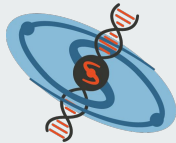




Toward the detection of sulfur reservoir(s) in the JWST era ?

A. Taillard, R. Martín-Doménech, H. Carrascosa, G. M. Muñoz Caro, J. A. Noble, E. Dartois, D. Navarro-Almaida, Á. Sánchez-Monge, A. Fuente

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SUL4LIFE



Introduction - The missing sulfur problem

- Sulfur is the 10th most abundant element in the Universe ([Asplund+2009](#))
- In the ISM, small molecules (e.g. H₂S) believed to act as a **catalyst**
- Sulfur abundance is still uncertain in some regions of the ISM by **several orders of magnitude**
- **Main molecules detected in gas-phase:** SO, SO₂, CS, HCS⁺, H₂CS, C₂S and C₃S

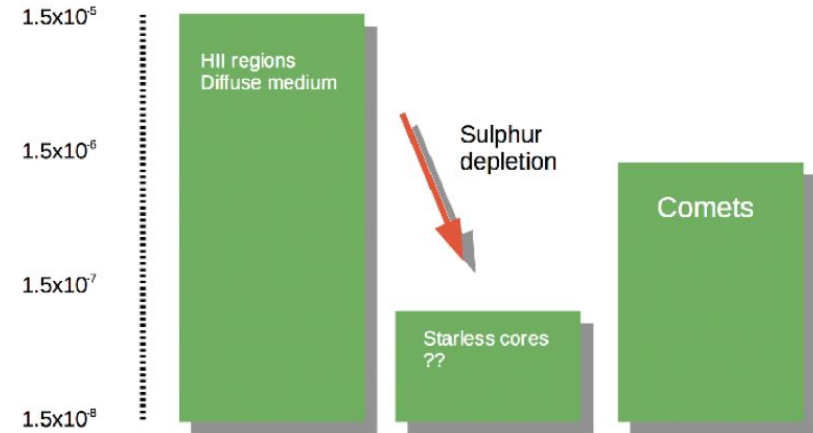
A UNIFIED REPRESENTATION OF GAS-PHASE ELEMENT DEPLETIONS IN THE INTERSTELLAR MEDIUM*

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Received 2009 February 23; accepted 2009 June 1; published 2009 July 13

9. SULFUR: A TROUBLESOME ELEMENT



In-situ observations from 67P comet

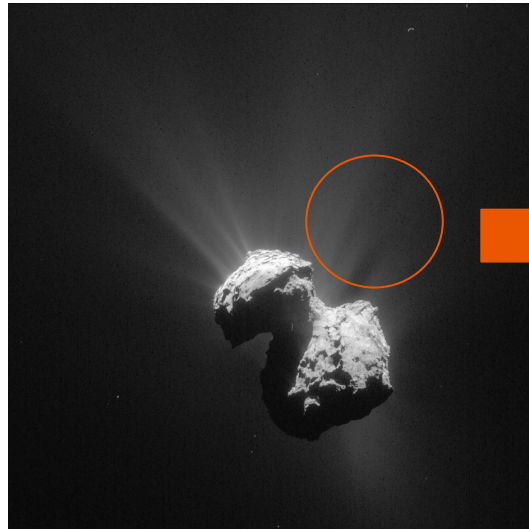
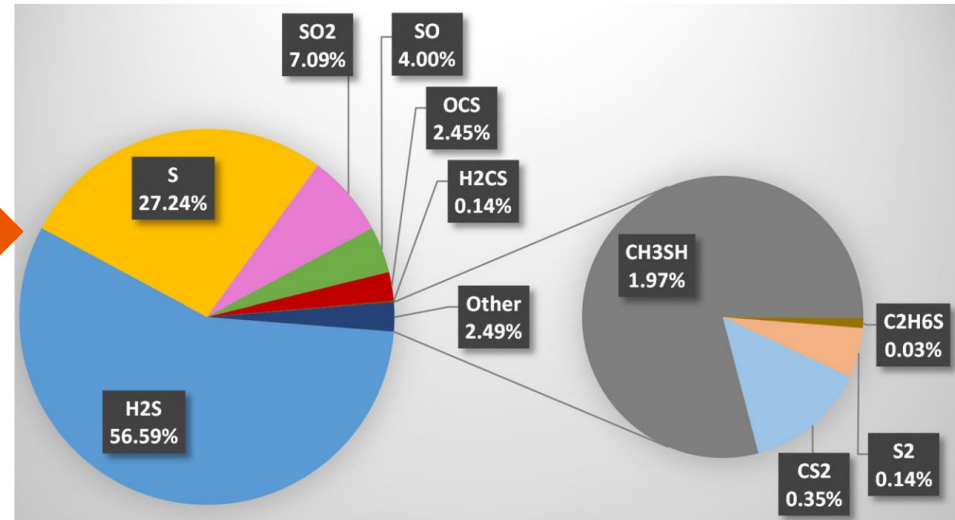


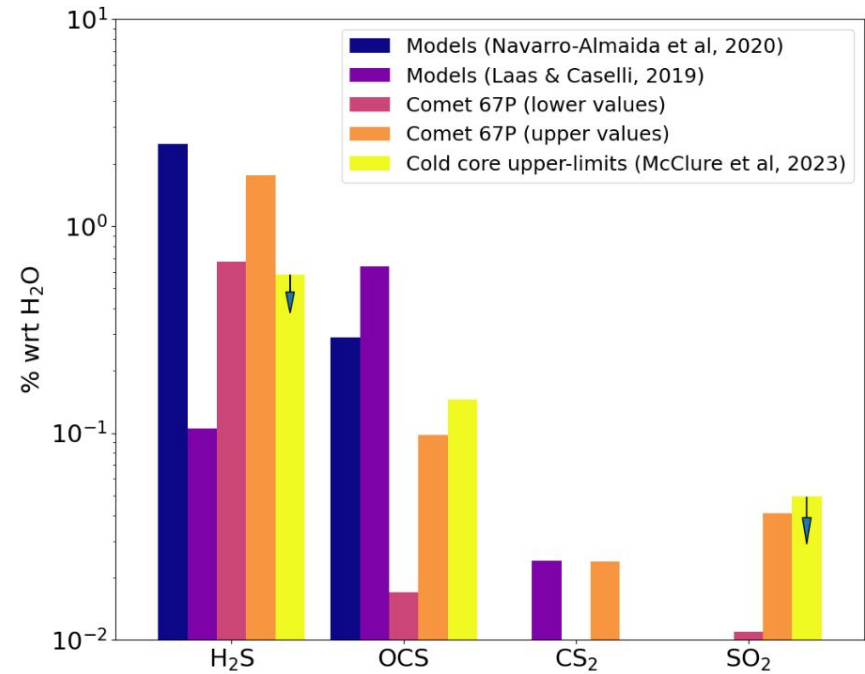
Image credits: ESA/Rosetta/NAVCAM



Calmonte et al. 2016

In chemical models ?

- More than **95%** locked in ices
- Varies a lot depending of initial parameters
- H_2S , SO and OCS are the main molecules predicted



Ice detection so far

- Only **TWO** species identified with only one solidly detected: **OCS**
- Their abundances would account for less than 5% of the total sulfur

Where is the rest ?

