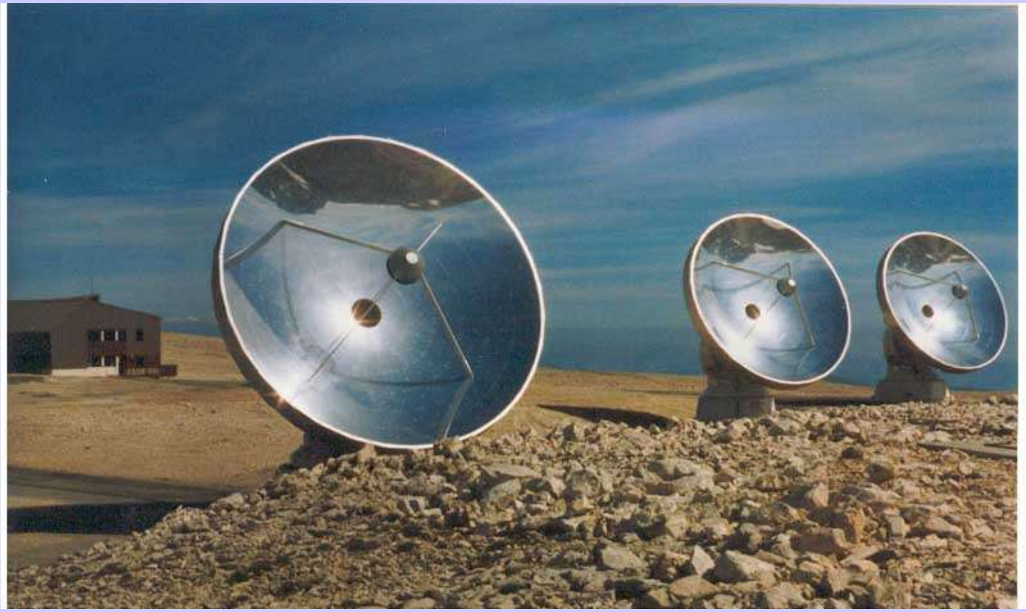
# *Hunting for Molecules*



The IRAM telescopes

# *First spectral features in the interstellar medium*

- 1904 Hartmann "fixed line" Ca K interstellar line
- 1910s Barnard dark clouds → extinction and scattering from dust grains
- 1920s Statistics on atomic spectral lines (Na, Ca,...)
- Eddington (1937) What about molecules ?
- Merril (1936) New bands :λ5780, λ5797, λ6278, λ6284 The Diffuse Interstellar Bands, attributed to molecules by Russel (1935) Carrier still unknown !!
- Dunham (1937) weak feature λ4300
- CH Identification (Swings & Rosenfeld, 1937)
- CN (Mc Kellar 1940, Adams 1941), $CH^+$ (Douglas and Herzberg 1941)

# *First explanations, predictions*

1950s Kramers & ter Haar, Bates & Spitzer

- Formation and destruction processes (low density, two body reactions, radiative association)
- First estimate of gas density ($10^{3}$ $cm^{-3}$)
- Suggestion of grain evaporation ($CH_4$)

Predictions that solely diatomic molecule will be found

CN excitation temperature 2.3K (Mc Kellar 41)

→ Estimate of the CMB temperature

- 1950s new field of Radioastronomy→ new possibilities for molecules

# *First explanations, predictions*

1955 Townes lists possible interstellar molecules

| Molecule | Found or not | Comment |
|---|---|---|
| CaH | No | Ca depleted |
| CO | Yes | 1970 |
| $CO^+$ | Yes | 1993 |
| CS | Yes | 1971 |
| NO | Yes | 1978 |
| $H_2O$ | Yes | 1969(maser), space |
| $N_2O$ | No | Earth Atmosphere |
| HCN | Yes | 1971 |
| $CH_2$ | Yes | 1989, space 2005 |
| $NH_2$ | Yes | 1992 |
| $NH_3$ | Yes | 1968 |
| $O_3$ | No | Earth Atmosphere |

# *Interstellar and Circumstellar molecules today*

Hydrogen

| | | | | |
|---|---|---|---|---|
| $H_2$ | $HD$ | $H_3^+$ | $H_2D^+$ | $D_2H^+$ |

Carbon chains and cycles

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $CH$ | $CH^+$ | $C_2$ | $CH_2$ | $CCH$ | $C_3$ | $CH_3$ | $C_2H_2$ | $l-C_3H$ | $c-C_3H$ |
| $CH_4$ | $C_4$ | $c-C_3H_2$ | $l-C_3H_2$ | $C_4H$ | $C_5$ | $C_2H_4$ | $C_5H$ | $l-H_2C_4$ | $HC_4H$ |
| $CH_3CCH$ | $C_6H$ | $C_6H_2$ | $HC_6H$ | $C_7H$ | $CH_3C_4H$ | $C_8H$ | $C_6H_6$ | | |

Species with O, and/or H and C

| | | | | | | |
|---|---|---|---|---|---|---|
| $OH$ | $H_2O$ | $O_2$? | $CO$ | $CO^+$ | $HCO^+$ | $HOC^+$ |
| $HCO$ | $C_2O$ | $CO_2$ | $H_3O^+$ | $HOCO^+$ | $H_2CO$ | $C_3O$ |
| $HCOOH$ | $CH_2CO$ | $H_2COH^+$ | $CH_3OH$ | $CH_2CHOH$ | $HC_2CHO$ | $C_5O$ |
| $CH_3CHO$ | $c-C_2H_4O$ | $CH_3OCHO$ | $CH_2OHCHO$ | $CH_3COOH$ | $CH_2CHOH$ | $(CH_3)_2O$ |
| $CH_3CH_2OH$ | $CH_2CHCHO$ | $CH_3CH_2CHO$ | $HOCH_2CH_2OH$ | $(CH_3)_2CO$ | $CO(CH_2OH)_2$ | |

Species with N, and/or H and C

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $N_2$ | $NH$ | $CN$ | $NH_2$ | $HCN$ | $HNC$ | $N_2H^+$ | $NH_3$ | $HCNH^+$ |
| $H_2CN$ | $HCCN$ | $C_3N$ | $CH_2CN$ | $CH_2NH$ | $HC_3N$ | $HC_2NC$ | $NH_2CN$ | $C_3NH$ |
| $HC_4N$ | $CH_3CN$ | $CH_3NC$ | $HC_3NH^+$ | $C_5N$ | $CH_3NH_2$ | $C_2H_3CN$ | $HC_5N$ | $CH_3C_3N$ |
| $C_2H_5CN$ | $HC_7N$ | $CH_3C_5N$ ? | $HC_9N$ | $HC_{11}N$ | | | | |

Species with N, O and/or H and C

| | | | | |
|---|---|---|---|---|
| $NO$ | $HNO$ | $N_2O$ | $HNCO$ | $NH_2CHO$ |

Species with S, Si and other elements

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SH$ | $CS$ | $SO$ | $SO^+$ | $NS$ | $SiH$ | $SiC$ | $SiN$ | $SiO$ | $SiS$ |
| $HCl$ | $NaCl$ | $AlCl$ | $KCl$ | $HF$ | $AlF$ | $CP$ | $PN$ | $H_2S$ | $C_2S$ |
| $SO_2$ | $OCS$ | $HCS^+$ | $c-SiC_2$ | $SiCN$ | $NaCN$ | $MgCN$ | $MgNC$ | $H_2CS$ | $HNCS$ |
| $C_3S$ | $c-SiC_3$ | $SiH_4$ | $SiC_4$ | $CH_3SH$ | $C_5S$ | $FeO$ | $AlNC$ | $SiNC$ | |

Deuterated species

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $HDO$ | | $CCD$ | $DCO^+$ | $DCN$ | $DNC$ | $N_2D^+$ | $NH_2D$ | $ND_2H$ | $ND_3$ |
| $HDCO$ | | $D_2CO$ | $HDS$ | $DC_3N$ | $DC_5N$ | $C_4D$ | $CH_2DCCH$ | $CH_3CCD$ | |
| $HDCS$ | $CH_2DCN$ | $D_2S$ | $CH_2DOH$ | $CD_2HOH$ | $CD_3HOH$ | $CH_3OD$ | $c-C_3HD$ | $HDCS$ | $D_2CS$ |

**Molecular ions**, CSE, ISM & CSE, galaxies

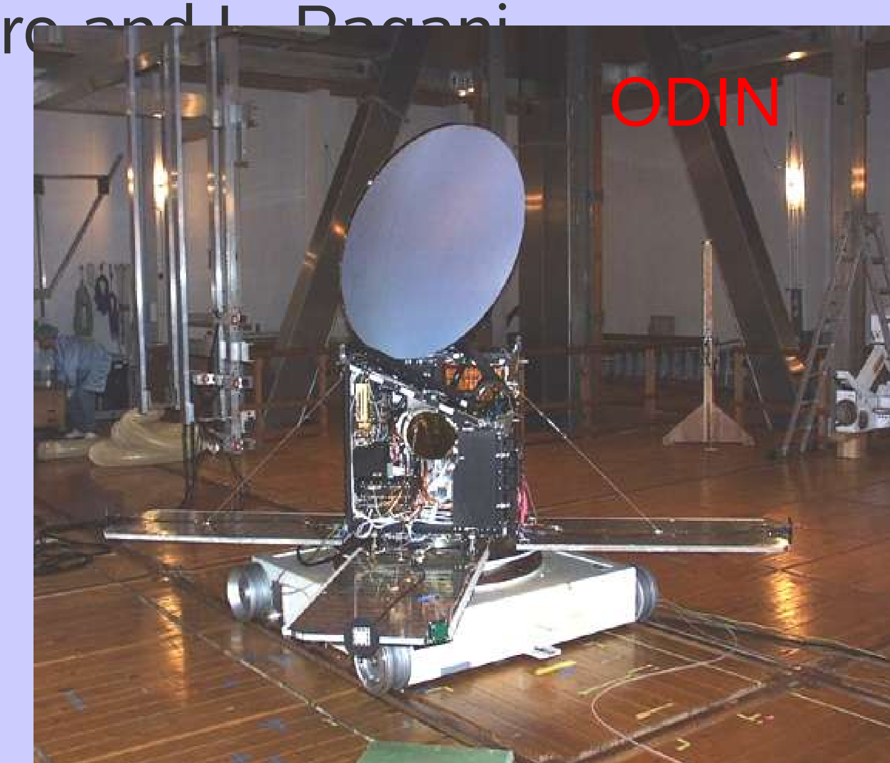
# *Lessons from the first years*

- Advanced instrumentation → high resolution & high sensitivity spectrometers, large telescopes
- Deep search , no a priori against new ideas
- Tight coupling with physics → line identification, chemistry, ...

