Influence of nuclear spin conversion of H_2 molecules on the chemistry of the interstellar medium - Experiment and modelling

Japhar Michoud

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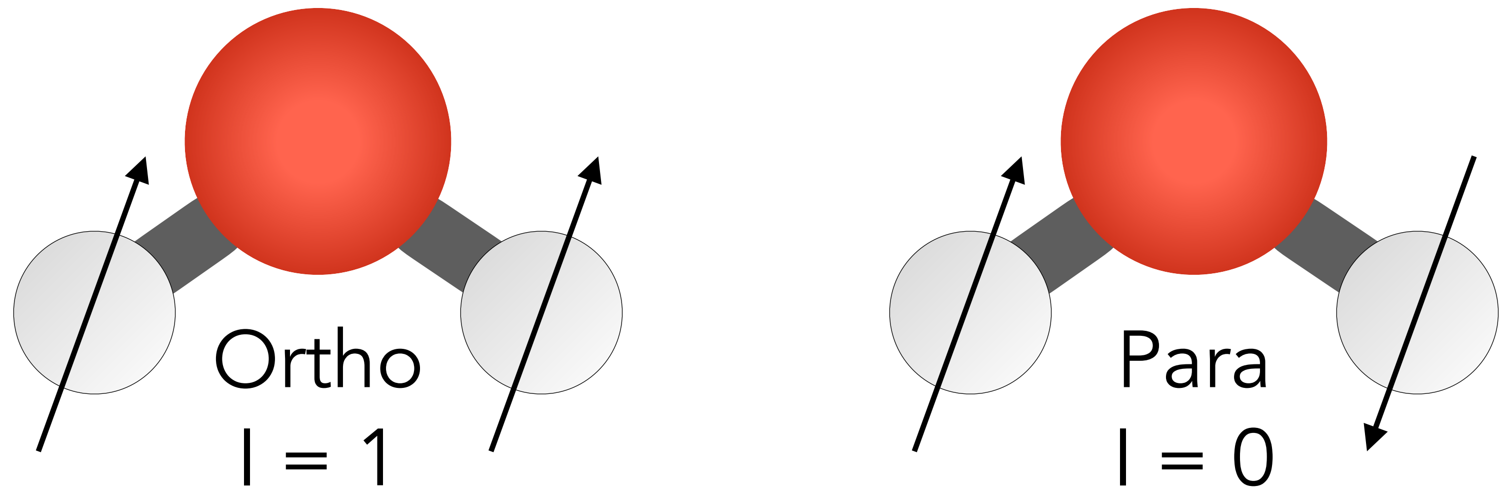
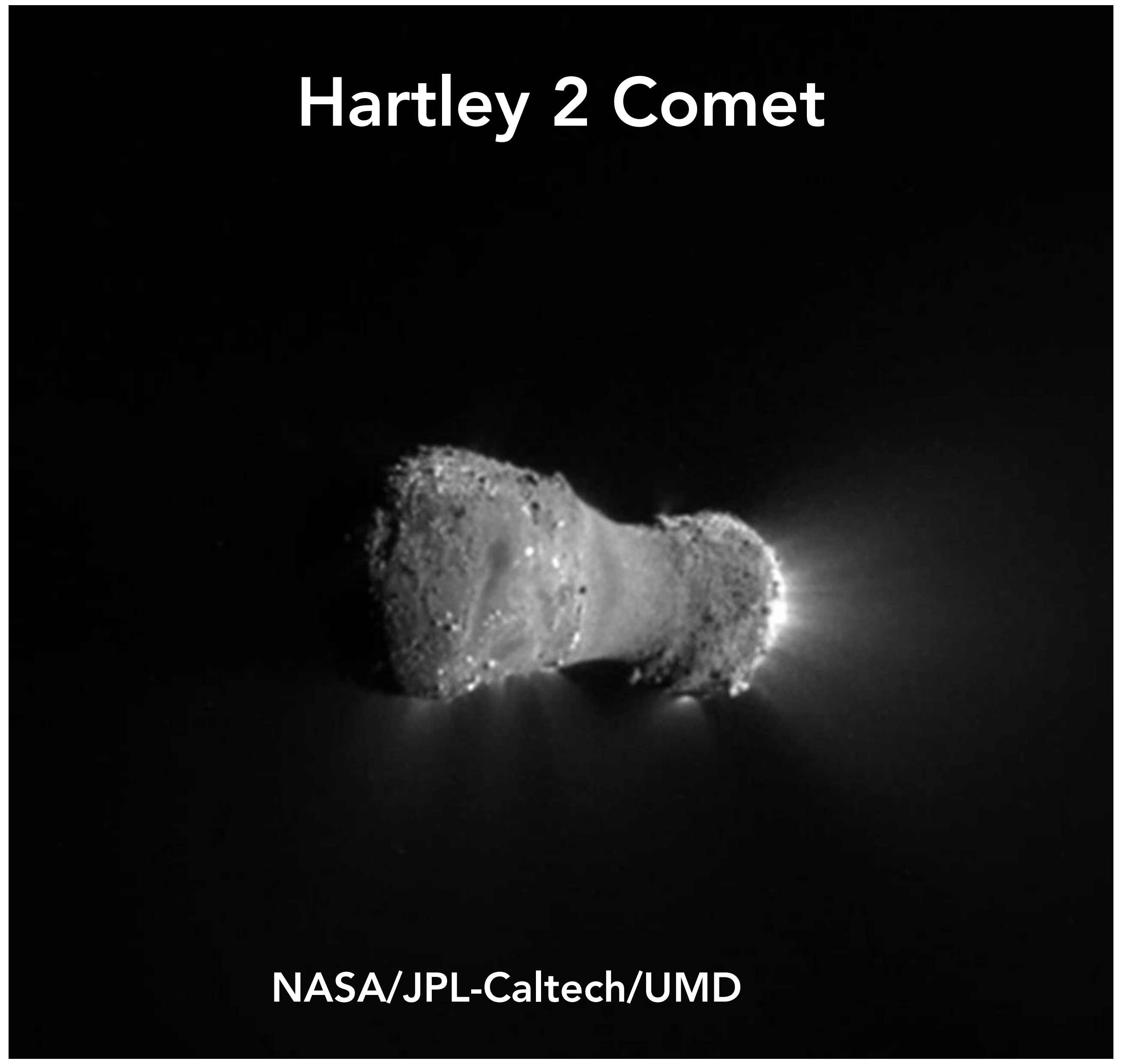
Nicolas Paladini

ORTHO TO PARA RATIO (OPR) IN THE INTERSTELLAR MEDIUM (ISM)

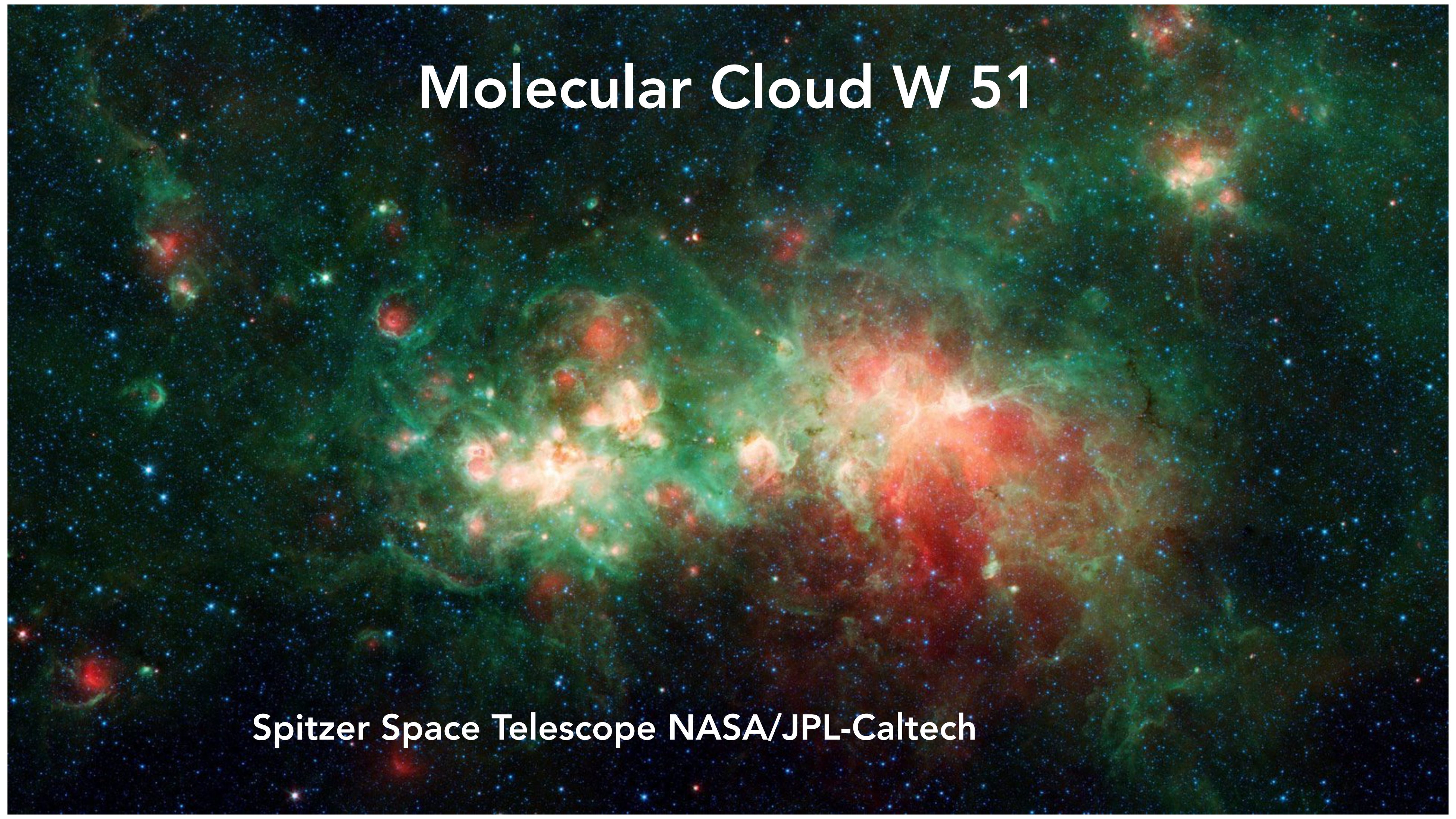
Why look at the OPR in the ISM?

- Parameter tracer such as the temperature of the medium?
- Impact on the chemistry of the ISM?





OPR = 2.59 ± 0.13
Bonev and al. Icarus 222 (2013)



OPR = 3.2 ± 0.1
N. Flagey and al. ApJ 762 11 (2013)

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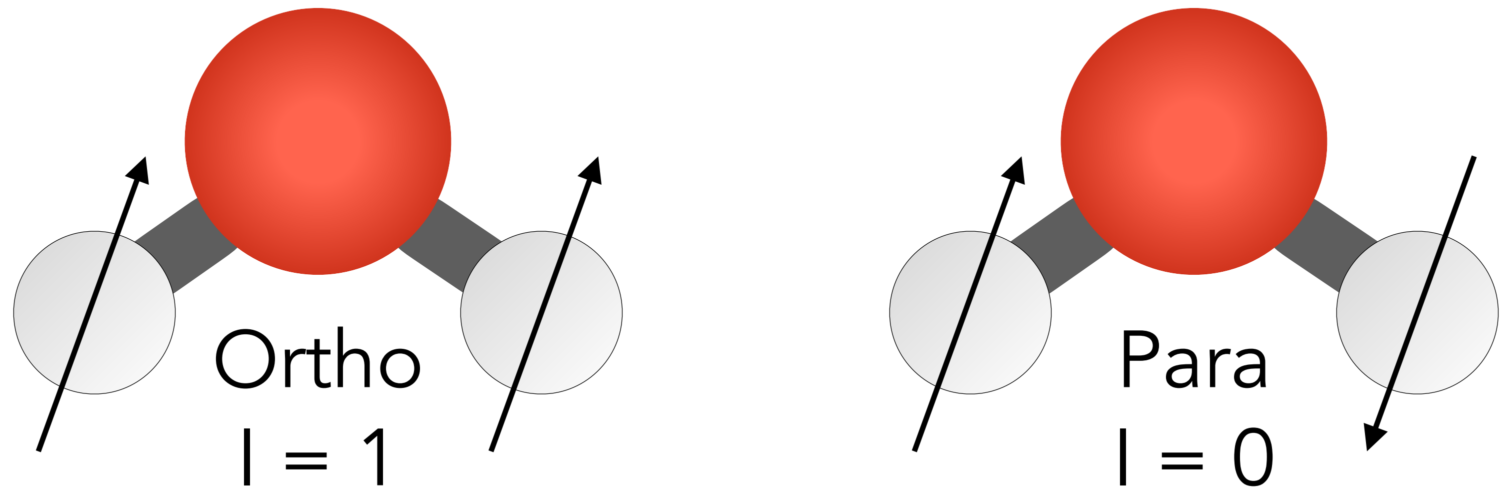

