

CARBON CHEMISTRY AND CARBON BALANCE IN EVOLVED STARS: THE CASE OF IRC +10216

*Synergy ALMA/Herschel &
other telescopes and lambdas*

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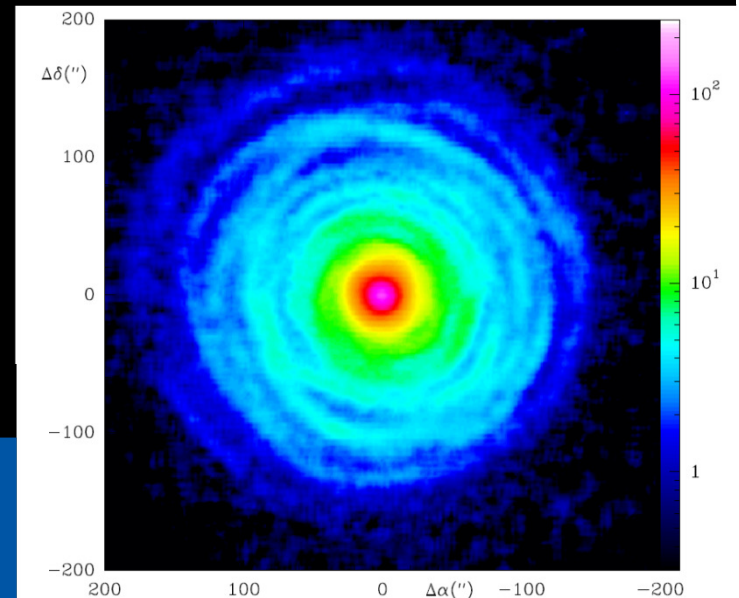


Main Collaborators:

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Luis Velilla, G. Quintana Lacaci

NANOCOSMOS: C: Joblin, J.A. Gago



AGB stars exhibit a large dynamical range of temperatures, Densities and molecular abundances.

Angular resolution from a few milliarcseconds to several arcseconds is needed to characterize the physics and chemistry of these objects.

Chemistry requires the observation of abundant and key species without no permanent dipole moment (C_2H_2 , CH_4 , SiH_4 , C_3 , ...).

A single line with a given angular resolution will ONLY provide a very limited view of the reality of the object.

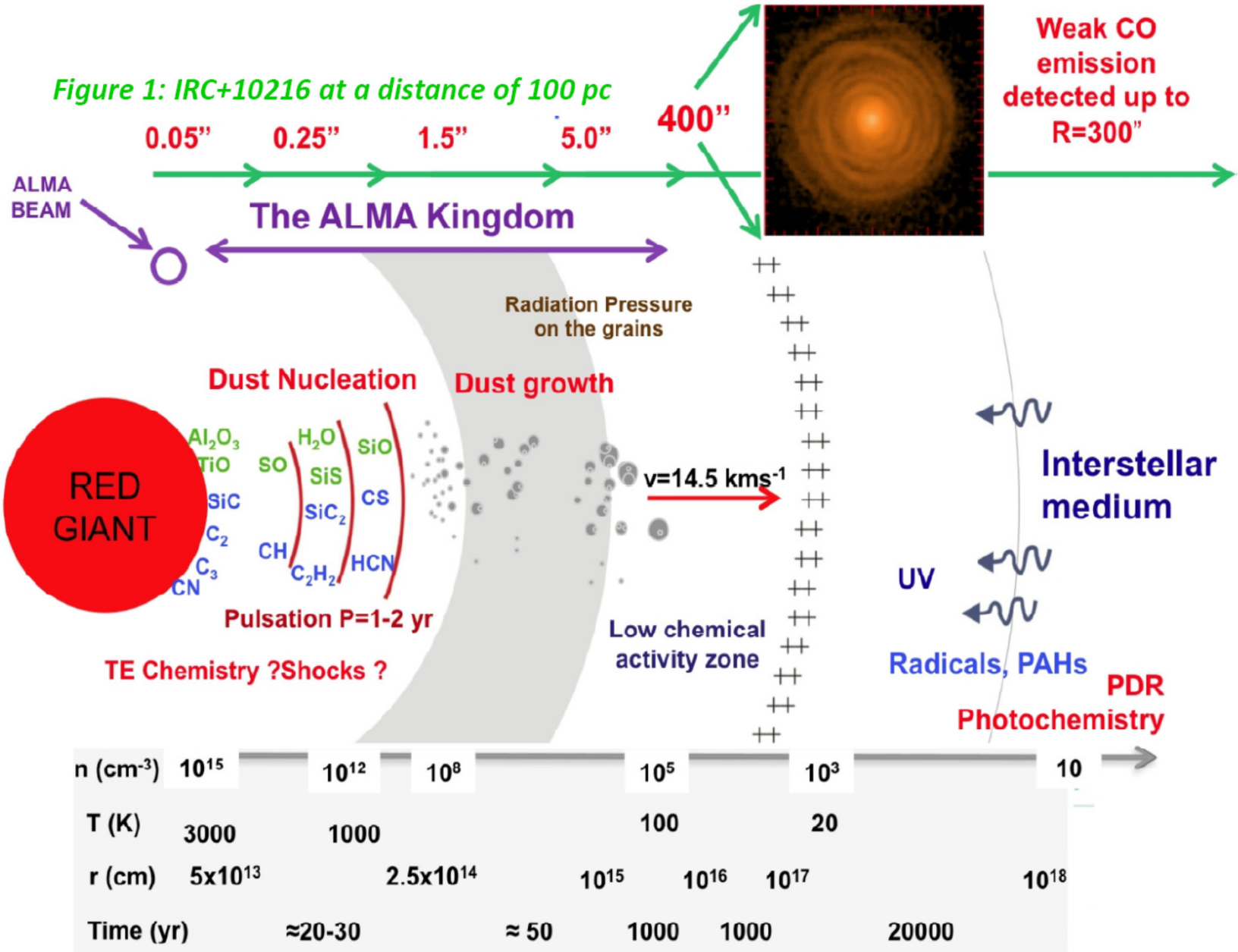
Synergy between radio and infrared, single dish and interferometric observations absolutely mandatory.

For the synergy ALMA/Herschel in the ISM see the talk of Belen Tercero

Inner shells

Outer shells

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



The Herschel archive contains far-IR spectra taken with PACS and SPIRE of a large number of objects

The ISO archive contains hundreds of spectra of evolved stars in the near, mid and far infrared domain

Spitzer archive contains very sensitive data of hundreds of objects

Ground based mm/submm telescopes have, and could still provide, line surveys of a few objects of perhaps 10-20 objects i

ALMA will provide selected frequency observations of a large number of stars but only line surveys for 1-3 objects

The NANOCOSMOS Synergy project will provide line surveys of hundreds of evolved stars in the 30-50, 70-116 GHz domain

→ λ -synergy is needed to get the maximum scientific output for physics and chemistry of AGBs and post-AGBs in the ALMA era

IRC +10216:

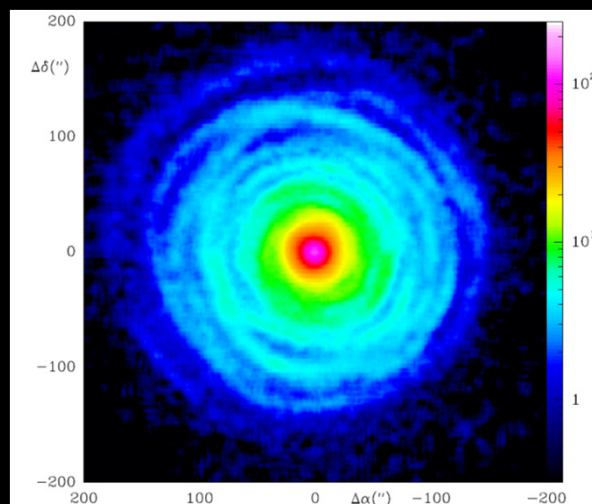
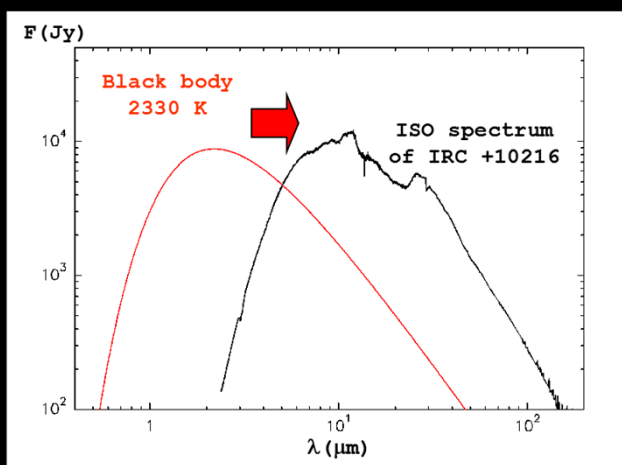
Chemical study of the envelope



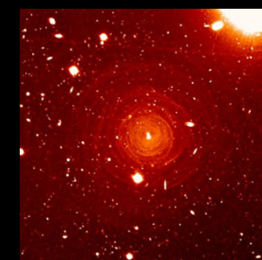
l 10 mm; ESO/La Silla
B. Stecklum & H.-U. Käußl

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

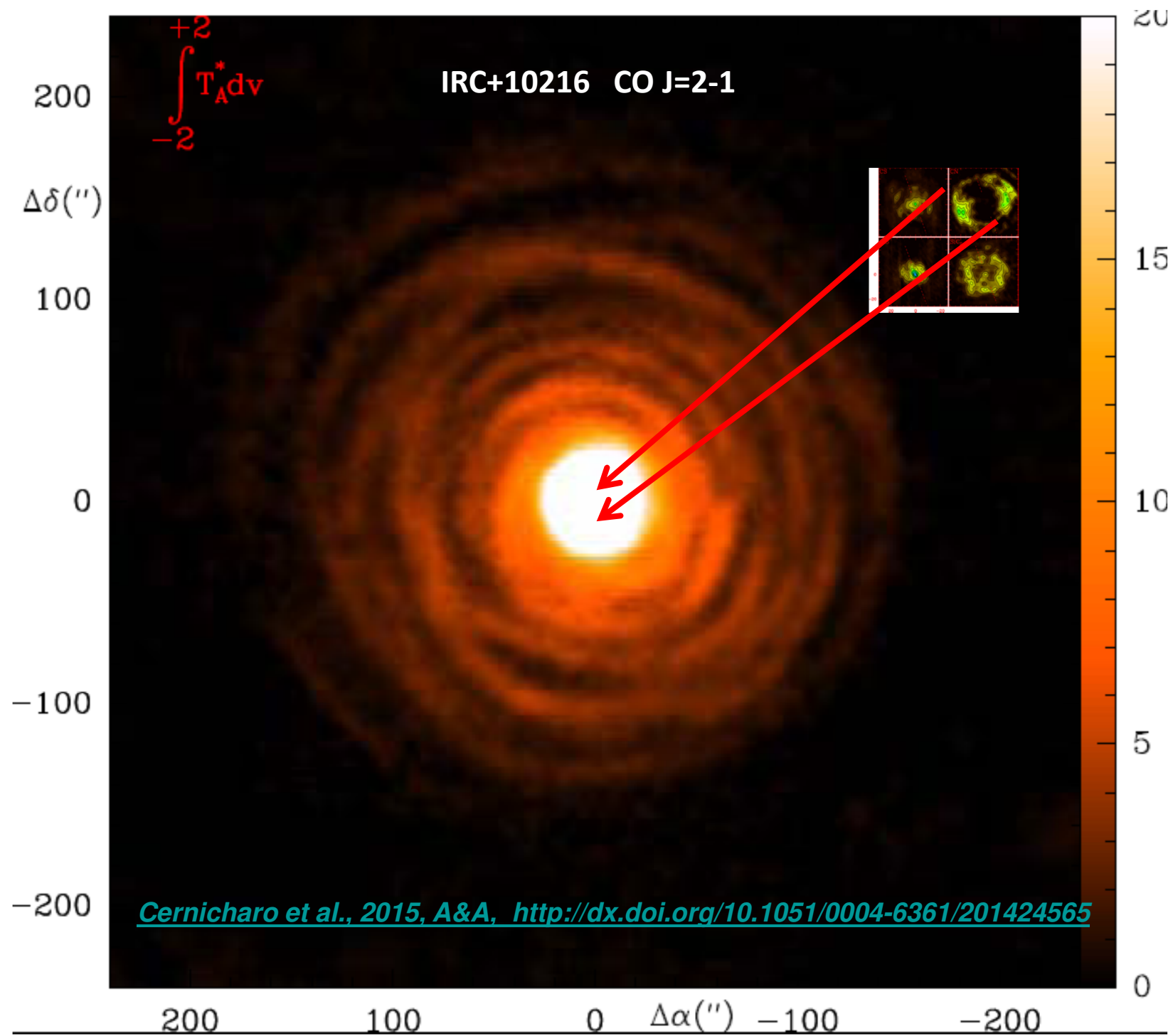
- IRC+10216 is a prototype of C-rich stars
- 50% of the molecules known in space have been detected in its CSE

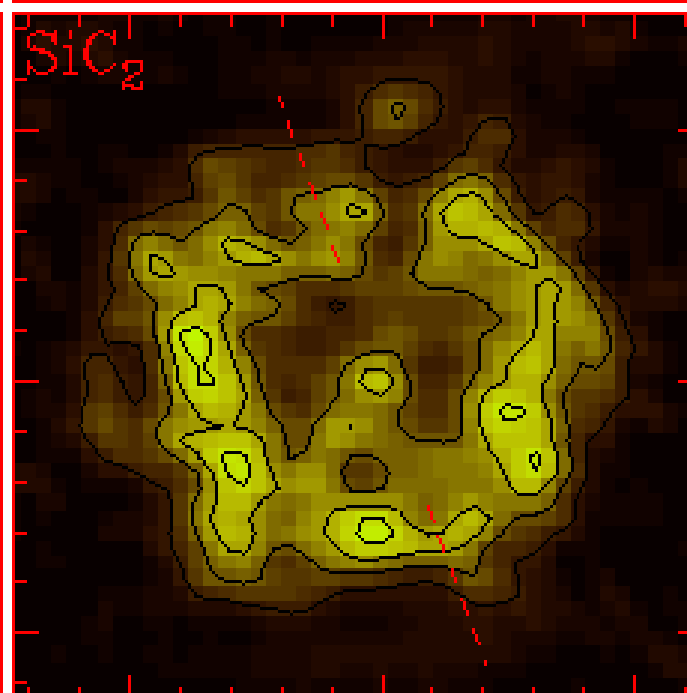
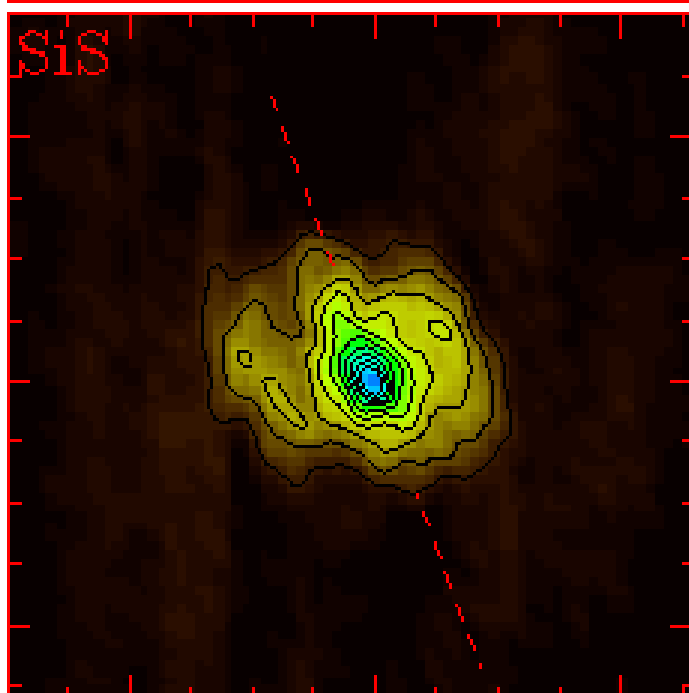
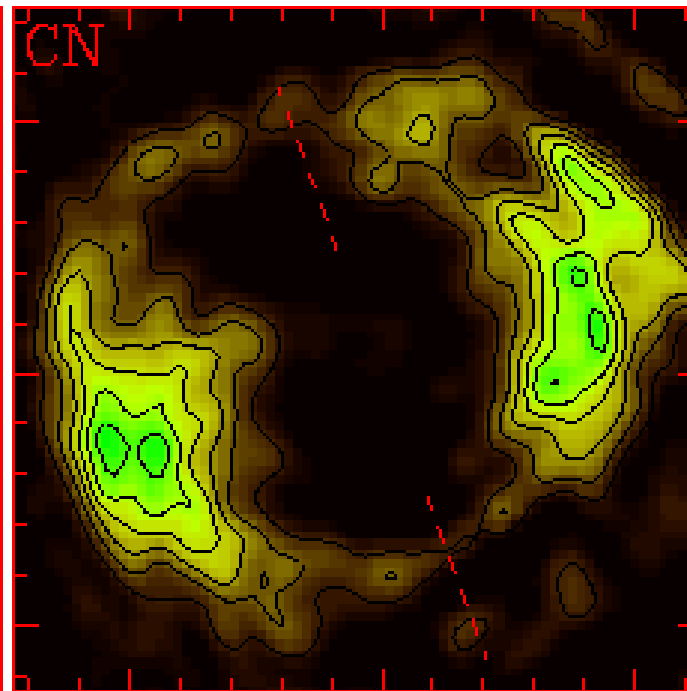
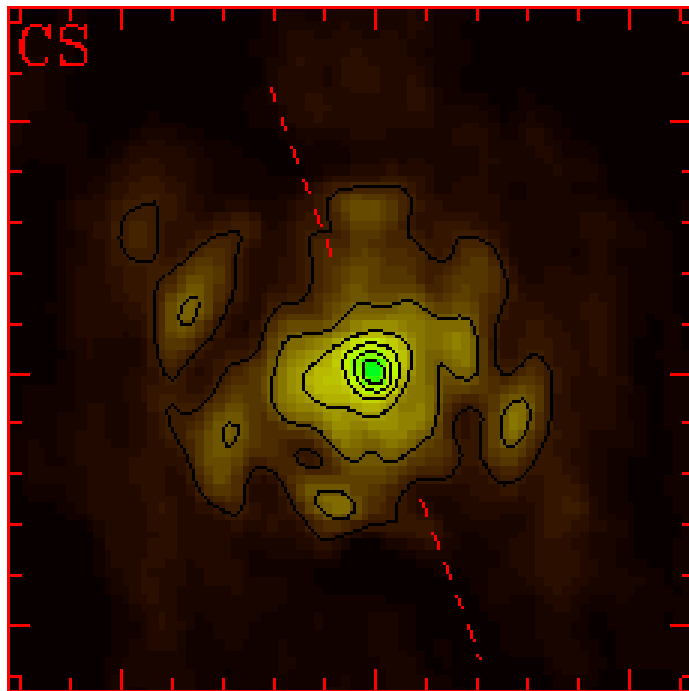


Cernicharo et al, 2015,
Leao et al., 2006



METHODS : Astronomical observations at all frequencies
Radiative transfer modelling, Dynamical Evolution, Chemical modelling,....





Guélin &
Coworkers

PdBI data
3'' resolution

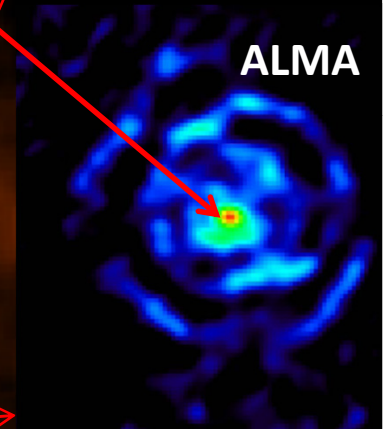
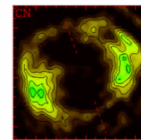
Radicals C_nH
and C_nN are
found in the
molecular
ring at 14''
from CW Leo

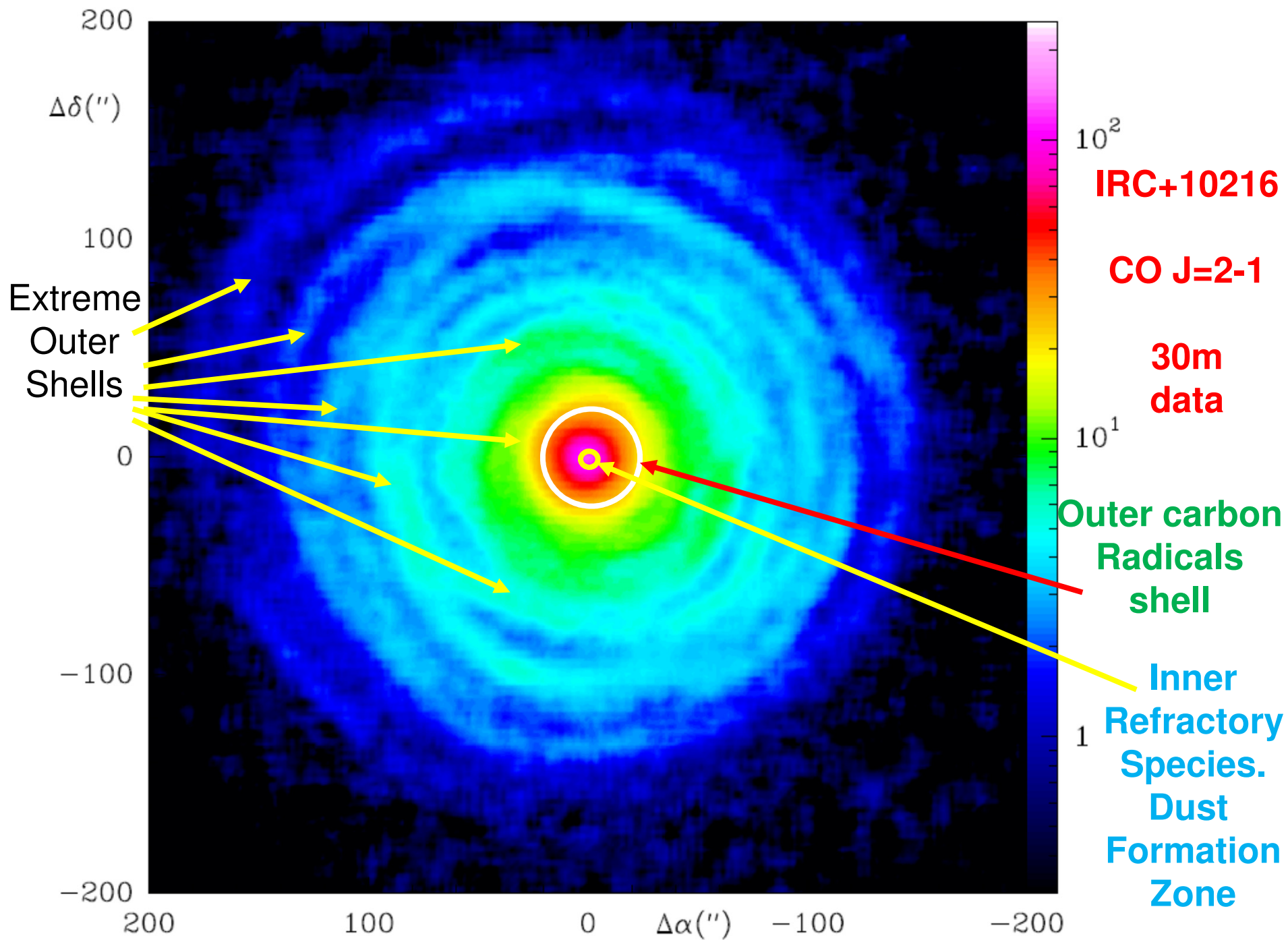
20
0
-20

20 0 -20

The chemical composition of the dust formation zone of IRC+10216

CO (2-1)
30m IRAM



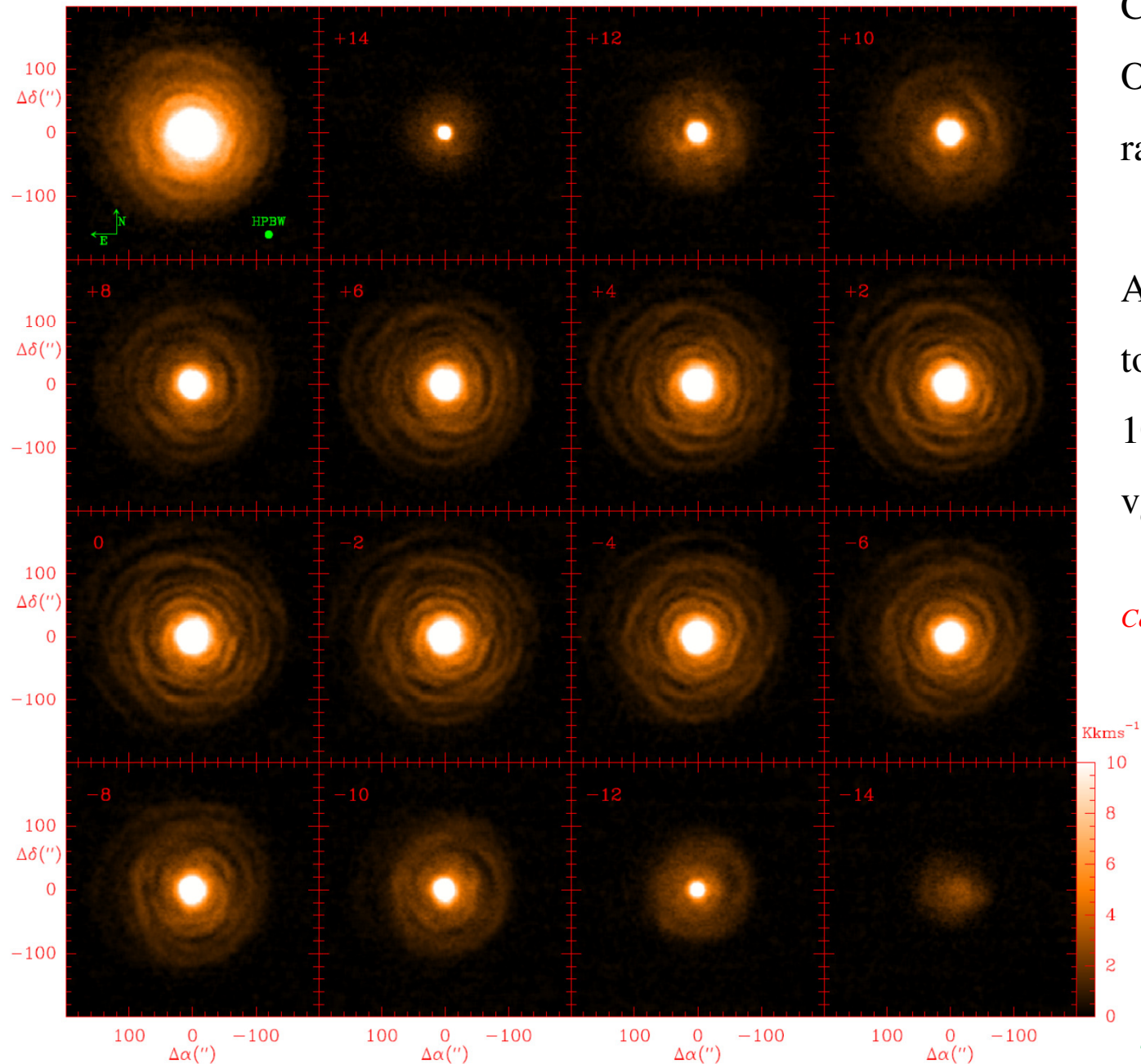


The Physical and Chemical Conditions in the middle and external zones of IRC+10216

*Tools: Line Surveys in mm/submm
domains*

*Ground based telescopes, Herschel,
ALMA*

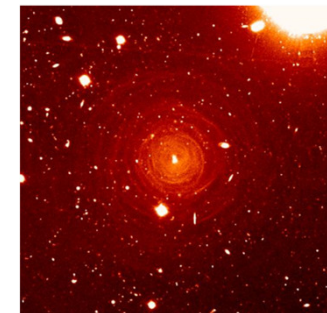
IRC+10216 at large scales



CO J=2-1 velocity maps as
Observed with the 30m
radiotelescope.

