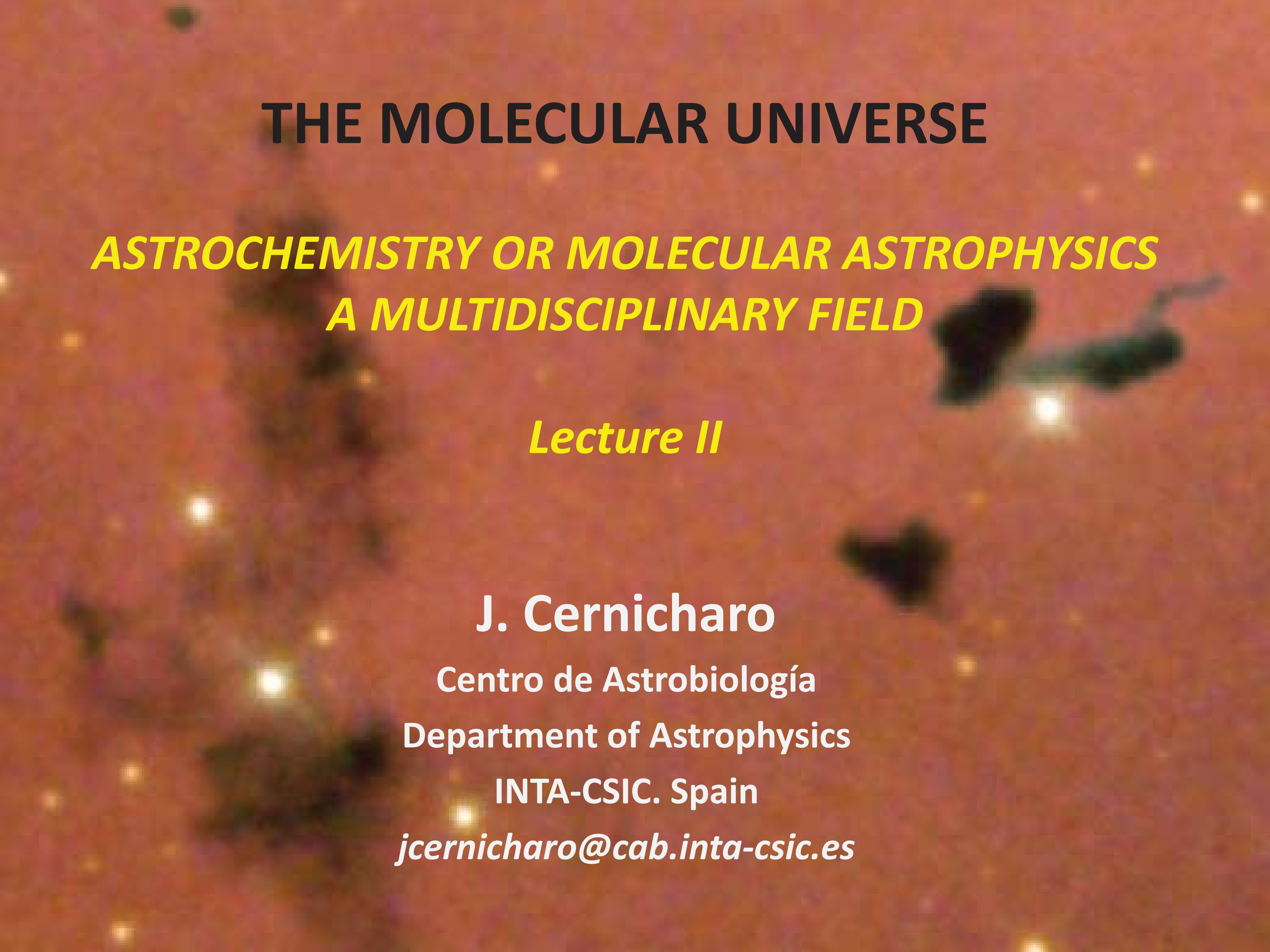

THE MOLECULAR UNIVERSE

ASTROCHEMISTRY OR MOLECULAR ASTROPHYSICS A MULTIDISCIPLINARY FIELD

Lecture II

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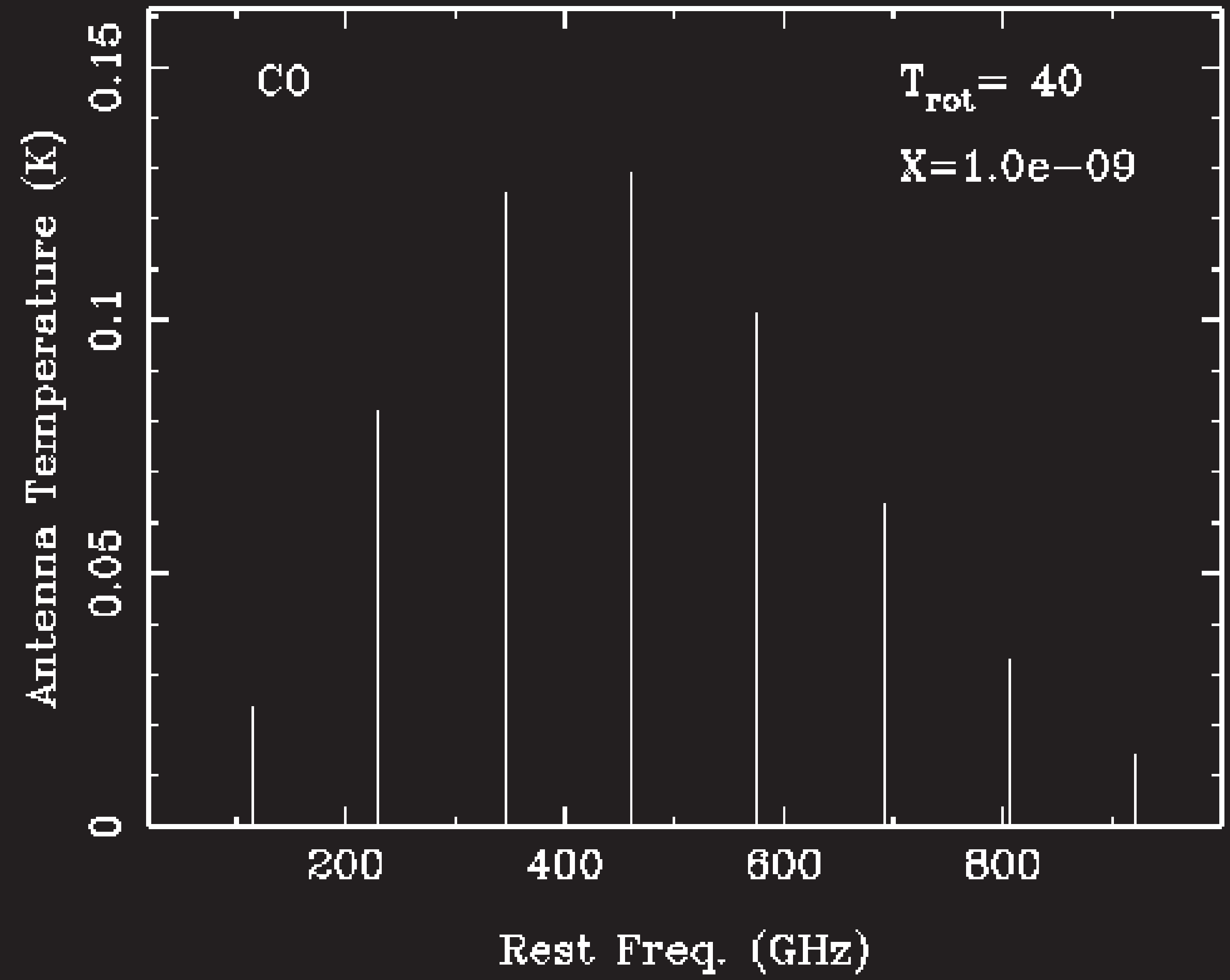
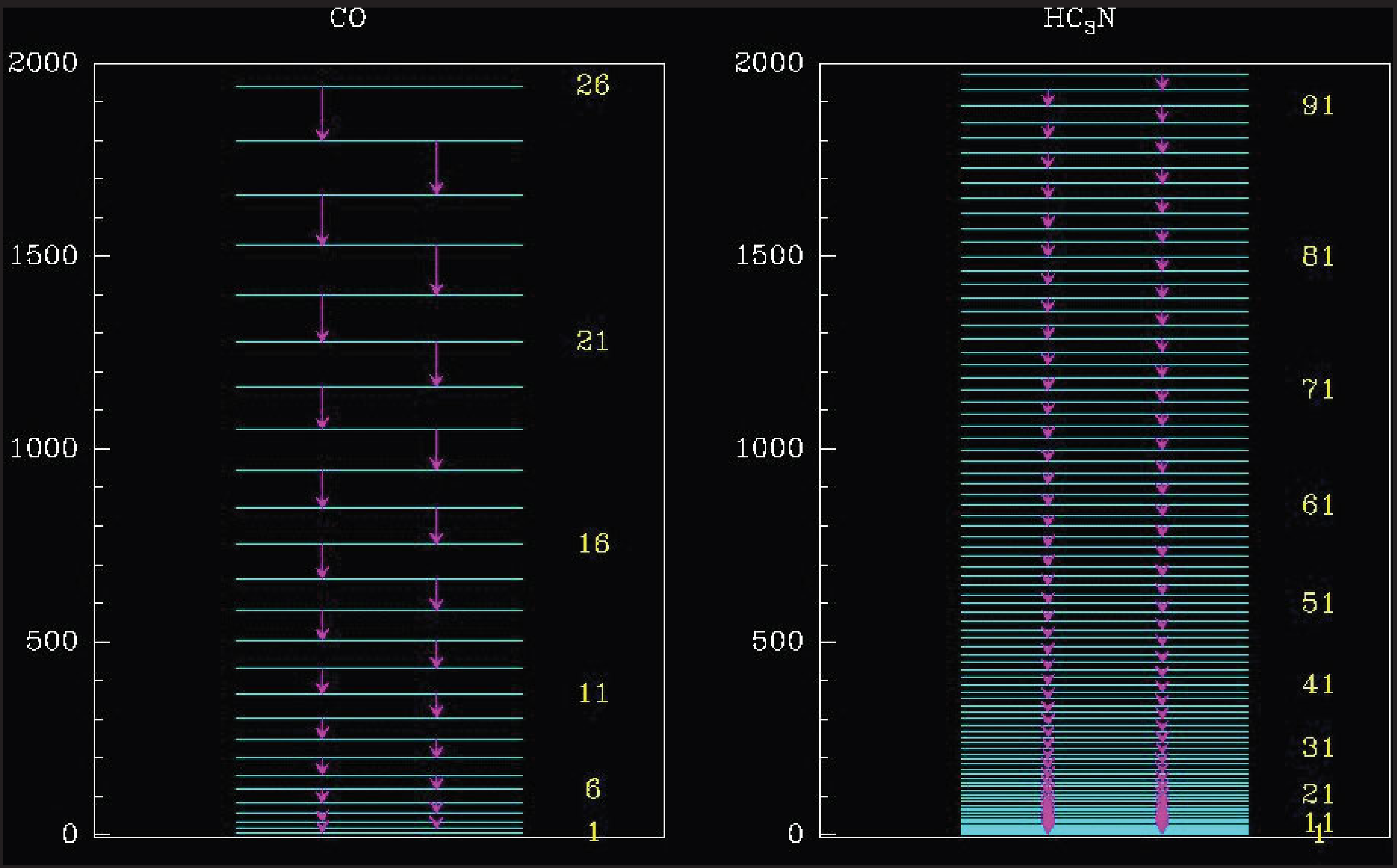
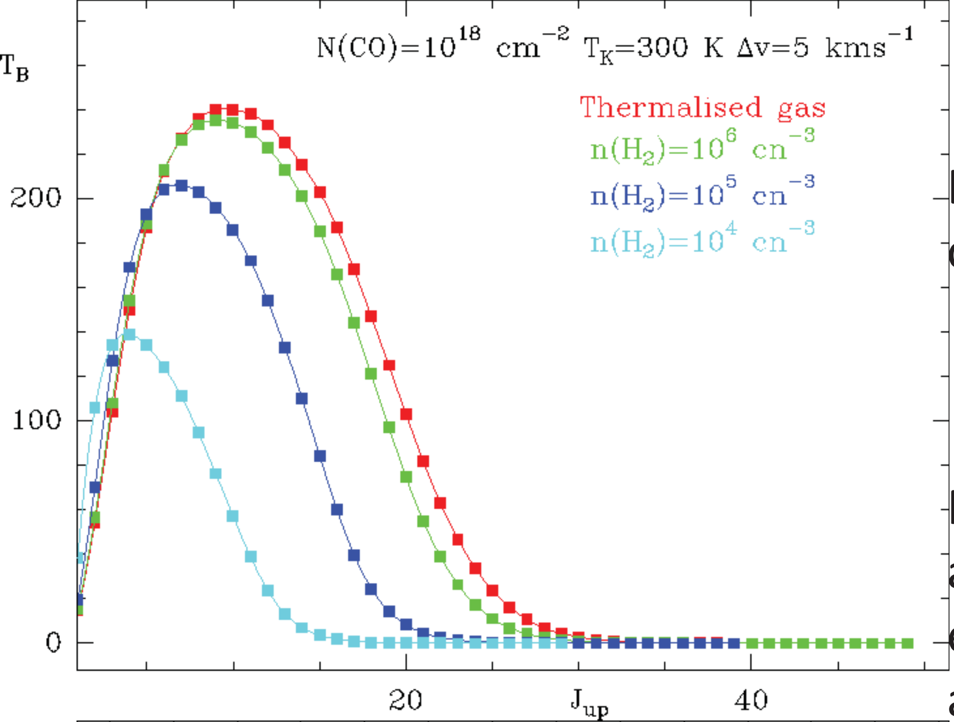
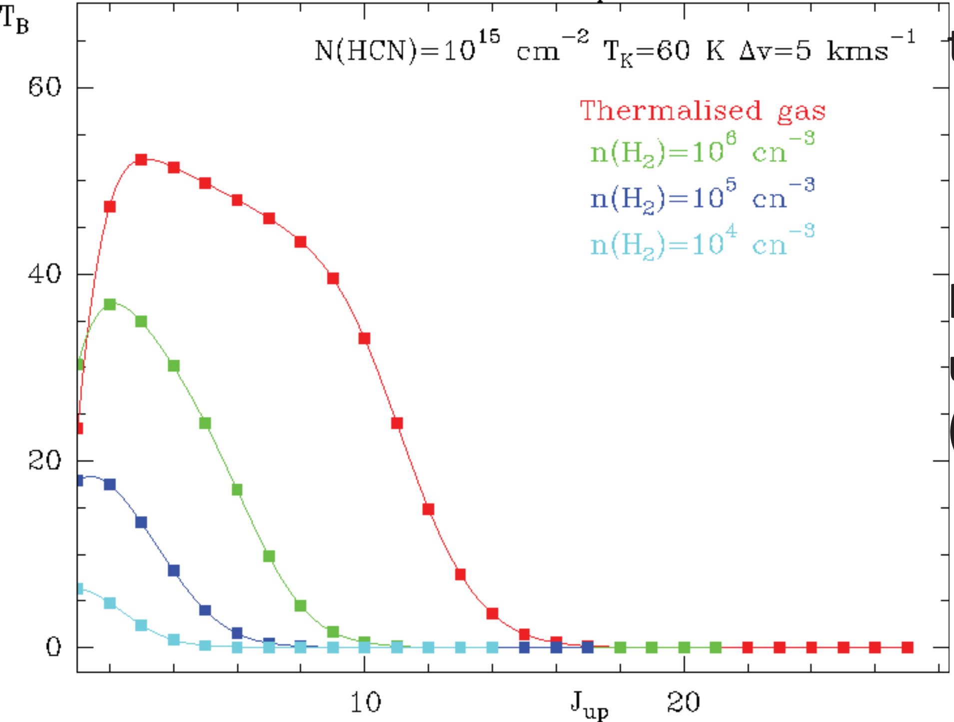


ROTATIONAL SPECTRUM OF CARBON MONOXIDE



Selection rules ΔJ=±1



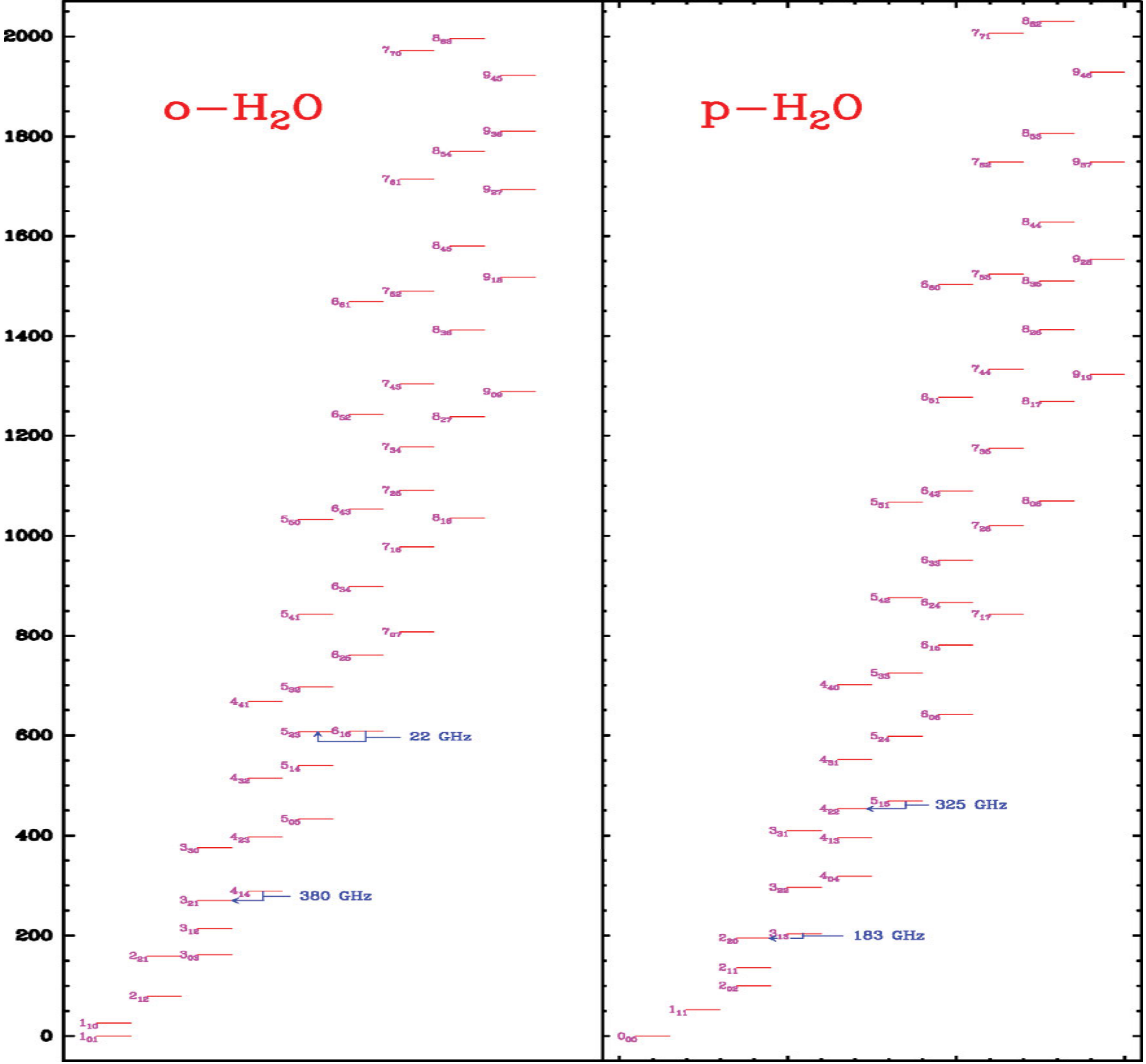


By selecting the appropriate molecule we can trace different physical conditions.

Molecules with low dipole moment, as CO, are easily excited through collisions with H_2, even for low volume densities. Under some assumptions these molecules could trace the kinetic temperature of the gas.

High dipole moment molecules could be used as tracer of the gas volume density ($n(H_2)$).

Pcm2l.exe

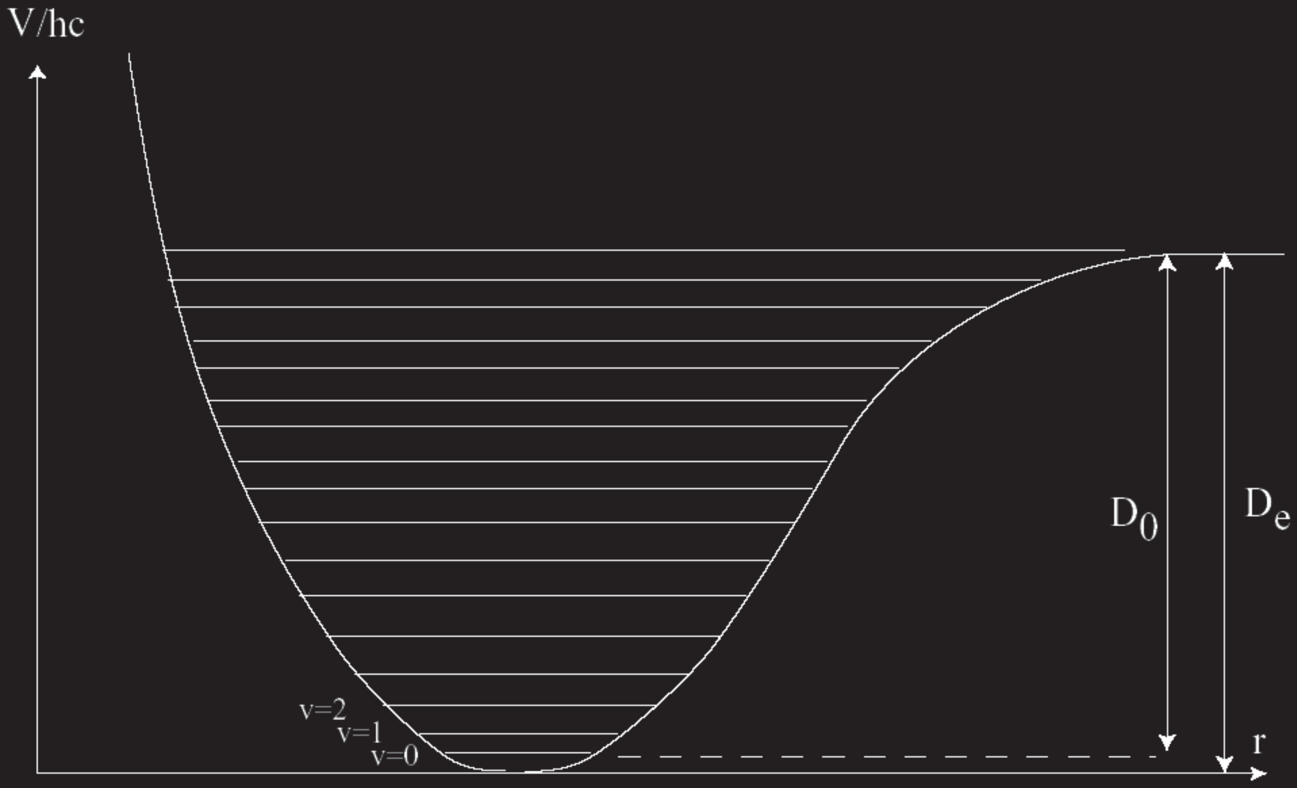


o−H$_2$O
p−H$_2$O
0
200
400
600
800
1000
1200
1400
1600
1800
2000
1_{01}
1_{10}
2_{12}
2_{21}
3_{03}
3_{12}
3_{21}
4_{14}
380 GHz
3_{30}
4_{23}
5_{05}
4_{32}
5_{14}
5_{23}
6_{16}
22 GHz
4_{41}
5_{32}
6_{25}
7_{07}
5_{41}
6_{34}
7_{16}
5_{50}
6_{43}
8_{18}
7_{25}
7_{34}
8_{27}
6_{52}
9_{09}
7_{43}
8_{36}
6_{61}
7_{52}
9_{18}
8_{45}
9_{27}
7_{61}
8_{54}
9_{36}
9_{45}
7_{70}
8_{63}
0_{00}
1_{11}
2_{02}
2_{11}
2_{20}
3_{13}
183 GHz
3_{22}
4_{04}
4_{13}
3_{31}
4_{22}
5_{15}
325 GHz
4_{31}
5_{24}
6_{06}
4_{40}
5_{33}
6_{15}
7_{17}
6_{24}
5_{42}
6_{33}
7_{26}
5_{51}
8_{08}
6_{42}
7_{35}
8_{17}
6_{51}
9_{19}
7_{44}
8_{26}
8_{35}
6_{60}
7_{53}
9_{28}
8_{44}
9_{37}
7_{62}
8_{53}
9_{46}
7_{71}
8_{62}

A few facts…

Continuous term spectra and dissociation

If oscillator has more energy E' than, hcD_e, then $r \rightarrow \infty$ and molecule dissociates. For $E' > hcD_e$, system has excess energy (kinetic energy) after dissociation. $\therefore$ $(K.E)_{\text{atoms}} > 0$ and not quantized.



