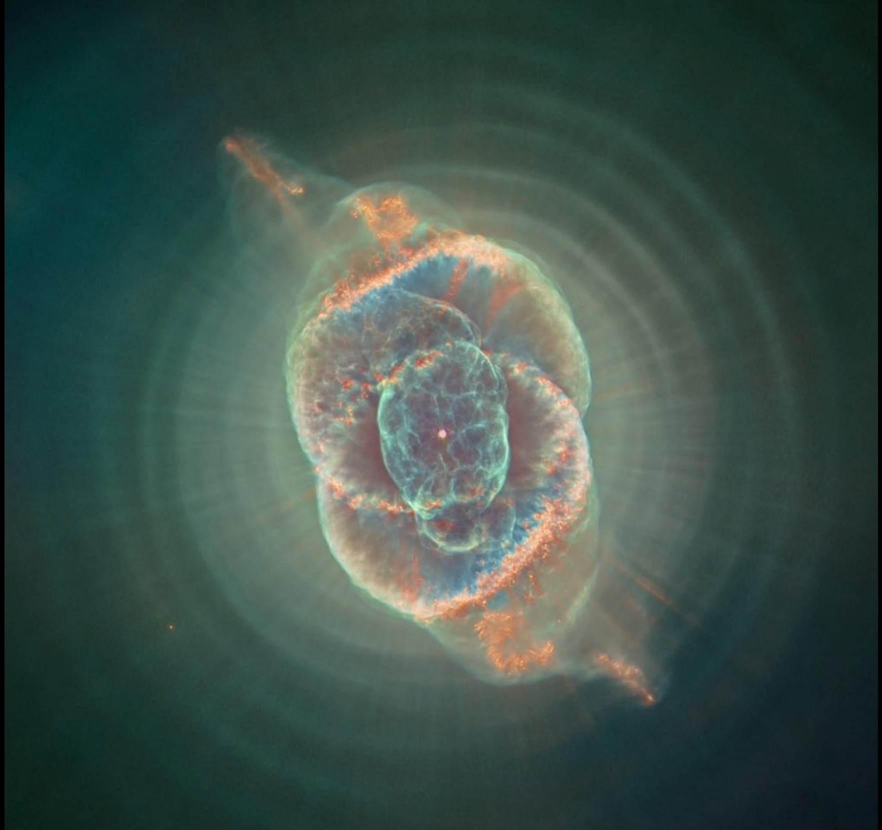
Today in Astronomy 106: heavy elements to molecules

- Today's chemical elements: summary of the nuclear-chemical evolution of the Universe
- Molecules
- Chemistry of the interstellar medium: long chains of carbon atoms in space
- Aromatic (benzene-ring) molecules in space
- Formation of molecules, on dust-grain surfaces and in the gas phase



NGC 6543, the Cat's Eye Nebula, remnant of a dead Solar-type star. (HST/STScI/NASA)

What is the heaviest element made during the first three minutes of the Big Bang?

A. Uranium B. Oxygen C. Beryllium
D. Lithium E. Helium

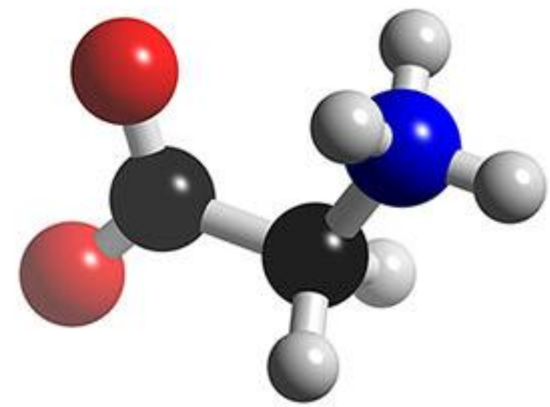
What is the mass number, A (total of protons and neutrons), of the heaviest element made by the Big Bang?

A. 6 B. 7 C. 8 D. 9 E. 10

The evolution of interstellar matter: emergence of molecules

The heavy-element-enriched material from normal stellar death, *via* mass loss/planetary nebula/white dwarf, comes out in two forms:

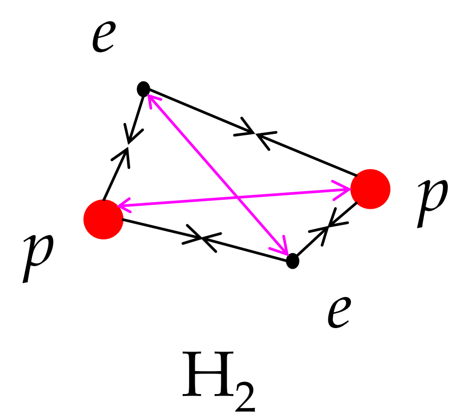
- Gas, mostly (99%).
- **Dust**: initially disorganized clumps of high-melting-point (a.k.a. **refractory**) materials, like C, Si, Mg, and Fe. Small: 100-100,000,000 atoms

