

# **Class 4: Chemistry and thermodynamics**

**ASTR 4008 / 8008, Semester 2, 2022**

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# Outline

- Chemistry
  - Hydrogen
  - Carbon / oxygen
- Thermodynamics
  - Heating processes
  - Cooling process
  - Temperature and isothermality

# H<sub>2</sub> molecules

## Background

- Hydrogen can form H<sub>2</sub> molecules, binding energy 4.5 eV
- In most of the ISM, hydrogen is NOT in this form, and is instead free atomic H; this is the only form that produces the 21 cm line
- However, star formation seems to occur pretty much exclusively in gas where most of the hydrogen is in the form of H<sub>2</sub>
- Our goal is to understand why this is, and what physical processes are responsible for the chemical transition between atomic H and H<sub>2</sub>

# The two-hydrogen system

## Proof that even the simplest things are incredibly complicated

- In order for an H<sub>2</sub> molecule to form from two free H atoms, some process must remove the 4.5 eV binding energy
- At the low densities of the ISM, 3-body reactions are very unlikely, so radiation is a natural mechanism:  $X + Y \rightarrow XY + h\nu$
- However, this process is greatly suppressed for H<sub>2</sub> due to symmetry, because the 2H system is symmetric so the electric dipole operator almost vanishes; symmetry broken only by spin-orbit coupling, effect at order  $\alpha^4 \sim 10^{-9}$
- Instead, formation of H<sub>2</sub> is mostly by surface catalysis on dust grains; excess energy mostly goes into heating the grain

# The H<sub>2</sub> formation rate

## Steps to form a molecule

- Formation requires: (1) sticking, (2) migration, (3) chemical binding, (4) ejection
- Rate can be written

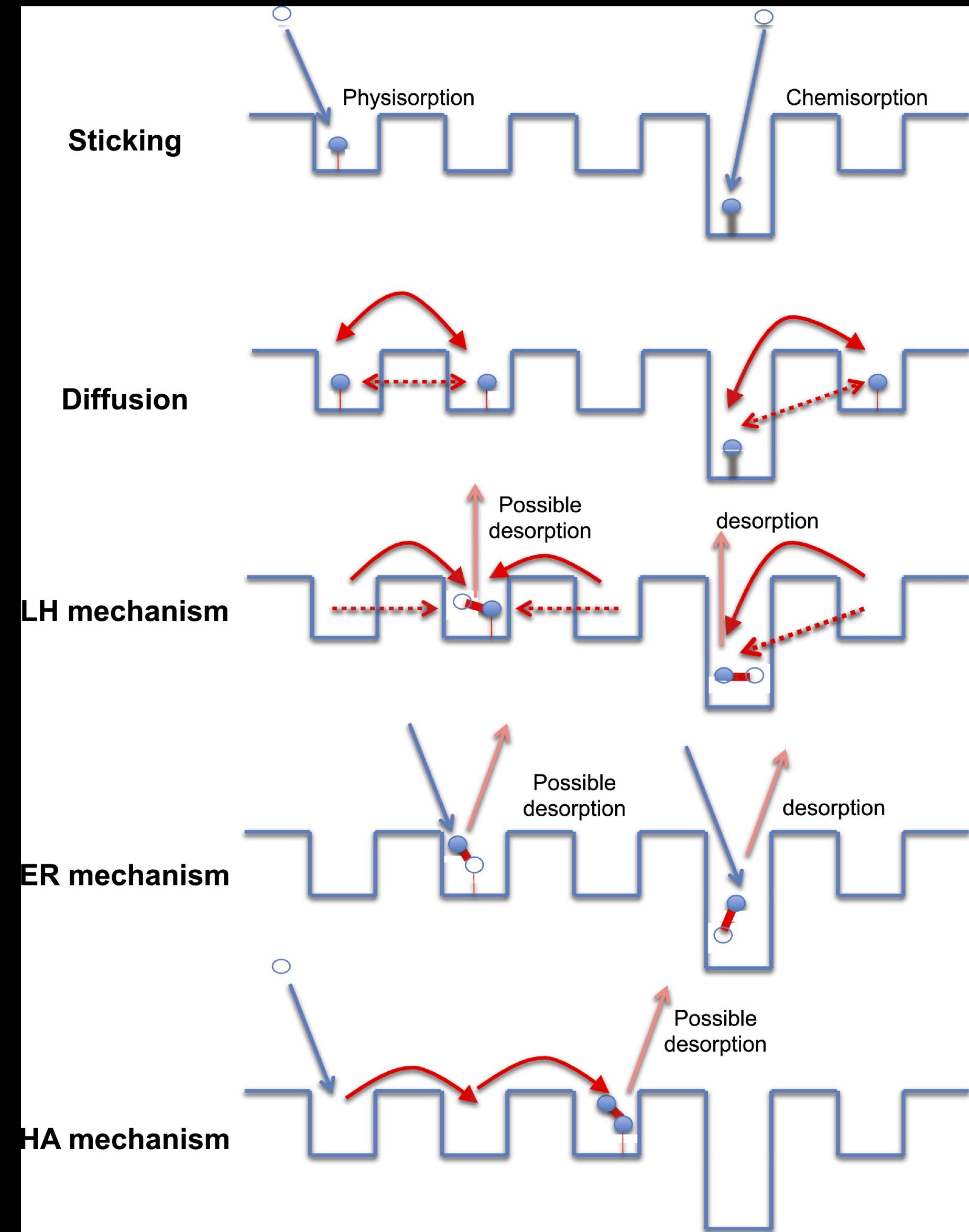
$$\frac{1}{2} S(T, T_{\text{gr}}) \eta(T_{\text{gr}}) n_{\text{gr}} n_{\text{H}} \sigma_{\text{gr}} v_{\text{H}}$$

