Gas-phase chemistry in the ISM and the primordial Universe

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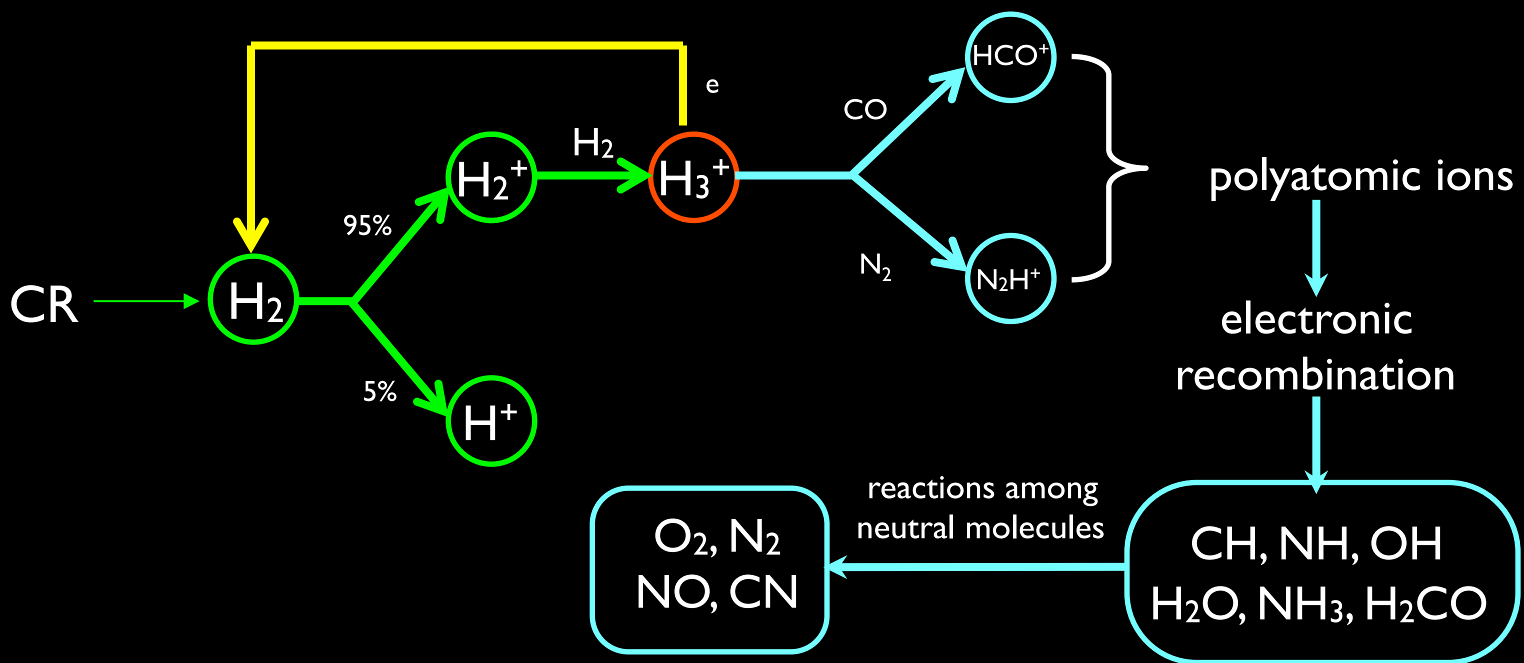
Fundamental gas-phase reactions in molecular clouds



Reactions and reaction rates

- A+B → P (two-body reaction)

$$\frac{dn_{\mathrm{P}}}{dt} = k\, n_{\mathrm{A}} n_{\mathrm{B}}$$

units of k : $\mathrm{cm^3\ s^{-1}}$

- A+photon → P (photoreaction)

$$\frac{dn_{\mathrm{P}}}{dt} = k\, n_{\mathrm{A}}$$

units of k : $\mathrm{s^{-1}}$

- A+B+C → P (three-body reaction)

$$\frac{dn_{\mathrm{P}}}{dt} = k\, n_{\mathrm{A}} n_{\mathrm{B}} n_{\mathrm{C}}$$

units of k : $\mathrm{cm^6\ s^{-1}}$

Two-body reactions, thermal rate

$$k(T) = \int_0^\infty \sigma(v) v f(v) 4\pi v^2 \, dv \equiv \langle \sigma v \rangle$$

Where σ is the cross section of the process and *f(v)* the maxwellian distribution of relative velocities

$$f(v) = \left(\frac{\mu}{2\pi k_\mathrm{B} T} \right)^{3/2} \exp\left(-\frac{\mu v^2}{2 k_\mathrm{B} T} \right)$$

Chemical networks

A system of ODEs

$$\frac{dx_{\rm P}}{dt} = \boxed{k_{\rm 2b}(T_{\rm gas})n}\, x_{\rm A}x_{\rm B} + \boxed{k_{3b}(T_{\rm gas})\, n^2}\, x_{\rm A}x_{\rm B}x_{\rm C} - \boxed{k_{\rm d}(T_{\rm rad})}\, x_{\rm P} + \ldots$$

for the fractional abundances

$$x_i \equiv \frac{n_i}{n}$$

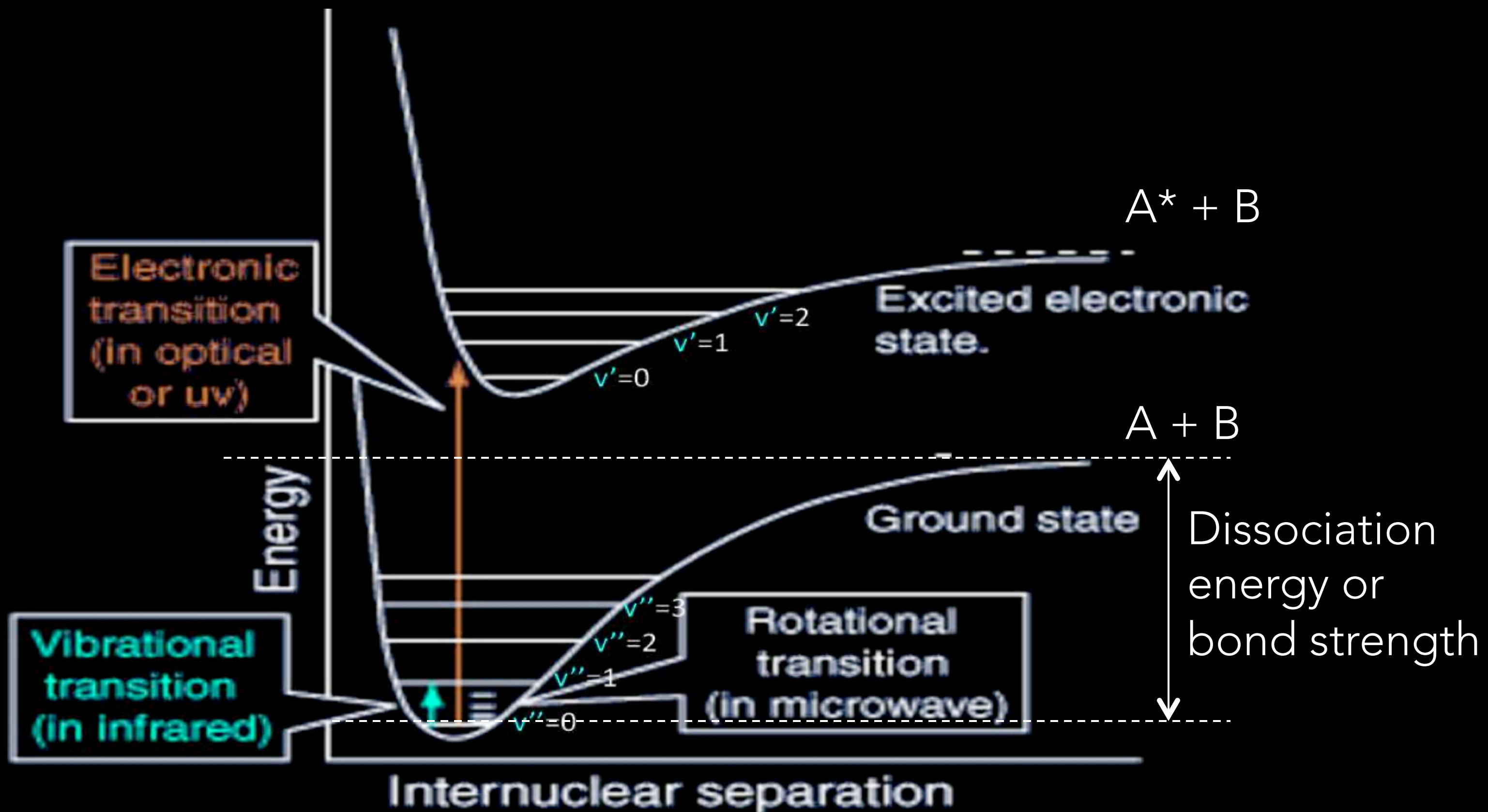
k_{2b}, k_{3b} depend on T_{gas}; k_d depend on spectrum (photons, CRs)
Usually $k \sim T_{gas}{}^{\alpha}$, but activation energy $k \sim \exp(-E_A/k_B T_{gas})$

Needs n, T_{gas}, T_{rad}

- $n(r)$, $T_{gas}(r)$, $T_{rad}(r)$ fixed (e.g. cloud chemistry)
- $n(t)$, $T_{gas}(t)$, $T_{rad}(t)$ prescribed (e.g. early Universe)
- $n(r,t)$, $T_{gas}(r,t)$, $T_{rad}(r,t)$ dynamics-chemistry coupled (e.g. star formation)

→ see talk by T. Haugbølle on Tuesday

Energy levels of a diatomic molecule



Chemical reactions in the ISM

- Low temperatures: T=10-100 K, E=1-10 meV.
  Only exothermal reactions are possible

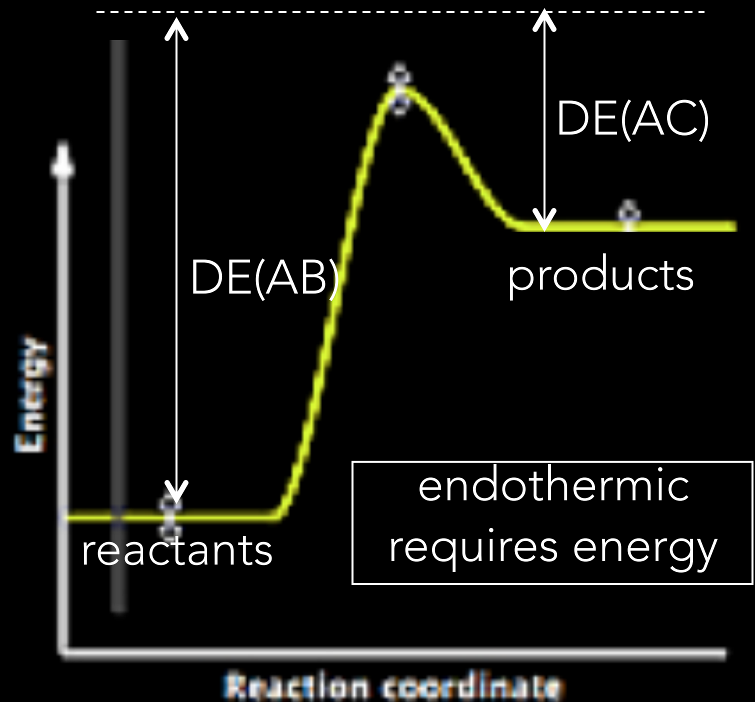
- Low density: $n=10^3$-10^6 cm^{-3}. Only two-body reactions.
  (3-b frequent in the Earth's atmosphere $n=10^{19}$ cm^{-3})

- Some reactions, even if exothermal, have a potential barrier (activation energy). Not possible if the temperature is too low.

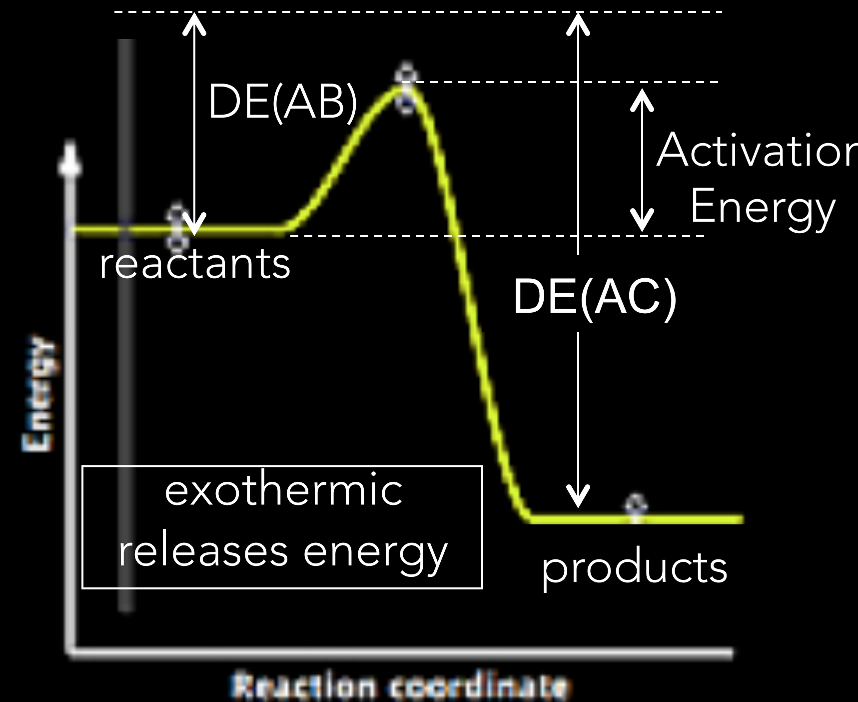
- Shocks and turbulence generate warm zones where endothermal reactions can occur (shock chemistry)

$AB + C \rightarrow AC + B$

$\Delta H = H(\text{products}) - H(\text{reactants}) > 0$



$\Delta H = H(\text{products}) - H(\text{reactants}) < 0$



$C^+ + H_2 \rightarrow CH^+ + H$
$DE(H_2)=4.5$ eV
$DE(CH^+)=4.1$ eV
endothermic by 0.4 eV
(important in shocks)

$OH + H_2 \rightarrow H_2O + H$
$DE(H_2)=4.5$ eV
$DE(H_2O)=5.1$ eV
but 0.14 eV barrier
(important in shocks and hot cores)

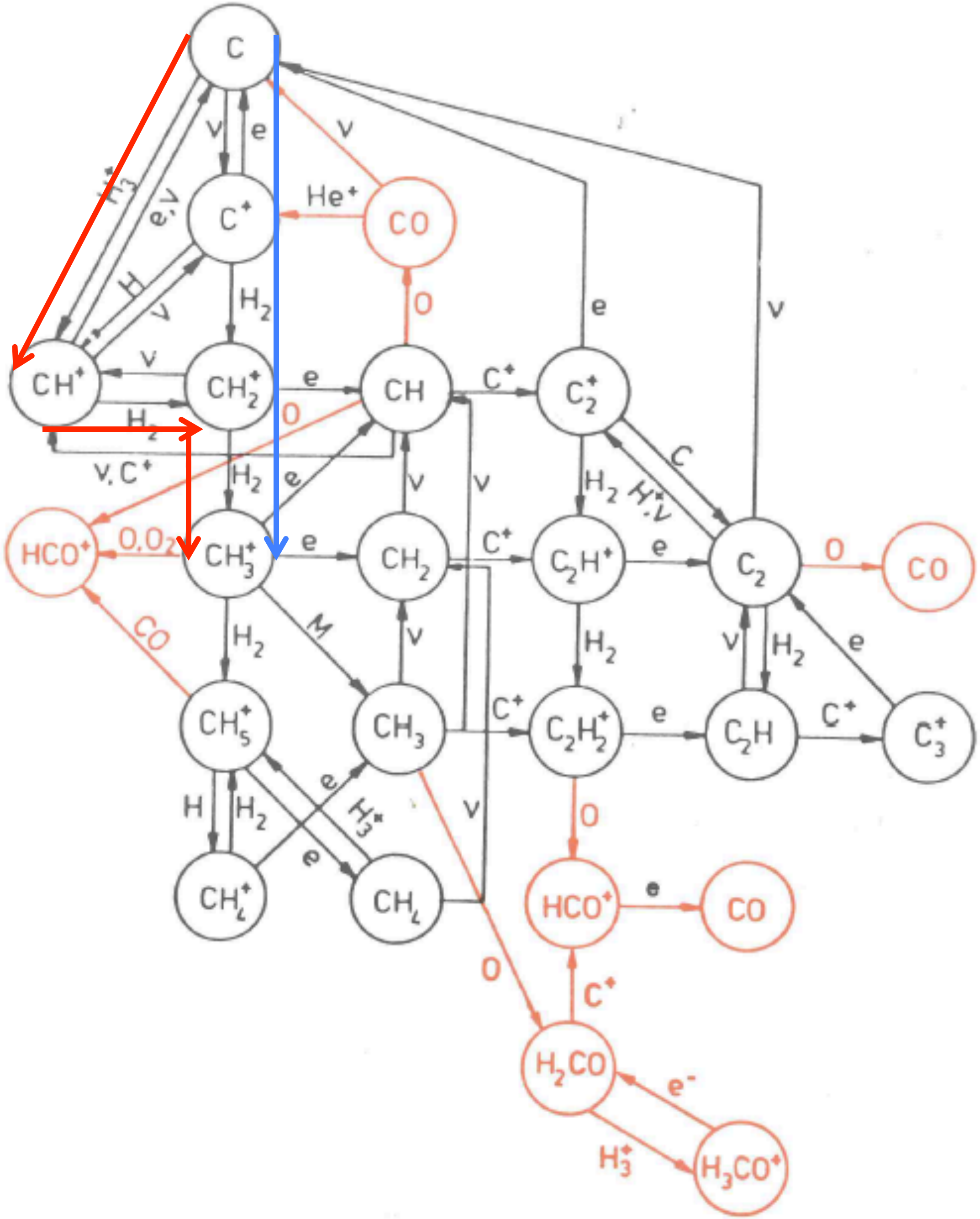
C chemistry

in diffuse clouds

- C + ISRF (IP 13.3eV) $\rightarrow$ C^+ + e ($x_e = 10^{-4}$)
- $C^+ + H_2 \rightarrow CH^+$ NO (endothermic ΔE=0.4 eV)
- $C^+ + H_2 \rightarrow CH_2^+$ radiative association, slow

in dense clouds

- $C + H_2 \rightarrow CH$ NO (endothermic ΔE=1 eV)
- $C + H_3^+ \rightarrow CH^+$ charge transfer, fast
- $CH^+ + H_2 \rightarrow CH_2^+$ } hydrogen abstraction
- $CH_2^+ + H_2 \rightarrow CH_3^+$ } hydrogen abstraction
- $CH_3^+ + e \rightarrow CH, CH_2$ dissociative recombination
- formation of hydrocarbons


