Astrochemistry (1)

Planets and Astrobiology (2023)
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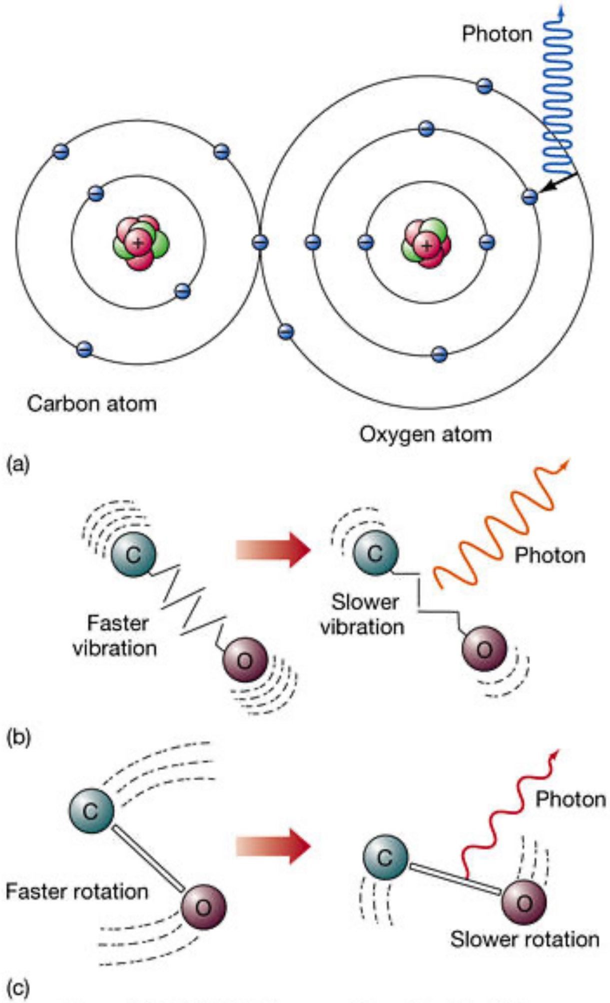
Molecular spectra

- Molecular spectra are much more complex than atomic spectra

- Molecular lines result from the combination of different types of transitions
  - Electronic
  - Vibrational
  - Rotational

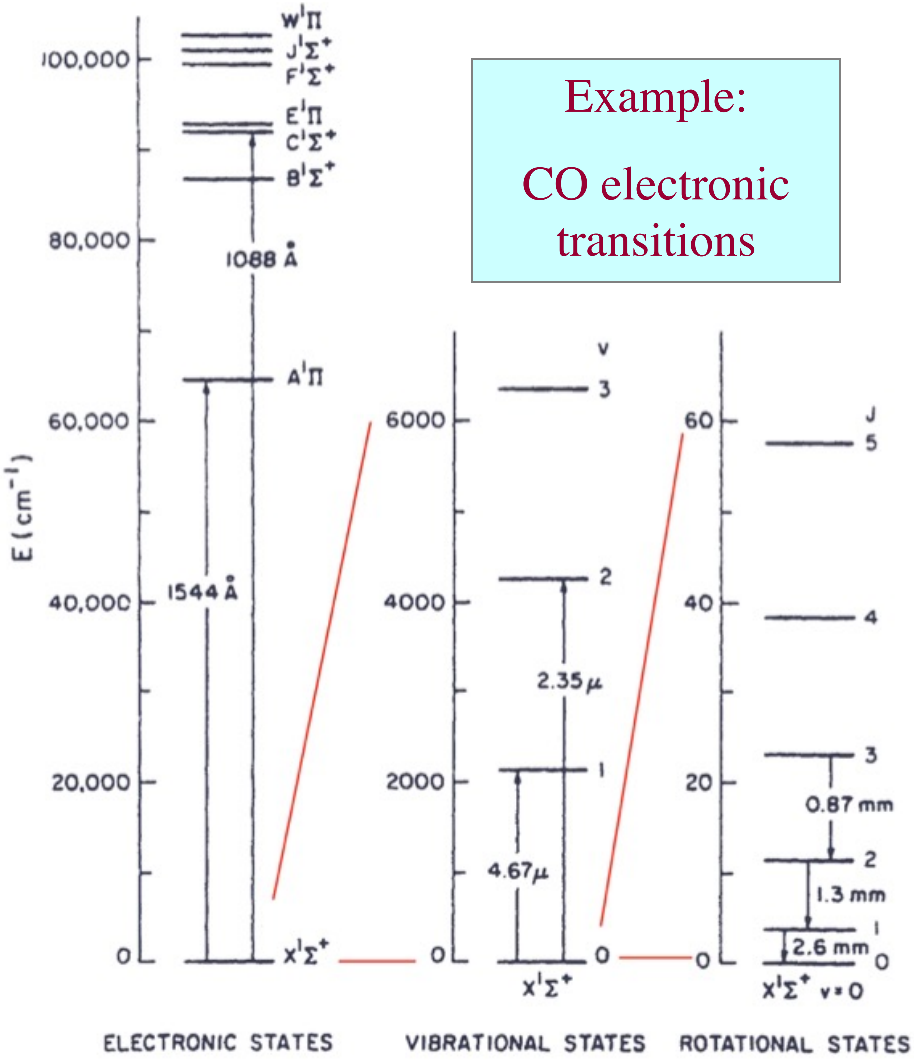
Example in figure: CO molecule



Electronic transitions in molecules

- Electronic transitions in molecules are equivalent to the electronic transitions in atoms
  - Typical energies are in the order of some eV

    They generally lie in the optical/UV spectral range
  - However, when observed at high spectral resolution, they can be solved in vibrational sub-levels which, in turn, can be solved in rotational sub-levels



Example:

CO electronic transitions

Vibrational transitions

- Between energy levels that result from the quantization of vibrational modes
  - They are mostly "stretching" modes

    (variations of interatomic distances)

    Stretching is the only possible mode for diatomic molecules

    Complex molecules also have "bending" and "deformation" modes
- The quantum number v indicates the vibrational state of the system

