Paleo-spectroscopy: retrieve and complement past data for radioastronomy searches

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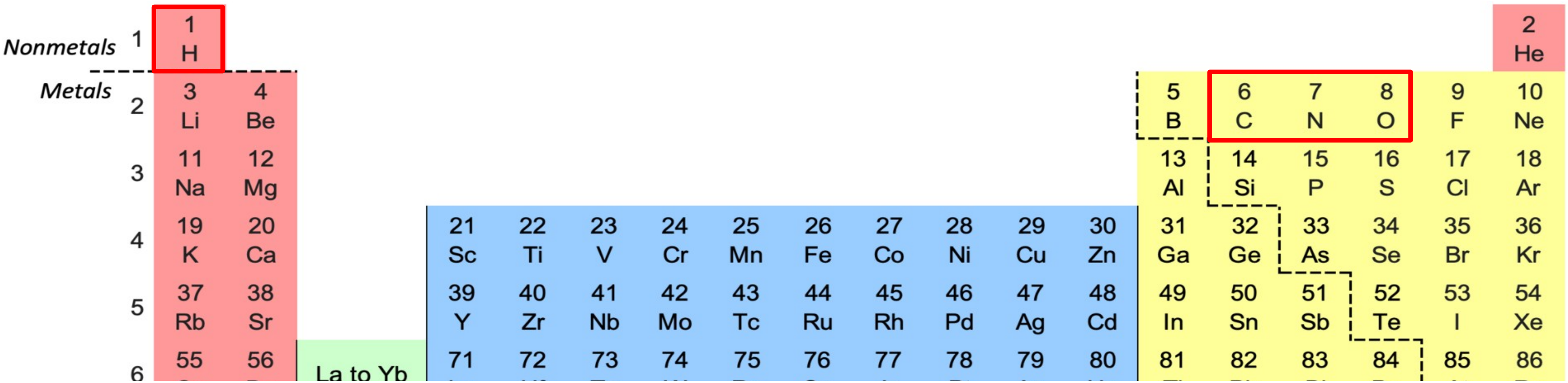
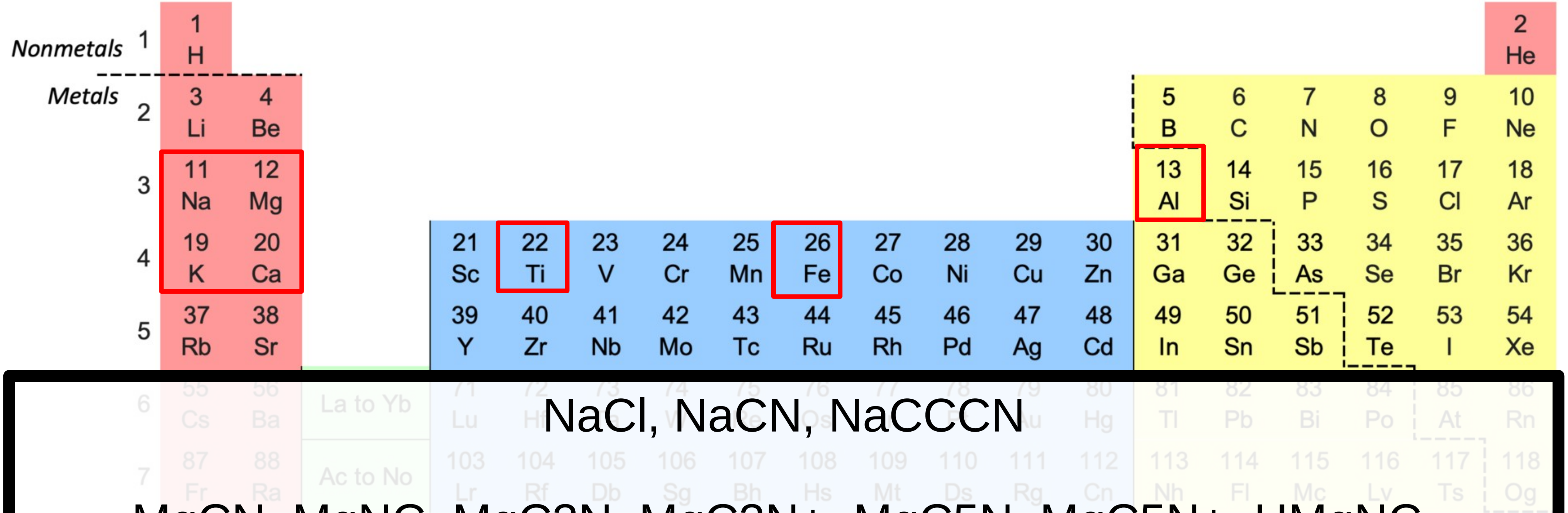
Molecules in space

