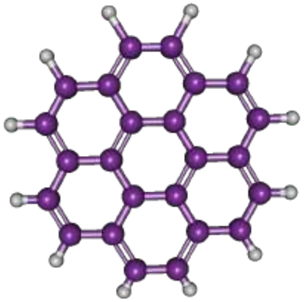


Mesoscopic Astrochemistry: a sprinkle of Dust and PAHs

Alessandra Candian - University of Amsterdam

NanoSpace

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

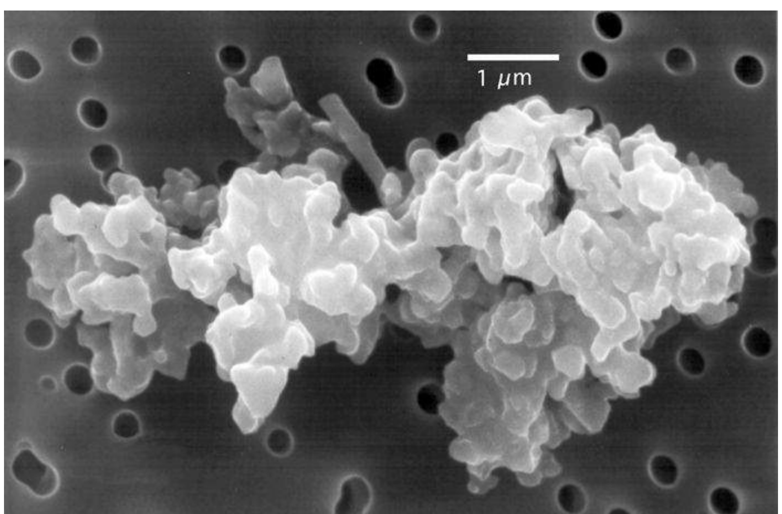
Origins Center

NWO

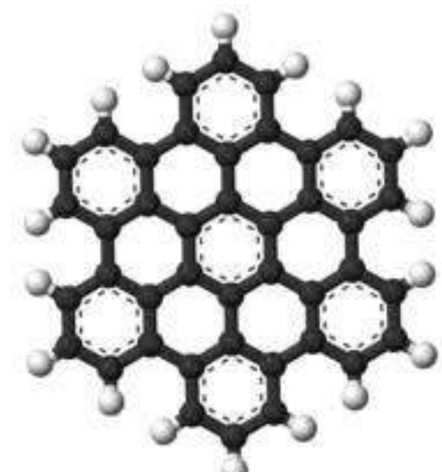
DAN Dutch Astrochemistry Network III

Overview

- Interstellar dust grains:
  - composition and properties
- Polycyclic Aromatic Hydrocarbon (PAH) molecules and large hydrocarbons
  - detection, properties, role in ISM, hot topics



Jessberger et al, 2001 -



A tour of the dusty Universe

Q: How do we know that there is interstellar dust?

A tour of the dusty Universe

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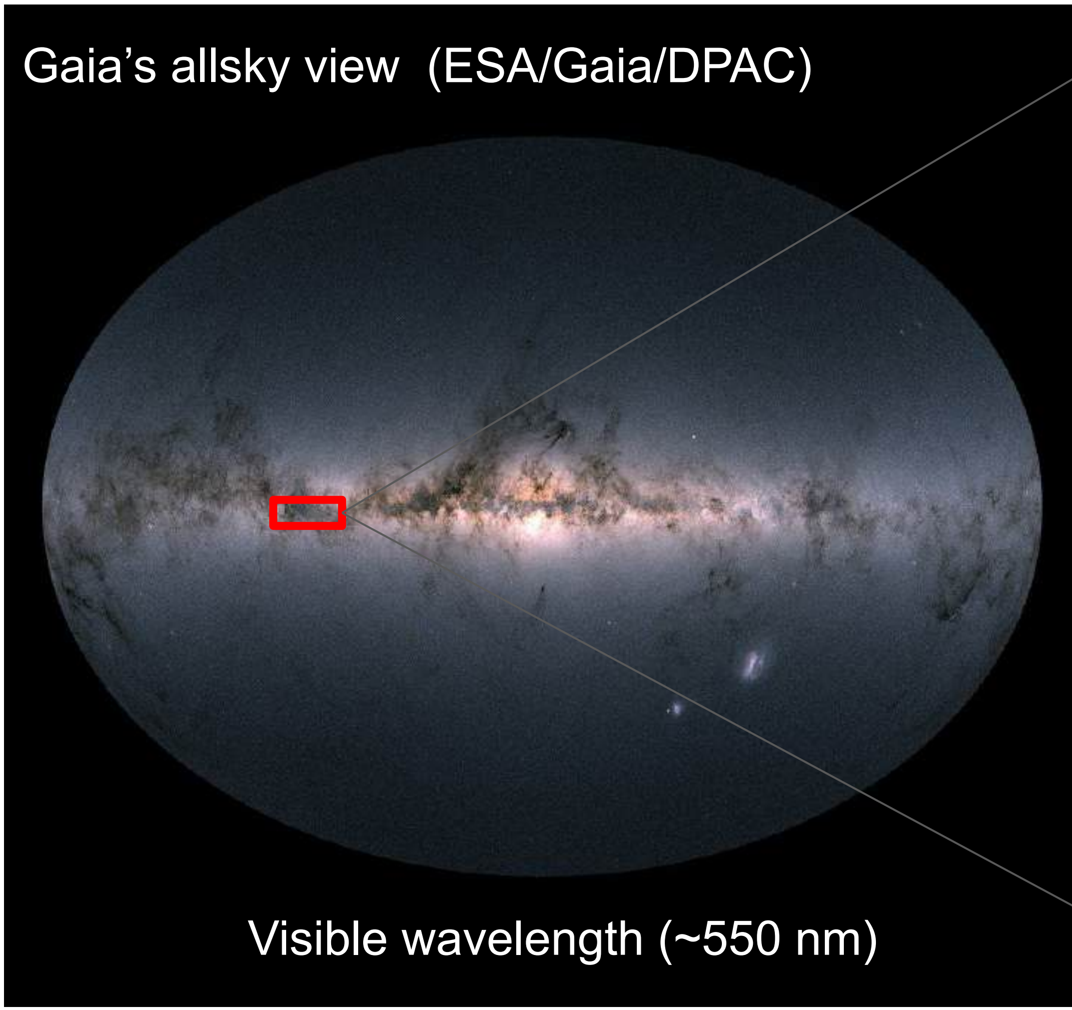
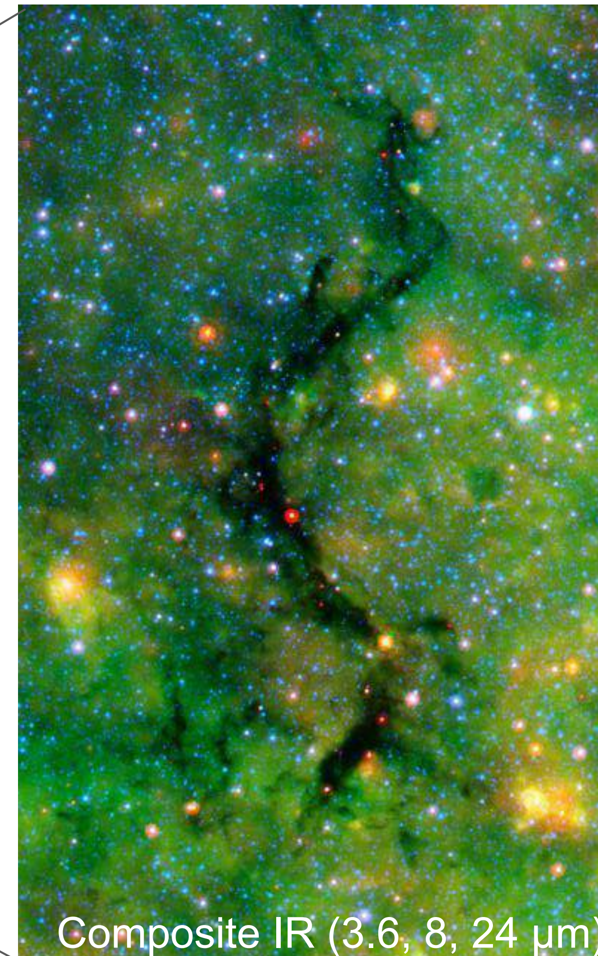
A1: Because it interacts with light => absorption of light



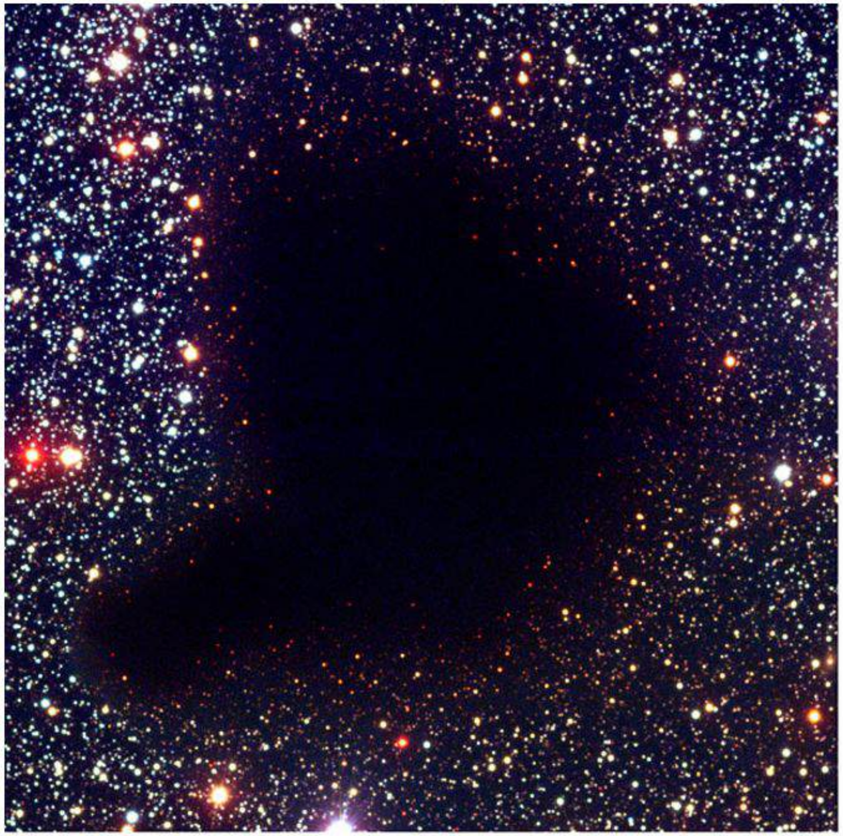


NASA, JPL-Caltech/S. Carey (SSC/Caltech)

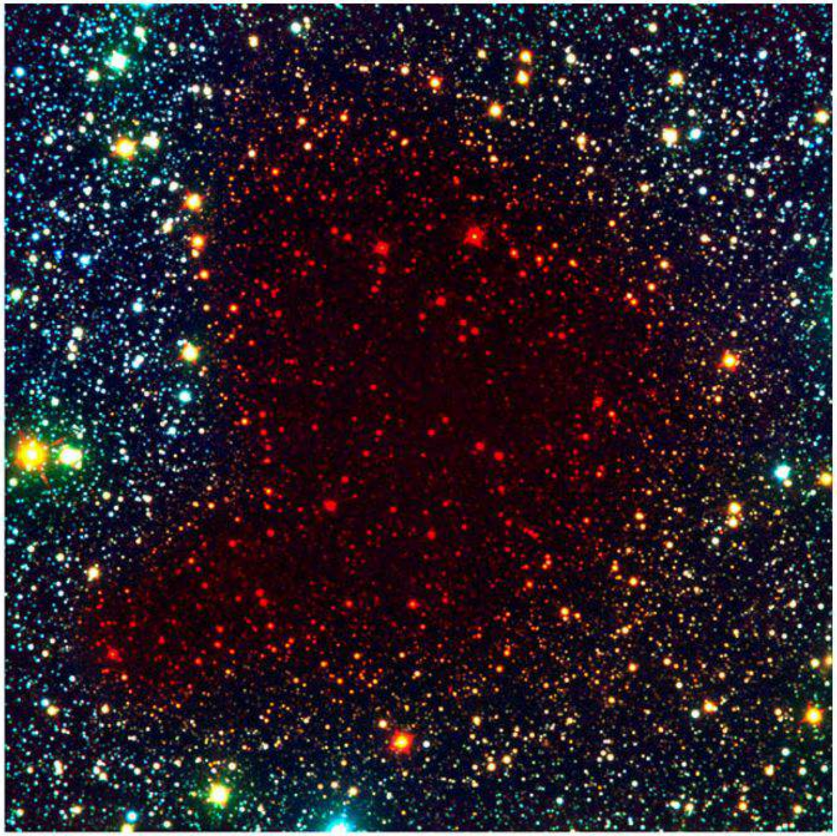
A tour of the dusty Universe

Q: How do we know that there is IS dust?

A1: Because it interacts with light => Reddening



B, V, I

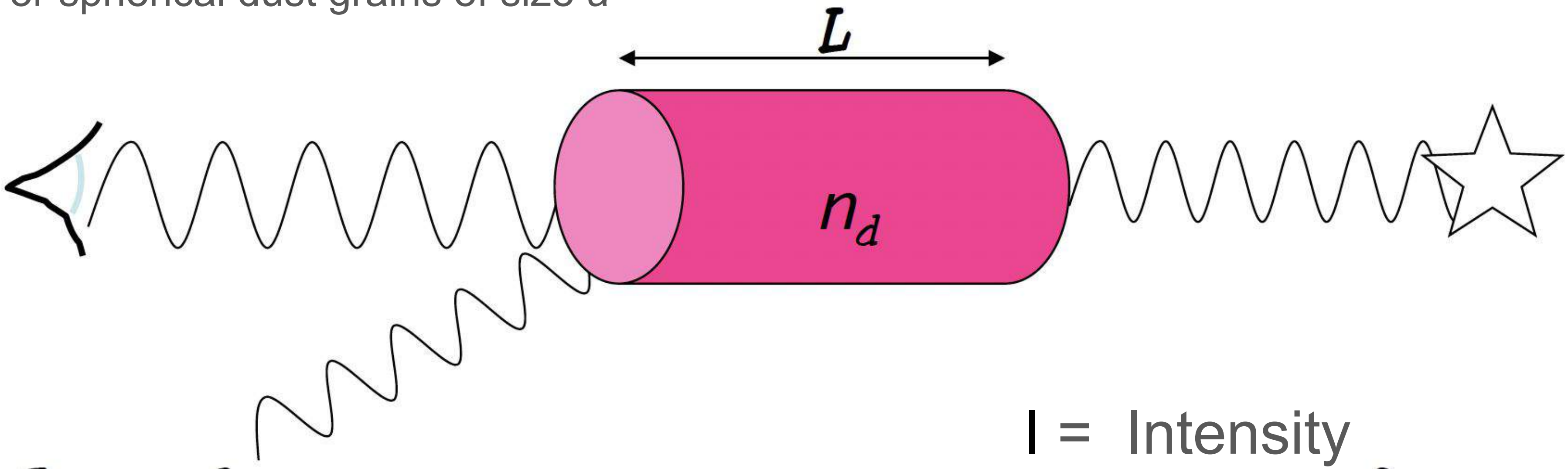


B, I, K

Blok Globule B68, ESO

Dust extinction

For spherical dust grains of size *a*



$$I = I_0 e^{-\tau}$$

where

$$\tau = \int n_d \, dL \, C_{ext} = N_d \, C_{ext}$$

Optical depth

I = Intensity
n_d = number density
C_{ext} = extinction cross-section

$$C_{ext} = \frac{E_{abs}}{E_{inc} / m^2} \sim \pi a^2$$

Extinction curves

$$A_\lambda = -2.5 \log (I/I_0) = 1.086\ \tau$$

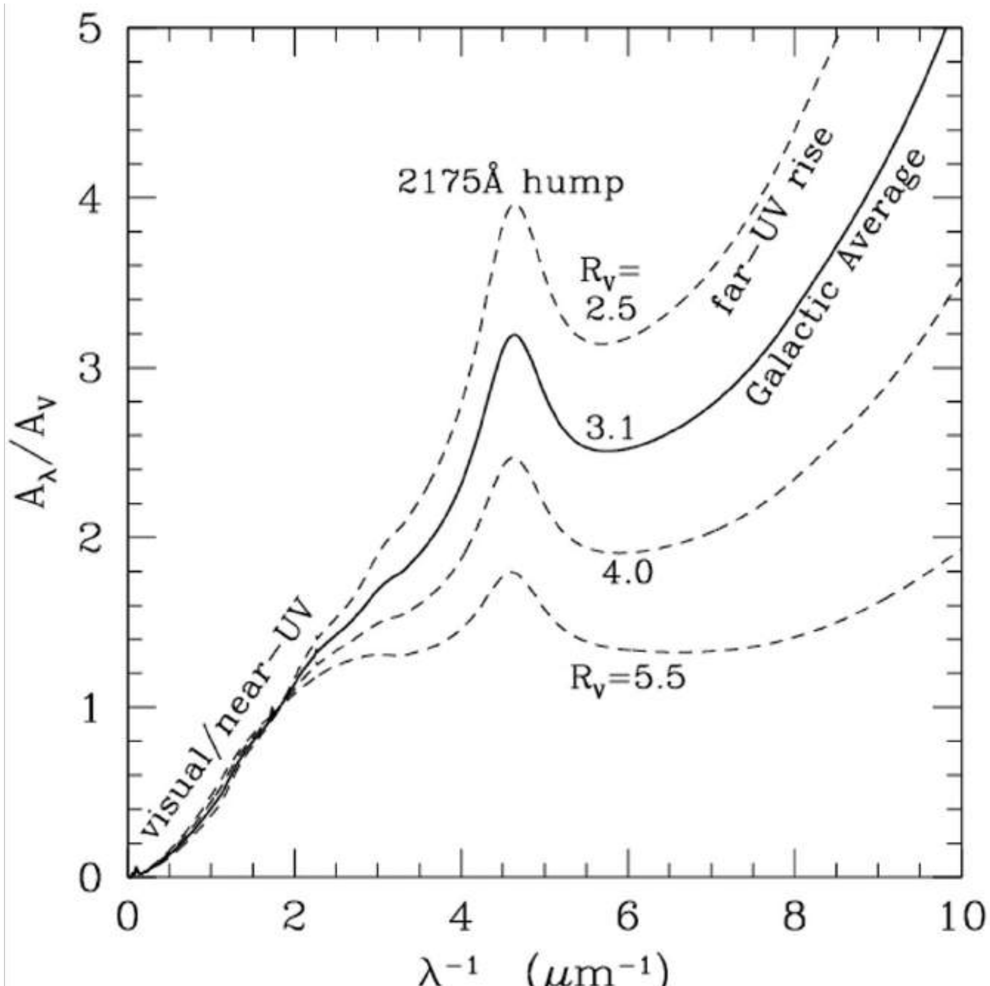


Figure courtesy of A. Li

Extinction curves are characterized by one parameter

$$R_V = A_V / E_{B-V}$$

R_v is **environment-dependent:**

- 3.1 in diffuse ISM
- 4-6 in molecular clouds

Extinction curves

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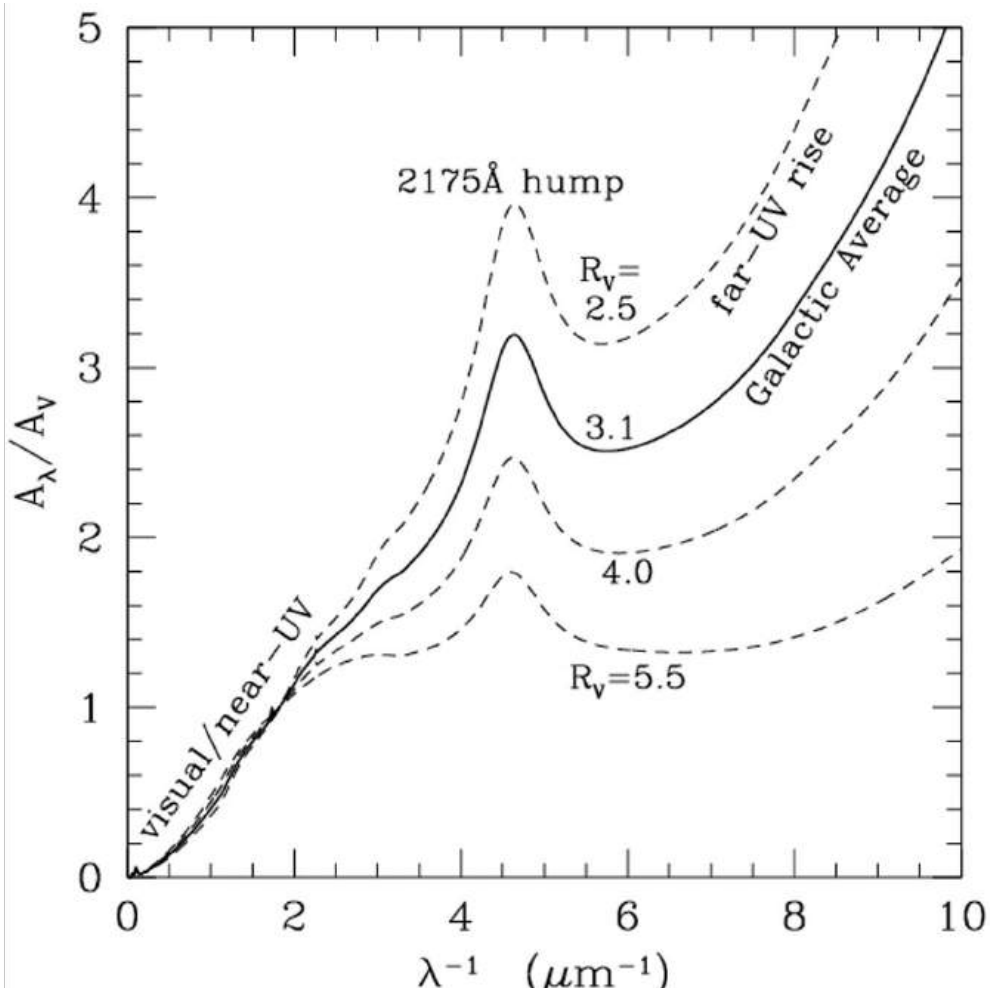

Figure courtesy of A. Li

Extinction curves are characterized by one parameter

$$R_V = A_V / E_{B-V}$$

R_v is **environment-dependent:**

- 3.1 in diffuse ISM
- 4-6 in molecular clouds

Main features:

- Rising with $\lambda^{-1.7}$ in the IR and λ^{-1} in the visible
- Prominent 217.5 nm (4.6 μm^{-1}) bump + Far-UV rise

Extinction curves

$$A_\lambda = -2.5 \log (I/I_0) = 1.086\,\tau$$

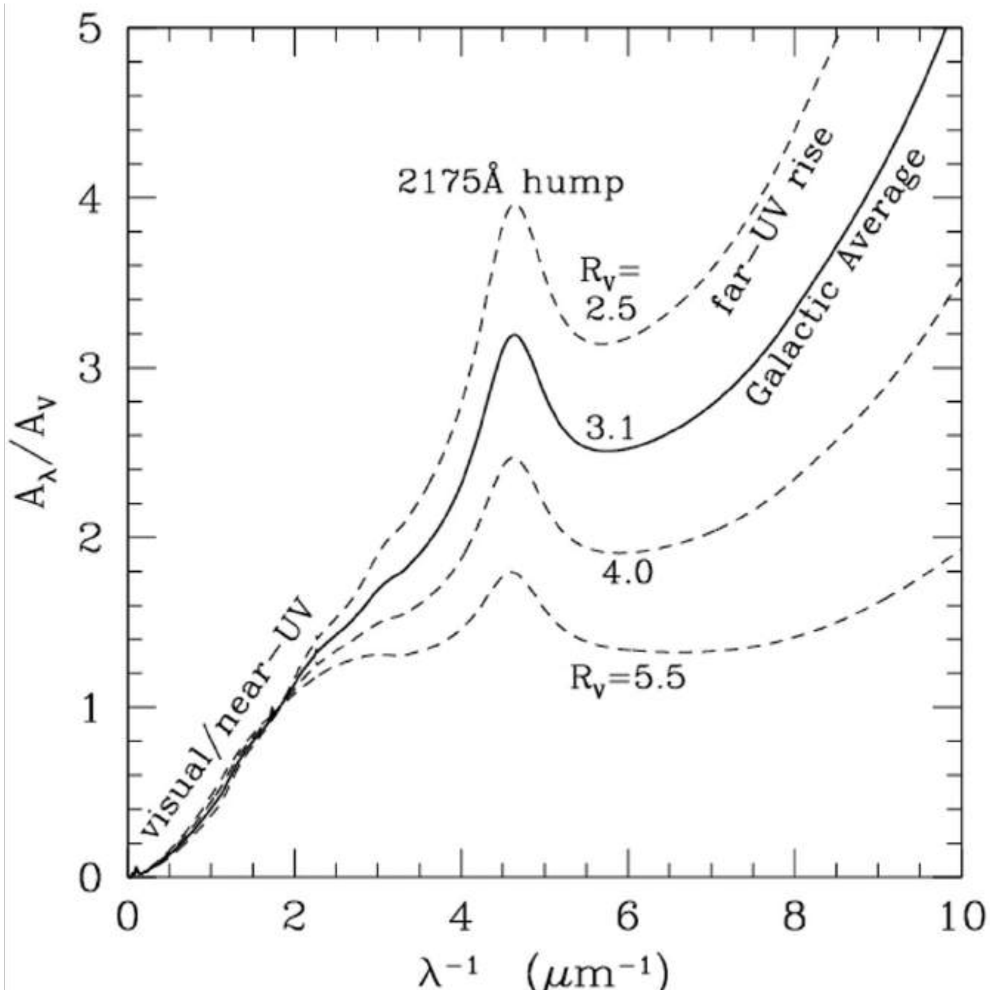

Figure courtesy of A. Li

To model extinction curves we need

1) size distribution (1-300 nm)

$n(a) \propto a^{-\beta}$ with $a_{min} < a < a_{max}$

(small grains for the FUV rise, large grains for visual IR extinction)

2) refractive index $m(\lambda)$

3) two populations of materials: silicates and graphite

Extinction curves

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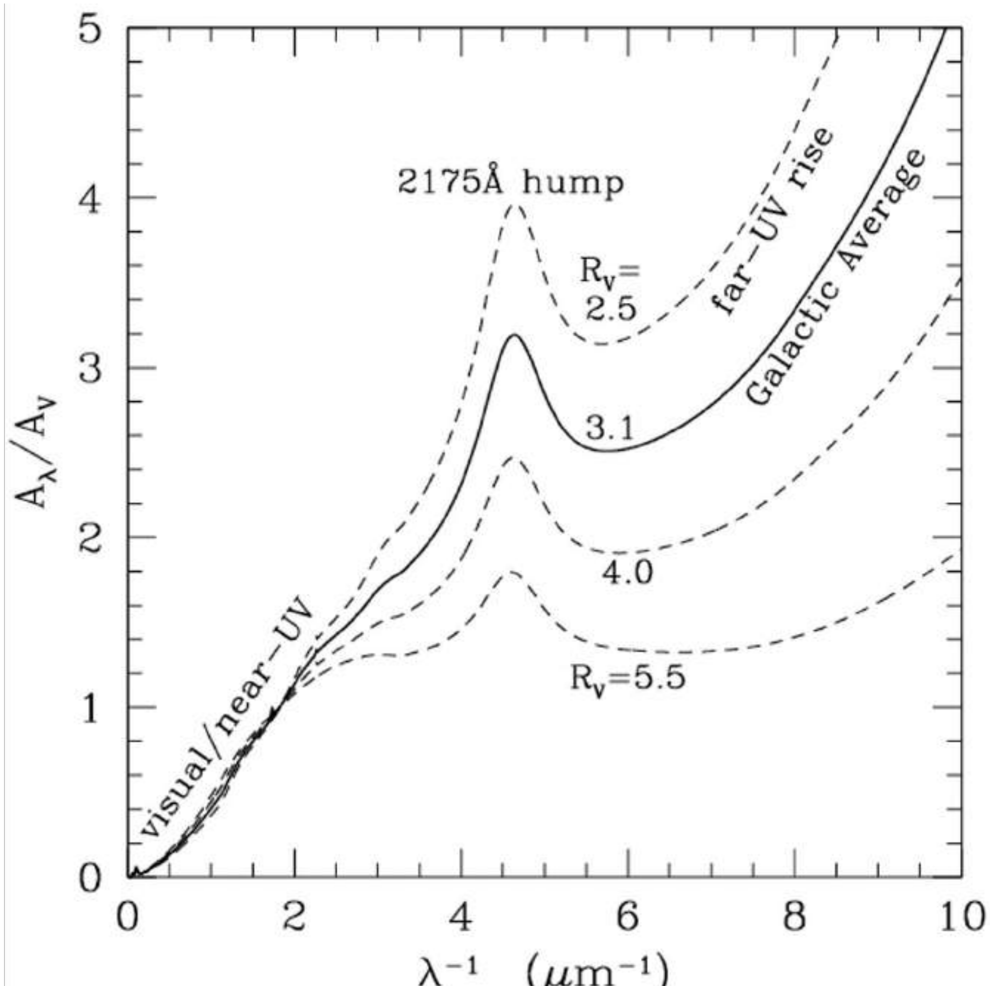

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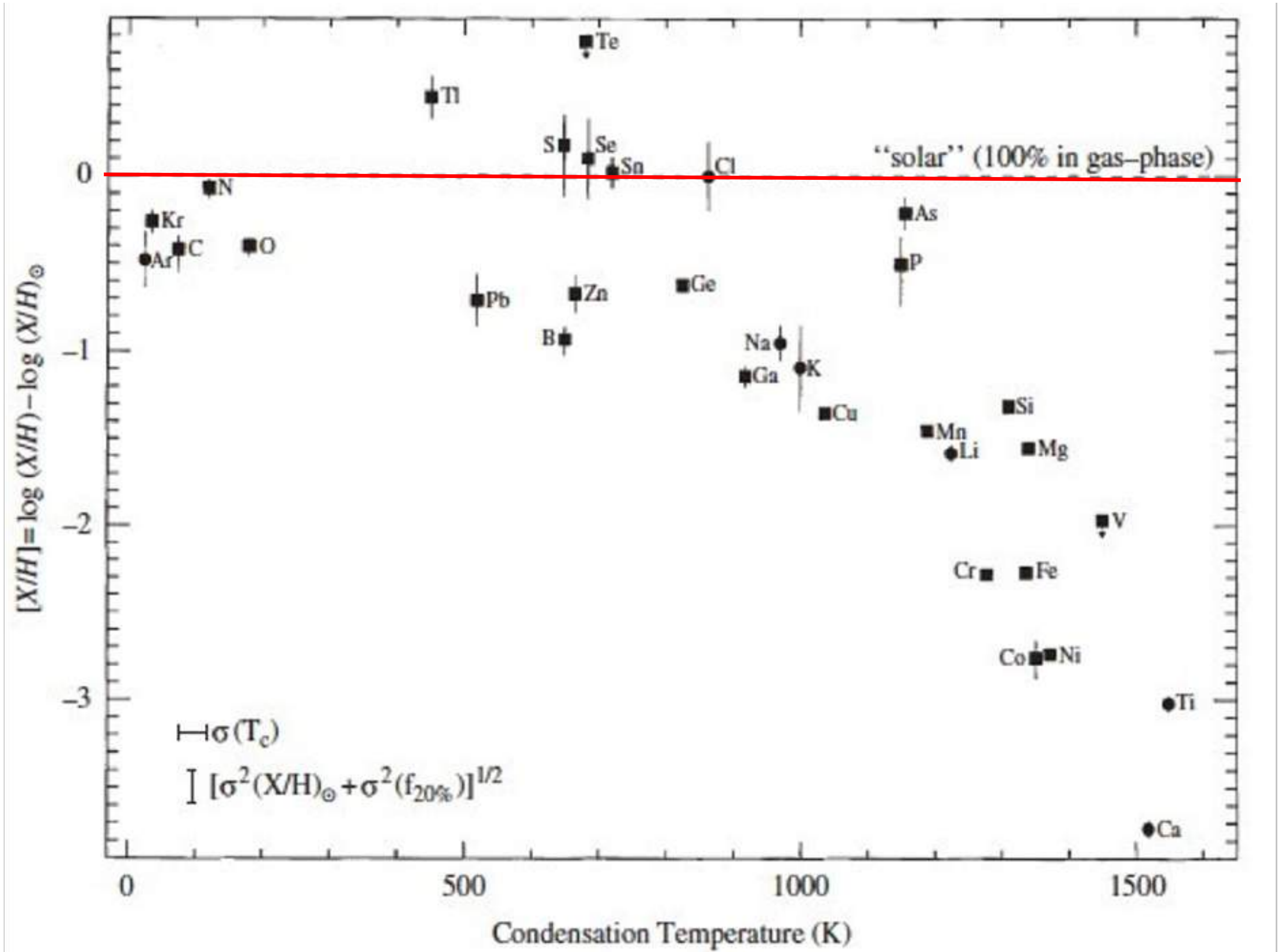
??