- 3 types of “hunt for molecules” :
    - Deep search, no a priori → “line survey”
    - Dedicated search based on chemical reason-ing (families e.g. cyanopolyynes)
    - Dedicated search, based on chemical model + spectroscopy (e.g; $C_2$, $H_2D^+$, $CF^+$)

# *Water and the Oxygen chemistry*

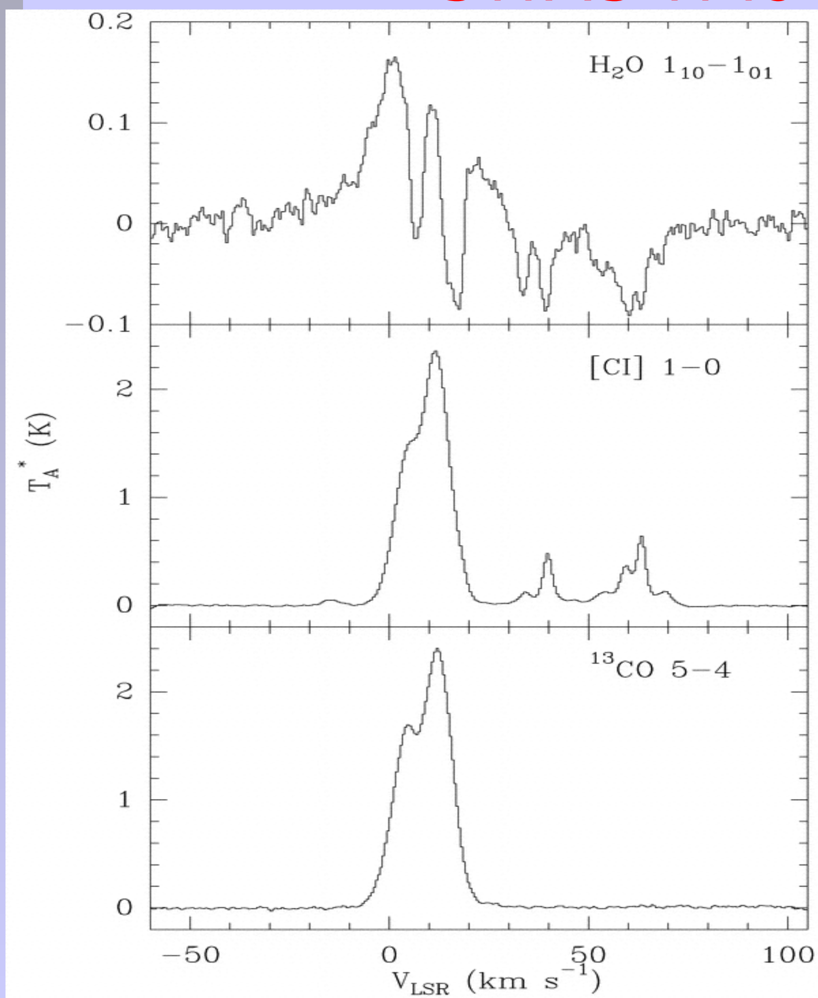
- O chemistry, difficult to study from ground, dedicated space missions for $H_2O$, $O_2$ . $H_2O$ main grain mantle constituant.
- See talks by J. Cernicharo and L. Pagani.

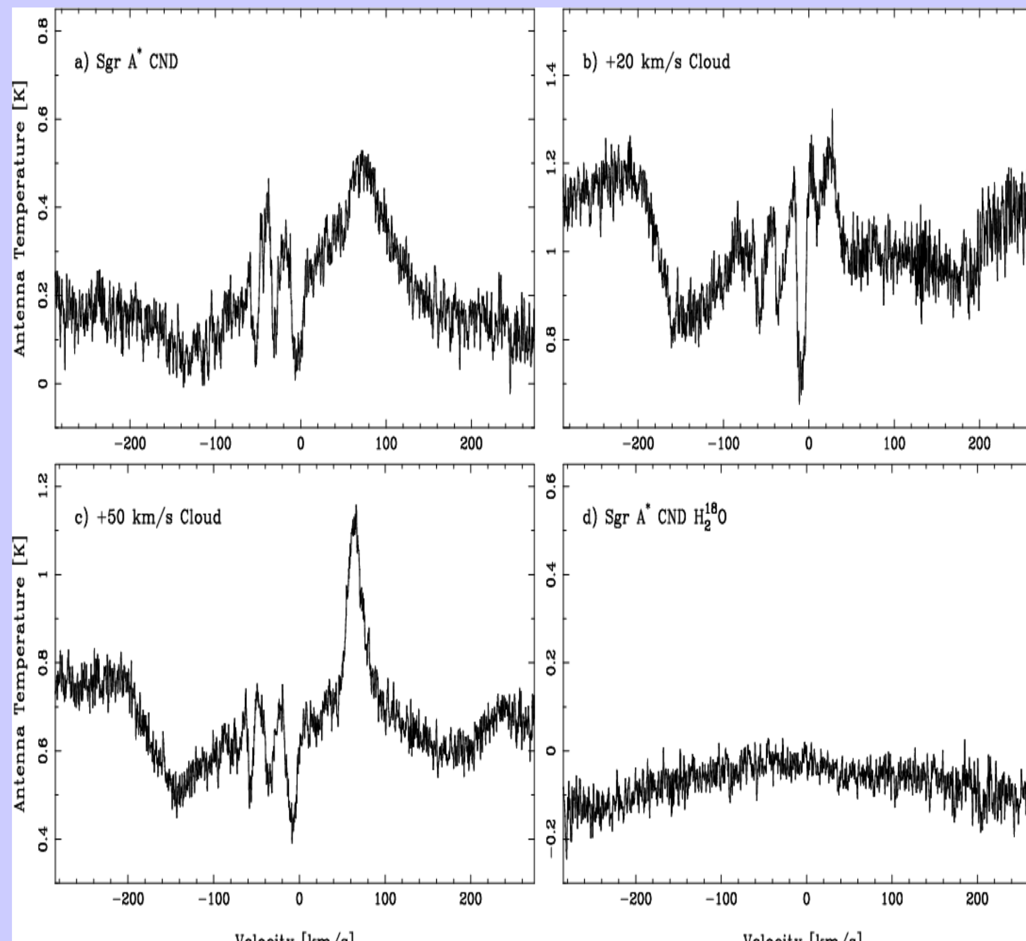
# *Water and the Oxygen chemistry*

Prominent absorption for the $H_2O$ submillimeter ground state lines

SWAS W49




ODIN
Galactic Center



# *Deuterium chemistry*

- 1970s Molecular ions are recognized as key species for ISM chemistry
- Detection of $DCO^+$, DCN, $N_2D^+$ , ..

Main D fractionation reactions :

$$H_3^+ + HD \rightarrow H_2D^+ + H_2$$
$$HD_2^+ + HD \rightarrow D_2H^+ + H_2$$
$$D_2H^+ HD \rightarrow D_3^+ + H_2$$
$$CH_3^+ + HD \rightarrow CH_2D^+ + H_2 , \ldots$$

$\rightarrow$ Search for $H_3^+$ and $H_2D^+$

# *Looking for $H_2D^+$*

Phillips et al. 1985
Yes ?

L46 PHILLIPS *ET AL.* Vol. 294

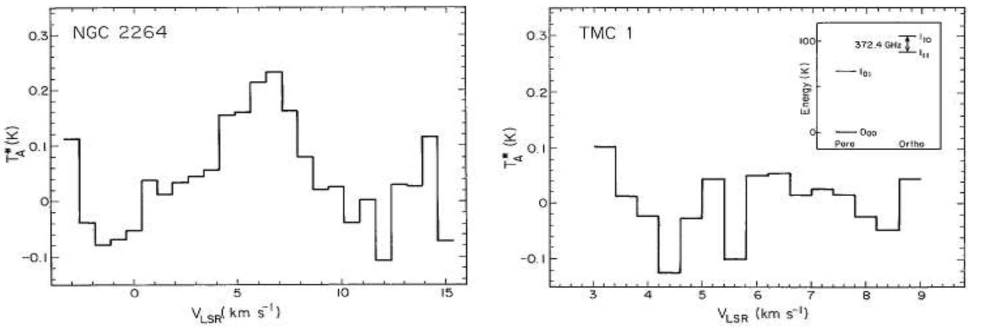



FIG. 1a FIG. 1b

FIG. 1.—(*a*) A spectrum taken in the vicinity of the $H_2D^+$ line, toward the molecular cloud NGC 2264. The velocity scale has been established using a rest frequency of 372.4213 GHz. Individual channels are spaced by 0.75 km s$^{-1}$. (*b*) A spectrum taken in the vicinity of the $H_2D^+$ line, toward TMC-1. Channels are spaced by 0.4 km s$^{-1}$. Inset is the energy-level diagram for the lower lying $H_2D^+$ transitions.