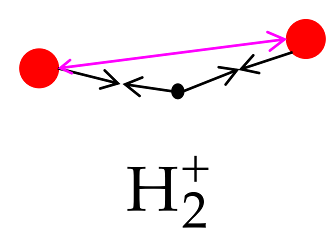


The heavy-element-enriched gas and dust mixes into the existing ISM, and **profoundly** affects the nature of the ISM, as the presence of dust and the higher concentration of heavy elements lead to the formation of lots of molecules.

Molecular binding

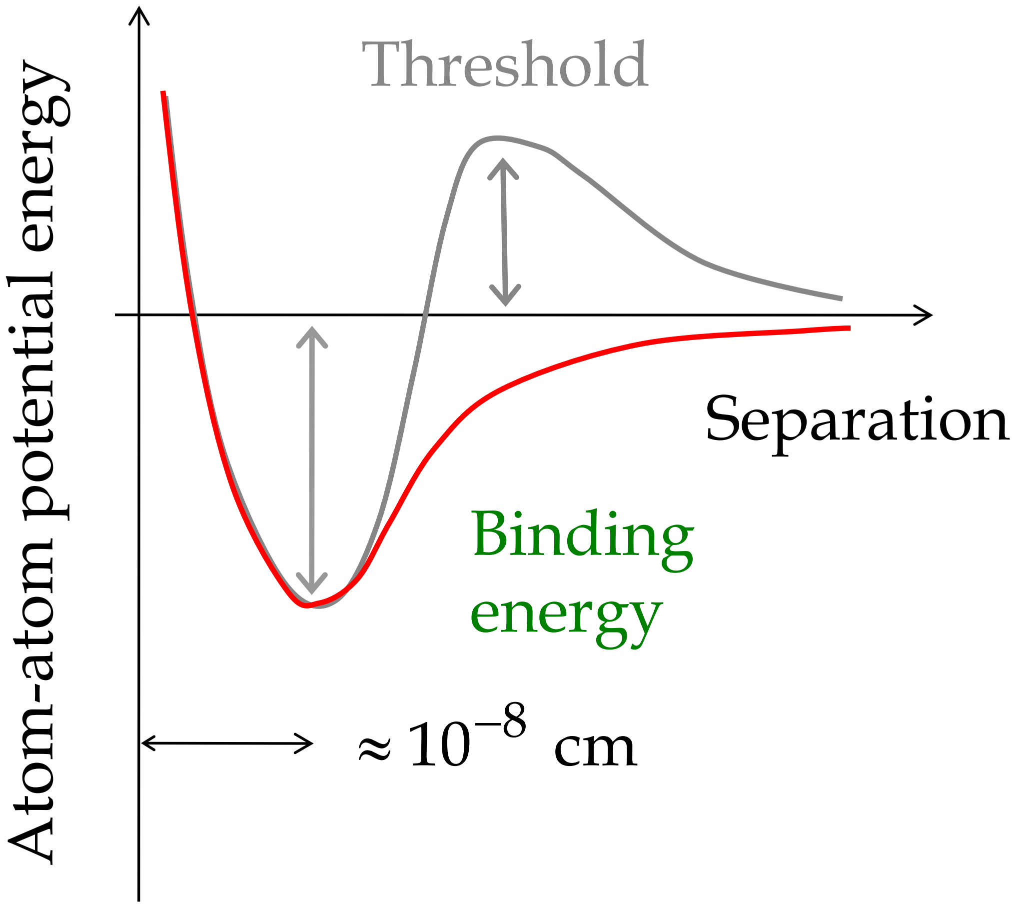
- Like atoms, molecules are held together by the **electrostatic force**, with the nuclei of the participating atoms typically about 10^{-8} cm apart.
  - Binding is a result of the balance between the attraction of the nuclei for each other's electrons, and the repulsion of the nuclei and the electrons. Bond = electron sharing.
  - Thus molecules tend to be fragile, but can have complex structure.
  - Nothing obliges them to be neutral (not ionized).