A tour of the dusty Universe

Q: How do we know that there is IS dust?

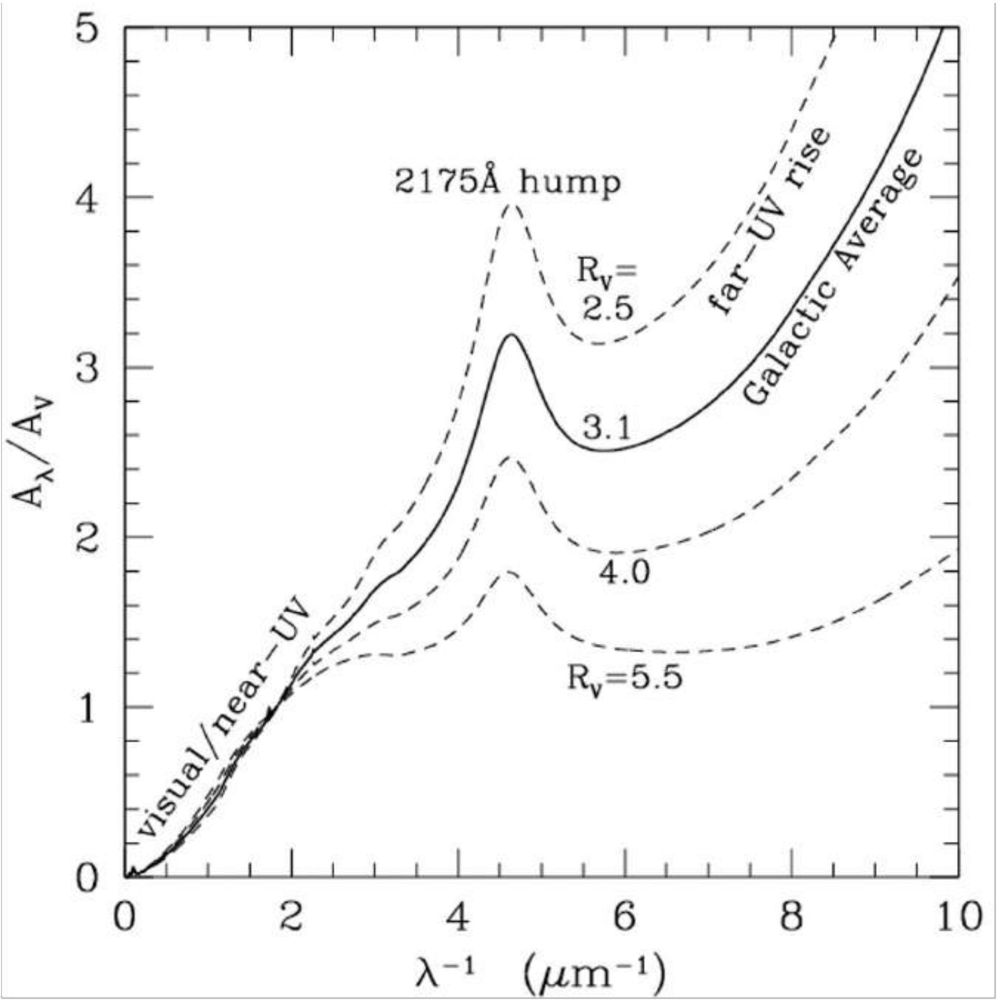
A2: Because some elements are missing from the gas-phase



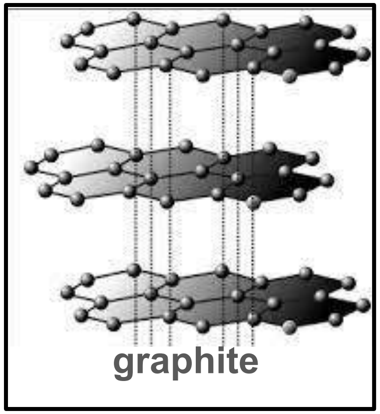
Dust composition

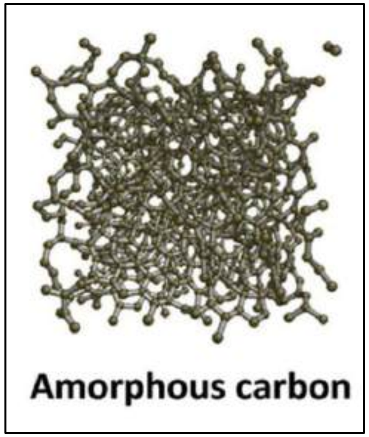
Dust composition

1) UV Bump at 2175 Å in the extinction curve



"graphitic-like" material
π → π* transition ~2000 Å

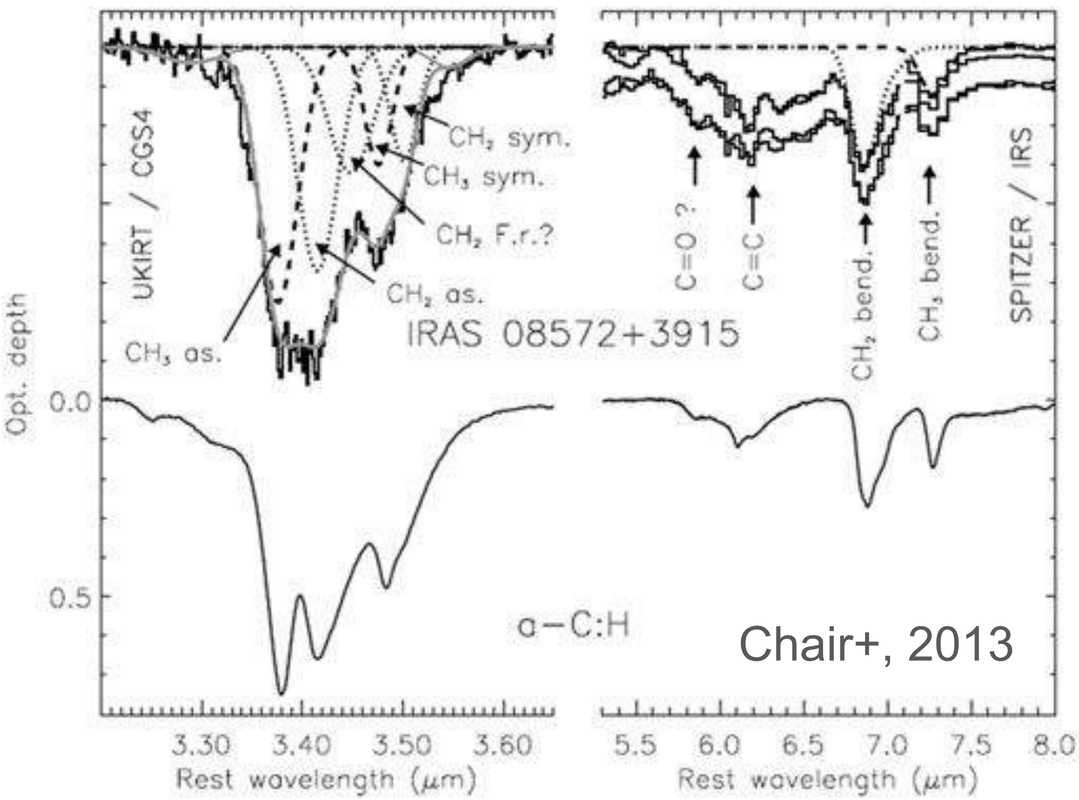


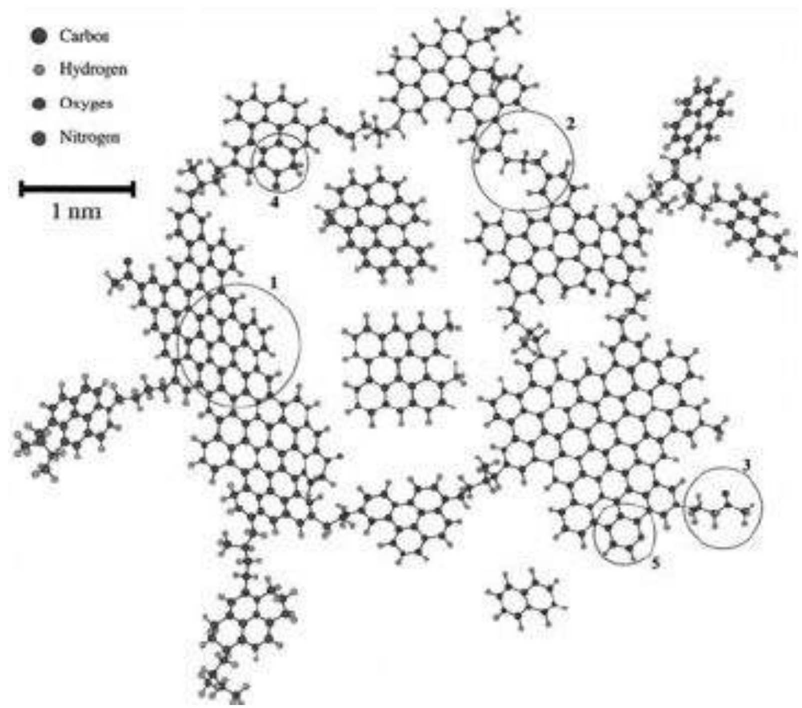


Position & width depend on "material" properties

Dust composition

2) Infrared absorption features in the diffuse ISM



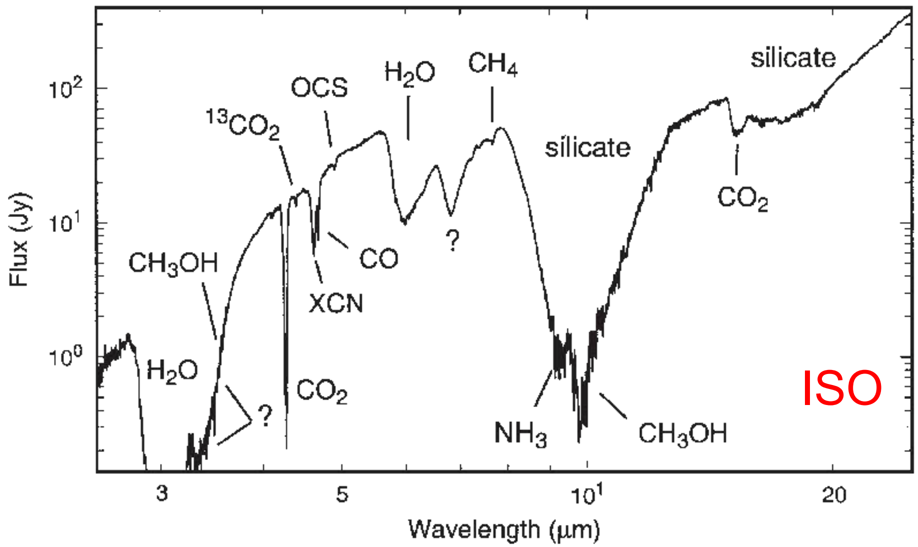


More C-dust

Consistent with vibrations of several types of C-H bonds and C-C bonds (Dartois et al. 2007)

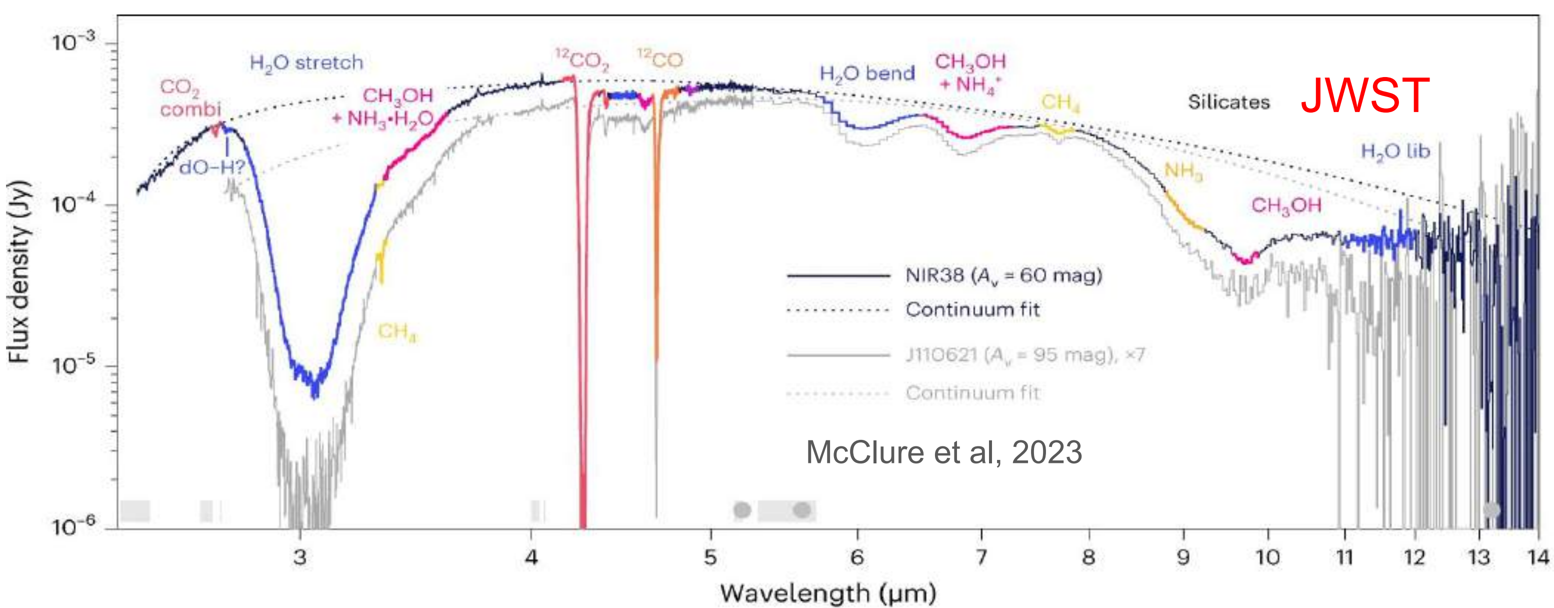
Dust composition

3) IR absorption features in the "dense" ISM



- Features at 9.7 and 18 μm, due to O-Si-O modes (mostly Mg and Fe-rich)
- Different ice features, e.g. water at 3 μm

Dependence on A_V!



Dust composition

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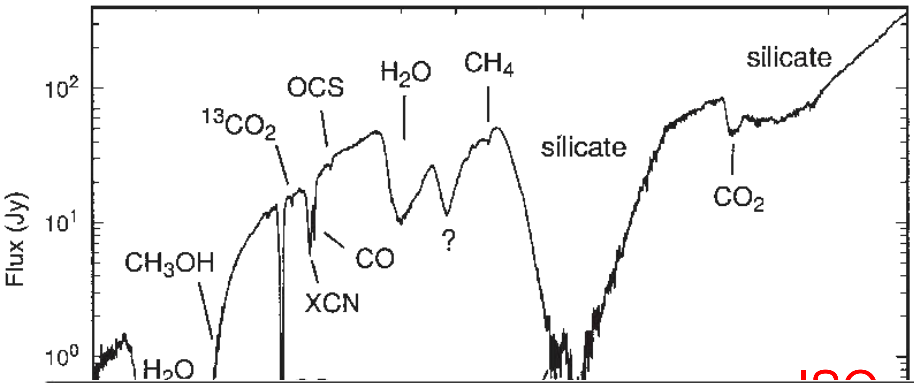

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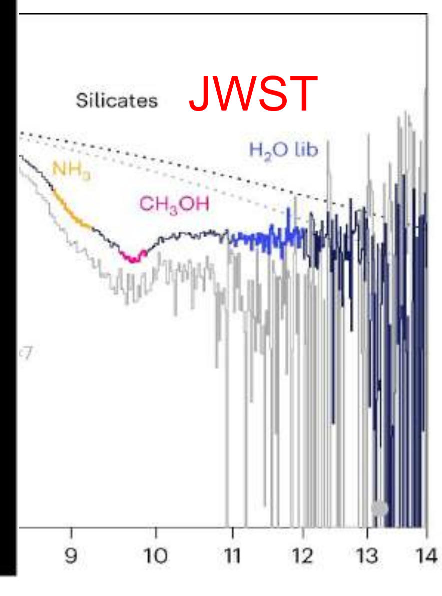

Dust temperature

Dust temperature is set by radiative energy balance $\Gamma_{abs} = \Gamma$

$$\Gamma_{\rm abs} = 4\pi\sigma_{\rm d}\int_0^\infty Q(\lambda)J(\lambda){\rm d}\lambda,$$

$$\Gamma_{\rm em} = 4\pi\sigma_{\rm d}\int_0^\infty Q(\lambda)B(T_{\rm d},\lambda){\rm d}\lambda,$$

with
J(λ)= mean intensity of the radiation field,
Q(λ)= efficient of the dust (abs and em.)
T_d= dust temperature
$B(T_d,\lambda)$= Planck function for $T=T_d$

In the diffuse ISM, considering stellar light and efficiencies typical for Silicate and Carbon dust:

$$T_{\rm sil} = 13.6\left(\frac{1\mu{\rm m}}{a}\right)^{0.06}{\rm K}.$$

and

$$T_{\rm gra} = 15.8\left(\frac{1\,\mu{\rm m}}{a}\right)^{0.06}{\rm K}.$$

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EXERCISE: (in pairs) Calculate the Silicate dust temperature for particles of sizes:

1) a = 10 nm
2) a = 2.5 μm

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EXERCISE: (in pairs) Calculate the Silicate dust temperature for particles of sizes:

1) a = 10 nm => T_{sil} ~18 K
2) a = 2.5 μm => T_{sil} ~13 K

Dust temperature

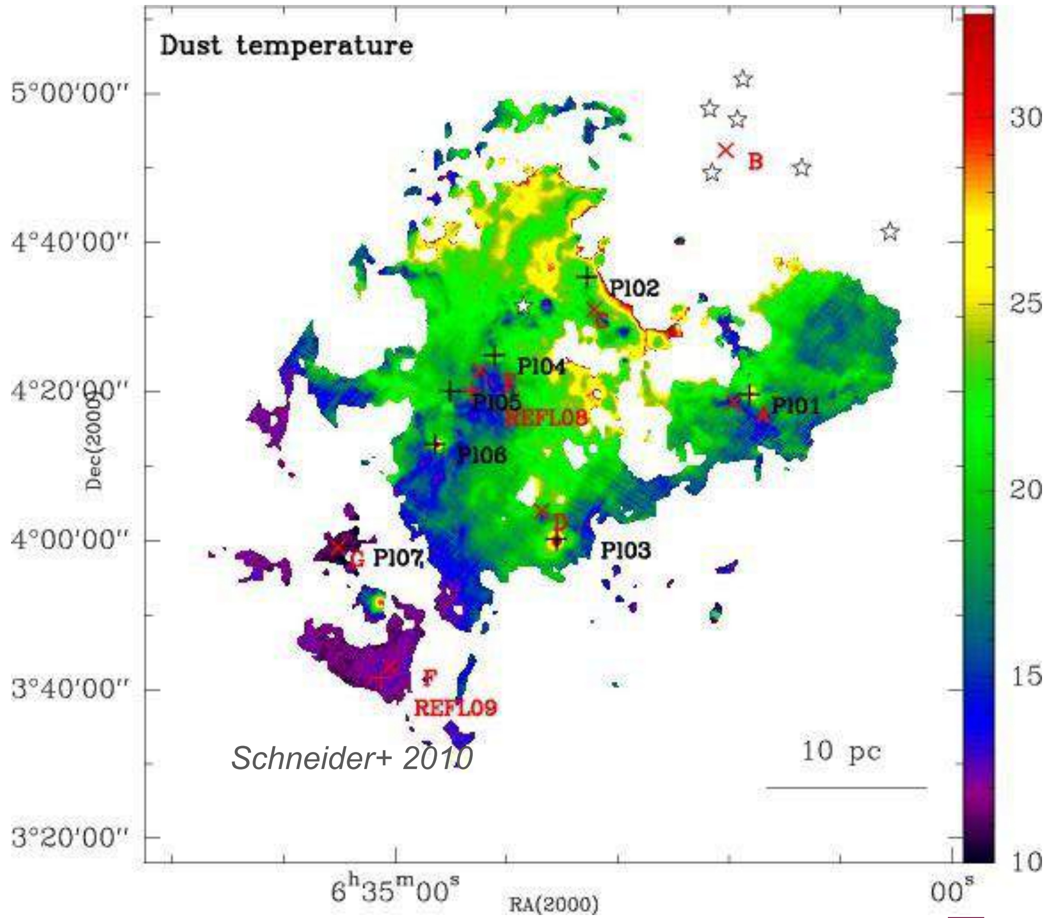
Dust temperature is set by radiative energy balance $\Gamma_{abs} = \Gamma_{em}$

Star-forming region, central star with Luminosity L and distance d.

Dust temperature

Dust temperature is set by radiative energy balance $\Gamma_{abs} = \Gamma_{em}$

Star-forming region, central star with Luminosity L and distance d.

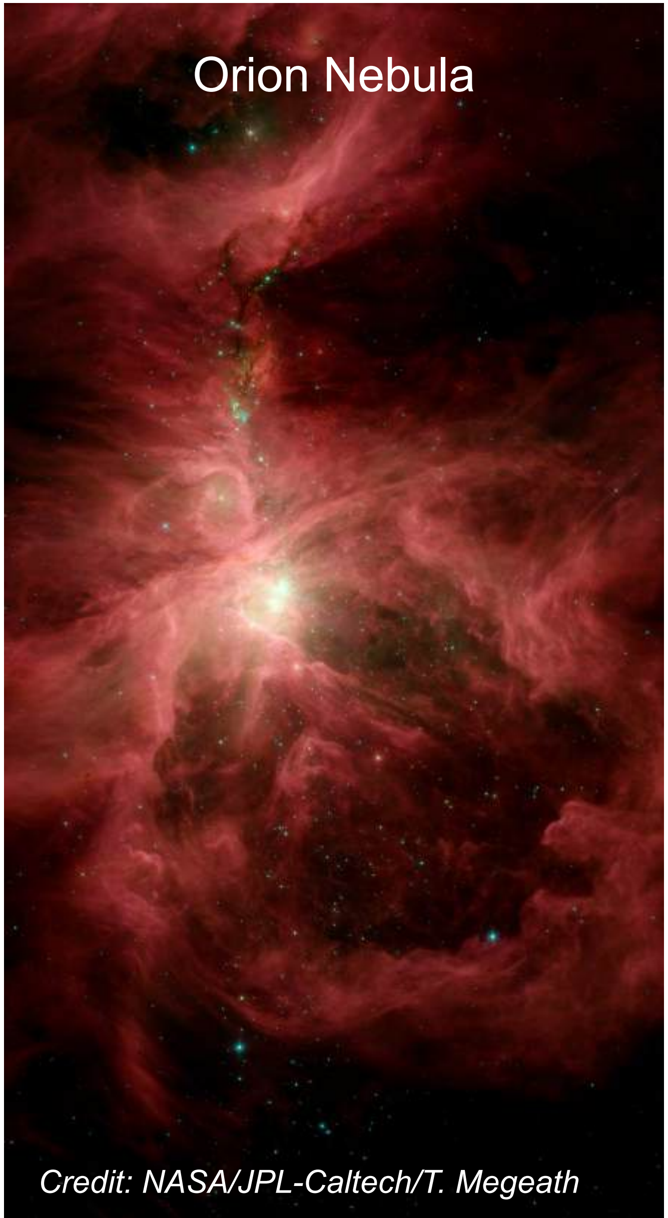


Schneider+ 2010

$T_d \sim (Q_{UV}/Q_{IR})^{1/4}[L/(16\ \pi\sigma d^2)]^{1/4}$

T_d depends on distance from star!

