Synthesis of Complex Organics in the Late Stages of Stellar Evolution

Sun Kwok

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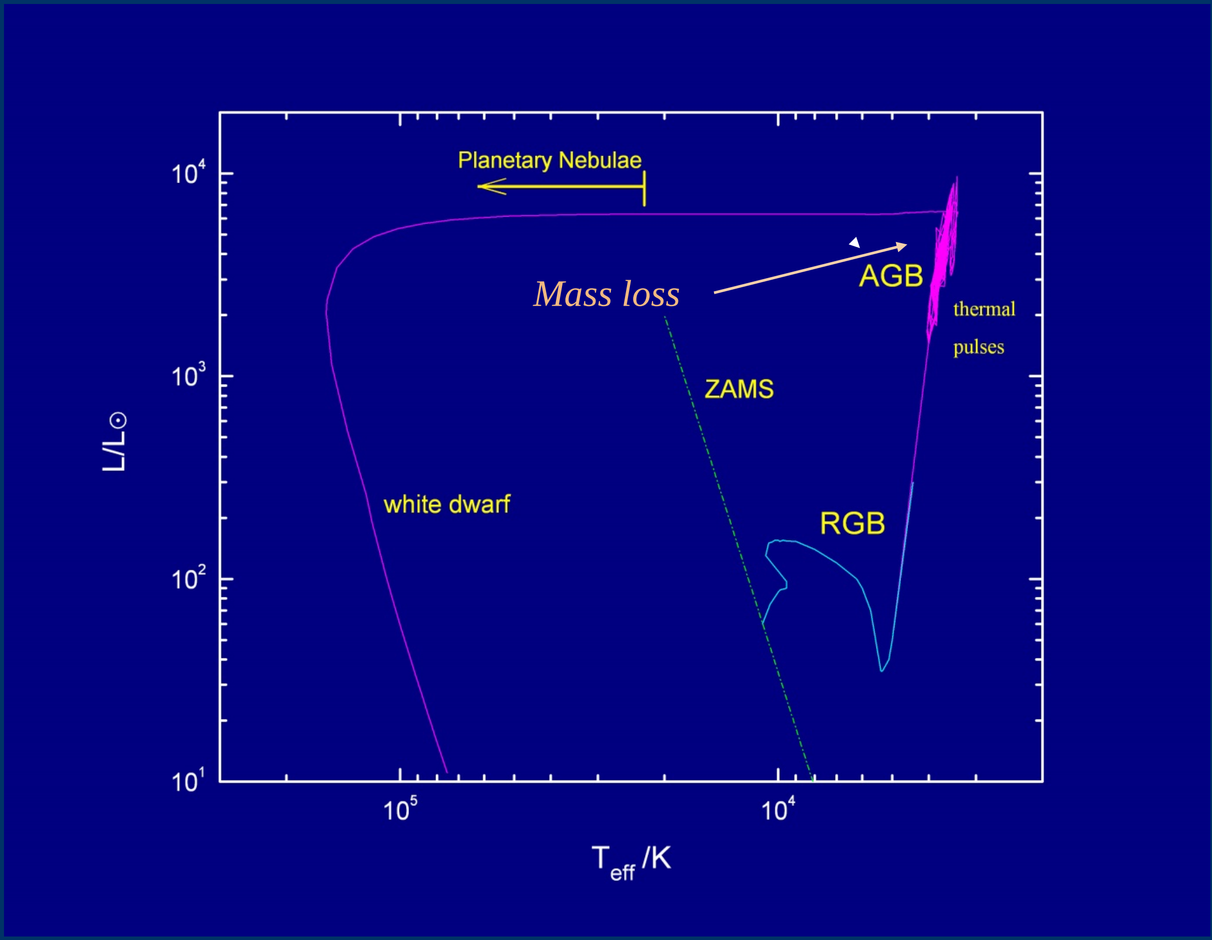
Evolution of intermediate mass (1-$8\ M_\odot$) stars and the synthesis of carbon

- Triple-α reaction (He→C)
- Slow neutron capture (s-process) (Y, Zr, Ba, La, Ce, Pr, Nd, Sm, Eu, etc)
- Thermal pulse and dredge up
- *Manifestation of mass loss in molecular emission and infrared excess from dust*

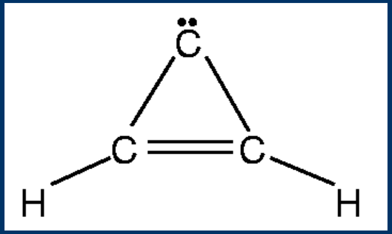


$3\ M_\odot$ track

Bloecker

Molecular synthesis in the stellar winds of AGB stars

- Rotational transitions of over 70 molecules have been detected in the circumstellar envelopes of AGB stars
- Inorganics: CO, SiO, SiS, NH_3, $AlCl$, ..
- Organics: C_2H_2, CH_4, H_2CO, CH_3CN, ..
- Radicals: CN, C_2H, C_3, HCO^+
- Rings (C_3H_2), chains (HC_9N)



AGB stars are prolific molecular factories

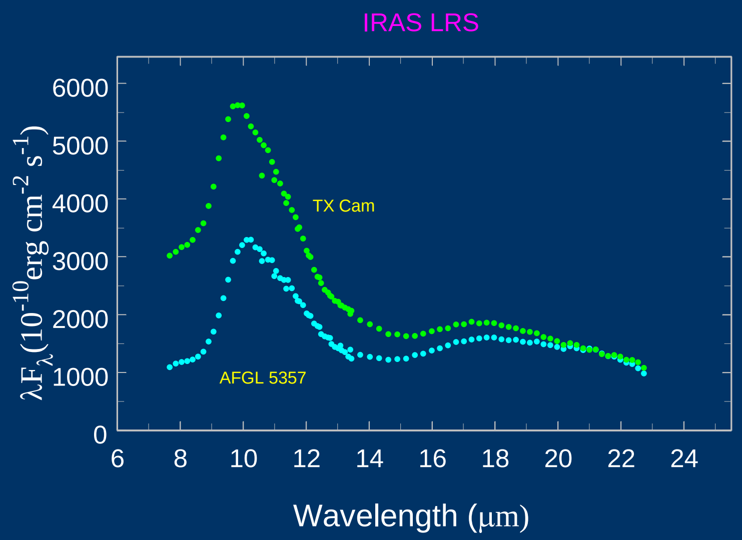
Condensation of solids:

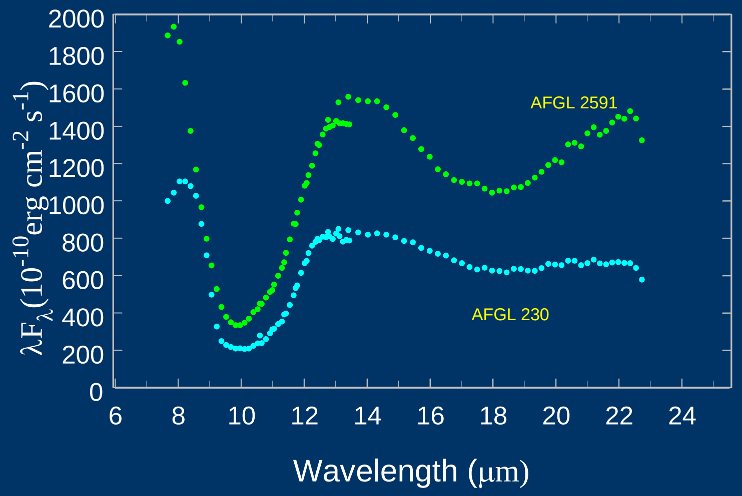
Amorphous Silicates

- IRAS Low Resolution Spectrometer
- Over 11,000 spectra processed and classified (Kwok et al. 1997)
- Seen in both emission and self absorption

9.7 μm: Si-O stretch

18 μm: O-Si-O bend

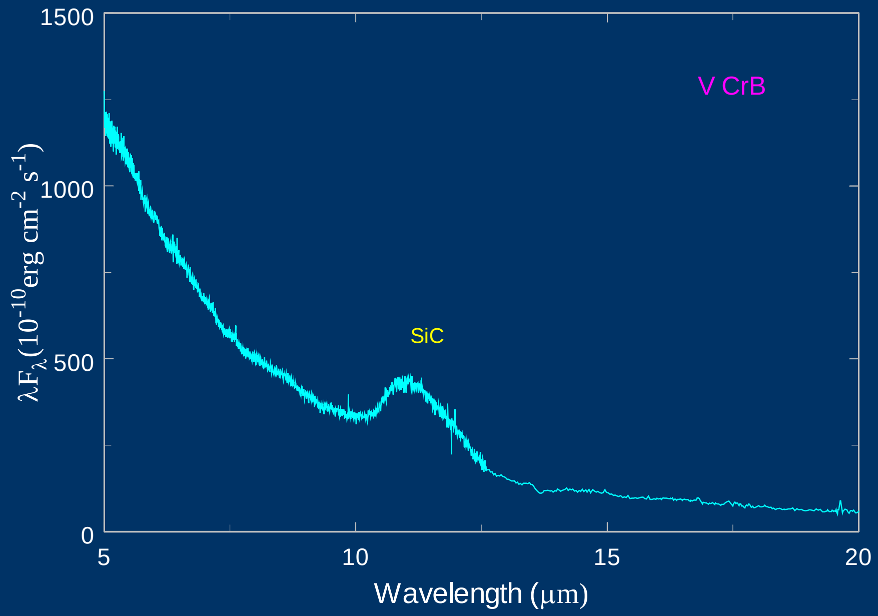




Direct condensation from gas to solid results in disordered structure

Silicon Carbide

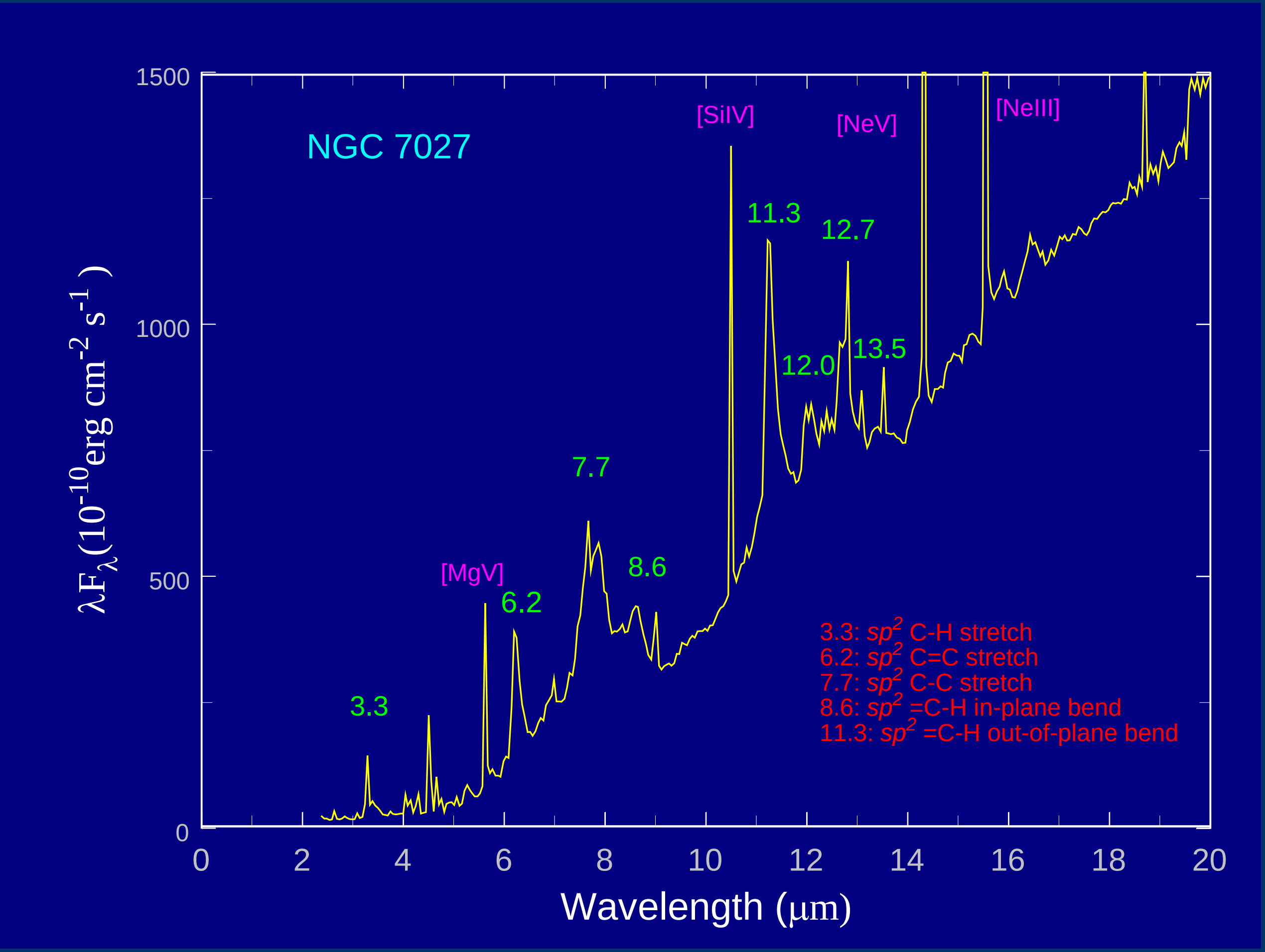
- 4000 stars detected to have amorphous silicates by IRAS LRS
- 700 stars detected in SiC
- M stars: silicates, C stars: SiC



Do dust in planetary nebulae has the same chemical composition as dust in AGB stars?

