Unlocking the Chemistry of the Heavens

Solid state pathways towards molecular complexity in space

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Nederlandse Organisatie voor Wetenschappelijk Onderzoek

Universiteit Leiden

LASSIE

FOM

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The laboratory perspective

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Molecules detected in the I[illegible]M/CSM

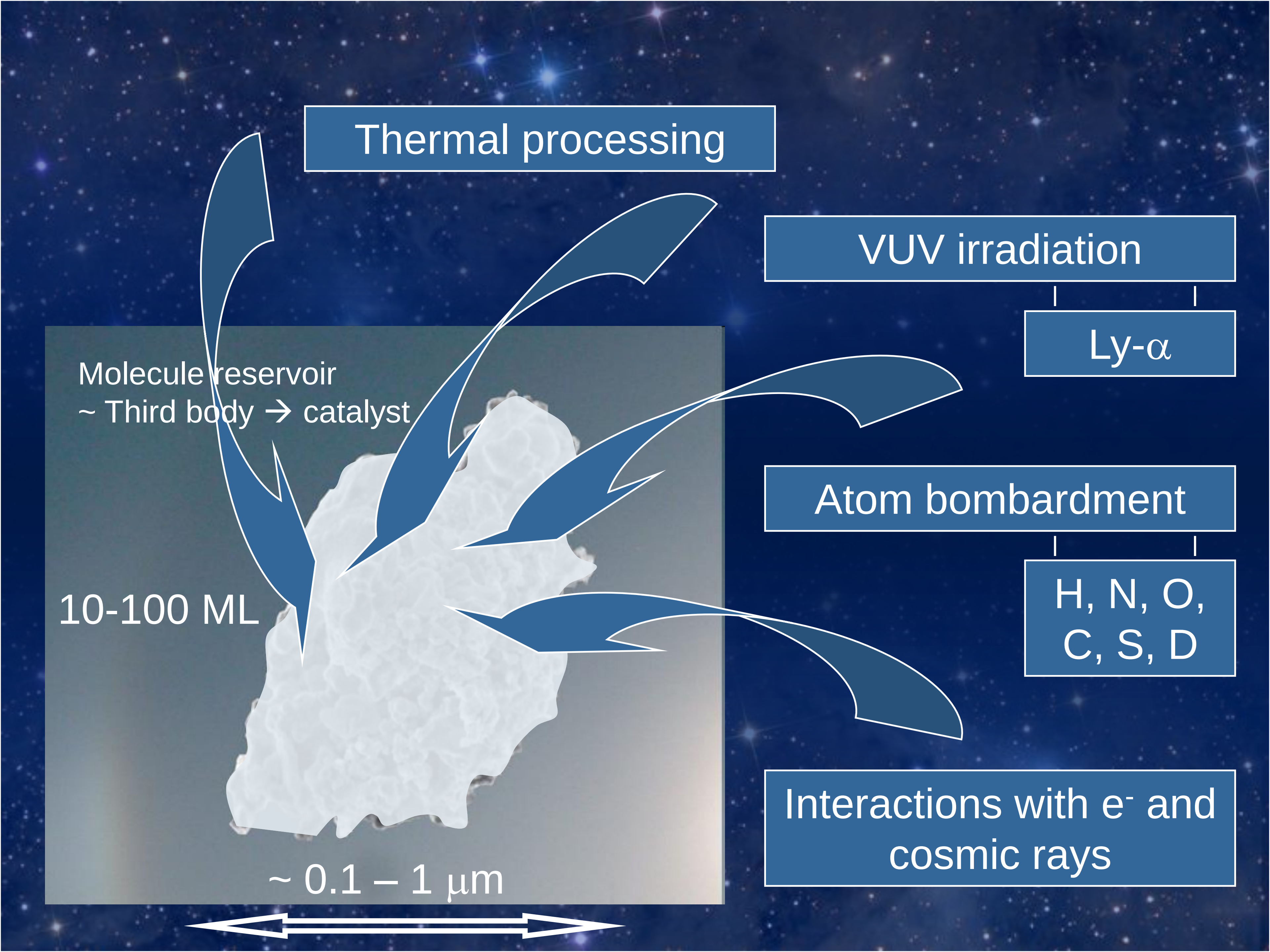
Regular species, ions, exotic radical[illegible]mplex molecules

2		3		4	[illegible]	[illegible]	7	8-9	10-13
H_2	PN	C_3	OCS	[illegible]	[illegible]	C_5H	C_6H	[illegible]	CH_3C_5N
AlF	SO	C_2H	NaCN	[illegible]	[illegible]	$l\text{-}H_2C_4$	CH_2CHCN	[illegible]	$(CH_3)_2CO$
AlCl	SO^+	C_2O	[illegible]	[illegible]	C_4Si	C_2H_4	[illegible]	[illegible]	$(CH_2OH)_2$
C_2	SiN	[illegible]	[illegible]	[illegible]	$l\text{-}C_3H_2$	CH_3CN	[illegible]	[illegible]	CH_3CH_2CHO
CH	[illegible]	[illegible]	[illegible]	C_3S	$c\text{-}C_3H_2$	[illegible]	[illegible]	H_2C_6	
[illegible]	[illegible]	[illegible]	NH_2	C_2H_2	CH_2CN	[illegible]	[illegible]	CH_2OHCHO	[illegible]
[illegible]	[illegible]	HCO	H_3^+	HCCN	[illegible]	[illegible]	$c\text{-}C_2H_4O$		[illegible]
CO	HF	HCO^+	SiCN	[illegible]	[illegible]	[illegible]	CH_2CHOH	[illegible]	[illegible]
CO^+	SH	HCS^+	SiNC	[illegible]	[illegible]	HC_2CHO	C_6H^-	[illegible]	[illegible]
CP	CF^+	HOC^+	[illegible]	[illegible]	[illegible]	NH_2CHO		[illegible]	(C_6H_6)
SiC	FeO	[illegible]	[illegible]	[illegible]	H_2CHN	C_5N	[illegible]	[illegible]	
HCl	SiH	[illegible]	[illegible]	H_2CO	H_2C_2O	[illegible]	[illegible]	HC_7N	$HC_{11}N$
KCl	O_2	[illegible]	[illegible]	H_2CN	H_2NCN	[illegible]	[illegible]	C_8H	
NH	CN^-	HNO		H_2CS	[illegible]	[illegible]		CH_3CONH_2	LARGE STUFF
NO		MgCN		[illegible]	[illegible]			C_8H^-	
NS		MgNC		[illegible]	[illegible]				PAHS ?
NaCl		N_2H^+		[illegible]	C_4H^-				C_{60}, C_{70}
OH		N_2O		CH_3	$CCCN^-$				

Reactions in the gas phase

Reactions on icy grains

Gas-grain interactions



Thermal processing
VUV irradiation
Ly-α
Atom bombardment
H, N, O,
C, S, D
Interactions with e- and
cosmic rays
Molecule reservoir
~ Third body → catalyst
10-100 ML
~ 0.1 – 1 μm

Research goals in solid state ice chemistry

- Spectroscopy of ice (IR & UV/VIS).
- Physical ice behavior: thermal desorption & ice segregation.

  Burke and Brow… RAS 2004, Fayolle et al. A&A, 2011.

- Atom additi… ons in ice.

  Watanabe and … A&A 2007, Cuppen et al. and Ioppo…

- VUV phot… photodesorption, photodissoc… sing.

  Caro et al. Scie… and ApJ 2009.

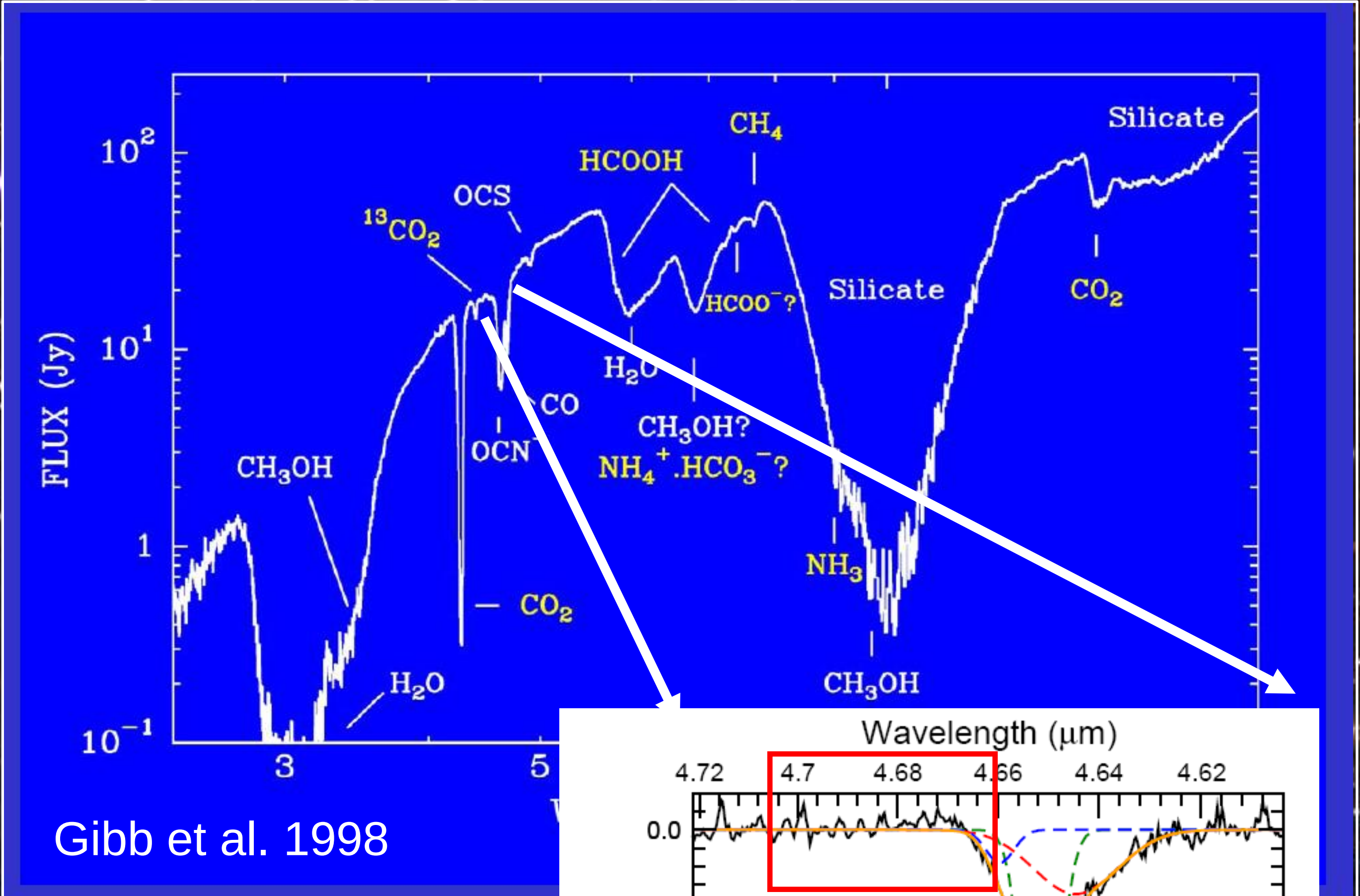
- Cosmic ray … ice

  Palumbo et al. A&A 2006.

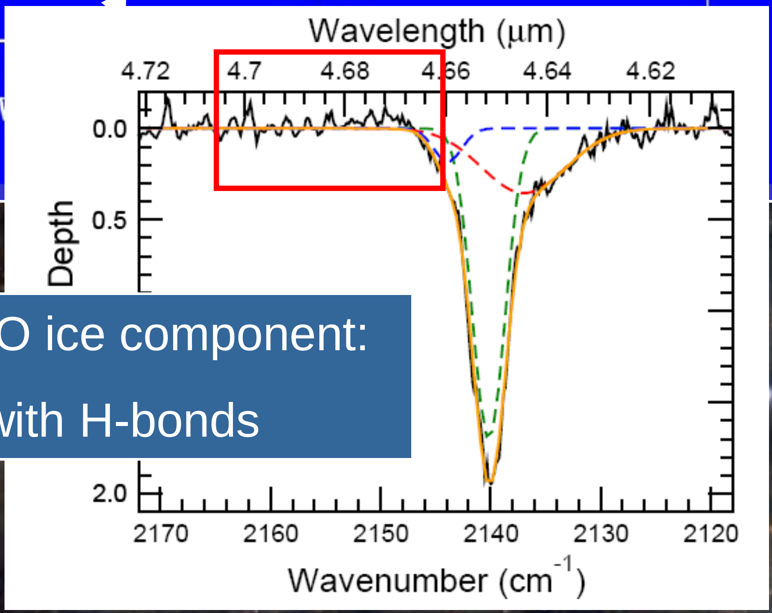
- Molecular complexity in ice, where does it end ?

1. Spectroscopy of ice

CO ice: water poor or water rich ?



Gibb et al. 1998



Red or Broad CO ice component:

