Astrochemistry (1)

Planets and Astrobiology (2018-2019)
G. Vladilo

Interstellar molecules

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

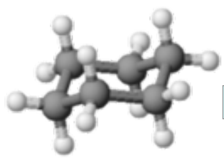
Species	Name	Source
Hydrocarbons		
C_2H_4	Ethene	circ
HC_4H	Butadiyne	circ
H_2C_4	Butatrienylidene	circ, cc, lc
C_5H	Pentadiynyl	circ, cc
CH_3C_2H	Propyne	cc, lc
C_6H	Hexatriynyl	circ, cc, lc
C_6H^-	Hexatriynyl ion	circ, cc, lc
H_2C_6	Hexapentaenylidene	circ, cc, lc
HC_6H	Triacetylene	circ
C_7H	Heptatriynyl	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 <u>saturated</u> molecule <u>not detected</u> in the ISM

    Cyclohexane, C_6H_{12}



Cyclohexane

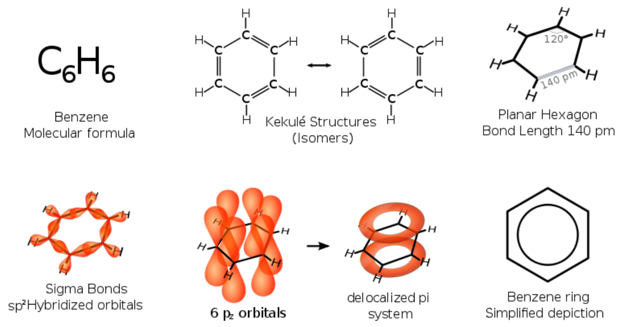
  - Example of <u>unsaturated</u> molecule <u>detected</u> in the ISM

    Benzene, C_6H_6

Benzene

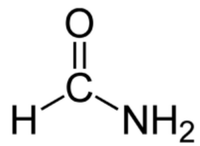
- Aromatic ring
  - Stable electronic structure that results from the superposition of atomic orbitals; the electrons are delocalized and shared by all atoms
- Plays an important role in astrochemistry
  - Starting point for the formation of complex aromatic compounds

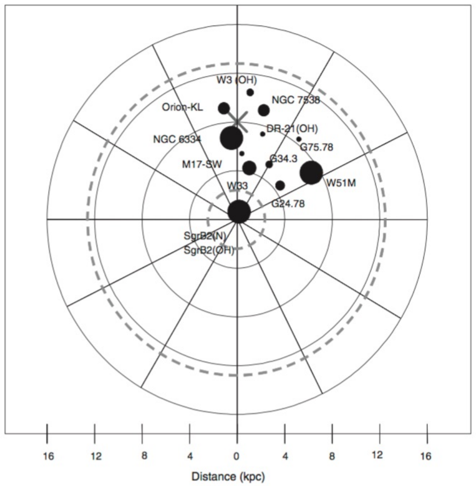
    PAHs=Polycyclic Aromatic Hydrocarbon



Formamide

An interstellar molecule of prebiotic interest





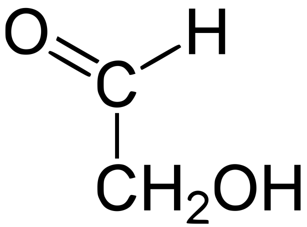
Detected multiple rotational transitions in the sub-millimetric spectral range in molecular clouds at different locations in the Galaxy

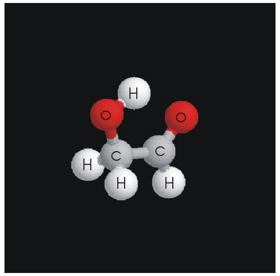
Adande et al. (2013)

Complex organic molecules in the interstellar medim

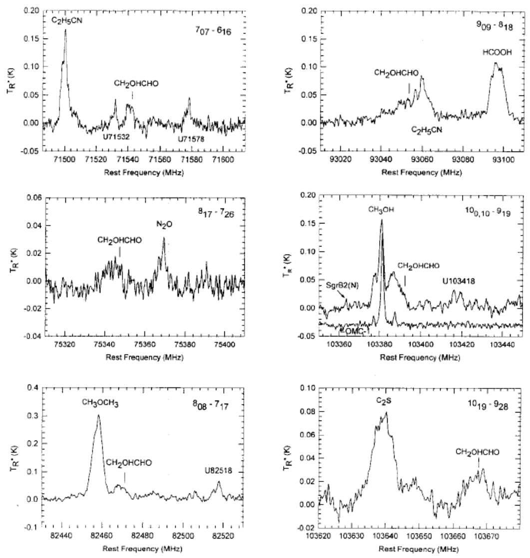
- Glycolaldehyde ($C_2H_4O_2$)
  - Simplest sugar
  - First intermediate product of the reaction which starts with formaldehyde (H_2CO) and leads to the formation of various sugars and finally of ribose, one of the DNA building blocks

