INTERSTELLAR MEDIUM

- Stefano Bovino -

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

- Is to study the chemical processes which destroy and form atoms/molecules relevant to understand the ISM
- Gas phase chemistry
- Chemistry on dust grains

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	$X + YZ \rightarrow XY + Z$	$10^{-11} - 10^{-9}$

Gas-phase chemical reactions

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

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

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

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

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 $\rightarrow$ P (two-body reactions)
2. A + photon $\rightarrow$ P (photo-reactions)
3. A + B + C $\rightarrow$ P (three-body reactions)

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

$$\frac{dn_P}{dt} = k(T)n_A \quad (2)$$ units of $k(T)$: s^{-1}

$$\frac{dn_P}{dt} = k(T)n_A n_B n_C \quad (3)$$ units of $k(T)$: $cm^6\ s^{-1}$

Different mechanisms

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

- Continuum absorption

Cross-section Intensity

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

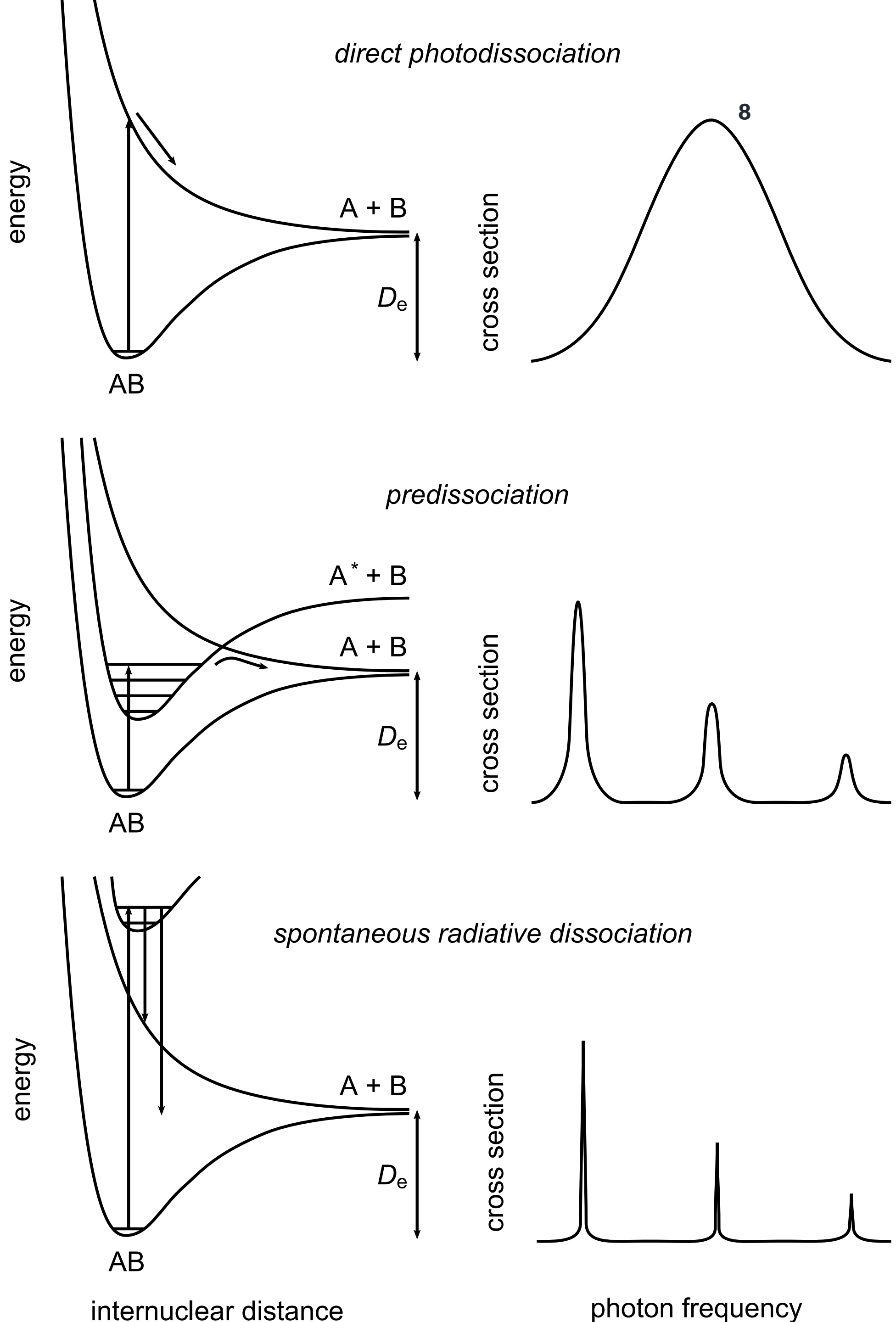
- Line absorption for one line (one needs to sum over all the transitions)