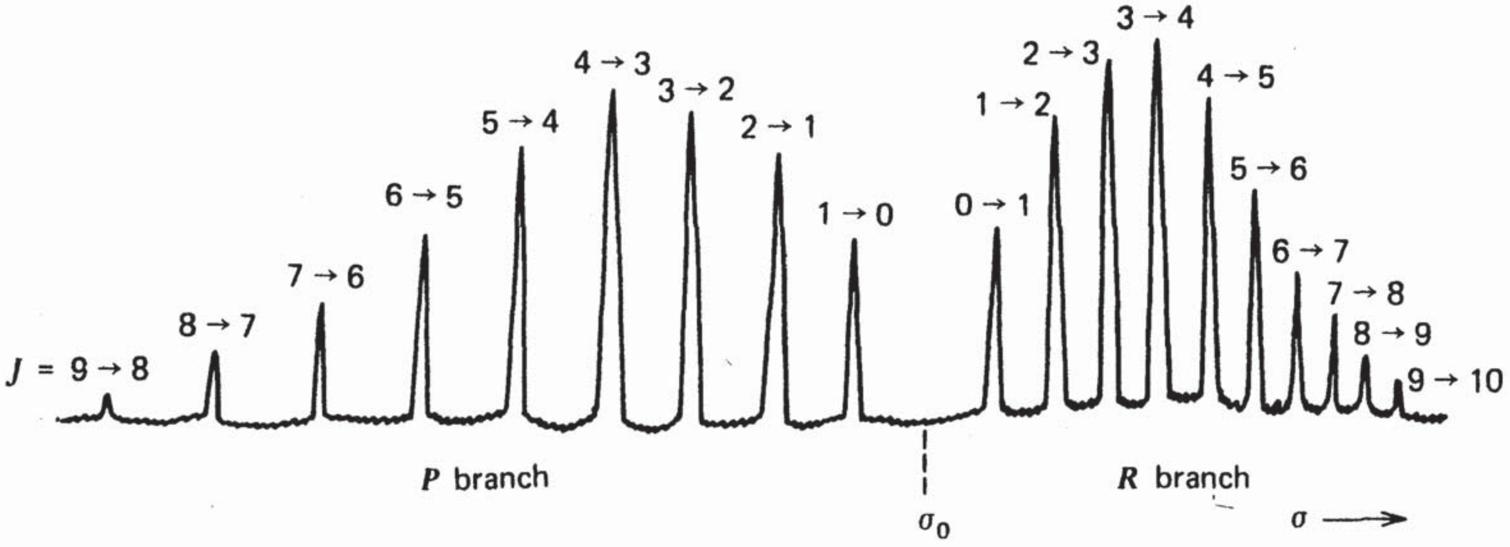


Fig. 4.9 Rotational fine structure of a vibration–rotation band of a diatomic molecule. Note the decreasing spacing with increasing *J* in the *R* branch, and the increasing spacing with increasing *J* in the *P* branch.

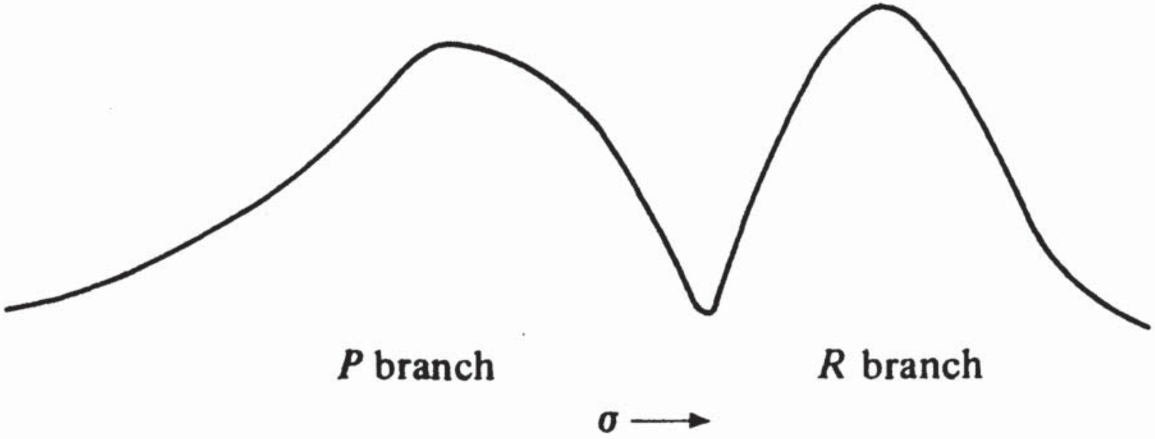
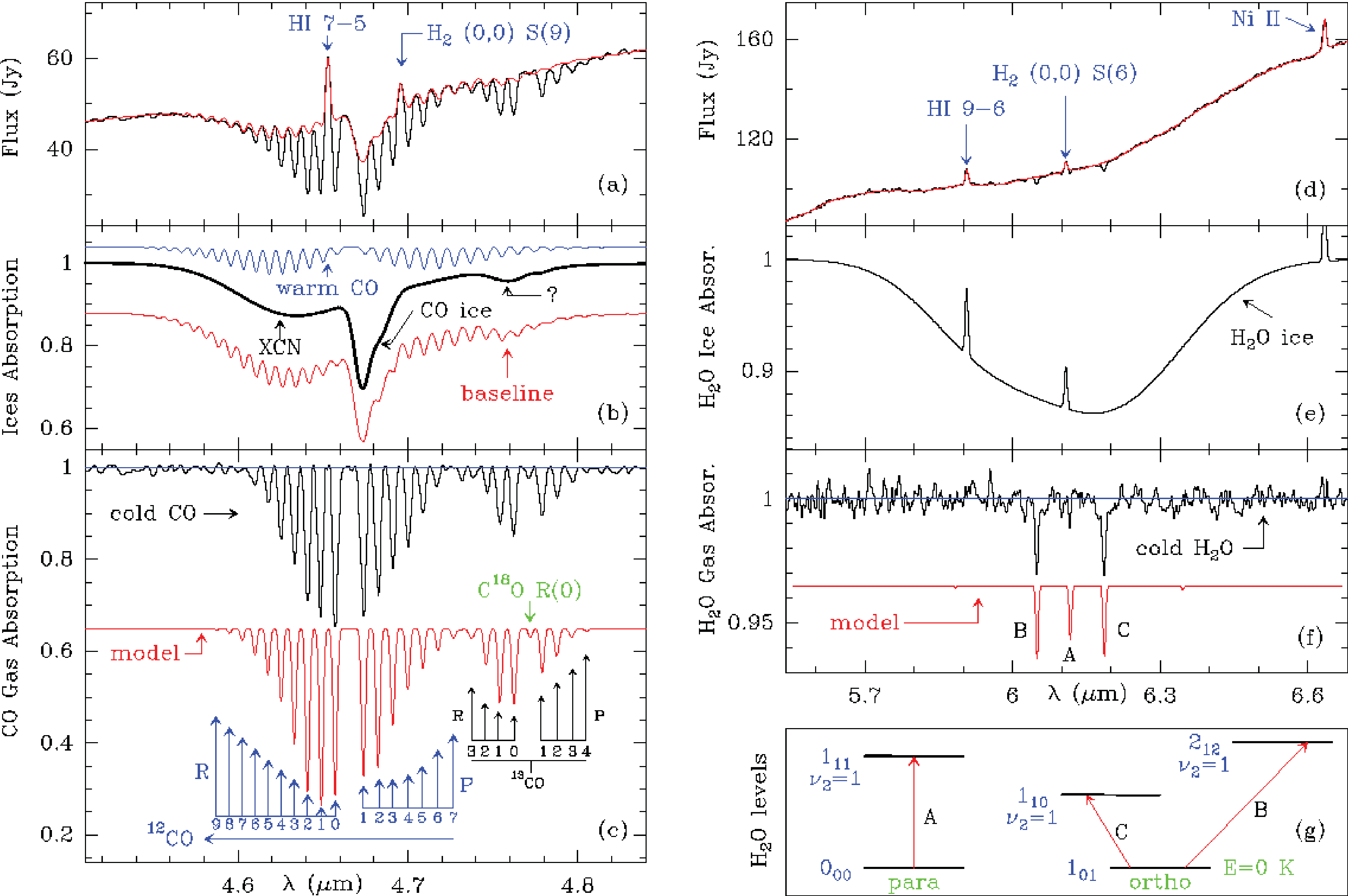


Fig. 4.10 Appearance of a vibration–rotation band of a diatomic molecule under low resolution.

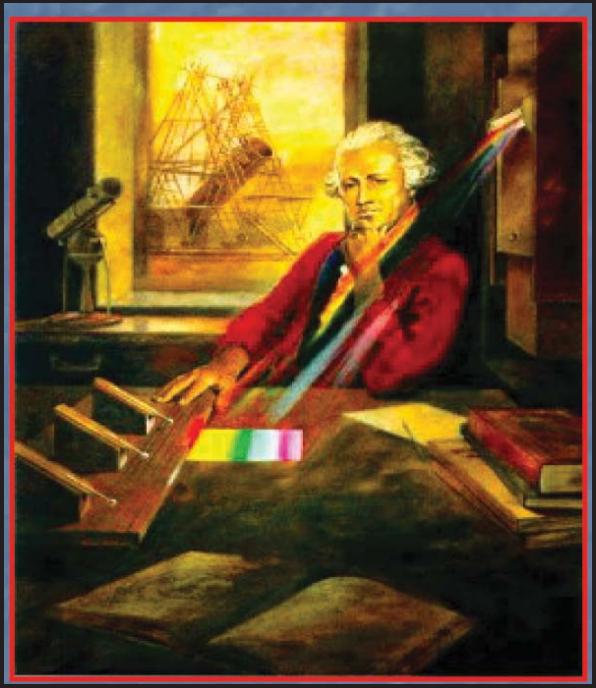
Perhaps in dark clouds infrared effects are much less important. The kinetic temperature is too low to pump vibrational levels. But !!!!

(Moneti, Cernicharo & Pardo ApJ Letters,2001)



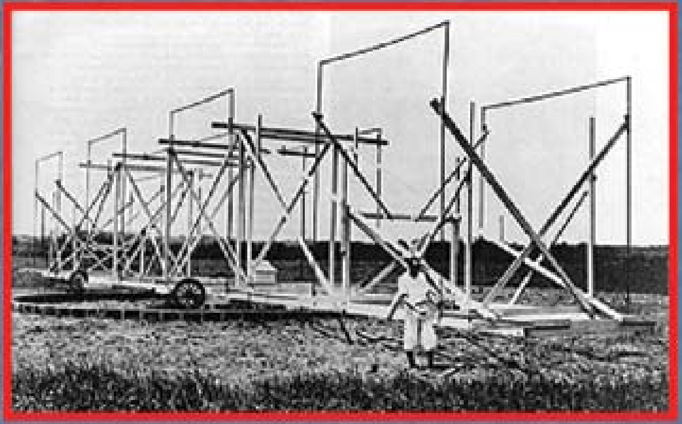
History of Radioastronomy

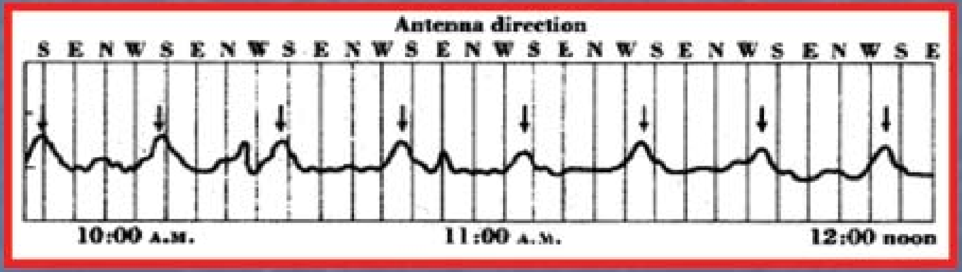
Continuum & Lines



William Herschel noticed that the highest temperature was measured in a portion of the spectrum beyond the red where no sunlight was visible

INFRARED RADIATION





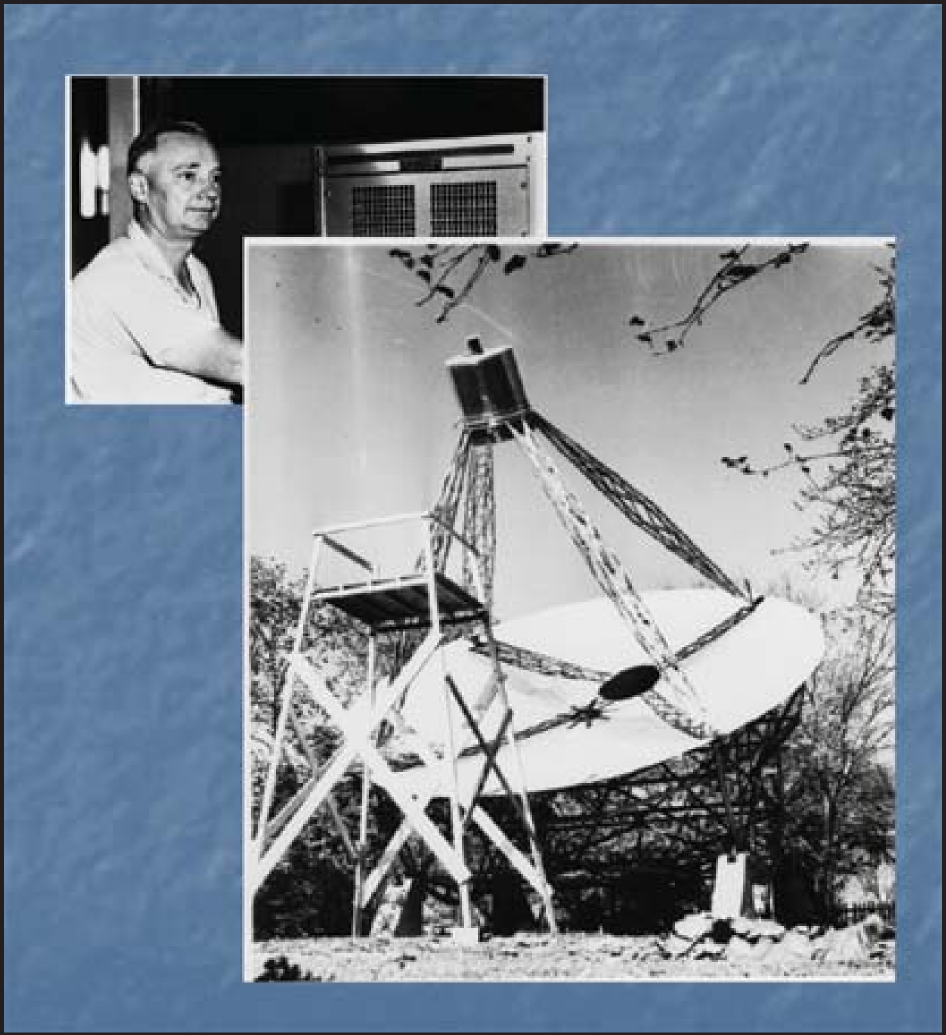
Bell Labs asks K. Jansky to investigate perturbations of radio voice transmission between USA and Europe. He builts an antenna of 30x4 m that rotates every 20 minutes. He discovers a “steady hiss static of unknown origin”.

1933-35 Jansky resolves mystery

The source of the radiation is established to be in a fixed direction of the sky with the following approximatecoordinates:

RA: 18h dec: -10 deg

(The Galactic Center)

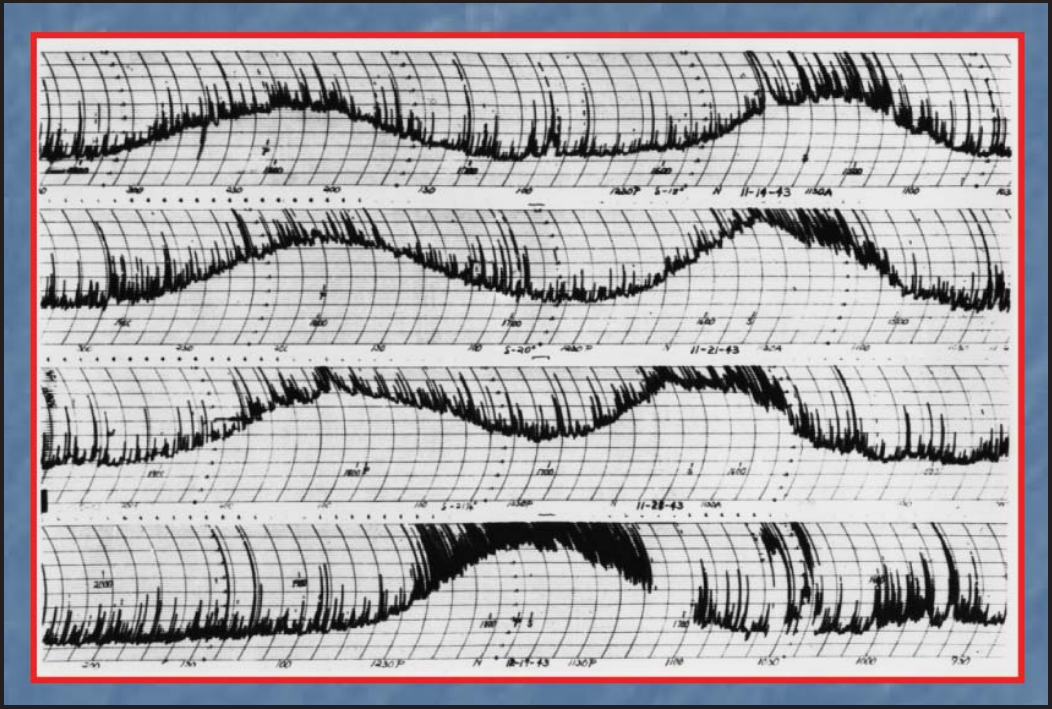


G. Reber was interested in investigating the nature of the signals revealed by Janky's experiment. He could not get a job to do this due to great depression so he built this radiotelescope in his back yard.

Aprox. 10 m diameter, amplification of several million on the receiver placed within the cylinder at the focus. Signals recorded on a chart.

The parabolic design concentrates waves of all wavelengths to the same focus.

The first radio map of the Galaxy



First two receivers (3300 and 900 MHz failed to detect signals from outer space.

Finally, a third receiver at 160 MHz (1.9 meter wavelength made detection of the radio emission from the Milky Way and the Sun (broad features on the chart readings). Narrow peaks are due to interference with automobile engine sparks.

The first radio map of the Galaxy

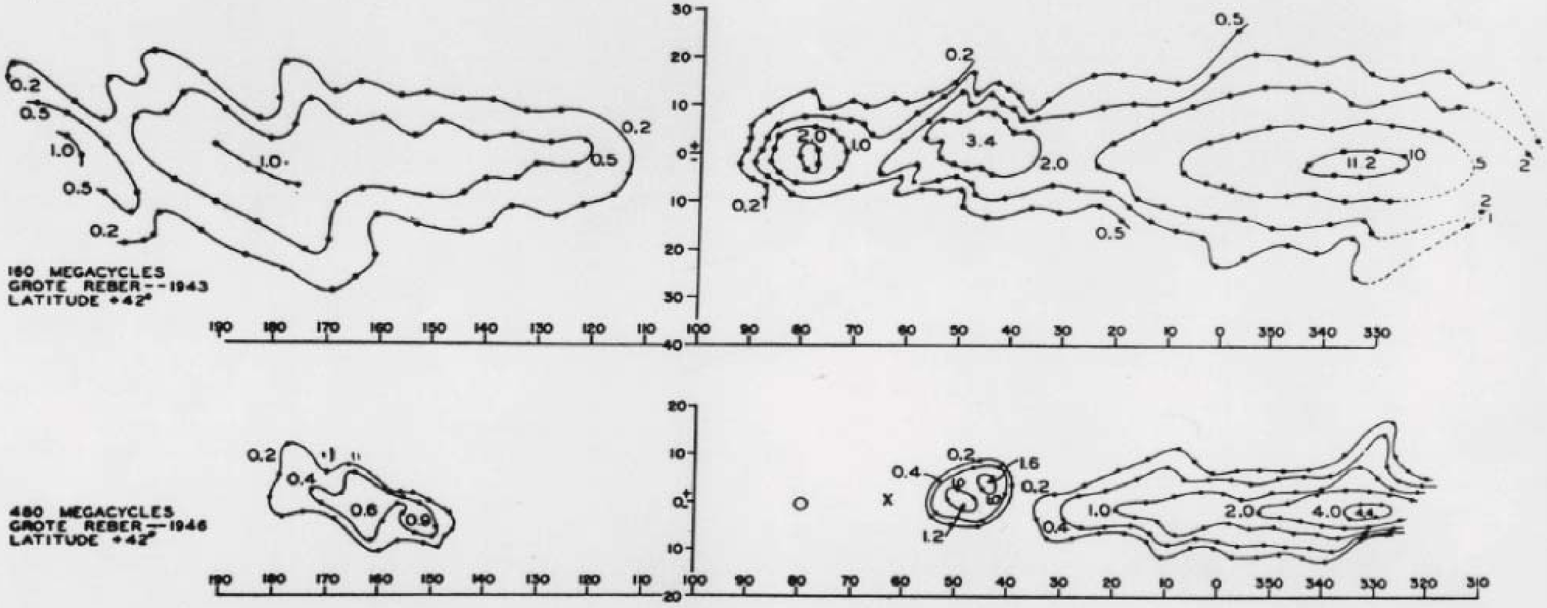
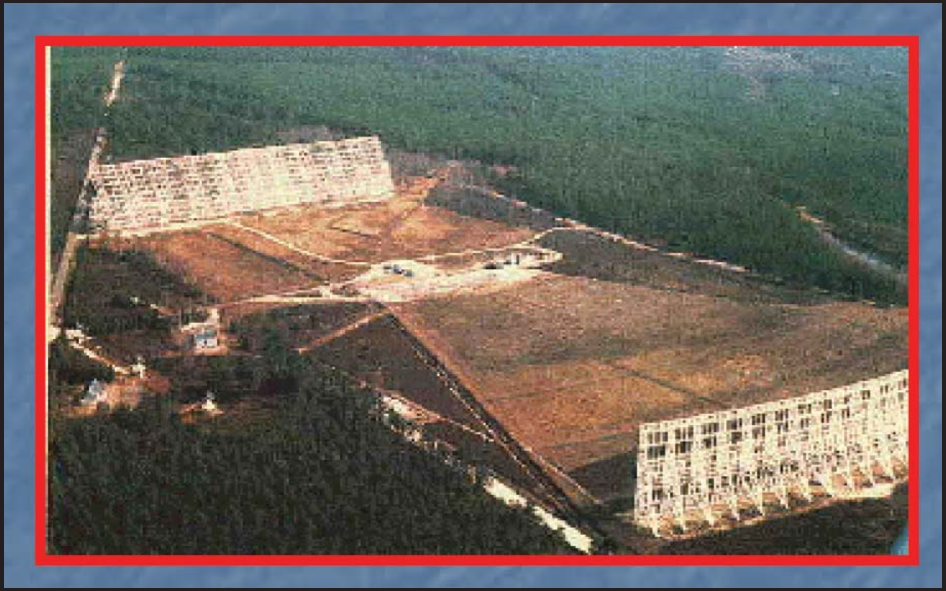


FIG. 7—Contours of constant intensity at 160 MHz and 480 MHz, taken at Wheaton, Illinois.

Reber presented his results in the form of contour diagrams showing that the brightest areas correspond to the Milky Way, specially towards its center. Other bright radio sources such as Cygnus and Cassiopeia were also discovered for the first time.

…essentially centimeter wavelengths



Nancay

Effelsberg

Present day facilities:

millimeter and submillimeter single antenna

Present day falicilities:

millimeter interferometry

What do we detect with a Radiotelescope?

