

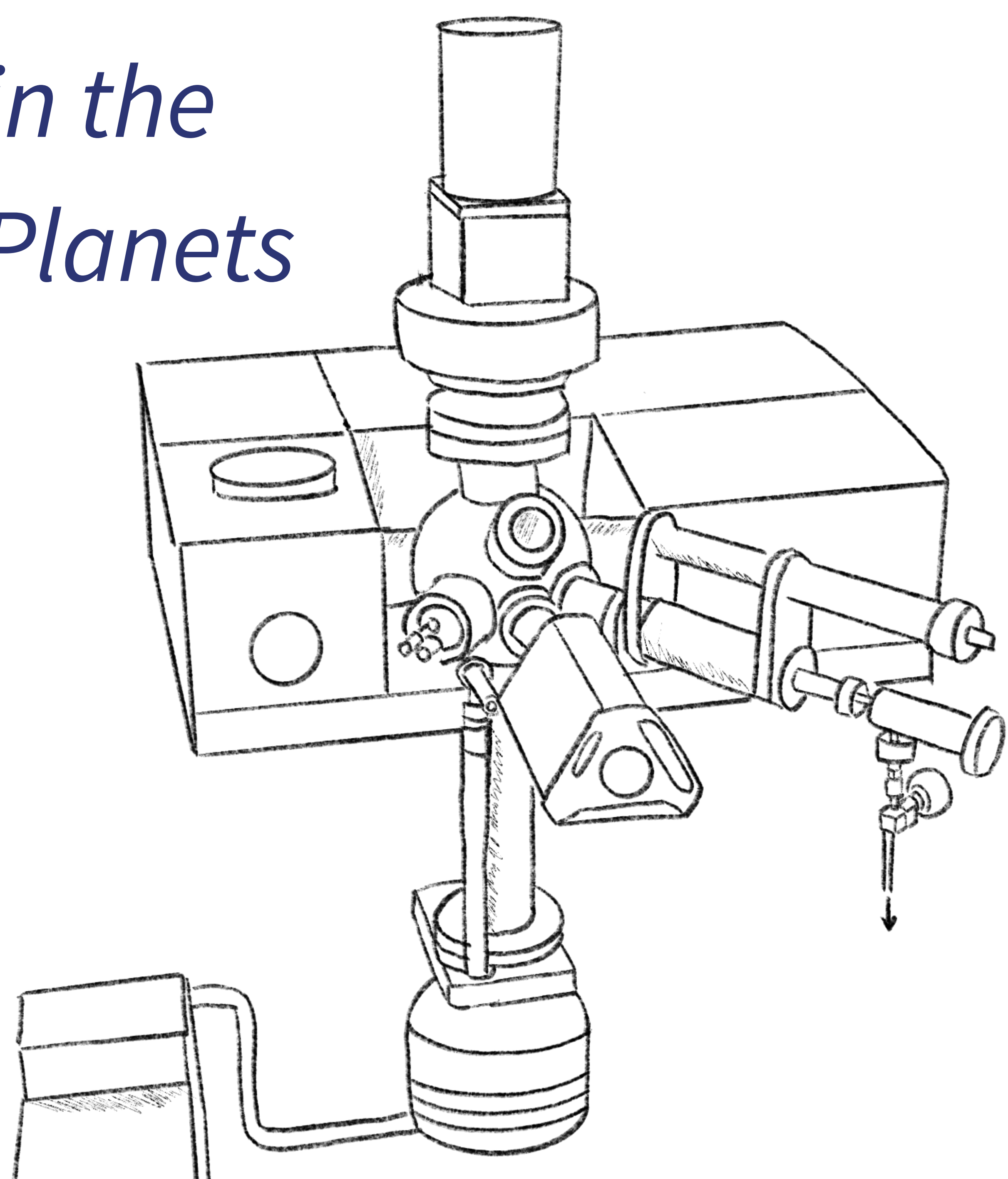
# *Organosulfur Chemistry in the Birthplaces of Stars and Planets*

*Suchitra Narayanan*

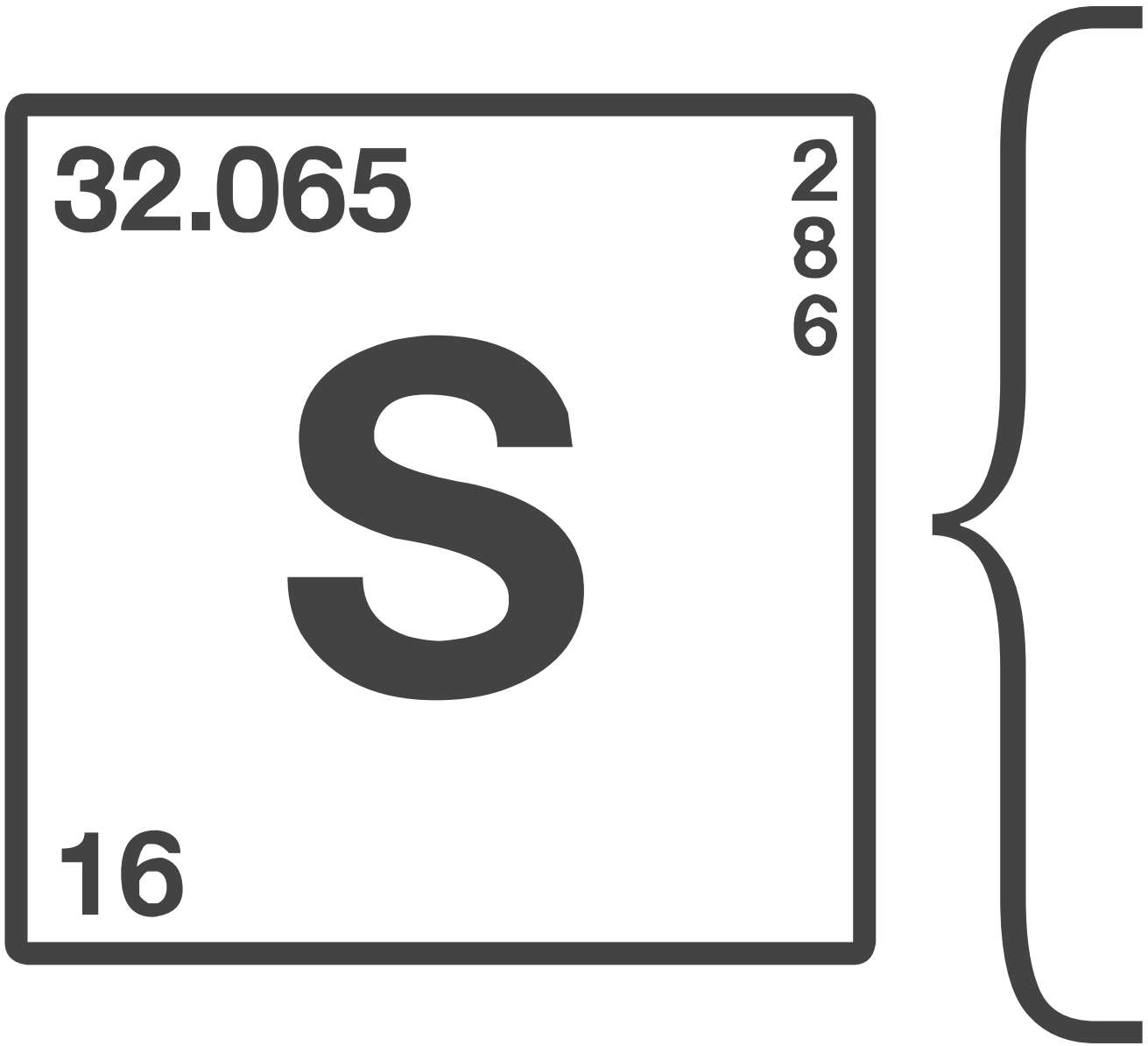
NSF Graduate Research Fellow & PEO Scholar

Advised by Karin I. Öberg & Jonathan P. Williams  
Center for Astrophysics | Harvard & Smithsonian  
Institute for Astronomy, University of Hawai'i at Mānoa

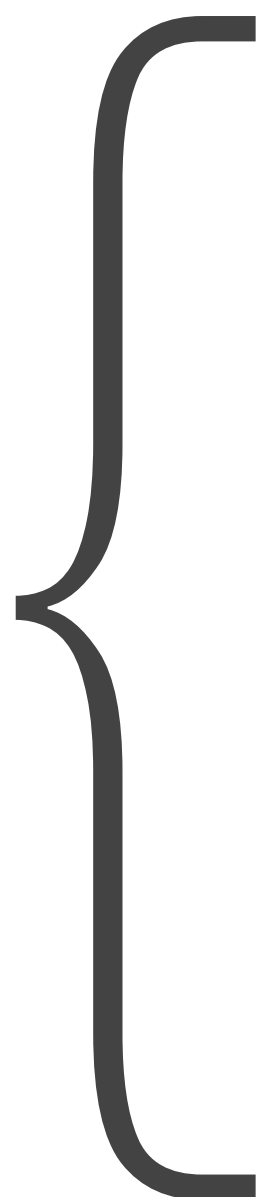
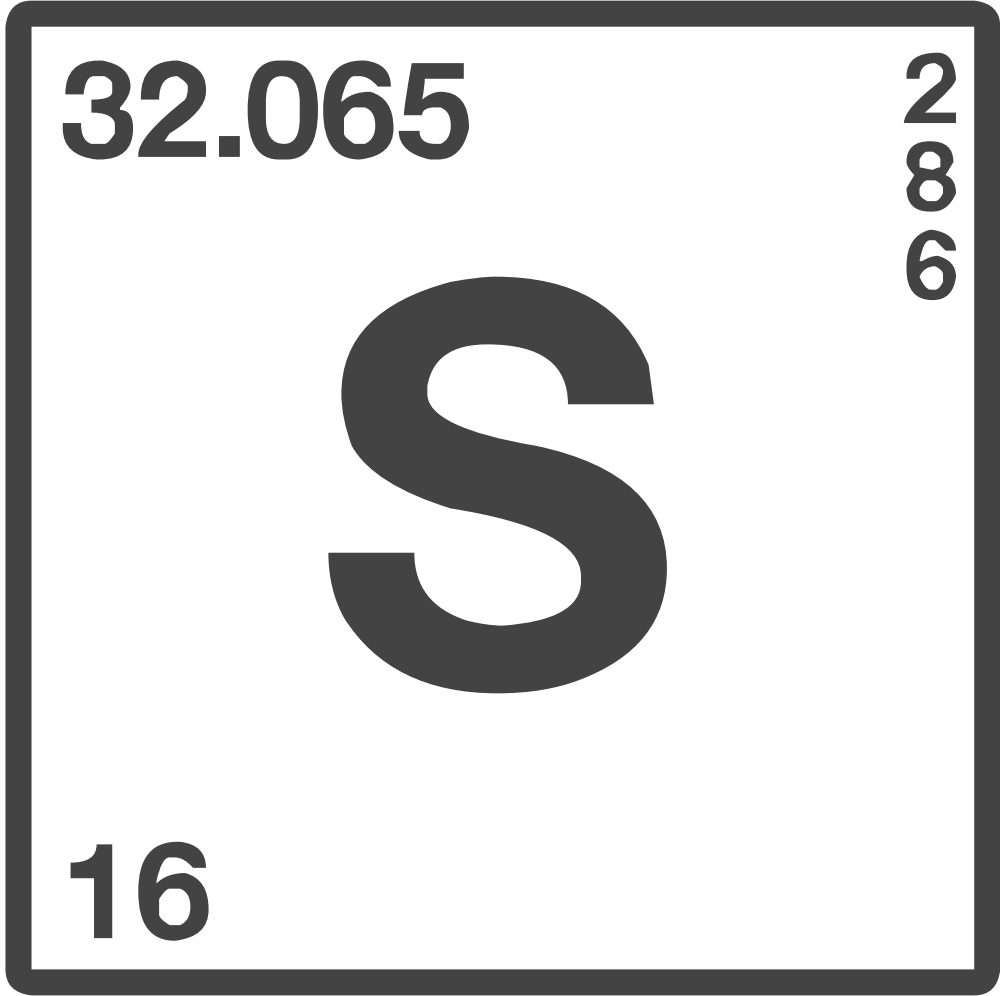
ExoPAG 31, 245th Meeting of the AAS · 12 January 2025



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



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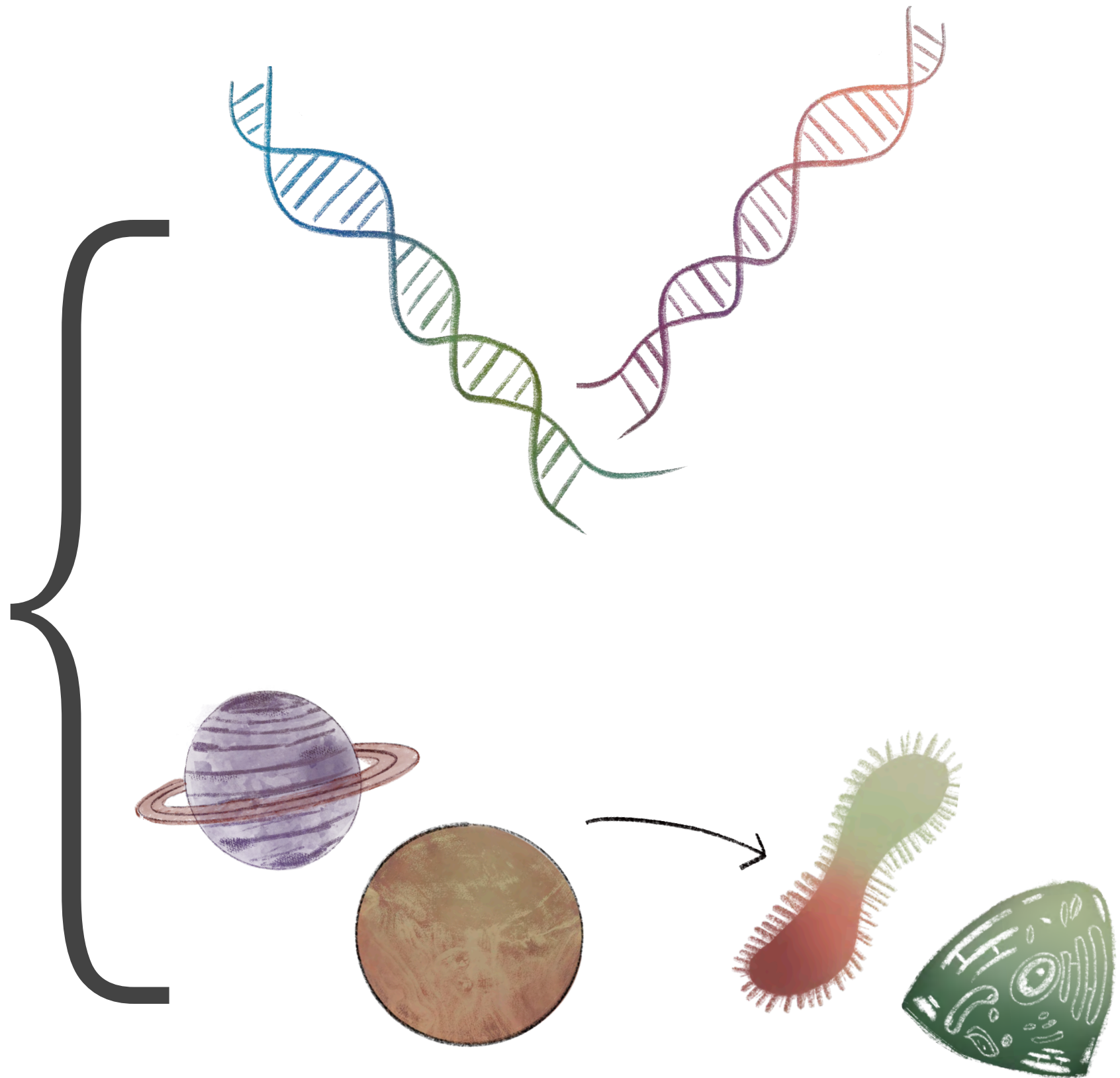
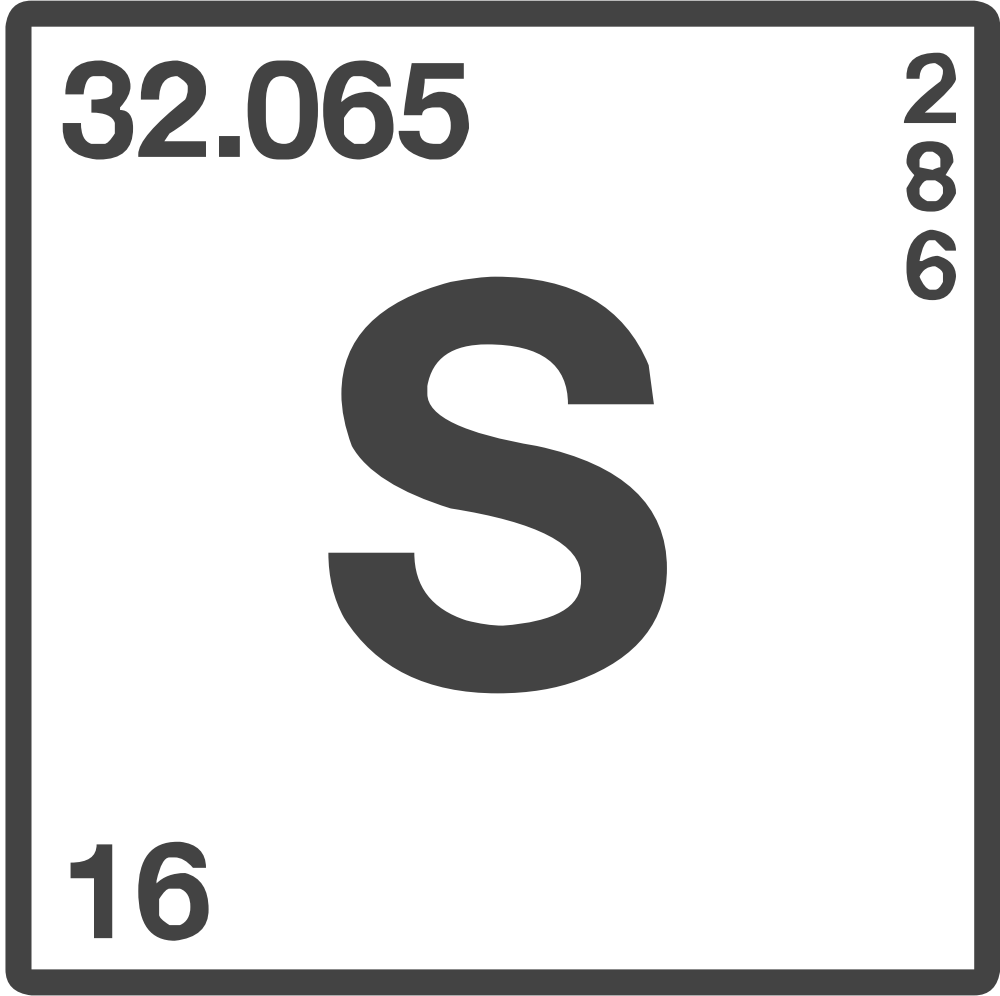


## *(Astro)biology*

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



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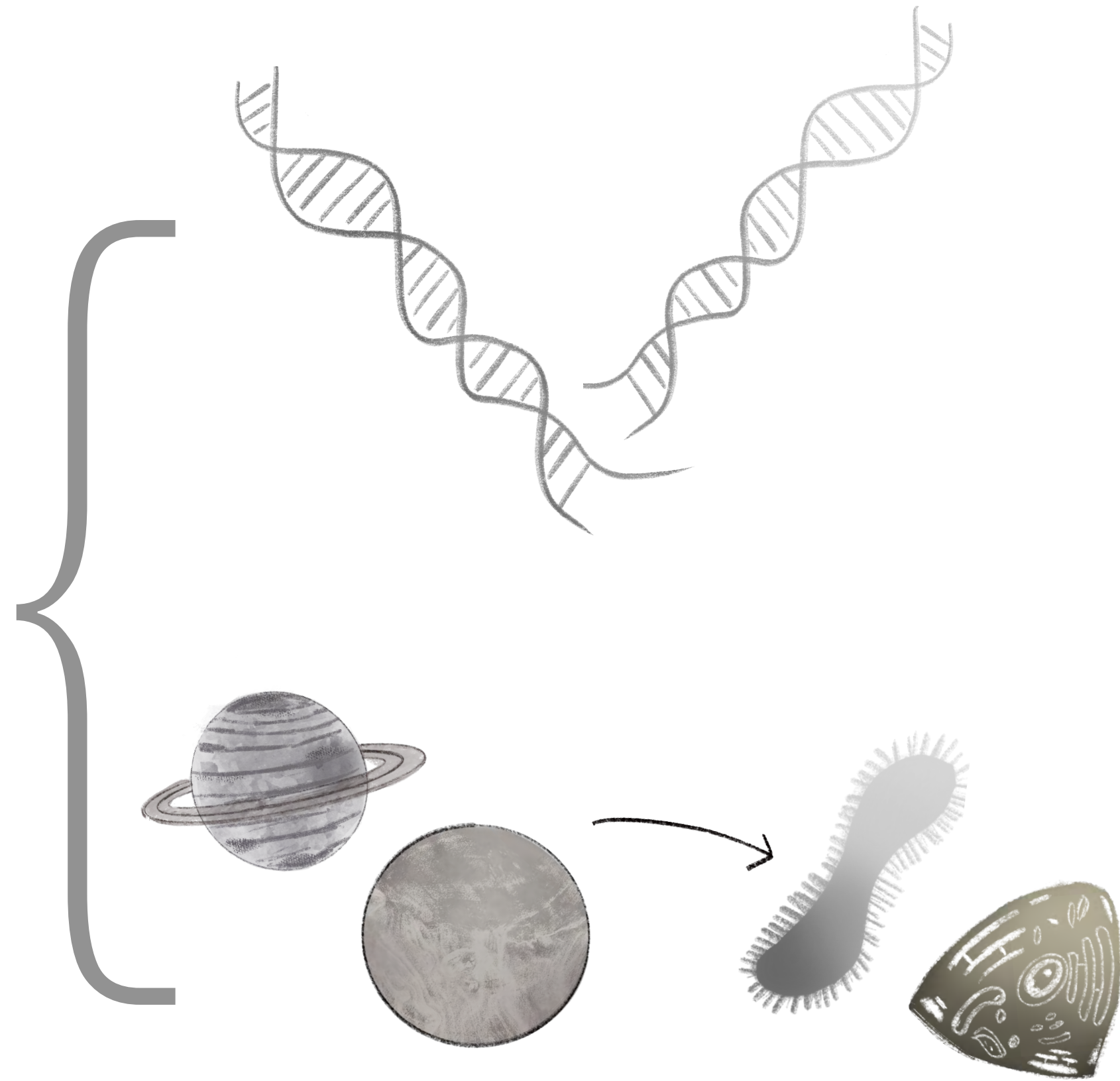
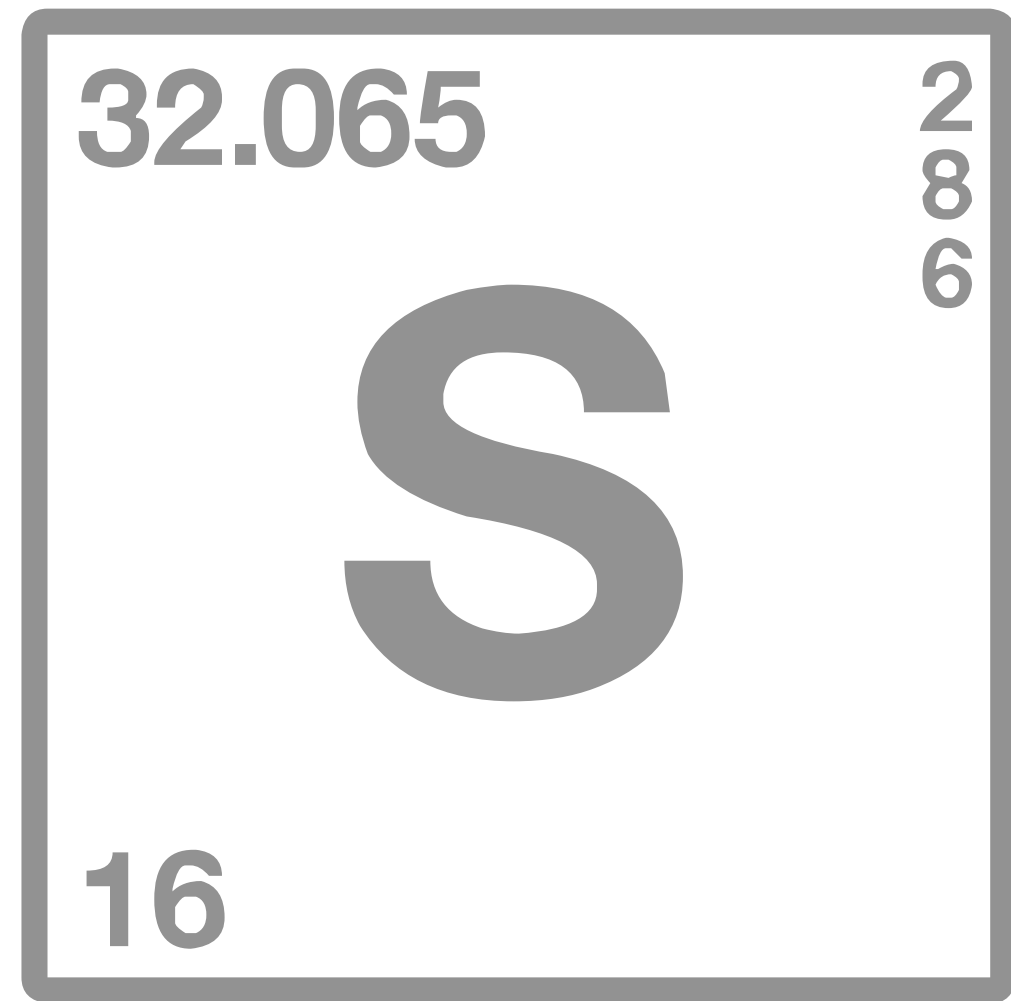
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origins of life as we know it require the presence of S-bearing organics (+ nitriles) in prebiotic conditions



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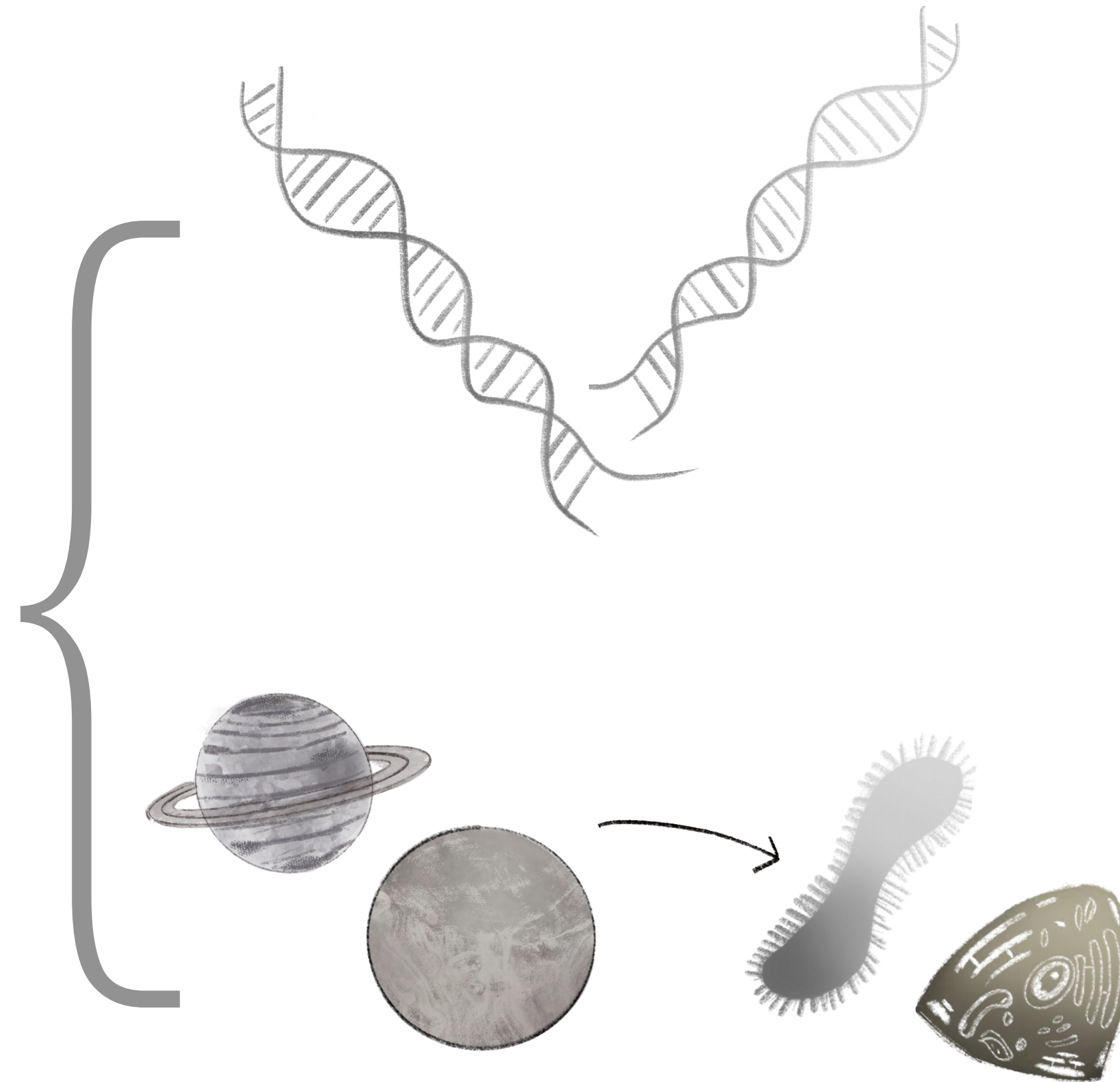
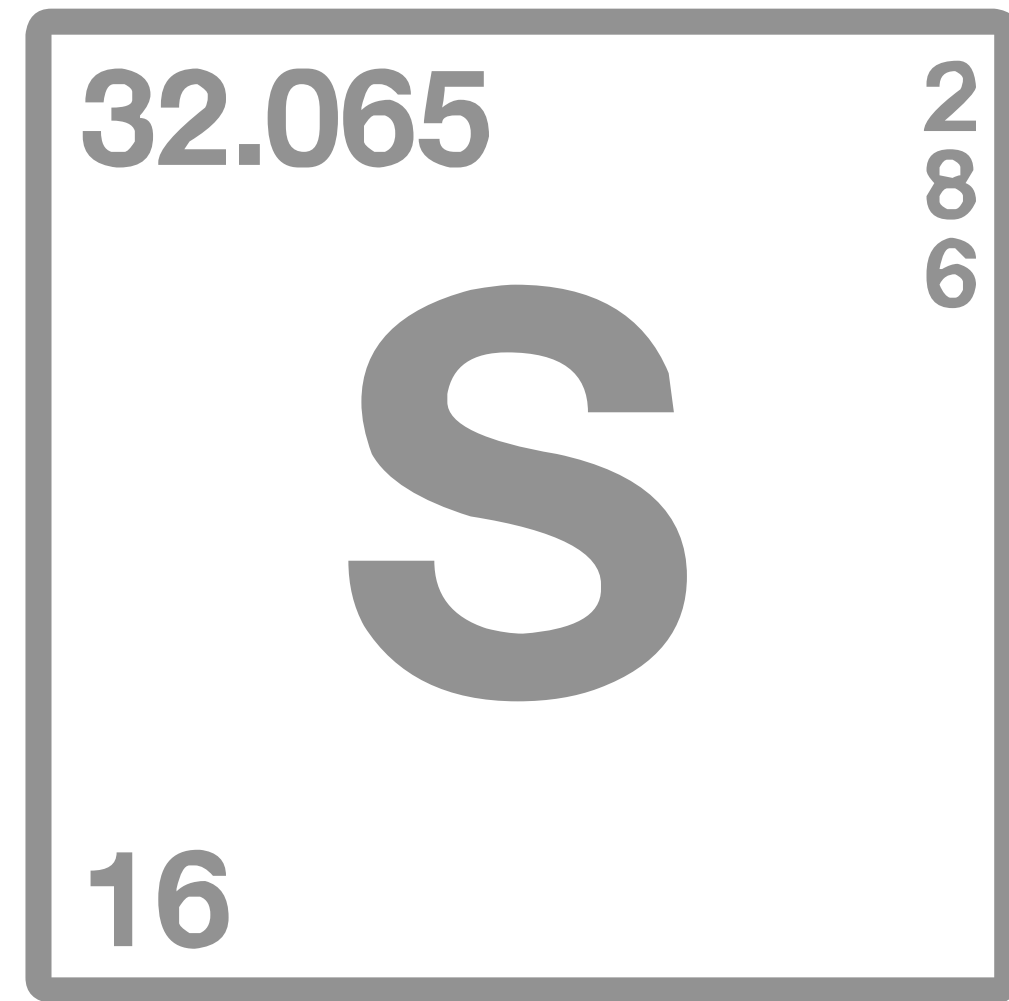
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*...but we can't account for ~95% of the Universe's S budget*

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

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



# Theoretical modelers leverage the periodic table

1 1A 1A <b>H</b> Hydrogen 1.008																	18 VIIIA 8A <b>He</b> Helium 4.003
3 <b>Li</b> Lithium 6.941	4 <b>Be</b> Beryllium 9.012											5 <b>B</b> Boron 10.811	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998	10 <b>Ne</b> Neon 20.180
11 <b>Na</b> Sodium 22.990	12 <b>Mg</b> Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 <b>Al</b> Aluminum 26.982	14 <b>Si</b> Silicon 28.086	15 <b>P</b> Phosphorus 30.974	16 <b>S</b> Sulfur 32.066	17 <b>Cl</b> Chlorine 35.453	18 <b>Ar</b> Argon 39.948
19 <b>K</b> Potassium 39.098	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.956	22 <b>Ti</b> Titanium 47.88	23 <b>V</b> Vanadium 50.942	24 <b>Cr</b> Chromium 51.996	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Iron 55.933	27 <b>Co</b> Cobalt 58.933	28 <b>Ni</b> Nickel 58.693	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.39	31 <b>Ga</b> Gallium 69.732	32 <b>Ge</b> Germanium 72.61	33 <b>As</b> Arsenic 74.922	34 <b>Se</b> Selenium 78.09	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 84.80
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Lanthanide Series	57 <b>La</b> Lanthanum 138.906	58 <b>Ce</b> Cerium 140.115	59 <b>Pr</b> Praseodymium 140.908	60 <b>Nd</b> Neodymium 144.24	61 <b>Pm</b> Promethium 144.913	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.966	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.925	66 <b>Dy</b> Dysprosium 162.50	67 <b>Ho</b> Holmium 164.930	68 <b>Er</b> Erbium 167.26	69 <b>Tm</b> Thulium 168.934	70 <b>Yb</b> Ytterbium 173.04	71 <b>Lu</b> Lutetium 174.967
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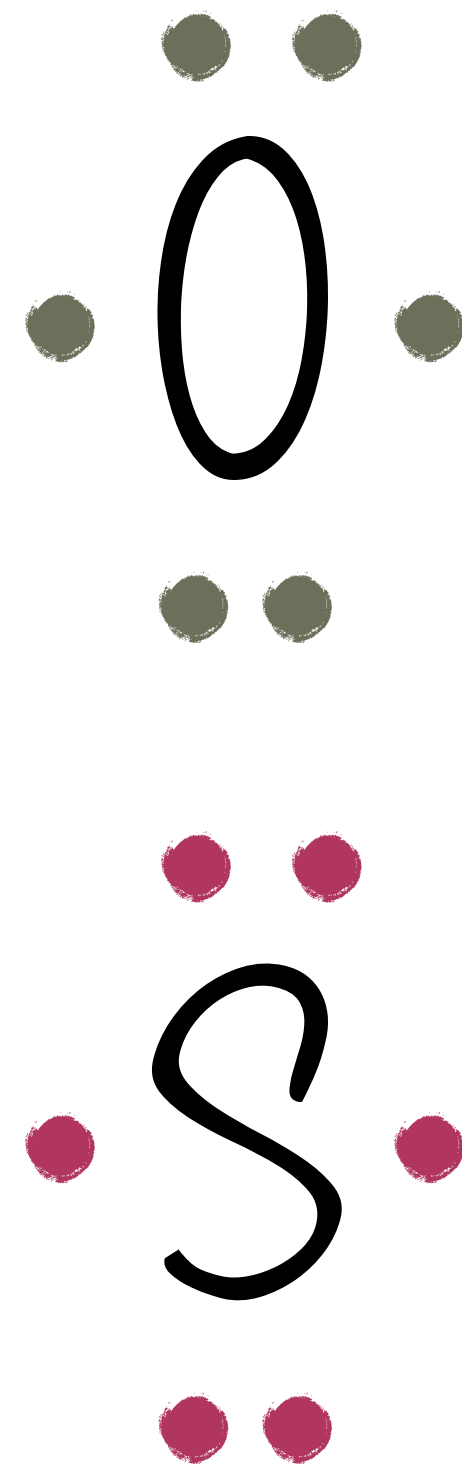
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*Same-group elements have identical # of valence electrons*