C
C⁺
CO
He⁺
CH⁺
CH₂⁺
CH
C₂⁺
HCO⁺
CH₃⁺
CH₂
C₂H⁺
C₂
CO
CH₅⁺
CH₃
C₂H₂⁺
C₂H
C₃⁺
CH₄⁺
CH₄
HCO⁺
CO
H₂CO
H₃CO⁺

O chemistry

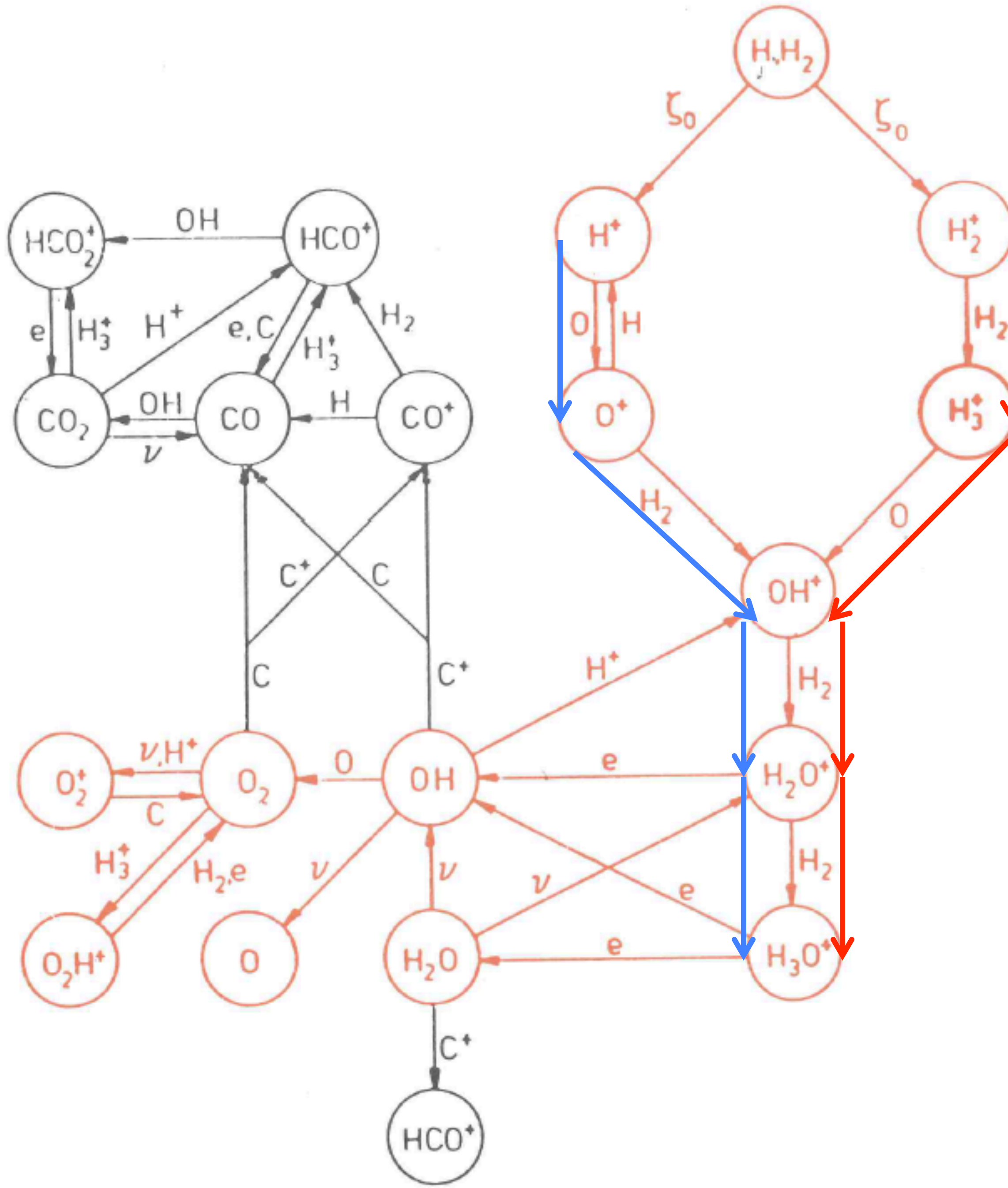
- $O + H^+ \rightarrow O^+ + H$ charge transfer
- $O^+ + H_2 \rightarrow OH^+$

or

- $O + H_3^+ \rightarrow OH^+$ charge transfer

followed by

- $OH^+ + H_2 \rightarrow H_2O^+$
- $H_2O^+ + H_2 \rightarrow H_3O^+$
- $H_3O^+ + e \rightarrow O, OH, H_2O$ dissociative recombination



H, H2
ζ0
ζ0
H+
H2+
O
H
H2
O+
H3+
H2
O
OH+
HCO2+
OH
HCO+
e
H3+
H+
e, C
H3+
H2
CO2
OH
CO
H
CO+
ν
C+
C
C
C+
H+
H2
O2+
ν, H+
O2
O
OH
e
H2O+
C
H3+
H2, e
ν
ν
ν
e
H2
O2H+
O
H2O
e
H3O+
C+
HCO+

Types of reactions

Collisional processes:

1. ion-neutral reactions $A^+ + B \rightarrow C^+ + D$
2. radiative association $A + B \rightarrow AB + h\nu$
3. dissociative recombination $AB^+ + e \rightarrow A + B$
4. neutral-neutral reactions $A + B \rightarrow C + D$
5. charge transfer $A^+ + B \rightarrow A + B^+$

Photoprocesses:

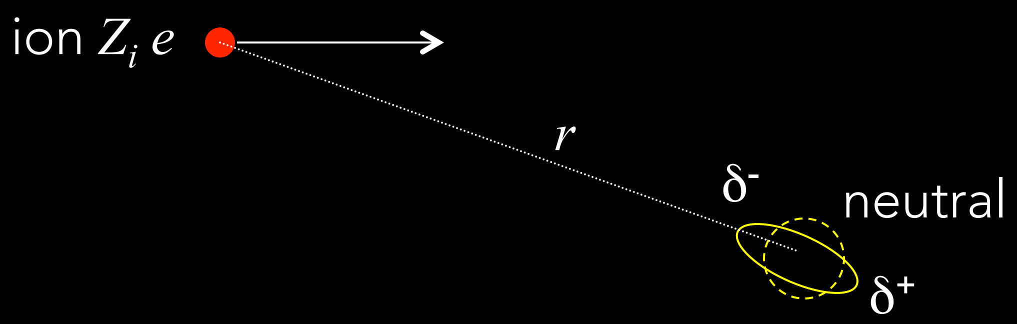
1. photodissociation $AB + h\nu \rightarrow A + B$
2. photoionization $AB + h\nu \rightarrow AB^+ + e$

(see talks by W.-F. Thi, T. Grassi, D. Seifried on Wednesday)

1. Ion-neutral reactions

$A^+ + B \rightarrow C^+ + D$

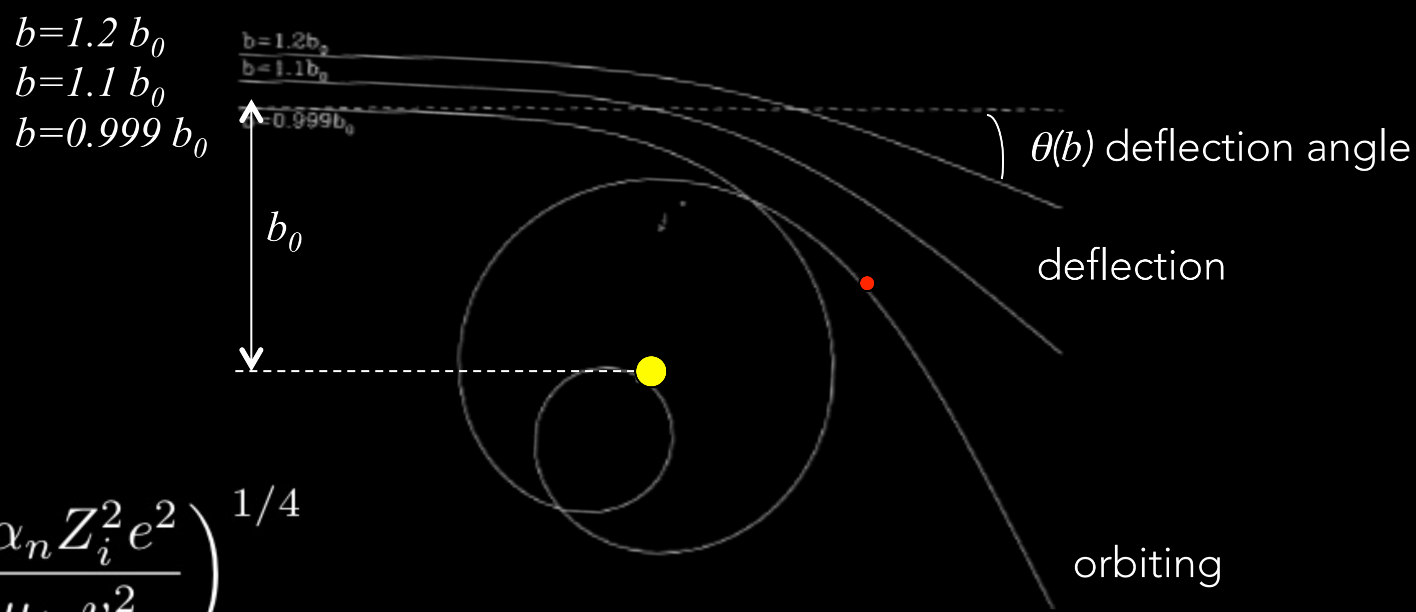
- Often have no activation barrier
- The approaching ion induces an electric dipole in the neutral that attracts the ion



- Long-range attractive potential $V_{in} = -\frac{\alpha_n Z_i^2 e^2}{2r^4}$

  $\alpha_n \approx 1$ Å^3 polarizability of neutral species

Orbits in r^{-4} potential

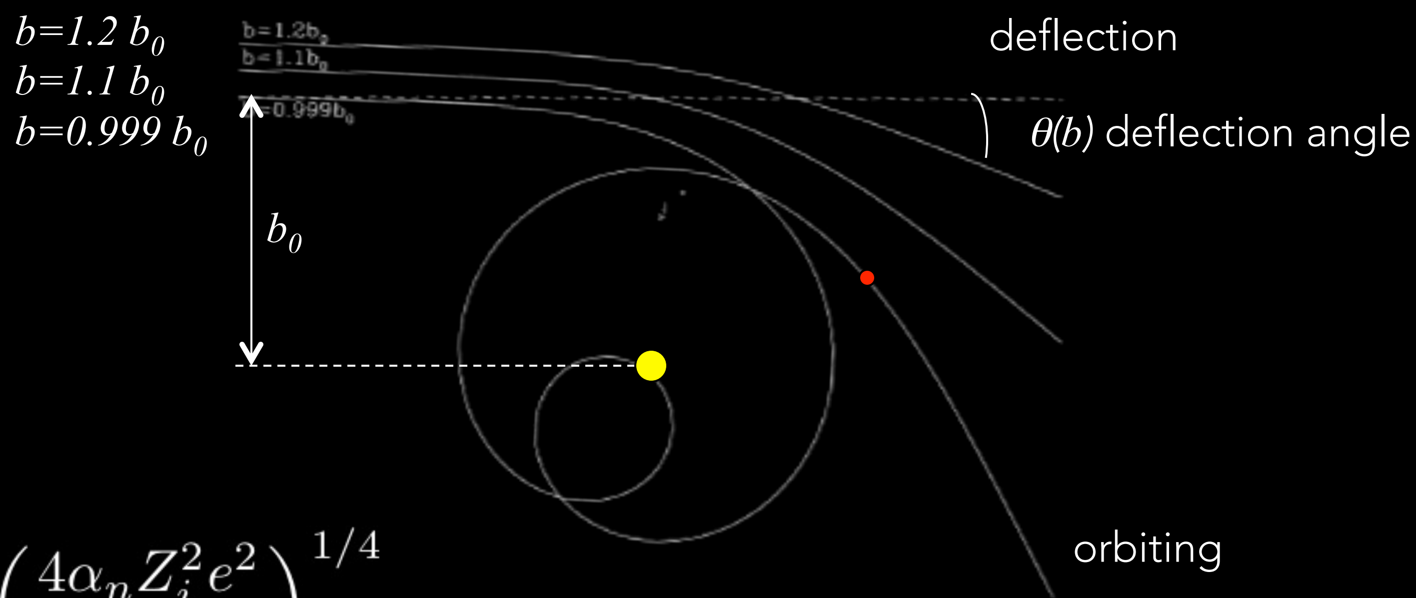


$$b_0 = \left(\frac{4\alpha_n Z_i^2 e^2}{\mu_{in} v^2}\right)^{1/4}$$

$$\sigma = \pi b_0^2 = 2\pi Z_i e \left(\frac{\alpha_n}{\mu_{in}}\right)^{1/2} \frac{1}{v}$$ Langevin cross section

$$\langle \sigma v \rangle = 2\pi Z_i e \left(\frac{\alpha_n}{\mu_{in}}\right)^{1/2} \equiv k_{\rm L} \approx 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$ independent on T

Orbits in r^{-4} potential



$$b_0 = \left(\frac{4\alpha_n Z_i^2 e^2}{\mu_{in} v^2} \right)^{1/4}$$

- If $b<b_0$ reactive collision
- If $b>b_0$ deflection (ion-neutral momentum transfer)

Reaction cross section:

$$\sigma = 2\pi \int_0^{b_0} b\,db = \pi b_0^2 = 2\pi Z_i e \left(\frac{\alpha_n}{\mu_{in}}\right)^{1/2} \frac{1}{v}$$

This is the Langevin cross section. The Langevin rate is

$$\langle \sigma v \rangle = 2\pi Z_i e \left(\frac{\alpha_n}{\mu_{in}}\right)^{1/2} \equiv k_{\mathrm{L}}$$ independent on T

Numerical value, with $\alpha \approx 1$ Å^3, $\mu_{in} \approx m_H$:

$k_L \approx 10^{-9}$ cm^3 s^{-1}

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

- a "cornerstone" reaction in molecular clouds:

H_2 ionized by photons, CRs, X-rays, reacts with ambient H_2

May proceed by proton transfer:

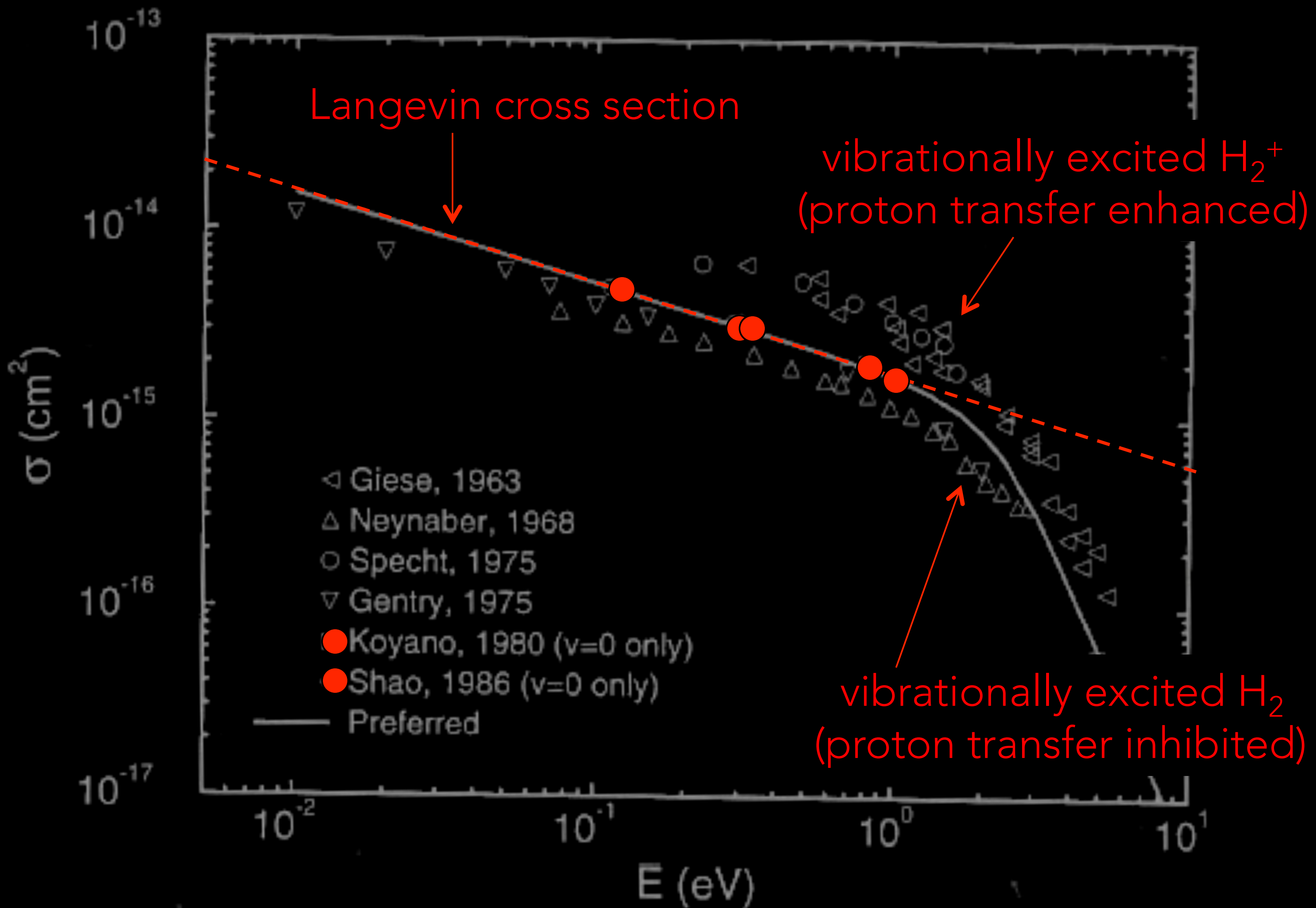
$H_2^+ + H_2 \rightarrow (H^+H_2) + H$ $\Delta H=2.3$ eV