  (for v=0 the vibrational energy is not null)

$$E^{vib} = \hbar\omega_e(\mathrm{v} + \frac{1}{2})$$

$$\mathrm{v} = 0, 1, 2, \ldots$$

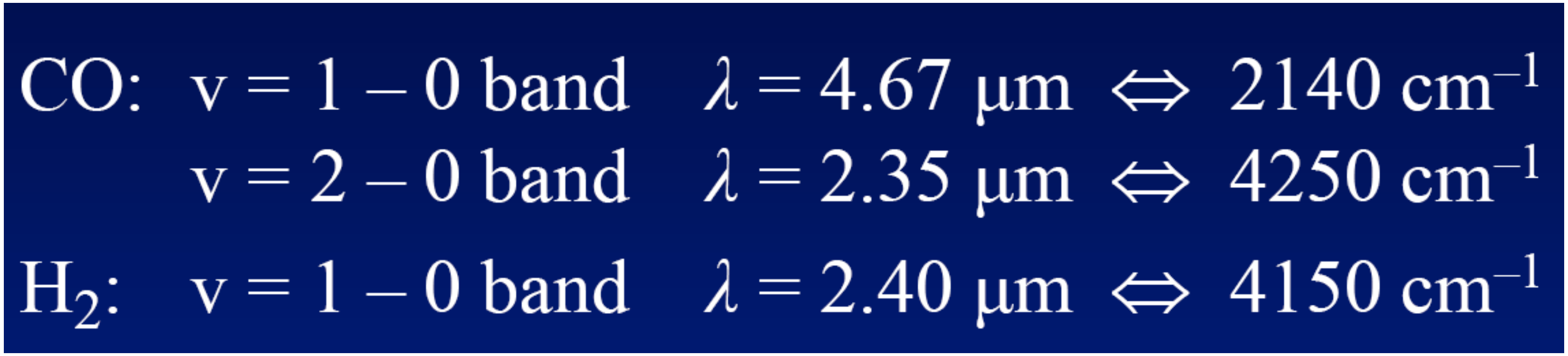
As v varies in a given molecule, the vibrational energy levels are equidistant

For different molecules the separation of the vibrational levels is a function of the reduced mass μ

For instance, H_2, HD e D_2 produce different vibrational spectra

Vibrational transitions

- The typical energies of vibrational modes lie in the range 0.1 e 0.3 eV
  - The corresponding wavelength λ lies in the near IR



$$\begin{array}{llll} \mathrm{CO:} & v = 1-0 \text{ band} & \lambda = 4.67\ \mu\mathrm{m} \Leftrightarrow & 2140\ \mathrm{cm}^{-1} \\ & v = 2-0 \text{ band} & \lambda = 2.35\ \mu\mathrm{m} \Leftrightarrow & 4250\ \mathrm{cm}^{-1} \\ \mathrm{H_2:} & v = 1-0 \text{ band} & \lambda = 2.40\ \mu\mathrm{m} \Leftrightarrow & 4150\ \mathrm{cm}^{-1} \end{array}$$

The energy of the transitions scales as λ^{-1} and can be expressed in cm^{-1}

Conversion factor: $1\ \mathrm{cm}^{-1} = 1.24 \times 10^{-4}$ eV

- Every chemical group has a characteristic vibrational energy
  - Examples: C–H stretch, C≡H stretch, CH_2 angle bending

    Different complex molecules that have in common a chemical group will show the same vibrational transitions characteristic of that group

      Problem of identification of complex molecules

Rotational transitions

- Result from the quantization of the molecular rotational energies
  - The rotation can take place around the main axis of inertia
  - For complex molecules it could be a form of internal rotation
- Rotational transitions have energies in the order of ~ 10^{-3} eV
  - The wavelength λ generally lies in the millimetric or sub-millimetric spectral bands
- Rotational states are identified with the quantum number *J*

Example: CO

$$\begin{array}{lllll}
\mathrm{CO} & J = 1 - 0 & \nu = 115\ \mathrm{GHz} & \Leftrightarrow & \lambda = 2.6\ \mathrm{mm} \\
 & J = 2 - 1 & \nu = 230\ \mathrm{GHz} & \Leftrightarrow & \lambda = 1.3\ \mathrm{mm} \\
 & J = 3 - 2 & \nu = 345\ \mathrm{GHz} & \Leftrightarrow & \lambda = 0.87\ \mathrm{mm}
\end{array}$$

Roto-vibrational transitions

- Vibrational transitions can be decomposed in rotational levels, the combination of the two giving rise to a roto-vibrational band

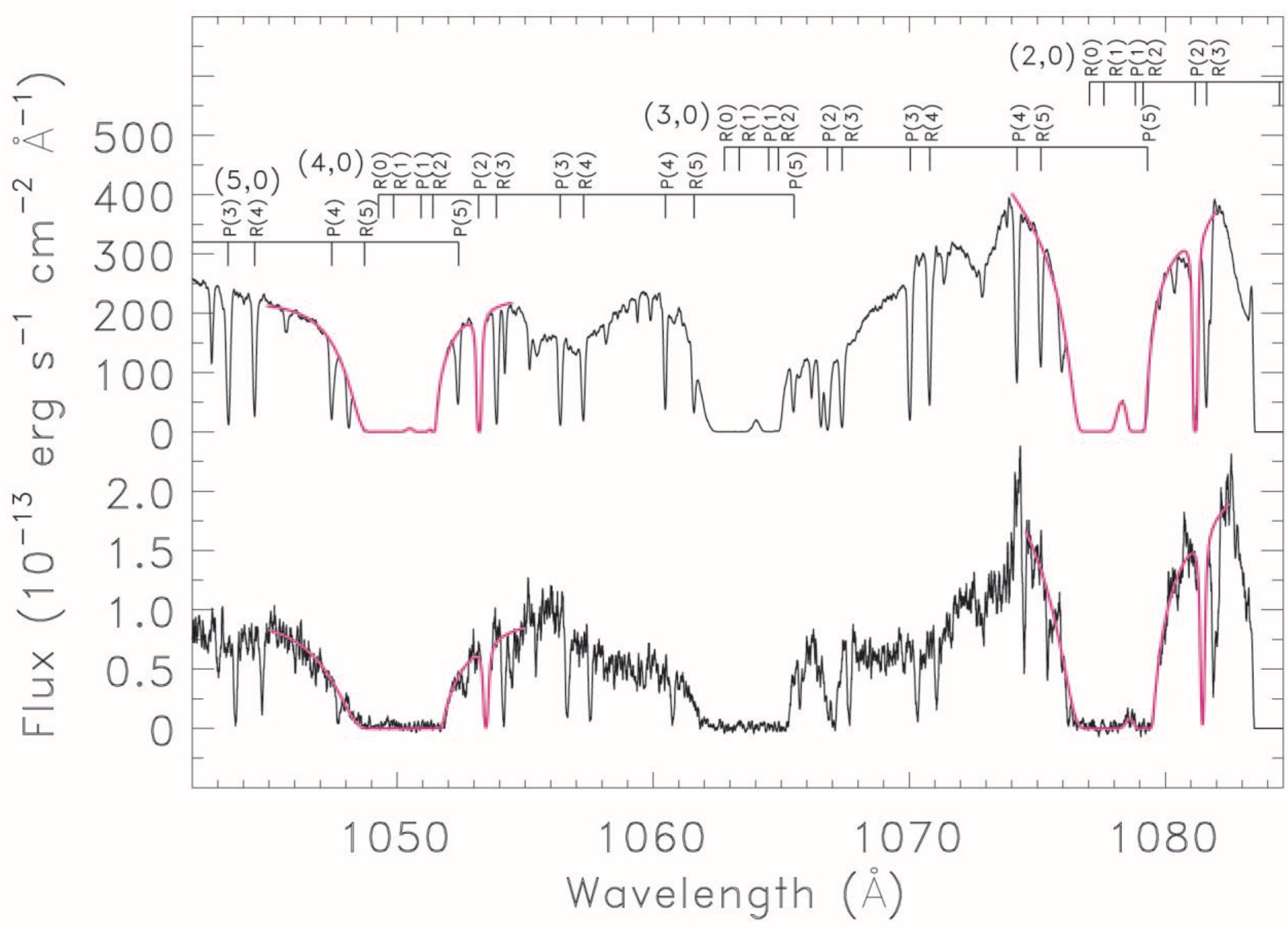
- Selection rules:
  - There are no restrictions on the variation of the vibrational state, Δv
  - Variations of angular momentum are constrained by the selection rules $\Delta J = 0, \pm 1$

