

The physics of interstellar photon-dominated regions (PDRs)

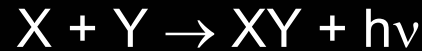
Chemistry I+II
(based on lecture notes by E. van Dishoeck, Leiden)

SS 2007

Basic Molecular Processes

Formation processes

radiative association:

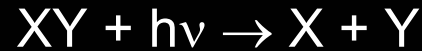


grain surface reaction:

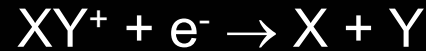


Destruction processes

photodissociation:



dissociative recombination:

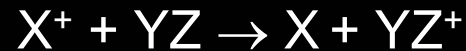


Rearrangement processes

ion-molecule reaction:



charge transfer reaction:



neutral-neutral reactions:



Destruction processes

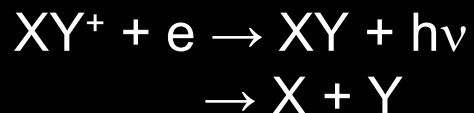
4. Dissociative recombination

atomic ions:



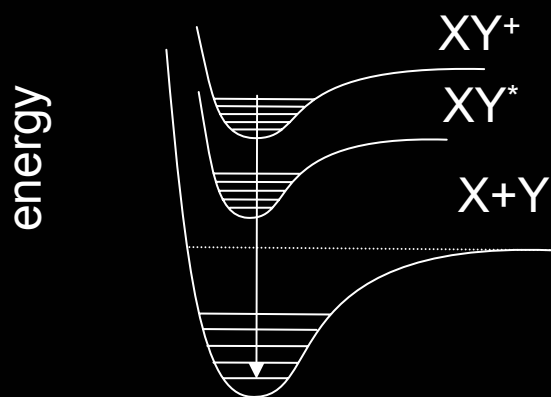
radiative $\Rightarrow$ slow

molecular ions:

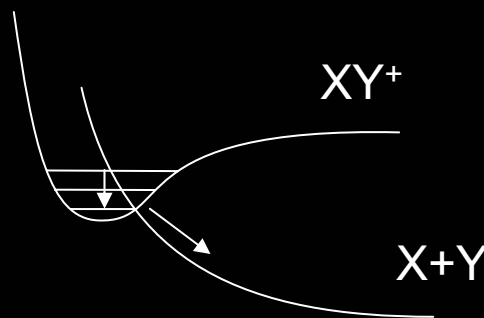


radiative $\Rightarrow$ slow

dissociative $\Rightarrow$ very rapid at low T



slow

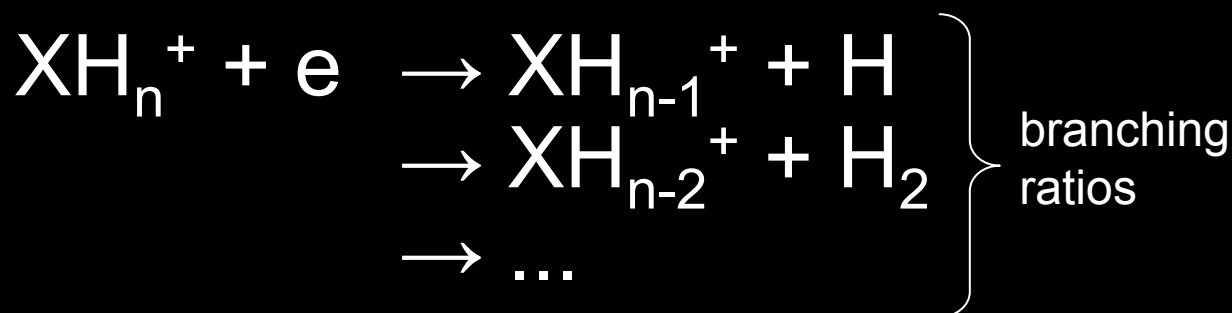


rapid

Need curve crossing between XY^+ and repulsive XY potential for reaction to proceed fast. Occurs for most molecular ions.

Destruction processes

- major uncertainties in models: products

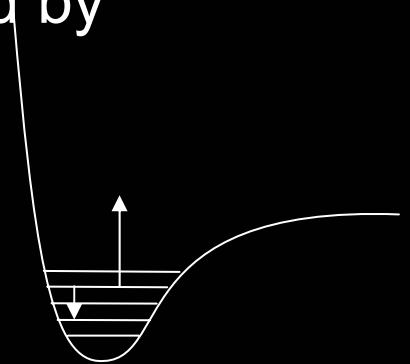
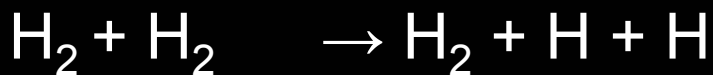
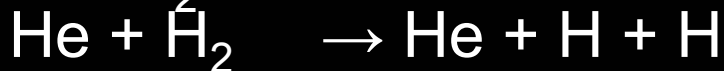
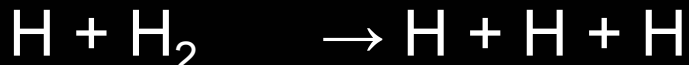


		Vejby_C et al. '97	Williams et al. '96
Example: $\text{H}_3\text{O}^+ + e$	$\rightarrow \text{H}_2\text{O} + \text{H}$	33%	5%
	$\rightarrow \text{OH} + \text{H}_2$	18%	36%
	$\rightarrow \text{OH} + \text{H} + \text{H}$	48%	29%
	$\rightarrow \text{OH} + \text{H}_2 + \text{H}$	1%	30%
3-body products			

Destruction processes

5. Collision induced dissociation

If T is high enough ($T > 5000\text{K}$), H_2 is destroyed by collisions



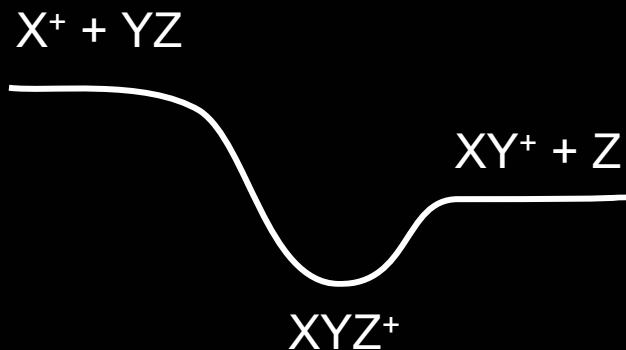
H_2 has no permanent dipole moment $\Rightarrow$ significant population in high ν levels at high $T \Rightarrow$ large dissociation rate

CO has small dipole moment $\Rightarrow$ radiative stabilisation rapid
 $\Rightarrow$ not much pop. in high ν
 $\Rightarrow$ small dissociation rate

Rearrangement processes

7. Ion-molecule reactions

long-range attraction: ion-(induced) dipole $\sim 1/R^4$
 $\Rightarrow$ rapid at low T if reaction is exothermic

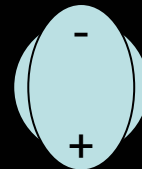


collision energy in ISM ~ 0.01 eV
 $\Rightarrow$ calculation of collision cross
section via potential surface
calculation requires high precision

Rearrangement processes



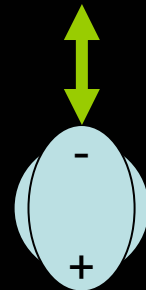
impact parameter
 b



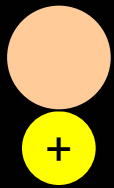
Rearrangement processes



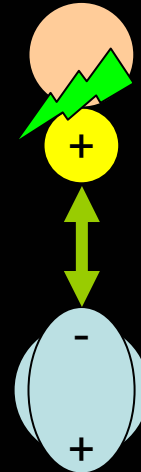
critical impact
parameter b_c



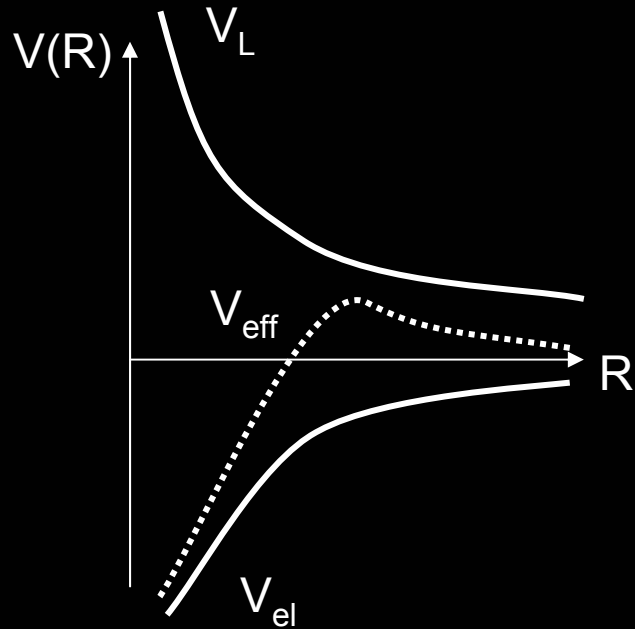
Rearrangement processes



critical impact
parameter b_c



Rearrangement processes



centrifugal potential $V_L = \frac{\mu b^2 v^2}{2R^2}$

ion induced dipole $V_{el} = -\frac{e^2 \alpha}{2R^4}$

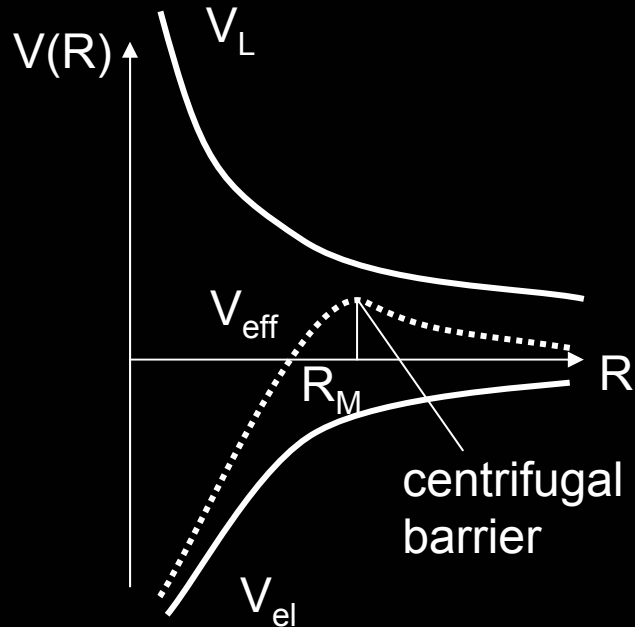
$$V_{eff} = -\frac{e^2 \alpha}{2R^4} + \frac{\mu b^2 v^2}{2R^2}$$

μ : reduced mass

α : polarizability ($\sim 10^{-24} \text{ cm}^3$)

$L = m b v$: angular momentum in centrifugal potential

Rearrangement processes



$$V_{eff} = -\frac{e^2 \alpha}{2R^4} + \frac{\mu b^2 v^2}{2R^2}$$

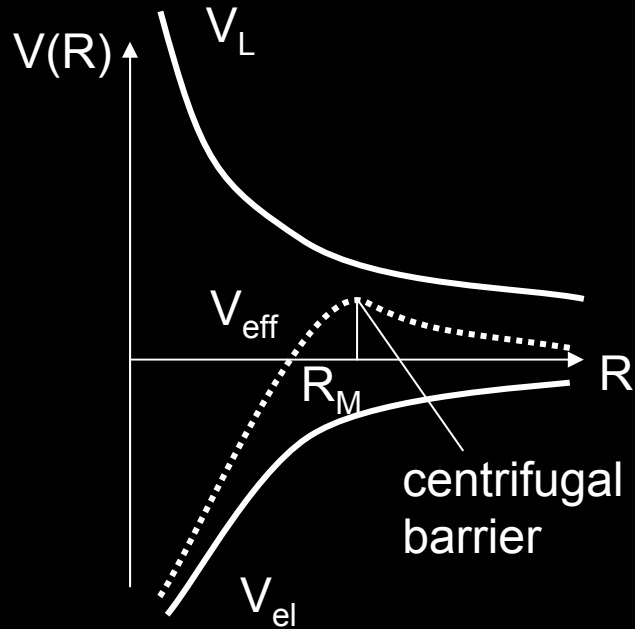
$$\max V_{eff} : \frac{(\mu b^2 v^2)^2}{2\alpha e^2} \quad \text{at} \quad R_M^2 = \frac{2\alpha e^2}{\mu b^2 v^2}$$

barrier can only be surmounted if:

$$\frac{1}{2} \mu v^2 > \frac{(\mu b^2 v^2)^2}{2\alpha e^2}$$

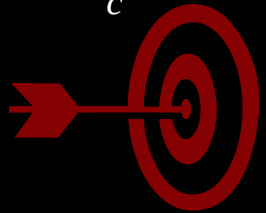
critical impact parameter $b_c = \left(\frac{4\alpha e^2}{\mu v^2} \right)^{1/4}$

Rearrangement processes



critical impact parameter: $b_c = \left(\frac{4\alpha e^2}{\mu v^2} \right)^{1/4}$

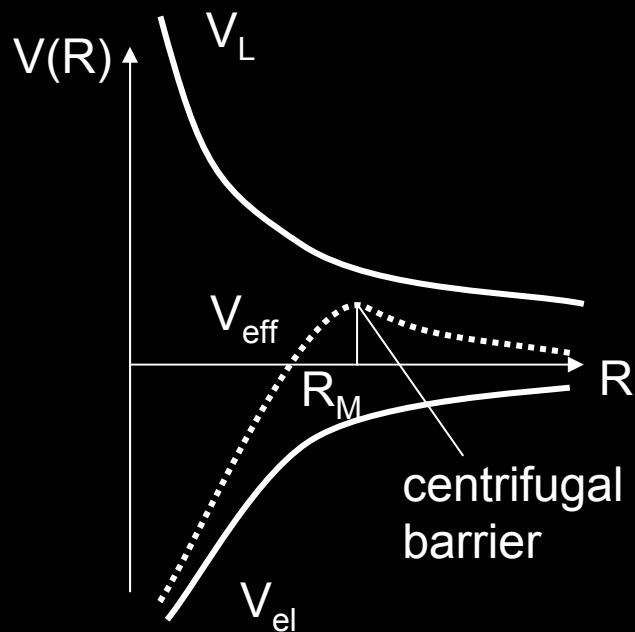
cross section for reaction: $\sigma = \pi b_c^2$



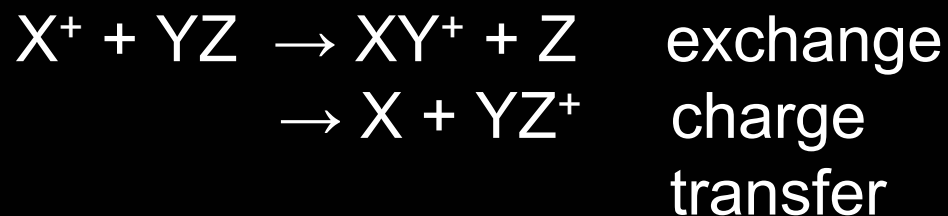
collision frequency: $k = \langle \sigma v \rangle = 2\pi \left(\frac{\alpha e^2}{\mu} \right)^{1/2}$

$\Rightarrow k \sim 10^{-9} \text{cm}^3 \text{s}^{-1}$, independent of T !