IR view of a star forming region

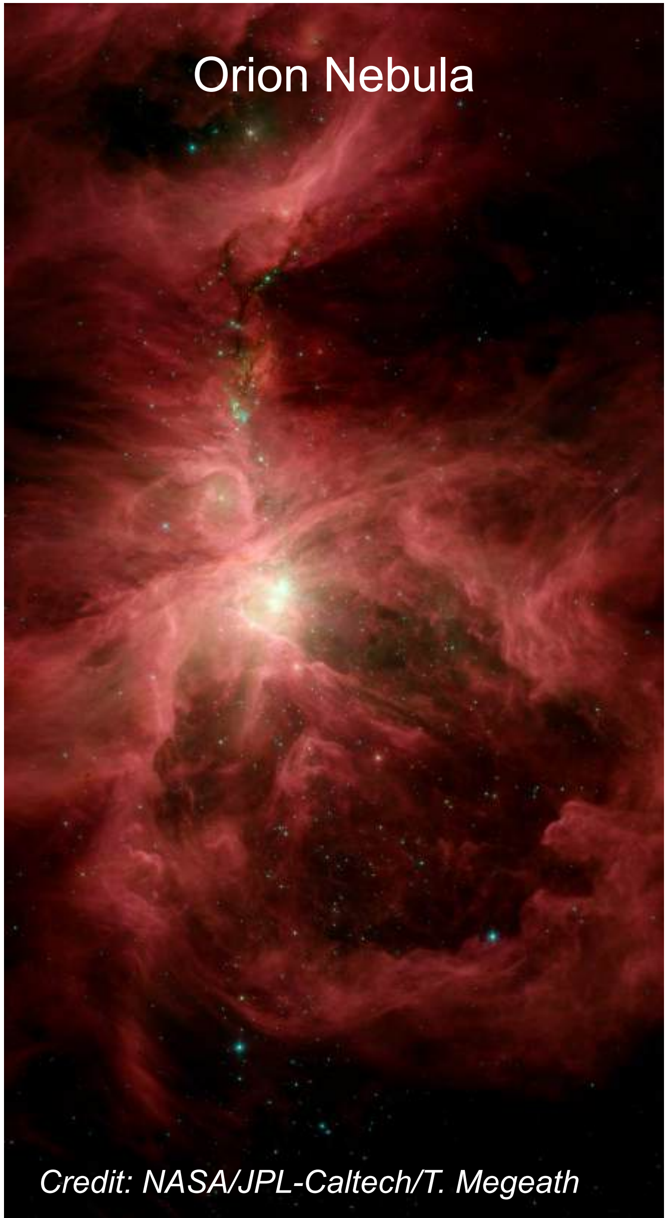


1980s IRAS => strong and extended emission in the mid infrared (12 μm)

↓

cannot be solid dust in radiative equilibrium. **Why?**

IR view of a star forming region



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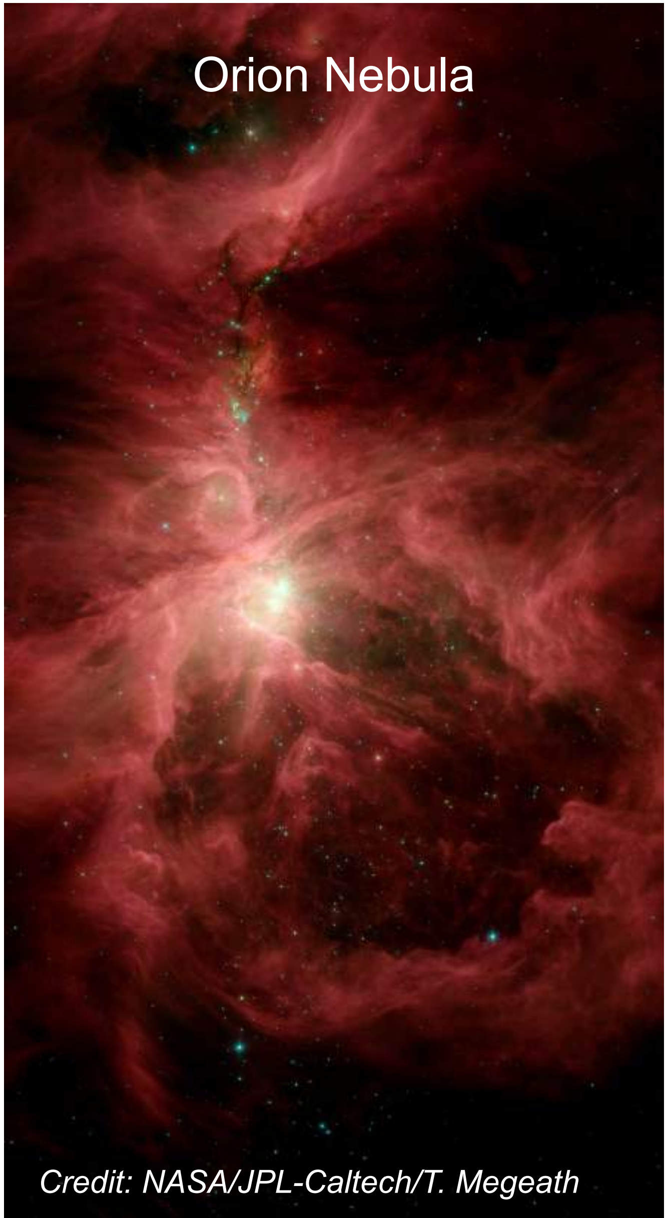
$$\lambda_{\rm peak} = \frac{b}{T}$$

T= 242 K for 12 μm

IR view of a star forming region



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TOO HOT, TOO FAR AWAY

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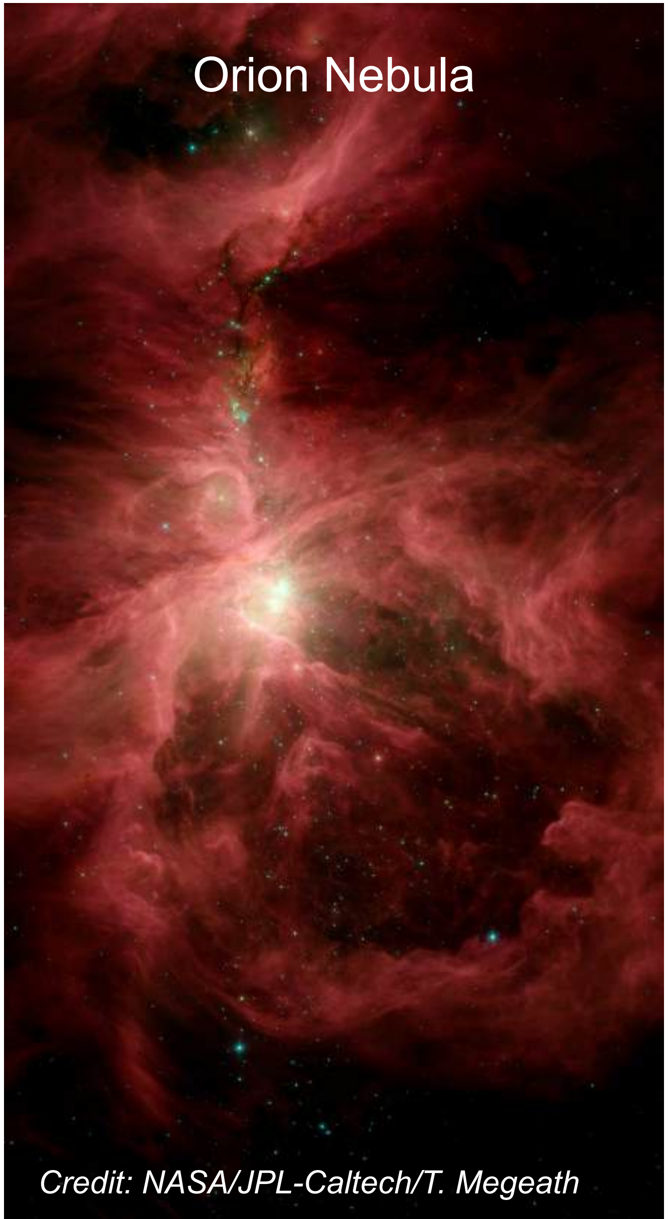

Credit: NASA/JPL-Caltech/T. Megeath

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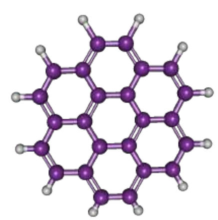
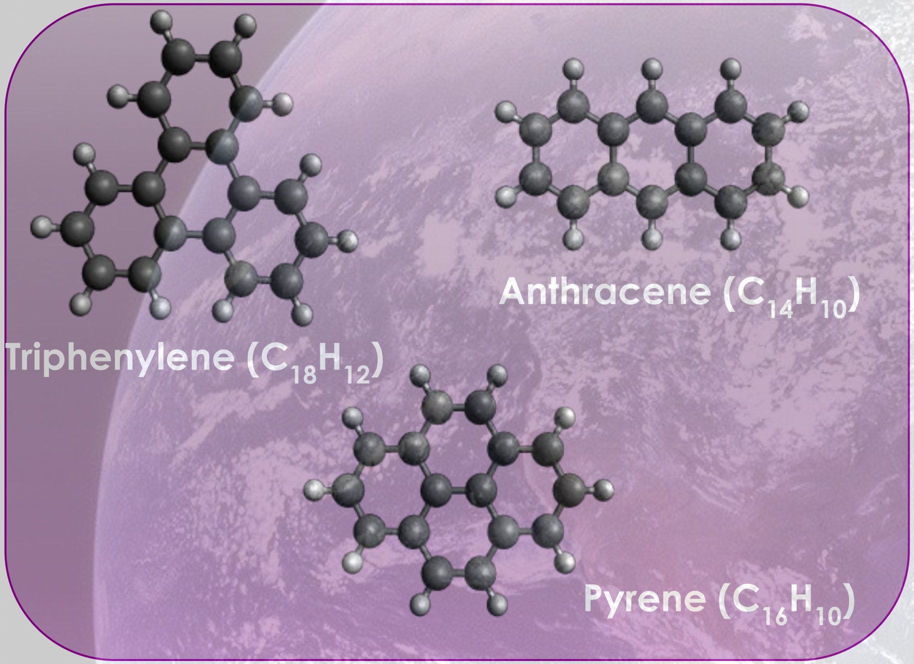
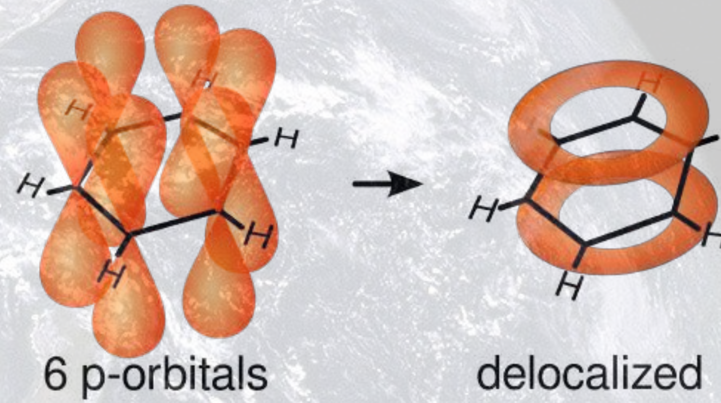


POLYCYCLIC
AROMATIC
HYDROCARBONS

Polycyclic Aromatic Hydrocarbons





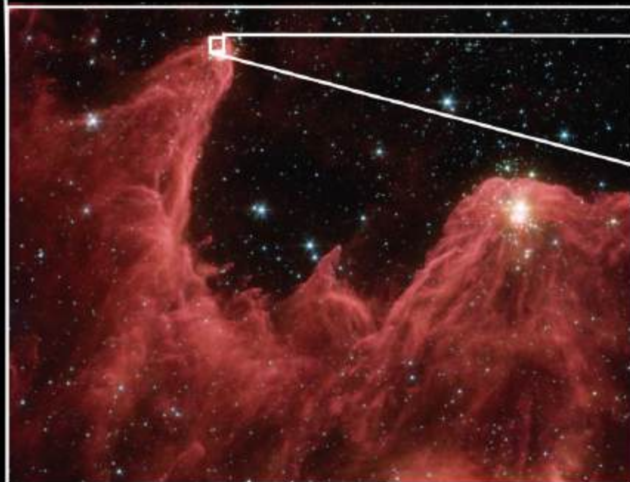
Aromaticity = e^- delocalization

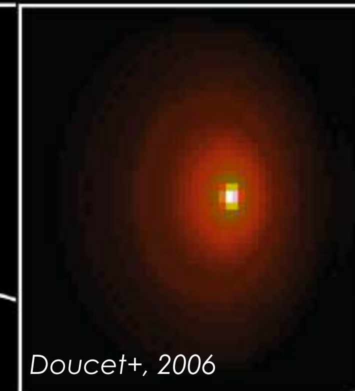
On Earth they are

1) the product of combustion chemistry (high T and density)
2) pollutant of water and of air
3) carcinogenic => they link to and deform DNA

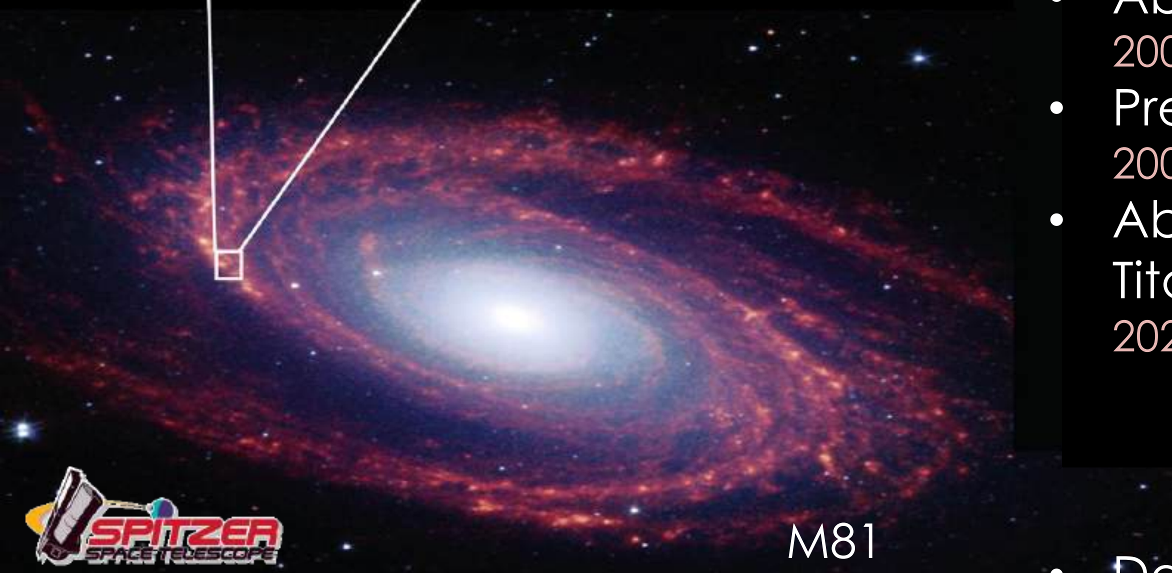
PAH emission is strong and ubiquitous!

Protoplanetary Disk





Star-forming Region

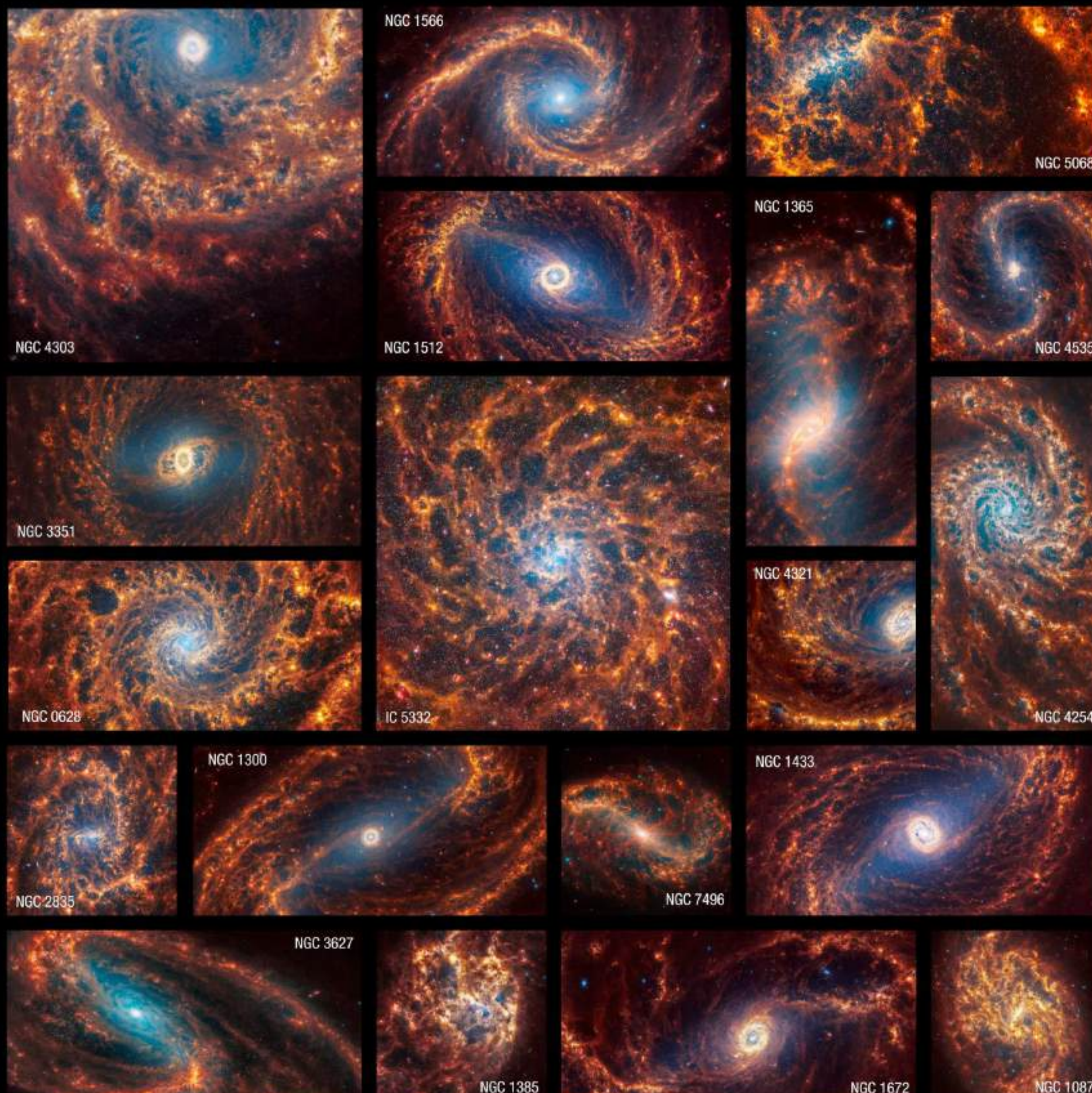


Up to ~20% of IR flux from a galaxy

- Abundant in meteorites (Sephton 2002; Sabbah+, 2017)
- Present in comets and IDPs (Li, 2008; Clemett+ 2010)
- Abundant in the atmosphere of Titan (Lopez-Puertas+, 2013; Cours+, 2020)

- Detected up to z ~ *4* (Riechers+, 2014; *Li, 2020)*

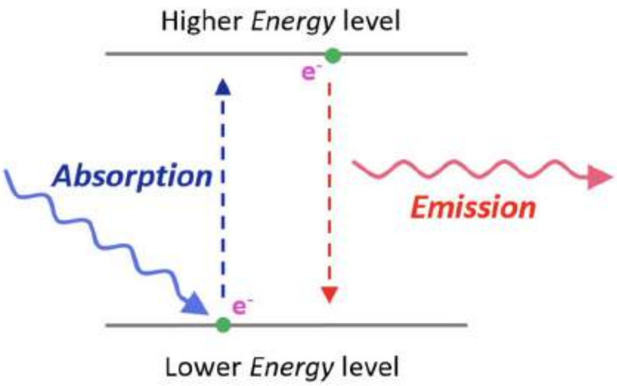
PAH emission seen by JWST



PHANGS collaboration 2024

PAH excitation mechanism

- For small molecules, electronic excitation and de-excitation happens at the same wavelength



PAH excitation mechanism

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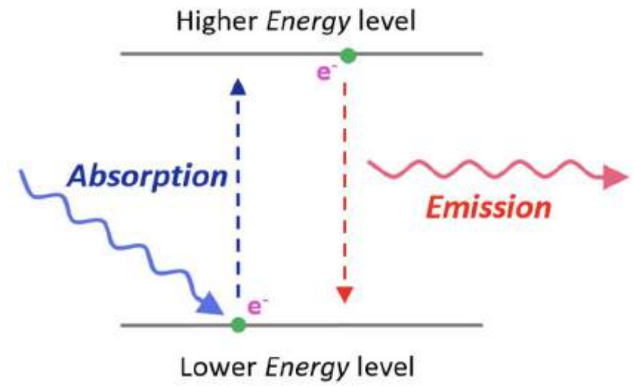
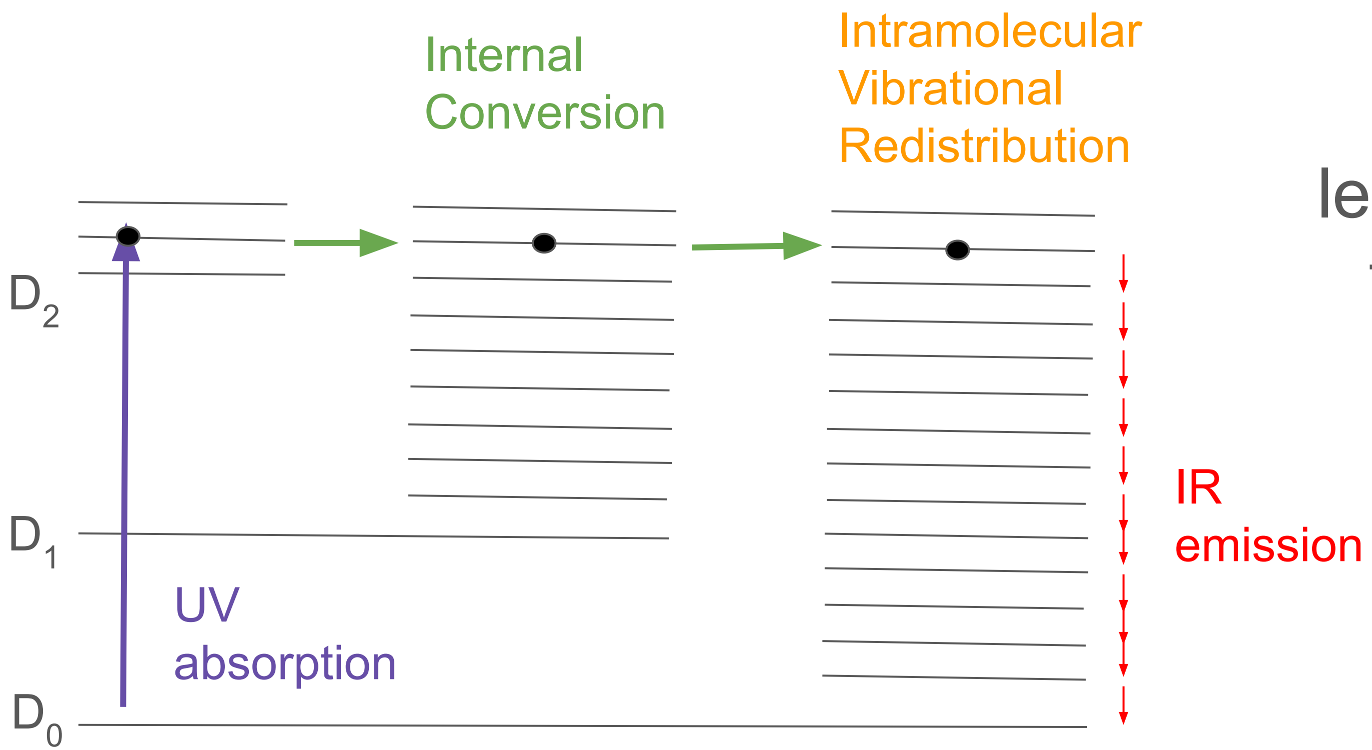


but PAHs behave differently!



UV photon absorption leads to infrared fluorescence

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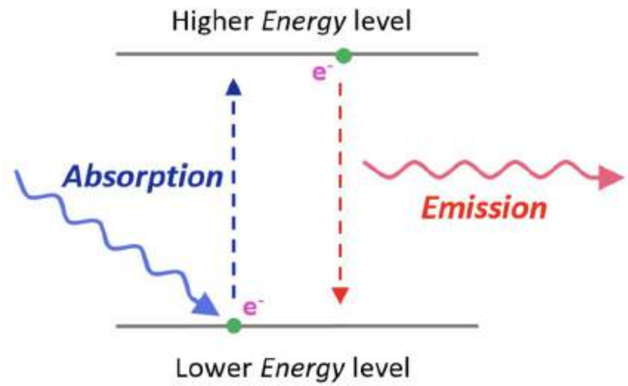

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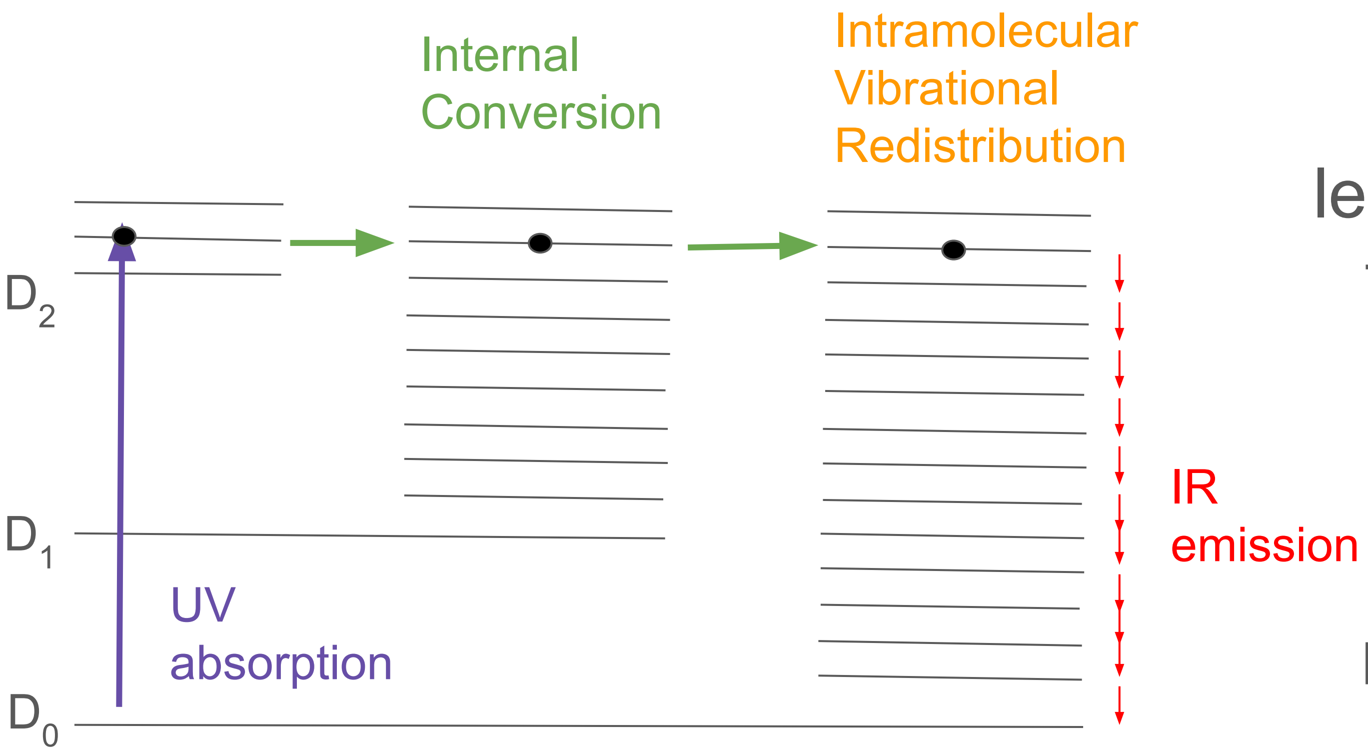
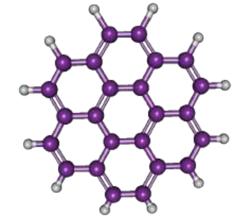
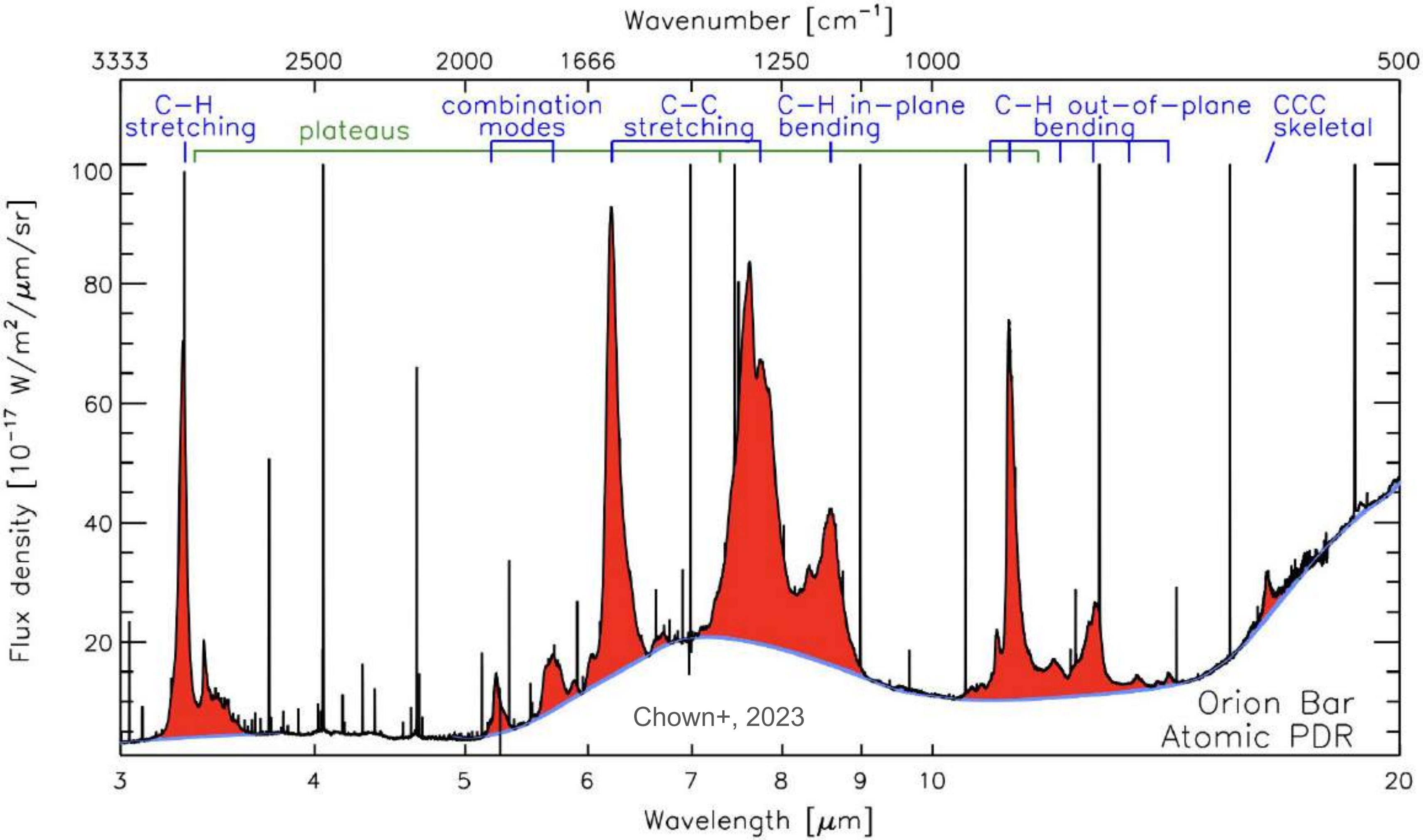