and atom transfer

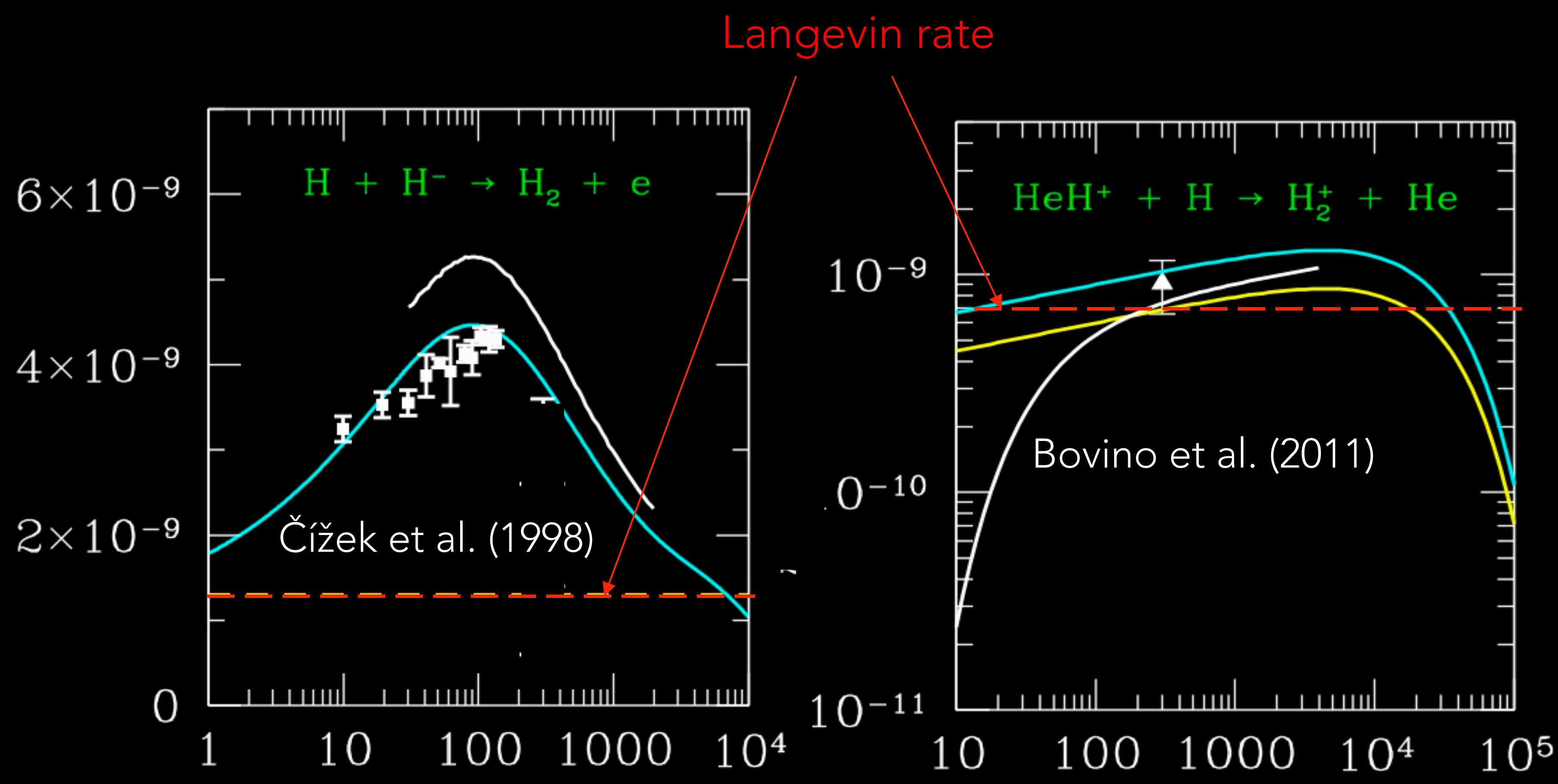
$H_2^+ + H_2 \rightarrow (H_2^+H) + H$ $\Delta H=0.5$ eV

- If both H_2 and H_2^+ are in their v=0, proton transfer dominates.
- Otherwise, it depends.

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



Linder, Janev & Botero (1995)



Langevin rate
H + H⁻ → H₂ + e
6×10⁻⁹
4×10⁻⁹
2×10⁻⁹
0
1
10
100
1000
10⁴
Čížek et al. (1998)
HeH⁺ + H → H₂⁺ + He
10⁻⁹
10⁻¹⁰
10⁻¹¹
10
100
1000
10⁴
10⁵
Bovino et al. (2011)

Momentum transfer cross section

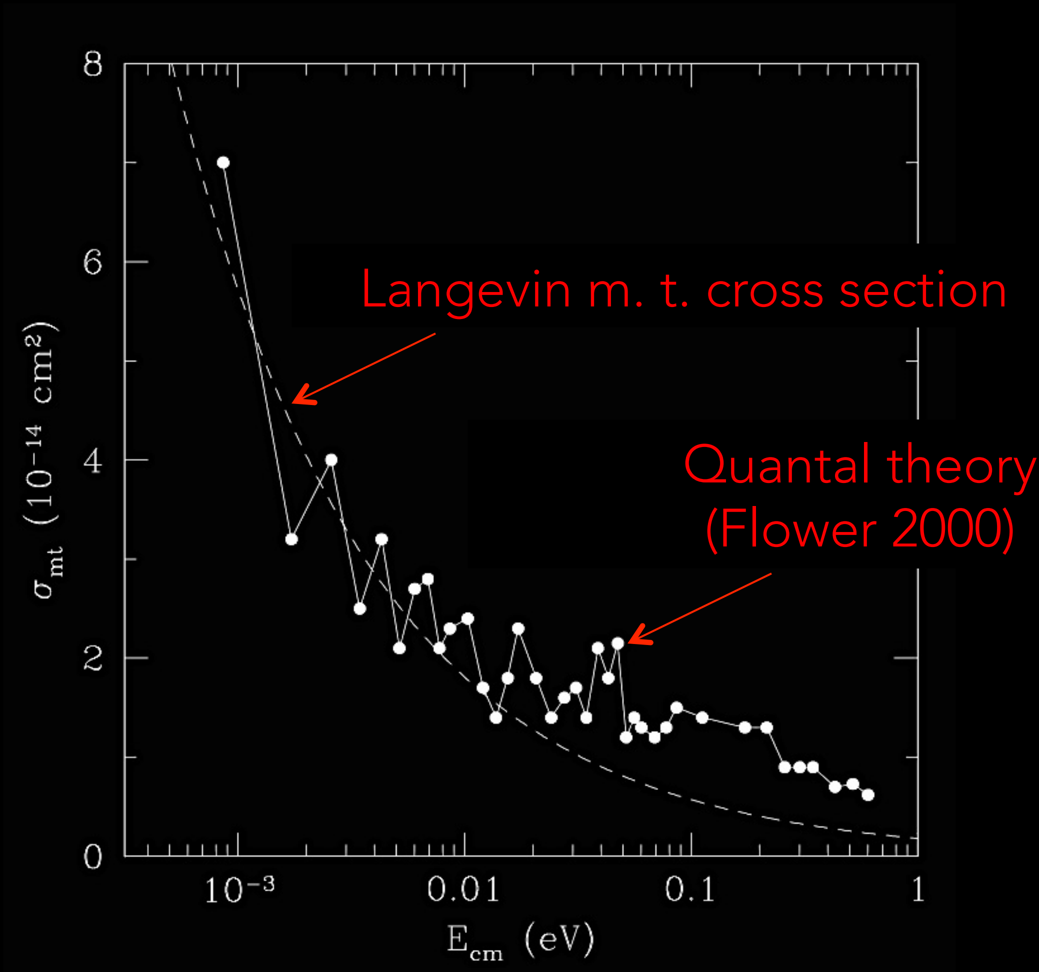
- elastic (i.e. non-reactive) collisions
- momentum exchange between ions and neutrals
- important for MHD codes

$$\sigma_{mt} = 2\pi \int_{b_0}^{\infty} (1 - \cos\theta) b \, db = 2.21\pi Z_i e \left(\frac{\alpha_n}{\mu_{in}}\right)^{1/2} \frac{1}{v}$$

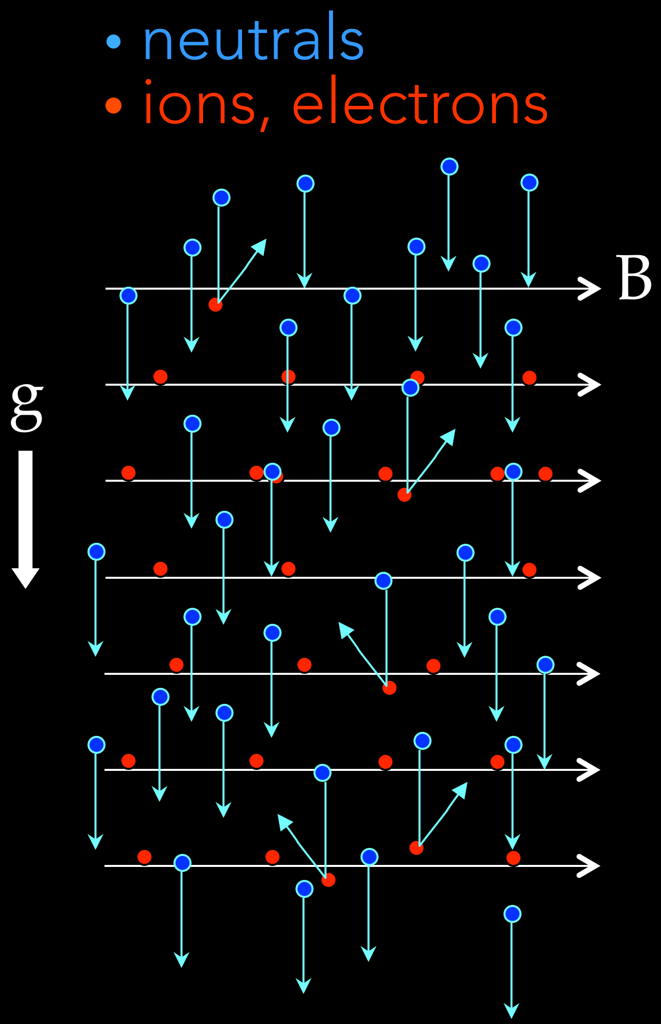
where $\theta(b)$ = scattering angle. Only 1.105 times Langevin c.s.

- Contribution of $b<b_0$ can be included assuming orbiting collisions result in isotropic scattering with $\langle\cos\theta\rangle = 0$: factor 2.21 → 2.41

Example: $HCO^+ + H_2$ momentum transfer



Ambipolar diffusion



- The field acts on neutrals indirectly through collisions between neutral and charged particles: frictional force mediated by momentum-transfer collisions.
- The field and the ions slip through the neutrals (ion-slip or ambipolar diffusion);
- The momentum-transfer cross section ion-neutrals controls the process.

2. Radiative association

$$A + B \rightarrow AB + h\nu$$

- Collision product stabilized through photon emission
- $t_{collision} \approx a_0/v \approx 10^{-13}$ s   if v=0.5 km s^{-1}
- $t_{radiative} \approx A_{ul}^{-1} \approx 10^{-7}$ s   dipole electronic transition

$$\sigma \approx (\pi a_0^2)(t_{collision}/t_{radiative}) \approx 10^{-6} a_0^2$$

$$k_{rad.\ ass.} = \langle \sigma v \rangle \approx 10^{-17}\ cm^3\ s^{-1}$$

- Generally slow, independent on T. Needs large dipole moments because $A_{ul} \sim d^2$

$C + H \rightarrow CH + h\nu$ $k_{rad.\ ass.} = 1.0 \times 10^{-17}\ cm^3\ s^{-1}$

$C^+ + H \rightarrow CH^+ + h\nu$ $k_{rad.\ ass.} = 1.7 \times 10^{-17}\ cm^3\ s^{-1}$

$C^+ + H_2 \rightarrow CH_2^+ + h\nu$ $k_{rad.\ ass.} = 6.0 \times 10^{-16}\ cm^3\ s^{-1}$

- Semiclassical estimates of radiative association rate for primordial molecules (Lepp & Shull 1984):

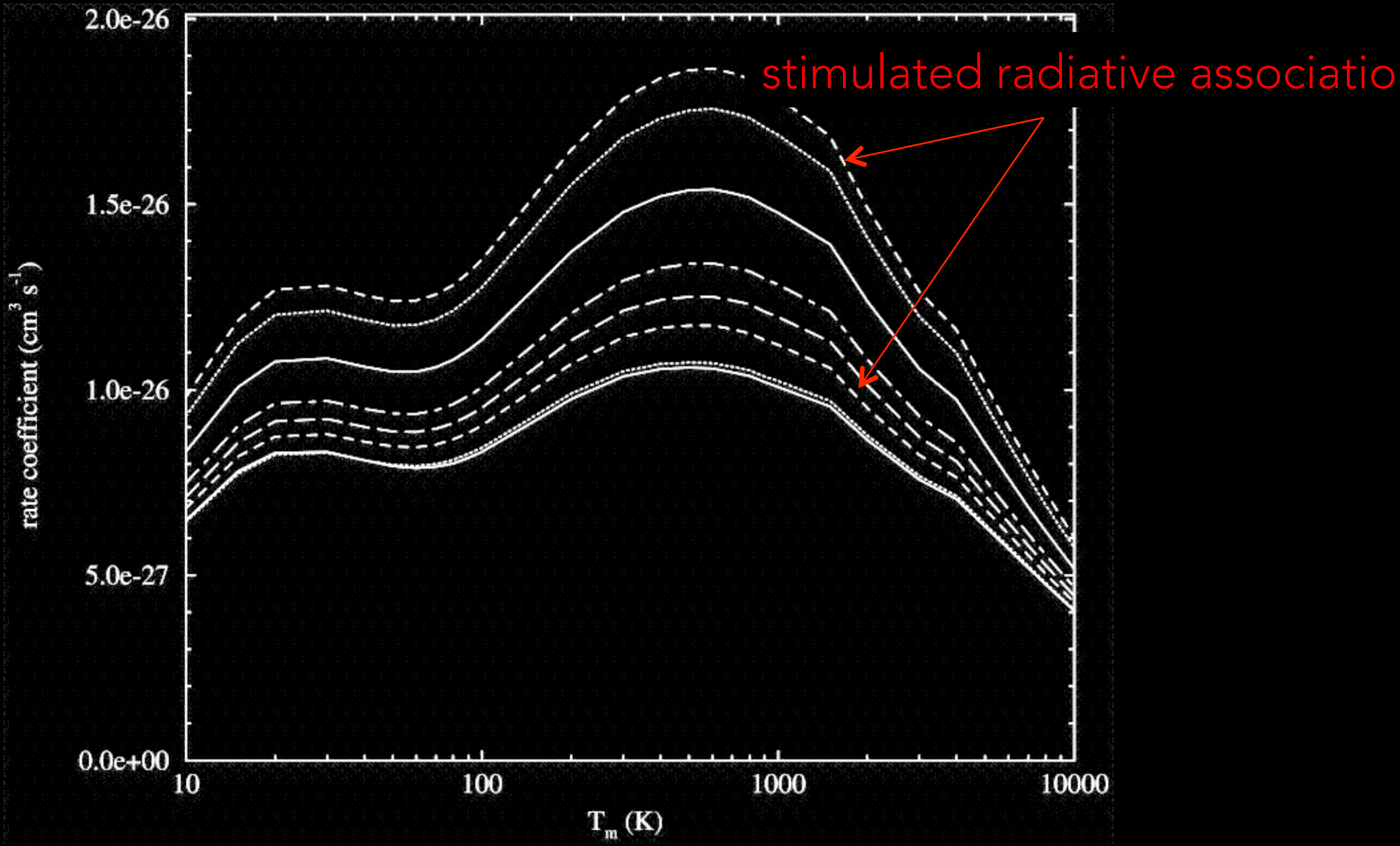
H_2 (d=0) $\rightarrow k_{H2} \approx 0$
HD (d=6x10^{-4} debyes) $\rightarrow k_{HD} \approx 10^{-25}$ cm^3 s^{-1}
LiH (d=6 debyes) $\rightarrow k_{LiH} \approx 10^{-17}$ cm^3 s^{-1}

- Warning: semiclassical results can be overestimated!

