How chemical complexity flourishes on dust grains: CH3SH formation in cold molecular clouds

Kruczkiewicz, F.

Towards New Frontiers
10 – 14 March, ESO Garching

How chemical complexity flourishes on dust grains:

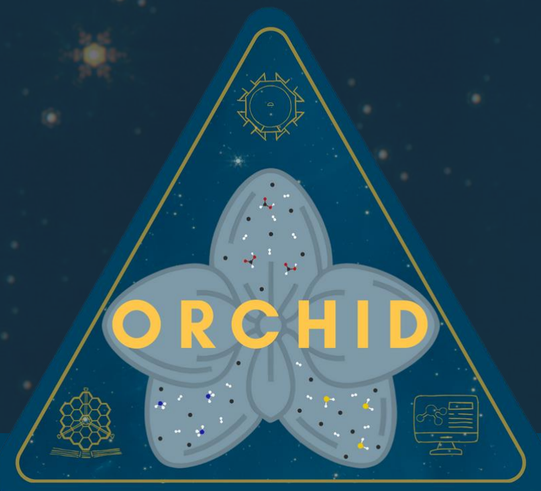
CH_3SH formation on cold molecular clouds

Dr. Franciele Kruczkiewicz

Marie Curie Skłodowska Actions (MSCA) Individual Fellow

Laboratory for Astrophysics (LfA), Leiden University

The Netherlands



LEIDEN LABORATORY for ASTROPHYSICS

Universiteit Leiden
Leiden Observatory

Sterrewacht Leiden

MARIE CURIE ACTIONS

How do molecules form in astrophysical environments, and what can they tell us about the physical and chemical conditions of the regions where they are detected?

How do molecules form in astrophysical environments, and what can they tell us about the physical and chemical conditions of the regions where they are detected?

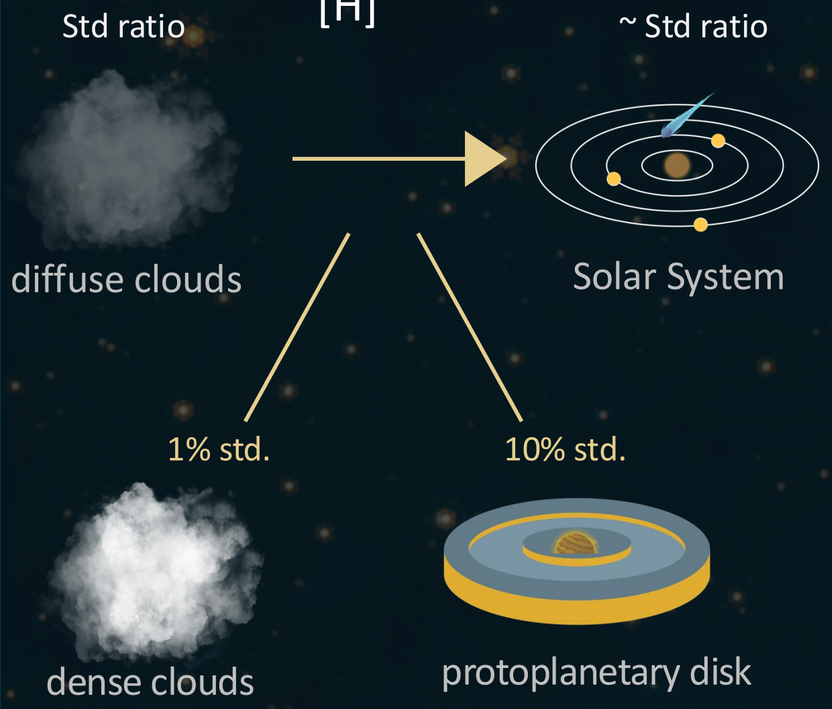
Sulfur-bearing species:

Simple: H_2S, OCS, H_2CS, CS_2, SO_2, S_8, NH_4SH
Complex: CH_3SH, CH_3CH_2SH, CH_2CHSH, $HSCH_2CH_2SH$

Sulfur chemistry ... and how different works this week address it

S-depletion problem

$$\frac{[S]}{[H]} \approx 10^{-5}$$



Angèle Taillard
Julia Santos
Katerina Slavicinska

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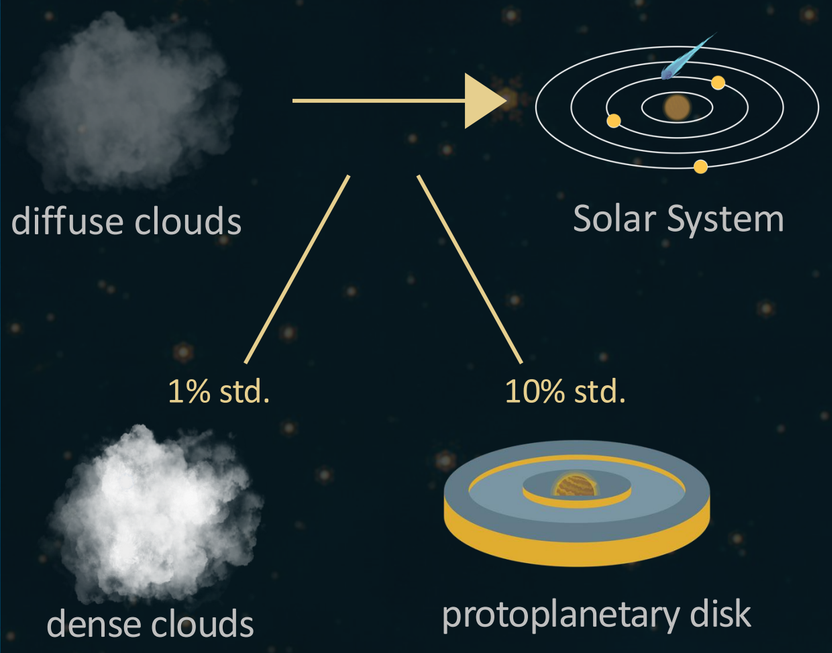

Angèle Taillard
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S solid-state chemistry

$$S^+_{gas} \longrightarrow \textbf{S-precursor}_{ice}$$

↓

energetic processing (UV/CRs)
non-energetic processing
(atoms/radicals)

↓

S-bearing-product

Rafael Martin Domenech
Julia Santos
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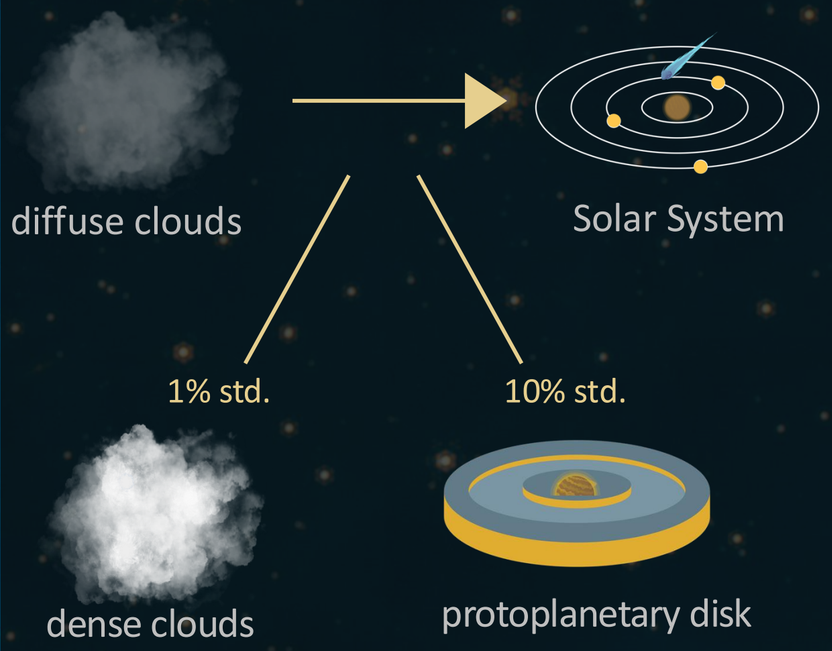
Std ratio

~ Std ratio



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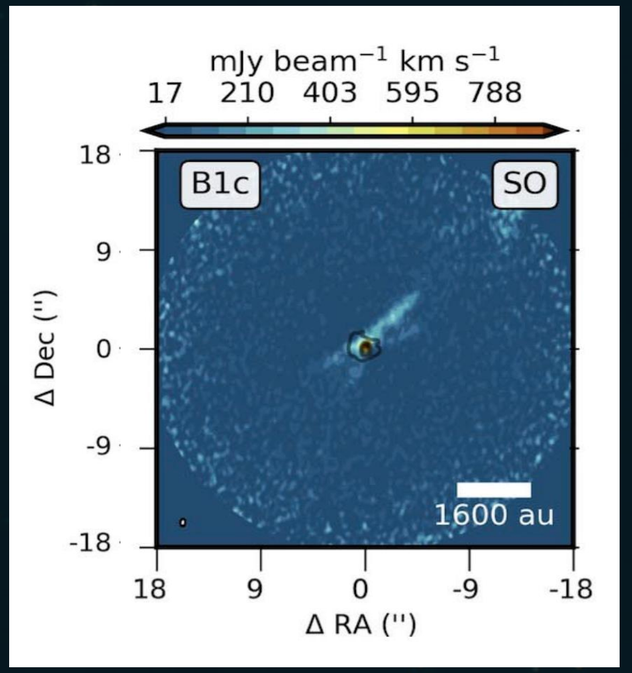
S-bearing species as a tracer



Tychoenic+21

Maria Teresa Valdivia Mena
Laura Colzi

+Posters: Miguel Sanz-Novo, Laura Schöller

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S-depletion problem

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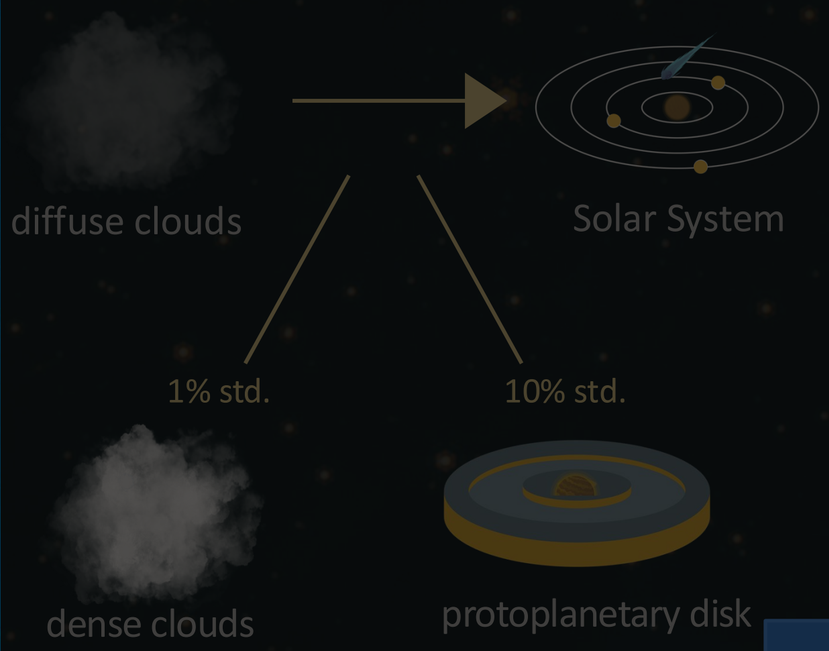


S solid-state chemistry

$S^+_{gas} \longrightarrow$ **S-precursor**$_{ice}$

↓

energetic processing (UV/CRs)
non-energetic processing (atoms/radicals)

↓

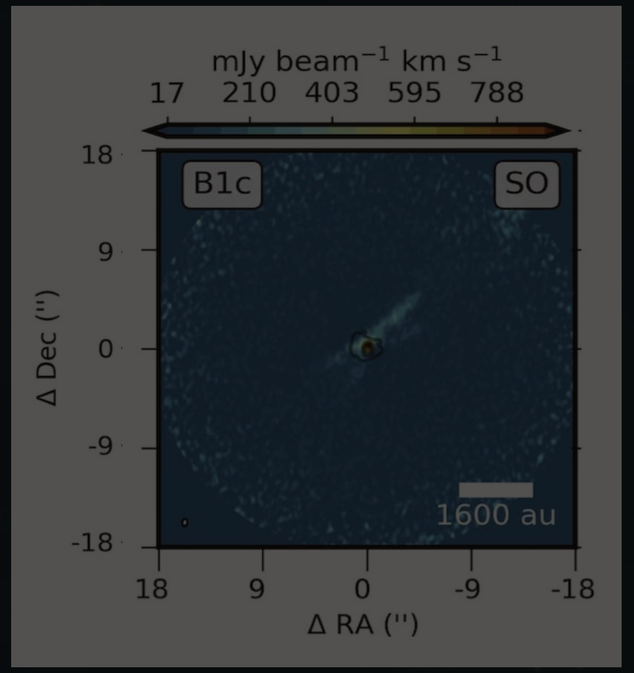
S-bearing-product

this work

$H_2S + H_2/H/C \longrightarrow CH_3SH$

a.k.a Methyl Mercaptan

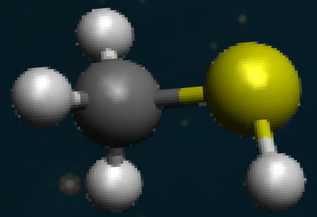
S-bearing species as a tracer



Tychoenic+21

CH_3SH: the target molecule

- First CH_3SH detection:
  - Sgr B2 Turner 1977; Linke+1979
- First CH_2DSH detection:
  - IRAS 16293-2422 **Bunn+2025**

