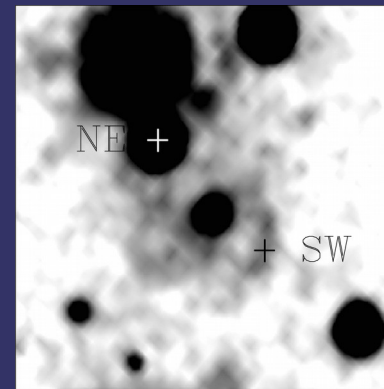
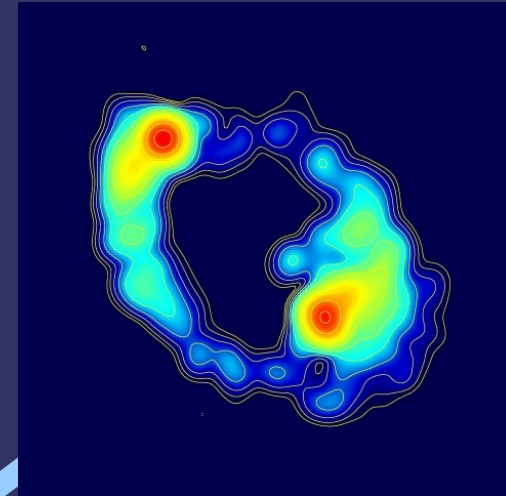


# Molecules in absorption at intermediate redshifts



Sébastien Muller

Onsala Space Observatory, Nordic ARC  
Department of Space, Earth and Environment  
Chalmers University of Technology, Sweden

The Cosmic Cycle of Dust and Gas in the Galaxy  
Quy Nhon, Vietnam, 2018 July 11th



EUROPEAN ARC  
ALMA Regional Centre || Nordic

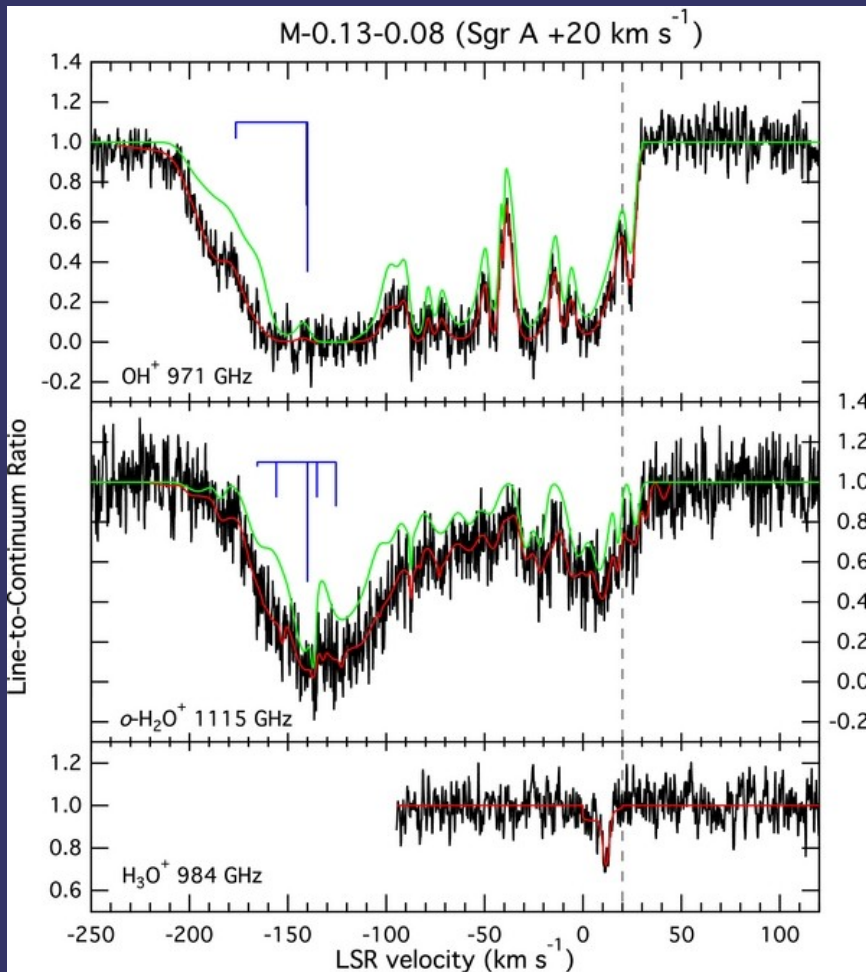
# Molecules in absorption

- Very sensitive ... provided there is a background continuum
- No signal dilution by distance (as sensitive at high-z than local)

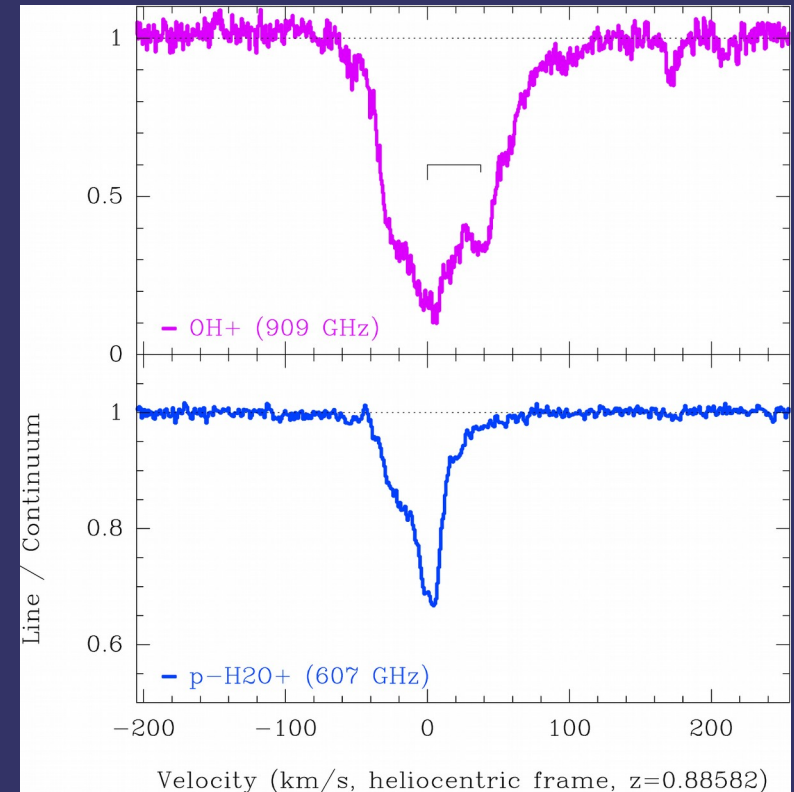
# Molecules in absorption

- Very sensitive ... provided there is a background continuum
- No signal dilution by distance (as sensitive at high-z than local)

