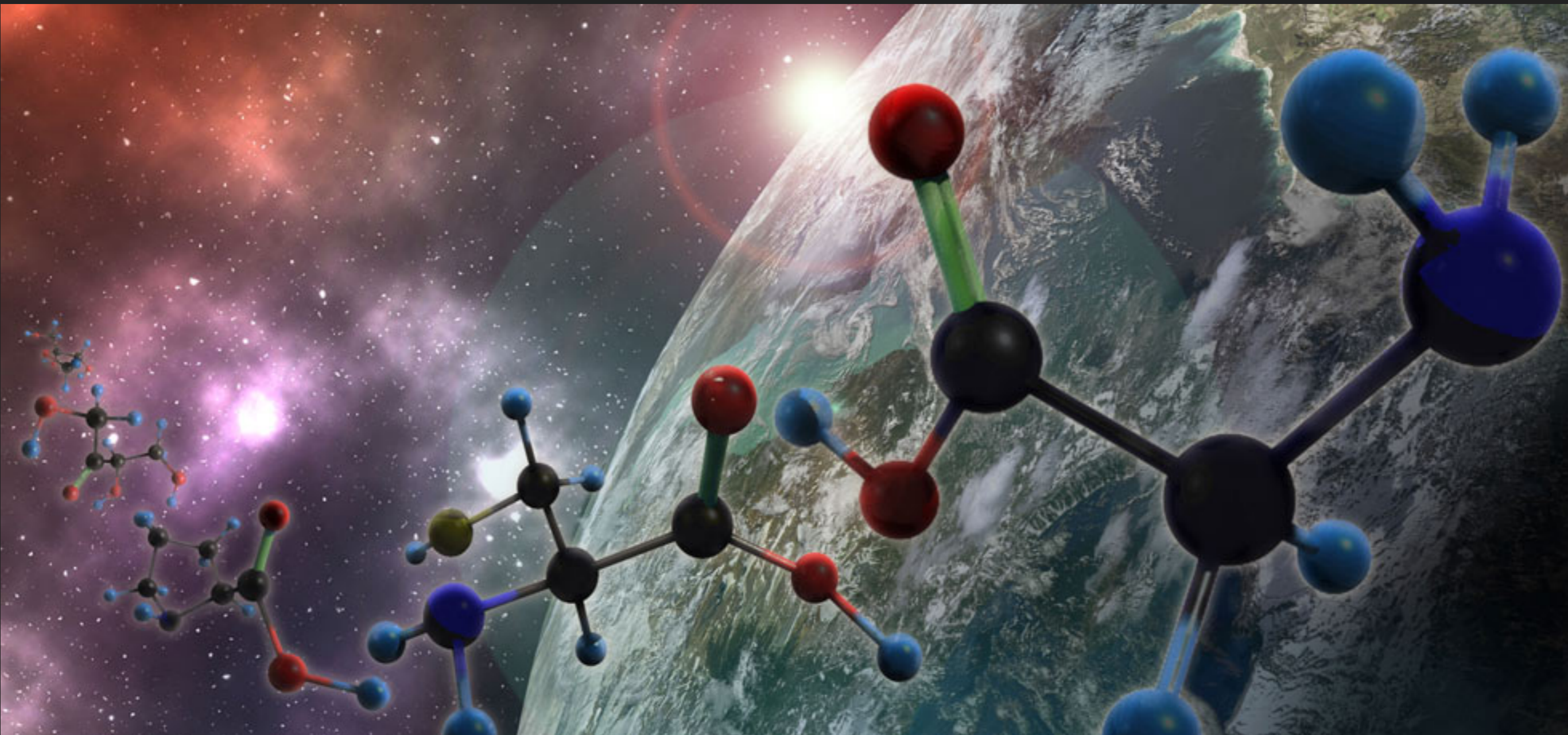


# LECTURE 6

STEFANO BOVINO

UNIVERSIDAD DE CONCEPCIÓN



# Dust

- We have talked about gas-radiation, all processes occurring at specific frequencies (absorption) or range of frequencies (ionization)
- Dust interact with light in a wide range of wavelengths



# The role of dust in the ISM

- Dust accounts for 1% of the total matter in the ISM
- Formed by micro-sized particles
- Extremely important for
  - Chemistry and physics of the ISM
  - Energy balance of Galaxy (heating/cooling/extinction)
  - Evolution of interstellar clouds and SF
  - Depletion and evaporation of heavy elements

# Interaction matter-dust-radiation < 4 >

- Dust scatters, absorbs, and re-radiates starlight
  - Reflection nebula (blue scattered light)
  - Transmitted light (reddening)
- $1:10^{12}$  photons reaches our telescope because of extinction
- Energy is absorbed and re-emitted in the IR (~20% of the total luminosity of the Galaxy)



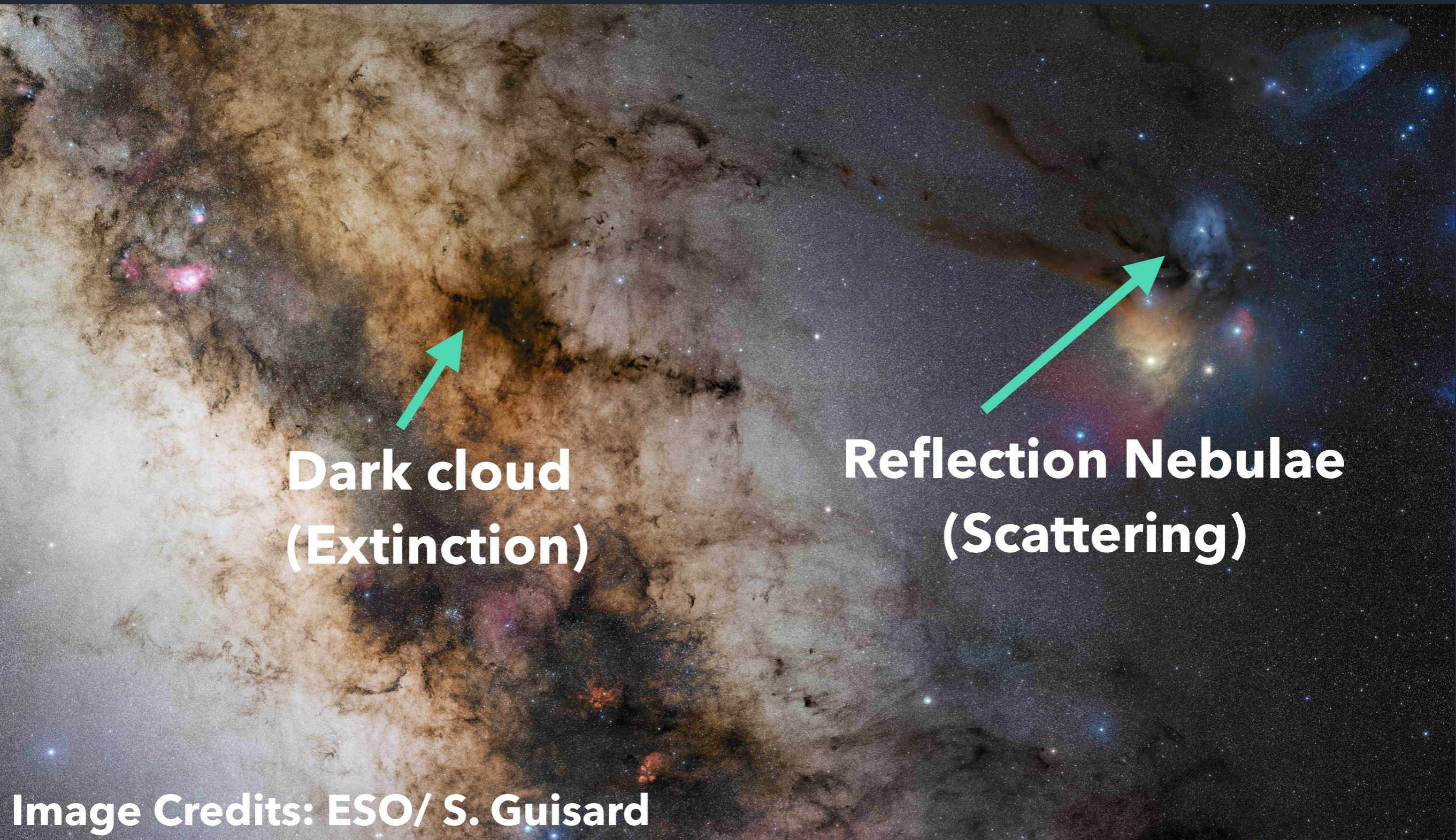
# Interaction matter-dust-radiation < 5 >

- Photoelectric heating
- Surface mantle or ices (gas-grain interaction)
- Chemistry

# How do we learn about dust

- Extinction: wavelength dependence of how dust attenuates (absorbs & scatters light)
- Polarization
- Thermal emission from grains
- Depletion of elements from the gas relative to expected abundance





**Dark cloud  
(Extinction)**

**Reflection Nebulae  
(Scattering)**

**Image Credits: ESO/ S. Guisard**



# Dust history

**1784** - William Herschel "Hole in the sky"

**By eyes** - Ophiuchus, Barnard 86: observed regions devoid of stars!





# Dust history

## 1847 - Wilhelm Struve

- Star counts (distribution of stars with distance)
- Number of stars over volume declines with distance from the Sun
- Struve proposed:
  - The existence of some obscuring material
  - Uniformly distributed in space
  - That affects the intensity of starlight
- **Stars less bright (because of dust) and apparently further away**



# Dust history

## William Herschel



1784

Ophiuchus, Barnard 86

**obs. regions devoid of stars?**

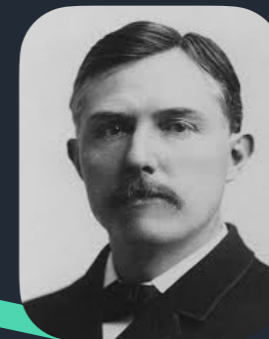
## Wilhelm Struve



1847

**Starlight suffers absorption!**

## Edward Emerson Barnard



1910-1927

Some interstellar material obscures (absorb and scatter) starlight! **They are not "holes in the sky".**



# Dust history

## 1930s - Robert Trumpler

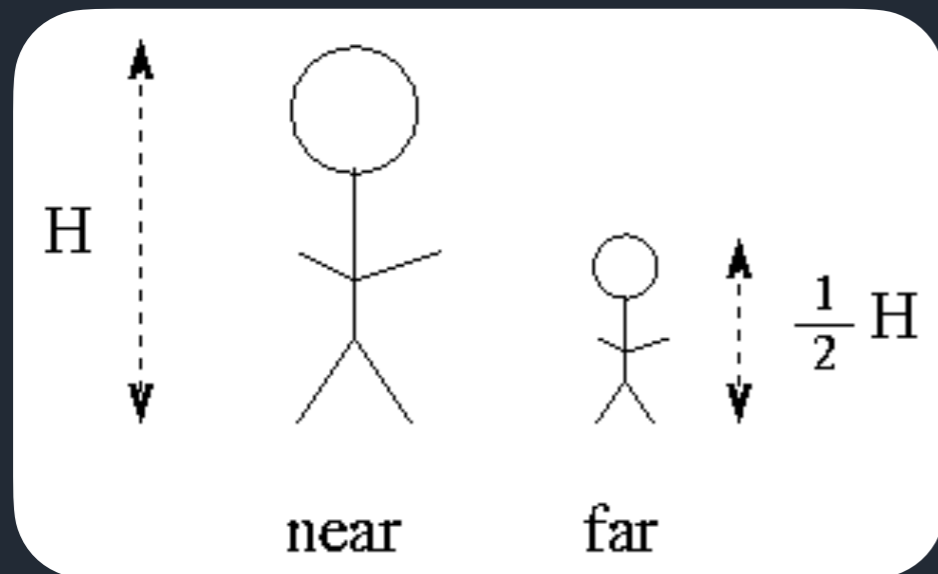
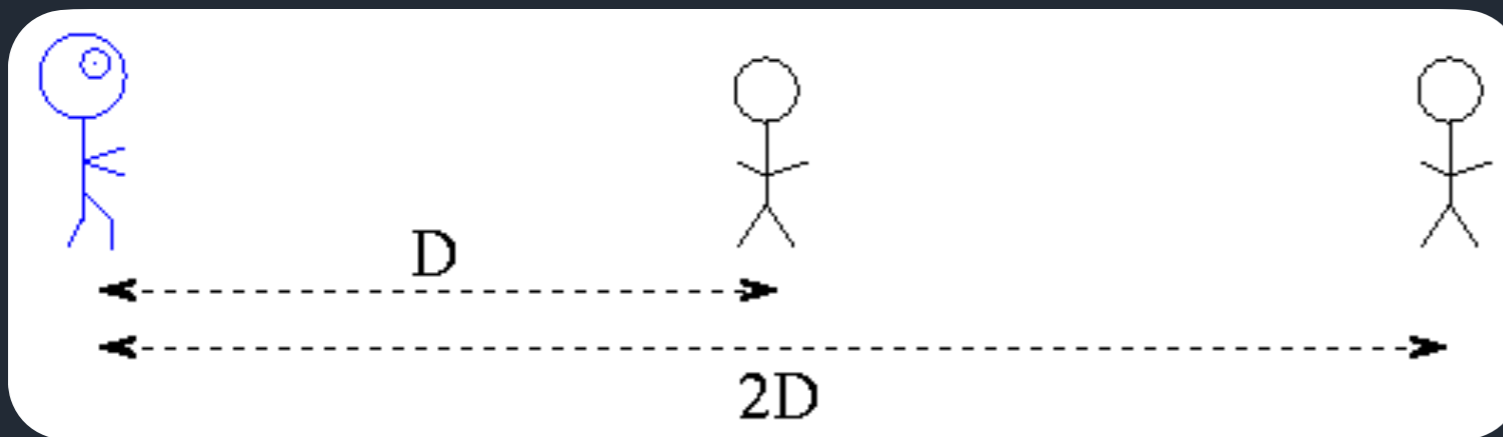
1. He used two different methods to determine the distance to each cluster
  - one based on brightness
  - the other based on size

### Diameter distance

1. First, he divided the clusters into groups, based on the number of stars in each and the degree of central concentration
2. He assumed that clusters in the same group had the same size
3. From the size he calculated the distance (small far / large near)

# Dust history

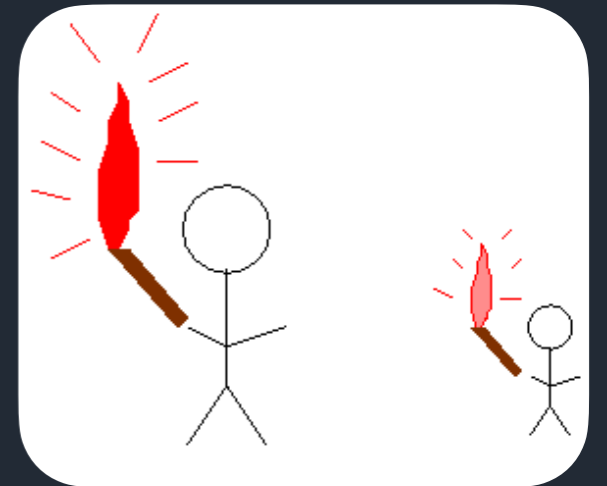
1930s - Robert Trumpler



# Dust history

## 1930s - Robert Trumpler

1. He applied the inverse square law to individual star
  - spectral class of a star yielded its absolute magnitude
  - photographic plates provided each star's apparent magnitude



## Photometric distance

1. Assuming that light travelled freely through space, he calculated the distance to each star, and averaged them to find the distance to each cluster.

# Dust history

1930s - Robert Trumpler

1. Followed Struve's hypothesis
2. Calculated the average amount of extinction per unit distance (incredibly close to what we know now)

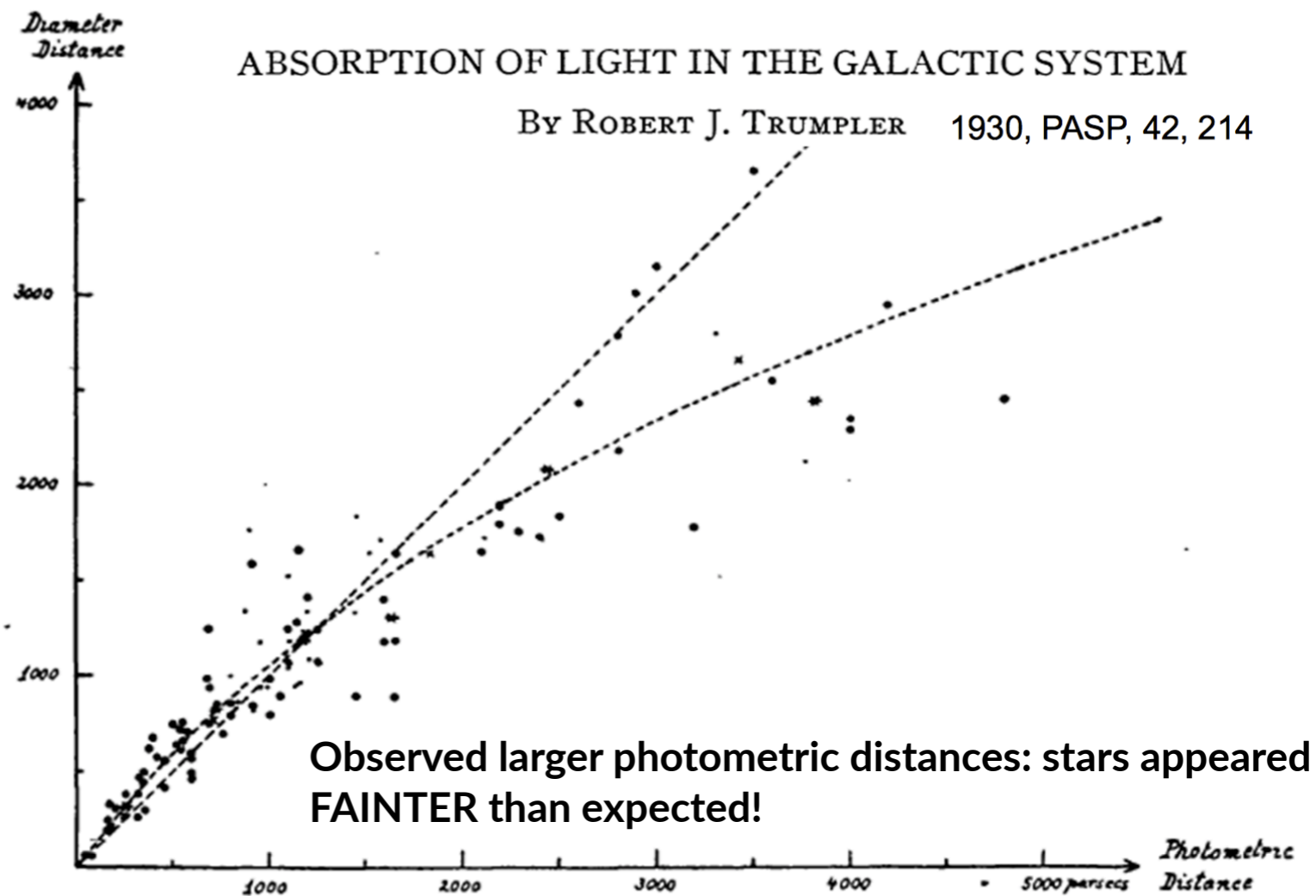
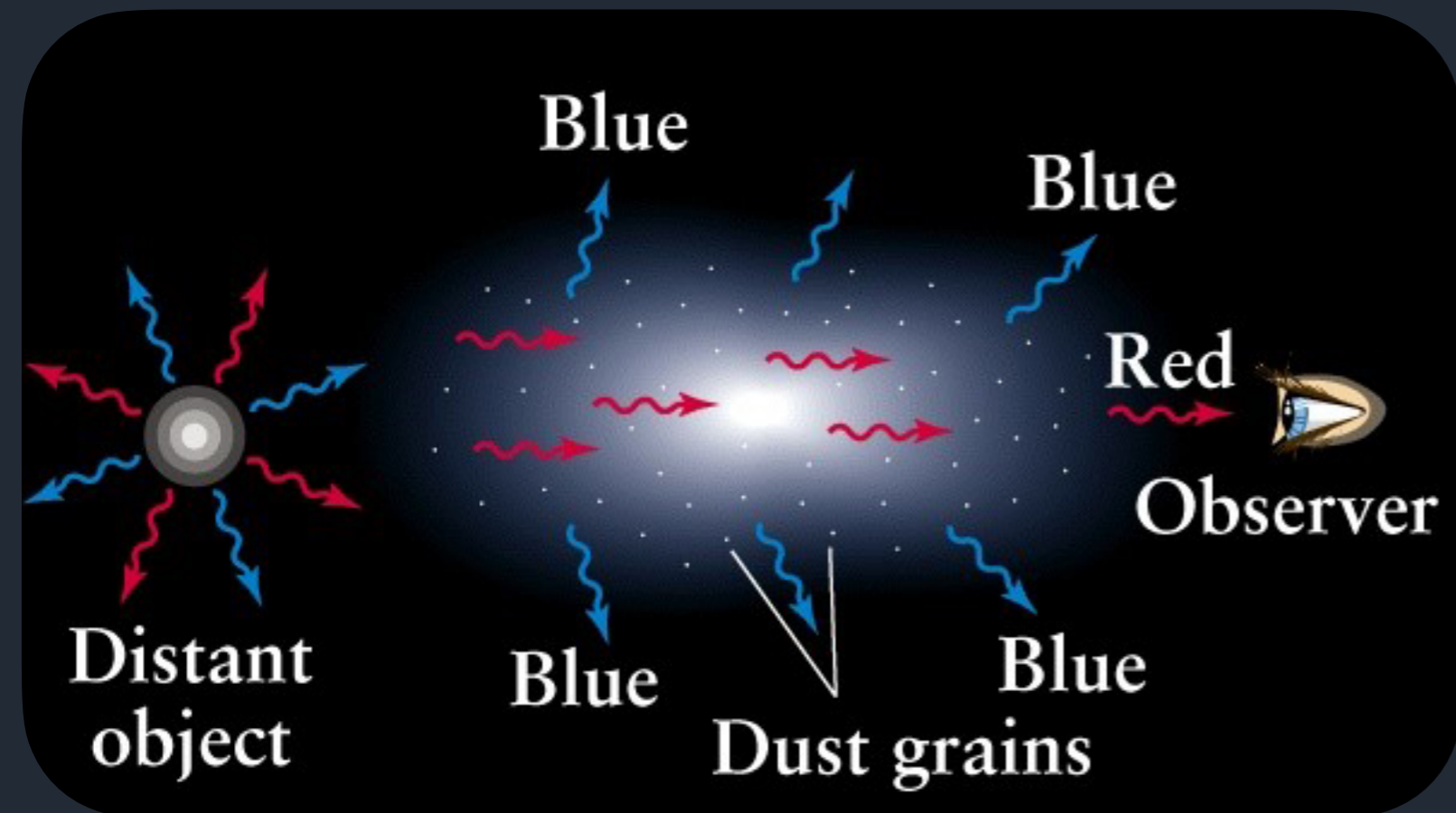


