INTERSTELLAR MEDIUM

- Stefano Bovino -

Collisions and chemistry in the ISM

Collisions

Govern many key processes in the ISM

- Distribute energy
- Ionize the medium (collisional ionization)
- Recombination (radiative recombination)
- Excitation and loss of energy via de-excitation
- Govern chemistry (reactions)
- Gas-dust interaction and grain-grain

Collisions: different types of

- **Elastic collisions**: only kinetic energy is exchanged (momentum)
  - viscosity (resistance to flow)
  - electrical conductivity (resistance to electrical currents)
  - thermal conductivity (resistance to heat flow)

- **Inelastic collisions**: kinetic and internal energy is exchanged
  - excitation/de-excitation processes

- **Reactive collisions**: chemical structure changes
  - (control chemistry of ISM)

Collisions: rate coefficients

- It is important to become comfortable with the definition of collisional rate or collisional rate coefficients
- How these depend on temperature

Collisions: rate coefficients

$$f(v)dv = 4\pi v^2 \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu v^2}{2k_B T}\right) dv$$

$$k(T) = \langle \sigma v \rangle = 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \int_0^\infty \sigma(v) v^3 \exp\left(-\frac{\mu v^2}{2k_B T}\right) dv$$

Collisions: different types of

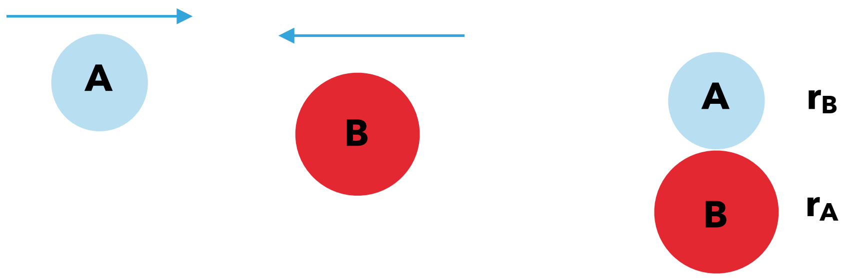
- Neutral-neutral
- Charged-neutral
- Charged-charged

Depends on the type of interaction (long-range)

Neutral-neutral

No attractive forces (hard spheres interaction)

$$\sigma = \pi (r_A + r_B)^2$$



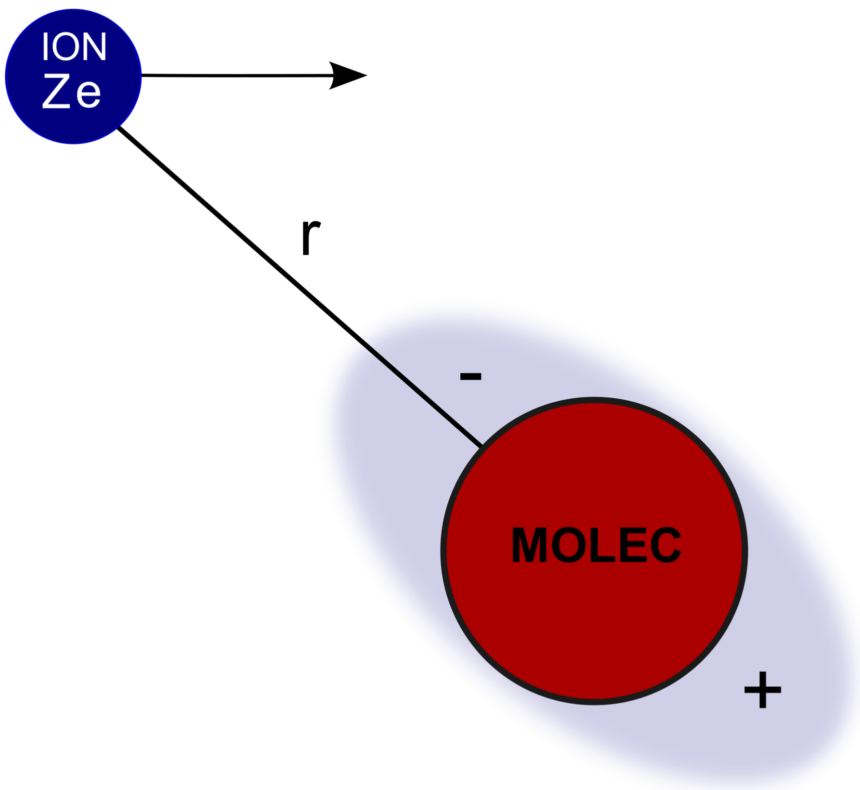
$$k = \sigma v_{AB} = \pi (r_A + r_B)^2 \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2}$$

Charged-neutral

Polar molecules have a permanent dipole moment
Charges can induce a dipole moment in non-polar molecules

ION-NEUTRAL INTERACTION

$$U(r) = -\frac{\alpha Z^2 e^2}{2r^4}$$

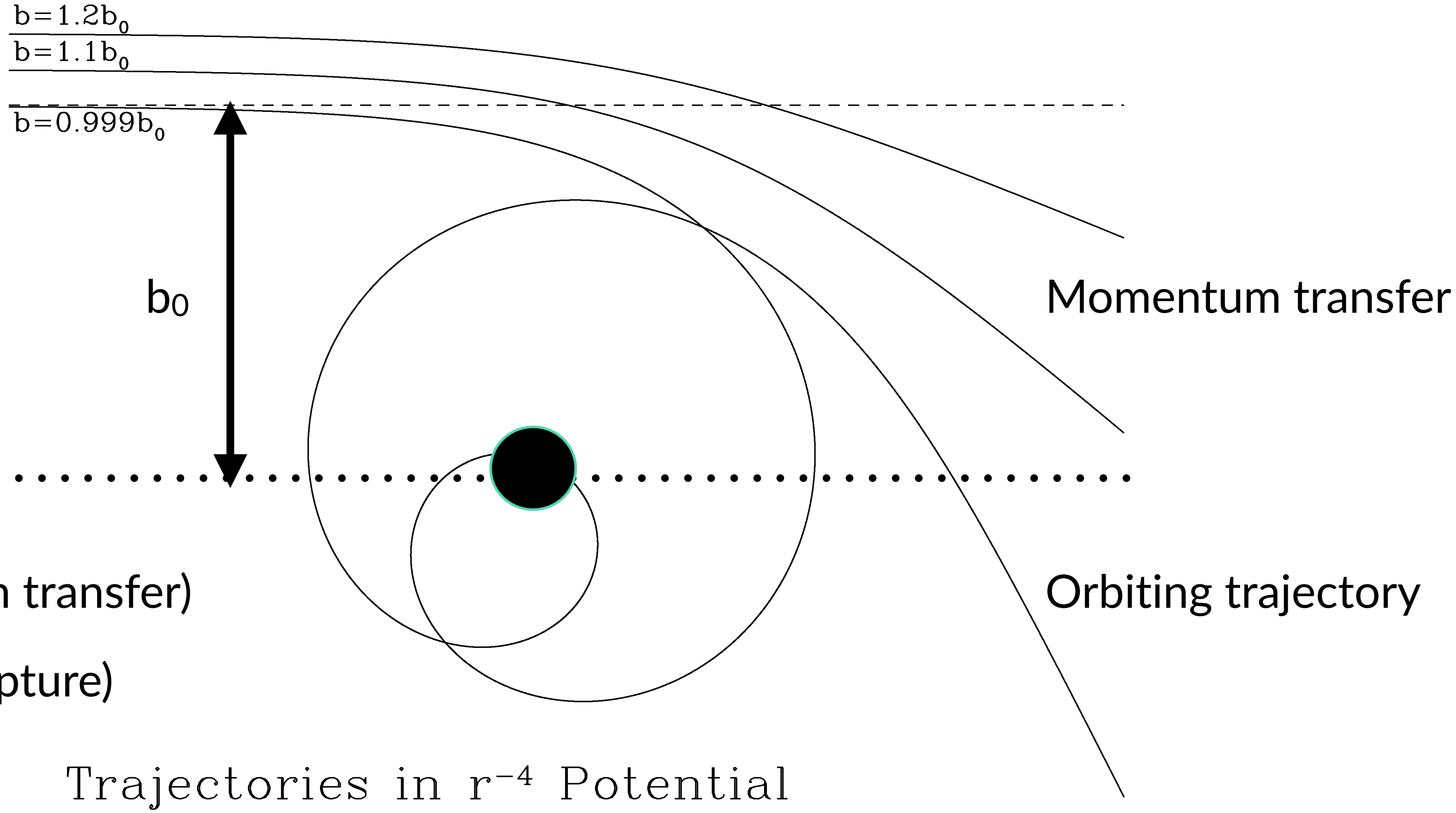


Polarizability indicates how easy the molecule electrons can be displaced by an electric field

Charged-neutral

Polar molecules have a permanent dipole moment
Charges can induce a dipole moment in non-polar molecules

$$U(r) = -\frac{\alpha Z^2 e^2}{2r^4}$$



$b > b_0$ No collision (momentum transfer)

$b < b_0$ Orbiting trajectories (capture)

Charged-neutral

$$b_0^2 = \sqrt{\frac{4\alpha e^2}{\mu v^2}}$$

$$\sigma = \pi b_0^2$$

Polarizability indicates how easy the molecule electrons can be displaced by an electric field

