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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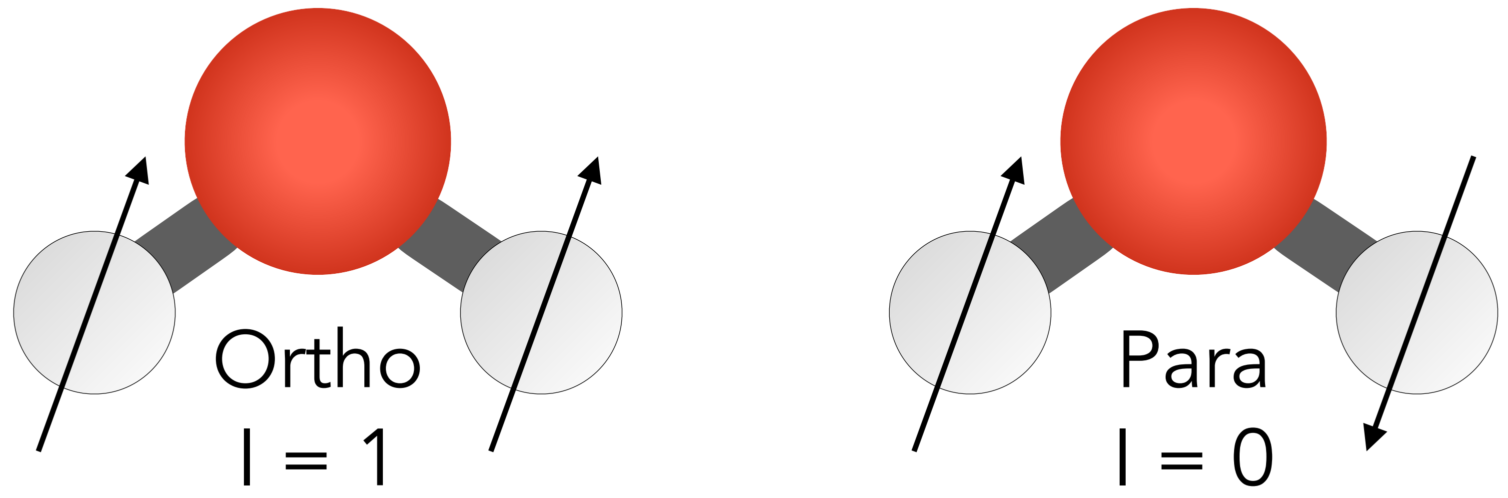
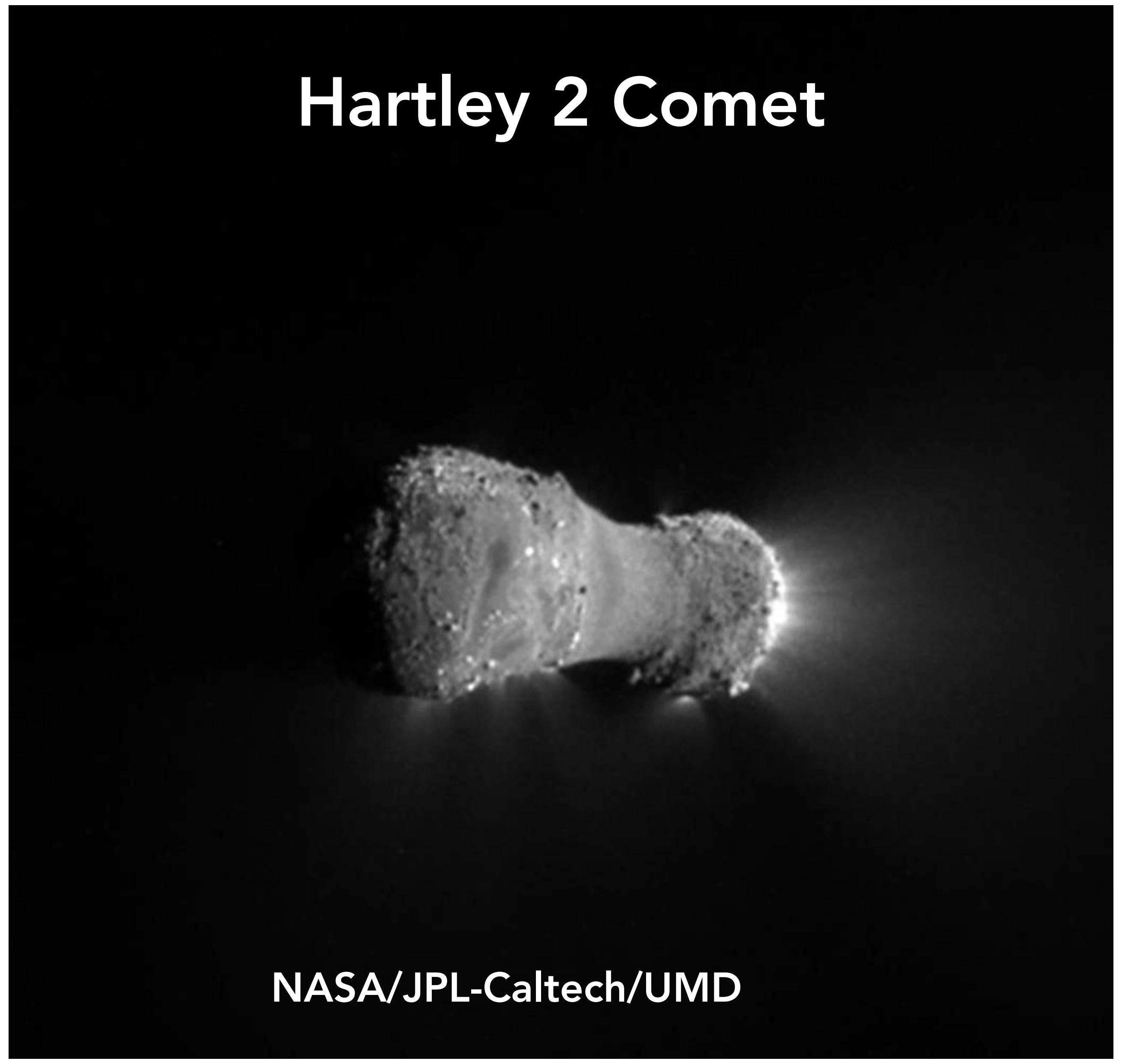
Nicolas Paladini

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

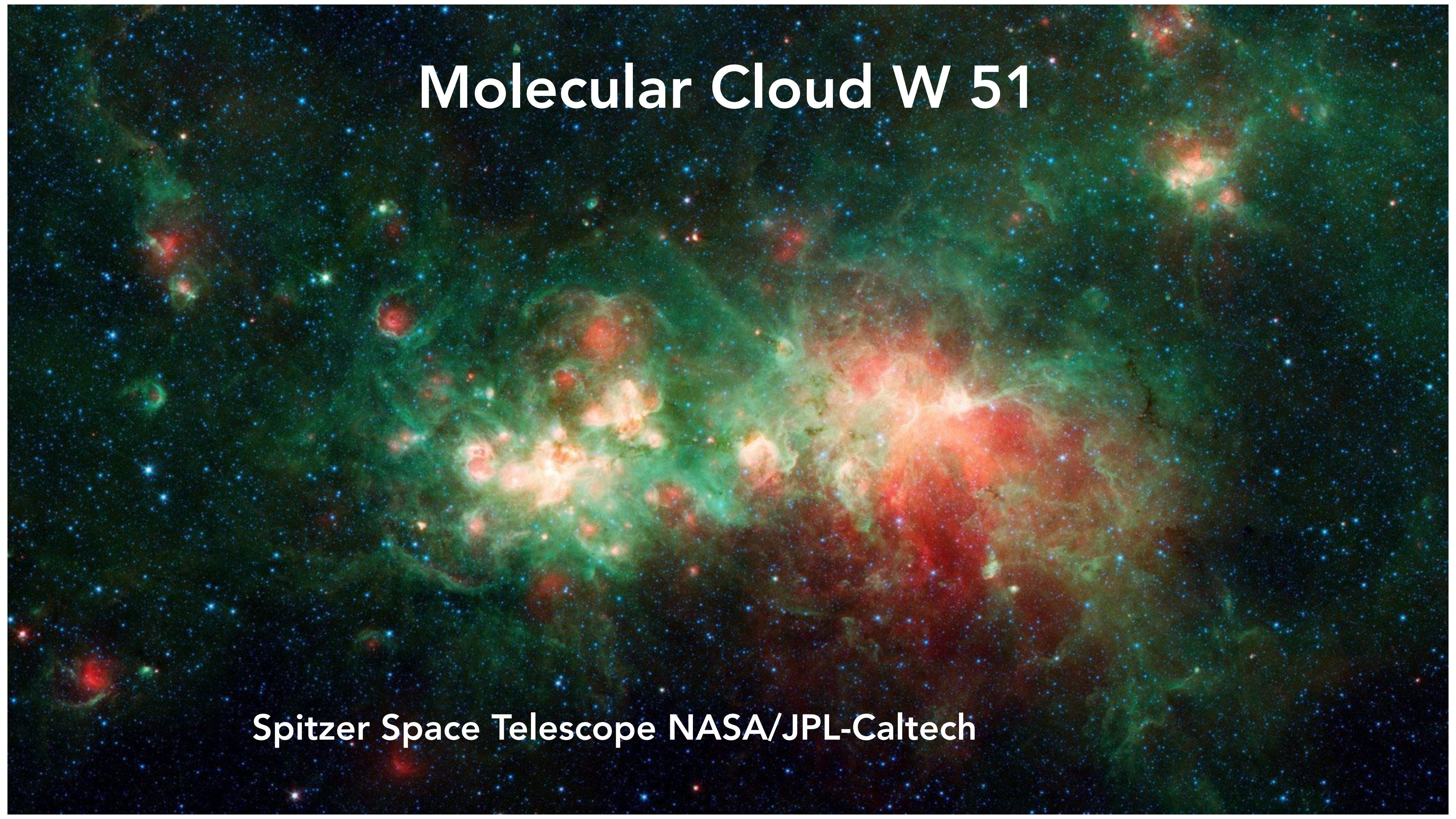
Why look at the OPR in the ISM?