Unidentified infrared emission bands

(Russell et al. 1977)

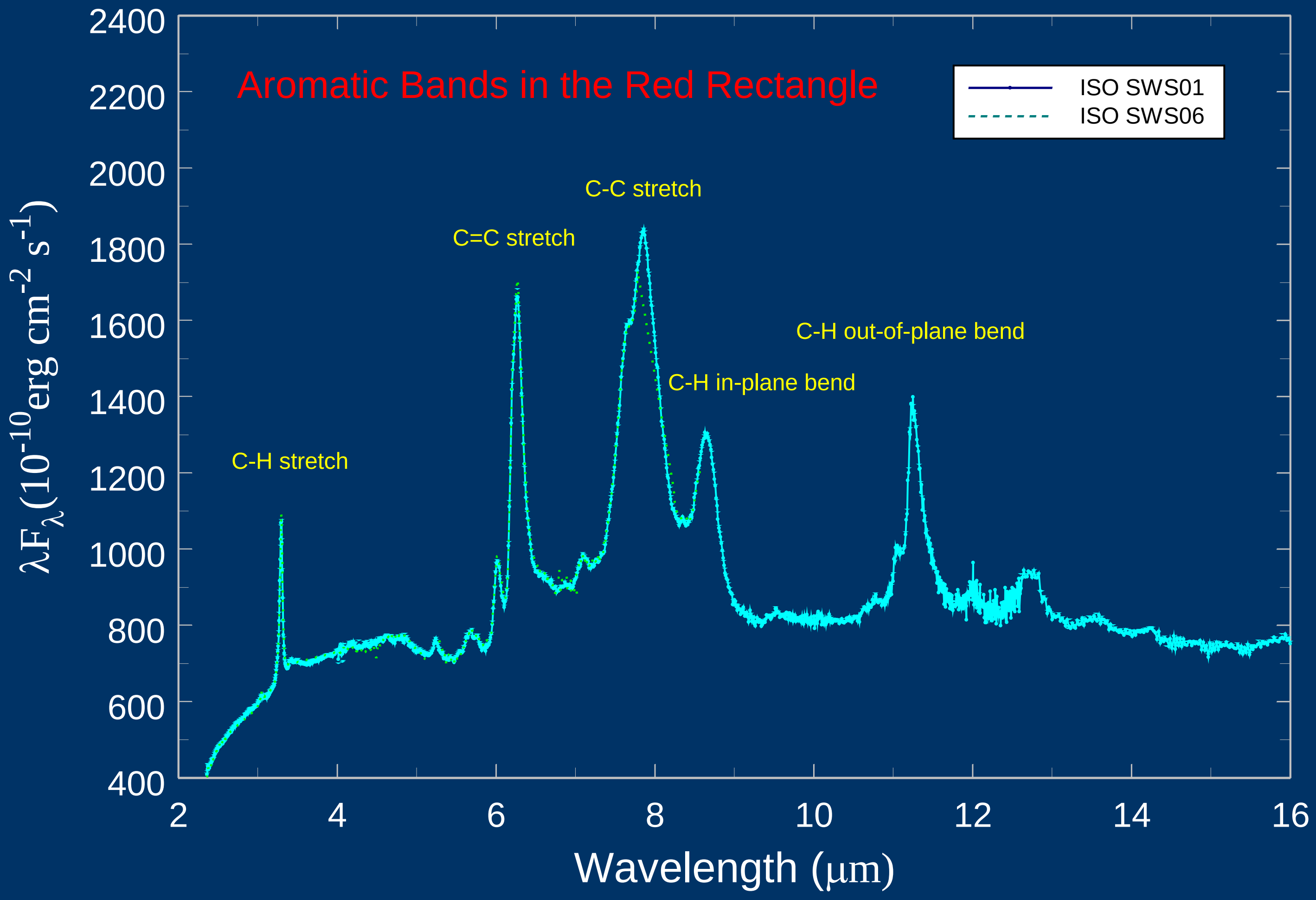


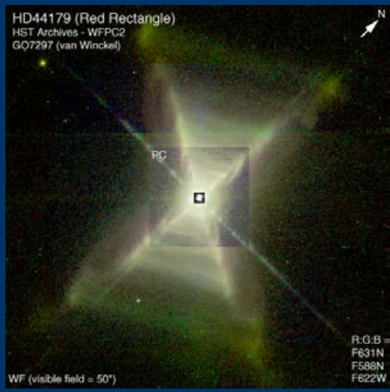
3.3: sp^2 C-H stretch
6.2: sp^2 C=C stretch
7.7: sp^2 C-C stretch
8.6: sp^2 =C-H in-plane bend
11.3: sp^2 =C-H out-of-plane bend

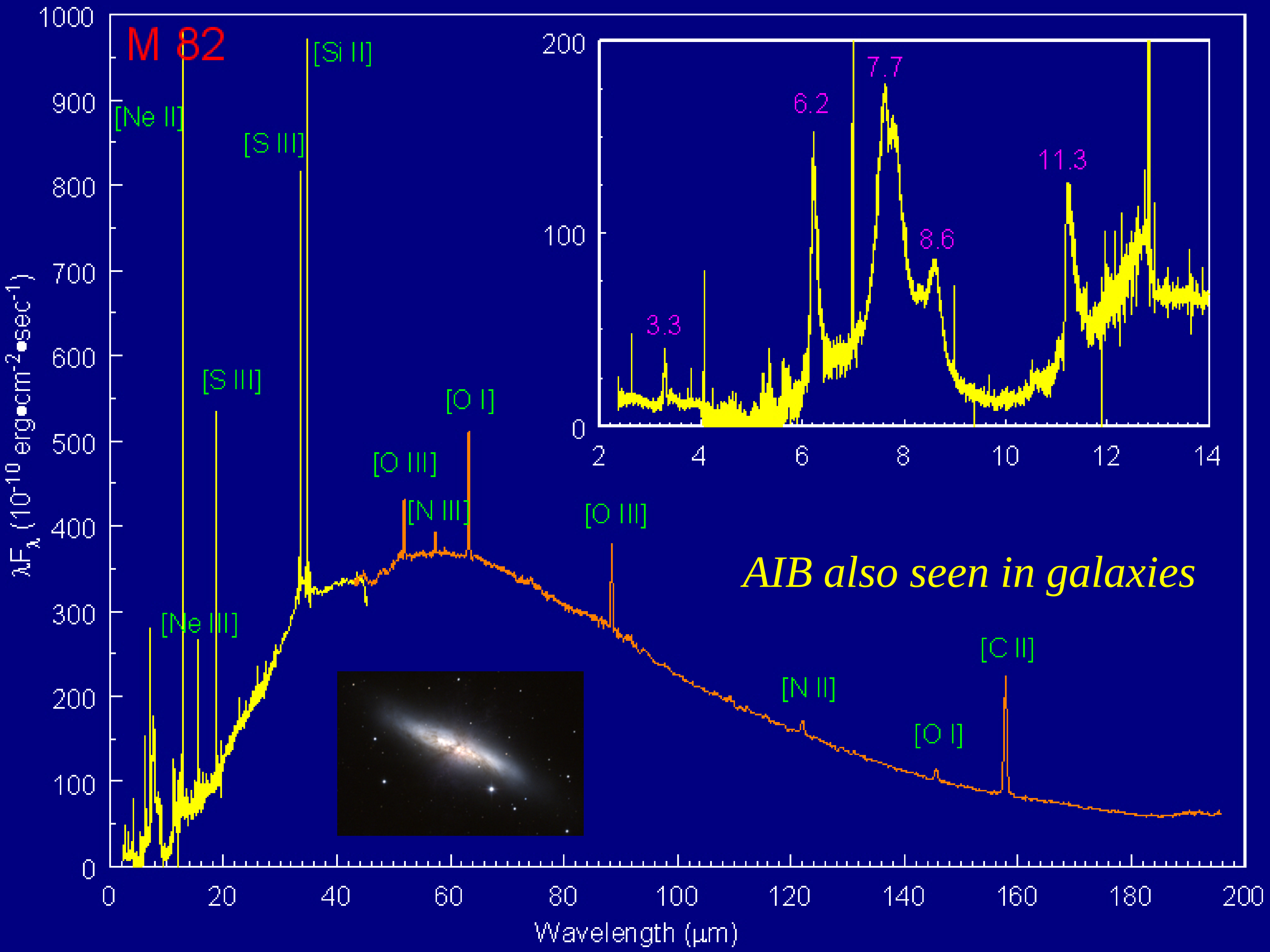
Aromatic nature first proposed by: Knacke 1977, Duley & Williams 1979, 1981; Puetter et al. 1979

Stretching and bending modes of aromatic compounds

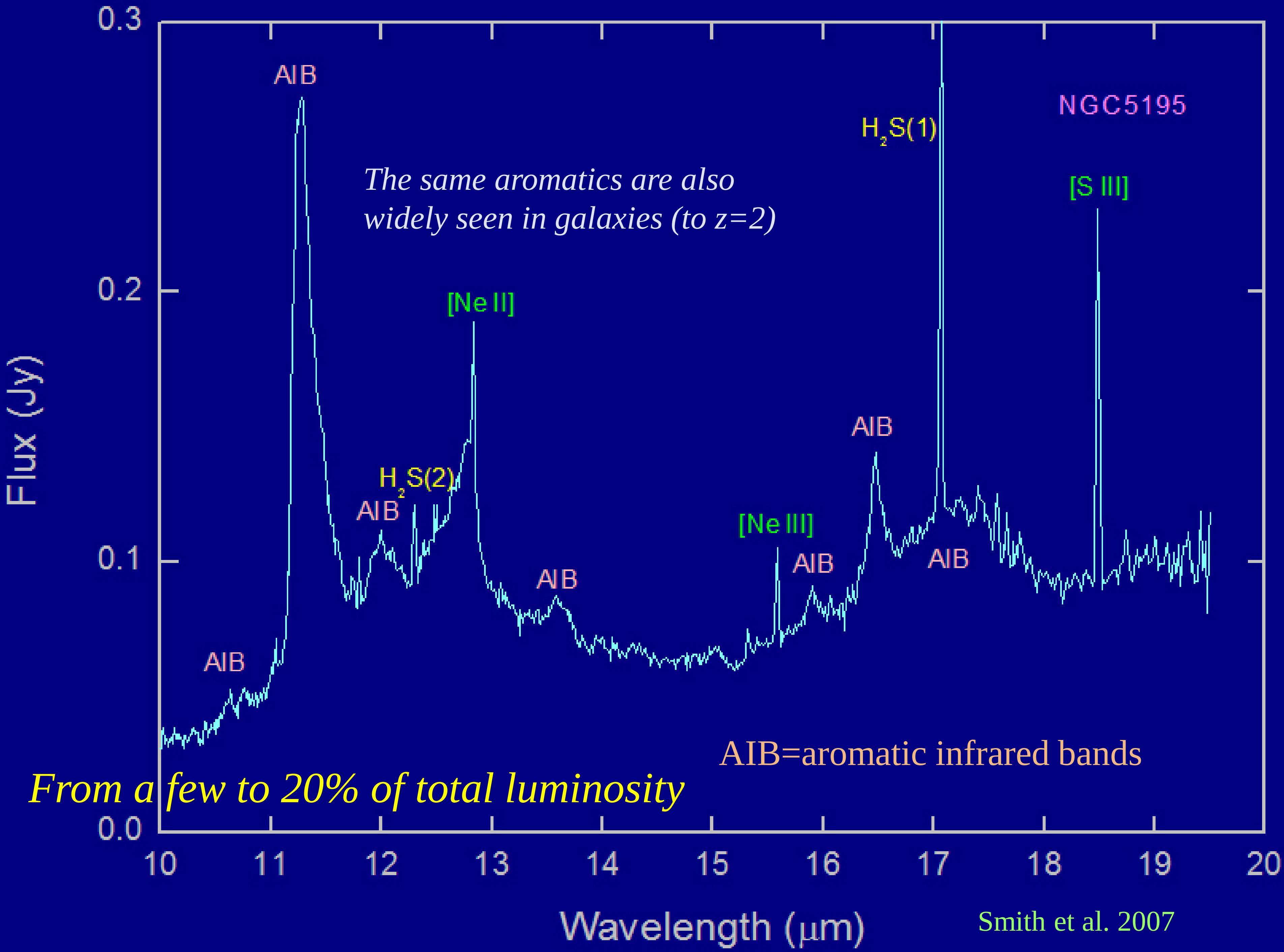
AIB seen in reflection nebulae, HII regions, diffuse ISM, and galaxies







AIB also seen in galaxies



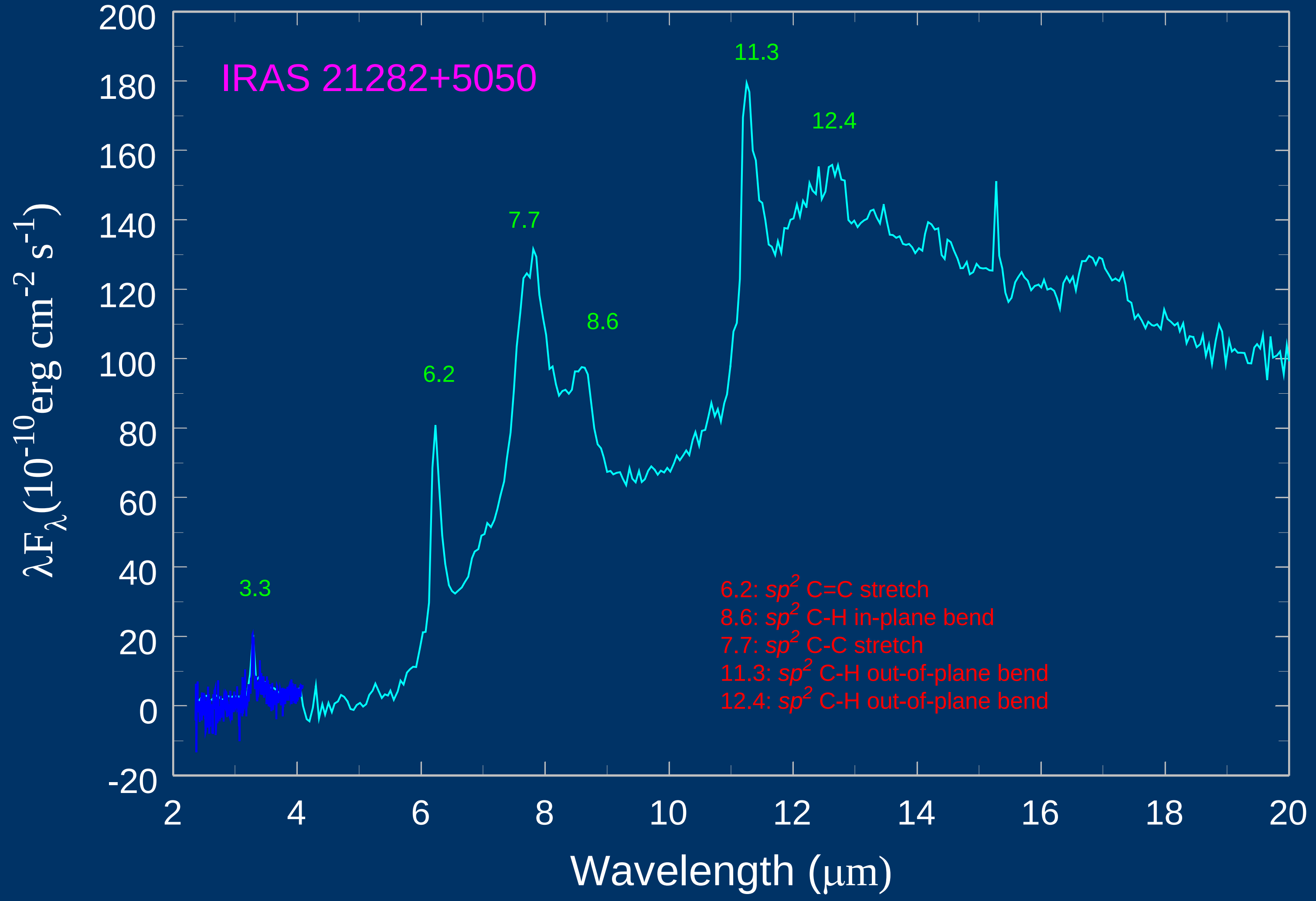
The same aromatics are also widely seen in galaxies (to z=2)

AIB=aromatic infrared bands

From a few to 20% of total luminosity

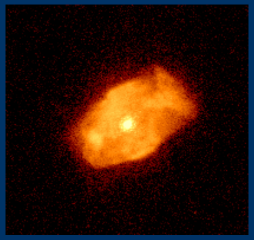
Smith et al. 2007

AIB are detected in many planetary nebulae. Since the carrier is synthesized in situ, PN are the best objects to study their origins



6.2: sp^2 C=C stretch
8.6: sp^2 C-H in-plane bend
7.7: sp^2 C-C stretch
11.3: sp^2 C-H out-of-plane bend
12.4: sp^2 C-H out-of-plane bend

A young PN



When are the aromatic compounds synthesized?

