Organosulfur Chemistry in the Birthplaces of Stars and Planets

Suchitra Narayanan

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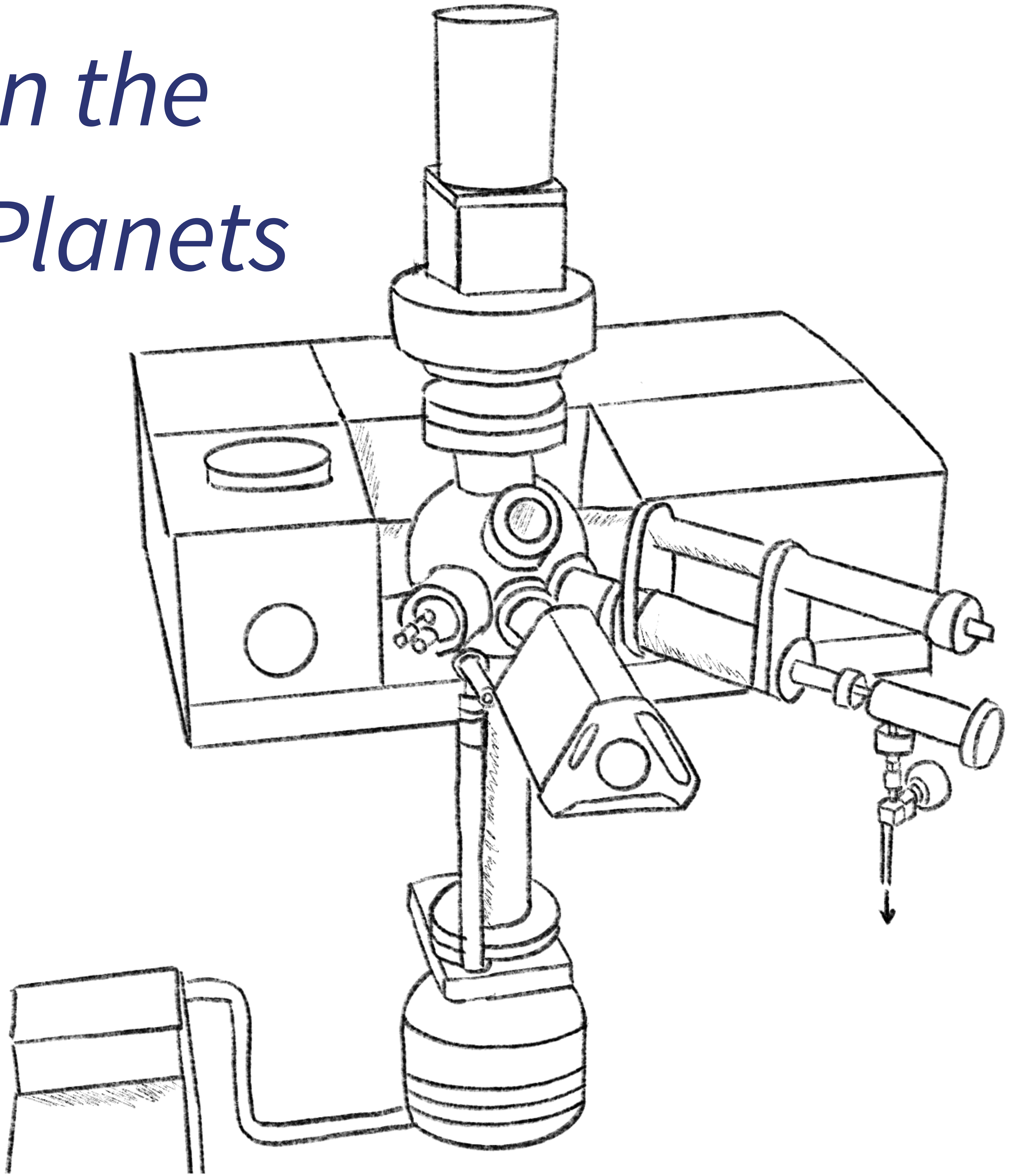
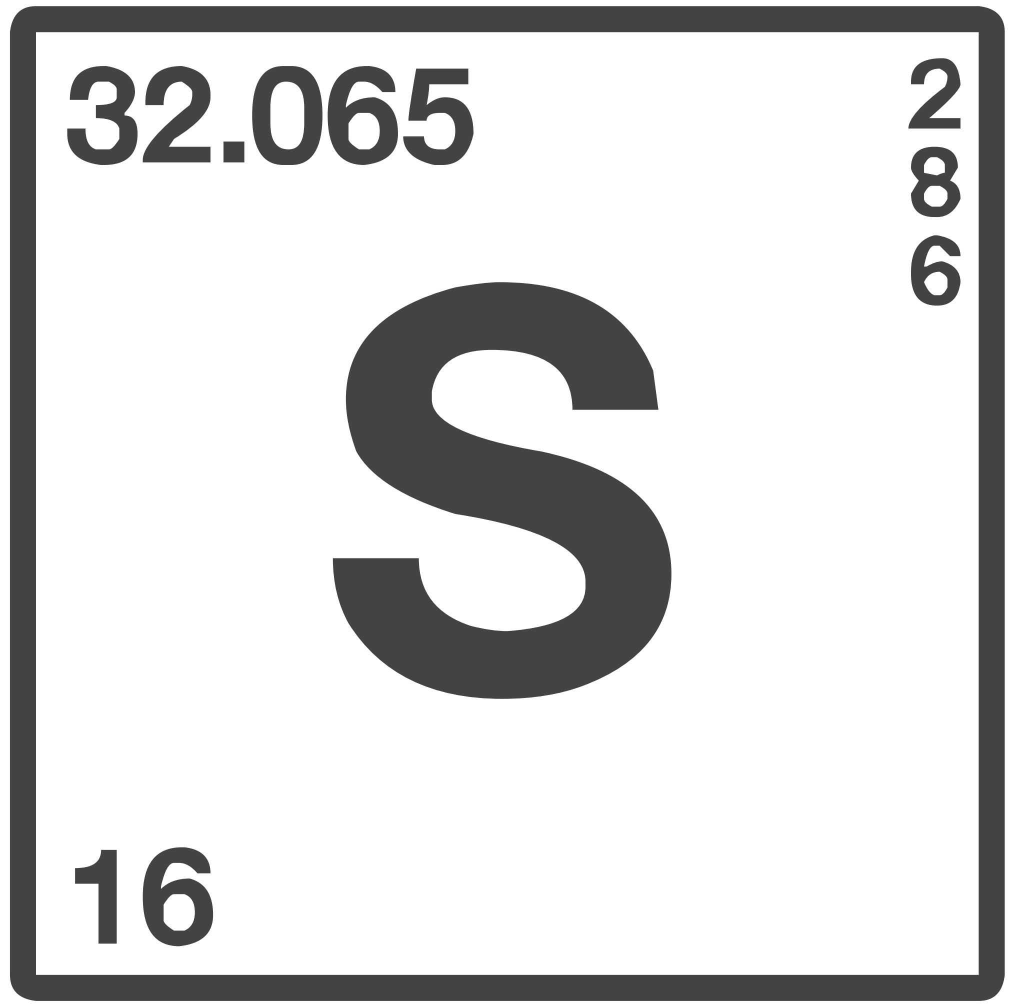
ExoPAG 31, 245th Meeting of the AAS · 12 January 2025



Sulfur is important in (but not limited to) two contexts



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32.065
2
8
6
S
16

(Astro)biology

sulfur is present in amino acids, proteins, lipids (even primordial Earth's genetic alphabet!)

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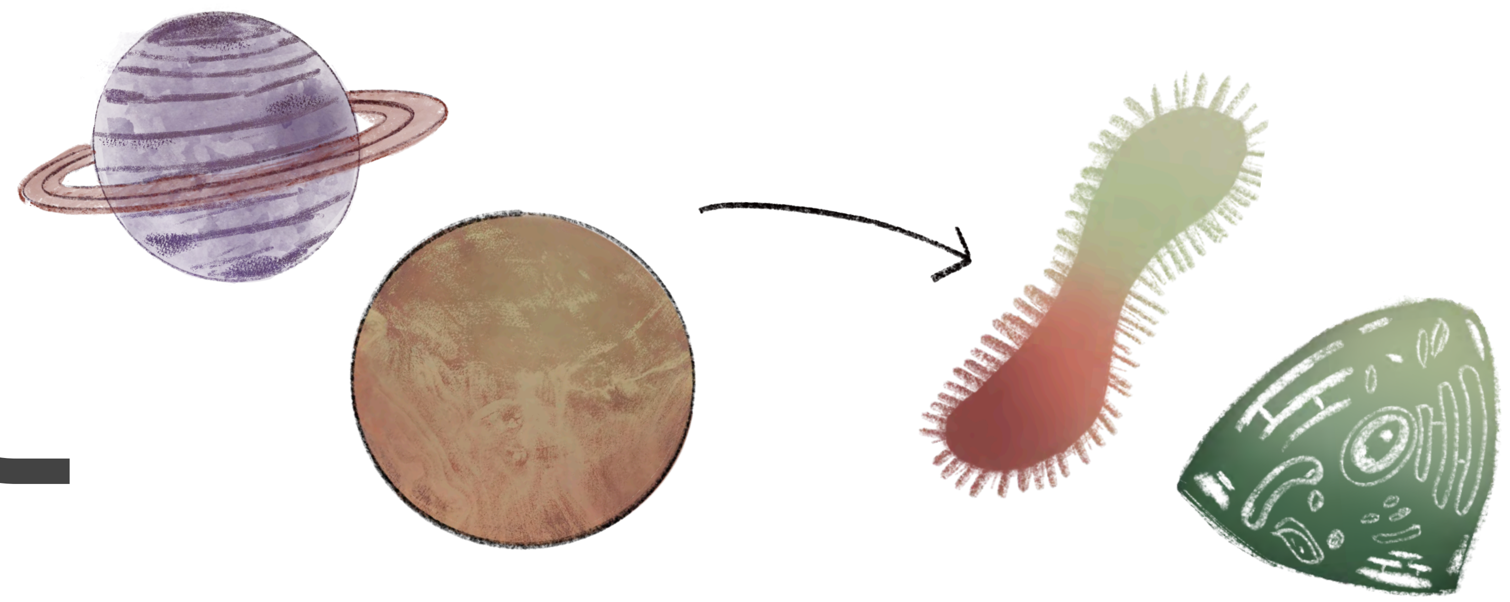

Planetary habitability

origins of life as we know it require the presence of S-bearing organics (+ nitriles) in prebiotic conditions

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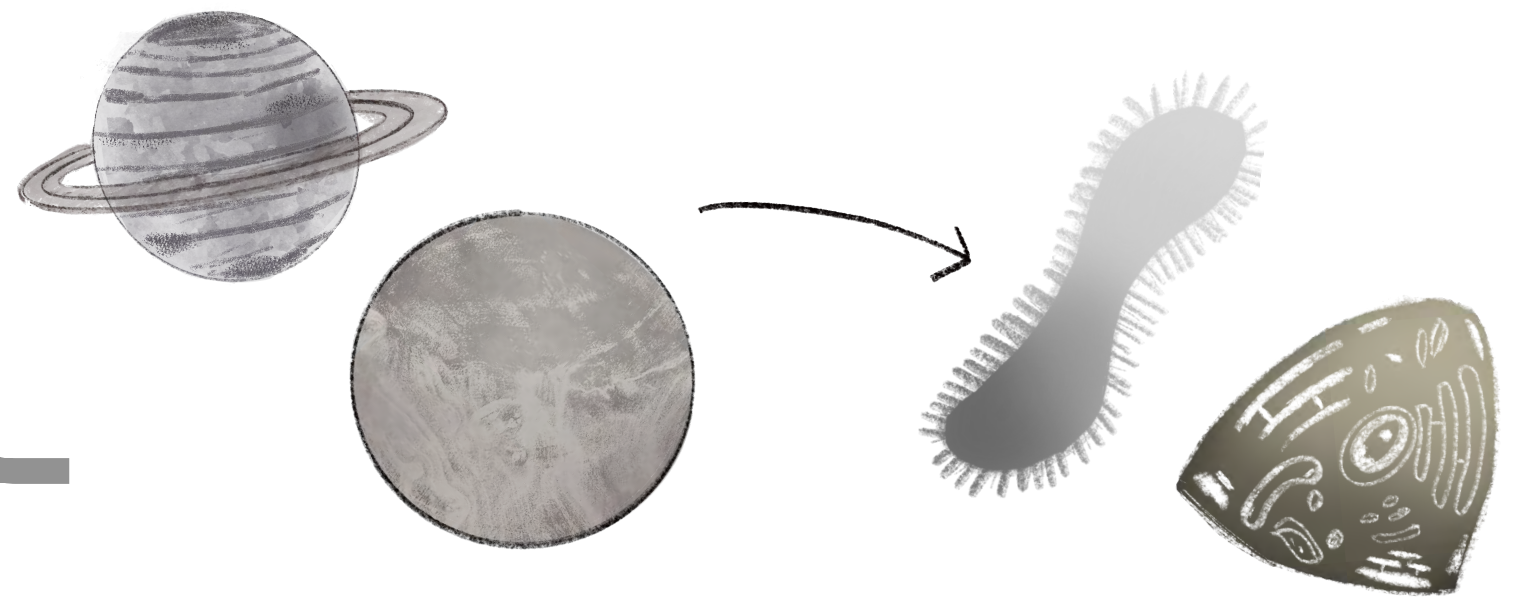

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...but we can't account for ~95% of the Universe's S budget

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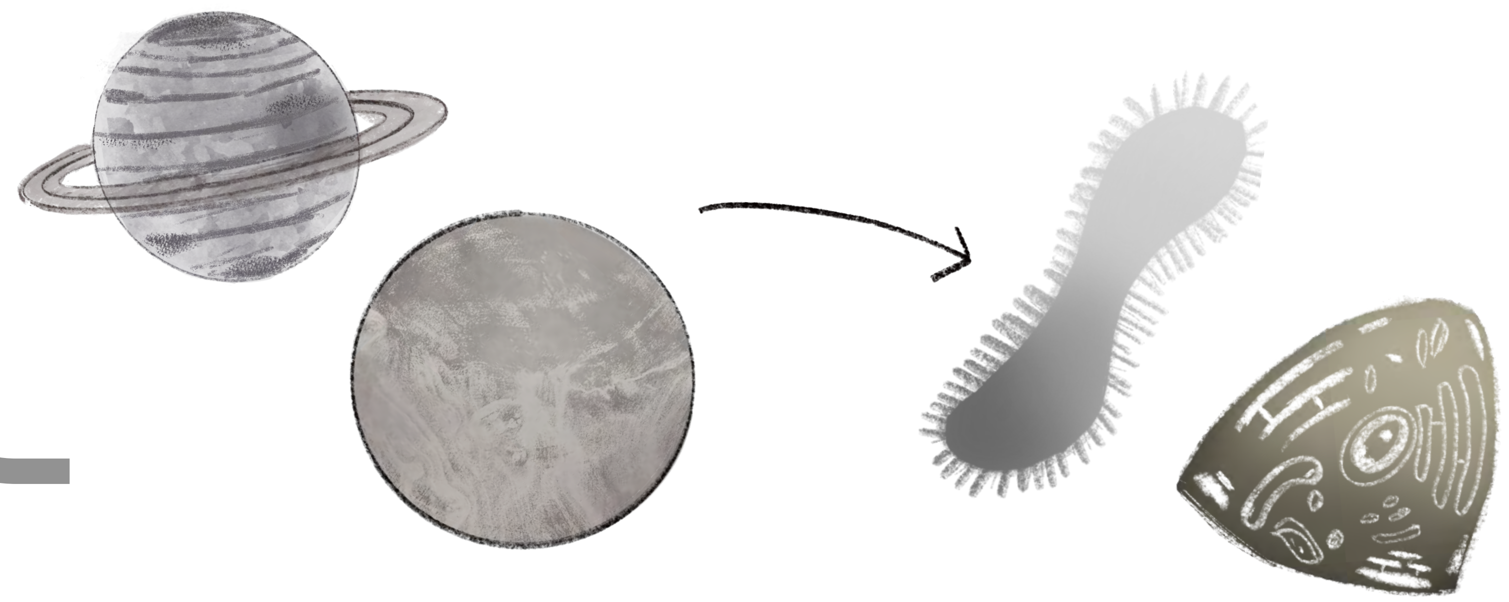

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...but we can't account for ~95% of the Universe's S budget

→ called the "missing sulfur problem" since the 1990s

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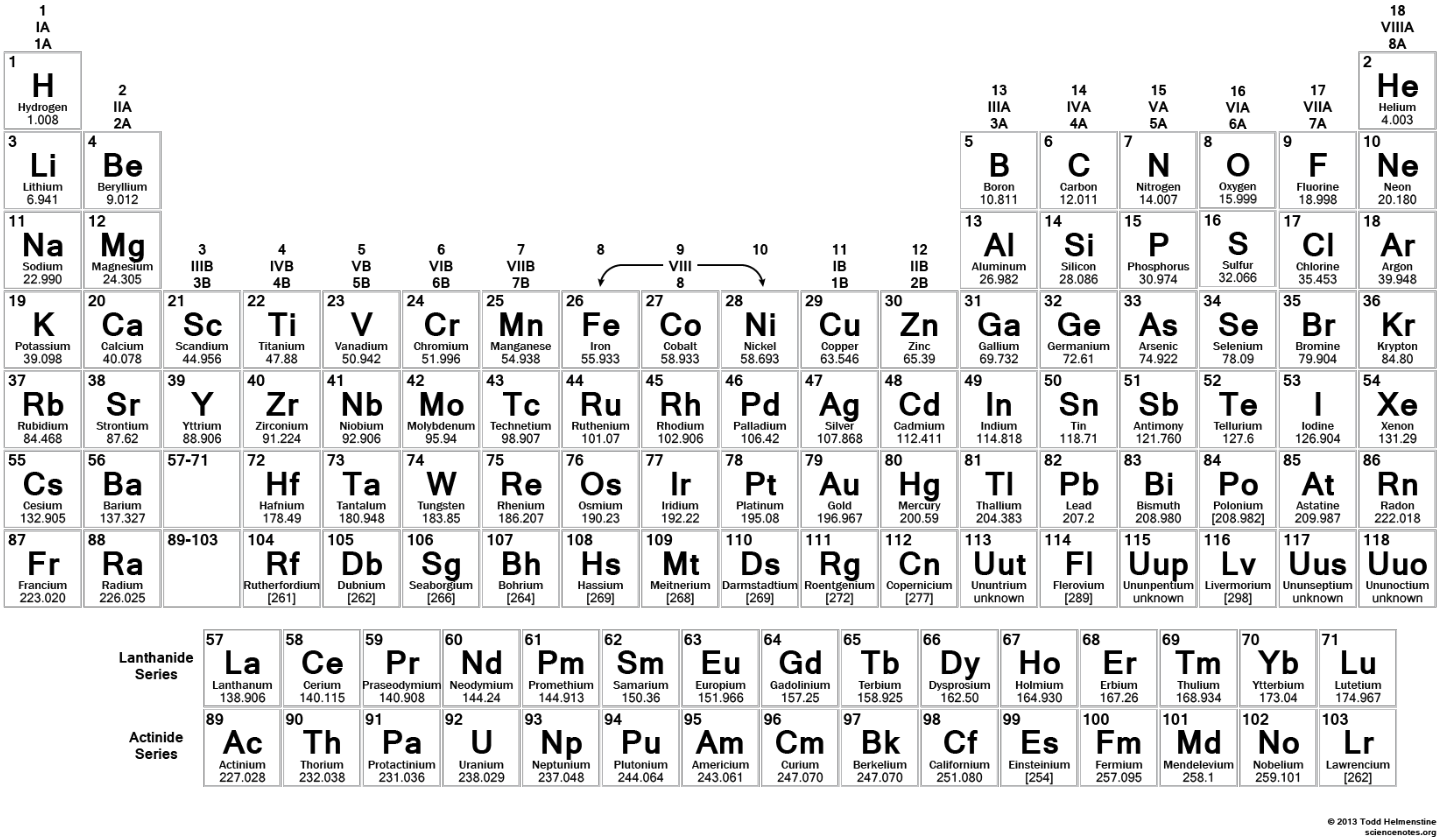
How can we understand sulfur if it’s hard to observe?

Theoretical modelers leverage the periodic table



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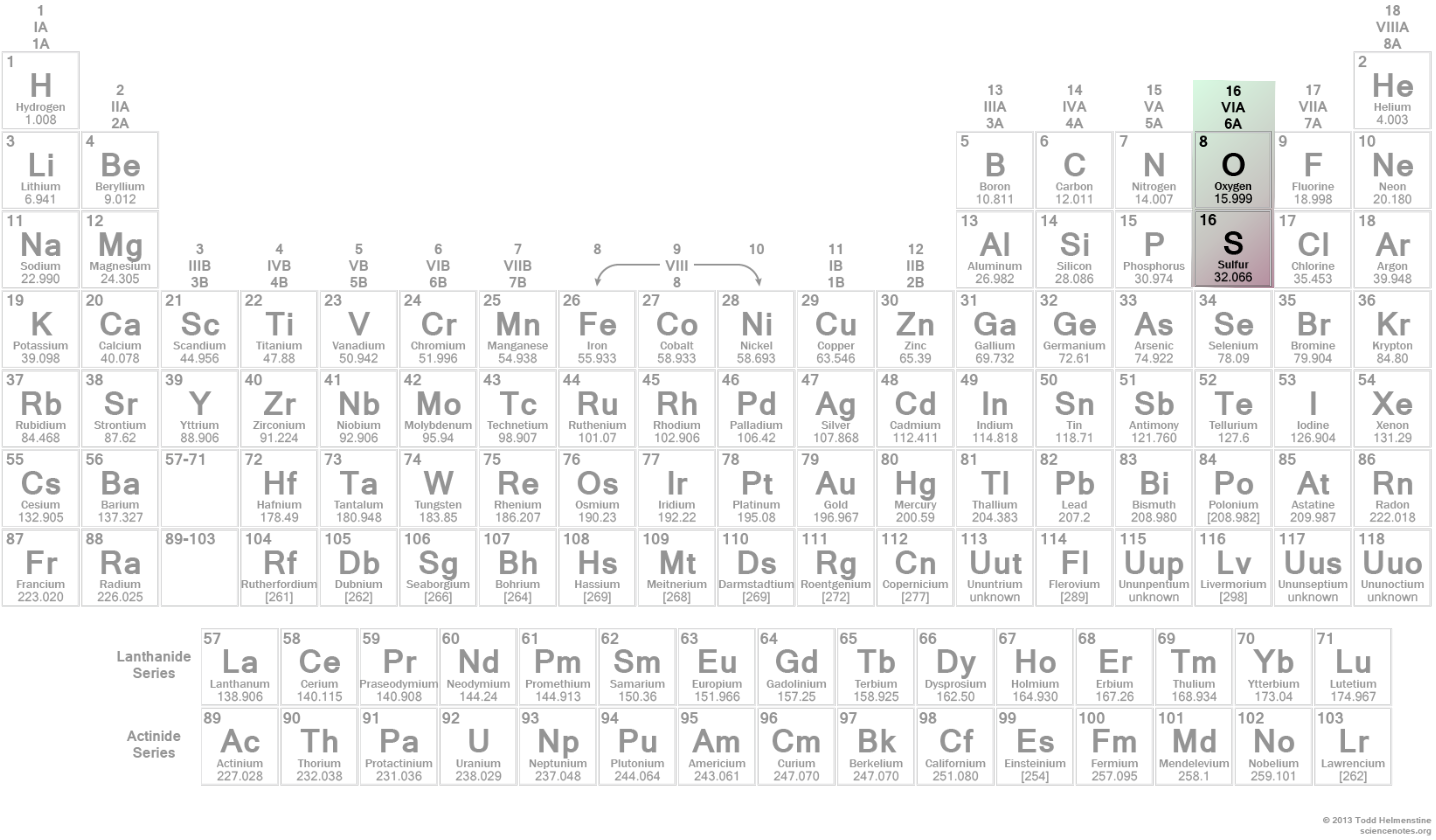

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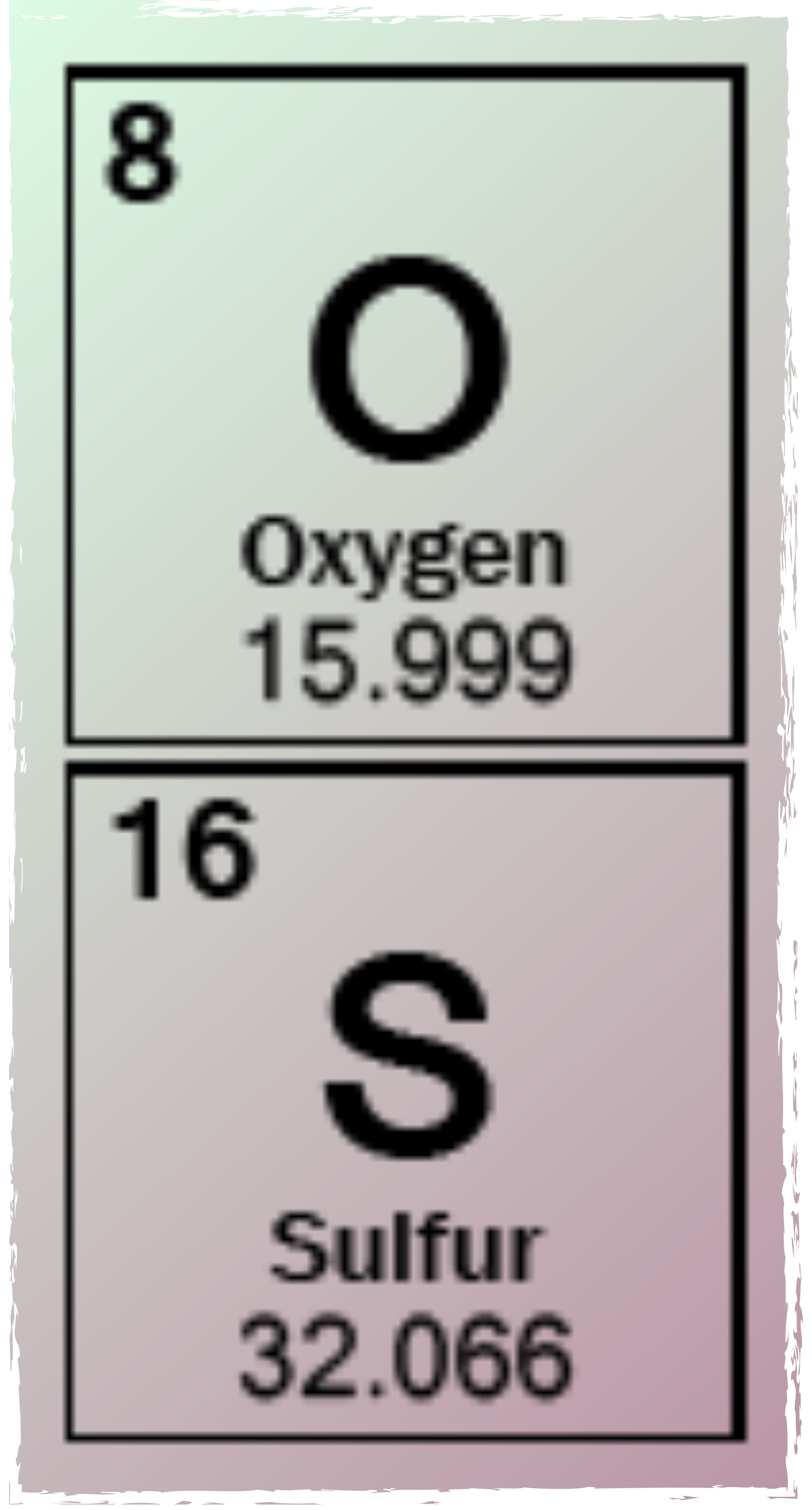
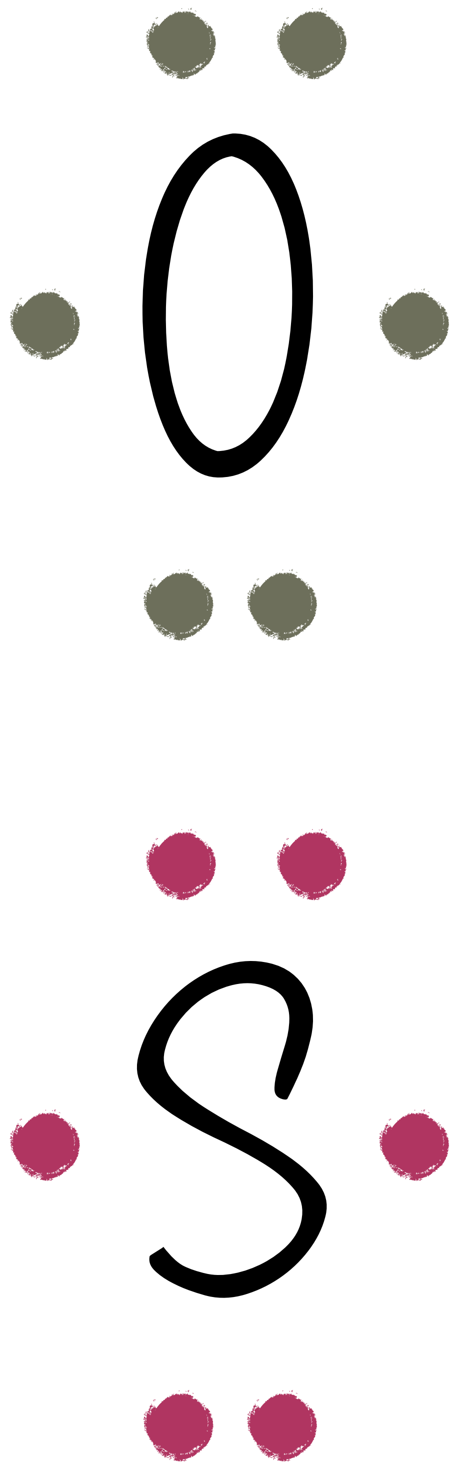
Same-group elements have identical # of valence electrons





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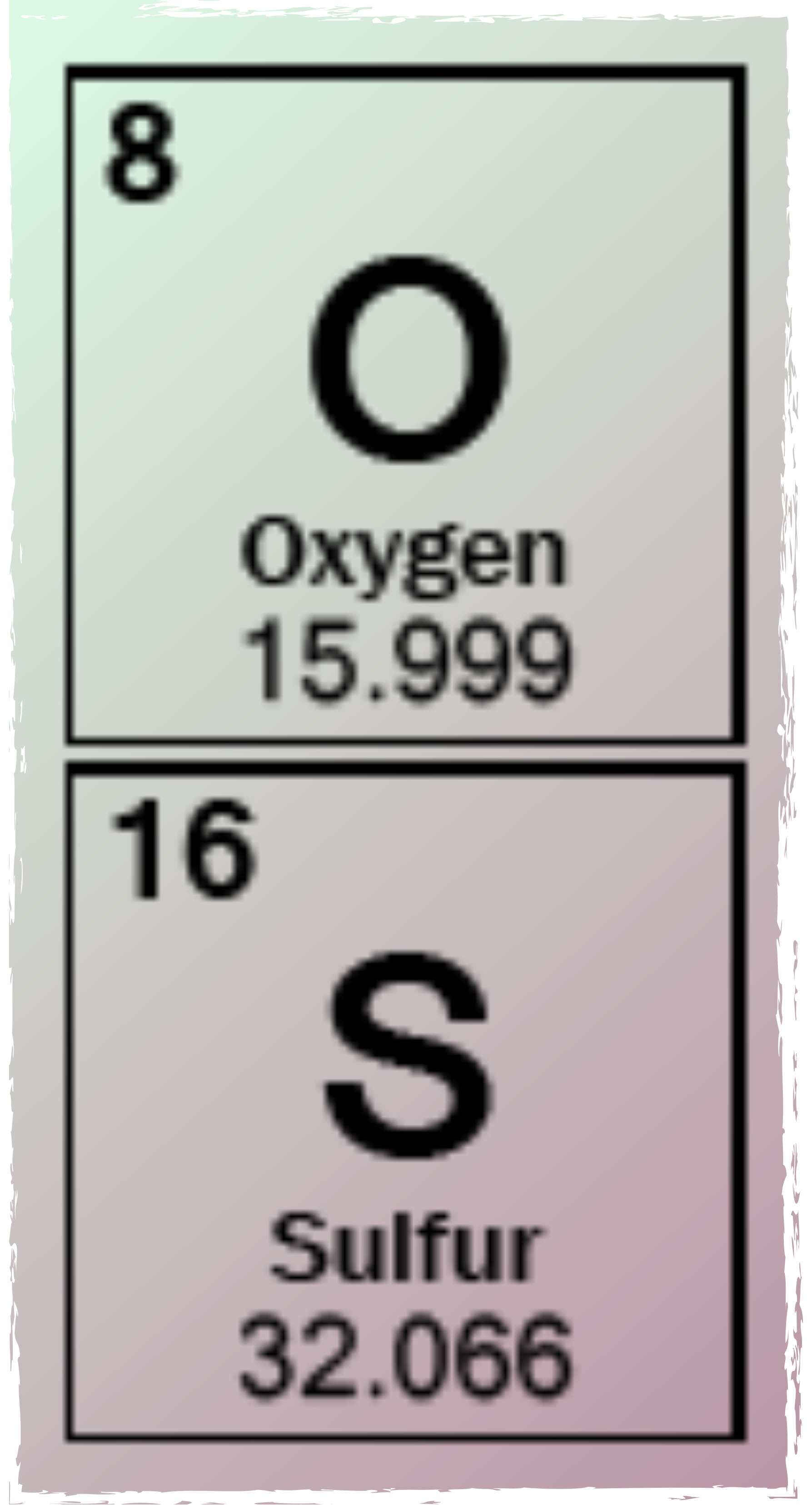