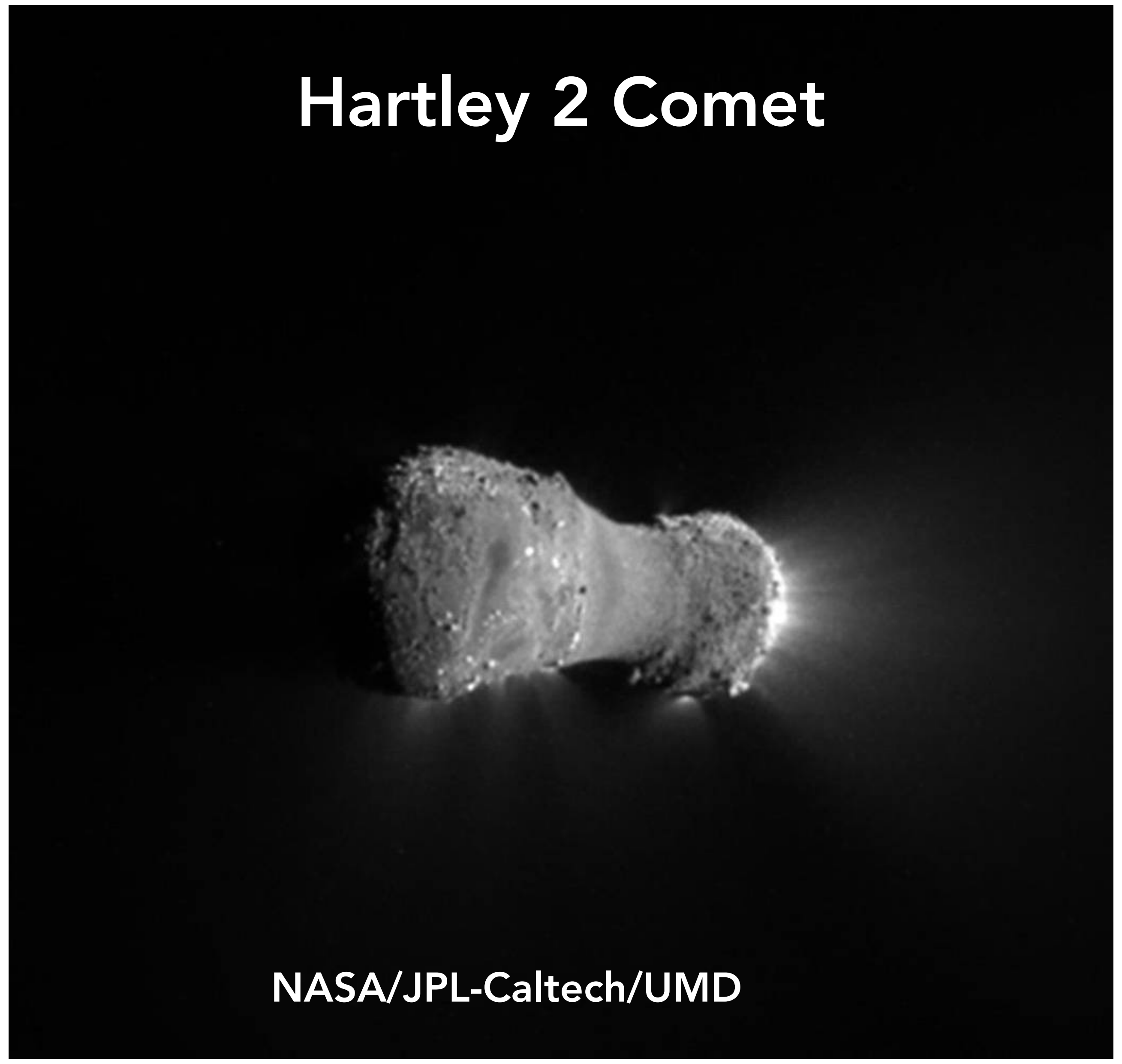

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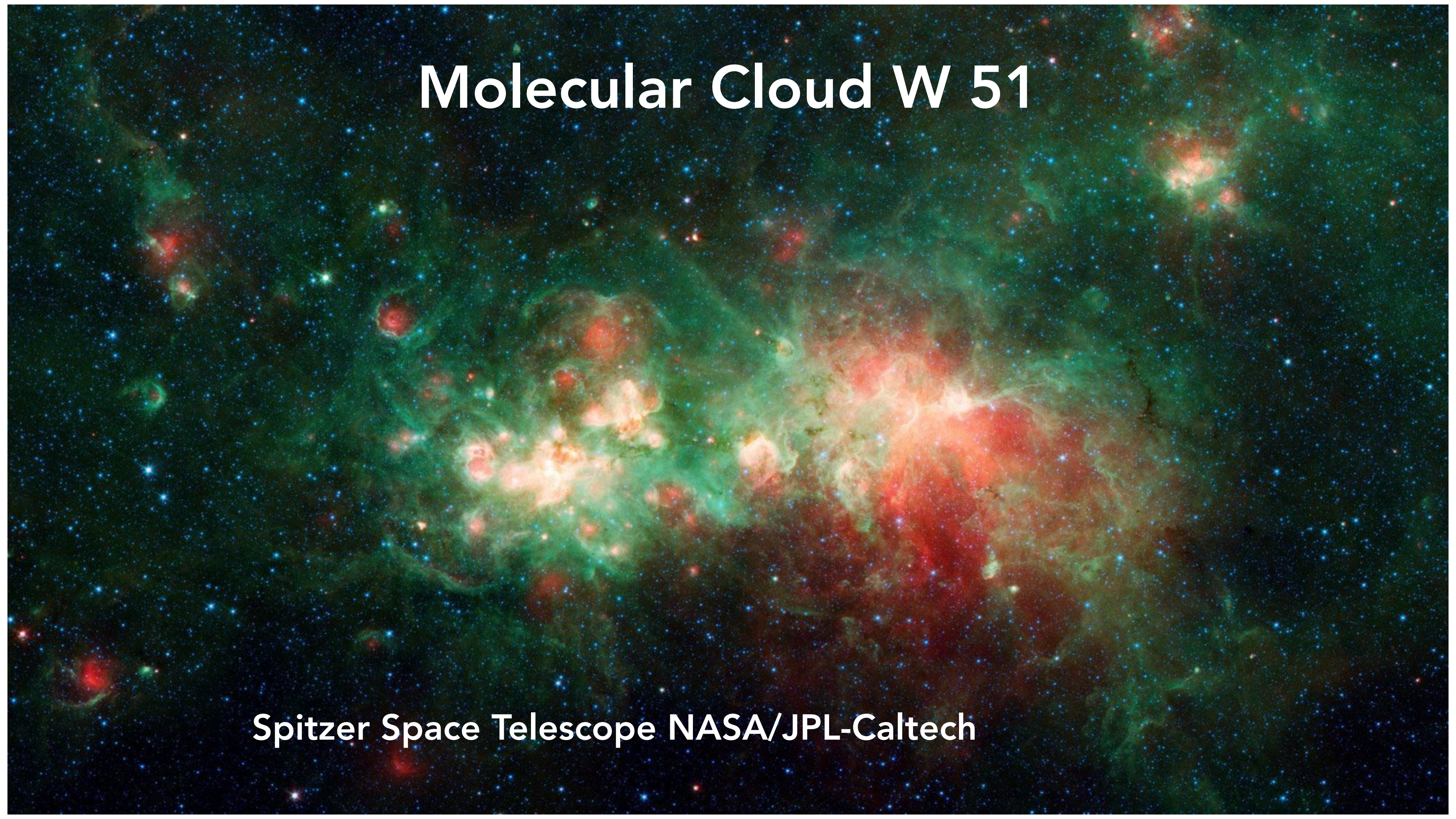

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ONE OF THE LOWEST OPR VALUES REPORTED IN THE ISM

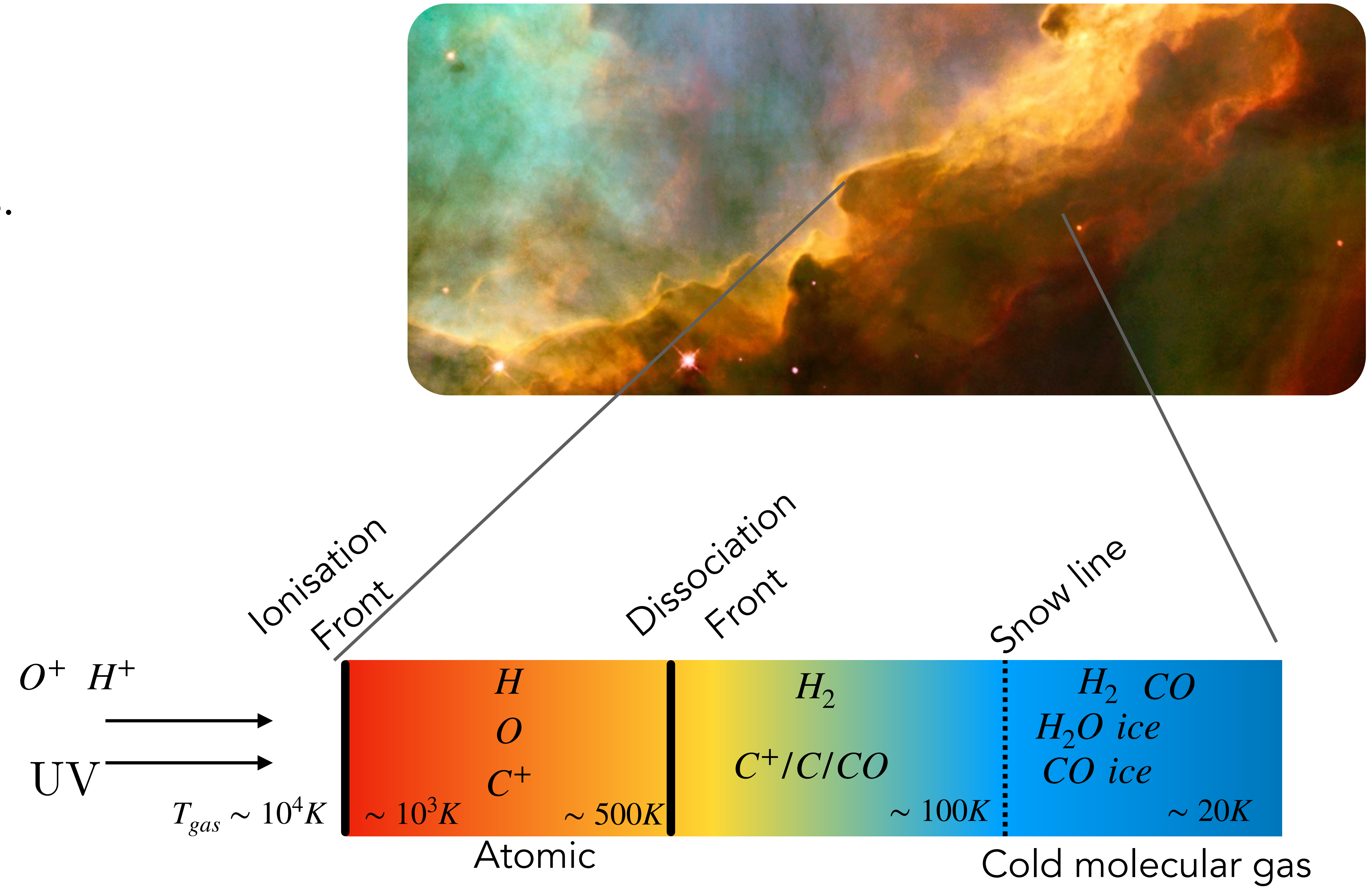
MEUDON PDR CODE (Photo Dissociated Region)

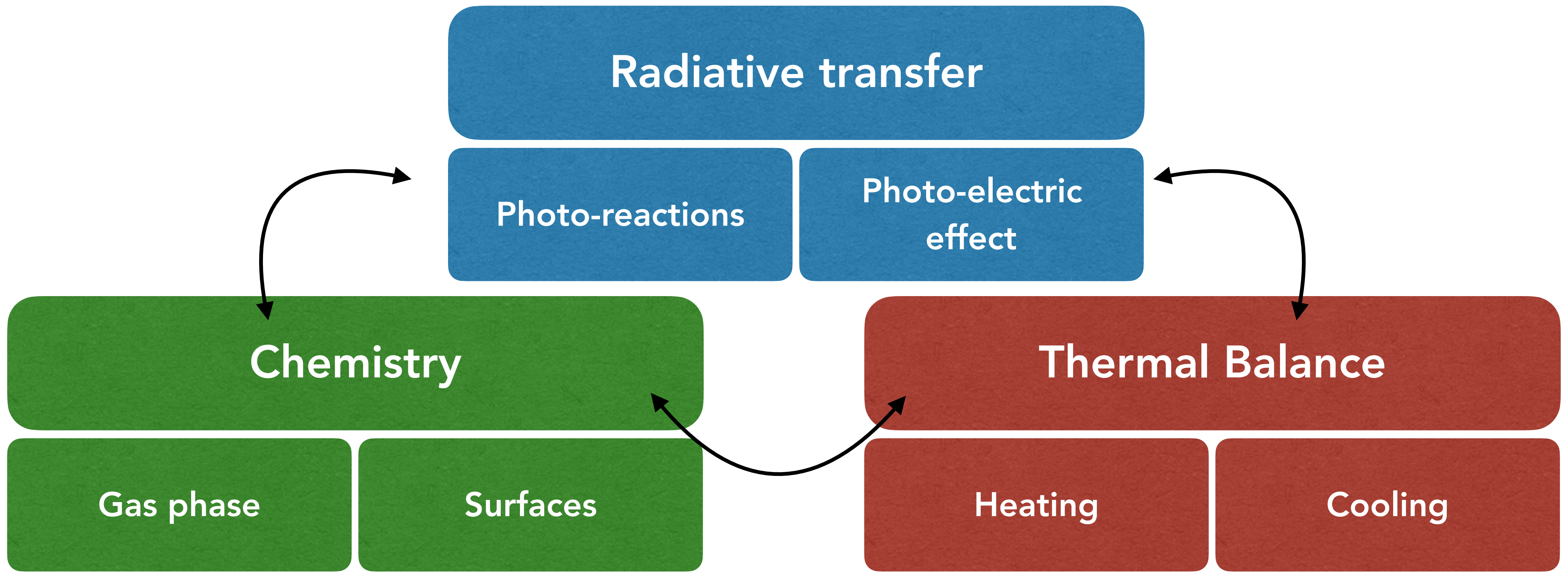
PDR CODE :

- Computes the atomic and molecular structure of interstellar clouds.
- Analysis of physical and chemical processes

MAIN PARAMETERS :

- G_0 (UV intensity radiation field), stellar spectrum
- Density, pressure, user profile density : clumps
- Metallicity and elemental abundances
- Cosmic ray ionisation rate
- Grain properties





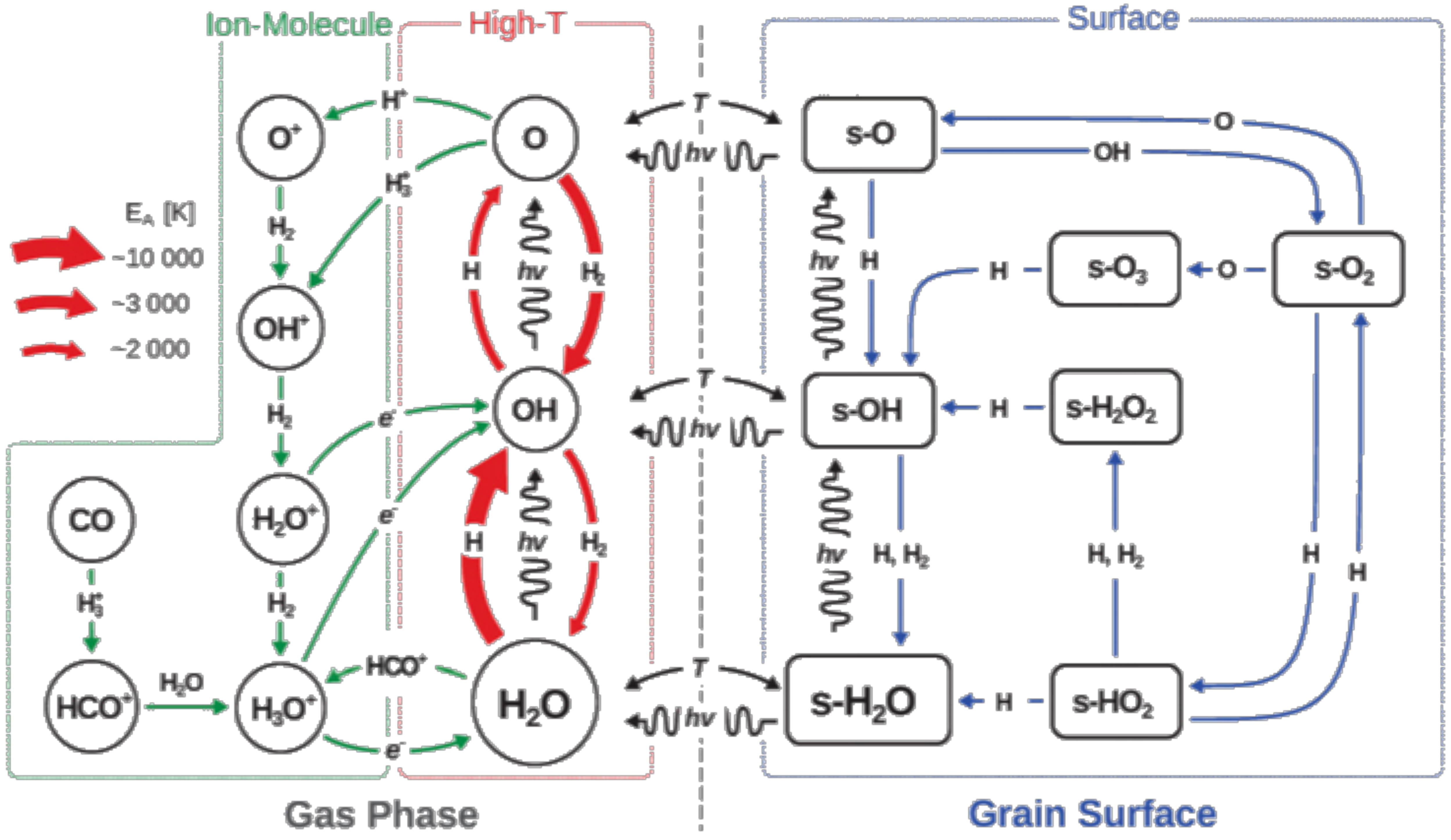
- Abundances of hundreds species
- Excitation in levels
- Gas & grains temperatures
- Intensities (H_2, CO, H_2O, ...)
- Column densities of species

H_2 IN THE CHEMICAL CHAIN REACTION OF WATER FORMATION

Why the study of H_2 is so important for the interstellar medium?