CO interacting with H-bonds

H_2O

CO_2

CO

NH_3

CH_3OH

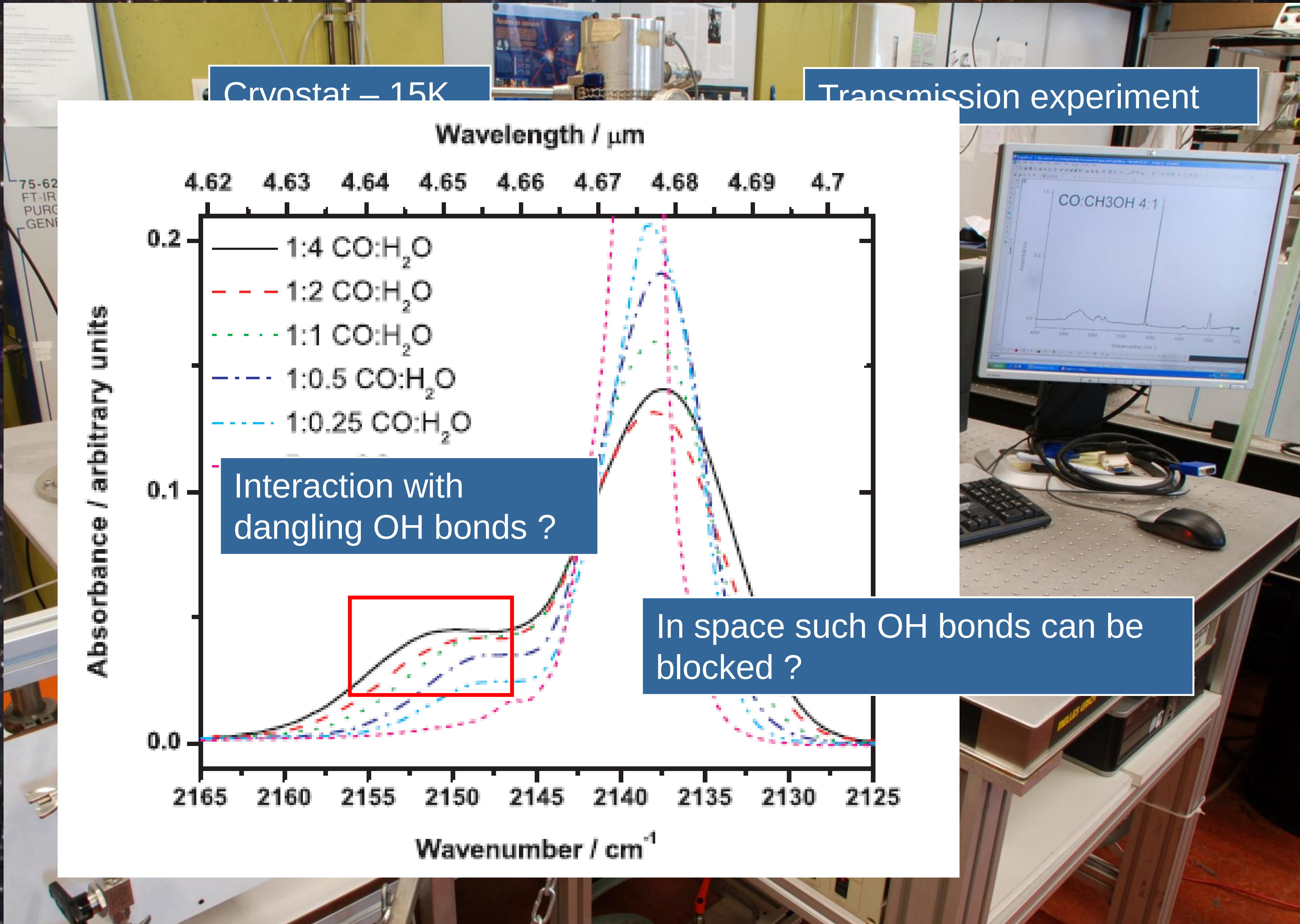
CH_4

H_2CO

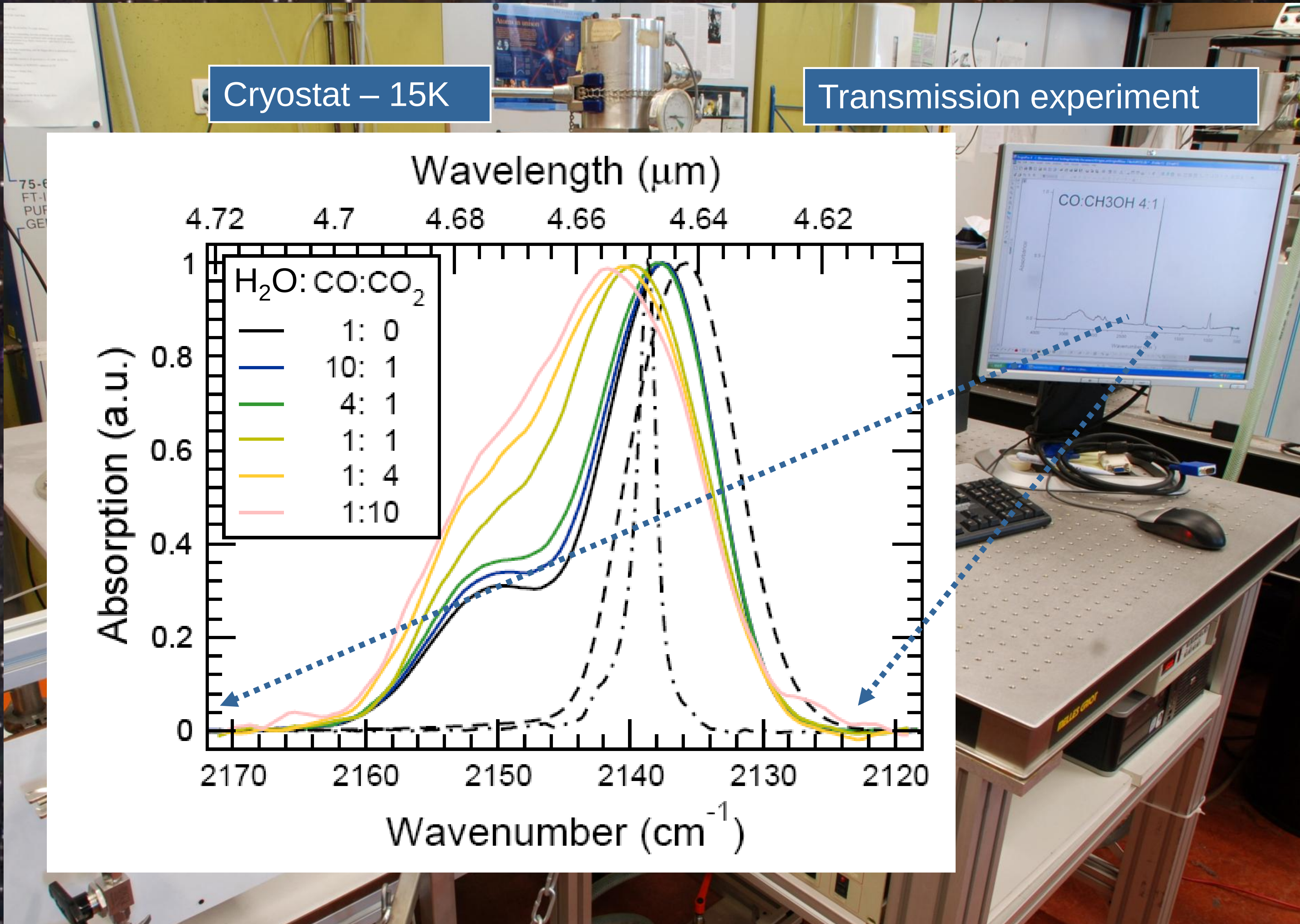
HCOOH

OCS

HCN

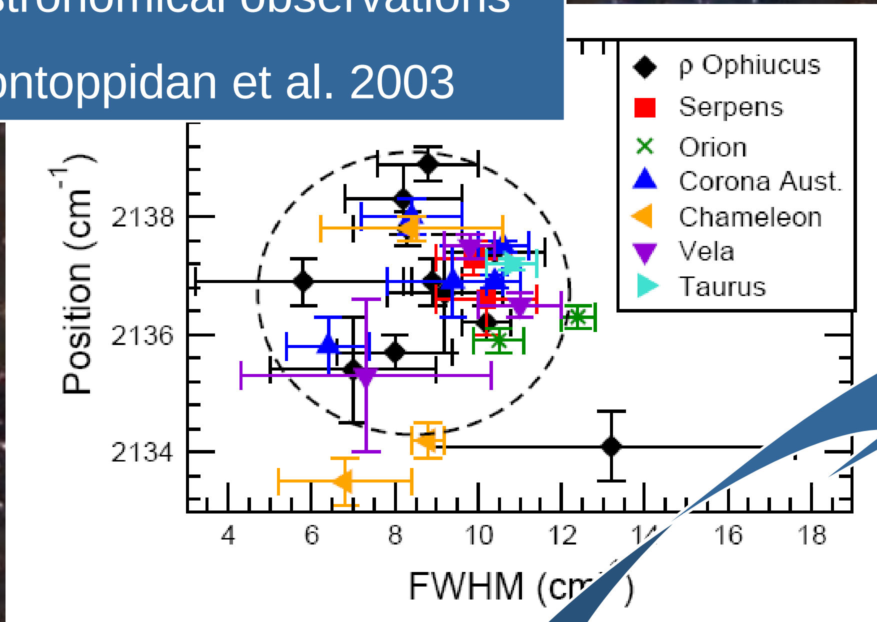


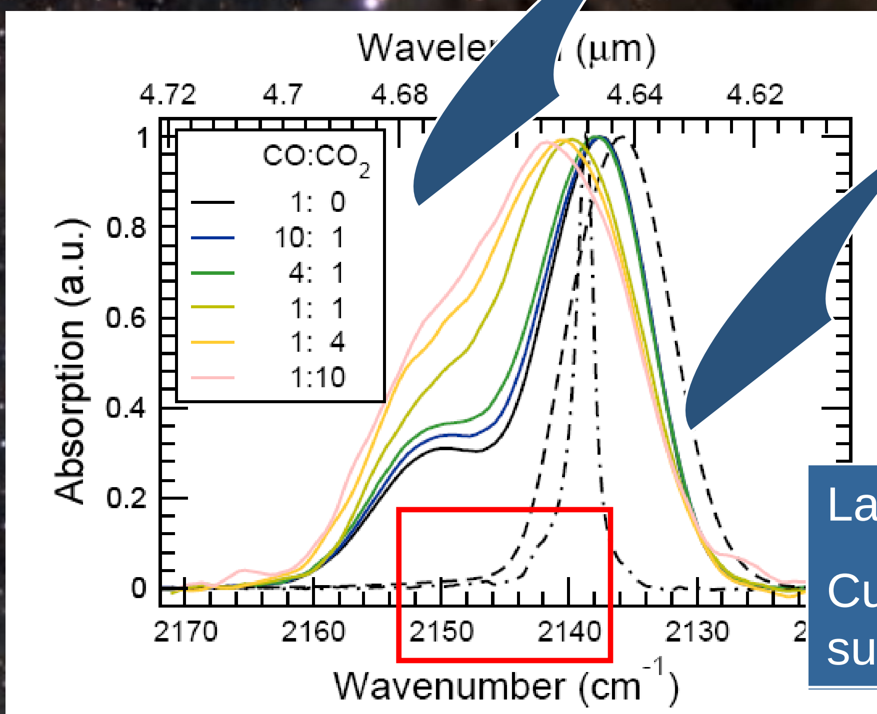
Cryostat – 15K
Transmission experiment
Wavelength / µm
4.62
4.63
4.64
4.65
4.66
4.67
4.68
4.69
4.7
Absorbance / arbitrary units
0.2
0.1
0.0
1:4 CO:H2O
1:2 CO:H2O
1:1 CO:H2O
1:0.5 CO:H2O
1:0.25 CO:H2O
2165
2160
2155
2150
2145
2140
2135
2130
2125
Wavenumber / cm-1
Interaction with dangling OH bonds ?
In space such OH bonds can be blocked ?
CO:CH3OH 4:1

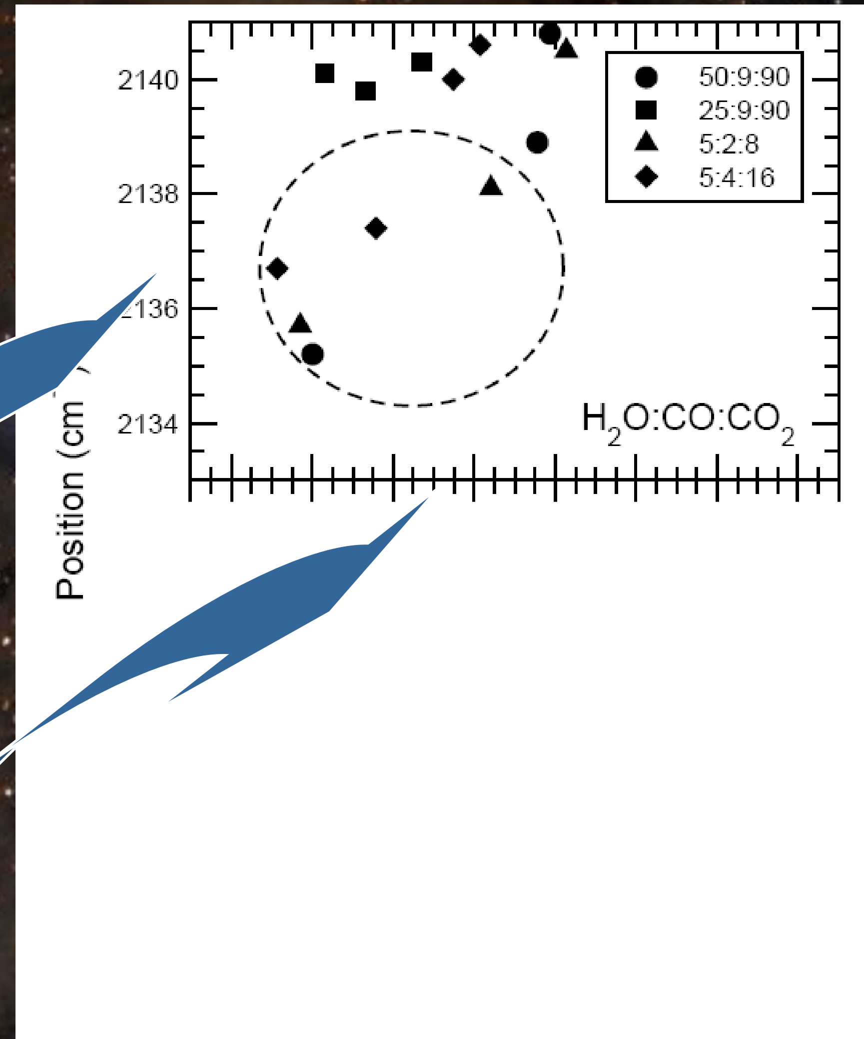

Cryostat – 15K
Transmission experiment
Wavelength (μm)
4.72
4.7
4.68
4.66
4.64
4.62
Absorption (a.u.)
1
0.8
0.6
0.4
0.2
0
H$_2$O: CO:CO$_2$
1: 0
10: 1
4: 1
1: 1
1: 4
1:10
2170
2160
2150
2140
2130
2120
Wavenumber (cm^{-1})
CO:CH3OH 4:1

Astronomical observations

Pontoppidan et al. 2003





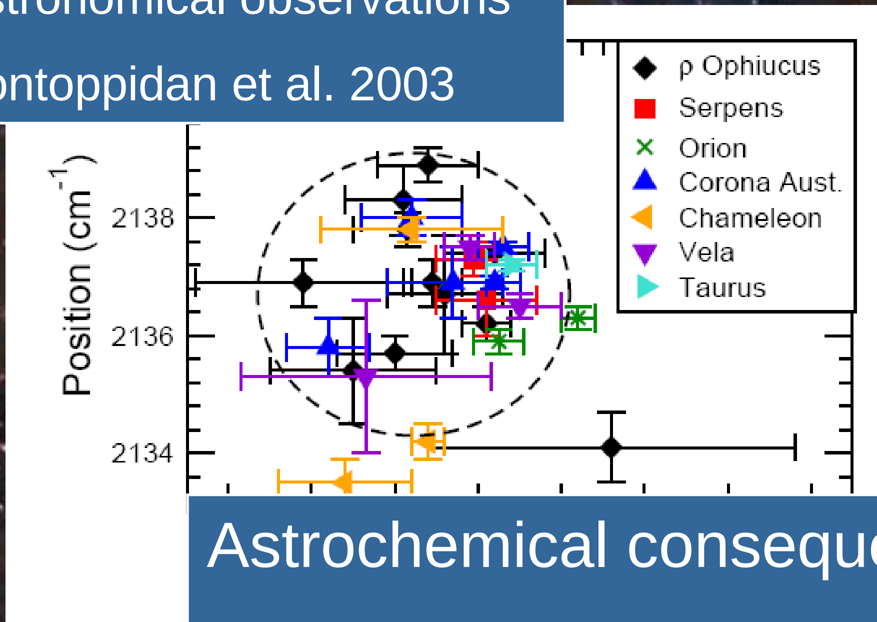


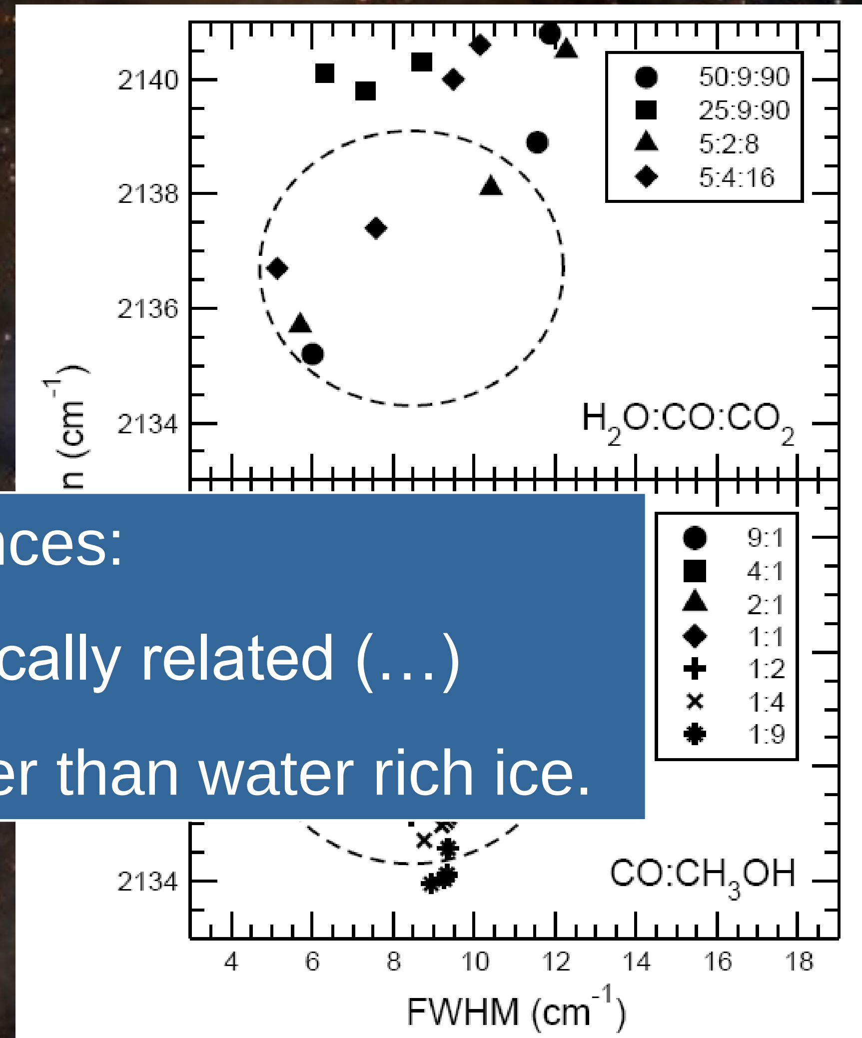
Laboratory data

Cuppen et al. MNRAS, submitted

Astronomical observations

Pontoppidan et al. 2003

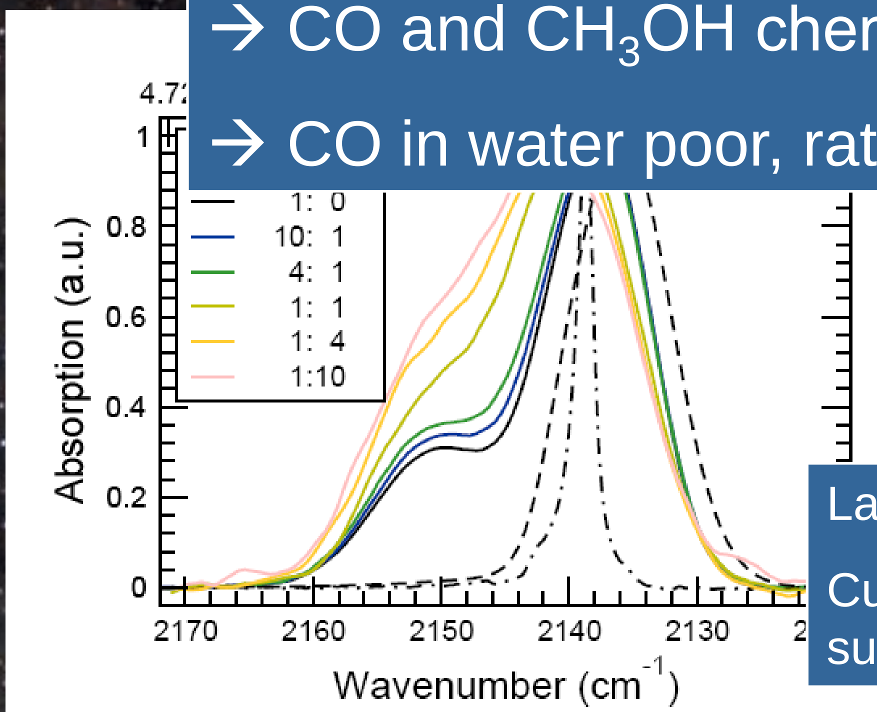




Astrochemical consequences:

→ CO and CH_3OH chemically related (…)

→ CO in water poor, rather than water rich ice.



Laboratory data

Cuppen et al. MNRAS, submitted

2. Atom addition reactions

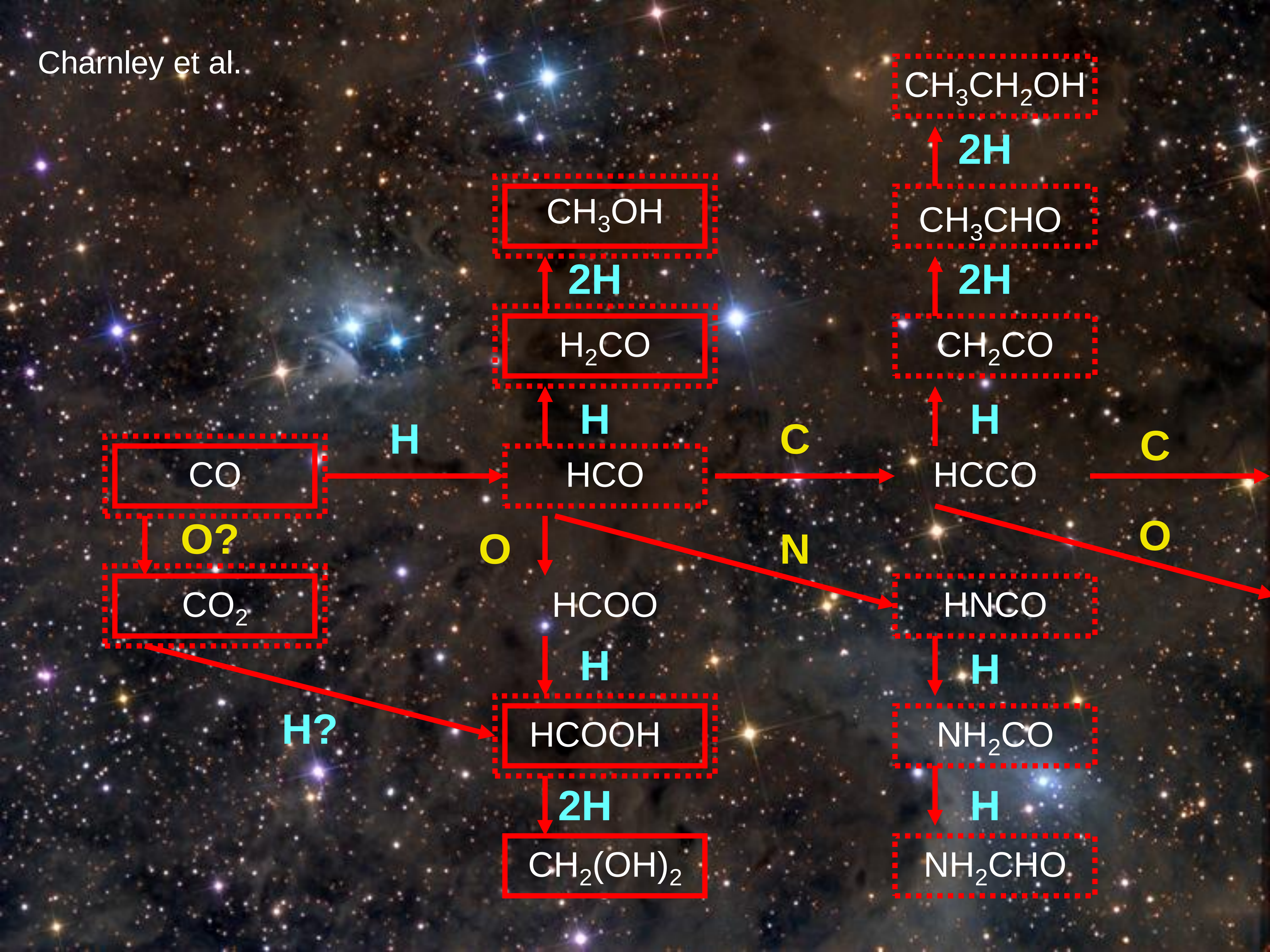
$CO + H$ — Hiraoka et al. ApJ. 1998/2002, Watanabe et al. ApJ 2002-2004, Fuchs et al. A&A 2007