Molecular binding (continued)

- Atoms bind into molecules if the potential energy is less than that of the separated atoms.
- Two neutral atoms or similarly-charged ions exhibit thresholds at separations larger than that for minimum binding energy.
- **Ion-neutral pairs, or oppositely-charged ions, have zero threshold.**



A few questions for you (non-PRS)

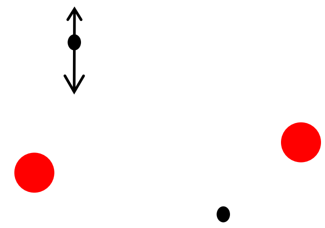
- Do you suppose everyday terrestrial chemistry is mostly neutral-neutral or ion-molecule?
- What do you suppose the typical threshold for neutral-neutral biochemical reaction is, typically, in **temperature units**?
- Why do you suppose this typical value is the size it is?

Quantum behavior of molecules

- On the distance scale of molecular bonds (about 10^{-8} cm), electrons behave as waves instead of particles.
  - Probability-density waves, again.
  - Waves can **interfere** with one another, constructively or destructively. (Particles can't.)
  - As a result, electrons in molecules can't have any energy they want: only certain energies are allowed (quantization of molecular electronic energy levels).
  - But nuclear position influences the electron structure, **and** vice versa.
  - Thus energies of molecular **vibration** and **rotation** are quantized too.

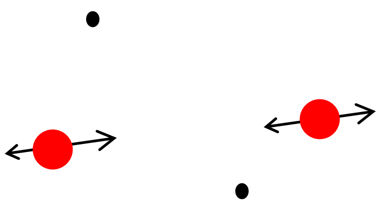
Energies of different bound states of molecules

Electronic energies



- Different states correspond to electrons in different configurations.
- Energy differences correspond typically to visible and ultraviolet wavelengths (0.1-1 μm).

Vibrational energies

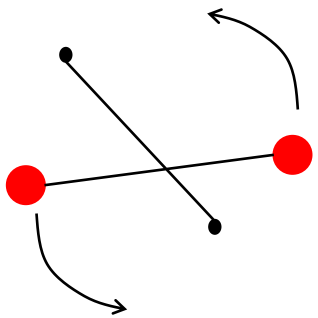


- Different states: different modes of vibration of the nuclei, either along or transverse to the bonds: like different notes on a guitar string.
- Energy differences correspond typically to near and mid infrared wavelengths (1-50 μm).

Energies of different bound states of molecules (continued)

Rotational energies

- Different states: rotation of the molecule by quantized amounts, about various different axes.
- Energy differences correspond typically to far-infrared and millimeter wavelengths (50 μm-10 mm).