Sticking probability  $\uparrow$   $S(T, T_{\text{gr}})$   
 Migration probability  $\uparrow$   $\eta(T_{\text{gr}})$   
 Grain density  $\uparrow$   $n_{\text{gr}}$   
 H density  $\uparrow$   $n_{\text{H}}$   
 Grain cross section  $\uparrow$   $\sigma_{\text{gr}}$   
 H thermal speed  $\uparrow$   $v_{\text{H}}$

- Generally simplified to

$$\text{Rate} = \mathcal{R} n n_{\text{H}}$$

Rate coefficient,  $\approx 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  in Milky Way  $\uparrow$   $\mathcal{R}$   
 Number density of H nuclei, regardless of chemical state  $\uparrow$   $n$



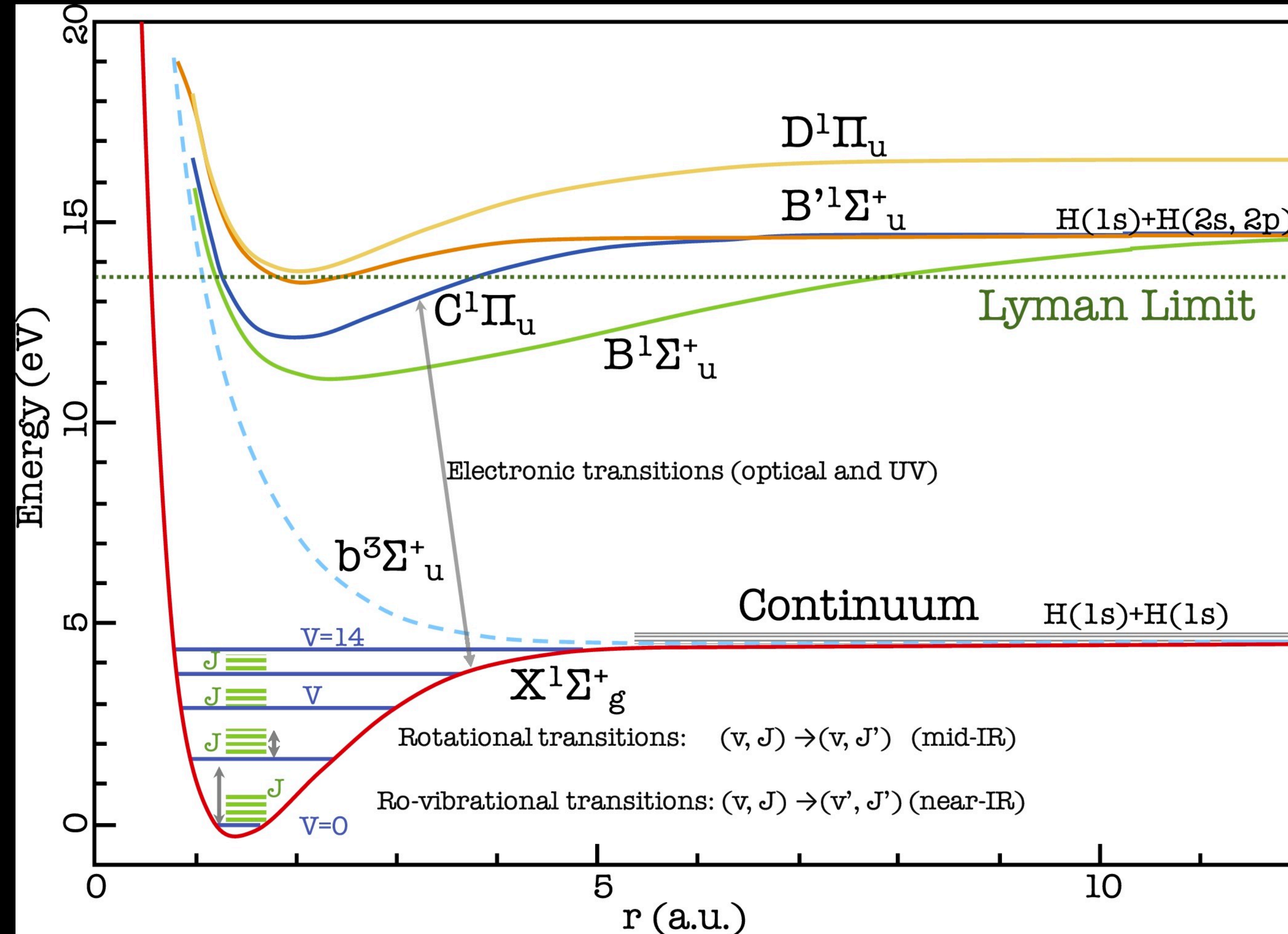
Wakelam+ 2017 review

# H<sub>2</sub> destruction mechanism

- Main destruction mechanism is by radiation, but H<sub>2</sub> can't absorb 4.5 eV photons for same reason it can't emit them
- However, higher energy photons can excite into a higher, non-symmetric electronic state, which has higher energy than ground state
- First two excited electronic states have vibrational and rotational states with energies < 13.6 eV above ground, can be excited by photons with energies from 11.2 - 13.6 eV; hot stars produce lots of these
- Since there are many (v,J) transitions form a band: Lyman-Werner band
- Once excited, H<sub>2</sub> molecule can then de-excite into unbound electronic state; dissociation probability ~10-15%, depending on exactly which excited state molecule is in



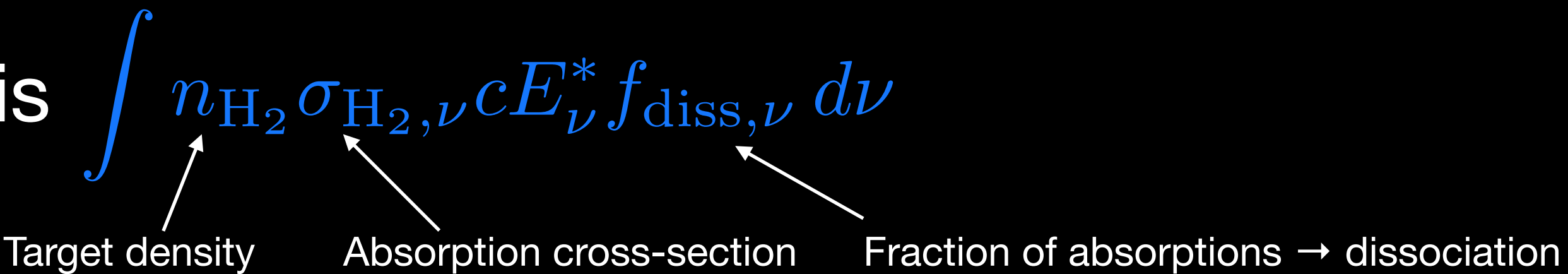
# Level structure of H<sub>2</sub> molecule