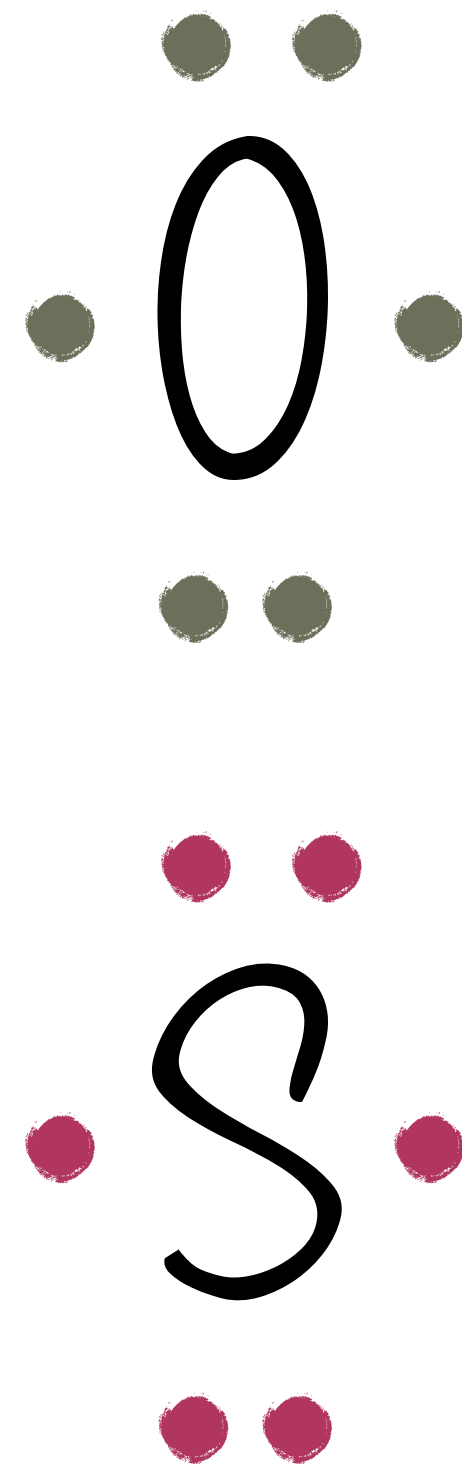
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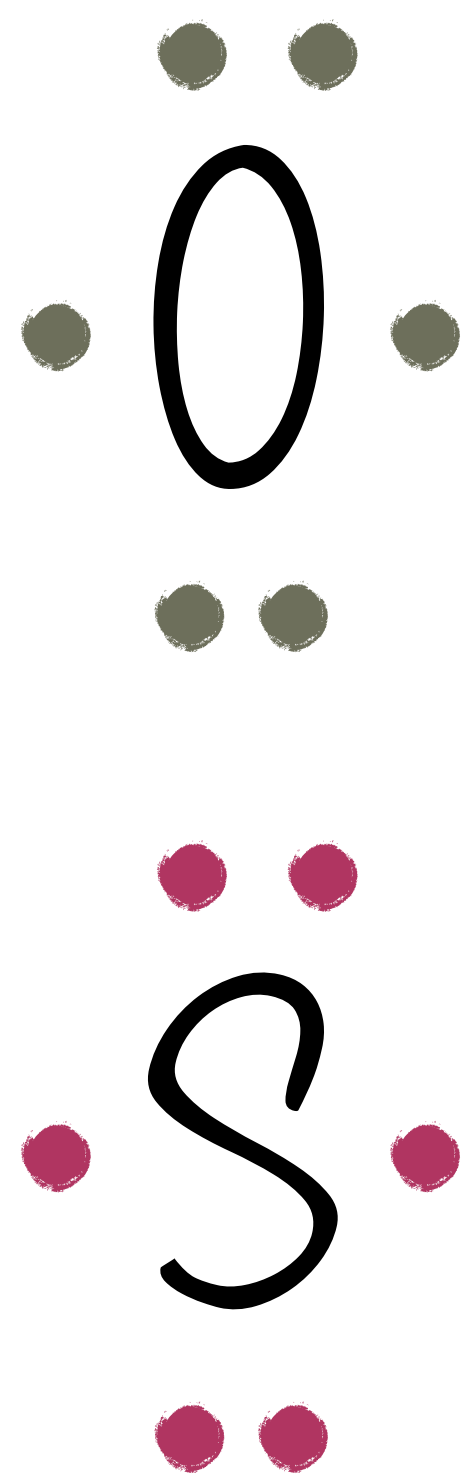
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----------------------------	-----------------------------



*Valence electrons are responsible for an element's reactivity*

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8	O	Oxygen	15.999
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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*

*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

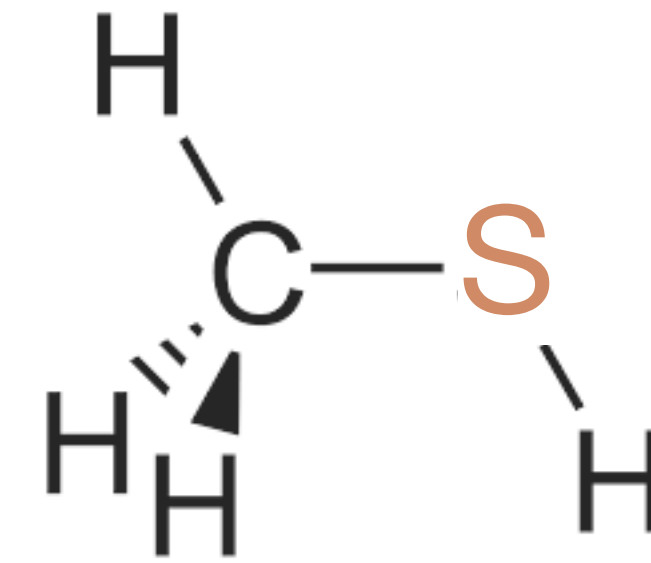


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A sulfur compound containing a C–H bond

“Simplest” complex organosulfur: **methyl mercaptan**

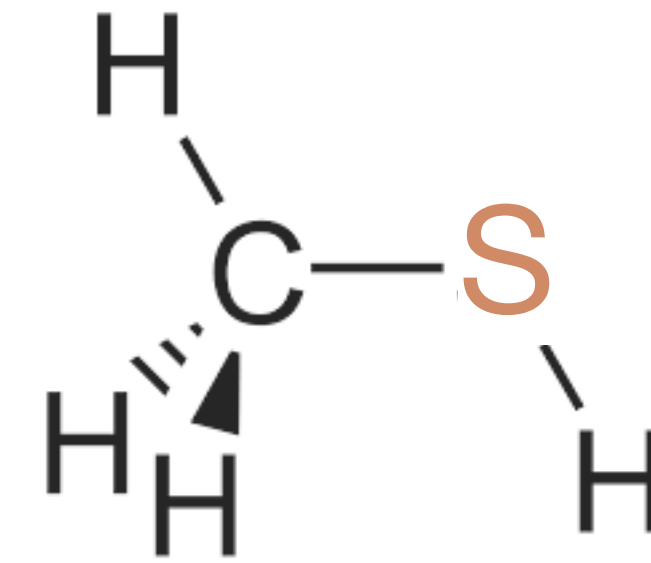


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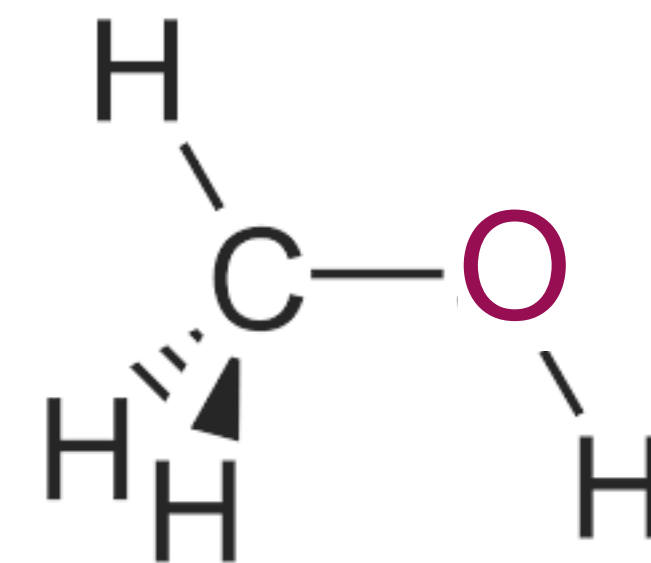
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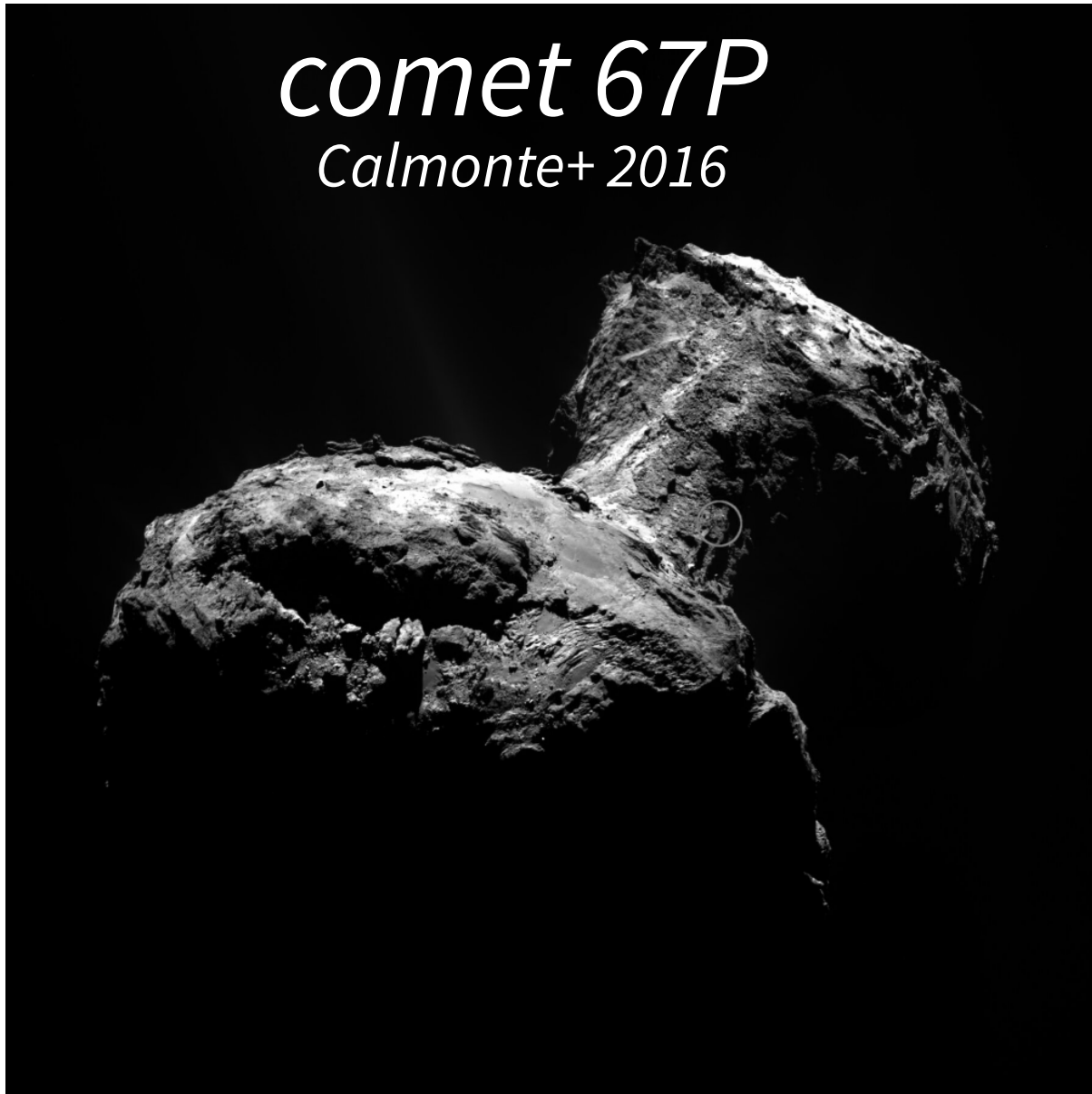
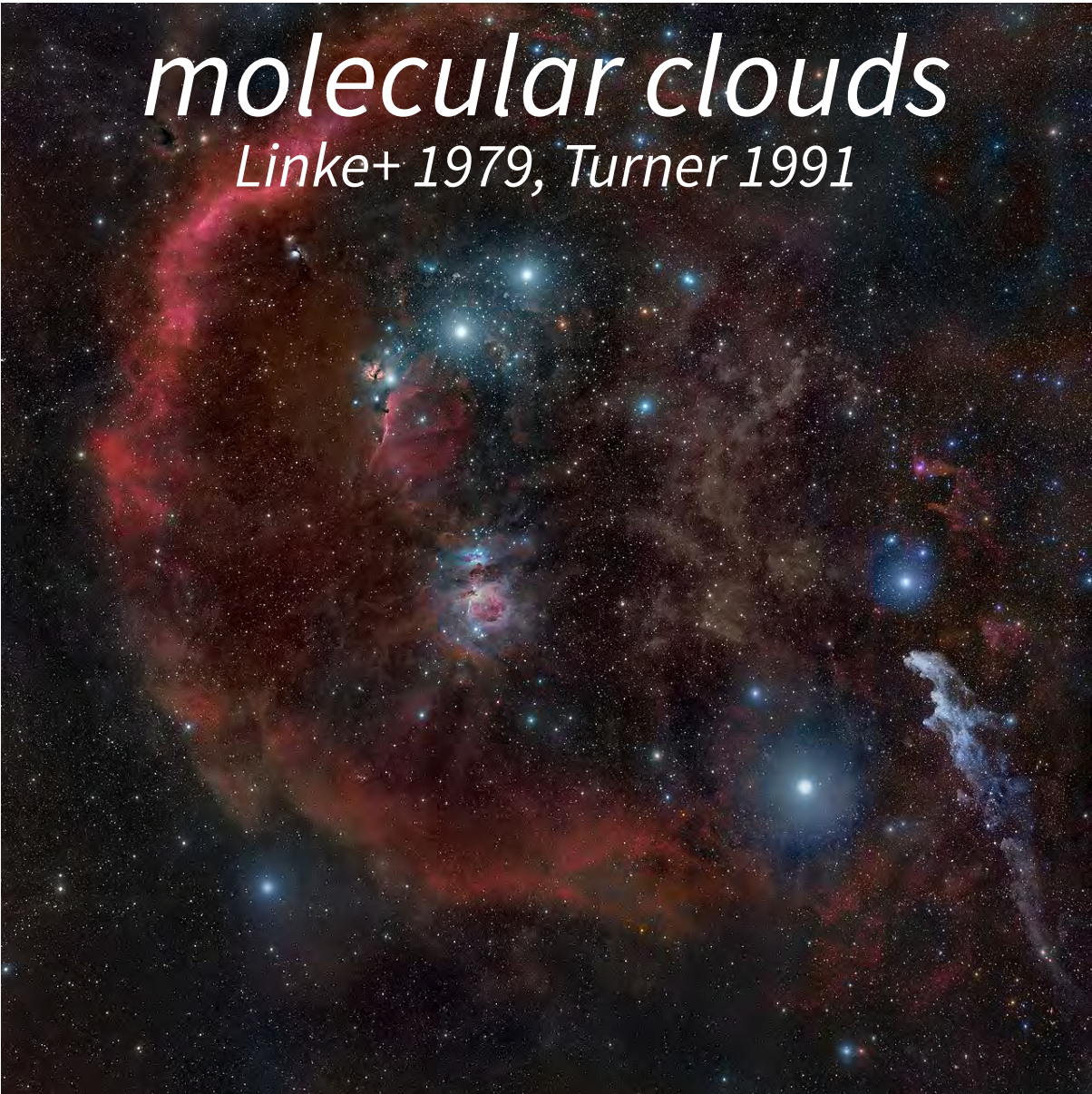


Analogous to its well-understood counterpart, **methanol**





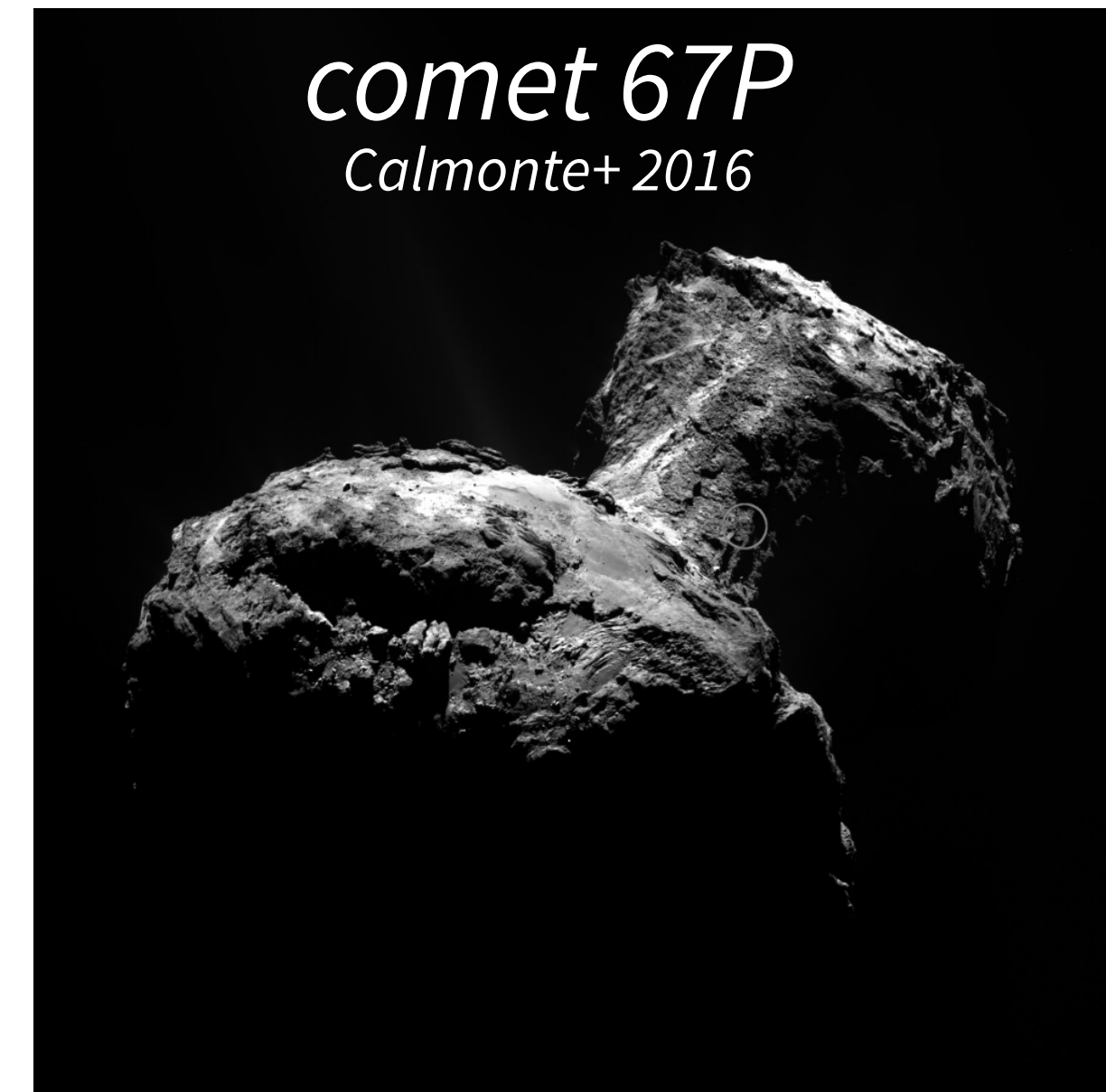
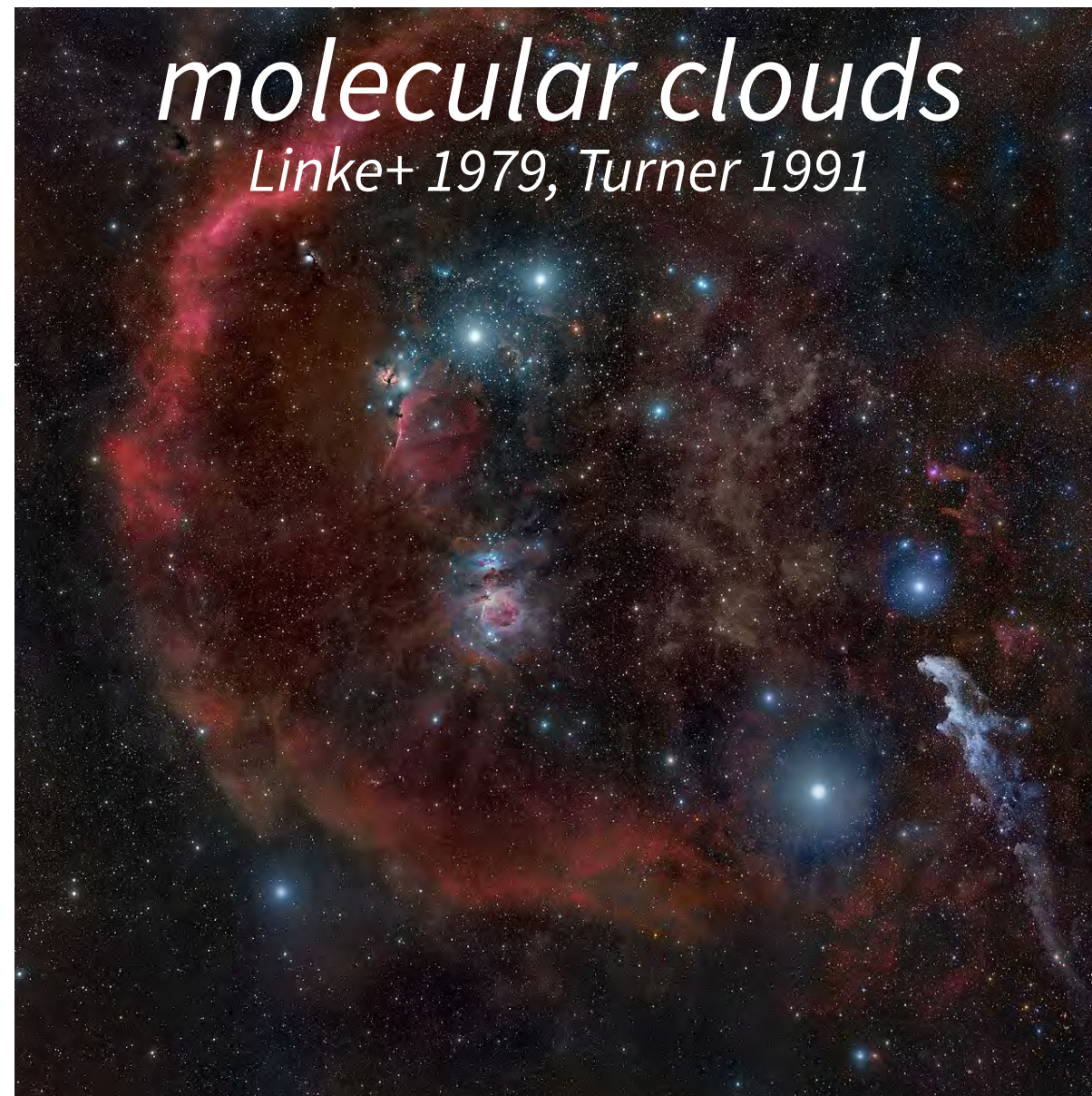
# *CH<sub>3</sub>SH (methyl mercaptan) has been detected towards*



*Image credits: Rogelio B. Andreo/ESO/ESA*



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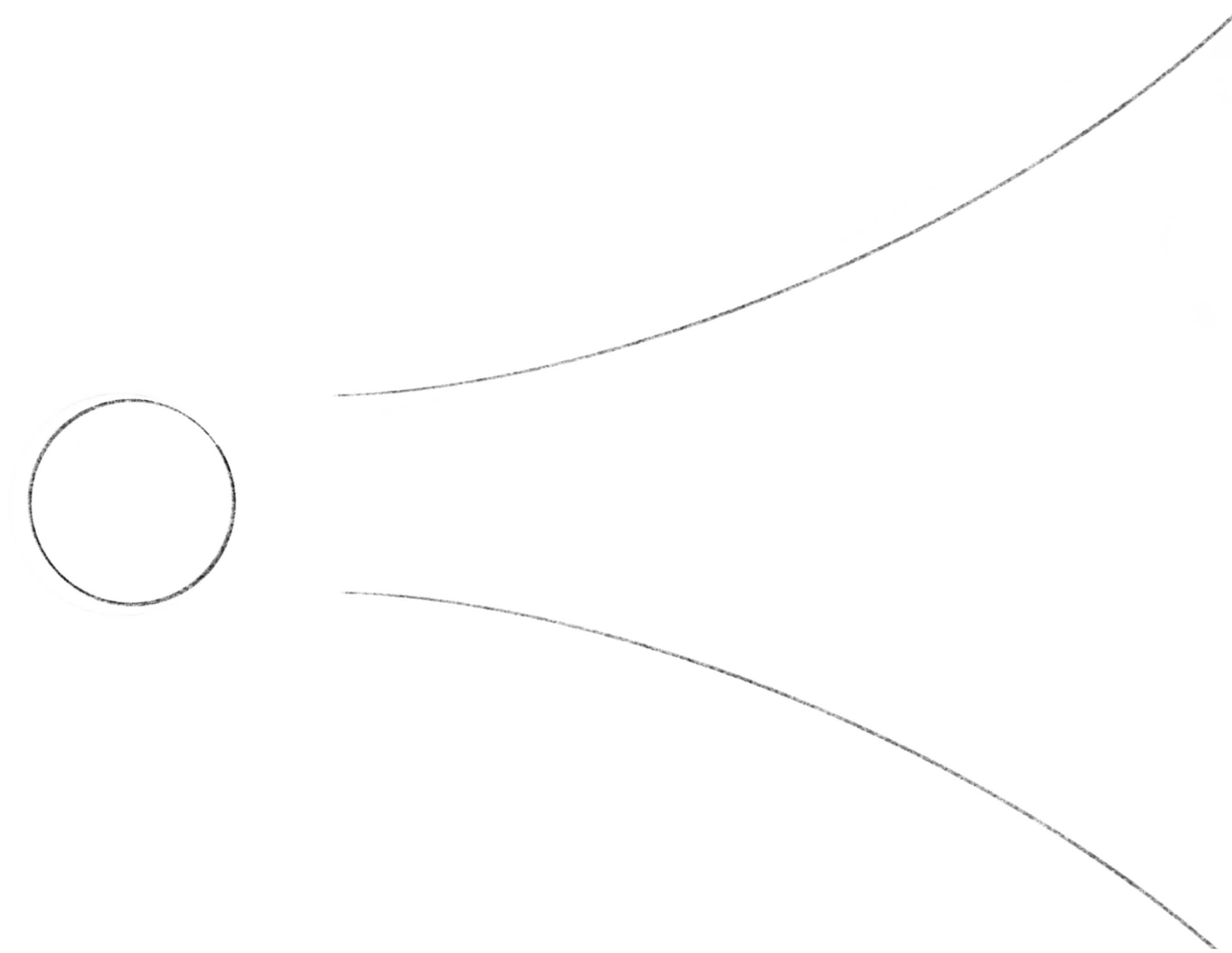


*Image credits: Rogelio B. Andreo/ESO/ESA*

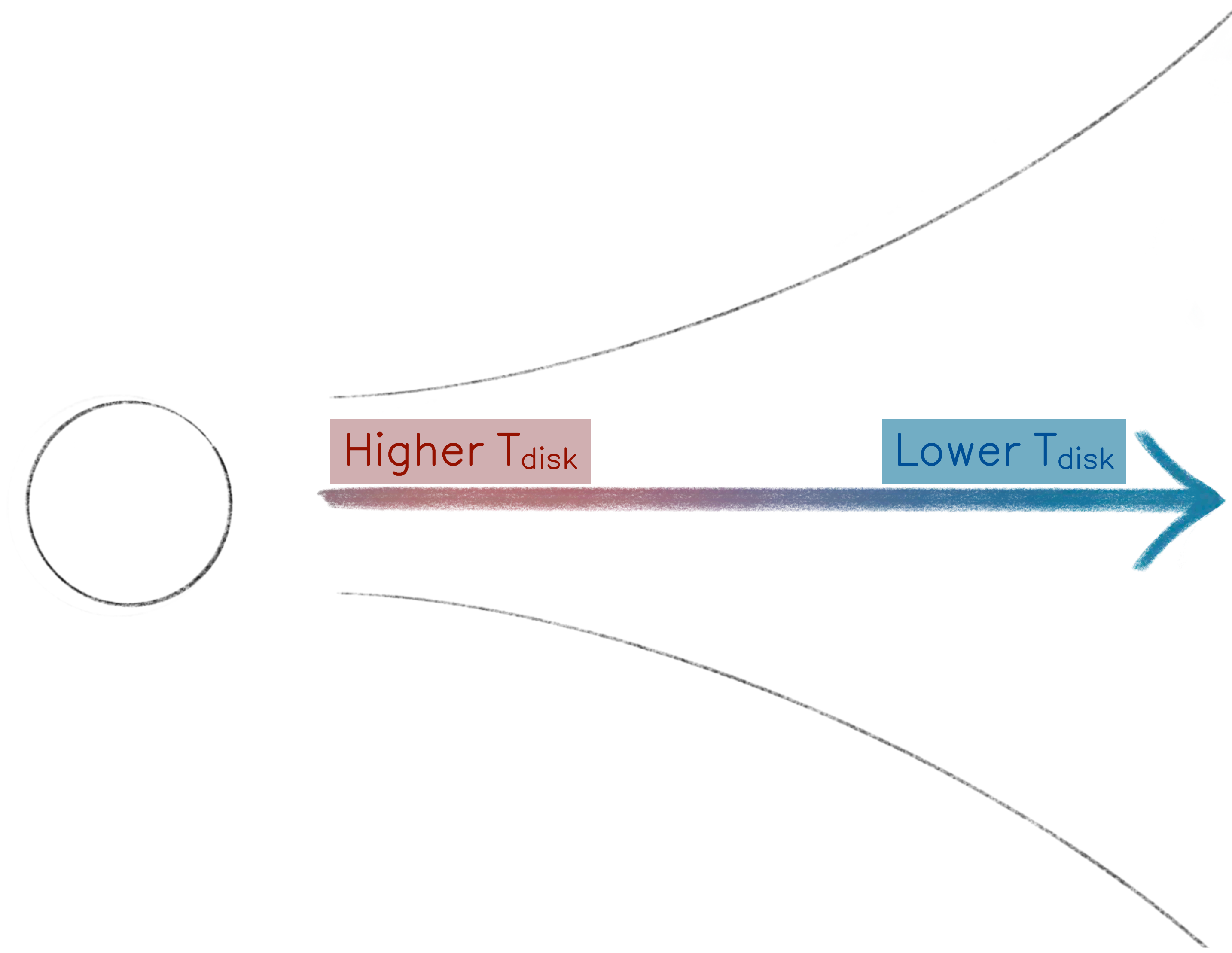
*To understand whether organosulfurs are a possible sulfur sink, we must empirically characterize its fundamental astrochemical properties*



