

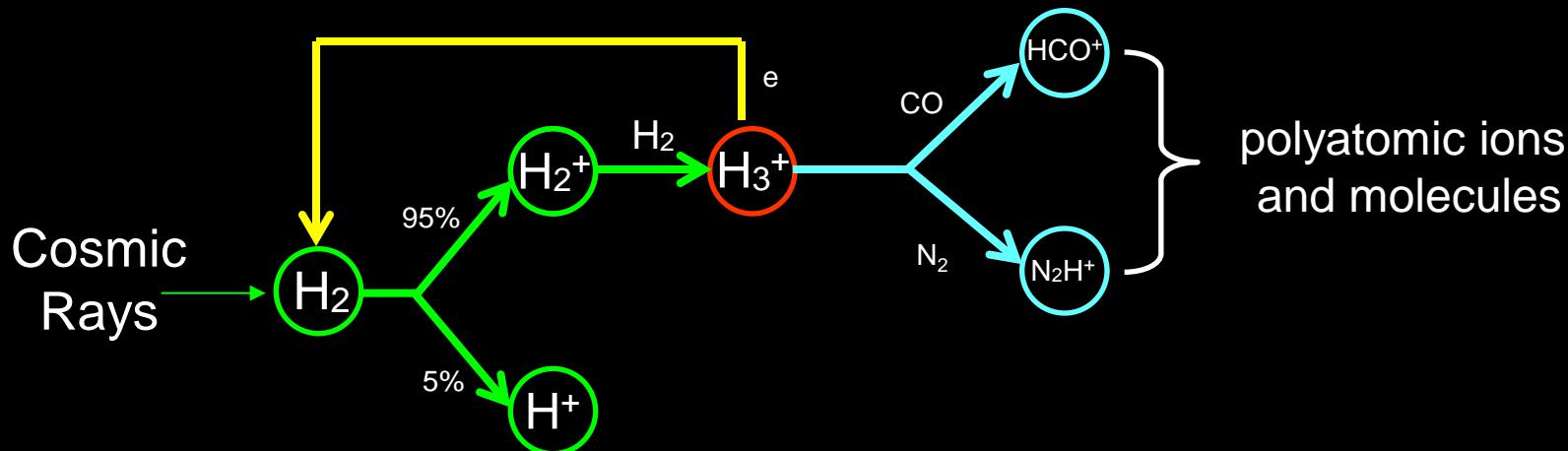
# Gas-phase chemistry in the ISM and the primordial Universe

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# Fundamental gas-phase reactions in molecular clouds



# Reactions and reaction rates

- $A + B \rightarrow P$  (two-body reaction)

$$\frac{dn_P}{dt} = k n_A n_B \quad \text{units of } k : \text{cm}^3 \text{ s}^{-1}$$

- $A + \text{photon} \rightarrow P$  (photoreaction)

$$\frac{dn_P}{dt} = k n_A \quad \text{units of } k : \text{s}^{-1}$$

- $A + B + C \rightarrow P$  (three-body reaction)

$$\frac{dn_P}{dt} = k n_A n_B n_C \quad \text{units of } k : \text{cm}^6 \text{ s}^{-1}$$

## 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  $\sigma$  is the cross section of the process and  $f(v)$  the Maxwellian distribution of relative velocities

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

# Chemical networks

A system of ODEs like

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

where

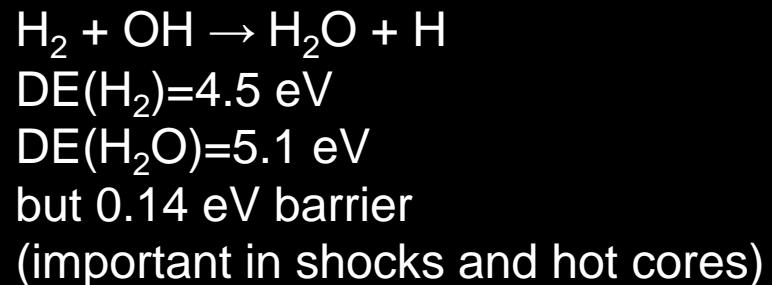
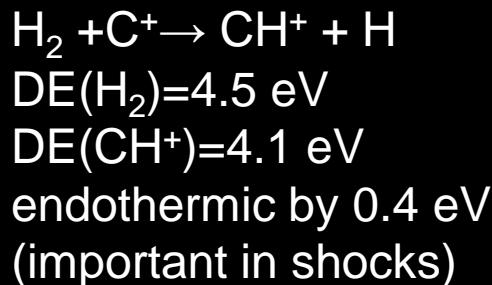
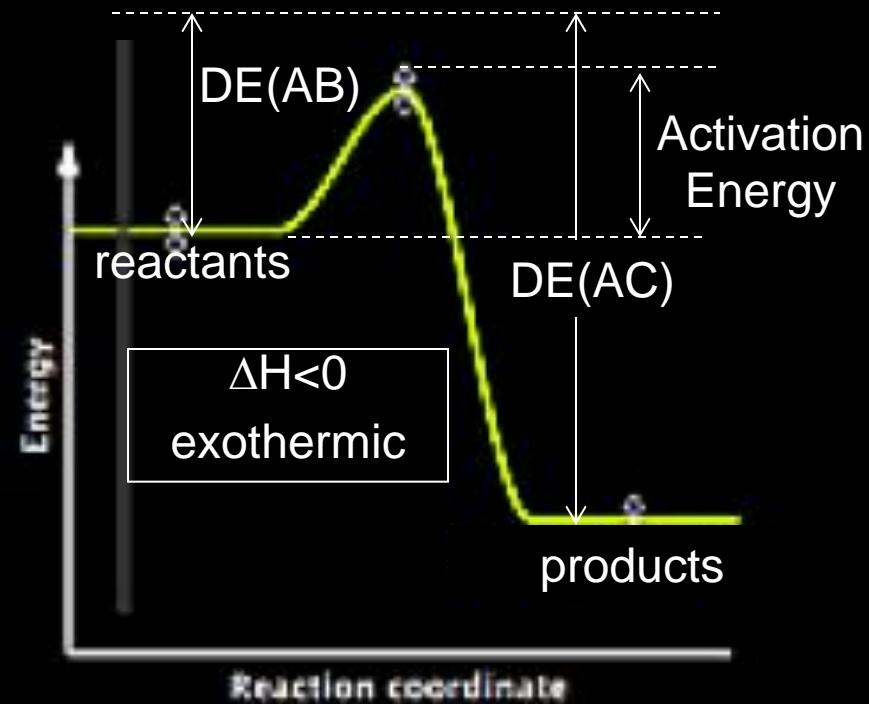
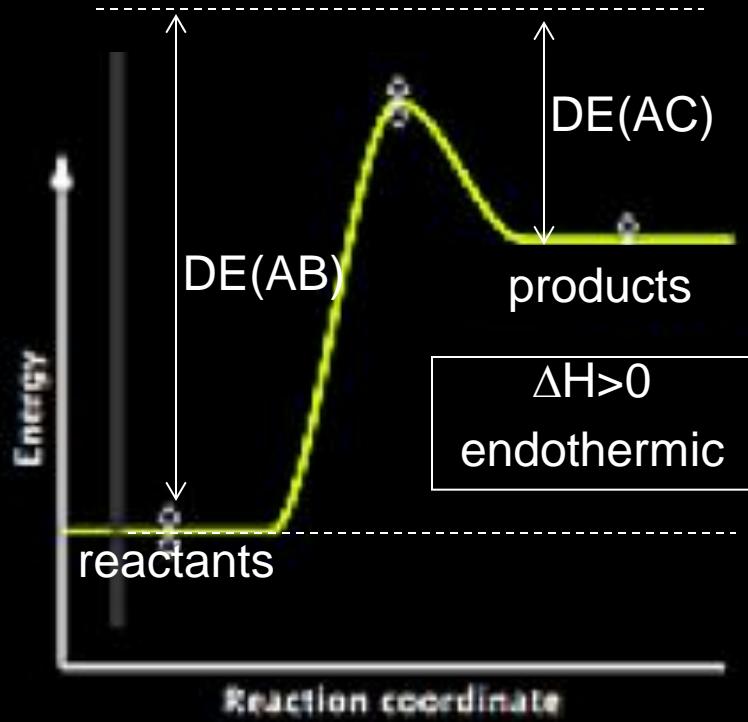
$$x_i \equiv \frac{n_i}{n}$$

Needs  $n, T_{\text{gas}}, T_{\text{rad}}$

- $n, T_{\text{gas}}, T_{\text{rad}}$  fixed (e.g. cloud chemistry)
- $n(t), T_{\text{gas}}(t)$  prescribed (e.g. early Universe)
- $n(t), T_{\text{gas}}(t)$  coupled to chemistry (e.g. magnetic collapse)

# Chemical reactions in the cold ISM

- Low temperatures:  $T=10-100\text{ K}$ ,  $E=1-10\text{ meV}$ .  
Only exothermal reactions are possible
- Low density:  $n=1-10^6\text{ cm}^{-3}$ . Only two-body reactions.  
(3-b frequent in the Earth's atmosphere  $n=10^{19}\text{ cm}^{-3}$ )
- 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)