- H_2 is the most abundant molecule in the interstellar medium
- For a given reaction, the reaction rate may be different depending on whether H_2 is ortho or para (Dislaire *et al* A&A 537, A20 (2012))

$\Longrightarrow$ The OPR of H_2 can have a great impact on the chemistry



E. F. van Dishoeck and al. Chem. Rev. 2013, 113, 12, 9043–9085

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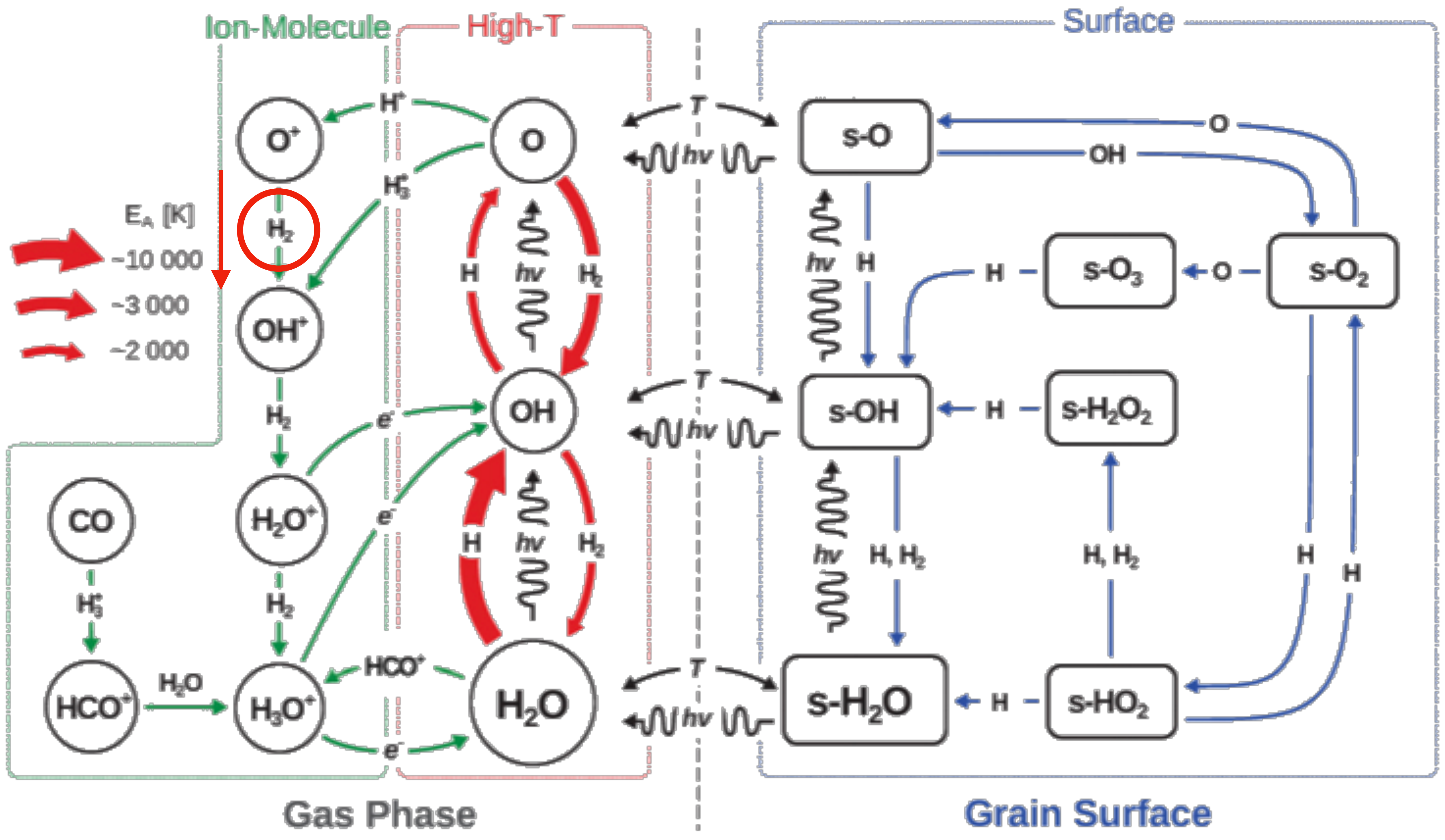

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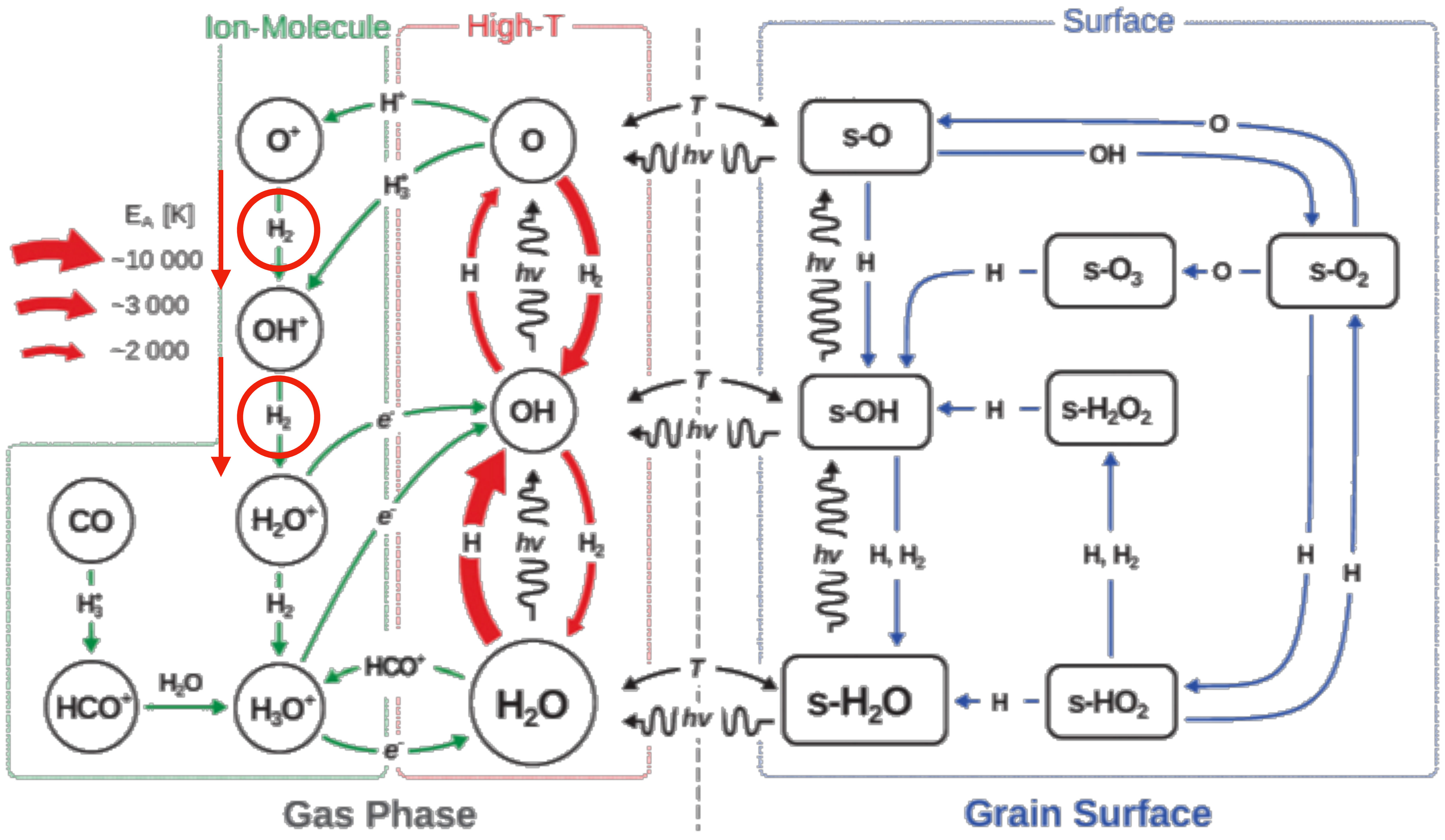

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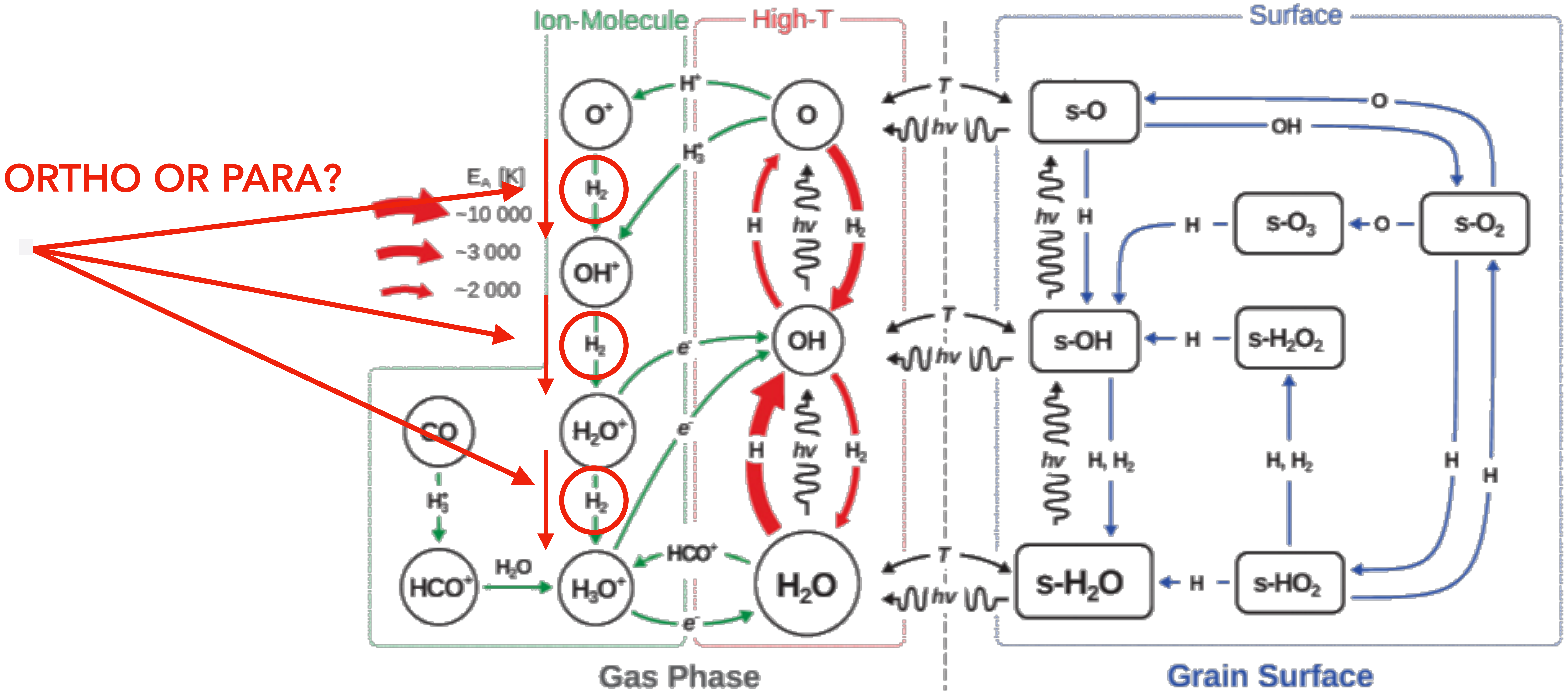

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PROCESSES THAT GOVERN THE ORTHO TO PARA RATIO IN THE PDR CODE

(i) Chemistry

(ii) Excitation

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(i) Chemistry

Chemical equation :

$$A + X\text{-}o \longrightarrow B + C \quad k_1$$

Differential equations for X specie :

$$\frac{dn(X)}{dt} = -\,k_1 n(A) f_X^o n(X)$$

→ **Modification of reaction rates depending on the ortho / para aspect of the species**

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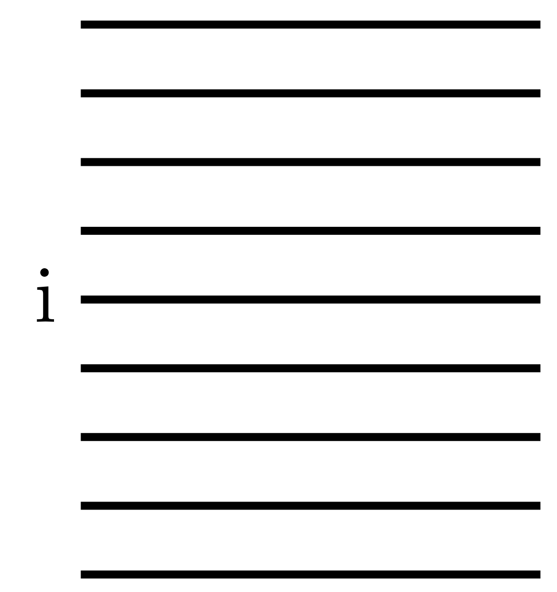
(ii) Excitation

Different processes that populate and depopulate a i-level for a given specie :

- Radiative processes
- Collisional processes
- Formation processes
- Destruction processes



Energy levels for a given species

Example for H_3^+ with two equations :

$$\begin{cases} H_2^+\text{-}o \;+\; H_2\text{-}o \;\longrightarrow\; H_3^+\text{-}p \;+\; H & k_1 \\ H_3^+\text{-}p \;+\; e^- \;\longrightarrow\; H_2\text{-}p \;+\; H & k_2 \end{cases}$$

$$\frac{dn(H_3^+, i)}{dt} = k_1 \cdot f^o_{H_2^+} \cdot f^o_{H_2}\; n(H_2^+) n(H_2)\; Boltz_{para}(i) \;-\; k_2 \cdot f^p_{H_3^+}\; n(e^-) n(H_3^+) \cdot Z^D_{para}(i)$$

- The excitation is calculated for 4 ortho/para species : H_2 , H_2O, H_2O^{18} and H_3^+
- **X-o** and **X-p** are not chemical species in the PDR code
- The excitation computation in quantum states is only made for the **X** specie