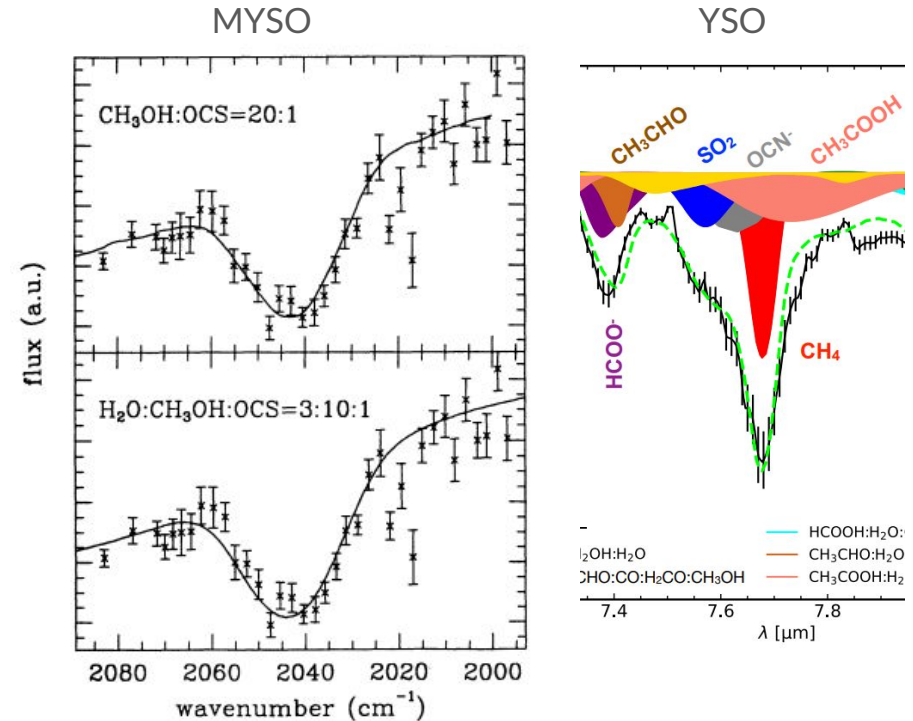
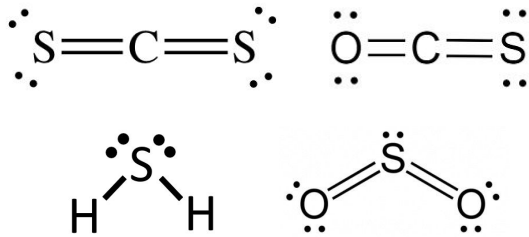
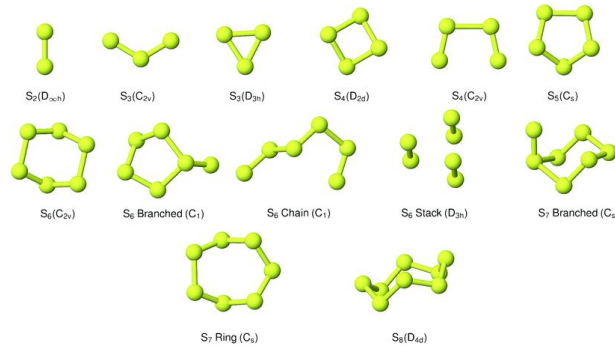


FIG. 7b

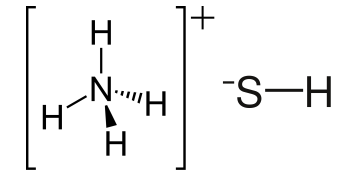
What reservoirs are we considering ?



“Simple”
molecules



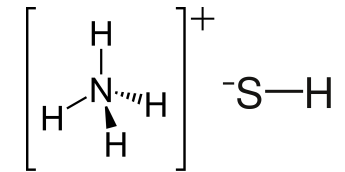
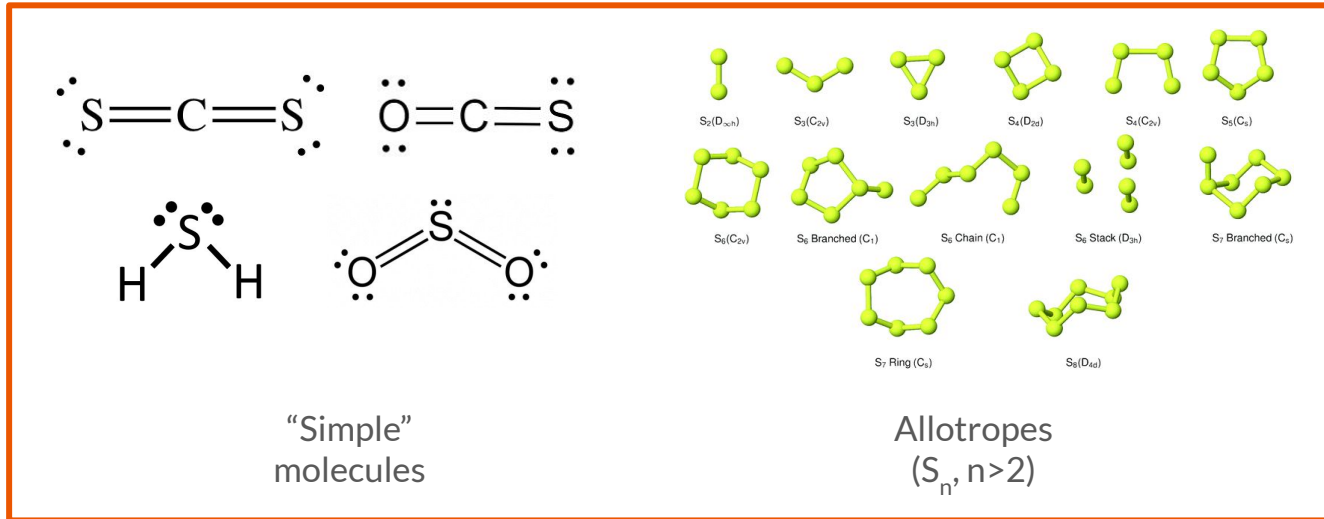
Allotropes
(S_n , $n > 2$)
Cazaux et al. 2022



Salts
Vitorino et al. 2024
Slavicinska et al. 2024

- Locked in ice mantles or (semi-)refractory components ?
- We are still missing ~ 95% of the sulfur... Can JWST help us ?

What reservoirs are we considering ?

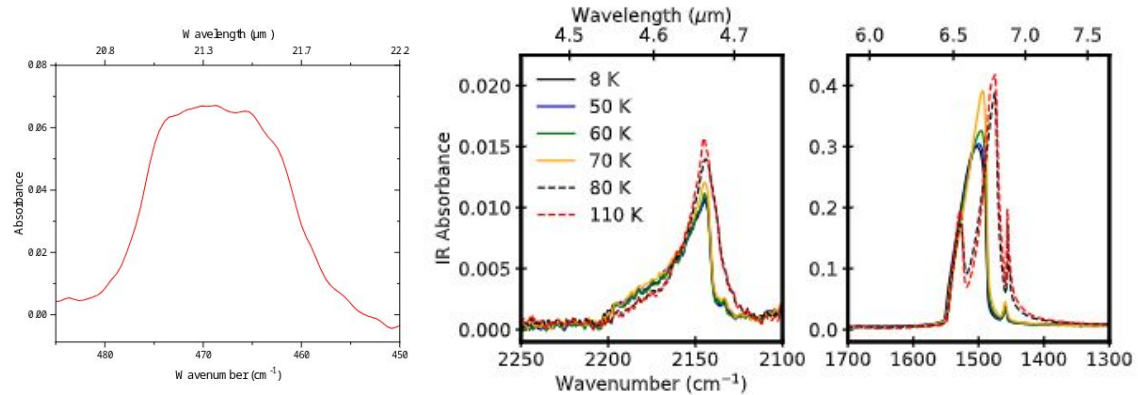


Salts
 Vitorino et al. 2024
 Slavicinska et al. 2024

- Locked in **ice mantles** or **(semi-)refractory** components ?
- We are still missing ~ 95% of the sulfur... Can JWST help us ?