UV photon absorption leads to infrared fluorescence

PAHs "cool" down vibrating

PAH vibrations





Vibrations cannot lead to identification of specific molecules

Allamandola et al, 1989
Leger & Puget, 2989

PAH excitation: timescales

- **Timescale for PAH emission**

10^{-12} s (IC)+ 10^{-12} s (IVR)+ 1s (IR emission) ~ 1s

PAH excitation: timescales

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- **Timescale for UV absorption of PAHs** (Tielens, 2005)

$$\tau_{\rm UV} = k_{\rm UV}^{-1} = (4\pi\sigma_{\rm UV}(\rm PAH)\mathcal{N}_{\rm UV})^{-1} \simeq \frac{1.4\times10^9}{N_{\rm c} G_0}\,{\rm s},$$

Exercise (in pairs)

A. Considering a standard size PAH (N_c=50), calculate how often a PAH absorbs a UV photon
   a. in the diffuse ISM (G_0=1)
   b. in a photo-dominated region ($G_0=10^4$)

B. Describe how the internal energy of PAHs changes with time

PAH excitation: timescales

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10^{-12} s (IC)+ 10^{-12} s (IVR)+ 1s (IR emission) ~ 1s

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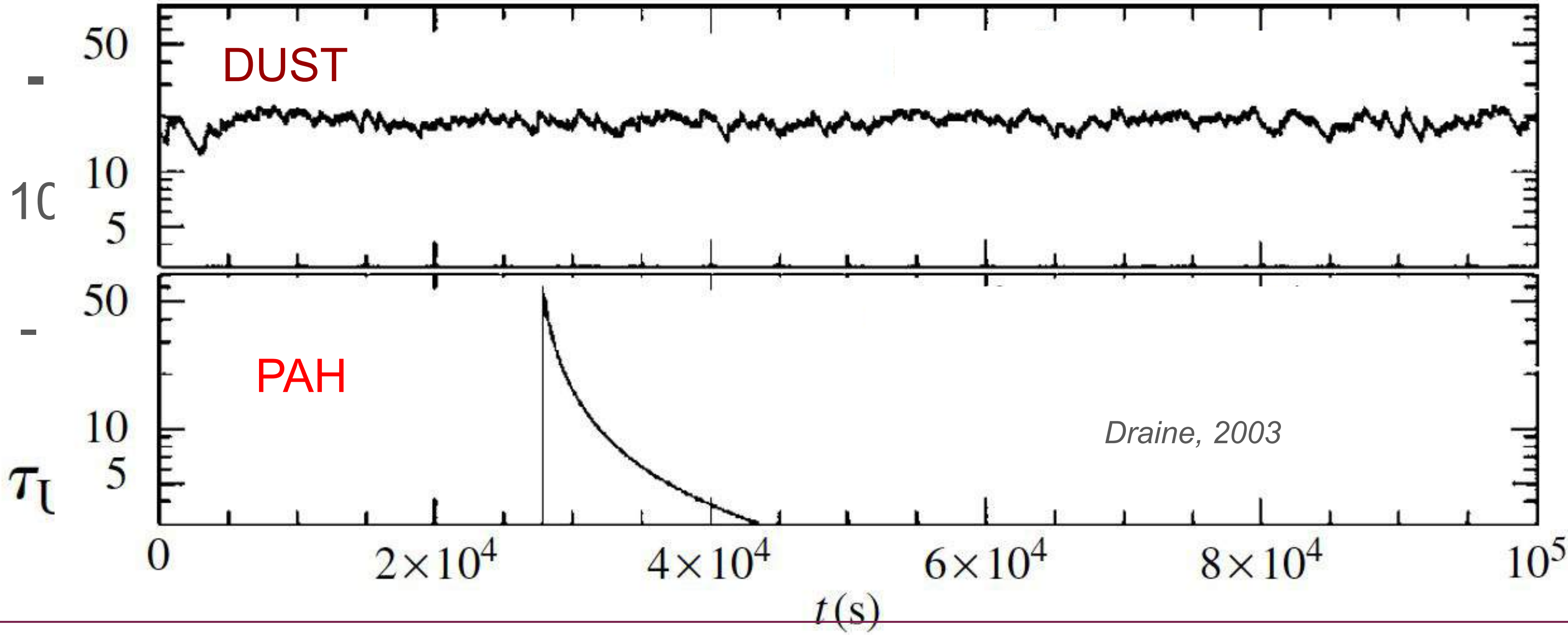

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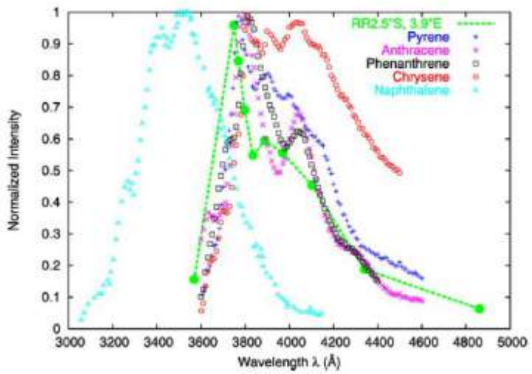
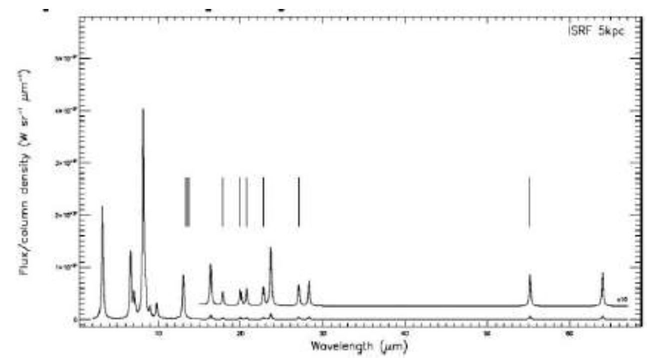
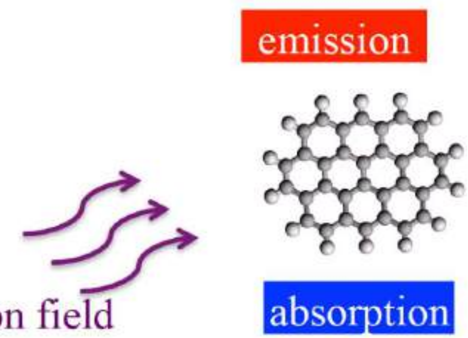
PAH photophysics: a unified vision



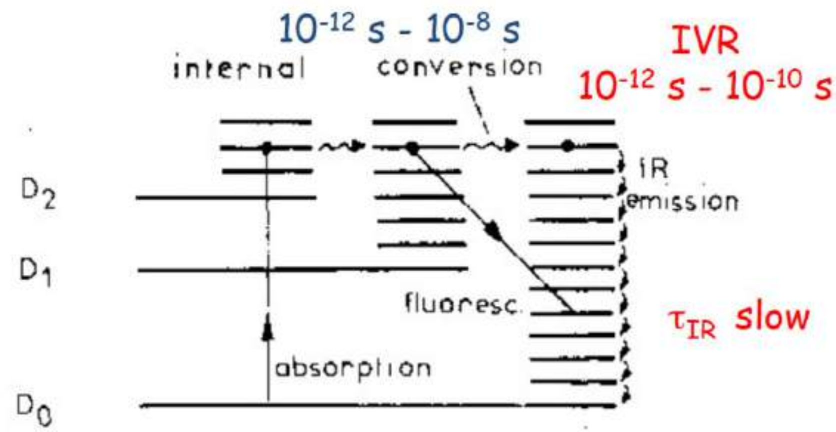
Fluorescence



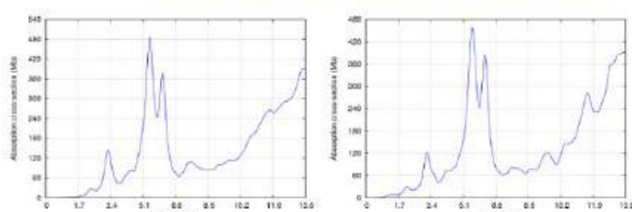
Vibrational emission



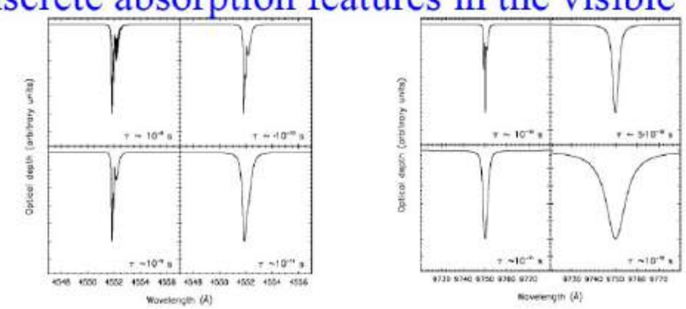
UV radiation field



Broad absorption in the UV

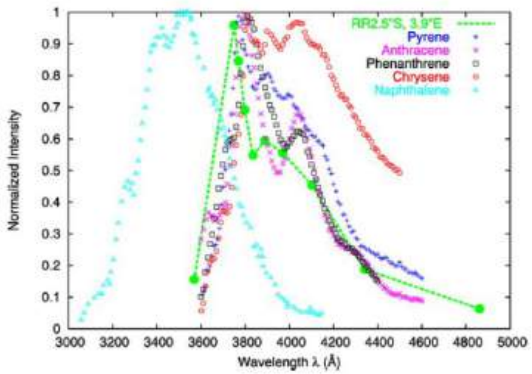


Discrete absorption features in the visible

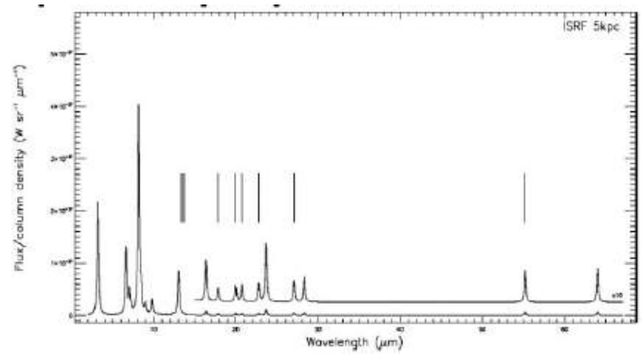


Courtesy of C. Joblin

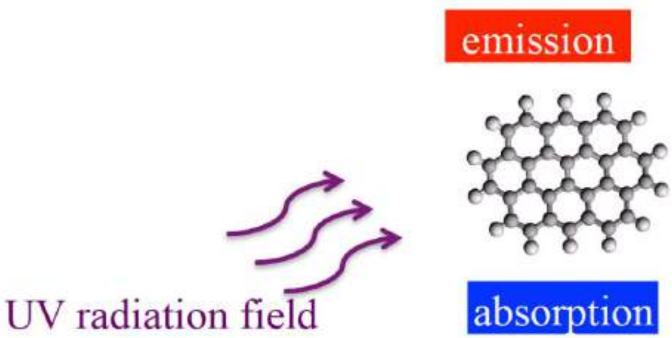
PAH photophysics: a unified vision

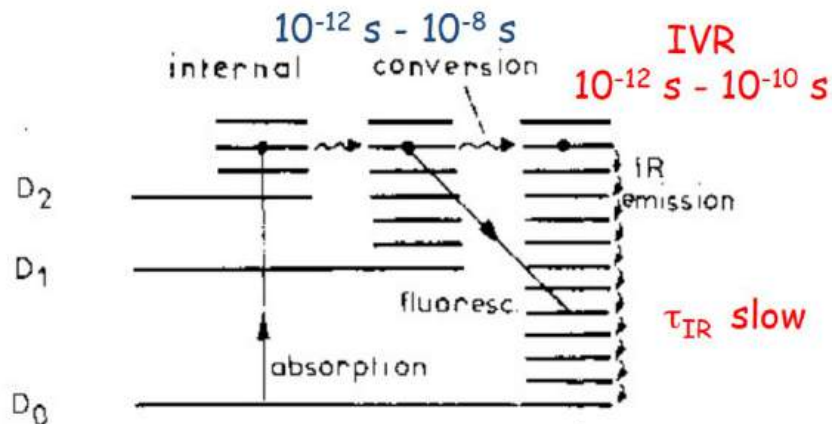


Fluorescence

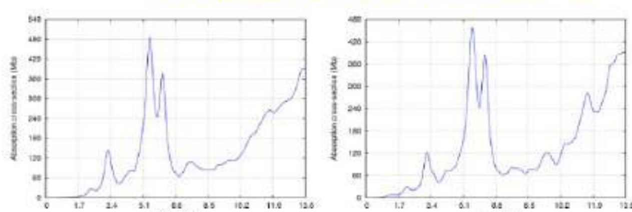


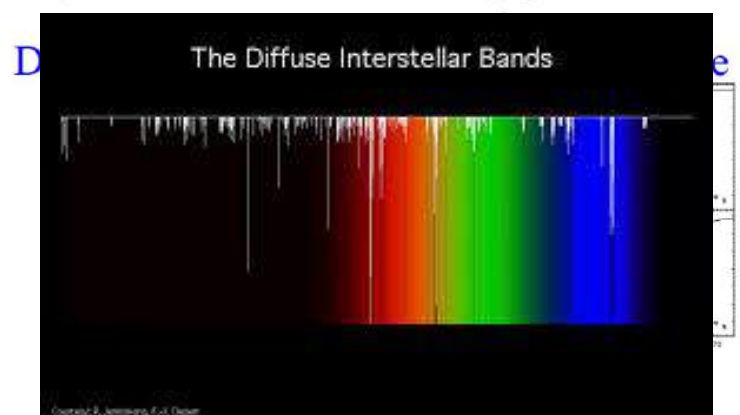
Vibrational emission





Broad absorption in the UV





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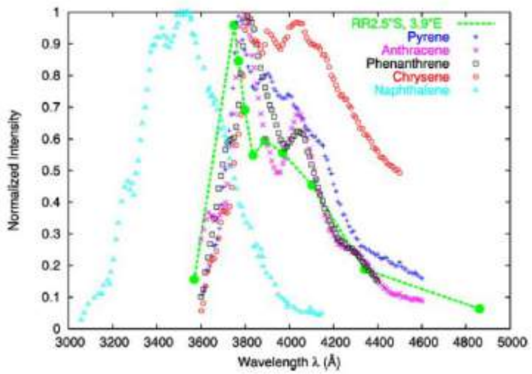
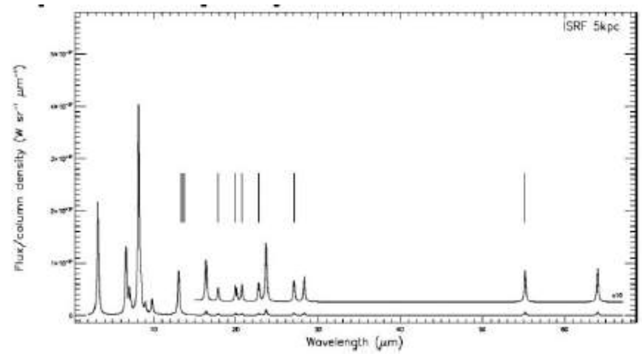
PAH photophysics: a unified vision

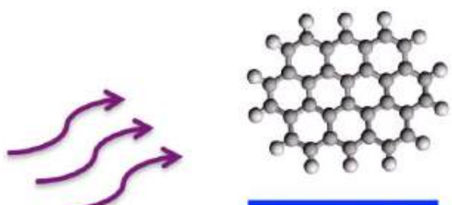


Fluorescence



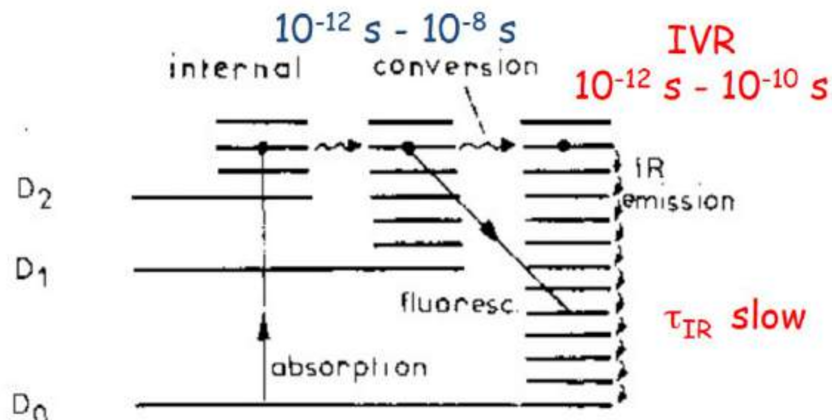
Vibrational emission

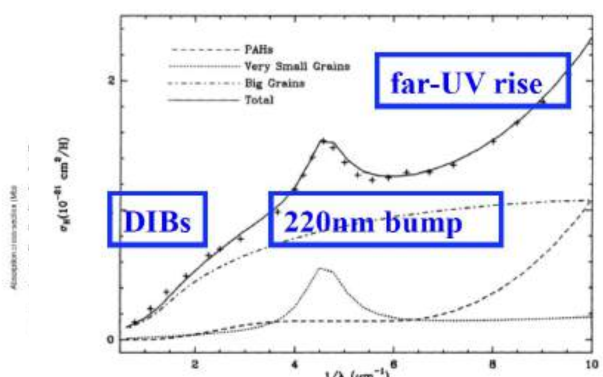
emission

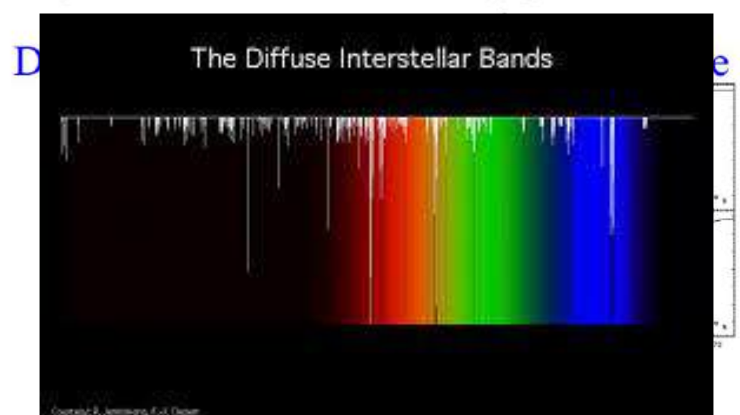


UV radiation field

absorption

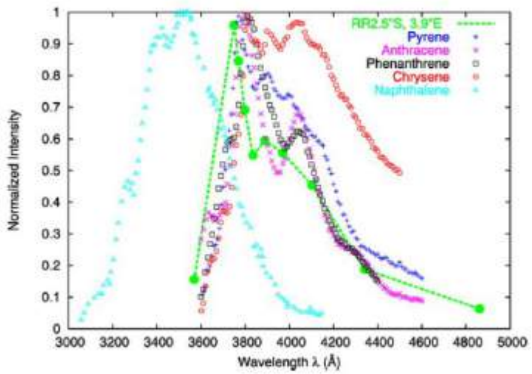




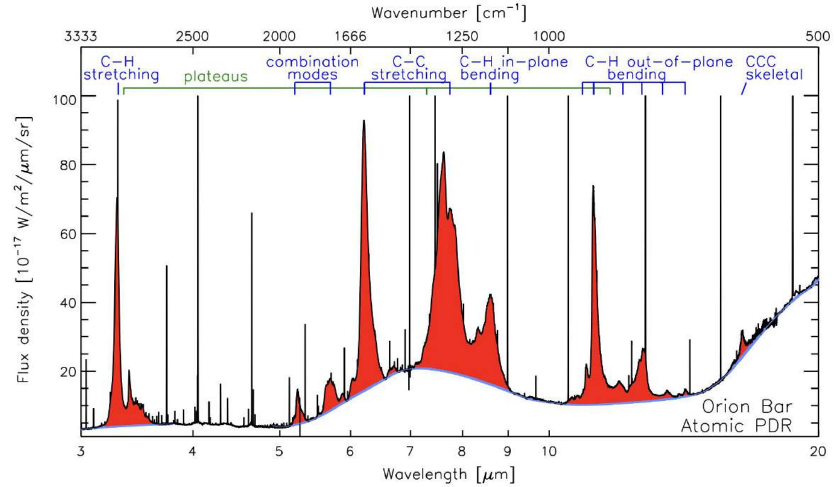


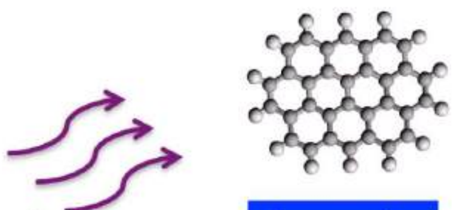
Courtesy of C. Joblin

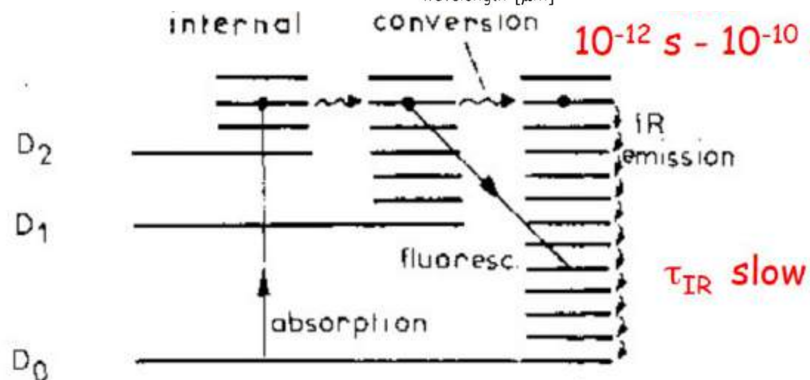
PAH photophysics: a unified vision

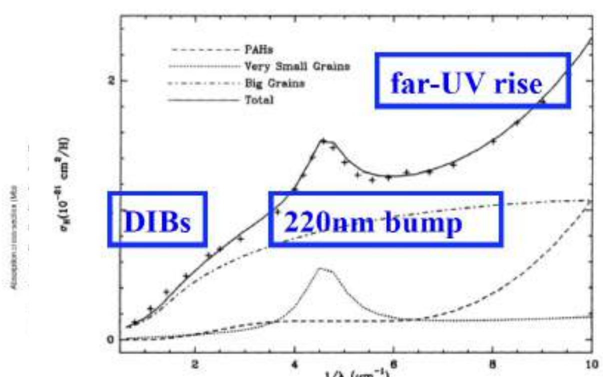


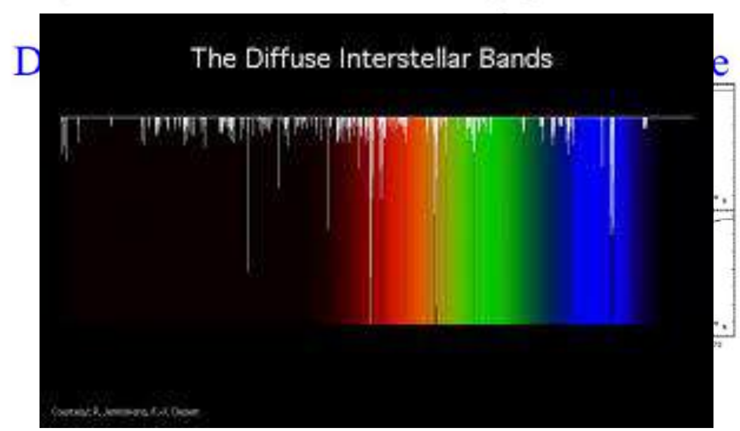
Fluorescence









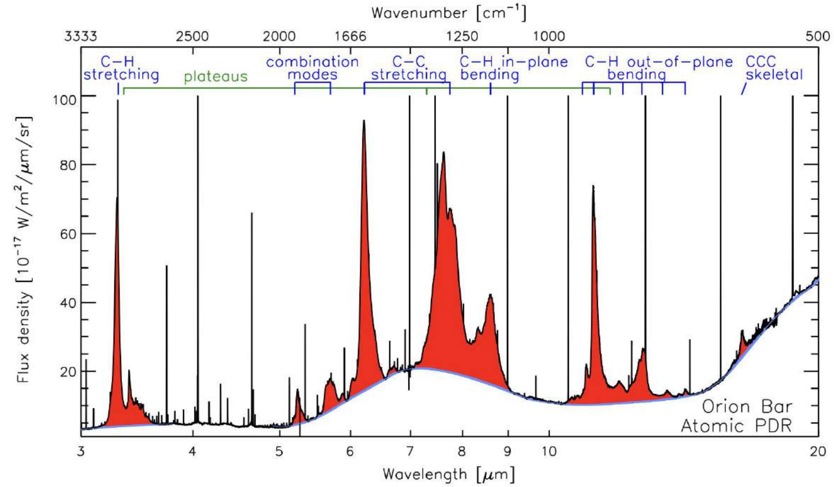


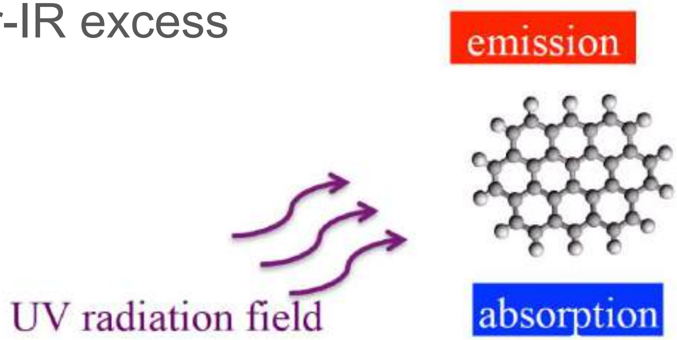
Courtesy of C. Joblin

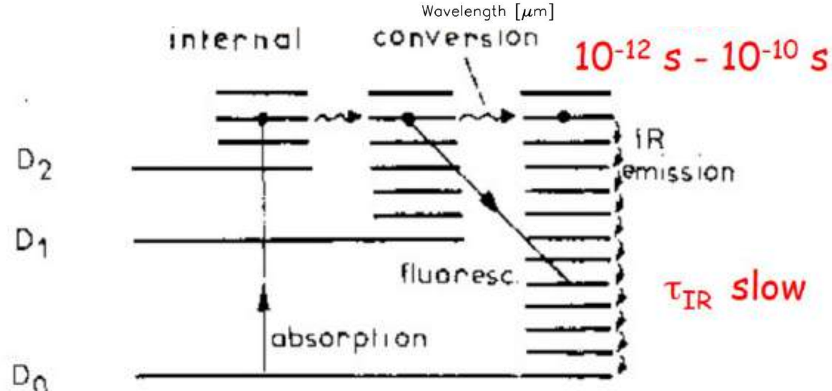
PAH photophysics: a unified vision

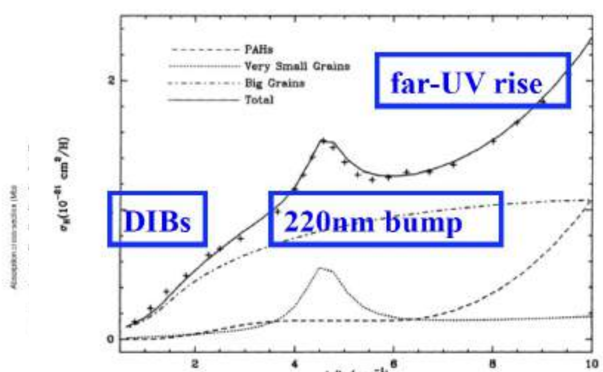
Fluorescence

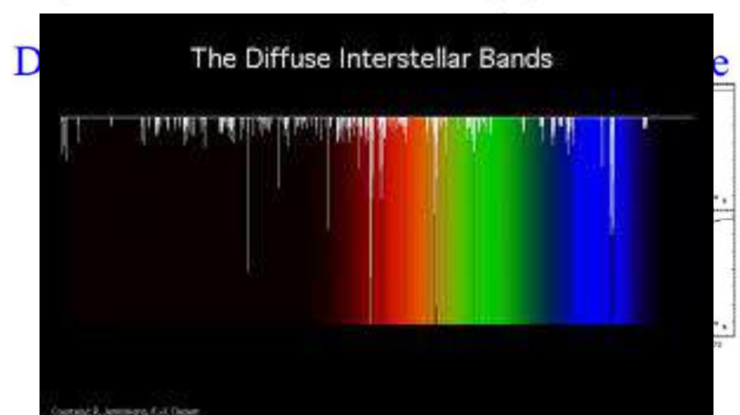
near-IR excess











Courtesy of

PAH emission process*

After absorption of a UV photon

heat capacity for harmonic oscillators

$$h\nu_{\rm UV} = \int_{T_0}^{T_1} C_V(T)\,{\rm d}T, \quad \text{where} \quad C_V = k\sum_{i=1}^{s}\left(\frac{h\nu_i}{kT}\right)^2 \frac{\exp[h\nu_i/kT]}{(\exp[h\nu_i/kT]-1)^2},$$