FIG. 1.—Comparison of the distances of 100 open star clusters determined from apparent magnitudes and spectral types (abscissae) with those determined from angular diameters (ordinates). The large dots refer to clusters with well-determined photometric distances, the small dots to clusters with less certain data (half weight). The asterisks and crosses represent group means. If no general space absorption were present, the clusters should fall along the dotted straight line; the dotted curve gives the relation between the two distance measures for a general absorption of  $0^m.7$  per 1000 parsecs.

# Dust history

**1930s** - Robert Trumpler: interstellar reddening



1 - Blue-light strongly absorbed and scattered by dust (size similar to blue wavelengths)

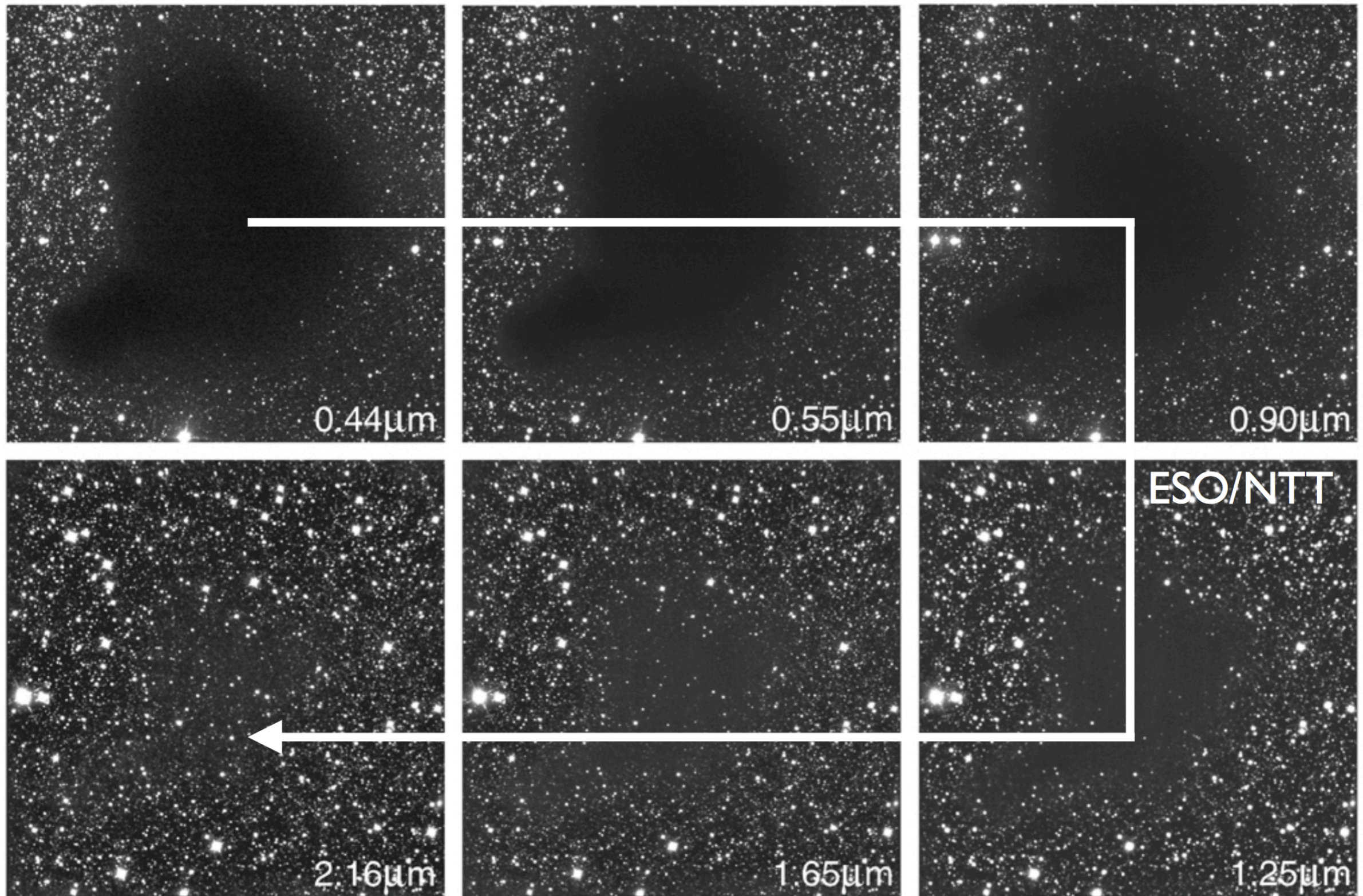
2 - Objects appears redder that they really are

$$A_{\lambda} \propto \lambda^{-1}$$

**Joel Stebbins 1939**



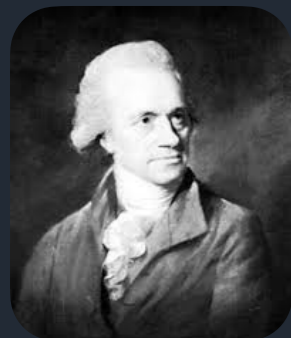
$$A_{\lambda} \propto \lambda^{-1}$$





# Dust history

Herschel



1784

Ophiuchus,  
Barnard 86  
**obs. regions  
devoid of stars?**

Struve



1847

**Starlight  
suffers  
absorption!**

Barnard



1910-1927

Some interstellar  
material obscures  
(absorb and scatter)  
starlight! **They are  
not "holes in the  
sky".**

**First estimate of  
the extinction  
coefficient**

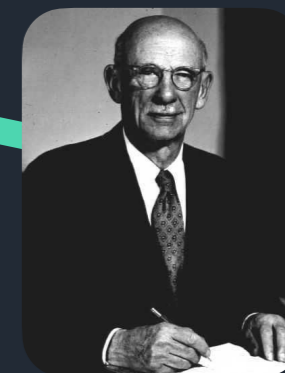
Trumpler



1930

**They are solid  
particles!**

Stebbins



1939



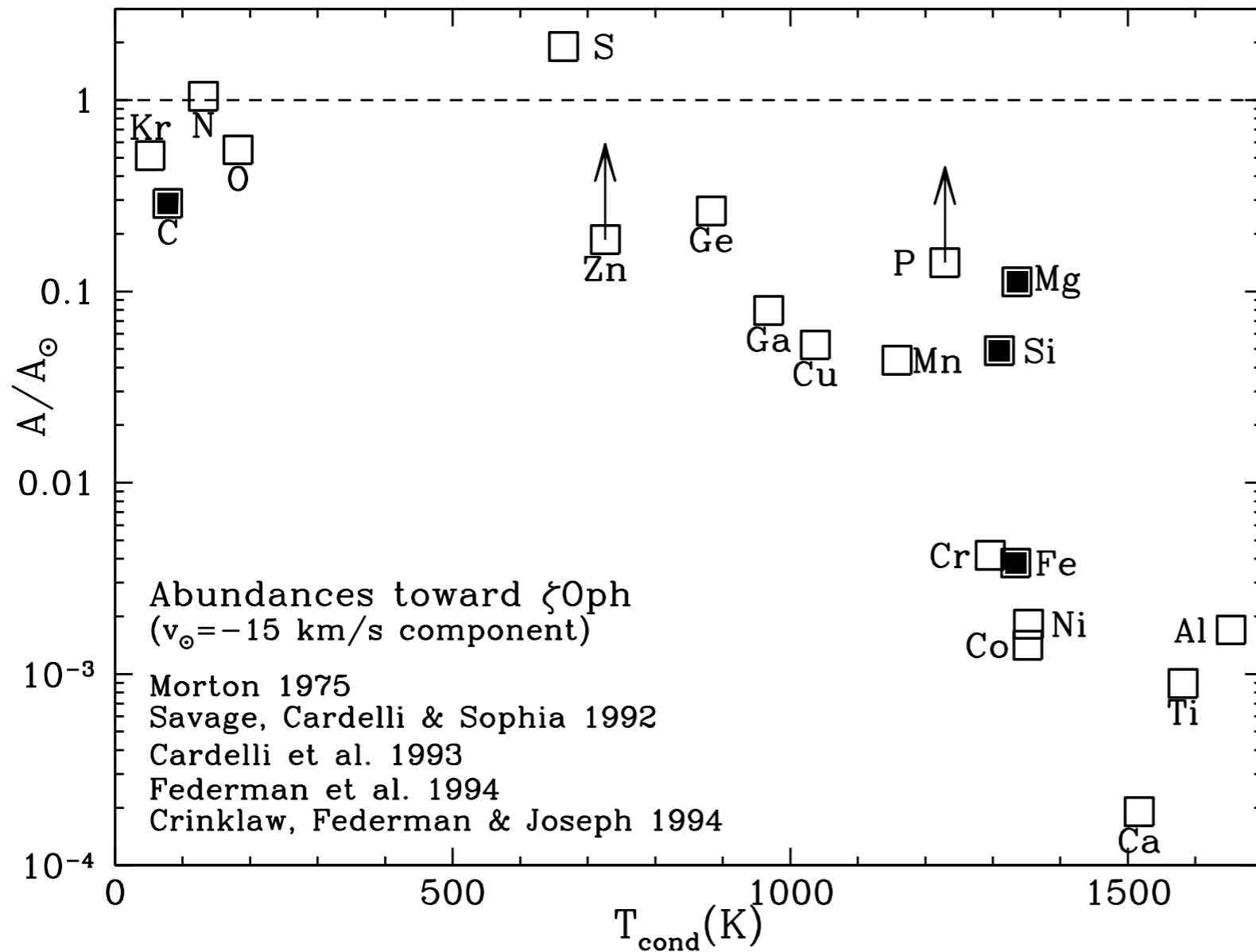
# What is made of the interstellar dust?

---

- Ideal approach: spectroscopic features
  - Would uniquely identify the material
  - Would allow to measure the amounts of each material
- For dust is difficult
  - Optical and UV absorption is continuum
  - Spectral features are broad, difficult to identify

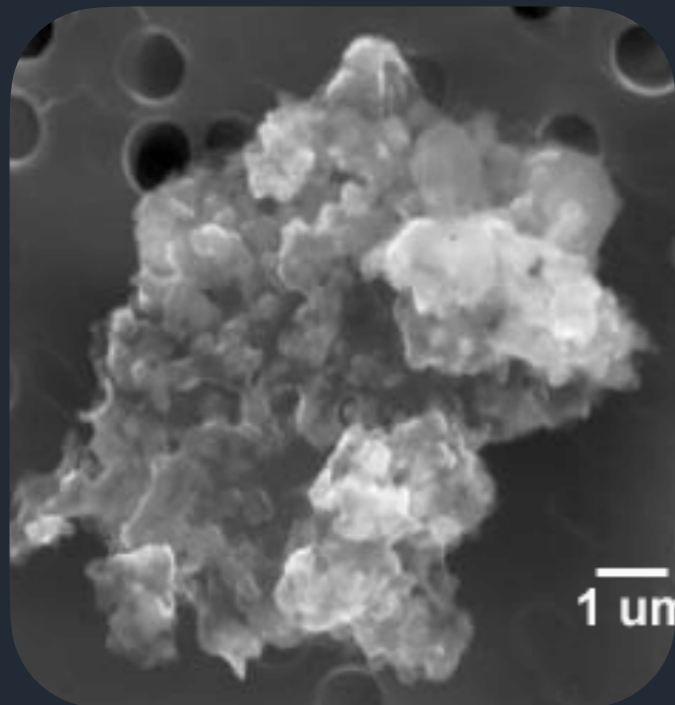
**What materials could plausibly be present in the ISM?**

# Abundances constraints



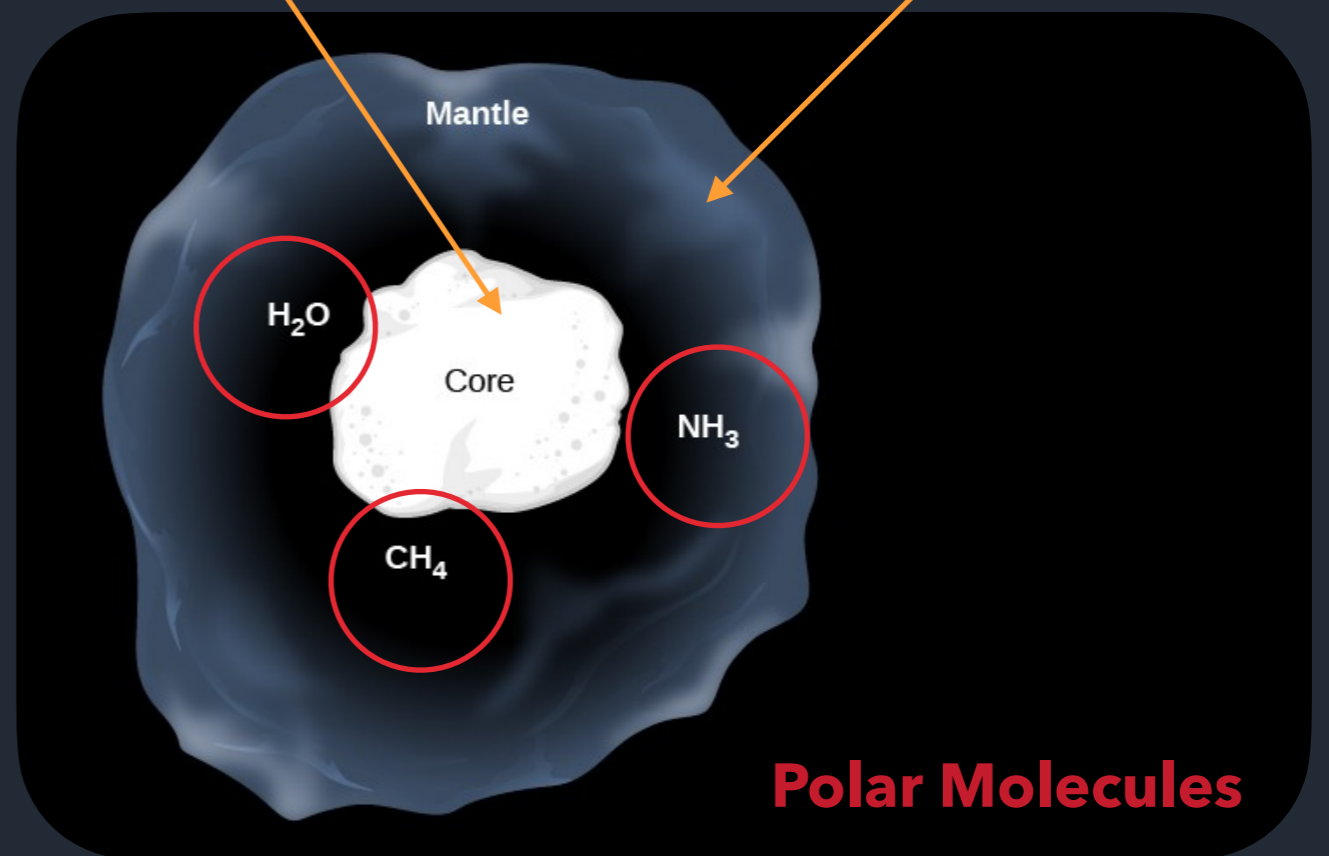
- Silicates, pyroxene, olivine
- Oxides of Si, Mg, Fe
- Carbon solids
- Hydrocarbons (PAH)
- Carbides
- Metallic Fe