Charged-neutral

$$k = \sigma v = \pi b_0^2 v = 2\pi e v \sqrt{\frac{\alpha}{\mu v^2}}$$

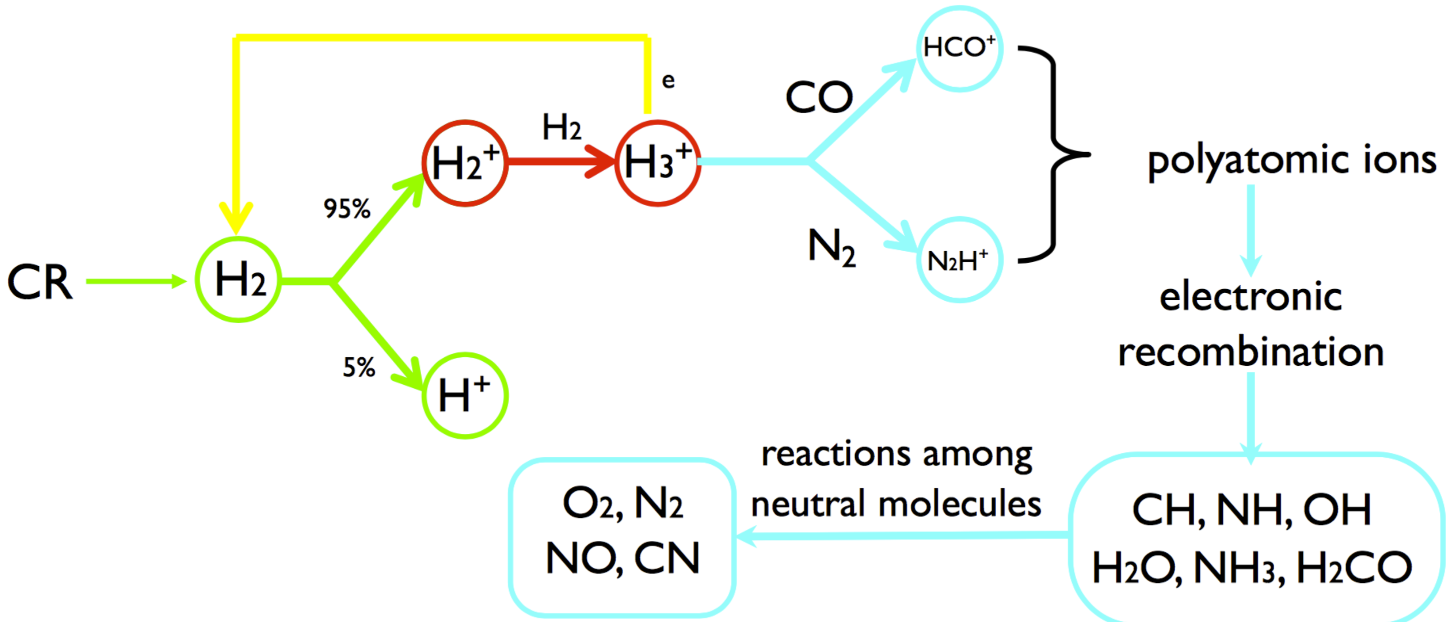
$$k = k_L = 2\pi e \sqrt{\frac{\alpha}{\mu}}$$

Charged-neutral

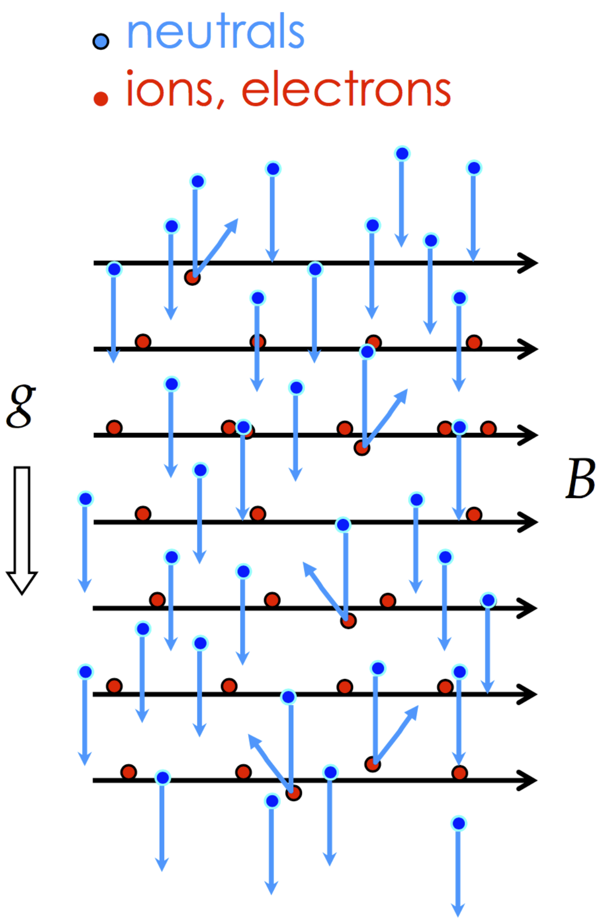
Example: $H_2^+ + H_2 \rightarrow H_3^+ + H$

- a "cornerstone" reaction in molecular clouds:

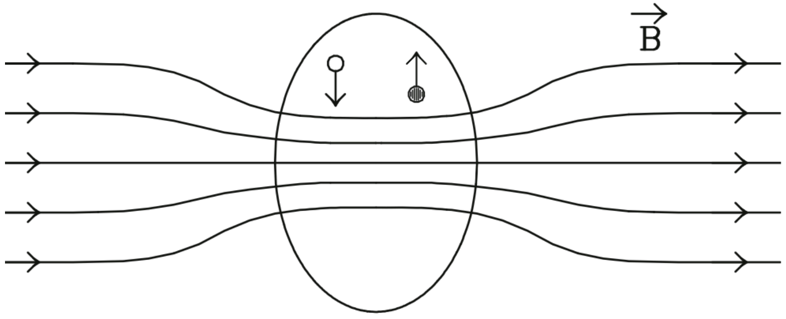
H_2 ionized by photons, CRs, X-rays, reacts with ambient H_2



Charged-neutral (momentum transfer)



- Charged particles (ions and electrons)are "attached" to B-field lines.
- Neutrals feel the gravitational field and "slip" trough the B-field.
- However neutrals collide with ions → the B-field acts on neutrals indirectly through collisions (ambipolar diffusion).
- The process is controlled by elastic collisions (momentum-transfer cross section).



Charged-charged interaction

- **Collisional ionization**: when the gain in kinetic energy is larger than the ionization potential of the collider.
- **Inelastic collision electrons-ions:** responsible for much of the line radiation emitted by hot gas, from H II regions to supernova remnants
- How electrons distribute their energy among other gas particles (e.g. **photoelectric heating**)

General comments on kinetics

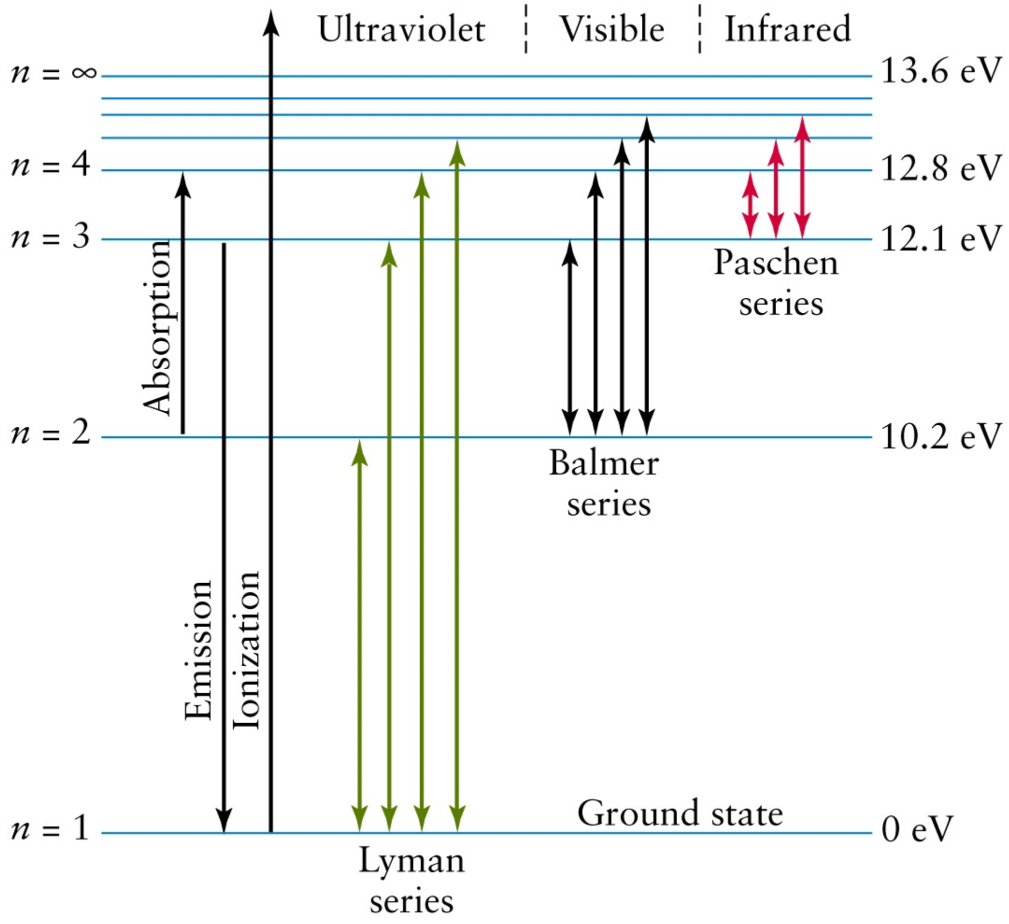
1. A + B → P (two-body reactions)
2. A + photon → P (photo-reactions)
3. A + B + C → P (three-body reactions)

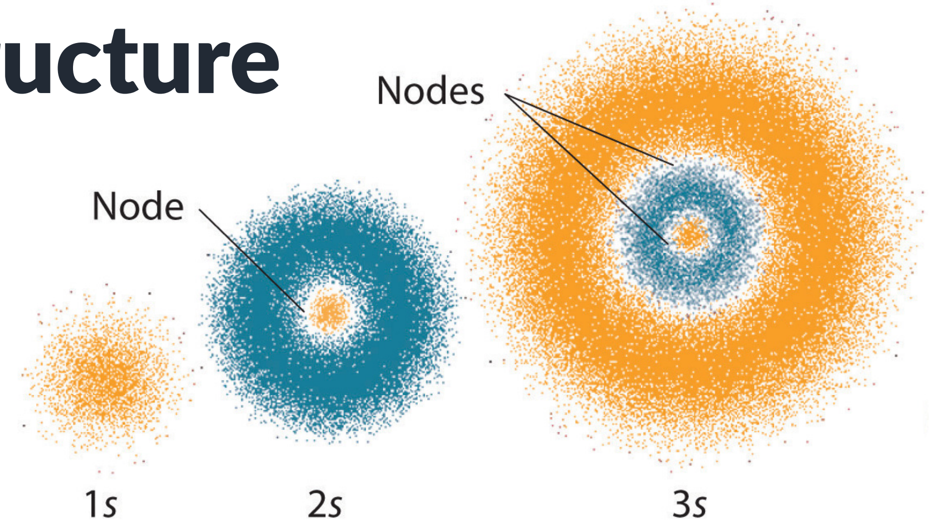
$$\frac{dn_{\mathrm{P}}}{dt} = k(T)n_{\mathrm{A}}n_{\mathrm{B}} \qquad (1)$$ units of $k(T)$: $\mathrm{cm^3\ s^{-1}}$