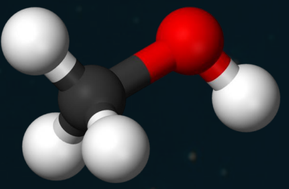


CH_3SH
Methyl Mercaptan

$$CS \xrightarrow{+H} HCS \xrightarrow{+H} H_2CS \xrightarrow{+H} CH_3S \xrightarrow{+H} CH_3SH$$

Lamberts+18

CH_3SH is the
S-analogue of CH_3OH



CH_3OH
Methanol

$$CO \xrightarrow{+H} HCO \xrightarrow{+H} H_2CO \xrightarrow{+H} CH_3O \xrightarrow{+H} CH_3OH$$

Watanabe+02; Fuchs+09; Chuang+16, 17;
Fedoseev+17; Santos+22

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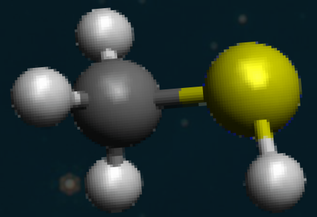


CH_3SH
Methyl Mercaptan

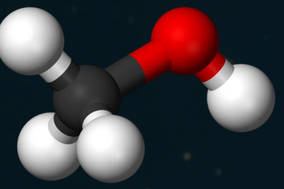
$$\mathbf{CS} \xrightarrow{+H} \mathbf{HCS} \xrightarrow{+H} \mathbf{H_2CS} \xrightarrow{+H} \mathbf{CH_3S} \xrightarrow{+H} \mathbf{CH_3SH}$$

Lamberts+18

CH_3SH is the
S-analogue of CH_3OH

Beyond CS hydrogenation:

What alternative pathways lead to CH_3SH formation, and what do they reveal about sulfur chemistry in star-forming environments?



CH_3OH
Methanol

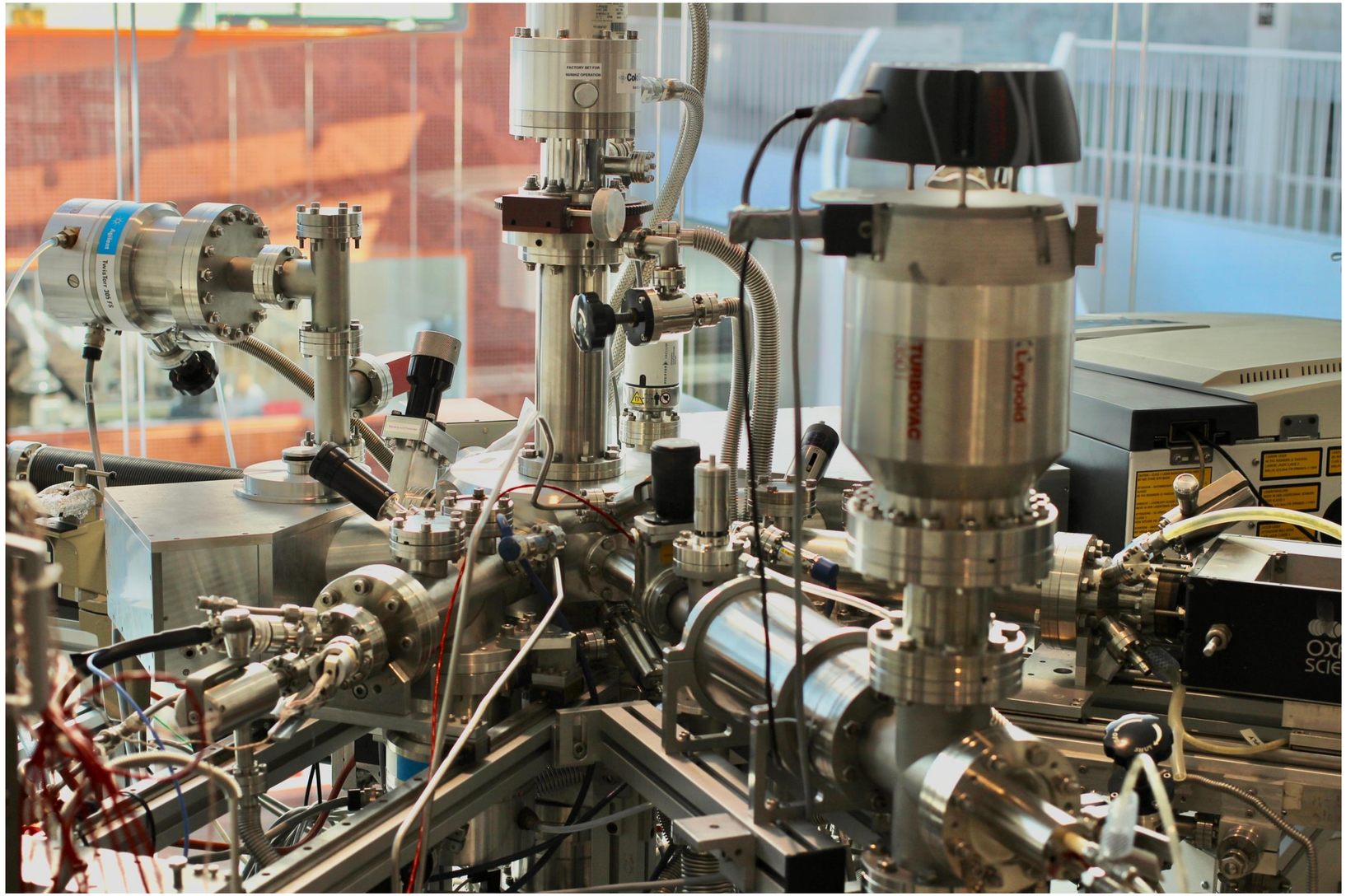
$$\mathbf{CO} \xrightarrow{+H} \mathbf{HCO} \xrightarrow{+H} \mathbf{H_2CO} \xrightarrow{+H} \mathbf{CH_3O} \xrightarrow{+H} \mathbf{CH_3OH}$$

Watanabe+02; Fuchs+09; Chuang+16, 17;
Fedoseev+17; Santos+22

SURFRESIDE^3

T = 10 – 450 K
P_{base} = 1 x 10^{-9} mbar

SURFace REactions SImulation DEvice III



Iopollo+2011; Qasim+2020;

SURFRESIDE^3

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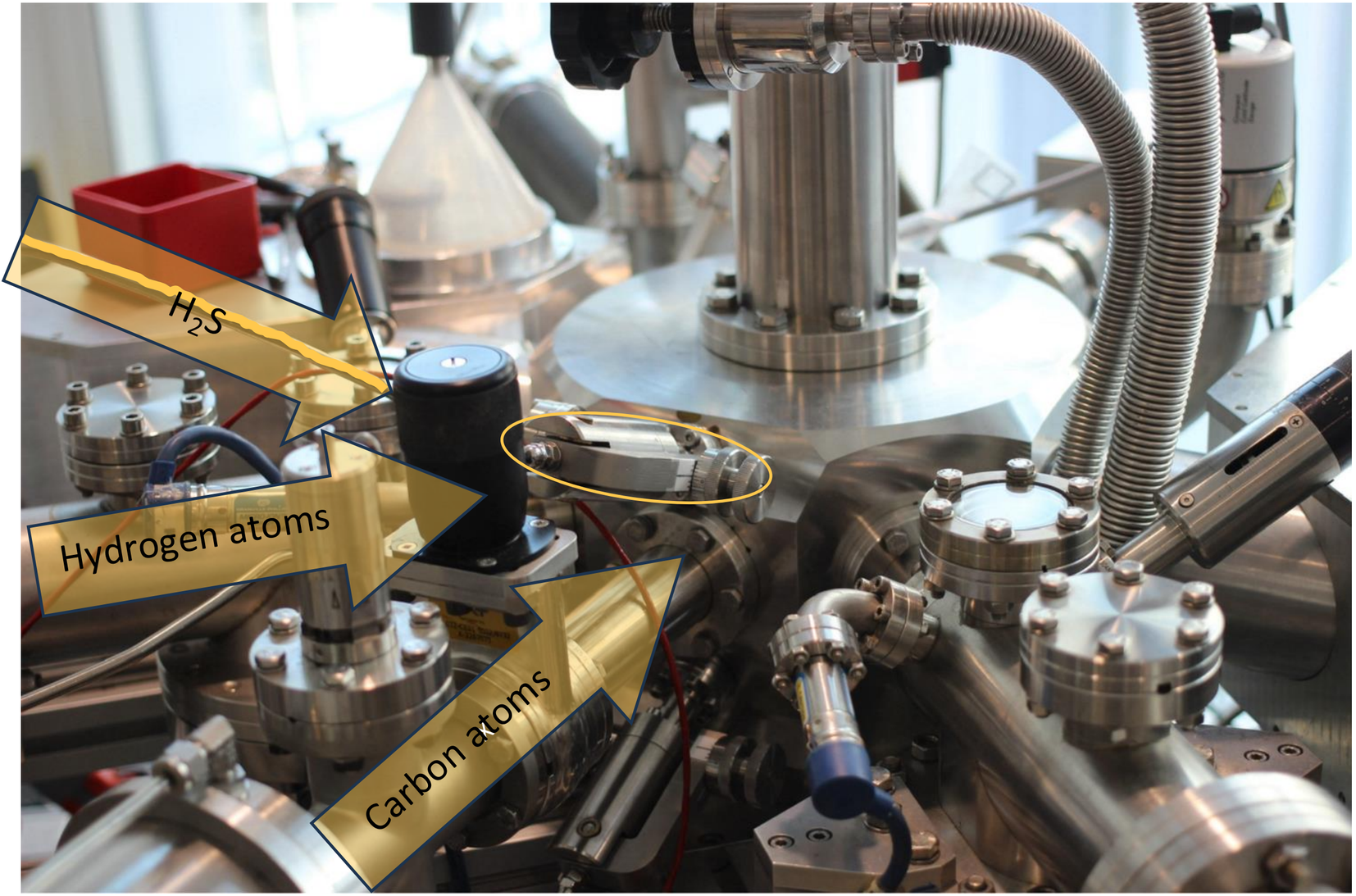