Rearrangement processes



possible processes:



many experiments performed at room T, some at low T. Most reactions proceed at Langevin rate, but some exceptions known!

Rate coefficients for ion-polar molecule reactions may be factors of 10-100 larger than Langevin values at low T, because $V(R) \sim R^{-2}$ (eg. $C^+ + OH \rightarrow CO^+ + H$
 $H_3^+ + CS \rightarrow HCS^+ + H_2$)

Rearrangement processes

- long range attraction: weak van der Waals interaction $\sim 1/R^6$ (Woon & Herbst '97)



μ_1 : dipole moment of CN

α_2 : polarizability of C_2H_2

α_1 : polarizability of CN

I : ionization potential

$$V_{el}(R) = -\frac{C_6}{R^6} - \frac{\mu_1^2 \alpha_2}{R^6}$$

dispersion coefficient $C_6 = \frac{3}{2} \frac{I_1 I_2}{I_1 + I_2} \alpha_1 \alpha_2$

Rearrangement processes

- simpler: $V_{el}(R) = -\frac{\alpha_1 \alpha_2}{R^6} I$

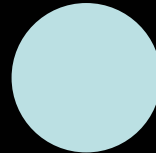
$$k = \langle \sigma v \rangle \approx \pi \cdot 13.6 \left(\frac{\alpha_1 \alpha_2}{\mu} I \right)^{1/3} \langle v^{1/3} \rangle \approx 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

$$\Rightarrow k_{n-n} \ll k_{i-n}$$

$\Rightarrow$ neutral-neutral reactions
unimportant (exception:
reactions with radicals)

Rearrangement processes

- comparison:
simple hard sphere collision without
electromagnetic interaction



Rearrangement processes

- comparison:

simple hard sphere collision without
electromagnetic interaction

(Bohr's radius: $r = 5.3 \times 10^{-11} \text{ m} = 5.3 \times 10^{-9} \text{ cm}$)

$R \approx 10^{-10} \text{ m} = 10^{-8} \text{ cm}$

$\Rightarrow \sigma = R^2 \pi = 3 \times 10^{-16} \text{ cm}^2, v \approx 10^4 \text{ cm/s}$

$k = \sigma v$	$\approx 3 \times 10^{-12}$	$\text{cm}^3 \text{s}^{-1}$	} Factor ≈ 1000	} Factor ≈ 10
$k_{\text{ion-neutral}}$	$\approx 10^{-9}$	$\text{cm}^3 \text{s}^{-1}$		
$k_{\text{neutral-neutral}}$	$\approx 4 \times 10^{-11}$	$\text{cm}^3 \text{s}^{-1}$		

Rearrangement processes

Comparison of effective cross section and radii
(assumption: $v=10^4$ cm s⁻¹)

$\sigma = \frac{k}{v}$ $r = \sqrt{\frac{\sigma}{\pi}}$		σ [cm ²]	r [cm]
	hard sphere	3×10^{-16}	10^{-8}
	ion-neutral	10^{-13}	2×10^{-7}
	neutral-neutral	4×10^{-15}	4×10^{-8}

- dipole induction enlarges the effective target radius by a factor of 20 !
- van der Waals induction enlarges r_{eff} by ~ 4

Rearrangement processes

- Adiabatic capture approximation (AC)
 - if collision energy $< V_{\text{eff}}(R) \Rightarrow \text{react. prob}=0$
 - if collision energy $> V_{\text{eff}}(R) \Rightarrow \text{react. prob}=1$

(ignores angular dependencies, short range effects, quantum effects, activation energies)

With AC theory, the rate coefficient is:

$$k(T) \propto T^{-\frac{2}{n} + \frac{1}{2}} \quad \text{as } T \rightarrow 0$$

for potentials of form r^{-n}

Rearrangement processes

$k(T) \propto T^{-\frac{2}{n} + \frac{1}{2}}$ as $T \rightarrow 0$, for potentials of form r^{-n}

interaction		low T dependence
charge-induced dipole	r^{-4}	T^0
charge-dipole	r^{-2}	$T^{-1/2}$
charge-quadrupole	r^{-3}	$T^{-1/6}$
dipole-dipole	r^{-3}	$T^{-1/6}$
dipole-quadrupole	r^{-4}	T^0
dispersion	r^{-6}	$T^{1/6}$

neutral-neutral reactions typically factor 5 smaller than ion-molecule reactions at low T

Time scales

rate coefficient :	k	$[\text{cm}^3 \text{s}^{-1}]$
rate :	$k n_A n_B$	$[\text{cm}^{-3} \text{s}^{-1}]$
reaction time :	$t \cong (k n)^{-1}$	$[\text{s}^{-1}]$

Time scales

rad.association $\text{C} + \text{H} \rightarrow \text{CH} + h\nu$ $k = 10^{-17} \text{ cm}^3 \text{ s}^{-1}$
 $\rightarrow t = 10^{17} \frac{1}{n} \text{ s}$
 $t_{n=10^4} = 10^{13} \text{ s} \hat{=} 3 \times 10^5 \text{ yr}$

photodiss. $\text{CO} + h\nu \rightarrow \text{C} + \text{O}$ $k = 2 \times 10^{-10} \text{ s}^{-1}$
 $\rightarrow t = 5 \times 10^9 \text{ s}$
 $t_{n=10^4} = 160 \text{ yr}$

Time scales

diss.
recomb.

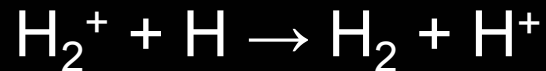
$$\text{HCO}^+ + \text{e}^- \rightarrow \text{CO} + \text{H} \quad k = 1.1 \times 10^{-7} \left(\frac{300 \text{ K}}{T} \right) \text{cm}^3 \text{s}^{-1}$$
$$k_{T=15\text{K}} = 2.2 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$$
$$\rightarrow t = 4.6 \times 10^5 \frac{1}{n_e} \text{s}$$
$$t_{n_e=1} \approx 5 \text{ d}$$

ion-molecule
reaction

$$\text{CO} + h\nu \rightarrow \text{C} + \text{O} \quad k = 2.08 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$$
$$t = 4.8 \times 10^8 \frac{1}{[\text{H}_2]} \text{s}$$
$$t_{[\text{H}_2]=10^4} = 4.8 \times 10^4 \text{s}^{-1}$$
$$\approx 0.5 \text{ d}$$

Time scales

charge transf.
reaction

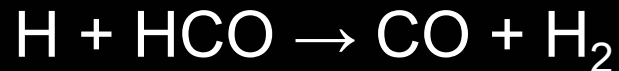


$$k = 6.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

$$t = 1.6 \times 10^9 \frac{1}{n} \text{ s}$$

$$t_{[H]=10^4} = 1.6 \times 10^5 \approx 2 \text{ d}$$

neutral-neutral
reaction



$$k = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

$$t = 5 \times 10^9 \frac{1}{n} \text{ s}$$

$$t_{n=10^4} = 5 \times 10^5 \text{ s}^{-1}$$

$$\approx 6 \text{ d}$$

Time scales

CR ionization

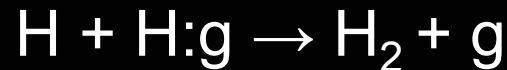


$$k = 10^{-17} \text{ s}^{-1}$$

$$t = 10^{17} \frac{1}{n} \text{ s}$$

$$t_{[H]=10^4} = 10^{13} \text{ s} \approx 3.2 \times 10^5 \text{ yr}$$

dust-surface
reaction



$$k = 10^{-17} \text{ cm}^3 \text{ s}^{-1}$$

$$t = 2.7 \times 10^9 \frac{1}{n} \text{ yr}$$

$$t_{n=10^4} = 2.7 \times 10^5 \text{ yr}$$

Time scales

Example: ratio H_2/H

$$\frac{d}{dt}[H_2] = -k_{diss}[H_2] + k_{form}[H] \stackrel{!}{=} 0$$

$$\frac{[H_2]}{[H]} = \frac{k_{form}}{k_{diss}} = \frac{t_{diss}}{t_{form}} = \frac{634 \text{ yr}}{2.7 \times 10^9 \text{ yr}} \cdot n = 2.4 \times 10^{-7} n \text{ cm}^{-3}$$

$\Rightarrow$ all hydrogen is atomic, unless FUV is attenuated

but: H_2 is detected

diffuse clouds: $[H_2]/[H] \approx 1$

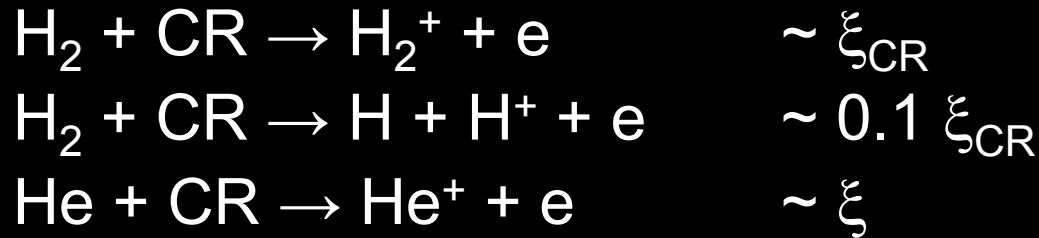
dense clouds: $[H_2]/[H] \gg 1$

$\Rightarrow$

- dust extinction
- self shielding

Degree of Ionization

- electron production:



radiative recombination of atomic ions too slow
 $\Rightarrow$ charge exchange from $\text{H}^+, \text{He}^+ \rightarrow$ molecular
ions ($10\text{-}100 \text{ } 1/n \text{ yr cm}^{-3}$)

followed by dissociative recombination of
molecular ions ($0.3 \text{ } 1/n_e \text{ yr cm}^{-3}$)

Degree of Ionization

$$\frac{d}{dt}[\text{mol.ions}] = -\frac{1}{t_{diss.rec.}}[\text{mol.ions}] + \xi[\text{He}] \stackrel{!}{=} 0$$

$$= -\frac{1}{0.3 \text{ yr cm}^{-3}} n_e^2 + \xi \frac{1}{10} n = 0$$

$$n_e \approx 10^{-4} \text{ cm}^{-3} \sqrt{n}$$

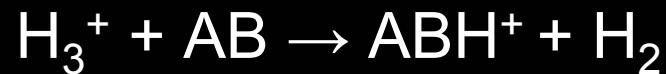
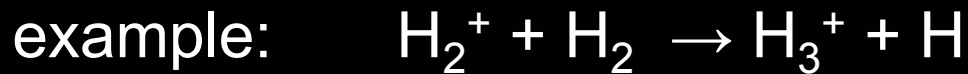
$$t_{diss.rec} \approx 3 \times 10^3 \text{ yr} \sqrt{\frac{1}{n}}$$

compared to: exchange reactions $t \approx 10^{-3} \dots 10^{-2} \text{ yr } 1/n$
 rad. associations $t \approx 10^4 \text{ yr } 1/n$

⇒ many other reactions occur before 1 dissoc. recombination destroys ions/electrons

Degree of Ionization

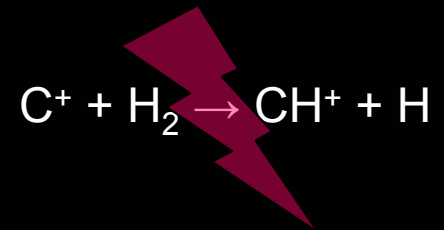
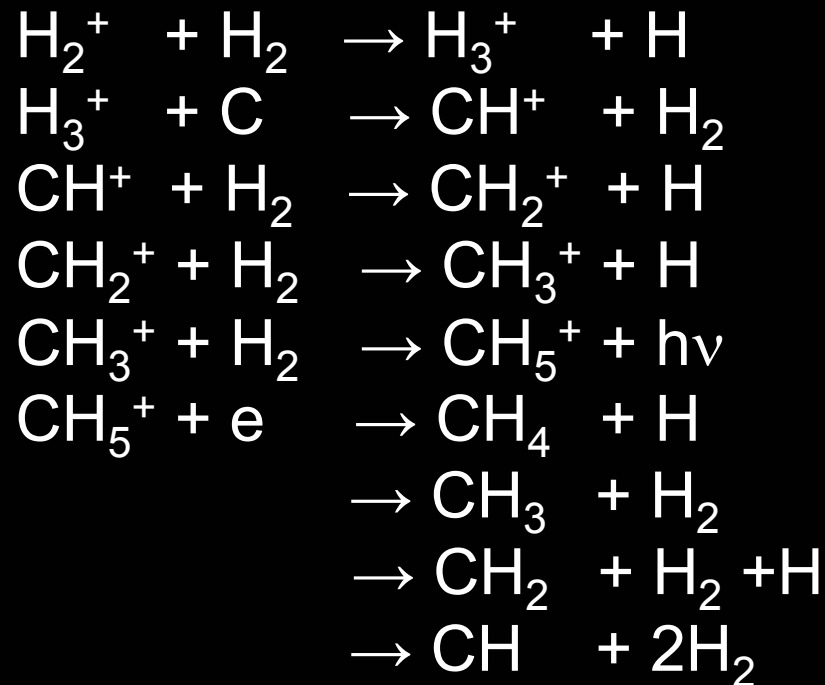
⇒ Ion – Molecule – Scheme:



...