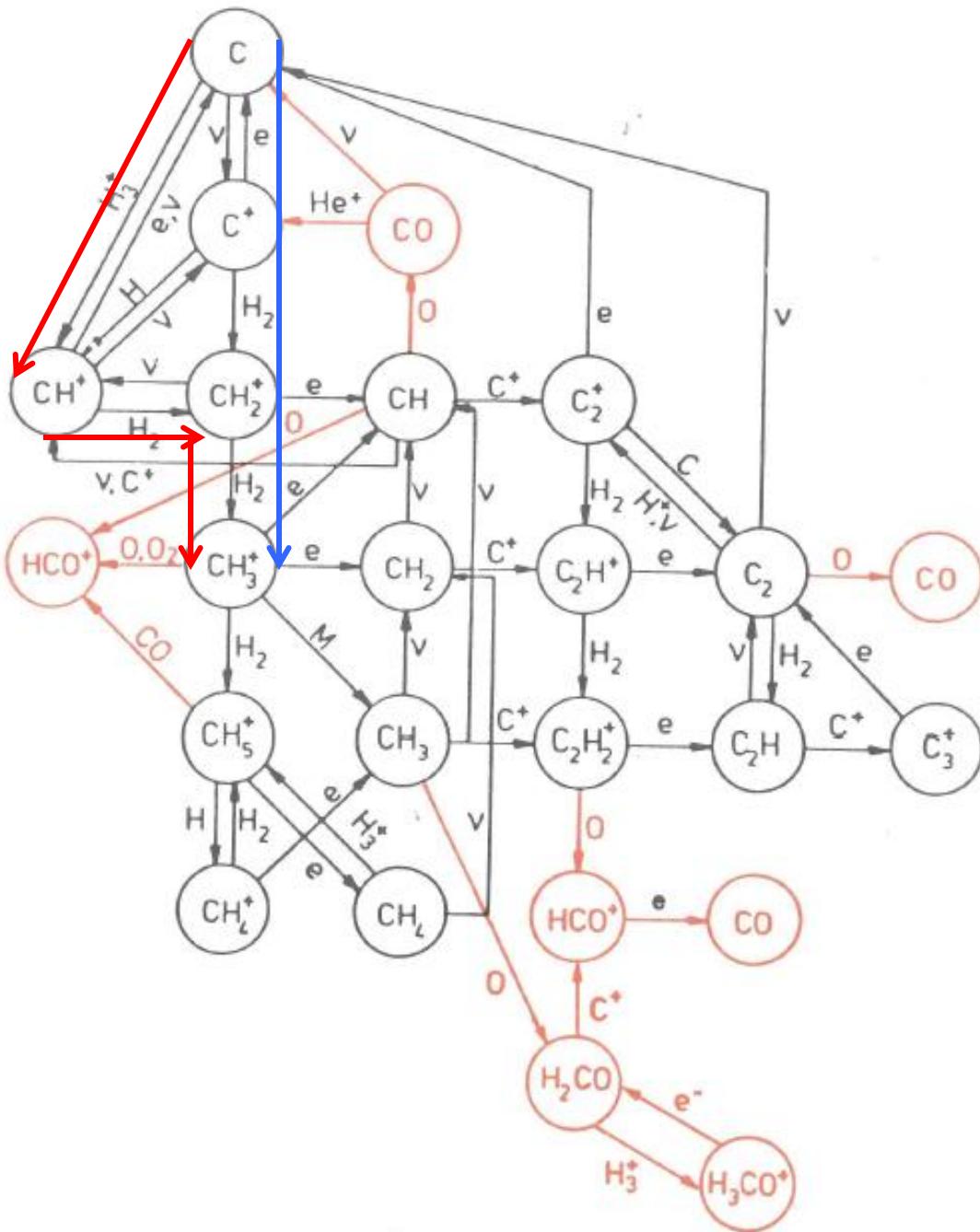
# Example: C chemistry

## in diffuse clouds

- $\text{C} + h\nu (\text{IP}=11.2 \text{ eV}) \rightarrow \text{C}^+ + \text{e}^- \rightarrow x_e = 10^{-4}$
- $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$  NO (endothermic  $\Delta E=0.4 \text{ eV}$ )
- $\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + h\nu$  radiative association, slow

## in dense clouds

- $\text{C} + \text{H}_2 \rightarrow \text{CH} + \text{H}$  NO (endothermic  $\Delta E=1 \text{ eV}$ )
- $\text{C} + \text{H}_3^+ \rightarrow \text{CH}^+ + \text{H}_2$  fast
- $\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}$
- $\text{CH}_2^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H}$  } hydrogen abstraction
- $\text{CH}_3^+ + \text{e}^- \rightarrow \text{CH}, \text{CH}_2$  dissociative recombination



# Types of reactions

## Collisional processes:

- ion-neutral reactions  $A^+ + B \rightarrow C^+ + D$
- radiative association  $A + B \rightarrow AB + h\nu$
- dissociative recombination  $AB^+ + e \rightarrow A + B$
- neutral-neutral reactions  $A + B \rightarrow C + D$
- charge transfer  $A^+ + B \rightarrow A + B^+$

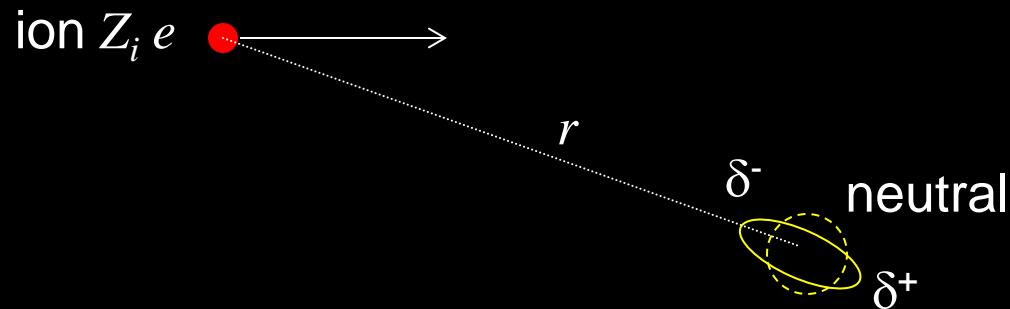
## Photoprocesses:

- photodissociation  $AB + h\nu \rightarrow A + B$
- photoionization  $AB + h\nu \rightarrow AB^+ + e$

# 1. Ion-neutral reactions

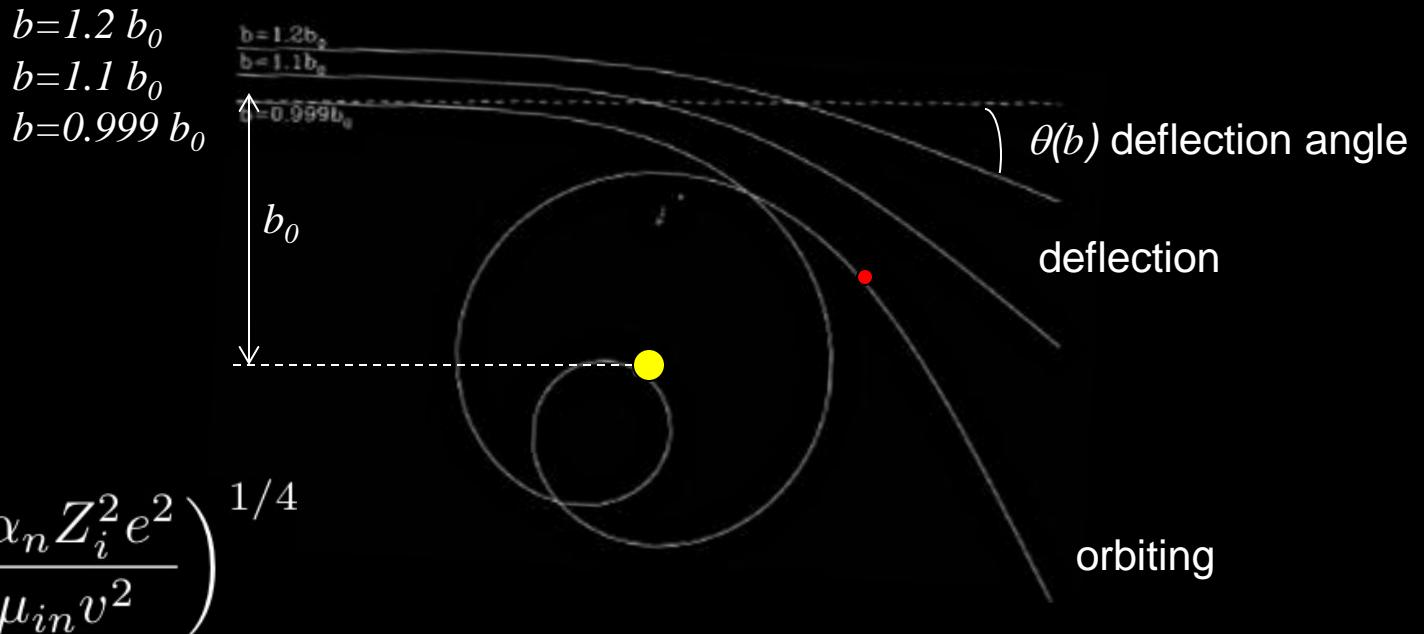


- Often have no activation barrier
- The approaching ion induces an electric dipole in the neutral that attracts the ion



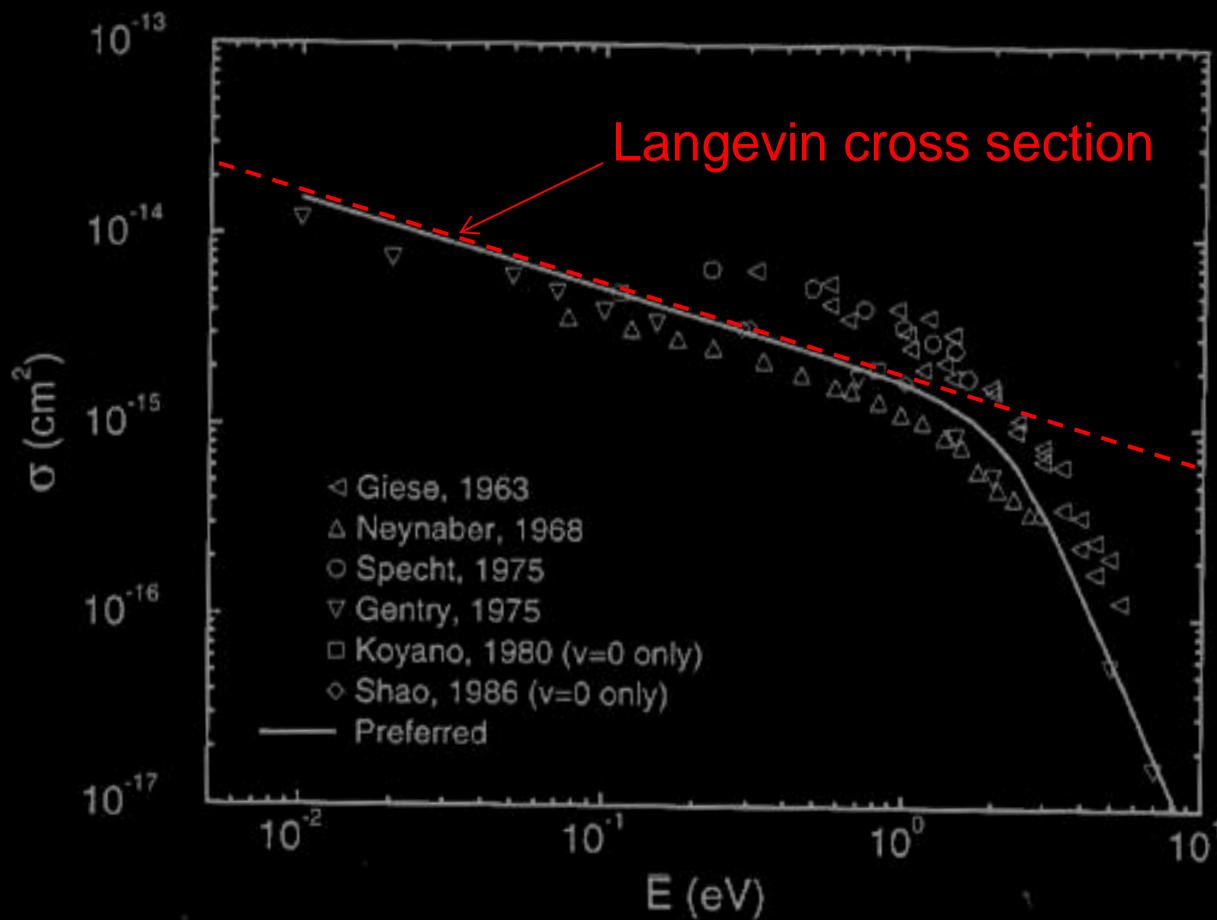
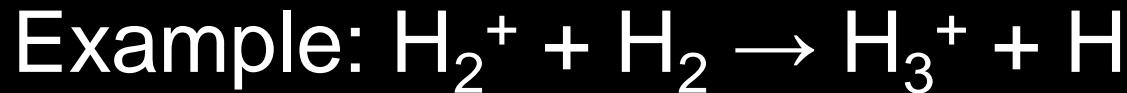
- Long-range attractive potential  $V_{in} = -\frac{\alpha_n Z_i^2 e^2}{2r^4}$   
 $\alpha_n \approx 1 \text{ \AA}^3$  polarizability of neutral species