- So far, according to The Cologne Database for Molecular Spectroscopy: *about 300 molecules have been detected in the interstellar medium or circumstellar shells.*
- The constituents of most of them are light atoms (H, C, O, N) but also heavier atoms are present.



Metals III/IV period



NaCl, NaCN, NaCCCN

MgCN, MgNC, MgC3N, MgC3N+, MgC5N, MgC5N+, HMgNC, HMgC3N, MgC2, MgC2H, MgC4H, MgC4H+, MgC6H, MgC6H+

AlF, AlCl, AlNC, AlO, AlOH

KCl, KCN CaNC FeCN TiO, TiO2

Nonmetals

HF, CF+, AlF

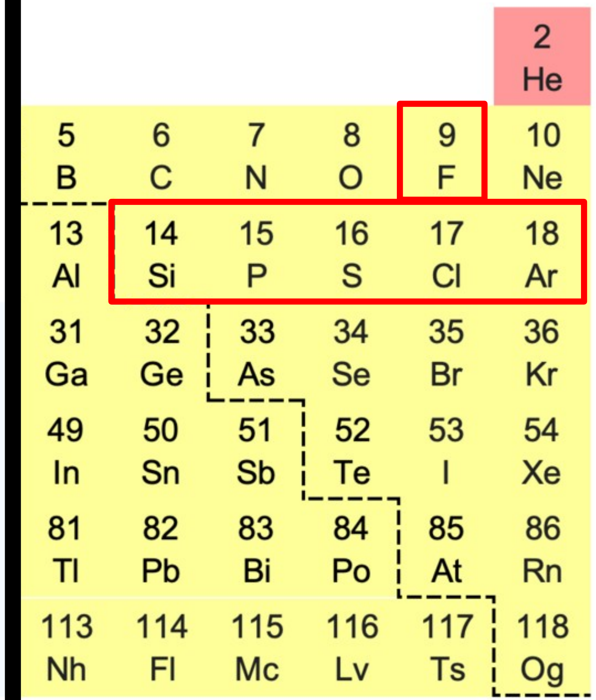
SiC, SiN, SiO, SiS, SiP?, SiH?, SiH4*, SiCN, SiNC, Si2C, C4Si, c-SiC2, c-SiC3, **SiH3CN**, **CH3SiH3**

CP, SiP?, PNPO, PO+, PH3, HCP, CCP

SH+, SH, SO, SO+, SO2, NS, NS+, CS, H2S, OCS, HCS+, HS2, HCS, HSC, NCS, C2S, C3S, C4S, C5S, HCCS, HCCS+, HC3S+, HC4S, H2CS, H2C2S, H2C3S, HCCCHS, HNCS, HSCN, **HC(S)CN**, **HC(O)SH**, **CH3SH**, **CH3CH2SH**

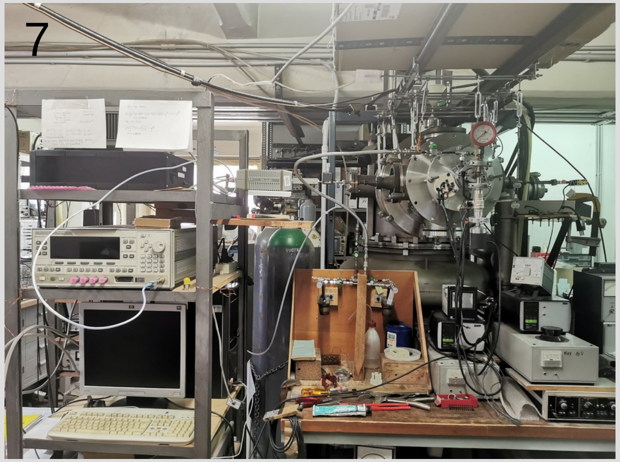
HCl, HCl+, H2Cl+, KCl, AlCl, NaCl, **CH3Cl**

ArH+



Free-jet mw/mmw spectroscopy lab.

