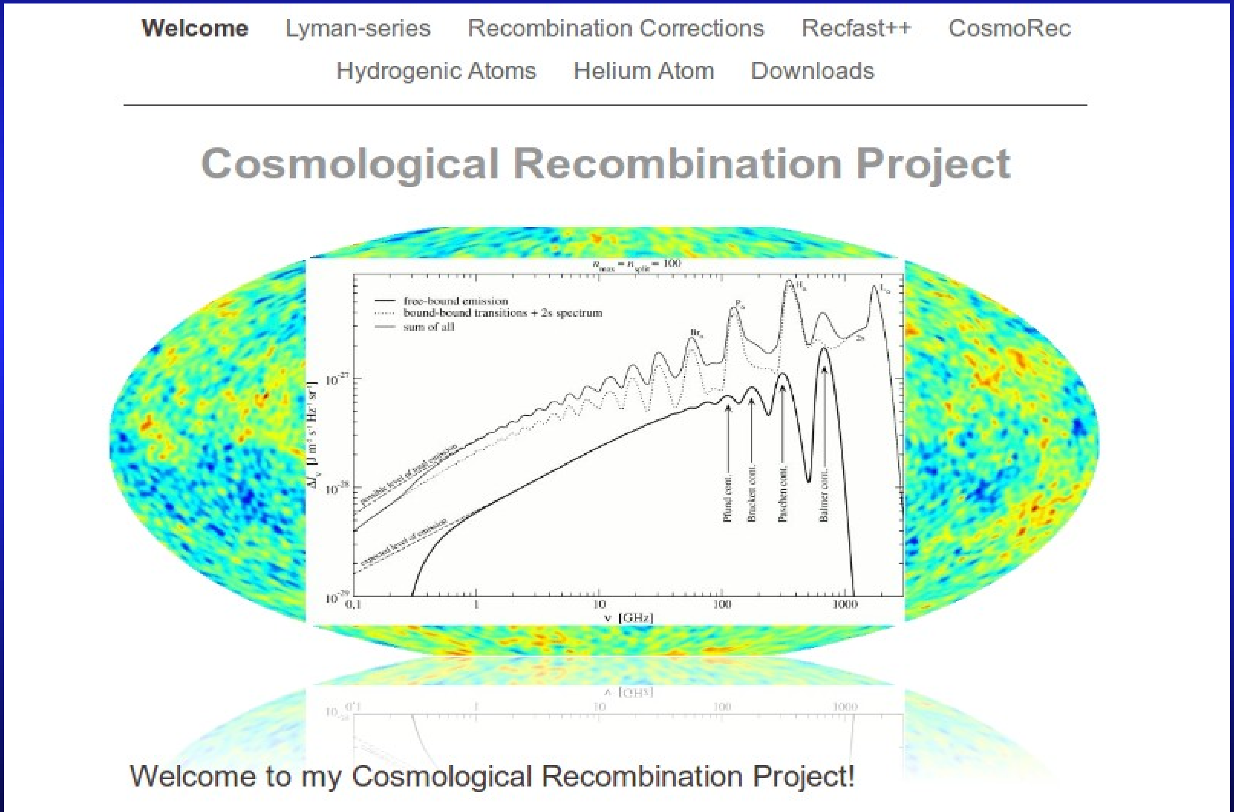
$$A^+ + e^- \longrightarrow A + h\nu$$

He^{++} He^+
H^+

- molecular radiative cascade

$$H_2(v) \longrightarrow H_2(v') + h\nu$$

PRIMORDIAL ATOMIC RECOMBINATION



CosmoRec

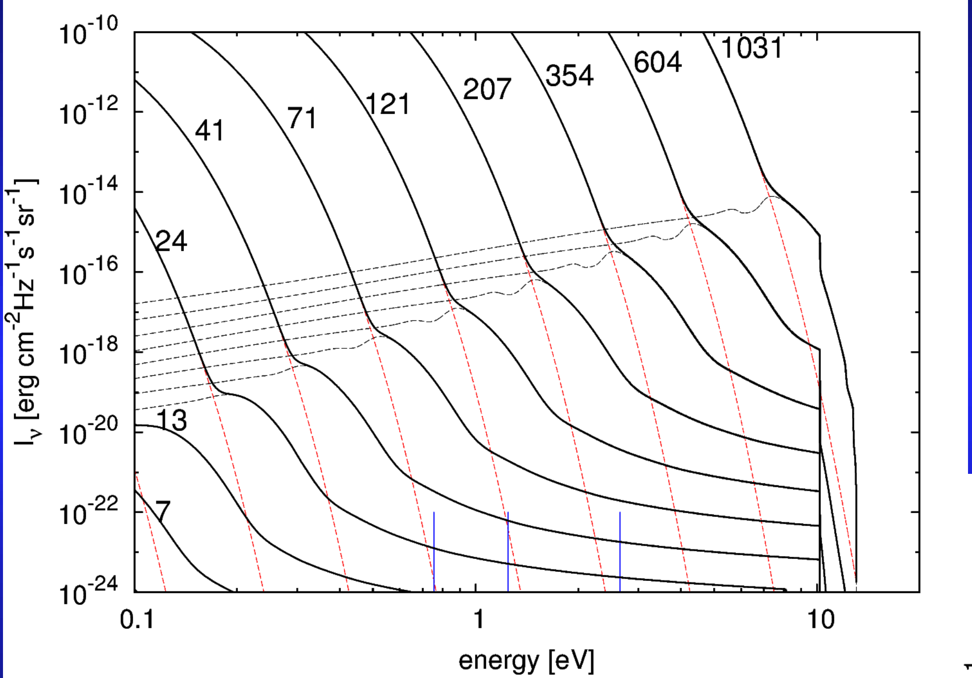
by

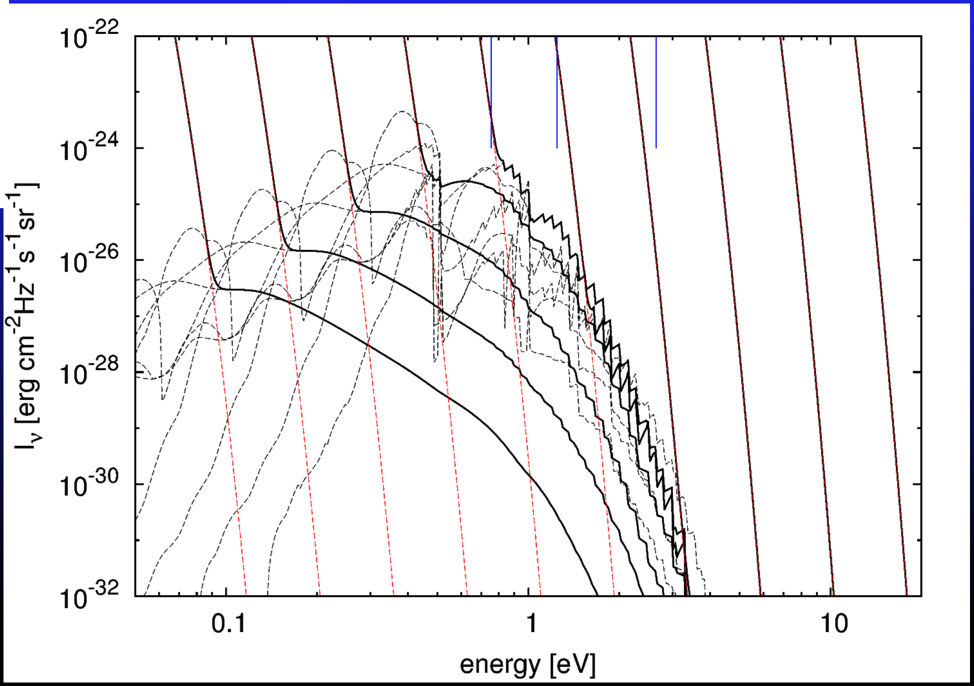
Jens Chluba

- effective multi-level approach;
- fast and accurate (~1.3 sec)
- solves a detailed radiative transfer problem for Ly-n
- available @ www.Chluba.de/CosmoRec