Angular scales corresponds
to a time evolution of
10000 yr for $d=120$ pc and
 $v_{\text{exp}}=14.5$ km/s (400").

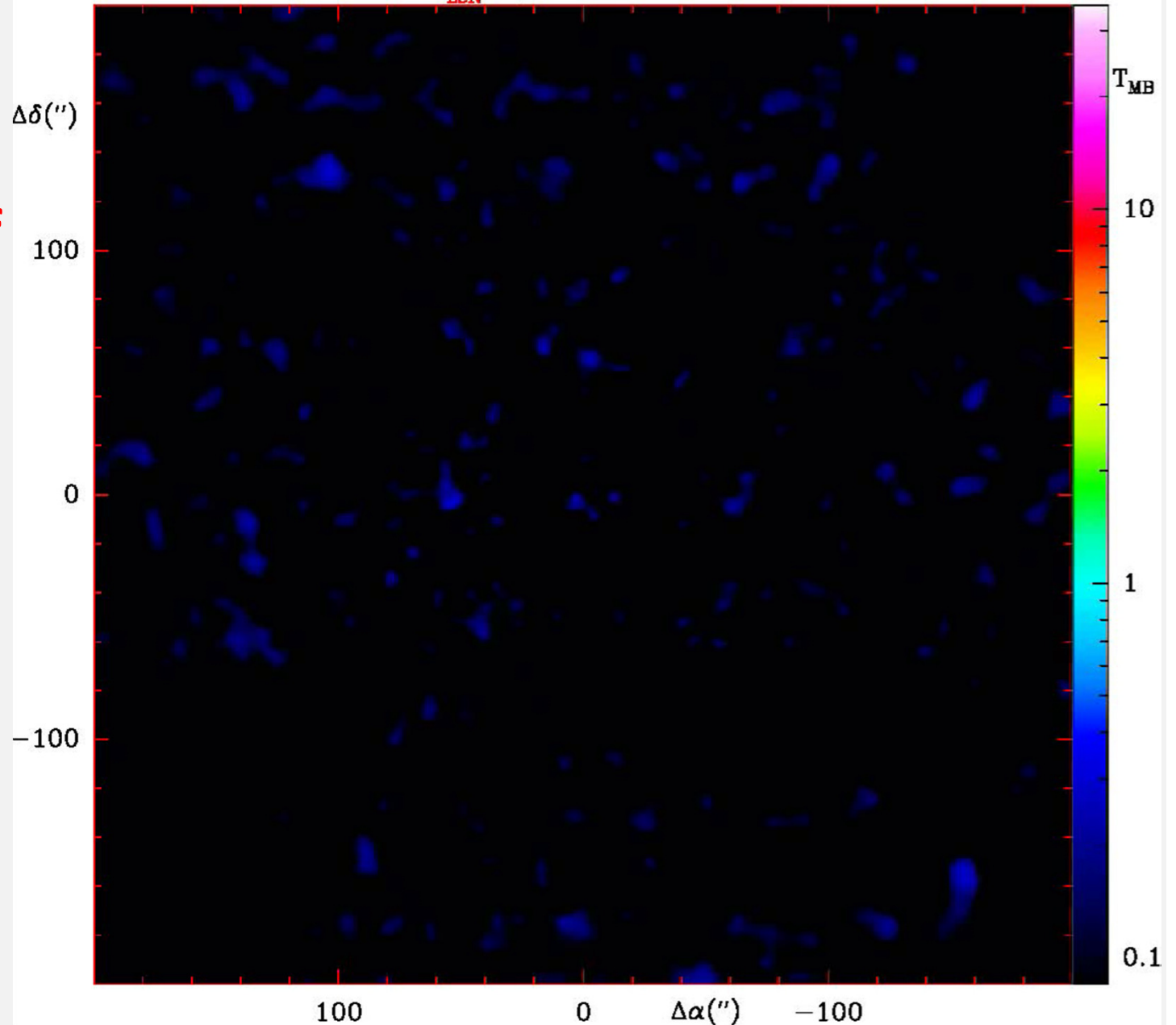
Cernicharo et al. (2015) A&A,

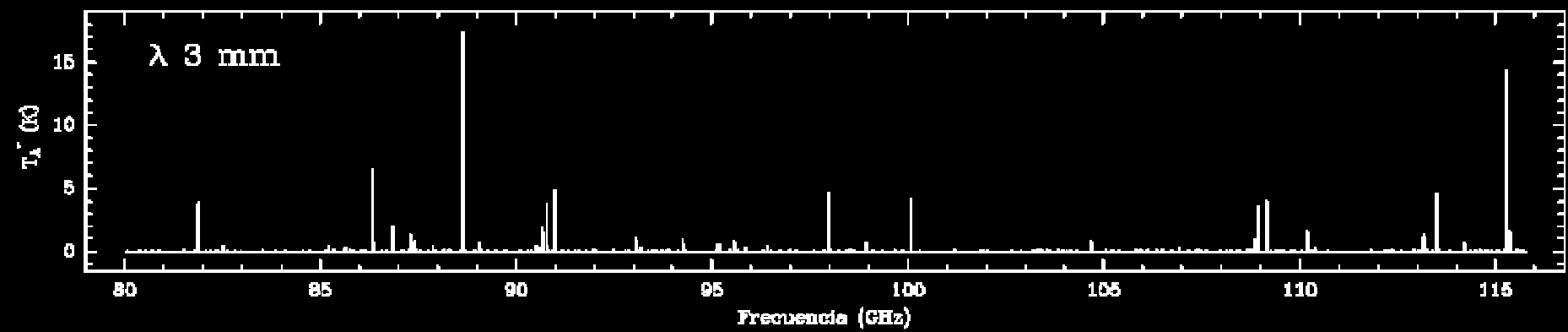
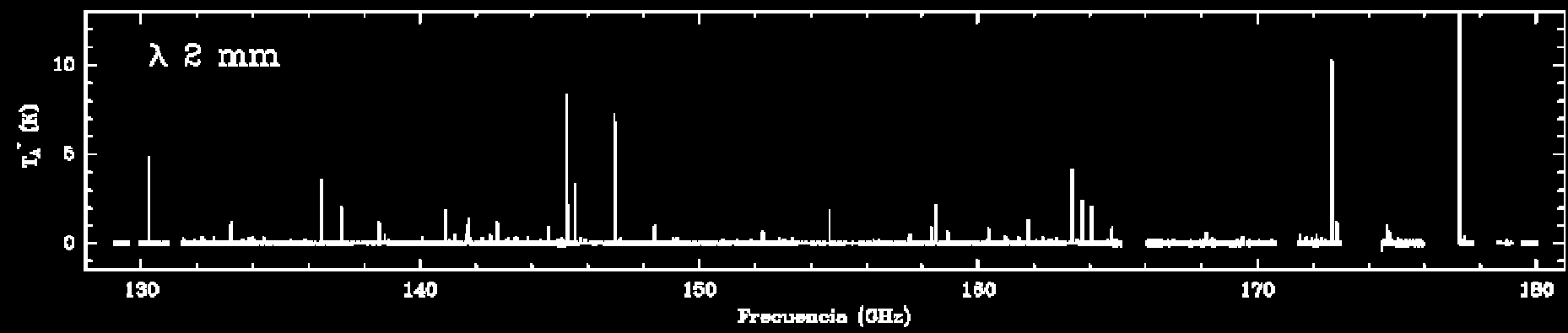
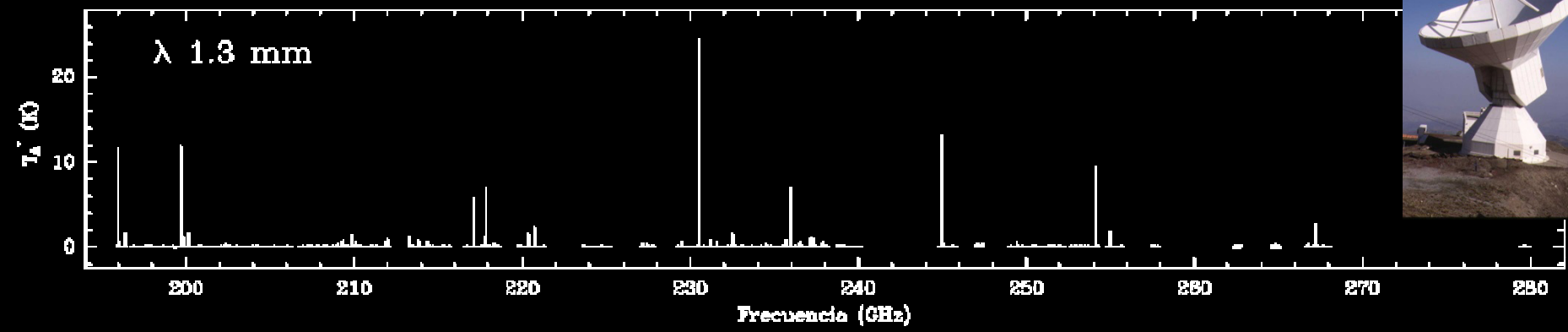


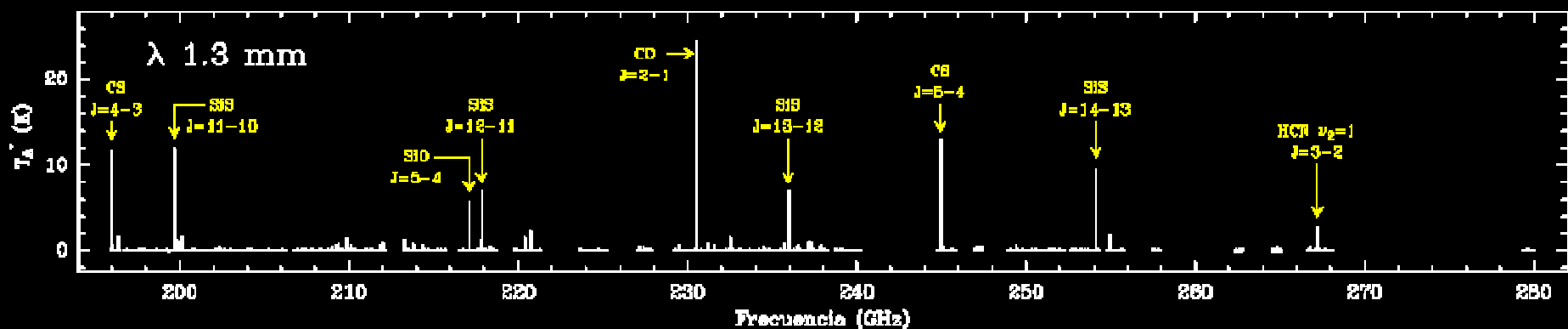
Scattered light (Leao et al. 2006)

**The 3D view of
IRC+10216
from CO
J=2-1
30m IRAM
radiotelescope
Observations**

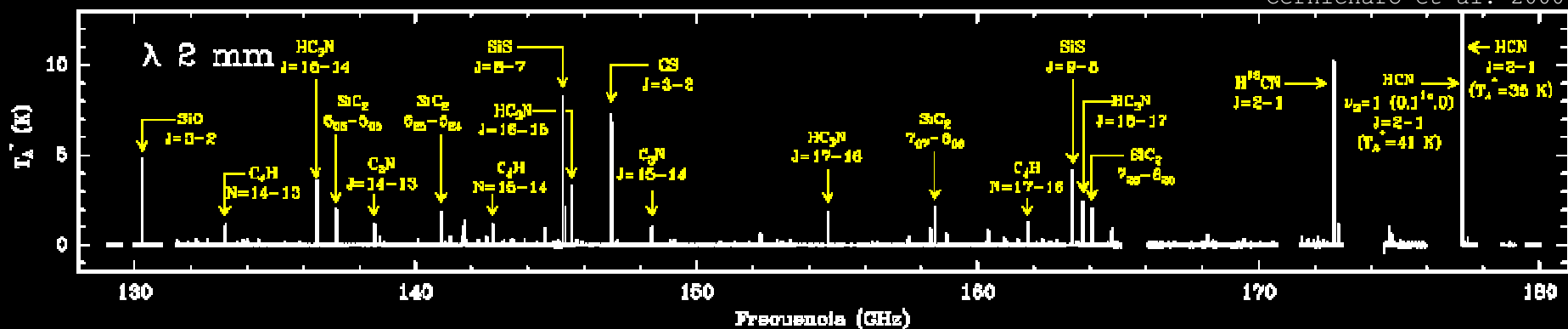
Observed $T_{\text{MB}}(^{12}\text{CO } J=2-1)$ in IRC+10216 with the IRAM 30m Telescope
 $V_{\text{LSR}} - V_* = -17.1 \text{ Km s}^{-1}$



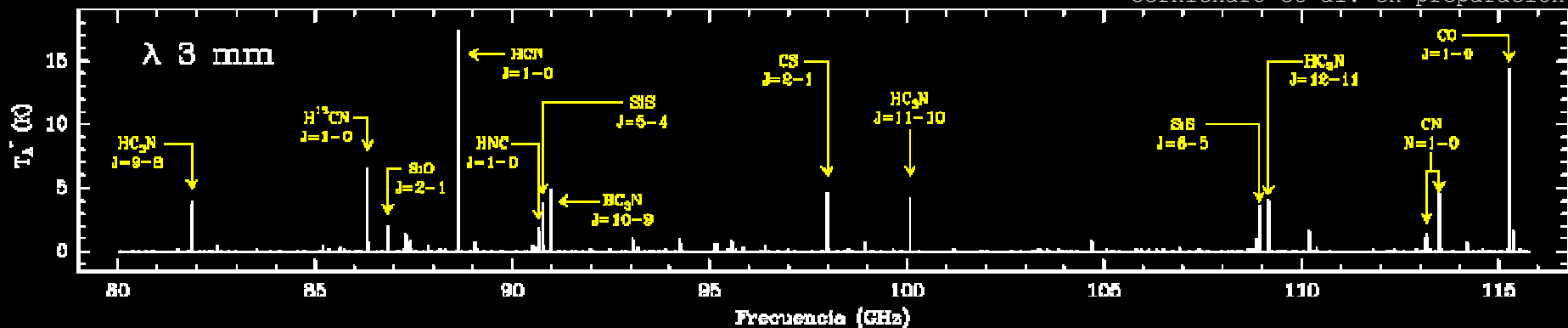




Cernicharo et al. 2000



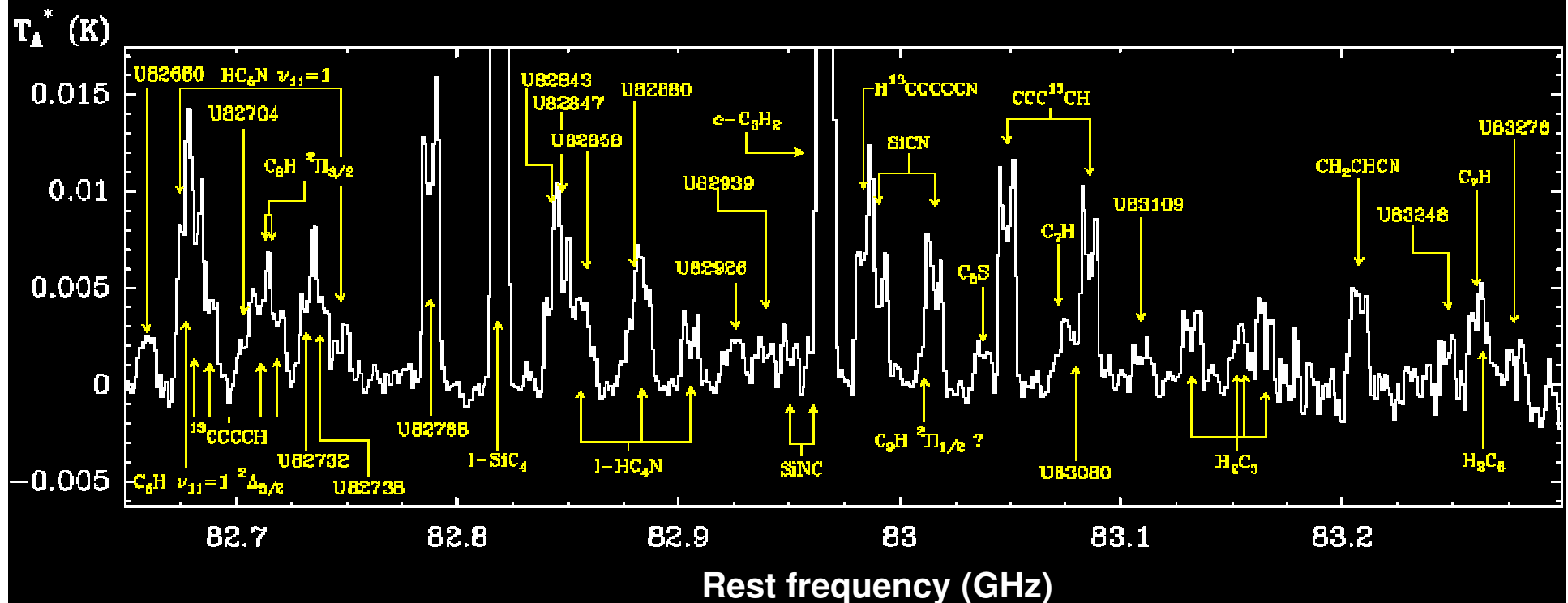
Cernicharo et al. en preparación



METHODS: Radio astronomical observations

Line survey at $\lambda=3$ mm carried out with the IRAM 30-m radio telescope:

- 80.05–115.75 GHz
- 1339 emission lines (~ 37 lines/GHz)
- 1100 assigned to rotational transitions of 70 molecules (+all isotopologues and vibrationally excited states)
- 240 unassigned lines (only 31 with $T_A^* > 10$ mK)
- high sensitivity: $\text{rms}(T_A^*) < 1$ mK for most frequencies



10⁻³ CO 1 (-3)

Complete analysis of all species in the 30m line survey

10⁻⁴

C₂H₂ 8 (-5)

HCN 2 (-5)

10⁻⁵

CH₄ 3.5 (-6)

C₂H 3 (-6)

C₄H 2.5 (-6)

C₂ 1 (-6)

C₃ 1 (-6)

NH₃ 2 (-6)

CN 1.7 (-6)

HC₃N 1.4 (-6)

SiC₂ 1.2 (-6)

SiS 1 (-6)

10⁻⁶

C₃N 4 (-7) CS 5 (-7)

SiH₄ 2.2 (-7)

SiO 1.2 (-7)

10⁻⁷

H₂O 1 (-7)

C₅ 1 (-7)

HC₅N 2 (-7)

HNC 1 (-7)

OH 4 (-8)

1-C₃H 5 (-8)

C₆H 4 (-8)

C₅H 3 (-8)

c-C₃H₂ 3 (-8)

CH₃C₂H 3 (-8)

c-C₃H 2 (-8)

C₂H₄ 2 (-8)

H₂C₄ 1.4 (-8)

CH₃CN 3 (-8) C₂S 3 (-8)

HC₇N 2 (-8)

C₃S 1.2 (-8)

SiC 4 (-8)

HCP 2.5 (-8)

AlCl 3.5 (-8)

NaCN

10⁻⁸

H₂CO 1.3 (-8)

C₈H 8 (-9)

HC₉N 8 (-9)

CH₂CN 7 (-9)

HC₂N 6 (-9)

C₅N 4 (-9)

C₇H 3 (-9)

HCCNC 4 (-9)

C₂H₃CN 4 (-9)

C₅N⁻ 2.3 (-9)

HC₄N 2 (-9)

C₃N⁻ 1.1 (-9)

H₂CS 7 (-9)

H₂S 4 (-9)

C₅S 1.2 (-9)

SiN 8 (-9)

c-SiC₃ 4 (-9)

SiC₄ 3 (-9)

SiCN 2 (-9)

SiNC 1.1 (-9)

CP 1 (-8)

PH₃ 8 (-9)

PN 1 (-9)

C₂P 1 (-9)

MgNC 8 (-9)

AlF 7.5 (-9)

NaCl 1 (-9)

AlNC 1 (-9)

10⁻⁹

HCO⁺ 7 (-10)

HNCCC 5 (-10)

MgCN 5 (-10)