Silicon		Sulfur		Chlorine	
dimethylsilane	C_2H_8Si	thioglycolic acid	$C_2H_4O_2S$	2-chloropropanoic acid	$C_3H_5ClO_2$
trimethylsylanol	$C_3H_{10}OSi$	dimethyl sulfoxide	C_2H_6OS	3-chloropropanoic acid	$C_3H_5ClO_2$
		thioacetamide	C_2H_5NS		
		cysteamine	C_2H_7NS		
		1-propanethiol	C_3H_8S		
		2-propanethiol	C_3H_8S		
		1,3-propanedithiol	$C_3H_8S_2$		
		thioglycerol	$C_3H_8O_2S$		
		sulfanilamide	$C_6H_8N_2O_2S$		



Free Jet Absorption Stark Modulated Microwave Spectrometer
Range 60-78 GHz
Resolution 0.3 MHz

6 C	7 N	8 O	9 F
14 Si	15 P	16 S	17 Cl

Molecular Beam Fourier Transform Microwave Spectrometer
Range 6-18 GHz
Resolution 0.01 MHz

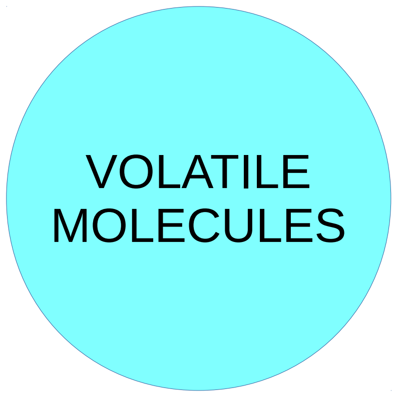
Cold cases

Silicon		Sulfur		Chlorine	
dimethylsilane	C_2H_8Si	thioglycolic acid	$C_2H_4O_2S$	2-chloropropanoic acid	$C_3H_5ClO_2$
		dimethyl sulfoxide	C_2H_6OS		
		thioacetamide	C_2H_5NS		
		cysteamine	C_2H_7NS		
		1/2-propanethiol	C_3H_8S		

- The spectra of the lightest and more volatile compounds were measured and assigned decades ago.
- Why investigate them again?

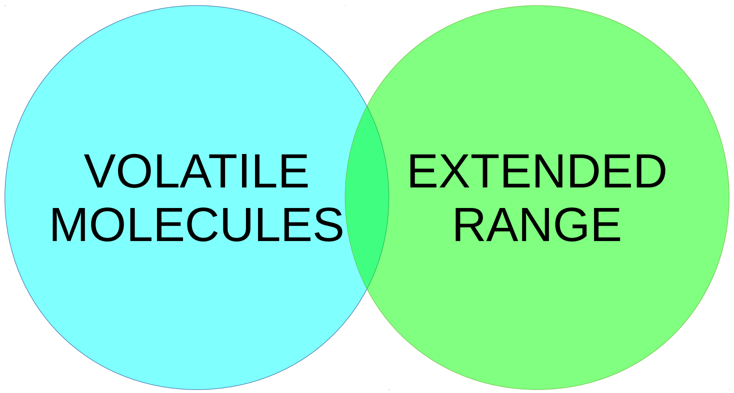
- 1 -

- Light and volatile molecules are the best candidates to be observed by radio-telescopes.