Wakelam+ 2017 review

# Formation-destruction balance

- Let  $E_\nu^*$  be number density of LW-band photons of frequency  $\nu$

- Destruction rate is  $\int n_{\text{H}_2} \sigma_{\text{H}_2, \nu} c E_\nu^* f_{\text{diss}, \nu} d\nu$   


Target density      Absorption cross-section      Fraction of absorptions → dissociation

- Since  $f_{\text{diss}, \nu} \sim \text{constant}$ , chemical balance set by

$$n_{\text{H}} n_{\text{R}} \approx f_{\text{diss}} \int n_{\text{H}_2} \sigma_{\text{H}_2, \nu} c E_\nu^* d\nu$$

- Note: LHS scales as  $n^2$ , RHS as  $n$ , so gas will tend to be more  $\text{H}_2$ -dominated at high density



# Simple slab model

for  $\text{H} \rightarrow \text{H}_2$  transition

- Photon flux incident on surface of slab; photon conservation:

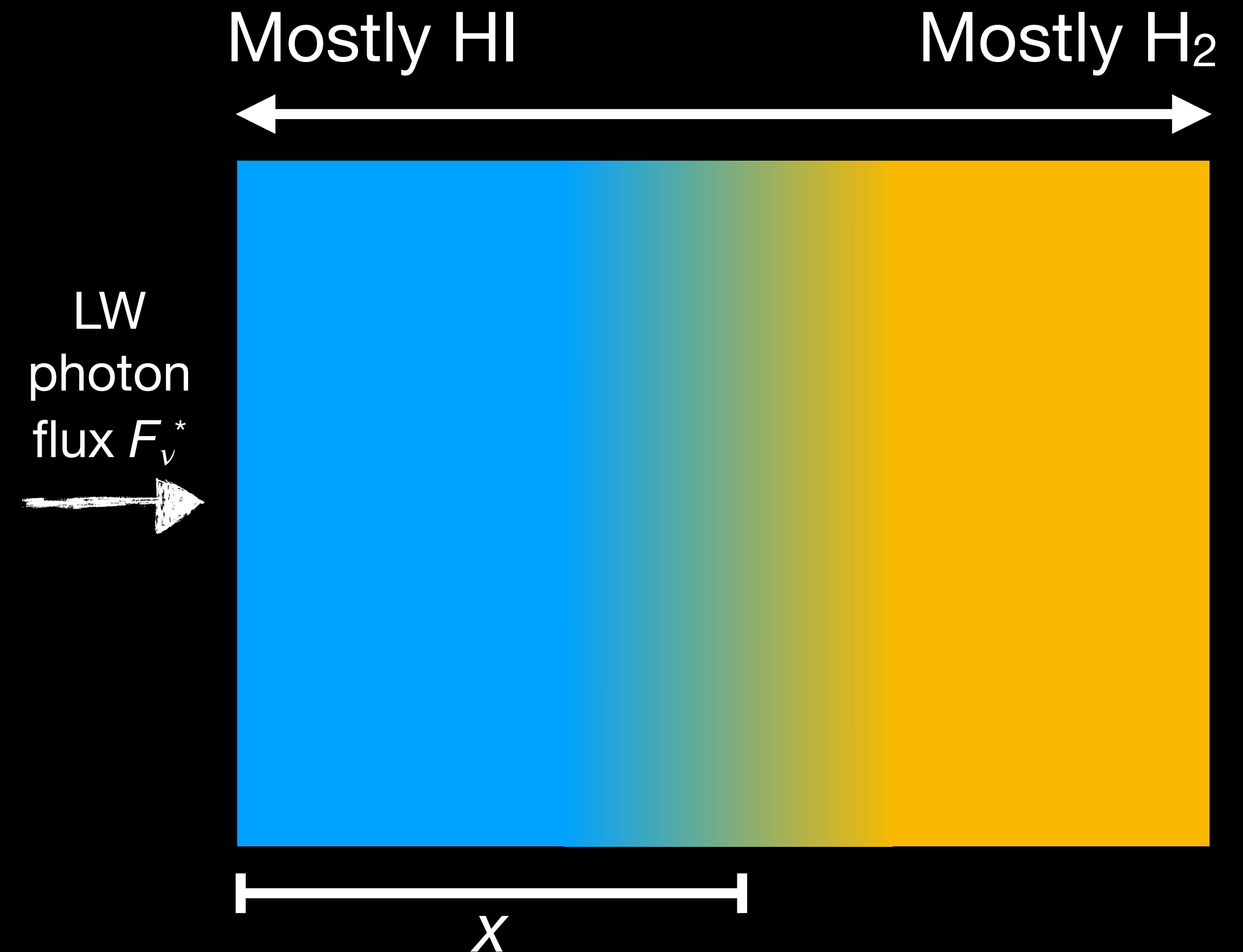
$$\frac{dF_\nu^*}{dx} = c \frac{dE_\nu^*}{dx} = -n_{\text{H}_2} \sigma_{\text{H}_2, \nu} c E_\nu^*$$