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

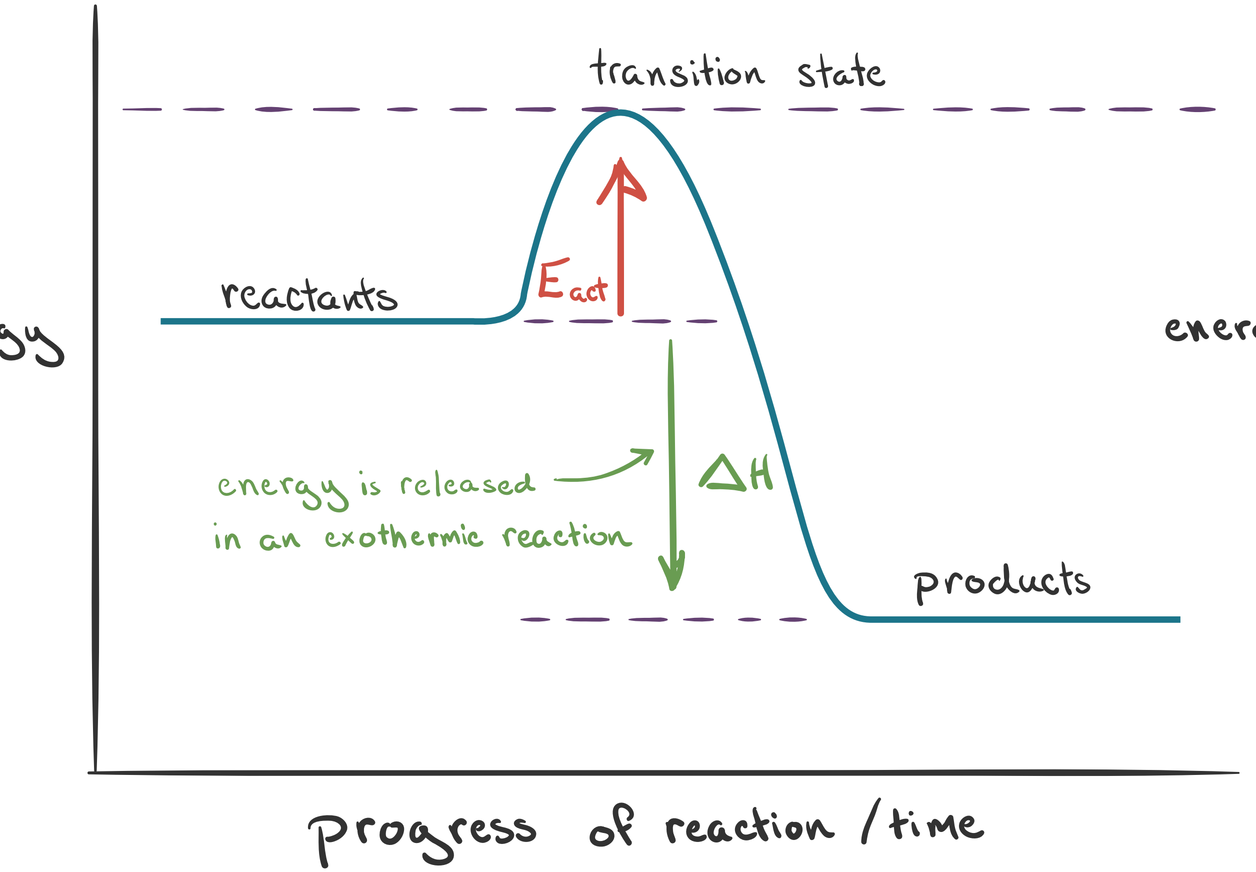
oscillator strength

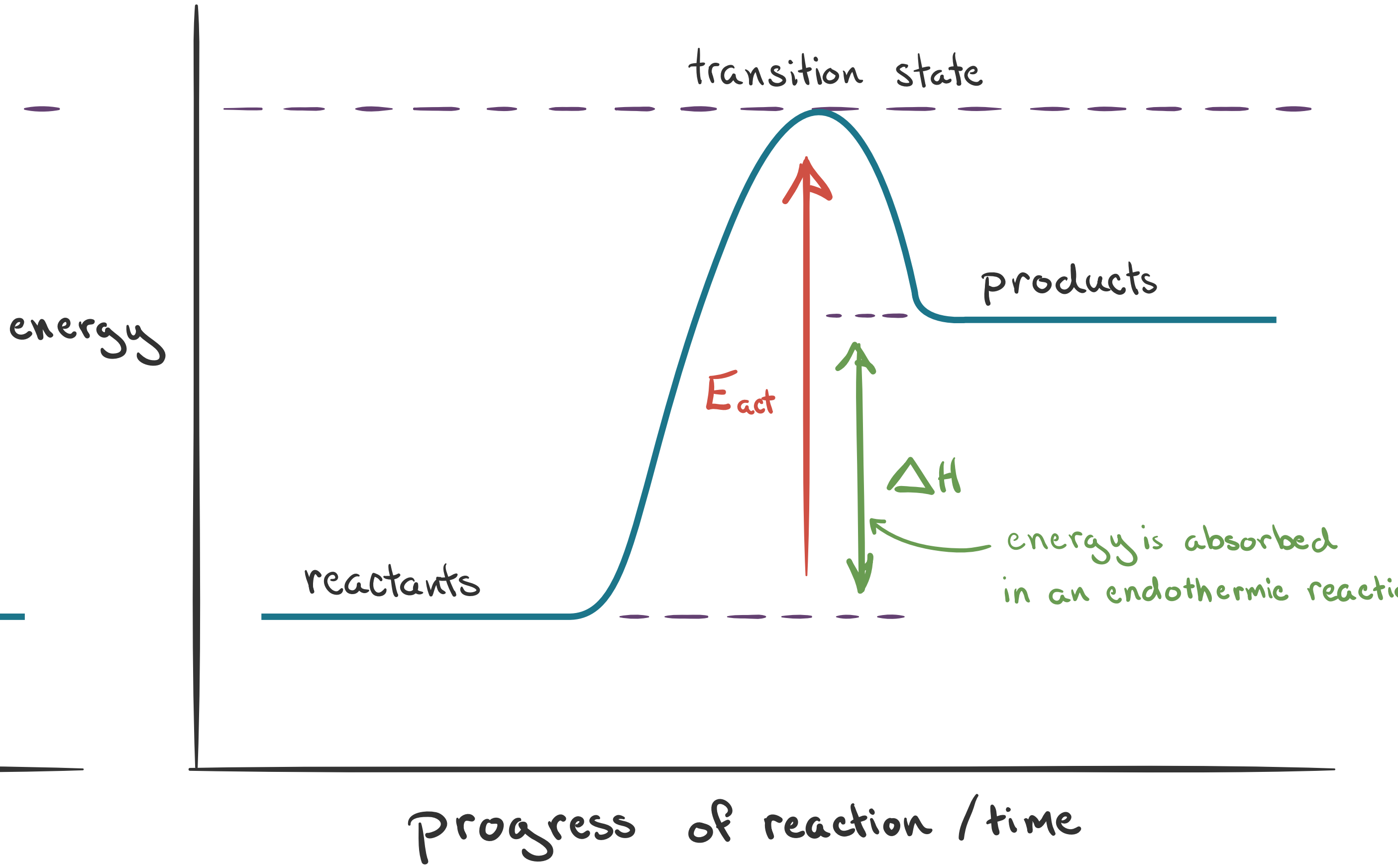
Dissociation probability

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

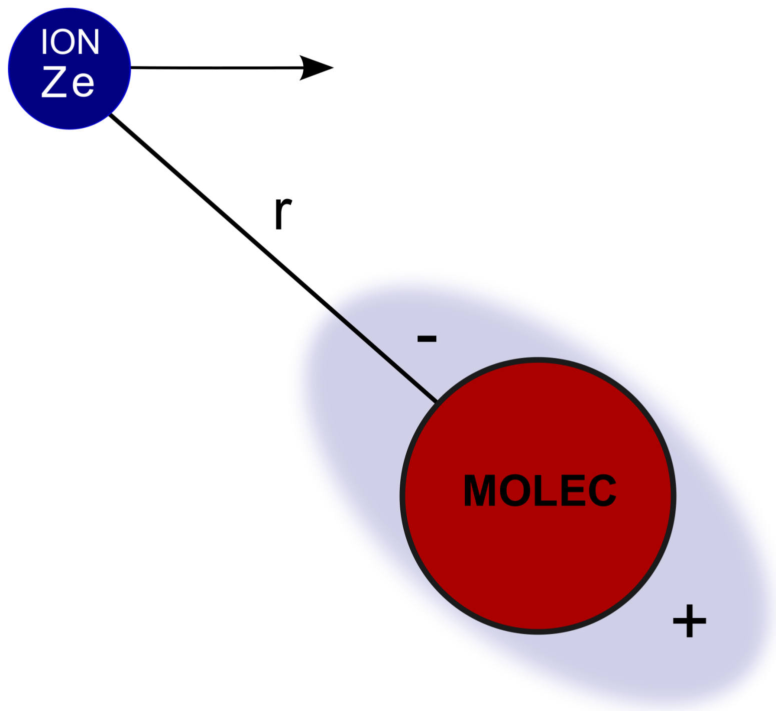
These reactions are important when the gas is warm:

- 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*

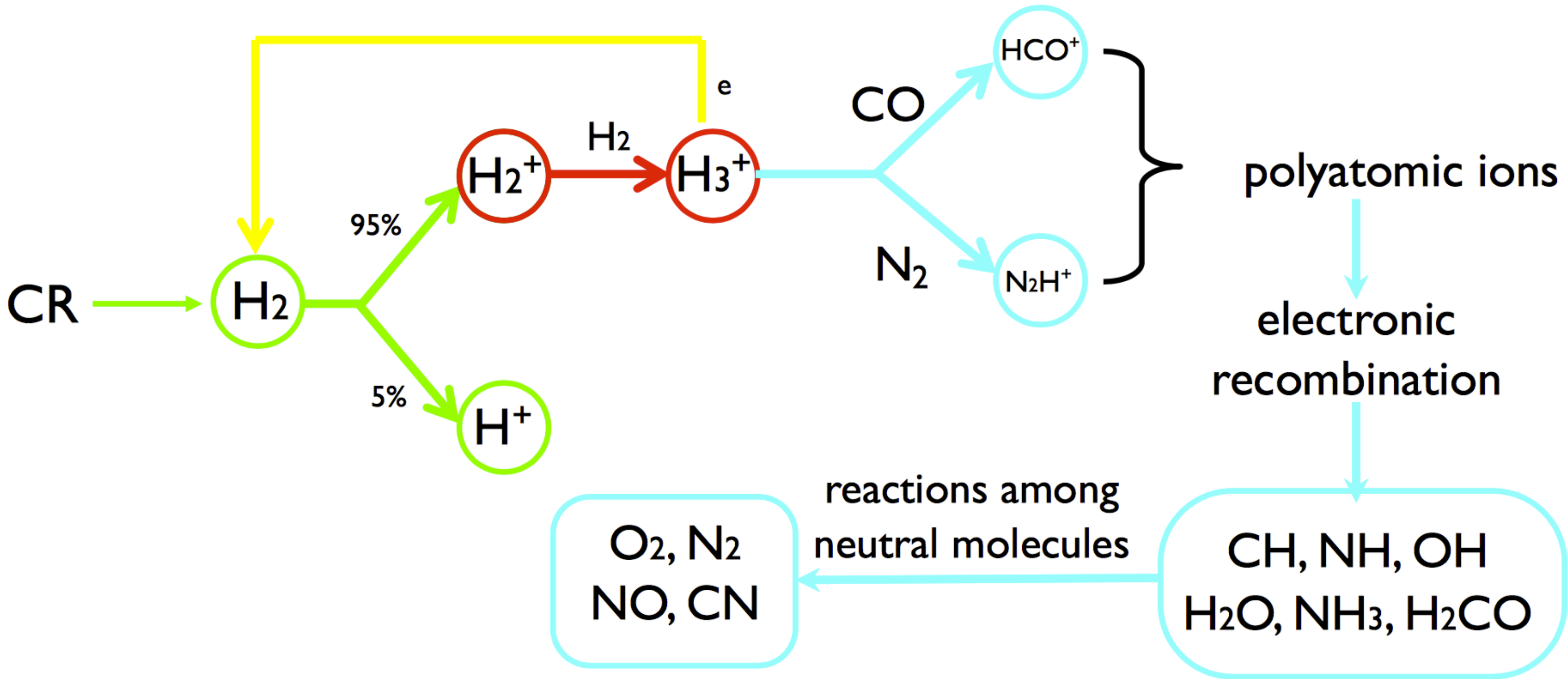
reaction	α
$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1 (–9)
$H_3^+ + O \rightarrow OH^+ + H_2$	8.0(–10)
$H_3^+ + CO \rightarrow HCO^+ + H_2$	1.7 (–9)
$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	5.9 (–9)
$OH^+ + H_2 \rightarrow H_2O^+ + H$	1.1 (–9)
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	6.1(–10)
$C^+ + OH \rightarrow CO^+ + H$	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 $k = \alpha$.