http://www.cita.utoronto.ca/~jchluba/Science_Jens/Recombination/Welcome.htm

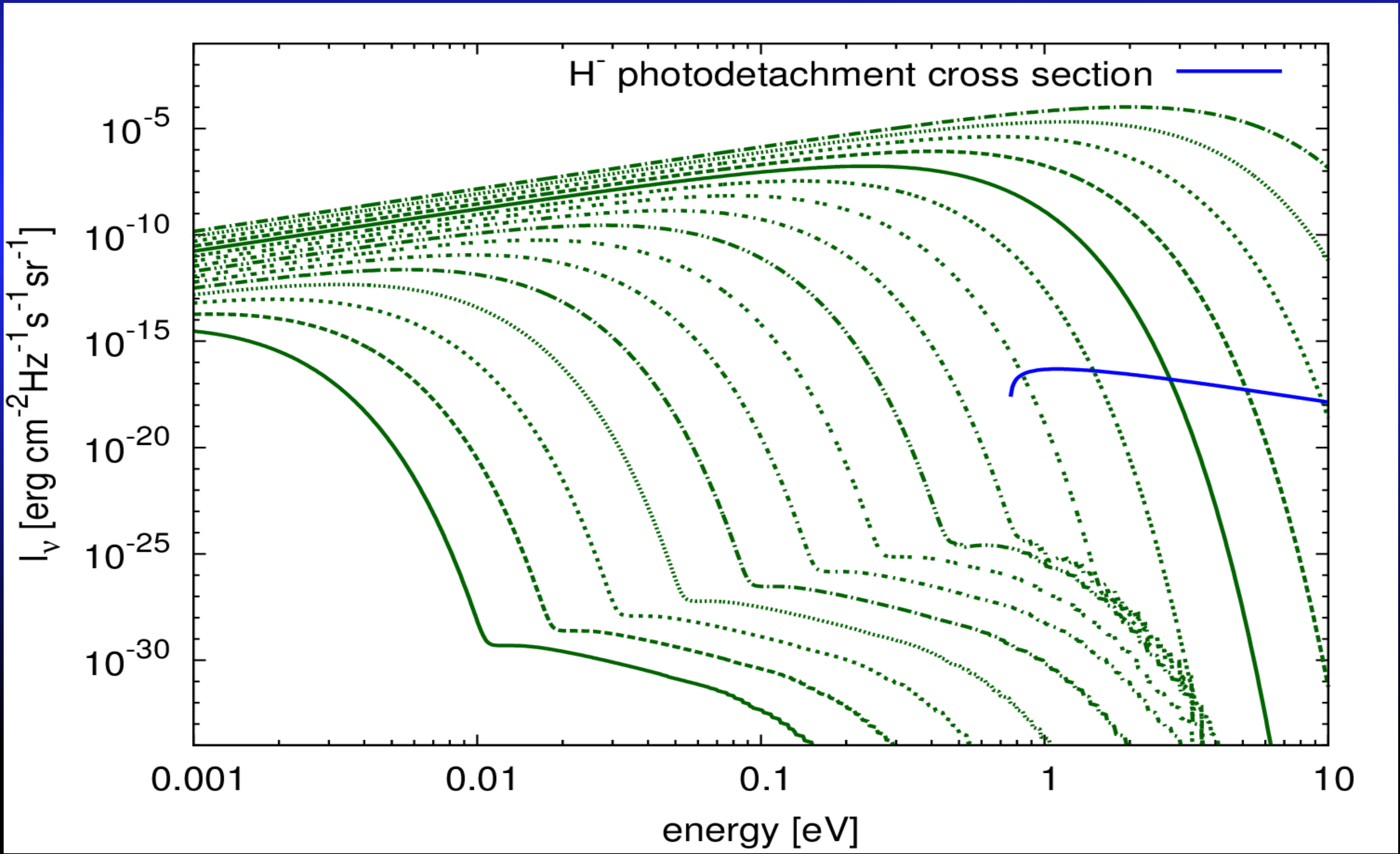
SPECTRAL DISTORTIONS



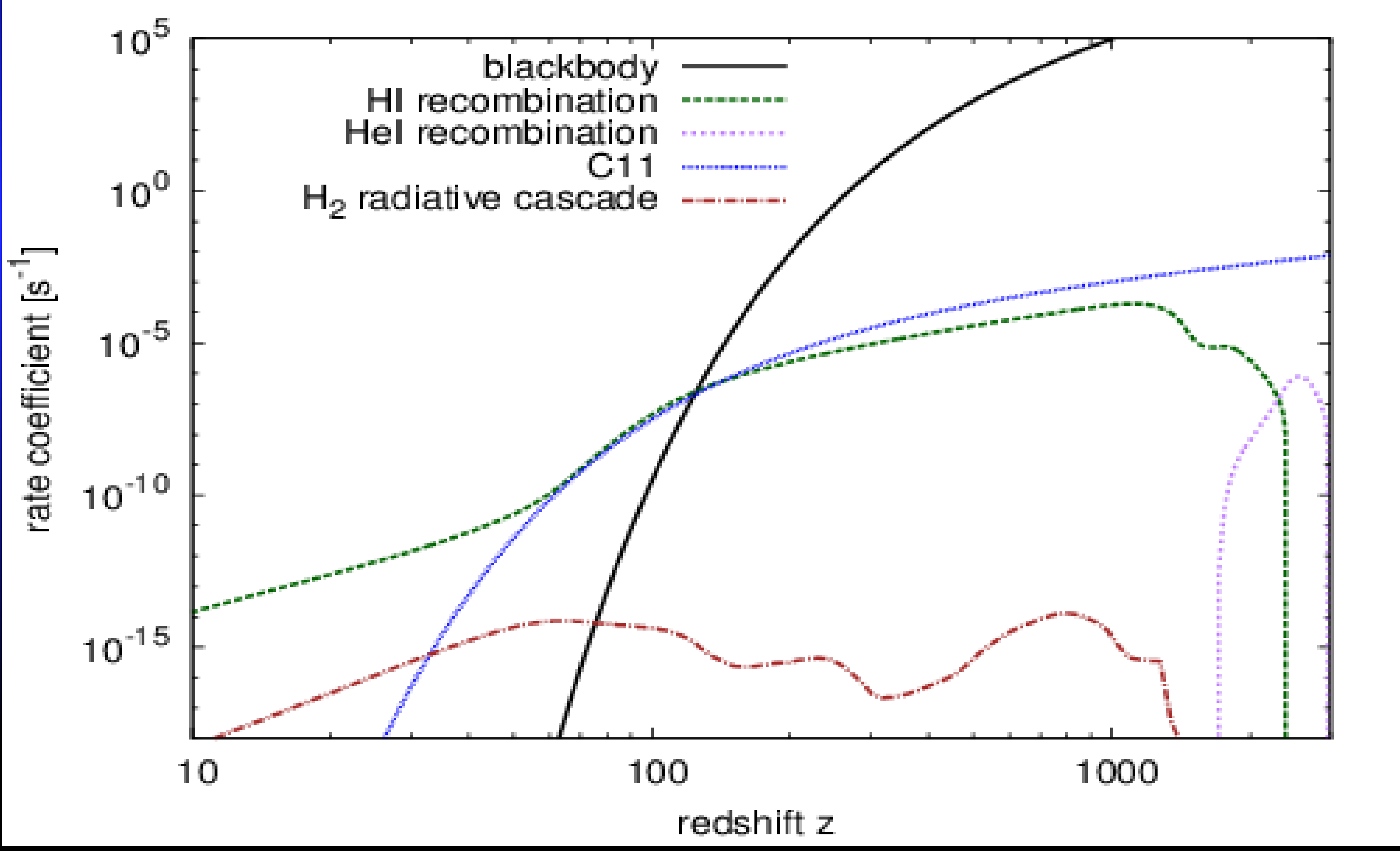


Coppola et al. 2013
MNRAS **434** (1) 114-122

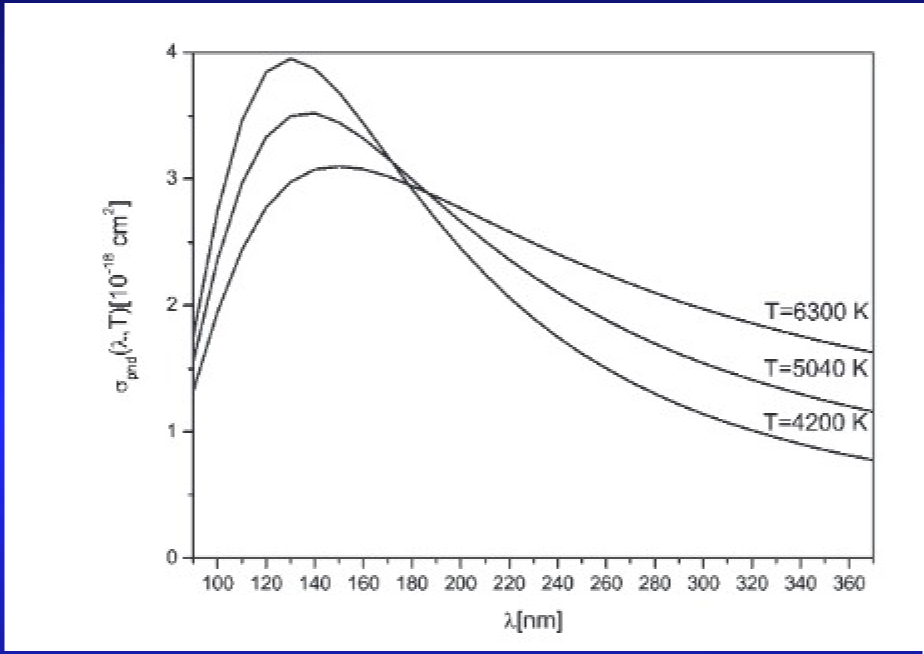
SPECTRAL DISTORTIONS

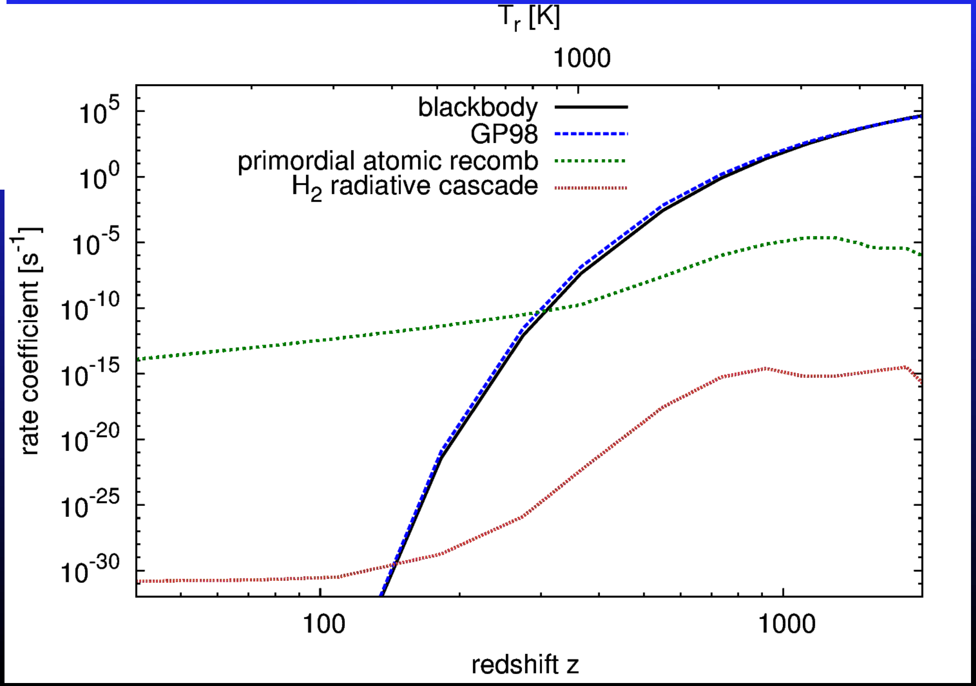


SPECTRAL DISTORTIONS: H^- photodetachment

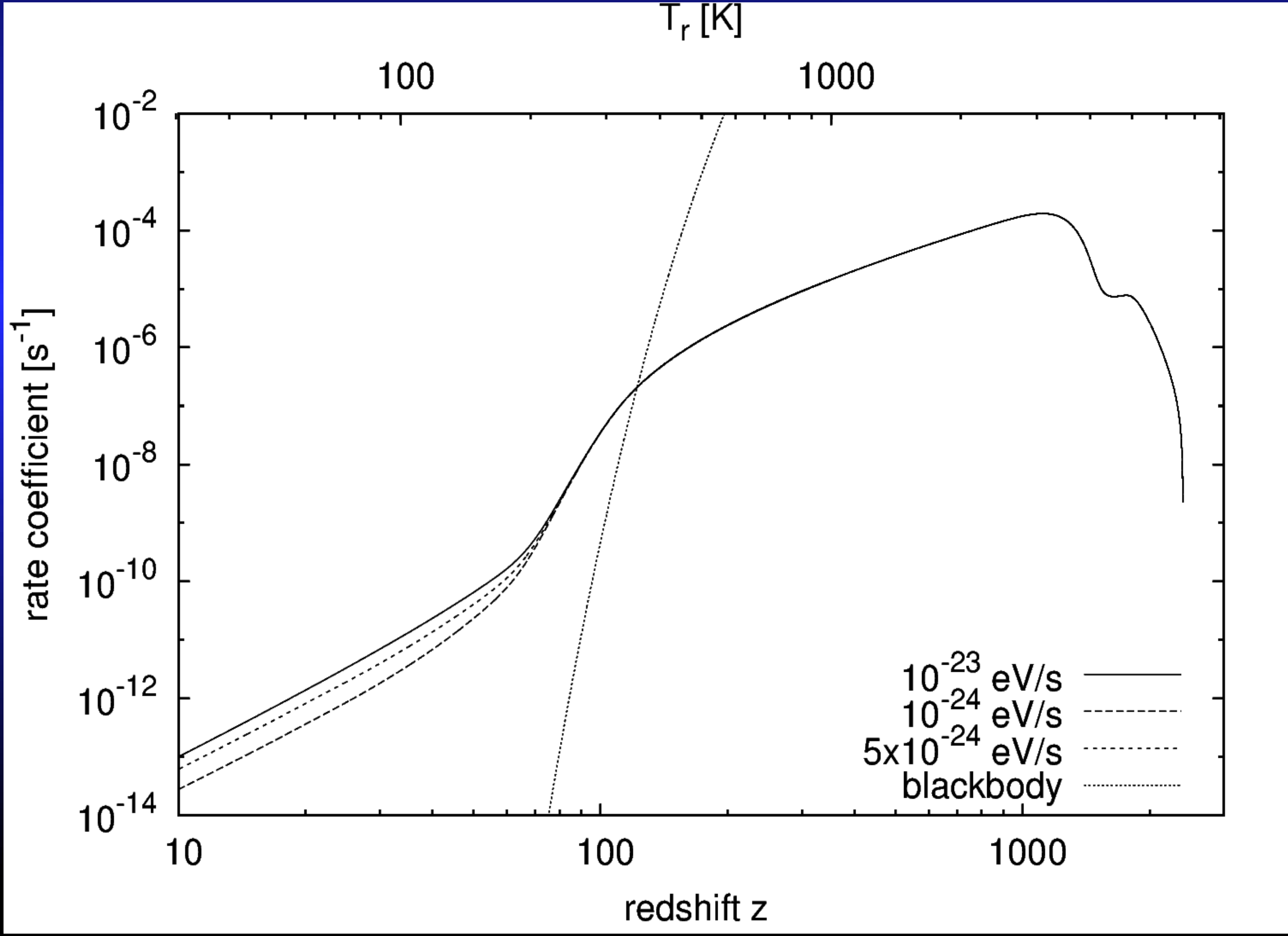


SPECTRAL DISTORTIONS: H_2^+ photodissociation

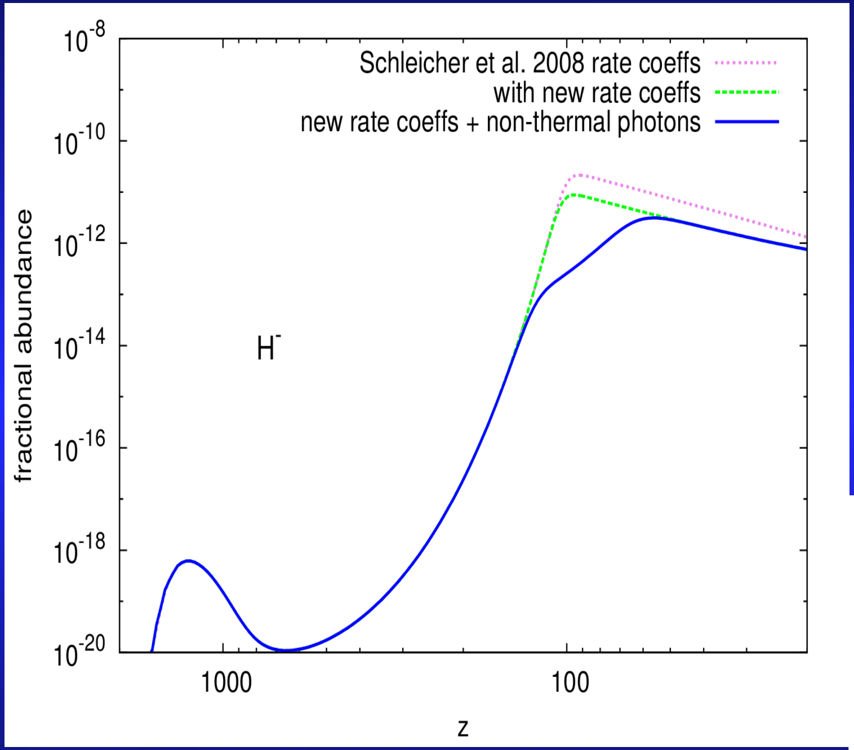


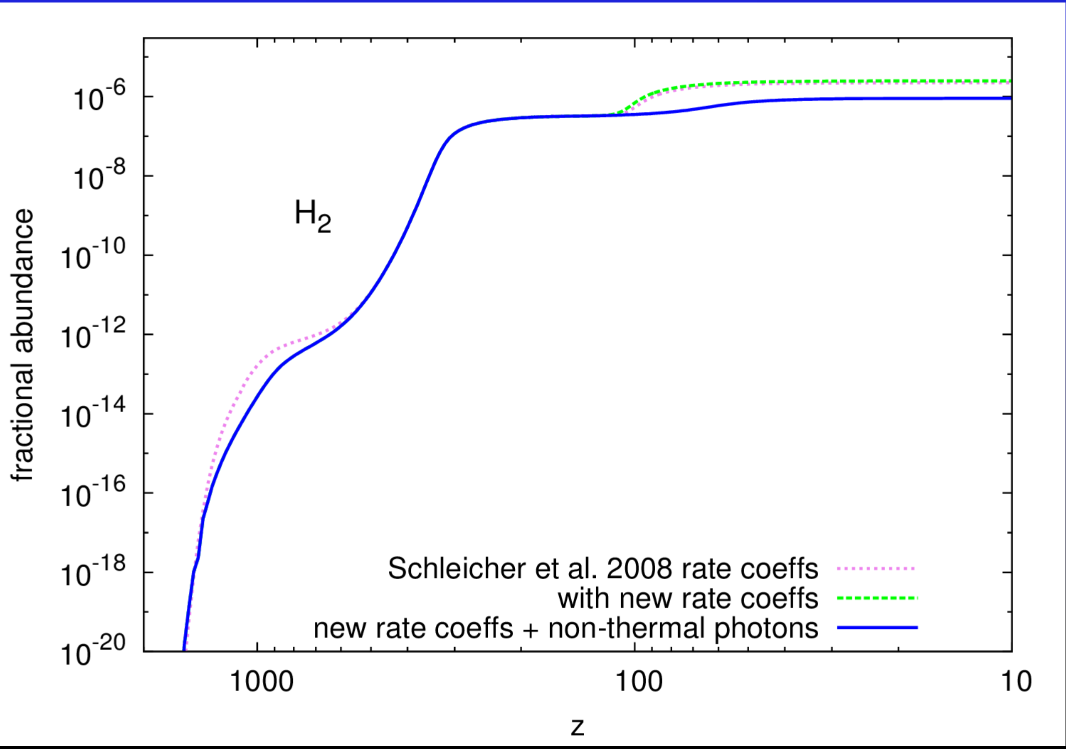


SPECTRAL DISTORTIONS: DARK MATTER ANNIHILATION

