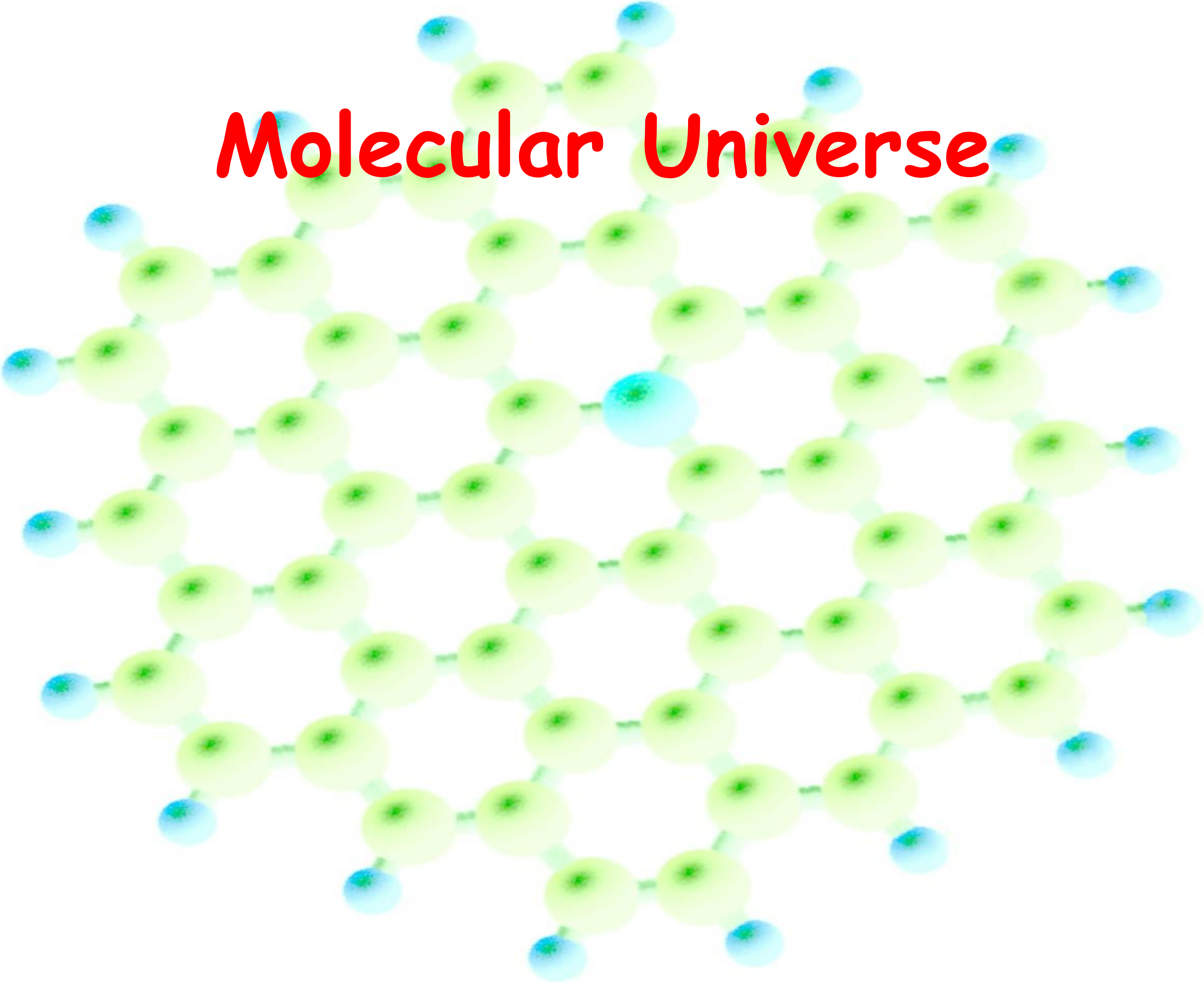
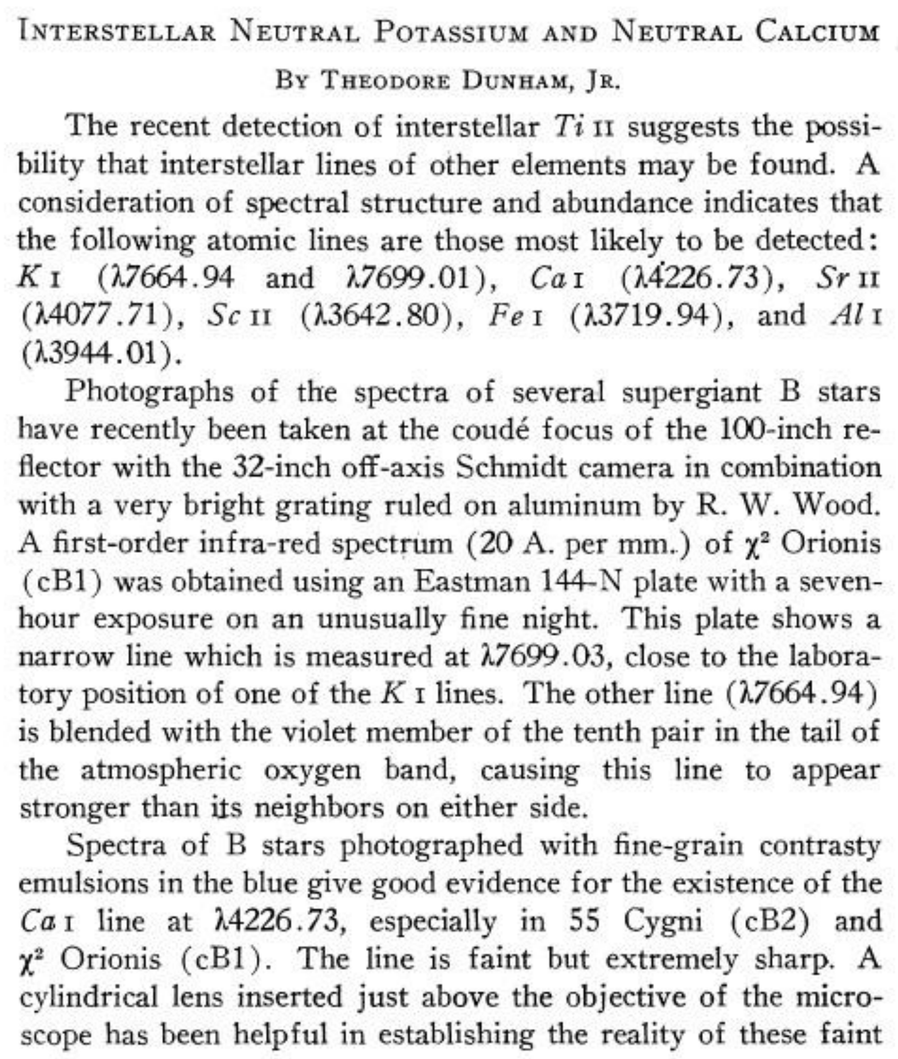
Molecular Universe





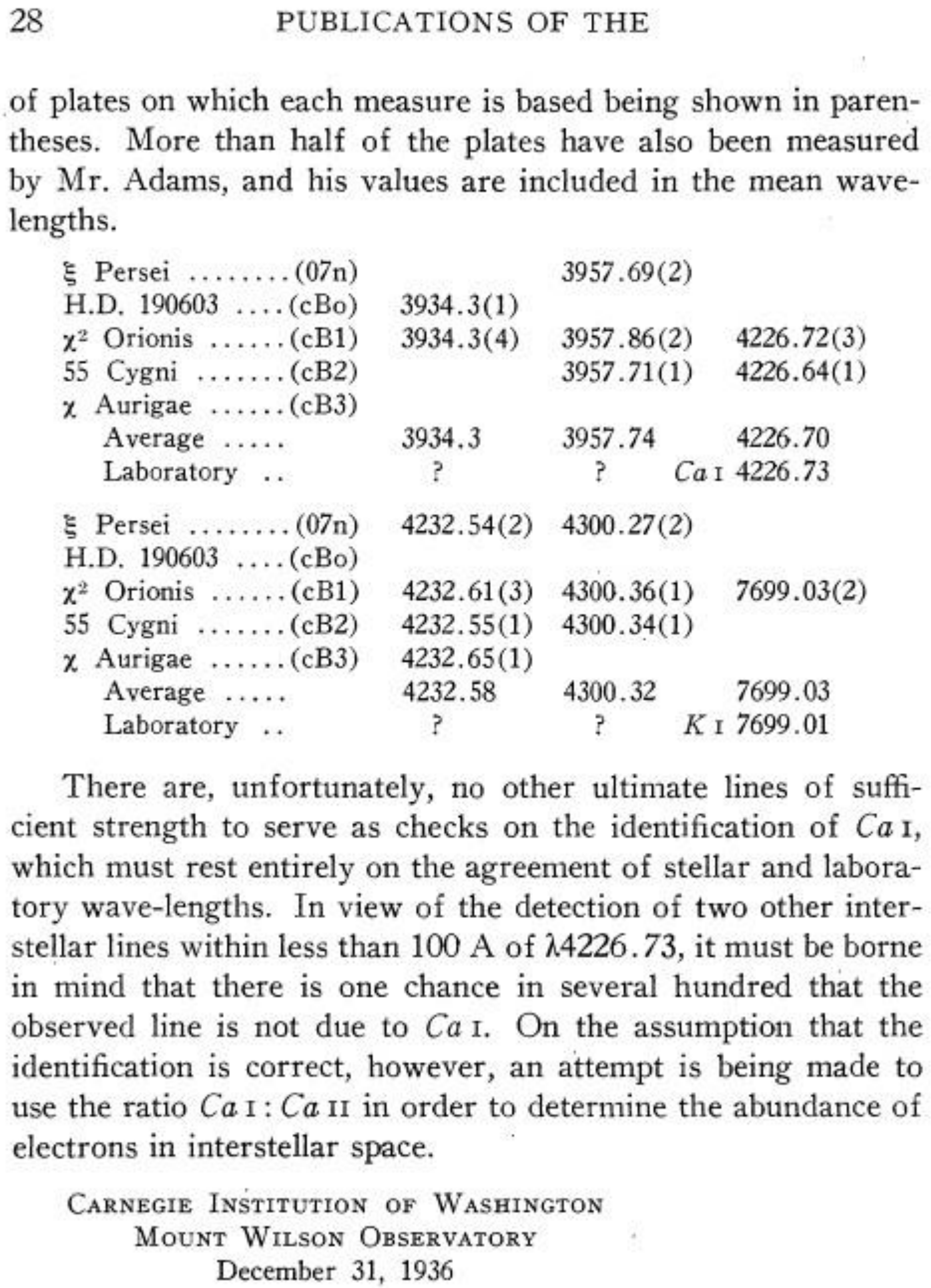
INTERSTELLAR NEUTRAL POTASSIUM AND NEUTRAL CALCIUM

BY THEODORE DUNHAM, JR.

The recent detection of interstellar *Ti* II suggests the possibility that interstellar lines of other elements may be found. A consideration of spectral structure and abundance indicates that the following atomic lines are those most likely to be detected: *K* I (λ7664.94 and λ7699.01), *Ca* I (λ4226.73), *Sr* II (λ4077.71), *Sc* II (λ3642.80), *Fe* I (λ3719.94), and *Al* I (λ3944.01).

Photographs of the spectra of several supergiant B stars have recently been taken at the coudé focus of the 100-inch reflector with the 32-inch off-axis Schmidt camera in combination with a very bright grating ruled on aluminum by R. W. Wood. A first-order infra-red spectrum (20 A. per mm.) of χ^2 Orionis (cB1) was obtained using an Eastman 144-N plate with a seven-hour exposure on an unusually fine night. This plate shows a narrow line which is measured at λ7699.03, close to the laboratory position of one of the *K* I lines. The other line (λ7664.94) is blended with the violet member of the tenth pair in the tail of the atmospheric oxygen band, causing this line to appear stronger than its neighbors on either side.

Spectra of B stars photographed with fine-grain contrasty emulsions in the blue give good evidence for the existence of the *Ca* I line at λ4226.73, especially in 55 Cygni (cB2) and χ^2 Orionis (cB1). The line is faint but extremely sharp. A cylindrical lens inserted just above the objective of the microscope has been helpful in establishing the reality of these faint



of plates on which each measure is based being shown in parentheses. More than half of the plates have also been measured by Mr. Adams, and his values are included in the mean wave-lengths.

ξ Persei ....(07n)		3957.69(2)	
H.D. 190603 ....(cBo)	3934.3(1)		
χ^2 Orionis ......(cB1)	3934.3(4)	3957.86(2)	4226.72(3)
55 Cygni ....(cB2)		3957.71(1)	4226.64(1)
χ Aurigae ......(cB3)			
Average	3934.3	3957.74	4226.70
Laboratory ..	?	?	*Ca* I 4226.73

ξ Persei ....(07n)	4232.54(2)	4300.27(2)	
H.D. 190603 ....(cBo)			
χ^2 Orionis ......(cB1)	4232.61(3)	4300.36(1)	7699.03(2)
55 Cygni ....(cB2)	4232.55(1)	4300.34(1)	
χ Aurigae ......(cB3)	4232.65(1)		
Average	4232.58	4300.32	7699.03
Laboratory ..	?	?	*K* I 7699.01

There are, unfortunately, no other ultimate lines of sufficient strength to serve as checks on the identification of *Ca* I, which must rest entirely on the agreement of stellar and laboratory wave-lengths. In view of the detection of two other interstellar lines within less than 100 A of λ4226.73, it must be borne in mind that there is one chance in several hundred that the observed line is not due to *Ca* I. On the assumption that the identification is correct, however, an attempt is being made to use the ratio *Ca* I : *Ca* II in order to determine the abundance of electrons in interstellar space.

CARNEGIE INSTITUTION OF WASHINGTON
MOUNT WILSON OBSERVATORY
December 31, 1936

Dunham, 1937, *PASP*, **49**, 26-28

NOTES

CONSIDERATIONS REGARDING INTERSTELLAR MOLECULES

ABSTRACT

An attempt has been made to compute the numbers of certain molecules in interstellar space. The results obtained are unfavorable to Saha's identification of one of Merrill's interstellar lines with Na_2. A search for the bands of CH, OH, NH, CN, and C_2 would appear to be promising.

Attention has recently been drawn to the subject of molecules in interstellar space by H. N. Russell,[1] P. Swings,[2] A. S. Eddington,[3] and M. N. Saha,[4] whose aims were essentially the interpretation of new interstellar lines of rather diffuse character, discovered by P. W. Merrill.[5] In the paper by Swings, a tentative identification of two of Merrill's lines with rotatory oscillation bands of CO_2 is suggested; the theoretical width of molecular interstellar bands is calculated and found to be in good agreement with the observations; and finally the importance of the dissociation of molecules in a radiation field is advocated. Later on, Saha published the statement that one of Merrill's bands (λ 6283) was certainly due to the Na_2 molecule (transition $1\Sigma \leftrightarrow 1\Sigma$; $v'' = 0$, $v' = 8$) and that another line (λ 5780) might provisionally be attributed to NaK ($v'' = 0$, $v' = 5$). We do not believe that Saha's identification is correct; actually the experimental and theoretical investigations of the Na_2 spectrum and the determination of the corresponding Franck-Condon diagram by Loomis and Nile[6] and by Loomis and Nusbaum[7] indicate clearly that several other bands of Na_2 ($v'' = 0$ to $v' = 5, 6, 7, 9, 10$) are

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[1] *M.N.*, **95**, 635, 1935.

[2] *Ibid.*, **97**, 212, 1937.

[3] *Observatory*, **60**, 99, 1937.

[4] *Nature*, **139**, 840, 1937.

[5] *Pub. A.S.P.*, **46**, 206, 1934; *Ap. J.*, **83**, 126, 1936.

[6] *Phys. Rev.*, **32**, 873, 1928.

[7] *Ibid.*, **40**, 380, 1932.

Swings, Rosenfeld, 1937, *ApJ*, **86**, 483-486

For a triatomic molecule (such as CO_2, assuming the reaction $CO + O$), we get

$$\frac{n_{AB_2}}{n_A n_B^2} = 4 \cdot 10^{-15} .$$

Thus triatomic molecules like CO_2 must be rare compared with diatomic compounds. In the case of Na_2, Eddington has given the maximum value to 10^{-6} atom per cubic centimeter for the density of neutral Na atoms in interstellar space. This would give us

$$n_{Na_2} = 2 \cdot 10^{-22} ,$$

which seems an extremely low value.

On the other hand, most of the H, O, N, and C atoms must be in their neutral state in interstellar space; we may safely assume that for these elements the atomic populations per cubic centimeter are not much smaller than unity, say between 1 and 10^{-3} atom per cubic centimeter. For diatomic compounds, such as H_2, OH, CH, NH, O_2, CO, CN, etc., the numbers of molecules would thus not be much smaller than the numbers of interstellar Ca^+ and Na atoms; but there would be less than 10^{-14} CO_2 molecules per cubic centimeter; this is rather unfavorable to the identification of CO_2. A search for the interstellar bands of CH, OH, NH, CN, and C_2 seems most interesting and promising. An interstellar line observed by Dunham[9] at λ 4300.3 may be due to CH. The only absorption lines of the (0, 0), $^2\Delta \leftarrow {}^2\Pi$ transition of this molecule, starting from the lowest rotational level, are λ 4300.24 and λ 4303.86. The second line could not be observed as a stationary line in an early B star, as it would be blended with λ 4303.82 O II. But the first would give an interpretation of the interstellar line observed by Dunham; the corresponding absorbing molecules would all be in their lowest level, in complete analogy with the case of Ti^+ atoms.

We may notice the influence of the adopted values for the temperature, the dilution factor, and the abundances. Actually if the temperature of radiation T_0 and the temperature of matter T_1 are identical, we may apply the formulae of thermodynamic equilibrium with the dilution factor δ and obtain the foregoing formula. If we suppose

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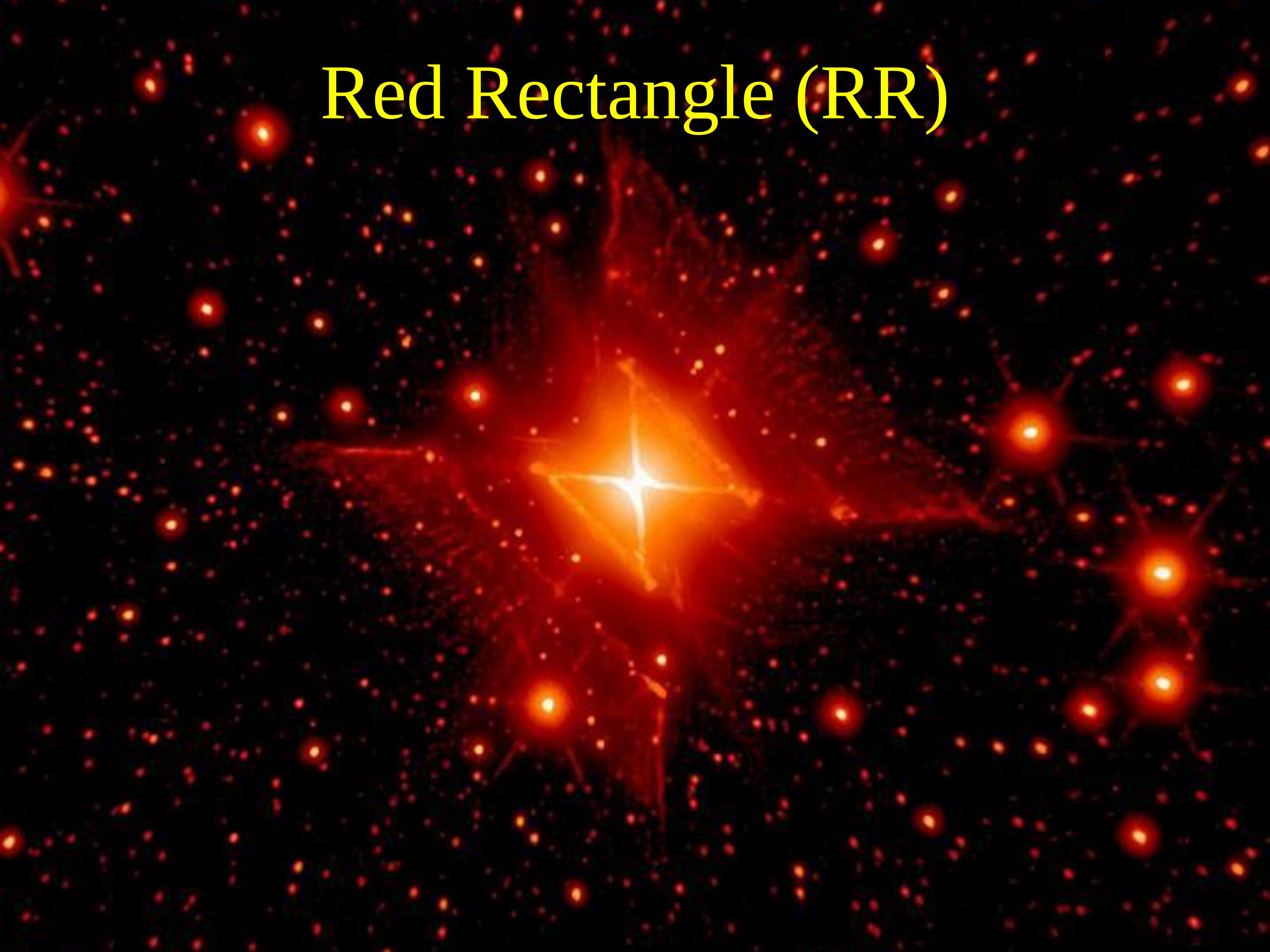
[9] Pub. *A.S.P.* **49**, 26, 1937.

Red Rectangle (RR)



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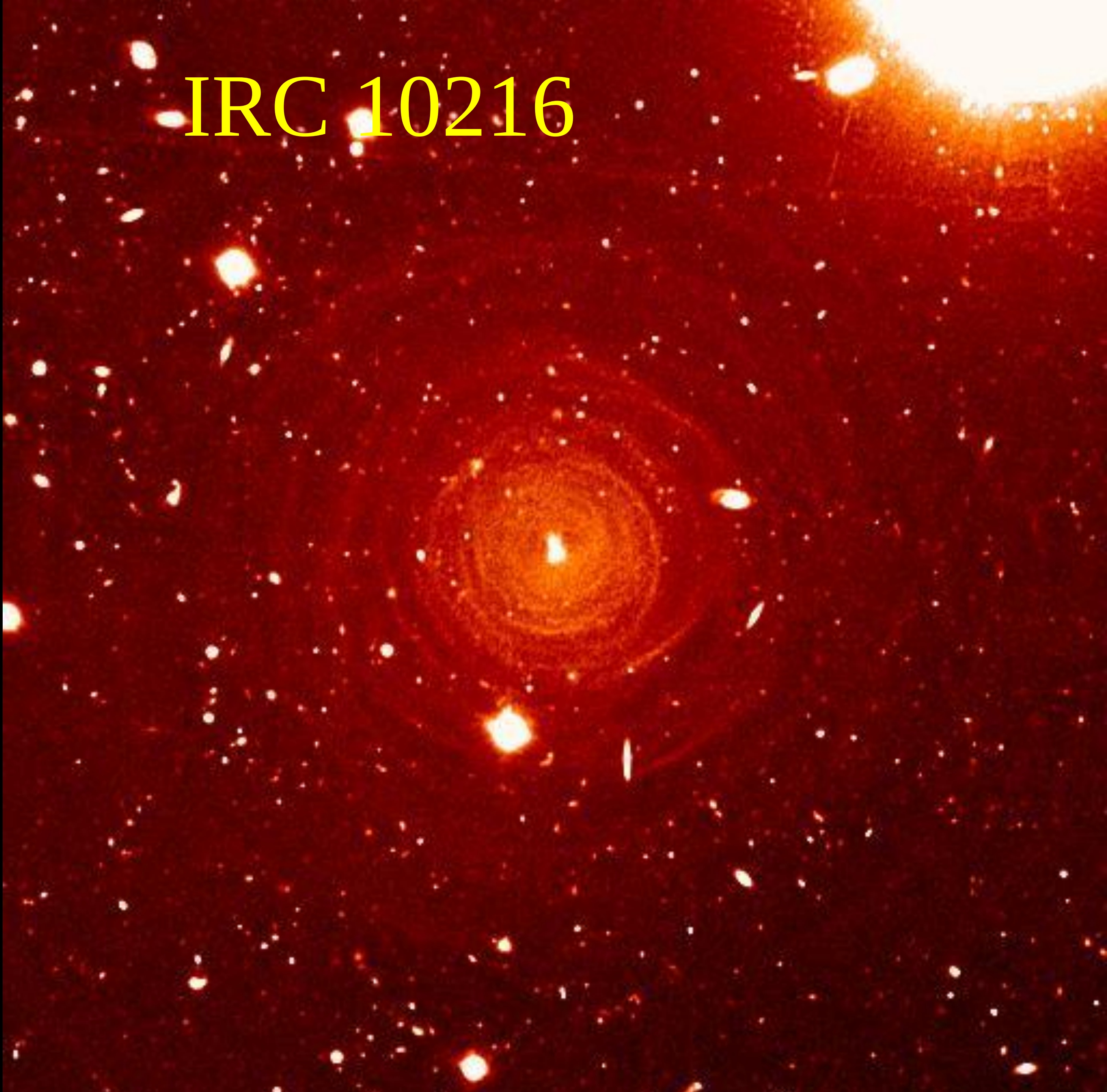
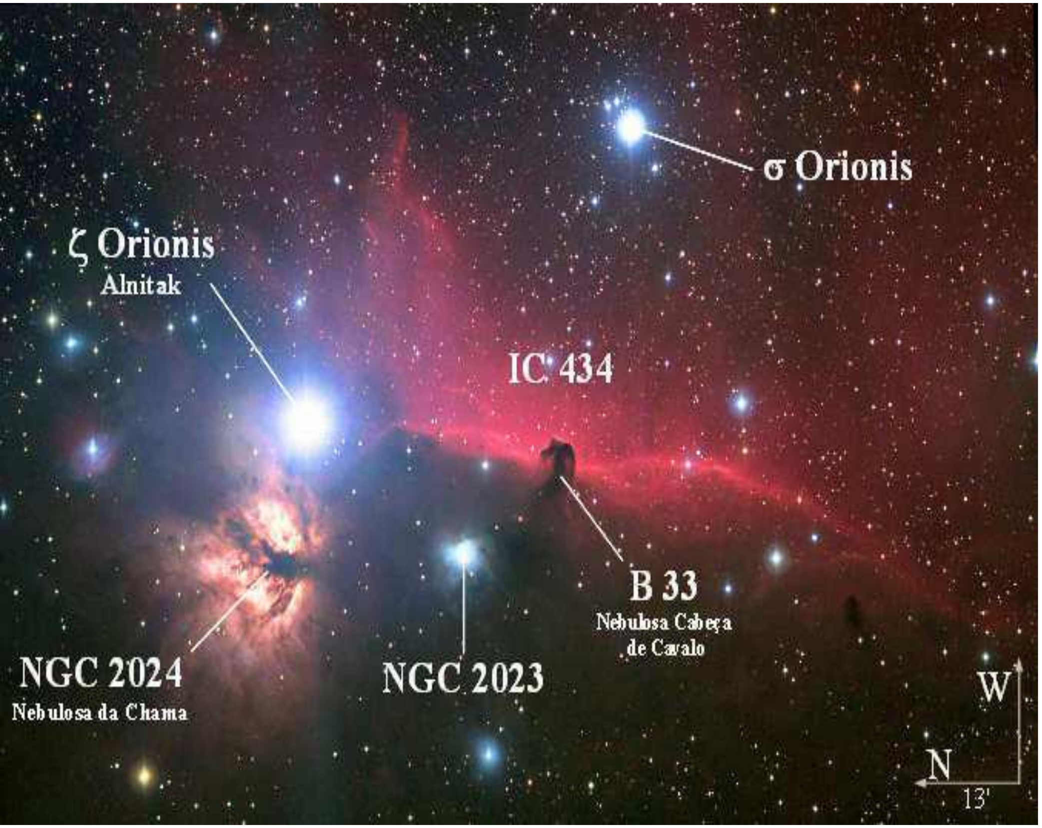