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

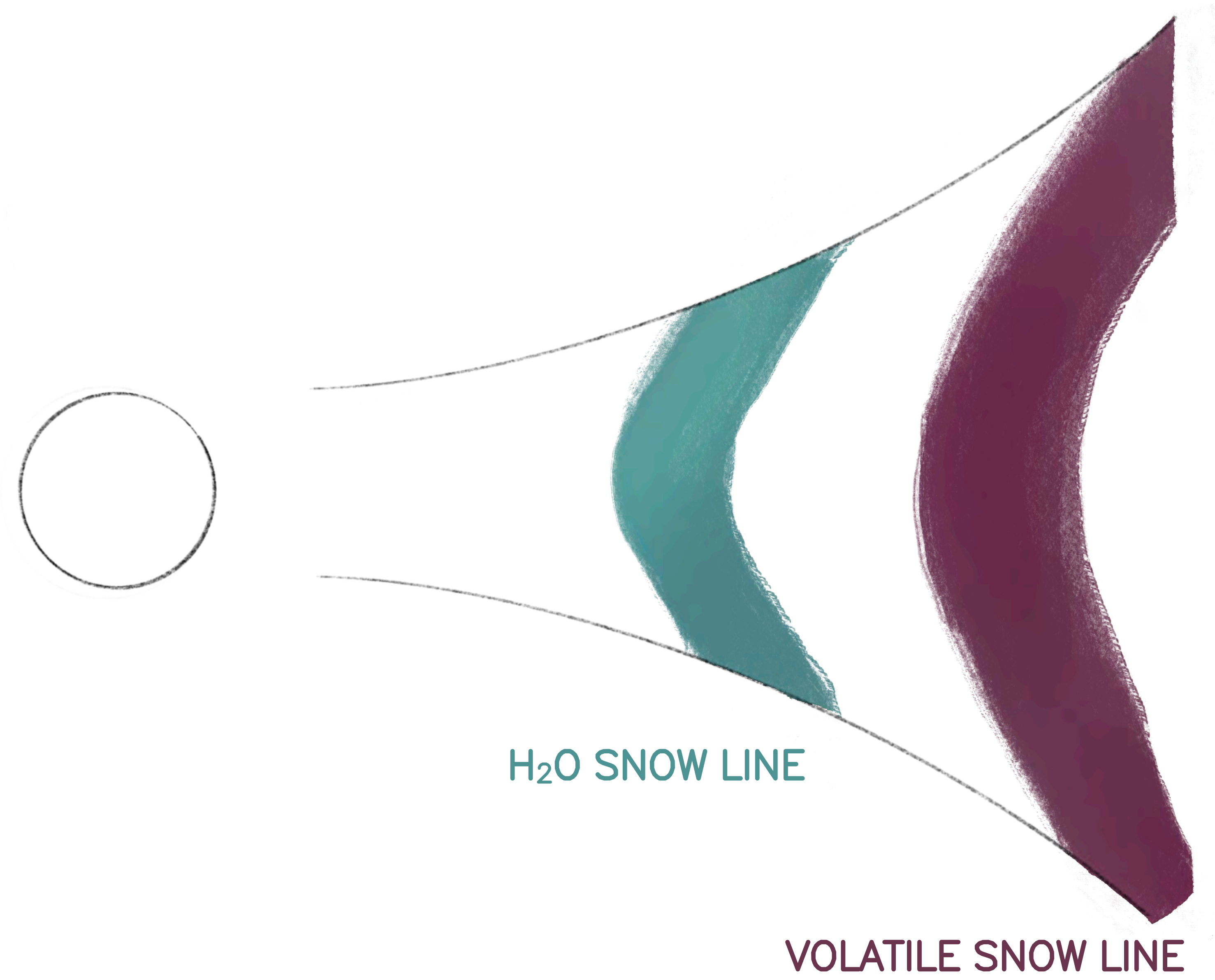


# Molecules condense out as a function of $R_{disk}$ (or $T_{disk}$ )...

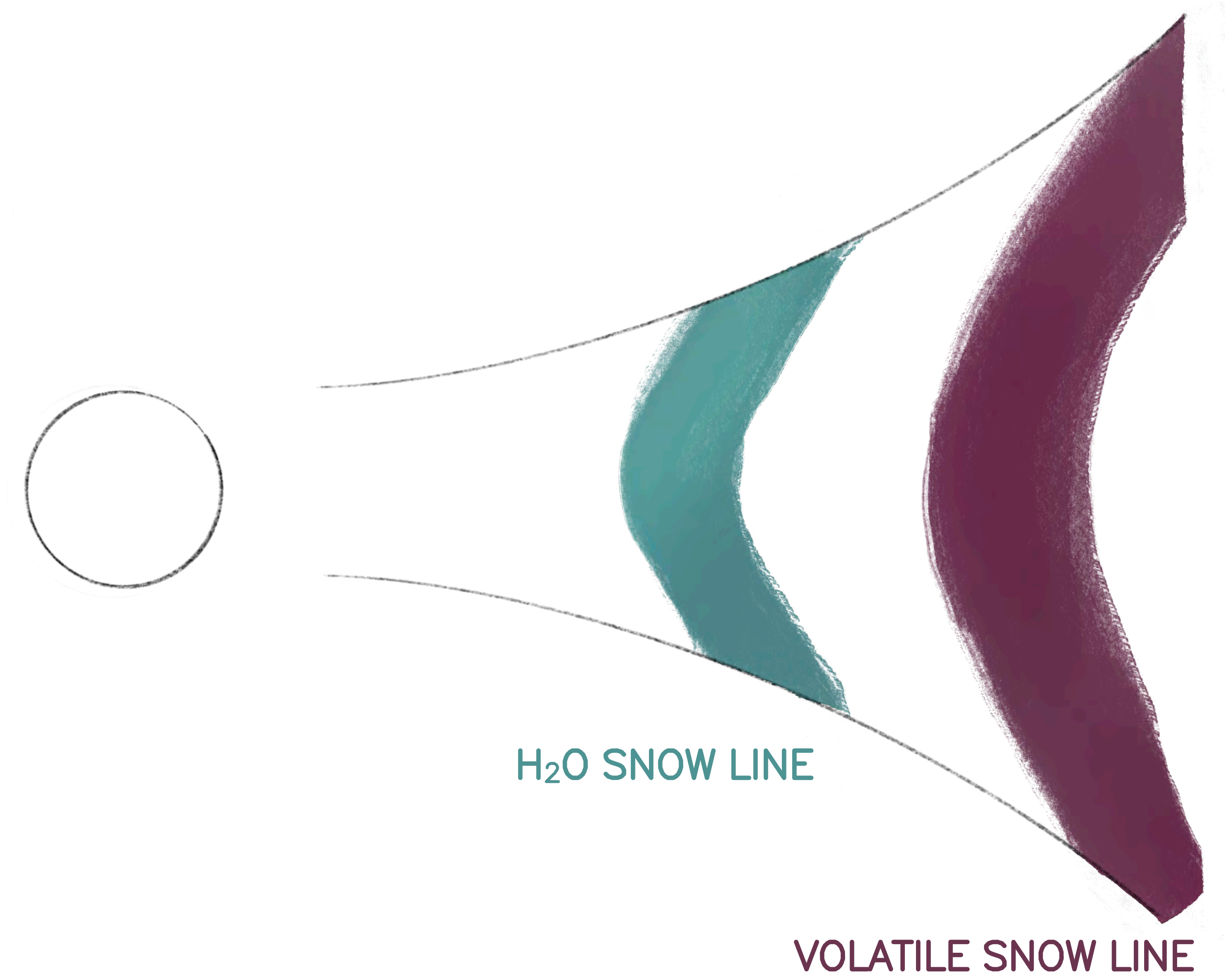




*...forming snow lines which represent the ice-gas boundary*

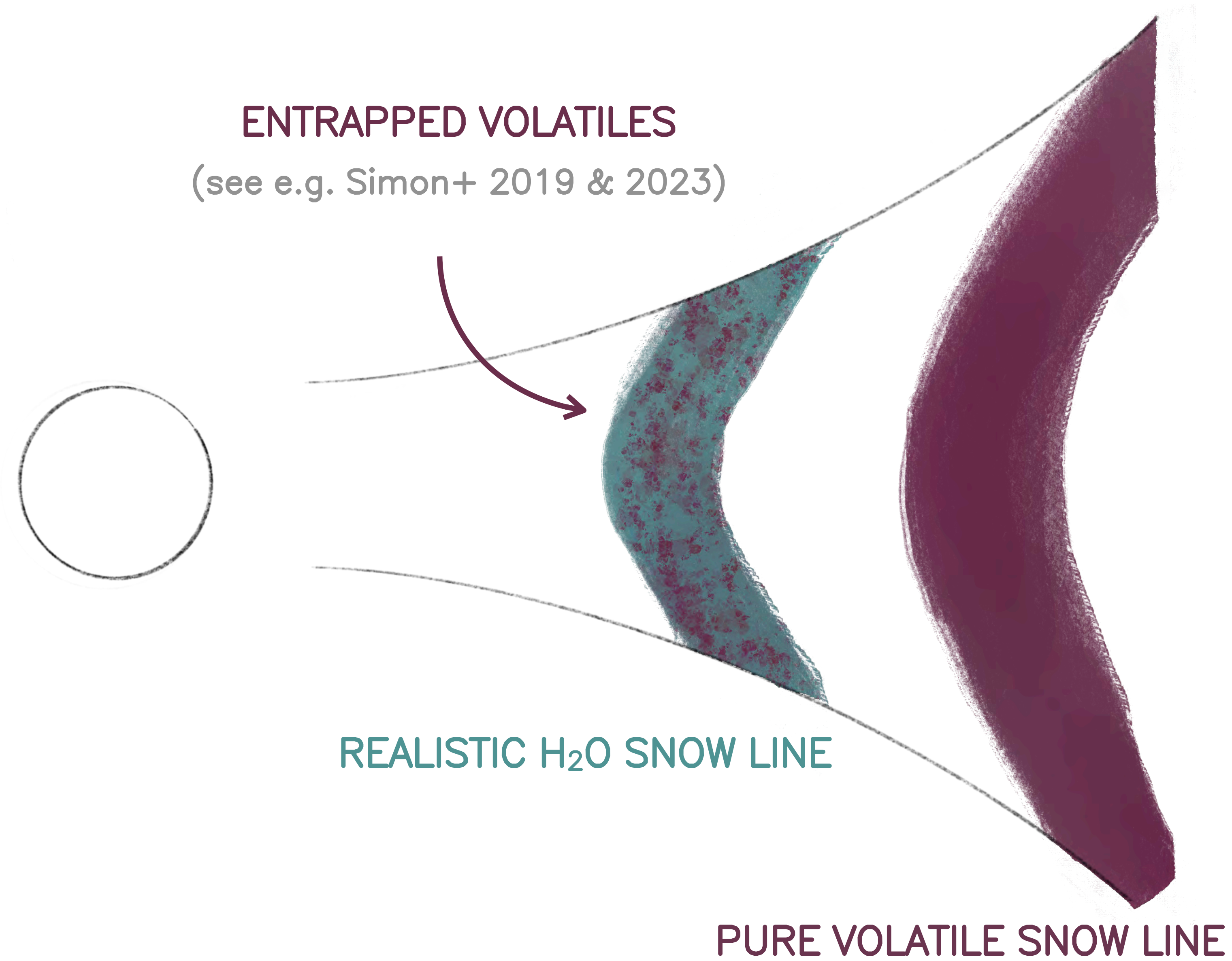


*However, realistic ices are mixtures of H<sub>2</sub>O + other volatiles*

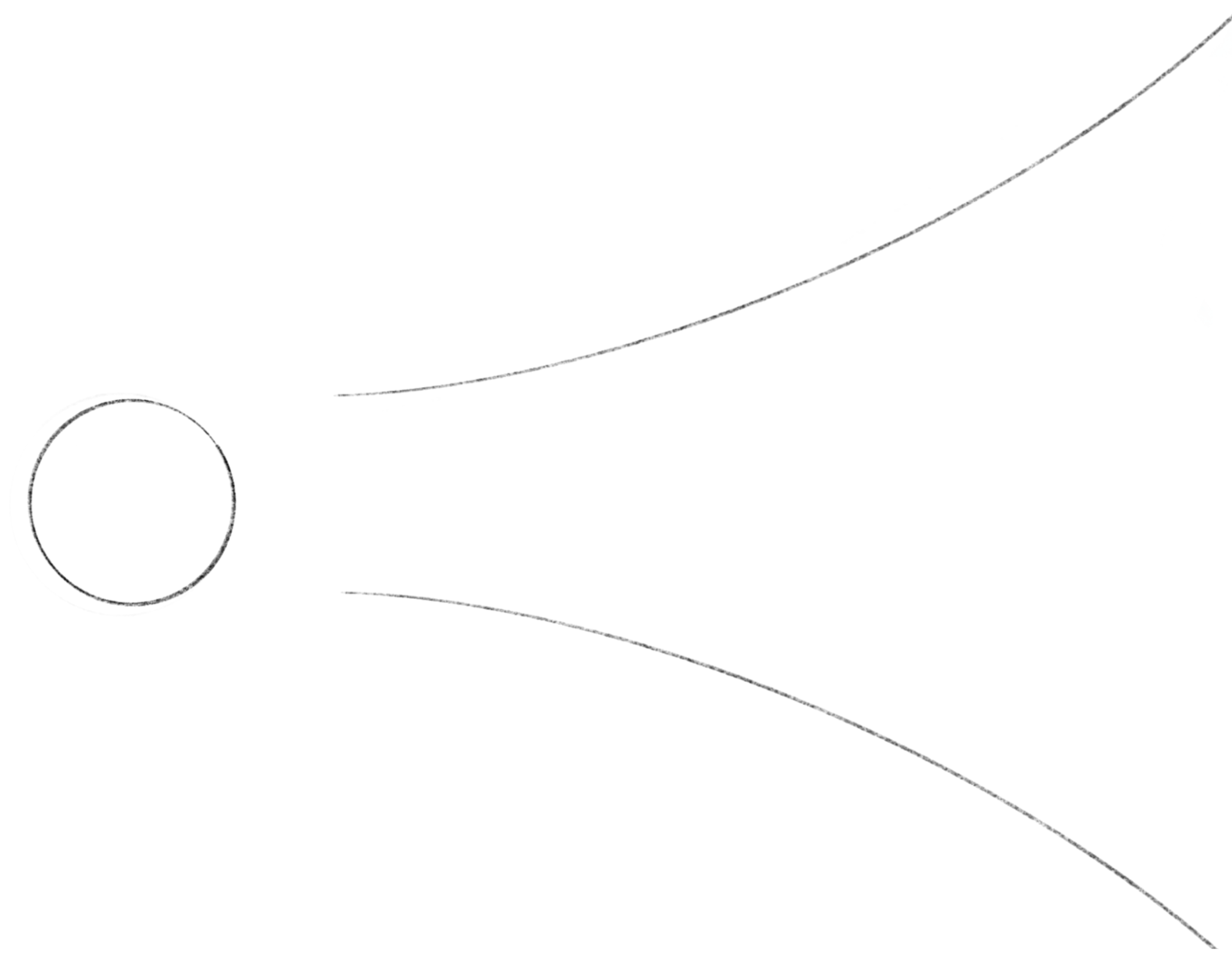




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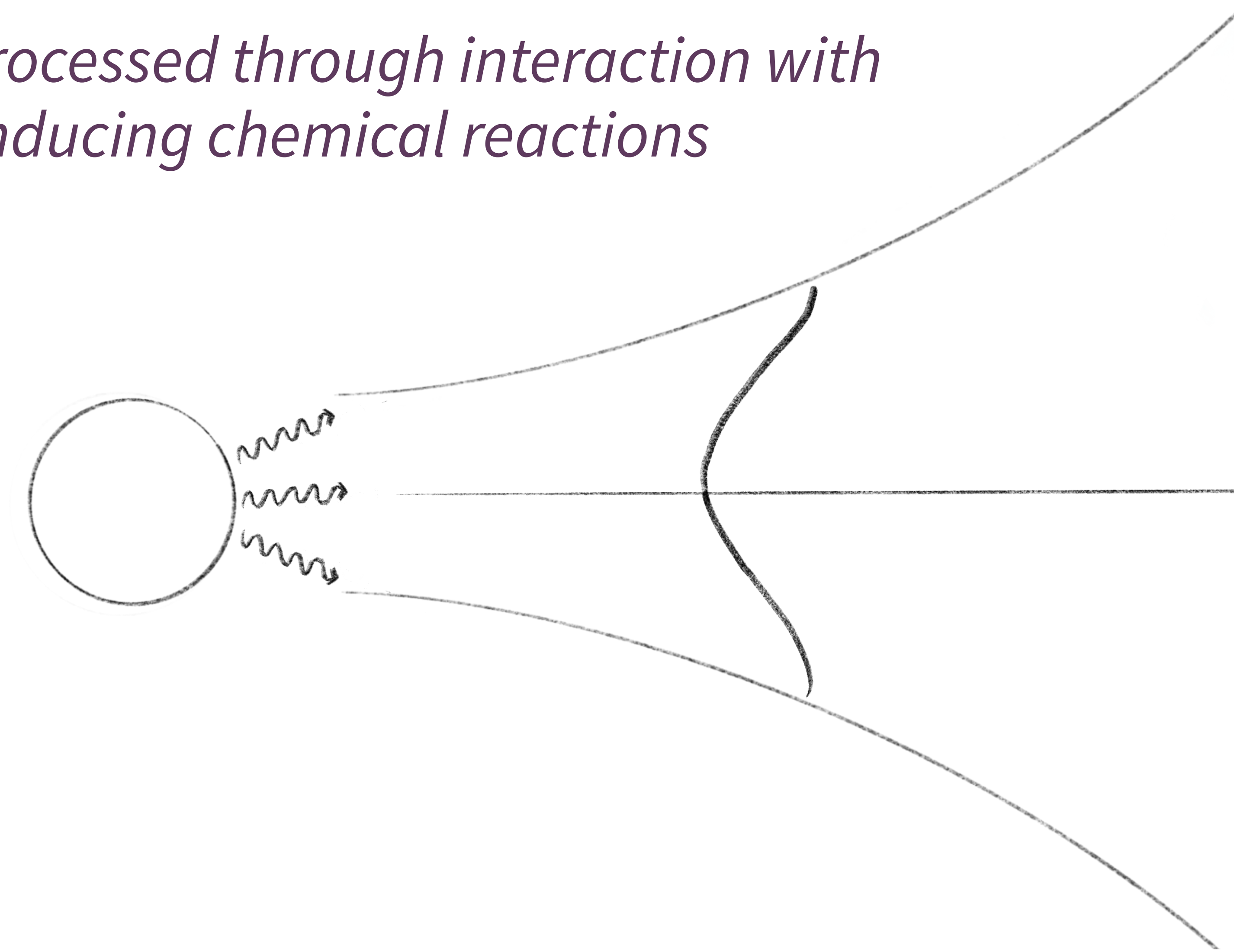
## 2 & 3. How is $CH_3SH$ formed and destroyed?





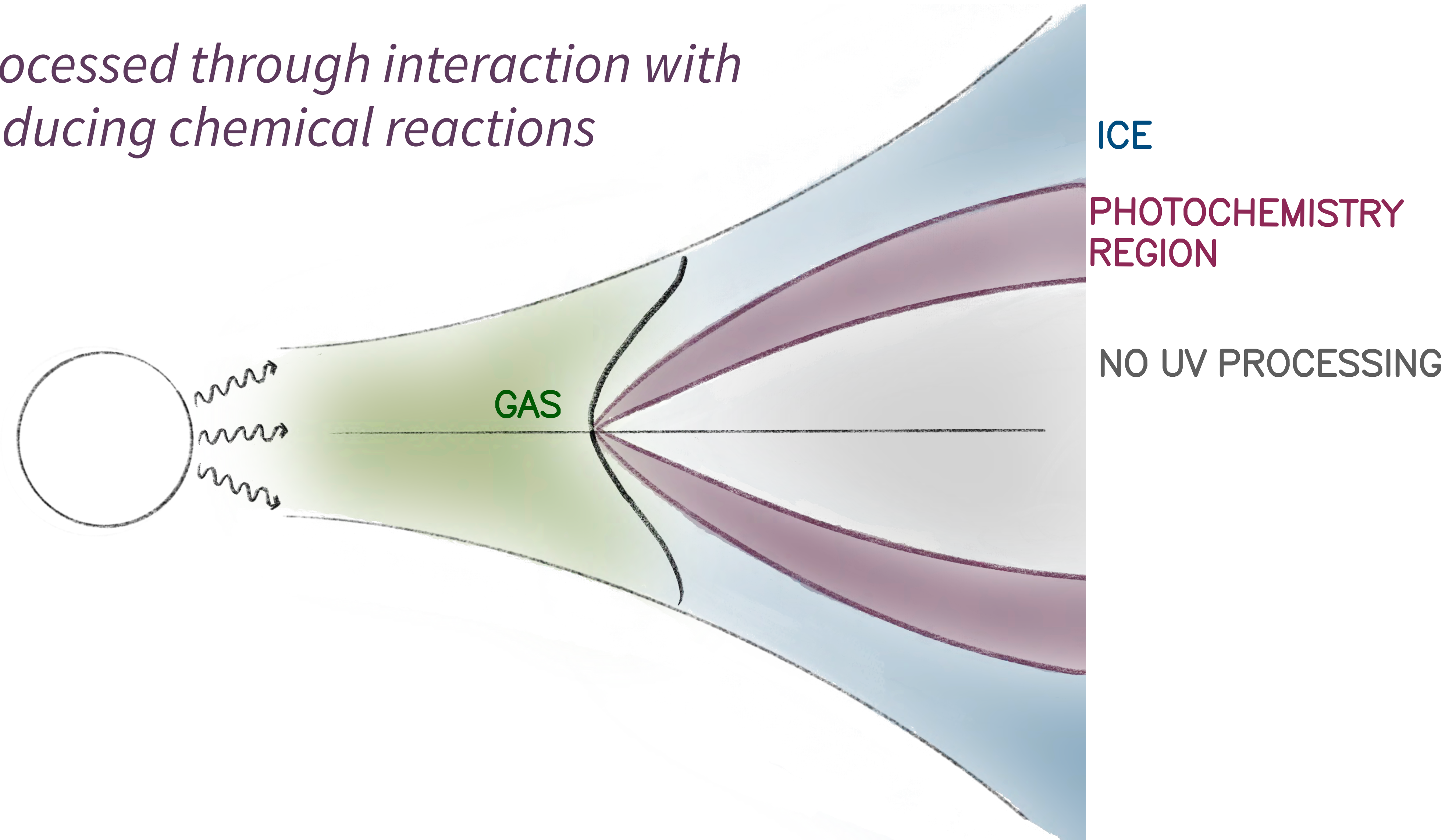
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*Ices can be processed through interaction with UV photons inducing chemical reactions*



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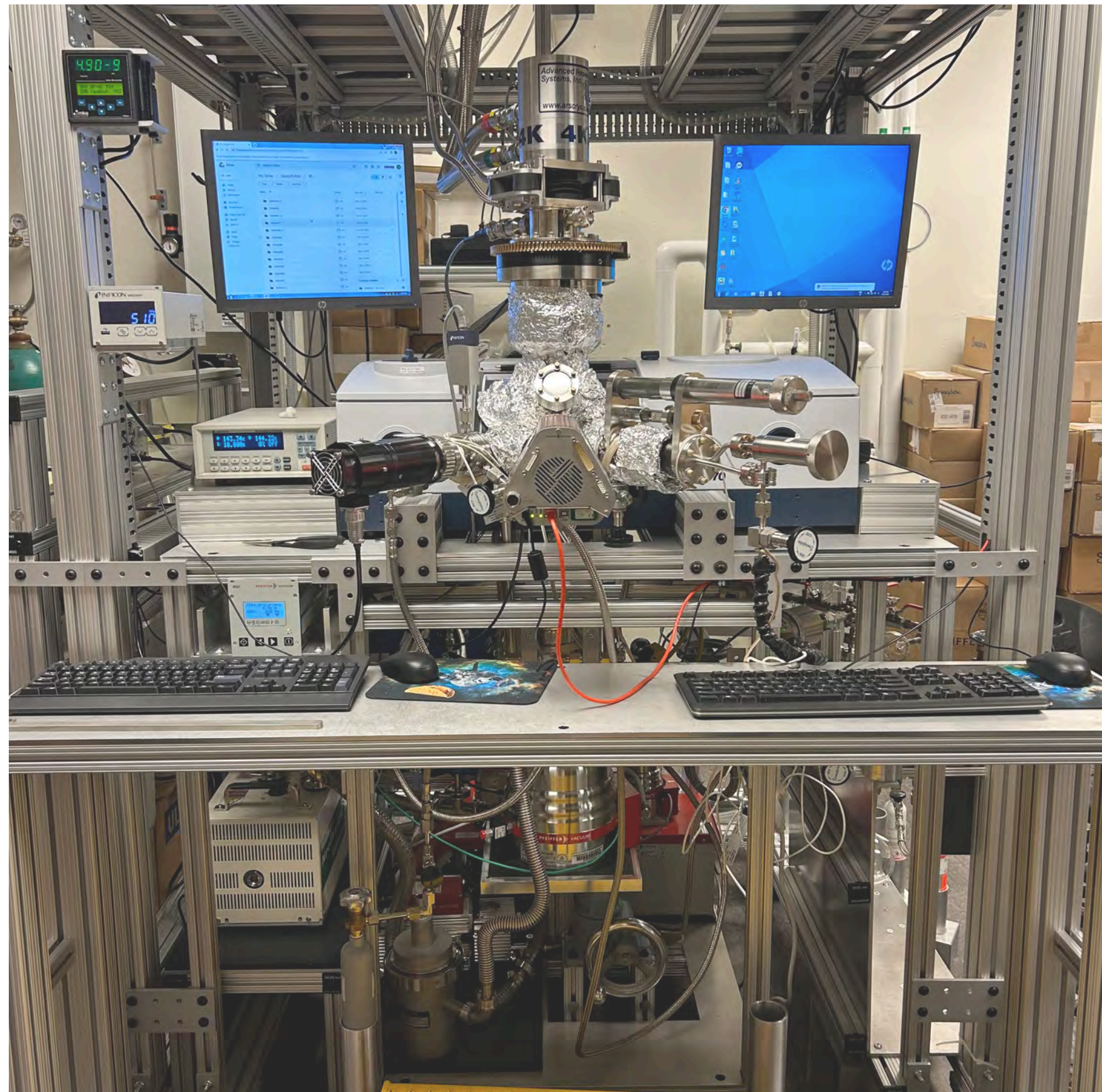
# *How do we simulate disk conditions in the laboratory?*

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



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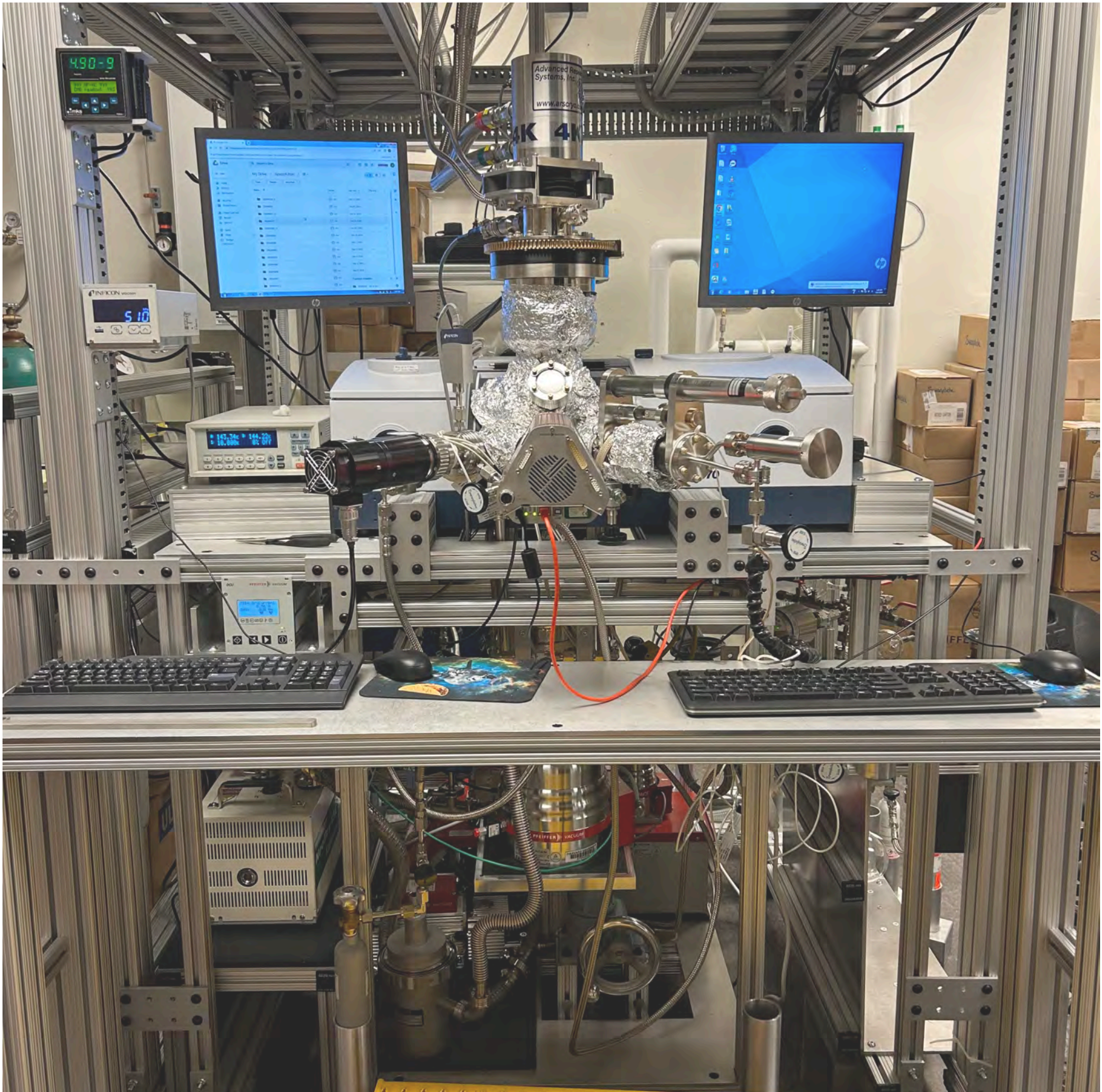


**SIMPLEST**

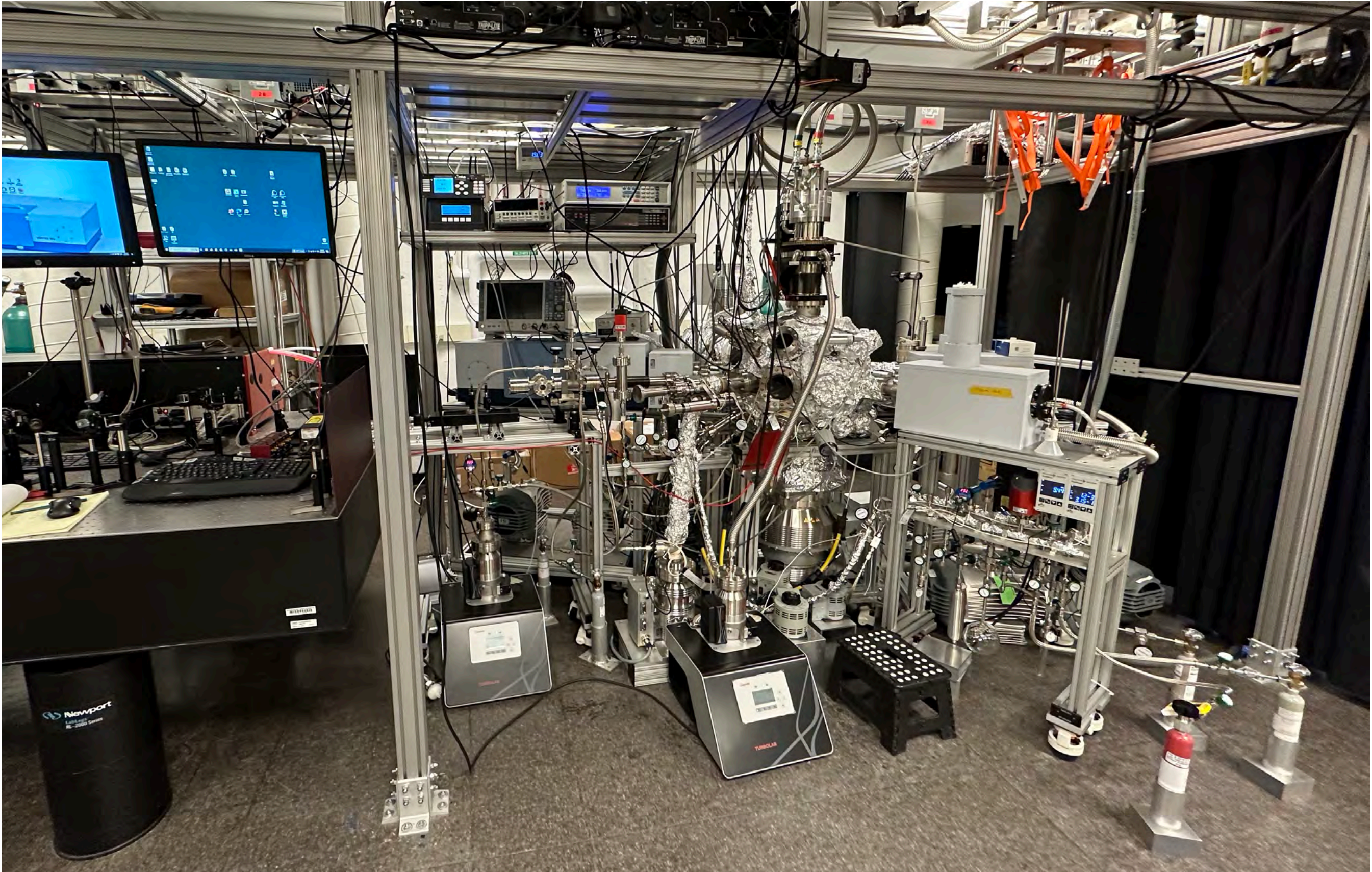


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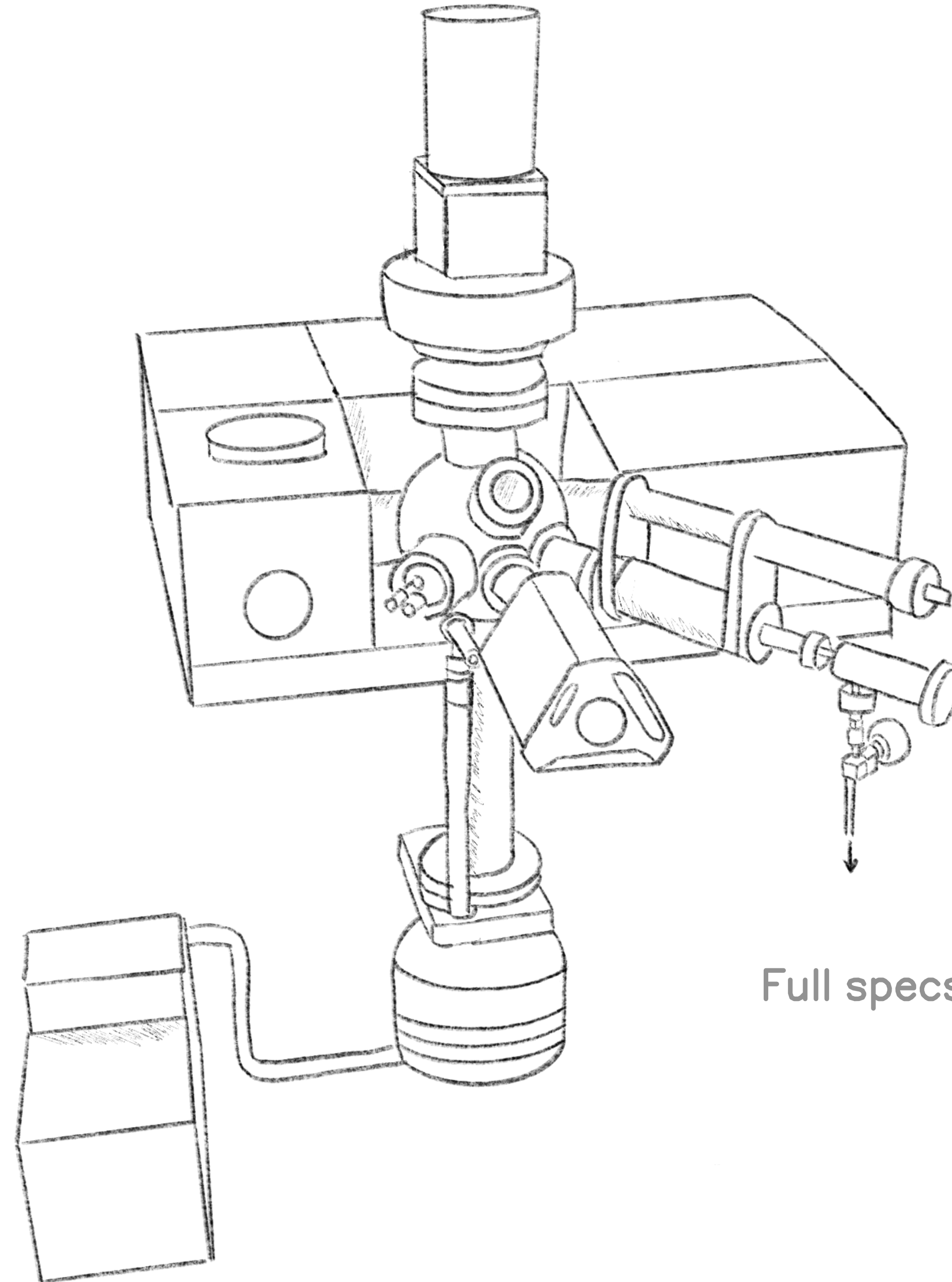
SIMPLEST



MOST COMPLEX



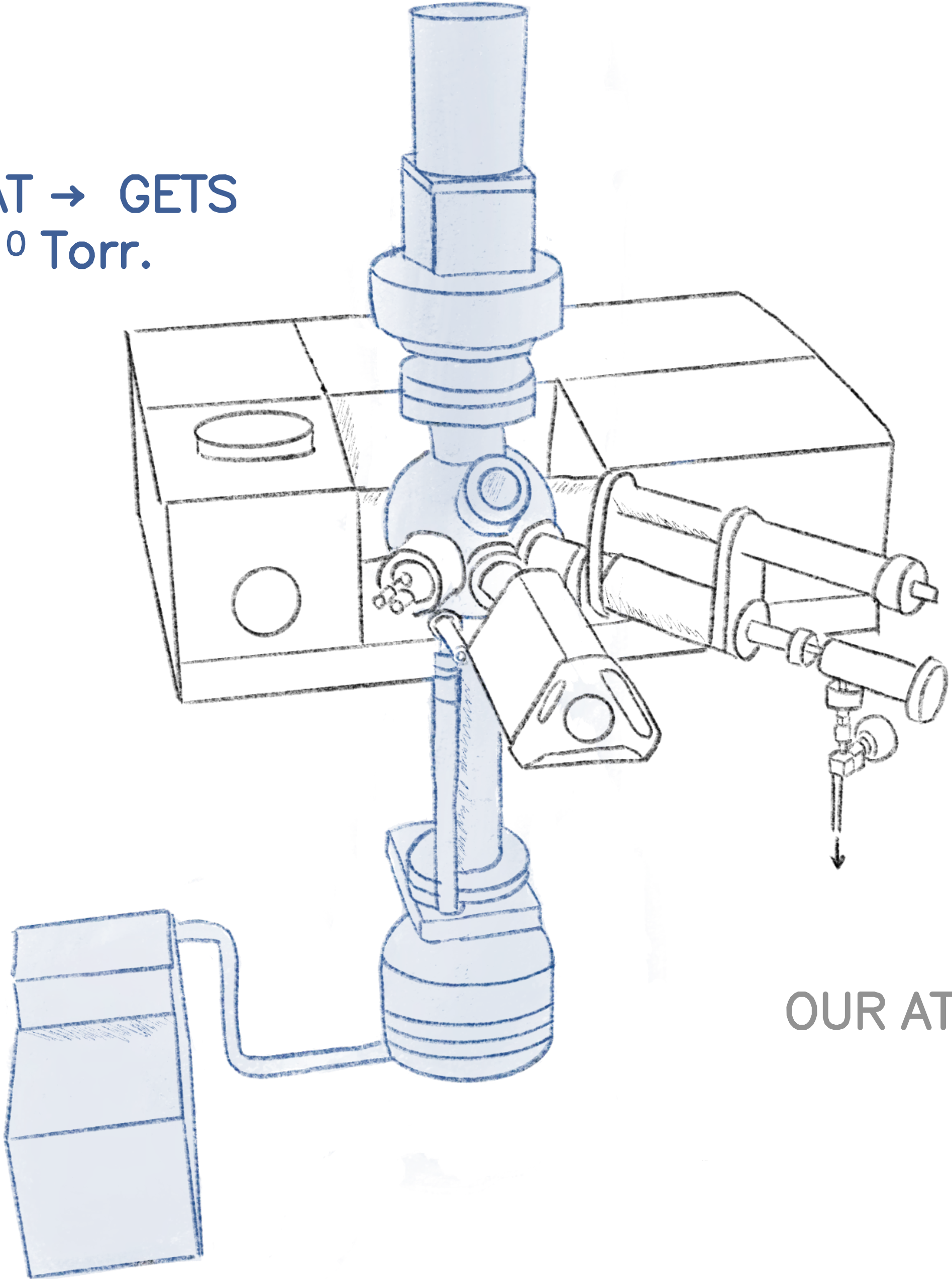
# Brief experimental procedure



Full specs in Simon+ 2023.

