The Chemistry of Circumstellar Envelopes

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Advanced School on Infrared and Submillimeter Astrophysics: Quito, 5-16 March 2018

The Chemistry of Circumstellar Envelopes

1.- Introduction

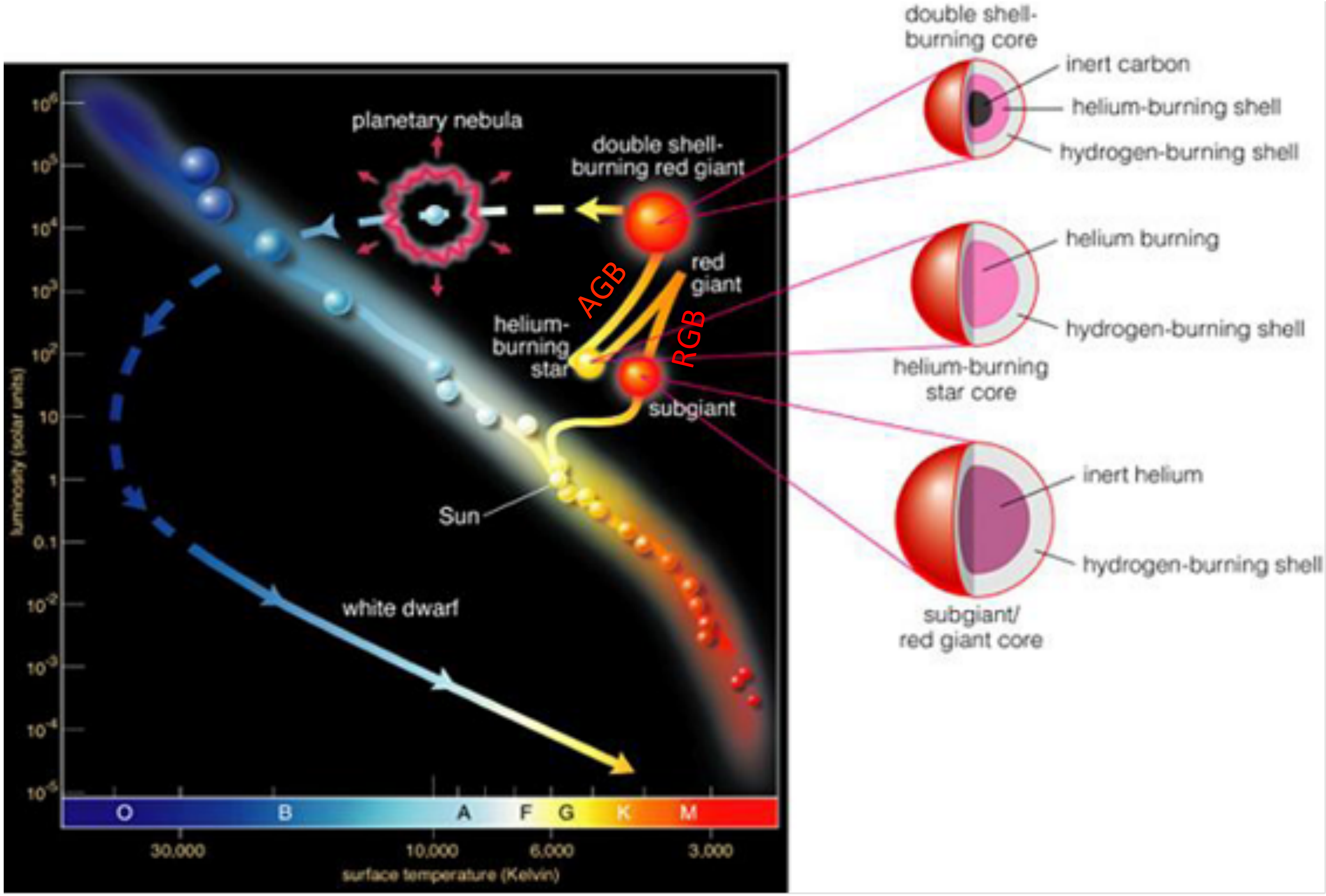
2.- Chemical equilibrium

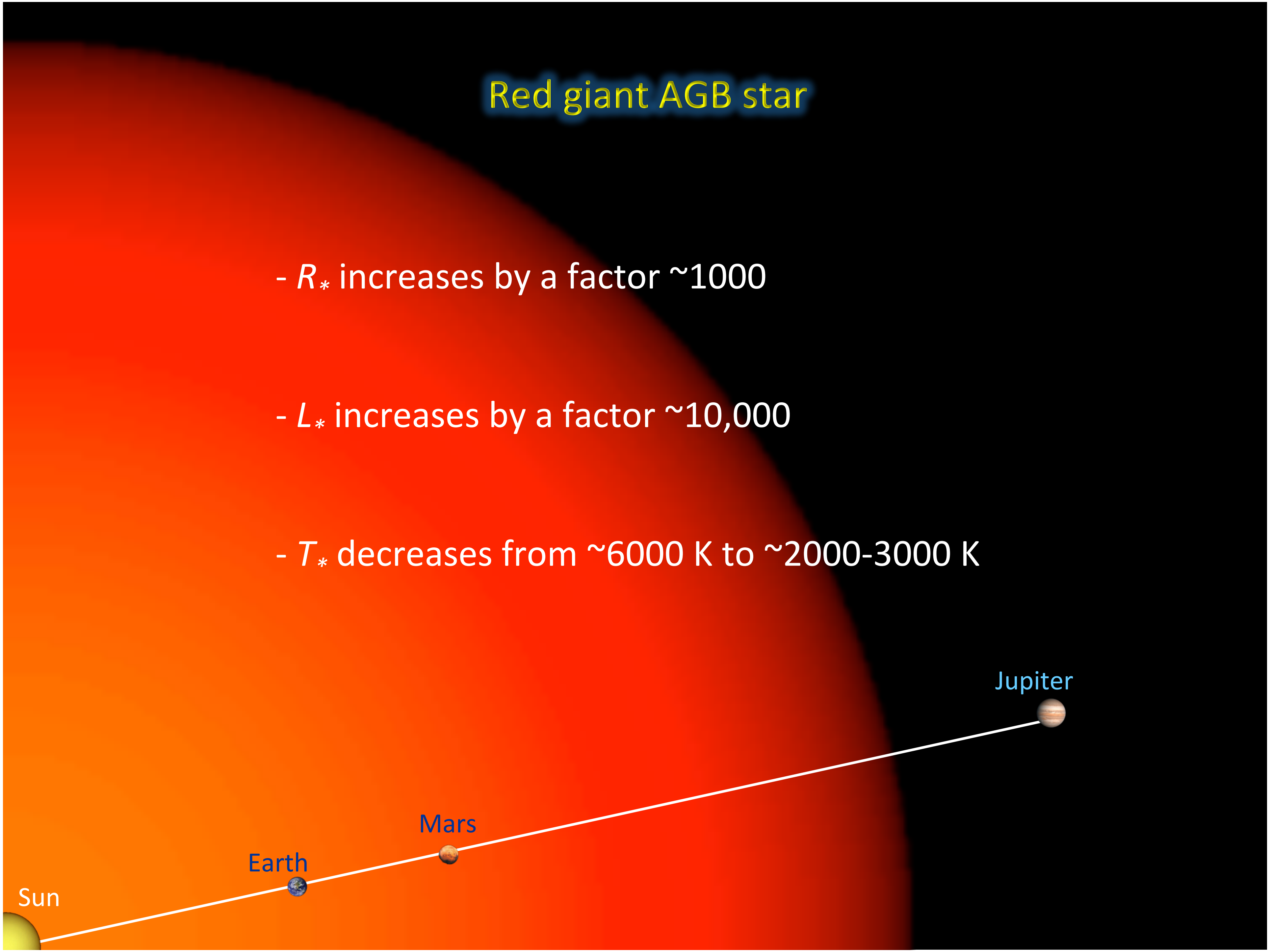
3.- Non-equilibrium chemistry: chemical kinetics

4.- Circumstellar chemistry: standard scenario

5.- Circumstellar chemistry: non-standard findings

Evolved stars in the H-R diagram (the AGB phase)



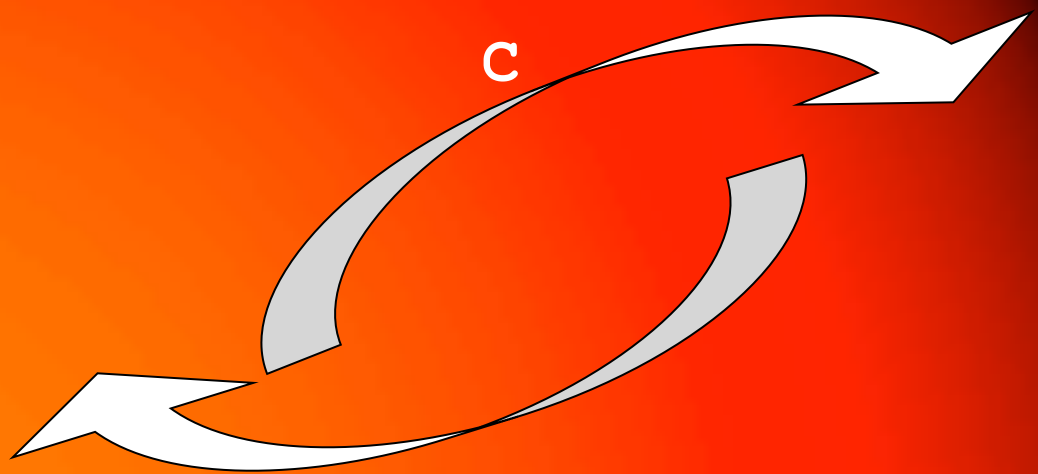

Red giant AGB star
- R_* increases by a factor ~1000
- L_* increases by a factor ~10,000
- T_* decreases from ~6000 K to ~2000-3000 K
Jupiter
Mars
Earth
Sun

The [C]/[O] ratio in AGB stars

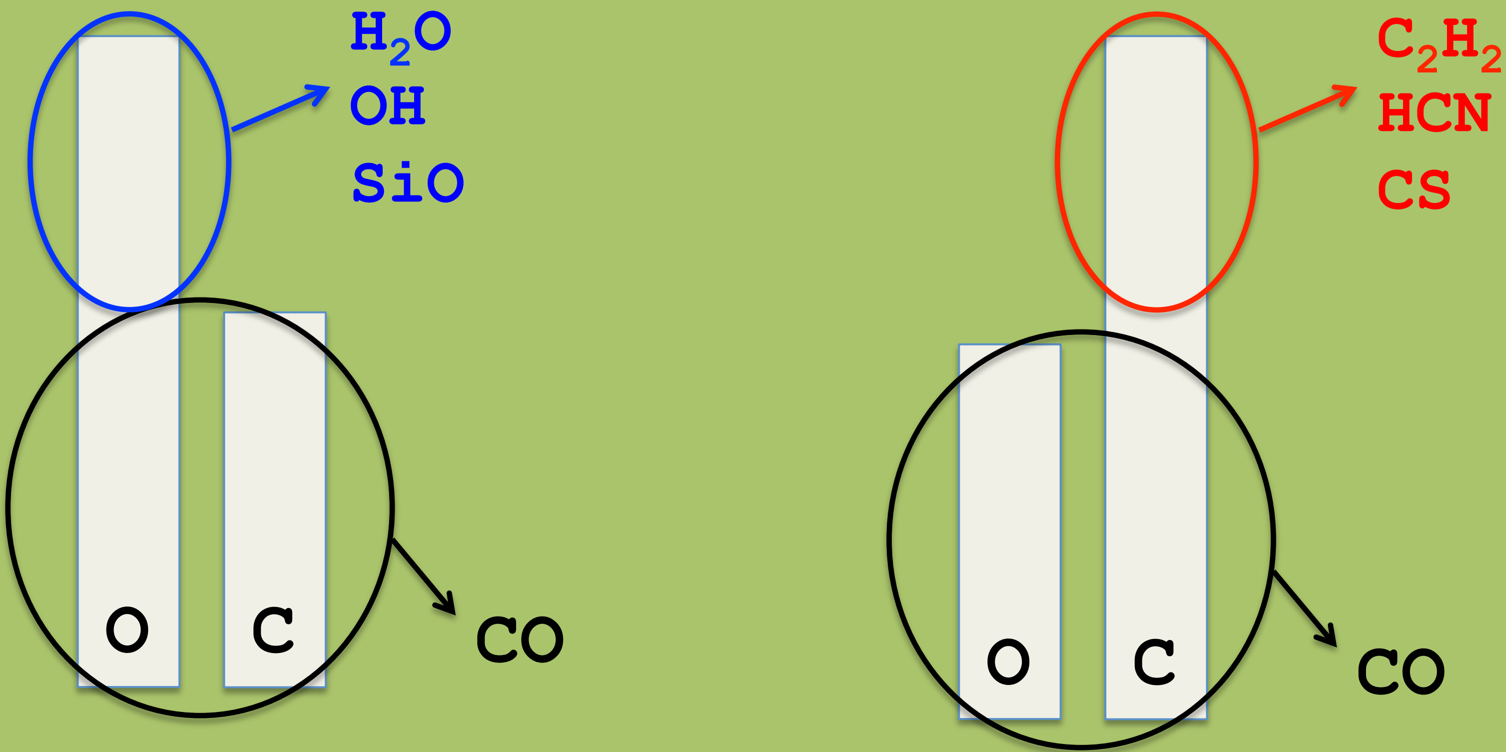
usually at the stellar surface:
[O] > [C] (oxygen-rich)

if enough C is brought to the surface:
[C] > [O] (carbon-rich)

convective processes: dredge-up



The [C]/[O] ratio in AGB stars



Circumstellar chemistry in the stellar atmosphere: Chemical equilibrium

(Thermo)Chemical equilibrium

At high densities and high temperatures,
chemical timescales become short,
and the chemical composition is given by chemical equilibrium
(where the Gibbs energy of the system is minimum).

Caution! The expression "chemical equilibrium" is sometimes used
to refer to a steady state, which may be completely out of thermochemical equilibrium

Chemical equilibrium is rarely found in interstellar or circumstellar clouds
because of the low densities.
We typically find it in atmospheres of cool stars, brown dwarfs, and planets.

(Thermo)Chemical equilibrium: Basics

Simple case: pure hydrogen gas

$$H_2 \rightleftharpoons H + H$$

depends on T

$$K_P = \frac{P_H P_H}{P_{H_2}}$$

total pressure

$$P = P_H + P_{H_2}$$

conservation equation

$$\frac{P_H^2}{K_P} + P_H - P = 0$$

$$\begin{cases} P_H = \dfrac{-1+\sqrt{1+4P/K_P}}{2/K_P} \\ P_{H_2} = P - \left(\dfrac{-1+\sqrt{1+4P/K_P}}{2/K_P}\right) \end{cases}$$

(Thermo)Chemical equilibrium: Basics

General case: multiple elements

T
P
ε_i
$K_{p,n}$

→

$$\varepsilon_i kT = p_i + \sum_{n=1}^{N_i} \frac{(p_i)^{h_n} (p_j)^{c_n} (p_k)^{o_n} \ldots}{K_{p,n}}$$

...

...

→

Sistema de ecuaciones algebraicas no lineal

Newton-Raphson

→

p_n

Astron. & Astrophys. 23, 411—431 (1973)

Molecular Abundances in Stellar Atmospheres. II.