Indriolo+15



**OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>  
toward the Galactic center**

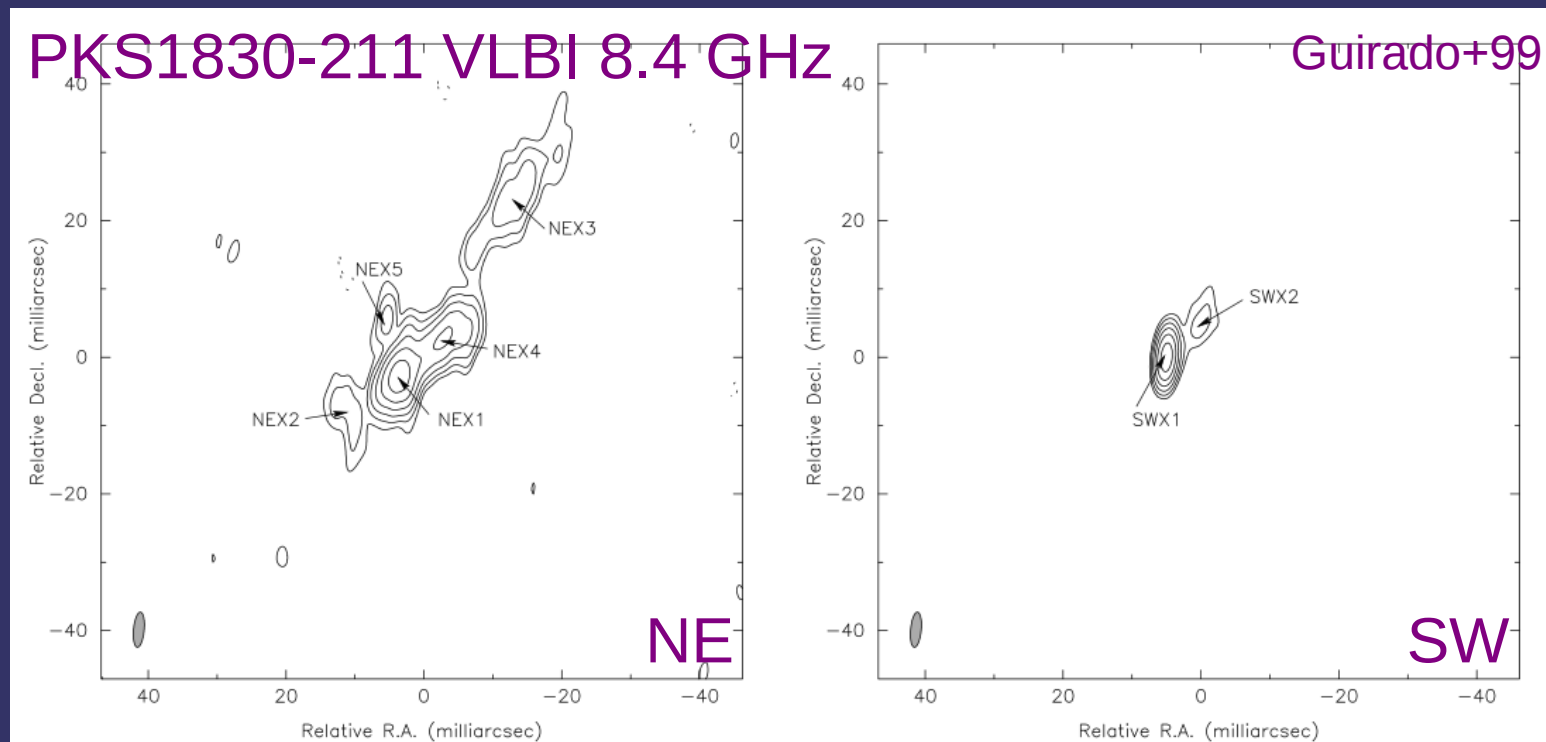


Muller+16

**OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>  
@z=0.89 toward PKS1830-211**

# Molecules in absorption

- Very sensitive ... provided there is a background continuum
- No signal dilution by distance (as sensitive at high-z than local)
- Outstanding angular resolution = size of the continuum illumination  
Quasars have emission size of ~few mas  
1 mas = 8 pc @z=0.89  
But ... along a line of sight = cylinder of absorption



**Fig. 1.** Maps of the NE image (*left*) and SW image (*right*) of PKS 1830–211 at 8.4 GHz. Contours are -1,1,2,4,8,1

# Molecules in absorption

- Very sensitive ... provided there is a background continuum
- No signal dilution by distance (as sensitive at high- $z$  than local)
- Outstanding angular resolution = size of the continuum illumination  
Quasars have emission size of  $\sim$ few mas  
 $1 \text{ mas} = 8 \text{ pc} @z=0.89$   
But ... along a line of sight = cylinder of absorption
- In diffuse gas, the excitation of polar molecules is simple  
(low-collision regime, coupling with CMB photons)
- Line-to-continuum ratio can be converted directly into opacity  
Get (robust) column densities and chemical abundances
- Easy line identification (only low-energy levels populated, no confusion)

# Extragalactic radio-mm molecular absorbers

| Source              | z(abs) | Background continuum flux (Jy @3mm) | N(H <sub>2</sub> ) (cm <sup>-2</sup> ) | Molecules detected   |
|---------------------|--------|-------------------------------------|--|--|
| Cen A               | 0.002  | 6                                   | 2 x 10 <sup>20</sup>                   | CO, OH, NH <sub>3</sub> , CN, HCO <sup>+</sup> , HCN, N <sub>2</sub> H <sup>+</sup> , C <sub>2</sub> H, CS, H <sub>2</sub> CO, C <sub>3</sub> H <sub>2</sub> |
| 3C293               | 0.045  |                                     | 2 x 10 <sup>19</sup>                   | CO, HCO <sup>+</sup> , HCN   |
| 4C31.04             | 0.060  |                                     | 1 x 10 <sup>19</sup>                   | CO, HCO <sup>+</sup> , HCN   |
| PKS 1413+135        | 0.247  | 0.5                                 | 5 x 10 <sup>20</sup>                   | CO, CN, HCO <sup>+</sup> , HCN, HNC  |
| B 1504+377          | 0.673  | 0.4                                 | 5 x 10 <sup>20</sup>                   | CO, HCO <sup>+</sup> , HCN, HNC  |
| B 0218+357          | 0.685  | 0.5<br>lensed                       | 4 x 10 <sup>21</sup>                   | CO, NH <sub>3</sub> , H <sub>2</sub> O, HCO <sup>+</sup> , HCN, HNC, C <sub>2</sub> H, CS, H <sub>2</sub> S, H <sub>2</sub> CO                               |
| PKS 0132-097        | 0.765  | 0.4<br>lensed                       |  | OH, CO, HCO <sup>+</sup>   |
| <b>PKS 1830-211</b> | 0.886  | 2-3<br>lensed                       | 2 x 10 <sup>22</sup>                   | <b>&gt; 50 species</b> (not incl. isotopic variants)   |

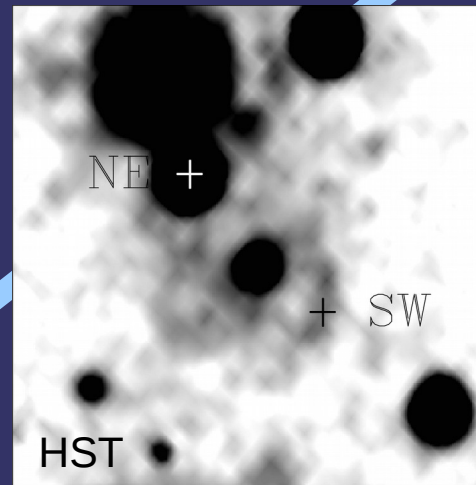
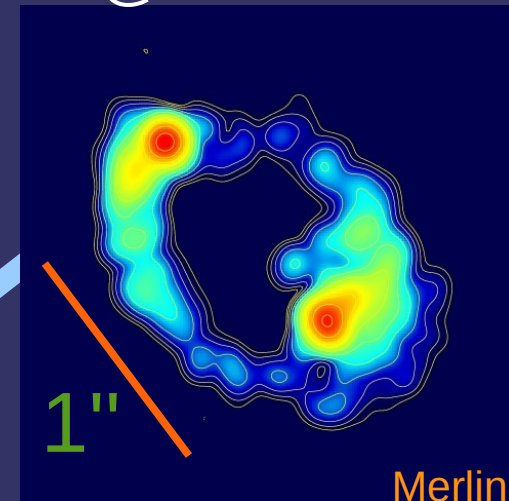
@z>0.1

See Combes 2008, Wiklind et al 2018

# The line(s) of sight to PKS1830-211

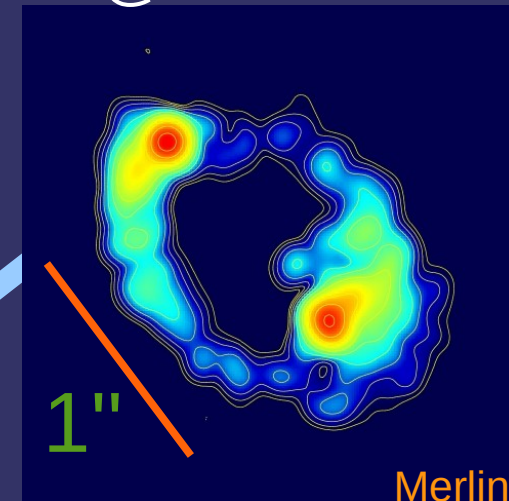
Foreground  
nearly face-on spiral galaxy  
@  $z=0.89$

Lensed blazar  
@  $z=2.5$

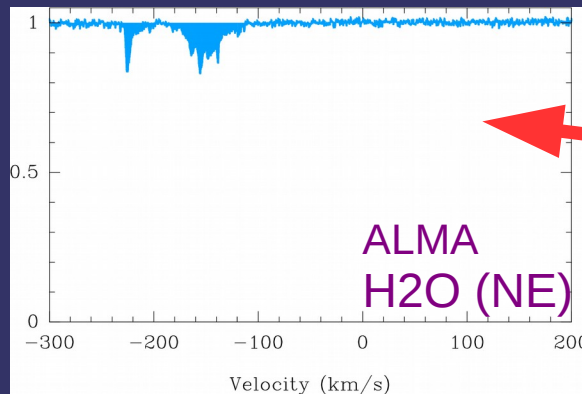
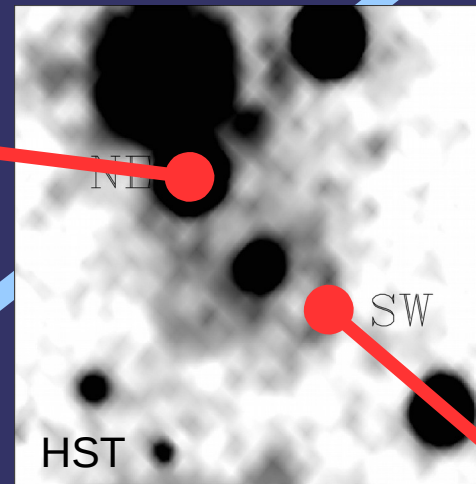