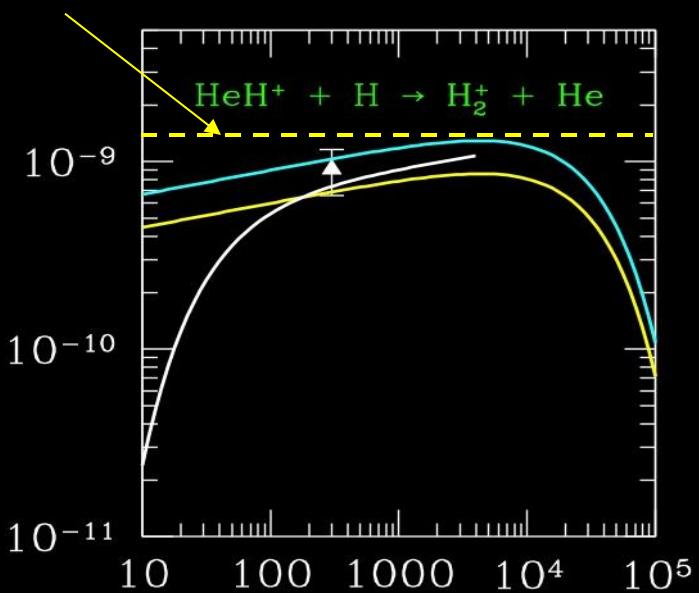
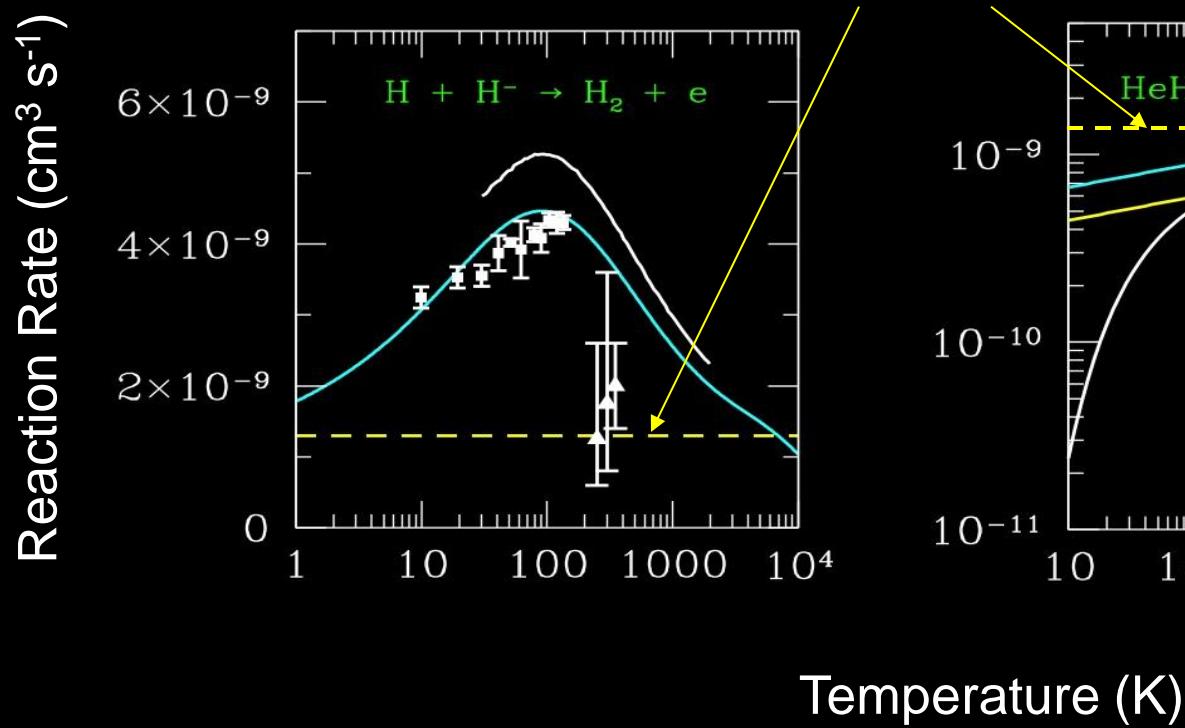
# Orbits in $r^{-4}$ potential



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

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





Temperature (K)

# Momentum transfer cross section

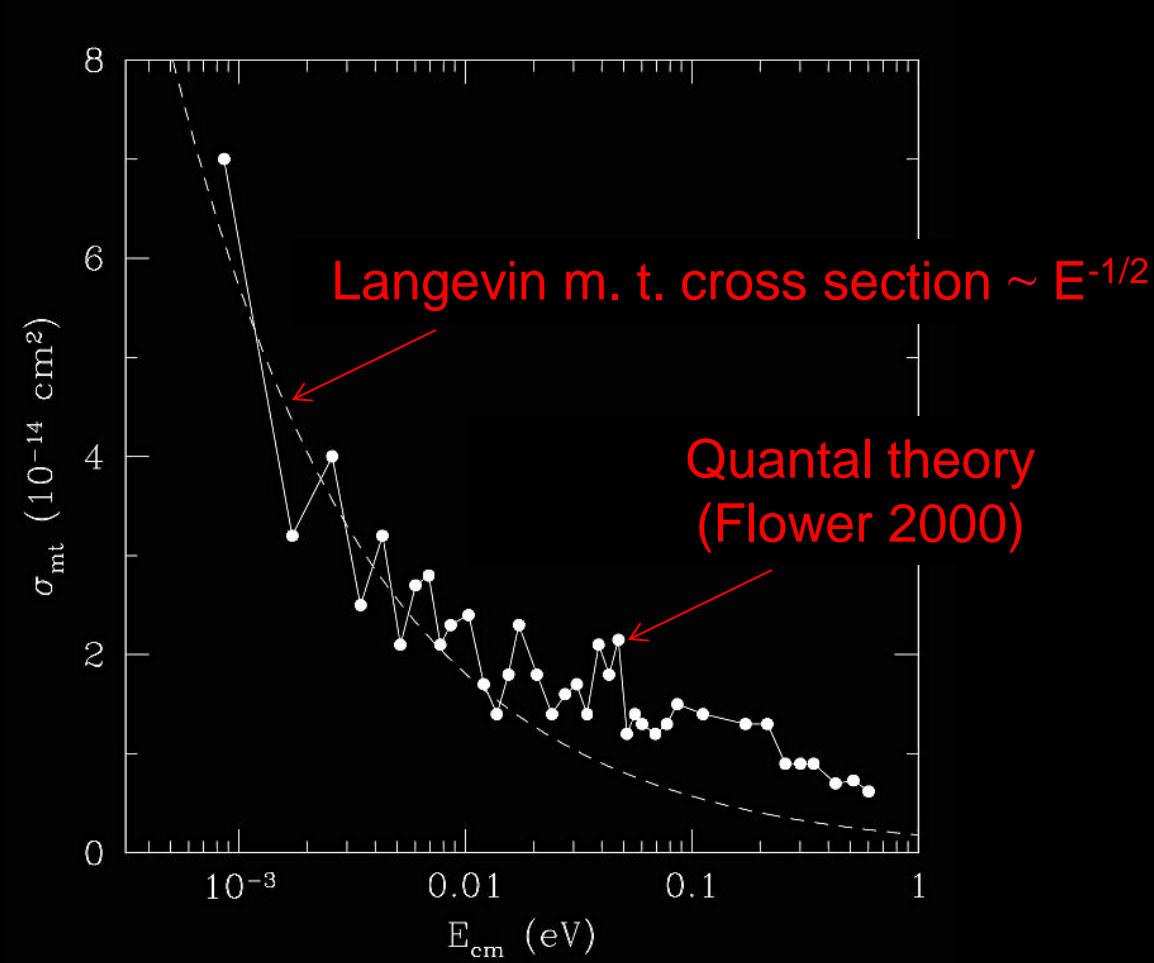
- elastic collisions
- momentum exchange between ions and neutrals
- important for MHD models

$$\sigma_{mt} = 2\pi \int_0^\infty (1 - \cos \theta) b \, db$$

Where  $\theta(b)$  = scattering angle  
(if  $b < b_0$  scattering assumed isotropic)

$$\langle \sigma v \rangle_{\text{mt}} = 2.41\pi Z_i e \left( \frac{\alpha_n}{\mu_{in}} \right)^{1/2} = 1.21 \langle \sigma v \rangle$$