Continuum

- Free-free
- Synchrotron
- Dust

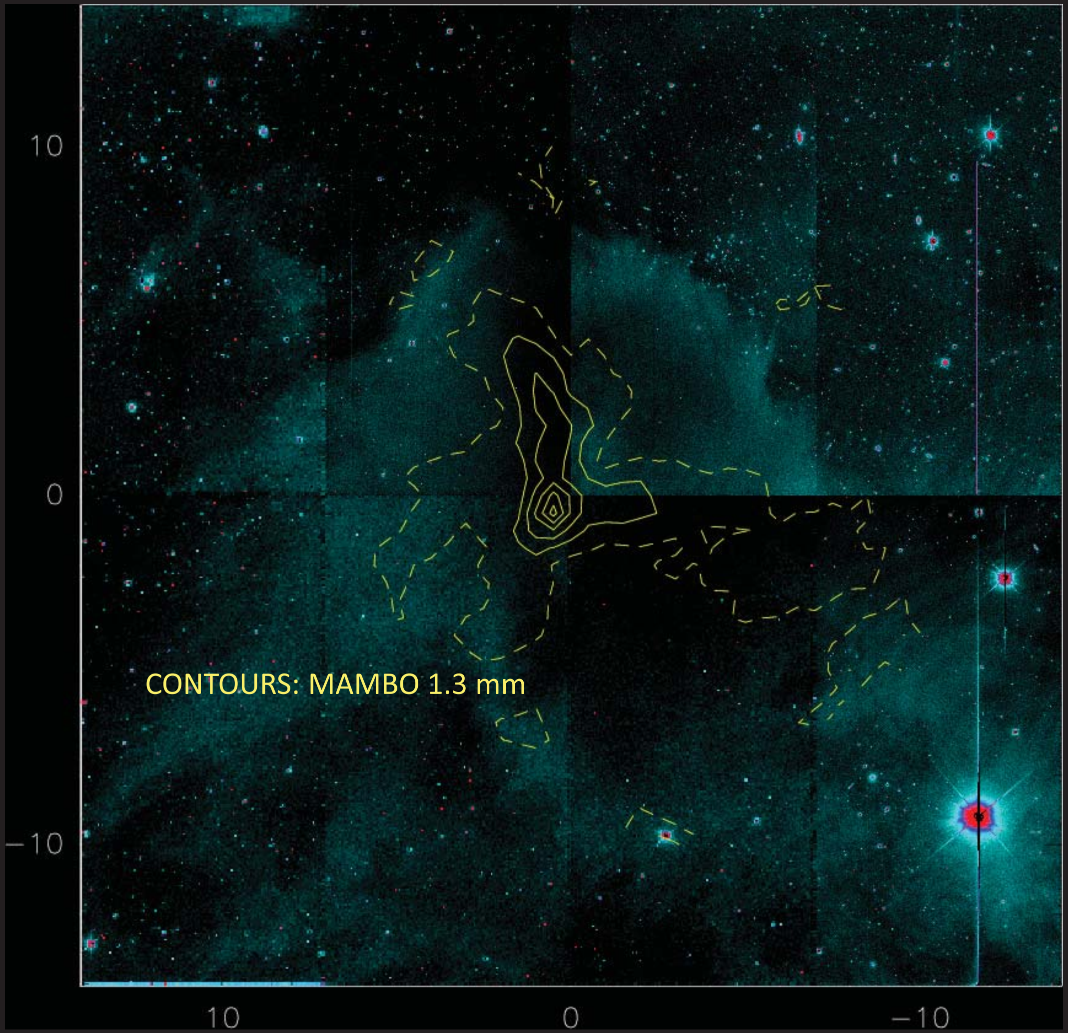
Line Radiation

- “Normal” molecular lines
- Masers
- atomic (HI fine structure or recombination)

What do we detect with a Radiotelescope? (II)

CONTINUUM EMISSION (from dust, thermal, synchrotron,…)

IMAGE: CFHT BAND K



CONTOURS: MAMBO 1.3 mm

Dust radiation

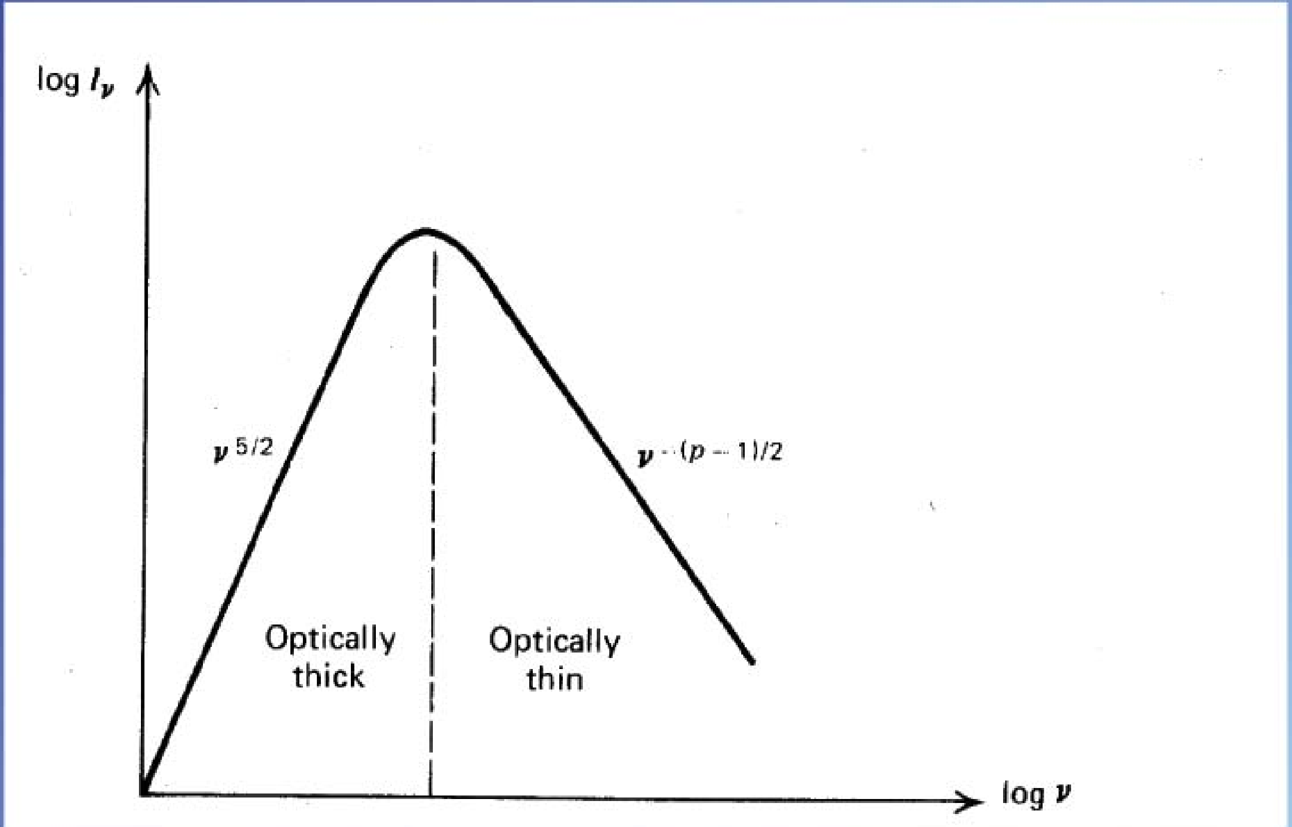
- Mass absorption coefficient

$$\kappa = \kappa_0 \left(\frac{\nu}{230\,\mathrm{GHz}} \right)^{\beta} \mathrm{cm}^2\,\mathrm{g}^{-1}$$

- κ_0 is typically 0.4 $\mathrm{cm}^2\ \mathrm{g}^{-1}$ in the ISM, but can vary with
  - Grain size
  - Grain properties (fluffy, ice mantle)
- β is around 2 in the ISM, and lower (1 or so) in disks (grain growth)

Synchrotron radiation

- Radiation by relativistic electrons through gyration around magnetic fields
- $I_\nu \propto \nu^{-\alpha}$ with $\alpha \approx 0.6$
- Visible in low radio range
- Information about magnetic fields and relativistic electrons



Free-Free radiation

- Free-Free or Bremsstrahlung
  - Acceleration of electrons by protons in plasma

$$\tau_\nu = 8.24 \times 10^{-2} T_e^{-1.35} \nu^{-2.1} EM$$

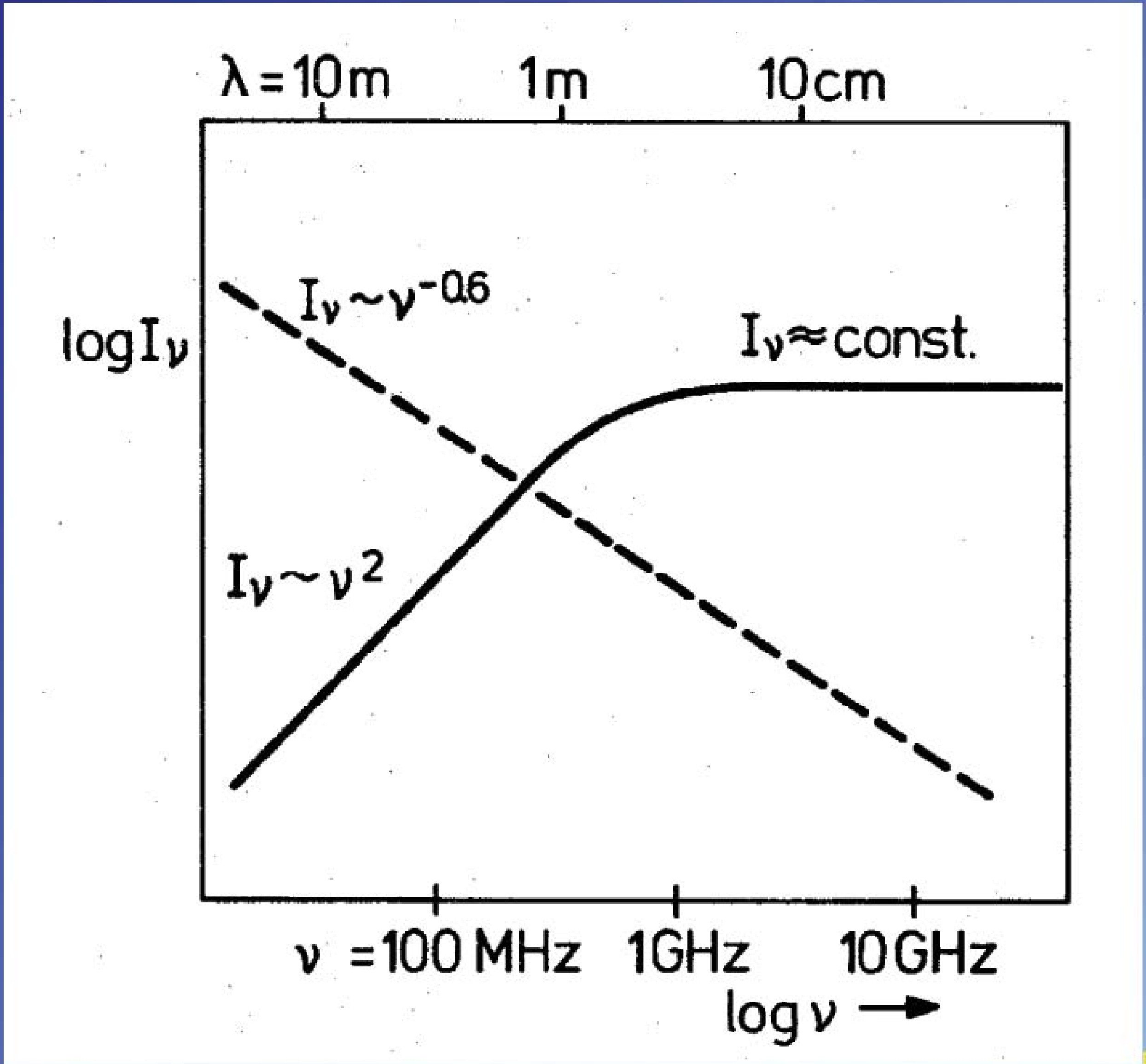
$EM = \int n_e^2 dr$ Emission measure

n_e electron density

$$I_\nu \propto \left\{ \begin{array}{c} \nu^2 T_e \text{ for } \tau_\nu \gg 1 \\ \nu^{-0.1} T_e^{-0.35} EM \text{ for } \tau_\nu \ll 1 \end{array} \right\}$$ Rayleigh-Jeans

Peter Schilke

Synchrotron/Free-Free radiation

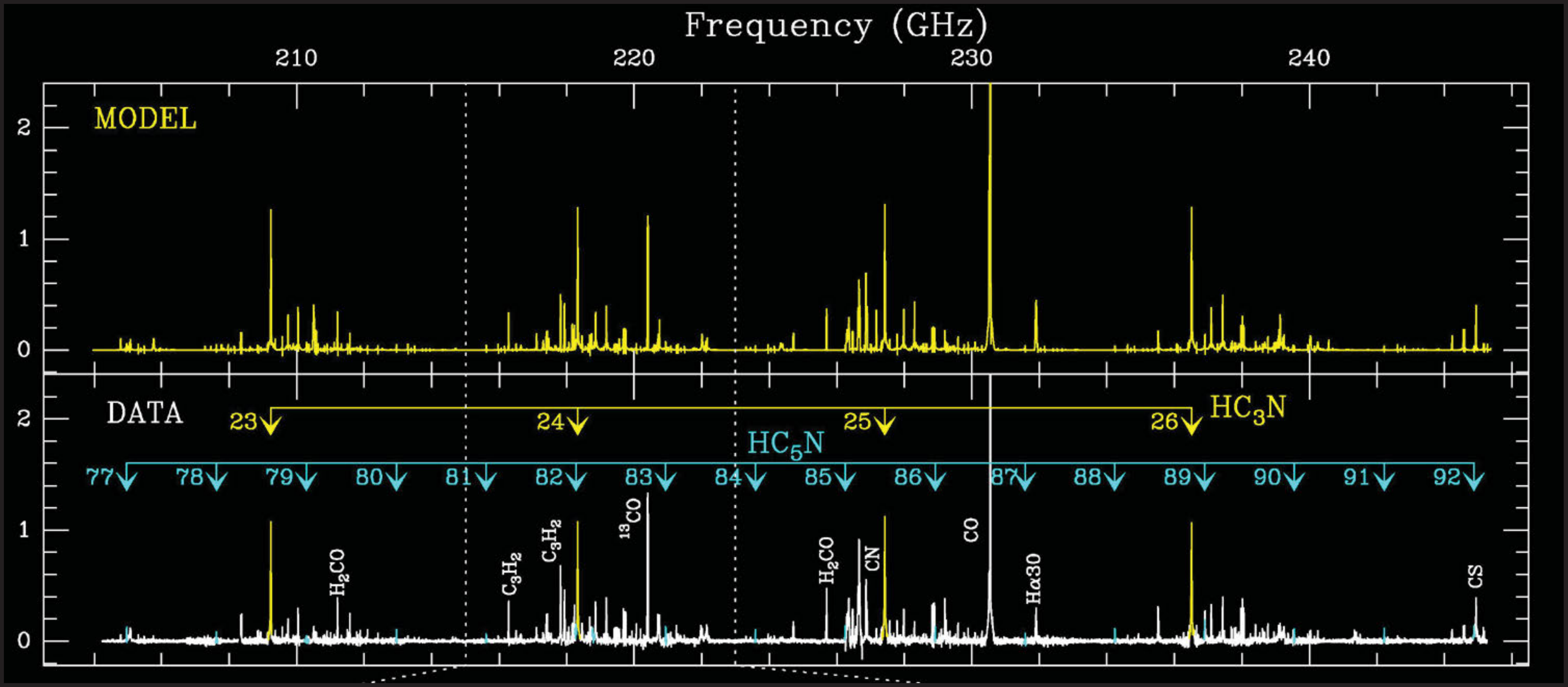


Peter Schilke

Free-Free radiation

- Determines Parameters of HII regions
  - Electron density
  - Electron temperature (with recombination lines)
  - Number of Lyman continuum photons
    - Gives hint to nature of exciting star

What do we detect with a Radiotelescope?



From Pardo et al.

SPECTRAL LINES (generally from molecules)

Why looking for low abundance species ?

- **Some times these species play a crucial role in the chemistry and in the dynamical evolution of the clouds.**
- **Each molecule brings information from different regions of molecular clouds.**
- **From a spectral point of view (molecular physics) many of these molecules have been never observed in the Earth (complex radicals) : Lab. Chemistry.**
- **Gas phase and dust grain chemistry need of clear discrimators**
- **Except for hot cores and corinos all complex molecules have low abundances**
- **Note that a low dipole moment molecule will produce weak lines even if its abundance is similar to that of HCO^+**
- **Key Molecules such as C_2H_2, CH_4, C_2H_4,…, do not have pure rotational spectrum and very little information is available on their abundances**

- How to interpret spectra with thousands of lines ?

  We need laboratory spectroscopy

- What methods have to be implemented to deal with these expected line forests ?

  We need collaboration with software developers under the supervision of specialists

- What we get from line surveys ?

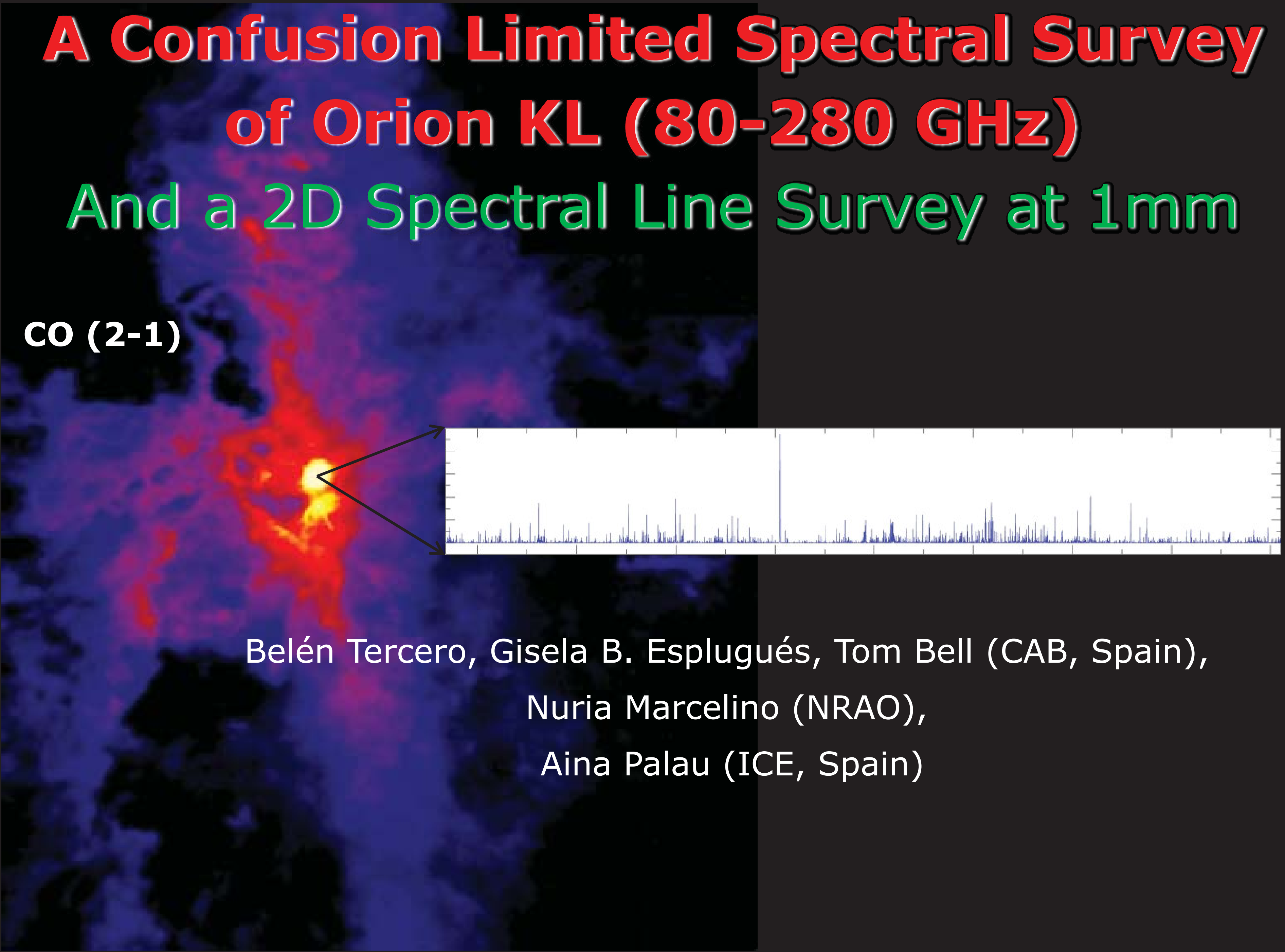
  We need modeling : chemical, physical, dynamical evolution of the gas,...

- To look for new molecules we need *more sensitive instruments.*
- To look for new physical and chemical processes we need *more sensitive instruments*
- To understand the evolution of gas from protoplanetary disks to high redshift objects we need *more sensitive instruments* :

HERSCHEL & ALMA & eVLA & ELT & ...

A Confusion Limited Spectral Survey of Orion KL (80-280 GHz)

And a 2D Spectral Line Survey at 1mm



Belén Tercero, Gisela B. Esplugués, Tom Bell (CAB, Spain),

Nuria Marcelino (NRAO),

Aina Palau (ICE, Spain)

Line Surveys in Orion-KL

- The closest (brightest) massive star forming region, contains several compact objects
- Prototypical source: observed extensively at mm and submm wavelengths
- Exhibits an intense and prolific spectrum
- Many spectral line surveys performed in the last 20 years (ground and space) covering most of the 70 to 2000 GHz domain.
- Very rich and complex chemistry (warm gas-phase, shocks, grain mantle evaporation/desorption, etc.)

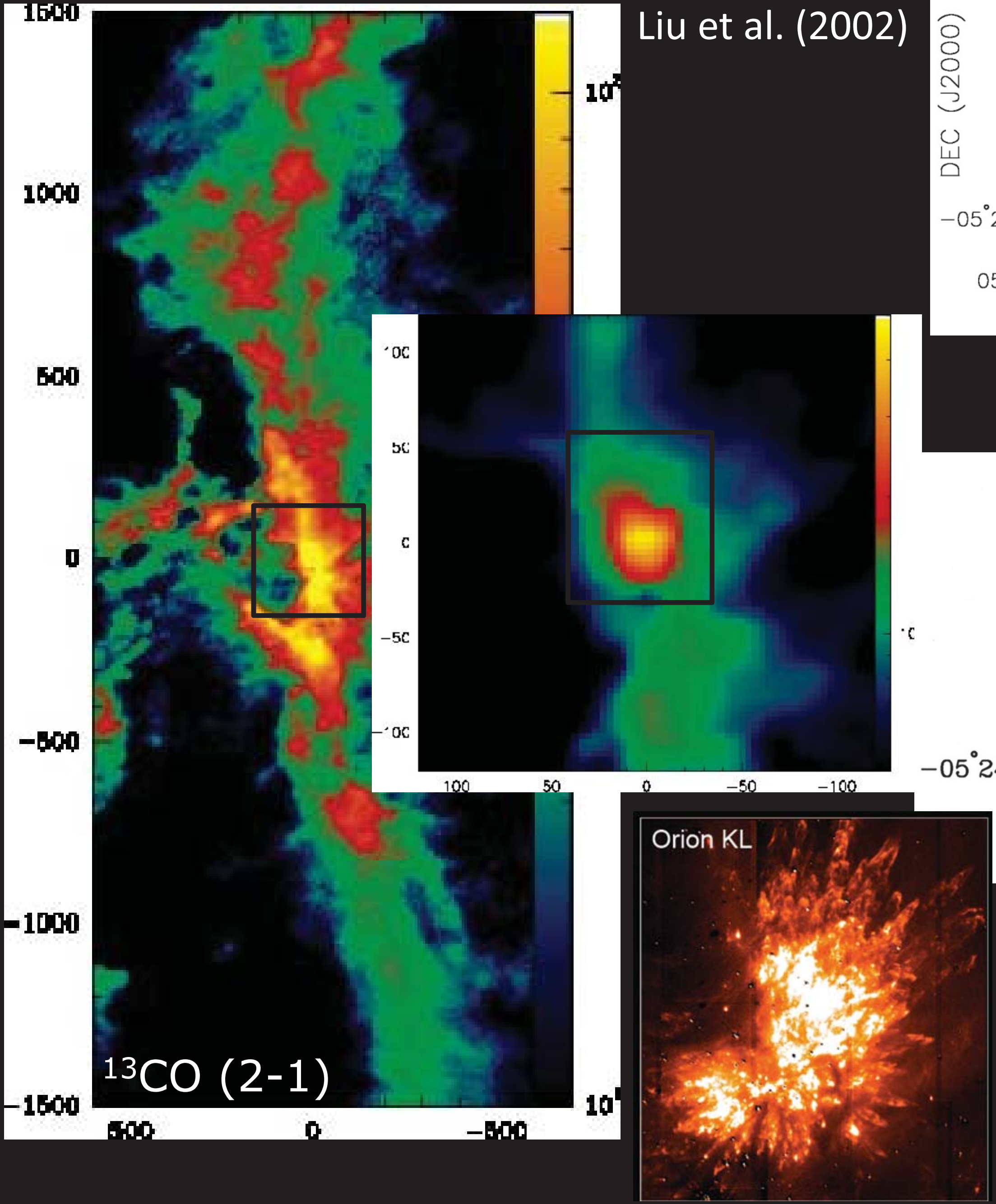
Cloud components of Orion-KL

- *Extended Ridge:* gas-phase ion-molecule chemistry; C-rich molecules (CS, CN, CCH), lack of O-rich species

- *Compact Ridge:* shocked gas, release of oxygen from grains; abundant in complex organic molecules (CH_3OH, $HCOOCH_3$, CH_3OCH_3, etc.)

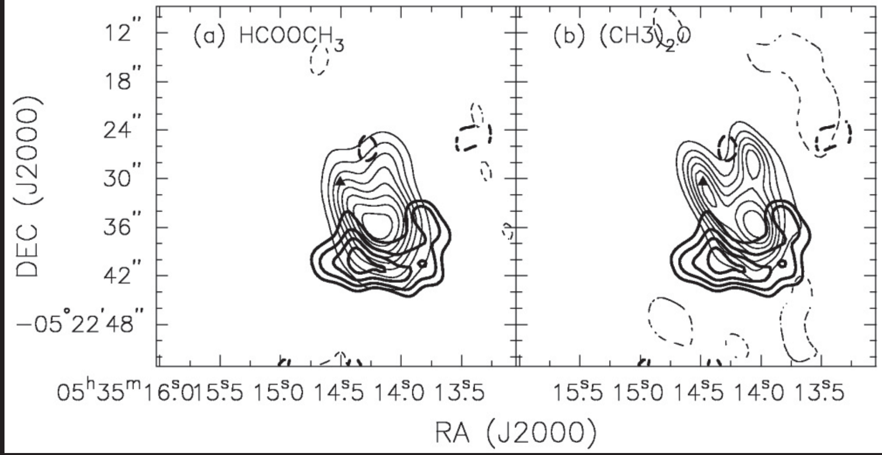
- *Hot Core:* warm gas-phase with N-rich and H-saturated species from grains; NH_3, HDO, CH_3CN, CH_3CH_2CN, etc.