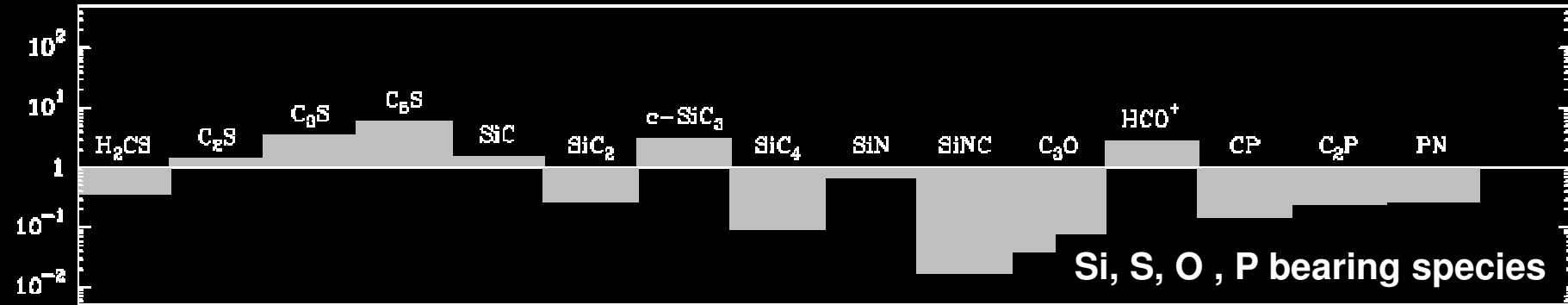
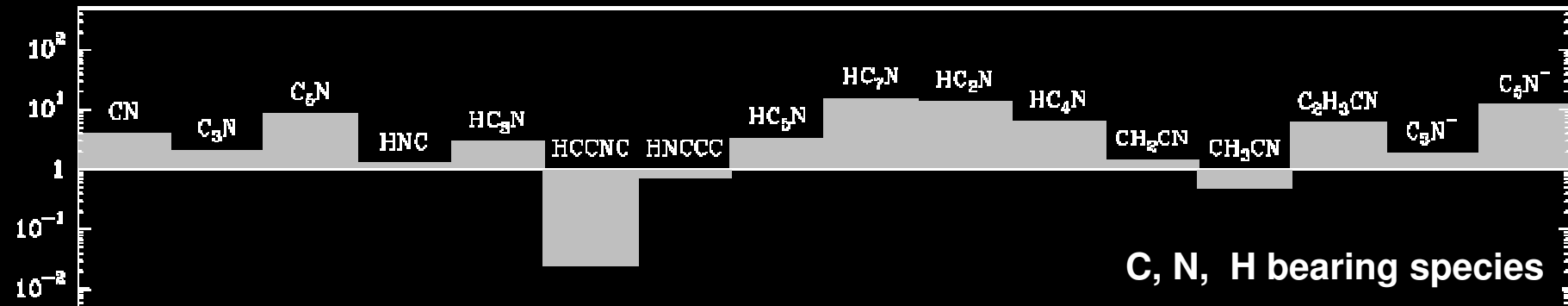
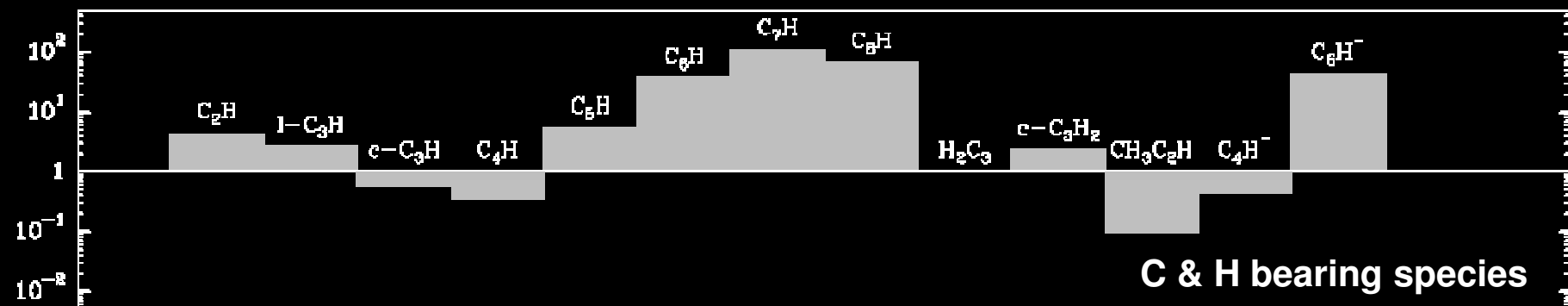
10⁻¹⁰

C₄H⁻ 3 (-10)

KCl 2.5 (-10)

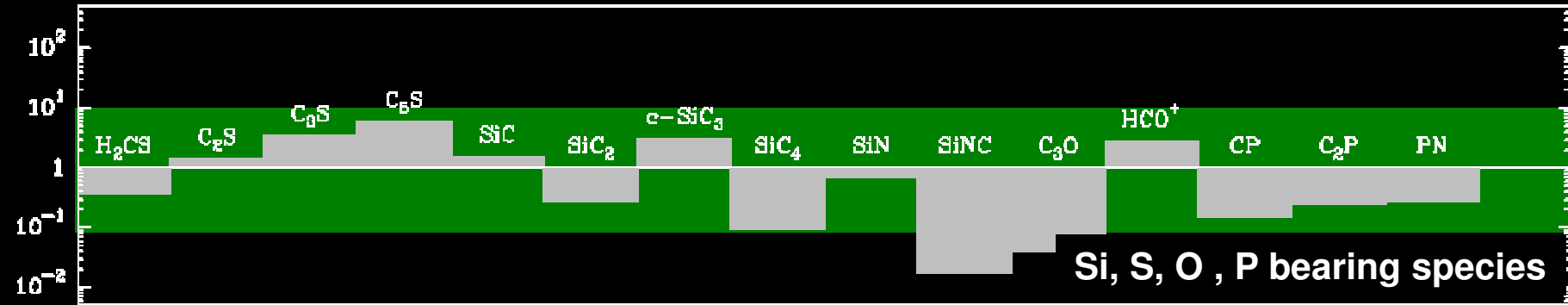
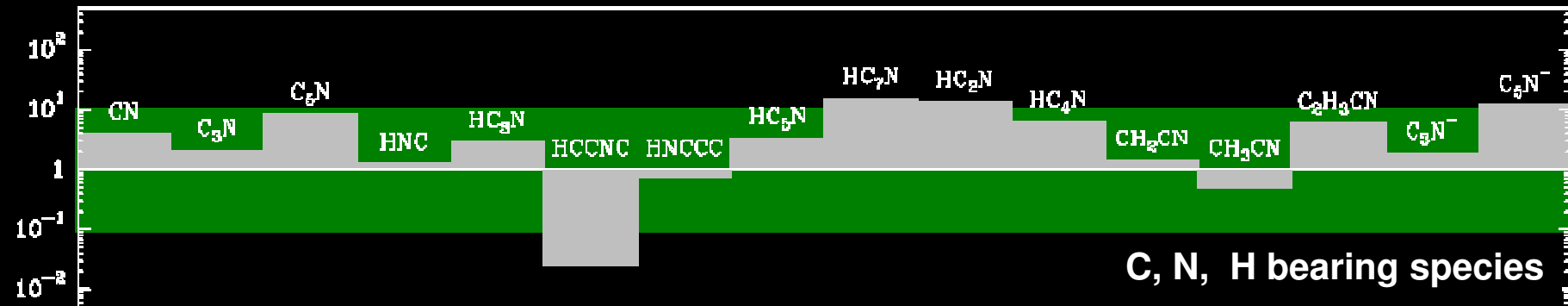
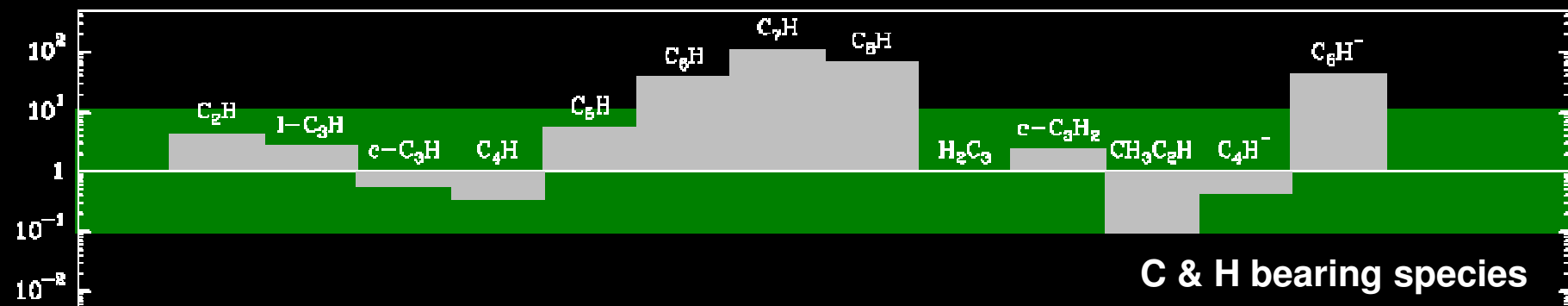
RESULTS: THE OUTER ENVELOPE --- Chemical kinetic models

N_{calc}/N_{obs}



RESULTS: THE OUTER ENVELOPE --- Chemical kinetic models

N_{calc}/N_{obs}



Anions in IRC+10216

2006 C_6H^- en IRC +10216 y TMC-1 (McCarthy et al.)

2007 C_4H^- en IRC +10216 (Cernicharo et al.)

2007 C_8H^- en IRC +10216 y TMC-1 (Remijan et al.; Brünken et al.)

2008 C_3N^- en IRC +10216 (Thaddeus et al.)

2008 C_5N^- en IRC +10216 (Cernicharo et al.)

Additional detections:

C_6H^- en L1527 (Sakai et al. 2007)

C_4H^- en L1527 (Agúndez et al. 2008)

C_6H^- en L1544 y L1521F (Gupta et al. 2009)

DETECTION OF C_5N^- AND VIBRATIONALLY EXCITED C_6H IN IRC +10216¹

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 Received 2008 July 2; accepted 2008 October 8; published 2008 October 29

ABSTRACT

We report the detection in the envelope of the C-rich star IRC +10216 of four series of lines with harmonically related frequencies: B1389, B1390, B1394, and B1401. The four series must arise from linear molecules with mass and size close to those of C_6H and C_5N . Three of the series have half-integer rotational quantum numbers; we assign them to the ${}^2\Delta$ and ${}^2\Sigma^-$ vibronic states of C_6H in its lowest (ν_{11}) bending mode. The fourth series, B1389, has integer J with no evidence of fine or hyperfine structure; it has a rotational constant of 1388.860(2) MHz and a centrifugal distortion constant of 33(1) Hz; it is almost certainly the C_5N^- anion.

TABLE 2
 DERIVED ROTATIONAL CONSTANTS

Series	B (MHz)	D (Hz)	N_{lines}	J -Range
B1389	1388.860(2)	33(1)	13	8, 29–40
B1390	1389.878(7)	−35(3)	9	59/2–79/2
B1394	1394.609(10)	32(4)	22	29–41 ^a
B1401	1401.559(26)	139(7)	7	59/2–75/2

C₅N⁻ : Identification based on comparison with ab initio calculations by Botschwina & Oswald (2008)

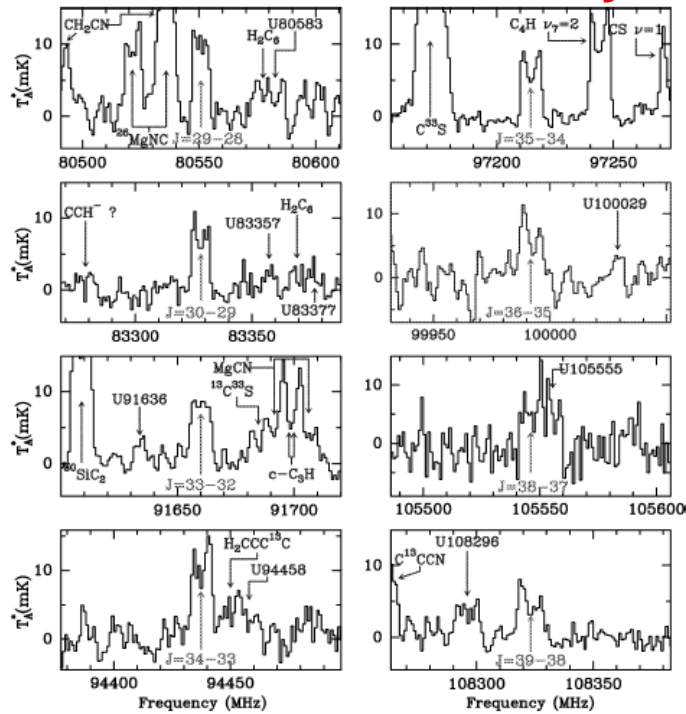


FIG. 1.—Spectra of IRC +10216 observed with the IRAM 30 m telescope, showing lines from the B1389 series assigned here to C_5N^- . The marginal weak line U83278 is worth noting, because it is within 0.1 MHz of the $J = 1-0$ line of CCH^- (see text). [See the electronic edition of the Journal for a color version of this figure.]

Very little is known about the chemical properties of anions. A lot of work to be done !!

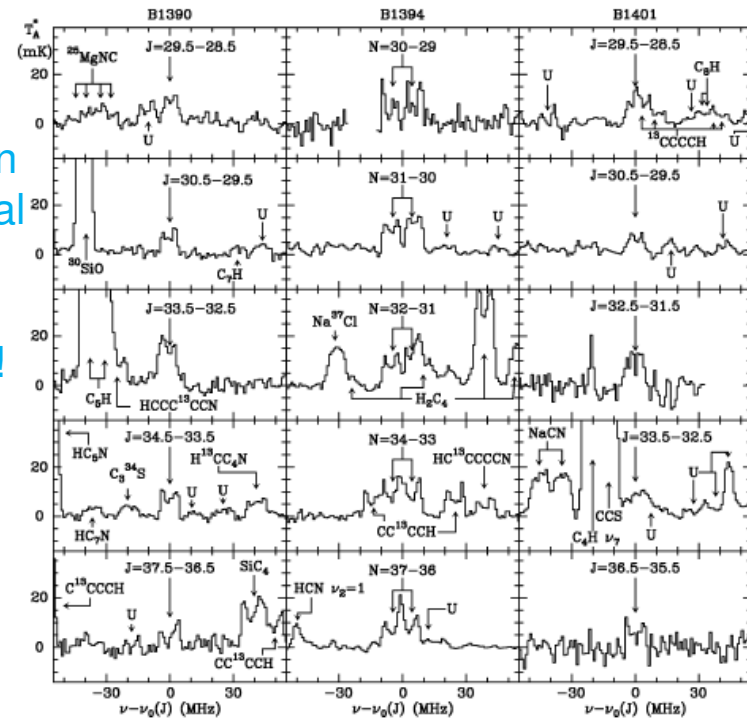
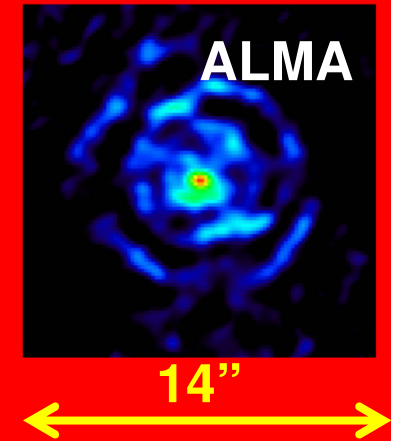


FIG. 2.—Spectra of IRC +10216 observed with the IRAM 30 m telescope showing selected lines pertaining to the series B1390, B1394, and B1401. These three series of lines are assigned to vibronic states of the ν_{11} bending mode of C_6H .

The Physical and Chemical Conditions in the innermost regions of IRC+10216



A mandatory step to understand the chemistry of the whole envelope

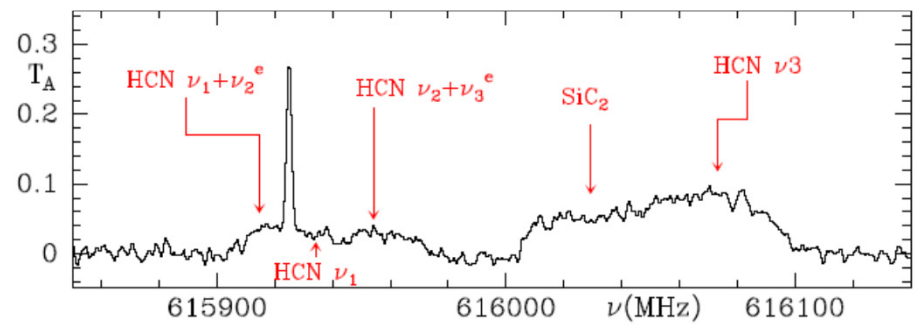
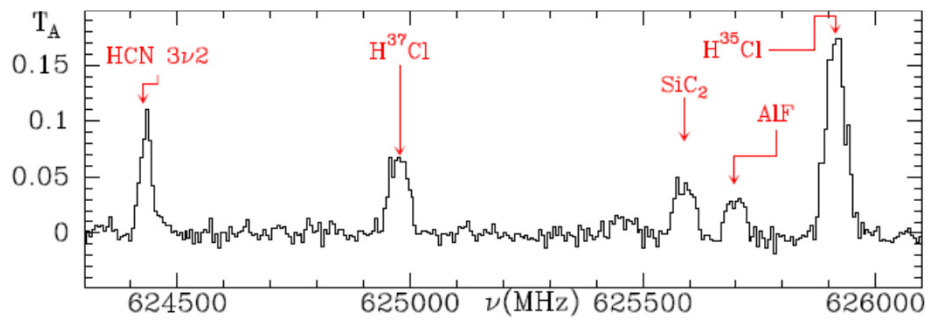
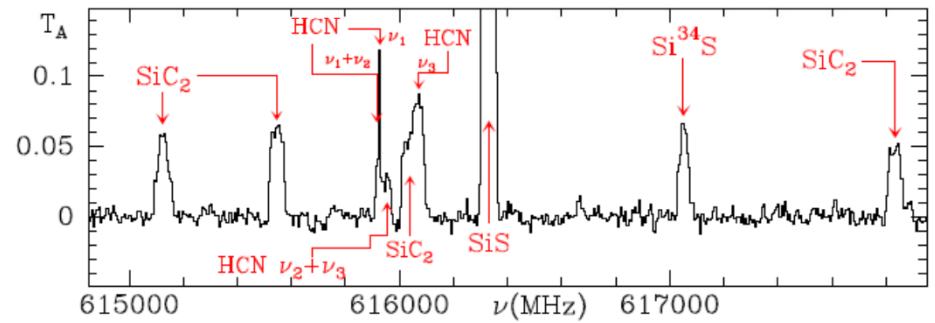
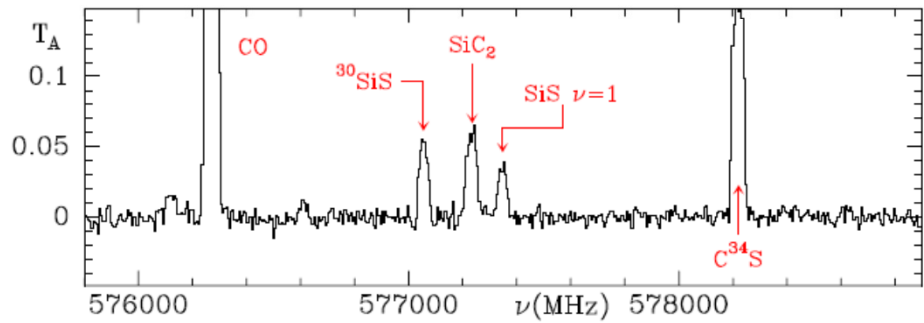
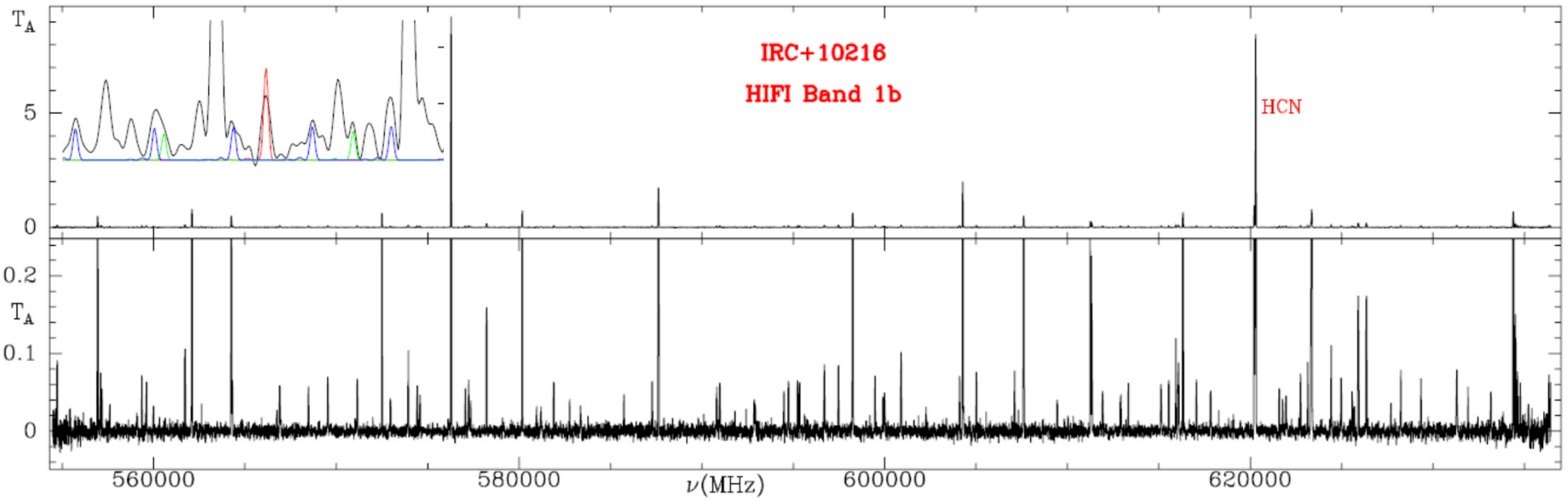
IR Tools: Line Surveys in the Far, Mid, and Near Infrared with ISO & Herschel & Ground Based Telescopes

Millimeter/Submillimeter tools: Herschel & ALMA

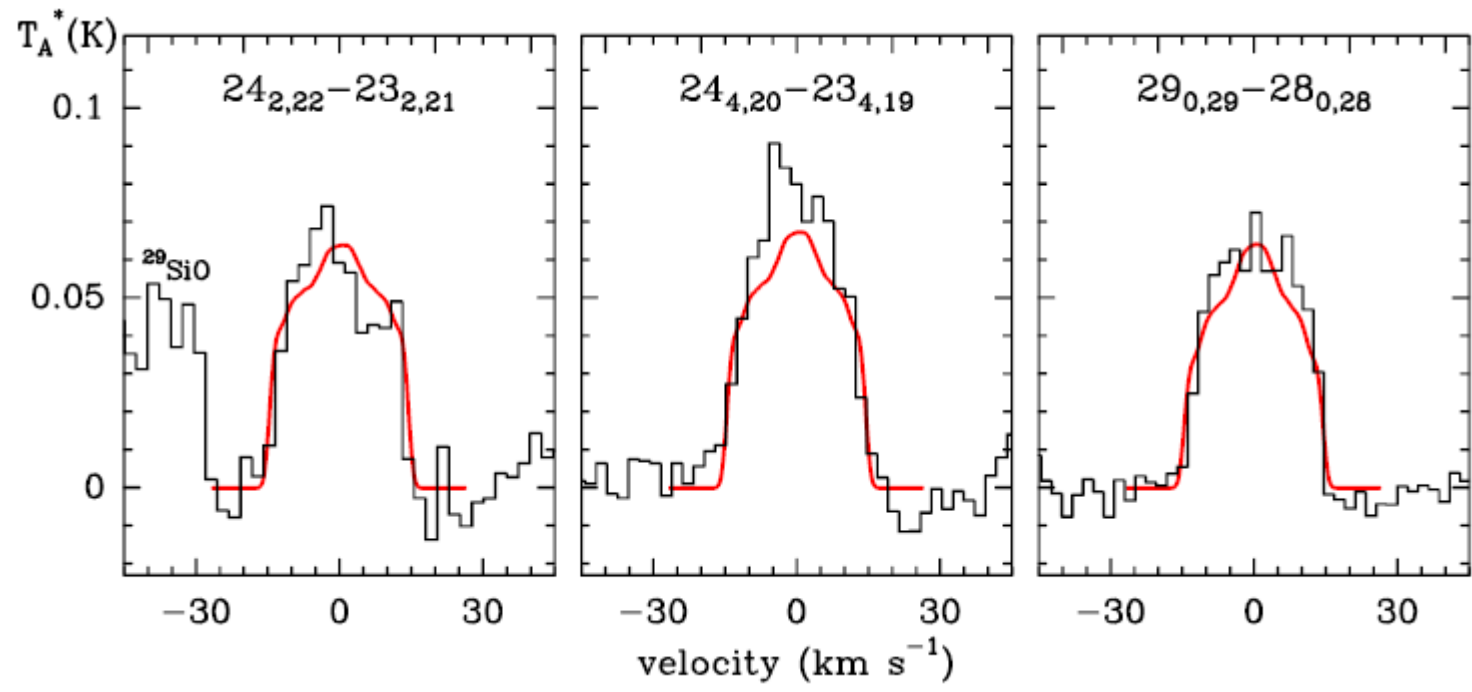
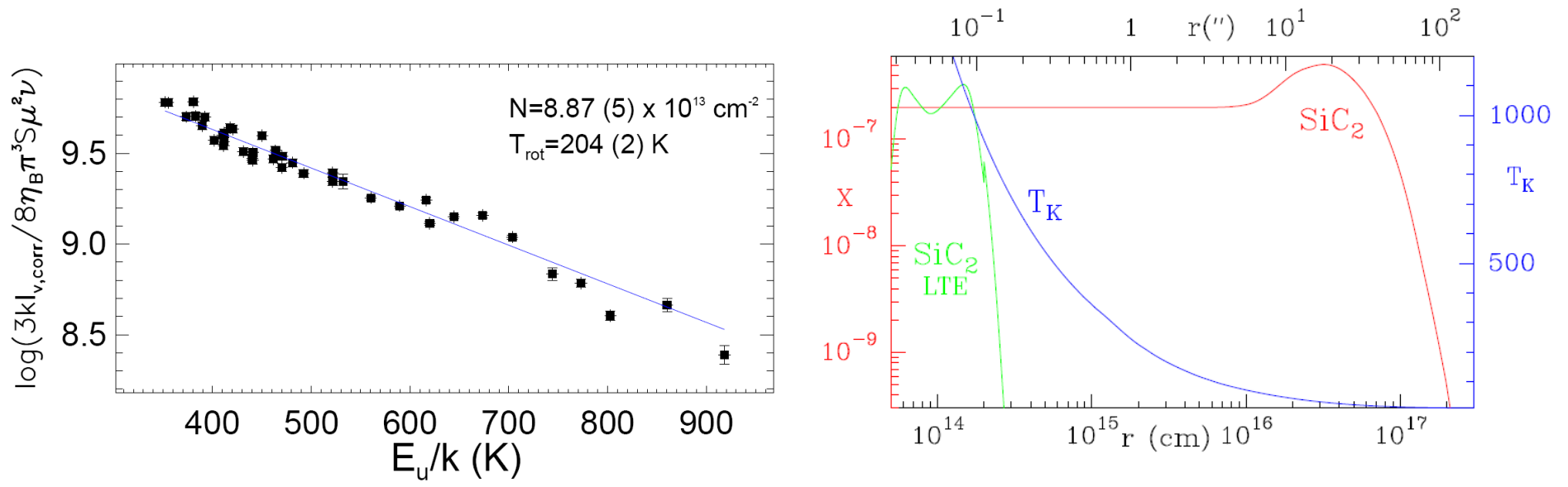
The Herschel view of IRC+10216:

The middle and inner zone of the CSE

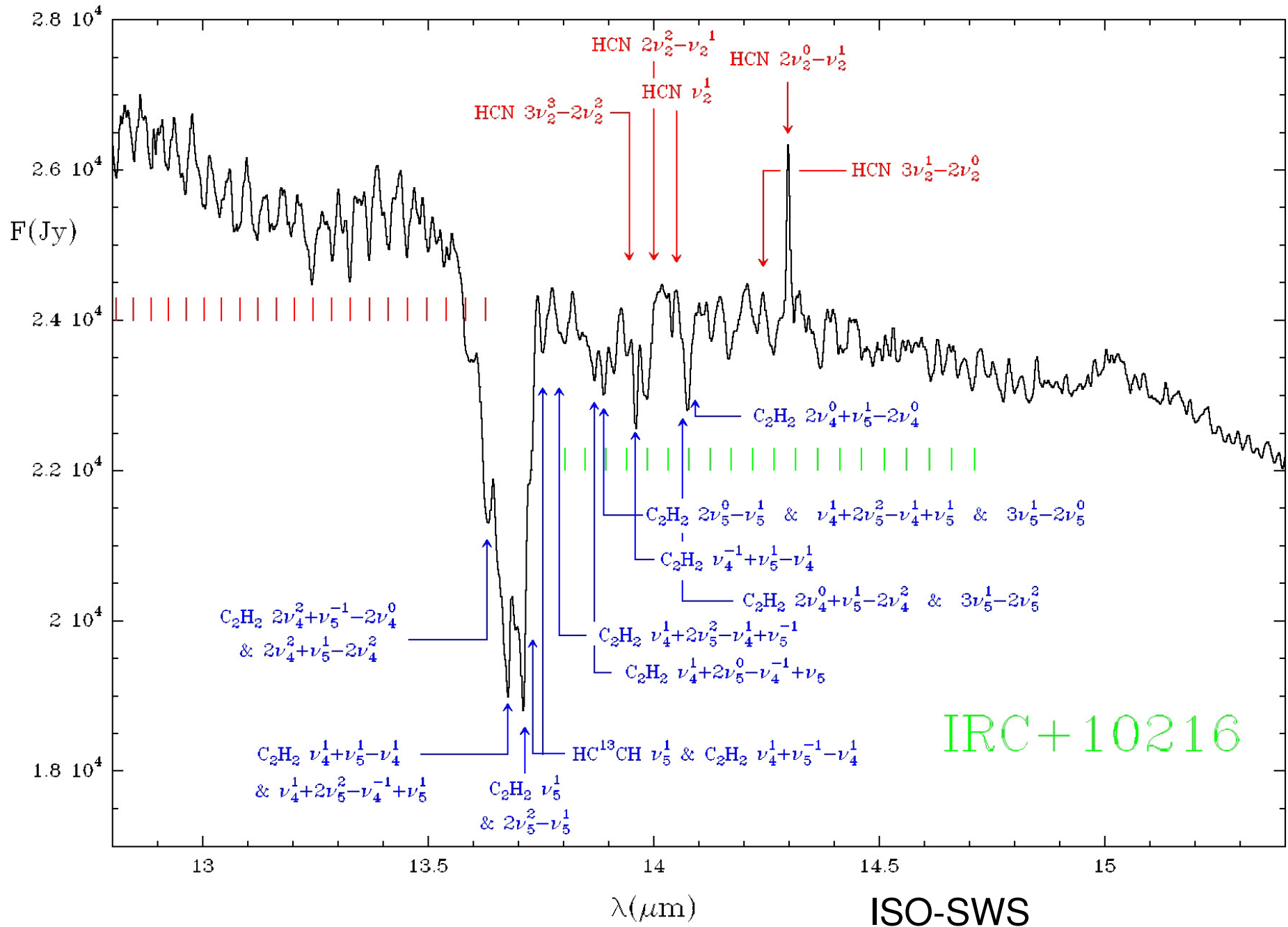
- Observed with the three instruments on board Herschel
- Continuum and spectroscopic observations
- **Full line survey with HIFI :**
 - * Infrared pumping
 - * Time variability of the molecular emission
 - * SiC₂ as the most abundant species containing SiC bonds
 - * Lack of emission from light Carbon-rich species such as C₃H₂, C₂H, C₃H, C₃



Cernicharo et al., 2011, A&A, 521, L8

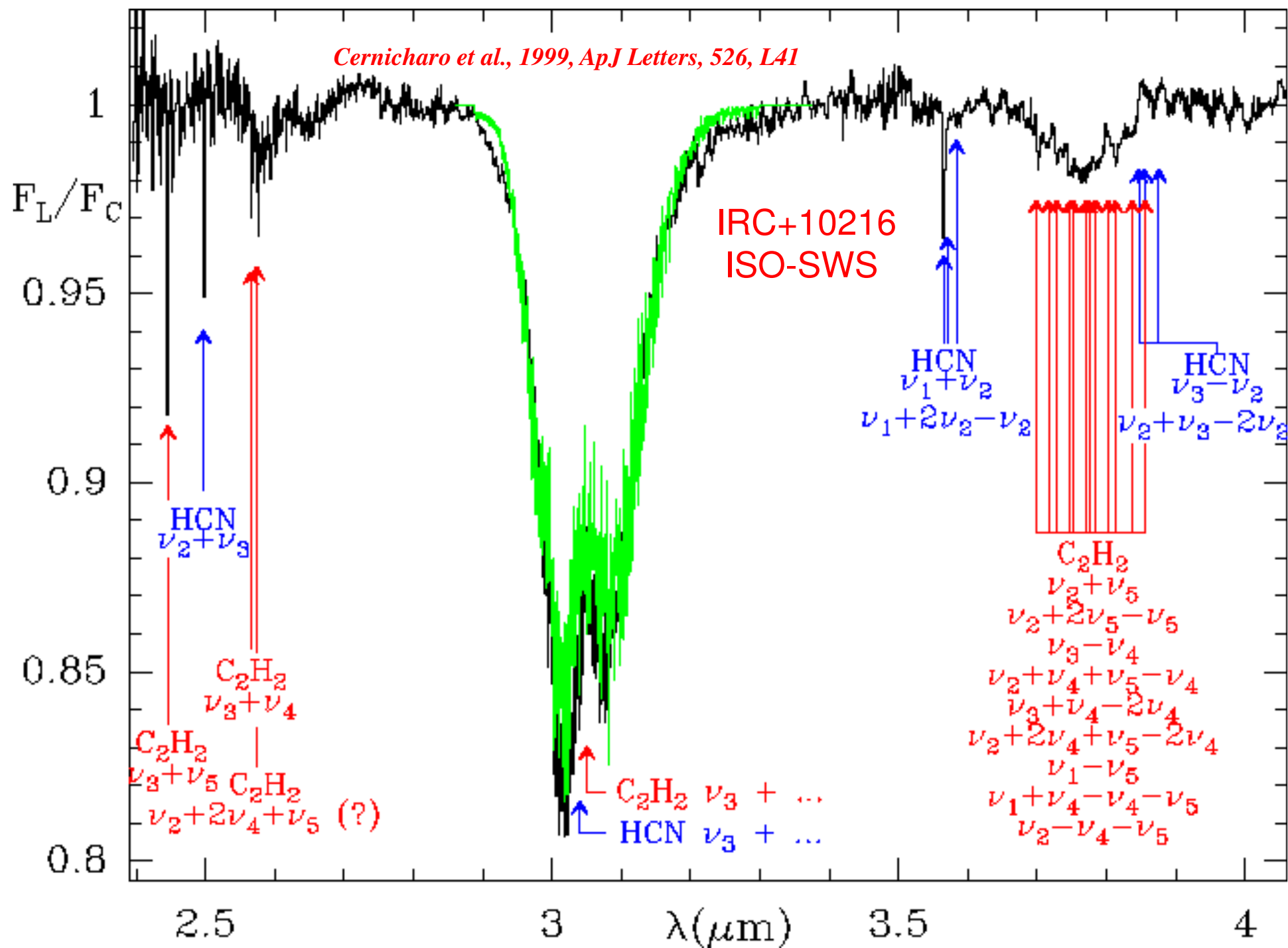


Cernicharo et al. 2010, A&A, 521, L8



Cernicharo et al., 1999, ApJ Letters, 526, L41

Cernicharo et al., 1999, ApJ Letters, 526, L41



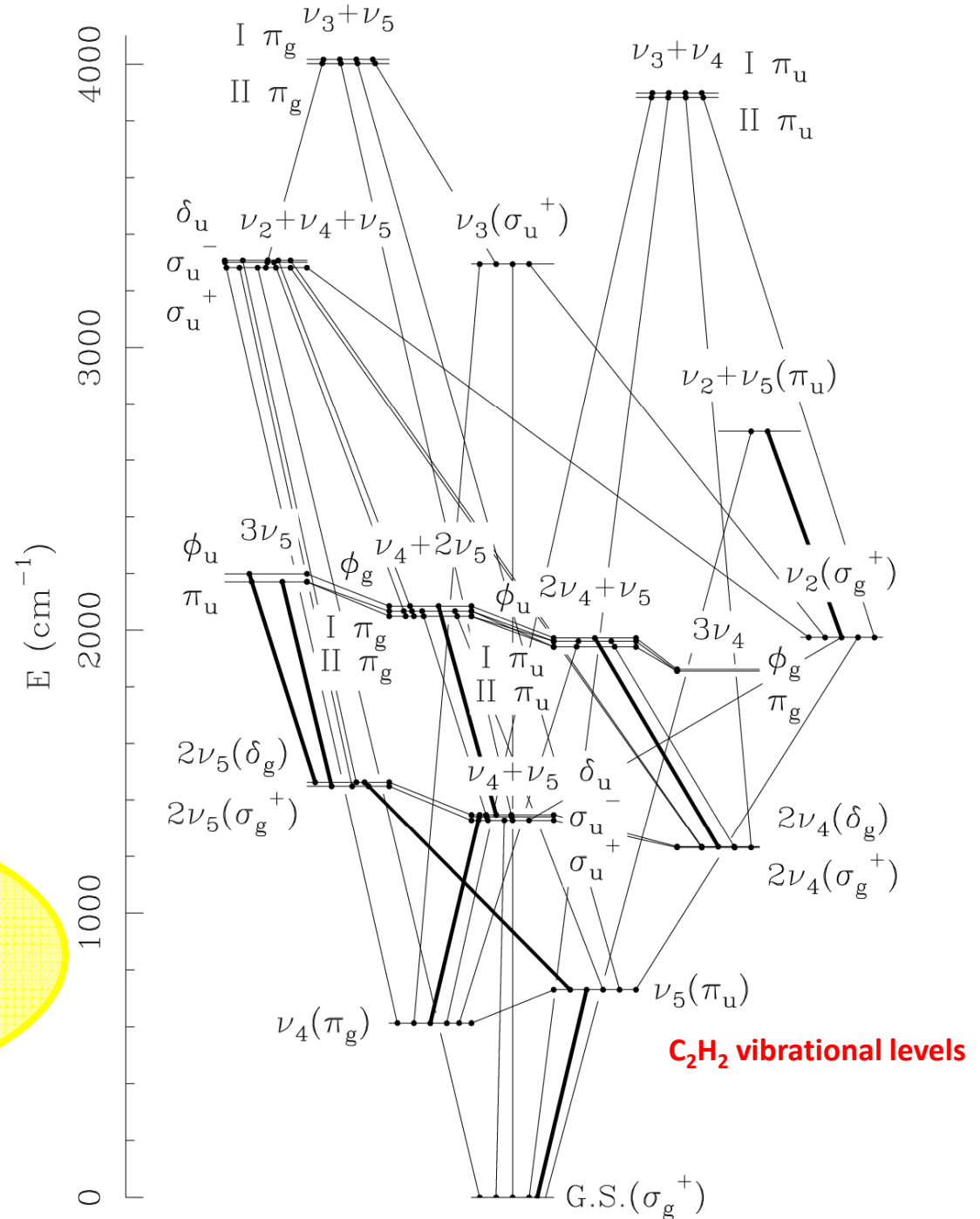
Observations of C_2H_2 and HCN with TEXES at the IRTF

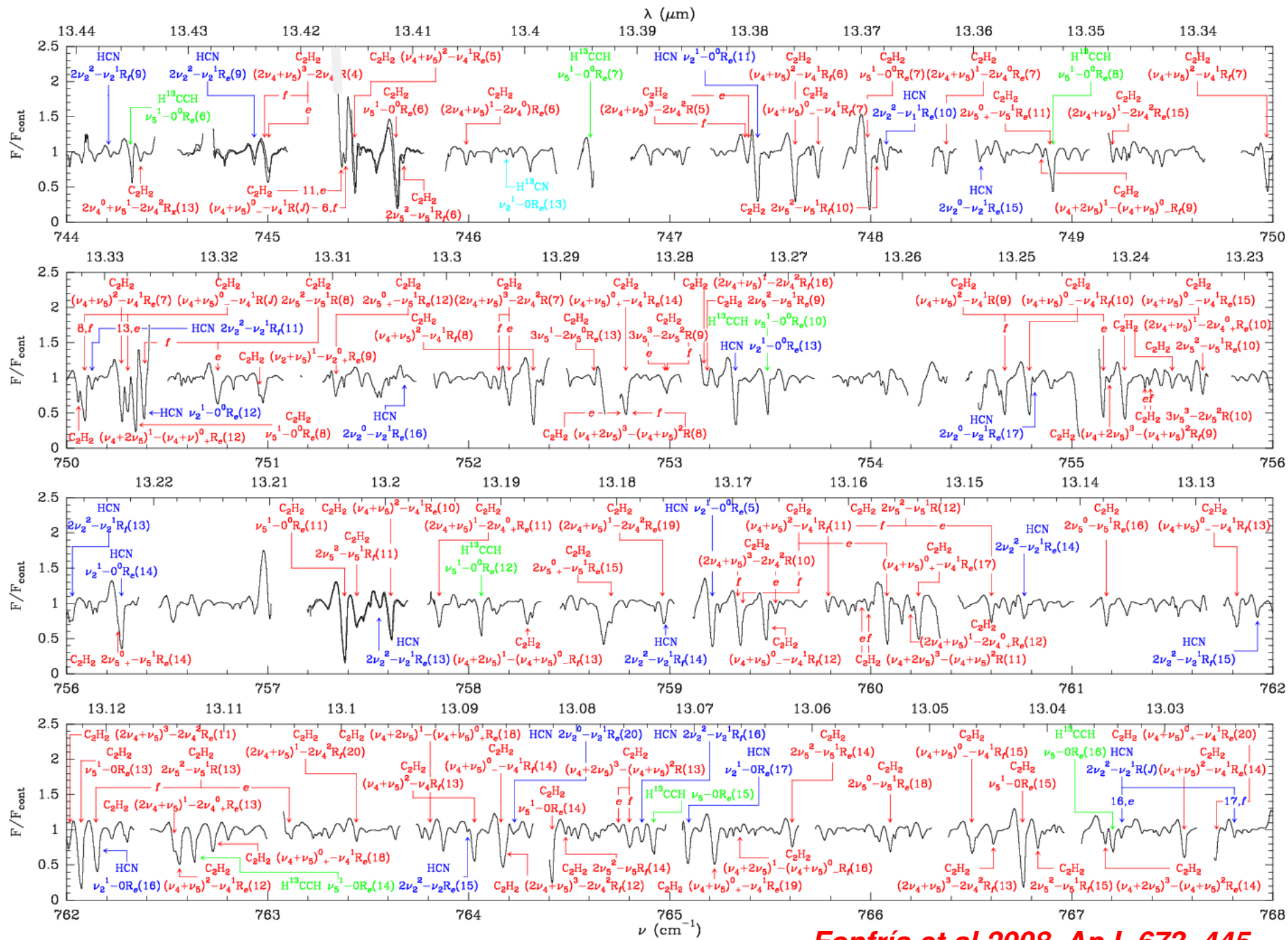
PhD of J.Pablo Fonfría
(Fonfría et al., 2008, ApJ)

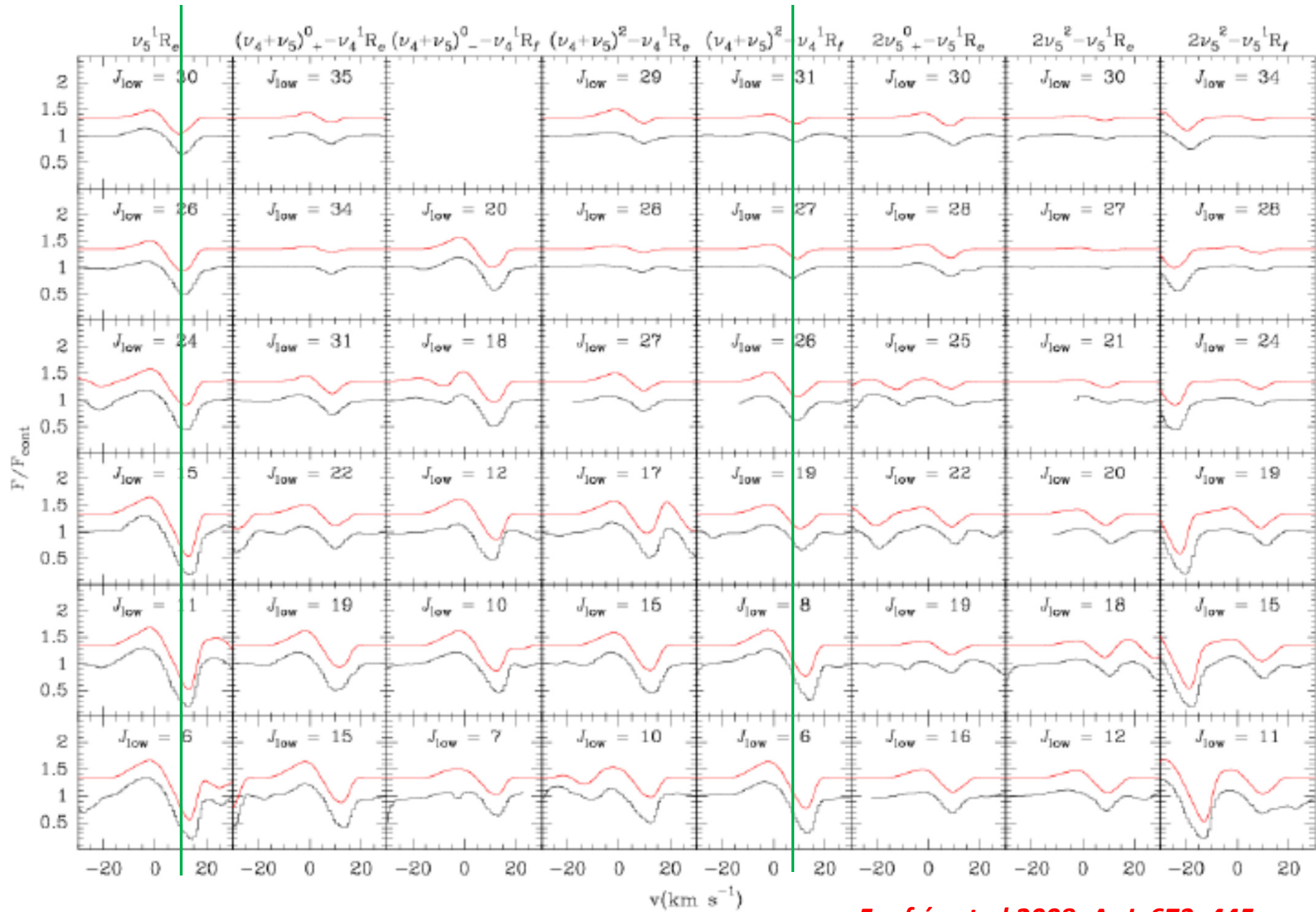
TEXES::Lacy et al., 2002,
PASP, 114, 153

$720-900\text{ cm}^{-1}$
 $11.1-13.9\text{ }\mu\text{m}$

Spectral resolution 75000
4 km/s (0.008 cm^{-1})







DATA

MODEL C₂H₂ + HCN + ISOTOPES

Fonfría et al 2008, ApJ, 673, 445

RESULTS

$x(\text{C}_2\text{H}_2)$

Z I	$7.5 \cdot 10^{-6}$
Z II	$8.0 \cdot 10^{-5}$
Z III	$8.0 \cdot 10^{-5}$

$x(\text{HCN})$

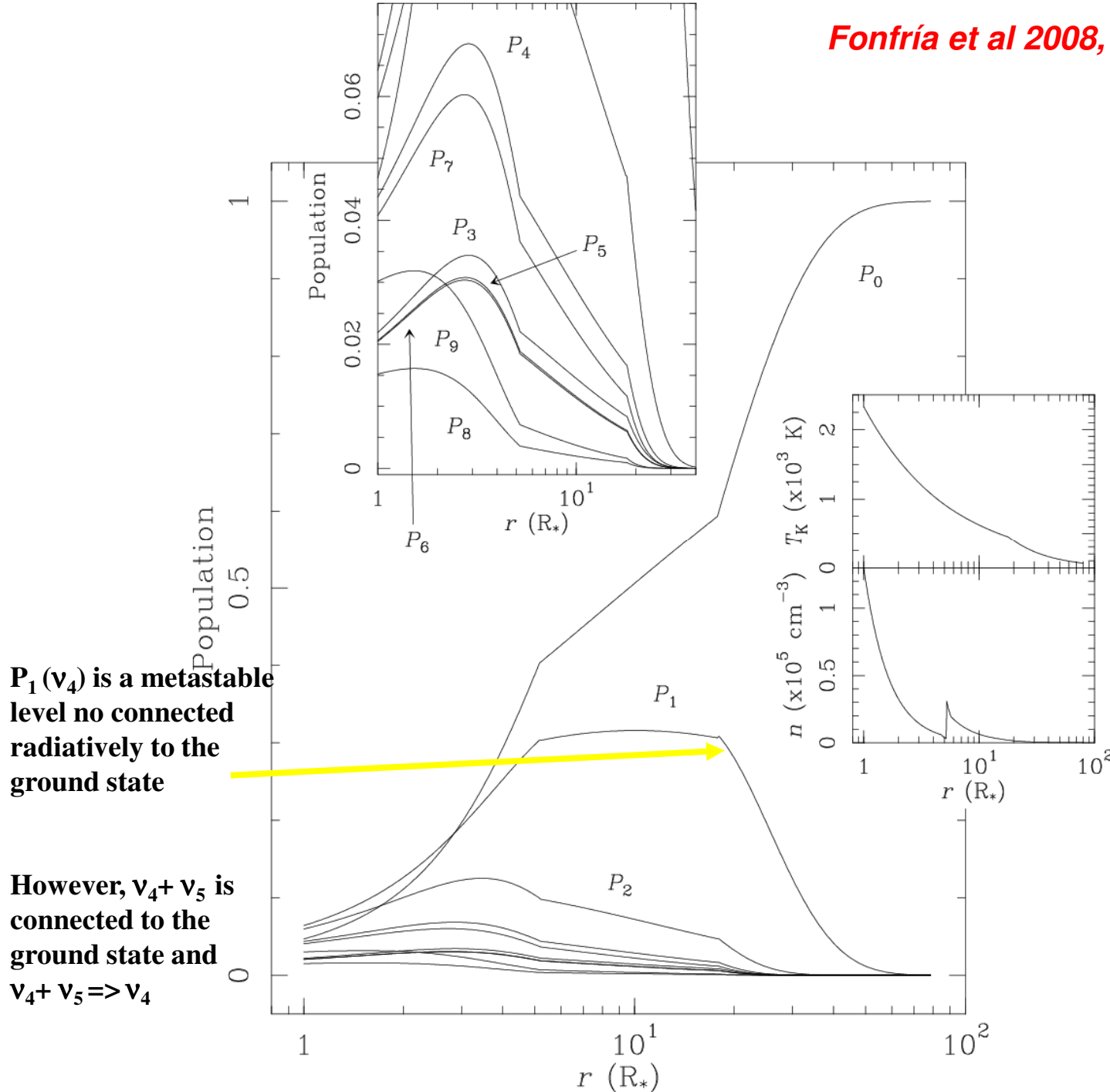
Z I	$2.5 \cdot 10^{-5}$
Z II	$5.0 \cdot 10^{-5}$
Z III	$5.0 \cdot 10^{-5}$