- Integrate over  $\nu$ , divide by  $c$ :

$$\frac{dE_*}{dx} = - \int n_{\text{H}_2} \sigma_{\text{H}_2, \nu} E_\nu^* d\nu$$

- Use chemical balance to rewrite RHS:

$$\frac{dE_*}{dx} = - \frac{n_{\text{H}} n \mathcal{R}}{c f_{\text{diss}}}$$



# Slab model solution

- Simplify by approximating  $\text{H} \rightarrow \text{H}_2$  transition as sharp, so  $n \approx n_{\text{H}}$  in zone dominated by H
- In this case, we have analytic solution  $E^*(x) = E_0^* - \frac{n^2 \mathcal{R}}{c f_{\text{diss}}} x$
- Transition is located a point where  $E^*(x) \approx 0$ ; column through this region is
$$N_{\text{H}} = n x_{E^*=0} = \frac{c f_{\text{diss}} E_0^*}{n \mathcal{R}}$$
- LW photon density in Solar neighbourhood  $E_0^* \approx 7.5 \times 10^{-4} \text{ cm}^{-3}$ ,  $n \approx 100 \text{ cm}^{-3} \Rightarrow N_{\text{H}} = 7.5 \times 10^{20} \text{ cm}^{-3}$ ,  $\Sigma \approx 10 \text{ M}_{\odot} \text{ pc}^{-2}$
- Explains why MW is mostly atomic H: mean surface density is at or below this value, so most is in “atomic shielding zone” rather than “molecular zone”