*thermal approximation (Leger+, 1989; Schutte+, 1993)

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The emission in the vibrational mode (i) can be expressed as

$$k^i_{\mathrm{IR},v} = v \times A_i^{1,0} \times \exp(-vh\nu_i/kT) \times (1 - \exp(-h\nu_i/kT))$$

Einstein coefficient

*thermal approximation (Leger+, 1989; Schutte+, 1993)

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$$k^i_{\rm IR} = \sum_v k^i_{{\rm IR},v} = A_i^{1,0} \times [\exp(h\nu_i/kT) - 1]^{-1}$$

Total IR emission in the mode *i*

*thermal approximation (Leger+, 1989; Schutte+, 1993)

PAH emission process*

After absorption of a UV photon

heat capacity for harmonic oscillators

vibrational frequencies

$$h\nu_{\mathrm{UV}} = \int_{T_0}^{T_1} C_V(T)\,\mathrm{d}T, \quad \text{where} \quad C_V = k\sum_{i=1}^{s}\left(\frac{h\nu_i}{kT}\right)^2 \frac{\exp[h\nu_i/kT]}{(\exp[h\nu_i/kT]-1)^2},$$

We need frequency (cm^{-1}) and intensities of the vibrational modes for PAH molecules => Computational Chemistry

PAH IR Spectral Database

Ames Research Center

Theoretical spectral database of:

Polycyclic Aromatic Hydrocarbons

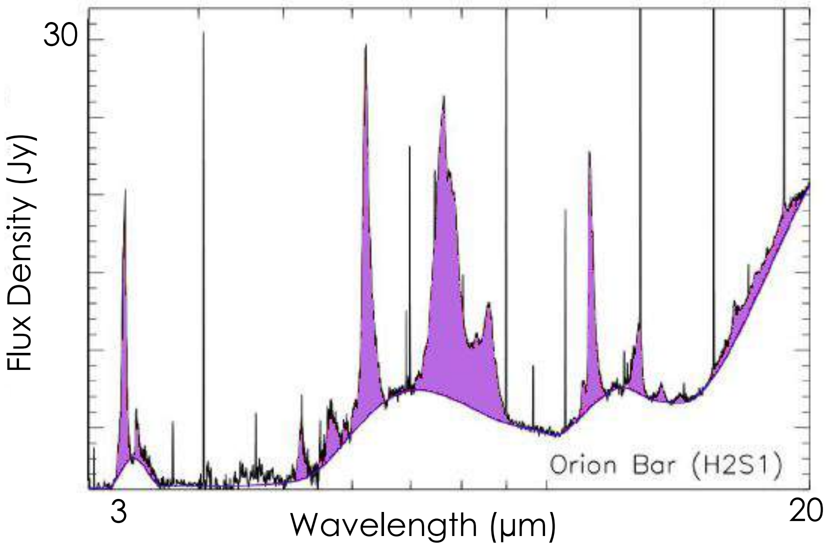
Cagliari - Toulouse Database

$$k_{\mathrm{IR}}^i = \sum_v k_{\mathrm{IR},v}^i = A_i^{1,0} \times [\exp(h\nu_i/kT) - 1]^{-1}$$

Total IR emission in the mode *i*

*thermal approximation (Leger+, 1989; Schutte+, 1993)

A population of AstroPAH



See Tielens, 2008

Quantum Chemistry ↔ Experiments

Quantum Chemistry ↔ Observations

Experiments ↔ Observations

Charge
++/+/0/
-?

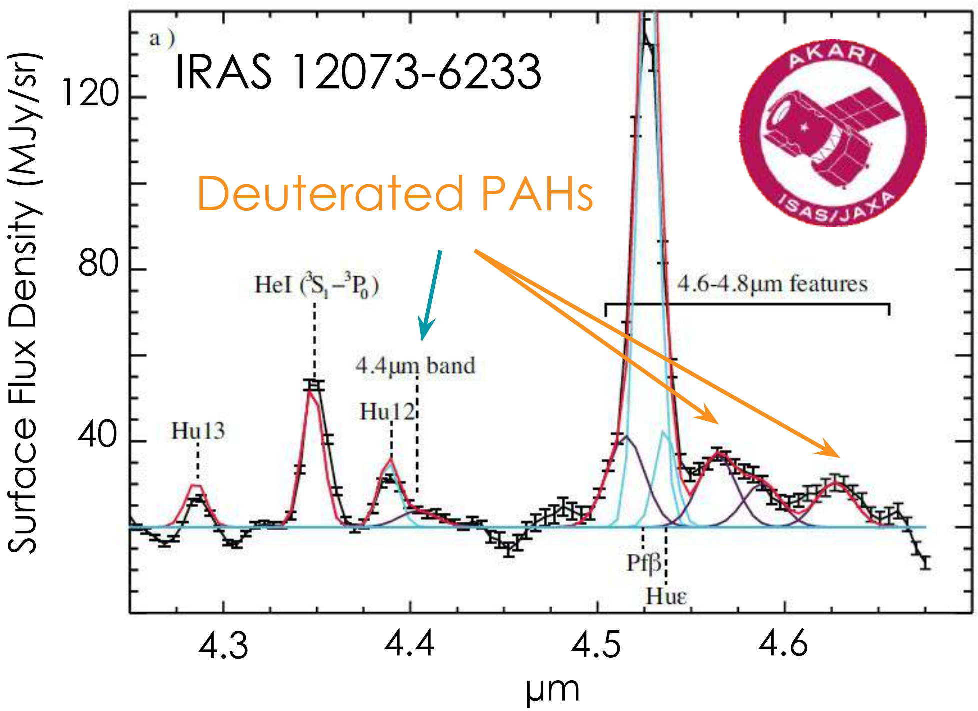
Size
Nc>40

Members

Subst.
N,O,Si,D

Funct. Groups
$-CH_3$
-OH

A population of AstroPAH

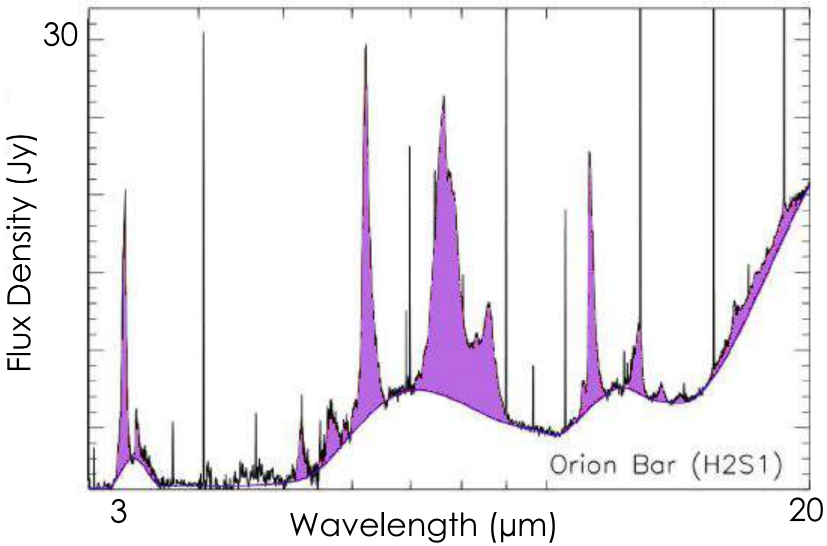


Large fluctuation of D in the ISM
Incorporated in PAHs?

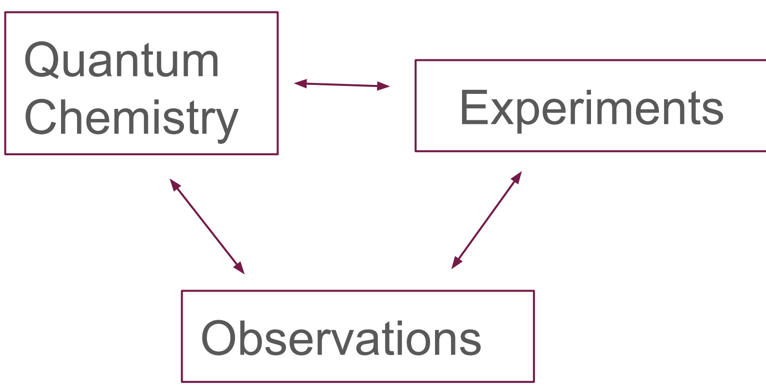
(Yang+, 2020; Wiersma, 2021; Boersma + 2023)

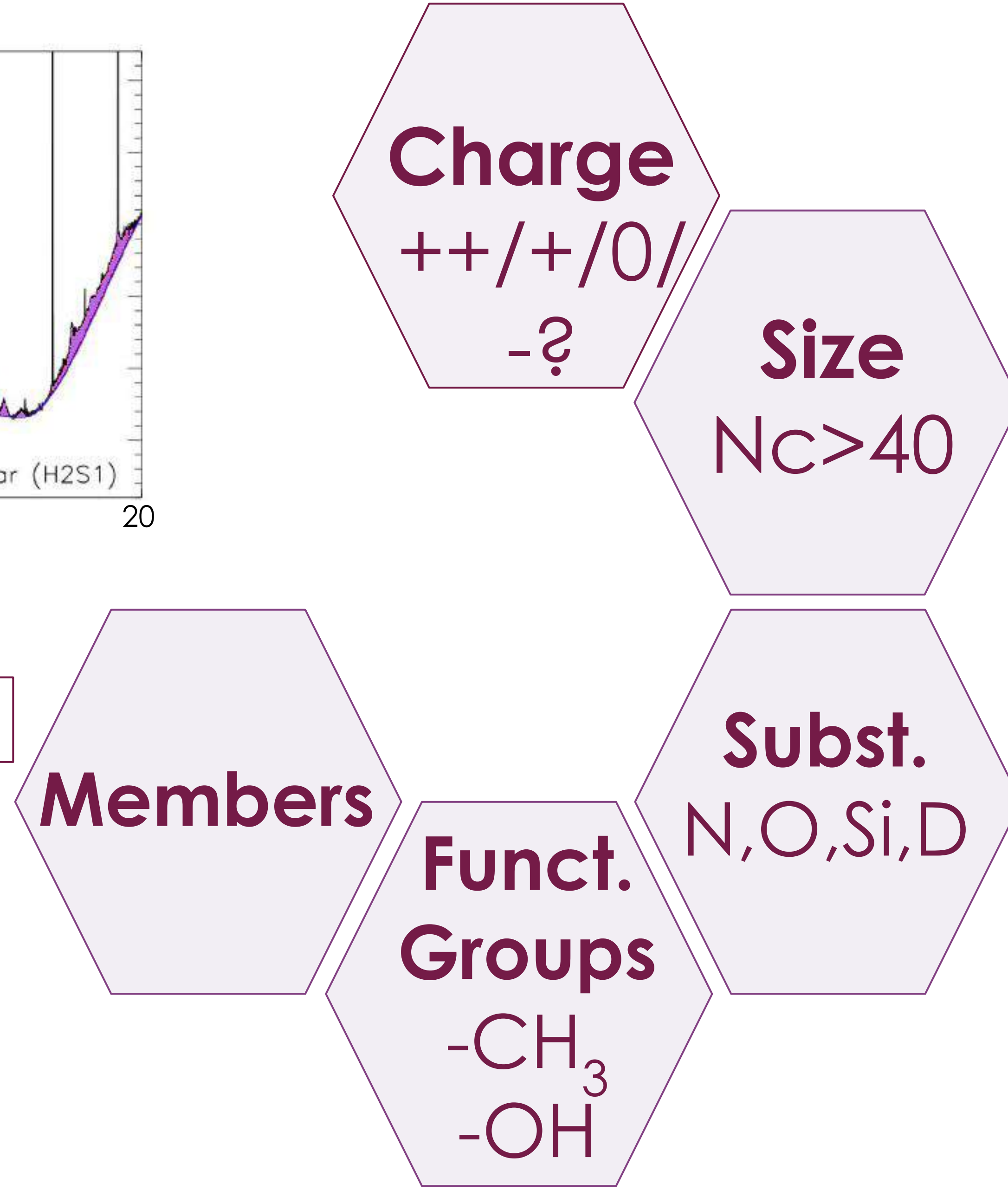
Subst.
N,O,Si,D

A population of AstroPAH

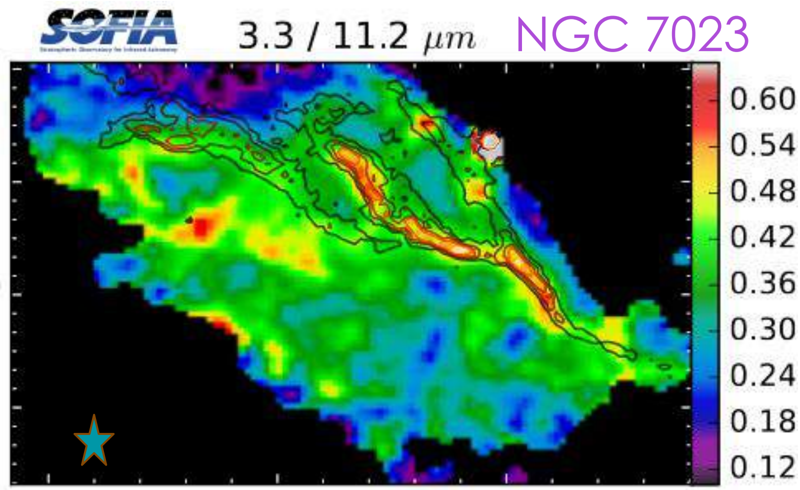


See Tielens, 2008





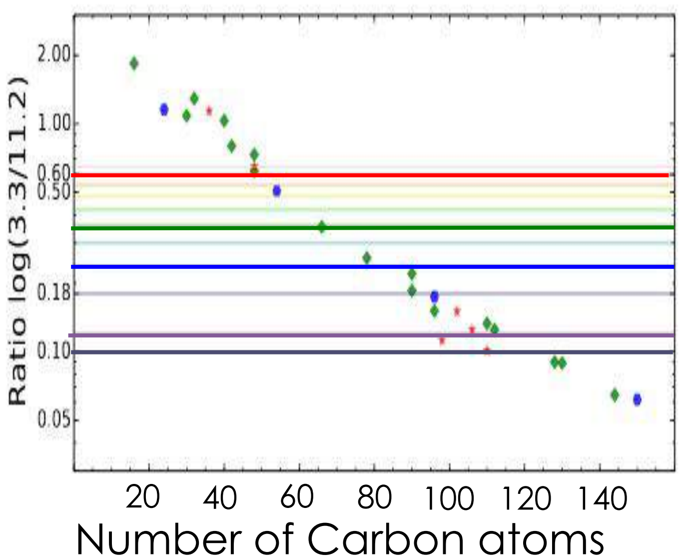
A population of AstroPAH



3.3/11.2 band ratio as **proxy** for **size** of emitting PAHs

Ricca+ 2012; Maragkoudakis+, 2020
Lemmens+, 2024

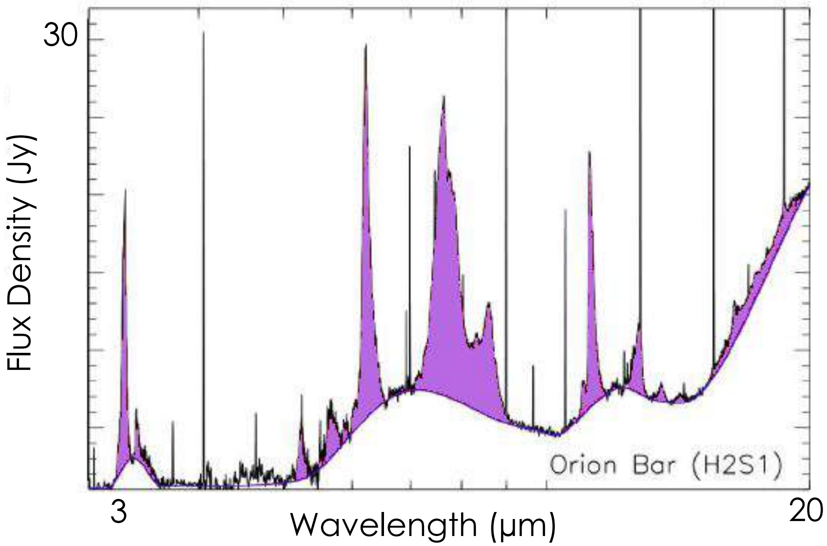
Size
Nc>40



Croiset+, 2016

First determination of the size distribution of PAHs across an object [50-120] Nc

A population of AstroPAH



See Tielens, 2008

Quantum Chemistry

Experiments

Observations

Charge
++/+/0/-?

Size
Nc>40

Members

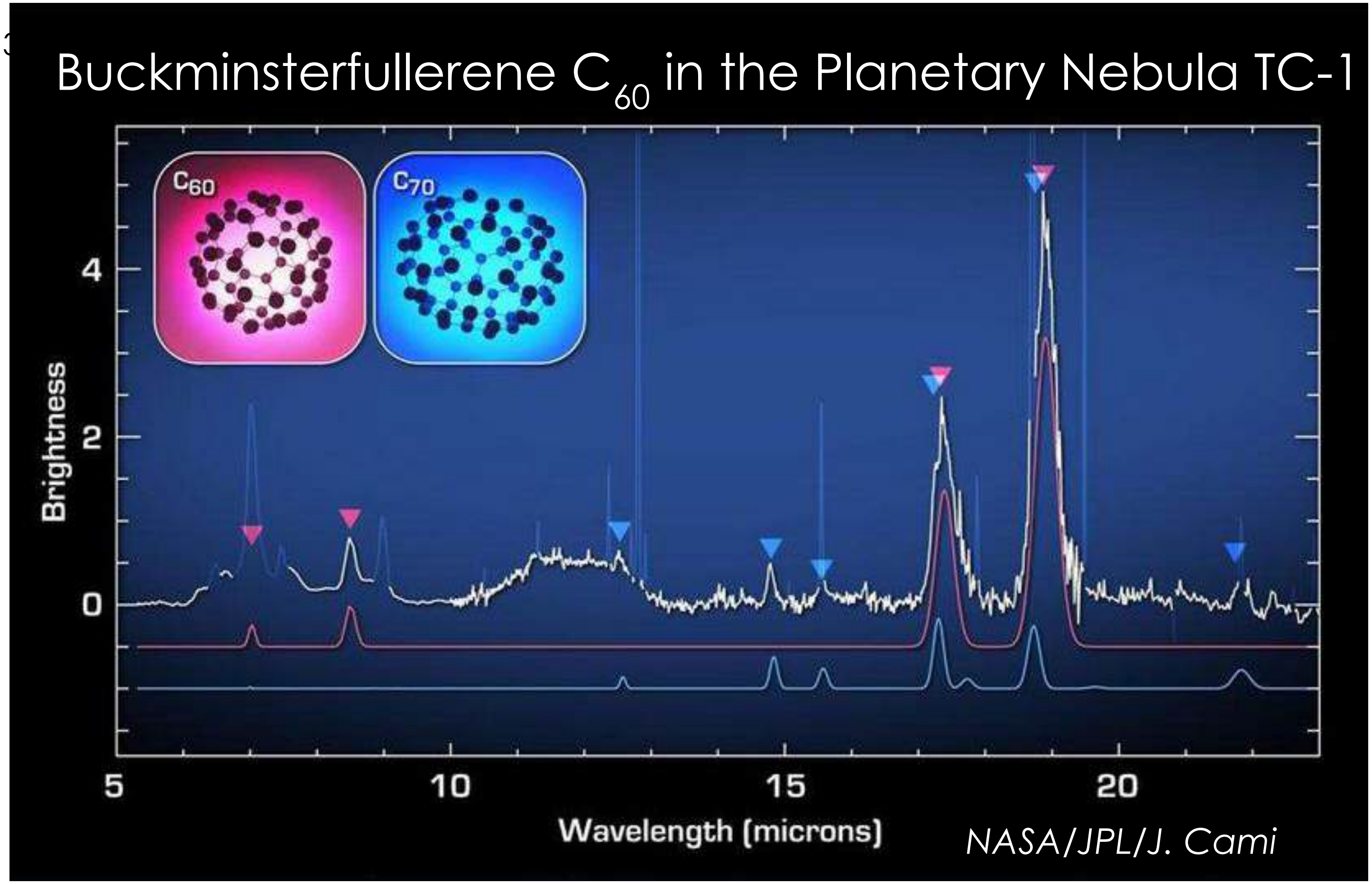
Subst.
N,O,Si,D

Funct. Groups
$-CH_3$
-OH

A population of AstroPAH

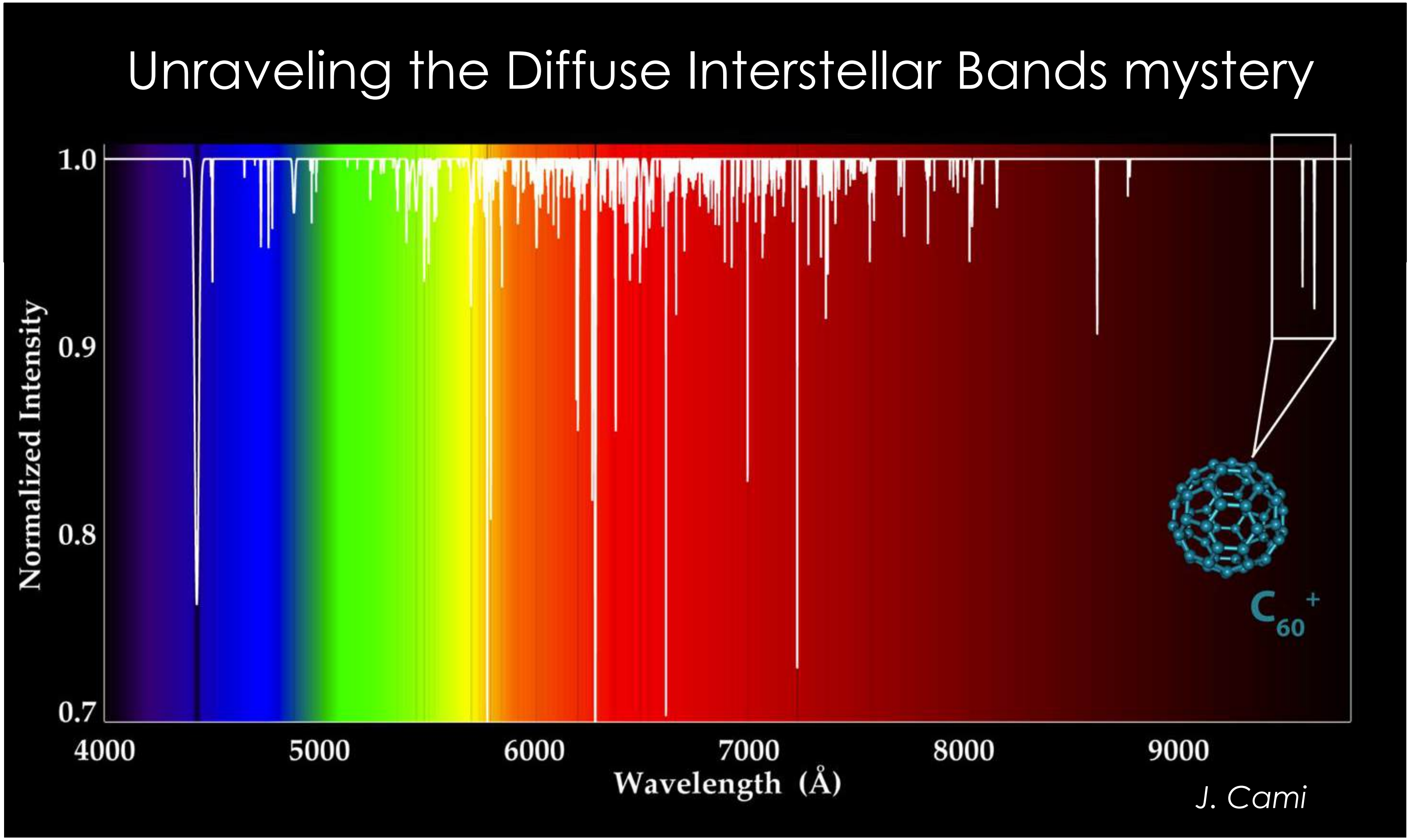
Members

A population of large Organics



Also detected in other planetary nebulae, in reflection nebulae, a young stellar object and the diffuse ISM. *(Sellgren+, 2007, 2010; Otsuka+, 2013; Roberts+, 2012; Rubin+, 2011)*

A population of large Organics

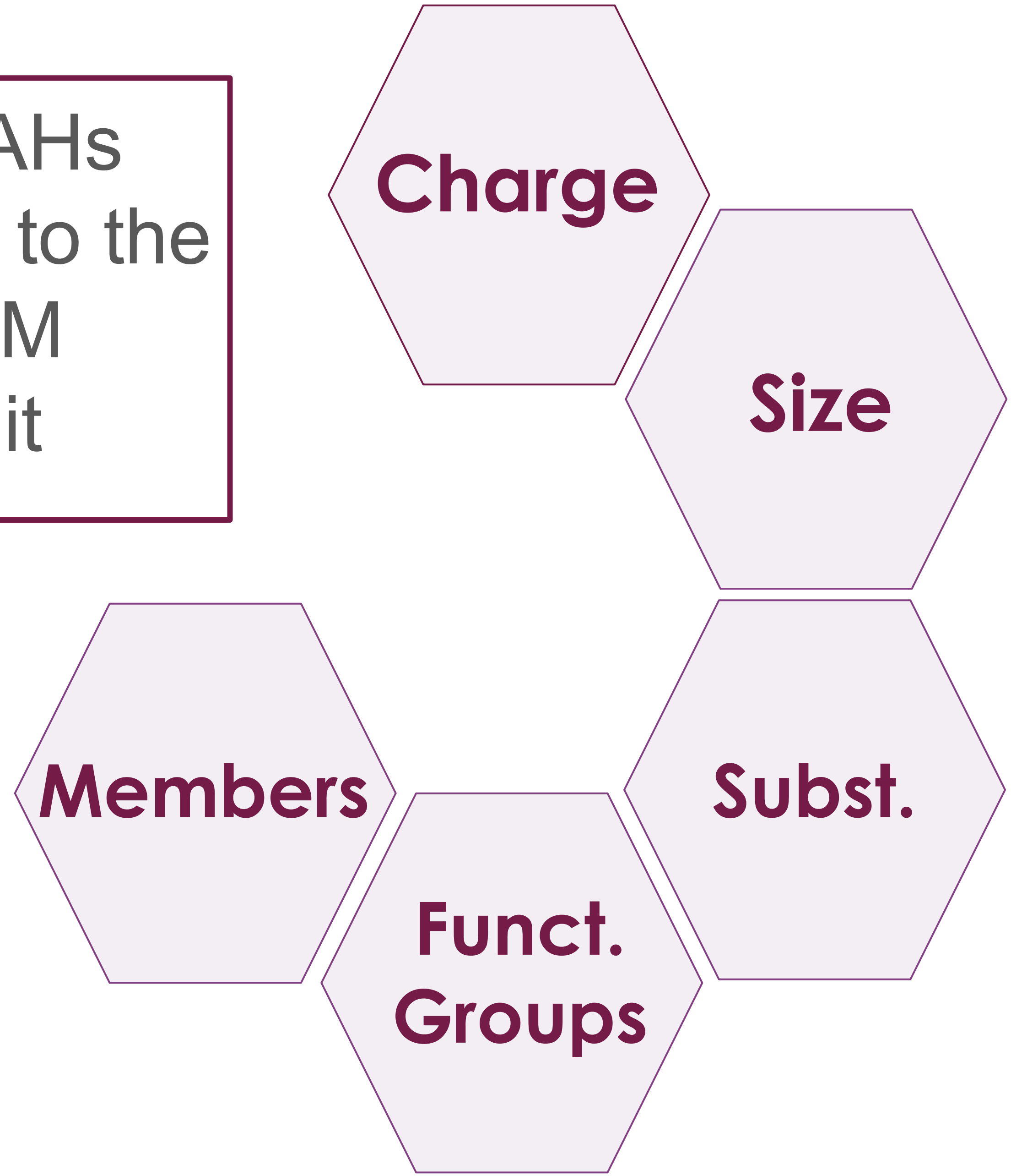


Campbell +, 2015
Cordiner+, 2019
Linnartz+, 2020

Also, C_{60}^{+} IR detection in the diffuse ISM
(Berné+,2017)