Depending on the value ΔJ the bands are called as follows:

$\Delta J = -1$ “P branch”
$\Delta J = \;\; 0$ “Q branch” (but J=0 → J=0 is forbidden)
$\Delta J = +1$ “R branch”

H_2 absorption lines

- Observations with high resolution spectroscopy show the extreme complexity of the molecular spectrum



H_2 emission

- Molecular hydrogen is a symmetric molecule
  - The electric dipole moment is zero

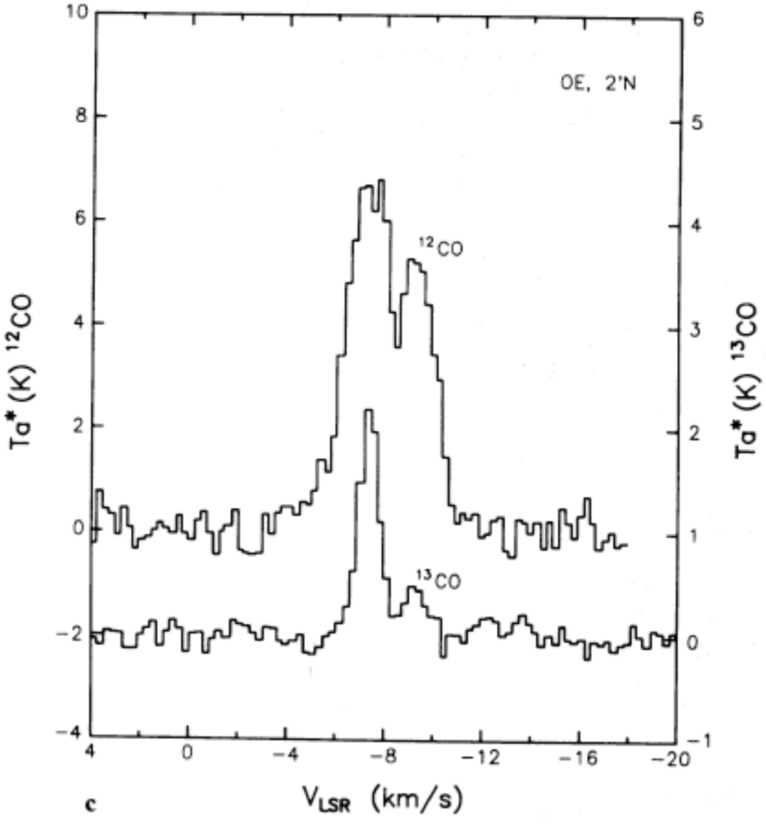
    Rotational transitions are forbidden, even though electronic transitions are allowed
- Quadrupole transitions are possible, but very weak
  - Their energies are much higher than the typical rotational energies
  - Can only be observed in relatively warm regions

    Thanks to the abundance of H_2 some of these transitions have been observed in the mid IR
- Due to the lack of H_2 emissions it is hard to map the distribution of molecular hydrogen in galaxies
  - UV absorptions require (rare) bright background sources and are not suited to map the molecular gas, especially in dust-rich regions, where the background sources are obscured

Molecular emission spectra in the millimetric band

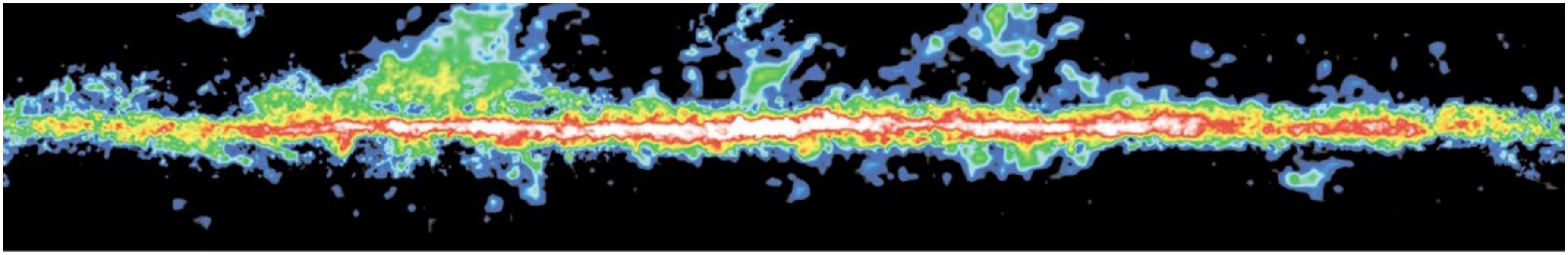
- CO emission lines

  $J = 1–0$ at 2.6 mm
- Advantages
  - CO is relatively abundant and has rotational transitions (not a symmetric molecule)
  - the dipole moment is relatively small and the molecule can be easily excited also in gas with relatively low density
- Used as a tracer of H_2
- If the emission is too strong one can use less abundant istotopes, such as ^{13}CO, to obtain optically thin emissions



Molecular emission in the millimetric band

- OH, NH_3, H_2O (1965)
  In the radio band
- First measurement of CO emission (1970)
- Maps of the Galactic distribution of CO (1970's and 1980's)
  Tracer of molecular gas in the Galaxy