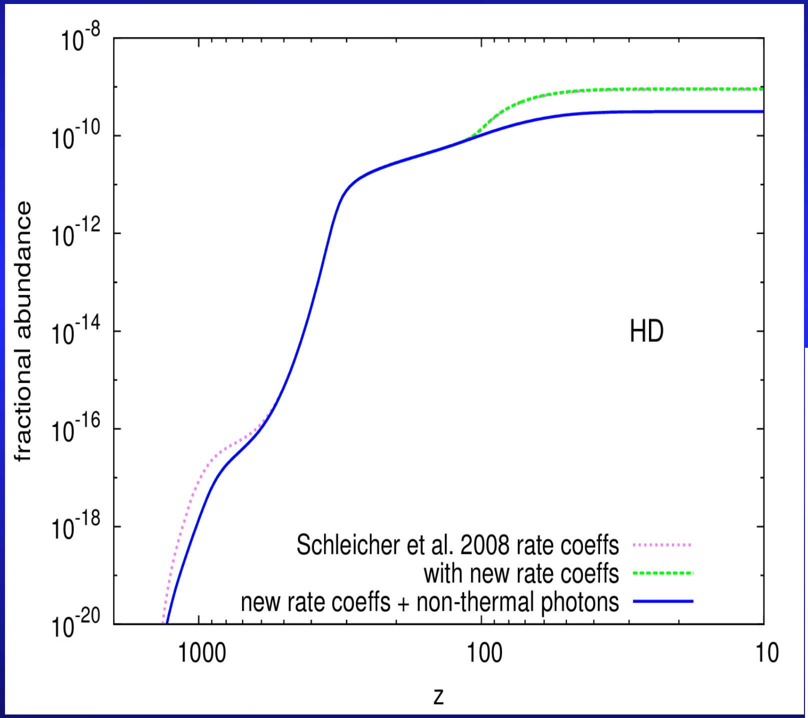


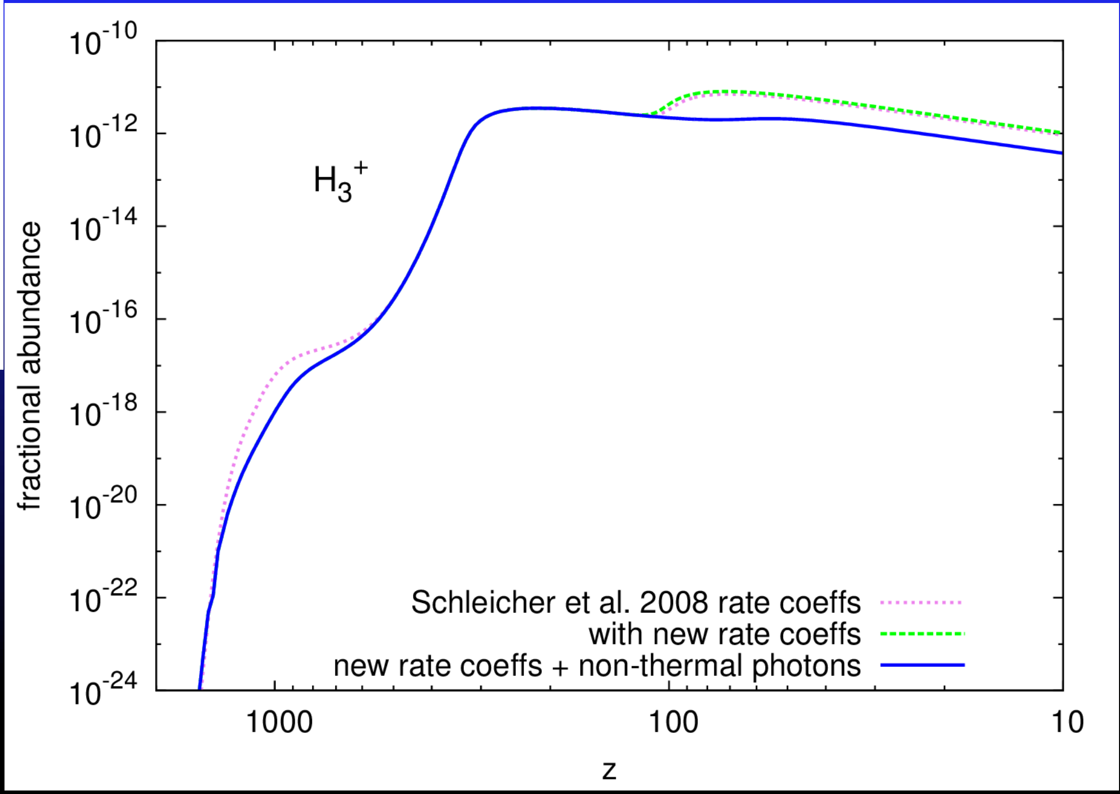
SPECTRAL DISTORTIONS



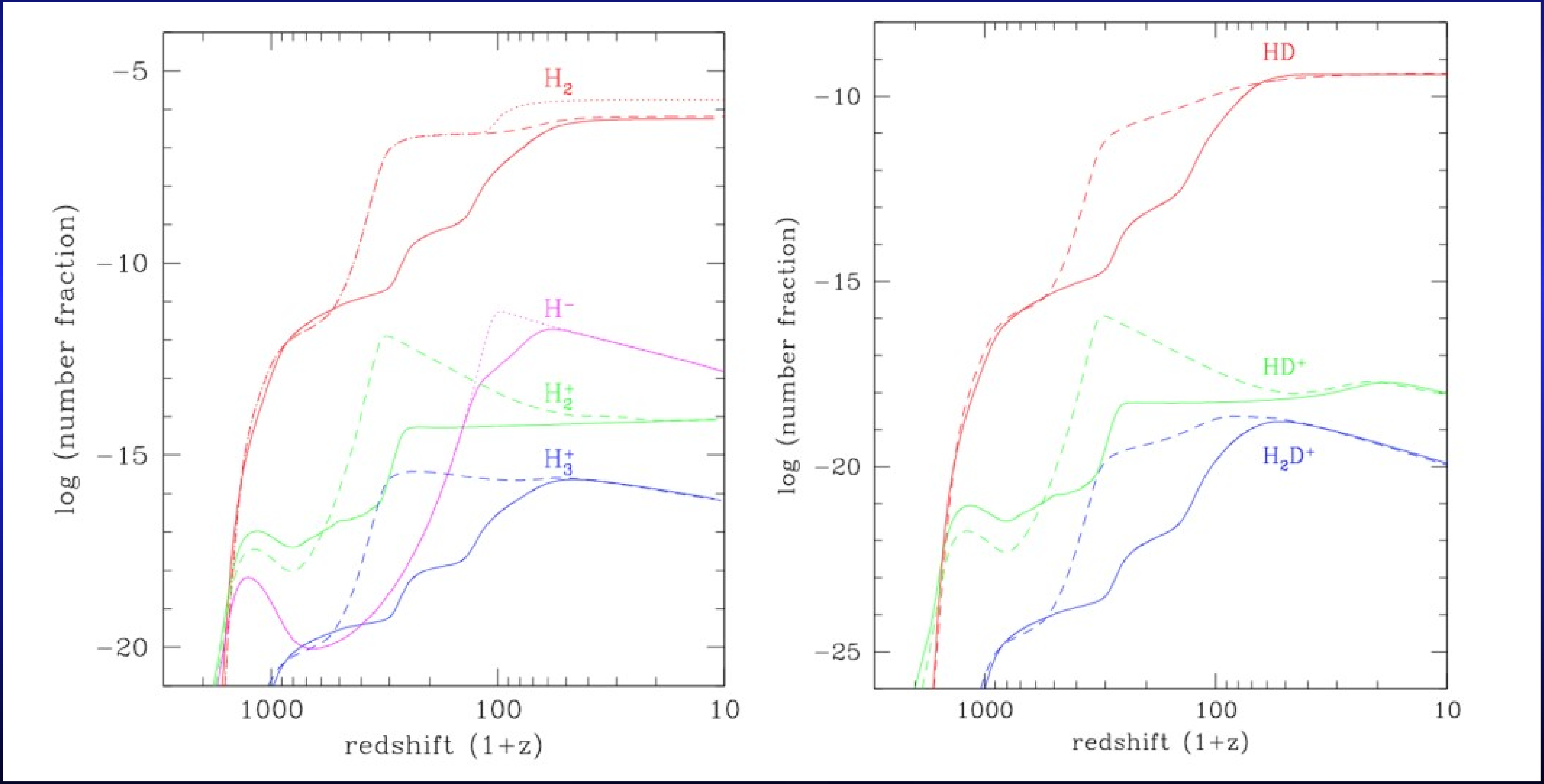


SPECTRAL DISTORTIONS





" MODIFIED" FRACTIONAL ABUNDANCES



Galli & Palla, Annual Review of Astronomy and Astrophysics, **51,** 163-206, 2013

MOVING TO PREGALACTIC SHOCKS...

- Steady state shock
- 1D, plane symmetric
- Homogeneous IGM @ fixed z

pre-shock region	post-shock region
T_1	T_2
ρ_1	ρ_2
u_1	u_2

PREGALACTIC SHOCKS: APPROXIMATIONS

$J\nu$ ⟶ CMB @ z = 10

- no external radiation field (only CMB);