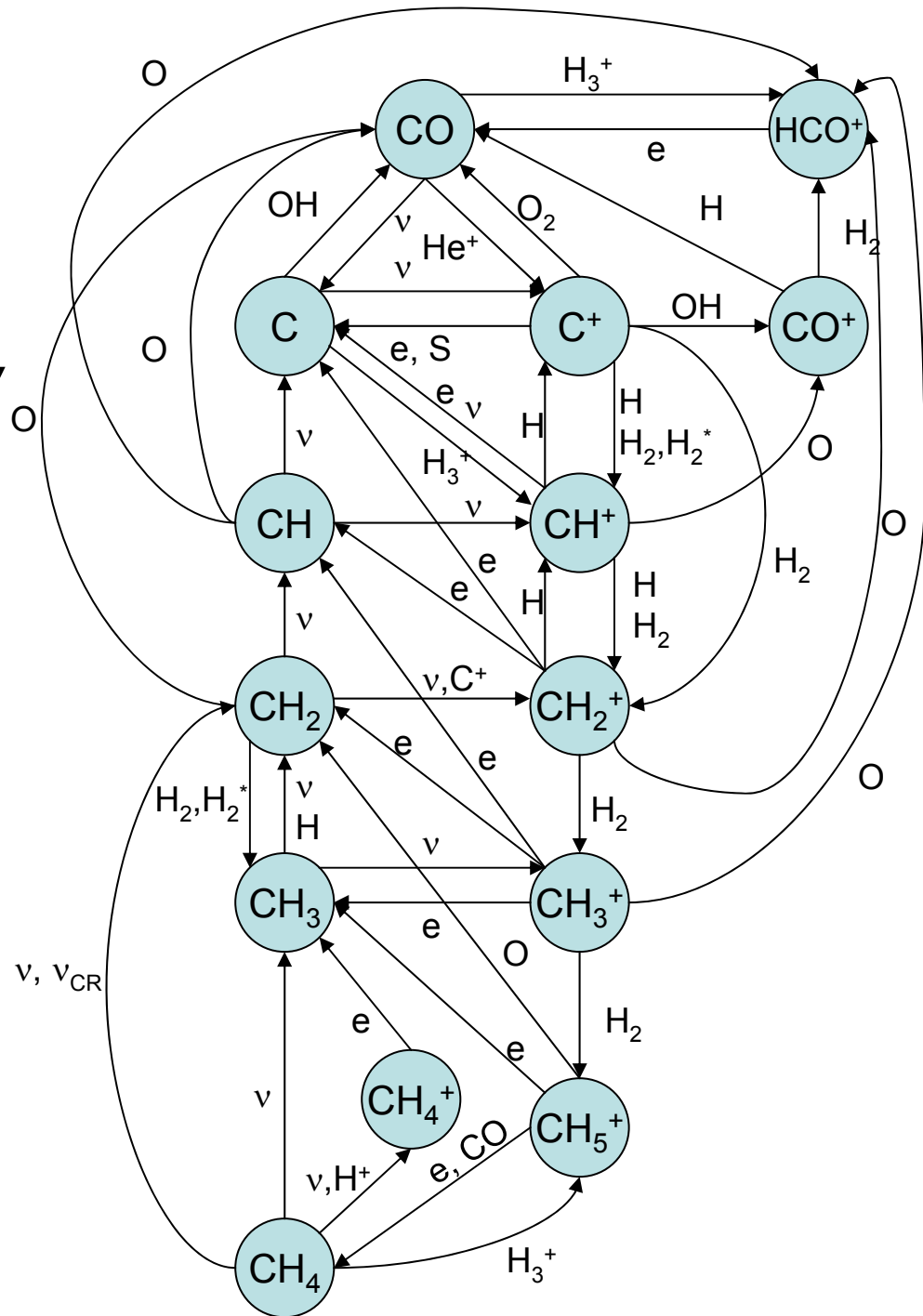
Degree of Ionization

⇒ Ion – Molecule – Scheme:



The carbon roadmap

- Like any roadmap, this network describes *how to get from A to B*.
- Like on any roadmap, *some paths are quick some are slow*.
- Unlike any normal roadmap some *slow paths may become very quick* under certain conditions



Example: Diffuse Cloud

starting point: C^+

collision with H_2 :

$\Delta E = 4600K$

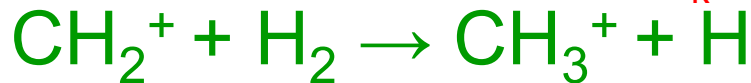


instead:

$k \approx 10^{-15} \text{ cm}^3 \text{ s}^{-1}$



$k \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1}$



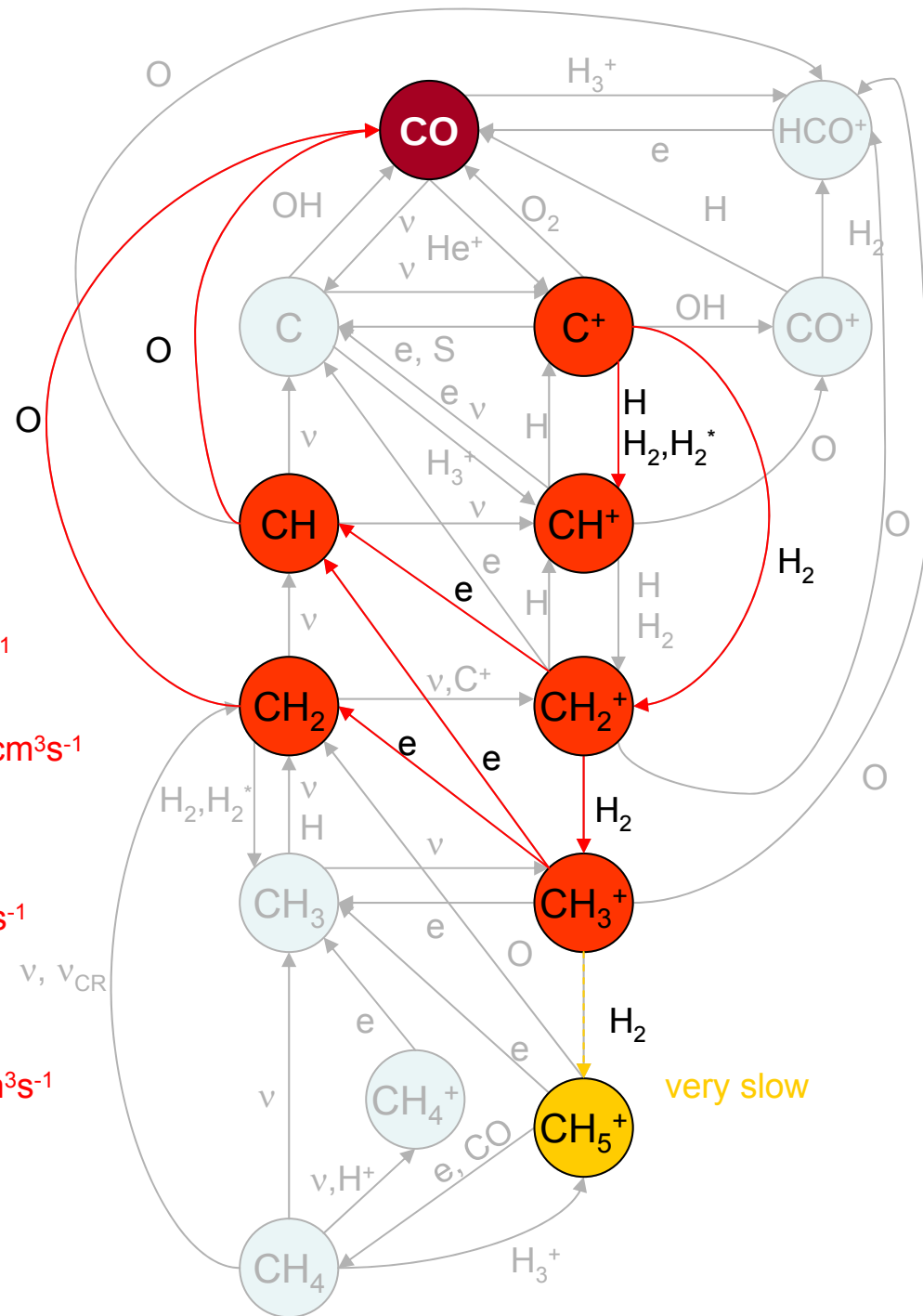
then:

$k \approx 10^{-7} \text{ cm}^3 \text{ s}^{-1}$



and:

$k \approx 10^{-10} \text{ cm}^3 \text{ s}^{-1}$



Example: **PDR**

high FUV intensity heats
the gas at the surface

→ some slow routes
become quick

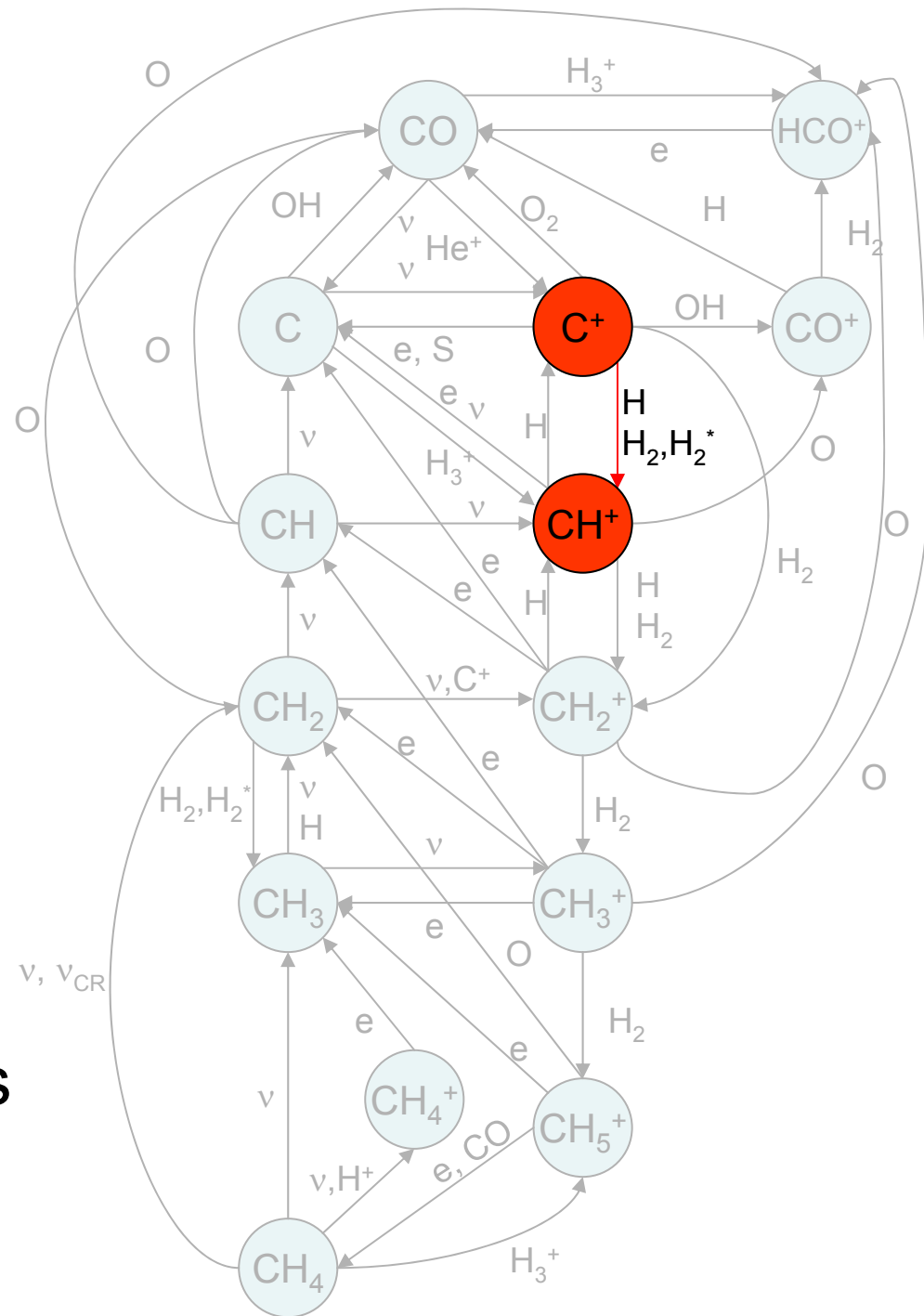


endothermic reactions

become possible

activation energy barriers

become surmountable

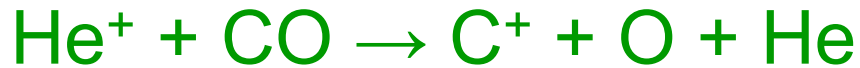


Example: **Dark Cloud**

cold and dense:

$T=10\text{ K}$, $n=10^4\text{-}10^5\text{ cm}^{-3}$

carbon locked in CO



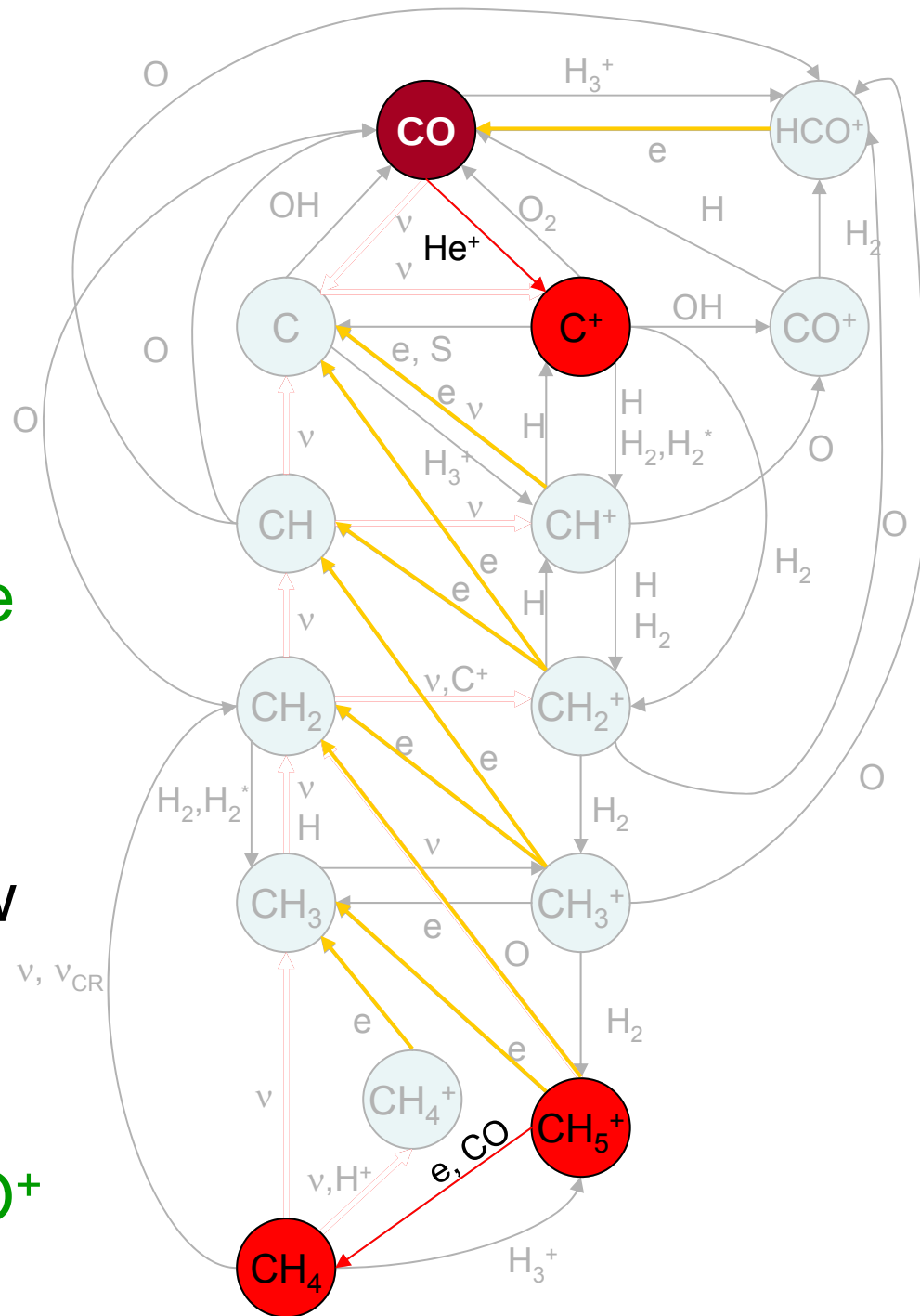
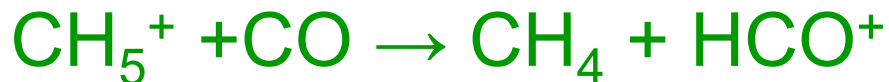
FUV fully absorbed

some roads vanish

some roads become slow

e.g. reactions with e^-

but:

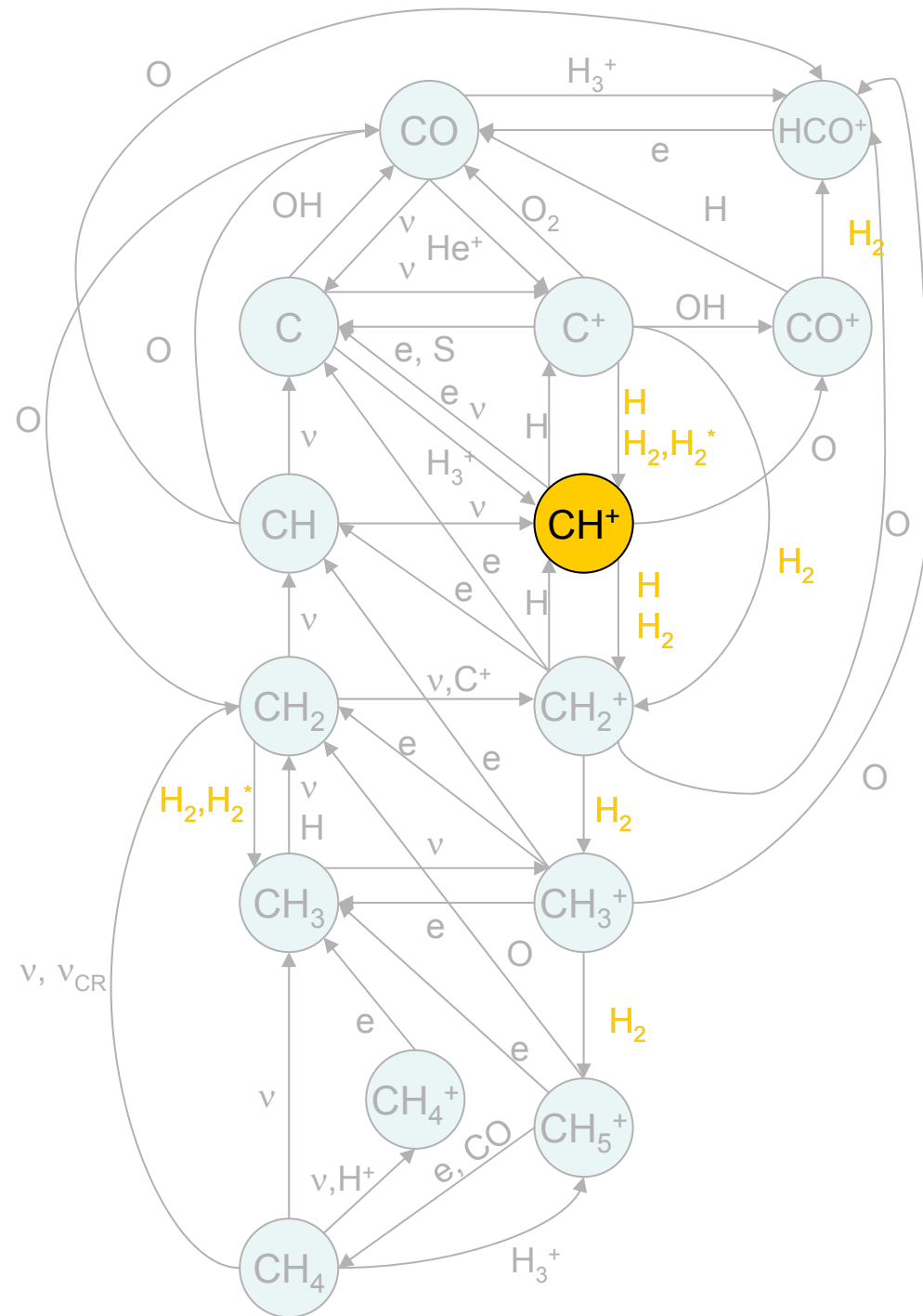


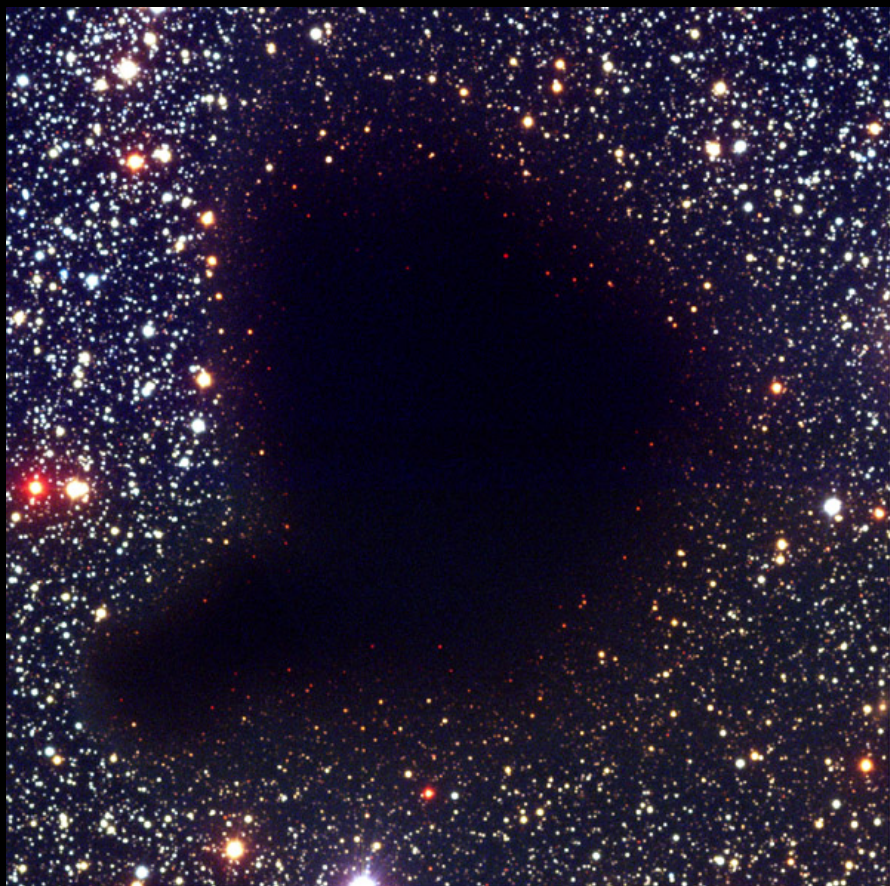
Looks 'simple', but:

CH^+ a factor 100 too low

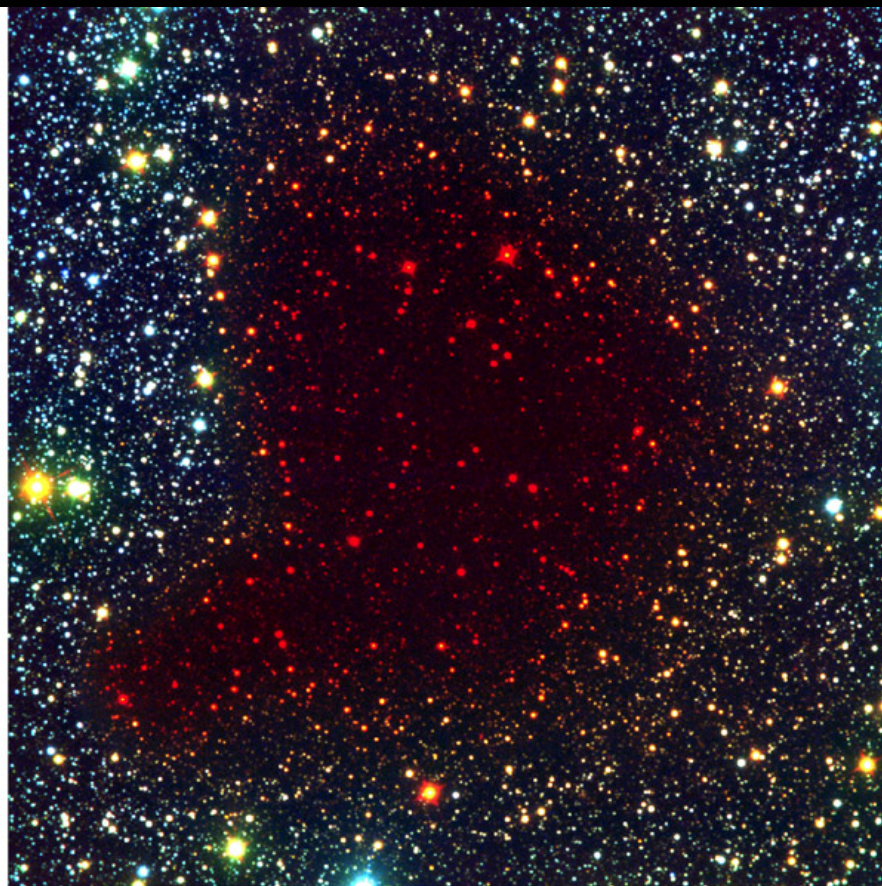
H_2 formation not fully understood

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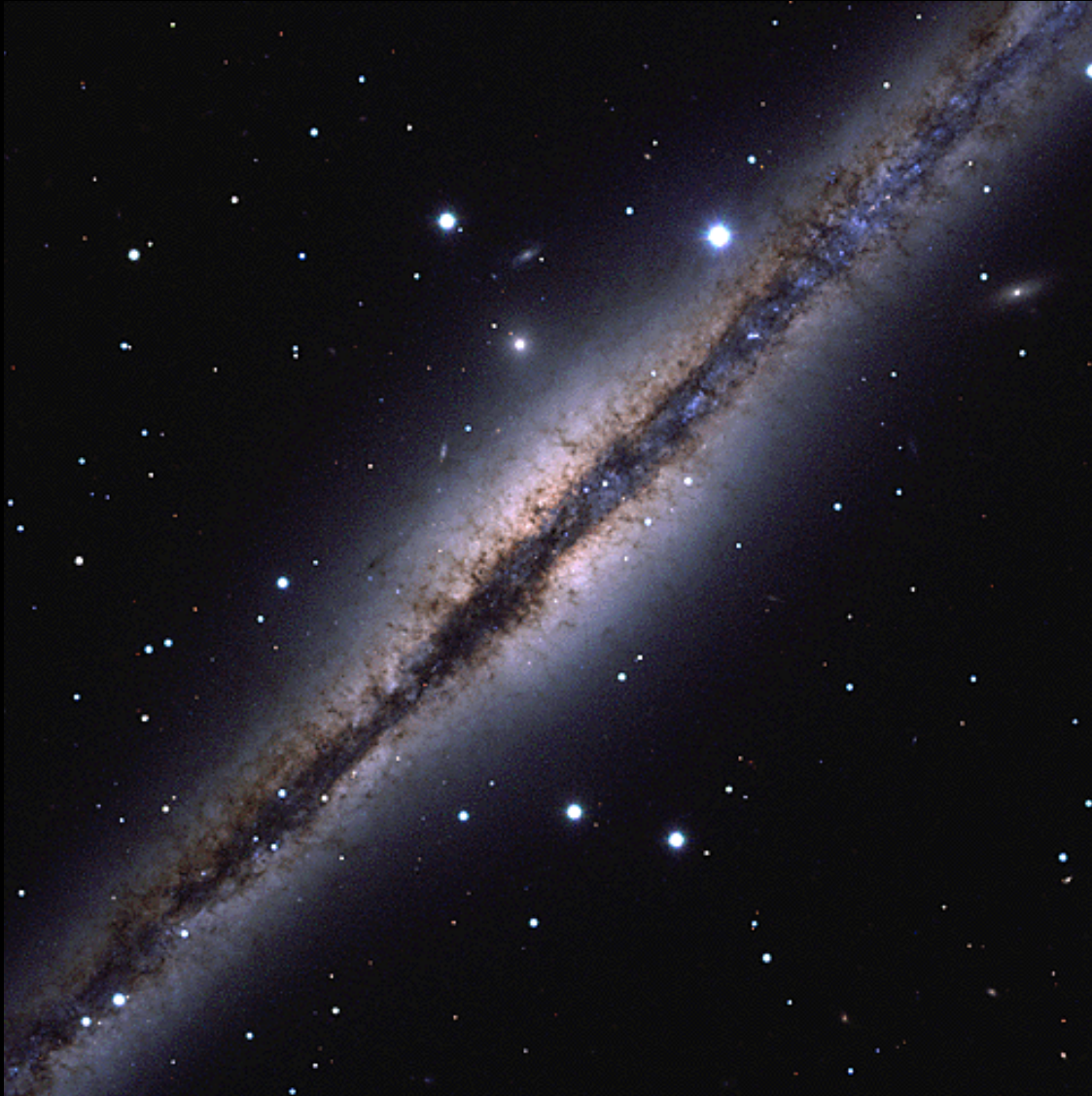
B, V, I



B, I, K

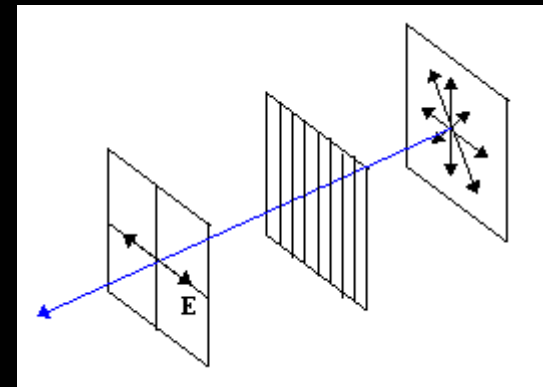
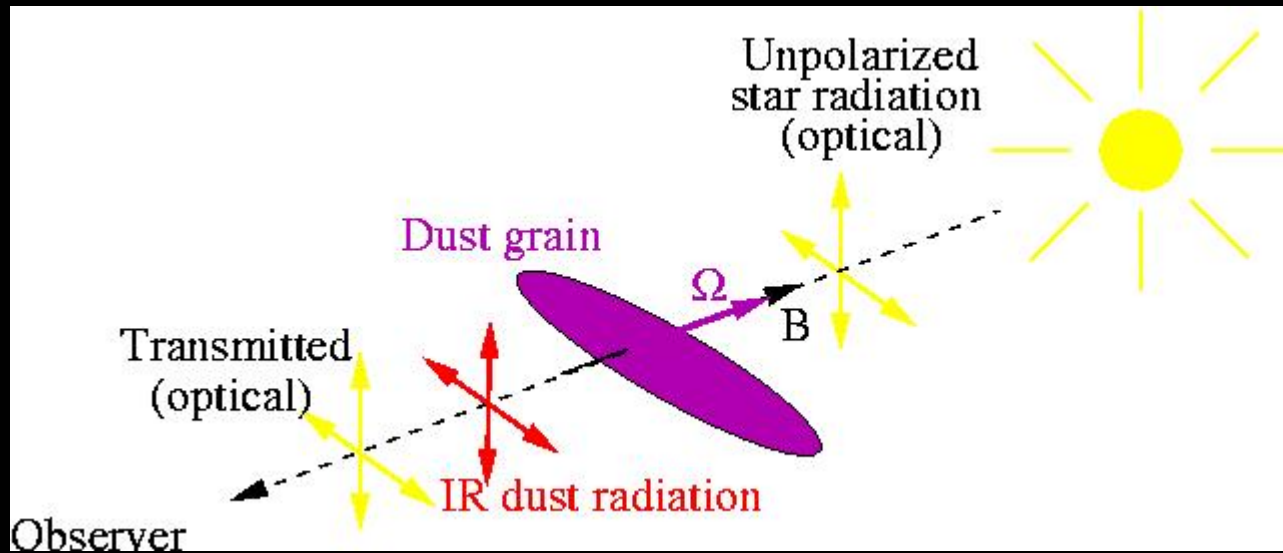
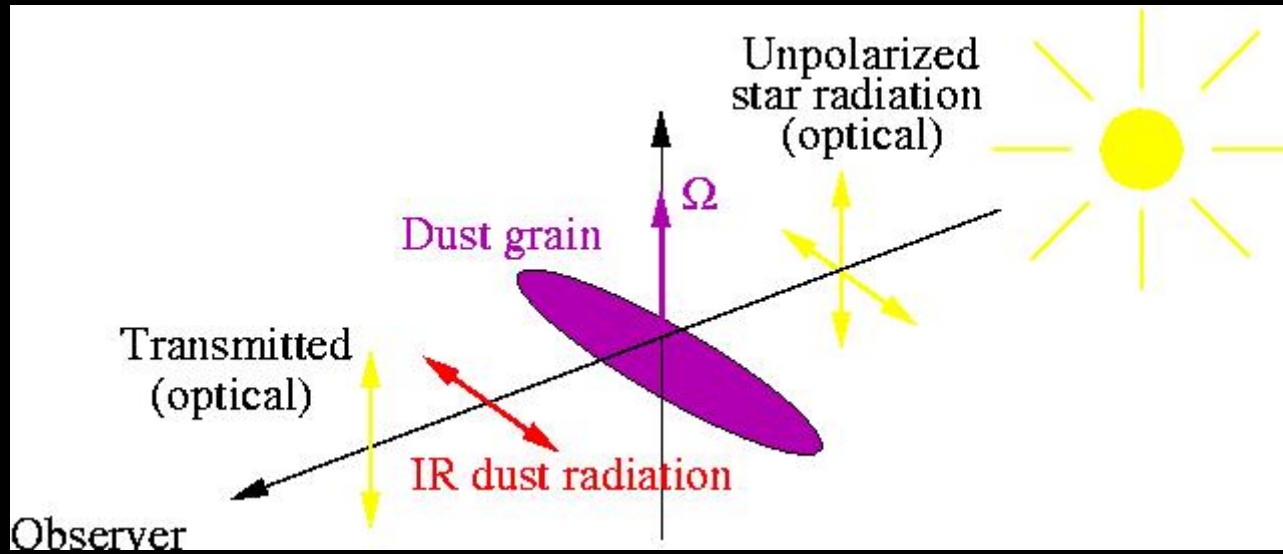
Pre-Collapse Black Cloud B68 (comparison)
(VLT ANTU + FORS 1 - NTT + SOFI)

