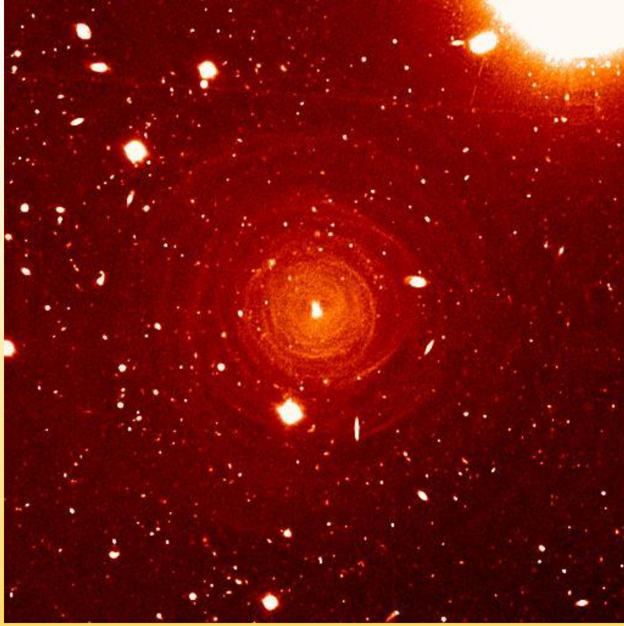
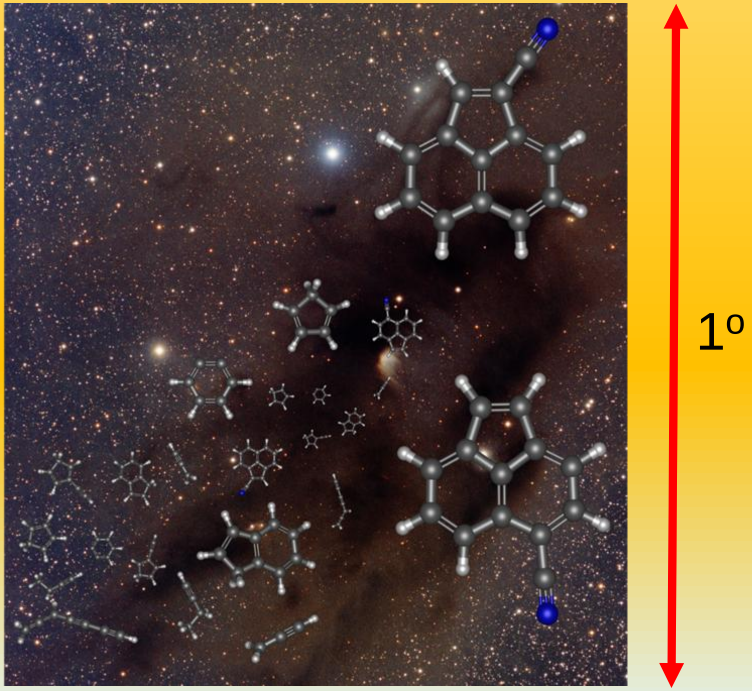
Carbonaceous chemistry with ALMA Band 2: The case of IRC+10216 (and TMC-1…)

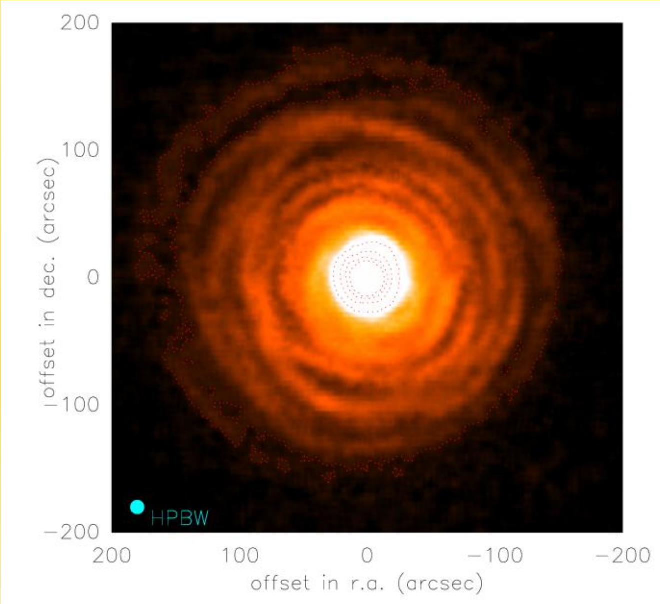
José Cernicharo
IFF (CSIC)
Department of Molecular Astrophysics
Spain
jose.cernicharo@csic.es



IRC+10216 : Optical view

TMC-1 T_K=10 K





IRC+10216 : ^{12}CO J=2-1

What we understand by carbonaceous chemistry ??

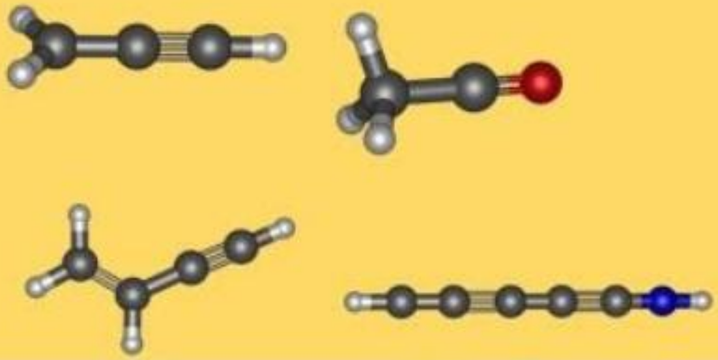
Species such as CO, HCN, HCO^+, HNC, CCH contain carbon but

real carbon chemistry in space means the detection and chemical analysis of species such as:

CCH, CCCH, CCCCH, CCCCCH, CCCCCCH,….
CCH^-, $CCCCH^-$, $CCCCCCH^-$,
HCN, HC_3N, HC_5N, HC_7N, HC_9N, ….
C_3N, C_5N, C_3N^-, C_5N^-, C_7N^-,…
CH_2CHCCH, $CH_2CCHCCH$, CH_2CCHC_4H,,,
and
Individual PAHs containing five/six-C rings and > 20 carbon atoms

Where these species are found and how ALMA can help us in understanding how they have been formed ?

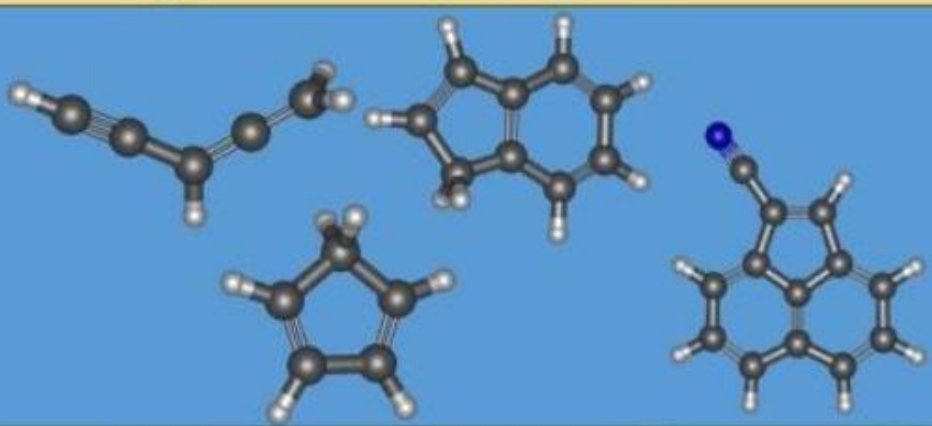
Which is the best frequency to study carbonaceous chemistry in space



W-Band 71.5-91.5 GHz

Molecules of 3-6 atoms

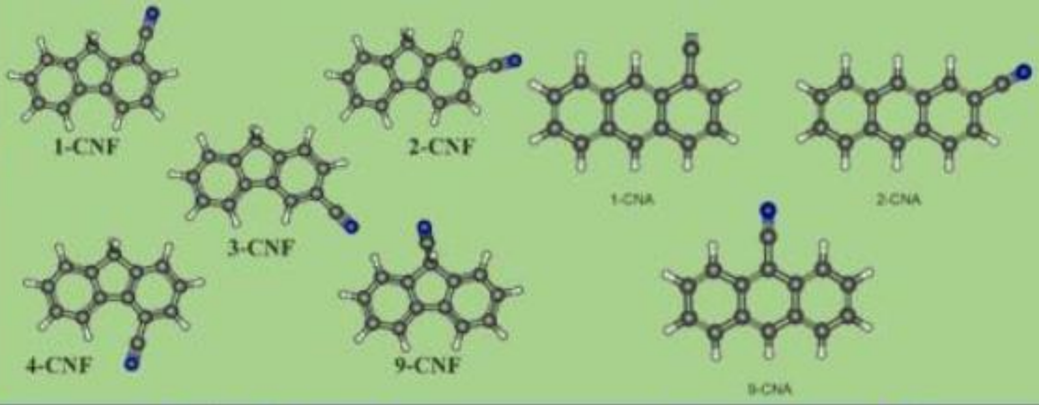
IRAM 30m line surveys
ALMA BAND 2
(67-116 GHz)



Q-Band 31.1-50.3 GHz

Molecules of 6-20 atoms

QUIJOTE LINE SURVEY:
DARK CLOUD (also
GOTHAM)



K-Band 18-32 GHz

Molecules of >20 atoms

THE ASTROPHYSICAL JOURNAL, 438:259–264, 1995 January 1

CONFIRMATION OF INTERSTELLAR METHYLENE

J. M. HOLLIS
NASA Goddard Space Flight Center, Space Data Computing Division, Code 930, Greenbelt, MD 20771
P. R. JEWELL
National Radio Astronomy Observatory, Campus Building 65, 949 North Cherry Avenue, Tucson, AZ 85721-0655
AND
F. J. LOVAS
National Institute of Standards and Technology, Molecular Physics Division, Building 221, Room B265, Gaithersburg, MD 208

Received 1994 May 9; accepted 1994 July 7

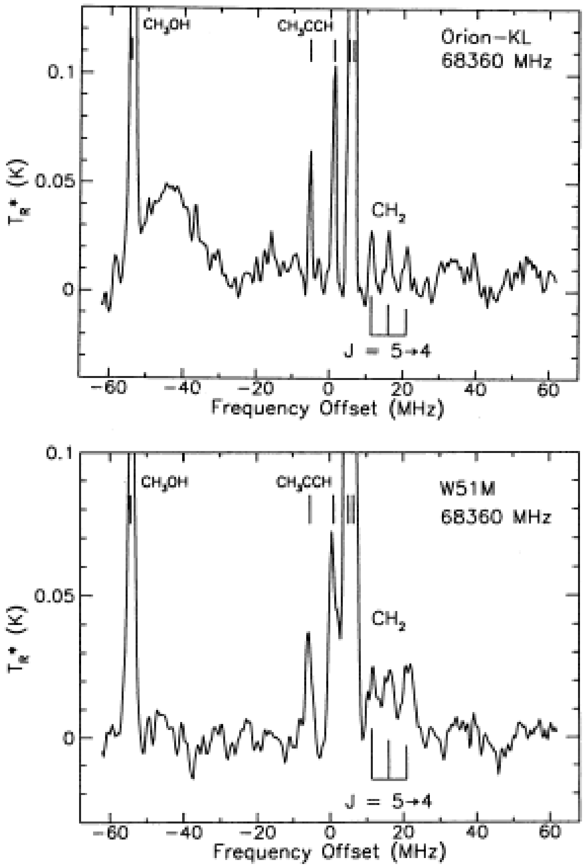


FIG. 1.—Spectra showing the $F = 6–5$, 5–4, and 4–3 hyperfine structure of the $J = 5–4$ fine-structure levels of the $N_{KK} = 4_{04}–3_{13}$ rotational transition of CH_2 at 391 kHz channel spacing. *Upper:* the Orion–KL abscissa is the frequency offset relative to 68,360 MHz for the signal bandpass, assuming a source V_{LSR} of $+9.0$ km s^{-1}. The broad spectral feature near -40 MHz is thought to be a harmonic instrumental artifact (see § 2.3). *Lower:* the W51 M abscissa is the frequency offset relative to 68,360 MHz for the signal bandpass, assuming a source V_{LSR} of $+57.1$ km s^{-1}. Shown below the CH_2 positions are hyperfine fiducials with relative intensities expected for LTE.

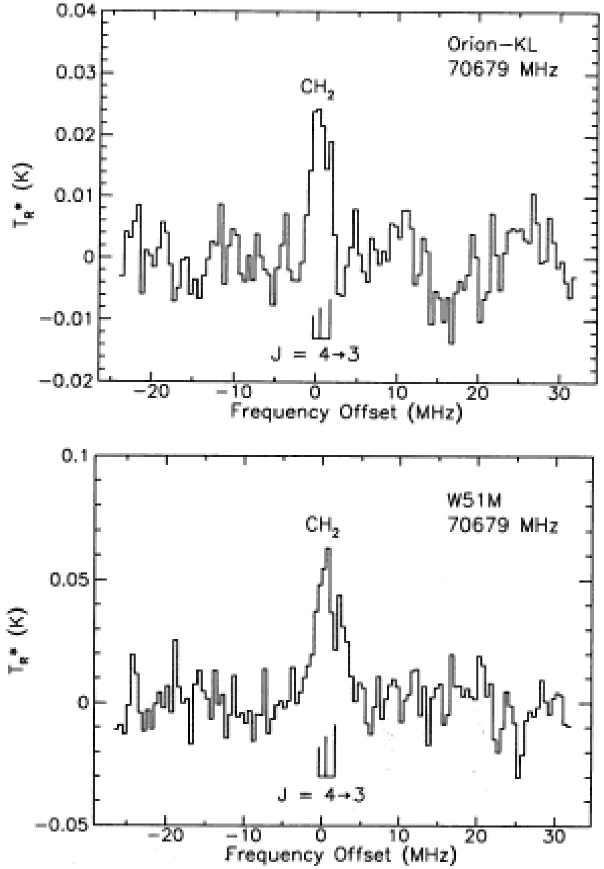


FIG. 2.—Spectra showing a blend of the $F = 5–4$, 4–3, and 3–2 hyperfine structure of the $J = 4–3$ fine-structure levels of the $N_{KK} = 4_{04}–3_{13}$ rotational transition of CH_2 at 500 kHz resolution. *Upper:* the Orion–KL abscissa is the frequency offset relative to 70,679 MHz for the signal bandpass, assuming a source V_{LSR} of $+9.0$ km s^{-1}. *Lower:* the W51 M abscissa is the frequency offset relative to 70,679 MHz for the signal bandpass, assuming a source V_{LSR} of $+57.1$ km s^{-1}. Shown below the CH_2 position are hyperfine fiducials with relative intensities expected for LTE.

CH_2

E_{upp}=224 K

Band 2

but very high
Energy=>
Hot cores
and corinos
AGBs

fundamental lines
In the submm

CARBON CHEMISTRY
IRC +10216 (Cw Leo)

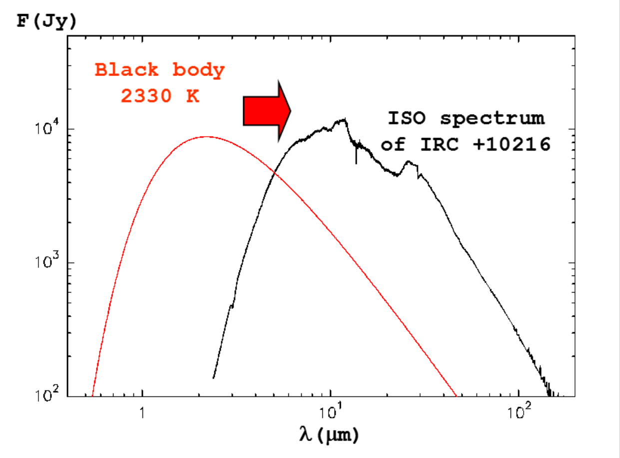
Chemical study of the envelope

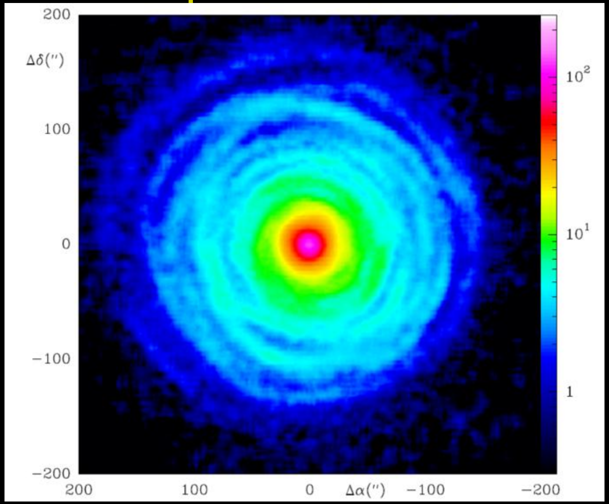
l 10 mm; ESO/La Silla
B. Stecklum & H.-U. Kaüfl

¿Why is so interesting the study of chemical composition of IRC +10216?

- IRC+10216 is a prototype of C-rich stars (mass loss rate of 10^{-5} M_O/yr)

- All metal-bearing species known in space have been detected in this CSE





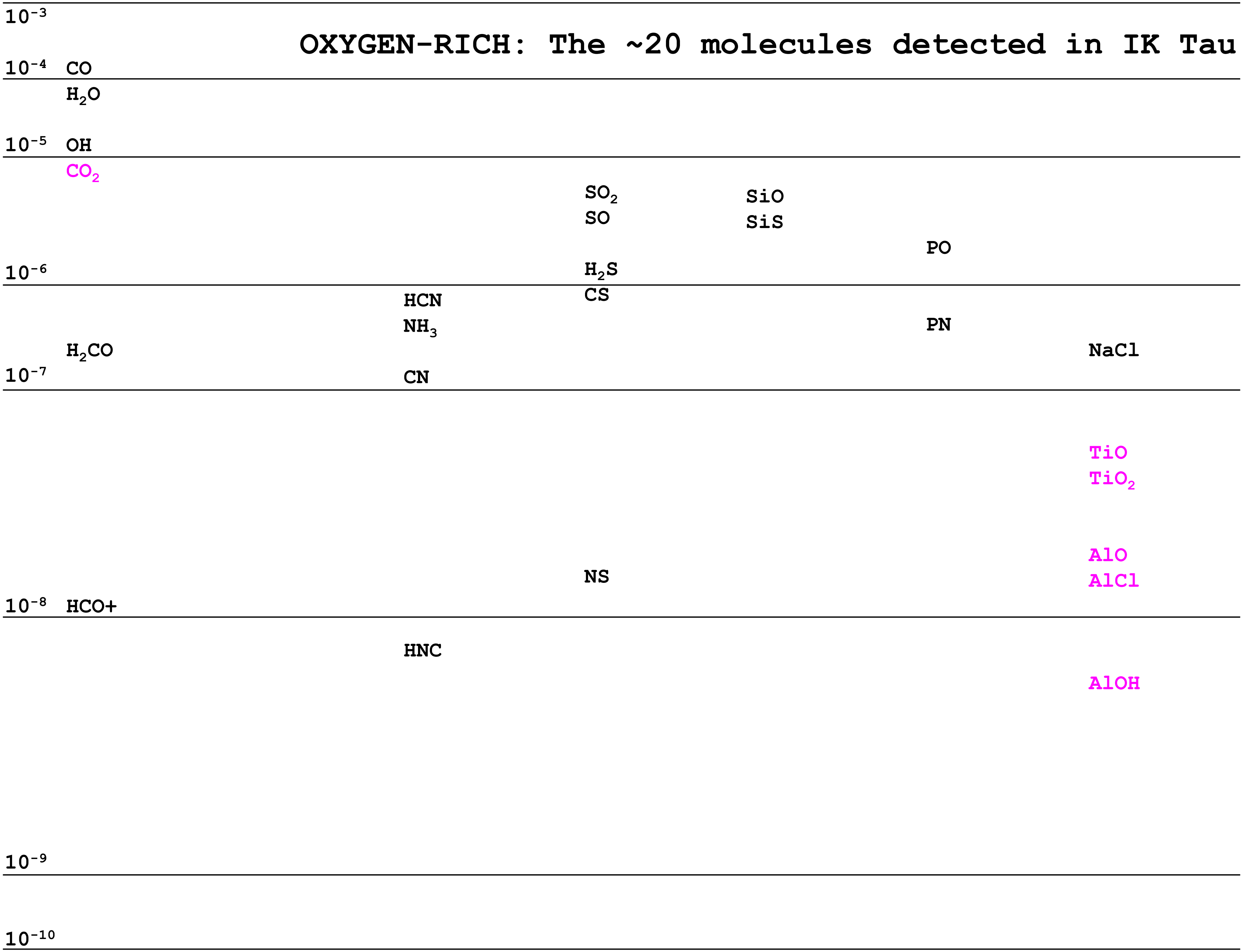
Cernicharo et al, 2015,
Leao et al., 2006

METHODS : Astronomical observations at all frequencies, high and médium angular resolution
Radiative transfer modelling, Dynamical Evolution, Chemical modelling,….