Data from the lab

- We compiled the available band parameters from literature
- New measurements were done for S_8 and CS_2 by our team

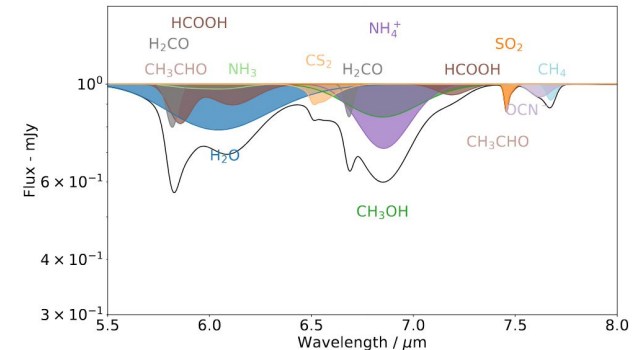
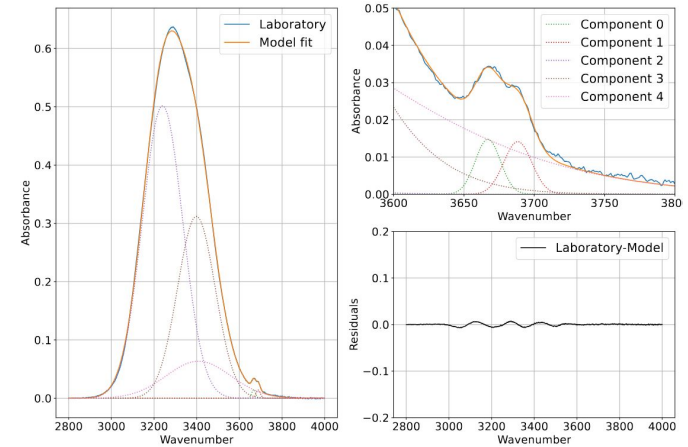


Molecule	Wavenumber (cm ⁻¹)	Wavelength (μm)	Band strength (cm/molecule)	Modes	Reference
H ₂ S ₂	2590.0	4.02	2.40×10^{-17}	S-H stretch	Cazaux et al. (2022) ^a
H ₂ S	2547.0	3.94	1.69×10^{-17}	S-H stretch	Yarnall & Hudson (2022)
CS	1270.0	7.87	-	C-S sym. stretch	Bohn et al. (1992)
CS ₂	1502.0	6.66	1.06×10^{-16}	C-S asym. stretch	This work
CS ₂	2145.0	4.66	2.09×10^{-18}	C-S combination	This work
OCS	514.0	19.46	1.80×10^{-18}	C-S bending	Hudgins et al. (1993)
OCS	2025.0	4.94	1.50×10^{-16}	C-O sym. stretch	Hudgins et al. (1993)
SO ₂	1335.0	7.49	1.47×10^{-17}	S-O asym. stretch	Garozzo et al. (2008)
SO ₂	1149.0	8.70	2.20×10^{-18}	S-O sym. stretch	Garozzo et al. (2008)
SO	1130.0	8.85	2.20×10^{-18}	S-O stretch	Garozzo et al. (2008)
S ₃	680.0	14.71	$\sim 2.50 \times 10^{-17}$	S-S stretch	Estimated value (see the text)
S ₄	665.0	15.04	$\sim 5.00 \times 10^{-17}$	S-S stretch	Estimated value (see the text)
S ₈	471.0	21.23	1.50×10^{-19}	S-S stretch	This work ^b

Synthetic Ice Spectra generator (SynthIceSpec, Taillard et al, in prep)

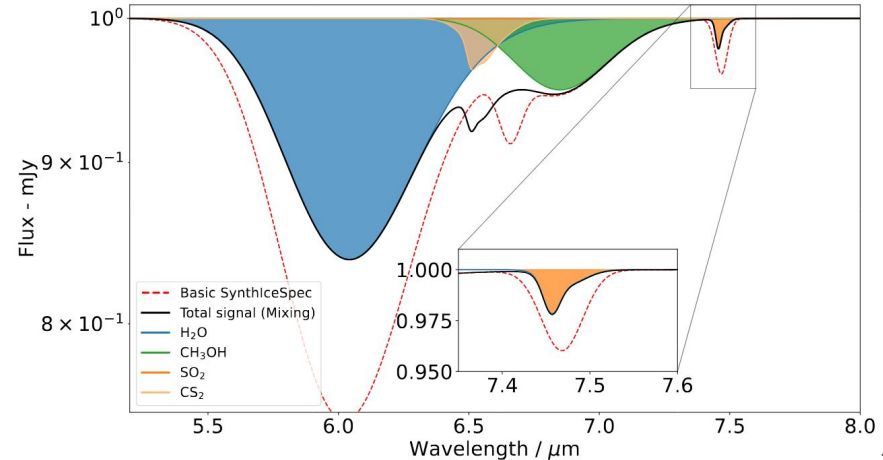
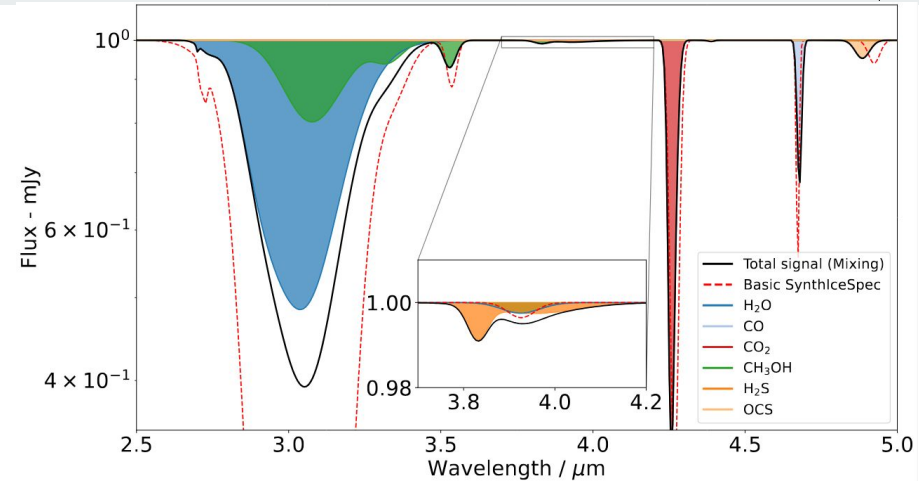
- Based on simple approximations:
 - Each vibrational mode can be represented by a Gaussian (or a combination of Gaussians)
 - Superimposed on the IR spectrum of a background object
 - + Silicates features included
 - Intensity of each band is obtained by multiplying the assumed column density N by the corresponding {band strength and FWHM} (τ)

$$N = \frac{1}{A} \int_{band} \tau_v dv,$$



Adding a bit of mixing

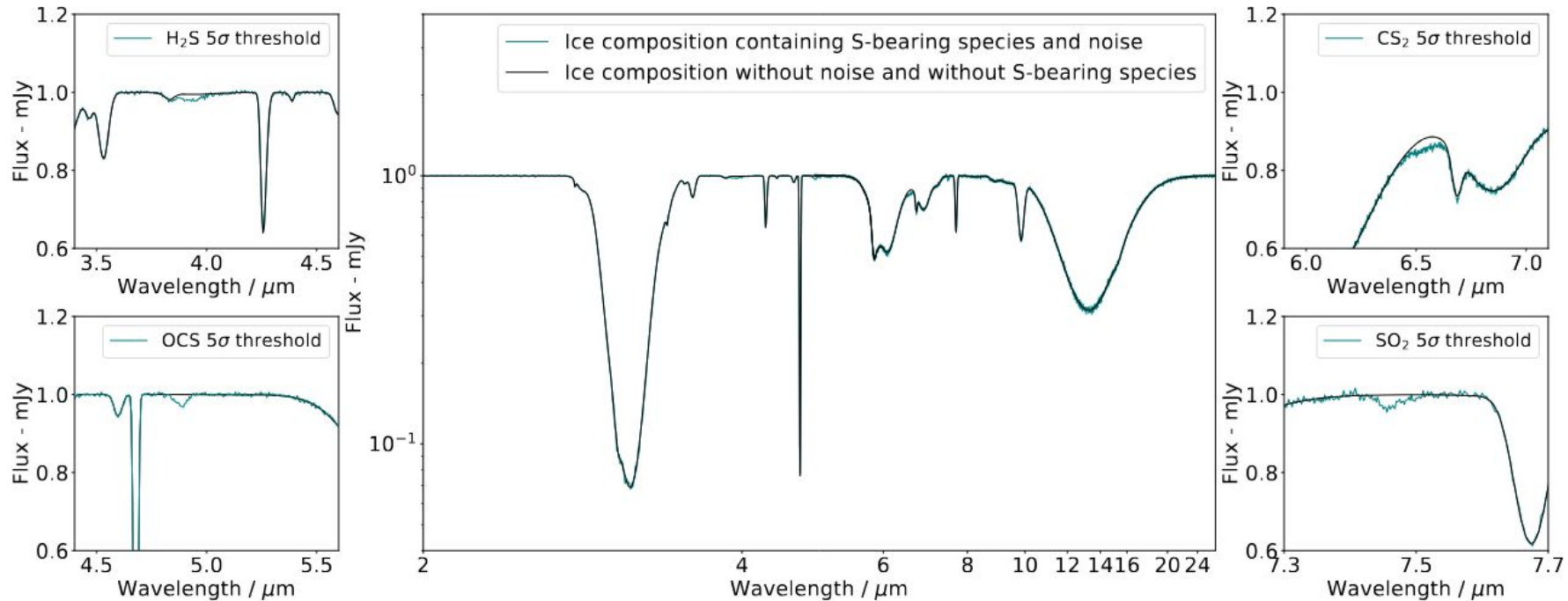
- Considering a $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}_2$ (9:1:2) mixing (Ehrenfreund+1999), we adjusted the band position, width and shape of these four species in SynthIceSpec
- In a similar way, we used mixing with H_2O for all the other molecules present
 - The bands widths/positions/strengths are affected
 - Species overlap in a very simple ice composition
- Adding noise based on real JWST observations (McClure+2023)