- steady, plane-parallel shock wave propagating through the homogeneous medium which is at rest and consists of a pure hydrogen gas
- no gravitational forces from external sources
- cosmological adiabatic cooling neglected

pre-shock region	post-shock region
T_1	T_2
ρ_1	ρ_2
u_1	u_2

⟶

PREGALACTIC SHOCKS: JUMP CONDITIONS ACROSS THE SHOCK FRONT

$$\rho_2 v_2 = \rho_1 v_s$$

$$\rho_2 v_2^2 + p_2 = \rho_1 v_s^2 + p_1$$

$$v_2\left(\frac{\rho_2 v_2^2}{2} + \frac{\gamma_2}{\gamma_2 - 1} p_2\right) = v_s\left(\frac{\rho_1 v_s^2}{2} + \frac{\gamma_1}{\gamma_1 - 1} p_1\right)$$

mass
momentum
energy

} conservation

pre-shock region	post-shock region
T_1	T_2
ρ_1	ρ_2
v_1	v_2

PREGALACTIC SHOCKS: INITIAL CONDITIONS

$$\mathrm{H} \rightleftharpoons \mathrm{H}^+ + e^-$$

$$\mathrm{He} \rightleftharpoons \mathrm{He}^+ + e^-$$

$$\mathrm{He}^+ \rightleftharpoons \mathrm{He}^{++} + e^-$$

$$\mathrm{D} \rightleftharpoons \mathrm{D}^+ + e^-$$

$$\rho_1 u_1 = \rho_2 u_2$$

$$p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2$$

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2}$$

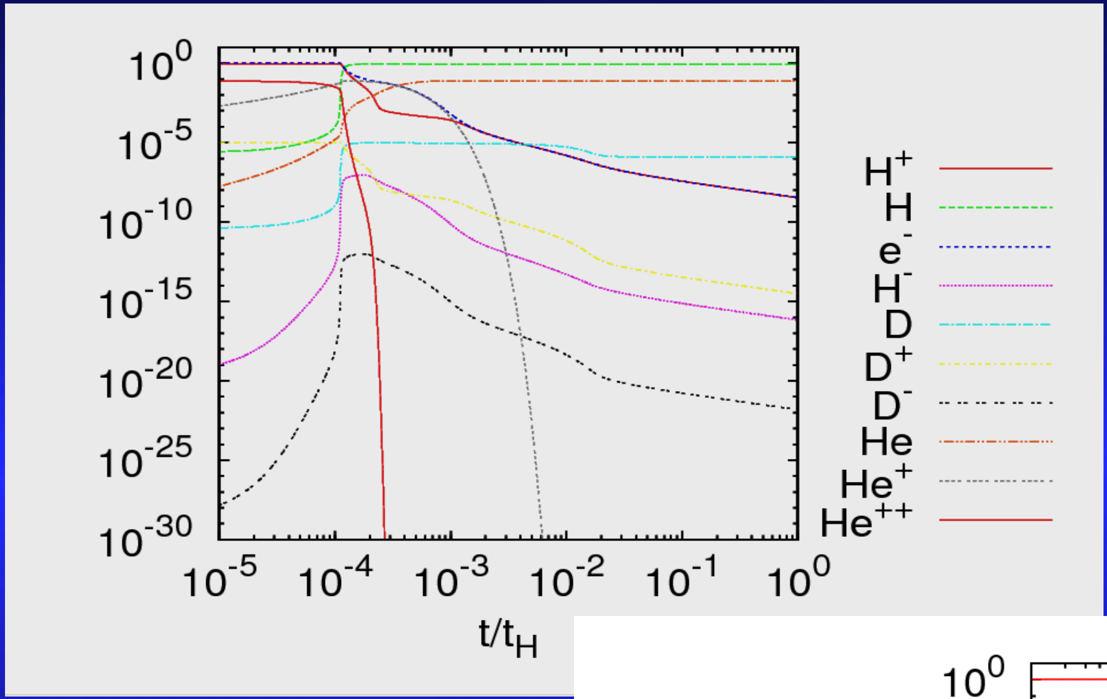
$$h_1 = \frac{5}{2}\frac{n_1 k_B T_1}{\rho_1}$$