$O + H/D$ — Mokrane et al. ApJ 2009, Dulieu et al. A&A, 2010,

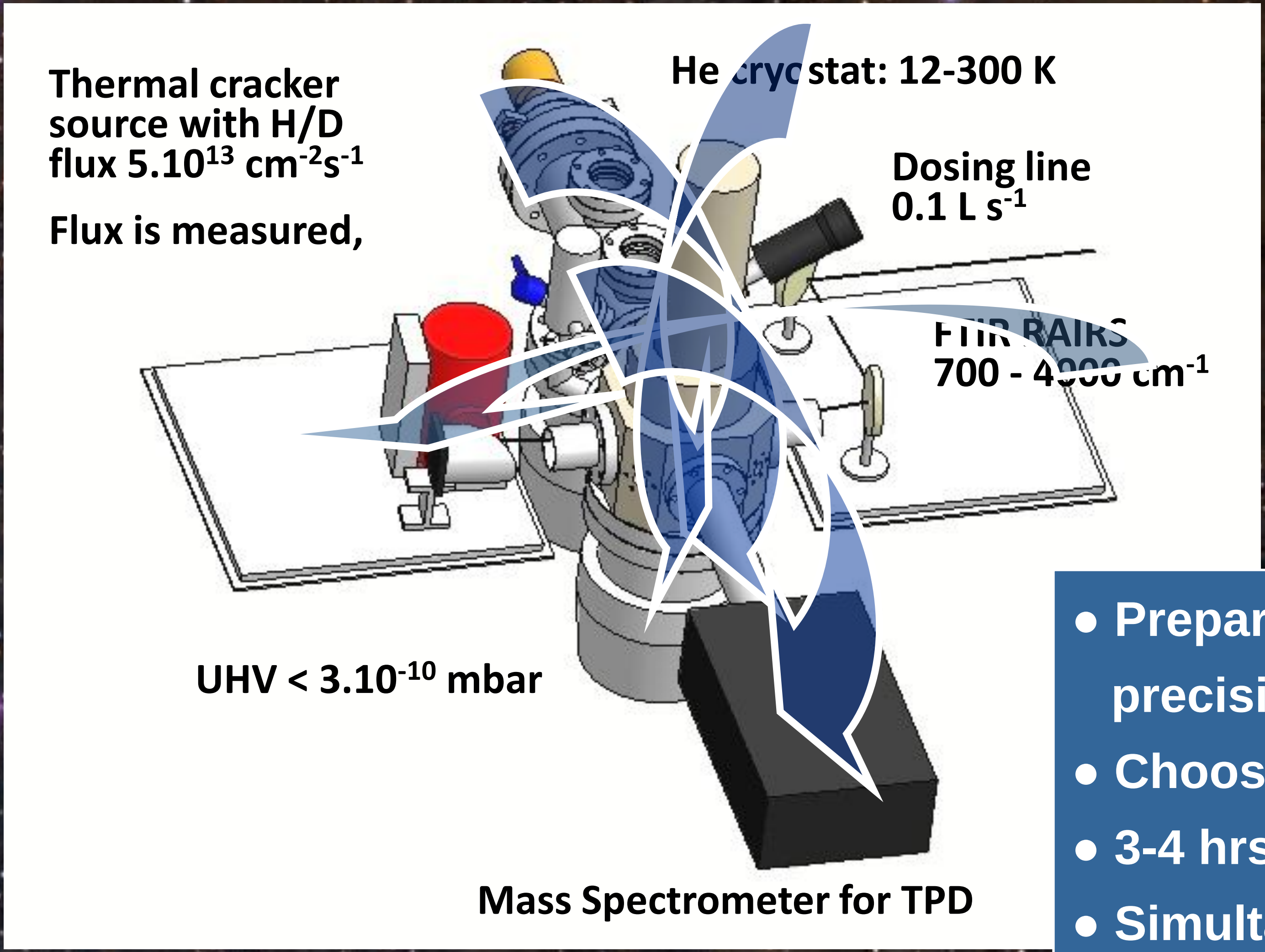
$O_2 + H/D$ — Miyauchi et al. CPL 2008, Ioppolo et al. ApJ 2008, Oba et al. ApJ 2009, Ioppolo et al. PCCP 2010, Cuppen et al. PCCP 2010

$O_3 + H/D$ — Romanzin et al. JCP 2011

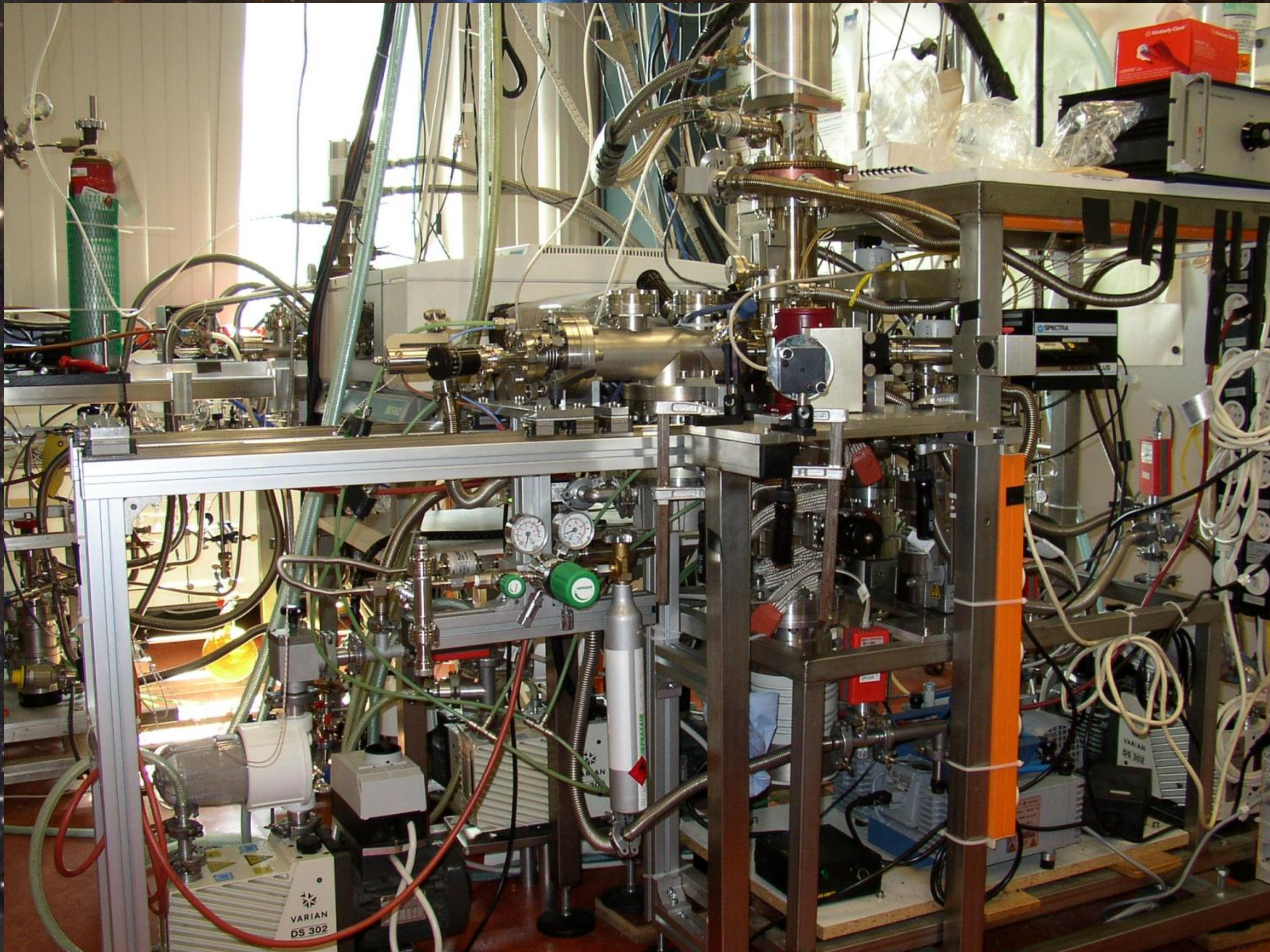
$CO{:}O_2 + H$ — Ioppolo et al. MNRAS 2011

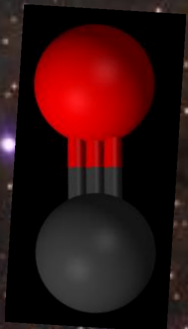

Charnley et al.
CH_3CH_2OH
2H
CH_3OH
CH_3CHO
2H
2H
H_2CO
CH_2CO
H
H
H
C
C
CO
HCO
HCCO
O?
O
N
O
CO_2
HCOO
HNCO
H
H
H?
HCOOH
NH_2CO
2H
H
$CH_2(OH)_2$
NH_2CHO

Hydrogenation reactions

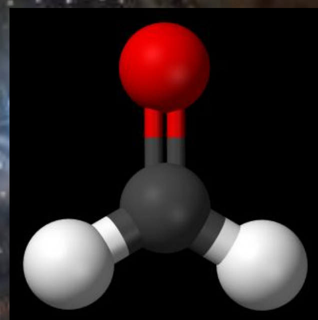


- Prepare ice – ML precision
- Choose final T
- 3-4 hrs H or D-flux
- Simultaneous RAIRS
- TPD finishing touch

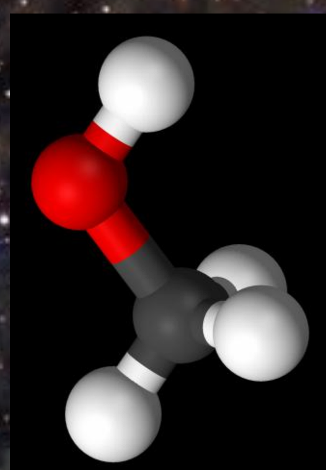

VARIAN
DS 302

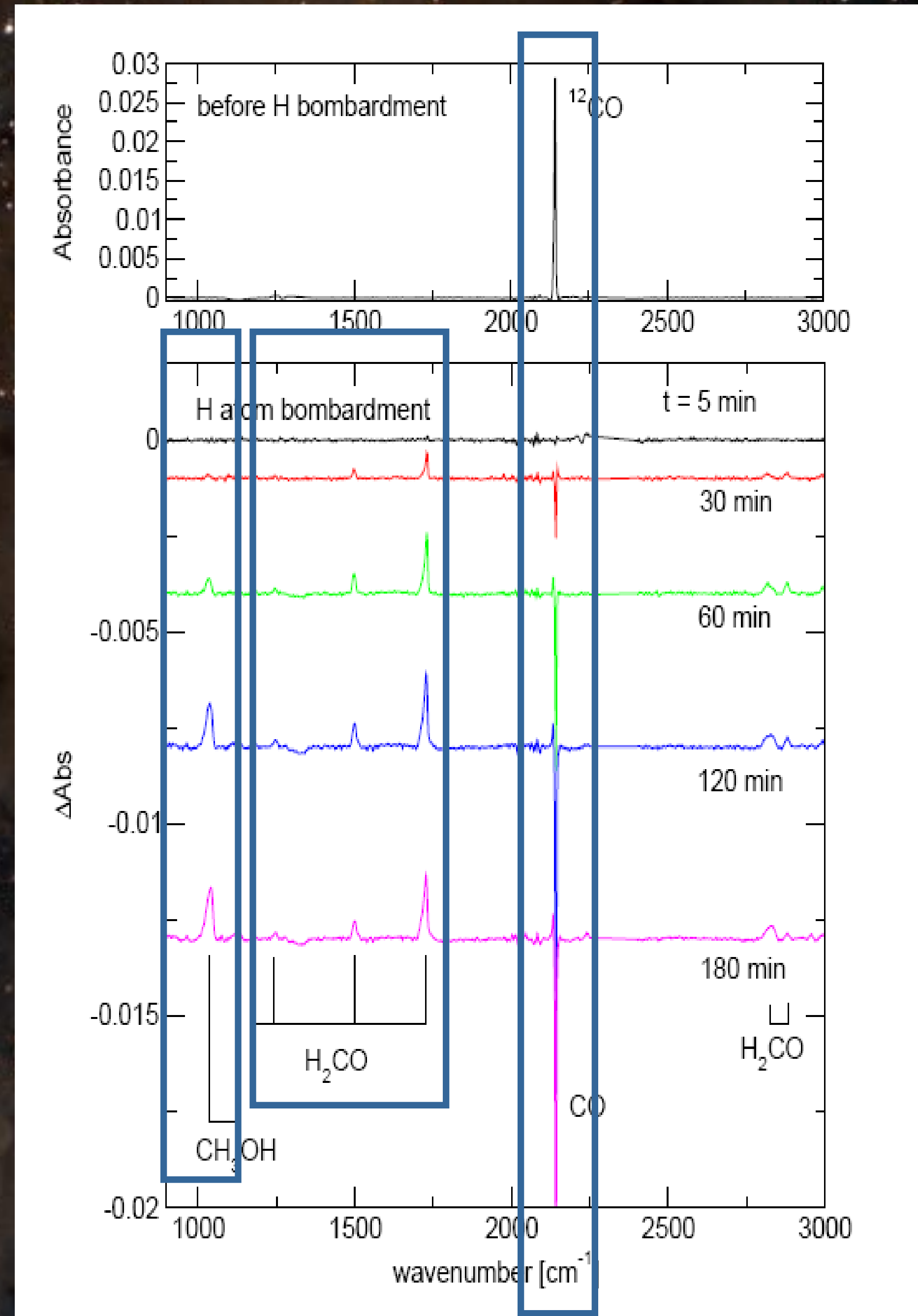


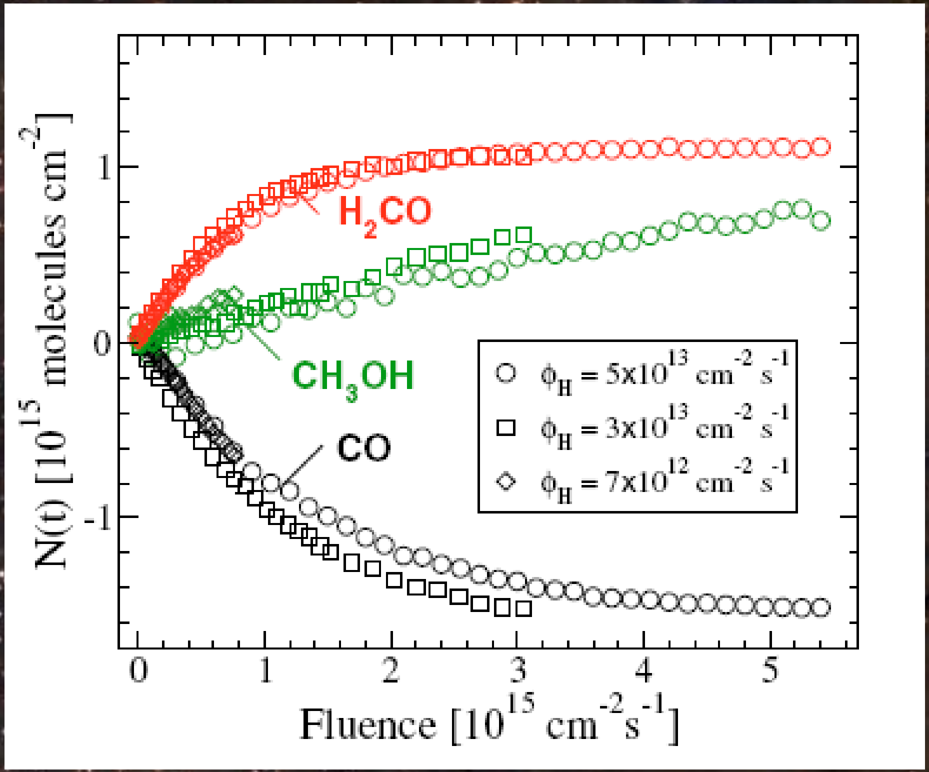
$CO \rightarrow_{2H} H_2CO$



$H_2CO \rightarrow_{2H} CH_3OH$







Fuchs et al. and Cuppen et al. A&A 2009

Using Monte Carlo simulations

► T-dependent reaction barriers / diffusion rates.
► Conversion towards interstellar conditions / timescales.

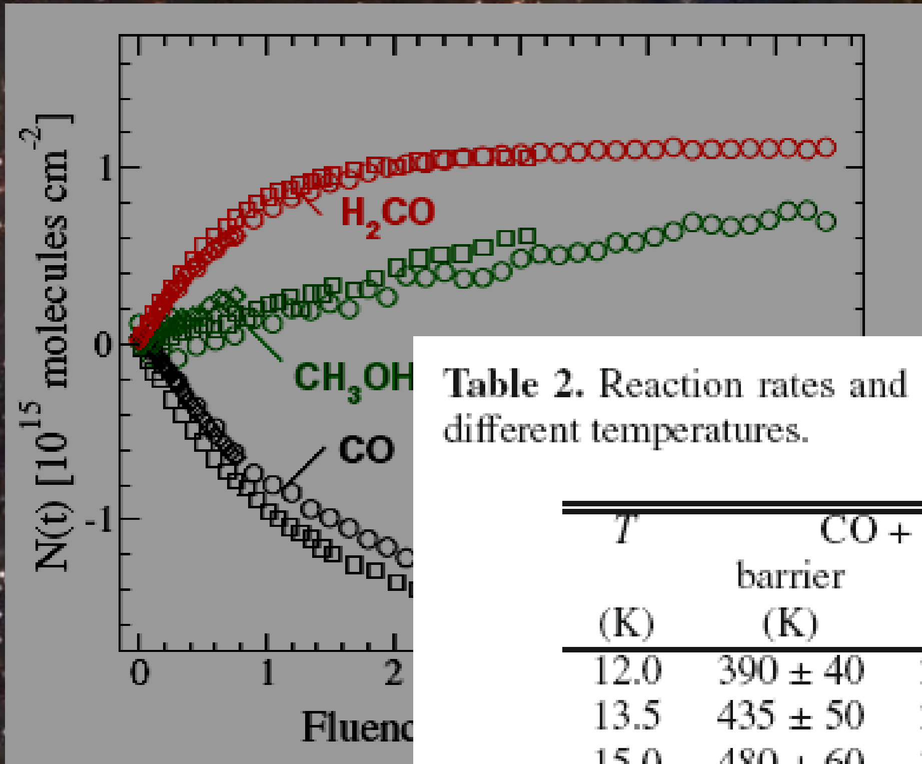


Table 2. Reaction rates and barriers for CO + H and H_2CO + H for different temperatures.

T (K)	CO + H barrier (K)	CO + H rate (s^{-1})	H_2CO + H barrier (K)	H_2CO + H rate (s^{-1})
12.0	390 ± 40	2×10^{-3}	415 ± 40	2×10^{-4}
13.5	435 ± 50	2×10^{-3}	435 ± 50	2×10^{-3}
15.0	480 ± 60	3×10^{-3}	470 ± 60	5×10^{-3}
16.5	520 ± 70	4×10^{-3}	490 ± 70	2×10^{-2}