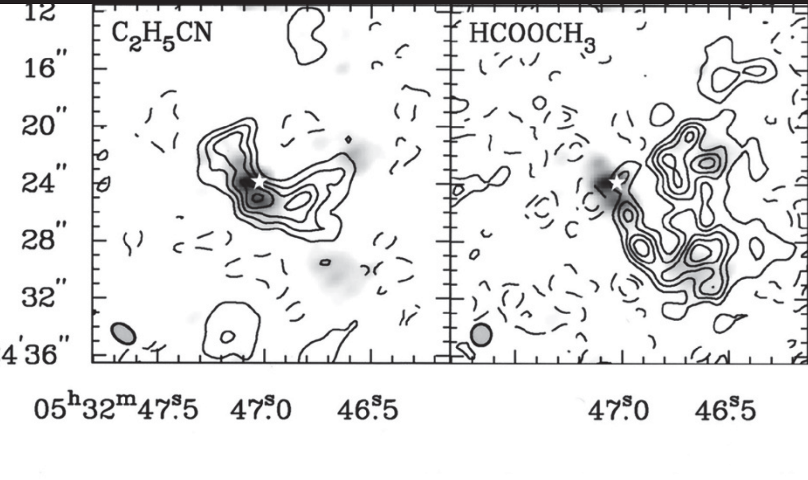
- *Plateau:* outflows; high velocity wings of CO and HCO^+; SiO, SO, SO_2, etc.; and maser emission (H_2O, OH, SiO)



BIMA

Liu et al. (2002)





OVRO

Blake et al. (1996)

IRAM 30m Line Surveys:

- Freq. range: 80 – 280 GHz → multiple transitions from the same species
- Spectral resolution: ~1 MHz (3–1 km/s)
- HPBW = 29 – 9’’
- Line confusion limited survey → deep insight into the chemistry, and detection of new molecules (isotopologs and vibrationally excited states)

Ground Based observations of high Mass star forming regions

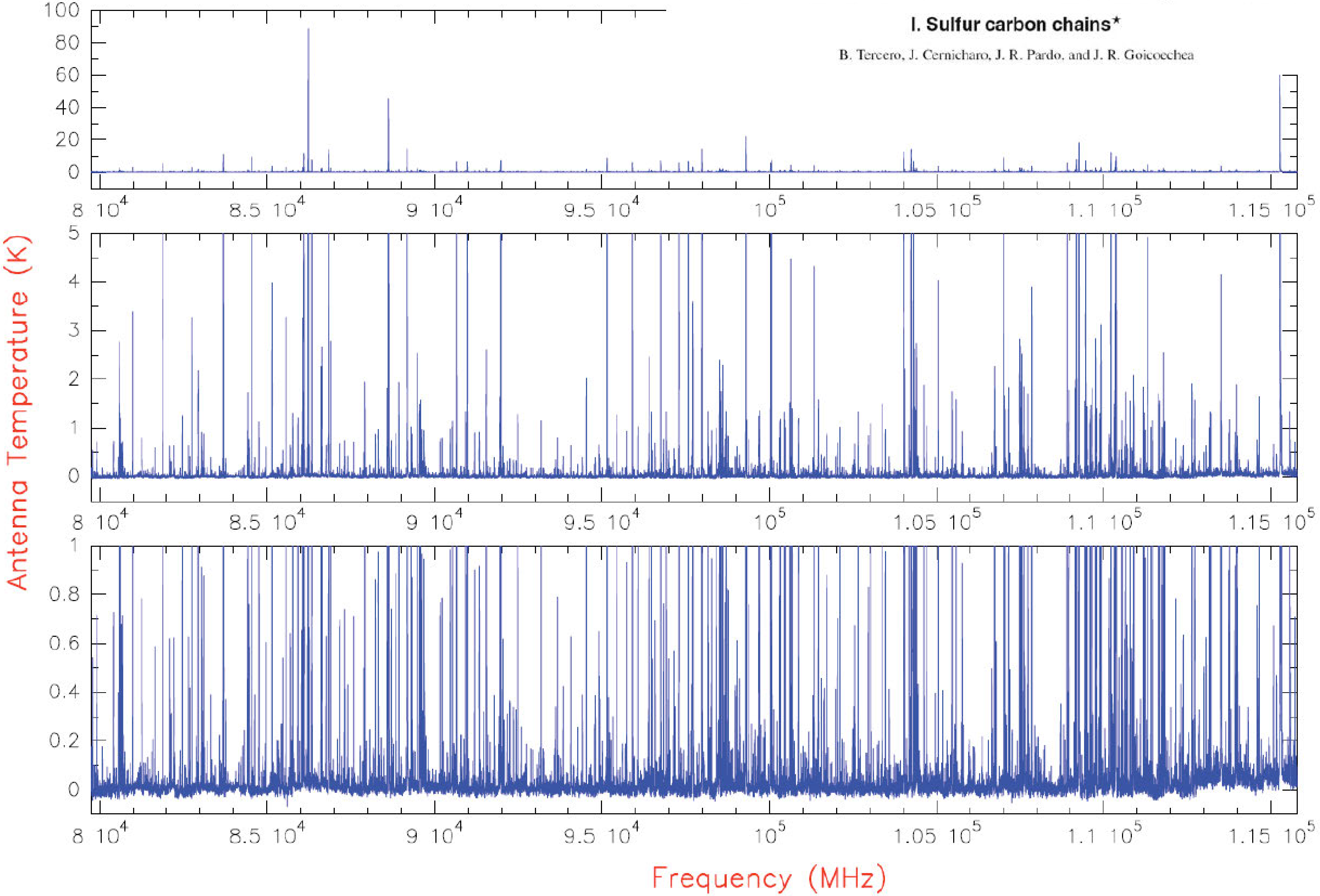
&A 517, A96 (2010)
OI: 10.1051/0004-6361/200913501
ESO 2010

A&A 517,

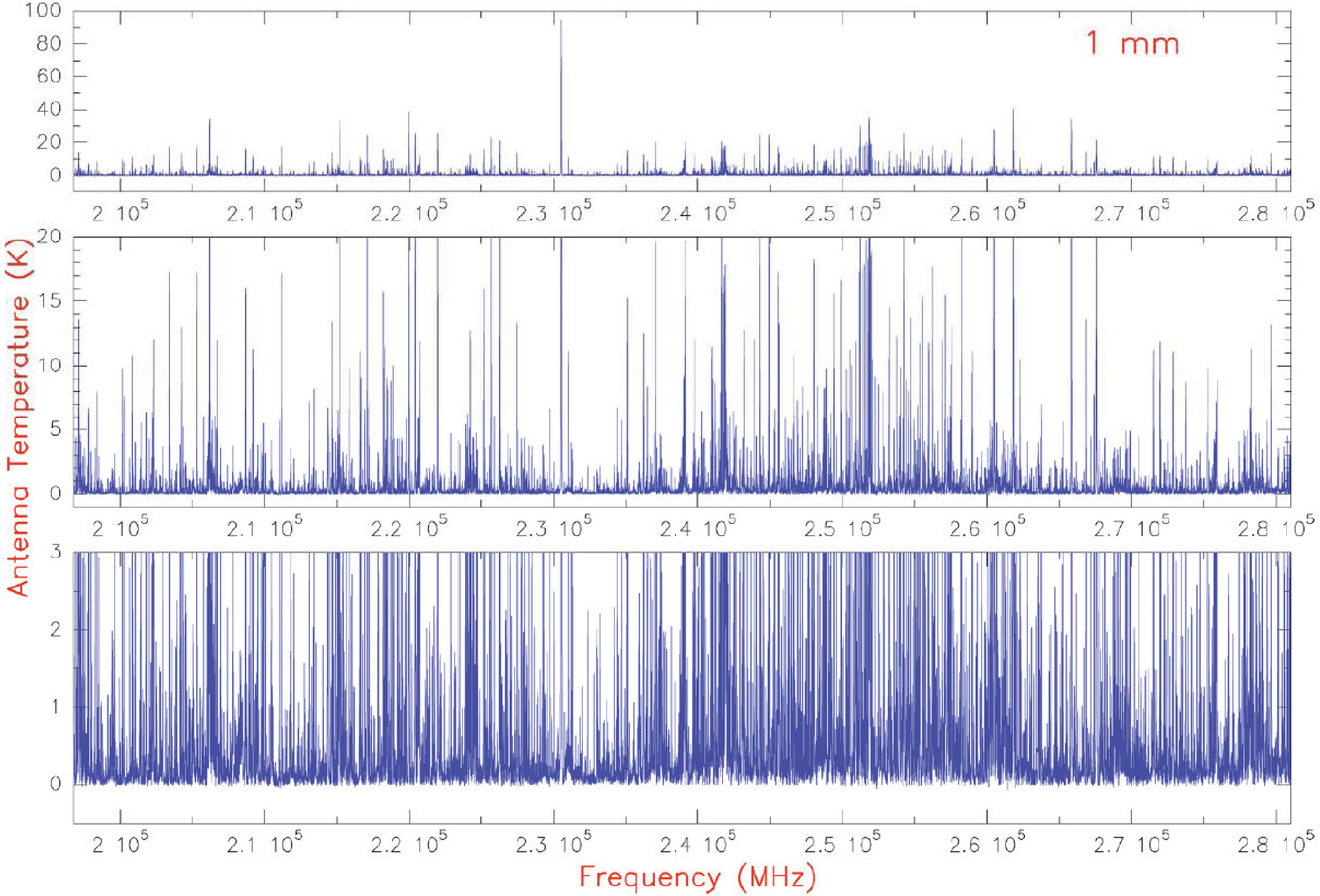
A line confusion limited millimeter survey of Orion KL

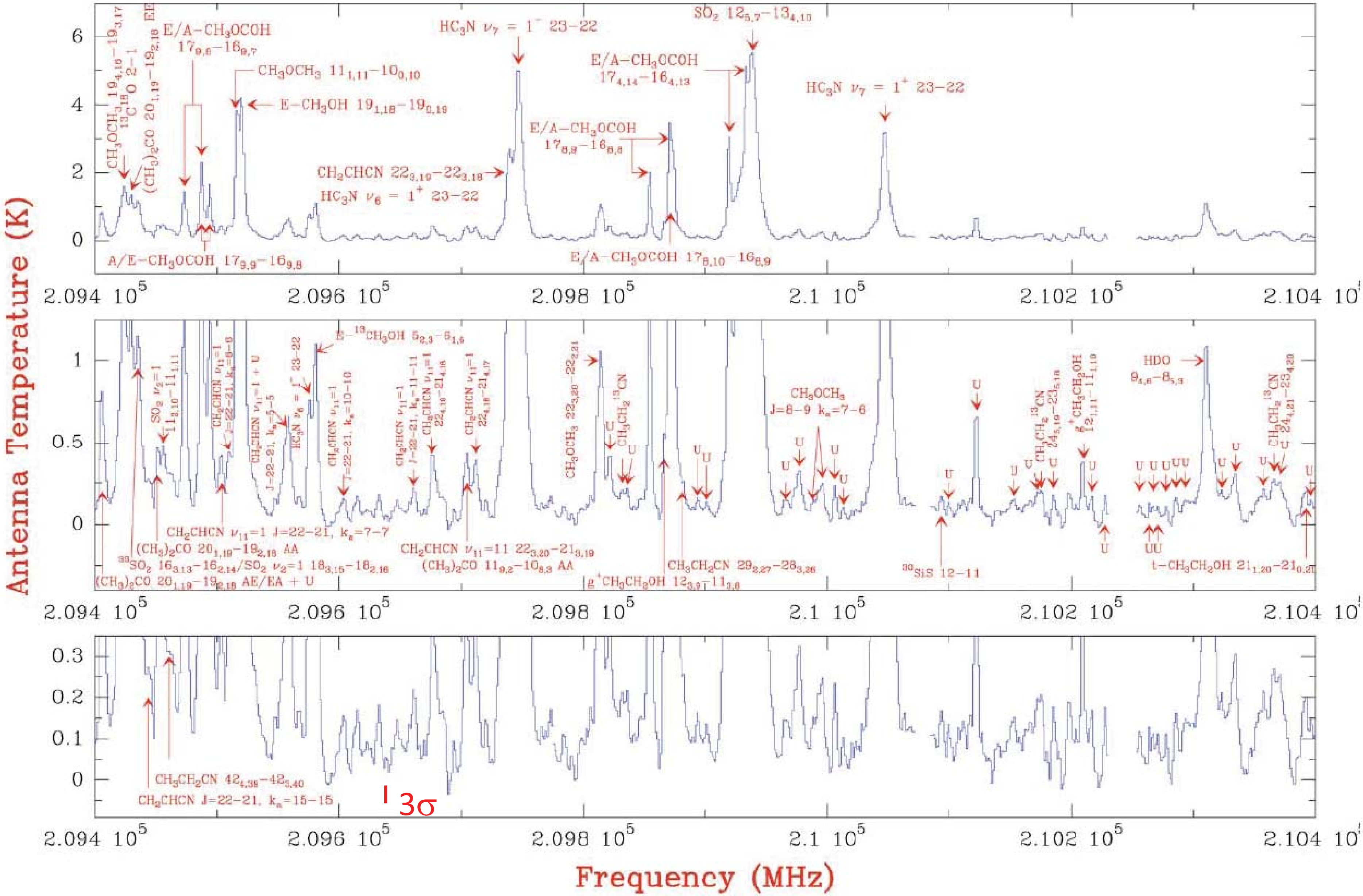
I. Sulfur carbon chains*

B. Tercero, J. Cernicharo, J. R. Pardo, and J. R. Goicoechea



A&A 517, A96 (2010)



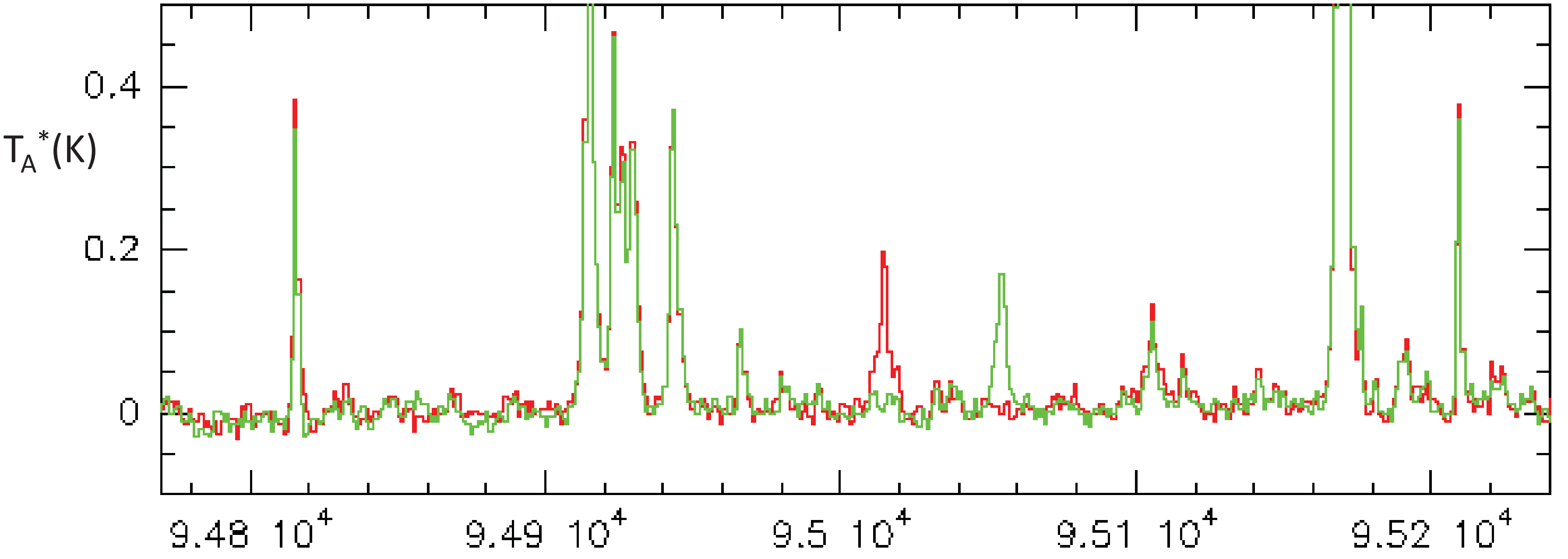


LINE CONFUSION LIMIT REACHED. WHAT TO DO ?

ALMA WILL BE 8 times more sensitive than the 30-m radio telescope

BARRIDO ESPECTRAL
Reducción de las observaciones

Eliminación de la banda imagen:
tomamos el mismo espectro desplazado en 20 MHz

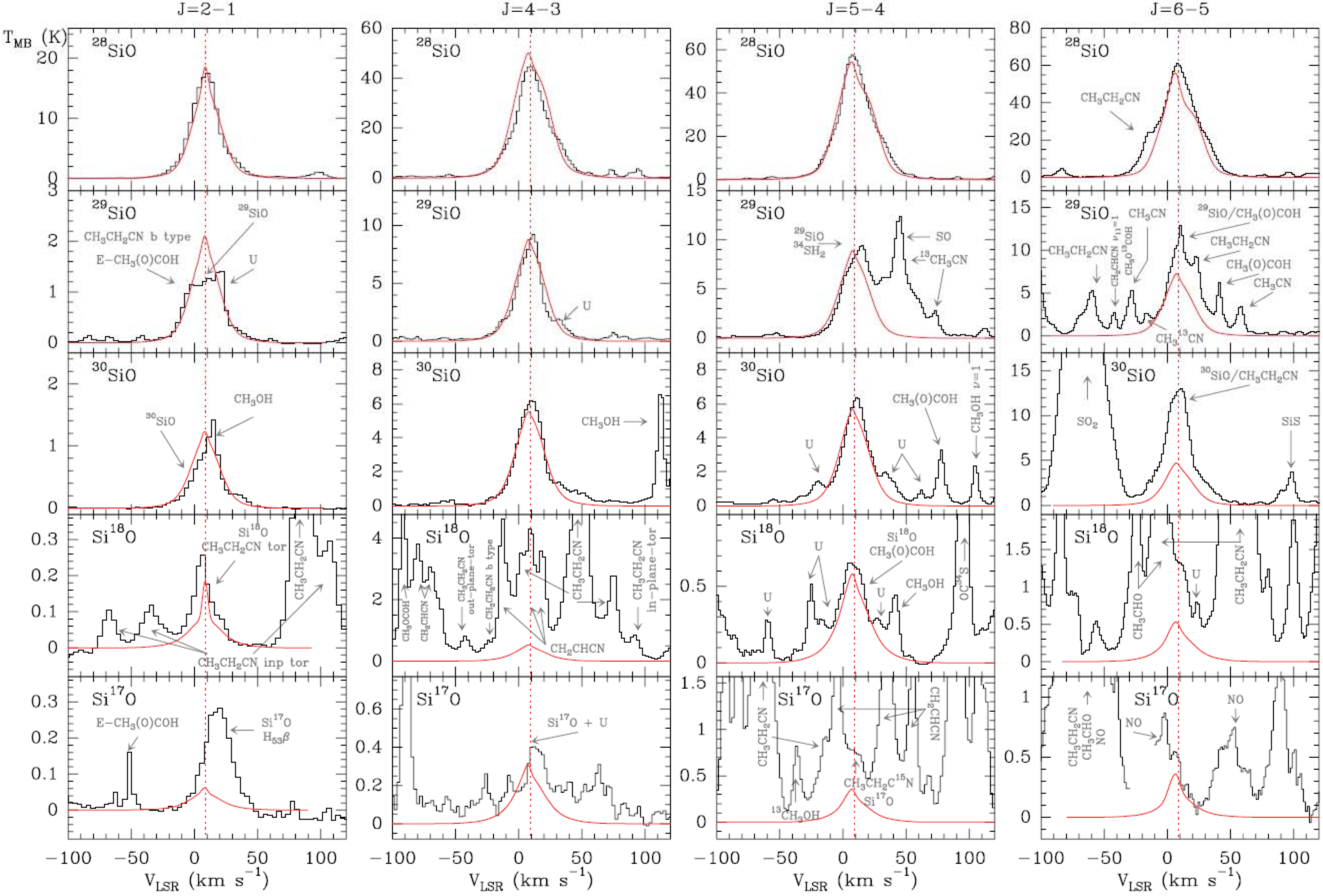


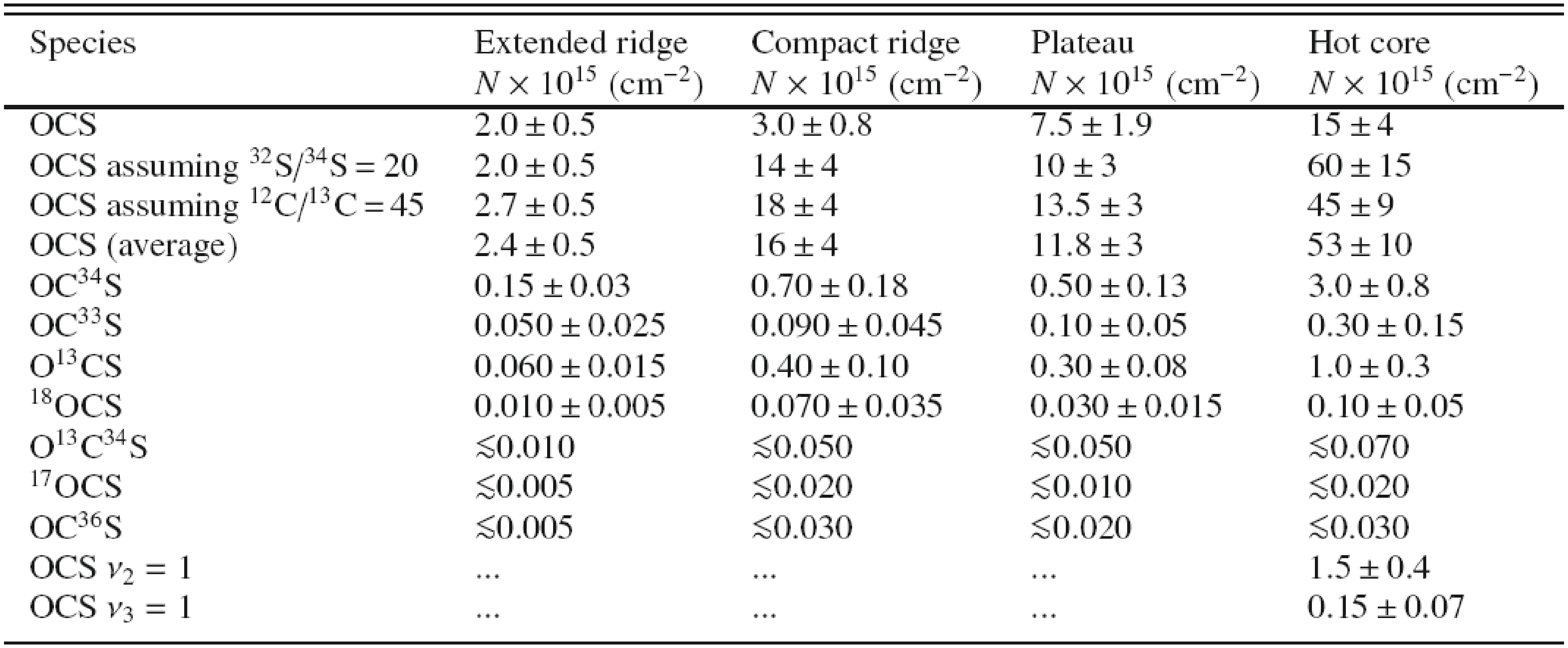
IRAM 30m Line Surveys:

- 15000 lines detected (above confusion limit), of which 10000 have been assigned to 44 molecules and their isotopologues

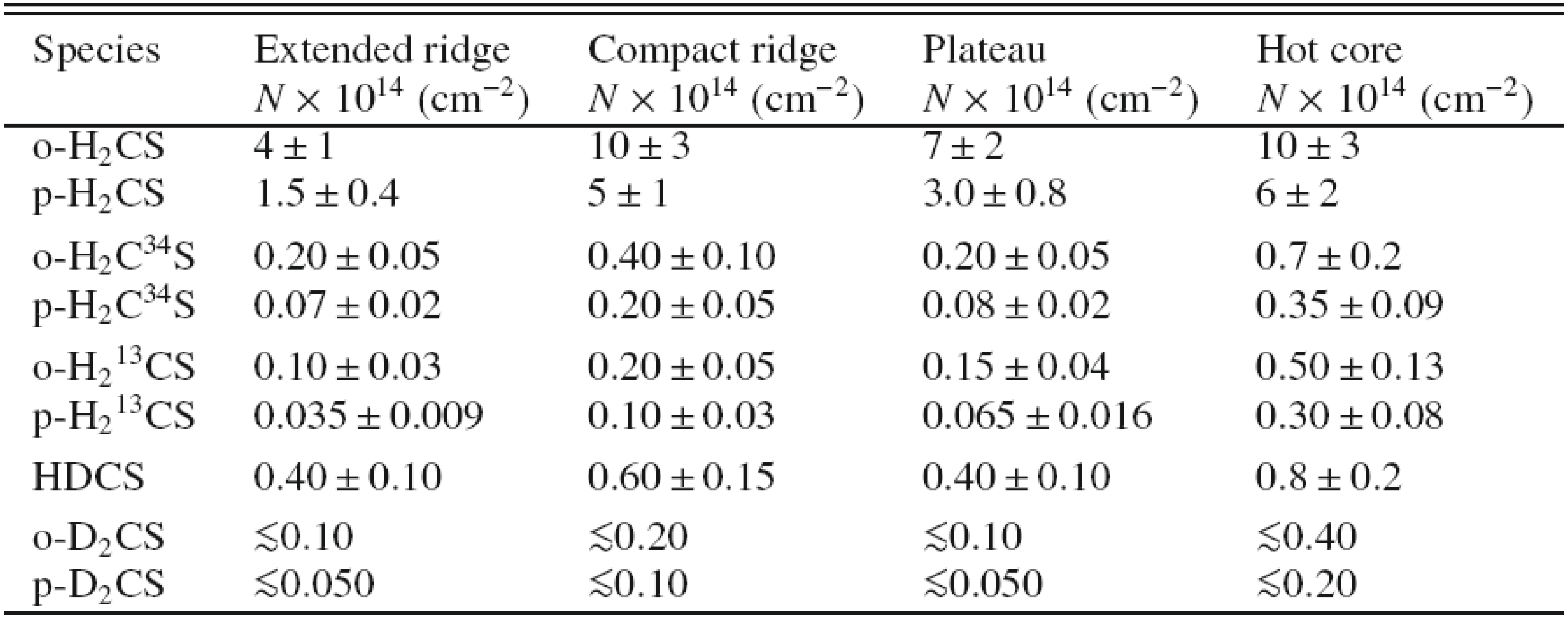
- New detections of multiple isotopic substitutions (^{18}O, D) of $HCOOCH_3$ and CH_3CH_2CN, for which new laboratory measurements were needed (Collaboration with Lille Spectroscopy Group).