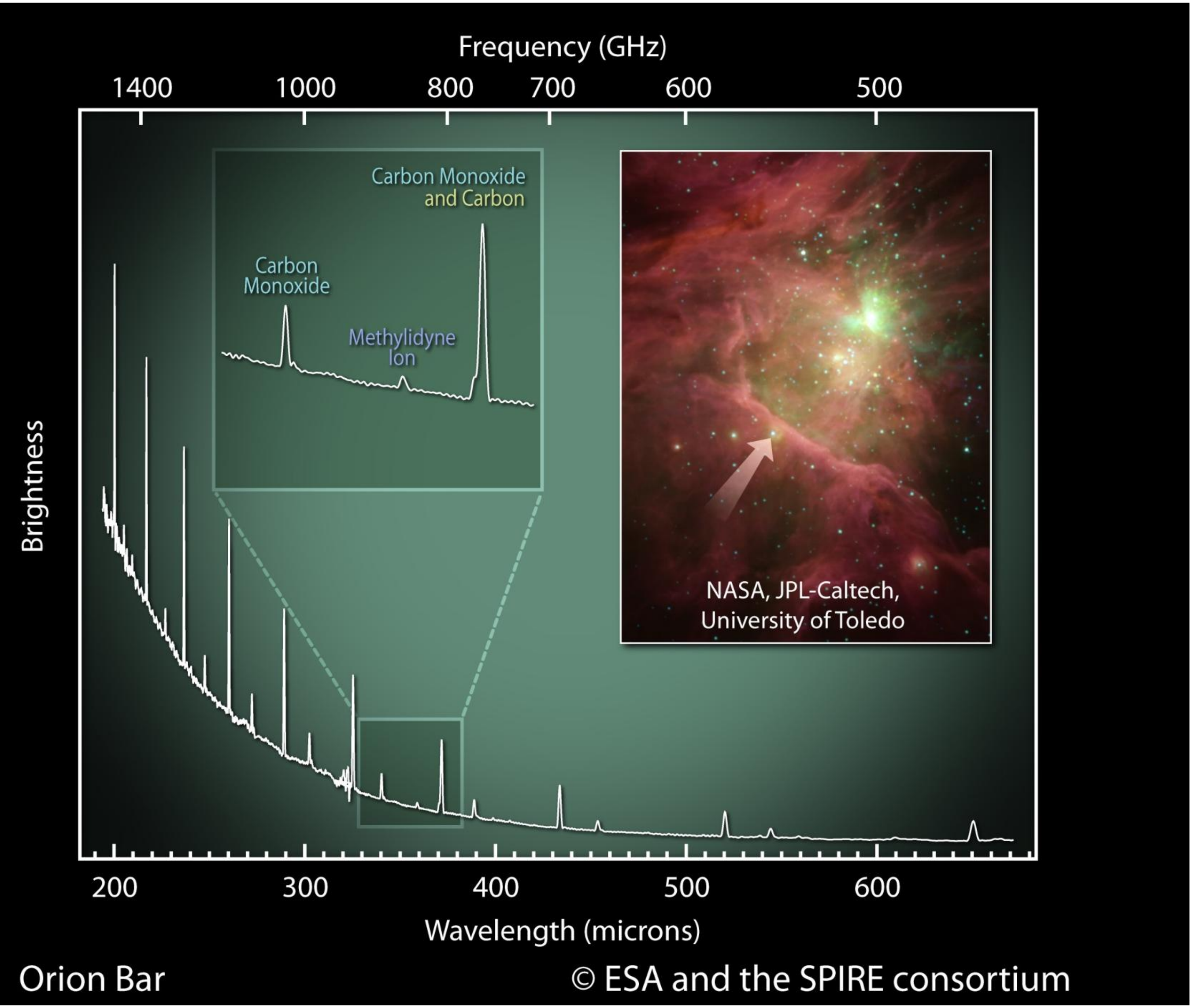


Linear and symmetrical molecules have fewer vibrational and rotational states than complex, bent ones.

- Thus they have fewer, and stronger, spectral lines, and are easier to detect and identify.

Molecular upshot: we can identify molecules in interstellar clouds and measure their abundances

- Every molecule has a distinctive set of electronic, vibrational and rotational energy levels, and thus a distinctive spectrum: thus molecules can be identified positively.
- Again, the wavelengths and strengths of the spectral lines can be measured in the laboratory, usually to very high precision and accuracy.
- Also again, the relative brightness of lines of a given species can be used to determine density, temperature, and pressure of the emitting region.
- Thus the relative brightness of lines of different species can be used to determine relative abundances.



Example rotational molecular-line spectrum

Mostly CO and ^{13}CO, and many others including CH^+. Done with the SPIRE instrument on the new ESA/NASA Herschel Space Observatory.

Number of atoms in molecule

2	3	4	5	6	7	8	9	10	11	12	13
H_2	C_3	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	$CH_3OC_2H_5$	$HC_{11}N$
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH_3)_2CO$			
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	NH_2CH_2COOH			
C_2	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO			
CH	CH_2	C_3S	c-C_3H_2	CH_3NC	$HCOCH_3$	H_2C_6	HC_7N				
CH+	HCN	C_2H_2	CH_2CN	CH_3OH	NH_2CH_3	CH_2OHCHO	C_8H				
CN	HCO	CH_2D^+	CH_4	CH_3SH	c-C_2H_4O	CH_2CHCHO					
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	CH_2CHOH						
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO							
CP	HOC^+	HNCO	HCOOH	NH_2CHO							
CSi	H_2O	HNCS	H_2CHN	C_5N							
HCl	H_2S	$HOCO^+$	H_2C_2O	HC_4N							
KCl	HNC	H_2CO	H_2NCN								
NH	HNO	H_2CN	HNC_3								
NO	MgCN	H_2CS	SiH_4								
NS	MgNC	H_3O^+	H_2COH^+								
NaCl	N_2H^+	NH_3									
OH	N_2O	SiC_3									
PN	NaCN	C_4									
SO	OCS										
SO^+	SO_2										
SiN	c-SiC2										
SiO	CO_2										
SiS	NH_2										
CS	H_3^+										
HF	SiCN										
SH	AlNC										
FeO	SiNC										

Amino acid (glycine)

Alcohols (methanol, ethanol)

Sugar (glycoaldehyde)

Organic acids (formic, acetic)