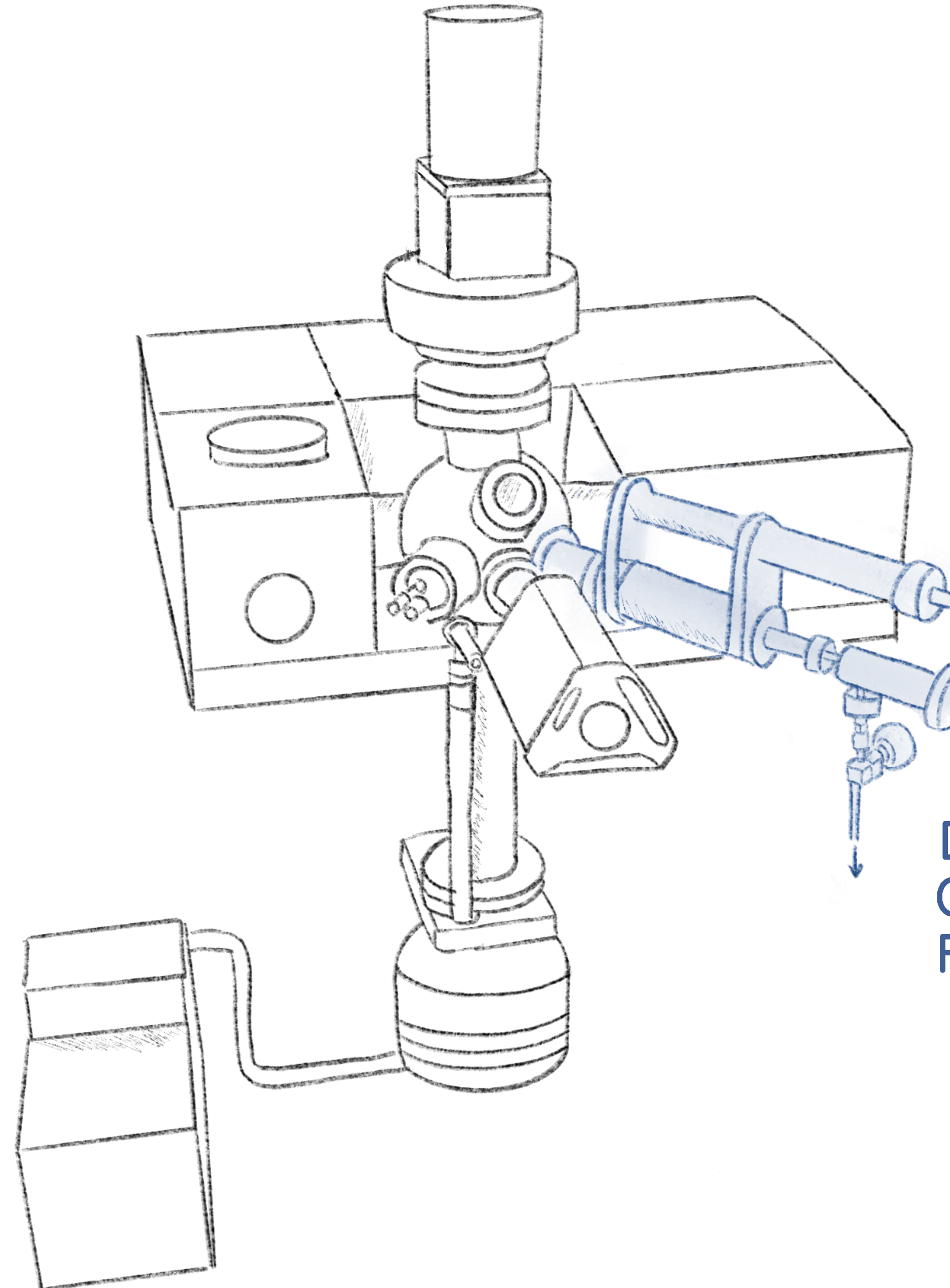
# We first get to low $T$ , low $P$

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



OUR ATMOSPHERE IS 760 Torr...

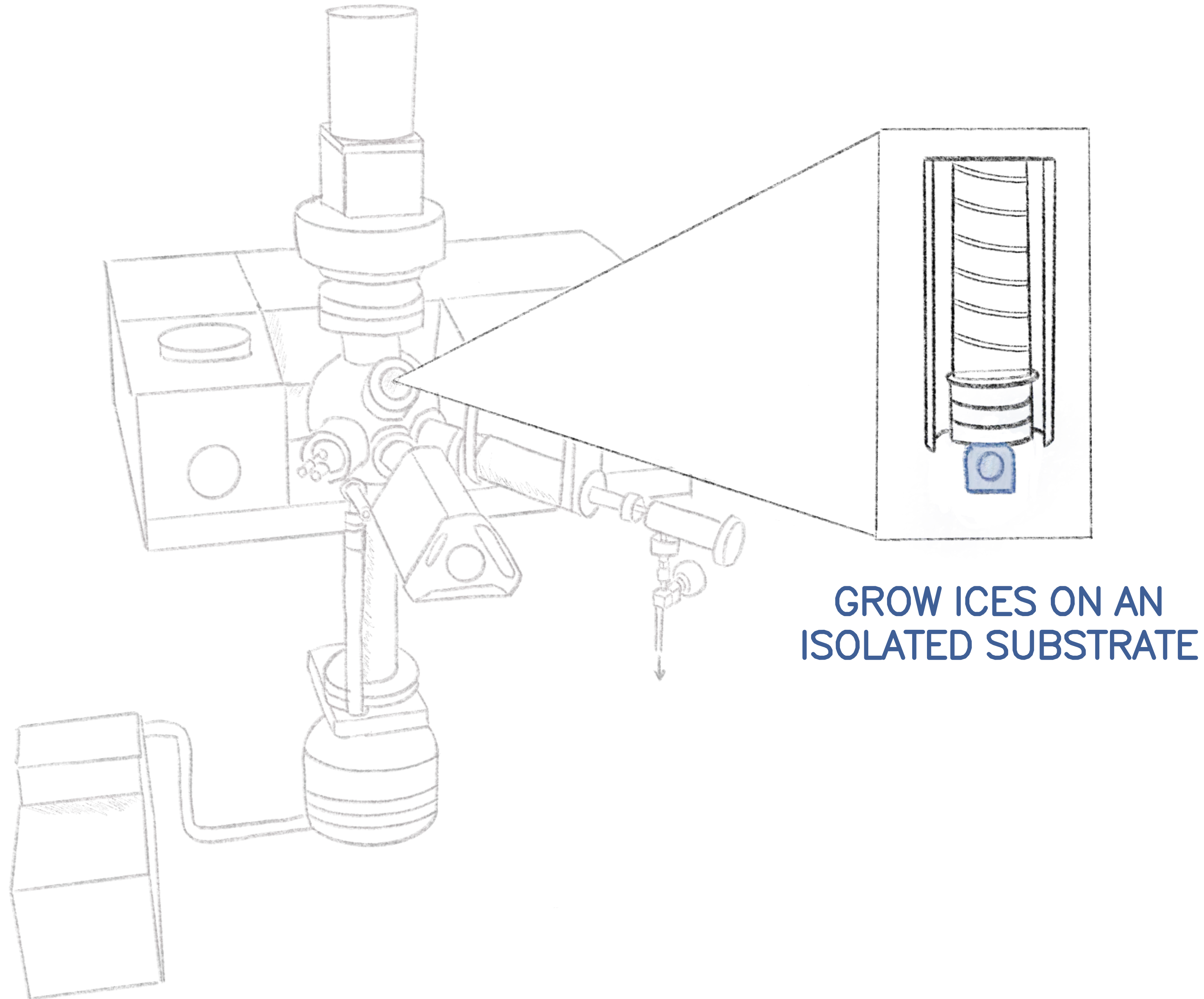
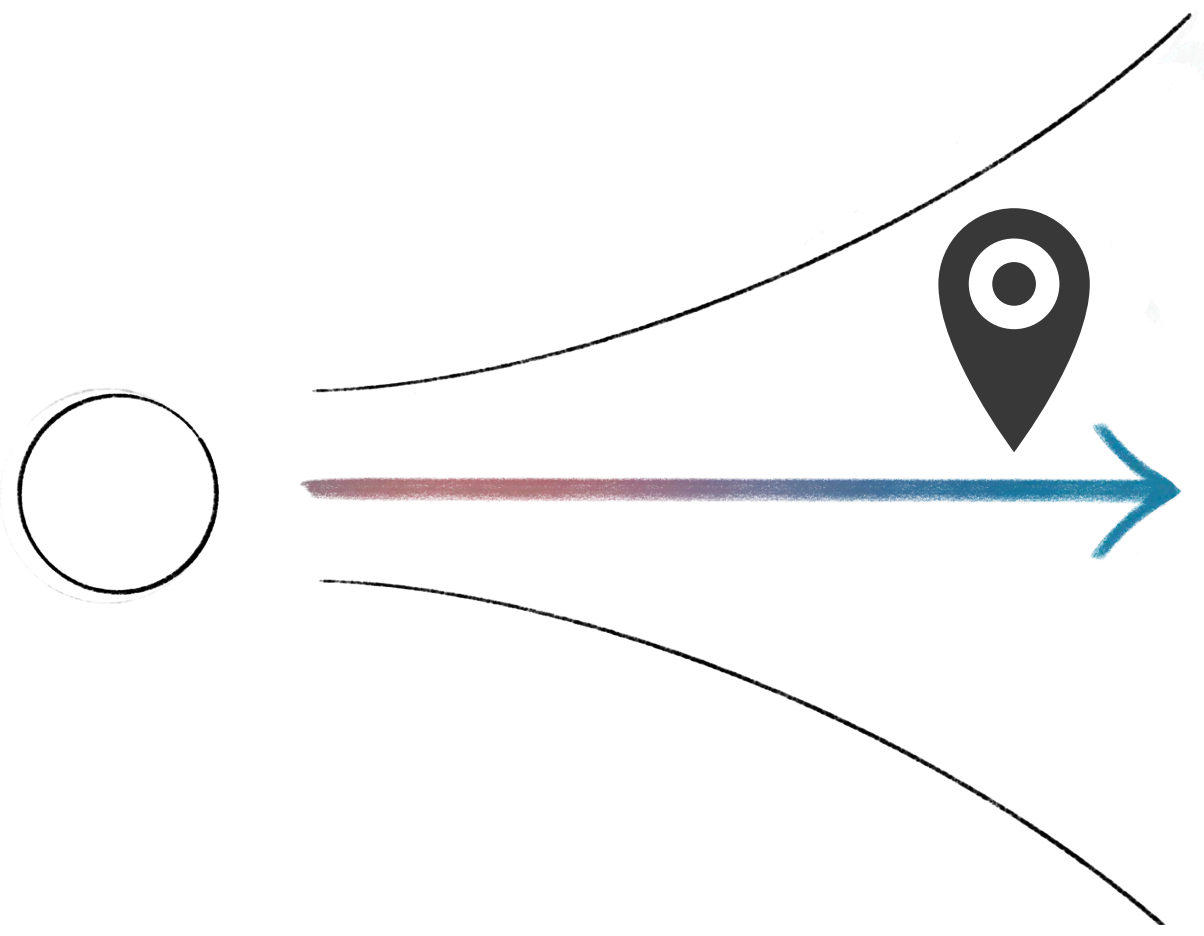
# Introduce molecules into chamber



DOSER THAT CONNECTS TO A GAS LINE WHERE WE MIX OUR REACTANTS (i.e.  $\text{CH}_3\text{SH}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ )

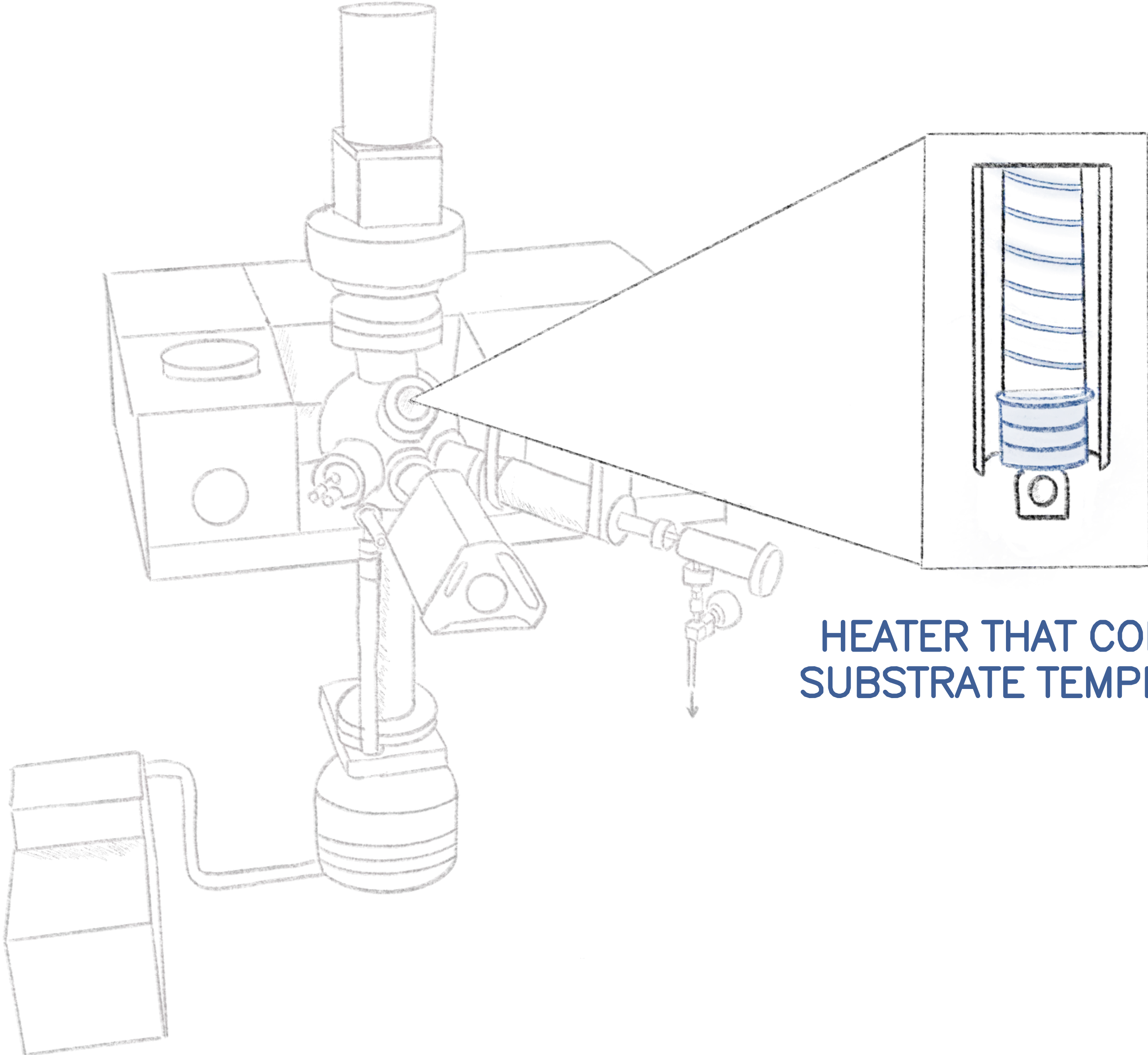
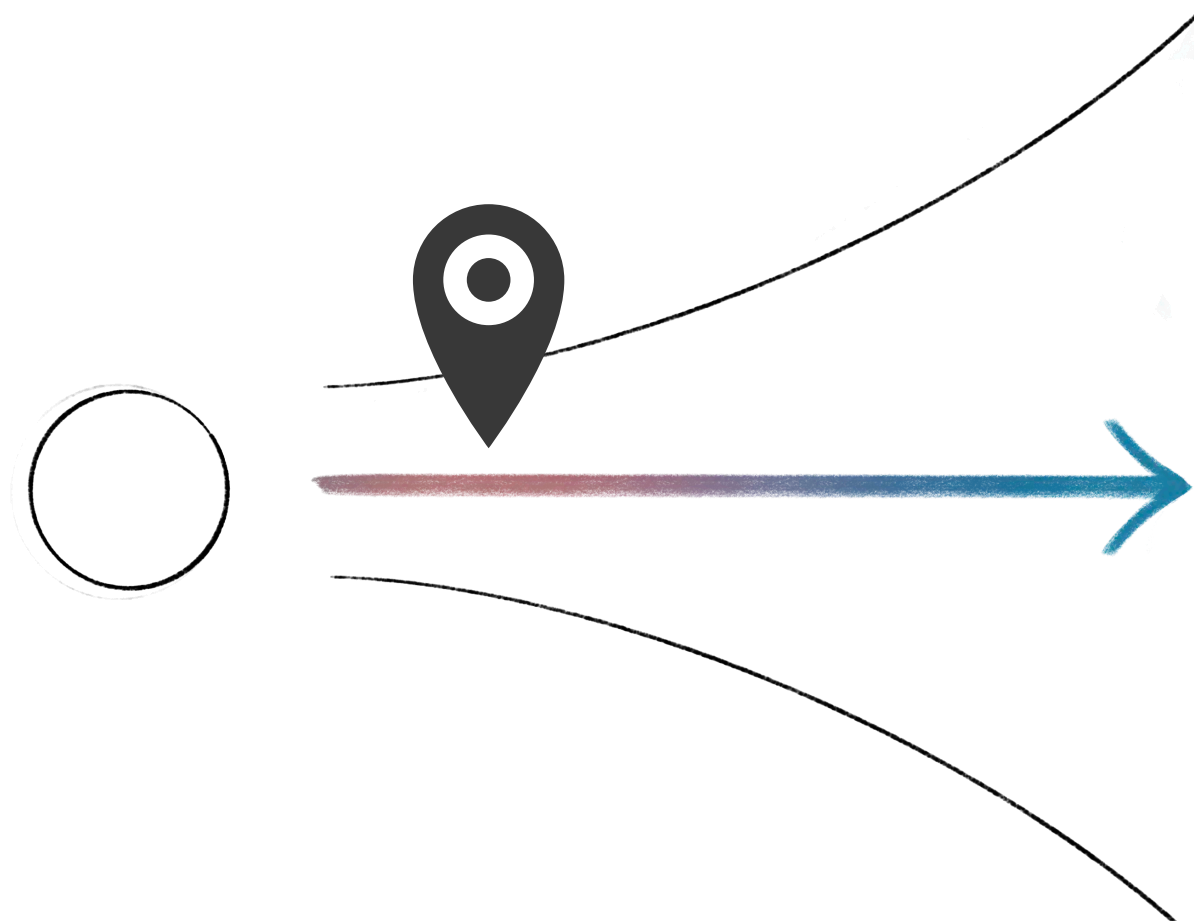


# Form ices on an infrared (IR) inactive substrate



GROW ICES ON AN ISOLATED SUBSTRATE

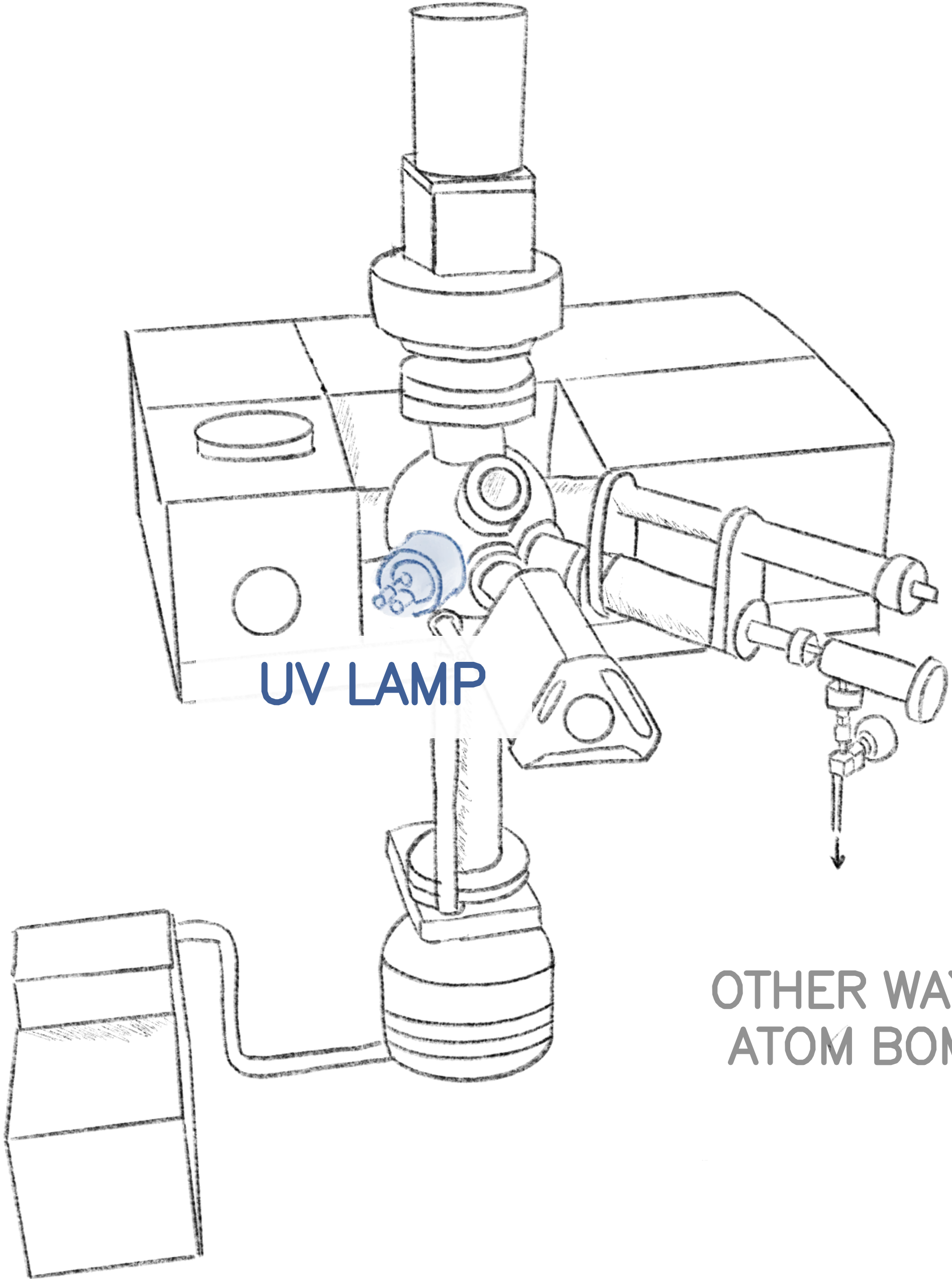
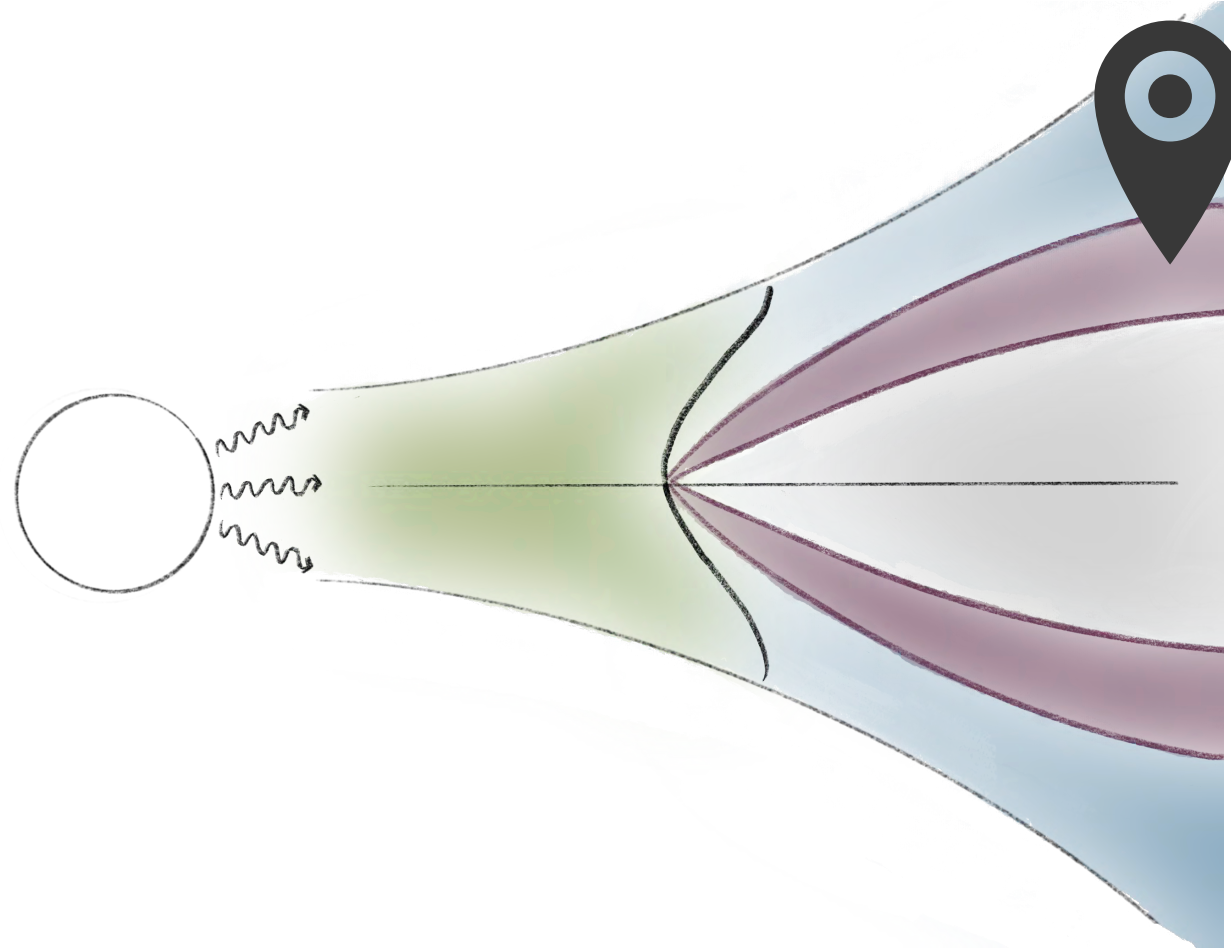
# We can process the ice thermally



**HEATER THAT CONTROLS  
SUBSTRATE TEMPERATURE**

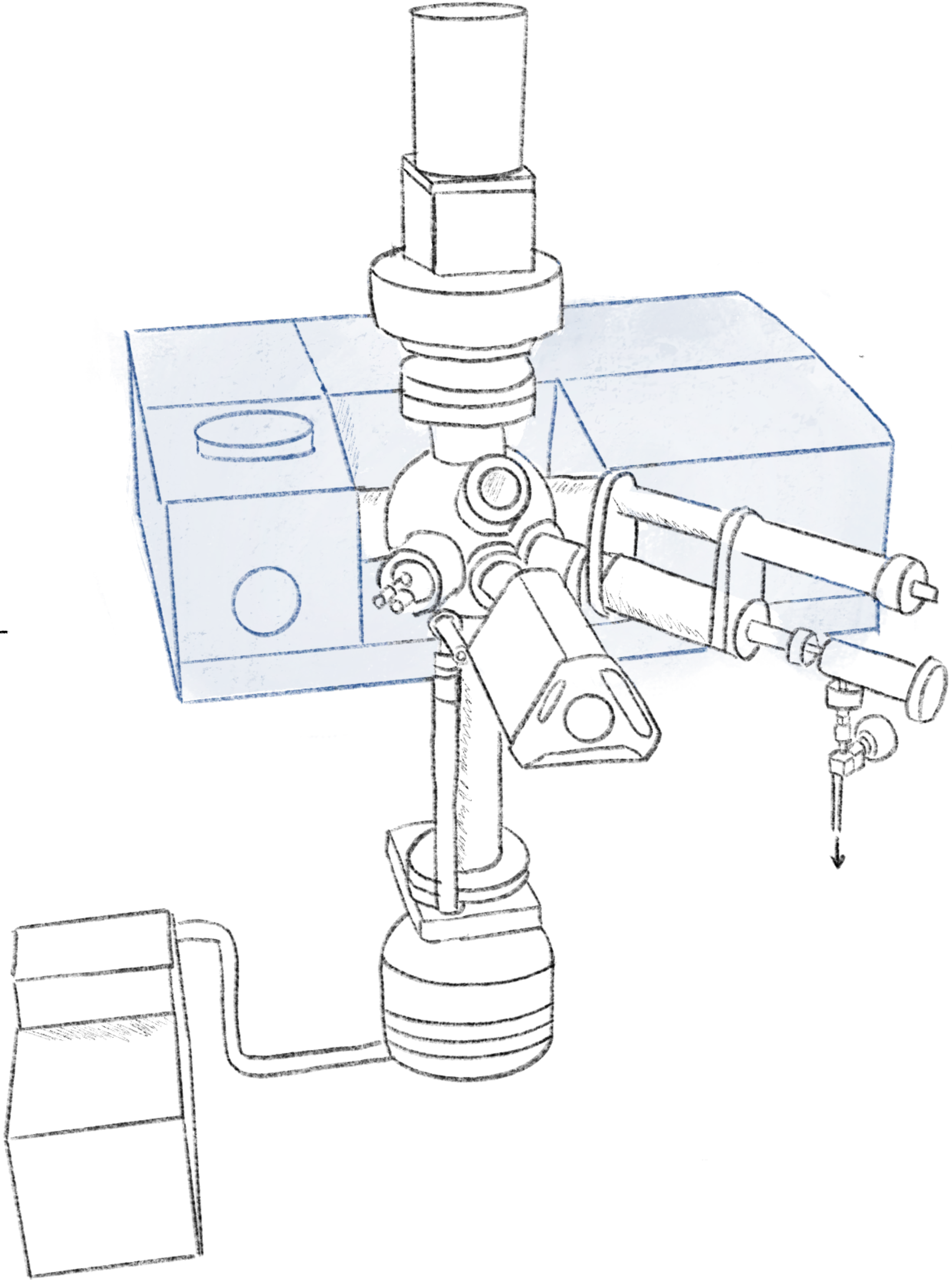
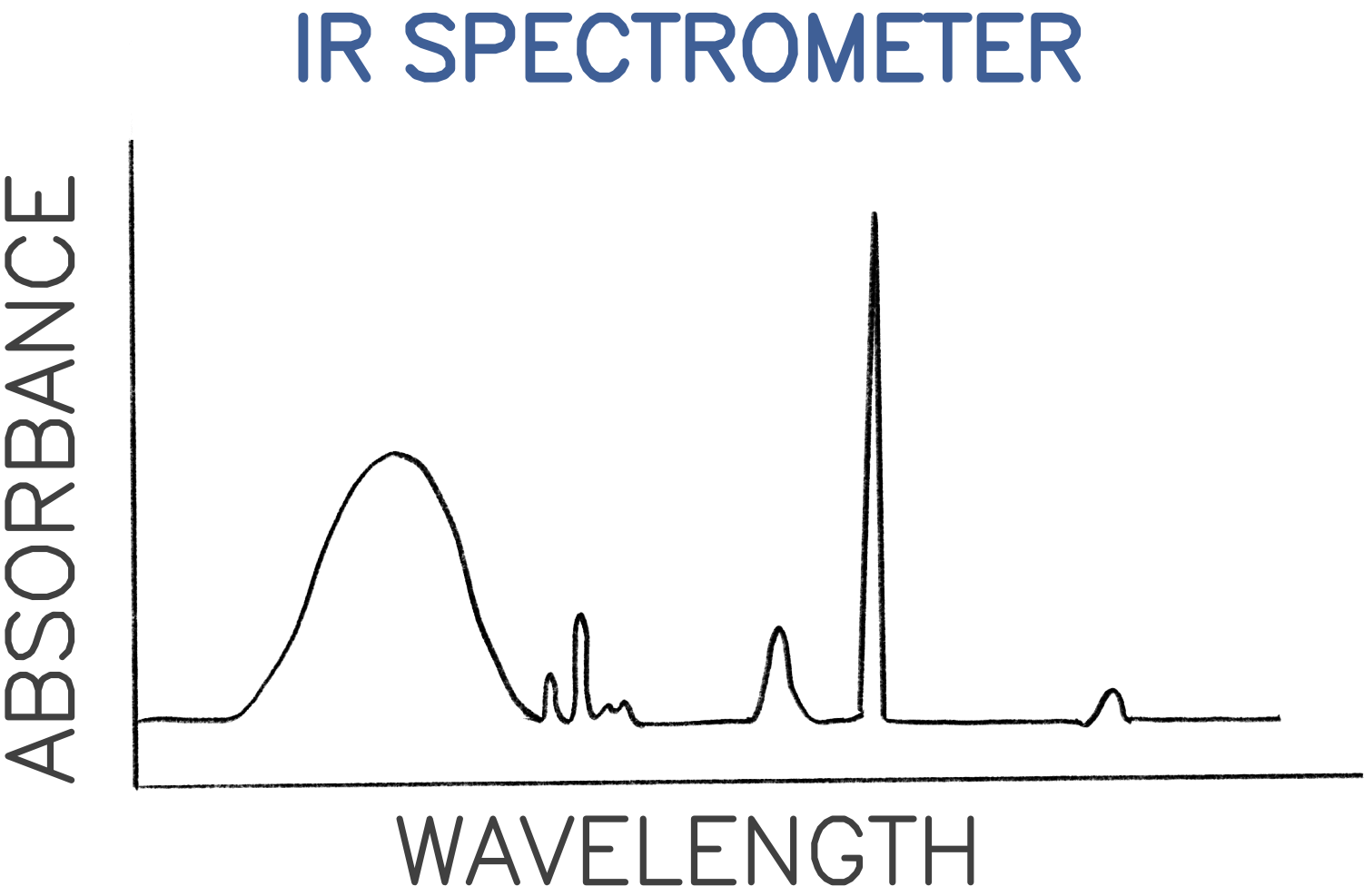


# We can also process the ice via irradiation



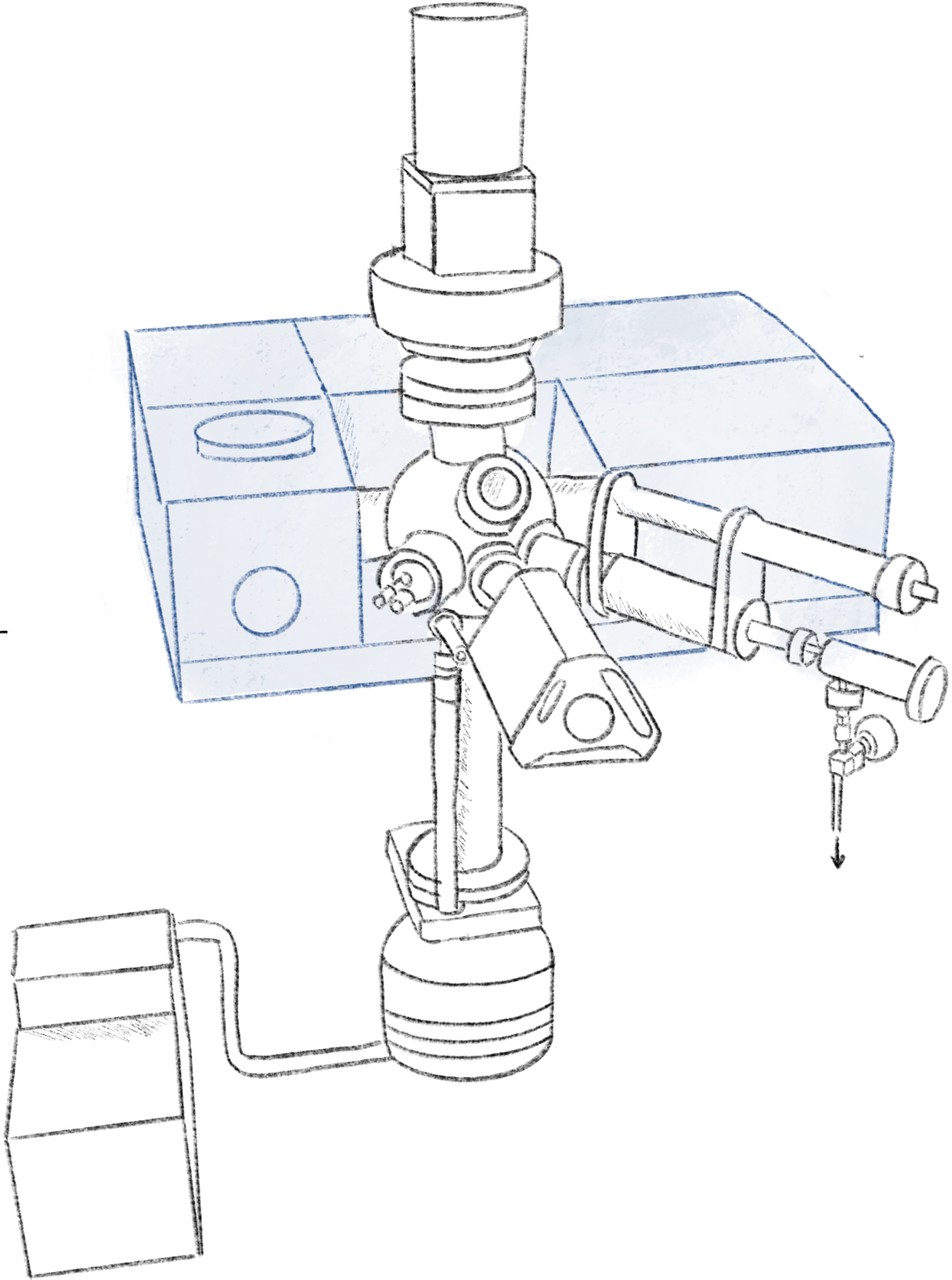
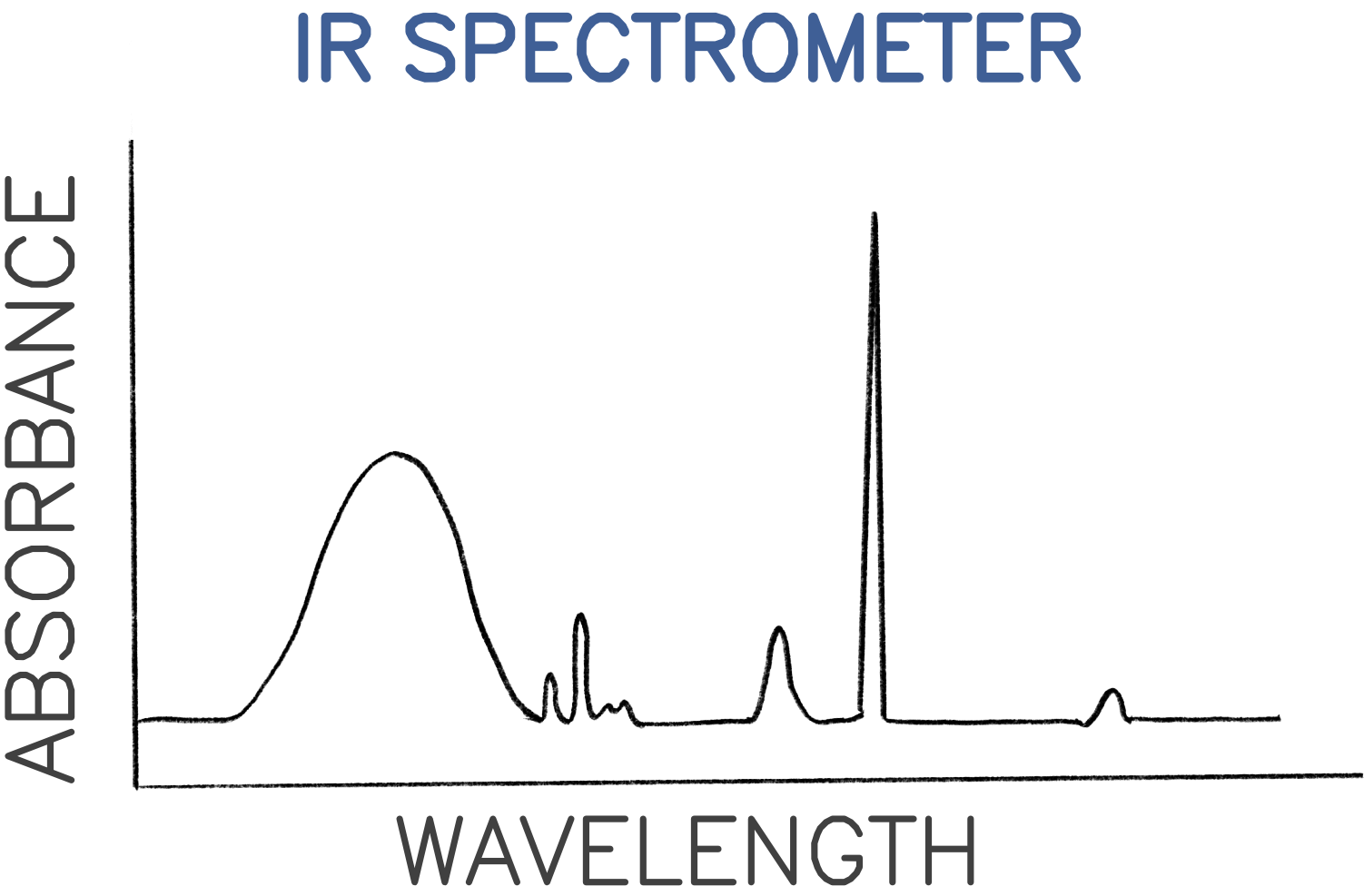
OTHER WAYS INCLUDE ELECTRON OR ATOM BOMBARDMENT AND LASERS.