T. Tsuji*
Observatoire de Paris-Meudon

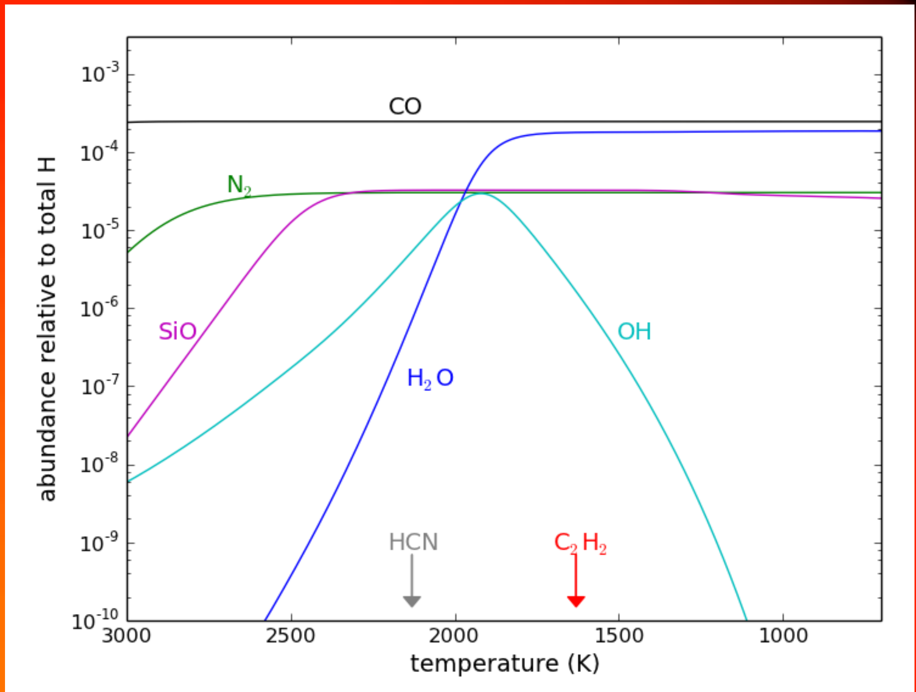
Received March 31, revised September 22, 1972

Summary. Chemical equilibria of 36 elements are solved for the physical conditions of cool stellar atmospheres. It is found that the molecular species formed (monoxide, dioxide, halide etc.) and the degree of molecular association, (i.e. the fraction of atoms locked in molecules) are well correlated with the position of each element (both Group and atomic weight) in the periodic table.
In the atmospheres of carbon-rich stars, molecular formation is generally less important than in oxygen-rich atmospheres except for some carbon compounds. The metal oxides in oxygen-rich atmospheres are generally replaced by metal carbides, especially by dicarbides, in carbon-rich atmospheres. The formation of carbides in carbon-rich atmospheres, however, is less effective than that of the corresponding metal oxides in oxygen-rich atmospheres. In carbon stars, it is shown that the Si/S ratio plays a critical role just like the C/O ratio.

Key words: equilibrium constants – chemical equilibrium – molecular abundance – atmospheres of cool stars

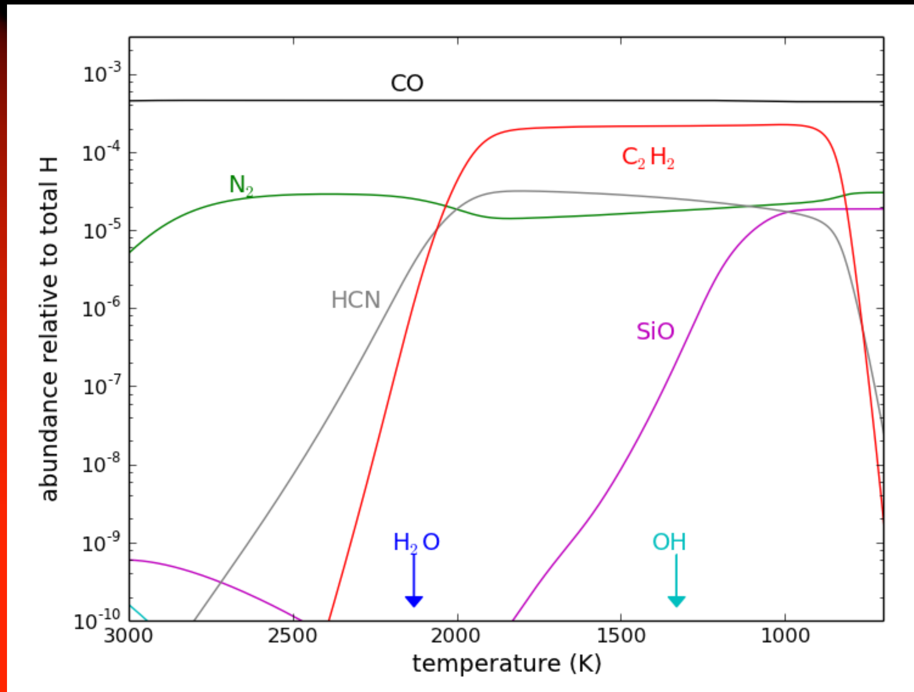
Chemical equilibrium in red giant AGB stars

oxygen-rich star: [C]/[O] < 1



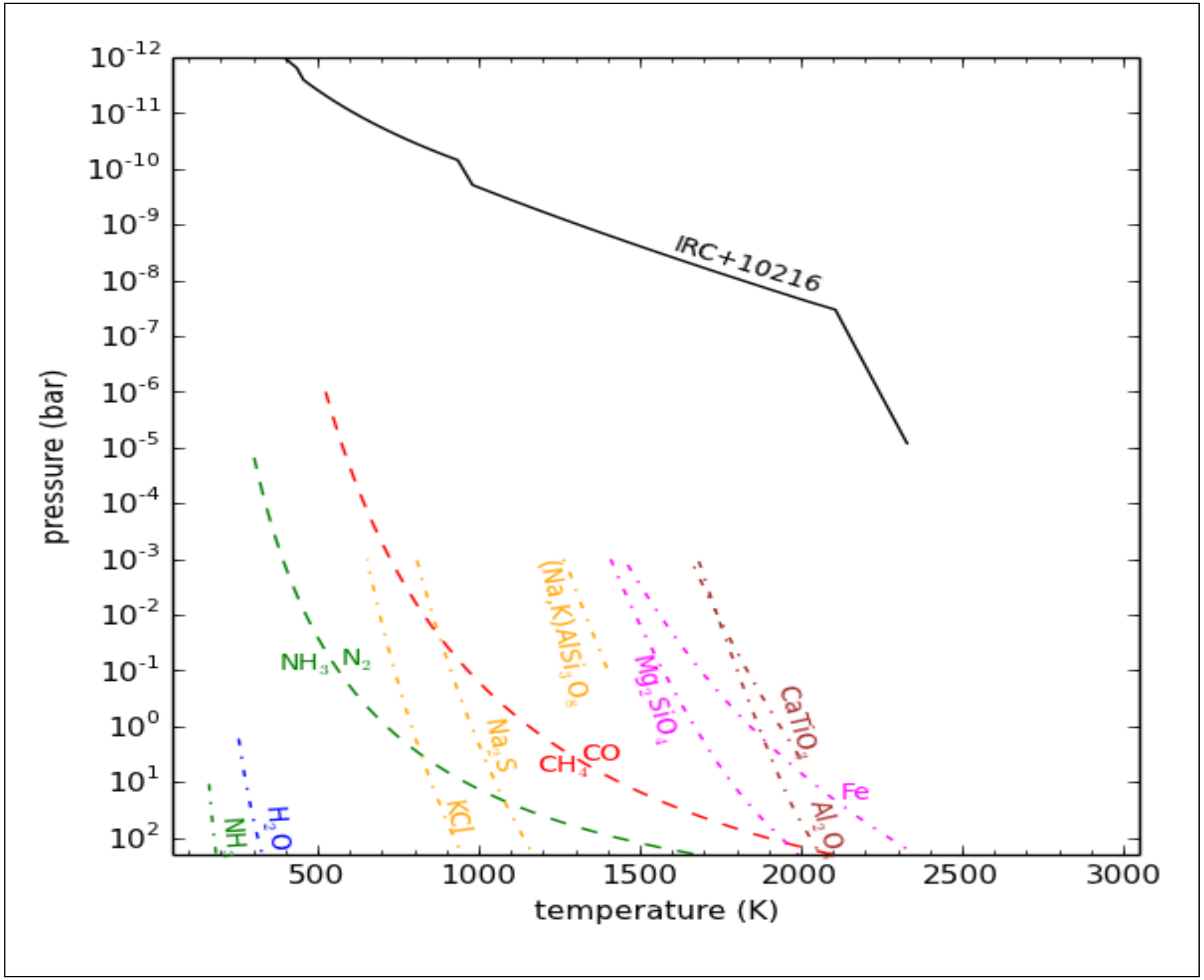
oxygen-bearing molecules
H_2O, SiO, OH, …

carbon-rich star: [C]/[O] > 1



carbon-bearing molecules:
C_2H_2, HCN, CS, …

Dust: expected from chemical equilibrium

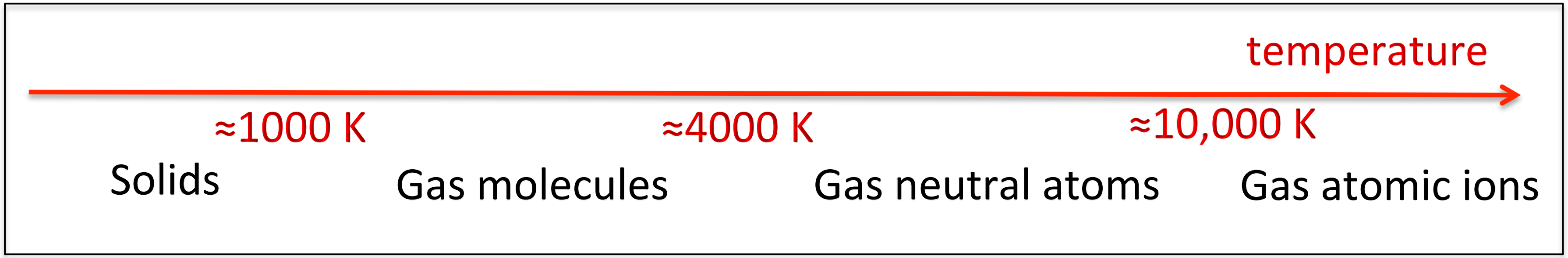


(Thermo)chemical equilibrium: Summary

The chemical composition of matter is at chemical equilibrium at high temperatures and high densities.

Chemical equilibrium does only depend on:

- temperature
- pressure
- elemental composition



For the conditions of AGB atmospheres, composition largely depends on C/O:

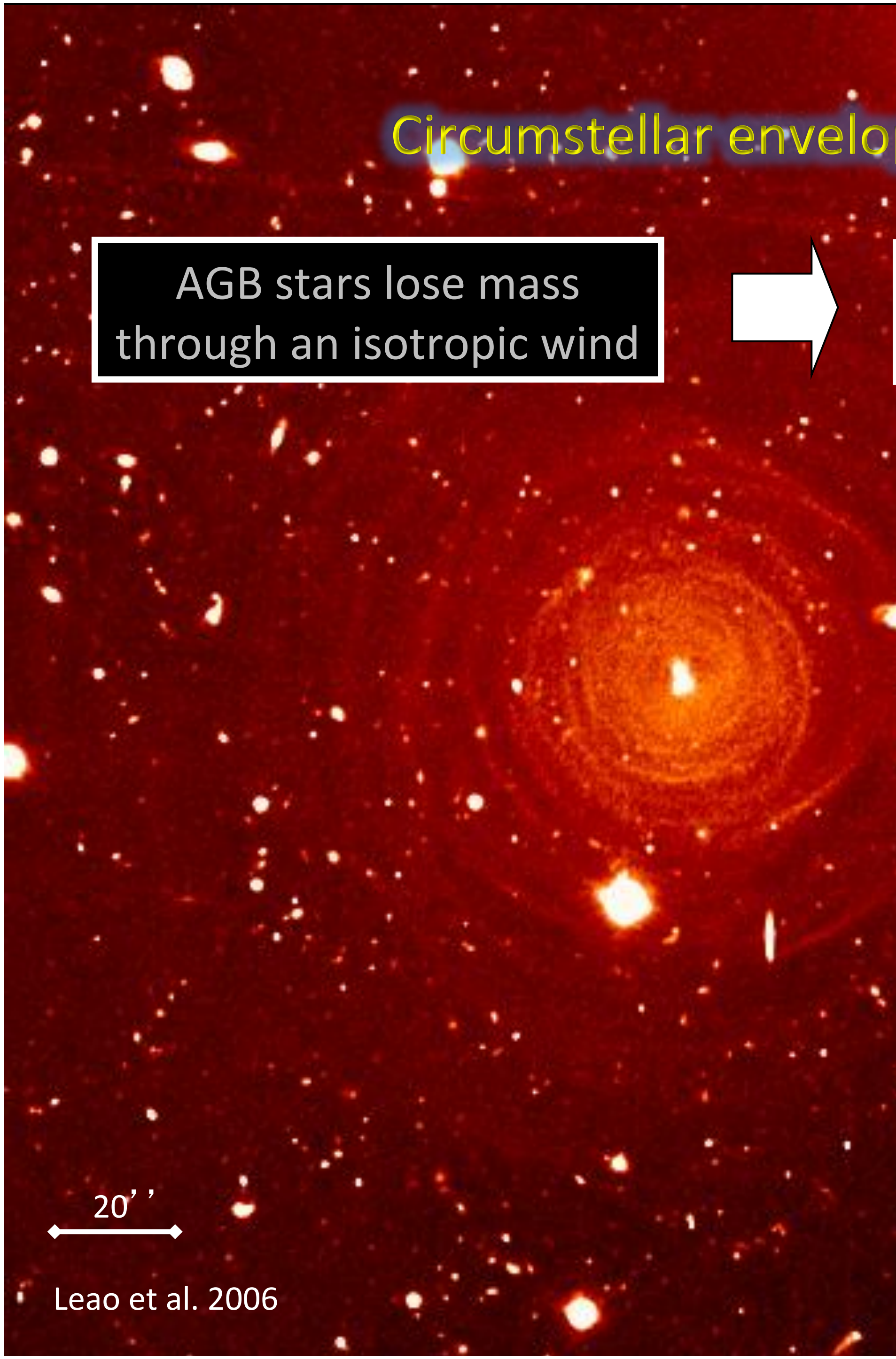
- O-rich chemistry if $C/O < 1$
- C-rich chemistry if $C/O > 1$

Circumstellar chemistry beyond the stellar atmosphere:
Non-equilibrium chemistry: chemical kinetics