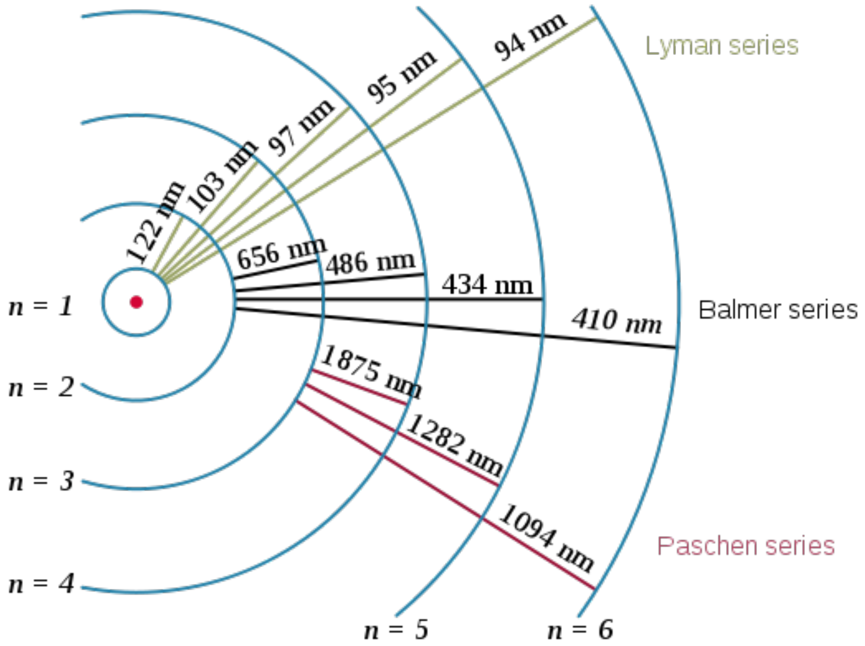
$$\frac{dn_{\mathrm{P}}}{dt} = k(T)n_{\mathrm{A}} \qquad (2)$$ units of $k(T)$: $\mathrm{s^{-1}}$

$$\frac{dn_{\mathrm{P}}}{dt} = k(T)n_{\mathrm{A}}n_{\mathrm{B}}n_{\mathrm{C}} \qquad (3)$$ units of $k(T)$: $\mathrm{cm^6\ s^{-1}}$

Quick (re)-view of the atom structure







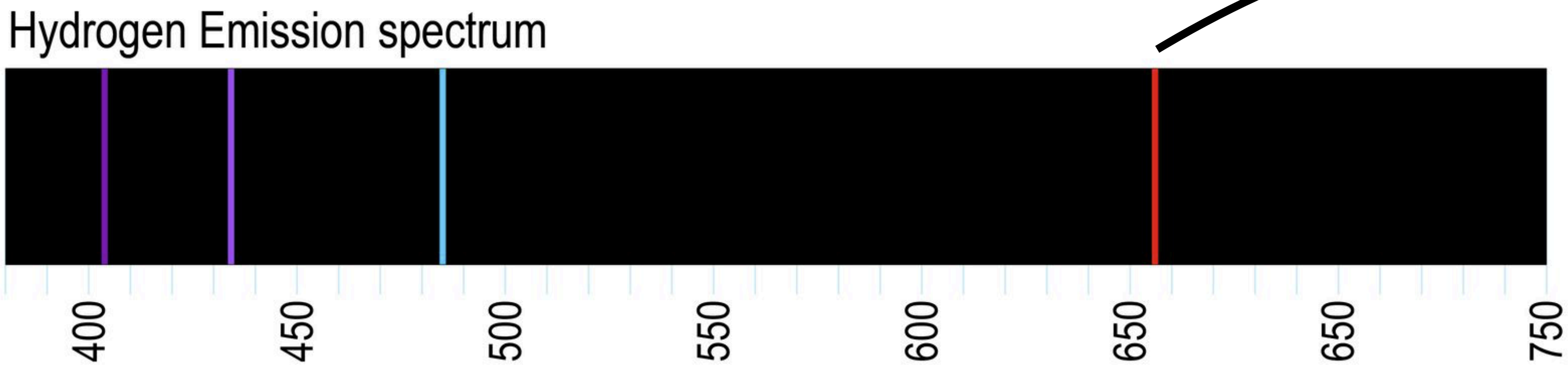
$$E_n = -\left(\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\right)\frac{1}{n^2} \qquad n = 1, 2, \ldots$$

H-alpha line (orange) (n=3-> n=2)

Balmer represents the strongest line

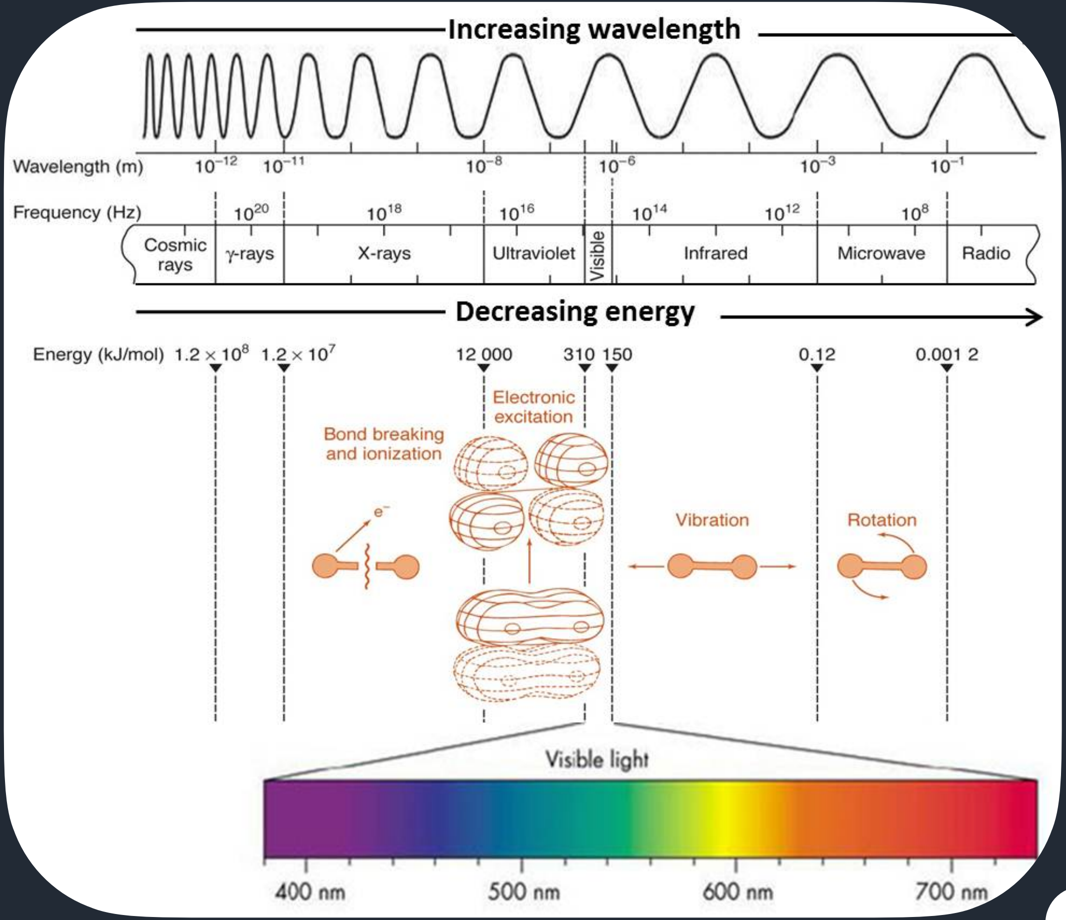
UV radiation ionize H which then recombines

Produce a cascade between the levels (electron jumps through levels)



Balmer line (656 nm)