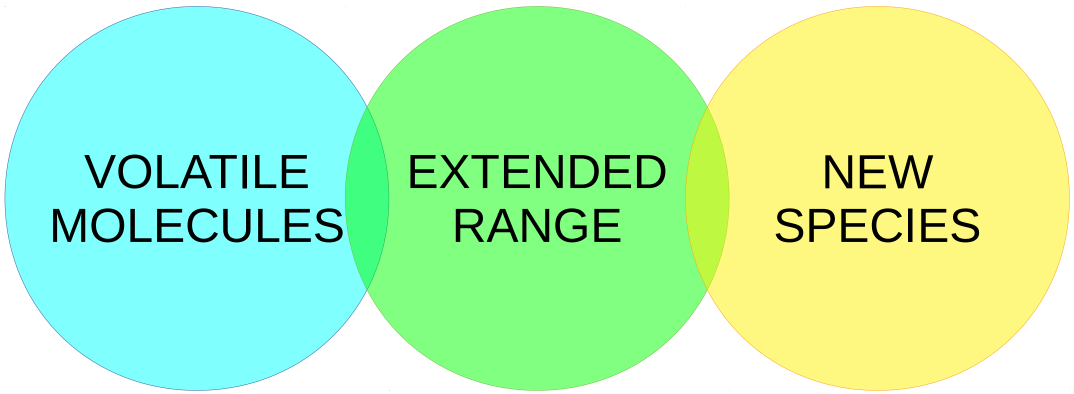
- 2 -

- The observed frequency range can be extended in order to measure additional transition lines and improve the predictive power of the model.



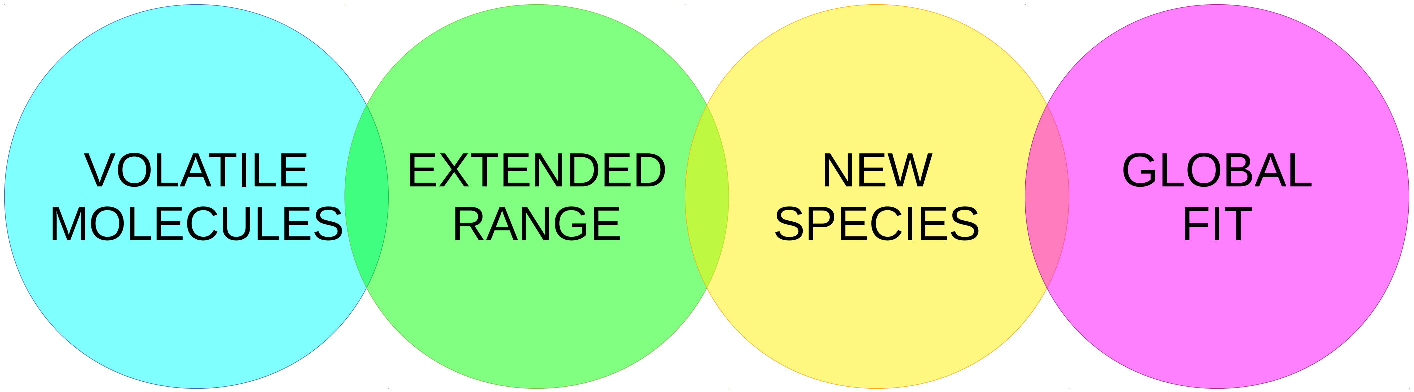
- 3 -

- In the case of flexible molecules, measurements performed with supersonic expansion, which induces a cooling of the internal degrees of freedom, can lead to the observation of isomers unseen before and sometimes redefine their relative stability scale.



- 4 -

- Often the already known data are not fitted together, therefore it is necessary to collect and merge all the available information and build a global model.
- This is the case of molecules characterized by nuclear quadrupole coupling interactions or large amplitude motions as the methyl internal rotation.
- Nowadays, it is possible to fit all these spectral features together, providing a reliable description of the fine and hyperfine structure, which can be much helpful in the assignment of crowded astronomic surveys.