# C / O chemistry

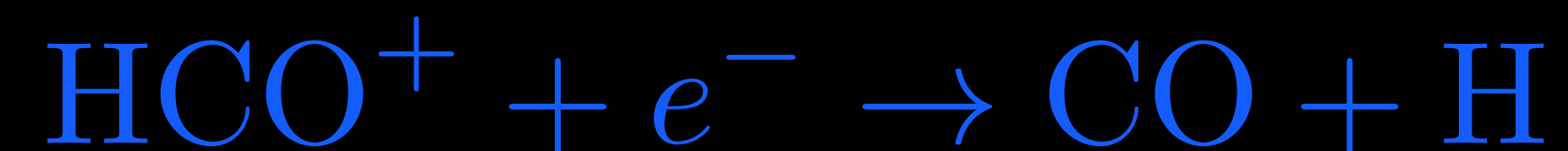
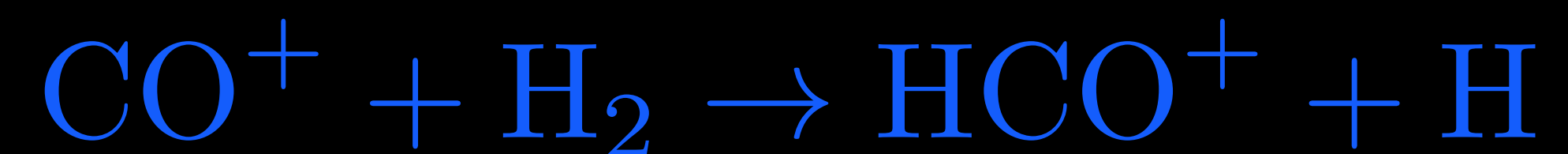
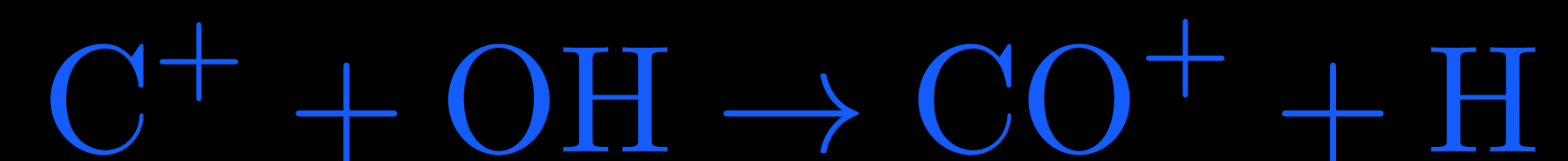
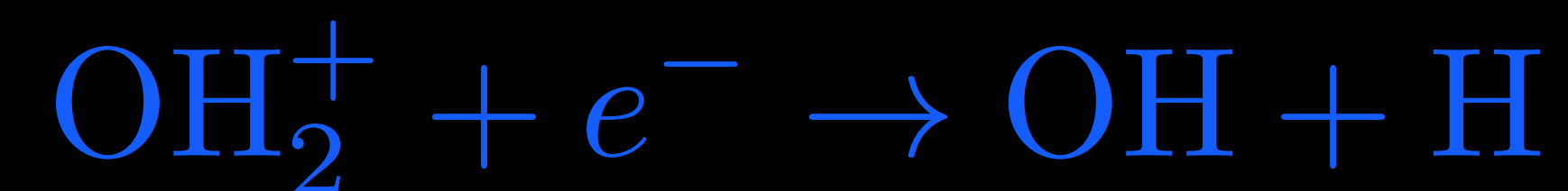
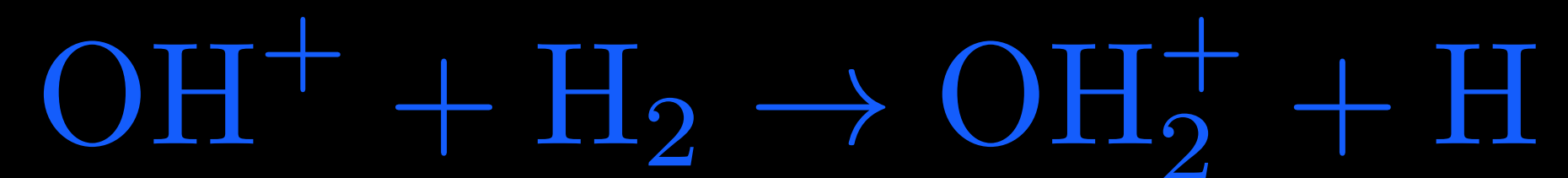