# The line(s) of sight to PKS1830-211

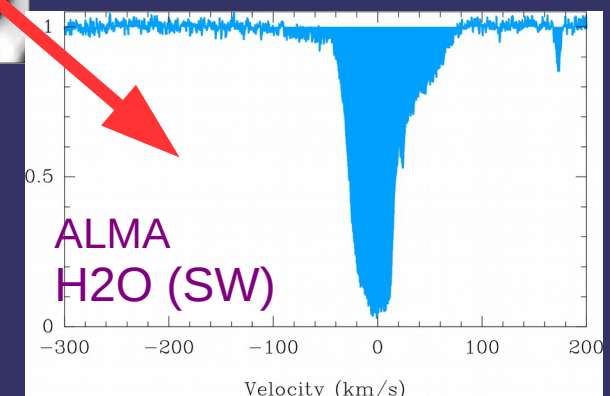
Lensed blazar  
@  $z=2.5$



Absorber =  
nearly face-on spiral galaxy  
@  $z=0.89$



$N(\text{H}_2) \sim 1 \times 10^{21} \text{ cm}^{-2}$



$N(\text{H}_2) \sim 2 \times 10^{22} \text{ cm}^{-2}$

~ mas / pc scale





# Chemical inventory toward the SW los

| <u>1 atom</u> | <u>2 atoms</u>  | <u>3 atoms</u>              | <u>4 atoms</u>              | <u>5 atoms</u>                      | <u>6 atoms</u>           | <u>7 atoms</u>                      |
|---------------|-----------------|-----------------------------|-----------------------------|-------------------------------------|--------------------------|-------------------------------------|
| H             | <u>CH</u> (*)   | <u>NH<sub>2</sub></u>       | <u>NH<sub>3</sub></u>       | <u>CH<sub>2</sub>NH</u>             | <u>CH<sub>3</sub>OH</u>  | <u>CH<sub>3</sub>NH<sub>2</sub></u> |
| C             | <u>CH+</u> (*)  | <u>H<sub>2</sub>O</u> (**)  | <u>H<sub>2</sub>CO</u> (**) | <u>c-C<sub>3</sub>H<sub>2</sub></u> | <u>CH<sub>3</sub>CN</u>  | <u>CH<sub>3</sub>CCH</u>            |
|               | <u>OH</u>       | <u>H<sub>2</sub>O+</u>      | <u>I-C<sub>3</sub>H</u>     | <u>I-C<sub>3</sub>H<sub>2</sub></u> | <u>NH<sub>2</sub>CHO</u> | <u>CH<sub>3</sub>CHO</u>            |
|               | <u>OH+</u>      | <u>C<sub>2</sub>H</u>       | <u>HNCO</u>                 | <u>H<sub>2</sub>CCN</u>             |                          |                                     |
|               | <u>HF</u>       | <u>HCN</u> (**)             | <u>HOCO+</u>                | <u>H<sub>2</sub>CCO</u>             |                          |                                     |
|               | <u>CN</u>       | <u>HNC</u> (**)             | <u>H<sub>2</sub>CS</u>      | <u>C<sub>4</sub>H</u>               |                          |                                     |
|               | <u>CO</u> (**)  | <u>N<sub>2</sub>H+</u>      |                             | <u>HC<sub>3</sub>N</u>              |                          |                                     |
|               | <u>CF+</u>      | <u>HCO+</u> (***)           |                             |                                     |                          |                                     |
|               | <u>SH+</u> (*)  | <u>HCO</u>                  |                             |                                     |                          |                                     |
|               | <u>HCl</u> (*)  | <u>HOC+</u>                 |                             |                                     |                          |                                     |
|               | <u>ArH+</u> (*) | <u>H<sub>2</sub>S</u> (**)  |                             |                                     |                          |                                     |
|               | <u>SiO</u> (**) | <u>H<sub>2</sub>Cl+</u> (*) |                             |                                     |                          |                                     |
|               | <u>CS</u> (*)   | <u>HCS+</u>                 |                             |                                     |                          |                                     |
|               | <u>NS</u>       | <u>C<sub>2</sub>S</u>       |                             |                                     |                          |                                     |
|               | <u>SO</u>       |                             |                             |                                     |                          |                                     |
|               | <u>SO+</u>      |                             |                             |                                     |                          |                                     |

51 species detected

+ 24 isotopic variants (\*)

Including 14 hydrides

All (exc. H and OH) observed at mm/submm  
e.g., Muller et al. 06, 11, 13, 14, 16, 17  
PdBI, ATCA, ALMA cycle 0,1,2

@ z=0.89 !

Upper limits on D-species, H<sub>2</sub>F+, O<sub>2</sub>, ...

# Chemical inventory toward the NE los

1 atom

2 atoms

3 atoms

4 atoms

5 atoms

6 atoms

7 atoms

H

CH

NH<sub>3</sub>

C

CH+ (\*)

H<sub>2</sub>O

H<sub>2</sub>CO

c-C<sub>3</sub>H<sub>2</sub>

OH

H<sub>2</sub>O+

OH+

C<sub>2</sub>H

HF

HCN

HNC

CO

HCO+

ArH+ (\*)

H<sub>2</sub>Cl+ (\*)

19 species detected

+ 3 isotopic variants (\*)

Including 10 hydrides

All (exc. H and OH) observed at mm/submm  
e.g., Muller et al. 06, 11, 13, 14, 16, 17

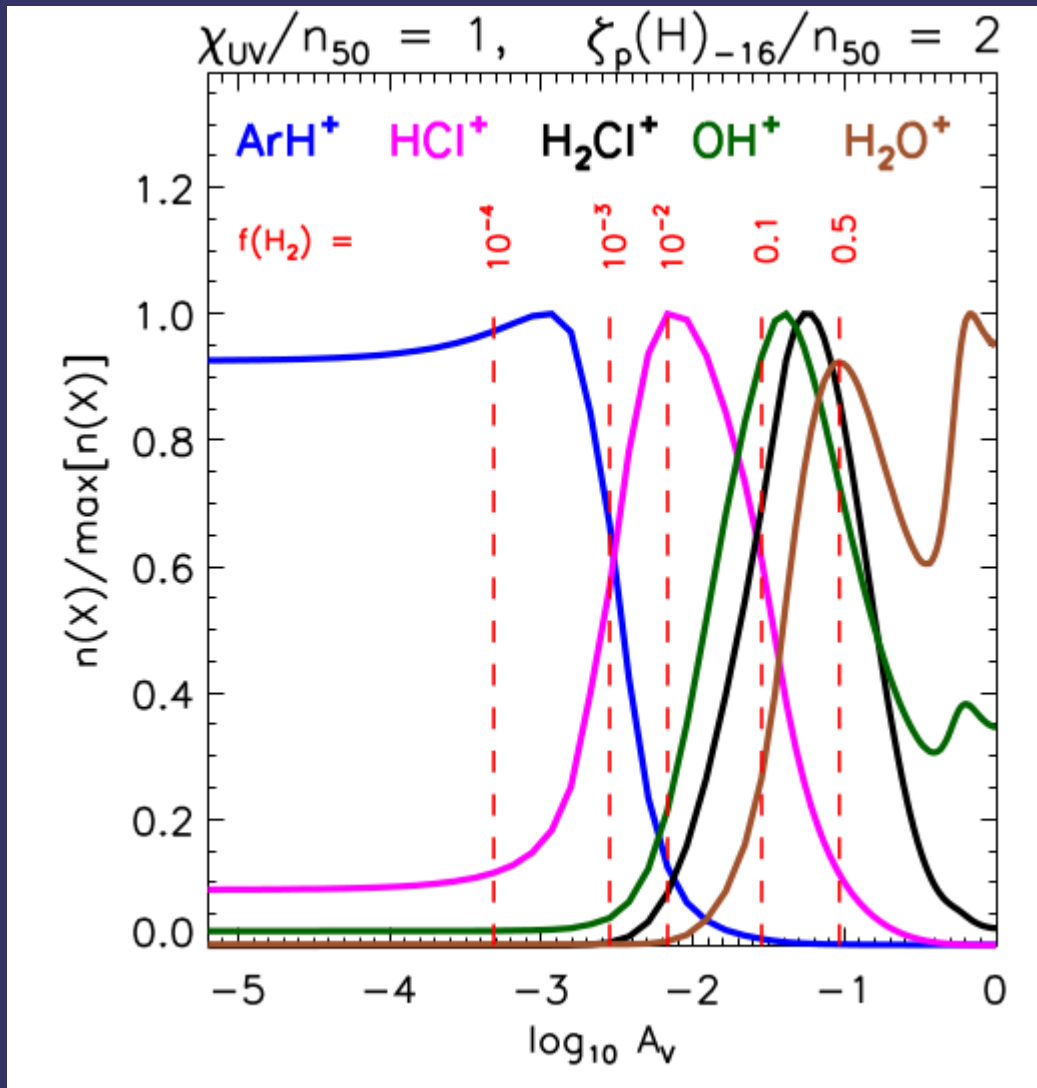
PdBI, ATCA, ALMA cycle 0,1,2,3

@ z=0.89 !