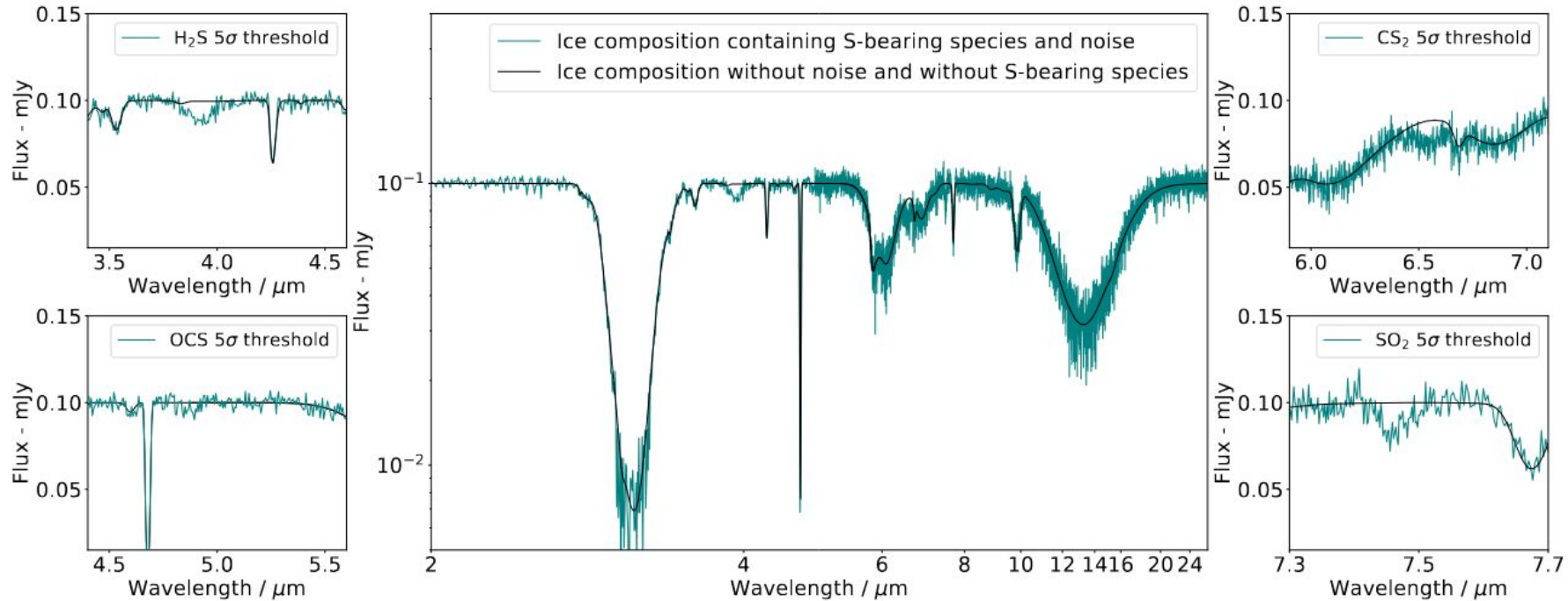
Detectability in 3 science cases (data from Boogert+2015)

Molecule	Column density (molecule/cm ⁻²) (% H ₂ O)		
	Dense cloud	LYSO	MYSO
H ₂ O	9.3×10 ¹⁸	5.0×10 ¹⁸	5.0×10 ¹⁸
CO	2.3×10 ¹⁸ (25.0%)	1.3×10 ¹⁸ (25.0%)	3.5×10 ¹⁷ (7.0%)
CO ₂	2.4×10 ¹⁸ (26.0%)	1.3×10 ¹⁸ (26.0%)	9.5×10 ¹⁷ (19.0%)
CH ₃ OH	7.4×10 ¹⁷ (8.0%)	3.0×10 ¹⁸ (6.0%)	4.5×10 ¹⁷ (9.0%)
NH ₃	0	3.5×10 ¹⁷ (7.0%)	3.5×10 ¹⁷ (7.0%)
NH ₄ ⁺	0	4.0×10 ¹⁷ (8.0%)	5.5×10 ¹⁷ (11.0%)
CH ₄	0	1.5×10 ¹⁷ (3.0%)	1.0×10 ¹⁷ (2.0%)
OCN ⁻	0	2.0×10 ¹⁷ (4.0%)	3.0×10 ¹⁶ (0.6%)
HCOOH	3.7×10 ¹⁷ (4%)	1.0×10 ¹⁷ (2.0%)	2.0×10 ¹⁷ (4.0%)
CH ₃ CHO	0	5.0×10 ¹⁷ (1.0%)	2.7×10 ¹⁷ (5.5%)
H ₂ CO	0	1.0×10 ¹⁷ (2.0%)	2.5×10 ¹⁷ (5.0%)

Dense cloud environment - 1 mJy



Dense cloud environment - 0.1 mJy



5 sigma detection thresholds % to water

Molecule	Column density (molecule/cm ⁻²) (% H ₂ O)		
	Dense cloud	LYSO	MYSO
H ₂ O	9.3×10 ¹⁸	5.0×10 ¹⁸	5.0×10 ¹⁸
	Detection thresholds of sulfur species (assuming rms level derived from McClure et al. (2023) , of 0.003 and 0.005 mJy for NIRSPEC and MIRI respectively)		
H ₂ S (1 mJy)	6.5×10 ¹⁶ (0.7%)	1.1×10 ¹⁷ (2.2%)	6.5×10 ¹⁶ (1.3%)
H ₂ S (0.10 mJy)	5.1×10 ¹⁷ (5.5%)	5.2×10 ¹⁷ (10.5%)	4.3×10 ¹⁷ (8.6%)
H ₂ S (0.04 mJy)	9.0×10 ¹⁷ (9.7%)	6.6×10 ¹⁷ (13.2%)	8.2×10 ¹⁷ (16.5%)
OCS (1 mJy)	6.5×10 ¹⁵ (0.07%)	5.0×10 ¹⁵ (0.1%)	5.0×10 ¹⁵ (0.1%)
OCS (0.1 mJy)	1.4×10 ¹⁶ (0.15%)	3.0×10 ¹⁶ (0.6%)	3.0×10 ¹⁶ (0.6%)
OCS (0.04 mJy)	2.8×10 ¹⁶ (0.3%)	6.5×10 ¹⁶ (1.3%)	6.0×10 ¹⁶ (1.2%)
CS ₂ (1 mJy)	0.9×10 ¹⁶ (0.1%)	1.0×10 ¹⁶ (0.2%)	1.0×10 ¹⁶ (0.2%)
CS ₂ (0.1 mJy)	4.6×10 ¹⁶ (0.5%)	4.5×10 ¹⁶ (0.9%)	4.5×10 ¹⁶ (0.9%)
CS ₂ (0.04 mJy)	1.3×10 ¹⁷ (1.4%)	1.0×10 ¹⁷ (2.0%)	1.1×10 ¹⁷ (2.1%)
SO ₂ (1 mJy)	1.8×10 ¹⁶ (0.2%)	2.5×10 ¹⁶ (0.5%)	2.0×10 ¹⁶ (0.4%)
SO ₂ (0.1 mJy)	1.2×10 ¹⁷ (1.3%)	1.5×10 ¹⁷ (3.0%)	1.1×10 ¹⁶ (2.2%)
SO ₂ (0.04 mJy)	2.3×10 ¹⁷ (2.5%)	2.6×10 ¹⁷ (5.2%)	2.1×10 ¹⁷ (4.2%)

