Class 4: Chemistry and thermodynamics

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Outline

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

H_2 molecules

Background

- Hydrogen can form H_2 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_2
- Our goal is to understand why this is, and what physical processes are responsible for the chemical transition between atomic H and H_2

The two-hydrogen system

Proof that even the simplest things are incredibly complicated

- In order for an H_2 molecule to from 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_2 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 is H_2 is mostly by surface catalysis on dust grains; excess energy mostly goes into heating the grain

The H_2 formation rate

Steps to form a molecule

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

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

Grain density

Grain cross section

H thermal speed

H density

Migration probability

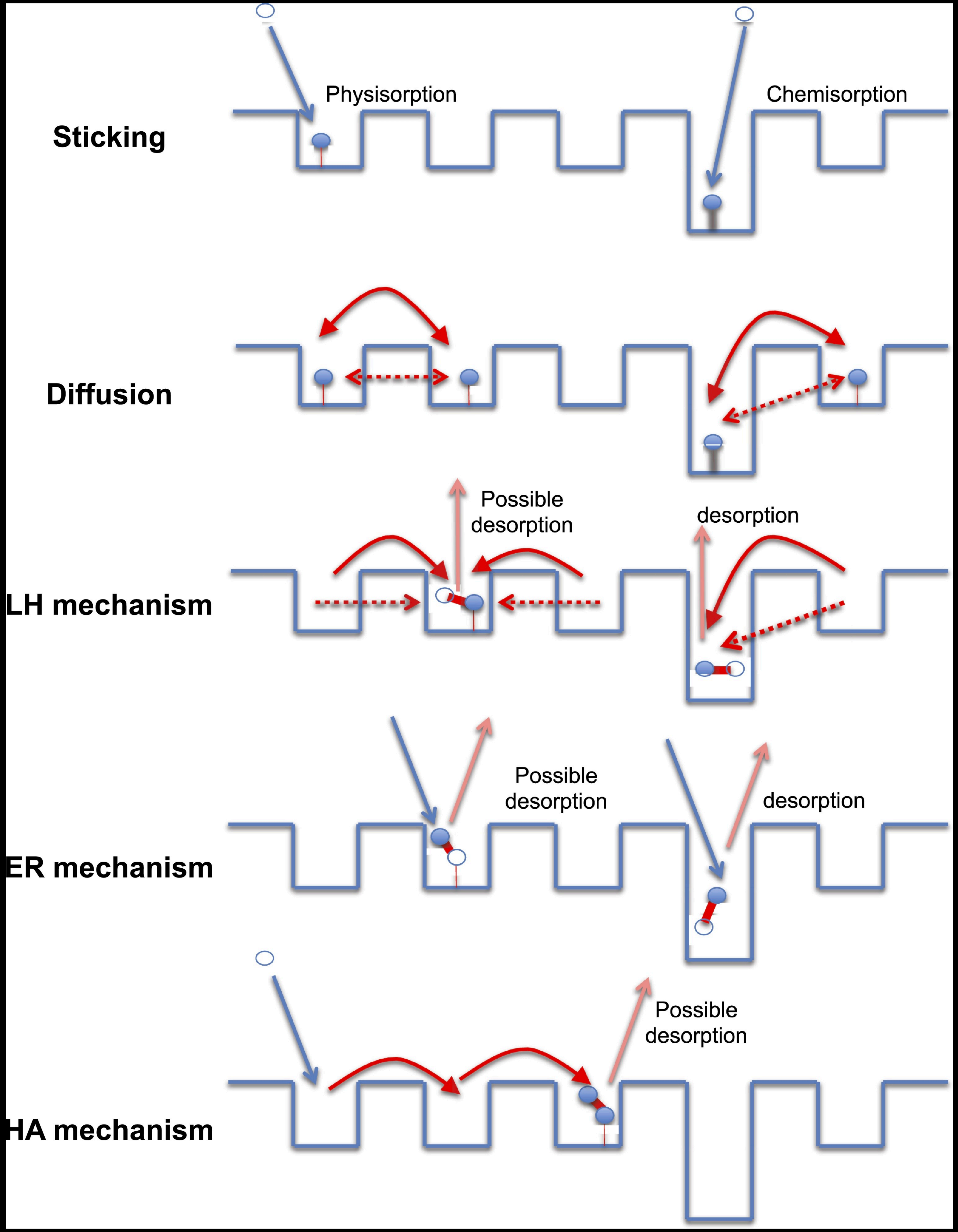
Sticking probability

- Generally simplified to

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

Number density of H nuclei, regardless of chemical state

Rate coefficient, ≈ 3×10^{-17} $\mathrm{cm}^3\ \mathrm{s}^{-1}$ in Milky Way

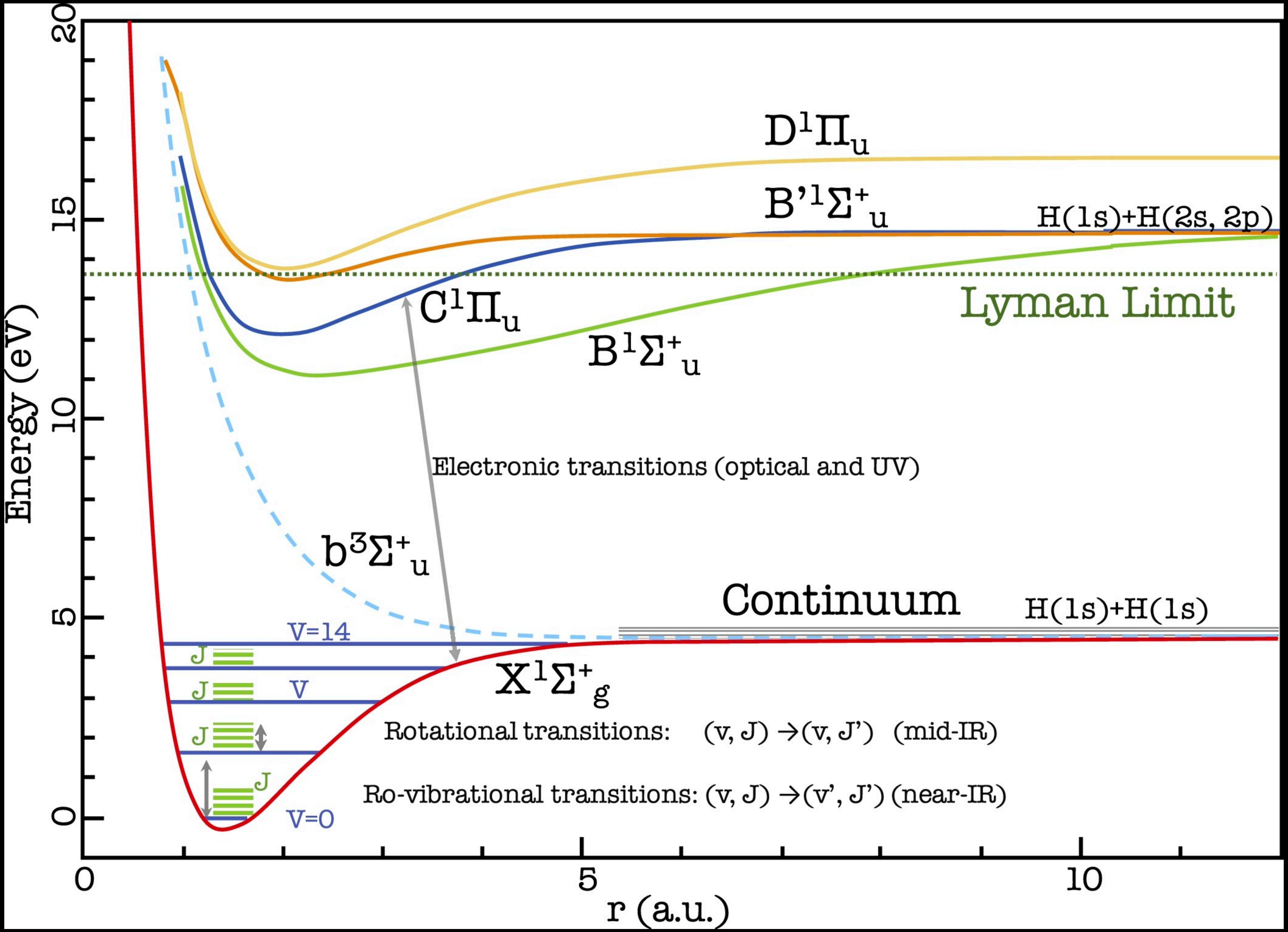


Wakelam+ 2017 review

H_2 destruction mechanism

- Main destruction mechanism is by radiation, but H_2 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_2 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_2 molecule