- AIB features not seen in the progenitor AGB stars (dynamical age ~10^4 yr)
- AIB features are strong in young planetary nebulae (age <10^4 yr)
- Have to study the missing link between AGB and PN phases

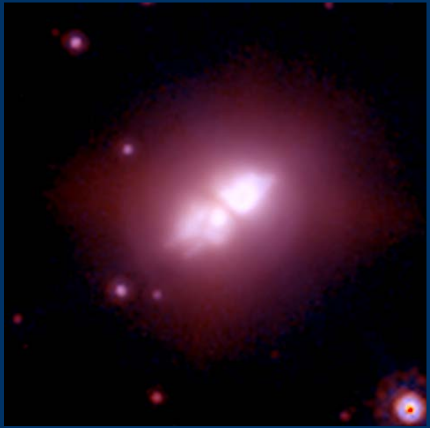
Proto-planetary nebulae

- Objects in transition between AGB and PN stages *(about several thousand years)*
- Difficult to identify because the nebulae of PPN are neutral and do not have emission lines
- ~30 PPN were discovered from their IR properties as the result of follow up of IRAS survey (Kwok 1993, *Ann. Rev. Astr. Ap.*, 31, 63)

PPN as imaged by the HST

The
Silkworm
Nebula

The Cotton
Candy
Nebula



The Walnut
Nebula

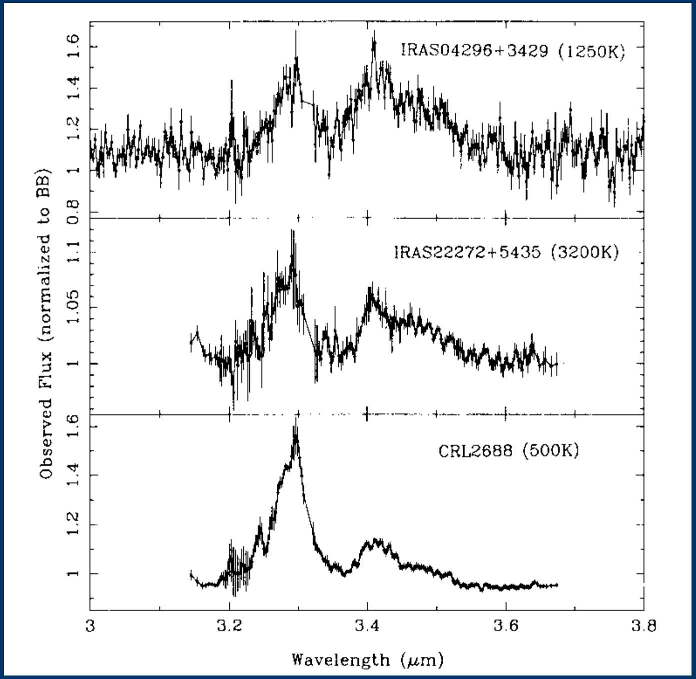
The Water
Lily Nebula

Reflected starlight, not emission!

The Spindle Nebula

3.4 μm aliphatic C-H stretch

- 3.38 μm: asymmetric CH_3
- 3.42 μm: asymmetric CH_2
- 3.46 μm: lone C-H group
- 3.49 μm: symmetric CH_3
- 3.51 μm: asymmetric CH_2

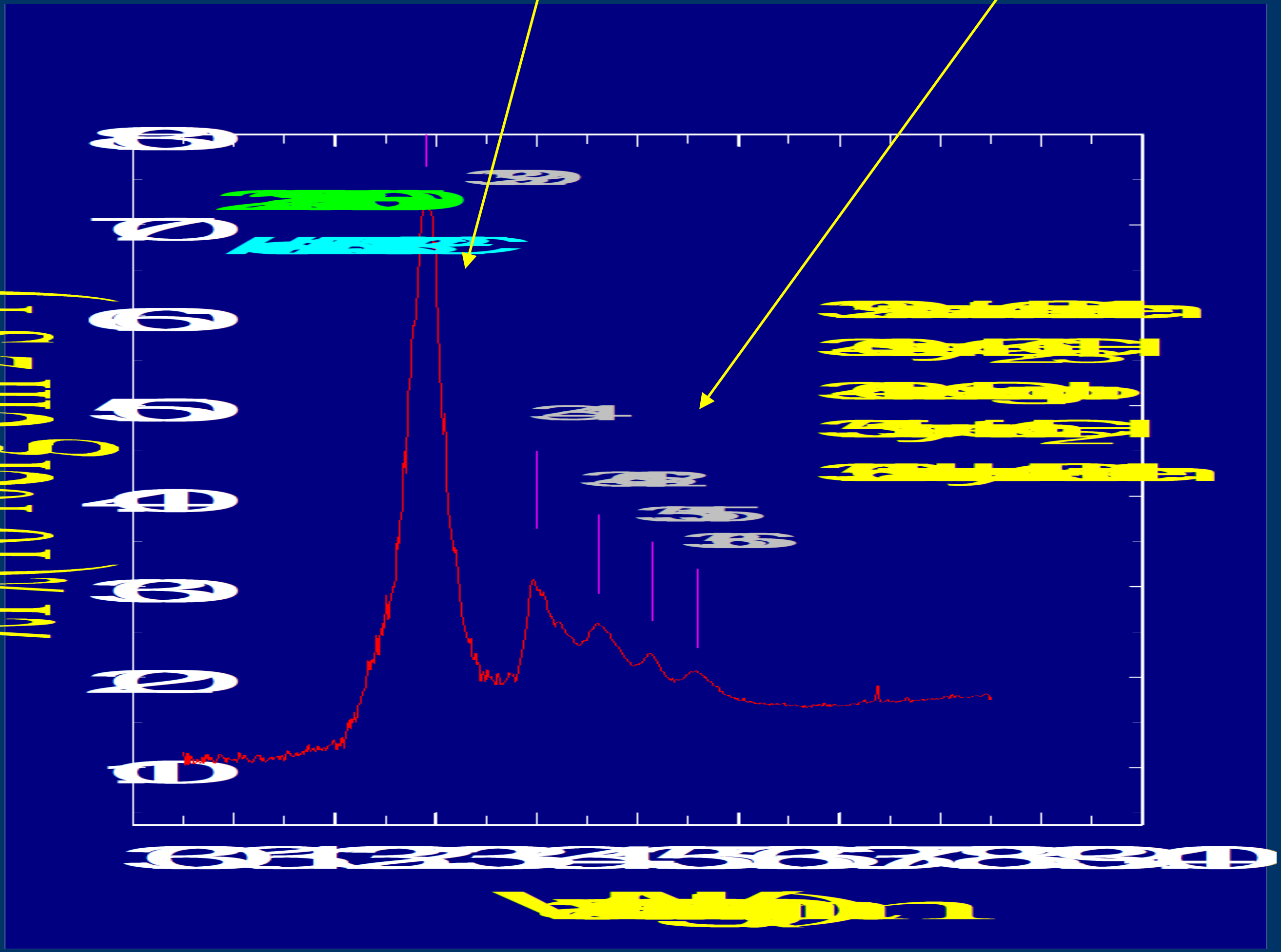


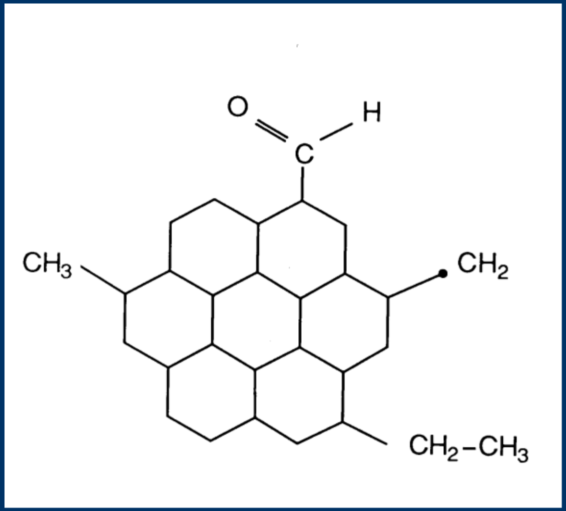
Infrared spectroscopy reveals aliphatic features

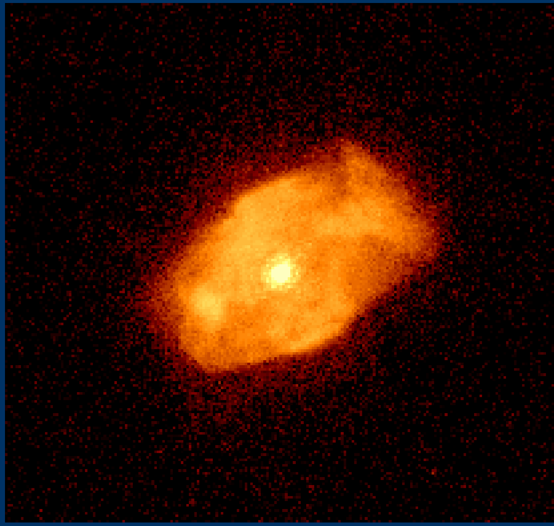
Aliphatic sidegroups

aromatic

aliphatic



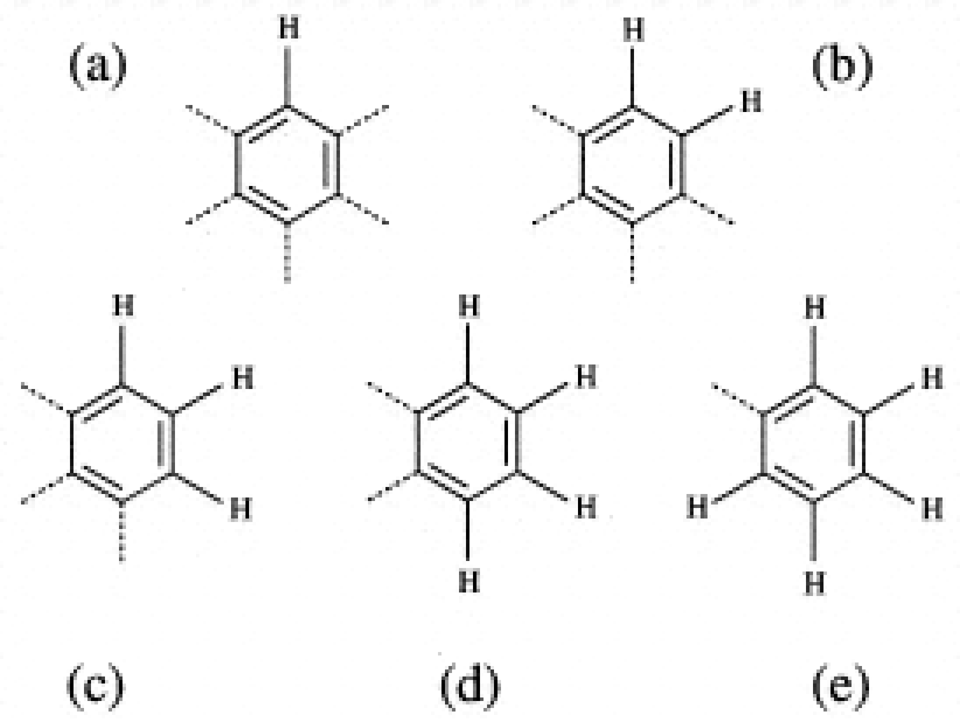




Number of CH groups in aromatic rings

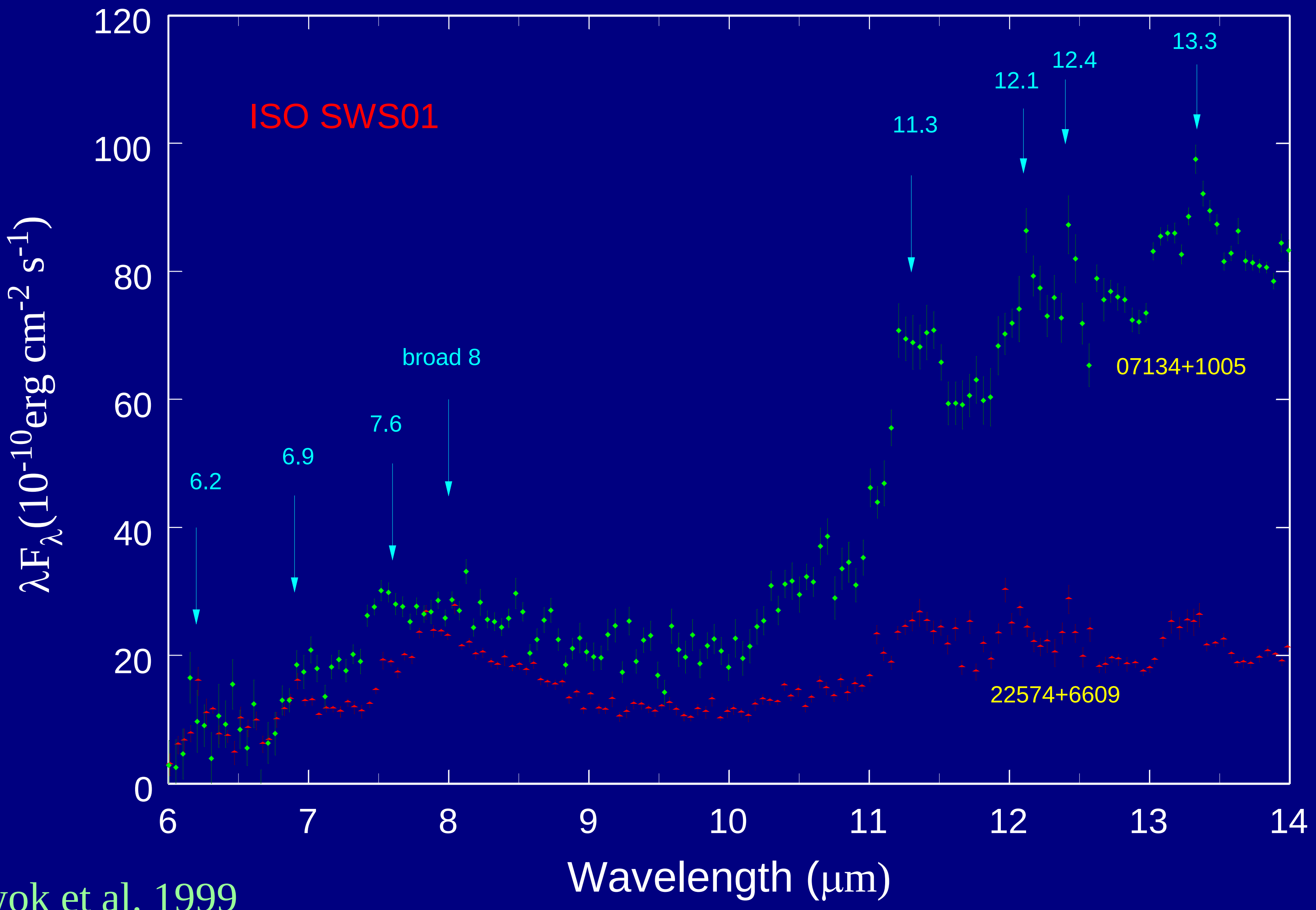
Their out of plane bending mode frequencies are different

- Solo: 11.1-11.6 µm
- Duo: 11.6-12.5 µm
- Trio:12.4-13.3 µm
- Quarto: 13-13.6 µm



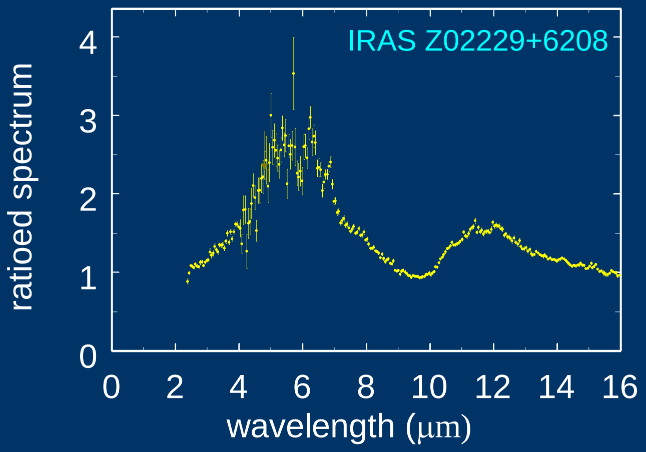
Hugdins and Allamandola 1999

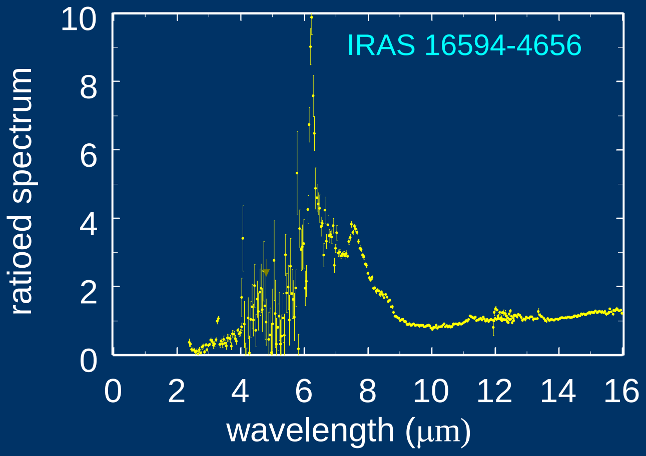
The number of rings in each aromatic unit is small