# Hydrides as critical diagnostics of the physics and chemistry of the ISM

# Chemical predictions

## Physics and chemistry of diffuse clouds



e.g. Neufeld & Wolfire 2016:

Ingredients:

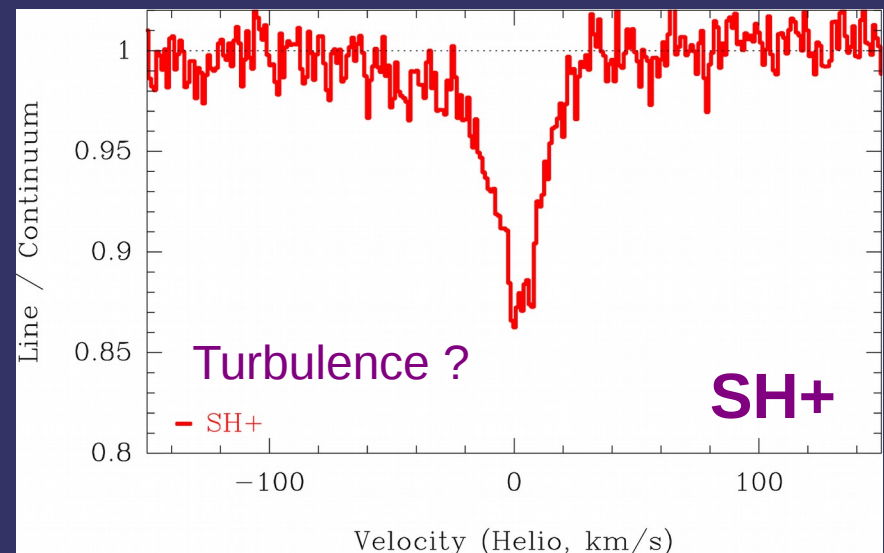
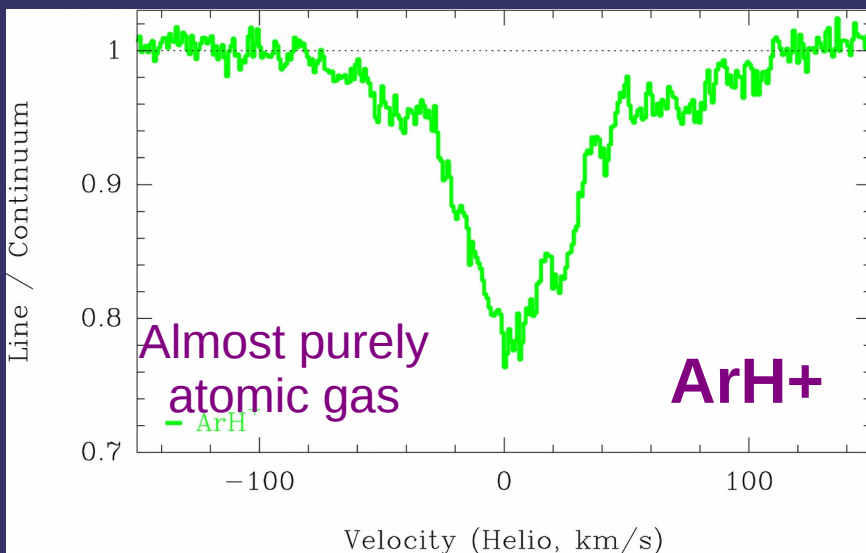
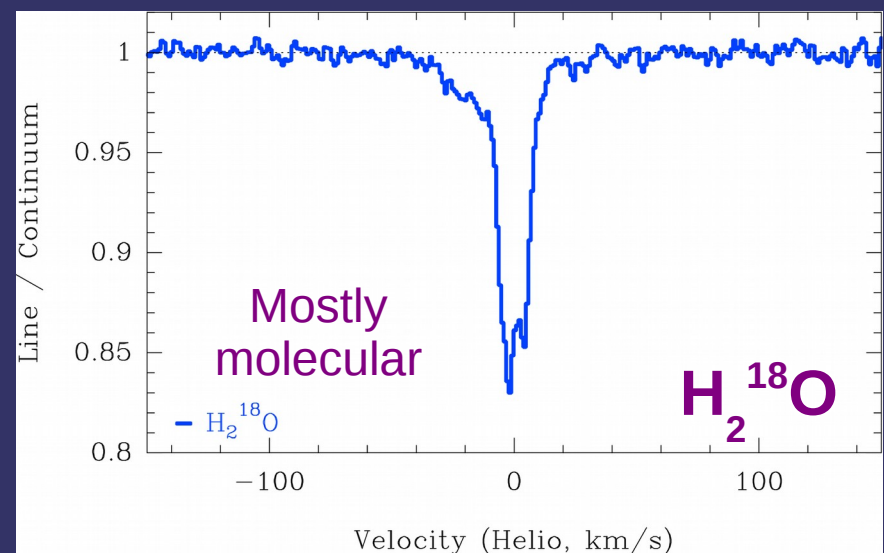
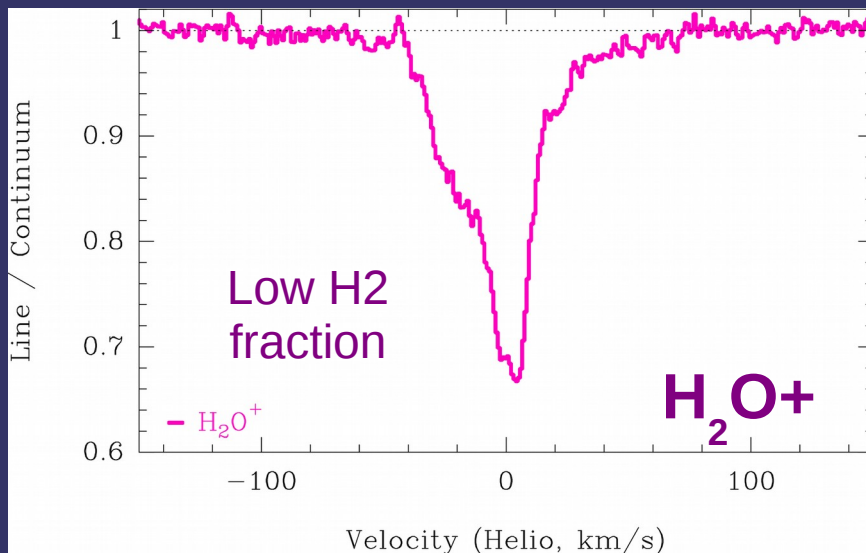
UV radiation field  
Cosmic-ray ionization  
Cloud extinction  
Chemistry

Sequence:

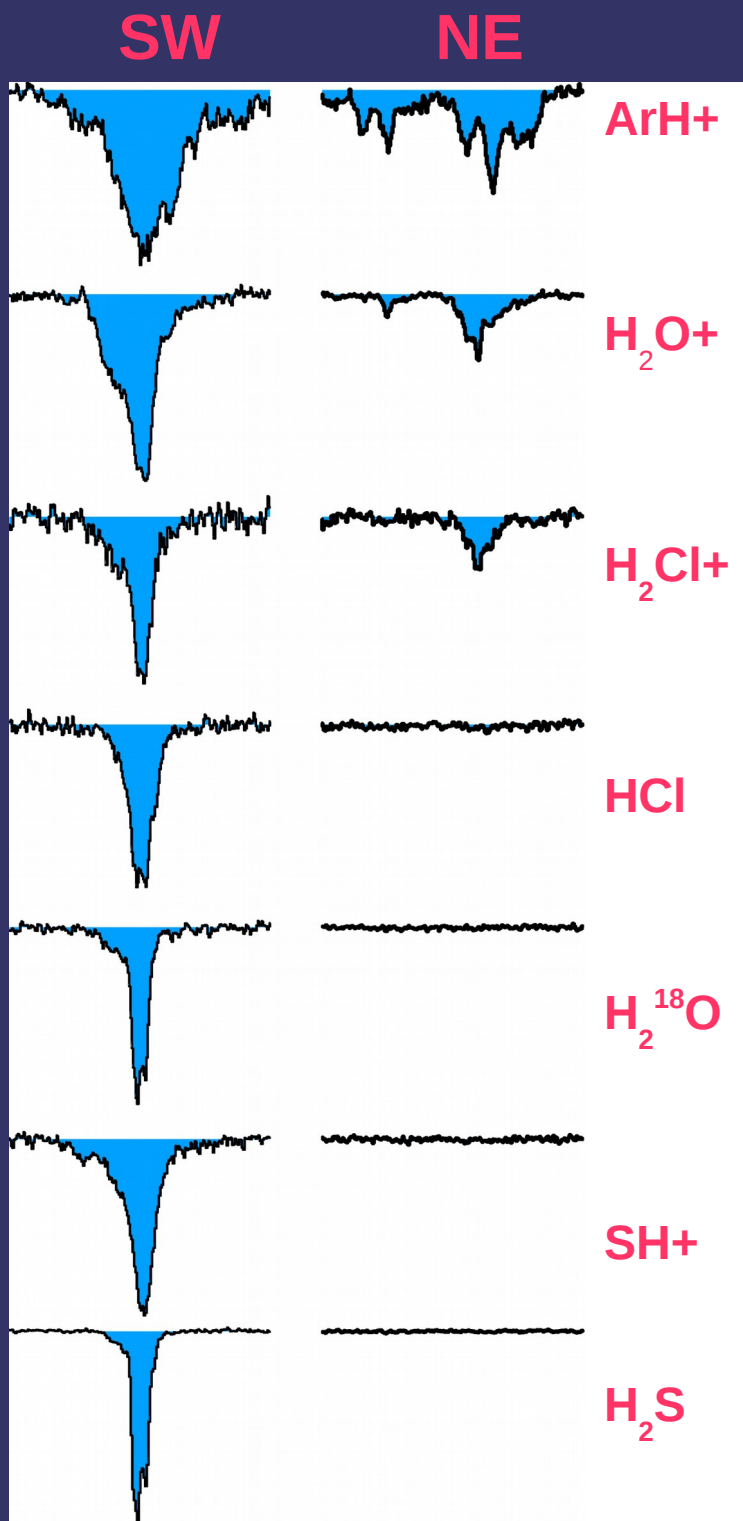
ArH<sup>+</sup> - HCl<sup>+</sup> - H<sub>2</sub>Cl<sup>+</sup> - OH<sup>+</sup> - H<sub>2</sub>O<sup>+</sup>