# What is made of the interstellar dust?

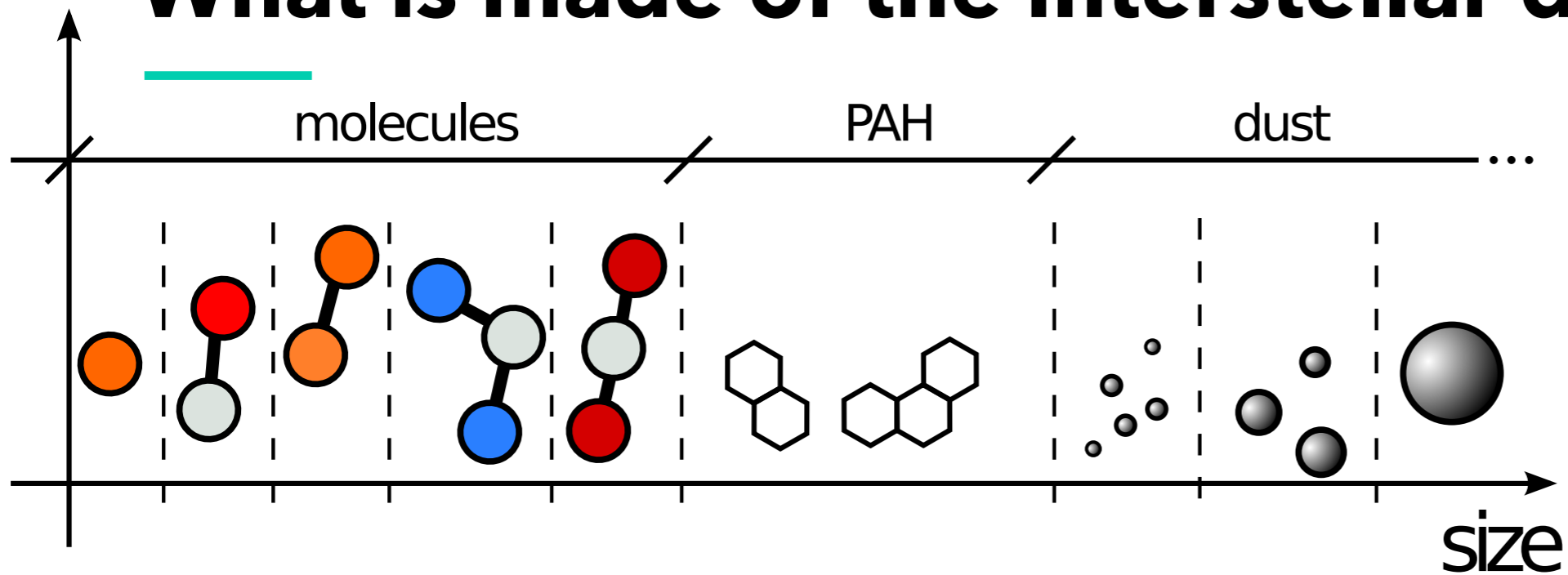


**Silicates/Carbonaceous**

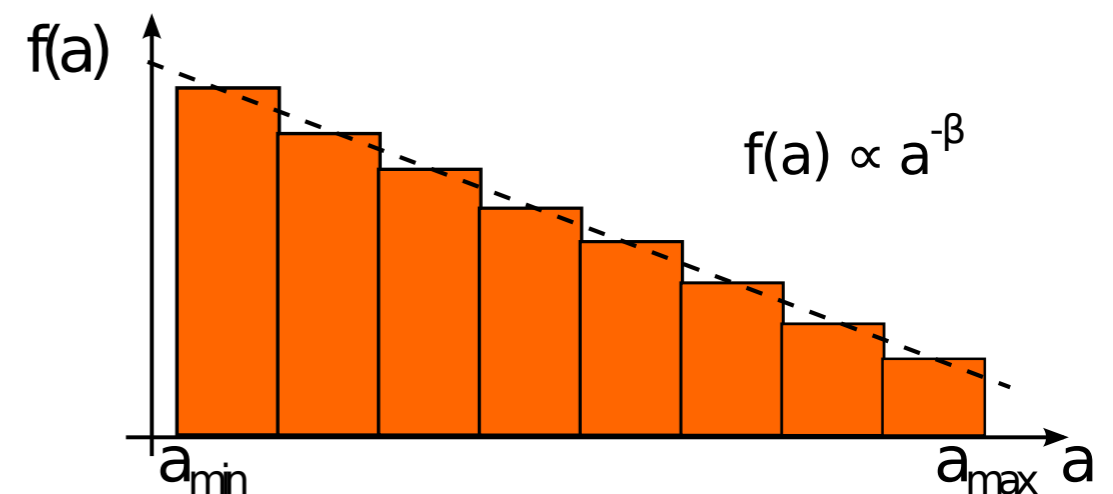
**Ice mantles**



# What is made of the interstellar dust?



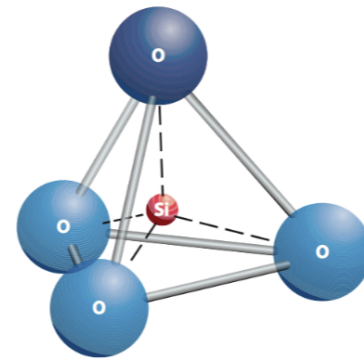
- Silicates (olivine and pyroxenes)
- Carbonaceous (HAC + PAH)
- Typical size  $\sim 0.1$  micron
- MRN distribution (power-law, does not include PAH)



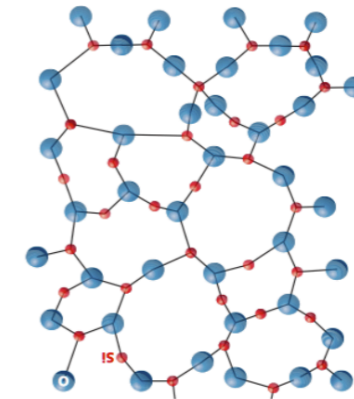


# Silicates

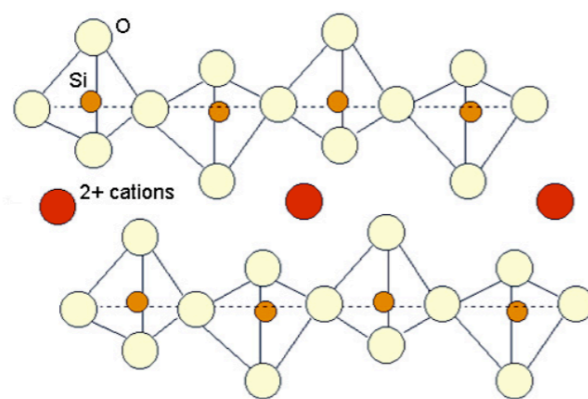
- 9.7  $\mu$  m Si-O stretching mode
- 18  $\mu$  m O-Si-O bending mode
- Low crystallinity in the ISM, increasing in brown dwarf disks



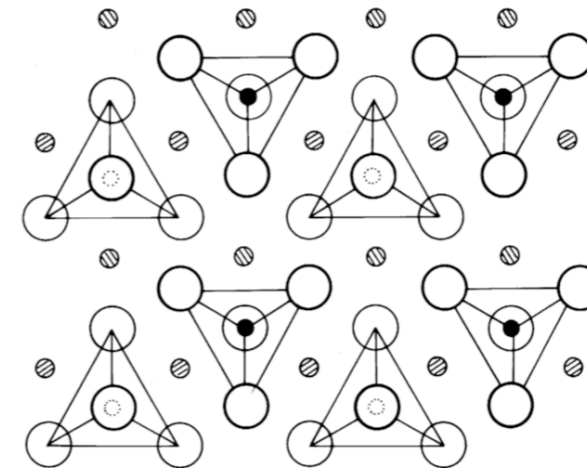
Basic building block



Amorphous silicate



Pyroxene  $Mg_x Fe_{1-x} SiO_3$



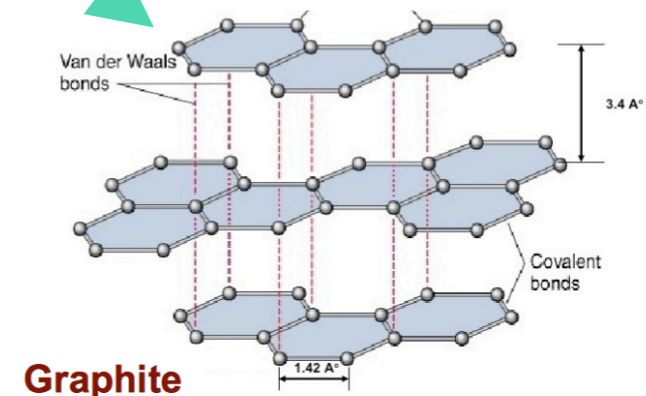
Olivine  $Mg_{2x} Fe_{2-2x} SiO_4$

Henning 2010

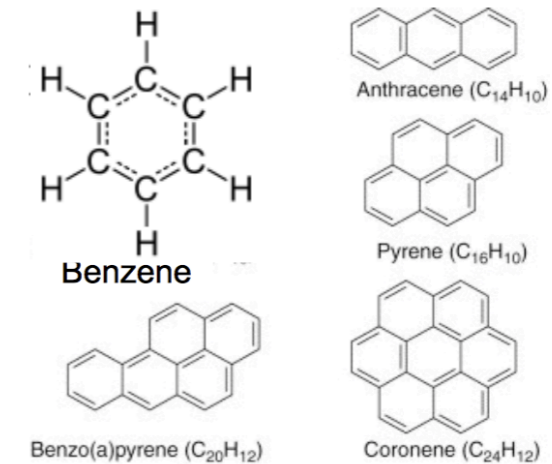
# Carbonaceous

Each of these sheets is graphene

- Graphite (Stecher 1965, Draine&Lee1984, Li&Draine2001)
  - C atoms: three  $sp^2$  (sigma) +  $\pi$  orbitals
  - $\pi + 217.5 \text{ nm} \rightarrow \pi^*$
  - BUT: variations in the peak position!
- Hydrogenated amorphous carbon (HAC, a-C:H)
  - Mennella et al. (1998) - 217 nm bump due to UV processed HAC
  - $3.4 \mu\text{m}$  feature - aliphatic C-H stretch
  - Jones et al. - HAC is less resilient than graphite - reproduces better variations of C gas phase abundances
  - Jones PoS(LCDU2013)001: review of current knowledge about ISM dust
- Polycyclic aromatic hydrocarbon (PAH)
  - Strong extinction in 200-250 nm region
  - Solid state emission 3.3, 6.7, 7.6, 8.6, and  $11.3 \mu\text{m}$

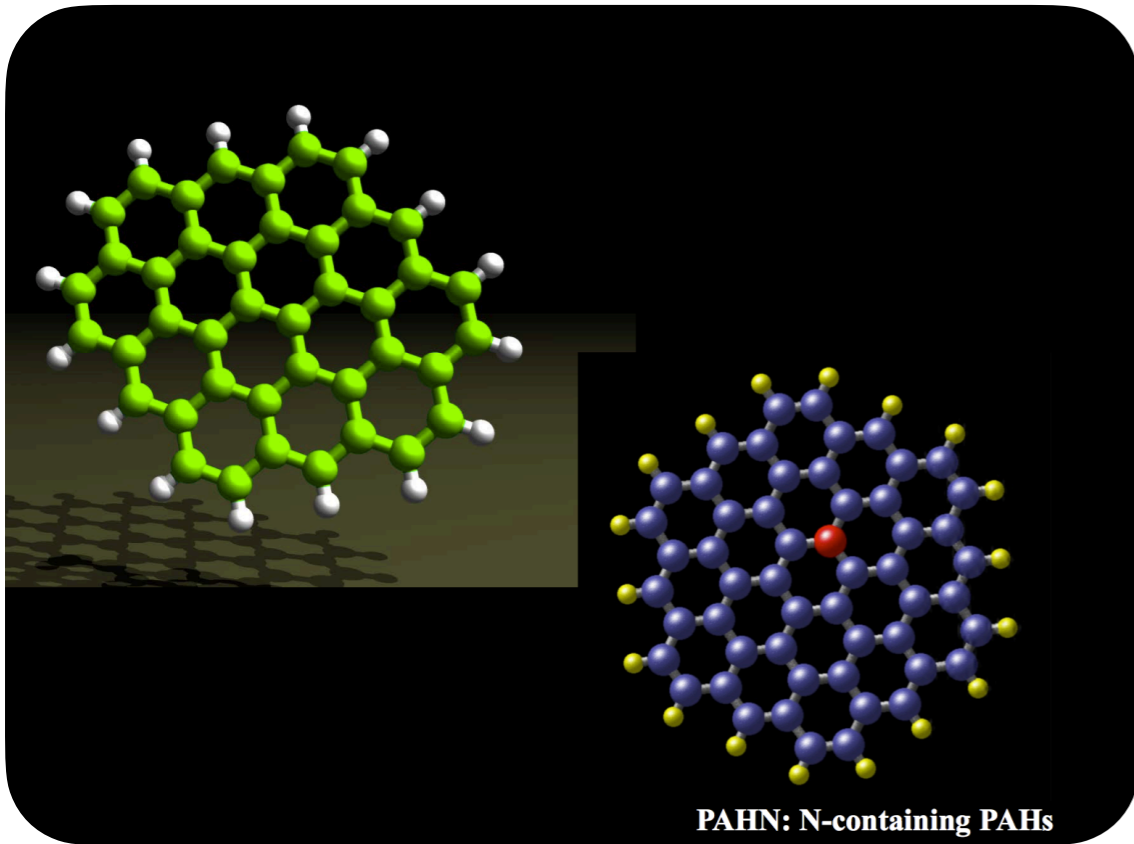


## PAH





# PAH

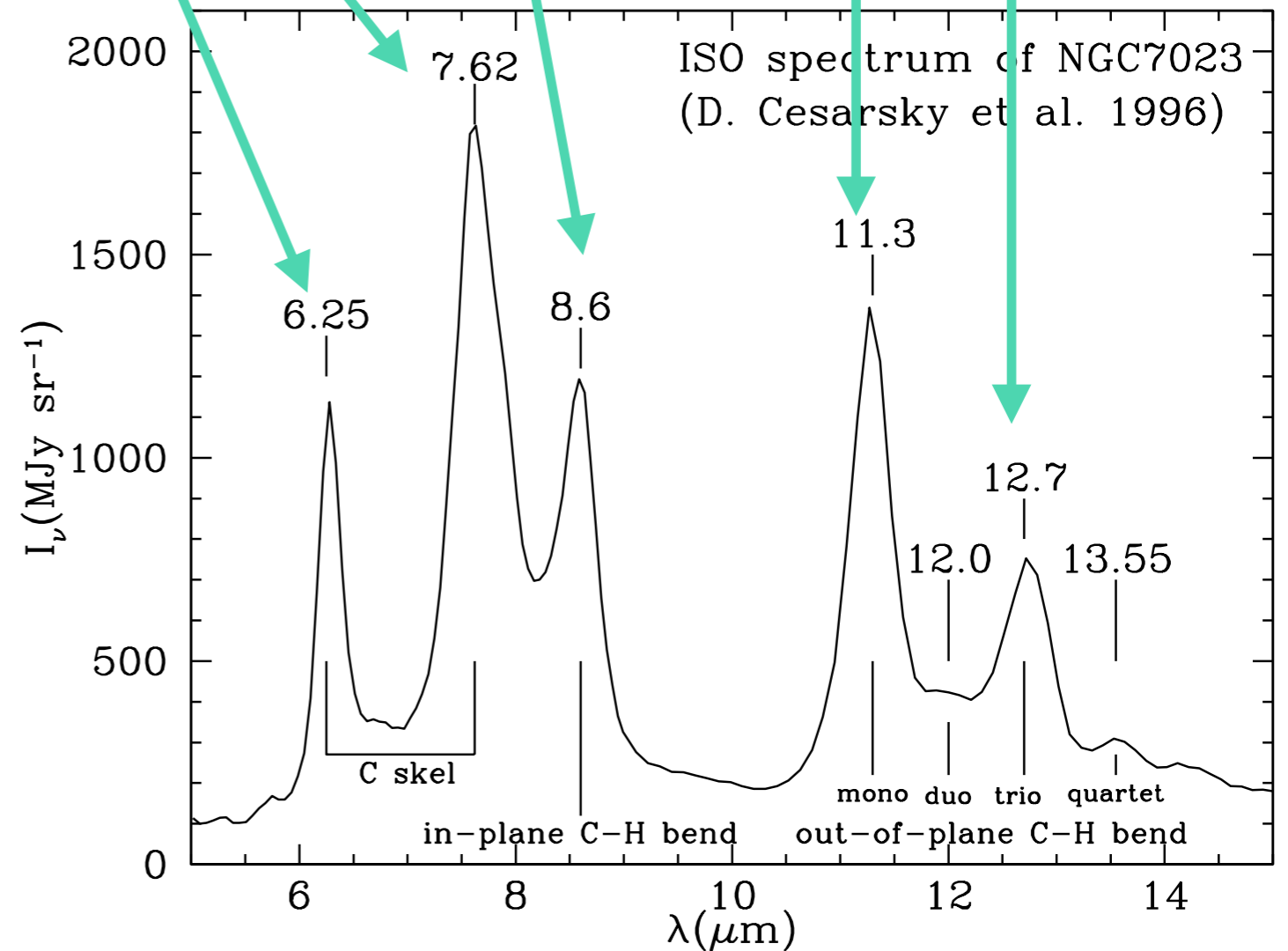


- vibrational emission bands at 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 micron