→ **The population X-o and X-p are finally deduced from this computation**

COMPARISON BETWEEN TWO MODELS WITH AND WITHOUT ORTHO PARA CHEMISTRY

Tested model : Diffuse cloud

PDR without ortho/para chemistry

$cm^3 s^{-1}$

Reaction	α	β
$H_2^+ + H_2 \longrightarrow H_3^+ + H$	$2.27 \cdot 10^{-9}$	-0.06
$H_2 + crp \longrightarrow H_2^+ + e^-$	$9.6 \cdot 10^{-1}$	0.00

PDR with ortho/para chemistry

$cm^3 s^{-1}$

Reaction	α	β
$H_2^+\text{-}o + H_2\text{-}o \longrightarrow H_3^+\text{-}p + H$	$7.57 \cdot 10^{-10}$	-0.06
$H_2^+\text{-}o + H_2\text{-}o \longrightarrow H_3^+\text{-}o + H$	$1.51 \cdot 10^{-9}$	-0.06
$H_2^+\text{-}p + H_2\text{-}o \longrightarrow H_3^+\text{-}p + H$	$1.51 \cdot 10^{-9}$	-0.06
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$H_2\text{-}o + crp \longrightarrow H_2^+\text{-}o + e^-$	$9.6 \cdot 10^{-1}$	0.00
$H_2\text{-}p + crp \longrightarrow H_2^+\text{-}p + e^-$	$9.6 \cdot 10^{-1}$	0.00

$$k = \alpha \left(\frac{T}{300} \right)^{\beta} e^{-\gamma / T}$$

$$\gamma = 0$$

T. Oka, J. Mol. Spectr. 228 (2), 635-639 (2004)
K.N. Crabtree, and al. Atrophys. J. 729 (1), 15 (2011)

COMPARISON BETWEEN TWO MODELS WITH AND WITHOUT ORTHO PARA CHEMISTRY

Excitation temperature of H_2 deduced :

-Without ortho/para chemistry : $T_{01} = 63.565\ K$

-With ortho/para chemistry : $T_{01} = 63.583\ K$

Excitation temperature of H_3^+ deduced :

-Without ortho/para chemistry : $T(H_3^+) = 47.860\ K$

-With ortho/para chemistry : $T(H_3^+) = 25.965\ K$

→ Decrease of the H_3^+ excitation temperature

→ Good agreement with H_3^+ and H_2 temperatures observed in the ISM

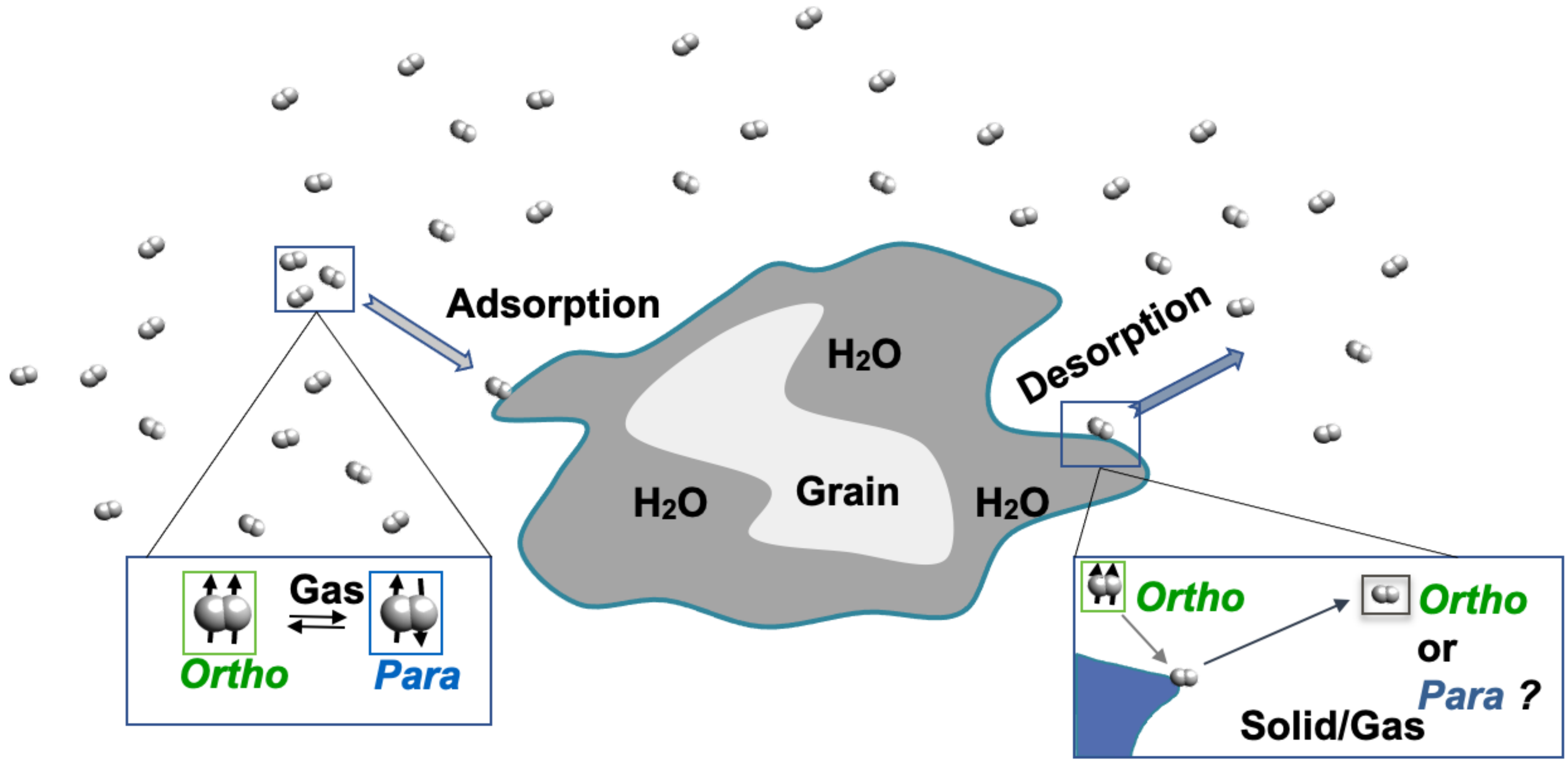
Quantity	Units	ζ Per[a, b]	X Per[a, c]	HD 154368[c]	HD 73882[c]	HD 110432[c, d]
			H_3^+ Results			
$N(1, 1)$	$(10^{13}\ \mathrm{cm}^{-2})$	4.09 ± 0.53	3.34 ± 0.69	7.43 ± 1.24	6.08 ± 0.12	3.11 ± 0.05
$N(1, 0)$	$(10^{13}\ \mathrm{cm}^{-2})$	2.53 ± 0.29	3.29 ± 0.45	2.83 ± 0.74	2.94 ± 0.48	2.11 ± 0.17
p_3[e]		0.62 ± 0.04	0.50 ± 0.06	0.72 ± 0.06	0.67 ± 0.04	0.60 ± 0.02
$T(H_3^+)$	(K)	28 ± 4	46^{+21}_{-13}	20 ± 4	23 ± 3	30 ± 2
			H_2 Results			
$\log[N(0)]$	(cm^{-2})	20.51 ± 0.09	20.76 ± 0.03	21.04 ± 0.05	20.99 ± 0.08	20.40 ± 0.03
$\log[N(1)]$	(cm^{-2})	20.18 ± 0.09	20.42 ± 0.06	20.54 ± 0.15	20.50 ± 0.07	20.27 ± 0.04
p_2[f]		0.68 ± 0.06	0.69 ± 0.04	0.76 ± 0.07	0.76 ± 0.05	0.57 ± 0.03
T_{01}	(K)	58 ± 6	57 ± 4	51 ± 8	51 ± 6	68 ± 5

K.N. Crabtree, and al. Atrophys. J. 729 (1), 15 (2011)

More results on H_3^+ temperature in Le Bourlot et al. (coming very soon)

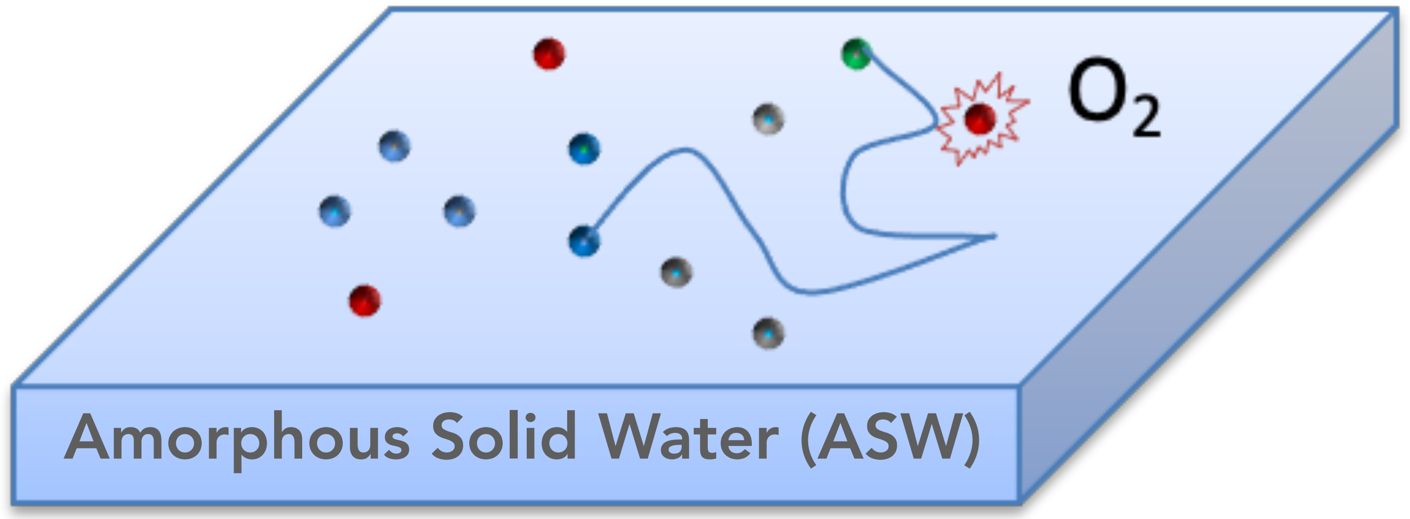
ORTHO-PARA SELECTIVITY OF H_2 OF DESORPTION PROCESSES

Behaviour of the nuclear spin isomers at the solid-gas interface ?



Molecular hydrogen on ASW

NSC in presence of O_2 traces



Molecular Hydrogen Diffusion

At 10K

O_2	t (min) IR Vib	t (min) Laser *FORMOLISM* (1)	t (min) Laser *Sugimoto* (2)	t (min) Laser *Ueta* (3)
0.2 %		H_2 : 3.7 (1) D_2 : 11 (1)		
0.1 %	H_2 : 30 (2)			
0.02 %		D_2 : 51 (4)		
0 %	H_2 : 220 (17)	H_2 : >300	H_2 : 8 (2) D_2 : 49 (38)	H_2 : 52 (5)
Coverage	1ML	0.3 - 0.75 ML	1 - 2 ML	0.3 - 1 ML

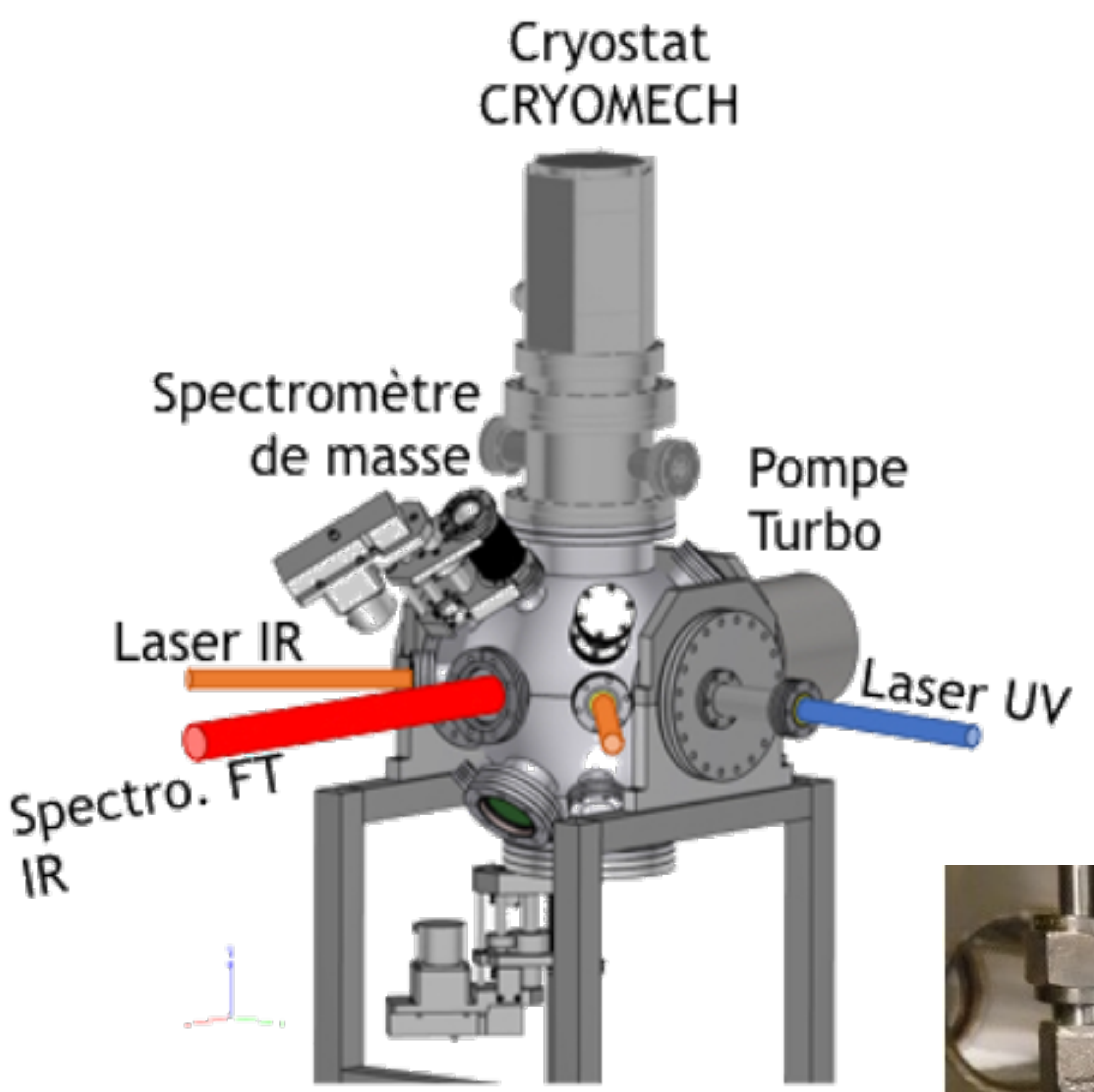
(1) Chehrouri, Fillion et al PCCP 2011
(2) Sugimoto & Fukutani Nature Physics 2011
(3) Ueta, Watanabe, Hama, Kouchi PRL 2016