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





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



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

OPR = 0.2 - 0.5
Y. Choi et al. A&A 572 L10 (2014)

ONE OF THE LOWEST OPR VALUES REPORTED IN THE ISM

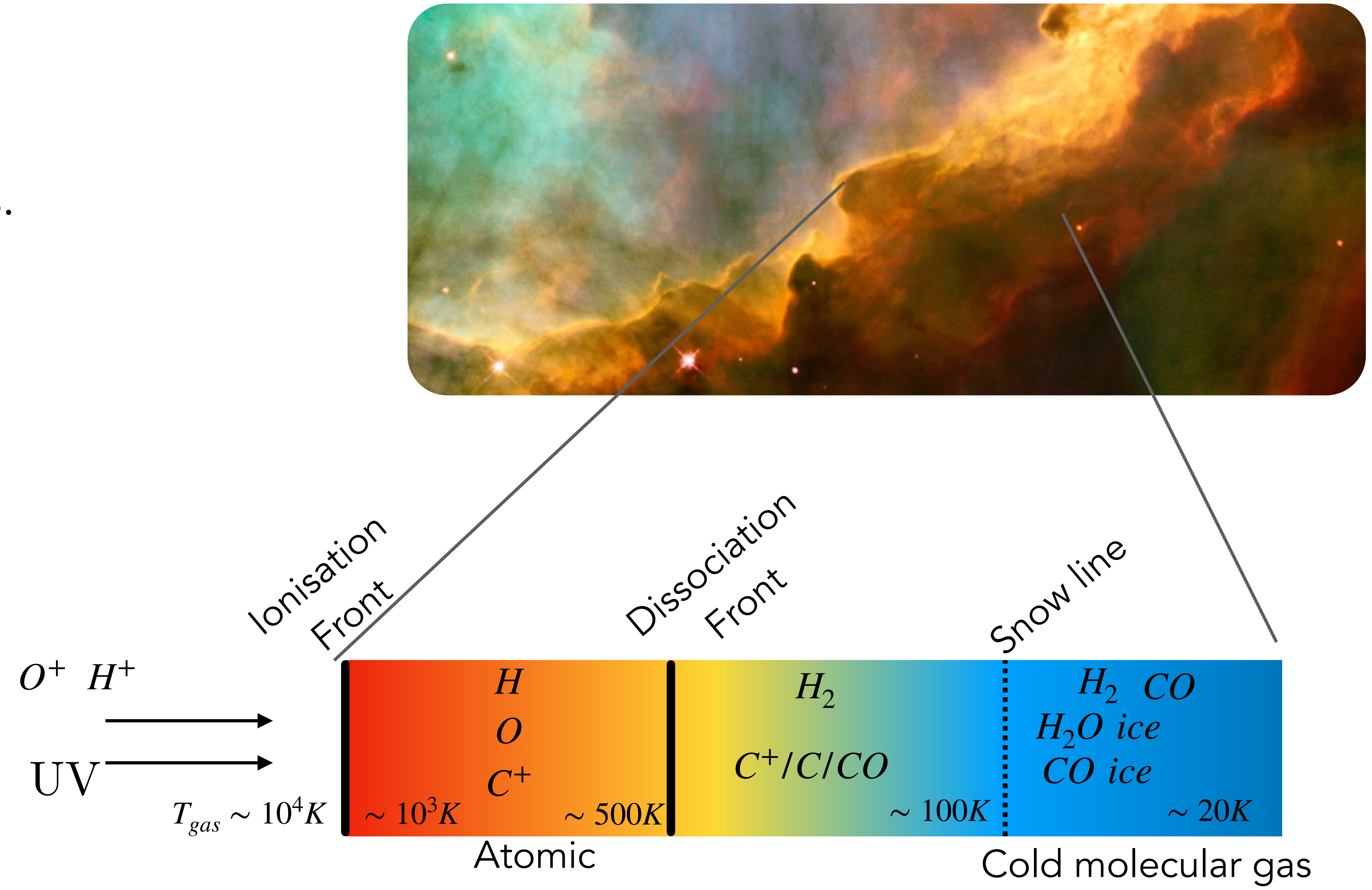
MEUDON PDR CODE (Photo Dissociated Region)

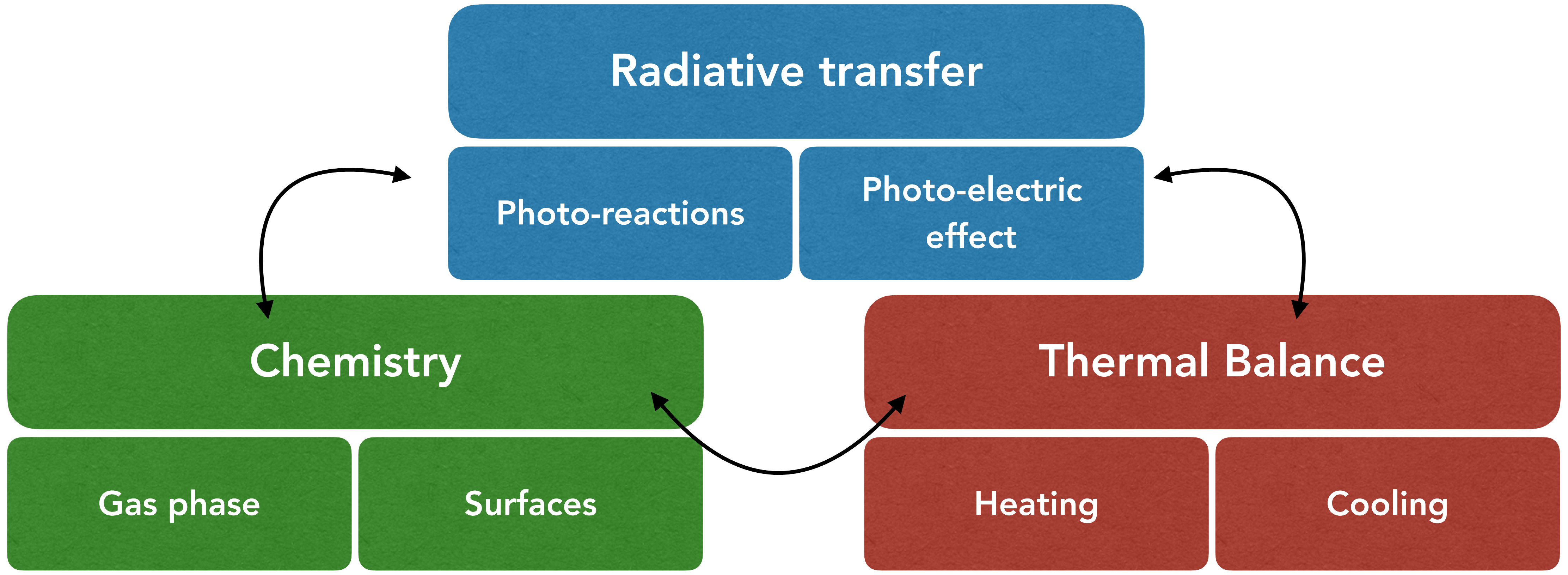
PDR CODE :