- 5000 lines remain unidentified above the confusion limit (0.05 K at 3mm, 0.1 K at 2mm and 1mm)


J=2−1
J=4−3
J=5−4
J=6−5
T_MB (K)
28SiO
29SiO
30SiO
Si18O
Si17O
CH3CH2CN b type
E−CH3(O)COH
29SiO
U
CH3OH
30SiO
Si18O
CH3CH2CN tor
CH3CH2CN
CH3CH2CN inp tor
E−CH3(O)COH
Si17O
H53β
CH3OH
CH3OCOH
CH2CHCN
CH3CH2CN out−plane−tor
CH3CH2CN b type
CH3CH2CN
CH3CH2CN in−plane−tor
CH2CHCN
Si17O + U
29SiO
34SH2
SO
13CH3CN
CH3(O)COH
CH3OH ν=1
OC34S
CH3OH
CH3CH2CN
CH2CHCN
CH3CH2C15N
Si17O
13CH3OH
CH3CH2CN
CH2CHCN ν11=1
CH3O13COH
CH3CN
29SiO/CH3(O)COH
CH3CH2CN
CH3(O)COH
CH3CN
CH313CN
SO2
30SiO/CH3CH2CN
SiS
CH3CHO
CH3CH2CN
CH3CH2CN
CH3CHO
NO
NO
V_LSR (km s−1)
−100
−50
0
50
100



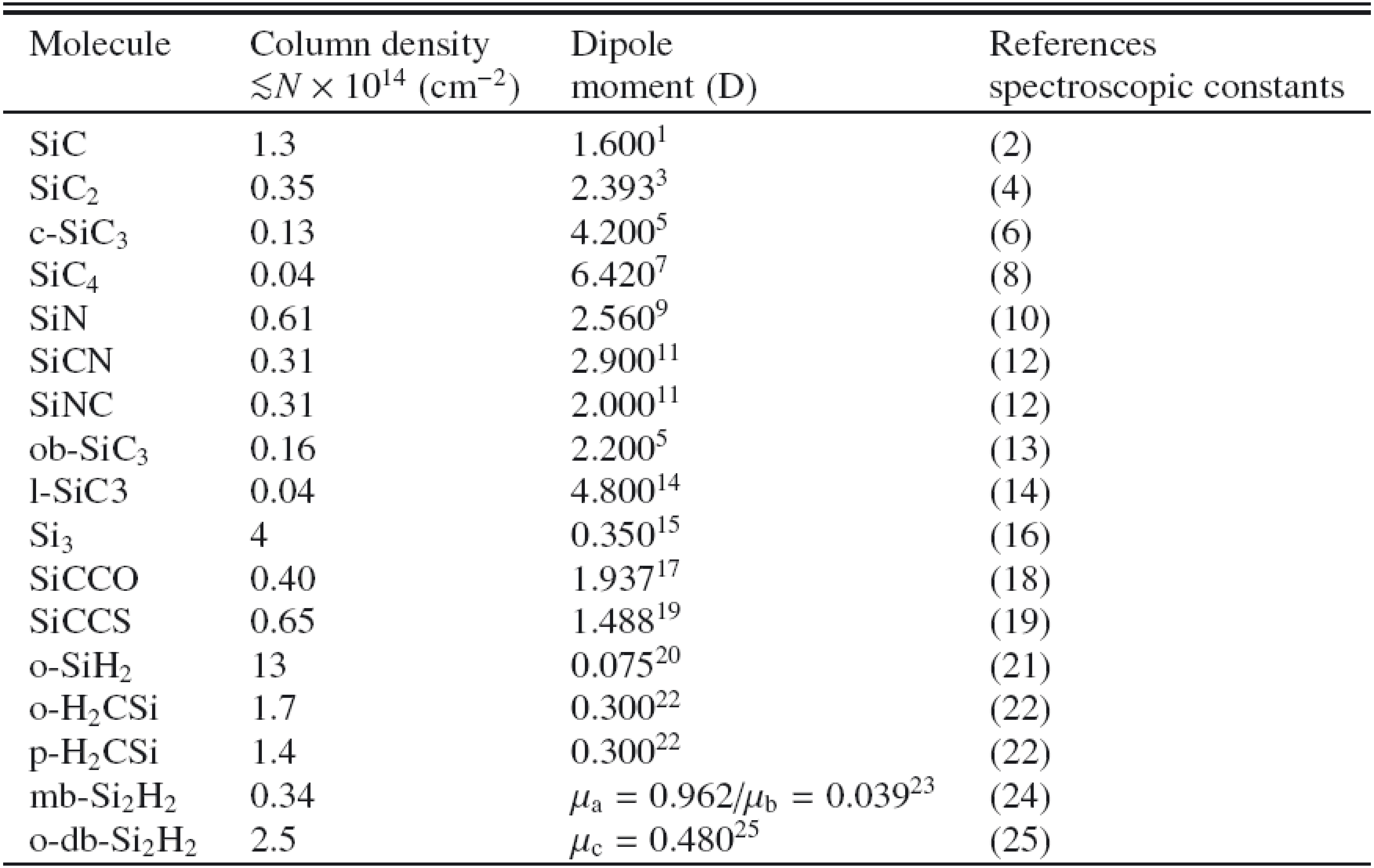
Species	Extended ridge $N \times 10^{15}$ (cm^{-2})	Compact ridge $N \times 10^{15}$ (cm^{-2})	Plateau $N \times 10^{15}$ (cm^{-2})	Hot core $N \times 10^{15}$ (cm^{-2})
OCS	2.0 ± 0.5	3.0 ± 0.8	7.5 ± 1.9	15 ± 4
OCS assuming $^{32}S/^{34}S = 20$	2.0 ± 0.5	14 ± 4	10 ± 3	60 ± 15
OCS assuming $^{12}C/^{13}C = 45$	2.7 ± 0.5	18 ± 4	13.5 ± 3	45 ± 9
OCS (average)	2.4 ± 0.5	16 ± 4	11.8 ± 3	53 ± 10
$OC^{34}S$	0.15 ± 0.03	0.70 ± 0.18	0.50 ± 0.13	3.0 ± 0.8
$OC^{33}S$	0.050 ± 0.025	0.090 ± 0.045	0.10 ± 0.05	0.30 ± 0.15
$O^{13}CS$	0.060 ± 0.015	0.40 ± 0.10	0.30 ± 0.08	1.0 ± 0.3
^{18}OCS	0.010 ± 0.005	0.070 ± 0.035	0.030 ± 0.015	0.10 ± 0.05
$O^{13}C^{34}S$	$\lesssim 0.010$	$\lesssim 0.050$	$\lesssim 0.050$	$\lesssim 0.070$
^{17}OCS	$\lesssim 0.005$	$\lesssim 0.020$	$\lesssim 0.010$	$\lesssim 0.020$
$OC^{36}S$	$\lesssim 0.005$	$\lesssim 0.030$	$\lesssim 0.020$	$\lesssim 0.030$
OCS $v_2 = 1$	...	...	...	1.5 ± 0.4
OCS $v_3 = 1$	...	...	...	0.15 ± 0.07



Species	Extended ridge $N \times 10^{14}$ (cm^{-2})	Compact ridge $N \times 10^{14}$ (cm^{-2})	Plateau $N \times 10^{14}$ (cm^{-2})	Hot core $N \times 10^{14}$ (cm^{-2})
o-H_2CS	4 ± 1	10 ± 3	7 ± 2	10 ± 3
p-H_2CS	1.5 ± 0.4	5 ± 1	3.0 ± 0.8	6 ± 2
o-$H_2C^{34}S$	0.20 ± 0.05	0.40 ± 0.10	0.20 ± 0.05	0.7 ± 0.2
p-$H_2C^{34}S$	0.07 ± 0.02	0.20 ± 0.05	0.08 ± 0.02	0.35 ± 0.09
o-$H_2{}^{13}CS$	0.10 ± 0.03	0.20 ± 0.05	0.15 ± 0.04	0.50 ± 0.13
p-$H_2{}^{13}CS$	0.035 ± 0.009	0.10 ± 0.03	0.065 ± 0.016	0.30 ± 0.08
HDCS	0.40 ± 0.10	0.60 ± 0.15	0.40 ± 0.10	0.8 ± 0.2
o-D_2CS	$\lesssim 0.10$	$\lesssim 0.20$	$\lesssim 0.10$	$\lesssim 0.40$
p-D_2CS	$\lesssim 0.050$	$\lesssim 0.10$	$\lesssim 0.050$	$\lesssim 0.20$

From Tercero et al., 2010, A&A, 517, A96 & 2011, A&A, 528, A26

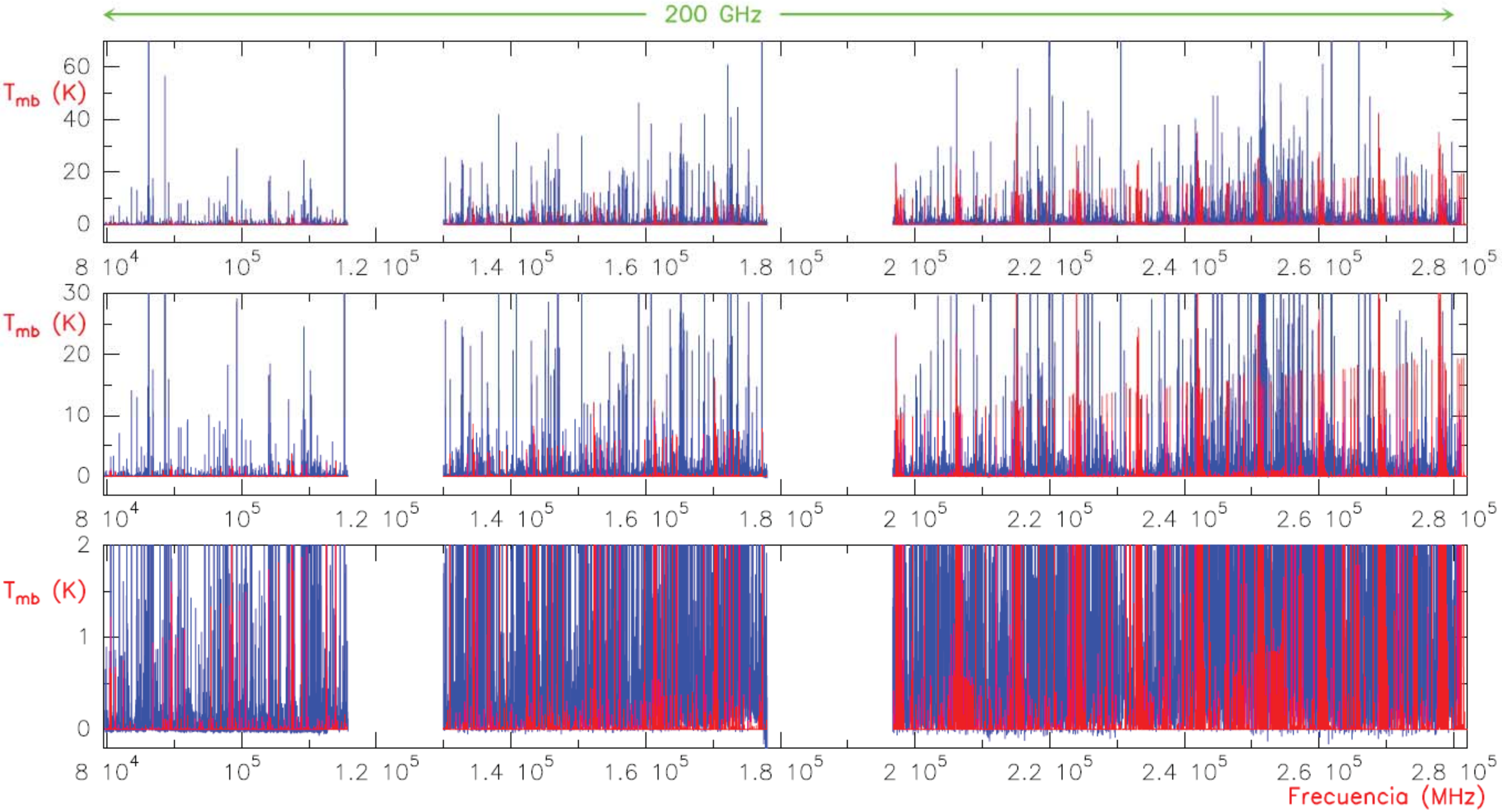
Using MADEX: upper limits to the column density of hundreds of potentially interesting species



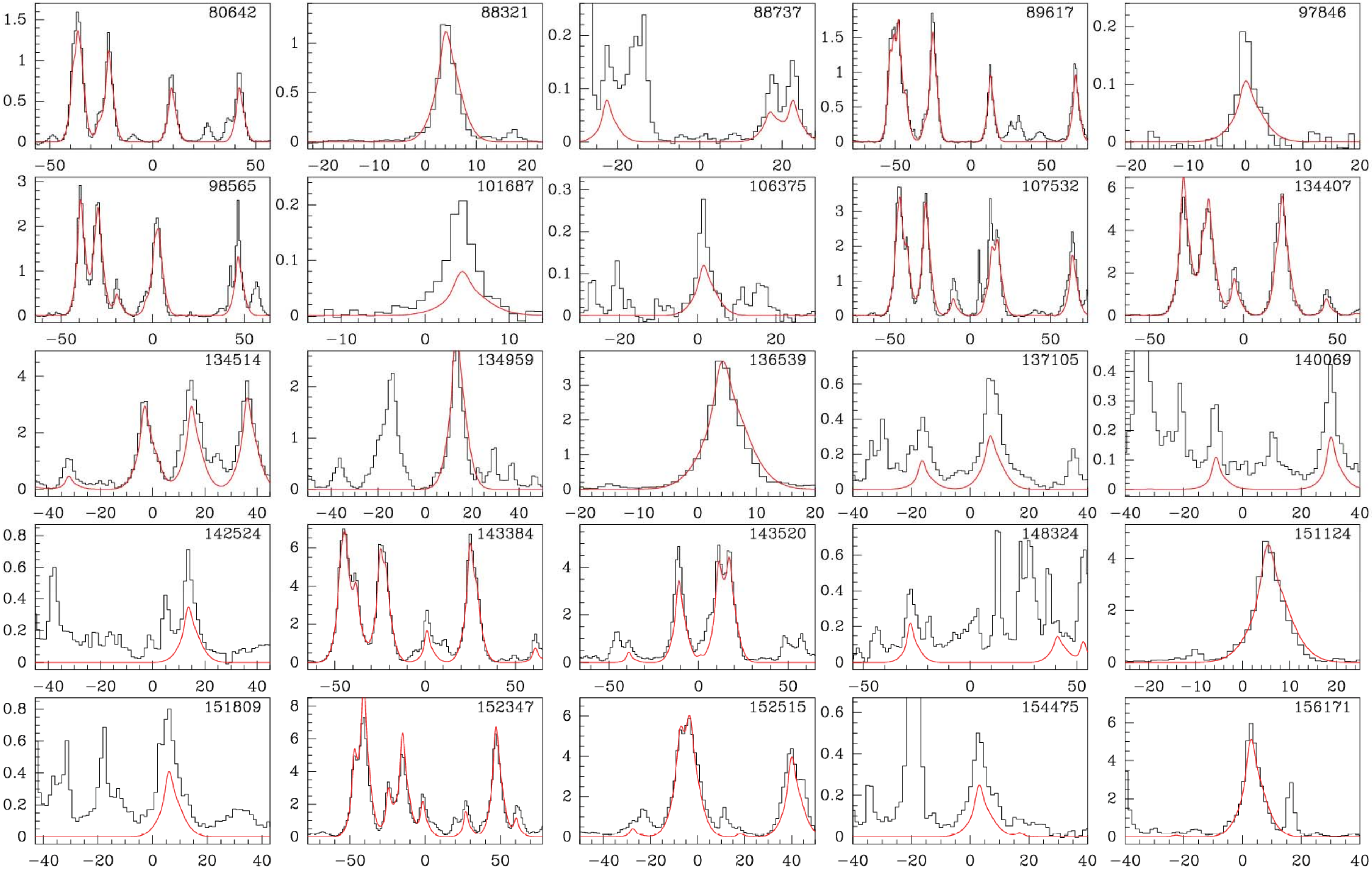
Molecule	Column density $\lesssim N \times 10^{14}$ (cm^{-2})	Dipole moment (D)	References spectroscopic constants
SiC	1.3	1.600[1]	(2)
SiC_2	0.35	2.393[3]	(4)
c-SiC_3	0.13	4.200[5]	(6)
SiC_4	0.04	6.420[7]	(8)
SiN	0.61	2.560[9]	(10)
SiCN	0.31	2.900[11]	(12)
SiNC	0.31	2.000[11]	(12)
ob-SiC_3	0.16	2.200[5]	(13)
l-SiC3	0.04	4.800[14]	(14)
Si_3	4	0.350[15]	(16)
SiCCO	0.40	1.937[17]	(18)
SiCCS	0.65	1.488[19]	(19)
o-SiH_2	13	0.075[20]	(21)
o-H_2CSi	1.7	0.300[22]	(22)
p-H_2CSi	1.4	0.300[22]	(22)
mb-Si_2H_2	0.34	$\mu_a = 0.962/\mu_b = 0.039$[23]	(24)
o-db-Si_2H_2	2.5	$\mu_c = 0.480$[25]	(25)

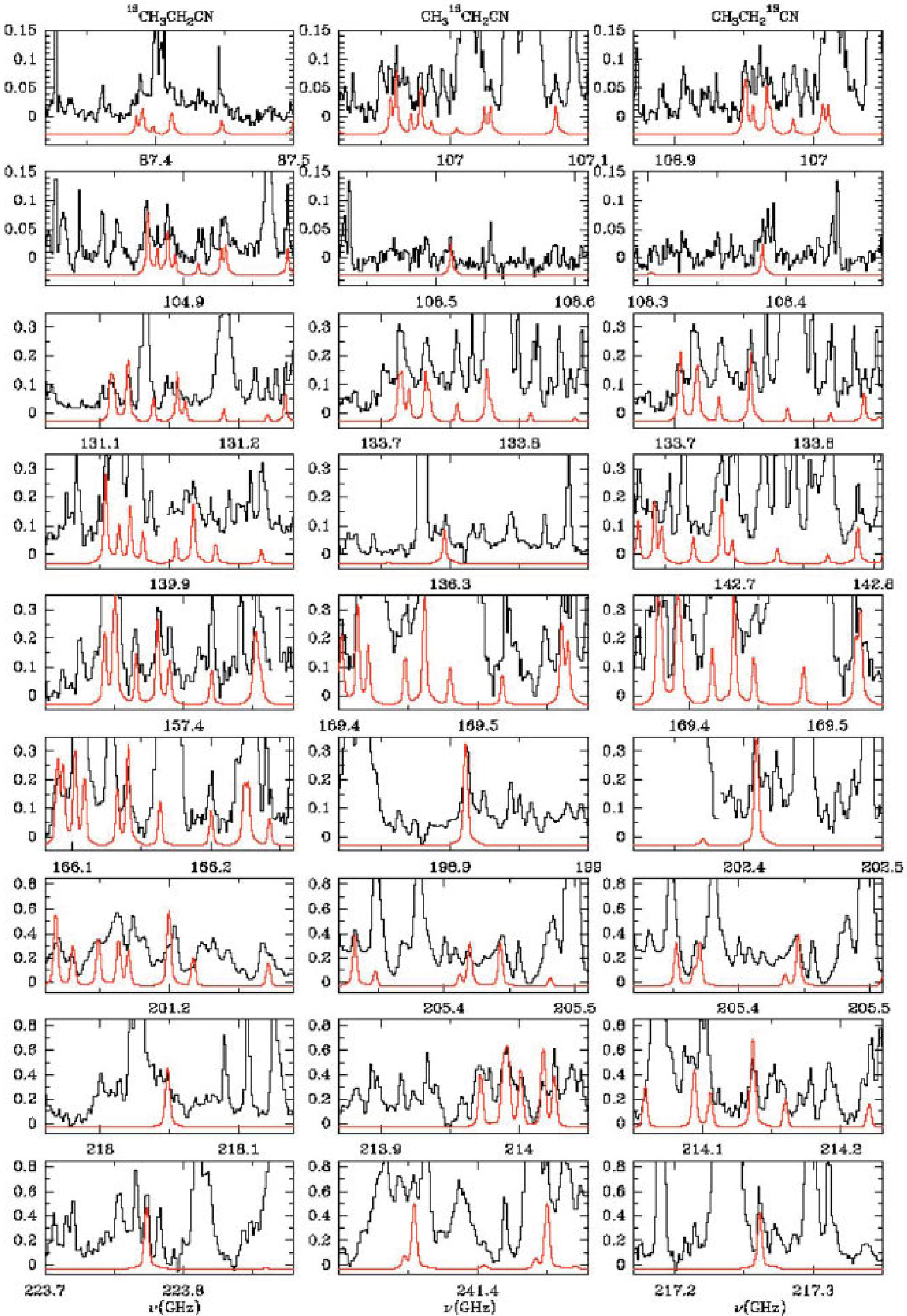
From Tercero et al., 2011, A&A, 528, A26

Ethyl Cyanide (The Contaminator), CH_3CH_2CN



Ethyl Cyanide, CH_3CH_2CN (ground state)





Collaboration with L. Margules, I. Kleiner et al. ➔

More than 800 lines from the isotopes of CH_3CH_2CN

Around 600 lines from the vibrational excited states of ethyl cyanide

More than 400 lines from those of CH_3OCOH

Around 800-1000 lines identified every 2 years in Orion. All lines above confusion limit could be identified around 2020 !!!

Belen started her PhD based on this line survey in 2006.

When combined with HEXOS data=> Work for a long period

ALMA ?