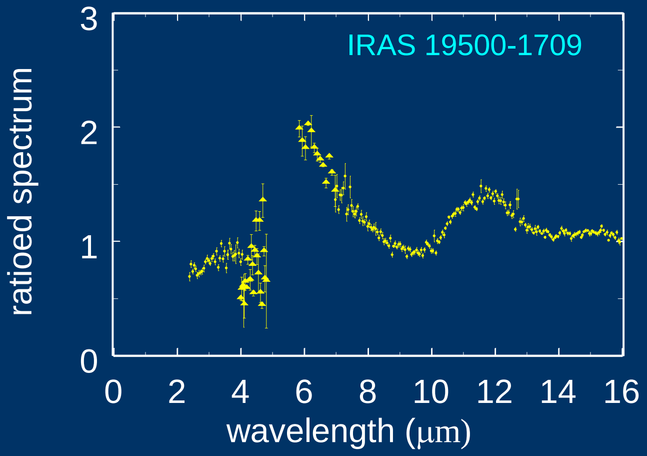


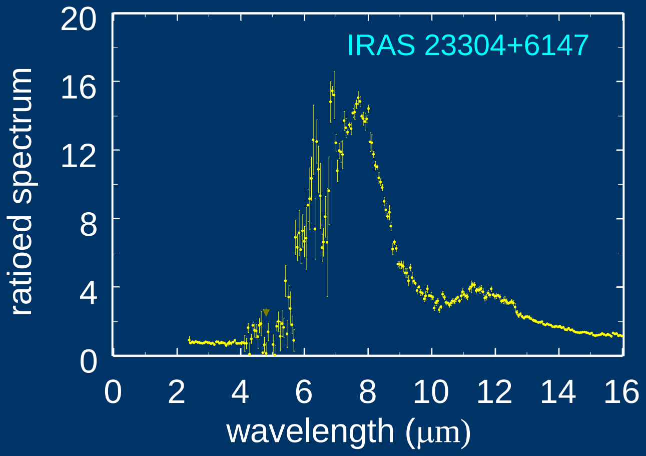
Kwok et al. 1999

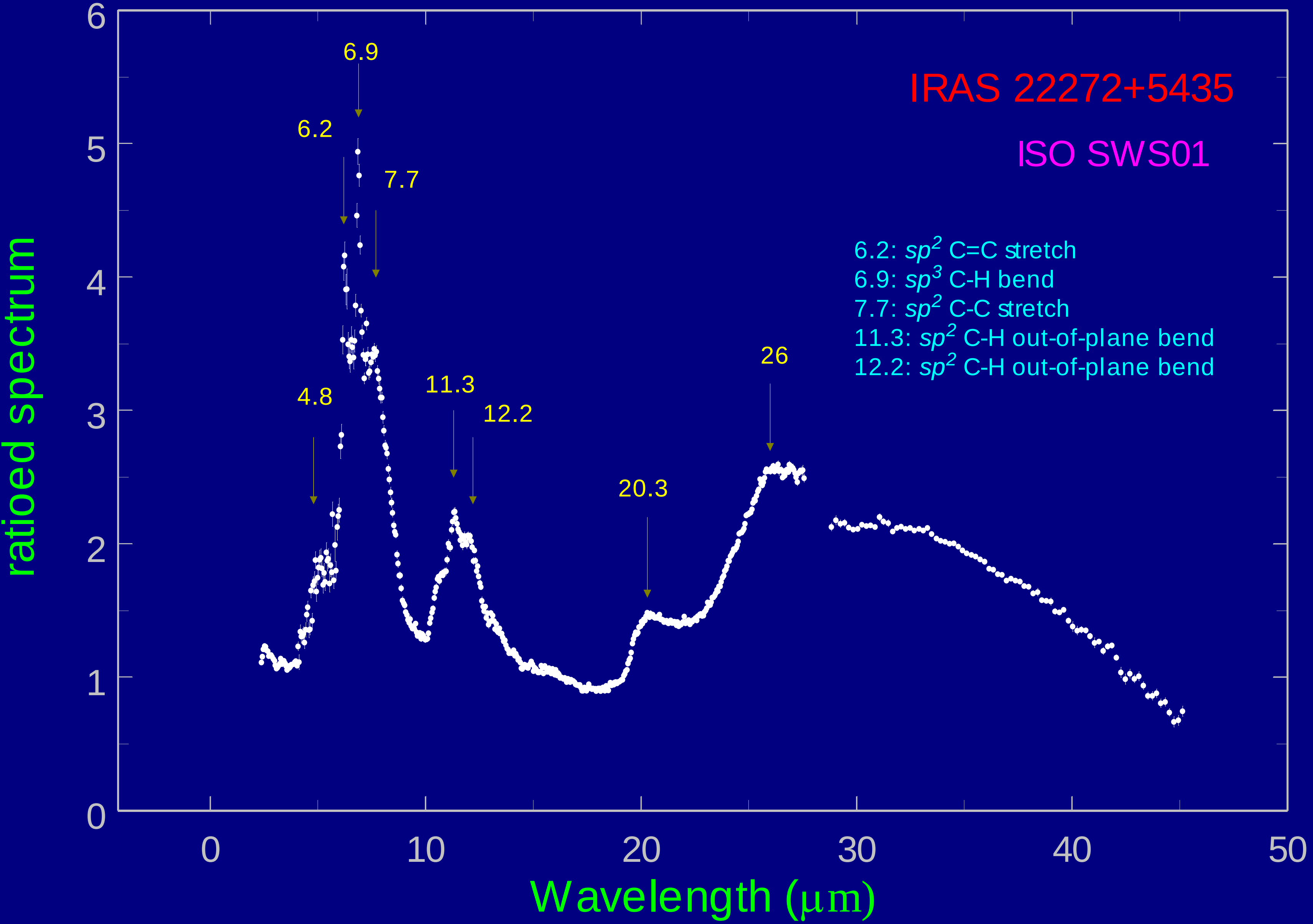
Broad emission plateaus





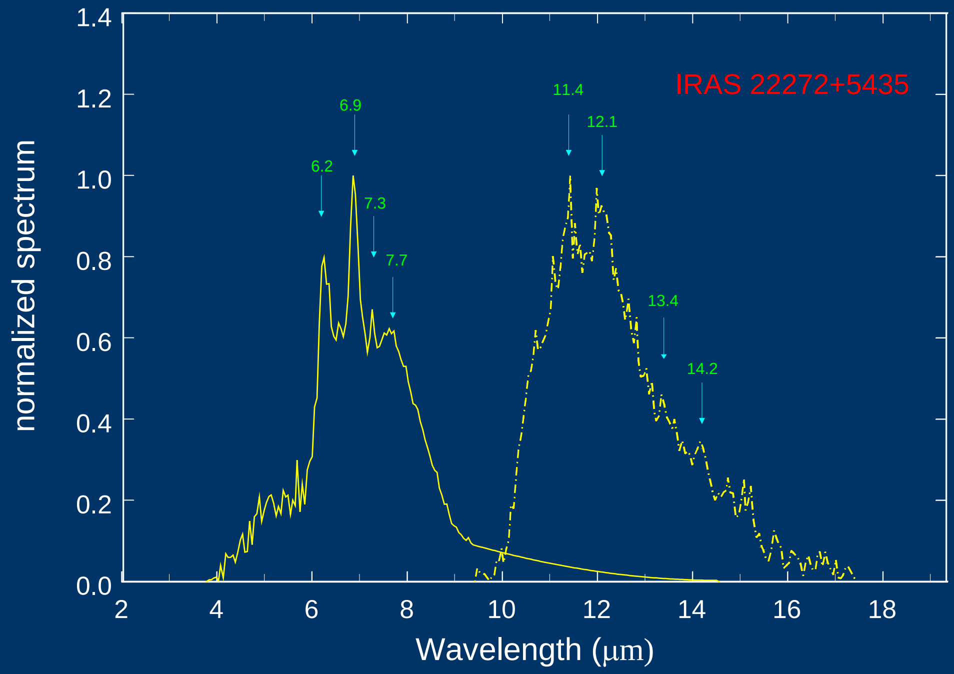


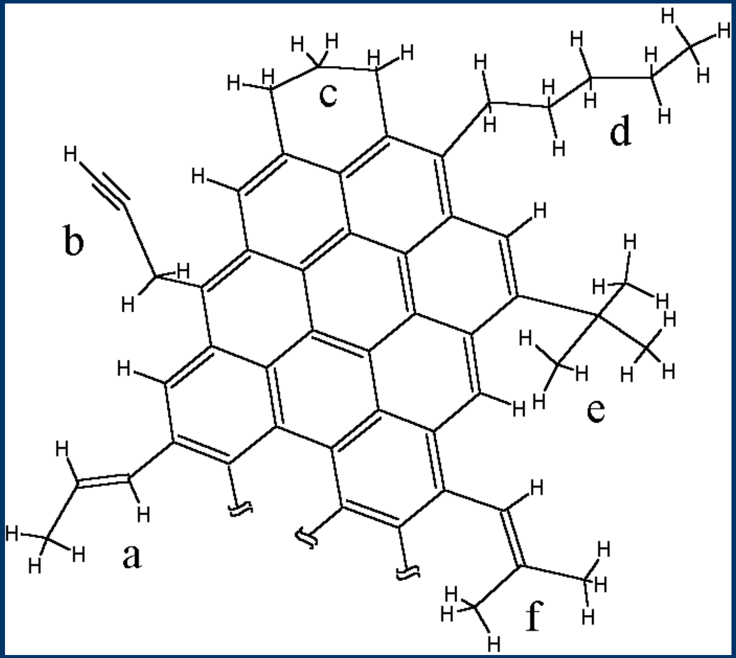




6.2: *sp*^{2} C=C stretch
6.9: *sp*^{3} C-H bend
7.7: *sp*^{2} C-C stretch
11.3: *sp*^{2} C-H out-of-plane bend
12.2: *sp*^{2} C-H out-of-plane bend

Aliphatic in-plane and out-of-plane bending modes





Kwok et al. 2001

- 8μm plateau: $-CH_3$ (7.25 μm), $-C(CH_3)_3$ (8.16 μm, “e”), $=(CH_3)_2$ (8.6 μm, “f”)
- 12 μm plateau: C-H out-of-plane bending modes of alkene (“a”, “b”), cyclic alkanes (9.5-11.5 μm, “c”), long chains of $-CH_2-$ groups (13.9 μm, “d”).

The Unidentified Infrared Emission bands phenomenon

- Aromatic features: 3.3, 6.2, 7.7, 8.6, and 11.3 μm
- Aliphatic features: 3.4 and 6.9 μm
- Features at 15.8, 16.4, 17.4, 17.8, and 18.9 μm (in PPN, Kwok et al. 1999, in reflection nebulae, Sellgren et al. 2007, in galaxies, Sturm et al. 2000)
- Broad plateau features at 8, 12, and 17 μm.

What is the chemical structure of the carrier?

The PAH hypothesis

(Allamandola et al. 1989, Puget & Léger 1989)

- the UIE features are the result of infrared fluorescence from small (~50 C atoms) gas-phase PAH molecules being pumped by far-ultraviolet photons (Tielens 2008, *Ann. Rev. Astr. Ap.*, **46**, 289)
- The central argument for the PAH hypothesis is that single-photon excitation of PAH molecules can account for the 12 μm excess emission observed in cirrus clouds in the diffuse interstellar medium by *IRAS* (Sellgren 1984, 2001).

Problems with the PAH model

- PAH molecules have well-defined sharp features but the UIE features are broad
- PAHs primarily excited by UV, with little absorption in the visible, but UIE features are seen in PPN and reflection nebulae with no UV radiation
- The strong and narrow predicted gas phase features in the UV are not seen in interstellar extinction curves → upper limits of 10^{-10}-10^{-8} (Clayton et al. 2003, Salama et al. 2011, Gredel et al. 2011)
- No specific PAH molecules have been detected in spite of the fact that the vibrational and rotational frequencies are well known

Expected from IR: $3x10^{-7}$ (Tielens 2008)

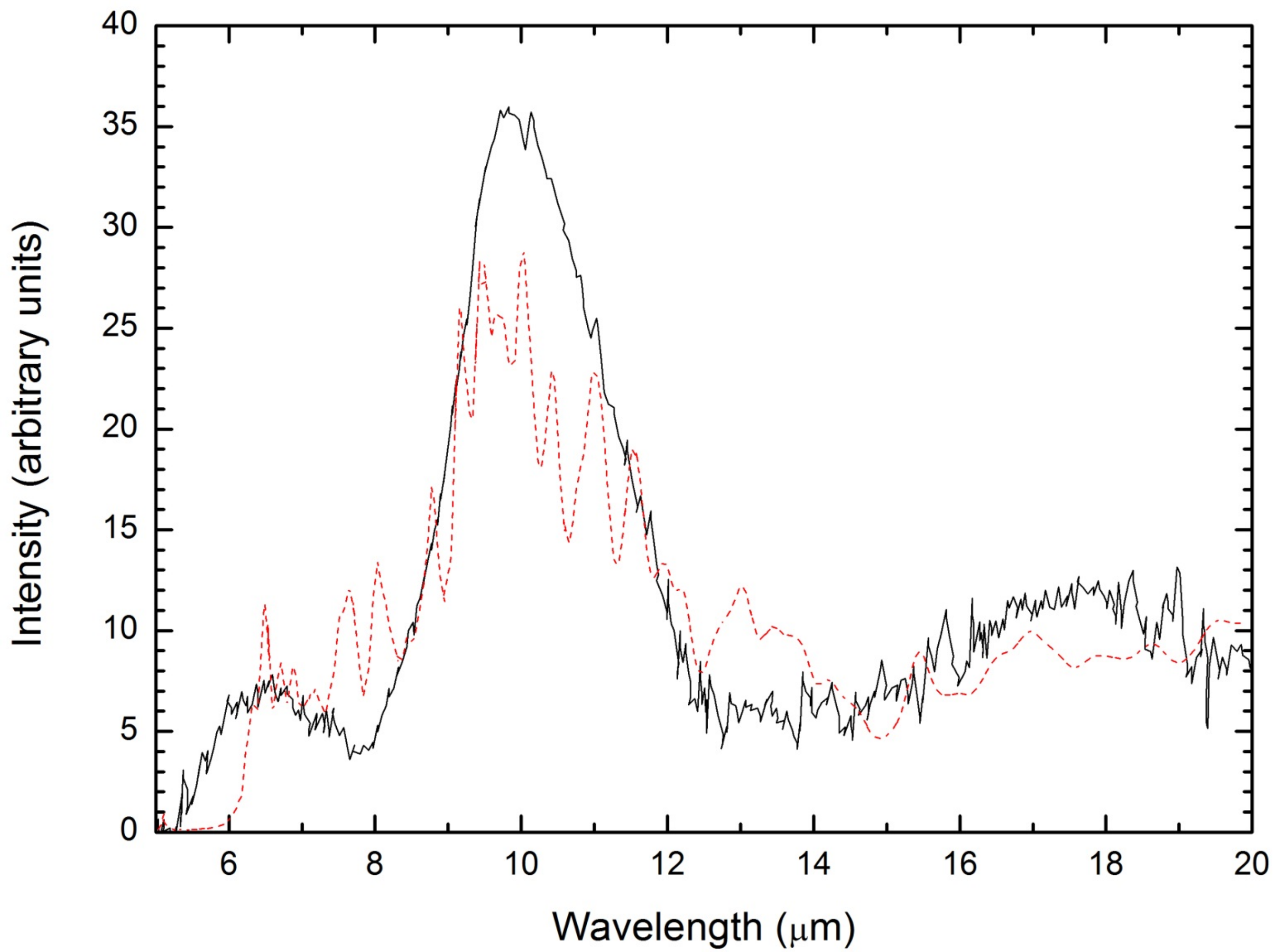
Problems with the PAH model

- “No PAH emission spectrum has been able to reproduce the UIE spectrum w.r.t. either band positions or relative intensities” (Schlemmer et al. 1994, Cook et al. 1996, Cook & Saykally 1998, Wagner et al. 2000)
- The shapes and peak wavelengths of UIE features are independent of temperature of exciting star
- In order to fit the astronomical observations, the PAH model has to appeal to a mixture of PAH of different sizes, structures (compact, linear, branched) and ionization states, as well as artificial broad intrinsic line profiles (Cami 2011).