Sagittarius B2

Horse Head Nebula

Nebulosa Cabeça de Cavalo



- É um arquétipo de PDR e de nuvem molecular
- Distância moderada ($d \simeq 400\ pc$)
- Geometria simples
- Campo de radiação FUV bem conhecido (60 unidades de Draine)
- A estrela *Sigma Orionis* (A=O9.5V, T= 32.000 K; B=B0.5V, T= 32.000 K; C=A2V; D=B2V; E=B2Vp) ioniza a região, (Gerin, 2009)
- Temperatura Cinética $T_K \approx 15$ K
- Pressão térmica $P \approx 4 \times 10^6$ K cm^{-3}

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Chemical complexity in the Horsehead Photo-Dissociation Region

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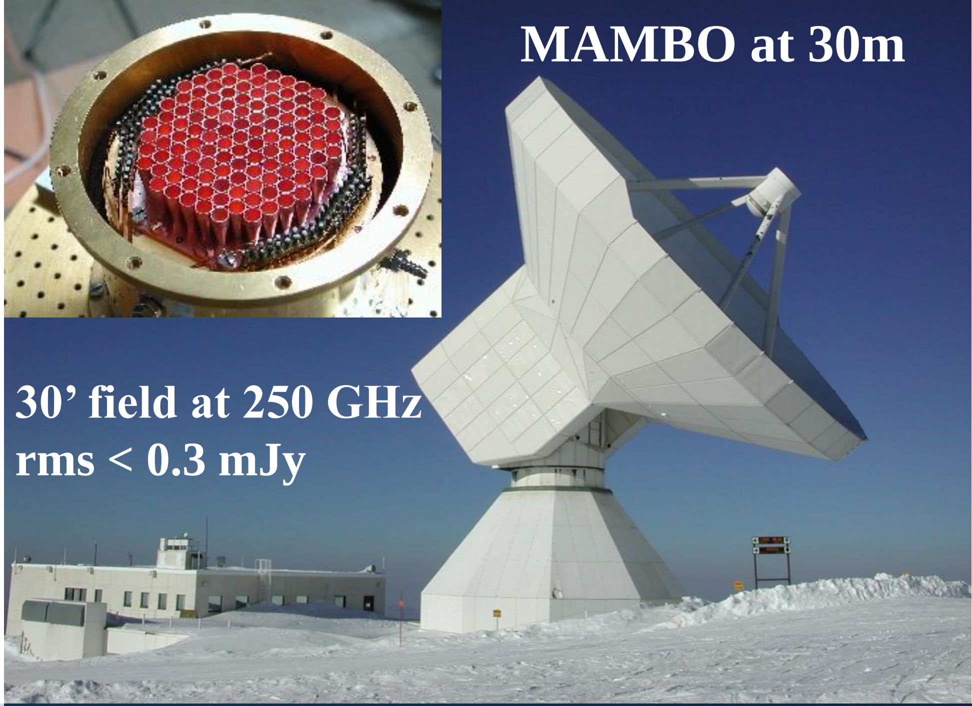
The interstellar medium is known to be chemically complex. Organic molecules with up to 11 atoms have been detected in the interstellar medium, and are believed to be formed on the ices around dust grains. The ices can be released into the gas-phase either through thermal desorption, when a newly formed star heats the medium around it and completely evaporates the ices; or through non-thermal desorption mechanisms, such as photodesorption, when a single far-UV photon releases only a few molecules from the ices. The first one dominates in hot cores, hot corinos and strongly UV-illuminated PDRs, while the second one dominates in colder regions, such as low UV-field PDRs. This is the case of the Horsehead were dust temperatures are $\simeq 20-30$ K, and therefore offers a clean environment to investigate what is the role of photodesorption. We have carried-out an unbiased spectral line survey at 3, 2 and 1mm with the IRAM-30m telescope in the Horsehead nebula, with an unprecedented combination of bandwidth, high spectral resolution and sensitivity. Two positions were observed: the warm PDR and a cold condensation shielded from the UV field (dense core), located just behind the PDR edge. We summarize our recently published results from this survey and present the first detection of the complex organic molecules HCOOH, CH_2CO, CH_3CHO and CH_3CCH in a PDR. These species together with CH_3CN present enhanced abundances in the PDR compared to the dense core. This suggests that photodesorption is an efficient mechanism to release complex molecules into the gas-phase in far-UV illuminated regions.

Table 2 Summary of abundances with respect to total hydrogen nuclei ($N_H = N(X)/(N(H) + 2\,N(H_2))$) toward the PDR and dense core. The column densities of the total hydrogen nuclei are $N_H = 3.8 \times 10^{22}$ cm^{-2} (PDR) and $N_H = 6.4 \times 10^{22}$ cm^{-2} (dense core).

Species	Beam	PDR		Core		Ref.
	(″)	Abundance	Offsets	Abundance	Offsets	
$C^{18}O$	6.5×4.3	1.9×10^{-7}	(-6,4)	-	-	Pety *et al.* [20]
C_2H	7.2×5.0	1.4×10^{-8}	(-6,4)	-	-	Pety *et al.* [20]
c-C_3H	28	2.7×10^{-10}	(-10,0)	-	-	Teyssier *et al.* [31]
l-C_3H	28	1.4×10^{-10}	(-10,0)	-	-	Teyssier *et al.* [31]
c-C_3H_2	6.1×4.7	1.1×10^{-9}	(-6,4)	-	-	Pety *et al.* [20]
l-C_3H_2	27	$< 4.6 \times 10^{-11}$	(-10,0)	-	-	Teyssier *et al.* [31]
C_4H	6.1×4.7	1.0×10^{-9}	(-6,-4)	-	-	Pety *et al.* [20]
C_6H	28	2.2×10^{-11}	(-6,4)	-	-	Agúndez *et al.* [32]
CS	10	2.0×10^{-9}	(4,0)	2.9×10^{-9}	(21,15)	Goicoechea *et al.* [33]
$C^{34}S$	16	9.2×10^{-11}	(4,0)	9.1×10^{-11}	(21,15)	Goicoechea *et al.* [33]
HCS^+	29	1.7×10^{-11}	(4,0)	1.2×10^{-11}	(21,15)	Goicoechea *et al.* [33]
HCO	6.7×4.4	8.4×10^{-10}	(-5,0)	$< 8.0 \times 10^{-11}$	(20,22)	Gerin *et al.* [21]
HCO^+	28	9.0×10^{-10}	(-5,0)	3.9×10^{-9}	(20,22)	Goicoechea *et al.* [34]
$H^{13}CO^+$	6.8×4.7	1.5×10^{-11}	(-5,0)	6.5×10^{-11}	(20,22)	Goicoechea *et al.* [34]
HOC^+	28	4.0×10^{-12}	(-5,0)	-	(20,22)	Goicoechea *et al.* [34]
CO^+	10	$< 5.0 \times 10^{-13}$	(-5,0)	-	(20,22)	Goicoechea *et al.* [34]
DCO^+	12	-	(-5,0)	8.0×10^{-11}	(20,22)	Pety *et al.* [23]
CF^+	25	5.7×10^{-10}	(-5,0)	$< 6.9 \times 10^{-11}$	(20,22)	Guzmán *et al.* [22]
C_3H^+	27	3.1×10^{-11}	(-5,0)	-	(20,22)	Pety *et al.* [35]
$o-H_2CO$	6.1×5.6	1.9×10^{-10}	(-5,0)	1.5×10^{-10}	(20,22)	Guzmán *et al.* [36]
$p-H_2CO$	6.1×5.6	9.5×10^{-11}	(-5,0)	5.0×10^{-11}	(20,22)	Guzmán *et al.* [36]
HDCO	18	-	(-5,0)	2.5×10^{-11}	(20,22)	Guzmán *et al.* [36]
D_2CO	24	-	(-5,0)	1.6×10^{-11}	(20,22)	Guzmán *et al.* [36]
CH_3OH-E	6.1×5.6	7.0×10^{-11}	(-5,0)	1.0×10^{-10}	(20,22)	Guzman *et al.* [24]
CH_3OH-A	6.1×5.6	5.3×10^{-11}	(-5,0)	1.3×10^{-10}	(20,22)	Guzman *et al.* [24]
CH_3CN	27	2.5×10^{-10}	(-5,0)	7.9×10^{-12}	(20,22)	Gratier *et al.* [37]
CH_3NC	25	4.1×10^{-11}	(-5,0)	$< 7.8 \times 10^{-12}$	(20,22)	Gratier *et al.* [37]
HC_3N	30	6.3×10^{-12}	(-5,0)	7.9×10^{-12}	(20,22)	Gratier *et al.* [37]
$t-HCOOH$	29	5.2×10^{-11}	(-5,0)	1.4×10^{-11}	(20,22)	This work
$o-CH_2CO$	30	1.3×10^{-10}	(-5,0)	4.2×10^{-11}	(20,22)	This work
$p-CH_2CO$	26	1.8×10^{-11}	(-5,0)	7.3×10^{-12}	(20,22)	This work
CH_3CHO-E	27	1.4×10^{-11}	(-5,0)	3.9×10^{-12}	(20,22)	This work
CH_3CHO-A	27	5.4×10^{-11}	(-5,0)	2.0×10^{-11}	(20,22)	This work
CH_3CCH	29	4.4×10^{-10}	(-5,0)	3.0×10^{-10}	(20,22)	This work

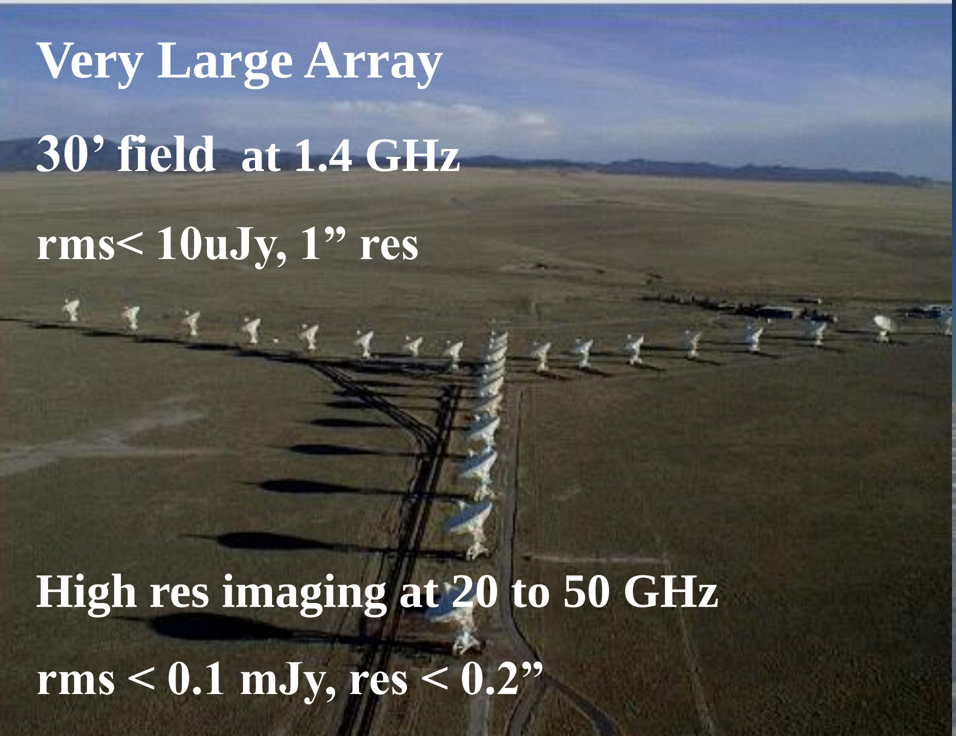
Powerful suite of existing cm/mm facilites

First glimpses into early galaxy formation



MAMBO at 30m

30’ field at 250 GHz
rms < 0.3 mJy



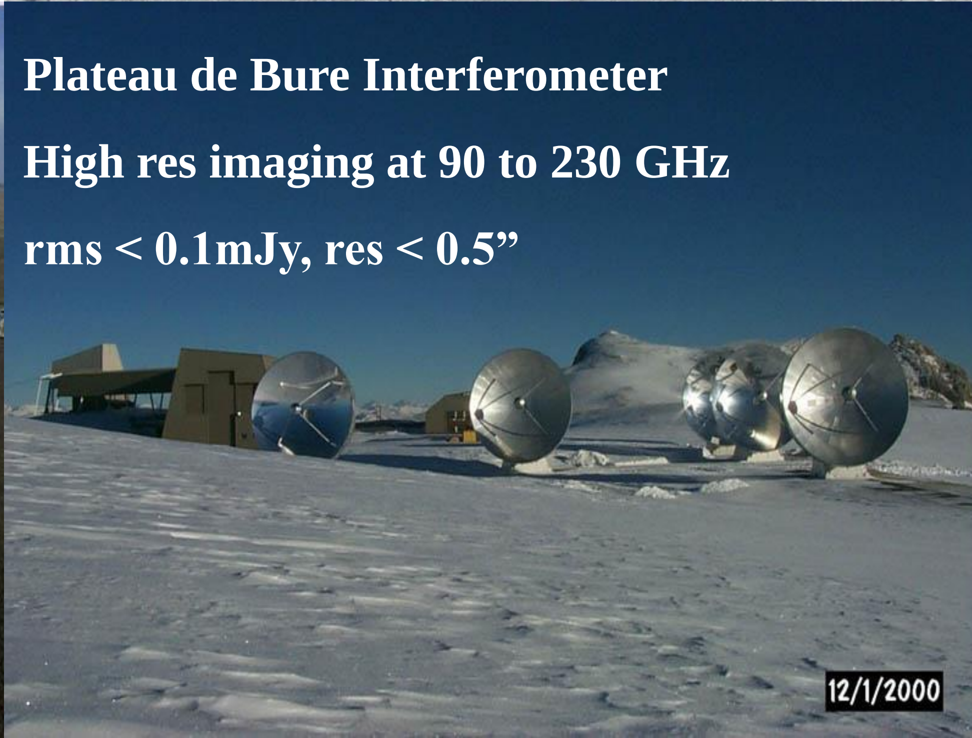
Very Large Array

30’ field at 1.4 GHz

rms< 10uJy, 1” res

High res imaging at 20 to 50 GHz

rms < 0.1 mJy, res < 0.2”

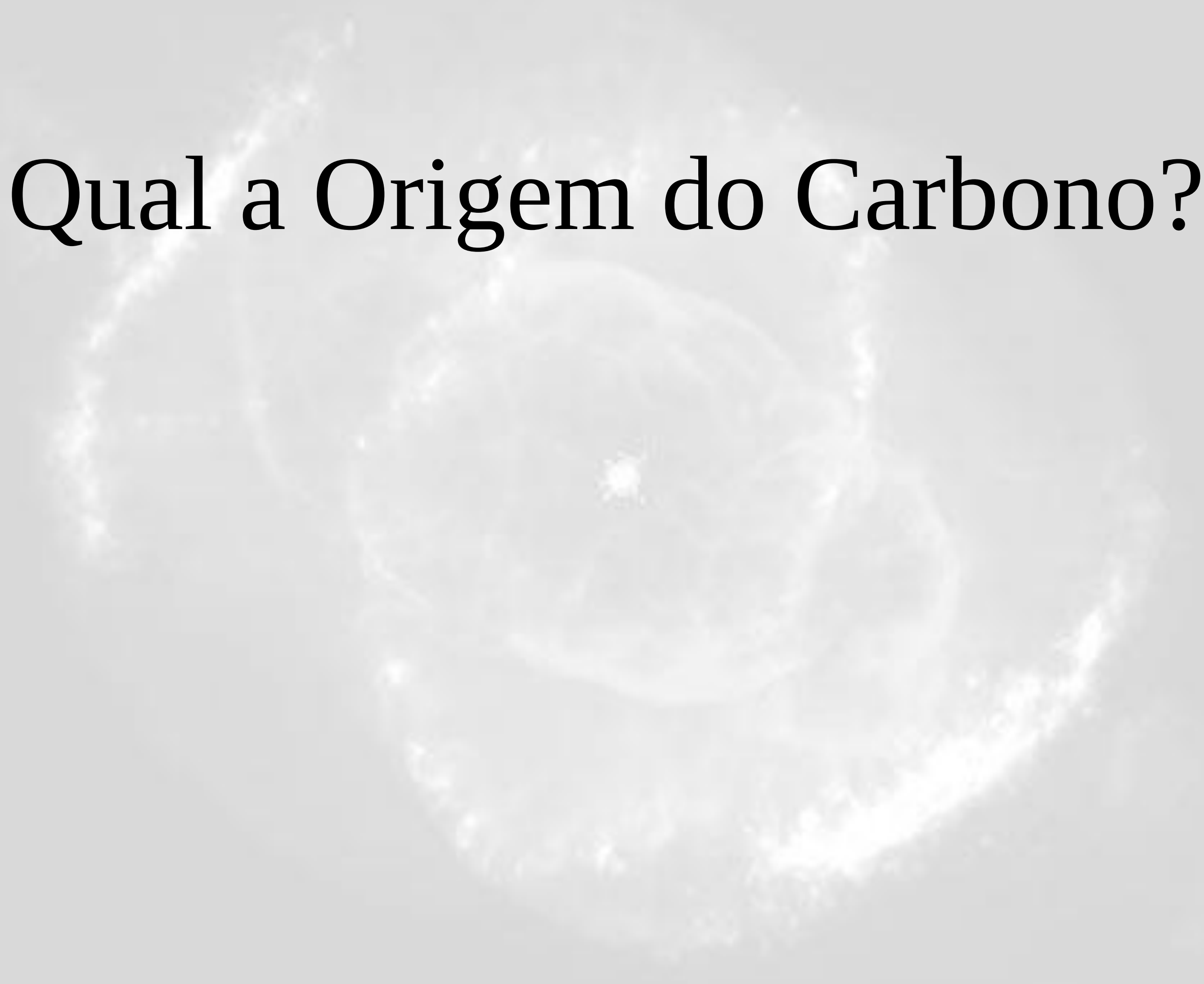


Plateau de Bure Interferometer

High res imaging at 90 to 230 GHz

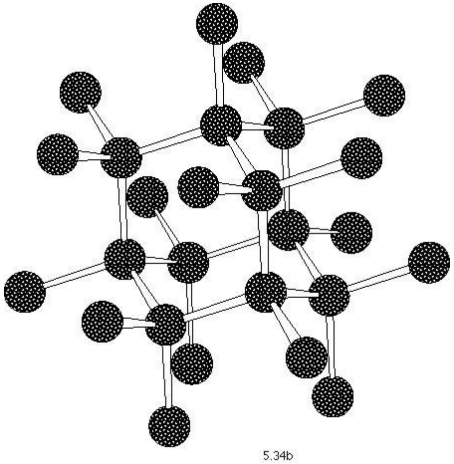
rms < 0.1mJy, res < 0.5”

Qual a Origem do Carbono?

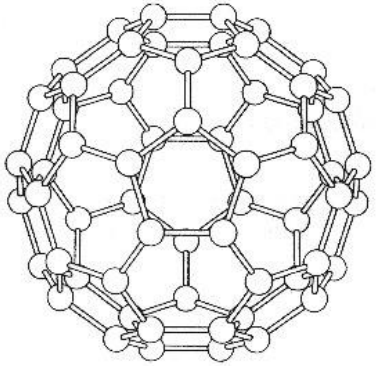


Large carbonaceous molecules in space

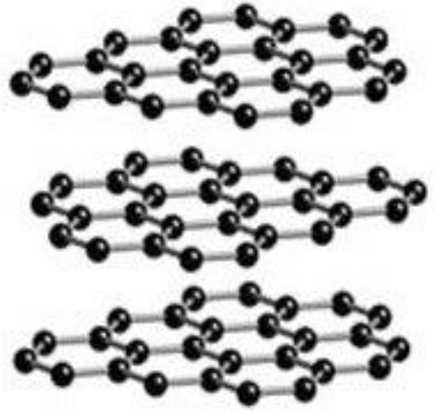
Diamond <<

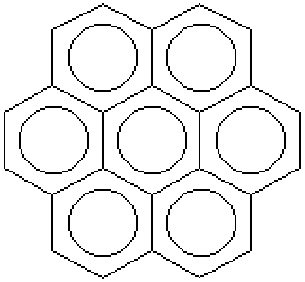


Fullerenes ~ 0.5 %



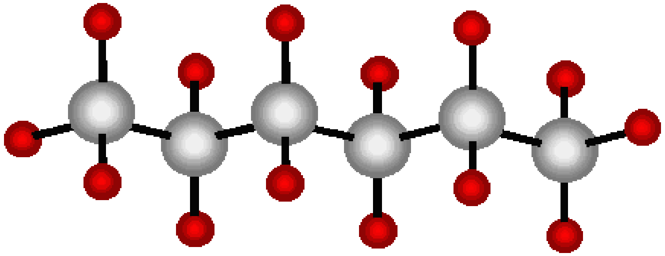
Graphite ?



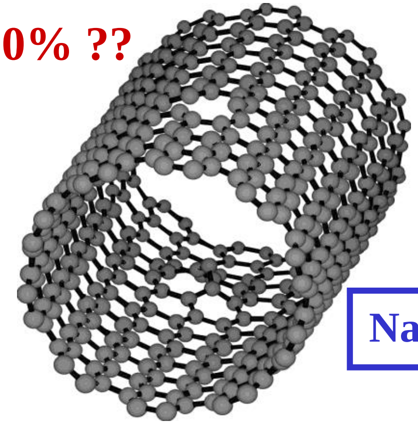


PAHs ~ 15 %

C-chains ~ 0.1%

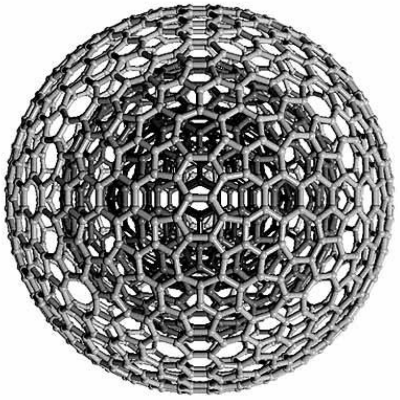


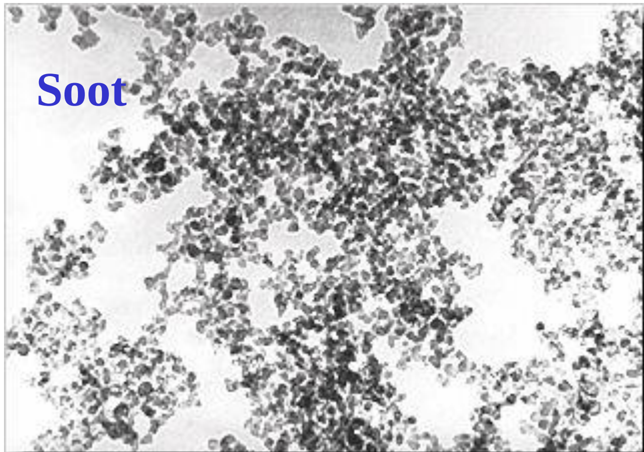
> 50% ??