Dust



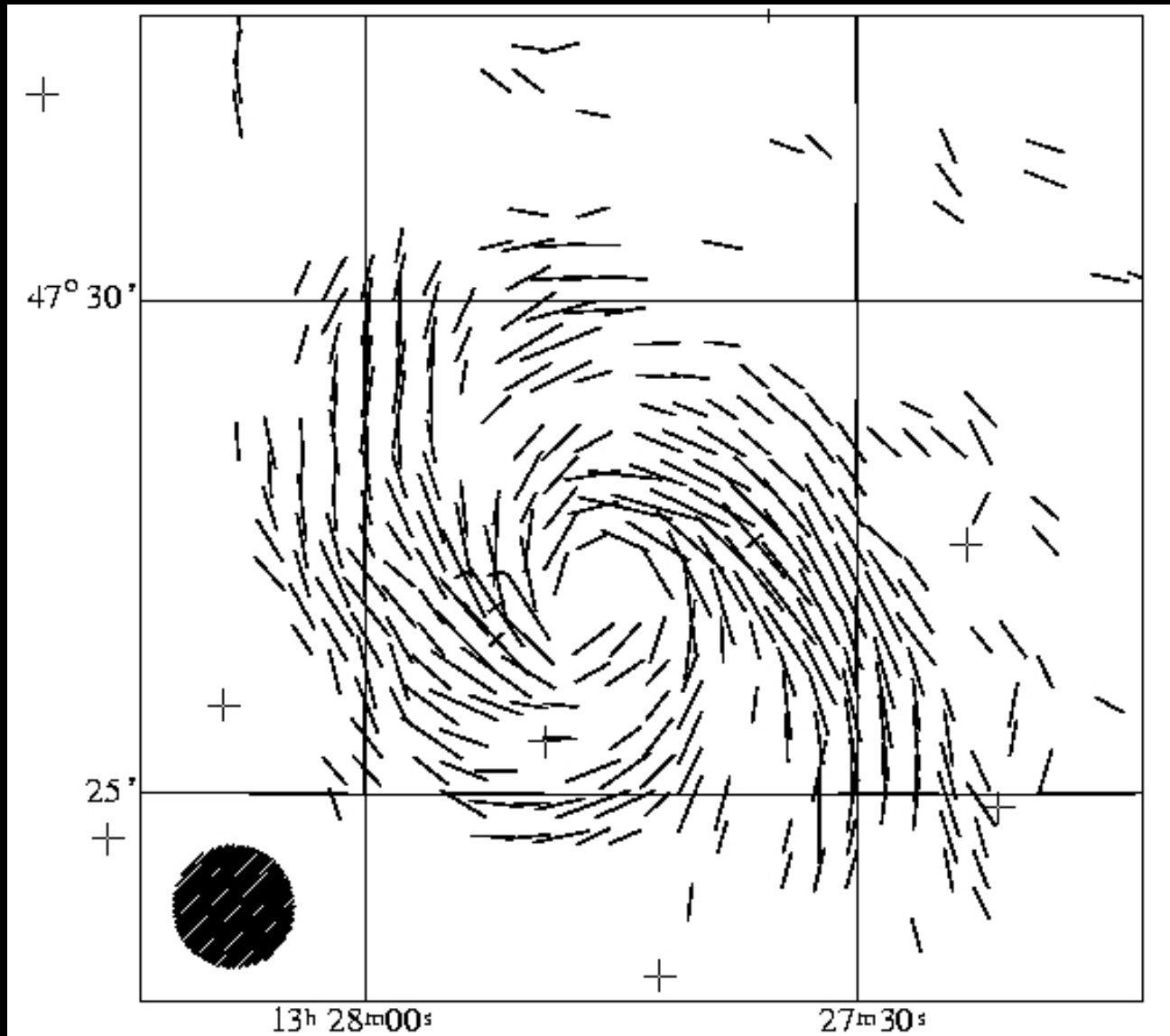
NGC 891

Dust

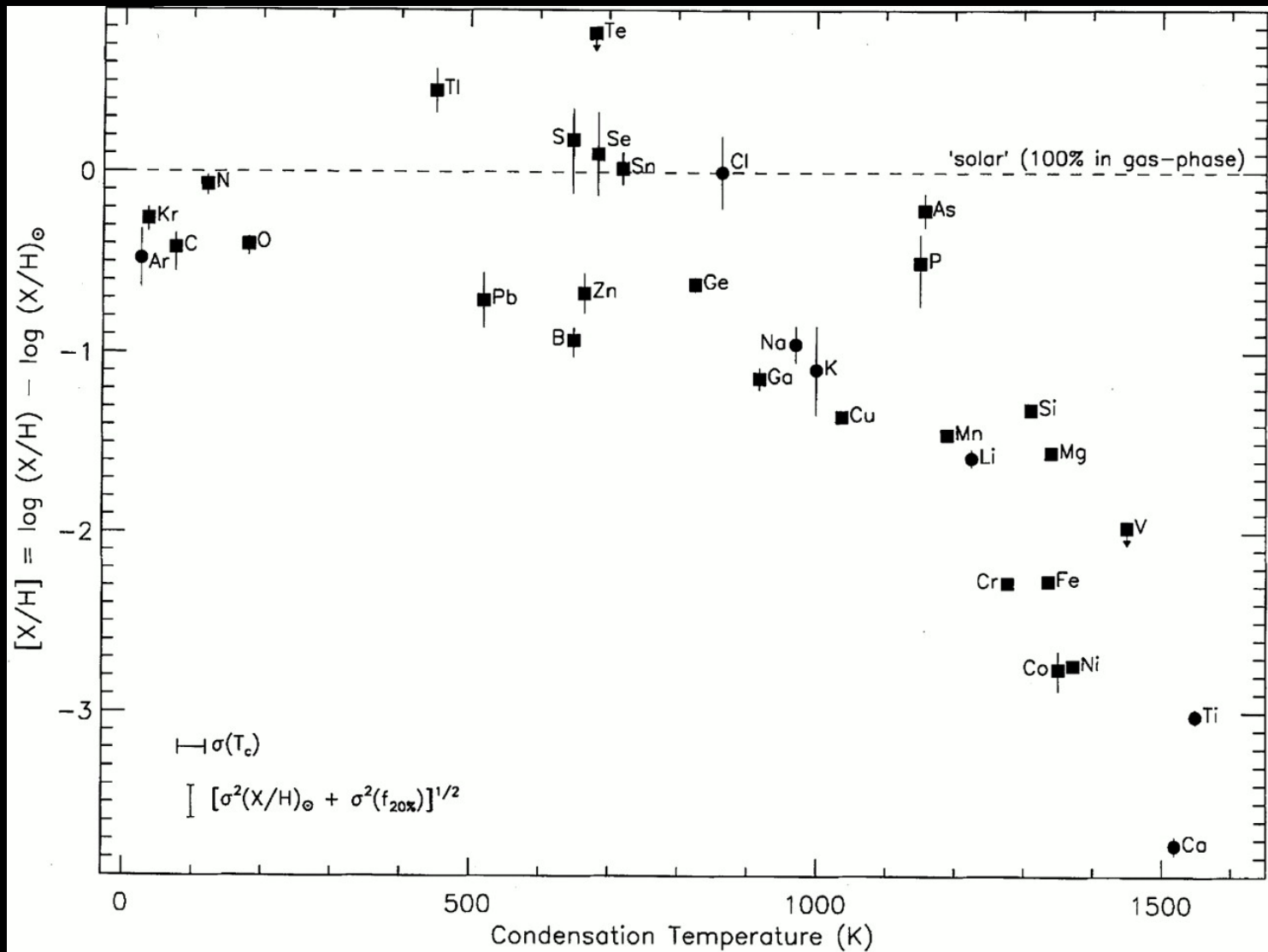


Davis Greenstein Effect

Dust

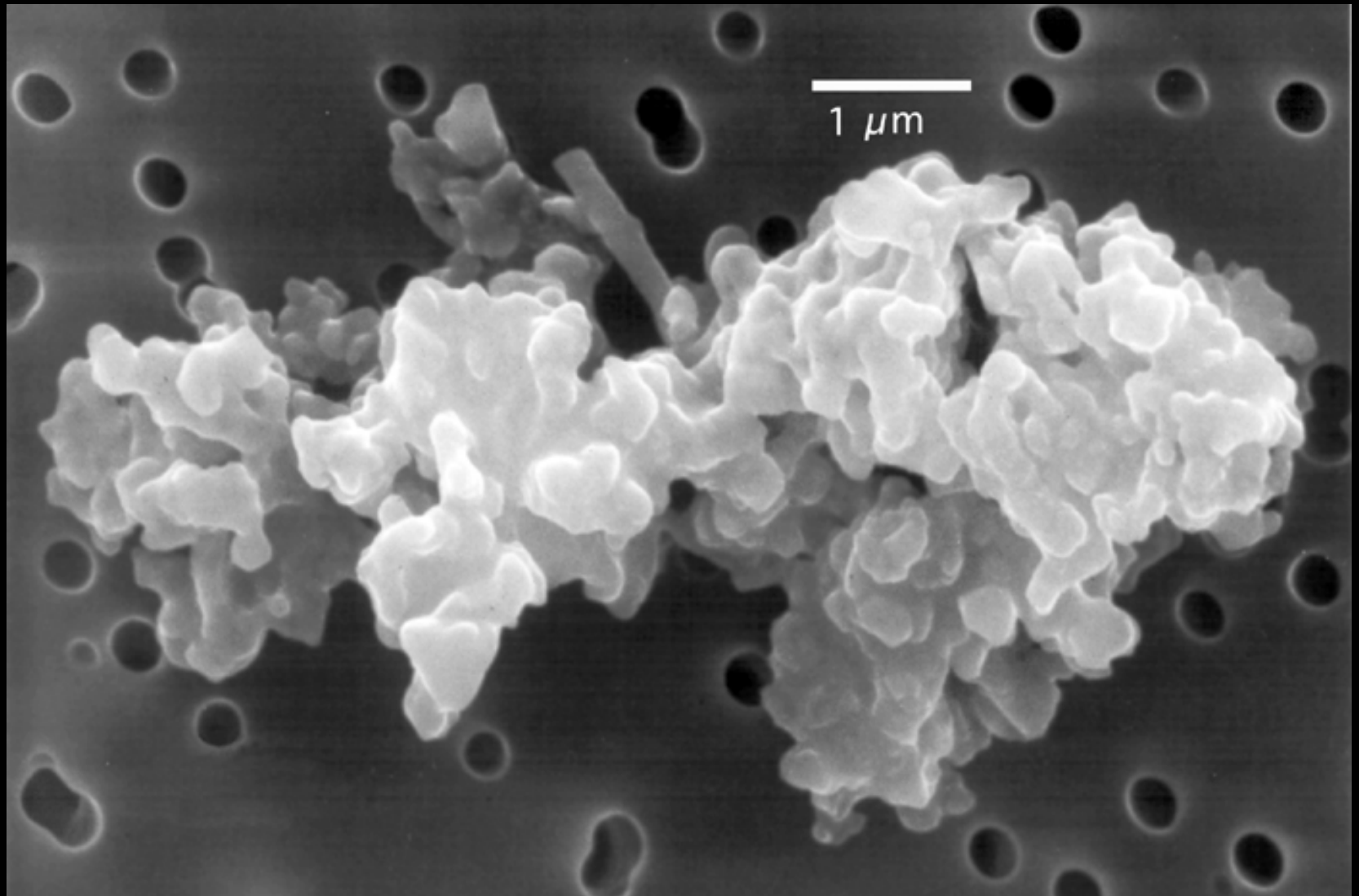


Magnetic field
orientation in the
Galaxy M51
(Berkhuijsen et
al. 1975).