Fitting of UIE by PAHs

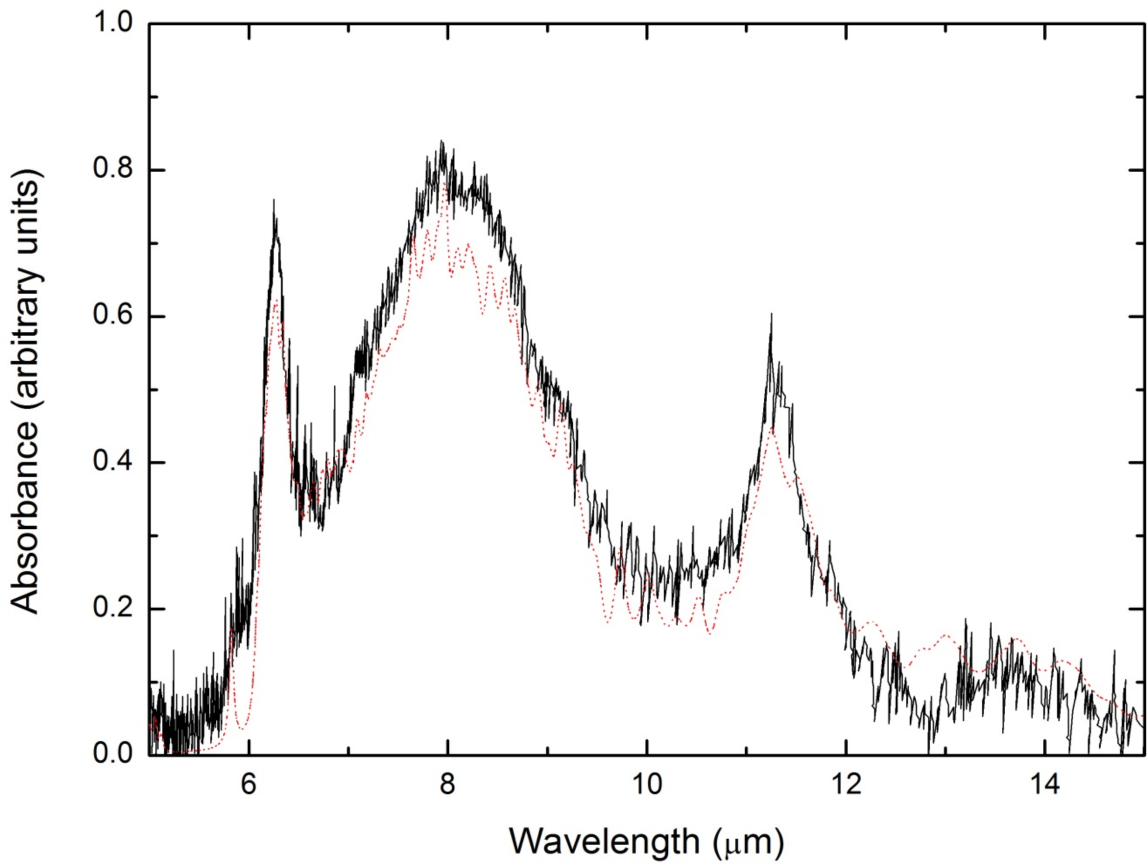
- NASA Ames PAH database and fitting routines (Boersma et al. 2014).
- 700 computational and 75 experimental spectra of PAH molecules and ions.
- Size range from 6 to 384 C atoms
- Charged states: neutral, anion (–), and cations (+ , ++, and + + +).

silicates

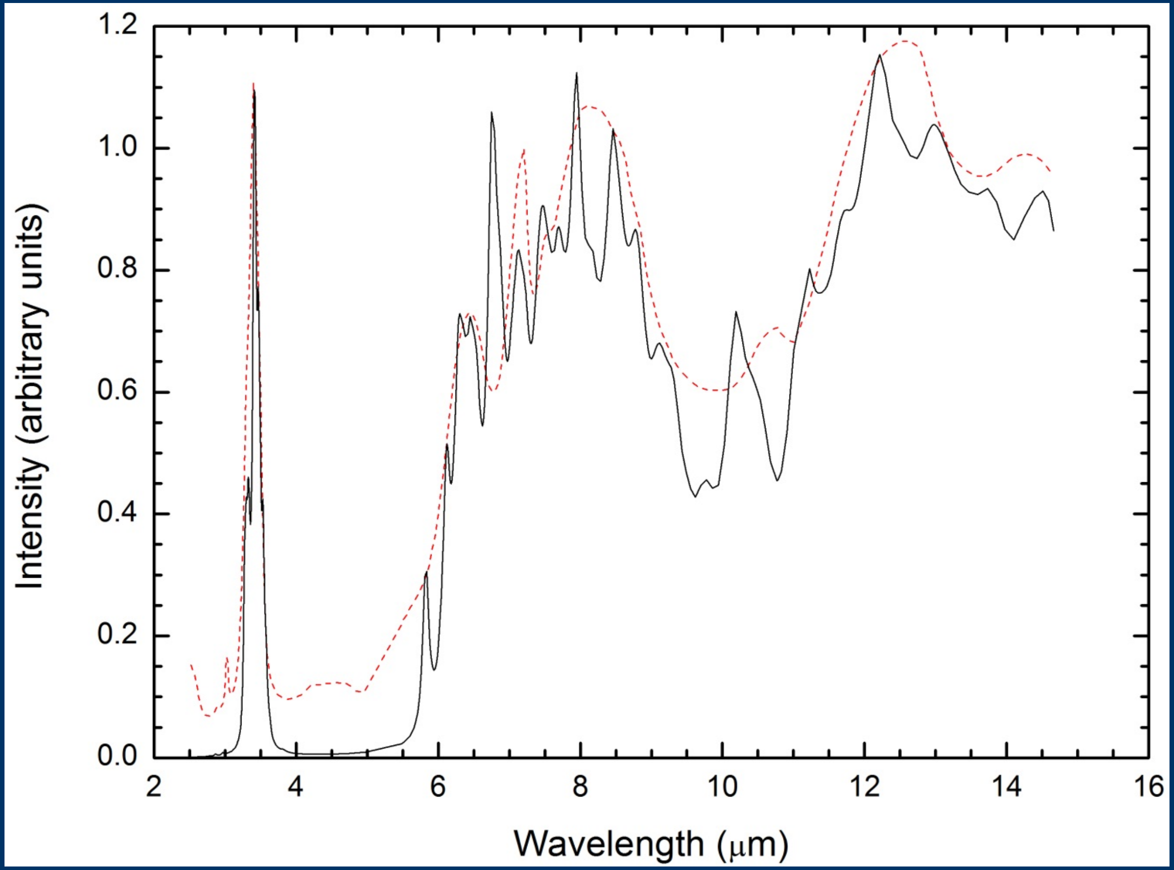


Intensity (arbitrary units)
0
5
10
15
20
25
30
35
40
6
8
10
12
14
16
18
20
Wavelength (μm)

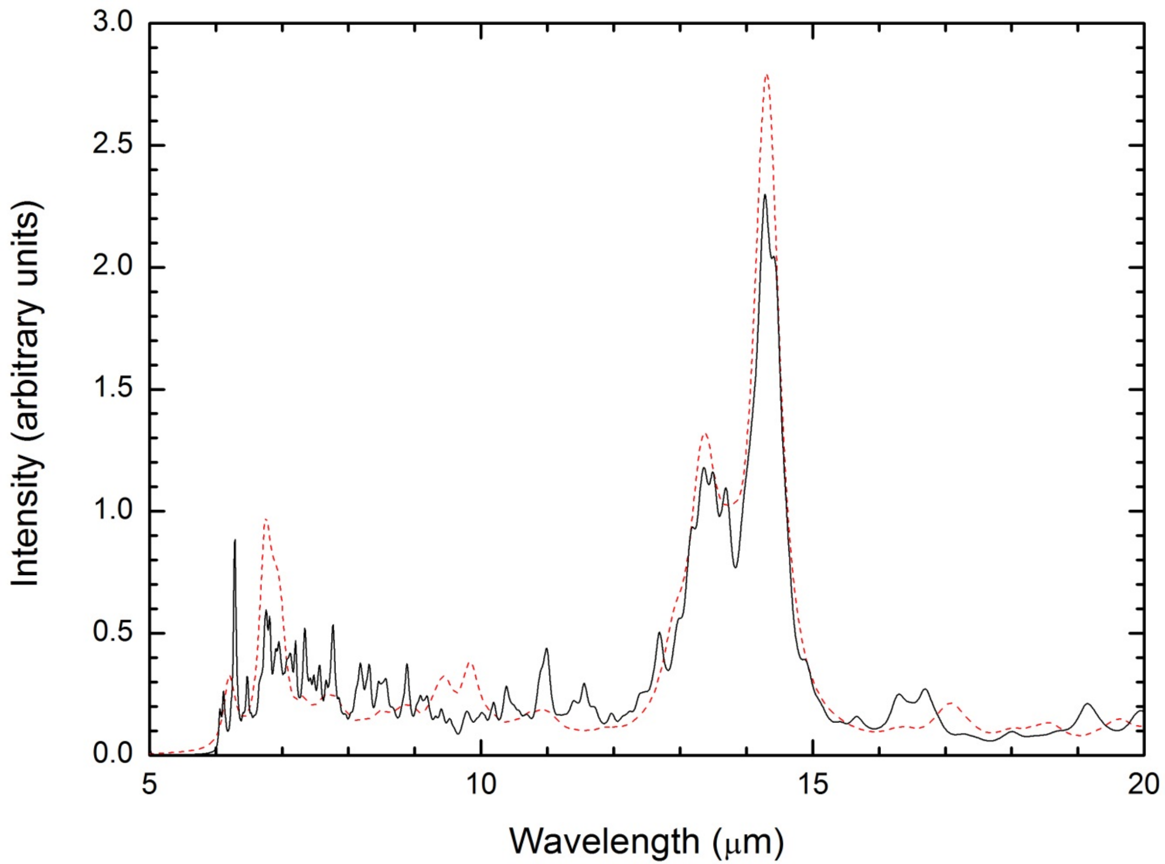
Coal

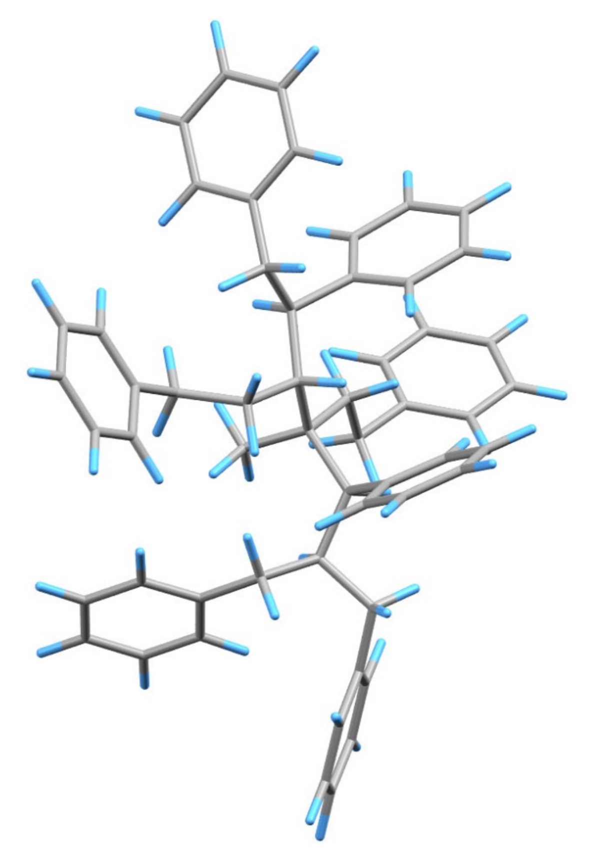

1.0
0.8
0.6
0.4
0.2
0.0
Absorbance (arbitrary units)
6
8
10
12
14
Wavelength (μm)