Nanotubes

C-onions

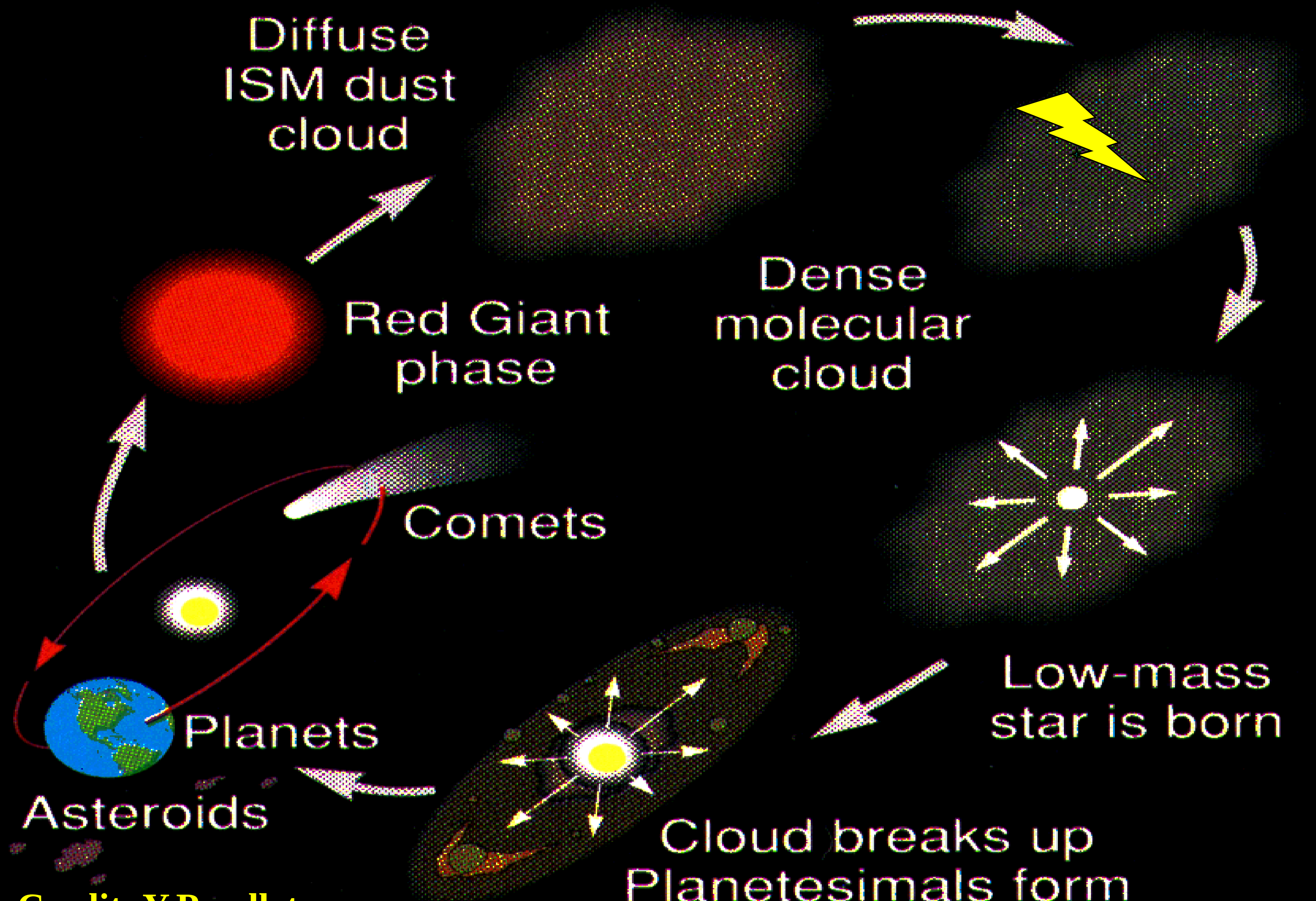




Soot

Ehrenfreund & Charnley 2000

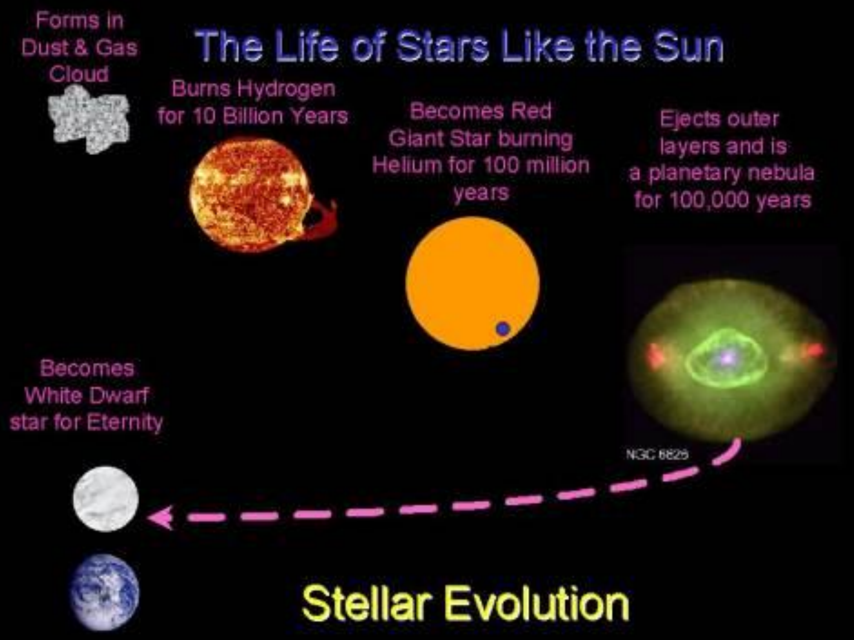
Life cycle of a low-mass star

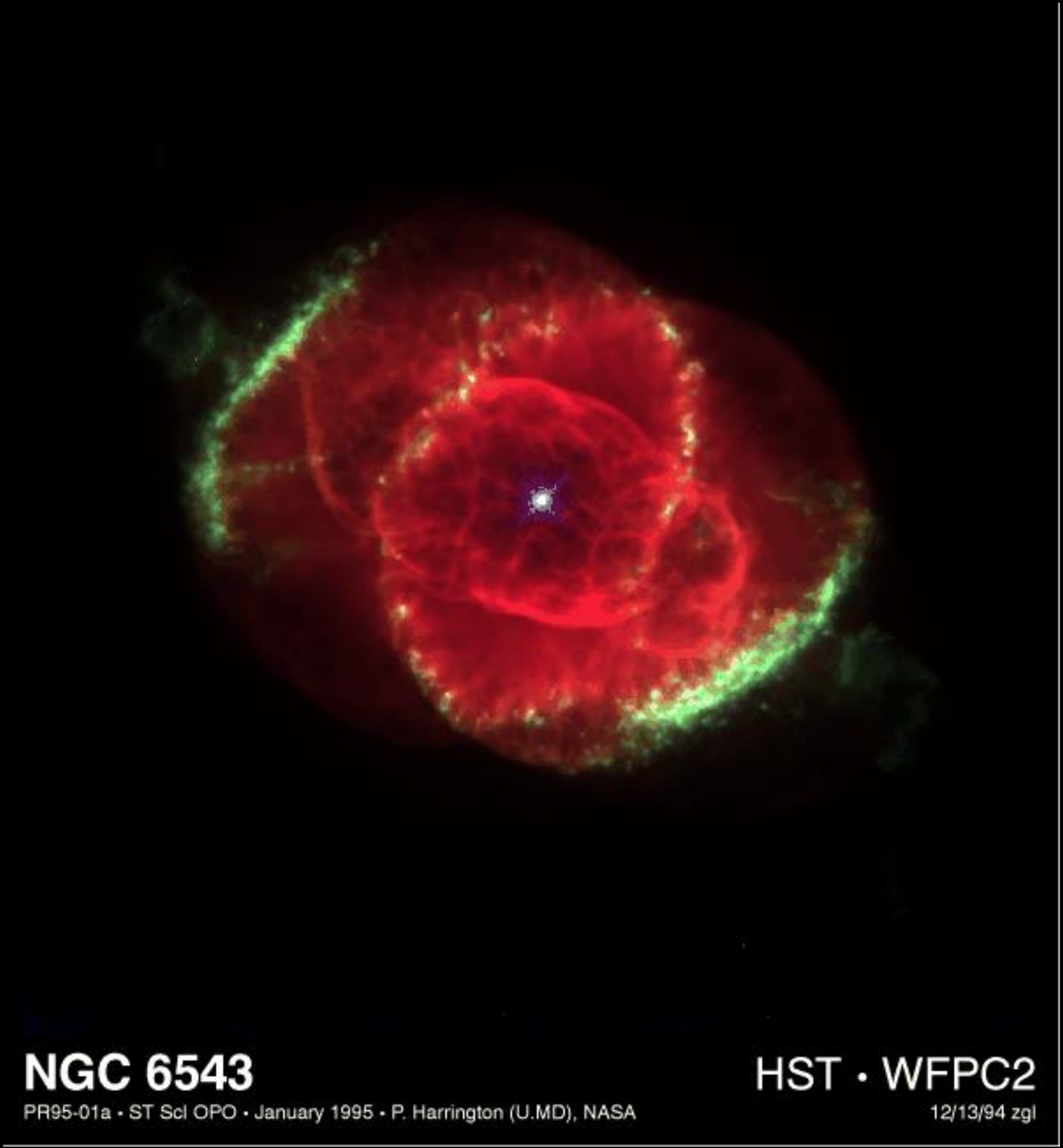


Credit: Y.Pendleton

Nebulosas Planetárias

- O Sol vai morrer assim
- Estrelas com massas menores que 8 vezes a massa do Sol
- Núcleo ⇒ anã branca
- Camadas exteriores ⇒ nebulosa planetária
- C, N
- Tempos: até varios Ganos
- Promovem as condições pré-bióticas.



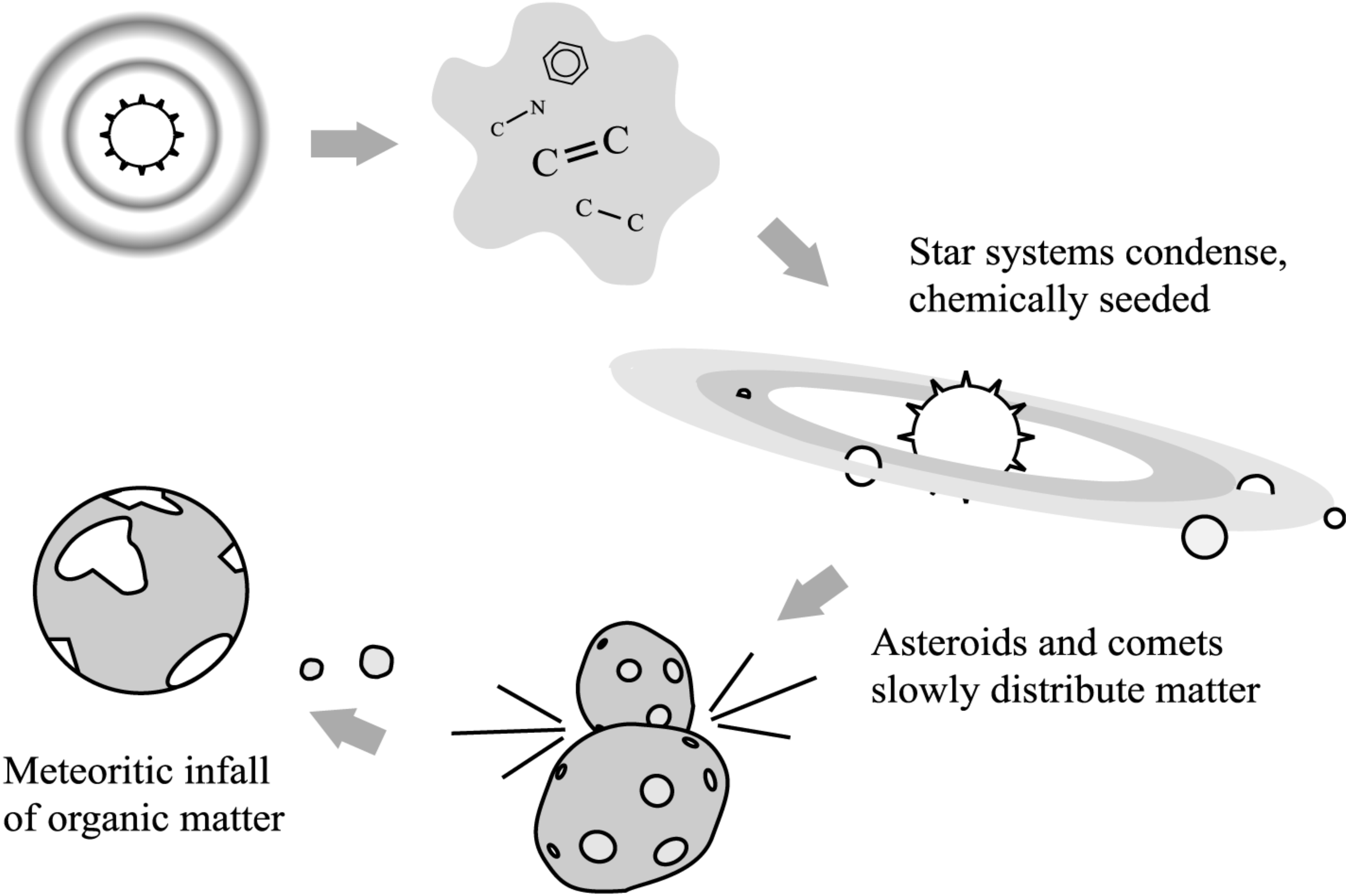


NGC 6543

PR95-01a • ST ScI OPO • January 1995 • P. Harrington (U.MD), NASA

HST • WFPC2

12/13/94 zgl



Complex carbon chemistry
in circumstellar envelopes

Organic chemistry in
interstellar clouds

Star systems condense,
chemically seeded

Asteroids and comets
slowly distribute matter

Meteoritic infall
of organic matter

O Nitrogênio e a Vida

SIGA A VIDA

- Siga a água (Follow the water)
- Siga o carbono
- ⇒ Siga o nitrogênio
- Siga o fósforo
- Siga a energia
- Siga a entropia
- Siga a informação
- Siga o significado

Why Nitrogen?

- N is the fourth more abundant chemically active element in the Universe
- N is one of the elements (together with N, C, O and P) entering in the composition of the carrier of biological information in Earth (DNA)
- N allows the assembling of a number of complex, heterocyclic, assymetric compounds
- The odd-valence of N compounds introduces asymmetries, which are a necessary condition for information storage

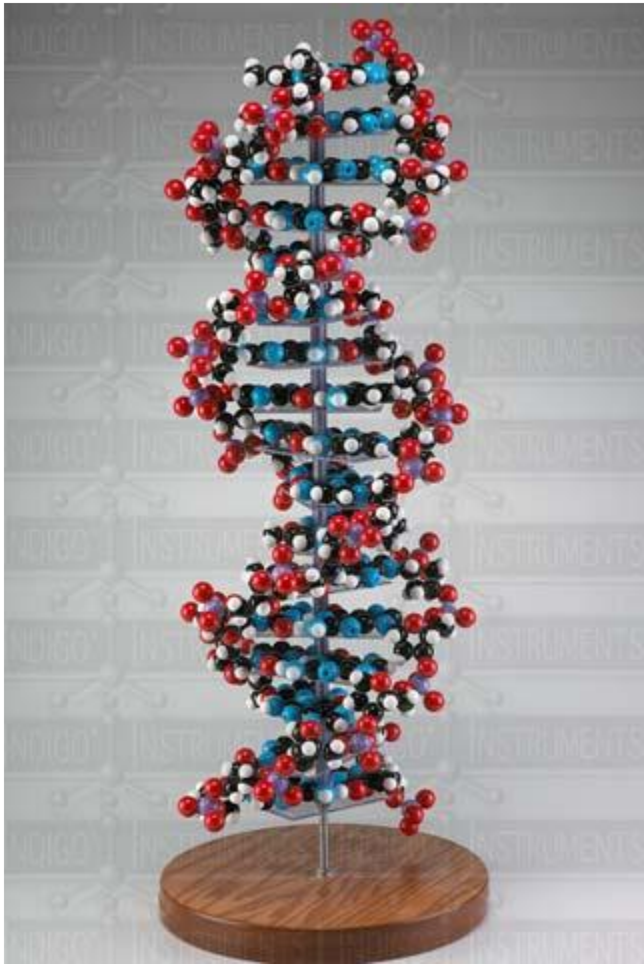
Four types of organic macromolecules in living systems.

Most of the molecules in the living systems are water (H_2O) and large organic macromolecules:

- Carbohydrates
- Lipids
- Proteins
- Nucleic Acids

Nucleic acids (DNA/RNA)

- Deoxyribonucleic acid (DNA), is a nucleic acid that contains the (genetic) instructions used in the development and functioning of all known living organisms.
- Collection of nucleotides linked together in long polymers – the largest macromolecule



Nucleotide

Each nucleotide:
1) Five-carbon sugar molecule
2) One or more phosphate groups
3) Nitrogen-containing compound – nitrogenous base

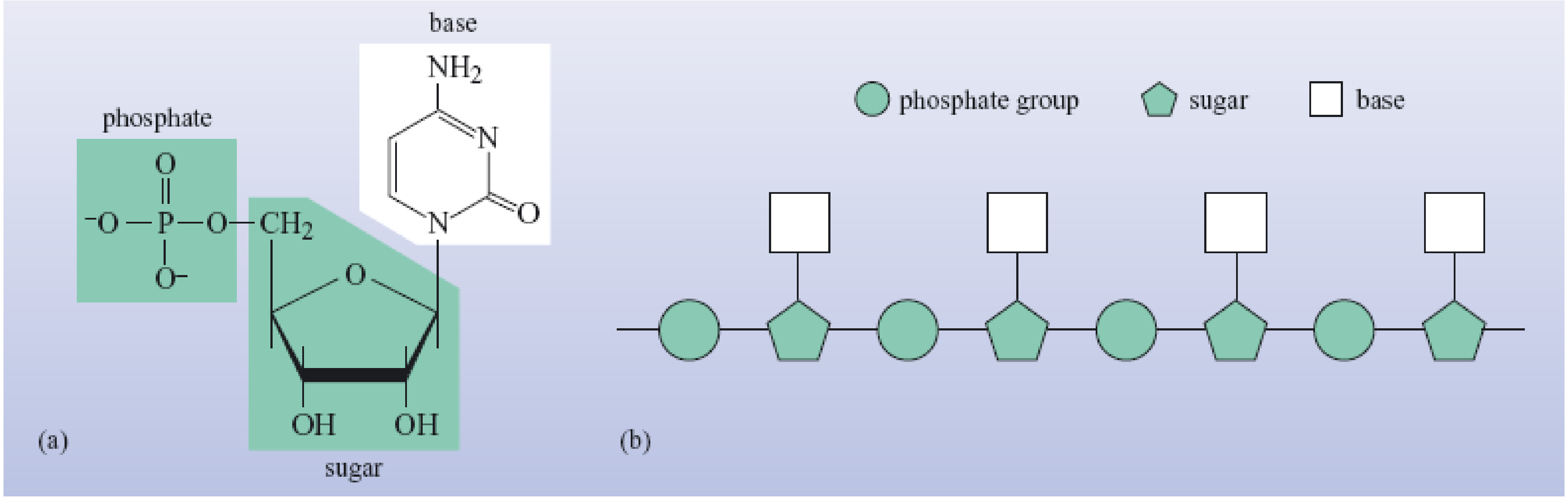


Figure 1.7 (a) The structure of a nucleotide consisting of a phosphate group, sugar molecule and nitrogenous base (cytosine in this instance). (b) Nucleotides polymerize by simple reactions that involve the loss of water to form nucleic acids. ((a) Zubay, 2000)

Watson and Crick (1953) realized that DNA have a double helix.

DNA strand	DNA strand
A	T
T	A
G	C
C	G

A can link only with T
G can link only with C

Two DNA strands are “complimentary” to each other

Strand

Hydrogen bond (weak)

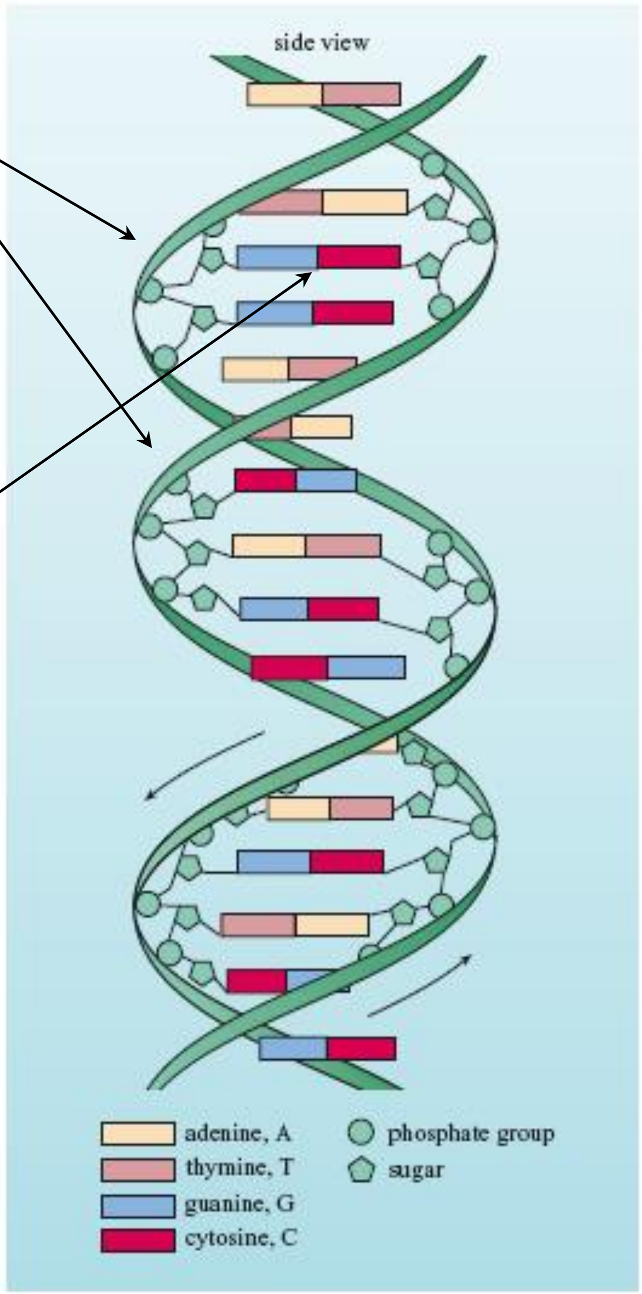


Figure 1.9 The DNA double helix. Note that the ‘ribbons’ are not real, but are there to illustrate the nature of the double helix.

DNA vs. RNA

- Deoxyribonucleic acid (DNA) – deoxyribose sugar
- Ribonucleic acid (RNA) – ribose sugar

Four bases:

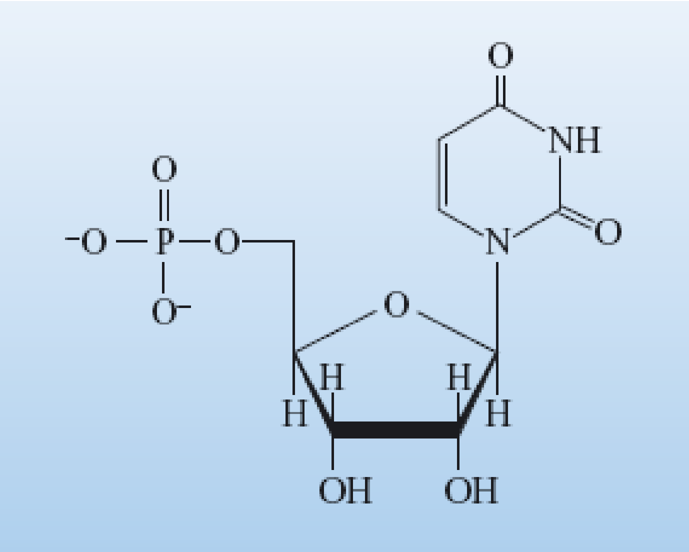
DNA RNA

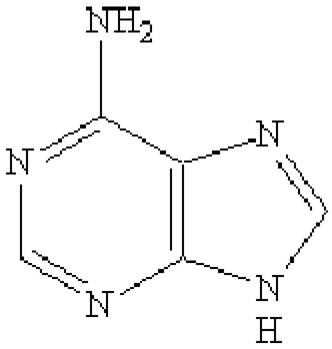
A – adenine – A

G – guanine – G

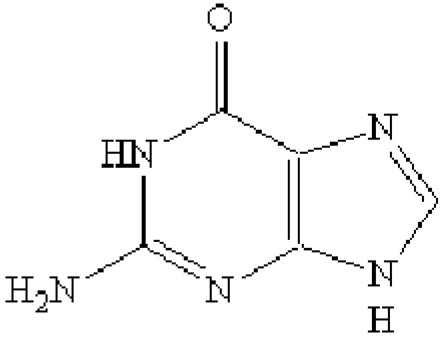
C – cytosine – C

T – thymine U – uracil



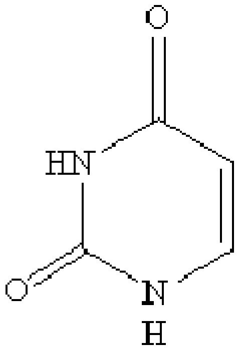


Adenine

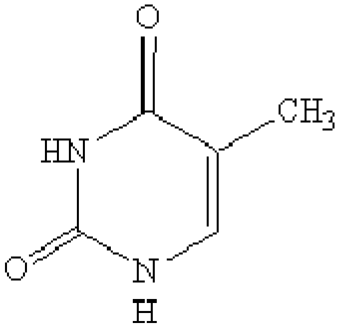


Guanine

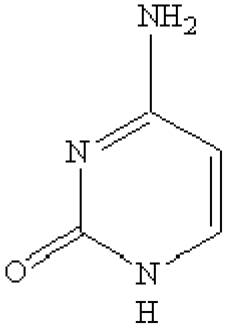
Purines



Uracil

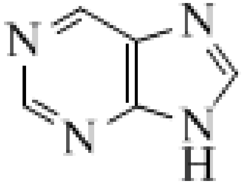


Thymine

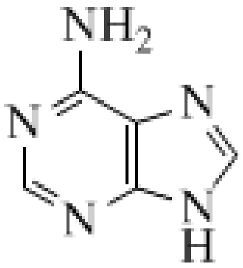


Cytosine

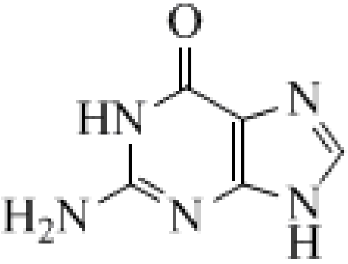
Pyrimidines



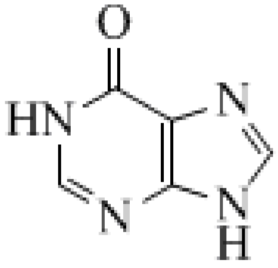
purine
1



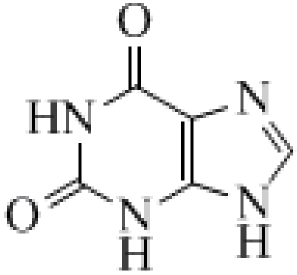
adenine
2



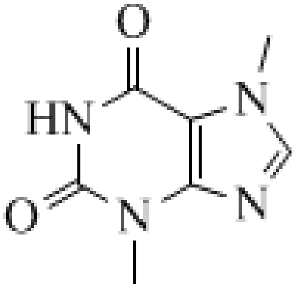
guanine
3



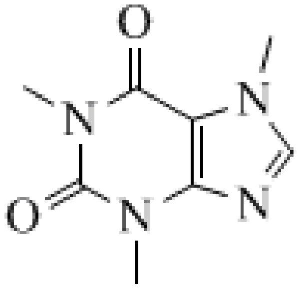
hypoxanthine
4



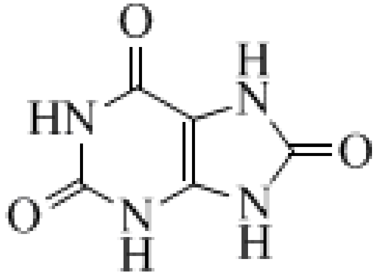
xanthine
5



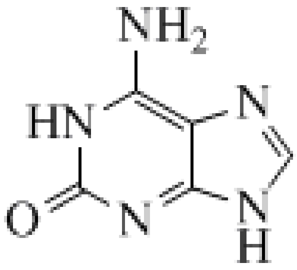
theobromine
6



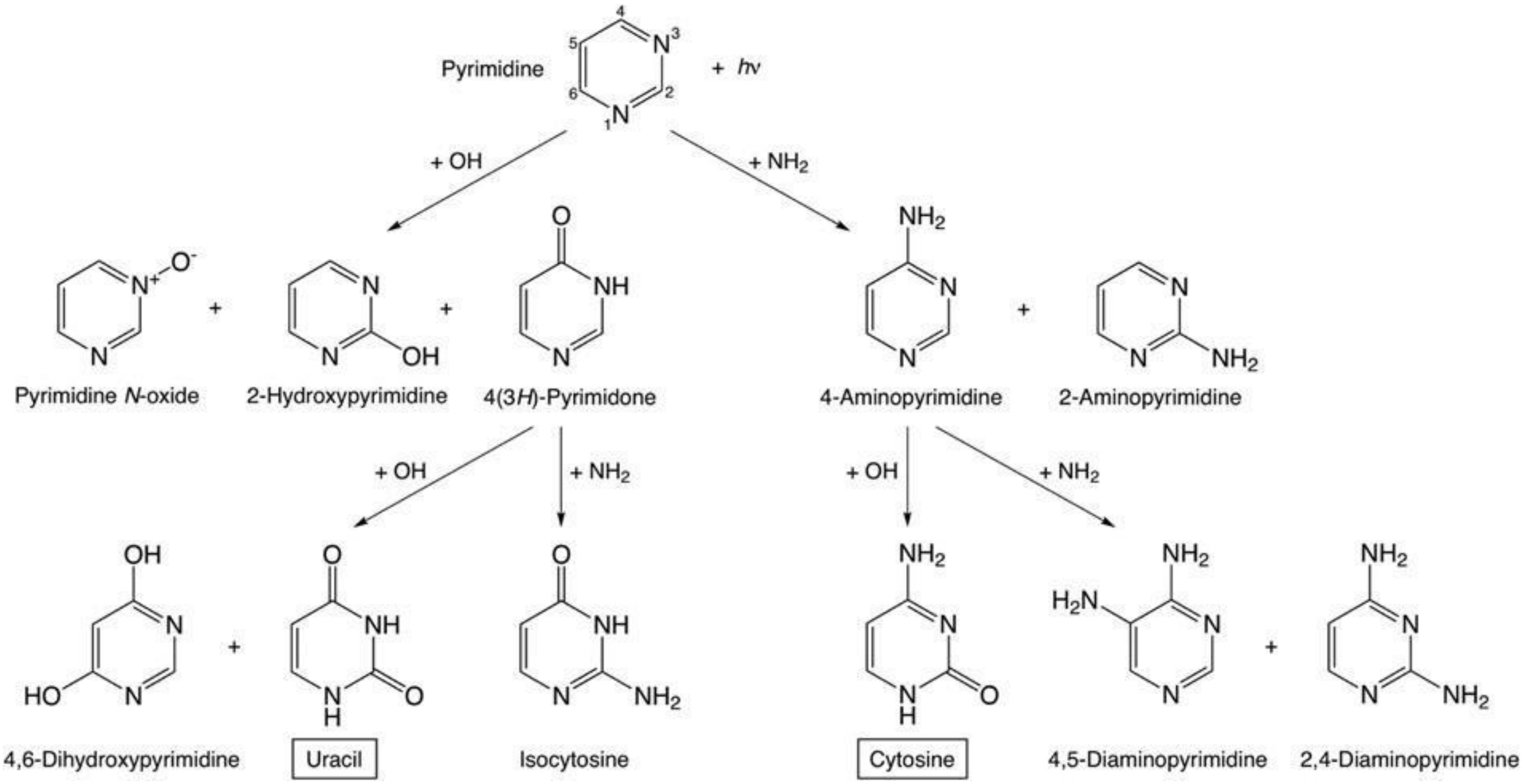
caffeine
7



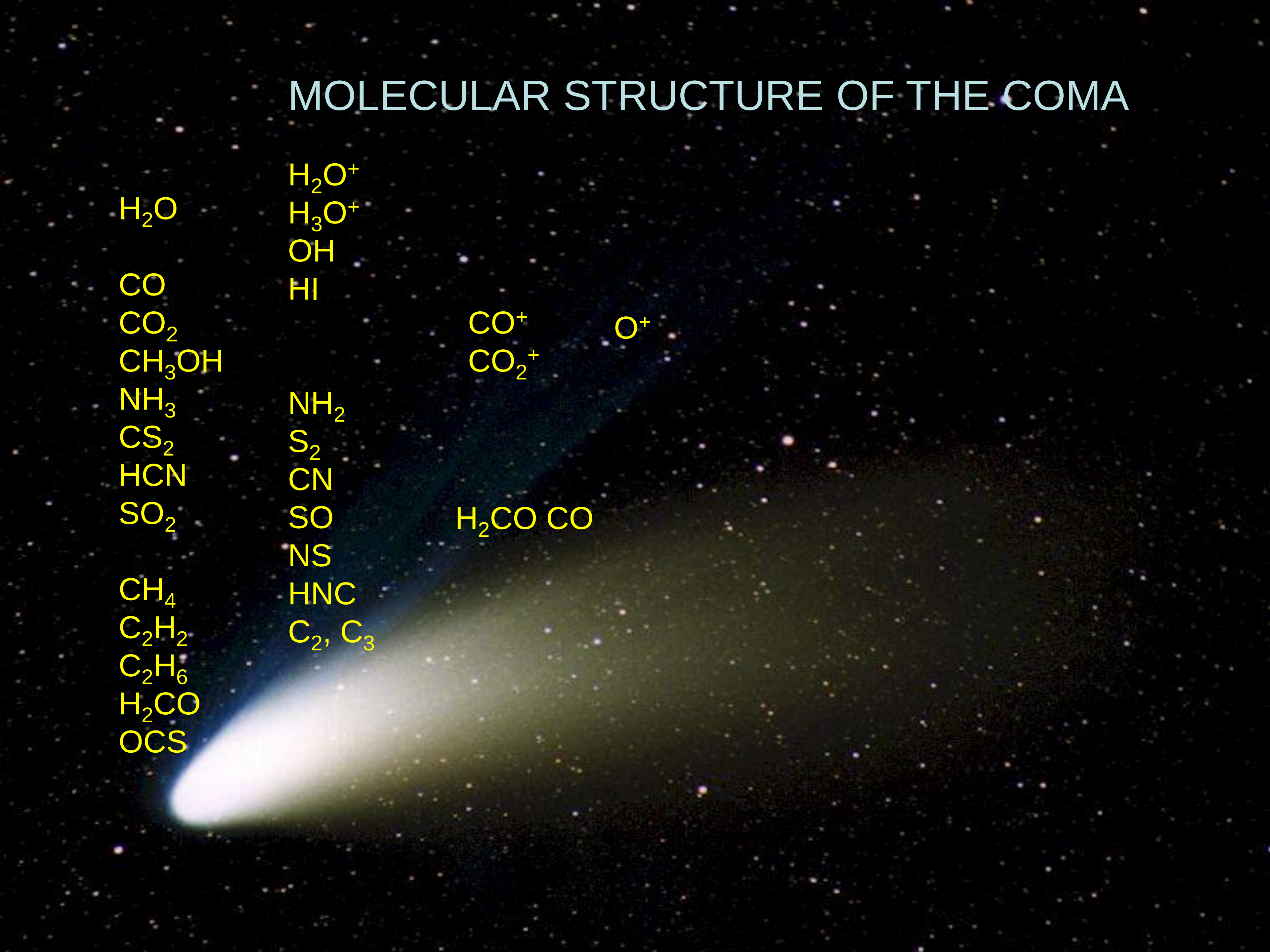
uric acid
8



isoguanine
9


Pyrimidine
+ hν
+ OH
+ NH2
Pyrimidine N-oxide
2-Hydroxypyrimidine
4(3H)-Pyrimidone
4-Aminopyrimidine
2-Aminopyrimidine
+ OH
+ NH2
+ OH
+ NH2
4,6-Dihydroxypyrimidine
Uracil
Isocytosine
Cytosine
4,5-Diaminopyrimidine
2,4-Diaminopyrimidine