Generic formula for sugars
$C_n(H_2O)_n$



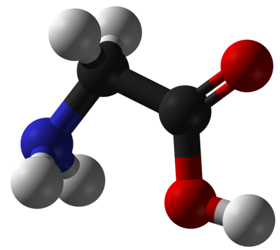


- Detection of glycolaldehyde (CH_2OHCHO)
  - First detection of interstellar sugar
  - Detected in the millimetric band towards Sagittarius B2(N), a source in the direction of the Galactic center (Hollis et al. 2000)
  - Also observed by ALMA around a young, solar-type star

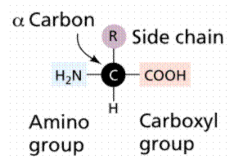


Complex organic molecules in the interstellar space
The case of glycine

- Glycine is the simplest aminoacid found in biological proteins (NH_2CH_2COOH)
  - Its existence in the interstellar space would demonstrate the existence of chemical pathways potentially able to synthesise basic ingredients of life molecules in the interstellar space
  - The “lateral group” R is simply a hydrogen atom

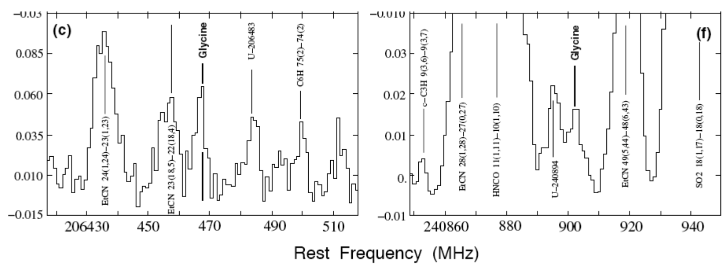


Conventional depiction of aminoacids



Tentative evidence for interstellar glycine

- Glycine (NH_2CH_2COOH)
  - Several emission lines attributed to interstellar glycine have been reported
    Kuan et al. (2003)



  - The identification is not confirmed by a subsequent analysis performed by testing a larger number of lines expected for glycine
    Snyder et al. (2005)

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

Interstellar dust
The solid phase component of the ISM

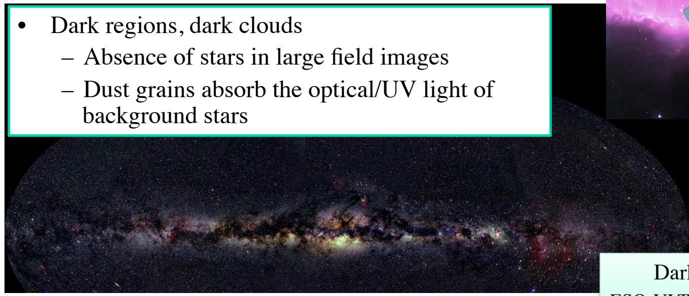
Importance of interstellar dust in astronomy

- Effects on astronomical observations
  - Reddening and extinction of astronomical sources
  - Depletion of chemical abundances in the interstellar gas
- Physical effects in the interstellar medium
  - Transformation of UV photons into IR photons
  - Cooling of the ISM by means of thermal emission
- Effects on planetary formation
  - Essential ingredient of planetary formation in protoplanetary
- Importance in astrochemistry
  - Catalyst for the formation of interstellar molecules

Observational evidence of interstellar dust (1)

The Horsehead Nebula

- Dark regions, dark clouds
  - Absence of stars in large field images
  - Dust grains absorb the optical/UV light of background stars



Dark cloud B68
ESO-VLT Alves et al. (2001)

In some cases, dark clouds are associated with pre-stellar cores

Observational evidence of interstellar dust (2)
Reflection nebulae

- Dust grains in reflection nebulae scatter the stellar photons
- A detailed study of reflection nebulae provides information on some physical properties of the grains
  - Albedo
    Ratio between scattering and extinction cross-sections of dust grains
  - Phase function
    Angular distribution of scattered light

Observational evidence of interstellar dust (3)

Galactic infrared emission

- Thermal emission from interstellar dust
  - Dust is heated by interstellar radiation
  - The infrared emission cools the gas
- Galactic infrared emission maps the distribution of interstellar dust

  1983, IRAS satellite
  - All sky map in the bands at12, 25, 60 e 100 μm
  - The emission is concentrated in the Galactic plane
  - IR clouds ("cirrus") found outside the Galactic plane

Composite mid-and far-infrared intensity observed in the 12, 60, and 100 μm wavelength bands. Mosaic of IRAS Sky Survey Atlas images. Emission from interplanetary dust in the solar system, the "zodiacal emission," was modeled and subtracted.