- Fully quantal calculations:

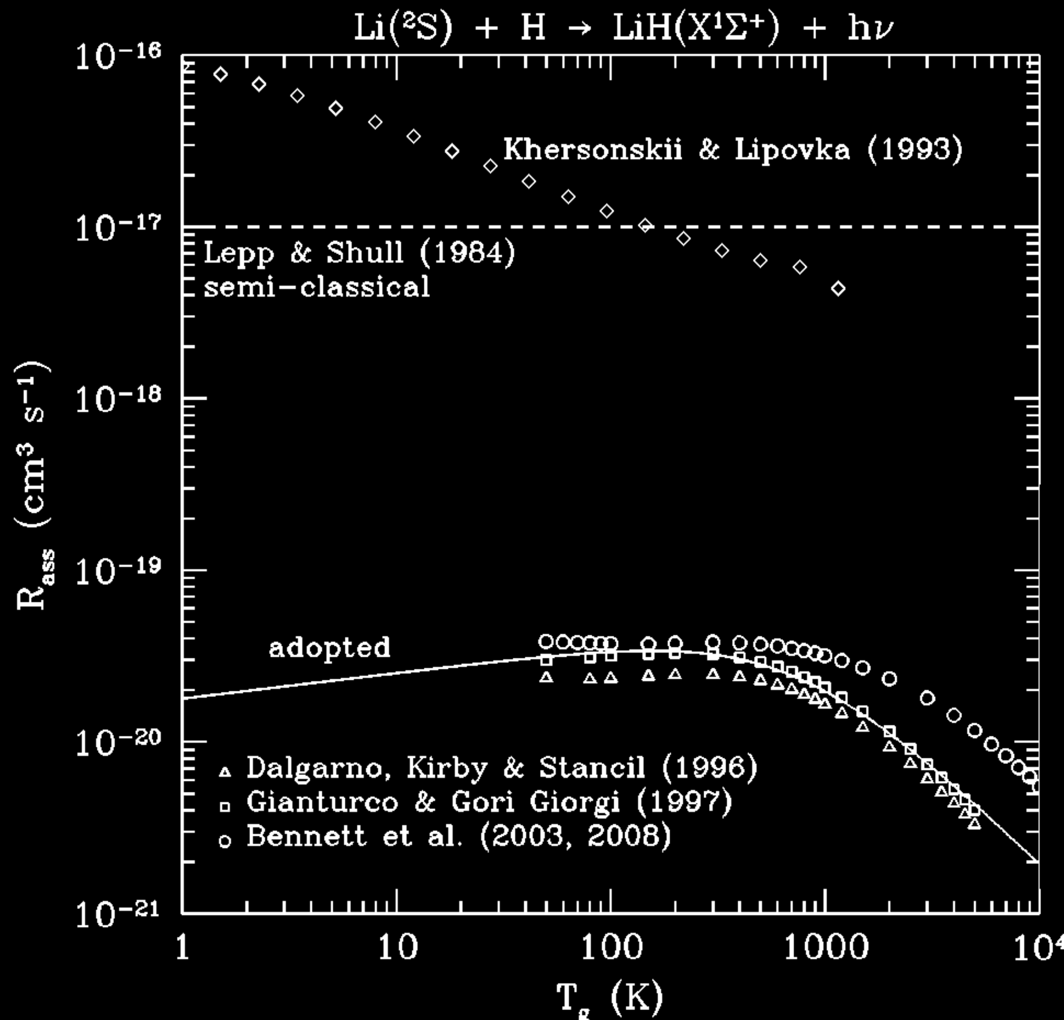
$k_{HD} \approx 10^{-26}$ cm^3 s^{-1} (Stancil & Dalgarno 1997)
$k_{LiH} \approx 10^{-20}$ cm^3 s^{-1} (Dalgarno et al. 1996)

H + D → HD + hν



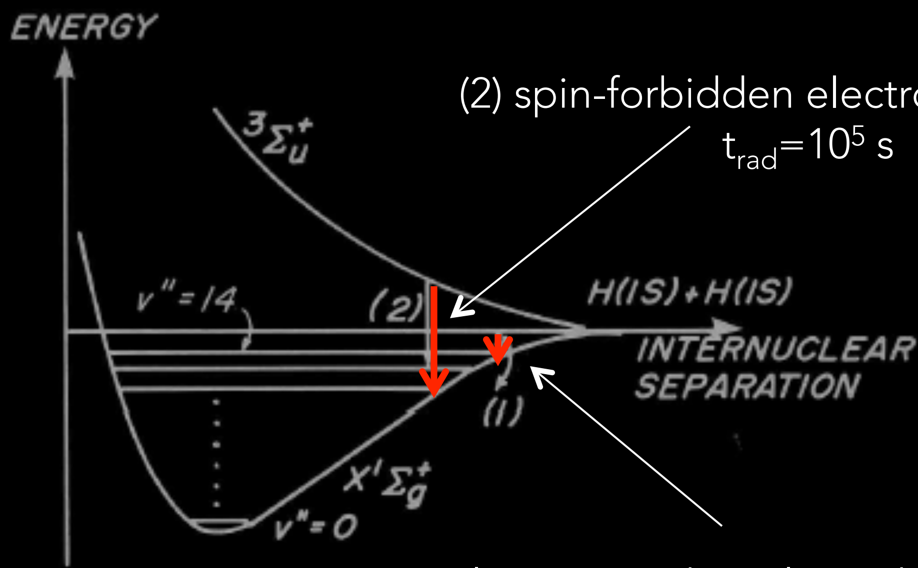
Stancil & Dalgarno (1997)

Li + H → LiH + hν



Li(²S) + H → LiH(X¹Σ⁺) + hν
Khersonskii & Lipovka (1993)
Lepp & Shull (1984)
semi-classical
adopted
Dalgarno, Kirby & Stancil (1996)
Gianturco & Gori Giorgi (1997)
Bennett et al. (2003, 2008)
R_ass (cm³ s⁻¹)
10⁻¹⁶
10⁻¹⁷
10⁻¹⁸
10⁻¹⁹
10⁻²⁰
10⁻²¹
1
10
100
1000
10⁴
T_g (K)

- Does not work for H + H → H_2 + hν



(2) spin-forbidden electronic transition $t_{rad}=10^5$ s

(1) electric quadrupole rovibrational transition within the ground electronic state $t_{rad}=10^7$ s

- (1) $k_{rad.\ ass.} = 10^{-31}\ cm^3\ s^{-1}$ (2) $k_{rad.\ ass.} = 10^{-29}\ cm^3\ s^{-1}$

- Needs a third body to remove excess energy that cannot be radiated away

$$\mathrm{H + H + H \rightarrow H_2 + H}$$

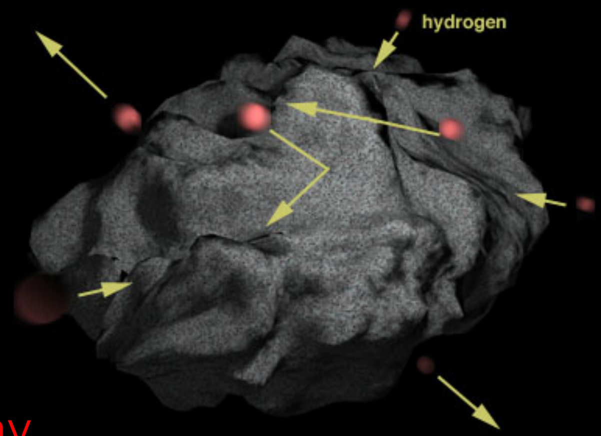
rate k ≈ 5.5x10^{-29} (T/°K)$^{-1}$ cm^{6} s^{-1} (uncertain)

important only at high density (n>10^{8} cm^{-3})

- Or a catalyst (dust grain): $\mathrm{H+H \rightarrow H_2}$

$$\frac{dn_{\mathrm{H_2}}}{dt} = k\, n_{\mathrm{H}} n_{\mathrm{g}} \qquad k = \frac{1}{2}(\pi a^2) v S \gamma$$

v = speed of H atoms in gas-phase
a = grain radius
S = sticking probability
γ = surface reaction probability

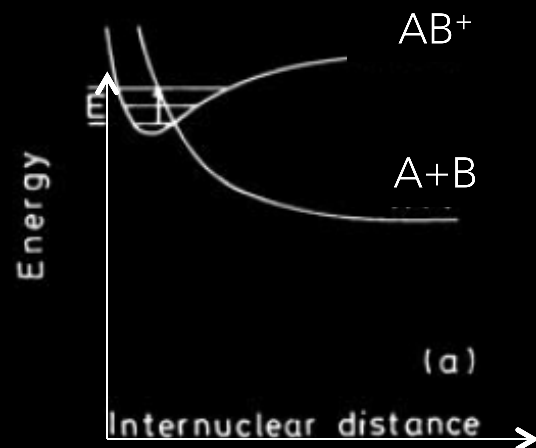


→ see talks by W.-F. Thi and T. Grassi on friday

3. Dissociative recombination

$AB^+ + e \rightarrow A + B$

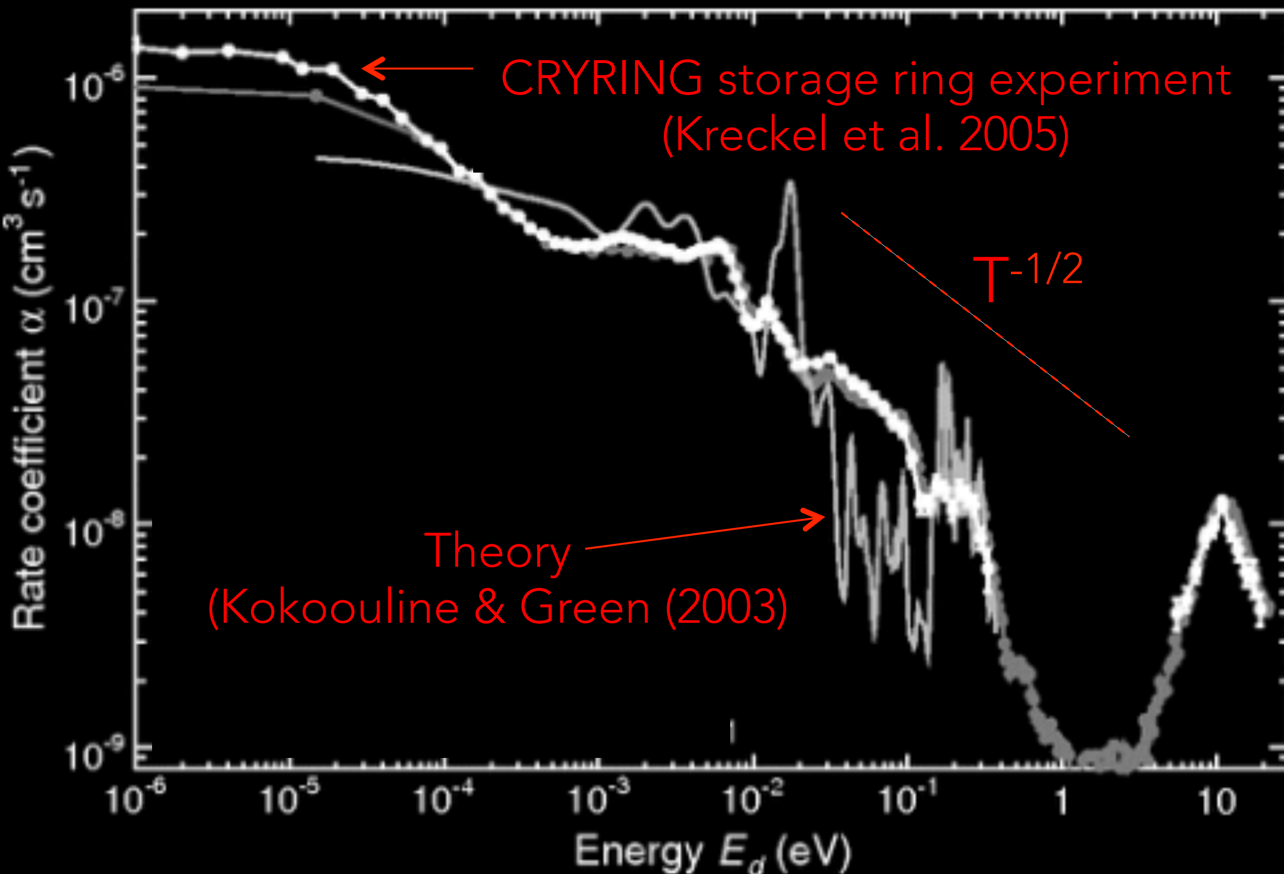
- Electron excites transition of stable AB^+ ion to a repulsive state of AB molecule which crosses the energy curve of the ion.



- Example: $HCO^+ + e \rightarrow H + CO$ (important CO source)
- Theoretically complex, experimentally difficult
- Large rate coefficient: $10^{-7} – 10^{-6}$ cm^3 s^{-1} at T=10 K proportional to $T^{-1/2}$ for a Maxwellian distribution

Dissociative recombination of H_3^+

$H_3^+ + e \rightarrow H + H + H$ (64%)
$H_3^+ + e \rightarrow H_2 + H$ (36%)



4. Neutral-neutral reactions

A + B → C + D

- if $b < R_1 + R_2$ ≈ a few a_0 (``hard-sphere'' model)

  $$\sigma = \pi (R_1 + R_2)^2 \approx 10^{-15}\ \mathrm{cm}^2$$

  $$\langle \sigma v \rangle = \pi (R_1 + R_2)^2 \left(\frac{8kT}{\pi \mu_{mn}} \right)^{1/2} \approx 10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1} \text{ at } T=10\ \mathrm{K}$$

- Correction for attractive Van der Waals forces at larger b (fluctuations in the dipole of one species induce a dipole in the other)

  $$V_{nm}(r) = -\frac{\alpha_n \alpha_m}{r^6} I_{nm} \qquad I_{nm} = \langle I_n + I_m \rangle$$

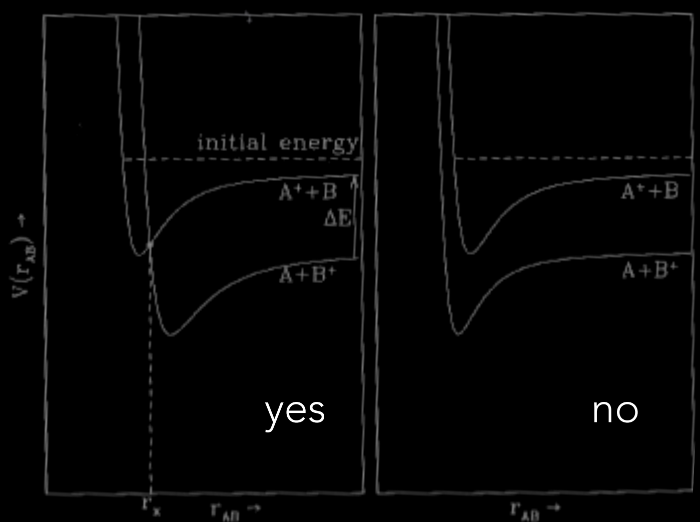
  $$\langle \sigma v \rangle = 13.5\pi \left[\frac{\alpha_n \alpha_n I_{nm}}{\mu_{mn}} \left(\frac{8kT}{\pi \mu_{mn}} \right)^{1/2} \right]^{1/3} \approx 10^{-11} \left(\frac{T}{100\ \mathrm{K}} \right)^{1/6}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$$

5. Charge transfer reactions

$$A^+ + B \rightarrow A + B^+$$

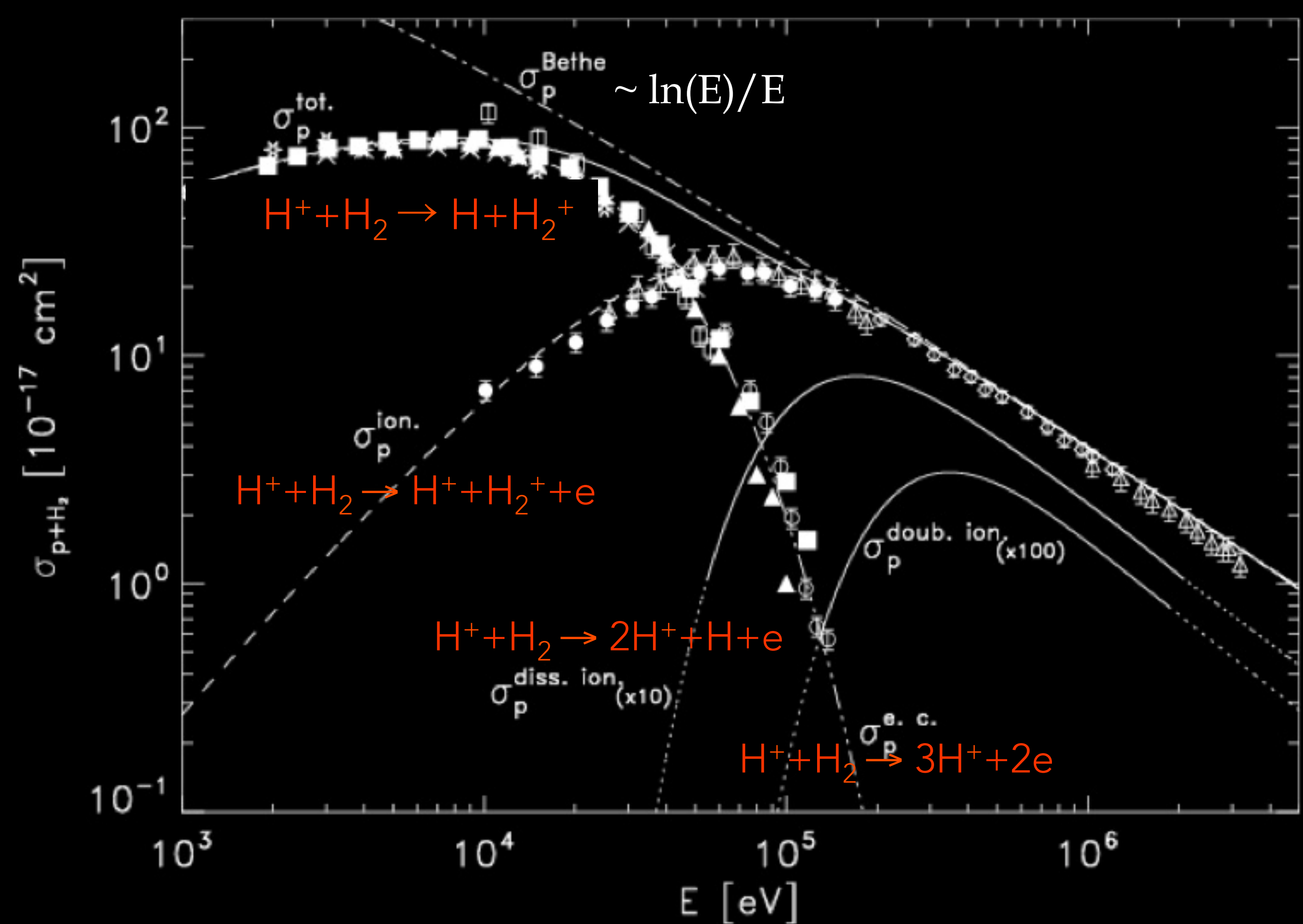
- $t_{collision} = a_0/v \approx 10^{-13}$ s   if $v \approx 0.5$ km s^{-1}
- $t_{telectron\ transfer} = h/\Delta E \approx 10^{-15}$ s   if $\Delta E \approx I_A - I_B \approx 1$eV (released)
- Requires exhothermicity and "level crossing": potential energy curves of $A^+ + B$ and $A+B^+$ must intersect.
- Reaction rate fast $k=10^{-9}$ cm^3 s^{-1} and independent on T

Exhothermal, level crosing



Exhothermal, no level crosing

$H^+ + H_2$: charge transfer vs. collisional ionization



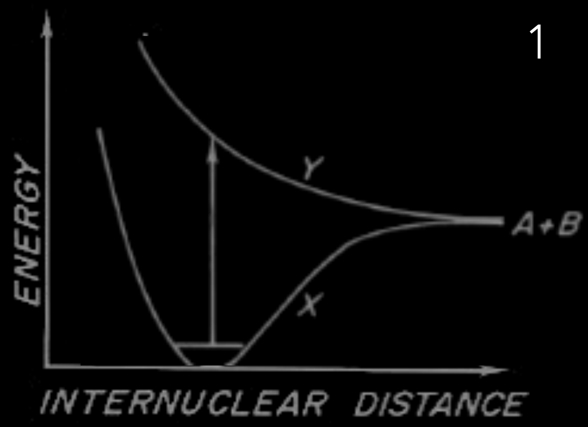
Padovani et al. (2009)

6. Photodissociation

$$AB + h\nu \rightarrow A + B$$

Transition from a bound state to:

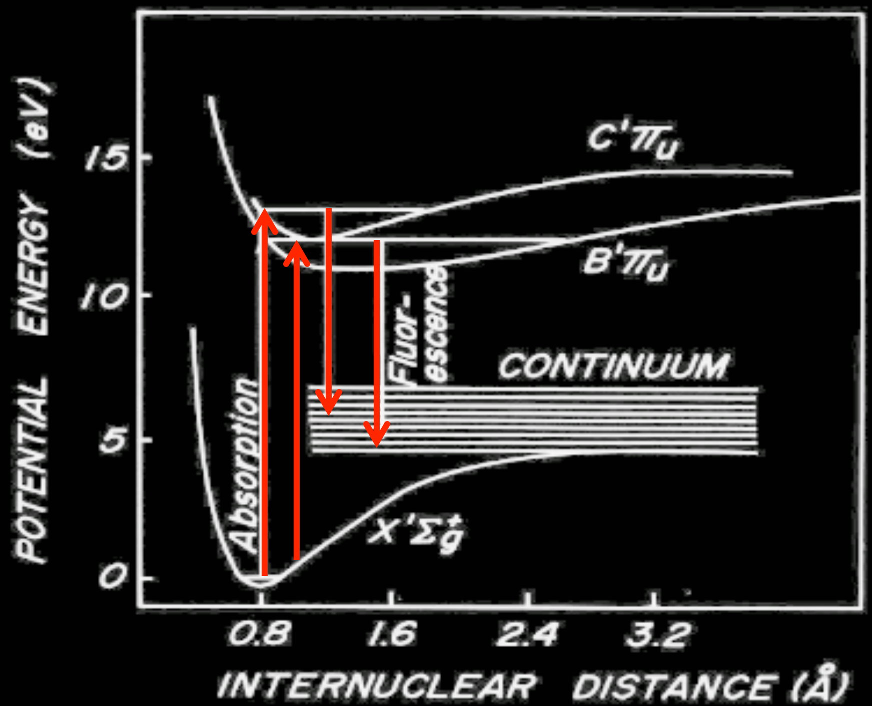
1. a repulsive state (photodissociation)
2. a bound state that decays into the continuum of the lower state by emitting a photon (two-step photodissociation)



Photodissociation of H_2 follows 2

Photodissociation of H_2

- Principal destruction process of H_2 in the ISM
- First step: absorption of a resonance line photon (E=11.2-13.6 eV) from ground state X to excited level B or C
- Second step: spontaneous decay to the vibrational continuum of X (~15% of the time), leading to dissociation.