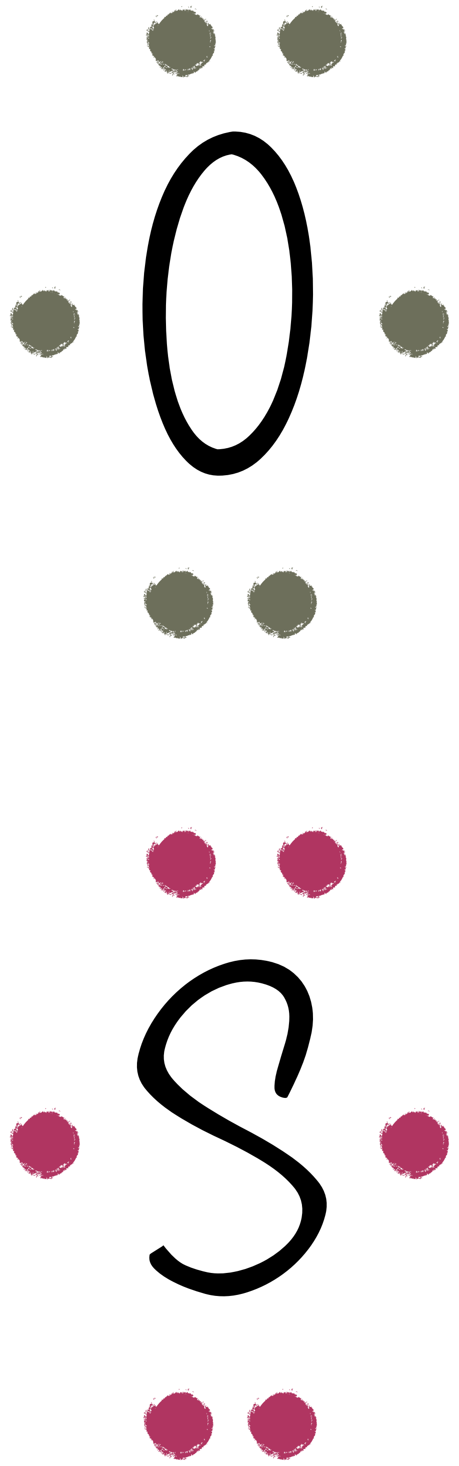

Valence electrons are responsible for an element's reactivity

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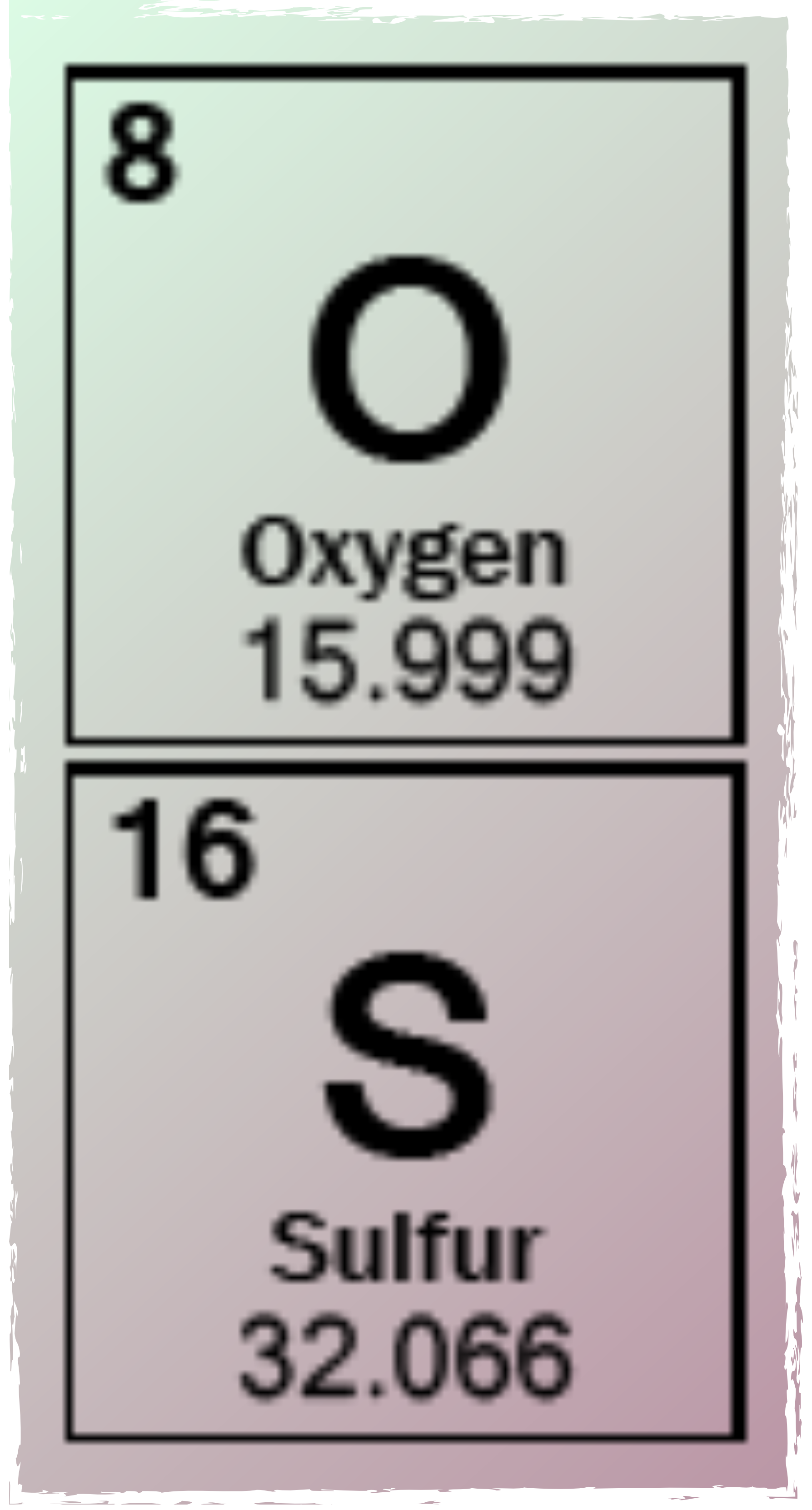

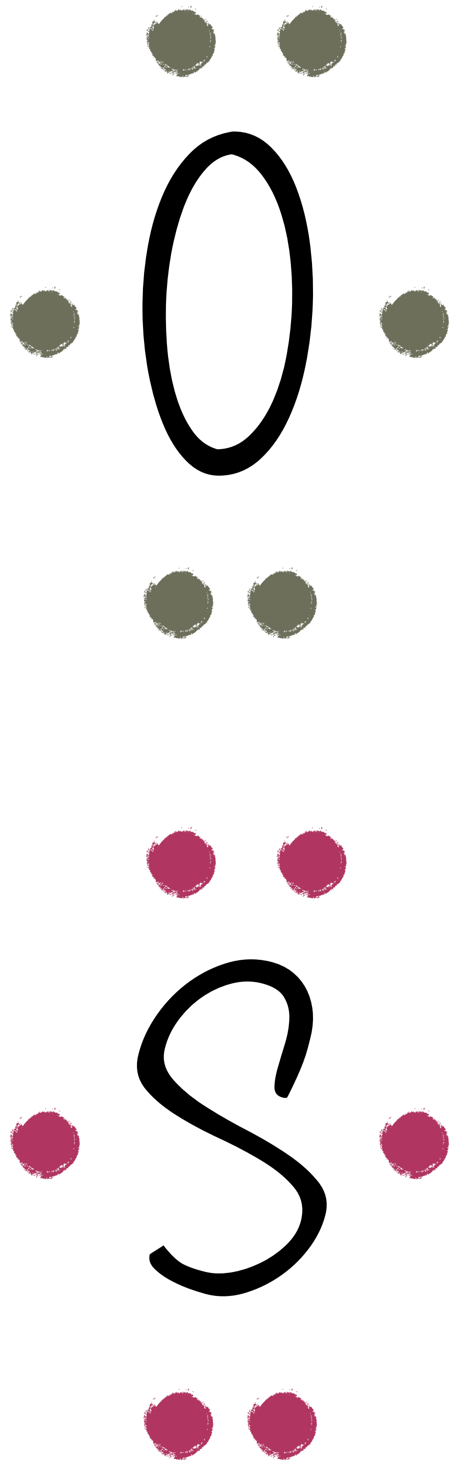

Valence electrons are responsible for an element's reactivity

⇒ *We can infer how sulfur-bearing molecules form using their oxygen analogs*

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The most updated astrochemical model predicts most of the "missing" sulfur to be locked in ices, namely organosulfurs

(Laas + Caselli 2019)

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A sulfur compound containing a C—H bond

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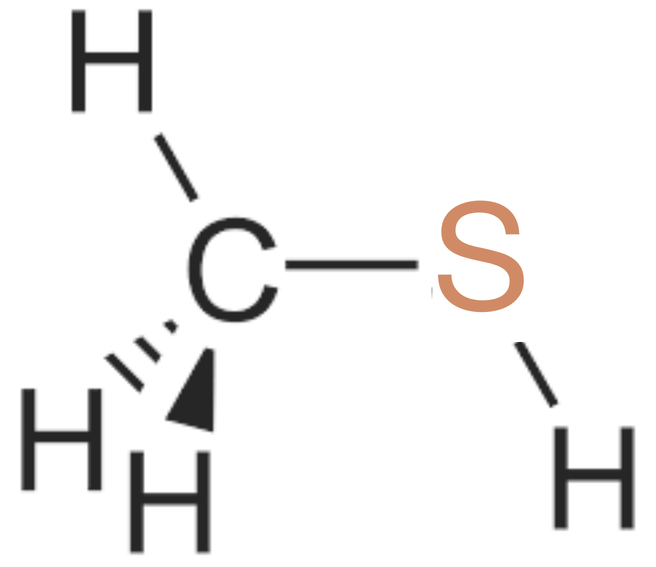
"Simplest" complex organosulfur: **methyl mercaptan**



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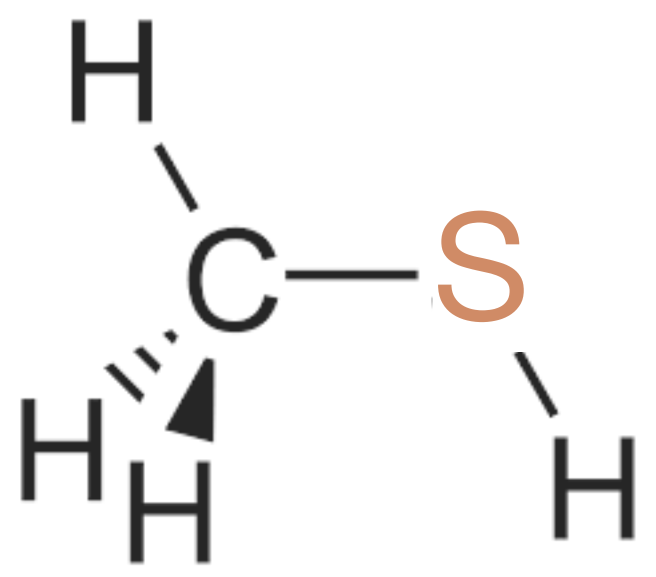
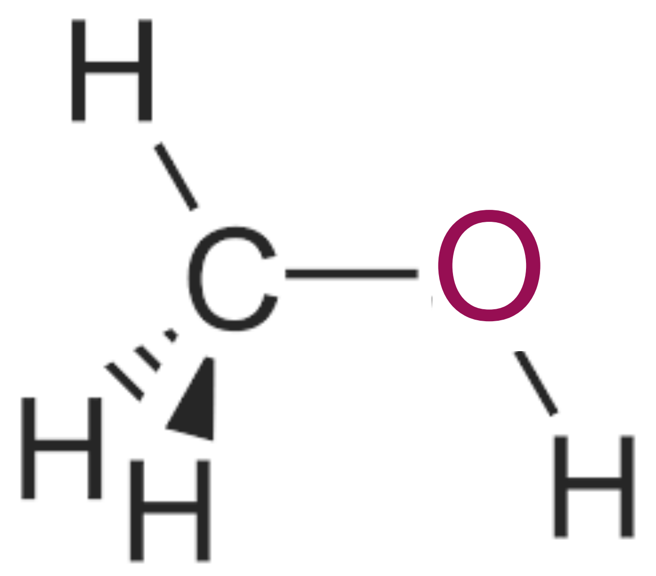


Analogous to its well-understood counterpart, **methanol**



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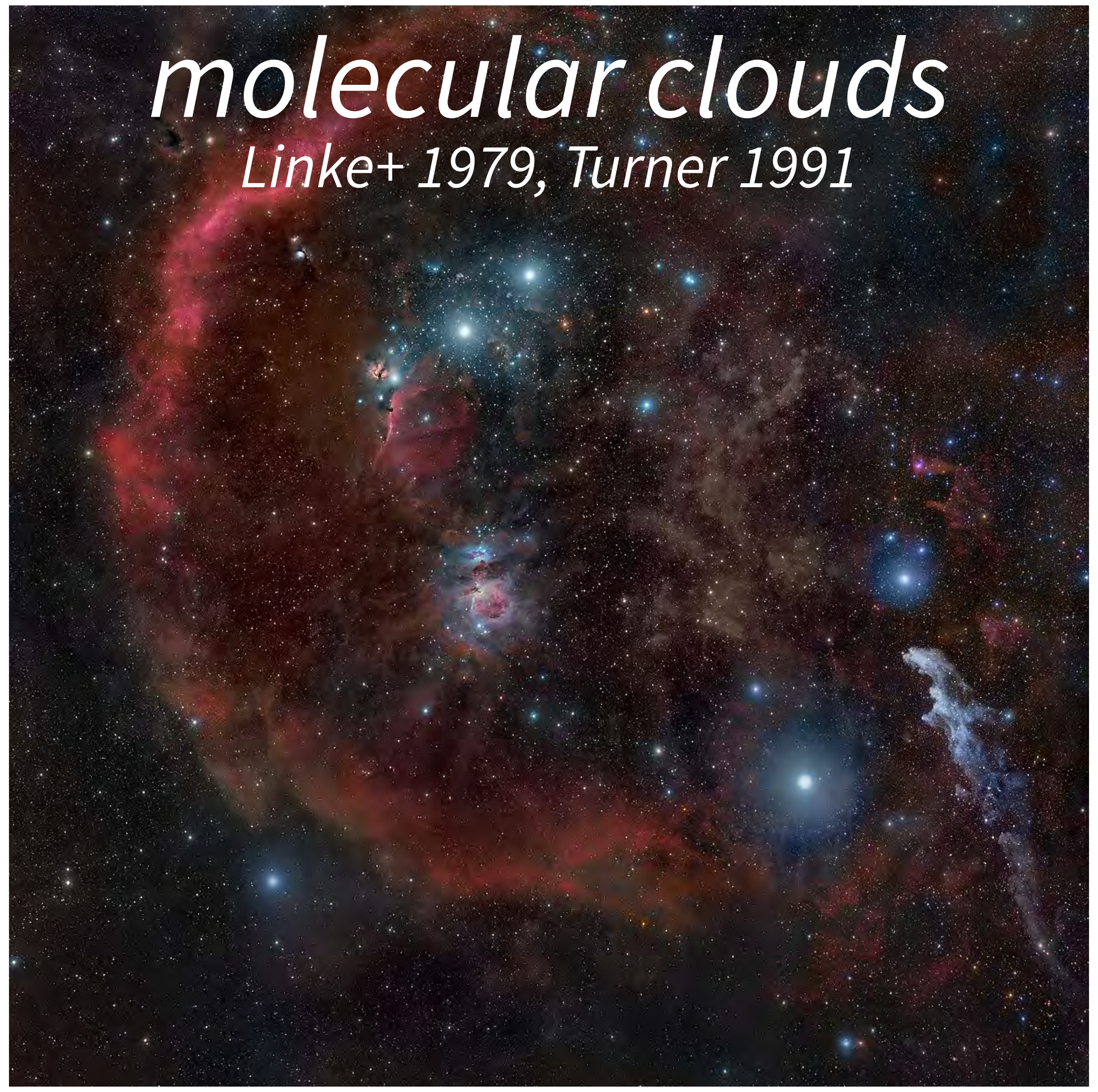
CH_3SH (methyl mercaptan) has been detected towards



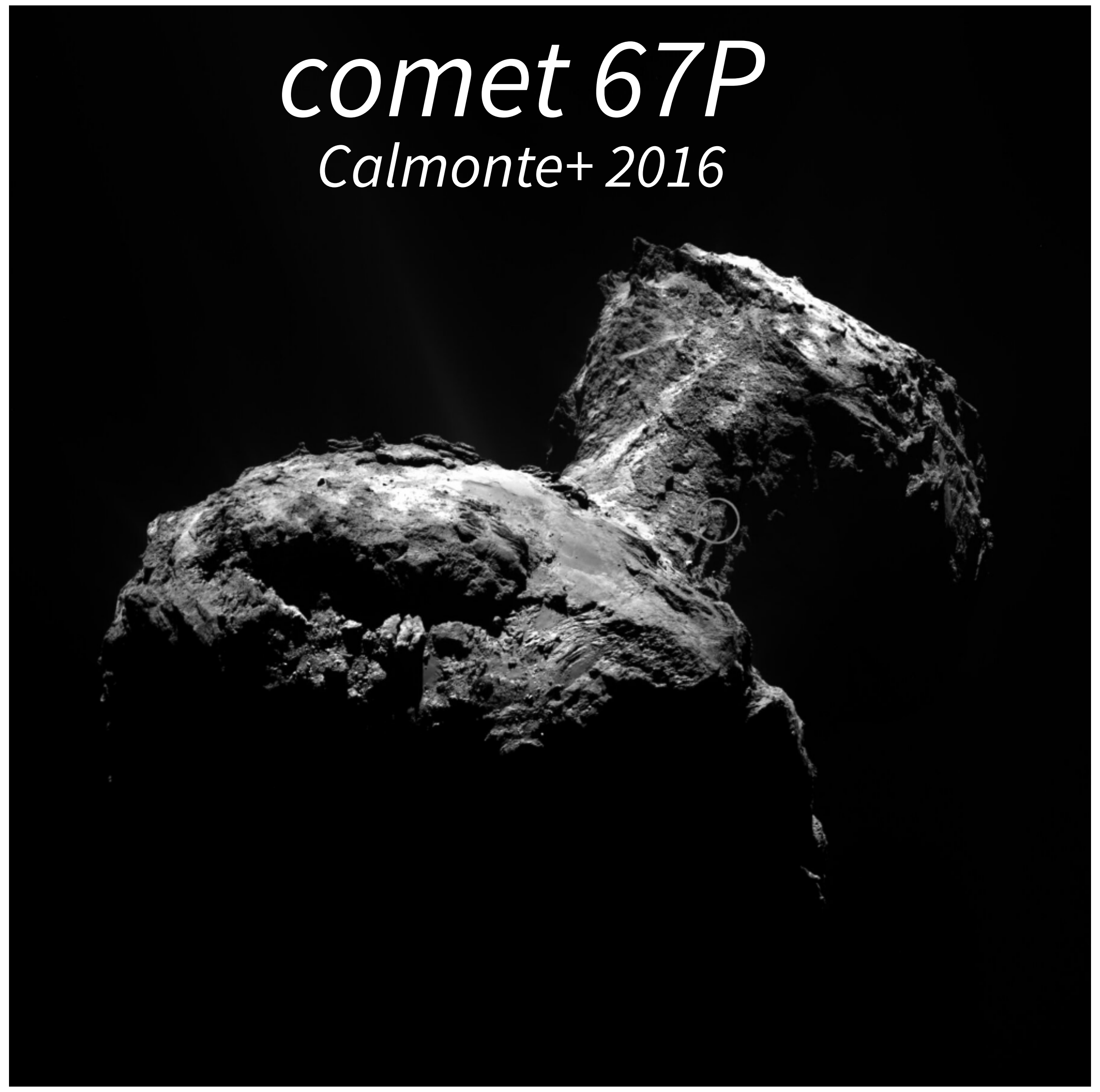


Image credits: Rogelio B. Andreo/ESO/ESA

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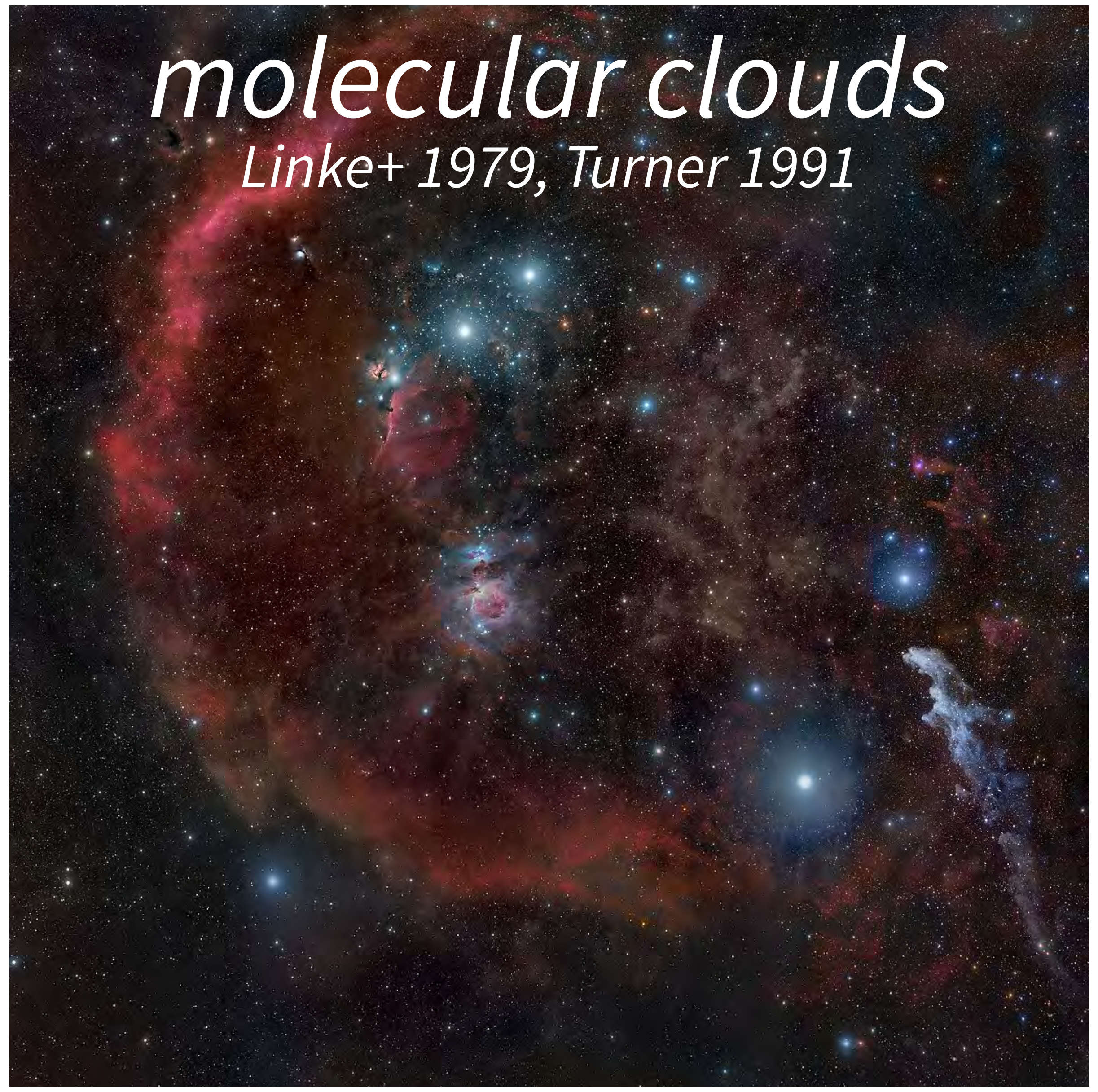

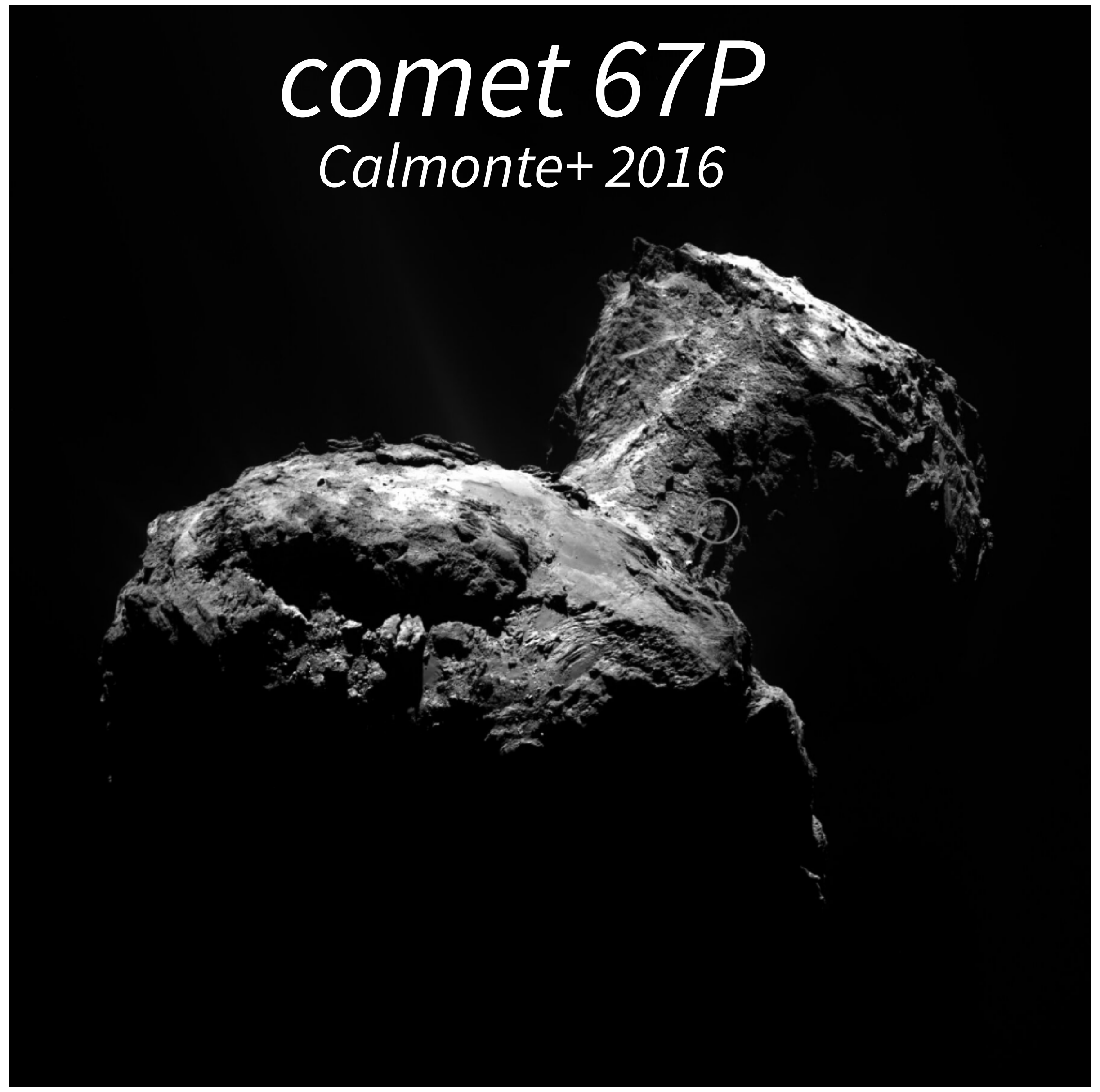

Image credits: Rogelio B. Andreo/ESO/ESA

To understand whether organosulfurs are a possible sulfur sink, we must empirically characterize its fundamental astrochemical properties

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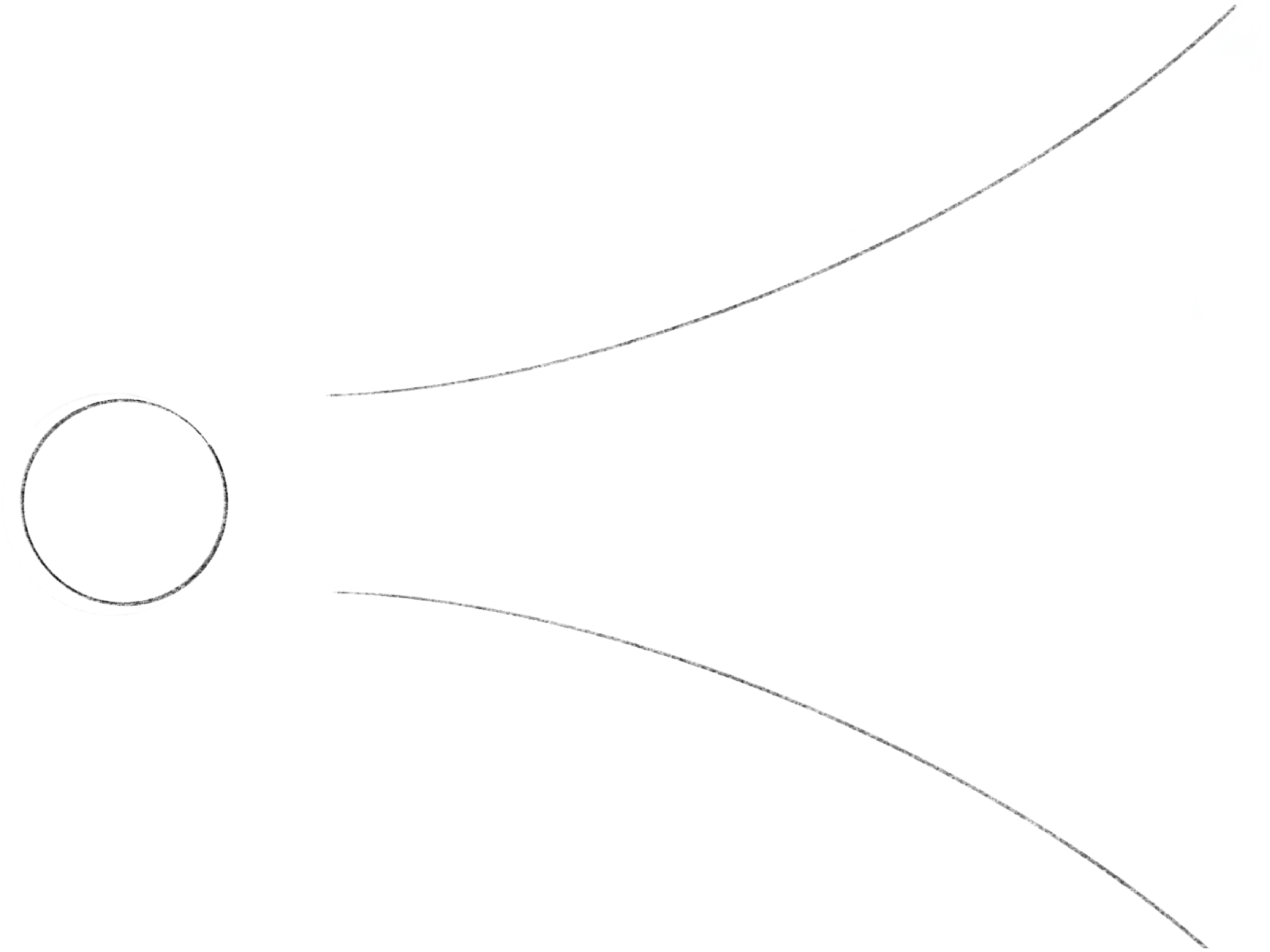
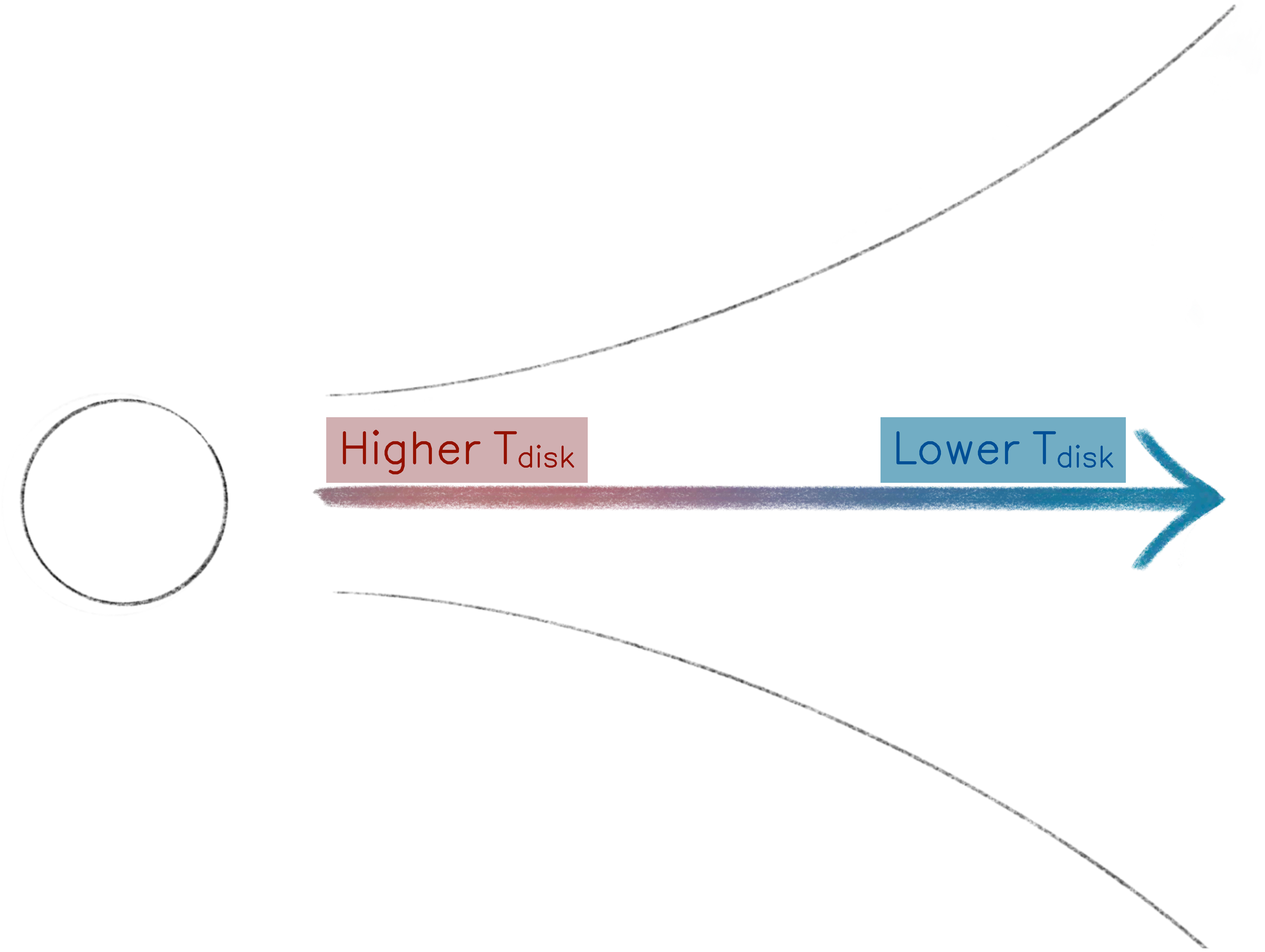
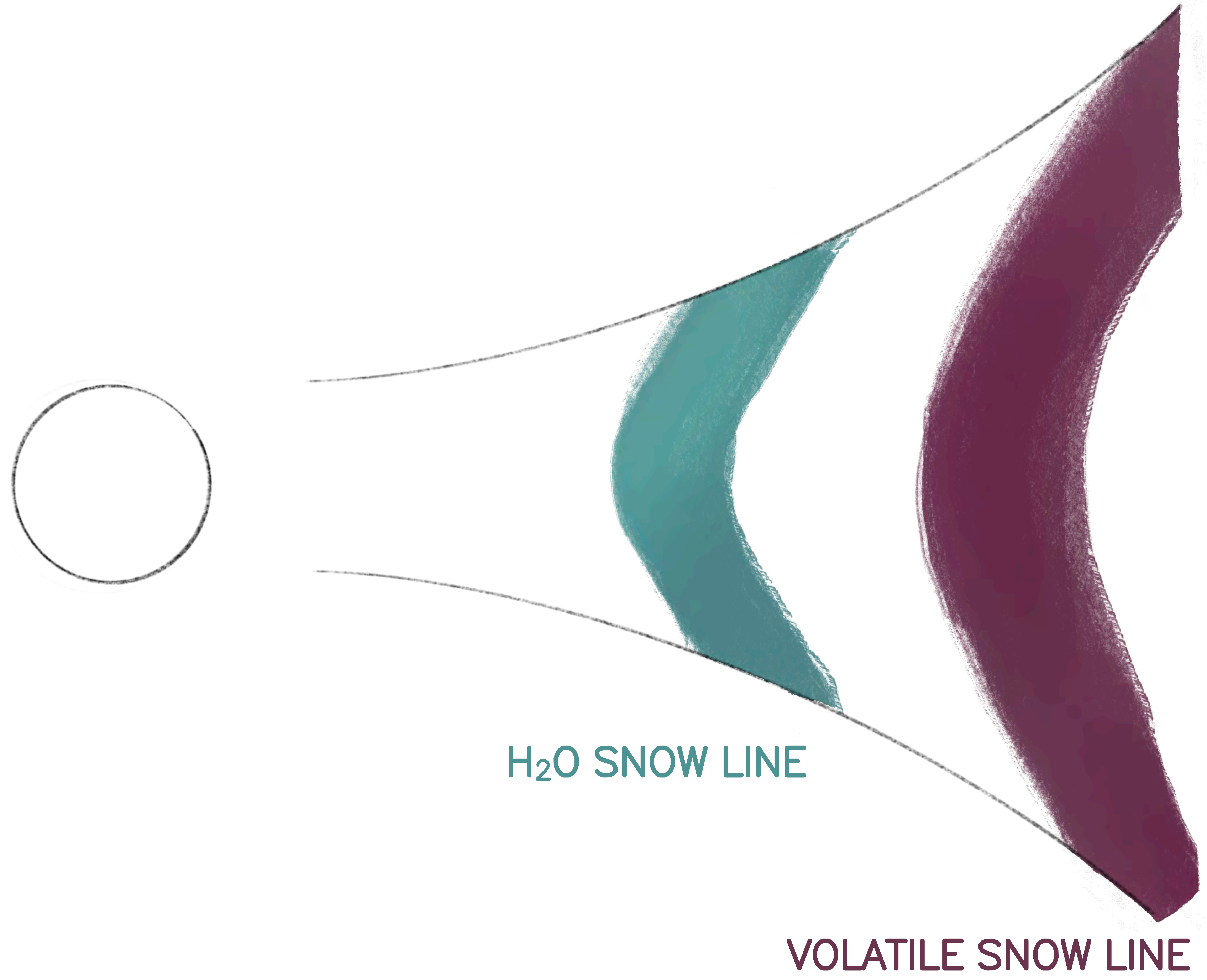
1. When is CH_3SH in its gas or ice phase?