- 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

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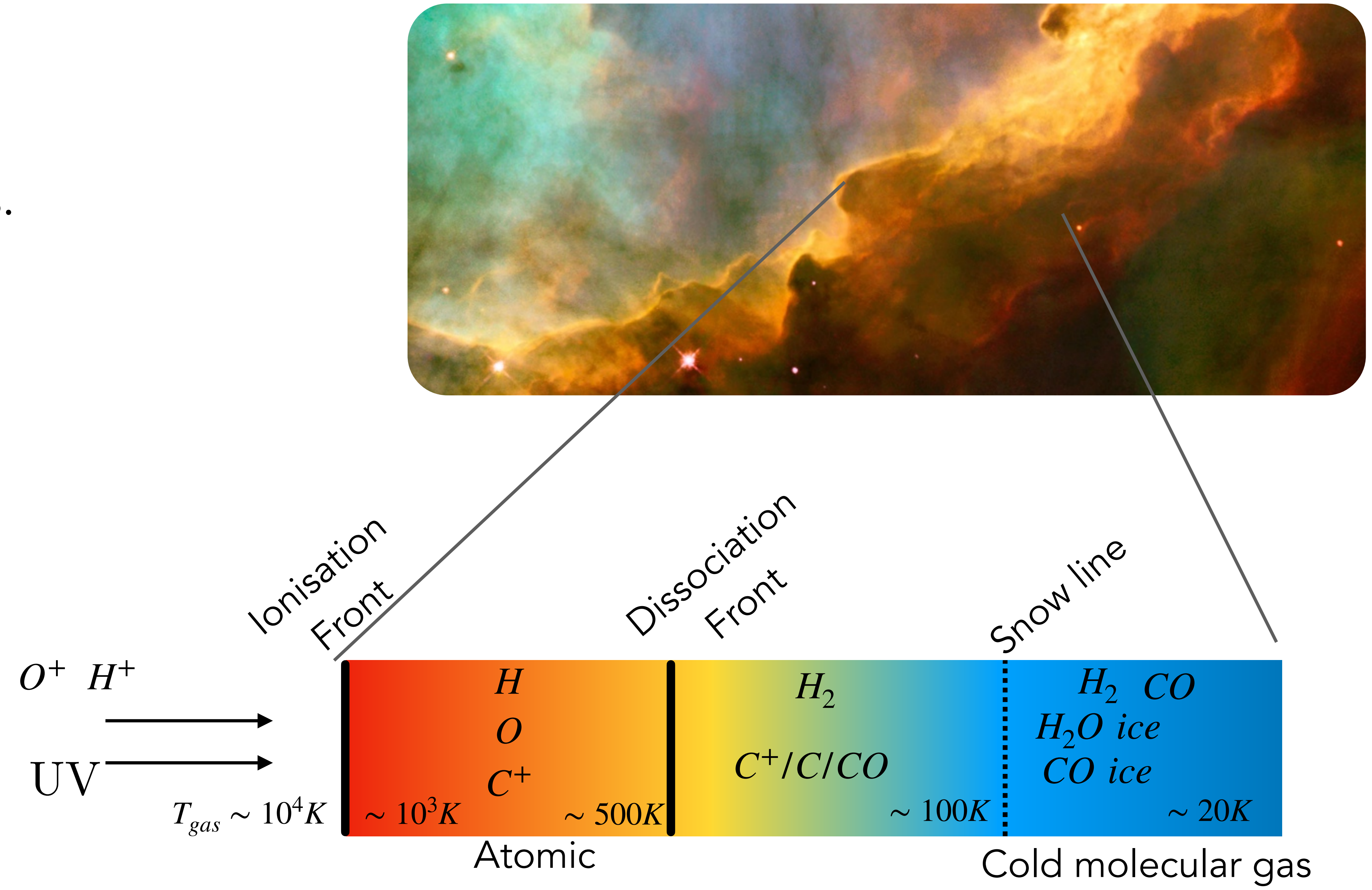

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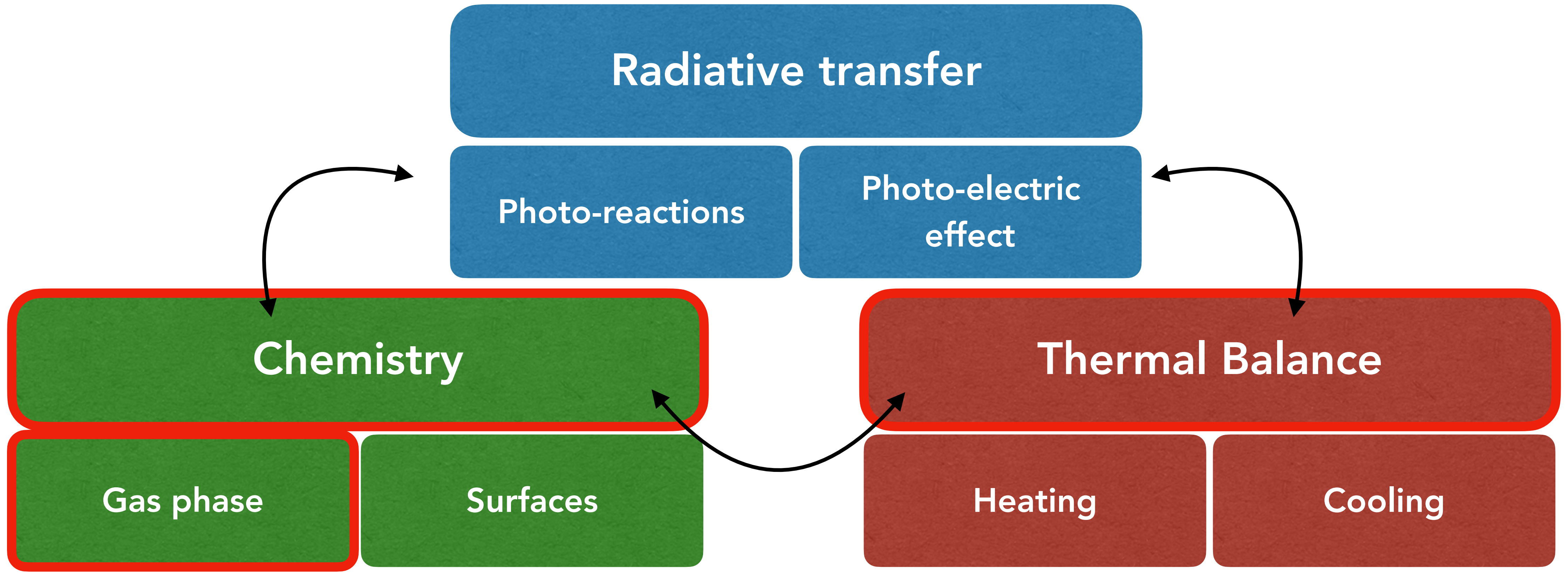

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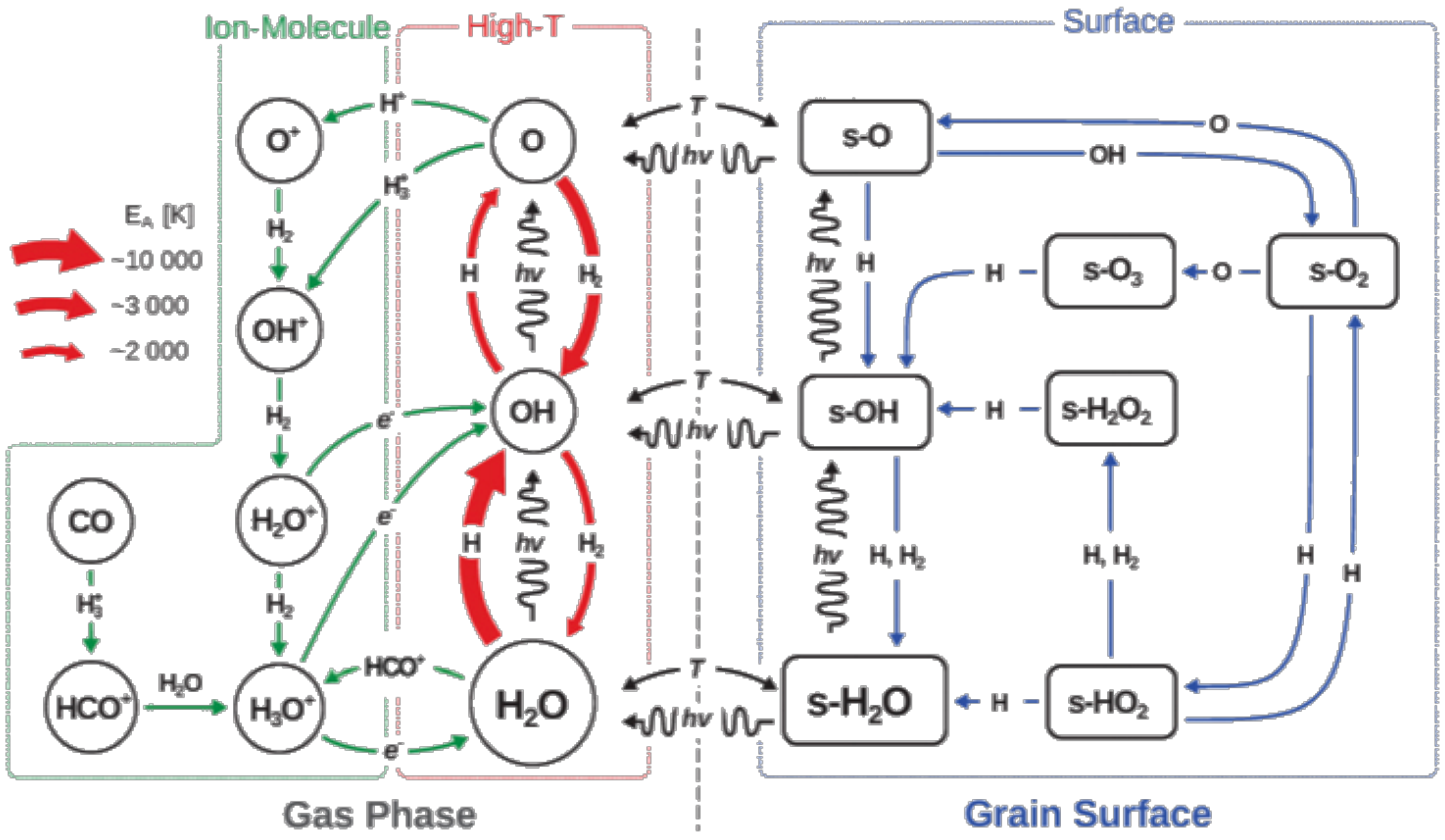
H_2 IN THE CHEMICAL CHAIN REACTION OF WATER FORMATION