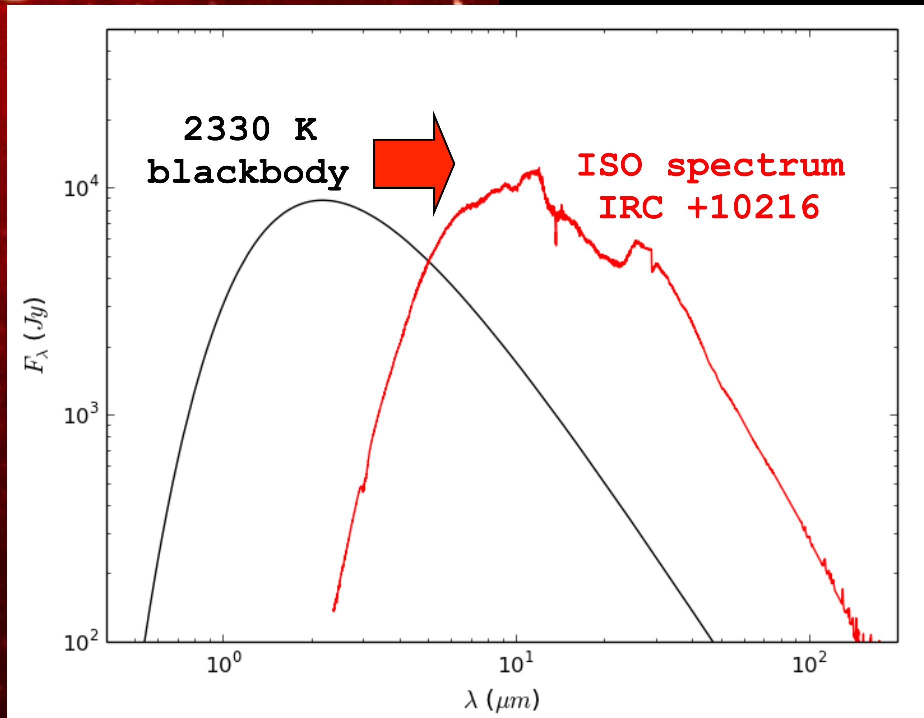
Circumstellar envelopes around AGB stars

AGB stars lose mass through an isotropic wind

producing an extended circumstellar envelope of gas and dust

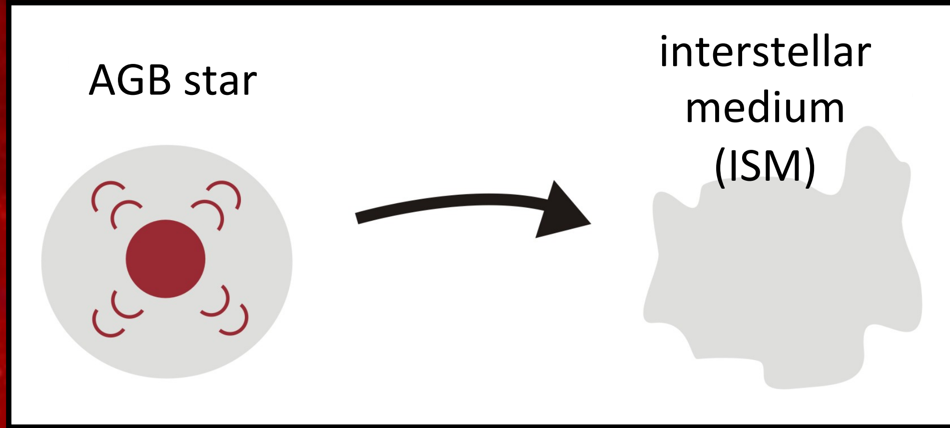


Leao et al. 2006



Circumstellar envelopes around AGB stars

AGB ejecta are the main suppliers of recycled matter to the ISM



… and the main sites of formation of interstellar dust

Non-equilibrium chemistry: Chemical kinetics

$$A + B \rightarrow C + D$$

$$\frac{-dn(A)}{dt} = \frac{-dn(B)}{dt} = \frac{dn(C)}{dt} = \frac{dn(D)}{dt} = k\, n(A)\, n(B)$$

dt → time !!!

k → k: rate constant (depends on temperature)

$k = A\, T^n\, e^{-(Ea/RT)}$

$T(t)$
$n(t)$
n_i^0
k_j

→

$$\frac{dn_i}{dt} = \underbrace{\sum_{j=1}^{N_f} k_j \prod_{l=1}^{N_{reac}^j} n_{j,l}}_{\text{formación de i}} - \underbrace{\sum_{m=1}^{N_d} k_m n_i \prod_{s=1}^{N_{reac}^m} n_{m,s}}_{\text{destrucción de i}}$$

...

...

→

Sistema de ecuaciones diferenciales ordinarias no lineal

Runge-Kutta

→

$n_i(t)$

Non-equilibrium chemistry: Chemical kinetics

Example: pure hydrogen gas in expansion

$$H_2 \rightleftharpoons H + H$$

State 1:
Pure hydrogen gas at a given pressure and temperature:
n_H and n_{H2} at chemical equilibrium

$$H_2 \rightleftharpoons H + H$$

$$\mathrm{H} + \mathrm{H} + \mathrm{H} \rightarrow \mathrm{H_2} + \mathrm{H} \qquad k_{\mathrm{M,H}} = 8.82 \times 10^{-33}\ \mathrm{cm^6 s^{-1}}$$

$$\mathrm{H} + \mathrm{H} + \mathrm{H_2} \rightarrow \mathrm{H_2} + \mathrm{H_2} \qquad k_{\mathrm{M,H_2}} = 2.65 \times 10^{-31} T^{-0.6}\ \mathrm{cm^6 s^{-1}}$$

$$\mathrm{H_2} + \mathrm{H} \rightarrow \mathrm{H} + \mathrm{H} + \mathrm{H} \qquad k_{\mathrm{d,H}} = 1.11 \times 10^{-9} T^{0.36} e^{-52043/T}\ \mathrm{cm^3 s^{-1}}$$

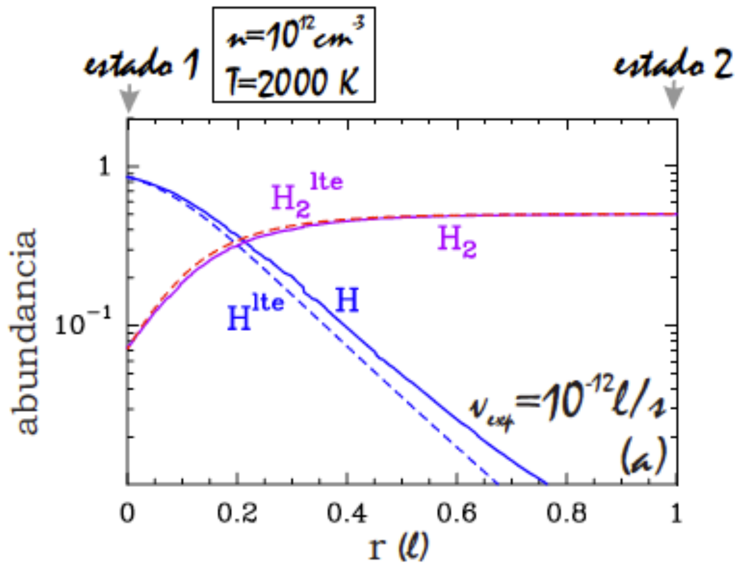
$$\mathrm{H_2} + \mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{H} + \mathrm{H_2} \qquad k_{\mathrm{d,H_2}} = 3.32 \times 10^{-8} T^{-0.24} e^{-52043/T}\ \mathrm{cm^3 s^{-1}}$$

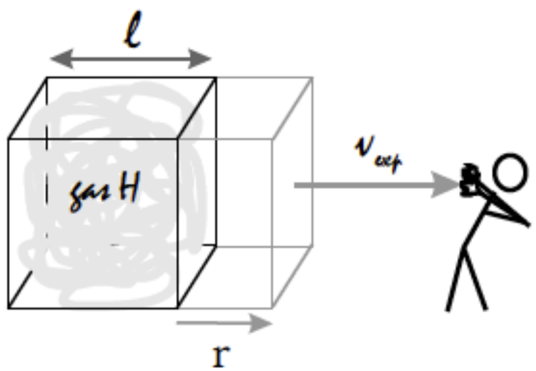
$$\frac{dn_{\mathrm{H}}}{dt} = \overbrace{\left(2k_{\mathrm{d,H}} n_{\mathrm{H_2}} n_{\mathrm{H}} + 2k_{\mathrm{d,H_2}} n_{\mathrm{H_2}}^2\right)}^{\text{formation rate of H}} - \overbrace{\left(2k_{\mathrm{M,H}} n_{\mathrm{H}}^3 + 2k_{\mathrm{M,H_2}} n_{\mathrm{H}}^2 n_{\mathrm{H_2}}\right)}^{\text{destruction rate of H}}$$

$$\frac{dn_{\mathrm{H_2}}}{dt} = \underbrace{\left(k_{\mathrm{M,H}} n_{\mathrm{H}}^3 + k_{\mathrm{M,H_2}} n_{\mathrm{H}}^2 n_{\mathrm{H_2}}\right)}_{\text{formation rate of H}_2} - \underbrace{\left(k_{\mathrm{d,H}} n_{\mathrm{H_2}} n_{\mathrm{H}} + k_{\mathrm{d,H_2}} n_{\mathrm{H_2}}^2\right)}_{\text{destruction rate of H}_2}$$

Non-equilibrium chemistry: Chemical kinetics

Example: pure hydrogen gas in expansion





Chemical kinetics: Summary

Chemical kinetics: get abundances as a function of time

Need to consider many chemical reactions with their associated rate coefficients

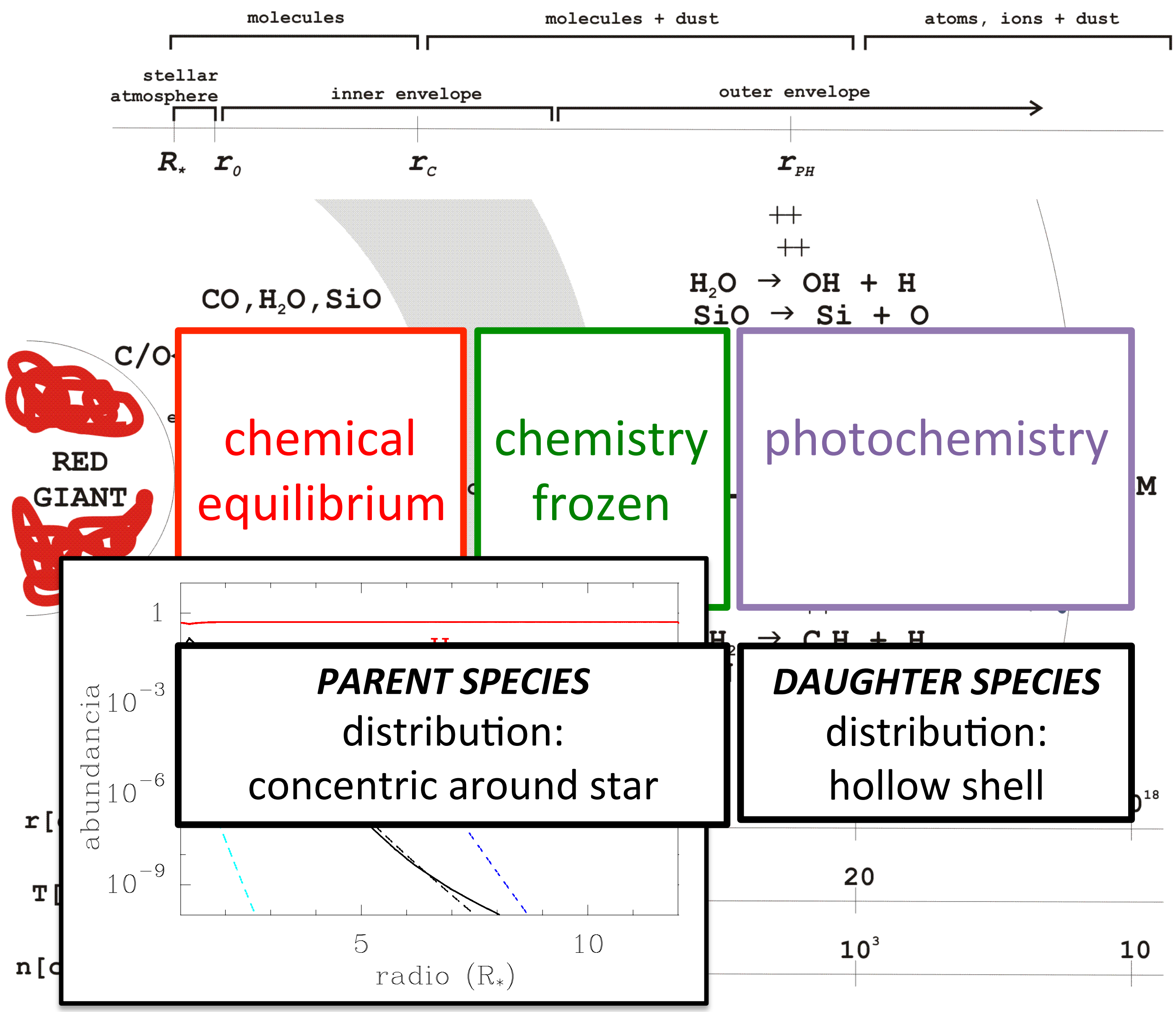
Chemical time scale (τ_{chem}):

- if τ_{chem} is short → chemical equilibrium
- if τ_{chem} is long → chemical abundances are frozen

Circumstellar chemistry in envelopes around AGB stars:

the standard scenario

Circumstellar chemistry in envelopes around AGB stars

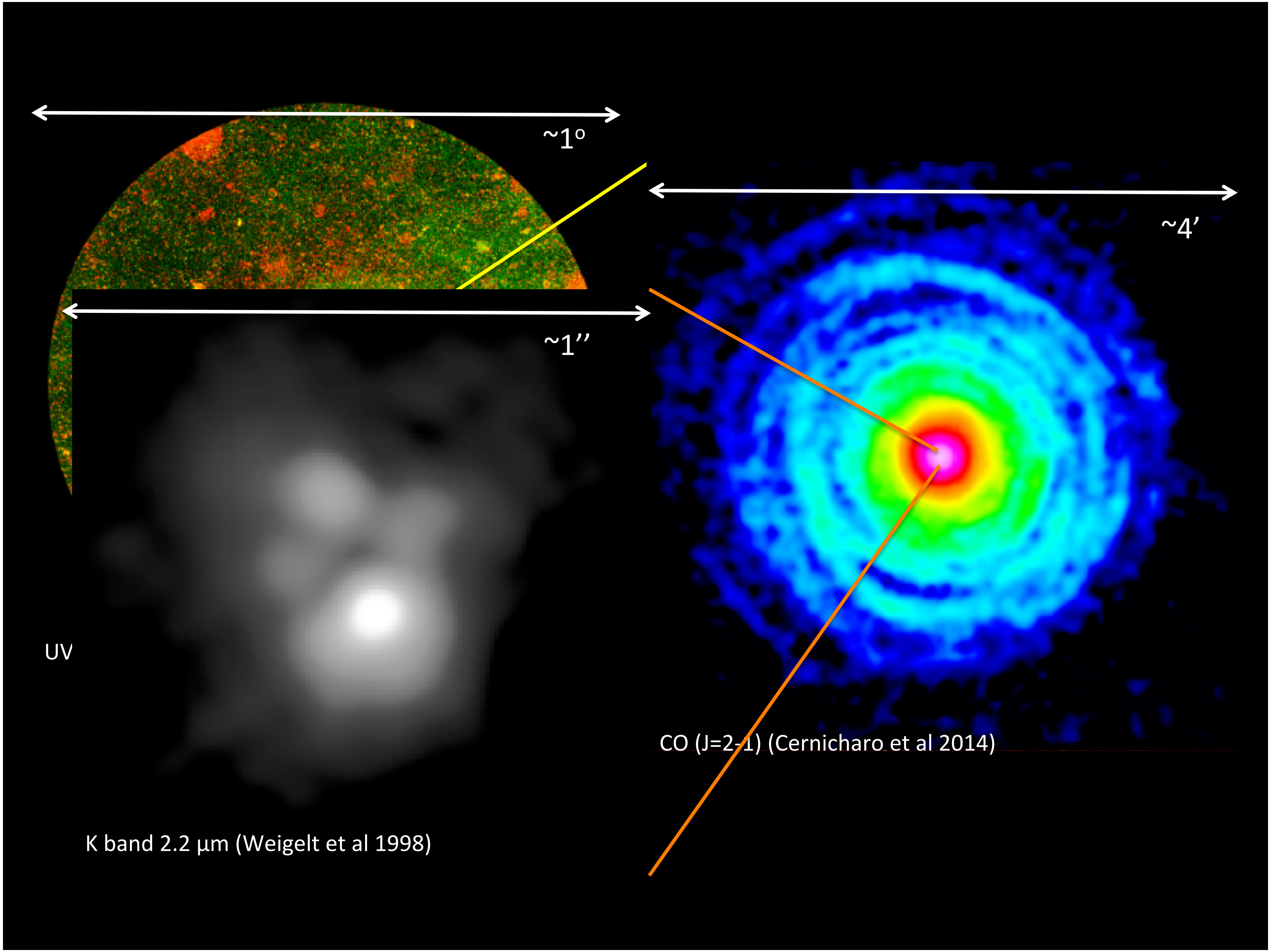


λ 1.65 mm
2MASS

IRC +10216

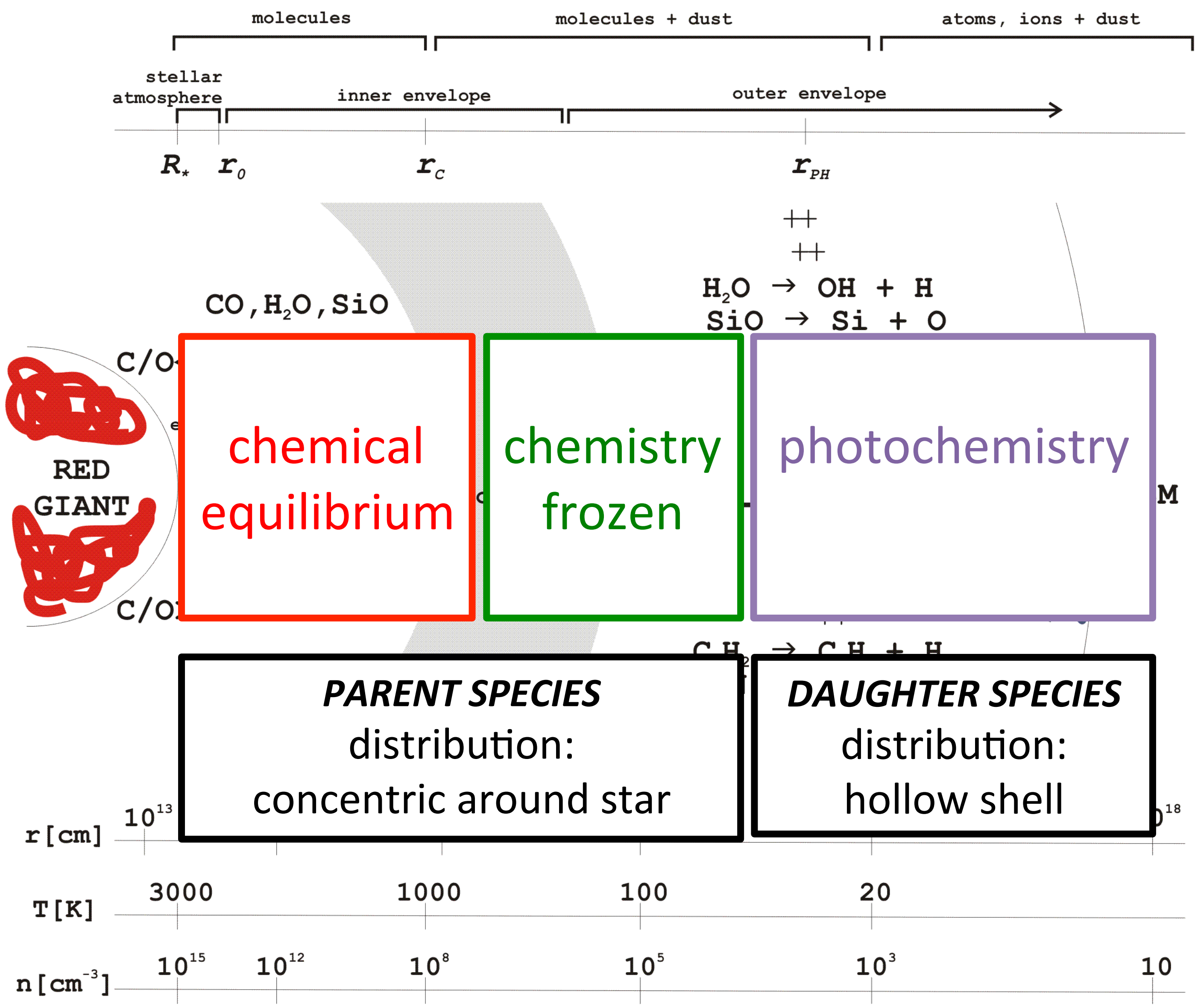
- Nearest carbon-rich AGB star (~130 pc)
- Brightest object at 5-10 μm (outside solar system)

- Mass loss and dust formation processes can be studied in detail in IRC +10216
- IRC +10216 is an excellent chemical laboratory (>80 molecules detected)

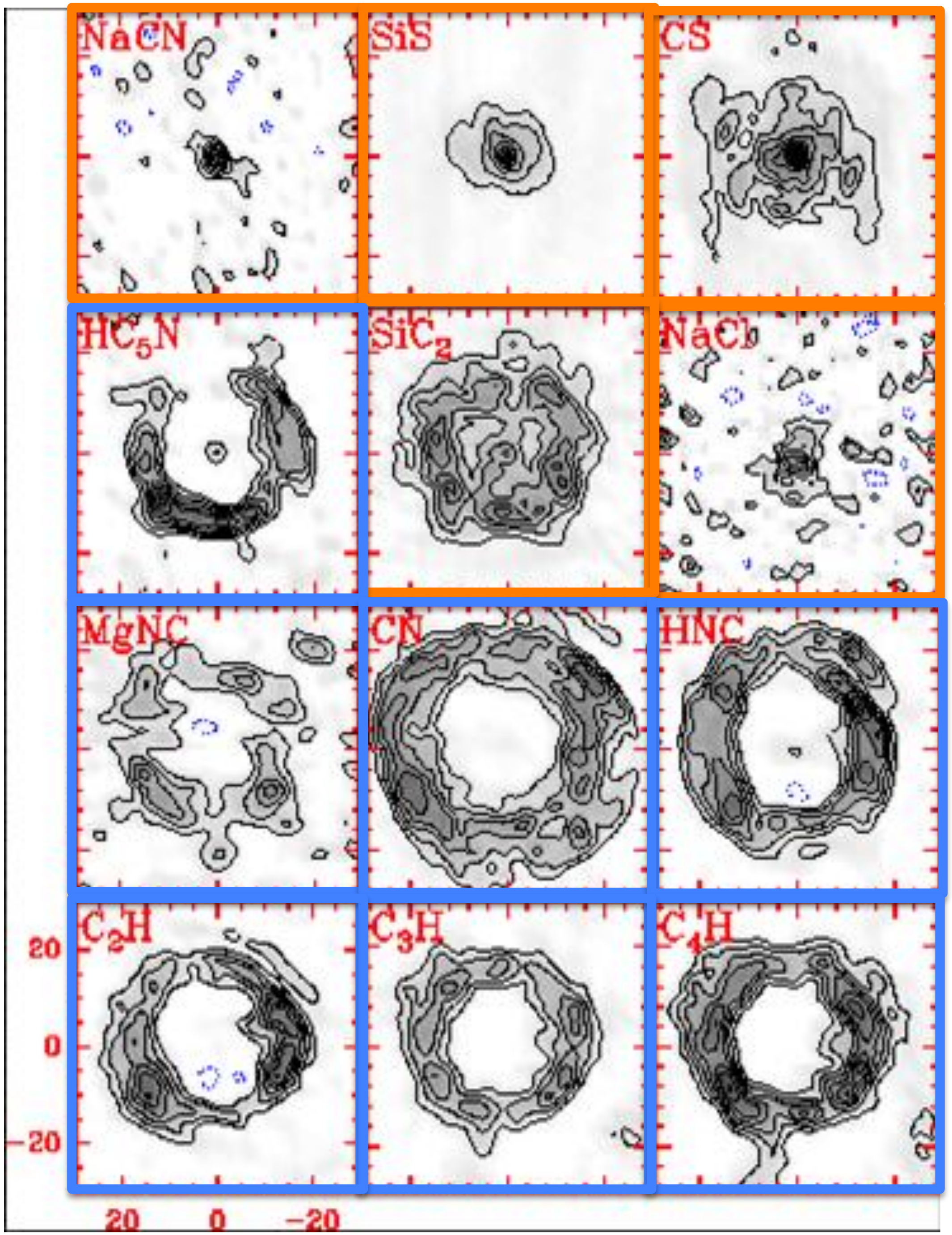

~1°
~4′
~1″
UV
CO (J=2-1) (Cernicharo et al 2014)
K band 2.2 µm (Weigelt et al 1998)

10^{-3}	CO						
10^{-4}							
		C_2H_2					
			HCN				
10^{-5}							
		CH_4					
		C_2H	NH_3				
		C_4H	CN				
		C_2	HC_3N		SiC_2		
10^{-6}		C_3			SiS		
			C_3N	CS	Si_2C		
					SiH_4		
			HC_5N		SiO		HCl
10^{-7}	H_2O	C_5	HNC				
		$l\text{-}C_3H$	CN^-				
	OH	C_6H			SiC		
		C_5H	CH_3CN	C_2S			AlCl
		$c\text{-}C_3H_2$					
		CH_3C_2H					
		$c\text{-}C_3H$	HC_7N			HCP	
		C_2H_4					NaCN
	H_2CO	H_2C_4		C_3S			
10^{-8}						CP	HF
		C_8H	HC_9N	H_2CS	SiN	PH_3	MgNC
			CH_2CN				AlF
			HC_2N				
			C_5N				
		C_7H	HCCNC				
		H_2C_6	C_2H_3CN	H_2S	$c\text{-}SiC_3$		
		C_6H^-	C_5N^-		SiC_4		
	C_3O	C_8H^-	HC_4N		SiCN		
		H_2C_3	C_3N^-	C_5S	SiNC	PN	NaCl
10^{-9}						C_2P	AlNC
	HCO^+		HNCCC				MgCN HMgNC
		C_4H^-					KCl FeCN KCN
10^{-10}							

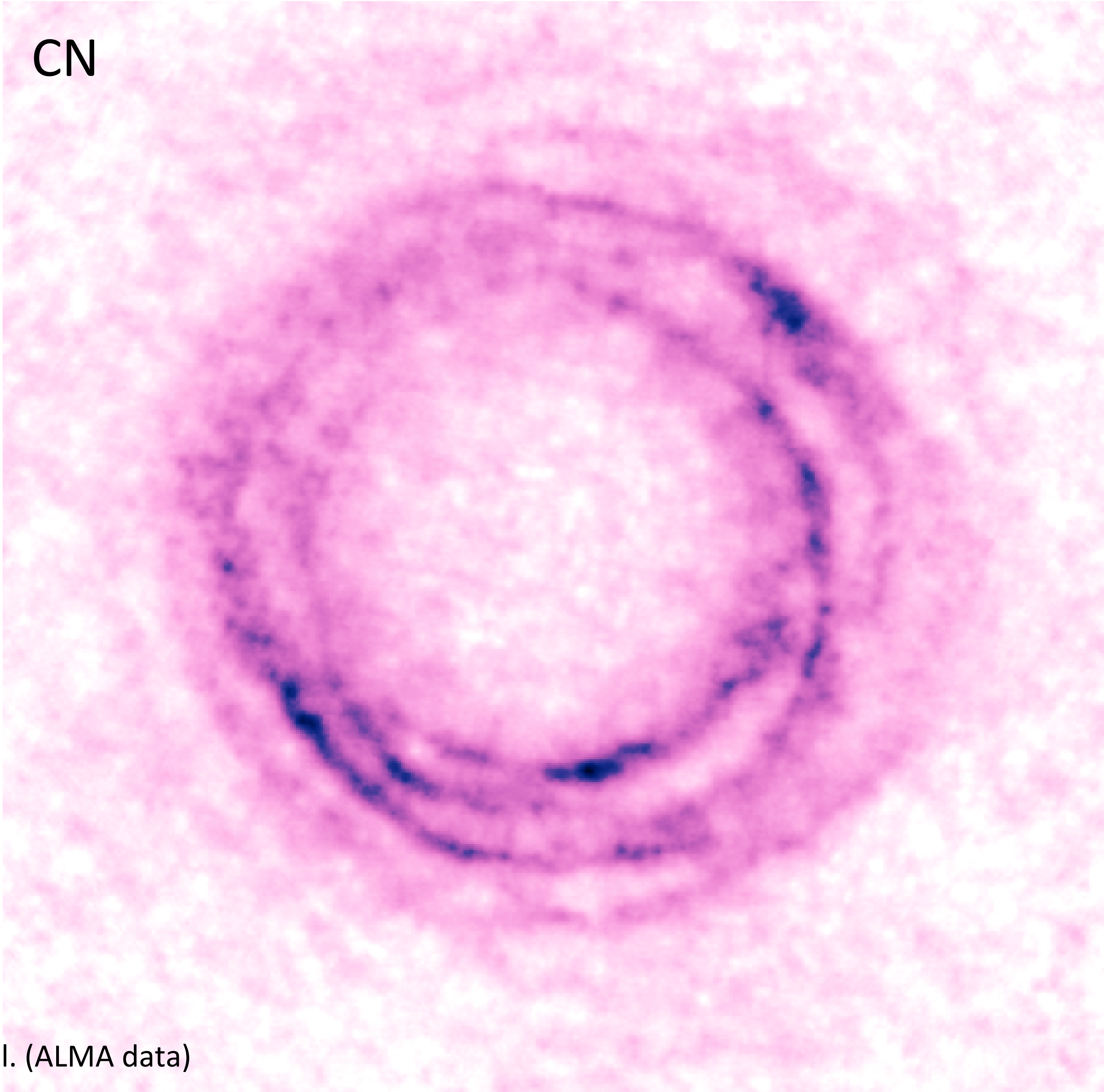
Circumstellar chemistry in envelopes around AGB stars