Water

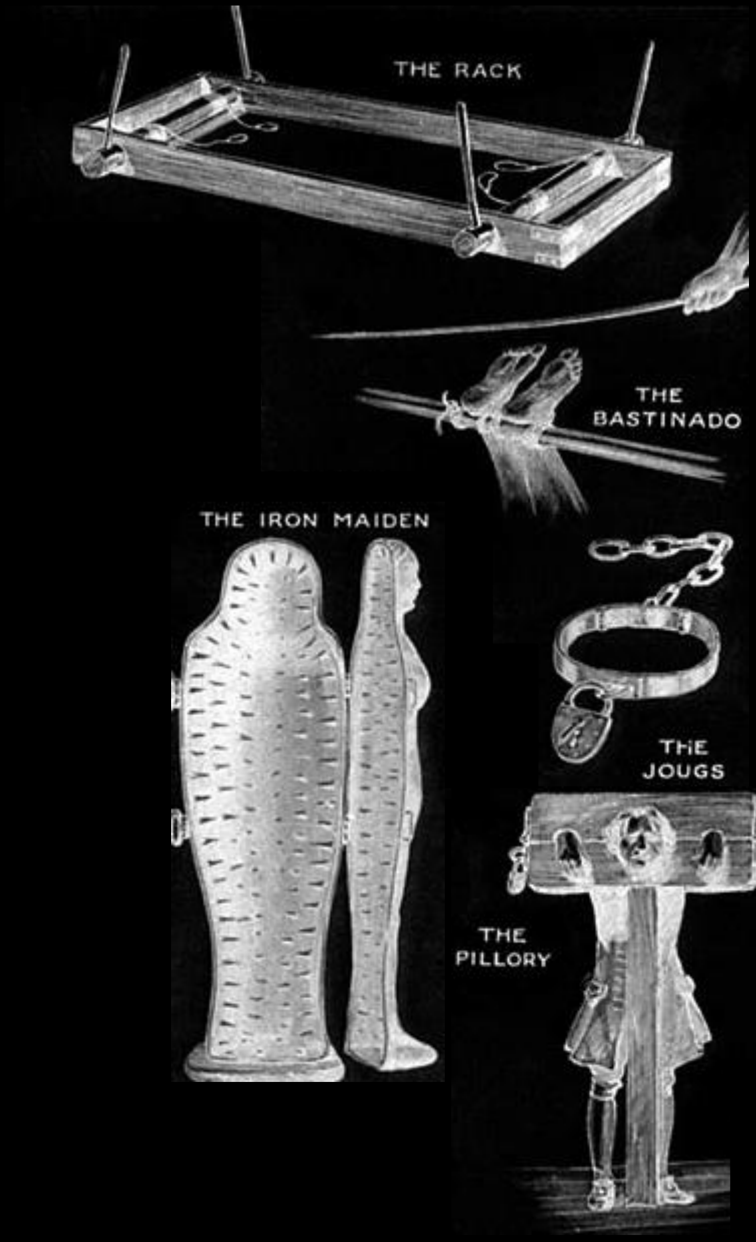
Today's interstellar molecules

Note the long carbon chains (11 Cs!), many radicals and ions, and quite a few of the simpler molecules of life.

(Al Wooten, NRAO)

Mid-lecture **Break**

- Homework #1 is due Wednesday by midnight.
- Last pre-exam recitation today, 2 PM, B&L 315.
- **Exam #1 is Friday, on WeBWorK, in any 75-minute window between 10 AM and 6 PM.**
- A practice exam will appear on WeBWork on Thursday.



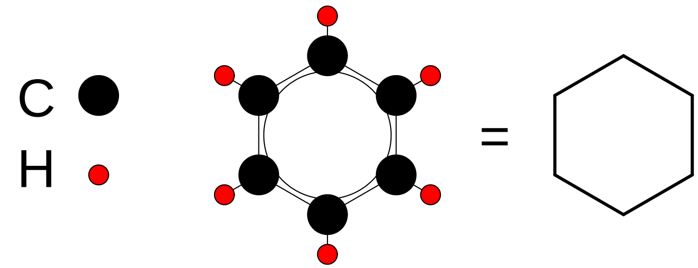
What element necessary for human life is absent from the current inventory of interstellar molecules?

A. Nitrogen
B. Phosphorus
C. Sulfur
D. Sodium
E. These are all present

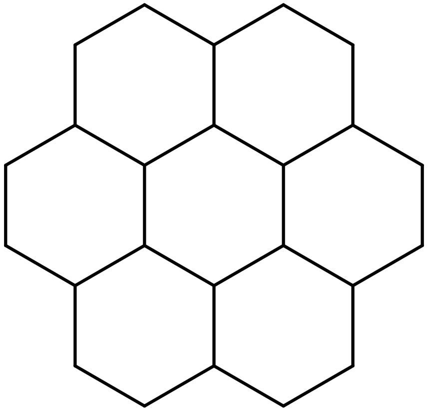
Aromatic molecules in space

In addition to these, there is also a well-known and abundant class of **aromatic ring molecules** in interstellar clouds.

- Archetype of aromatic rings: **benzene**, C_6H_6.
- In space are "polycyclic aromatic hydrocarbons" (**PAH**s), with 20-50 carbon atoms and hydrogens around the edges.
- We know them from their vibrational spectra, which blend together the signatures of different-size PAHs.