Nitrogenated Organic Compounds in Astrobiology



MOLECULAR STRUCTURE OF THE COMA

H_2O

CO
CO_2
CH_3OH
NH_3
CS_2
HCN
SO_2

CH_4
C_2H_2
C_2H_6
H_2CO
OCS

H_2O^+
H_3O^+
OH
HI

NH_2
S_2
CN
SO
NS
HNC
C_2, C_3

CO^+
CO_2^+

H_2CO CO

O^+

On the Photographic Spectrum of Comet b 1881*.

On the evening of June 24, I directed the reflector furnished with the spectroscopic and photographic arrangements described in my paper "On the Photographic Spectra of Stars" † to the head of the comet, so that the nucleus should be upon one half of the slit. After one hour's exposure the open half of the slit was closed, the shutter withdrawn from the other half, and the instrument then directed to Arcturus for 15 minutes.

After development, the plate presented a very distinct spectrum of the comet, together with the spectrum of the star, which I have already described in the paper referred to above.

The spectrum of the comet consists of a pair of bright lines in the ultra-violet region, and a continuous spectrum which can be traced from about F to some distance beyond H.

The bright lines, a little distance beyond H, with an approximate wave-length from 3870 to 3890, appear to belong to the spectrum of carbon (in some form, possibly in combination with hydrogen), which I observed in the spectra of the telescopic comets of 1866 and 1868.

In the continuous spectrum shown in the photograph, the dark lines of Fraunhofer can be seen.

This photographic evidence supports the results of my previous observations in the visible spectra of some telescopic comets. Part of the light from comets is reflected solar light, and another part is light of their own. The spectrum of this light shows the presence in the comet of carbon, possibly in combination with hydrogen.

On the next night, June 25, a second photograph was obtained with an exposure of an hour and a half. This photograph, notwithstanding the longer exposure, is fainter, but shows distinctly the two bright lines and the continuous spectrum, which is too faint to allow the Fraunhofer lines to be seen.

I have since measured the photographs of the comet's spectrum, and I find for the two strong bright lines the wave-lengths 3883 and 3870. The less refrangible line is much stronger, and a faint luminosity can be traced from it to a little beyond the second line 3870. There can be, therefore, no doubt that these lines represent the brightest end of the ultra-violet group which appears under certain circumstances in the spectra of the compounds of carbon. Professors Liveing and Dewar have found for the strong line at the beginning of this group the wave-length 3882·7, and for the second line 3870·5.

I am also able to see upon the continuous solar spectrum, a distinct impression of the group of lines between G and *h*, which is usually associated with the group described above. My measures for the less refrangible end of this group give a wave-length of 4230, which agrees as well as can be expected with Professors Liveing and Dewar's measure 4220.

$N\equiv C-C\equiv N$

$\cdot C\equiv N$

In their paper "On the Spectra of the Compounds of Carbon" (Proc. Roy. Soc. vol. xxx. p. 494), Professors Liveing and Dewar show that these two groups indicate the presence of cyanogen, and are not to be seen in the absence of nitrogen. If this be the case, the photograph gives undoubted evidence of the presence of nitrogen in the comet, in addition to the carbon and hydrogen shown to be there by the bright groups in the visible part of the spectrum. On this hypothesis we must further suppose a high temperature in the comet unless the cyanogen is present ready formed.

I should state that Mr. Lockyer regards the two groups in the photograph, and the groups in the visible spectrum, to be due to the vapour of carbon at different heat-levels (Proc. Roy. Soc. vol. xxx. p. 461).

It is of importance to mention the strong intensity in the photograph of the lines 3883 and 3870, as compared with the continuous spectrum, and the faint bright group beginning at 4230. At this part of the spectrum, therefore, the light emitted by the cometary matter exceeded by many times the reflected solar light. I reserve for the present the theoretical suggestions which arise from the new information which the photographs have given us.

1881 July 9. W. Huggins.

CORRESPONDENCE.

To the Editor of 'The Observatory.'

The Grave of Flamsteed.

Sir,—

Believing that any circumstances, however trivial, relating to the personal history of the Rev. John Flamsteed will be received with interest, I have thought that the readers of the 'Observatory,' and astronomers generally, will be glad to be informed of a few facts lately come into my possession, which clear up a doubtful point regarding the resting-place of the remains of the first Astronomer Royal. These facts have been gleaned principally from the registered copy of the will of Mrs. Margaret Flamsteed, his widow, now preserved in the Principal Registry of the Court of Probate, Somerset House.

Flamsteed died at the Royal Observatory on 1719, December 31; and in the parish register of Burstow, in Surrey, the record of his burial is entered thus:—"1719–20. Jan: ye 12th. The Rev^{d} Mr. John Flamsteed, Rector of this Parish." Up to the present time there appears to have been some uncertainty as to the locality of his grave, whether it was in the chancel or the churchyard. There was no known documentary evidence one way or the other; but it has always been supposed to be in the chancel; and a *tradition*, brought down probably from rector to rector, has assigned a

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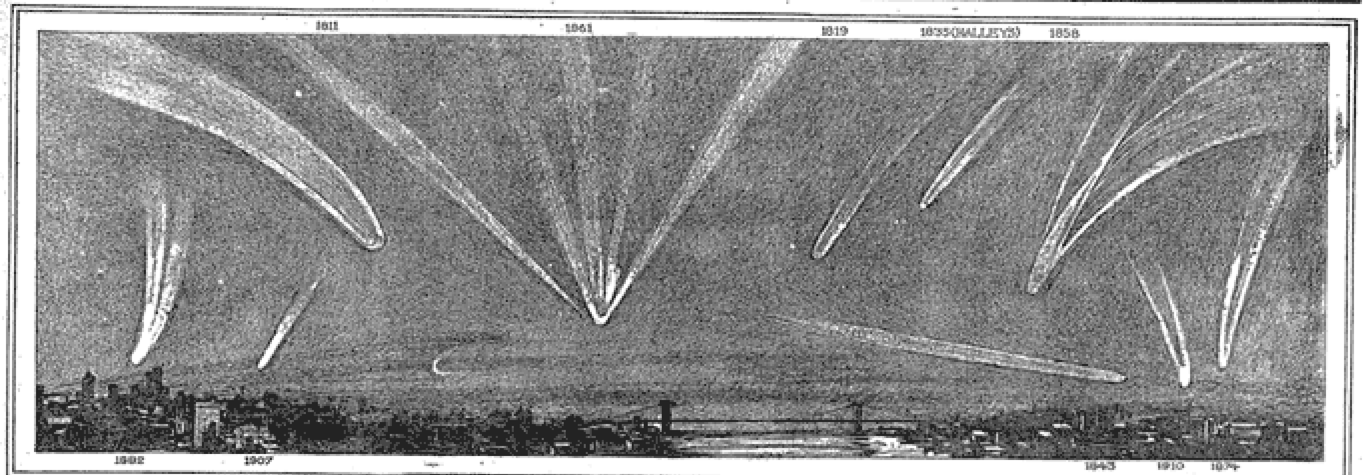
[*] From the 'Proceedings of the Royal Society,' No. 213. Communicated by the Author.

[†] Phil. Trans. 1880, p. 669.

Der Komet kommt!

FEARS OF THE COMET ARE FOOLISH AND UNGROUNDED



How the Famous Comets of History Looked and How They Compare in Size.

Mary Proctor Tells of Similar Scares in the Past, Occurring Every Time These Blazing Visitors Were Expected, and All Proved Groundless.

By MARY PROCTOR.

A DISMAL report is circulating to the effect that Halley's comet is about to cause the destruction of our planet, and as we draw nearer the fateful date of May 18, a grave feeling of apprehension is excited in the minds of those who are very naturally afraid of something they cannot understand.

[illegible]

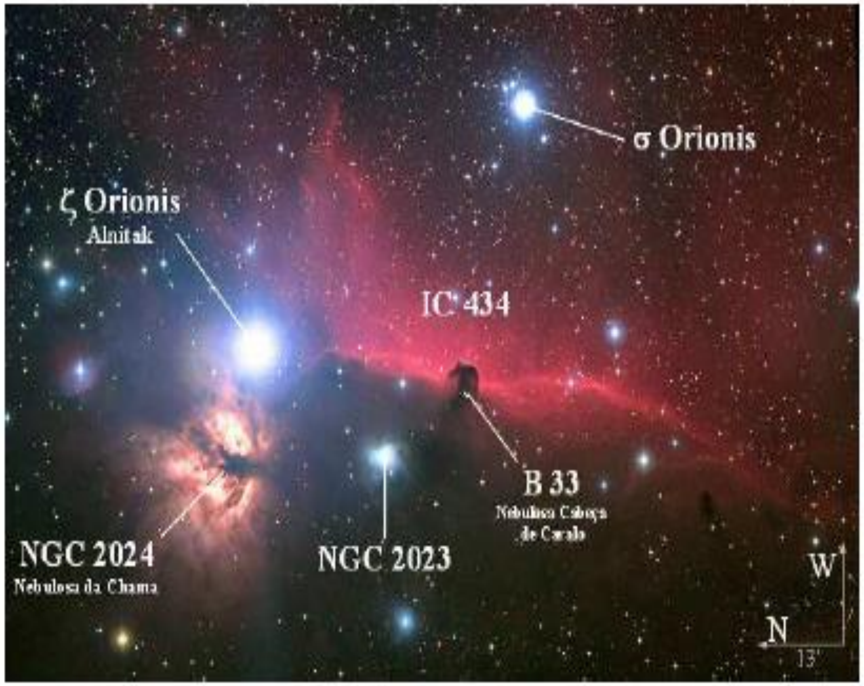
19 MAGGIO 1910!

Un angolo di strada, quando la Terra sarà invasa dai miasmi pestiferi della cometa di Halley.

Solo gli Automobilisti provvisti della **Bottiglia MICHELIN**, gonfiata con aria purissima, respireranno a loro piacere.... * * *

Horse Head Nebula

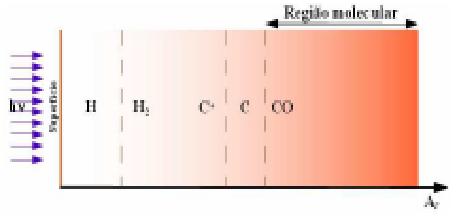
Nebulosa Cabeça de Cavalo



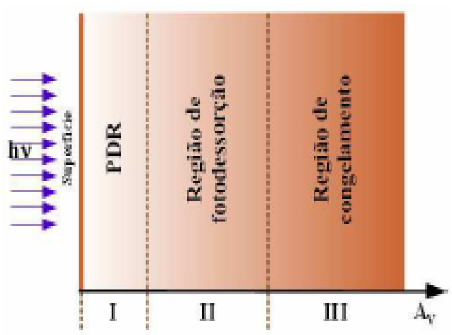
NASA, 2010

- É um arquétipo de PDR e de nuvem molecular;
- Distância moderada ($d \simeq 400\ pc$);
- Geometria simples;
- Campo de radiação FUV bem conhecido - 60 (Unidade de Draine);
- A estrela σ *Orionis* (O(9.5V) ioniza a região, conforme parametrizado por Gerin, 2009;
- Temperatura Cinética $T_K \sim 15K$;
- Pressão térmica $P \sim 4 \times 10^6\ Kcm^{-3}$

PDRs



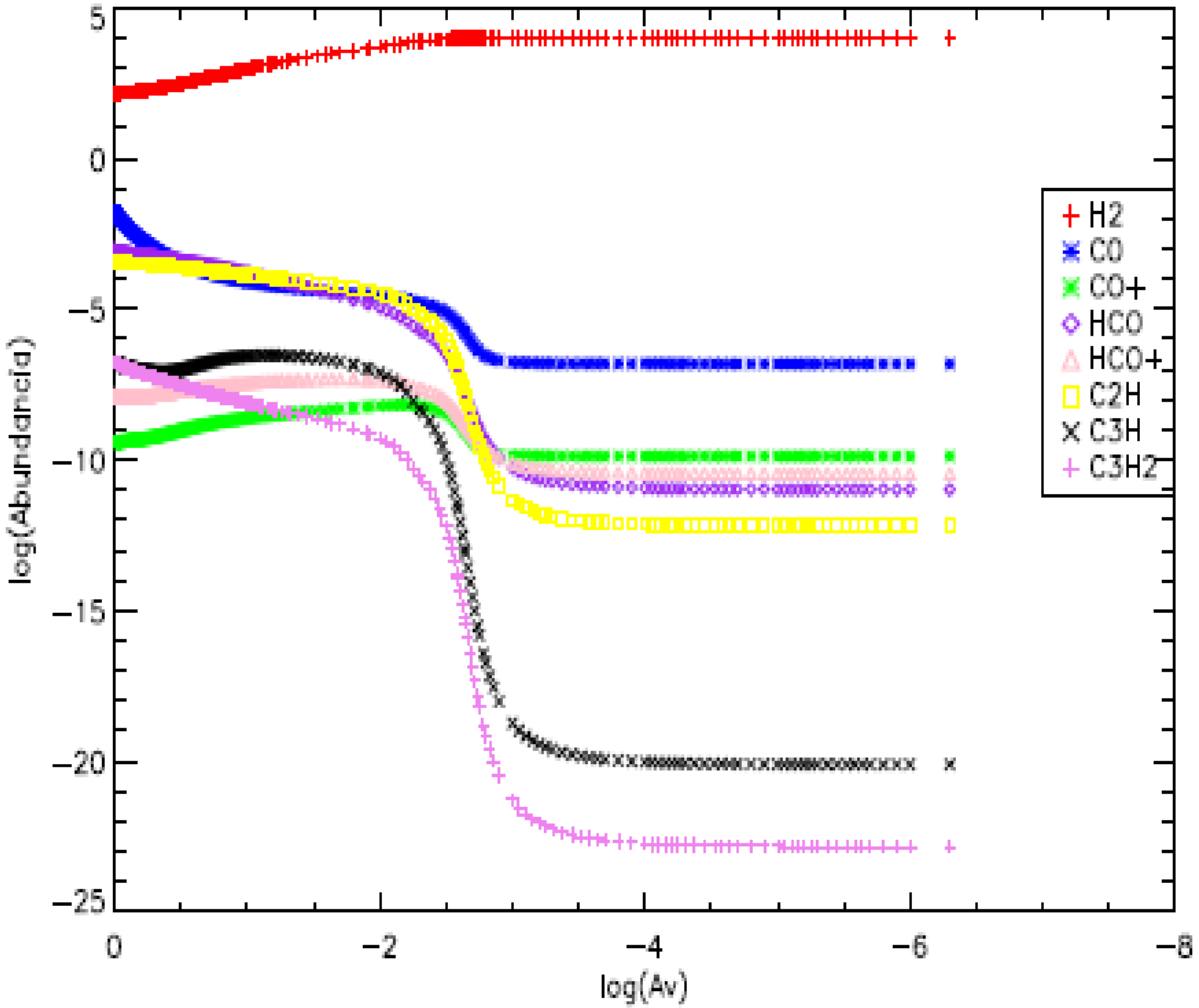
Le Petit, 2012



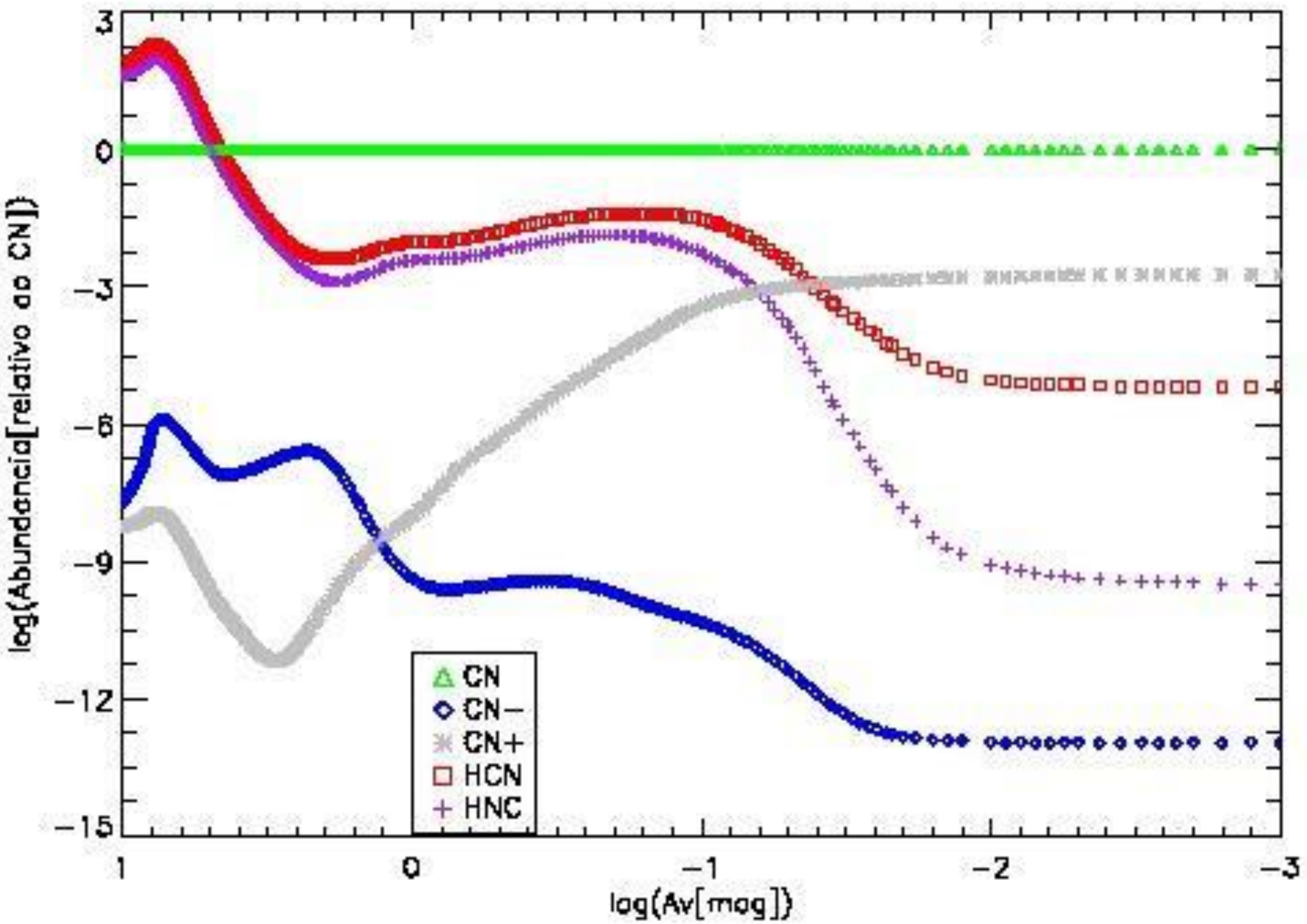
Le Petit, 2012

- PDR é definida como uma região onde as propriedades físicas e químicas do gás são determinadas por fótons penetrantes do ultravioleta distante ($6 < h\nu < 13.6eV$);
- No interior da nuvem as espécies mais importantes passam de íons para moléculas;
- A complexidade química aumenta, pois não são imediatamente destruídas pela radiação de alta energia;
- A densidade da nuvem e a intensidade do campo de radiação FUV determinam o tamanho e a estrutura química;
- Grãos na nuvem molecular determinam grande parte da curva de extinção da nuvem, catalisam algumas reações químicas e são responsáveis pela formação de hidrogênio molecular.

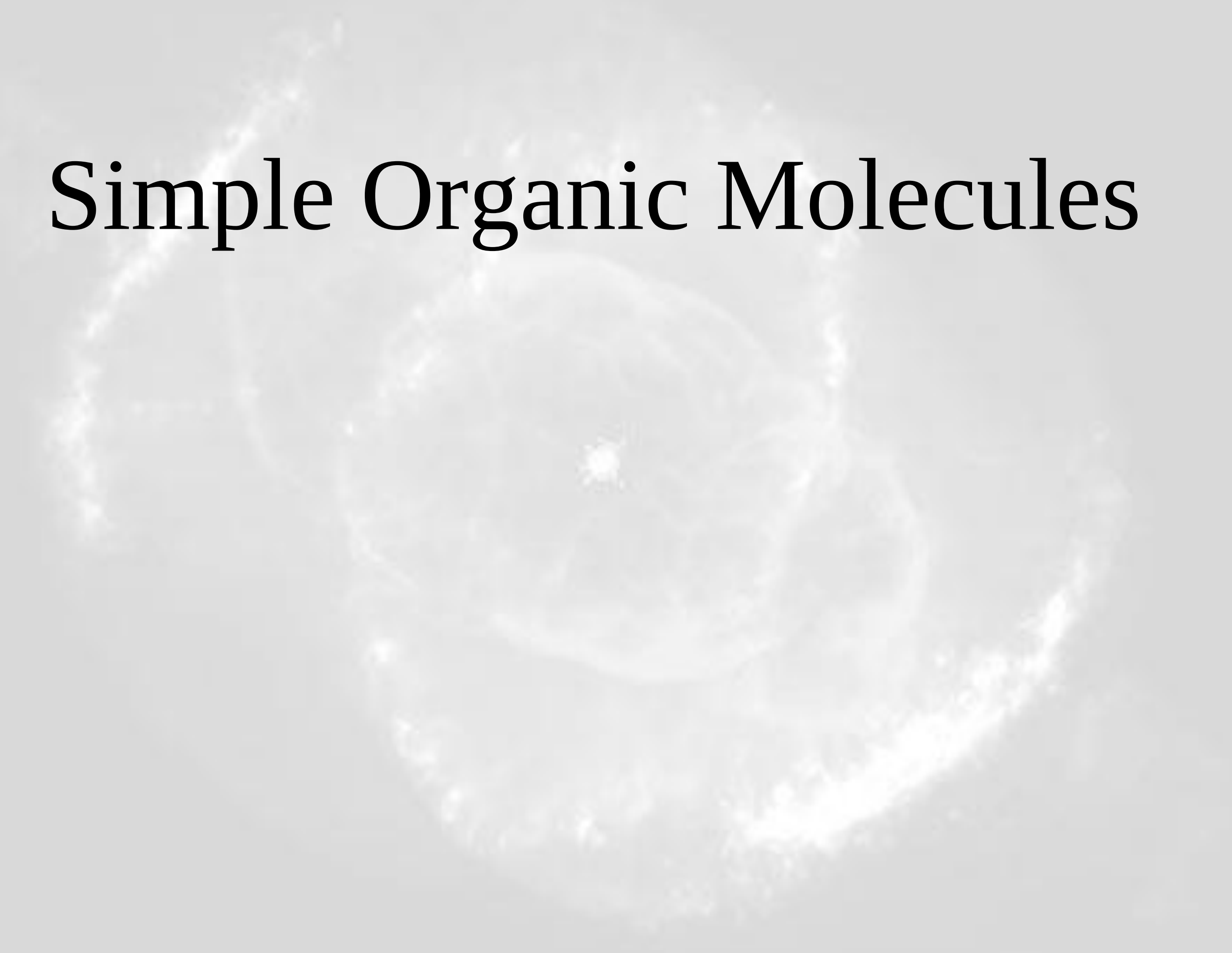
CHO Molecules



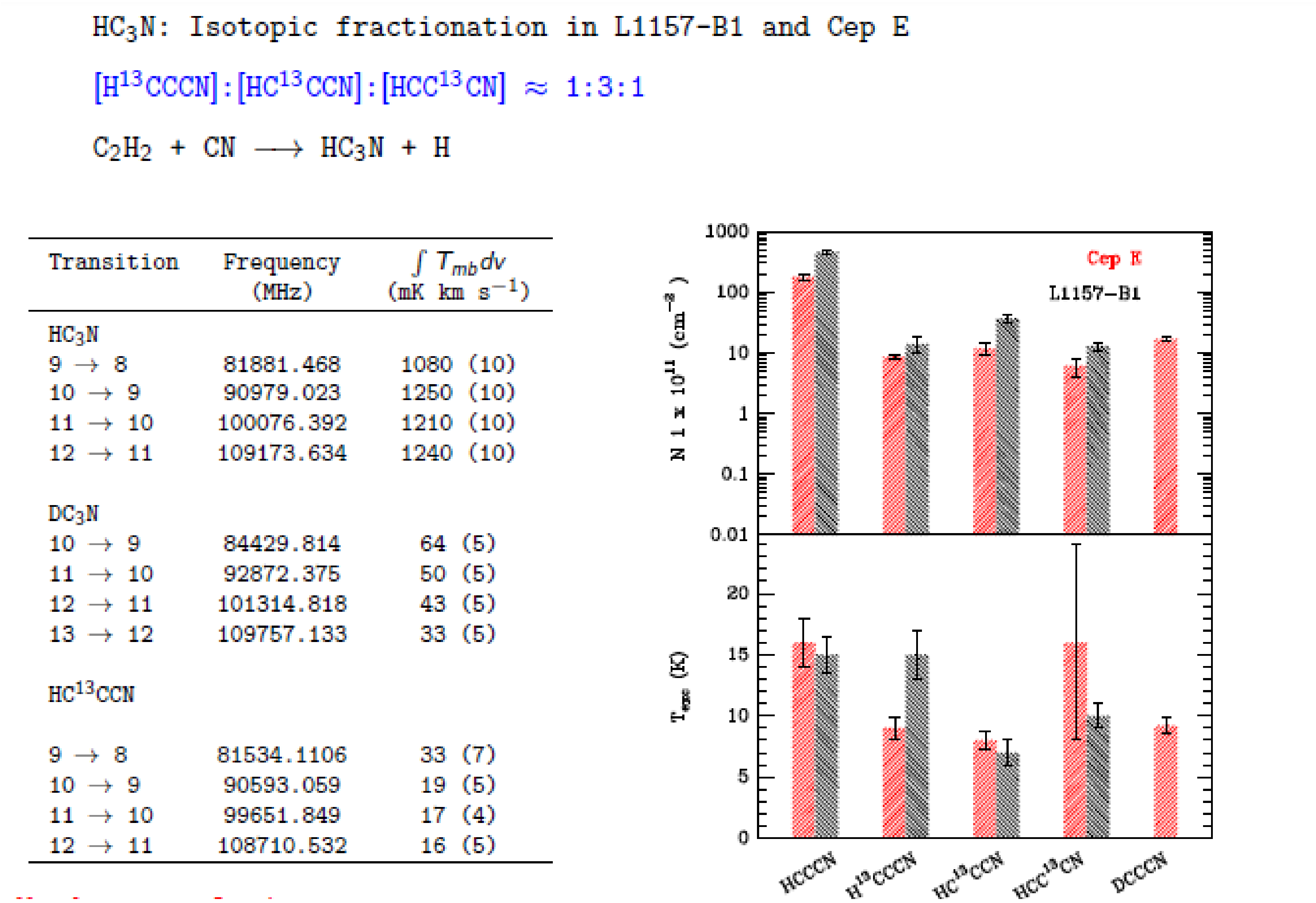
Nitrogenated Molecules (Abundances relative to CN)