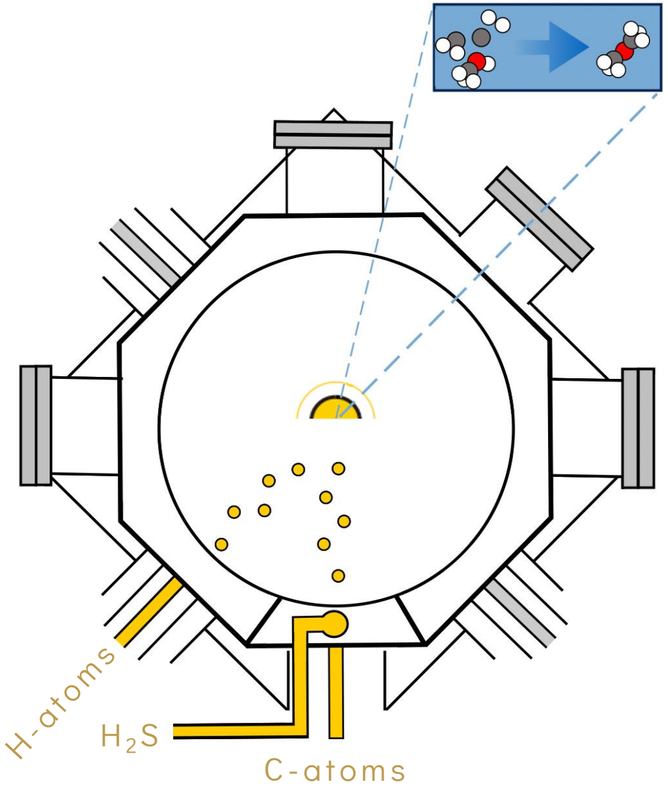

$C + H/H_2 + H_2S$

Ice samples prepared via vapor deposition

SURFRESIDE^3

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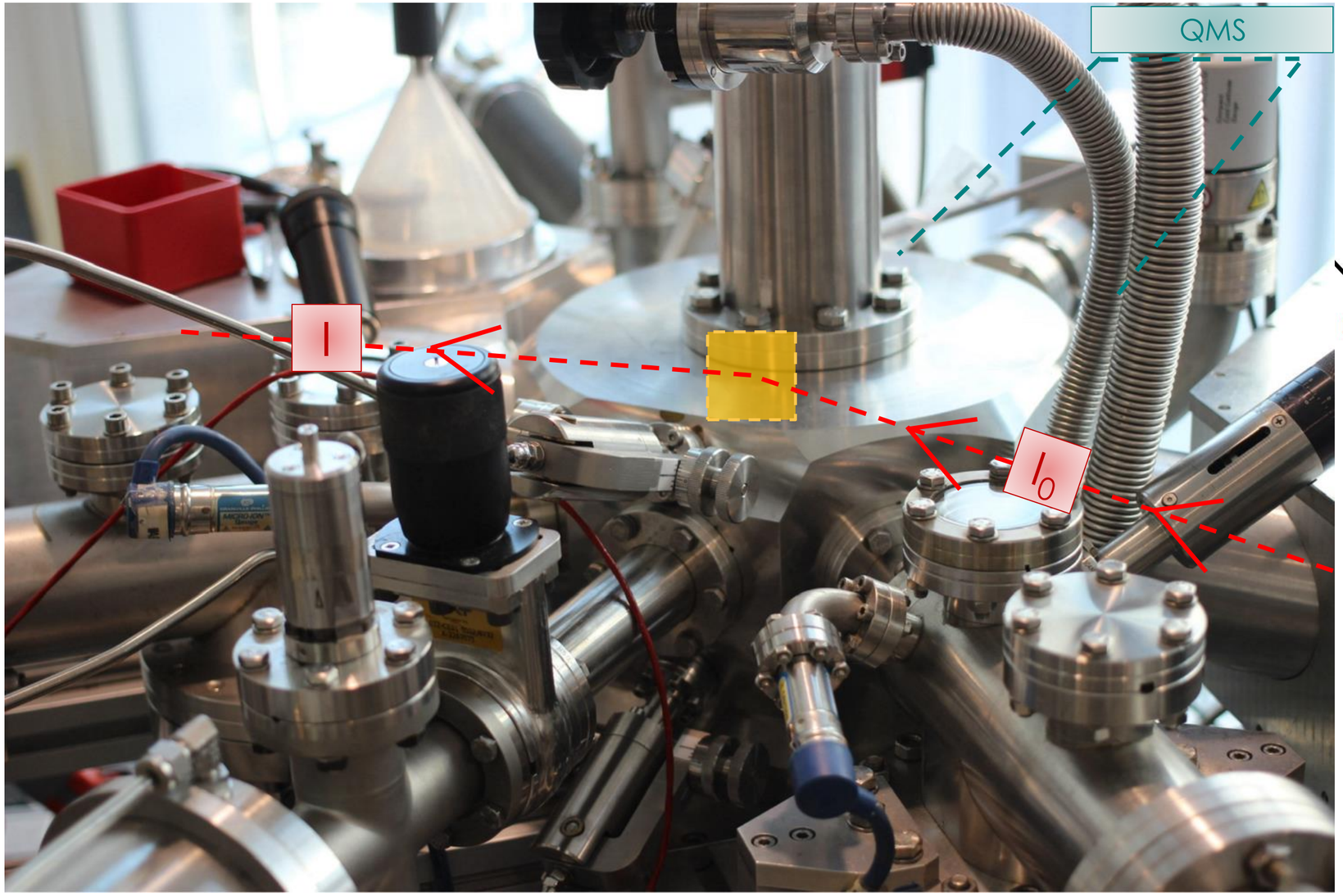
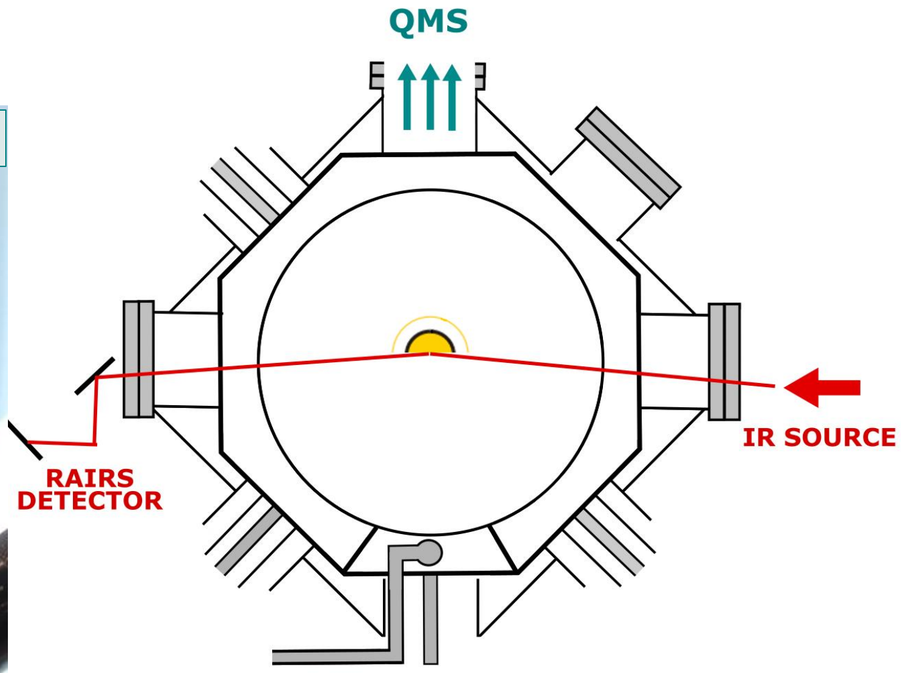
SURFace REactions SImulation DEvice III



Analysis

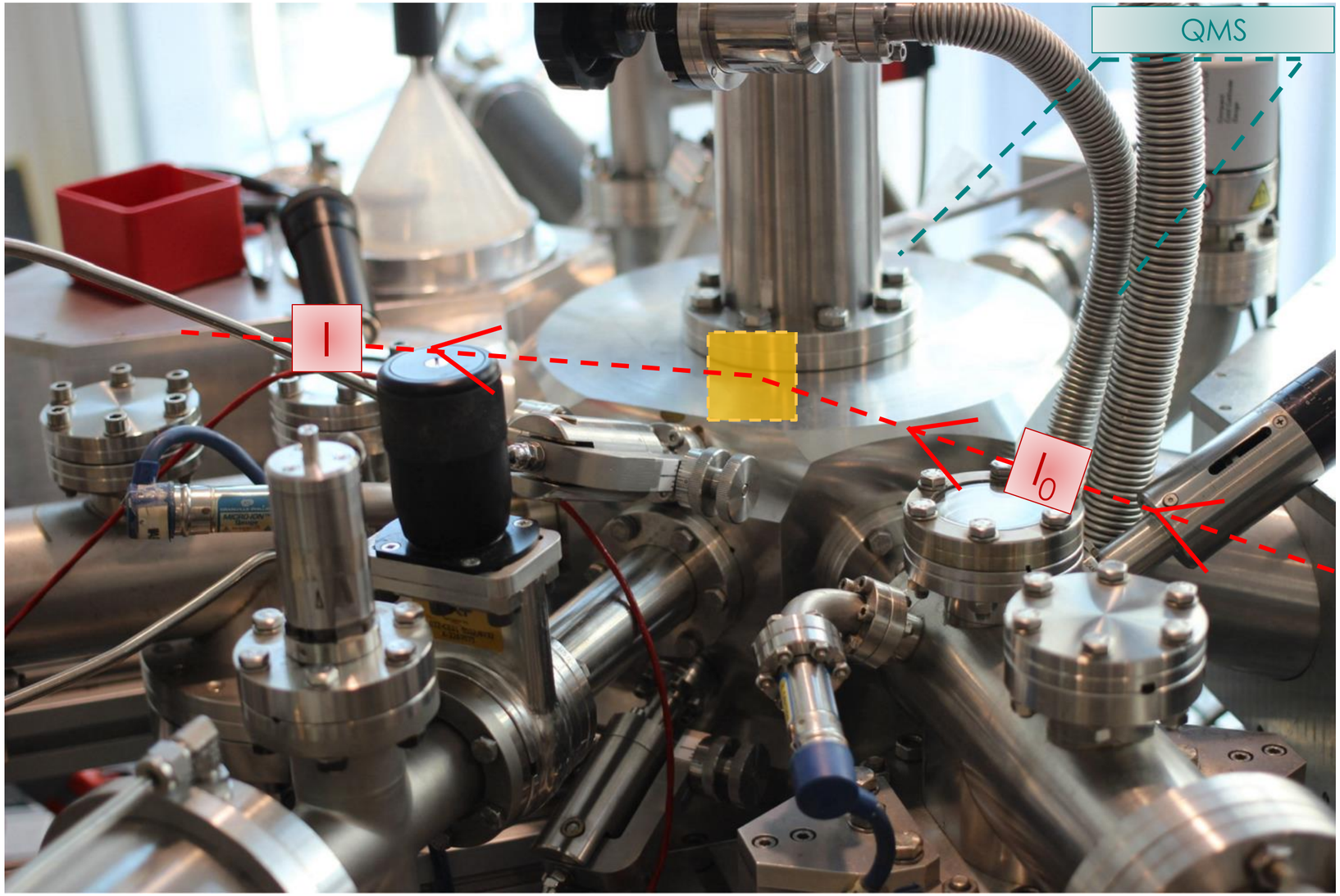


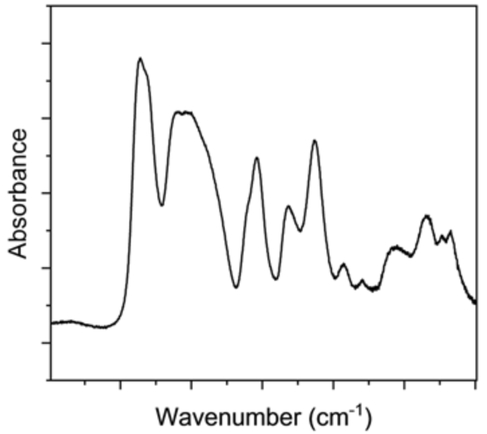
IR spectroscopy on reflection mode (RAIRS)
+
Quadrupole Mass Spectrometry (QMS) for Temperature Programmed Desorption (TPD)

SURFRESIDE^3

T = 10 – 450 K
P_{base} = 1 x 10^{-9} mbar

SURFace REactions SImulation DEvice III

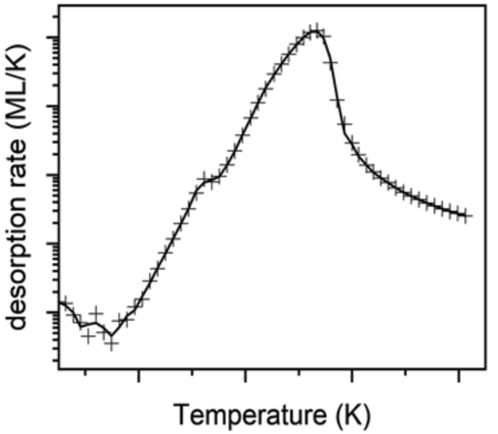




RAIRS

+

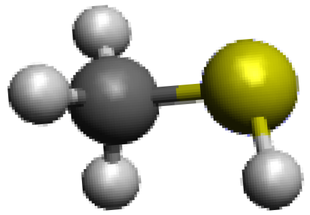
TPD signal



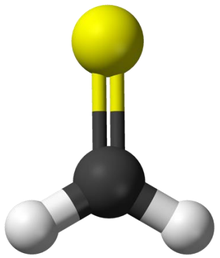
correlation allow assignment of newly formed species in the ice samples