Photodissociation rate

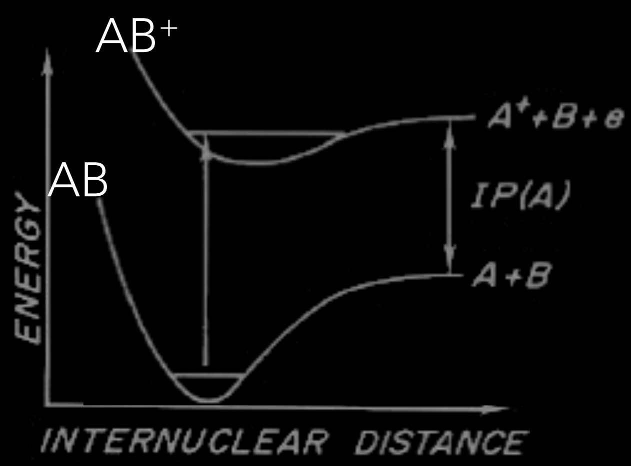
$$k_{\mathrm{ph}} = 4\pi \int_0^\infty \frac{J(\nu)}{h\nu} \sigma_{\mathrm{ph}}(\nu)\, d\nu$$

- $J(\nu)$ is the specific intensity (in erg cm^{-2} s^{-1} $ster^{-1}$ Hz^{-1})
- $\sigma_{ph}(\nu)$ is the photodissociation cross section (in cm^{-2})
- k_{ph} is the photodissociation rate in s^{-1}
-
- Typical values 10^{-11} (H_2) – 10^{-9} s^{-1} (CH, CN, O_2, H_2CO)

7. Photoionization

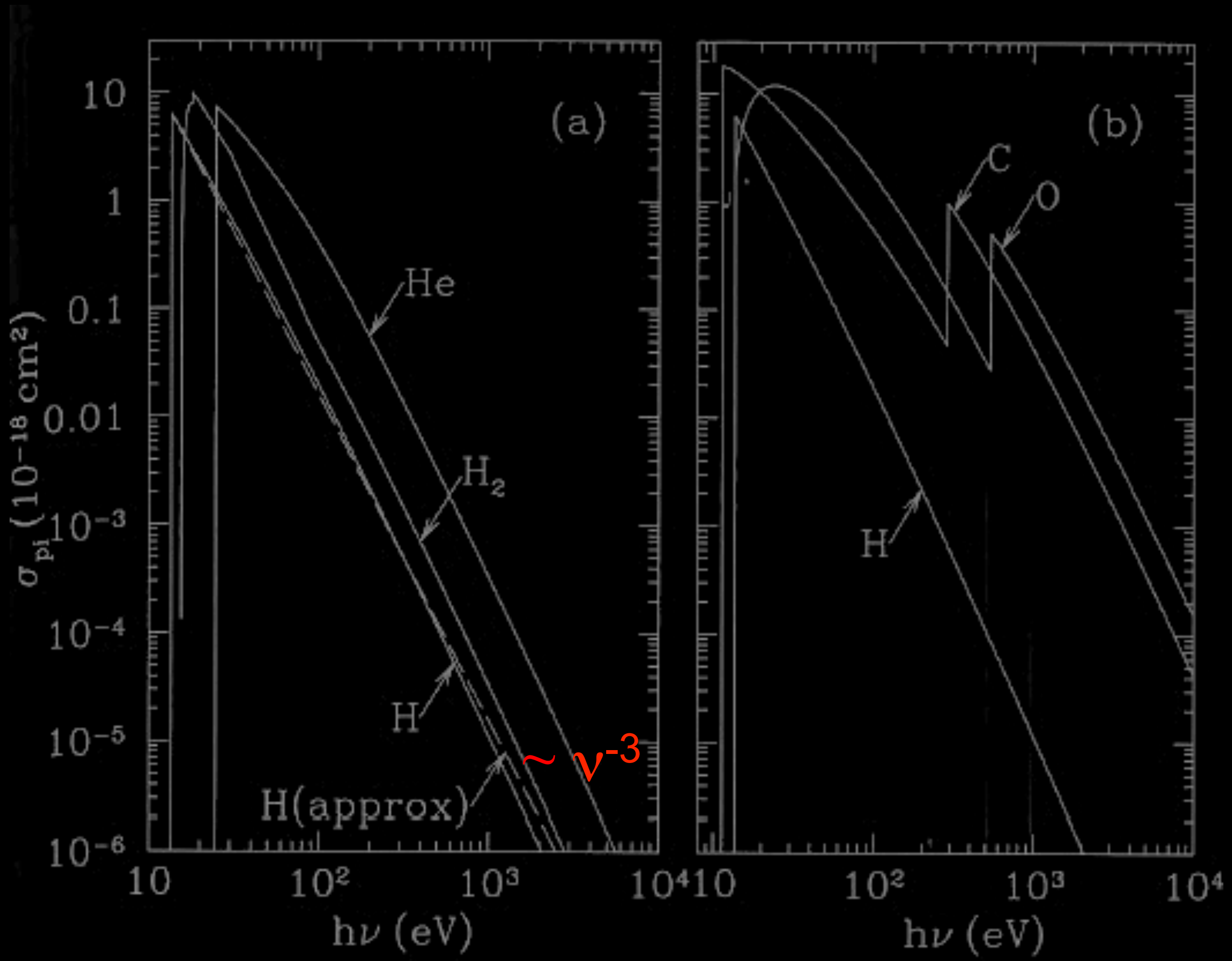
$$AB + h\nu \rightarrow AB^+ + e$$

- Similar to photodissociation
- Transition from a bound state of AB to a bound state of AB^+ that lies above the A+B state by the ionization potential IP



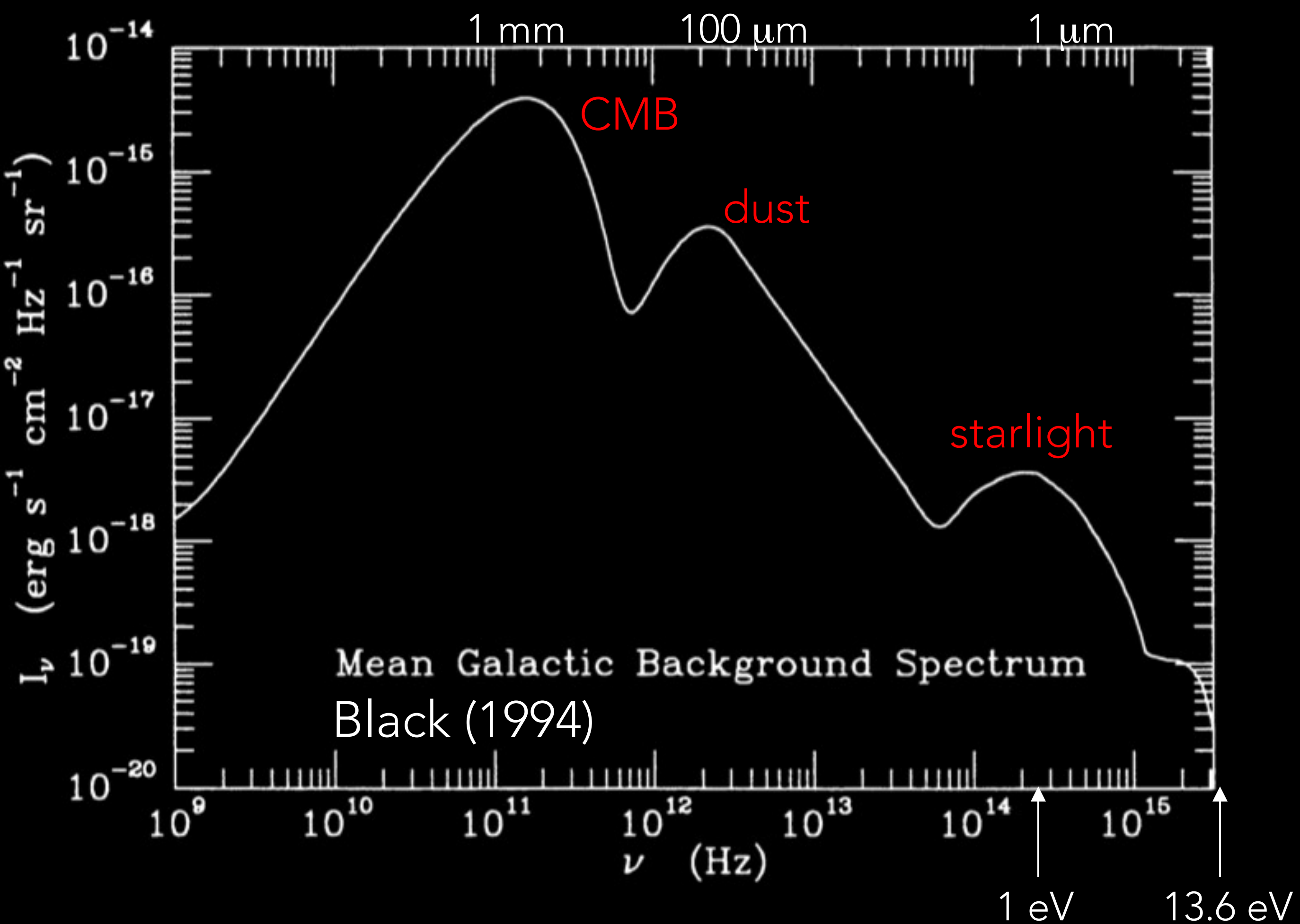
- I_{CH}=10.64 eV, I_{CO}=14.01 eV, I_{H2}=15.44 eV

Photoionization cross sections



Draine (2011)

Interstellar radiation spectrum



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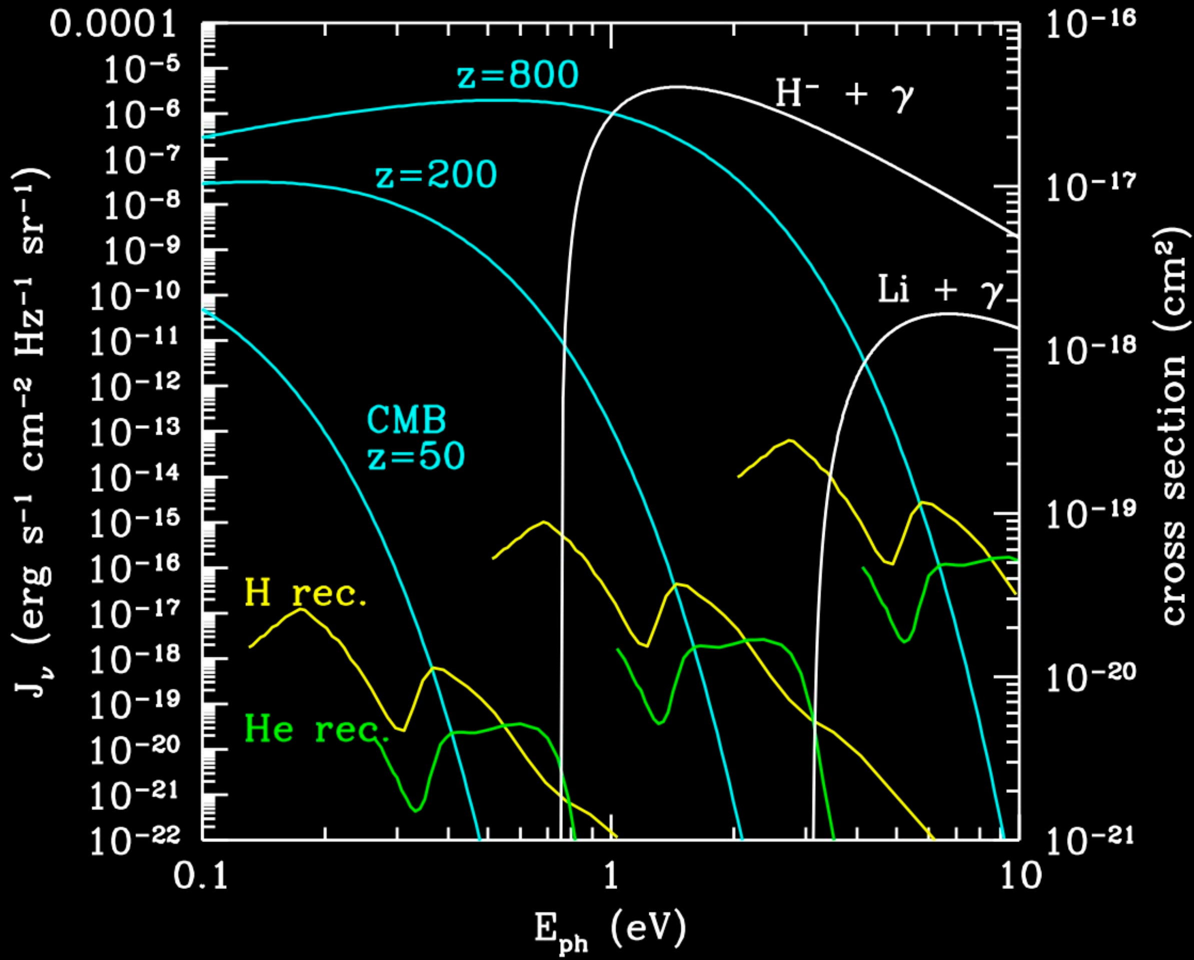


Switzer & Hirata (2005)
Hirata & Padmanabhan (2006)

Chemistry in the Early Universe

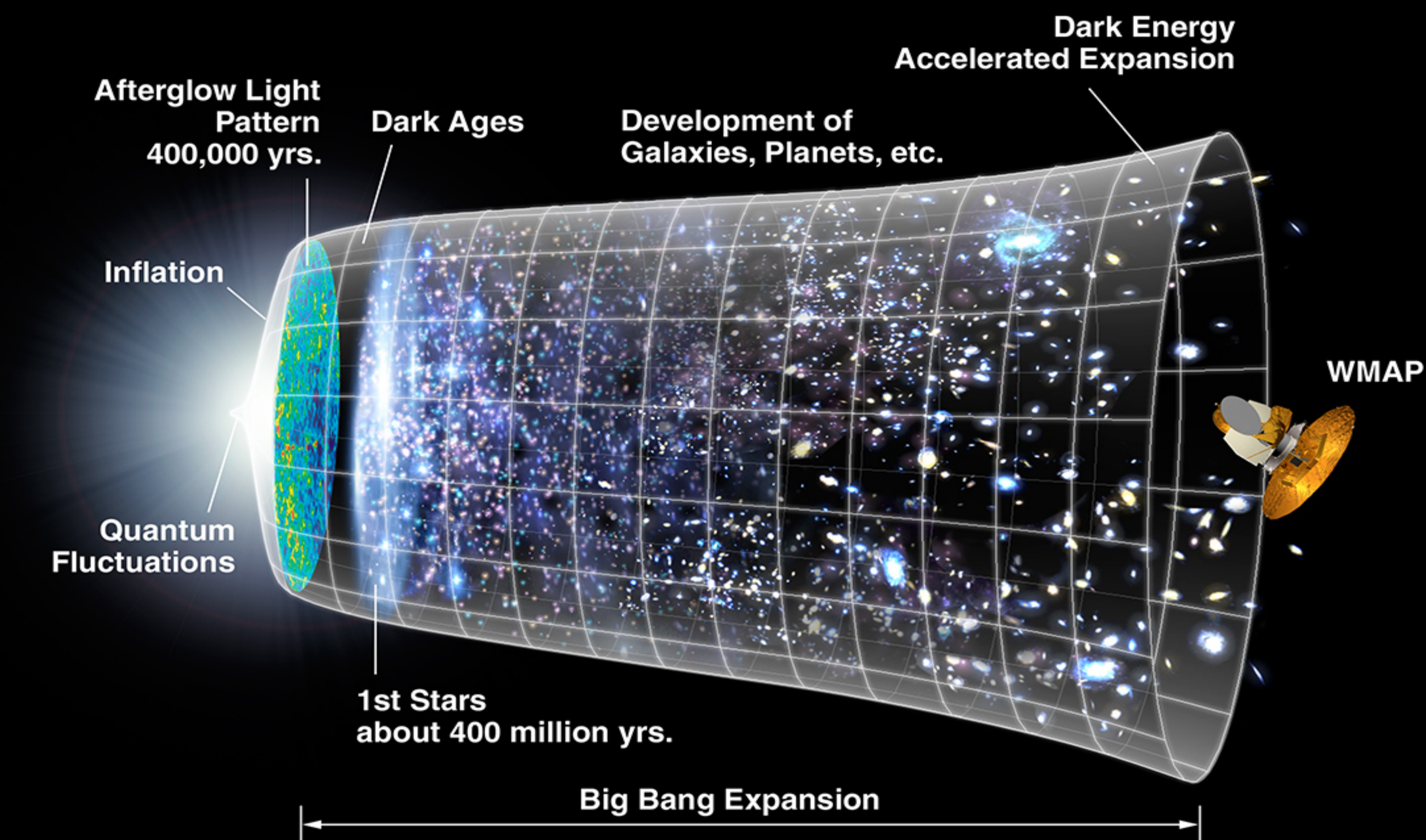
Unfavorable environment for chemical enrichment:

- rapid expansion
- strong radiation field (CMB)
- gas chemically inert (H=0.924, He=0.076, D=2x10^{-5}, Li=4x10^{-10})
- no solid particles (catalyzers)

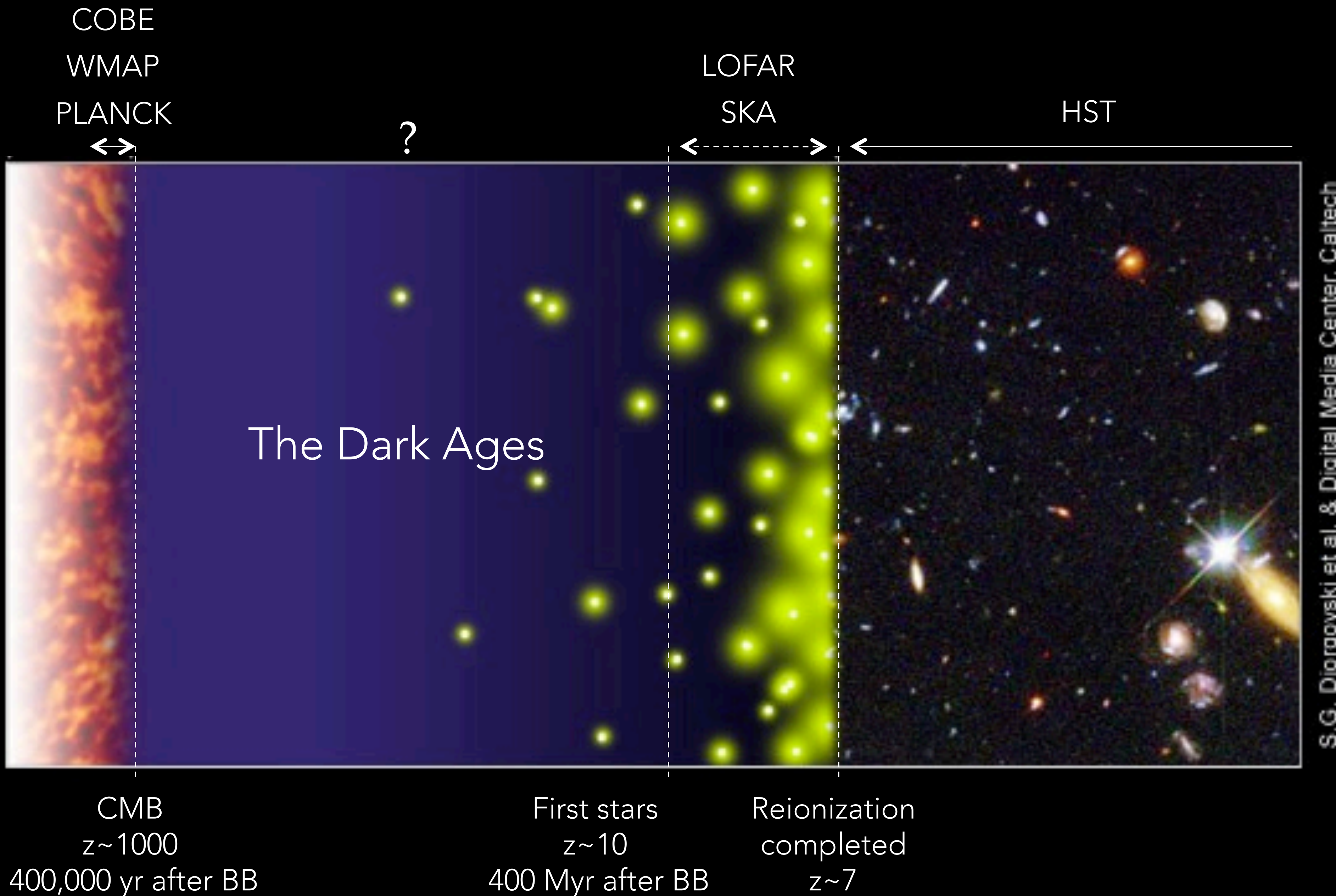
→ low molecular abundances

Main molecules and ions:

- Hydrogen subsystem: H_2, H_2^+, H_3^+, H^-, H_3^+
- Deuterium " ": HD, HD^+, H_2D^+
- Helium " ": He_2^+, HeH^+
- Lithium " ": LiH, LiH^+, $LiHe^+$



13.798 ± 0.037 billion years


COBE
WMAP
PLANCK
?
LOFAR
SKA
HST
The Dark Ages
S.G. Djorgovski et al. & Digital Media Center, Caltech
CMB
z~1000
400,000 yr after BB
First stars
z~10
400 Myr after BB
Reionization
completed
z~7

The cosmological background

the Dark Ages:

- start: after H recombination (z ~ 1000, t ~ 400,000 yr)
- end: formation of the first stars (z ~ 10, t ~ 400 million yr)

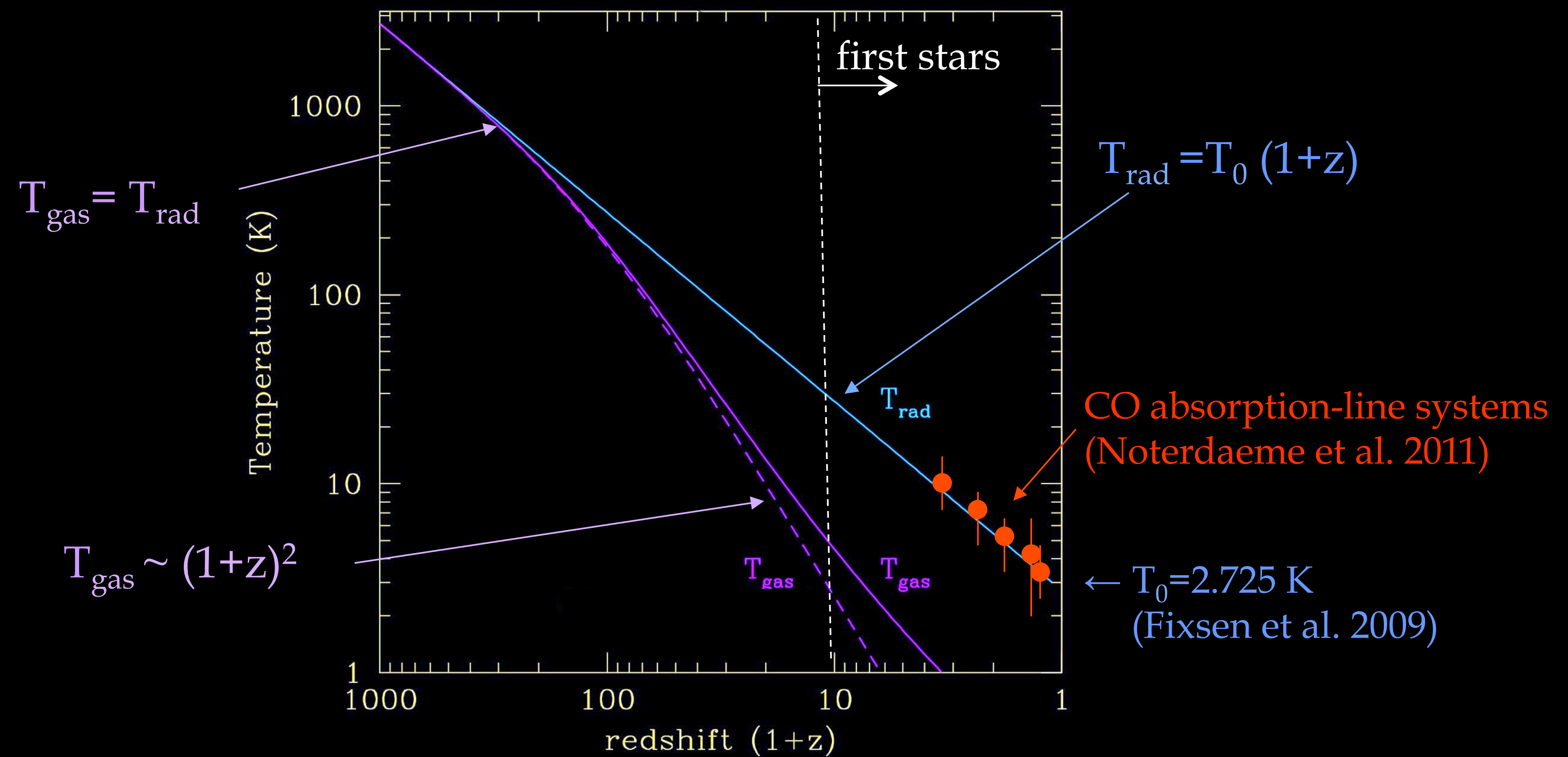
- Baryon density $n \approx 10^{-5} \Omega_b h^2 (1+z)^3 \ \mathrm{cm}^{-3}$
- Expansion rate $\frac{dt}{dz} \approx - \frac{10^{10}\ \mathrm{yr}}{h(1+z)\sqrt{\Omega_\Lambda + (1+z)^3 \Omega_m}}$
-
- Radiation field $T_r = T_0 (1+z)$

- Cosmological parameters $h, \Omega_b, \Omega_m, \Omega_\Lambda, T_0$

$\Omega_\Lambda = 0.726^{+0.013}_{-0.017}$ $100\ \Omega_b h^2 = 2.233^{+0.028}_{-0.038}$ $h = 0.734^{+0.072}_{-0.091}$ $T_0 = 2.726^{+0.0013}_{-0.0013}$ K

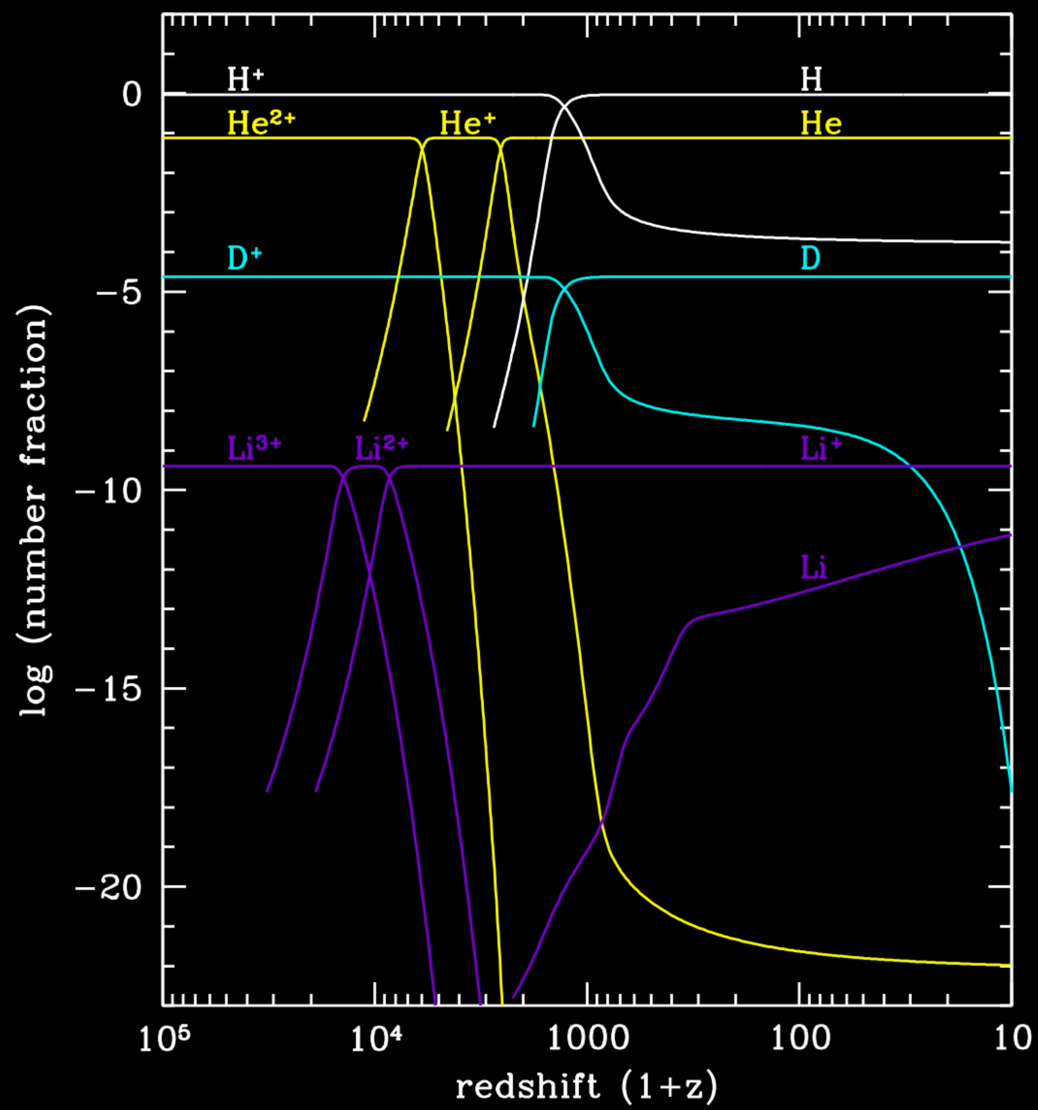
Spergel et al. (2003), Fixsen (2009)

Temperature of matter and radiation

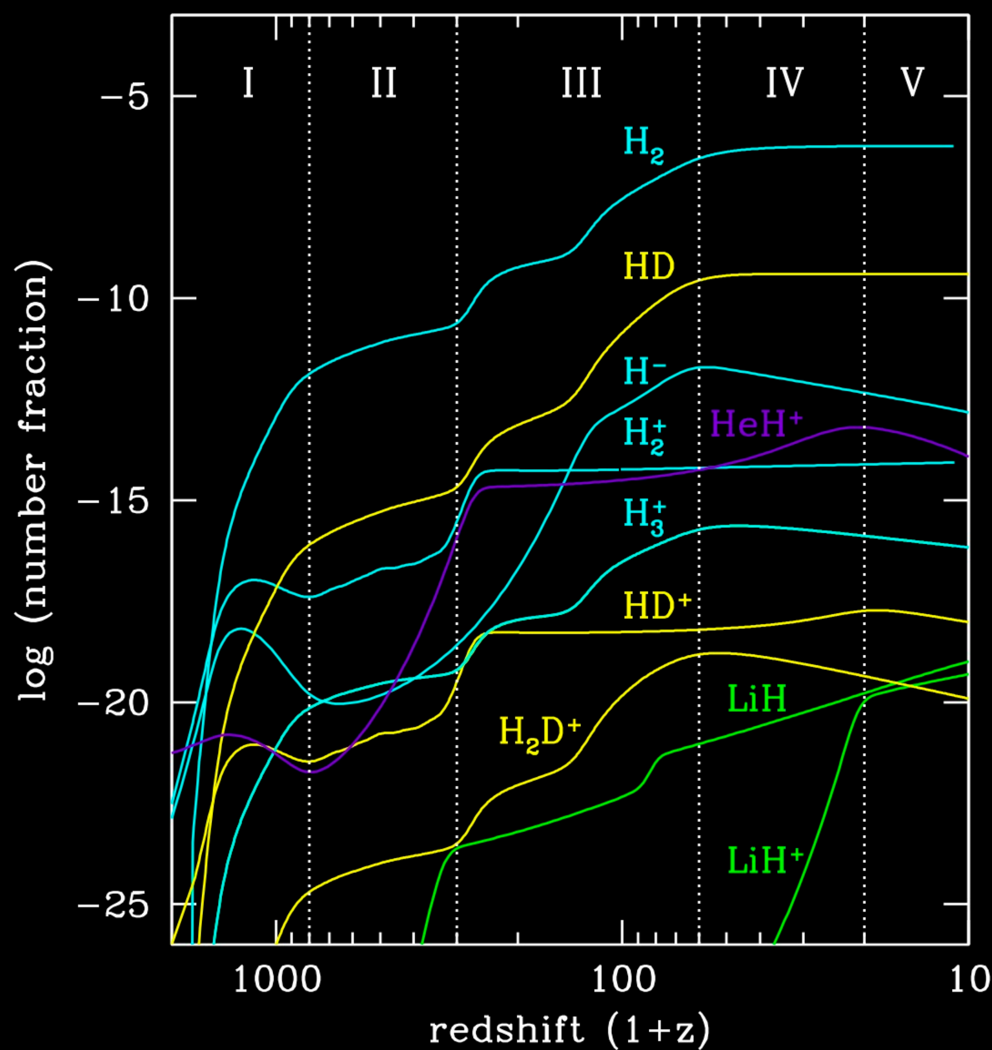


LCDM model: $h, \Omega_{\rm b}, \Omega_{\rm m}, \Omega_\Lambda, T_0$ from WMAP-7yr (Komatsu et al. (2011)

Ions and atoms in the Early Universe



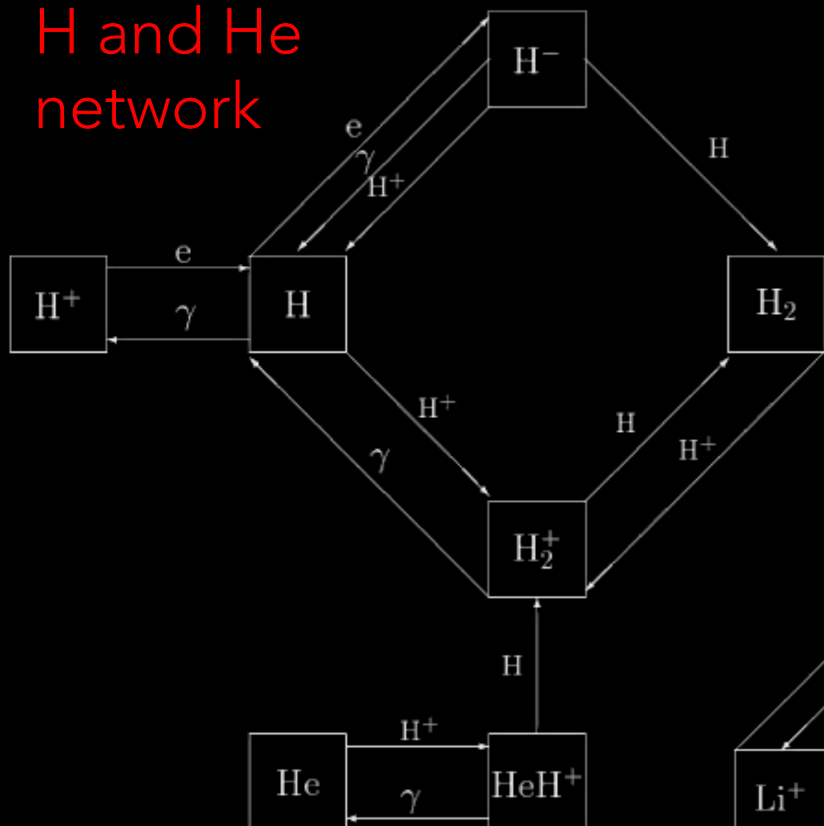
Molecules in the early Universe



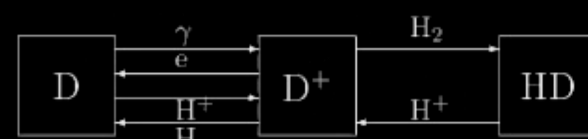
Galli & Palla (2013) Ann. Rev. Astron. Astrophys., Vol. 51, 163

Primordial chemistry networks (simplified)

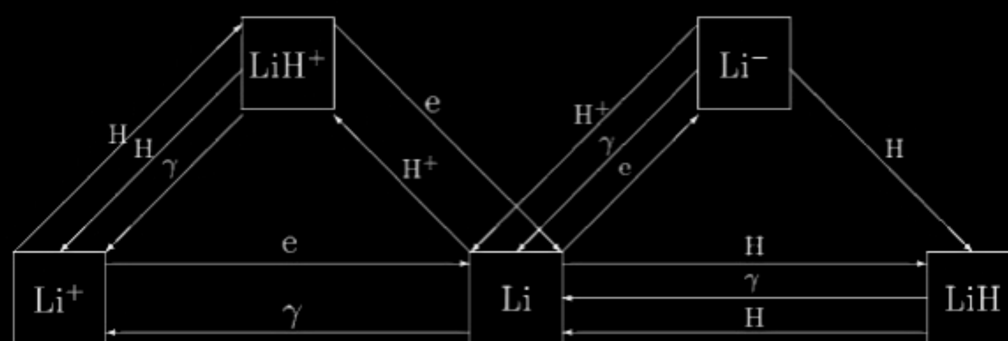
H and He network



D network



Li network



Recent advances in primordial chemistry

Recently computed with fully quantal methods → Gianturco, Bovino et al.