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



Charge-transfer

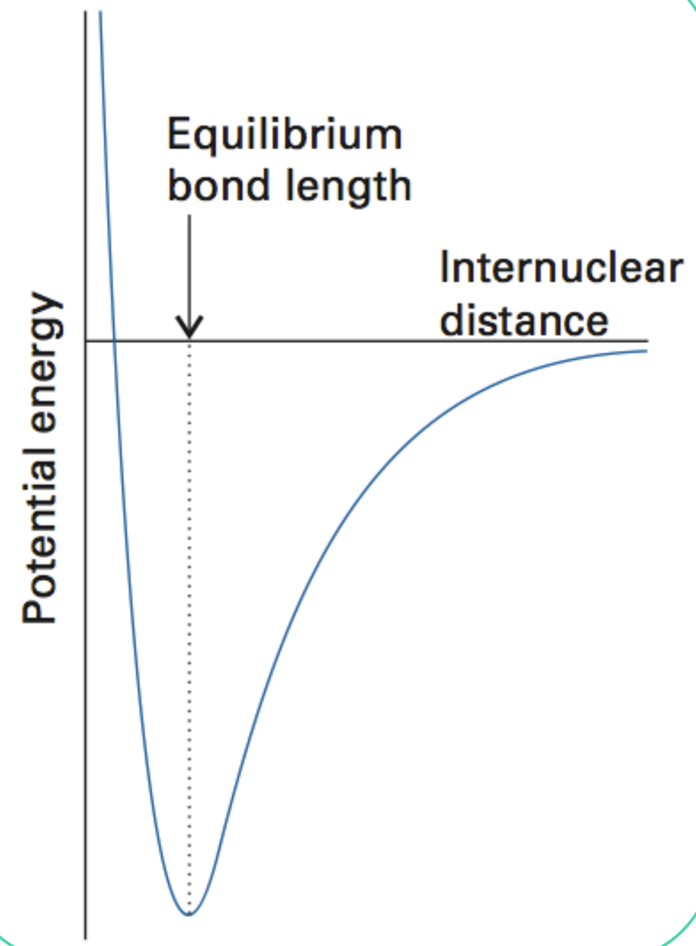
$$A^+ + B \rightarrow A + B^+$$

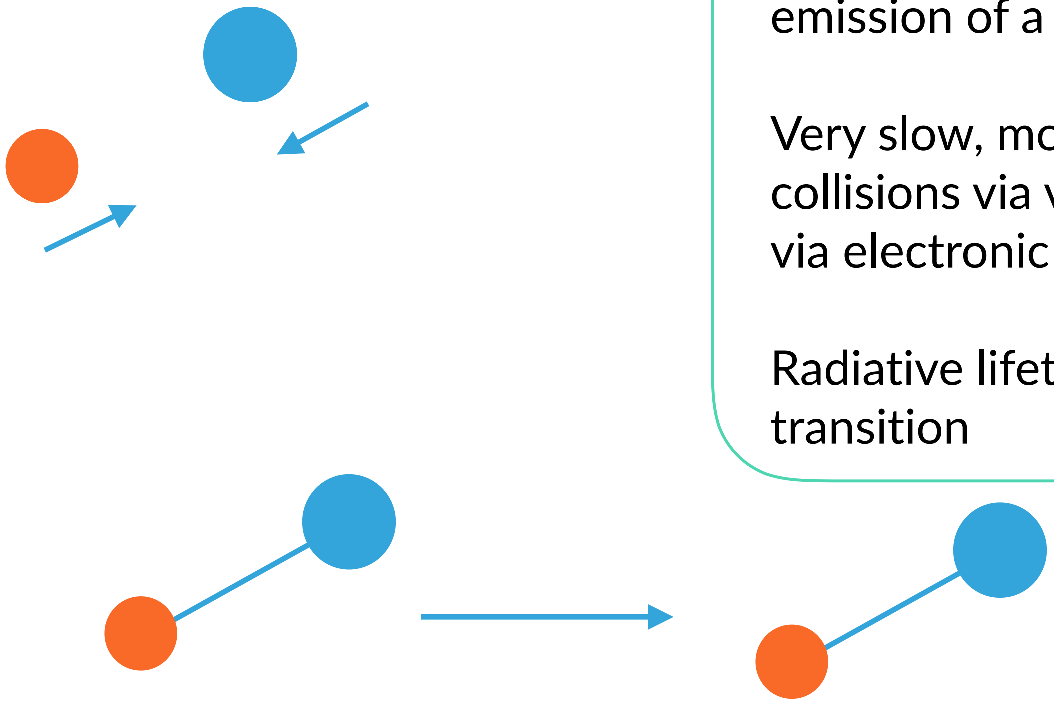
Important in setting the ionization balance