Observational evidence of interstellar dust (4)

Infrared absorptions

- Observations of background sources with strong IR emission along lines of sight intersecting dust-rich regions
  - Vibrational bands of solid compounds are detected in absorption
- Ice and organic compounds
  - H_2O, CO, CO_2, CH_3OH …
- Silicates
  - 9.7 μm e 18 μm

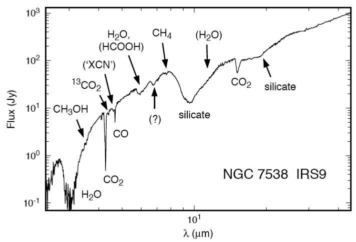
    Stretching vibration modes of Si−O bonds and bending vibration modes O−Si−O modes, respectively

Examples of silicates

Pyroxenes: $Mg_xFe_{(1-x)}SiO_3$

Olivines: $Mg_{2y}Fe_{2(1-y)}SiO_4$

ISO SWS spectrum in the mid-IR (2.4 to 45 μm) towards the young stellar cluster NGC7538 IRS9 embedded in a molecular cloud (Whittet et al. 1996)



Vibration modes of interstellar solids: ice and dust

A high spectral resolution is required to discriminate between different types of silicates

Pyroxenes: $Mg_xFe_{(1-x)}SiO_3$

Olivines: $Mg_{2y}Fe_{2(1-y)}SiO_4$

Molecule	Mode	λ (μm)
H_2O	O–H stretch	3.05
	H–O–H bend	6.0
	libration	13.3
NH_3	N–H stretch	2.96
	umbrella	9.35
CH_4	C–H stretch	3.32
	C–H deformation	7.69
CO	C–O stretch	4.67
CO_2	C–O stretch	4.27
	O–C–O bend	15.3
CH_3OH	O–H stretch	3.08
	C–H stretch	3.35
	C–H stretch	3.53
	O–H bend, C–H deformation	6.89
	C–O stretch	9.75
$MgSiO_3$	Si–O stretch	9.7
	O–Si–O bend	19.0
Mg_2SiO_4	Si–O stretch	10.0
	O–Si–O bend	19.5
$FeSiO_3$	Si–O stretch	9.5
	O–Si–O bend	20.0
Fe_2SiO_4	Si–O stretch	9.8
	O–Si–O bend	20.0
SiC	Si–C stretch	11.2

Observational evidence of interstellar dust (5)

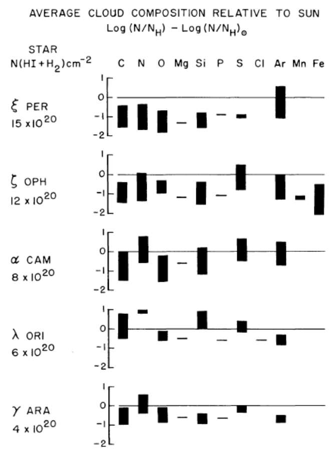
Elemental depletions

Gas-phase interstellar abundances are measured with high-resolution UV spectroscopy

The interstellar (resonance) transitions of the main ionization stages of the most abundant astrophysical elements are found in the UV range

The measurements of interstellar abundances indicate that:

- For most elements the interstellar abundances X/H, measured in the gas phase, are lower than the corresponding solar abundances
- This deficiency is known as "interstellar depletion"



Interstellar depletions

- Interpretation

  a fraction of the atoms is incorporated in dust grains and, as a result, is not counted in the gas-phase column density measurements

- Galactic interstellar depletions are calculated assuming that the total abundance of the interstellar medium (gas plus dust) is solar

$$\delta_X = \log_{10} (N_X/N_H) - \log_{10} (X/H)_{sun}$$

  This expression is equal to the definition of [X/H], but the physical meaning is completely different

- Interstellar depletions vary
  - between different elements
  - in different types of interstellar regions

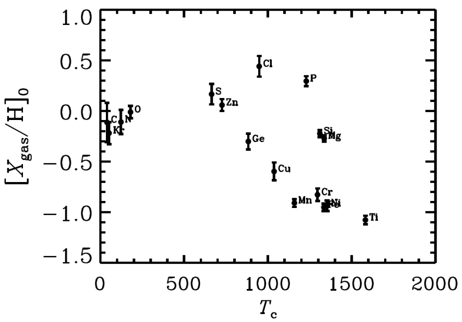
Element-to-element variations of interstellar depletions

- Refractory elements
  - Strong depletions

    e.g., Ti, Ni, Fe, Cr, Mn, ..
- Volatile elements
  - Weak depletions

    e.g., S, Zn

- Correlation between depletion and condensation temperature
  - Empirical evidence that supports the interpretation of depletions in terms of incorporation of a fraction of elements in dust form



Condensation temperature

Temperature at which the 50% of an element condenses to a solid compound in a cooling gas of solar chemical composition

See Lodders K, 2003, ApJ, 591, 1220

Variations of depletions in different types of interstellar regions

- Cold and dense clouds
  - Strong depletions
- Warm and hot gas
  - Weak depletions

- Further evidence that depletions are due to the incorporation of atoms in dust form
  - Dust grains survive (or grow by accretion) in cold and dense clouds
  - Dust grains tend to be destroyed in hot, low density regions