# Data product 1: IR spectra → characterize ice phase



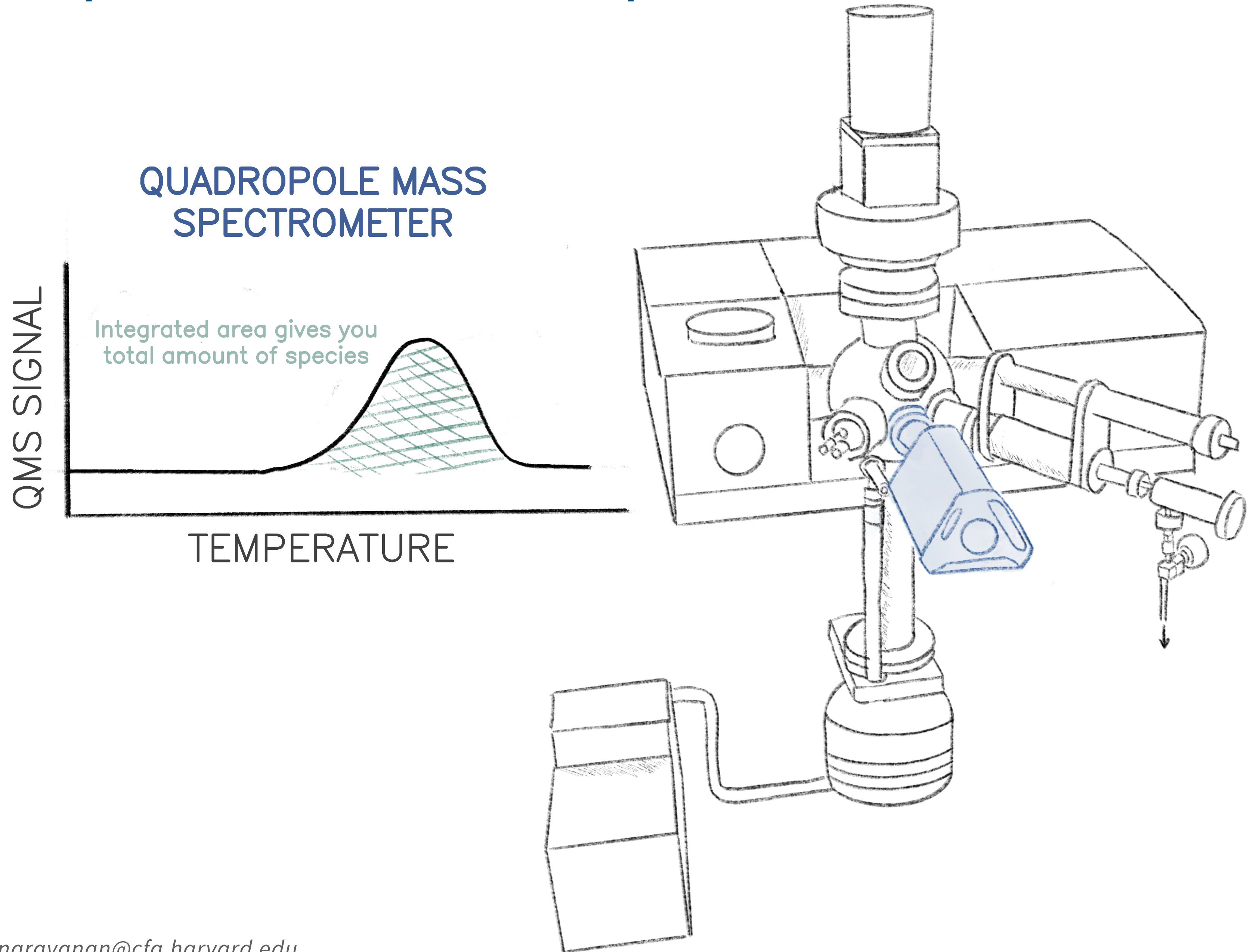


# Data product 1: IR spectra → characterize ice phase



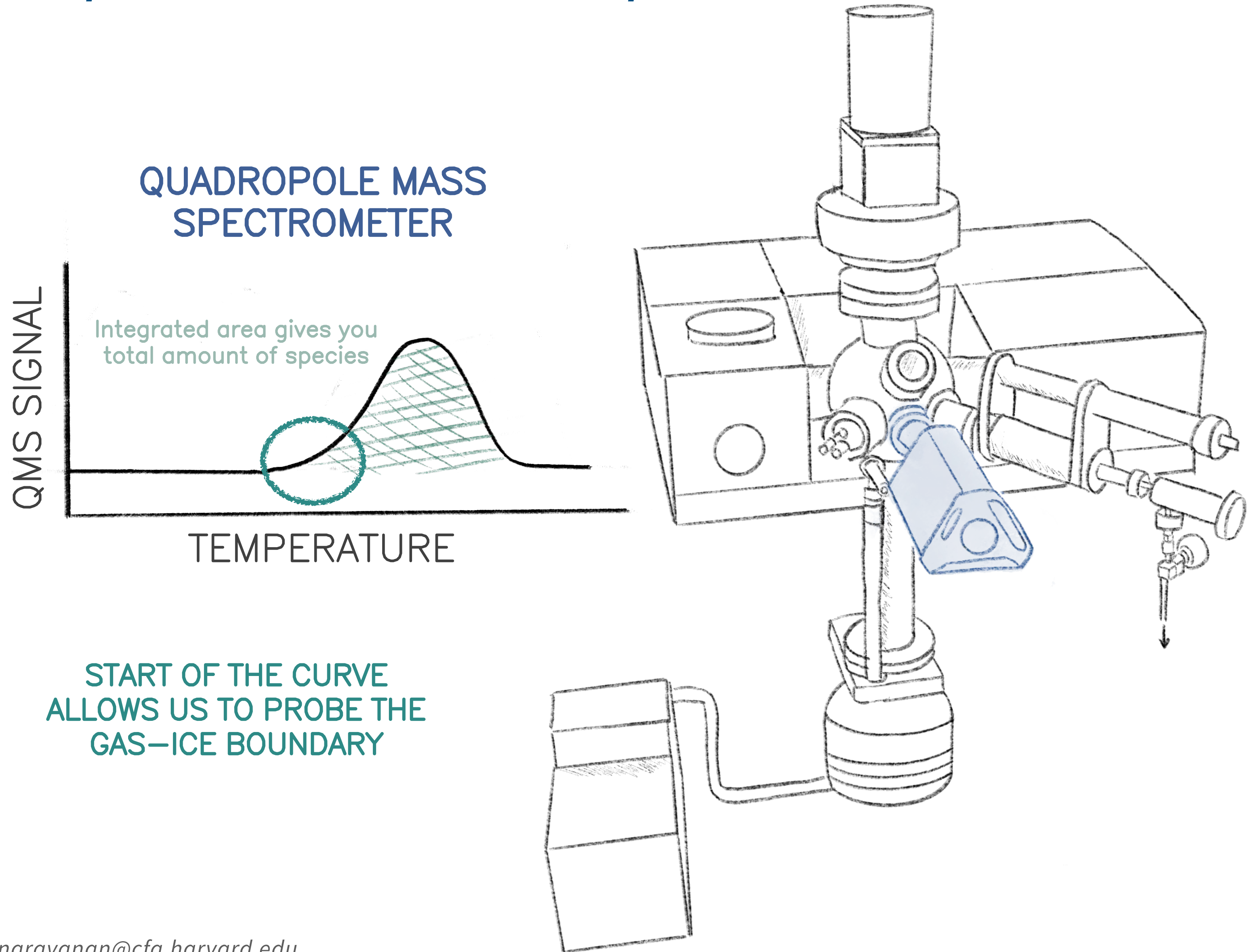
CAN COMPARE LAB + JWST SPECTRA TO UNDERSTAND ICE COMPOSITION  
(see Berger+ 2024)

# Data product 2: mass spectra → characterize gas phase



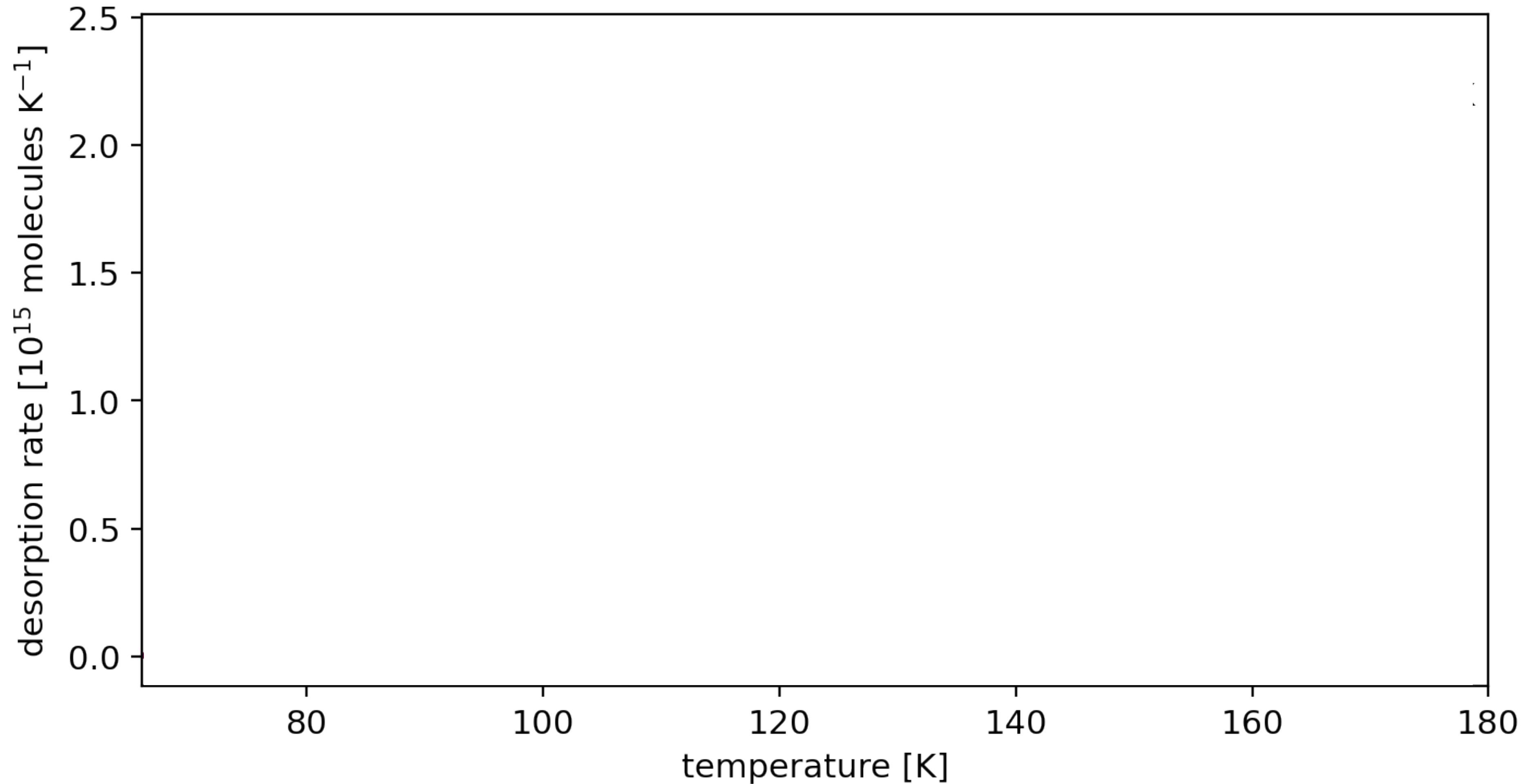


# Data product 2: mass spectra → characterize gas phase



# Temperature programmed desorption (TPD) curves

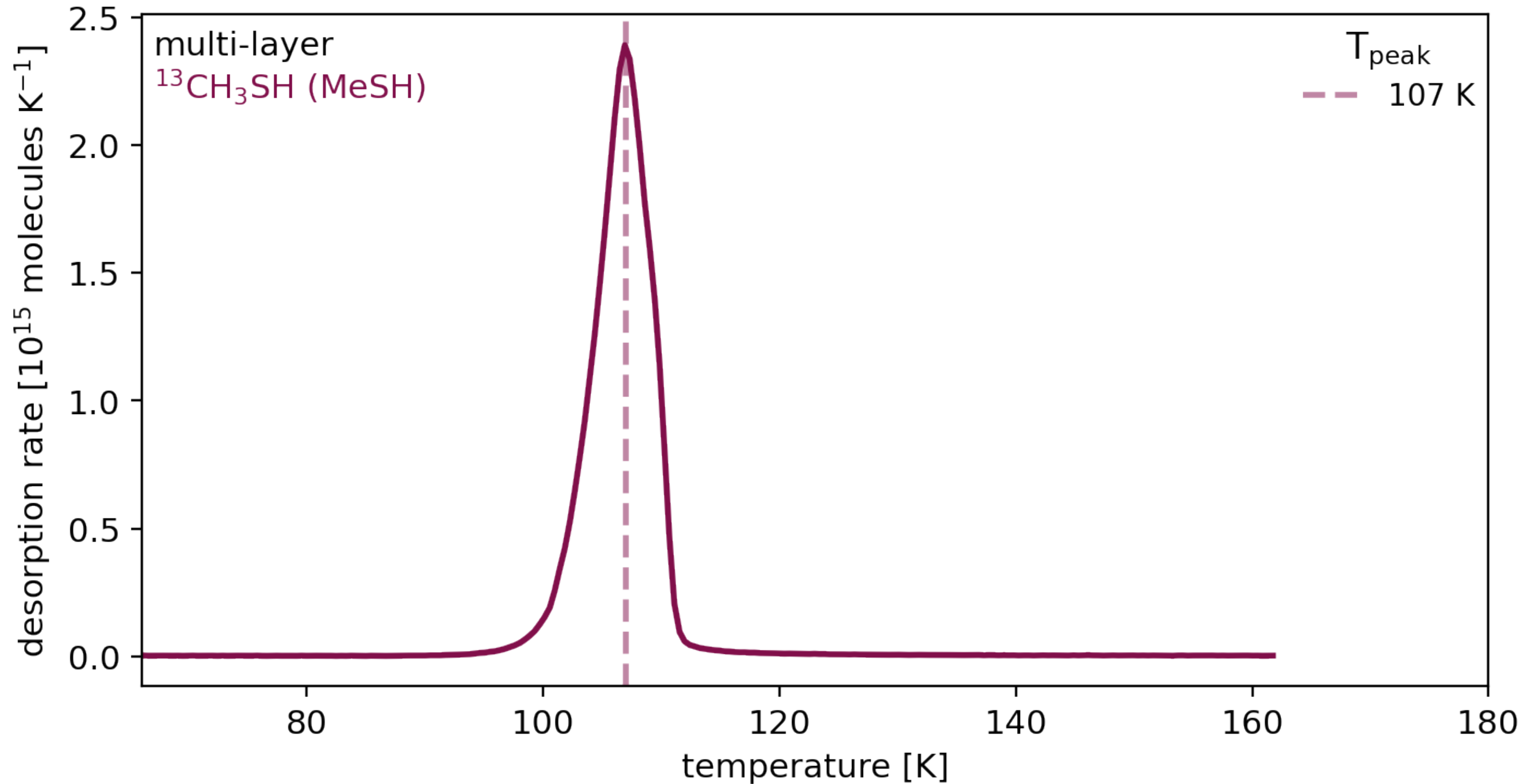
What temperature would  $\text{CH}_3\text{SH}$  desorb off of grains  $\rightarrow$  can predict snow line location





# Temperature programmed desorption (TPD) curves

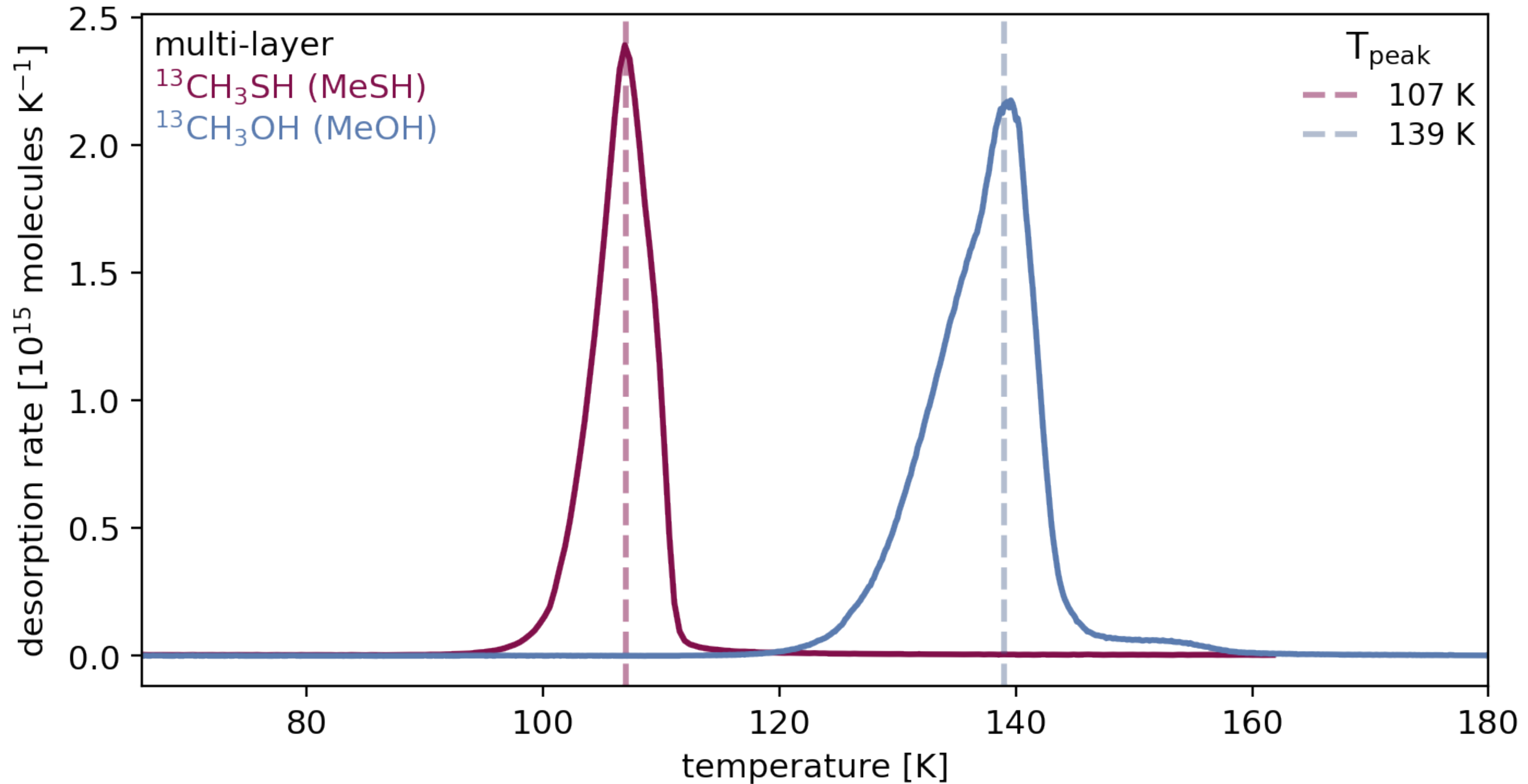
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All results are from Narayanan+, ApJ, in review

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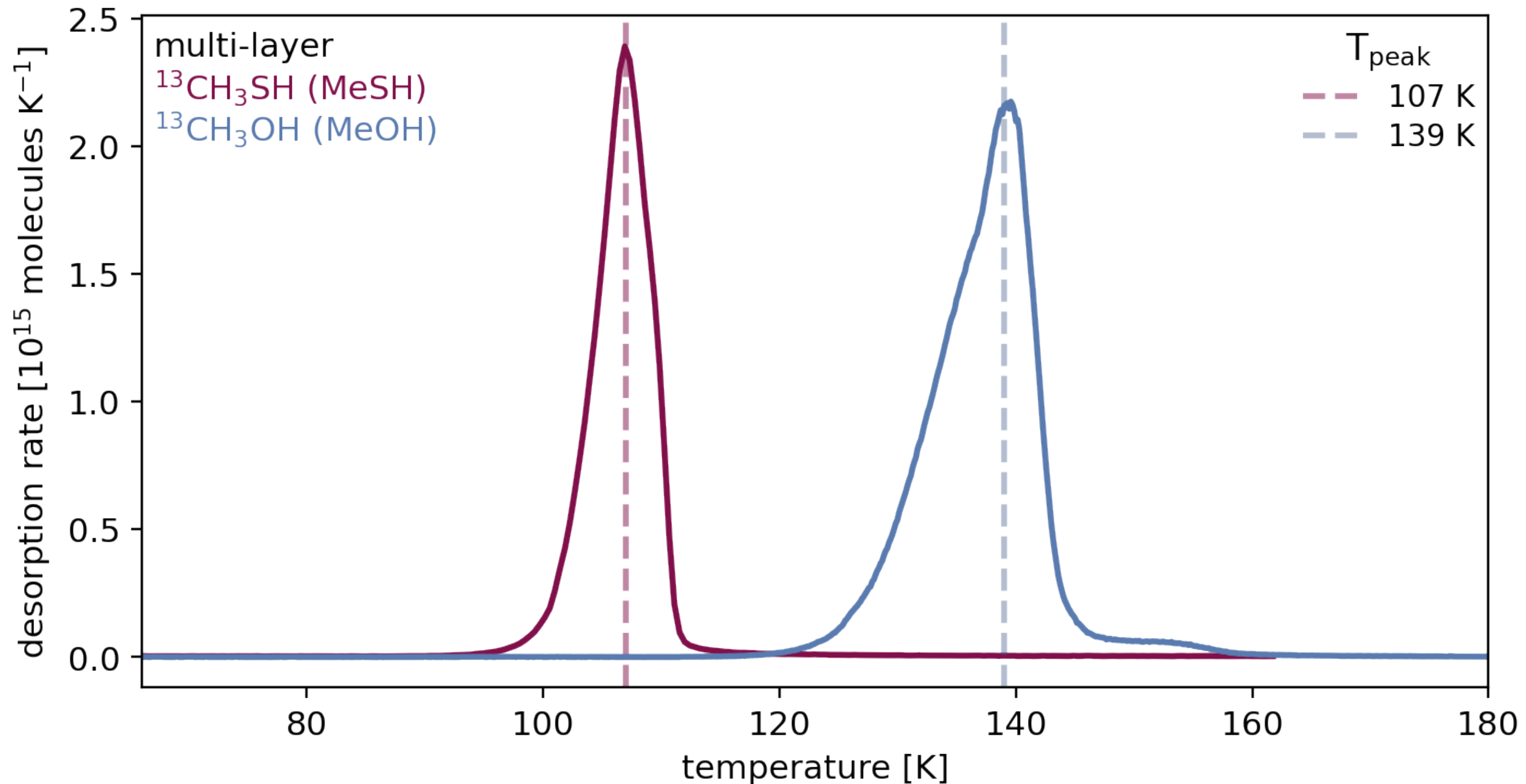


All results are from Narayanan+, ApJ, in review



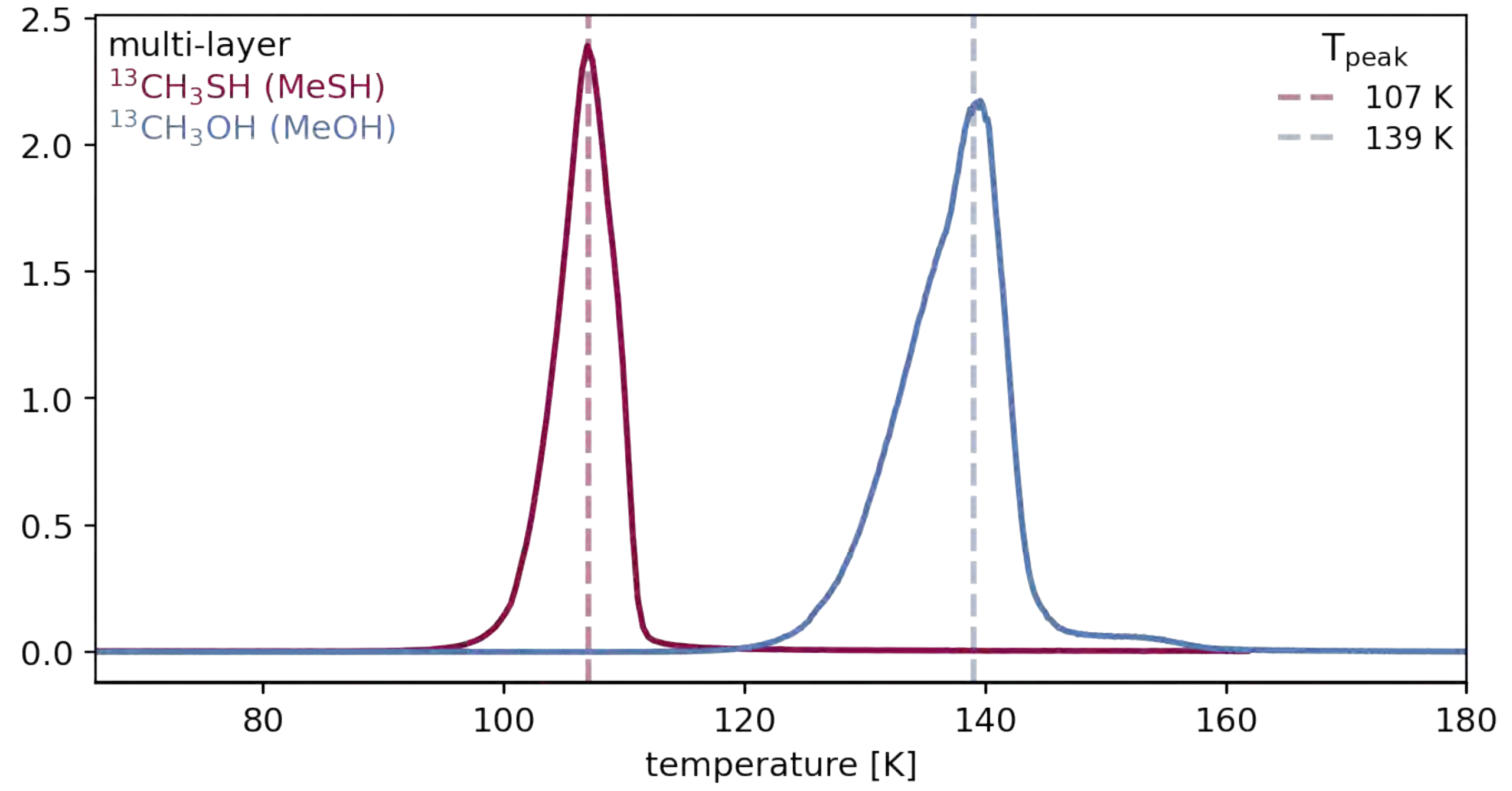
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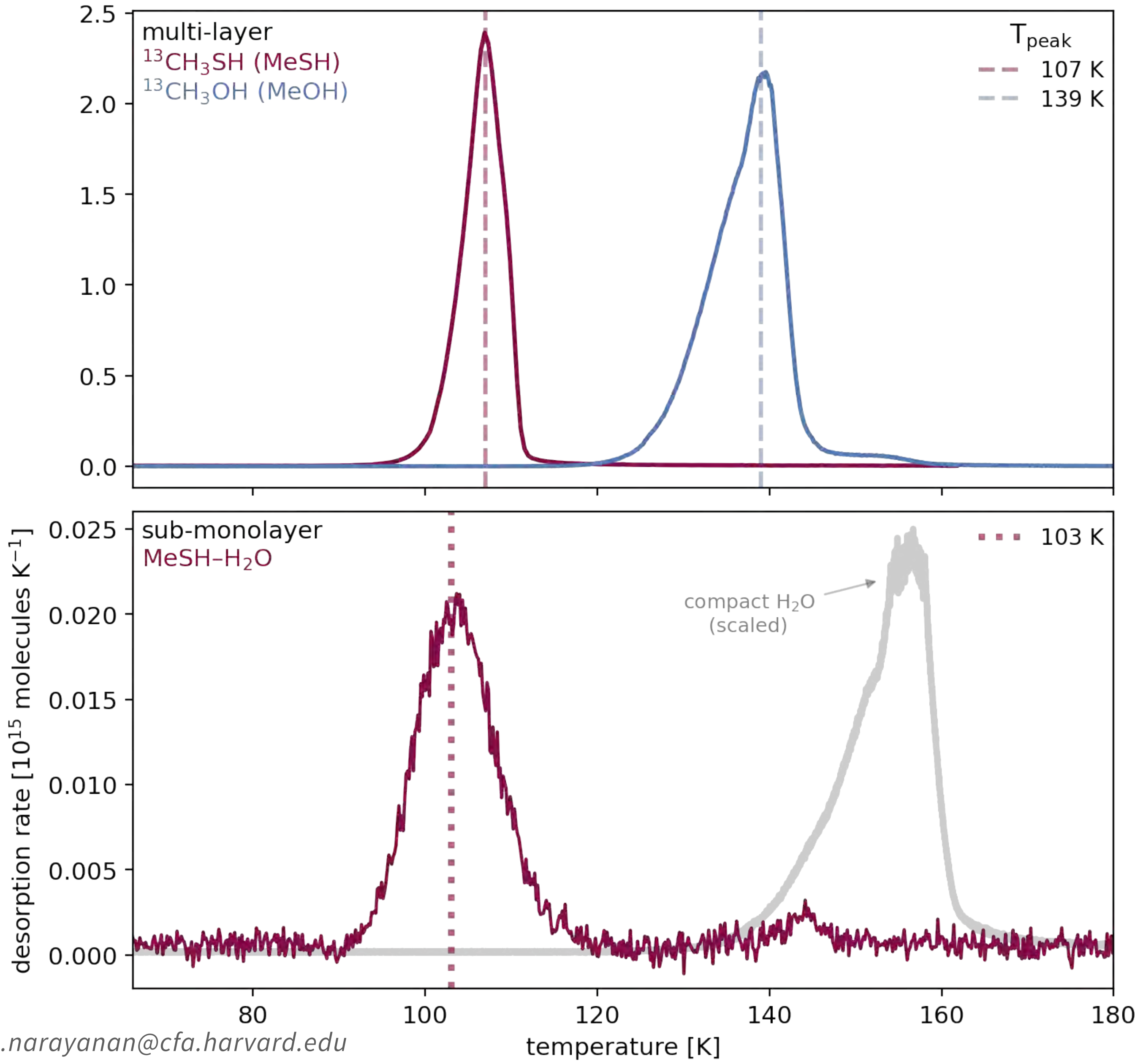
$\Rightarrow$   $\text{CH}_3\text{SH}$  is more volatile than  $\text{CH}_3\text{OH}$  because it desorbs at a lower temperature