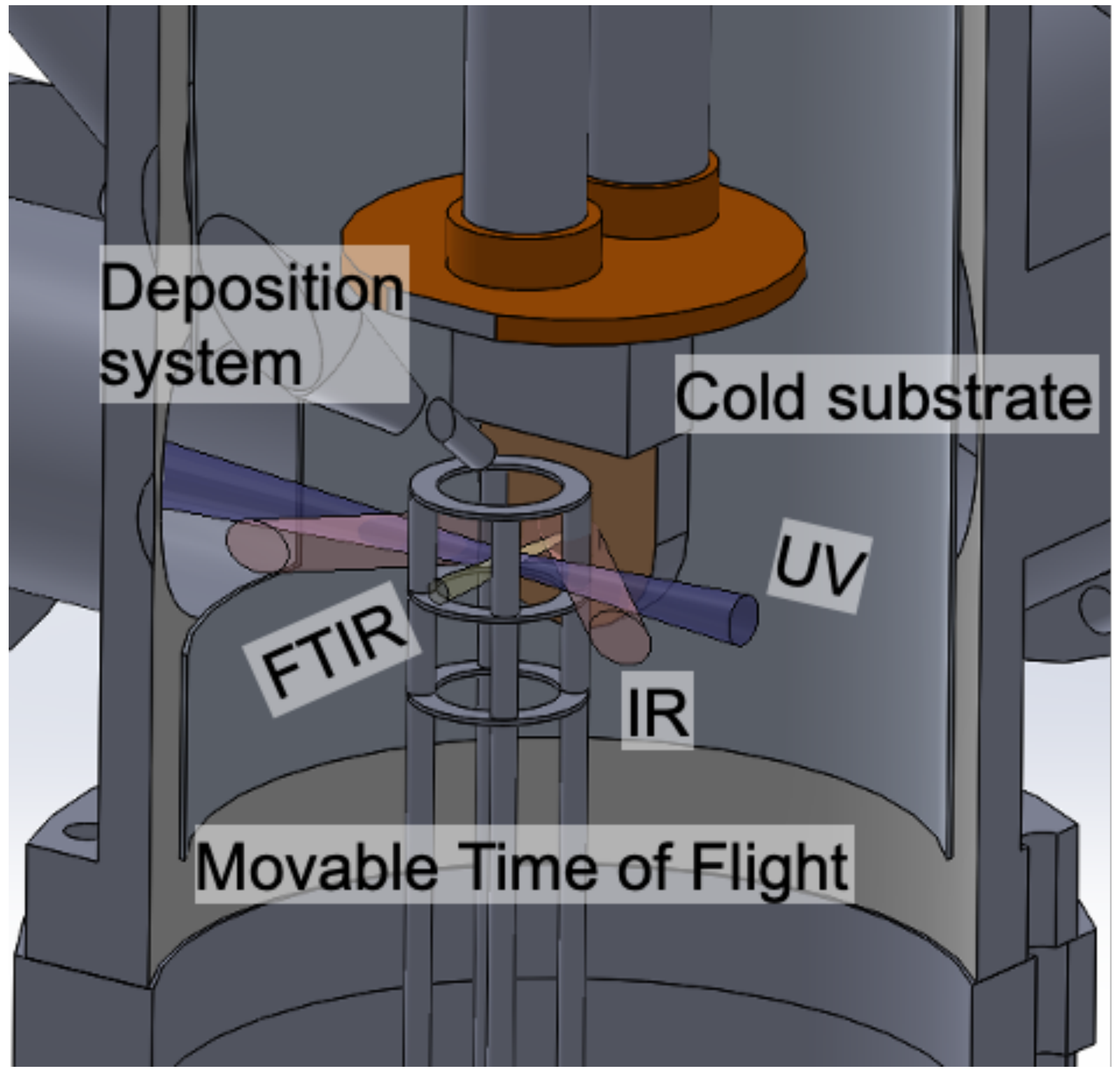
Solid H_2 at 4 K : 1.5 days
Gas H_2 (2 bars, 293K) : 12.8 days (DG)

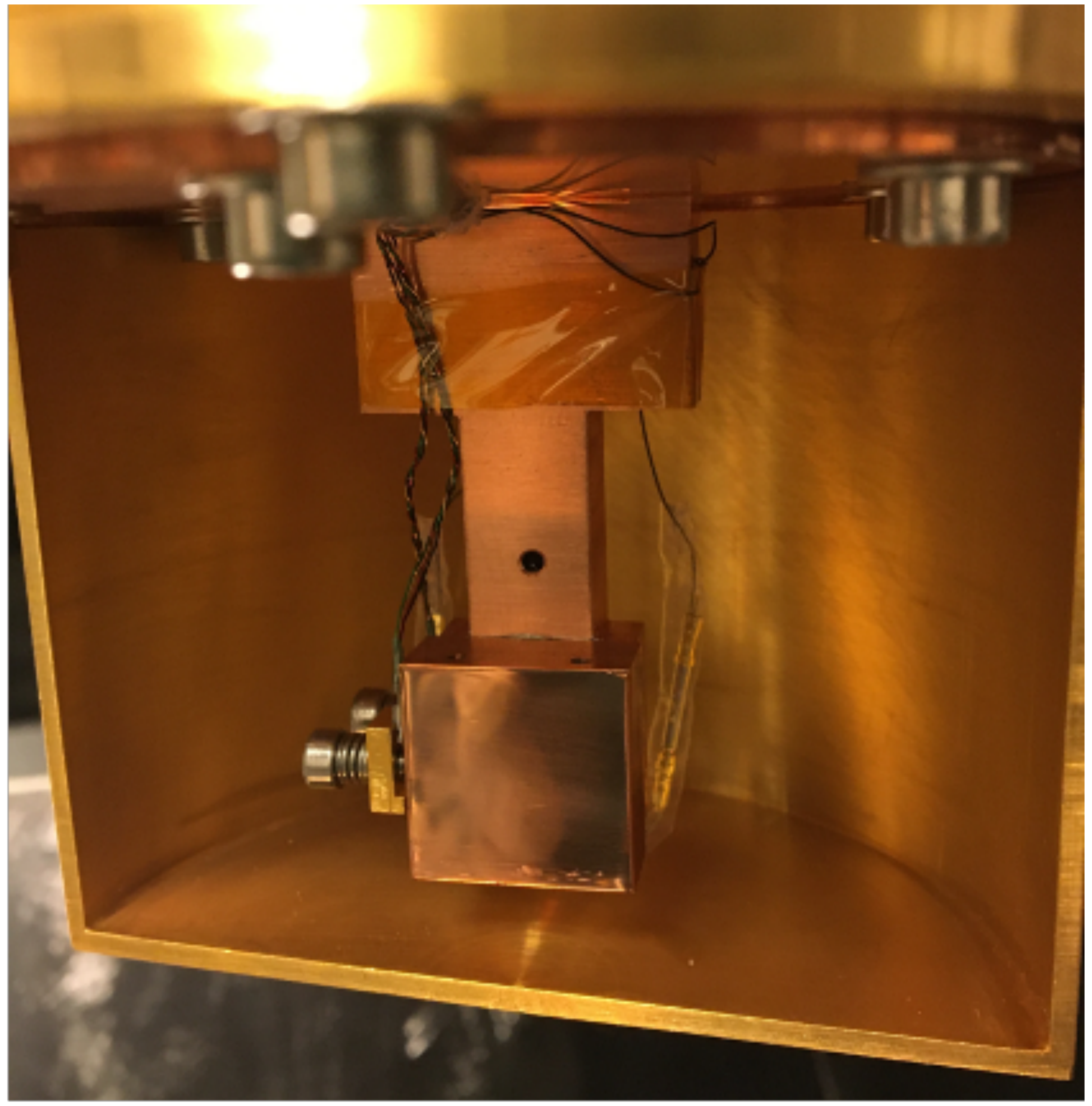
COSPINU2

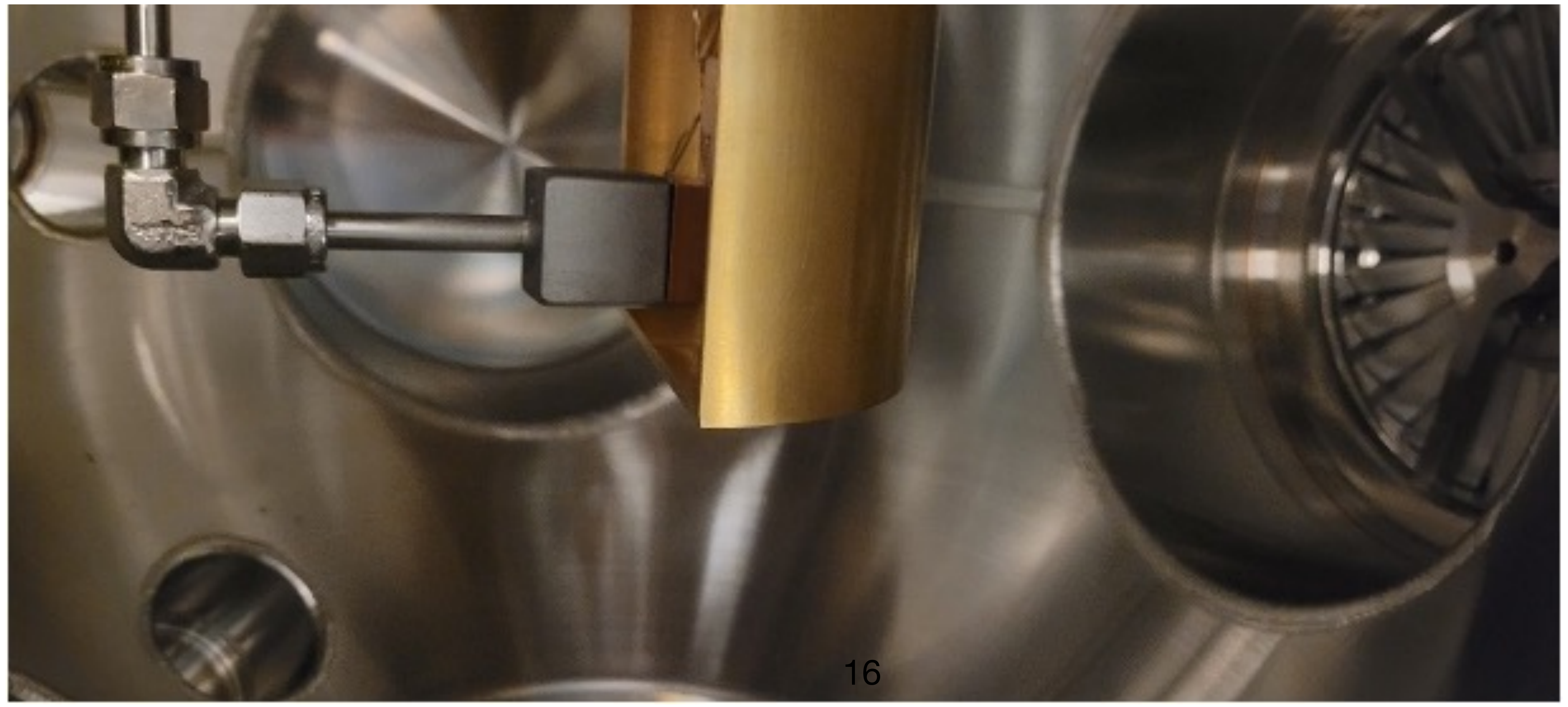
Methods :

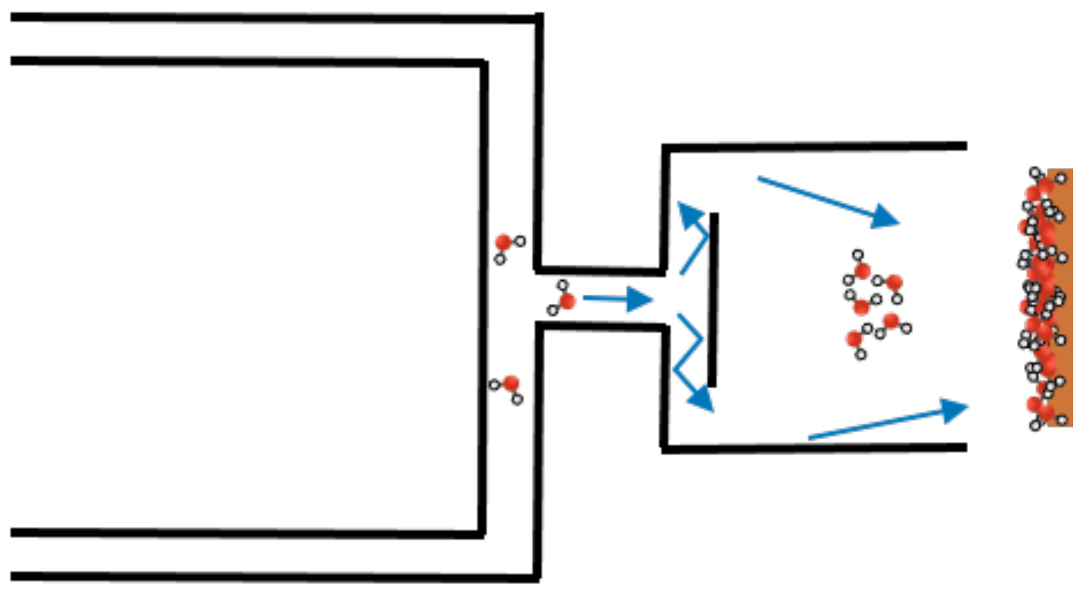
Experimental set-up under Ultra High Vacuum chamber (3.10^{-10} mbar) at low temperature (6K) to produced controlled icy films coated with H_2 isotopologues