Chemical bonds of interstellar molecules

- Atoms in interstellar molecules are held together by covalent bonds
  - Superposition of the atomic orbitals
  - Sharing of the eletrons in external shells
- Typical energies of covalent bonds
  - ~100 kcal/mol ⇒ ~ 4 eV
- In the harsh conditions of the ISM the molecules can be easily dissociated
  - Kinetic temperatures in excess of ~10^4 K would dissociate molecules by collisions
  - Photons with energies up to13.6 eV can penetrate HI regions and photodissociate molecules
  - Interstellar molecules can survive in cold regions protected by the interstellar radiation field

Interstellar chemical reactions

Formation of bonds

- Radiative association

  Between neutrals and ions

- Reactions on the surface of dust grains

  Also between neutrals

  example: H_2 formation

Destruction of bonds

- Photo-dissociation
- Dissociative recombination

$$X^+ + Y \rightarrow XY^+ + h\nu$$

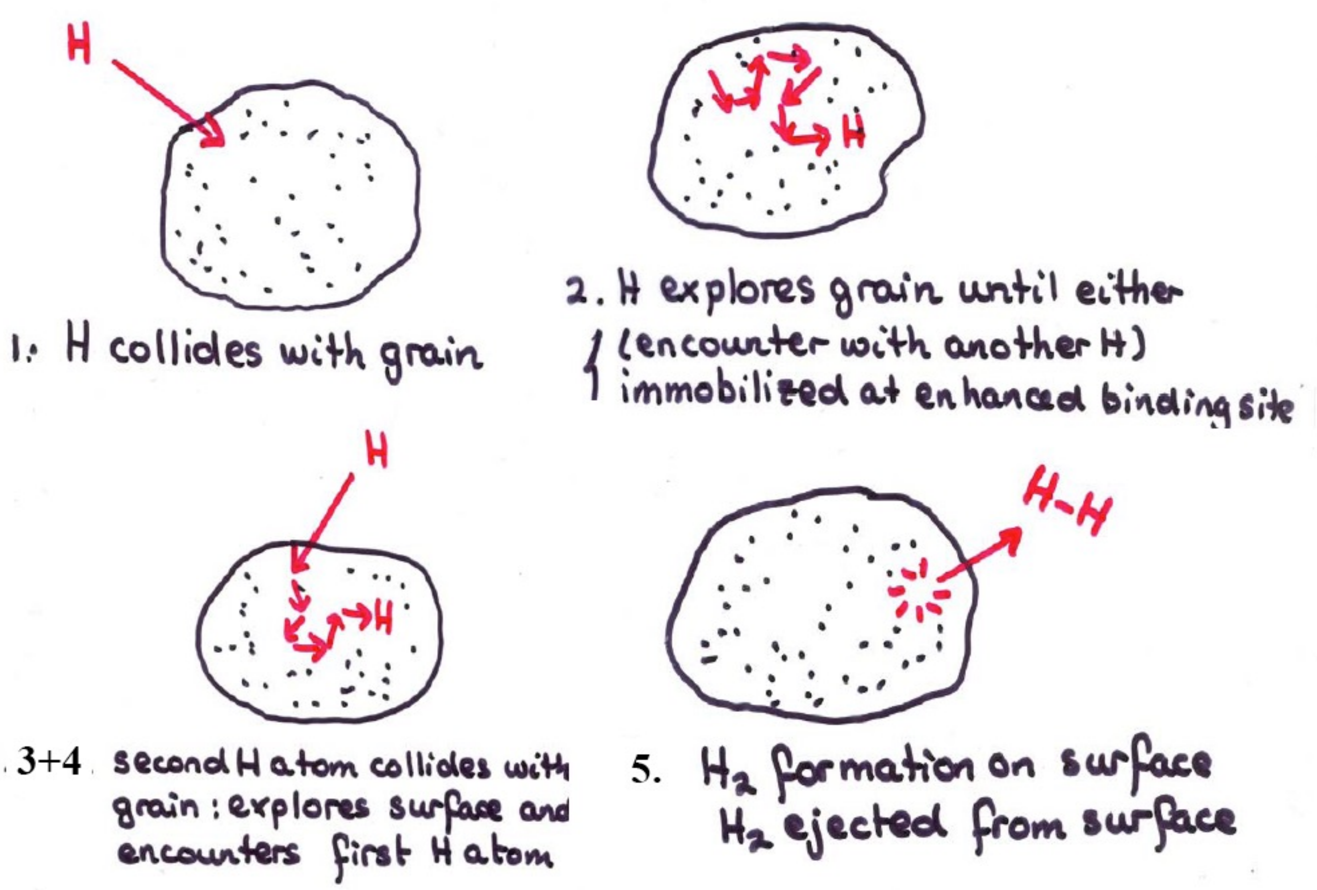
$$X + Y{:}g \rightarrow XY + g$$

$$XY + h\nu \rightarrow X + Y$$

$$XY^+ + e \rightarrow X + Y$$

H_2 formation on dust grains

Credits: van Dishoeck



1. H collides with grain

2. H explores grain until either
{ (encounter with another H)
immobilized at enhanced binding site

3+4. second H atom collides with grain: explores surface and encounters first H atom

5. H_2 formation on surface
H_2 ejected from surface

Interstellar molecules

- About two hundreds gas-phase molecular species have been detected so far
- Besides simple molecules with a few atoms, also relatively complex molecules with a larger number of atoms have been detected

http://www.astro.uni-koeln.de/cdms/molecules

  - Observational bias:

    Different types of molecules are observed in different types of interstellar or circumstellar regions

    Some of them are only observed in dense molecular clouds

    Symmetric molecules are harder to detect: they could be more abundant than what observed