# Pure vs. layered thermal desorption

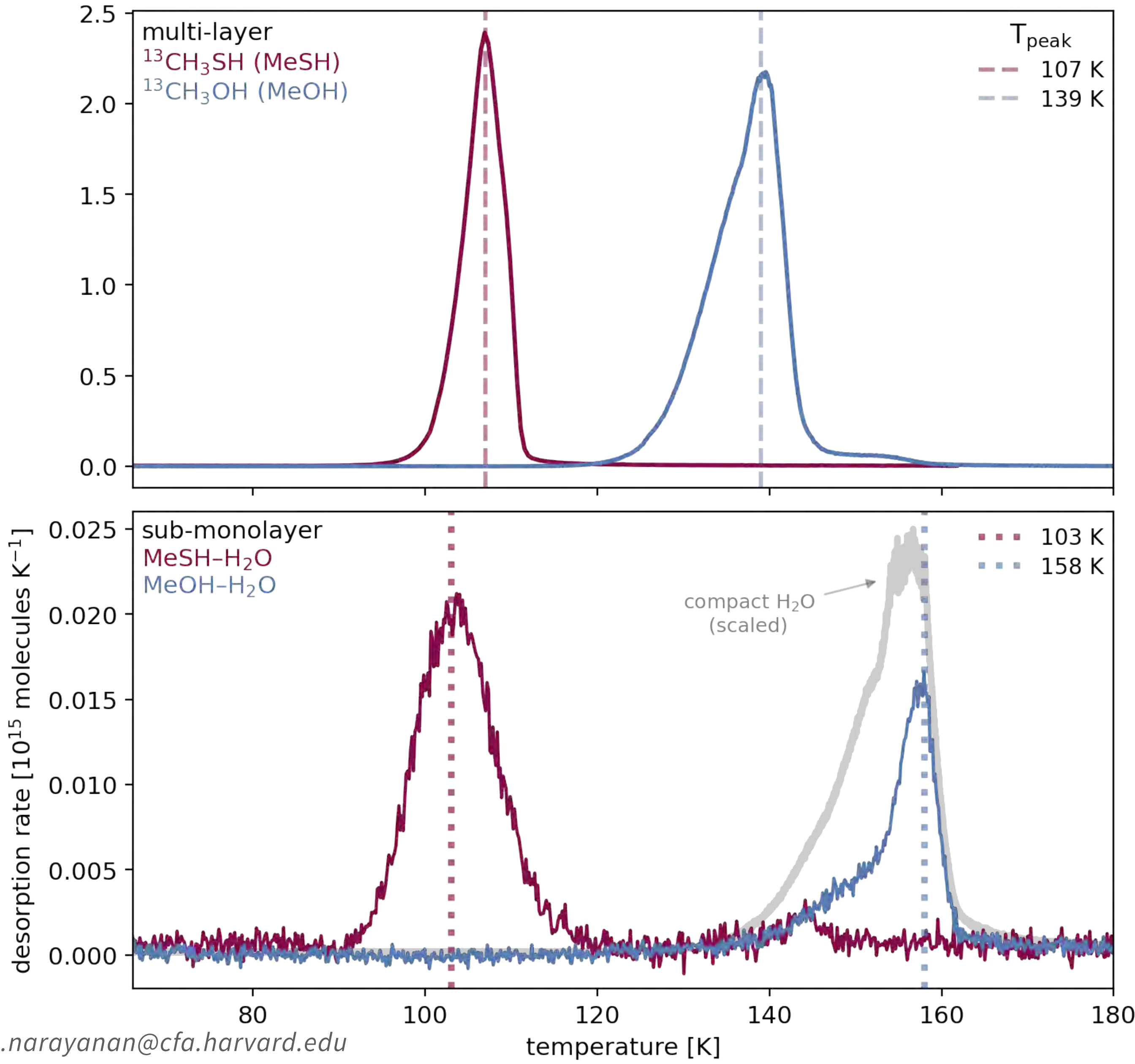




# Pure vs. layered thermal desorption

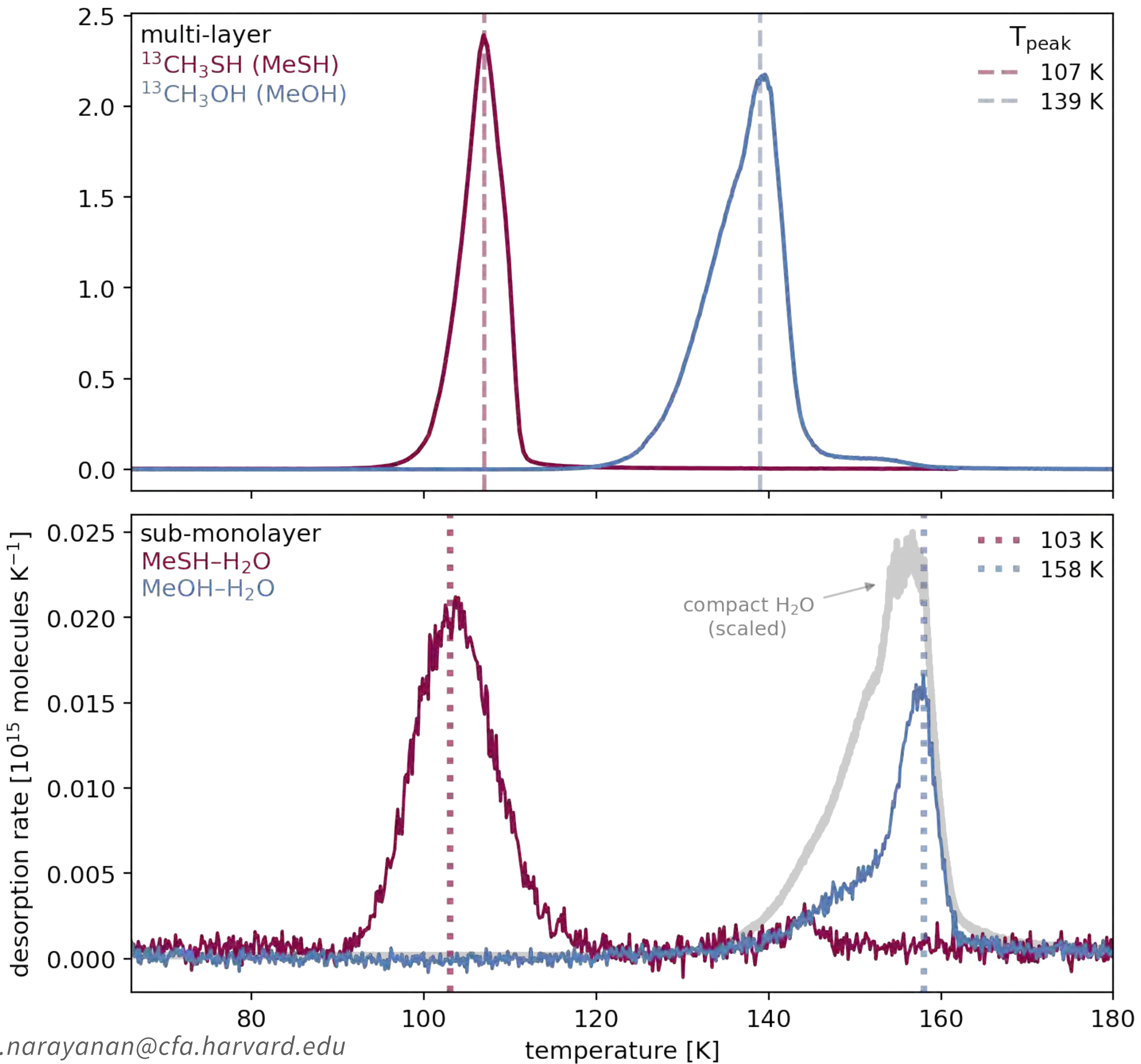


# Pure vs. layered thermal desorption



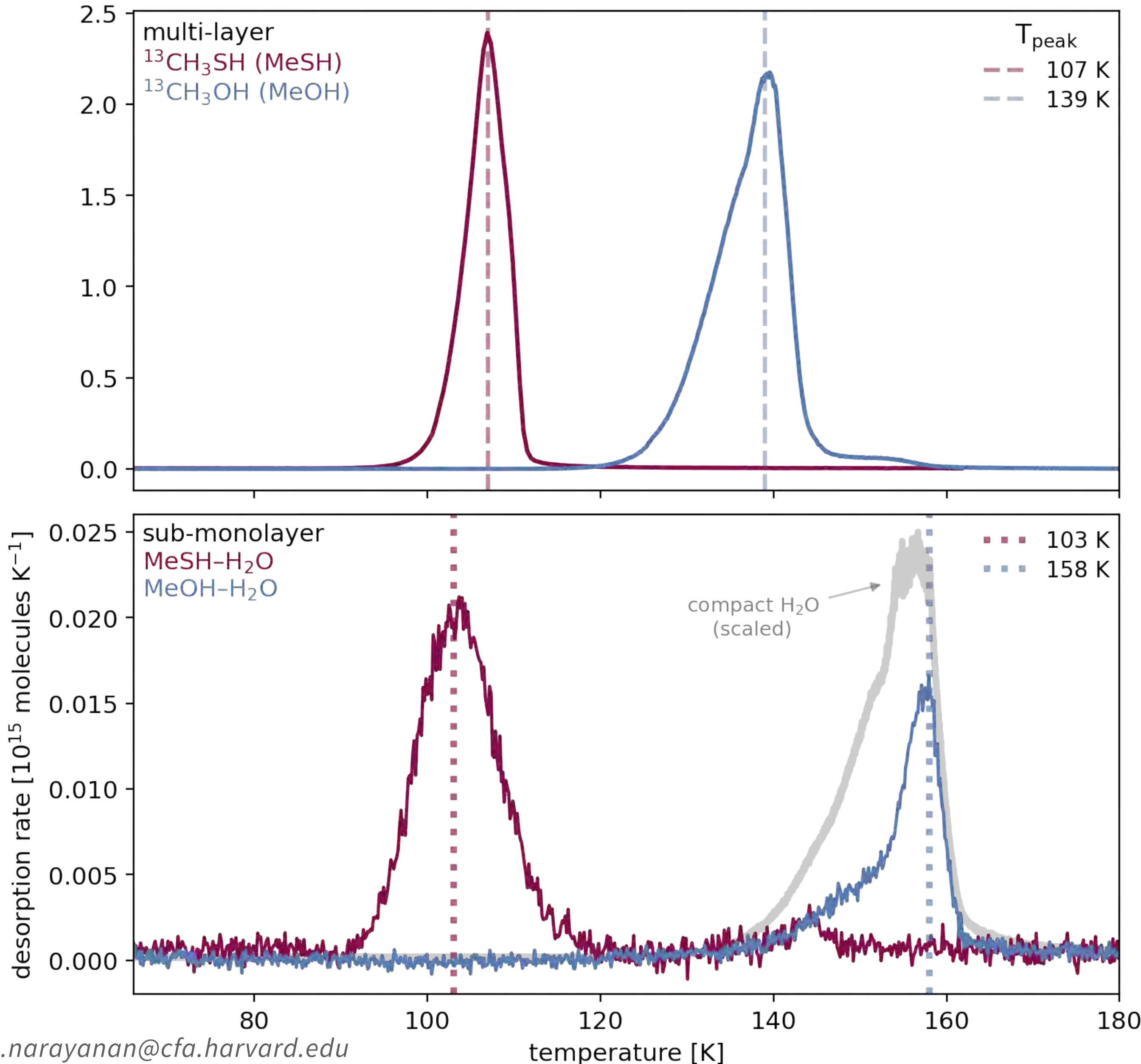


# Pure vs. layered thermal desorption



⇒ CH<sub>3</sub>SH is indifferent to whether it binds to itself or to water; CH<sub>3</sub>OH interacts with water significantly

# Pure vs. layered thermal desorption



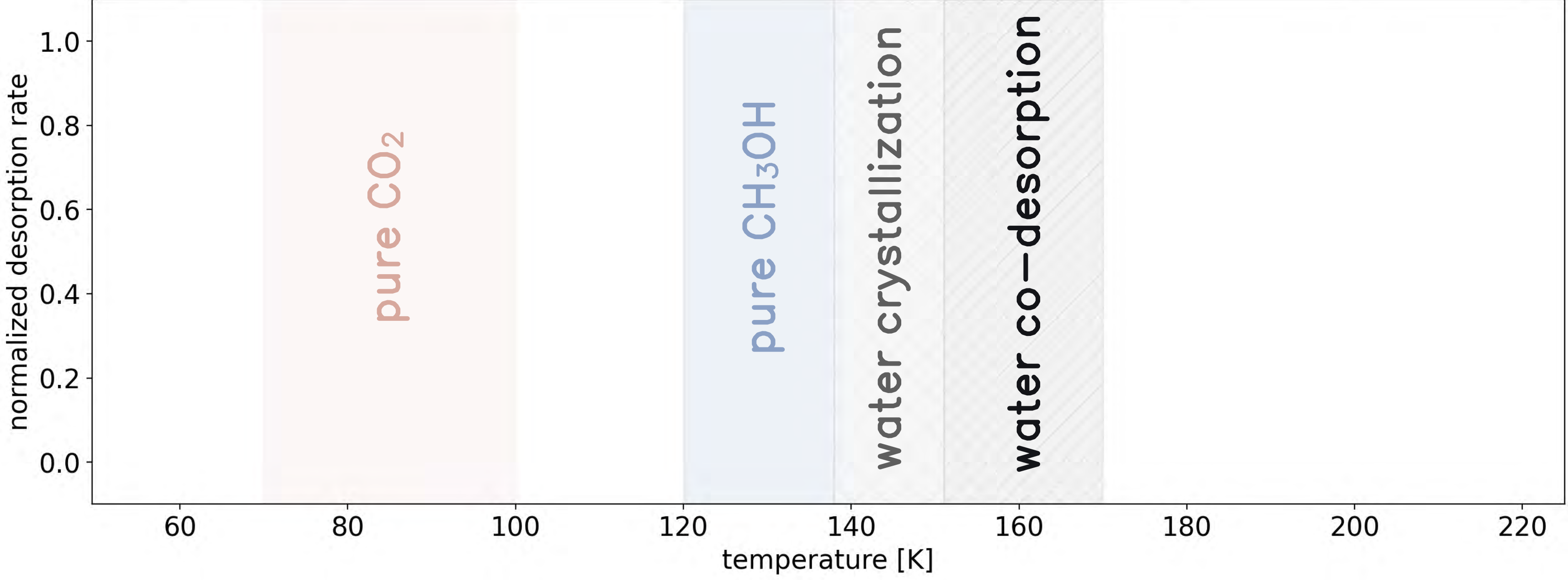
⇒  $\text{CH}_3\text{SH}$  is indifferent to whether it binds to itself or to water;  $\text{CH}_3\text{OH}$  interacts with water significantly

We can infer that  $\text{CH}_3\text{SH}$  snow line would be further out than  $\text{CH}_3\text{OH}$ 's

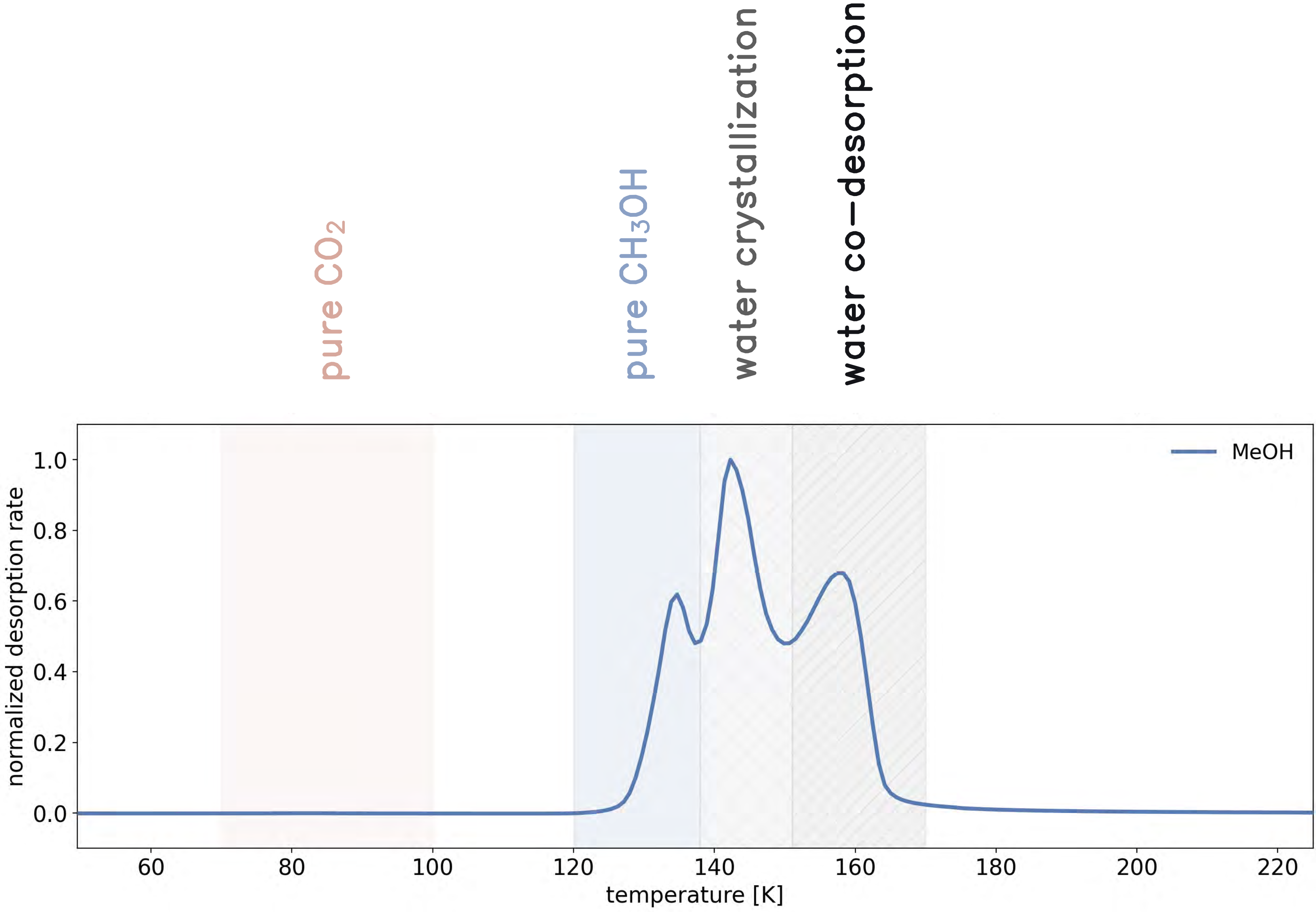
(computed this quantitatively... can chat later)



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

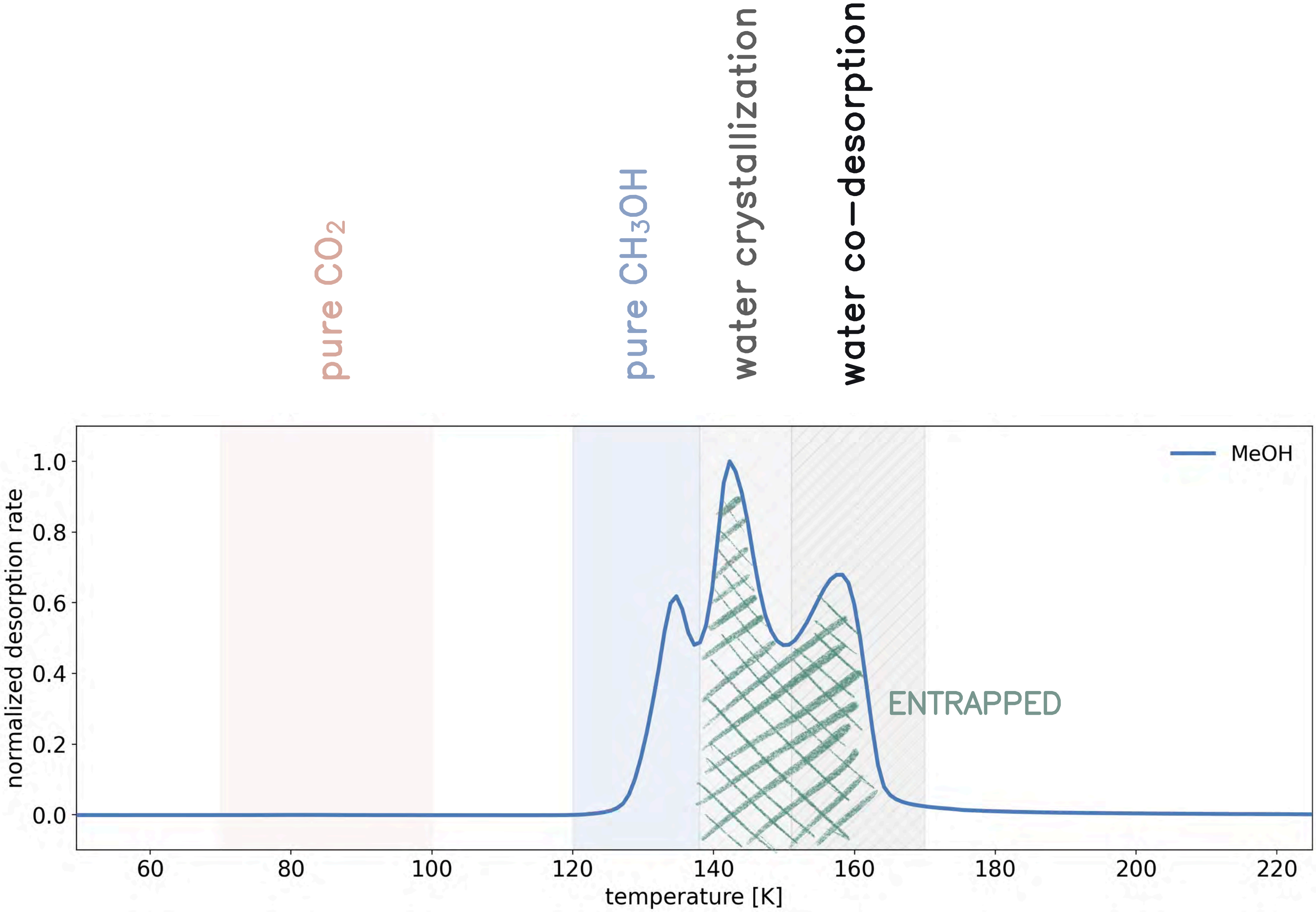


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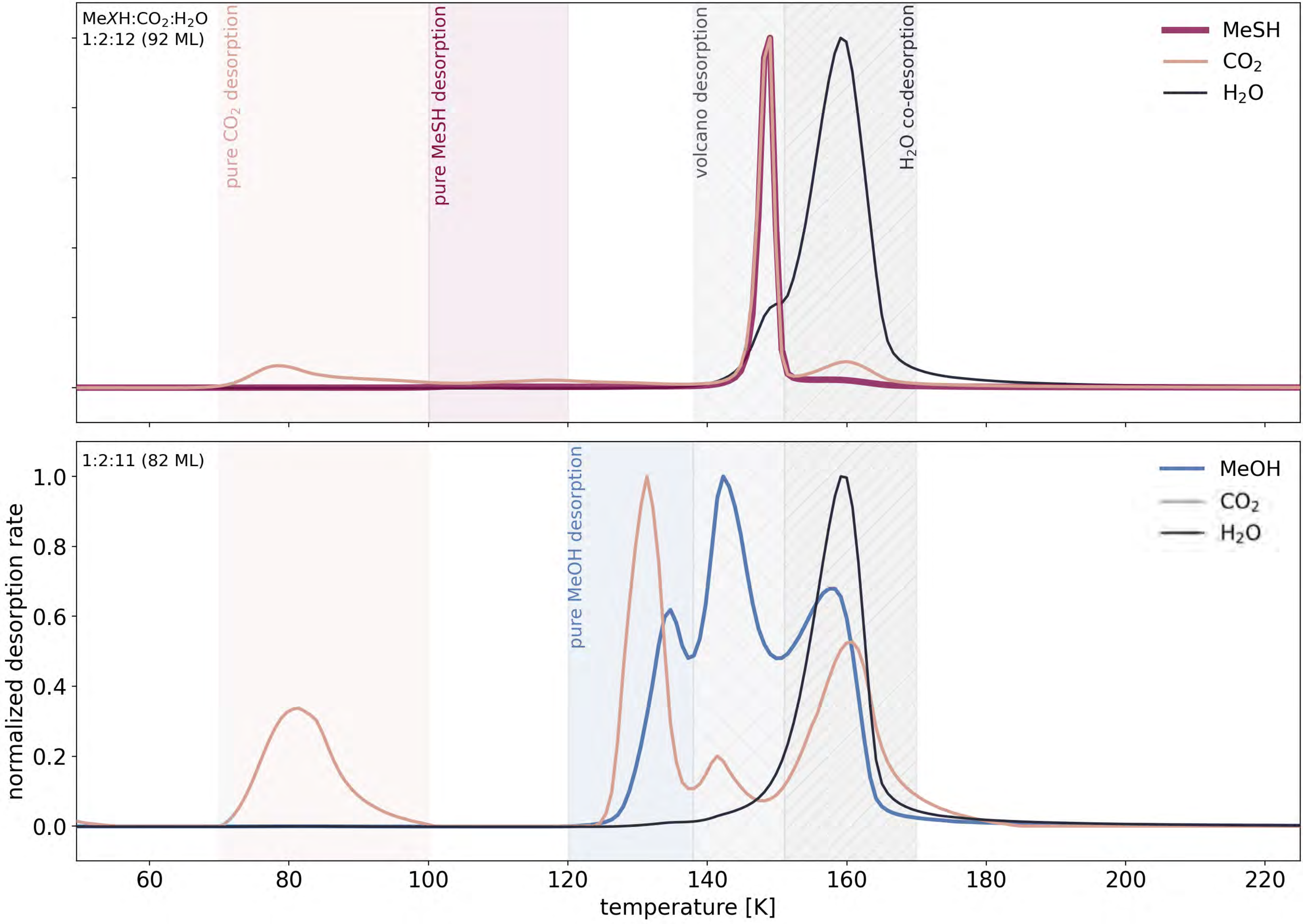




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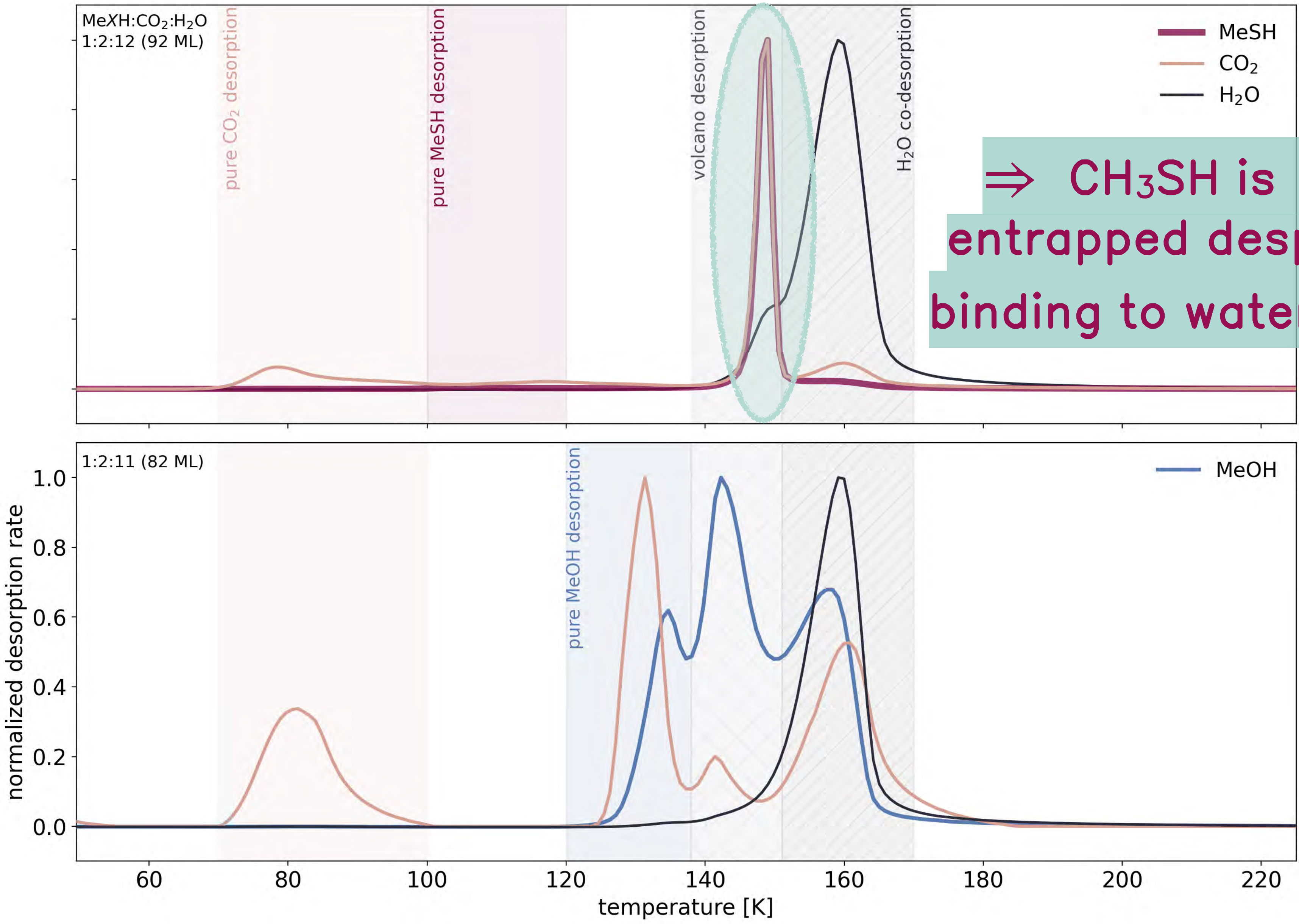


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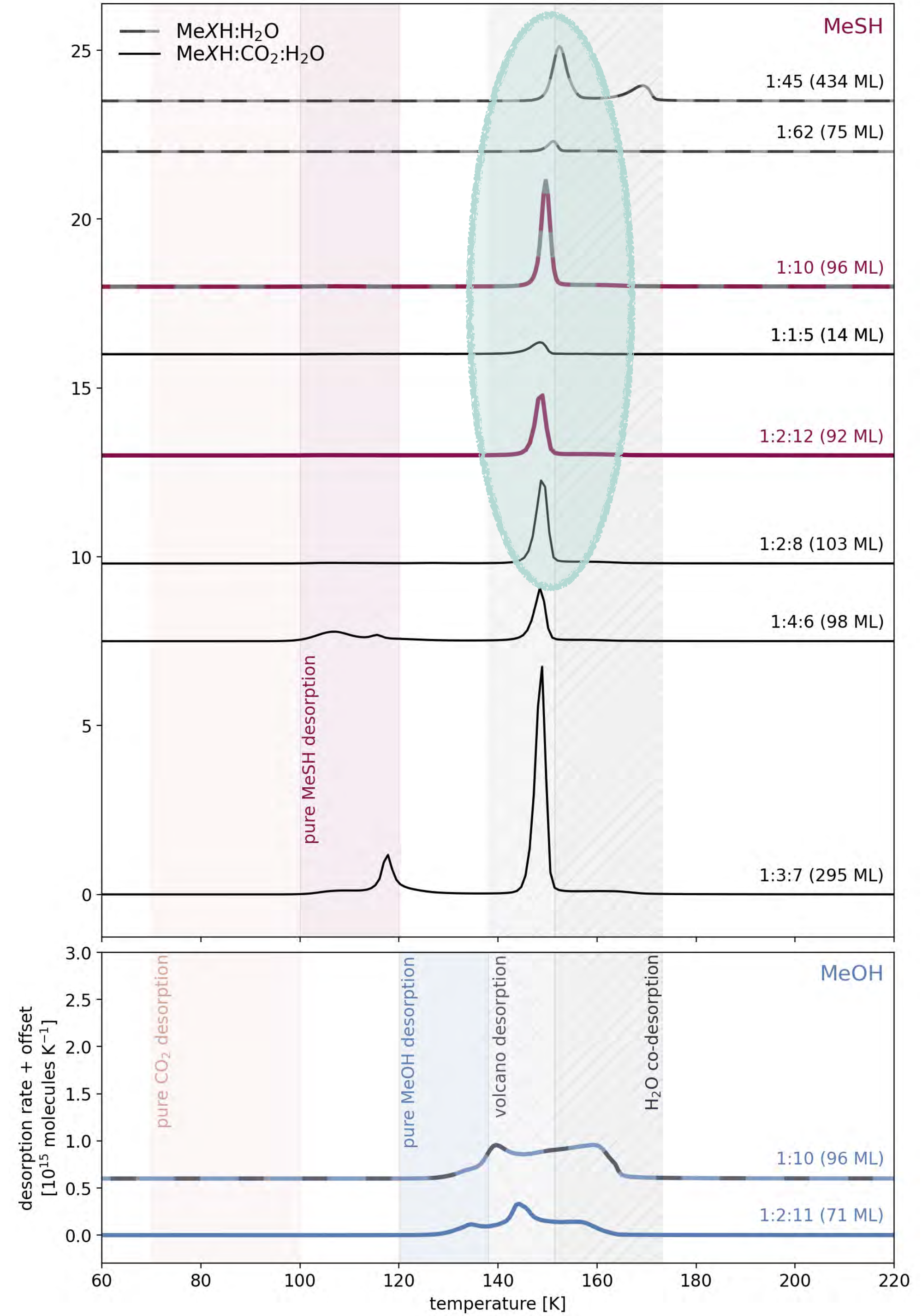
# Entrapment in realistic 3-component ices ( $CH_3XH:CO_2:H_2O$ )



⇒ CH<sub>3</sub>SH is 100% entrapped despite not binding to water...why?



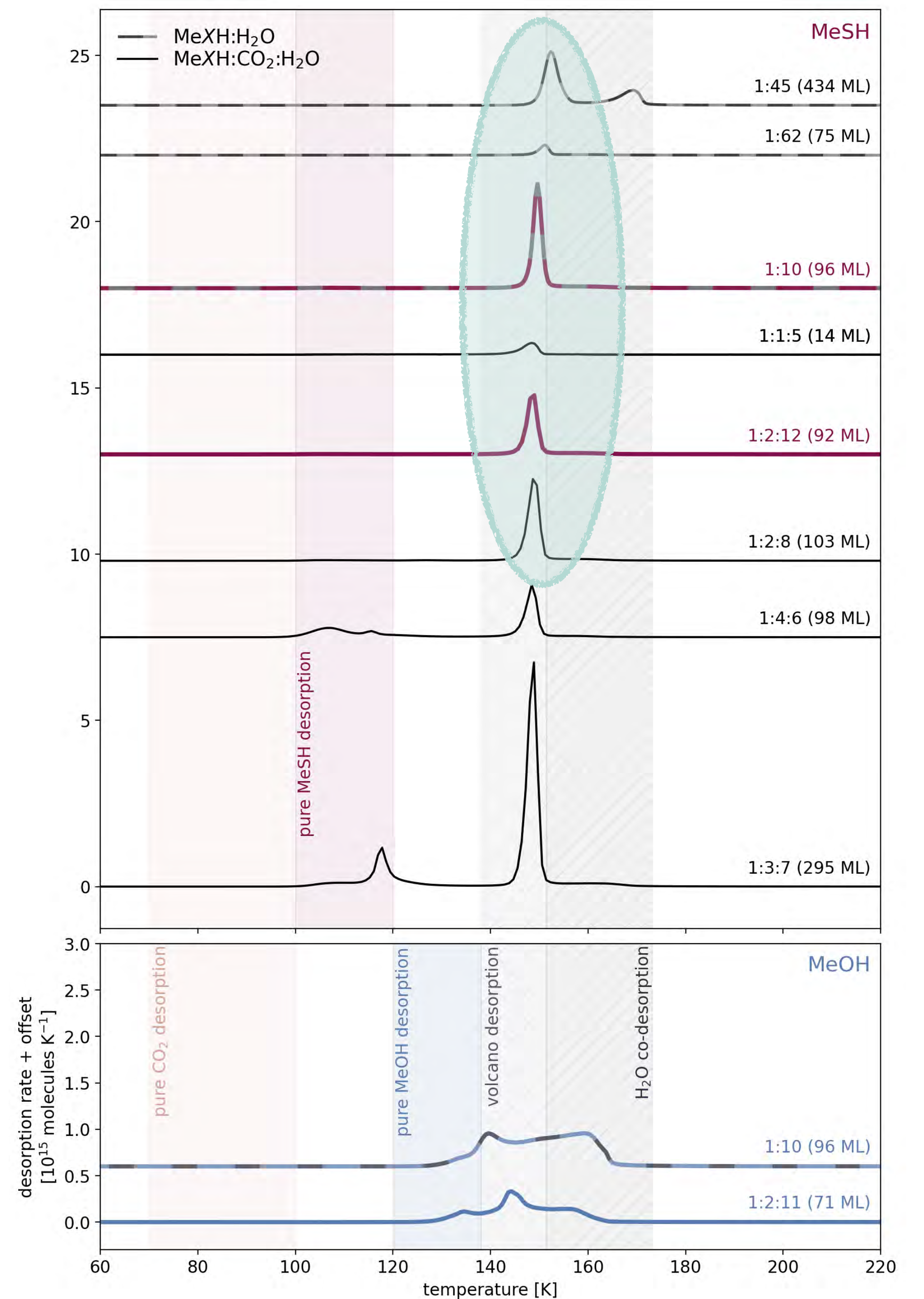
*In all entrapment experiments that were not CH<sub>3</sub>SH-rich we see 100% entrapment that has never been seen before.*





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⇒ CH<sub>3</sub>SH's size inhibits its ability to diffuse through the water matrix.