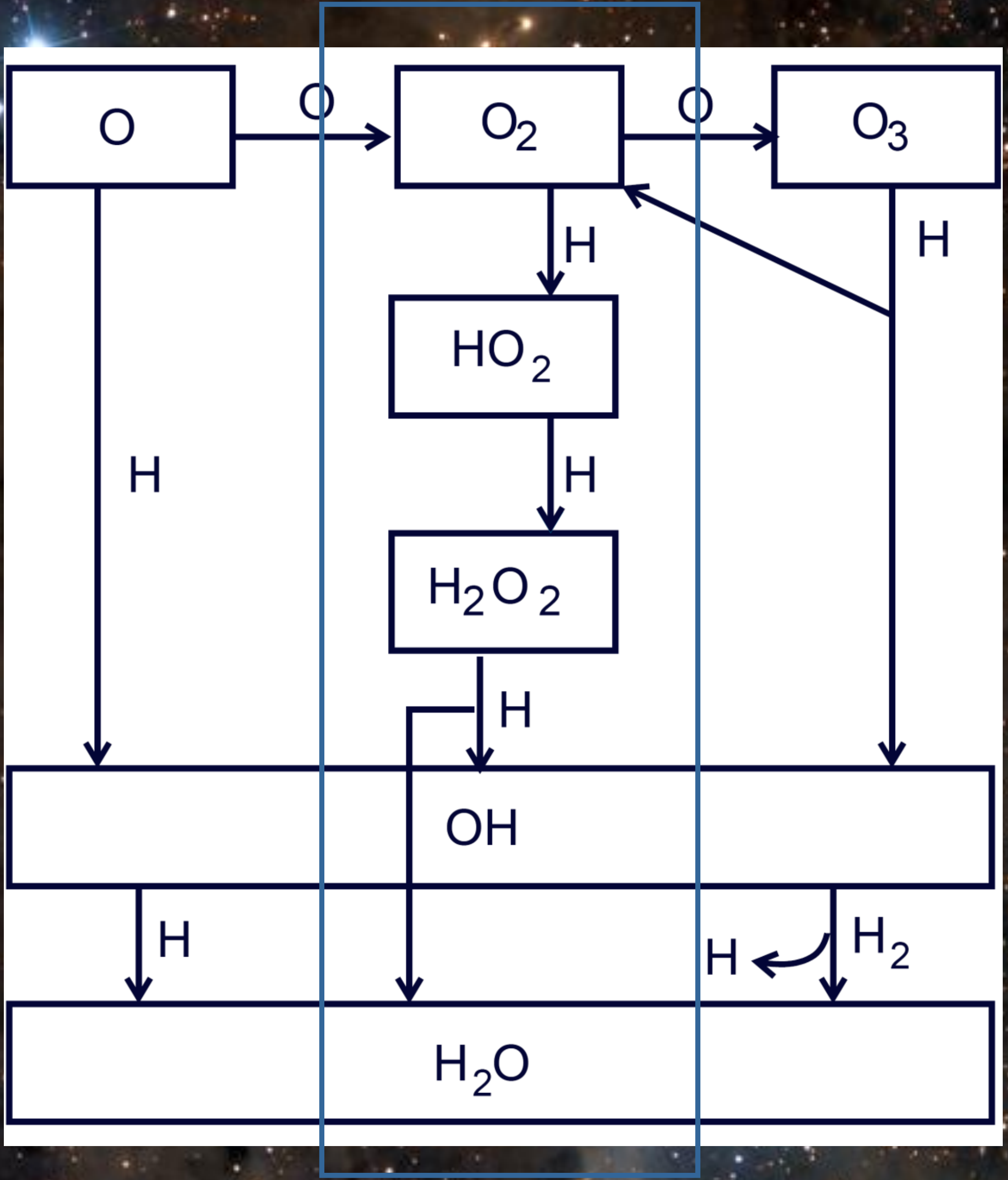
Fuchs et al. and Cuppen et al. A&A 2009

Using Monte Carlo simulations

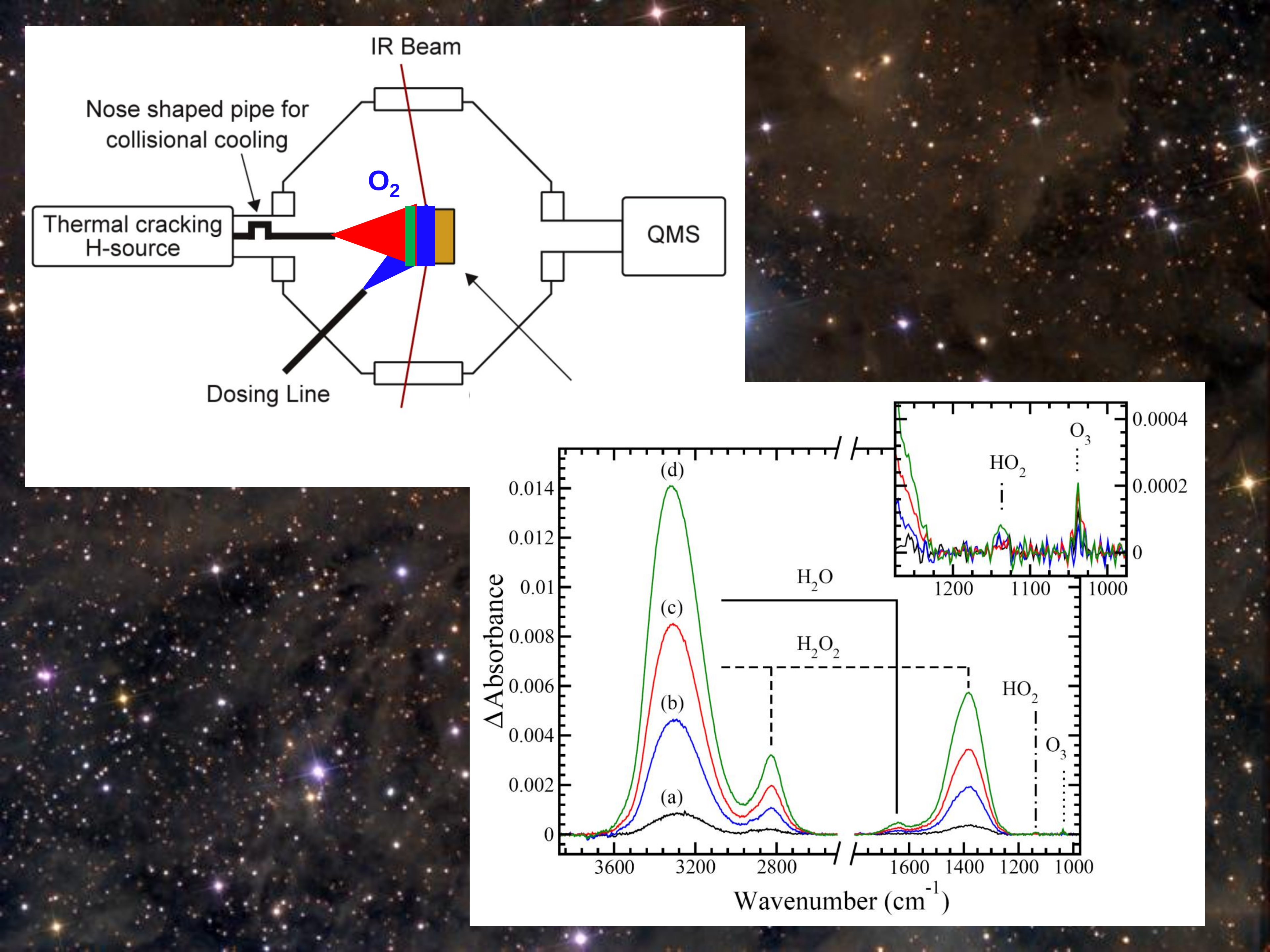
► T-dependent reaction barriers / diffusion rates.
► Conversion towards interstellar conditions / timescales.

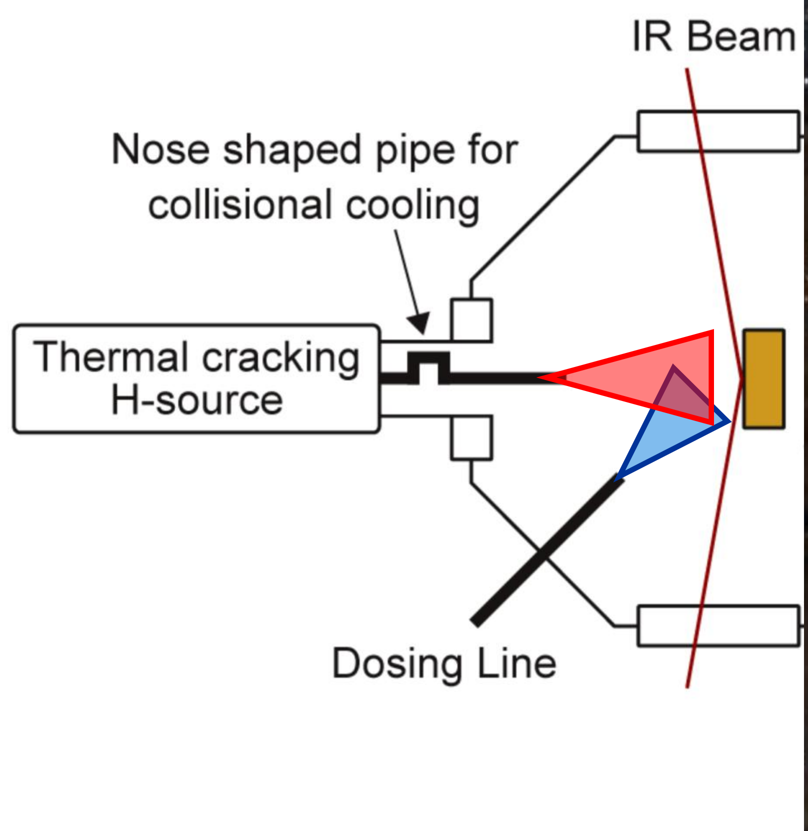
How about water ?

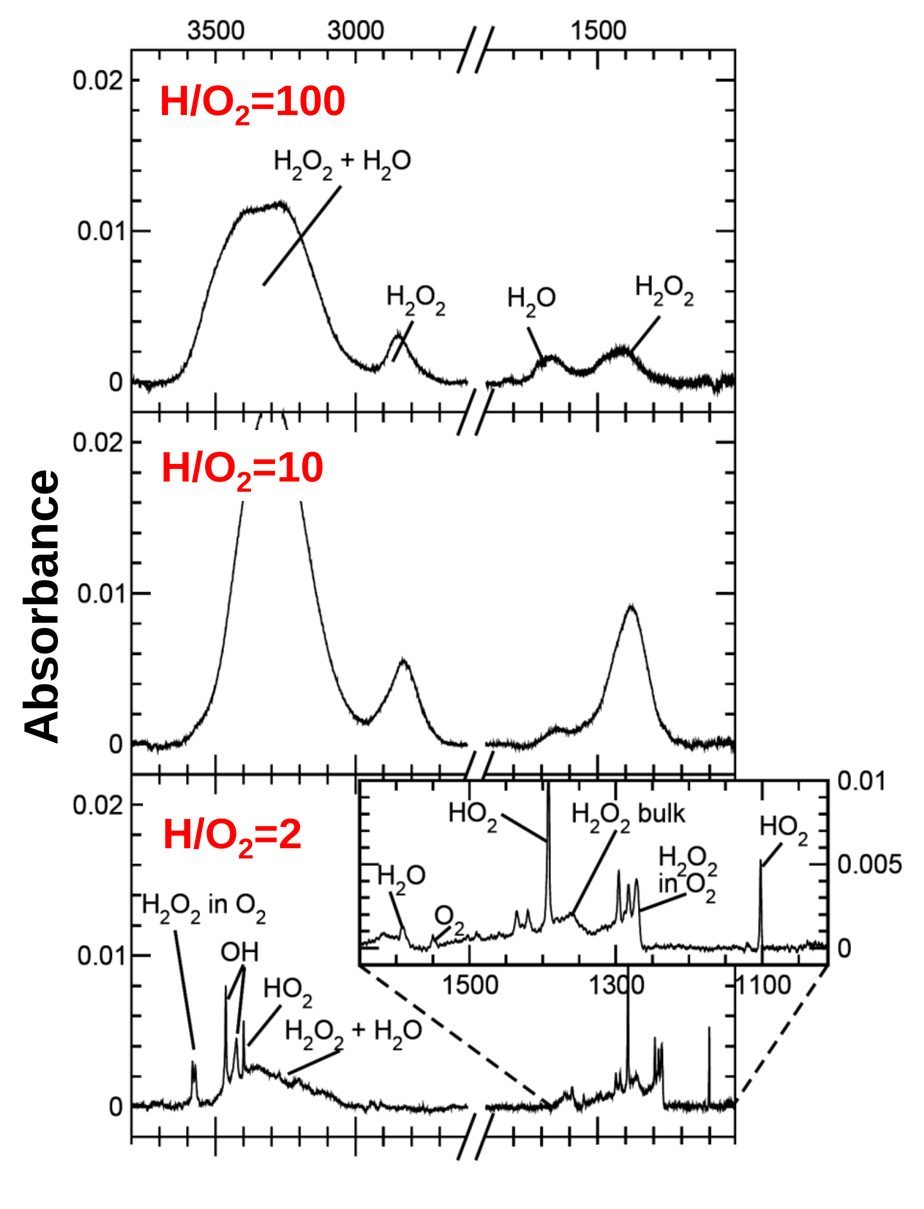
(More also in the next talk)



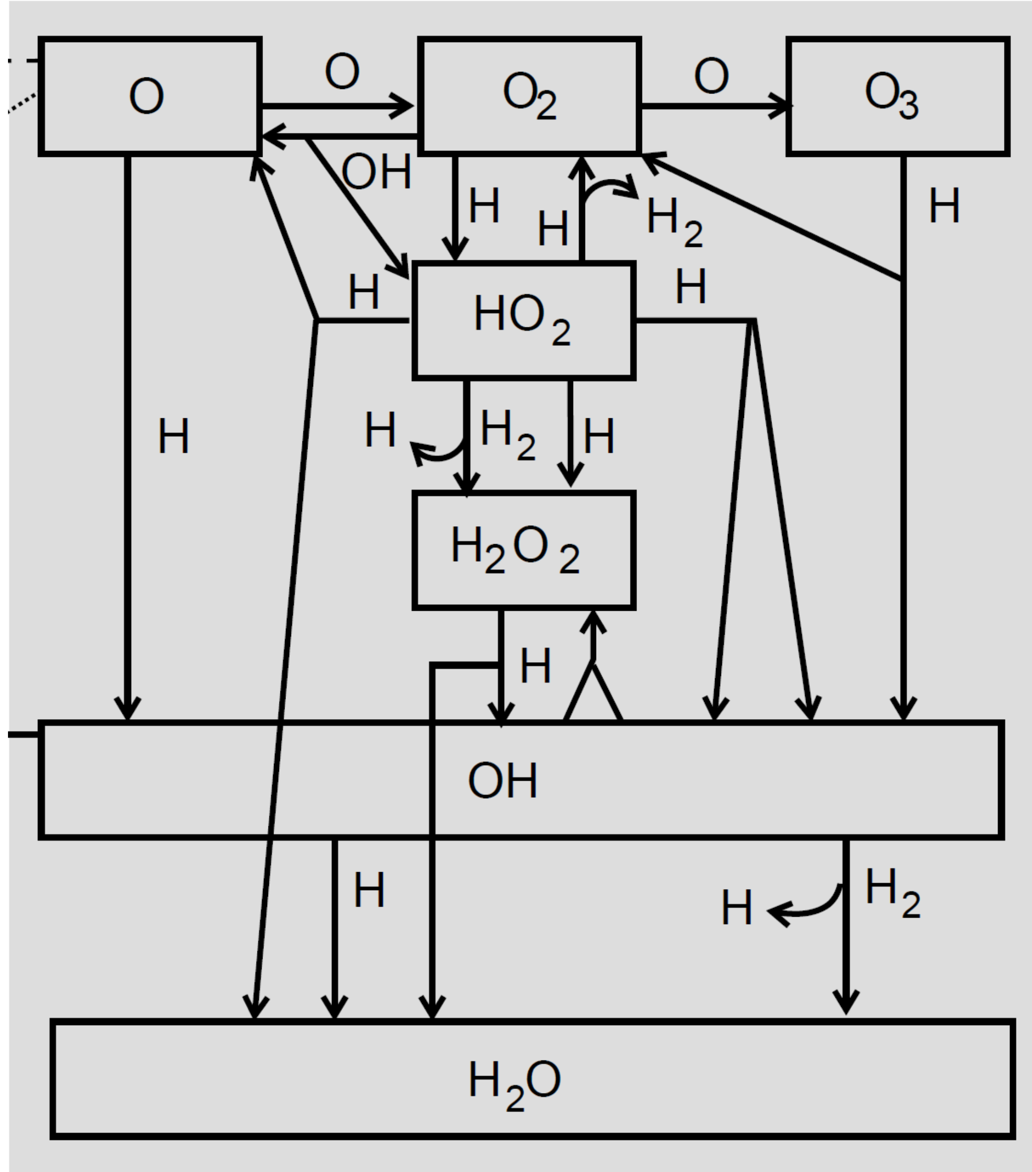
Tielens and Hagens, 1982


IR Beam
Nose shaped pipe for collisional cooling
O_2
Thermal cracking H-source
QMS
Dosing Line
ΔAbsorbance
Wavenumber (cm^{-1})
(a)
(b)
(c)
(d)
H_2O
H_2O_2
HO_2
O_3
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
3600
3200
2800
1600
1400
1200
1000
0.0004
0.0002
0

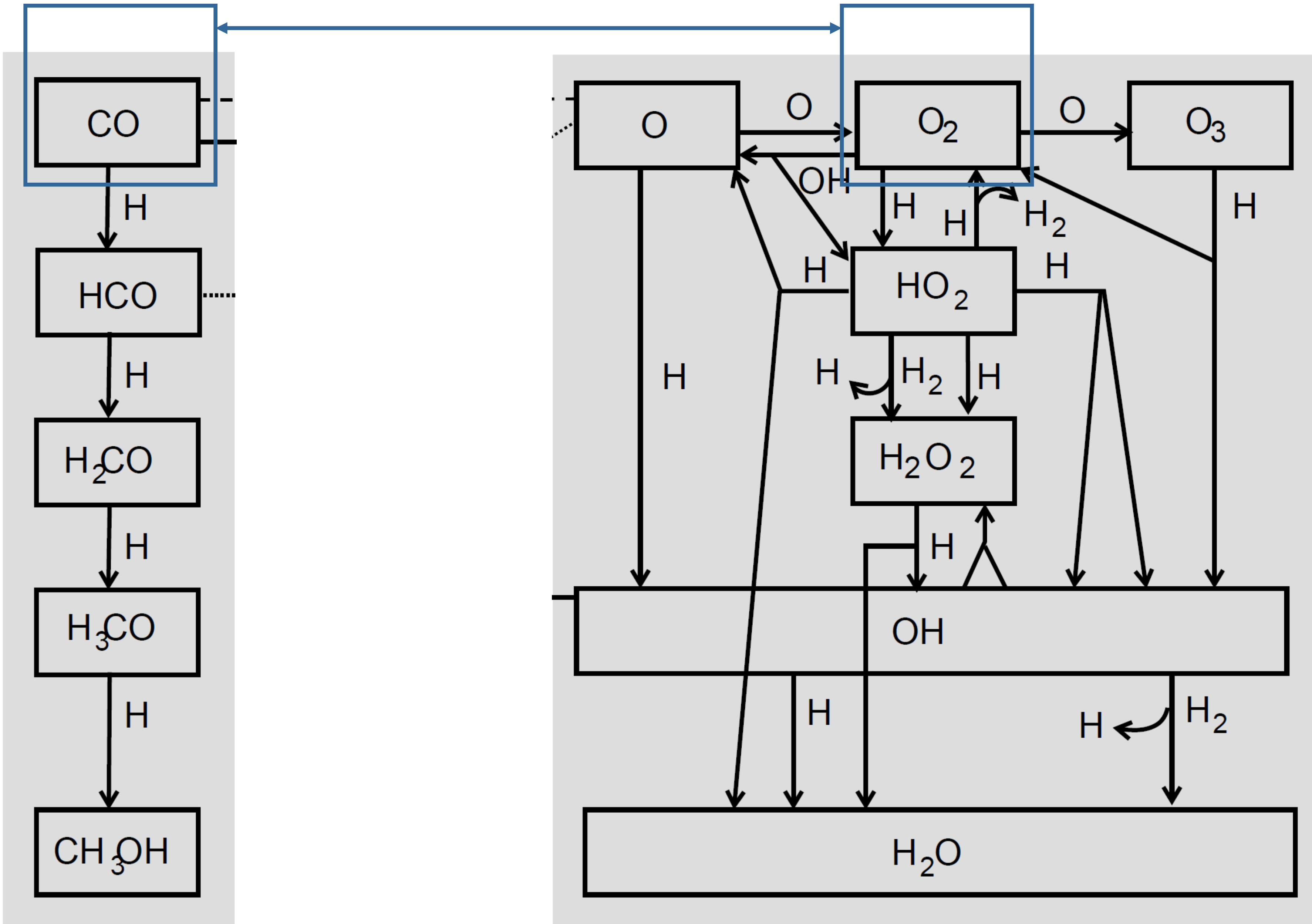


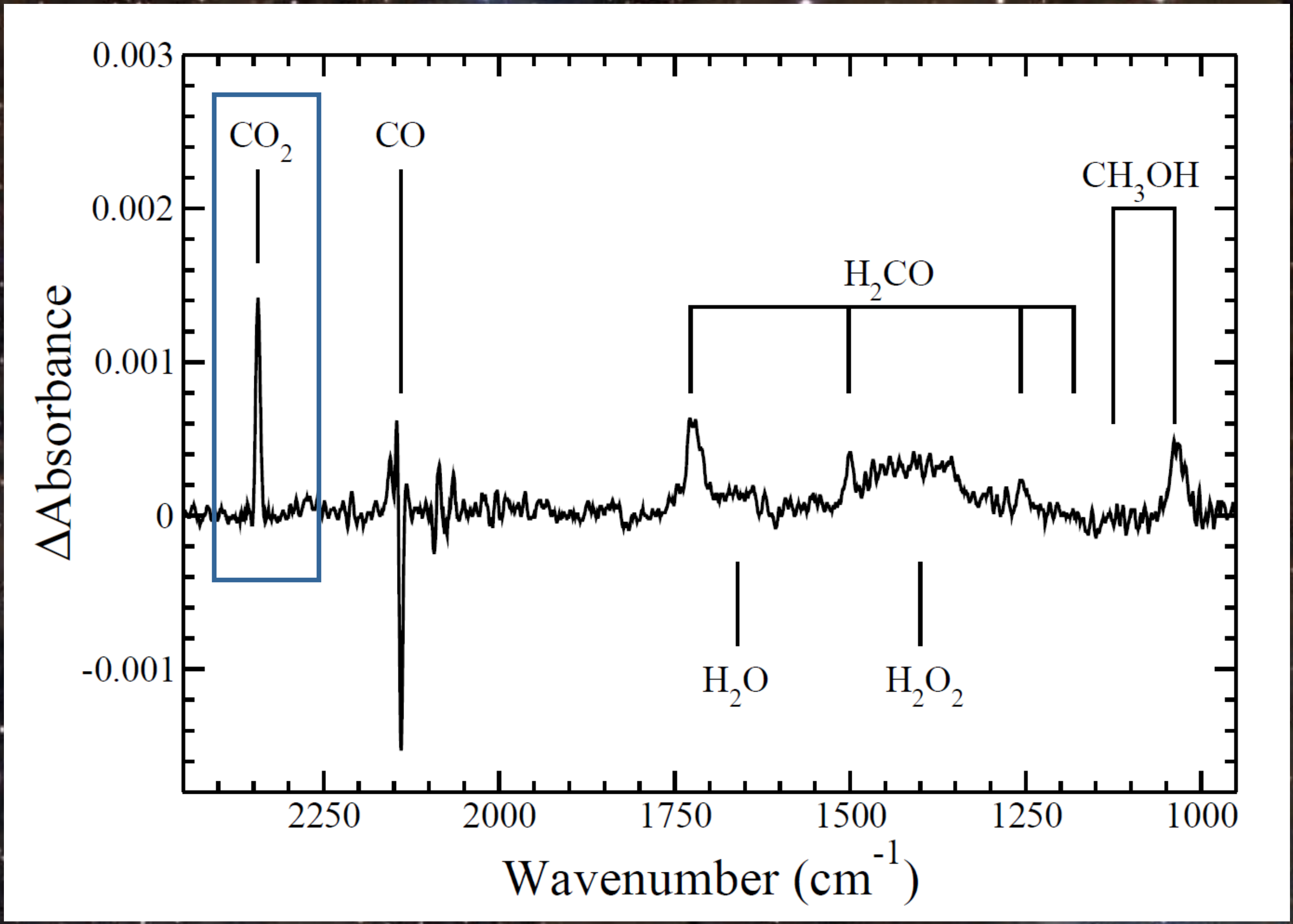


By changing H/O_2 ratio different stages of the reaction network can be probed.