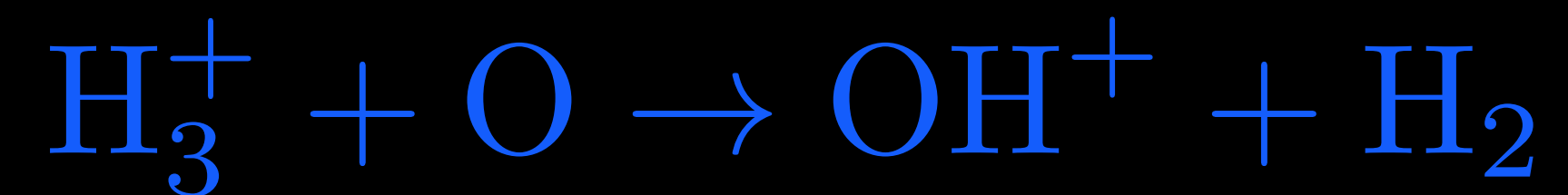
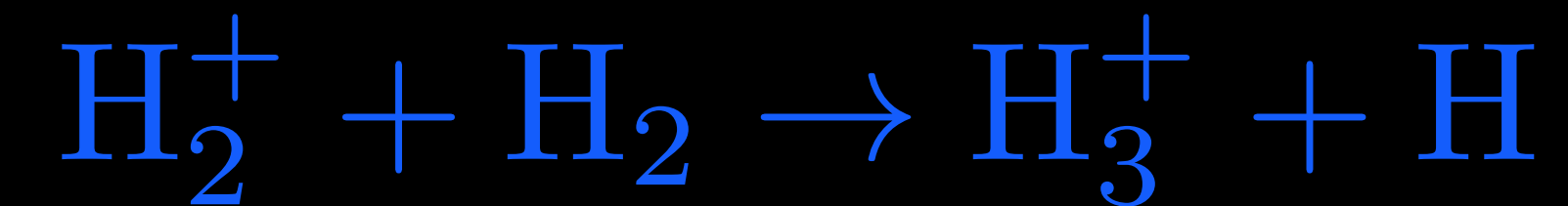
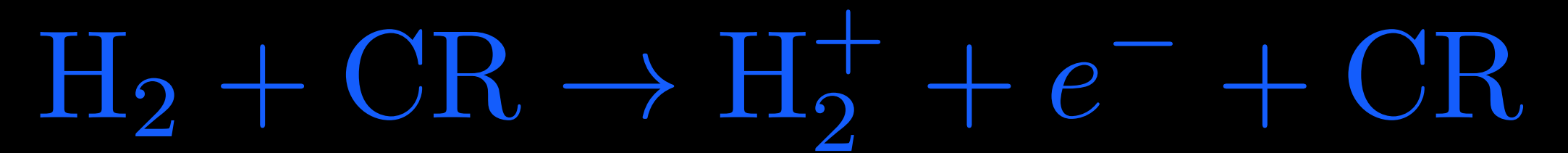
The next two most abundant elements (that have chemistry, i.e., not He)