Molecules: adding degrees of freedom

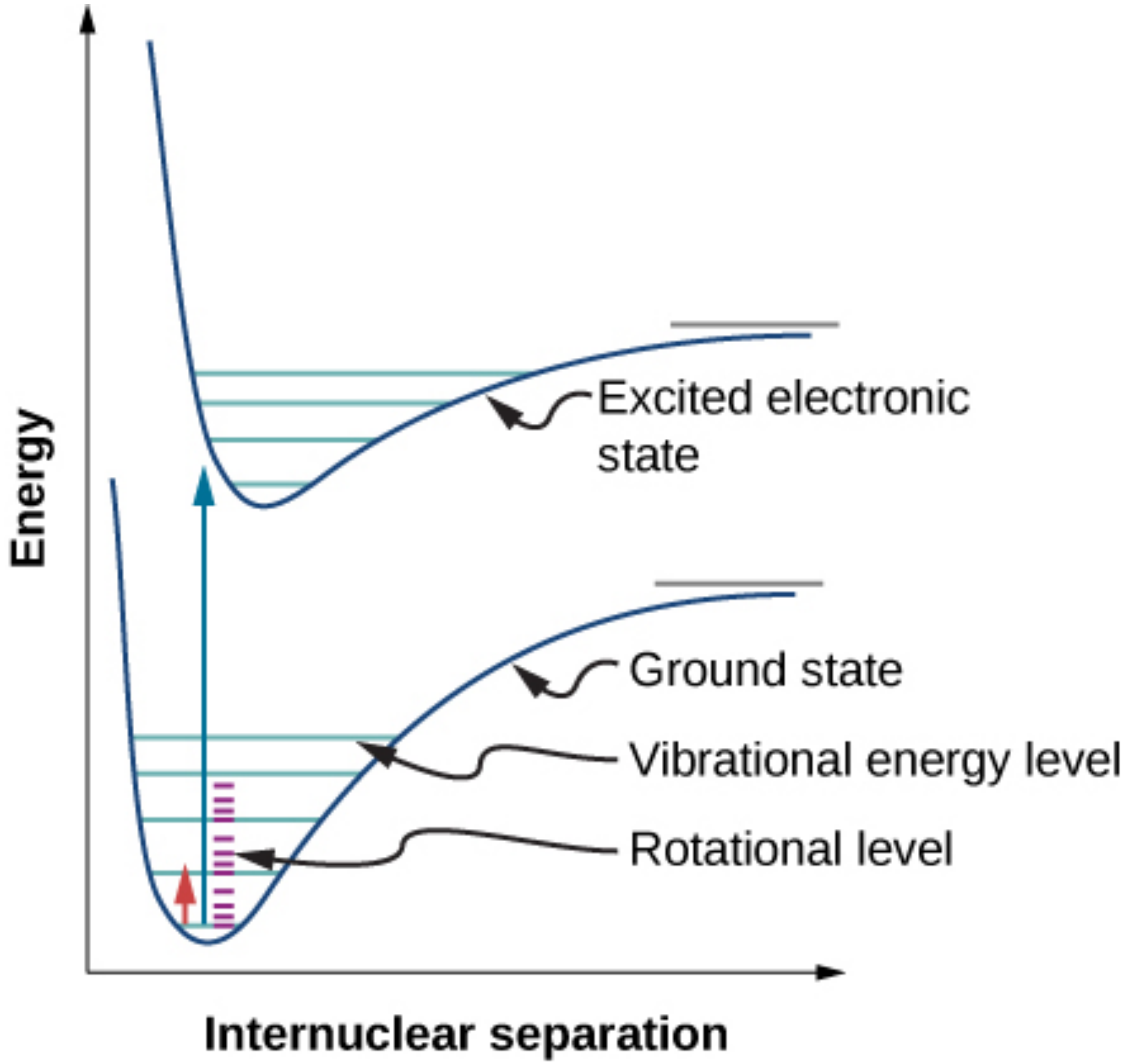


Energy

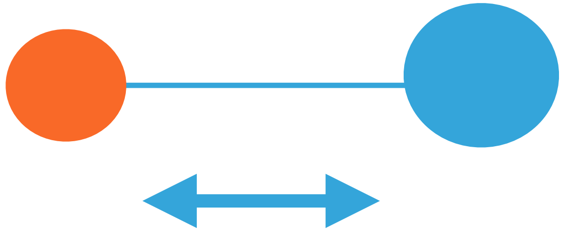
$$E_{tot} \sim E_{el} + E_{vib} + E_{rot}$$

Order of magnitudes

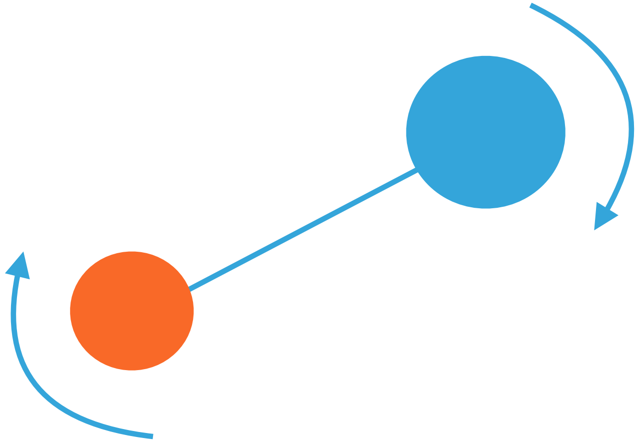
Transitions	Energy (eV)	Temperature (K)	λ
Electronic	4 eV	40,000 K	visible and UV
Vibrational	0.1 eV	1,000 K	NIR/MIR ($\sim$2-20μm)
Rotational	$<$ 0.01 eV	$<$ 100 K	mm/submm