CARBON-RICH: The ~100 molecules detected in IRC+10216

10^{-3}	CO						
10^{-4}							
		C_2H_2					
			HCN		PAHs expected here !!!		
10^{-5}							
		CH_4					
		C_2H	NH_3				
		C_4H	CN		SiC_2		
		C_2	HC_3N		SiS		
10^{-6}		C_3			Si_2C		
			C_3N	CS	SiH_4		
					SiO		
			HC_5N				HCl
10^{-7}	H_2O	C_5	HNC				
		l-C_3H	CN-		SiC		
	OH	C_6H					
		C_5H	CH_3CN	C_2S			AlCl
		c-C_3H_2					
		CH_3C_2H					
		c-C_3H	HC_7N			HCP	
		C_2H_4			CH_3SiH_3		NaCN
	H_2CO	H_2C_4		C_3S			MgC_4H MgC_6H
10^{-8}					SiN	CP	HF
		C_8H	HC_9N	H_2CS		PH_3	MgNC
			CH_2CN				AlF
			HC_2N				MgC_3N
			C_5N		c-SiC_3,l-SiC_3		MgC_5N $HMgC_3N$
		C_7H	HCCNC		SiC_4,l-SiC_5,		MgC_2H
		H_2C_6	C_2H_3CN	H_2S	SiC_6		
		C_6H-	C_5N-		SiCN		MgC_4H^+ MgC_6H^+
	C_3O	C_8H-	HC_4N		SiNC		MgC_3N^+ MgC_5N^+
		H_2C_3	C_7N-	C_5S		PN	NaCl CaC_2
10^{-9}			C_3N-			C_2P	AlNC
	HCO+		HNCCC				MgCN HMgNC
		C_4H-					KCl FeCN KCN
10^{-10}		$C_{10}H-$					CaNC NaC_3N FeC

OXYGEN-RICH: The ~20 molecules detected in IK Tau



10^{-3}

10^{-4} CO

H_2O

10^{-5} OH

CO_2

SO_2

SO

SiO

SiS

PO

H_2S

10^{-6}

HCN

CS

NH_3

PN

H_2CO

NaCl

10^{-7}

CN

TiO

TiO_2

AlO

NS

AlCl

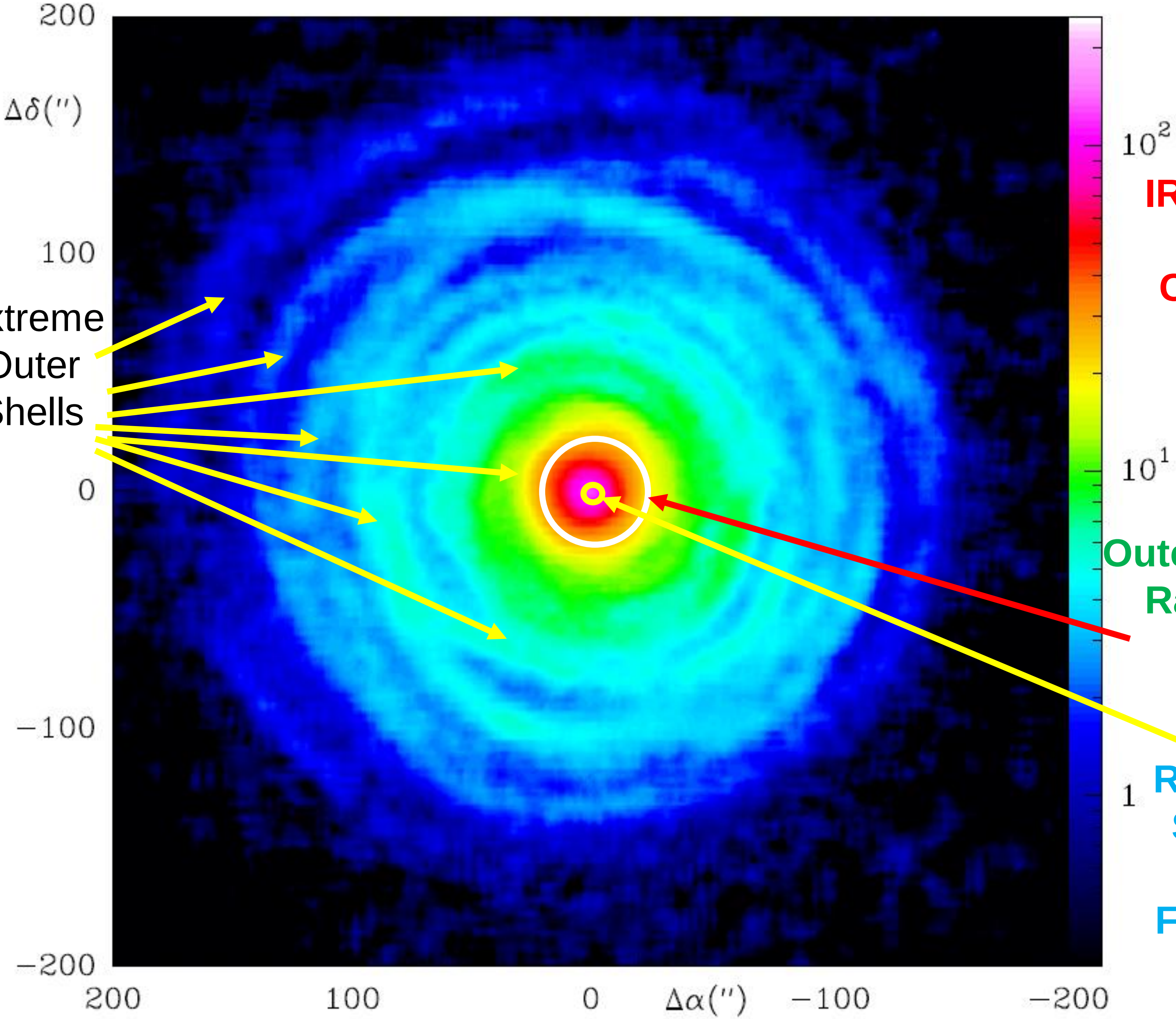
10^{-8} HCO+

HNC

AlOH

10^{-9}

10^{-10}



IRC+10216

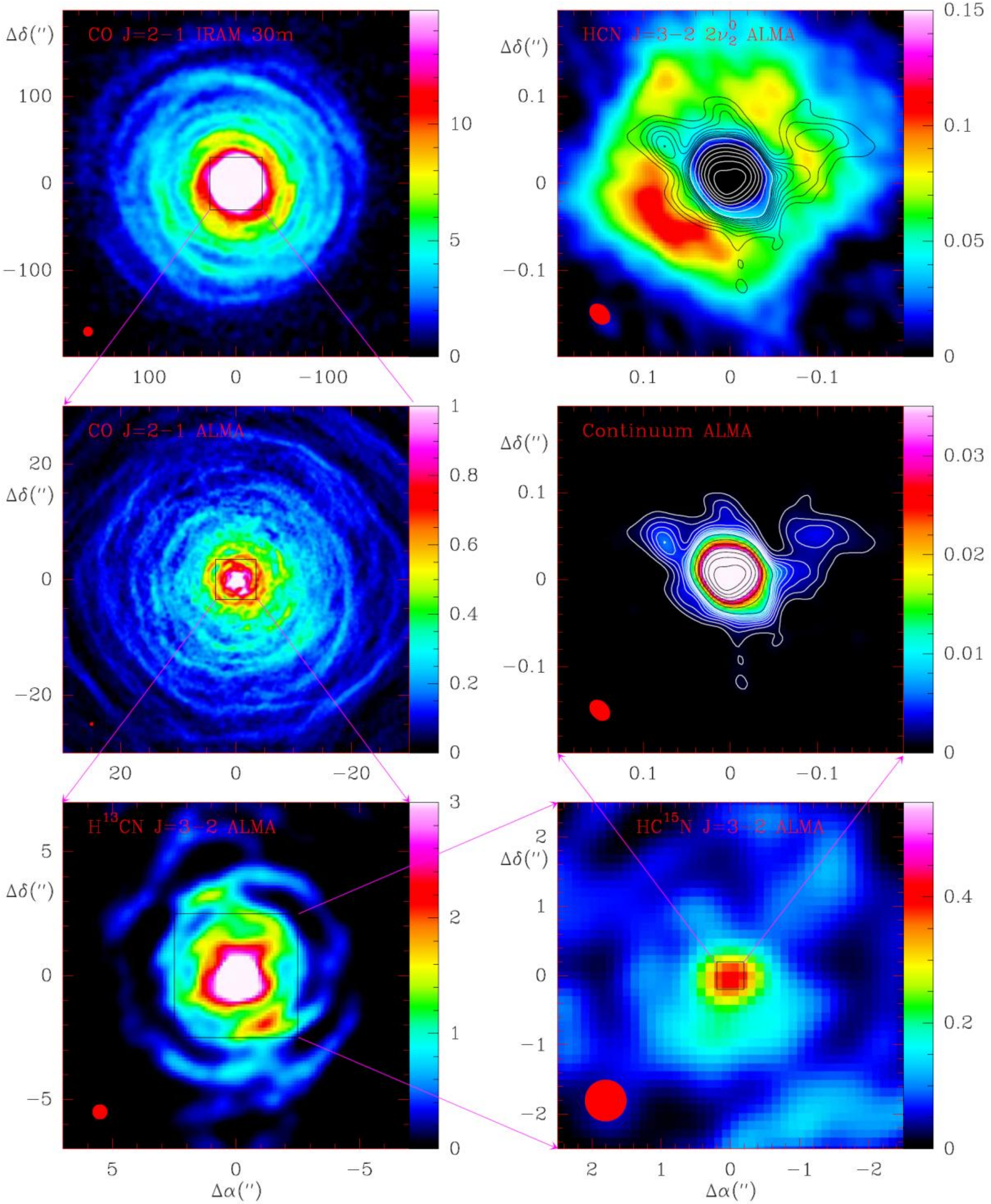
CO J=2-1

30m data

Extreme
Outer
Shells

**Outer carbon
Radicals
shell**

**Inner
Refractory
Species.
Dust
Formation
Zone**



IRC+10216
CO, HCN, H^{13}CN

From 400” (angular Resolution 11”)

down to

0.3” (angular resolution 0.02”)

Inner shells

Outer shells

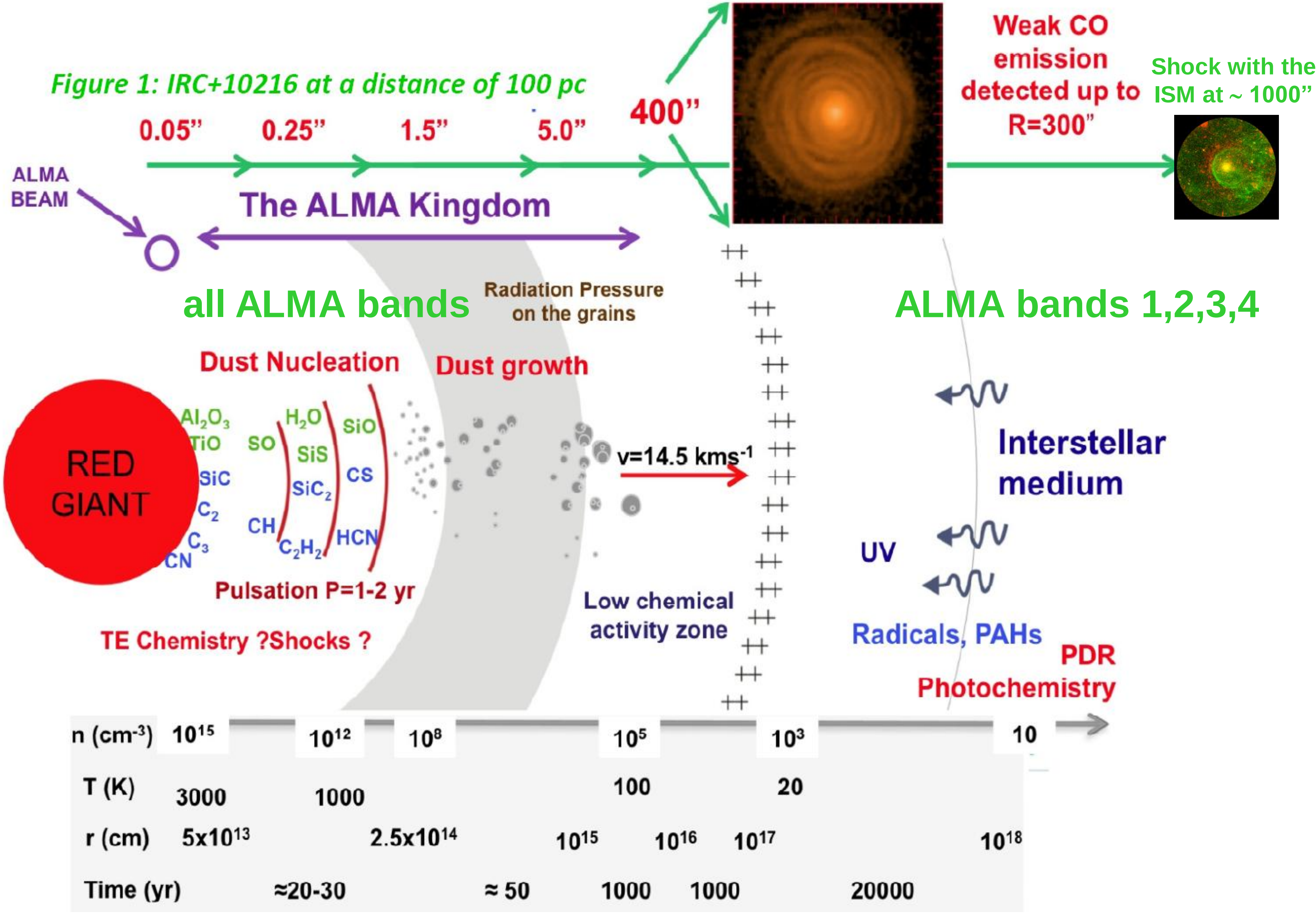


Figure 1: IRC+10216 at a distance of 100 pc

0.05” 0.25” 1.5” 5.0” 400”

Weak CO emission detected up to R=300”

Shock with the ISM at ~ 1000”

ALMA BEAM

The ALMA Kingdom

all ALMA bands

Radiation Pressure on the grains

ALMA bands 1,2,3,4

Dust Nucleation

Dust growth

RED GIANT

Al_2O_3
TiO
SiC
C_2
C_3
CN

SO
CH

H_2O
SiS
SiC_2
C_2H_2

SiO
CS
HCN

v=14.5 kms^{-1}

Interstellar medium

UV

Pulsation P=1-2 yr

TE Chemistry ?Shocks ?

Low chemical activity zone

Radicals, PAHs

PDR Photochemistry

n (cm^{-3}) 10^{15} 10^{12} 10^{8} 10^{5} 10^{3} 10

T (K) 3000 1000 100 20

r (cm) 5x10^{13} 2.5x10^{14} 10^{15} 10^{16} 10^{17} 10^{18}

Time (yr) ≈20-30 ≈ 50 1000 1000 20000

Astrochemistry of the inner layers

THE DUST FORMATION ZONE EXPLORED IN THE NEAR, MID AND FAR INFRARED

AND IN THE MILLIMETER EMISSION OF HUNDREDS OF UNIDENTIFIED LINES

For high spectral resolution IR data see **Fonfría et al., 2008, ApJ**

The ALMA view of IRC+10216: A forest of U Lines at 1mm

HCN in high energy vibrational levels (>10000 K)

SiC$_2$ in v$_3$ and 2v$_3$,…

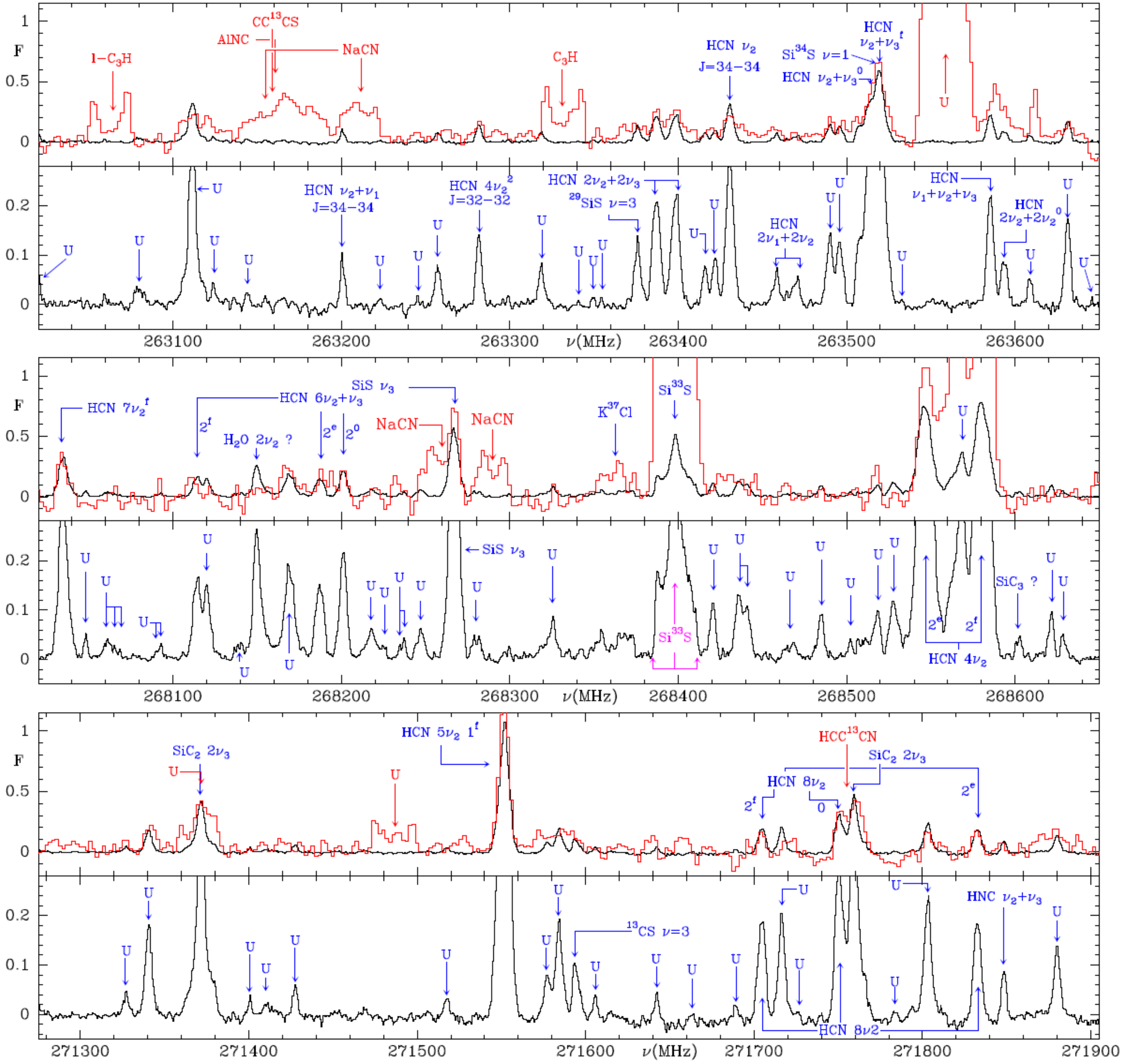
SiS up to v=10 (& isotopologues)

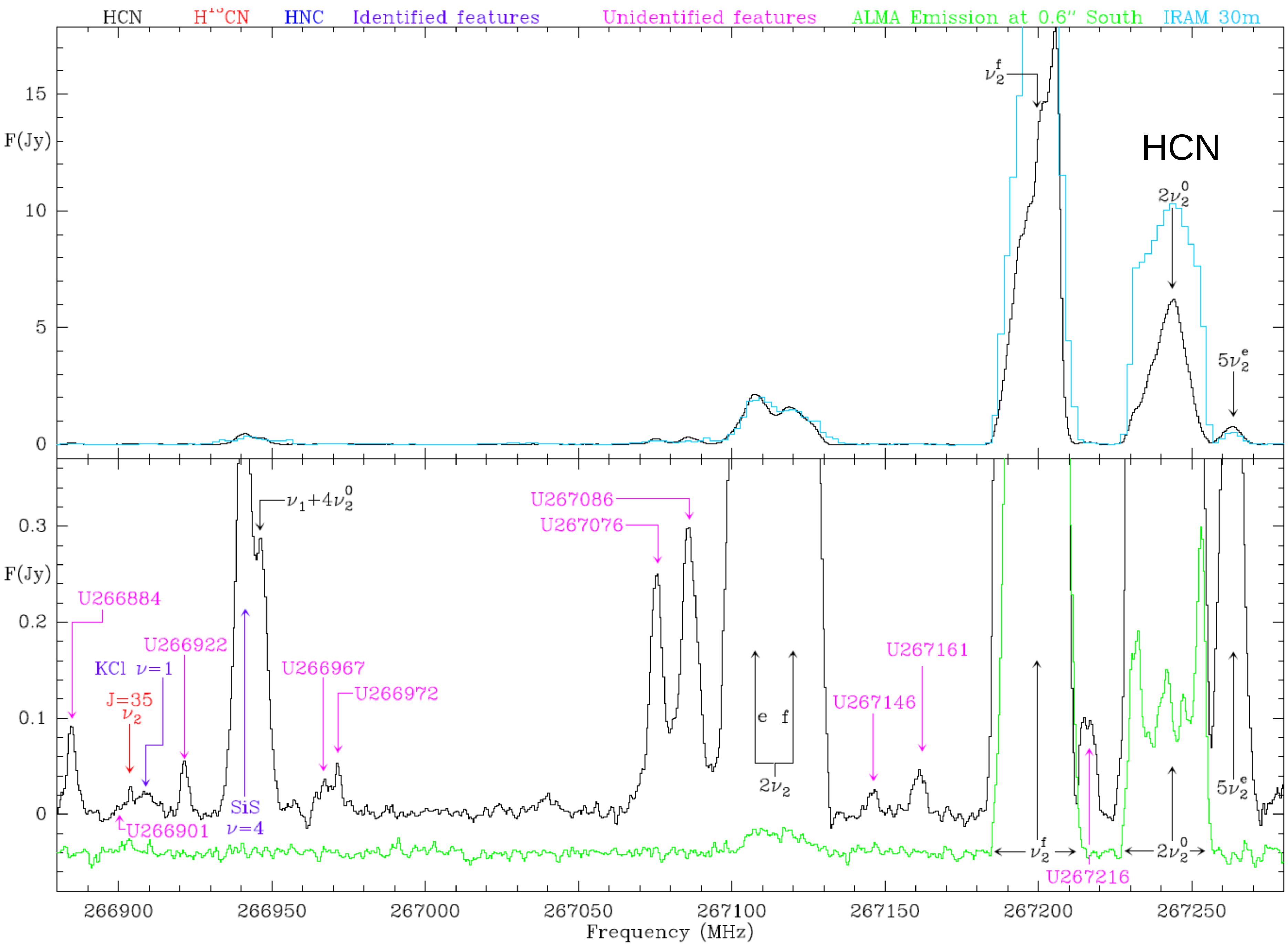
SiO up to v=3 (& isotopologues)