Pagani et al. 1992
No
also Boreiko et al. 1993

475

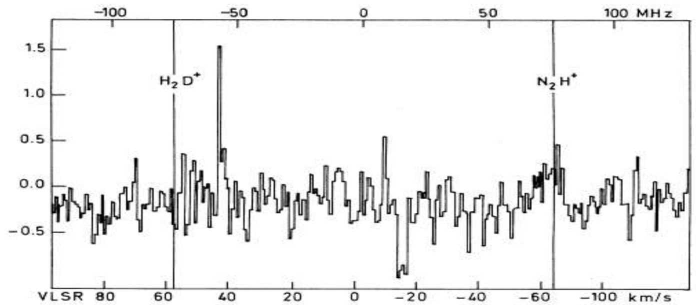



**Fig. 2.** Spectrum taken toward NGC 6334. The $N_2H^+$ ($J$:4→3) line is detected (0.4 K). Vertical axis is antenna temperature. The horizontal axis is only relative to the center of the backend. Actual positions of the lines in the backend are indicated by the vertical lines

# *Looking for $H_2D^+$- 2 - from the ground*

Van Dishoeck et al., 1992
No

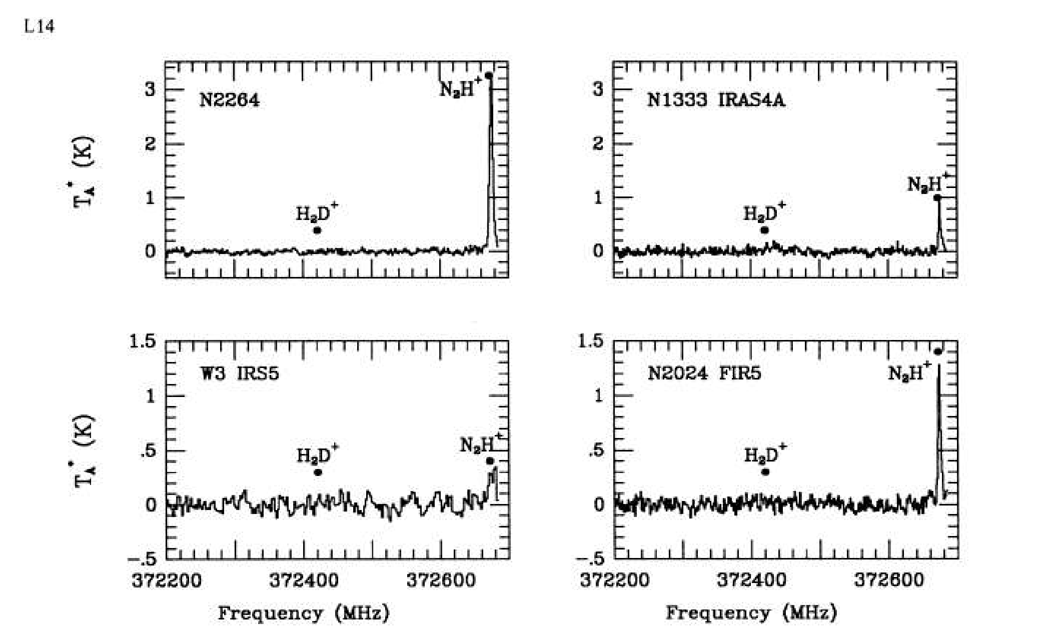
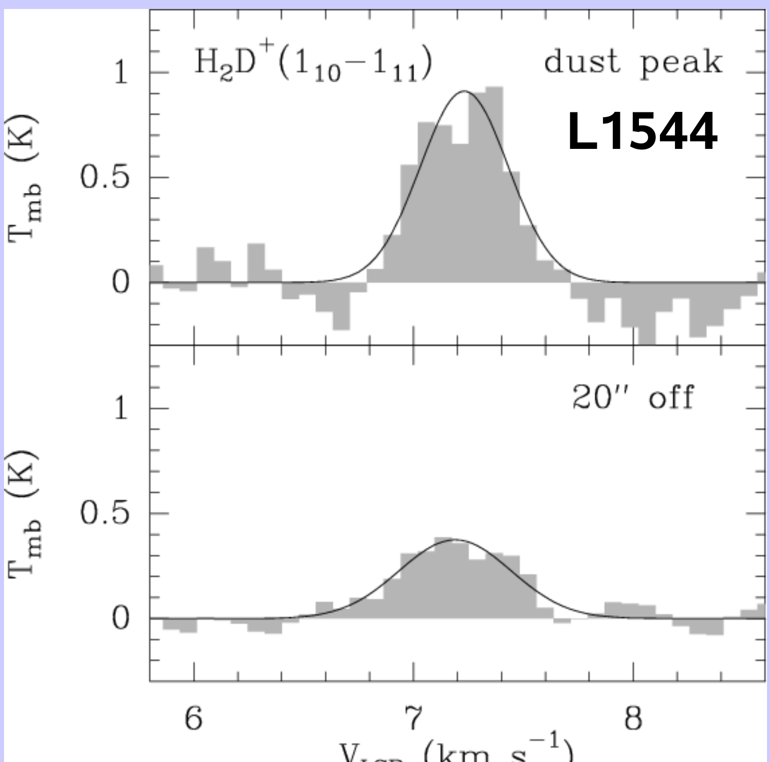


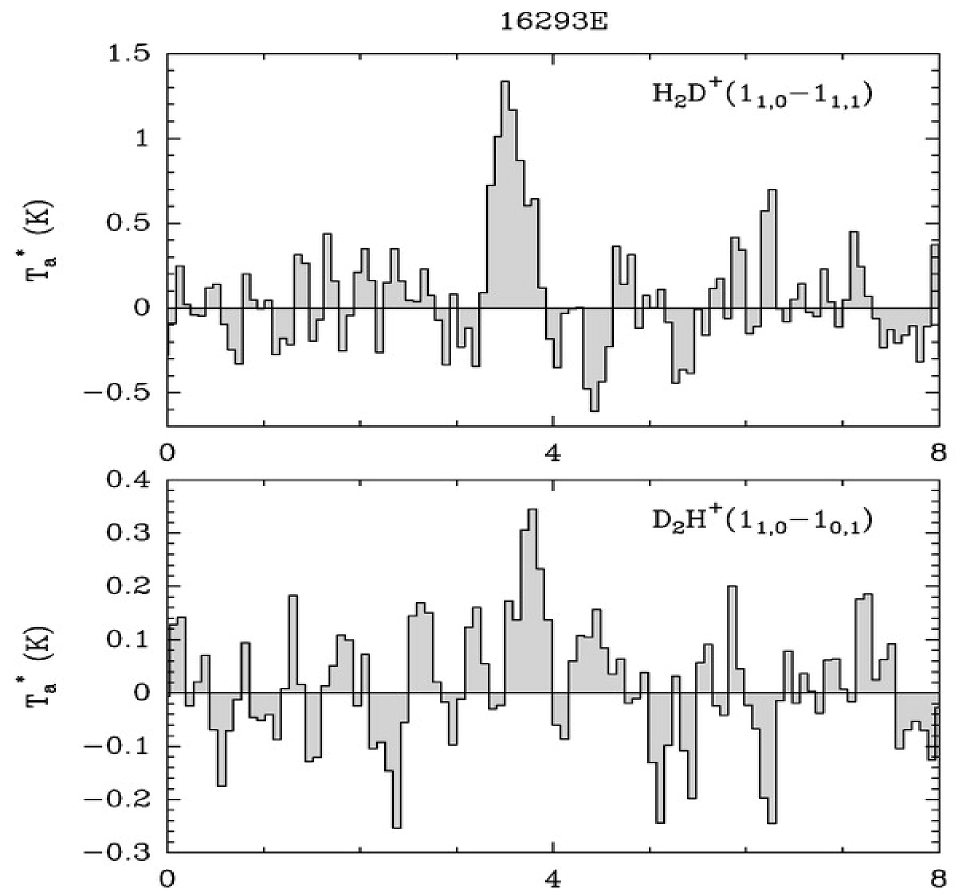

**Fig. 1.** Observed spectra at 372 GHz toward four of the five sources. The spectra toward NGC 2264, NGC 1333 IRAS 4A and NGC 2024 FIR5 have been smoothed to 1 MHz resolution, and that toward W3 IRS5 to 2 MHz resolution.




Stark et al., 1999
Caselli et al. 1999
Yes !!