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 may have a great impact on the chemistry



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

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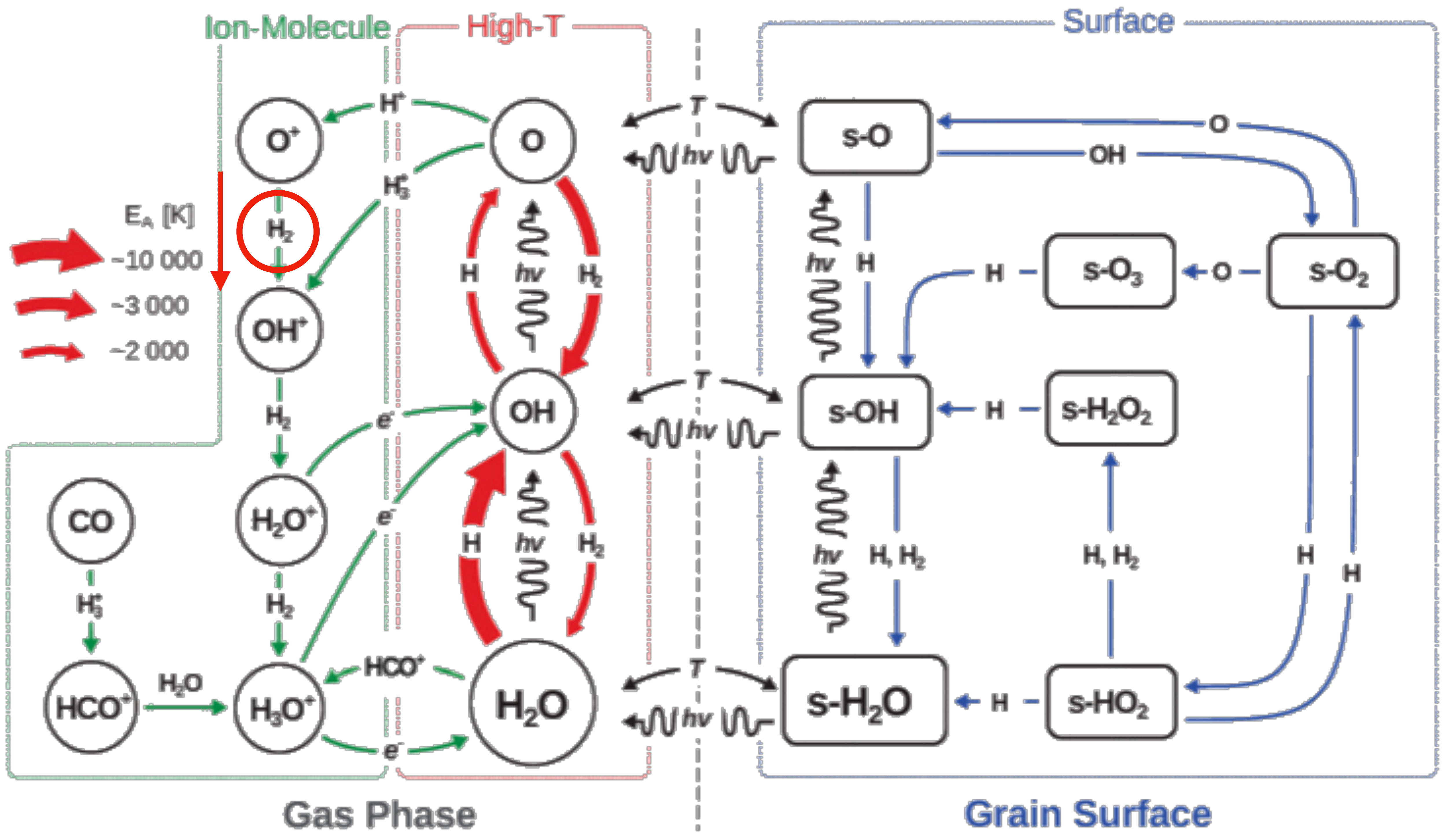

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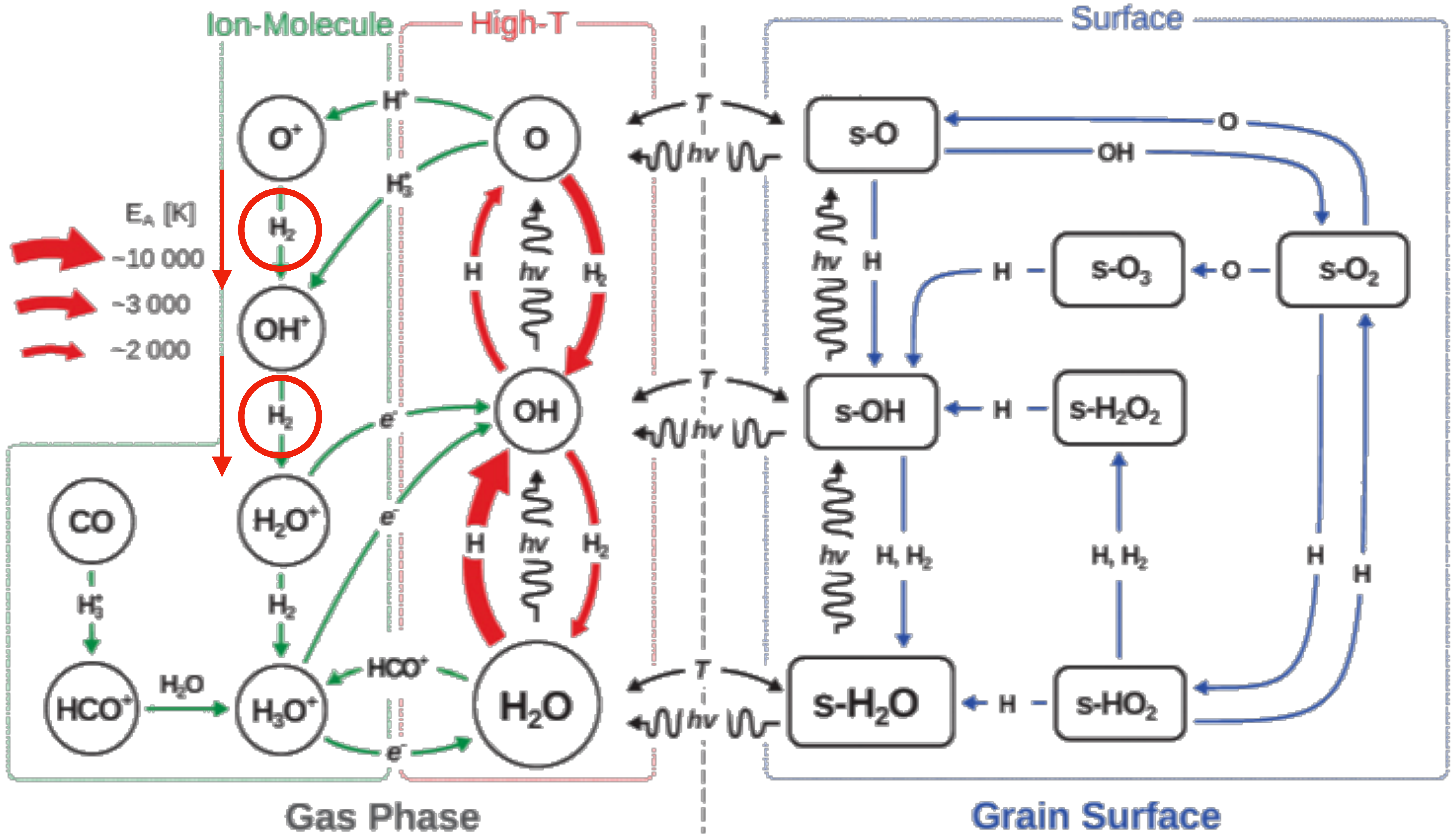