IRC +10216:
distribution of molecules

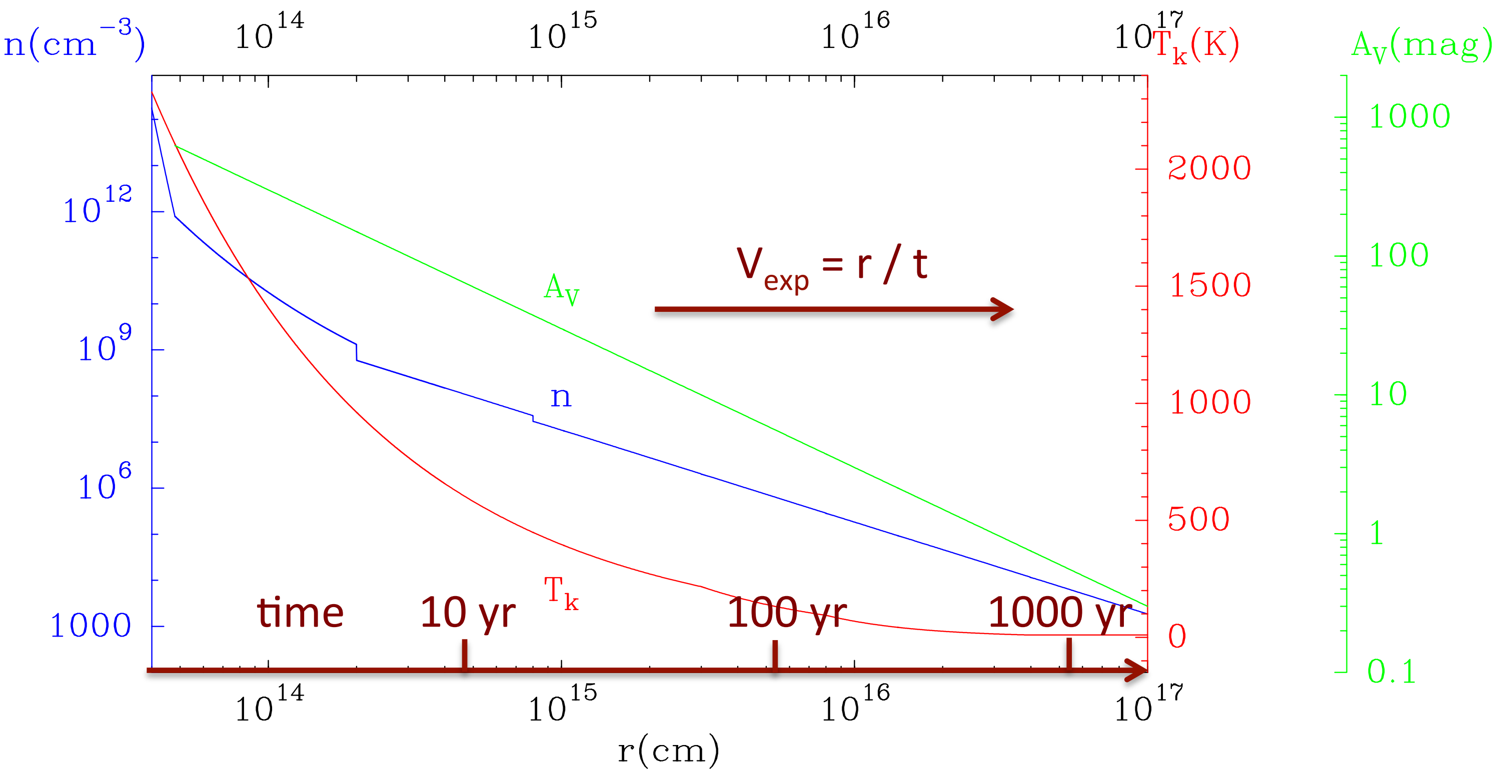


Guélin et al. (IRAM PdBI data)



Agúndez et al. (ALMA data)

Circumstellar chemistry in envelopes around AGB stars



$T(t)$
$n(t)$
n_i^0
k_j

$$\frac{dn_i}{dt} = \underbrace{\sum_{j=1}^{N_f} k_j \prod_{l=1}^{N_{reac}^j} n_{j,l}}_{\text{formación de i}} - \underbrace{\sum_{m=1}^{N_d} k_m n_i \prod_{s=1}^{N_{reac}^m} n_{m,s}}_{\text{destrucción de i}}$$

...

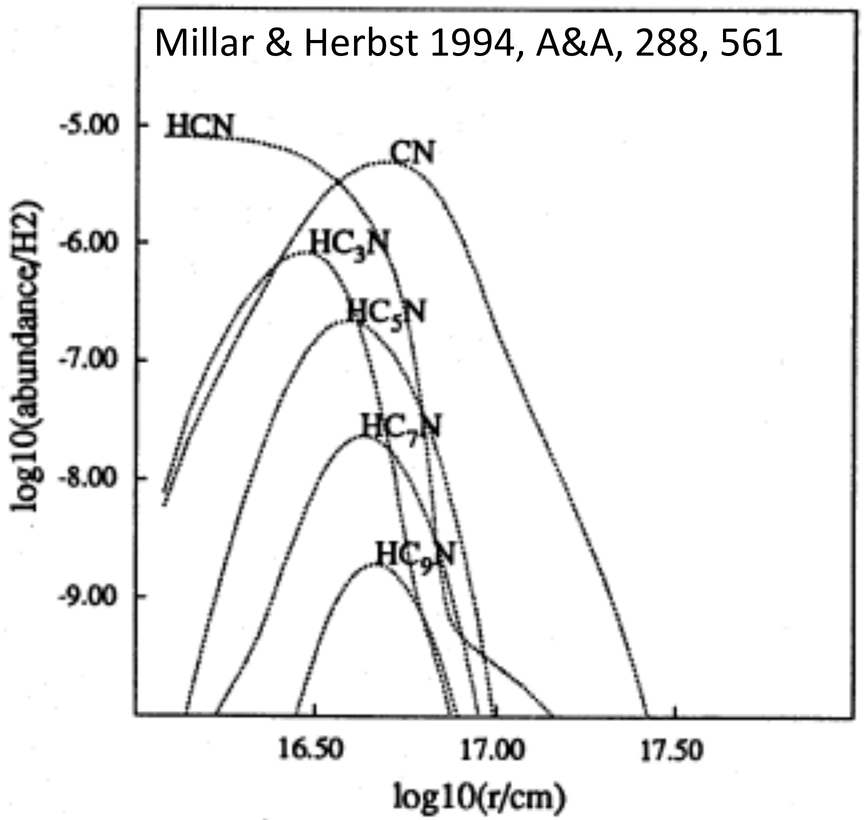
...

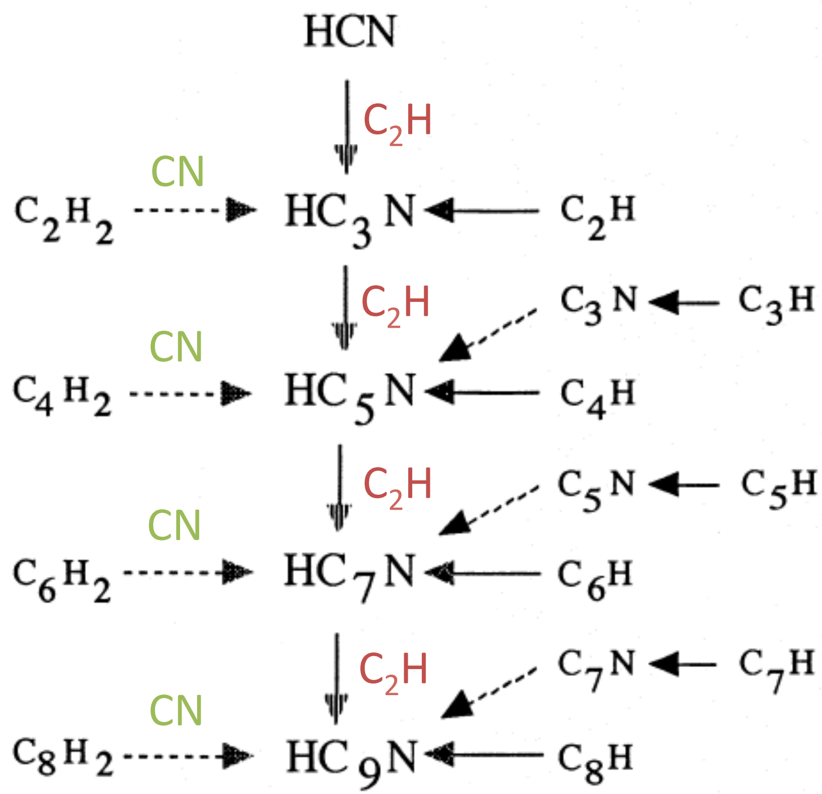
Sistema de ecuaciones diferenciales ordinarias no lineal

Runge-Kutta

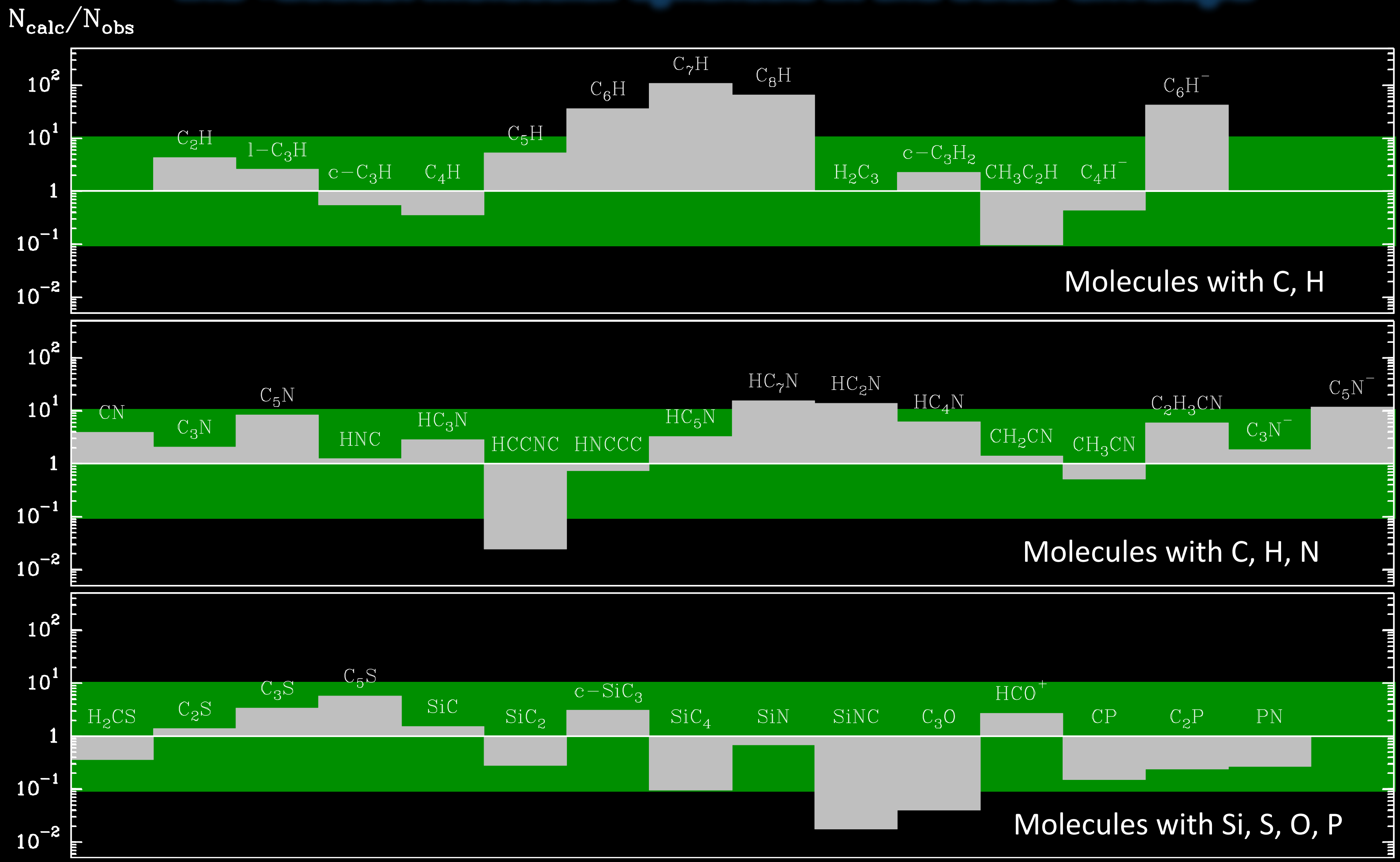
$n_i(t)$

IRC +10216: molecular synthesis in the outer envelope





IRC +10216: molecular synthesis in the outer envelope



Circumstellar chemistry in envelopes around AGB stars:

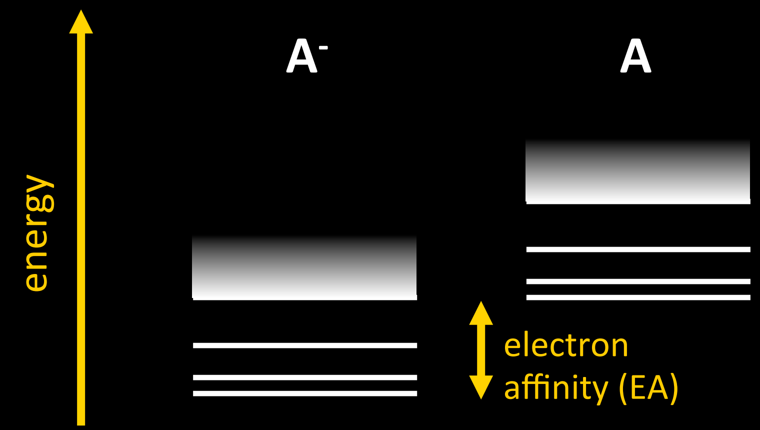
Some specific types of circumstellar molecules:

- Negatively charged molecules
- Metal-containing molecules

Negatively charged molecules

Negatively charged molecules

Thermodynamics — Anion formation favoured



Kinetics — Anion formation slow

$$\mathbf{A + e^- \rightarrow A^- + } \boldsymbol{h\nu}$$

except for species *A* with a high *EA* and large size (C_4H, C_6H, C_8H, C_3N, C_5N, …

Negatively charged molecules

The Astrophysical Journal, 652: L141–L144, 2006 December 1

LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION C_6H^-

M. C. McCarthy,[1] C. A. Gottlieb,[1] H. Gupta,[1,2] and P. Thaddeus[1]
Received 2006 September 28; accepted 2006 October 17; published 2006 November 20

ABSTRACT

The negative molecular ion C_6H^- has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that C_6H^- is the carrier of the series of lines with rotational constant 1377 MHz first observed by K. Kawaguchi et al. in IRC +10216. The column density of C_6H^- toward both sources is 1%–5% that of neutral C_6H. These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

Anion-to-neutral abundance ratios in IRC +10216

$[C_4H^-]/[C_4H]$ . . .	0.074 %	$[CN^-]/[CN]$ . . .	0.25 %
$[C_6H^-]/[C_6H]$	6.8 %	$[C_3N^-]/[C_3N]$ . . .	0.42 %
$[C_8H^-]/[C_8H]$	26 %	$[C_5N^-]/[C_5N]$	58 %