# *Looking for $D_2H^+$- from the ground*

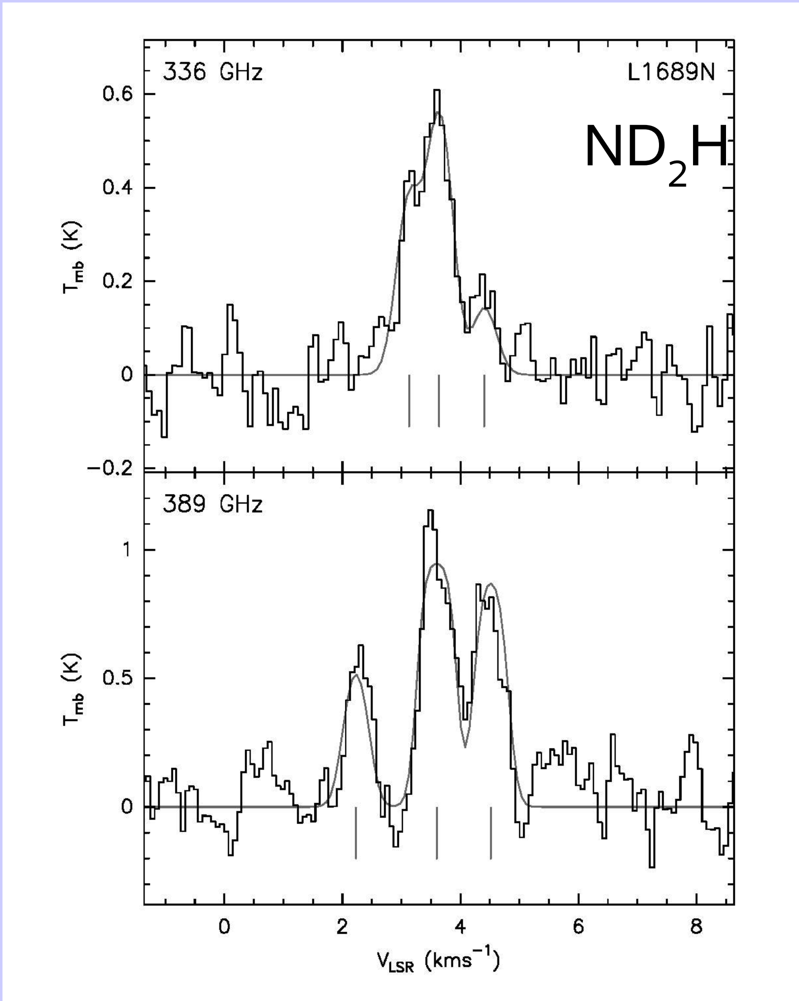
- D ions are the main positive ions
- Large depletions (CO freeze out) & high densities, low x(e)
- → very large fractionation ($D/H > 10\%$ vs $10^{-5}$)



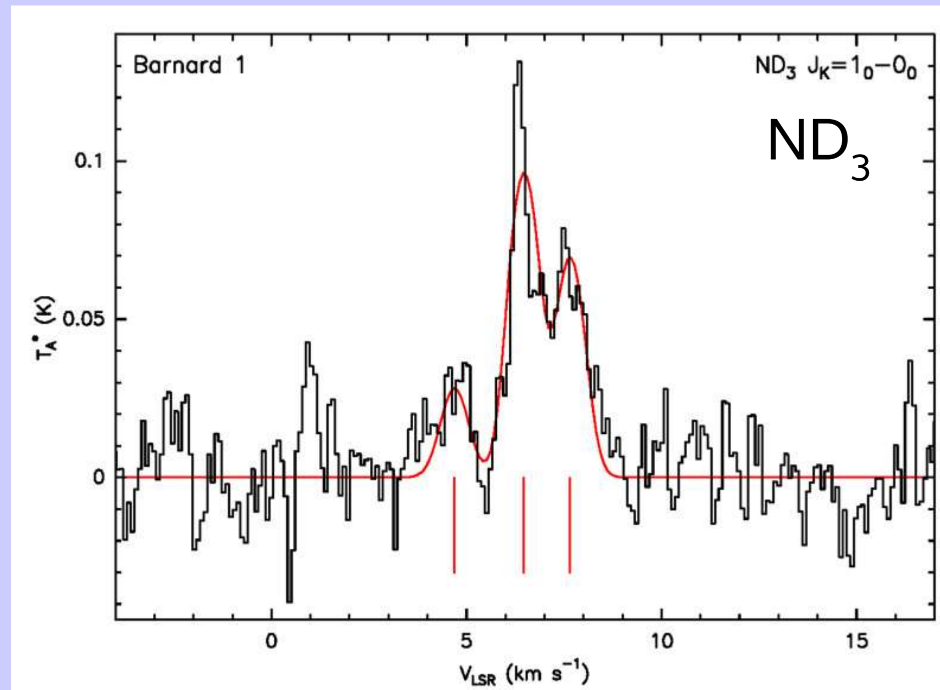

Vastel et al. 2004

Yes

# *Multiply deuterated molecules*




Lis et al. 2003, 2005



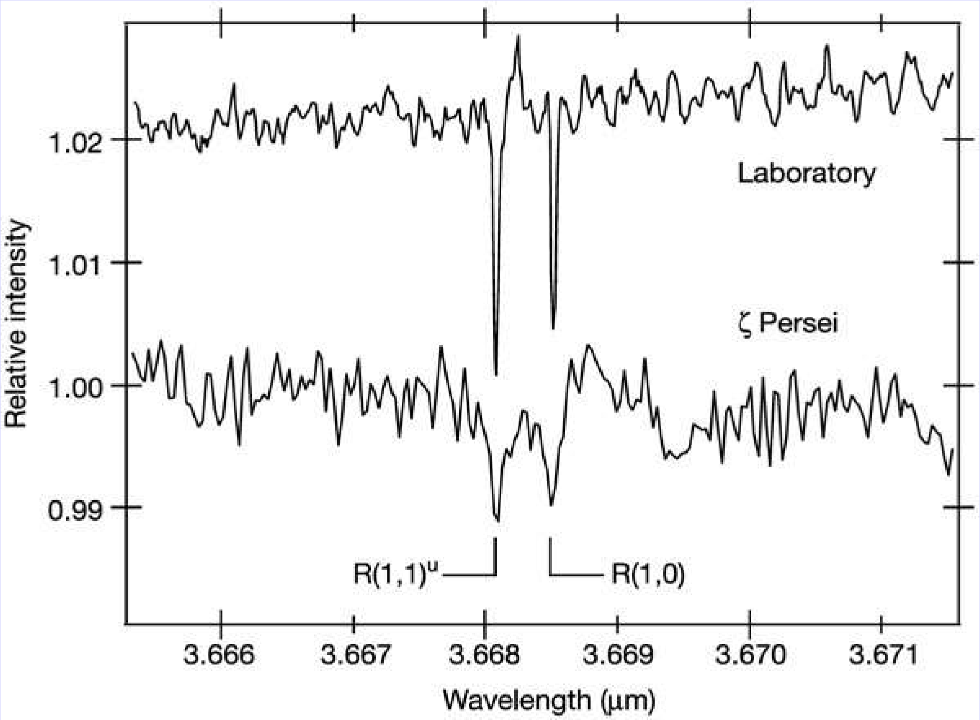

- 2000s,detection of several multiply deuterated species
- Formation ? Gas phase (assisted by depletions)
- Dust phase (D – H substitution on grain mantles)

# *Reactive species*

- $H_3^+$ key species for initiating the ion – molecule chemistry

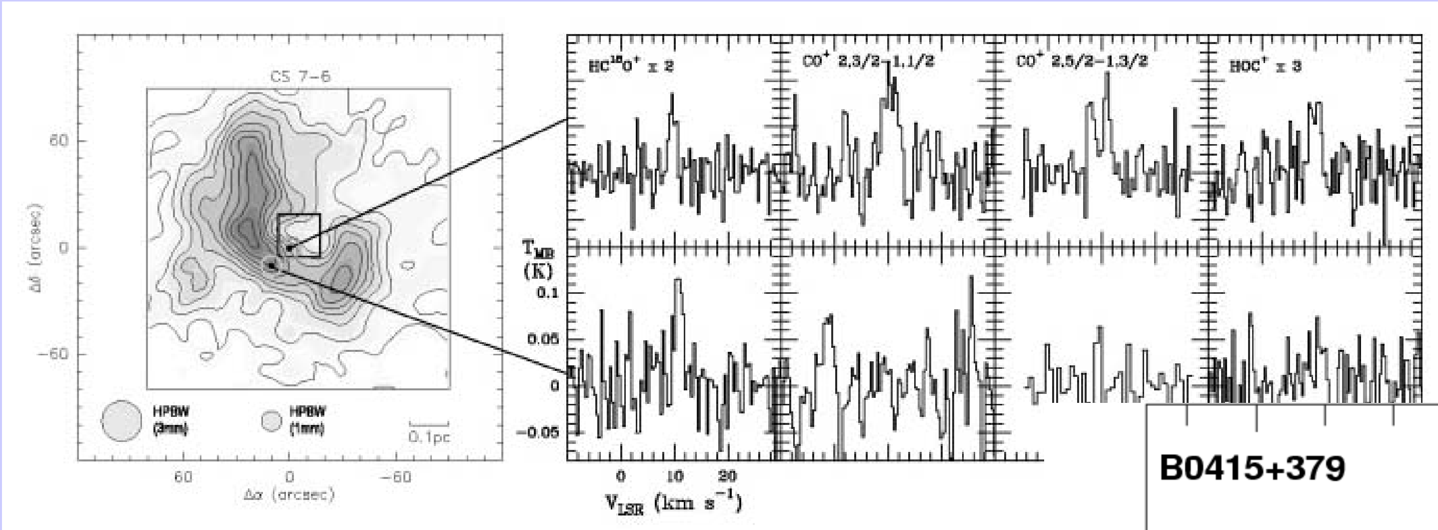
Vibration lines near 3.67 µm

Rate of Dissociative recombination , key parameter for IS chemistry.