Vibrational mode of Carbon skeleton

Bending mode of C-H  
In plane

Bending mode of C-H  
Out of plane



# How does the dust appear to us globally?

## Milky Way galactic plane

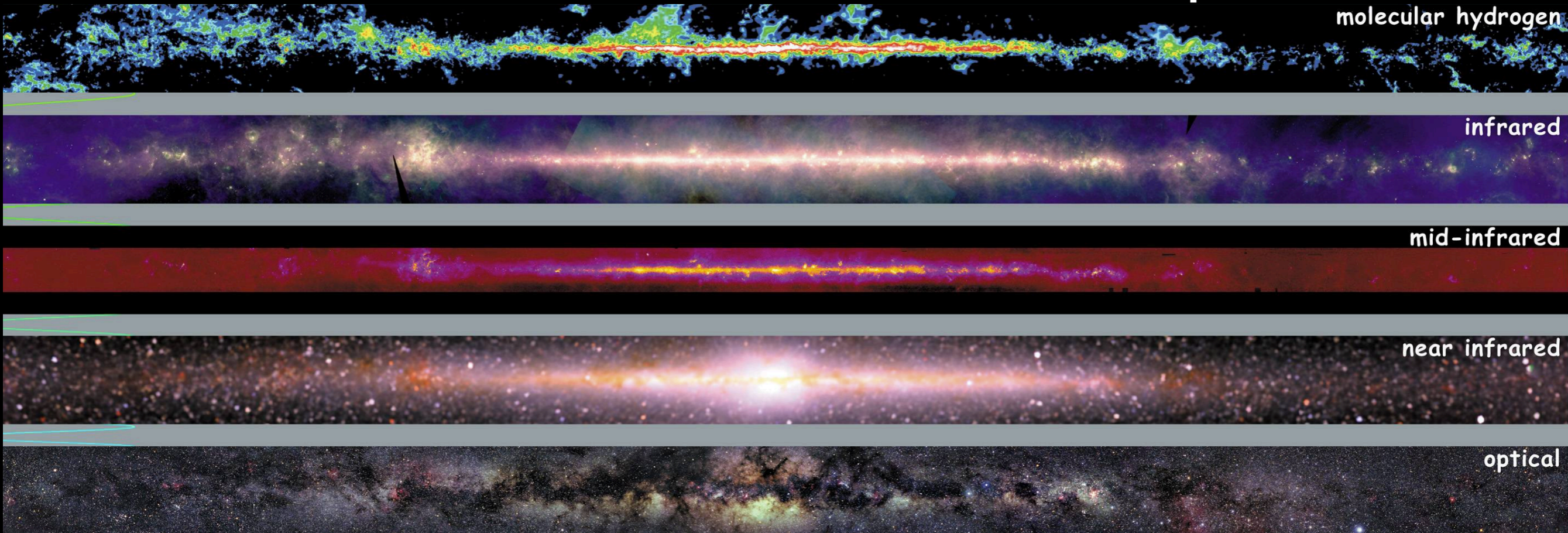
molecular hydrogen

infrared

mid-infrared

near infrared

optical



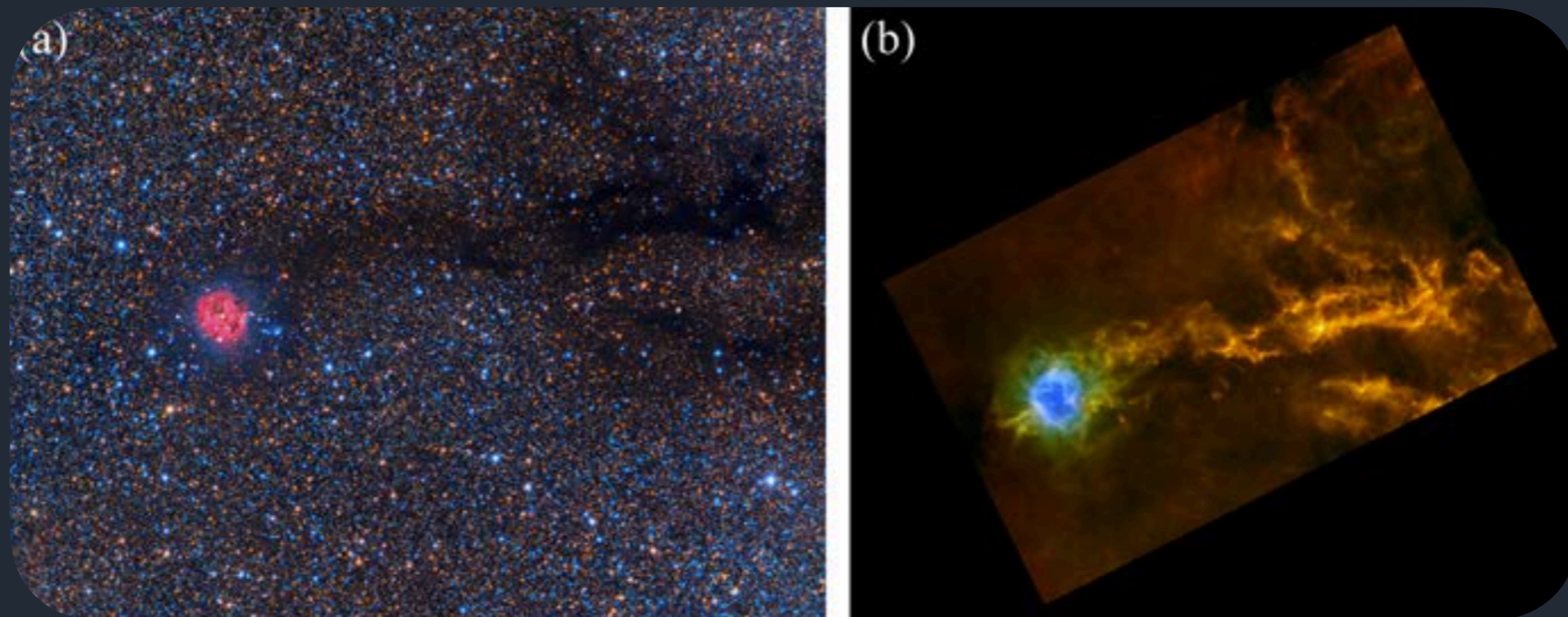


# How does the dust appear to us globally?

## Cocoon Nebula and trail of dark interstellar dust clouds:

(a) in the visible (credit and copyright: Tony Hallas);

(b) in the infrared (credit: ESA, SPIRE & PACS Consortia, Doris Arzoumian [CEA, Saclay] *et al.*);





# Infrared spectroscopy of dust

- Astronomical spectra:
  - ISO: 2 – 200  $\mu\text{m}$
  - SOFIA: 60 – 200  $\mu\text{m}$
  - Spitzer: 5 – 40  $\mu\text{m}$
  - Herschel: 40 – 260  $\mu\text{m}$
  - James Webb Space Telescope: 0.6 – 28  $\mu\text{m}$
- Ground-based telescopes:  $\sim 1\text{--}3 \mu\text{m}$  (VLT)
- Laboratory spectroscopy!



# Summarising

- **Up to mid-20th century:** dust was an annoying “fog” that prevented clear view of stars and galaxies
- The main task was to disperse that fog (theoretically)
- **Now:** dust affects every aspects of the formation of stars, galaxies and planets

# How and where dust form?

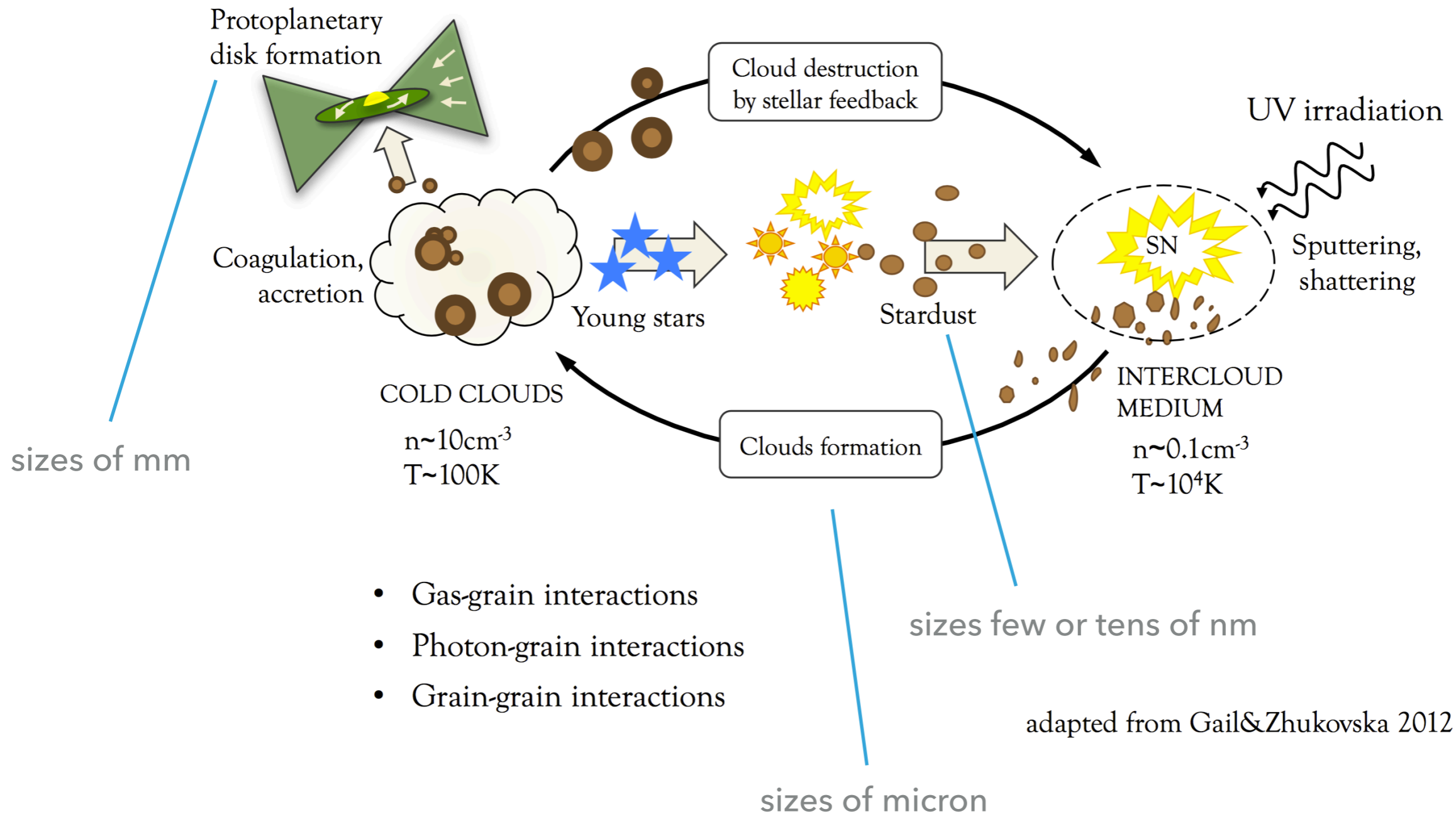
- Dust form mainly in AGB stars and SNe
- Once formed is injected in the ISM
- In the ISM can be re-processed via radiation and chemical reactions
- This can change their chemical structure and nature
- Main formation process: nucleation (and condensation)
- Need to enter a zone with high pressure and high temperature

# AGB stars

- Cool stars at the end of their lives
- Already burned most of H and He
- Their envelopes contain a richness of dust-related elements (C, Si, O) -> result of thermonuclear reactions
- The envelope eventually drifts away from the star by radiation pressure
- AGB stars: C-rich and O-rich



# Lifecycle of dust grains



adapted from Gail&Zhukovska 2012

**Table 5.1** A list of the main contributors to gas and dust in the Milky Way, with estimated injection rates<sup>a</sup> ( $M_{\odot} \text{ pc}^{-2} \text{ Myr}^{-1}$ ).

Source	Gas	Carbon dust	Silicate dust
AGB (C-rich)	750	3	
AGB (O-rich)	750		5
OB stars	30		
Wolf–Rayet	100	0.1	
Red supergiants	20		0.03
Novae	6	0.3	0.03
SN type Ia		0.3	2
SN type II	100	2	10

<sup>a</sup>Data are taken from Tielens *et al.* (2005),<sup>4</sup> Massey *et al.* (2005),<sup>5</sup> and Ferrarotti & Gail (2006).<sup>6</sup>

If  $n(\text{O})/n(\text{C}) > 1$  : oxygen atoms react in the stellar atmosphere with Si and any other metals to form amorphous and crystalline oxide and silicates

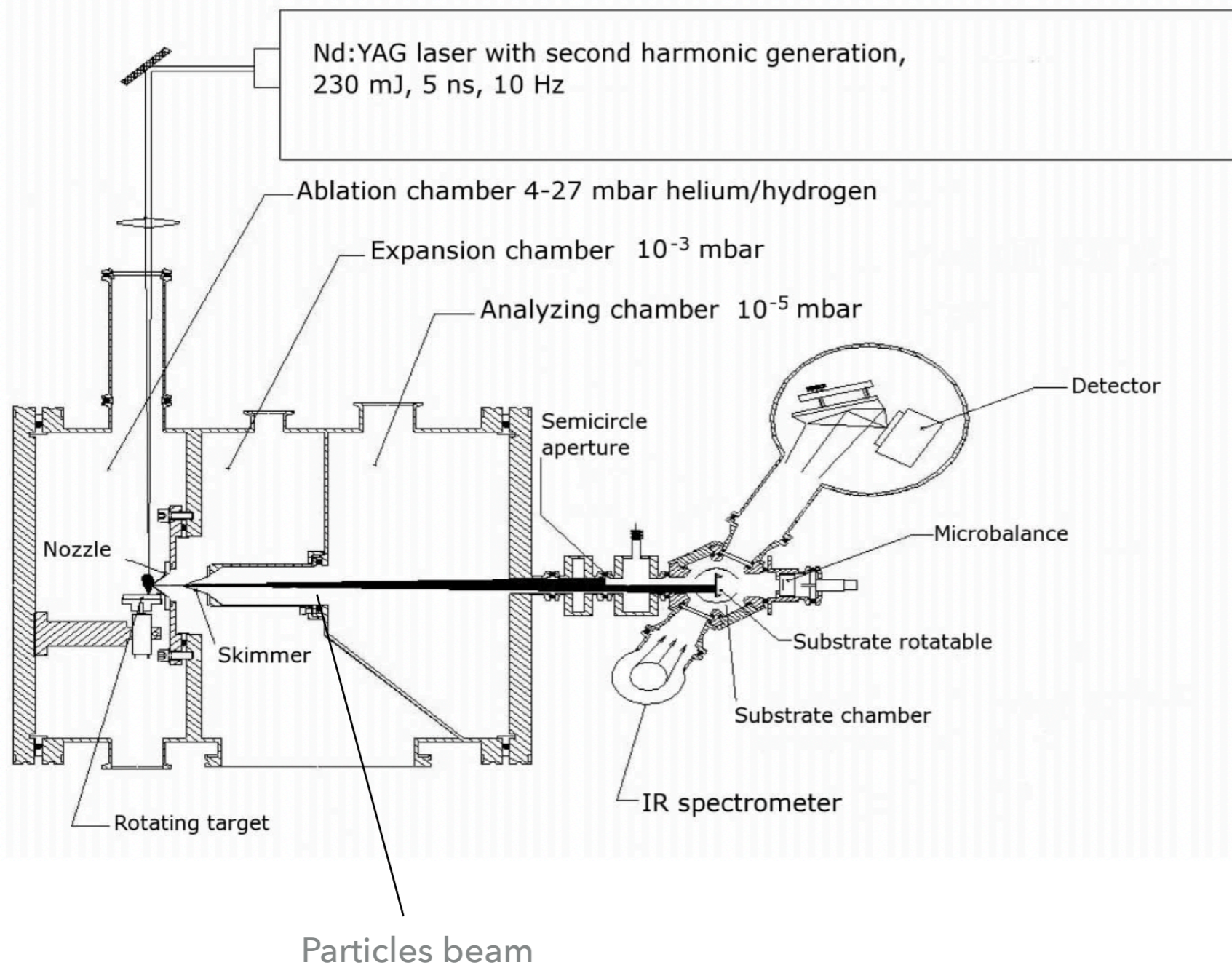
If  $n(\text{O})/n(\text{C}) < 1$  : carbon particles are into graphite or amorphous carbon grains

**Table 5.5** Chemical inventory in dust factories.

Material	AGB	Post-AGB	PN	Nova	RSG	WR	LBV	SN
Amorphous silicates	X	X	X	X	X		X	X
Crystalline forsterite	X	X	X		X		X	
Crystalline enstatite	X	X	X		X		X	
Chromite	X							X
Aluminium oxide	X			X				X
Spinel	X							X
TiO <sub>2</sub>	X				X			
Hibonite	X							
MgO	X							
Fe	X							X
PAHs	X	X	X	X	X	X	X	
a-C:H	X	X	X	X		X		
Graphite	X	X		X				X
Diamond		X						X
SiC	X	X	X	X				X
Other carbides	X							X
Si <sub>3</sub> N <sub>4</sub>								X
MgS	X	X	X				X	



# Dust formation in laboratory



## STEP 1

Pulsed laser ablation of graphite, MgSi, FeSi or MgFeSi targets

## STEP 2

condensation of the evaporated species in a quenching atmosphere of a few mbar

He/H<sub>2</sub> for carbon grains

He/O<sub>2</sub> for silicate grains



# Dust formation in laboratory

Electron microscopy

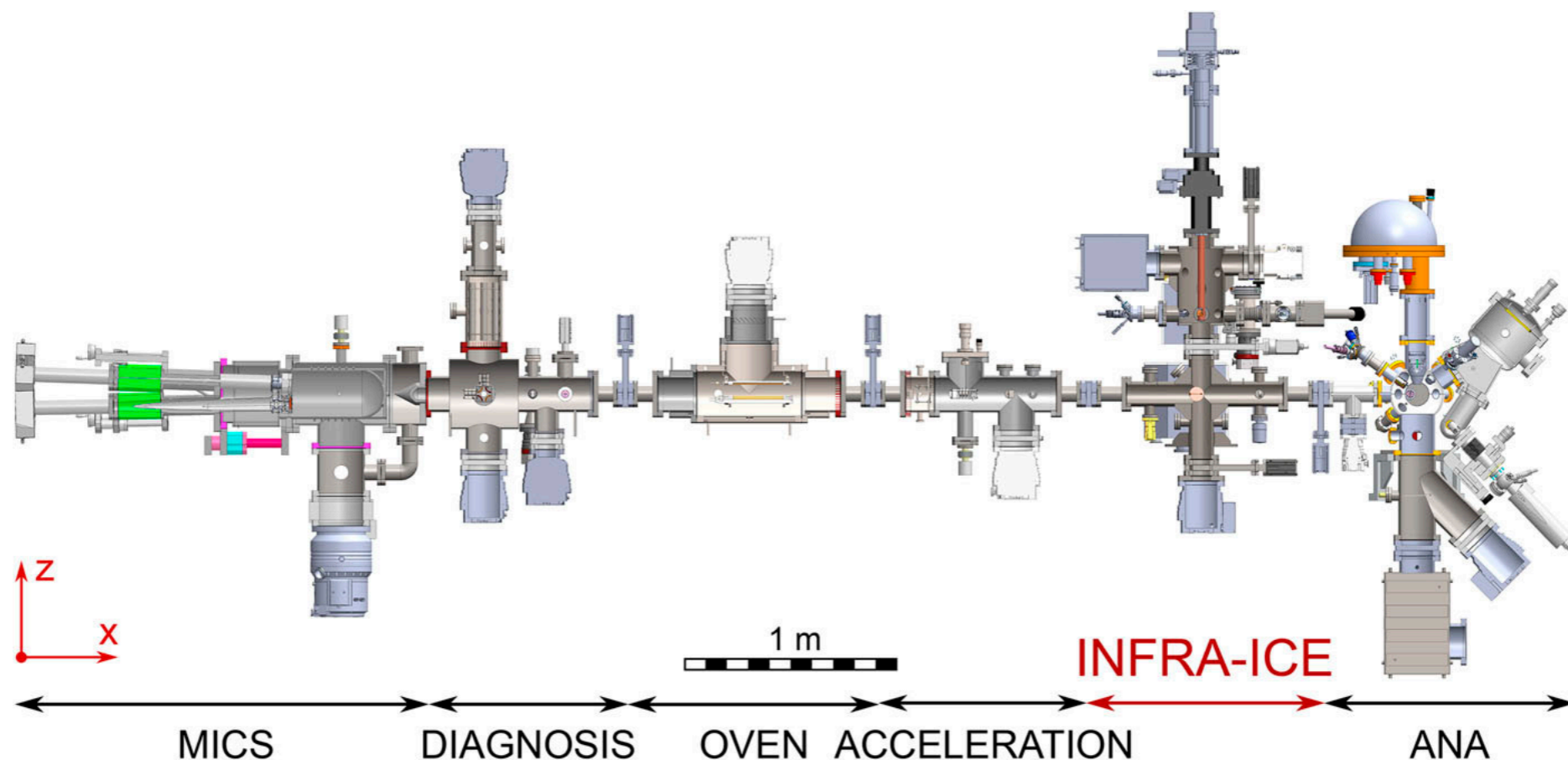
5 nm

100 nm

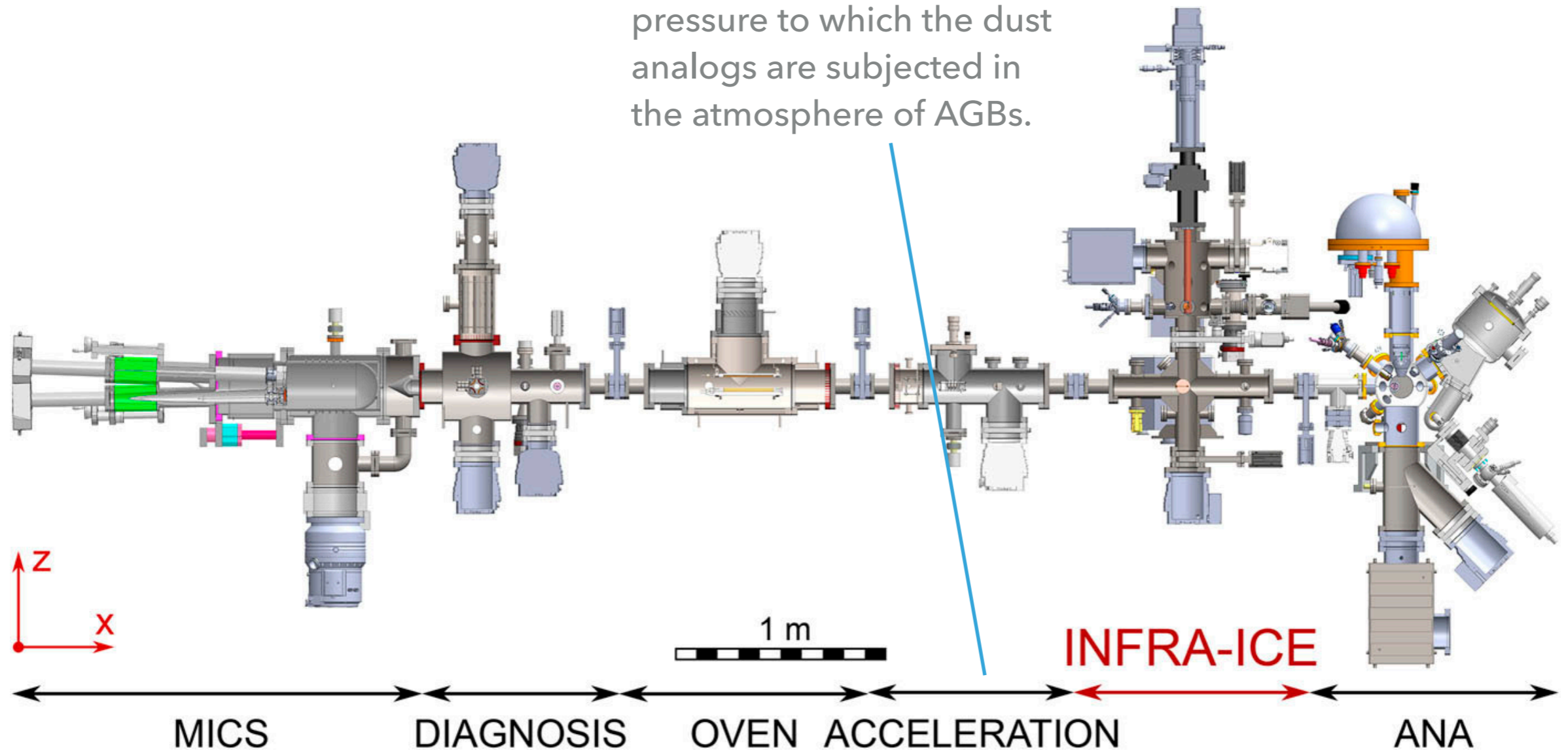


# Dust formation in laboratory

Stardust machine aimed at mimicking the journey of dust grains from their formation @1000-1500 K to their structure modification in the ISM (exposed to UV, CRs) up to the formation of ices in cold and dense regions



simulate the radiation pressure to which the dust analogs are subjected in the atmosphere of AGBs.