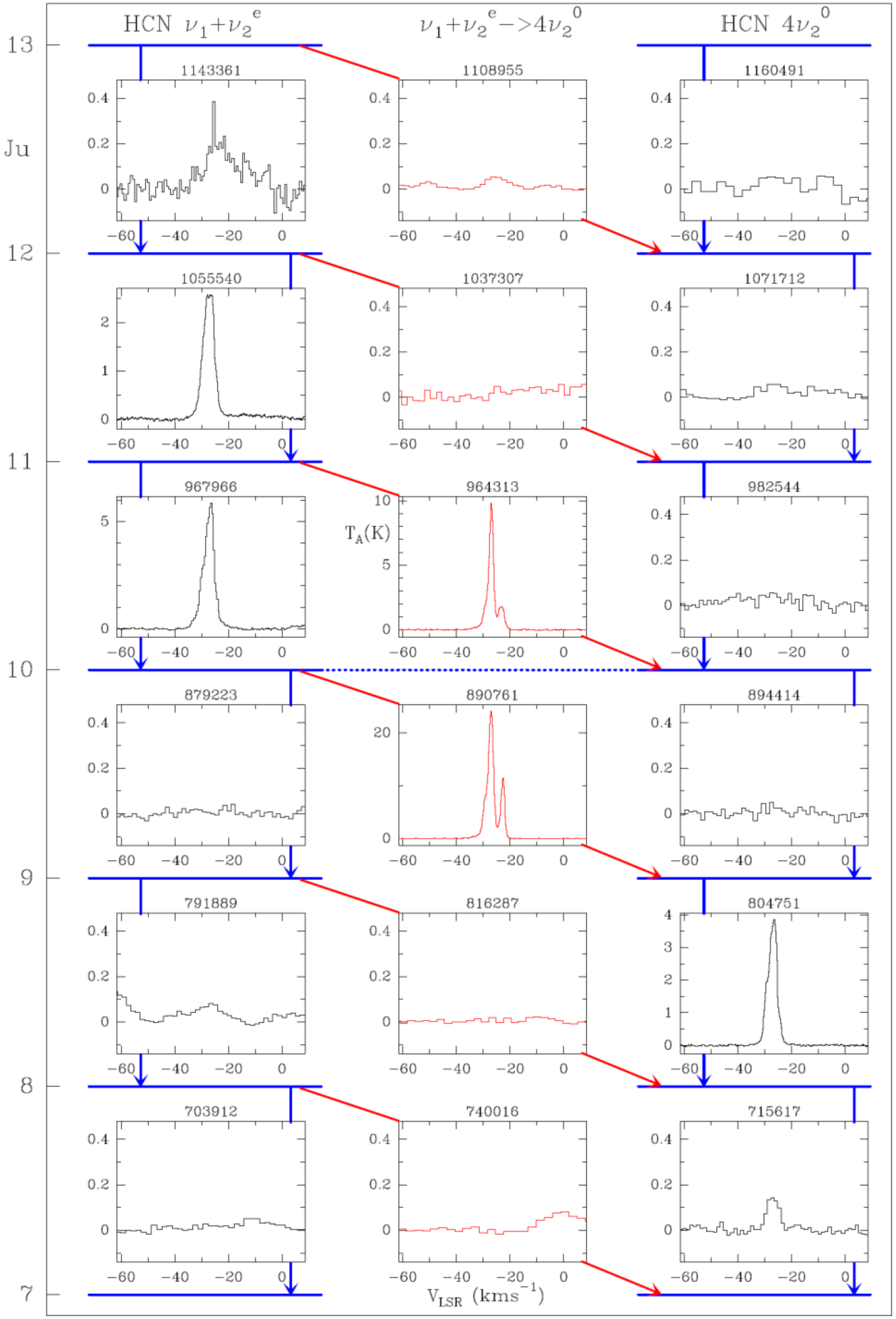
HNC in vibrational levels up to 10000 K

+ hundreds of U lines

Cernicharo et al., 2013
ApJ Letters, 778, L25

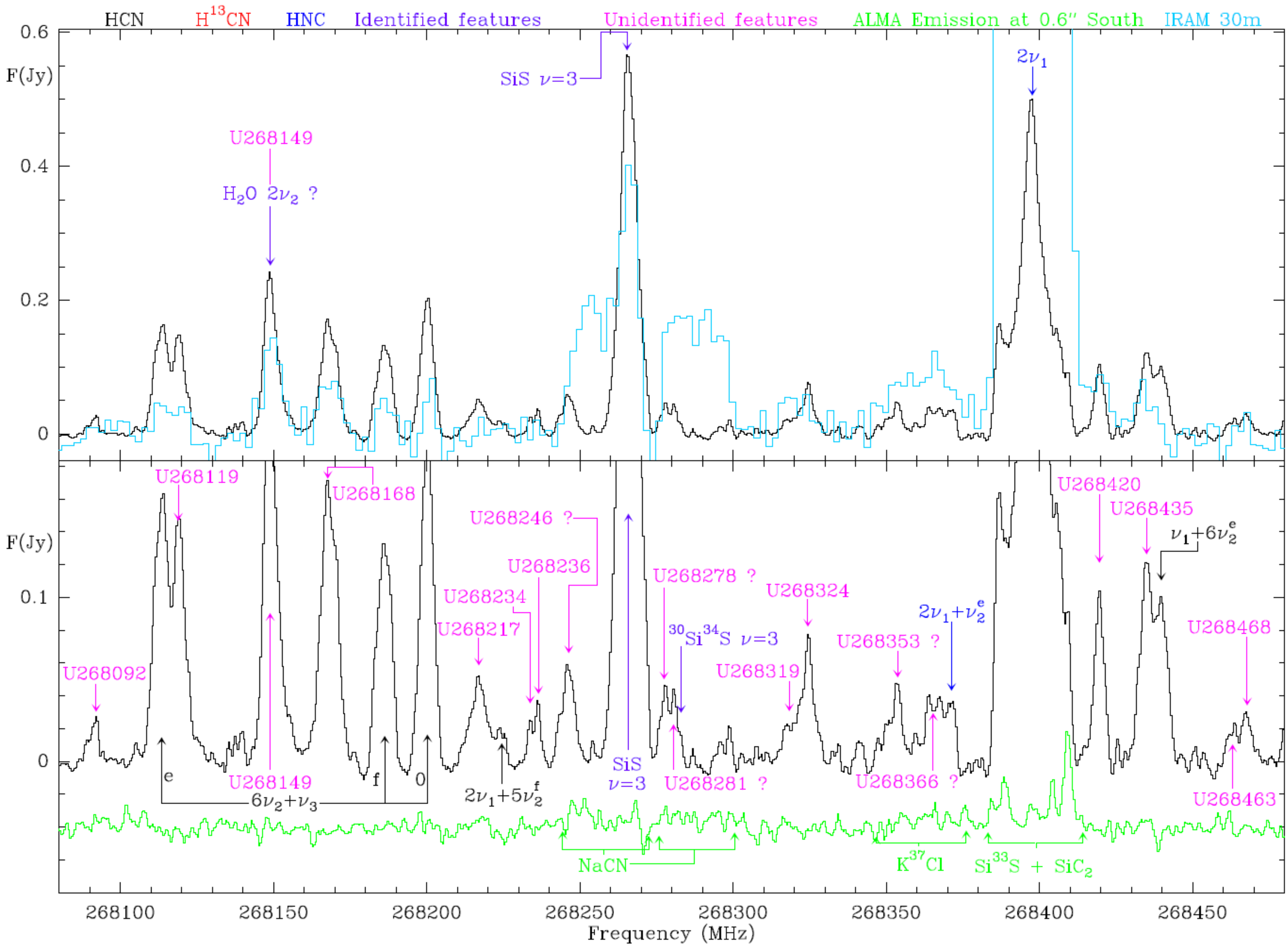



HCN
H13CN
HNC
Identified features
Unidentified features
ALMA Emission at 0.6″ South
IRAM 30m
HCN
ν_2^f
$2\nu_2^0$
$5\nu_2^e$
F(Jy)
15
10
5
0
0.3
0.2
0.1
0
$\nu_1+4\nu_2^0$
U267086
U267076
U266884
U266922
KCl ν=1
J=35
ν_2
U266967
U266972
SiS
ν=4
U266901
e
f
$2\nu_2$
U267161
U267146
ν_2^f
U267216
$2\nu_2^0$
$5\nu_2^e$
266900
266950
267000
267050
267100
267150
267200
267250
Frequency (MHz)



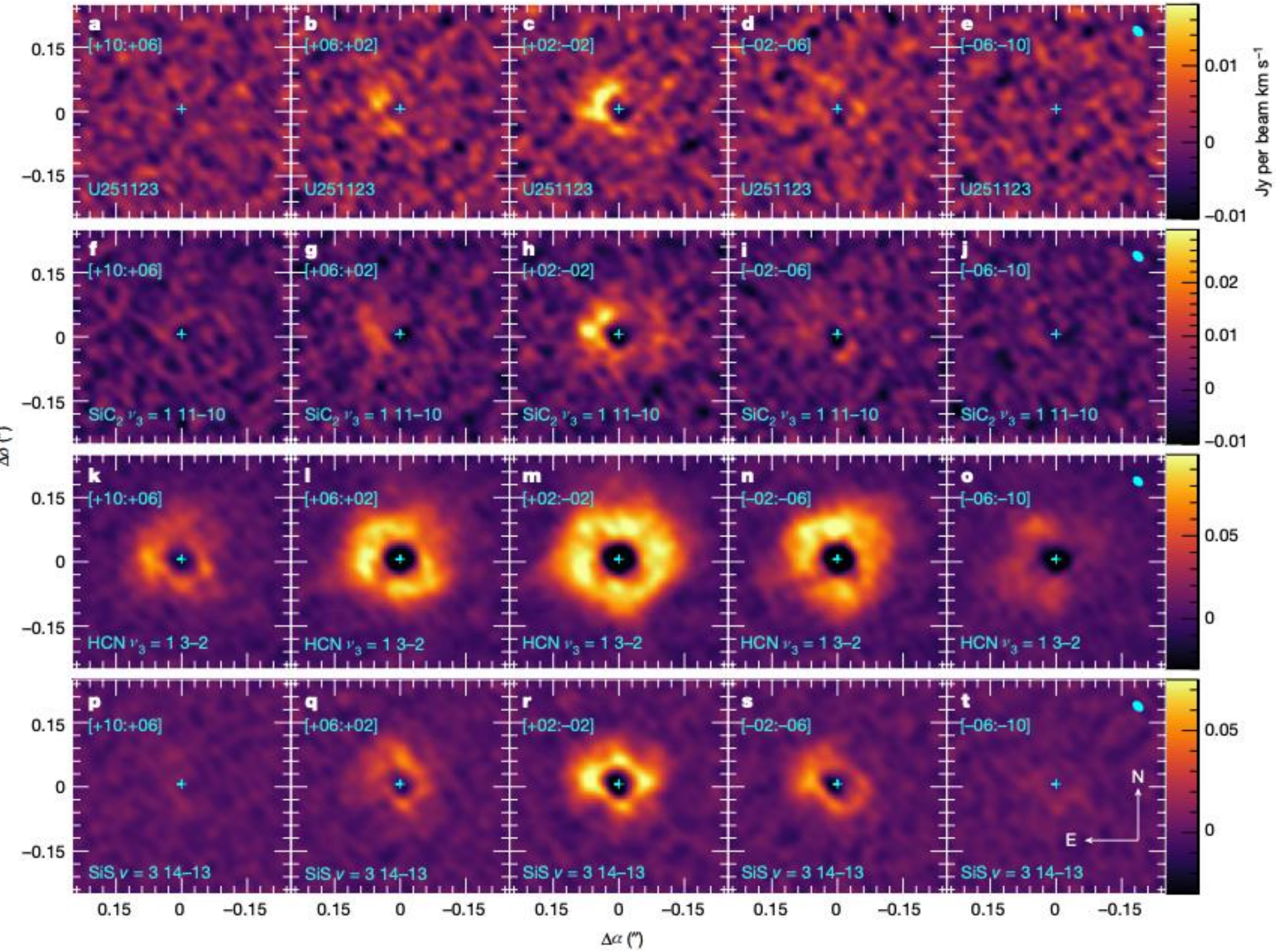
HCN **maser** transitions between the $(1,1^{1e},0)$ and $(0,4^0,0)$ vibrational states with the rotational levels from J = 7 to J = 13, observed towards IRC+10216 in 2010 May using **Herschel/HIFI**. Spectra are arranged from left to right: **(left)** the rotational lines in the $(1,1^{1e},0)$ vibrational state, **(right)** the rotational lines in the $(0,4^0,0)$ vibrational state, **(middle)** the cross-ladder lines between two vibrational states. The intensity scale is antenna temperature in K. The frequency of each line is labelled at the top of the panel in MHz. Blue solid horizontal lines represent the rotational levels, and the blue dotted line marks the J=10 rotational levels of the different vibrational states which are strongly coupled by Coriolis interaction.

Yang et al. 2025, A&A, 696, A60



Between 80 and 270 GHz we have more than 1200 unknown narrow features

The ALMA view of the DFZ of IRC+10216: gas



Molecular emission:

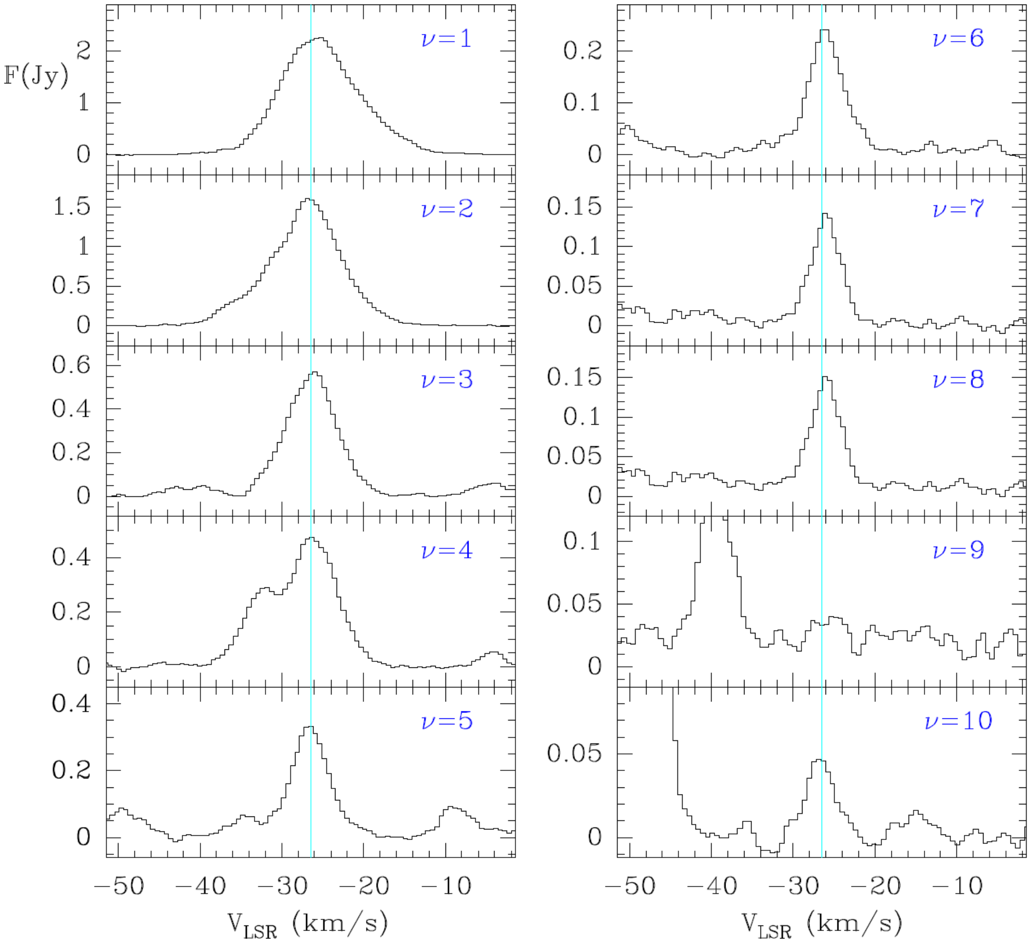
1) Shows clear departures from spherical symmetry

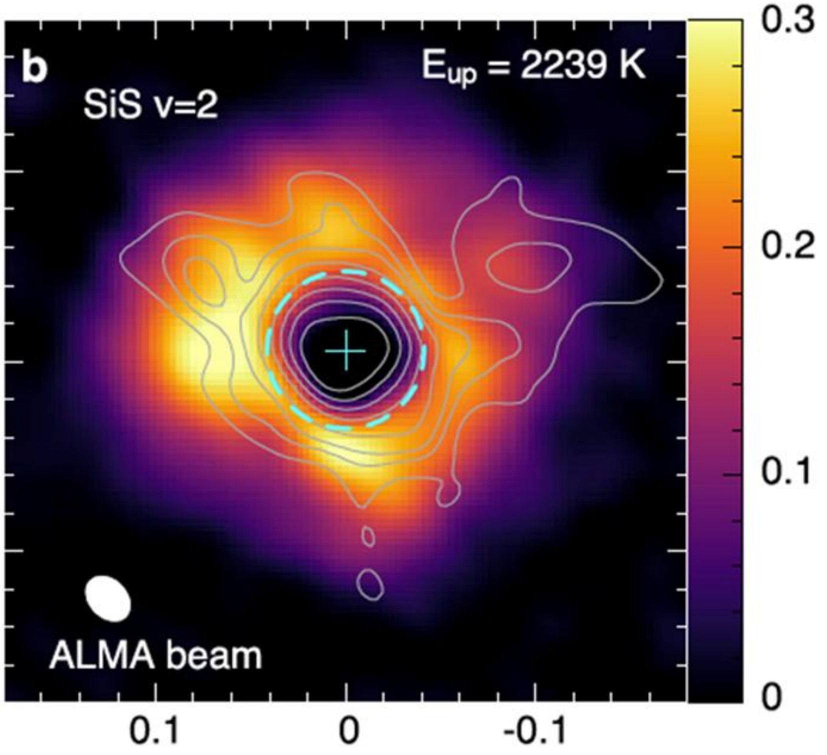
2) Different molecules show different spatial distributions

Anisotropic formation of dust grains and molecular gas hardly may be explained in a scenario of isotropic mass loss

Velilla-Prieto et al. 2023, Nature, 617, 696

SiS and other diatomic highly vibrationally excited (*v*=10)



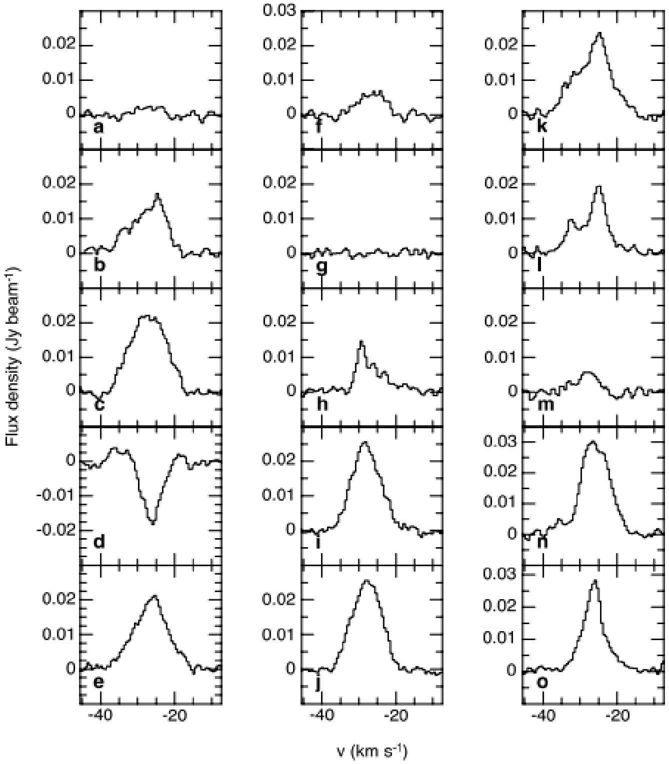


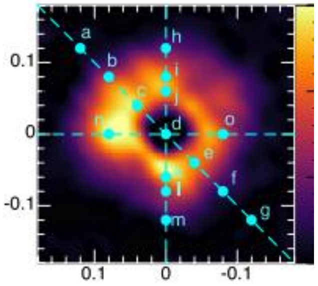
SiS v>3 is coming from a region 1-1.5R$_*$ (0.03-0.04”)

SiS v<3 is coming from the dust growth zone (1”)

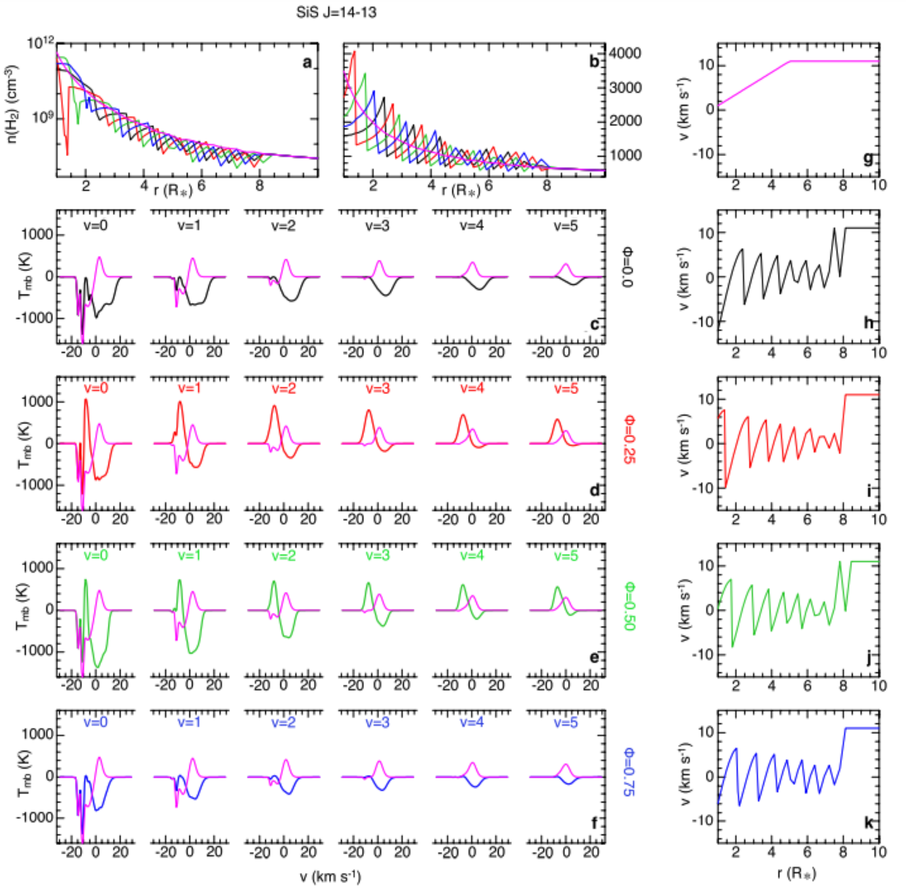
Alternative scenario : shocks

Models based on results by
Cherchneff et al. 2012





SiS v=2
J=14-13



Models do not support the presence of shocks
at the present angular resolution

Velilla-Prieto et al. 2023, Nature, 617, 696

Lack of SiC, TiC and other refractory species in the dust nucleation zone

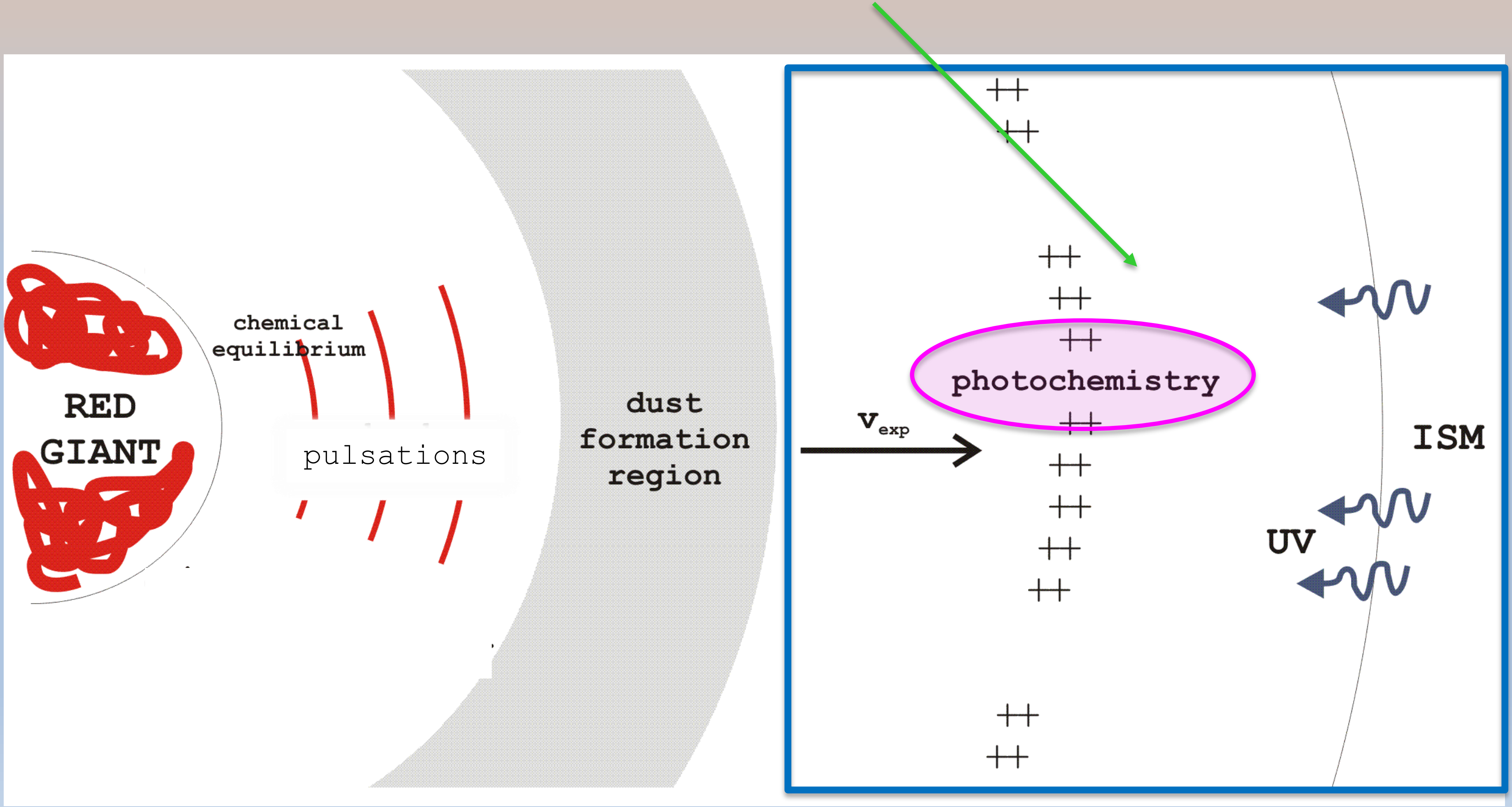
- SiC is not detected in the survey (through SiC v=1 and ^{29}SiC). It is formed in the external layers f rom photo-dissociation of SiC_2 and Si_2C.
- The most abundant species in gas phase containing a SiC bond are SiC_2 and Si_2C. Additional SiC-bearing species needed to explain the observed SiC grain feature ?
- However, none of the SiC_n molecules already detected in the external shells of IRC+10216 (SiC_3 up to SiC_6) are present in the dust formation zone. Si_nC_m are promising candidates but lacking laboratory spectroscopy.
- SiO and SiS very abundant with slowly decreasing abundance in the dust growth zone.
- No molecules with known spectrum containing Mg, Al, K, Na, Fe, Ti (oxides or carbides) detected in the dust formation zone. All of them (Metal-CN, Metal-C_nH) are formed in the external shell where radicals are formed (r∼14”).
- **Unknown molecules responsible for the forest of narrow U lines observed with ALMA. All of them participating in the dust nucleation and grain growth. These molecules disappear at distances >1”. Need for a detailed inventory of unknown-lines from cm to submm domains.**