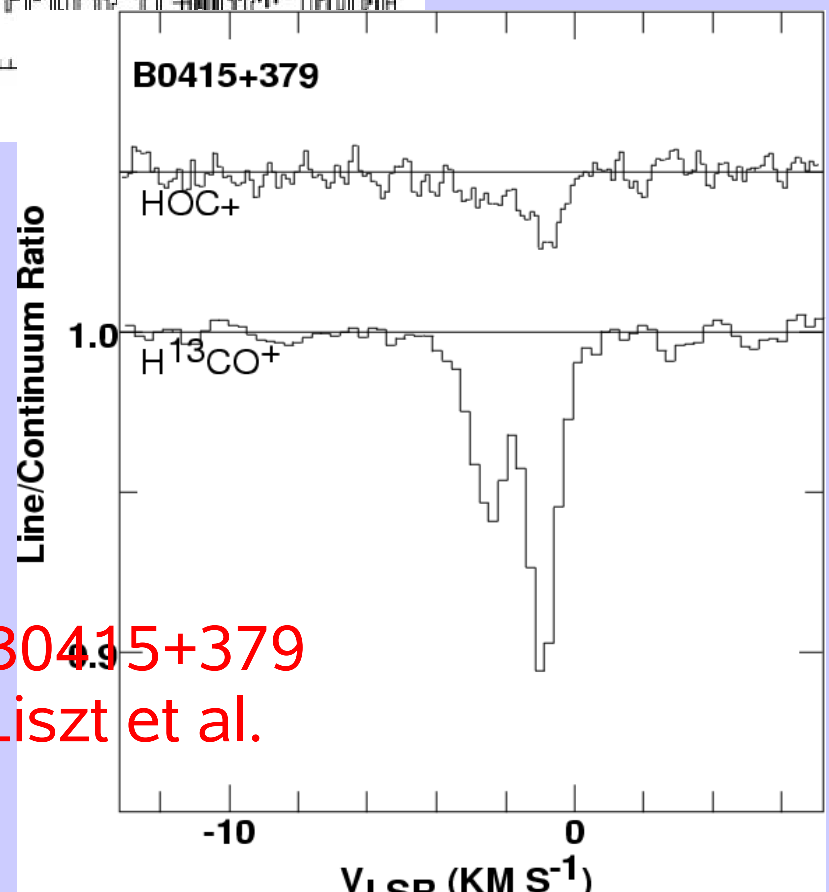



ζ Per
Mc Call et al. 2003

# *Reactive species, $CO^+$ and $HOC^+$*



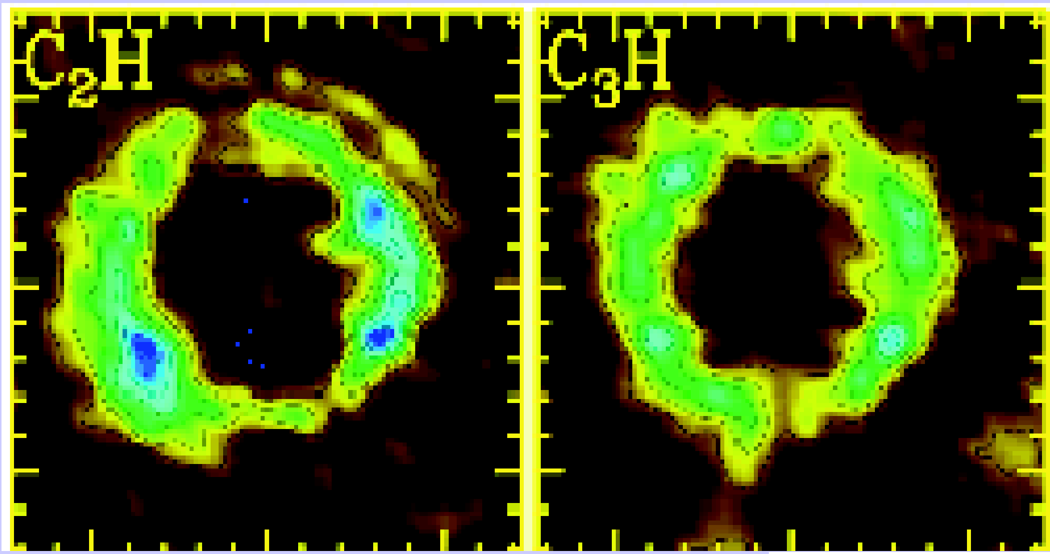

MonR2
Rizzo et al.
2003



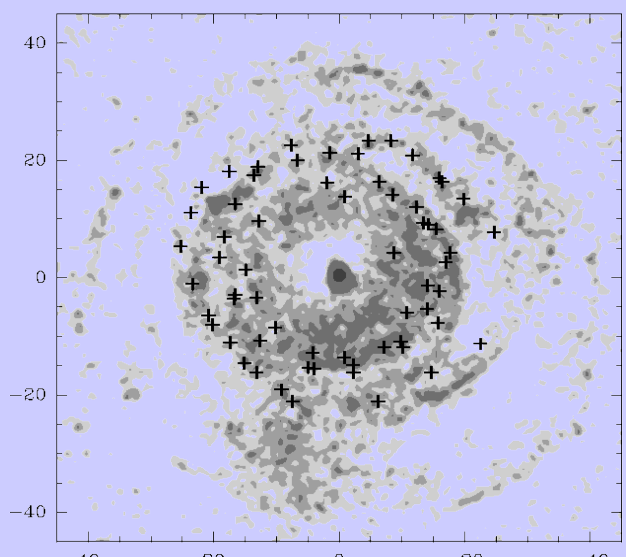

B0415+379
Liszt et al.

- Prediction of CO+ from chemical models, detection in PDRs and star forming regions , energetic inter-faces
- Other reactive species, $HOC^+$, $SO^+$ etc.

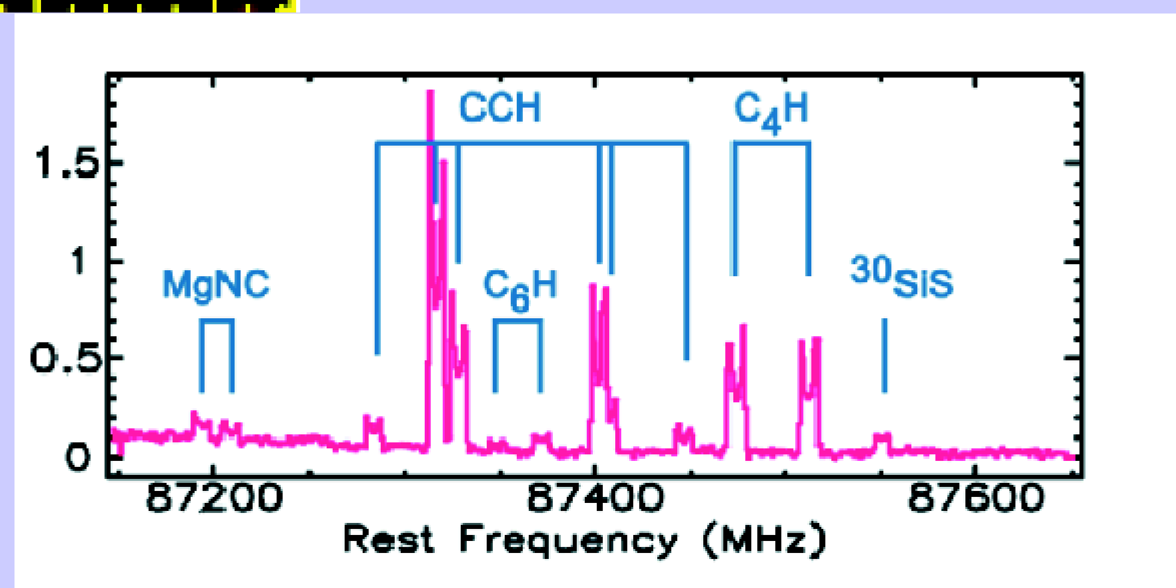
# *Carbon chains : carbon stars as molecule factories*




IRC+10216 very close carbon star . Envelope and atmosphere rich in exotic molecules, cyanopolyynes, chains, rings ...



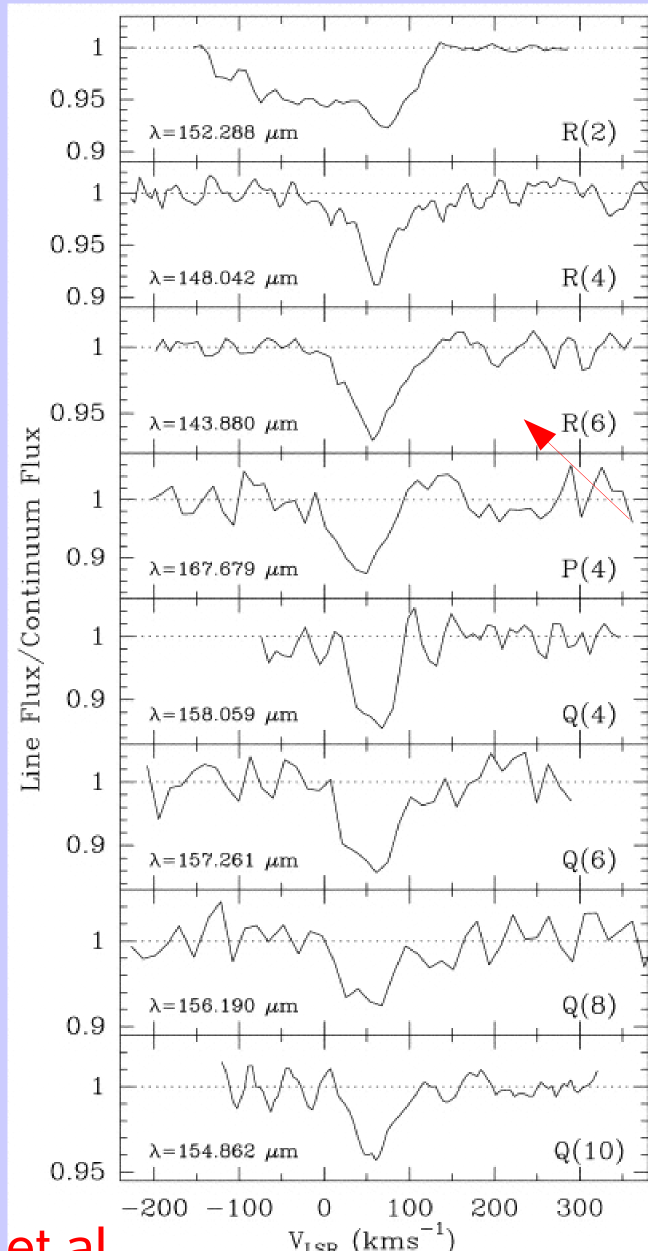

Mauron & Huggins .