Simple Organic Molecules



Using Isotopic Fractionation (D, C^{13}, N^{15}, O^{18}) to explore production channels

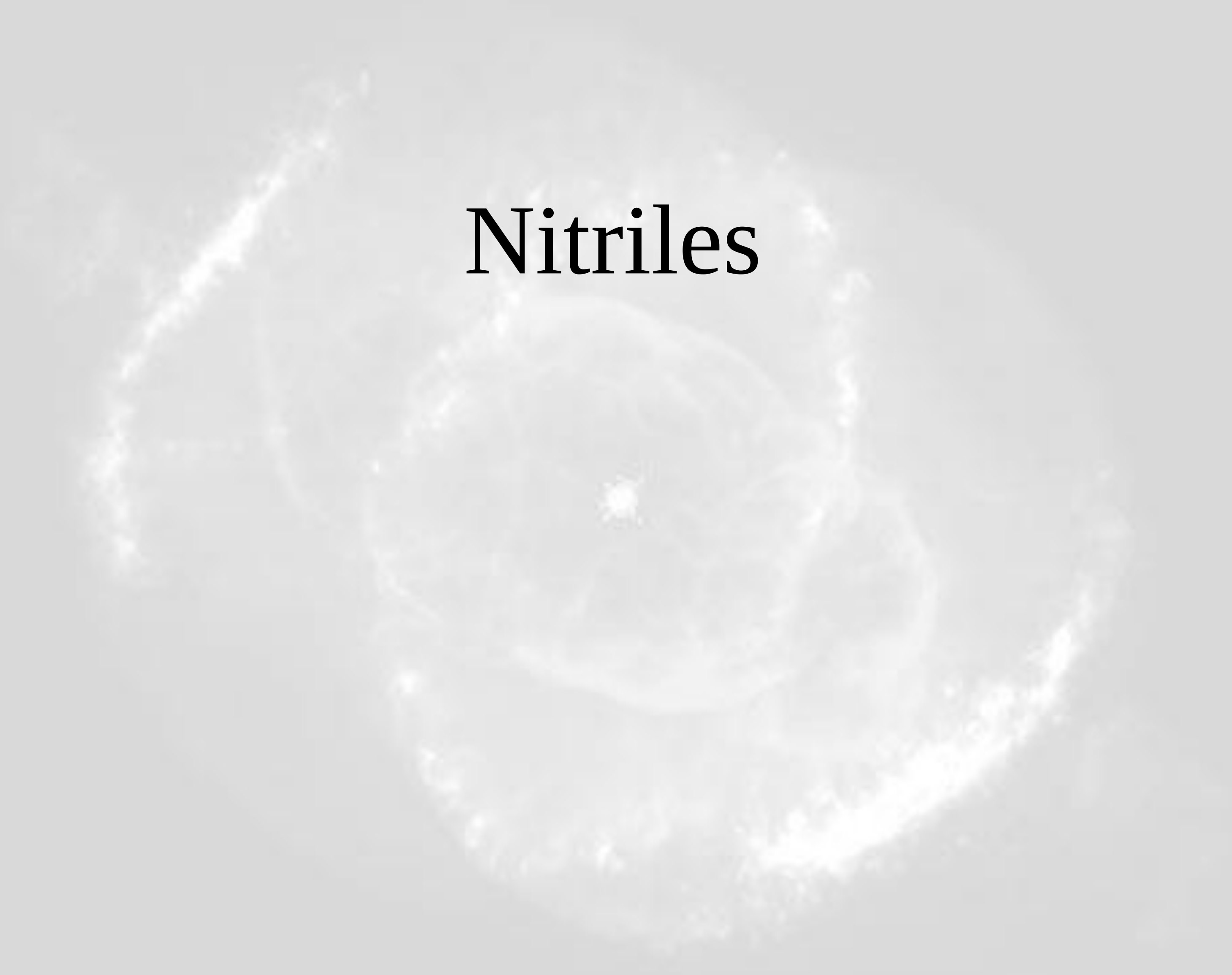


HC_3N: Isotopic fractionation in L1157-B1 and Cep E

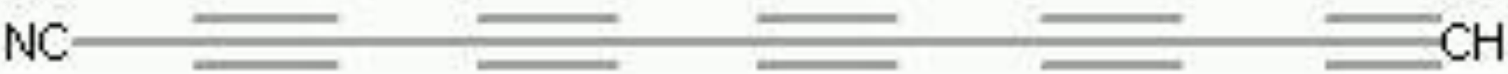
$[H^{13}CCCN]:[HC^{13}CCN]:[HCC^{13}CN] \approx 1:3:1$

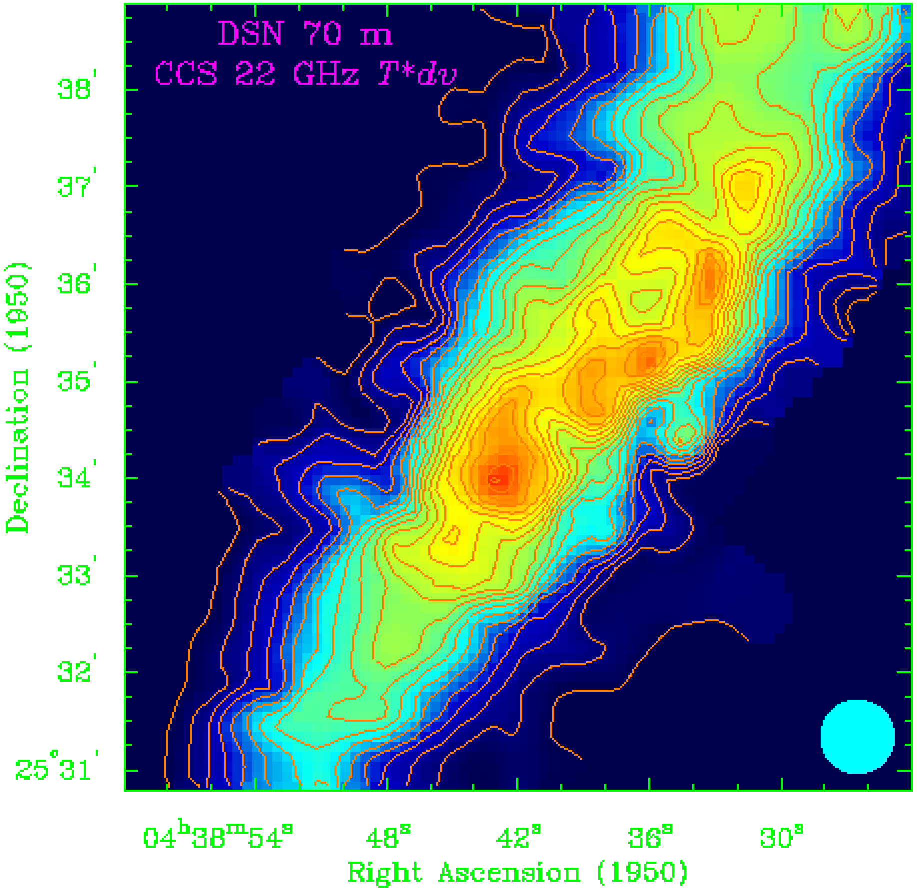
$C_2H_2 + CN \longrightarrow HC_3N + H$

Transition	Frequency (MHz)	$\int T_{mb} dv$ (mK km s^{-1})
HC_3N		
9 → 8	81881.468	1080 (10)
10 → 9	90979.023	1250 (10)
11 → 10	100076.392	1210 (10)
12 → 11	109173.634	1240 (10)
DC_3N		
10 → 9	84429.814	64 (5)
11 → 10	92872.375	50 (5)
12 → 11	101314.818	43 (5)
13 → 12	109757.133	33 (5)
$HC^{13}CCN$		
9 → 8	81534.1106	33 (7)
10 → 9	90593.059	19 (5)
11 → 10	99651.849	17 (4)
12 → 11	108710.532	16 (5)



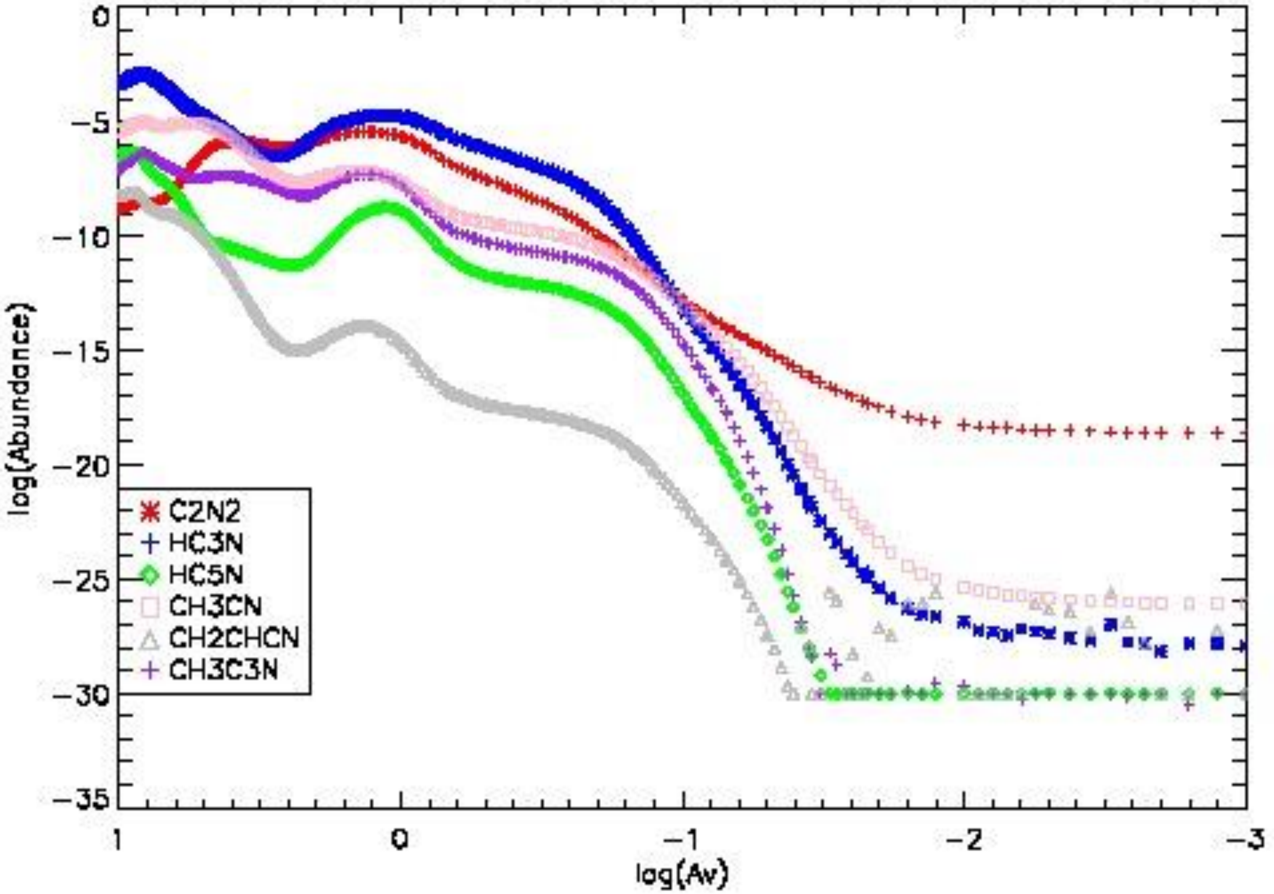
Nitriles



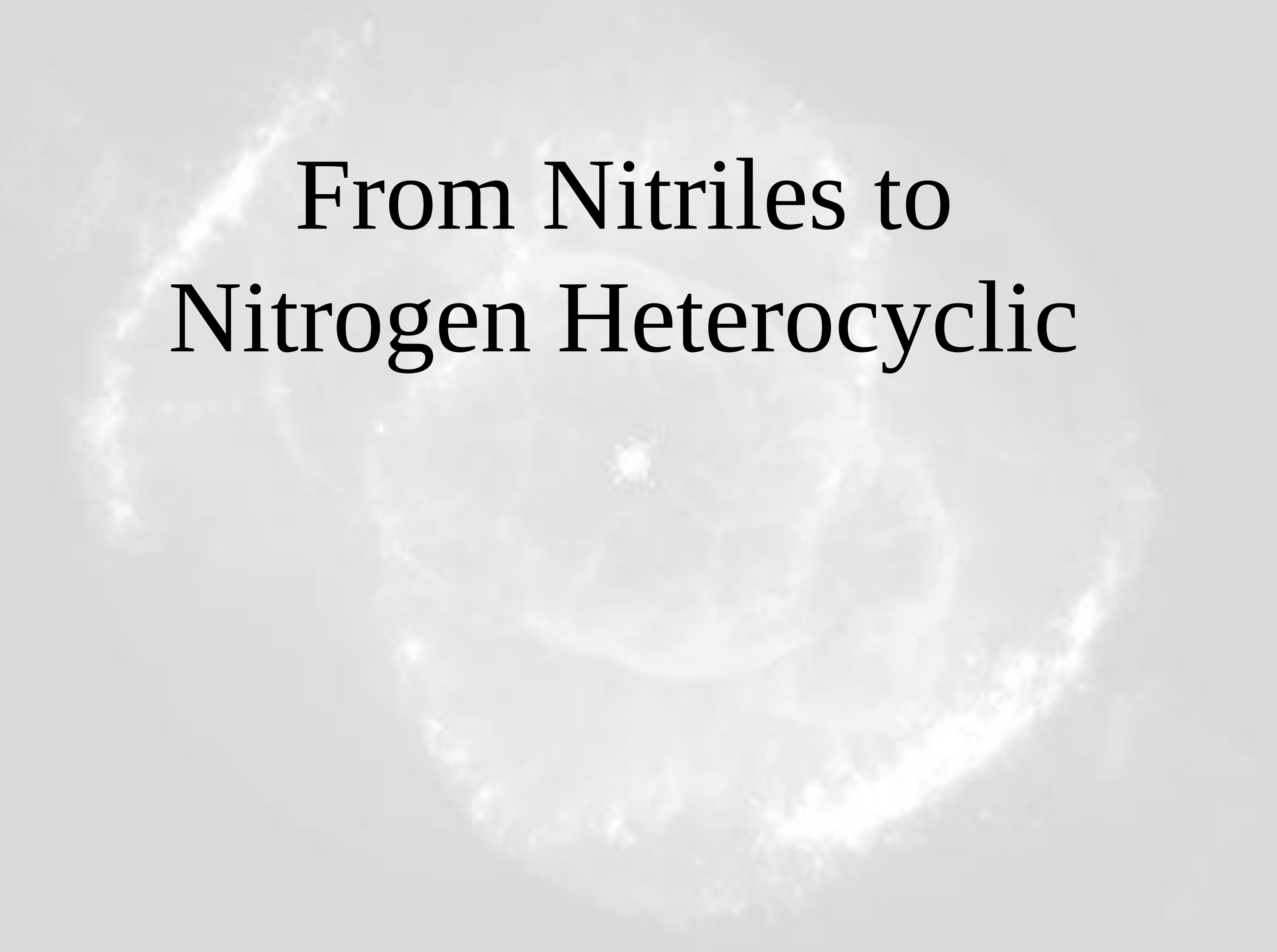


Bell et al. 1997. On the Detection of Cyanodecapentayne, HC11N, in TMC-1. *Astrophys. J.* 483, L61–L64

Nitriles

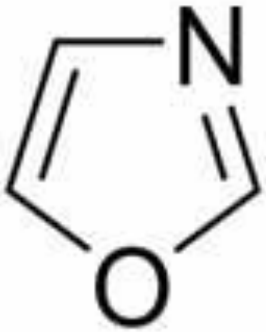


C_2N_2 – cyanogen
HC_3N – cyanoacetylene
HC_5N – cyanodiacetylene
CH_3CN – acetonitrile
CH_2CHCN – acrylonitrile
CH_3C_3N – methylcyanoacetylene

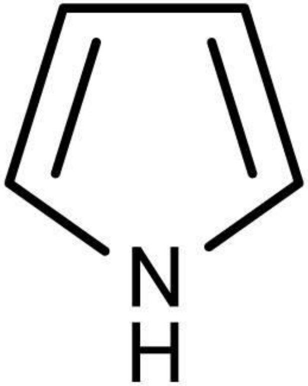


From Nitriles to Nitrogen Heterocyclic

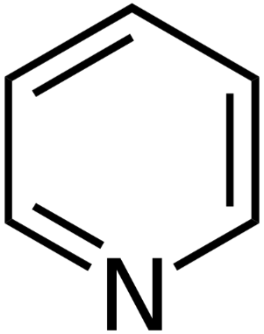
Simple heterocyclic compounds to be aimed in future observations of the interstellar and circumstellar medium



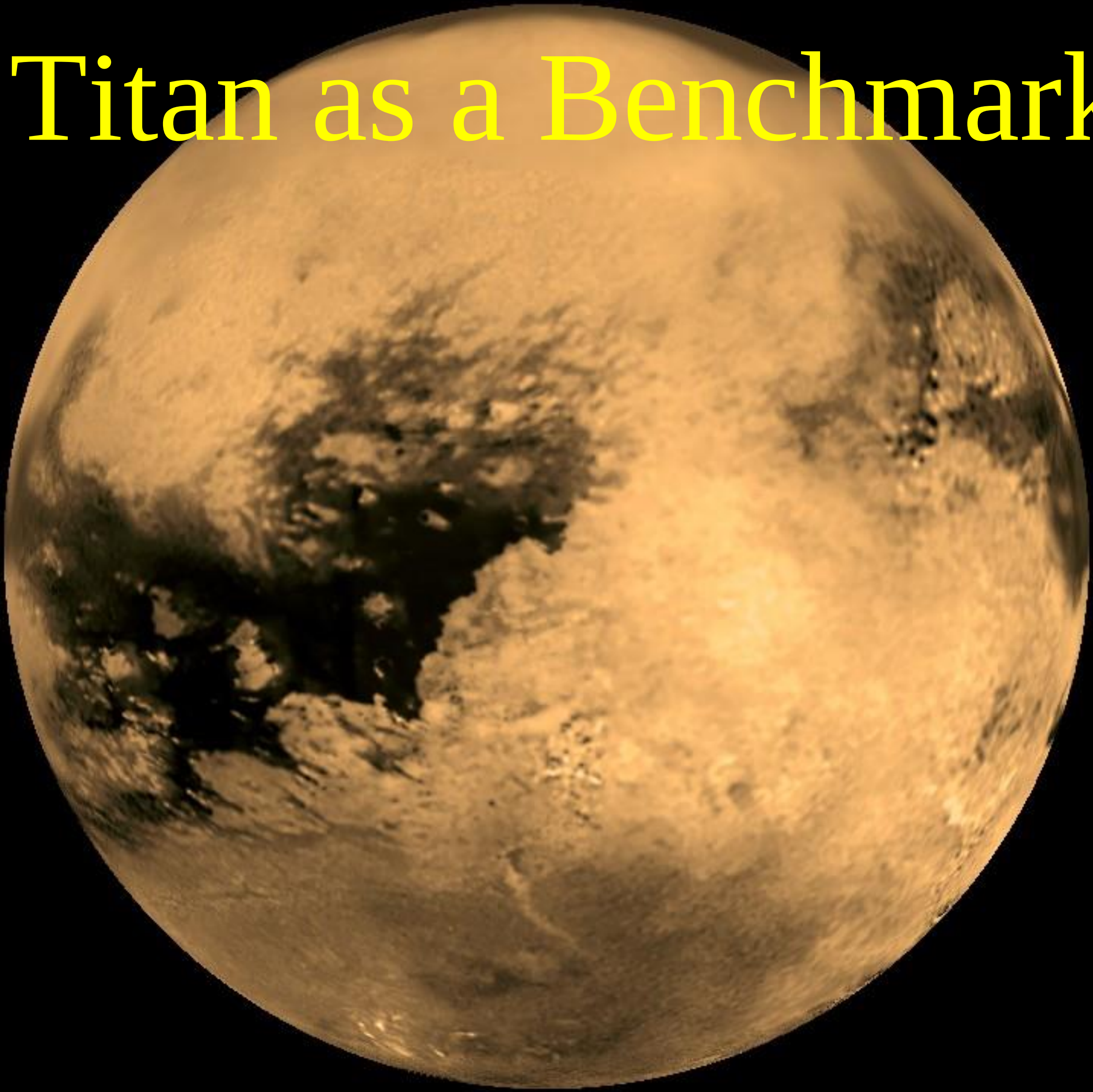
oxazole



pyrrole

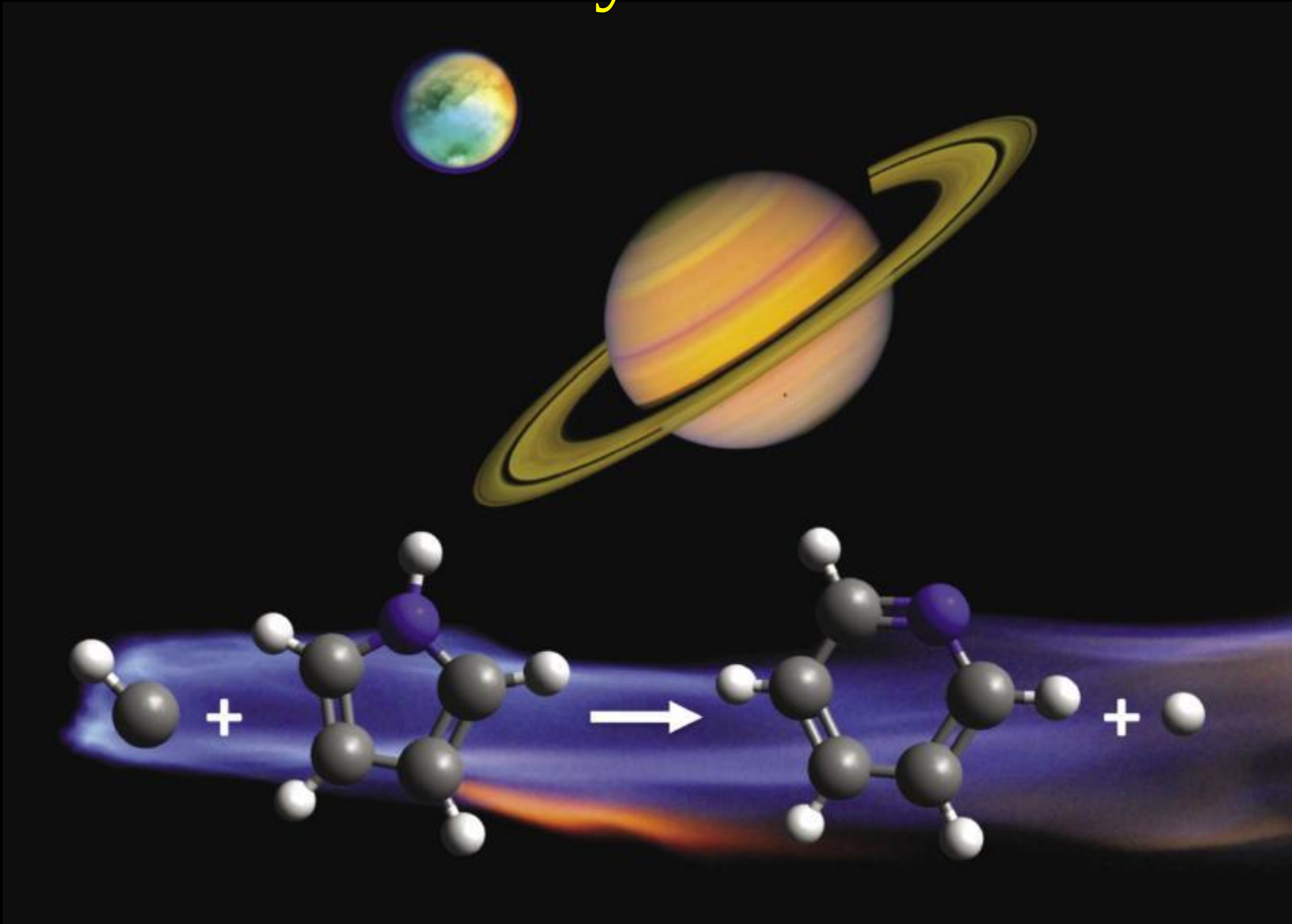


pyridine



Titan as a Benchmark

Formation of Pyridine in Titan



Produção de Heterocíclicos em Titan

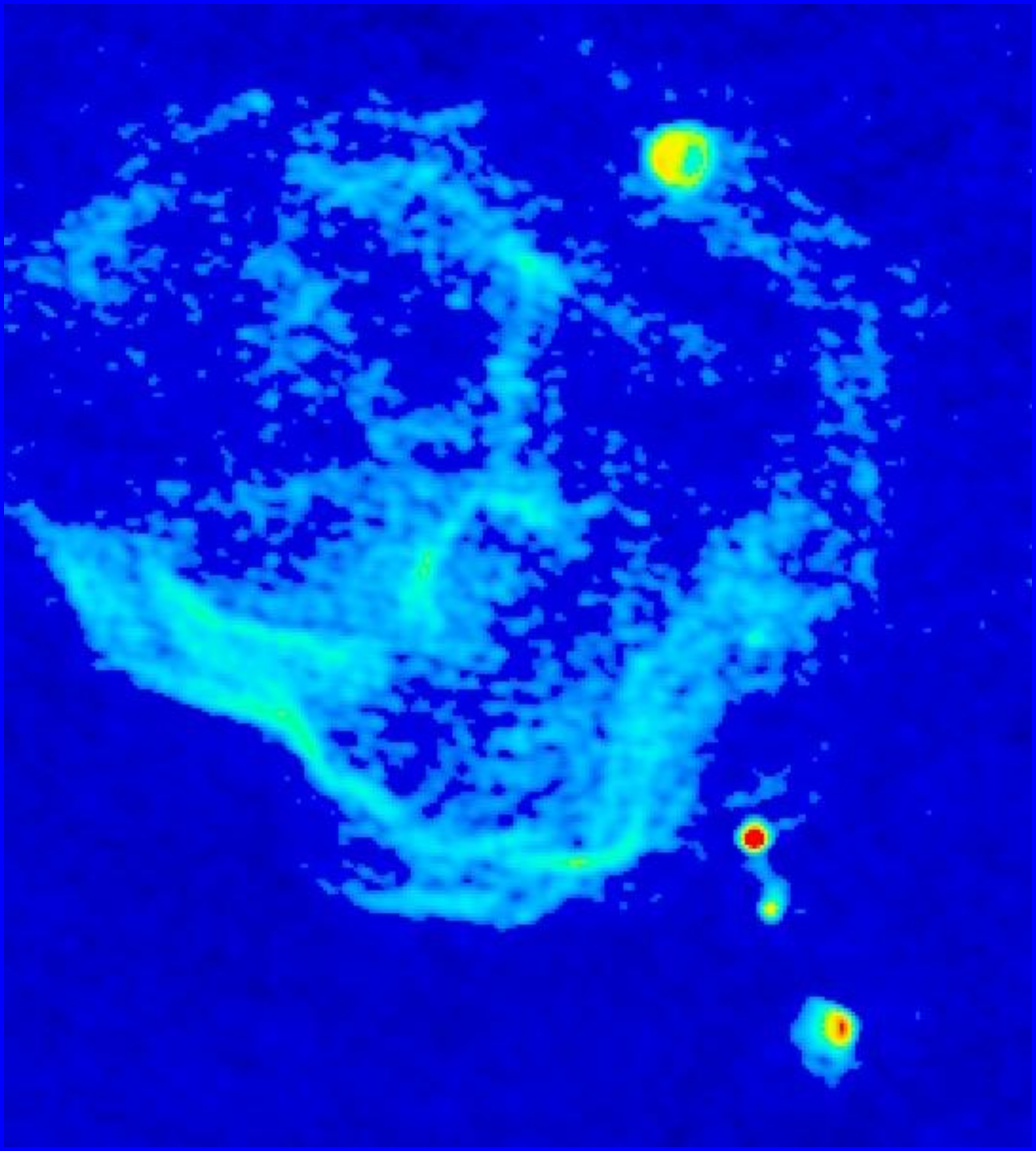
(Krasnopolsky, 2009)