*The difference between  $CH_3SH$  and  $CH_3OH$  is only ~15%*

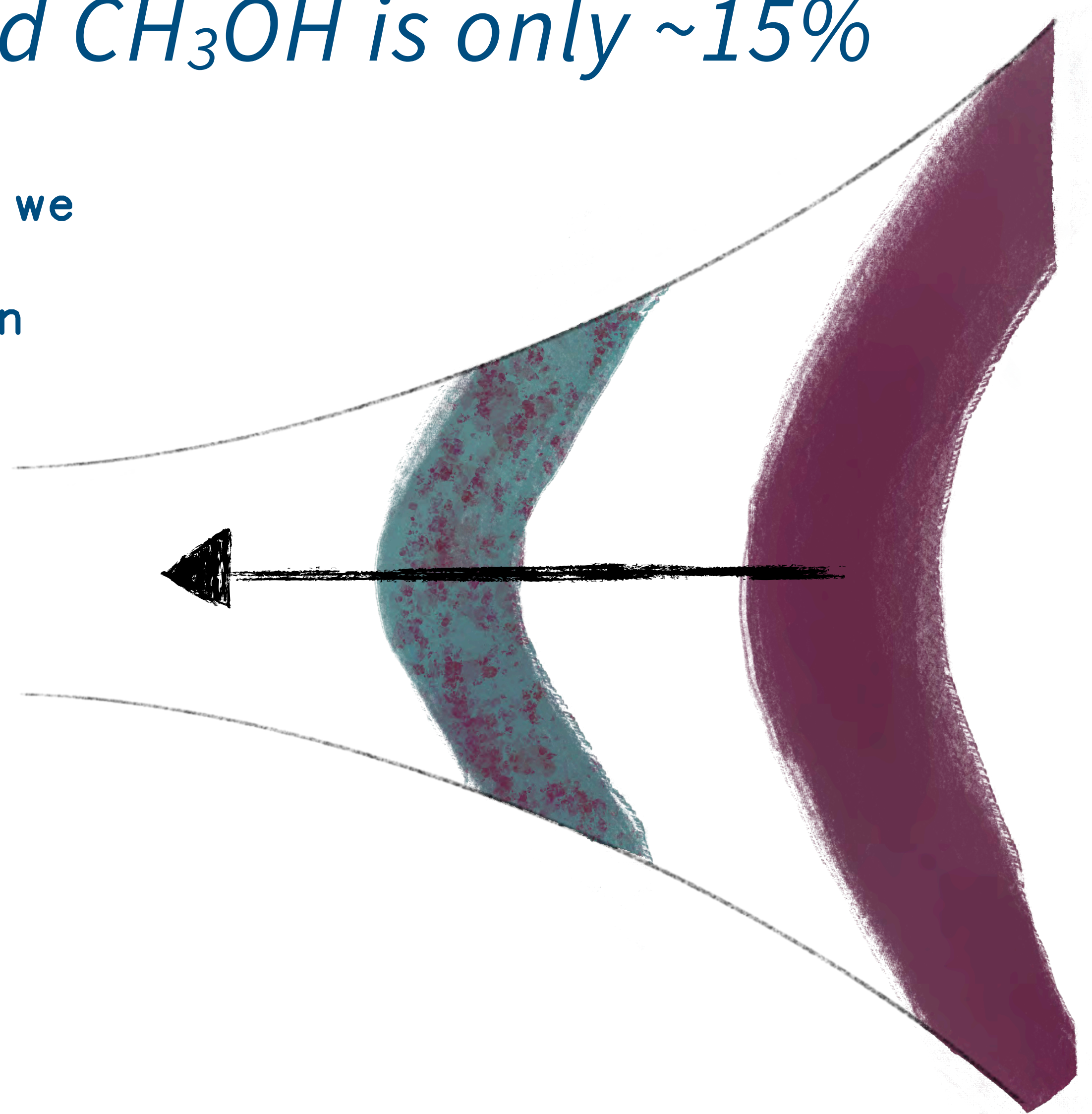
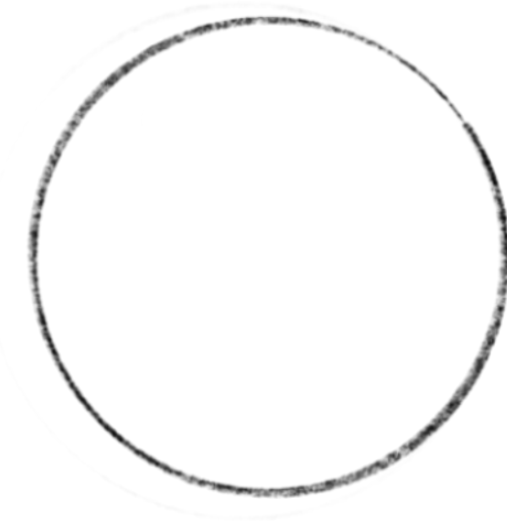


*The difference between  $CH_3SH$  and  $CH_3OH$  is only ~15%*

If prebiotic molecules larger than  $CH_3SH$  form with water, we would expect it to be available at very high concentrations at the water snow line where planets can overcome the meter-sized barrier

# The difference between $CH_3SH$ and $CH_3OH$ is only $\sim 15\%$

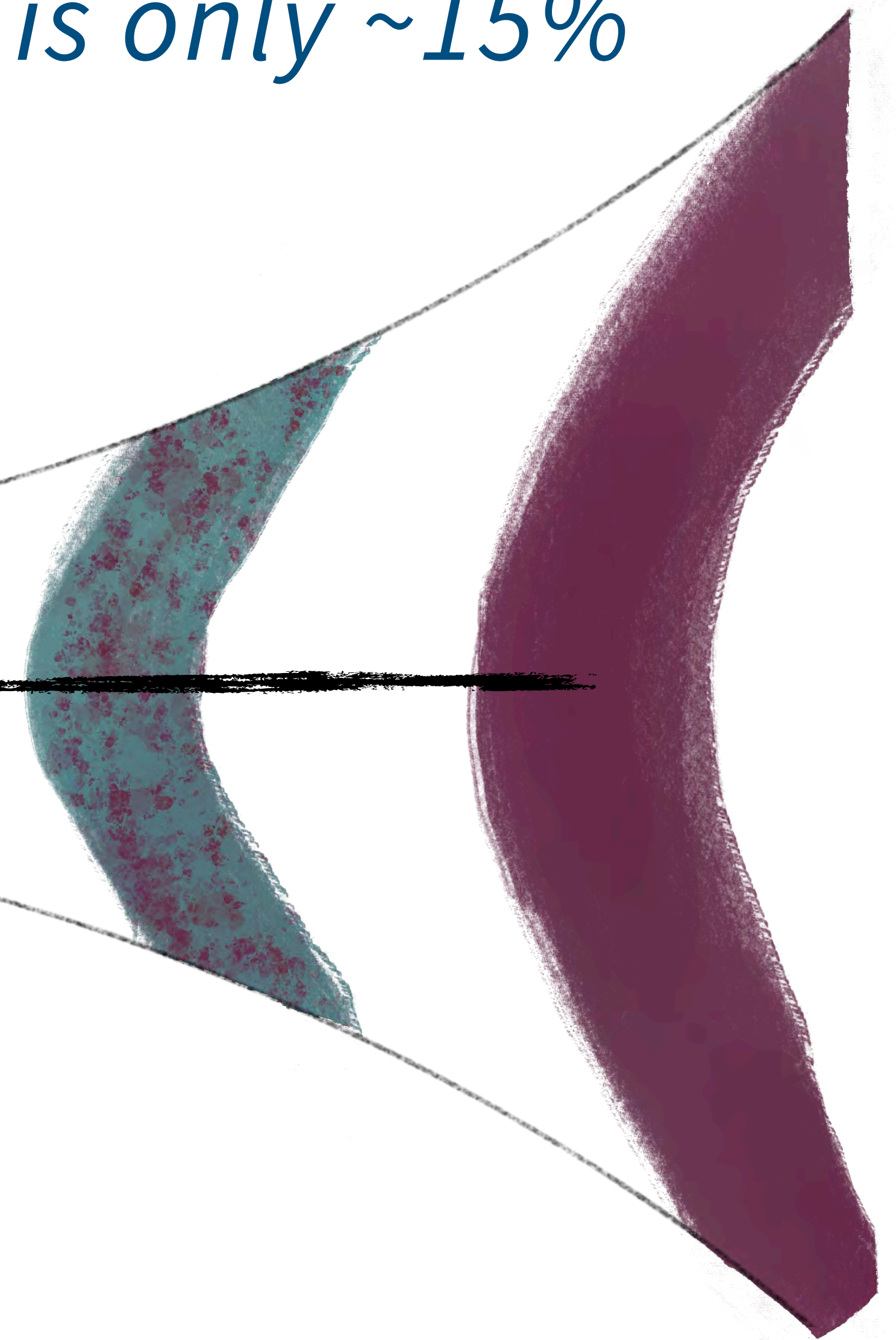
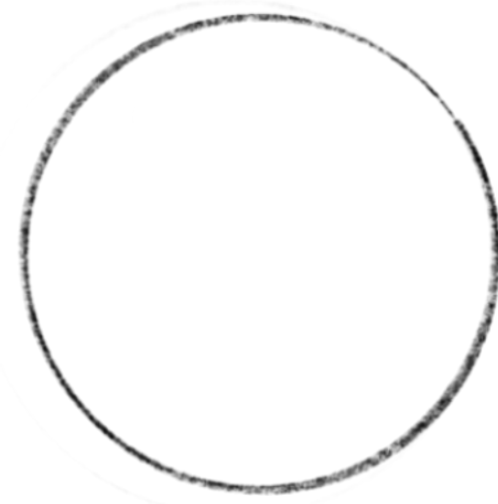
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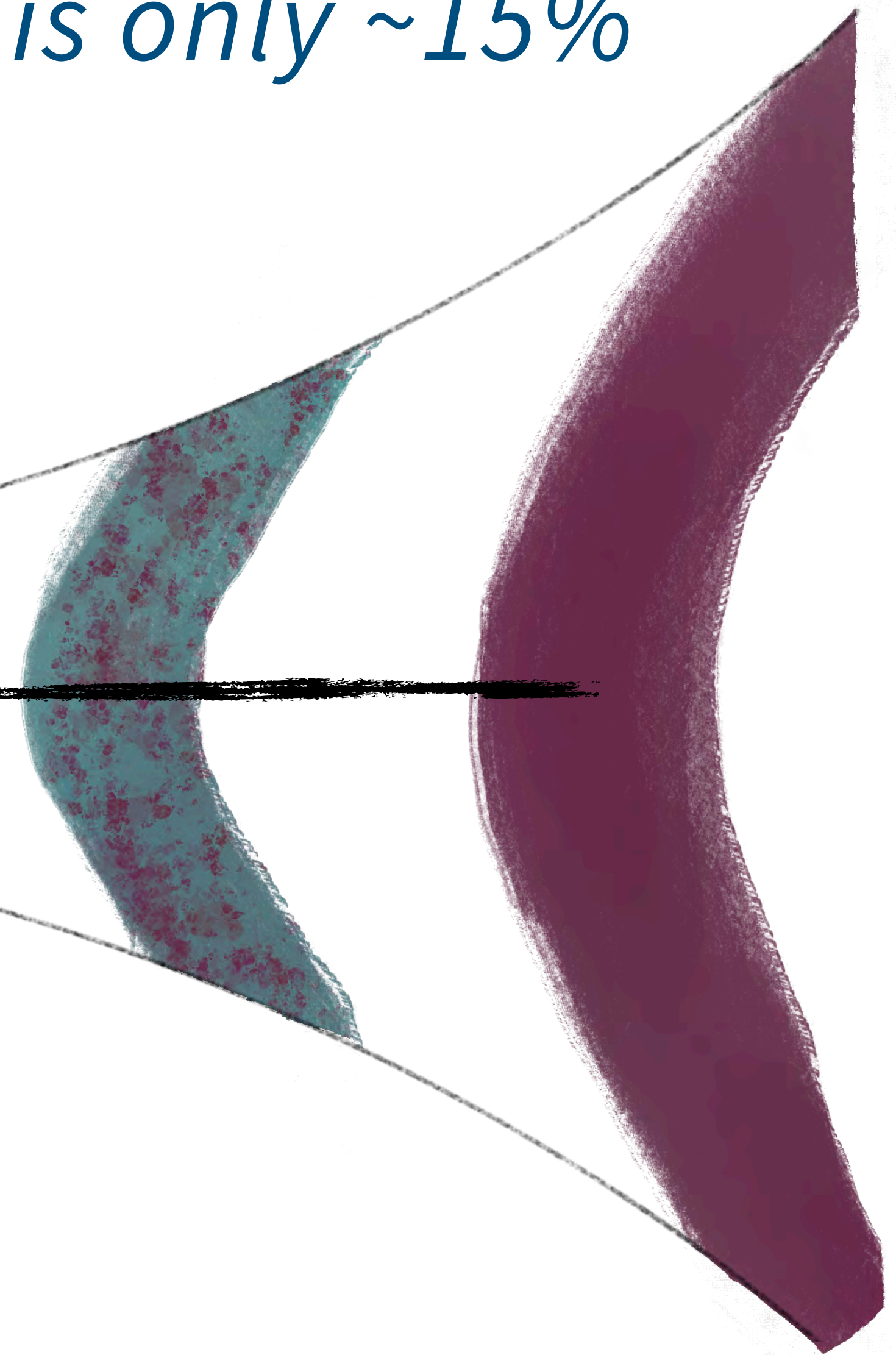
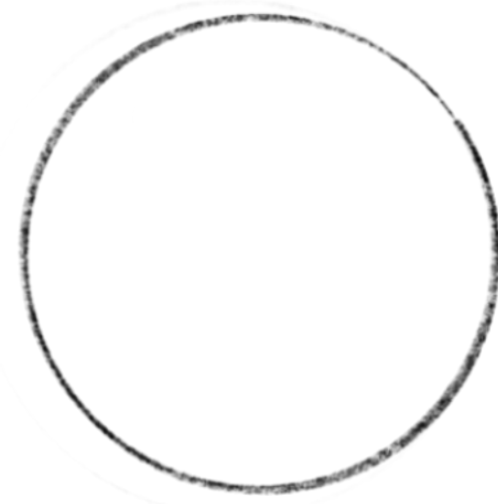
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→ We likely are severely underestimating the inventory of volatiles/organics close in the inner disk and thereby what goes into forming planets...

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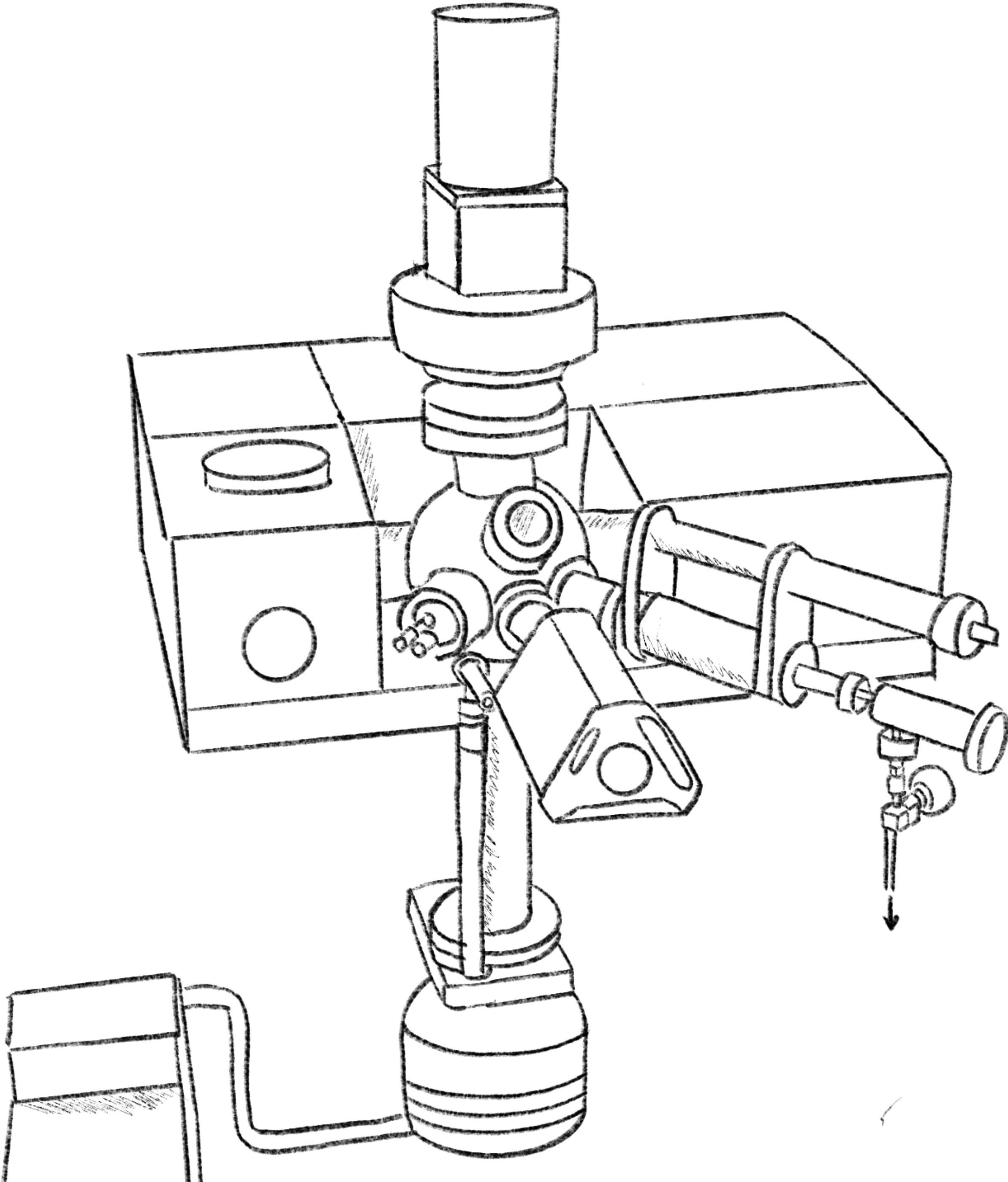
→ We likely are severely underestimating the inventory of volatiles/organics close in the inner disk and thereby what goes into forming planets...

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

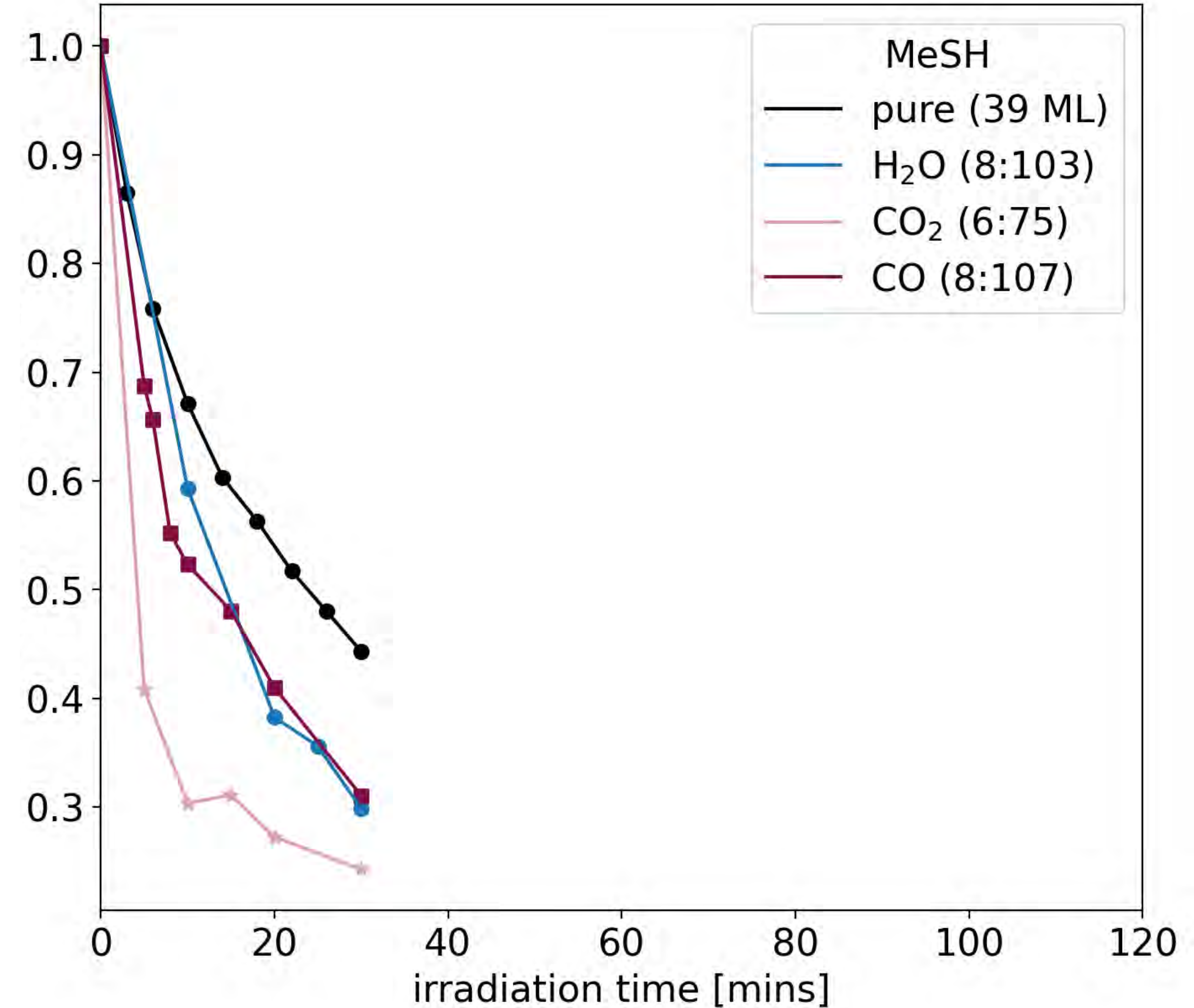
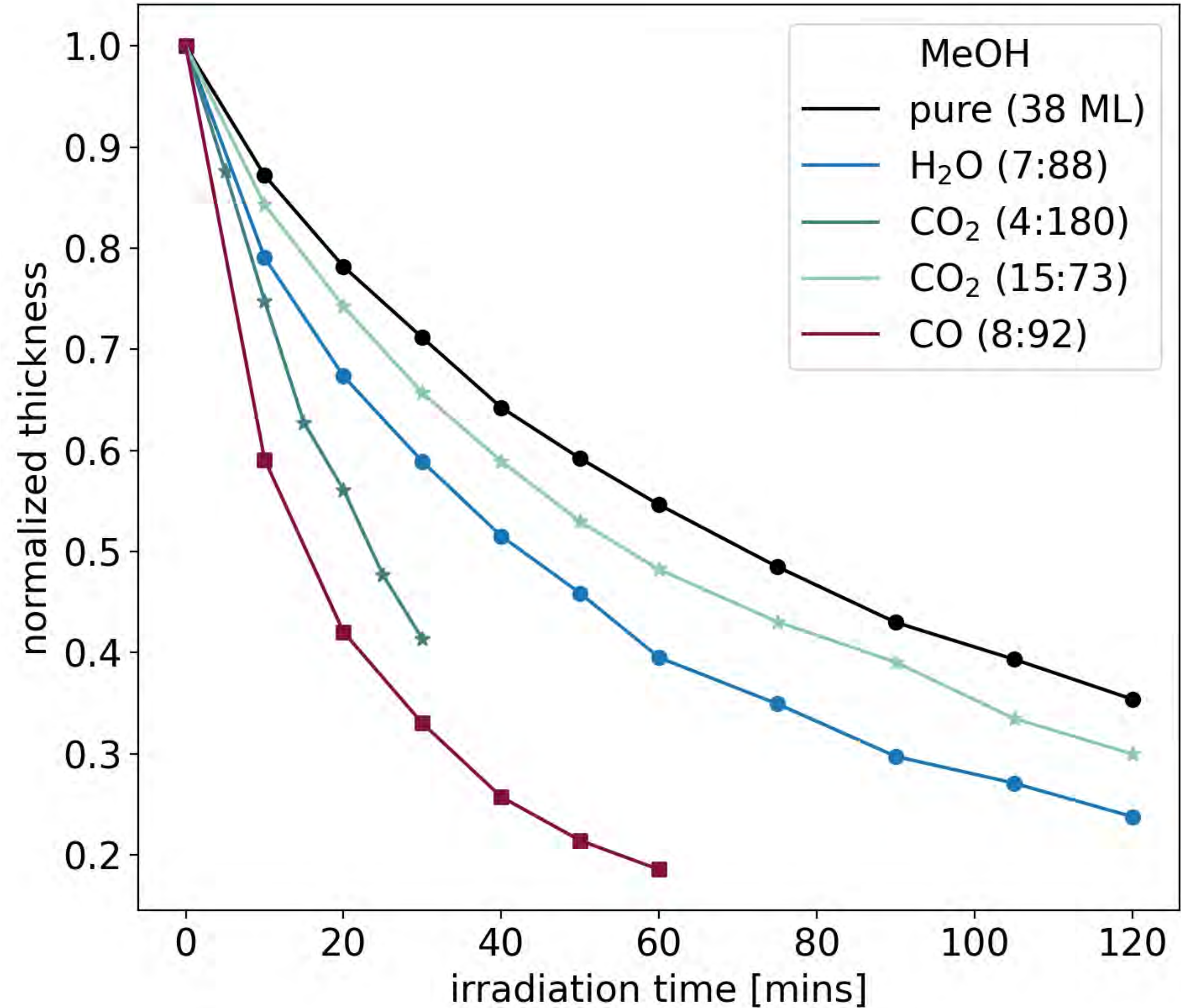
*\*If interested in more details, **my dissertation talk is Mon. 13 Jan, 3:10 pm** at YSO II / happy to chat over this week!*



*Appendix*

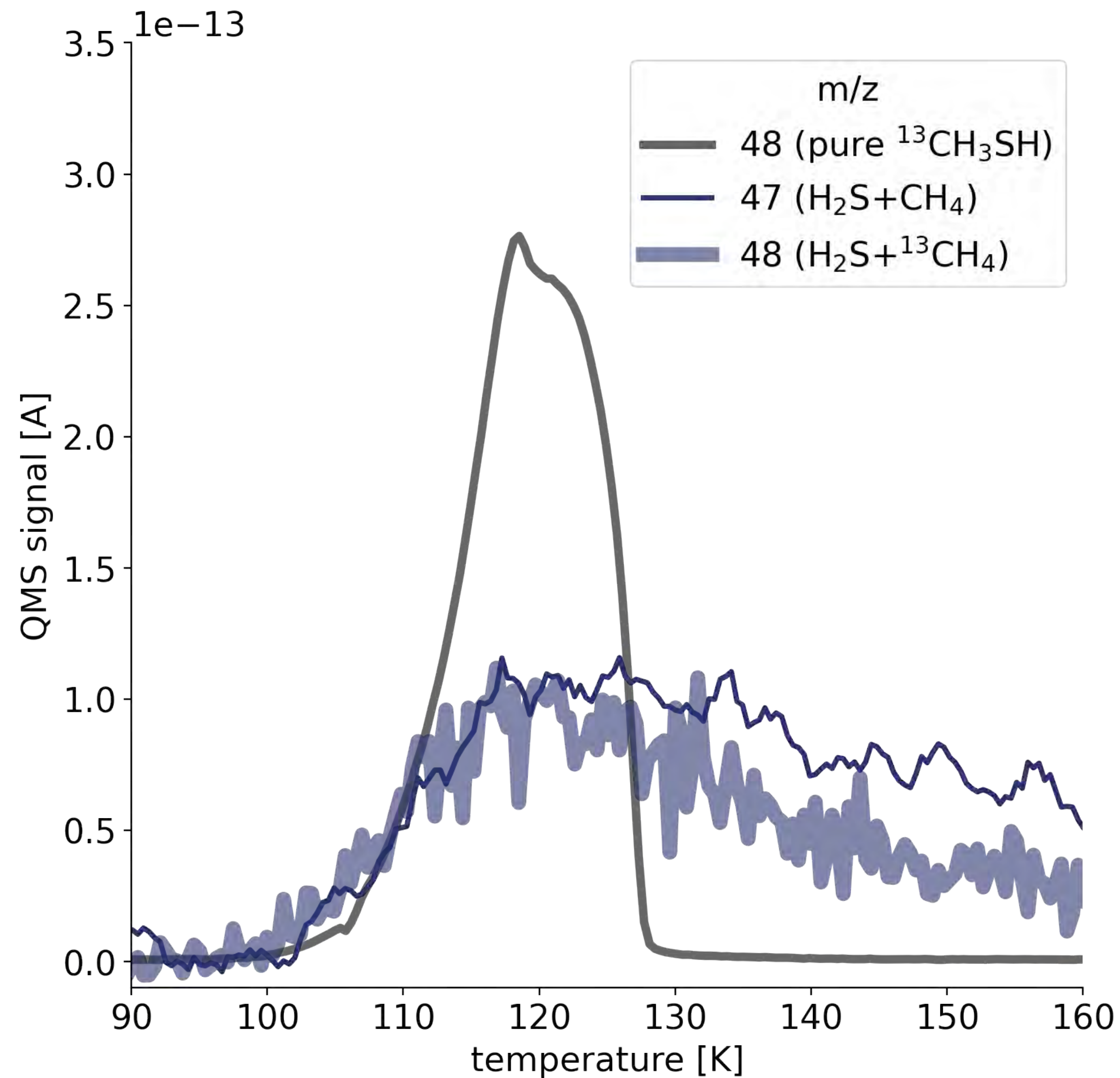


# *CH<sub>3</sub>SH is destroyed rapidly when exposed to same amount of UV photons*





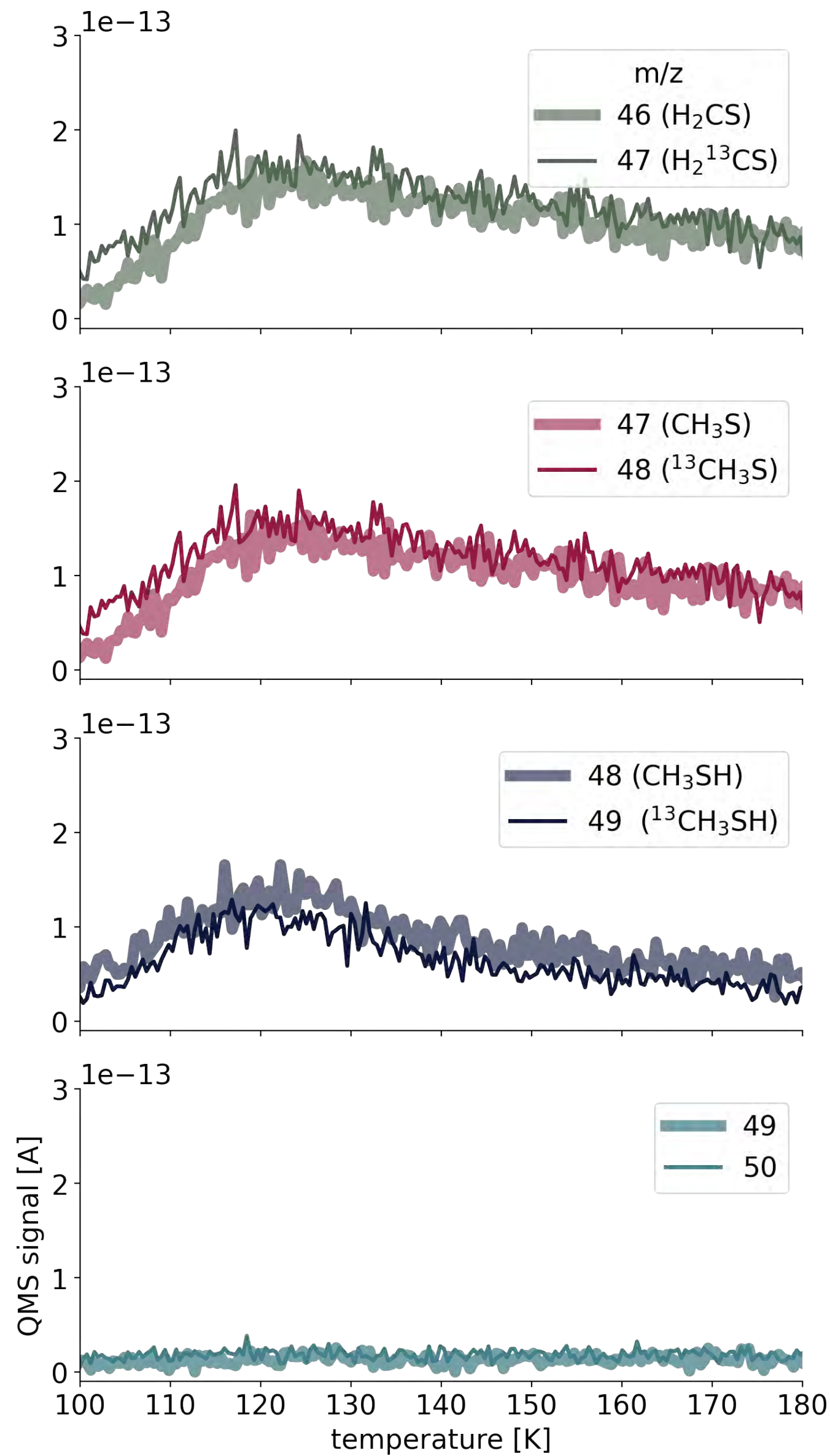
# Characterizing $\text{CH}_3\text{SH}$ formation via $\text{H}_2\text{S}+\text{CH}_4$ e- irr



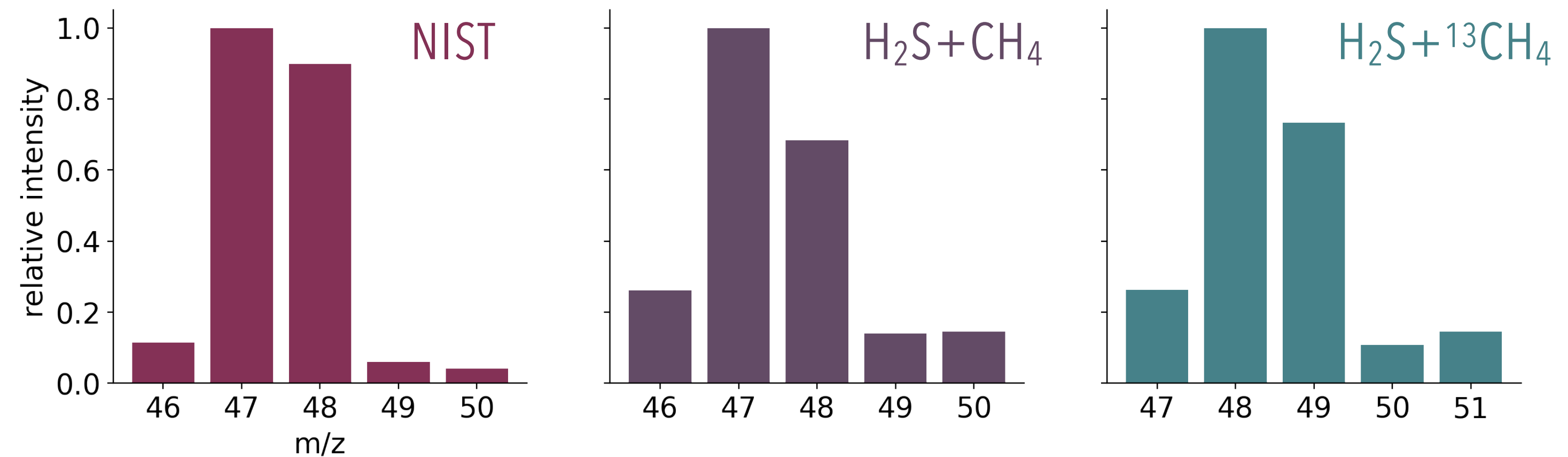
Fiducial experiment: 300 ML, 1:5 ( $\text{H}_2\text{S}:\text{CH}_4$ ), irradiation at 10 K for 120 mins ( $\approx 5 \times 10^{18}$  eV/cm<sup>2</sup>)

- Confirm  **$\text{CH}_3\text{SH}$  is forming** based on TPD data following irradiation
  - $T_{\text{des}}$  matches literature value even with isotopic substitution ( $^{13}\text{CH}_4$ )
- Analogous to  $\text{CH}_3\text{OH}$  formation from  $\text{CH}_4$  and  $\text{H}_2\text{O}$  (relative rates are still being quantified)
- Note these are done in  $\text{CH}_4$ -dominated ices
- We form a lot of  $\text{S}_2$  and  $\text{S}_3$ ...