Elemental depletions as a function of condensation temperature (the temperature at which 50% of element condenses out in solid form)

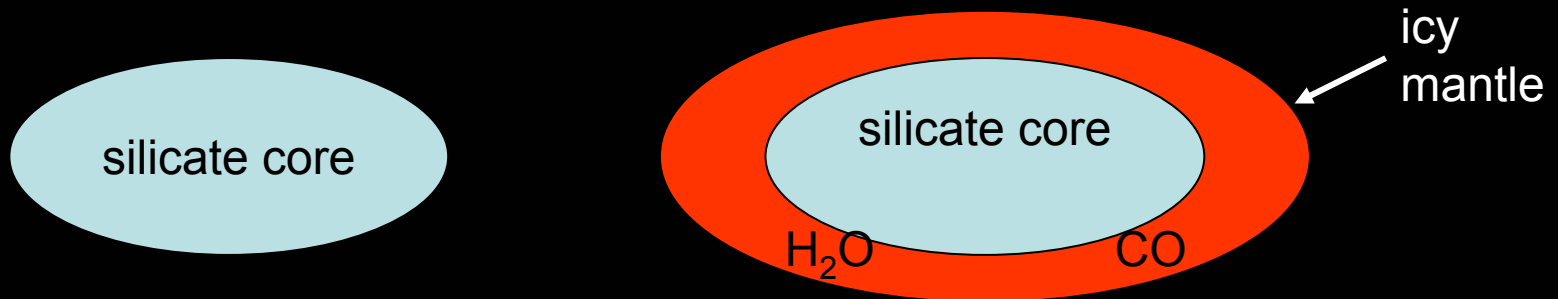
Dust

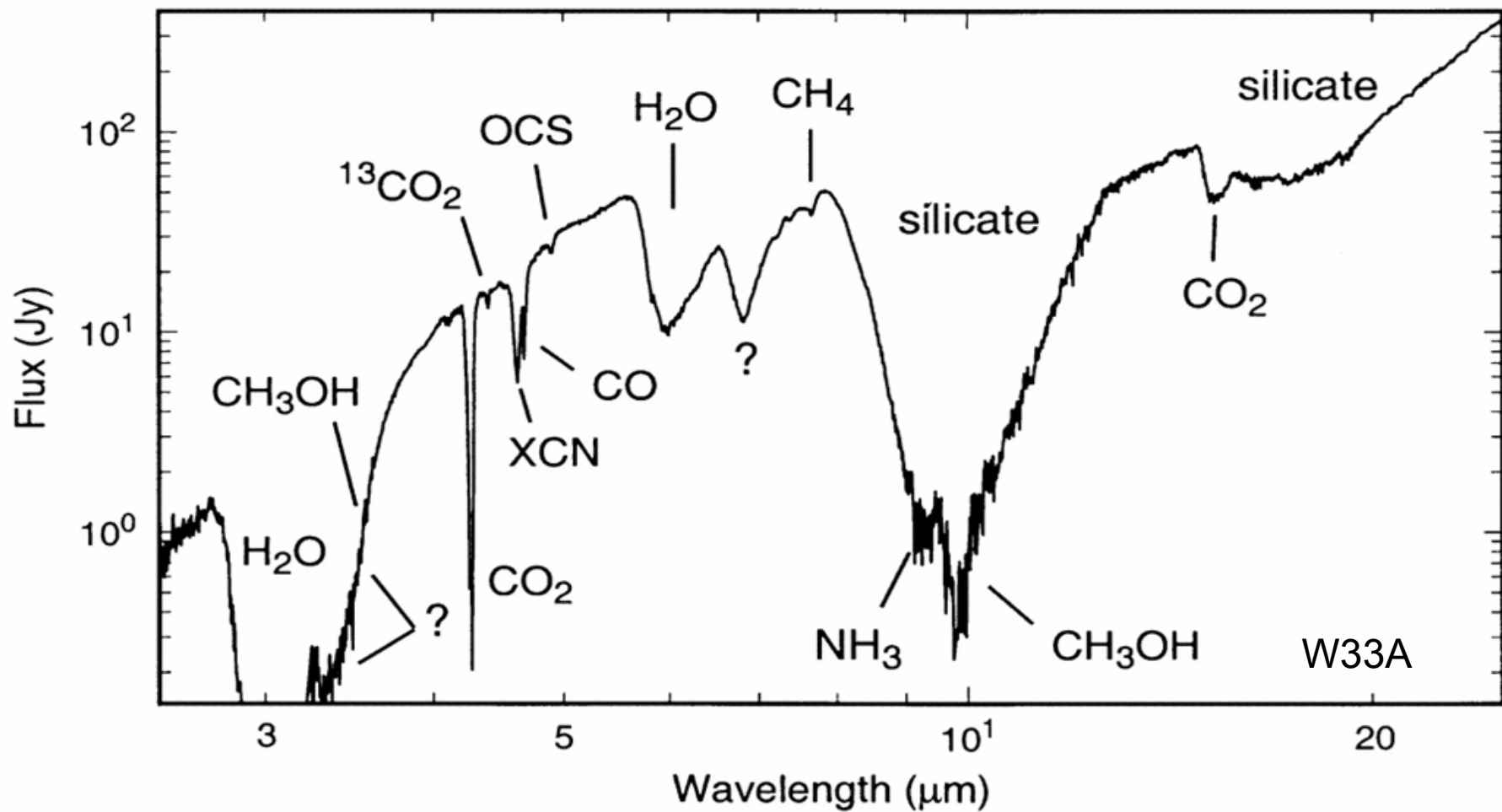


Dust

What is this dust composed of?

- amorphous silicates
 - observed depletion: most of Si, Mg, Fe, and 20% of O is contained in silicates (e.g. MgFeSiO_4 , i.e. Olivine)
 - shape of $9.7\mu\text{m}$ Si-O stretch and $18\mu\text{m}$ O-Si-O bending modes (Gillet & Forrest, '79), absorption features
 - optical extinction + polarization $\Rightarrow$ typical size $\sim 0.1\mu\text{m}$, elongated
 - wavelength dependence of extinction $\Rightarrow$ size distribution, e.g. $n(a) \sim a^{-3.5}$ $50\text{\AA}$ - $2500\text{\AA}$ (MRN)





Dust

- crystalline silicates
 - discrete, relatively sharp emission features found in spectra of old (post) AGB stars, PNe, and young stars with circumstellar disks, but not in ISM! (photons and ions tend to destroy lattice order)
 - features can be identified with Mg-rich crystalline silicates, e.g.

Mg_2SiO_4	fosterite
MgSiO_3	enstatite

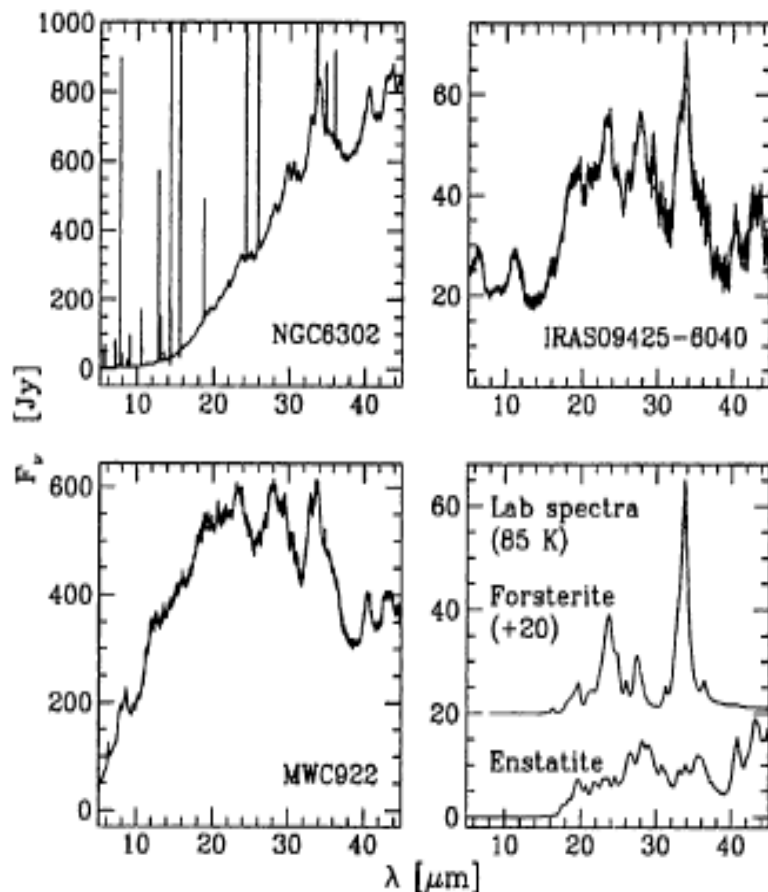


Figure 1. The spectrum of the planetary nebula NGC6302, the AGB star IRAS09425-6040 and the MWC922, which has an unknown evolutionary status, together with the laboratory spectra of forsterite (Mg_2SiO_4) and enstatite (MgSiO_3) multiplied with a blackbody of 85 K. The feature at $10\text{ }\mu\text{m}$ in IRAS09425-6040 is due to SiC.

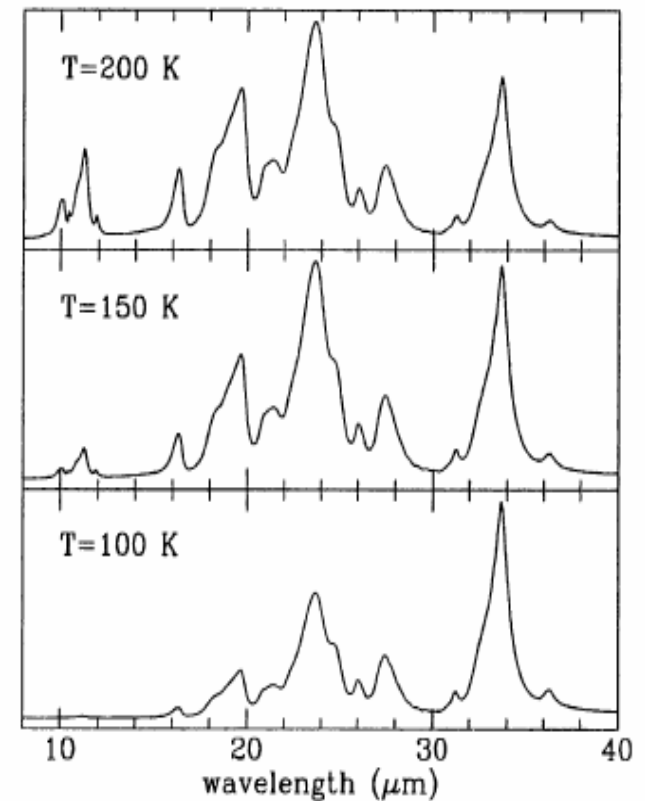


Figure 2. Laboratory transmission spectrum of forsterite, multiplied with blackbody curves of 200, 150 and 100 K. Note the decrease in the strength of the peaks in the $10\text{ }\mu\text{m}$ region when lowering the temperature.

Molster et al. 2000

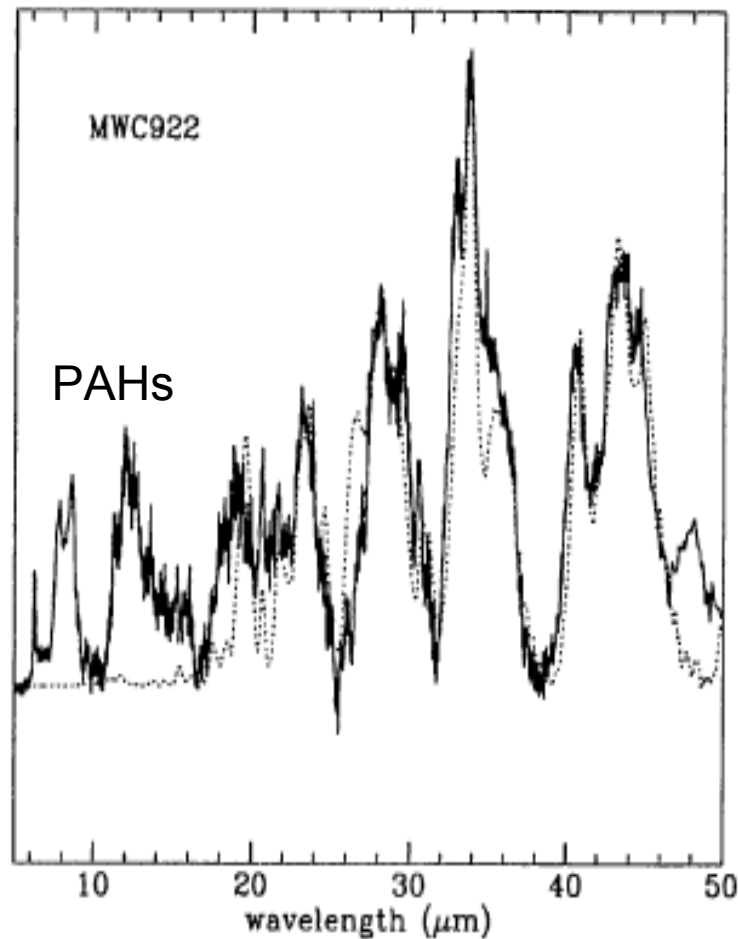


Figure 4. The model fit (dotted line) to the continuum subtracted spectrum of MWC922 (solid line). The derived temperature of the forsterite is respectively 90 and for enstatite (50% clino-enstatite and 50% ortho-enstatite) respectively 100. Note that this two component model already reproduces the observed features rather well. The mismatch at the shortest wavelengths is due to PAH features, which are not incorporated in the model.