$$\begin{aligned}
N_2 + h\nu \rightarrow\ & N + N^* \\
& N_2^+ + e \\
& N^+ + N^* + e \\
N_2 + e \rightarrow\ & N + N^* + e
\end{aligned}$$

$$\begin{aligned}
N_2 + \text{cosmic rays} \rightarrow\ & N_2^+ + e \\
& N^+ + N^* + e \\
& N^* + N \\
N_2 + e \rightarrow\ & N_2^+ + e + e \\
& N^+ + N^* + e + e \\
& N^* + N + e \\
N_2 + p \rightarrow\ & N_2^+ + e + p \\
& N^+ + N^* + e + p \\
& N^* + N + p
\end{aligned}$$

$$N^* + C_4H_6 \rightarrow C_4H_5N + H$$

$$C_3N + C_2H_6 \rightarrow C_5H_5N + H$$

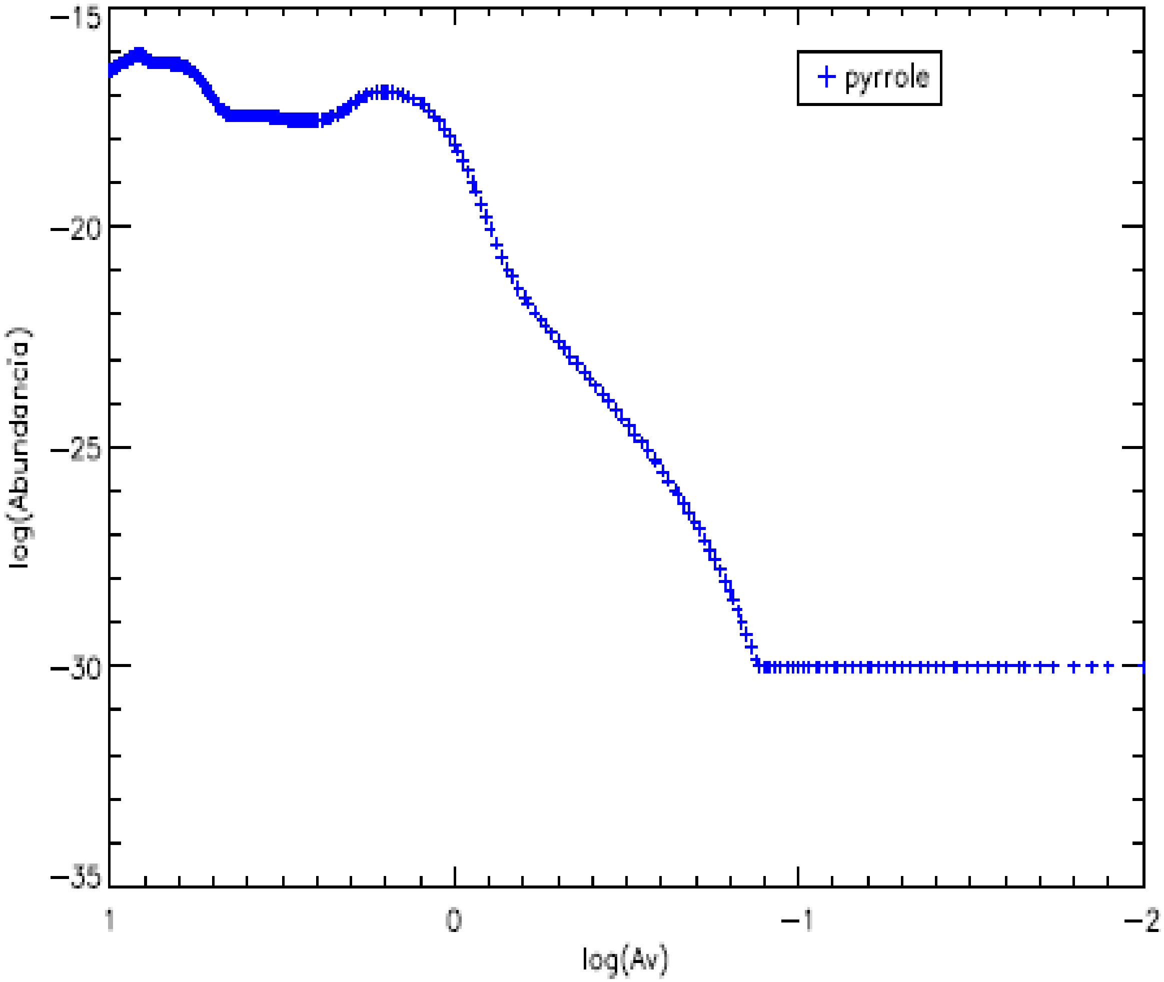


Propenal and Propanal in Sgr B2(N)

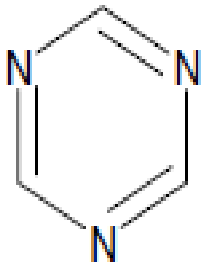
(Hollis et al. 2004)

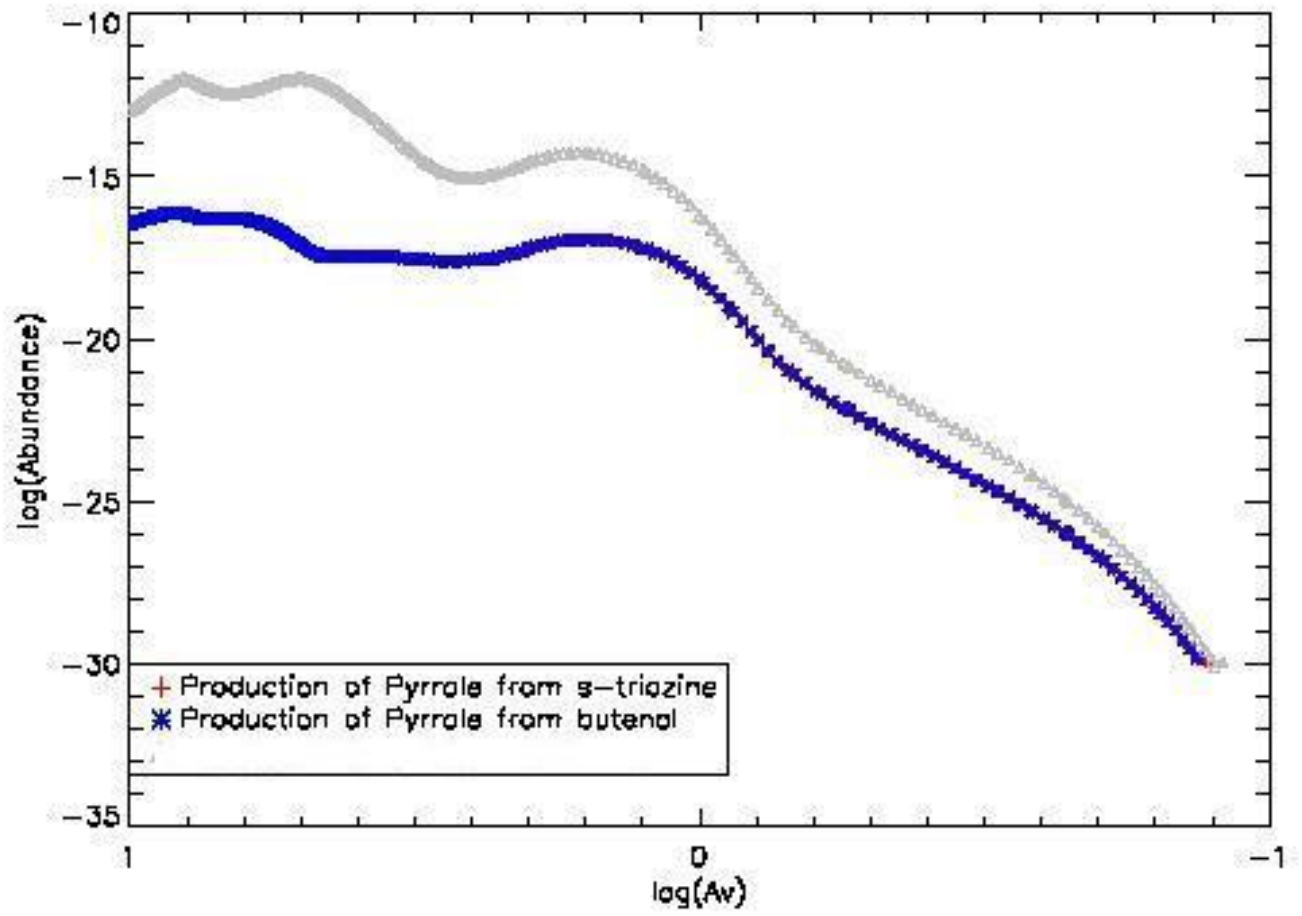
Formation of pyrrole from butenal

$$C_4H_6O + NH_3 \rightarrow C_4H_5N + H_2O + H_2$$



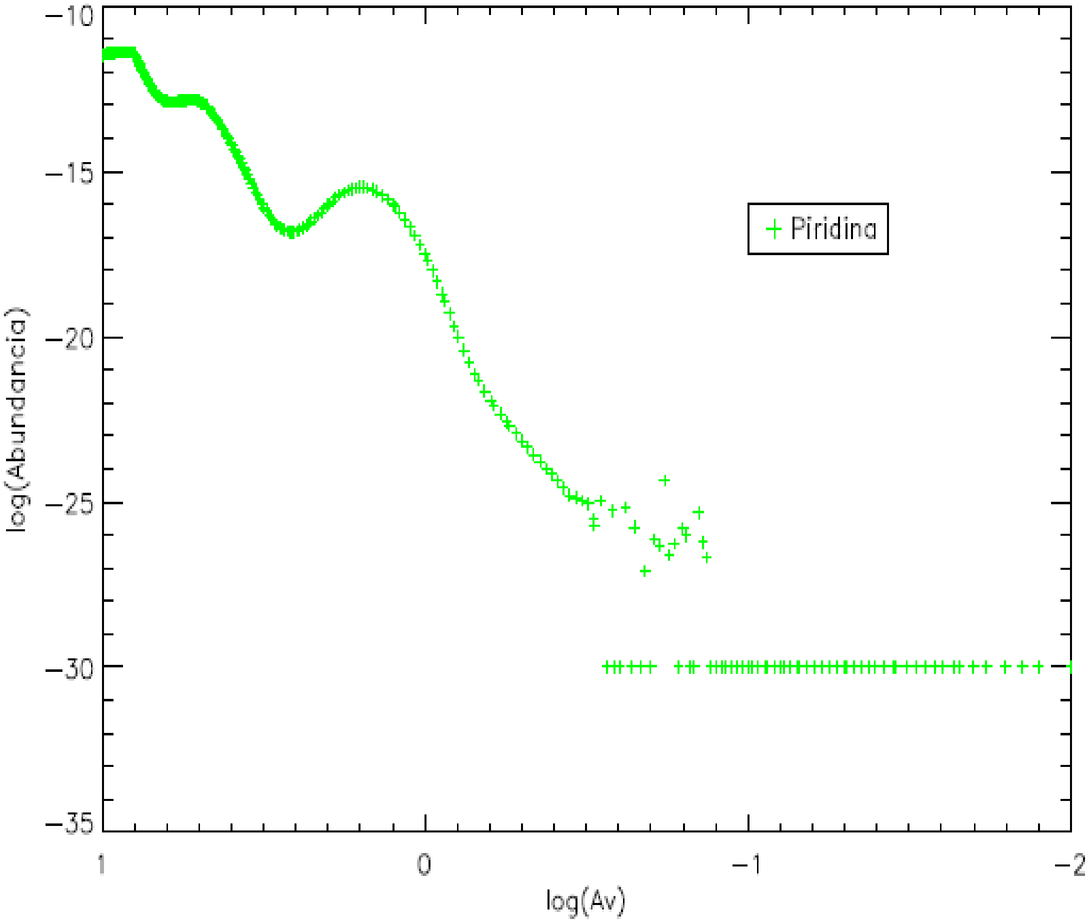
Formation of pyrrole from s-triazine



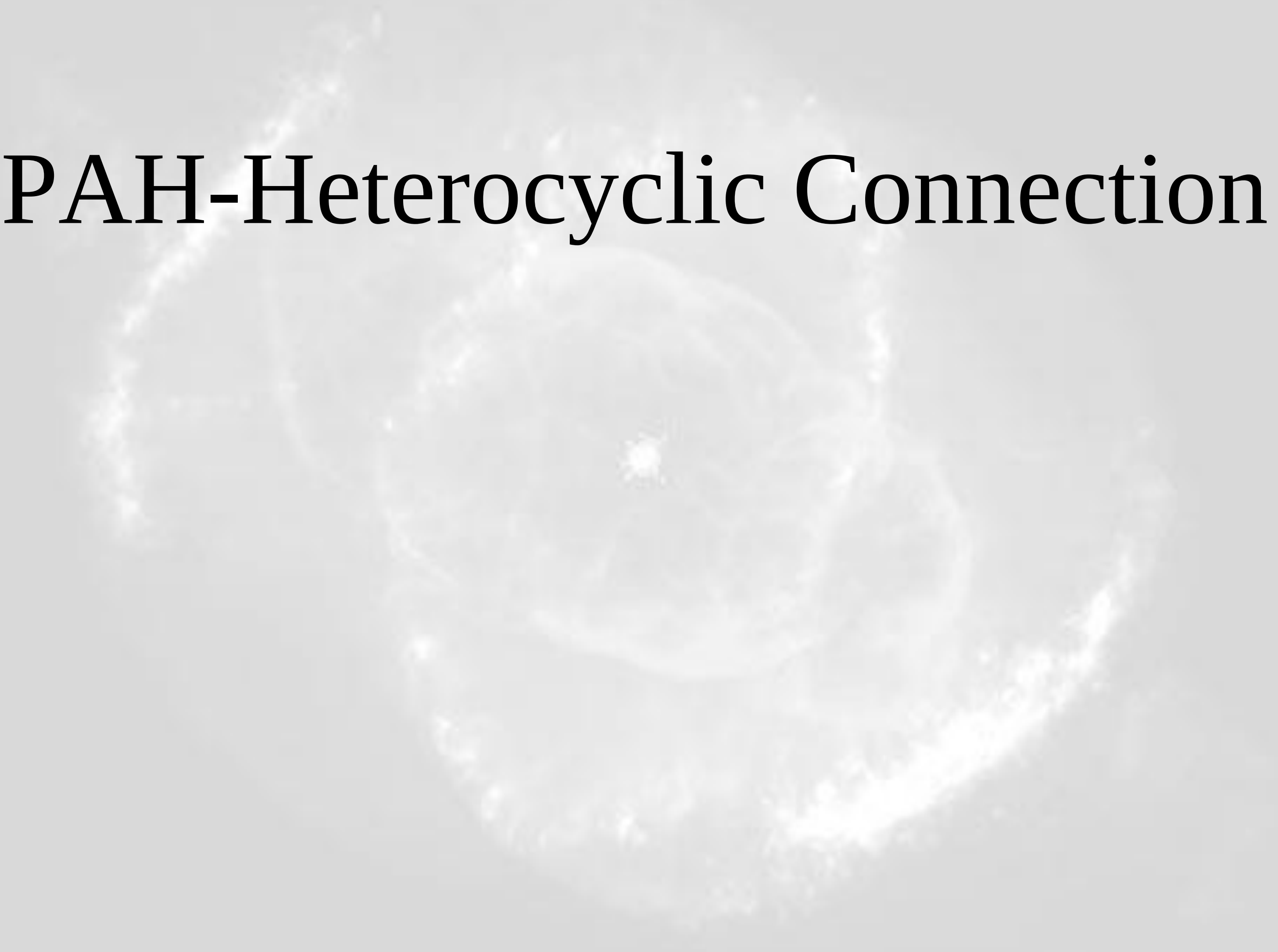


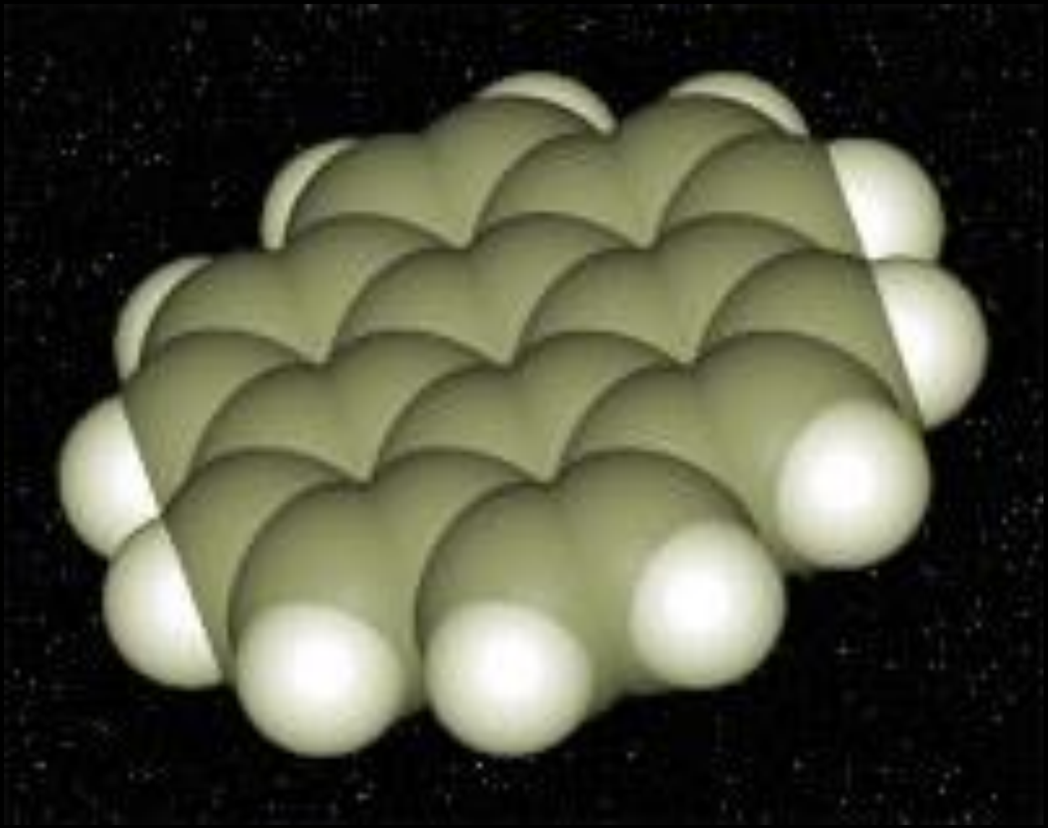
Formation of pyridine from pyrrole

$$CH + C_4H_5N \rightarrow C_5H_5N + H$$



PAH-Heterocyclic Connection





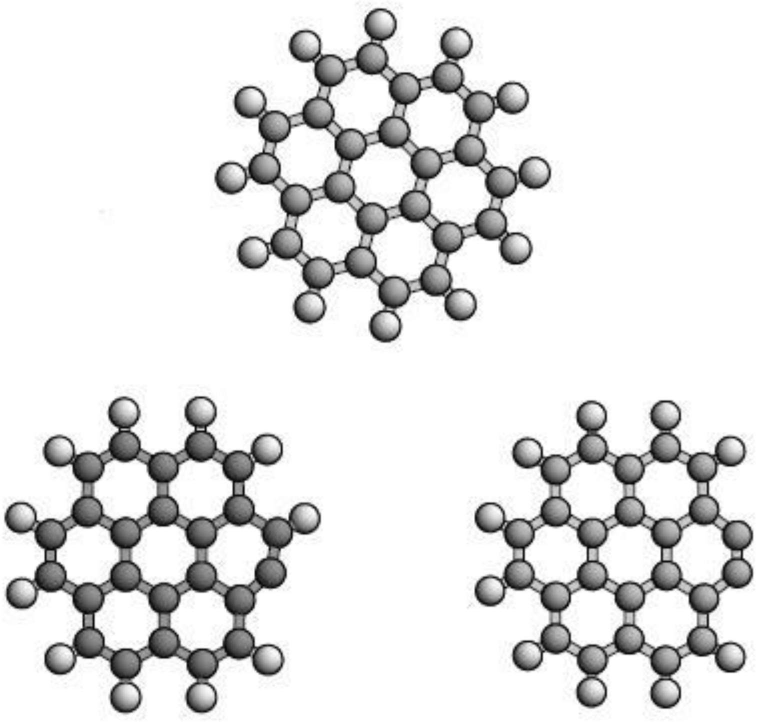
PAHs: extremamente resistentes

tempo de sobrivência no ISM ~ 1 Gano

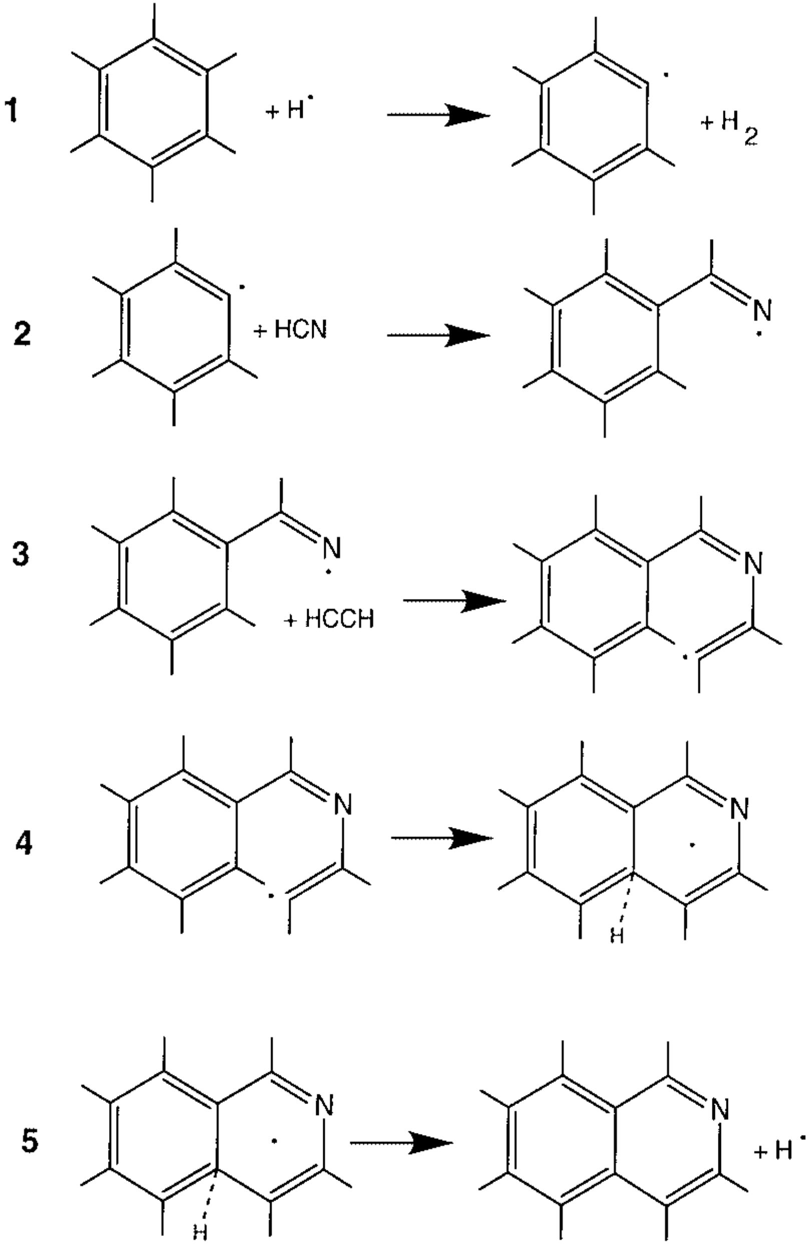
Desidrogenação de PAHs

O PAH pode perder hidrogênios, pois a energia necessária para a perda de um átomo de hidrogênio é 4,5 eV

Um parâmetro adicional que descreve um PAH é o seu grau de hidrogenação, $\alpha_{H/C}$

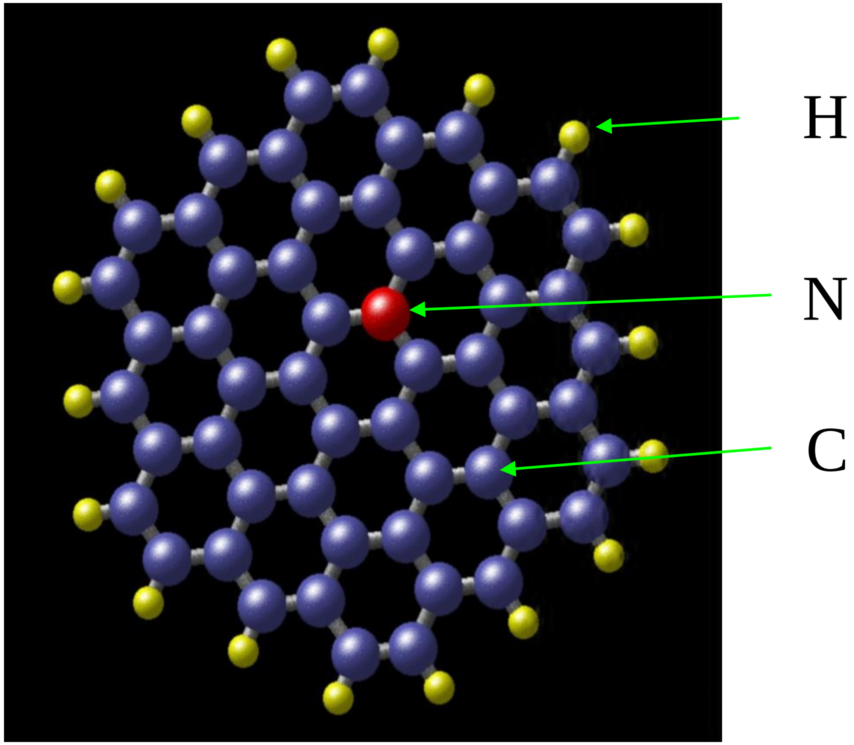


Incorporation of Nitrogen Atoms into PAHs



(Ricca et al. 2001)

Which PANHs viable?