A population of large Organics

This means that PAHs actively participate to the chemistry of the ISM and are altered by it



PAH Charge Balance

PAH Charge in the ISM

Ionisation potential

$$IP(Z) \simeq 4.4 + \left(Z + \frac{1}{2}\right) \frac{25.1}{N_c^{1/2}} \text{ eV}$$

For a PAH with N_c=50 in diffuse ISM (E<13.6 eV): +3, +2, +1, 0, -1

PAH Charge in the ISM

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For a PAH with N_c=50 in diffuse ISM (E<13.6 eV): +3, +2, +1, 0, -1

The PAH charge is set by the balance between photo-ionisation and e^- recombination rates

$$f(Z) = \frac{k_e(Z+1)}{k_{\text{ion}}(Z)} f(Z+1)$$

PAH Charge in the ISM

Ionisation potential

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Photoionisation:

$$k_{\rm ion}(Z) = \pi W \int_{\nu_Z}^{\nu_H} Y_{\rm ion}(Z,\nu)\sigma_{\rm abs}(Z,\nu)\frac{B_\nu(T_{\rm eff})}{h\nu}\mathrm{d}\nu \qquad (\mathrm{s}^{-1})$$

Astro

Molecule

PAH Charge in the ISM

Ionisation potential

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Astro

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Molecule

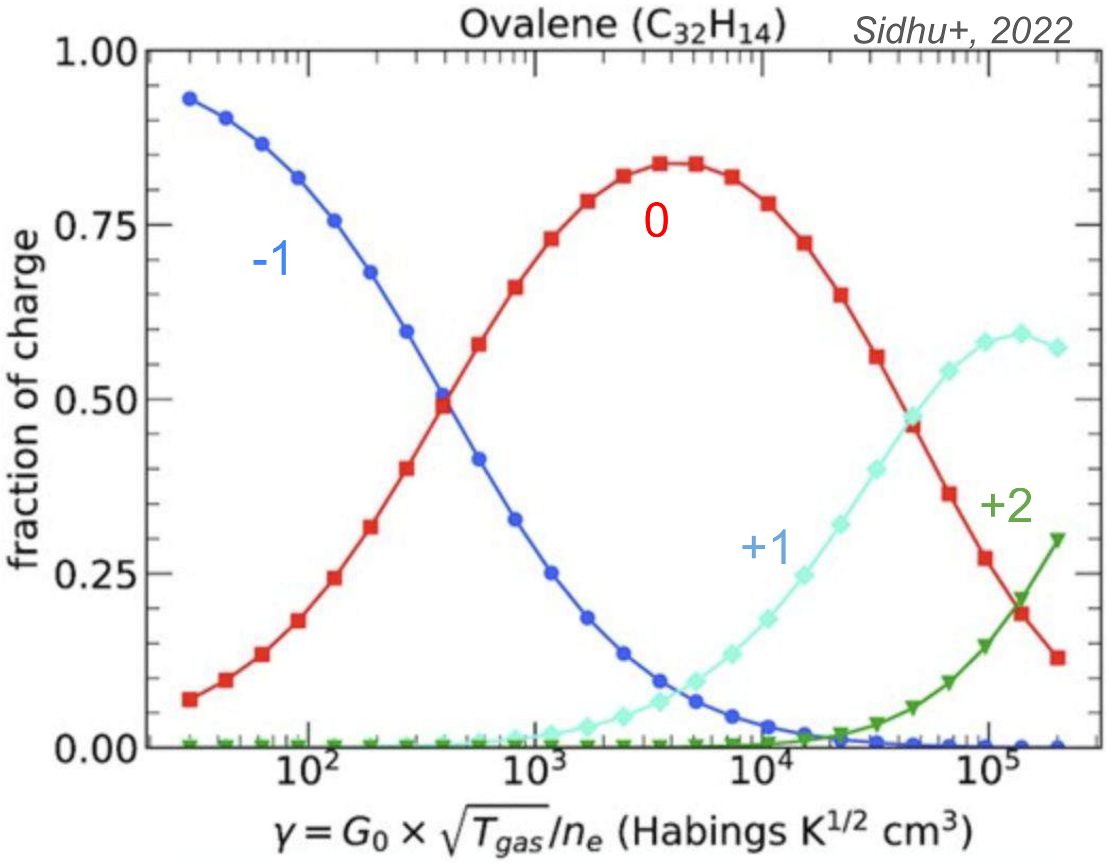
Electron recombination:

$$k_e(Z) = 1.3 \times 10^{-6} Z \, {\rm N}_C^{1/2} \left(\frac{300}{T_{\rm gas}}\right)^{1/2} n_e \qquad ({\rm s}^{-1})$$

Electron attachment:

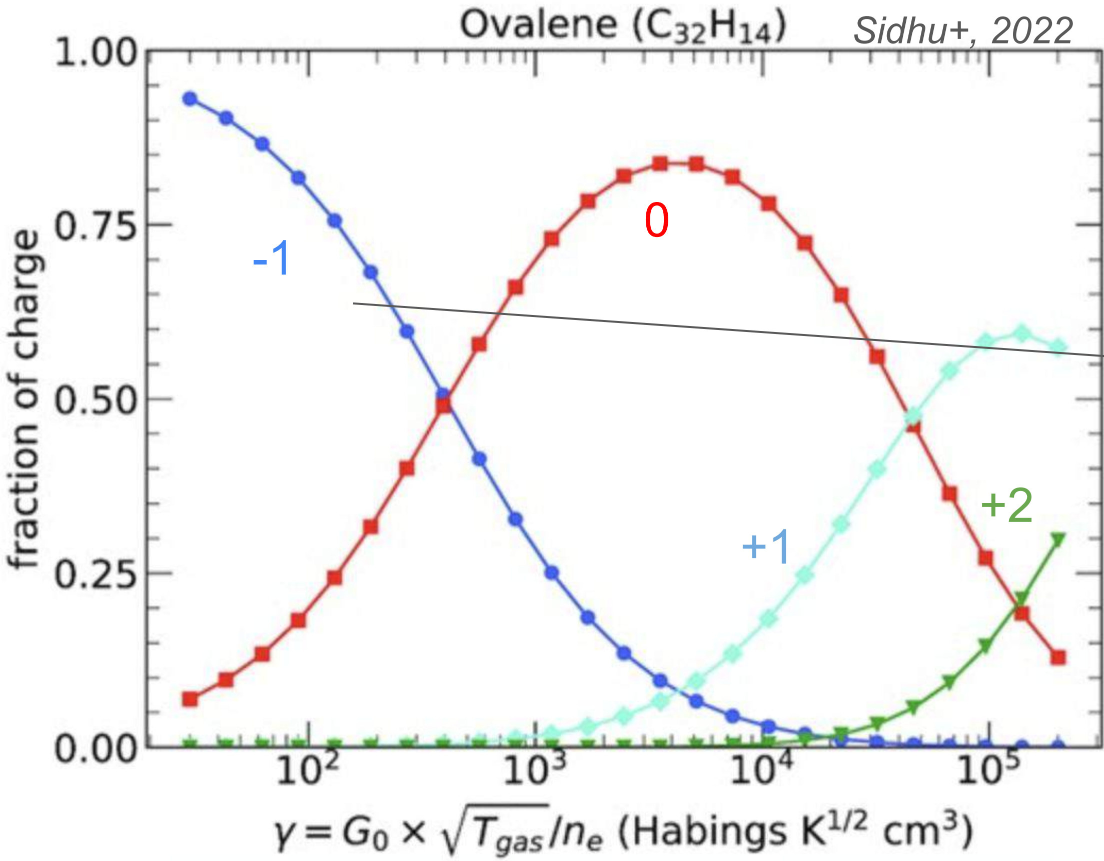
$$k_{ea}(Z=0) = 1.3 \times 10^{-7} s_e \, {\rm N}_C^{1/2} n_e \qquad ({\rm s}^{-1})$$

PAH Charge in the ISM



Dense clouds: $\gamma < 10^2$ => PAH mostly anions
ISM: $\gamma \sim 0.5\ 10^3$ => PAH mostly neutral
PDRs (star formation region, disks): $\gamma > 10^4$ => PAH mostly cations

PAH Charge in the ISM



PAH anions important for gas charge balance in dense clouds (Wakelam & Herbst, 2008)

Dense clouds: $\gamma < 10^2$ => PAH mostly anions
ISM: $\gamma \sim 0.5\ 10^3$ => PAH mostly neutral
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PAH Photodissociation

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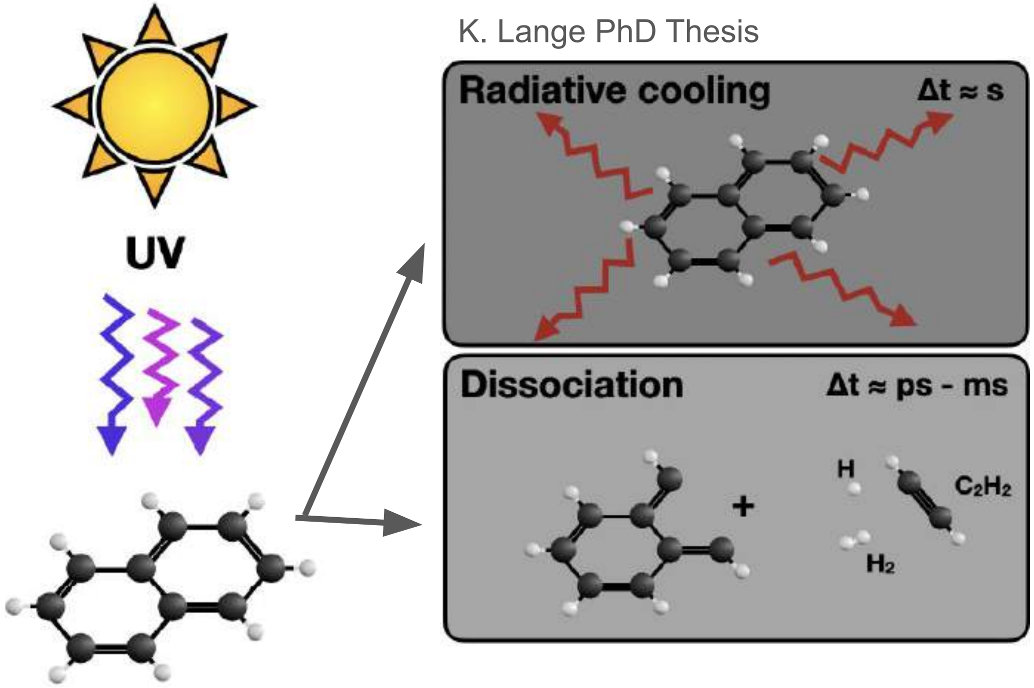
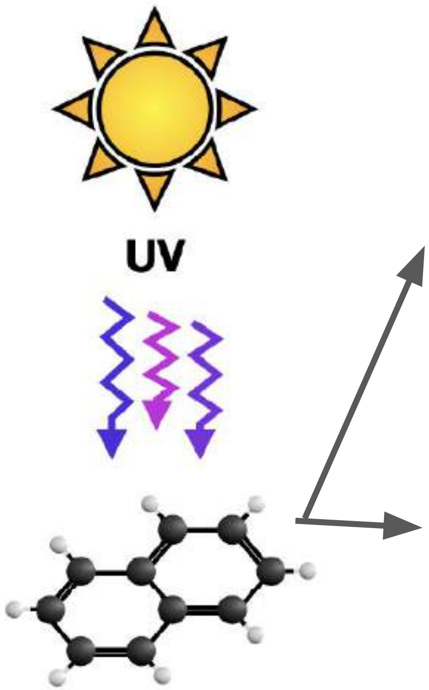


Dissociation depends on
- internal energy of PAH E
- Dissociation energy E_0
- degrees of freedom

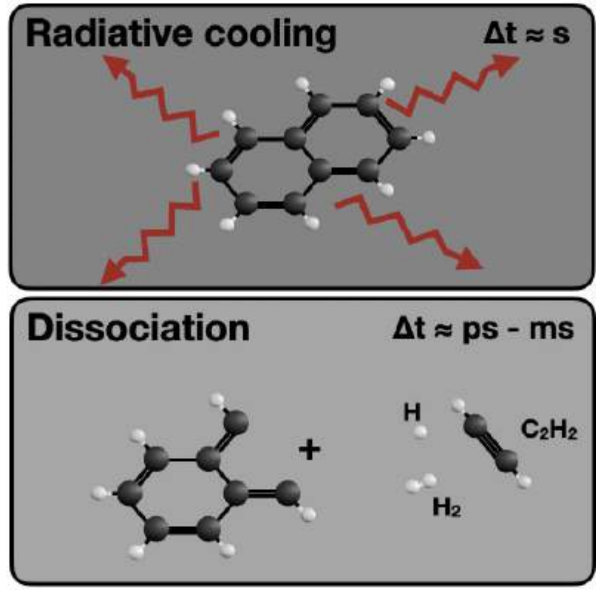
Vib. Density of States

$$\rho(E) = \frac{dN(E)}{dE}$$

PAH Photodissociation



K. Lange PhD Thesis



Dissociation depends on
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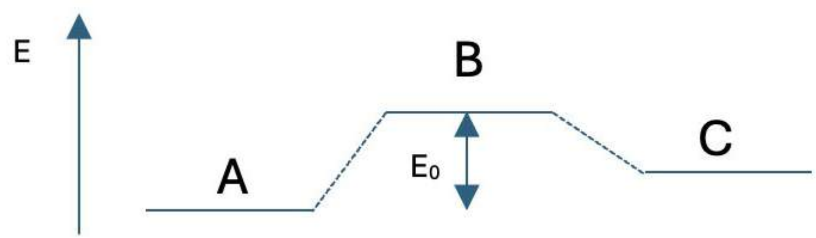
RRKM THEORY

Rice–Ramsperger–Kassel –Marcus theory

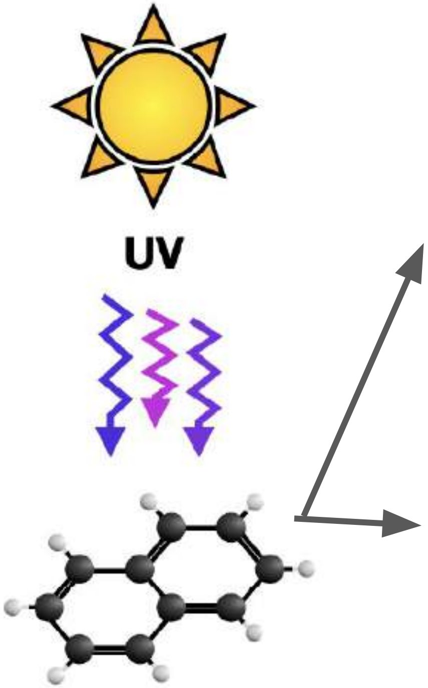


Sum of states B

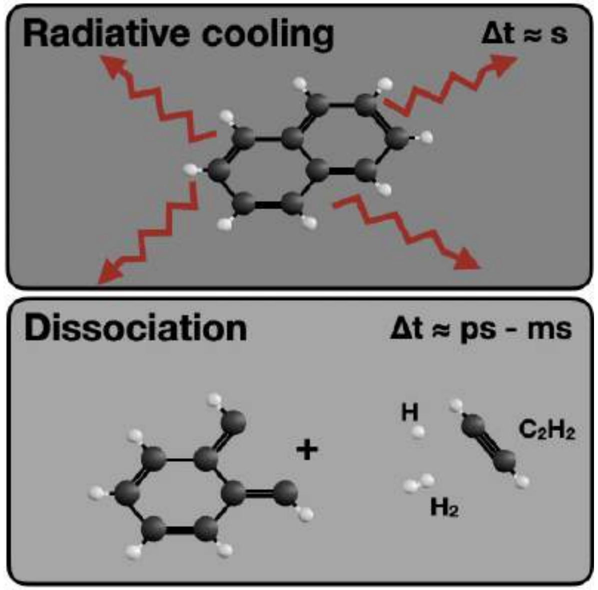
$$k_{\mathrm{RRKM}}(E) = \frac{W^{\star}(E - E_0)}{h\rho(E)},$$

Density of states A

PAH Photodissociation



K. Lange PhD Thesis



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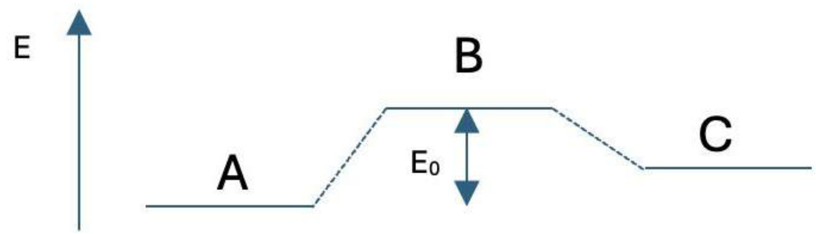
RRKM THEORY

Rice–Ramsperger–Kassel –Marcus theory



Sum of states B

$$k_{\mathrm{RRKM}}(E) = \frac{W^{\star}(E - E_0)}{h\rho(E)},$$

Density of states A

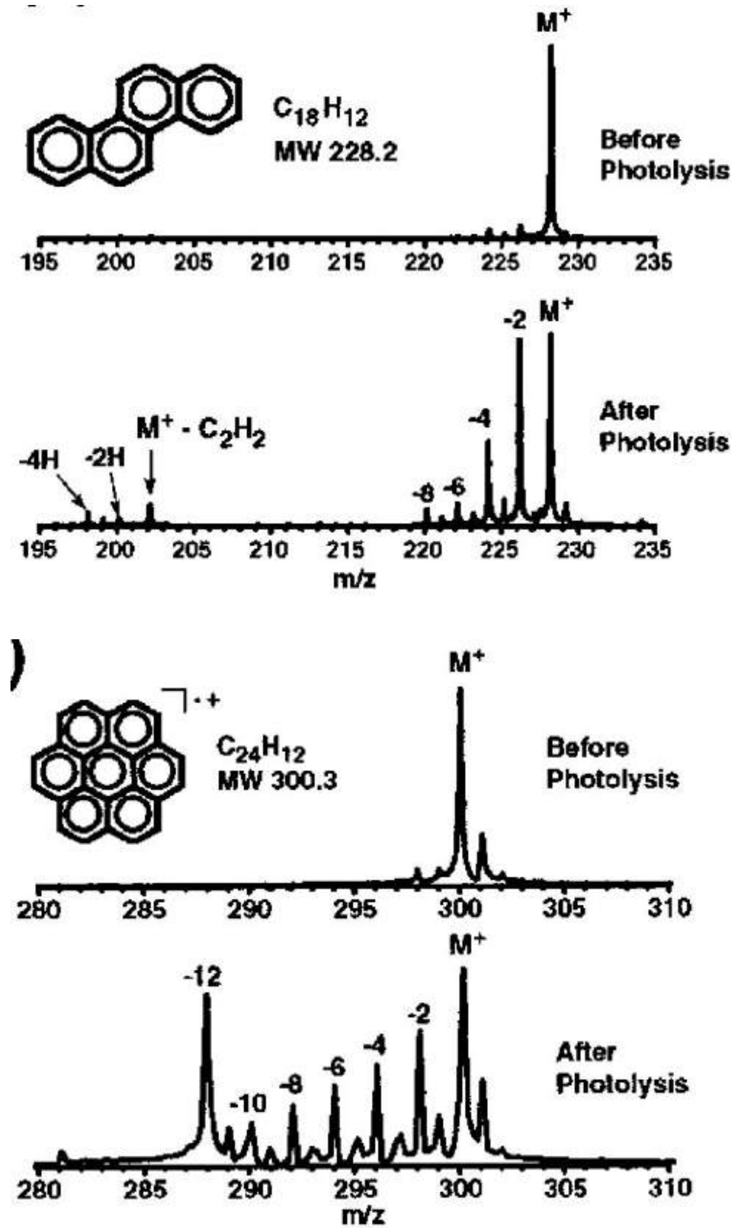
Ingredients needed:
1) vibrational modes A and B (Quantum Chemistry)
2) E_0 (Quantum Chemistry / experiments)

PAH Photodissociation

FROM THE LAB

Specific dissociation channels depend (mostly) on size

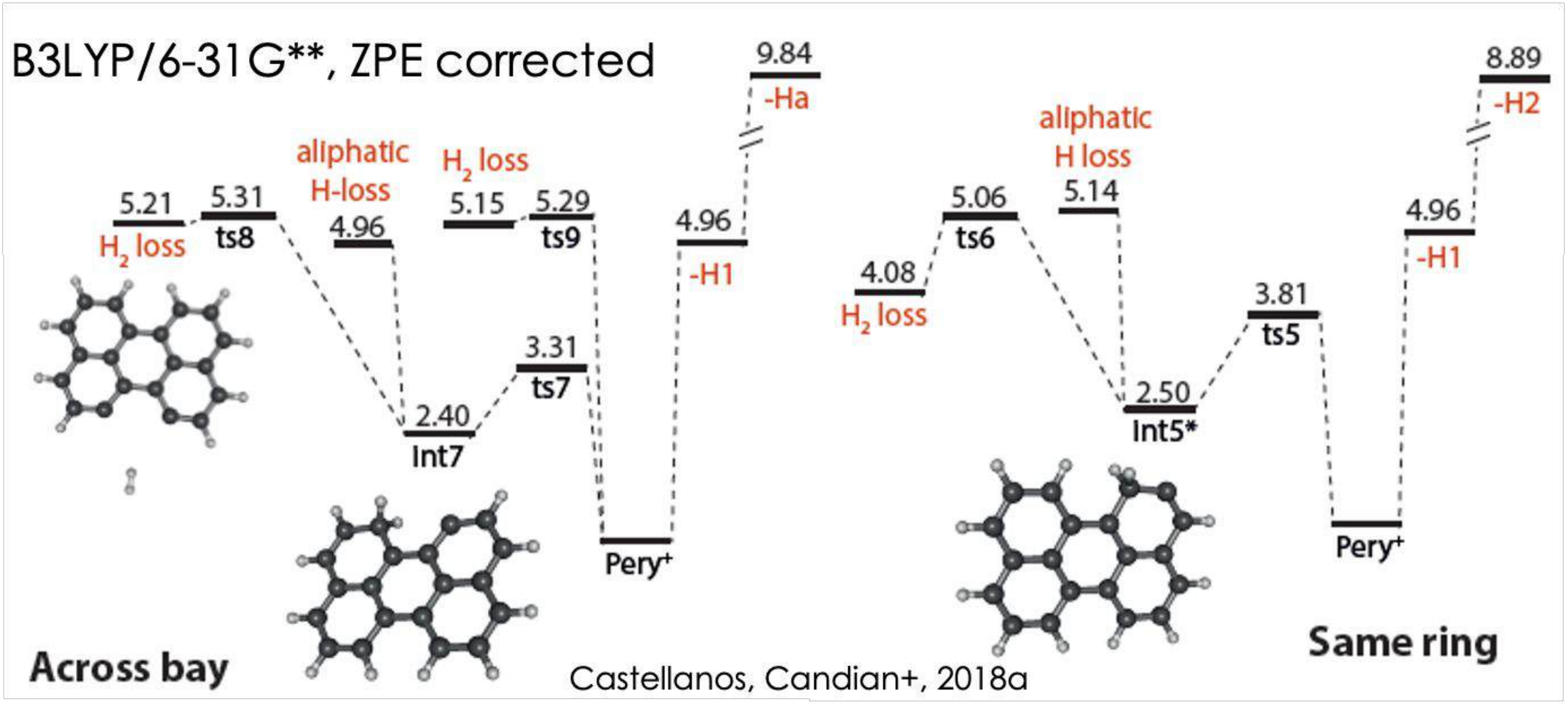
- $N_c > 24$ Only H/H_2 loss
- $N_c < 24$ H/H_2 and C_2H_2 loss at the same time



Ekern+ 1998

PAH Photodissociation: H loss

Reaction	Barriers (eV)
1st H loss	4.96 (DE)
Aliph H loss	2.65/1.73(DE)
Tertiary H loss	1.10 (DE)
H_2 loss (bay)	5.29 (TS)
H_2 loss	2.56/1.85 (TS)



Castellanos, Candian+, 2018a

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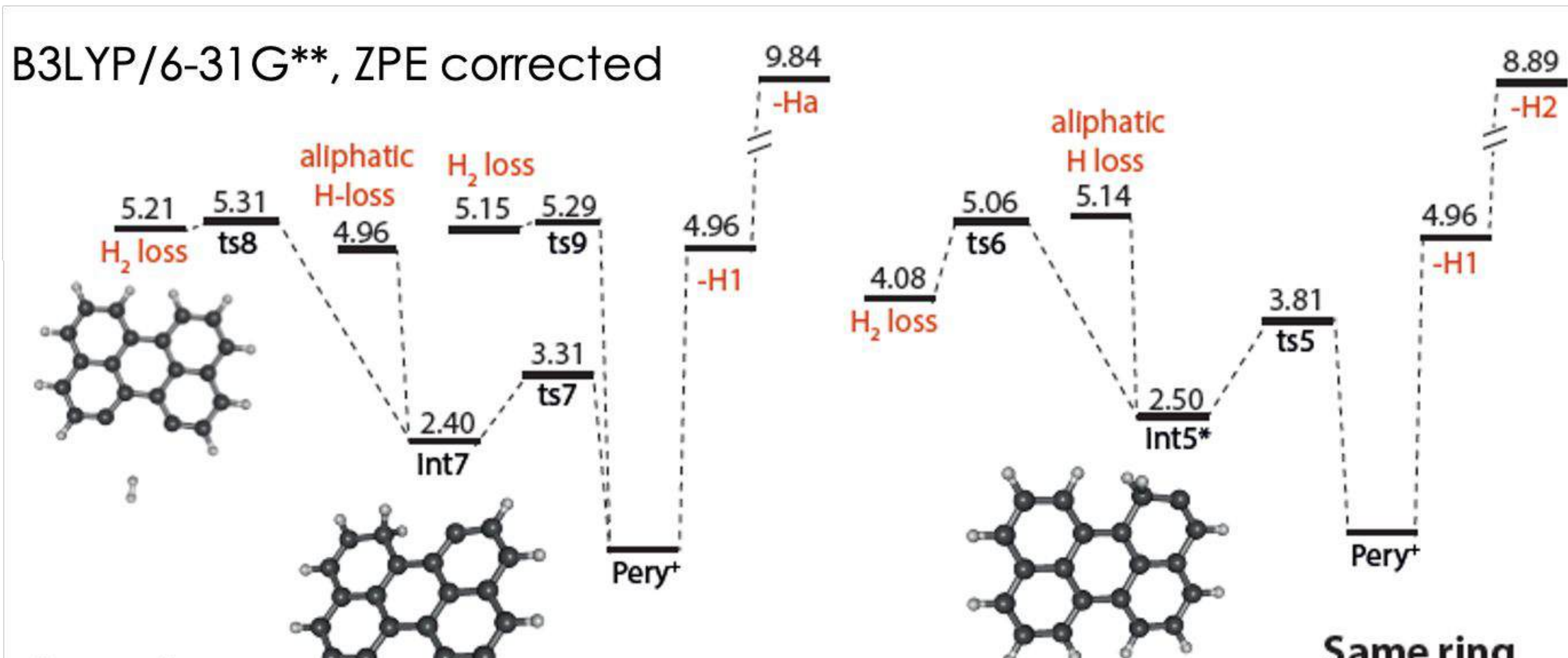
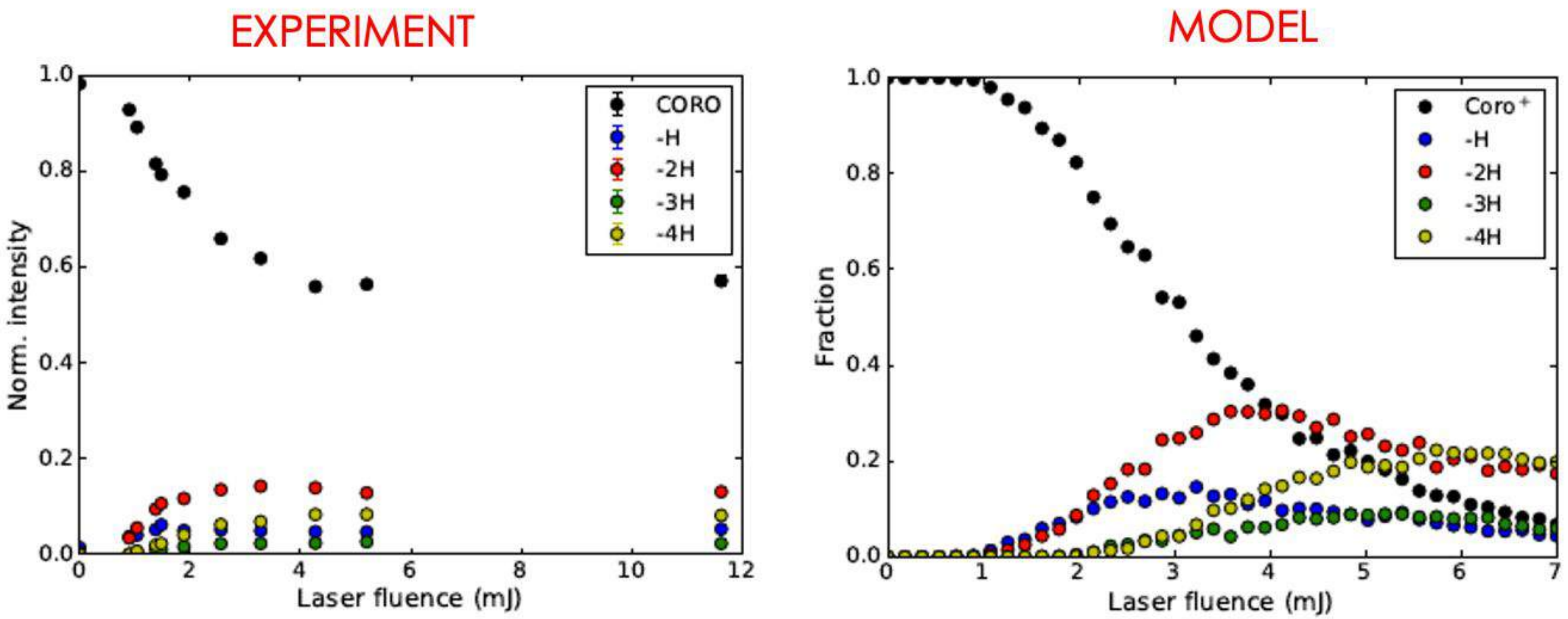
Isomerisation reactions have lower barrier than direct H or H_2 loss!