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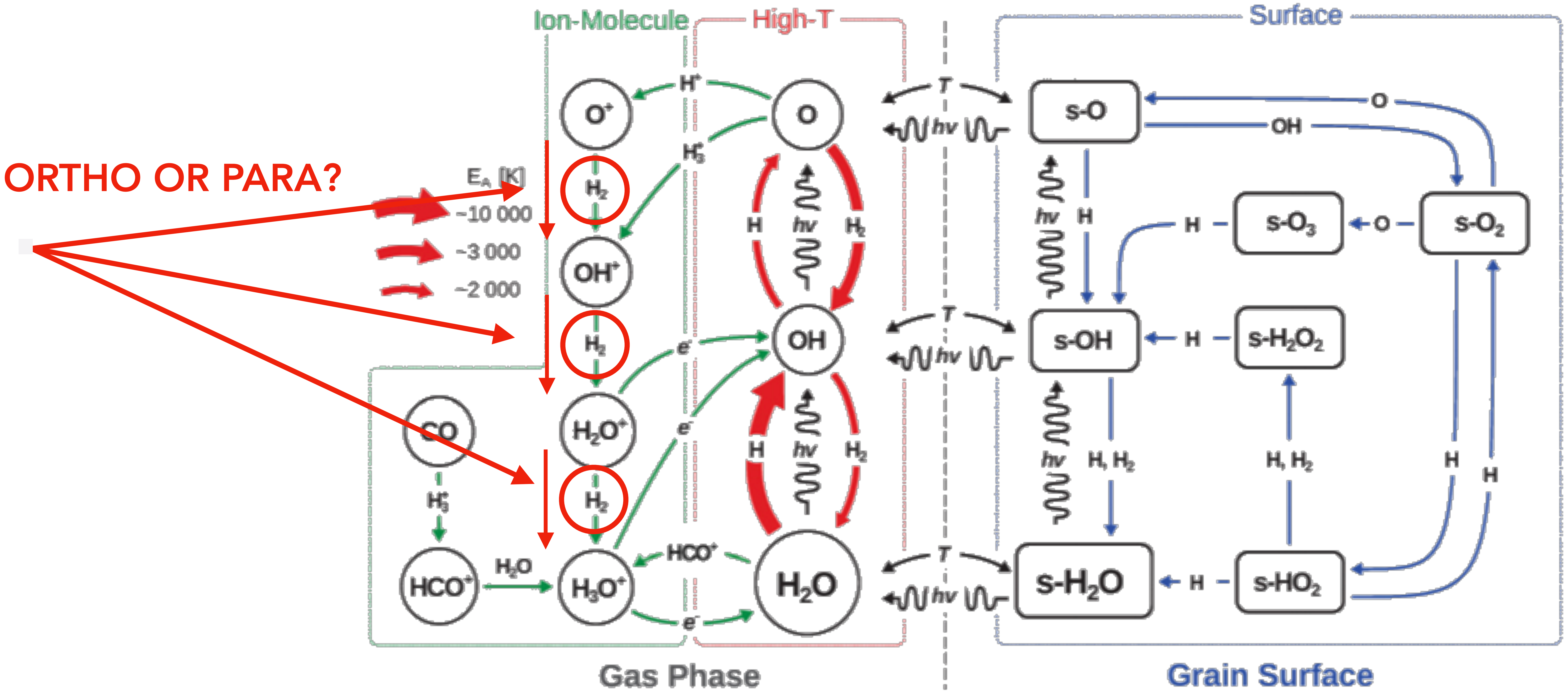

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PROCESSES THAT GOVERN THE ORTHO TO PARA RATIO IN THE PDR CODE AND H_2O CHEMISTRY

(i) Chemistry

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

$$H_3O^+ + e^- \longrightarrow H_2O + H \quad k$$

$$\downarrow$$

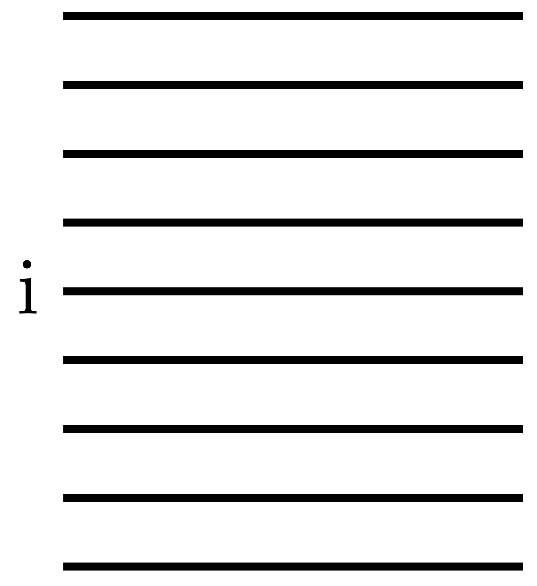
$$\begin{cases} H_3O^+\text{-}o + e^- \longrightarrow H_2O\text{-}o + H & k_1 = k \\ H_3O^+\text{-}p + e^- \longrightarrow H_2O\text{-}p + H & k_2 = k/2 \\ H_3O^+\text{-}p + e^- \longrightarrow H_2O\text{-}o + H & k_3 = k/2 \end{cases}$$