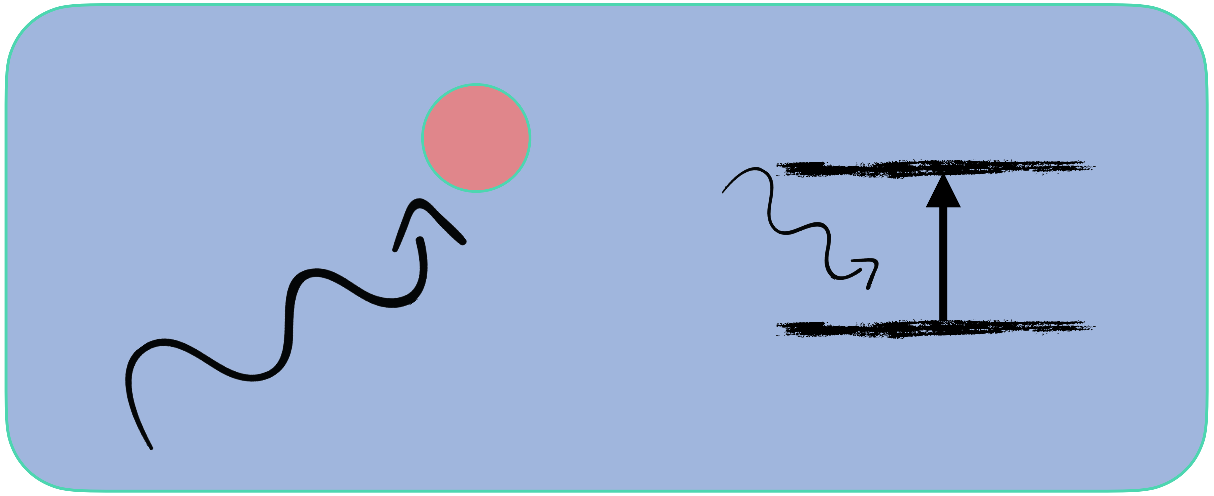


$$E_{vib} = \hbar\omega(v + \frac{1}{2})$$

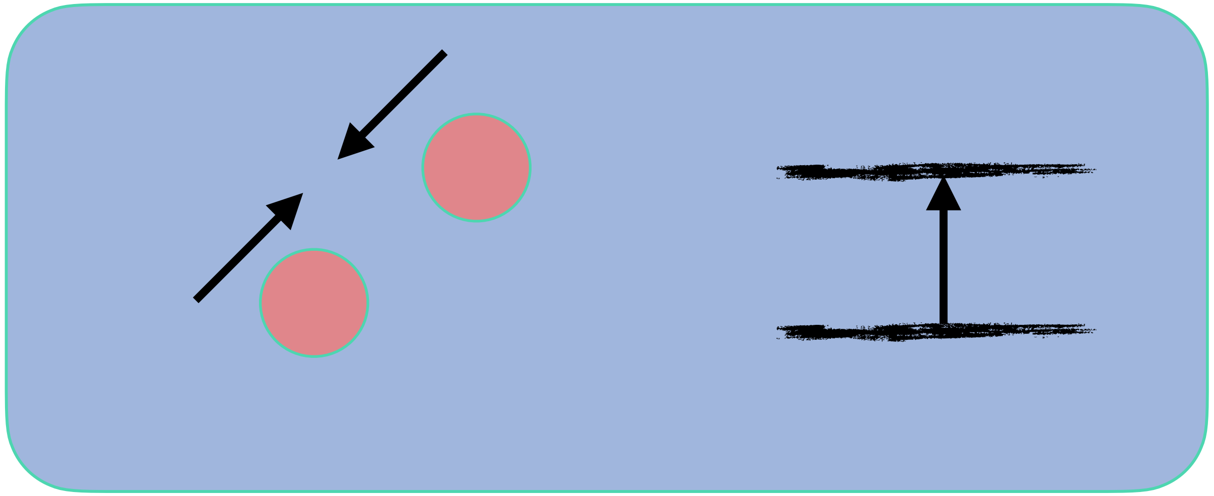


$$E_{rot} = BJ(J+1)$$

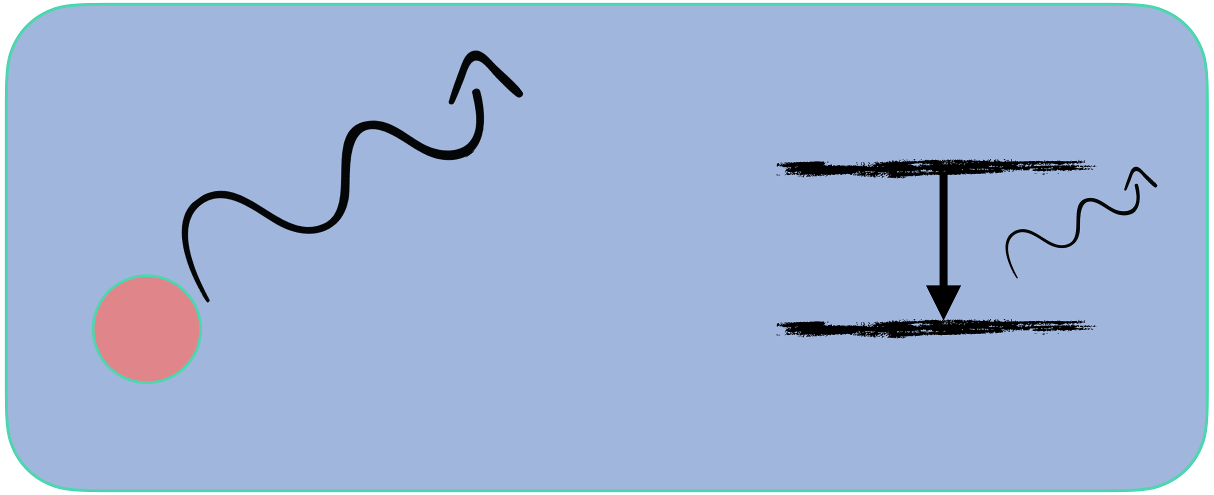




RADIATIVE EXCITATION

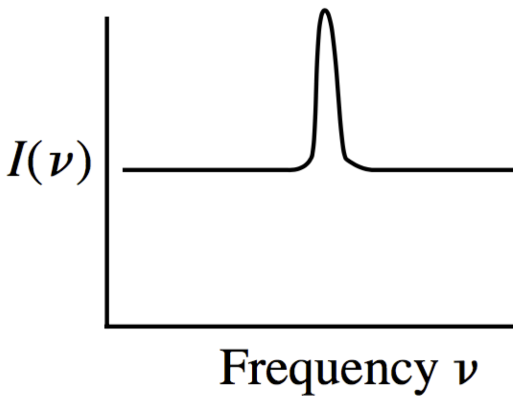


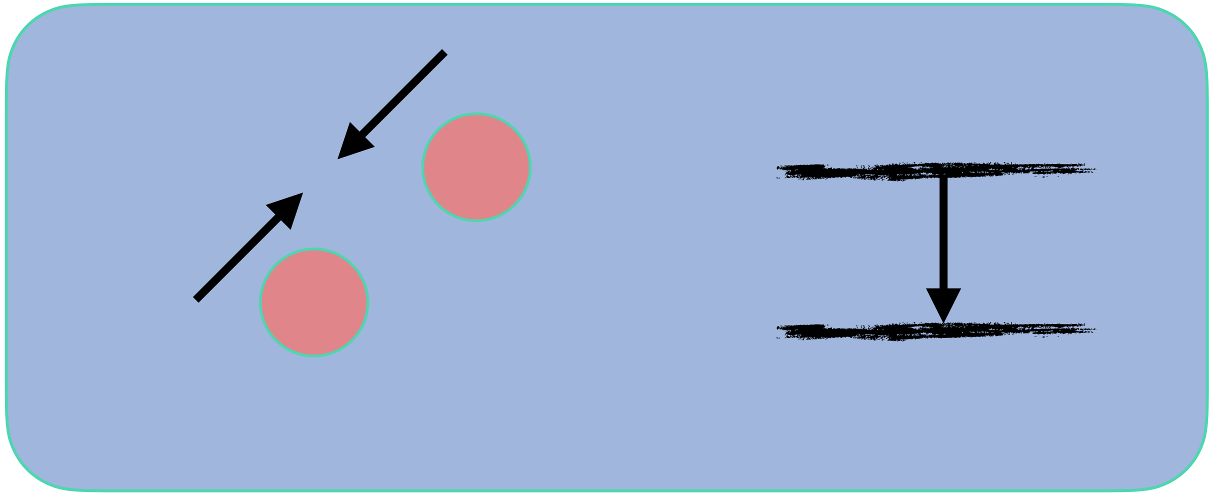
COLLISIONAL EXCITATION



RADIATIVE DE-EXCITATION
(spontaneous)

(a) Emission line

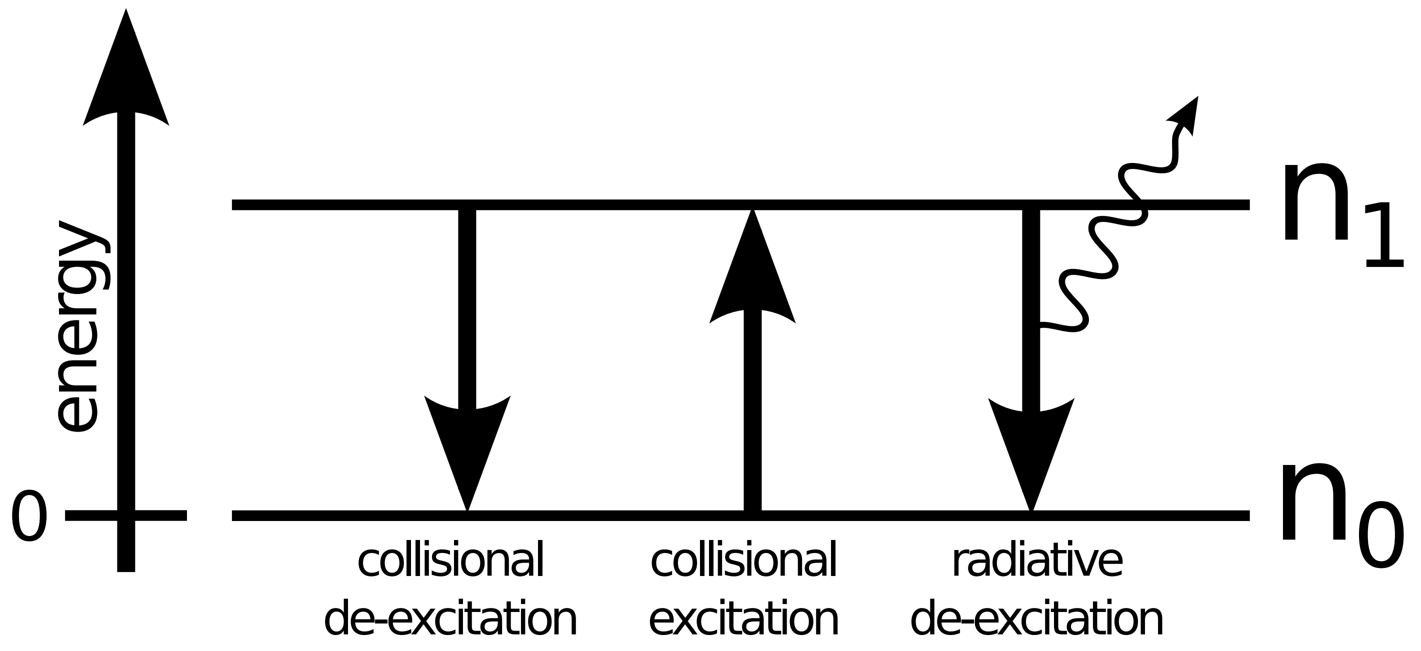


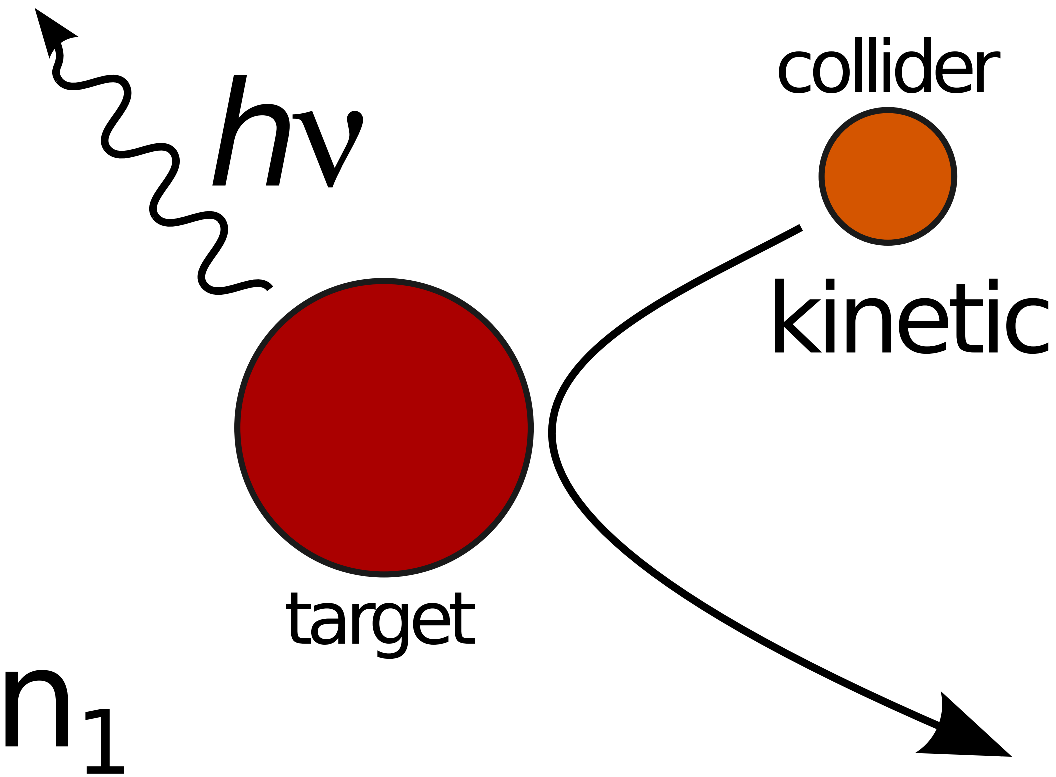


COLLISIONAL DE-EXCITATION

Collisions: a sketch

- Radiative processes:
  - Radiation by atoms/molecules/ions excited by collisions transfer part of the kinetic energy into radiation