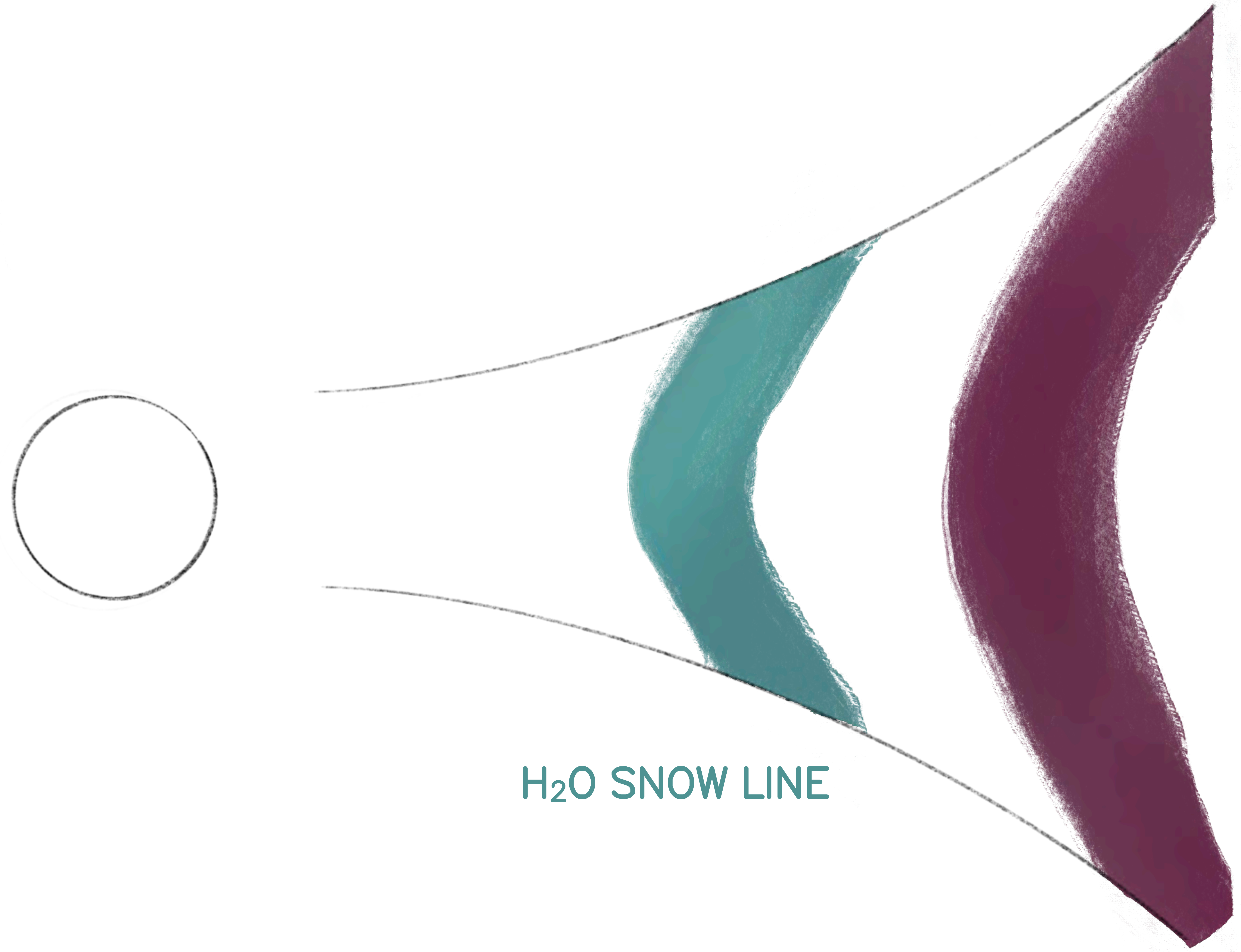
Molecules condense out as a function of R_{disk} (or T_{disk})...



...forming snow lines which represent the ice-gas boundary



However, realistic ices are mixtures of H_2O + other volatiles



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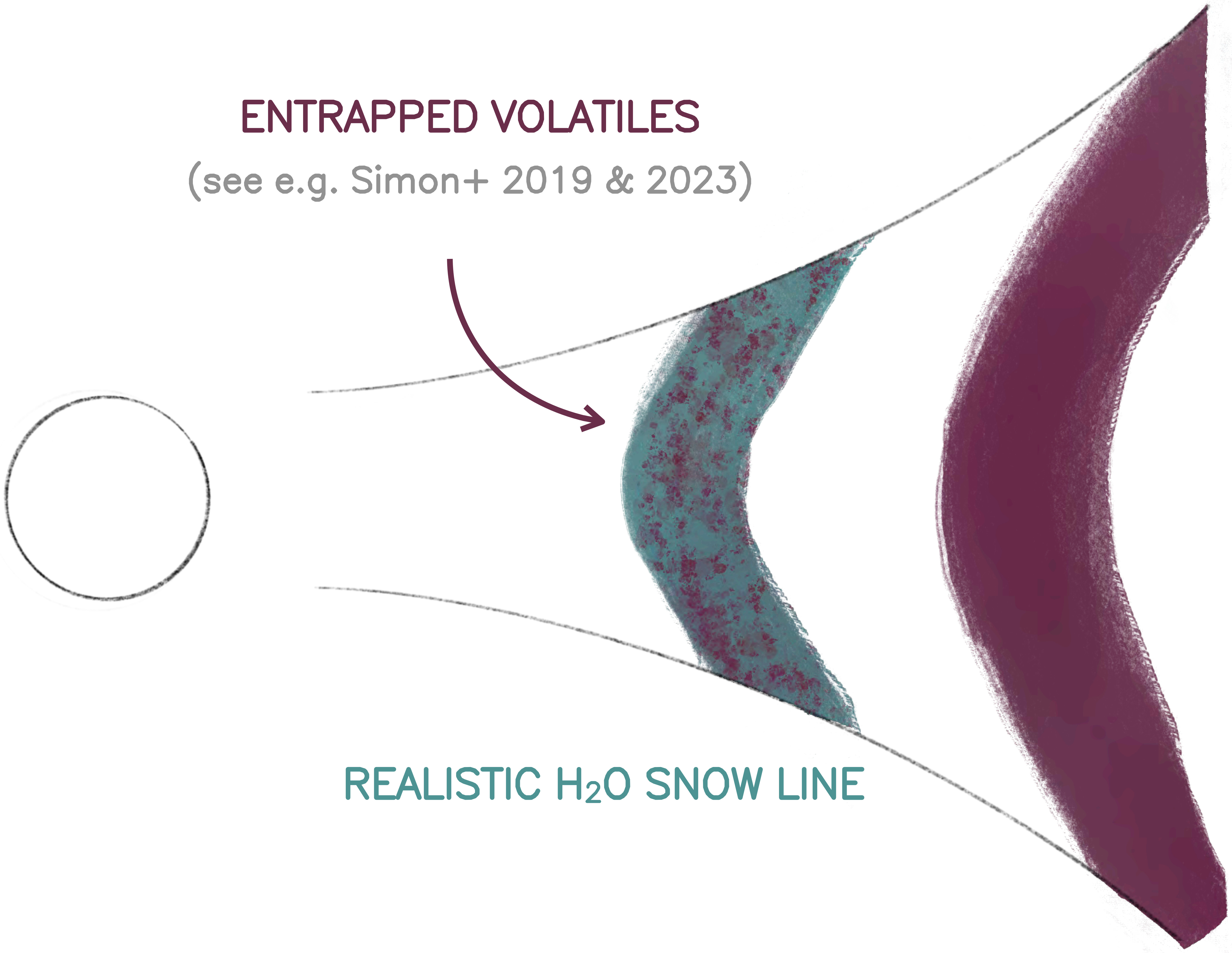
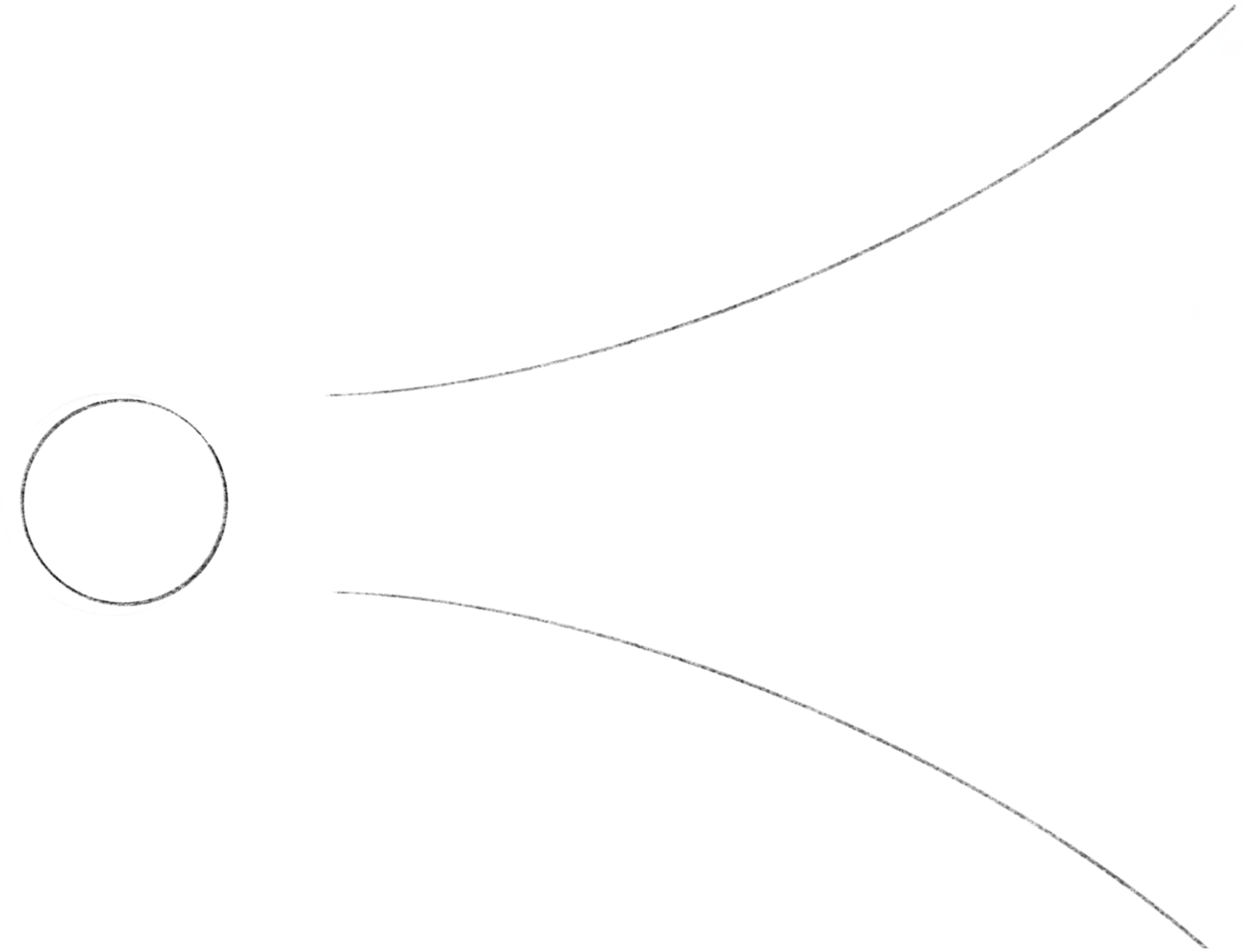


2 & 3. How is CH_3SH formed and destroyed?



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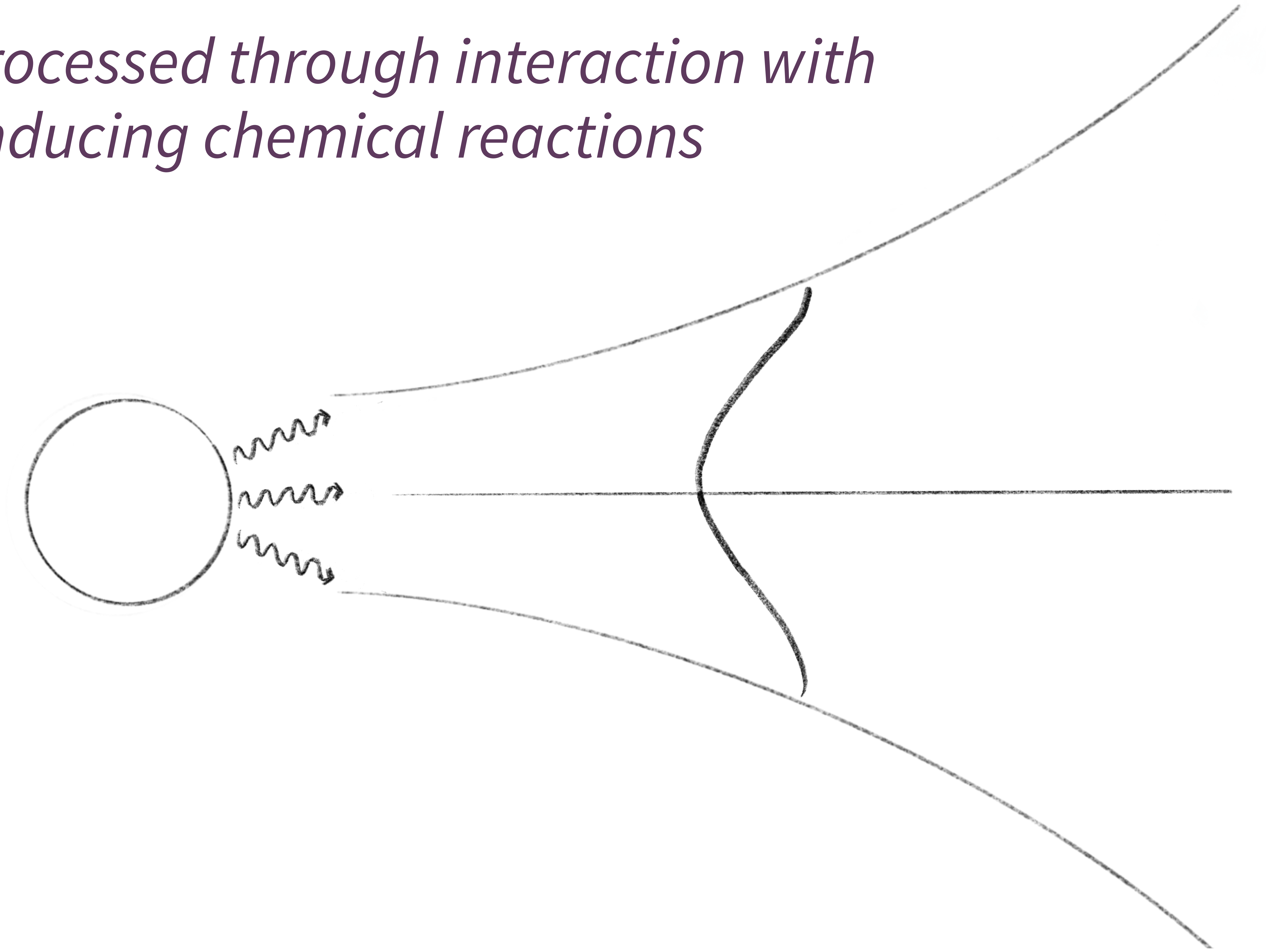
Ices can be processed through interaction with UV photons inducing chemical reactions



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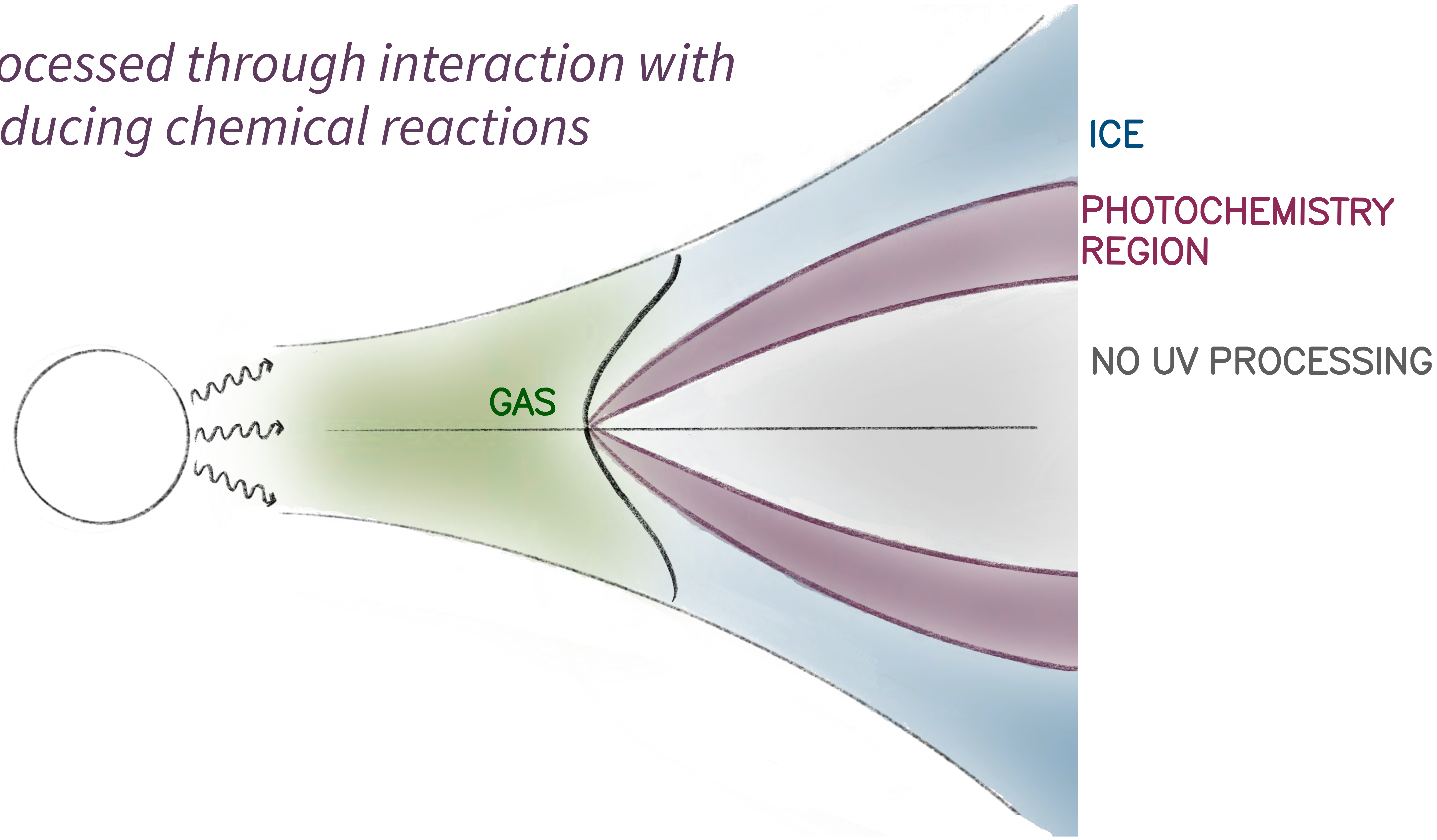

How do we simulate disk conditions in the laboratory?

Ultra-high vacuum chambers (we have 4 in the Öberg Astrochemistry Lab at CfA!)

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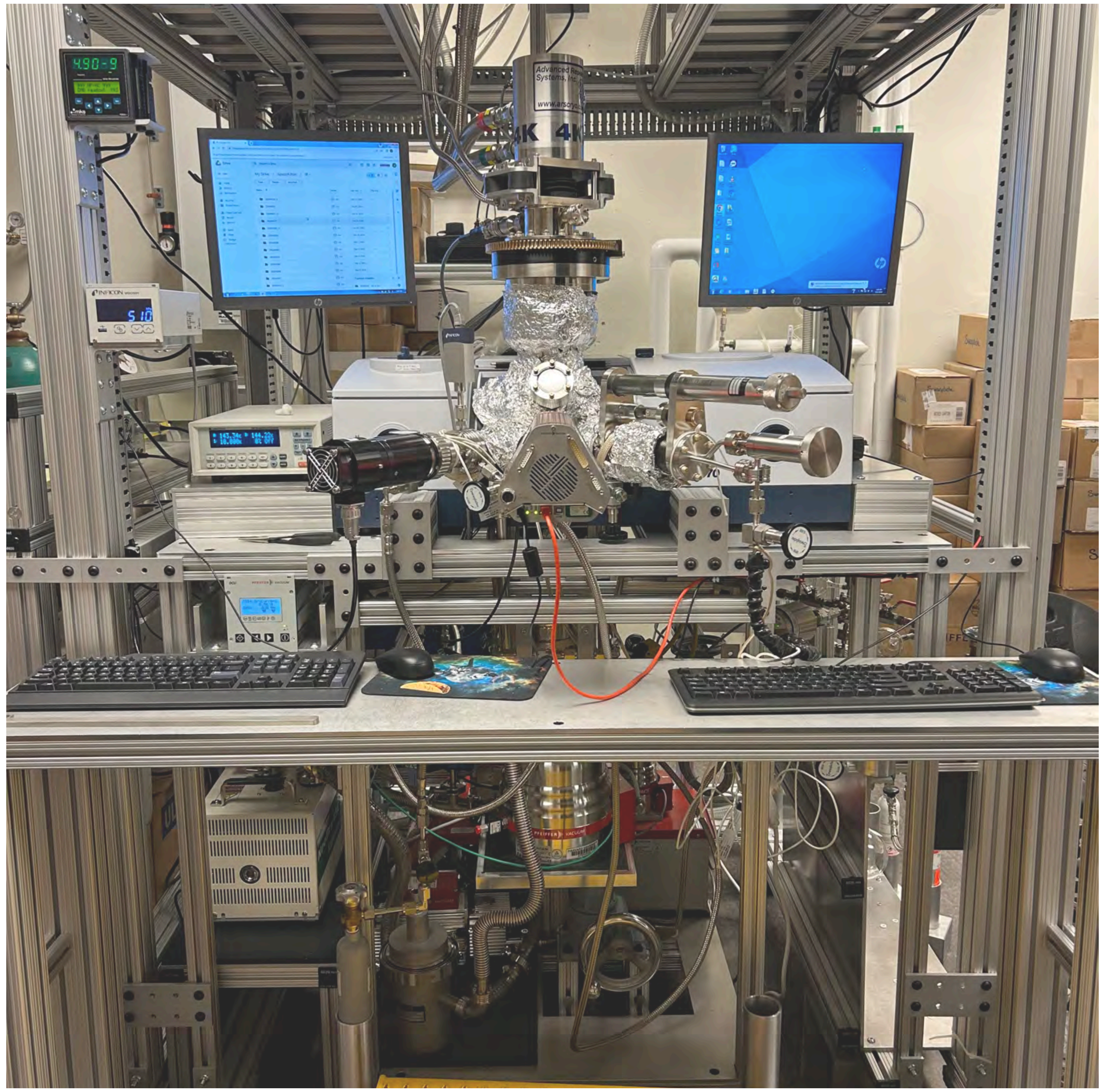

SIMPLEST

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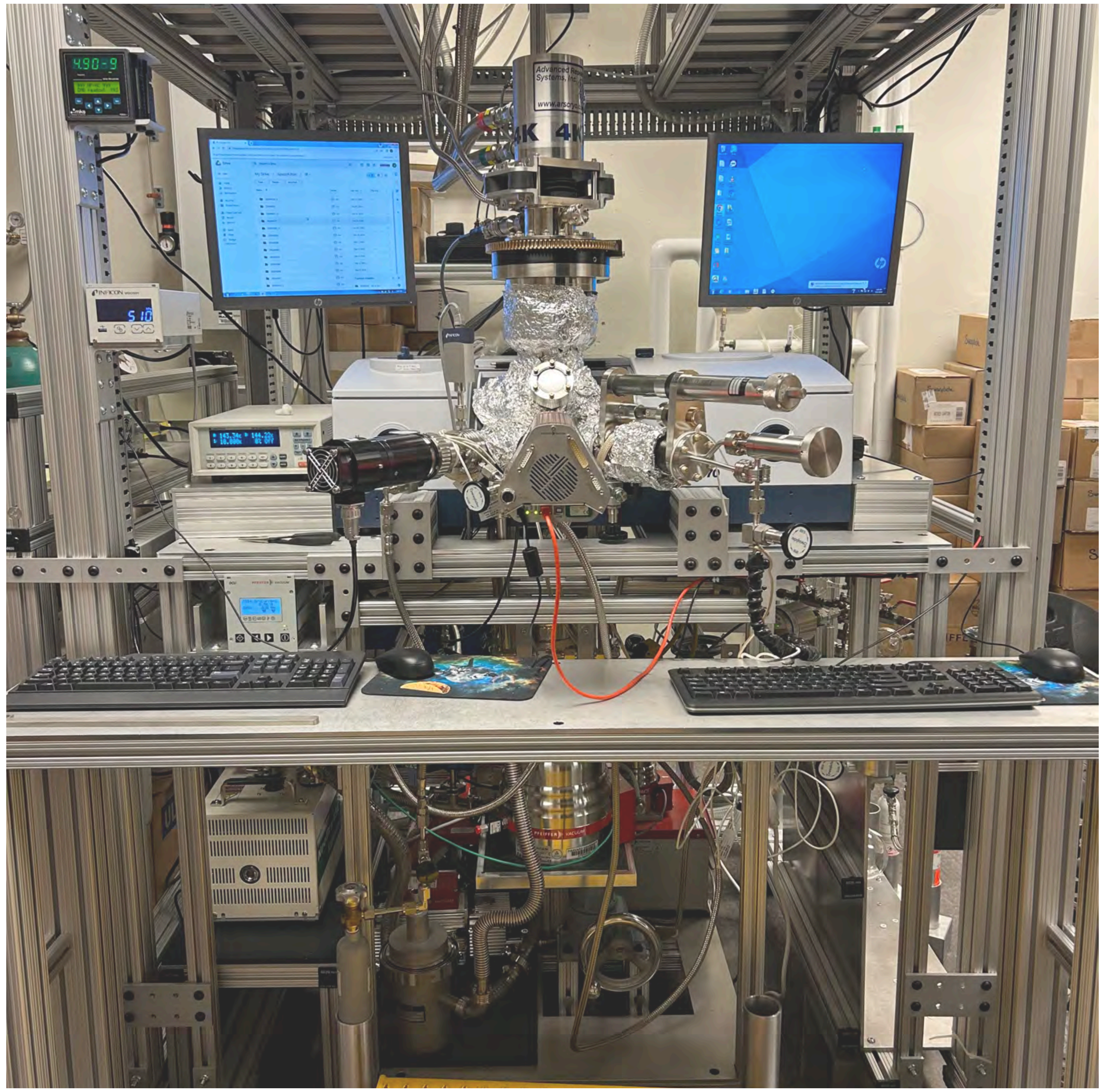

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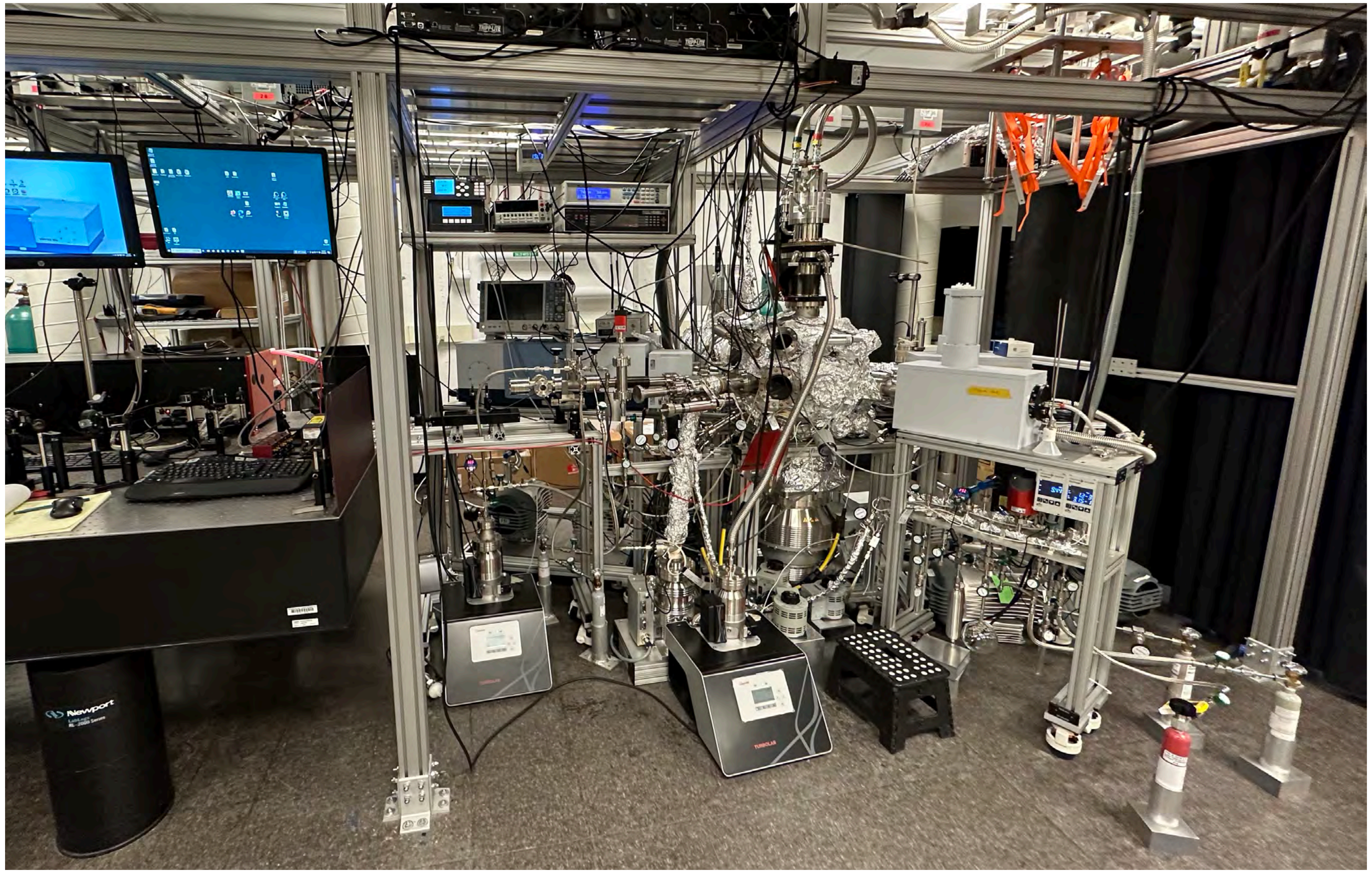

MOST COMPLEX

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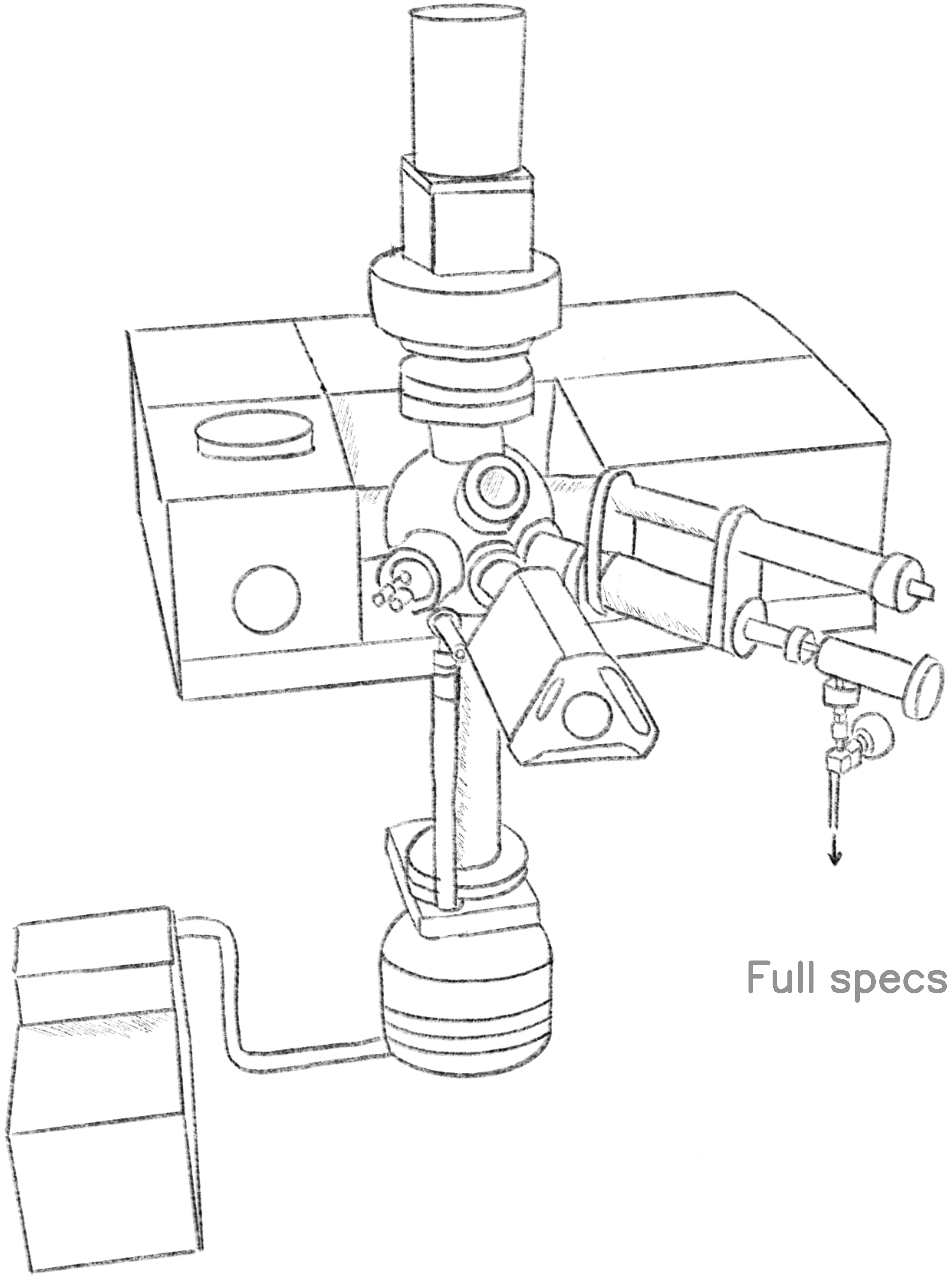
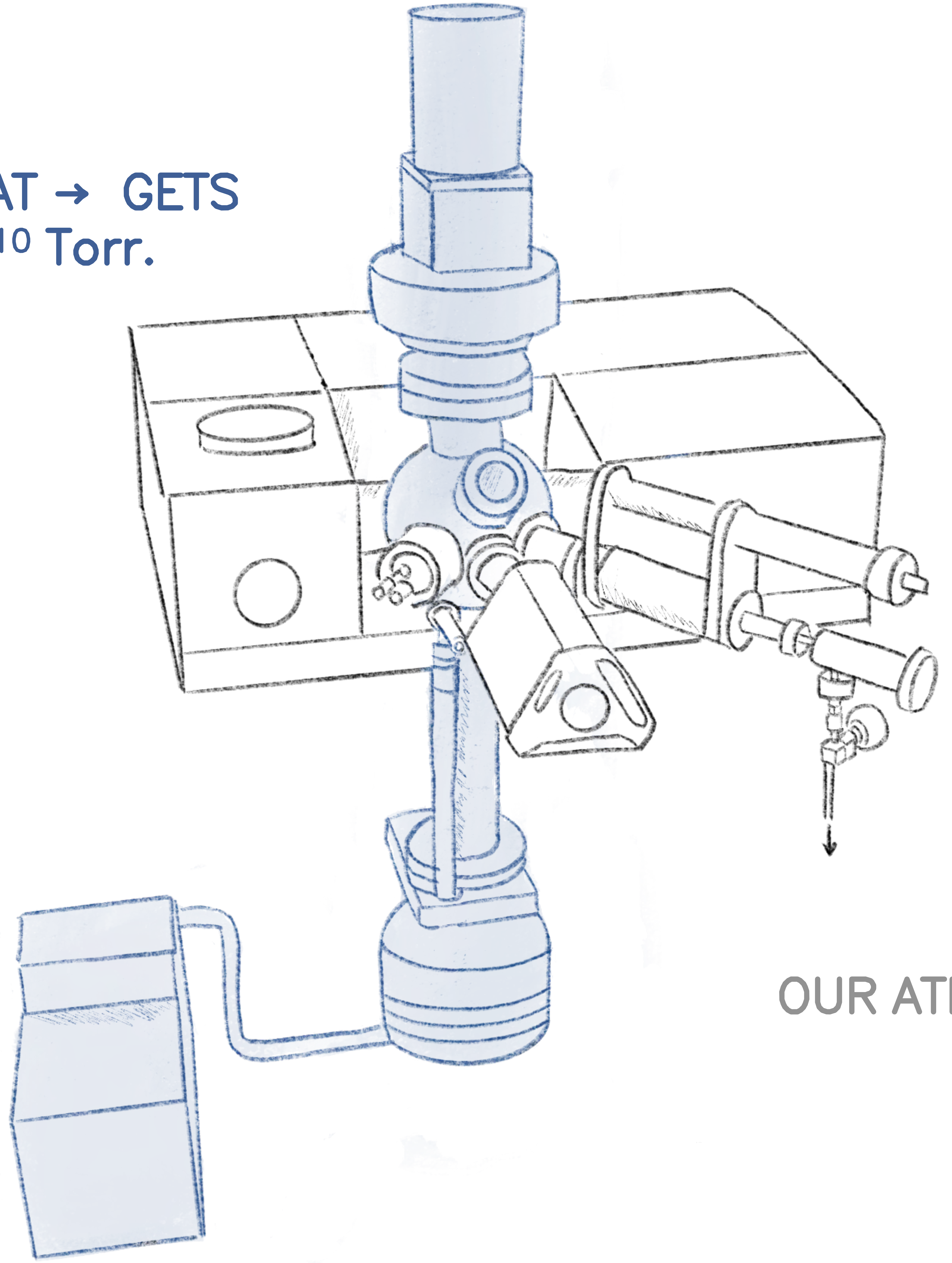
Brief experimental procedure



Full specs in Simon+ 2023.