Wakelam+ 2017 review

Formation-destruction balance

- Let E_ν^* be number density of LW-band photons of frequency ν
- Destruction rate is $\int n_{\mathrm{H}_2} \sigma_{\mathrm{H}_2,\nu} c E_\nu^* f_{\mathrm{diss},\nu} \, d\nu$

  Target density

  Absorption cross-section

  Fraction of absorptions → dissociation

- Since $f_{\mathrm{diss},\nu}$ ~ constant, chemical balance set by

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

- Note: LHS scales as n^2, RHS as n, so gas will tend to be more H_2-dominated a high density

Simple slab model

for H → H_2 transition

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

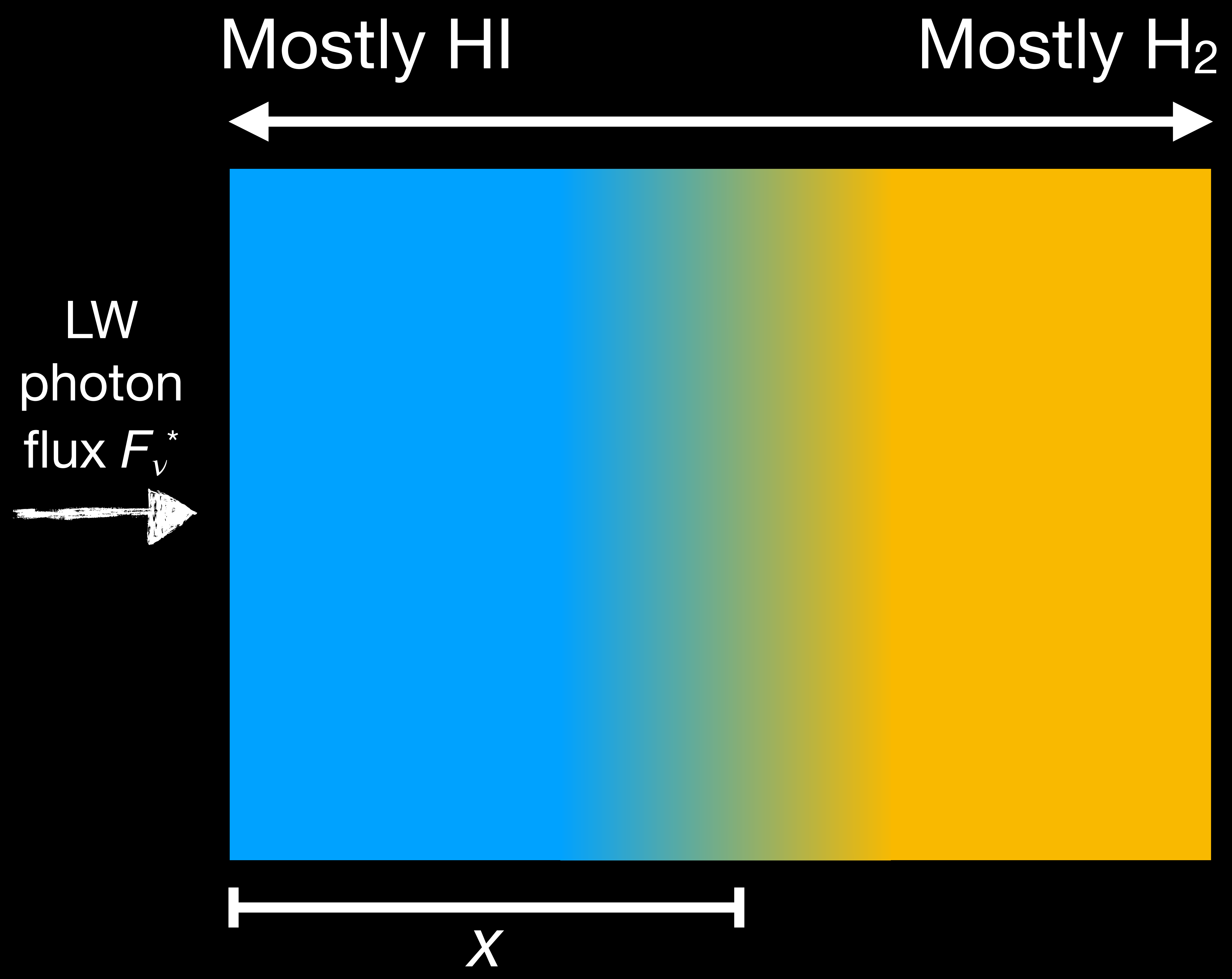
$$\frac{dF^*_\nu}{dx} = c\frac{dE^*_\nu}{dx} = -n_{\mathrm{H}_2}\sigma_{\mathrm{H}_2,\nu} c E^*_\nu$$