Sym. Species	No	Approximate type of mode	Freq. Value	Infrared Value
a'	1	CH3 d-str	3001	3001 VS
a'	2	CH2 s-str	2955	2955 VS
a'	3	CH3 s-str	2900	2900 S
a'	4	CN str	2254	2254 VS
a'	5	CH3 d-deform	1465	1465 S
a'	6	CH2 scis	1433	1433 S
a'	7	CH3 s-deform	1387	1387 M
a'	8	CH2 wag	1319	1319 M
a'	9	C-CN str	1077	1077 S
a'	10	CC str	1005	1005 M
a'	**11**	**CH3 rock**	**836**	836 W
a'	**12**	**CCC deform**	**545**	545 M
a'	**13**	**CCN bend**	**226**	226 M
a	14	CH3 d-str	3001	3001 VS
a	15	CH2 a-str	2849	2849 S
a	16	CH3 d-deform	1465	1465 S
a	17	CH2 twist	1256	1256 VW
a	18	CH3 rock	1022	
a	**19**	**CH2 rock**	**786**	786 M
a	**20**	**CCN bend**	**378**	378 M
a	**21**	**Torsion**	**222**	

Possible vibrational levels of CH_3CH_2CN in Orion:

ν_{21}, ν_{20}, ν_{19}, ν_{11}, ν_{12}, ν_{13}

$\nu_{21}+\nu_{20}$, $\nu_{21}+\nu_{19}$, ν_{21},

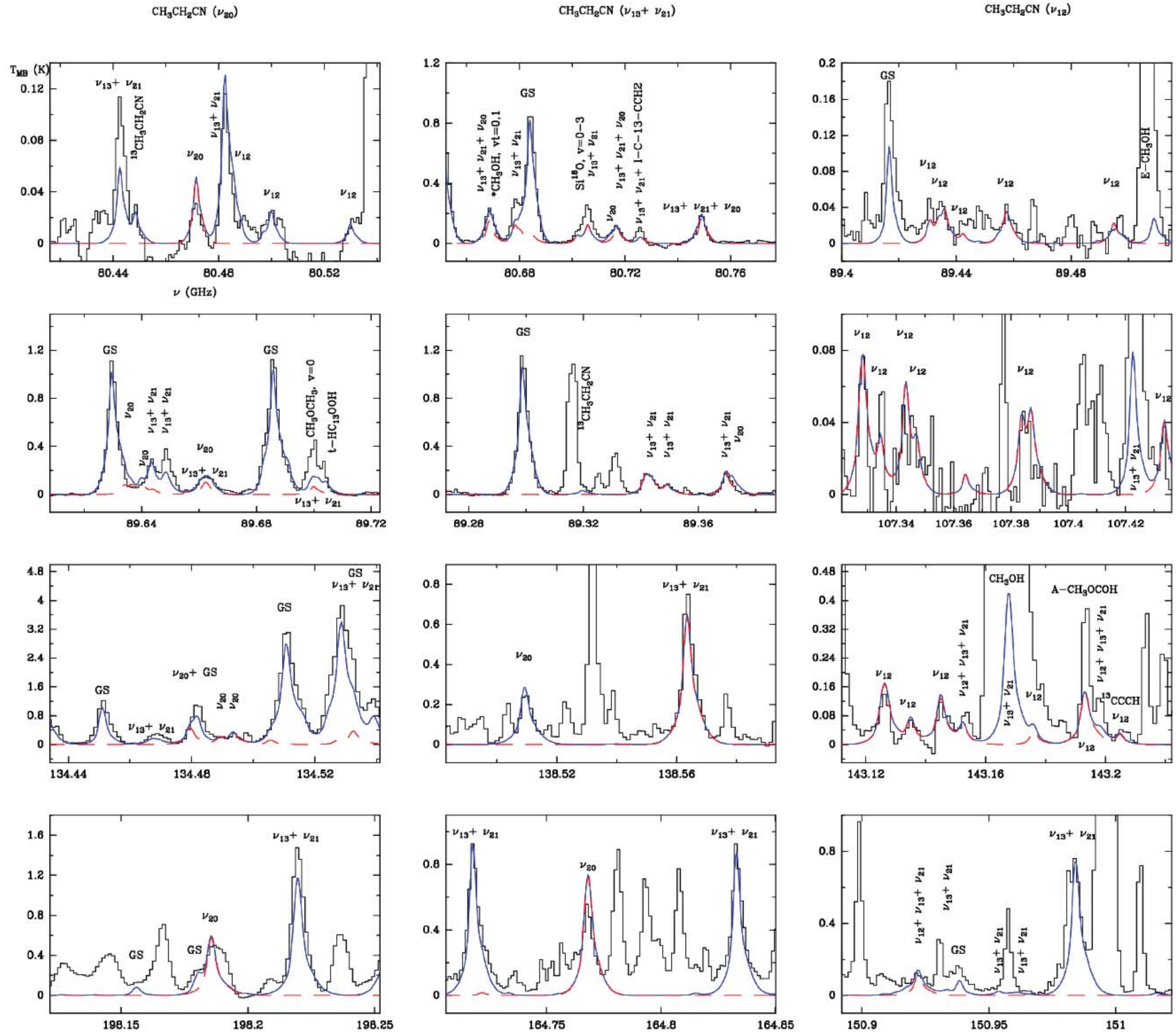
$\nu_{12}+\nu_{13}$, ……

For a vibrational temperature of 300 K all these levels will have a contribution 10 times larger than that of the isotopes ^{13}C !!!

Collaboration with J.L. Alonso (Valladolid, Spain) and J. Pearson et al. (JPL)

many of these levels have been detected (in progress for all levels below 1000 cm^{-1})

Strong perturbations, complex Hamiltonians.


CH3CH2CN (ν20)
CH3CH2CN (ν13+ ν21)
CH3CH2CN (ν12)
TMB (K)
ν (GHz)
ν13+ ν21
13CH3CH2CN
ν20
ν13+ ν21
ν12
ν12
ν12
80.44
80.48
80.52
GS
ν13+ ν21+ ν20
*CH3OH, vt=0,1
ν13+ ν21
Si18O, v=0-3
ν13+ ν21
ν20
ν13+ ν21+ ν20
ν13+ ν21+ 1-C-13-CCH2
ν13+ ν21+ ν20
80.68
80.72
80.76
GS
ν12
ν12
ν12
ν12
ν12
E-CH3OH
89.4
89.44
89.48
GS
ν20
ν20
ν13+ ν21
ν13+ ν21
ν20
ν13+ ν21
GS
CH3OCH3, v=0
t-HC13OOH
ν13+ ν21
89.64
89.68
89.72
GS
13CH3CH2CN
ν13+ ν21
ν13+ ν21
ν13+ ν21
ν20
89.28
89.32
89.36
ν12
ν12
ν12
ν12
ν12
ν12
ν13+ ν21
107.34
107.36
107.38
107.4
107.42
GS
ν13+ ν21
ν20+ GS
ν20
ν20
GS
GS
ν13+ ν21
134.44
134.48
134.52
ν20
ν13+ ν21
138.52
138.56
CH3OH
A-CH3OCOH
ν12
ν12
ν12
ν12+ ν13+ ν21
ν13+ ν21
ν12
ν12+ ν13+ ν21
13CCCH
ν12
ν12
143.12
143.16
143.2
GS
GS
ν20
ν13+ ν21
198.15
198.2
198.25
ν13+ ν21
ν20
ν13+ ν21
164.75
164.8
164.85
ν12+ ν13+ ν21
ν13+ ν21
GS
ν13+ ν21
ν13+ ν21
ν13+ ν21
150.9
150.95
151
0.12
0.08
0.04
0
1.2
0.8
0.4
0.2
0.16
4.8
4
3.2
2.4
1.6
0.48
0.32
0.24
0.6

	Hot core HOT	Hot core COLD	Plateau HOT	Plateau COLD
d_{sou}	4	7	15	25
offset	5	5	5	5
v_{exp}	5	5	13	22
v_{LSR}	5	5	3	3
T_{ETL}	**240**	**150**	**130**	**60**
CH_3CH_2CN (G.S.)	$2.50\text{x}10^{16}$	$1.50\text{x}10^{16}$	$4.00\text{x}10^{15}$	$2.00\text{x}10^{15}$
CH_3CH_2CN (inp-tor)	$3.12\text{x}10^{15}$	$1.88\text{x}10^{15}$	$5.00\text{x}10^{14}$	$2.50\text{x}10^{14}$
CH_3CH_2CN (outp)	$1.25\text{x}10^{15}$	$7.50\text{x}10^{14}$	$2.00\text{x}10^{14}$	$1.00\text{x}10^{14}$
$^{13}CH_3CH_2CN$	$5.21\text{x}10^{14}$	$3.12\text{x}10^{14}$	$8.33\text{x}10^{13}$	$4.17\text{x}10^{13}$
$CH_3{}^{13}CH_2CN$	$5.21\text{x}10^{14}$	$3.12\text{x}10^{14}$	$8.33\text{x}10^{13}$	$4.17\text{x}10^{13}$
$CH_3CH_2{}^{13}CN$	$5.21\text{x}10^{14}$	$3.12\text{x}10^{14}$	$8.33\text{x}10^{13}$	$4.17\text{x}10^{13}$
A-CH_2DCH_2CN	$\lesssim 4.54\text{x}10^{14}$	$\lesssim 2.73\text{x}10^{14}$	$\lesssim 7.27\text{x}10^{13}$	$\lesssim 3.64\text{x}10^{13}$
S-CH_2DCH_2CN	$\lesssim 4.54\text{x}10^{14}$	$\lesssim 2.73\text{x}10^{14}$	$\lesssim 7.27\text{x}10^{13}$	$\lesssim 3.64\text{x}10^{13}$
CH_3CH_2CN (v_{12})	**$4.17\text{x}10^{14}$**	**$2.50\text{x}10^{14}$**	**$6.67\text{x}10^{13}$**	**$3.33\text{x}10^{13}$**
CH_3CHDCN	$\lesssim 2.72\text{x}10^{14}$	$\lesssim 1.63\text{x}10^{14}$	$\lesssim 4.35\text{x}10^{13}$	$\lesssim 2.17\text{x}10^{13}$
$CH_3CH_2C^{15}N$	$1.47\text{x}10^{14}$	$8.82\text{x}10^{13}$	$2.35\text{x}10^{13}$	$1.18\text{x}10^{13}$

E_{vib}=800 K

What is the role of vibrationally excited molecules in chemistry ?

Slow reactions involving ground state species could become very fast using the vibrational energy reservoir to overpass possible activation barriers.

See Agúndez et al (2010, ApJ, 713, 662) for C^+ and $H_2(v=1)$

In high mass star forming regions such as Orion KL the contribution to the spectral density from diatomic and triatomic molecules is through their isotopologues:

SiO, ^{29}SiO, ^{30}SiO, $Si^{18}O$, $Si^{17}O$
CS, ^{13}CS, $C^{34}S$, $C^{33}S$
HCO^+, DCO^+, $H^{13}CO^+$, $HC^{18}O^+$, $HC^{17}O^+$
HCN, DCN, $H^{13}CN$, $HC^{15}N$,….

Lines from the vibrationally excited states of some of them are detected but are weak (lowest vibrational energies ≈ 700-1000 cm^{-1}).

However, for heavy species the main contribution to the confusion is through their vibrationally excited states.

For T_{vib}=300 K all molecules having vibrationally excited states around 200 cm-1 will have $N_{ground} / N_{vib} \approx 3$ while $^{12}C/^{13}C \approx 45$

Orion, the nightmare

- Chemical abundances show a stratification over scales of a few arcseconds.
- Observations with telescopes such as the 30-m reach the spectral confusion limit in a few minutes of observing time (ALMA could be a nightmare).
- Vibrationally excited species more important than isotopologues !!!

$^{12}C/^{13}C \approx 45$, $^{32}S/^{34}S \approx 20$, $^{14}N/^{15}N \approx 250$

$CH_3CH_2CN(v=0)/CH_3CH_2CN(bending) \approx 4\text{-}5$ for $T_{vib}=250$ K

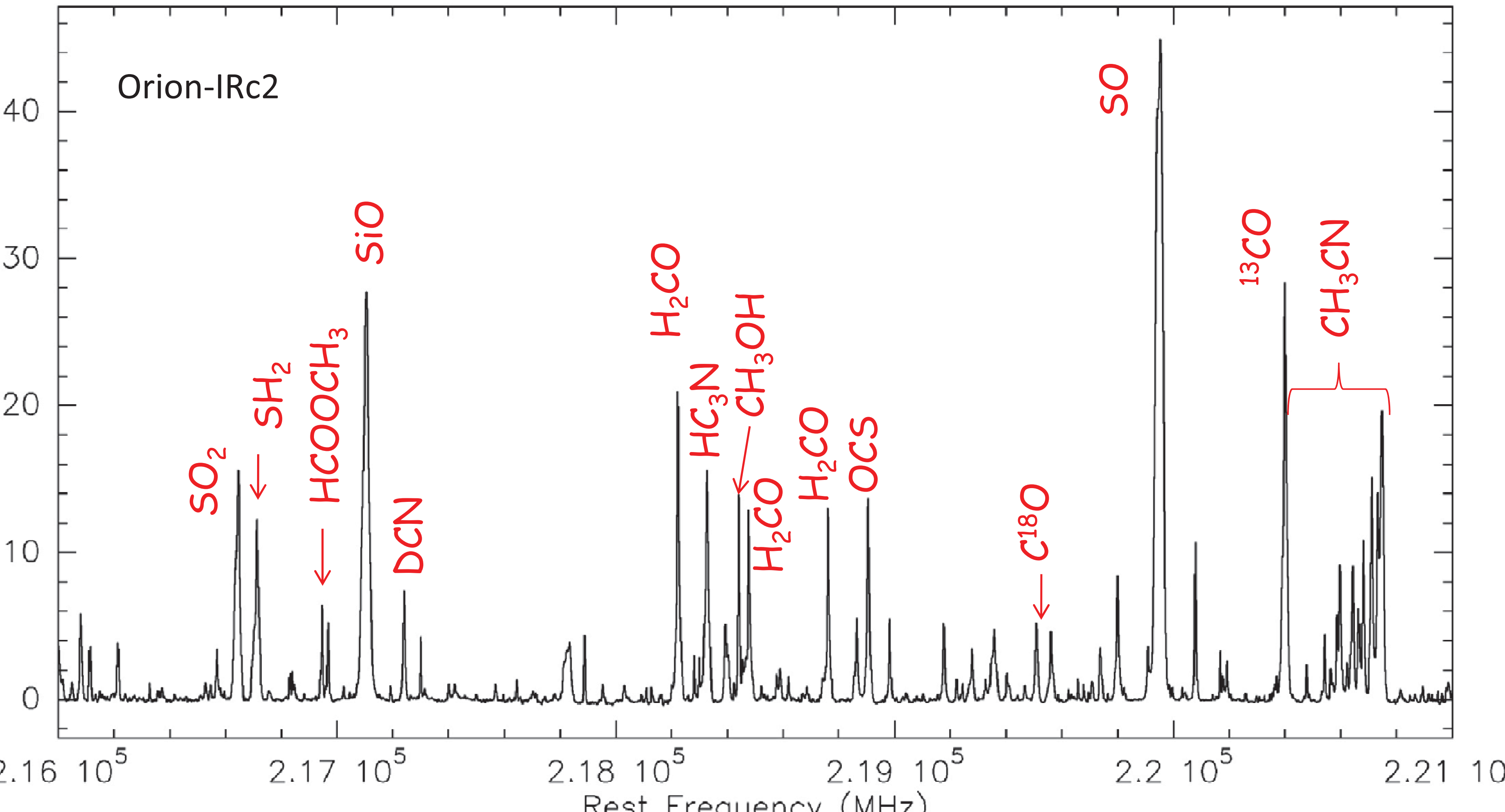
IRAM 30m Line Surveys:

- 2x2′ maps (fully sampled) centred on IRc2
- Freq. range: 200 – 282 GHz
- HERA (3x3 pixels, 1 GHz) + EMIR (4 GHz)
- Spectral resolution: 2 MHz (~2.6 km/s)
- HPBW = 12 – 9′′ Orion-KL source components can be resolved
- Spatial Sampling 4″
- Confusion limited in 30″x30″

→

- Observations completed, now in the reduction process…

2-D Line Survey



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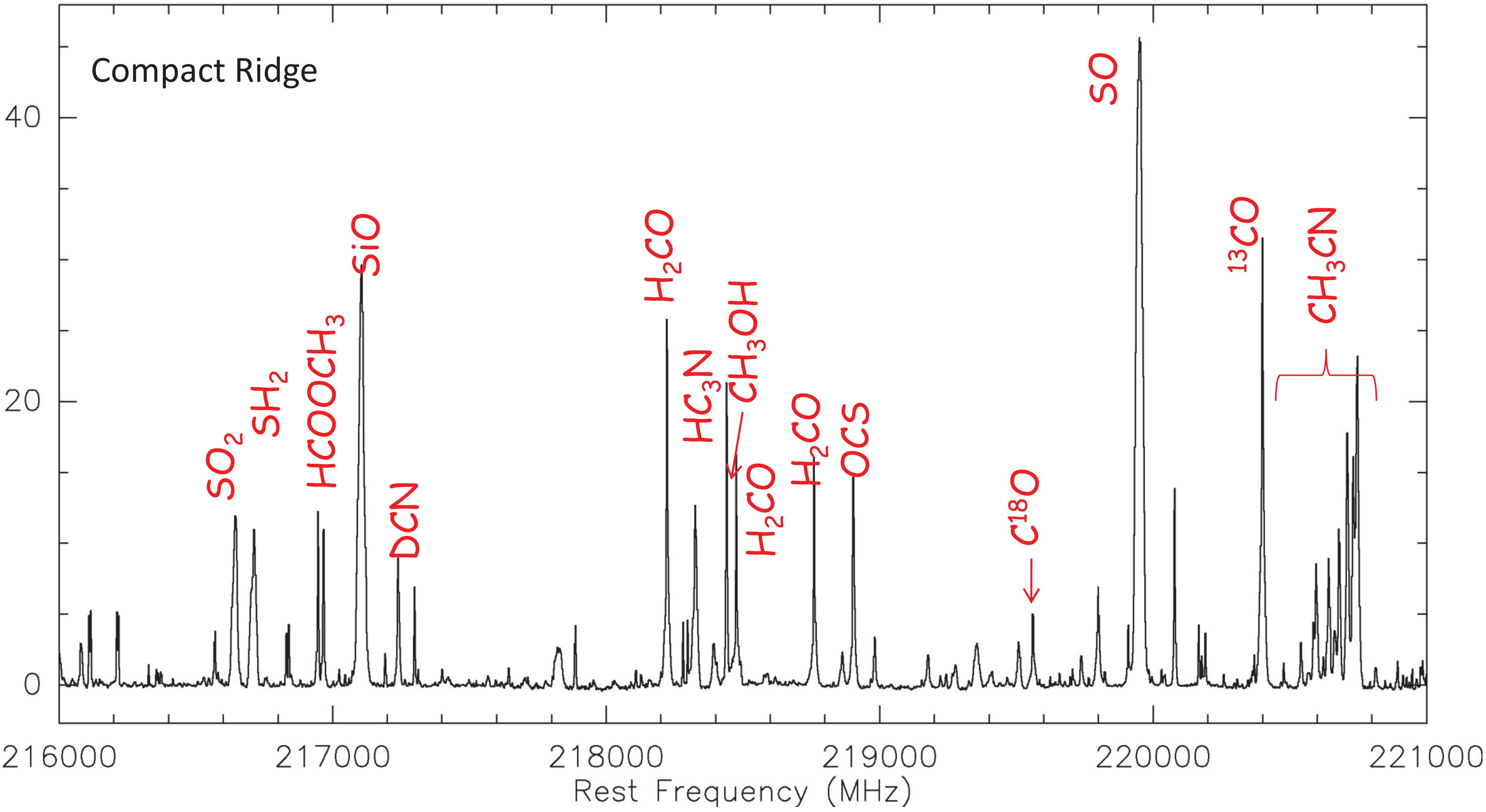

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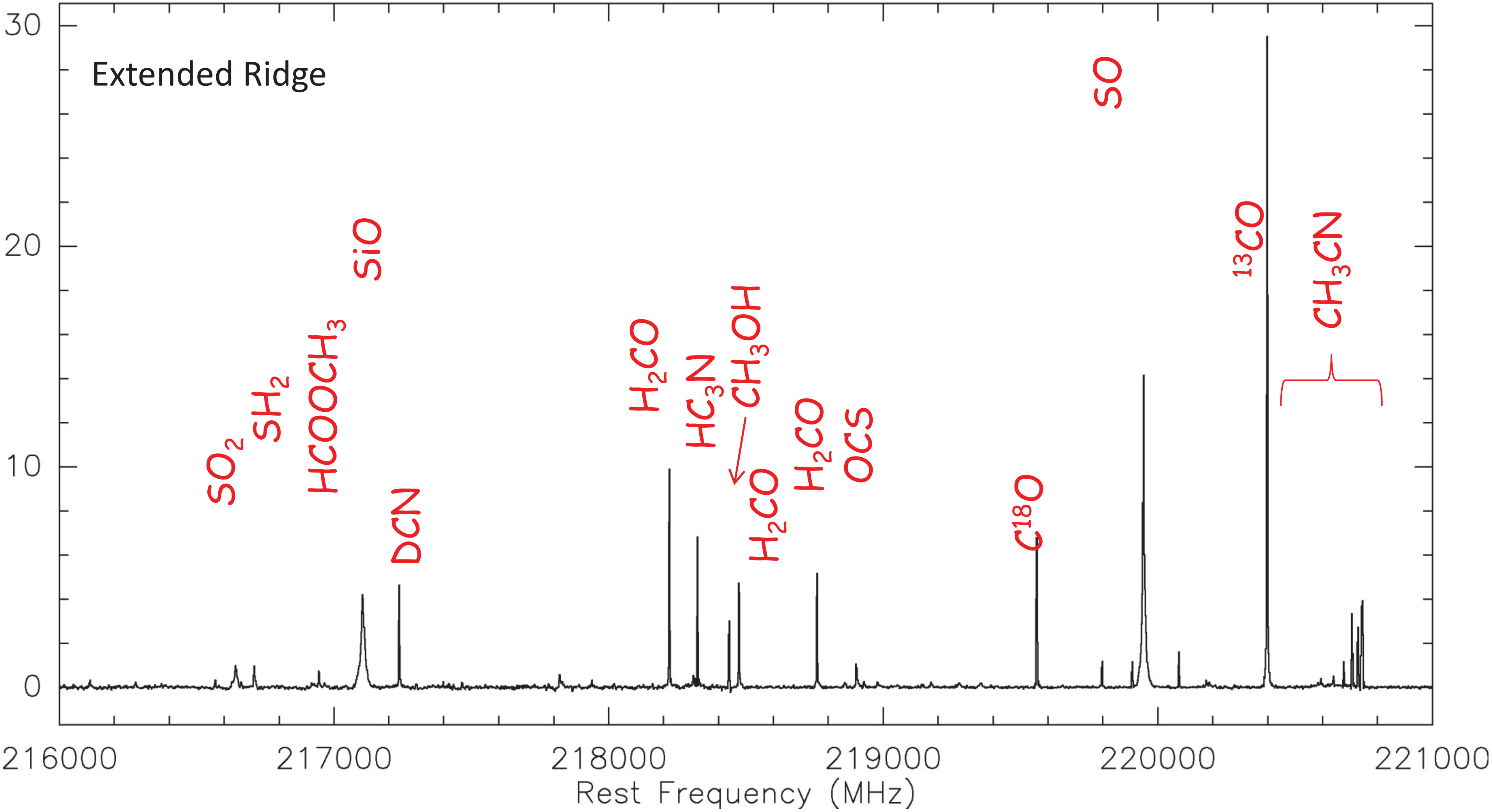

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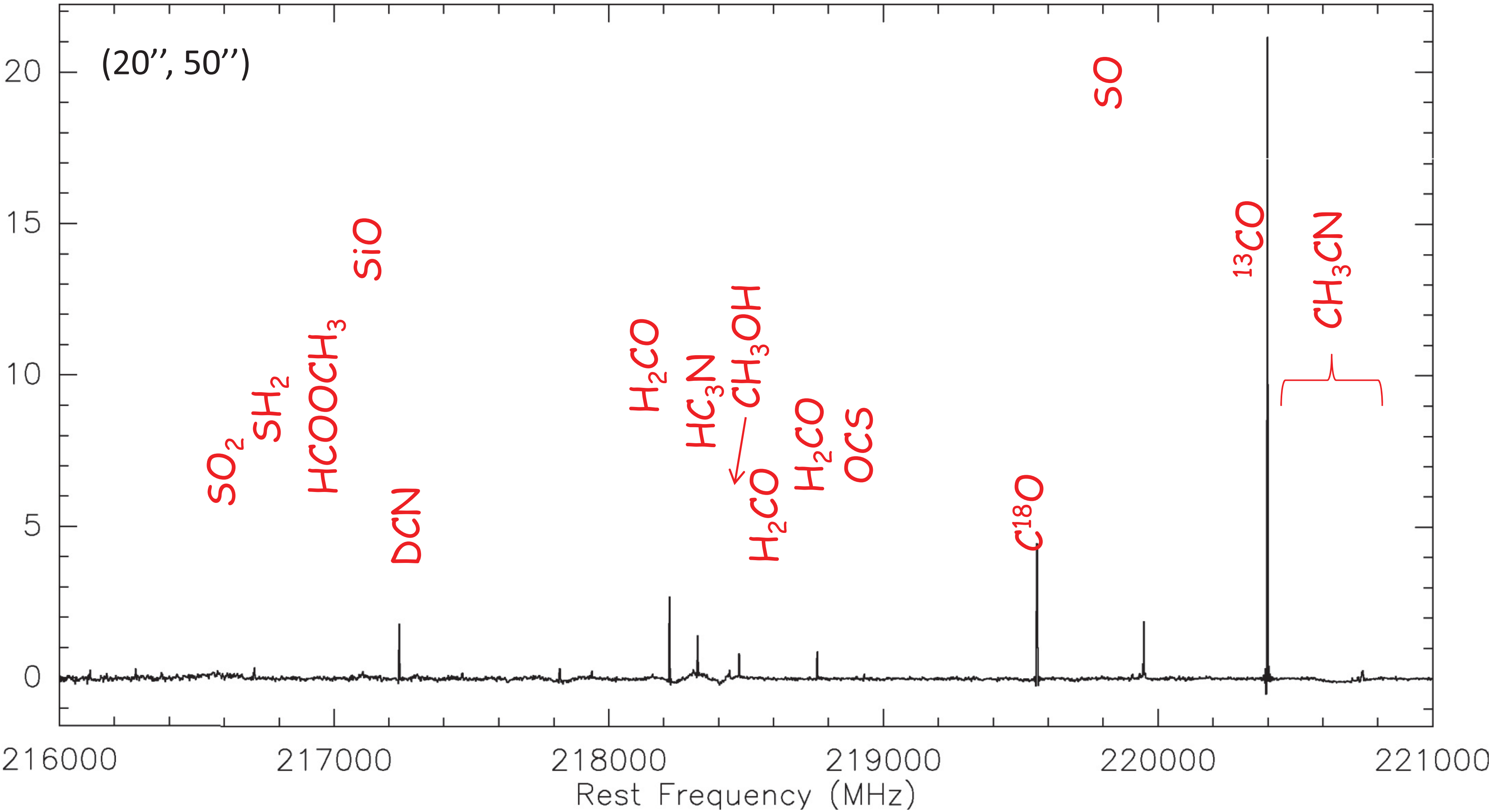
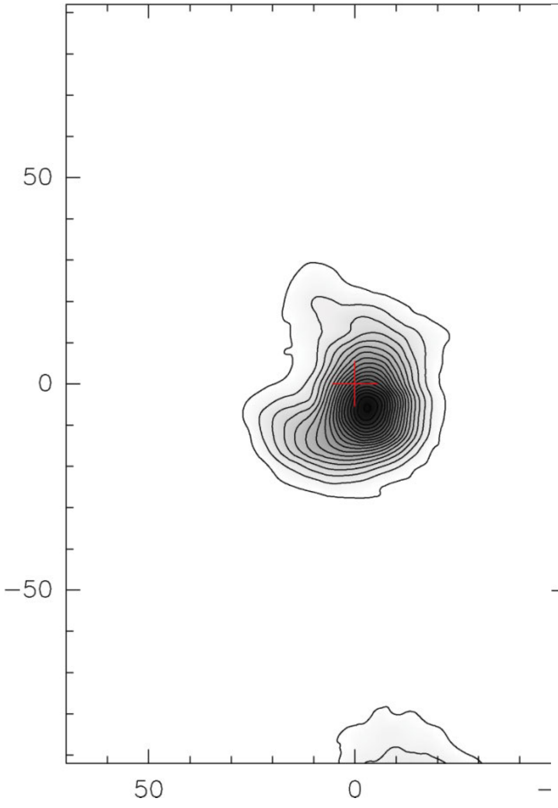
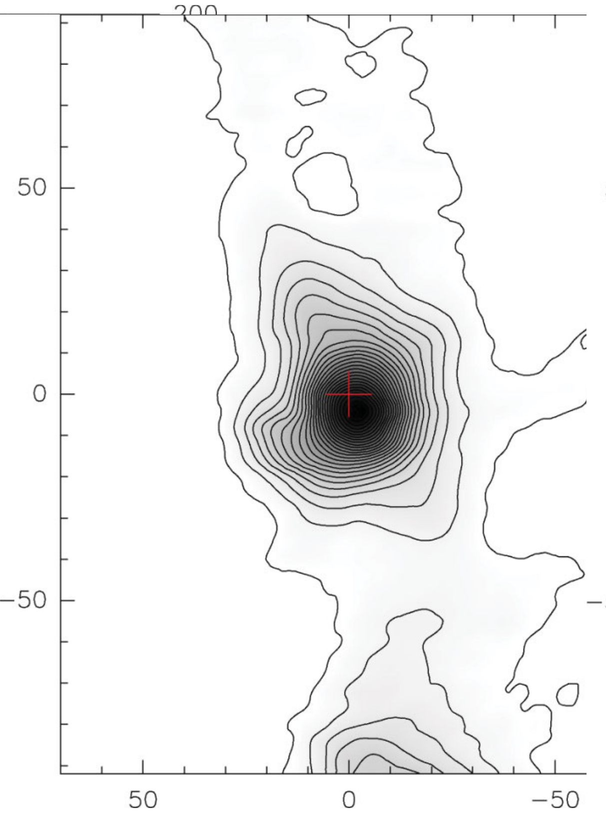


