Microphysical processes

Simon Glover

Astrochemistry

- In the last lecture, we discussed collisions that change the internal energy of the target atom/molecule, but leave it chemically unaltered

- However, collisions can also lead to **chemical** changes

- Study of this in an astrophysical context is known as **astrochemistry**

- As in the last lecture, we will look at this with a simple semi-classical approach

- Several important differences between terrestrial chemistry and astrochemistry:
    - Very low densities — two-body processes dominate
    - Often, very low temperatures (e.g. in GMCs, T ~ 20 K); hence, endothermic reactions suppressed
    - Much more H, He than any other element

Reaction terminology

- Gain or loss of electrons:

Radiative recombination	$\mathrm{A}^+ + \mathrm{e}^- \rightarrow \mathrm{A} + \gamma$
Dissociative recombination	$\mathrm{AB}^+ + \mathrm{e}^- \rightarrow \mathrm{A} + \mathrm{B}$
Collisional ionization	$\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{A}^+ + \mathrm{e}^- + \mathrm{e}^-$
Electron attachment	$\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{A}^- + \gamma$
Electron detachment	$\mathrm{A}^- + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}^-$
Charge transfer	$\mathrm{A}^+ + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{B}^+$

- Gain or loss of atoms:

Radiative association	$A + B \rightarrow AB + \gamma$
Atom transfer	$AB + C \rightarrow A + BC$
Atom exchange	$AB + CD \rightarrow AC + BD$
Collisional dissociation	$AB + C \rightarrow A + B + C$

- Photochemistry:

Photodetachment	$A^- + \gamma \rightarrow A + e^-$
Photoionization	$A + \gamma \rightarrow A^+ + e^-$
Photodissociation	$AB + \gamma \rightarrow A + B$

- How do we determine rate of a chemical reaction?

- Start by considering simple two-body gas-phase reactions

- For a reaction between reactants A, B, the reaction rate per unit volume can be written as:

$$R_{\rm AB} = k_{\rm react} n_{\rm A} n_{\rm B}$$

Here, n_A, n_B are the number densities of the reactants and k_{react} is the **reaction rate coefficient**

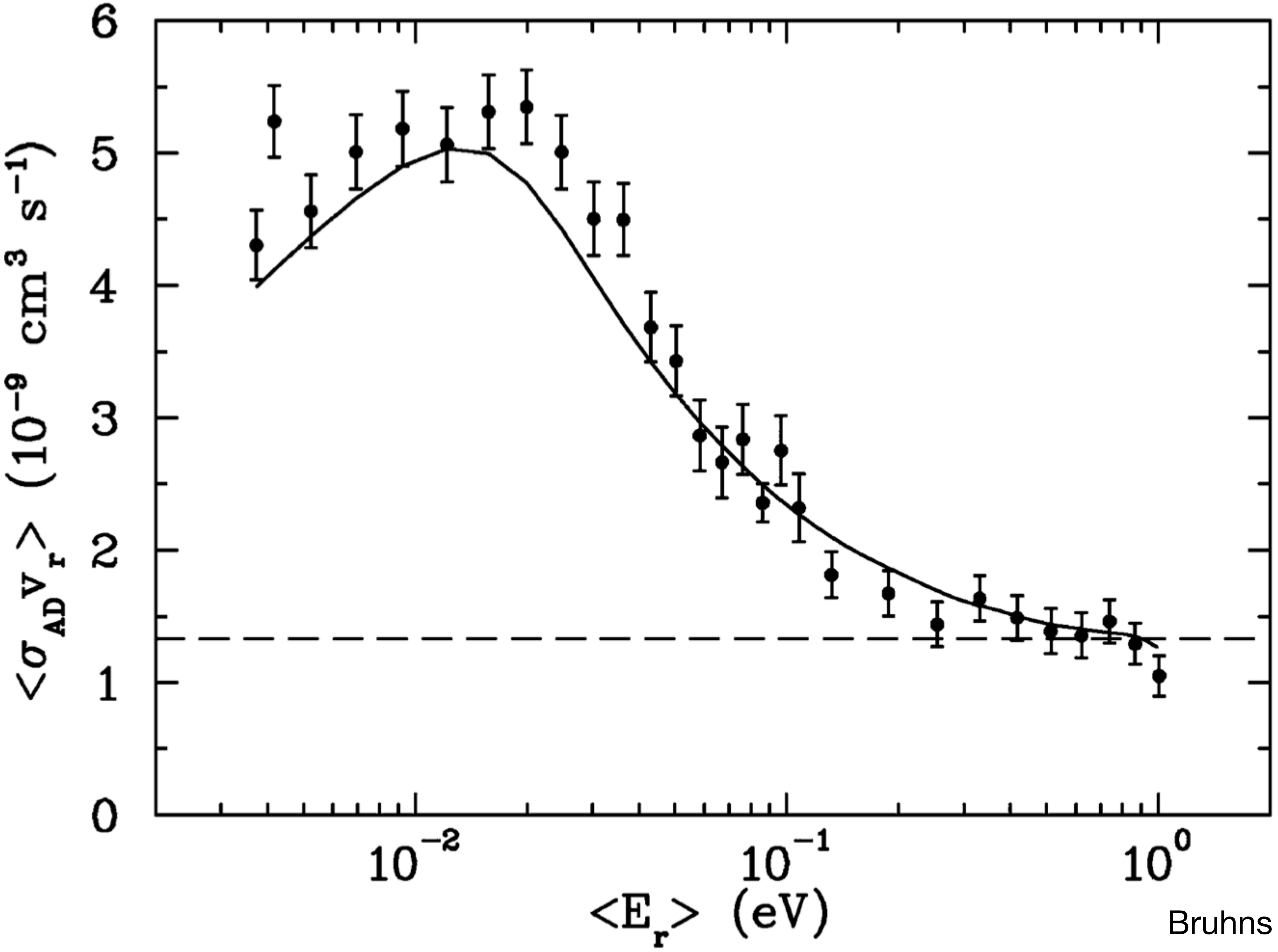
- Can write reaction rate coefficient in terms of a velocity-dependent cross-section:

$$k_{\mathrm{react}} = \int_0^\infty \sigma_{\mathrm{AB,react}}(v) v f(v) \mathrm{d}v$$

- Usually a good approximation to take velocity distribution function f(v) to be Maxwellian

- To determine k_{react}, hence need to calculate or measure the reaction cross-section

Associative detachment of H- with H



Bruhns et al., 2010

Datapoints — experimental measurement
Solid, dashed lines — theoretical models

- Semi-classical approach: assume we can write cross-section as product of **collision cross-section** and **reaction probability**

$$\sigma_{\mathrm{AB,react}} = p_{\mathrm{react}}\sigma_{\mathrm{AB,coll}}$$

- Collision cross-section depends on long range interaction between particles, can often be treated classically
- Reaction probability depends on short-range behaviour; accurate treatment requires QM (but can often be estimated)

The hard sphere approximation

- Simplest possible approximation: assume no long-range interaction between particles
- Cross-section is then simply:

$$\sigma_{\mathrm{AB,coll}} = \pi \left(\frac{d_A + d_B}{2} \right)^2$$

where d_A, d_B are sizes of the reactants

- For atoms, sizes are ~ 10^{-8} cm (to within factor of 2), so typical cross-sections are ~ few times 10^{-16} cm^2

- Since cross-section is independent of velocity:

$$k_{\mathrm{react}} = \sigma_{\mathrm{AB,coll}}\, p_{\mathrm{react}} \int_0^{\infty} v f(v) \mathrm{d}v = \sigma_{\mathrm{AB,coll}}\, p_{\mathrm{react}} \left\langle v_{\mathrm{r}} \right\rangle$$

- Mean relative velocity:

$$\left\langle v_{\mathrm{r}} \right\rangle = \left(\frac{8kT}{\pi\mu} \right)^{1/2}$$

where μ is the reduced mass

- Evaluating this yields a value ~ $10^{-11}\ p_{\mathrm{react}}\ (T/\mu)^{1/2}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, with μ in atomic mass units

- Key points to note:
  - Rate increases with temperature
  - Inverse dependence on reduced mass

- Reasonable approximation for non-polar neutral reactants

Ion-neutral collisions

- Electric field of ion induces dipole moment in otherwise non-polar atom or molecule

- Corresponding electrostatic interaction scales as $F \sim R^{-5}$, so potential describing the interaction scales as $V \sim R^{-4}$

- Lagrangian for system:

$$L = \frac{1}{2}\mu \dot{R}^2 + \frac{1}{2}\mu R^2 \dot{\phi}^2 - V(R)$$

- Corresponding equations of motion:

$$l \equiv \mu R^2 \dot{\phi} = \text{constant}.$$

$$\mu \ddot{R} = \frac{l^2}{\mu R^3} - \frac{\partial V}{\partial R}.$$

- Can write second of these in terms of an effective potential:

$$\mu \ddot{R} = -\frac{\partial V_{\text{eff}}}{\partial R}.$$

$$V_{\text{eff}}(R) = V(R) + \frac{l^2}{2\mu R^2}.$$

- Corresponding equations of motion:

$$l \equiv \mu R^2 \dot{\phi} = \text{constant}.$$

Angular momentum conservation

$$\mu \ddot{R} = \frac{l^2}{\mu R^3} - \frac{\partial V}{\partial R}.$$

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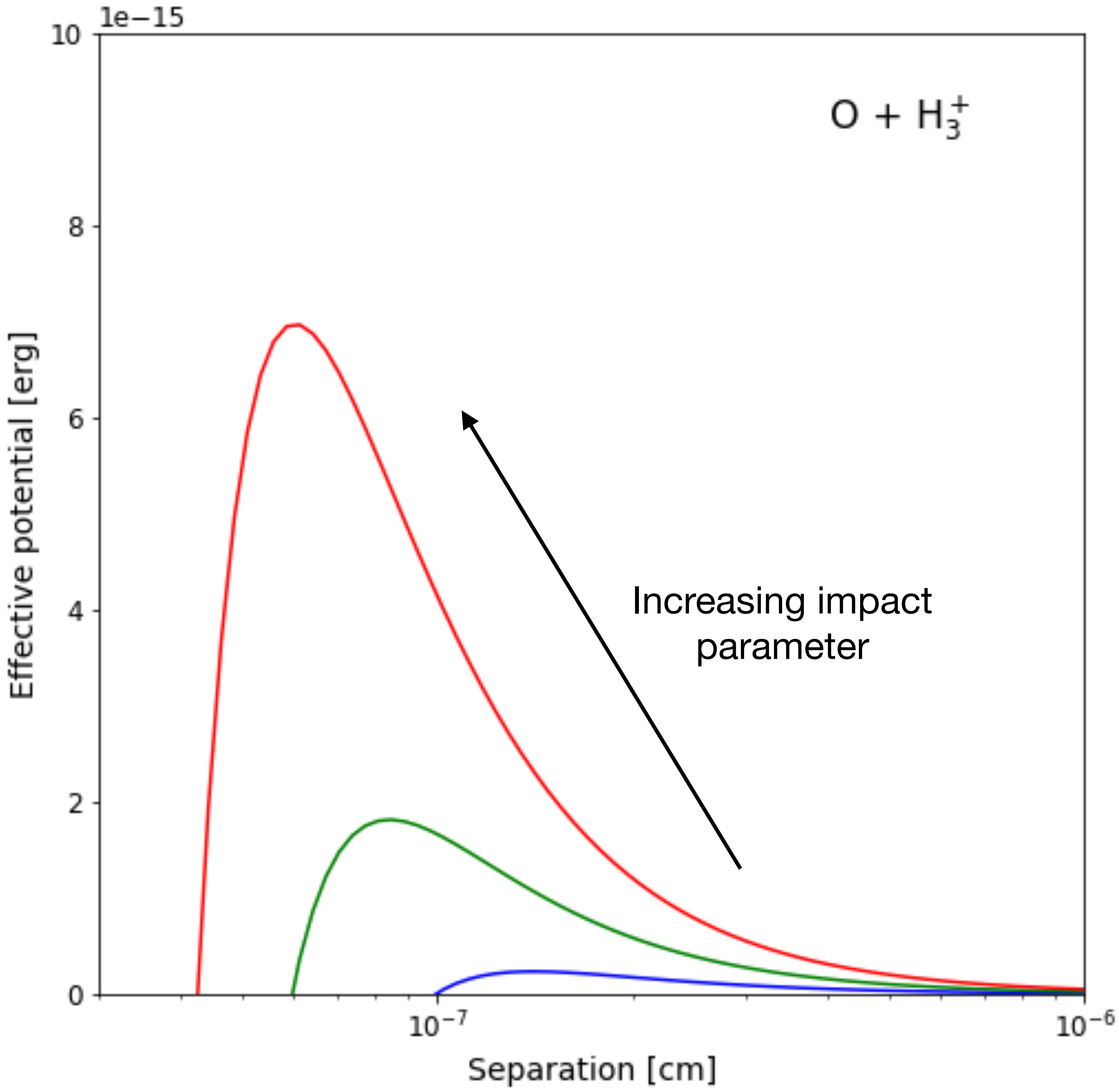

1e−15
10
8
6
4
2
0
Effective potential [erg]
10^{-7}
10^{-6}
Separation [cm]
$O + H_3^+$
Increasing impact parameter

- V_{eff} small at large distances, negative (attractive) at small distances

- Peak at intermediate distances owing to non-zero angular momentum — the **centrifugal barrier**

- Height of barrier depends on angular momentum, hence on initial kinetic energy and impact parameter

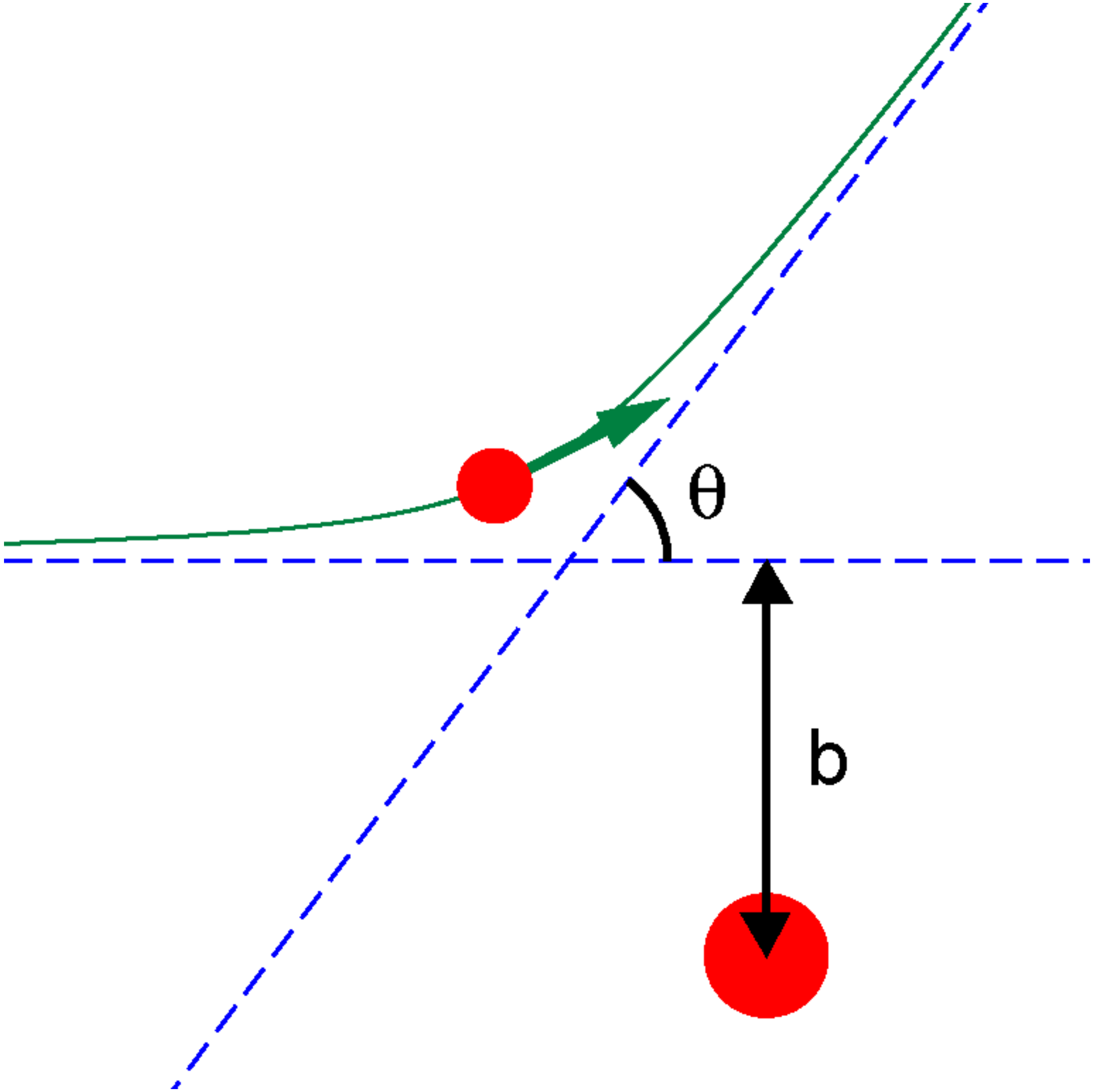


Image credit: Wikipedia (User:Tonatsu)

- For a reaction to be possible, reactant must be able to make it over barrier

- At given initial energy E_i, implies reactions only possible for collisions with impact parameter less than b_{max}:

$$b_{\rm max} = \left(\frac{2\alpha q^2}{E_i}\right)^{1/4}.$$

- Here, α is the **polarizability** — measure of how easy it is to polarize neutral reactant

- For given E_i, height of barrier exceeds E_i when $b > b_{max}$

- Note: in the general case, expression for b_{max} depends on form of interaction potential — this form is specifically for induced dipole interactions

- Effective cross-section for reaction:

$$\sigma = \pi b_{\text{max}}^2 = \pi \left(\frac{2\alpha q^2}{E_i} \right)^{1/2} .$$

- Note that b_{max} can be much larger than actual physical size of target reactant

- Note also inverse dependence on energy!

- In terms of velocity, this is:

$$\sigma = \pi b_{\mathrm{max}}^2 = \frac{2\pi q}{v}\left(\frac{\alpha}{\mu}\right)^{1/2}.$$

- Hence, reaction rate coefficient is:

$$\begin{aligned} k_{\mathrm{react}} &= 2\pi q \left(\frac{\alpha}{\mu}\right)^{1/2} \int_0^\infty f(v) p_{\mathrm{react}} \mathrm{d}v, \\ &\simeq 2\pi q \left(\frac{\alpha}{\mu}\right)^{1/2}, \end{aligned}$$

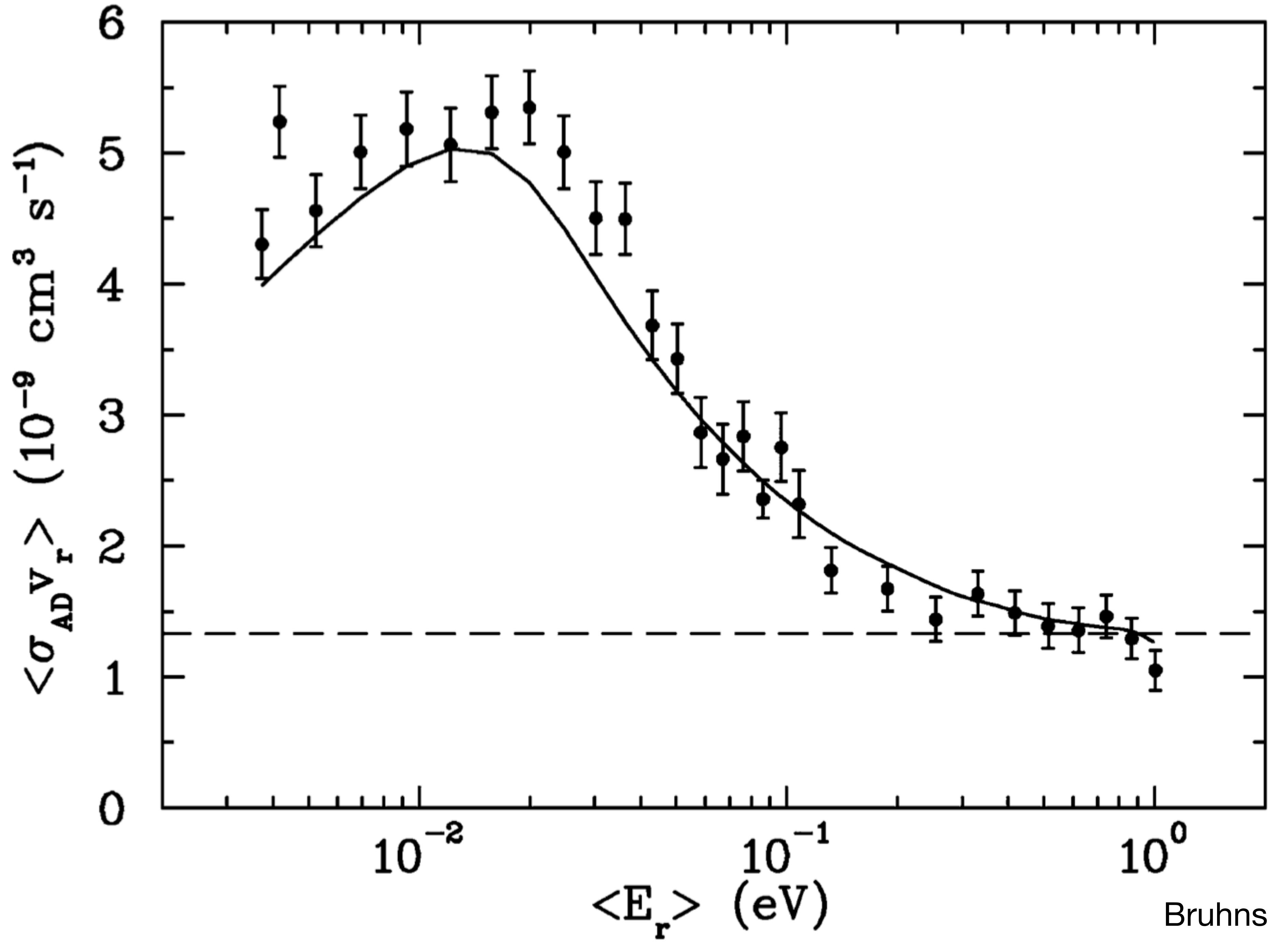
where second line assumes $p_{\mathrm{react}} \sim 1$