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

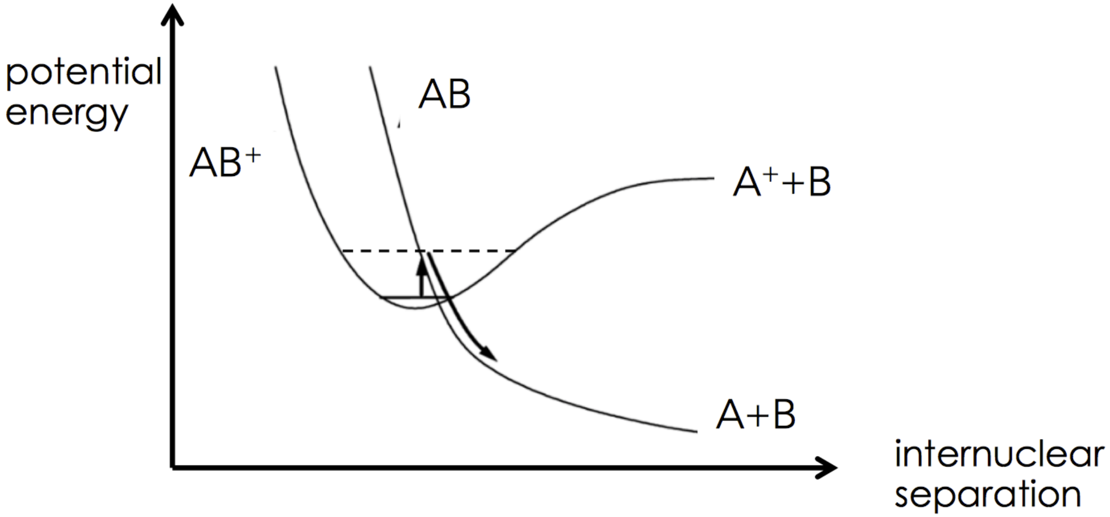
$$X + Y \rightleftarrows XY^* \rightarrow XY + \gamma$$

Dissociative recombination

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

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

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



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

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

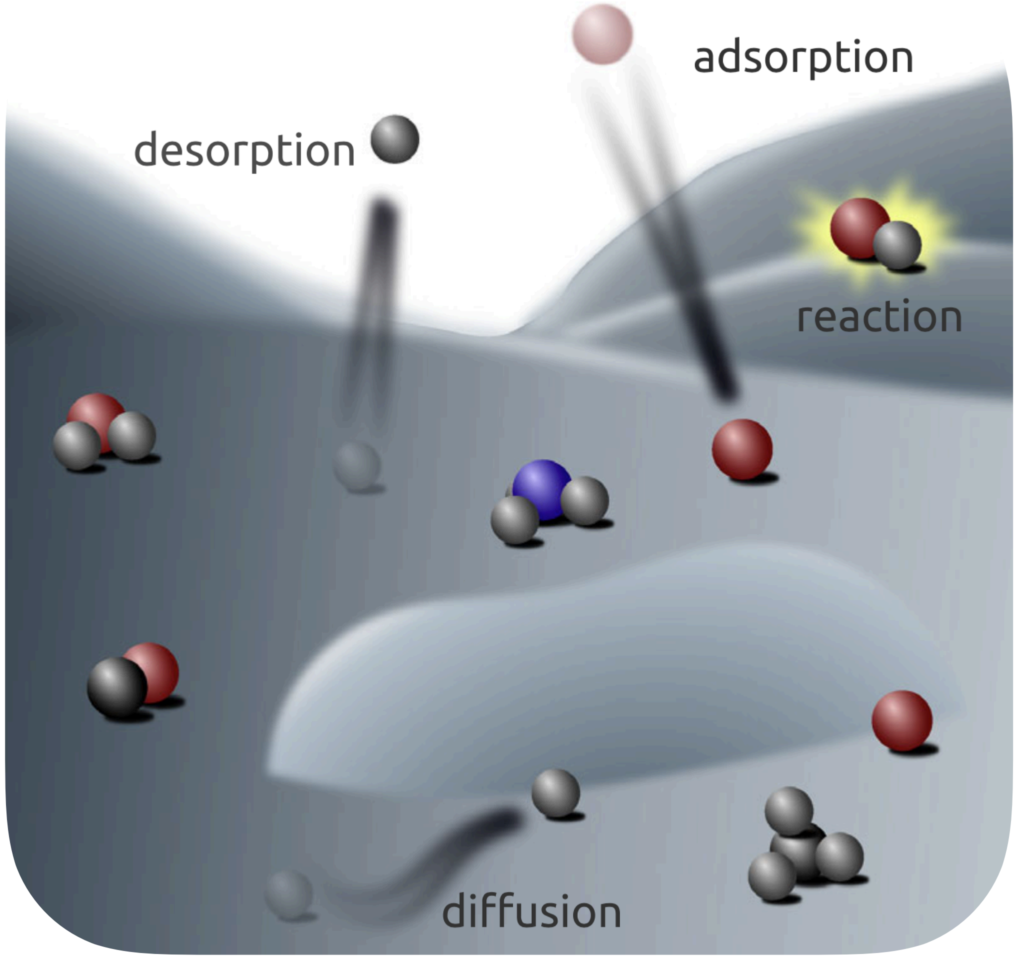
$$\mathrm{A} + \mathrm{B} + \mathrm{M} \leftrightarrow \mathrm{AB} + \mathrm{M}$$