- Integrate over ν, divide by c:

$$\frac{dE_*}{dx} = -\int n_{\mathrm{H}_2}\sigma_{\mathrm{H}_2,\nu} E^*_\nu \, d\nu$$

- Use chemical balance to rewrite RHS:

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



Slab model solution

- Simplify by approximating H → H_2 transition as sharp, so $n \approx n_H$ in zone dominated by H
- In this case, we have analytic solution $E^*(x) = E_0^* - \frac{n^2\mathcal{R}}{cf_\mathrm{diss}}x$
- Transition is located a point where $E^*(x) \approx 0$; column through this region is

$$N_\mathrm{H} = nx_{E^*=0} = \frac{cf_\mathrm{diss}E_0^*}{n\mathcal{R}}$$

- LW photon density in Solar neighbourhood $E_0^* \approx 7.5 \times 10^{-4}$ cm^{-3}, $n \approx 100$ cm^{-3} ⇒ $N_H = 7.5 \times 10^{20}$ cm^{-3}, $\Sigma \approx 10\ M_\odot$ 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 H2 — 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_2 as a catalyst — part of the reason CO only exists where H_2 does
- All steps are ion-neutral or ion-ion reactions, so proceed ok at low temperature

$$\mathrm{H_2 + CR \rightarrow H_2^+ + e^- + CR}$$

$$\mathrm{H_2^+ + H_2 \rightarrow H_3^+ + H}$$

$$\mathrm{H_3^+ + O \rightarrow OH^+ + H_2}$$

$$\mathrm{OH^+ + H_2 \rightarrow OH_2^+ + H}$$

$$\mathrm{OH_2^+ + e^- \rightarrow OH + H}$$

$$\mathrm{C^+ + OH \rightarrow CO^+ + H}$$

$$\mathrm{CO^+ + H_2 \rightarrow HCO^+ + H}$$

$$\mathrm{HCO^+ + e^- \rightarrow CO + H}$$

CO destruction

and formation-destruction balance

- Destruction is by photodissociation — equivalent to LW band for CO
- Formation-destruction balance more complicated than for H2, because CO can't self-shield from UV (not abundant enough); instead, get shielded by dust and by cross-shielding by overlapping lines of H2
- Bottom line: transition from C^+ to CO as dominant carbon species occurs at dust extinction of 1 - 2 mag in V band; equivalent to ~30 $M_\odot$ 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_2, but C is still C^+ or CO: hard to observe!

Heating processes

Photoelectric effect

- In atomic ISM, main heating process is the grain photoelectric effect: UV photons (~8 - 13.6 eV) knock fast electrons off dust grains, which then thermalise and share their energy
- Heat rate per H nucleus approximately

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

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 ~1-2; opacities a factor of ~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_2 (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_2, excitation of H_2 followed by collisional de-excitation
- Net heating rate for MW CR flux: $\Gamma_{\mathrm{CR}} \sim 2 \times 10^{-27}$ erg s^{-1} 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 is the density is $\gtrsim$ few × 10^5 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, H_2 cannot radiate, so main coolant is CO (or 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*:

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

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

Electric dipole moment; μ = 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):

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

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

Degeneracy

Partition function

Heating-cooling balance

Temperature and isothermality

- Set $\mathit{\Gamma}_{\mathrm{CR}} = \mathit{\Lambda}_{\mathrm{CO}}$ and solve; solution is $T \approx 10$ K; result very insensitive to exact choice of J or to variations in $\mathit{\Gamma}_{\mathrm{CR}}$, since cooling rate is almost exponentially sensitive to T

- Also important to evaluate cooling timescale: energy per H nucleus is ≈ (1/2)(3/2) kT, so time to return to thermal equilibrium after a perturbation is

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

- By contrast, we will see later that timescale of hydrodynamic flows is ~1 - 10 Myr; implication is that no hydrodynamic process can perturb the temperature much ⇒ molecular gas is (at least approximately) *isothermal*