**INFRA-ICE**

MICS  
PRODUCTION

DIAGNOSIS  
ANALYSIS

OVEN  
HEATING

ACCELERATION

ANA

1 m

z  
x

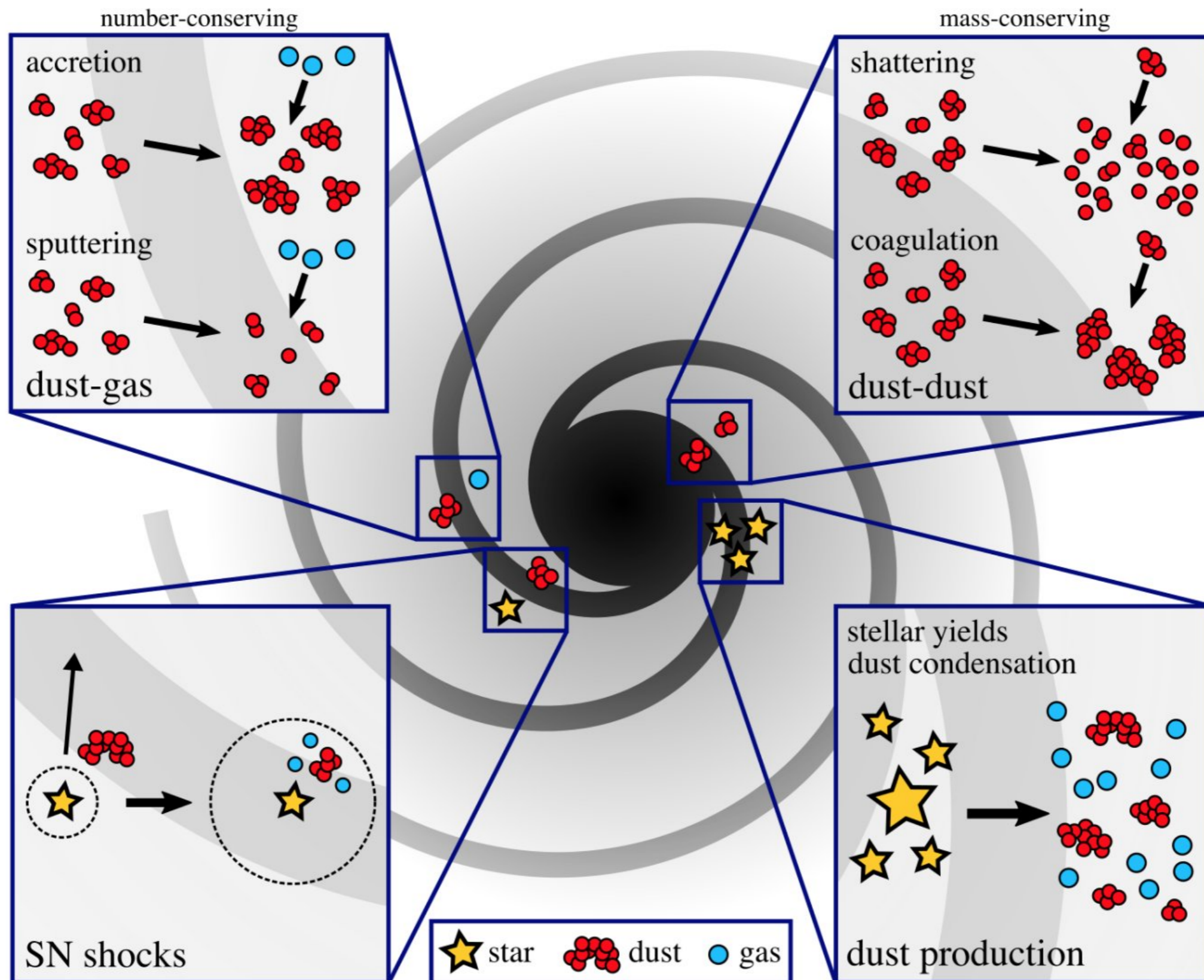
dust analogs are ionized, accelerated, and focused by an electron impact ionizer

heating of the particle beam to temperatures of up to 1400 K via three 2 kW infrared lamps

charge, production rate, and the mass of the analogs

Multiple ion cluster source  
Magnetron sputter sources

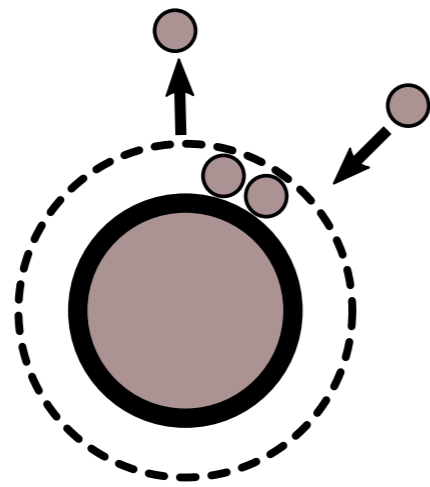




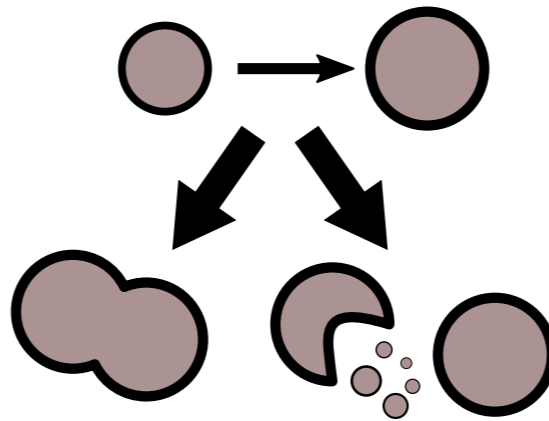
**Figure 8.** Schematic illustration of the lifecycle of dust within a galaxy. Graphics depict stars (yellow), dust grains (red), and gas-phase metals (blue) in the ISM. Dust grains are produced through stellar evolution, interact with other dust grains and gas-phase metals through collisional processes, and can be destroyed near SNe. Collisional processes are divided into those that conserve grain number (top left) and those that conserve grain mass (top right). Accretion and sputtering change total dust mass by growing or shrinking individual grains, while shattering and coagulation preserve overall mass but affect the number of grains.



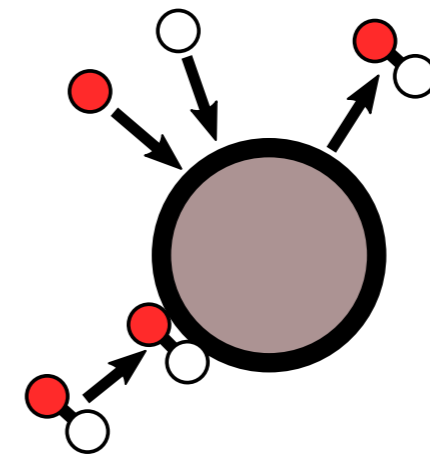
## DUST PHYSICS: SHATTERING-SPUTTERING-GROWTH



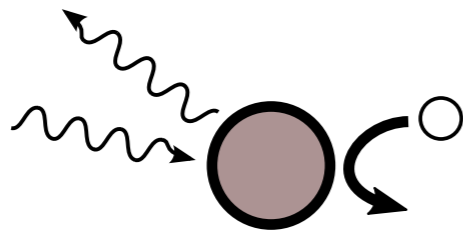
GROWTH  
EVAPORATION



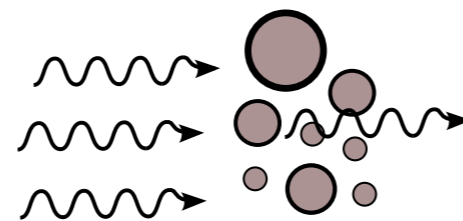
COAGULATION  
FRAGMENTATION



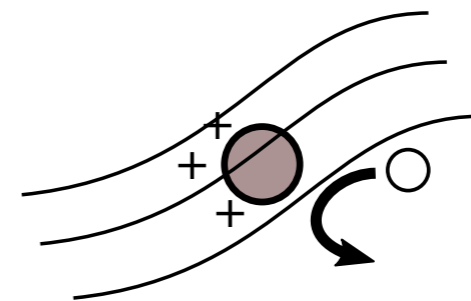
CATALYSIS  
FREEZE-OUT



COOLING



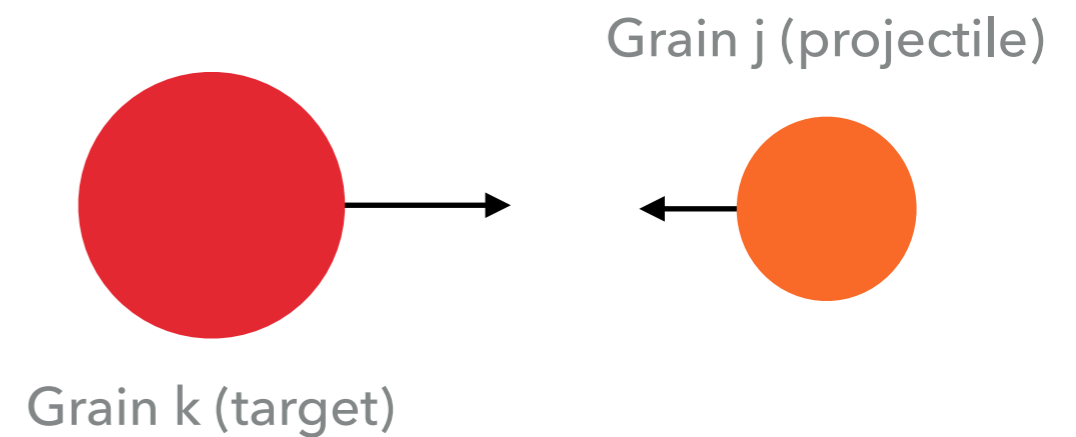
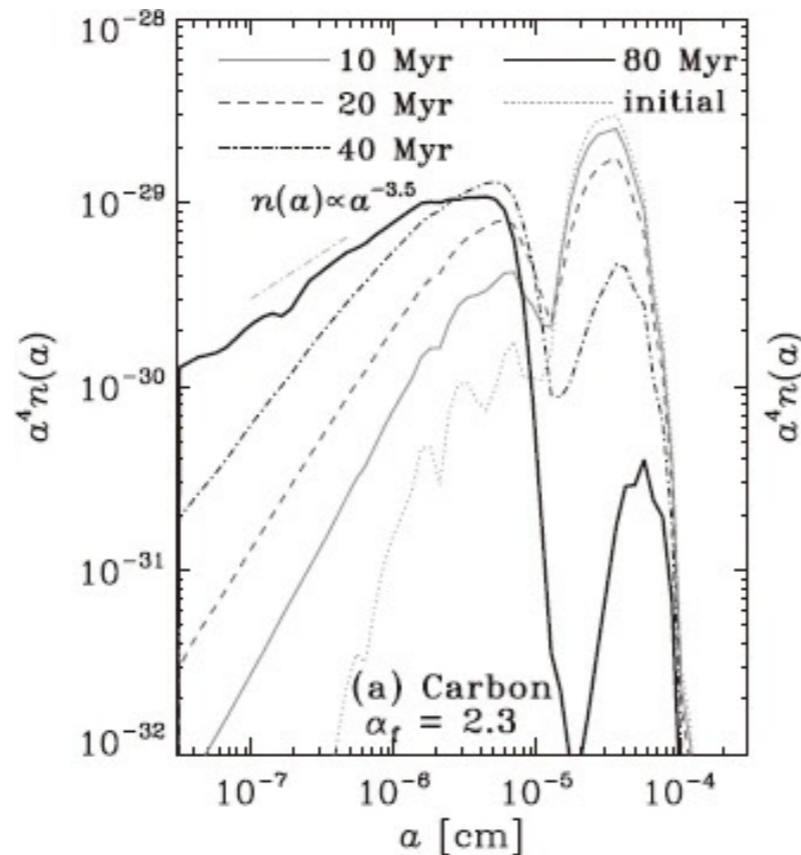
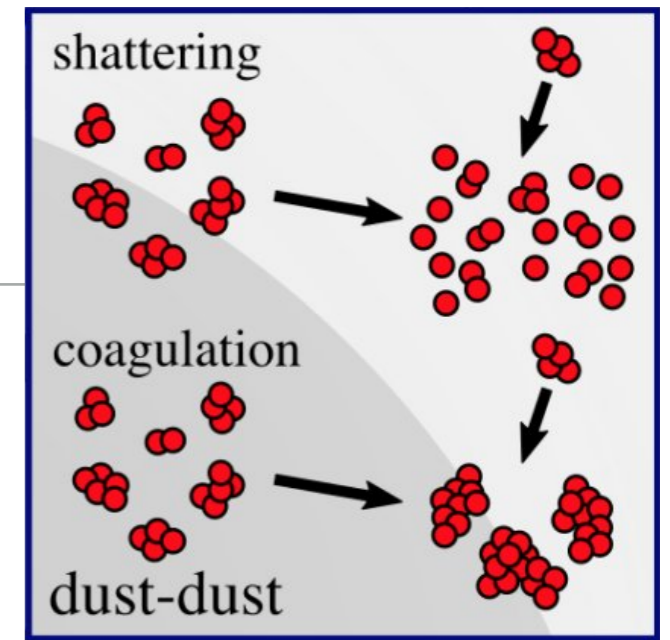
OPACITY



NON-IDEAL MHD

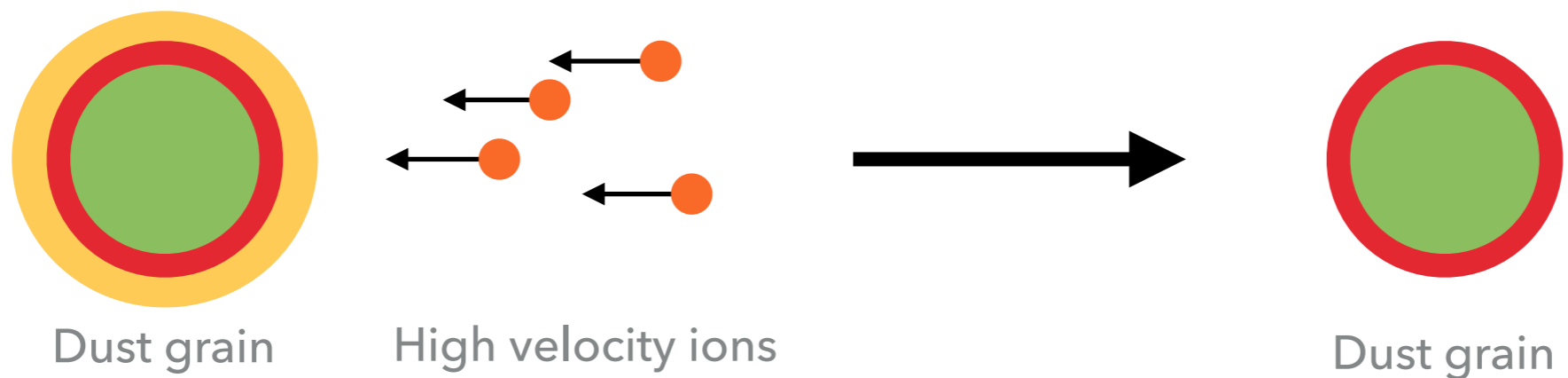
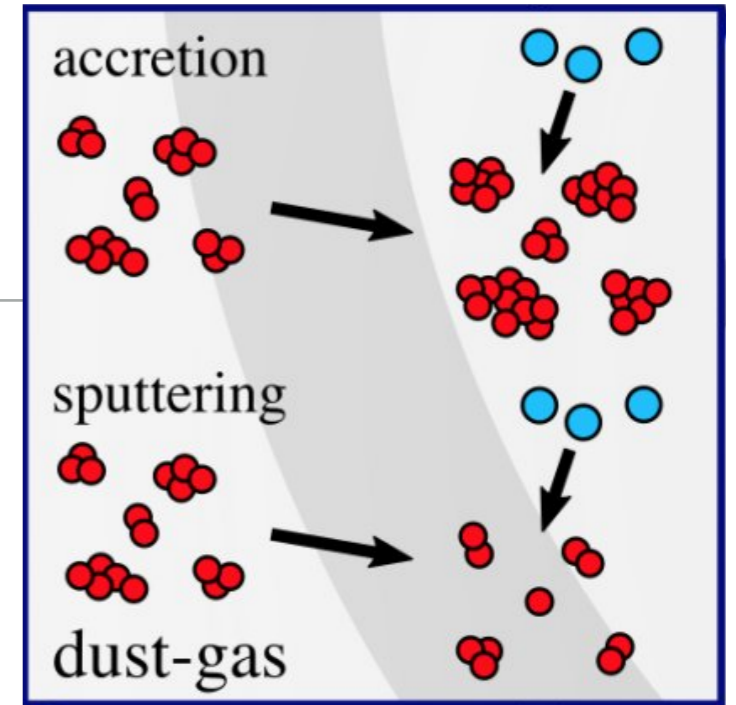
# SHATTERING