Negatively charged molecules

A^- formation:

$$A + e^- \xrightarrow{k_{ra}} A^- + h\nu$$ *radiative electron attachment*

A^- destruction:

$$A^- + H \xrightarrow{k_H} AH + e^-$$ *reaction with H atoms*

$$A^- + C^+ \xrightarrow{k_+} A + C$$ *neutralization with C^+ cations*

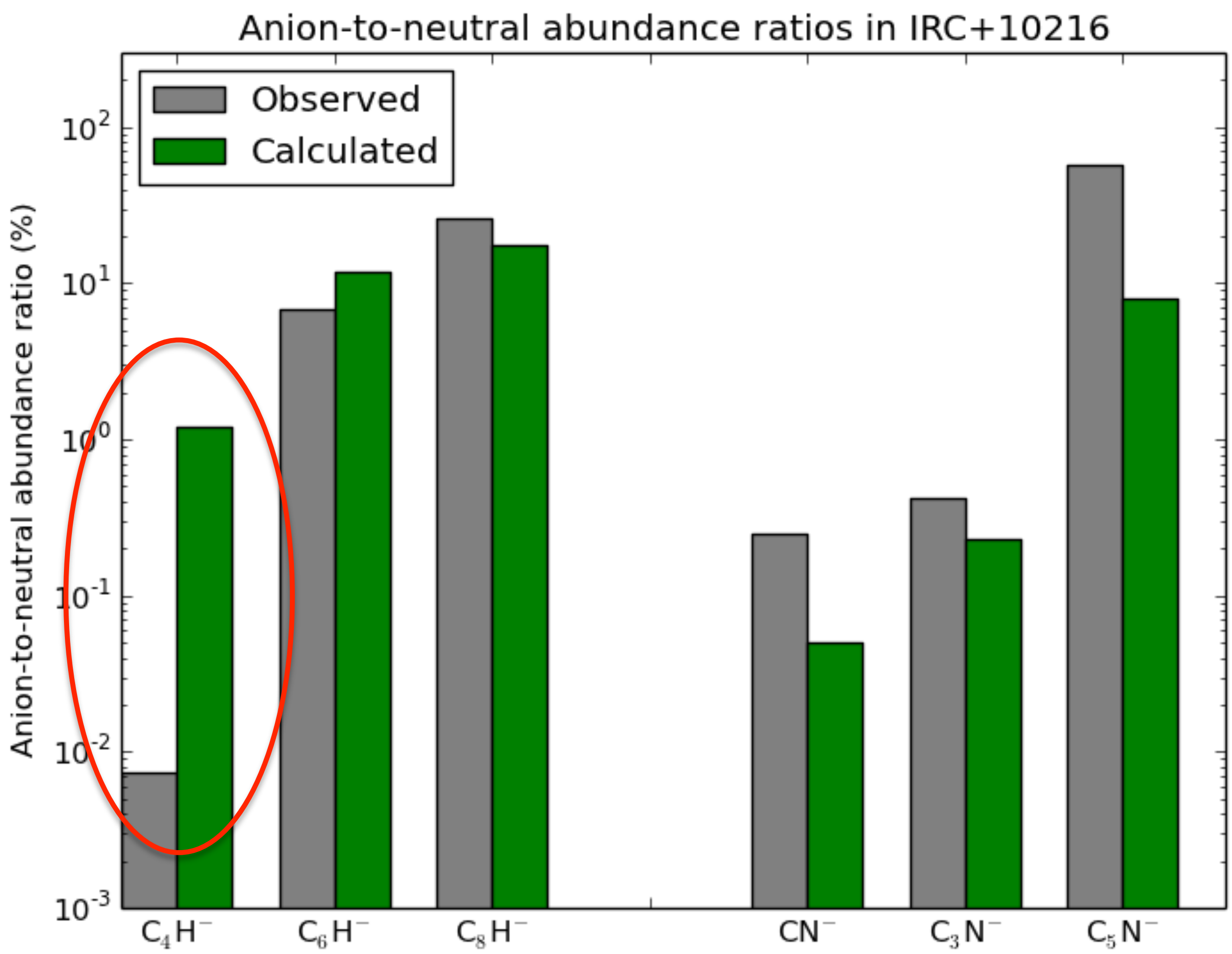
$$A^- + h\nu \xrightarrow{\Gamma_A} A + e^-$$ *photodetachment*

---

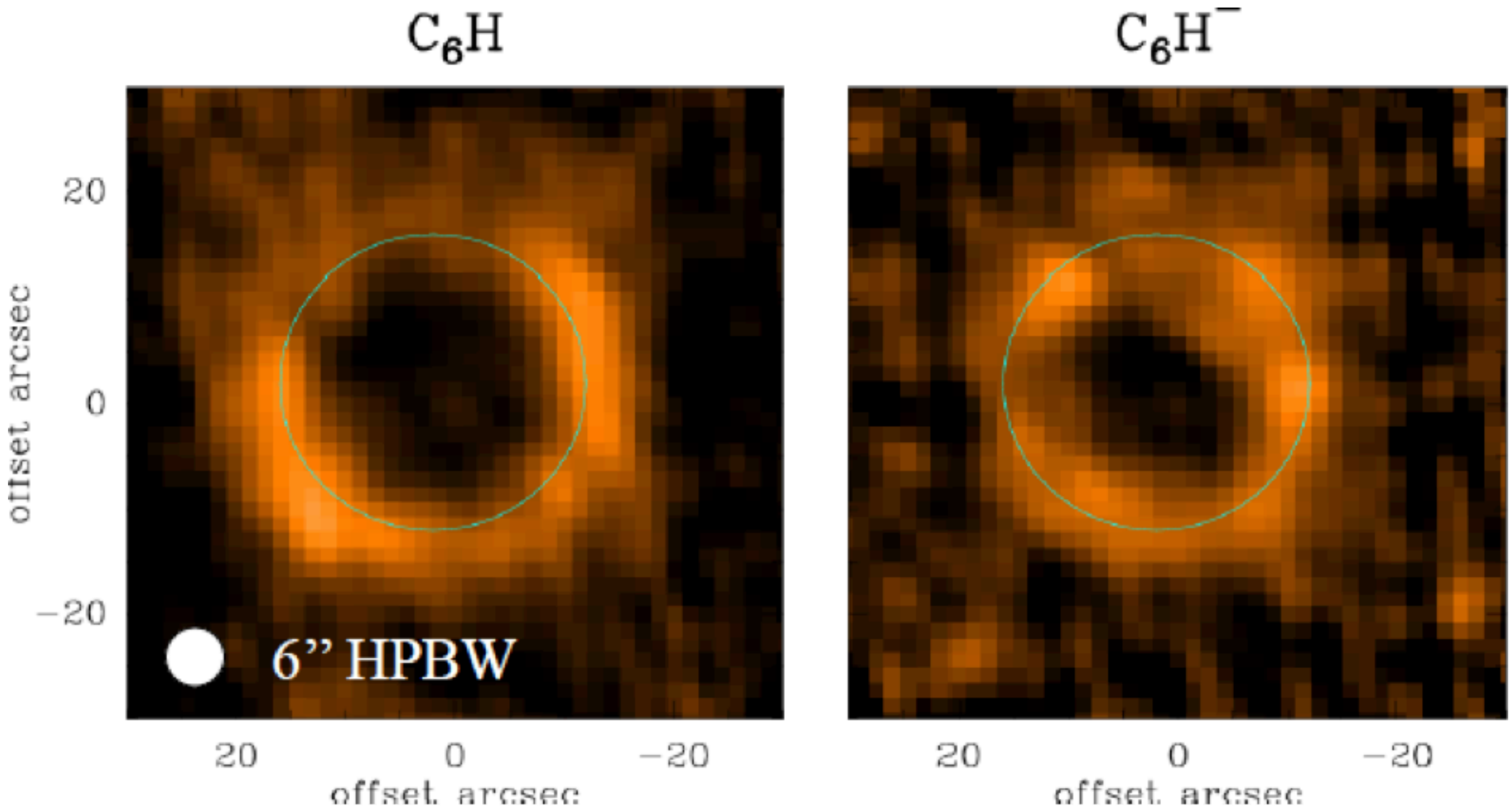
steady state

$$\frac{[A^-]}{[A]} = \frac{k_{ra}[e^-]}{k_H[H] + k_+[C^+] + \Gamma_A/n}$$

Negatively charged molecules: IRC+10216



Negatively charged molecules: IRC+10216



NOEMA data (Guélin et al.)

Metal-containing molecules

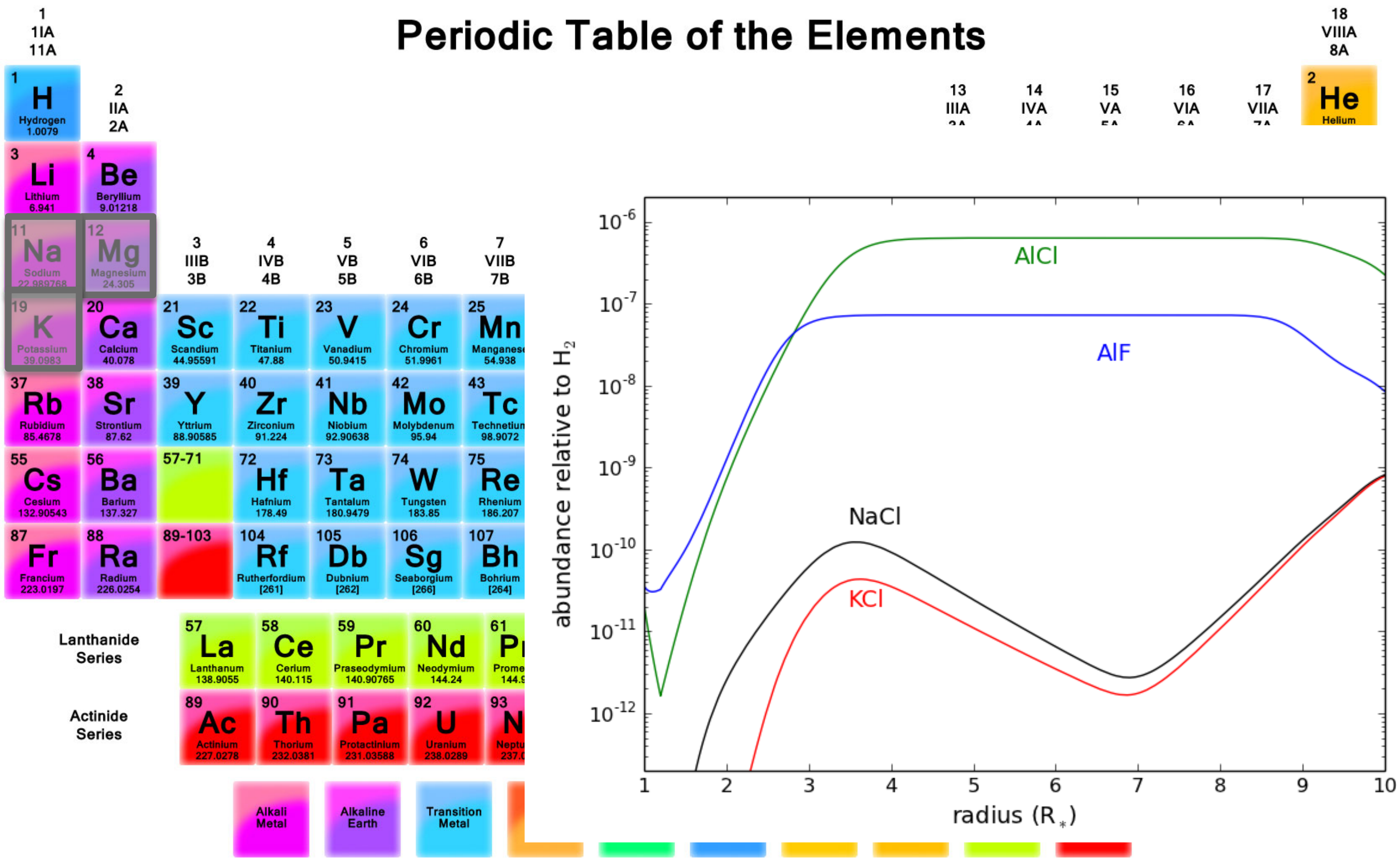
Metal-containing molecules

Astron. Astrophys. 183, L10–L12 (1987)

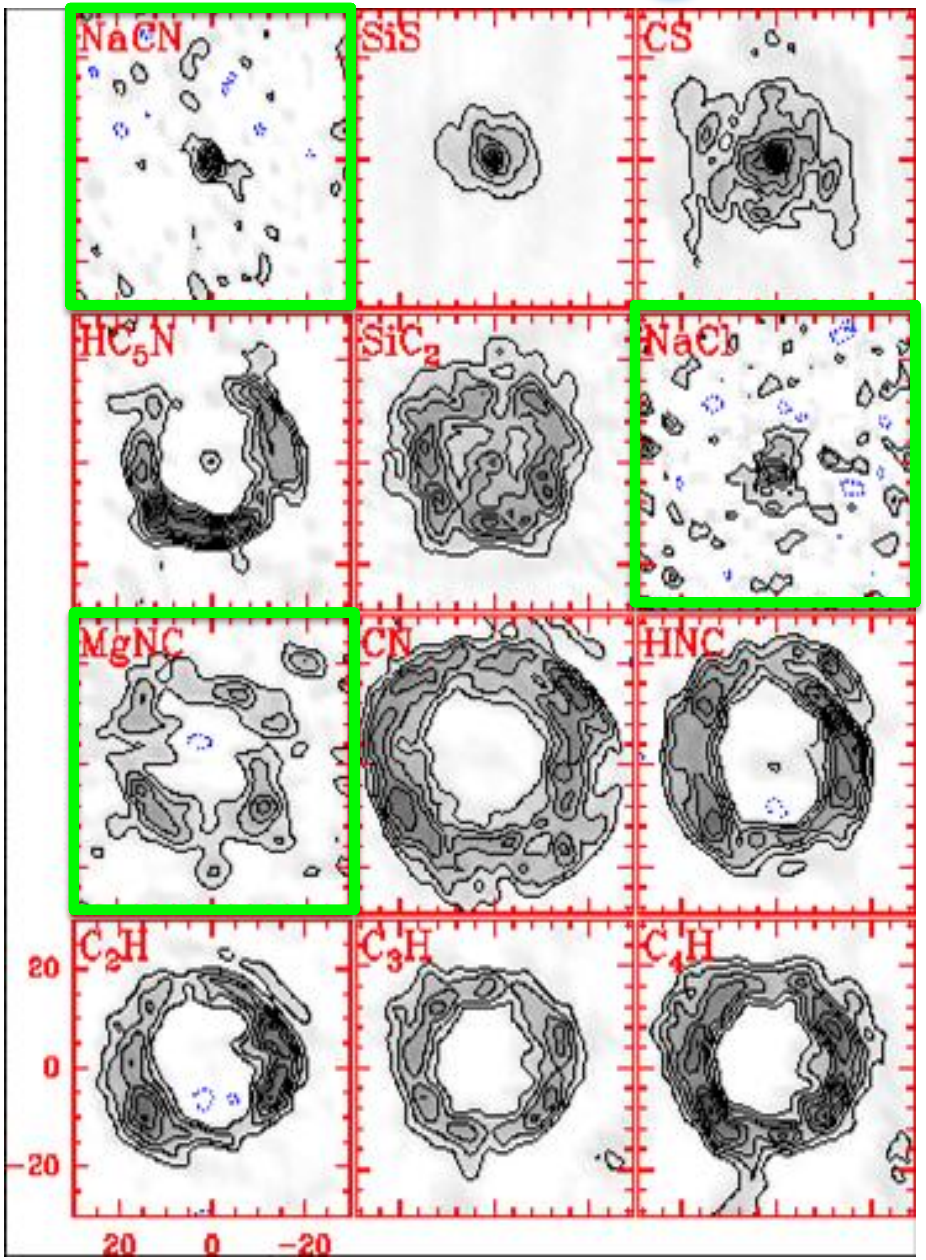
Metals in IRC+10216: detection of NaCl, AlCl, and KCl, and tentative detection of AlF

J. Cernicharo[1,2] and M. Guélin[1]

AlCl, AlF, AlNC
NaCl, NaCN
KCl, KCN
MgNC, MgCN, HMgNC
FeCN



Metal-containing molecules: IRC+10216



Guélin et al. (PdBI data)