We first get to low T, low P

CLOSED CYCLE HE CRYOSTAT → GETS DOWN TO 10 K AND 10^{-10} Torr.



OUR ATMOSPHERE IS 760 Torr...

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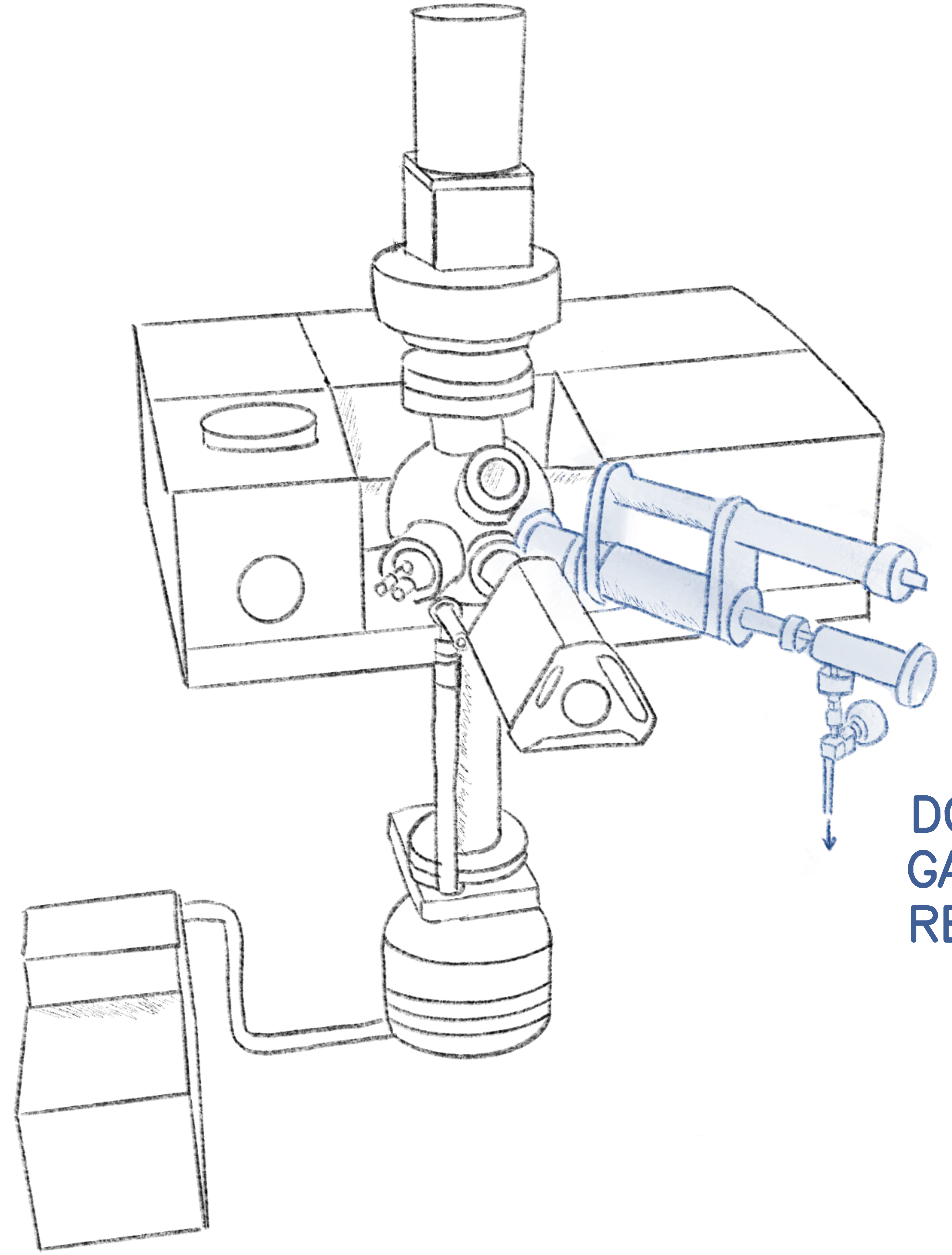
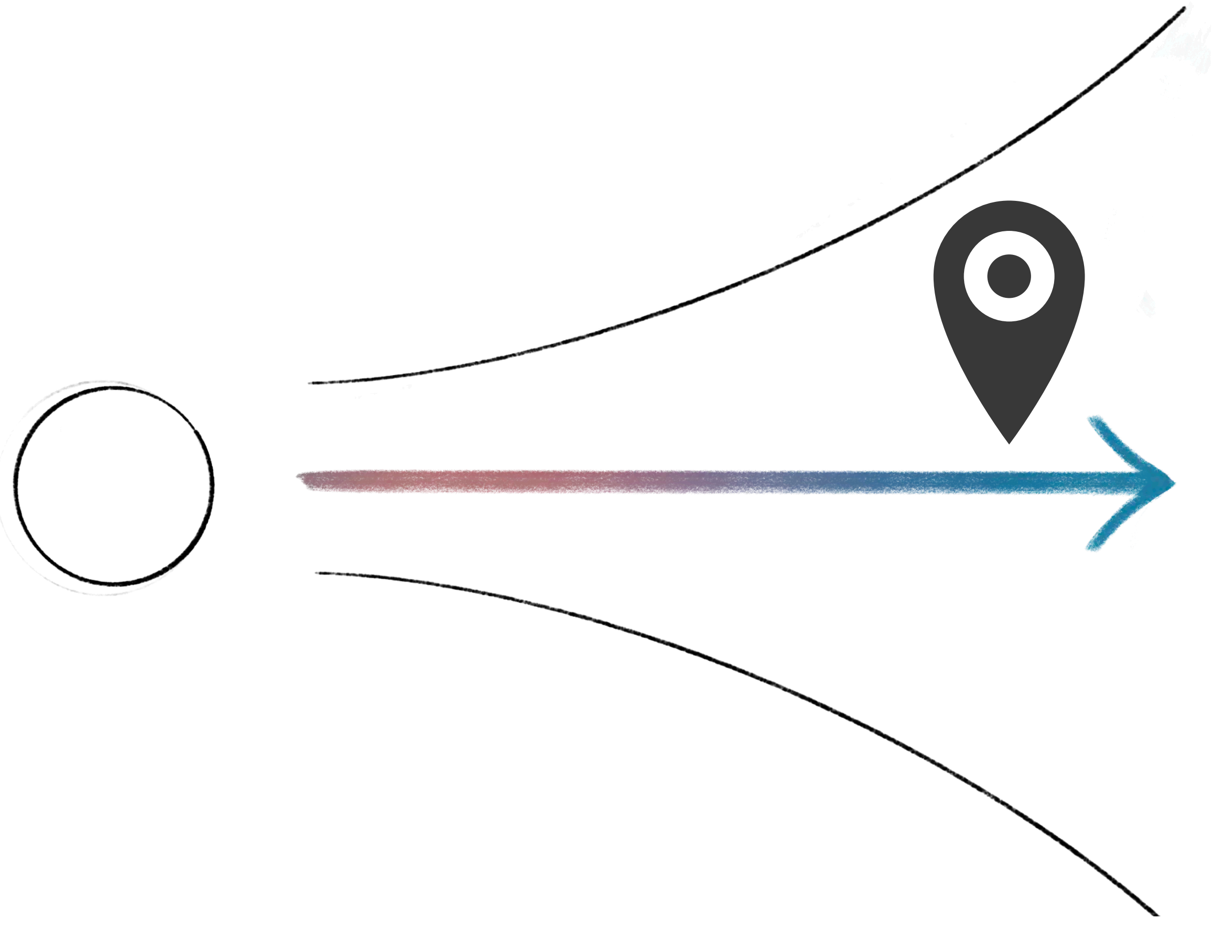
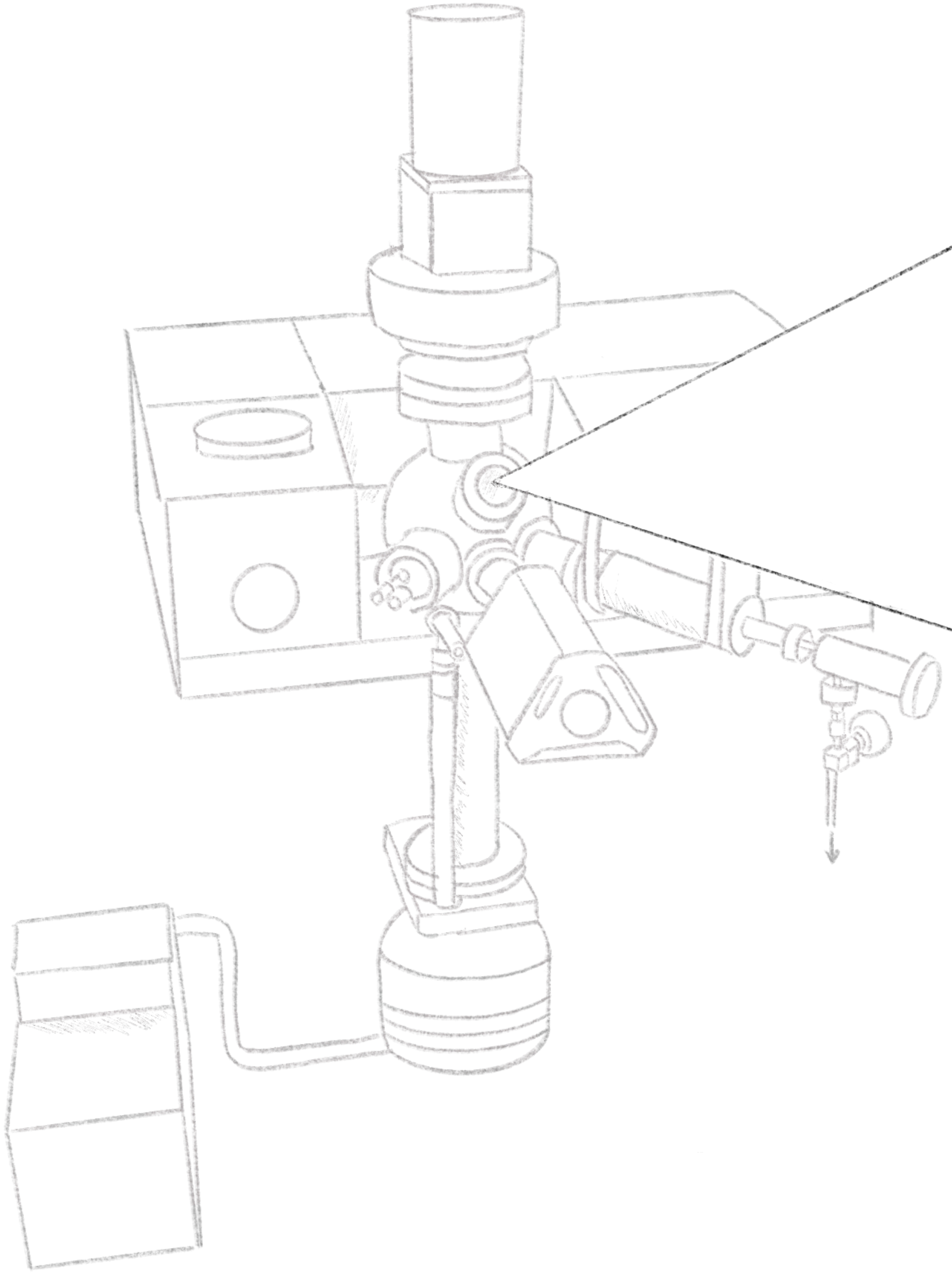
Introduce molecules into chamber



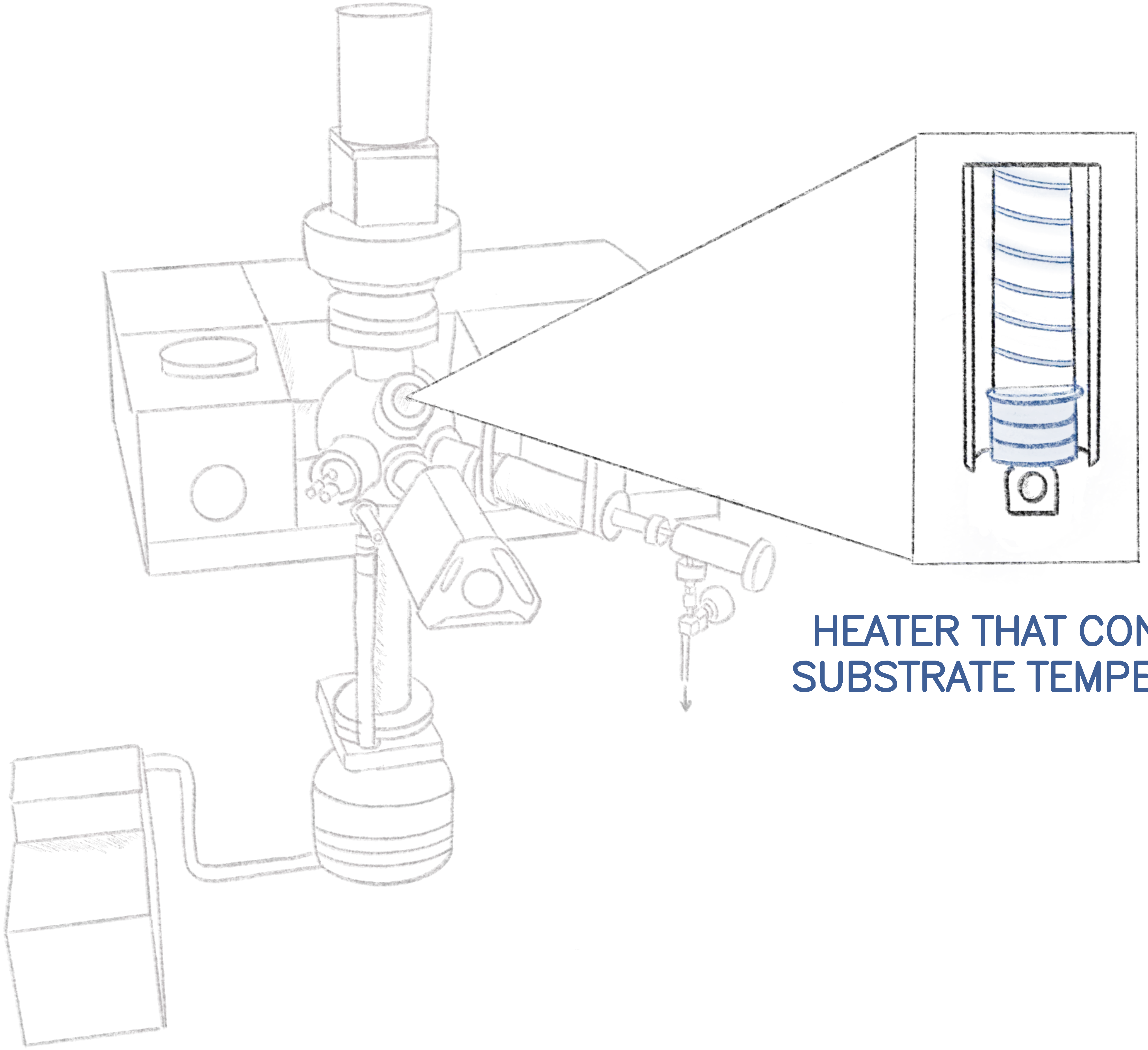
DOSER THAT CONNECTS TO A GAS LINE WHERE WE MIX OUR REACTANTS (i.e. CH_3SH, H_2O, CH_3OH)

Form ices on an infrared (IR) inactive substrate

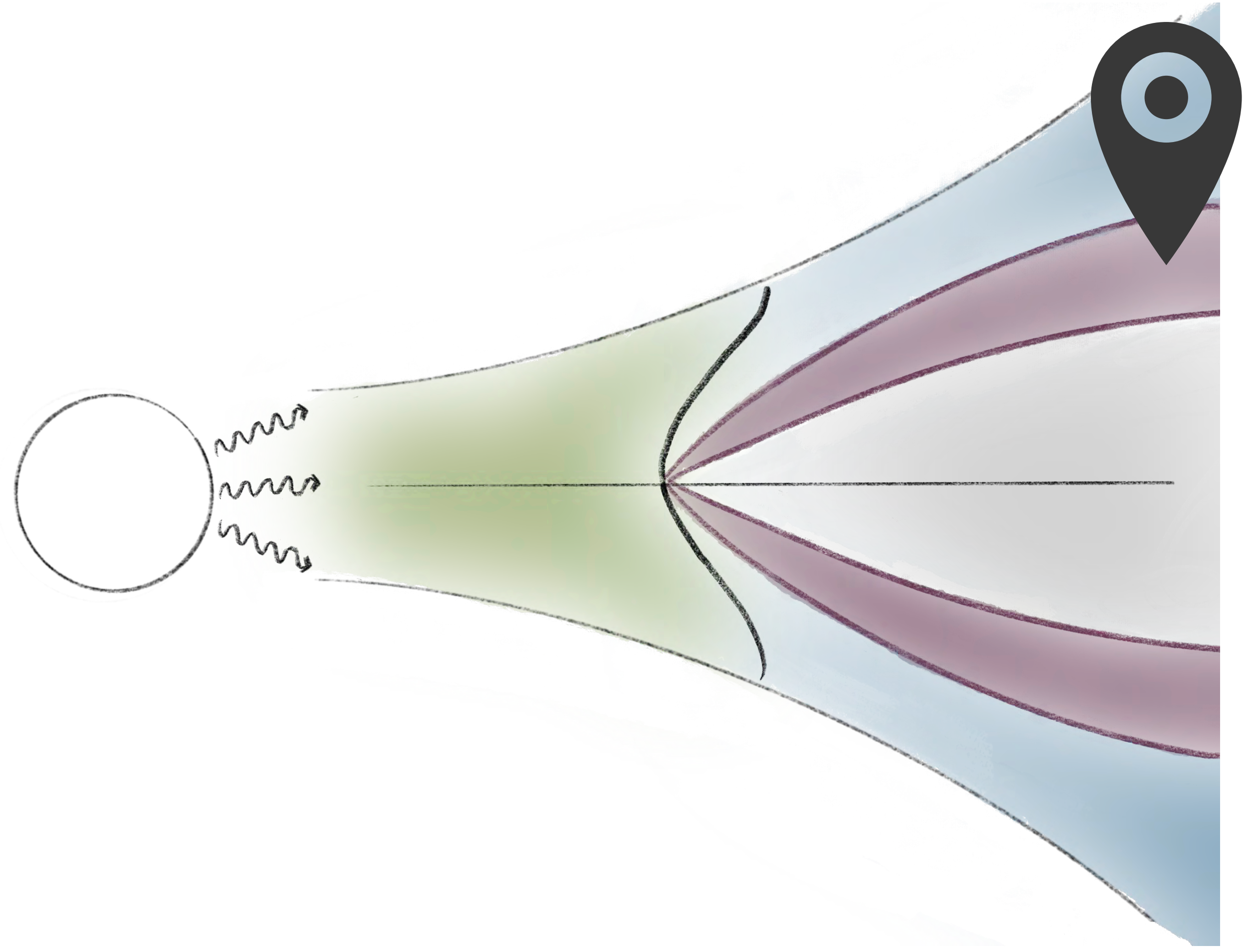


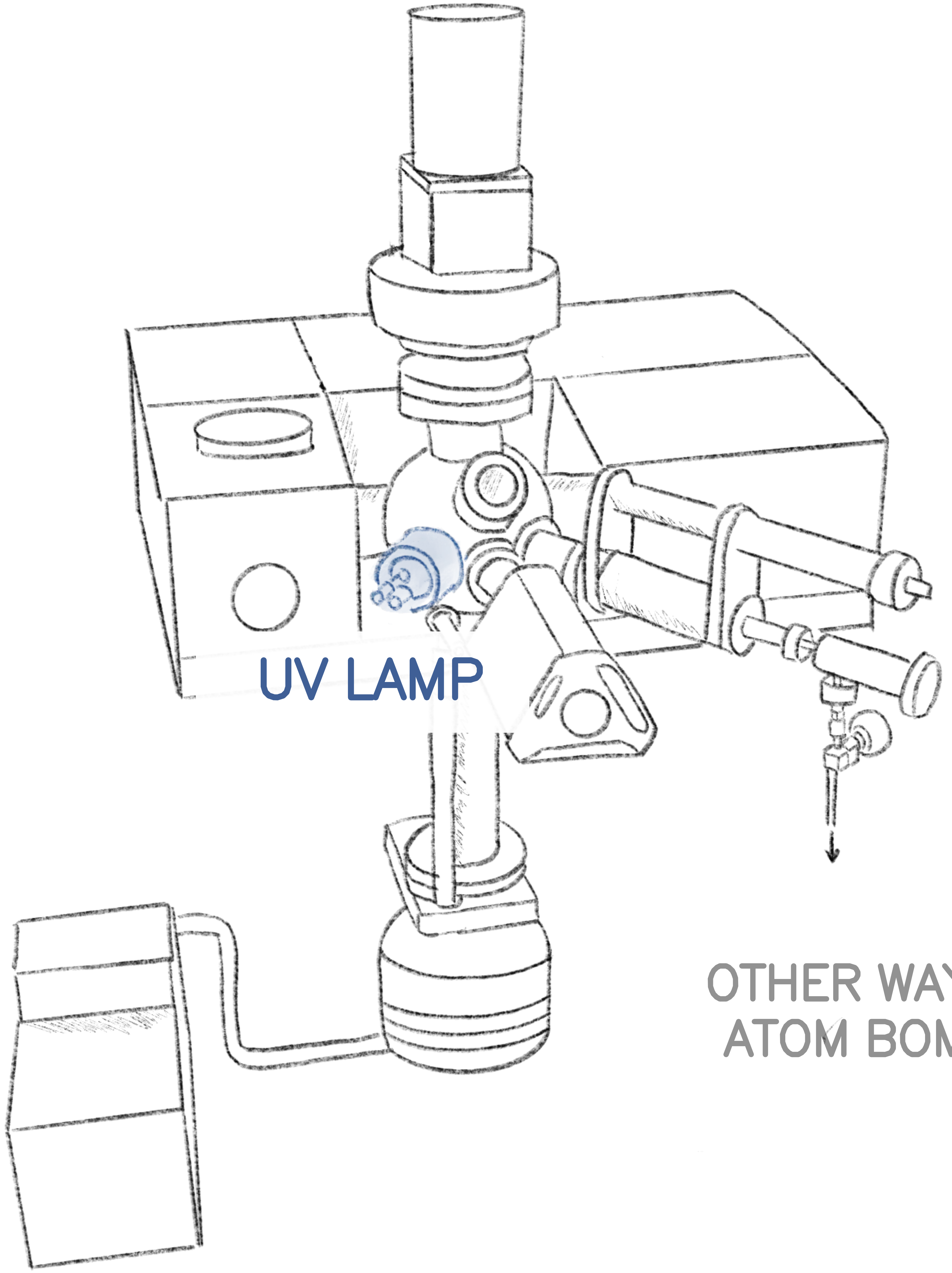


We can process the ice thermally



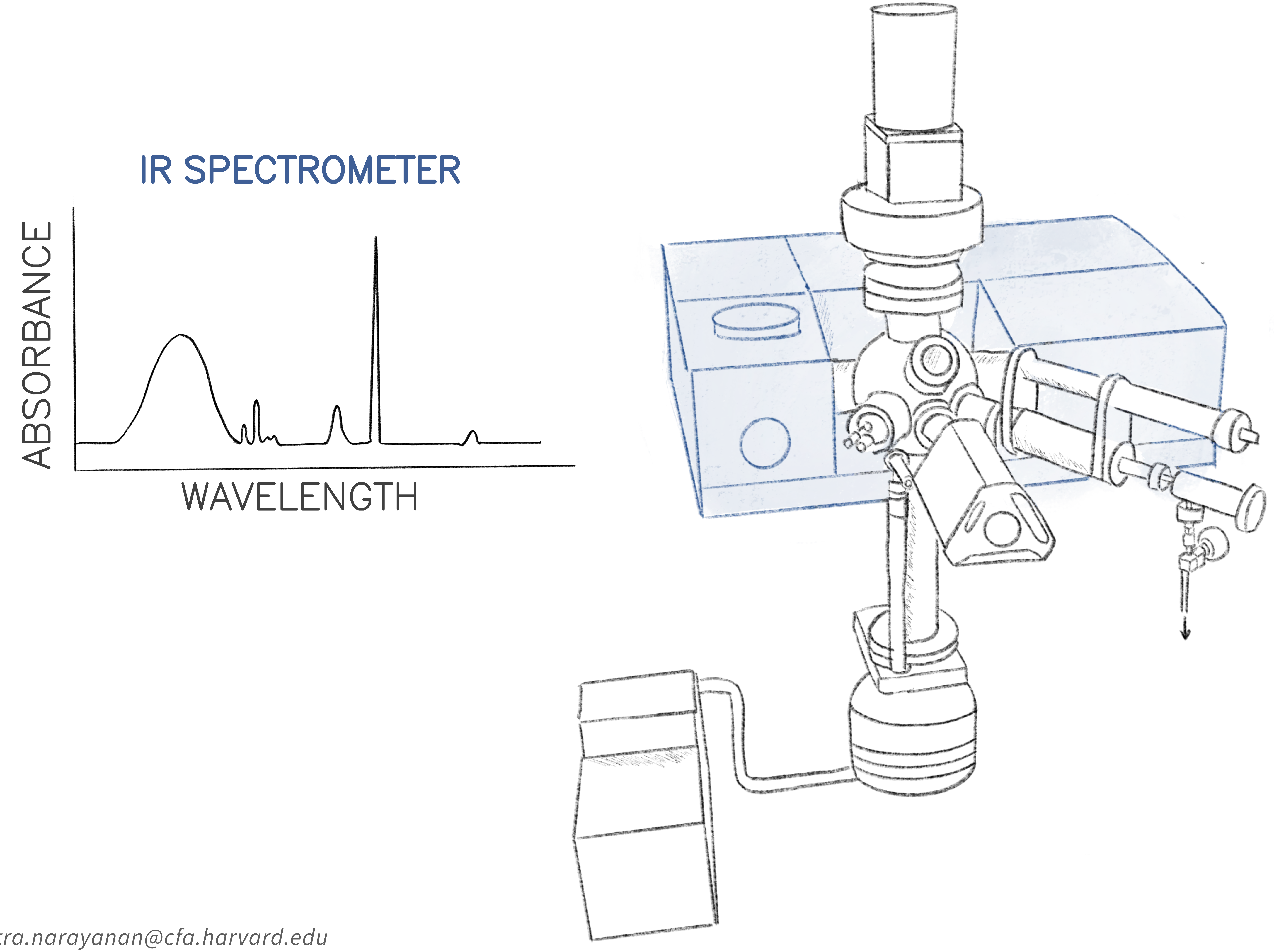
We can also process the ice via irradiation





OTHER WAYS INCLUDE ELECTRON OR ATOM BOMBARDMENT AND LASERS.