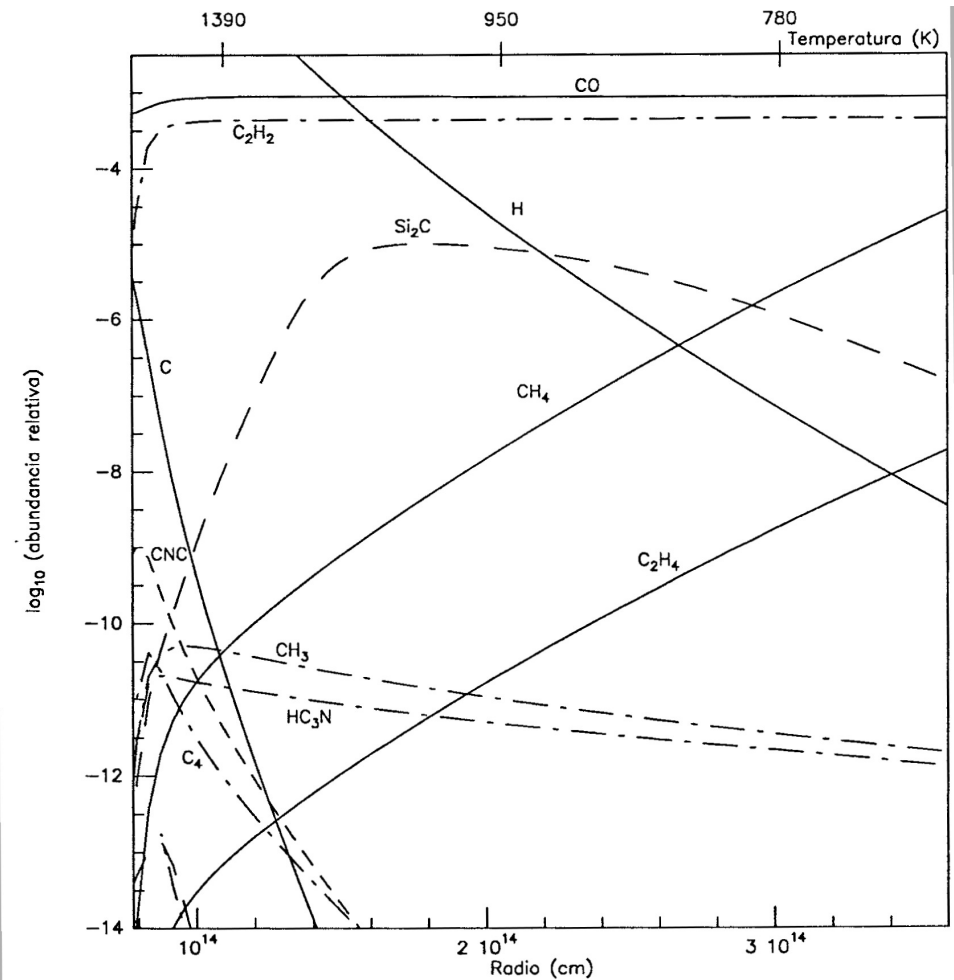
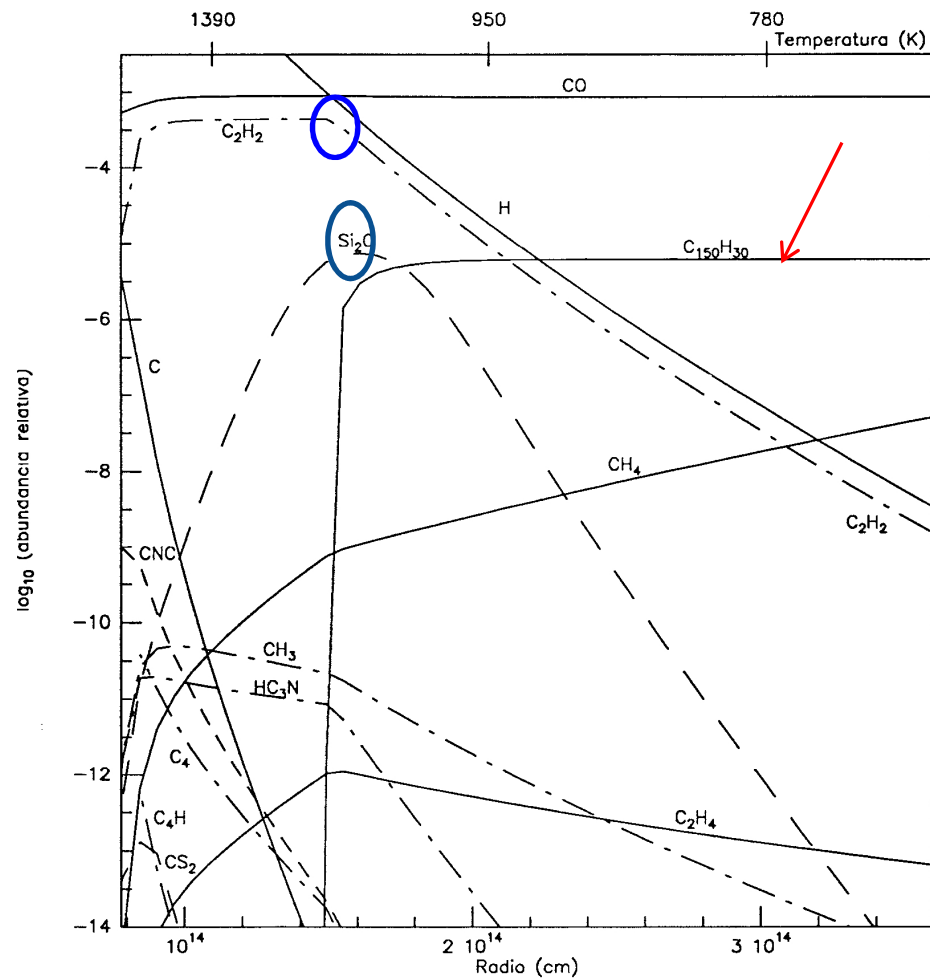
$^{12}\text{C}/^{13}\text{C}=41$

Z I 1- 5 R_*

Z II 5-20 R_*

Z III > 20 R_*





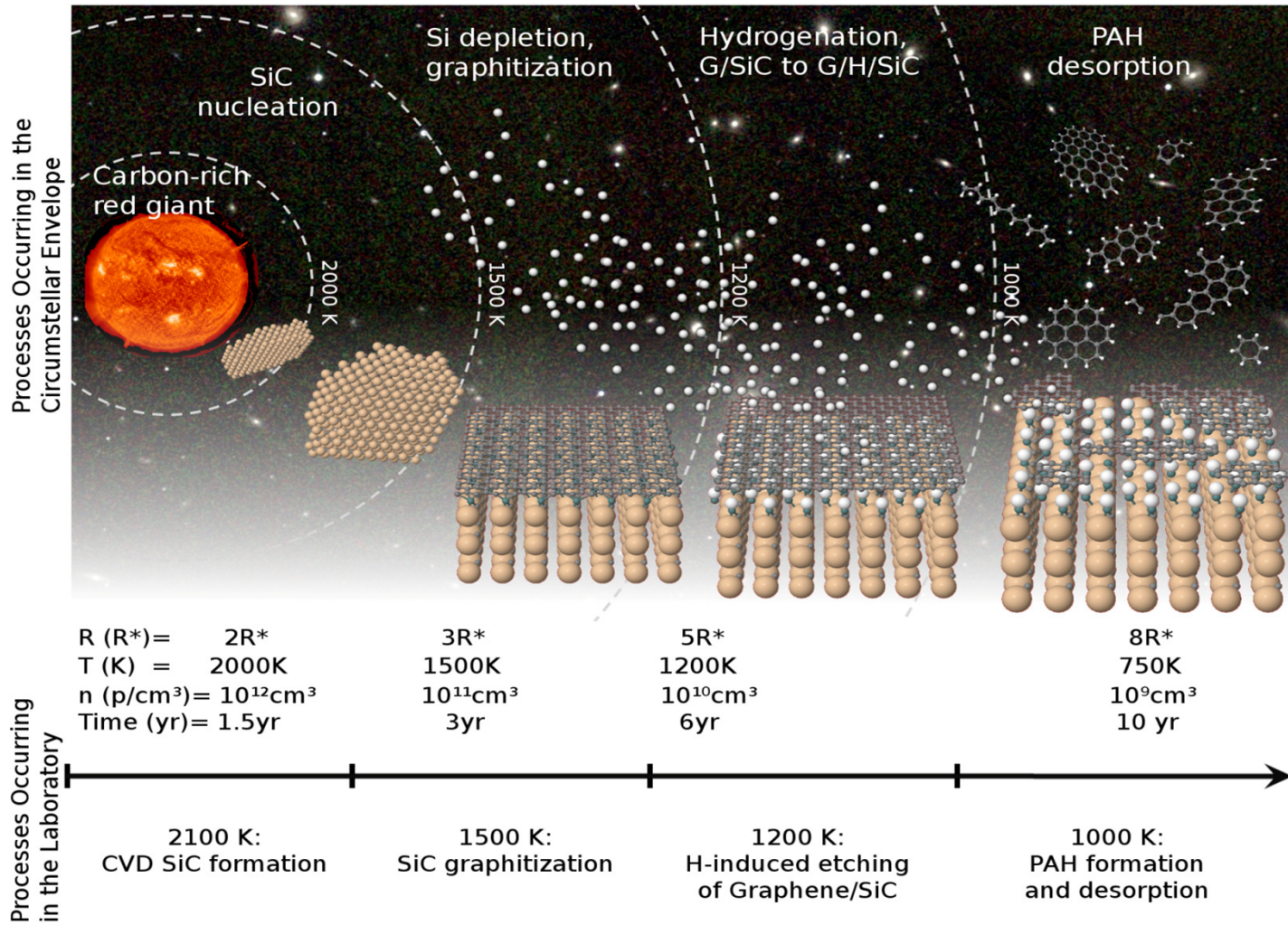
Thermodynamical Equilibrium

With PAHs

Without PAHs

NANOCOSMOS *A new path to form PAHs in evolved stars*

Merino, et al., 2014, Nature Comm. DOI: 10.1038/ncomms4054



ARTICLE

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Graphene etching on SiC grains as a path to interstellar polycyclic aromatic hydrocarbons formation

P. Merino¹, M. Švec², J.I. Martínez³, P. Jelinek², P. Lacovig⁴, M. Dalmiglio⁴, S. Lizzit⁴, P. Soukiassian^{5,6}, J. Cernicharo¹ & J.A. Martín-Gago^{1,3}

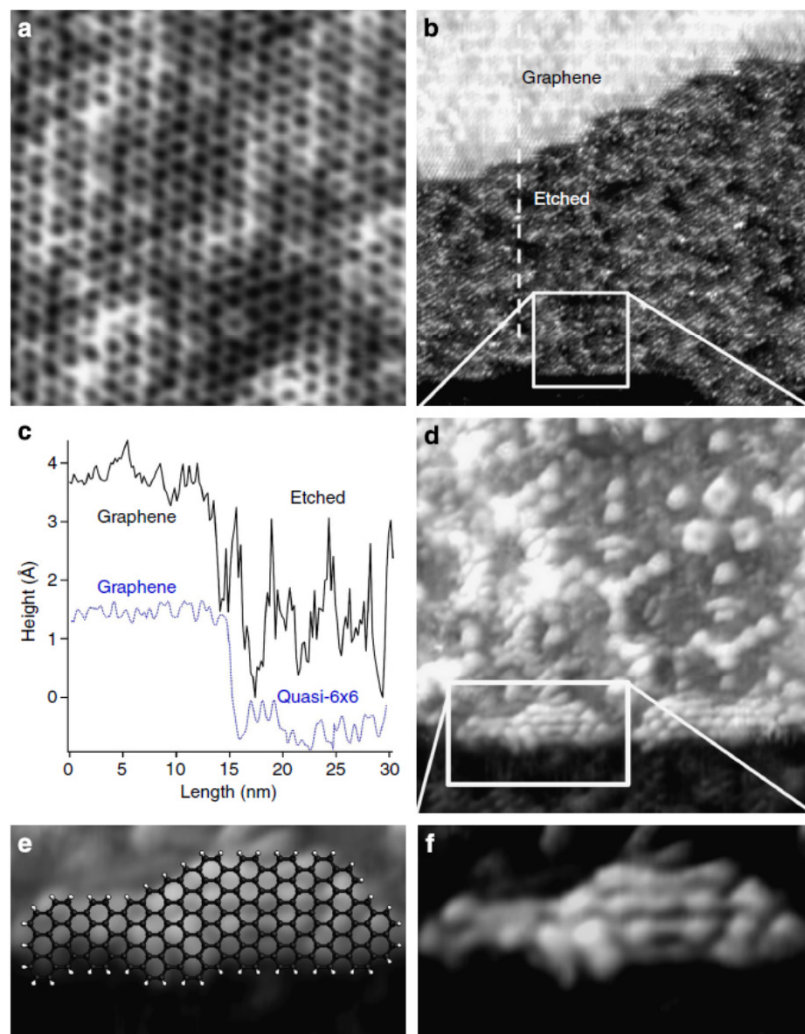


Figure 2 | Graphene etching on high-temperature and atomic H dose. (a) STM image ($5 \times 5 \text{ nm}^2$) showing a graphene region $V=100 \text{ mV}$; the small mesh corresponds to the atomic honeycomb atomic lattice of graphene. (b) The image shows at the upper side a graphene plane, whereas at lower part the surface has strongly roughened. $40 \times 40 \text{ nm}^2$ $V= -100 \text{ mV}$. (c) Profile on STM images recorded before (blue) and after (black) being exposed to atomic H with the surface kept at $1,200 \text{ K}$, taken along the dotted line indicated in. The total roughness (r.m.s.) of the surface increases from 0.22 to 0.69 \AA . (b,d-f) Series of STM images showing the graphene surface eroded after atomic H exposure at high temperature. (d) STM image ($10 \times 10 \text{ nm}^2$) recorded on the most eroded part that shows the formation on the surface of small molecules and nanostructures. $V= -200 \text{ mV}$ (f) STM image ($2.2 \times 4 \text{ nm}^2$) zooming in on a detail of the surface showing protrusions corresponding to localized molecular orbitals of a PAH-like molecule. (e) Overlaid optimized DFT model of a proposed PAH formed.

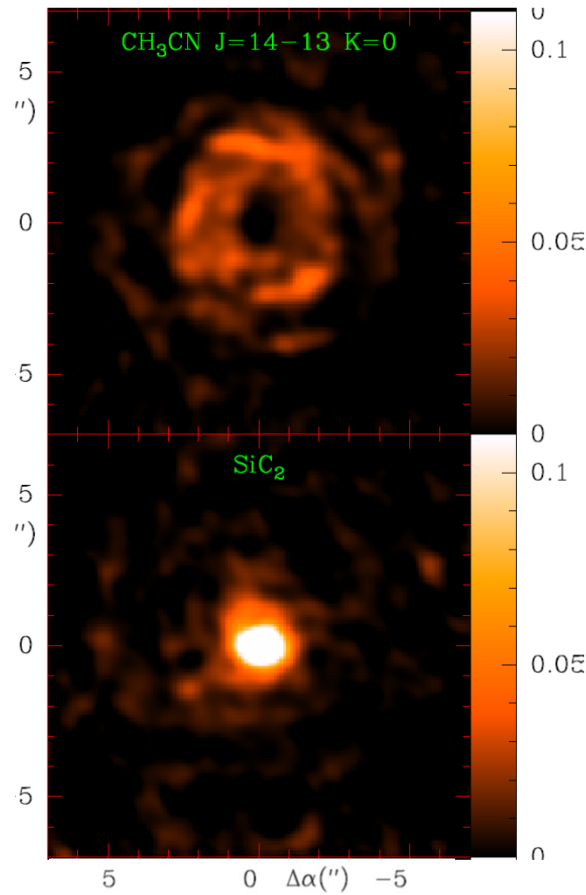
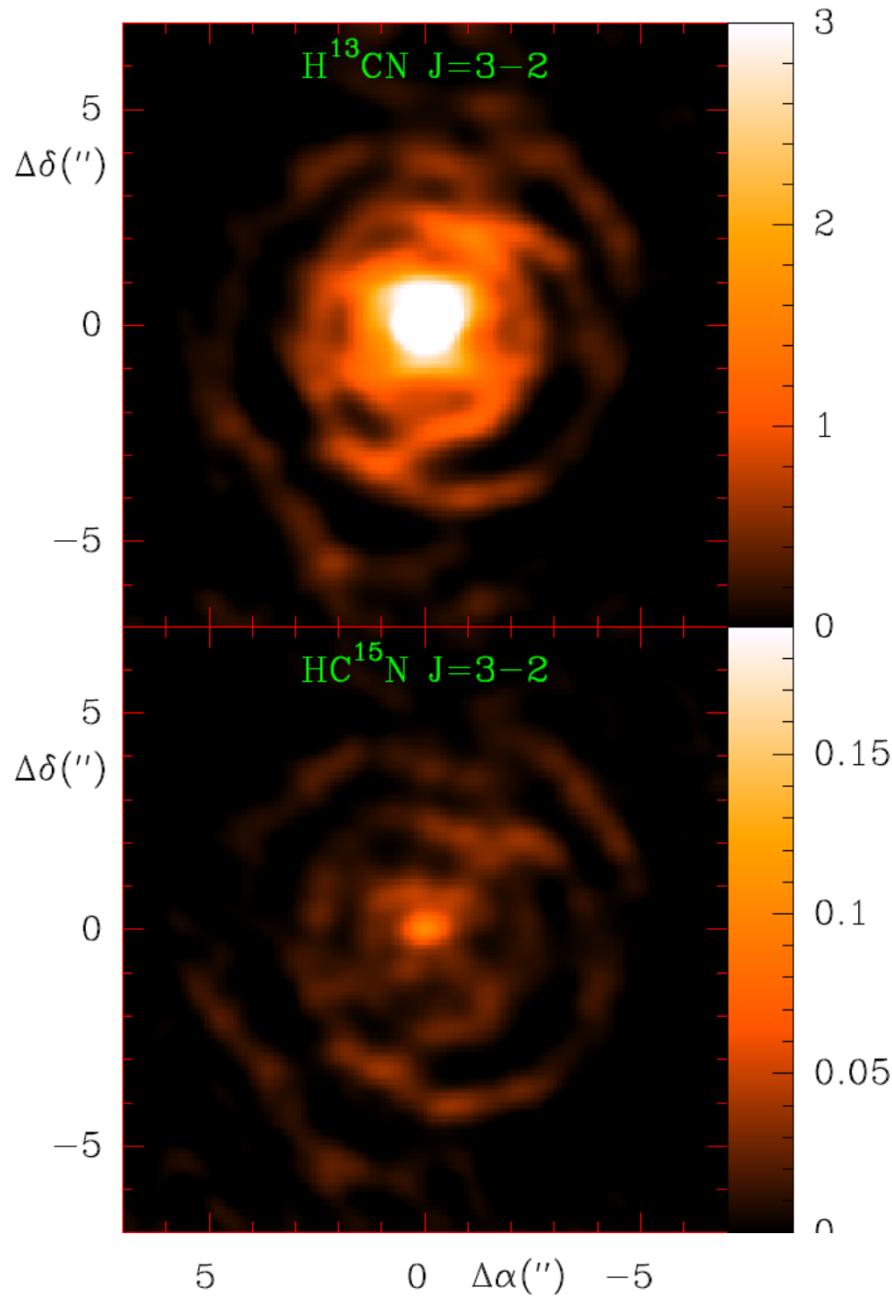
Carbon Balance in the dust formation zone

- In the region 1-5 stellar radii the total number of carbon atoms contained in C_2H_2 and HCN is a factor 5-10 less than for radii $> 5 R_*$. Most carbon locked in CO (and into the grains ?)
- If PAHs are formed in the 1-5 R_* zone from gas phase molecules then TE chemistry predicts the contrary of the observations, i.e., a decrease of the abundance of C_2H_2 , HCN, CH_4 , C_2H_4 , and even SiC_2 .
- Molecules as CH_4 , C_3 , C_5 , CN, C_2H_4 , C_2H_6 , and other small hydrocarbons should be abundant. Very little is known on the abundance of these species near the star. They deserve IR observations similar to those of Fonfría et al. for acetylene and hydrogen cyanide. (and also for Si bearing non polar species such as SiH_4 , Si_2 , ...)
- A detailed balance of Carbon has to be made in the innermost zones before concluding about the formation of large carbon-bearing species such as PAHs and the possible content of C in dust grains. Grain chemistry has to be considered.
- Mm/submm Line Surveys (ALMA): Polar Carbon species, CCH, C_nH , HCN, HNC, SiS, SiO, CS, CO,...

The ALMA view of IRC+10216

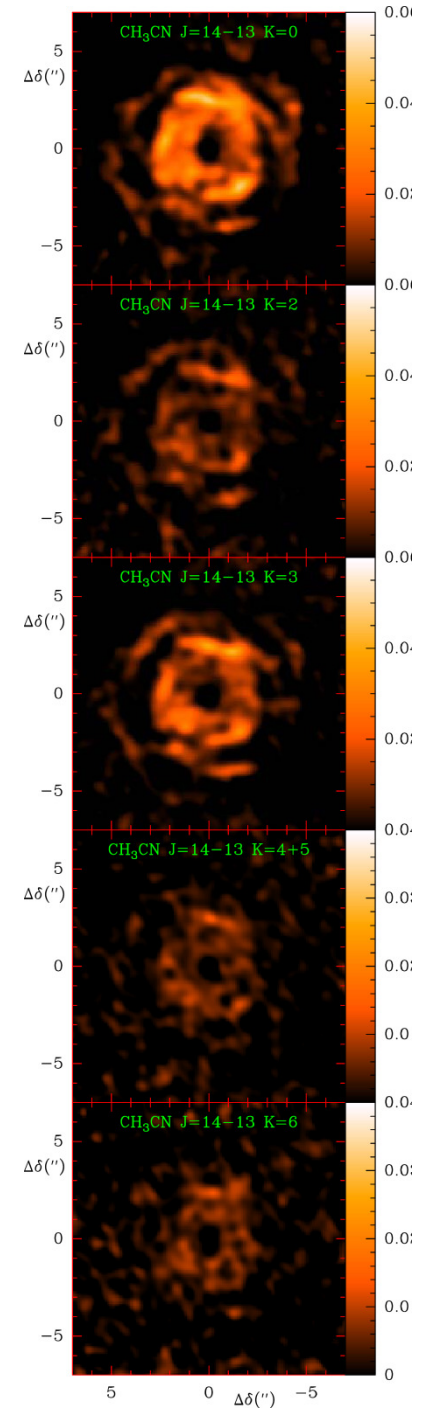
*tracing the dust formation zone
in the mm/submm domains*

The Spatial Distribution of Matter as seen by ALMA



$v-v_{\text{star}}=0 \text{ km/s maps}$

CH₃CN see Agundez et al. 2015, ApJ Letters, submitted



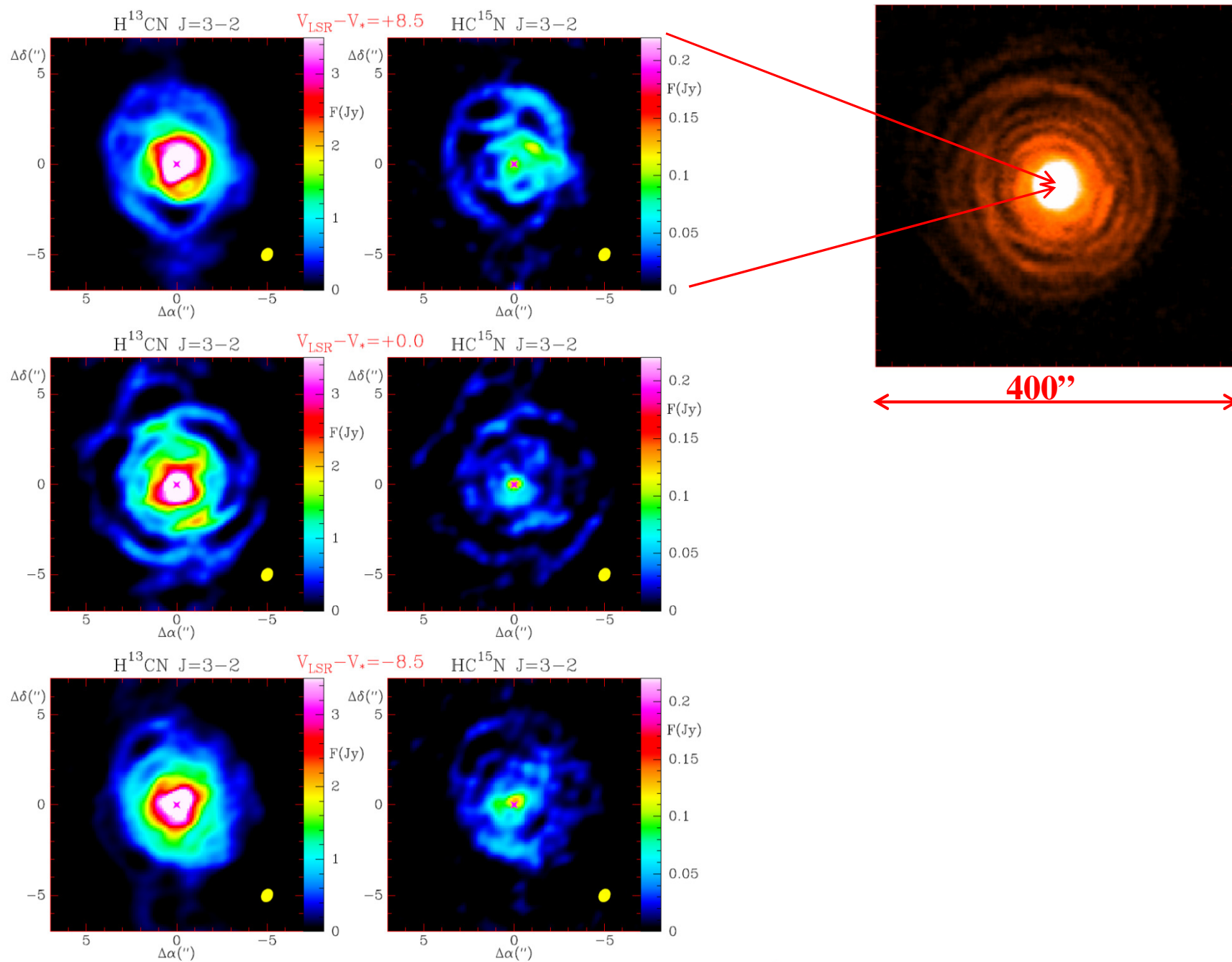


Figure 1. Spatial distribution of the brightness emission of the J=3-2 lines of H^{13}CN and HC^{15}N in the central region of IRC+10216. The synthetic beam of ALMA is shown in yellow. The central cross indicate the position of the continuum emission. This figure corresponds to three frames of the associated online video.