Hydrogenated Amorphous Carbon



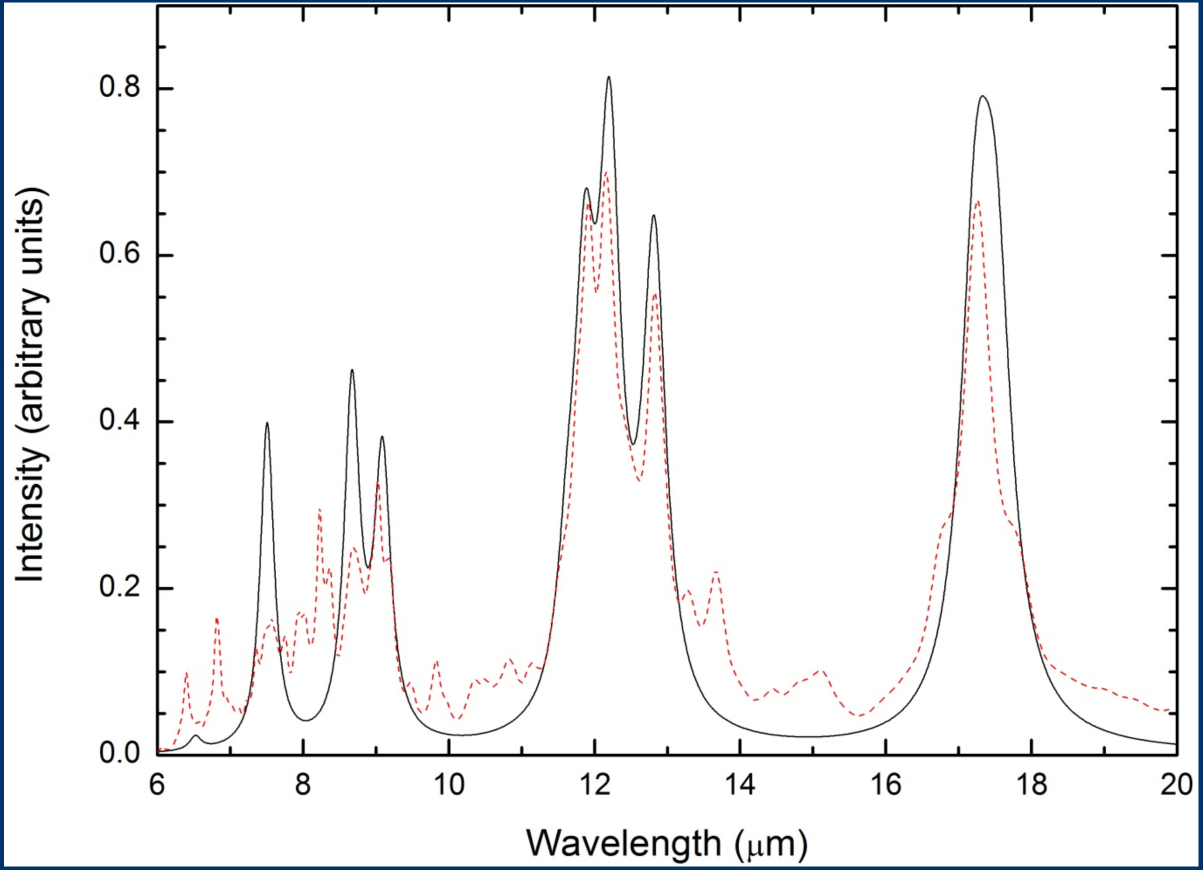
$C_{55}H_{56}$



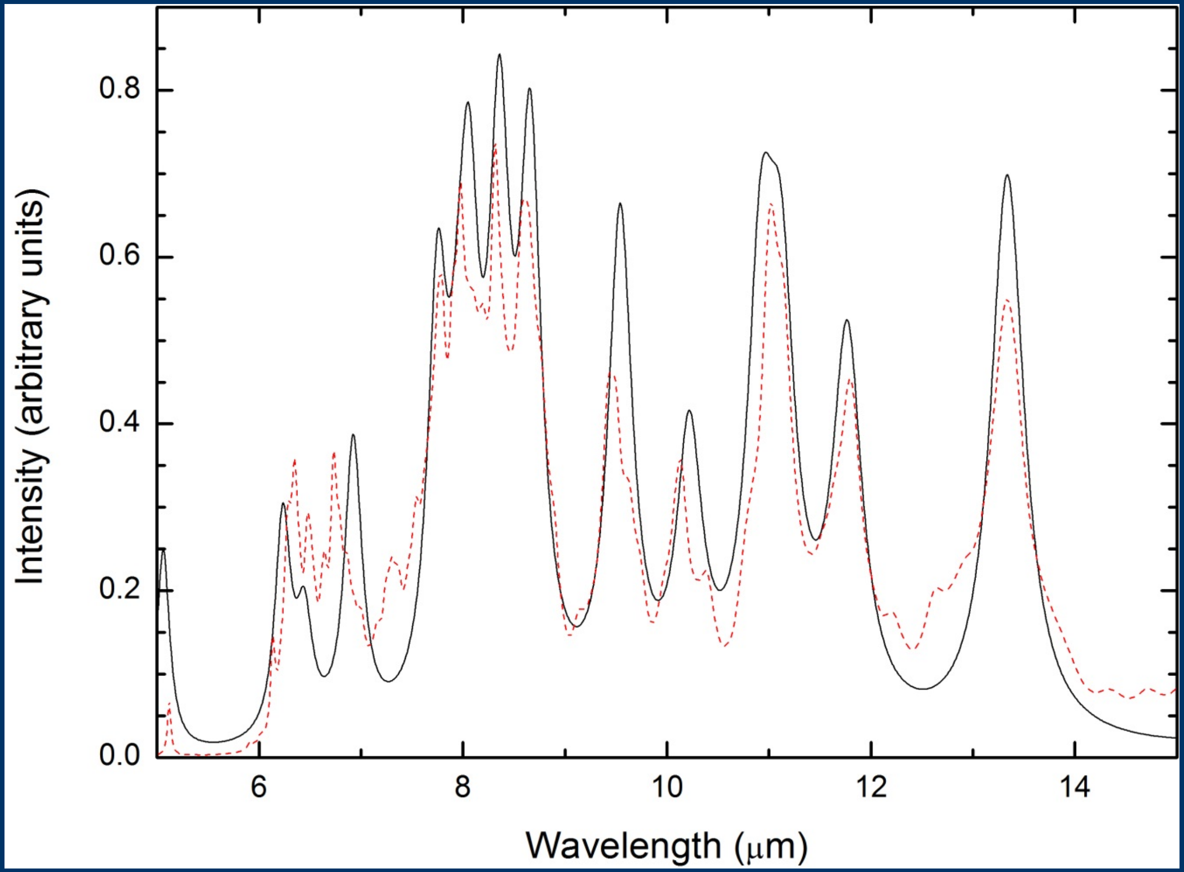


Zhang and Kwok 2015, ApJ, 798, 37

5 artificial features



10 Artificial features

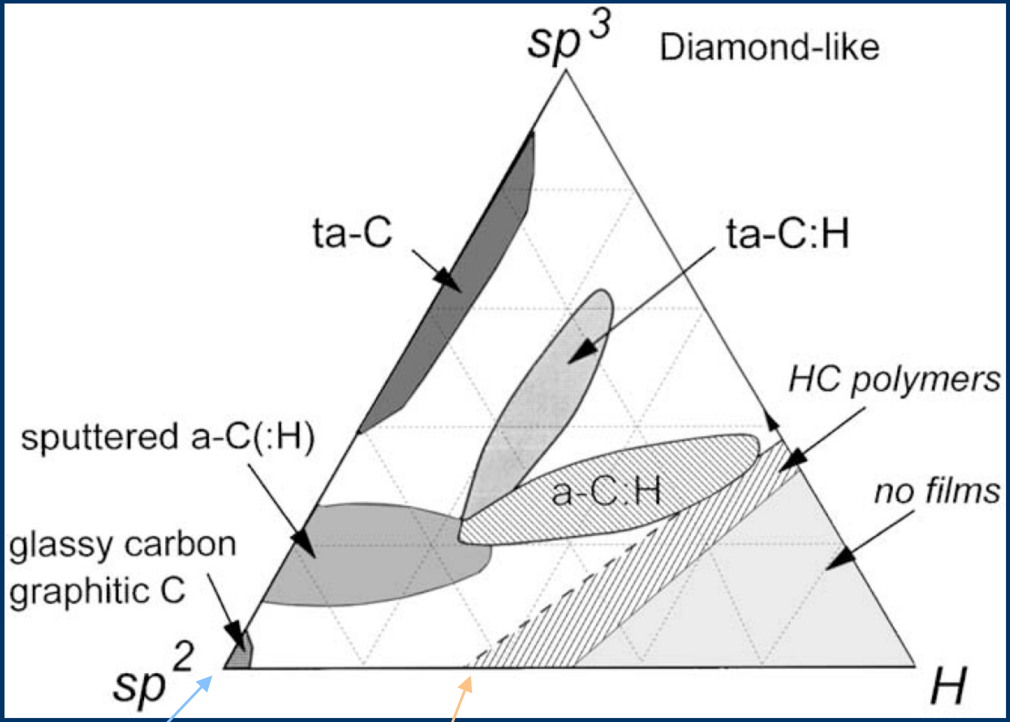


The PAH database model can fit anything!

If not PAH, then what is it?

Amorphous carbonaceous solids

- By introducing H into graphite (*sp*^{2}) and diamond (*sp*^{3}), a variety of amorphous C-H alloys can be created
- Geometric structures of different long- and short-range can be created by varying the aromatic to aliphatic ratio
- Different *sp*^{2}/*sp*^{3} hybridization ratios, mixed hybridization states



Robertson 2002

graphite

PAH

Laboratory synthesis of carbonaceous solids

- Microwave irradiation of plasma of 4-torr methane (Sakata et al. 1987, Godard et al. 2011)
- Hydrocarbon flame or arc-discharge in a neutral of hydrogenated atmosphere (Colangeli et al. 1995, Mennella et al. 2003)
- laser ablation of graphite in a hydrogen atmosphere (Scott and Duley 1996, Mennella et al. 1999, Jäger et al. 2008)
- Infrared laser pyrolysis of gas phase molecules (C_2H_4, C_4H_6)$\Rightarrow$C-based nanoparticles (Herlin et al. 1998)
- Photolysis of methane at low temperatures (Dartois et al. 2004)
- Flame combustion forming soot (Pino et al. 2008, Carpentier et al. 2012) (C_2H_2, C_2H_4, C_3H_6 mixed with O_2)

The simplest example: Hydrogenated Amorphous Carbon

- Aromatic rings of various sizes bonded peripherally to polymeric of hydrocarbon species
- A mixture of sp^2 and sp^3 bonded carbon
- Formed when H content exceeds 0.1 relative to C
- Similar to soot formed from the combustion of hydrocarbons

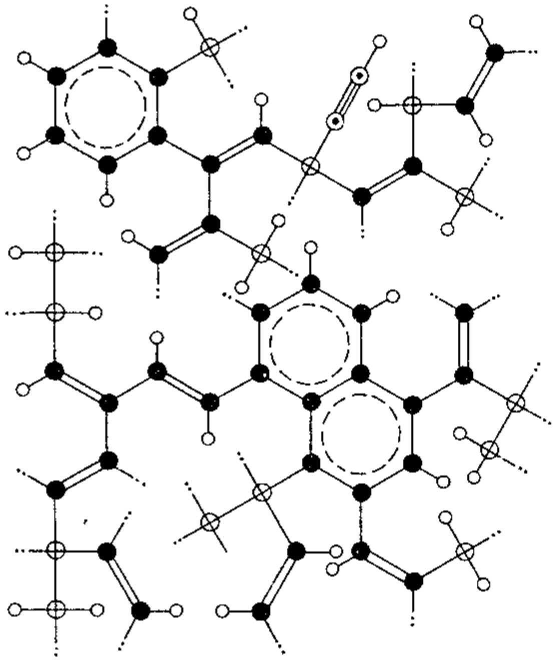
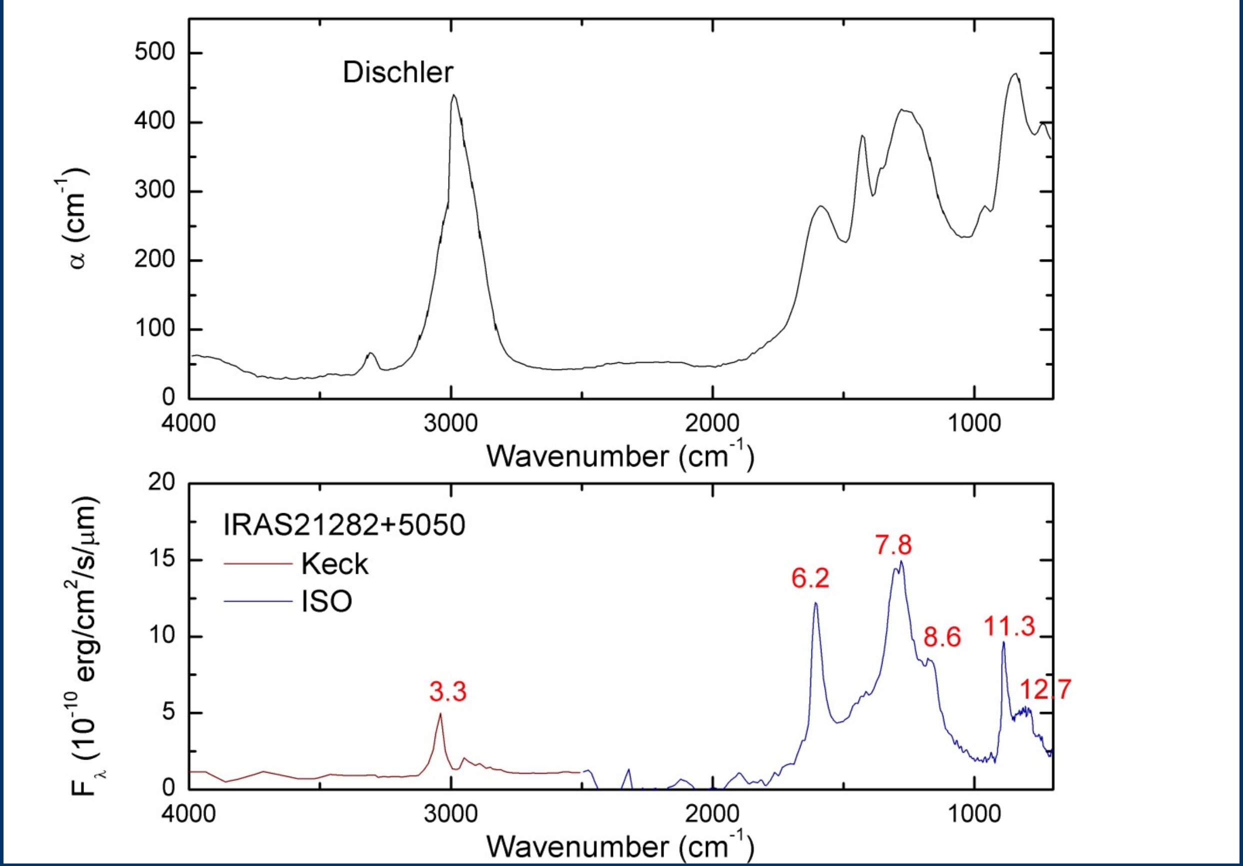


FIG. 1. Schematic diagram illustrating types of carbon atom bonding in HAC; sp^1 (circled dots), sp^2 (filled circles), sp^3 (circled crosses) and hydrogen atoms (open circles). Double dots indicate bonding to other atoms (not shown) or rare dangling bonds.

Jones, Duley, Williams 1990

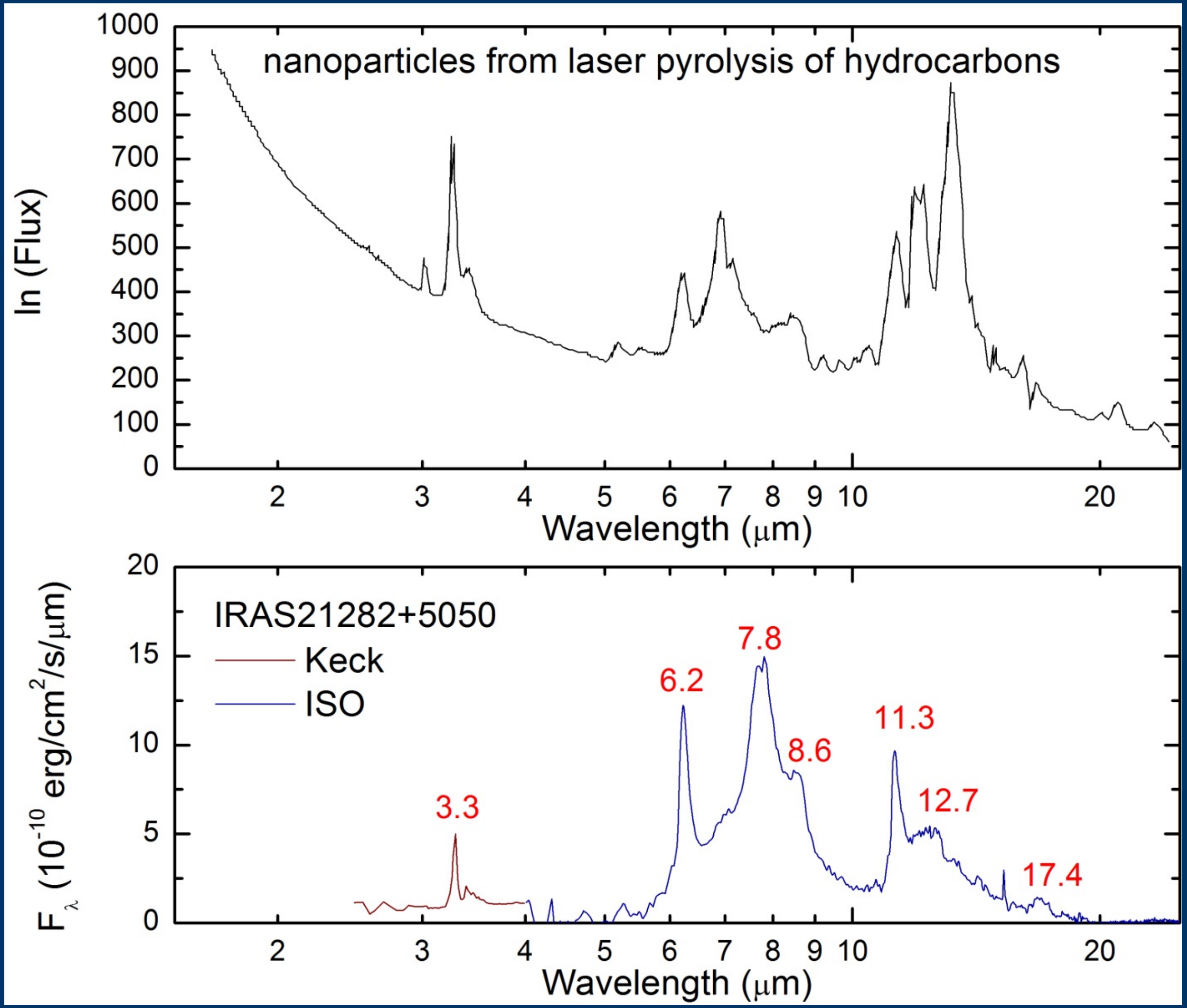
Natural products of combustion

- Soot: combustion of hydrocarbon molecules in a flame
- Islands of aromatic rings connected by aliphatic chains (Chung & Violi 2011)
- Sidegroups: methyl ($-CH_3$), methylene ($-CH_2$), carbonyl ($C{=}O$), aldehydic ($-HCO$), phenolic ($-OH$), and amino ($-NH_2$) (Pino et al. 2008)
- Similar processes at work in carbon-rich circumstellar envelopes