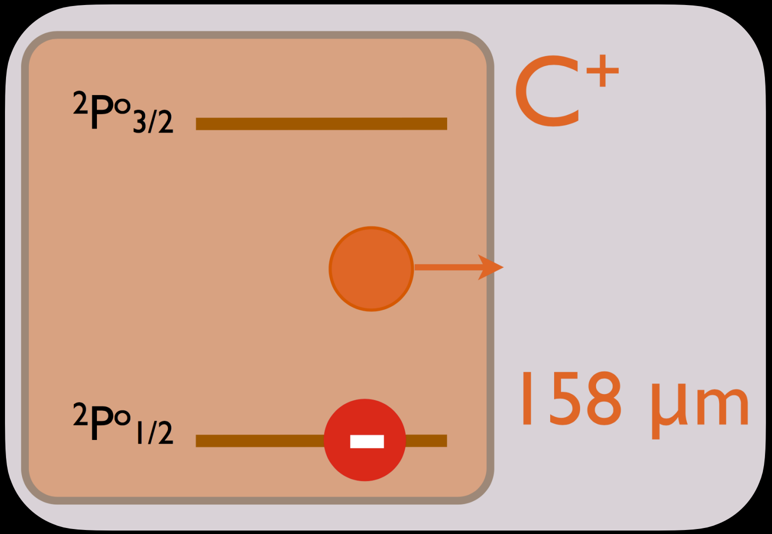


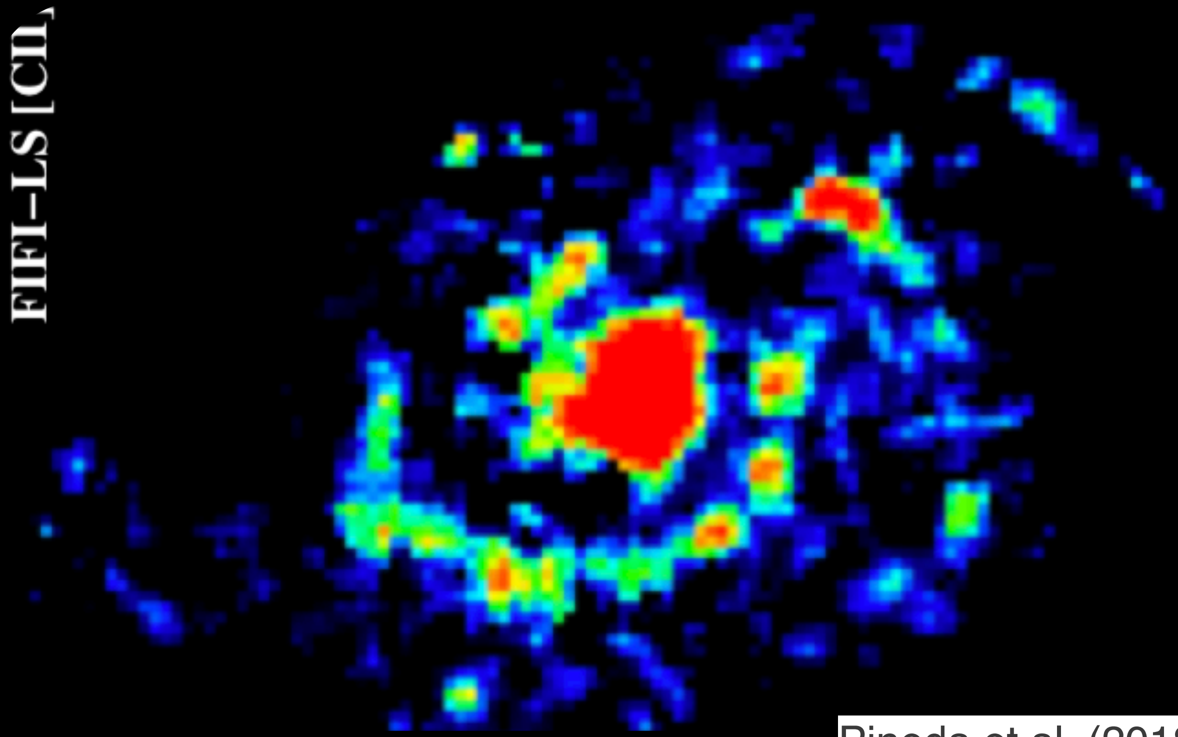


- electronic transitions → Vis/UV (Hubble Space Telescope)
  - H_2 + atoms observed directly
  - large oscillator strengths[1], minor species can be detected
- vibrational transitions → IR (Spitzer, Herschel)
  - both gas and solids observed
  - ices, silicates, oxides, PAH mid-far IR
  - molecules without permanent dipole moment (e.g. H_3^+, CH_4, CO_2)
  - moderate oscillator strengths
- rotational transitions → sub-mm (Herschel, ALMA)
  - bulk of interstellar molecules
  - high sensitivity to low abundances (down to 10^{-11} x_H)

Transitions	Energy (eV)	Temperature (K)	λ
Electronic	4 eV	40,000 K	visible and UV
Vibrational	0.1 eV	1,000 K	NIR/MIR (~2-20μm)
Rotational	< 0.01 eV	< 100 K	mm/submm

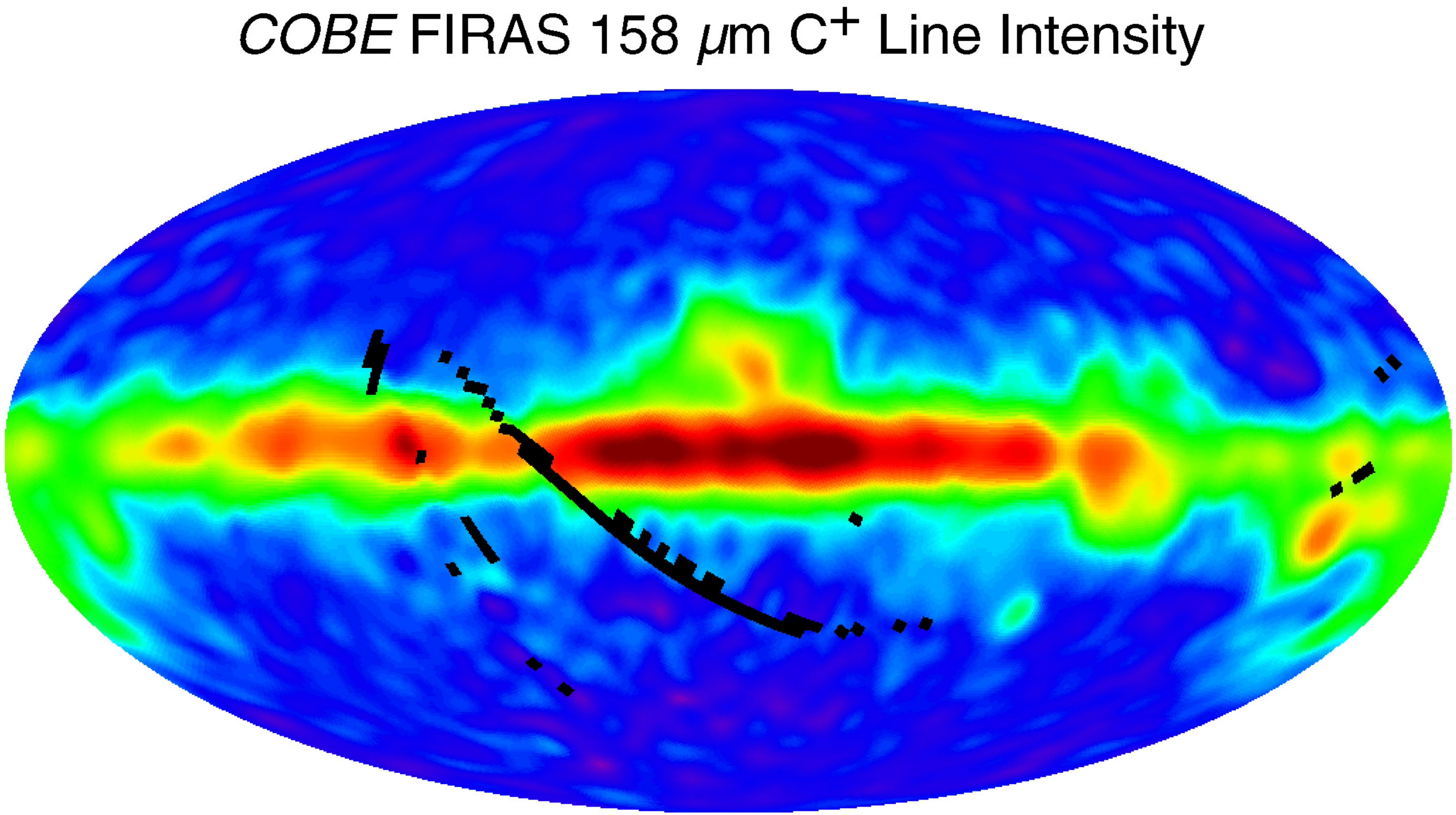
158 micron [CII] transition





Pineda et al. (2018)

158 micron [CII] transition



Interstellar chemistry

Astrochemistry

- Chemistry in the ISM is better known as “Astrochemistry”
- Tielens: “Astrochemistry describes a cosmic dance of the elements in which atoms are constantly reshuffled from one species to another”
- The “dance” is driven by different energy sources (including photons and cosmic rays)

The goal

- It is to study the chemical processes which destroy and form atoms/ molecules relevant to understand the ISM
- Gas phase chemistry

Gas-phase chemical reactions

		Typical rate coefficient ($cm^3\ s^{-1}$)
Bond Formation Processes		
Radiative association	$X + Y \rightarrow XY + h\nu$	$10^{-17} - 10^{-14}$
Grain surface formation	$X + Y{:}g \rightarrow XY + g$	$\sim 10^{-17}$
Associative detachment	$X^- + Y \rightarrow XY + e$	$\sim 10^{-9}$
Bond Destruction Processes		
Photodissociation	$XY + h\nu \rightarrow X + Y$	$10^{-10} - 10^{-8}\ s^{-1}$
Dissociative recombination	$XY^+ + e \rightarrow X + Y$	$10^{-7} - 10^{-6}$
Collisional dissociation	$XY + M \rightarrow X + Y + M$	$\sim 10^{-26}\ cm^6\ s^{-1}$
Bond Rearrangement Processes		
Ion–molecule exchange	$X^+ + YZ \rightarrow XY^+ + Z$	$10^{-9} - 10^{-8}$
Charge–transfer	$X^+ + YZ \rightarrow X + YZ^+$	10^{-9}
Neutral–neutral	$X + YZ \rightarrow XY + Z$	$10^{-11} - 10^{-9}$

Photochemistry

- Photons permeate the ISM (diffuse)
- Are then the dominant destruction agent for small molecules
- Typical bonding energies are 5-10 eV (~3000 Angstrom)

Photochemistry

1. A + B → P (two-body reactions)
2. A + photon → P (photo-reactions)
3. A + B + C → P (three-body reactions)

$$\frac{dn_{\mathrm{P}}}{dt} = k(T)n_{\mathrm{A}}n_{\mathrm{B}} \quad (1) \quad \text{units of } k(T)\text{: cm}^3\text{ s}^{-1}$$

$$\frac{dn_{\mathrm{P}}}{dt} = k(T)n_{\mathrm{A}} \quad (2) \quad \text{units of } k(T)\text{: s}^{-1}$$

$$\frac{dn_{\mathrm{P}}}{dt} = k(T)n_{\mathrm{A}}n_{\mathrm{B}}n_{\mathrm{C}} \quad (3) \quad \text{units of } k(T)\text{: cm}^6\text{ s}^{-1}$$

Different mechanisms

- Direct photodissociation (H_2O)
- Predissociation (CO, N_2)
- Two-step dissociation (H_2)