- $HeH^+ + H \rightarrow He + H_2^+$
- $LiH + H \rightarrow Li + H_2$
- $LiH^+ + H \rightarrow Li^+ + H_2$
- $LiH + H^+ \rightarrow Li + H_2^+$
- $LiHe^+ + H \rightarrow LiH^+ + He$
- $Li^+ + He \rightarrow LiHe^+ + g$
- $LiHe^+ + \gamma \rightarrow Li^+ + He$
- $LiHe^+ + e – Li + He$ (with Čurik)

Recently measured in the lab:

- $H^- + H \rightarrow H_2 + e$ ass. det. (Columbia Astroph. Lab., Kreckel et al. 2010)
- $H_3^+ + e \rightarrow 3H$ and $H_2 + H$ diss. rec. (CRYRING, TSR, McCall et al. 2004)

In progress:

- $H^- + H^+ \rightarrow H + H$ mut. neutr. (DESIREE - Manne Siegbahn Lab. Stockholm)

Still uncertain:

- $H + H + H \rightarrow H_2 + H$ three-body reaction (Bovino, Schleicher & Grassi 2014)

Hydrogen chemistry

H_2^+ channel

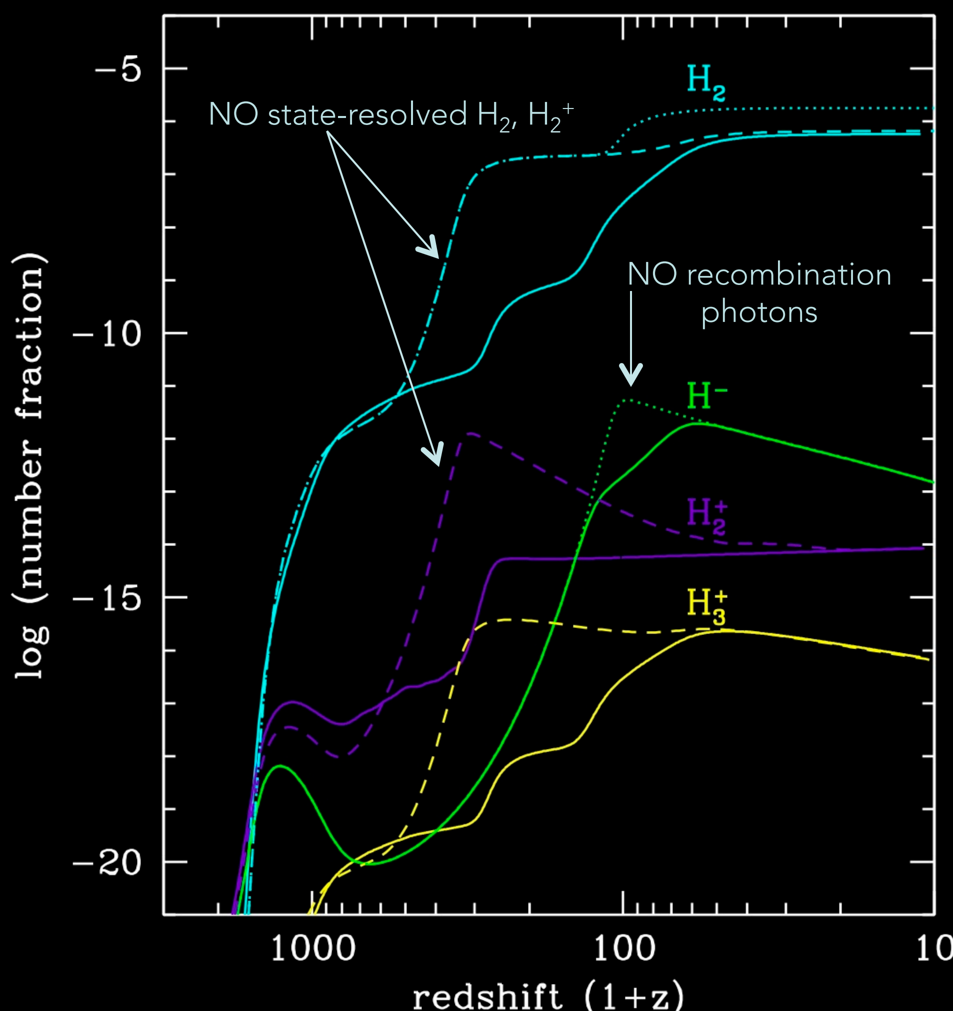
$H + H^+ \rightarrow H_2^+ + \gamma$

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

H^- channel

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

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



Galli & Palla (1998), Coppola et al. (2011)

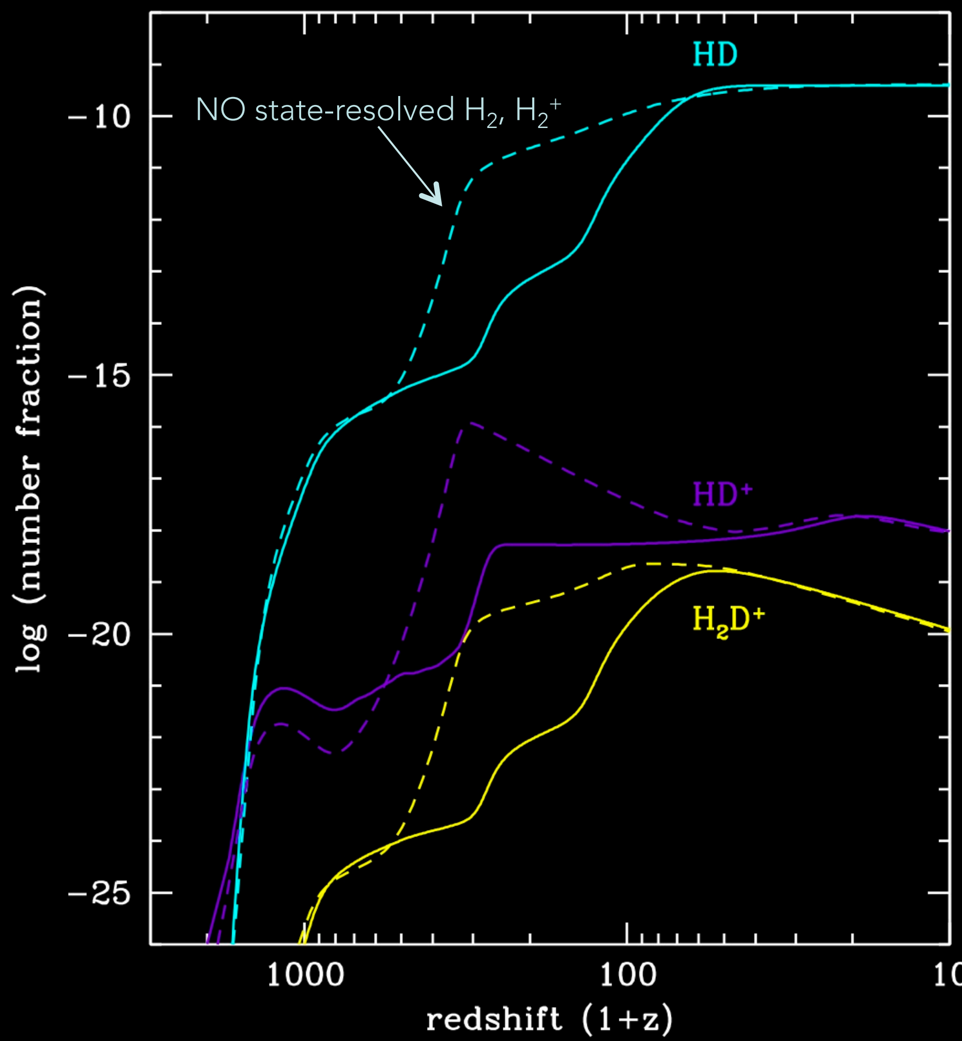
Deuterium chemistry

Formation of HD:

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

Destruction of HD:

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



Stancil et al. (1998), Galli & Palla (2002)

Helium chemistry

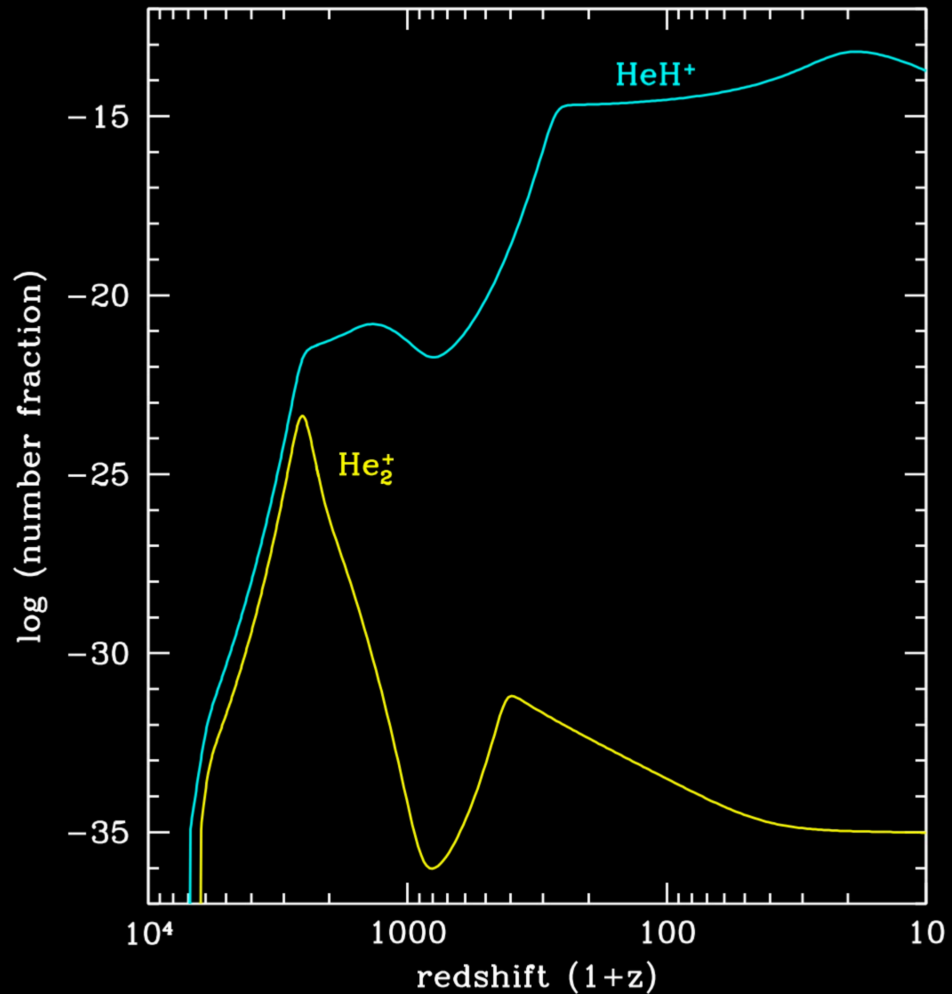
Formation:

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

Destruction:

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

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



Galli & Palla (1998), Bovino et al. (2011)

Lithium chemistry

Formation of LiH:

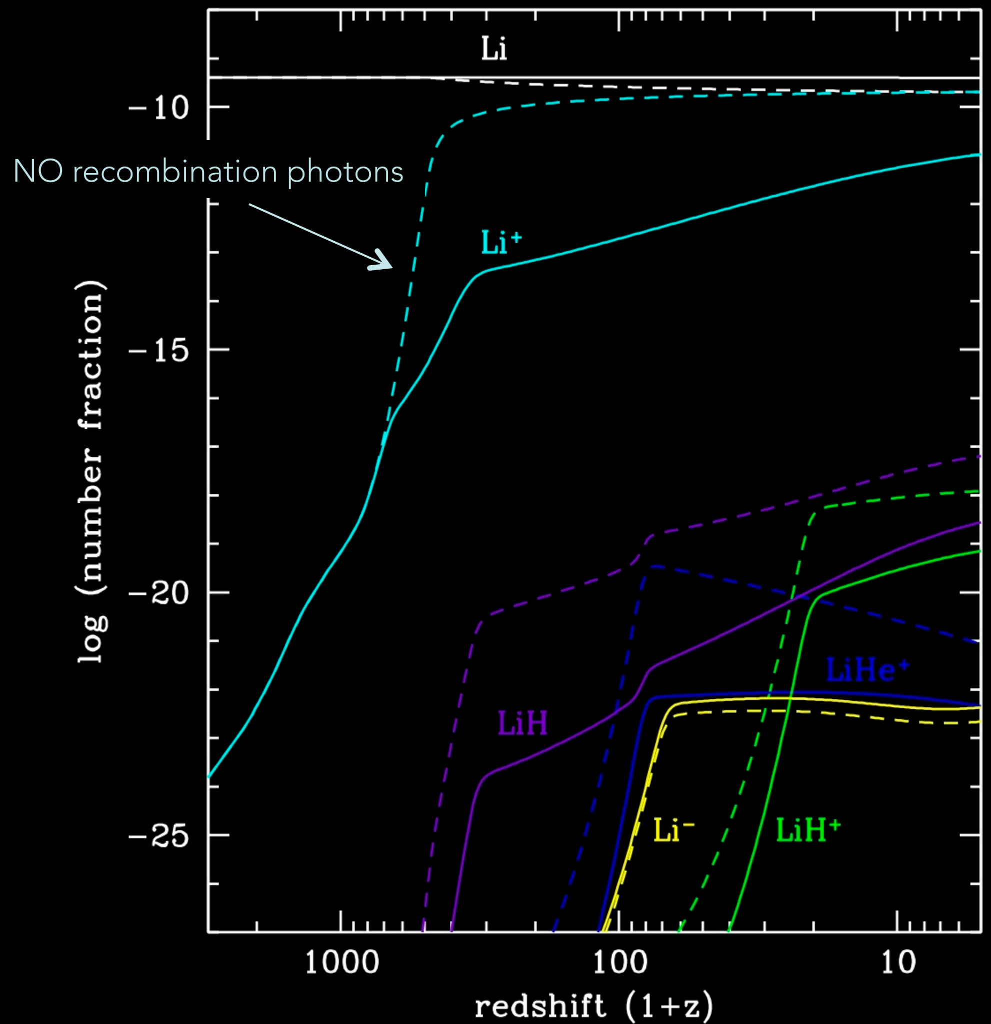
$Li + H \rightarrow LiH + \gamma$

$Li^- + H \rightarrow LiH + e^-$

Destruction of LiH:

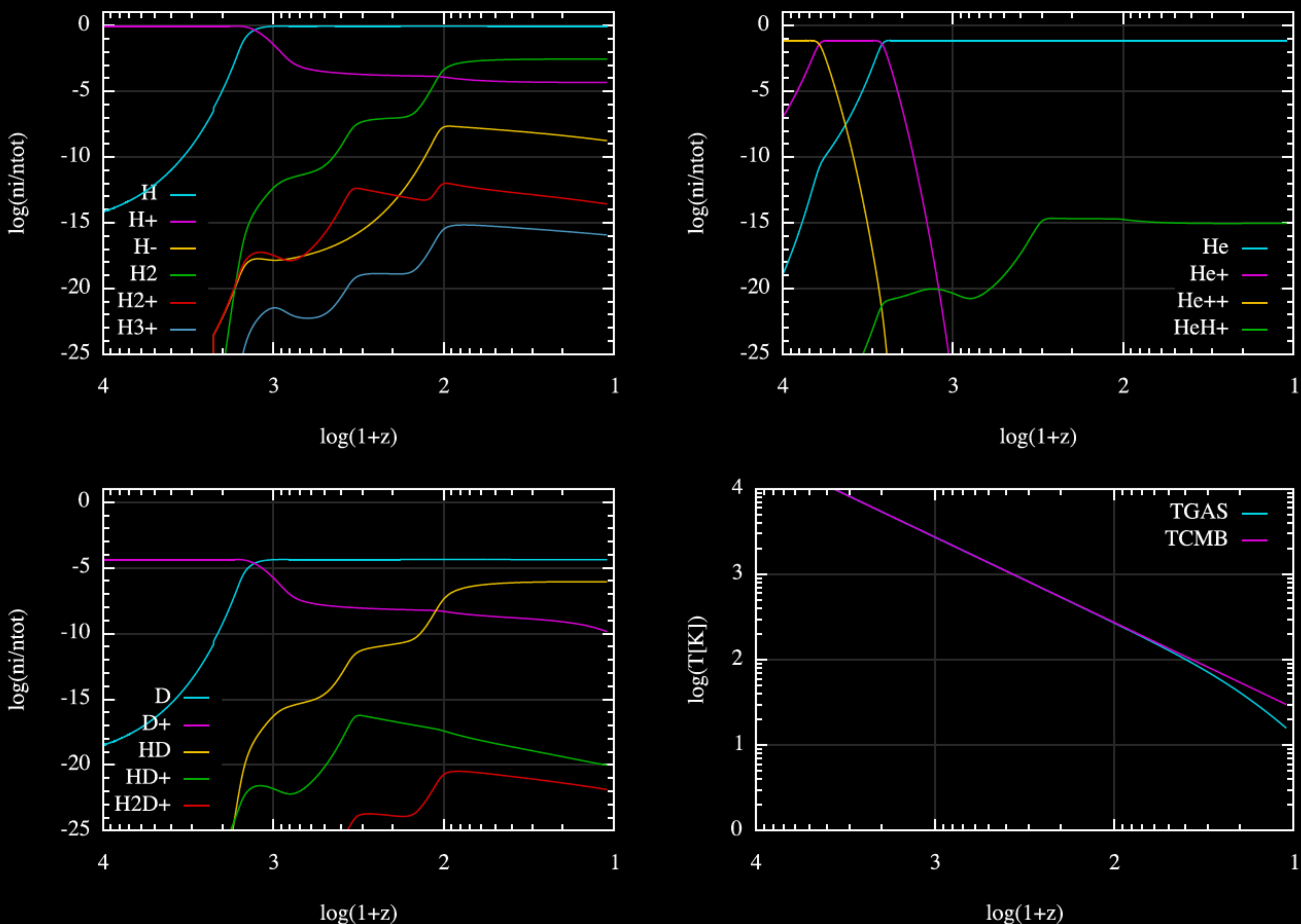
$LiH + \gamma \rightarrow Li + H$

$LiH + H \rightarrow Li + H_2$



Stancil et al. (1996), Bovino et al. (2011)

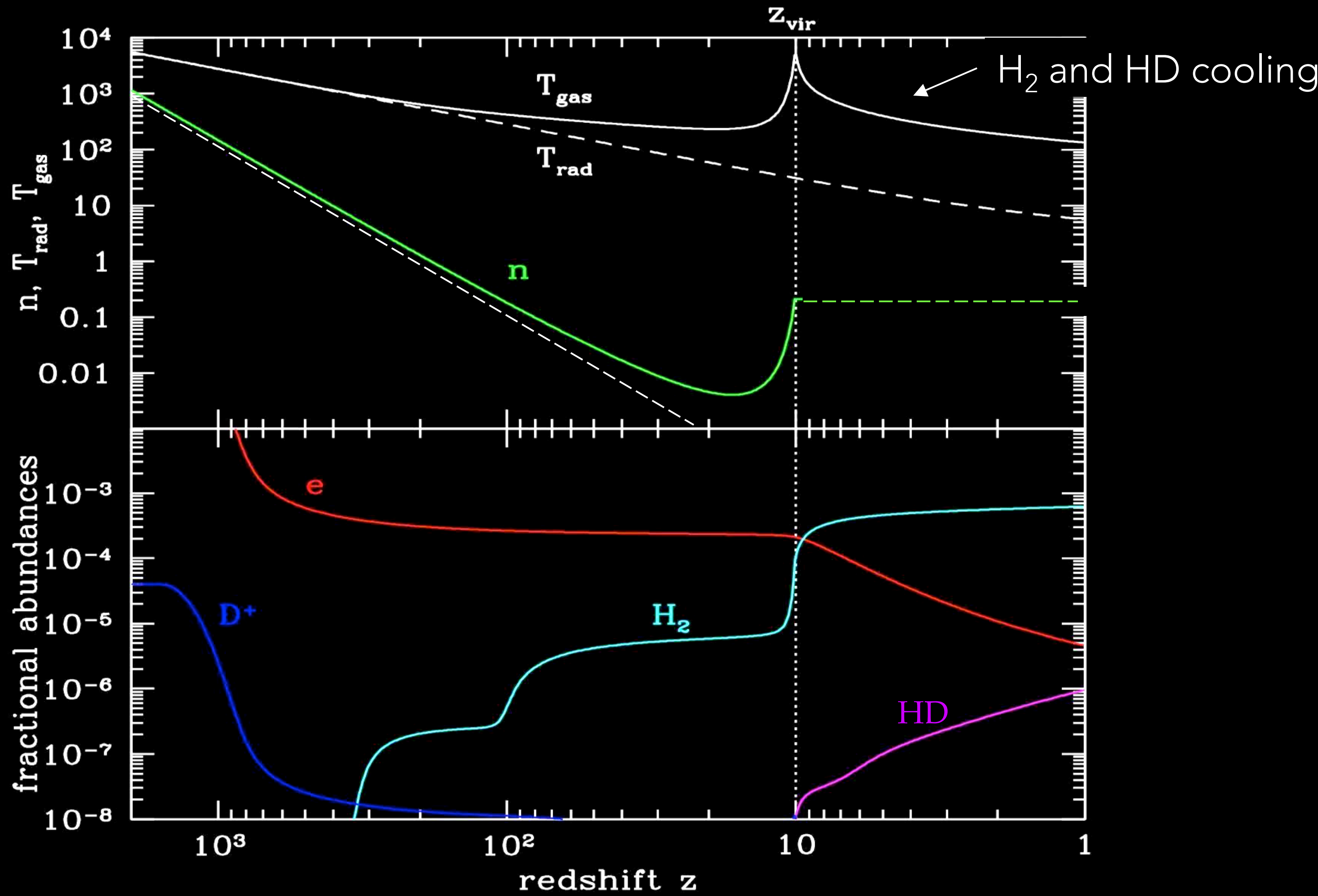
KROME!



log(ni/ntot)
log(1+z)
H
H+
H-
H2
H2+
H3+
He
He+
He++
HeH+
D
D+
HD
HD+
H2D+
log(T[K])
TGAS
TCMB

Evolution of an overdense region

Tegmark et al. (1997), Galli & Palla (2002)



→ see talk by D. Schleicher on Tuesday

Radiative cooling of interstellar gas

- Present-day ISM:

Very efficient cooling. Abundant species with low-lying energy levels (rotational transitions of ^{12}CO, ^{13}CO, $C^{18}O$, fine-structure splitting of C^+ and O). Gas cooling also by collisions with dust grains.

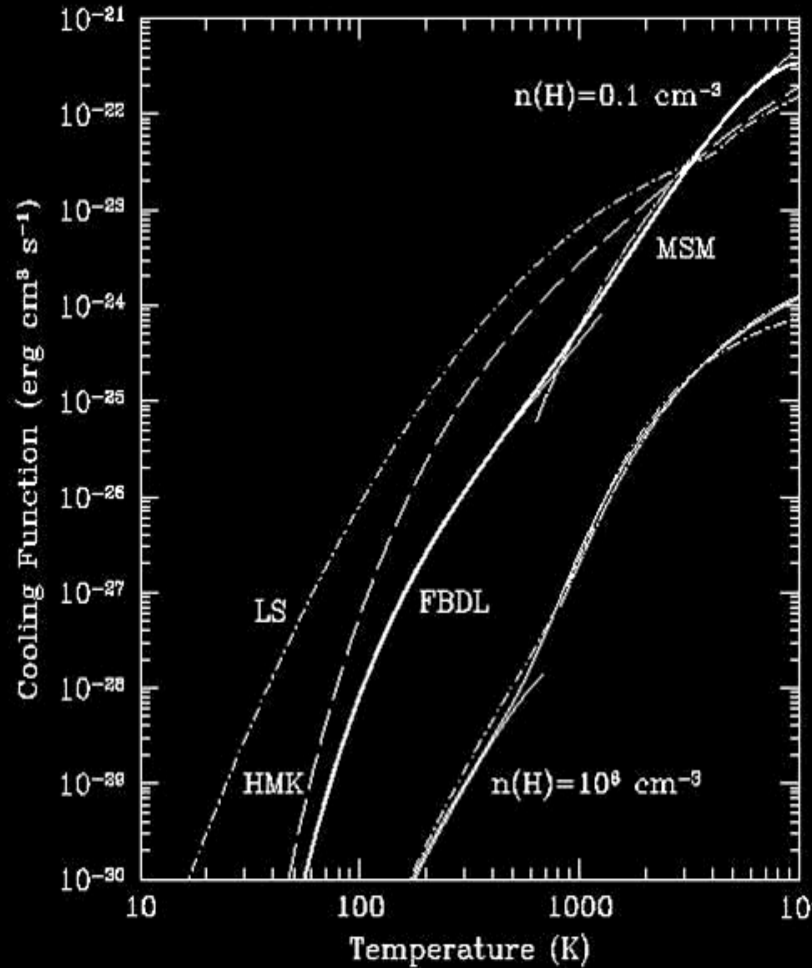
- Primordial Universe:

Inefficient cooling. Only H_2 and HD (minor species H_3^+, LiH). Lowest transitions H_2 (J=0-2 with ΔT=510 K, J=1-3 with ΔT=845 K) and HD (J=1-0 with ΔT=128 K, J=2-1 with ΔT=255 K). Excitation of H_2 and HD by collisions with H followed by radiative decay.

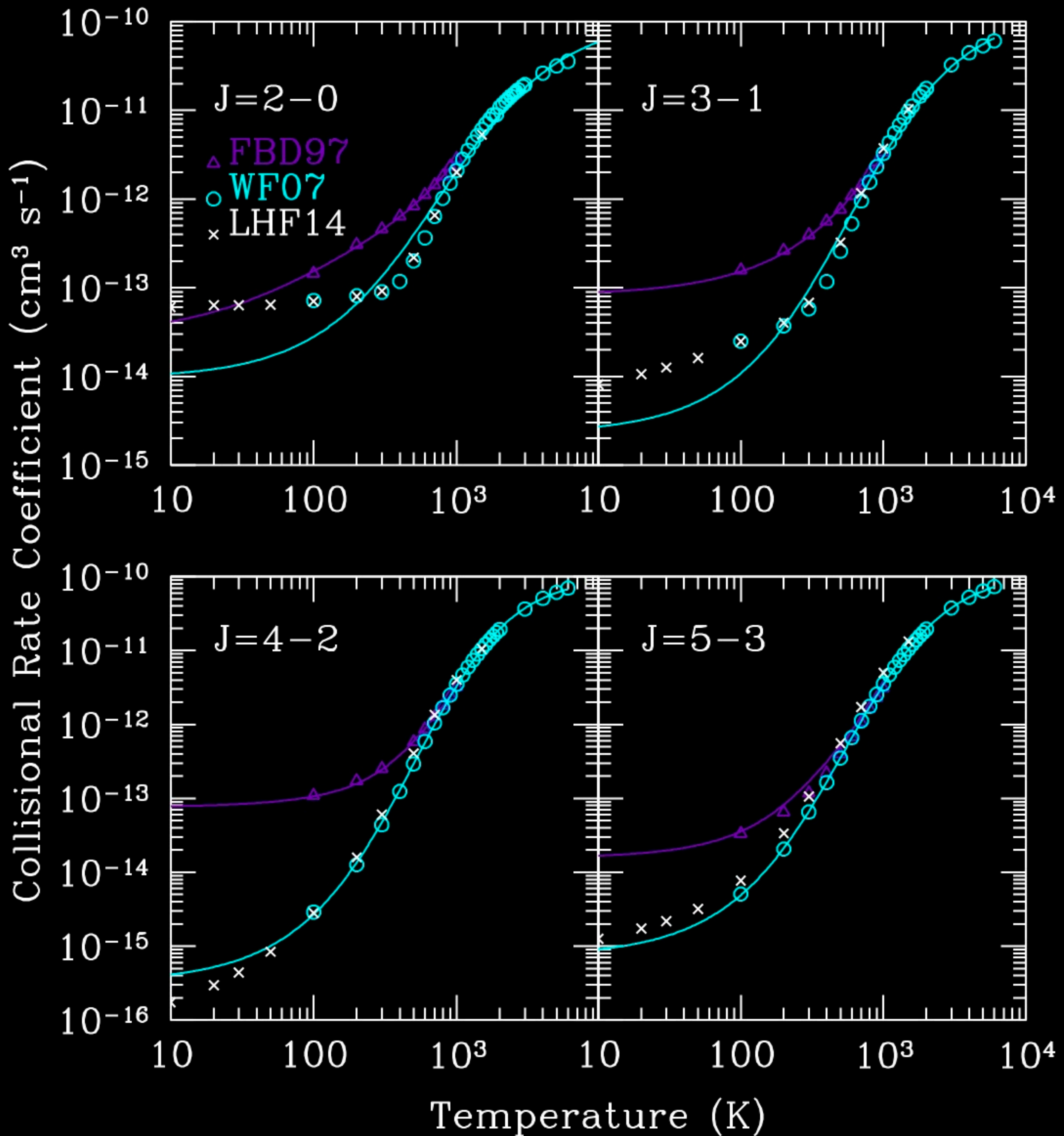
→ see talk by T. Grassi and S, Bovino on Tuesday

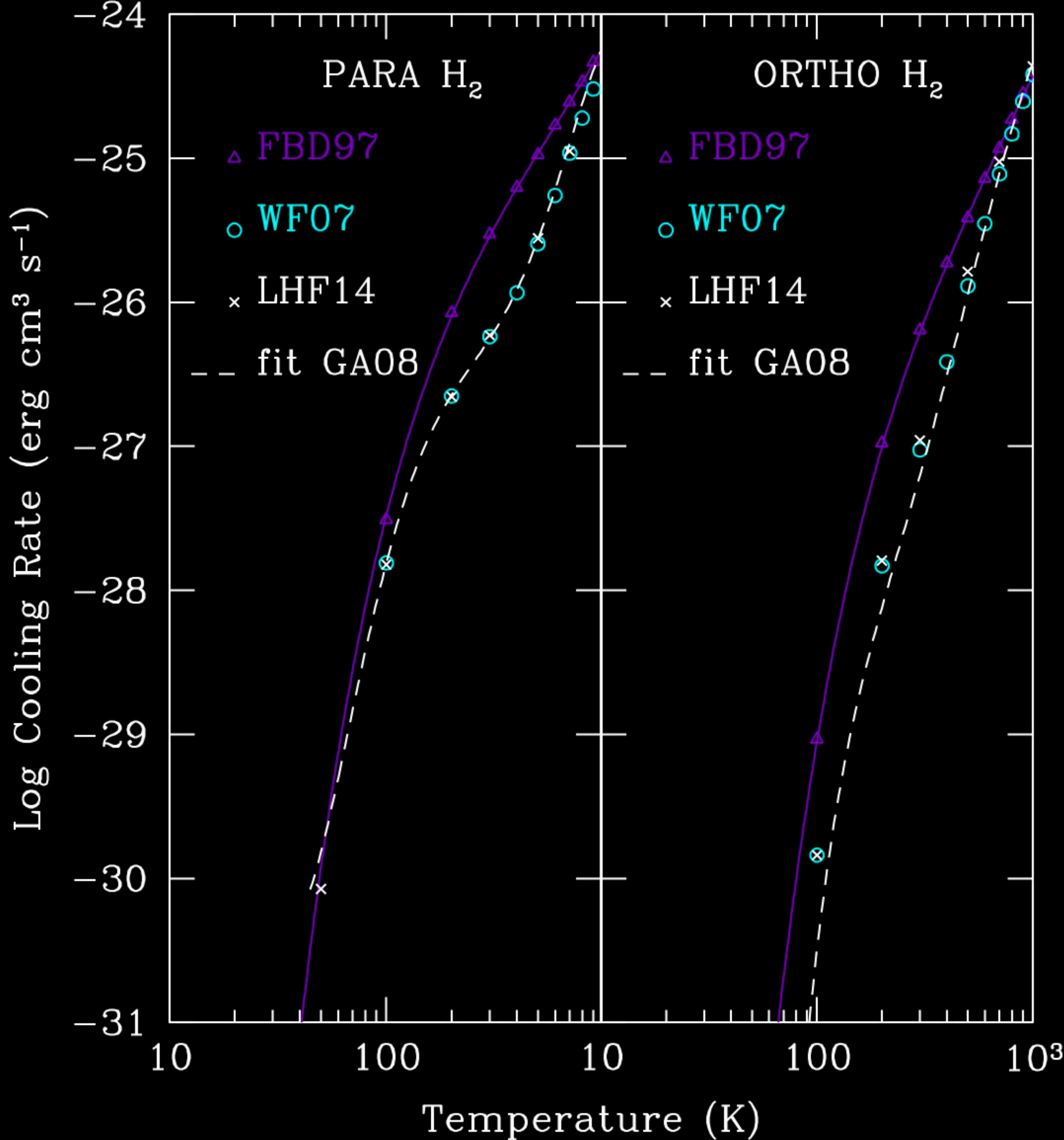
H_2 cooling

- Low-T rates for H-H_2 coll. exc. highly sensitive to adopted H_3 potential surface
- Galli & Palla (1998): coll. coeff. from Forrey et al. (1997) for T < 600 K, Mandy & Martin (1993) T > 600 K
- New set sof H-H_2 coll. coeff. (Wrathmall & Flower 2007; Lique et al. 2014)
- H_2-H_2 (Flower 2000)
- He-H_2 (Flower et al. 1998; Balakrishnan et al. 1999)



Galli & Palla (1998)


J=2−0
J=3−1
J=4−2
J=5−3
FBD97
WF07
LHF14
Collisional Rate Coefficient (cm^3 s^{-1})
Temperature (K)



Forrey et al. (1997), Wrathmall & Flower (2007), Lique et al. (2014)

Summary of primordial chemistry

- The first molecules are formed from gas-phase reactions after H and He recombination (z<1000).

- H_2, HD, and possibly H_3^+ control the thermodynamics of metal-free gas and determine the mass of the first stars. Li^+ controls the ionization fraction at high cloud densities.

- H^-, HeH^+ and Li dominate the optical depth of the primordial gas, but the induced spectral/spatial signatures in the CMB ($\Delta T/T < 10^{-7}$) are still below the sensitivity of current instruments ($\Delta T/T = 10^{-6}$).

- See Galli & Palla (2013) "The Dawn of Chemistry", ARAA vol. 51