C + H + H_2S: IR SPECTRA

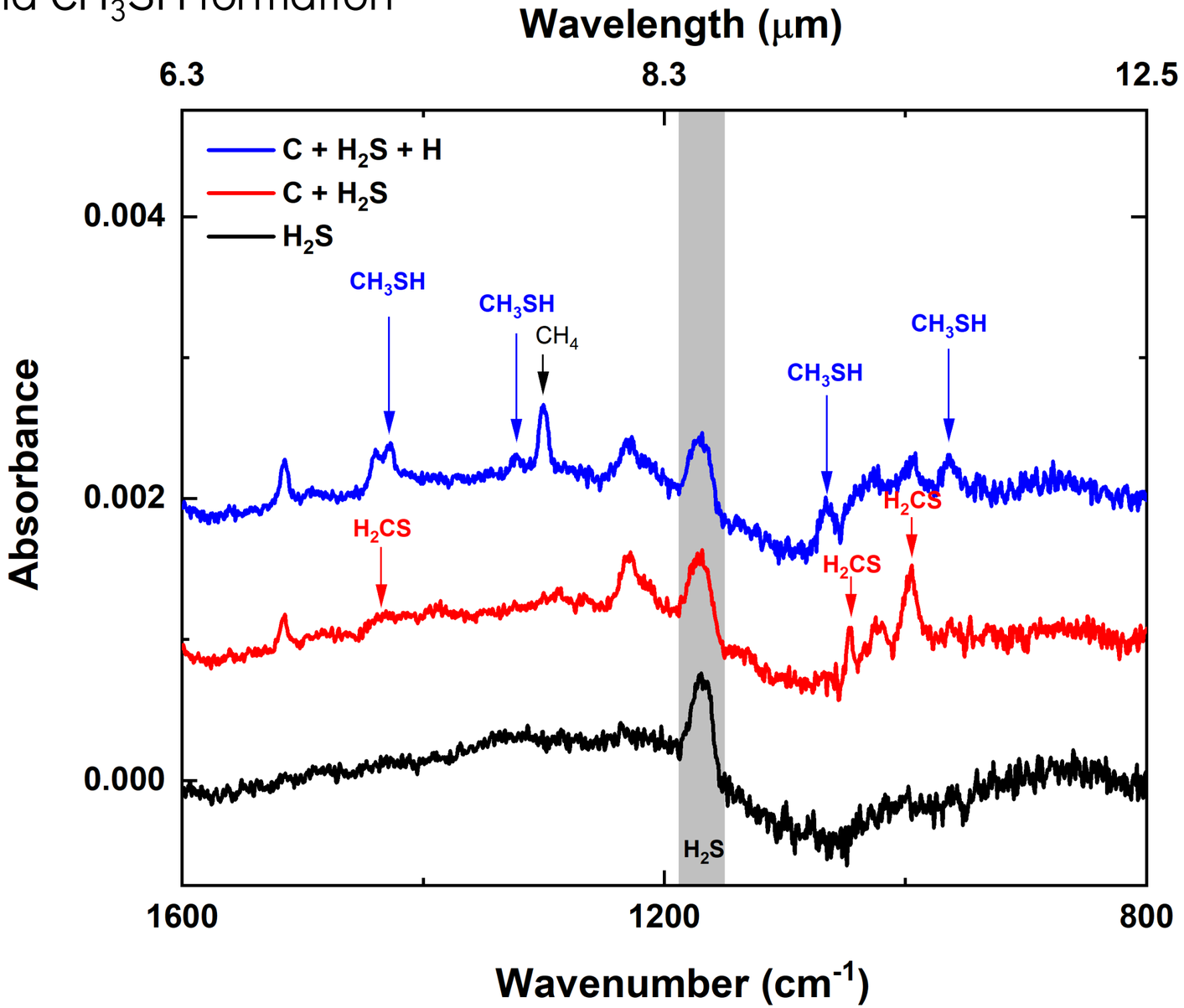
H_2CS and CH_3SH formation



CH_3SH
Methyl Mercaptan



H_2CS
Thioformaldehyde

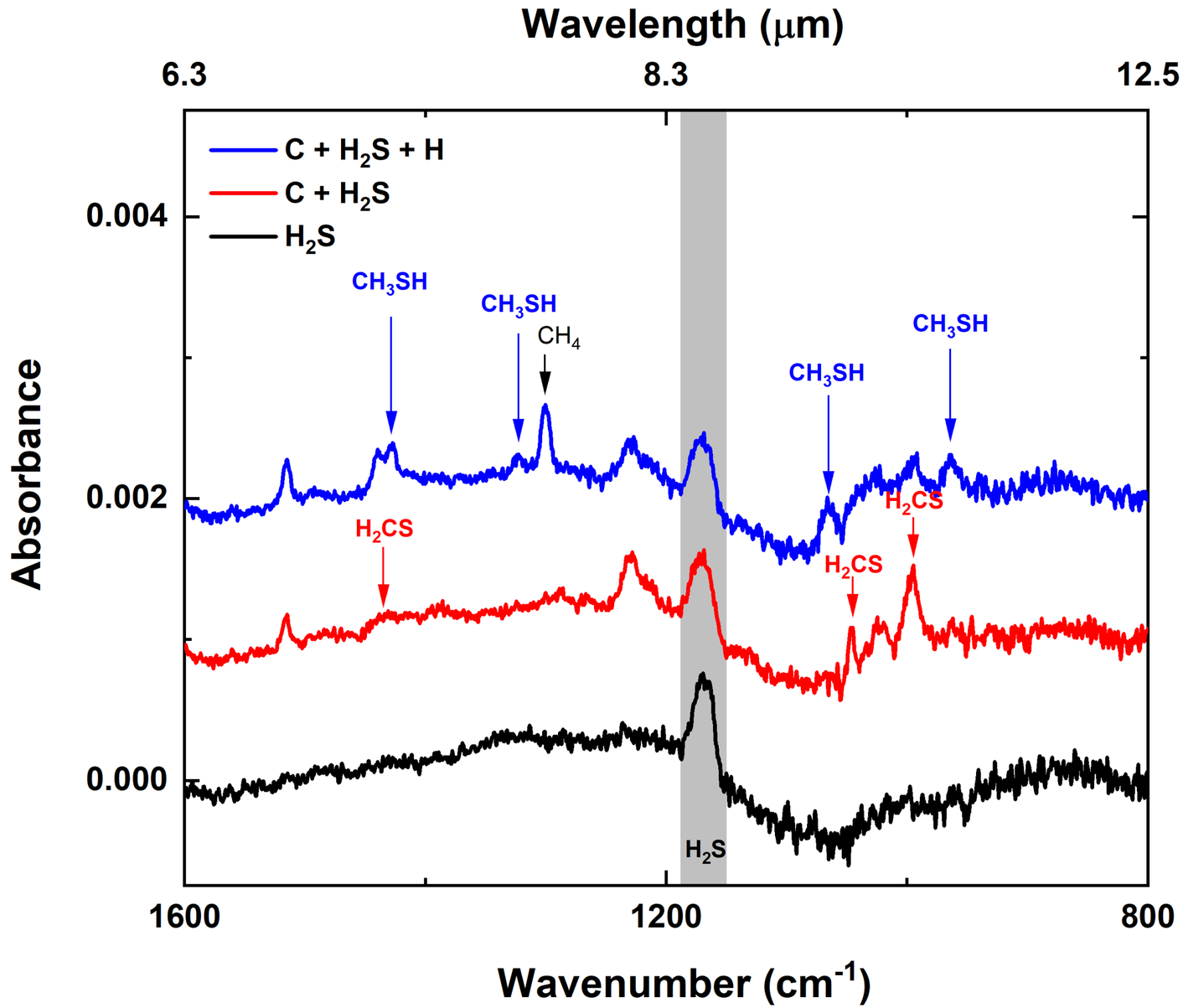


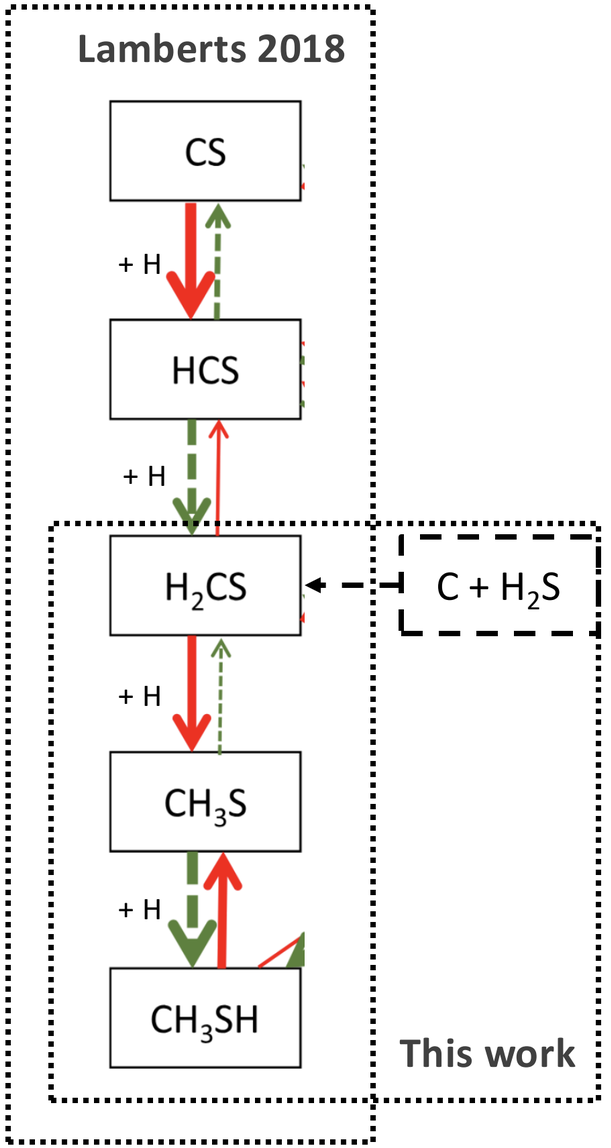
C + H + H_2S: IR SPECTRA H_2CS and CH_3SH formation

Competing reaction

$$C \xrightarrow{+H} CH_4$$

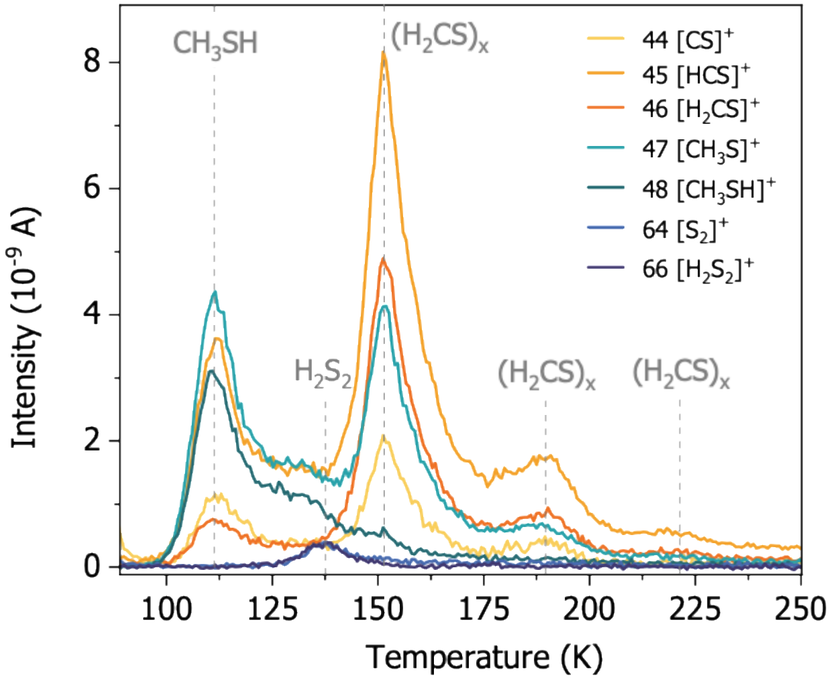
Qasim+20

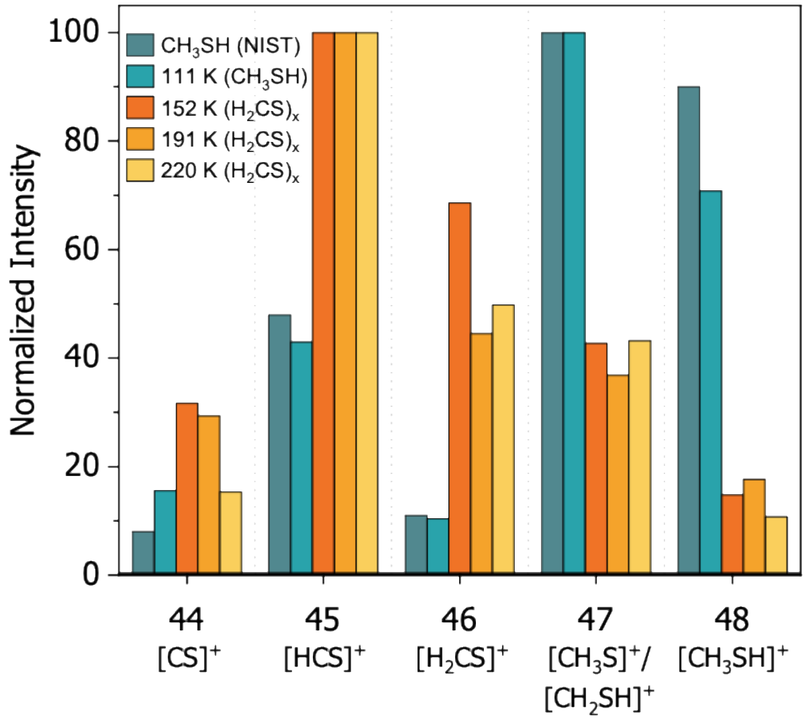




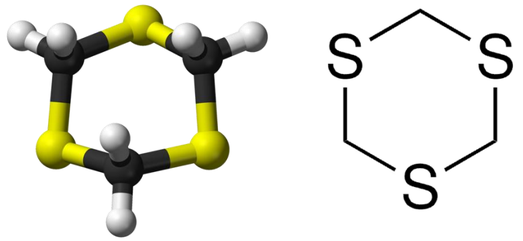
C + H + H_2S: TPD

H_2CS and CH_3SH desorb at different temperatures with distinct fragmentation patterns