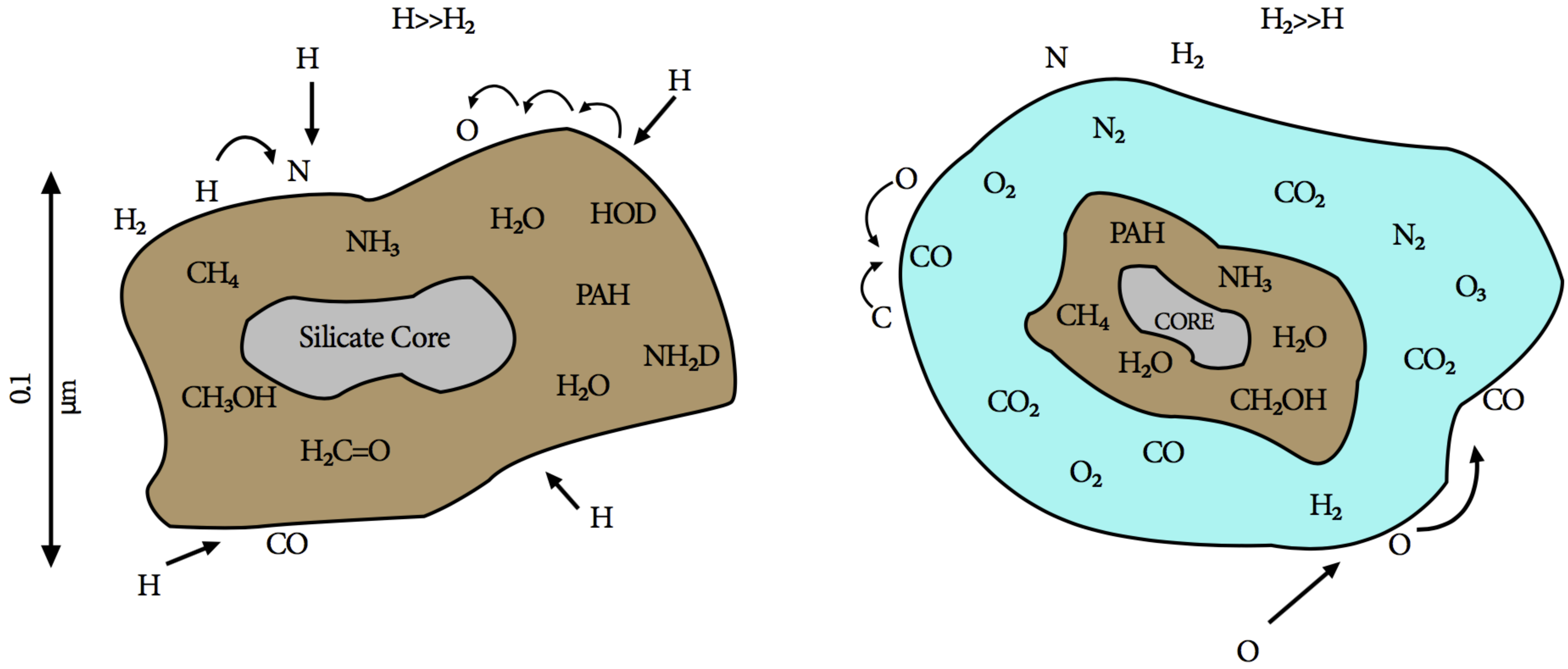
$$\mathrm{A} + \mathrm{B}^- \rightarrow \mathrm{AB} + \mathrm{e}$$