Astrochemistry of the outer layers

Line surveys with single dish telescopes and interferometers

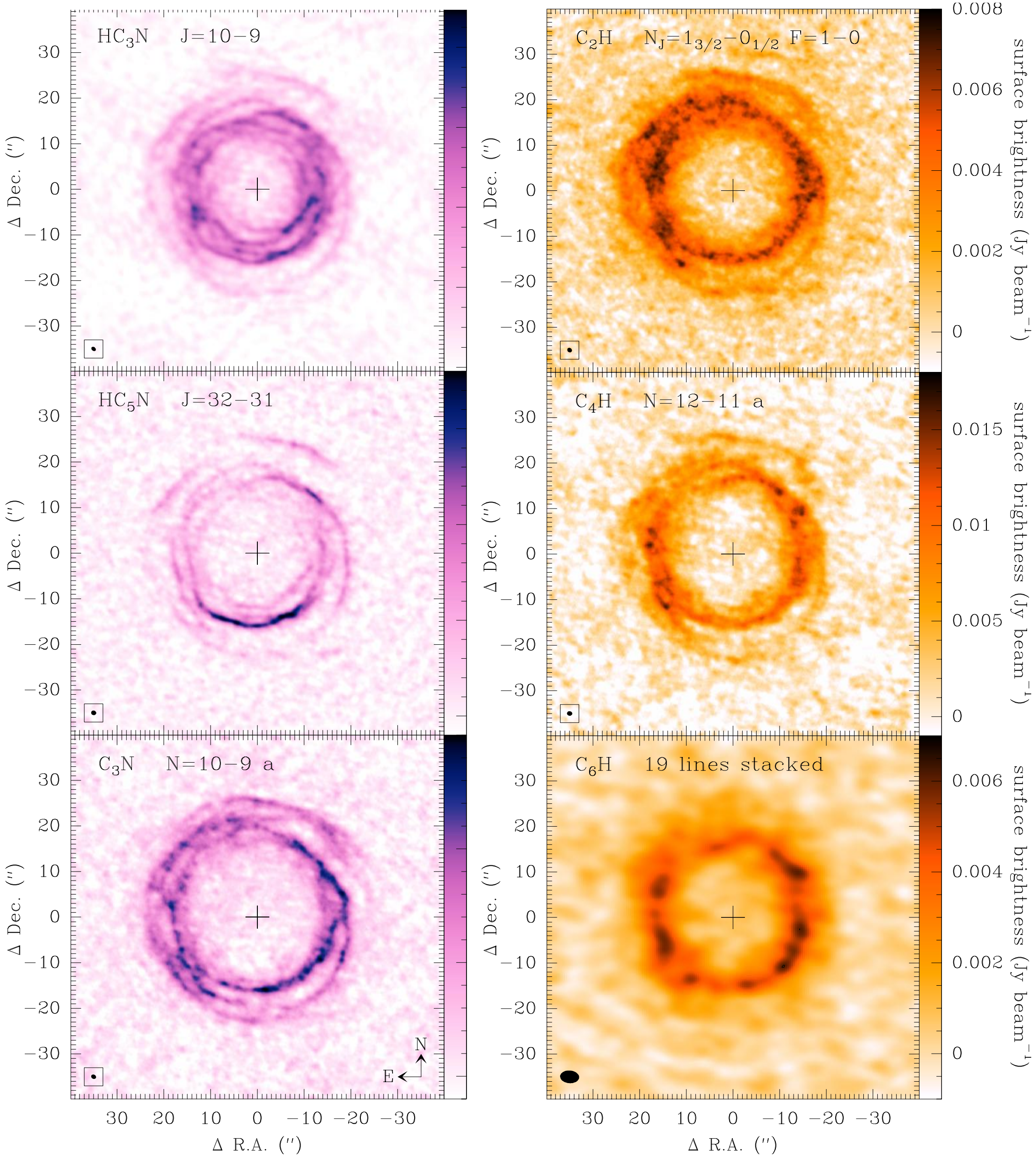
Broad frequency coverage needed to identify new species

30-350 GHz (IRAM 30m, Yebes 40m, ALMA bands 1,2+3,4)



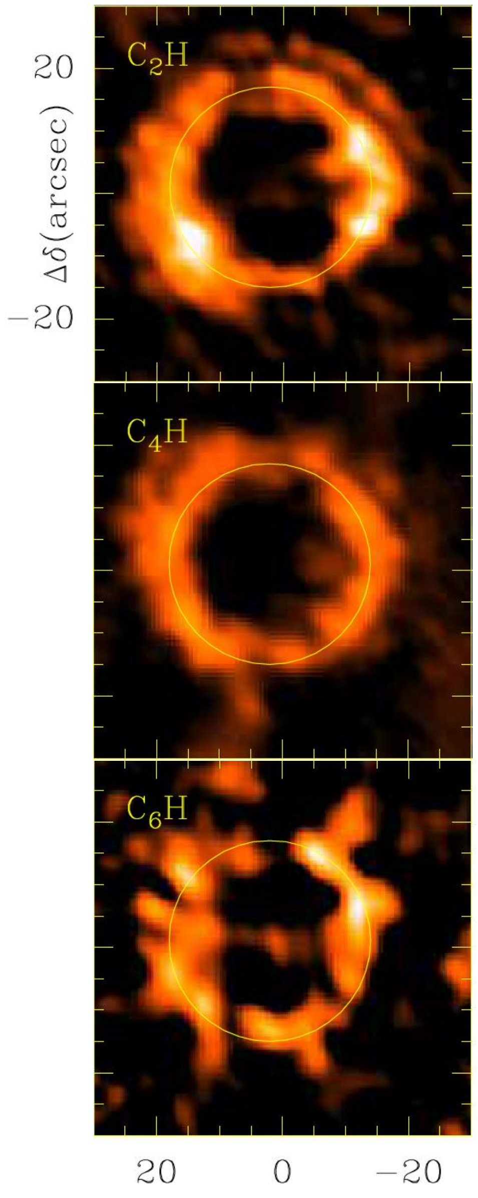
ALMA maps at 3mm

(Agúndez et al 2017)



IRAM Plateau de Bure 1990s

(Guélin et al 1999)

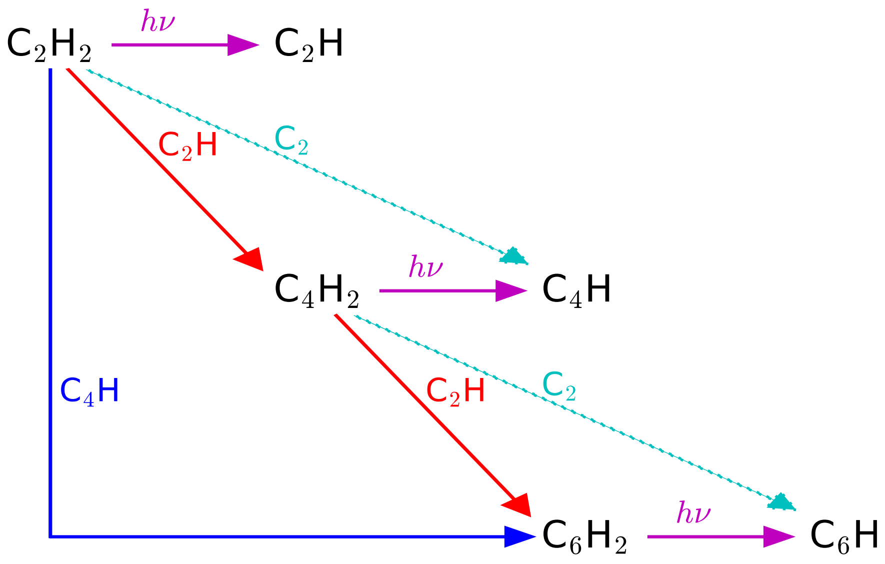


Several rings between 13-25” with a typical thickness of 1-2”

Carbon chain growth in IRC+10216

(Agúndez et al 2017)

Polyynes



$$C_2H_2 \xrightarrow{h\nu} C_2H$$

$$C_2H_2 \xrightarrow{C_2H} C_4H_2$$

$$C_2H_2 \xrightarrow{C_2} C_4H$$

$$C_4H_2 \xrightarrow{h\nu} C_4H$$

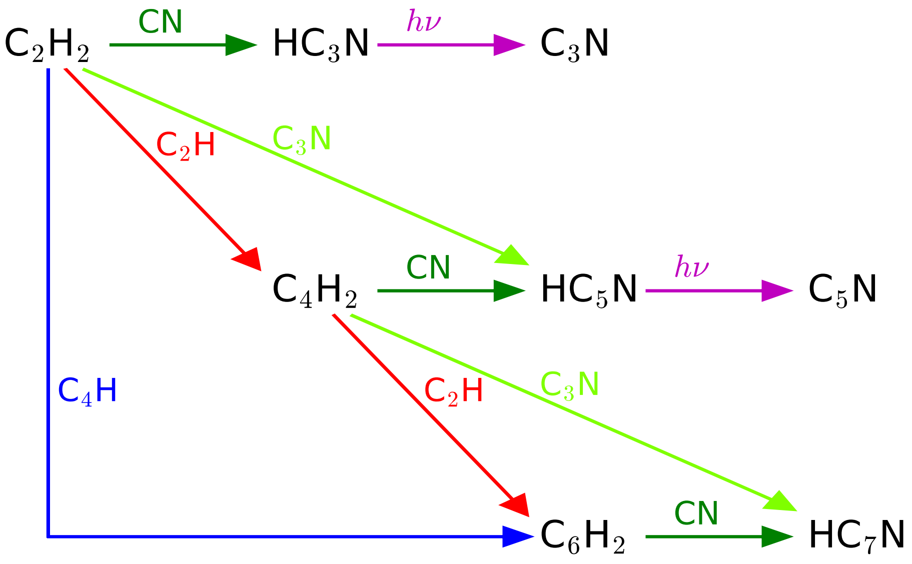
$$C_4H_2 \xrightarrow{C_2H} C_6H_2$$

$$C_4H_2 \xrightarrow{C_2} C_6H$$

$$C_2H_2 \xrightarrow{C_4H} C_6H_2$$

$$C_6H_2 \xrightarrow{h\nu} C_6H$$

Cyanopolyynes



$$C_2H_2 \xrightarrow{CN} HC_3N \xrightarrow{h\nu} C_3N$$

$$C_2H_2 \xrightarrow{C_2H} C_4H_2$$

$$C_2H_2 \xrightarrow{C_3N} HC_5N$$

$$C_4H_2 \xrightarrow{CN} HC_5N \xrightarrow{h\nu} C_5N$$

$$C_4H_2 \xrightarrow{C_2H} C_6H_2$$

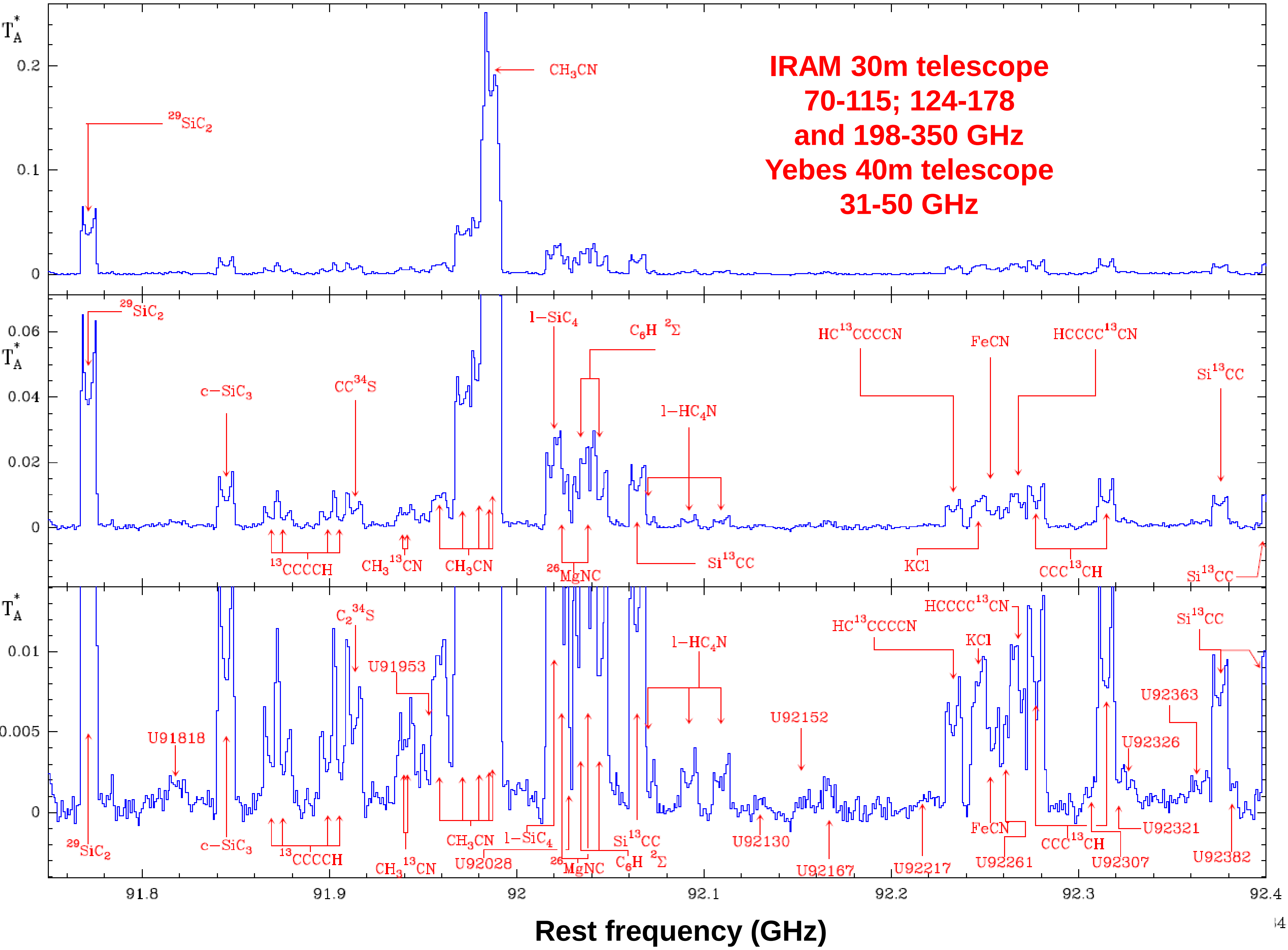
$$C_4H_2 \xrightarrow{C_3N} HC_7N$$

$$C_2H_2 \xrightarrow{C_4H} C_6H_2$$

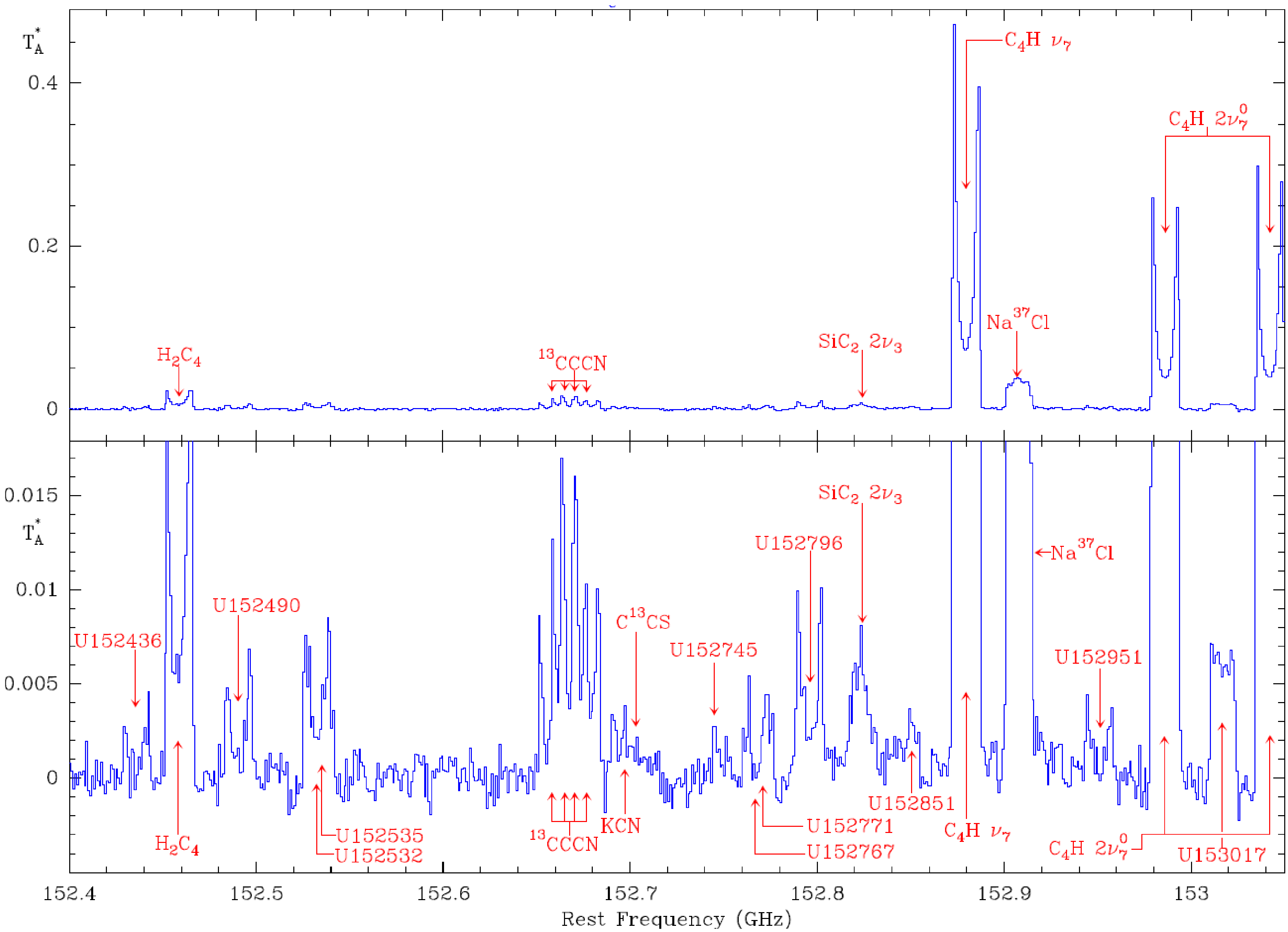
$$C_6H_2 \xrightarrow{CN} HC_7N$$

Photochemical polymerization of polyynes and cyanopolyynes in the outer envelope

No obvious photochemical route to aromatic molecules in the outer envelope
but C_nH and C_nN radicals are well explained