Data product 1: IR spectra → characterize ice phase



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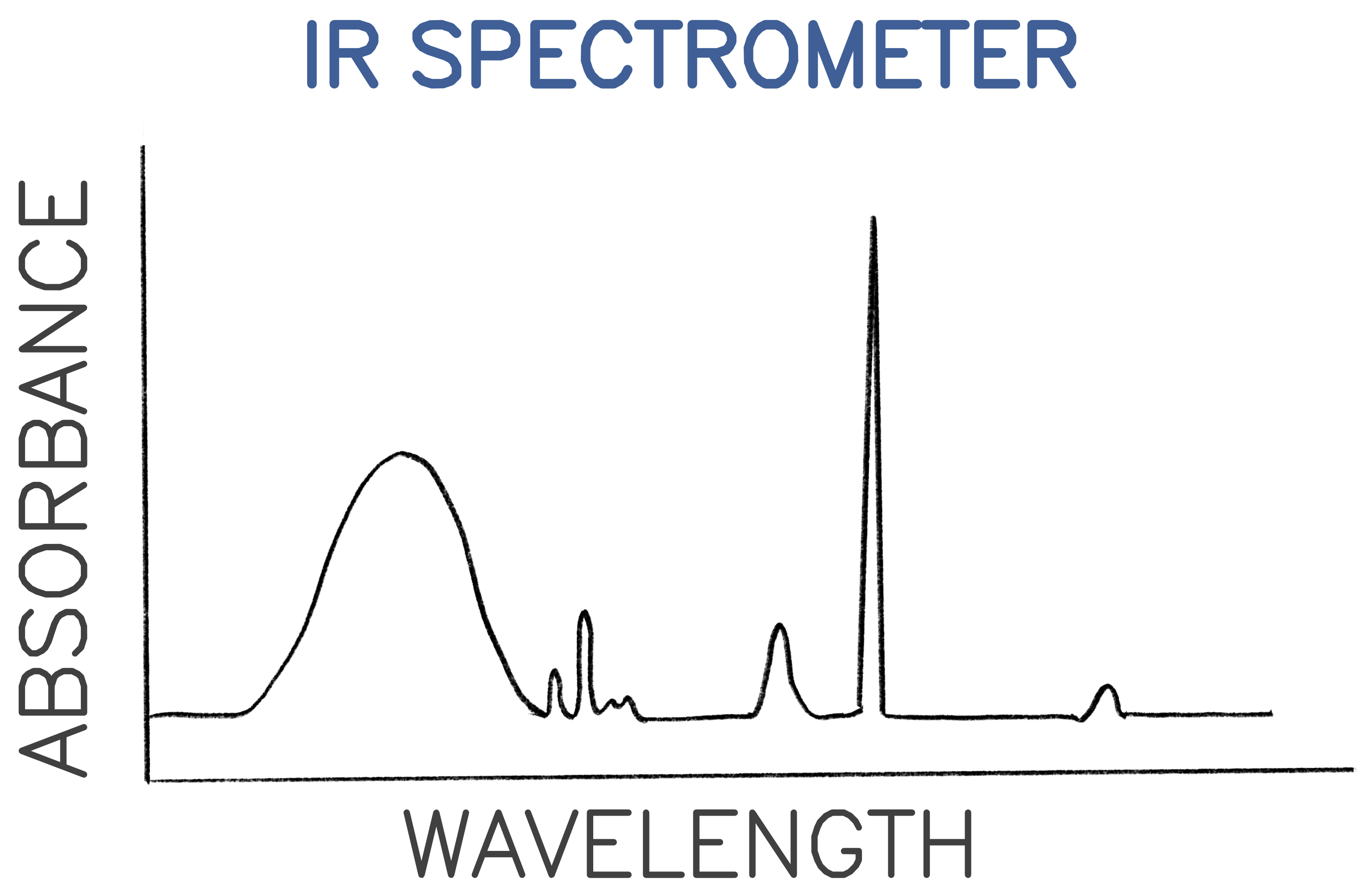

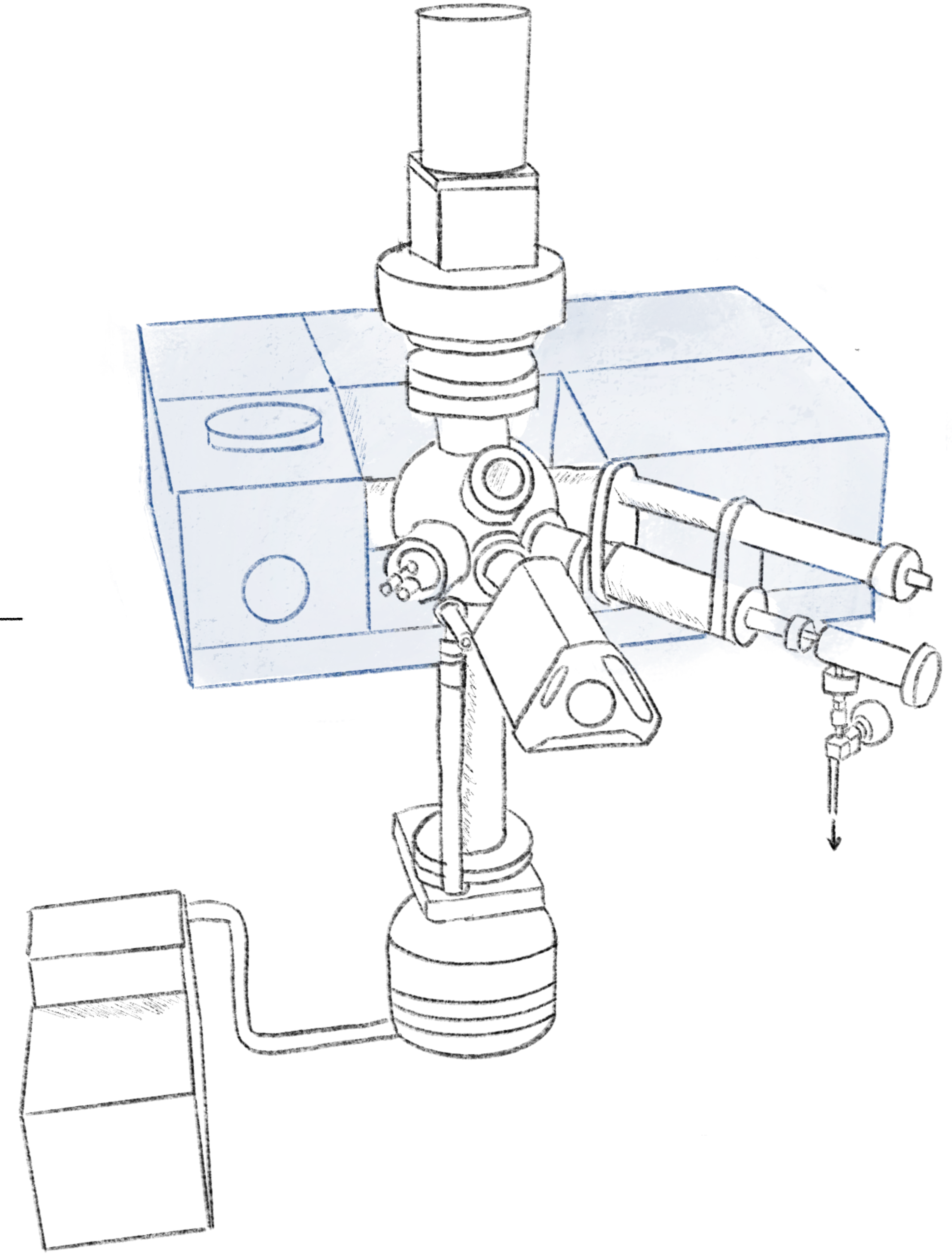

CAN COMPARE LAB + JWST SPECTRA TO UNDERSTAND ICE COMPOSITION

(see Berger+ 2024)

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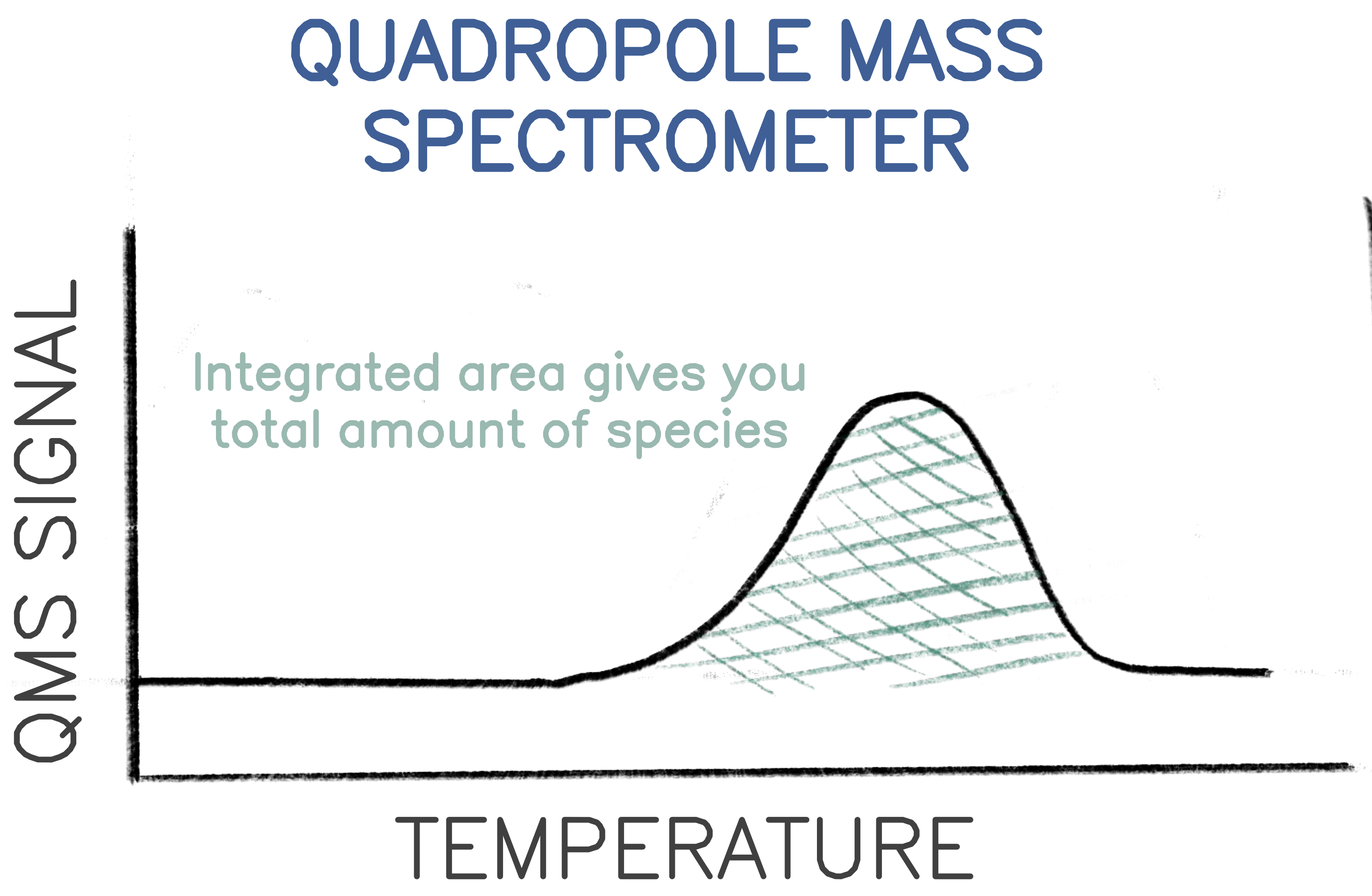
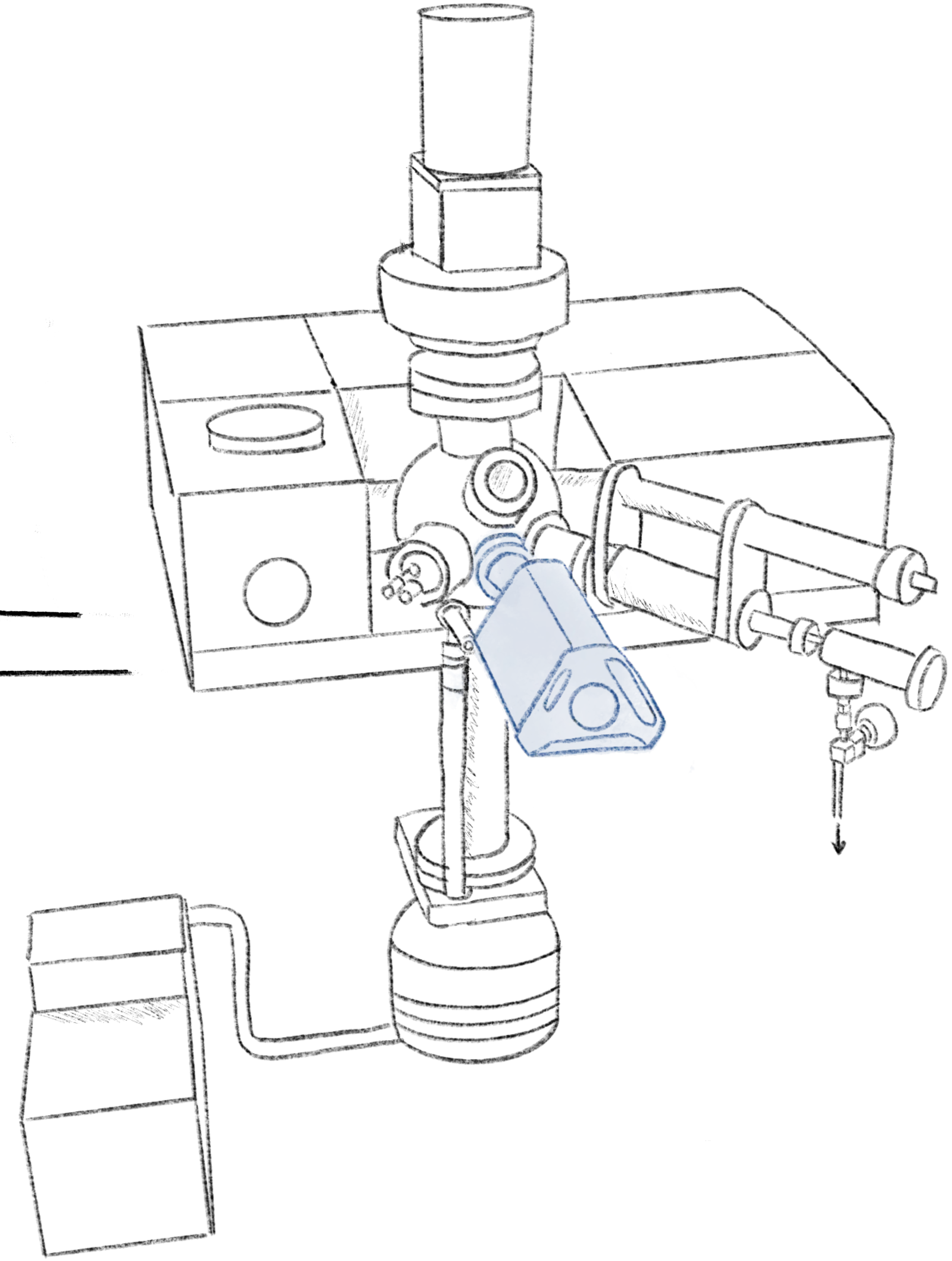
Data product 2: mass spectra → characterize gas phase





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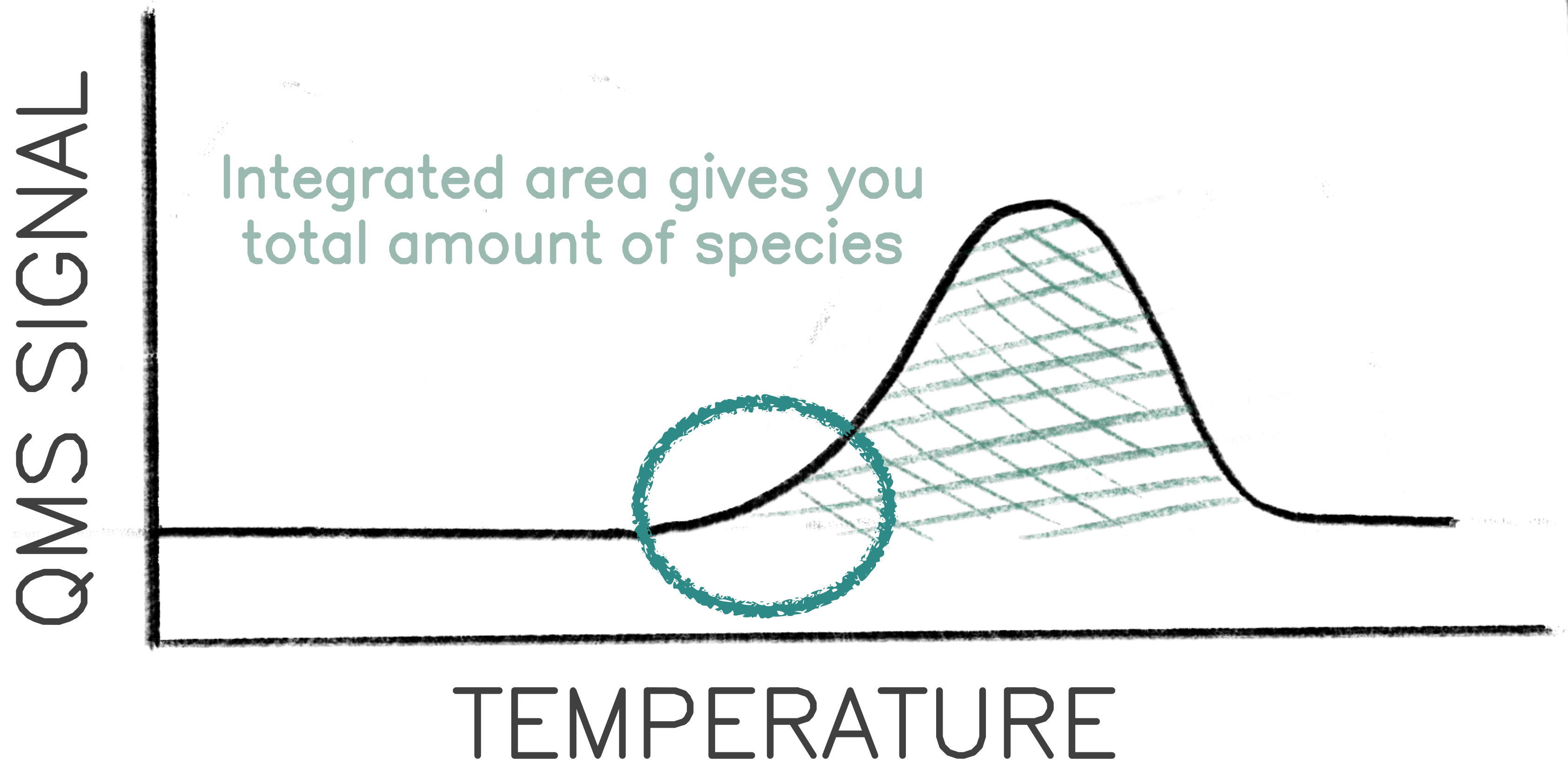
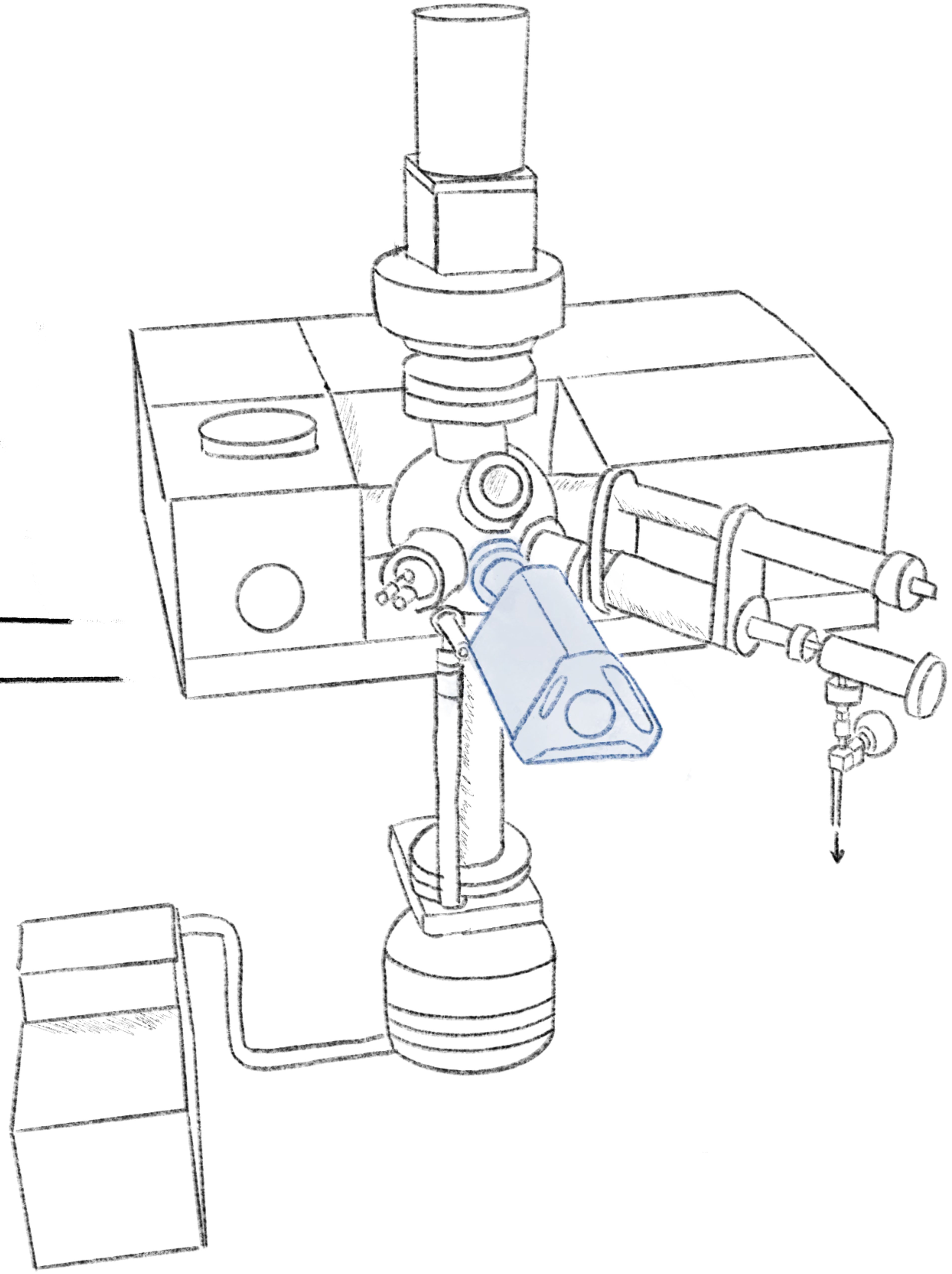
QUADROPOLE MASS SPECTROMETER



START OF THE CURVE ALLOWS US TO PROBE THE GAS—ICE BOUNDARY



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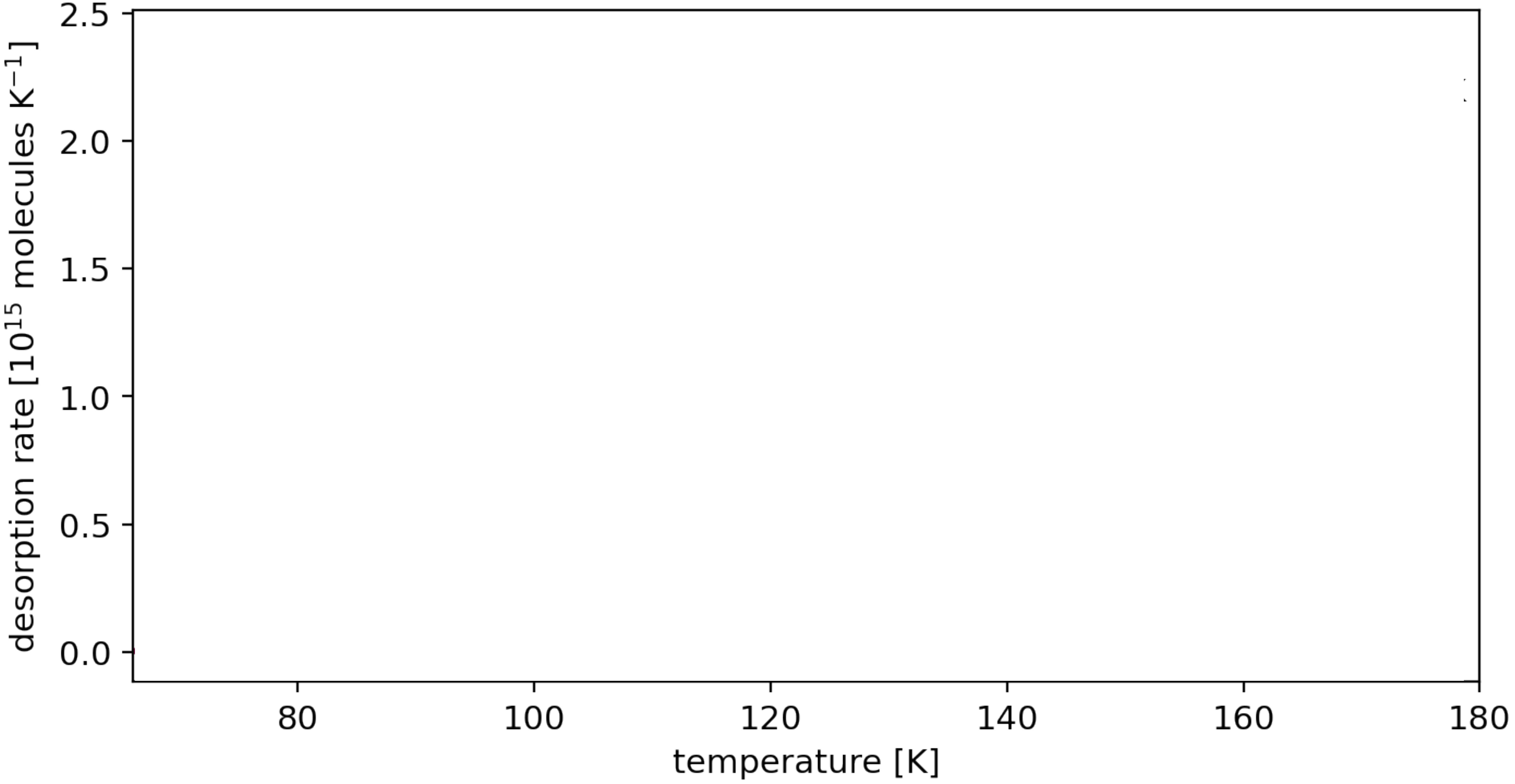
Temperature programmed desorption (TPD) curves

What temperature would CH_3SH desorb off of grains → can predict snow line location



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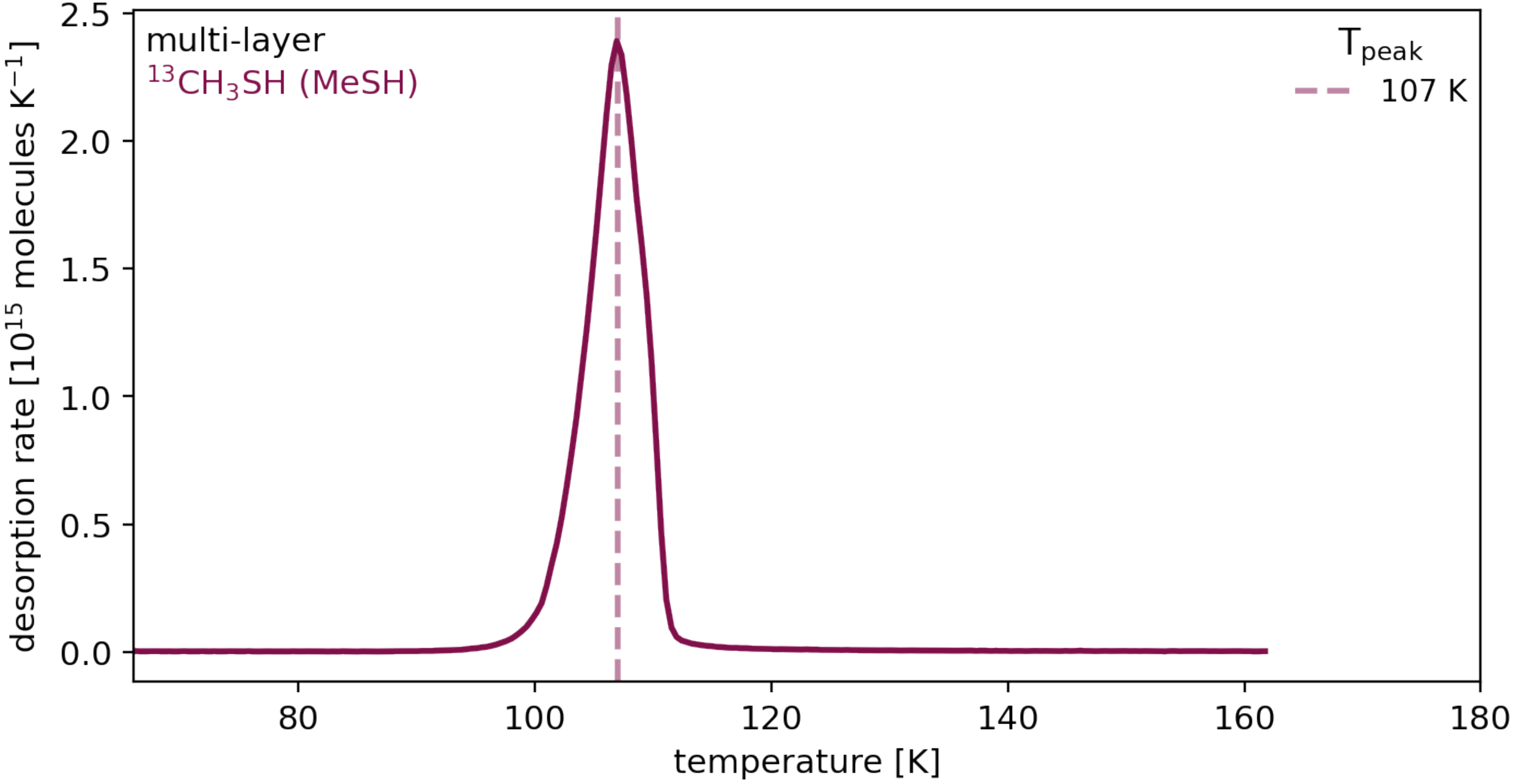

All results are from Narayanan+, ApJ, in review

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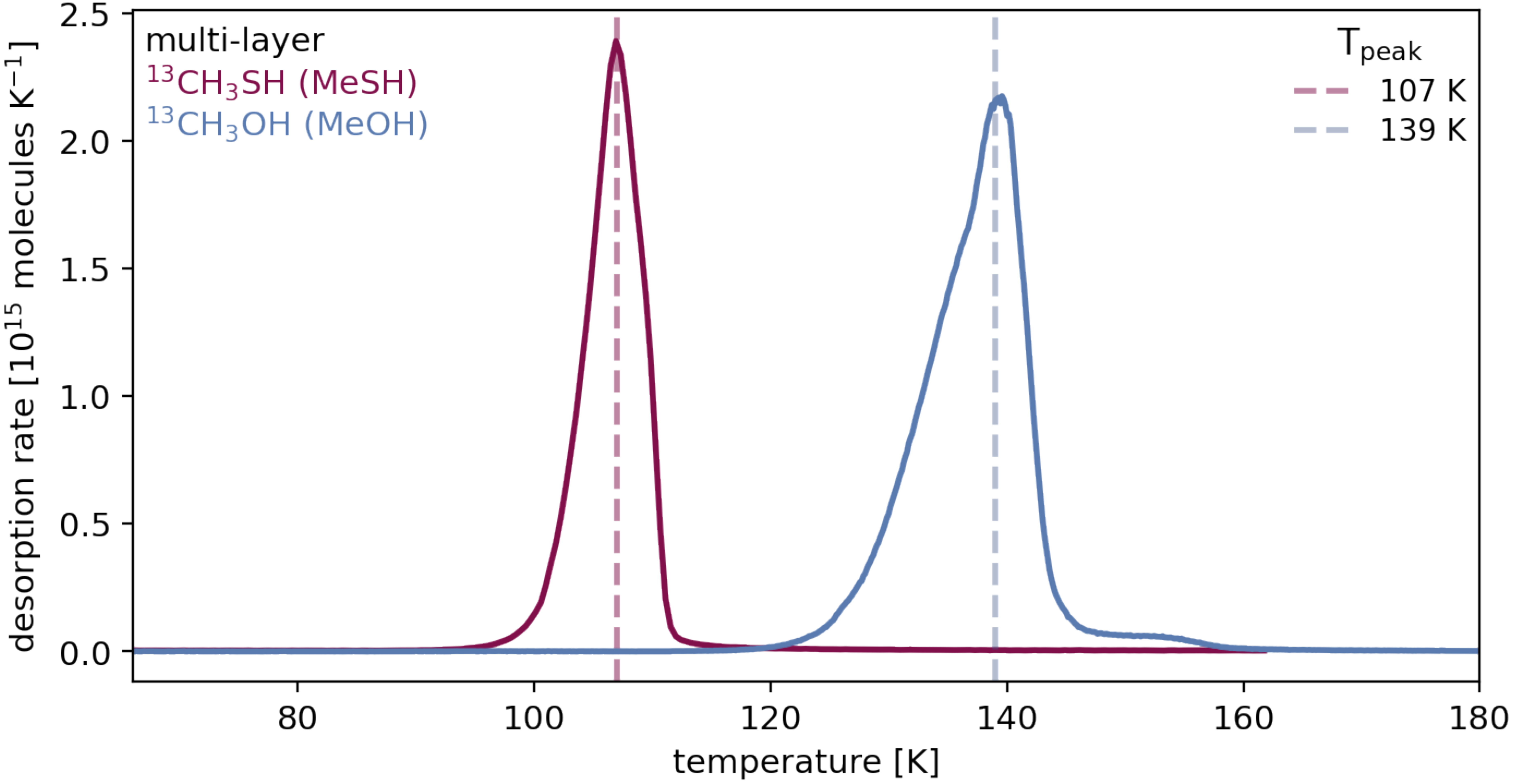

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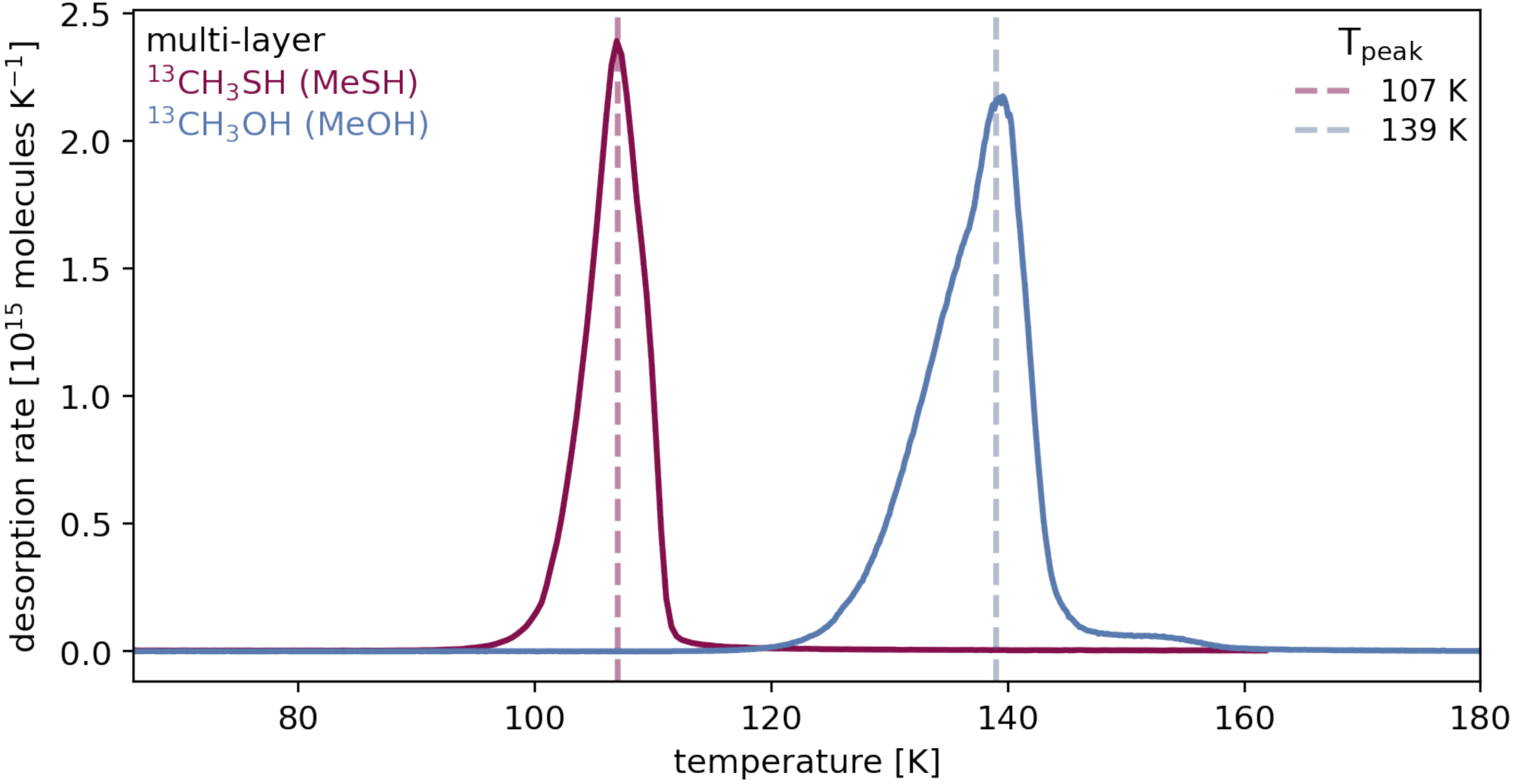