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

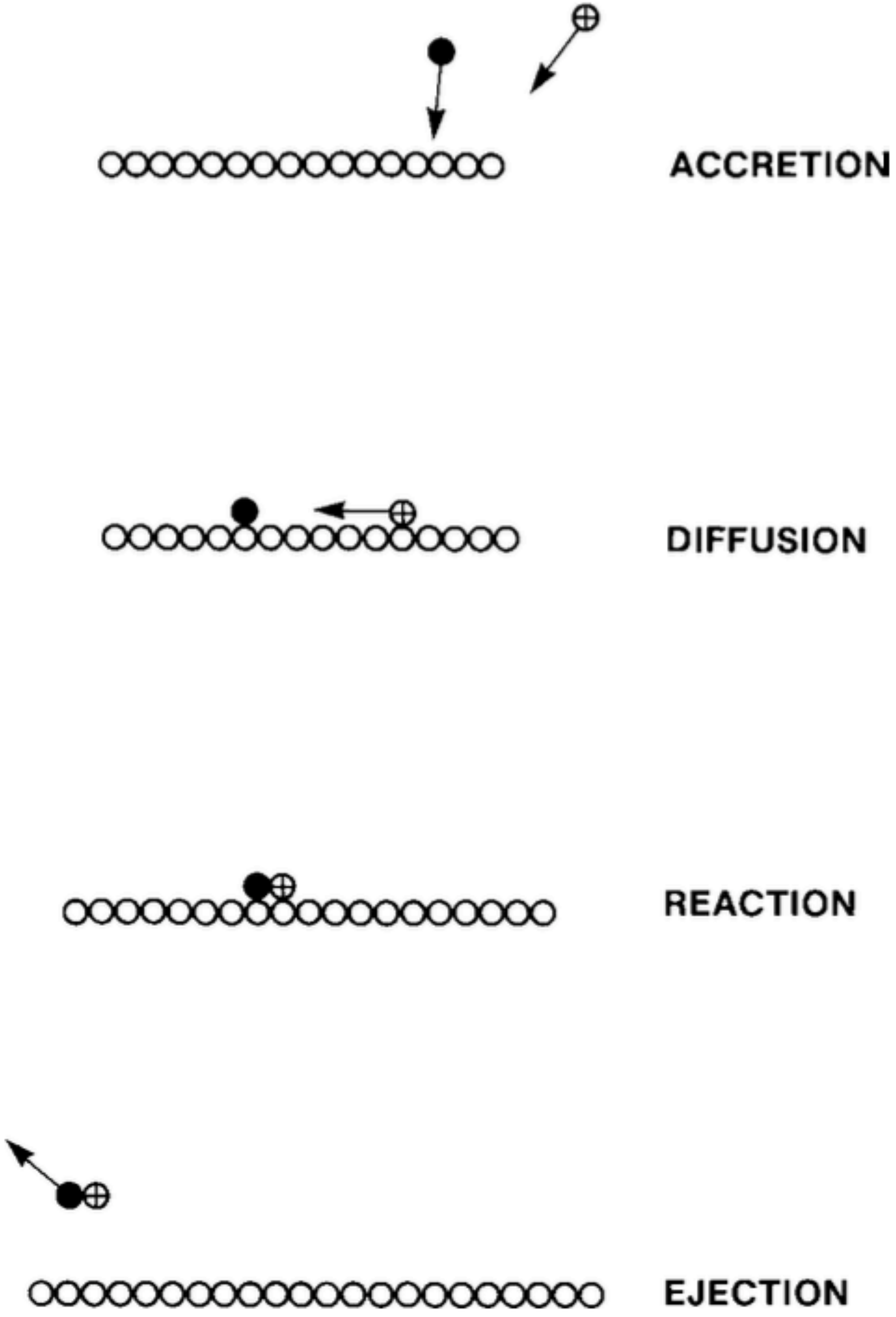
Grain-surface chemistry in pills

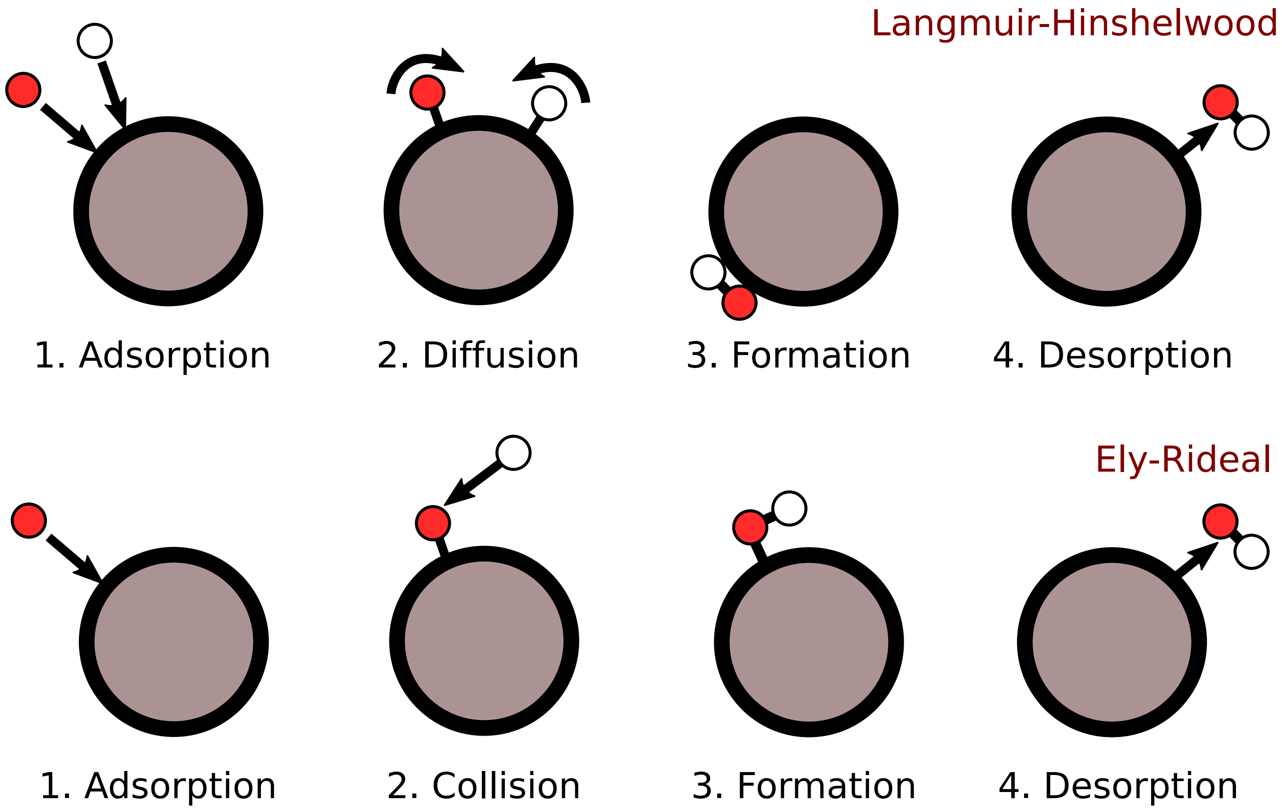
- Grains provide a surface on which accrete species
- These can meet and react