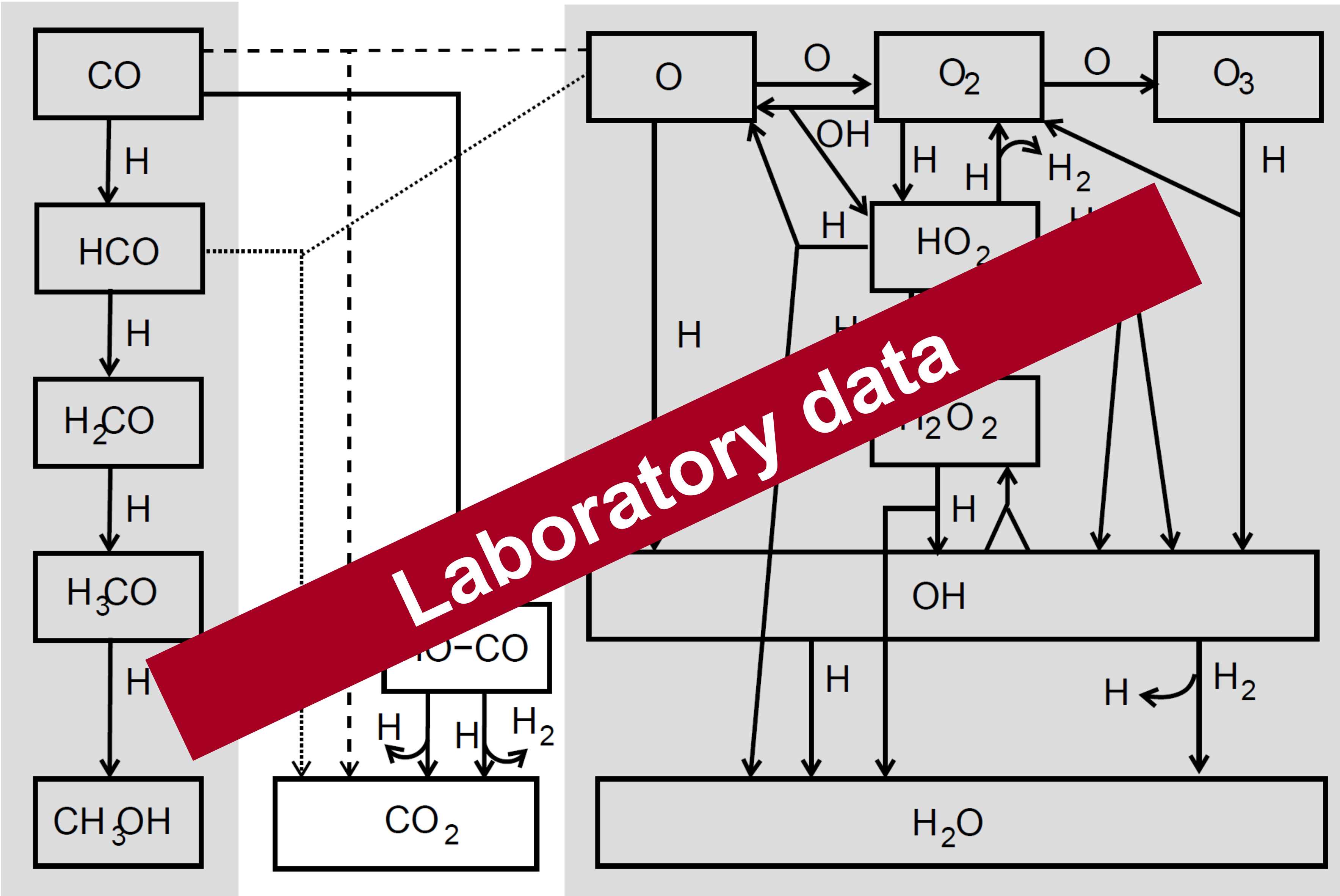


O
O
O_2
O
O_3
OH
H
H
H_2
H
H
HO_2
H
H
H
H_2
H
H_2O_2
H
OH
H
H
H_2
H_2O


CO
H
HCO
H
H2CO
H
H3CO
H
CH3OH
O
O
O2
O
O3
OH
H
H
H2
H
H
H
HO2
H
H2
H
H
H2O2
H
OH
H
H
H2
H2O



Ioppolo et al. MNRAS 2011

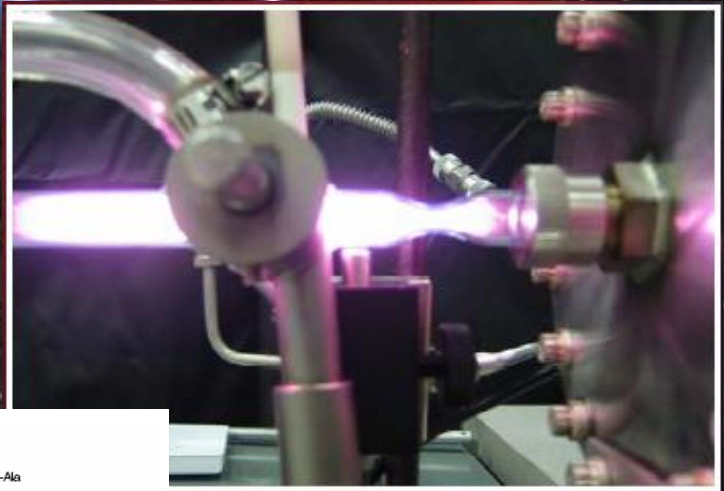


POSTERS: Ioppolo / Lamberts

3. VUV Spectroscopy of ice

Photo-desorption

Photo-processing



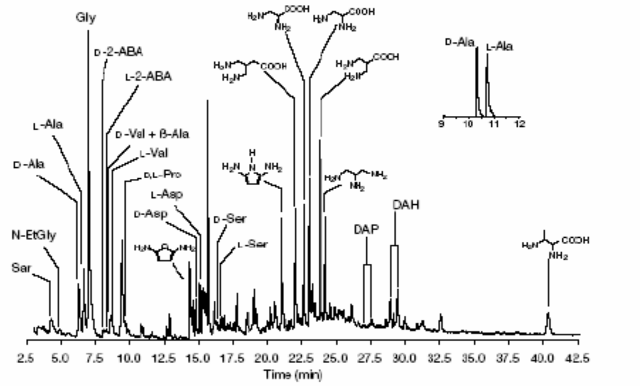
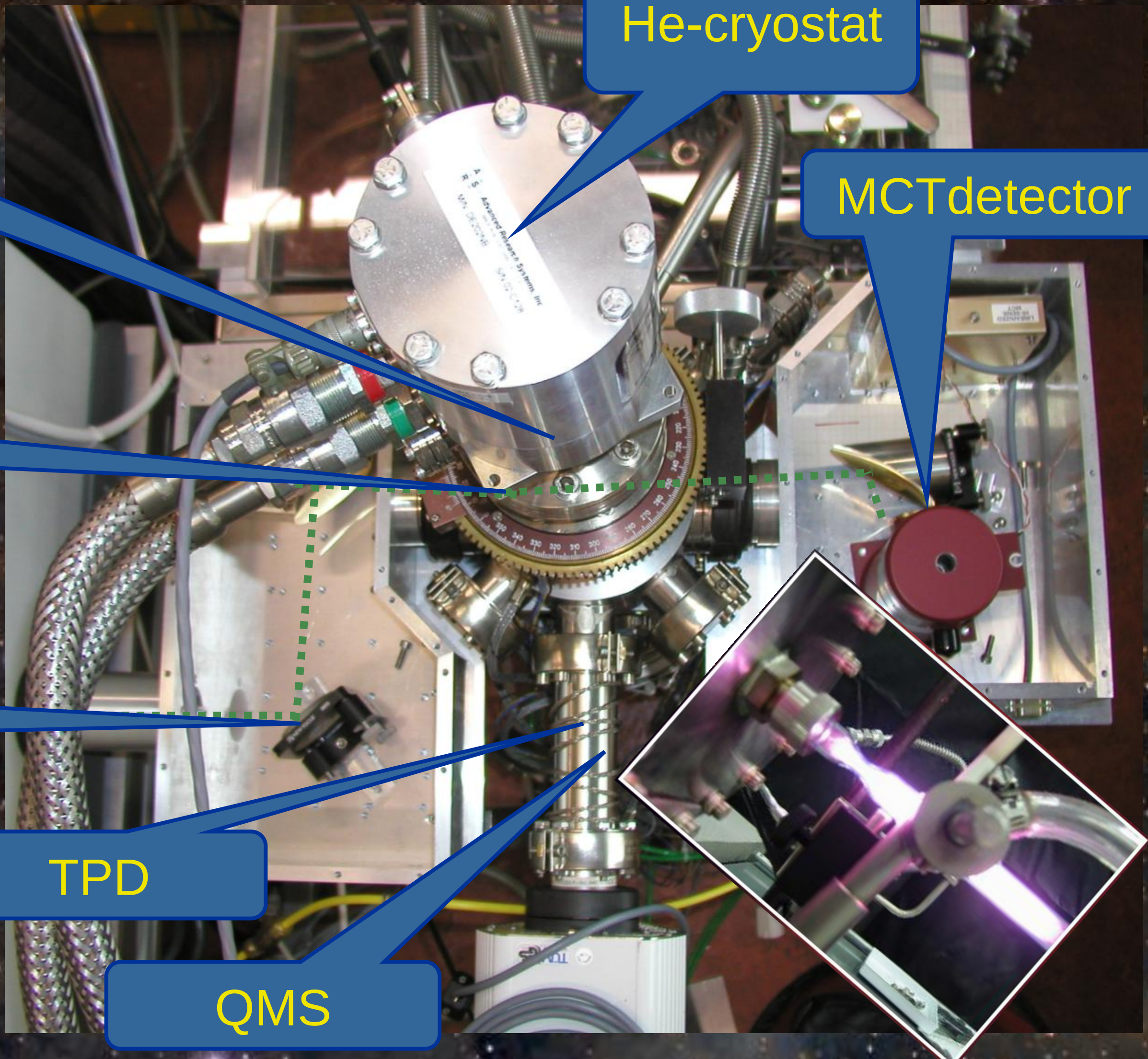
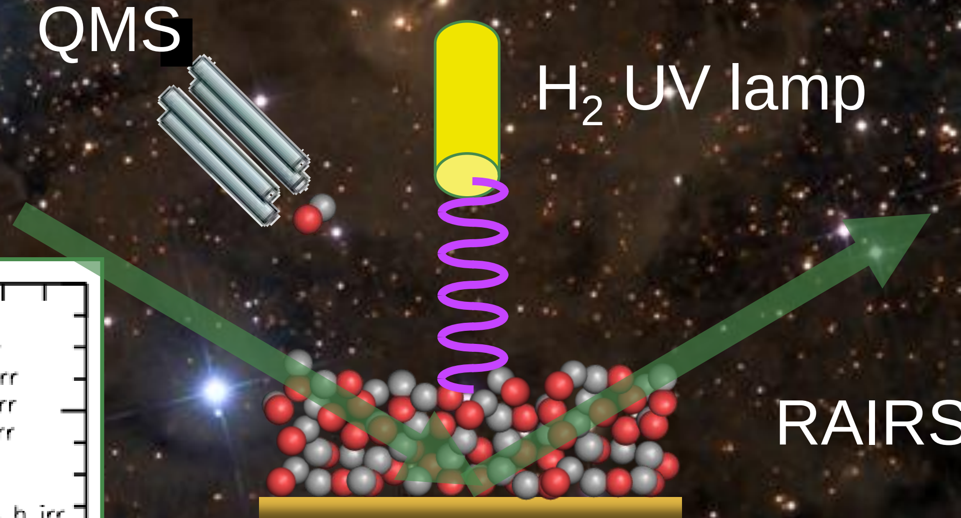


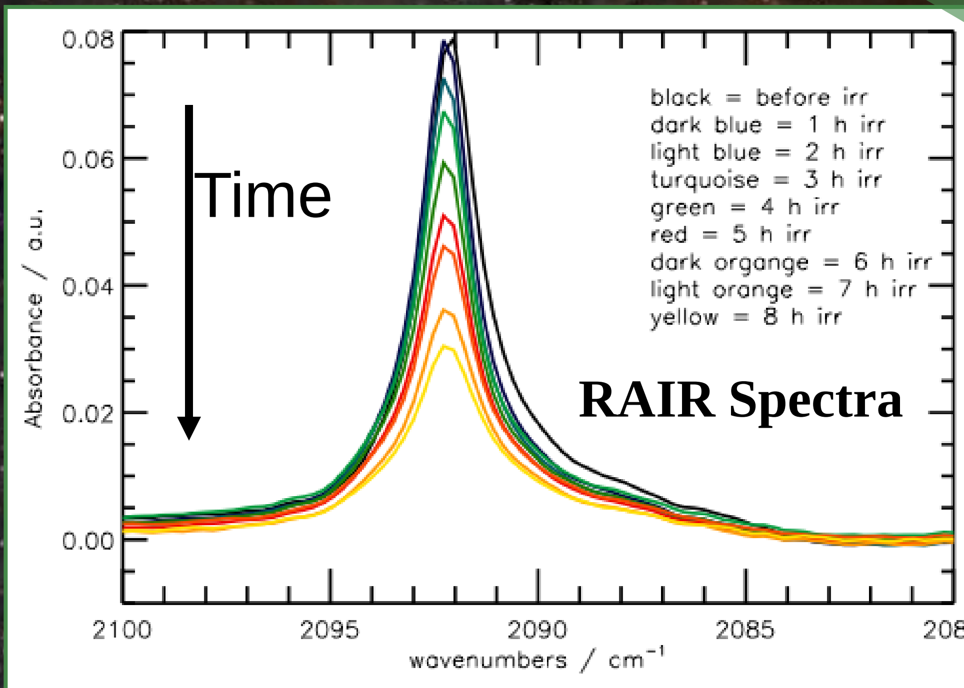
Fig. 2. Gas chromatogram showing a rich variety of amino acids and other compounds generated from a photo-processed ISM ice, containing H_2O, CH_3OH, NH_3, CO and CO_2. (Taken from G.M.M. Caro et al, Nature 416 (2002) 403.)

Caro et al.
Science 2002

UHV VUV Irradiation setup





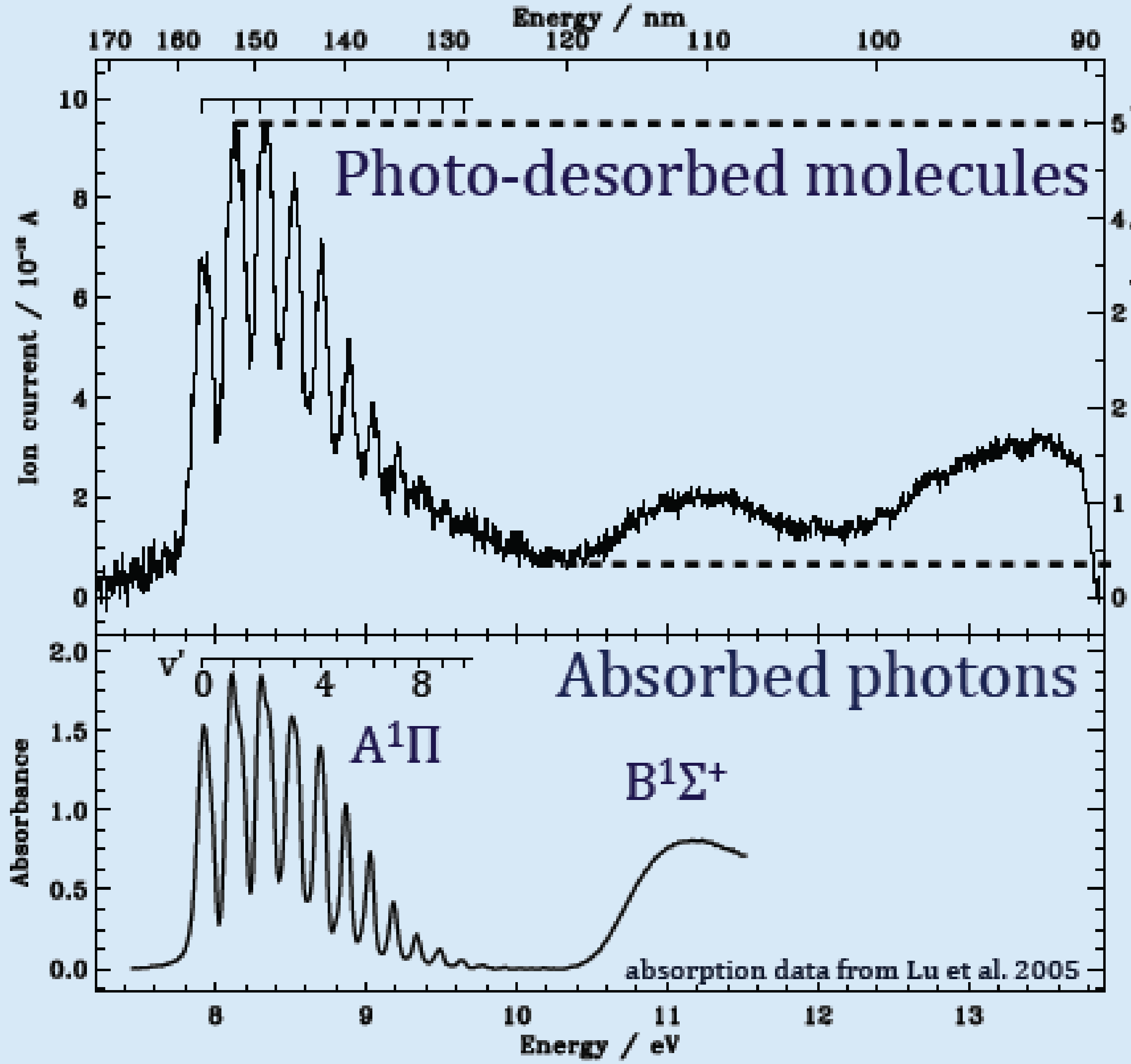


→ UV photodesorption rate

Oberg et al. 2007: 3.10^{-3} molecule / photon

Munoz-Caro et al. 2010: $3.5.10^{-2}$ molecule / photon

Frequency dependent CO ice photodesorption



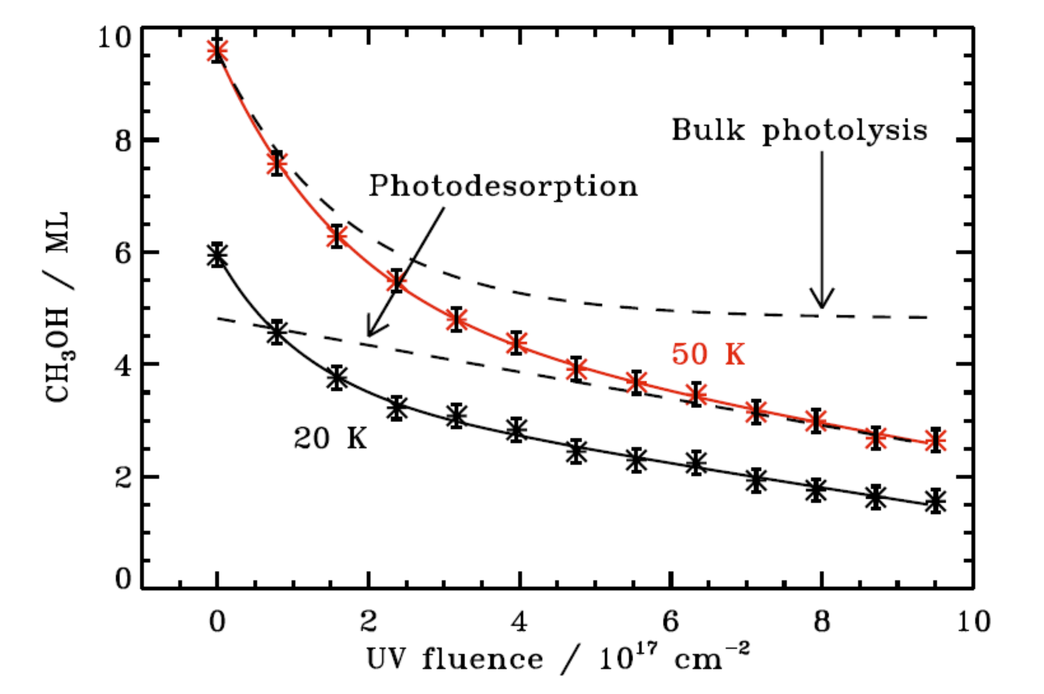
Maximum absorption
5.0×10^{-2} molecule.ph^{-1}