- This is the **Langevin rate** for the reaction

- Advantages of Langevin approach:
  - Little information necessary: q, α, reactant masses
  - Calculation trivial
  - Easy to calculate rates for large numbers of reactions

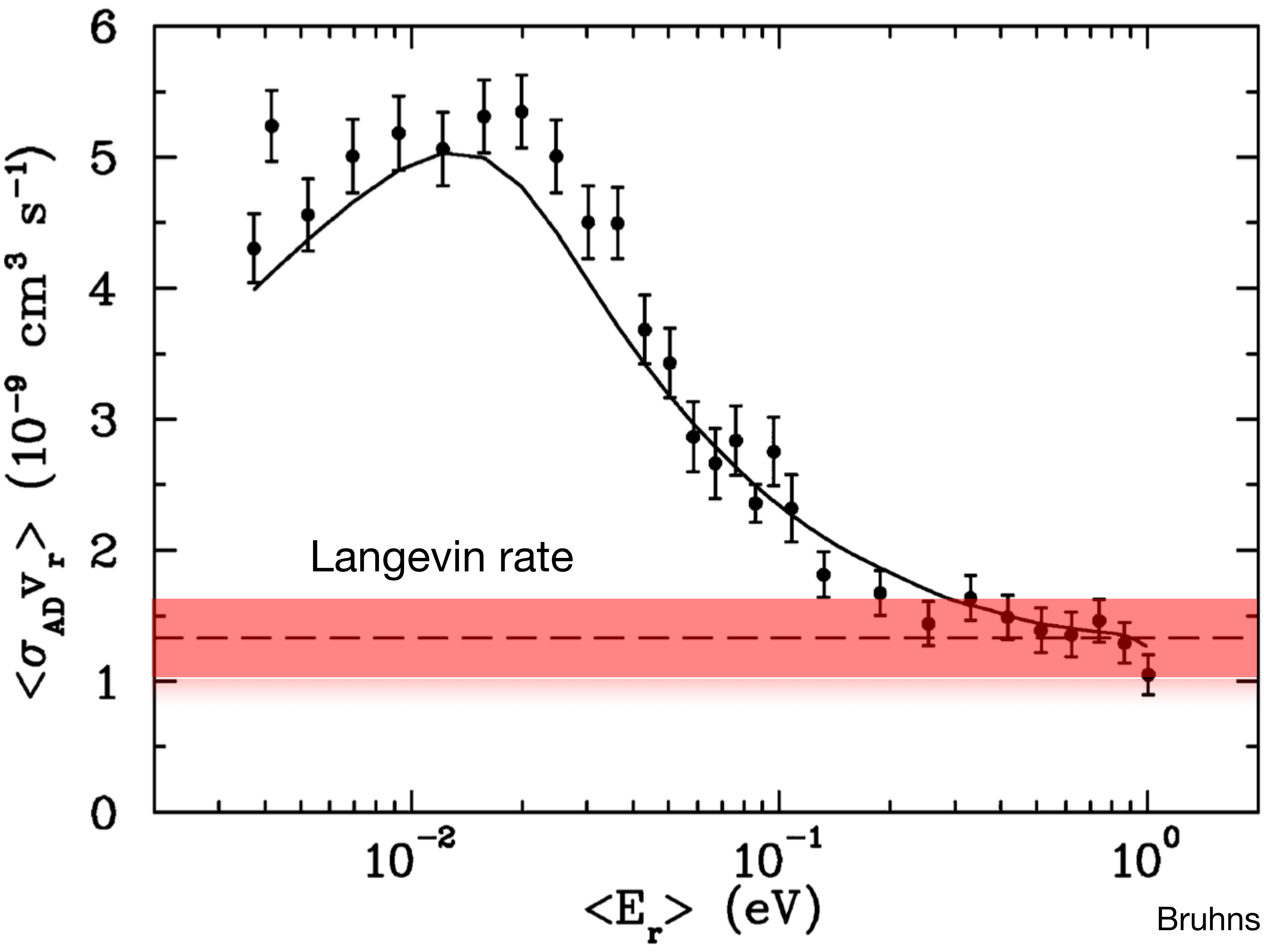
- Disadvantages:
  - Neglects short-range behaviour, assumes that all reactants that come close enough react
  - Limited accuracy — usually OK to within factor of 10

Associative detachment of H^- with H



Bruhns et al., 2010

Associative detachment of H- with H



Bruhns et al., 2010

- Procedure outlined here only applies to collisions between ions and non-polar neutrals

- Similar **capture theory** approaches can be developed for other types of long-range interaction
  - For a good review, see Tsikritea et al., 2022, J. Chem. Phys., 157, 060901

- In general, the stronger the long-range interaction, the stronger the anti-correlation of k_{react} and T
  - No interaction: $k_{react} \sim T^{1/2}$
  - Ion-induced dipole: $k_{react} \sim$ constant
  - Electrostatic (positive ion - electron): $k_{react} \sim T^{-1/2}$

Reaction probabilities

- Classical approach outlined previously assumes that all reactants react once they come close enough
- When is this a poor approximation?
    - Multiple reaction outcomes
    - Energy barrier
    - Radiative process

- Capture theory model tells us how often reactants come close enough to react

- BUT: same reactants can have more than one possible reaction, producing different products

- Capture theory tells us the rate of the **sum** of these different reactions — individual reactions have $p_{react} < 1$

- Example: dissociative recombination of H_3O^+

$$
\begin{aligned}
N_a(H_2O + H) &= 0.33 \pm 0.08 \\
N_b(OH + H_2) &= 0.18 \pm 0.07 \\
N_c(OH + H + H) &= 0.48 \pm 0.08 \\
N_d(O + H_2 + H) &= 0.01 \pm 0.04
\end{aligned}
$$

Vejby-Christensen et al. (1997)

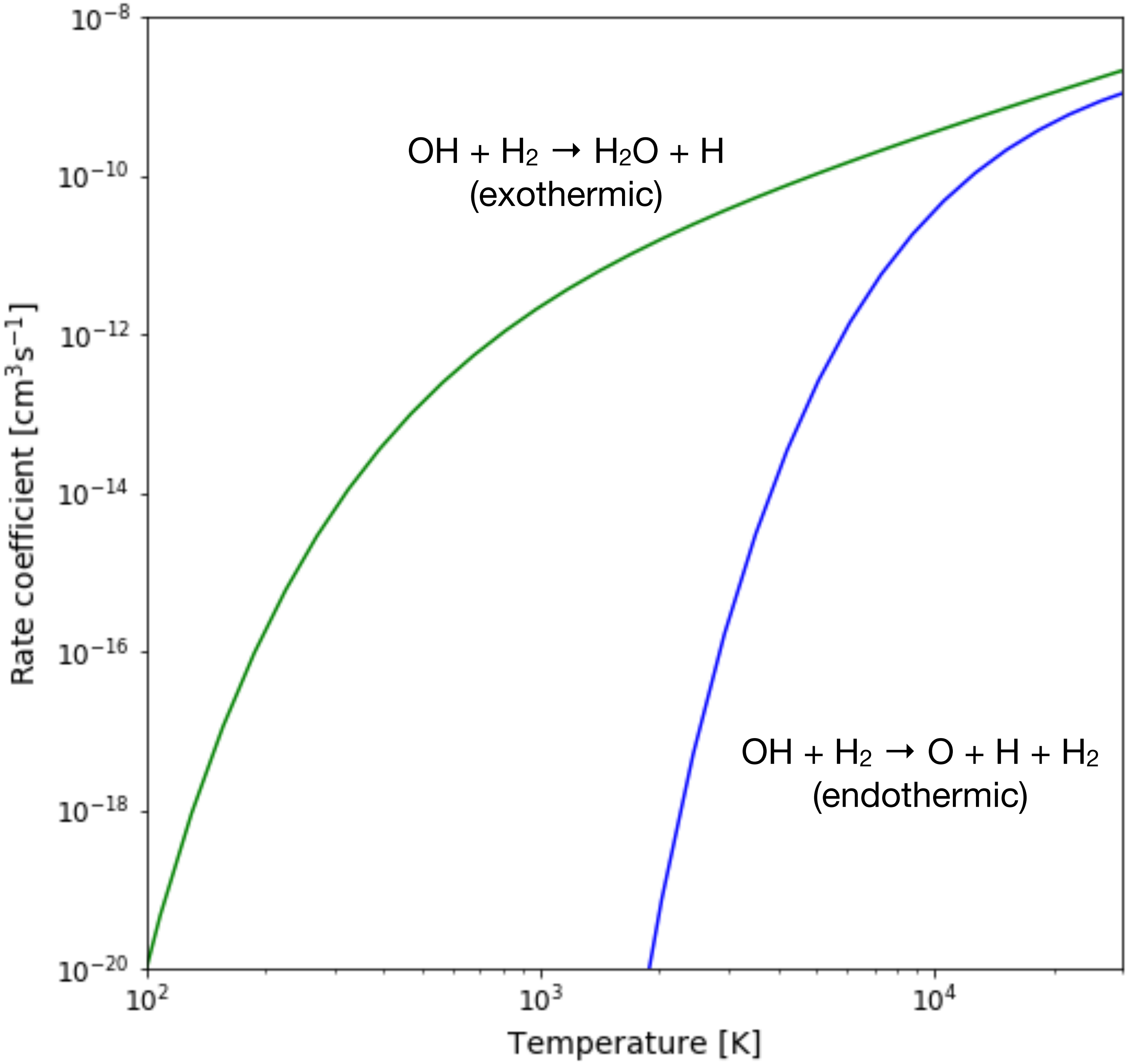
- If reaction is endothermic, need available kinetic energy to exceed required change in binding energy