Reaching peak abundance  
At increasing molecular fraction

# Comparison of SW line profiles



>> different gas components along the line of sight



## Comparison of the two los toward PKS1830-211

Enhanced NE / SW ratio


Diffuse gas tracers  
Low molecular fraction

No detection toward NE

High molecular fraction tracers

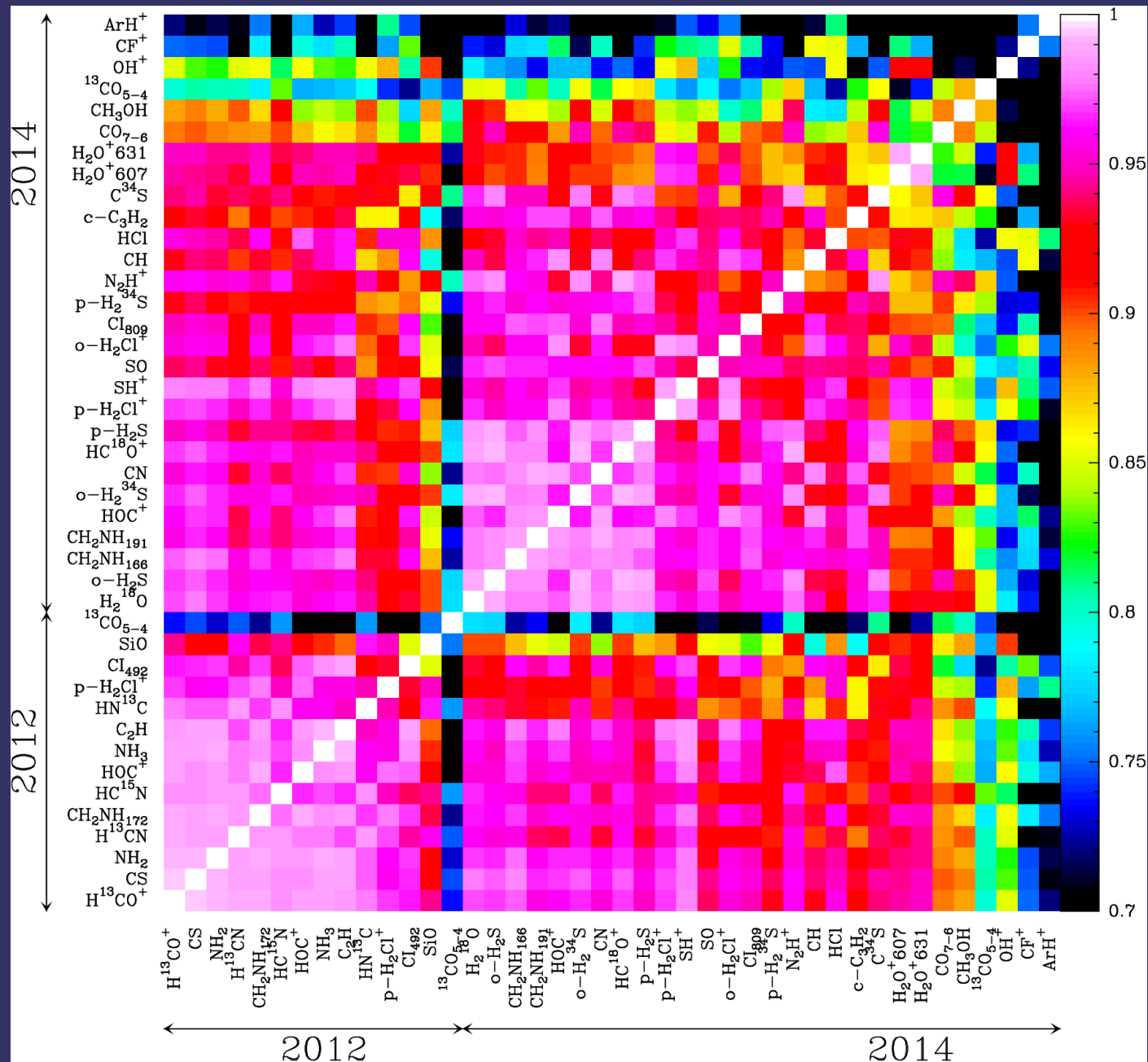
| Species            | Column densities (cm <sup>-2</sup> ) |                         | Ratio<br>SW/NE |
|--------------------|--------------------------------------|-------------------------|----------------|
|                    | SW                                   | NE                      |                |
| HI                 | 1.3 x 10 <sup>21</sup>               | 2.5 x 10 <sup>21</sup>  | 0.5            |
| ArH+               | 2.7 x 10 <sup>13</sup>               | 1.3 x 10 <sup>13</sup>  | 2.1            |
| OH+                | 1.6 x 10 <sup>15</sup>               | 7.6 x 10 <sup>14</sup>  | 2.2            |
| H <sub>2</sub> Cl+ | 1.4 x 10 <sup>13</sup>               | 3.7 x 10 <sup>12</sup>  | 3.8            |
| H <sub>2</sub> O+  | 2.7 x 10 <sup>14</sup>               | 7.0 x 10 <sup>13</sup>  | 3.9            |
| CH+                | 9.7 x 10 <sup>14</sup>               | 1.9 x 10 <sup>14</sup>  | 5.1            |
| CH                 | 7.7 x 10 <sup>14</sup>               | 3.5 x 10 <sup>13</sup>  | 22             |
| HF                 | >3.4 x 10 <sup>14</sup>              | 0.18 x 10 <sup>14</sup> | >19            |
| SH+                | 3.9 x 10 <sup>13</sup>               | <3.2 x 10 <sup>11</sup> | > 120          |

Tracers of increasing molecular fraction



→ multi-phase composition of the absorbing gas

# Chemical correlation – ALMA spectra – SW Ios



ArH<sup>+</sup> is the weird guy  
(tracing almost purely atomic)

CF<sup>+</sup>, <sup>13</sup>CO, CH<sub>3</sub>OH, OH<sup>+</sup>

Also different from the bulk of  
Standard molecules:

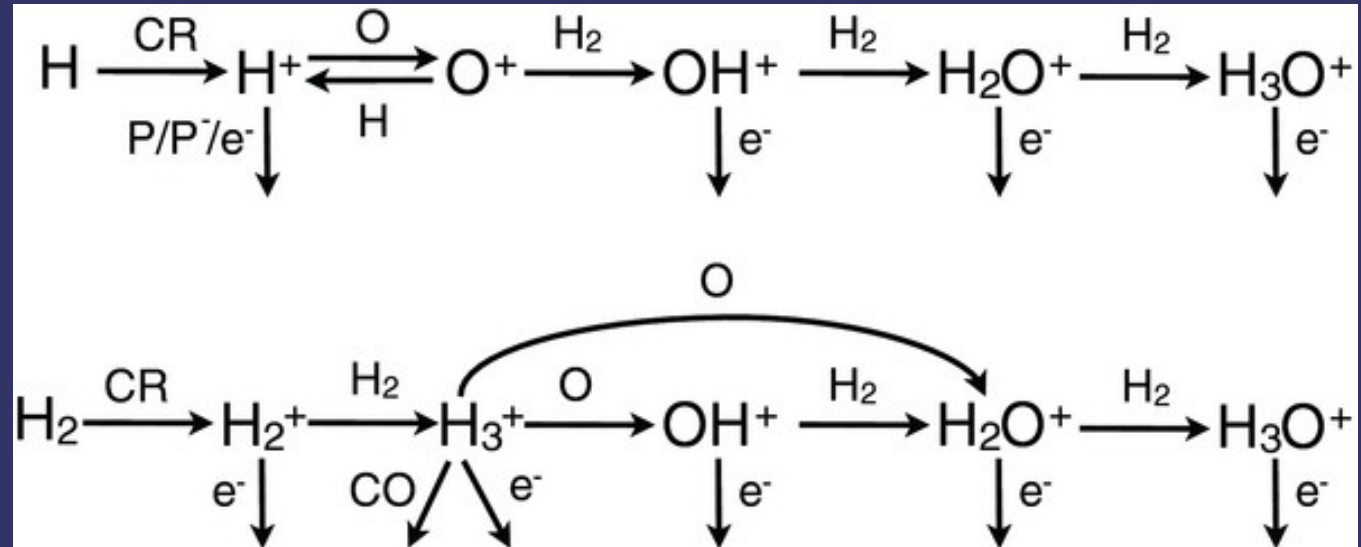
HCO<sup>+</sup>, HCN, CS, HOC<sup>+</sup>,  
CH<sub>2</sub>NH, NH<sub>3</sub>, ...