Between 300-400 more reactions with OP chemistry than without

(ii) Excitation

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

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

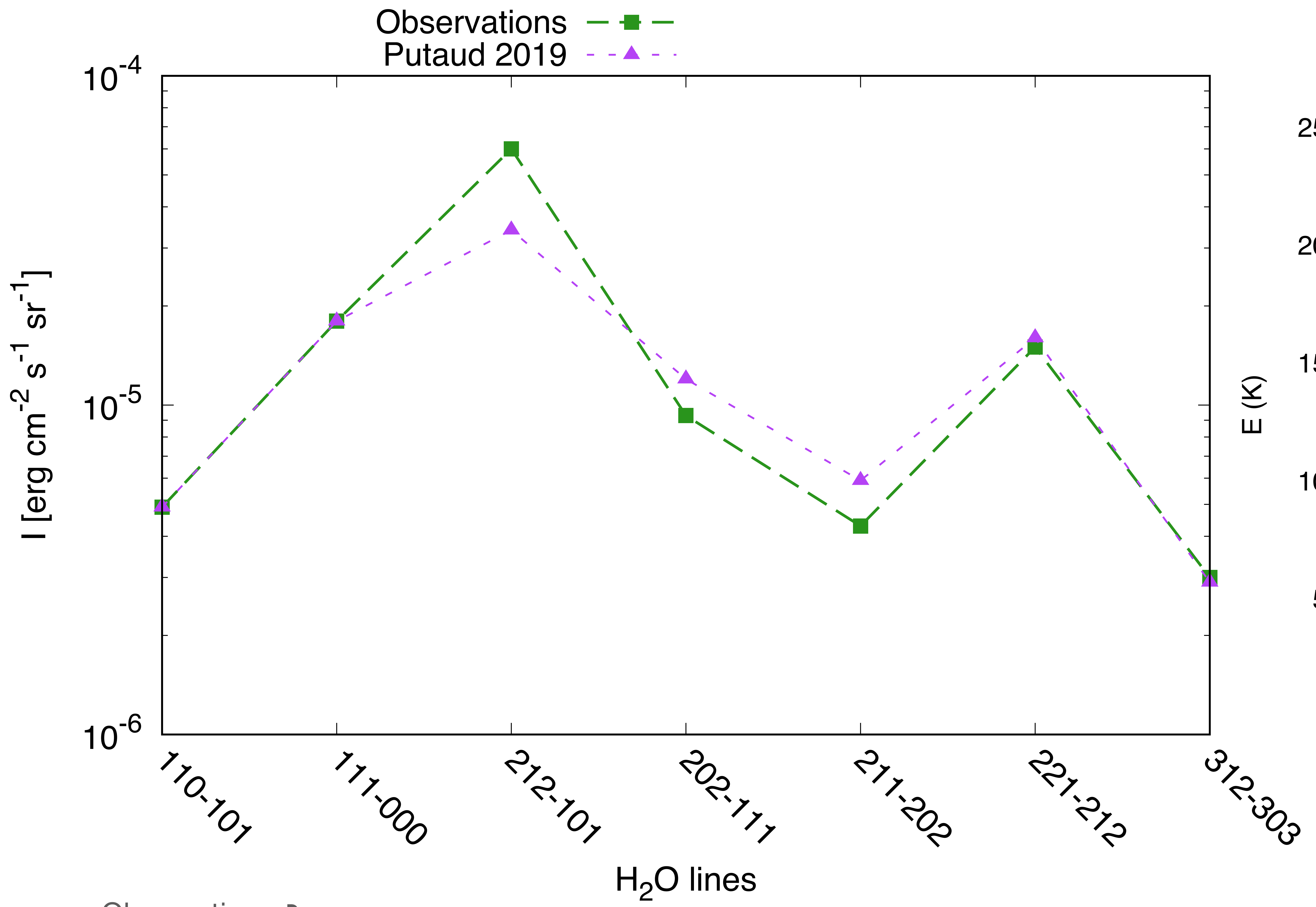


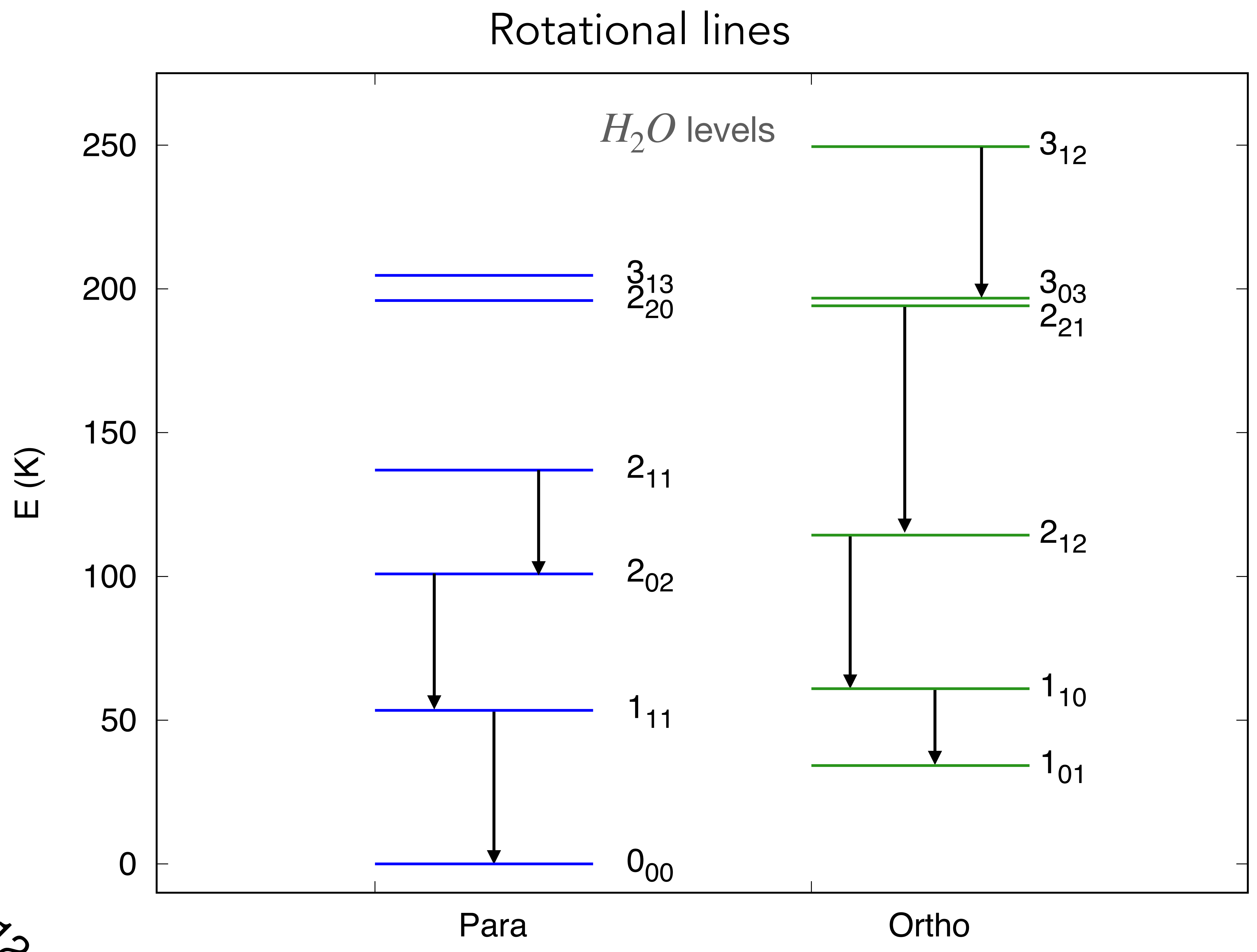
Energy levels for a given species

- The excitation is calculated for 4 ortho/para species : H_2 , H_2O, $H_2{}^{18}O$ 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** species while taking into account the ortho/para reactions of the **X** species