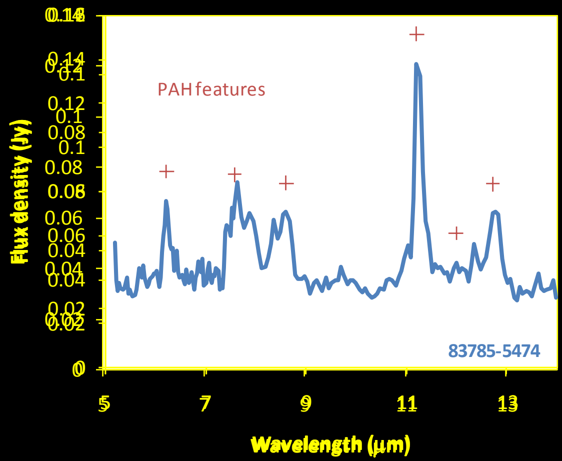


Benzene, C_6H_6



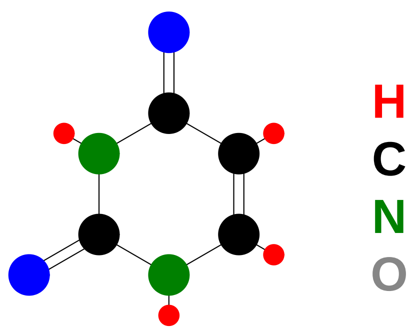
Coronene
$C_{24}H_{12}$

PAH emission from protoplanetary disks in the Orion Nebula. Spectra: Kyoung Hee Kim's Ph.D. dissertation, 2011. Image: HST/ STScI/ NASA.



Aromatic molecules in space

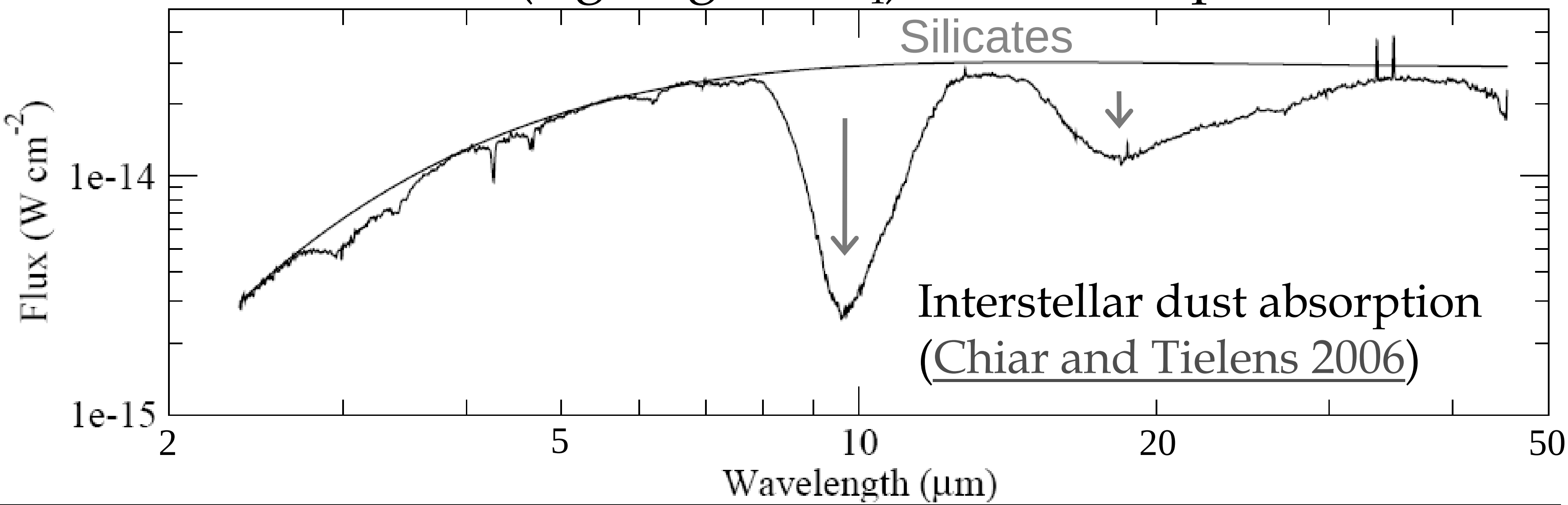
- So far no rotational transitions of PAH molecules have been seen, so molecules with specific numbers of C atoms haven't been identified. (Coming soon with *Herschel*.)
- No five- or six-member rings containing nitrogen have been identified yet either.
- Still, the complex PAHs are more easily excited (by UV light) and detected than the simpler ring molecules like the organic bases that make up DNA and RNA, so we expect these molecules also to exist in interstellar space, and to be detectable in the near future.