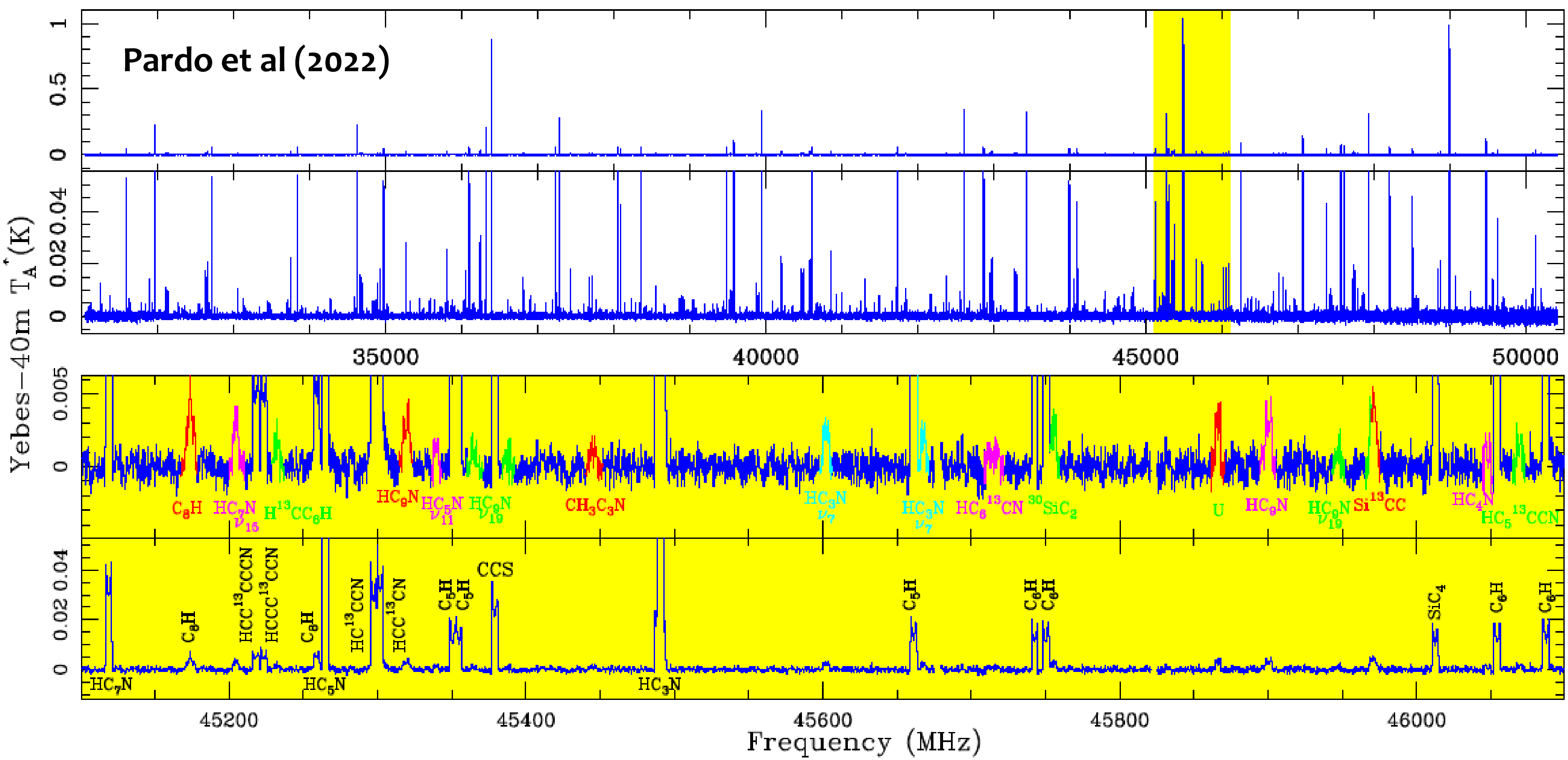


IRAM 30m telescope
70-115; 124-178
and 198-350 GHz
Yebes 40m telescope
31-50 GHz


T_A^*
0.4
0.2
0
C_4H ν_7
C_4H $2\nu_7^0$
$Na^{37}Cl$
SiC_2 $2\nu_3$
H_2C_4
$^{13}CCCN$
0.015
T_A^*
0.01
0.005
0
U152436
U152490
$C^{13}CS$
U152745
U152796
SiC_2 $2\nu_3$
$\leftarrow Na^{37}Cl$
U152951
H_2C_4
U152535
U152532
$^{13}CCCN$
KCN
U152771
U152767
U152851
C_4H ν_7
C_4H $2\nu_7^0$
U153017
152.4
152.5
152.6
152.7
152.8
152.9
153
Rest Frequency (GHz)

Yebes 40m telescope observing IRC+10216/TMC-1 in January 2021

The Yebes observatory is located in the region of La Mancha, the land of Don Quixote, at 950 m of altitude. It is around 60 km away from Madrid



Pardo et al (2022)

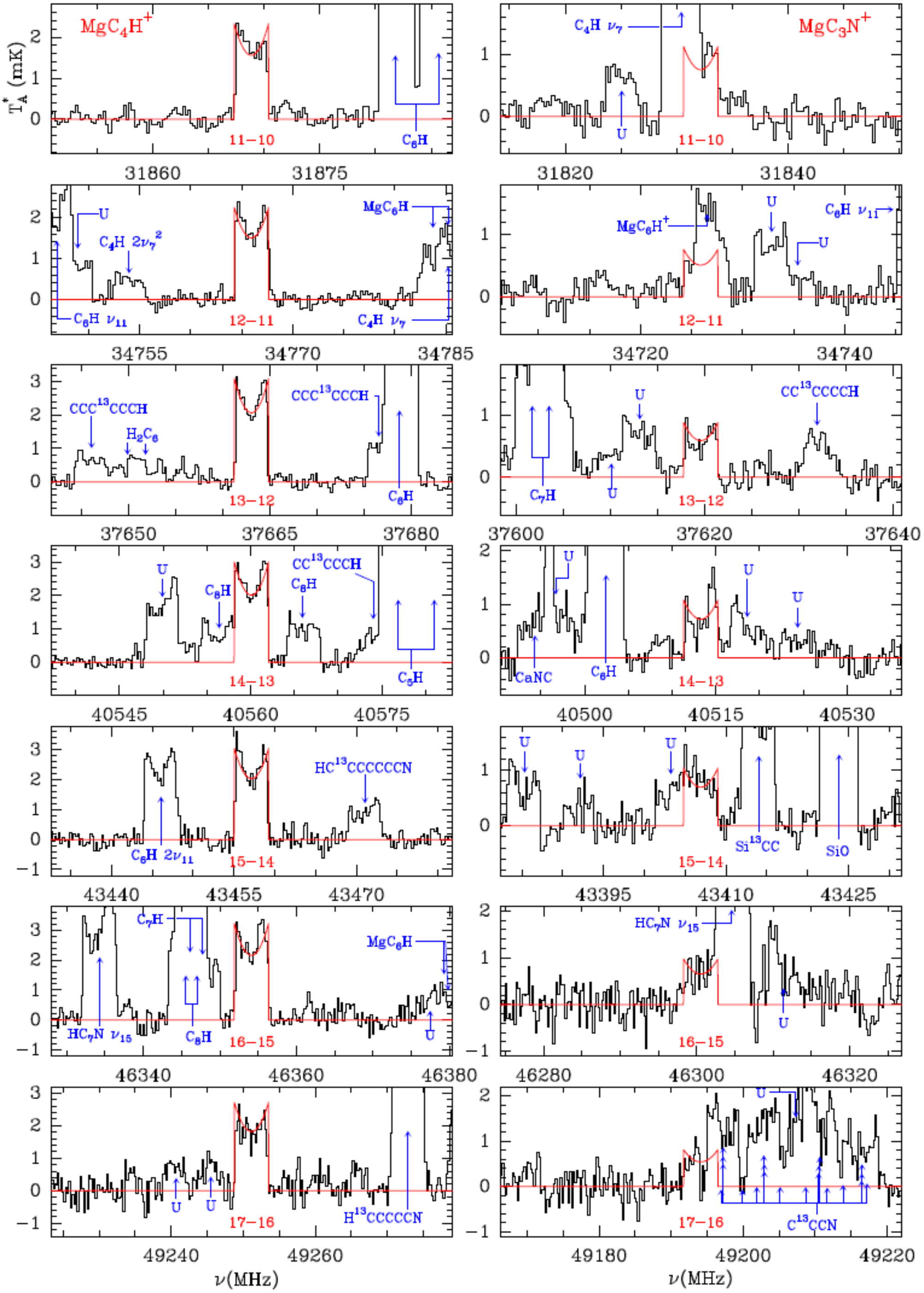


Fig. 1. Observations with the Yebes 40 m telescope toward IRC +10216. The left and right panels show the lines of B1449 and B1447 (MgC_4H^+ and MgC_3N^+), respectively. The line parameters are given in Tables A.1 and A.2, respectively. The abscissa corresponds to the rest frequency assuming a local standard of rest velocity of −26.5 km s^{-1}. The ordinate is the antenna temperature corrected for atmospheric and telescope losses in millikelvin. The red lines show the fitted line profiles adopting a terminal velocity of expansion of 14.5 km s^{-1} (Cernicharo et al. 2000).

How to identify new species from U-lines?

Looking for spectral patterns

We derive rotational constants and then we think about possible carriers (ab initio calculations)

Data from all telescopes (30m, 40m, ALMA)

A&A 672, L13 (2023)
https://doi.org/10.1051/0004-6361/202346467

Astronomy & Astrophysics

LETTER TO THE EDITOR

The magnesium paradigm in IRC +10216: Discovery of MgC_4H^+, MgC_3N^+, MgC_6H^+, and MgC_5N^+ ⋆

J. Cernicharo[1], C. Cabezas[1], J. R. Pardo[1], M. Agúndez[1], O. Roncero[1], B. Tercero[2,3], N. Marcelino[2,3],
M. Guélin[4], Y. Endo[5], and P. de Vicente[2]

Table 1. New series of lines in IRC +10216.

Series	B (MHz)	D (Hz)	Carrier	B_{calc} (a) (MHz)	D_{calc} (a) (Hz)	μ (D)	E_{up} range (K)	T_{rot} (K)	N (10^{11} cm^{-2})	N (neutral) (b) (10^{11} cm^{-2})
B1449	1448.5994±0.0013	63.45±1.15	MgC_4H^+	1447.01	63.6	13.5	9.2–78.0	17.4±0.3	4.8±0.3	220±5 (c)
B1447	1446.9380±0.0098	91.00±23.0	MgC_3N^+	1445.72	64.2	18.5	9.2–21.2	9.1±0.8	1.2±0.2	93±16 (c)
B599	598.7495±0.0011	6.13±0.43	MgC_6H^+	598.20	6.6	18.2	20.2–49.5	21.5±1.0	2.5±0.3	200±90 (d)
B594	594.3176±0.0026	4.92±1.16	MgC_5N^+	593.93	6.6	23.7	21.6–46.7	19.2±1.6	1.1±0.2	47±13 (d)

Line surveys of a carbon-rich star (IRC+10216; prototype of C-rich AGB star).

Polyatomic metal-bearing species are only detected towards the CSE of AGB stars (Mg, Na, Ca bearing species; 24 molecular species)

NaCl, KCl, AlCl, AlF (Cernicharo & Guélin 1987, A&A, 183, L10)
NaCN, MgNC, MgCN, AlCN, AlNC, KCN (see Cernicharo et al. 2023 and references therein)
HMgNC, HMgCCCN (Cabezas et al. 2013, A&A, 775, A133, Cabezas et al. 2023, 672, L12)
CaNC, CaC_2, NaCCCN (Cernicharo et al. 2019, A&A, 627, L4; Gupta et al., 2024, ApJ, 966, L28; Cabezas et al. 2023, A&A, 672, L12)
MgC_2 (Changala et al. 2022, ApJ, 940, L42)
MgC_3N,MgC_4H (Cernicharo et al. 2019, A&A, 630, L2)
MgC_5N,MgC_6H (Pardo et al. 2021, A&A, 652, L13)
MgC_3N^+, MgC_5N^+,MgC_4H^+, MgC_6H^+ (Cernicharo et al. 2023, A&A, 672, L13)

BUT NONE OF THE HYDROCARBONs FOUND IN TMC-1 WITH QUIJOTE or GOTHAM!!!!!

O-rich stars:
AlO, AlOH (Tenenbaum & Ziurys 2009, ApJ, 694, L59; Kaminski et al. 2016, A&A, 592, A42)
TiO, TiO_2 (Kaminski et al. 2013, A&A, 551, A113)

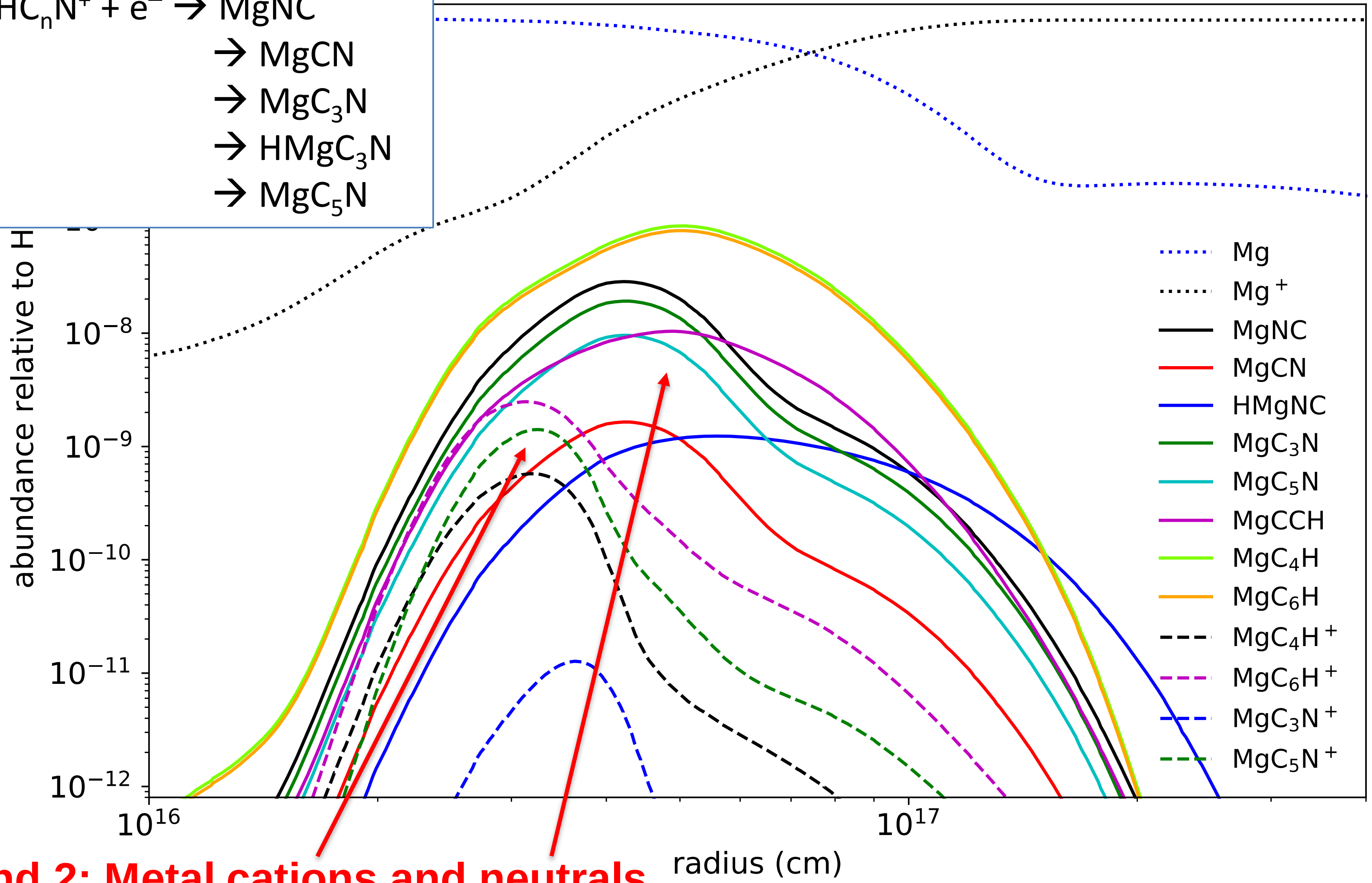
ALMA BAND 2+3 will help a lot in the identification of Metal-carbon chains (neutrals and cations). Moderate angular resolution of ~0.3-0.5” will provide key information on the chemistry

Metal chemistry in IRC+10216

Cernicharo et al (2019, 2023)
Pardo et al (2021)
Cabezas et al (2023)

$Mg^+ + HC_nN \rightarrow MgHC_nN^+ + h\upsilon$

$MgHC_nN^+ + e^- \rightarrow MgNC$
$\rightarrow MgCN$
$\rightarrow MgC_3N$
$\rightarrow HMgC_3N$
$\rightarrow MgC_5N$



Band 2: Metal cations and neutrals

Expected additional chemical complexity in the external layers

- Several hundreds of U-lines in our data awaiting potential carriers (inner and outer shells; probably different molecular species)
- Long chain metal-bearing species
- Cations of metal-bearing species
- Carbon radicals and anions
- Anions of metal-bearing species ?
- Fe, Ti, Cr –bearing species ?

- Chemical modelling of IRC+10216 (photochemistry) and TMC-1 (ion-neutral, radical-radical) => same abundances for many species but with very different formation paths ! Photo-dissociation regions.

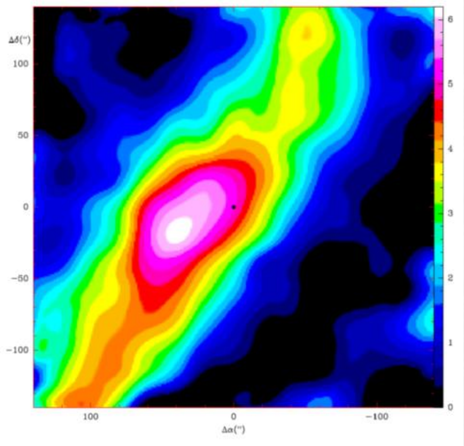
- **Close collaboration with spectroscopists and theoreticians is absolutely necessary to progress in discovering new molecules in IRC+10216 and in understanding chemical complexity (carbon, metals,…) in space**

- **Where, and when, PAHs are formed ?????**

Yebes 40m telescope observing TMC-1 in January 2021

The Yebes observatory is located in the region of La Mancha, the land of Don Quixote, at 950 m of altitude. It is around 60 km away from Madrid

Prior to QUIJOTE (2020) the radio telescope was built and equipped only for VLBI observations



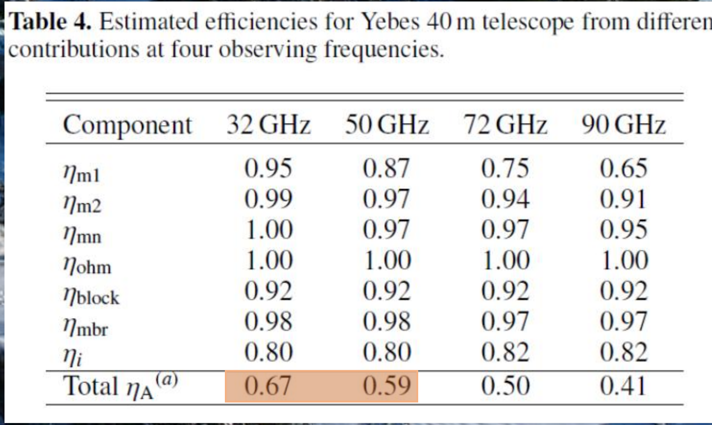


Table 4. Estimated efficiencies for Yebes 40 m telescope from differen
contributions at four observing frequencies.

Component	32 GHz	50 GHz	72 GHz	90 GHz
$\eta_{\rm m1}$	0.95	0.87	0.75	0.65
$\eta_{\rm m2}$	0.99	0.97	0.94	0.91
$\eta_{\rm mn}$	1.00	0.97	0.97	0.95
$\eta_{\rm ohm}$	1.00	1.00	1.00	1.00
$\eta_{\rm block}$	0.92	0.92	0.92	0.92
$\eta_{\rm mbr}$	0.98	0.98	0.97	0.97
η_i	0.80	0.80	0.82	0.82
Total $\eta_{\rm A}{}^{(a)}$	0.67	0.59	0.50	0.41

QUIJOTE's TEAM


Pablo de Vicente


Nuria Marcelino

Belén Tercero

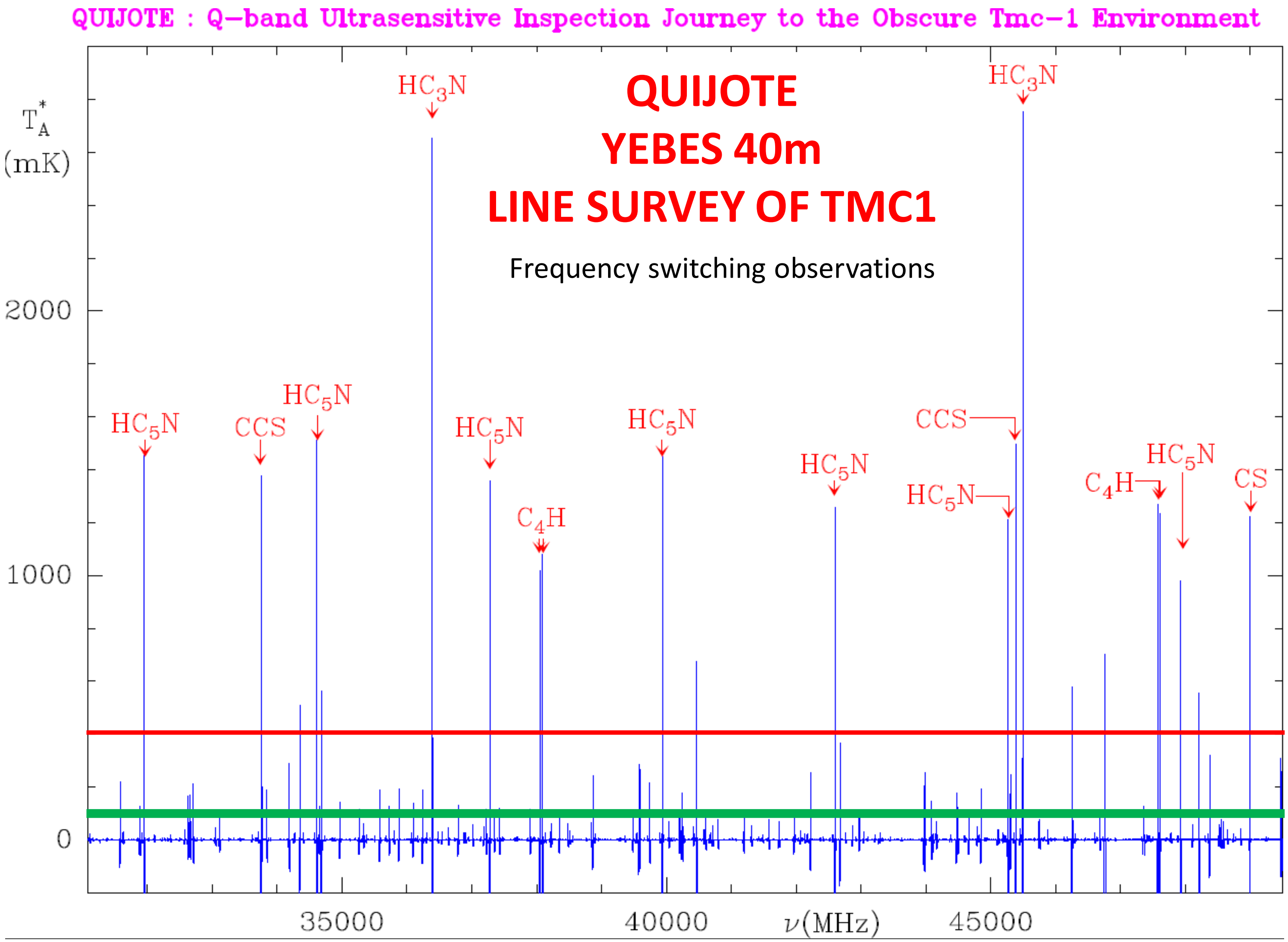

Carlos Cabezas



Raúl Fuentetaja


Marcelino Agúndez


José Cernicharo
(Pepe)