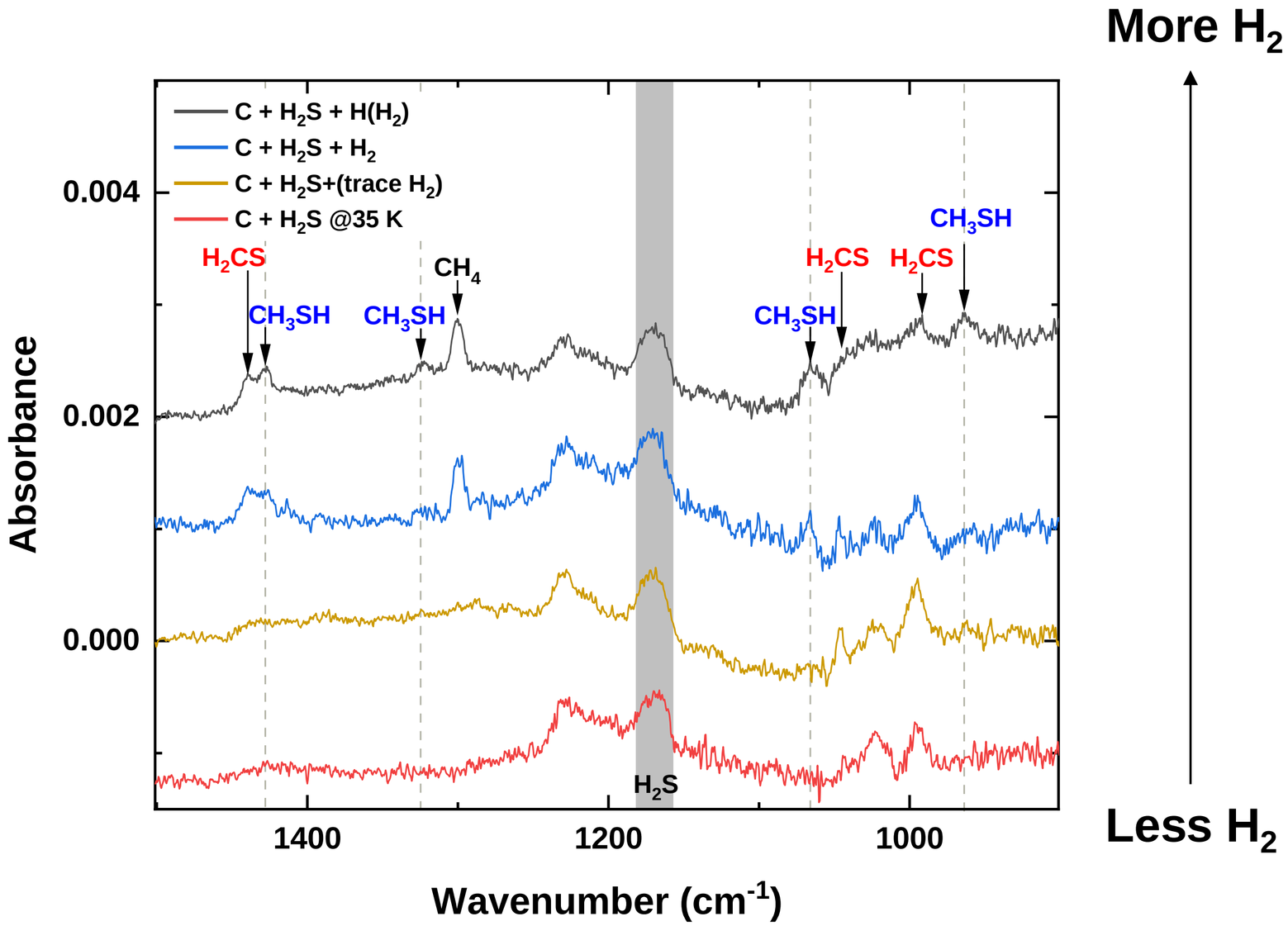


- CH_3SH
  - IR spectra and fragments match with NIST database
- H_2CS:
  - C + H_2S
  - T_{des} higher than expected, might be forming a trimer or bigger oligomers



C + H/H_2 + H_2S: IR SPECTRA

H_2CS and CH_3SH formation in various H/H_2 conditions



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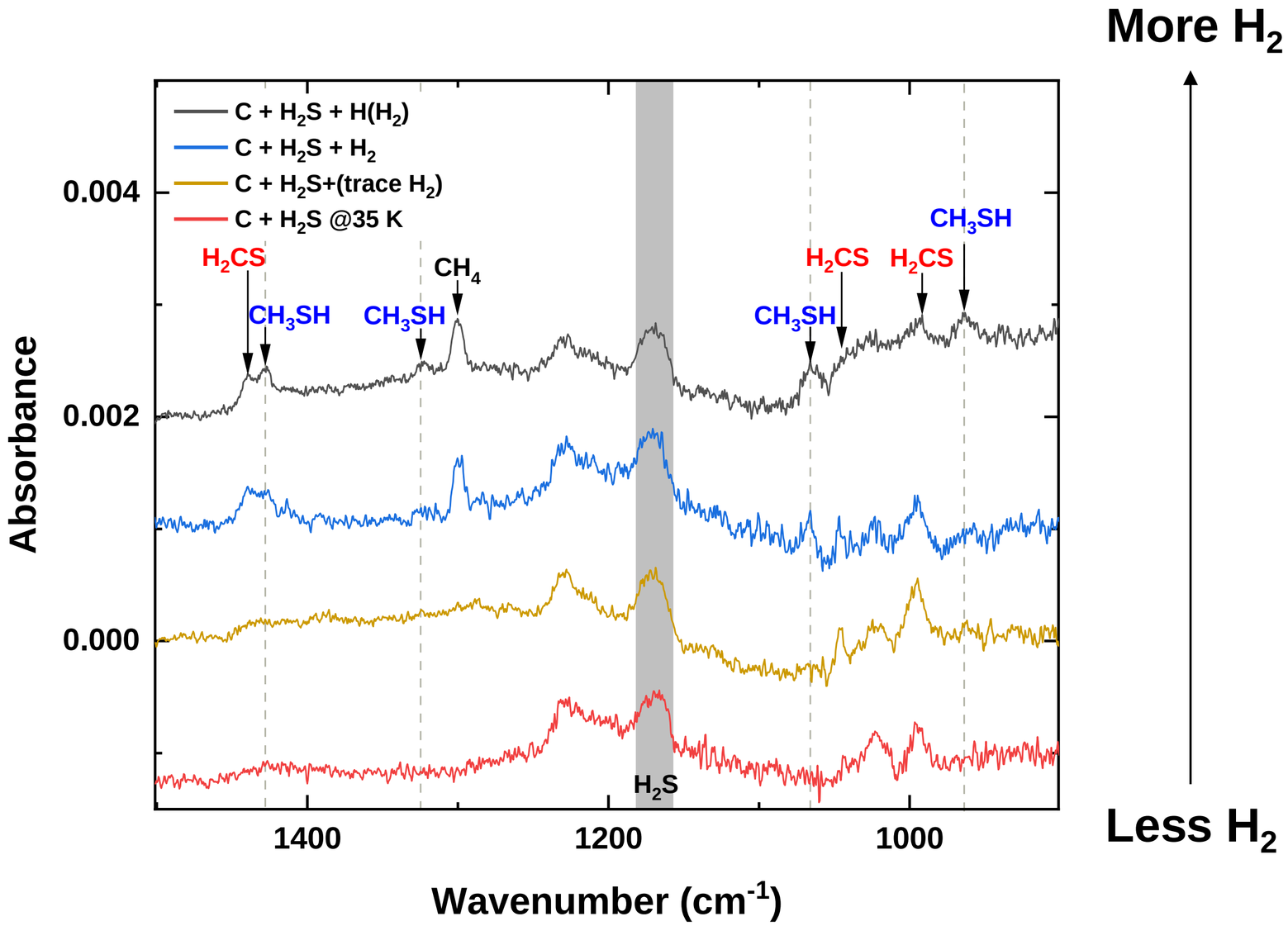
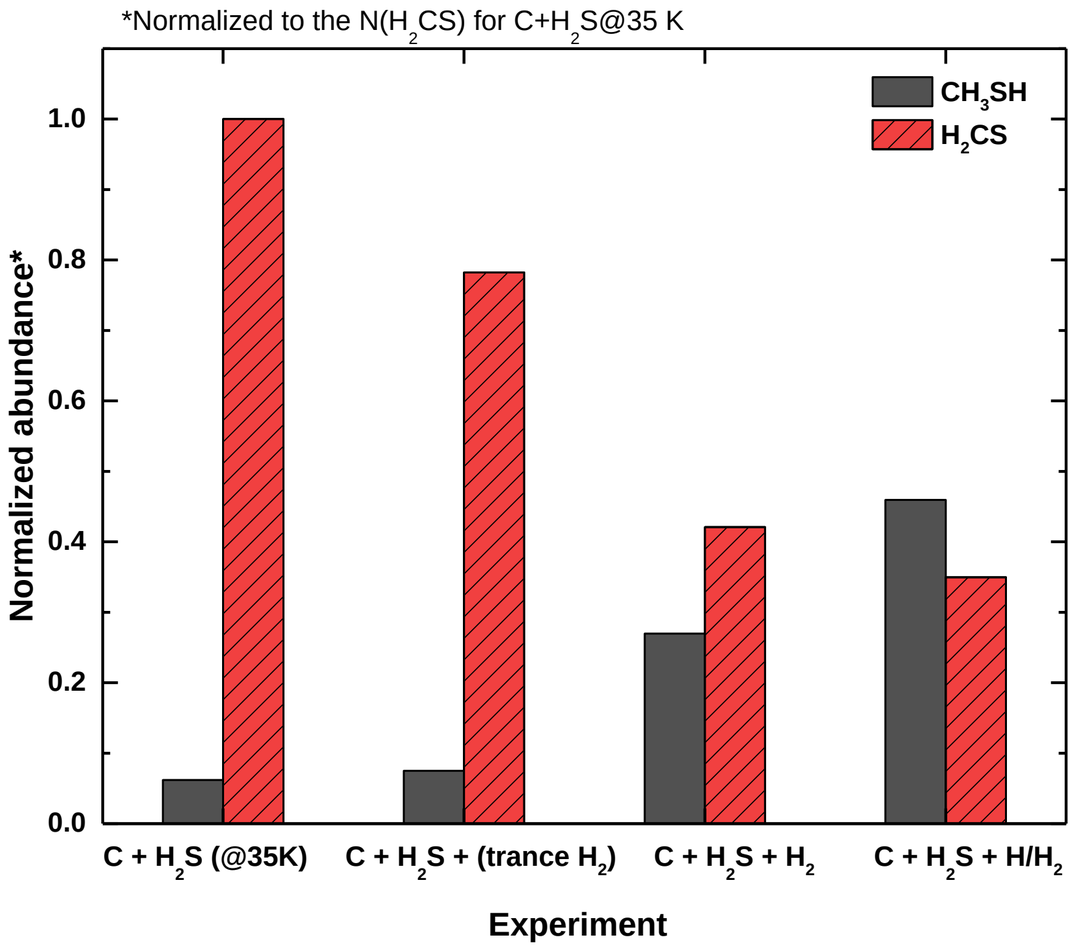