Castellanos, Candian+, 2018a

PAH Photodissociation: H loss

DFT → $$k_{\mathrm{RRKM}}(E) = \frac{W^{\star}(E - E_0)}{h\rho(E)}$$ → Monte Carlo Modelling



Castellanos, Candian +, 2018a

Isomerisation is fundamental to explain the experiments!

Chemical evolution of PAHs in ISM: charge and H coverage

PAH Kinetic model

- (multi) photon absorption
- real molecular properties

Reactions

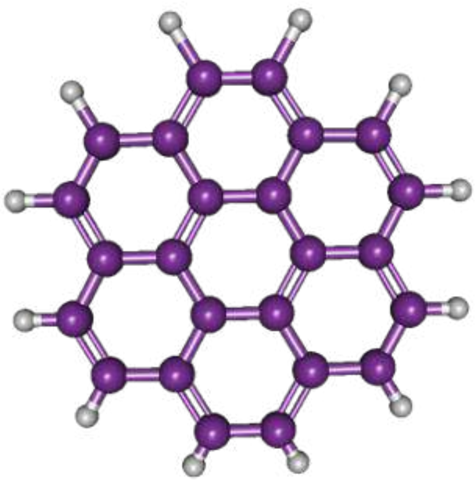
- e^- recombination/attachment
- H/H_2 photodissociation
- H addition (plenty of H gas)
- H_2 abstraction

Coronene family

$24 < N_c < 96$

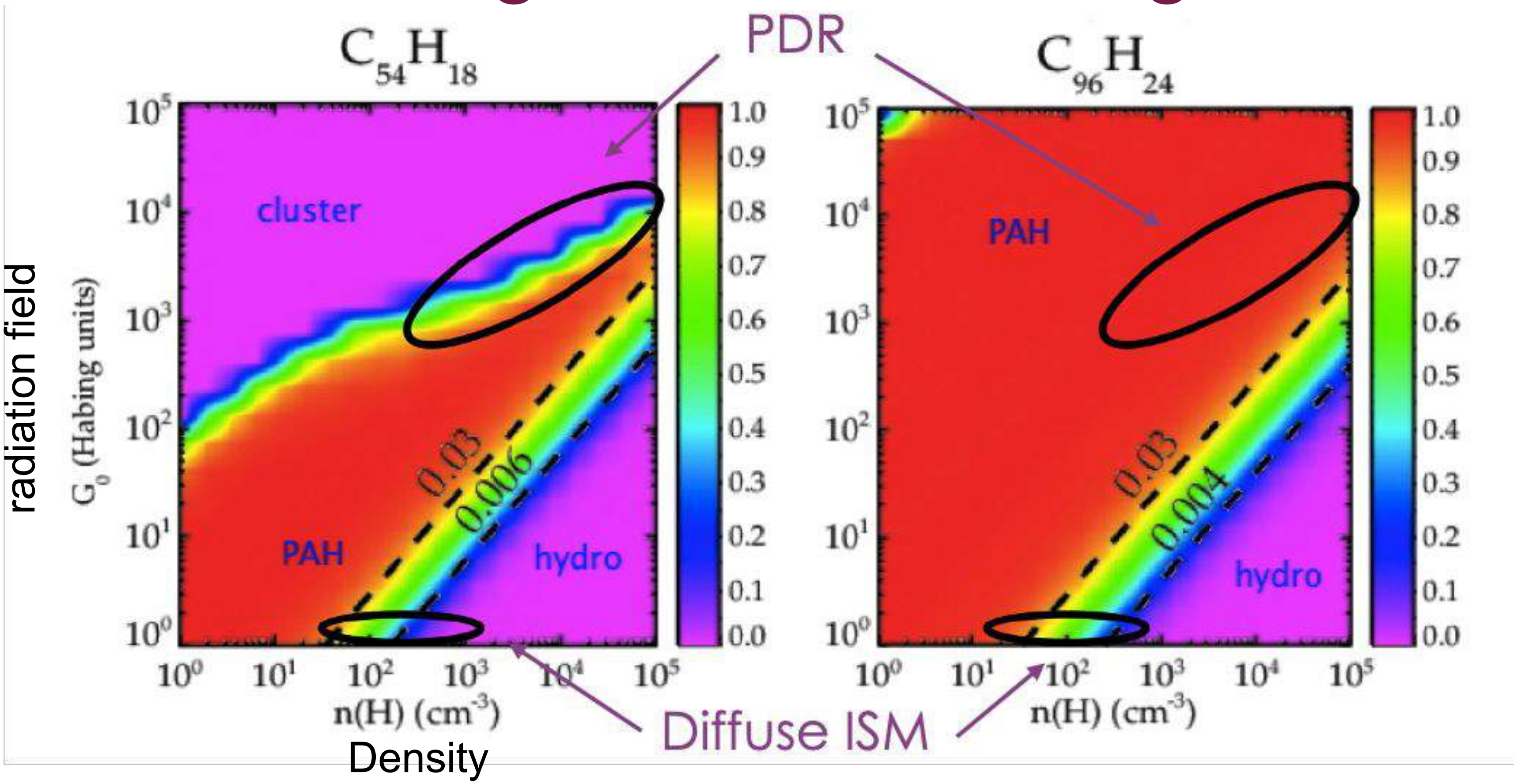
$Z = -1, 0, +1$

$N_h = [0, N\_edge+2]$



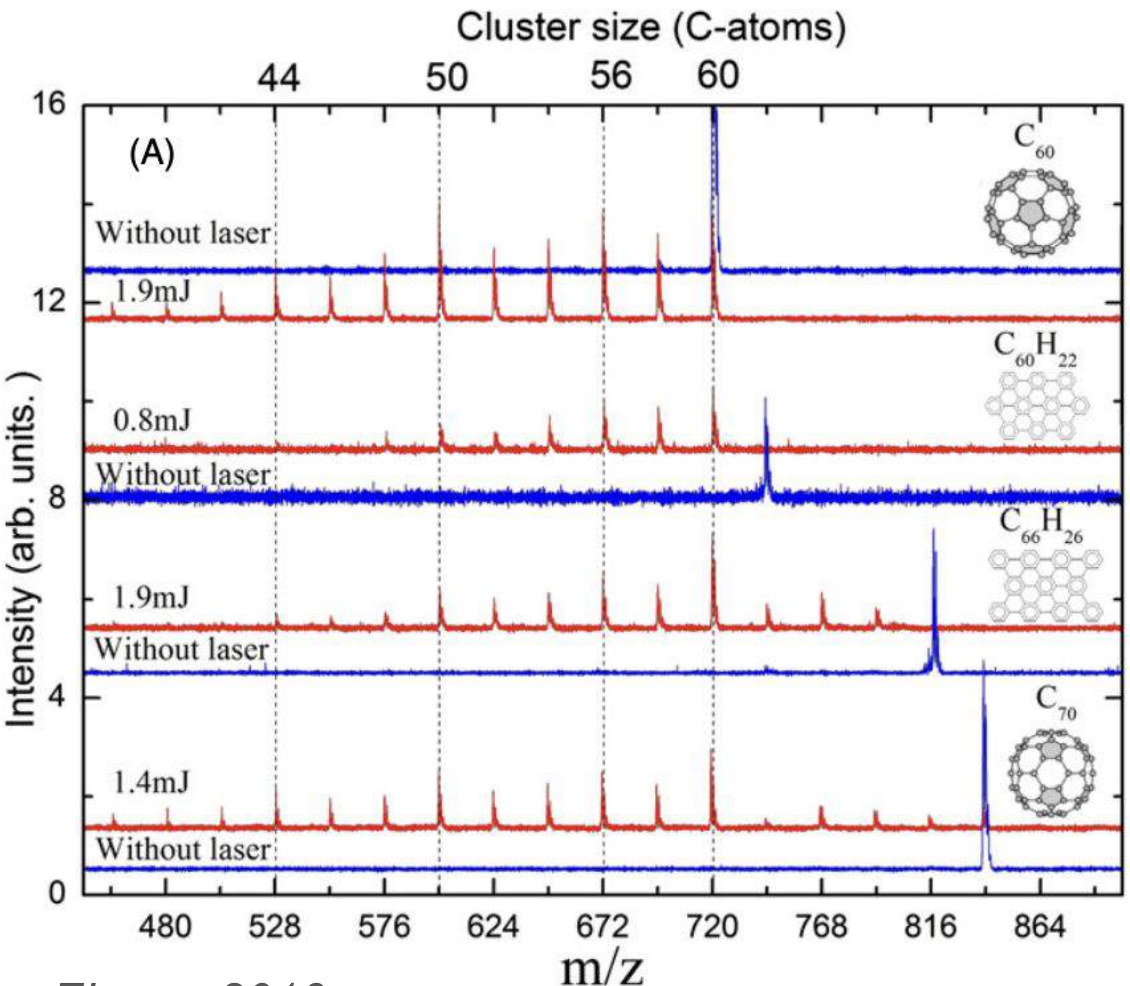
Le Page+, 2003
Montillaud+, 2013
Andrews, Candian & Tielens, 2016

Chemical evolution of PAHs in ISM: charge and H coverage



$N_c < 50$ completely dehydrogenated in most environments (clusters)
$50 < N_c < 80$ normally hydrogenated
$N_c > 80$ superhydrogenated (hydro)

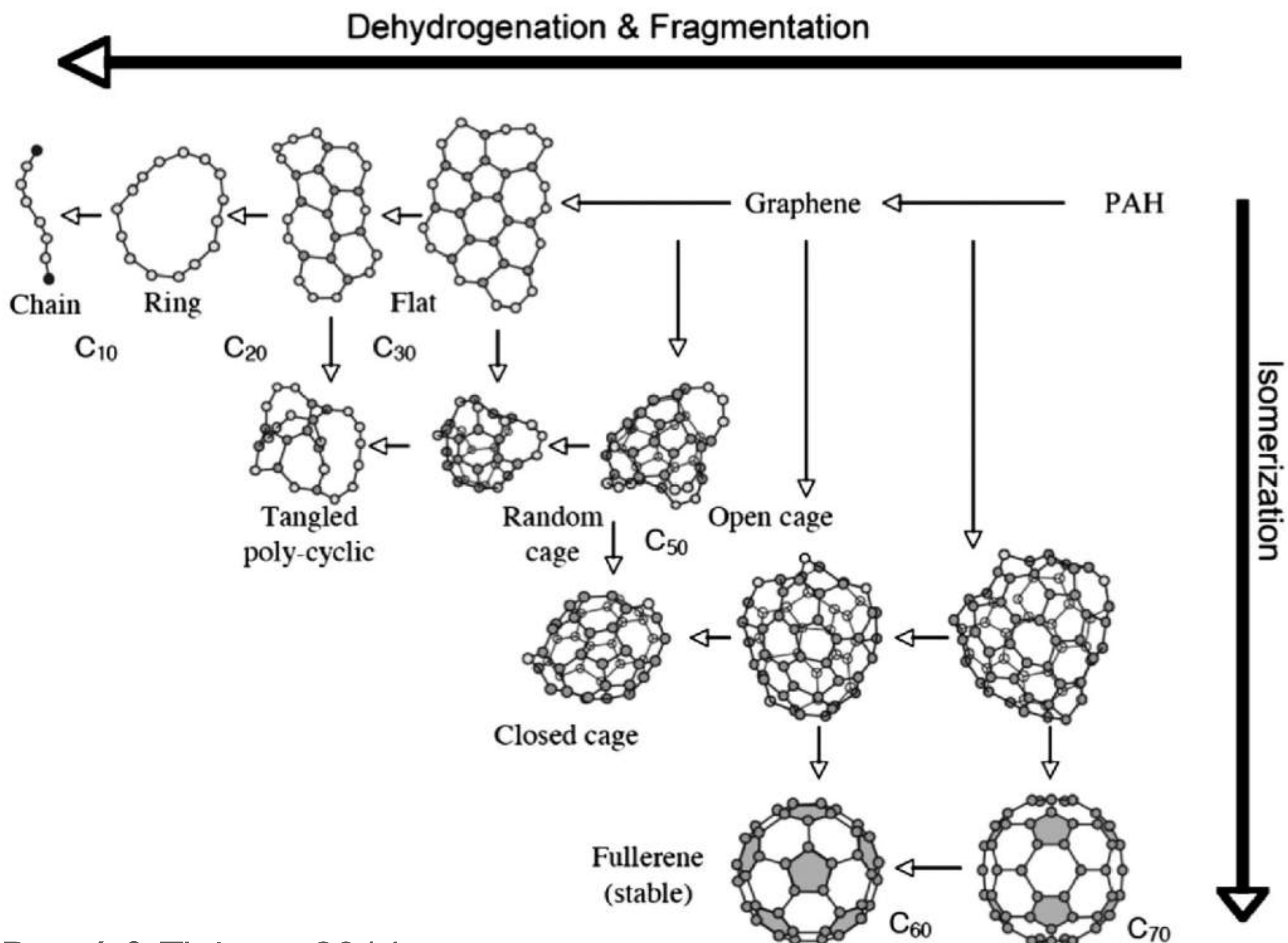
PAHs to C_{60}



Zhen+, 2016

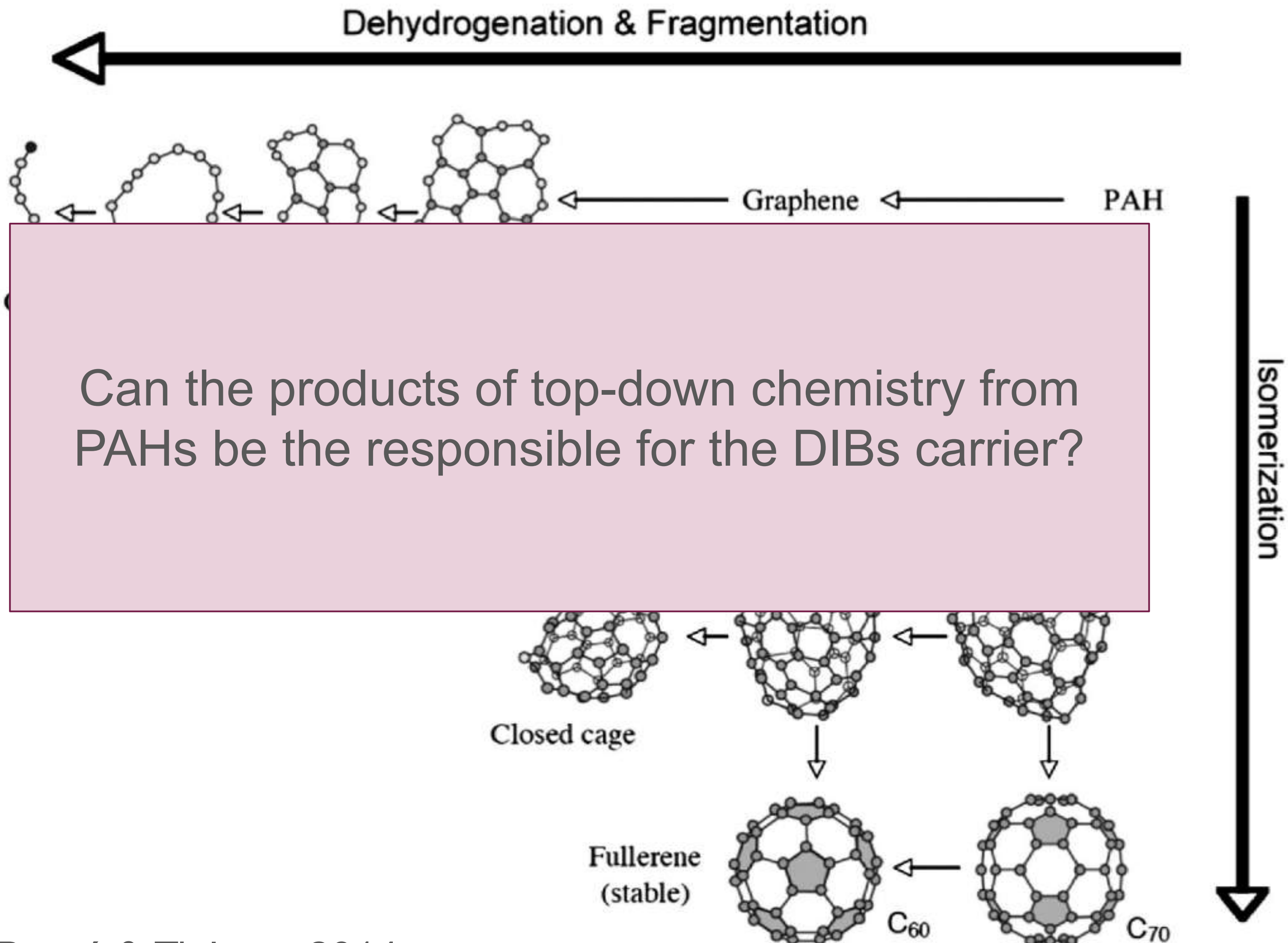
If PAH are large enough (more N_c>66) and there is enough UV irradiation => they convert into C_{60}

Top-down Carbon Chemistry



Berné & Tielens, 2014

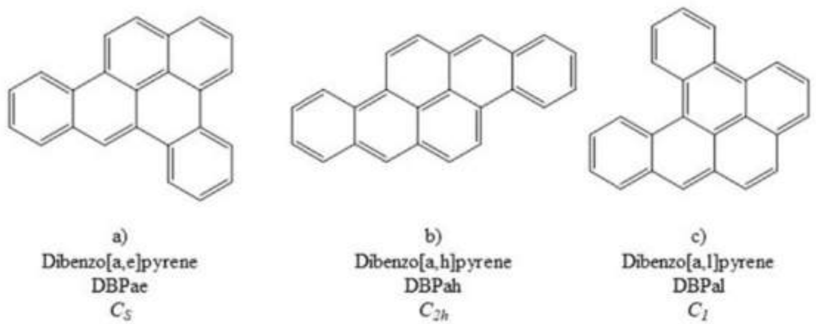
Top-down Carbon Chemistry



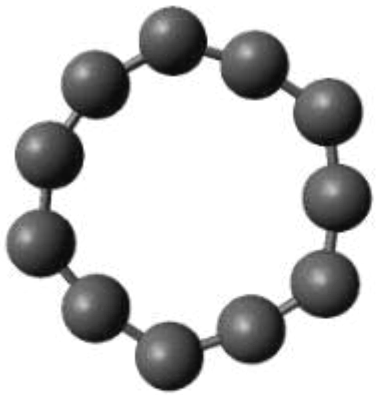
Can the products of top-down chemistry from PAHs be the responsible for the DIBs carrier?