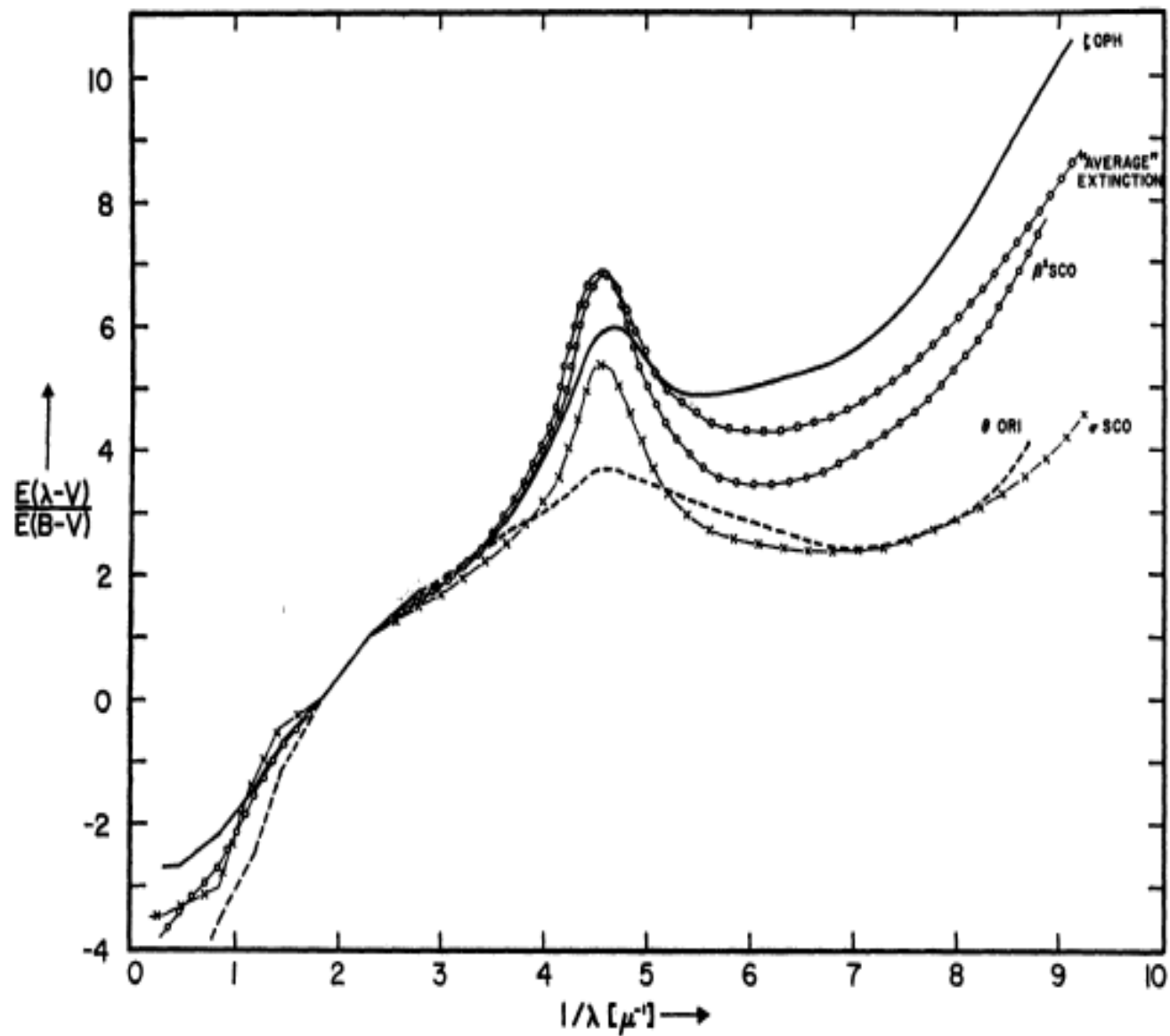
Molster et al. 2000

Dust

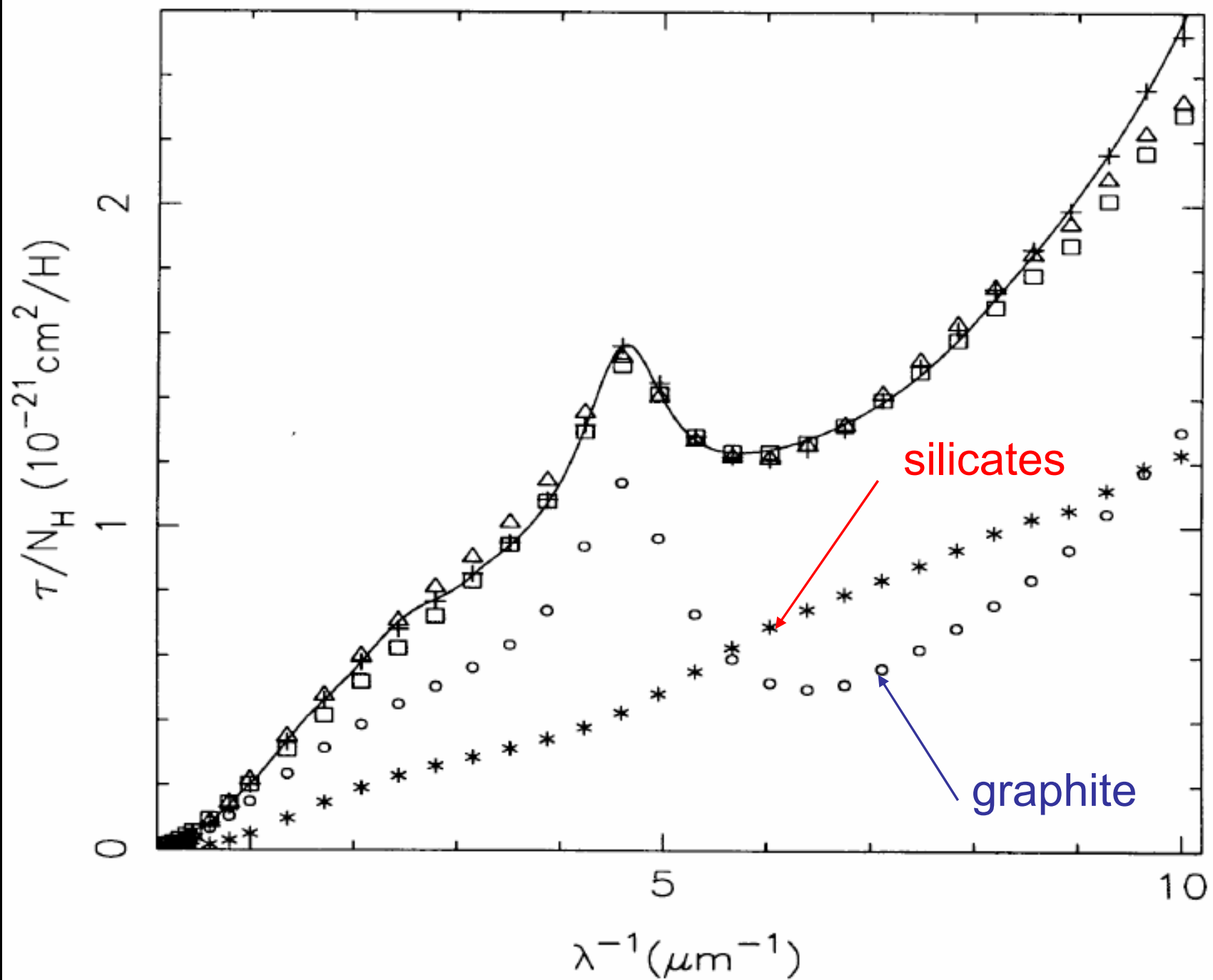
- crystalline silicates
 - fraction crystalline/anorphous ranges from few % to $\sim 50\%$, vs. $\leq$ few % in interstellar clouds

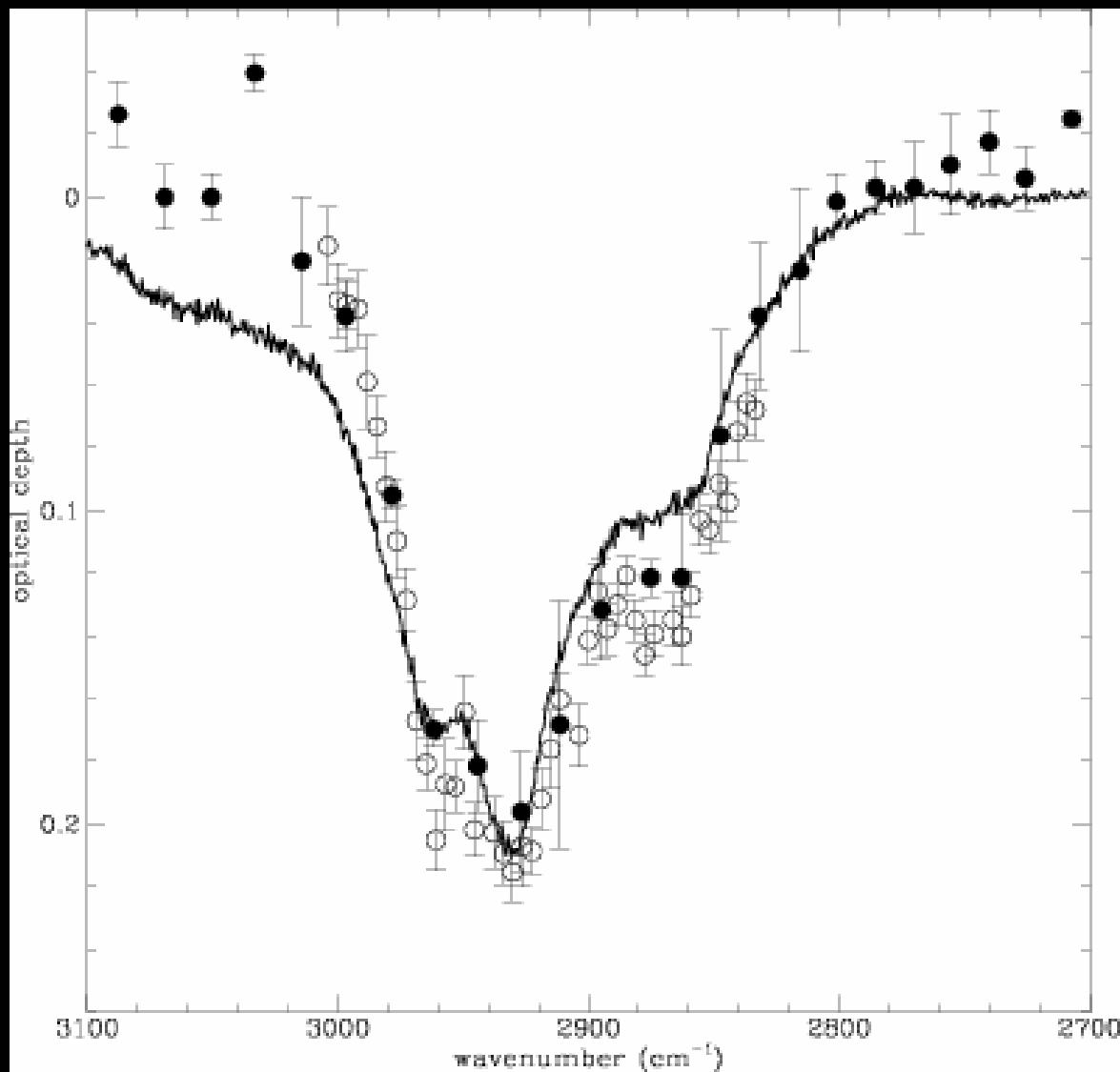
Dust

- carbonaceous material
 - 2175Å extinction bump $\Rightarrow$ ‘graphitic’ material
 - 3.4μm absorption diffuse ISM $\Rightarrow$ ‘aliphatic’
C_H (aliphatic means chain-like, i.e. does not contain ring structures)
 - mass extinction coefficient (opacity) $\Rightarrow$ ~60%
of C in solid form



Bless&Savage
1972





Galactic center
source IRS 6E
vs laboratory

Hydrogenated
carbon grains

Mennella et al.
2001

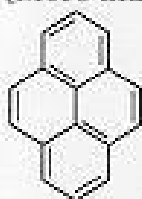
Dust

- PAHs
 - Series of discrete emission bands at 3.29 μm , 6.2 μm , 7.7 μm , 8.6 μm , 11.3 μm , ...
 - best fit by Polycyclic Aromatic Hydrocarbons with 20-100 carbon atoms containing ~1% of carbon abundance.

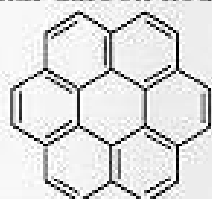
PAH Structures

Pericondensed

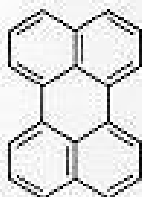
(More than one internal Carbon node)



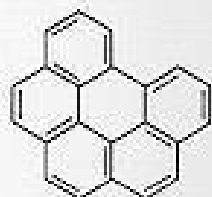
Pyrene
 $C_{16}H_{10}$



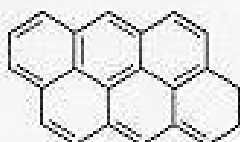
Coronene
 $C_{24}H_{12}$



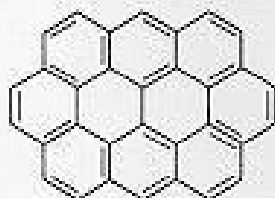
Perylene
 $C_{20}H_{12}$



Benzo[ghi]perylene
 $C_{22}H_{12}$



Antanthrene
 $C_{22}H_{12}$



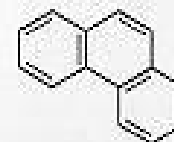
Ovalene
 $C_{32}H_{14}$

Catacondensed

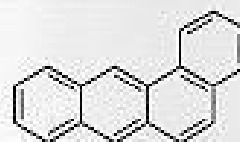
(No internal Carbon vertices)



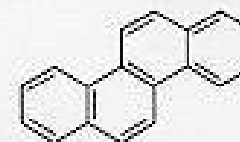
Naphthalene
 $C_{10}H_8$



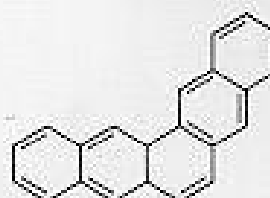
Phenanthrene
 $C_{14}H_{10}$



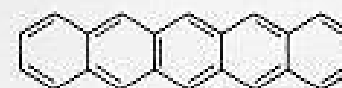
Tetraphene
 $C_{18}H_{12}$



Chrysene
 $C_{18}H_{12}$



Pentaphene
 $C_{22}H_{14}$



Pentacene
 $C_{22}H_{14}$

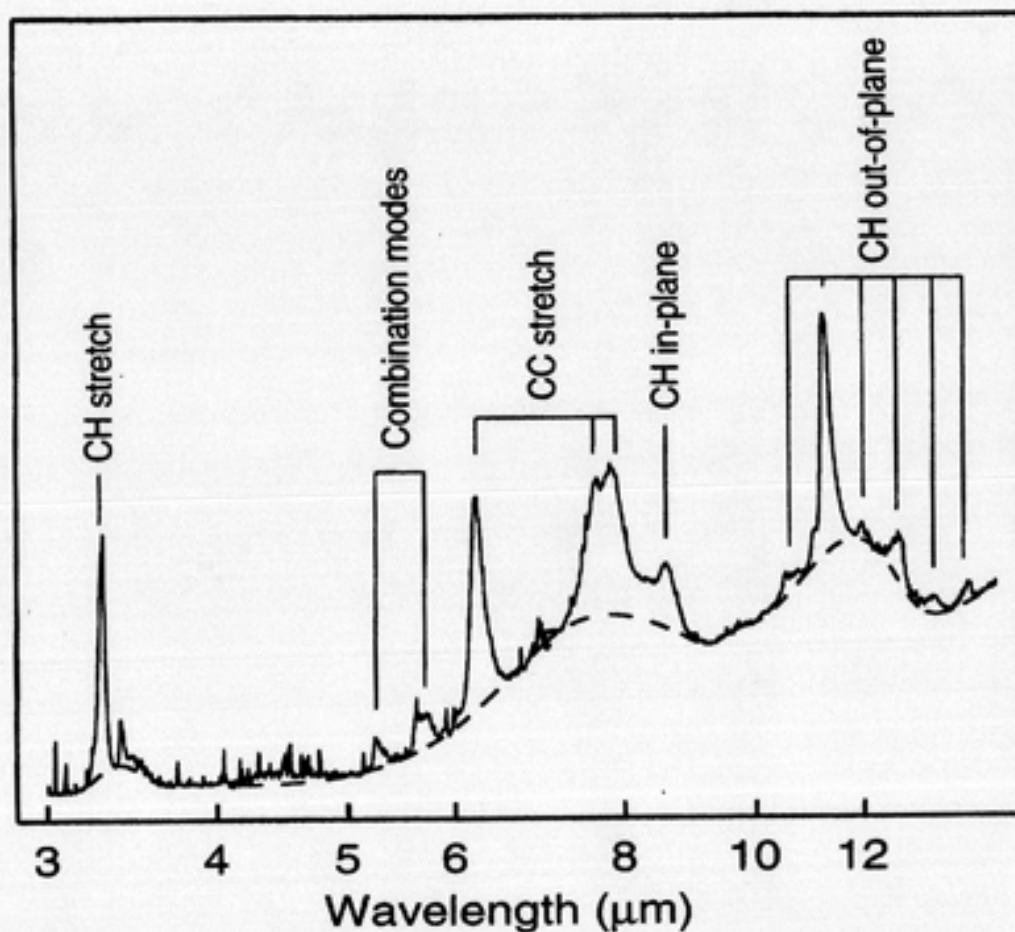
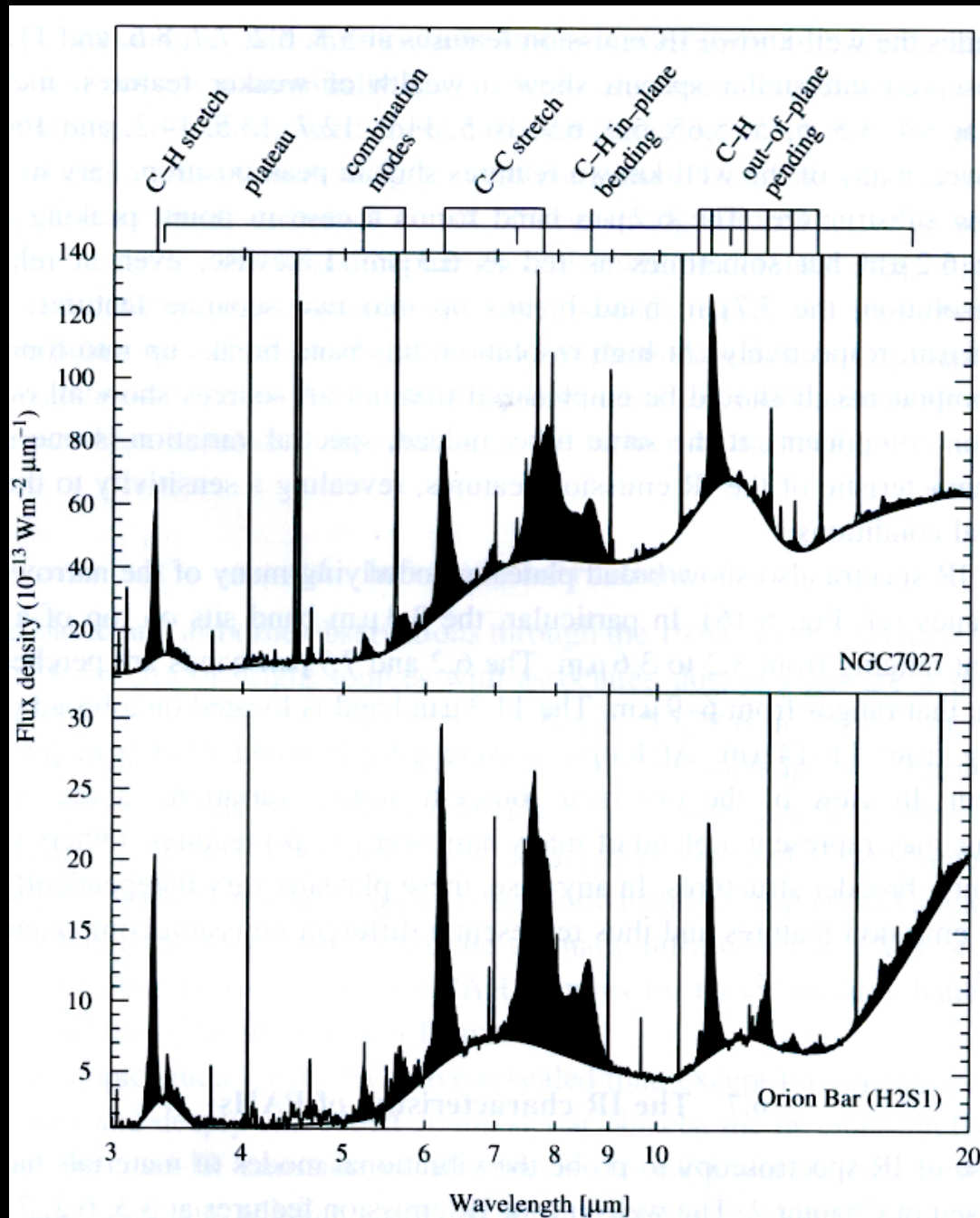