$C + H/H_2 + H_2S$

H_2CS and CH_3SH formation with different efficiencies

$C + H_2S \longrightarrow H_2CS$

the absence or with very low H/H_2, H_2CS dominates



Contributes to CH_4 formation

$$C \xrightarrow{+H_2} CH_2 \xrightarrow{+H_2} CH_4$$

Lamberts+2022

$$C \xrightarrow{+H_2} CH_2$$

$$CH_2 \xrightarrow{+H_2S} CH_3SH$$

formation of CH_3SH predominates

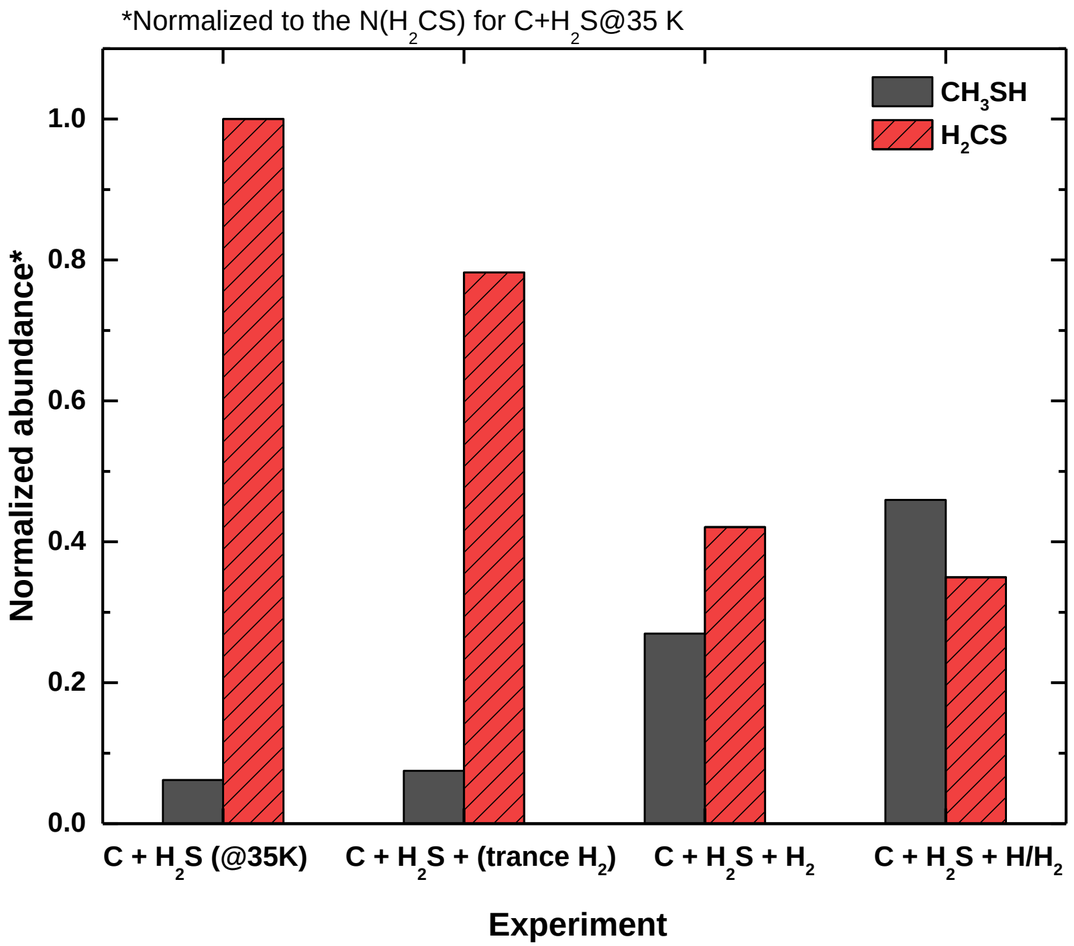
Less H/H_2 ⟶ **More H/H_2**

$C + H/H_2 + H_2S$

H_2CS and CH_3SH formation with different efficiencies

$C + H_2S \longrightarrow H_2CS$

the absence or with very low H/H_2, H_2CS dominates



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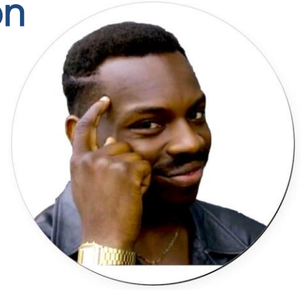
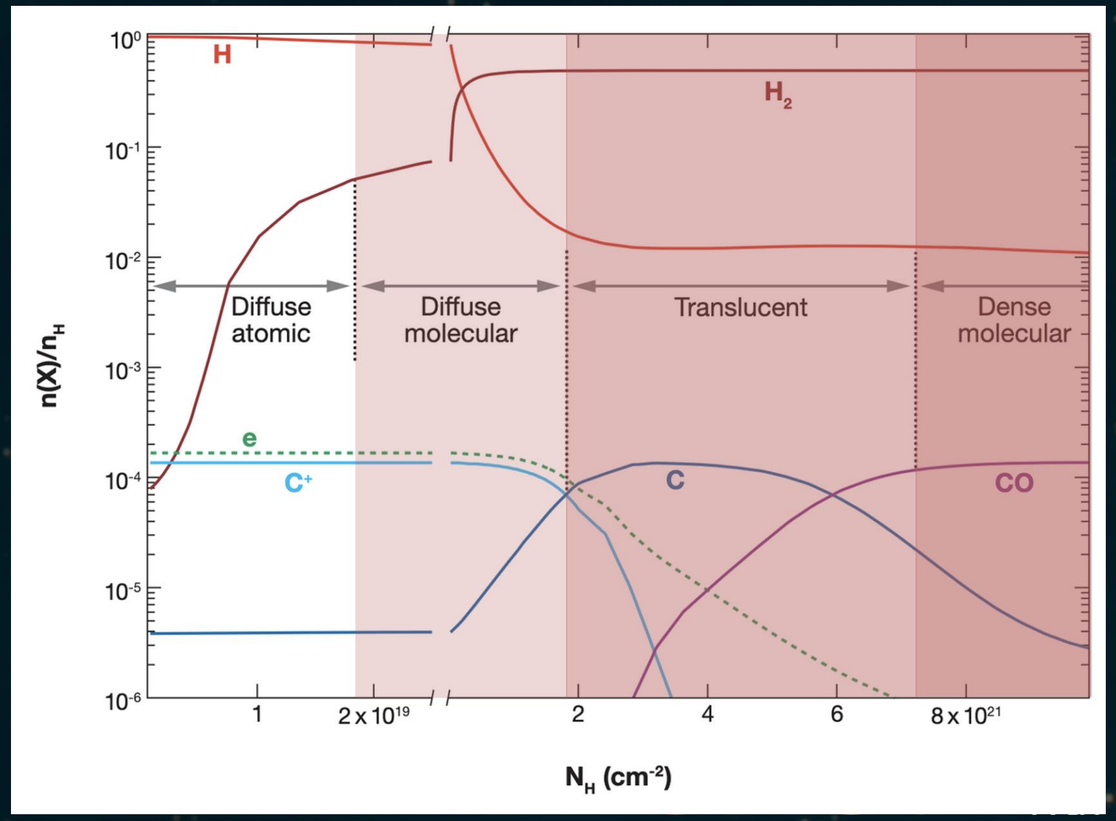
Beyond CS hydrogenation

Less H/H_2 ⟶ **More H/H_2**



Prestellar core chemistry

…and where C + H_2S + H_2 is relevant



Snow & McCall, 2006

van Dishoeck & Black (1989)

H_2 is 2 - 4 x more abundant than H!

Where

$H_2S_{(s)} + H_{2\,(g)} + C_{(g)}$

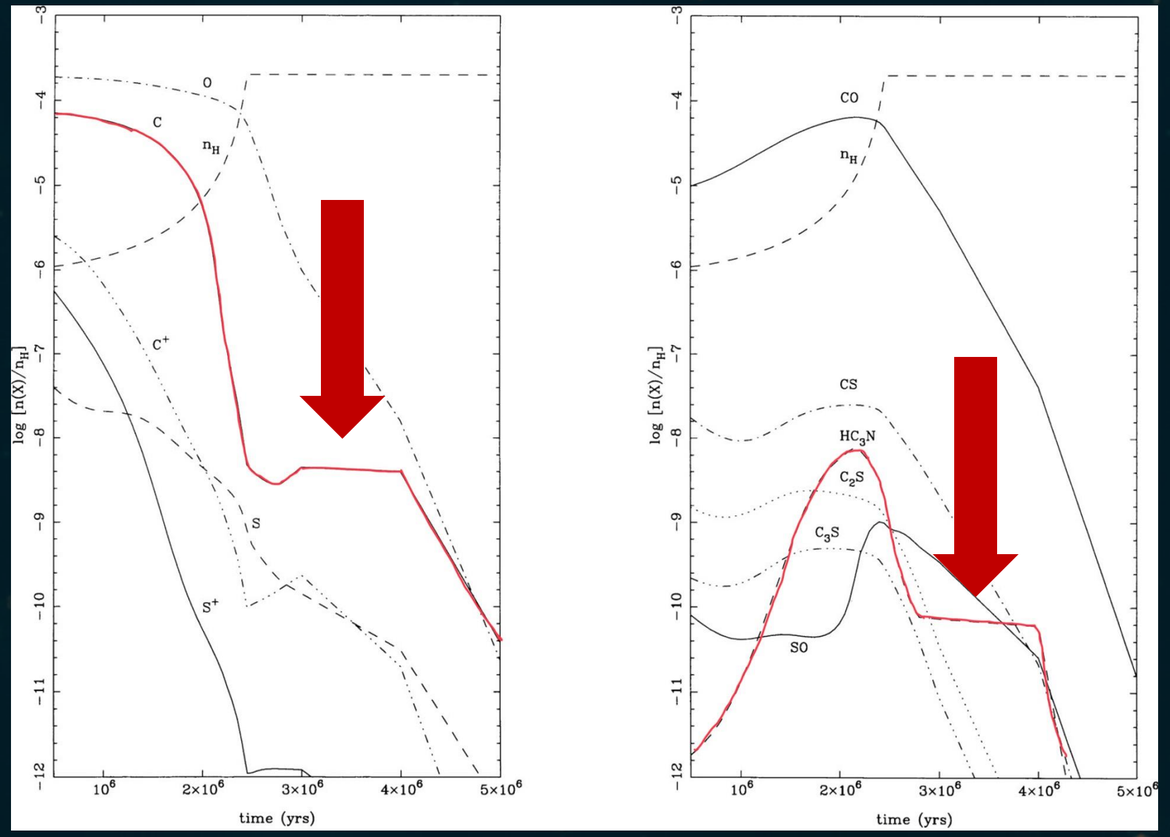
is available simultaneously?

Prestellar core chemistry

…and where C + H_2S + H_2 is relevant

At low abundances CO can be destroyed by He^+ and C atoms are available at denser regions

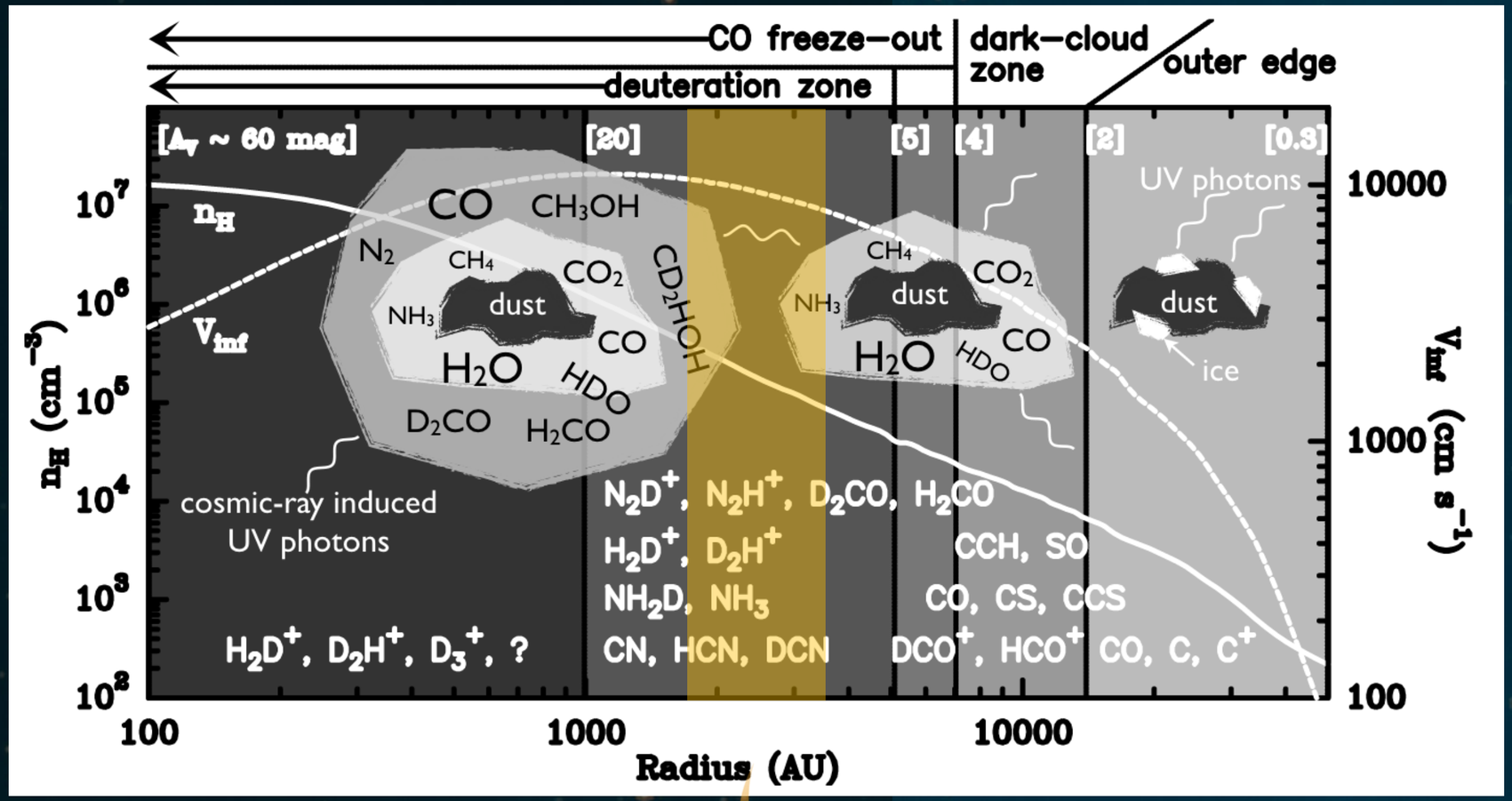
chemical model of a collapsing cloud



Ruffle+99

Prestellar core chemistry

Increasing density, decreasing temperature



Ceccarelli+PPVI 2014

$$H_2 \xrightarrow{cr} H_2^+ \xrightarrow{H_2} H_3^+$$

Central in gas-phase reactions

$$H_3^+ + HD \longrightarrow H_2D^+ + H_2 + 230\ K$$

Watson+1974

$$H_2S_{(s)} + H_2/H/C_{(g)}$$

Lab Astro meeting

Ringberg Castle, Oct24

Lab Astro meeting

Ringberg Castle, Oct24

Connection with observations

Deuteration fractions and S-chemistry

CH_3SH
Methyl Mercaptan

$$CS \xrightarrow{+H} HCS \xrightarrow{+H} H_2CS \xrightarrow{+H} CH_3S \xrightarrow{+H} CH_3SH$$