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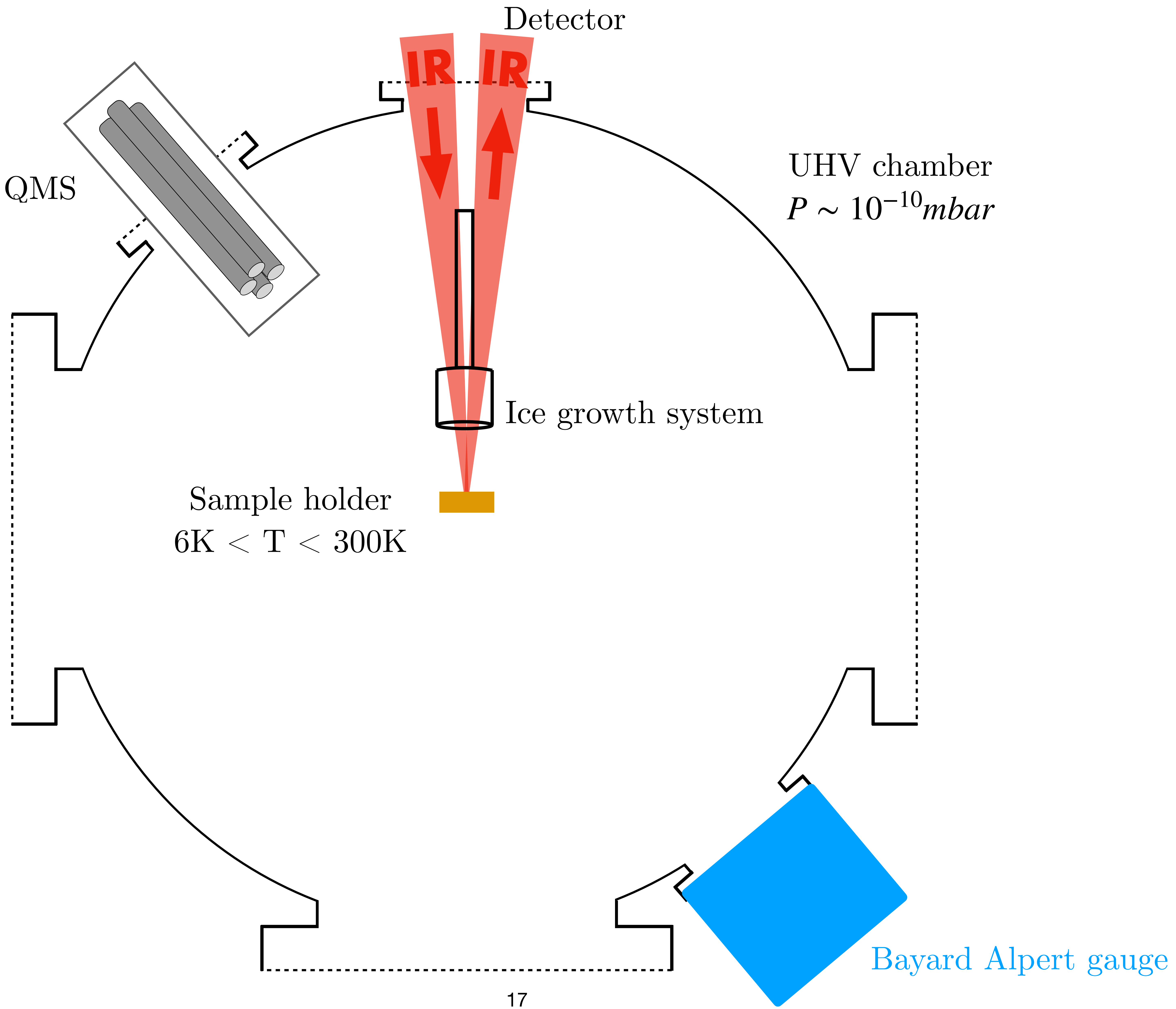
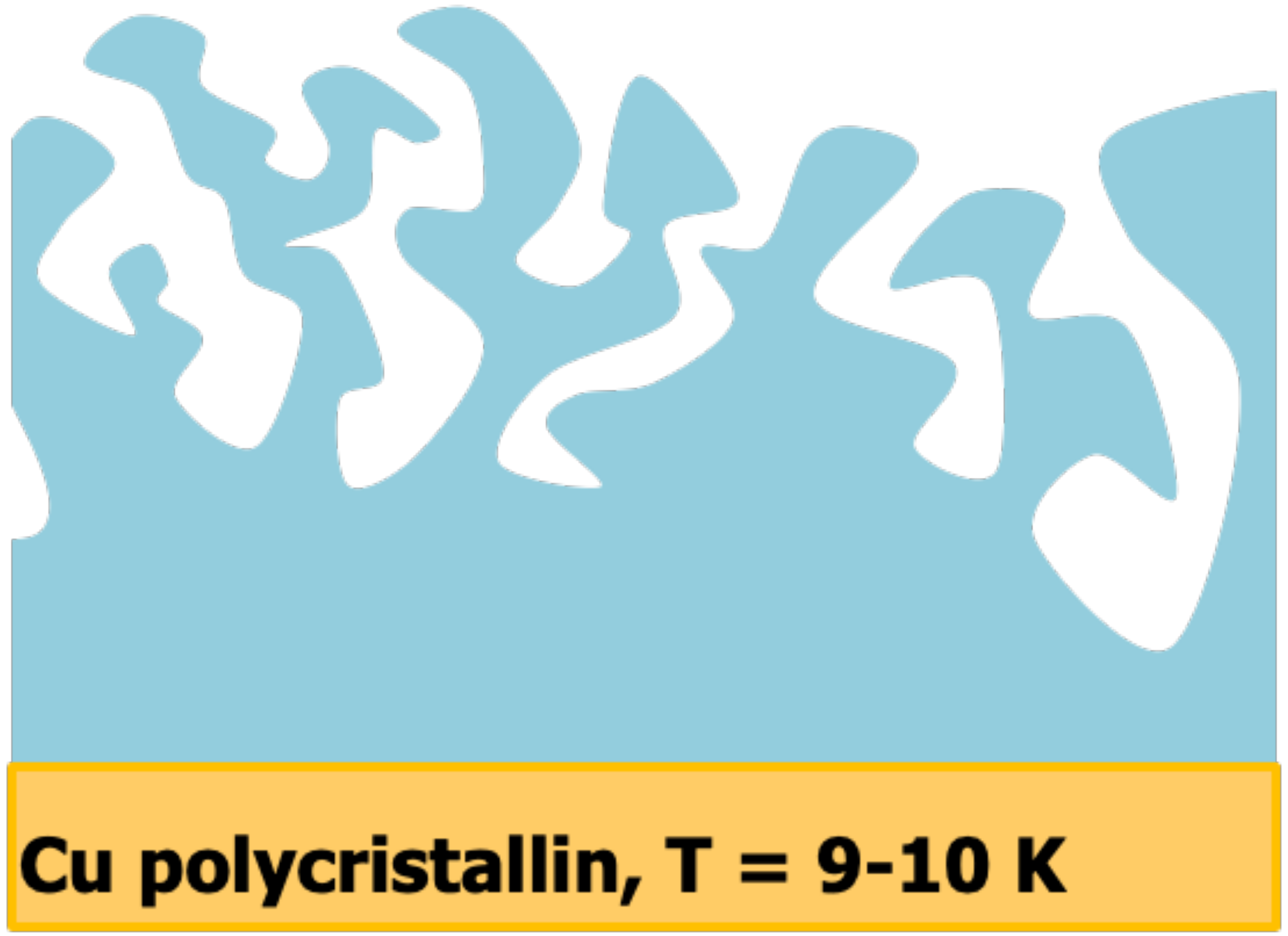


Detector
IR
IR
QMS
UHV chamber
$P \sim 10^{-10} mbar$
Ice growth system
Sample holder
6K < T < 300K
Bayard Alpert gauge

NSC ON ASW USING IR SPECTROSCOPY



Equivalent to 1000 ML of compact ices
H_2O amorphous and porous

Use of a special depostion technique to produce thick ices without destroying the background vacuum.
Allows to avoid redeposition during the duration of the experiment.

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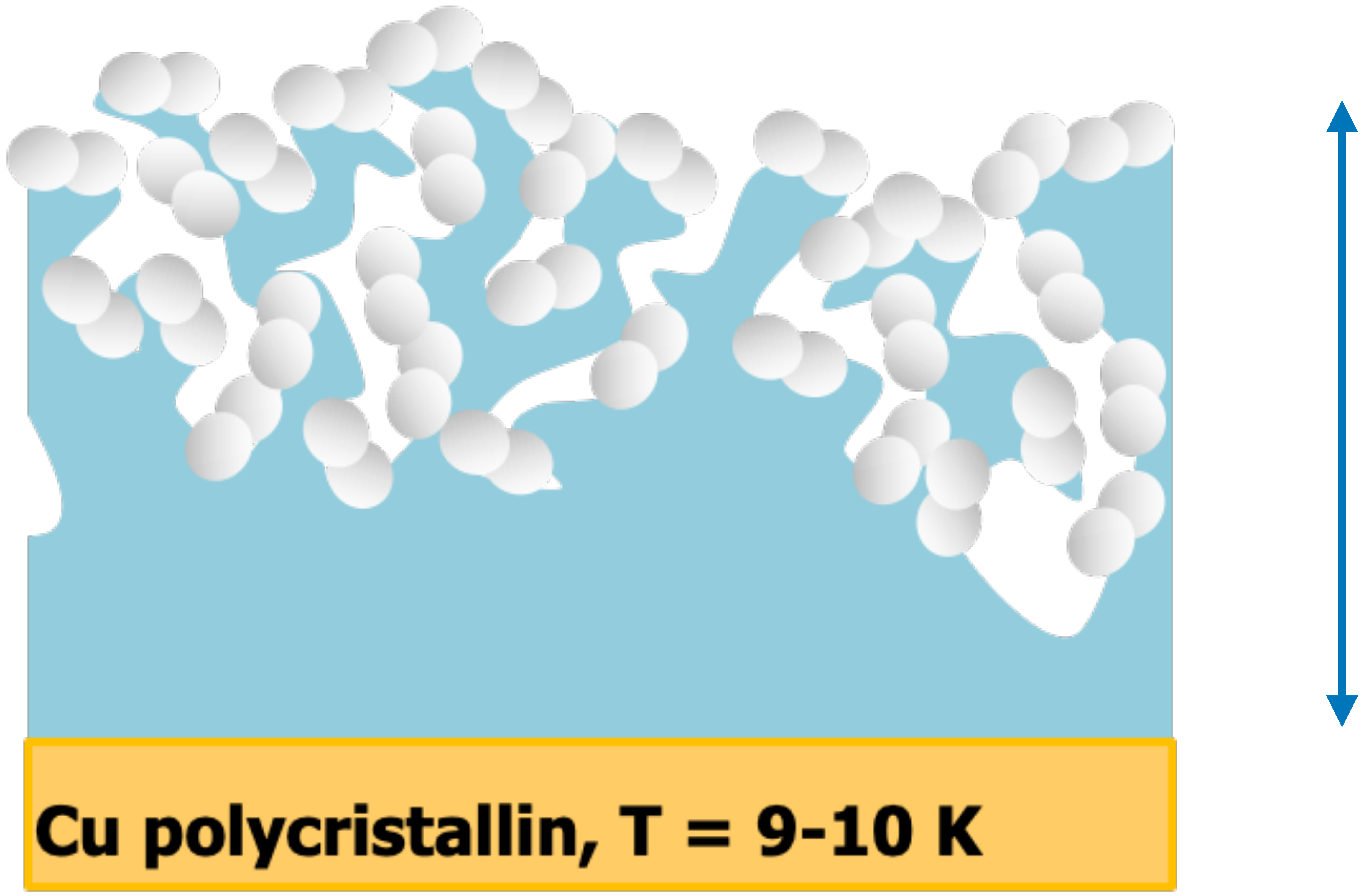

Surface (interface H_2O – vacuum) saturated with H_2

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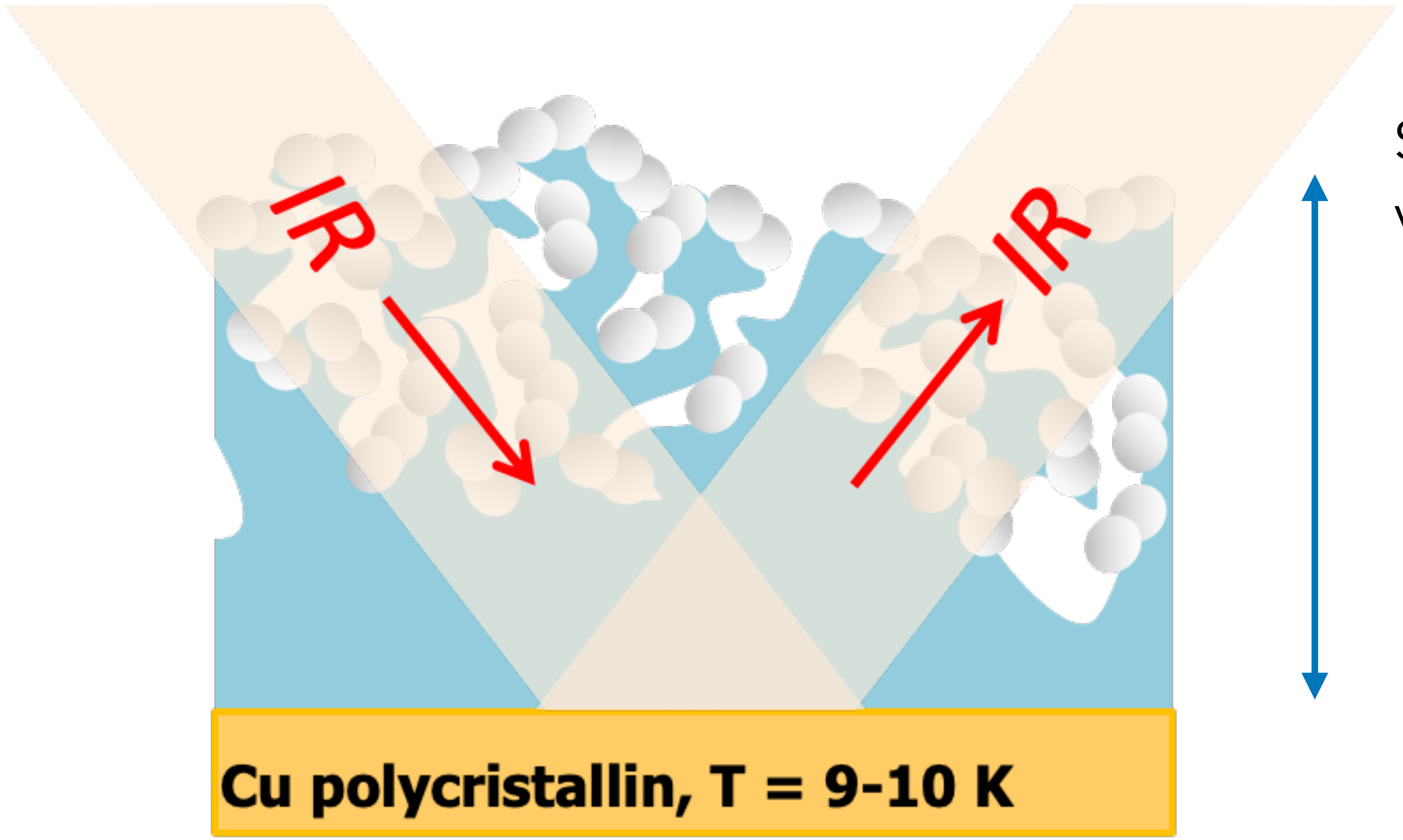
Fourier Transform IR spectroscopy (RAIRS)



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Equivalent to 1000 ML of compact ices

H_2O amorphous and porous

Equivalent to 1000 ML of compact ices H_2O amorphous and porous saturated with H_2. IR spectrum in the spectral range 4050-4200 cm^{-1} obtained with COSPINU2