Guélin et al.

# *Carbon chains, carbon clusters*

- Radio tele-scopes → Polar molecules
- Symmetric molecules ? Electronic tran-sitions ($C_2$, $C_3$) or vibration transitions ($C_2H_2$, …)

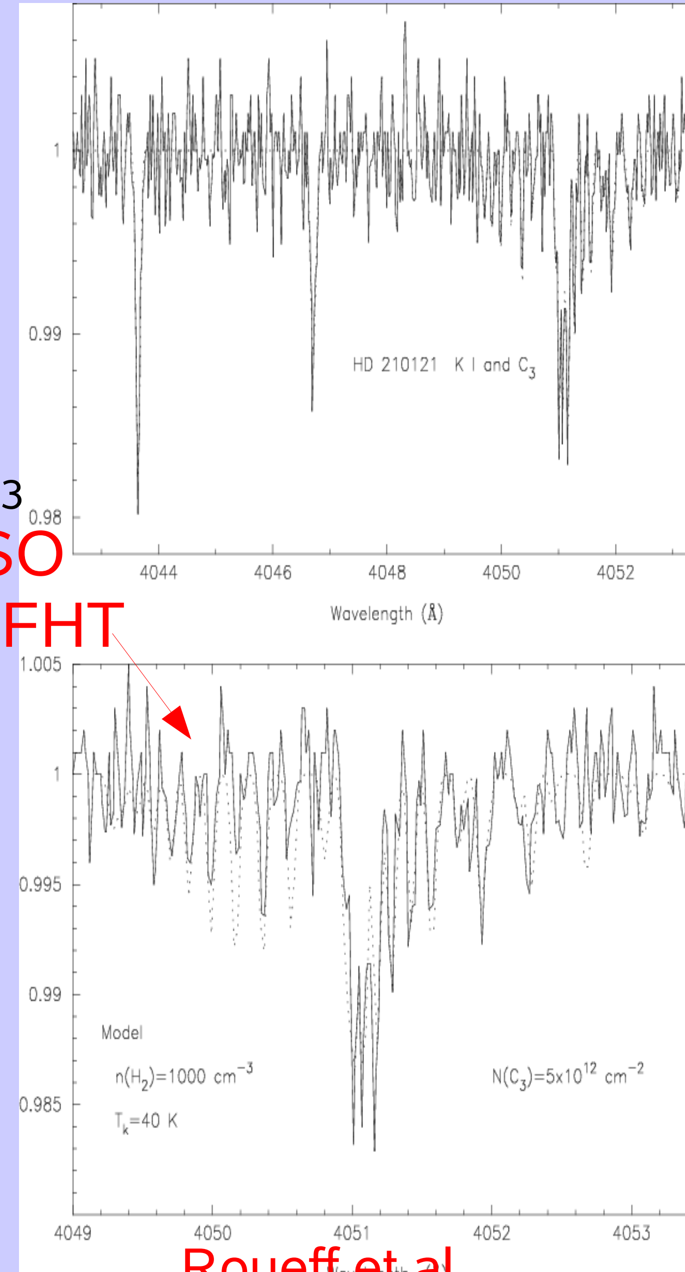



Cernicharo et al.

$C_3$

ISO

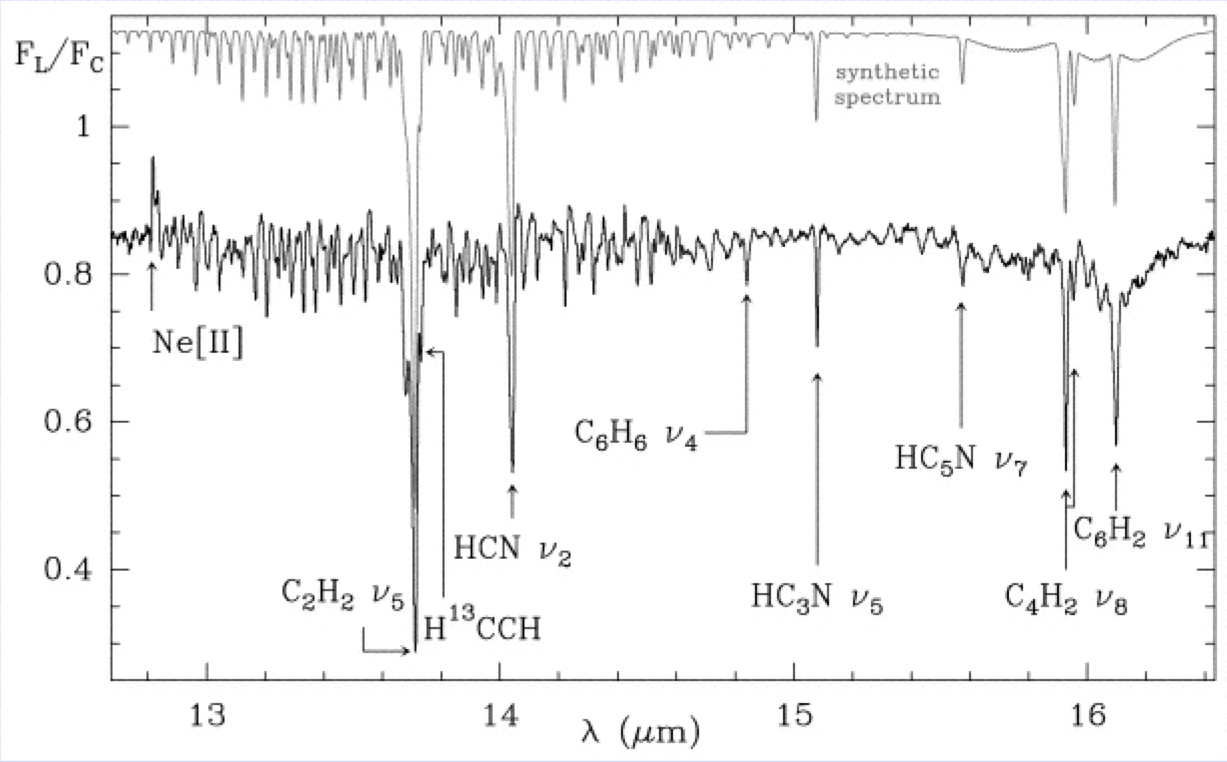
CFHT




Roueff et al.

# *Carbon chains*

IR & Radio spectroscopy, 2 complementary way for studying interstellar chemistry




CRL 618,
polymerization ?
Cernicharo et al.

# PAHs

- Macro molecules , proposed as carriers of IR emission bands. Play an important role for gas heating (Photo-electric effect), ionisation balance, chemistry ?
- No spectroscopic identification yet.

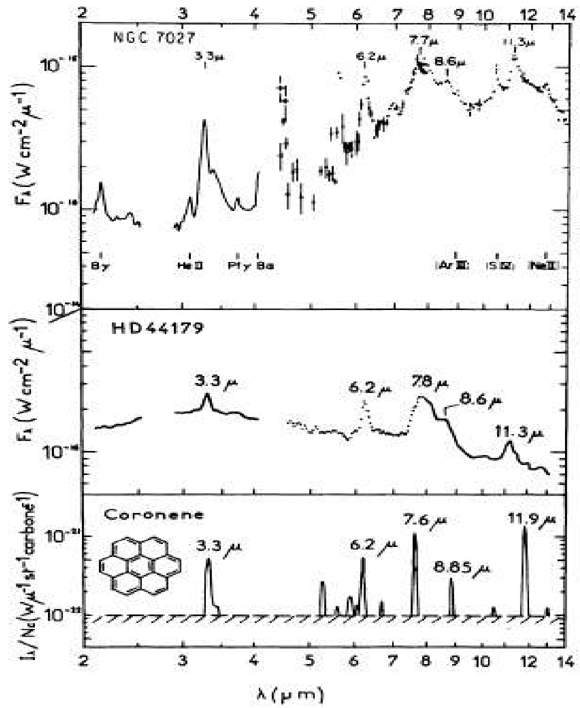
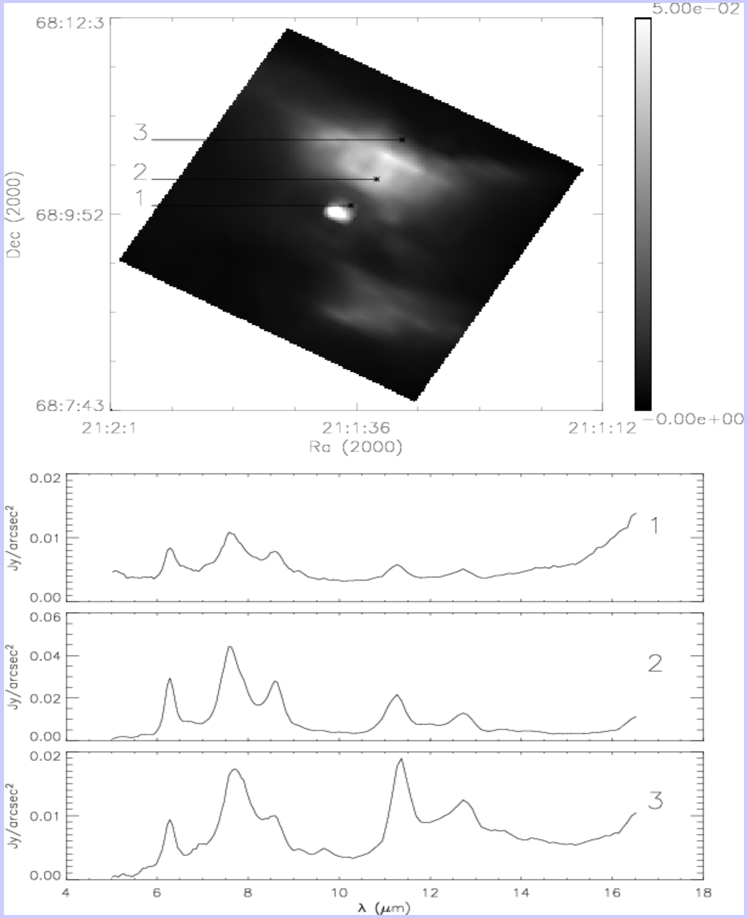