# Fraction of molecular hydrogen

## Cosmic-ray ionization rate of atomic hydrogen

OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> chemistry network:



Hollenbach et al 2012

The relative abundances of OH<sup>+</sup> / H<sub>2</sub>O<sup>+</sup> provide estimates of:

- the molecular fraction  $f(\text{H}_2)$

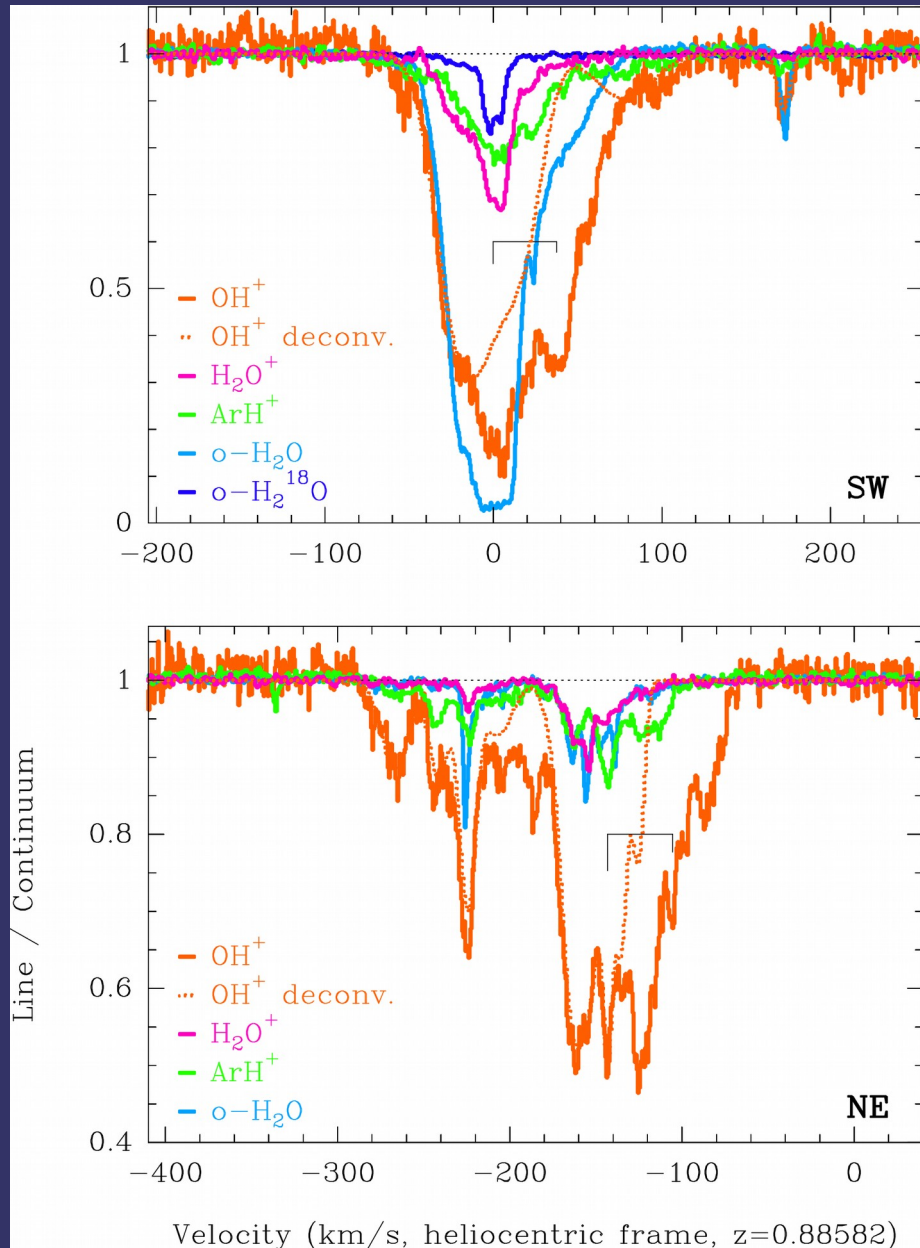
$$f_{\text{H}_2} = \frac{2x_e k_7 / k_4}{N(\text{OH}^+) / N(\text{H}_2\text{O}^+) - k_6 / k_4}$$

- the cosmic-ray ionization rate of atomic hydrogen

Indriolo et al 2015

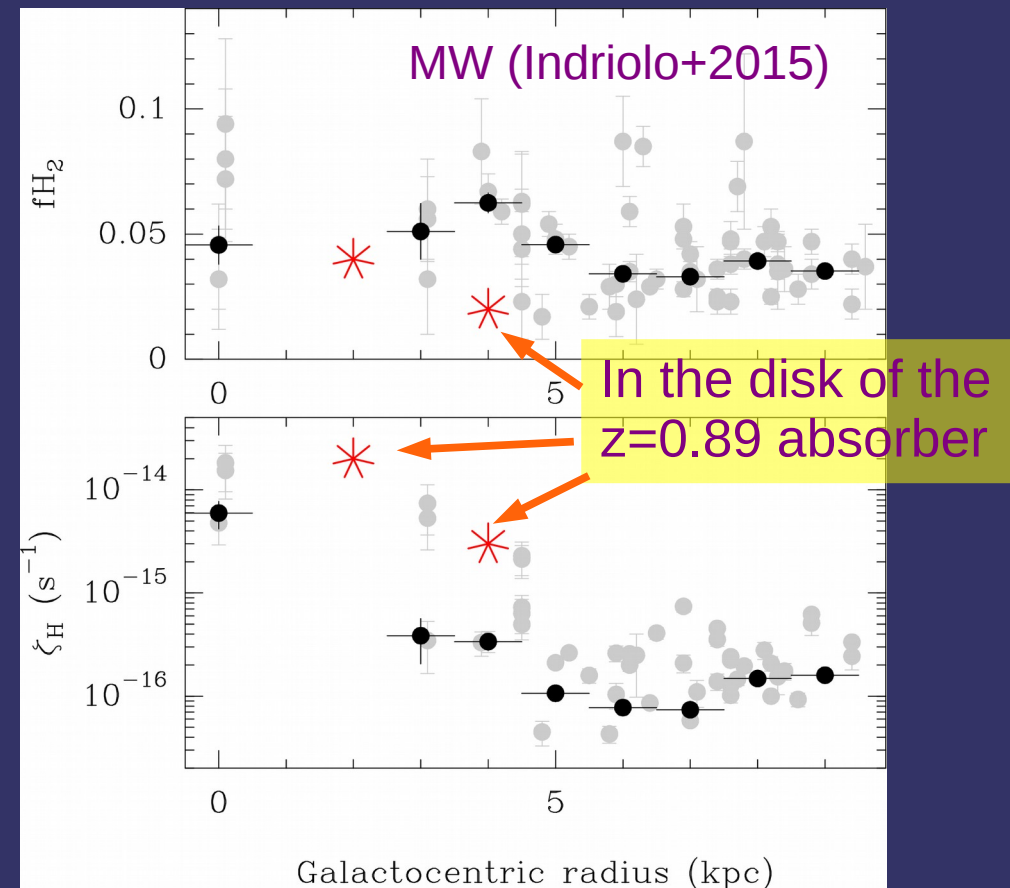
$$\epsilon_{\zeta\text{H}} = \frac{N(\text{OH}^+)}{N(\text{H})} n_{\text{H}} x_e \left[ \frac{k_7}{N(\text{OH}^+) / N(\text{H}_2\text{O}^+) - k_6 / k_4} + k_5 \right]$$

# Fraction of molecular hydrogen Cosmic-ray ionization rate of atomic hydrogen



Use  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  relative abundances  
See e.g. Hollenbach+2012, Indriolo+2015

(Caveat: fractional abundance of electrons)



# Summary “Chemistry in PKS1830”

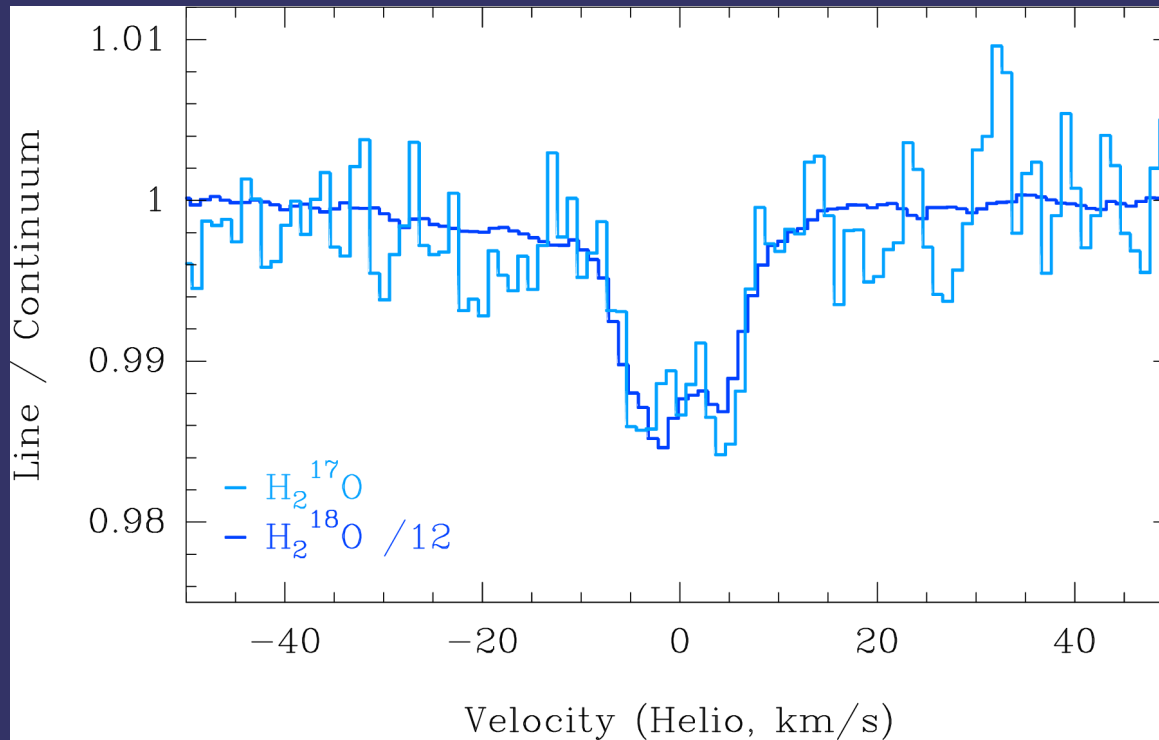
- Chemistry typical of diffuse/translucent clouds in the MW
- Hydrides reveals the multi-phase composition of the absorbing gas
- Observations of species difficult to observe from the ground at  $z=0$   
e.g.  $\text{H}_2\text{O}$ ,  $\text{OH}^+$ , ...
- Herschel in the MW (PRISMAS)  $\Leftrightarrow$  ALMA at  $z=0.89$   
e.g.,  $\text{CH}^+$ ,  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{HF}$ ,  $\text{ArH}^+$ , ...  
with high-quality spectral baseline and no contamination by emission
- Search for new interstellar molecules (or get deep upper limits)