- Continuum absorption

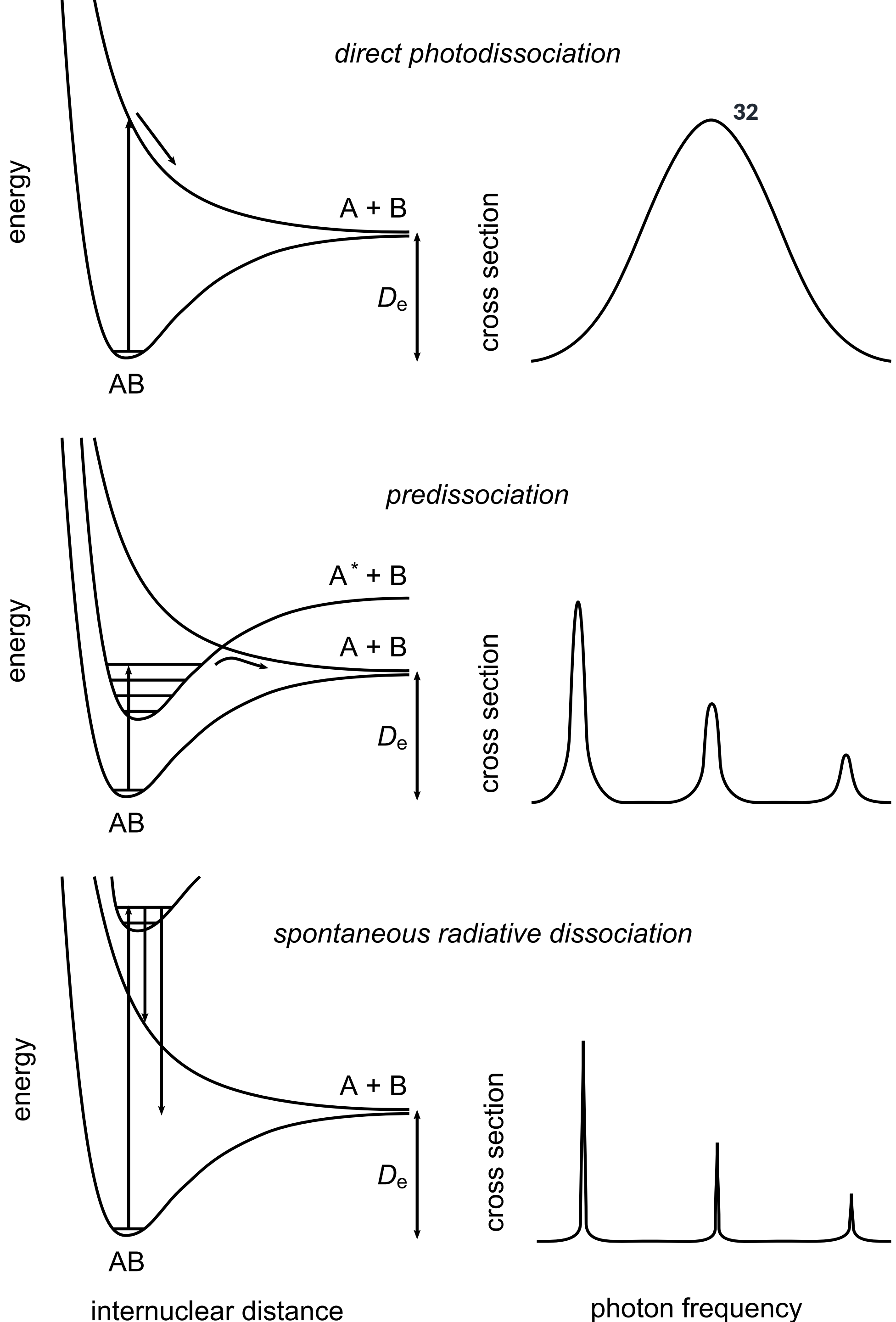
Cross-section — Intensity

$$k_{\rm pd}^{\rm cont} = \int_{\lambda_{\rm H}}^{\lambda_{\rm d}} \sigma(\lambda) I(\lambda) d\lambda \ \ {\rm s}^{-1}$$

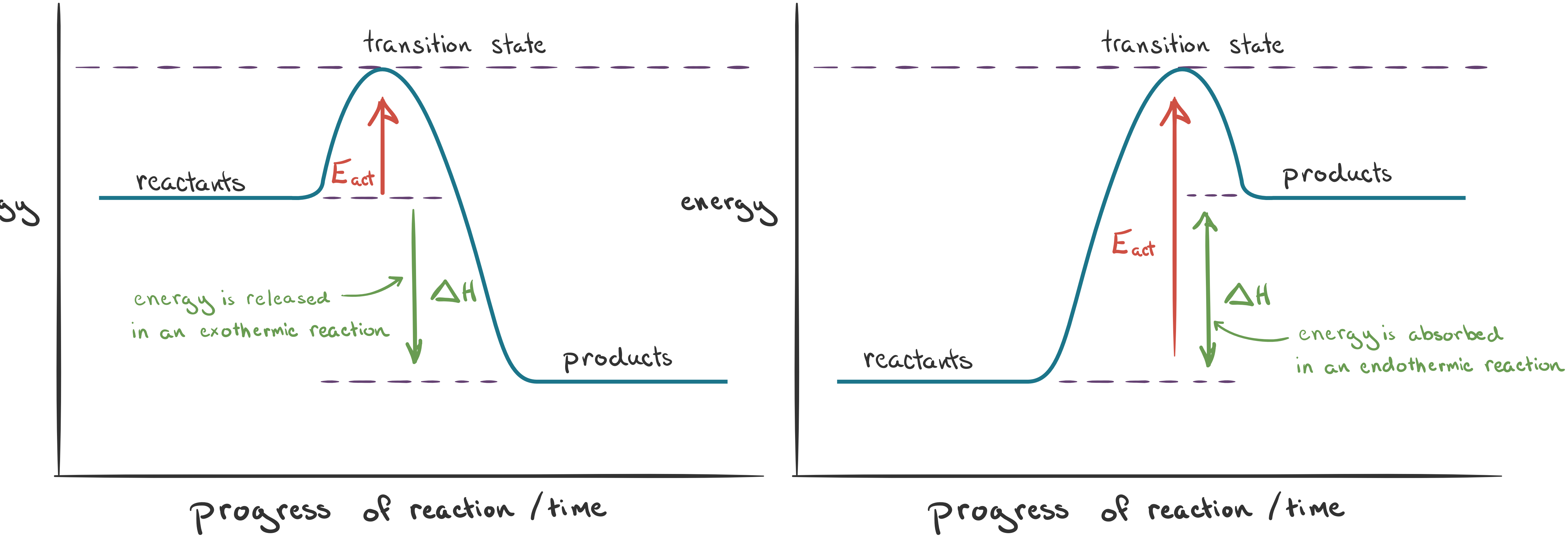
- Line absorption for one line (one needs to sum over all the transitions)

$$k_{\rm pd}^{\rm line} = \frac{\pi e^2}{mc^2} \lambda_{u\ell}^2 f_{u\ell} \eta_u x_\ell I(\lambda_{u\ell}) \ \ {\rm s}^{-1}$$

oscillator strength — Dissociation probability — Population of the lower level l



Neutral-neutral



$$A + B \leftrightarrow C + D + \Delta E$$

Neutral-neutral

Quite often reactions with barrier

A small barrier of 1000 K makes a reactions prohibitive at 100 K typical for diffuse ISM

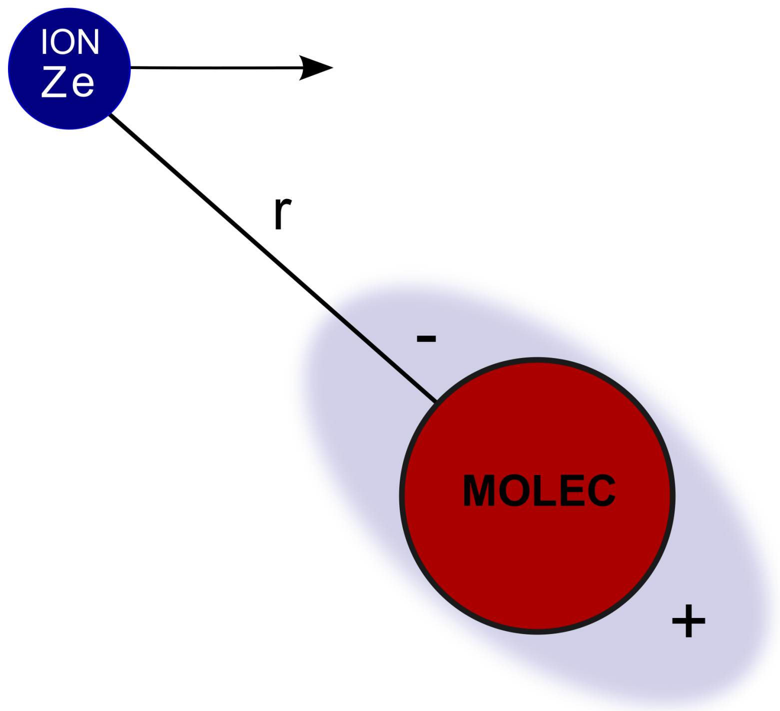
These reactions are important when the gas is warm:

- Stellar ejecta
- Hot cores
- Dense PDR
- Shocks

Ion-neutral reactions

Exothermic ion-neutral reactions are very rapid
Strong polarization-induced interaction potential

ION-NEUTRAL INTERACTION



$$\mu_D^{\text{induced}} = \alpha E$$

$$U(r) = -\frac{\alpha Z^2 e^2}{2r^4}$$

Long-range attractive potential

Polarizability indicates how easily the molecule electrons can be displaced by an electric field.

Ion-neutral reactions

1. Most of the times independent on T
2. Highly exothermic
3. Rate coefficient of the order of 10^{-9} cm^3 s^{-1}
4. A small amount of ionization can be very effective in driving interstellar chemistry
5. Proton transfer reactions from one species to another are of particular relevance

Examples

Table 4.4 *Neutral–neutral reactions* [a]

reaction	α	β	γ
$H_2 + O \rightarrow OH + H$	9.0(−12)	1.0	4.5(3)
$H + OH \rightarrow O + H_2$	4.2(−12)	1.0	3.5(3)
$H_2 + OH \rightarrow H_2O + H$	3.6(−11)		2.1(3)
$H + H_2O \rightarrow OH + H_2$	1.5(−10)		1.0(4)
$H + O_2 \rightarrow OH + O$	3.7(−10)		8.5(3)
$OH + O \rightarrow O_2 + H$	4.0(−10)		6.0(2)
$H_2 + C \rightarrow CH + H$	1.2(−9)	0.5	1.4(4)
$H + CH \rightarrow C + H_2$	1.2(−9)	0.5	2.2(3)
$C^+ + H_2 \rightarrow CH^+ + H$	9.4(−12)	1.25	4.7(3)

[a] Reaction rates of the form $k = \alpha (T/300)^\beta \exp[-\gamma/kT]$.