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

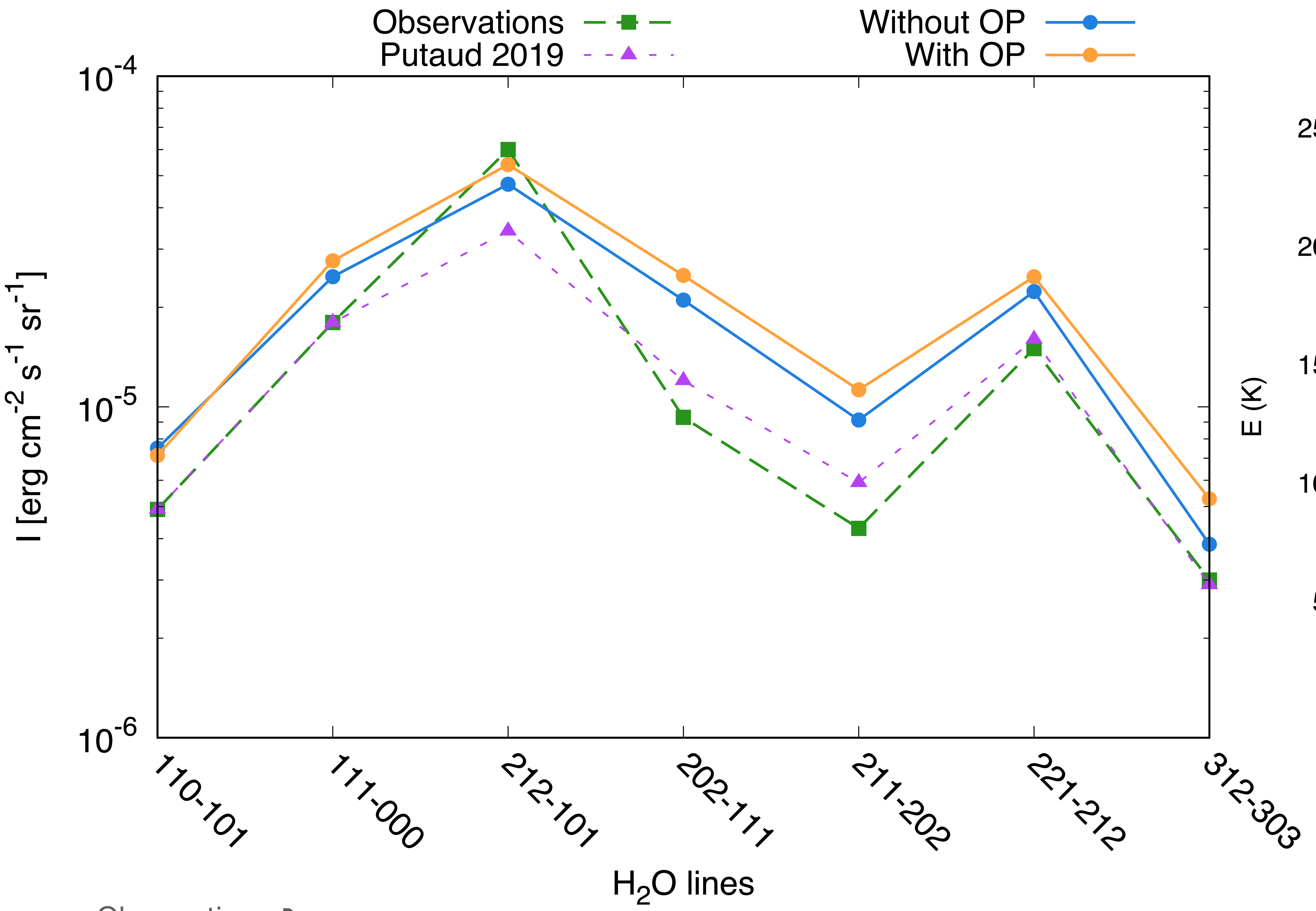
ORION BAR : H_2O CHEMISTRY

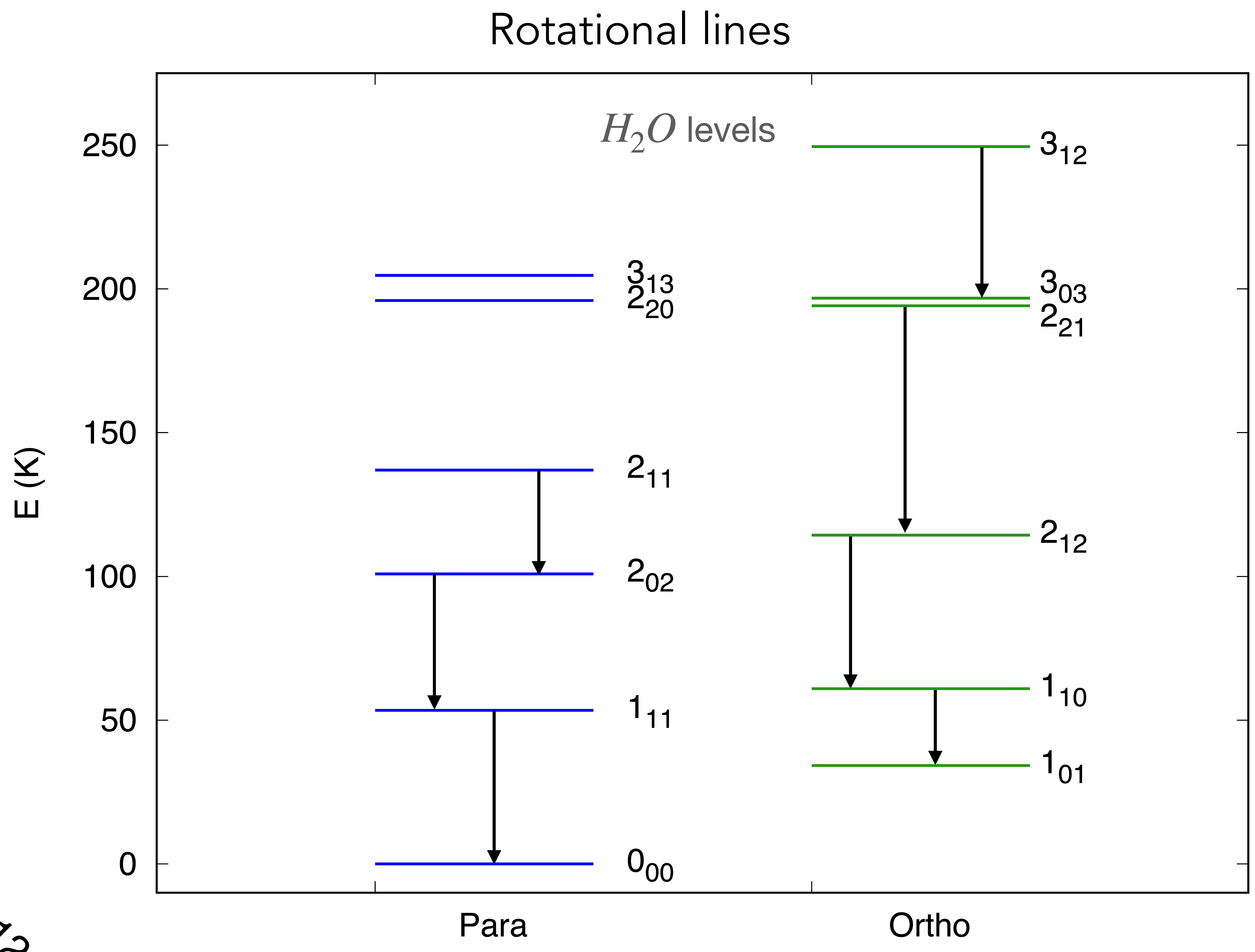




Observations
Putaud 2019 } T. Putaud et al. A&A 2019

ORION BAR : H_2O CHEMISTRY

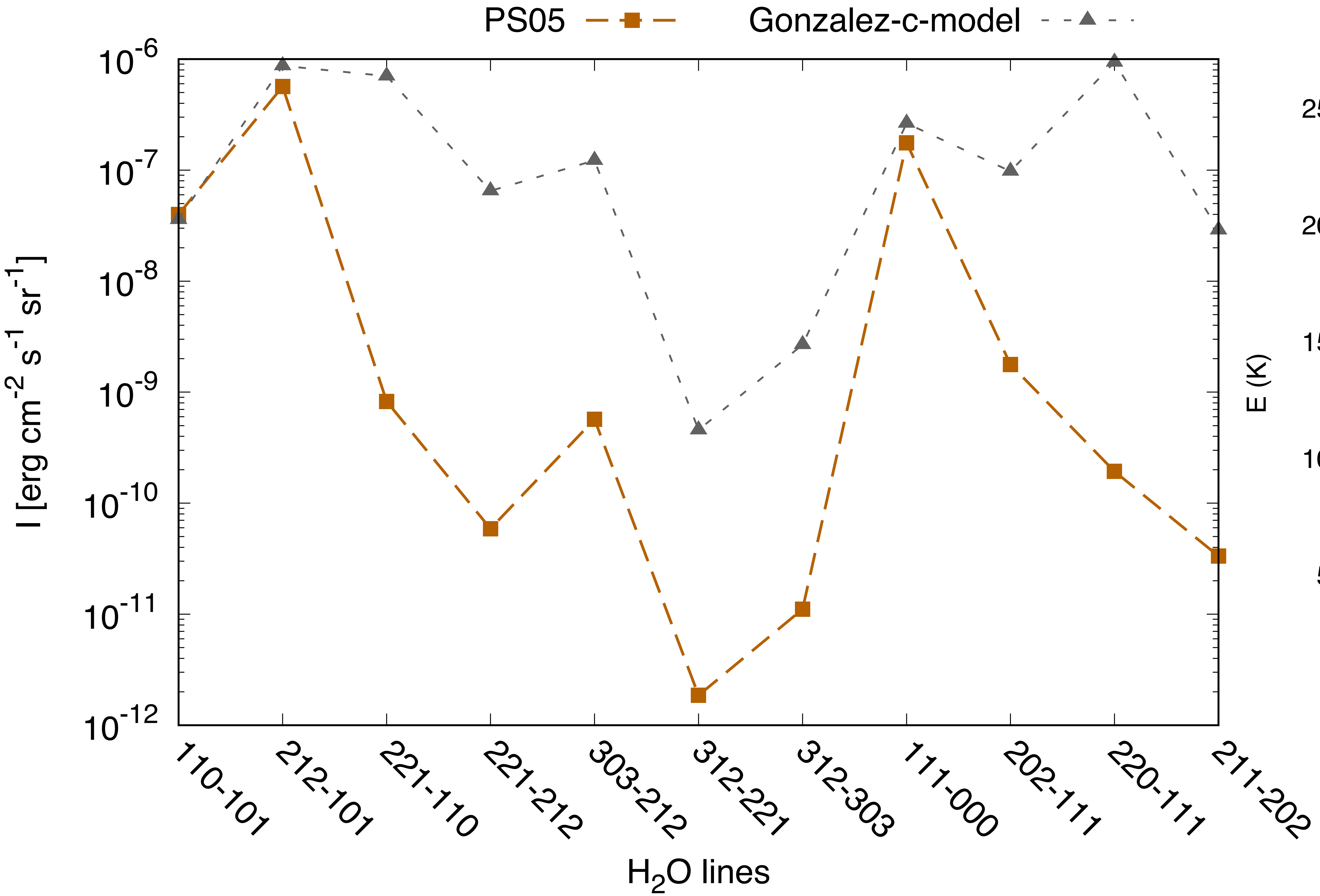


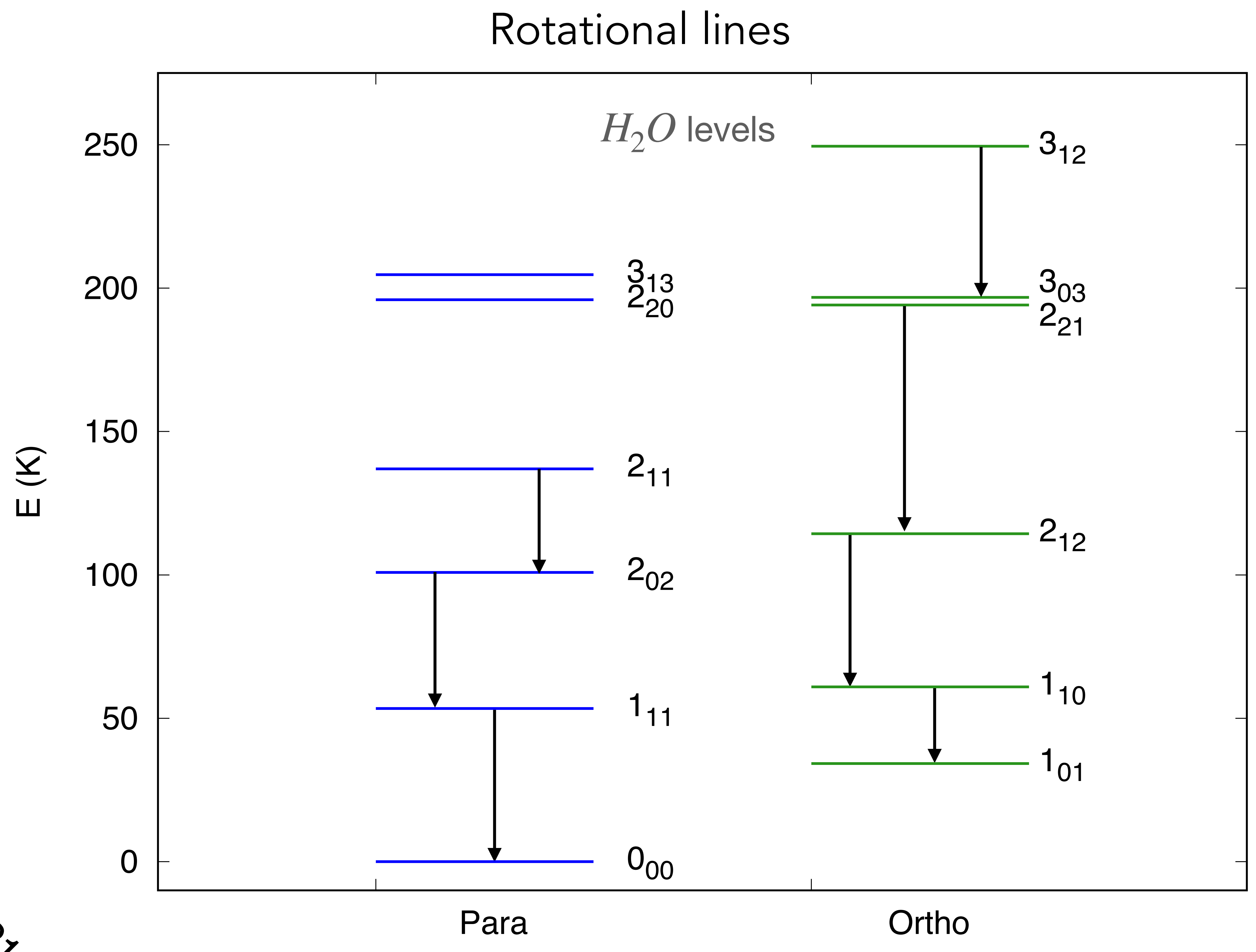


Observations } T. Putaud et al. A&A 2019
Putaud 2019

Ortho/para chemistry has little impact compared to other excitation processes

S140 : H_2O CHEMISTRY