- ▶ Grain-Grain collisions
- ▶ Redistribute grain mass into units of smaller sizes
- ▶ Distribution favors small size grains
- ▶ Can also cause vaporization and remove smaller grains entirely



# SPUTTERING

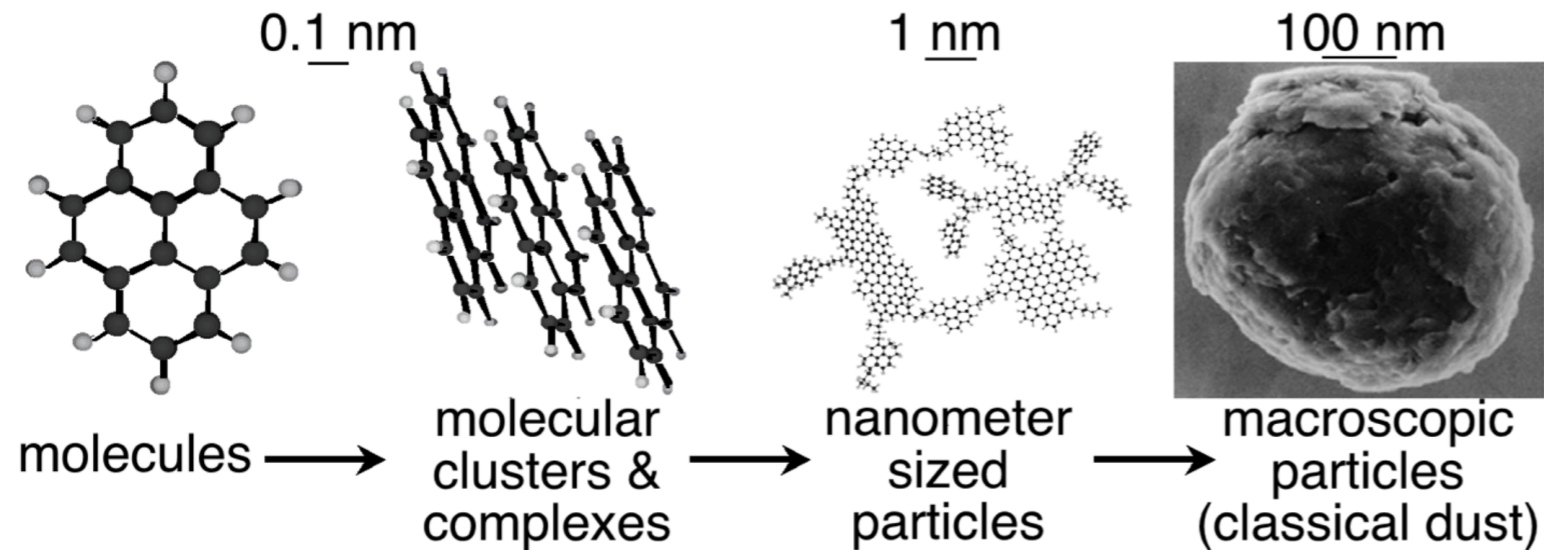
- ▶ Gas-Grain collisions
- ▶ Sufficiently high-energy needed
- ▶ Erosion
- ▶ Atoms and molecules can be ejected into the gas-phase
- ▶ Interstellar shocks



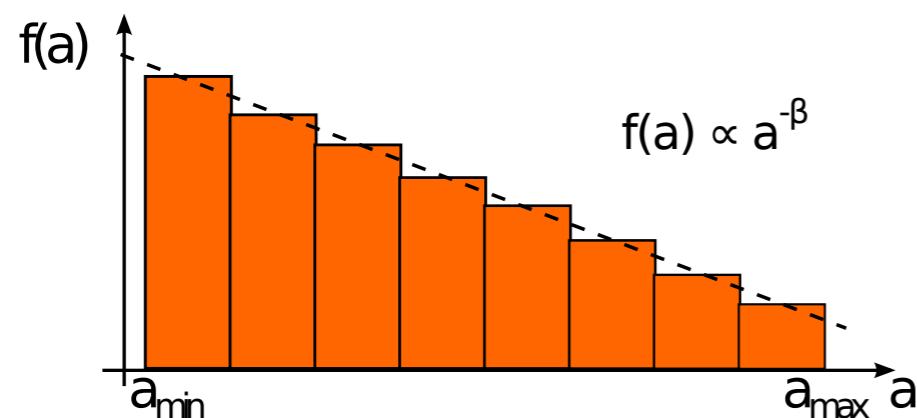
- 
- ▶ Gas-phase chemistry
  - ▶ Photochemistry
  - ▶ Grain-surface chemistry (This Lecture)
- 
- ▶ Gas-phase reactions cannot explain the whole range of molecular species and abundances observed
  - ▶ Dust accounts for 1% of the total matter in the ISM
  - ▶ Formed by micro-sized particles
  - ▶ Dust scatters, absorbs, and re-radiates starlight



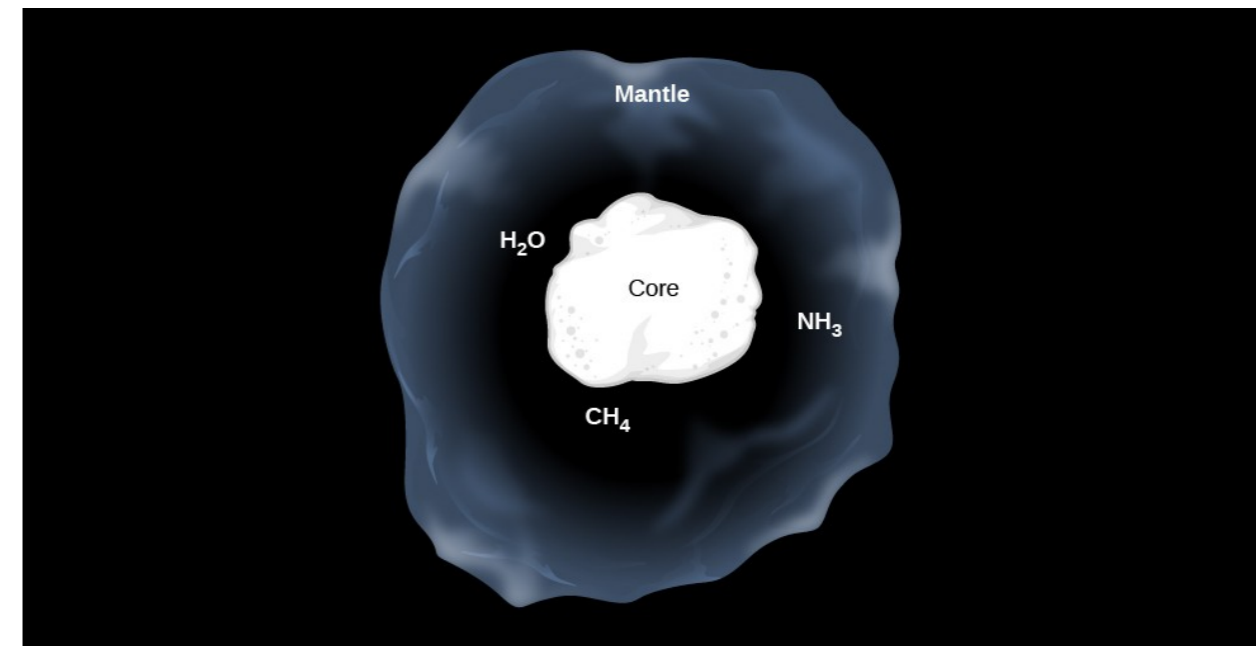
# GRAINS PROPERTIES SUMMARY



- Microscopic particles: atoms < size < clusters of molecules
  - Polycyclic Aromatic Hydrocarbons (PAHs): ~0.5–3nm (5–30 Å)
- Macroscopic particles: size >> molecules
  - Dust grains: > 3nm – 1cm



- Carbonaceous/silicates
- Size distribution (usually a single size in chemical models)
- Fluffy, porous structure (usually assumed spherical and compact)
- Molecules stick to dust surface:
  - ~ $10^6$  binding sites on 1000Å grain
  - a binding site has a size ~1Å
  - ~100–300 monolayers of ice



## IMPORTANCE OF DUST

- ▶ Dust allows for the formation of more complex molecules compared to gas-phase reactions
- ▶ Dust grains tend to be negatively charged in molecular clouds (see later)

COMPLEXITY

---

**HOW DOES H<sub>2</sub> FORM?**

## GAS-PHASE FORMATION PATHS

H<sub>2</sub> symmetric homonuclear molecule:

- ▶ no dipole moment
- ▶ strict selection rules for transitions
- ▶ difficult to observe in dense regions (even if most abundant molecule)
- ▶  $H + H \not\rightarrow H_2 \Rightarrow ({}^3\Sigma - {}^1\Sigma)$  transitions not allowed
- ▶  $H + H + H \not\rightarrow H_2 \Rightarrow$  only at high-densities
- ▶  $H^- + H \rightarrow H_2 + e^- \Rightarrow$  yes but not so efficient
- ▶  $H_2^+ + H \rightarrow H_2 + H^+ \Rightarrow$  yes but not so efficient

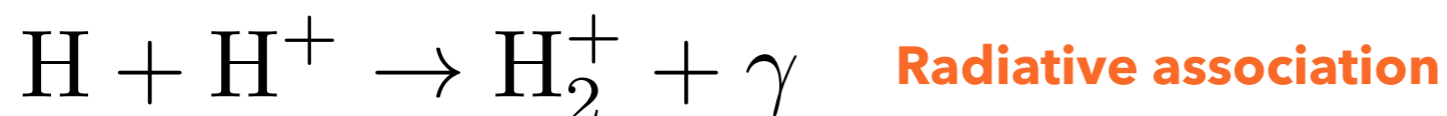
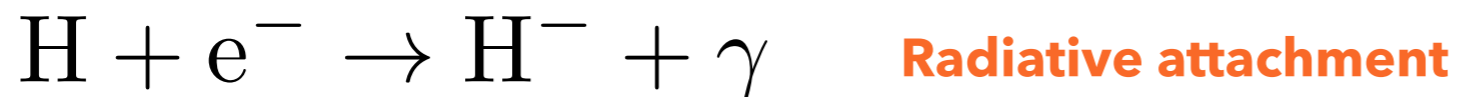
Cool Stars-envelope  
SNe ejecta  
Early Universe



Precursor formation slow



## GAS-PHASE FORMATION PATHS (CONT'D)

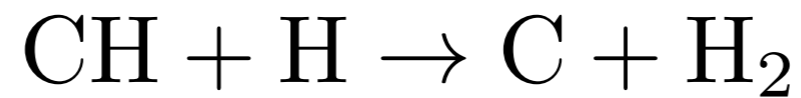


- ▶ Also easily destroyed by photodissociation and photodetachment

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

# CHICKEN-EGG PROBLEM

- ▶ Other channels can be considered (?)



It also forms from  $\text{H}_2$



## DUST GRAINS THEN!

- ▶ Mid-20th laboratory and theoretical work done
- ▶ If  $H_2$  forms on dust then also other molecules can do it?
- ▶ In particular the complexity in star-forming regions:

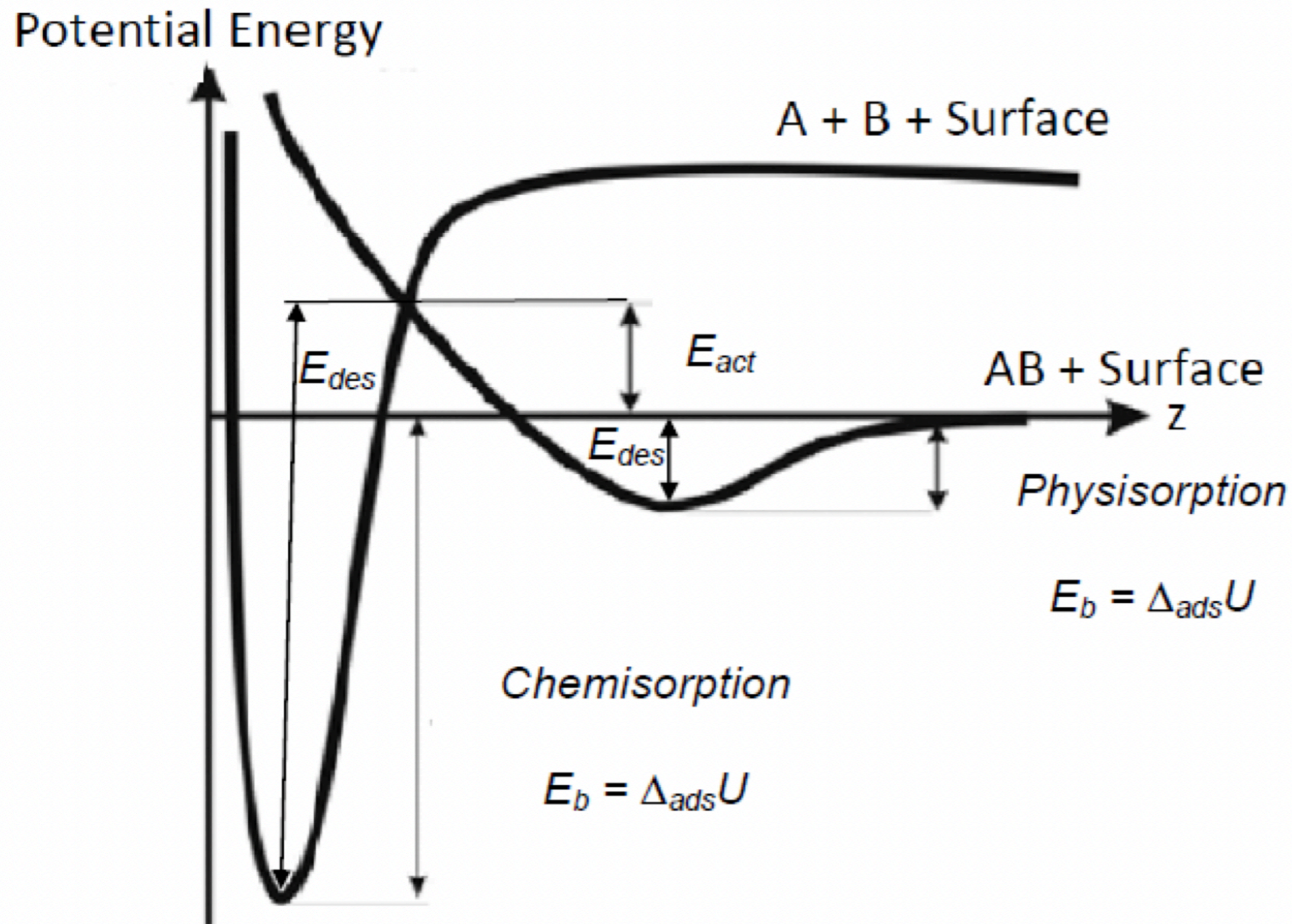
methanol ( $CH_3OH$ ), ethanol ( $C_2H_5OH$ ), dimethyl ether ( $CH_3OCH_3$ ), methyl formate ( $HCOOCH_3$ ), formic acid ( $HCOOH$ ), acetic acid ( $CH_3COOH$ ), propynal ( $HC_2CHO$ ), propenal ( $CH_2CHCHO$ ), propionaldehyde ( $CH_3CH_2CHO$ ), glycolaldehyde ( $CH_2OHCHO$ ), ethylene glycol ( $HOCH_2CH_2OH$ ), ethylene oxide ( $c-C_2H_4O$ ), acetaldehyde ( $CH_3CHO$ ), and ketene ( $H_2CCO$ )

---

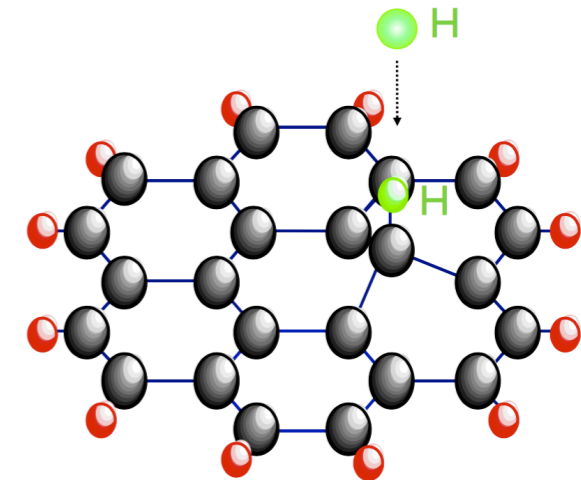
# INTERACTION BETWEEN ATOMS AND THE SURFACE

- ▶ **Physisorption:** van der Waals interaction (most common)
  - ▶ Induced dipole moments in the electrons shells of the gas-phase species and the surface atoms
- ▶ **Chemisorption:** real chemical bond (e.g. H-bond)
- ▶ Regulated by the sticking coefficient  $S$
- ▶ Represents the probability that an atom/molecule is adsorbed after collision
- ▶  $S$  depends on temperature, binding energy, and grain composition



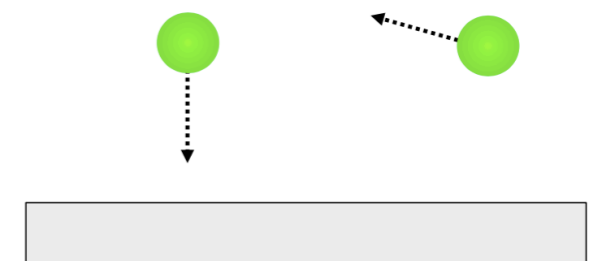


### Chemisorption



- Chemical bonds
- Binding energies:  $\sim 0.5\text{--}5\text{ eV}$   
or  $>20,000\text{ K}$

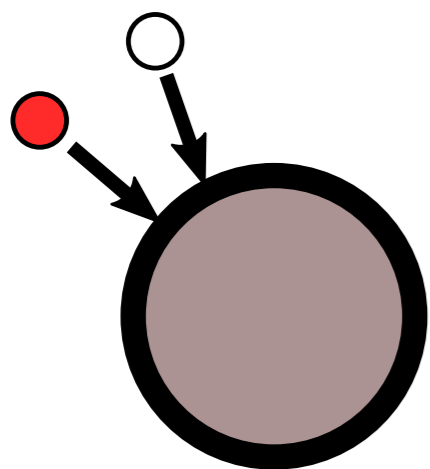
### Physisorption



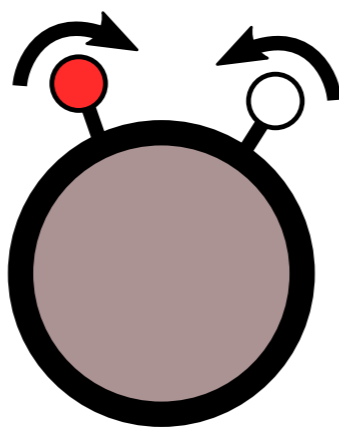
- Weak electrostatic van der Waals force
- Binding energies:  $\sim 10\text{--}100\text{ meV}$   
or  $\sim 100\text{--}10,000\text{ K}$