5 sigma detection thresholds % to water

Molecule	Column density (molecule/cm ⁻²) (% H ₂ O)		
	Dense cloud	LYSO	MYSO
H ₂ O	9.3×10 ¹⁸	5.0×10 ¹⁸	5.0×10 ¹⁸
Detection thresholds of sulfur species (assuming rms level derived from McClure et al. (2023) , of 0.003 and 0.005 mJy for NIRSPEC and MIRI respectively)			
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H ₂ S (0.04 mJy)	9.0×10 ¹⁷ (9.7%)	6.6×10 ¹⁷ (13.2%)	8.2×10 ¹⁷ (16.5%)
OCS (1 mJy)	6.5×10 ¹⁵ (0.07%)	5.0×10 ¹⁵ (0.1%)	5.0×10 ¹⁵ (0.1%)
OCS (0.1 mJy)	1.4×10 ¹⁶ (0.15%)	3.0×10 ¹⁶ (0.6%)	3.0×10 ¹⁶ (0.6%)
OCS (0.04 mJy)	2.8×10 ¹⁶ (0.3%)	6.5×10 ¹⁶ (1.3%)	6.0×10 ¹⁶ (1.2%)
CS ₂ (1 mJy)	0.9×10 ¹⁶ (0.1%)	1.0×10 ¹⁶ (0.2%)	1.0×10 ¹⁶ (0.2%)
CS ₂ (0.1 mJy)	4.6×10 ¹⁶ (0.5%)	4.5×10 ¹⁶ (0.9%)	4.5×10 ¹⁶ (0.9%)
CS ₂ (0.04 mJy)	1.3×10 ¹⁷ (1.4%)	1.0×10 ¹⁷ (2.0%)	1.1×10 ¹⁷ (2.1%)
SO ₂ (1 mJy)	1.8×10 ¹⁶ (0.2%)	2.5×10 ¹⁶ (0.5%)	2.0×10 ¹⁶ (0.4%)
SO ₂ (0.1 mJy)	1.2×10 ¹⁷ (1.3%)	1.5×10 ¹⁷ (3.0%)	1.1×10 ¹⁶ (2.2%)
SO ₂ (0.04 mJy)	2.3×10 ¹⁷ (2.5%)	2.6×10 ¹⁷ (5.2%)	2.1×10 ¹⁷ (4.2%)