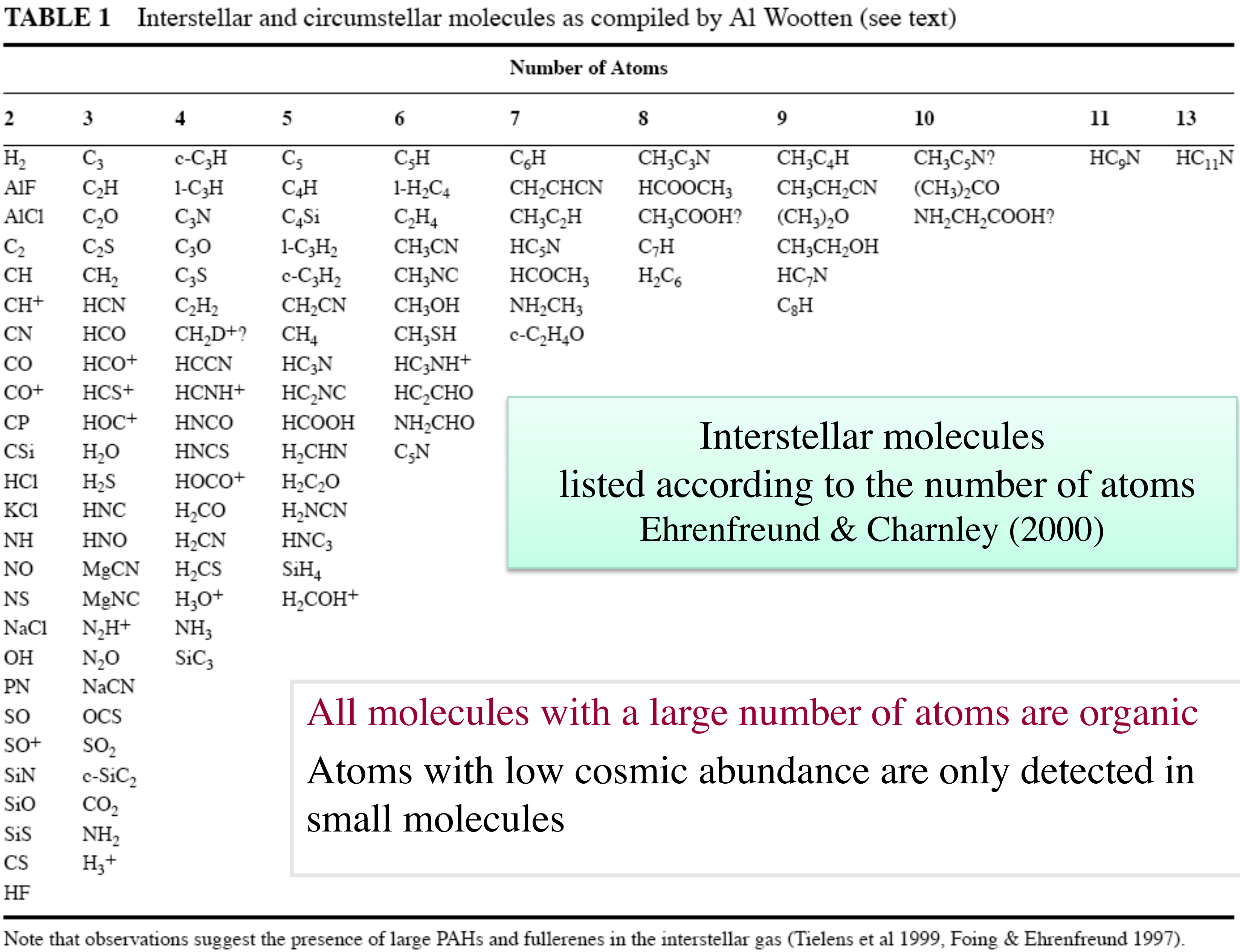


TABLE 1 Interstellar and circumstellar molecules as compiled by Al Wootten (see text)

Number of Atoms										
2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**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	$HC_{11}N$
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	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		C_8H			
CN	HCO	CH_2D^+?	CH_4	CH_3SH	c-C_2H_4O					
CO	HCO^+	HCCN	HC_3N	HC_3NH^+						
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							
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									
SO	OCS									
SO^+	SO_2									
SiN	c-SiC_2									
SiO	CO_2									
SiS	NH_2									
CS	H_3^+									
HF										

Note that observations suggest the presence of large PAHs and fullerenes in the interstellar gas (Tielens et al 1999, Foing & Ehrenfreund 1997).

Interstellar molecules
listed according to the number of atoms
Ehrenfreund & Charnley (2000)

All molecules with a large number of atoms are organic

Atoms with low cosmic abundance are only detected in small molecules

Small interstellar molecules

- Found in *diffuse* molecular clouds
  - molecular clouds with relatively low extinction
- Large molecules are absent in *diffuse* clouds because of:
  - physical conditions

    diffuse clouds are less protected from interstellar radiation field than denser molecular clouds
  - observational limitations

    diffuse clouds have relatively low column densities and this fact makes hard to detect large molecules, characterized by a low abundance