A PAH Channel for Production of Pyridine

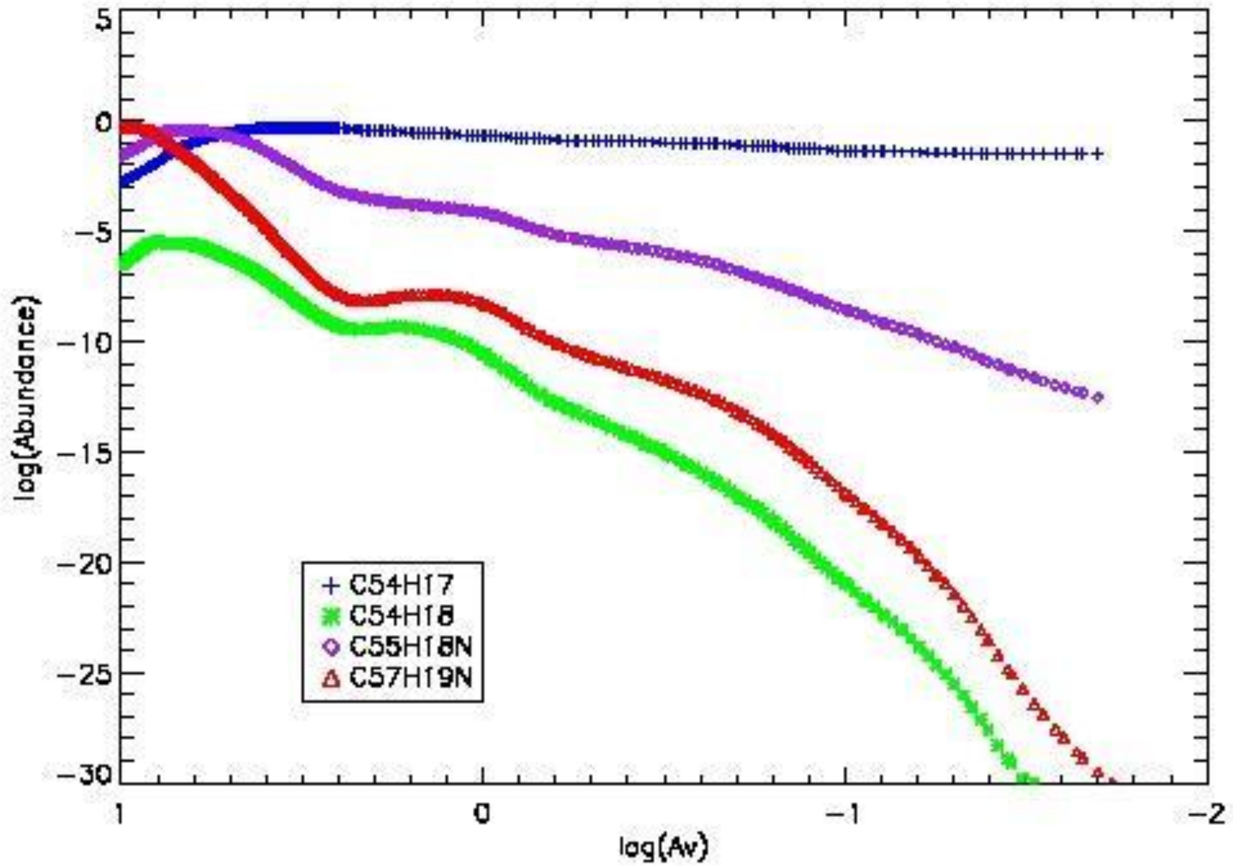
The PAHs have typically ~ 50 C atoms per PAH

Pericondensates with D_{6h} symmetry: $C_{6n^2}H_{6n}$

n=3 $\Rightarrow$ $C_{54}H_{18}$

$$C_{54}H_{18} + \gamma \rightarrow C_{54}H_{17} + H$$
$$C_{54}H_{18} + H \rightarrow C_{54}H_{17} + H_2$$
$$C_{54}H_{17} + HCN \rightarrow C_{55}H_{18}N + \gamma$$
$$C_{55}H_{18}N + C_2H_2 \rightarrow C_{57}H_{19}N + H$$
$$C_{57}H_{19}N + \gamma \rightarrow C_{54}H_{18} + HC_3N$$
$$C_{57}H_{19}N + C_2H_4 \rightarrow C_{54}H_{18} + C_5H_5N$$

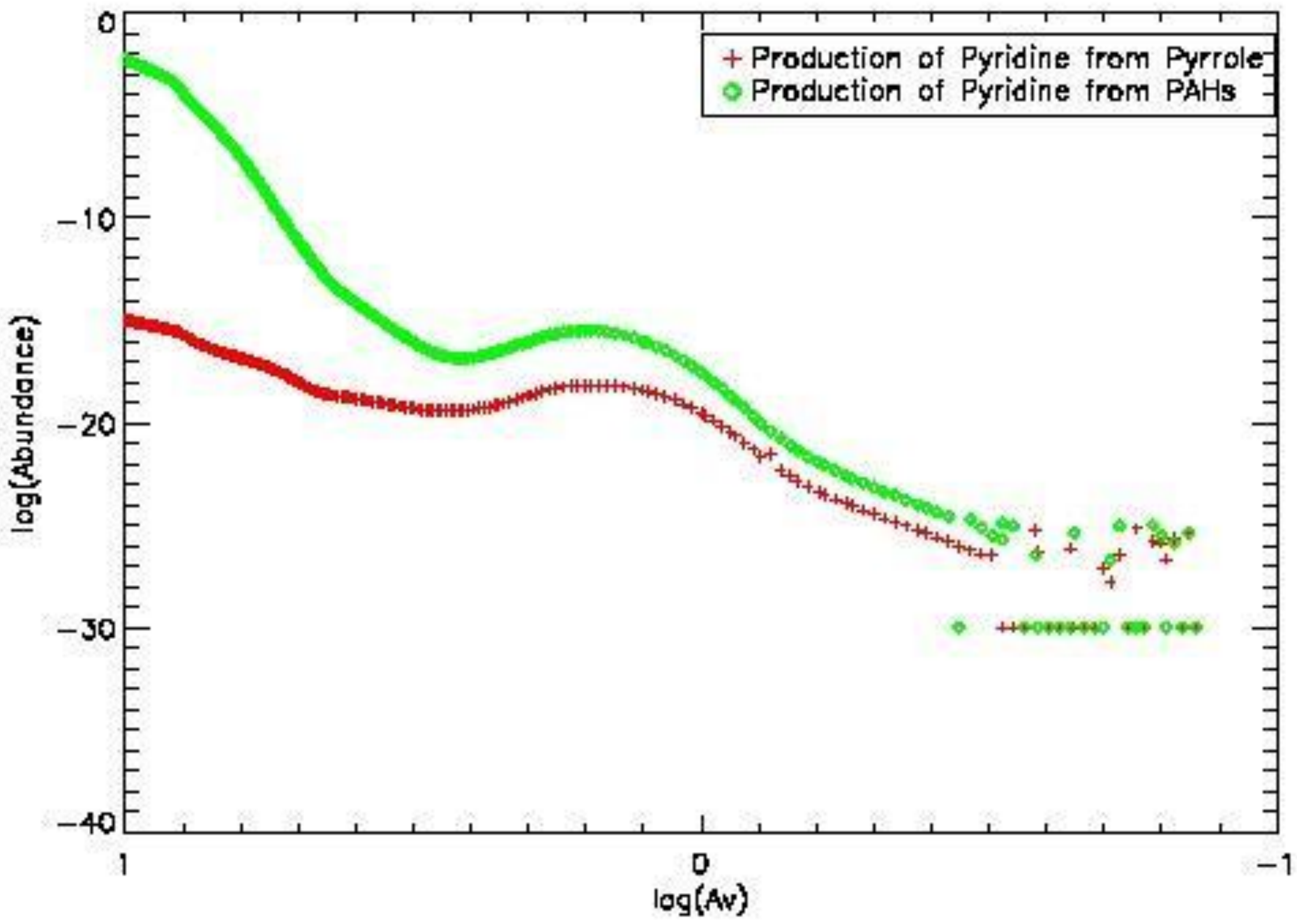
PAHs and PANHs (root PAH $C_{54}H_{18}$)



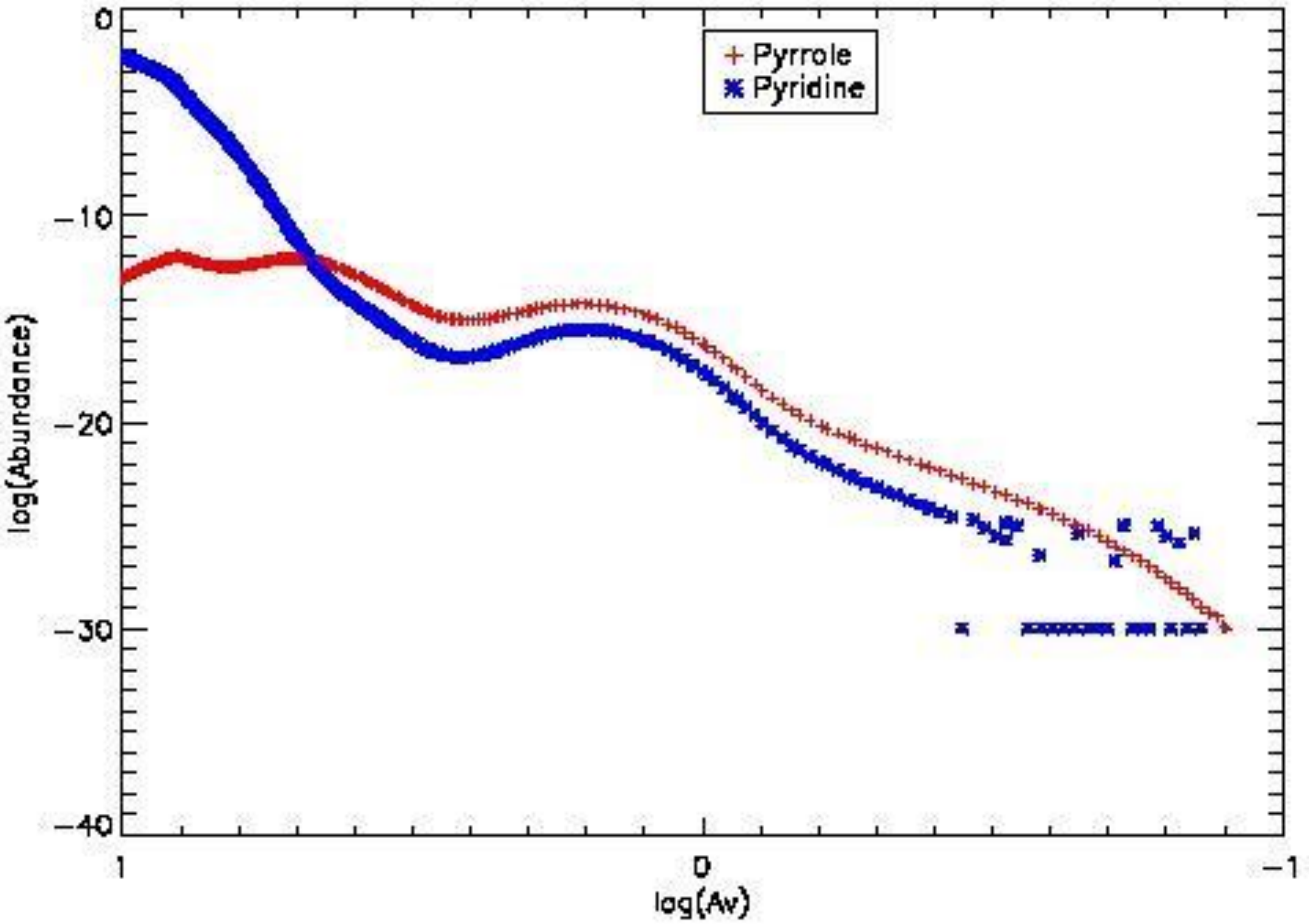
Pericondensates with D_{6h} symmetry: $C_{6n^2}H_{6n}$

n=3 ⇒ $C_{54}H_{18}$

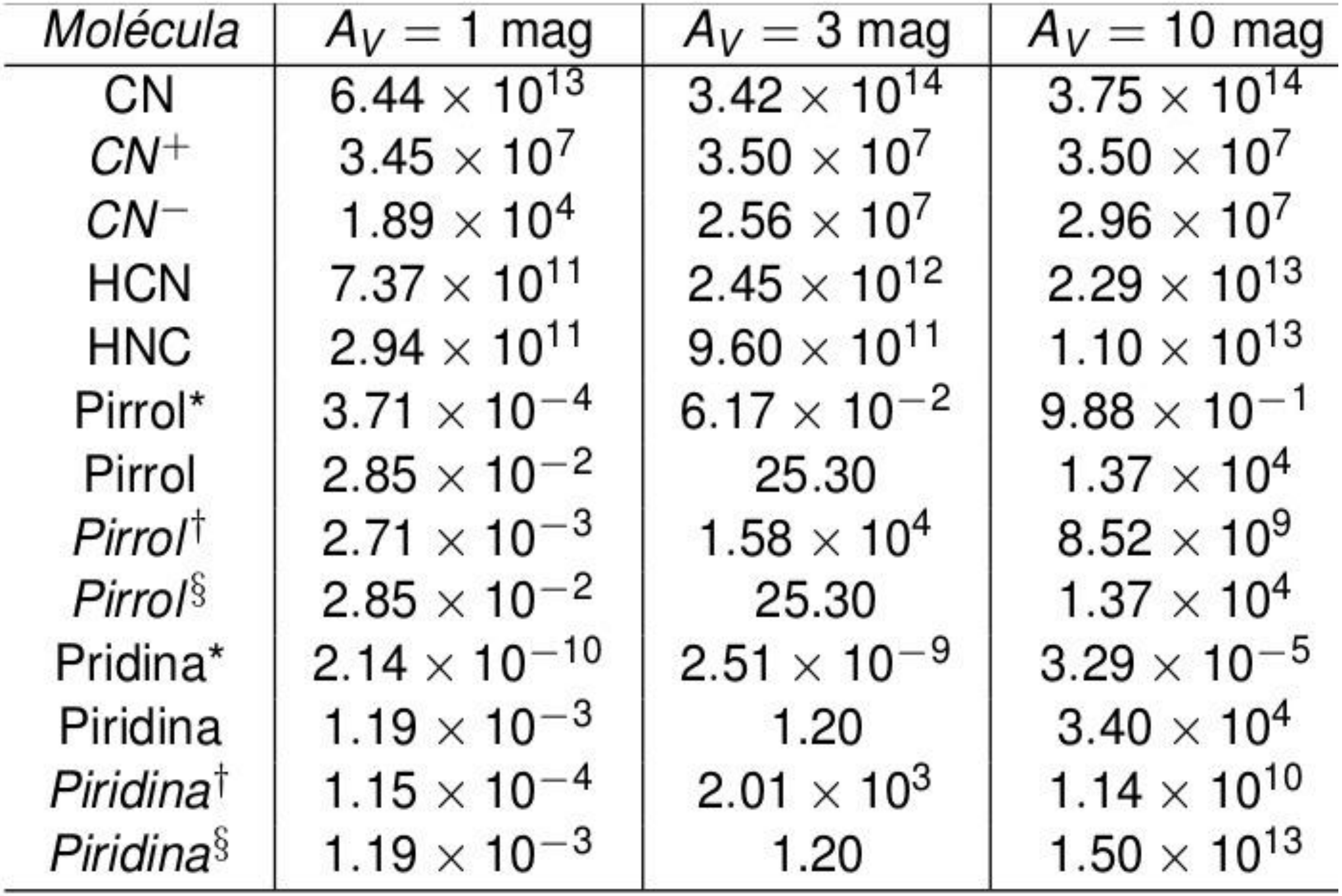
Channels for Production of Pyridine



Production of pyrrole vs. pyridine



Densidades de Coluna



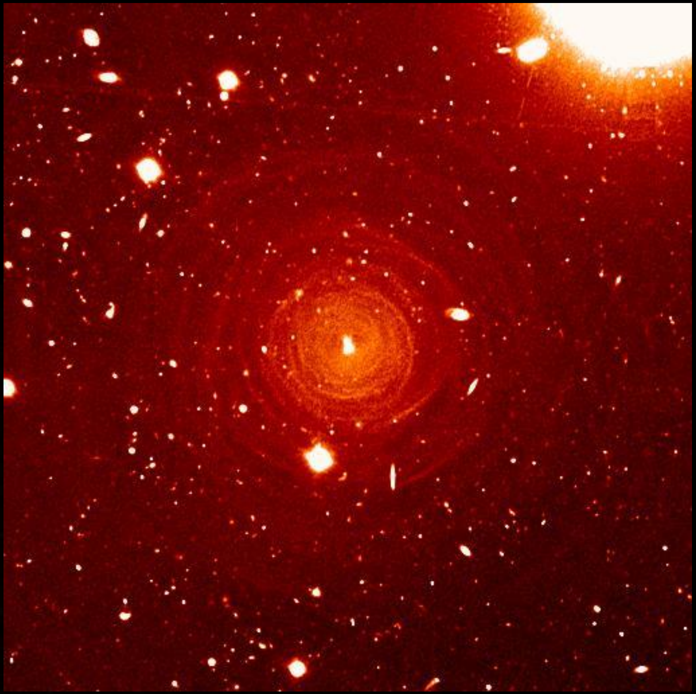
Molécula	$A_V = 1$ mag	$A_V = 3$ mag	$A_V = 10$ mag
CN	6.44×10^{13}	3.42×10^{14}	3.75×10^{14}
CN^{+}	3.45×10^{7}	3.50×10^{7}	3.50×10^{7}
CN^{-}	1.89×10^{4}	2.56×10^{7}	2.96×10^{7}
HCN	7.37×10^{11}	2.45×10^{12}	2.29×10^{13}
HNC	2.94×10^{11}	9.60×10^{11}	1.10×10^{13}
Pirrol*	3.71×10^{-4}	6.17×10^{-2}	9.88×10^{-1}
Pirrol	2.85×10^{-2}	25.30	1.37×10^{4}
Pirrol†	2.71×10^{-3}	1.58×10^{4}	8.52×10^{9}
Pirrol§	2.85×10^{-2}	25.30	1.37×10^{4}
Pridina*	2.14×10^{-10}	2.51×10^{-9}	3.29×10^{-5}
Piridina	1.19×10^{-3}	1.20	3.40×10^{4}
Piridina†	1.15×10^{-4}	2.01×10^{3}	1.14×10^{10}
Piridina§	1.19×10^{-3}	1.20	1.50×10^{13}

Searchs for Pyridine in the ISM

(Charnley et al. 2005)

IRC+10216 (AGB star)

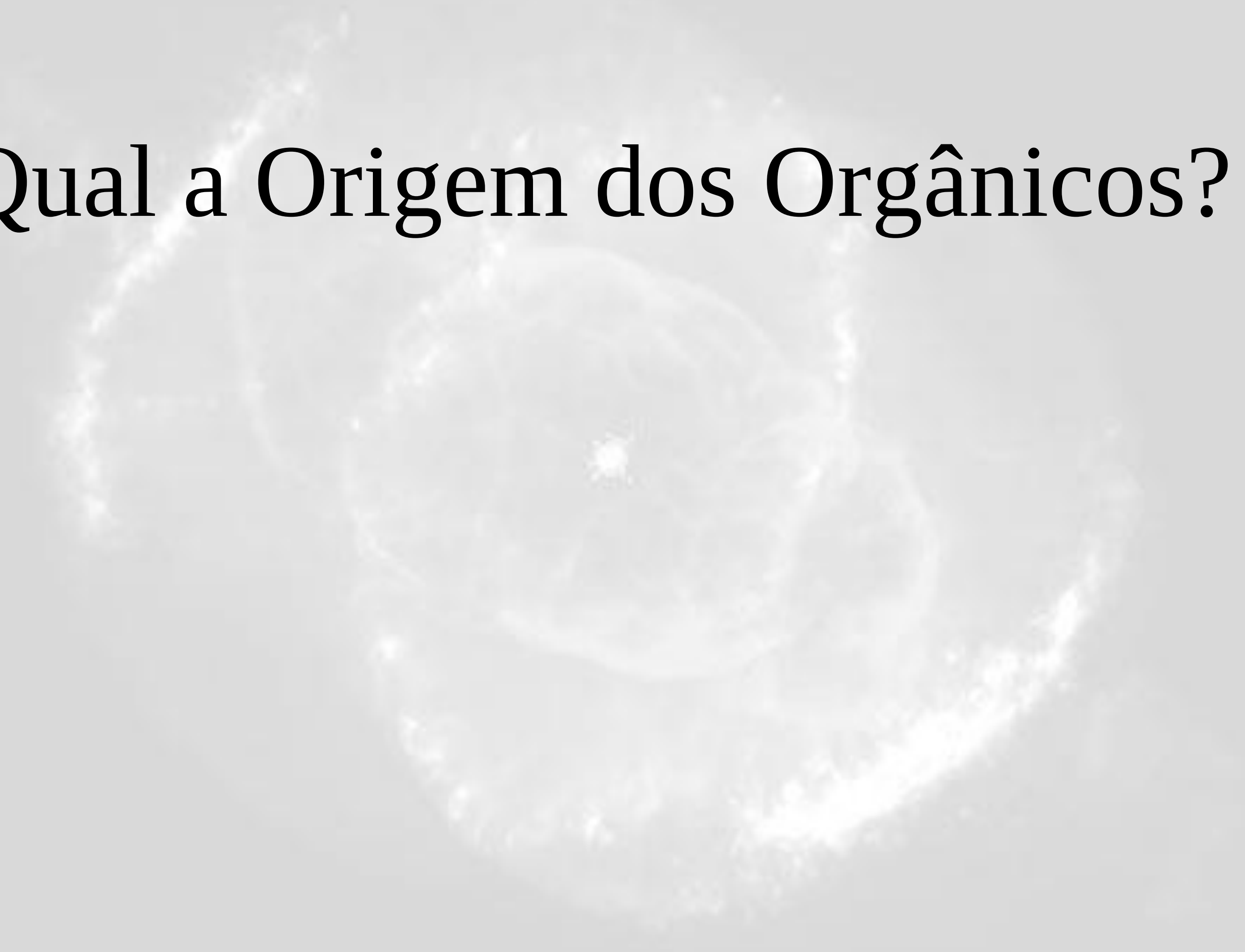
$N < 7.3\text{-}8.6 \times 10^{12}$ cm^2



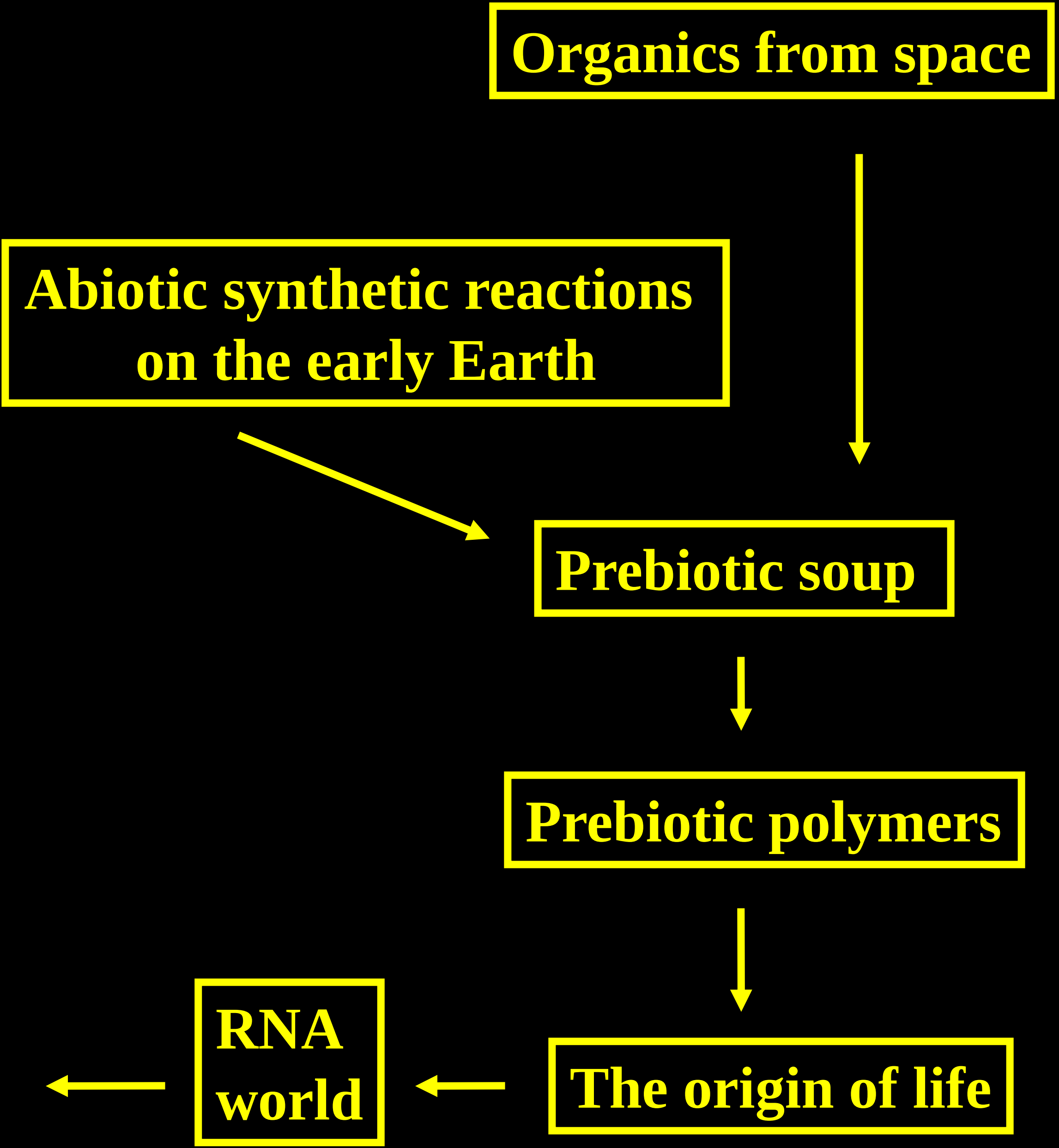
CRL 618 (PN)

$N < 2.3\text{-}2.7 \times 10^{13}$ cm^2

Qual a Origem dos Orgânicos?



EARTH TODAY



Organics from space

Abiotic synthetic reactions on the early Earth

Prebiotic soup

Prebiotic polymers

The origin of life

RNA world

Protein/DNA world (modern biochemistry)

Bada & Lazcano (Science, 2002)

Terrestrial vs. Extraterrestrial

- Terrestrial origin – organic synthesis occurred somewhere in the Earth environment
- Extraterrestrial origin – organic material was synthesized in space and was brought to Earth somehow

Problems with abiotic organic synthesis.