# Isotopic ratios and constraints on nucleosynthesis

For molecular absorbers at intermediate redshift  $z=0.68 - 0.89$ :

- Look-back time of about half the current age of the Universe
- Possible to measure isotopic ratios of C, N, O, S, Si, Cl, Ar
- Evolution effects already visible
- Low mass stars ( $< \sim 1.5$  Mo) have no time to contribute
  - >> Signature from massive star nucleosynthesis

# Oxygen



ALMA Cycle 1 & 2

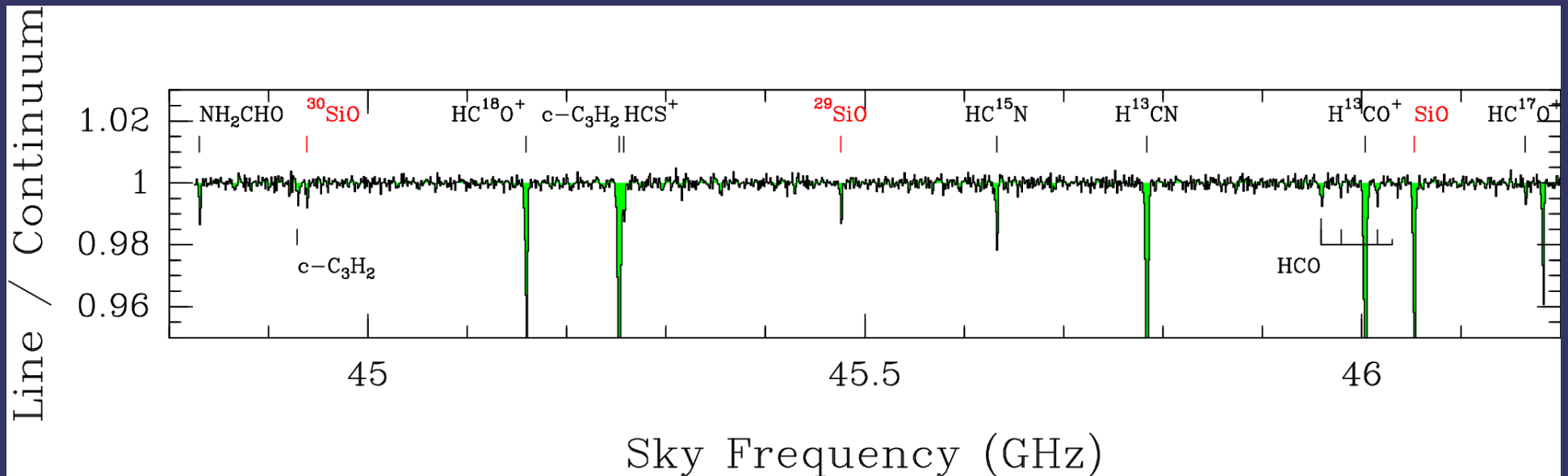
$$^{18}\text{O}/^{17}\text{O} = 12 \pm 2 \quad @ \quad z=0.89$$

Solar = 5.5

ISM = 3.5  $\pm$  0.2

AGB IRC+10216 = 0.7  $\pm$  0.2

# Silicon

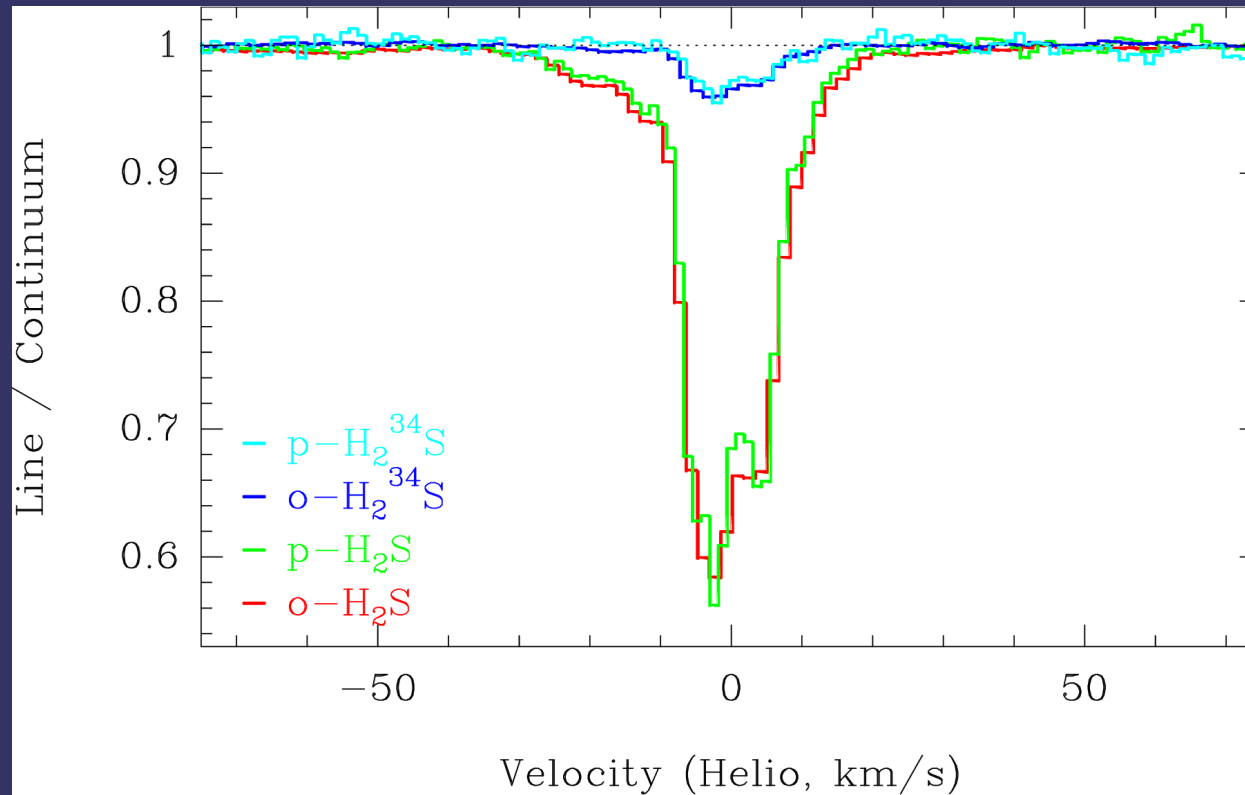


ATCA, Muller et al 2011, 2013

ATCA 2011  $\rightarrow$   $^{28}\text{Si}/^{29}\text{Si} = 6.5 \pm 0.5$  @  $z=0.89$   
 $\rightarrow$   $^{29}\text{Si}/^{30}\text{Si} = 1.8 \pm 0.3$

Earth and local ISM:  $^{28}\text{Si}/^{29}\text{Si} = 20$   
 $^{29}\text{Si}/^{30}\text{Si} = 1.5$

# Sulfur



$^{32}\text{S}/^{34}\text{S} \sim 12$  @  $z=0.89$

ALMA Cycle 2

Solar = 22

ISM =  $19 \pm 8$  (Lucas & Liszt 1998)

AGB IRC+10216 =  $21.8 \pm 2.6$  (Cernicharo et al 2000)

# Argon

Detection of argonium in SW & SW los:

$$^{36}\text{Ar}/^{38}\text{Ar} = 3.46 \pm 0.16 \quad (\text{SW})$$

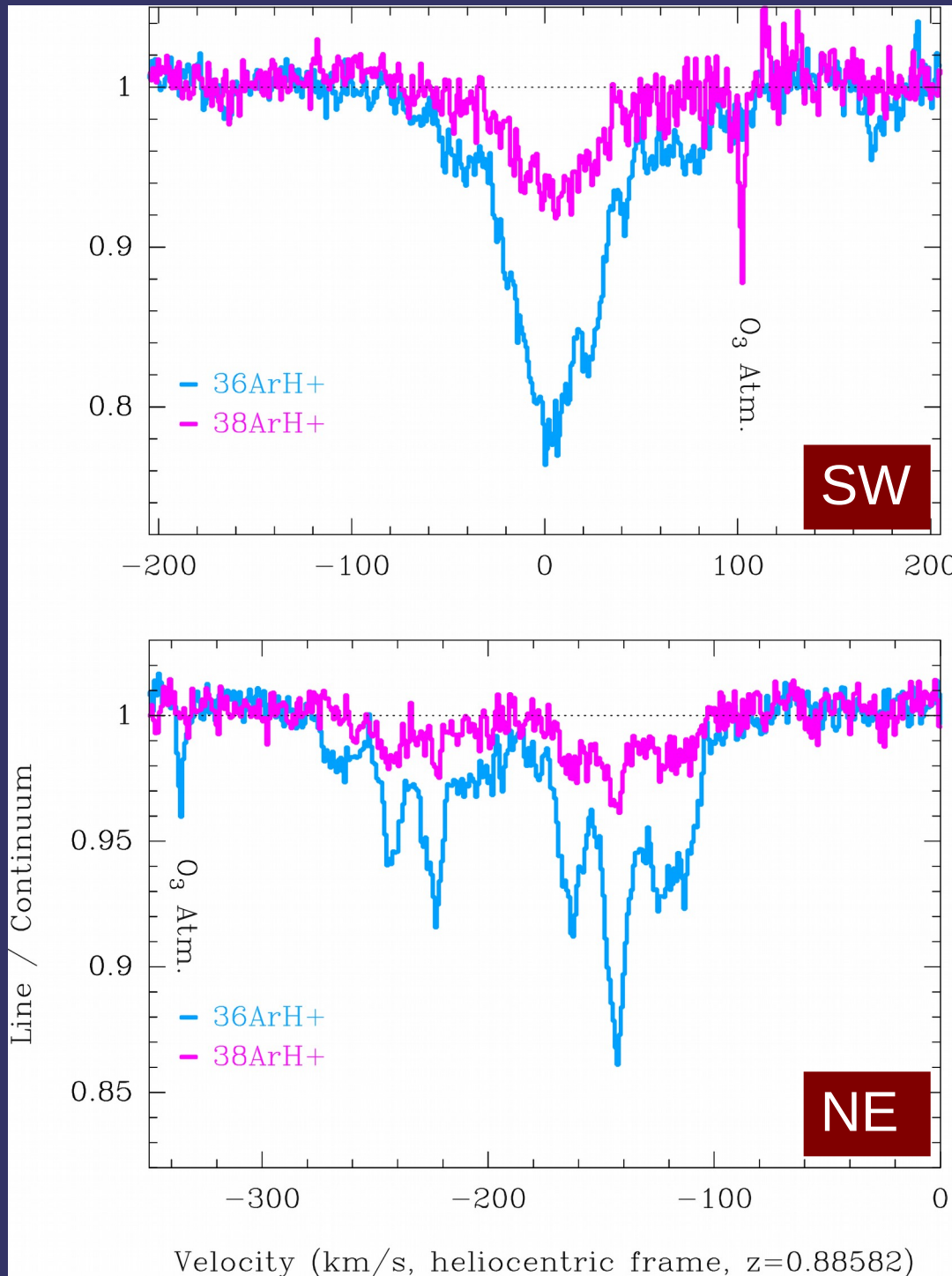
$$= 4.5 \pm 0.3 \quad (\text{NE})$$

@  $z=0.89$

Müller H., Müller S., et al 2015

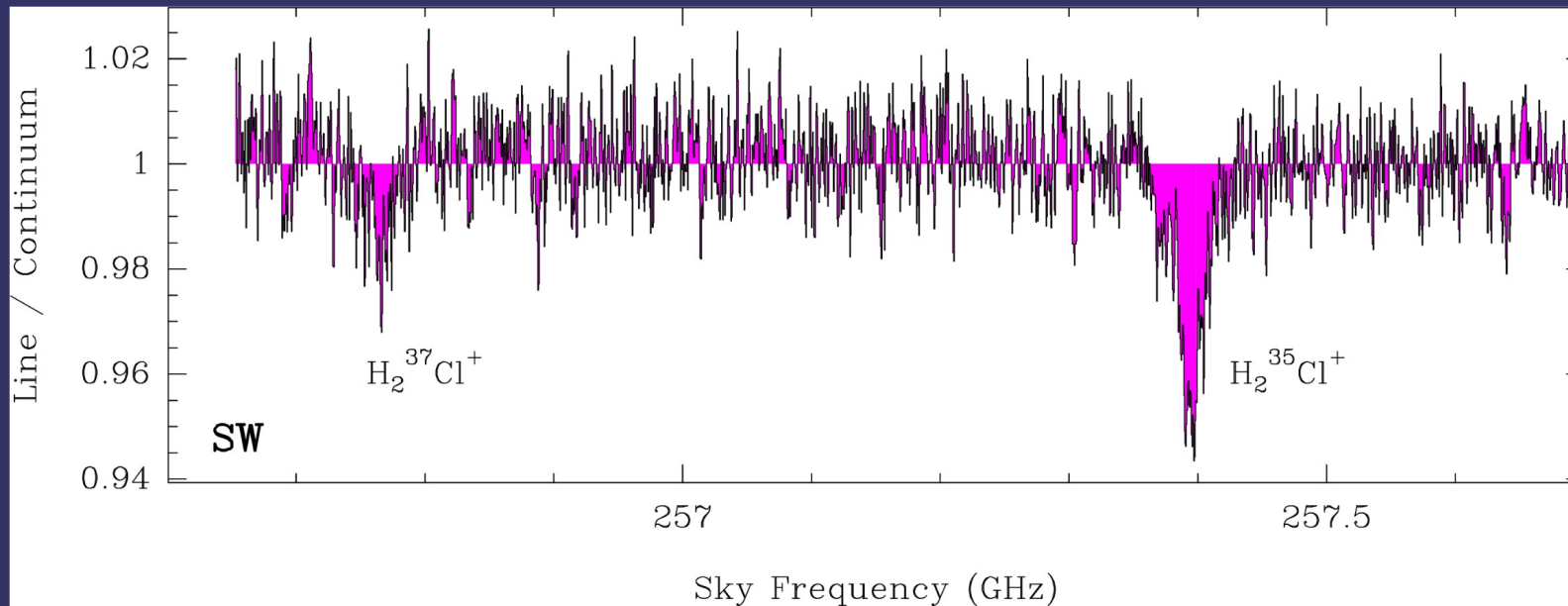
Solar value: 5.5

Alpha-elements Si, S, Ar all have different ratios than solar ...





# Chlorine

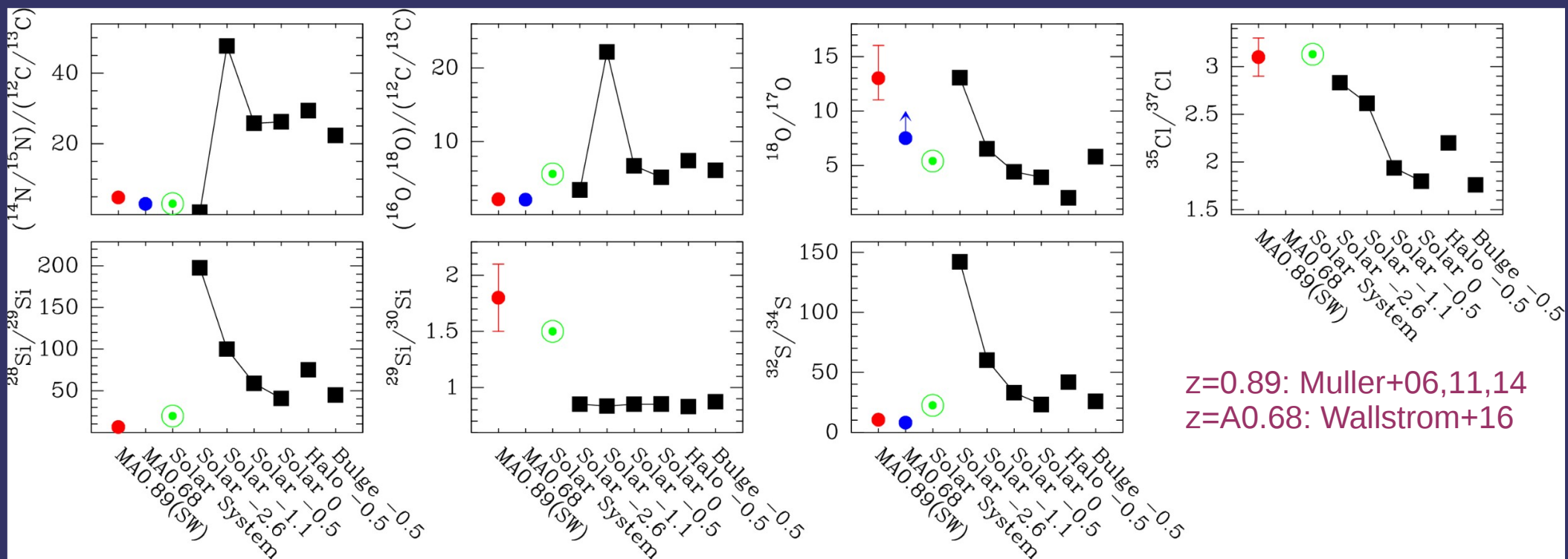


Detection of chloronium  $H_2^{35}Cl^+$  and  $H_2^{37}Cl^+$  toward PKS1830-211  
ALMA Cycle 0 – Muller et al 2014b

$$\rightarrow {}^{35}Cl/{}^{37}Cl = 3.1_{-0.2}^{+0.3} @z=0.89$$

- ${}^{35}Cl/{}^{37}Cl = 3.1$  Earth
- $= 3.1 \pm 0.6$  AGB IRC+10216 (Cernicharo et al 2000)
- $= 1 - 5$  in various Galactic sources (Cernicharo et al 2010, Peng et al 2010)

# Comparison with time / metallicity evolution models



Models from Kobayashi et al 2011

Solar neighbourhood at  $[\text{Fe}/\text{H}] =$

- 2.6 (metal-poor SNe II)
- 1.1 (SNe II + AGB)
- 0.5 (SNe II + AGB + SNe Ia)

Halo and Bulge components

But, what is the metallicity, IMF, SFR in the molecular absorbers ?

# Summary

Molecular absorbers at intermediate redshift:

- Probe the interstellar chemistry and physical conditions in the disk of distant galaxies

Molecules as cosmological probes:

- Evolution of the CMB temperature with redshift
- Test of invariance of fundamental constants
- Isotopic ratios and constraints on nucleosynthesis

Strong interests to find more absorbers, hopefully at  $z > 1$  !