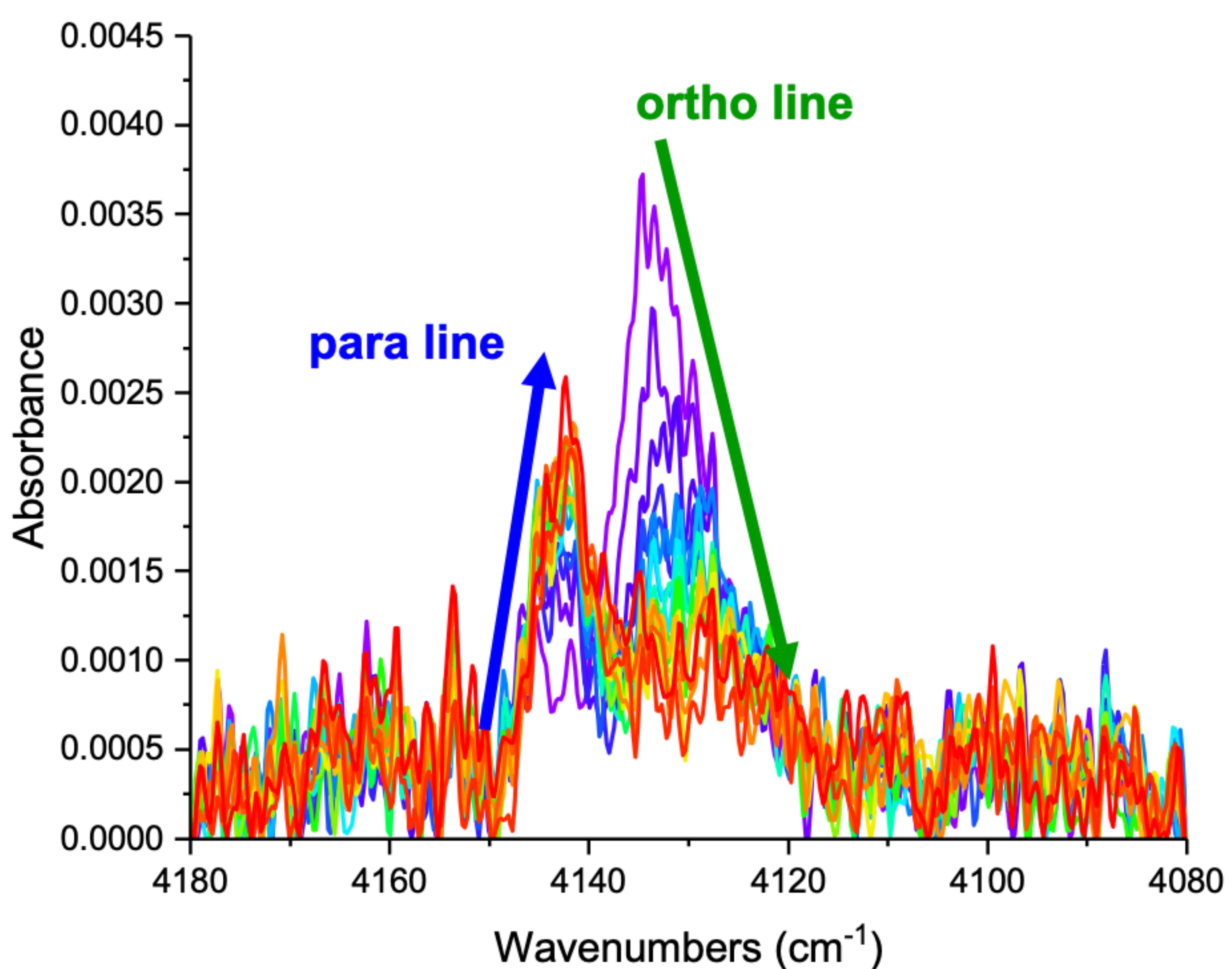
Gas phase

Q(0) line

4159.5 cm^{-1}

Q(1) line

4153.4 cm^{-1}



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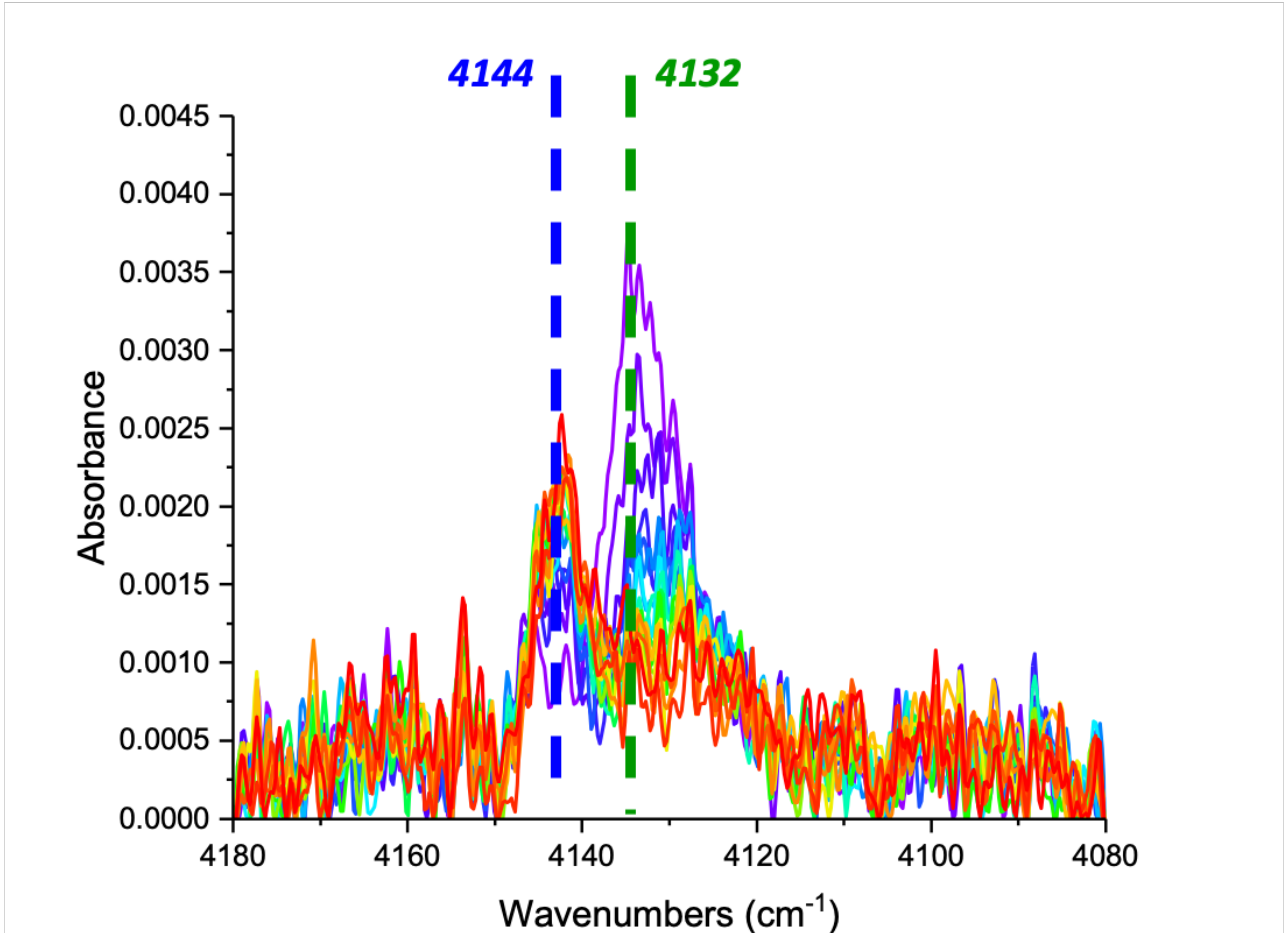

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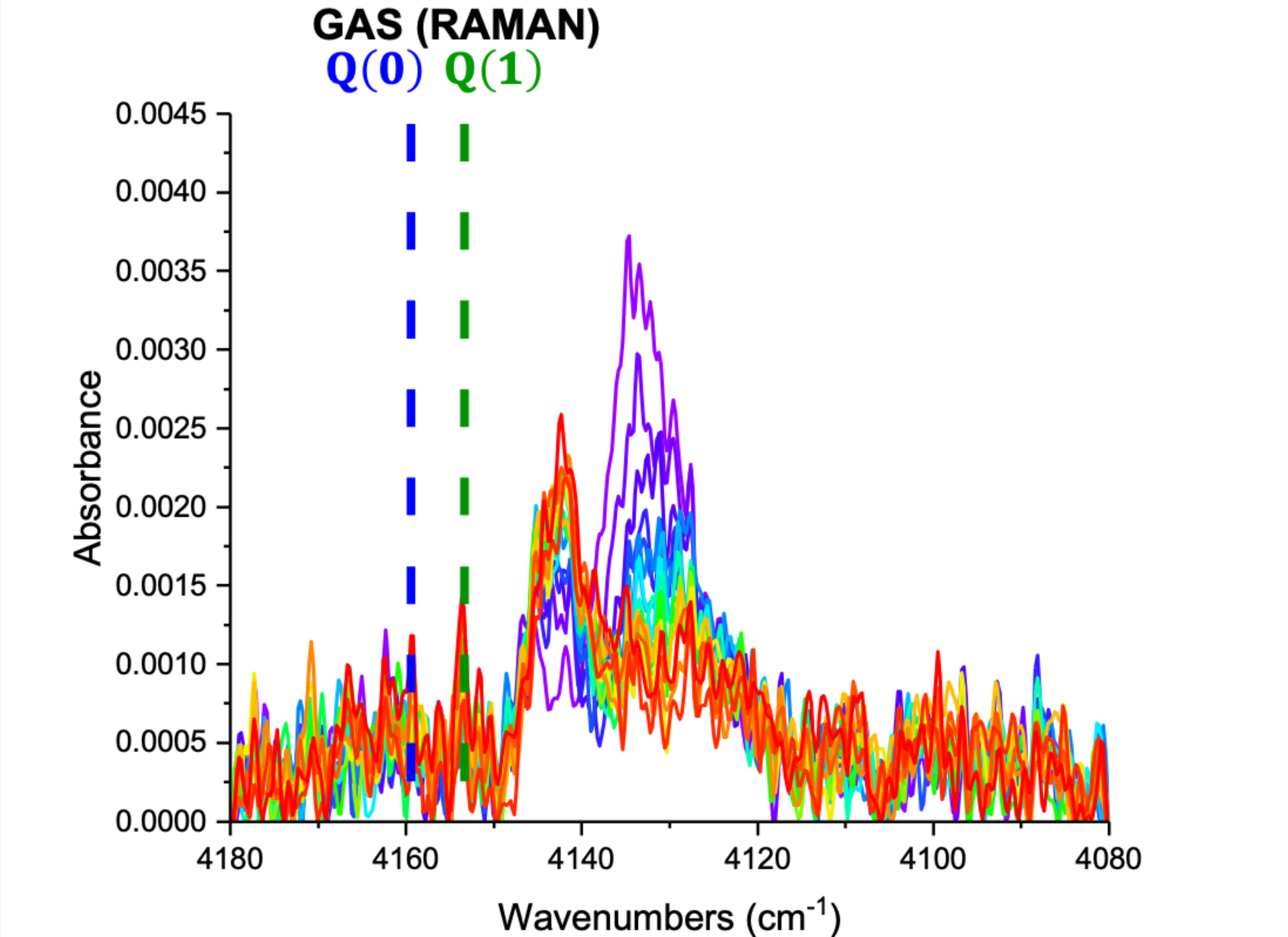

NSC ON ASW USING IR SPECTROSCOPY

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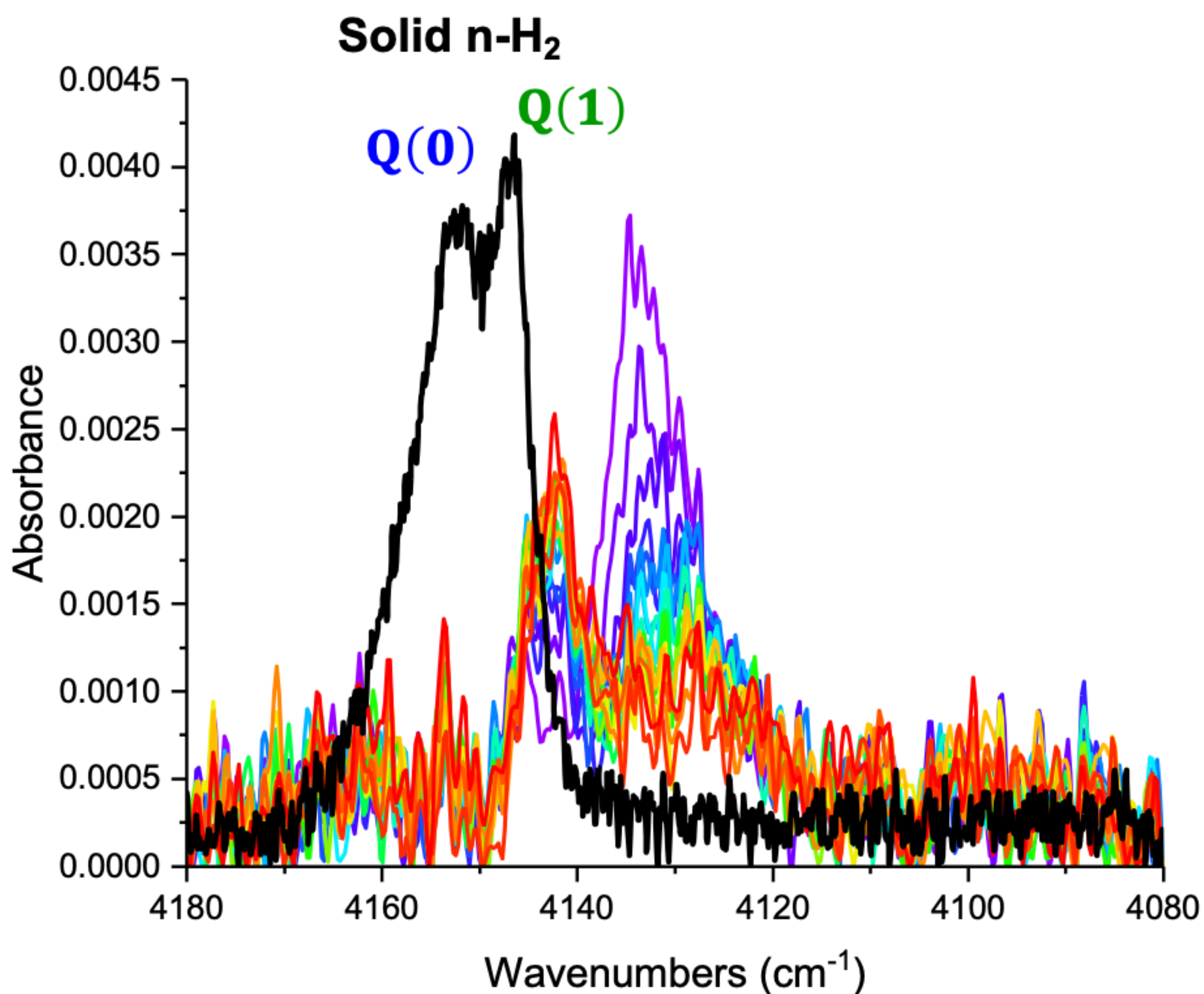
Solid n-H_2