⇒ CH_3SH is more volatile than CH_3OH because it desorbs at a lower temperature

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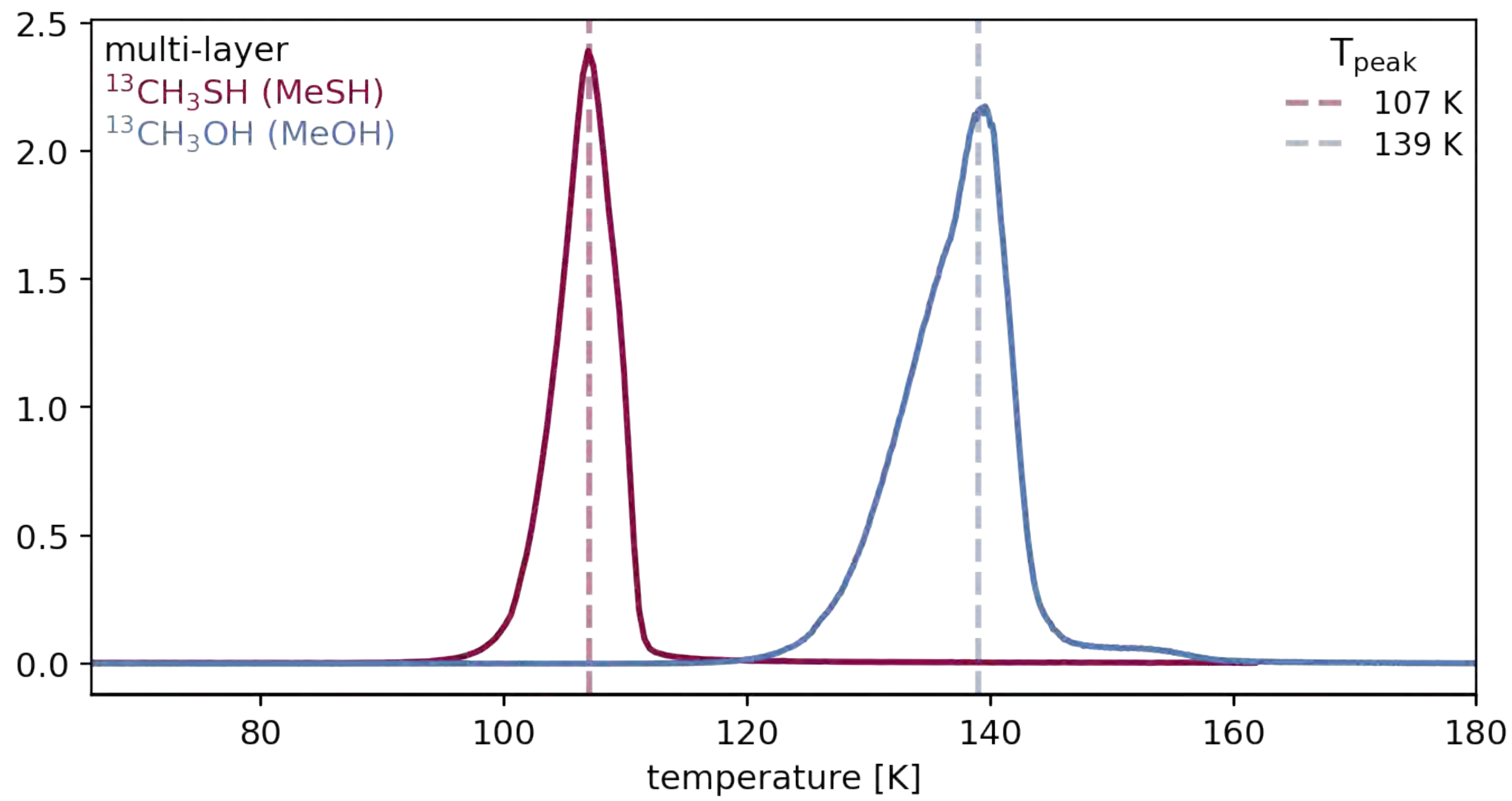
Pure vs. layered thermal desorption



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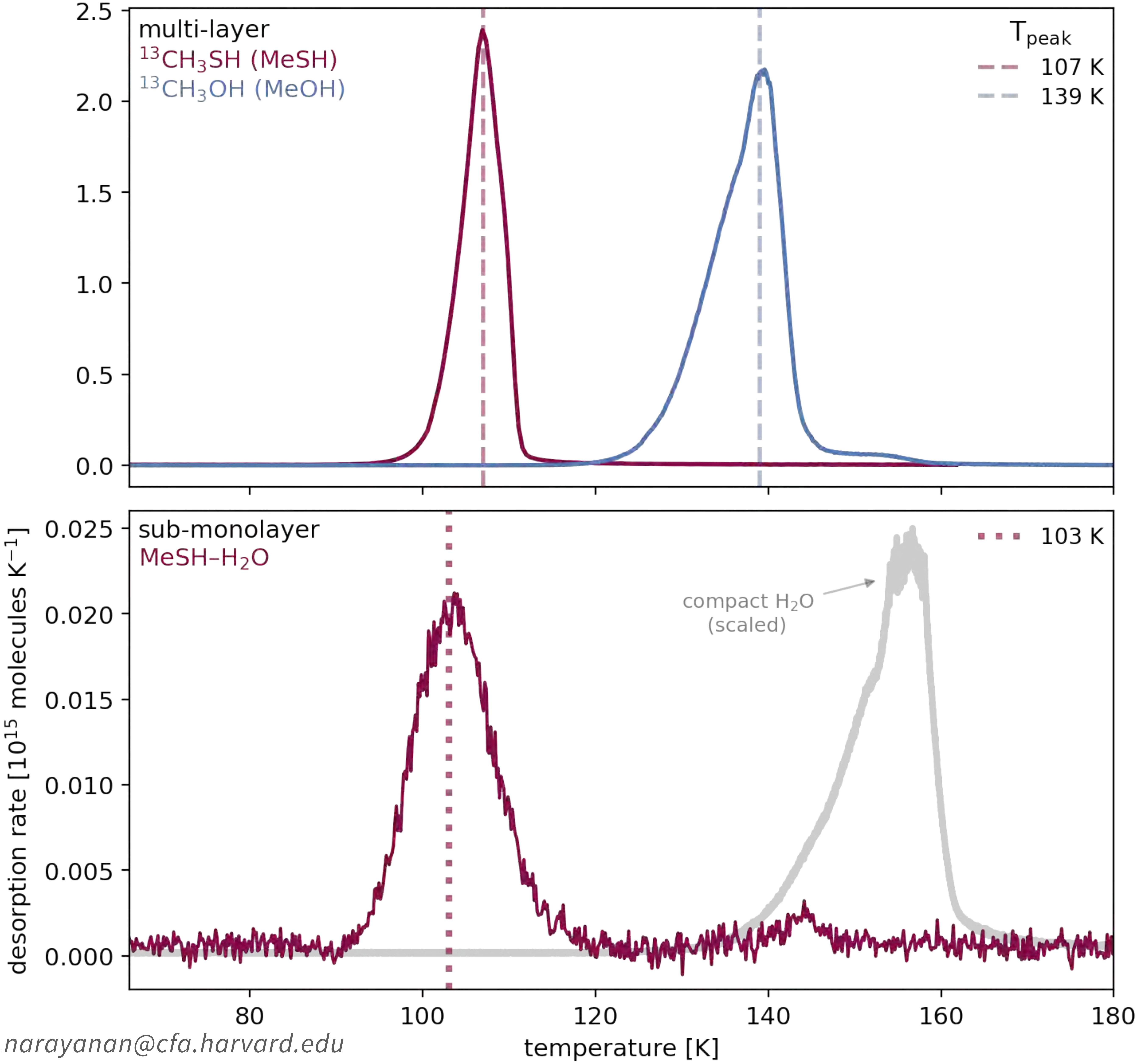

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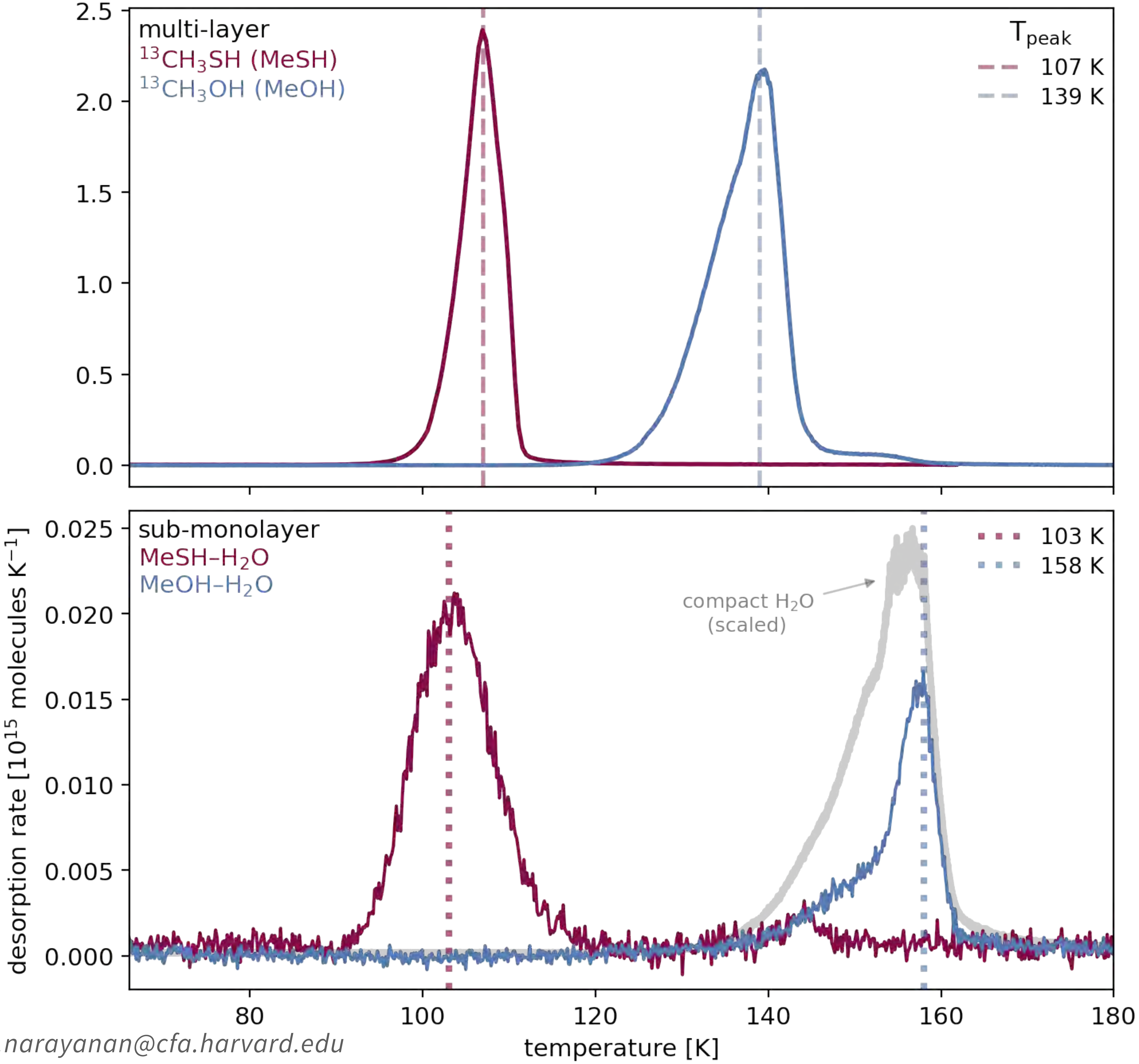

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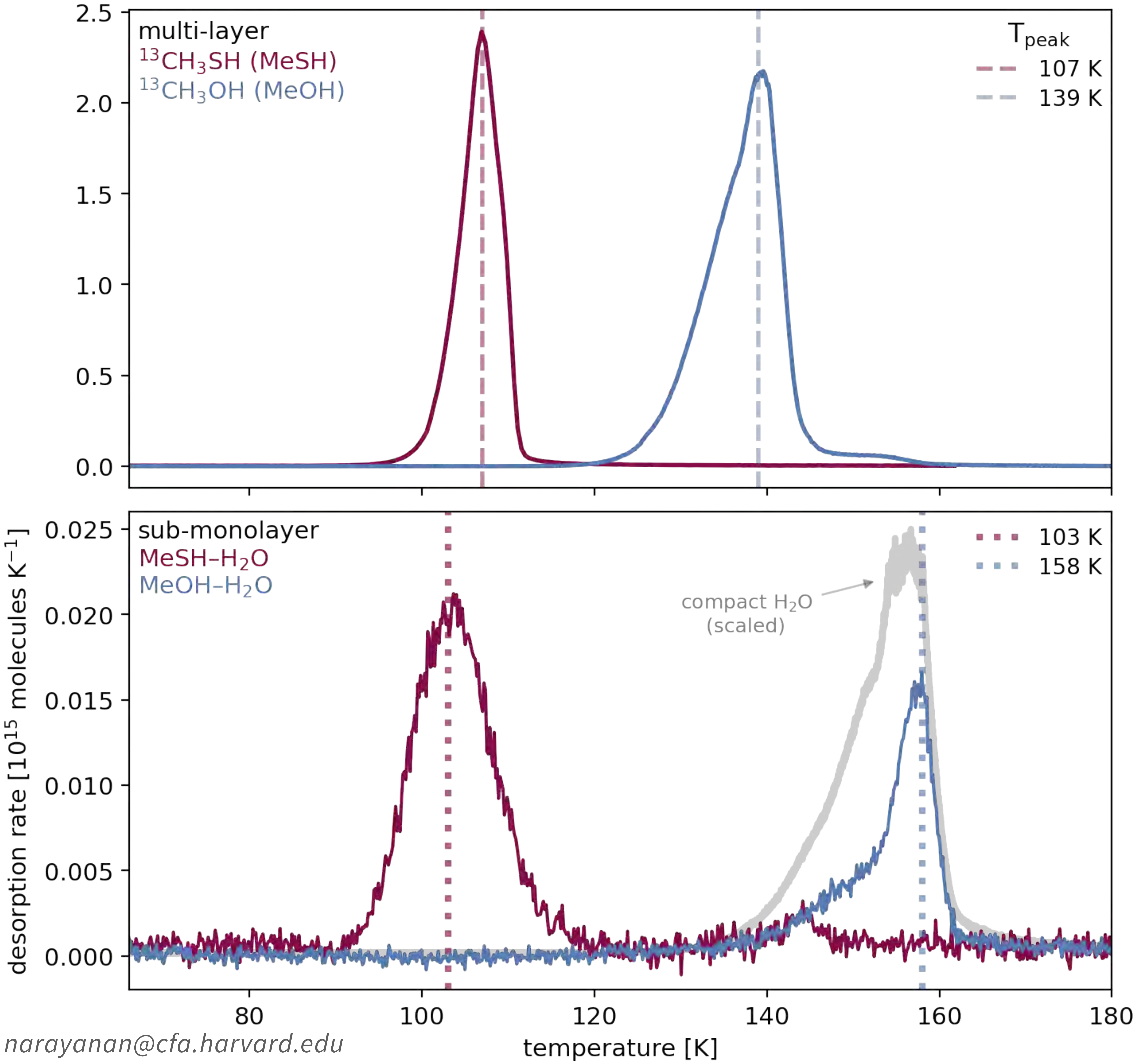

⇒ CH_3SH is indifferent to whether it binds to itself or to water; CH_3OH interacts with water significantly

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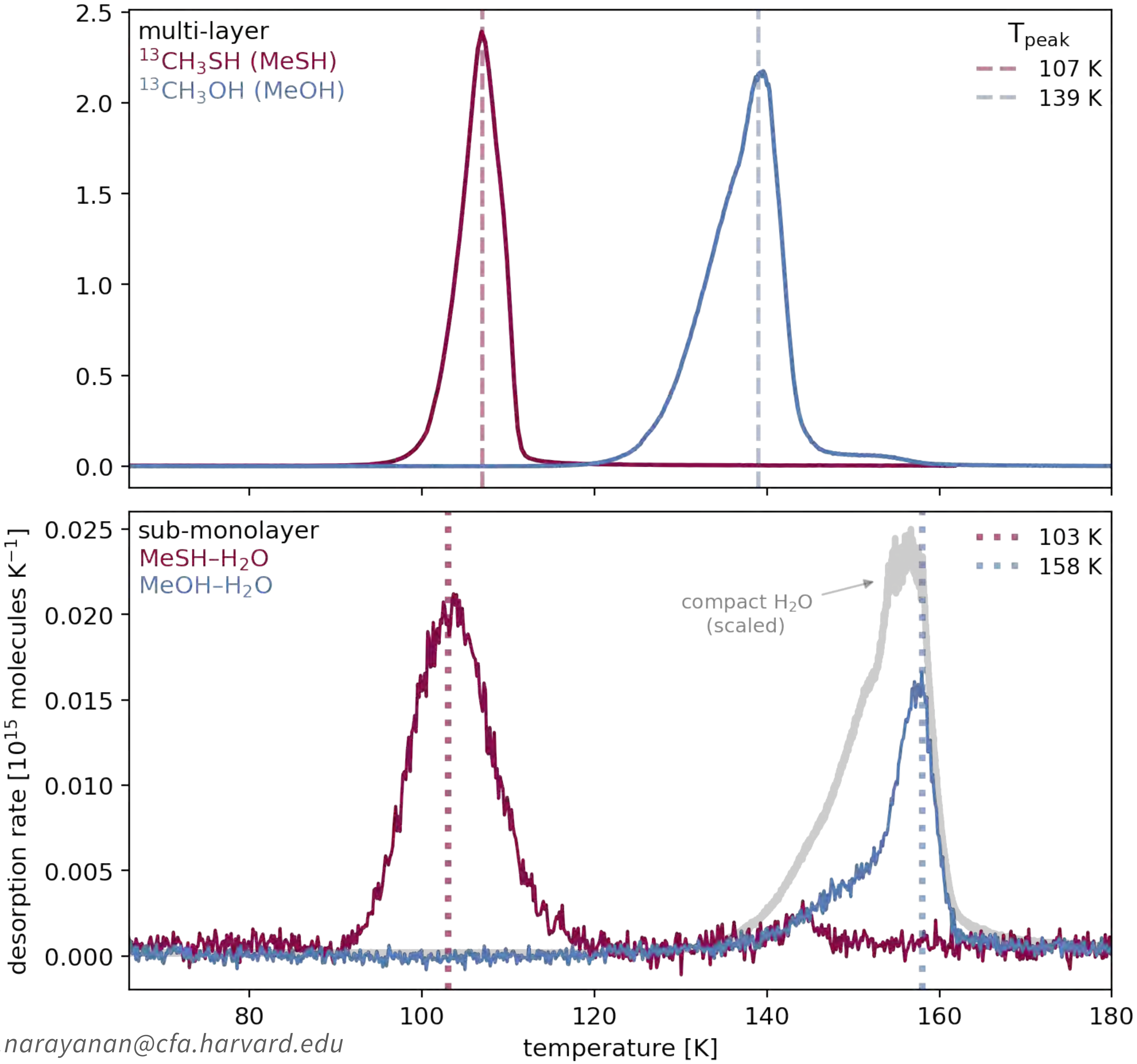

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We can infer that CH_3SH snow line would be further out than CH_3OH's

(computed this quantitatively… can chat later)

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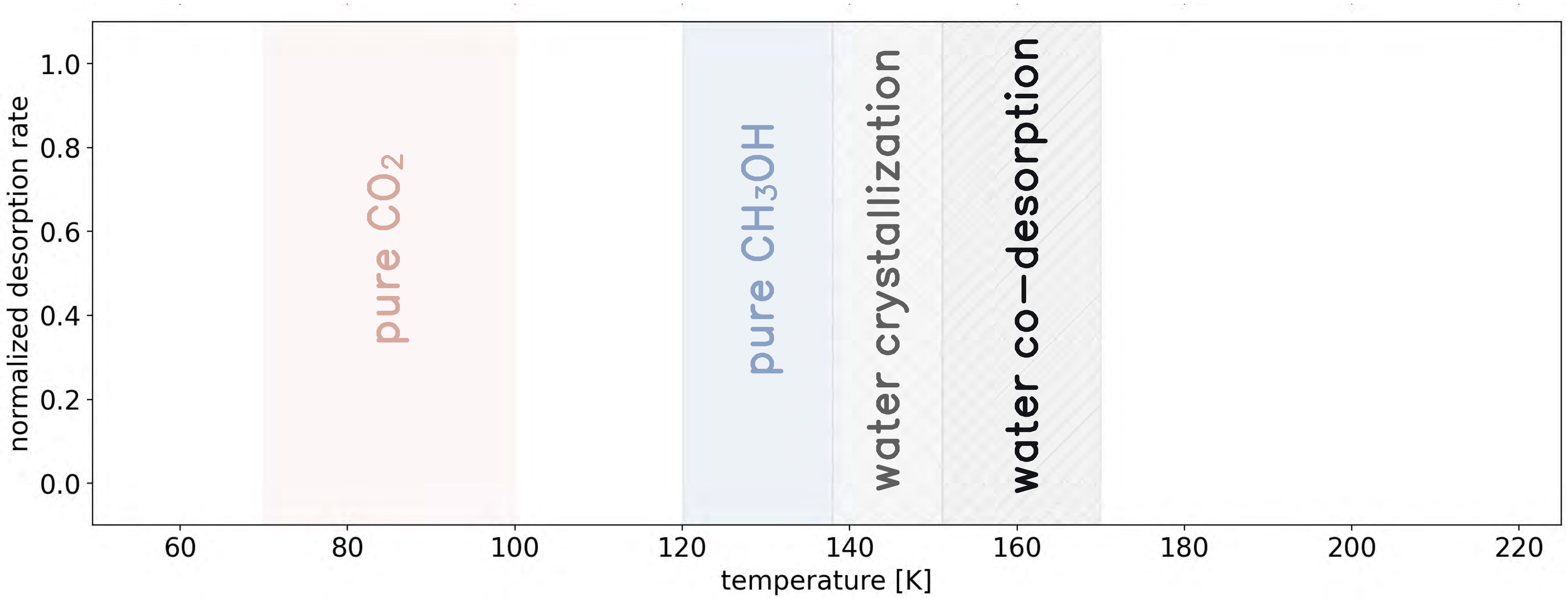
Entrapment in realistic 3-component ices ($CH_3XH:CO_2:H_2O$)



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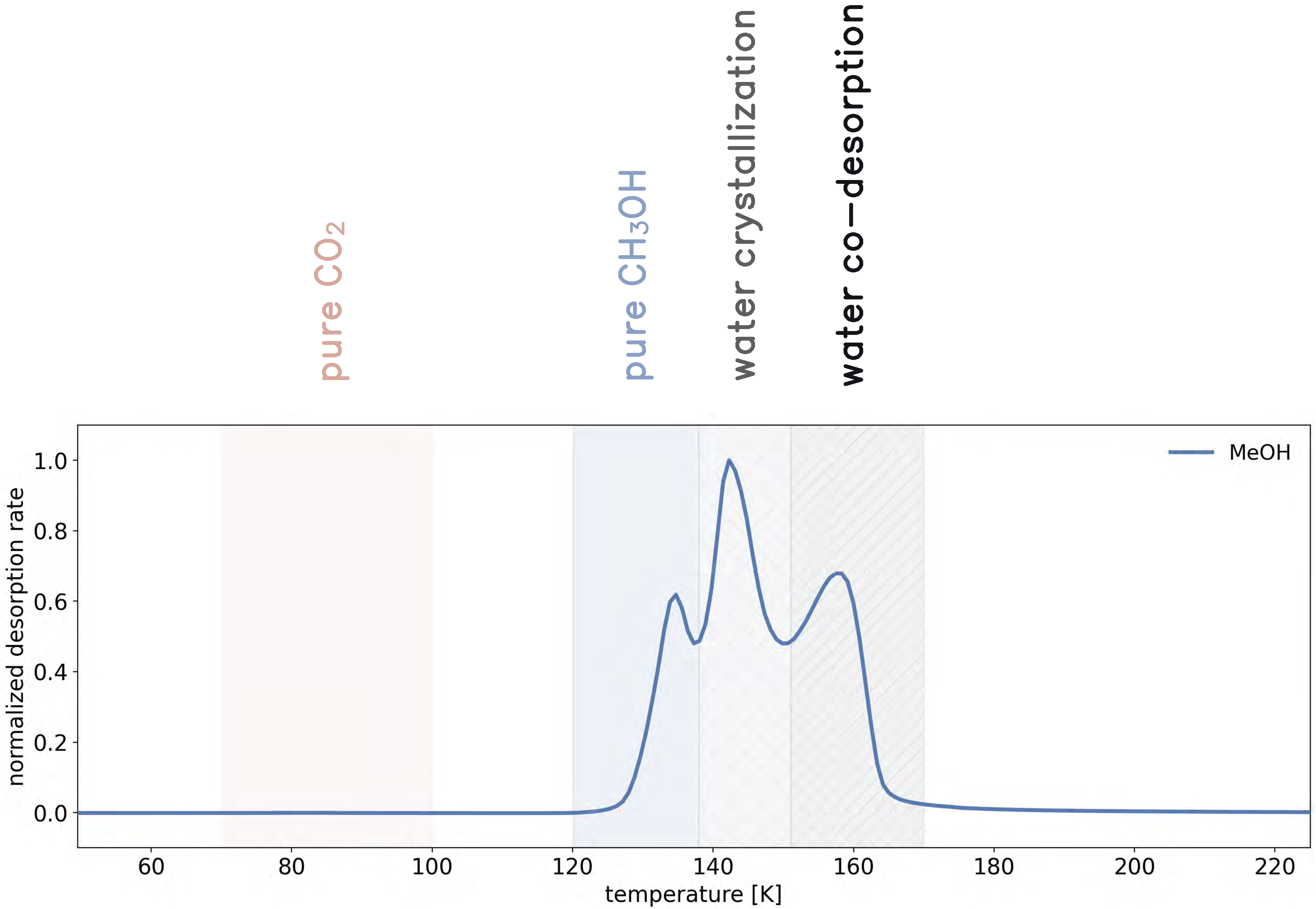

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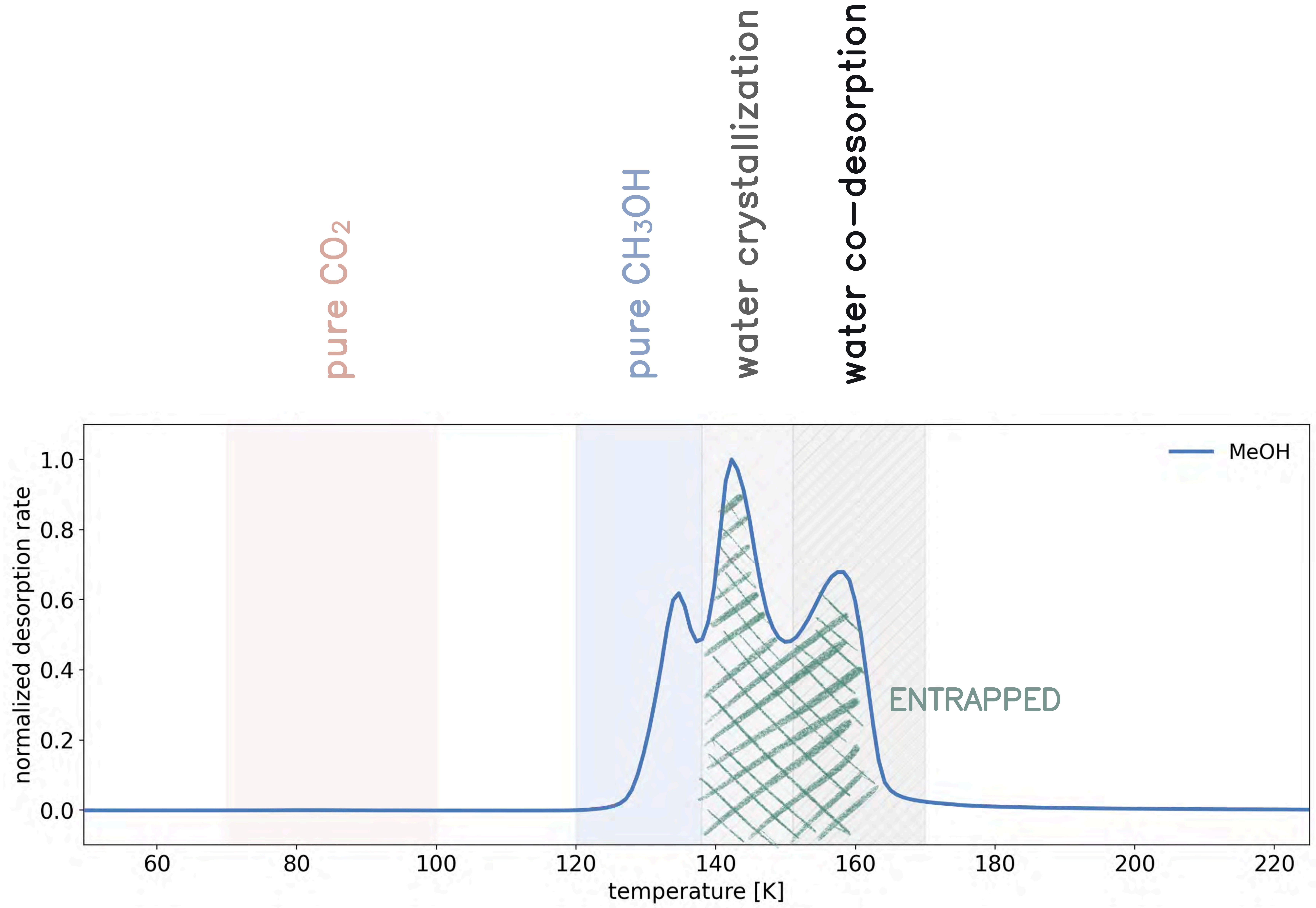

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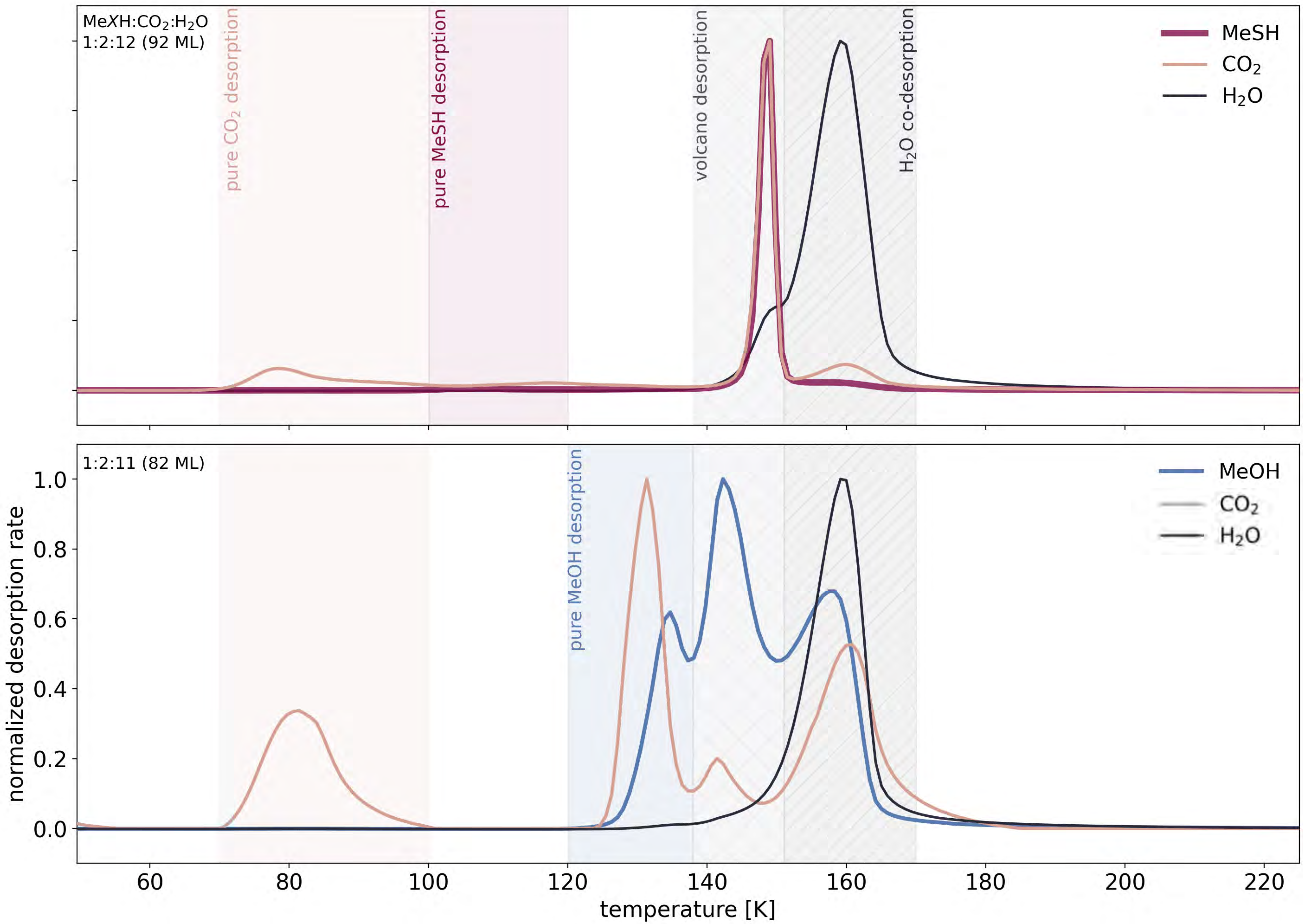

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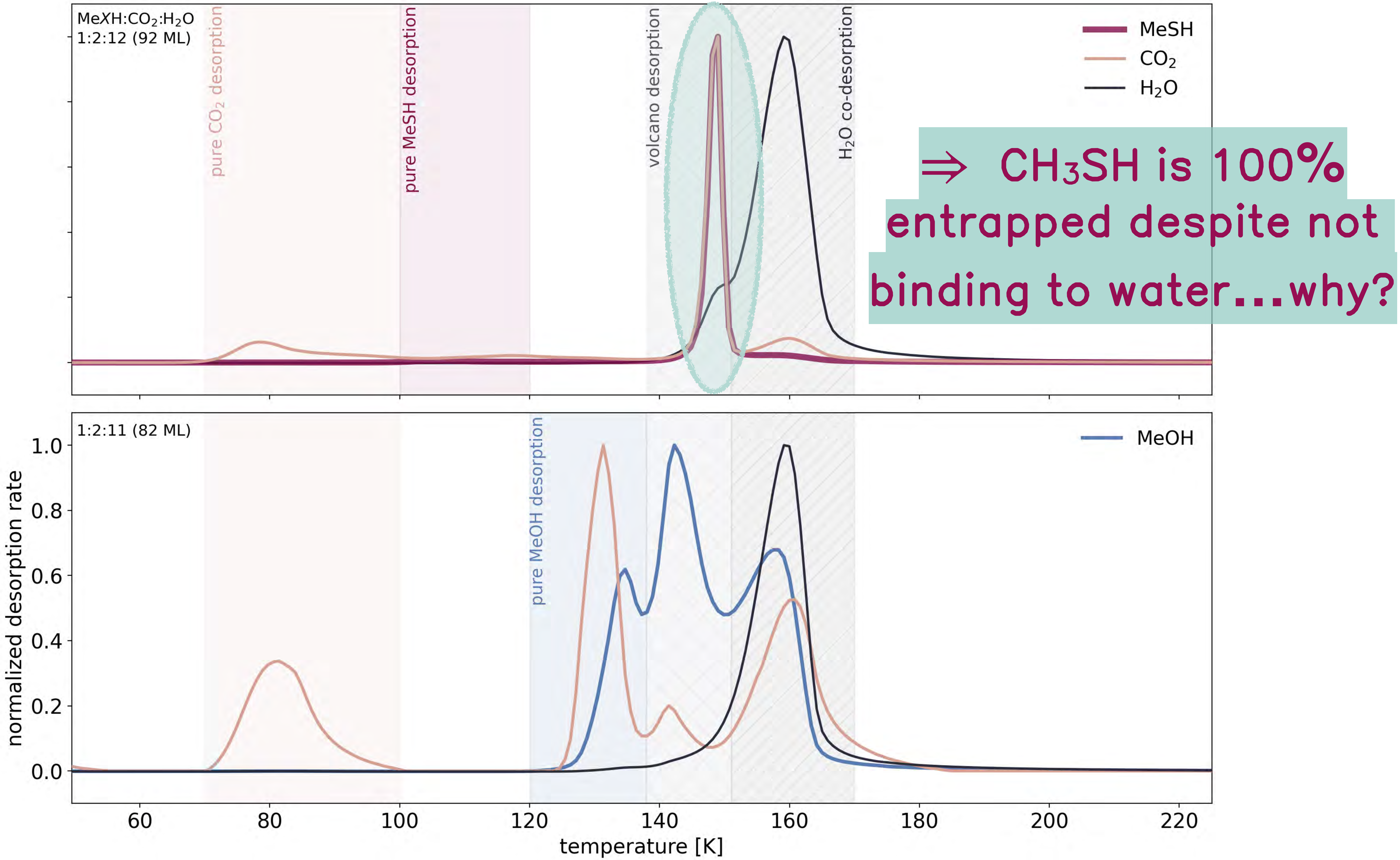