- Same also true for exothermic reactions if they have a non-negligible **activation energy**

- Collisions with insufficient energy have $p_{\rm react} = 0$

- If height of energy barrier is ΔE, this introduces a factor $\exp(-\Delta E/kT)$ into expression for rate coefficient

- Note: at typical molecular cloud temperatures, these terms can be very small


$OH + H_2 \rightarrow H_2O + H$
(exothermic)
$OH + H_2 \rightarrow O + H + H_2$
(endothermic)
Rate coefficient [$cm^3 s^{-1}$]
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
10^{-18}
10^{-20}
10^2
10^3
10^4
Temperature [K]

- Reactions that involve photon emission (e.g. radiative association, radiative recombination) have small p_{react}

- Probability of photon emission during collision:

$$p_{\text{react}} \simeq A_{\text{fb}} t_{\text{coll}}$$

A_{fb} = Einstein coefficient for transition from unbound to bound state; t_{coll} = collision time

- Typical collision times very short: $t_{\text{coll}} \sim 10^{-13}$ s

- Value of A_{fb} depends on nature of transition, but even for dipole-allowed transitions, rarely exceeds 10^9 s^{-1}

- Hence: even for allowed transitions, p_{react} ~ 10^{-4} or less

- Most collisions do not result in photon emission

- p_{react} even smaller (and reaction slower) if transition is forbidden (e.g. if end product has no dipole moment)

Photochemistry

- General term for chemical reactions induced by absorption of light

- At ISM densities, this typically implies interaction between single reactant and a photon — interactions involving multiple reactants and/or photons very rare

- Simplest cases: **photoionization** and **photodetachment**

- Note: latter is basically the same process, but involving a negative ion rather than neutral atom or positive ion

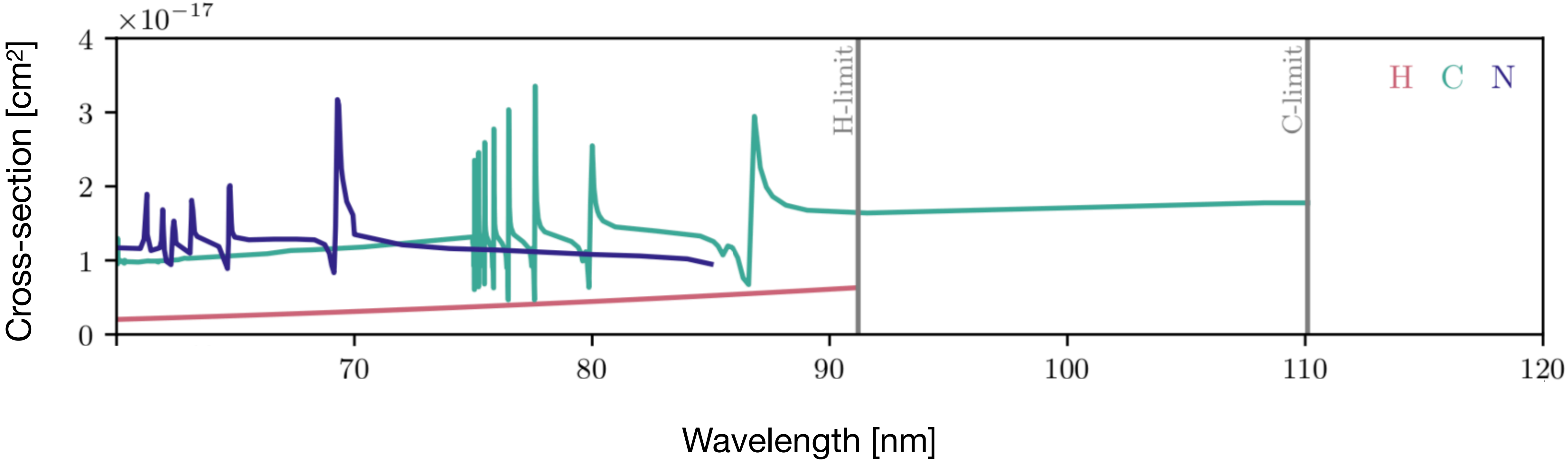
- Simplest photoionisation mechanism: absorption of photon leads to electron transition from bound state to continuum

- Minimum energy = **ionisation potential** of atom/molecule

- Any photons with energy above this value can cause photoionisation — smooth, continuous cross-section

- Example: photoionisation of H — the **only** case where we can compute the cross-section analytically!

- For any cases other than atomic H (or a hydrogenic ion), presence of additional ~~ions~~ e^- complicates matters
- Can get resonances in photoionisation cross-section
- These occur when photon energy is sufficient to expel one electron and simultaneously excite one or more additional electrons
- Close to resonances, cross-section much larger — can make significant contribution to total rate



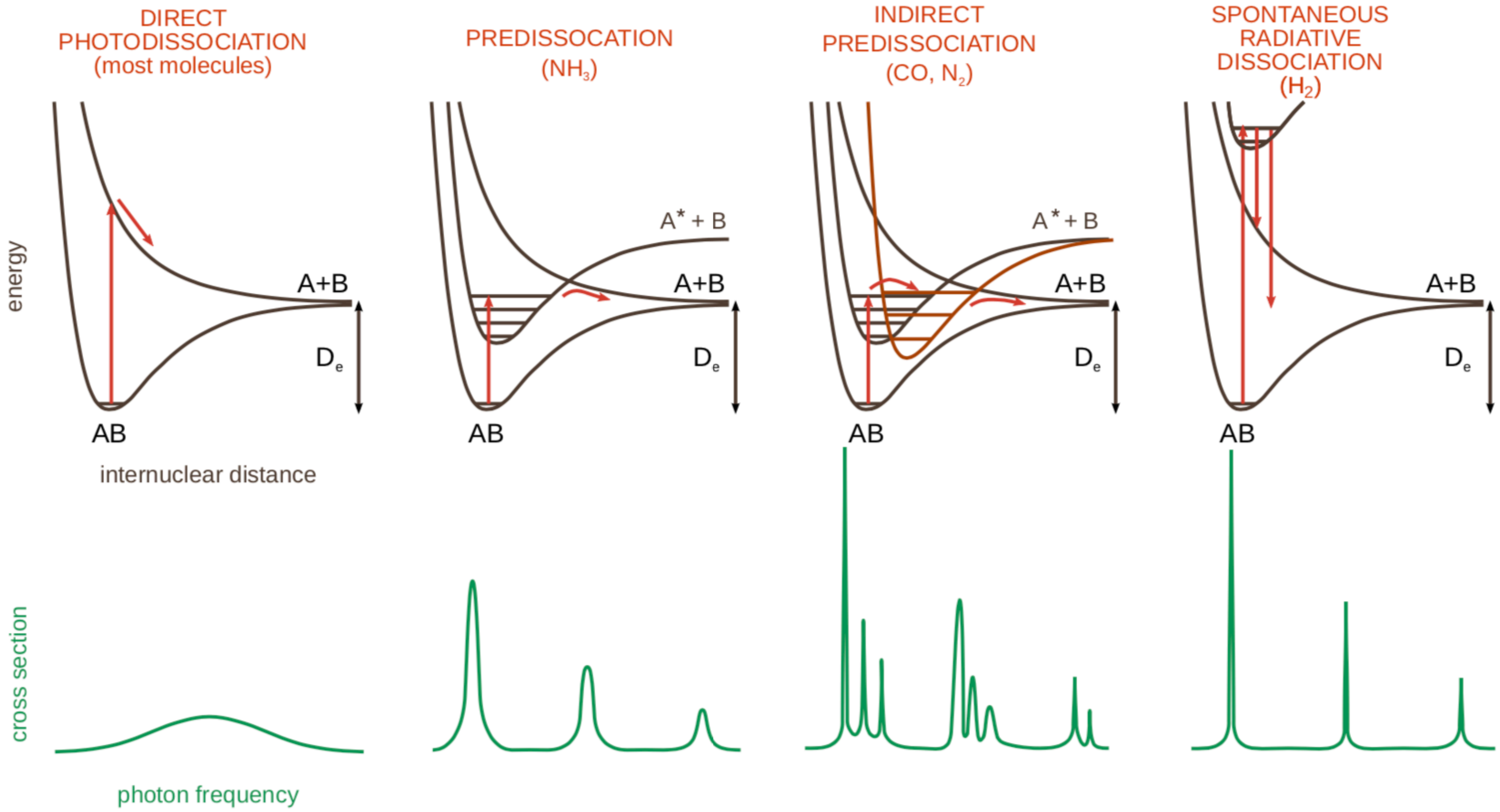
Heays et al (2017)

- Important distinction in ISM between reactants with first ionisation potentials above, below 13.6 eV

- For I > 13.6 eV, reactants can only be ionised by photons that can also ionise H
  - Since lots of H in ISM, photoionisation of these species typically only important inside HII regions
  - Important examples: He, N, O

- For I < 13.6 eV, reactants can be ionised by FUV and EUV photons that cannot ionise H
  - Typically found in singly ionised form in diffuse ISM
  - Important examples: C, S, Si

- **Photodissociation**: photon-induced transition involving break-up of molecule **without** loss of an electron
- Several different possible mechanisms
  - Direct photodissociaton
  - Predissociation
  - Indirect predissociation
  - Spontaneous radiative dissociation