# FORMATION ON DUST: MECHANISMS

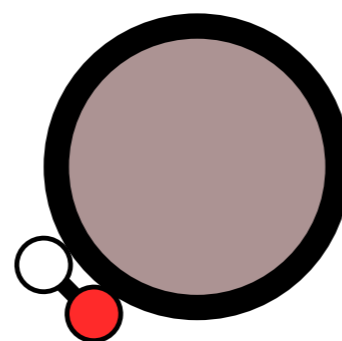
Langmuir-Hinshelwood



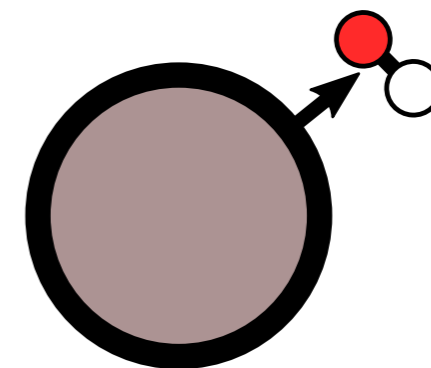
1. Adsorption



2. Diffusion

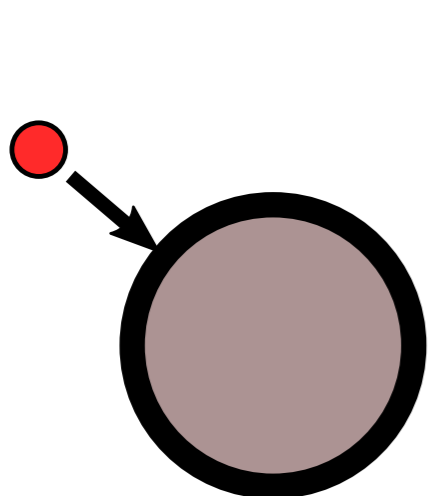


3. Formation

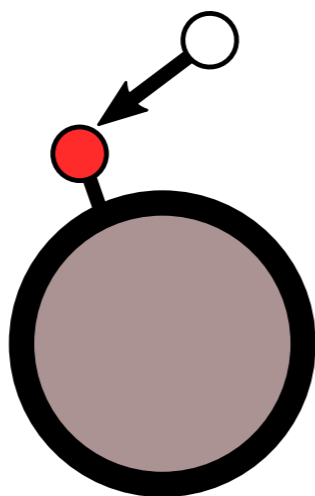


4. Desorption

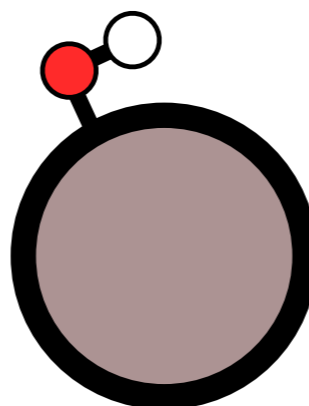
Ely-Rideal



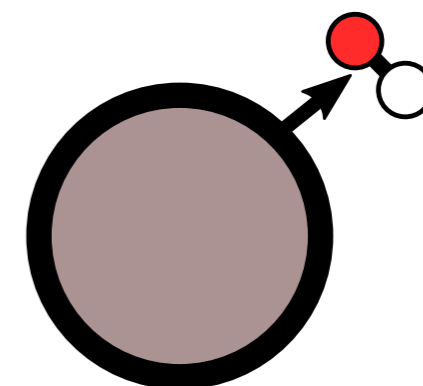
1. Adsorption



2. Collision

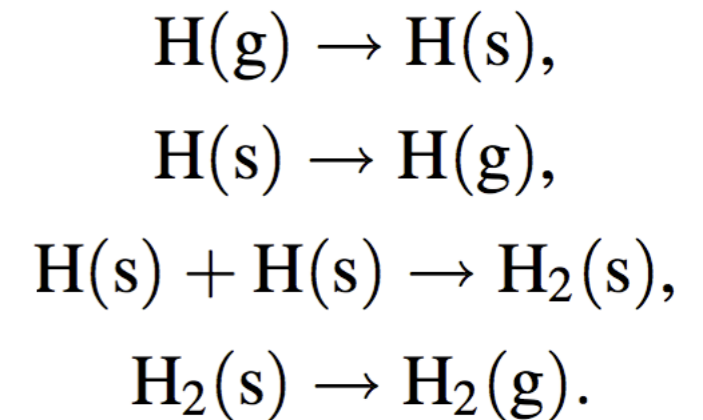


3. Formation



4. Desorption

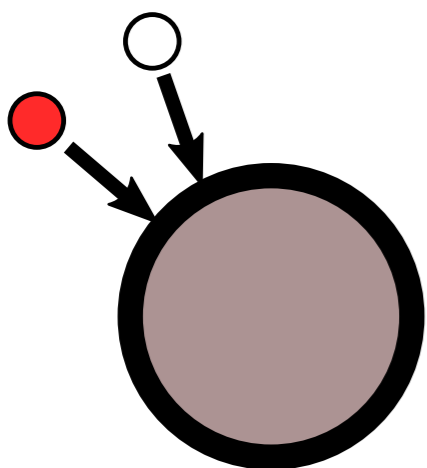
## ENERGY BALANCE



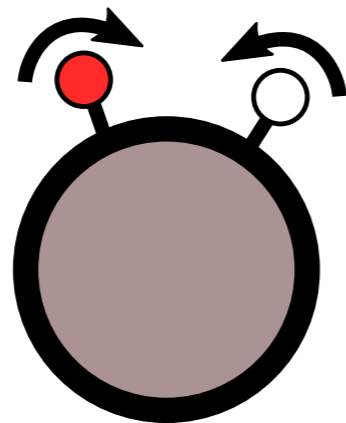
energy distributed as following

- ▶ 0.2 eV as kinetic energy
- ▶ 4.2 eV in roto-vibrational states of  $\text{H}_2$
- ▶ heating of grain negligible

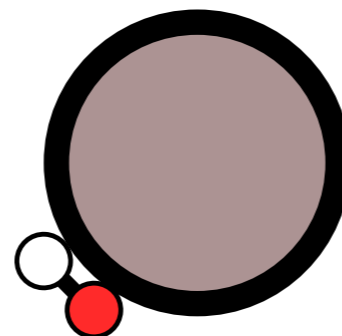
Langmuir-Hinshelwood



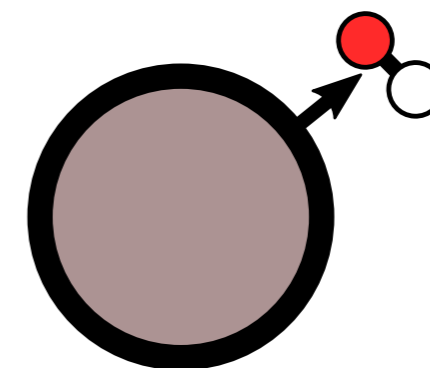
1. Adsorption



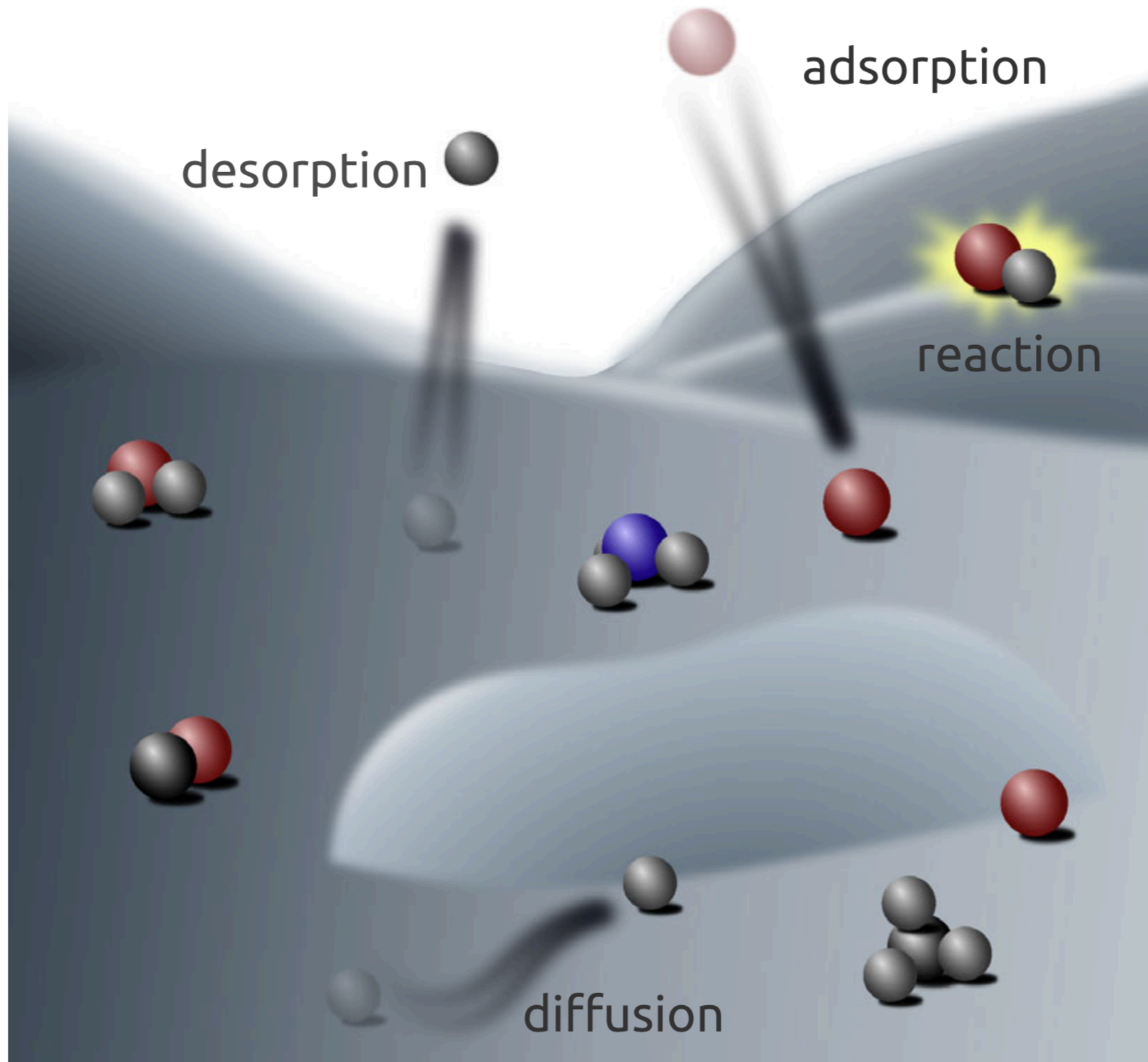
2. Diffusion



3. Formation

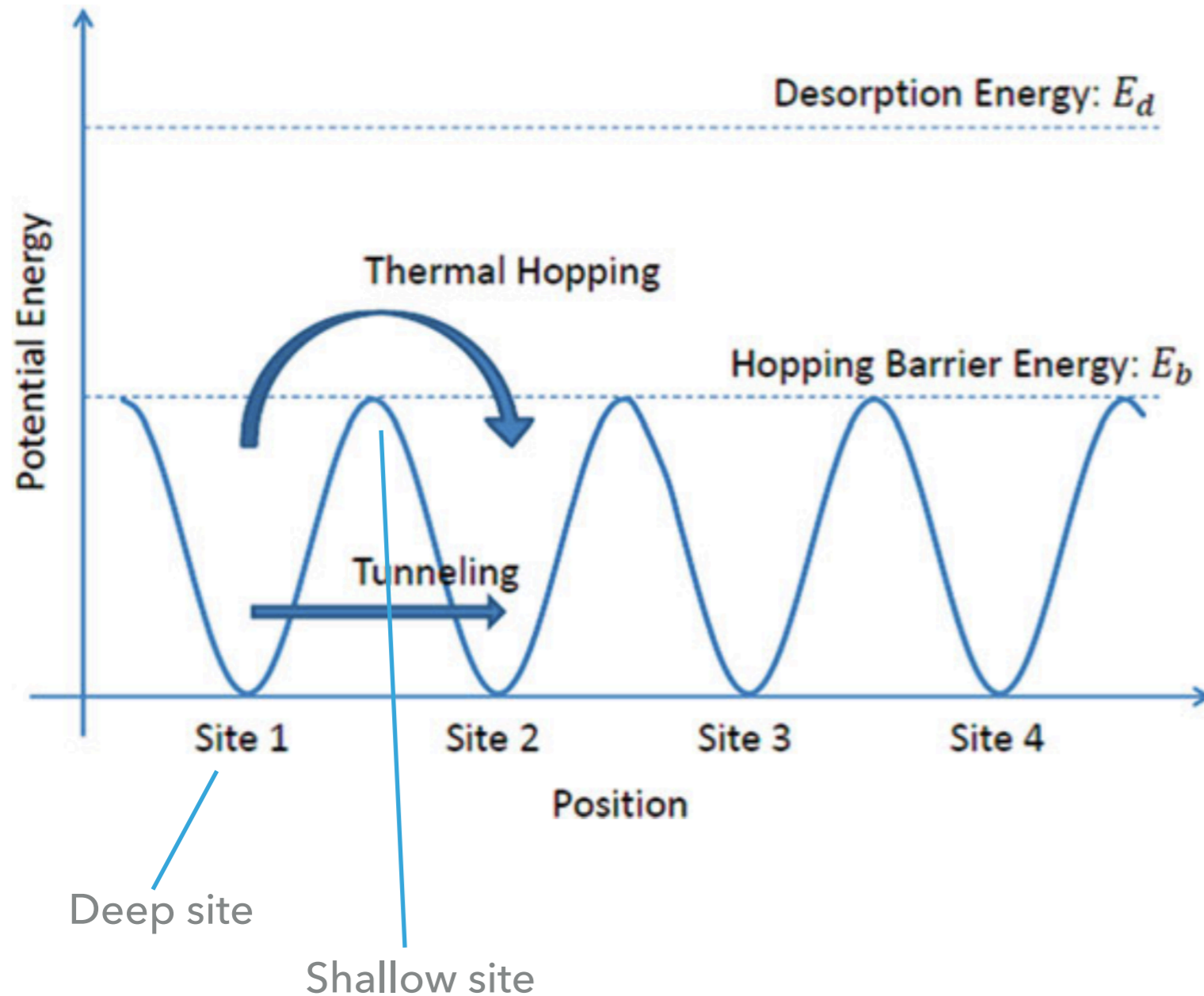


4. Desorption





# ADSORPTION / FREEZE-OUT

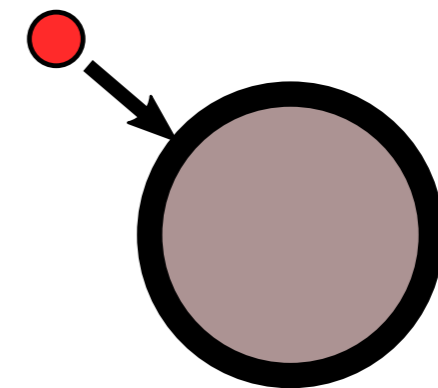


$$k_{\text{ads}} = \sigma n_d \langle v_i \rangle S$$

$$\sigma = \pi a^2$$

$$\langle v_i \rangle = \sqrt{\frac{8k_B T}{\pi m_i}}$$

$$R_{\text{ads}}^i = \sigma n_d n_i \langle v_i \rangle S$$

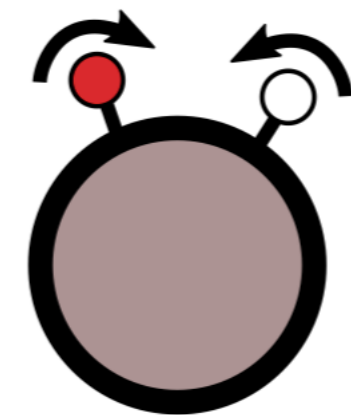
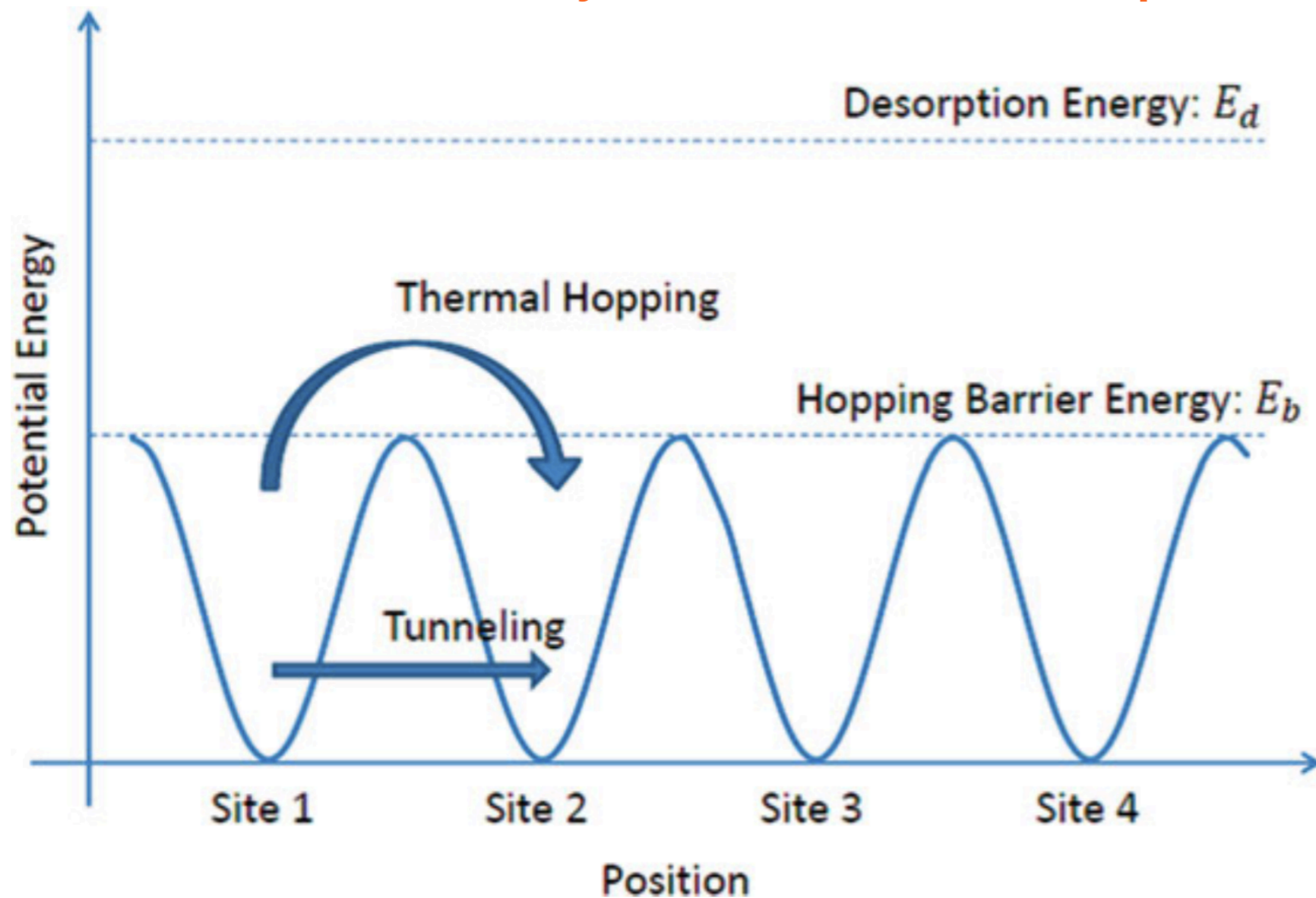


1. Adsorption

**It is a collisional process (as usual)**

# REACTIONS: 2-BODY

Density of sites and distribution depends on the surface!