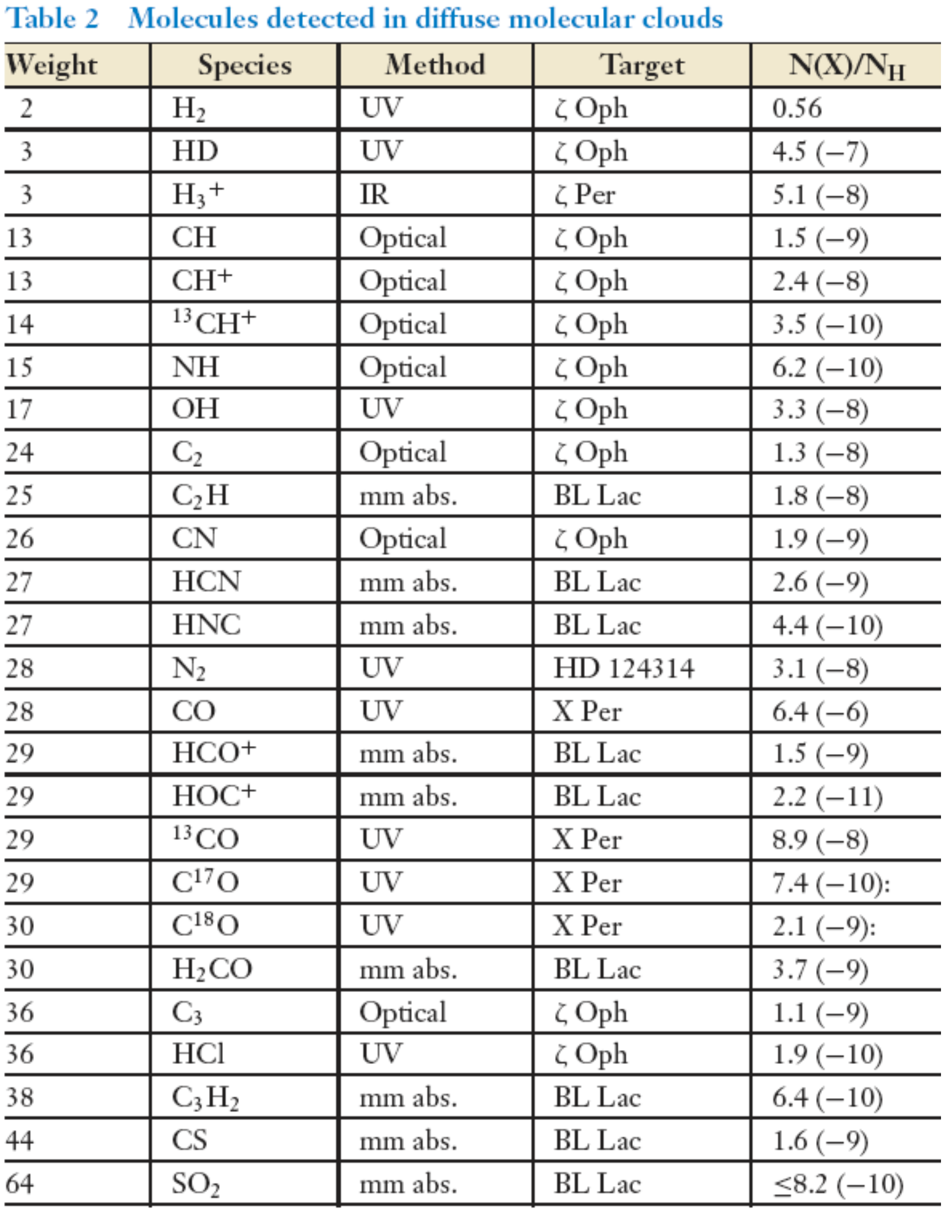


Table 2 Molecules detected in diffuse molecular clouds

Weight	Species	Method	Target	$N(X)/N_H$
2	H_2	UV	ζ Oph	0.56
3	HD	UV	ζ Oph	4.5 (−7)
3	H_3^+	IR	ζ Per	5.1 (−8)
13	CH	Optical	ζ Oph	1.5 (−9)
13	CH^+	Optical	ζ Oph	2.4 (−8)
14	$^{13}CH^+$	Optical	ζ Oph	3.5 (−10)
15	NH	Optical	ζ Oph	6.2 (−10)
17	OH	UV	ζ Oph	3.3 (−8)
24	C_2	Optical	ζ Oph	1.3 (−8)
25	C_2H	mm abs.	BL Lac	1.8 (−8)
26	CN	Optical	ζ Oph	1.9 (−9)
27	HCN	mm abs.	BL Lac	2.6 (−9)
27	HNC	mm abs.	BL Lac	4.4 (−10)
28	N_2	UV	HD 124314	3.1 (−8)
28	CO	UV	X Per	6.4 (−6)
29	HCO^+	mm abs.	BL Lac	1.5 (−9)
29	HOC^+	mm abs.	BL Lac	2.2 (−11)
29	^{13}CO	UV	X Per	8.9 (−8)
29	$C^{17}O$	UV	X Per	7.4 (−10):
30	$C^{18}O$	UV	X Per	2.1 (−9):
30	H_2CO	mm abs.	BL Lac	3.7 (−9)
36	C_3	Optical	ζ Oph	1.1 (−9)
36	HCl	UV	ζ Oph	1.9 (−10)
38	C_3H_2	mm abs.	BL Lac	6.4 (−10)
44	CS	mm abs.	BL Lac	1.6 (−9)
64	SO_2	mm abs.	BL Lac	≤8.2 (−10)

“Complex” interstellar molecules

(“complex” for interstellar standards, not for chemists)

- Complex interstellar molecules are hydrocarbons
- They are found in:
  - star-forming regions
  - circumstellar envelopes of evolved, late-type stars in the Asymptotic giant branch (AGB)
  - dense clouds in the direction of the Galactic center

Herbst & van Dishoeck (2009)

Examples of interstellar hydrocarbons

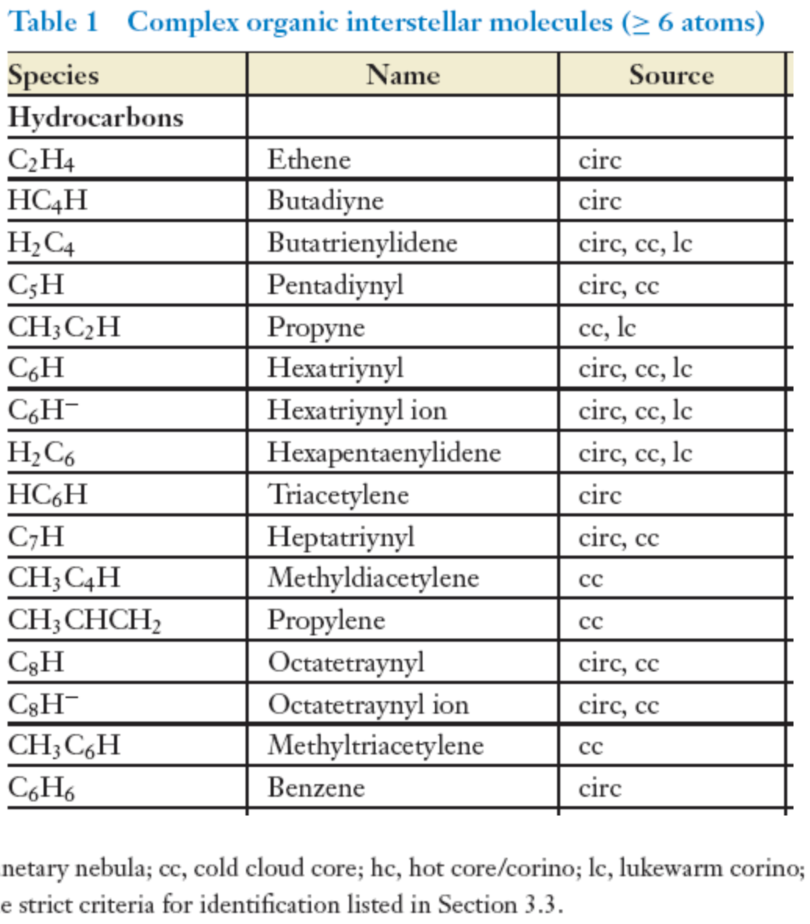


Table 1 Complex organic interstellar molecules (≥ 6 atoms)

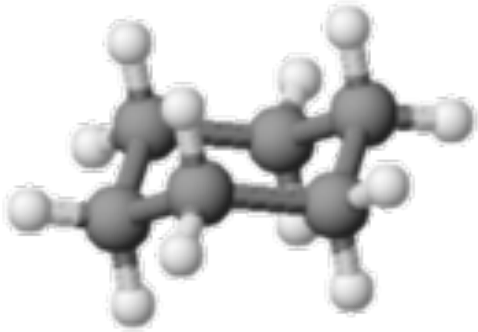
Species	Name	Source
Hydrocarbons		
C_2H_4	Ethene	circ
HC_4H	Butadiyne	circ
H_2C_4	Butatrienylidene	circ, cc, lc
C_5H	Pentadiynyl	circ, cc
CH_3C_2H	Propyne	cc, lc
C_6H	Hexatriynyl	circ, cc, lc
C_6H^-	Hexatriynyl ion	circ, cc, lc
H_2C_6	Hexapentaenylidene	circ, cc, lc
HC_6H	Triacetylene	circ
C_7H	Heptatriynyl	circ, cc
CH_3C_4H	Methyldiacetylene	cc
CH_3CHCH_2	Propylene	cc
C_8H	Octatetraynyl	circ, cc
C_8H^-	Octatetraynyl ion	circ, cc
CH_3C_6H	Methyltriacetylene	cc
C_6H_6	Benzene	circ

Abbreviations: circ, circumstellar envelope around evolved star/protoplanetary nebula; cc, cold cloud core; hc, hot core/corino; lc, lukewarm corino; gc, galactic center cloud; of, outflow. Not all of these molecules fulfill the strict criteria for identification listed in Section 3.3.