QUIJOTE
YEBES 40m
LINE SURVEY OF TMC1

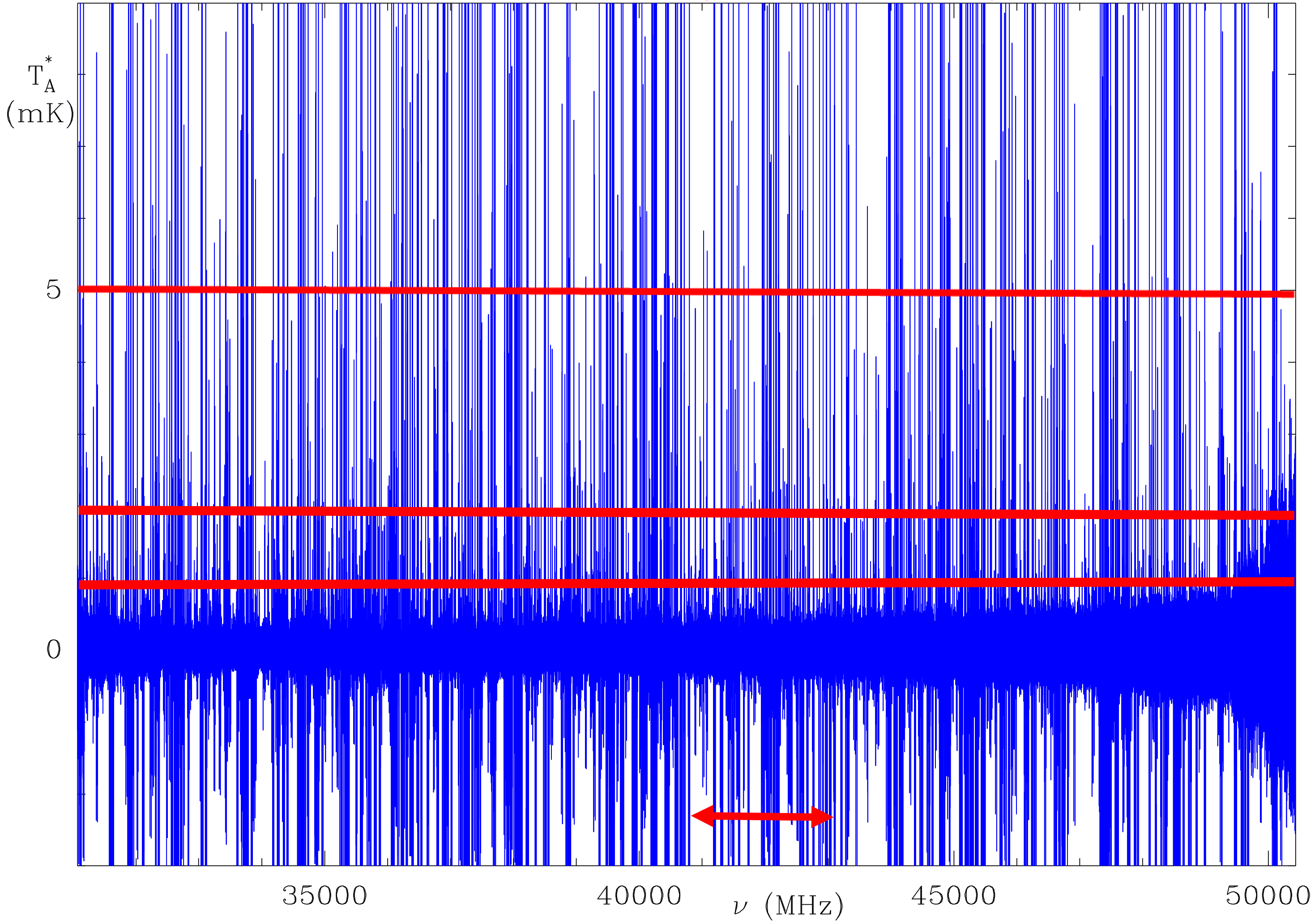
Frequency switching observations

only 22 lines above 400mK

A few more above 200 mK

First problem : all isotopologues of the carriers of the strong lines could be easily detected with QUIJOTE, but also those of the lines above the green line (100 mK). ^{13}C, D, ^{15}N, ^{34}S, ^{33}S

TMC-1 can not be considered any more as a line poor source



Above 5 mK several new species.

All lines have been IDENTIFIED

Below 5 mK: A forest of lines from isotopologues and unknown species

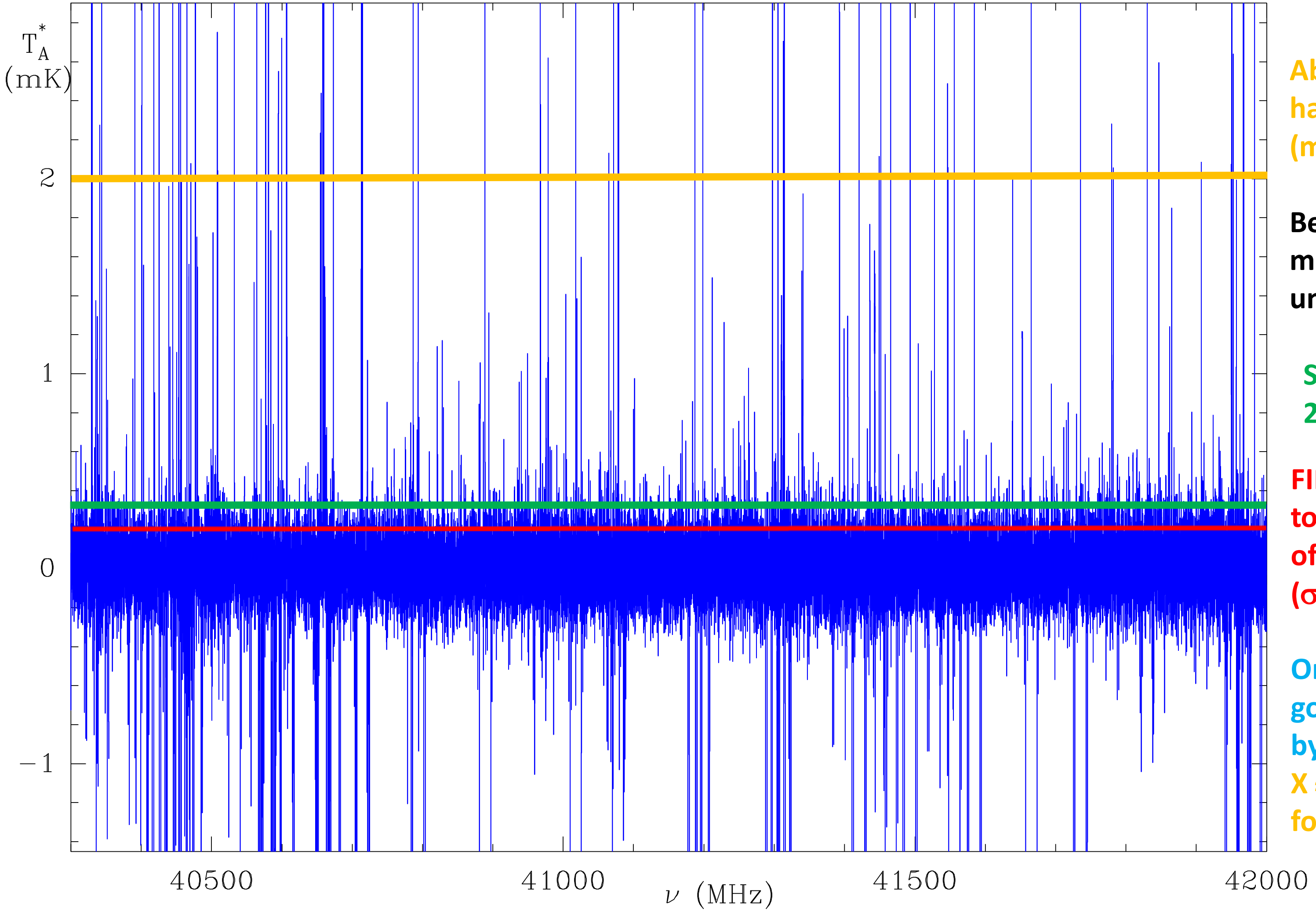
2 mK

1 mK

Data by Sept 2024

1500 hours of observing time

ULTRA DEEP SPECTRAL SURVEY: A LABORATORY FOR MOLECULAR SPECTROSCOPY



Above 2 mK most lines
have been assigned
(many new molecules)

Below 2 mK
most lines are
unidentified

Sensitivity by Sept.
2025 of 0.30 mK (5σ)

FINAL GOAL (2030)
to detect lines
of 0.20 mK at 5σ
(σ=0.04 mK)

On-going project;
goal to be reached
by 2029/2030
$X \approx 10^{-12}$
for very polar species

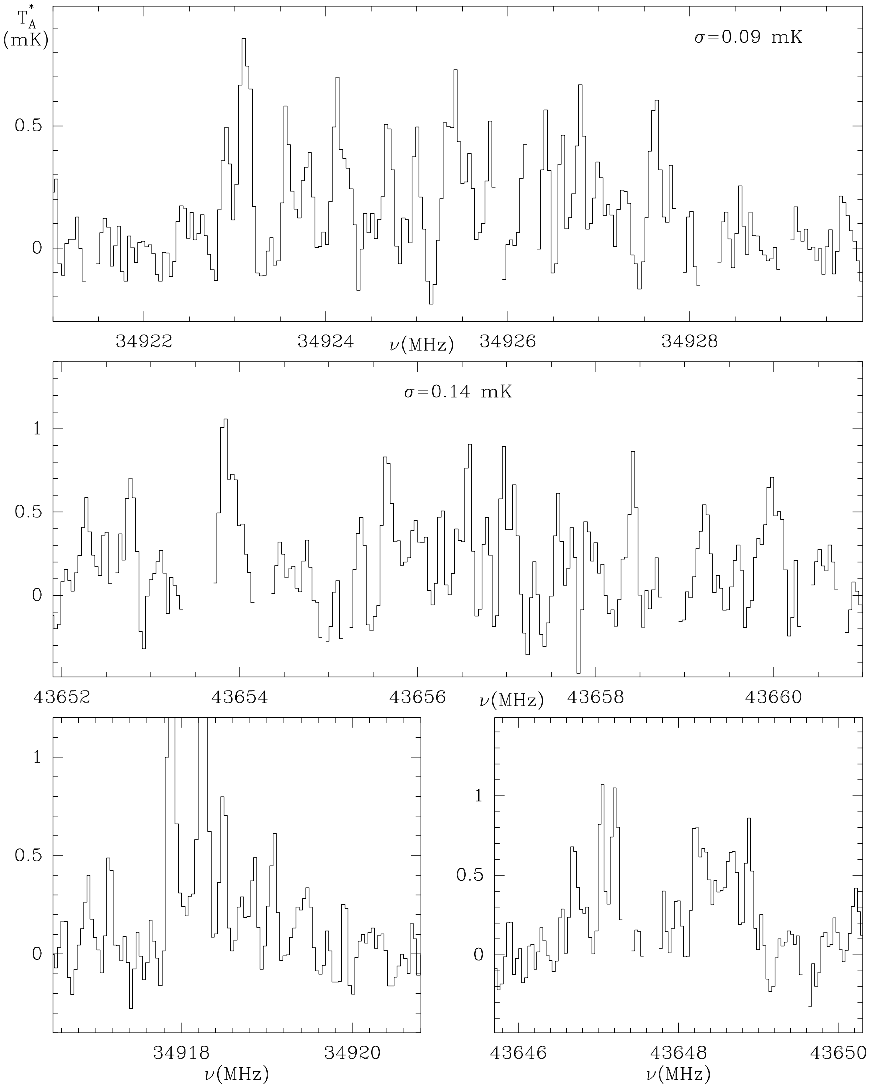
SPECTRAL PURITY

TMC-1 can not be considered as a poor line source at the QUIJOTE's sub mK level

Looking for specific spectroscopic patterns it is possible to discover new molecular species without any previous information on the frequencies.

TMC-1 is a chemical laboratory for molecular spectroscopy thanks to QUIJOTE and NANOCOSMOS.

QUIJOTE can now fight against the giant windmills of the forest of U-lines of TMC-1



ν_2/ν_1=1.249993 ≈ 5/4

Transitions N=5-4 and N=4-3 of a new radical ???

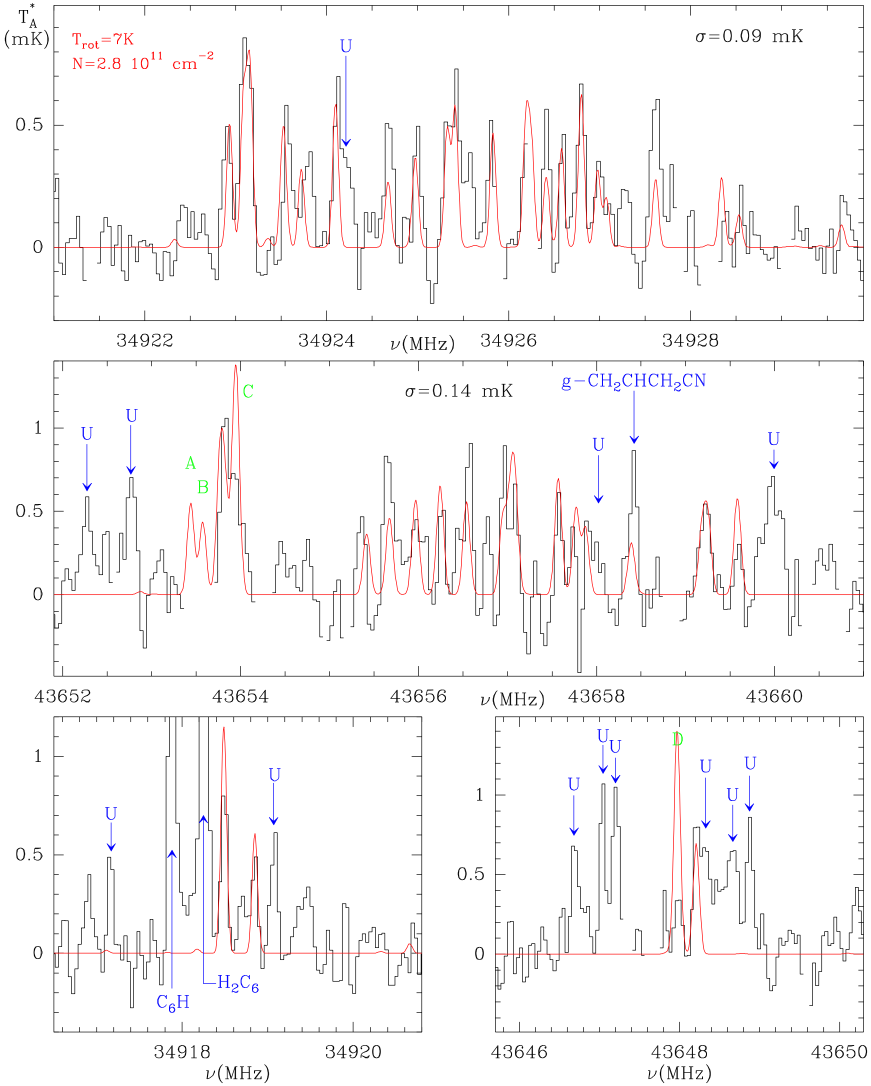
B or (B+C)/2 ≈ 4365 MHz

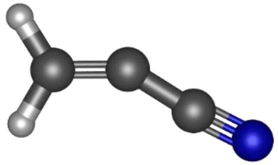
HCCCN has B=4549.1 MHz

H_2CCCN ???

Excellent data quality
All features are real.
Sensitivity continues
to increase with time.

Systematic instrumental
effects removed and
uncerstood



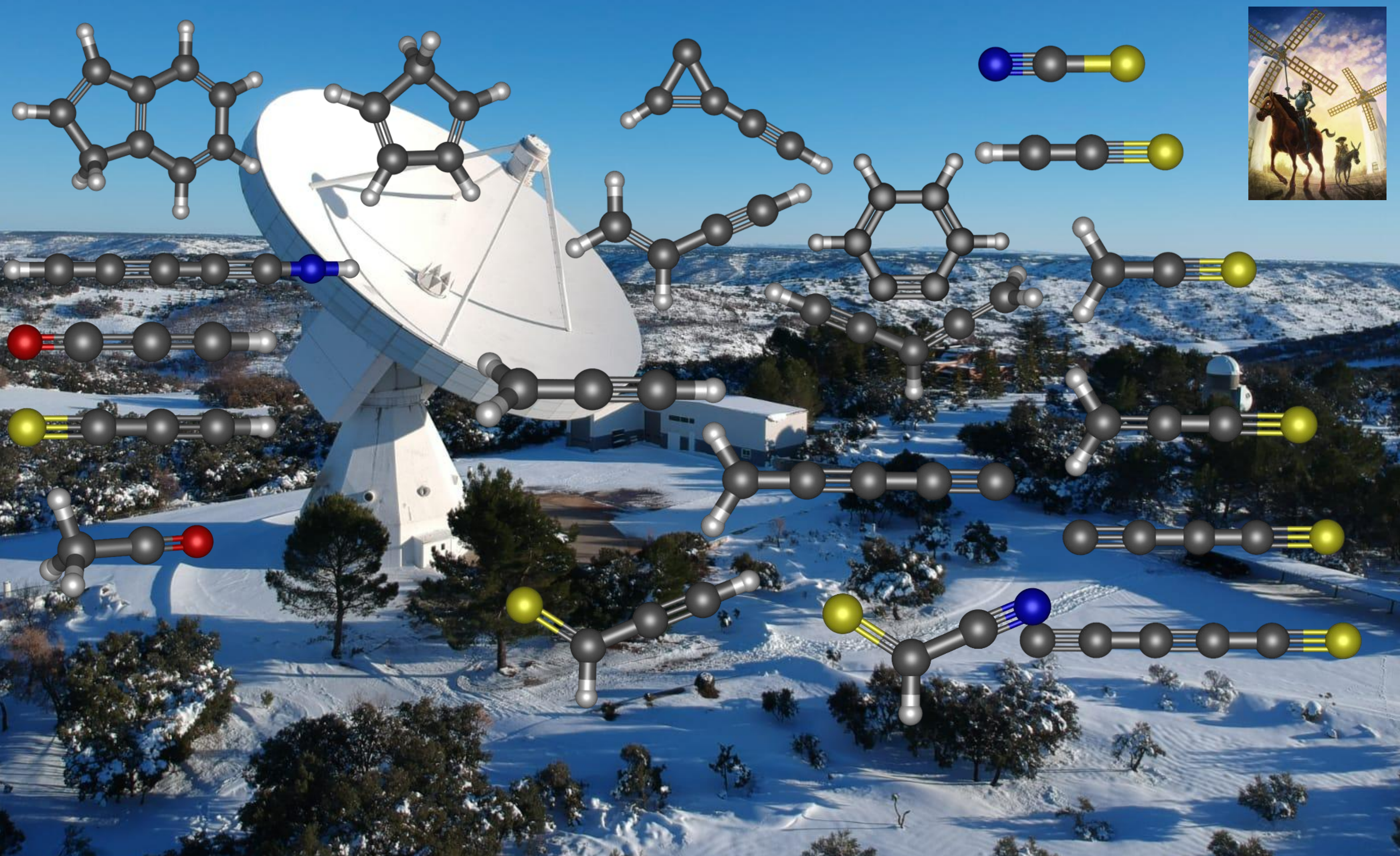


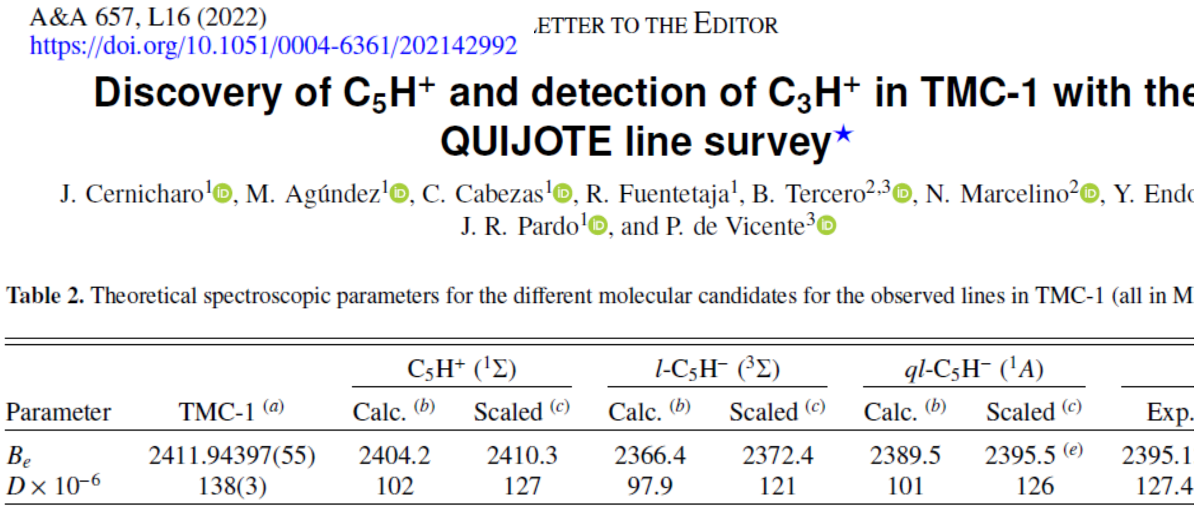
H_2CCCN radical
Cabezas et al. 2023,
A&A, 676, L5

Laboratory data from
Endo's team

QUIJOTE: Q-band Ultrasensitive Inspection Journey to the Obscure TMC-1 Environment

Cernicharo et al. (22 (+4) new species discovered in space by winter 2021)





A&A 657, L16 (2022)
https://doi.org/10.1051/0004-6361/202142992

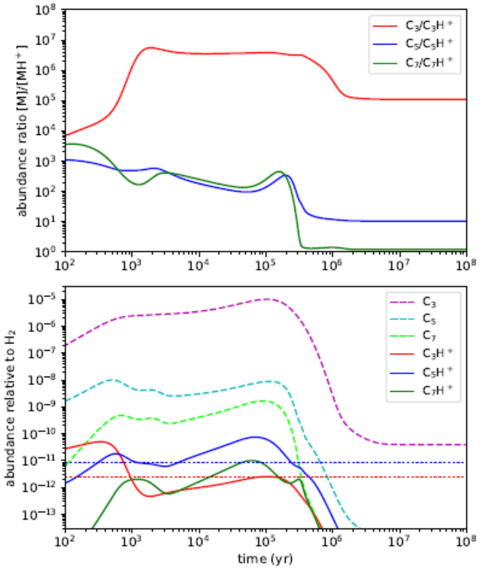
ETTER TO THE EDITOR

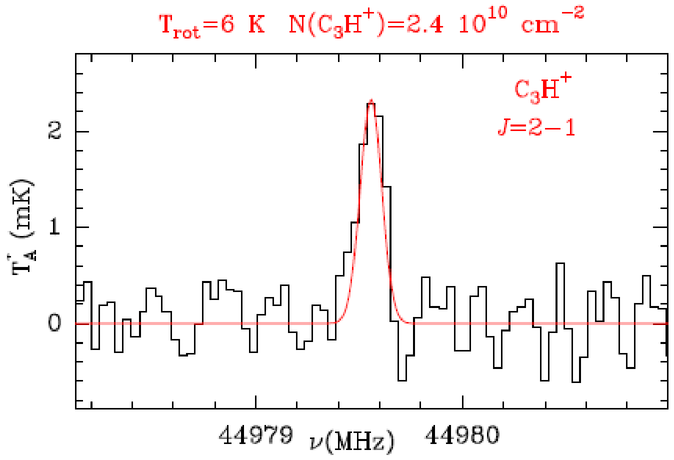
Discovery of C_5H^+ and detection of C_3H^+ in TMC-1 with the QUIJOTE line survey★