- Outside molecular clouds, carbon is mostly  $C^+$ , oxygen mostly O (class question to think about: why?)
- Inside molecular clouds, they can form CO
- Formation process very different from  $H_2$  — not symmetric so reactions can take place in gas phase
- However, direct also not simple  $C + O$  collision; instead, key process is ion-neutral collisions (class question to think about: why?)

# Reaction chain to CO

## One of a few possible

- Requires CR to create and initiate reaction chain
- Uses H<sub>2</sub> as a catalyst — part of the reason CO only exists where H<sub>2</sub> does
- All steps are ion-neutral or ion-ion reactions, so proceed ok at low temperature



# CO destruction

## and formation-destruction balance

- Destruction is by photodissociation — equivalent to LW band for CO
- Formation-destruction balance more complicated than for H<sub>2</sub>, because CO can't self-shield from UV (not abundant enough); instead, get shielded by dust and by cross-shielding by overlapping lines of H<sub>2</sub>
- Bottom line: transition from C<sup>+</sup> to CO as dominant carbon species occurs at dust extinction of 1 - 2 mag in V band; equivalent to  $\sim 30 M_{\odot} \text{ pc}^{-2}$  at Milky Way dust abundance
- Note: for low-dust galaxies, most molecular material may be in regions where H is mostly in H<sub>2</sub>, but C is still C<sup>+</sup> or CO: hard to observe!

# Heating processes

## Photoelectric effect

- In atomic ISM, main heating process is the grain photoelectric effect: UV photons ( $\sim 8 - 13.6$  eV) knock fast electrons off dust grains, which then thermalise and share their energy

- Heat rate per H nucleus approximately

$$\Gamma_{\text{PE}} \approx 4.0 \times 10^{-26} \chi_{\text{FUV}} Z'_d e^{-\tau_d} \text{ erg s}^{-1}$$

Dust abundance (normalised to local)      Optical depth to FUV photons  
FUV radiation field strength (normalised to local)

- In regions where CO forms, optical depth in visible light is at least  $\sim 1-2$ ; opacities a factor of  $\sim 5$  higher in FUV, so optical depth  $\gtrsim 5$
- This greatly suppresses FUV heating; typical rates  $\lesssim 10^{-28}$  erg s $^{-1}$ , small enough to be unimportant