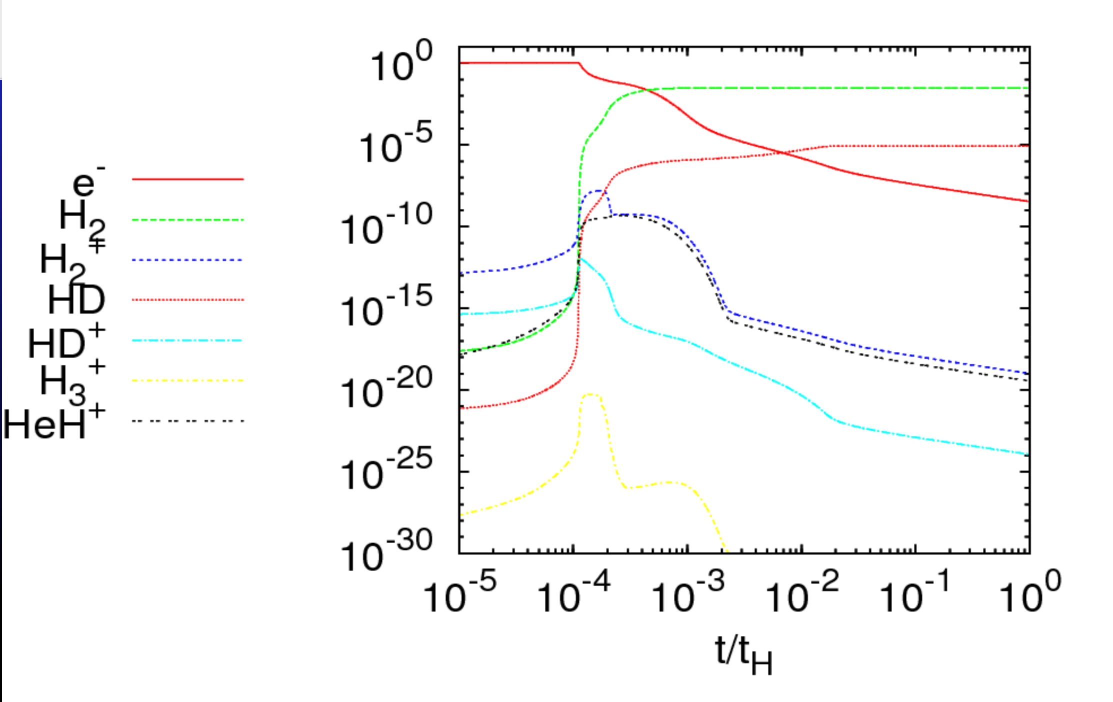
$$h_2 = \frac{5}{2}\frac{n_2 k_B T_2}{\rho_2} + \frac{(n_{2,H^+} I_H + n_{2,D^+} I_D + n_{2,He^+} I_{He})}{\rho_2}$$

v = 200 km/s

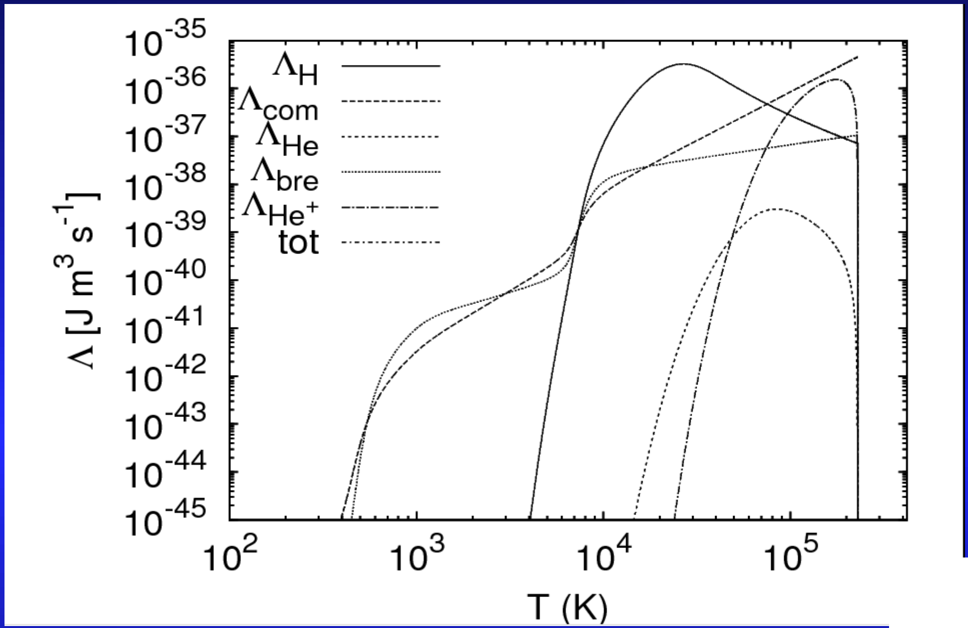
$$4v_1^2 y^2 - 5\left(v_1^2 + \frac{kT_1}{m_1}\right) y + v_1^2 + 5\frac{kT_1}{m1} - 2 \times I = 0$$