- Almost all organic carbon which we observe today is produced biologically (photosynthesis):

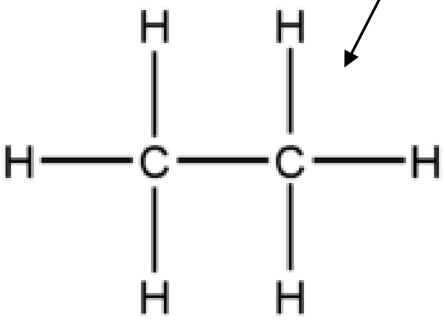
  $CO_2 + H_2O \rightarrow CH_2O + O_2$

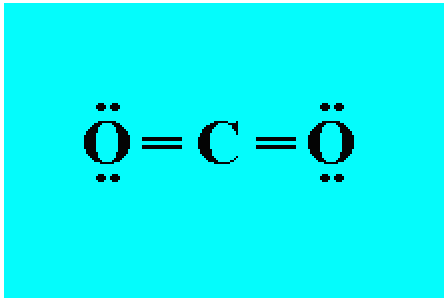
- Carbon which comes out of volcanoes is in a form of CO_2
- CO_2 gas mixture does not produc

organic molecules on its own

organic

inorganic



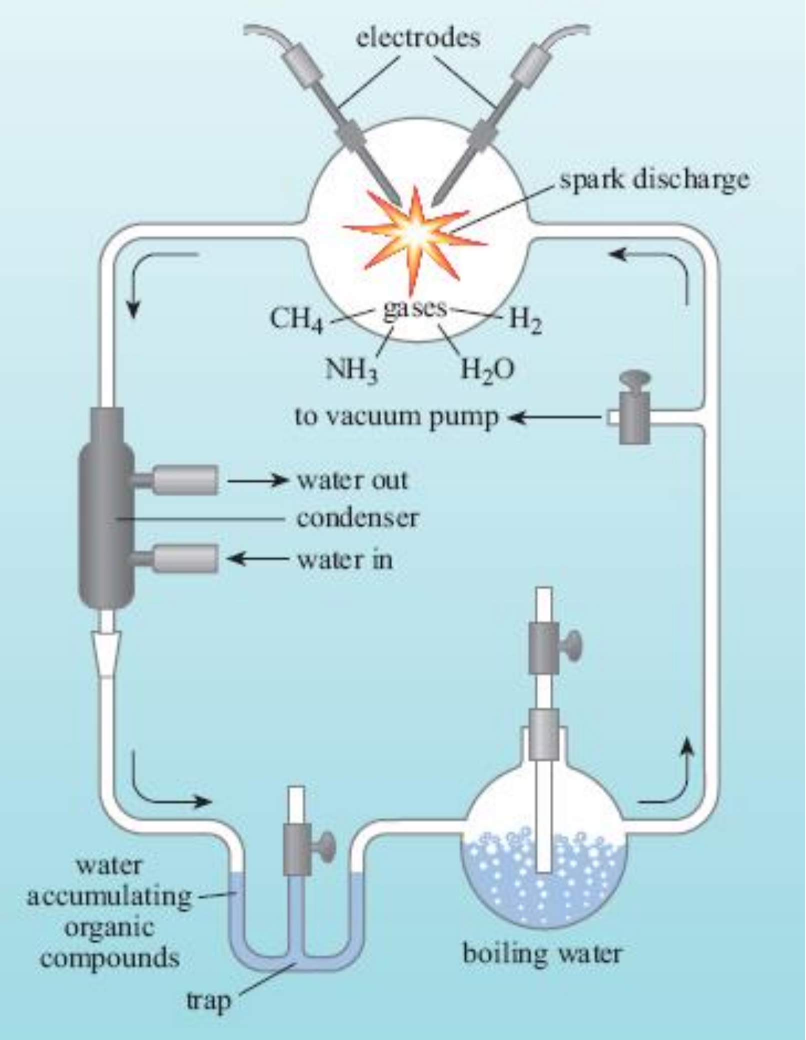


Urey-Miller Experiment

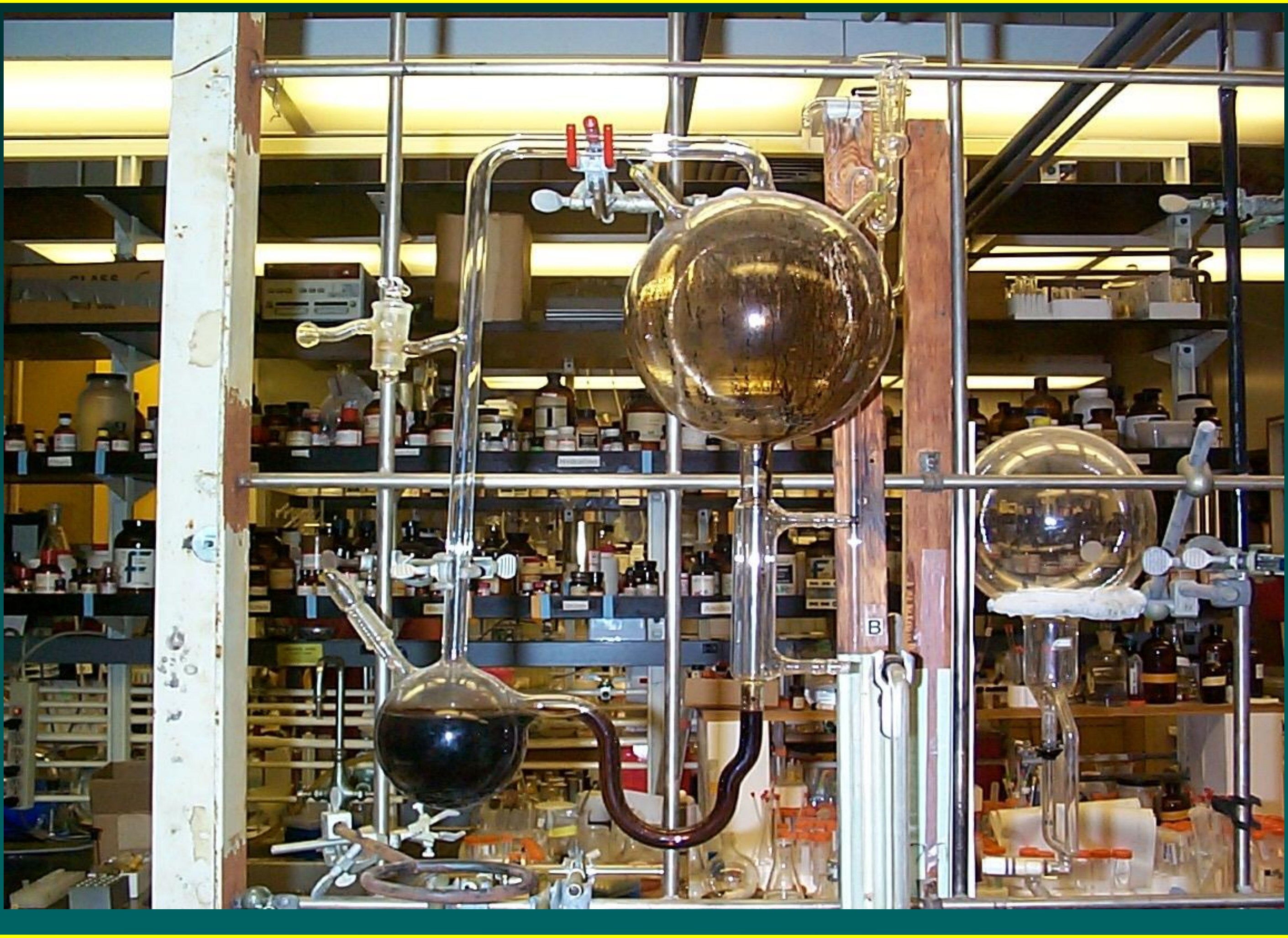
1) At some point scientists believed that the ancient atmosphere was rich in CH_4 and NH_3

2) But! Just mixing CH_4, NH_3, H_2O, H_2 would not produce any organic material

3) Miller showed that a spark discharge (lightning) would produce organic molecules up to 10-15% of the initial CH_4 by mass



The Miller-Urey-Experiment



FIRST EXPERIMENTAL FORMATION OF BIOLOGICALLY RELEVANT MOLECULES UNDER PREBIOTIC CONDIDTIONS

Formation of organic molecules in the gas phase

- UV can be used for organic synthesis as well
- The key is to produce carbon radicals
- $CH_4 + h\nu \rightarrow CH_3 + H$
- $CH_3 + CH_3 \rightarrow C_2H_6 + M$
- $C_2H_6 + h\nu \ldots \rightarrow C_2H$
- $C_{2n}H_2 + C_2H \rightarrow C_{2n+2}H_2 + H$
- Polymerization is extremely sensitive to O abundance

Advantages of Organic synthesis in the ancient atmosphere

- UM-like experiments produced many types of organic molecules which are used in proteins
- We would expect lightning and UV radiation in the prebiotic atmosphere
- No need to deliver organic material to Earth – it would be already here

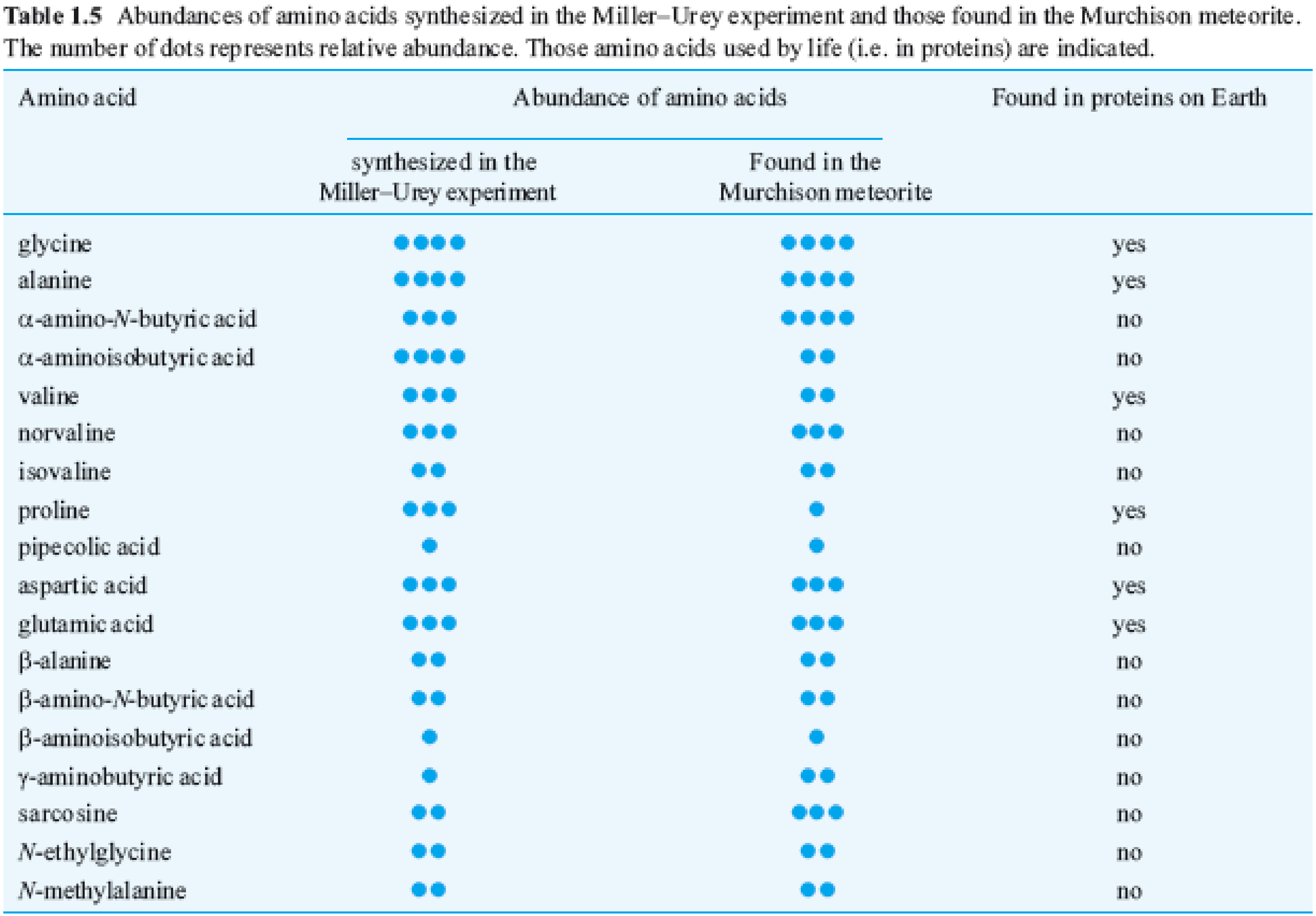
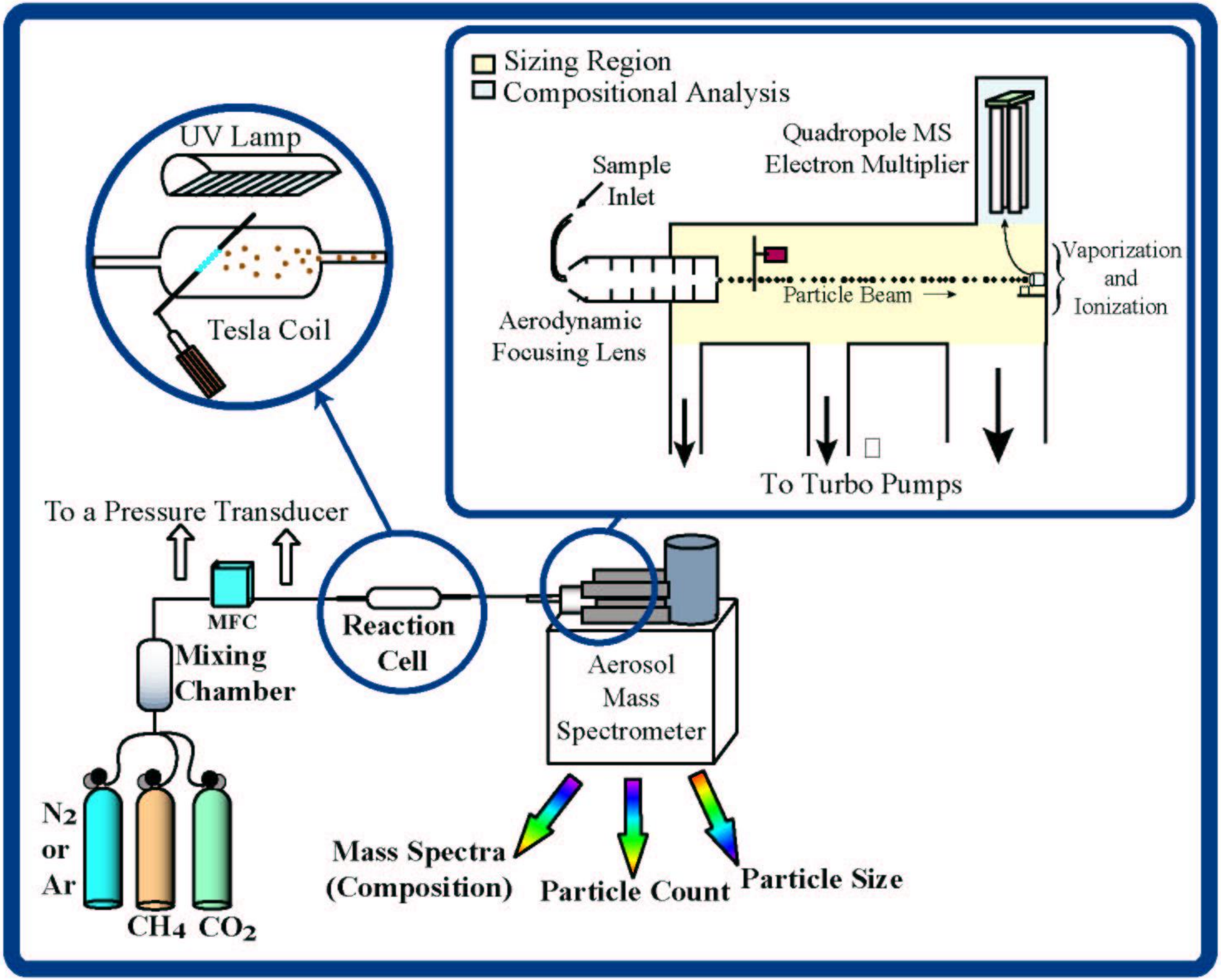


Table 1.5 Abundances of amino acids synthesized in the Miller–Urey experiment and those found in the Murchison meteorite. The number of dots represents relative abundance. Those amino acids used by life (i.e. in proteins) are indicated.

Amino acid	Abundance of amino acids		Found in proteins on Earth
	synthesized in the Miller–Urey experiment	Found in the Murchison meteorite	
glycine	●●●●	●●●●	yes
alanine	●●●●	●●●●	yes
α-amino-*N*-butyric acid	●●●	●●●●	no
α-aminoisobutyric acid	●●●●	●●	no
valine	●●●	●●	yes
norvaline	●●●	●●●	no
isovaline	●●	●●	no
proline	●●●	●	yes
pipecolic acid	●	●	no
aspartic acid	●●●	●●●	yes
glutamic acid	●●●	●●●	yes
β-alanine	●●	●●	no
β-amino-*N*-butyric acid	●●	●●	no
β-aminoisobutyric acid	●	●	no
γ-aminobutyric acid	●	●●	no
sarcosine	●●	●●●	no
N-ethylglycine	●●	●●	no
N-methylalanine	●●	●●	no

Difficulties for the organic synthesis via UM experiment

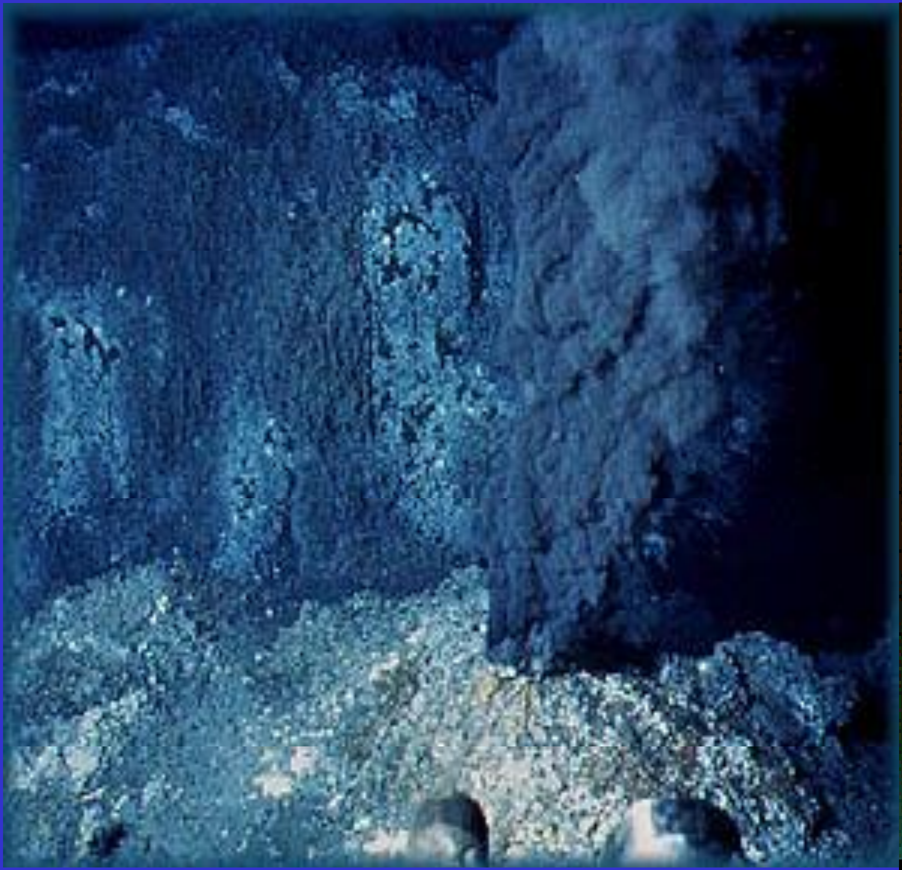
- It is hard to justify large amounts of NH_3 and CH_4 in the prebiotic atmosphere
- In the CO_2-rich atmosphere organic production by spark discharge is not very efficient
- If $CH_4/CO_2 < 0.1$ essentially no organic production

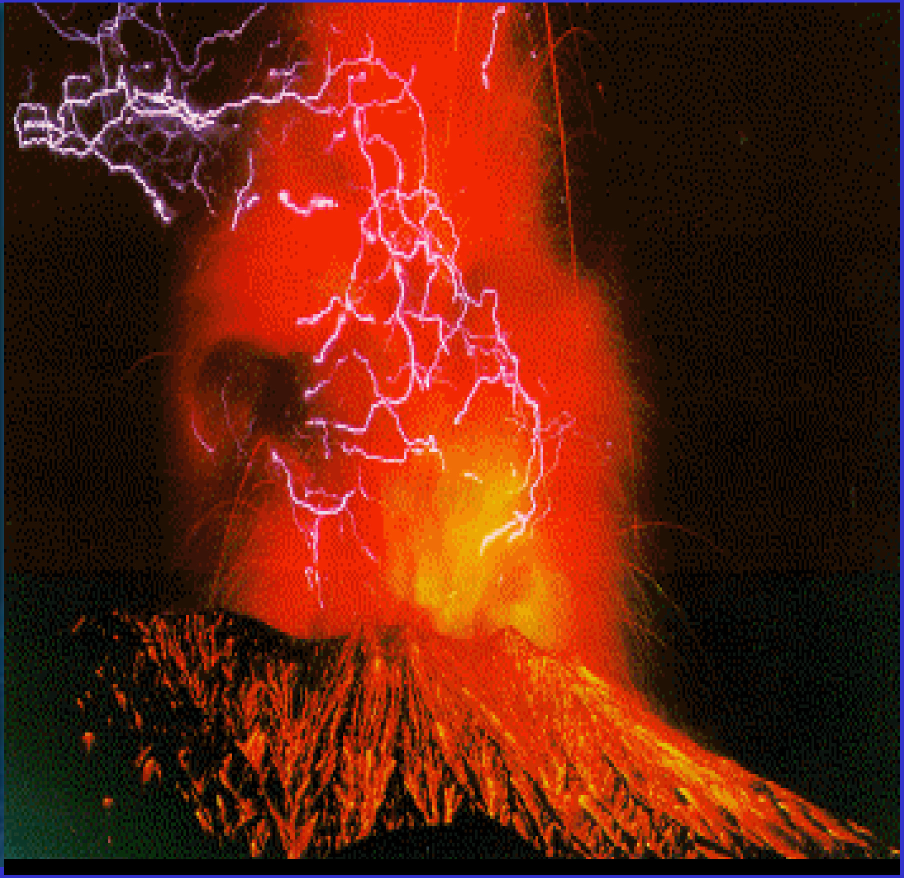


Trainer et al., 2005; 2006)

Alternative abiotic synthesis routes

- Black Smokers
- Volcanic outflows





Hydrothermal vents

- Fischer-Tropsch synthesis. Under high temperatures and pressures CO and H_2 can form hydrocarbons
- $(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$

  where 'n' is a positive integer

Advantages of Organic synthesis in the Hydrothermal Vents

- Hydrothermal vents were likely to be present in the prebiotic environment
- Organic synthesis requires only CO_2, H_2O and silicate rocks.
- Serpentinization:

$$3(Fe,Mg)_2SiO_4+nH_2O+HCO_3 \rightarrow 2Mg_3[Si_2O_5(OH_4)]+2Fe_3O_4+H_2O+CH$$

Olivine

Serpentine

Magnetite (spinel group)

- Spinel polymerization:

$$nCH_4+nFe_3O_4+nH_2O \rightarrow C_2H_6+Fe_2O_3+HCO_3+H^+$$

Difficulties of the organic synthesis via Hydrothermal Vents

- No clean catalysts in nature. Original Fischer-Tropsch reaction goes fast in the presence of iron and cobalt
- Only very simple organics can be generated. No amino-acids, no PAHs etc.

- Since both atmosphere and hydrothermal vents have problems producing organics we need to look somewhere else.

  Space!

Gaseous Pillars – Eagle Nebula

Key hole Nebula

Titan

Hale-Bopp

Murchinson

Extraterrestrial Delivery of Biogenic Molecules

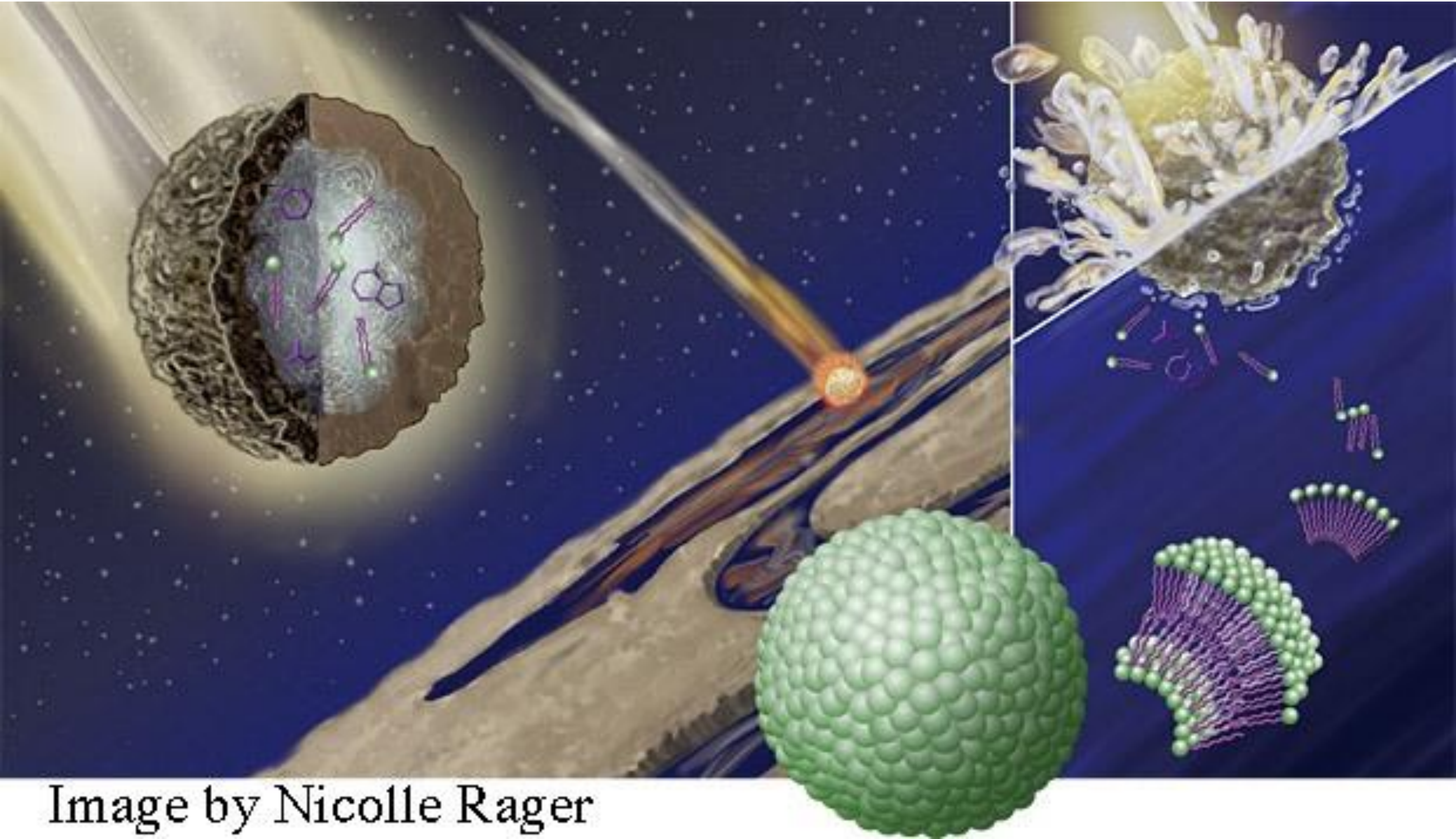


Image by Nicolle Rager

Major Sources (in kg/yr) of Prebiotic Organic Compounds in the Early Earth

Terrestrial Sources	kg/yr*
UV Photolysis	3 x 10^8
Electric Discharge	3 x 10^7
Shocks from impacts	4 x 10^2
Hydrothermal Vents	1 x 10^8
Extraterrestrial Sources	adapted from Chyba & Sagan (1992)
IDP’s	2 x 10^8
Comets	1 x 10^{11}
Total	10^{11}