# Not very efficient though...



- We use isotopic substitution for proof of concept
  - H<sub>2</sub>S+CH<sub>4</sub> (thicker line) and H<sub>2</sub>S+<sup>13</sup>CH<sub>4</sub> (thinner line)
  - Use the typical m/z values corresponding to CH<sub>3</sub>SH fragmentation
- Further confirm this is indeed CH<sub>3</sub>SH by taking the the mass spectrum at the desorption temperature (120 K) and compare to NIST's

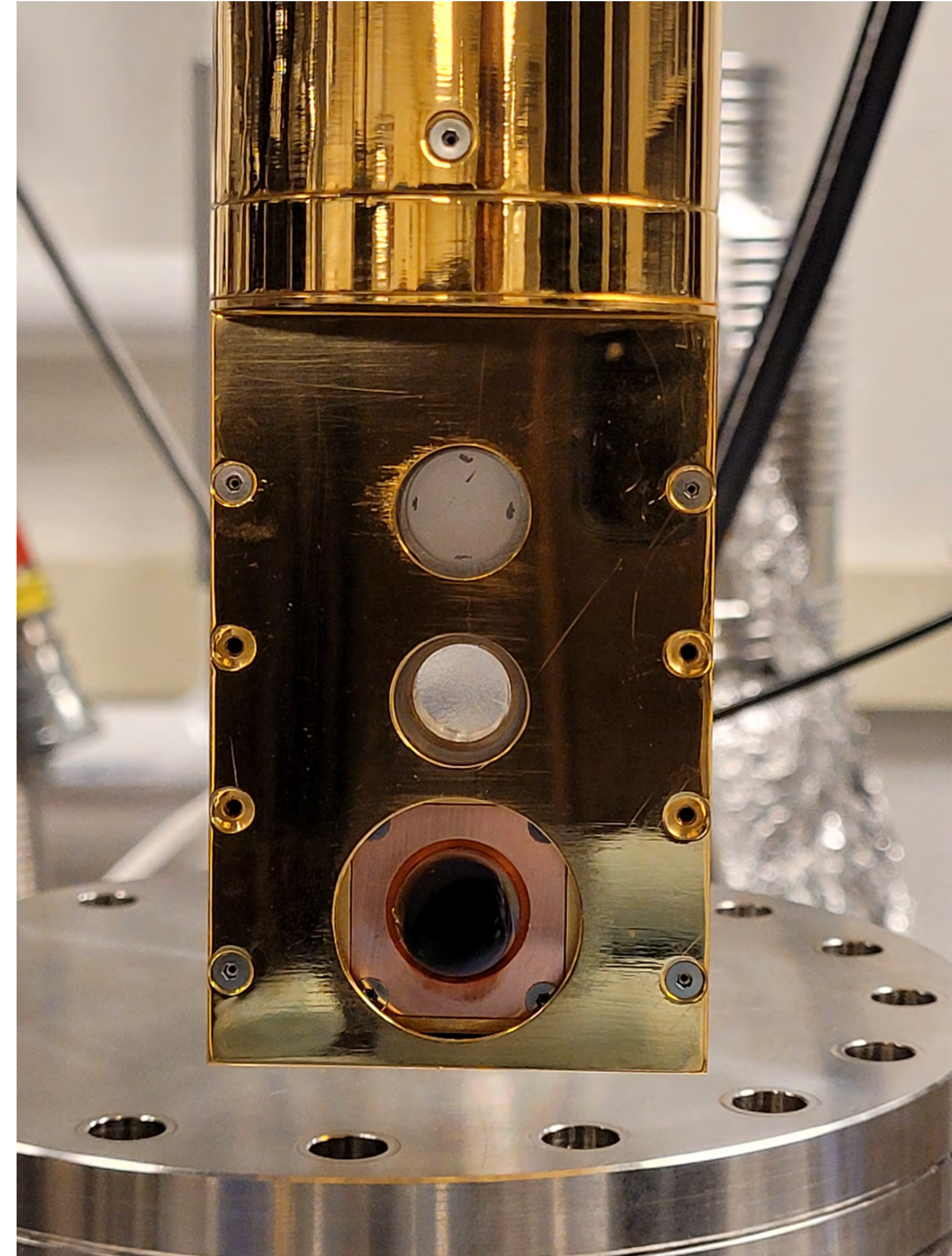
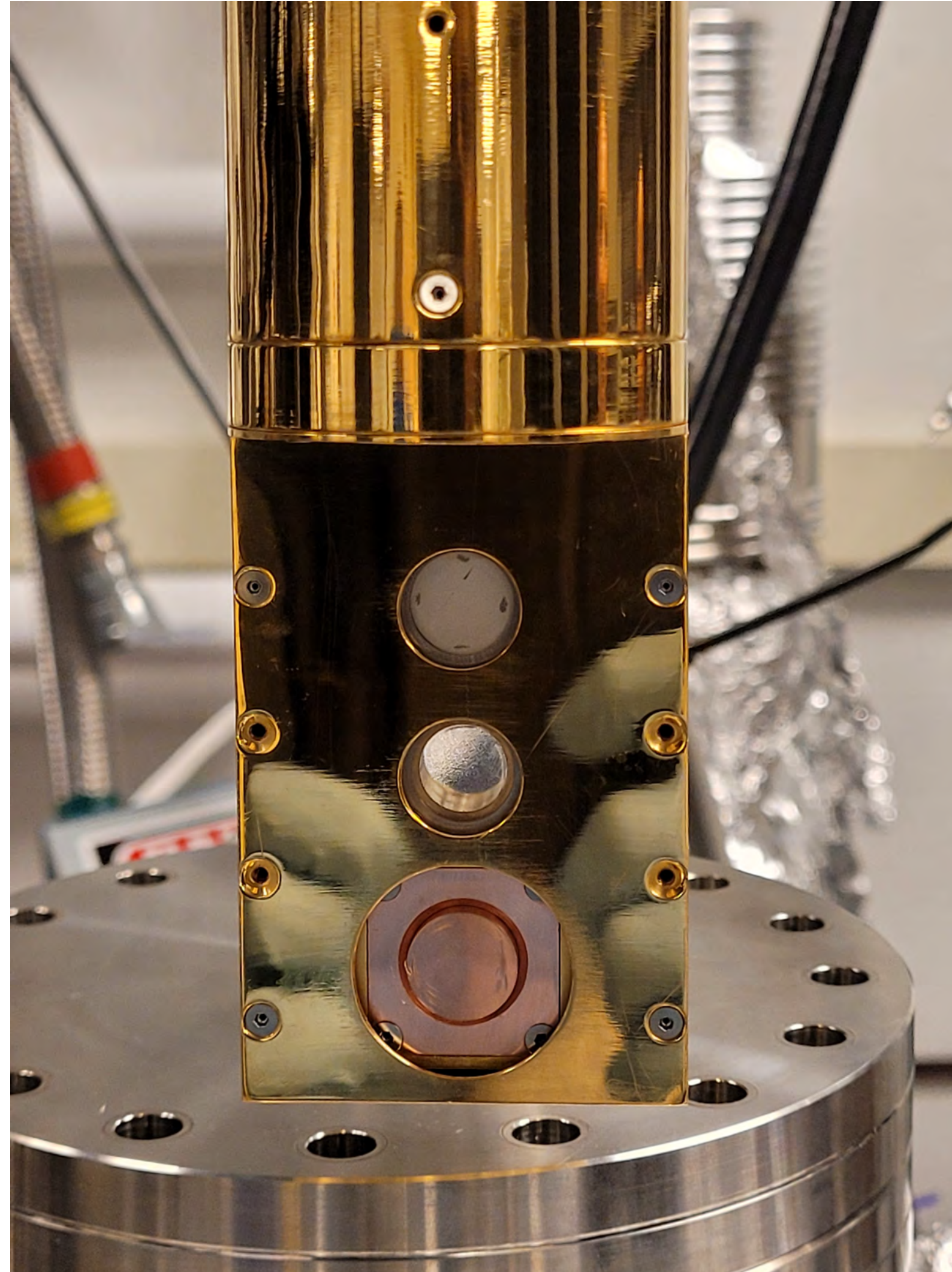


- Increase in production of 46/47 corresponds to build up of H<sub>2</sub>CS and H<sub>2</sub><sup>13</sup>CS
  - **Means the H<sub>2</sub>CS seen in disks is likely formed in the gas phase just like H<sub>2</sub>CO**



*Why aren't there many sulfur experiments?*

*Sulfur dirties the substrate pretty badly :(*



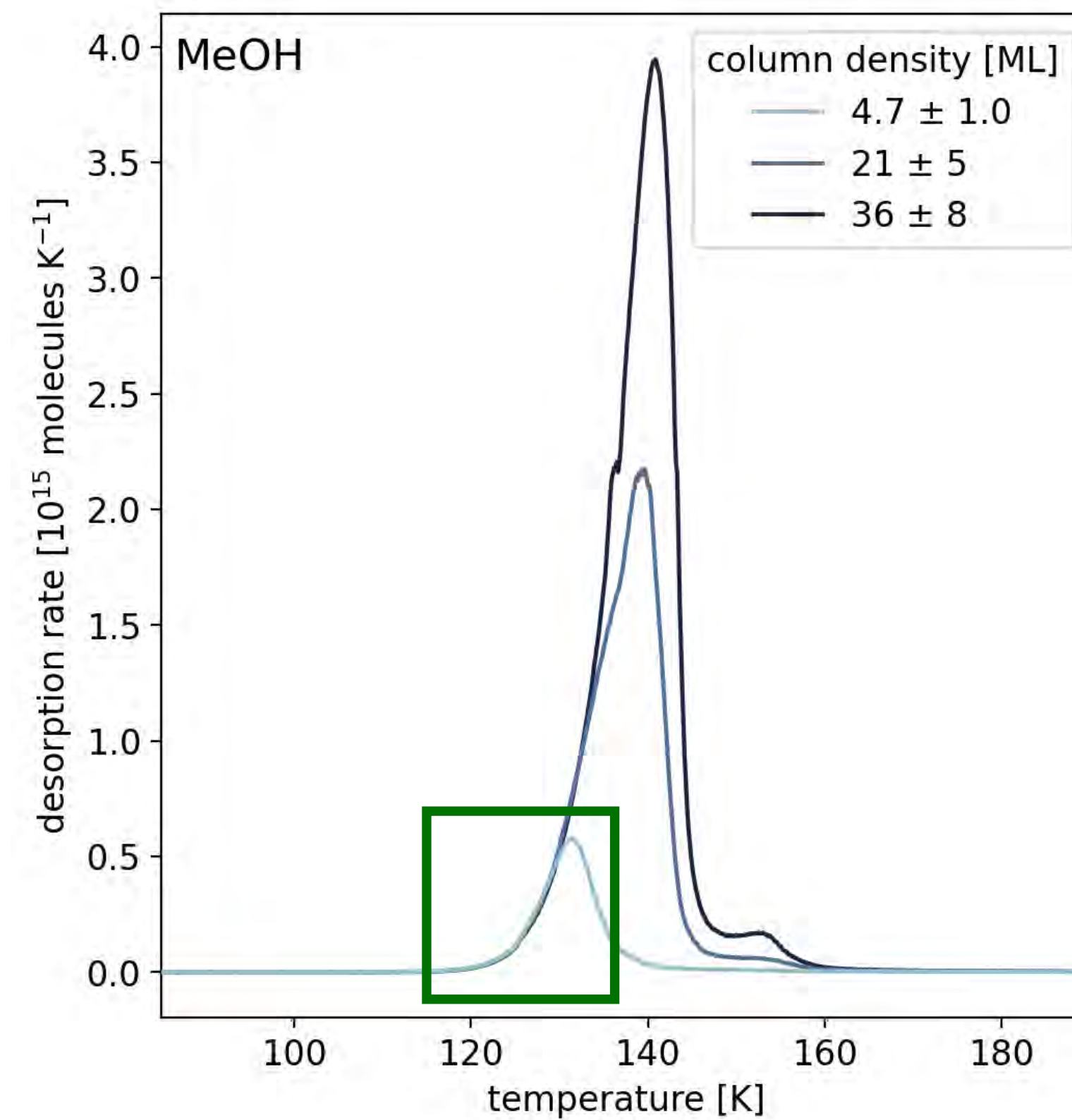
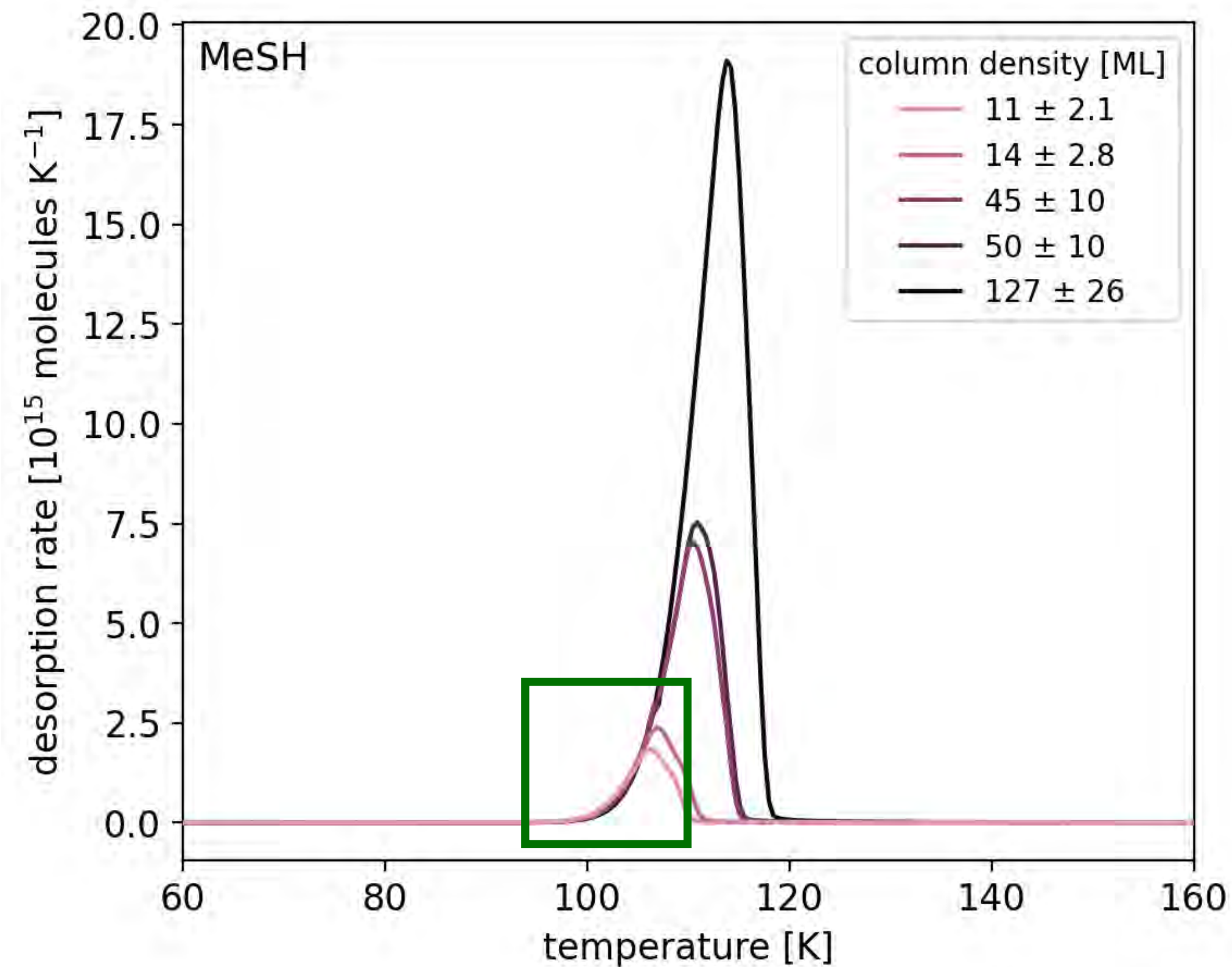


# Binding energies (BE) → proxy for sublimation fronts

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  $\nu + E_b$  [K]

DESORPTION RATE FROM TPD CURVE





# Estimating $E_b$ and $\nu$

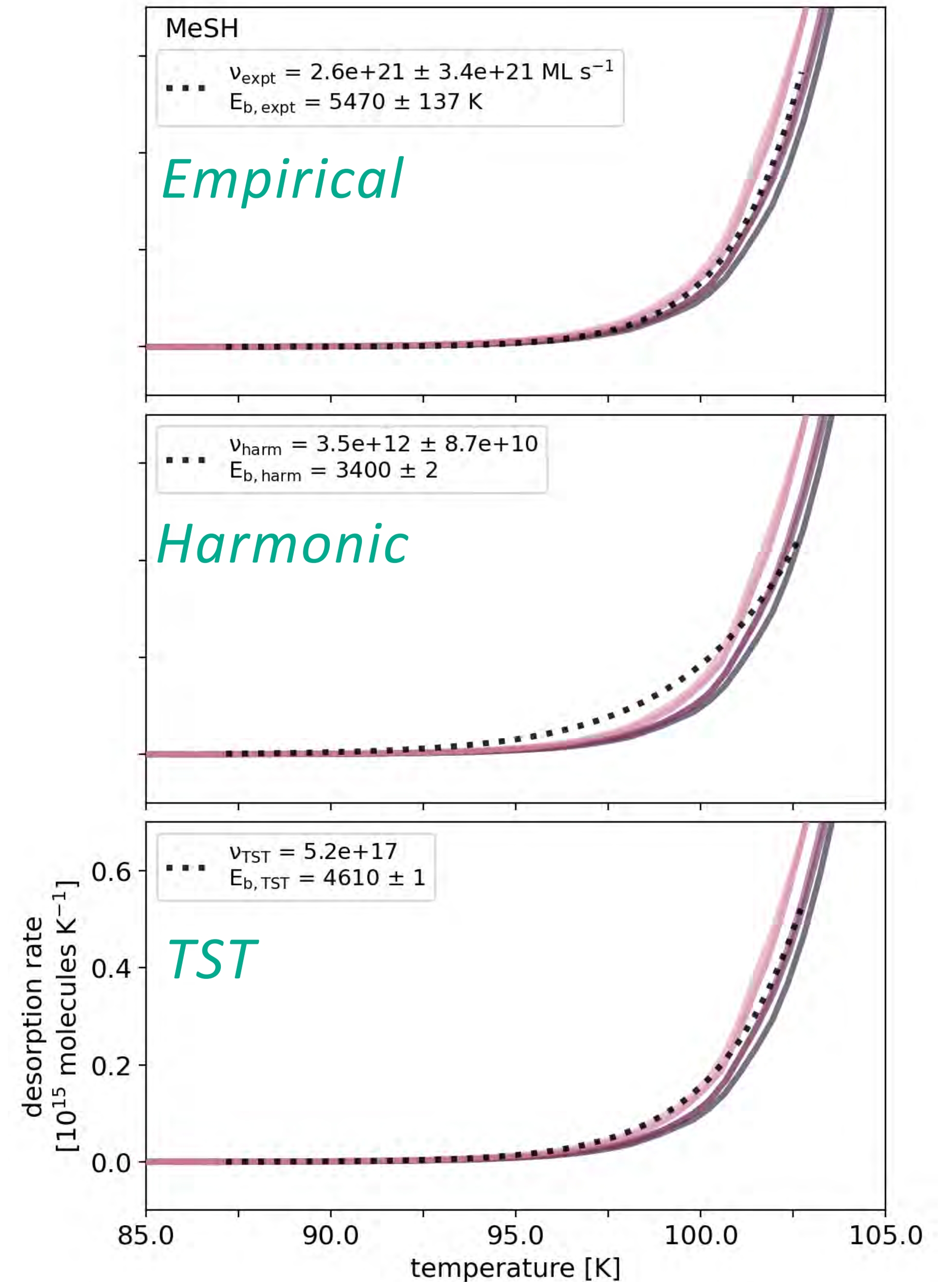
- Degeneracy between the two
  - Empirical fit
  - Harmonic approximation

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

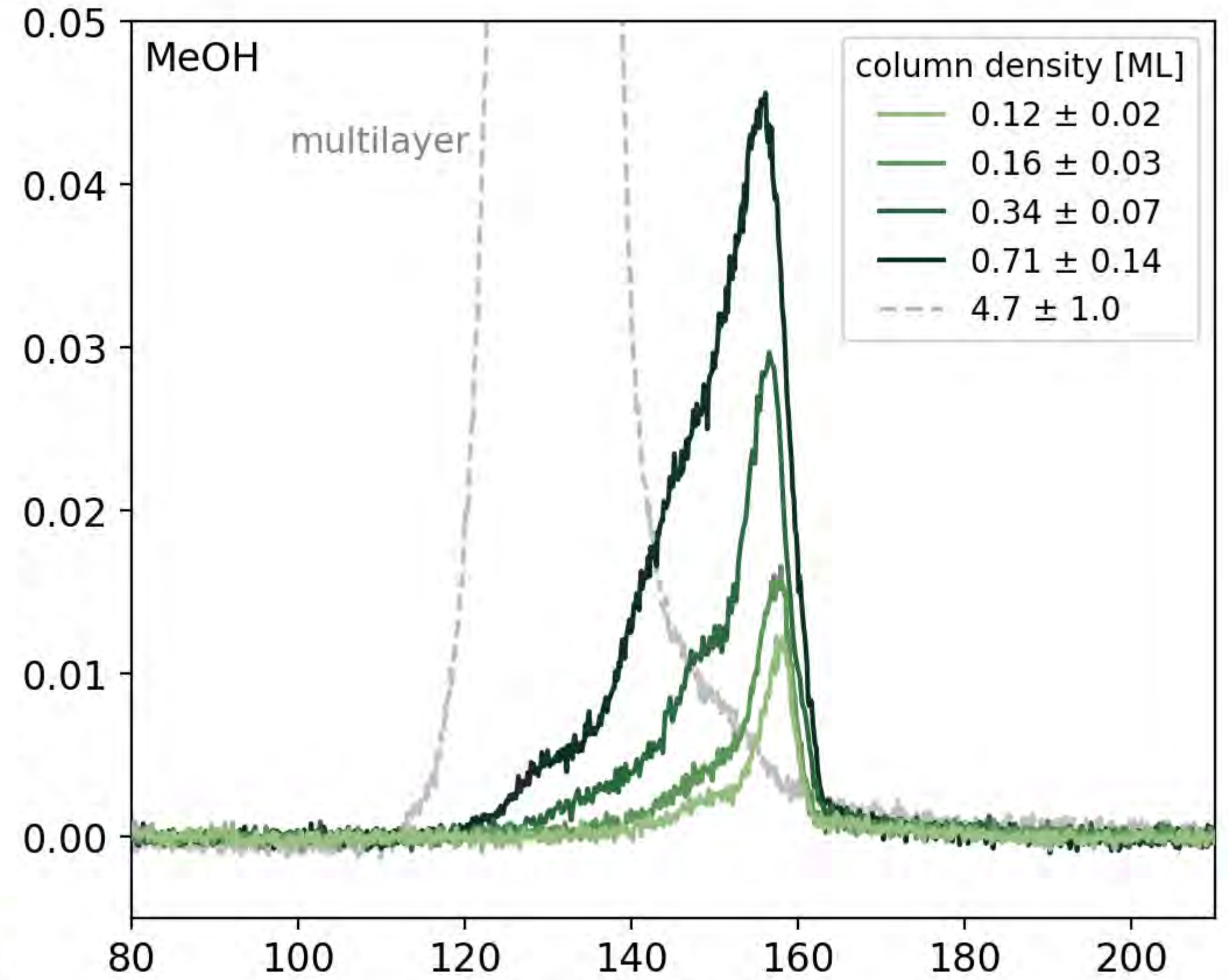
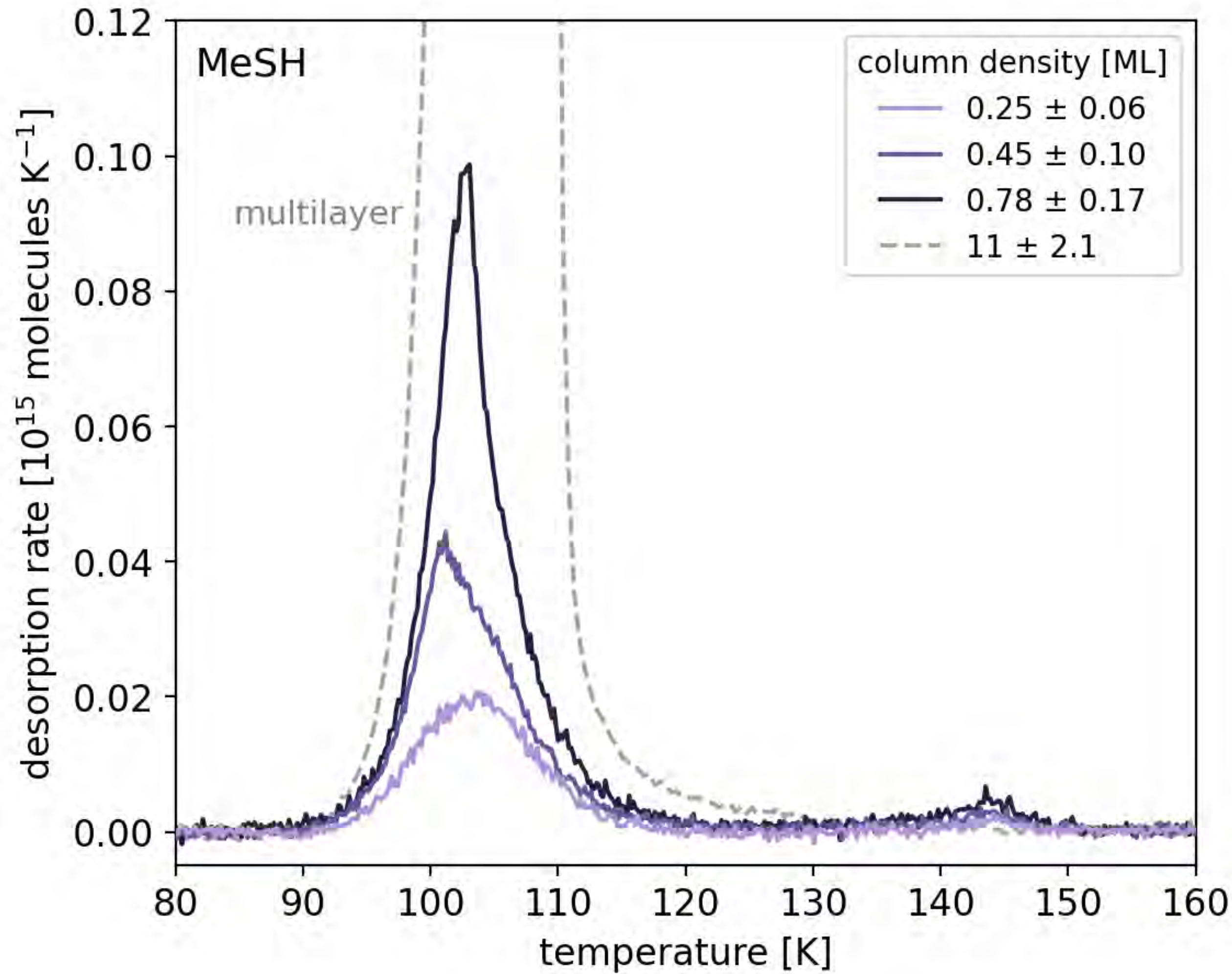
- Transition state theory (Minissale+ 2022)

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

- Bigger molecules are not well-described point masses

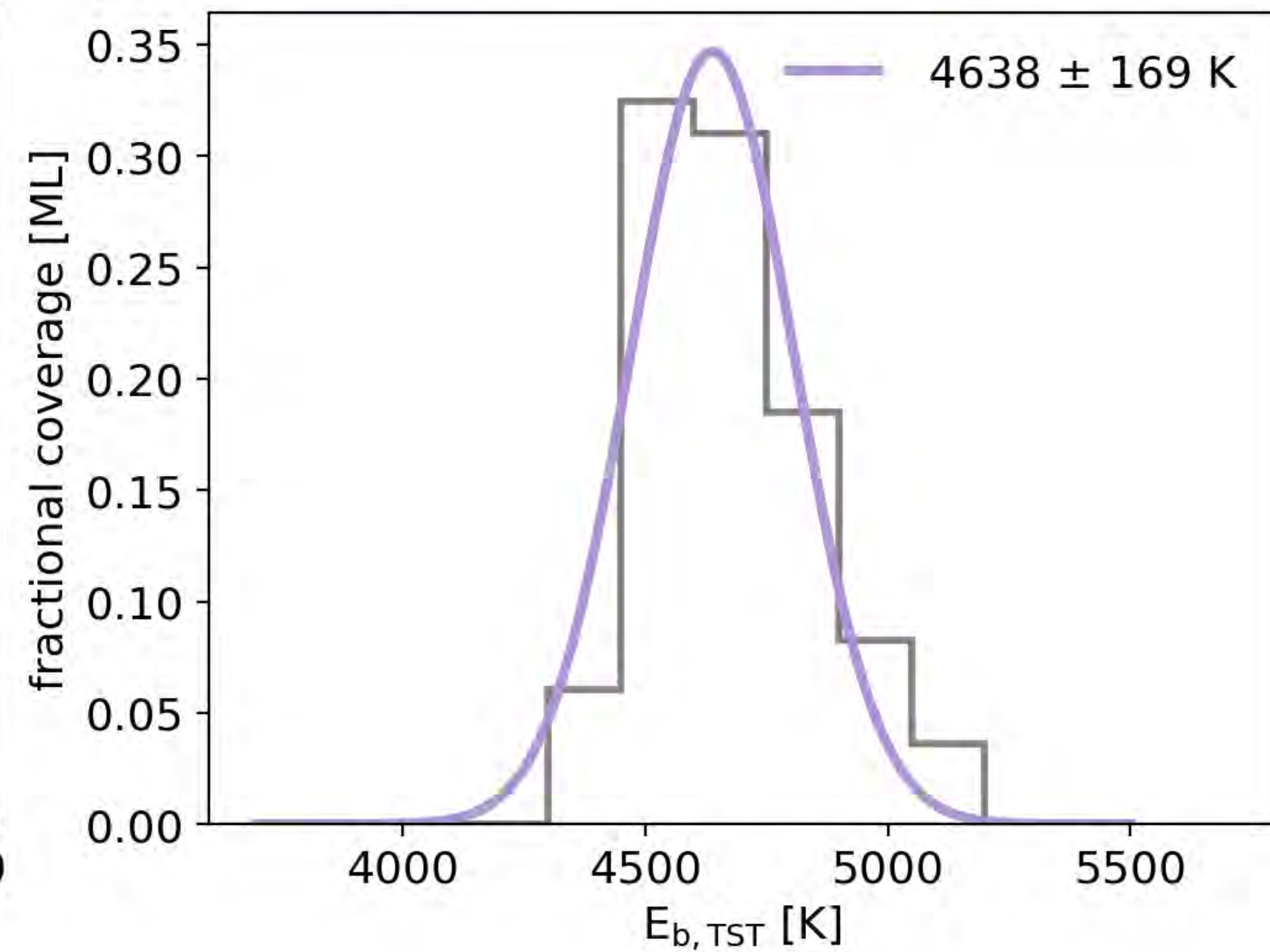
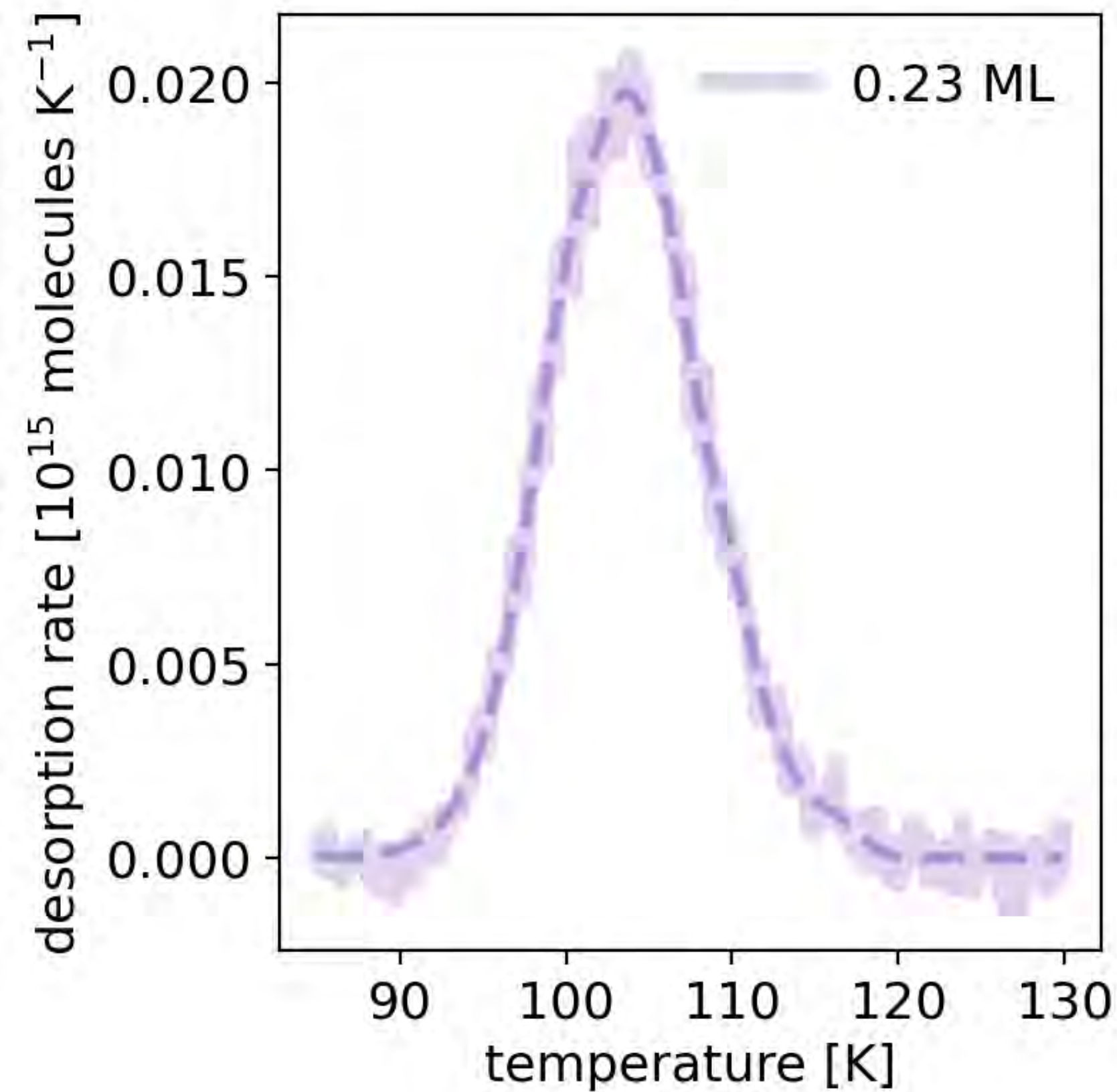


# All layered sub-monolayer TPD curves





*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

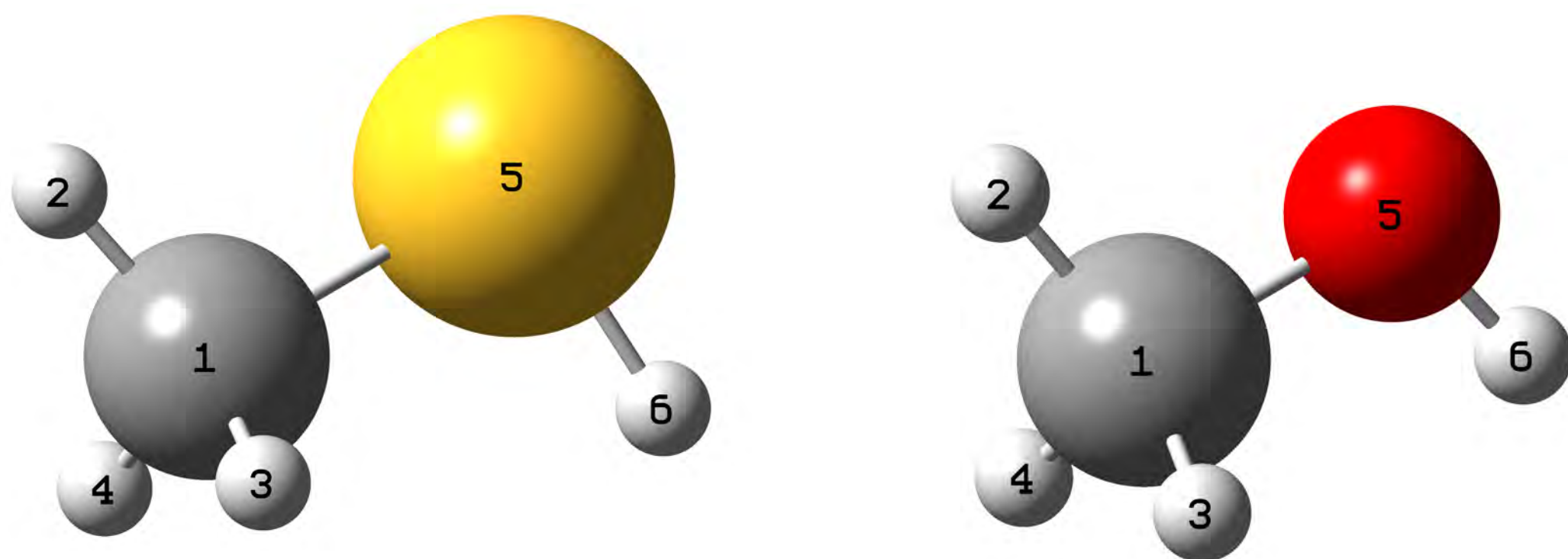
**Table 3.** Recommended TST-derived binding energies and pre-exponential factors.

	$n$	$E_{b, \text{TST}}$ [K]	$\nu_{\text{TST}}^a$	$T_{\text{peak}}^b$ [K]
MeSH–MeSH	0	$4610 \pm 110$	$5.2_{-1.0}^{+2.8} \times 10^{17}$	$106_{-6}^{+14}$
MeSH–H <sub>2</sub> O	1	$4640 \pm 170$	$4.9_{-0.9}^{+0.6} \times 10^{17}$	$104 \pm 5$
MeOH–MeOH	0	$5750 \pm 80$	$3.4_{-0.9}^{+1.5} \times 10^{17}$	$131_{-11}^{+14}$

⇒ Both MeSH binding energies are similar, MeOH-MeOH is higher, and MeOH-H<sub>2</sub>O should be higher



# Computational Calcs



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

Molecule A	Molecule B	$E_{b, \text{comp}}$ [K]
CH <sub>3</sub> SH	CH <sub>3</sub> SH	1642
CH <sub>3</sub> SH	H <sub>2</sub> O	2588
CH <sub>3</sub> OH	CH <sub>3</sub> OH	3105
CH <sub>3</sub> OH	H <sub>2</sub> O	3033

⇒ We see the opposite trend here...