Saturation of interstellar organic molecules

- Saturated hydrocarbons
  - The chain of carbon atoms are held by single bonds
  - The remaining carbon bonds are saturated with hydrogen atoms
- Interstellar organic molecules are usually not saturated
  - Example of saturated molecule not detected in the ISM

    Cyclohexane, C_6H_{12}



Cyclohexane

  - Example of unsaturated molecule detected in the ISM

    Benzene, C_6H_6

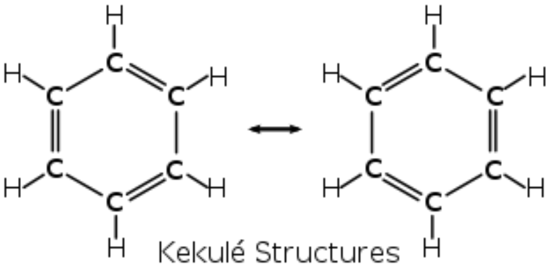
Benzene

- Aromatic ring
  - Stable electronic structure that results from the superposition of atomic orbitals; the electrons are delocalized and shared by all atoms
- Plays an important role in astrochemistry
  - Starting point for the formation of complex aromatic compounds

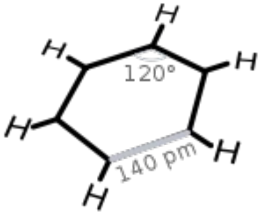
PAHs=Polycyclic Aromatic Hydrocarbon

C_6H_6

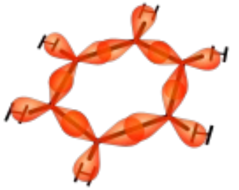
Benzene
Molecular formula



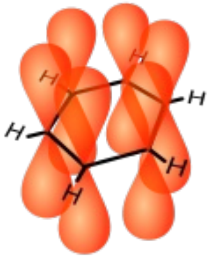
Kekulé Structures
(Isomers)



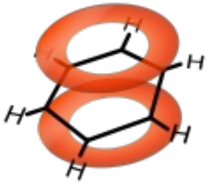
Planar Hexagon
Bond Length 140 pm



Sigma Bonds
sp^2 Hybridized orbitals



6 p_z orbitals

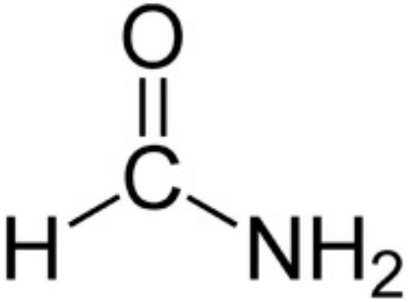


delocalized pi
system

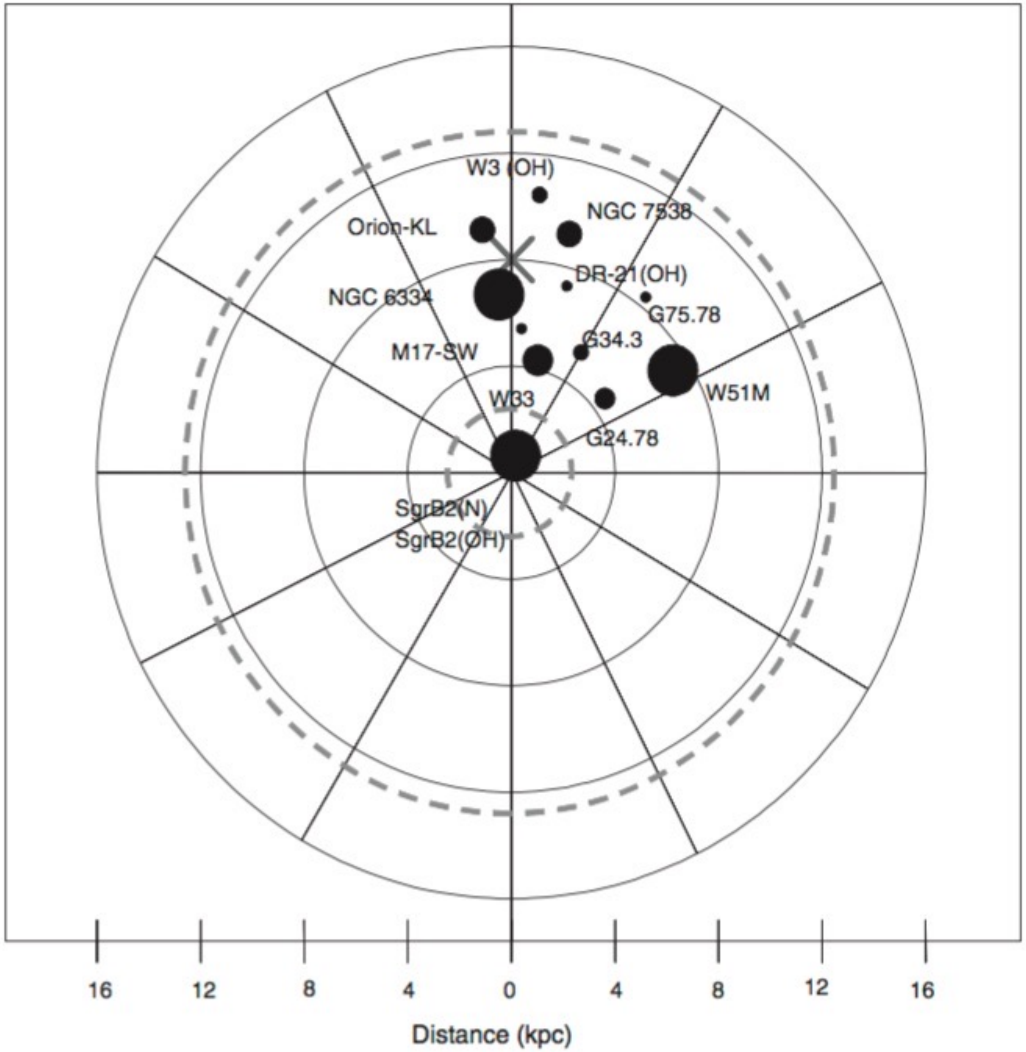
Benzene ring
Simplified depiction

Formamide

An interstellar molecule of prebiotic interest



Detected multiple rotational transitions in the sub-millimetric spectral range in molecular clouds at different locations in the Galaxy