ALMA Archive

- Project: Moving Past Small Number Statistics in Astrochemistry: A Molecular Survey of 25 Hot Cores, Brett McGuire et al. - **2019.1.00246.S**
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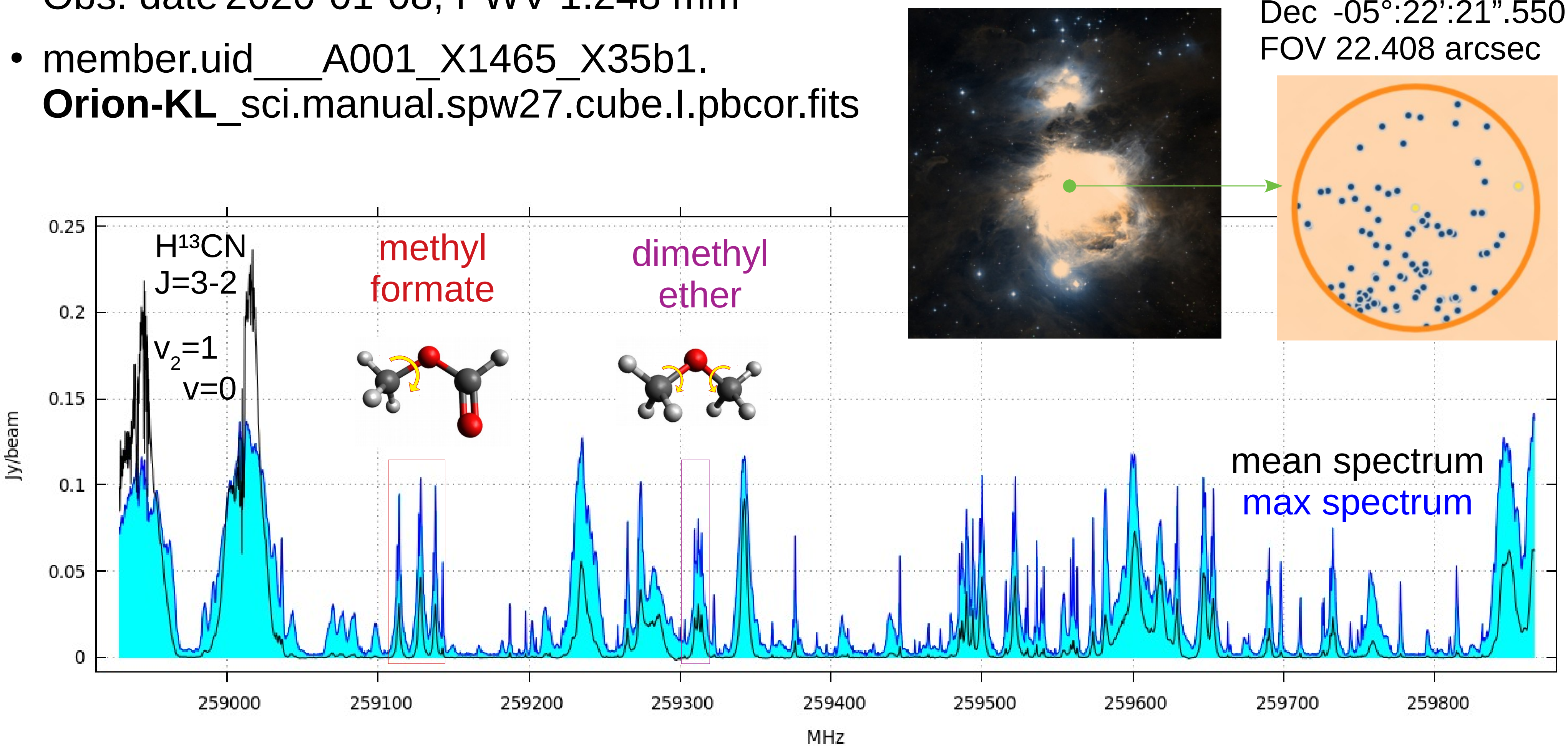
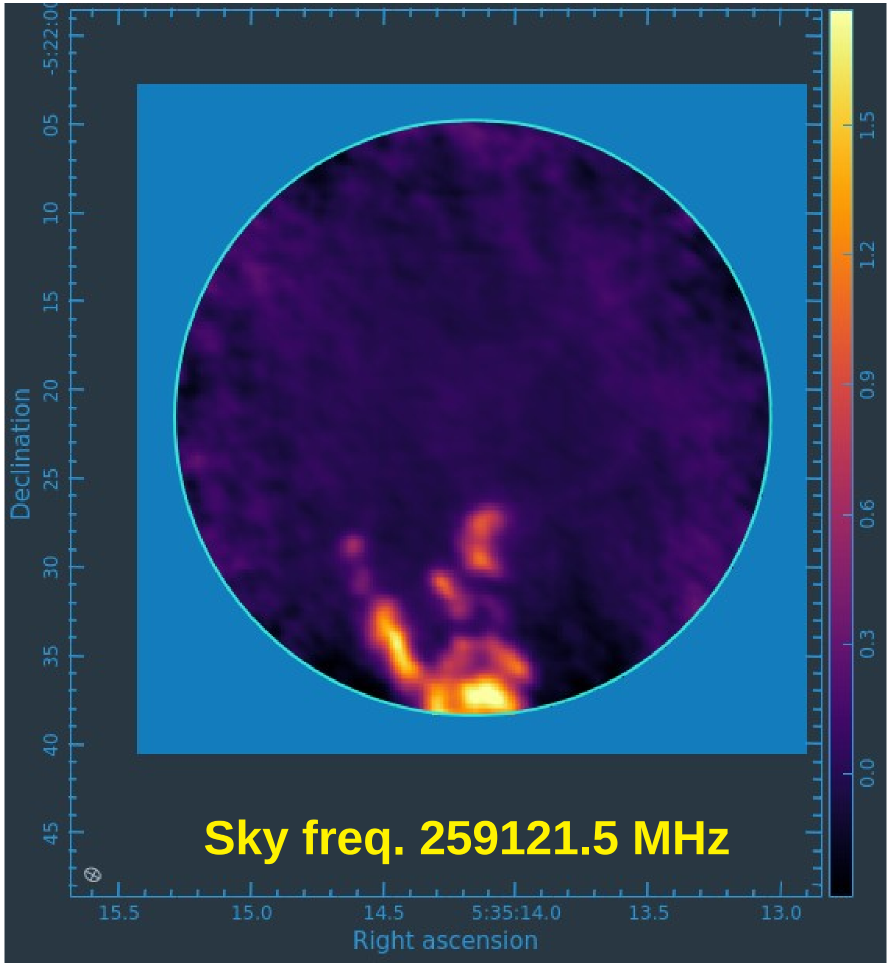