AlCl, AlF, AlNC
NaCl, NaCN
KCl, KCN
MgNC, MgCN, HMgNC
FeCN

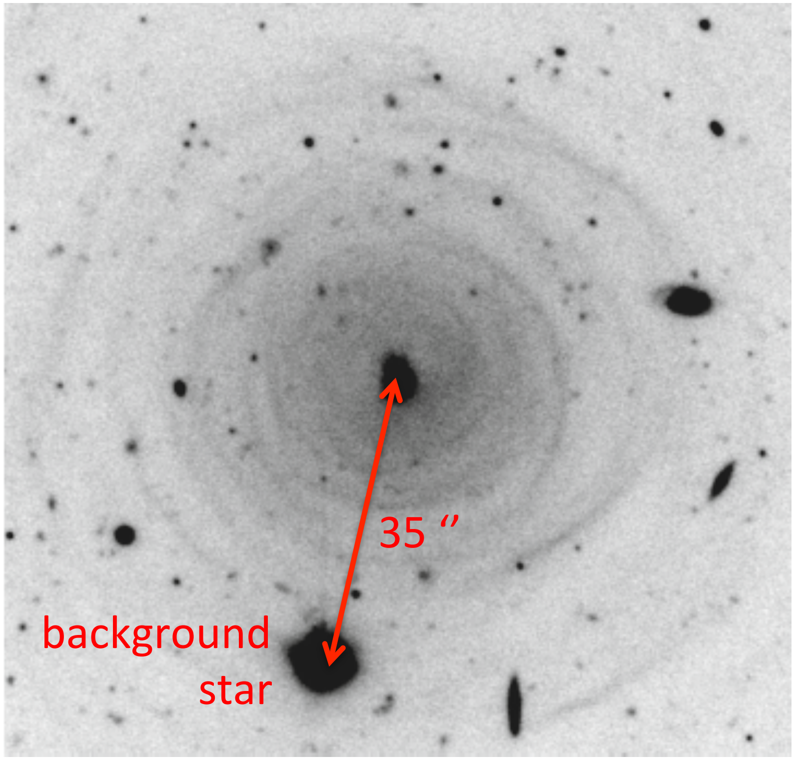
Some are distributed around the star
(NaCl, NaCN, KCl, AlCl, AlF)
formed in thermochemical equilibrium

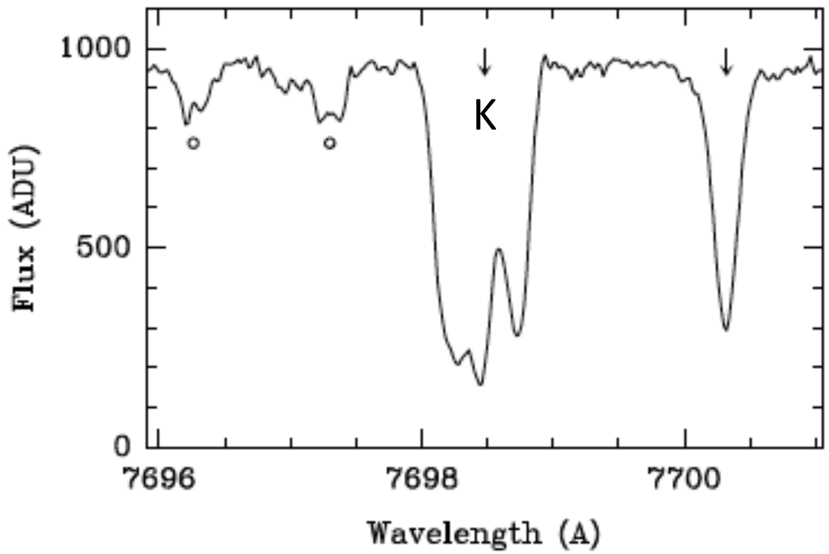
Some appear in the outer layers
(MgNC, ...)
formed by which processes ?

Metal-containing molecules: IRC+10216

Gas phase atomic metals in the circumstellar envelope of IRC+10216★

N. Mauron[1] and P. J. Huggins[2]





High gas phase abundance of neutral and ionized metal atoms in the outer envelope
Na, K, Ca, Cr, Fe

Metal-containing molecules: IRC+10216

Mon. Not. R. Astron. Soc. **282**, 807–819 (1996)

On the formation of metal cyanides and related compounds in the circumstellar envelope of IRC + 10216

Simon Petrie*

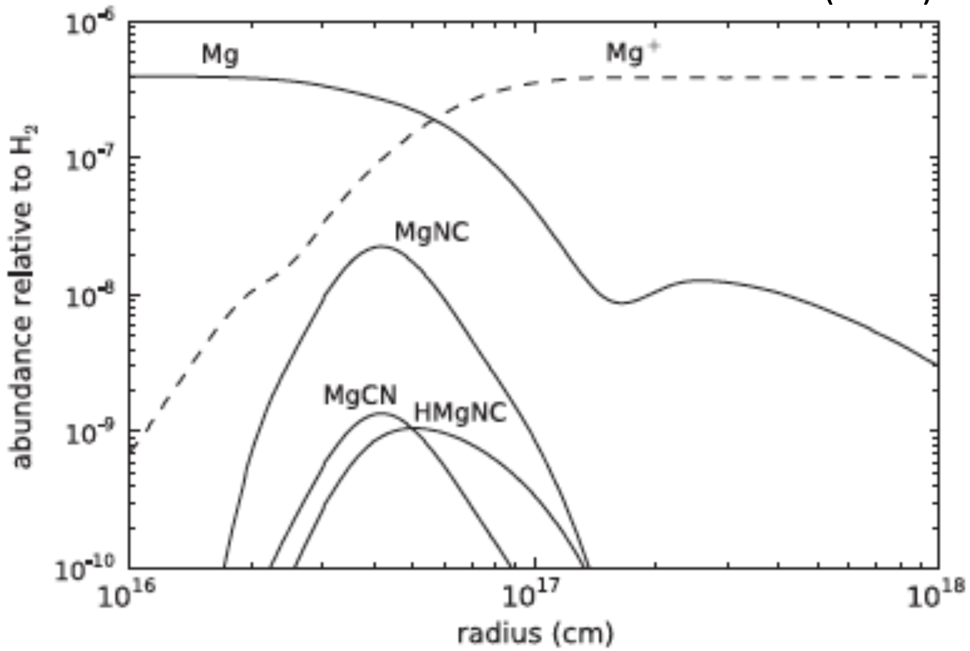
$M^+ + HC_{2n+1}N \rightarrow M(HC_{2n+1}N)^+ + h\nu$

$M(HC_{2n+1}N)^+ + e^- \rightarrow MCN + \ldots$

$MNC + \ldots$

$MC_3N + \ldots$

Cabezas et al. (2013)



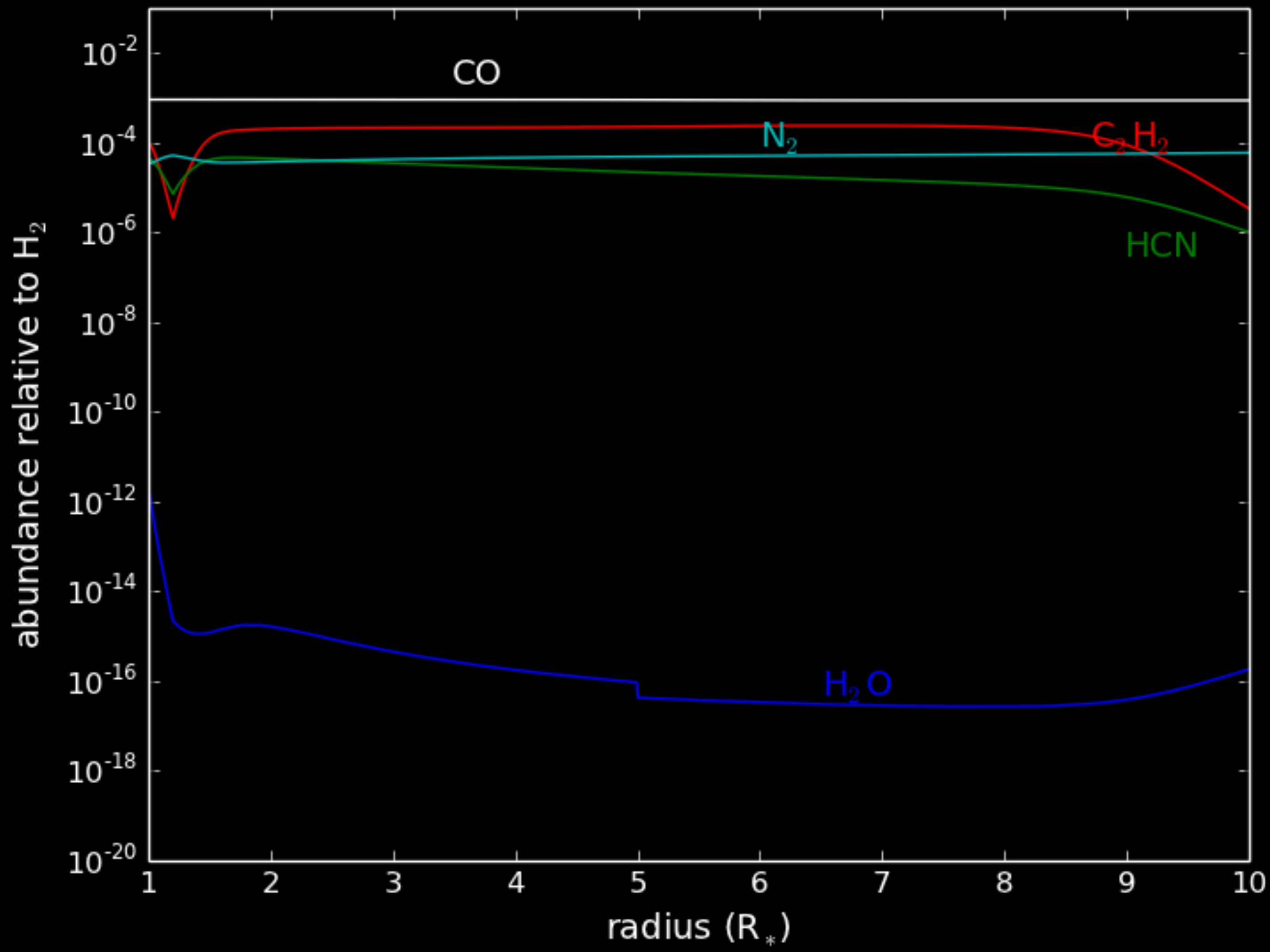
Possible formation route to (iso)cyanides (MgNC, MgCN, HMgNC, …)
in the outer envelope of IRC +10216

Circumstellar chemistry in envelopes around AGB stars:

non-standard chemistry unveiled by *Herschel* and ALMA

Water vapour in C-rich envelopes !

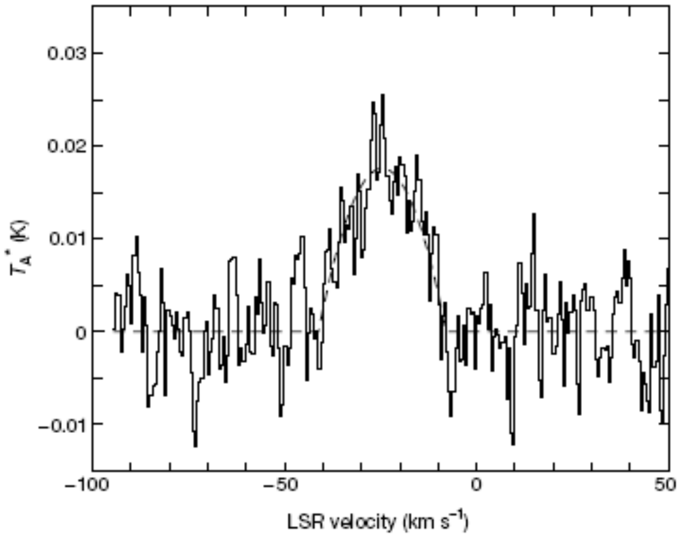
thermochemical equilibrium



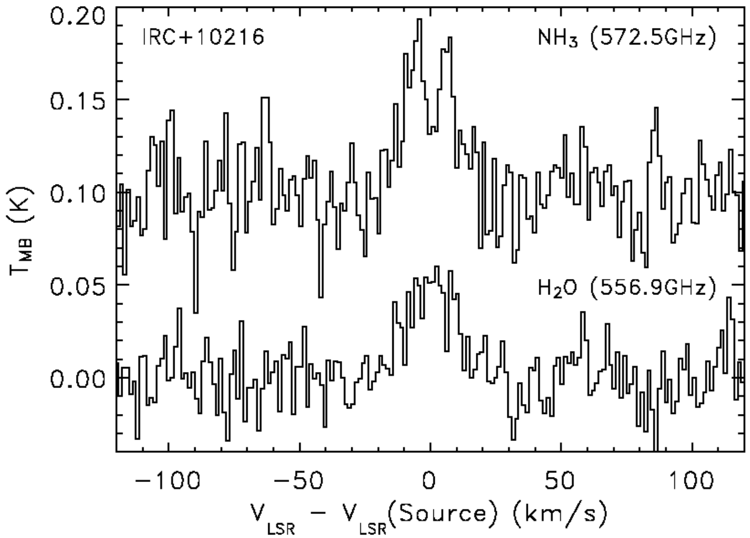
Water vapour in IRC+10216

H_2O $1_{1,0}$-$1_{0,1}$ at 556.936 GHz (E_{up} = 26.7 K)