Table 4.7 *Ion–molecule reactions*

reaction	α
$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1 (–9)
$H_3^+ + O \rightarrow OH^+ + H_2$	8.0 (–10)
$H_3^+ + CO \rightarrow HCO^+ + H_2$	1.7 (–9)
$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	5.9 (–9)
$OH^+ + H_2 \rightarrow H_2O^+ + H$	1.1 (–9)
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	6.1 (–10)
$C^+ + OH \rightarrow CO^+ + H$	7.7 (–10)
$C^+ + H_2O \rightarrow HCO^+ + H$	2.7 (–9)
$CO^+ + H_2 \rightarrow HCO^+ + H$	2.0 (–9)
$He^+ + CO \rightarrow C^+ + O + He$	1.6 (–9)
$He^+ + O_2 \rightarrow O^+ + O + He$	1.0 (–9)
$He^+ + H_2O \rightarrow OH^+ + H + He$	3.7 (–10)
$He^+ + H_2O \rightarrow H_2O^+ + He$	7.0 (–11)
$He^+ + OH \rightarrow O^+ + H + He$	1.1 (–9)

[a] Reaction rates are of the form $k = \alpha$.

Charge-transfer

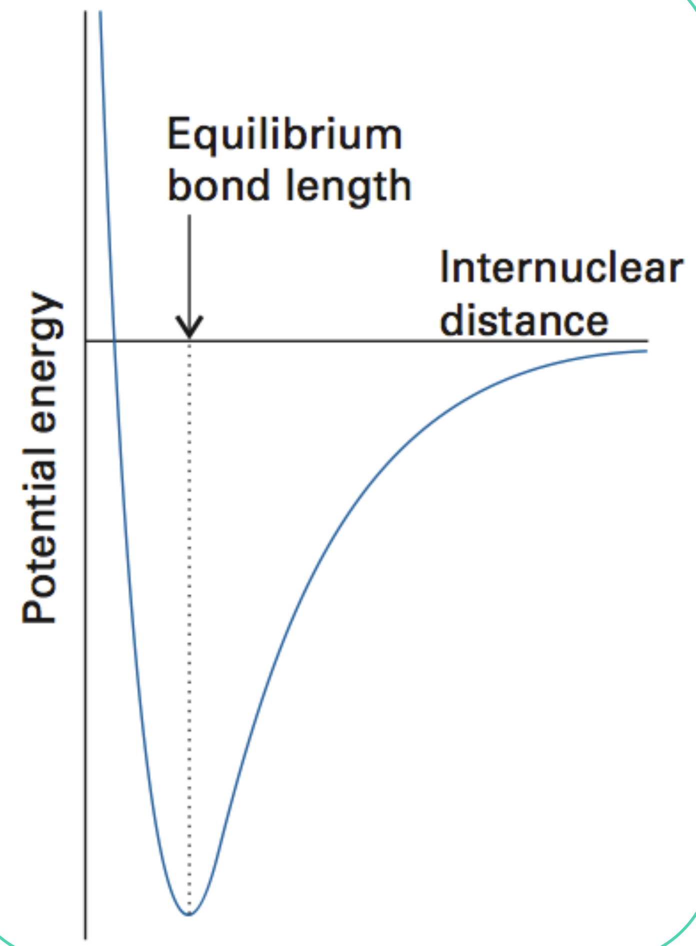
$$A^+ + B \rightarrow A + B^+$$

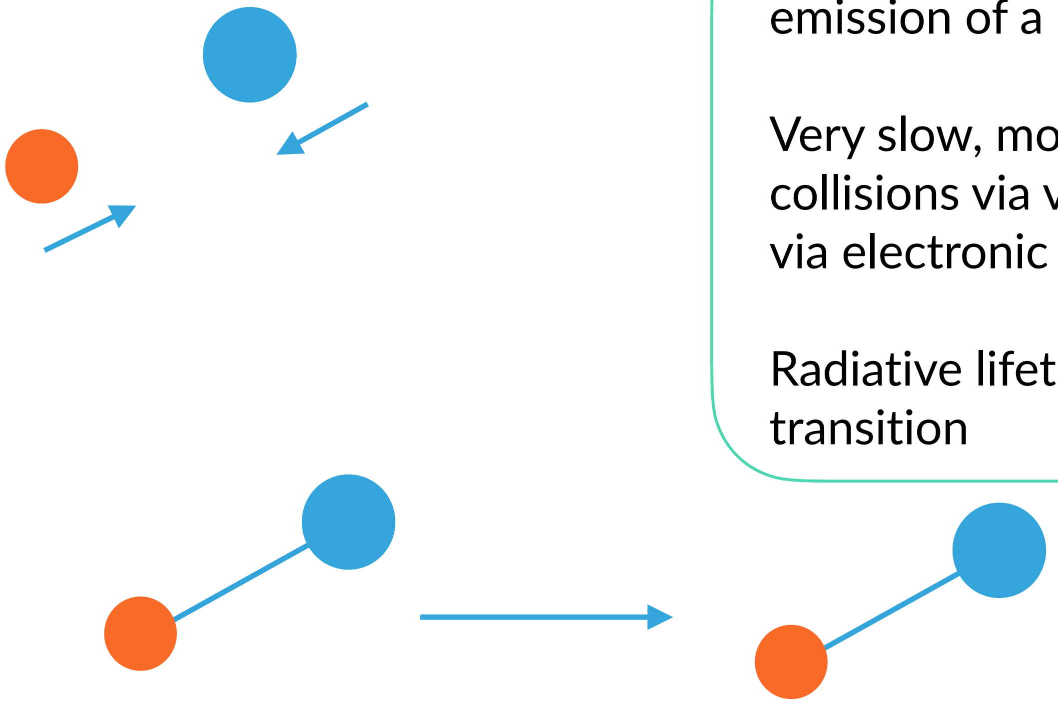
Important in setting the ionization balance

Pretty fast (10^{-9} cm^3 s^{-1})

O + H^+ particular relevant: drives interstellar chemistry making oxygen a reactive species

Radiative association





Collision product is stabilized through emission of a photon.

Very slow, molecules form every 1:10^{10} collisions via vibration, 1:10^5 via electronic

Radiative lifetime 10^{-7} s for an allowed transition

$$X + Y \rightleftarrows XY^* \rightarrow XY + \gamma$$

Dissociative recombination

- Involves capture of an electron by an ion to form a neutral in an excited electronic state that can dissociate

$$XY^{+} + e^{-} \rightarrow X + Y$$

- Fast: typical rate coefficients 10^{-7} cm^3 s^{-1}

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

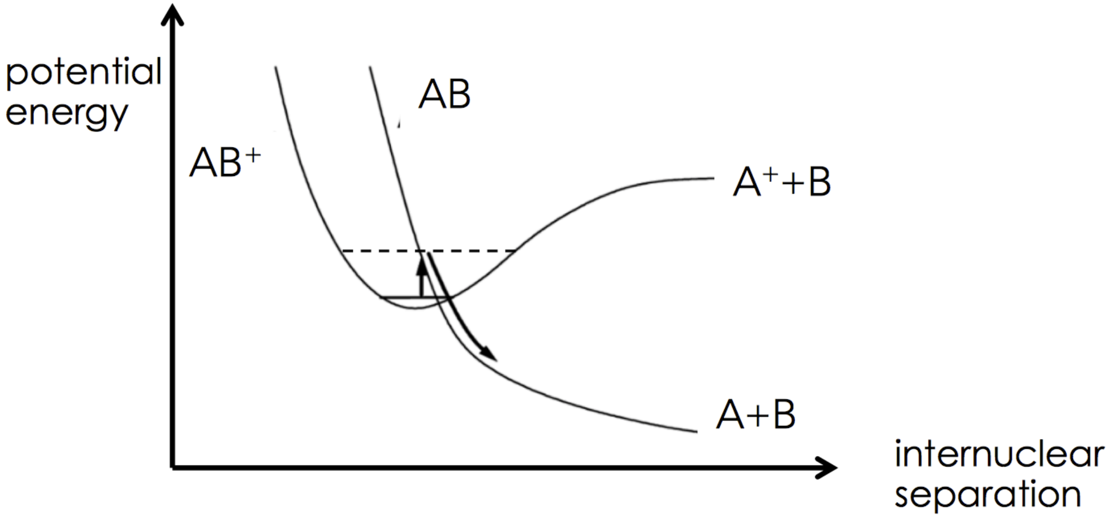


Table 4.11 *Electron recombination reactions*[a]

reaction	α	β
$OH^+ + e \rightarrow O + H$	3.8 (−8)	−0.5
$CO^+ + e \rightarrow C + O$	2.0 (−7)	−0.5
$H_2O^+ + e \rightarrow O + H + H$	2.0 (−7)	−0.5
$H_2O^+ + e \rightarrow OH + H$	6.3 (−8)	−0.5
$H_2O^+ + e \rightarrow O + H_2$	3.3 (−8)	−0.5
$H_3O^+ + e \rightarrow H_2O + H$	3.3 (−7)	−0.3
$H_3O^+ + e \rightarrow OH + H + H$	4.8 (−7)	−0.3
$H_3O^+ + e \rightarrow OH + H_2$	1.8 (−7)	−0.3
$H_3^+ + e \rightarrow H_2 + H$	3.8 (−8)	−0.45
$H_3^+ + e \rightarrow H + H + H$	3.8 (−8)	−0.45
$HCO^+ + e \rightarrow CO + H$	1.1 (−7)	−1.0
$CH^+ + e \rightarrow C + H$	1.5 (−7)	−0.4
$CH_2^+ + e \rightarrow CH + H$	1.4 (−7)	−0.55
$CH_2^+ + e \rightarrow C + H + H$	4.0 (−7)	−0.6
$CH_2^+ + e \rightarrow C + H_2$	1.0 (−7)	−0.55
$CH_3^+ + e \rightarrow CH_2 + H$	7.8 (−8)	−0.5
$CH_3^+ + e \rightarrow CH + H + H$	2.0 (−7)	−0.4
$CH_3^+ + e \rightarrow CH + H_2$	2.0 (−7)	−0.5

[a] Electron recombination rate coefficients are given as $k_{rec} = \alpha(T/300)^{\beta}$.

Other reactions

- Collisional dissociation/association: not very important in astrophysics
- In dense gas near stellar photospheres
- Or in dense circumstellar disks

$$A + B + M \leftrightarrow AB + M$$

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

- Associative detachment: neutral product stabilized through electron emission: important in early Universe

Literature

For a quick and understandable introduction to the chemistry of the ISM:

Tielens: The physics and chemistry of the ISM

For a deeper view see Introduction to Astrochemistry lectures @ stf.astropoyo.cl

Yamamoto: Introduction to Astrochemistry

BASICS TEXTBOOKS

Physics of Atoms and Molecules (Bransden&Joachain)

Physical Chemistry (McQuarrie & Simon)

Molecular Quantum Mechanics (Atkins & Friedman)