Lyman alpha
4.1×10^{-3} molecule.ph^{-1}

Fayolle et al., ApJ in preparation

POSTER Fayolle

UV irradiation of methanol ice



►Photodesorption ~ number of molecules in surface layer

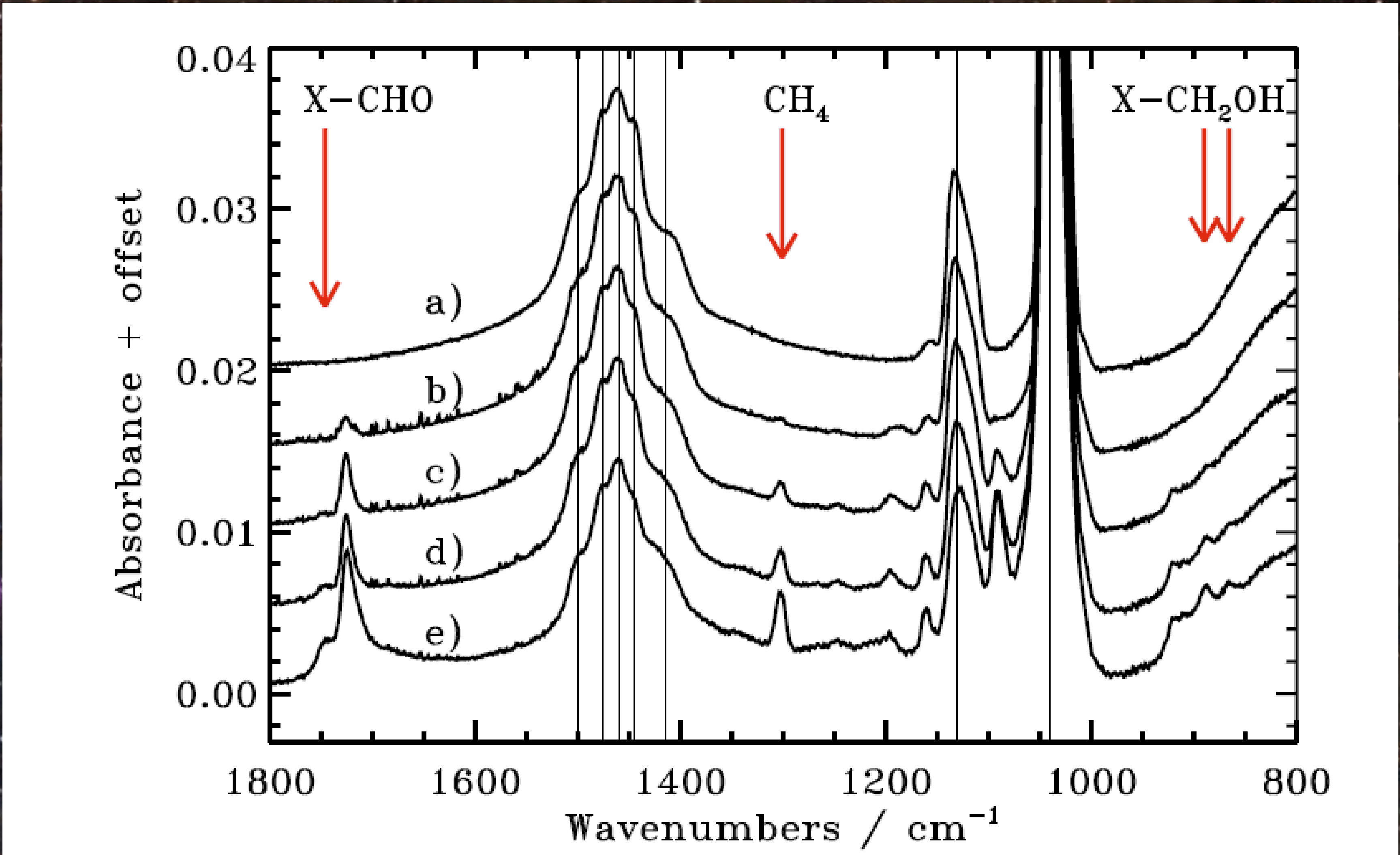
→ 0^{th} order process

►Photolysis ~ total number of molecules in the ice

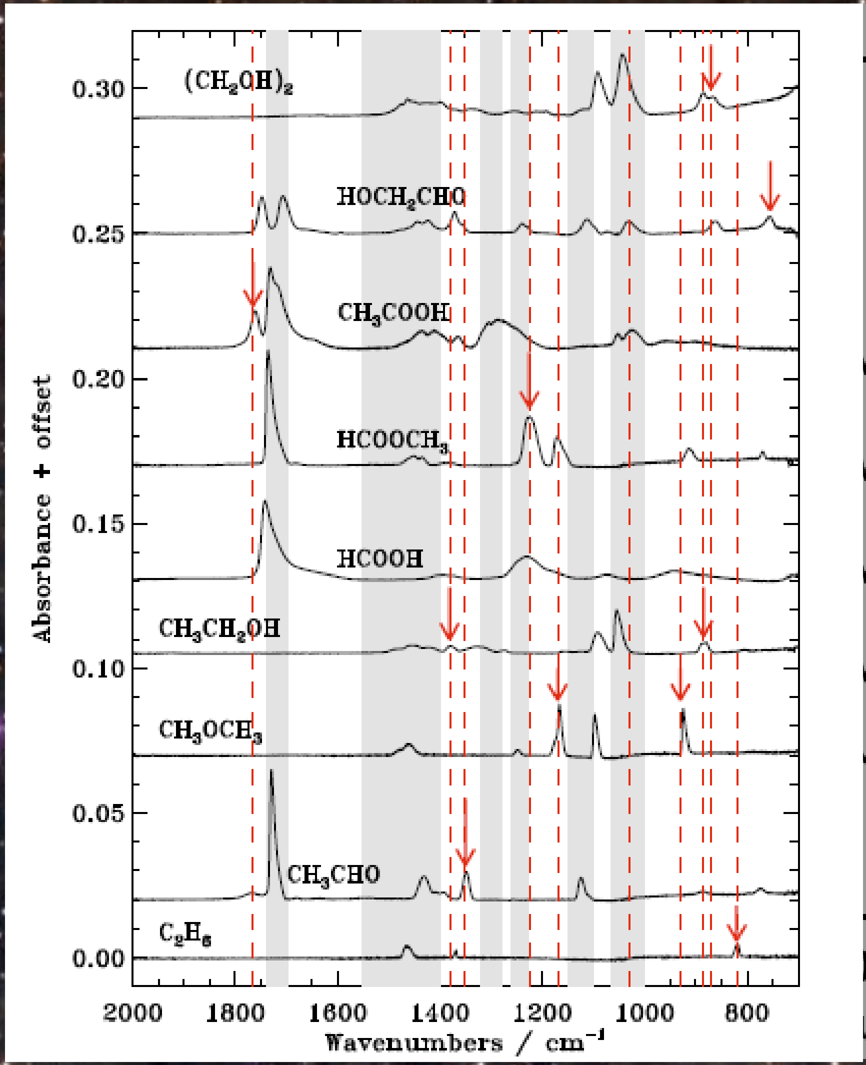
→ 1^{st} order process

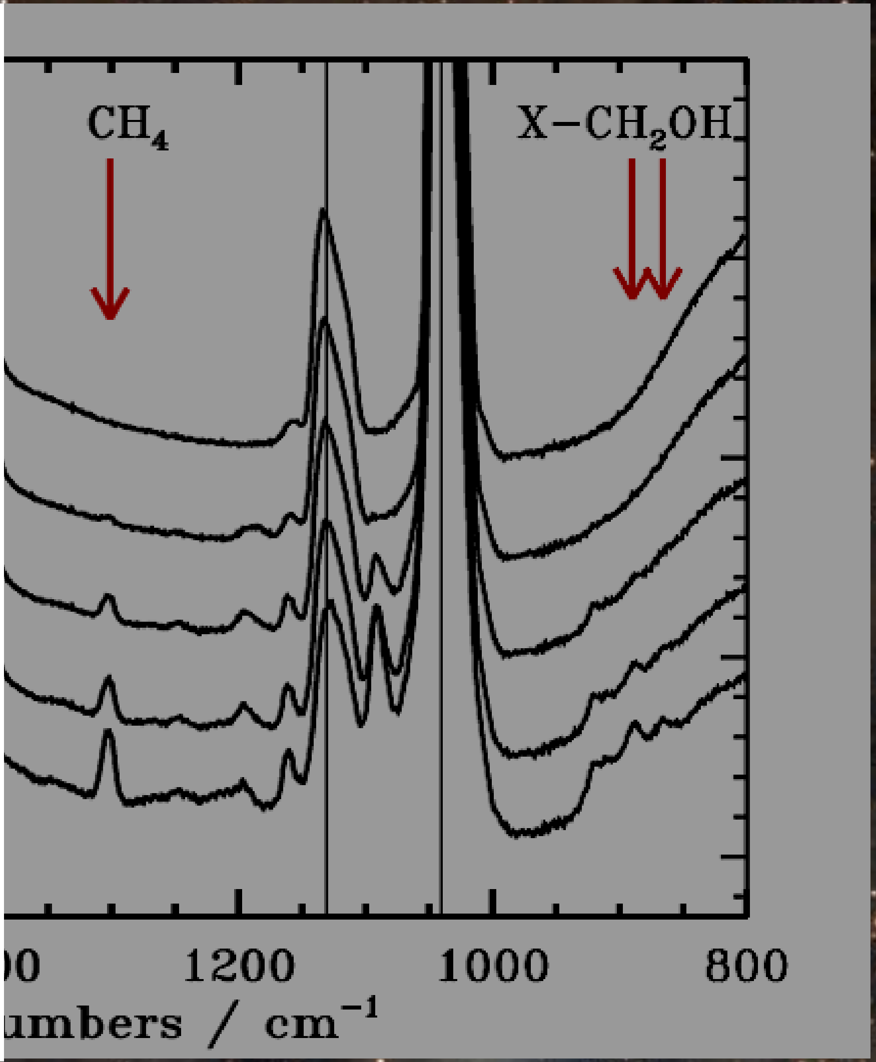
Öberg et al. A&A 2009

UV irradiation of methanol ice

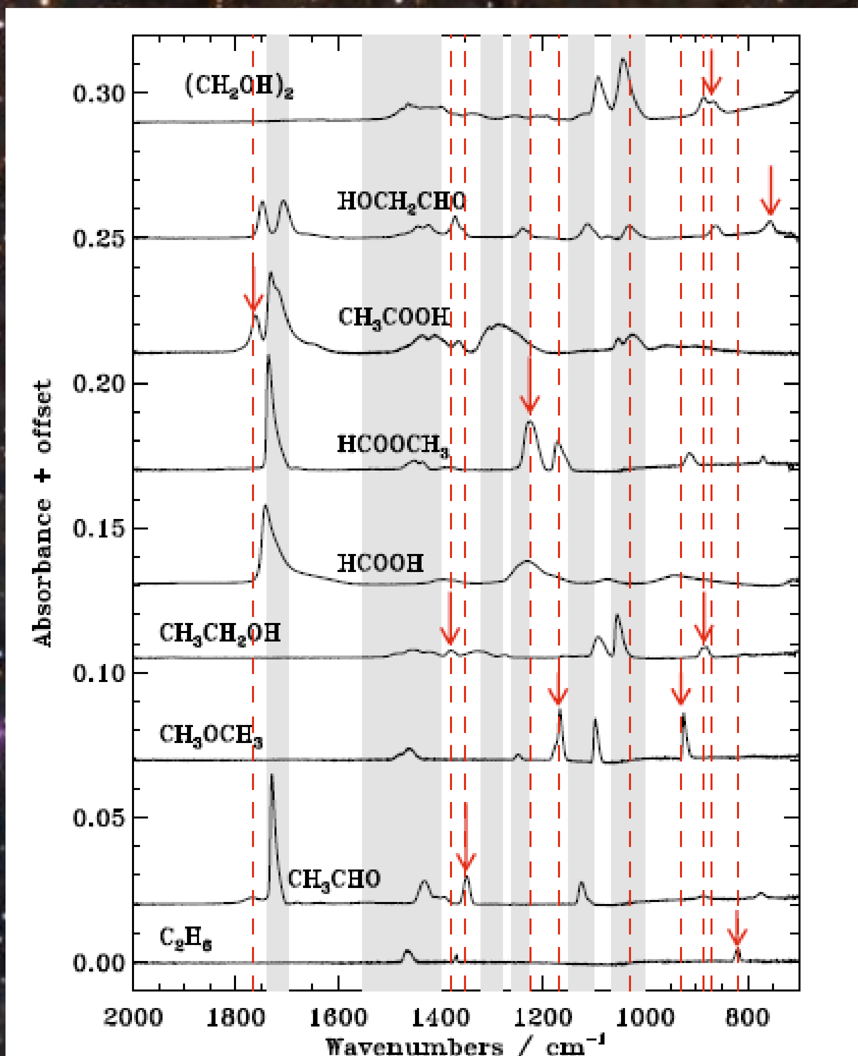


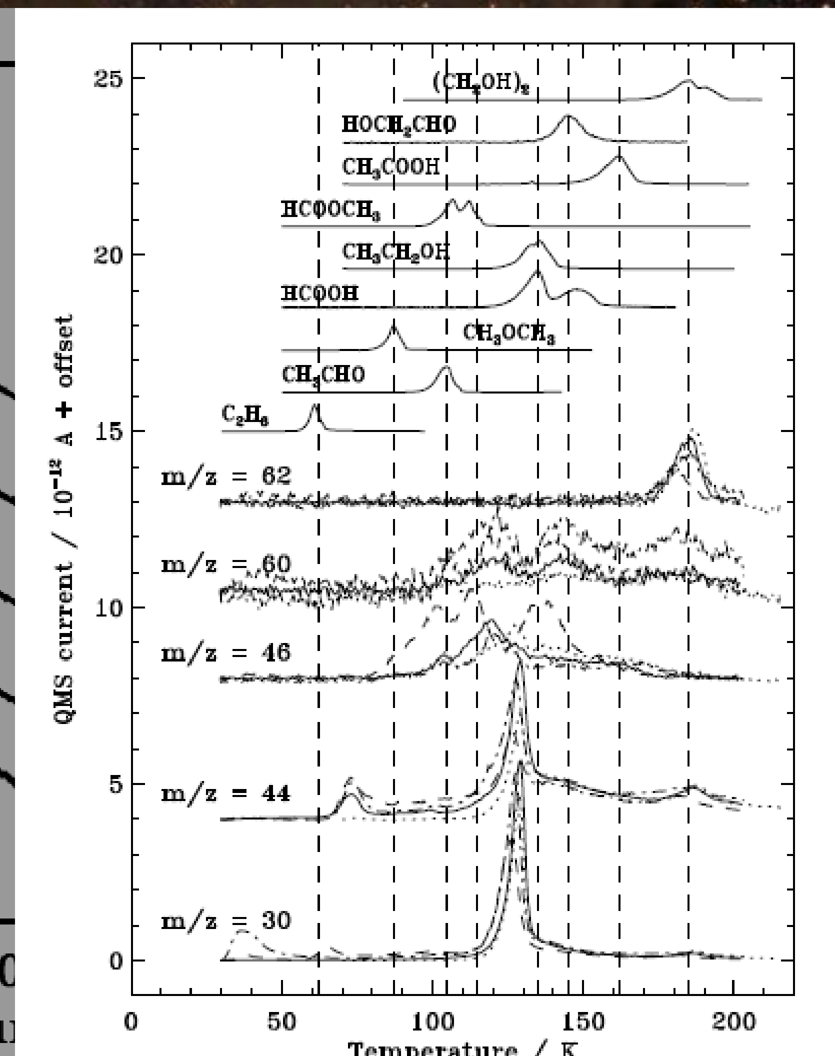
UV irradiation of methanol ice: RAIRS





UV irradiation of methanol ice: TPD





UV irradiation of methanol ice: TPD

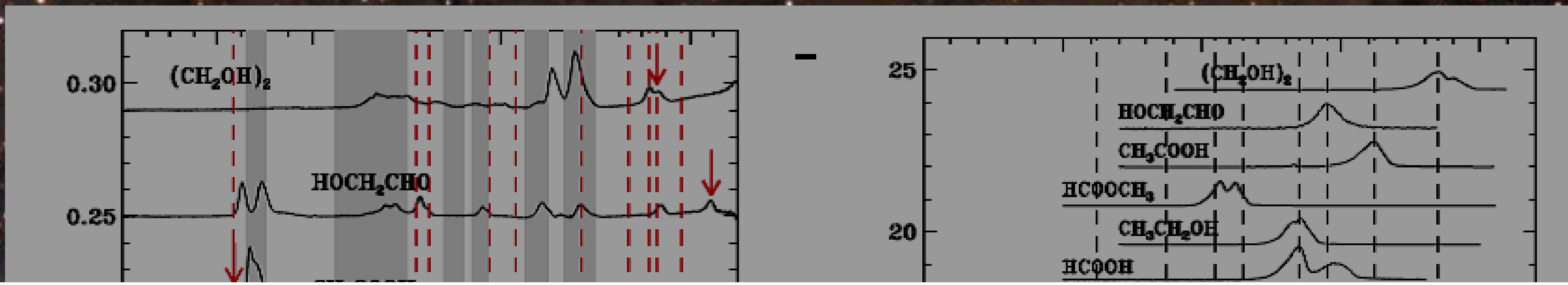
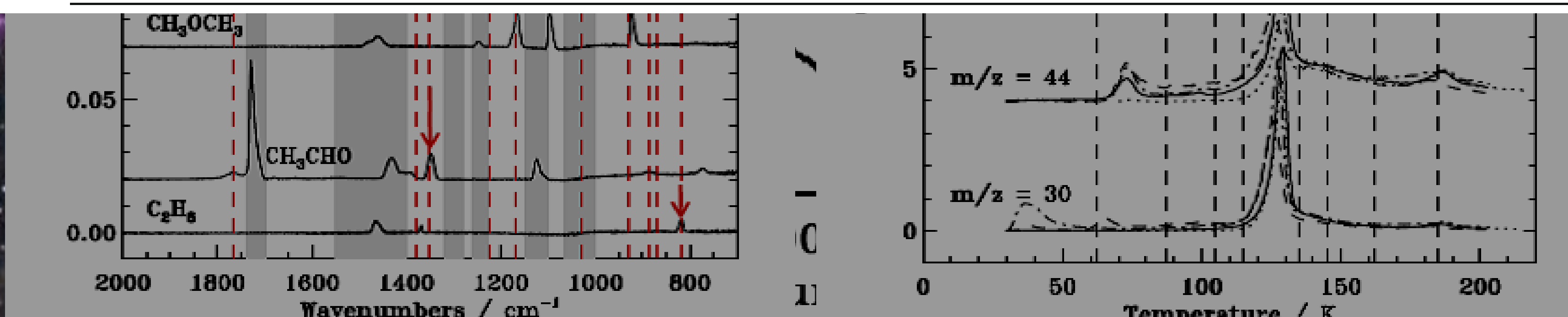


Table 6. Abundances of complex molecules relative to CH_3OH.