J. Cernicharo[1], M. Agúndez[1], C. Cabezas[1], R. Fuentetaja[1], B. Tercero[2,3], N. Marcelino[2], Y. End
J. R. Pardo[1], and P. de Vicente[3]

Table 2. Theoretical spectroscopic parameters for the different molecular candidates for the observed lines in TMC-1 (all in M

		C_5H^+ ($^1\Sigma$)		l-C_5H^- ($^3\Sigma$)		ql-C_5H^- (^1A)		
Parameter	TMC-1 $^{(a)}$	Calc. $^{(b)}$	Scaled $^{(c)}$	Calc. $^{(b)}$	Scaled $^{(c)}$	Calc. $^{(b)}$	Scaled $^{(c)}$	Exp.
B_e	2411.94397(55)	2404.2	2410.3	2366.4	2372.4	2389.5	2395.5 $^{(e)}$	2395.1
$D \times 10^{-6}$	138(3)	102	127	97.9	121	101	126	127.4





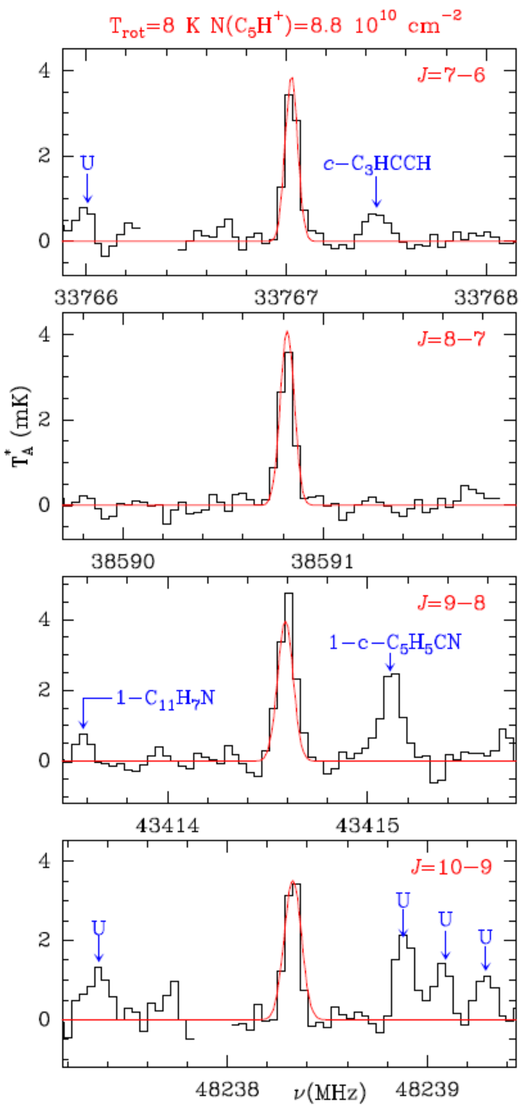
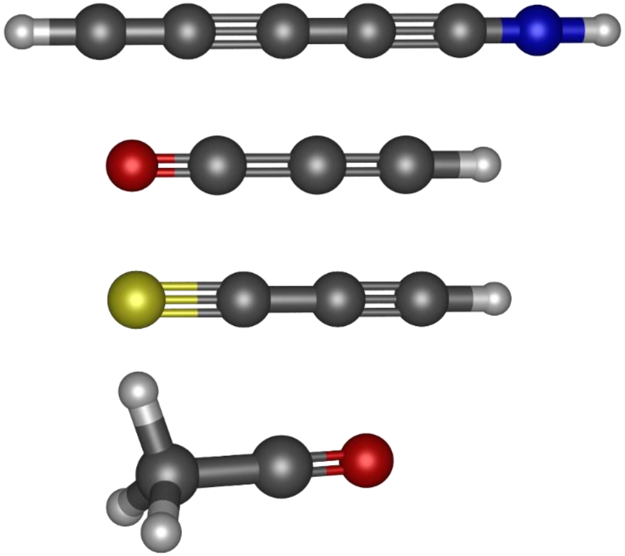


Fig. 1. Observed lines of C_5H^+ toward TMC-1. Line parameters are given in Table 1. The abscissa corresponds to the rest frequency assuming a local standard of rest velocity of 5.83 km s^{-1}. The ordinate is the antenna temperature corrected for atmospheric and telescope losses in mK. The red line shows the synthetic spectrum derived for T_{rot} = 8 K and N(C_5H^+) = 8.8 × 10^{10} cm^{-2}. Blank channels correspond to negative features produced in the folding of the frequency-switching data.

Broad band spectroscopy is mandatory. ALMA Band 2 (67-116 GHz) offers 50 GHz

TMC-1 as a spectroscopic laboratory

- **Detection of species WITHOUT previous laboratory data**. Searching for systematic spectral patterns in the data. Confirming assignments in the laboratory when possible and through ab initio calculations



- **HC_5NH^+** **Marcelino et al., 2020, A&A, 643, L6**
- **HC_3O^+** * **Cernicharo et al., 2020, A&A, 642, L17**
- **HC_3S^+** * **Cernicharo et al., 2021, A&A, 646, L3**
- **CH_3CO^+** * **Cernicharo et al., 2021, A&A, 646, L7**
- **C_5H^+** **Cernicharo et al., 2022, A&A, 657, L16**
- **HC_7NH^+** **Cabezas et al., 2022, A&A, 659, L8**
- **$HCCNCH^+$** **Agúndez et al., 2022, A&A, 659, L9**
- **$HCCS^+$** **Cabezas et al., 2022, A&A, 657, L4**
- **C_7N^-** **Cernicharo et al. 2023, A&A, 670, L19**
- **NC_4NH^+** **Agúndez et al. 2023, A&A, 669, L1**
- **$C_{10}H^-$** **GOTHAM, Remijan et al. 2023, ApJ, 944, L45**
- **And isotopologues such as HDCCN, Cabezas et al., 2021, A&A, 646, L1; CH_2DC_3N, Cabezas et al, 2021**

- Additionally, QUIJOTE has confirmed the previous detection of C_5N^- in IRC+10216 by detection of six narrow lines of this species in TMC-1 (**together with C_3N^-**). Rotational constants for these species have been improved.

TMC-1 : The sulfur factory

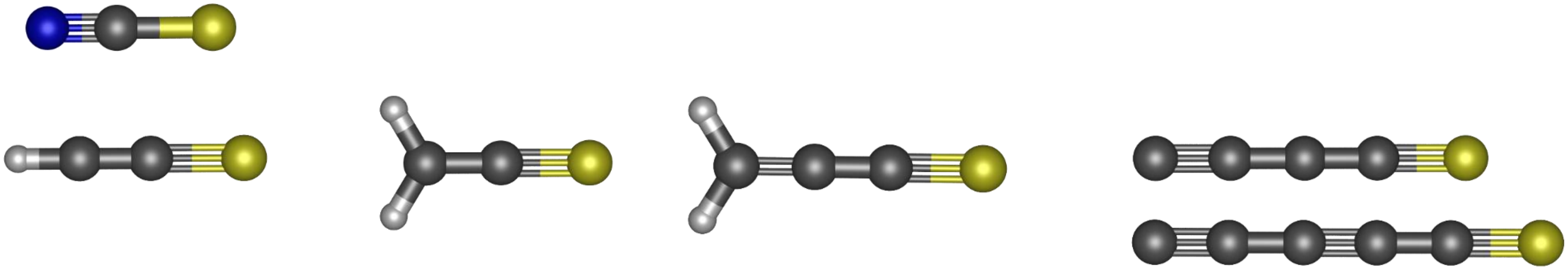
A&A 648, L3 (2021)
https://doi.org/10.1051/0004-6361/202140642

Astronomy & Astrophysics

Letter to the Editor

TMC-1, the starless core sulfur factory: Discovery of NCS, HCCS, H_2CCS, H_2CCCS, and C_4S and detection of C_5S★

J. Cernicharo[1], C. Cabezas[1], M. Agúndez[1], B. Tercero[2,3], J. R. Pardo[1], N. Marcelino[1], J. D. Gallego[3], F. Tercero[3], J. A. López-Pérez[3], and P. de Vicente[3]

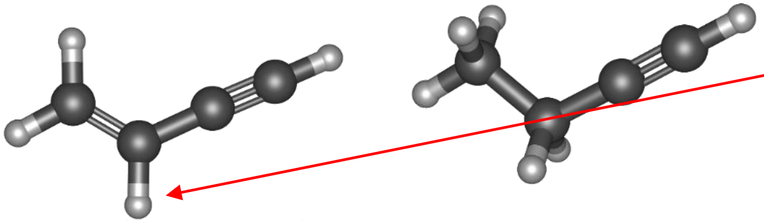


A total of 17 S-bearing species in TMC-1 between 2020 and 2025
All them sulphur-carbon chains

Pure hydrocarbons in TMC-1

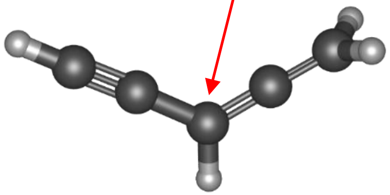
- **Discovery of several high abundant pure hydrocarbons, including three cycles (species with low dipole moment)**

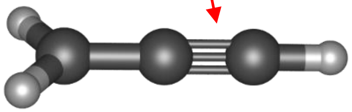
- **CH_2CHCCH**, Cernicharo et al. 2021, A&A, 647, L2 (together with HCCN, HC_4N, CH_3CH_2CN and tentatively CH_3CH_2CCH; confirmed recently)

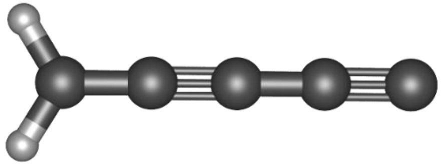


Very abundant species

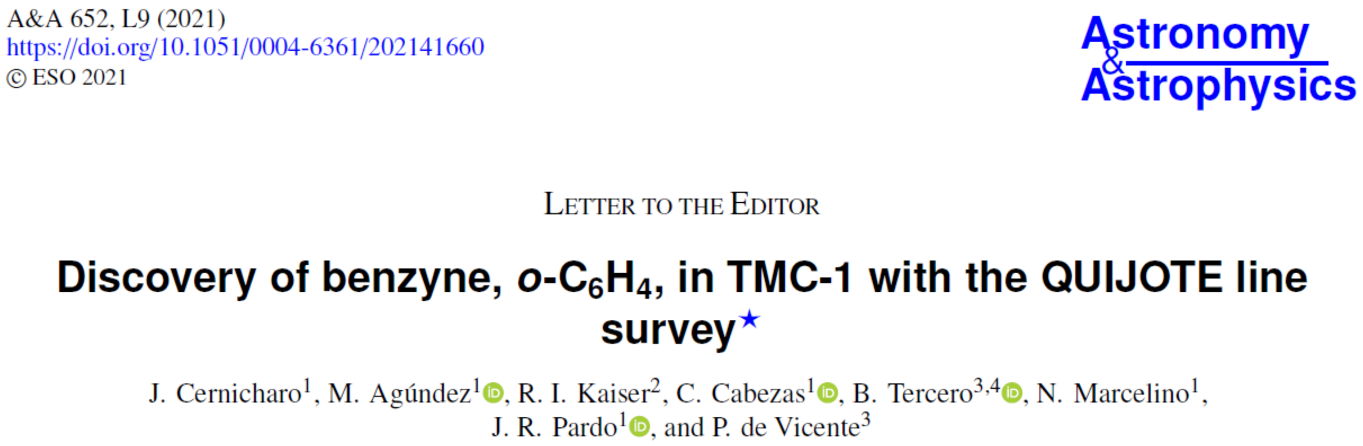
- **$H_2CCCHCCH$,** Cernicharo et al. 2021, A&A, 647, L3
- **$H_2CCCHCCCH$**, Fuentetaja et al. 2022, A&A, 663, L3
- **HCCCHCCC,** Fuentetaja et al., 2022, 667, L4
- **H_2CCCH,** Agúndez et al., 2021, 647, L10 **(extremely abundant !!!)**
- **c-C_5H,** Cabezas et al. 2022, A&A, 663, L2
- **H_2C_5,** Cabezas et al., 2021, A&A, 650, L9







None of these hydrocarbons have been found in IRC+10216



A&A 652, L9 (2021)
https://doi.org/10.1051/0004-6361/202141660
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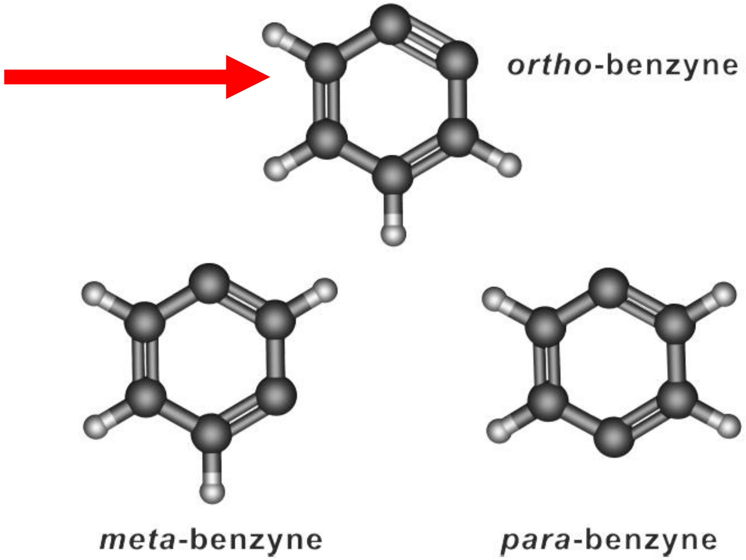
Astronomy & Astrophysics

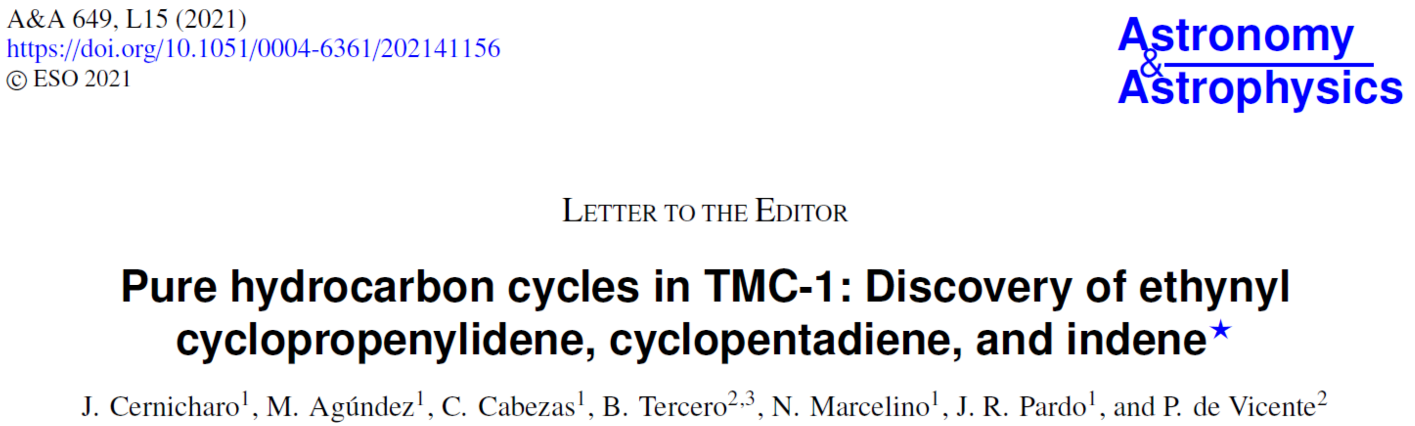
Letter to the Editor

Discovery of benzyne, o-C_6H_4, in TMC-1 with the QUIJOTE line survey[★]

J. Cernicharo[1], M. Agúndez[1], R. I. Kaiser[2], C. Cabezas[1], B. Tercero[3,4], N. Marcelino[1],
J. R. Pardo[1], and P. de Vicente[3]



None of these hydrocarbons have been found in IRC+10216



A&A 649, L15 (2021)
https://doi.org/10.1051/0004-6361/202141156

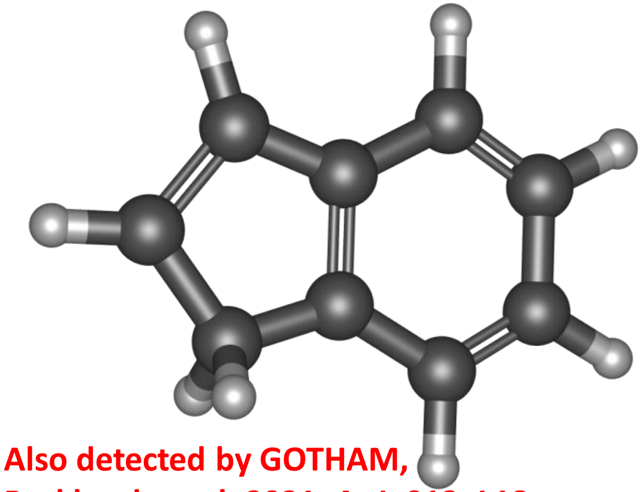
Astronomy & Astrophysics

Letter to the Editor

Pure hydrocarbon cycles in TMC-1: Discovery of ethynyl cyclopropenylidene, cyclopentadiene, and indene★

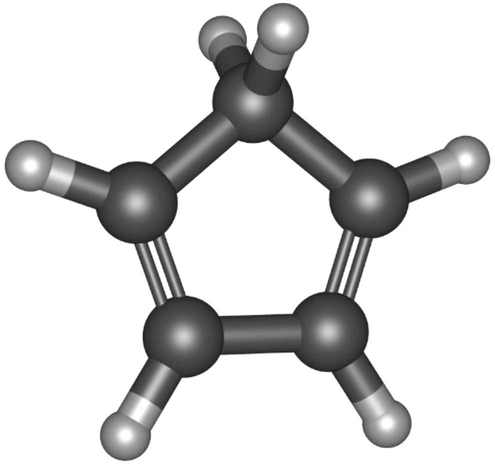
J. Cernicharo[1], M. Agúndez[1], C. Cabezas[1], B. Tercero[2,3], N. Marcelino[1], J. R. Pardo[1], and P. de Vicente[2]

Indene c-C_9H_8

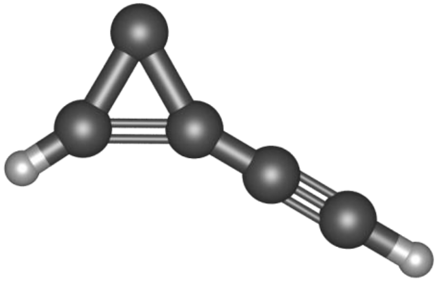


Also detected by GOTHAM, Burkhardt et al. 2021, ApJ, 913, L18

Cyclopentadiene c-C_5H_6

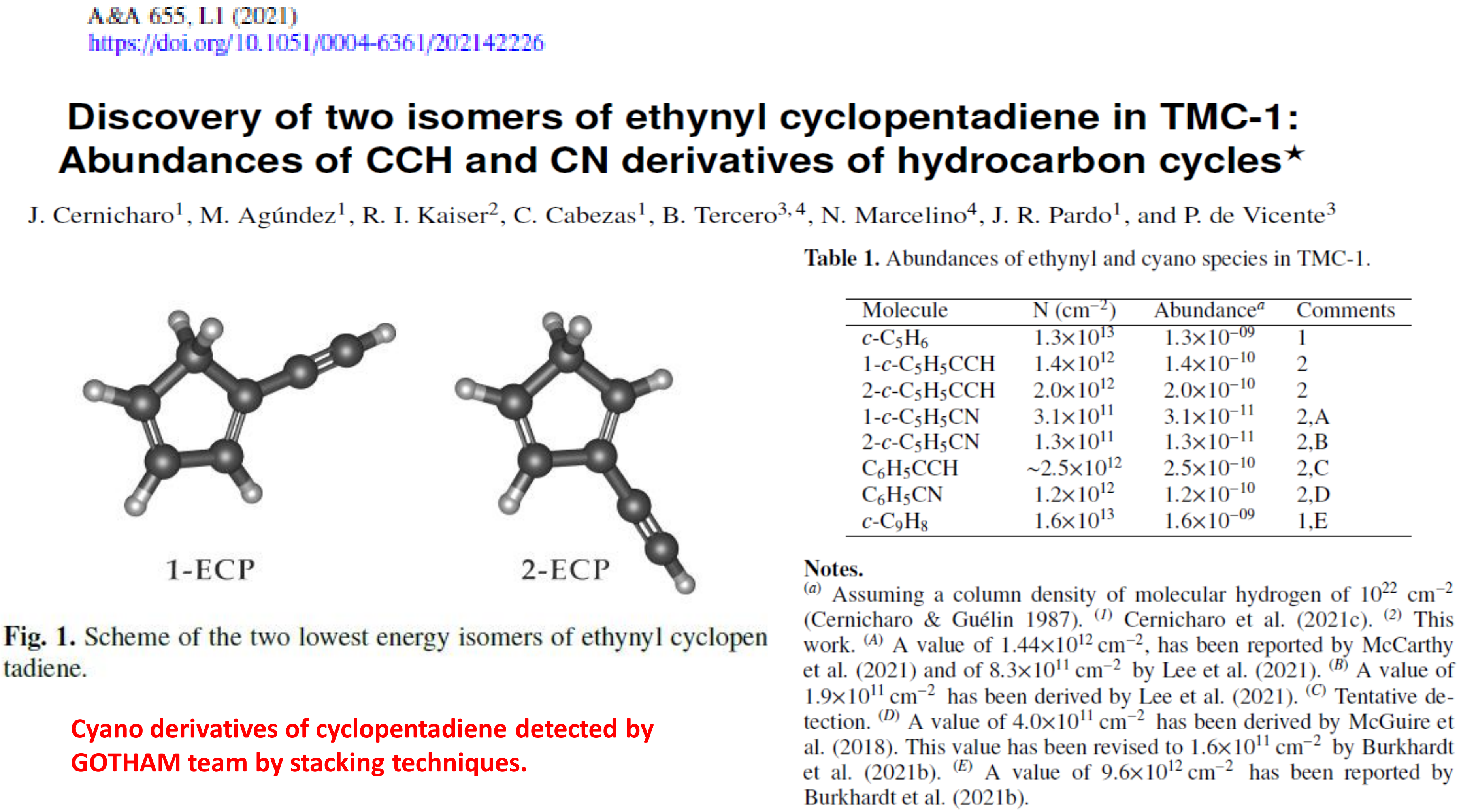


CN derivatives of cyclopentadiene detected by GOTHAM



Ethynyl cyclopropenylidene c-C_5H_2

None of these hydrocarbons have been found in IRC+10216



A&A 655, L1 (2021)
https://doi.org/10.1051/0004-6361/202142226

Discovery of two isomers of ethynyl cyclopentadiene in TMC-1: Abundances of CCH and CN derivatives of hydrocarbon cycles★

J. Cernicharo[1], M. Agúndez[1], R. I. Kaiser[2], C. Cabezas[1], B. Tercero[3,4], N. Marcelino[4], J. R. Pardo[1], and P. de Vicente[3]

1-ECP

2-ECP

Fig. 1. Scheme of the two lowest energy isomers of ethynyl cyclopentadiene.