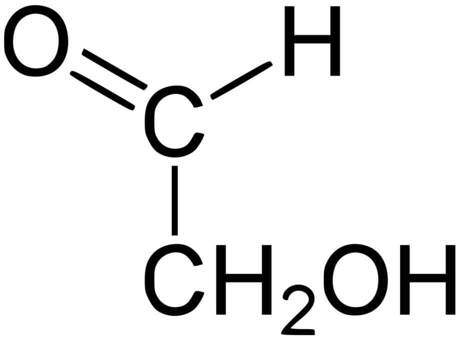


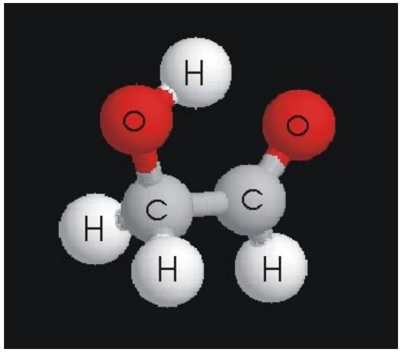
Adande et al. (2013)

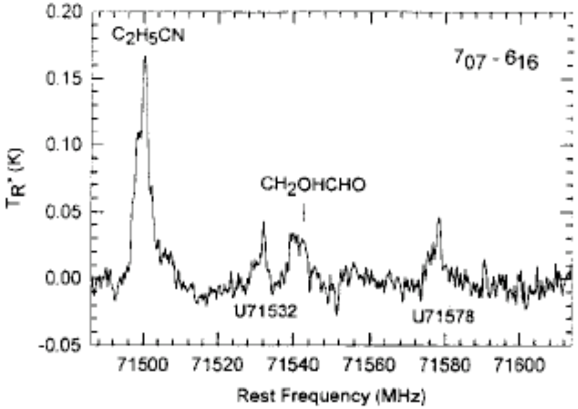
“Complex” organic molecules in the interstellar medium

Generic formula for sugars
$C_n(H_2O)_n$

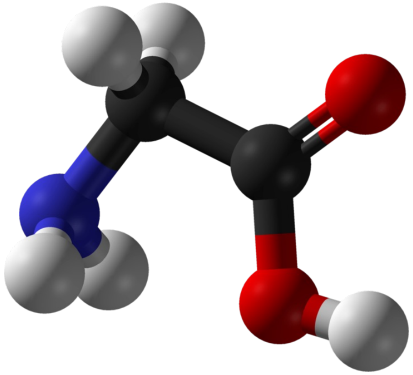
- Glycolaldehyde ($C_2H_4O_2$)
  - Simplest sugar
  - Detected in the millimetric band towards Sagittarius B2(N), a source in the direction of the Galactic center (Hollis et al. 2000)
  - Also observed by ALMA around a young, solar-type star
  - First intermediate product of the reaction which starts with formaldehyde (H_2CO) and leads to the formation of various sugars and finally of ribose, one of the DNA building blocks



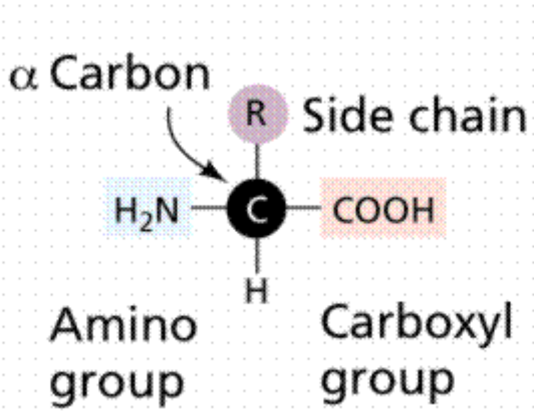




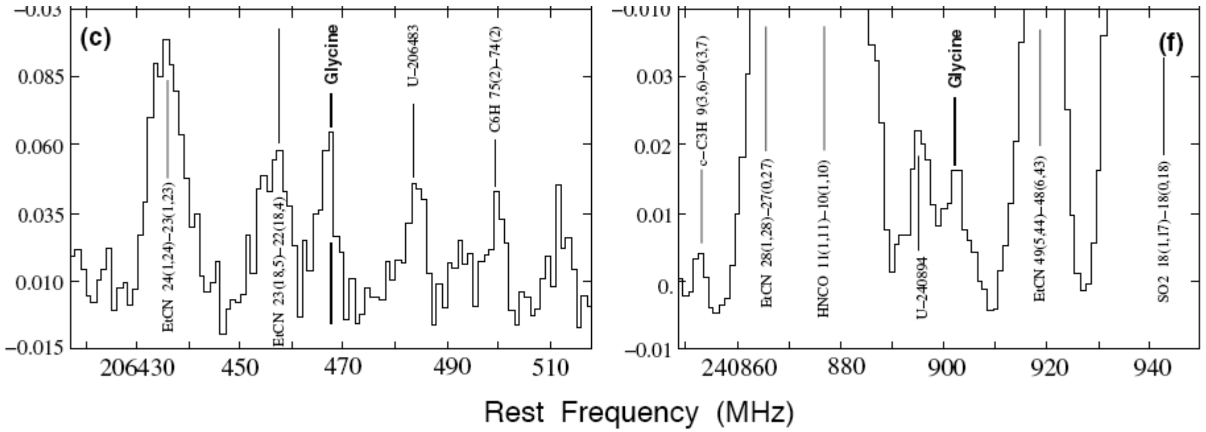
“Complex” organic molecules in the interstellar space
The case of glycine



Conventional depiction of aminoacids



- Glycine is the simplest biological aminoacid
  - Its presence in the space would demonstrate the existence of interstellar chemical pathways able to synthesise basic ingredients of biomolecules
  - Several claims of detection of interstellar glycine have been reported
  - However, its identification is hard to confirm



Which is the maximum complexity of interstellar organic molecules in the gas phase?

As molecular complexity increases, the identification of the molecule tends to become uncertain

Gas-phase molecules with a high number of atoms could be present in the interstellar medium, even though it is difficult to prove their existence