FIG. 2 : Observed "unidentified" IR emission bands in NGC 7027 and HD 44179, the Red Rectangle, (adapted from Russell et al, 1977 and 1978). Atomic fine structure lines are also present in the first spectrum. Calculated emission of coronene heated to 600 K (absorption spectrum of coronene from Sadtler Standard Spectra, 1959). The

**Léger & Puget, 1984**

**Rapacioli et al. 2005**



# Complex organic molecules

- Many organic molecules detected in hot cores → “line forest”, line blending and confusion. Identification ?
- High spatial resolution helps → interferometer
- Formation = Grain mantle ice processing + warm gas phase

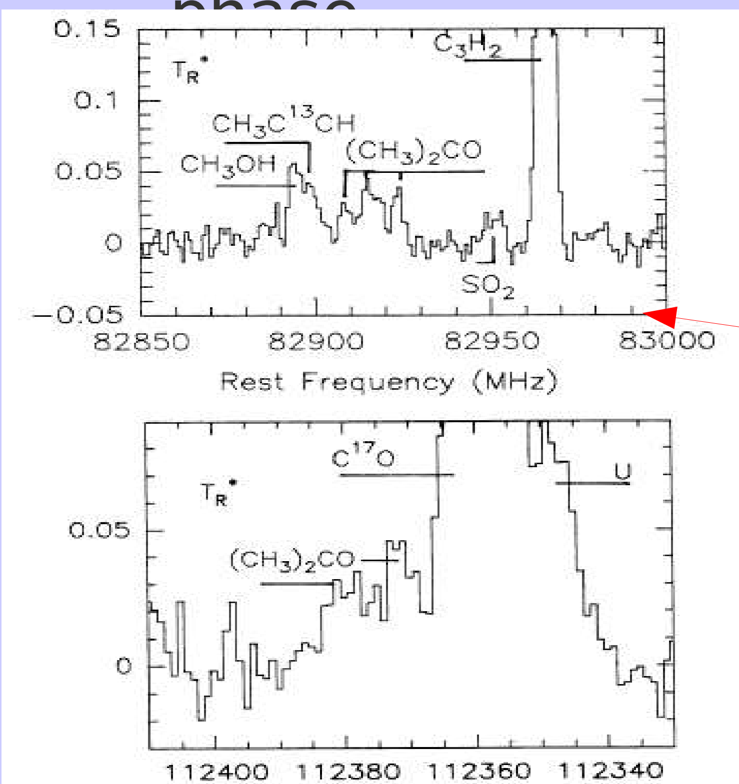
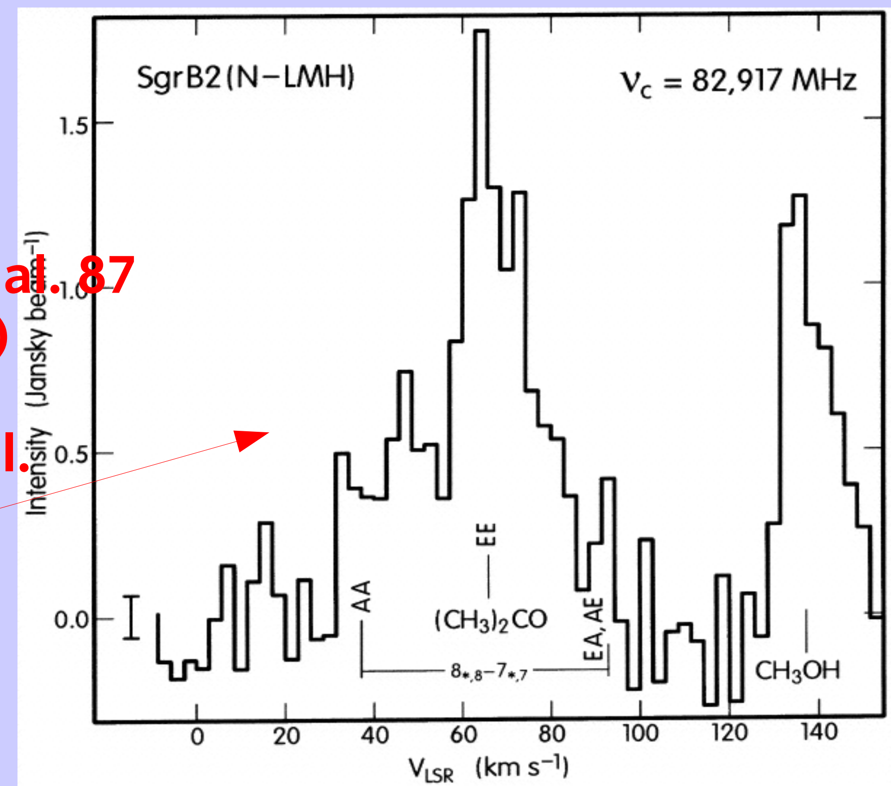



Figure 2: Same spectra as figure 1, with an enlarged scale.

Acetone

**Combes et al. 87 (IRAM 30m)**

**Snyder et al. 2003 BIMA**

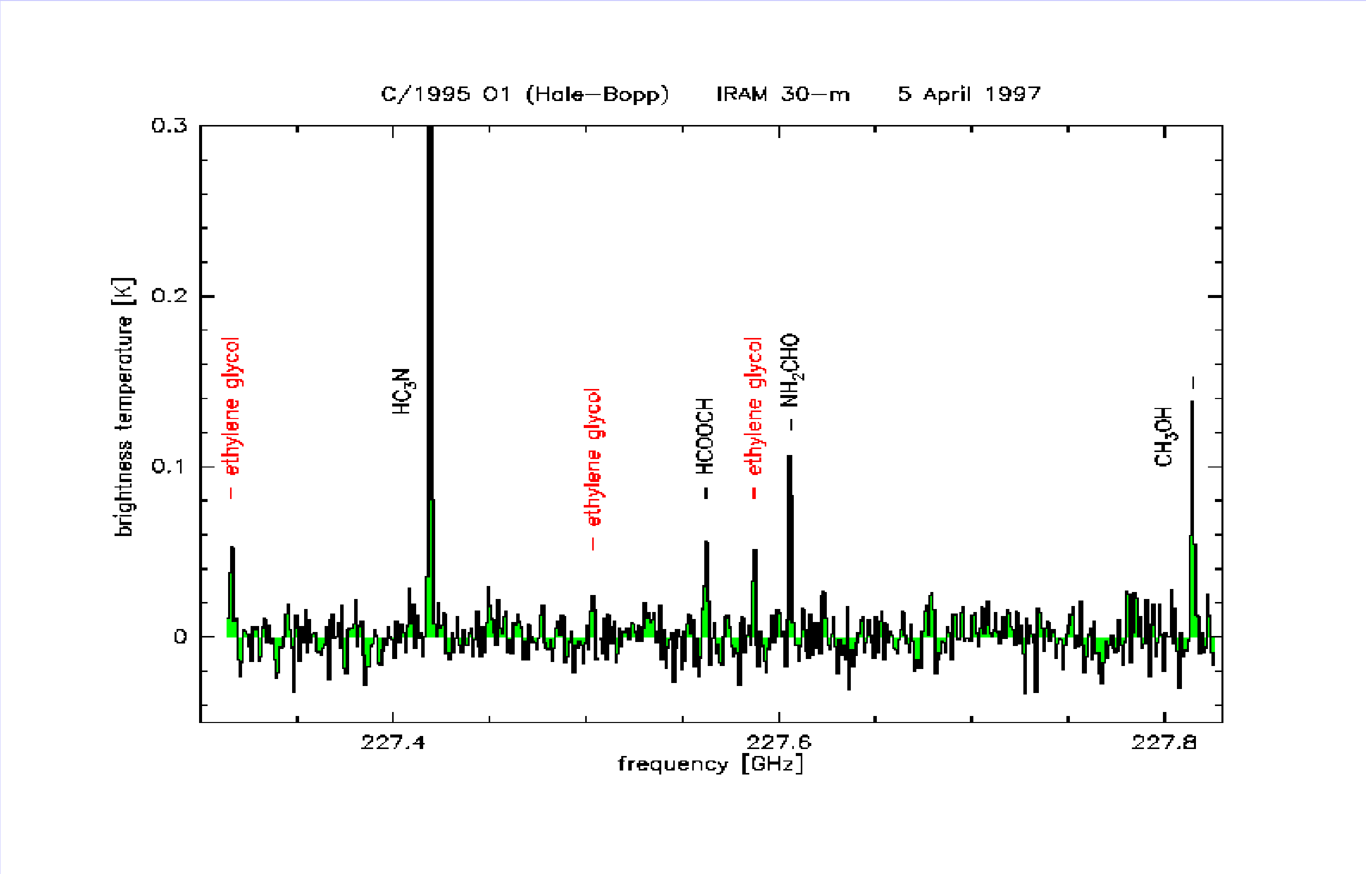


# *Molecular ices*

- In dense, dark clouds, condensation of atoms and molecules
- Hydrogenation, $H_2O$, CO, $CH_4$, ..
- Processing due to cosmic rays, UV photons
- Formation of more complex species ($CO_2$, $CH_3OH$)
- 
- Ice evaporation / sublimation in hot cores , release of processed material in the gas phase (eg $CH_3OH$, $H_2CO$) and formation of other species
- Connection to primordial solar system matter ? (cf comet studies)