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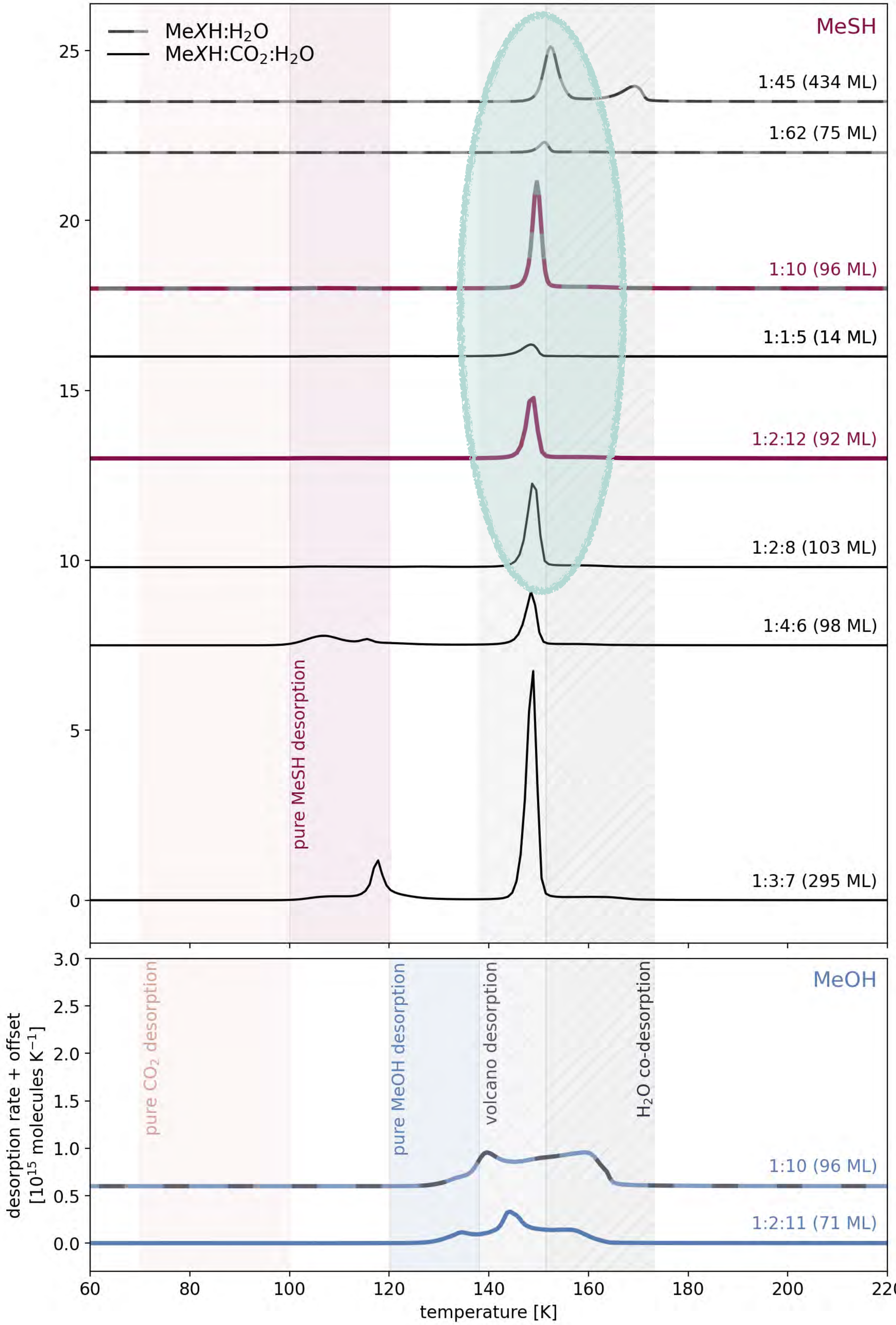
In all entrapment experiments that were not CH_3SH-rich we see ***100% entrapment*** *that has never been seen before.*



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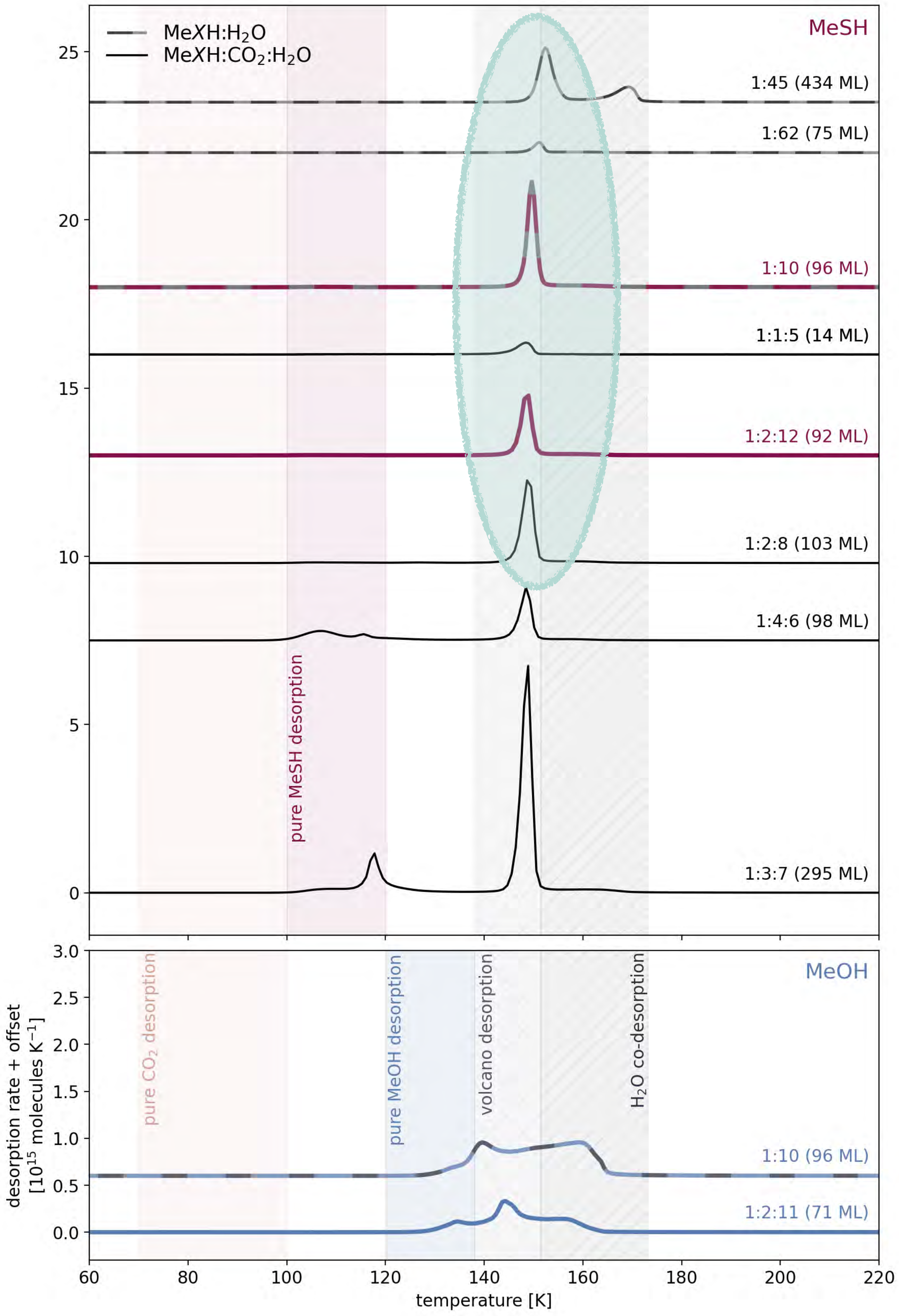
⇒ CH_3SH's size inhibits its ability to diffuse through the water matrix.



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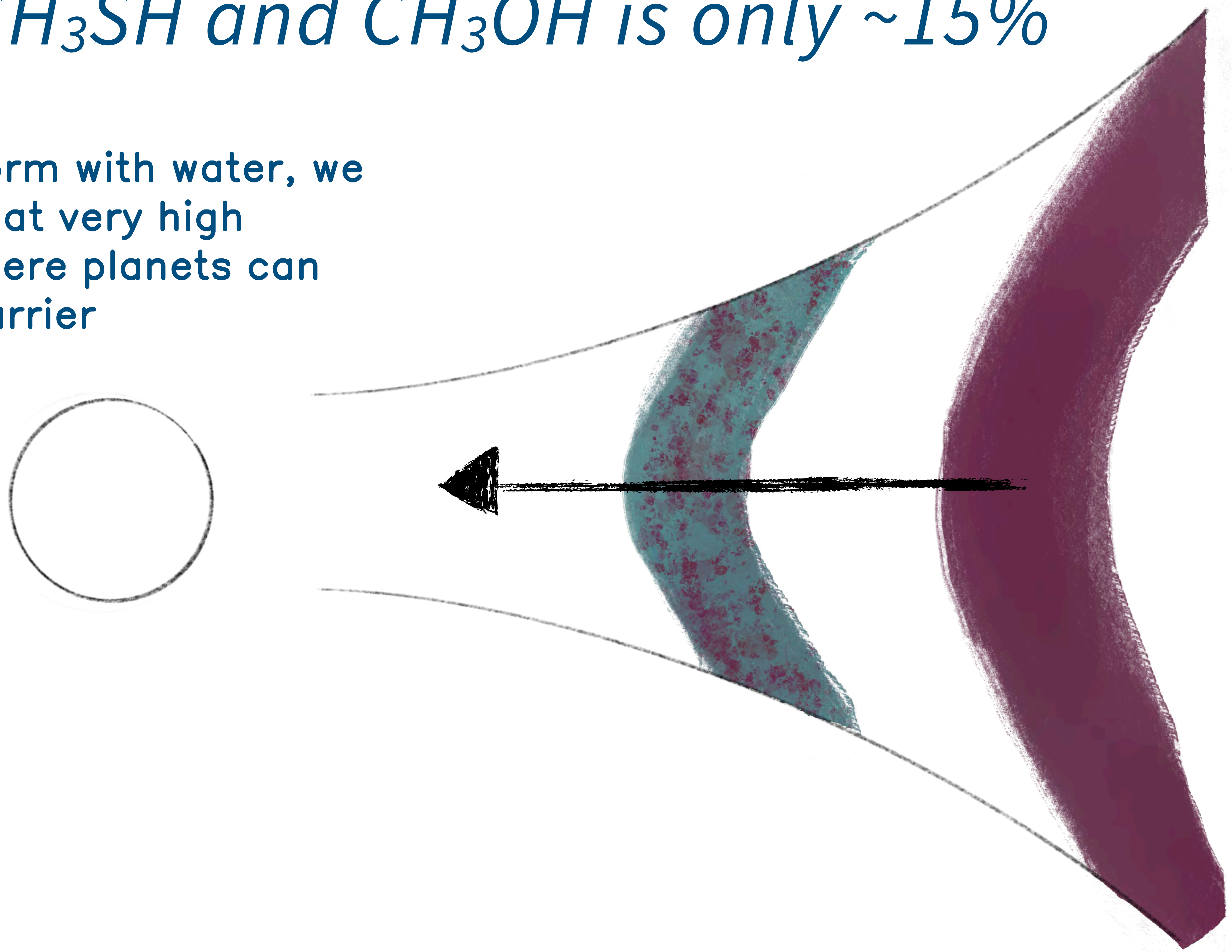

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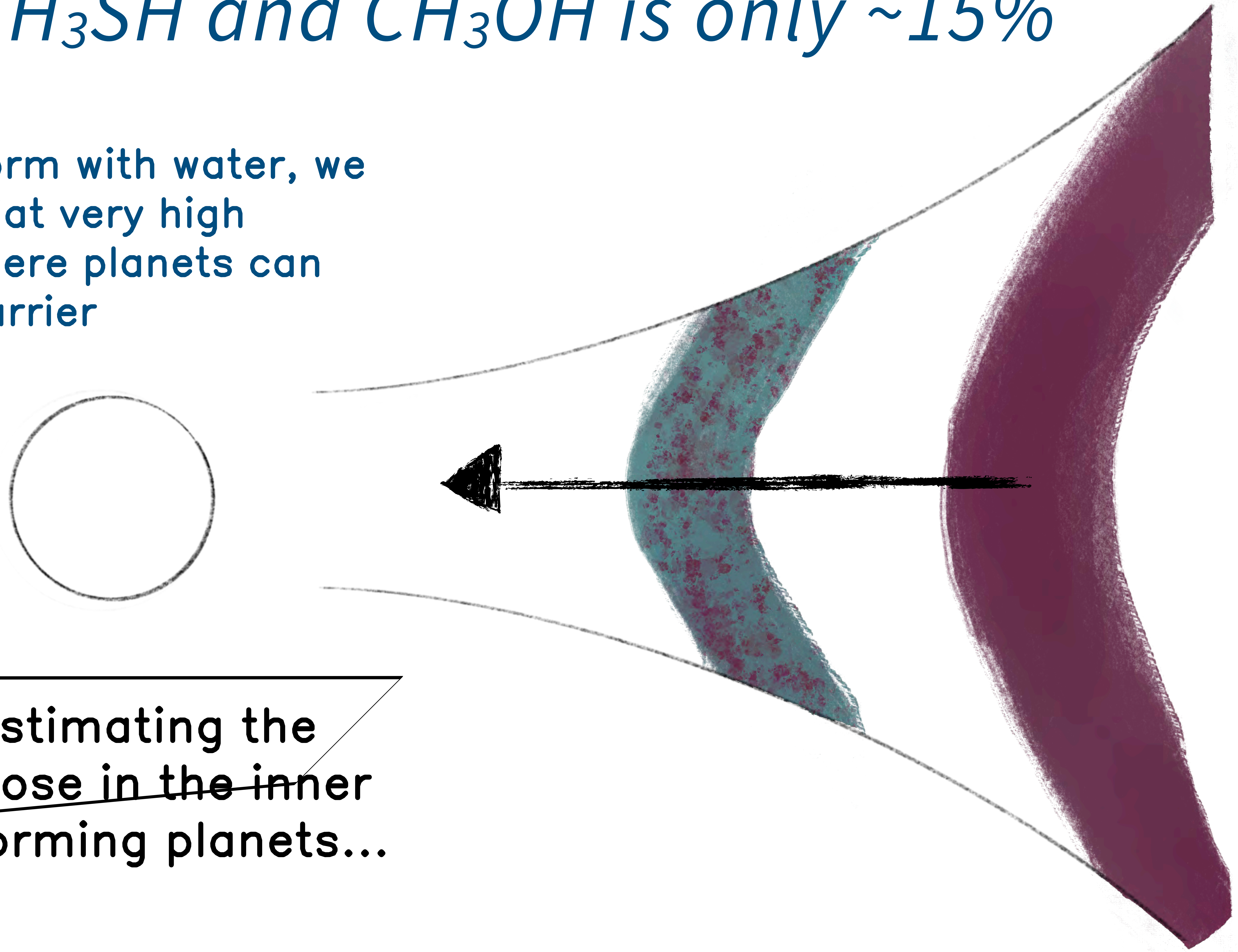

→ We likely are severely underestimating the inventory of volatiles/organics close in the inner disk and thereby what goes into forming planets…

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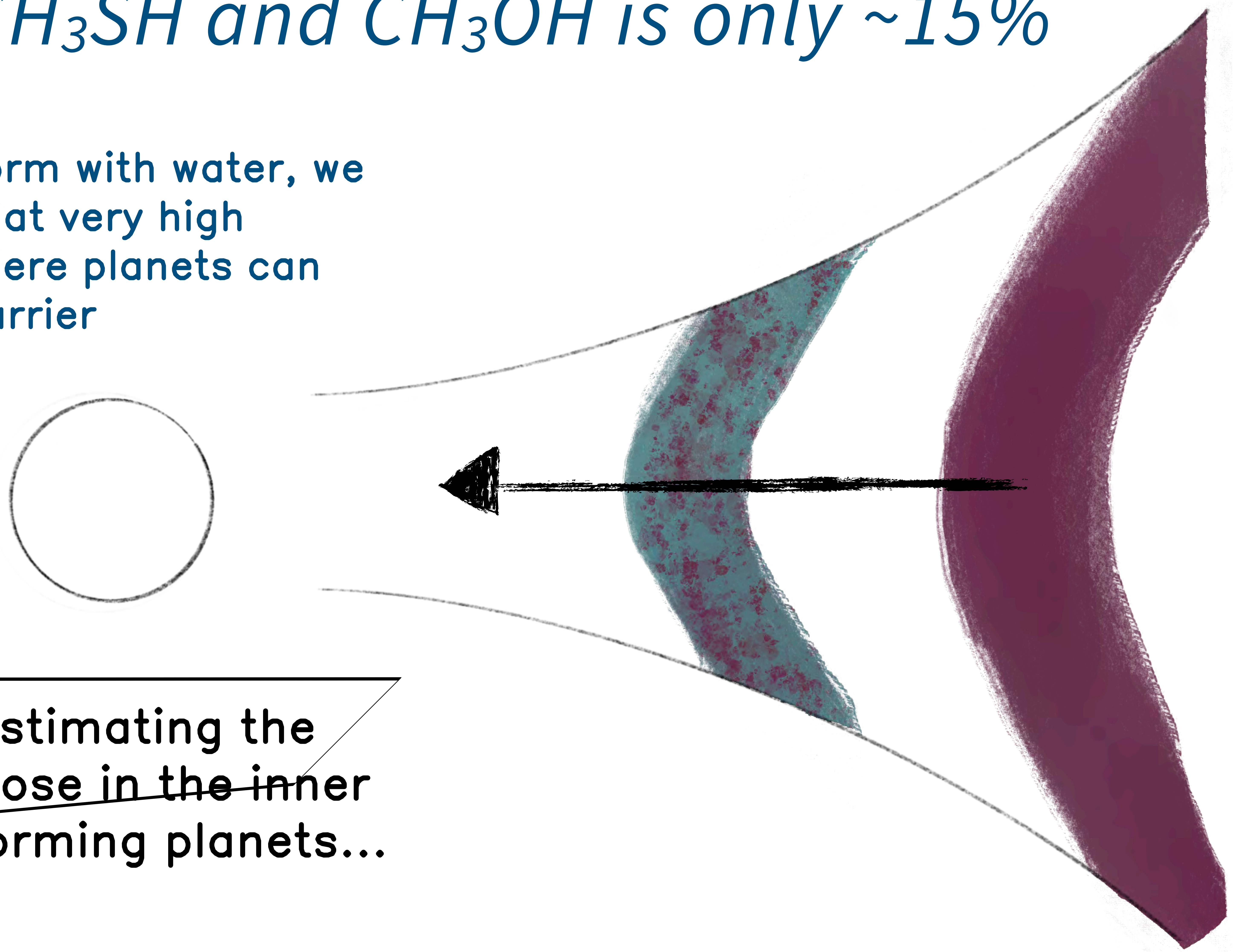

→ We likely are severely underestimating the inventory of volatiles/organics close in the inner disk and thereby what goes into forming planets...

(Spoiler: my formation and destruction experiments also show that S vs. O chemistry is fundamentally different)

If interested in more details, **my dissertation talk is Mon. 13 Jan, 3:10 pm at YSO II / happy to chat over this week!*

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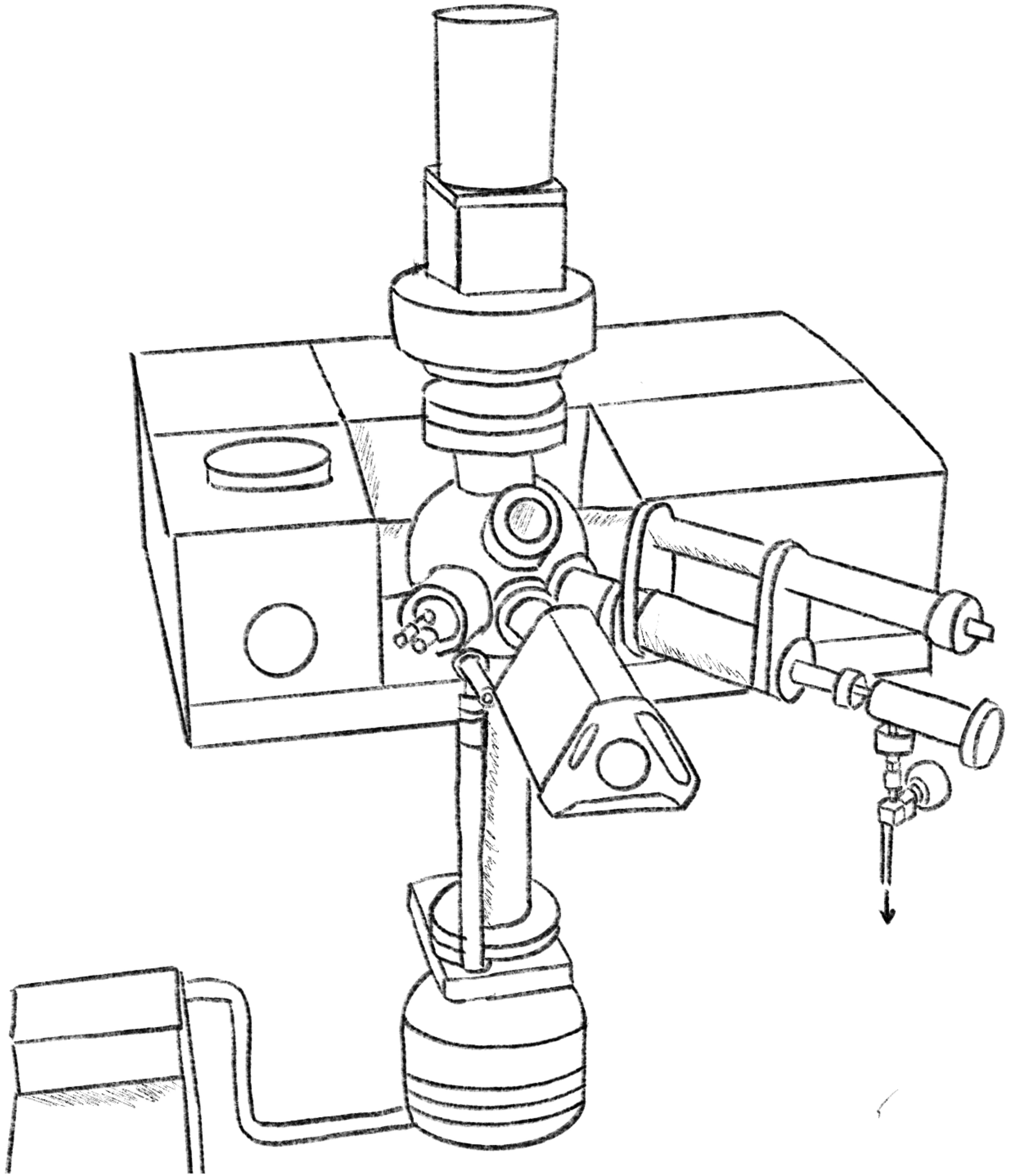
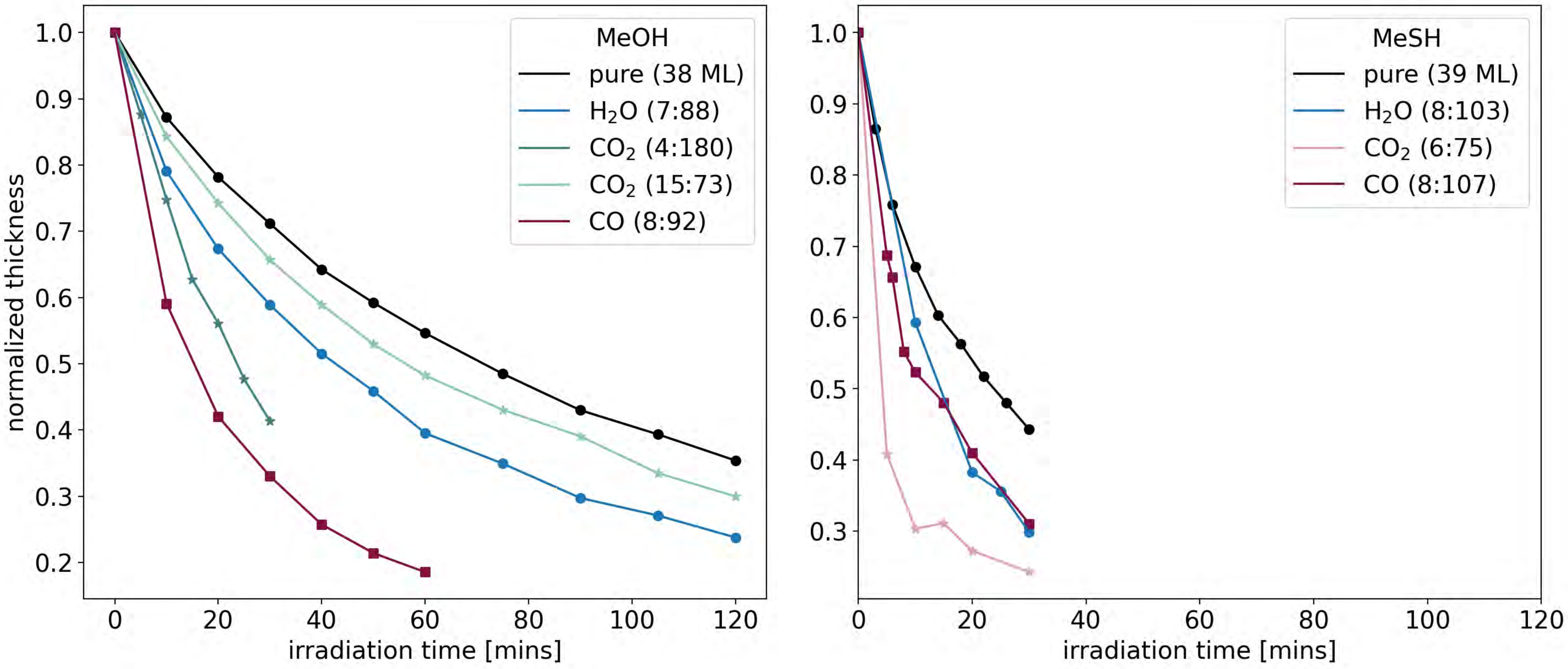
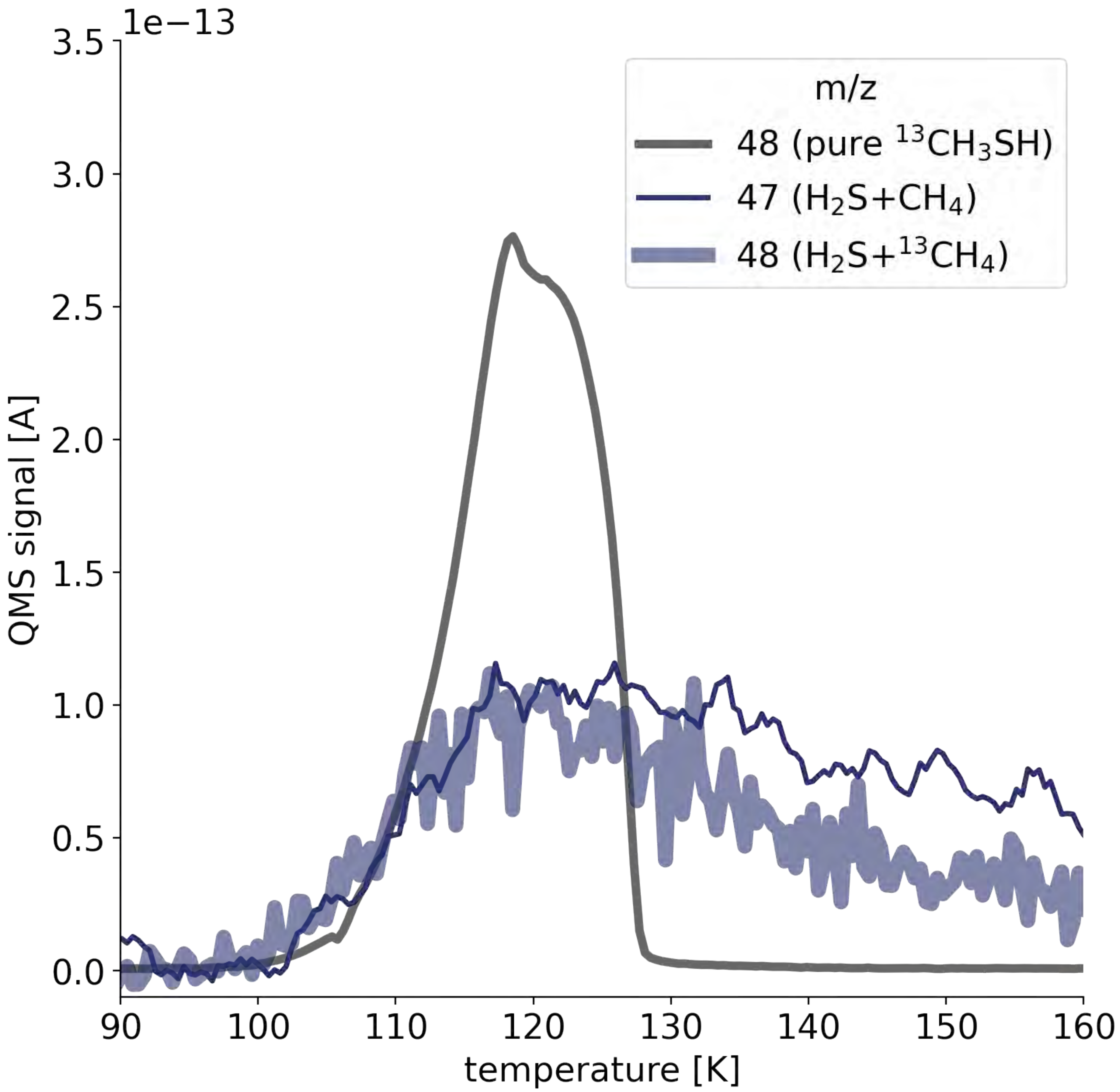
Appendix



CH_3SH is destroyed rapidly when exposed to same amount of UV photons



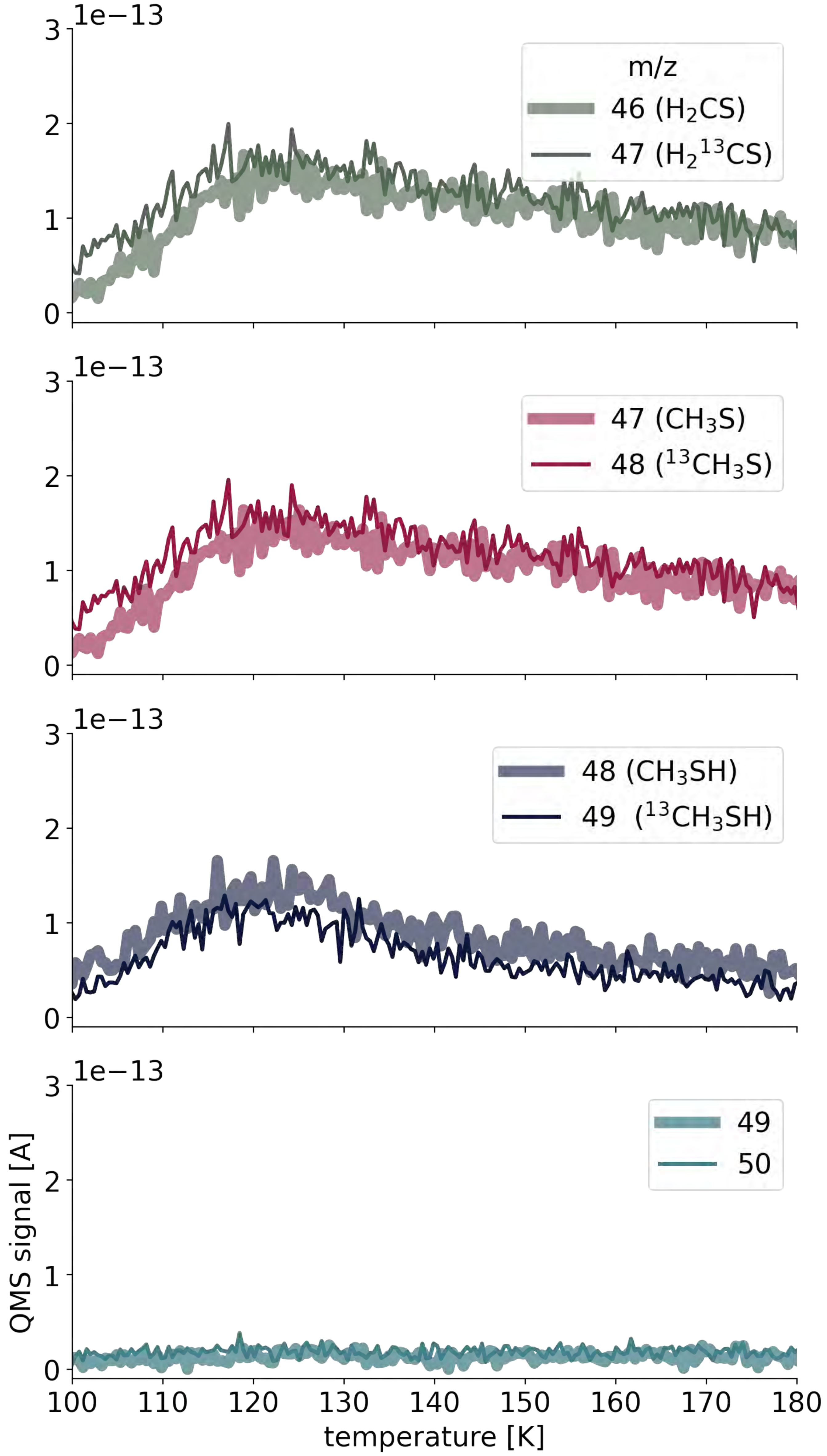
Characterizing CH3SH formation via H2S+CH4 e- irr