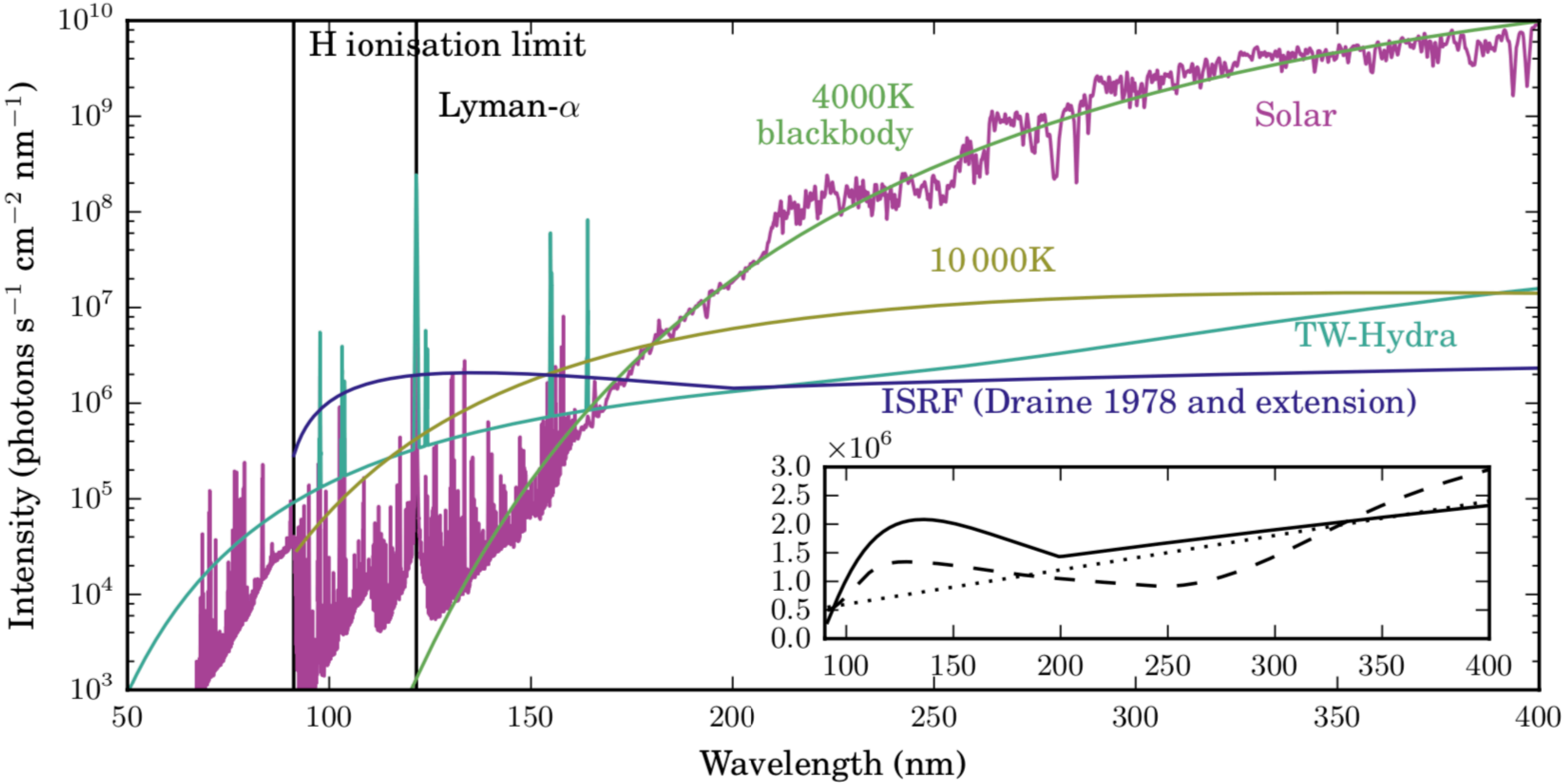
Heays et al (2017)

- Direct photodissociation:
    - Transition from bound to unbound electronic state
    - Broad, continuous cross-section
    - Dissociation probability is ~100%
    - Energy required must exceed molecular binding energy, but often not by much
    - Only important if transition allowed (i.e. doesn’t violate any selection rules)

- Predissociation:
  - Radiative transition to excited bound state
  - Non-radiative transition to repulsive electronic state
  - Line-driven (initial bound-bound transition), but short lifetime of excited state implies broad lines
- Indirect predissociation:
  - Similar to predissociation, but involves intermediate transitions to one or more excited bound states
- In both cases, dissociation probability < 100% (non-radiative transition competes with radiative decay to ground state)

- Spontaneous radiative dissociation:
  - Radiative transition to excited bound state
  - Radiative decay to ground state vibrational continuum
  - Line-driven; excited state long-lived, so lines narrow
  - Dissociation probability can be small, since significant probability that molecule decays back to bound state
  - Most important example: **molecular hydrogen** (H_2)

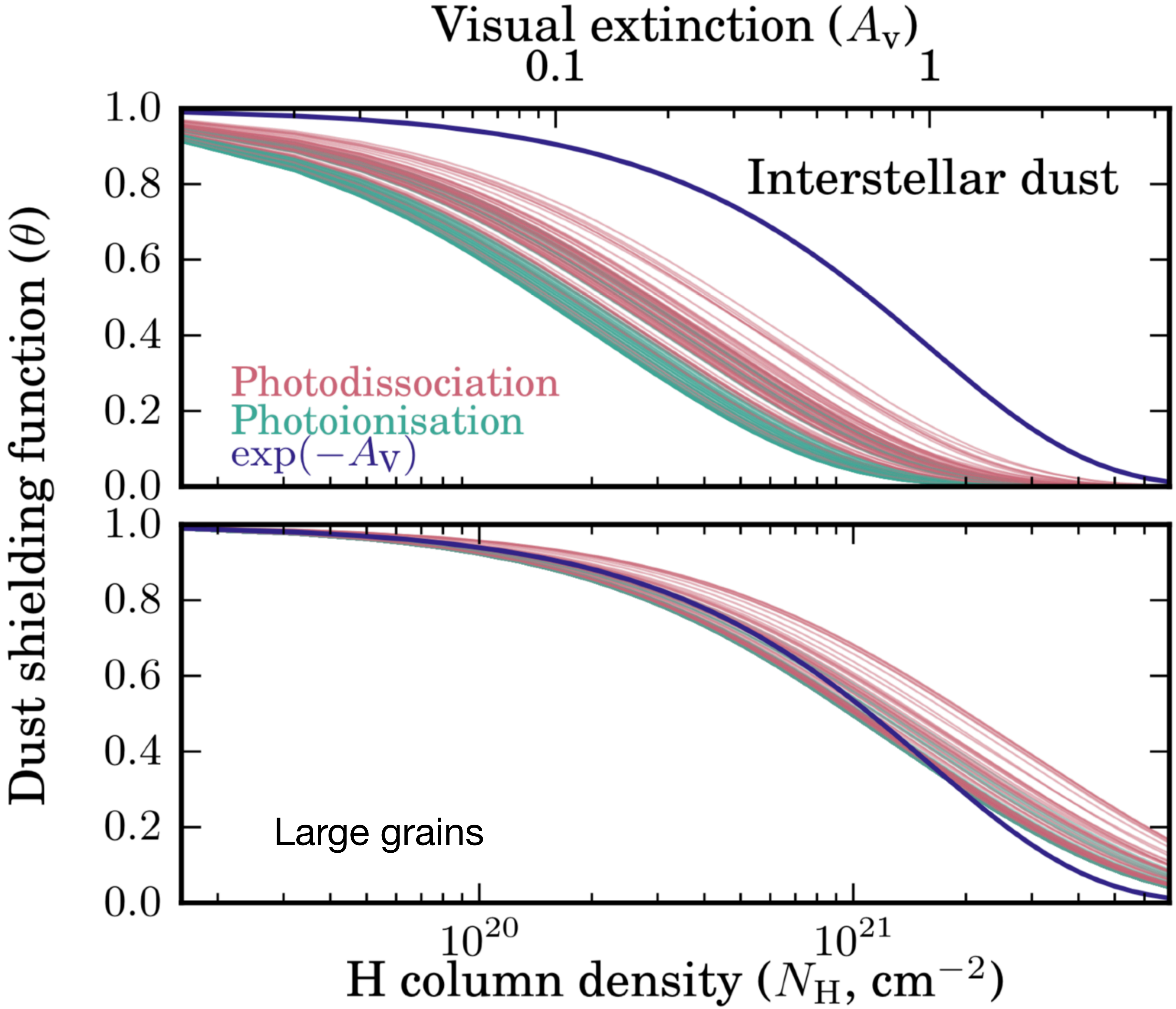
- What photon energies relevant?
  - Photoionisation, neutral atom/molecule: ~ 10 eV
  - Photodissociation: typically > 4 eV (~3000 Angstrom)
  - Very weakly bound species (e.g. H^-, O_3) need less
  - Photochemistry driven by **ultraviolet** radiation field



Heays et al (2017)

- Relative importance of different reactions depends on local UV radiation spectrum