2-D Line Survey

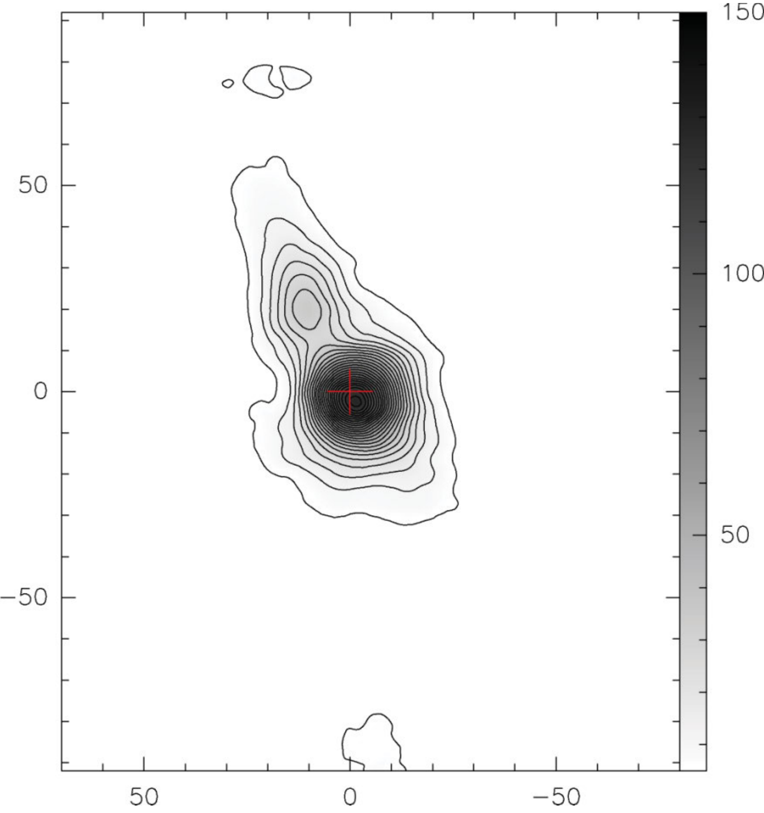
CH_3OH (4_{22}-3_{12} E)



H_2CO (3_{03}-2_{02})



HC_3N (24-23)



THE SPECTROSCOPY PROBLEM

- Weeds
- How to deal with future ALMA data ?
- What we need from laboratory groups ?
  - -isotopologues, vibrationally excited states
- Which direction have we to follow ?

=> high frequency (ALMA) => Physical processes

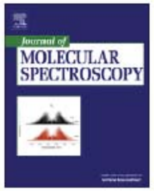
=> Low frequency (GBT, VLA, SKA) => Heavy species ?

Journal of Molecular Spectroscopy 278 (2012) 31–34

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms



Note

LA-MB-FTMW spectroscopy of AlCCH and AgCCH with a discharge source

Carlos Cabezas [a], Santiago Mata [a], Adam M. Daly [a], Agustín Martín [a], José L. Alonso [a,*], José Cernicharo [b,*]

[a] *Grupo de Espectroscopía Molecular (GEM), Edificio Quifima, Área de Química-Física, Laboratorios de Espectroscopia y Bioespectroscopia, Parque Científico UVa, Universidad de Valladolid, 47005 Valladolid, Spain*

[b] *Departamento de Astrofísica, Centro de Astrobiología CAB, CSIC–INTA Ctra. de Torrejón a Ajalvir km 4, 28850 Madrid, Spain*

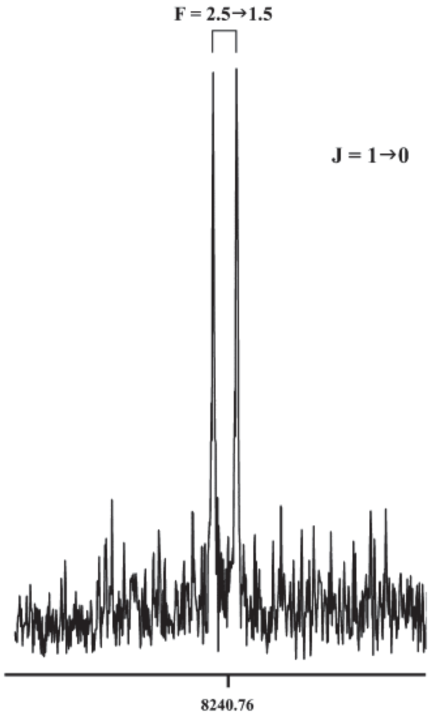


Fig. 1. $F = 2.5 \rightarrow 1.5$ hyperfine component of the $J = 1 \rightarrow 0$ rotational transition of CuCCH main isotopologue measured in this work in the 8.2 GHz frequency region. The line has been registered with 50 shots in the resonance frequency.

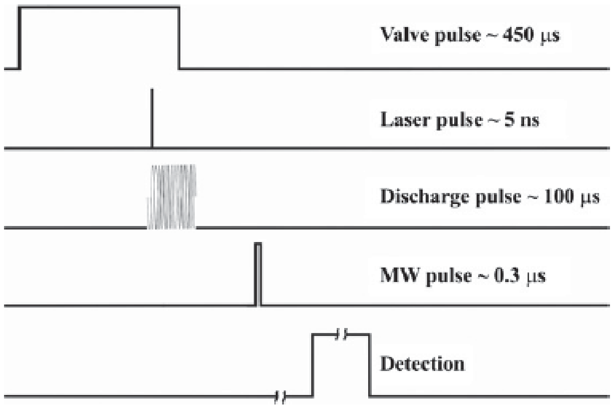


Fig. 3. Time diagram to the LA-MB-FTMW spectrometer for a single experimental cycle in the ablation-discharge configuration. When the system works without dc discharge the time sequence is the same excepting the discharge pulse.

Masers & Lasers : Where Astrophysics becomes pure physics

HCN LASERS

ON THE EXPLANATION OF THE SO-CALLED CN LASER*

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

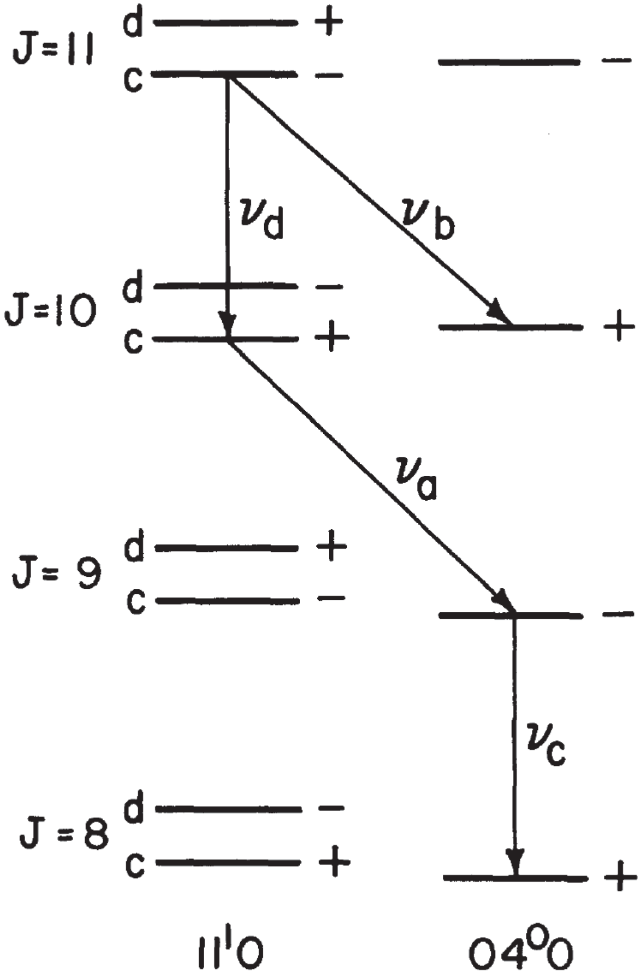
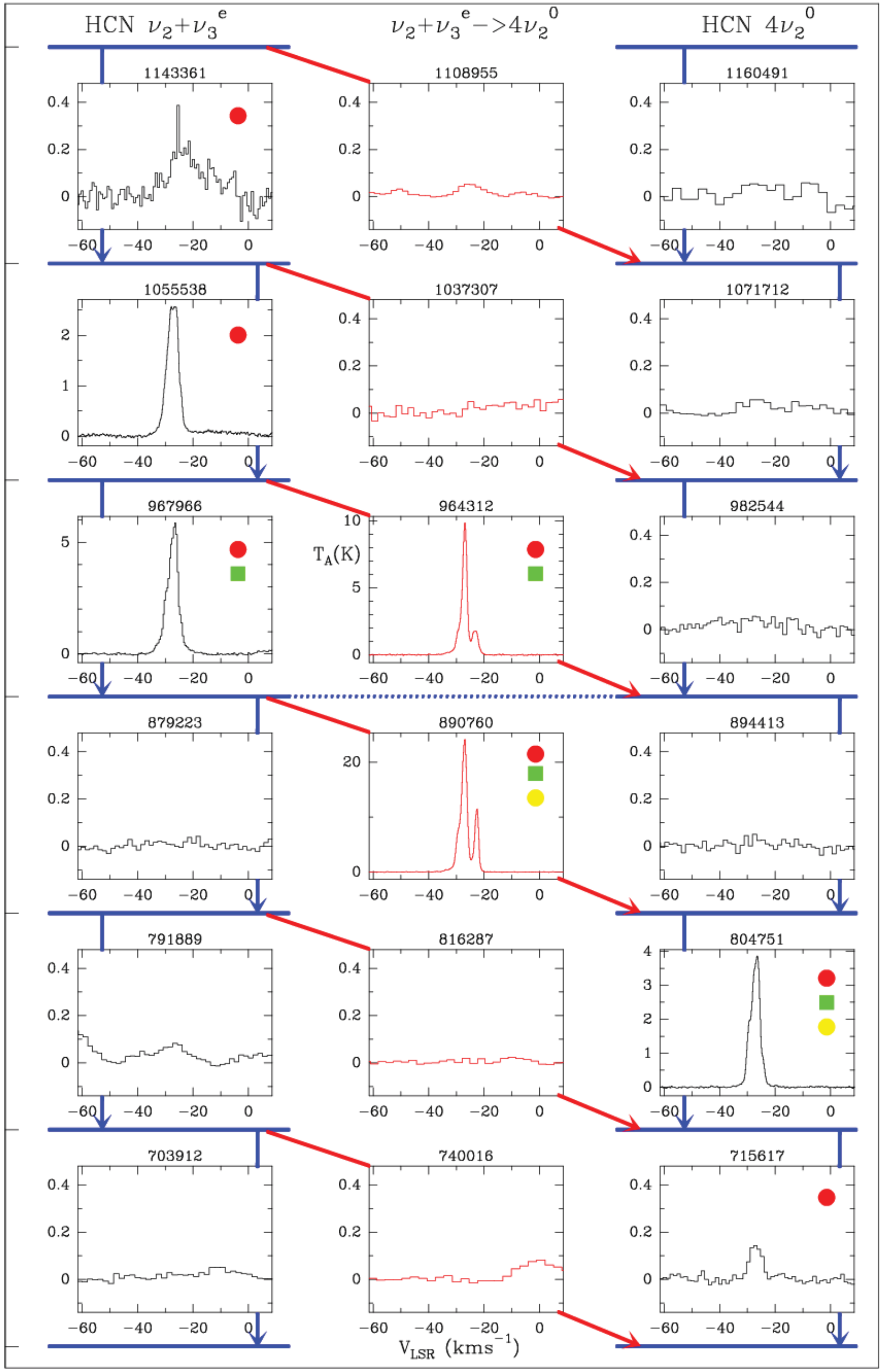
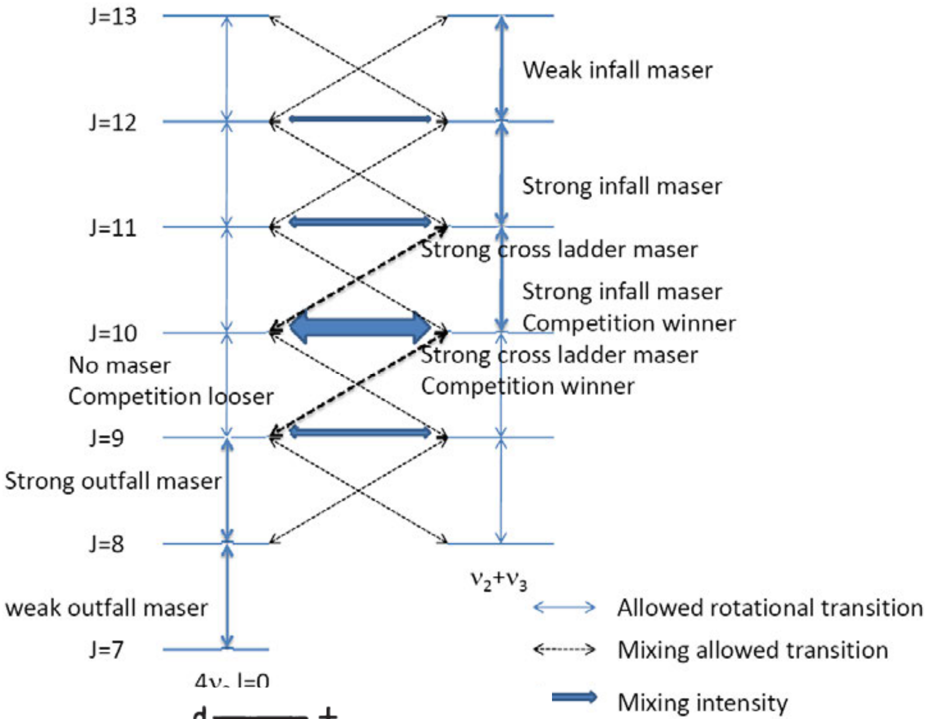


Fig. 1. Pattern of levels in HCN. The 11^10 level is split by *l*-type doubling.





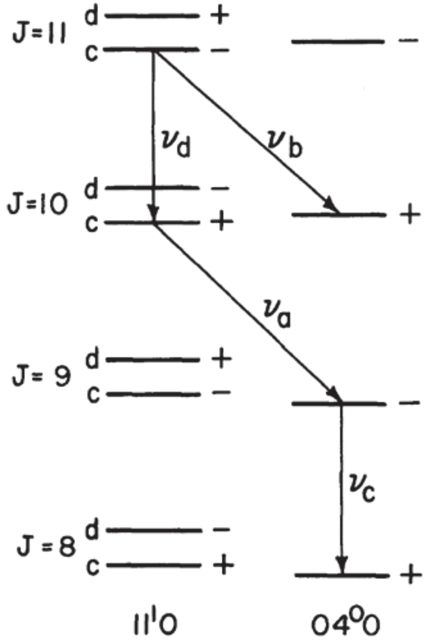


Fig. 1. Pattern of levels in HCN. The 11^10 level is split by l-type doubling.

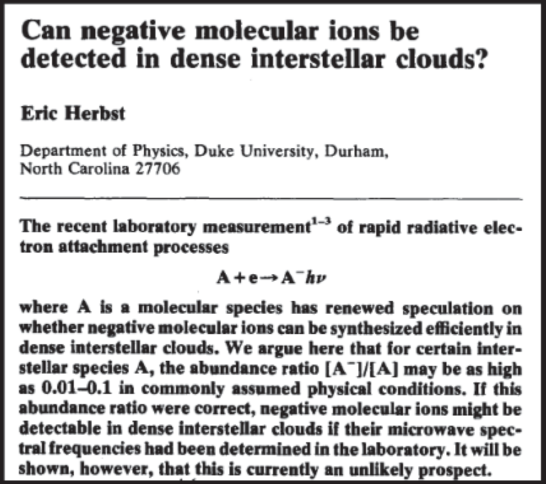
Anions: Where Astrophysics becomes chemical physics

ANIONS

¡ First detection of molecular anions in IRC+10216

C_6H^-, C_4H^-, C_8H^-, C_3N^-, C_5N^-

Thermodynamics The formation of the anion is favoured



Can negative molecular ions be detected in dense interstellar clouds?

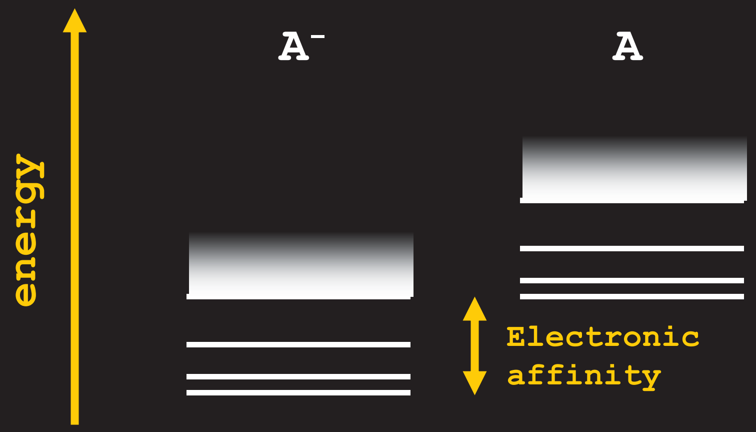
Eric Herbst

Department of Physics, Duke University, Durham, North Carolina 27706

The recent laboratory measurement[1–3] of rapid radiative electron attachment processes

$$A + e \rightarrow A^- h\nu$$

where A is a molecular species has renewed speculation on whether negative molecular ions can be synthesized efficiently in dense interstellar clouds. We argue here that for certain interstellar species A, the abundance ratio [A^-]/[A] may be as high as 0.01–0.1 in commonly assumed physical conditions. If this abundance ratio were correct, negative molecular ions might be detectable in dense interstellar clouds if their microwave spectral frequencies had been determined in the laboratory. It will be shown, however, that this is currently an unlikely prospect.



Kinetics The formation of the anion is NOT favoured

$$A + e^- \Leftrightarrow A^- + h\nu$$

Except for species with a high electronic affinity and a large size

e.g. C_4H, C_6H, C_8H, C_3N, C_5N, …

RESULTS: SPECIFIC RESULTS : ANIONS

History:

2006 C_6H^- in IRC +10216 and TMC-1 (McCarthy et al.)

RESULTS: SPECIFIC RESULTS : ANIONS

History:

2006 C_6H^- in IRC +10216 & TMC-1 (McCarthy et al.)

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

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

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

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

RESULTS: SPECIFIC RESULTS : ANIONS

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

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

2010 CN- in IRC+10216 (Agúndez et al.)

Additional detections:

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

C_4H^- in L1527 (Agúndez et al. 2008)

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

RESULTS: SPECIFIC RESULTS : ANIONS

History:

2006 C_6H^- in IRC +10216 & TMC-1 (McCarthy et al.)

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

2007 C_8H^- in IRC +10216 & TMC-1 (Remijan .)

2008 C_3N^- in IRC +10216 (Th

2008 C_5N^- in I

2)

IRC +10216
Is the only source where all anions have been observed
CN^-, C_4H^-, C_6H^-, C_8H^-, C_3N^-, C_5N^-

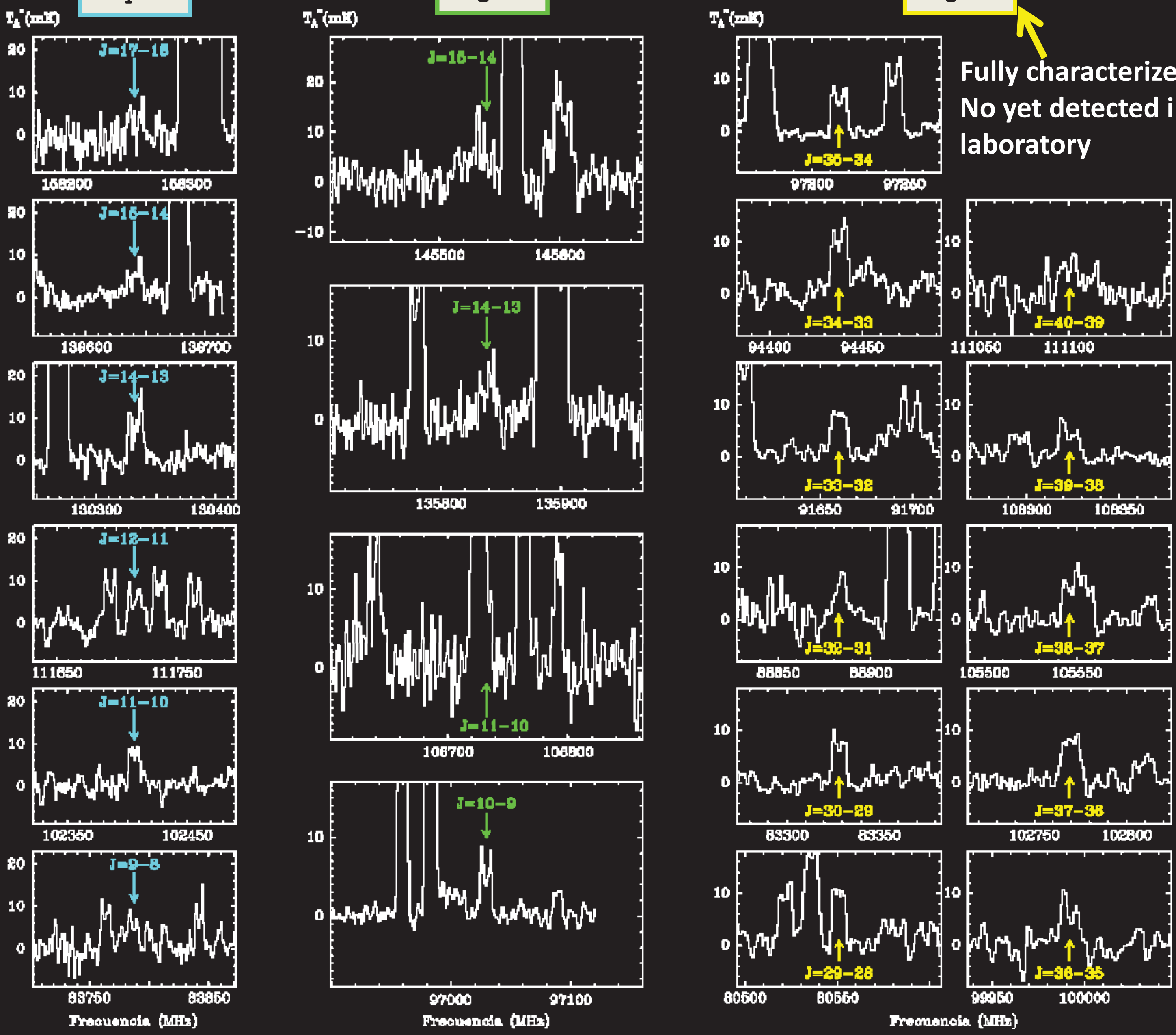
(Sakai et al. 2007)

C_4H^- in L1527 (Agúndez et al. 2008)

C_6H^- in L1544 & L1521F (Gupta et al. 2009)

RESULTS: SPECIFIC RESULTS : ANIONS

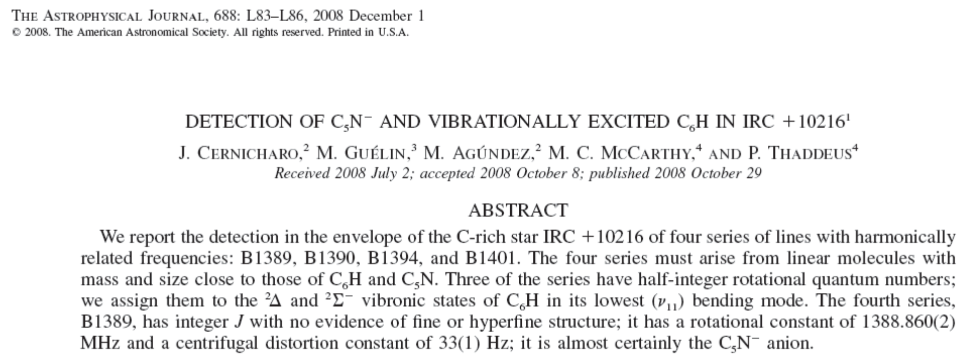
C_4H^- **C_3N^-** **C_5N^-**



Fully characterized in space
No yet detected in the
laboratory

Neutral species	Activation Energy (eV)	**Anion / Neutral (%)**	**rate** * **k_{ra} (astro)** cm^3s^{-1}	rate ** k_{ra} (theor) cm^3s^{-1}
C_2H	3.0	<0.0014	$< 10^{-11}$	$2.0\ 10^{-15}$
C_4H	3.6	0.0074	$4\ 10^{-11}$	$1.1\ 10^{-8}$
C_6H	3.8	6.8	$3\ 10^{-8}$	$6.2\ 10^{-8}$
C_8H	4.0	26.	$1.5\ 10^{-7}$	$6.2\ 10^{-8}$
CN	3.8	0.25	$2\ 10^{-9}$	$1.4\ 10^{-17\&}$
C_3N	4.6	0.42	$3\ 10^{-9}$	$2\ 10^{-10}$ @
C_5N	4.5	58. (?)	$5\ 10^{-7}$ (?)	