Cyano derivatives of cyclopentadiene detected by GOTHAM team by stacking techniques.

Table 1. Abundances of ethynyl and cyano species in TMC-1.

Molecule	N (cm^{-2})	Abundance^a	Comments
c-C_5H_6	1.3×10^{13}	1.3×10^{-09}	1
1-c-C_5H_5CCH	1.4×10^{12}	1.4×10^{-10}	2
2-c-C_5H_5CCH	2.0×10^{12}	2.0×10^{-10}	2
1-c-C_5H_5CN	3.1×10^{11}	3.1×10^{-11}	2,A
2-c-C_5H_5CN	1.3×10^{11}	1.3×10^{-11}	2,B
C_6H_5CCH	~2.5×10^{12}	2.5×10^{-10}	2,C
C_6H_5CN	1.2×10^{12}	1.2×10^{-10}	2,D
c-C_9H_8	1.6×10^{13}	1.6×10^{-09}	1,E

Notes.
(a) Assuming a column density of molecular hydrogen of 10^{22} cm^{-2} (Cernicharo & Guélin 1987). (1) Cernicharo et al. (2021c). (2) This work. (A) A value of 1.44×10^{12} cm^{-2}, has been reported by McCarthy et al. (2021) and of 8.3×10^{11} cm^{-2} by Lee et al. (2021). (B) A value of 1.9×10^{11} cm^{-2} has been derived by Lee et al. (2021). (C) Tentative detection. (D) A value of 4.0×10^{11} cm^{-2} has been derived by McGuire et al. (2018). This value has been revised to 1.6×10^{11} cm^{-2} by Burkhardt et al. (2021b). (E) A value of 9.6×10^{12} cm^{-2} has been reported by Burkhardt et al. (2021b).

None of these hydrocarbons have been found in IRC+10216

A&A, 690, L13 (2024)
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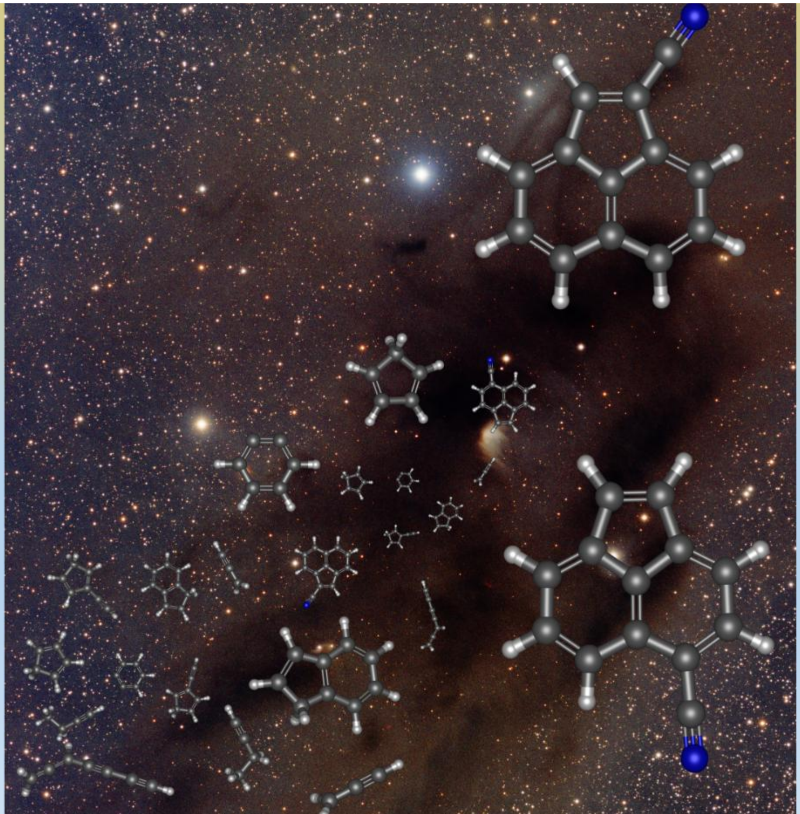
Astronomy & Astrophysics

LETTER TO THE EDITOR

Discovery of two cyano derivatives of acenaphthylene ($C_{12}H_8$) in TMC-1 with the QUIJOTE line survey★

J. Cernicharo[1,★★], C. Cabezas[1], R. Fuentetaja[1], M. Agúndez[1], B. Tercero[2,3], J. Janeiro[4], M. Juanes[5], R. I. Kaiser[6], Y. Endo[7], A. L. Steber[5], D. Pérez[4], C. Pérez[5], A. Lesarri[5], N. Marcelino[2,3], and P. de Vicente[2]



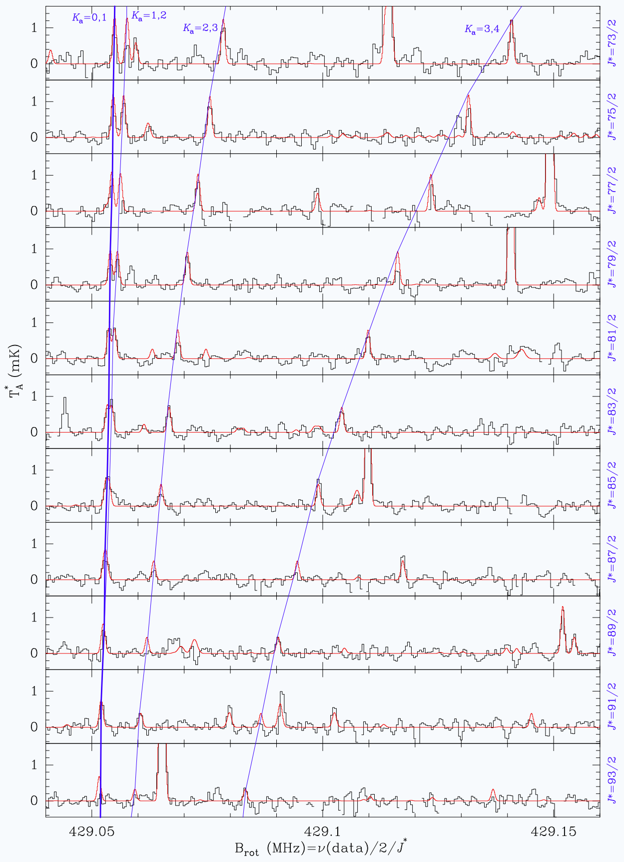
Detected and fully characterized in TMC-1

Synthetised in the chemical lab

Observed in the microwave laboratory

Space and laboratory rotational constants differ by less than 2 kHz

DISCOVERY OF TWO UNEXPECTED PAHs WITHOUT PREVIOUS LAB DATA PARTICULAR BEHAVIOUR OF THE Ka=0,1 LINES. HARMONIC RELATIONS WITH HALF INTEGERS QUANTUM NUMBERS



	B429	B444
***A* (MHz)**	1272.259(46)	1246.5655(67)
***B* (MHz)**	647.2573(135)	690.18796(258)
***C* (MHz)**	429.061350(271)	444.29786(37)
Δ_J (kHz)	20.25(82)	21.12(94)
Δ_{JK} (kHz)	11.80(84)	-17.16(103)
Δ_K (kHz)	-	-
δ_J (kHz)	-	-
δ_K (kHz)	-33.03(148)	-10.22(89)
N_{lines}	138	117
σ (kHz)	12.0	8.8

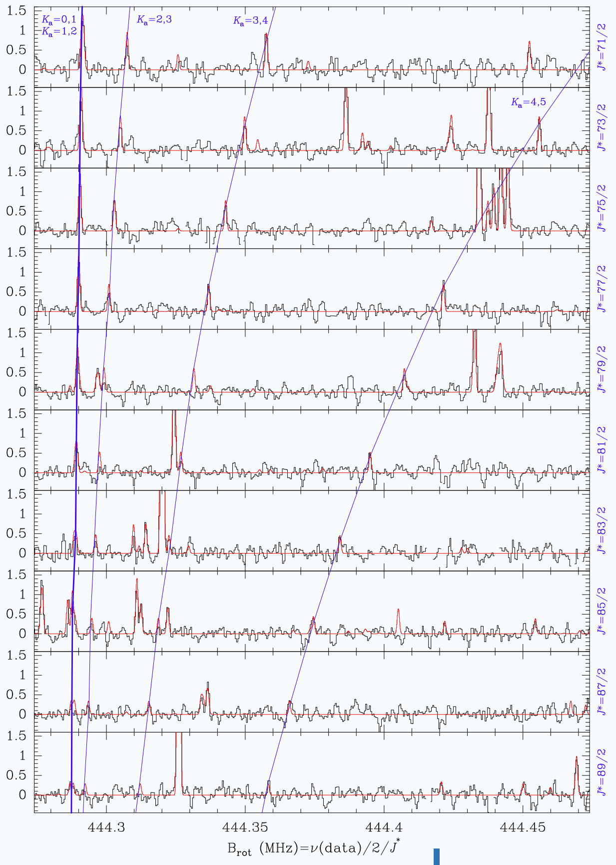
Both have large μ_a dipole moments

→ CN group?

Inertial defect Δ_c (I_c-I_b-I_a) ≈ -0.17 (amu Å^2)

→ planar heavy atom skeleton

Cyano-PAHs most promising candidates

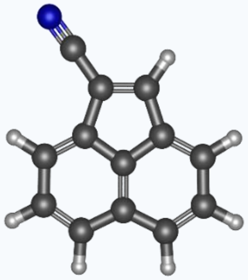


138 AND 117 INDIVIDUAL LINES. Identification without the shadow of a doubt !!!!!!
Spectral coverage needed to guarantee the identification !!! ALMA band 2

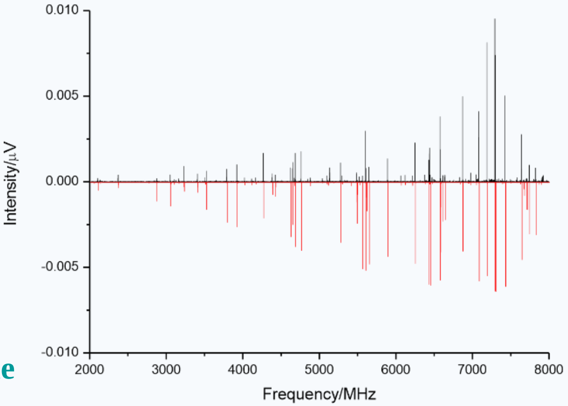
SERENDIPITY IN TMC-1: DISCOVERY OF TWO UNEXPECTED PAHs

	TMC-1	Theory	Lab	Lab+TMC-1
A **(MHz)**	1272.259(46)	1271.6	1272.173002(280)	1272.173142(246)
B **(MHz)**	647.2573(135)	647.4	647.282945(171)	647.282793(76)
C **(MHz)**	429.061350(271)	429	429.060379(174)	429.060651(60)
Δ_J (kHz)	20.25(82)	20.44	22.33(241)	21.21(133)
Δ_{JK}(kHz)	11.80(84)	11.3	9.28(225)	10.61(133)
Δ_K(kHz)	-	-30.04	[-30.04]	[-30.04]
δ_J(kHz)	-	6.88	-6.21(93)	-7.42(95)
δ_K (kHz)	-33.03(148)	32.23	-33.21(130)	-32.04(44)
χ_{aa} (MHz)	-	-4.37	-4.12606(280)	-4.12641(298)
χ_{bb} (MHz)	-	2.44	2.2166(34)	2.2158(36)
N_{lines}	138		313	451
σ (kHz)	10		7.2	8.7

	TMC-1	Theory	Lab	Lab+TMC-1
A **(MHz)**	1246.5655(67)	1248.9	1246.694127(220)	1246.694215(198)
B **(MHz)**	690.18796(258)	688.6	690.139405(155)	690.139409(82)
C **(MHz)**	444.29786(37)	443.8	444.297616(148)	444.297766(64)
Δ_J (kHz)	21.12(94)	20.8	22.05(227)	20.59(123)
Δ_{JK}(kHz)	-17.16(103)	-16.81	-18.36(205)	-16.57(122)
Δ_K(kHz)	-	-1.97	[-1.97]	[-1.97]
δ_J(kHz)	-	3.61	-2.48(101)	-2.18(97)
δ_K (kHz)	-10.22(89)	12.62	-11.85(202)	-14.31(53)
χ_{aa} (MHz)	-	-3.67	-3.43615(258)	-3.43536(274)
χ_{bb} (MHz)	-	1.69	1.52992(307)	1.5283(32)
N_{lines}	117		499	616
σ (kHz)	8.8		7.7	8.8

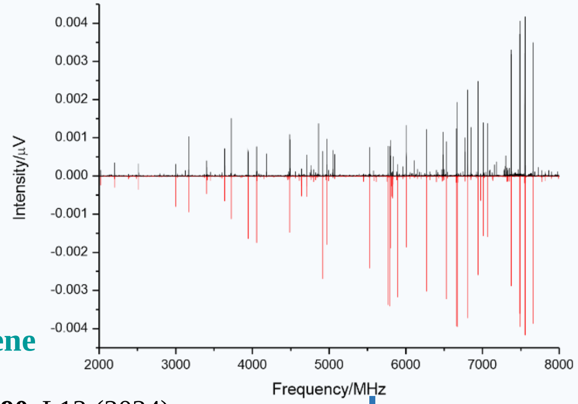


1-Cyanoacenaphthylene



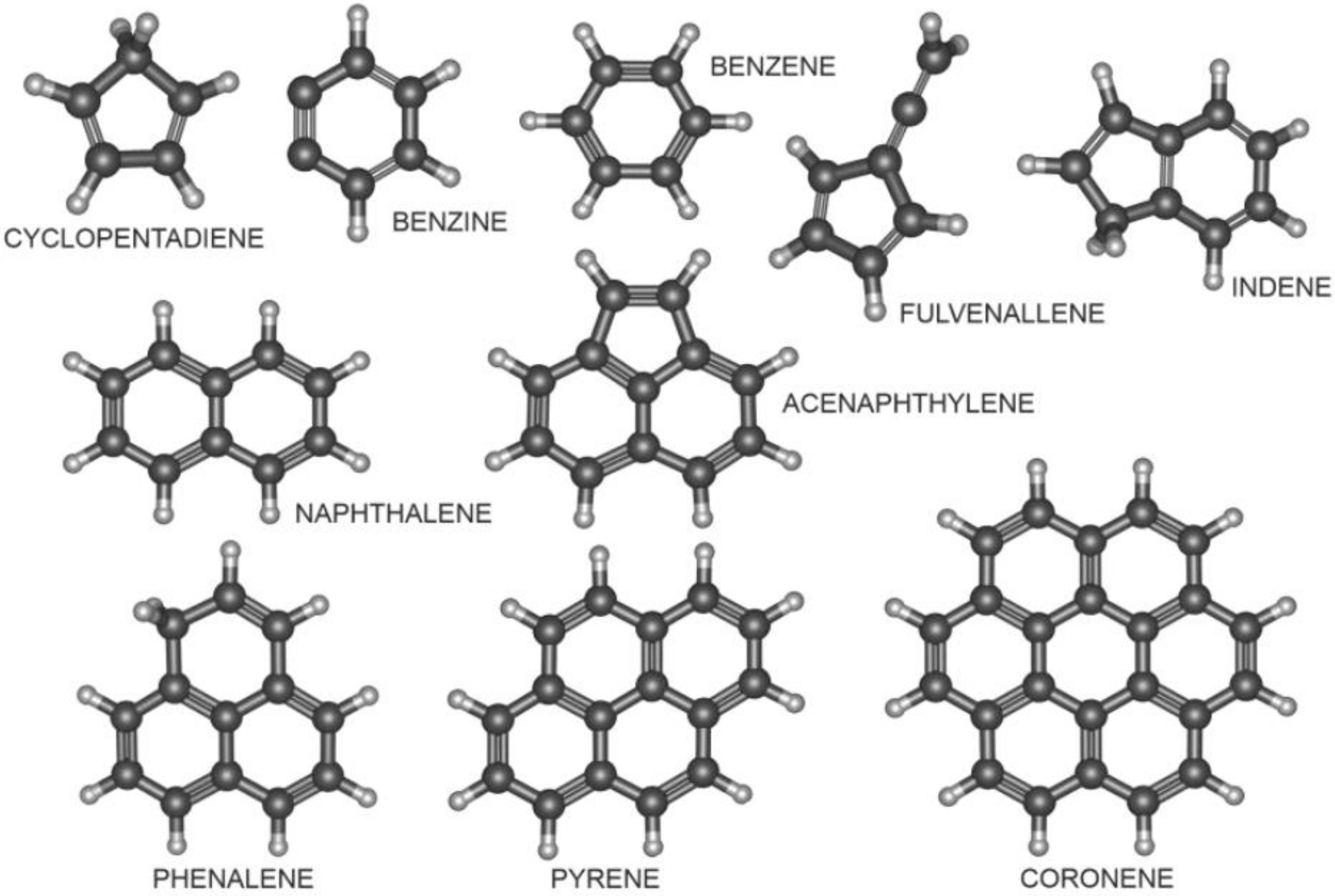
Experimental measurements by Prof. Lesarri @ UVa

5-Cyanoacenaphthylene



Cernicharo *et al.* A&A **690**, L13 (2024)

PAHs detected in TMC-1



None of them detected in IRC+10216…..

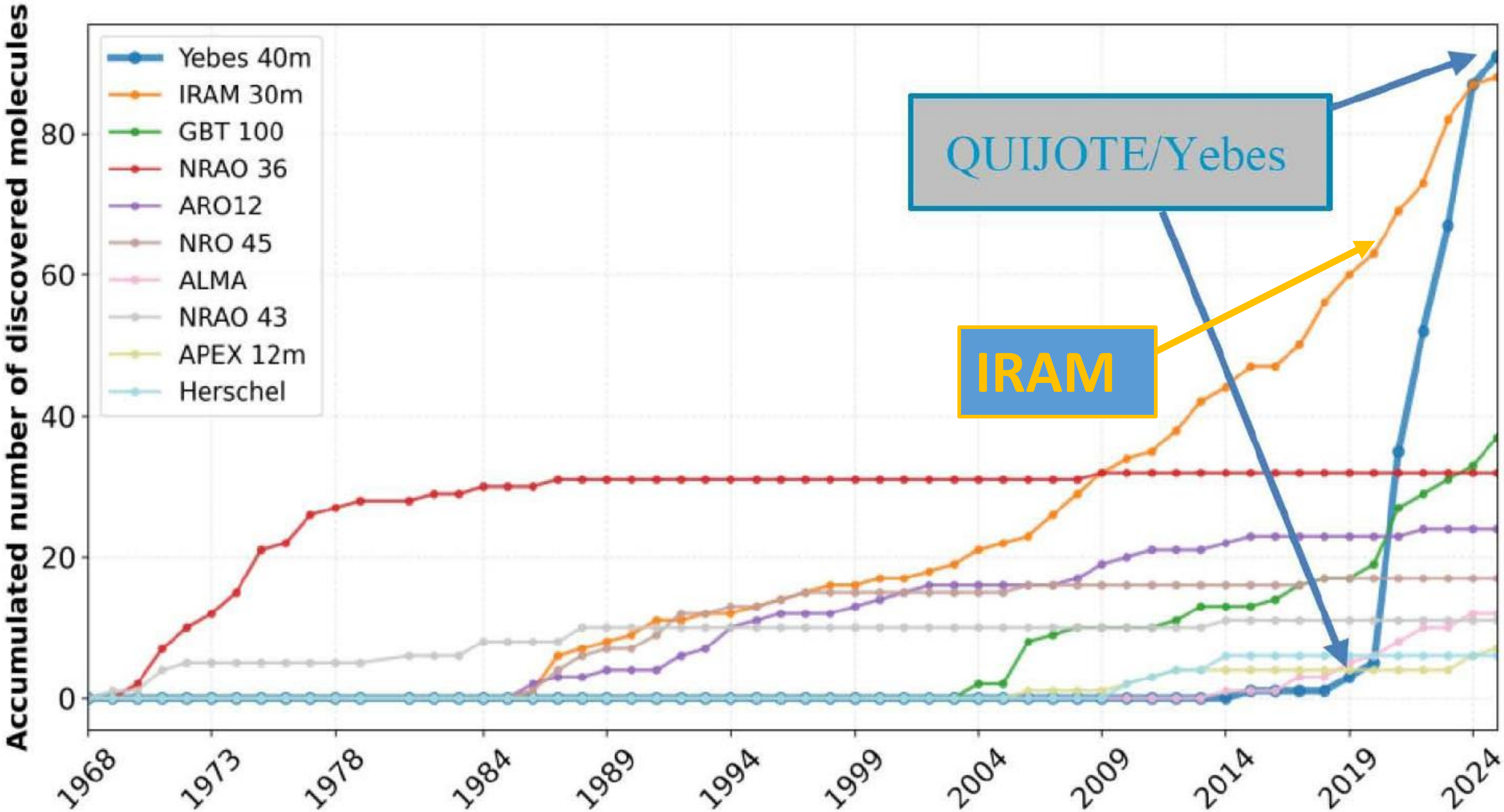


Figure 1: *Number of molecules detected as a function of time by the different radio observatories since the discovery of* H_2O *in 1968. The Yebes 40m radio telescope equipped with the Q-band Nanocosmos receiver is the instrument with the highest rate of detections in the world (blue thick line; most detections are produced by QUIJOTE and our observations of IRC+10216). The graph has been updated from a similar plot produced by McGuire (2022). The Nanocosmos receivers of the Yebes radio telescope were installed in 2019 and fully commissioned in 2020.*

The Yebes 40m telescope (Spain) is the instrument with the largest number of new molecular discoveries in space !!!!

What are the formation mechanism of PAHs in space?

QUIJOTE = TMC-1

But PAHs are observed everywhere in the IR .....

ALMA BAND 2+3 in its most compact configuration could help a lot in studying the chemistry of hydrocarbons in TMC-1.
For IRC+10216 a resolution of 0.3" will be enough for the external layers, but 0.01-0.02" for the dust formation zone

Single dishes can still help a lot in these studies