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

HCN in high energy vibrational levels (>10000 K)

SiC₂ in ν_3 and $2\nu_3, \dots$

SiS up to $\nu=10$ (& isotopologues)

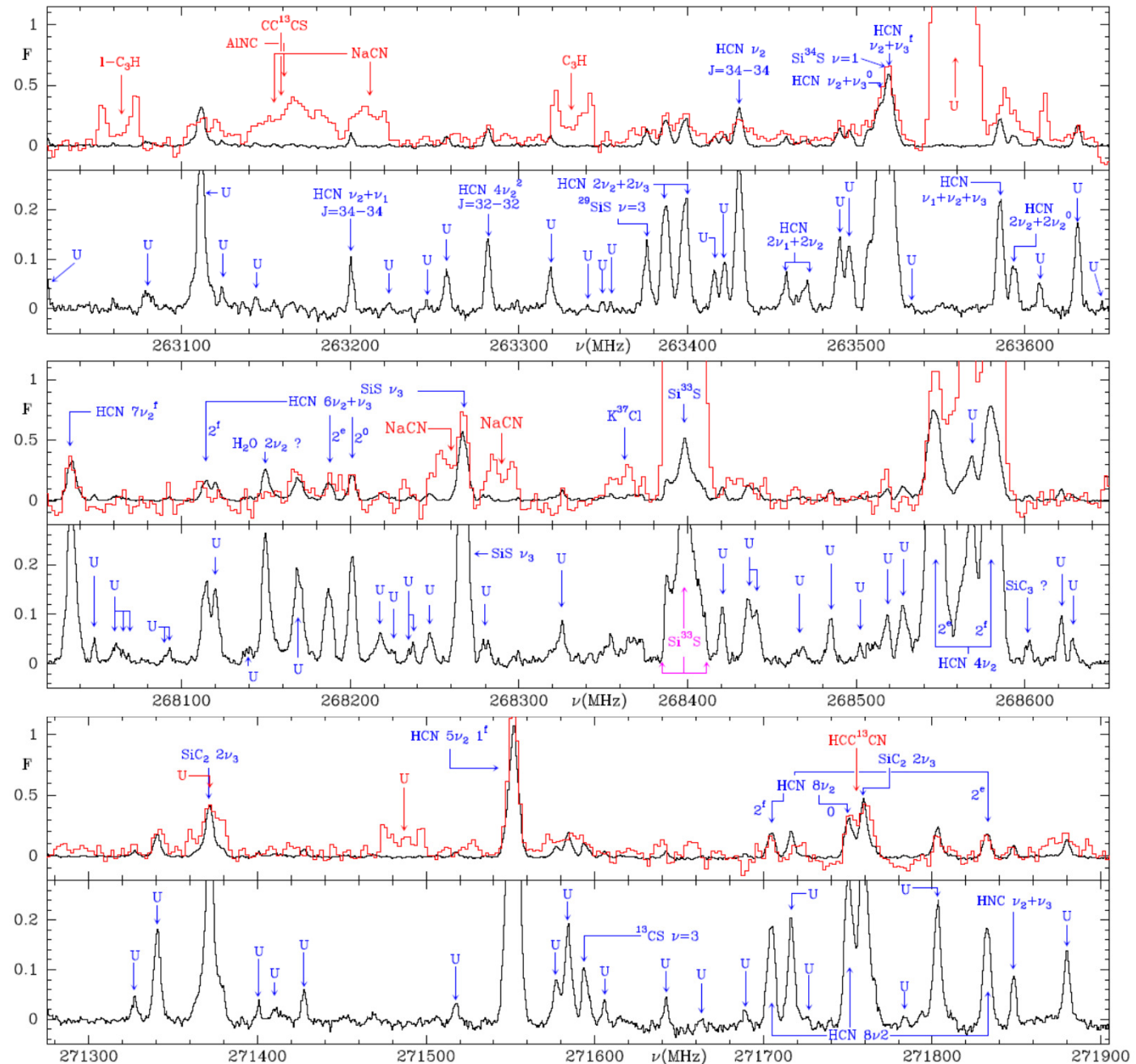
SiO up to $\nu=3$ (& isotopologues)

See Velilla Prieto 2015 ApJ Letters, submitted and his talk

HNC in vibrational levels up to 6000 K

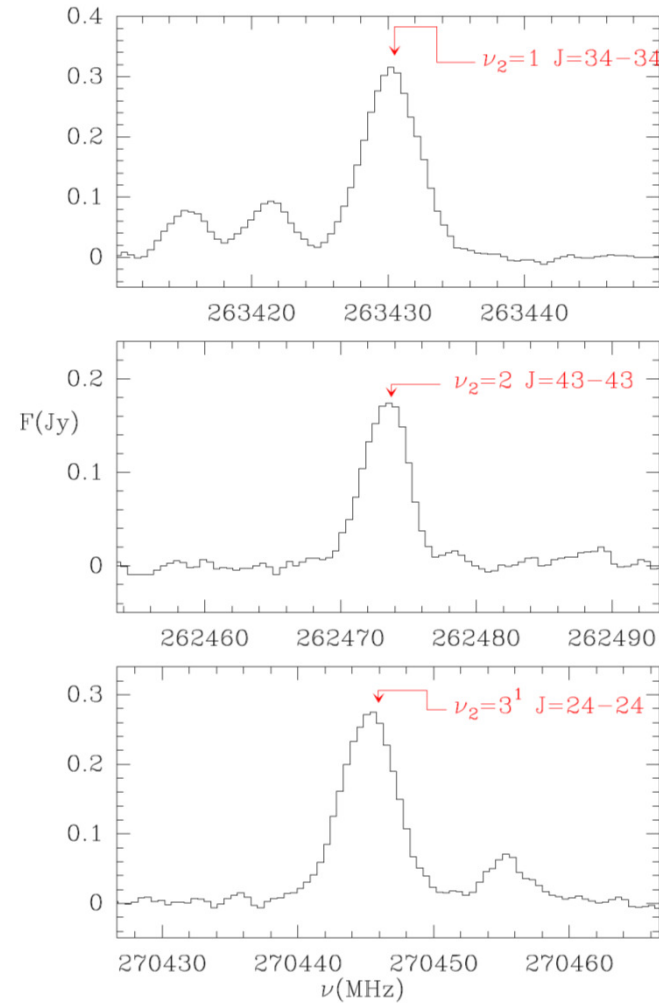
+ hundreds of U lines

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



What are the Carriers of the U lines ?

- I-doubling lines ($\Delta J=0$) of HCN detected for $\nu_2=1,2,3$.
- These lines are narrow and weak.
- Frequencies for I-doubling transitions from levels $iv_1+nv_2+jv_3$ $n>2$ are poorly known. They could be responsible for a few tens of lines



ON THE EXPLANATION OF THE SO-CALLED CN LASER*

HCN lasers....

David R. Lide, Jr. and Arthur G. Maki
 National Bureau of Standards
 Washington, D. C.
 (Received 19 May 1967)

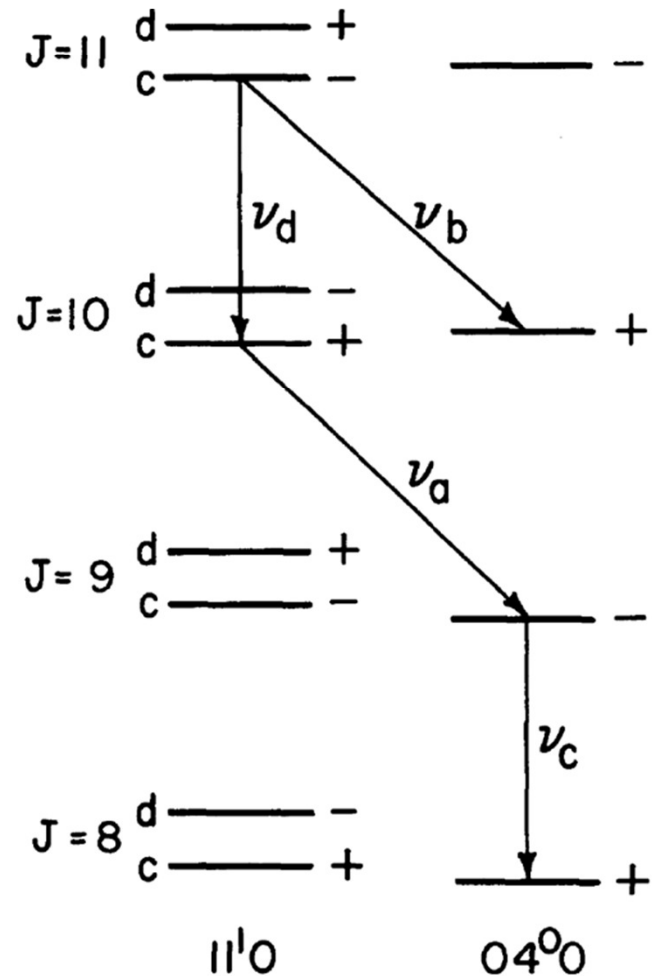
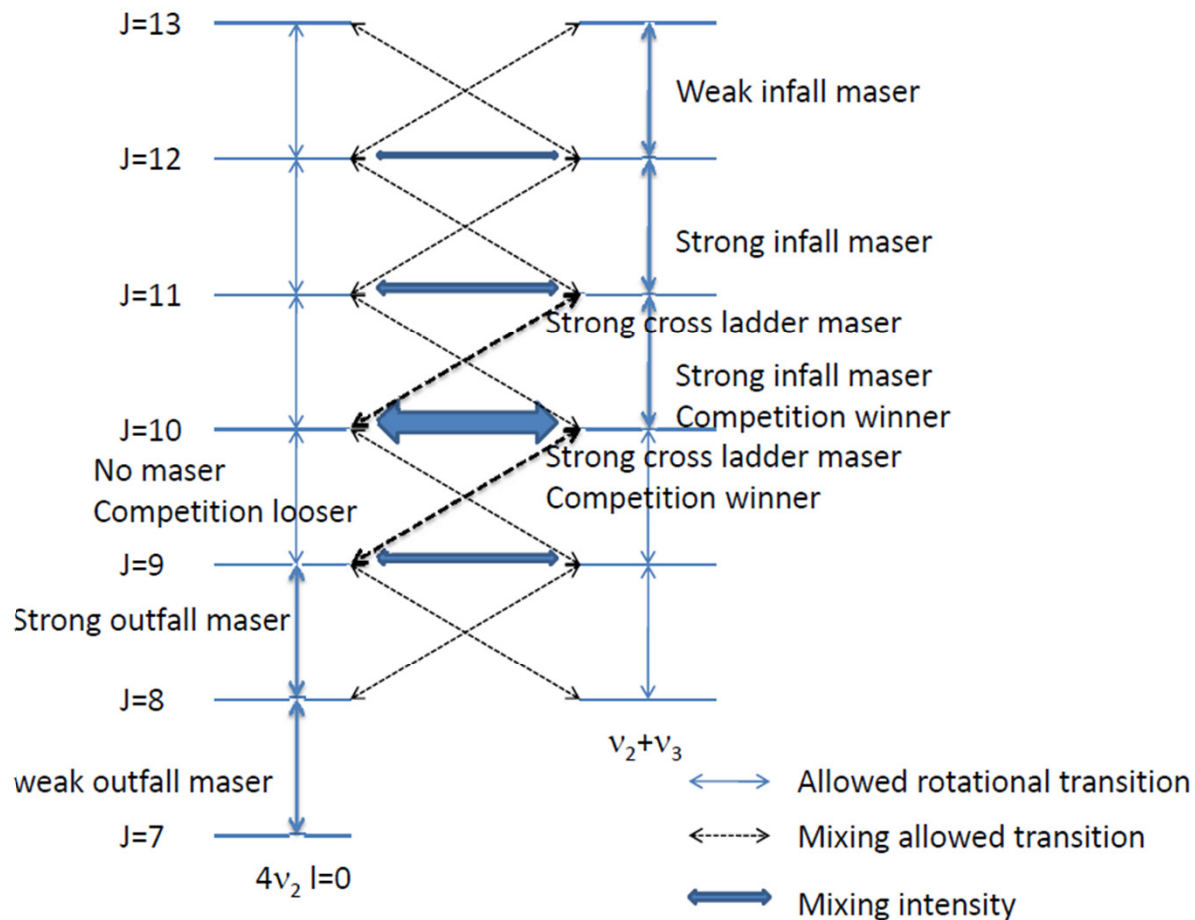


Fig. 1. Pattern of levels in HCN. The $11^1 0$ level is split by l -type doubling.

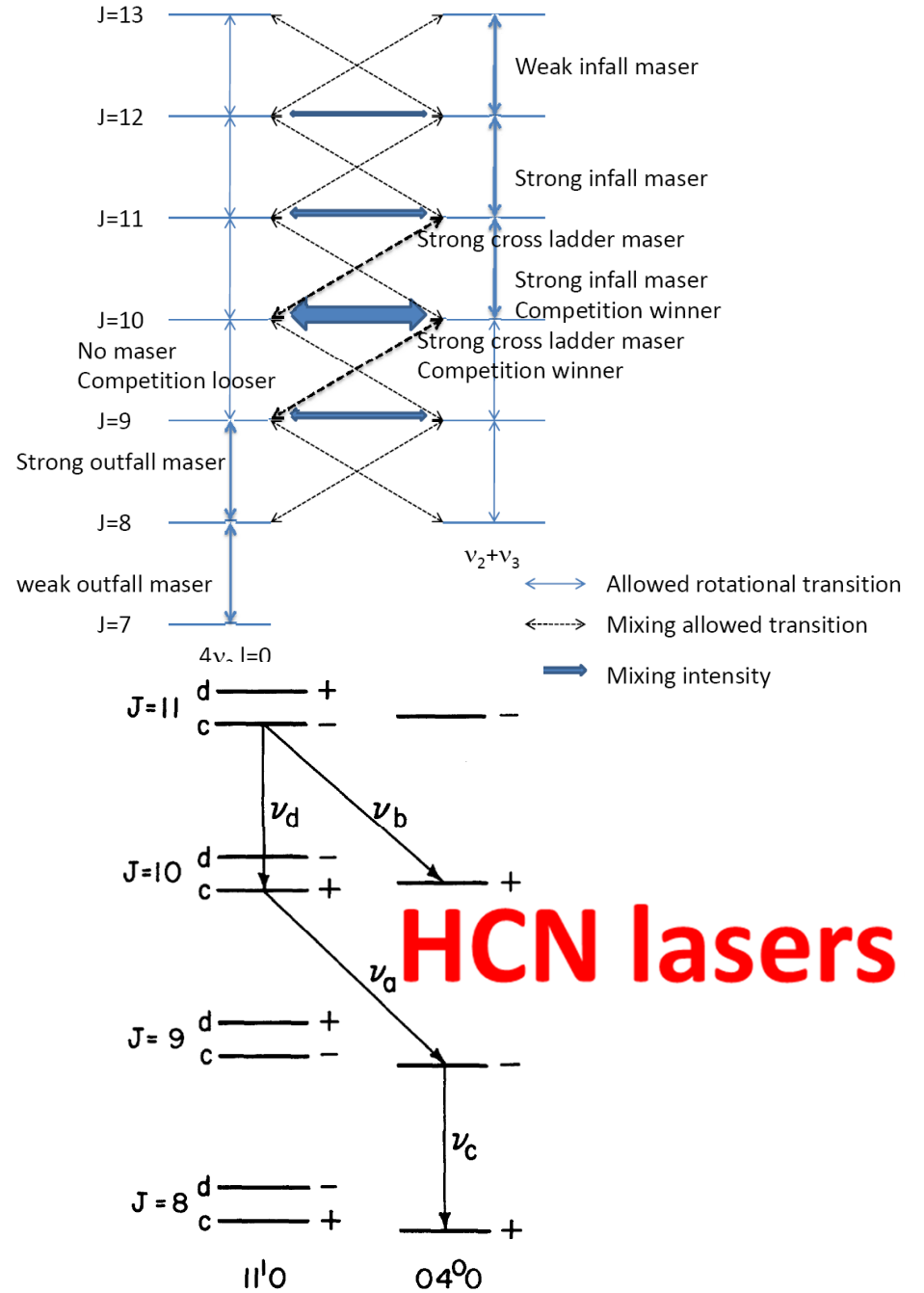
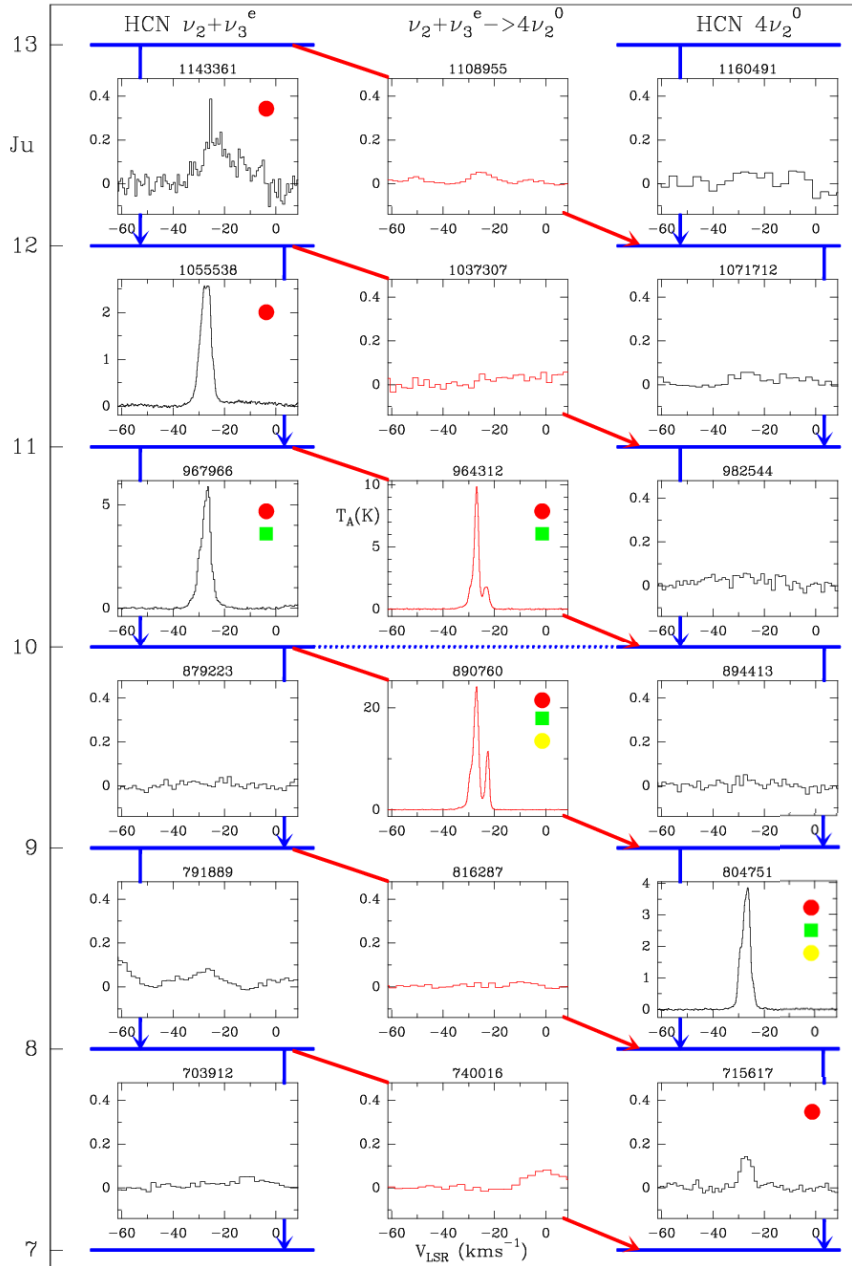
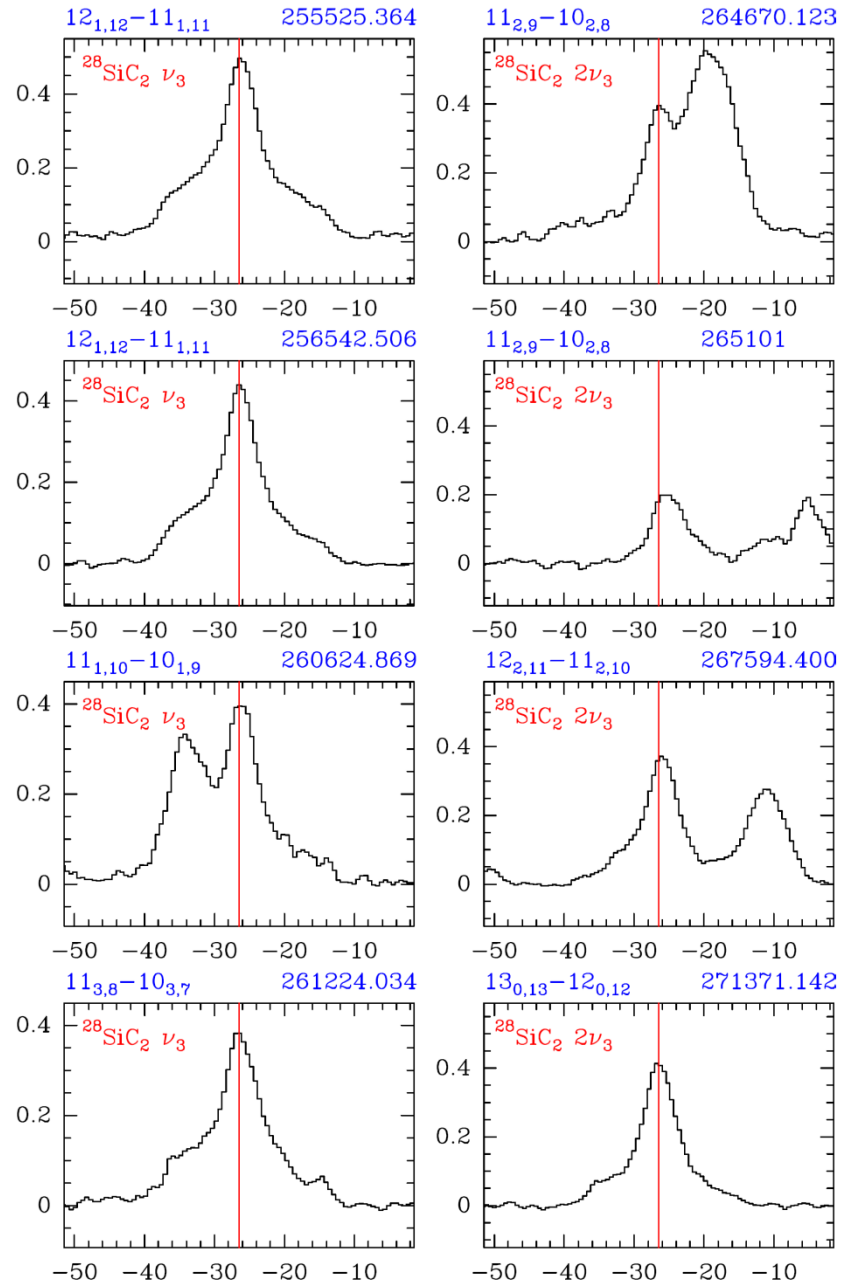