Lamberts+18

Beyond CS hydrogenation:

$$C \xrightarrow{+H_2} CH_2$$

$$CH_2 \xrightarrow{+H_2S} CH_3SH$$

Table 2
Column Density Ratios of CH_2DSH Compared with H_2CS, CH_3OH, and H_2CO toward IRAS 16293−2422 B

Ratio	Value (%)	
	IRAS 16293−2422 B	L1544
CH_2DSH/CH_3SH	5.5 ± 0.5	N/A
$HDCS/H_2CS$	10.0 ± 1.4	11.6 ± 1.8
H_2CS/CH_3SH	27.3 ± 7.71	2760.0 (lower limit)
$HDCS/CH_2DSH$	50 ± 11	N/A
CH_2DOH/CH_3OH	7.1 ± 2.0	21.5 ± 5.4
$HDCO/H_2CO$	6.8 ± 1.2	3.5 ± 2.2
H_2CO/CH_3OH	19.0 ± 5.4	282.3 ± 177.2
$HDCO/CH_2DOH$	18.3 ± 5.18	46.4 ± 12

Bunn+2025

Formation of CH_3SH from H_2CS is less efficient?
CH_3SH is still locked in the ice grains?

Wrap-up

From Experiments

- $C + H_2S \rightarrow H_2CS$
- $C + H_2S + H \rightarrow H_2CS$ and CH_3SH (plus competing reactions, such as CH_4)
- $C + H_2S + H_2 \rightarrow H_2CS$ and CH_3SH (plus competing reactions, such as CH_4)

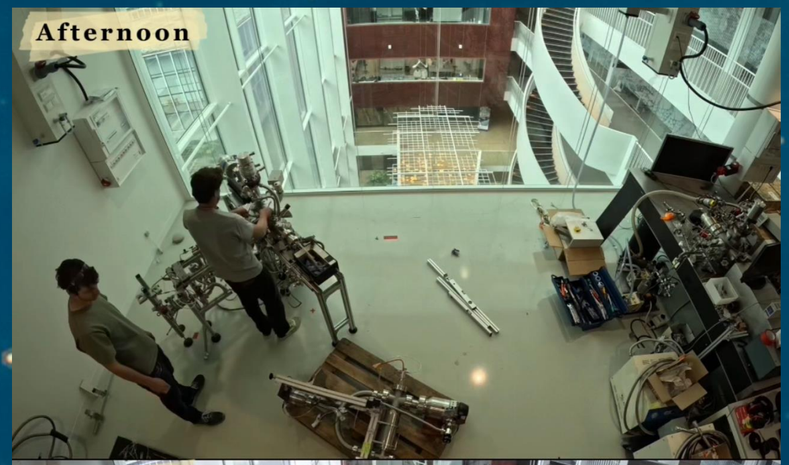
From observations:

- CO freeze-out + low temperatures:
  - At low abundances CO can be destroyed by He^+ and C atoms are available at denser regions (Ruffle+99)
  - Deuterium enrichment in gas and solid phases
  - Deuteration fractions of CH_3SH/CH_2DSH provide clues about the chemistry

Next steps:

- Include deuterium substitution reactions (D_2S/D_2) to understand in the detail the formation pathway of CH_3SH

Organic Reactions with Carbon and H in Interstellar Dust



This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 101153804

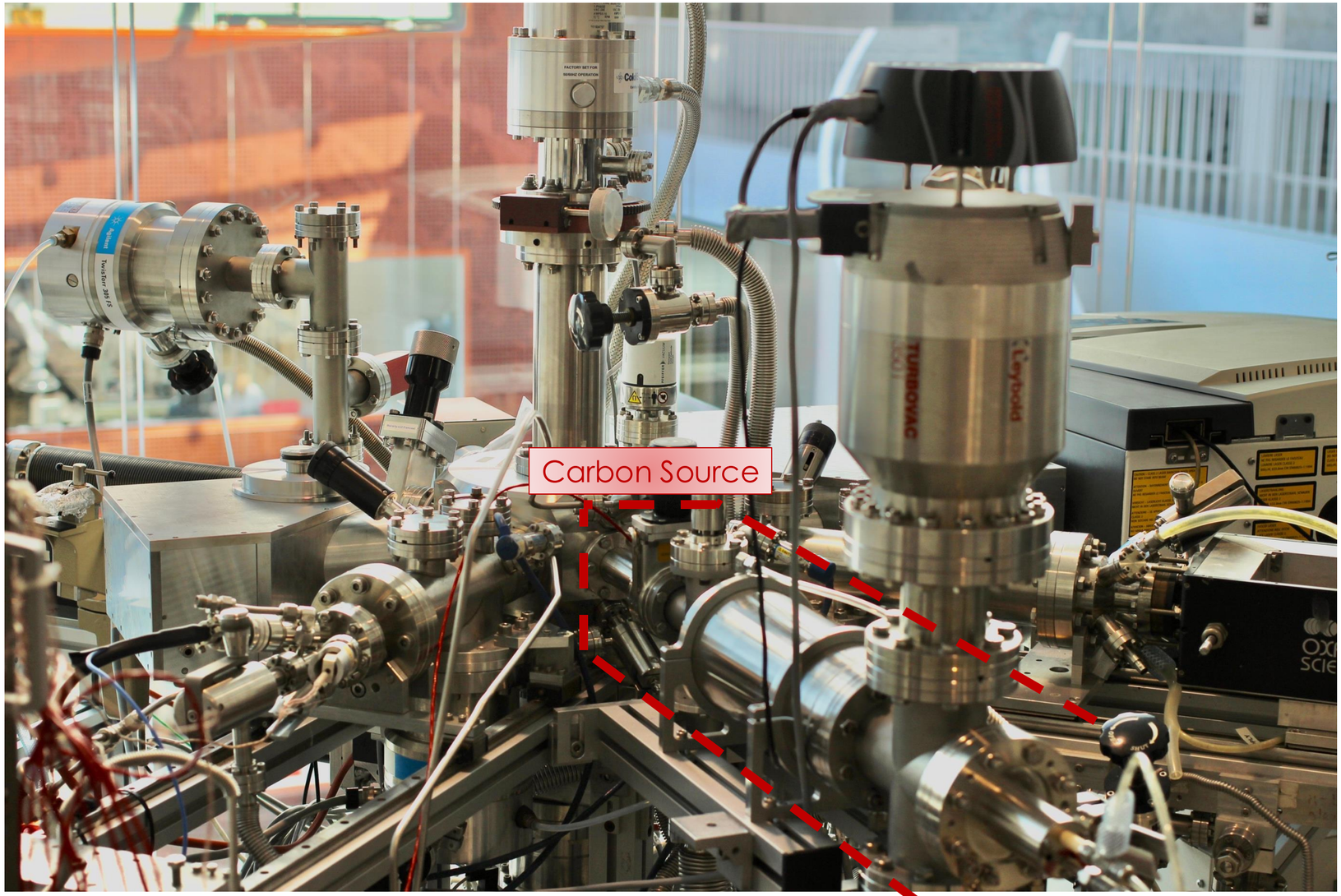
Universiteit Leiden
Leiden Observatory

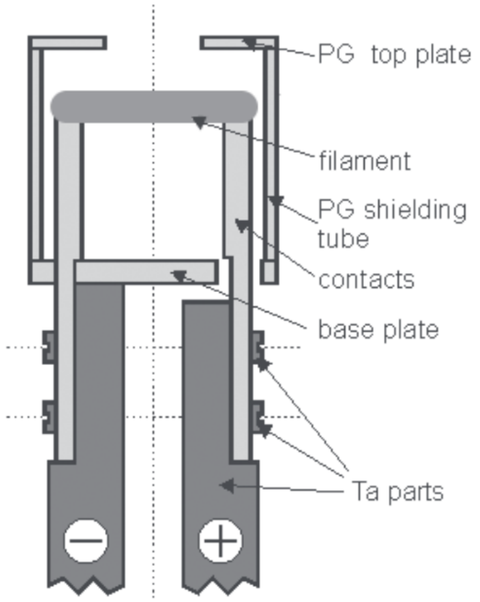
Sterrewacht Leiden

SURFRESIDE^3

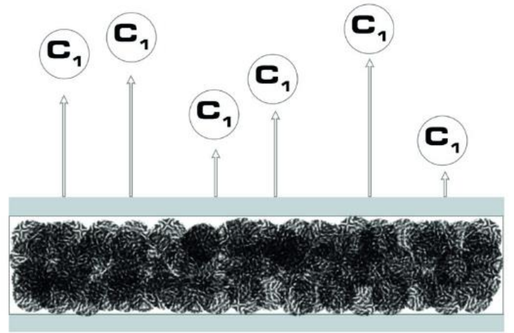
T = 10 – 450 K
P_{base} = 1 x 10^{-9} mbar

SURFace REactions SImulation DEvice III





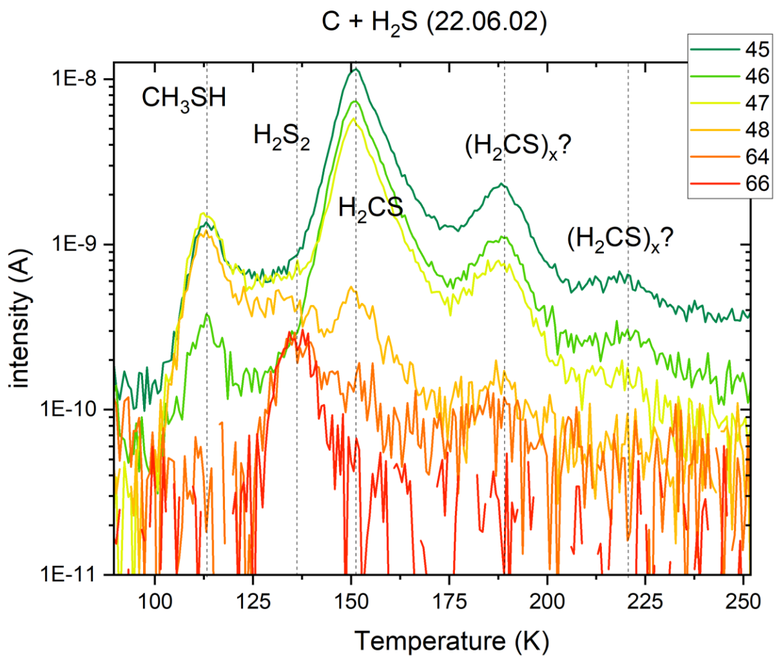
Main parts of the SUKO-A assembly

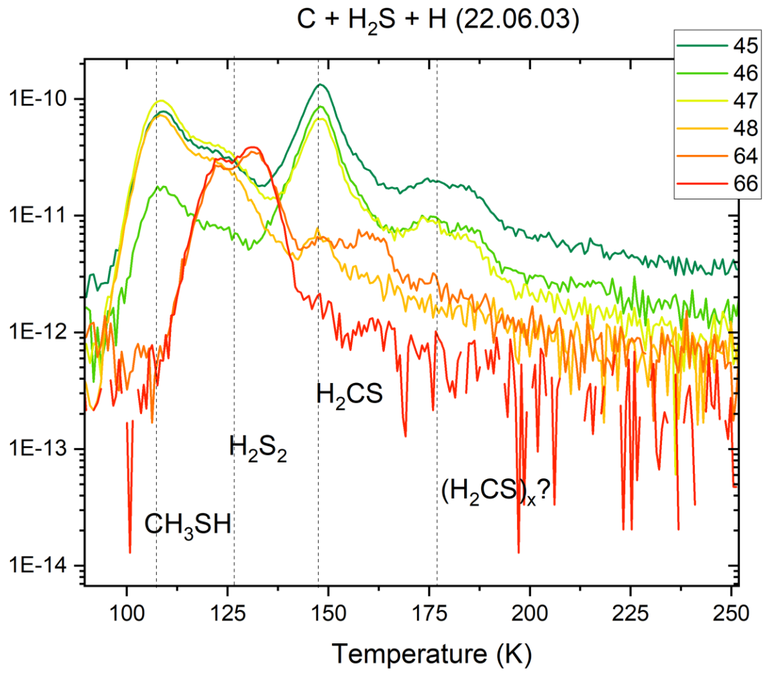


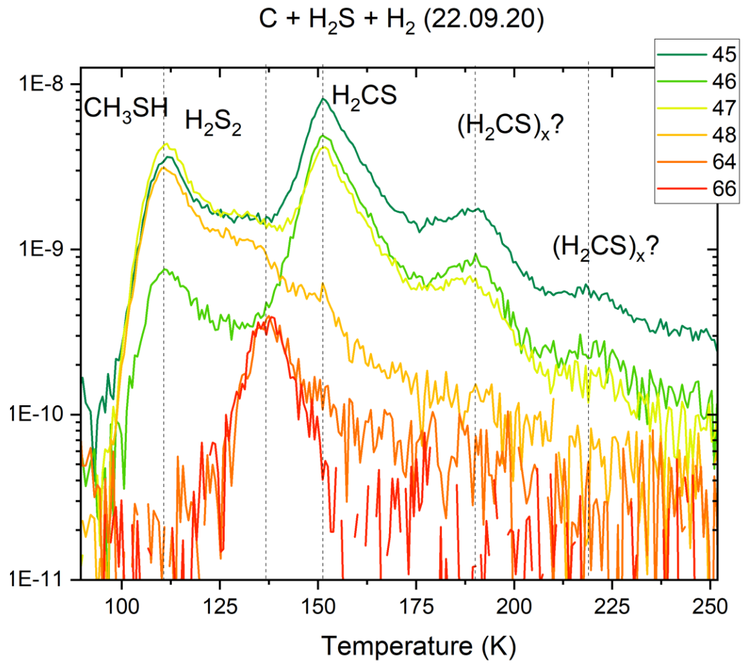
Schematic effusion of highly reactive C_1 carbon