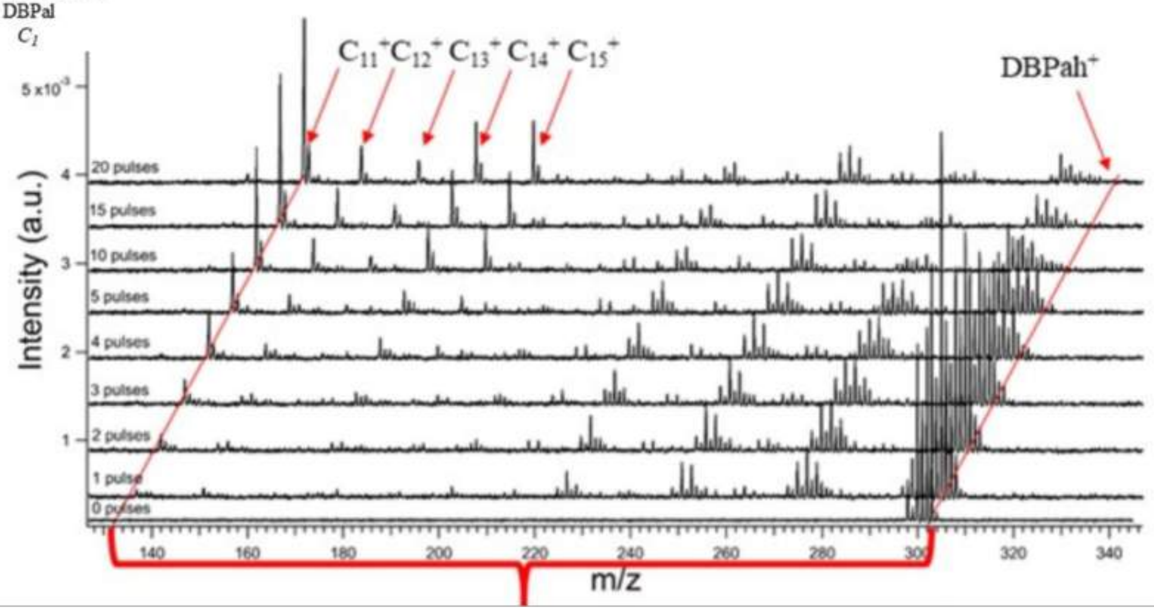
Berné & Tielens, 2014

Top-down Carbon Chemistry



$C_{24}H_{14}$ isomers lead to C_{11}- C_{15} carbon rings

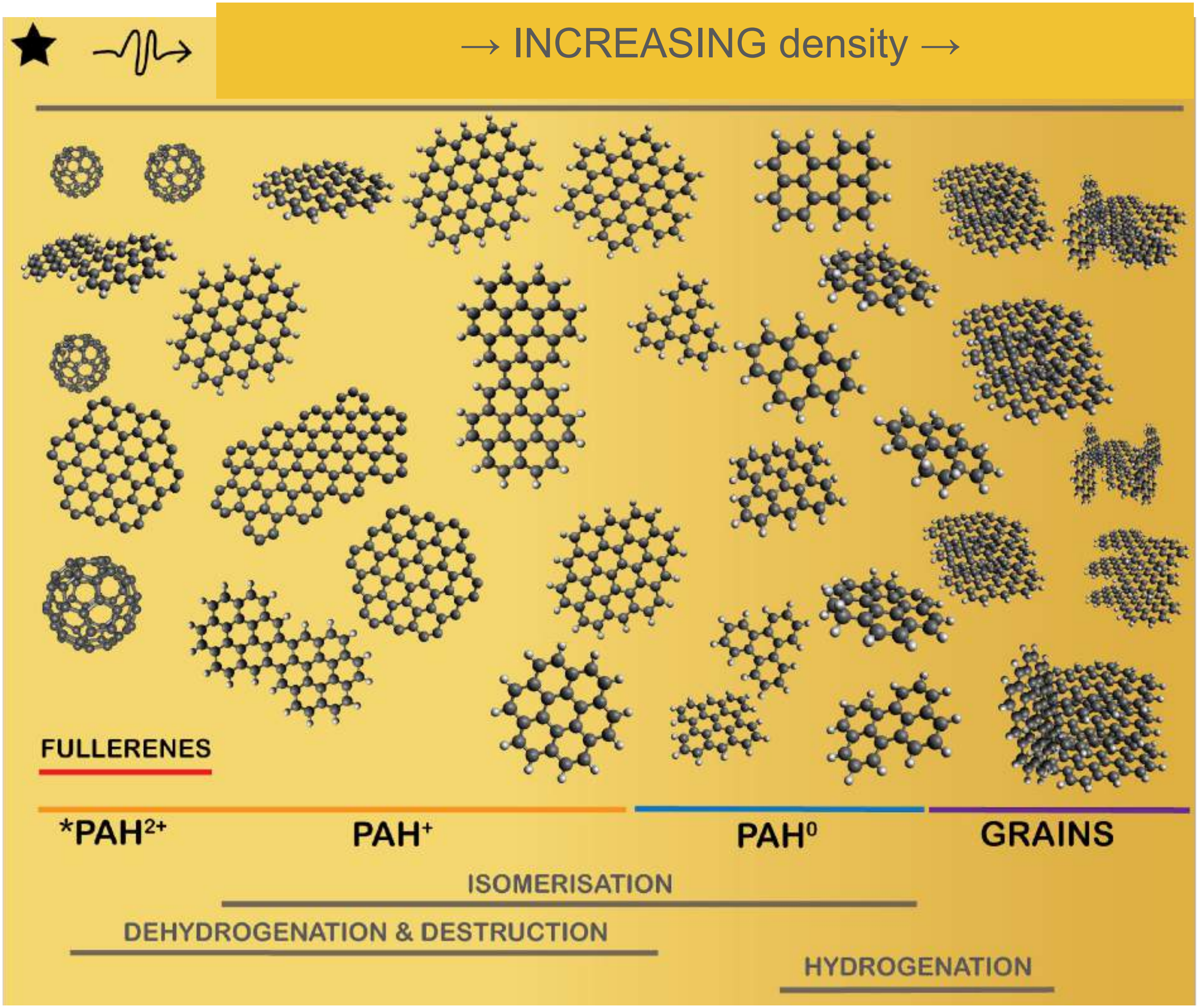




Hrodmarsson et al, Int. J. Mass. Spec., 2022

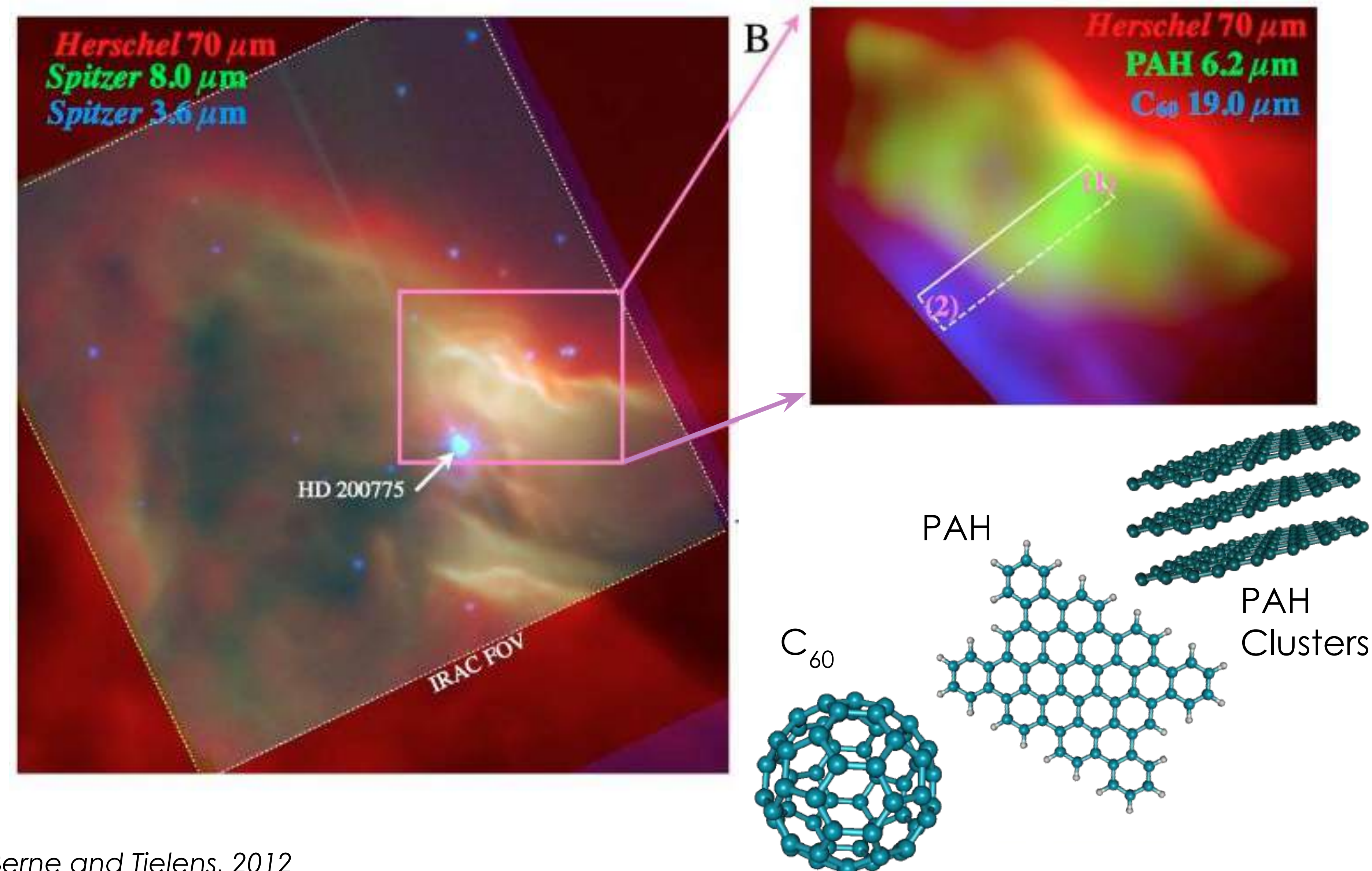
Berné & Tielens, 2014

Evolution of PAHs in PDRs



Candian & Petrignani, 2021

Top down chemistry in action

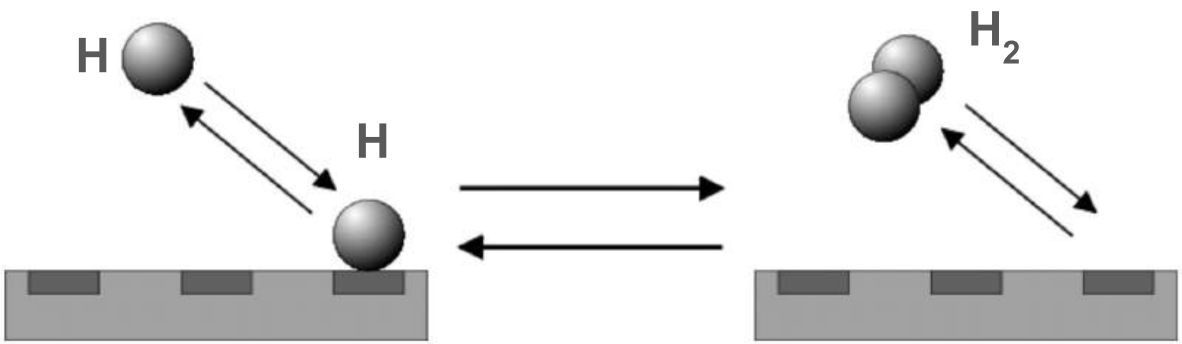


Berne and Tielens, 2012

H_2 formation on PAHs

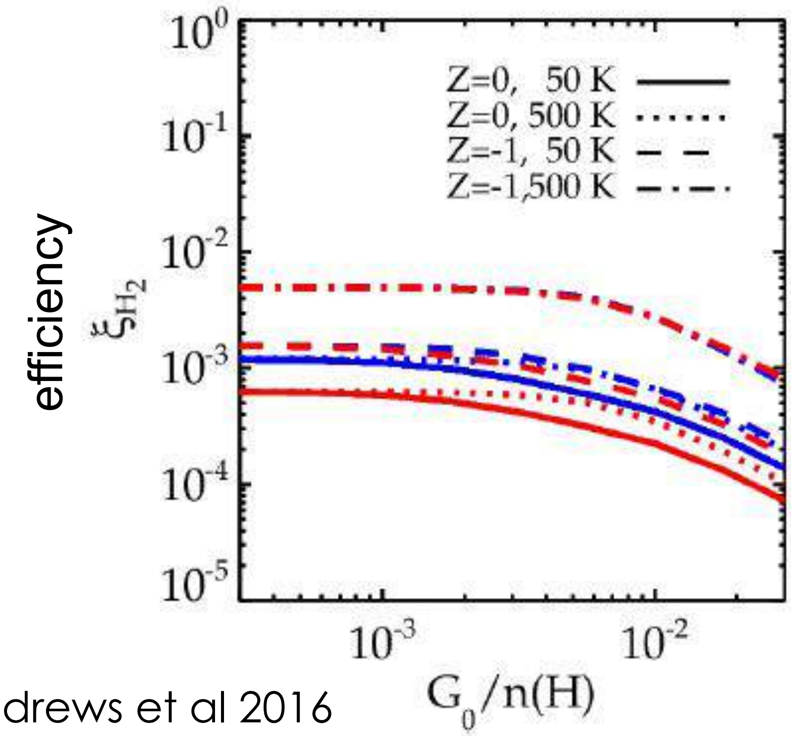
Andrews et al 2016

H_2 formation on PAHs



$HPAH + H = PAH + H_2$

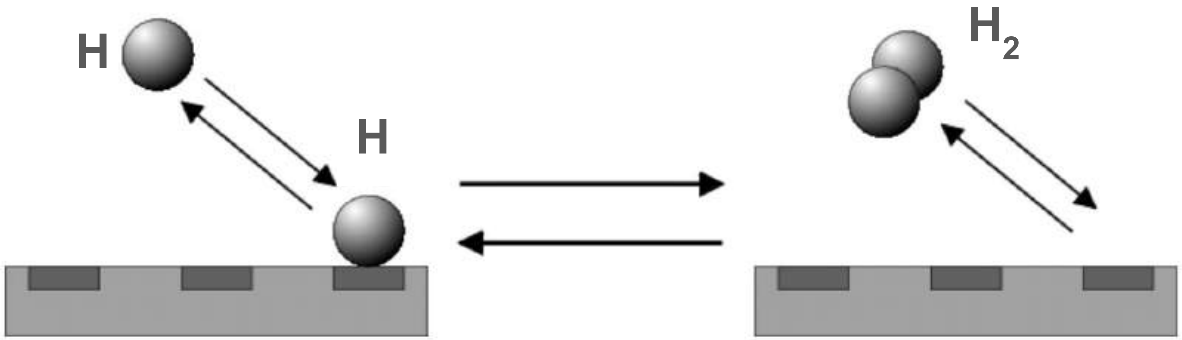
Eley-Rideal for H_2 abstraction on a PAH molecule



Andrews et al 2016

While the mechanism works from a chemical point of view (there is almost no barrier), its efficiency in the ISM is < 1%

H_2 formation on PAHs



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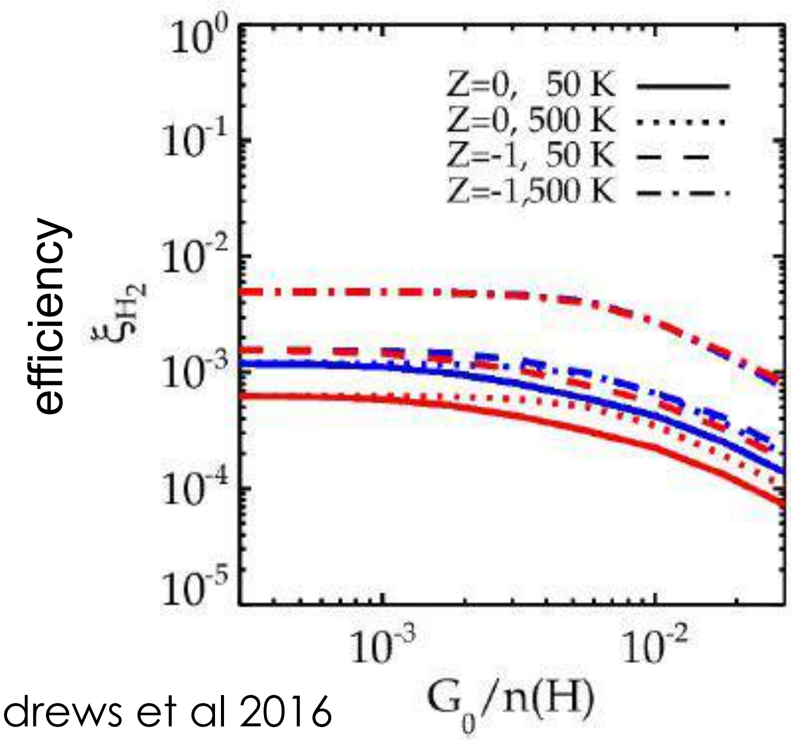


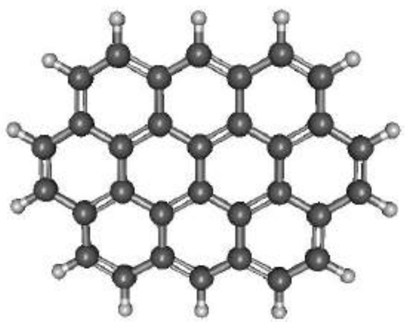
Andrews et al 2016

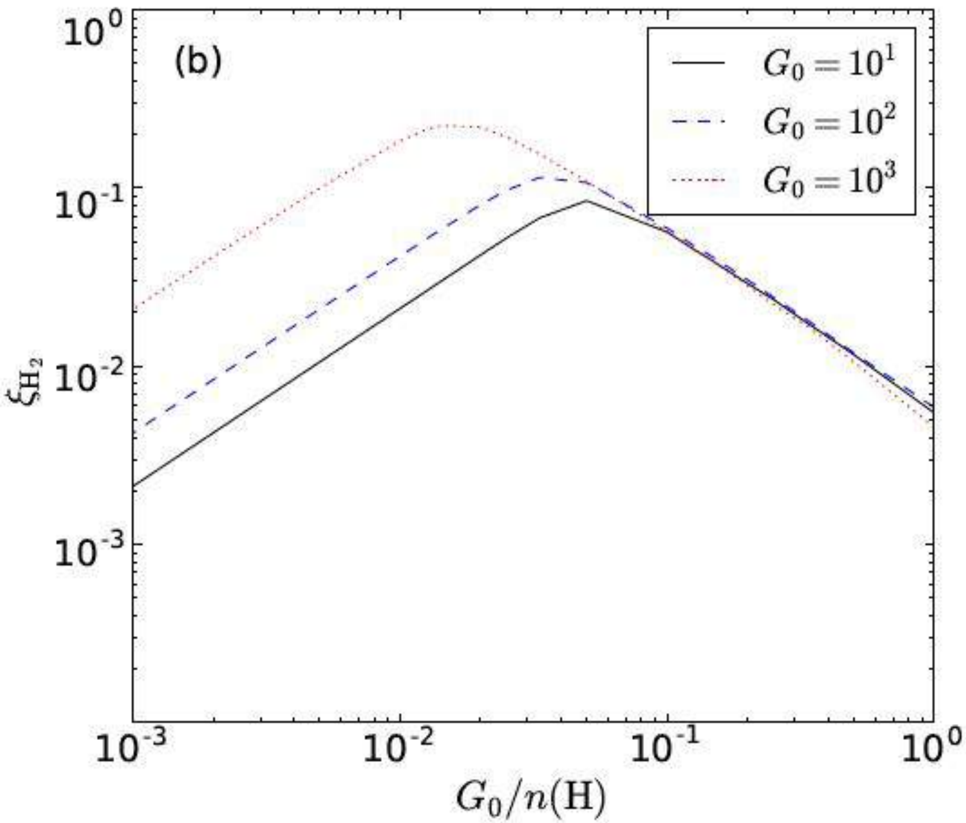
While the mechanism works from a chemical point of view (there is almost no barrier), its efficiency in the ISM is < 1%

What if considering H_2 photodissociation?

H_2 formation in PAHs (reprise)

Efficiency can go up to 10% but highly dependent on the shape of the molecule



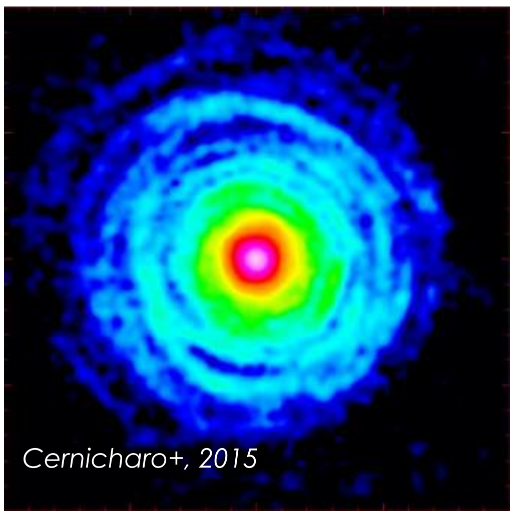


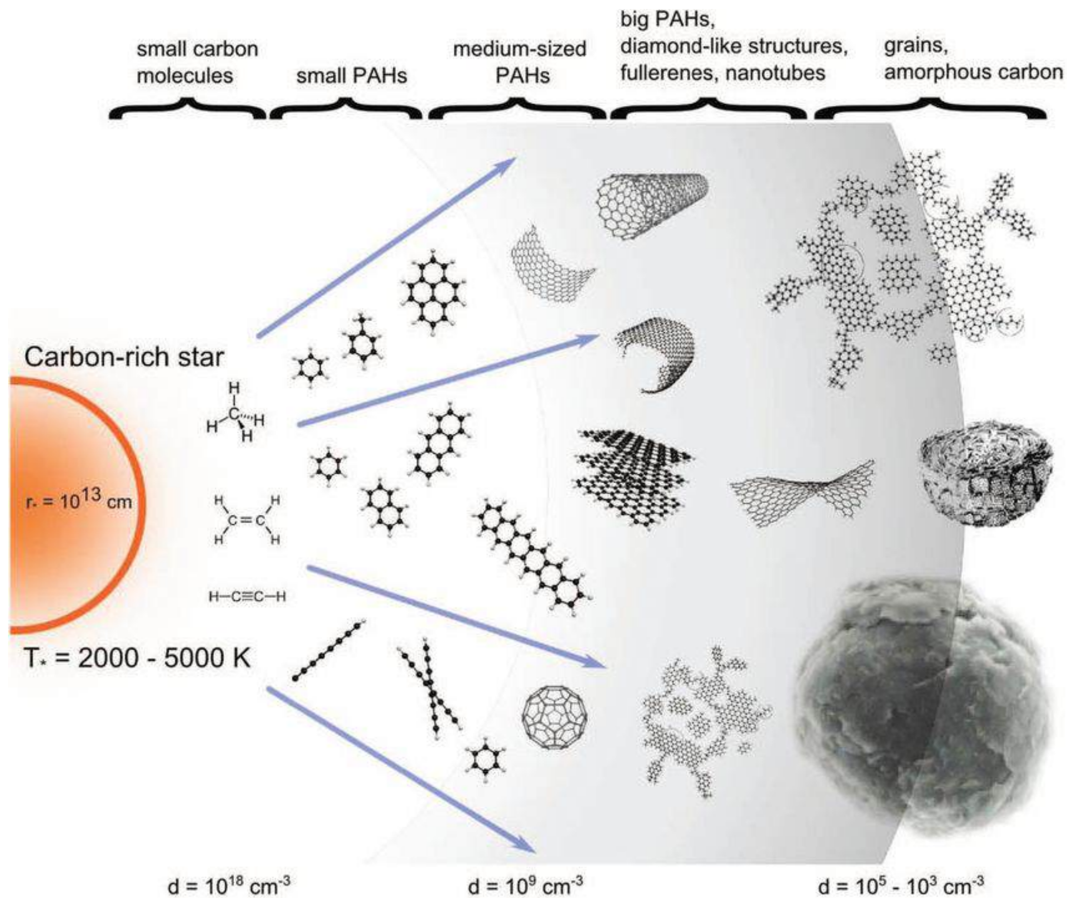
Castellanos, 2018b

PAH processes: hot topics

PAH processes: hot topics
PAH formation (high T)

Combustion chemistry in space –> C-rich (C/O>1) evolved stars
(Chercheff, 2011 but see Martínez+, 2019)



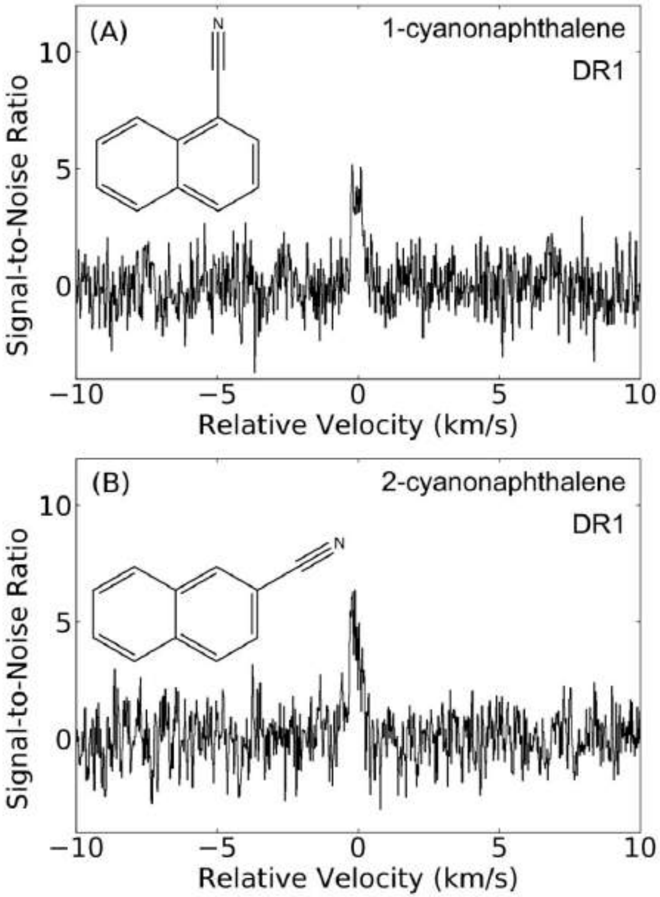


Models fail to predict

1) the abundance of PAH detected (but new routes Kaiser et al, 2021)
2) the diversity of populations

PAH processes: hot topics

PAH formation (low T)



McGuire+, 2021
Cernicharo+, 2022

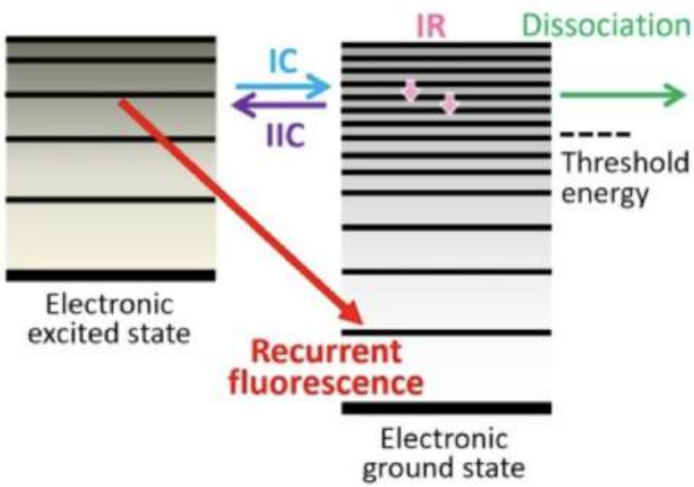
2-ring PAHs (CyanoPAHs and indene) detected via rotational transitions in cold clouds, but formation mechanism is unclear

- Formation of 1st ring (benzene) is the bottleneck
- Few small radical/ions hydrocarbons to start from in cold environments

Garcia de la Conception+, 2023; Rap+ 2022a, b

PAH processes: hot topics

Recurrent/Poincaré Fluorescence



Kosuda+, 2024

In a collisionless environment (ISM), Inverse Internal Conversion can happen => fluorescence from electronic excited states (Leger+, 1988), faster than IR emission.

Efficient stabilization of cyanonaphthalene by fast radiative cooling and implications for the resilience of small PAHs in interstellar clouds

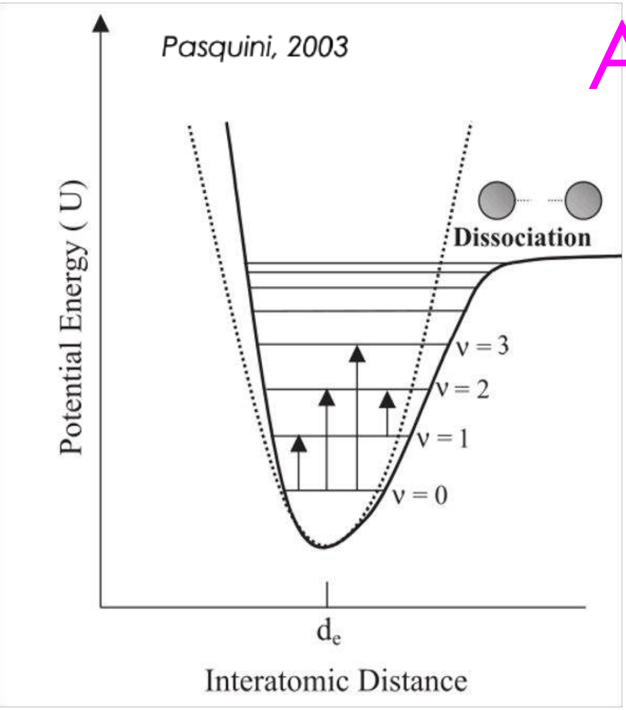
Mark H. Stockett, James N. Bull, Henrik Cederquist, Suvasthika Indrajith, MingChao Ji, José E. Navarro Navarrete, Henning T. Schmidt, Henning Zettergren & Boxing Zhu

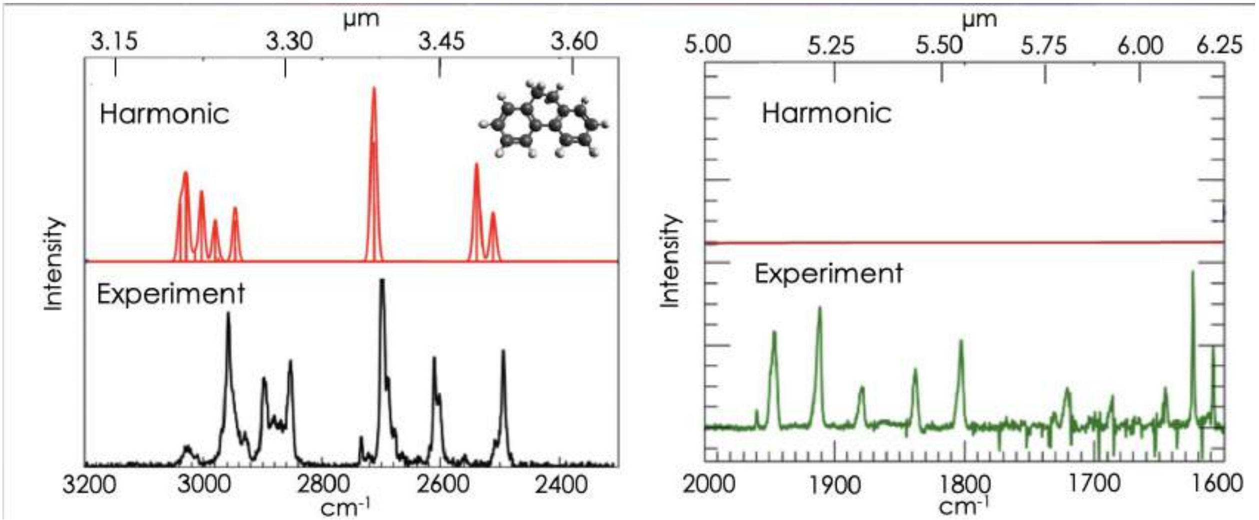
Nature Communications **14**, Article number: 395 (2023) | Cite this article

Effect of anharmonicity

PAH processes: hot topics

Anharmonicity

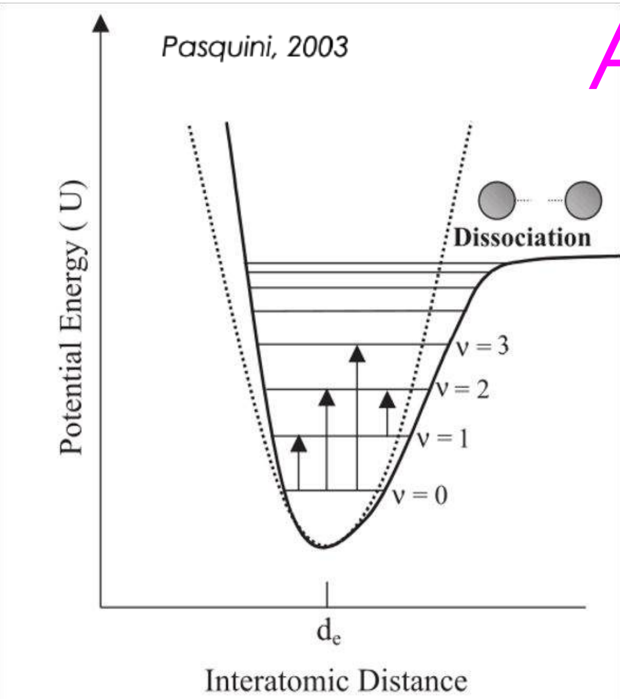


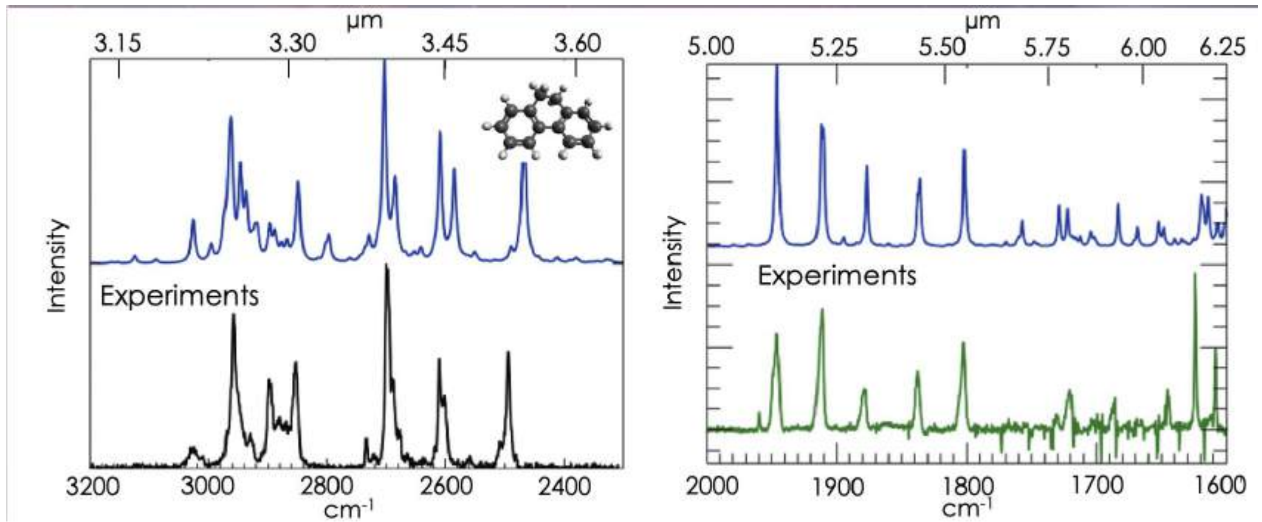


Mackie, Candian+, 2016-2018; Lemmens+, 2019-2021; Esposito+ , 2024a, b

PAH processes: hot topics

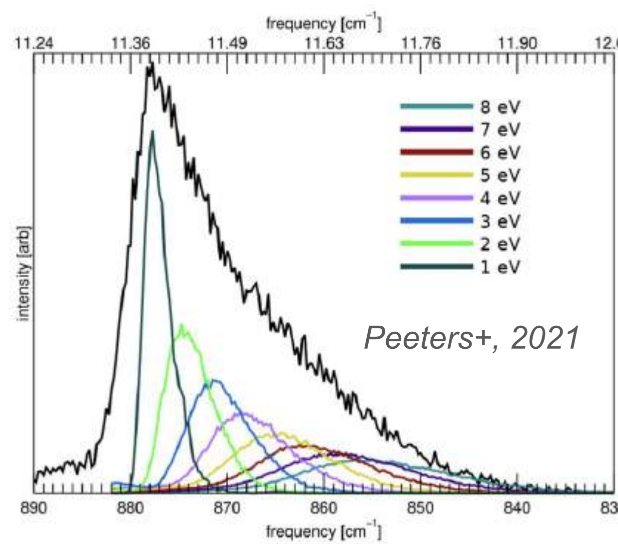
Anharmonicity





Mackie, Candian+, 2016-2018; Lemmens+, 2019-2021; Esposito+ , 2024a, b

We can model more accurately PAH emission bands, e.g. 11.2 μm / 893 cm^{-1}



Peeters+, 2021

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