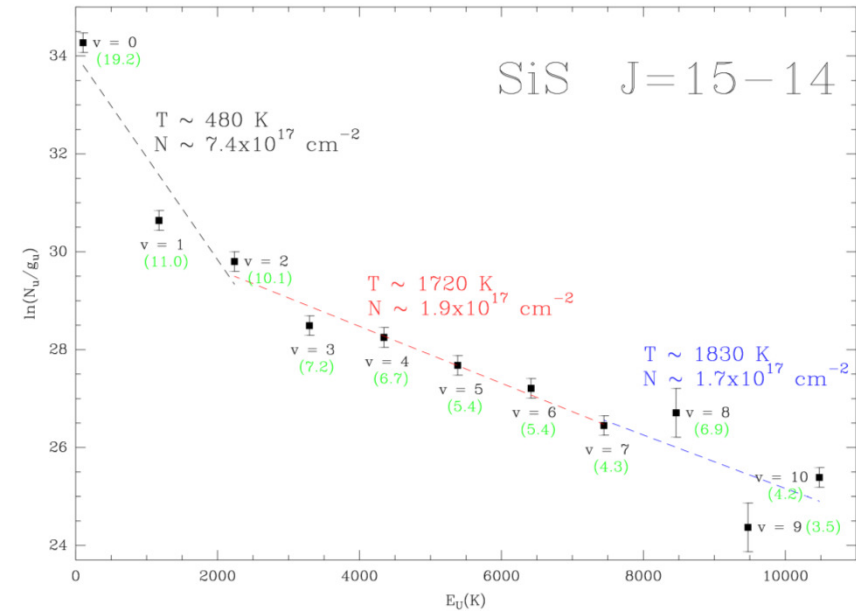
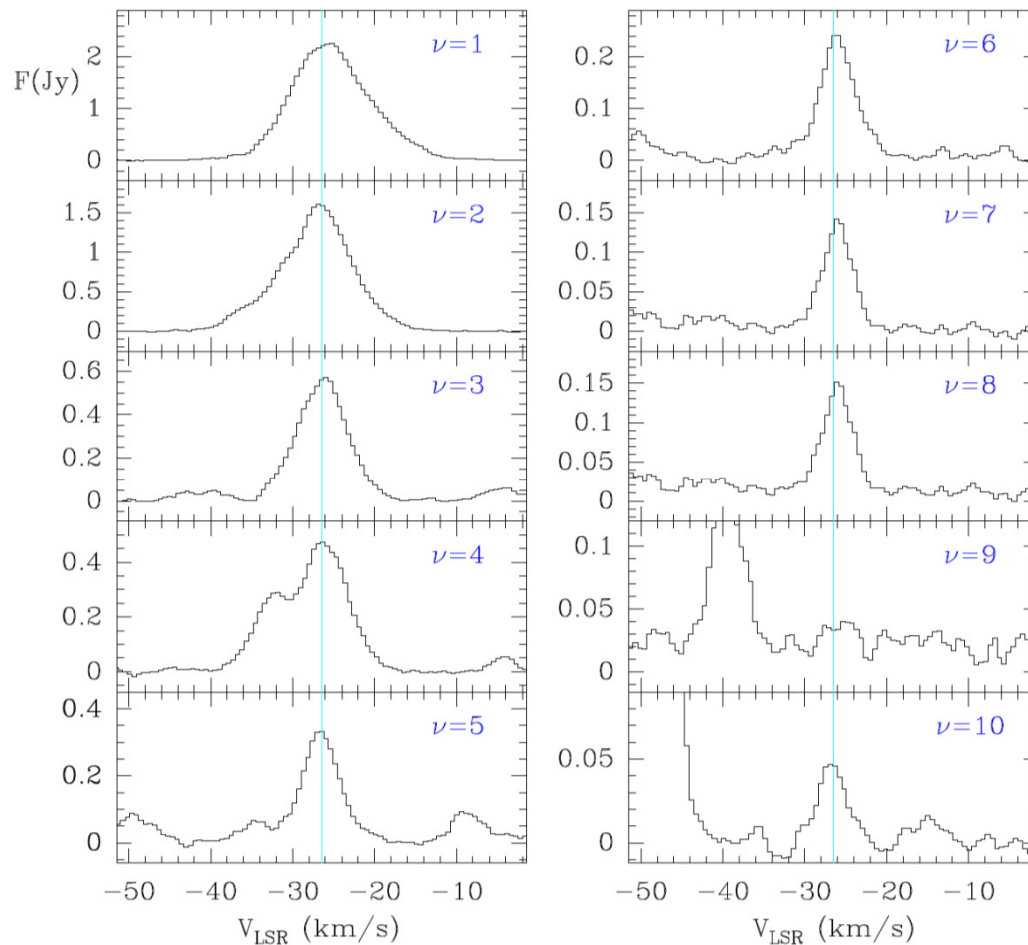
Fig. 1. Pattern of levels in HCN. The 11^1_0 level is split by l -type doubling.

SiC₂ vibrationally excited

- Several lines of SiC₂ and its isotopologues detected in $v_3=1,2$.
- Lines from other higher overtones of v_3 could be present. All together they could represent 20-30 lines.
- All emission in v_3 levels is restricted to a zone <1''



SiS and other diatomic highly vibrationally excited ($\nu=10$)



SiS $\nu>3$ is coming from a region $1-1.5R_*$ ($0.03-0.04''$)

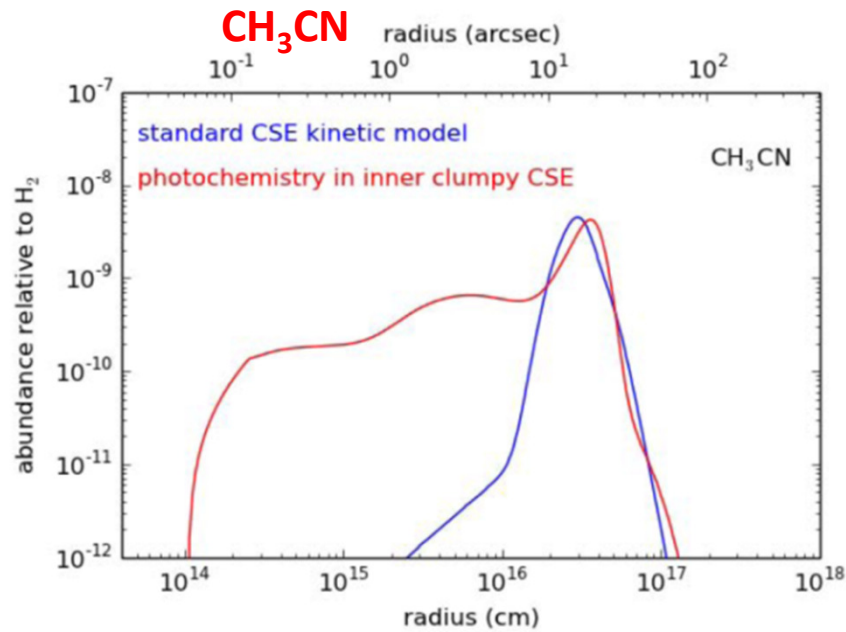
SiS $\nu<3$ is coming from the dust growth zone ($1''$)

Velilla Prieto 2015, ApJ Letters, and his next talk

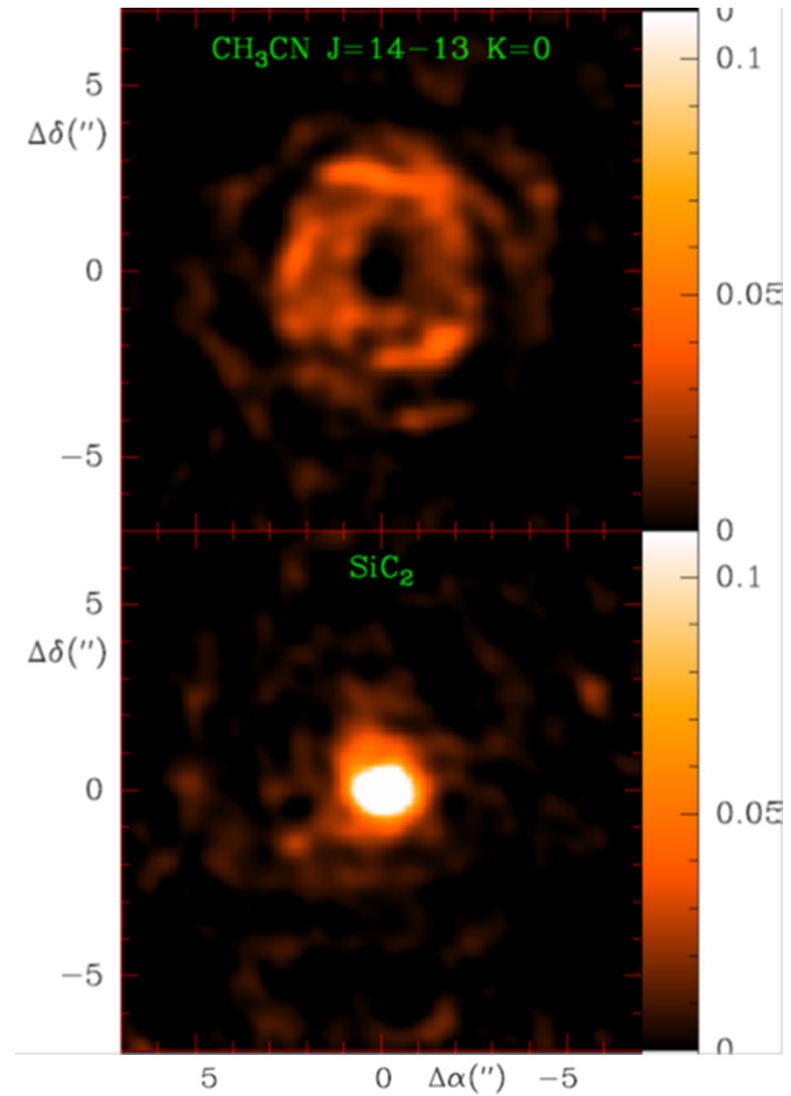
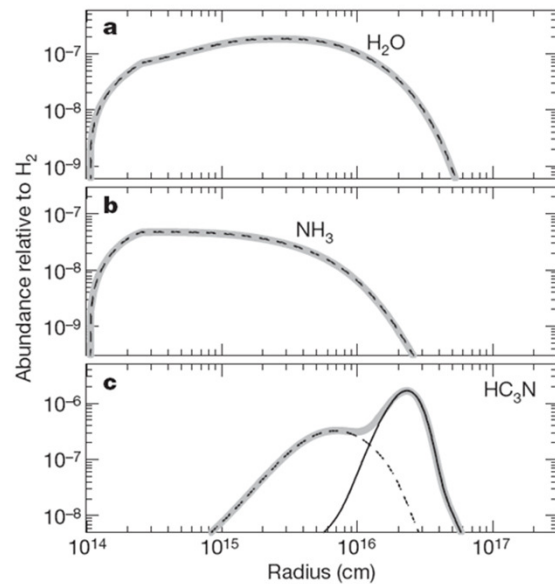
Similar plot than for HCN (Cernicharo et al., 2011, A&A, 529, L3)

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)
- The most abundant species in gas phase containing a SiC bond is SiC_2 .
Additional SiC-bearing species needed to explain the observed SiC grain feature ?
- Si_2C , SiC_n , Si_nC_m ? However, none of the SiC_n molecules already detected in the external shells of IRC+10216 are present in the dust formation zone. Si_nC_m 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) are formed in the external radical shell at $\sim 14''$ *(none of them observed with Herschel)*
- 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 $>1''$.



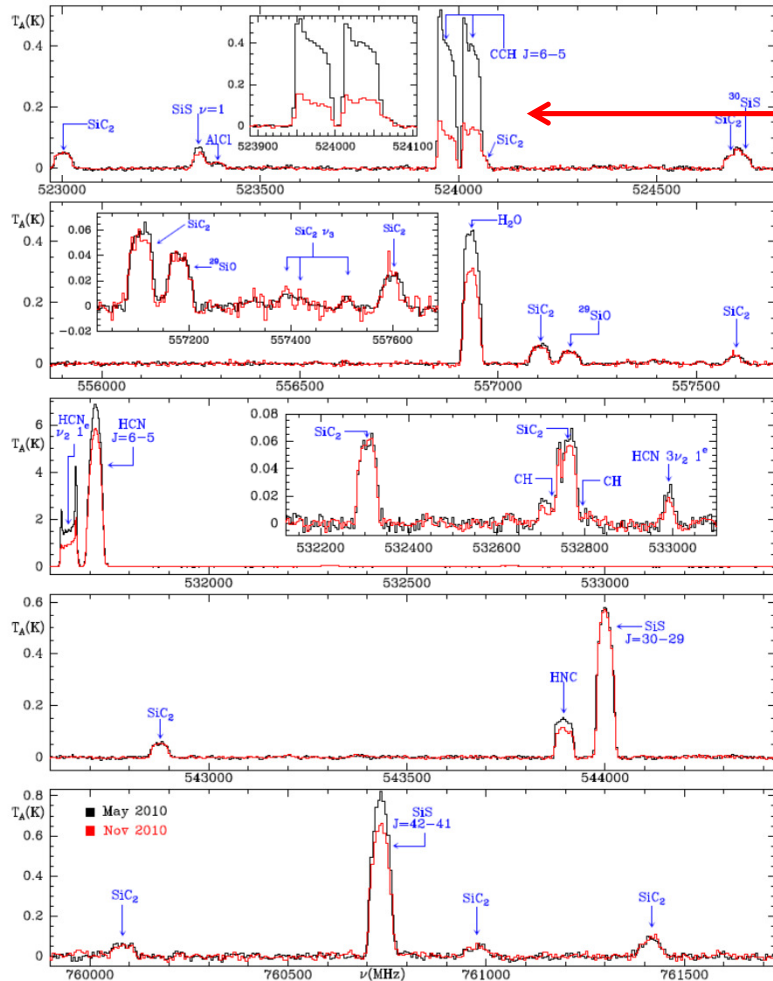
Photochemistry is playing a crucial role in the region $r > 1''$. Efficient for all AGBs with $dM/dt < 10^{-6}$. Clumpy structure of the envelope also allows photochemistry for higher mass loss rates (see Agúndez et al. 2010, ApJ, 724, L133, and Decin et al. 2010, Nature, 467, 64)



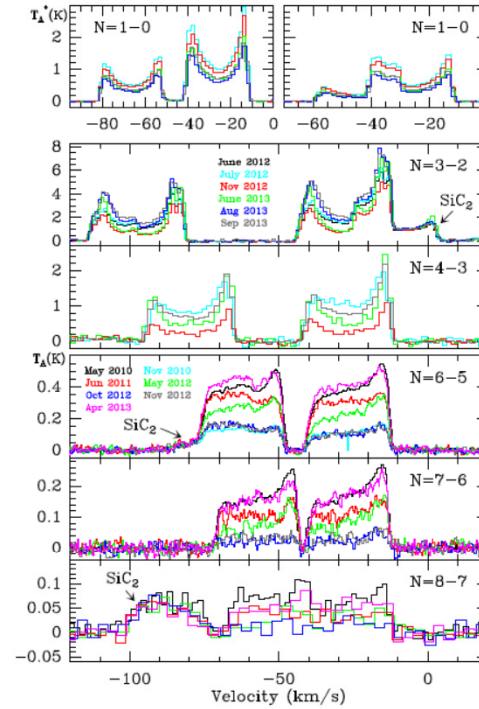
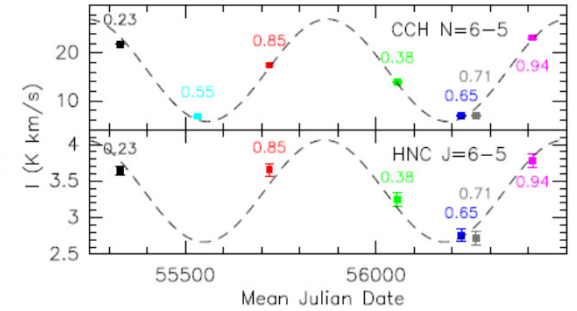
Agúndez et al., 2015, ApJ Letters submitted

DISCOVERY OF TIME VARIATION OF THE INTENSITY OF MOLECULAR LINES IN IRC+10216 IN THE SUBMILLIMETER AND FAR-INFRARED DOMAINS

J. CERNICHARO¹, D. TEYSSIER², G. QUINTANA-LACACI¹, F. DANIEL^{3,4}, M. AGÚNDEZ¹, L. VELLILLA-PRIETO¹,
 L. DECIN⁵, M. GUÉLIN⁶, P. ENCRENAZ⁷, P. GARCÍA-LARIO², E. DE BECK⁸, M. J. BARLOW⁹,
 M. A. T. GROENEWEGEN¹⁰, D. NEUFELD¹¹, AND J. PEARSON¹²

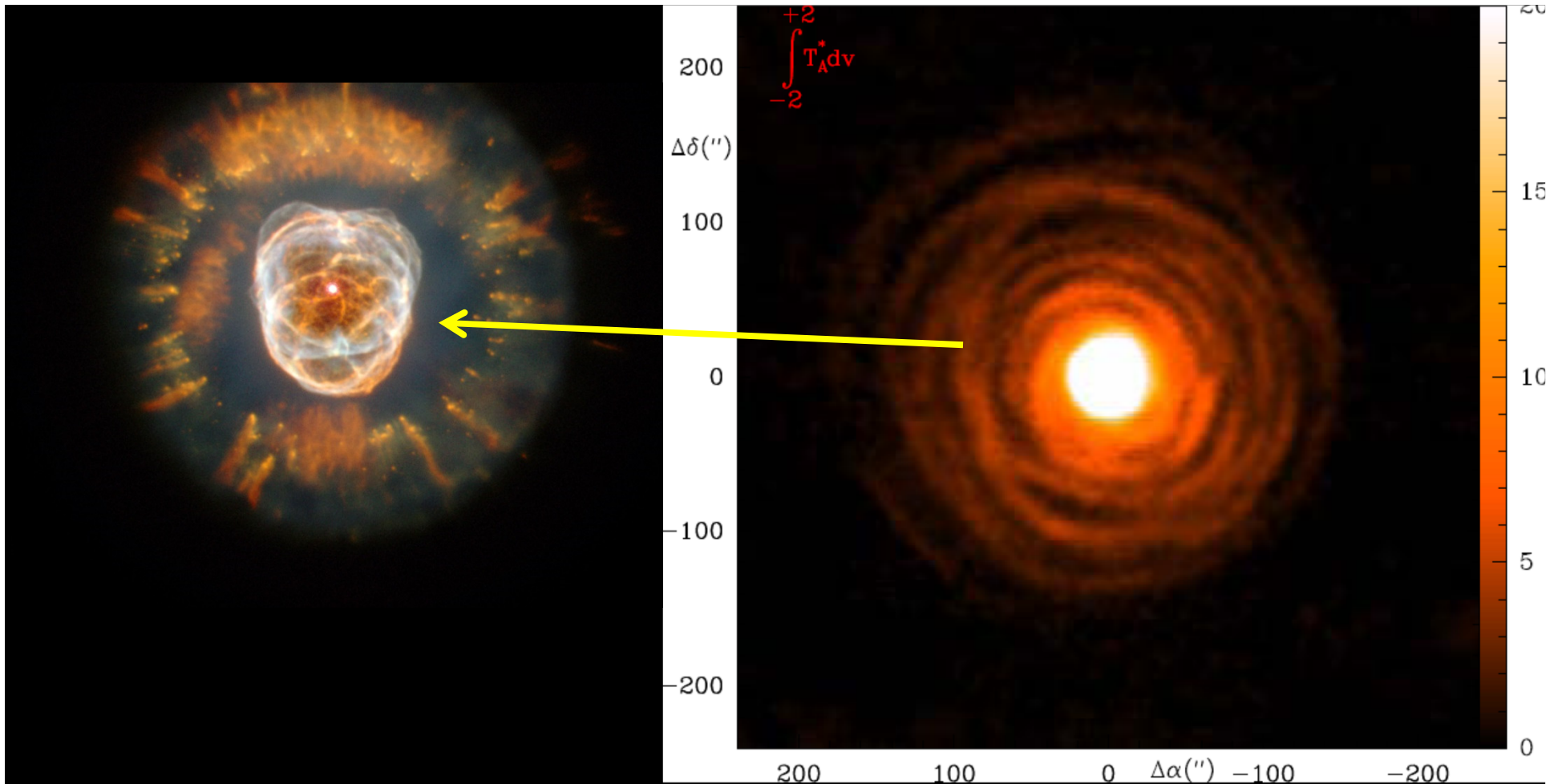


Six month variation



Line Intensities depend on the stellar phase. RT models to be revised !!!!!
WARNING FOR ALMA (AGBs): When having several configurations requested by observers try to get the data as close as possible in time...

Figure 1. Selected spectra observed with *Herschel* in 2010 May (black thin spectra; from Cernicharo et al. 2010b) and 2010 November (red thick spectra) at 543.5 GHz was taken in 2011 May. Windows within the panels show zooms to selected lines. Intensity scale is antenna temperature in K and frequency in MHz.

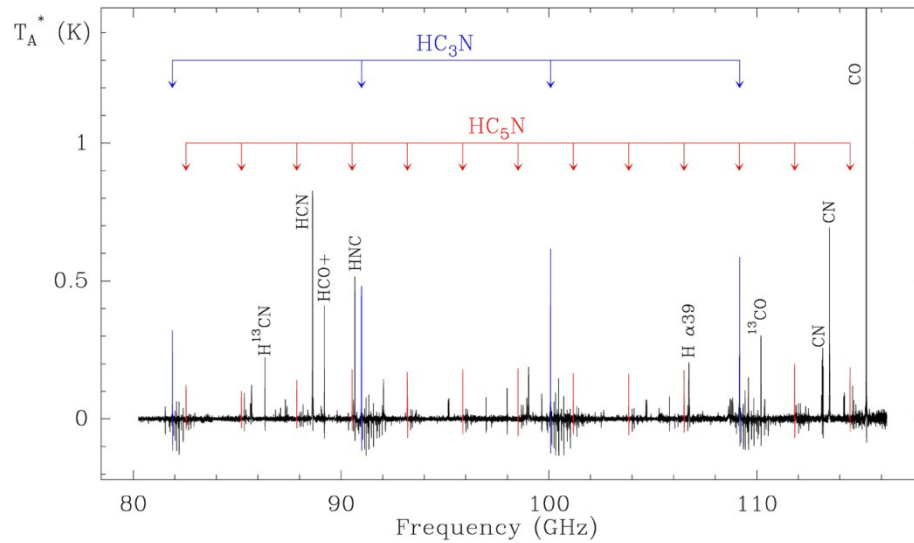


What will happens to IRC+10216 within a few hundreds/thousands years ?