Uracil
(simplest compo-
nent of RNA)

Dust grains in interstellar space

- Some are made of **amorphous** (randomly oriented, non—crystalline) **carbon** – these are the larger end of the particles whose smaller end are the PAHs molecules.
- Most are made of the ingredients of silicate minerals – e.g. Si, O, Mg and Fe – in the proportions found in common **silicate** minerals (e.g. $MgFeSiO_4$). Also amorphous.



Interstellar dust absorption (Chiar and Tielens 2006)

The origin of molecules

So, interstellar molecules can get quite complex, and many abundant species are based upon carbon.

- Molecular complexity is extraterrestrial.
- Carbon-based chemistry is not peculiar to Earth. (Recall also that Earth is rather poorly supplied with C.)

How do molecules form from atoms in the ISM? Three ways:

- Dust grain catalysis.
- Ion-molecule reactions.
- Neutral-neutral reactions in shocked material.

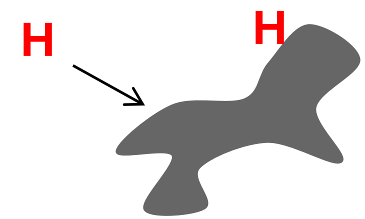
Why isn't all the ISM in molecular form?

- Ultraviolet starlight destroys molecules, when they're unprotected by lots of gas and dust.

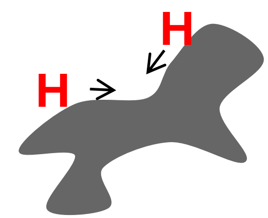
Dust grain catalysis

Perhaps surprisingly, the most abundant molecule, H_2, cannot form by combining two H atoms in gas. Instead its formation is **catalyzed** by dust grains.

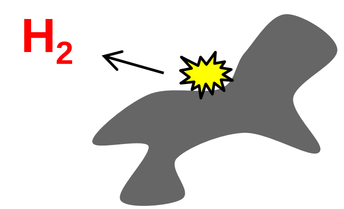
- A H atom, colliding with a dust grain, is not unlikely to stick, lightly, to the surface.



- Stuck lightly, it moves on the surface in response to surface charges and fields.



- If it finds another H atom, it can combine to form H_2.
  - The energy released in binding can kick the new molecule off the surface.
  - The grain goes away with the recoil momentum.



Ion-molecule reactions

Neutral-neutral reactions can have high threshold, but ion-molecule reactions have zero threshold.

- And there are always some ions around, as ultraviolet light and high-energy cosmic rays (CRs; mostly high-energy protons) ionize atoms and molecules:

$$\text{UV photon} + \mathrm{C} \rightarrow \mathrm{C}^+ + e^-$$

$$\mathrm{C}^+ + \mathrm{H} \rightarrow \mathrm{CH}^+ + \text{photon}$$

$$\mathrm{CH}^+ + \mathrm{O} \rightarrow \boxed{\mathrm{CO}} + \mathrm{H}^+$$

$$\mathrm{CR} + \mathrm{H}_2 \rightarrow \mathrm{H}_2^+ + e^- + \mathrm{CR}$$

$$\mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H}$$

$$\mathrm{H}_3^+ + \mathrm{CO} \rightarrow \boxed{\mathrm{HCO}^+} + \mathrm{H}_2$$