# Example: $\text{HCO}^+ + \text{H}_2$ momentum transfer



## 2. Radiative association



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

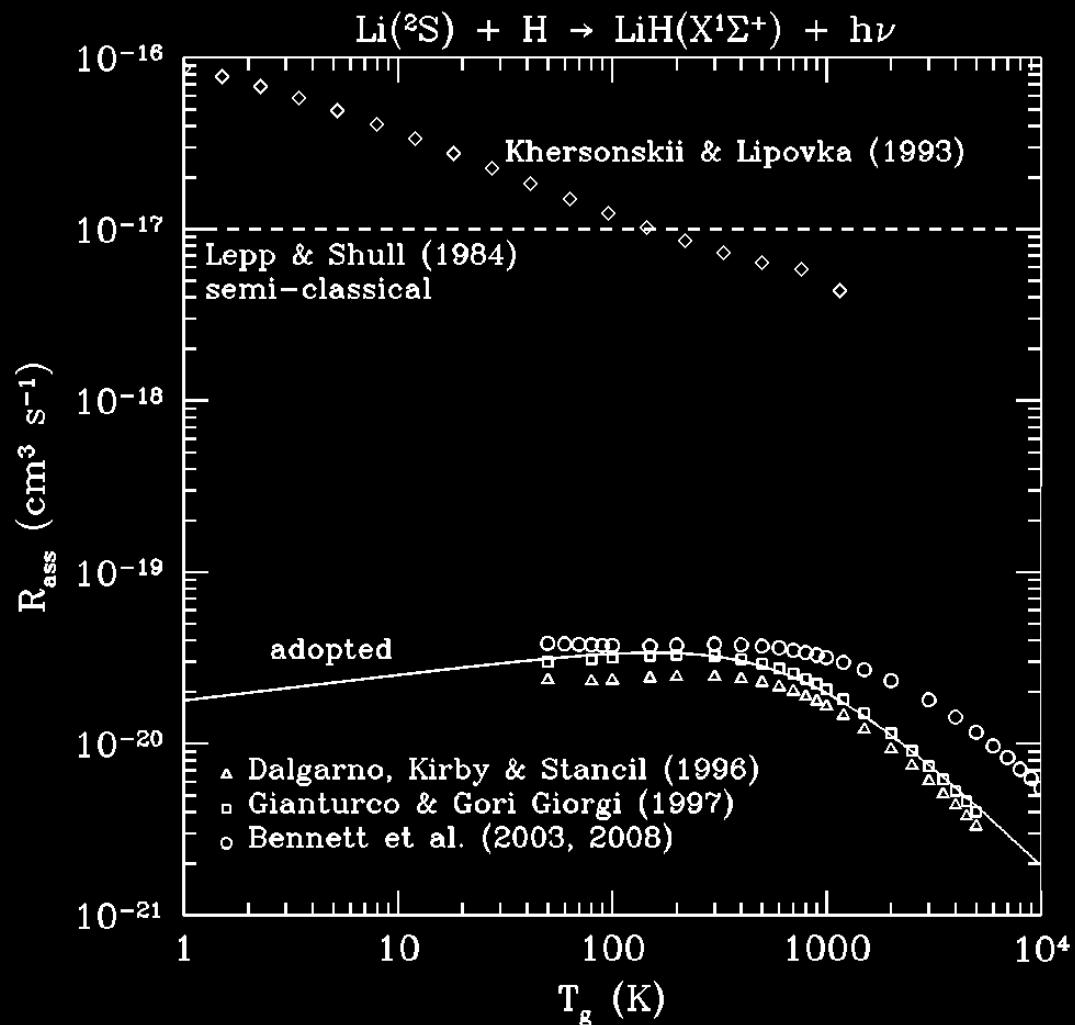
$$\sigma \approx (\pi a_0^2) (t_{\text{collision}}/t_{\text{radiative}}) \approx 10^{-6} a_0^2$$

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

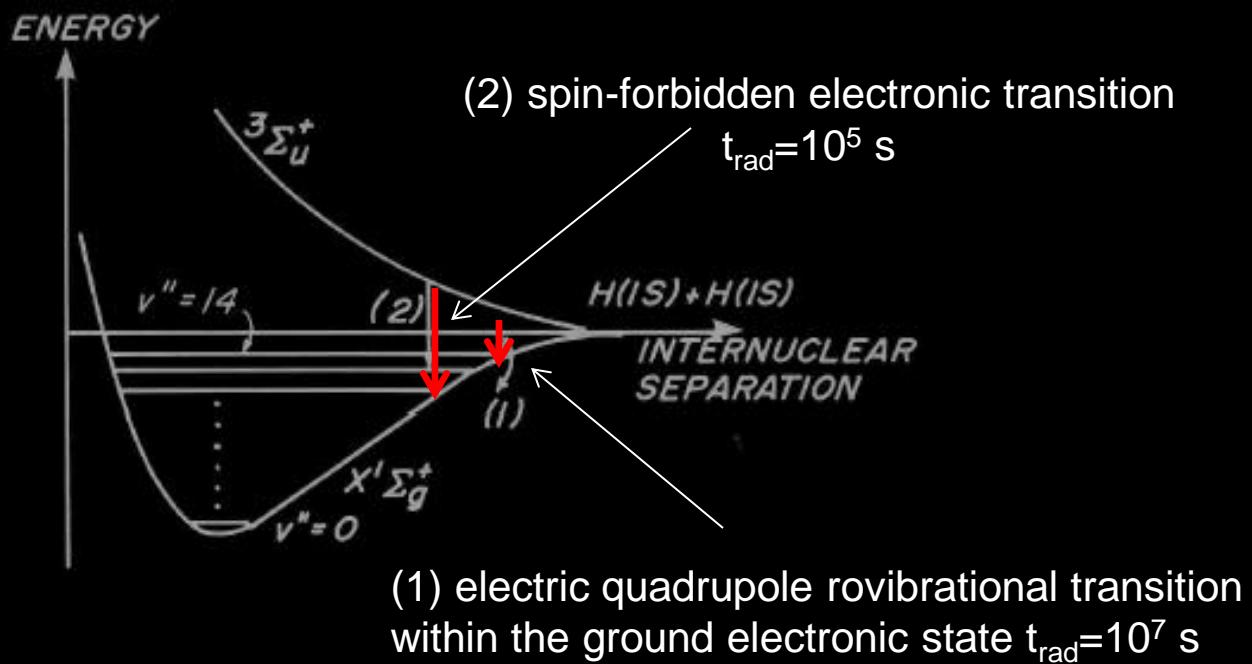
- Generally a slow process:



# Example: $\text{Li} + \text{H} \rightarrow \text{LiH} + h\nu$

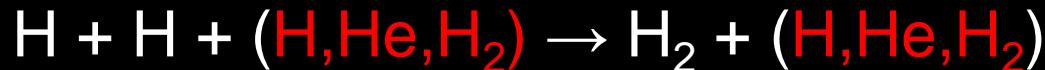


- Needs strong radiative transitions:  
does not work for  $H + H \rightarrow H_2 + h\nu$



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

- third body removes excess energy



rate  $k \approx 5 \times 10^{-29} (\text{T}/\text{°K})^{-1} \text{ cm}^6 \text{ s}^{-1}$  (uncertain)

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

- formation on grains  $\text{H} + \text{H} \rightarrow \text{H}_2$

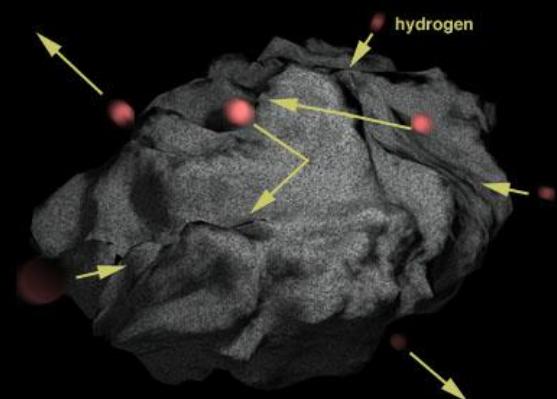
$$\frac{dn_{\text{H}_2}}{dt} = k n_{\text{H}} n_g \quad k = \frac{1}{2} (\pi a^2) v S \gamma$$

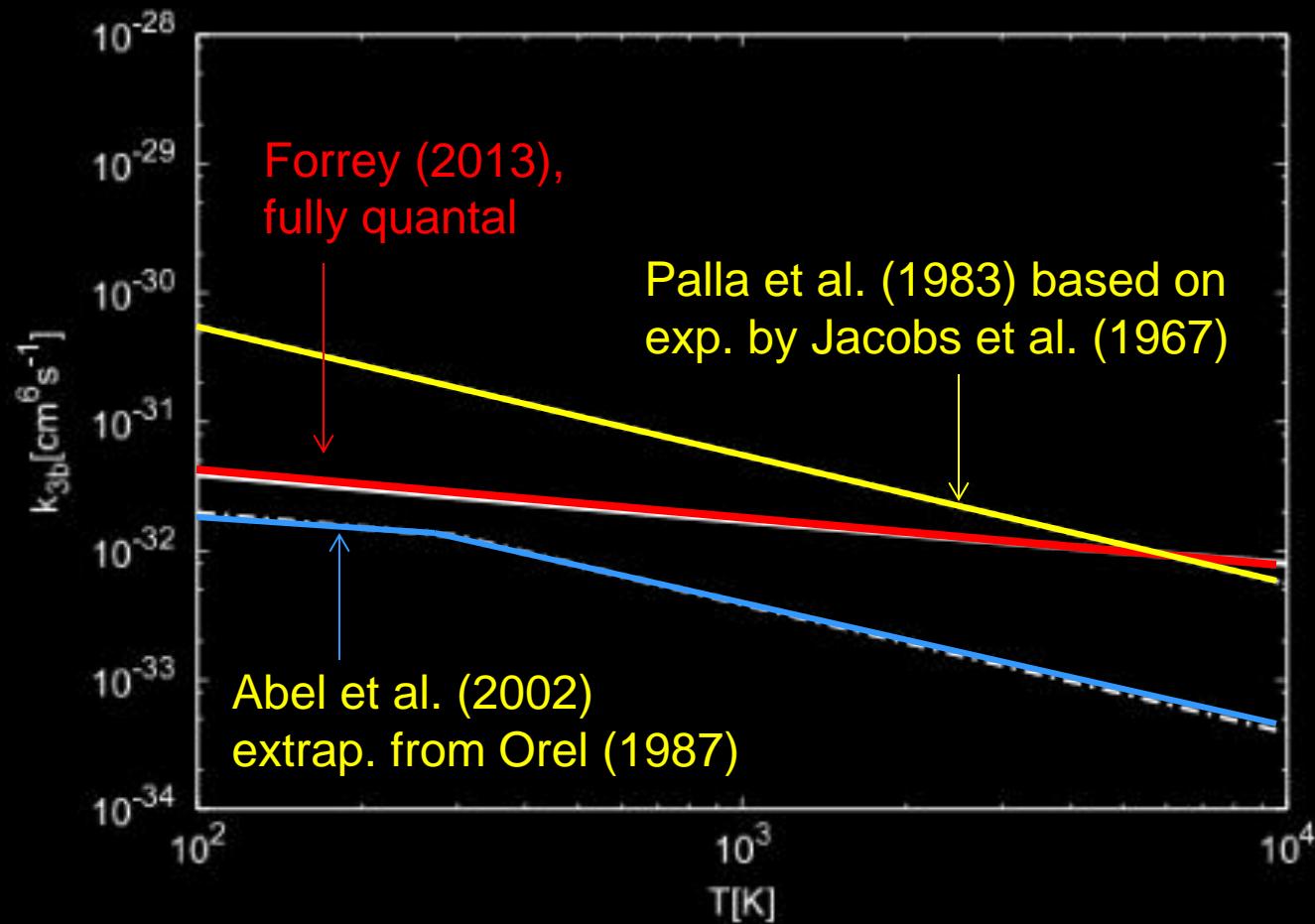
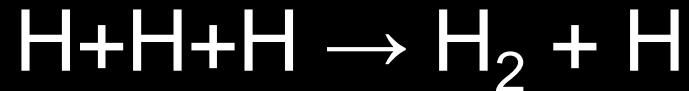
$v$  = speed of H atoms in gas-phase