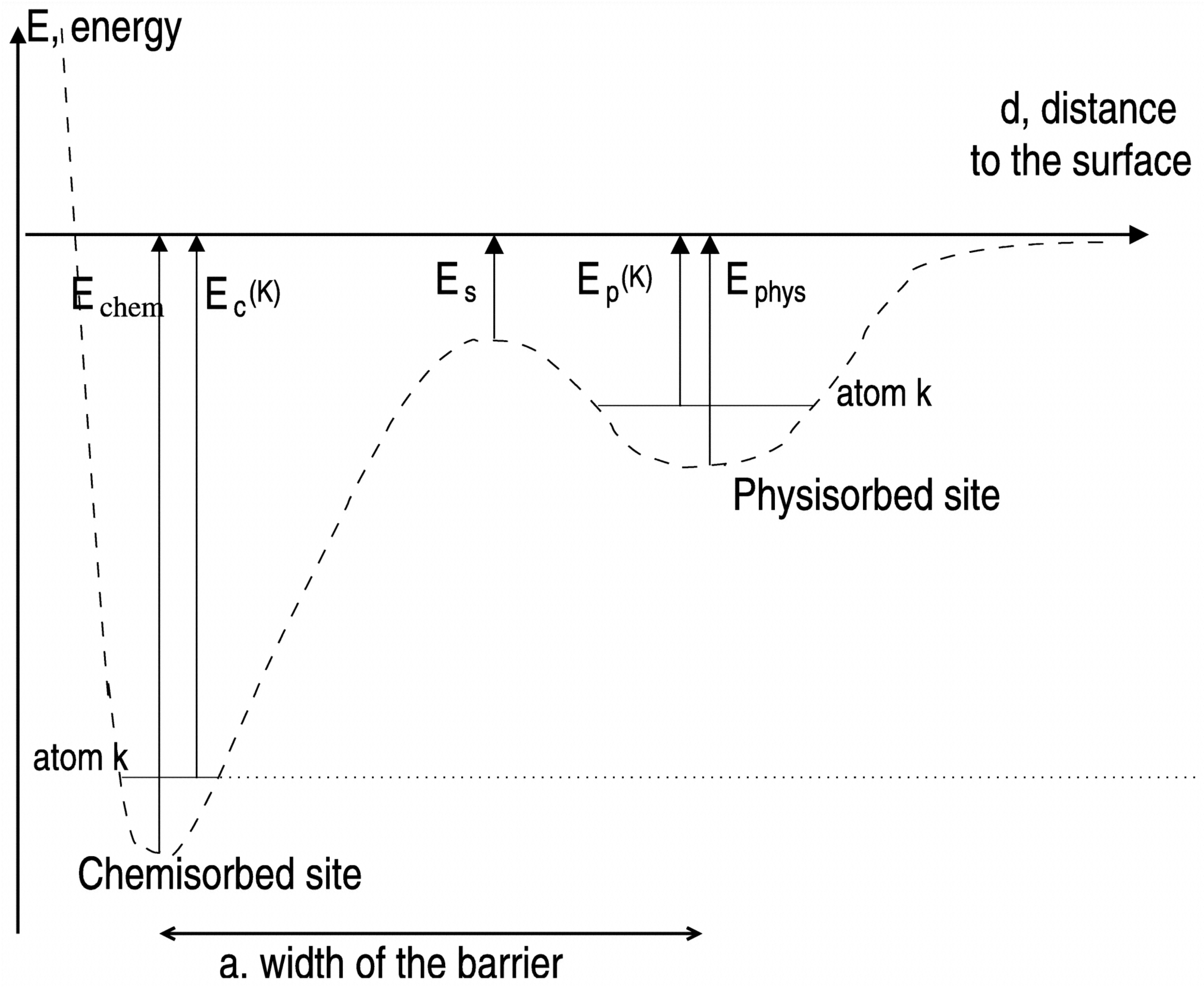


H>>H2
H
H
O
N
H
H2
NH3
H2O
HOD
CH4
PAH
Silicate Core
NH2D
CH3OH
H2O
H2C=O
CO
H
H
0.1 μm
H2>>H
N
H2
N2
O
O2
CO2
PAH
N2
CO
NH3
O3
CH4
CORE
H2O
C
H2O
CO2
CO2
CH3OH
CO
CO
O2
H2
O
O

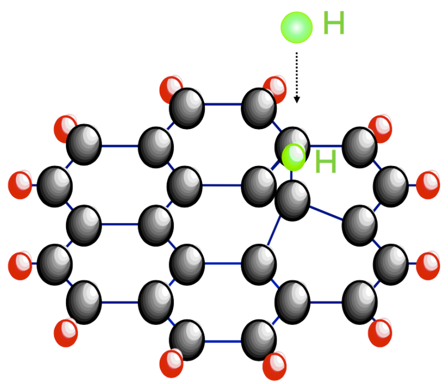

ACCRETION
DIFFUSION
REACTION
EJECTION


Langmuir-Hinshelwood
1. Adsorption
2. Diffusion
3. Formation
4. Desorption
Ely-Rideal
1. Adsorption
2. Collision
3. Formation
4. Desorption

Binding energy

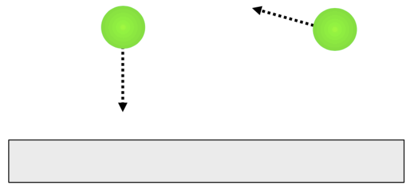


Chemisorption



- Chemical bonds
- Binding energies: ~ 0.5–5 eV or >20,000 K

Physisorption



- Weak electrostatic van der Waals force
- Binding energies: ~10–100 meV or ~100–10,000 K

Binding energy

Interstellar grains are porous

They are not regular in the shape: valleys and hills

Valleys (deep sites): chemisorbed sites
Hills (peak sites): physisorbed sites

Then we have also saddle points which represents barriers to the motion of the adsorbate across the surface

Chemisorbed sites are quickly covered with ice in cold environments: then physisorption is the only process

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