## 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:

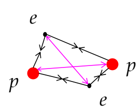
- Gas, mostly (99%).
- Dust: initially disorganized clumps of high-melting-point (a.k.a. refractory) materials, like C, Si, Mg, and Fe. Small: 100-100,000,000 atoms

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.

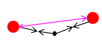


## Molecular binding

- 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).




$H_2$

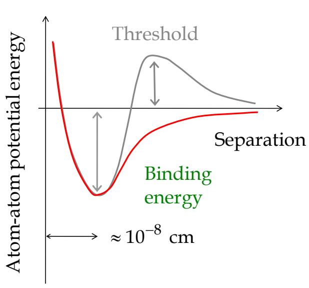


$H_2^+$



## 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

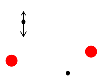
- ❑ On the distance scale of molecular bonds (about $10^{-8}$ cm), electrons behave as waves instead of particles.
  - Probability-density waves, again.
  - Waves can **interfere** with one another, constructively or destructively. (Particles can't.)
  - As a result, electrons in molecules can't have 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

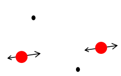
Electronic energies

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



Vibrational energies

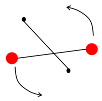
- ❑ Different states: different modes of vibration of the nuclei, either along or transverse to the bonds: like different notes on a guitar string.
- ❑ Energy differences correspond typically to near and mid infrared wavelengths (1-50 μm).



## 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.

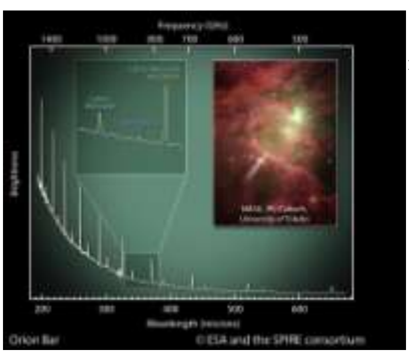
- Thus they have fewer, and stronger, spectral lines, and are easier to detect and identify.



## 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.



(c) University of Rochester 

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.
- Recitation, tomorrow, 12:30 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 Wednesday.



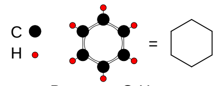
What element necessary for human life is absent from the current inventory of interstellar molecules?

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

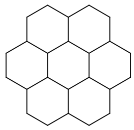
## Aromatic molecules in space

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.

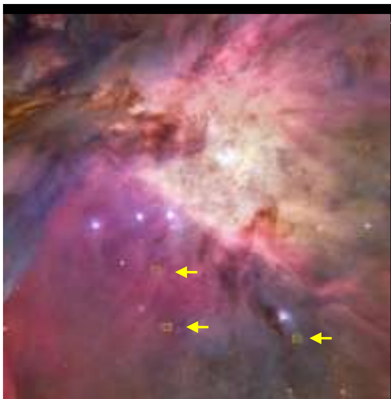



Benzene, $C_6H_6$

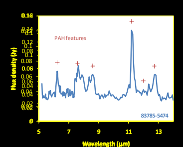


Coronene $C_{24}H_{12}$





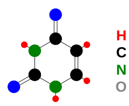
PAH emission from protoplanetary disks in the Orion Nebula. Spectra: Kyoung Hee Kim's Ph.D. dissertation, 2011. Image: HST/ STScI/ NASA.





## Aromatic molecules in space

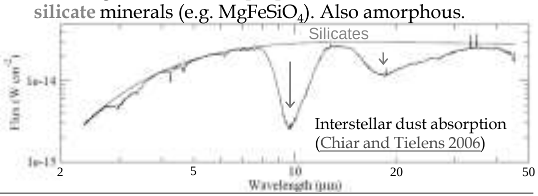
- So far no rotational transitions of PAH molecules have been seen, so molecules with specific numbers of C atoms haven't been identified. (Coming soon with *Herschel*.)
- No five- or six-member rings containing nitrogen have been identified yet either.
- Still, the complex PAHs are more easily excited (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 component 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.






## 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?

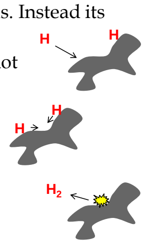
- Ultraviolet starlight destroys molecules, when they're unprotected by lots of gas and dust.



## 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:

$$\text{UV photon} + \mathrm{C} \rightarrow \mathrm{C}^+ + e^- \qquad \mathrm{CR} + \mathrm{H}_2 \rightarrow \mathrm{H}_2^+ + e^- + \mathrm{CR}$$

$$\mathrm{C}^+ + \mathrm{H} \rightarrow \mathrm{CH}^+ + \text{photon} \qquad \mathrm{H}_2^+ + \mathrm{H}_2 \rightarrow \mathrm{H}_3^+ + \mathrm{H}$$

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

$$\Downarrow$$

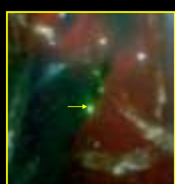
increasingly complex molecules



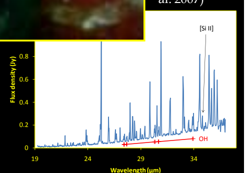
## Neutral-neutral reactions

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:

$$\mathrm{O} + \mathrm{H}_2 \rightarrow \mathrm{OH} + \mathrm{H}$$
$$\mathrm{OH} + \mathrm{H}_2 \rightarrow \boxed{\mathrm{H_2O}} + \mathrm{H}$$



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

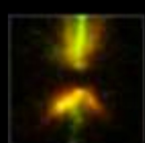


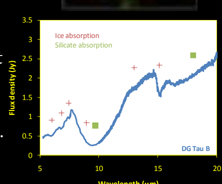



## More chemistry on grain surfaces

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.