Decreasing
flux



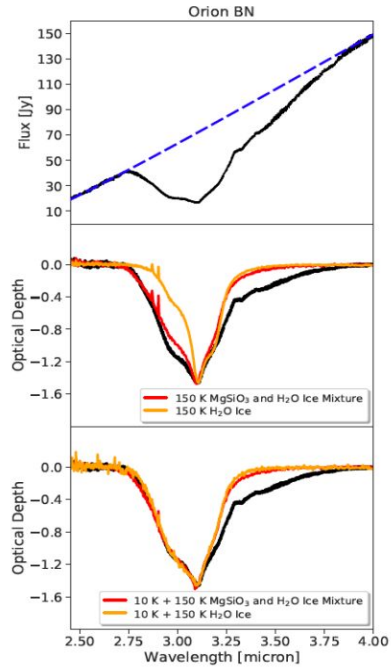
Increasing
column density



Crushing hope
and dreams



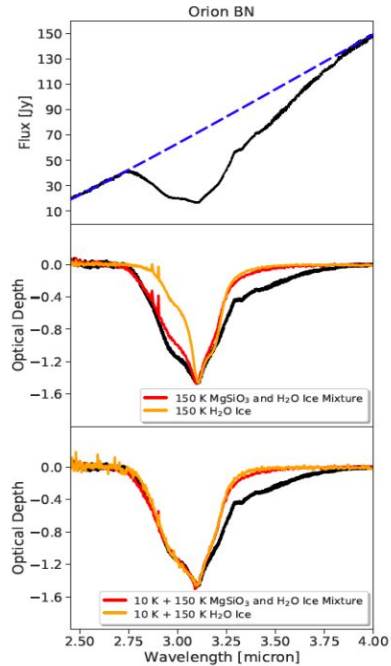
Model limitations



Scattering and/or
ice thermal processing

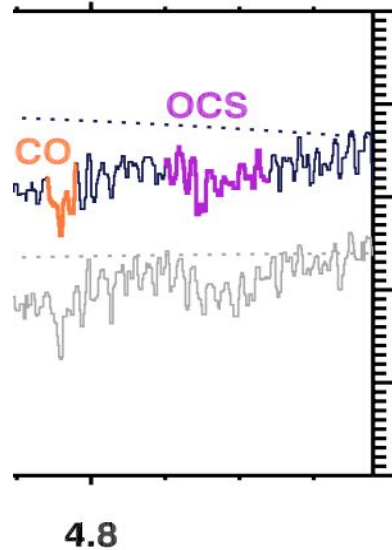
Potapov+2021

Model limitations



Scattering and/or
ice thermal processing

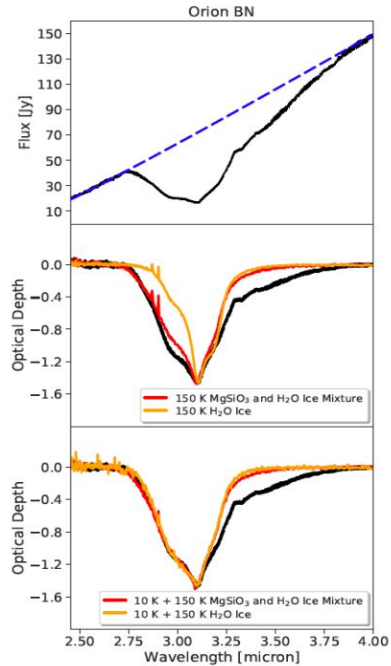
Potapov+2021



Photospheric lines

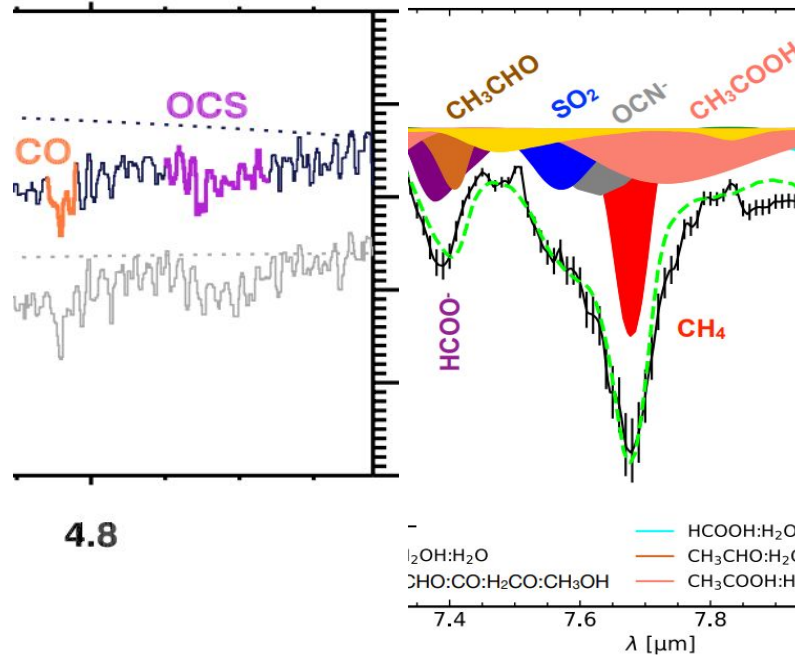
McClure+2023

Model limitations



Scattering and/or
ice thermal processing

Potapov+2021



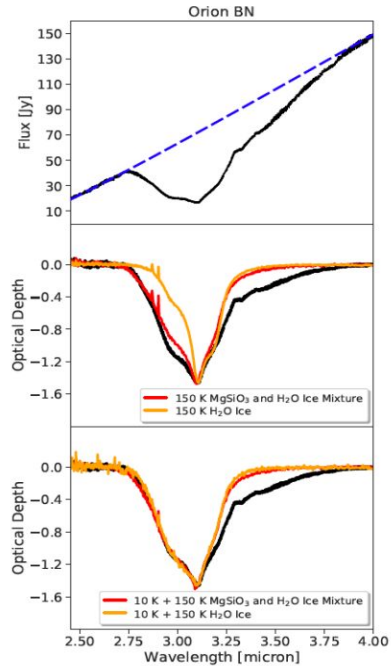
Photospheric lines

McClure+2023

Crowded area w/
abundant species

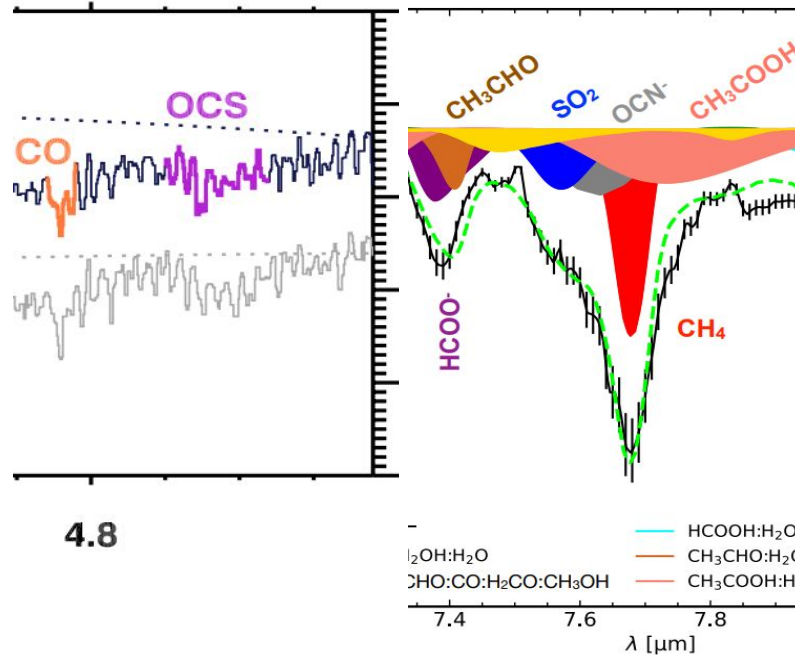
Rocha+2024

Model limitations



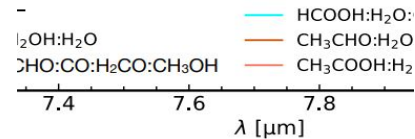
Scattering and/or
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Potapov+2021



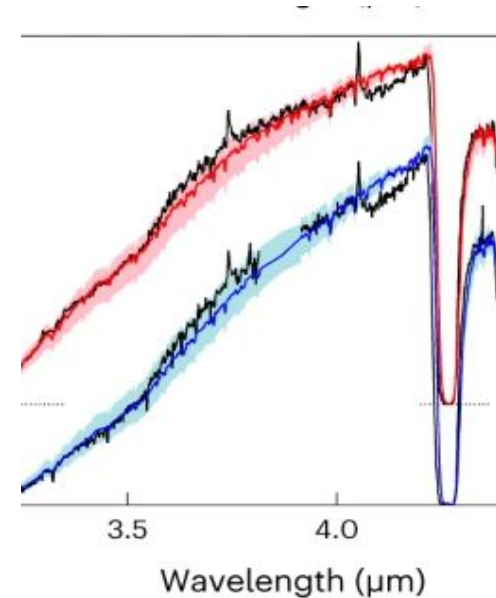
4.8
Photospheric lines

McClure+2023



Crowded area w/
abundant species

Rocha+2024



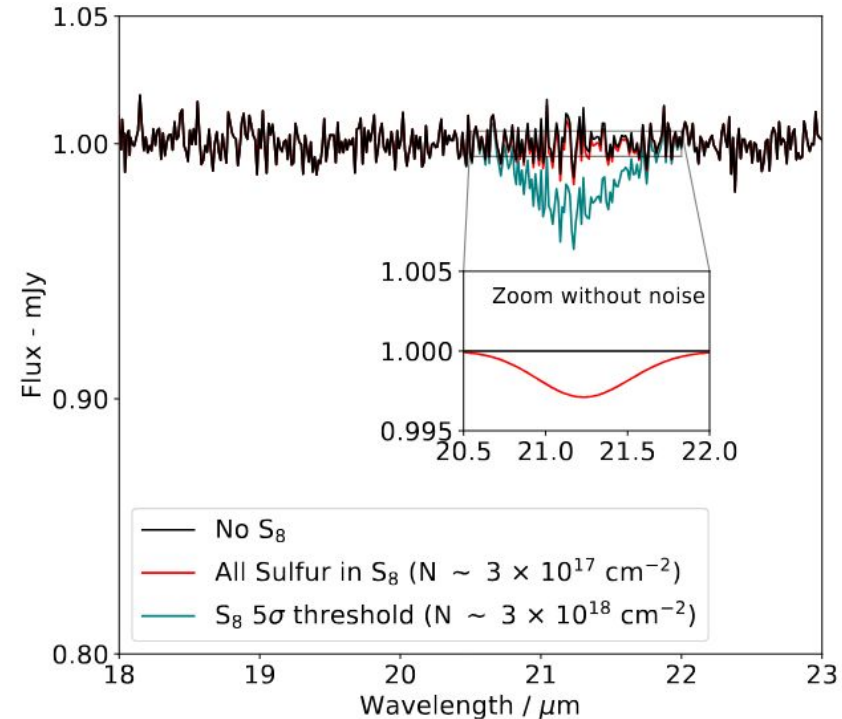
Grain growth

Dartois+2024

What about allotropes ? (S_n , $n > 2$)

- Allotropes are believed to be a solid S reservoirs, with possibly S_3 and S_4 detected in coma (67P, Calmonte+2016)...
- The solution ? Maybe, but not detectable !
- Even if we added all the **cosmic abundance** and locked it in S_8 , we would STILL not be able to detect it !

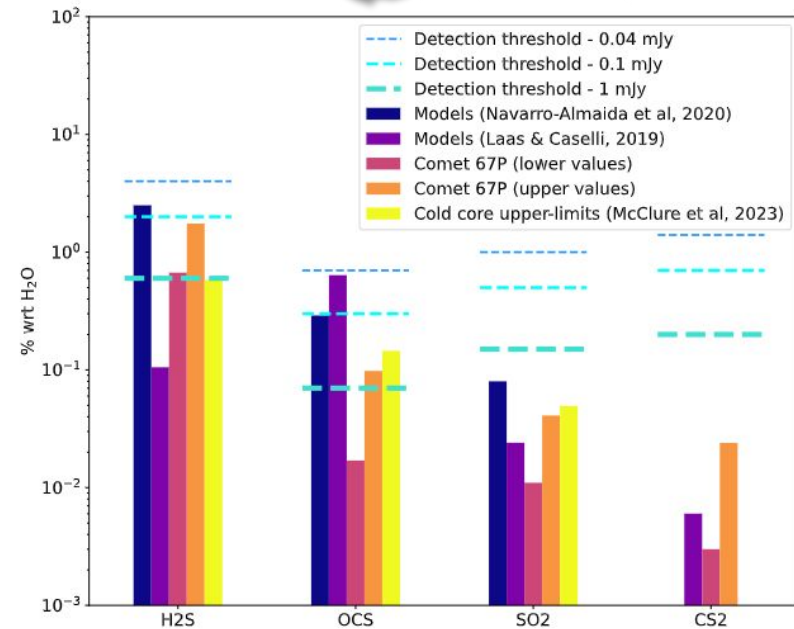
Cosmic abundance $\sim 1.5 \times 10^{-5} / H$ in a core with
 $N_{H_2} = 1.9 \times 10^{21} \text{ cm}^{-2}$, $A_v = 40$
 Conversion in column densities :
 $(1.5 \times 10^{-5}/8) * 1.9 \times 10^{21} * 40$



So what does it mean ?