# Heating processes

## Cosmic rays

- CRs can penetrate much more material than photons, so CR ionisation occurs even in dusty gas where photoelectric heating shuts off
- When CR hits H<sub>2</sub> (same process that kicks off CO formation), ejected electron has ~30-40 eV energy — heating source.
- Actual energy delivered is smaller, because energy not shared efficiently; much lost to secondary ionisations followed by radiative recombinations
- Main channels of heating: initiating exothermic chemical reactions, collisional dissociation of H<sub>2</sub>, excitation of H<sub>2</sub> followed by collisional de-excitation
- Net heating rate for MW CR flux:  $\Gamma_{\text{CR}} \sim 2 \times 10^{-27} \text{ erg s}^{-1} \text{ per H}$

# Cooling processes

## General considerations

- Diffuse gas is not an efficient radiator; generally transparent except at resonant frequencies
- Solid dust grains are efficient, but limited in their ability to cool gas by rate of gas-grain collisions; grains only cool gas if the density is  $\gtrsim \text{few} \times 10^5 \text{ cm}^{-3}$
- At lower density, main cooling process is collisionally-excited line emission: inelastic collision between two particles, resulting in one becoming excited and then radiatively de-exciting
- At molecular gas temperatures,  $\text{H}_2$  cannot radiate, so main coolant is CO (or  $\text{C}^+$  in regions where it dominates — homework problem)

# CO cooling

## The competition between excitation and opacity

- CO cooling is a competition:
  - low  $J$  levels easily excited, but photons mostly don't escape: a  $J = 1 \rightarrow 0$  can be absorbed by any molecule in the  $J = 0$  state, and there are lots of them
  - high  $J$  levels hard to excite, because  $E/kT$  is big, but there are few molecules capable of stopping the resulting photons from escaping
- Net effect of this competition is that cooling winds up being mostly dominated by the lowest- $J$  level for which most photons escape; usually  $J = 3 - 5$ , depending on cloud properties
- Can estimate cooling rate assuming 100% escape but LTE for this level (warning: this is *very* rough; doing better requires numerical approach)

# CO cooling rate

## CO as a quantum rotor

- CO is a quantum rotor; rotational states of a quantum rotor have energy and Einstein A:

$$E_J = hBJ(J+1) \quad A_{J,J-1} = \frac{512\pi^4 B^3 \mu^2}{3hc^3} \frac{J^4}{2J+1}$$

Rotation constant (set by moment of inertia);  $B = 57$  GHz for CO

Electric dipole moment;  $\mu = 0.112$  Debye for CO

- Total cooling rate per H = (# CO molecules per H) x (fraction of CO molecules in relevant  $J$  state) x (rate of photon emission) x (energy per photon):

$$\Lambda_{J,J-1} = x_{\text{em}} \frac{(2J+1)e^{-E_J/k_B T}}{Z(T)} A_{J,J-1} (E_J - E_{J-1})$$

Emitter abundance;  $x_{\text{em}} \approx 10^{-4}$  for CO

Degeneracy

Partition function

# Heating-cooling balance

## Temperature and isothermality

- Set  $\Gamma_{\text{CR}} = \Lambda_{\text{CO}}$  and solve; solution is  $T \approx 10 \text{ K}$ ; result very insensitive to exact choice of  $J$  or to variations in  $\Gamma_{\text{CR}}$ , since cooling rate is almost exponentially sensitive to  $T$
- Also important to evaluate cooling timescale: energy per H nucleus is  $\approx (1/2) (3/2) kT$ , so time to return to thermal equilibrium after a perturbation is

$$t_{\text{eq}} \sim \frac{(3/4)k_B T}{\Gamma_{\text{CR}}} \sim 10 \text{ kyr}$$

- By contrast, we will see later that timescale of hydrodynamic flows is  $\sim 1 - 10 \text{ Myr}$ ; implication is that no hydrodynamic process can perturb the temperature much  $\Rightarrow$  molecular gas is (at least approximately) *isothermal*