	IRAS 16293-2422/A[a,b]	Hot cores[c]	L1157[d]	MC G-0.02[e]	Hale-Bopp[f]	CH_3OH[g]	CH_3OH:CO[g]
CH_3OH	1/1	1	1	1	1	1	1
CH_3CHO	0.038/ < 0.0016	2.9[3.1] × 10^{-5}	–	0.033	0.010	0.01	<0.04
CH_3CH_2OH	–/0.031	0.019[0.012]	0.007	0.040	<0.042	0.1	<0.01
CH_3OCH_3	0.20/0.013	0.41[0.51]	–	0.050	–	0.04	<0.01
$HCOOCH_3$	0.30/0.0084	0.089[0.084]	0.019	0.037	0.033	<0.03	>0.08
$HOCH_2CHO$	–/–	–	–	0.01	<0.017	<0.04	>0.04
$(CH_2OH)_2$	–/–	–	–	0.01	0.10	0.4	<0.01



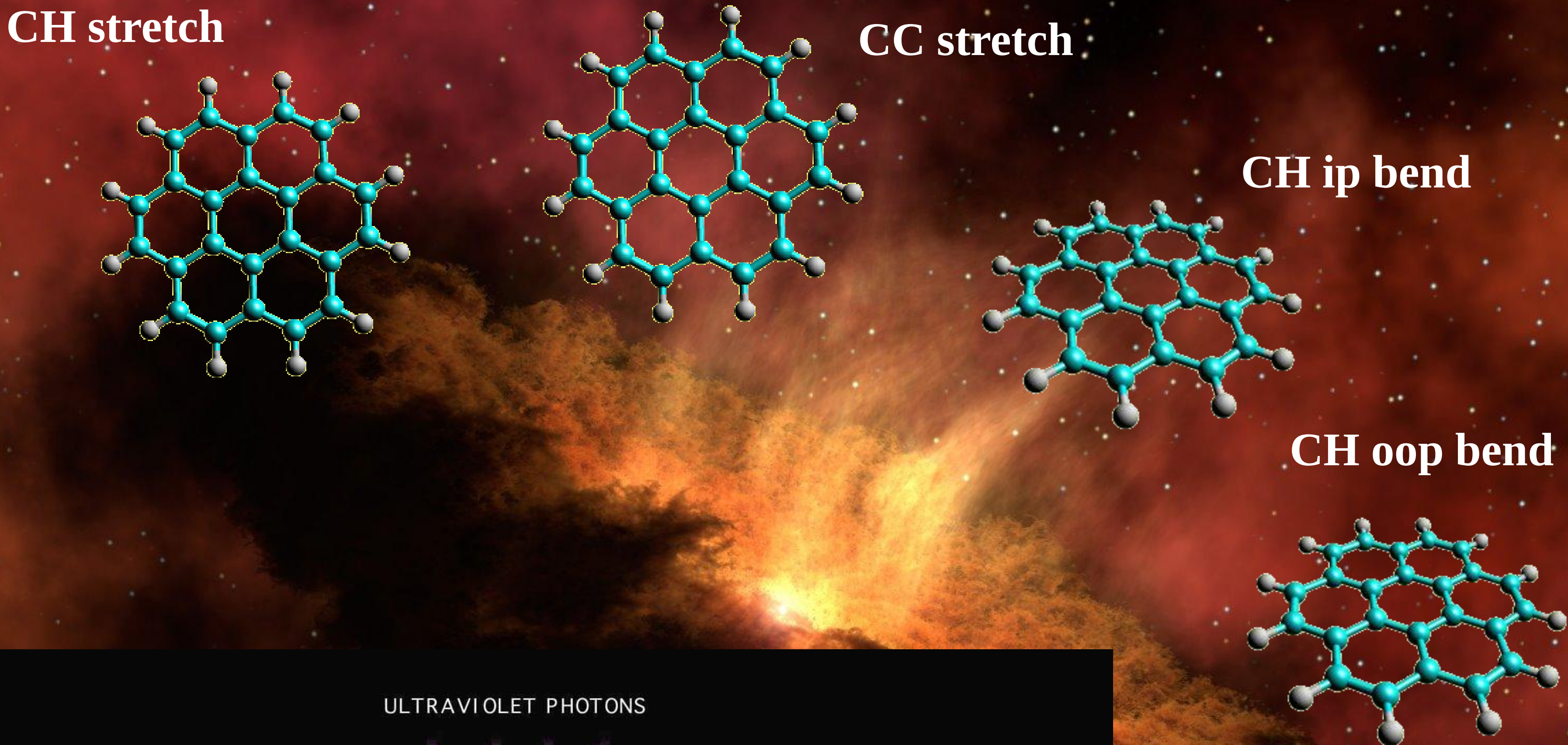
Warning:
How about ice boundary conditions ?

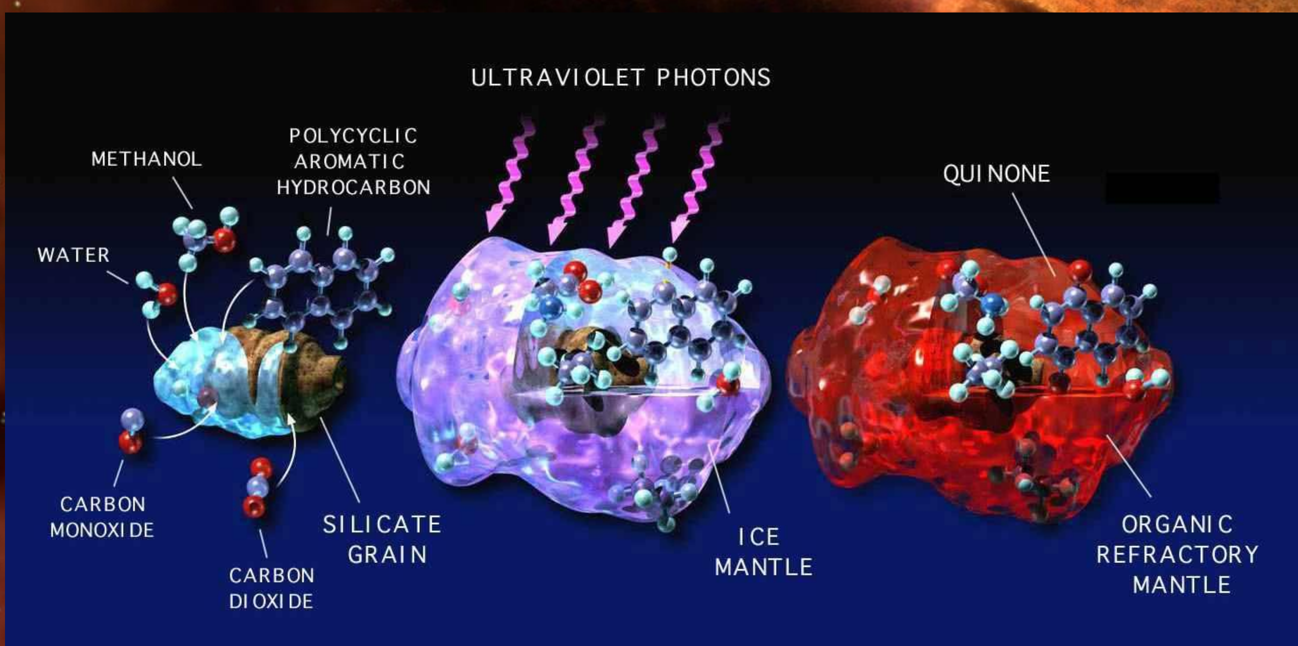
MATRI²CES: Mass Analysing Tool for Reactions in Interstellar ICES

POSTER: Isokoski & Bossa

4. Towards ‘real’ molecular complexity in interstellar ice

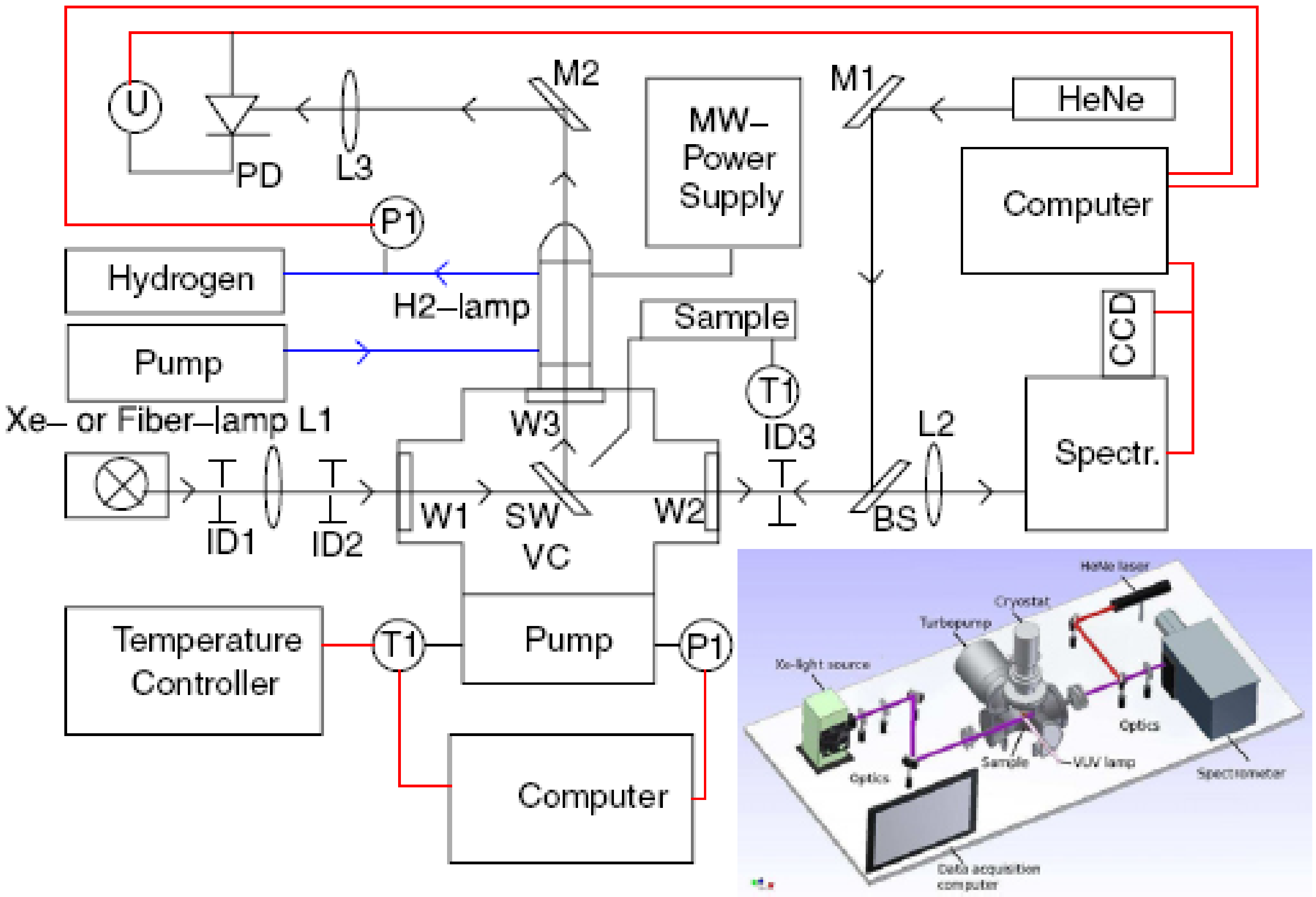
A different approach …



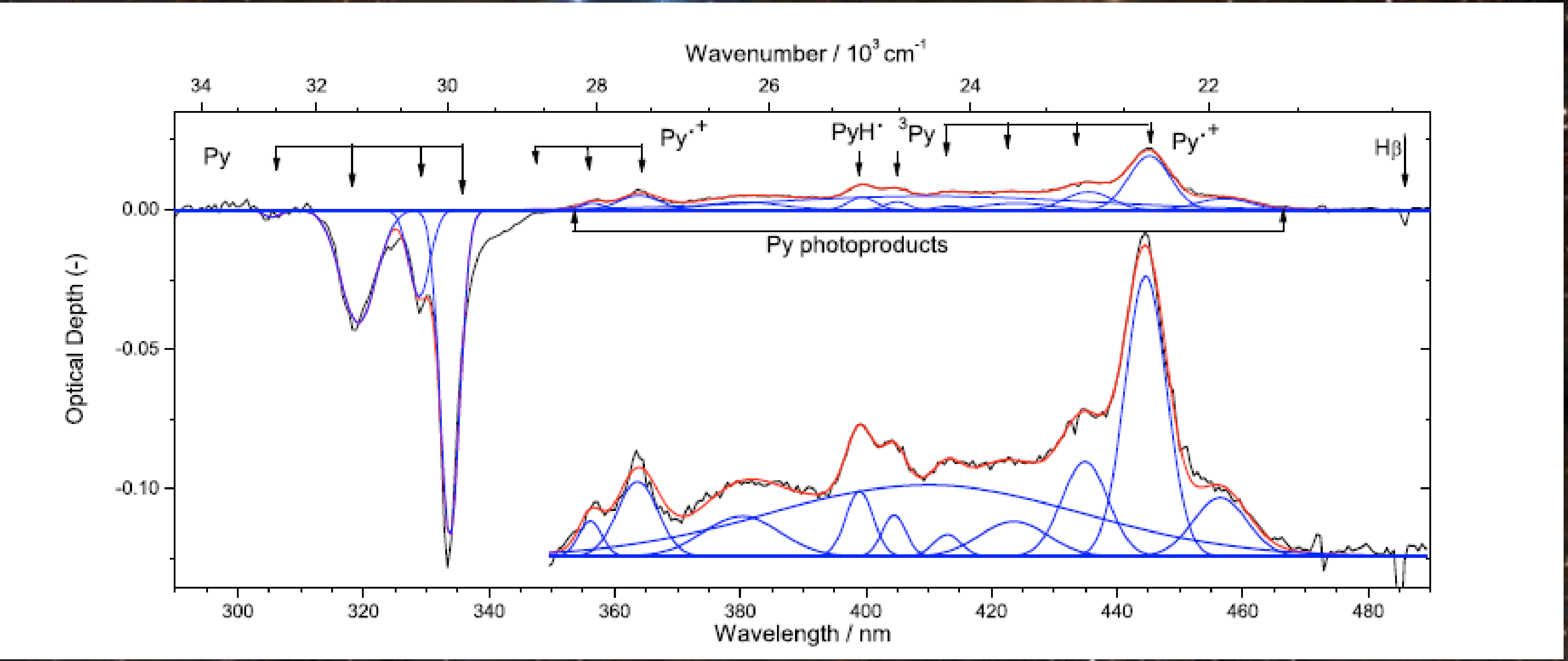


Courtesy
Allamandola

OASIS:
Optical Absorption Setup for Ice Spectroscopy



Bouwman et al. ApJ 2009, A&A 2010, 2011



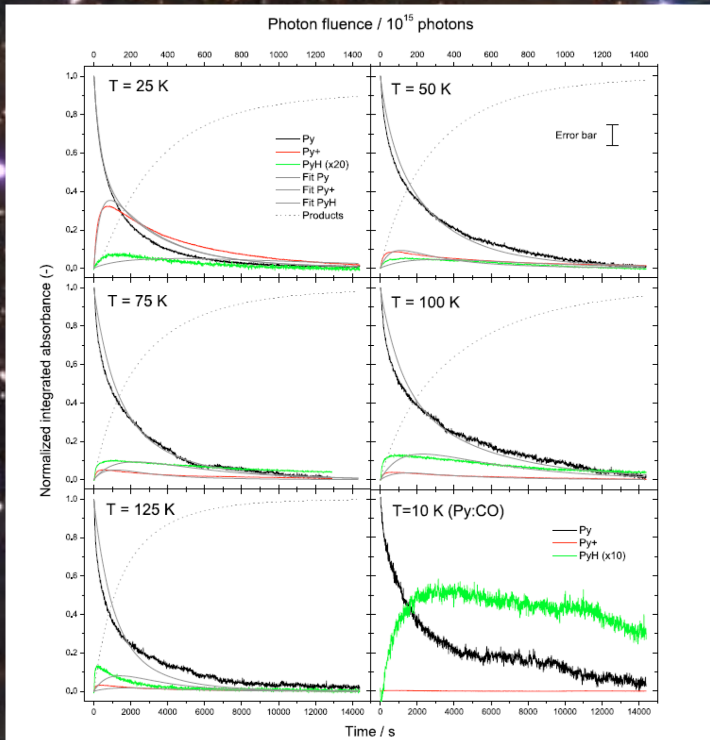
Pyrene:H_2O (1:10000) plus photo-products upon VUV irradiation

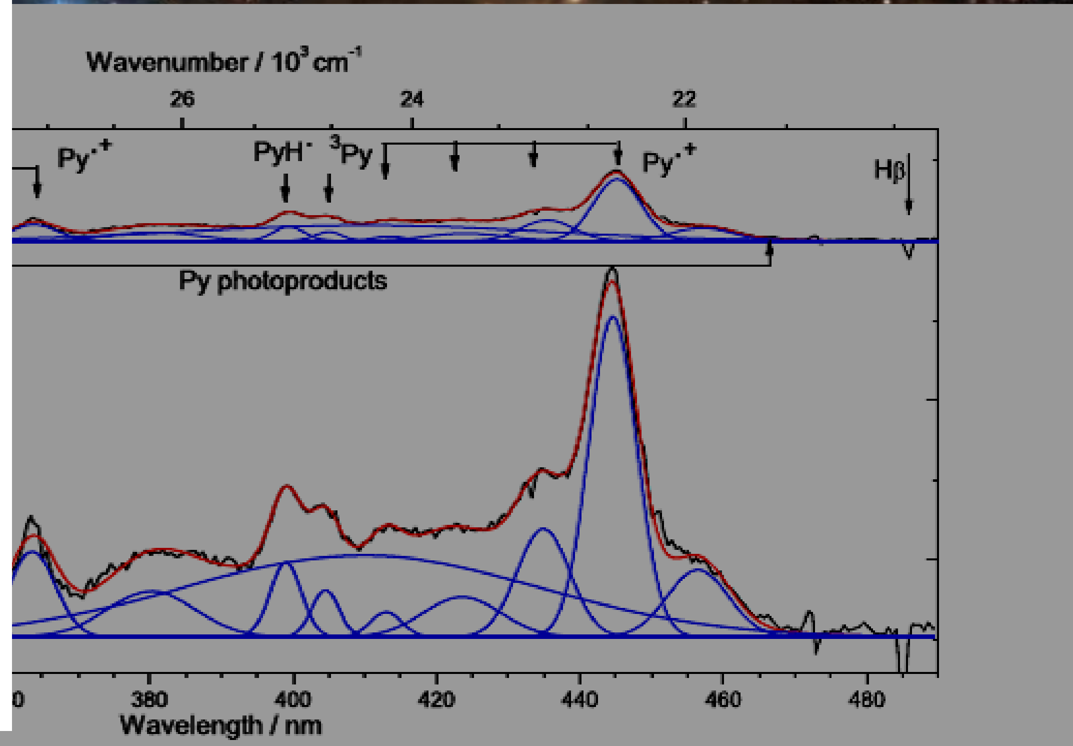
→ a way to search for PAHs in space - maybe

→ a way to understand photo-processing in ice – yes

→ complementary to previous IR work - absolutely

POSTER: Cuylle





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POSTER: Cuylle

Take Home Message

The molecular universe

has become ‘complex’