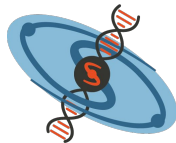
- **Hypothesis 1** : Sulfur all locked during the translucent phase in S_n (Cazaux+2022) or silicates
 - Little sulfur left to deplete from the gas-phase in later phases
 - If it's the case : undetectable and will remain as such
- **Hypothesis 2** : Sulfur is well distributed in the ices, so well that it is near impossible to detect any of these molecules because of band strength and/or low column density.
 - There might not be a “main” ice reservoir, we would have already detected it.
- Ice species left to **identify** : salt, S_n , ions...
 - Need to identify the precursors from the gas phase ?
- **Probably a mix of these**
 - **Limited to impossible detections with JWST**





Thank you very much for your attention!

Acknowledgments:

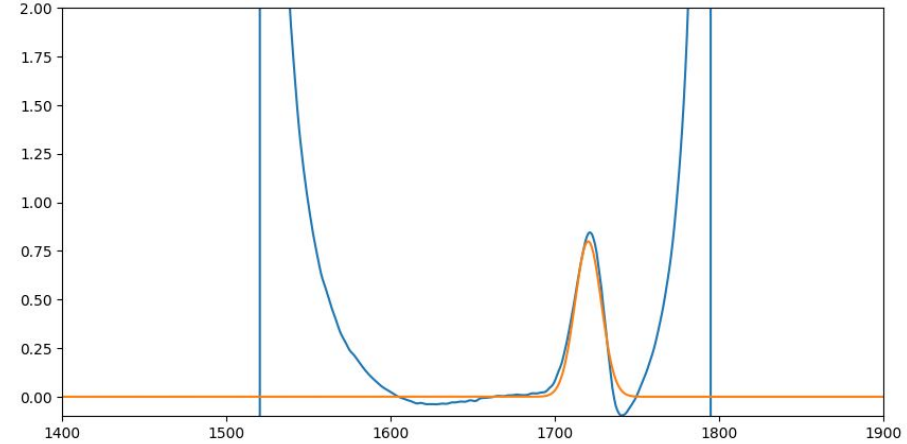
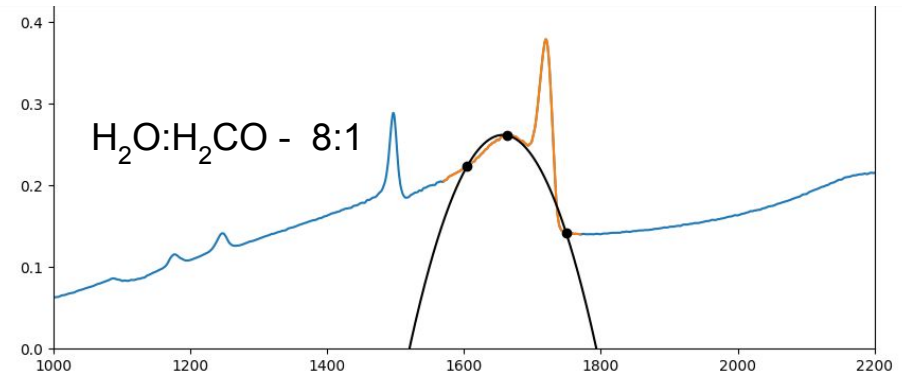
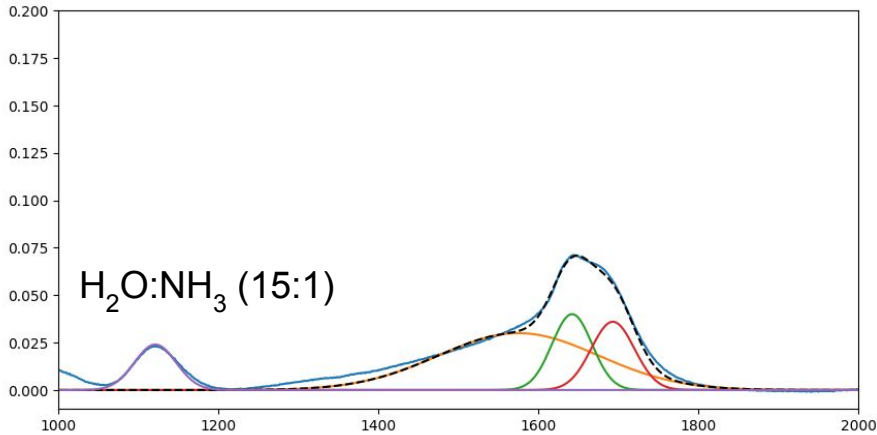
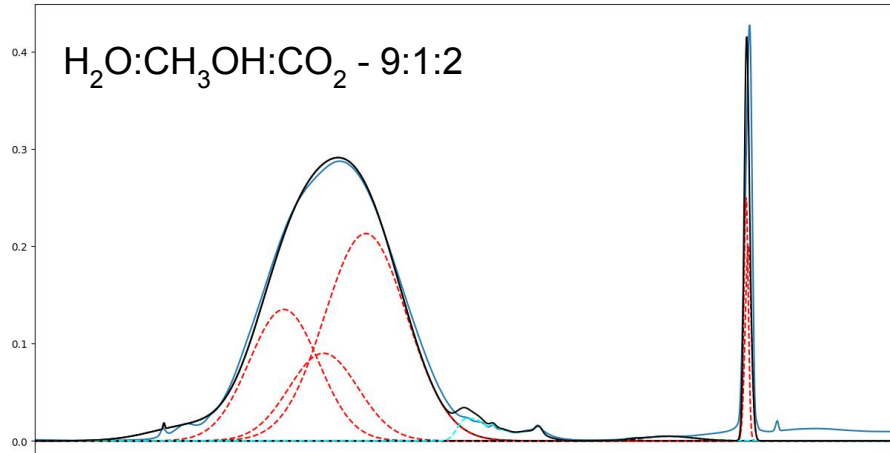


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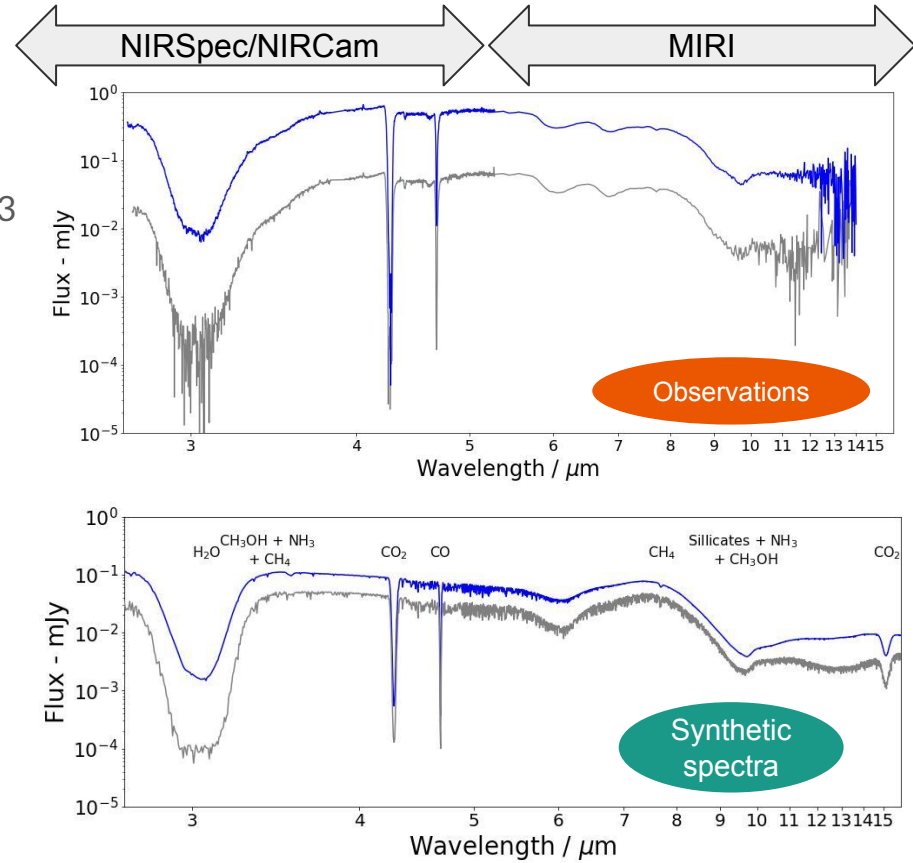
And of course thanks to the co-authors who helped a lot (and made thousands of comments on the draft :))