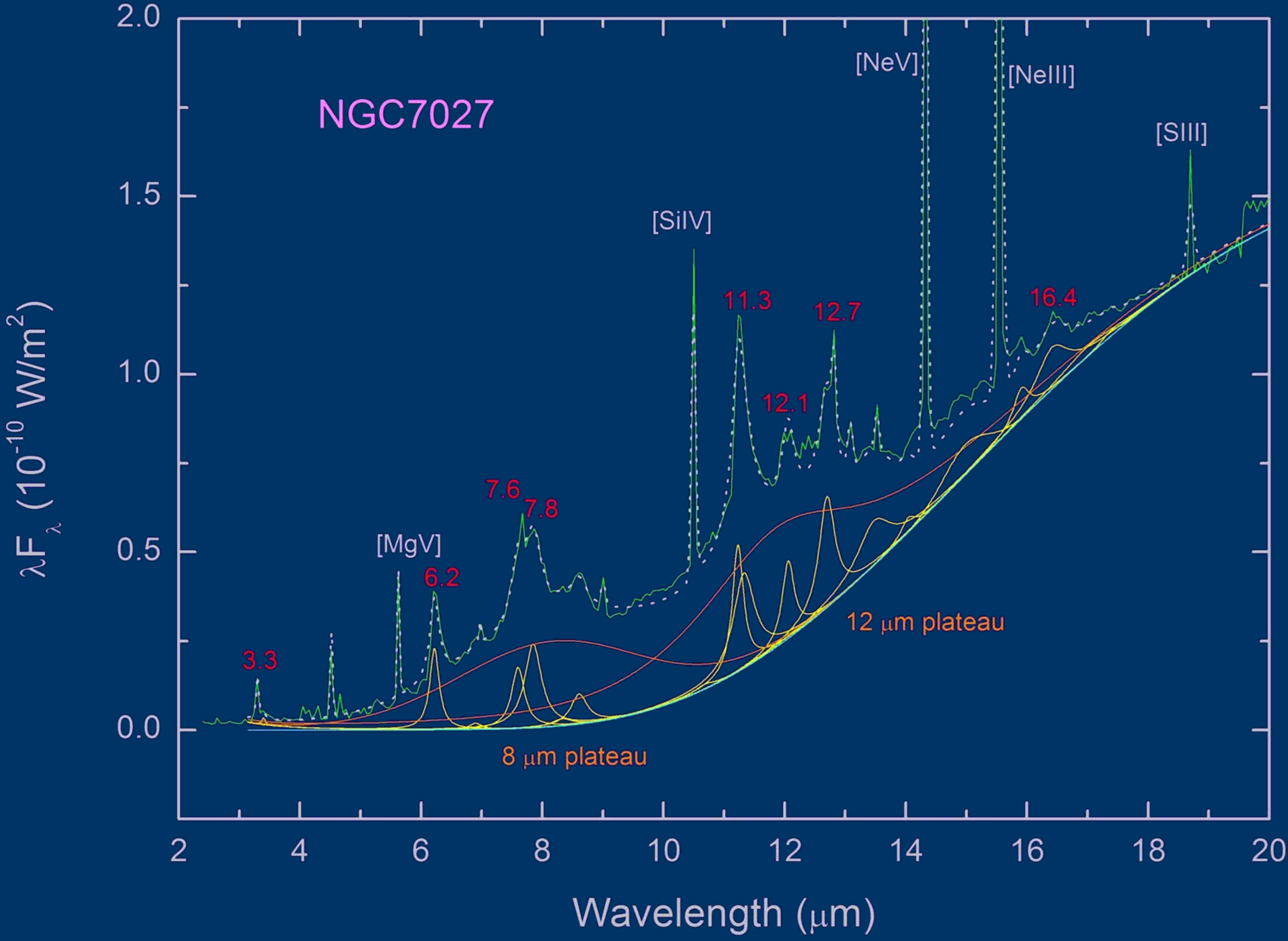


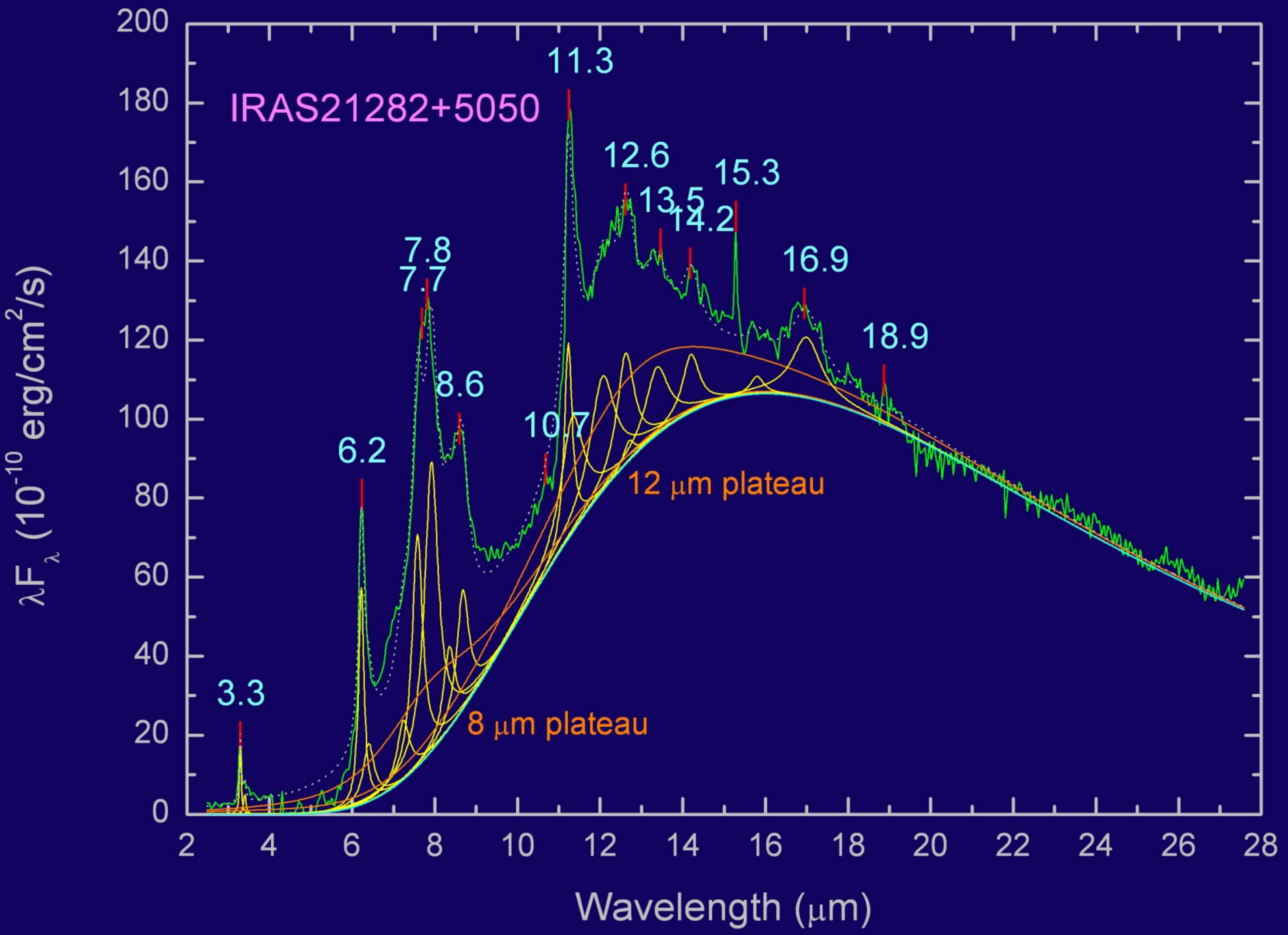
Band profiles naturally broad

Laboratory infrared spectra of hydrogenated amorphous carbon (top, Dischler 1983) compared to the astronomical spectrum of the planetary nebula IRAS 21282+5050.

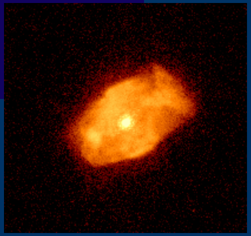


Comparison of the laboratory spectrum of nanoparticles produced by laser pyrolysis of hydrocarbons (Herlin et al. 1998) (top panel) with the astronomical spectrum of the planetary nebula IRAS 21282+5050 .

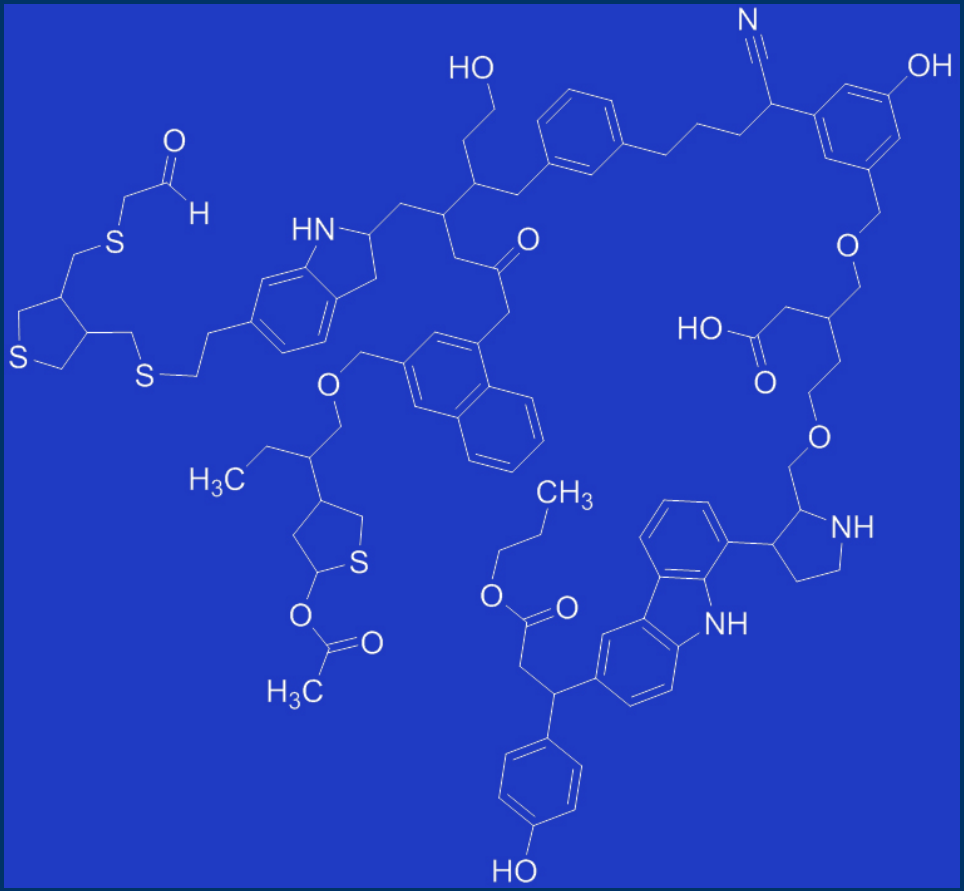

NGC7027
[NeV]
[NeIII]
[SIII]
[SiIV]
11.3
12.7
16.4
12.1
7.6
7.8
[MgV]
6.2
3.3
12 μm plateau
8 μm plateau
2.0
1.5
1.0
0.5
0.0
2
4
6
8
10
12
14
16
18
20
λF_λ (10^{-10} W/m^2)
Wavelength (μm)



Flux (2.4-27.6 μm): continuum 65%, AIB: 13%, aliphatic 17%



Mixed aromatic/aliphatic organic nanoparticles (MAON) as a component of interstellar dust



Complex organic solids with disorganized structures

- *Small units of aromatic rings linked by aliphatic chains*
- *Impurities of O, N, S*
- *A typical nanoparticle may contain multiple of this structures*

Kwok & Zhang 2011, *Nature*, **479**. 80
Kwok & Zhang 2013, *ApJ*, **771**, 5

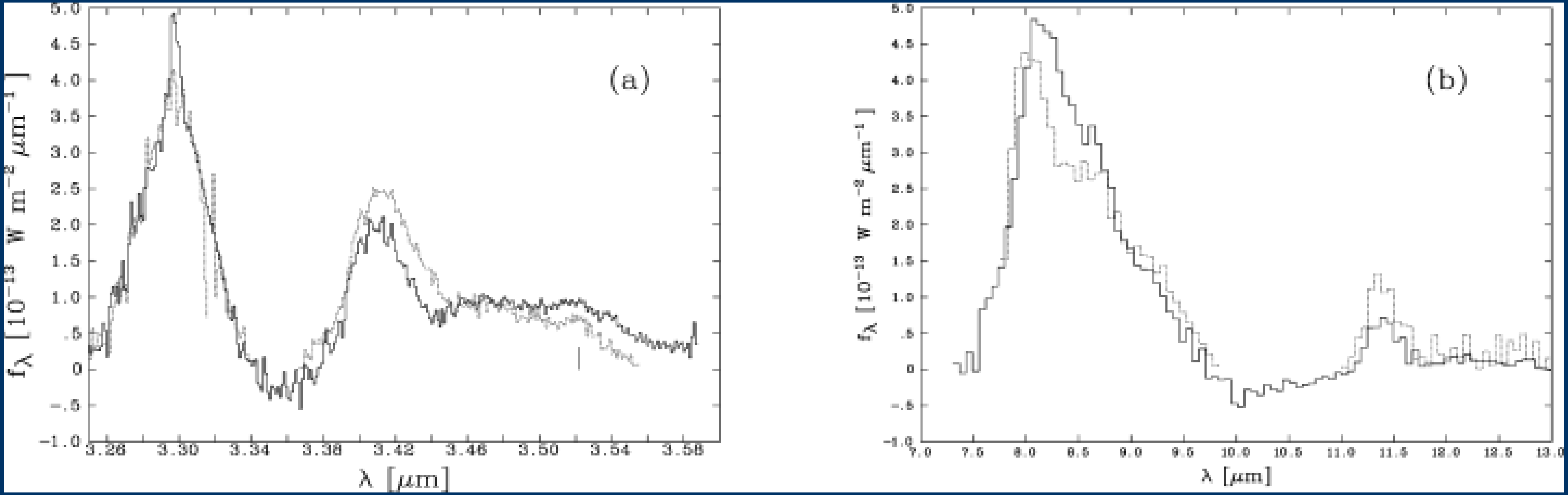
Properties of MAON

- Amorphous (no fixed structure)
- Contains rings of different sizes and chains of different lengths and random orientations
- Contains impurities
- 3-D (not 2-D)
- Exact aromatic to aliphatic ratio depends on radiation environment (photochemistry), original gas-phase components, and H content

How do they form?