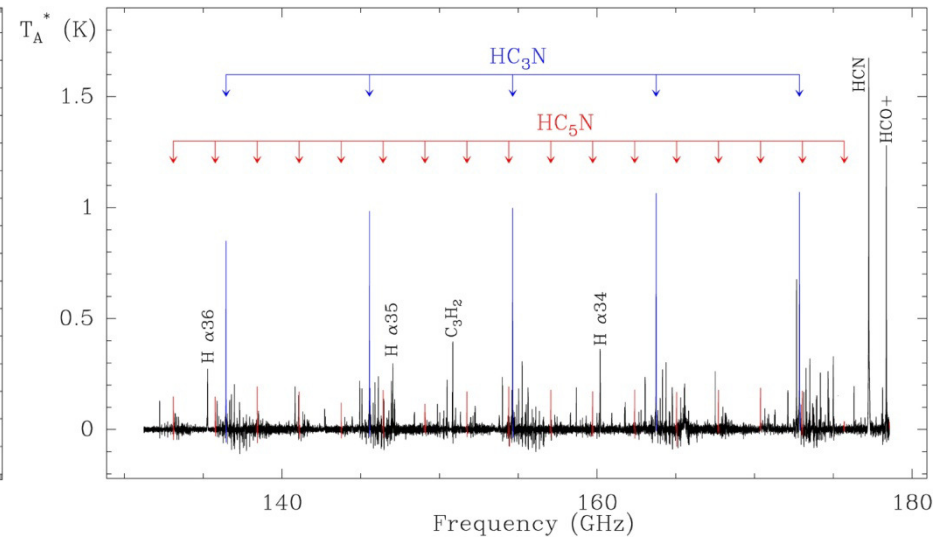
*It will evolve towards the Protoplanetary phase. The central star will become warmer and will irradiated from inside the CSE created in the AGB phase with a strong UV flux ($T_{star}=30000$ K and even higher in the PN phase) . **CRL618, CRL2688, Red Rectangle, NGC6302,.....***

CRL618 Spectral Line Survey: Pardo & Collaborators

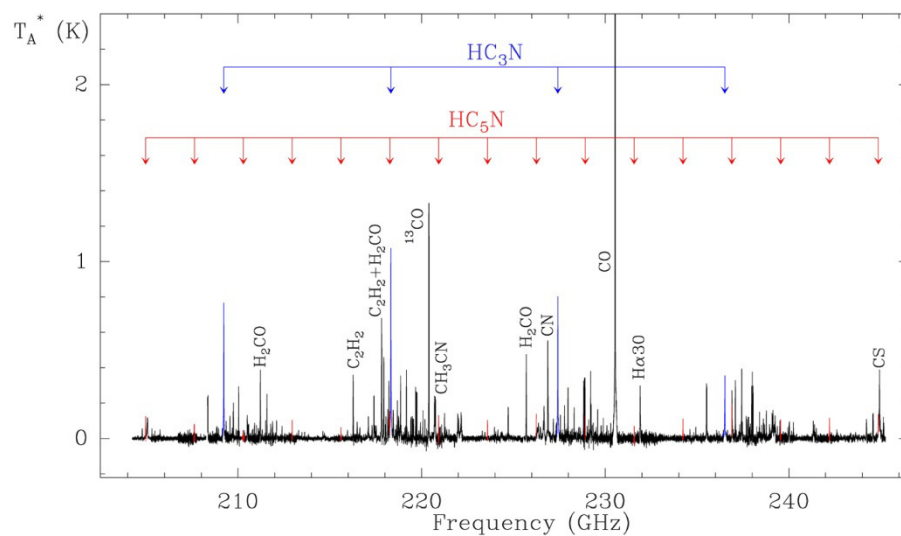
~ 3 mm



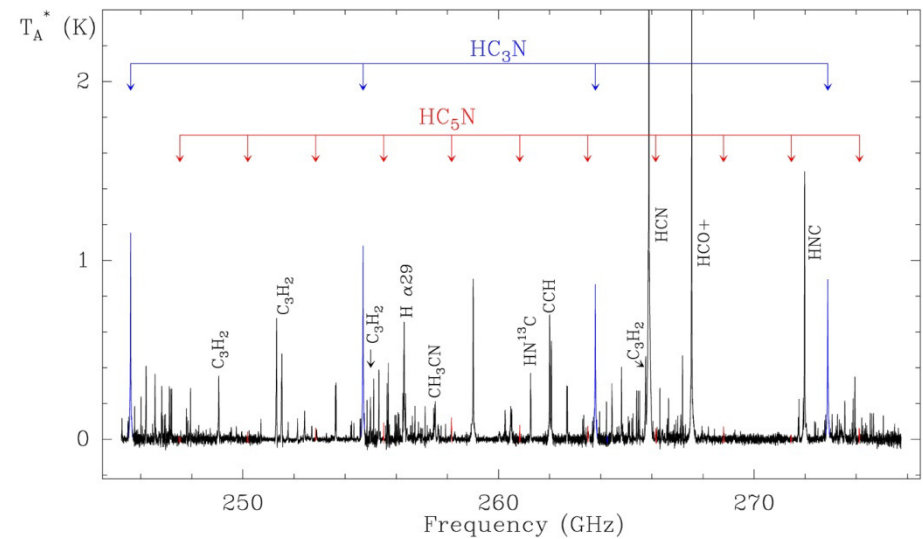
~ 2 mm



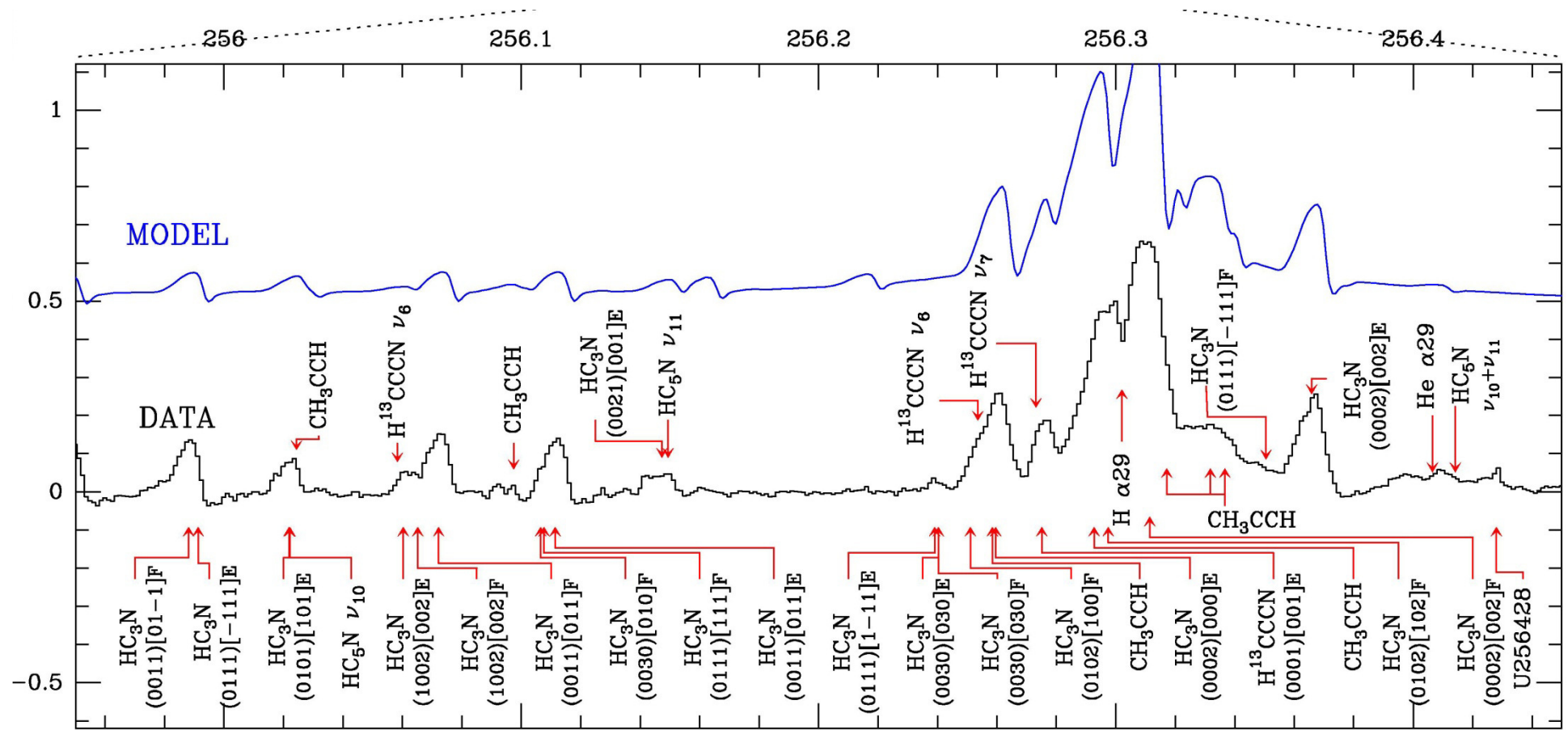
~ 1.3 mm

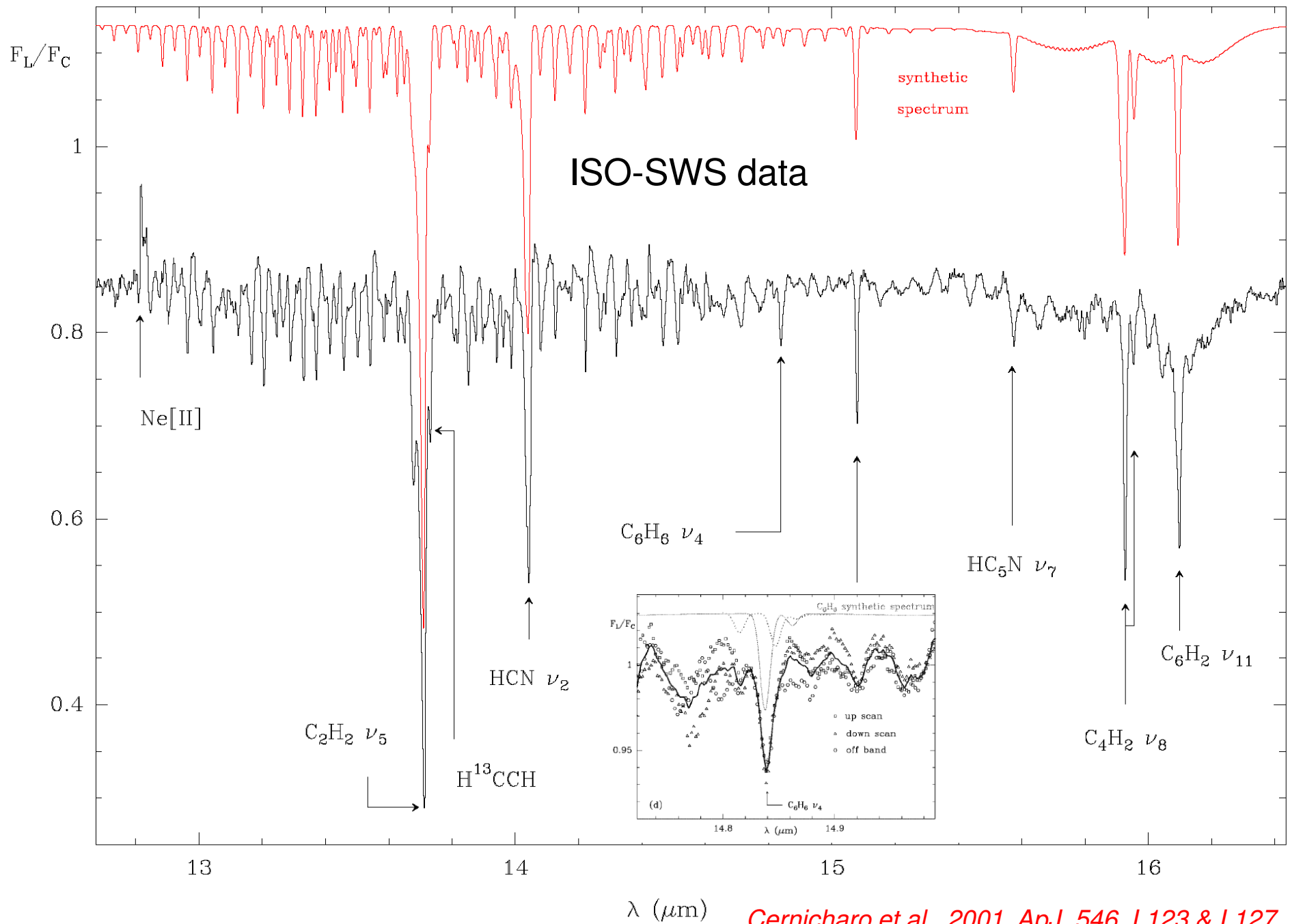


~ 1.0 mm



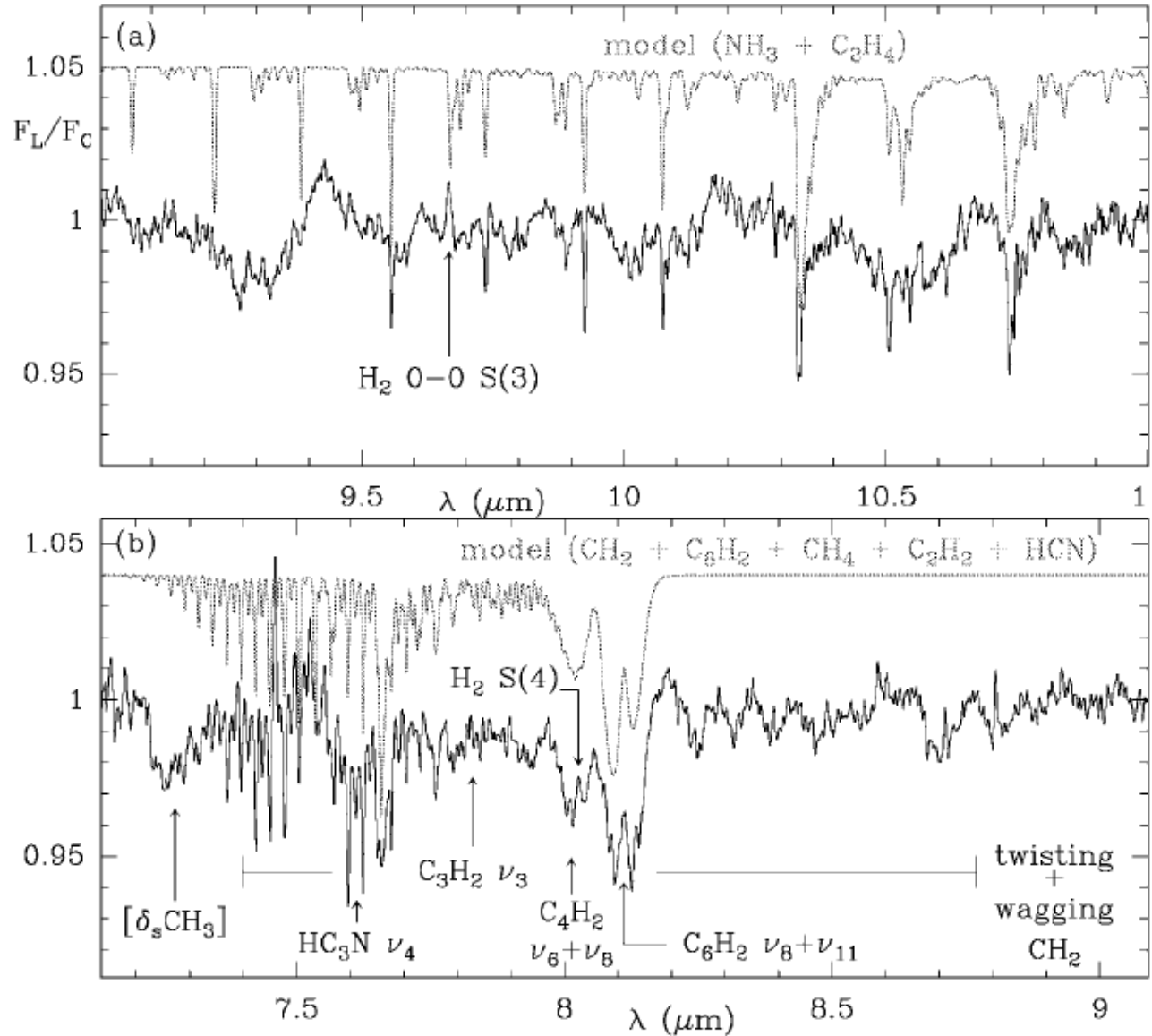
1 mm window : Data & final model





Cernicharo et al., 2001, ApJ, 546, L123 & L127

Cernicharo et al., ApJ, 546, L123 & L127

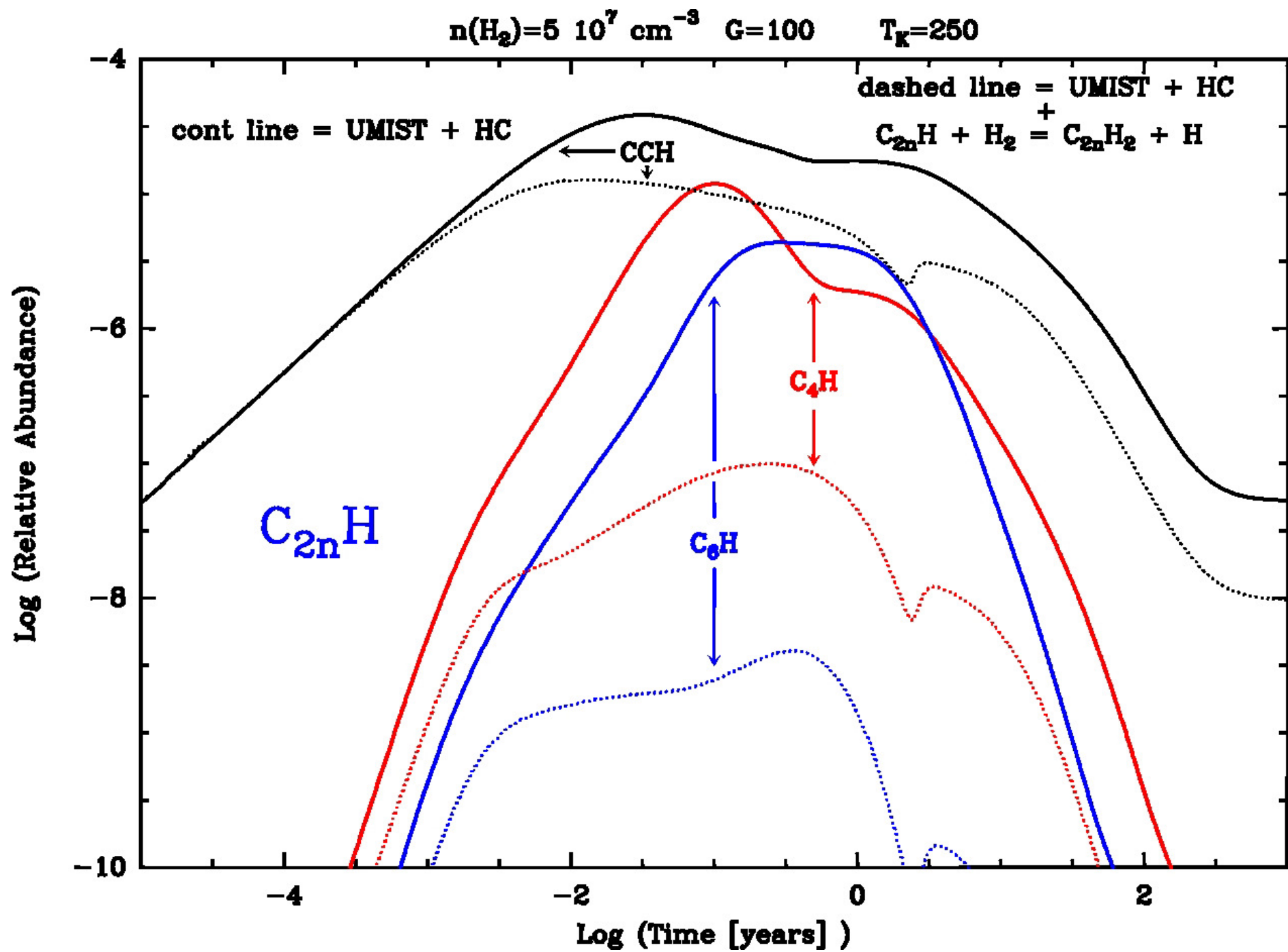


Many U-bands
in the mid-IR
all them in absorption.

Medium size
molecules 10-15
Atoms ??

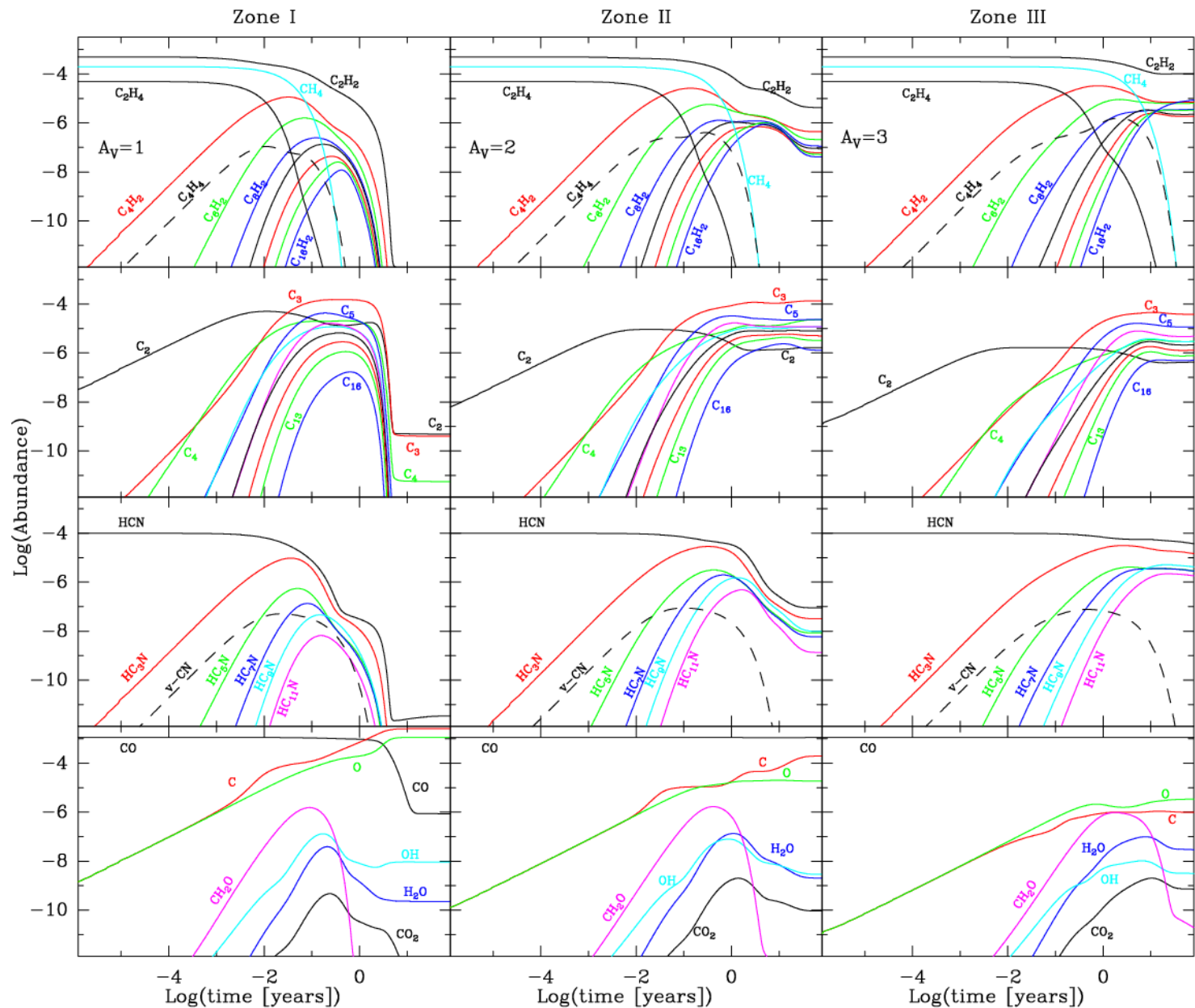
The source is rich in
polyacetylenes C_nH_2
but radicals C_nH are
lacking

Why IRC+10216 is rich in C_nH and CRL618 in C_nH_2 species ?



Looking for new molecules : Modelling

Chemical
modelling
specific
to a C-rich
PDR



Cernicharo
2004,
***ApJ*, 608, L41**



IR and radio data provide a powerful tool to study the chemistry of Carbon-rich evolved stars.

Herschel archival data excellent complement to focused ALMA observations

IR:..... C_2H_2 , CH_4 , C_2H_4 , SiH_4 , C_n

ALMA:.....

In some sources the spectral confusion will be huge.

In order to understand the message ALMA will send us a close collaboration with laboratory astrophysics (spectroscopy, chemistry, theory) has to be maintained and strengthen.

Dust formation and evolution: NANOCOSMOS

José Cernicharo

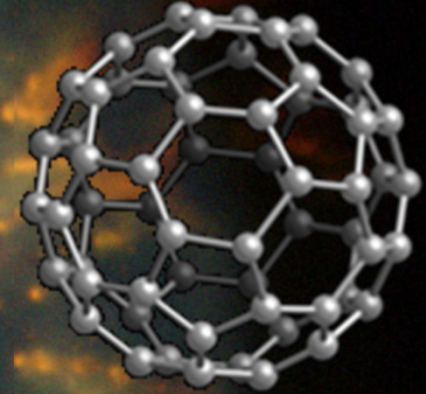
ICMM, CSIC, Spain

Christine Joblin,

IRAP, CNRS, France

José A. Martin-Gago,

ICMM, CSIC, Spain



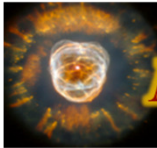
**Astronomers, Chemists, Physicists, and Engineers
working together at the frontiers of knowledge.**

*Understanding the formation of cosmic dust and chemical
complexity in Space and on Earth*



European Research Council
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HEMT RECEIVERS

**STARDUST
chamber**

**GAS EVOLUTION
chamber**

**PIRENEA/ESPOIRS
Upgrades**

**MOLECULAR
ANALYZER**

Technical Activities

OBSERVATIONS

High-res: ALMA, NOEMA
Surveys: 30m IRAM & 40m
IGN

IR: CARMENES/3.5 m Calar
Alto telescope. TEXES. VLTs

LABORATORY EXPERIMENTS

Spectroscopy
Dust formation & processing

THEORY- Quantum chemistry

Structure, energetics
Dynamics

MODELLING

Radiative transfer
Chemical models

Scientific Activities

**Determine gas
composition at the
dust formation zone**

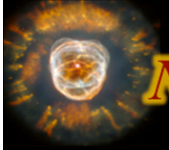
**Identify dust
nucleation seeds &
key processes**

**Create cosmic dust in
the laboratory**

**Identify dust growth
processes**

**Identify some key
catalytic reactions in
molecular formation**

GOALS



NANOCOSMOS

**THANK YOU
VERY MUCH
FOR YOUR ATTENTION**