- * M. Agundez (PhD thesis 2009); rates scaled to 300 K
- ** Herbst & Osumara 2008, @Petrie & Herbst 1997
- @ Petrie 1996



THE ASTROPHYSICAL JOURNAL, 688: L83–L86, 2008 December 1

DETECTION OF C_5N^- AND VIBRATIONALLY EXCITED C_6H IN IRC +10216[1]

J. CERNICHARO,[2] M. GUÉLIN,[3] M. AGÚNDEZ,[2] M. C. MCCARTHY,[4] AND P. THADDEUS[4]

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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.

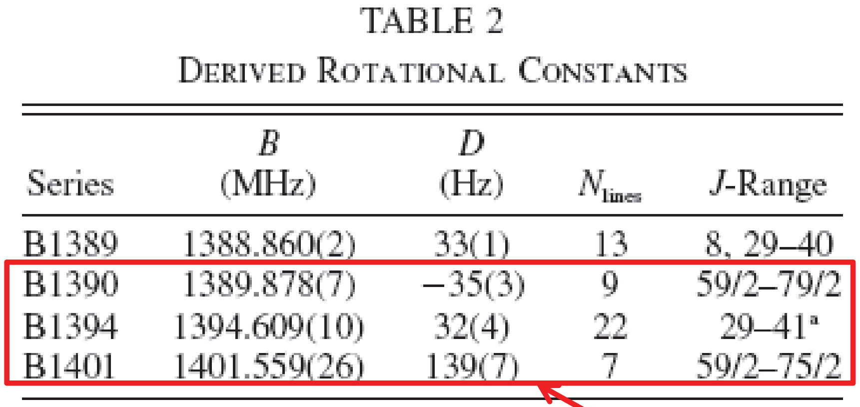

TABLE 2

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

C_6H vib

Identification of C_5N^- based on comparison with ab initio calculations by Botschwina & Oswald (2008)

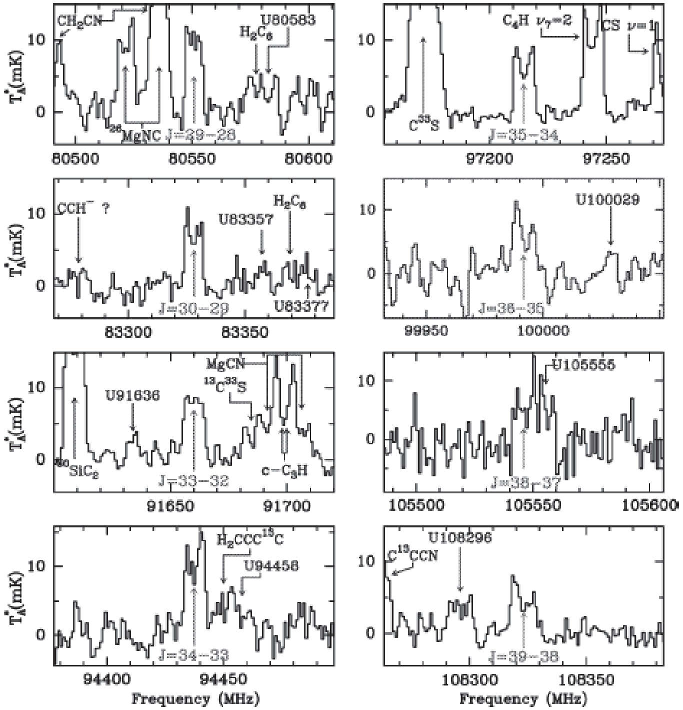

FIG. 1.—Spectra of IRC +10216 observed with the IRAM 30 m telescope, showing lines from the B1389 series assigned here to C_5N^-. The marginal weak line U83278 is worth noting, because it is within 0.1 MHz of the J = 1–0 line of CCH^- (see text). [*See the electronic edition of the Journal for a color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

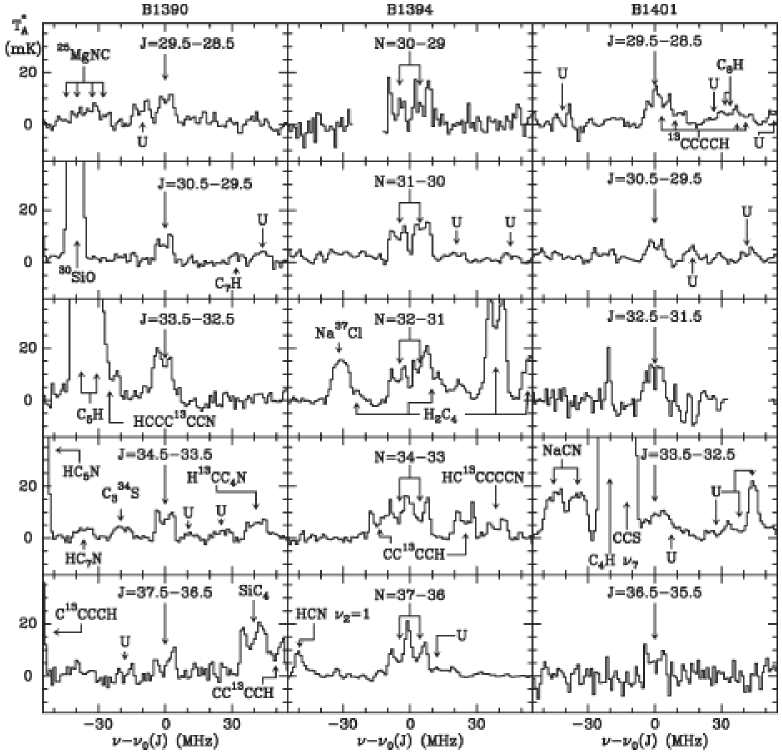

FIG. 2.—Spectra of IRC +10216 observed with the IRAM 30 m telescope showing selected lines pertaining to the series B1390, B1394, and B1401. These three series of lines are assigned to vibronic states of the ν_{11} bending mode of C_6H.

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Astronomy & Astrophysics

LETTER TO THE EDITOR

Astronomical identification of CN^-, the smallest observed molecular anion[★,★★]

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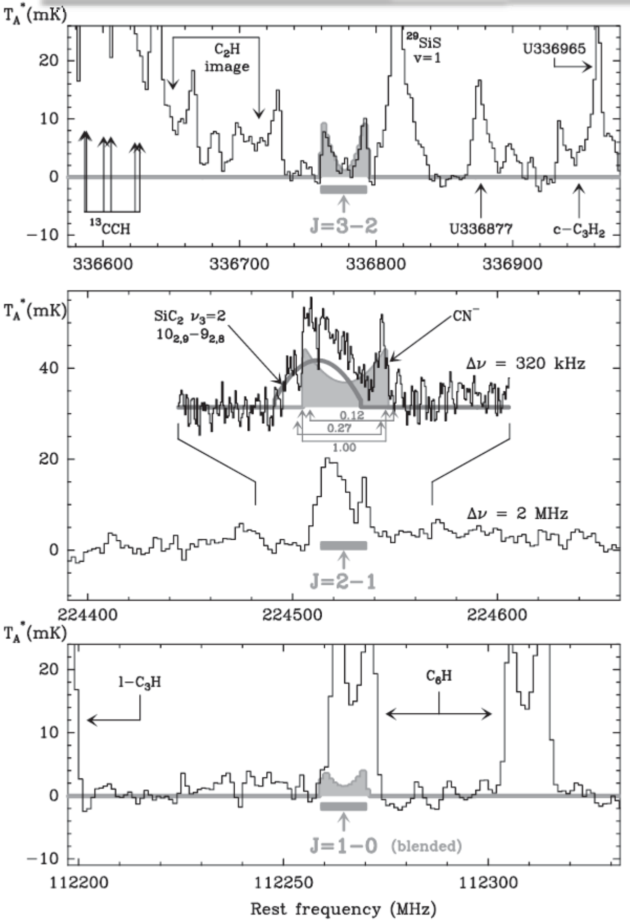
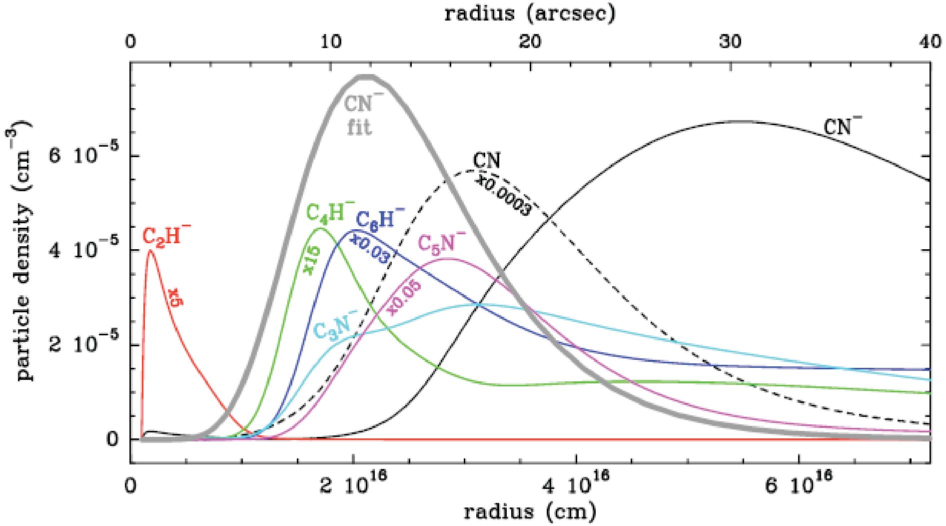
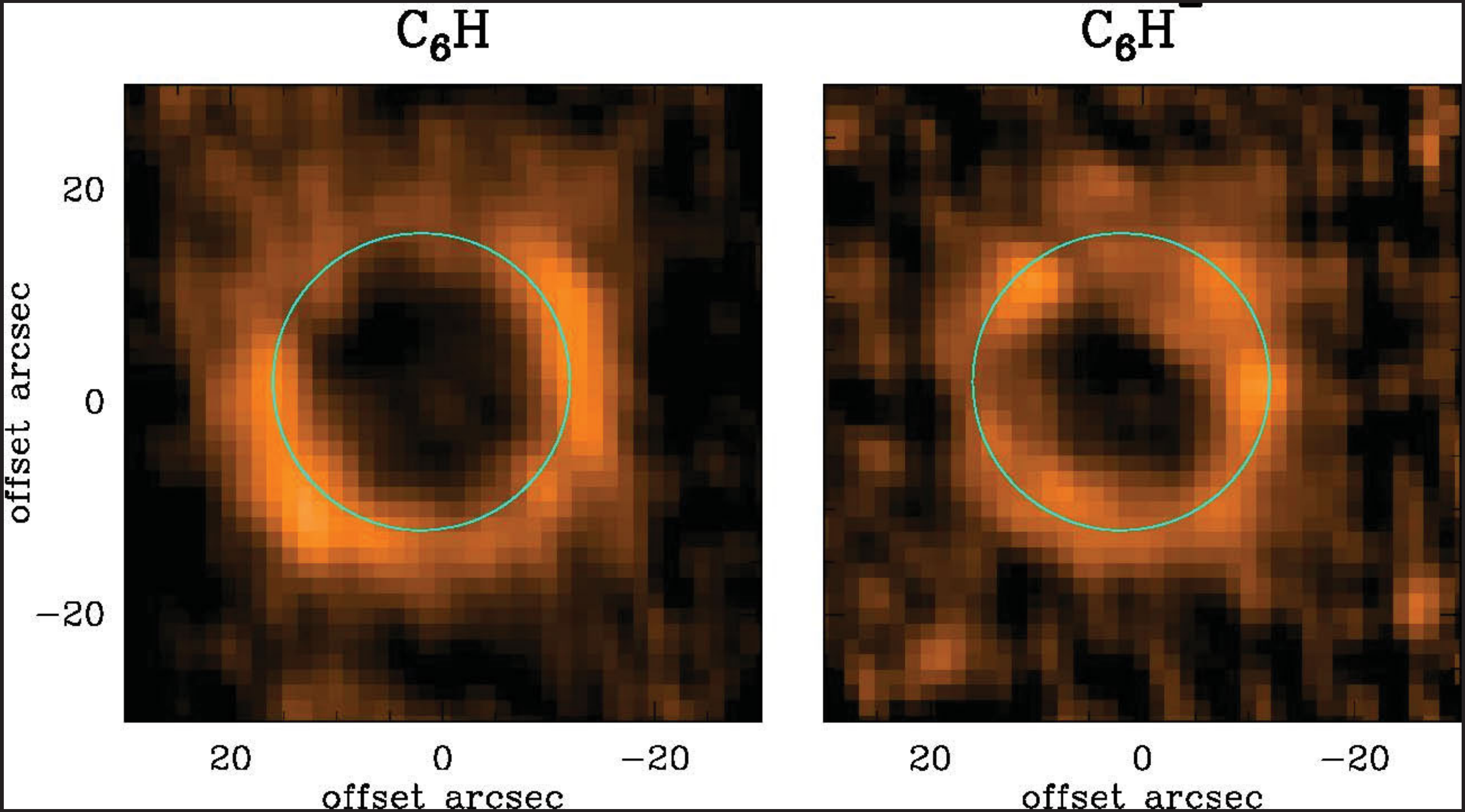


Table 1. Observed line parameters of CN^-.

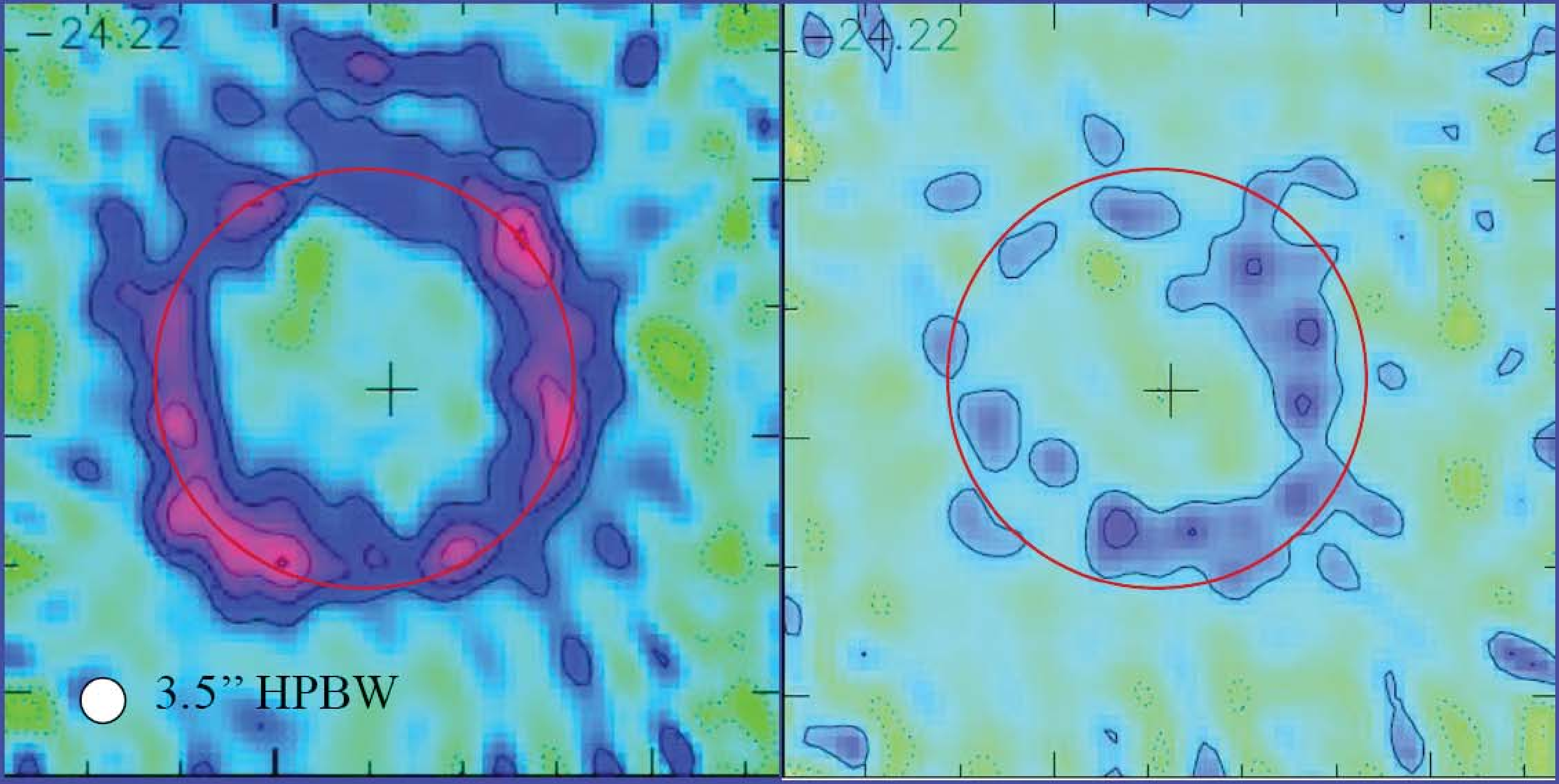
Transition	ν_0[a] (MHz)	$\nu_{\rm obs}$ (MHz)	$v_{\rm exp}$[b] (km s^{-1})	$\int T_A^* dv$ (K km s^{-1})
J = 1–0	112 264.8	112 264.8[c]	14.5[c]	~0.07(3)[d]
J = 2–1	224 525.1	224 525.4(5)	14.5[c]	0.23(7)[e]
J = 3–2	336 776.4	336 777.0(12)	15.0(10)	0.13(2)

Notes. Number in parentheses are 1σ uncertainties in units of the last digits. [(a)] Frequencies derived from the rotational constants reported by Amano (2008). [(b)] $v_{\rm exp}$ is the half width at zero level. [(c)] Fixed value. [(d)] Highly uncertain estimate. Line severely blended with a strong C_6H line. [(e)] Line blended with a SiC_2 ν_3 = 2 line.




C_6H
C_6H^-
20
0
−20
offset arcsec
20
0
−20
offset arcsec
20
0
−20
offset arcsec

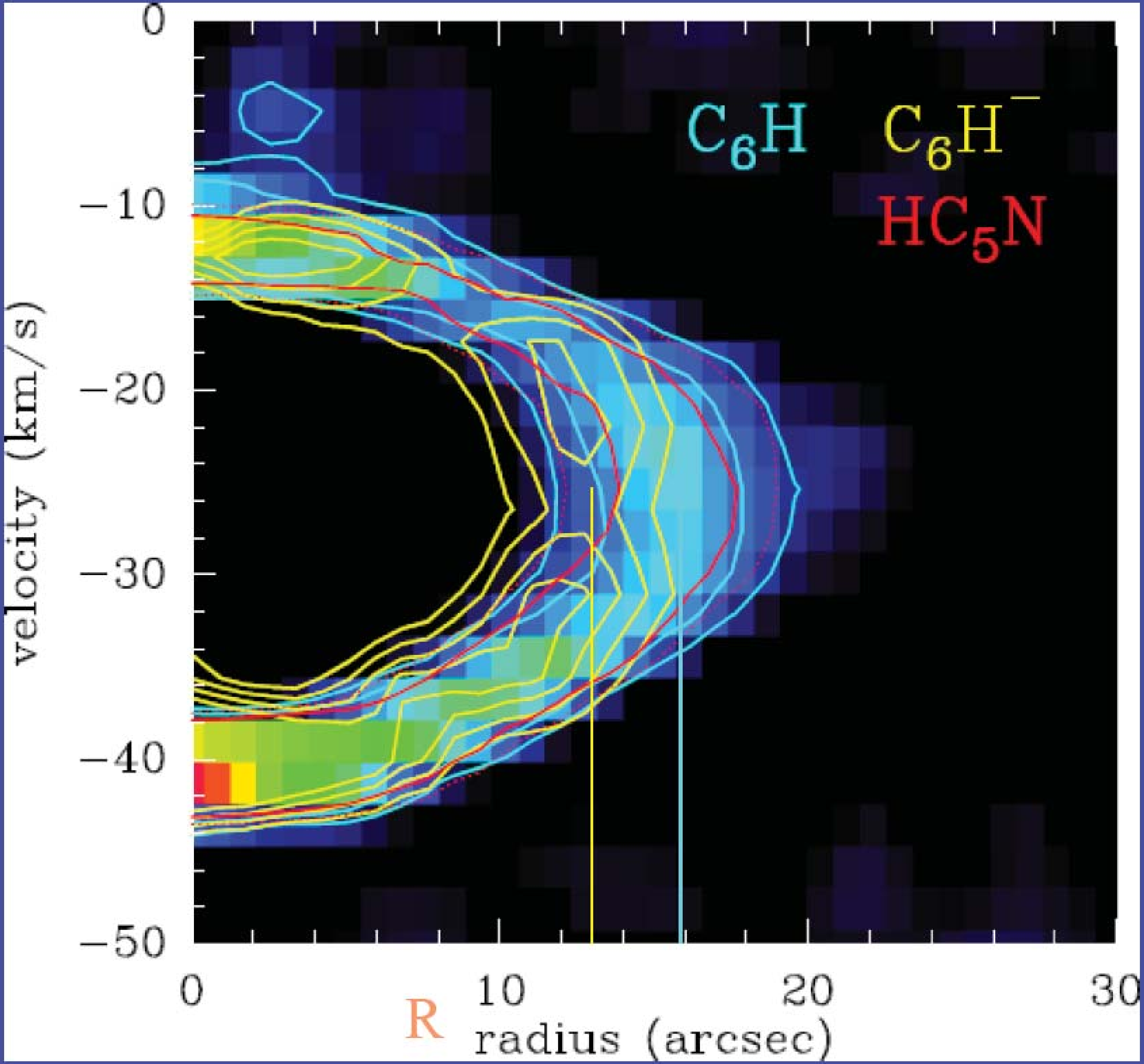
New high angular&spectral resolution map of anions *(PdBI, Guélin et al.)*



C_6H C_6H^-

M. Guélin et al., IAU Symp 280

Average intensity in concentric rings of radius R, for each velocity channel



First Conclusion:

C_6H^- and C_5N^- appear at smaller radii than predicted

C_4H^- appears further out than predicted

Second Conclusion:

The observed abundances of C_4H^- and CN^- disagree with predictions based on direct electron attachment on C_4H and CN

Other production mechanism for CN^- and other anions ?

$CN + e \Rightarrow CN^-$
$MgNC + e \Rightarrow CN^-$
$C_n^- + N \Rightarrow CN^- + C_{n-1}$
Dust grains

THE FINAL PRODUCT OF A DETAILED STUDY + GOOD INPUT FROM LABORATORY

- New Molecules
- Abundances for all species
- Isotopic abundances (nuclear evolution)
- Clear differentation of the different layers of the CSE
- Chemistry of exotic species (anions)
- A fine study of the missing reactions of the actual chemical networks

ALMA will surprise us in all fields. New experiments will be needed, new physical and chemical processes will be unveiled !!!