# *Comets and Planets*

- Radio sounding of cometary comae : same species as in the ISM (see talk by D. Bockelée)
- Radio sounding in planetary atmosphere (see talks af-ternoon session)



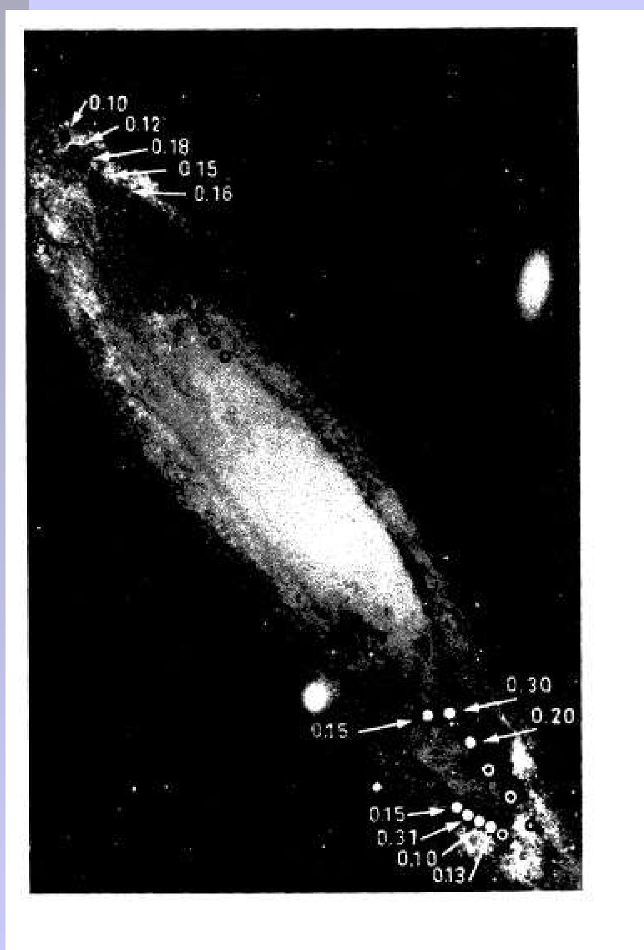

Ethylene Glycol, Hale Bopp

Crovisier et al.

# *Molecules everywhere*

1970s CO detected in external galaxies soon after detection in the ISM.

M31 (1977) and IRAM map



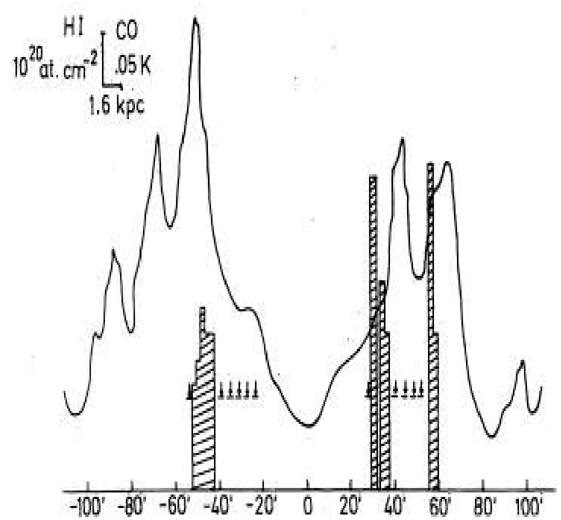
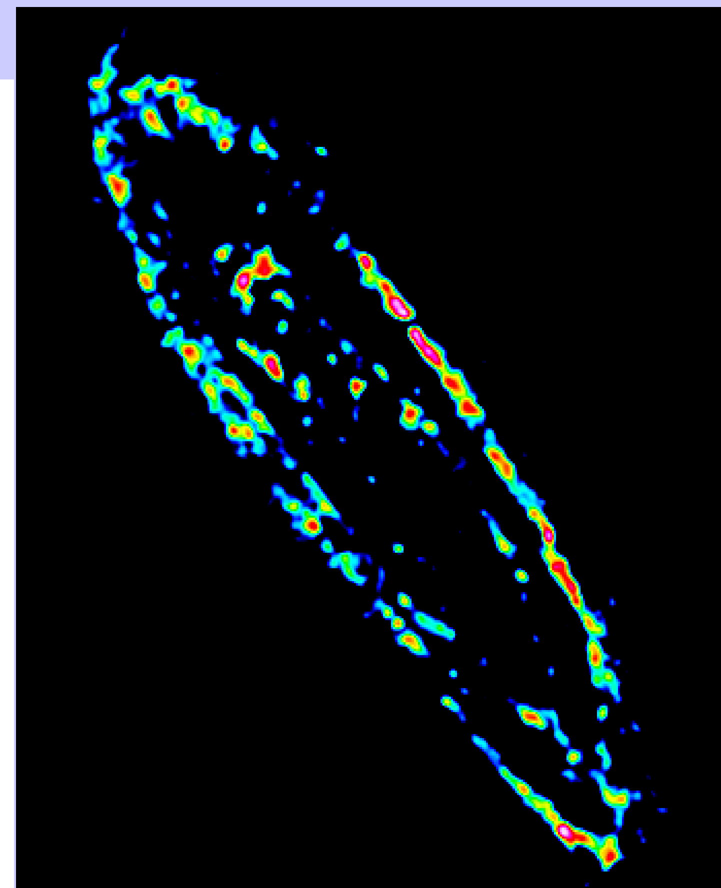
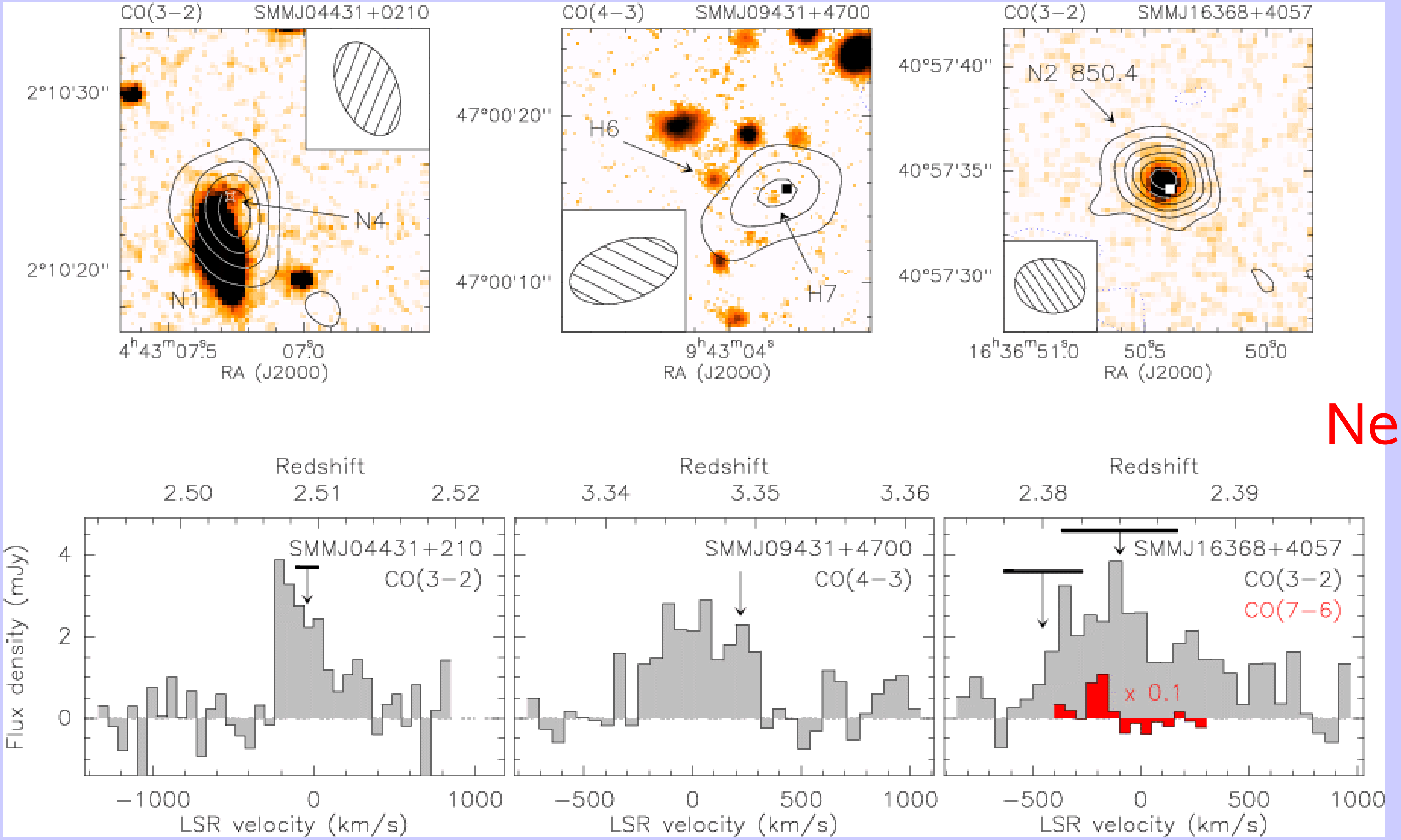




*Figure 2.* : Radial distribution of CO and HI in M31. The hydrogen distribution is the surface density along the major axis from Guibert (1975), the hatched histograms represent antenna temperatures obtained in CO. The arrows represent 3 σ limits.



# Molecules everywhere

- IRAM PdBI detections of high z galaxies (see talk by P. Cox)




Neri et al.

# *A promising future !*

- Powerful generation of instruments in operation
- Even more powerful in construction Herschel, ALMA, SOFIA, JWST ...