$a$  = grain radius

$S$  = sticking probability

$\gamma$  = surface reaction probability



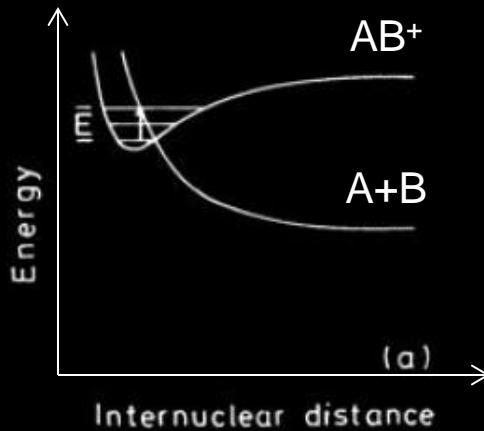


Bovino, Schleicher & Grassi (2014)

### 3. Dissociative recombination

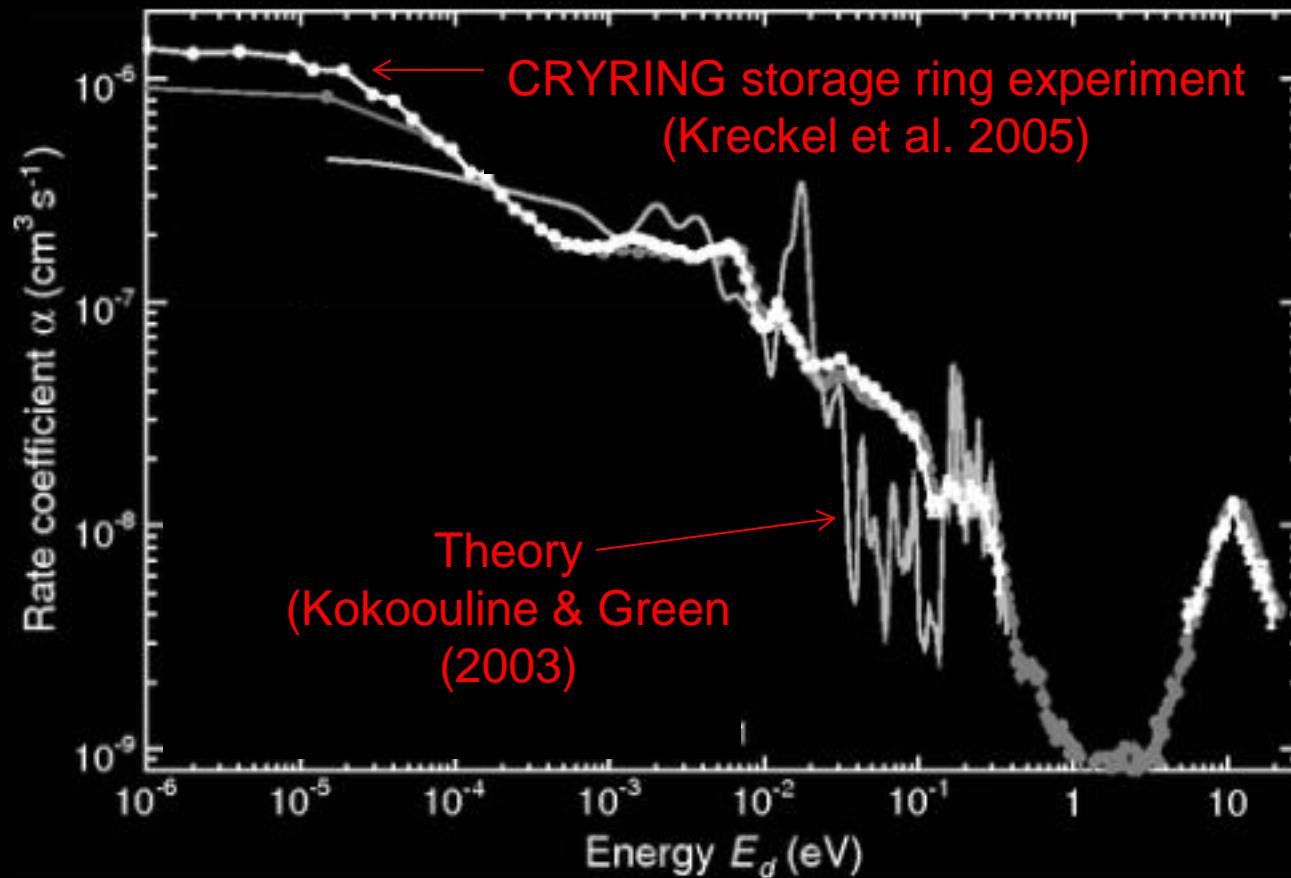
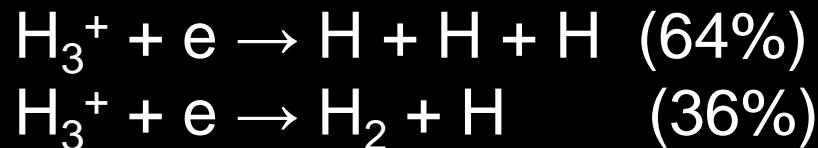


- Electron excites transition of stable  $AB^+$  ion to a repulsive state of  $AB$  molecule which crosses the energy curve of the ion.



- Theoretically complex experimentally difficult
- Branching ratio between various possible products

# Dissociative recombination of $\text{H}_3^+$



# 4. Neutral-neutral reactions



- if  $b < R_1 + R_2$      ``hard-sphere'' model

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

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

- At larger  $b$  attractive Van der Waals forces

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

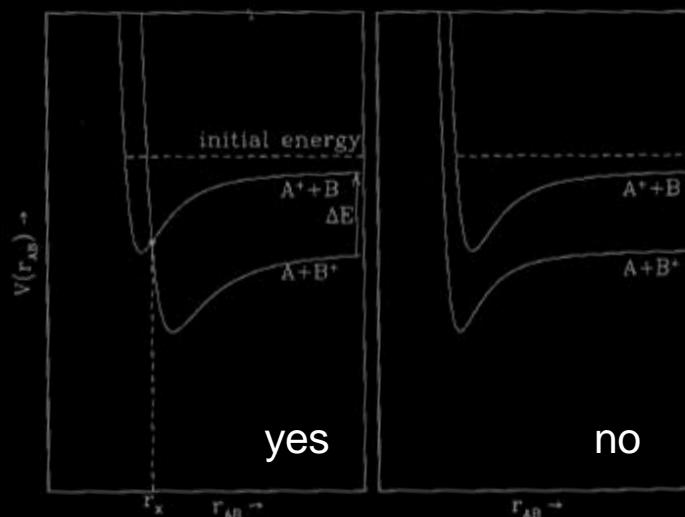
$$\langle \sigma v \rangle = 13.5\pi \left[ \frac{\alpha_n \alpha_n I_{nm}}{\mu_{mn}} \left( \frac{8kT}{\pi\mu_{mn}} \right)^{1/2} \right]^{1/3} \approx 10^{-11} \left( \frac{T}{100 \text{ K}} \right)^{1/6} \text{ cm}^3 \text{ s}^{-1}$$

# 5. Charge transfer reactions



Releases energy  $\Delta E = I(B) - I(A)$

- $t_{\text{collision}} = a_0/v \approx 10^{-13} \text{ s}$  if  $v \approx 0.5 \text{ km s}^{-1}$
- $t_{\text{transfer}} = h/\Delta E \approx 10^{-15} \text{ s}$  if  $\Delta E \approx 1 \text{ eV}$
- Requires level crossing



- Usually fast  $k = 10^{-9} \text{ cm}^3 \text{ s}^{-1}$

# Photoprocesses

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

- $J(\nu)$  is the specific intensity (in  $\text{erg cm}^{-2} \text{ s}^{-1} \text{ ster}^{-1} \text{ Hz}^{-1}$ )
- $\sigma_{\text{ph}}(\nu)$  is the cross section (in  $\text{cm}^{-2}$ )
- $k_{\text{ph}}$  is the rate in  $\text{s}^{-1}$
- 
- Typical photodestruction rates  $10^{-11} - 10^{-9} \text{ s}^{-1}$  (for ISRF)

→ see talk by S. Bovino

# Chemistry in the Early Universe

Unfavorable environment for chemical enrichment:

- rapid expansion
  - strong radiation field (CMB)
  - gas chemically inert ( $H=0.924$ ,  $He=0.076$ ,  $D=2\times 10^{-5}$ ,  $Li=4\times 10^{-10}$ )
  - 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 “ “:  $LiH$ ,  $LiH^+$ ,  $LiHe^+$