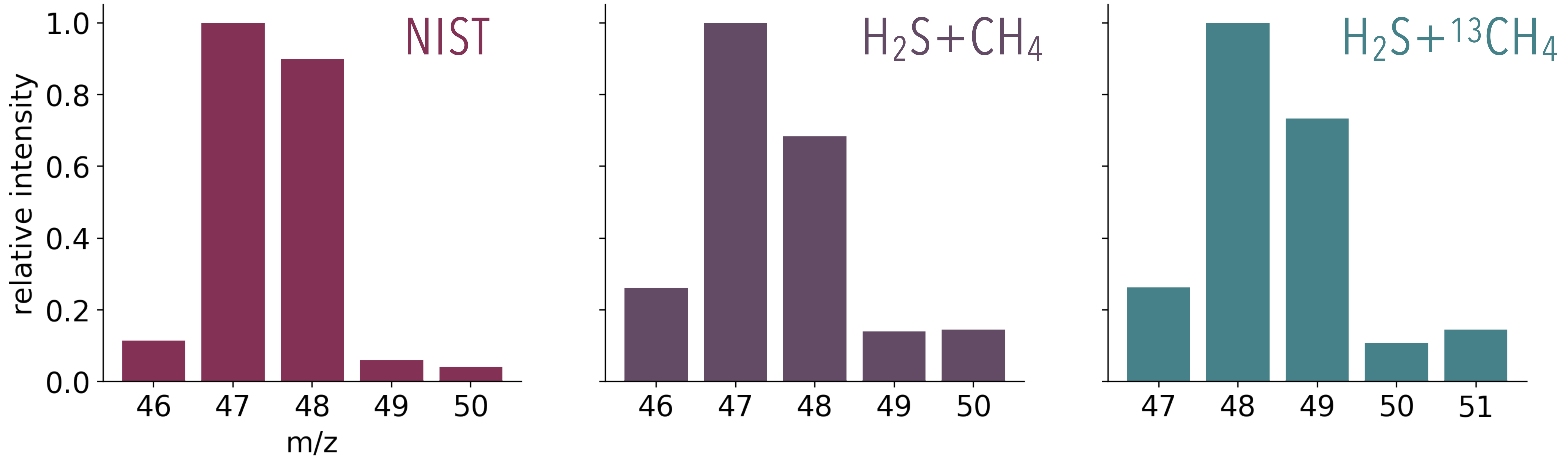
Fiducial experiment: 300 ML, 1:5 ($H_2S:CH_4$), irradiation at 10 K for 120 mins ($\approx 5 \times 10^{18}$ eV/cm^2)

- Confirm **CH_3SH is forming** based on TPD data following irradiation
  - T_{des} matches literature value even with isotopic substitution ($^{13}CH_4$)
- Analogous to CH_3OH formation from CH_4 and H_2O (relative rates are still being quantified)
- Note these are done in CH_4-dominated ices
- We form a lot of S_2 and S_3…

Not very efficient though…



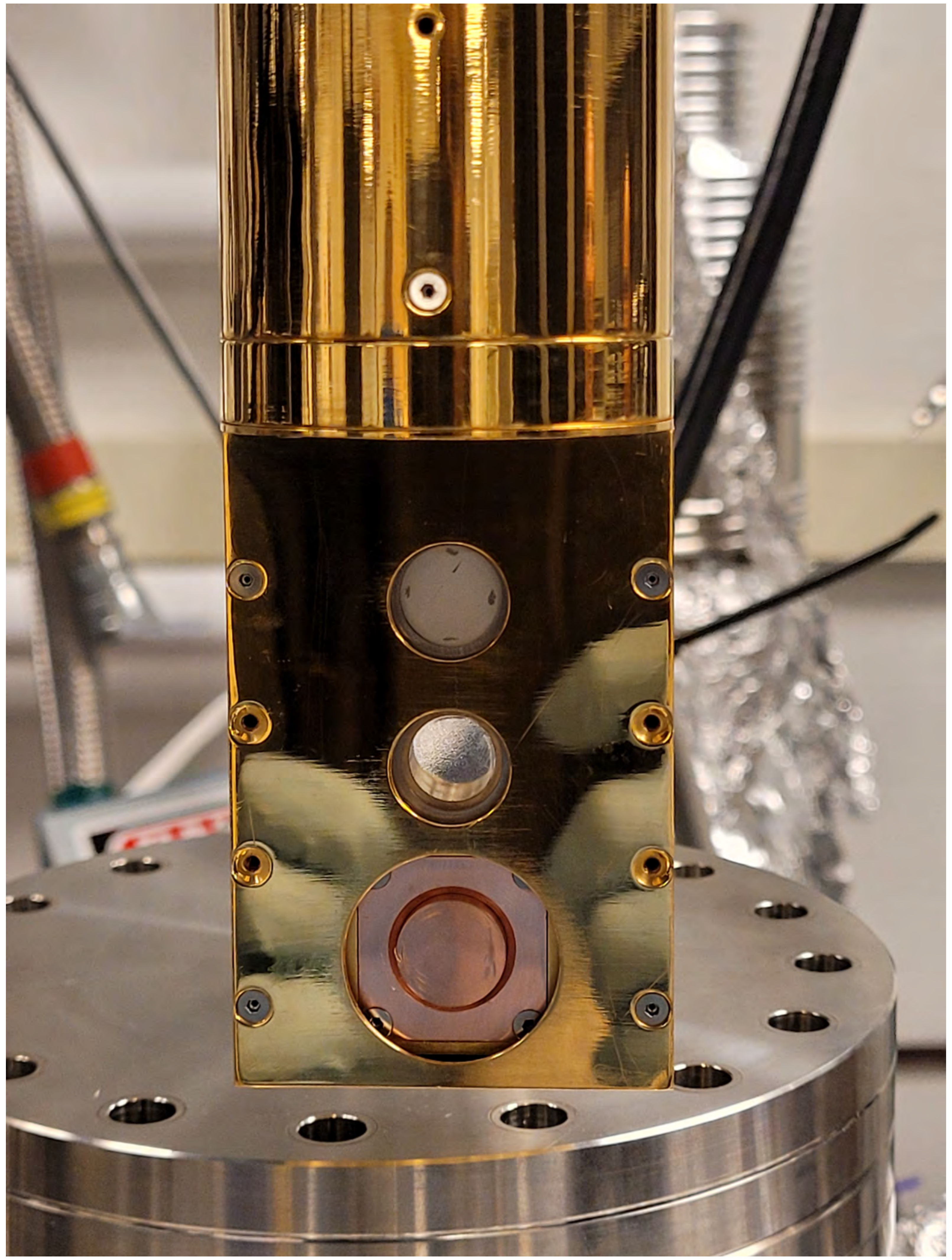
- We use isotopic substitution for proof of concept
  - H_2S+CH_4 (thicker line) and $H_2S+{}^{13}CH_4$ (thinner line)
  - Use the typical m/z values corresponding to CH_3SH fragmentation
- Further confirm this is indeed CH_3SH by taking the the mass spectrum at the desorption temperature (120 K) and compare to NIST's

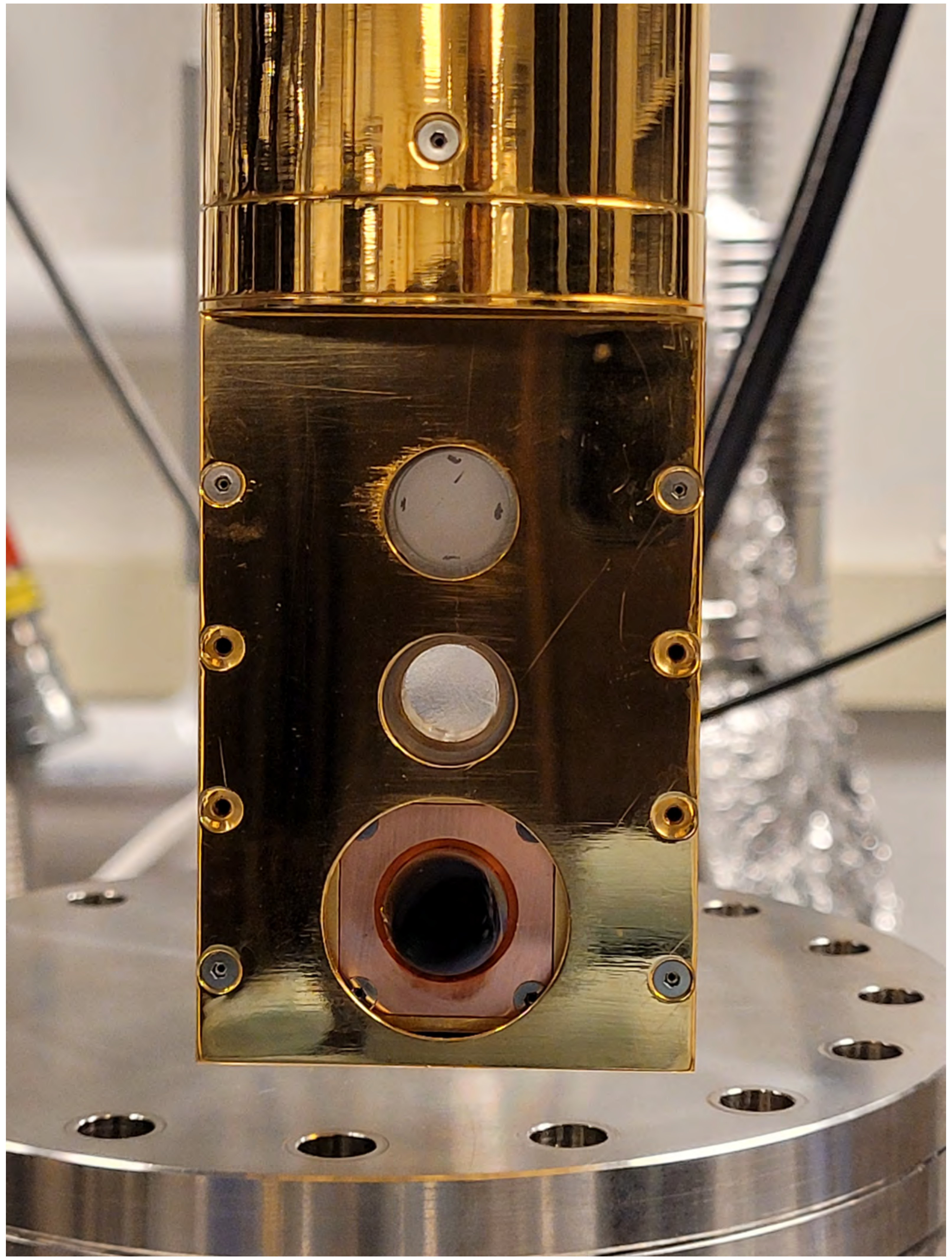


- Increase in production of 46/47 corresponds to build up of H_2CS and $H_2{}^{13}CS$
  - **Means the H_2CS seen in disks is likely formed in the gas phase just like H_2CO**

Why aren't there many sulfur experiments?

Sulfur dirties the substrate pretty badly :(





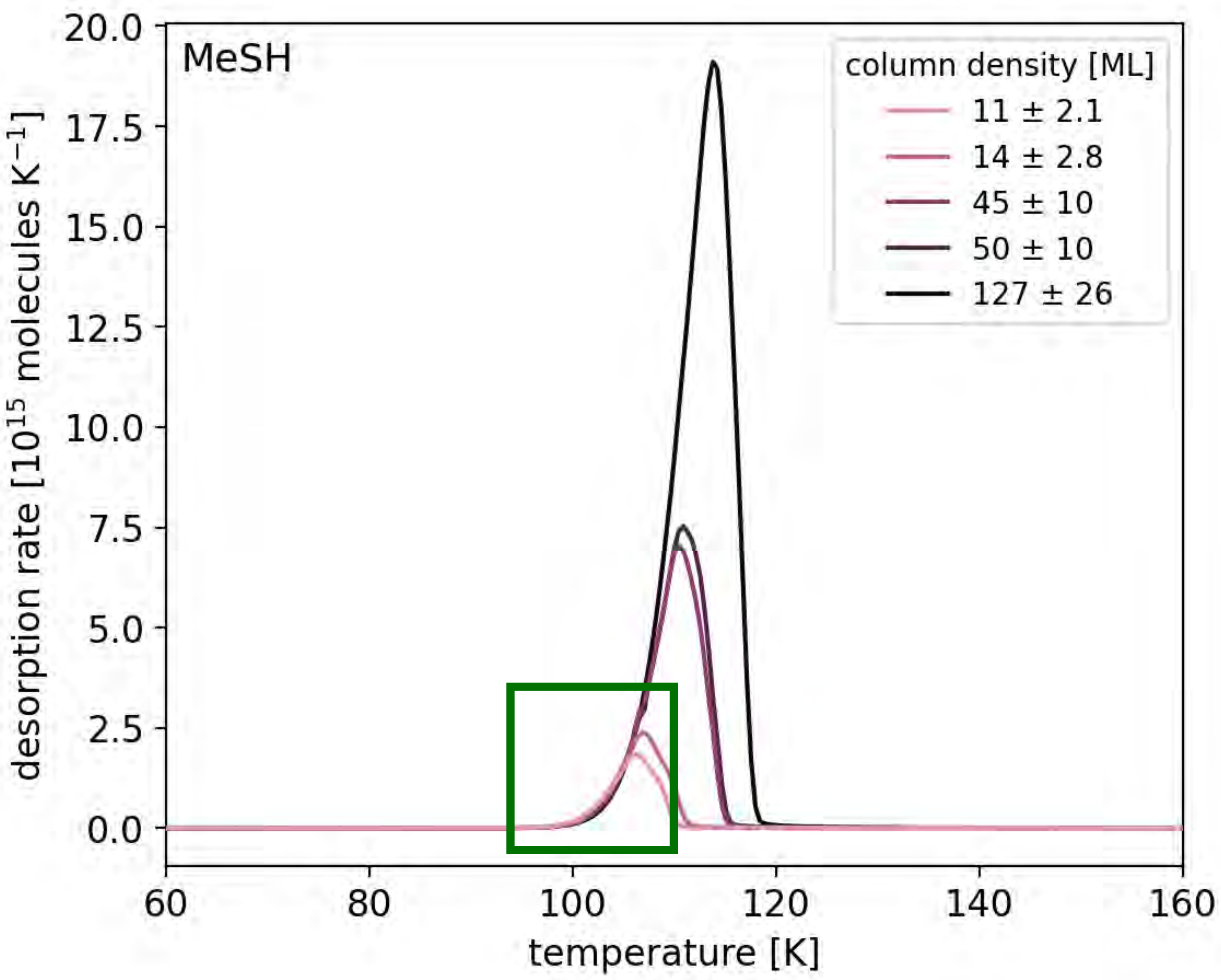
Binding energies (BE) → proxy for sublimation fronts

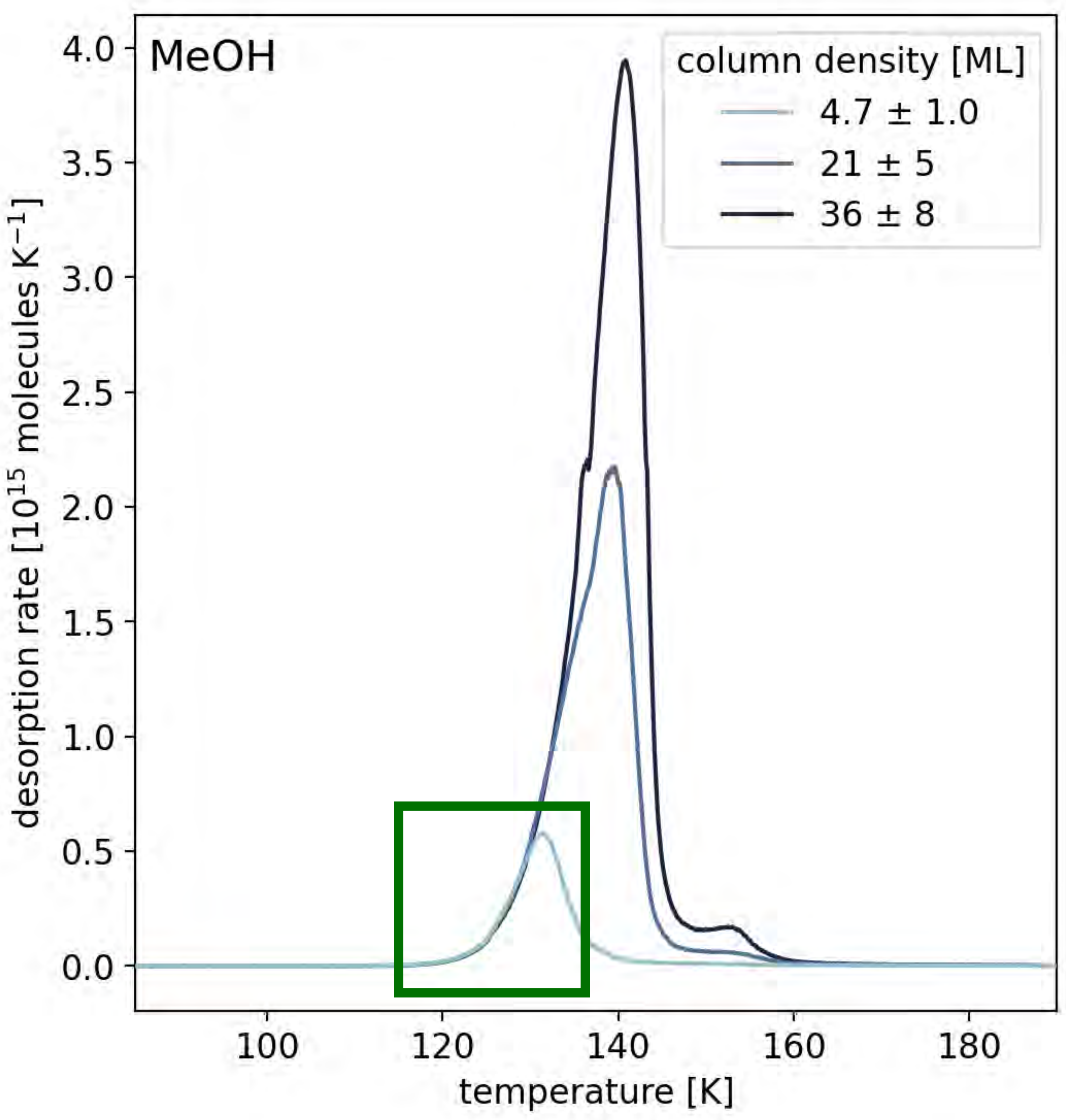
Experimentally-derived binding energies are necessary for astrochemical models

- well described using the Polanyi-Wigner equation: $-\frac{d\theta}{dT} = \frac{\nu}{\beta}\theta^n \exp\left[\frac{-E_b}{T}\right]$

FIT FOR ν + E_b [K]

DESORPTION RATE FROM TPD CURVE





Estimating E_b and ν

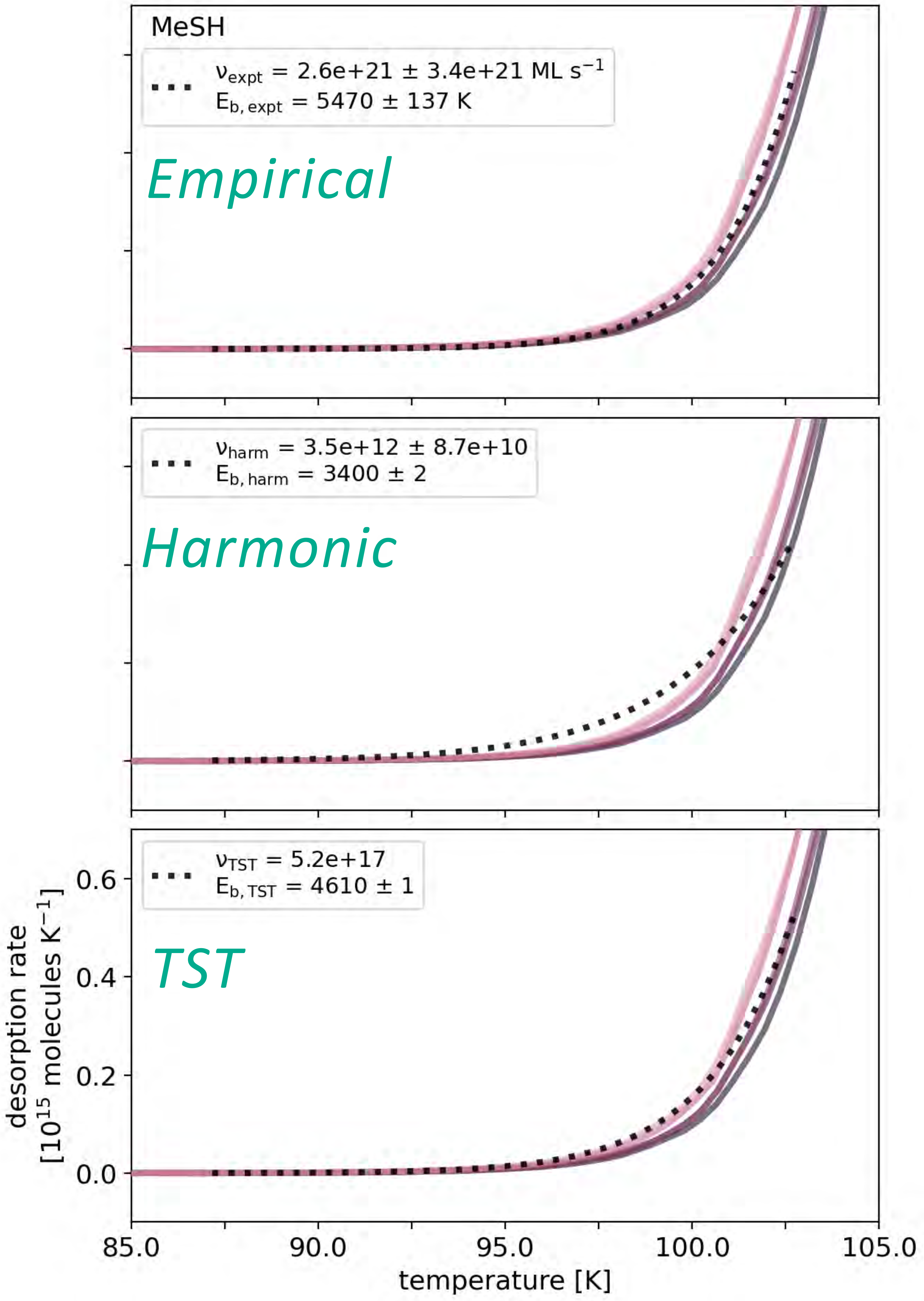
- Degeneracy between the two
  - Empirical fit
  - Harmonic approximation

$$\nu_{\text{harm}} = \sqrt{\frac{2N_s E_{b,\text{harm}}}{\pi^2 \mu m_{\text{H}}}}$$

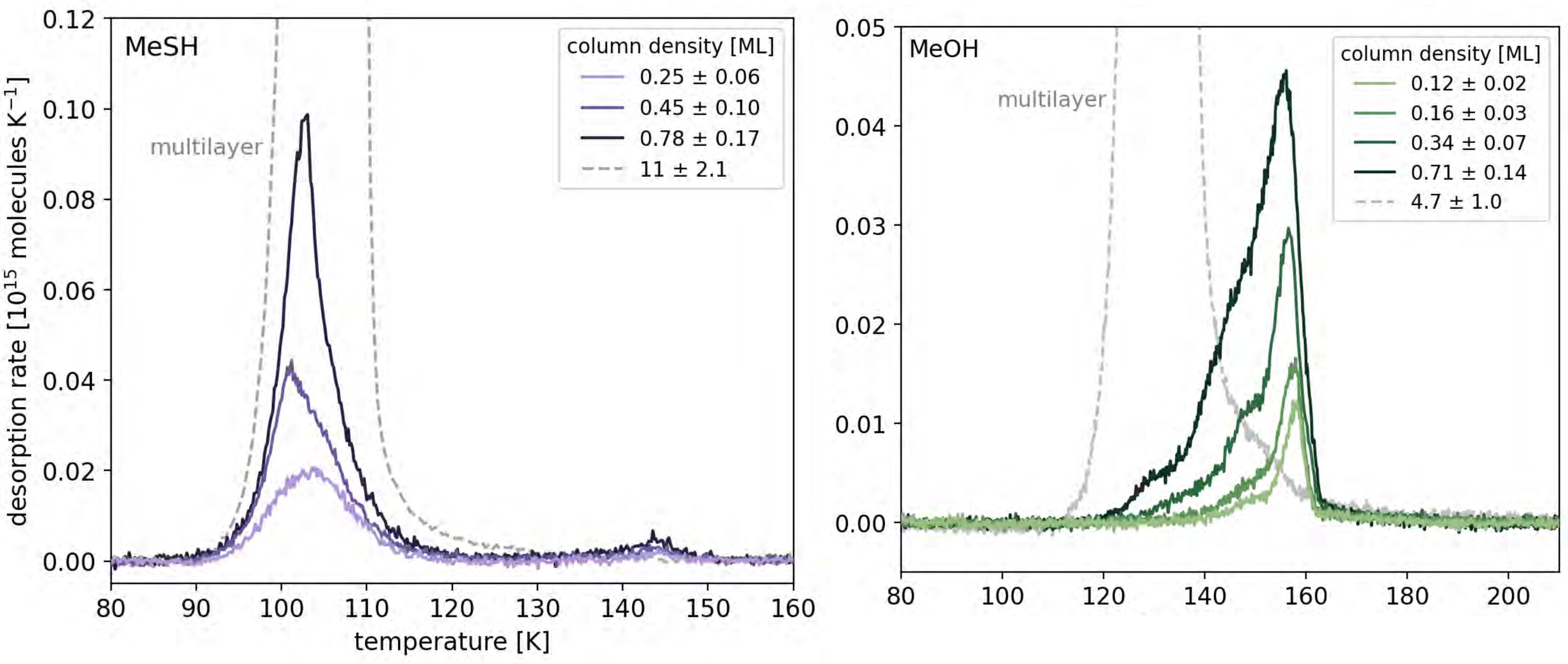
  - Transition state theory (Minissale+ 2022)

$$\nu_{\text{TST}} = \frac{k_B T_{\text{peak}}}{h} q^{\ddagger}_{tr,2D}\, q^{\ddagger}_{rot,3D}$$

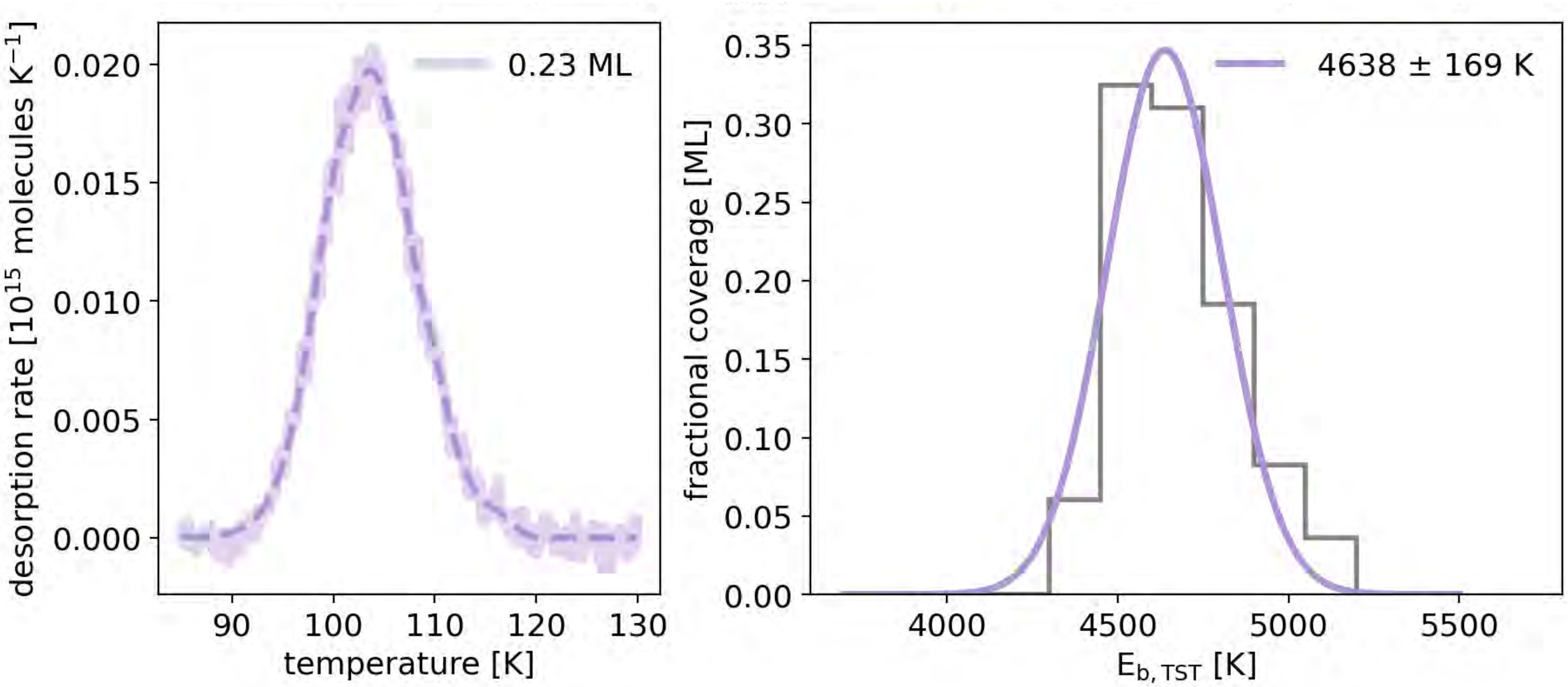
- Bigger molecules are not well-described point masses



All layered sub-monolayer TPD curves



At submonolayer regimes, we need to do a distribution of E_b



- Ice surfaces are not homogenous and due to topology constraints: different binding potentials

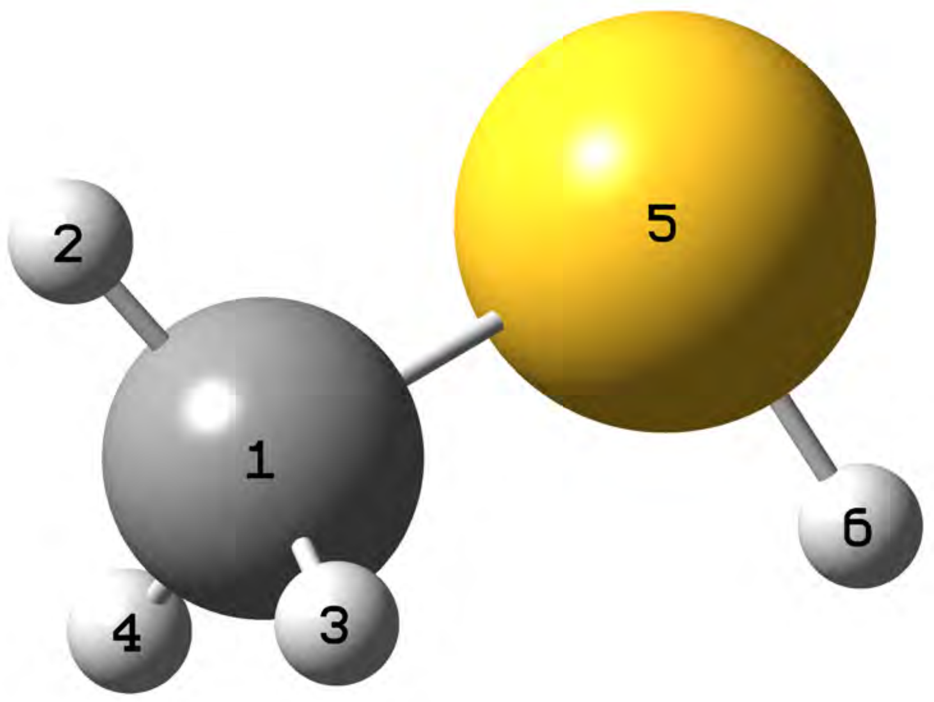
Summary of recommended binding energies

Table 3. Recommended TST-derived binding energies and pre-exponential factors.

	n	$E_{b,\,\mathrm{TST}}$ [K]	$\nu_{\mathrm{TST}}{}^{a}$	$\mathrm{T_{peak}}{}^{b}$ [K]
MeSH–MeSH	0	4610 ± 110	$5.2^{+2.8}_{-1.0} \times 10^{17}$	106^{+14}_{-6}
MeSH–H_2O	1	4640 ± 170	$4.9^{+0.6}_{-0.9} \times 10^{17}$	104 ± 5
MeOH–MeOH	0	5750 ± 80	$3.4^{+1.5}_{-0.9} \times 10^{17}$	131^{+14}_{-11}

⇒ Both MeSH binding energies are similar, MeOH-MeOH is higher, and MeOH-H_2O should be higher

Computational Calcs



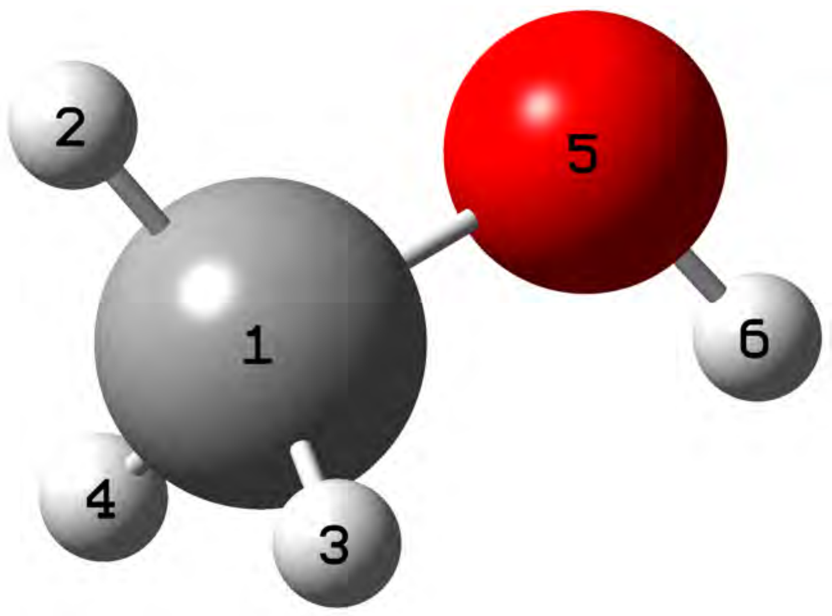


Table D3. Computationally-derived binding energies ($E_{b,\,\mathrm{comp}}$) obtained using Equation at the `M06-2X/aug-cc-pVDZ` level of theory.

Molecule A	Molecule B	$E_{b,\,\mathrm{comp}}$ [K]
CH_3SH	CH_3SH	1642
CH_3SH	H_2O	2588
CH_3OH	CH_3OH	3105
CH_3OH	H_2O	3033

⇒ We see the opposite trend here…