Acknowledgement

(Former) Post docs

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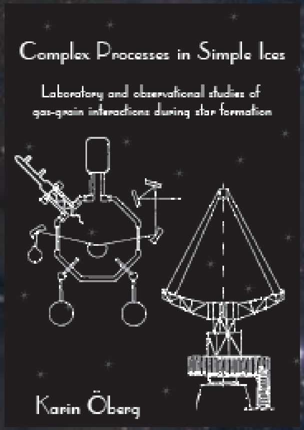

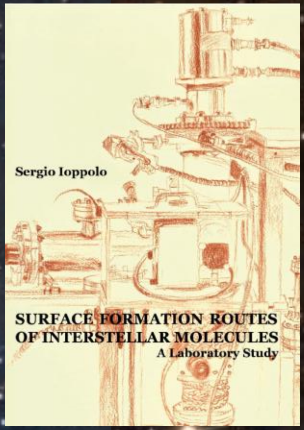

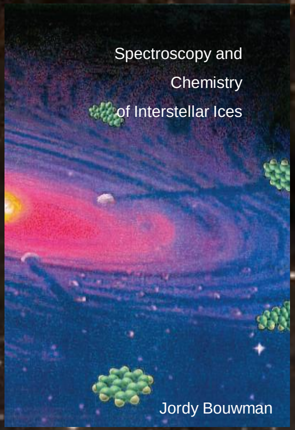

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Lou Allamandola (NASA)

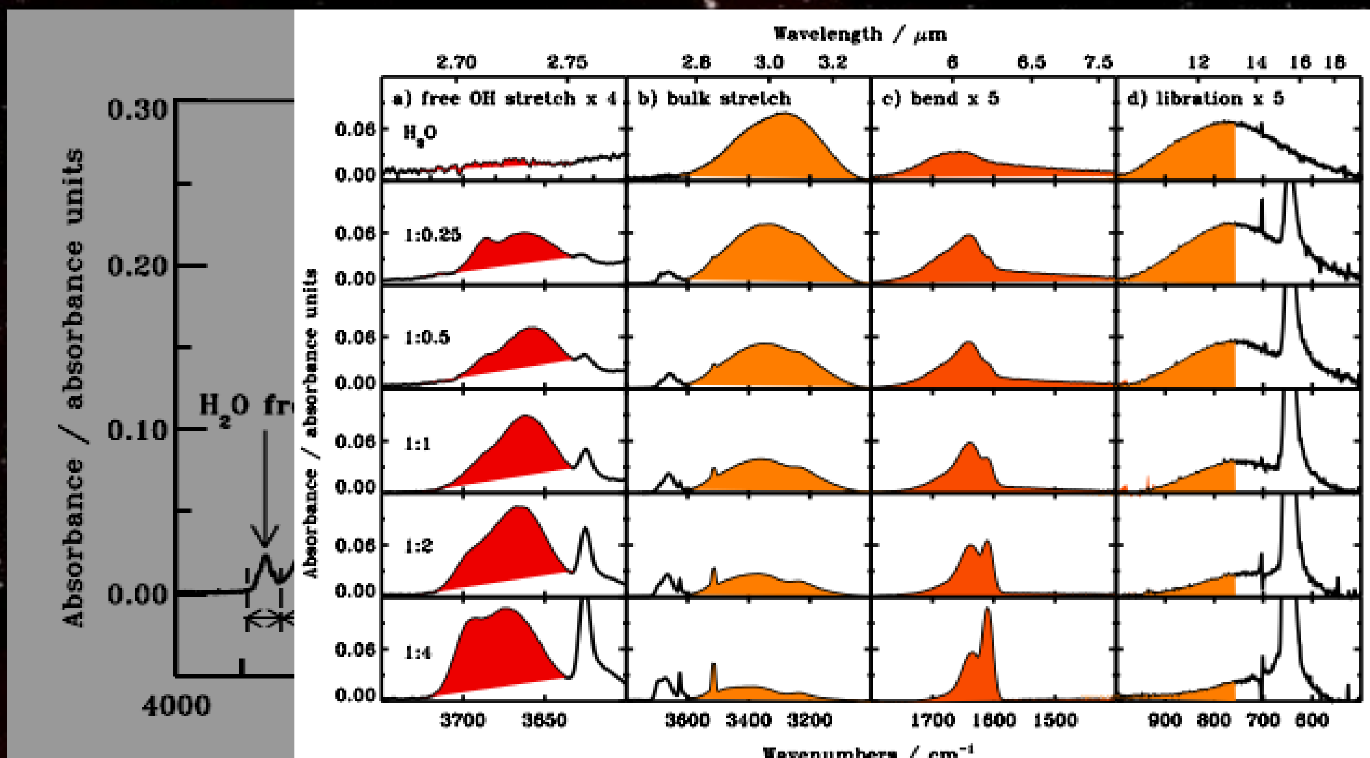
Thank you

http://www.laboratory-astrophysics.eu

Bottom-up approach

Research goals in solid state ice chemistry

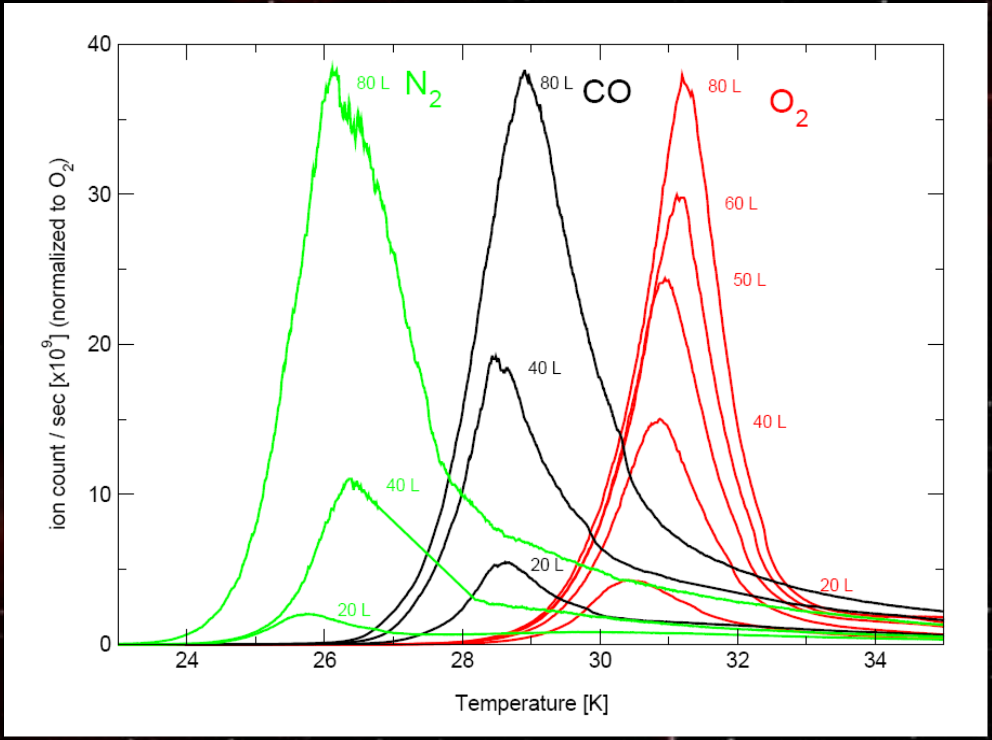
► Spectroscopy of ice (IR & UV/VIS)



Oberg et al. 2007

Research goals in solid state ice chemistry

- Spectroscopy of ice (IR & UV/VIS)
- Physical ice behavior: thermal desorption & segregation.



Acharyya et al. 2007

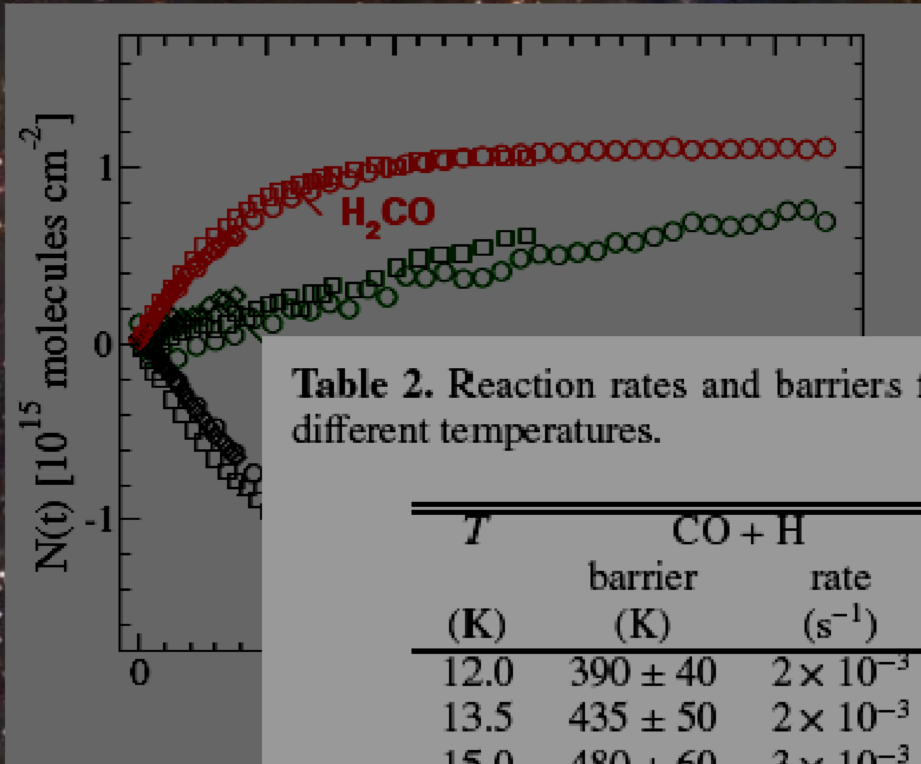
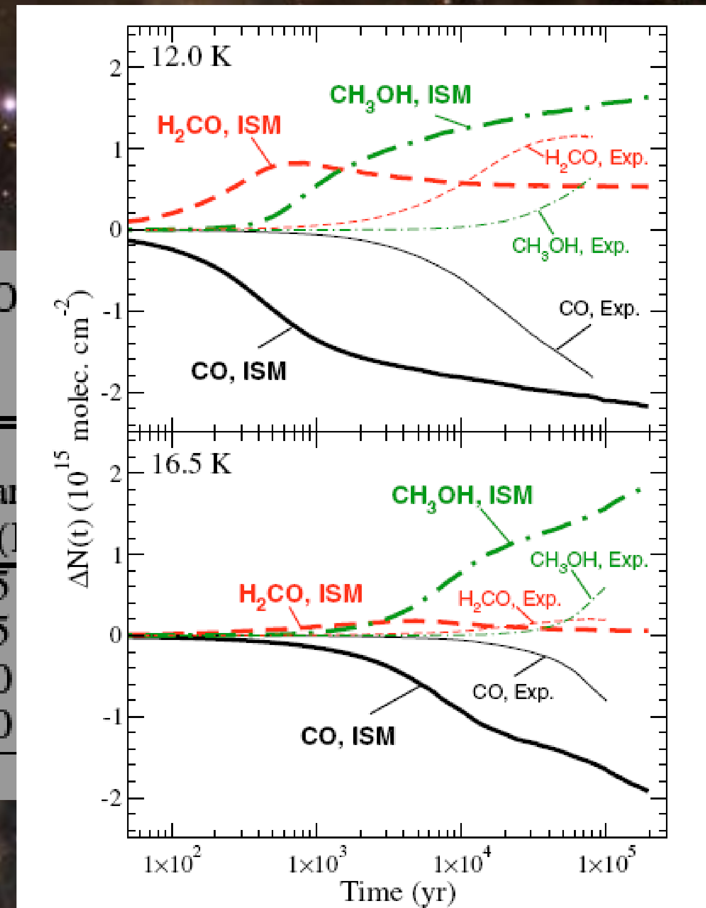


Table 2. Reaction rates and barriers for CO
different temperatures.

T	CO + H		
	barrier	rate	bar
(K)	(K)	(s^{-1})	(
12.0	390 ± 40	2×10^{-3}	415
13.5	435 ± 50	2×10^{-3}	435
15.0	480 ± 60	3×10^{-3}	470
16.5	520 ± 70	4×10^{-3}	490



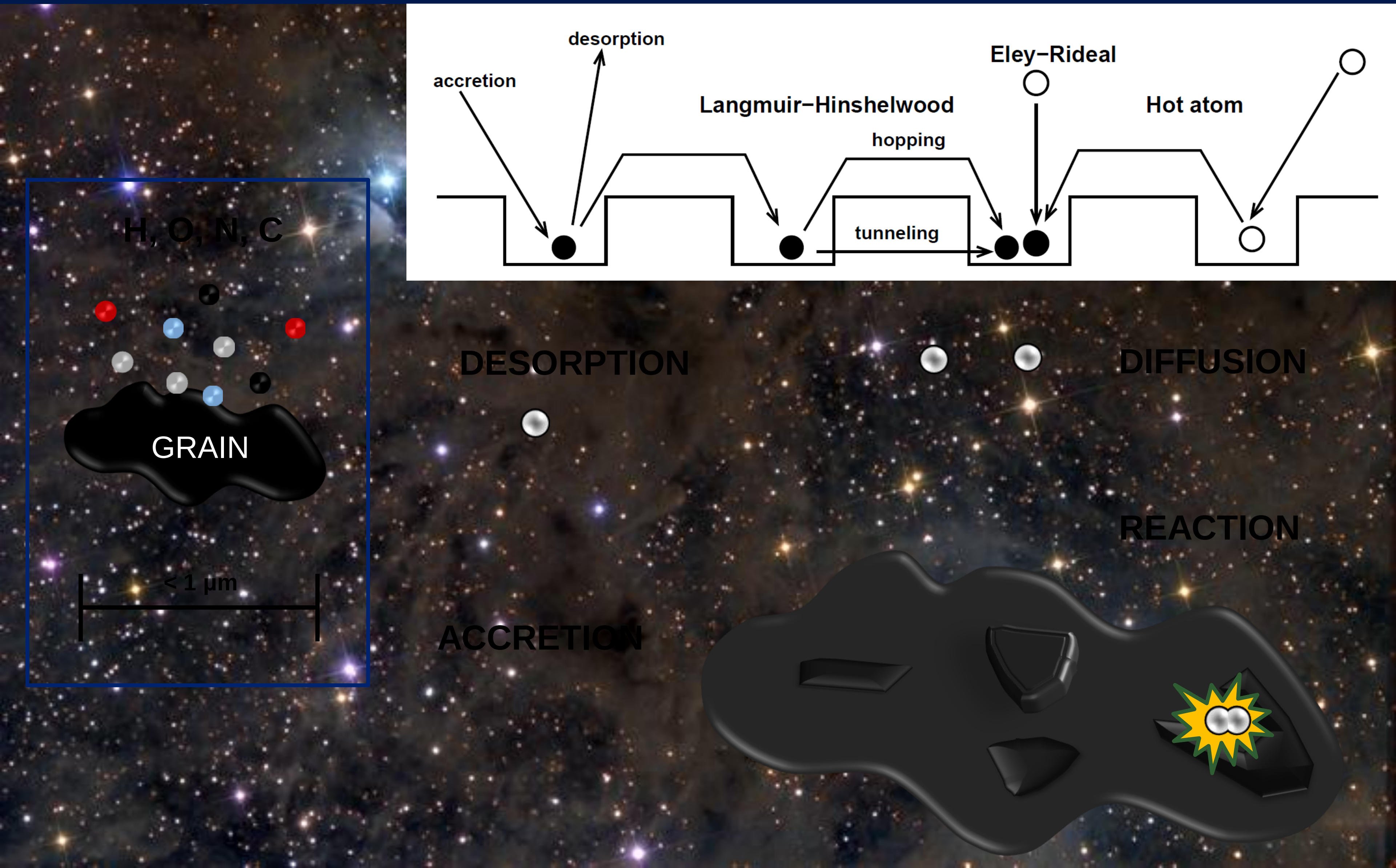
Fuchs et al. and Cuppen et al. A&A 2009

Using Monte Carlo simulations

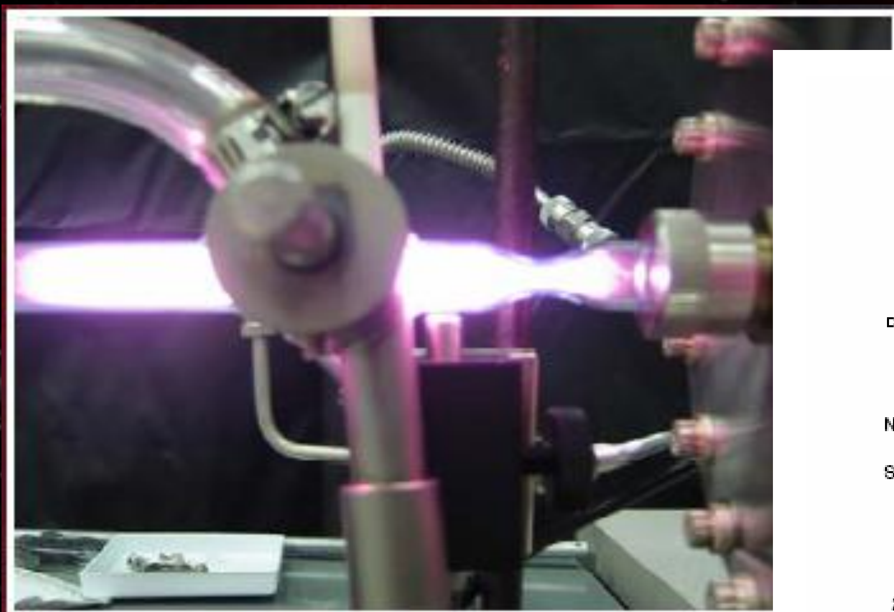
► **T-dependent reaction barriers / diffusion rates.**
► **Conversion towards interstellar conditions / timescales.**

Interstellar ice chemistry

Carbonaceous/Silicate Grains



Molecule	H_2O	CO	CO_2	CH_4	CH_3OH	H_2CO	OCS	NH_3	HCOOH	HCN
W33A	100	9	14	2	22	1.7-7	0.3	15	0.4-2	<3
Elias29	100	5.6	22	<1.6	<4	-	<0.1	<9.2	-	-



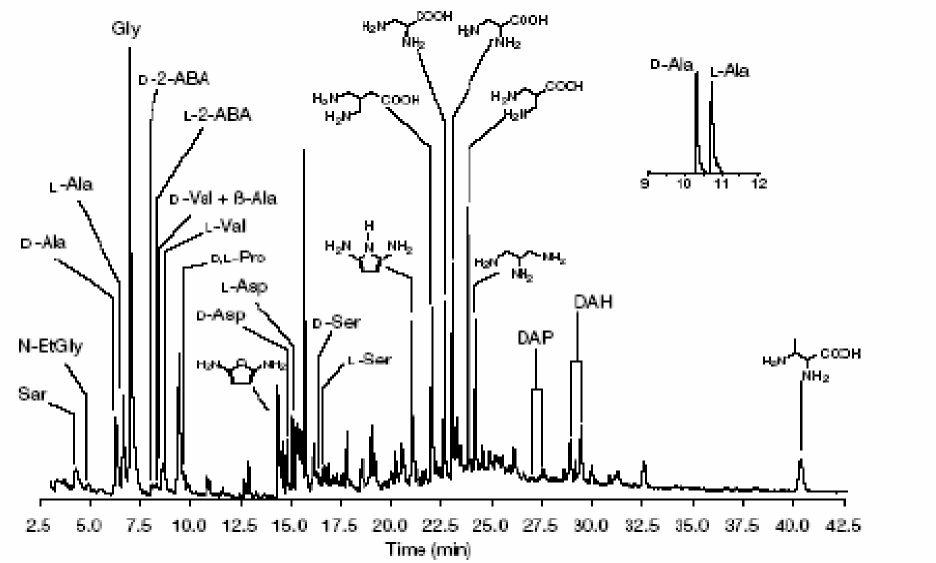


Fig. 2. Gas chromatogram showing a rich variety of amino acids and other compounds generated from a photo-processed ISM ice, containing H_2O, CH_3OH, NH_3, CO and CO_2. (Taken from G.M.M. Caro et al, Nature 416 (2002) 403.)

- **VUV lamp:**
- **►7 - 10.5 eV,**
- **►peaking around 121.6 nm**
- **►typically 5.10^{13} photons s^{-1} cm^{-2}**