COBE

WMAP

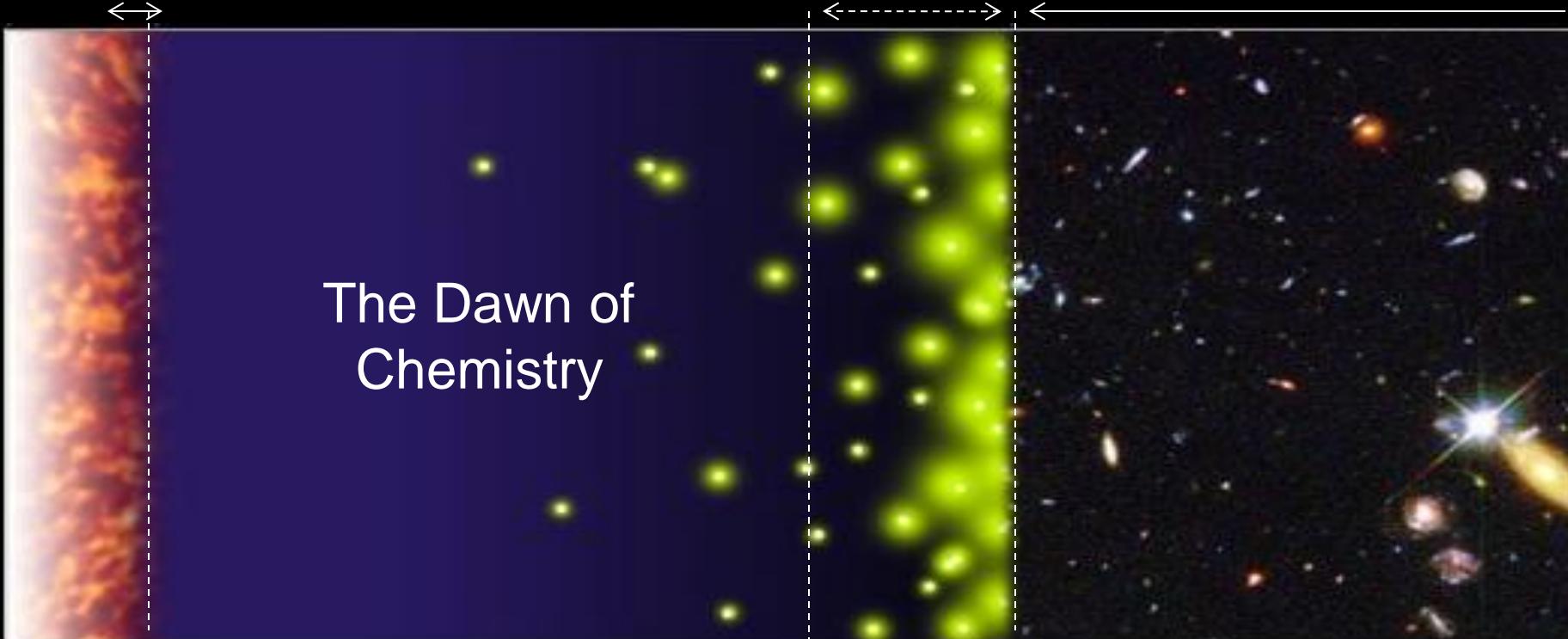
PLANCK

LOFAR

SKA

HST

The Dawn of  
Chemistry



CMB  
 $z \sim 1000$

First stars  
 $z \sim 10$

Reionization completed  
 $z \sim 7$

Now

redshift



400 Myr after BB

time



# The cosmological background

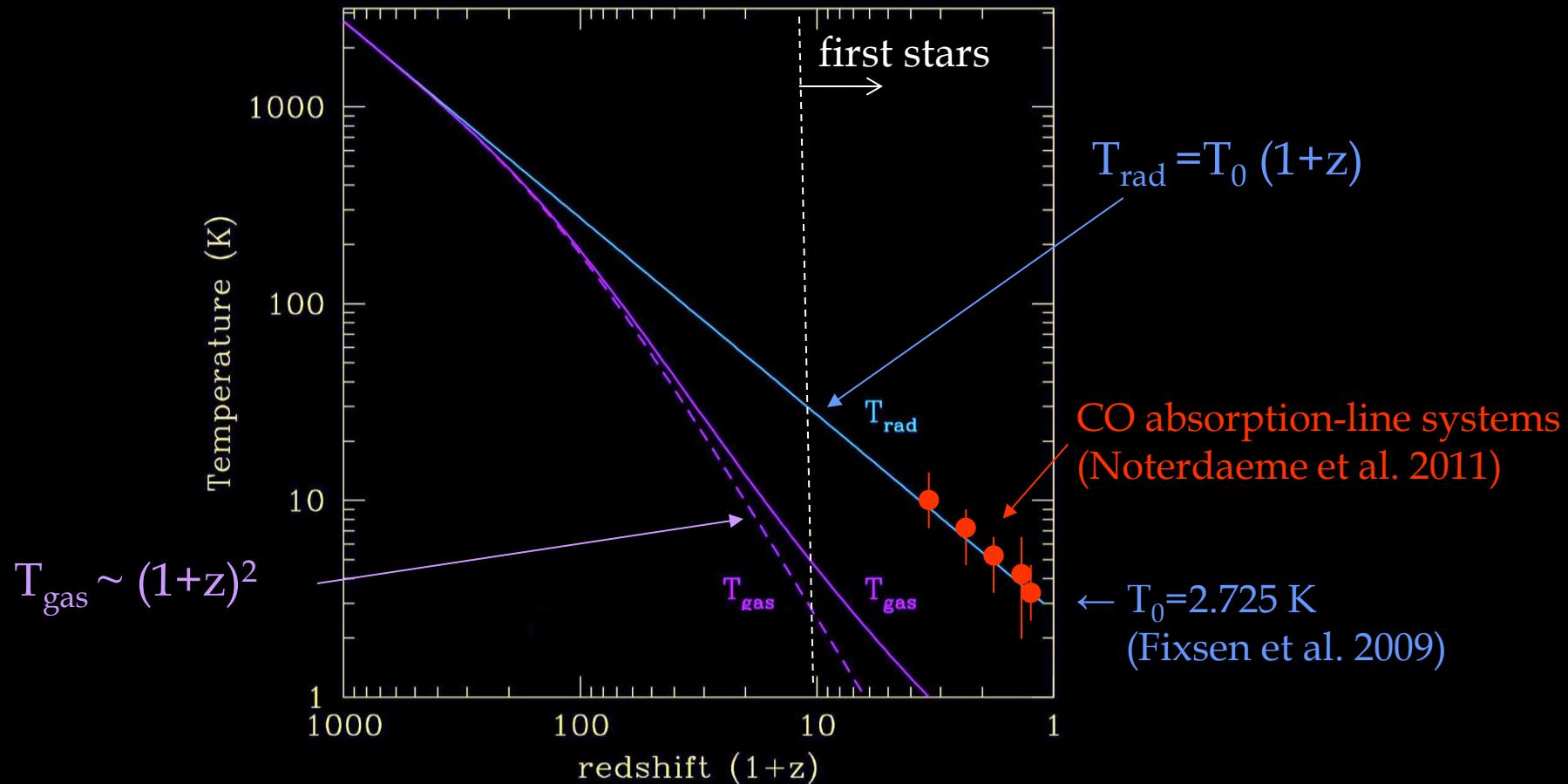
the Dark Ages:

- start: after H recombination ( $z \sim 1000$ ,  $t \sim 400,000$  yr)
- end: formation of the first stars ( $z \sim 10$ ,  $t \sim 400$  million yr)
- Baryon density  $n \approx 10^{-5} \Omega_b h^2 (1+z)^3 \text{ cm}^{-3}$
- Expansion rate  $dt/dz = -10^{10} \text{ yr}/h(1+z)\sqrt{\Omega_\Lambda + (1+z)^3\Omega_m}$
- Radiation  $T_{\text{rad}} = T_0(1+z)$
- Cosmological parameters ( $\Lambda$ CDM)  $h, \Omega_b, \Omega_m, \Omega_\Lambda, T_0$

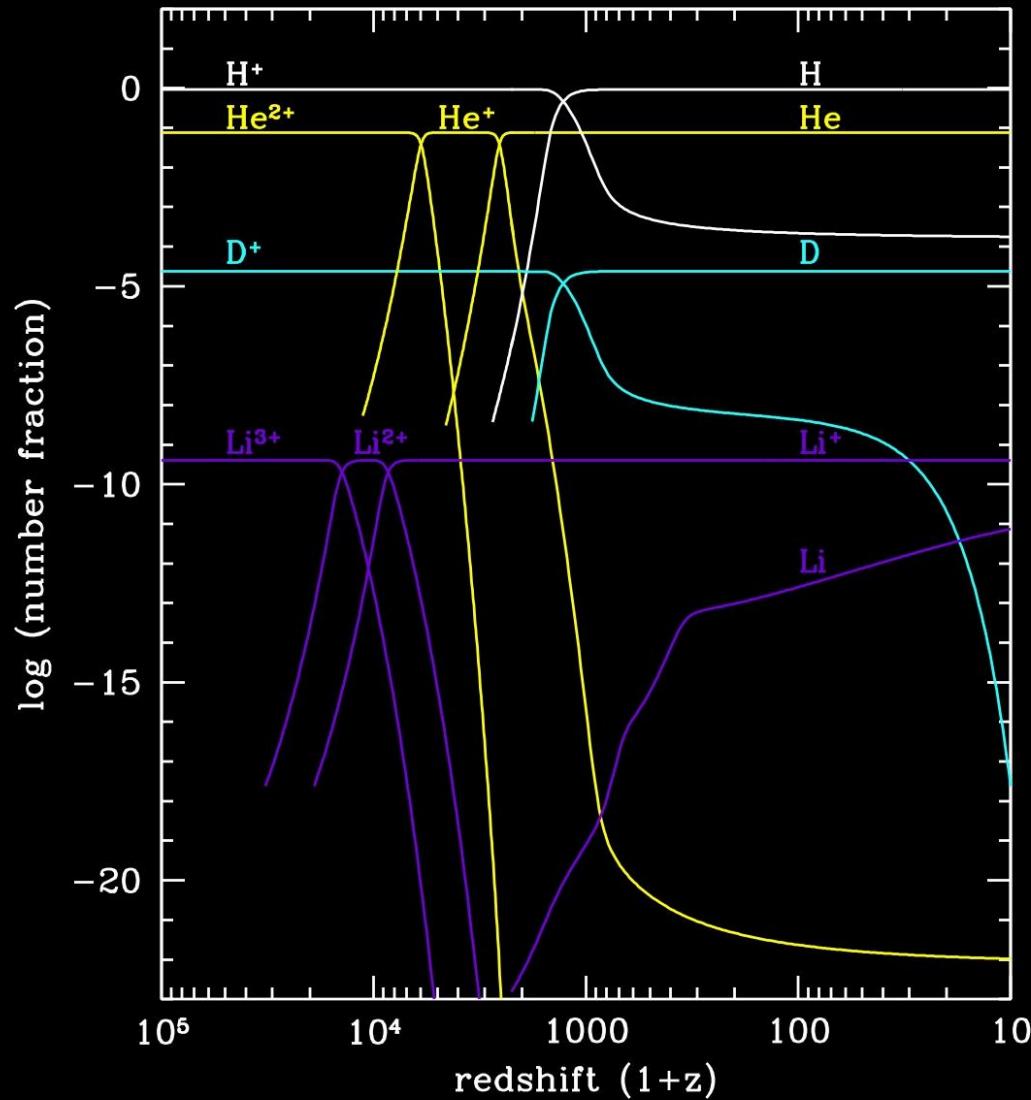
$$h = 0.704 \quad \Omega_b = 0.0455 \quad \Omega_m = 0.273 \quad \Omega_\Lambda = 0.727 \quad T_0 = 2.725 \text{ K}$$

Bennett et al. (2012) WMAP 9-yr, Fixsen (2009)