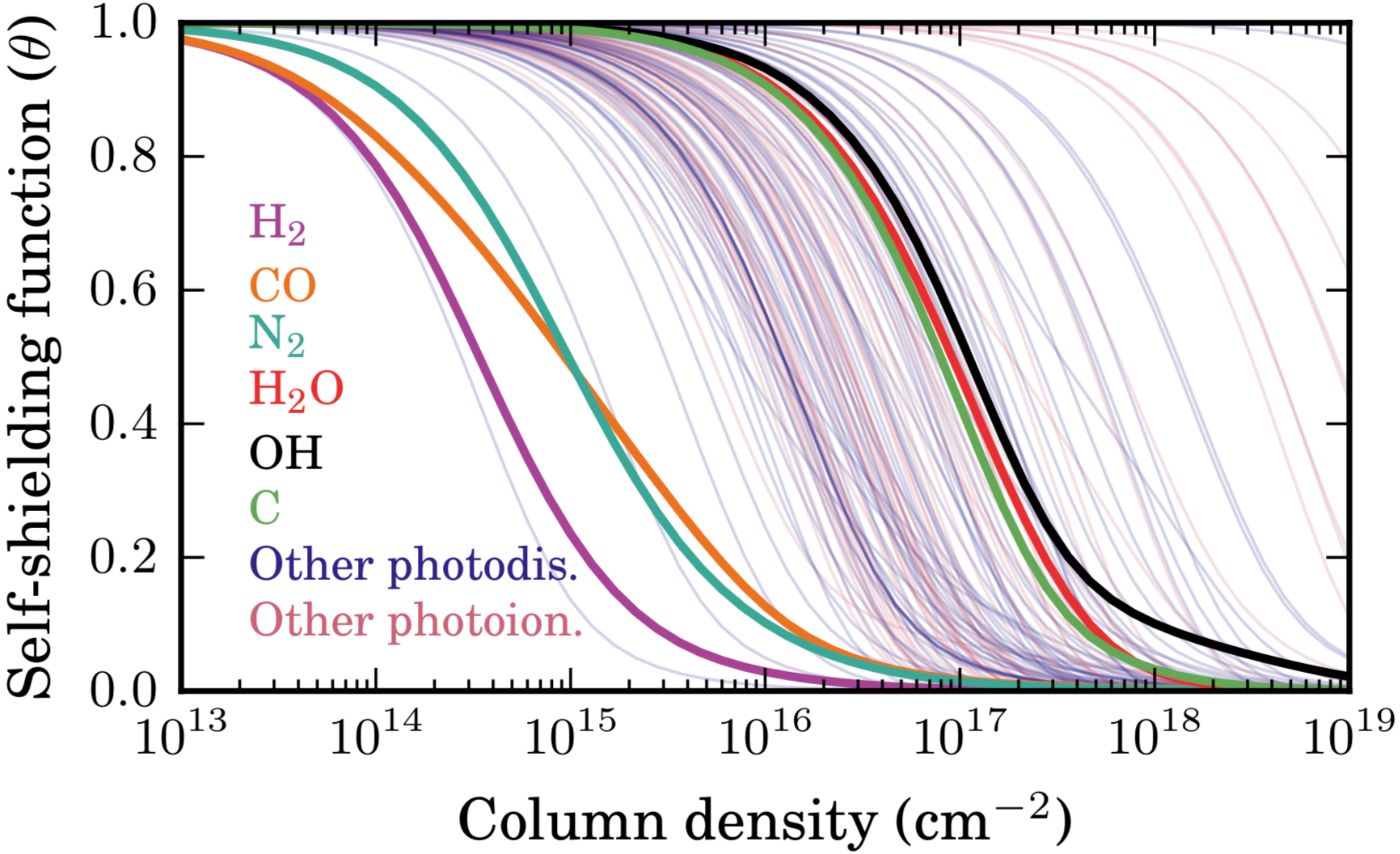
- Photochemical rates can be dramatically reduced by **shielding** of gas from incident radiation
- Two main processes:
  - Dust shielding
  - Self-shielding
- At solar metallicity, dust shielding becomes important for H column densities ~ 10^{21} cm^{-2} (A_V ~ 0.5)
- At lower Z, need much higher column density to get comparable A_V — dust shielding less effective



Heays et al (2017)

- For line-driven photodissociation, line absorption removes just those photons needed to cause photodissociation — process known as **self-shielding**

- Required column density depends on line widths (and hence on photodissociation mechanism)
    - Ranges from ~10^{15} cm^{-2} (e.g. H_2) — 10^{17} cm^{-2} (e.g. OH)
    - Important process for H_2, since H_2 column densities easily exceed this
    - Few other molecules have high enough column densities, so minor process for most species



Heays et al (2017)

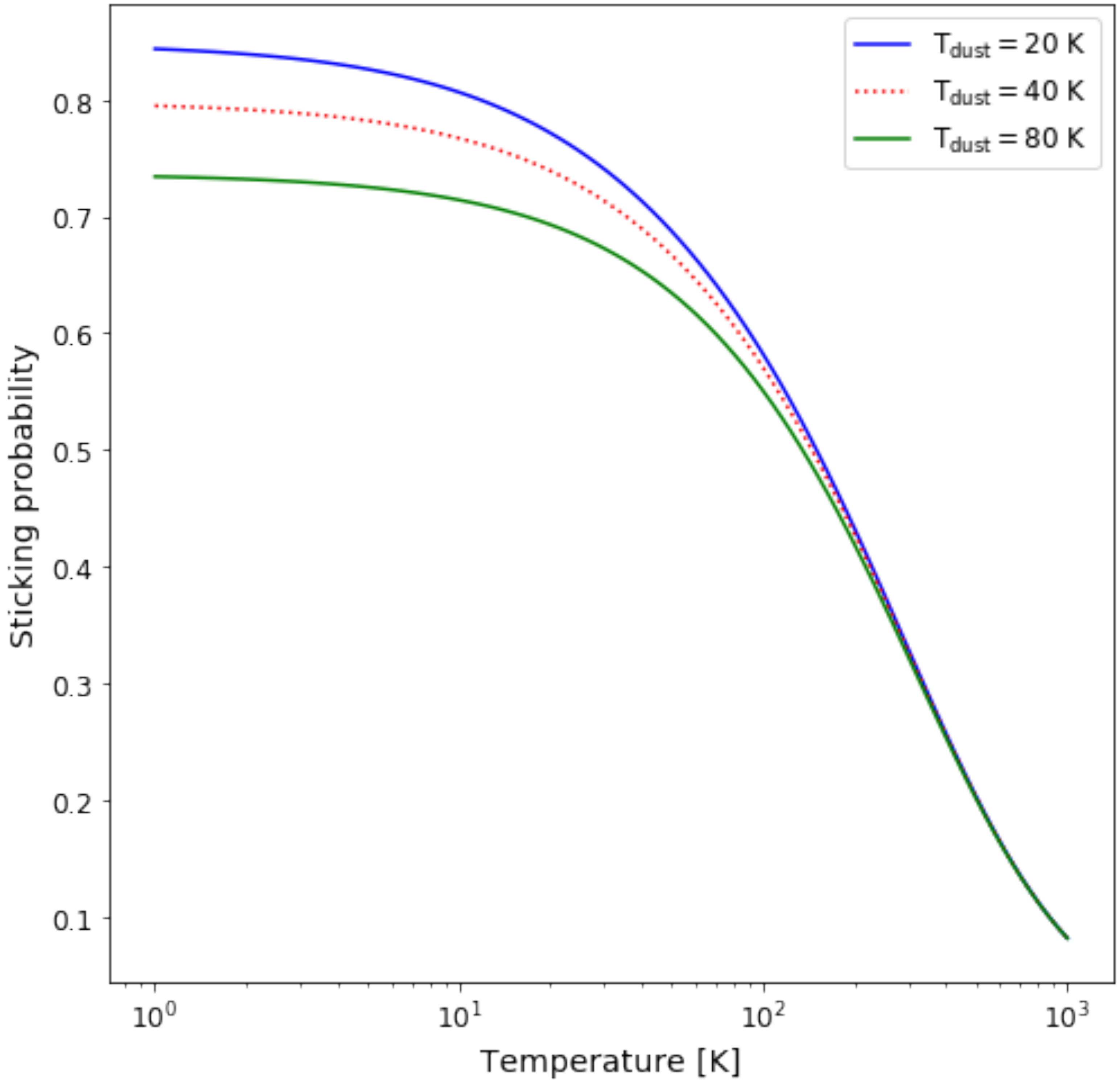
Grain surface chemistry

- So far, we have considered only processes in gas phase
- However, chemical reactions can also occur on the surface of dust grains
- Basic mechanism:
  - Adsorption of reactants onto grain surface
  - Reactants encounter each other and react
  - Desorption back into gas phase

Adsorption

- Atom or molecule encounters grain — rate at which this occurs can be treated classically
- Near surface, reactant attracted by van der Waals force
- If kinetic energy low, reactant can become physically bound to grain surface — **adsorption**
- If kinetic energy too high, reactant bounces off
- Probability of adsorption known as **sticking probability**

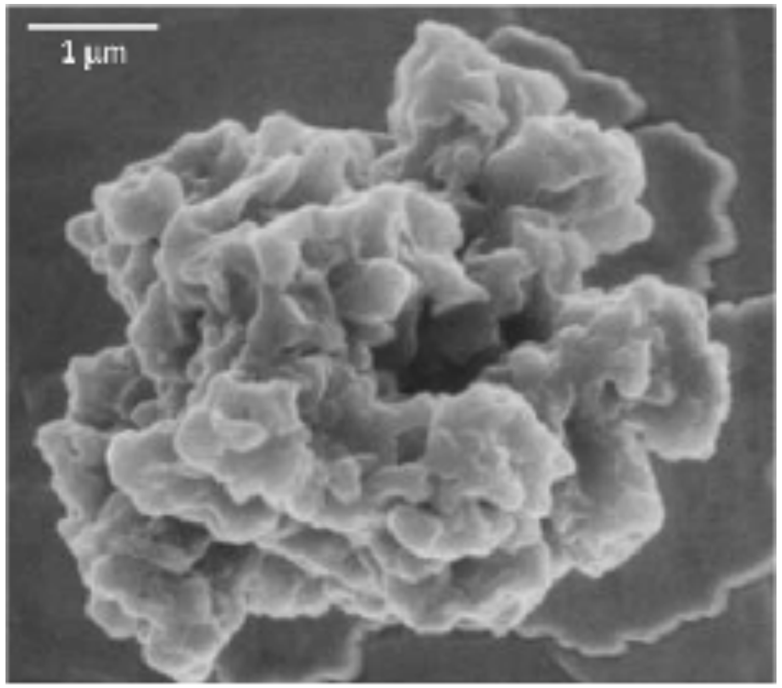
Sticking probability for atomic H



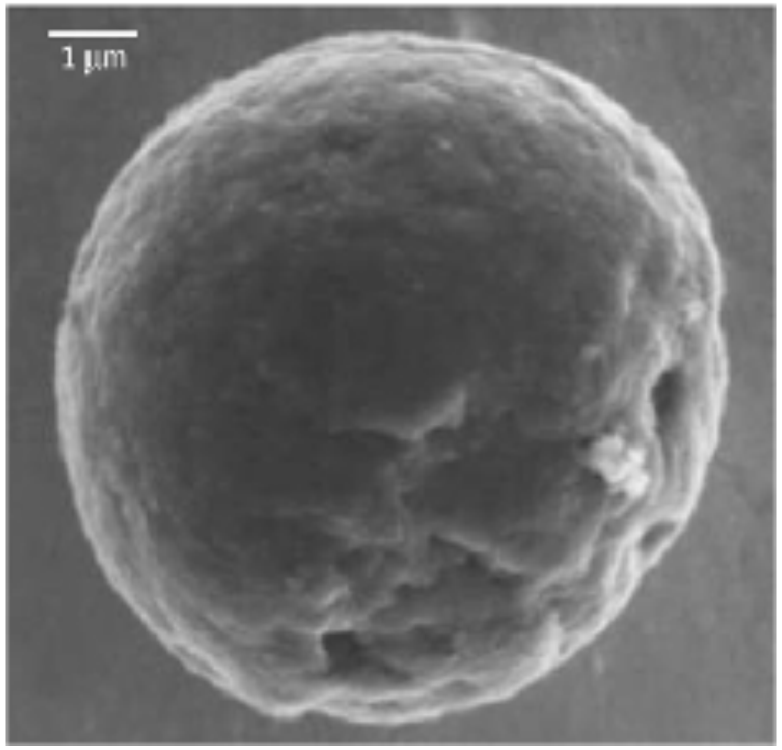
Motion on the surface

- van der Waals force weak — binding energy low
- Reactant can thermally “hop” around on surface
- Light reactants (especially atomic H) can also move around on surface by quantum tunnelling
- Effectiveness of hopping depends on size of binding energy and grain temperature