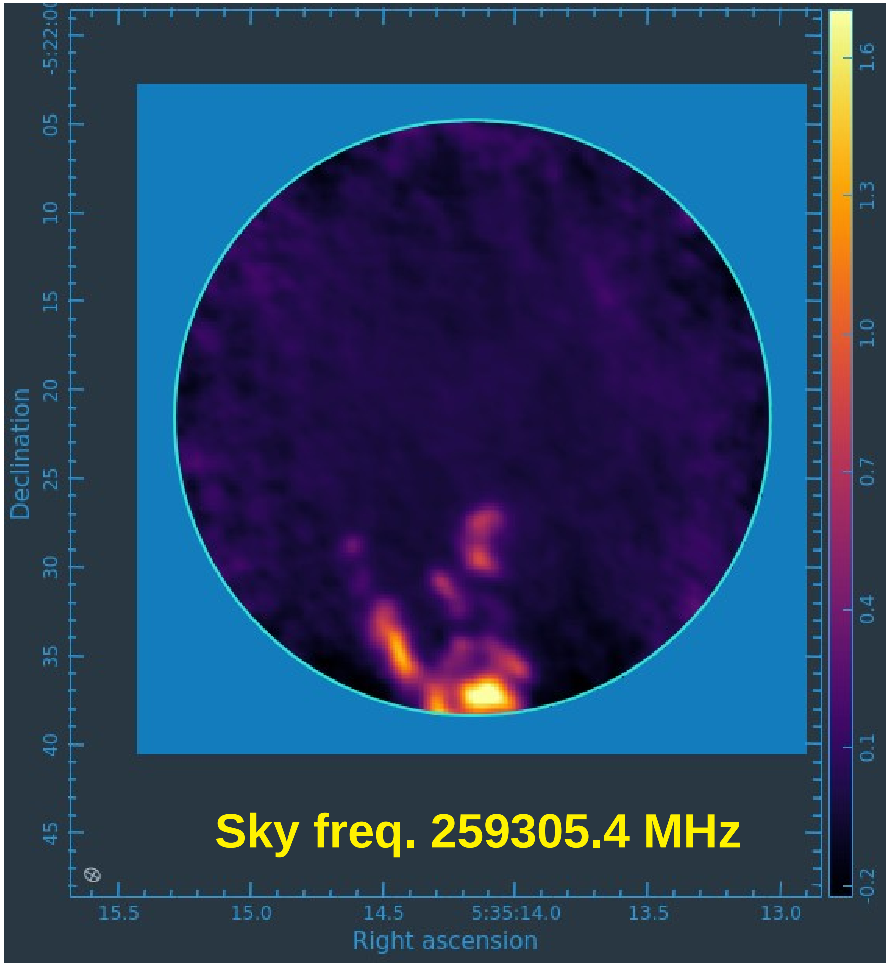
ALMA tools: CARTA

Cube Analysis and Rendering Tool for Astronomy

Methyl formate CH3OCHO

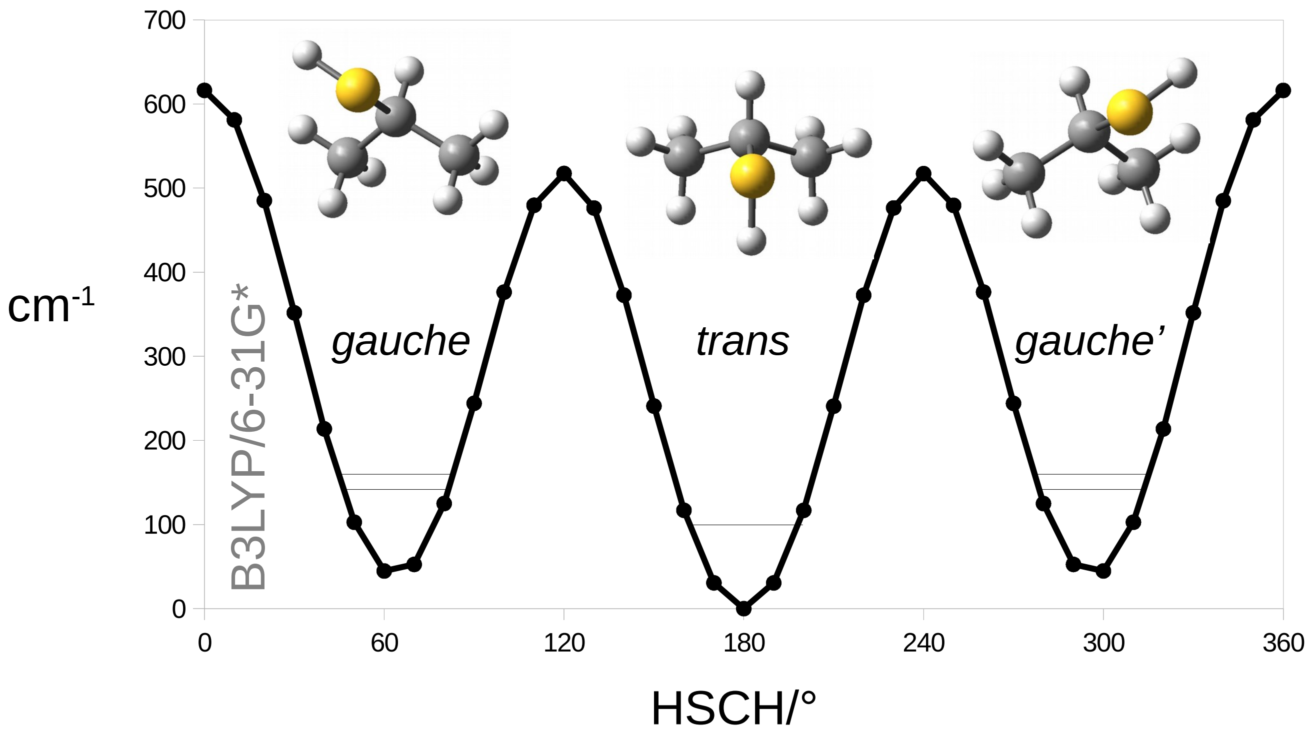


Dimethyl ether CH3OCH3



Alkanethiols / Alkyl mercaptans

- **CH3SH**
  SgrB2(N2), SgrB2(OH), G+0.693-0.027, Hot Core G327.3-0.6, IRAS 16293-2422
- **CH3CH2SH**
  SgrB2(N), G+0.693-0.027, Orion-KL?
- **works in progress:**
- **CH3CH2CH2SH**
- **CH3CH(SH)CH3**