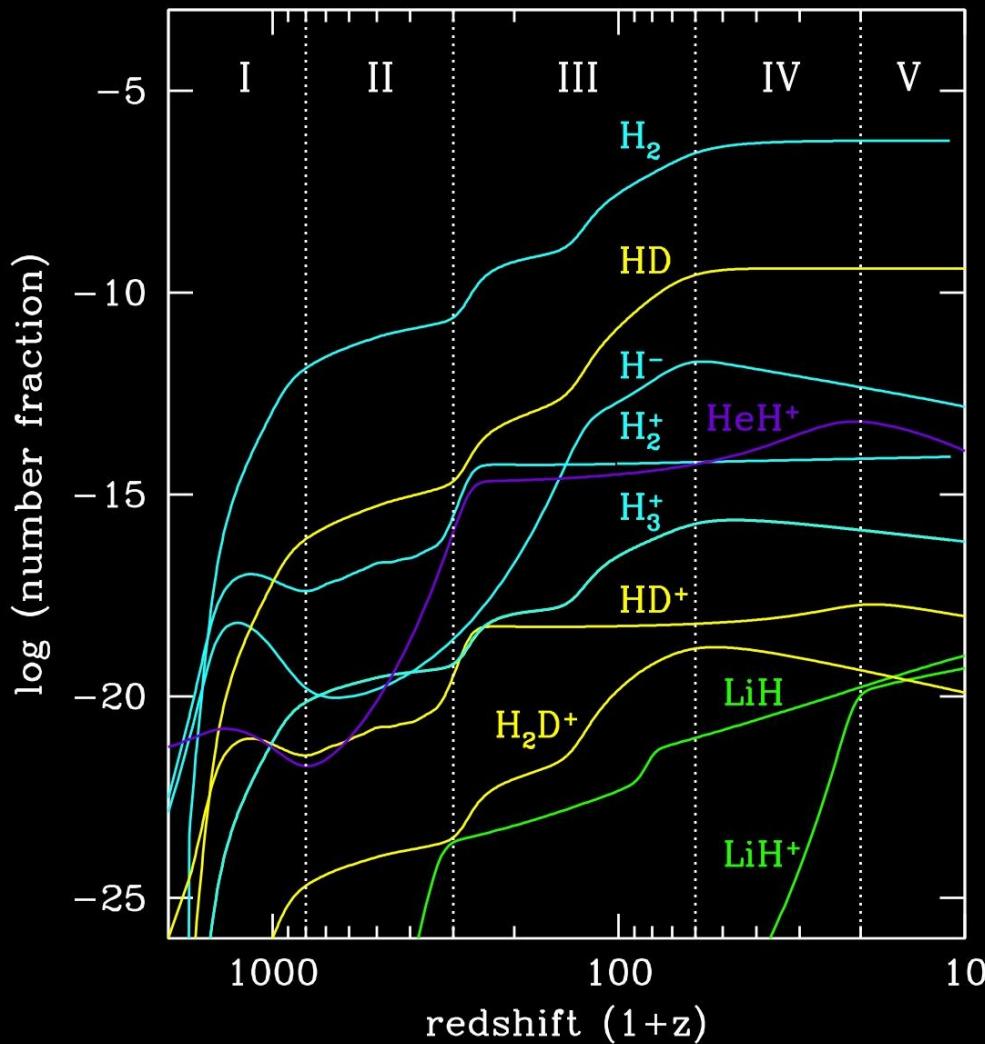
# Temperature of matter and radiation



# Ions and atoms in the Early Universe



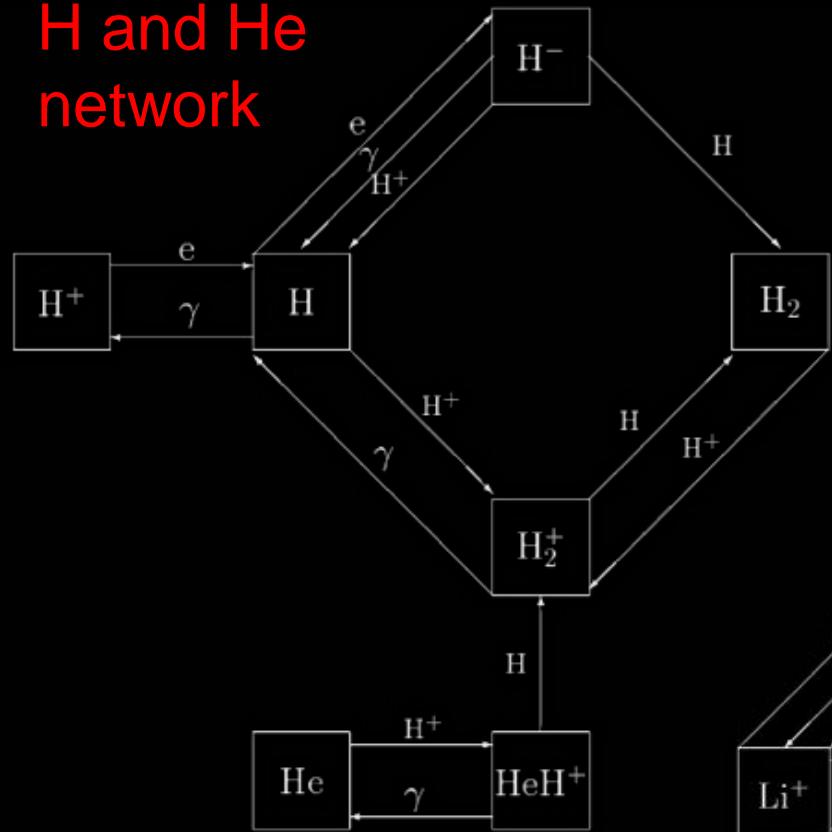
# Molecules in the early Universe



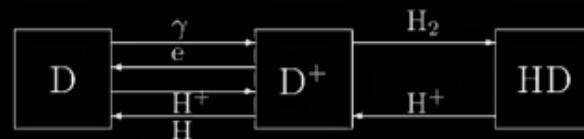
Galli & Palla (2013) Ann. Rev. Astron. Astrophys., Vol. 51, 163

# Primordial chemistry networks (simplified)

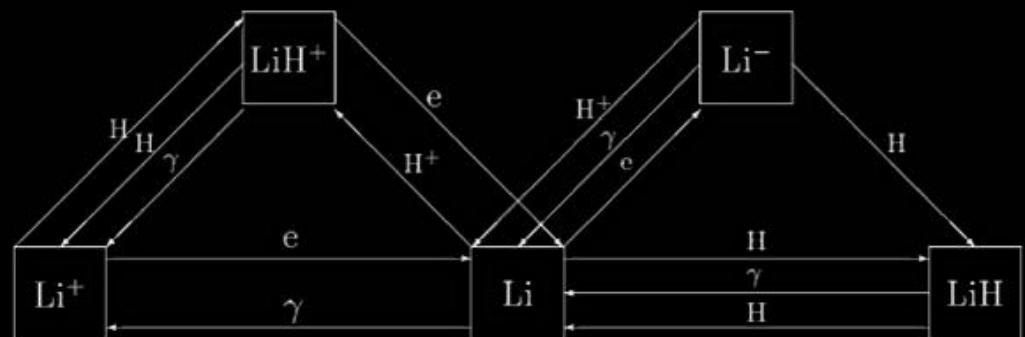
H and He  
network



D network



Li network



# Recent advances in primordial chemistry

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

- $\text{HeH}^+ + \text{H} \rightarrow \text{He} + \text{H}_2^+$
- $\text{LiH} + \text{H} \rightarrow \text{Li} + \text{H}_2$
- $\text{LiH}^+ + \text{H} \rightarrow \text{Li}^+ + \text{H}_2$
- $\text{LiH} + \text{H}^+ \rightarrow \text{Li} + \text{H}_2^+$
- $\text{LiHe}^+ + \text{H} \rightarrow \text{LiH}^+ + \text{He}$
- $\text{Li}^+ + \text{He} \rightarrow \text{LiHe}^+ + \gamma$
- $\text{LiHe}^+ + \gamma \rightarrow \text{Li}^+ + \text{He}$
- $\text{LiHe}^+ + \text{e} \rightarrow \text{Li} + \text{He}$  (with Čurik)

Recently measured in the lab:

- $\text{H}^- + \text{H} \rightarrow \text{H}_2 + \text{e}$  ass. det. (Columbia Astroph. Lab., Kreckel et al. 2010)
- $\text{H}_3^+ + \text{e} \rightarrow 3\text{H}, \text{ H}_2 + \text{H}$  diss. rec. (CRYRING, TSR, McCall et al. 2004)

In progress:

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

Still uncertain:

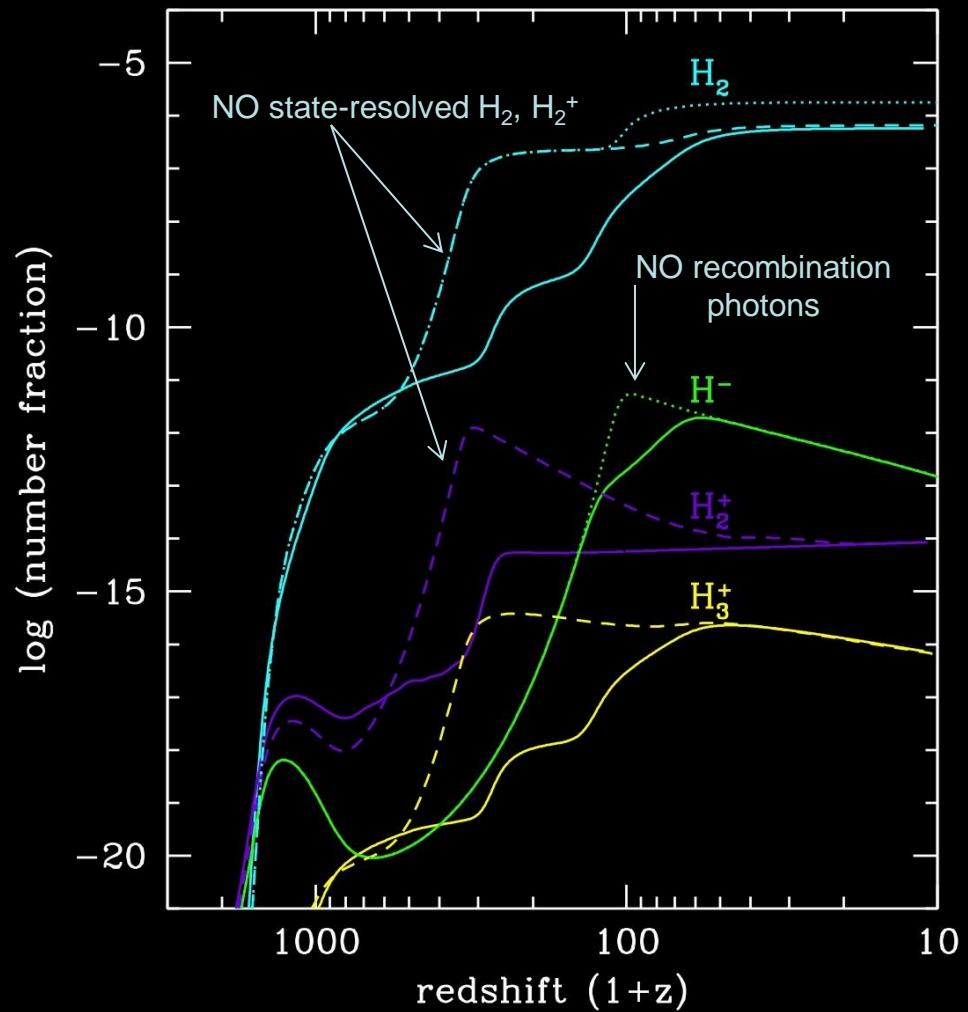
- $\text{H} + \text{H} + \text{H} \rightarrow \text{H}_2 + \text{H}$  three-body reaction (Bovino, Schleicher & Grassi 2014)