Rafa Martín-Doménech, Hector Carrascosa, Guillermo Muñoz Caro, Jenny Noble, Emmanuel Dartois,
David Navarro-Almaida, Álvaro Sánchez-Monge & Asunción Fuente

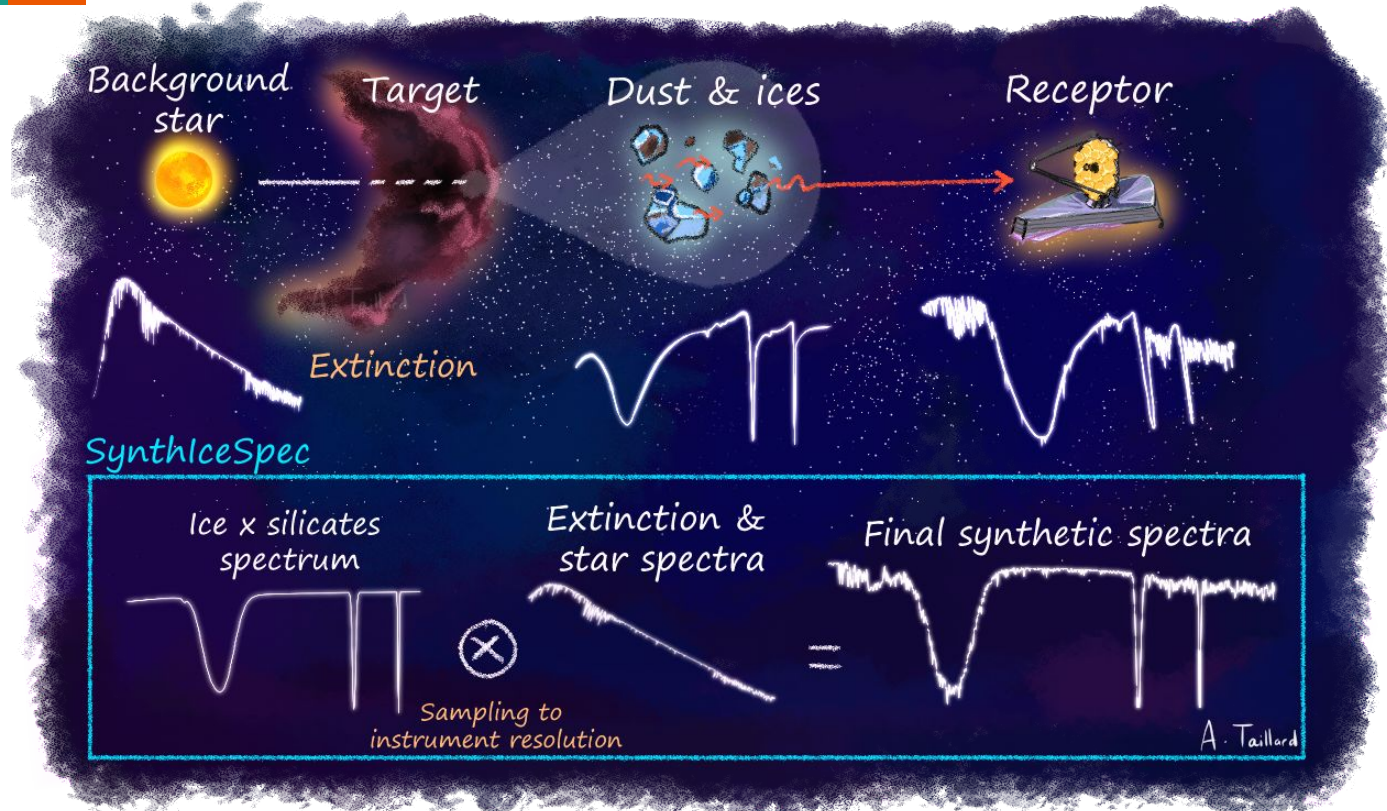




McClure+2023



SynthIceSpec principles (Taillard et al in prep)



S_8 new band strength

- Hector measured S_8 band strength, width and position in the following experiment (at CAB):
 - Hector made a 6 mg pellet (pastilla) of S_8 that he introduced in a Fourier-Transform IR spectrometer
 - Main feature detected at 21.36 μm (468 cm^{-1})
 - He measured the column density and deduced the band strength following the equation:

$$N = \frac{1}{A} \int_{\text{band}} \tau_\nu d\nu,$$

Band strength computed : $1.00 \times 10^{-19} \text{ cm/molecule}$

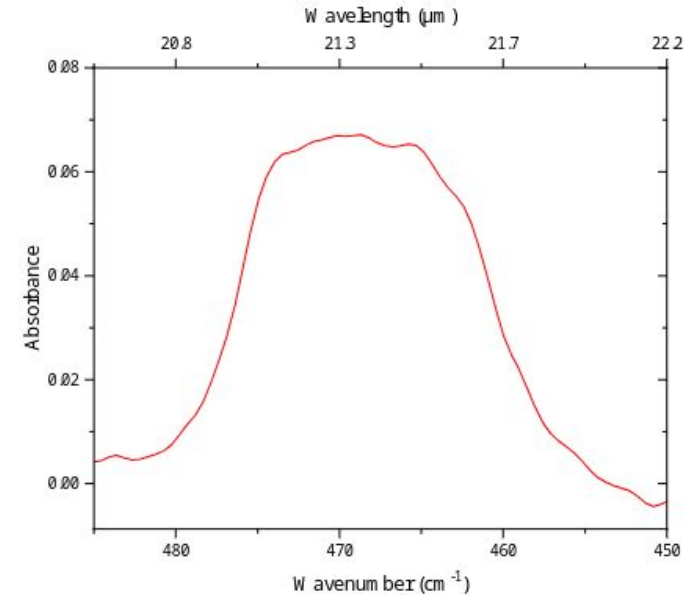


Fig. 1: Main IR feature corresponding to a S_8 pellet measured at the Centro de Astrobiología (CAB-CSIC, Spain)

CS₂ band strength

- Rafa made an experiment to compute the band strength, width and position of CS₂ (at CfA, Harvard & Smithsonian USA):
 - Rafa used a ultra-high-vacuum chamber to deposit CS₂ ice sample on a CsI substrate at 8 K and warmed it up to 130 K
 - No difference in spectra until 60 K
 - Shows transition from amorphous to crystalline
 - Features compared to 77 K ice sample from Yamada & Person 1964
 - New measurements : 1.1×10^{-16} (6.65 μm) and 2.1×10^{-18} (4.65 μm) cm/molecule

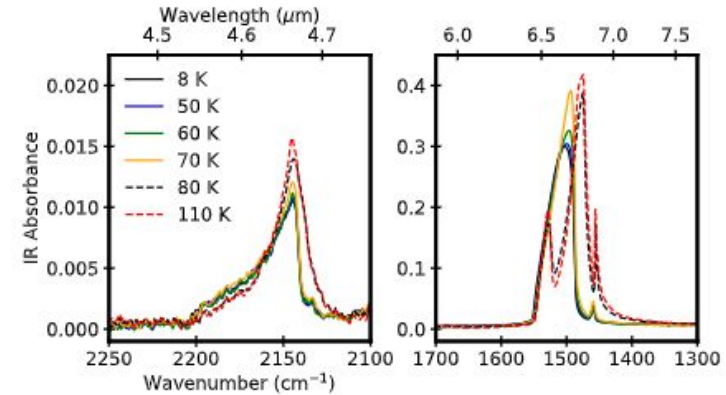


Fig. 2: Temperature evolution of the $\sim 4.65 \mu\text{m}$ (left panel) and $\sim 6.65 \mu\text{m}$ (right panel) CS₂ IR features. The $\sim 6.85 \mu\text{m}$ feature corresponding to ¹³CS₂ was observed in the red wing of the main CS₂ IR band (right panel). Transition from amorphous (solid lines) to crystalline (dashed lines) structure was observed above 60 K.