2-propanethiol

JOURNAL OF MOLECULAR SPECTROSCOPY 56, 257–269 (1975)

Microwave Spectrum and Rotational Isomerism in Isopropyl Mercaptan

JOHN H. GRIFFITHS AND JAMES E. BOGGS

A microwave investigation of isopropyl mercaptan has established the existence of both *trans* and *gauche* conformers, the *trans* being more stable by 57 cal mole^{-1}. Stark effect measurements give the dipole moments as 1.61 ± 0.2 D for the *trans* and 1.53 ± 0.2 D for the *gauche* species. The spectra of the isotopic species $(CH_3)_2CH^{32}SD$, $(CH_3)_2CH^{34}SH$, and $(CH_3)_2CH^{34}SD$ of the *trans* form have also been analyzed, providing a limited amount of structural data.

The rotational spectrum of the *gauche* isomer is noticeably influenced by inversion. Interactions between energy levels in the two lowest inversion states have been satisfactorily accounted for in terms of rotational constants, coupling parameters (G_a and G_c), and ΔE_0, the inversion level splitting. ΔE_0 is found to be 562.4 MHz for the ground state of $(CH_3)_2CHSH$ and 10.0 MHz for $(CH_3)_2CHSD$. A value of 1.98 kcal mole^{-1} has been calculated for the barrier to internal rotation of the -SH group in terms of a V_3 potential.

14-41 GHz

[MHz]	Global fit
A	7877.274(7)
B	4524.697(5)
C	3172.124(4)
D_J	1.22(1)e-3
D_{JK}	4.13(7)e-3
d_1	-0.391(9)e-3
d_2	-0.130(4)e-3
ΔE	562.50(2)
F_a	60.63(4)
F_c	96.37(3)
rms	0.16 🤔
N	56+49

60-78 GHz

Final remarks

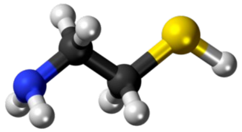
- Considering paleo-data allows for building **global spectral models** that can be used to disentangle astronomical surveys.
- However, some unexpected collateral difficulties must be taken into account:
  - Despite it seems trivial, it can be challenging retrieving not electronic supplementary material from authors, when decades have passed
  - Identifying typos or misleading assignments can be not so straightforward.
- To avoid the same kind of problems to next-generation scientists, besides a crude list of lines, it is necessary to provide the **I/O files** and the **model program** used for the fit.

Acknowledgments

Sonia Melandri

Luca Evangelisti

Wentao Song
Rotational spectroscopic study of cysteamine [64]



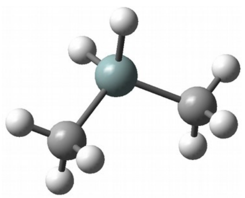
Giovanna Salvitti

Fufei Sun

Filippo Baroncelli

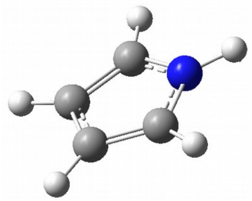
Emanuele Pizzano

Andrea Maggio
Free jet mmw torsion-rotation spectrum of a silicon containing molecule: dimethyl sylane [68]



Silvia Sigismondi

Cleo Whitcombe
Millimetre-wave spectroscopy of pyrrole: a model for astrophysical searches [62]



https://site.unibo.it/freejet/en

PRIN – 2020 BEYOND-2p
Astrochemistry beyond the Second Period Elements

https://beyond2p.weebly.com/

- UniPg, PI Nadia Balucani*
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- OA Arcetri, PI Claudio Codella
- UniBo, PI Sonia Melandri

Thank you for your attention!!!