# Hydrogen chemistry

$\text{H}_2^+$  channel



$\text{H}^-$  channel



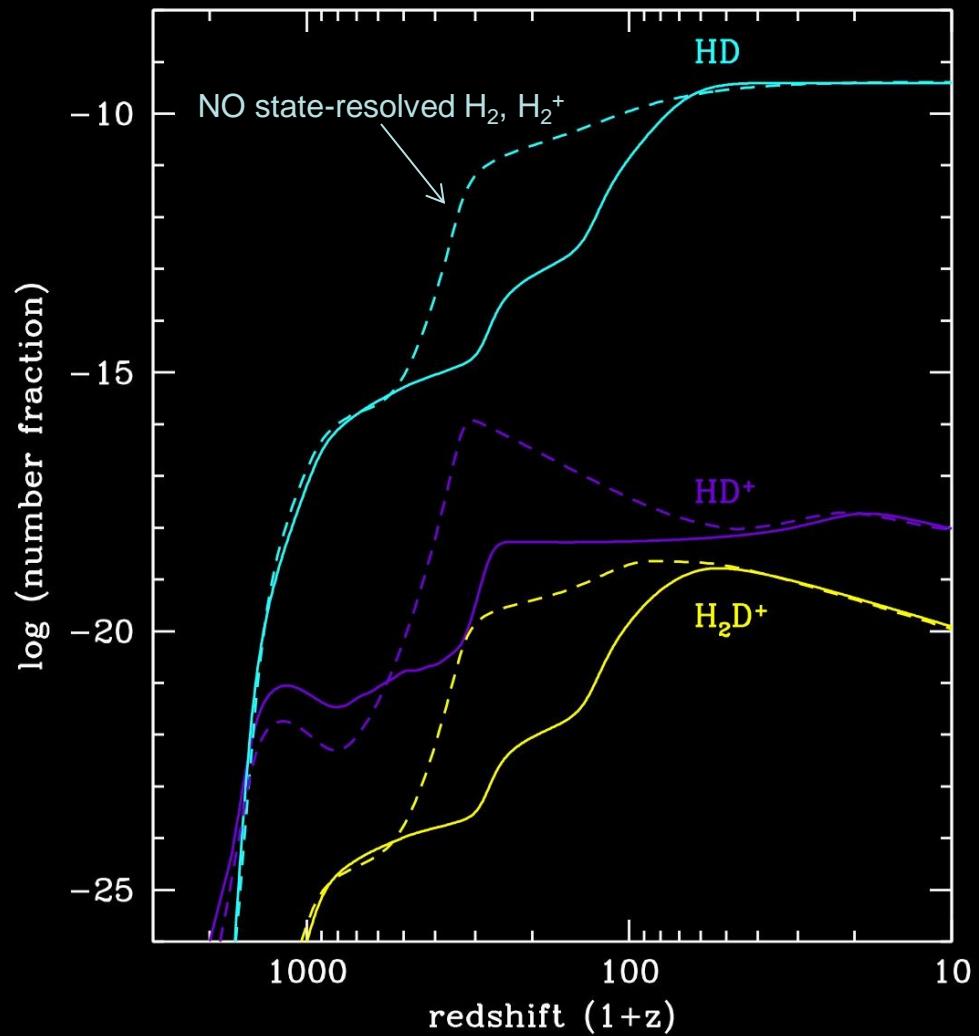
Galli & Palla (1998), Coppola et al. (2011)

# Deuterium chemistry

Formation of HD:



Destruction of HD:



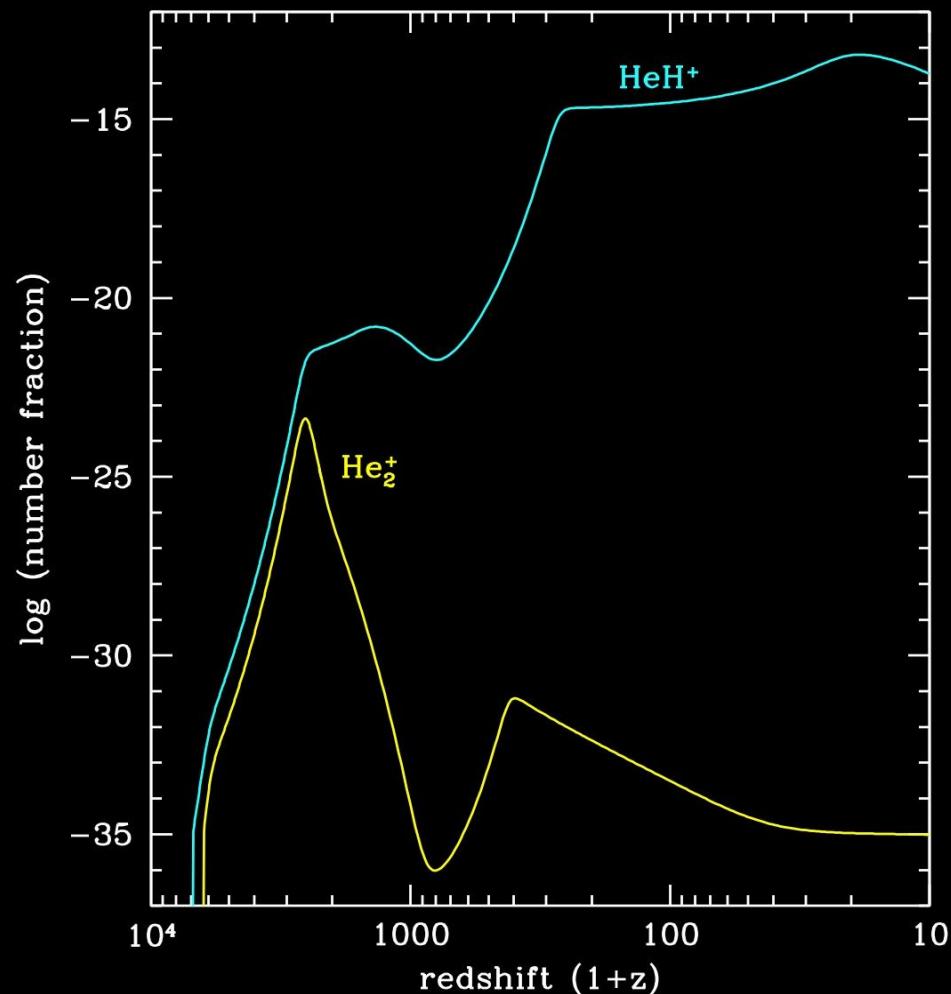
Stancil et al. (1998), Galli & Palla (2002)

# Helium chemistry

Formation:



Destruction:



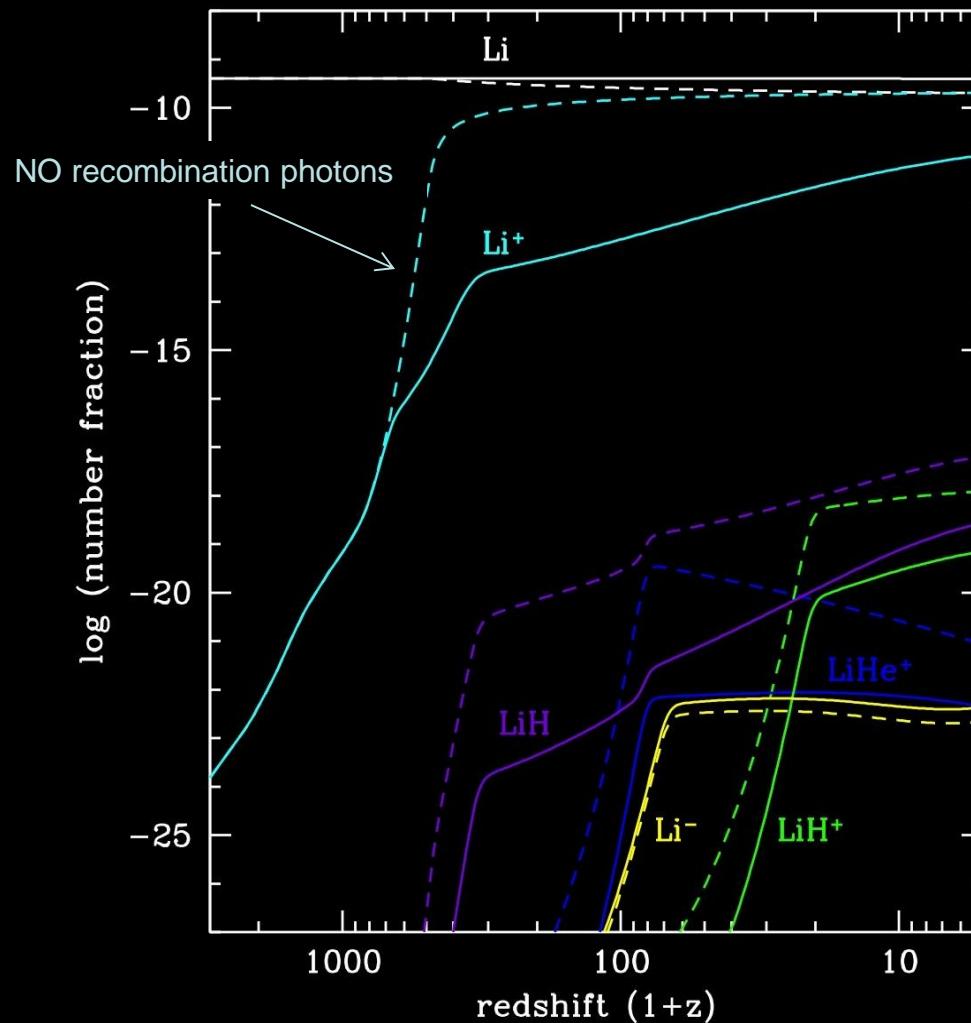
Galli & Palla (1998), Bovino et al. (2011)

# Lithium chemistry

Formation of LiH:



Destruction of LiH:



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

# KROME!