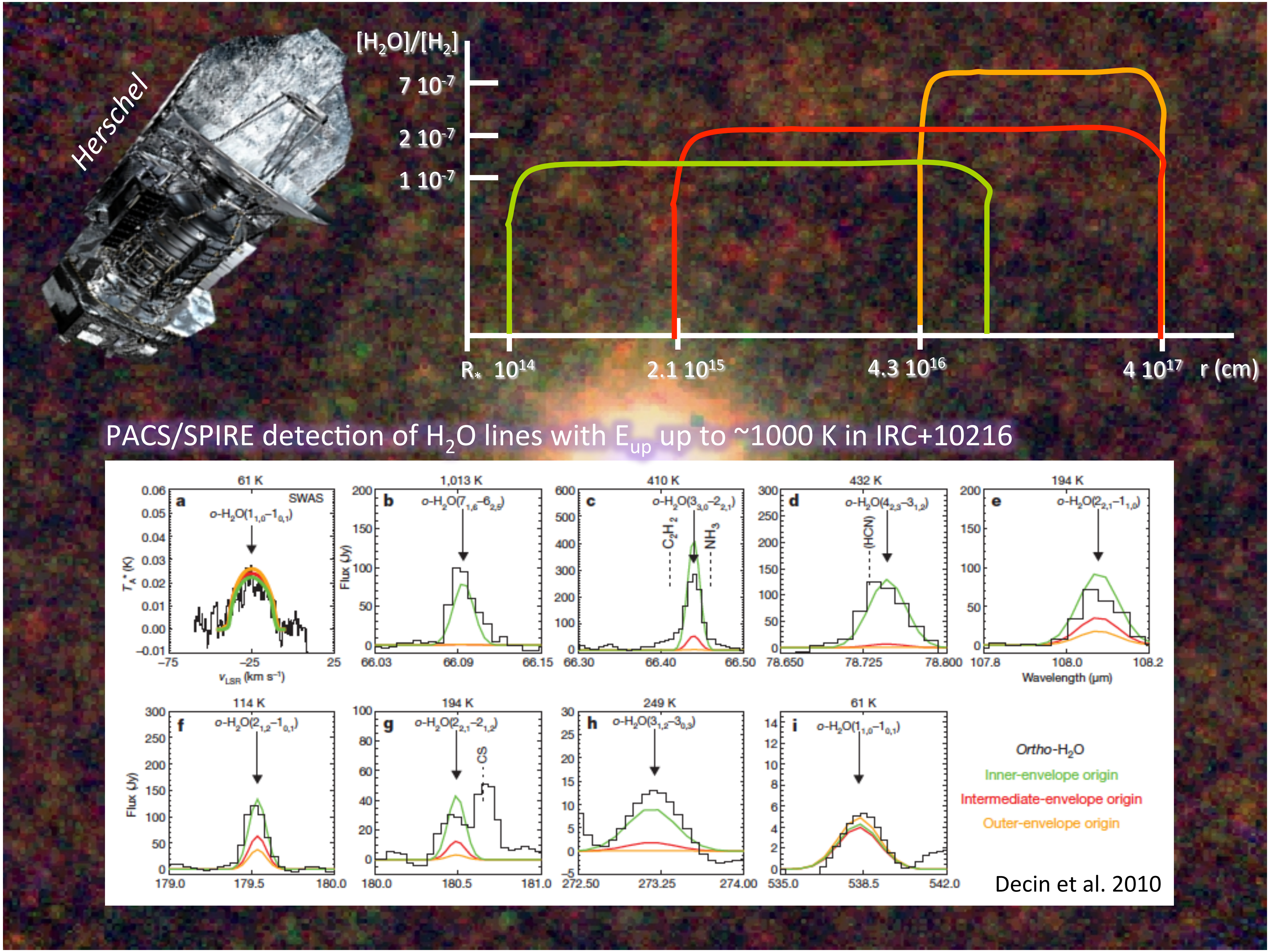
Melnick et al. 2001



Hasegawa et al. 2006

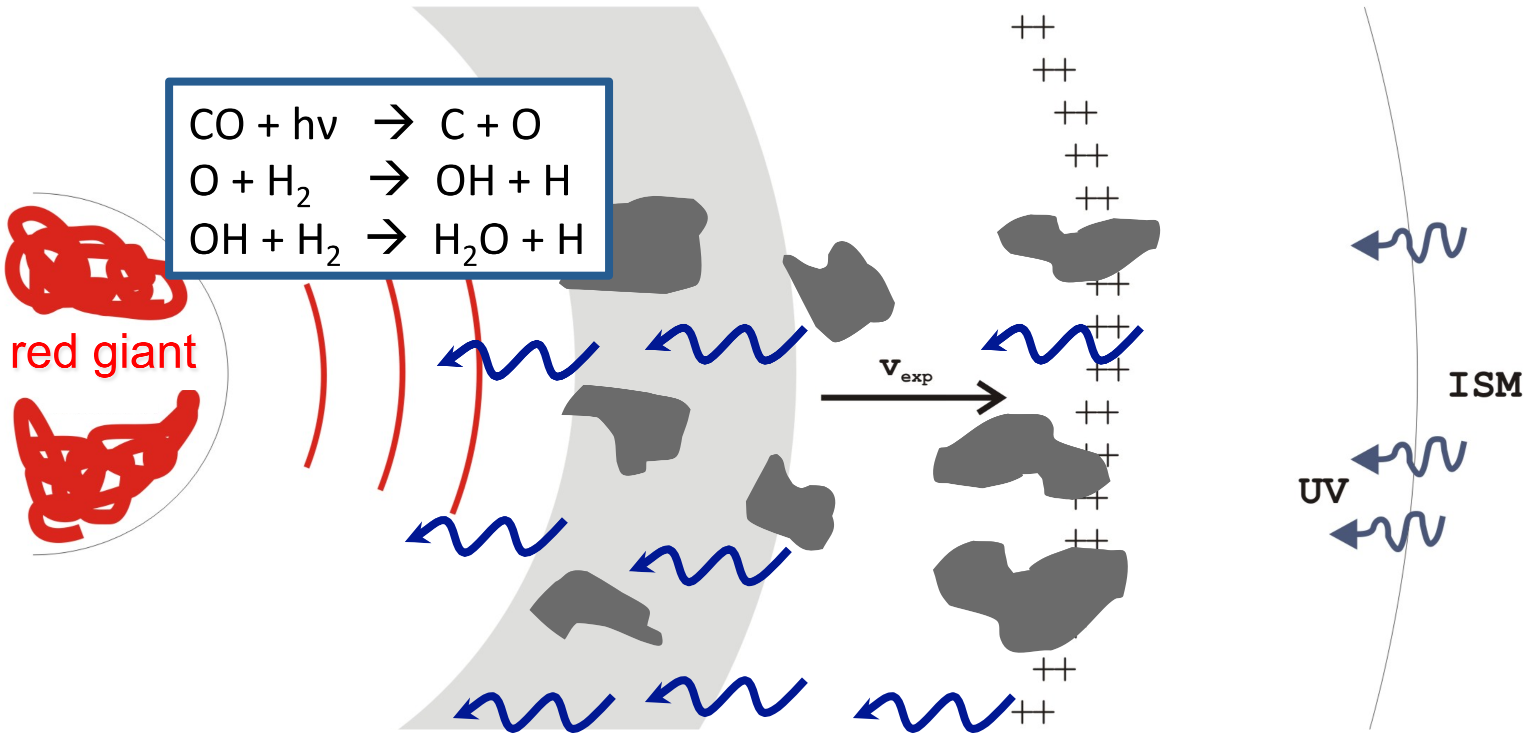


$[H_2O]/[H_2] = 4\times10^{-7} - 3\times10^{-6}$



Herschel
[H2O]/[H2]
7 10-7
2 10-7
1 10-7
R* 10^14
2.1 10^15
4.3 10^16
4 10^17
r (cm)
PACS/SPIRE detection of H2O lines with Eup up to ~1000 K in IRC+10216
61 K
a SWAS o-H2O(1_{1,0}–1_{0,1})
TA* (K)
vLSR (km s−1)
1,013 K
b o-H2O(7_{1,6}–6_{2,5})
Flux (Jy)
410 K
c o-H2O(3_{3,0}–2_{2,1})
C2H2
NH3
432 K
d o-H2O(4_{2,3}–3_{1,2})
(HCN)
194 K
e o-H2O(2_{2,1}–1_{1,0})
Wavelength (μm)
114 K
f o-H2O(2_{1,2}–1_{0,1})
194 K
g o-H2O(2_{2,1}–2_{1,2})
CS
249 K
h o-H2O(3_{1,2}–3_{0,3})
61 K
i o-H2O(1_{1,0}–1_{0,1})
Ortho-H2O
Inner-envelope origin
Intermediate-envelope origin
Outer-envelope origin
Decin et al. 2010

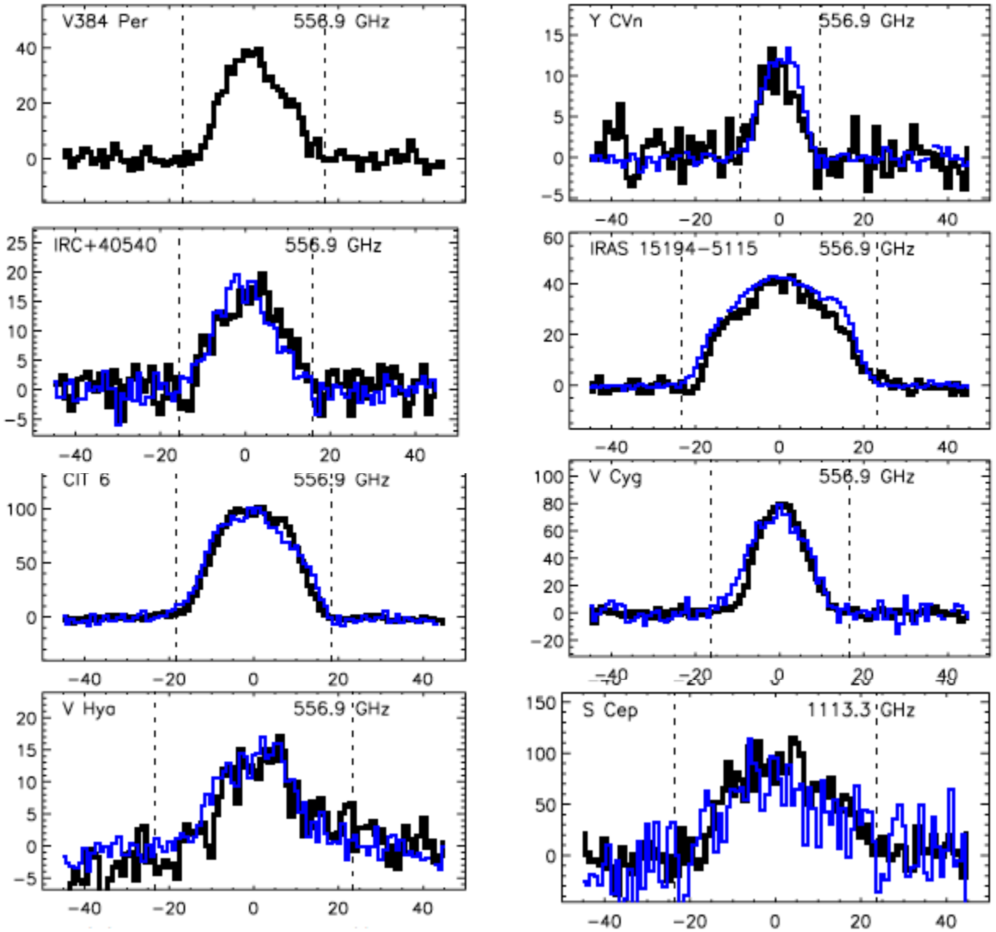
Clumpy envelope and photochemistry in the warm inner layers (Agúndez et al 2010)



Shock-induced chemistry in the inner layers (Cherchneff 2011)

Herschel HIFI finds that water vapour is ubiquitous around C-rich AGB stars

Neufeld et al. 2011

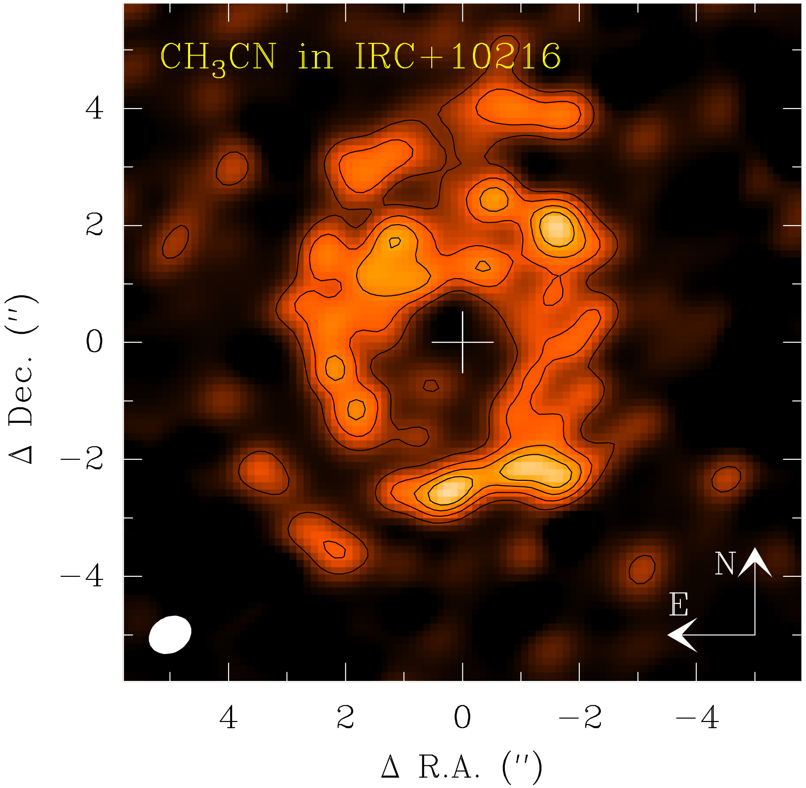


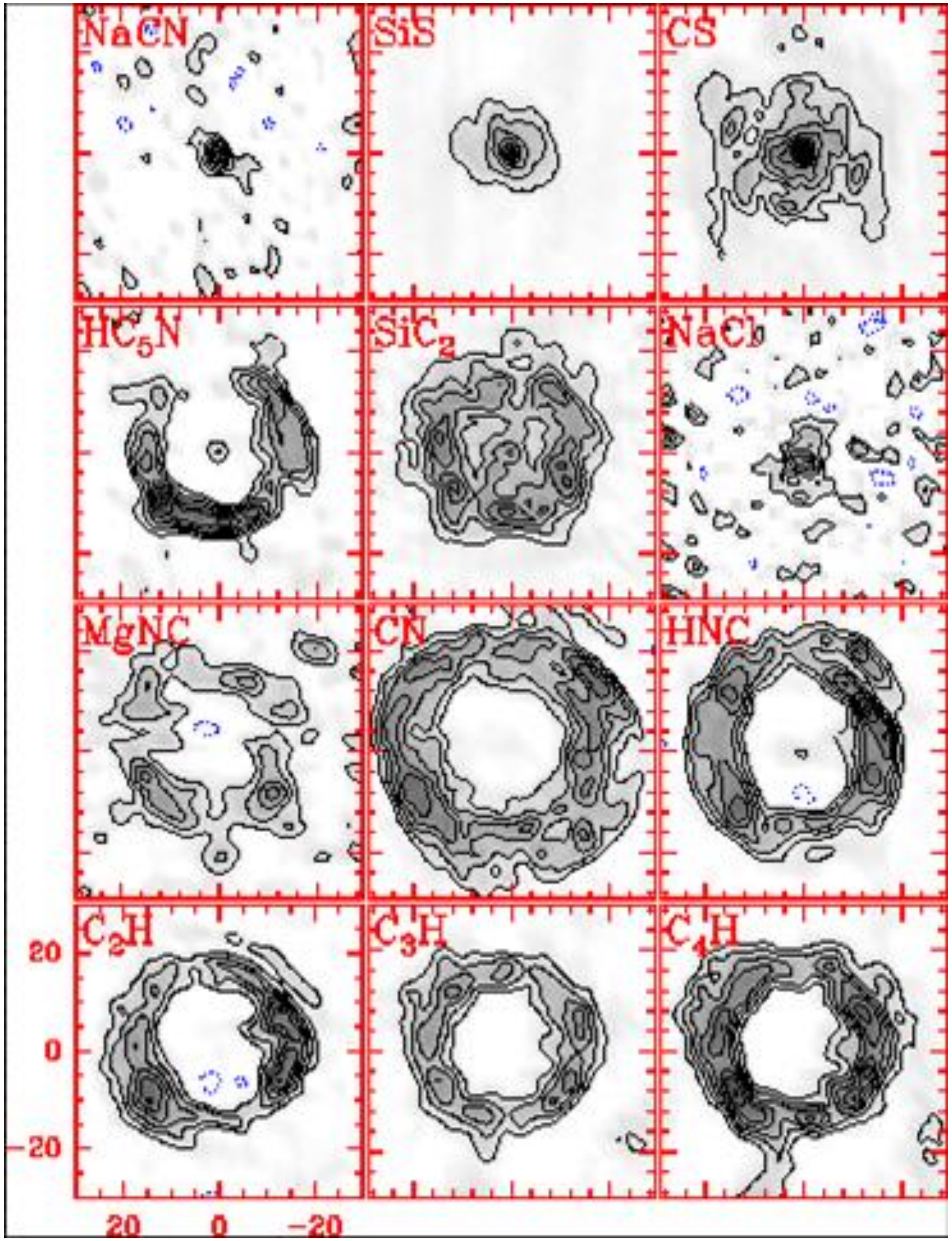
H_2O detected in all 8 C-rich AGB stars where it was searched for

There must be a kind of universal mechanism to form H_2O in CSEs of C-rich AGB stars

Non-standard distribution of CH_3CN in IRC+10216 !

ALMA observations





Circumstellar chemistry in envelopes around AGB stars