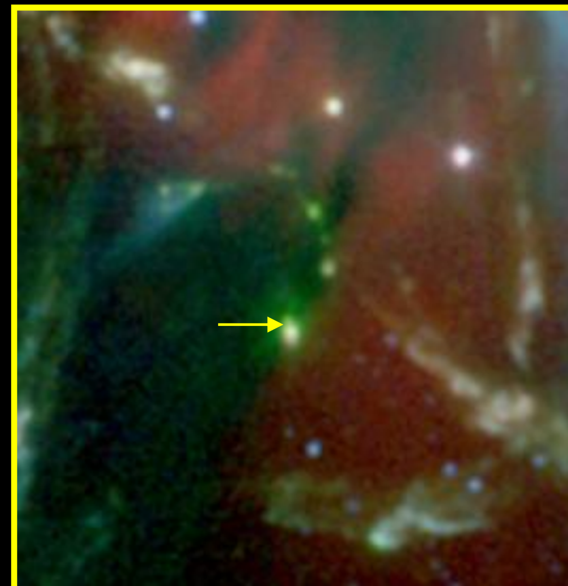
$$\Downarrow$$

increasingly complex molecules

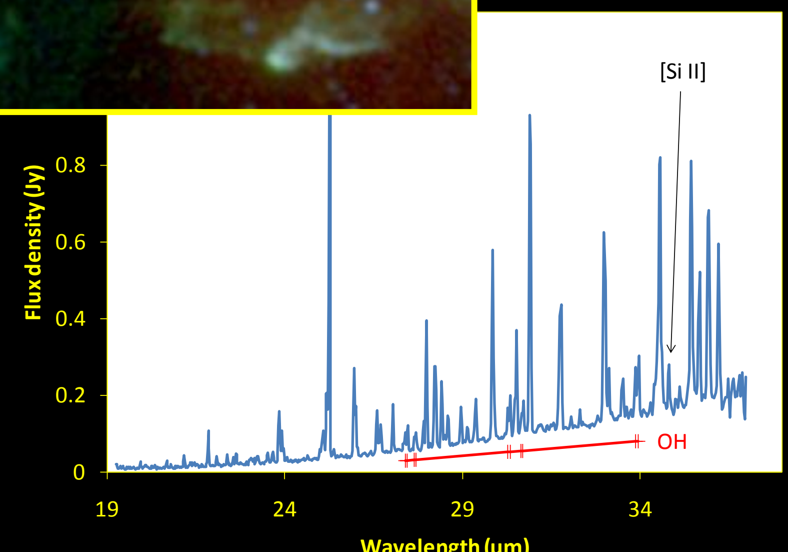
Neutral-neutral reactions

But when molecular matter is heated, as when a shock wave (supersonic disturbance, like a sonic boom) passes through, neutral-neutral reactions that have high thresholds, or are even endothermic (cost energy) can produce species abundantly that are hard to produce in large quantities otherwise:

$$O + H_2 \rightarrow OH + H$$
$$OH + H_2 \rightarrow \boxed{H_2O} + H$$



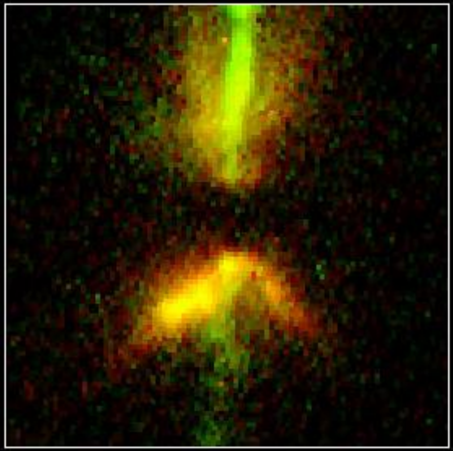
Water and OH emission in a proto-stellar accretion shock (Watson et al. 2007)

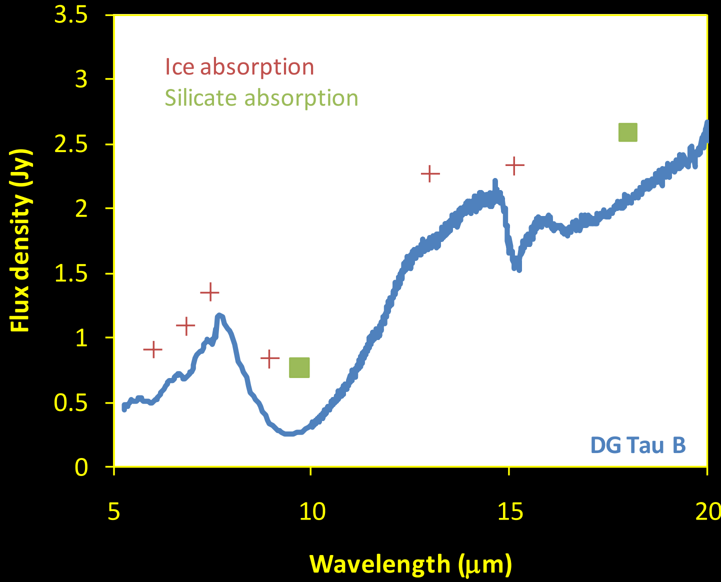


More chemistry on grain surfaces

In very cold regions, molecules can freeze onto the surfaces of dust grains, forming "ice mantles."

- Eventually if energy (e.g. UV light) is added, the dense concentration of molecules can react to produce even more complex molecules than froze out in the first place.
- Interstellar ethanol, for example, is thought to be made in this way.





DG Tau B image by *Hubble* (STScI/NASA), spectrum by *Spitzer* (Watson et al. 2004)

Dissociation of molecules

Molecules can be dissociated by UV starlight. But dust grains can absorb UV and simply warm up a little.

- A dusty layer of gas with about 10^{21} hydrogens per cm^2 attenuates the general interstellar UV radiation field sufficiently for molecules to form behind it.
- This layer, in which matter is mostly atomic, is called a **photodissociation** region.