Carbon in the ground state – (^{3}P)C

Commercial design MBE SUKO-A; Krasnokutski & Huisken 2014; Albar+17


C + H2S (22.06.02)
intensity (A)
1E-8
1E-9
1E-10
1E-11
CH3SH
H2S2
H2CS
(H2CS)x?
(H2CS)x?
45
46
47
48
64
66
100
125
150
175
200
225
250
Temperature (K)


C + H2S + H (22.06.03)
1E-10
1E-11
1E-12
1E-13
1E-14
H2CS
H2S2
(H2CS)x?
CH3SH
45
46
47
48
64
66
100
125
150
175
200
225
250
Temperature (K)

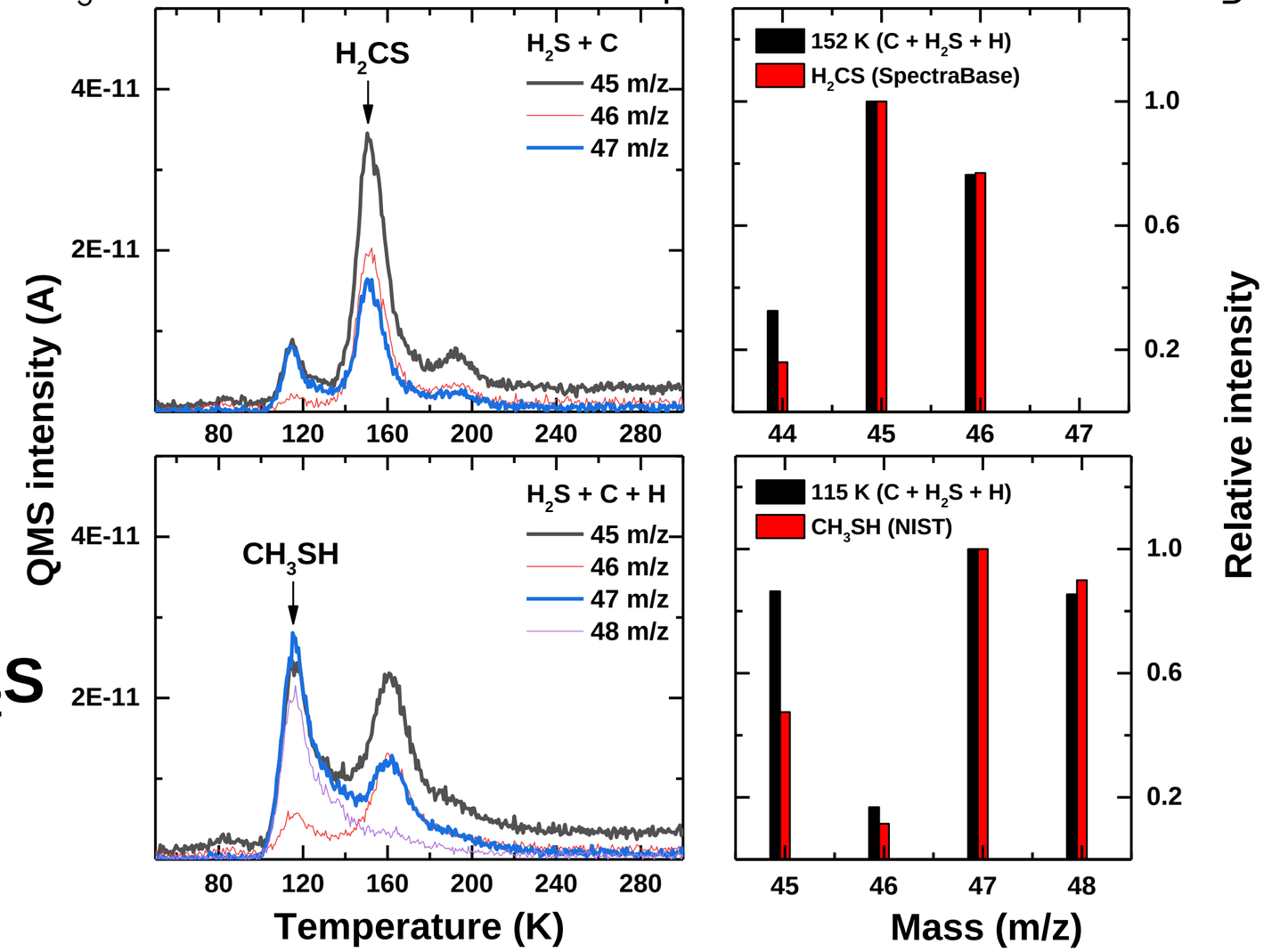

C + H2S + H2 (22.09.20)
1E-8
1E-9
1E-10
1E-11
CH3SH
H2S2
H2CS
(H2CS)x?
(H2CS)x?
45
46
47
48
64
66
100
125
150
175
200
225
250
Temperature (K)

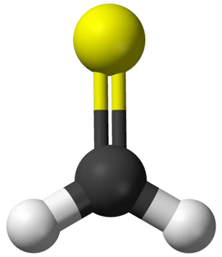
C + H + H_2S: TPD-QMS SPECTRA

H_2CS and CH_3SH desorb at different temperatures with distinct fragmentation patterns

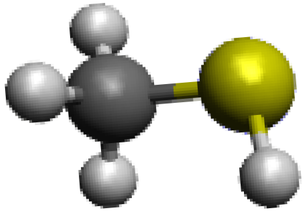
C + H_2S

C + H + H_2S





H_2CS
Thioformaldehyde



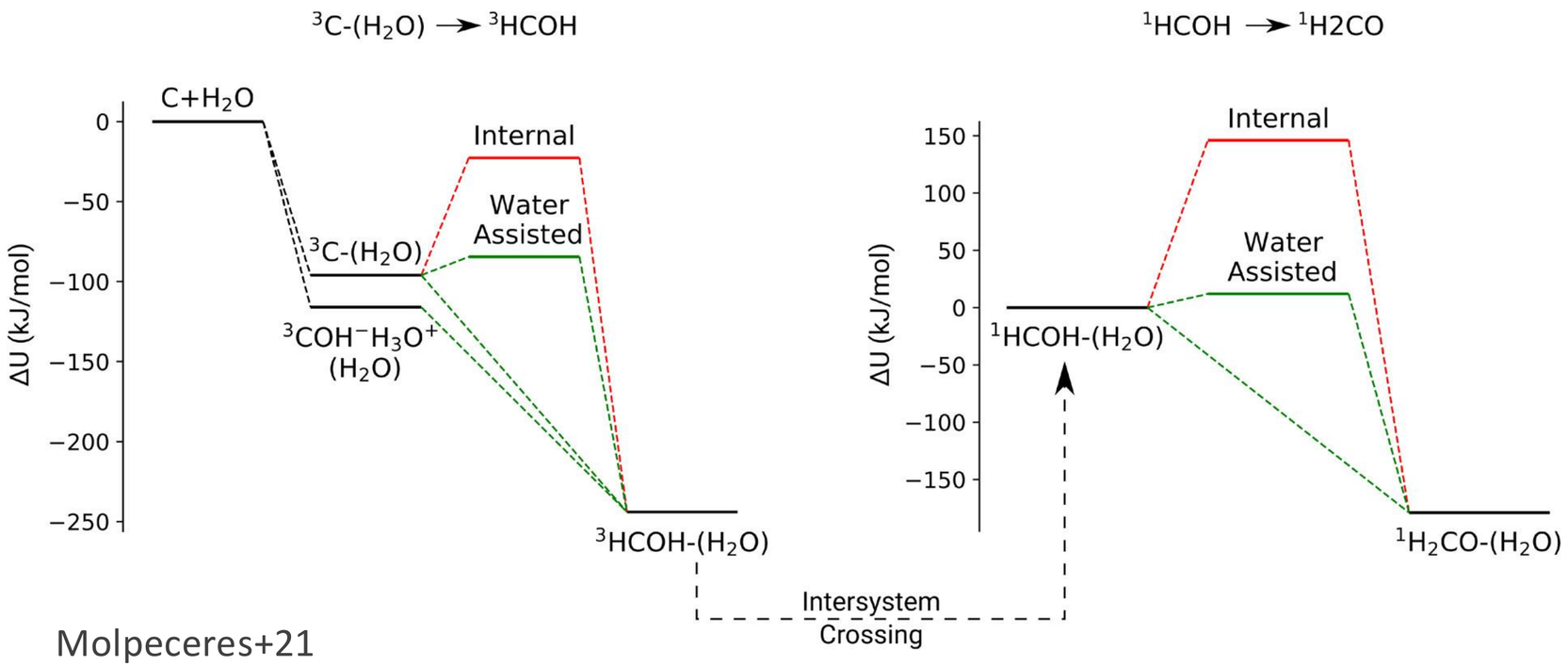
CH_3SH
Methyl Mercaptan

Which mechanisms and barriers are into play?

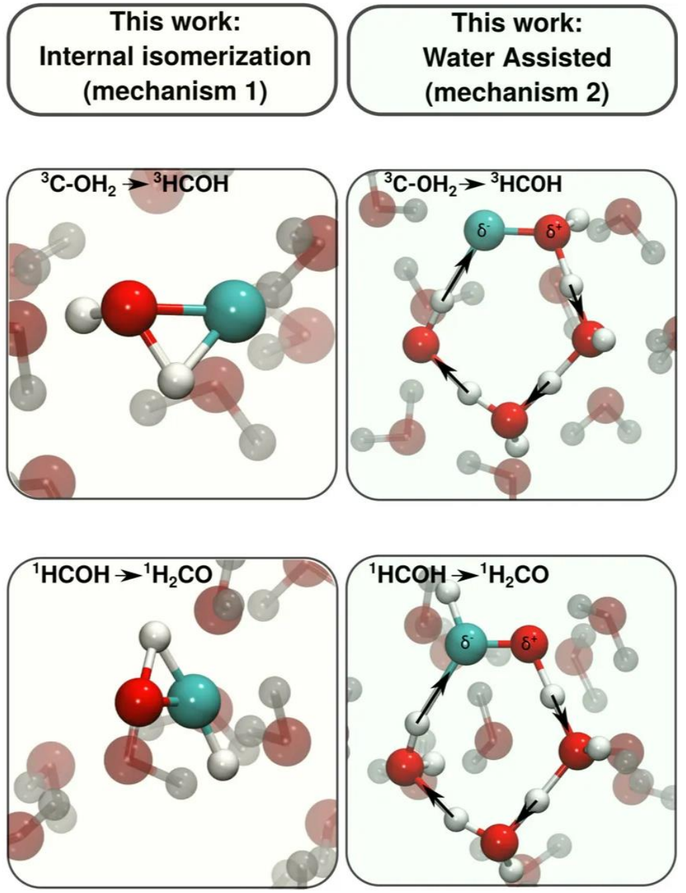
$C + H_2 + H_2S$

2) "H-assisted" mechanism

e.g. Molpecere+21, Ferrero+23



Molpeceres+21



Molpeceres+21

$C + H_2O \rightarrow H_2CO$

proceeds barrierless due to a catalytic effect provided by the H-bonded networks from water