Q(0) line

4153.0 cm^{-1}

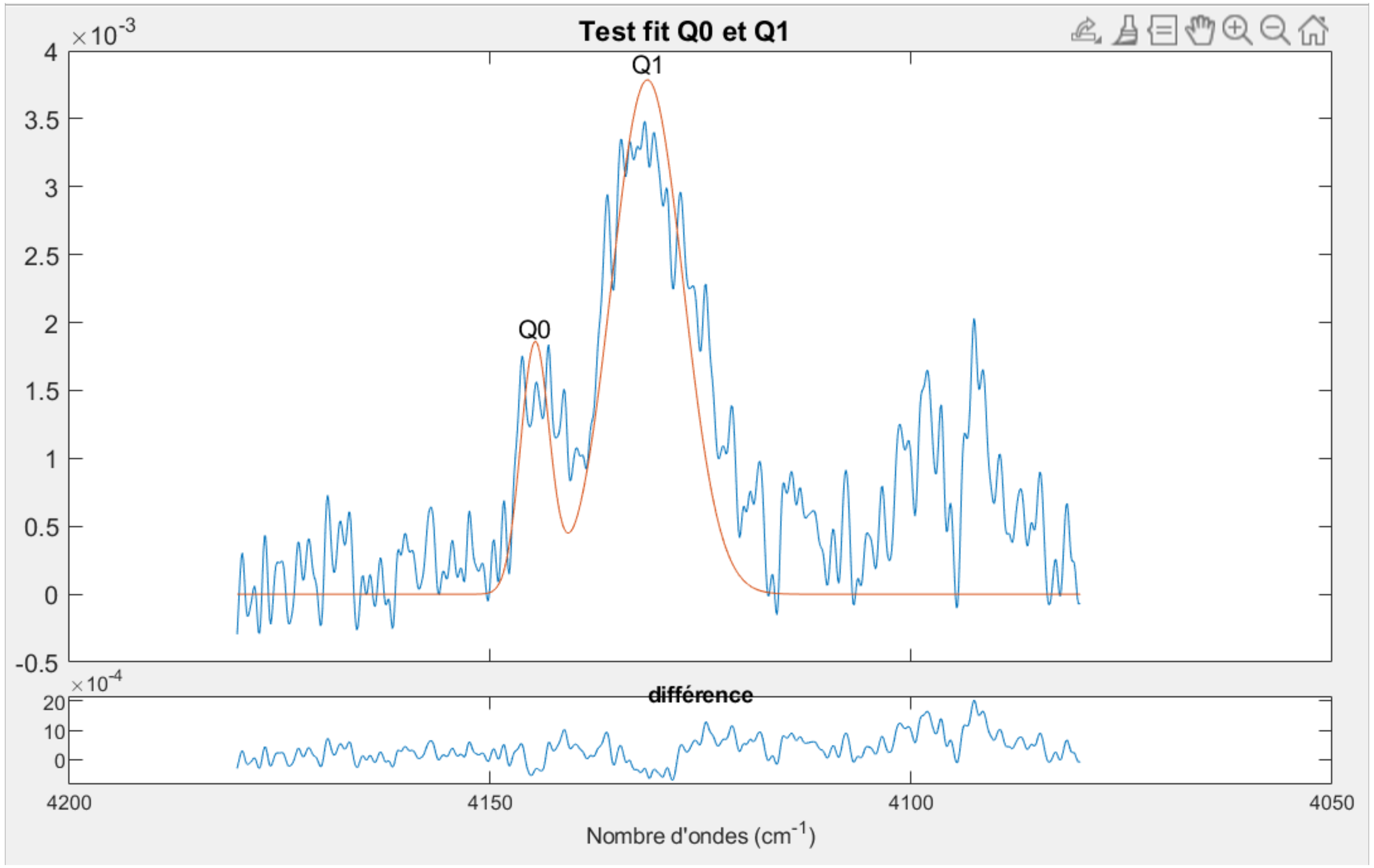
Q(1) line

4146.8 cm^{-1}



NSC ON ASW USING IR SPECTROSCOPY

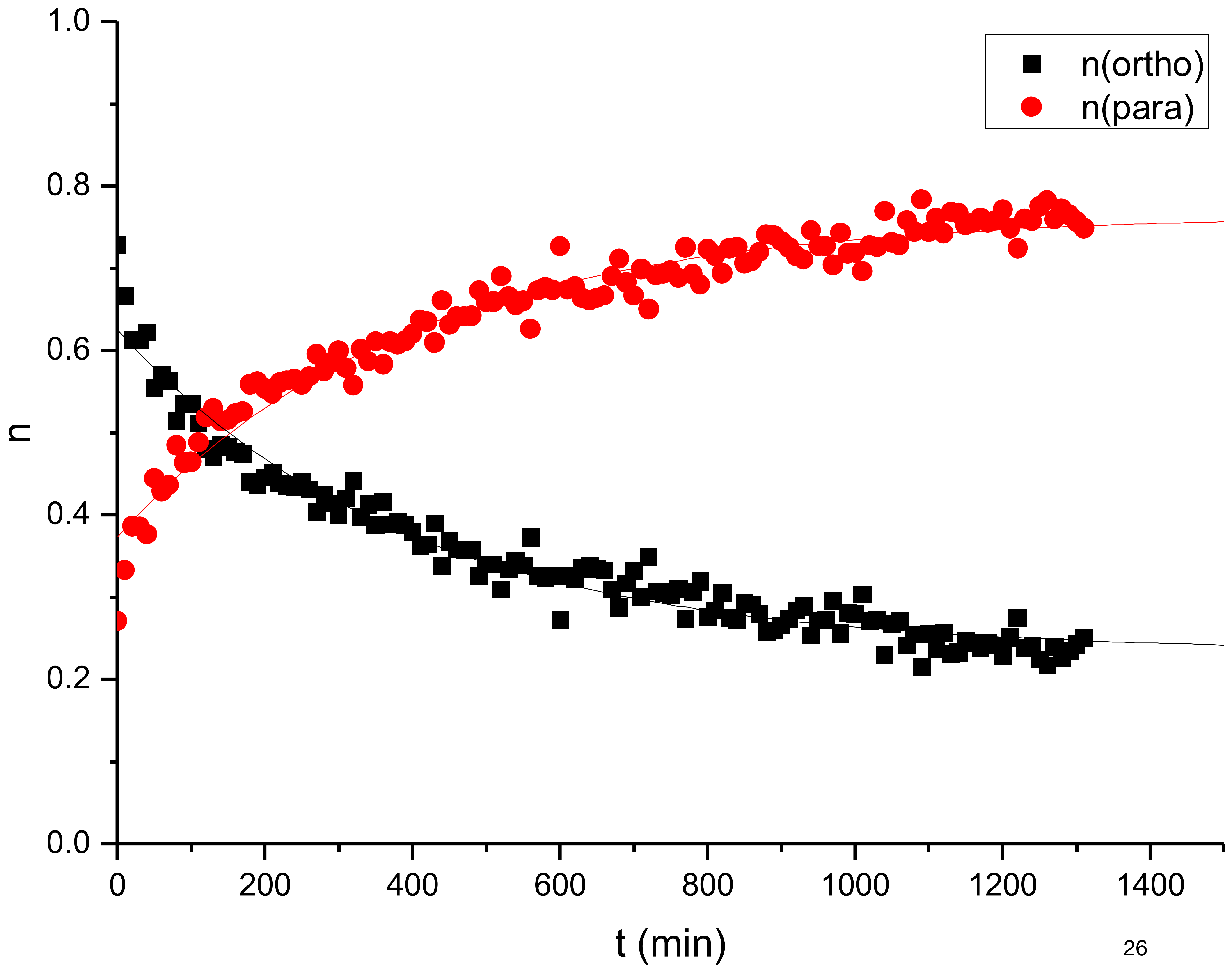
- Equivalent to 1000 ML of compact ices H_2O amorphous and porous saturated with H_2 at 10K
- IR spectrum in the spectral range 4050-4200 cm^{-1} obtained with COSPINU2
- Fitting procedure to be improved to correct better the baseline. Only the intensities are fitted up to now. Width of the Q(1) line is twice the width of the Q(0)



NSC ON ASW USING IR SPECTROSCOPY

Equivalent to 1000 ML of compact ices H_2O amorphous and porous saturated with H_2 at 10K

Time evolution of the fractional populations of the two species



Characteristic time :
390 ± 40 minutes

t (min) IR Vib	t (min) Laser *FORMOLISM* (1)	t (min) Laser *Sugimoto* (2)	t (min) Laser *Ueta* (3)
H_2 : 220 (17)	H_2 : >300	H_2 : 8 (2)	H_2 : 52 (5)
1ML	0.3 - 0.75 ML	1 - 2 ML	0.3 - 1 ML

→ **Same order of magnitude for the characteristic time of nuclear spin conversion**

(1) Chehrouri, Fillion et al PCCP 2011
(2) Sugimoto & Fukutani Nature Physics 2011
(3) Ueta, Watanabe, Hama, Kouchi PRL 2016

CONCLUSION

Modelisation :

- Same excitation temperature for H_2 with and without ortho/para chemistry
- Decrease of the temperature of H_3^+ with ortho/ para chemistry which is in good agreement with observations

- Next step : the oxygen chemistry to see the influence of H_2 on the production of ortho and para H_2O

↳ Integrate the UGAN network (University of Grenoble Alpes Astrochemical network)

  - Gas phase chemical reaction network
  - Grain surface interaction
  - Ortho/para aspect of the species

Reactional chain for water production in gas phase :

$$\begin{aligned} O^+ + H_2 &\longrightarrow OH^+ + H \\ OH^+ + H_2 &\longrightarrow H_2O^+ + H \\ H_2O^+ + H_2 &\longrightarrow H_3O^+ + H \\ H_3O^+ + e^- &\longrightarrow H_2O + H \end{aligned}$$

ORTHO/PARA CHEMISTRY →

$$\begin{cases} O^+ + H_2\text{-}o \longrightarrow OH^+ + H \\ O^+ + H_2\text{-}p \longrightarrow OH^+ + H \end{cases}$$

$$\begin{cases} OH^+ + H_2\text{-}o \longrightarrow H_2O^+\text{-}o + H \\ OH^+ + H_2\text{-}o \longrightarrow H_2O^+\text{-}p + H \\ OH^+ + H_2\text{-}p \longrightarrow H_2O^+\text{-}o + H \\ OH^+ + H_2\text{-}p \longrightarrow H_2O^+\text{-}p + H \end{cases}$$

$$\begin{cases} H_2O^+\text{-}o + H_2\text{-}o \longrightarrow H_3O^+\text{-}o + H \\ H_2O^+\text{-}o + H_2\text{-}o \longrightarrow H_3O^+\text{-}p + H \\ H_2O^+\text{-}o + H_2\text{-}p \longrightarrow H_3O^+\text{-}o + H \\ H_2O^+\text{-}o + H_2\text{-}p \longrightarrow H_3O^+\text{-}p + H \\ H_2O^+\text{-}p + H_2\text{-}o \longrightarrow H_3O^+\text{-}o + H \\ H_2O^+\text{-}p + H_2\text{-}o \longrightarrow H_3O^+\text{-}p + H \\ H_2O^+\text{-}p + H_2\text{-}p \longrightarrow H_3O^+\text{-}p + H \end{cases}$$

$$\begin{cases} H_3O^+\text{-}o + e^- \longrightarrow H_2O\text{-}o + H \\ H_3O^+\text{-}p + e^- \longrightarrow H_2O\text{-}o + H \\ H_3O^+\text{-}p + e^- \longrightarrow H_2O\text{-}p + H \end{cases}$$

CONCLUSION

Experiment :

- The NSC of H2 on ASW has been studied with different techniques.
  The measurements we made with SPICES and COSPINU2 give characteristic times very close.
  There is a large discrepancy with the data collected in the literature.

- Measurements with COSPINU2 will be done on a large time scale to investigate the temporal dynamics and the temperature dependence of the NSC

- Development are in progress to investigate the link between the OPR of H_2 we measure *in situ* and the OPR when the molecules are released in the gas phase from the surface through thermal and non thermal processes.

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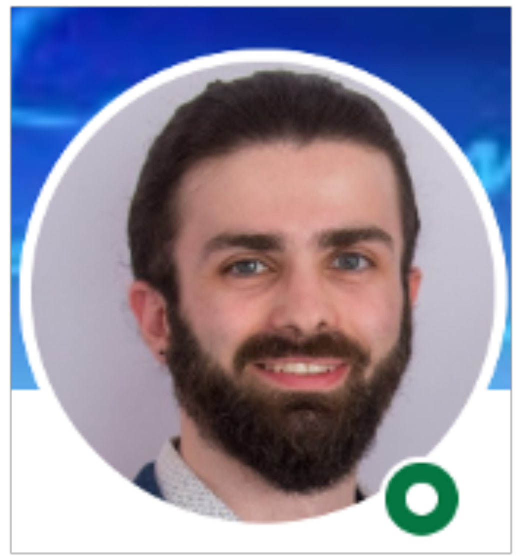
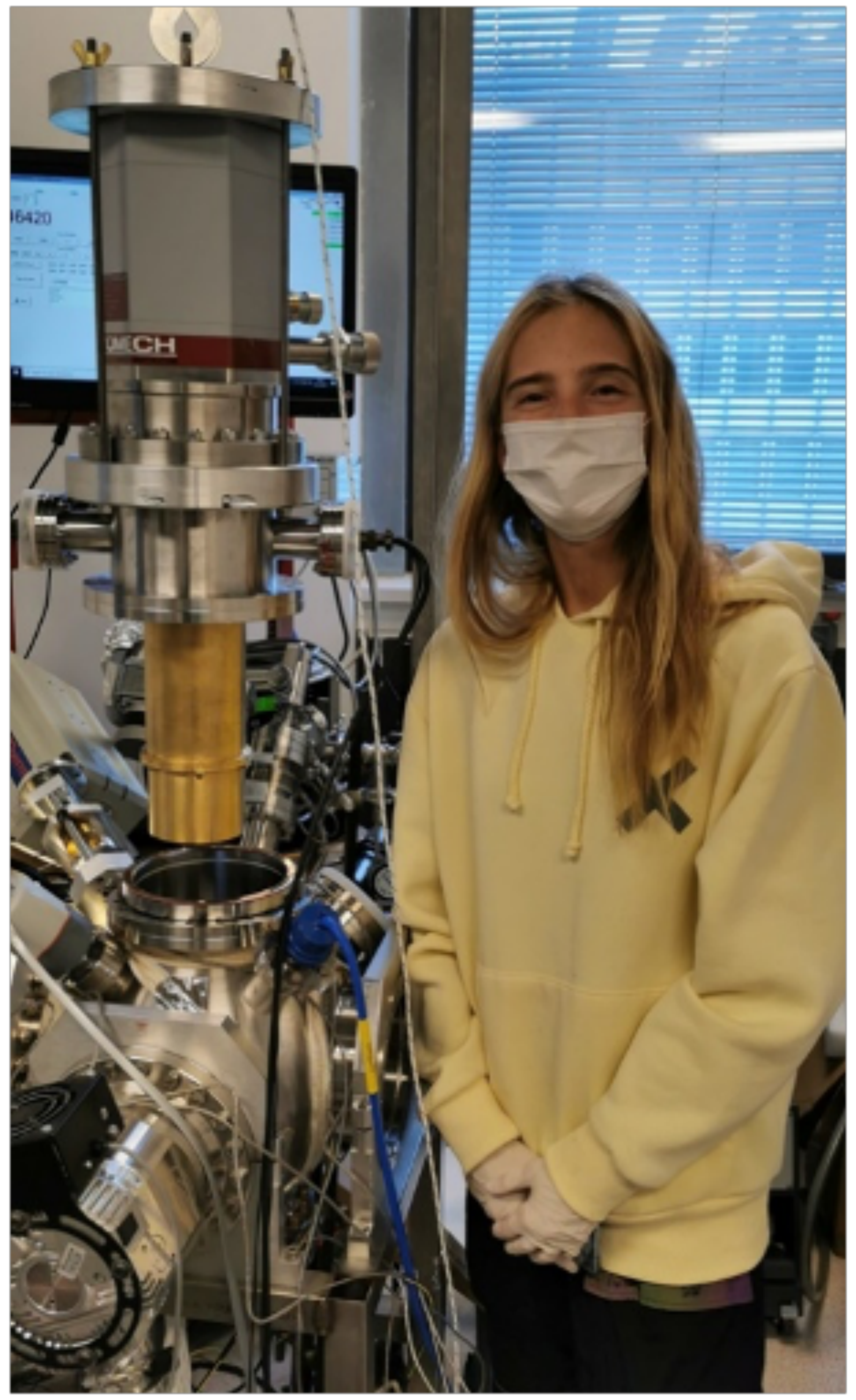


Alexandros Milpanis (M2 student)



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Thank you for your attention !