- Three possible outcomes:
  - Evaporation: reactant becomes unbound from surface
  - Reaction: encounter and reaction with another reactant
  - Trapping: atom forms a stronger bond with the surface, either due to surface geometry or due to formation of covalent chemical bound — **chemisorption**
- Once trapped, reactants generally cannot move around on surface
- Can still react, if encountered by mobile reactant or if it interacts directly with gas phase reactant



Silicon Carbide (SiC)



Graphite

- **Langmuir-Hinshelwood** mechanism:
  - Reaction between two adsorbed reactants
  - A(s) + B(s) → AB(s) [or AB(g)]
- **Eley-Rideal** mechanism:
  - Reaction between adsorbed reactant and gas-phase reactant
  - A(s) + B(g) → AB(g)

- Evaporation efficiency highly sensitive to binding energy and dust grain temperature:

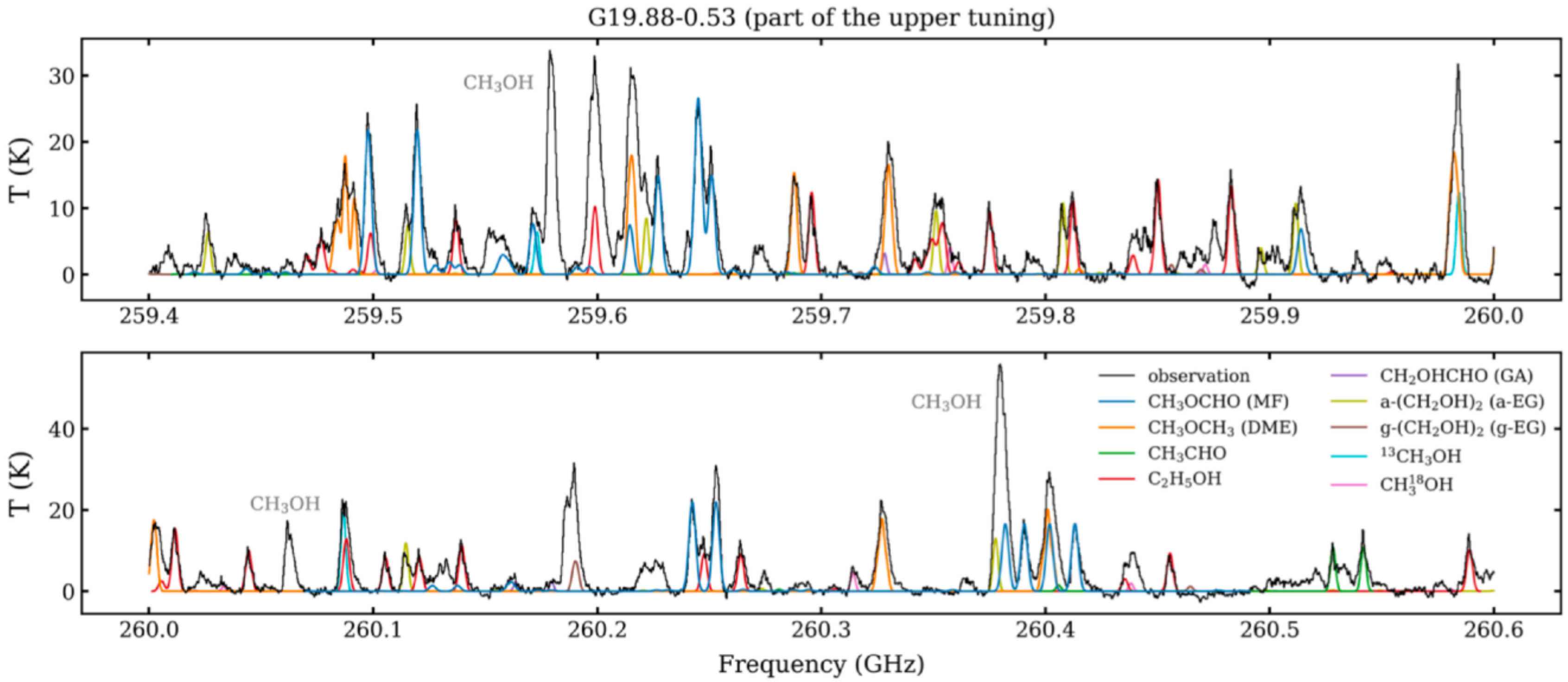
$$t_{\rm evap} \simeq 10^{-13} \exp\left(\frac{E_{\rm bind}}{T_{\rm dust}}\right) \,{\rm s}$$

- Examples for 20 K dust:
  - H_2 — $E_{bind}/k \sim 300$ K → $t_{evap} \sim 3 \times 10^{-7}$ s
  - CO — $E_{bind}/k \sim 900$ K → $t_{evap} \sim 3 \times 10^{6}$ s

- Doubling dust temperature reduces t_{evap} for CO to a small fraction of a second

- Warm dust chemically inefficient — difficult for species to remain on surface long enough to react
- Cold dust chemically efficient, but hard to get reaction products back into gas phase (unless weakly bound)
- BUT: what if dust is cold for a while, then warmed up?
- Expect considerable surface chemistry while dust is cold, products then ejected in gas phase once dust heated
- Strong observational evidence for this: **hot cores**

- Hot cores are small pockets of warm, dense molecular gas surrounding high mass protostars
- Protostellar heating implies high dust temperatures
- Hot cores observed to be chemically rich — particularly notable for high abundances of complex organics

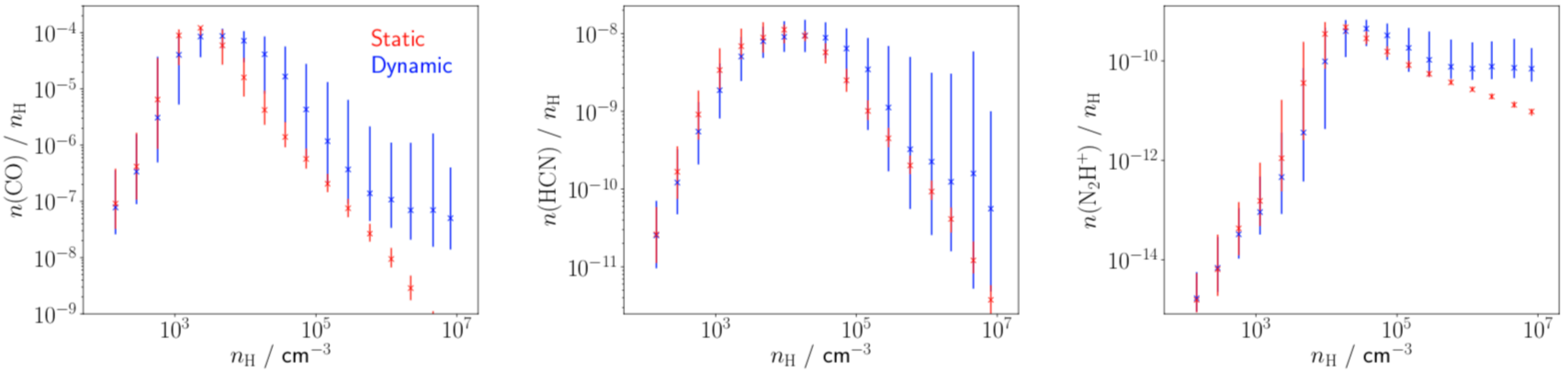


Chen et al. 2023

- In cold regions, difficult to remove molecules from grain surfaces, so at high densities find that some species **freeze-out** of gas phase

- Importance of freeze-out depends on binding energy: e.g. water is frozen out even at low density, but CO only at high density, and H_2 not at all

- Selective depletion of some species at high densities can lead to chemical changes in gas phase



Priestley et al. 2023

- Most important astrochemical role of dust: allows the formation of H_2 in large quantities at GMC densities

- Direct gas-phase formation of H_2 extremely slow — would need longer than age of Universe to convert all H to H_2

- Indirect formation possible via H- ion:

$$H + e^- \rightarrow H^- + \text{photon}$$

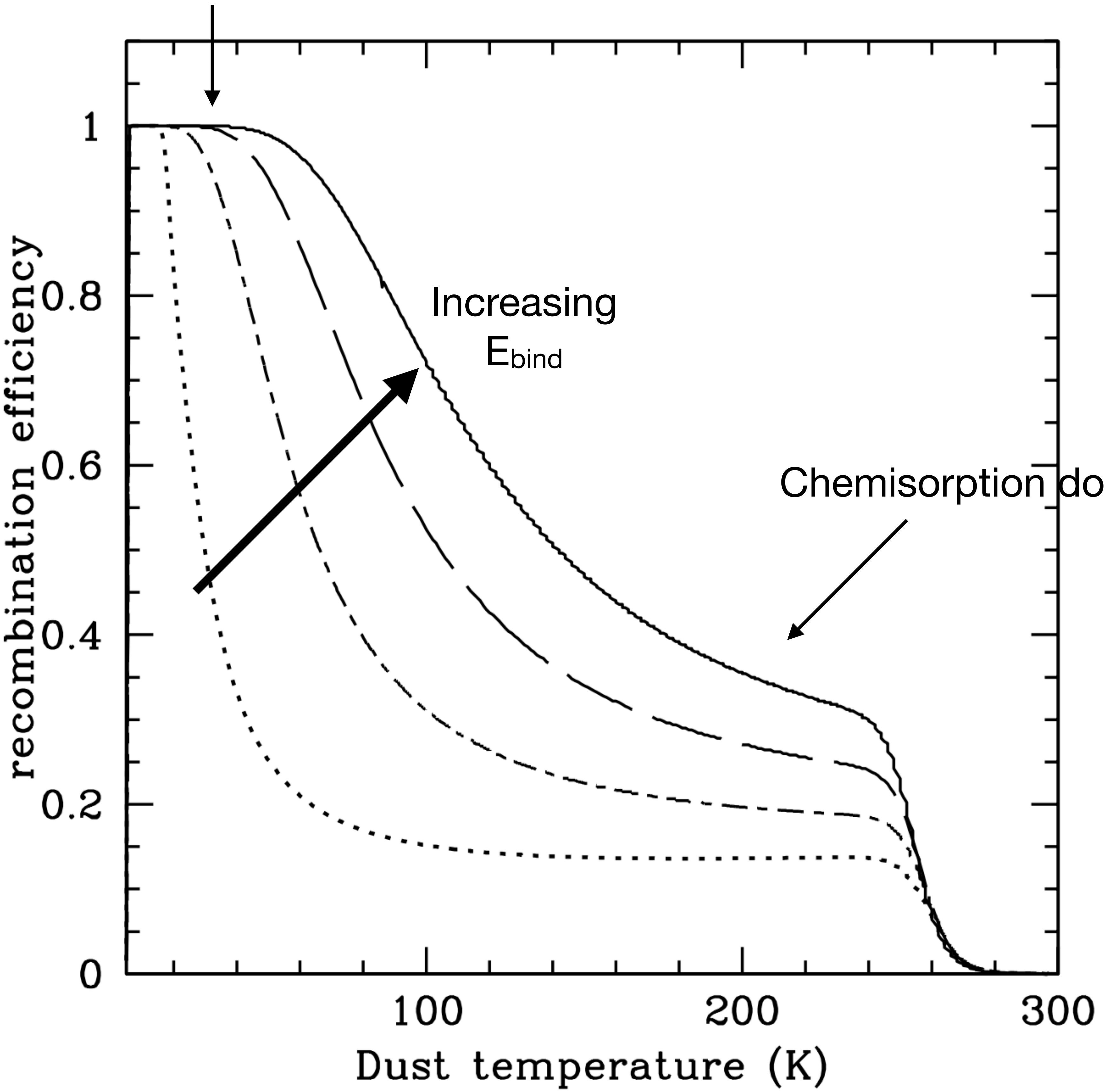
$$H^- + H \rightarrow H_2 + e^-$$

- Initial radiative association reaction slow (albeit ~12 orders of magnitude faster than H + H reaction)

- H^- pathway dominates H_2 formation in metal-free gas
- Limited by slow initiating reaction, dependence on e-
- Once gas recombines, H_2 formation stops
- Difficult to make H_2 fractions larger than ~1% in this way
- Other gas-phase pathways exist (e.g. via H_2^+, or three-body formation) but are less efficient at ISM densities
- Bottom line: gas-phase formation of H_2 ineffective

- Most H_2 in ISM forms via a grain surface reaction
- Formation efficiency ~ 1 for cold dust
- Sticking probability ~ 1 for cold gas
- To a first approximation, every H atom that collides with a grain ends up in an H_2 molecule
- H_2 formation rate therefore set by collision rate of H atoms with dust grains, hence by grain properties

Physisorption dominates



Increasing E_{bind}

Chemisorption dominates

Cazaux & Spaans (2004)

- For Milky Way dust, H2 formation rate in cold ISM is:

$$R_{\mathrm{H_2,dust}} \simeq 3 \times 10^{-17} \left(\frac{T}{100}\right)^{1/2} n n_{\mathrm{H}} \, \mathrm{cm^{-3}\, s^{-1}}$$

- Corresponding H_2 formation timescale:

$$t_{\mathrm{form,H_2}} \simeq \frac{1}{3 \times 10^{-17} n} \simeq 10^9 n^{-1} \, \mathrm{yr}$$

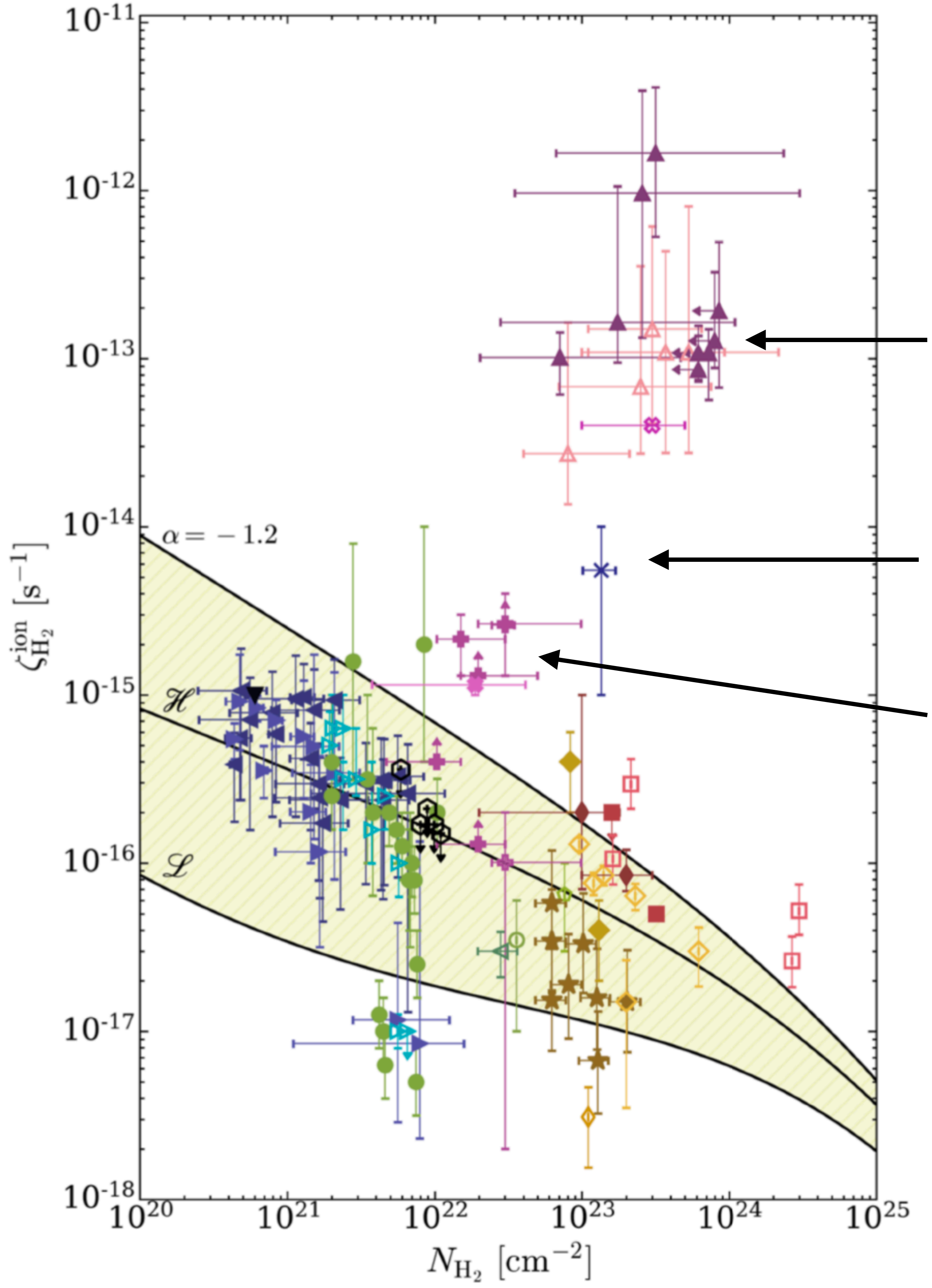
- GMC densities typically exceed 100 cm-3, implying H2 formation timescales of a few Myr

- Supersonic turbulence further accelerates this

Cosmic rays

- Low energy cosmic rays (CRs) also impact ISM chemistry
- Two effects:
    - Primary ionisation: CR collides with atom or molecule and collisionally ionises it
    - Secondary ionisation: high energy electron resulting from primary ionisation causes additional ionisations
- Often don’t distinguish between these processes

- Cosmic ray ionisation rate depends on:
  - Local energy density of low energy cosmic rays
  - Target atom/molecule — cross-section varies
- Low energy CRs lose significant energy while interacting with clouds → ionisation rate depends on N_H
- Short mean free path of low energy CRs in galaxy implies spatial variations in energy density can be large
  - E.g. considerable evidence for elevated energy density, ionisation rate in CMZ



CMZ in NGC 253

MW CMZ

Clouds near SN remnants

Padovani (2023)

- Cosmic rays play important role in initiating chemistry in dense molecular gas
  - Ion-neutral reactions often have no activation energy
  - Neutral-neutral reactions often have activation energy
  - At low T (~10-20 K), ion-neutral reactions much faster
- Cosmic rays can destroy molecules at high A_V, where UV photodissociation is ineffective
  - Efficient destruction of CO inside GMCs when CR ionisation rate is high?

Summary

- Gain considerable insight from treating reactions semi-classically, writing rate as product of collision rate, reaction probability
- Collision rate depends on long-range interaction
  - Strong interactions (e.g. Coulomb) yield higher rates that decrease with increasing T
  - Weak interactions yield smaller rates that remain constant or increase with T

- Often good approximation to take $p_{react} = 1$
- Important cases when this is not true:
    - Endothermic reactions — $p_{react} = 0$ if insufficient energy
    - Radiative association, recombination etc. — chance of emitting photon in any given collision small, $p_{react} << 1$
- Photoionisation, photodissociation play important role in ISM chemistry at low A_V, but negligible at high A_V
- Grain surface chemistry mostly only important at high densities (freeze out, desorption in hot cores)
    - **Major exception**: H_2 formation on grain surfaces

- CR ionisation also plays important role in ISM chemistry
- Dominated by low energy CRs
  - Spatial variation **within** clouds
  - Spatial variation **between** clouds
- Modelling of this in large simulations often still quite crude

Online resources

(A very incomplete list…)

- Grackle
  - Chemistry & cooling library
  - Fast, stable, but limited chemistry (H, H_2)
  - https://grackle.readthedocs.io/en/latest/
- KROME
  - Package for generating routines to solve rate equations
  - Comes with many pre-packaged networks
  - http://kromepackage.org

- Meudon PDR code
  - Photodissociation region chemistry, cooling in slab geometry
  - Very comprehensive list of physical processes
  - https://pdr.obspm.fr
- UCLCHEM
  - Gas-grain code for astrochemical modelling
  - Extremely extensive set of reactions
  - Needs radiation field as input
  - https://uclchem.github.io

- Note: many other PDR and astrochemistry codes available — these are just a couple of examples to get you started

- Reaction rate databases —curated compilations of chemical reaction rates:
  - UMIST database (https://umistdatabase.uk)
  - KIDA (https://kida.astrochem-tools.org)
  - Ewine van Dishoeck's compilation of photoionisation, photodissociation cross-sections:
    - https://home.strw.leidenuniv.nl/~ewine/photo/