PREGALACTIC SHOCKS: FRACTIONAL ABUNDANCES

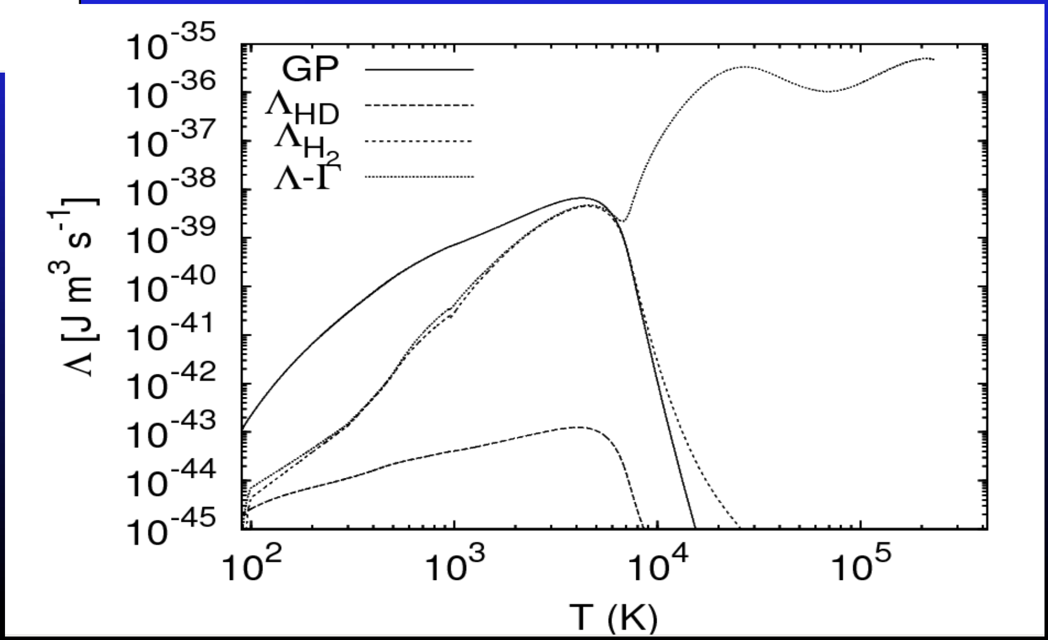




PREGALACTIC SHOCKS: COOLING FUNCTIONS

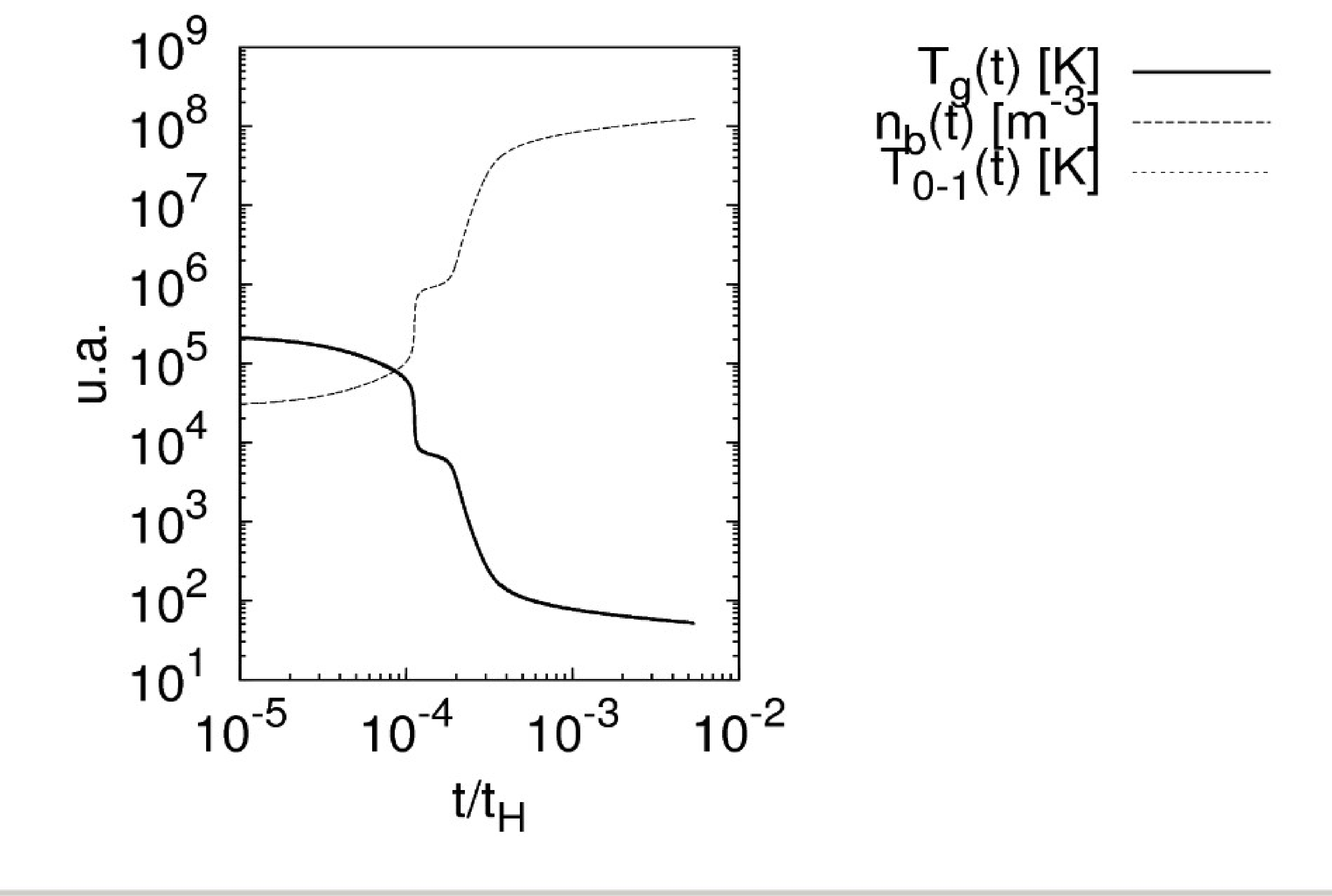


… @ high temperatures

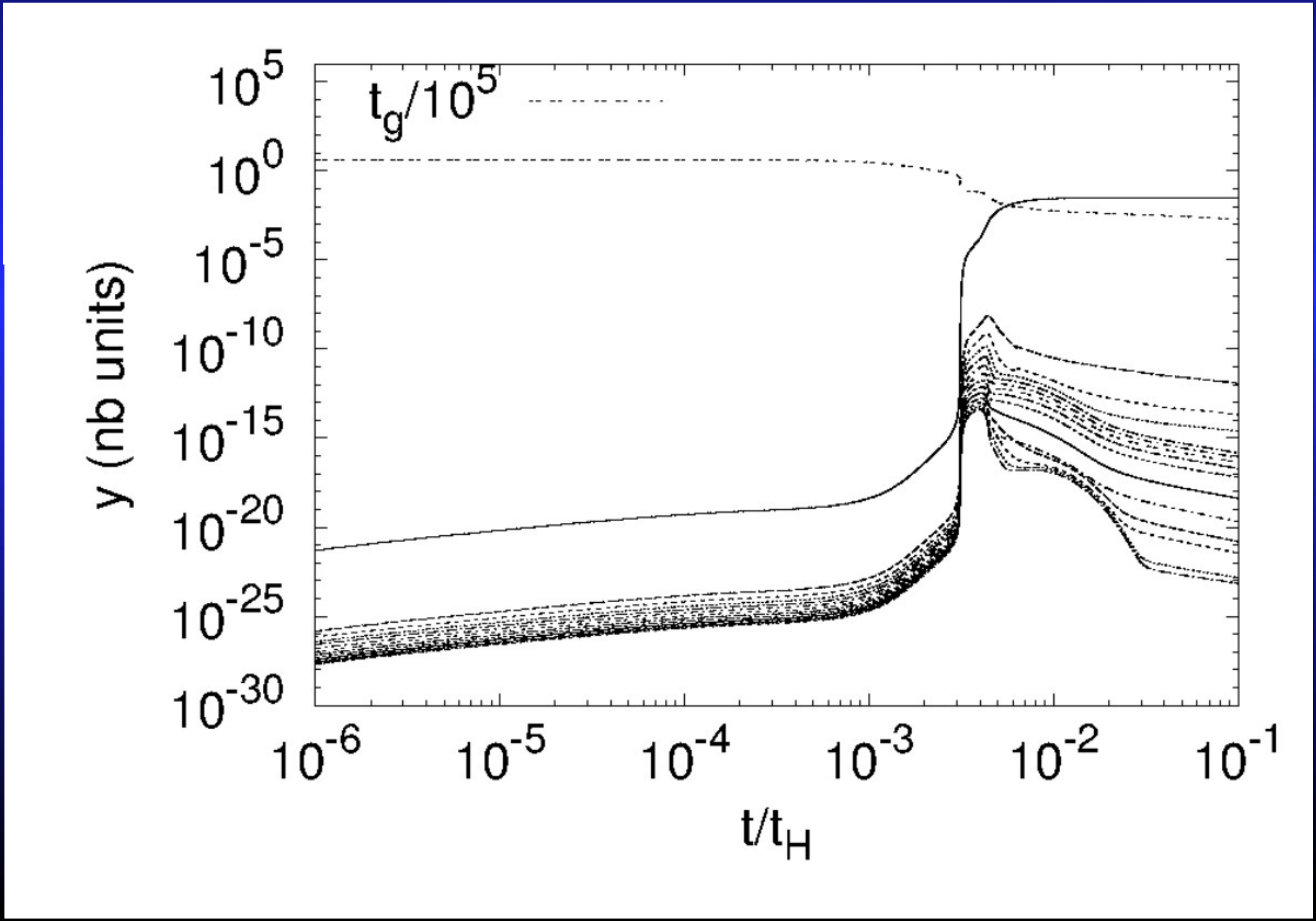


… @ low temperatures

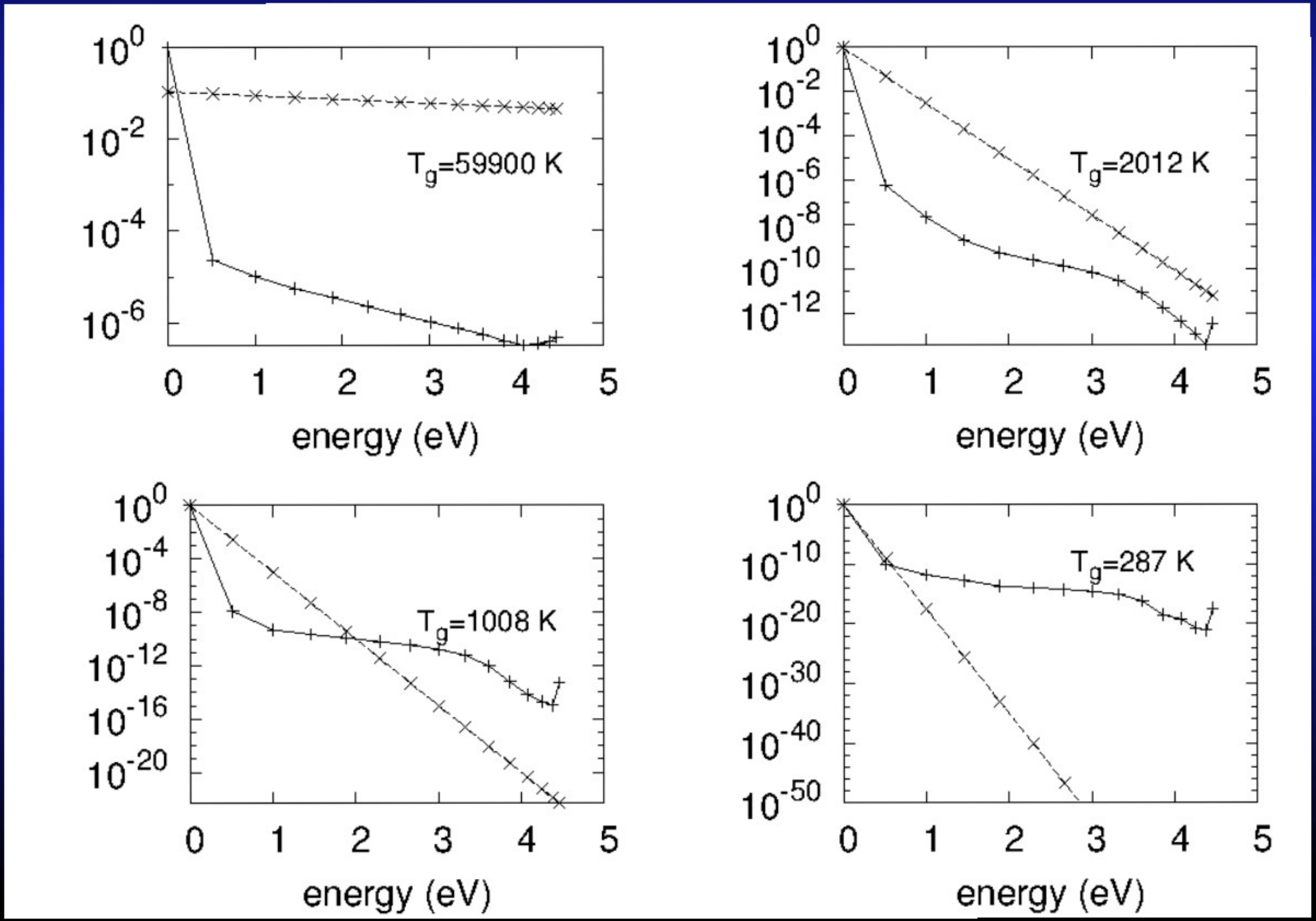
PREGALACTIC SHOCKS: TEMPERATURE AND DENSITY PROFILES



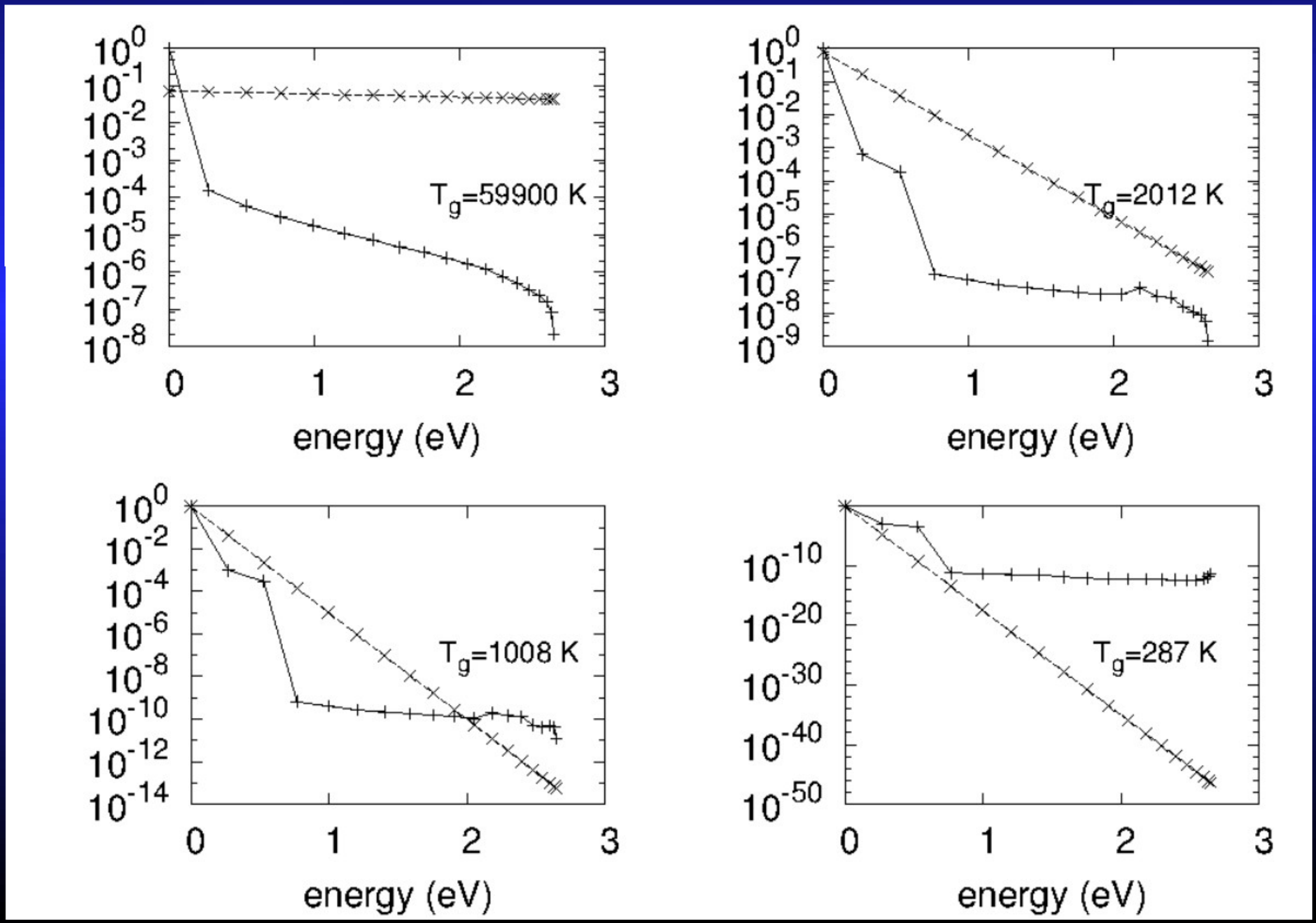
PREGALACTIC SHOCKS: H_2 DISTRIBUTION FUNCTIONS



PREGALACTIC SHOCKS: H_2 DISTRIBUTION FUNCTIONS



PREGALACTIC SHOCKS: H_2^+ DISTRIBUTION FUNCTIONS



COMMENTS AND PERSPECTIVES...

- state-to-state chemistry allows to estimate equilibrium/non-equilibrium distributions arising from the net of formation/destruction/”thermalization” processes introduced in the model

molecular vibration:
non-equilibrium distribution function: high deviations from LTE

- Non-equilibrium effects on photon distribution function → effects on the chemistry

- Effects on physical observables:
  - excitation temperatures
  - rate coefficients
  - heat transfer function
  - distortion photons

- What's going on...

  state-to-state approach for:
  - rotational levels (GS v)
  - electronic molecular resolution
  - non-equilibrium kinetics HD
  - 1-zone model

FOR MORE DETAILS...

"Vibrational level population of H_2 and H_2^+ in the early Universe"

Coppola CM, Longo S., Capitelli M., Palla F., Galli D.

ApJS 2011 193 **7**

"Non-equilibrium H_2 formation in the early Universe: energy exchanges, rate coefficients and spectral distortions"

Coppola CM, D'Introno R., Tennyson J., Galli D., Longo S.

ApJS 2012 198 **1**

"Non-thermal H_2 formation in the early Universe"

Coppola CM, Galli D., Palla F., Longo S., Chluba J.

MNRAS 2013 **434** (1) 114-122

COLLABORATORS LIST...

Savino Longo (Università degli Studi di Bari - Dipartimento di Chimica / CNR-IMIP)

Daniele Galli-Francesco Palla (INAF - Osservatorio di Arcetri)

Jonathan Tennyson (University College London)

Jens Chluba (Johns Hopkins University – Baltimore)

Roberto D'Introno – Giovanni Mizzi (Università degli Studi di Bari - Dipartimento di Fisica)

…ONGOING PROJECTS...
EUROPA: Early Universe: Research on Plasma Astrochemistry
International Space Science Institute (Bern)


THANKS...