- Surface temperature of red giants: 3000 degrees
- Solid grains condensed from gas in the stellar wind under near vacuum conditions
- Theoretically impossible, especially during the PPN phase
- Observationally we see aliphatics and aromatics form in PPN on time scales as short as hundreds of years
- In novae, they form on a time scale of days

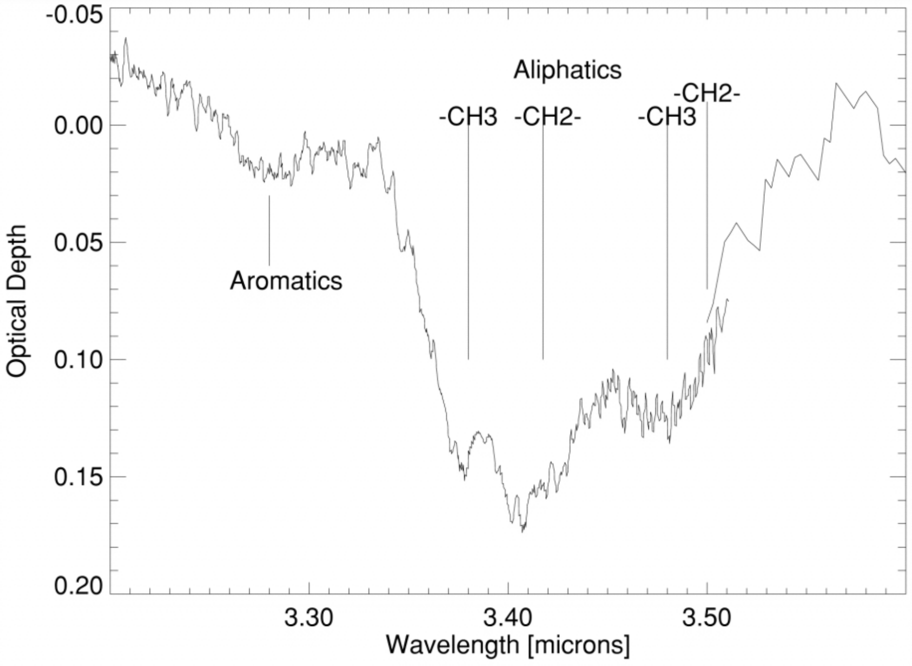
Aromatic & aliphatic features in novae



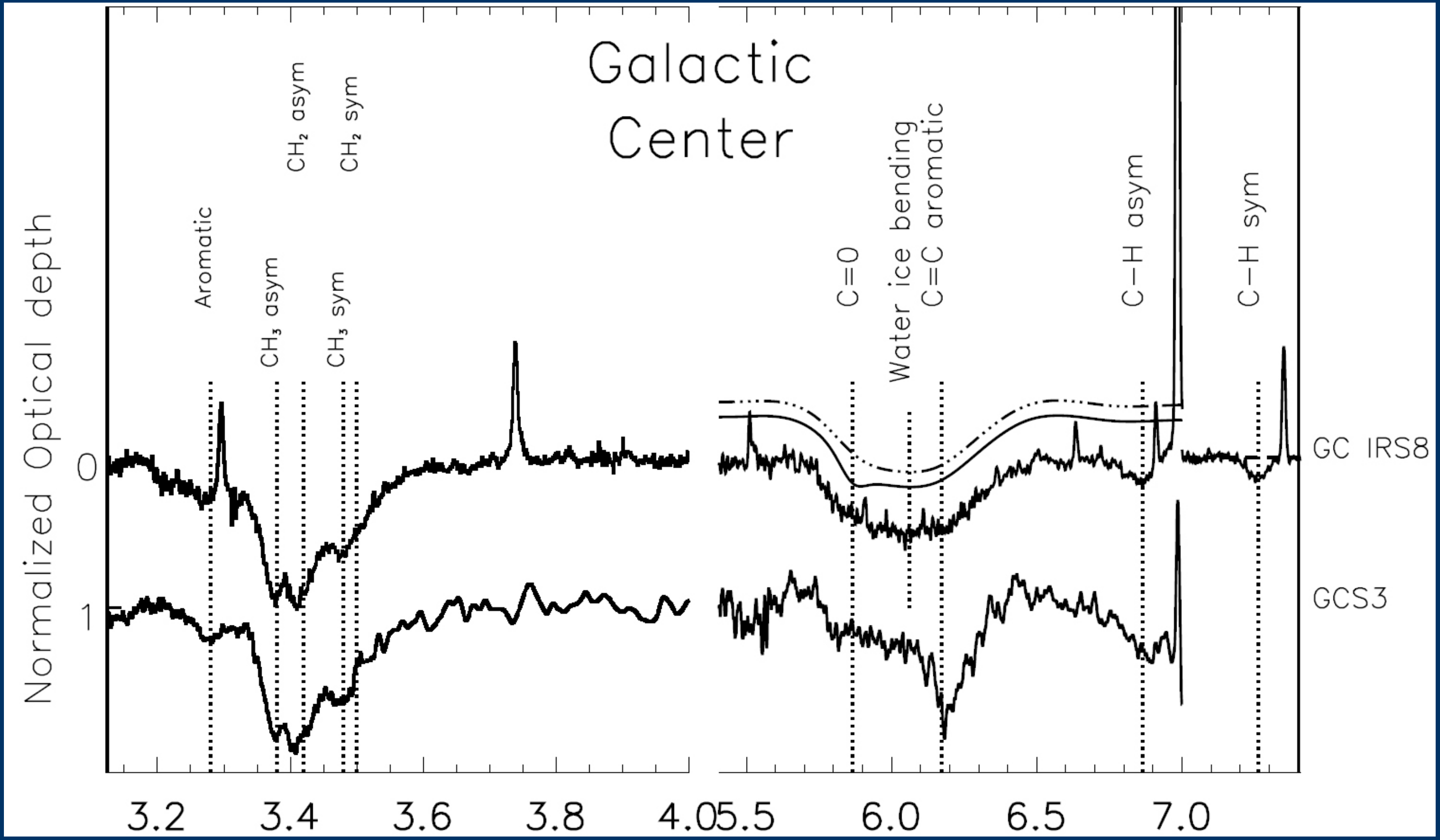
The 3.3 & 3.4 (left) and 8.2 and 11.4 µm features of Nova V705 Cas at 253 (solid line) & 320 (broken line) days after outburst (Evans et al. 2005)

Organic grains in the diffuse ISM

- 3.4 µm C–H stretch observed along the line of sight to the GC (Wickramasinghe & Allen 1983)
- Other sources: Sandford et al. 1991, Pendleton et al. 1994, Chiar et al. 2000
- 3.4 (stretching) and 6.9 µm (bending) aliphatic features in external galaxies: Spoon et al. 2004, Dartois et al. 2007



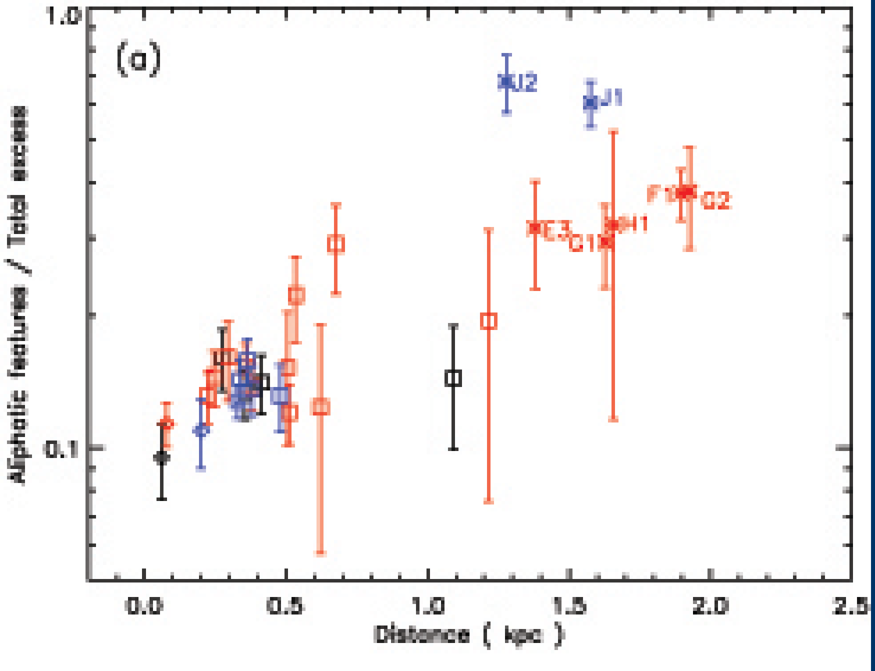
Aliphatics in diffuse ISM



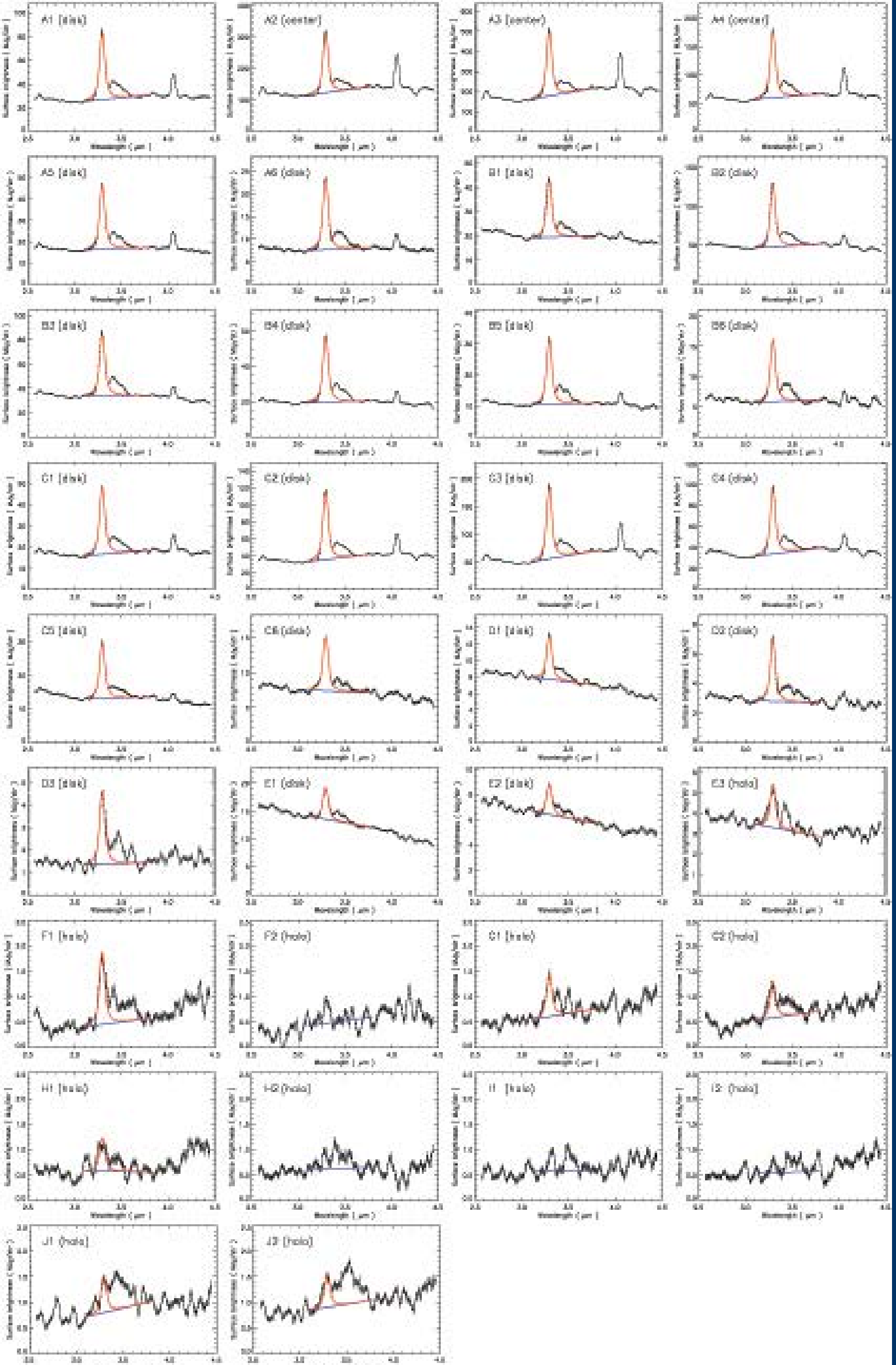
Dartois et al. 2004,
Chiar et al. 2002,
Dartois 2011

15% of C in sp^3 bonding

- Akari observations of M82
- 3.4 μm feature strength increases from disk to halo



Yamagishi et al. 2012

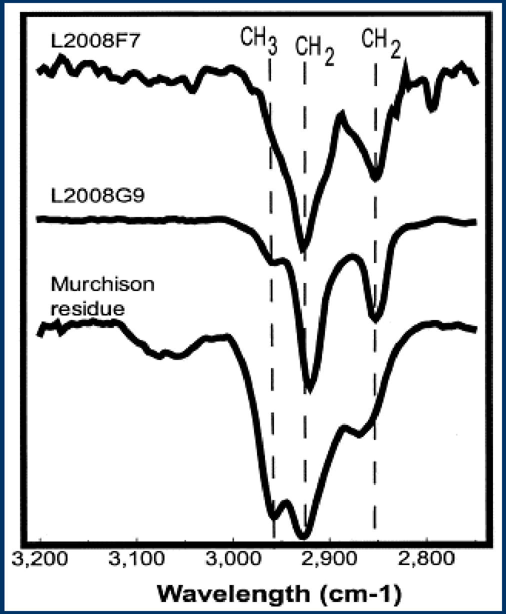


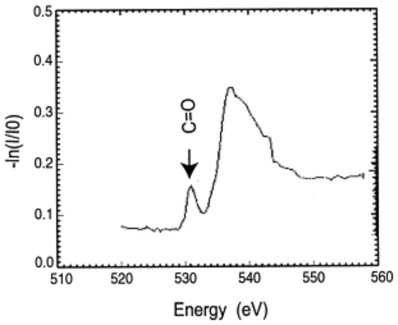
Organics in the Solar System

- Traditional picture: made up of minerals, metals, and ices
- Organic molecules and solids are found in planets and their satellites, asteroids, comets, meteorites, and minor bodies in the outer Solar System
- Origin of these organics: *were they made in the solar nebula or were they inherited from interstellar space?*

Interplanetary Dust

- Few microns to tens of microns in size (Brownlee 1978)
- Silicates (olivine & pyroxene)
- 10-12% carbon content
- 3.4 µm aliphatic feature and sometimes C=O group (Flynn et al. 2003)





O-XANES spectrum of IDP

The soluble component of carbonaceous chondrites

- Carboxylic acids, sulfonic and phosphonic acids, amino acids, aromatic hydrocarbons, heterocyclic compounds, aliphatic hydrocarbons, amines and amides, alcohols, aldehydes, ketones, and sugar related compounds
- >100 amino acids identified, much more than the 20 found in life on Earth
- Almost all biologically relevant organic compounds are present in carbonaceous meteorites

Schmidt-Kopplin et al. 2010, PNAS, 107, 2763

C and N isotopic ratios suggest interstellar origin (Martins et al. 2008; Nakamura-Messenger et al. 2006)

IOM in carbonaceous chondrites

- 70% of organic matter in IOM
- Destructive: thermal and chemical degradations followed by GC/MS
- Nondestrutive: NRM, FTIR, XNES, EPR, HRTEM
- Small (1-4) aromatic rings, short aliphatic chains, heteroelements (O, S, N) (Derenne & Robert 2010)
- Average abundance $C_{100}H_{46}N_{10}O_{15}S_{4.5}$ (Pizzarello & Shock 2010)

Carbonaceous condrites are products of abiotic organic chemistry: Nature can make complex organics without life

Summary

- Organic compounds are everywhere in the Universe (from solar system to ISM to galaxies)
- Detection of AIBs in galaxies with z~2 suggests that complex organics already present in the early history of the universe
- The observed features are consistent with the carrier being mixed aromatic/aliphatic organic nanoparticles (MAON)
- PPN, PN, and novae are the only objects that we have direct observations of organic synthesis
- Chemical evolution leading to complex organic compounds can take place over only a few thousand years in the circumstellar environment

Complex organics are routinely made by ordinary Sun-like stars

References

Kwok, S. 2004 The Synthesis of Organic and Inorganic Compounds in Evolved Stars, *Nature*, **430**, 985

Kwok, S. & Zhang, Y. 2011, Mixed aromatic/aliphatic organic nanoparticles as carriers of the unidentified infrared emission features, *Nature*, **479**, 80

Kwok, S. 2011, *Organic Matter in the Universe*, Wiley