2. Diffusion

$$k_{diff}^i = \nu_0^i \exp(-E_{diff}^i / T_d)$$

characteristic vibration frequency for the adsorbate species

$$k_{diff}^i = \nu_0^i \exp(-E_{diff}^i/T_d) \quad \nu_0^i = \sqrt{\frac{2n_s E_D^i}{\pi^2 m_i}}$$

**Table 6.1** Desorption energies and various timescales for some atoms and molecules

Species	$E_d/K^a$	10 K	$t_{hop}/s^b$ 20 K	40K	10 K
H	450	$1.7 \times 10^{-3}$	$2.3 \times 10^{-8}$	$8.2 \times 10^{-11}$	$1.0 \times 10^7$
H <sub>2</sub>	430	$9.3 \times 10^{-4}$	$2.0 \times 10^{-8}$	$9.3 \times 10^{-11}$	$2.0 \times 10^6$
OH	2850	$3.7 \times 10^{49}$	$4.3 \times 10^{18}$	1.4	$2.9 \times 10^{111}$
H <sub>2</sub> O	5700	$2.1 \times 10^{111}$	$2.7 \times 10^{49}$	$3.1 \times 10^{18}$	$1.2 \times 10^{235}$
N <sub>2</sub>	1000	$5.5 \times 10^9$	$7.6 \times 10^{-2}$	$2.8 \times 10^{-7}$	$2.8 \times 10^{31}$
CO	1150	$9.2 \times 10^{12}$	3.0	$1.7 \times 10^{-6}$	$8.6 \times 10^{37}$
CH <sub>4</sub>	1300	$1.2 \times 10^{16}$	$9.1 \times 10^1$	$8.0 \times 10^{-6}$	$2.0 \times 10^{44}$
H <sub>2</sub> CO	2050	$2.5 \times 10^{32}$	$1.4 \times 10^{10}$	$1.0 \times 10^{-1}$	$8.2 \times 10^{76}$
CH <sub>3</sub> OH	5530	$5.8 \times 10^{107}$	$5.3 \times 10^{47}$	$5.0 \times 10^{17}$	$7.0 \times 10^{227}$
HCOOCH <sub>3</sub>	6300	$3.9 \times 10^{124}$	$1.5 \times 10^{56}$	$9.7 \times 10^{21}$	$2.5 \times 10^{261}$
CH <sub>3</sub> OCH <sub>3</sub>	3150	$1.9 \times 10^{56}$	$1.2 \times 10^{22}$	$9.6 \times 10^4$	$4.8 \times 10^{124}$
C	800	$1.8 \times 10^5$	$3.7 \times 10^{-4}$	$1.7 \times 10^{-6}$	$4.3 \times 10^{22}$
O	800	$2.1 \times 10^5$	$4.3 \times 10^{-4}$	$2.0 \times 10^{-6}$	$4.9 \times 10^{22}$

# of sites per unit area

<sup>a</sup>Desorption energy

<sup>b</sup>Hopping timescale from one site to another, assuming that  $E_b = E_d/2$

<sup>c</sup>Evaporation timescale

<sup>d</sup>Timescale for quantum tunneling from one site to another

<sup>e</sup>Accretion timescale of molecules onto a single grain. The gas-phase abundance is set to 1 cm<sup>-3</sup>

# REACTIONS: BASIC EQUATIONS (1)

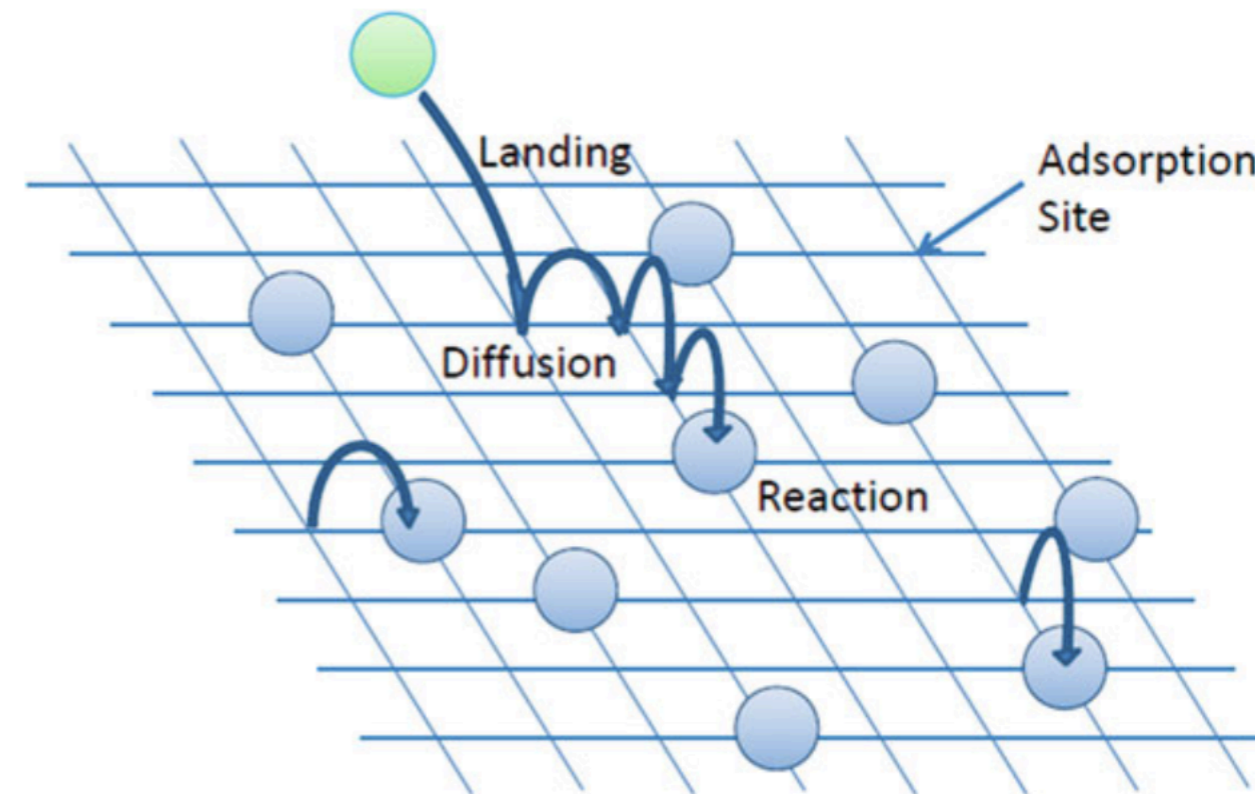
Area / typical distance between two subsequent sites (3 Angstrom)

$$N_{sites} = \frac{4\pi a^2}{a_{pp}^2}$$

$$k_{ik}^s = \frac{P_{ik}(k_{diff}^i + k_{diff}^k)}{N_{sites}n_d}$$

$$k_{diff}^i = \nu_0^i \exp(-E_{diff}^i/T_d)$$

$$P_{ik} = \alpha_{ik} \exp(-E_a/T_d)$$



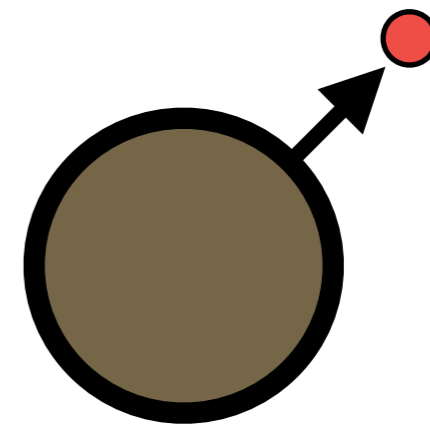
Normally taken to be 1 but if reactions involve a barrier we have to consider tunneling effects



## DESORPTION PROCESSES: THERMAL + NON-THERMAL

$$k_i^{des} = k_i^{des,th} + k_i^{des,cr}$$

$$k_i^{des,th} = \nu_0^i \exp\left(-\frac{E_D^i}{T_d}\right)$$



$$k_i^{des,cr} = f(70 \text{ K}) k_i^{des,th}(70 \text{ K})$$

$$f(70 \text{ K}) = \left( \frac{\zeta_{cr}}{1.3 \times 10^{-17} \text{ s}^{-1}} \right) 3.16 \times 10^{-19}$$

# HOW THE SYSTEM OF RATE EQUATIONS IS MODIFIED

Standard gas phase term

$$\frac{dn_i}{dt} = \sum_l \sum_j k_{lj}(T) n_l n_j - n_i \sum_j k_{ij}(T) n_j - (k_{ads}^i n_i + k_{des}^i n_i^s)$$

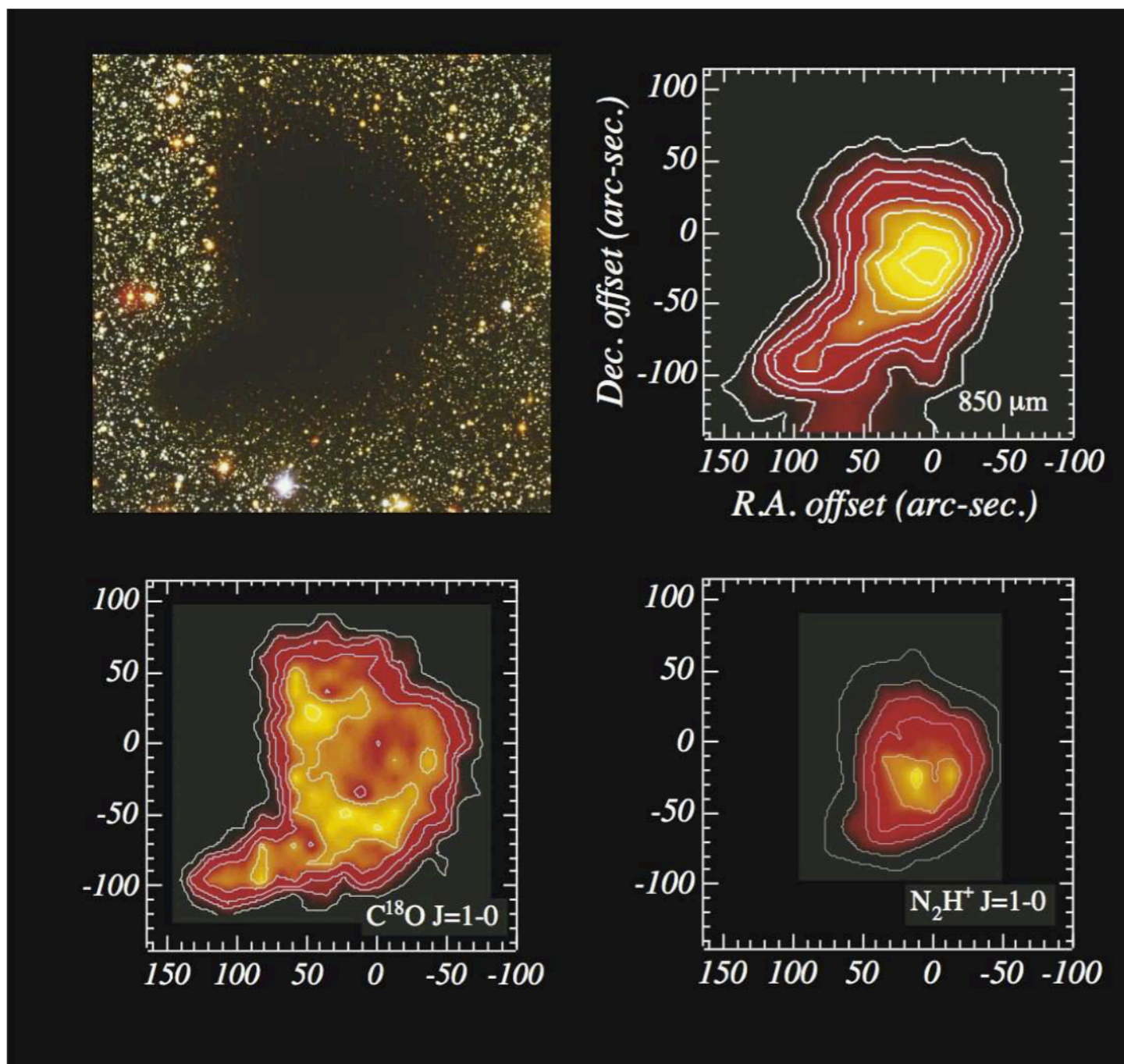
Gas-grain interaction term

$$\frac{dn_i^s}{dt} = \sum_l \sum_j k_{lj}(T) n_l^s n_j^s - n_i^s \sum_j k_{ij}(T) n_j^s + (k_{ads}^i n_i - k_{des}^i n_i^s)$$

2-body reactions on dust grains

---

**EXAMPLES**



$\text{N}_2\text{H}^+$

CO

$\text{H}_2\text{D}^+$

$\text{HCO}^+$

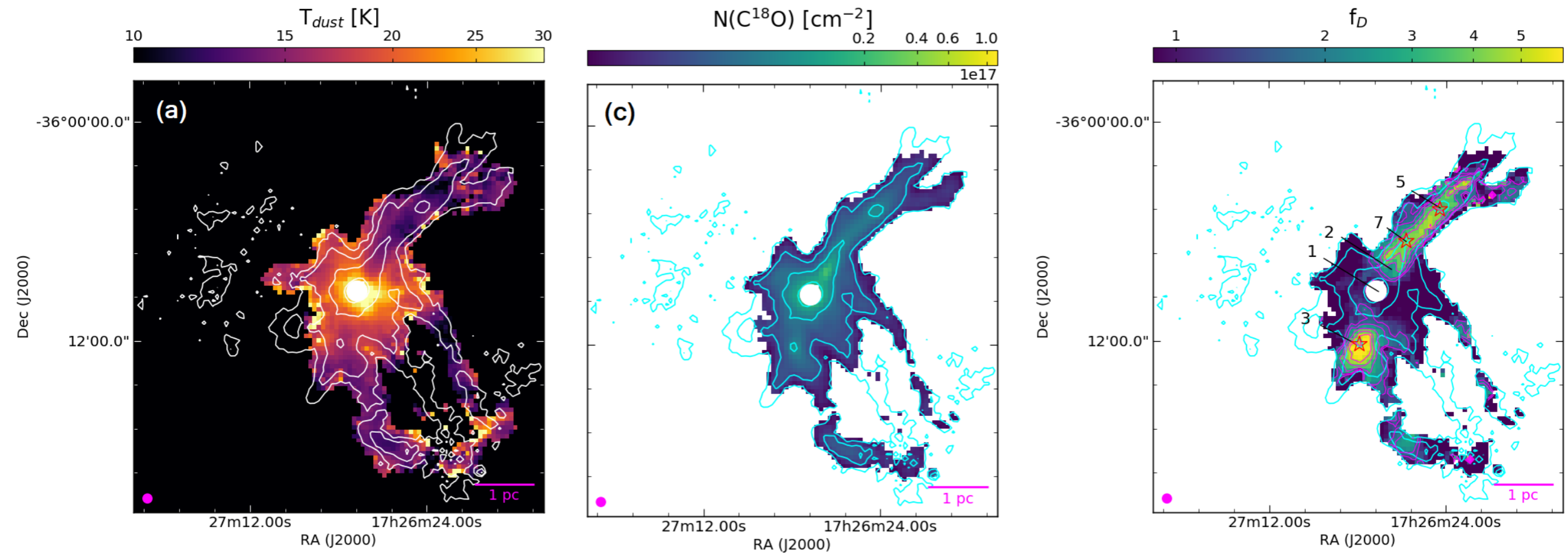
Freeze-out

Gas-grain chemistry

Figure 7: A deep optical image of the dark globule Barnard 68 (*top left*; Alves, Lada & Lada 2001) along with contour maps of integrated intensity from molecular emission lines of  $\text{N}_2\text{H}^+$  (contour levels: 0.3–1.8 by 0.3 K km s<sup>-1</sup>),  $\text{C}^{18}\text{O}$  (0.2–0.7 by 0.1 K km s<sup>-1</sup>), and 850 $\mu\text{m}$  dust continuum emission (10–70 by 10 mJy beam<sup>-1</sup>). Molecular data, with an angular resolution of  $\sim 25''$ , are from Bergin et al. (2002) and dust emission (angular resolution of 14.5'') from Bianchi et al. (2003).

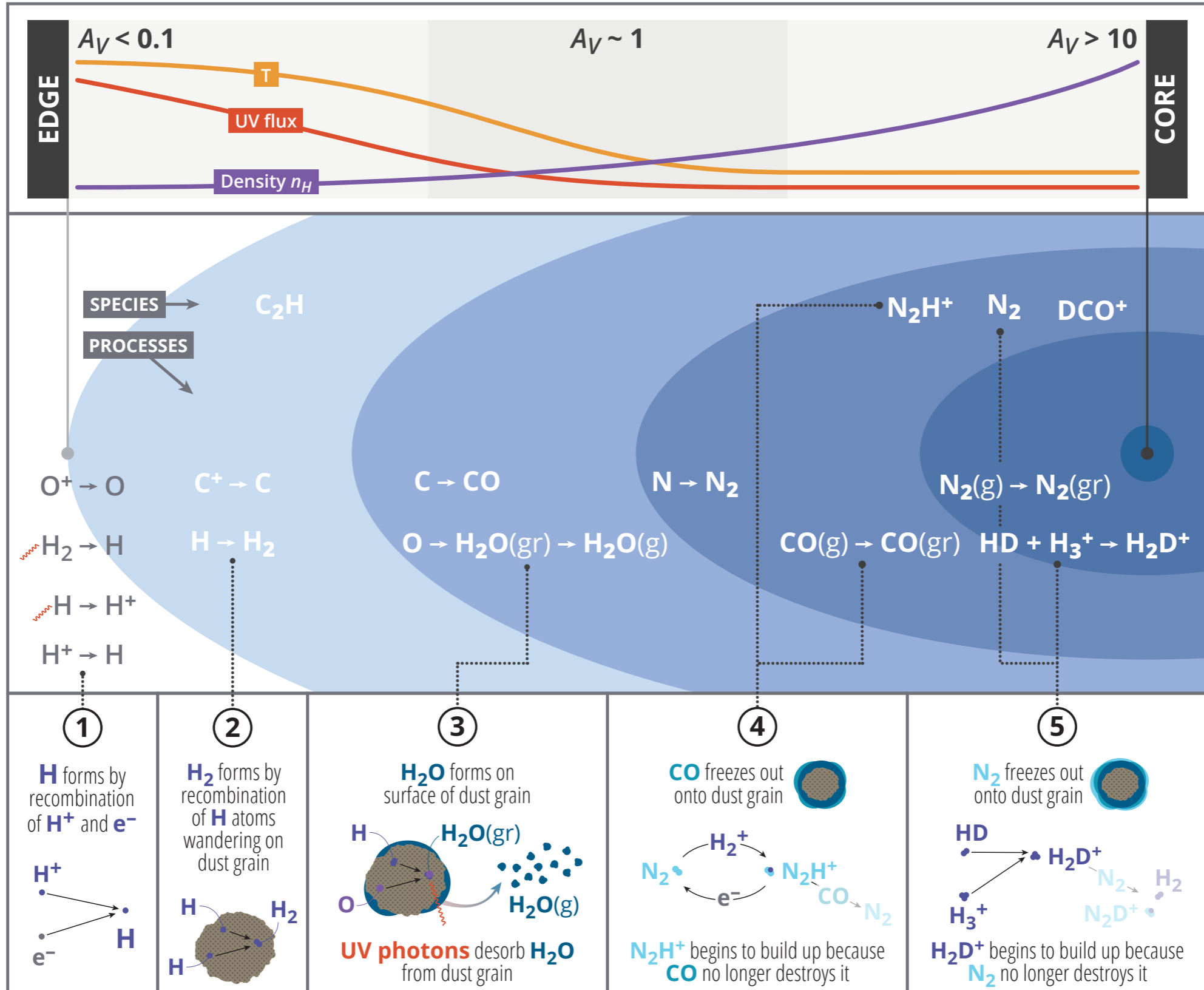


# G351 HIGH-MASS STAR-FORMING REGION (SABATINI,BOVINO+2019)



$$f_D = \frac{\text{expected } N(CO)}{\text{observed } N(CO)}$$

$$\tau = \frac{10^9}{n(H_2)} \text{ yr}$$



## Simulations results @30 kyr (Bovino+2019)