Figure 6.12. Assignment of aromatic features in the spectrum of the planetary nebula NGC 7027 to vibrational modes in PAHs. Figure courtesy of Emma Bakes, adapted from Bakes *et al* (2001).



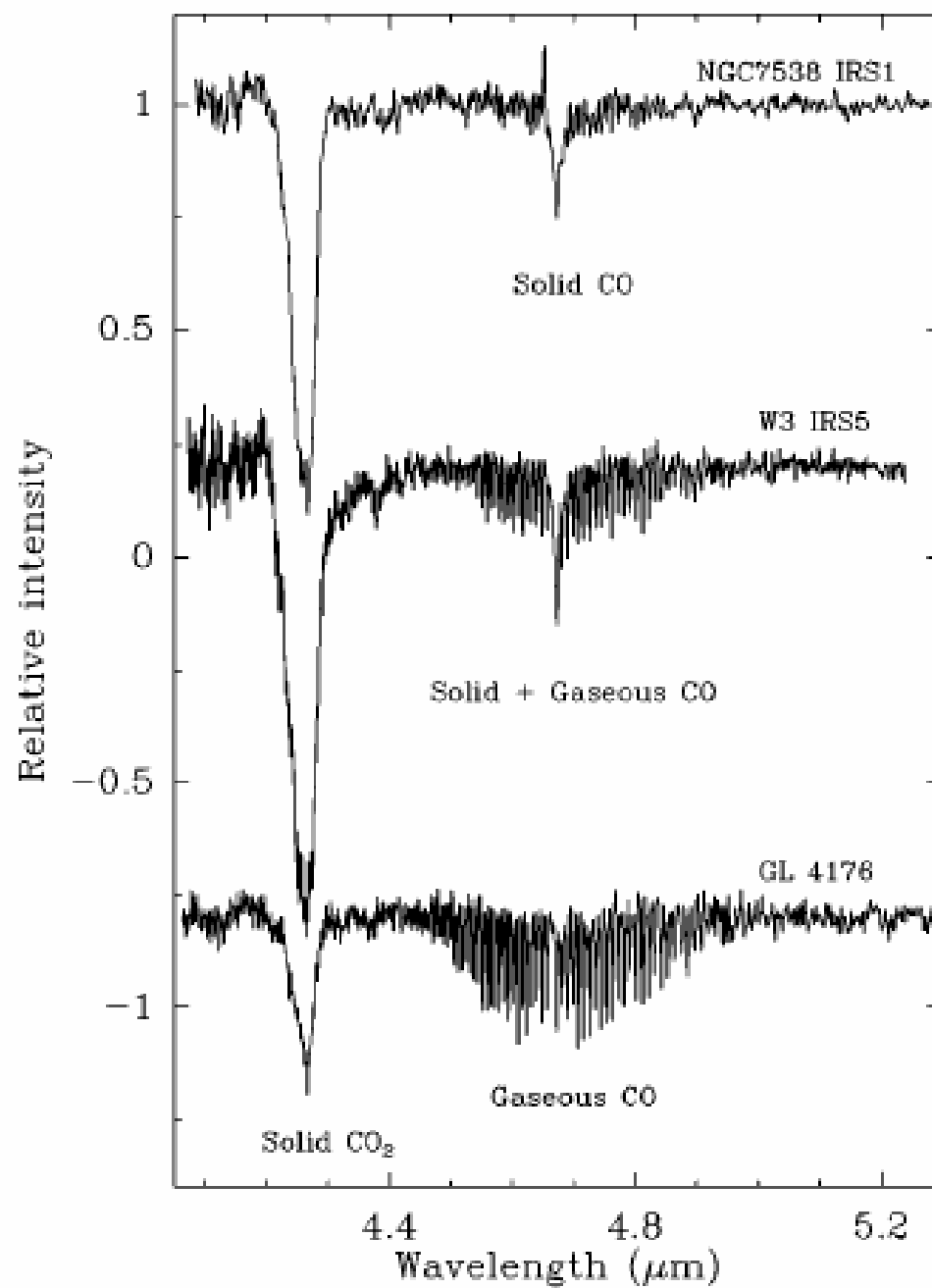
PAH
spectral
features in
IR spectra
of
NGC7027
(PN) &
Orion Bar
(PDR)

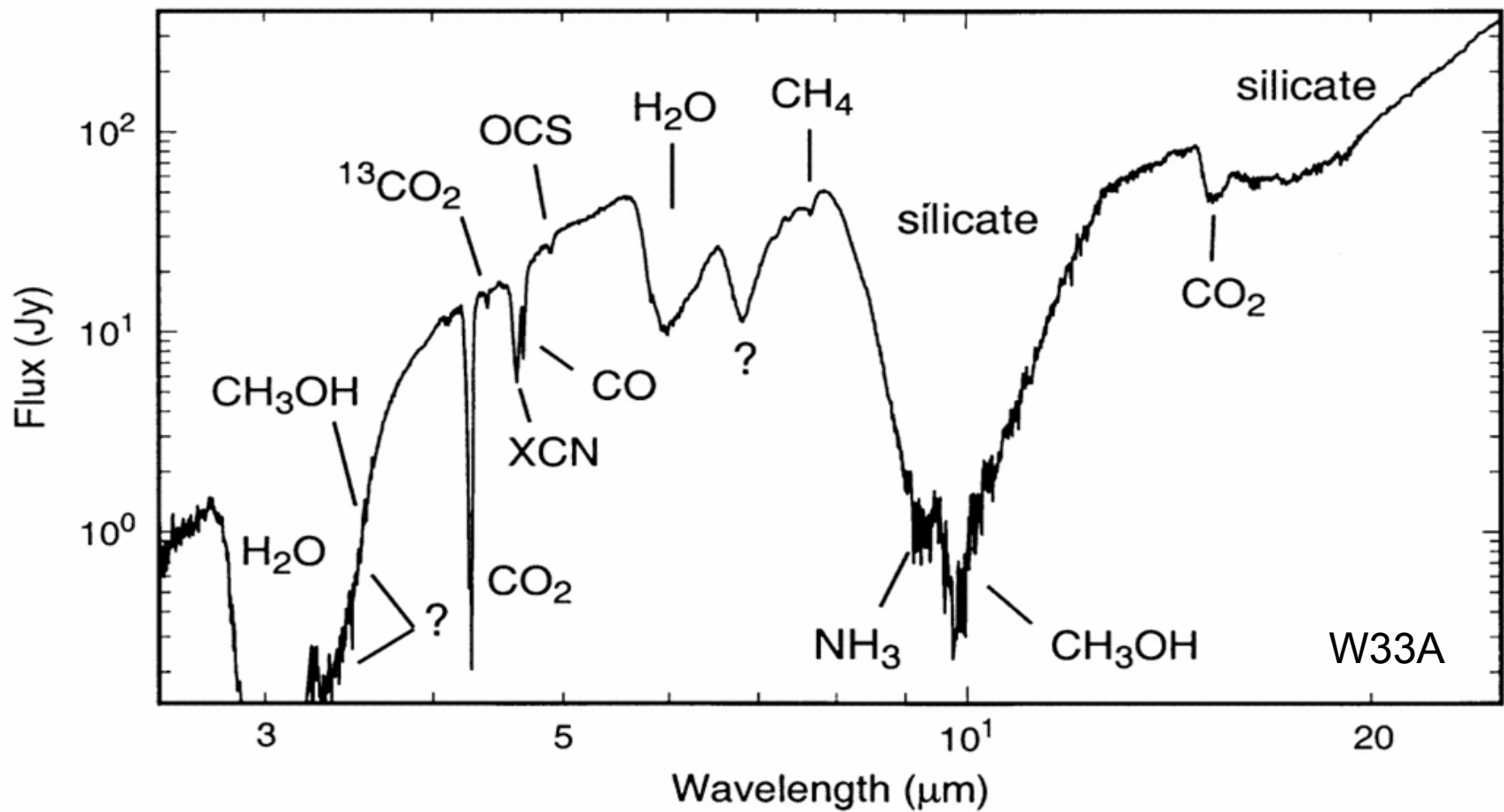
Dust

- Ices

- discrete absorption features in dense, cold

clouds:	3.1, 6.0 μm	H ₂ O ice
	4.27, 15.2 μm	CO ₂ ice
	4.67 μm	CO ice
	3.53, 9.75 μm	CH ₃ OH ice
	7.68 μm	CH ₄ ice

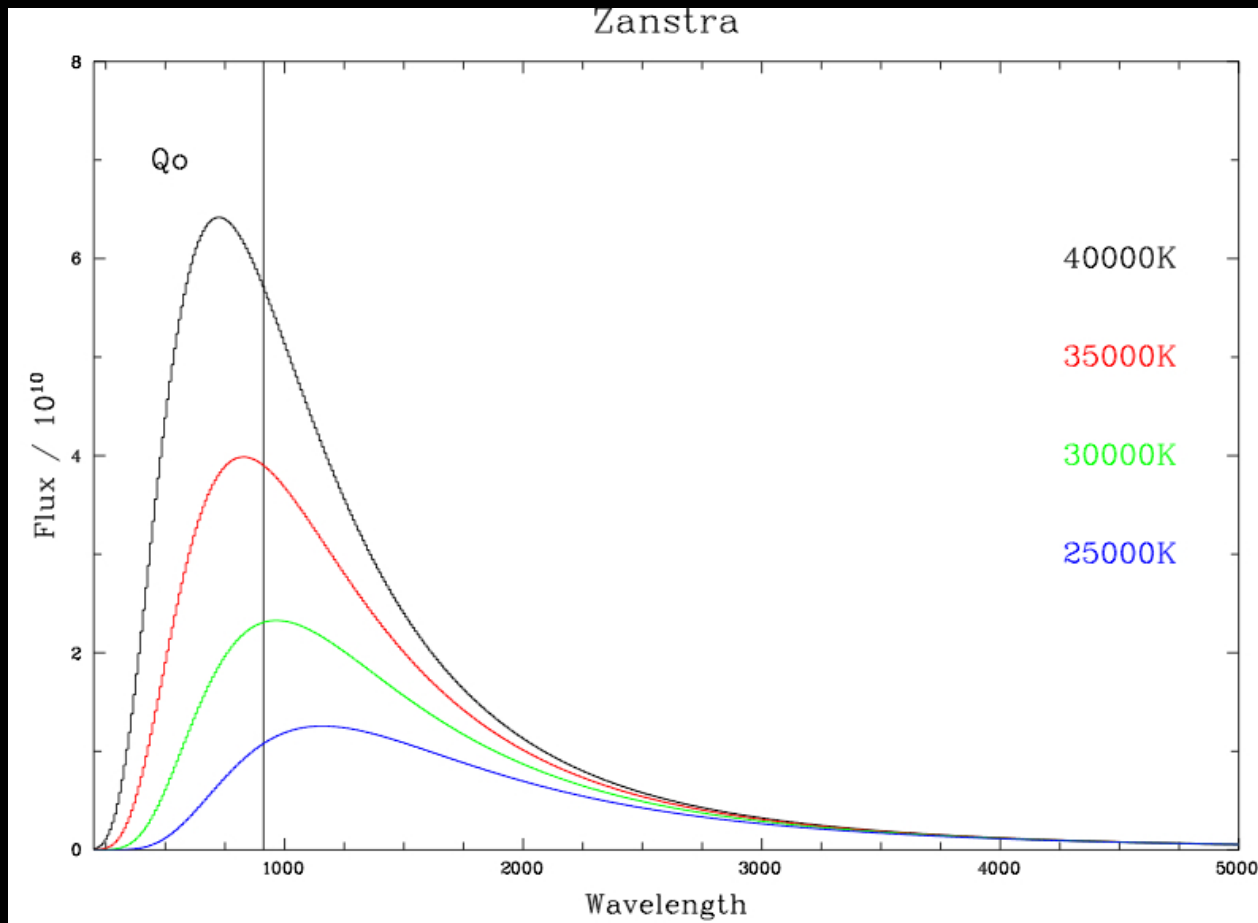




Dust

- Ices
 - ices can be distinguished from gas-phase by:
 - lack of rotational structure bands
 - broadening bands
 - shape of ice bands provides constraints on environmental molecules, e.g.:
 - H₂O-rich ices: “polar” ices
 - H₂O-poor ices: “apolar” ices

Review: Boogert & Ehrenfreund, astro-ph/0311163



Fraction of photons emitted by a star above 13.6eV increases rapidly with stellar temperature from 10^{-10} (Sun), to 10^{-5} (A0V, 10^4 K), 10% (B0V, $3 \cdot 10^4$ K), ~50% (O3V, $5 \cdot 10^5$ K).