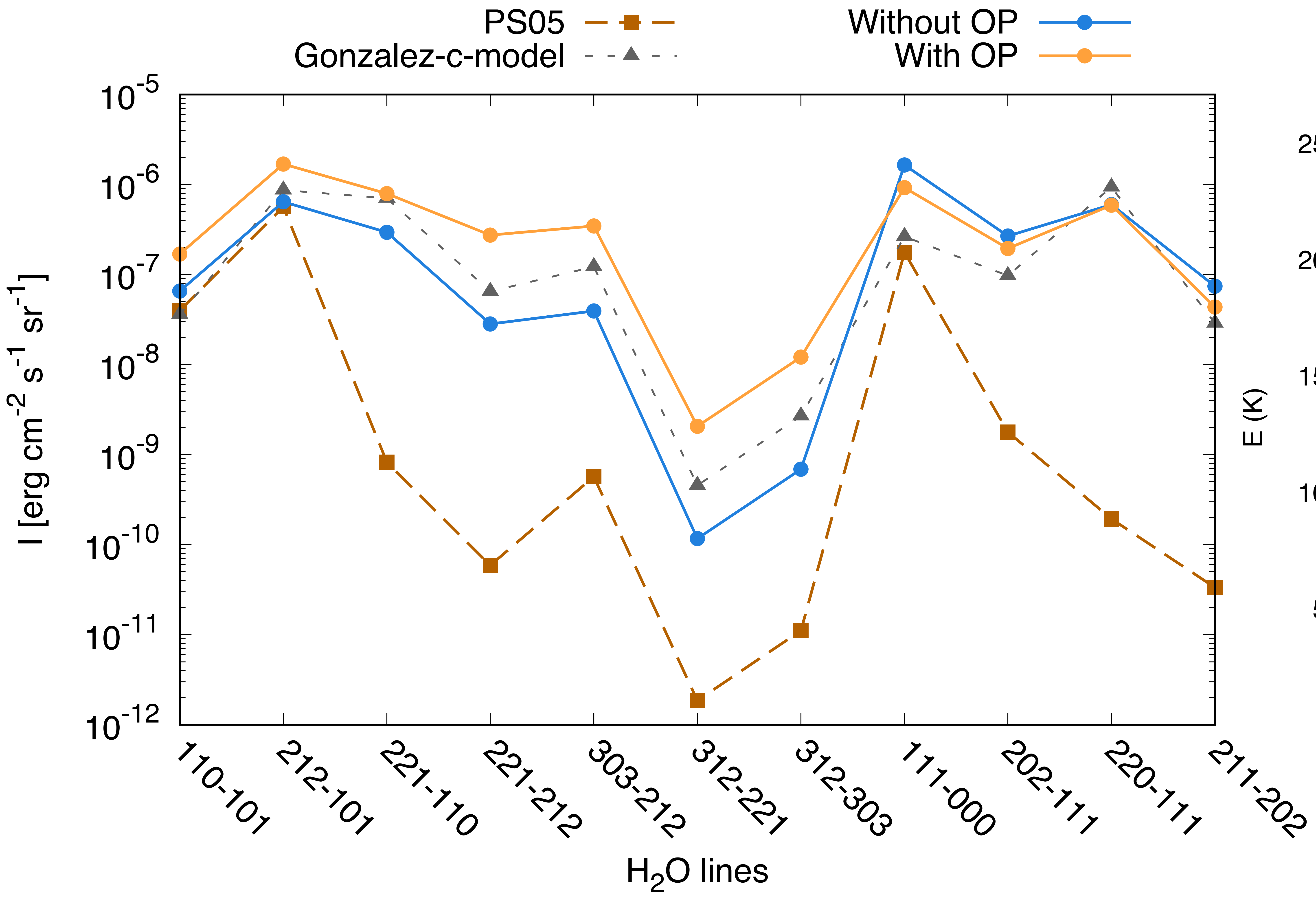


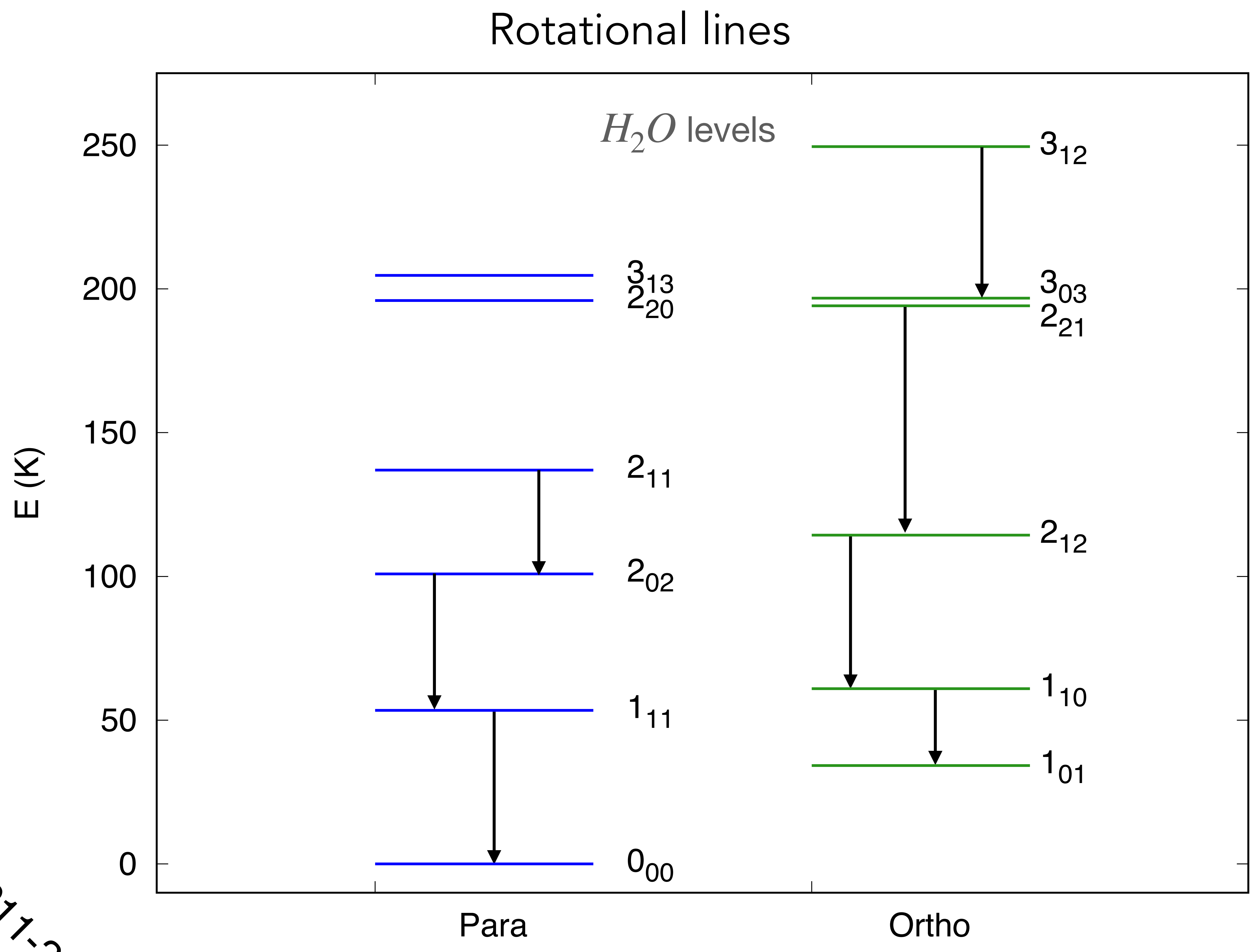


Gonzalez-c-model : Gonzalez et al A&A 2008

PS05 : Poelman & Spaans A&A 2005

S140 : H_2O CHEMISTRY





Gonzalez-c-model : Gonzalez et al A&A 2008
PS05 : Poelman & Spaans A&A 2005

Ortho/para chemistry has a greater impact compared to other excitation processes

CONCLUSIONS

Modelisation :

- Chemistry is in competition with other processes such as collisional and radiative processes

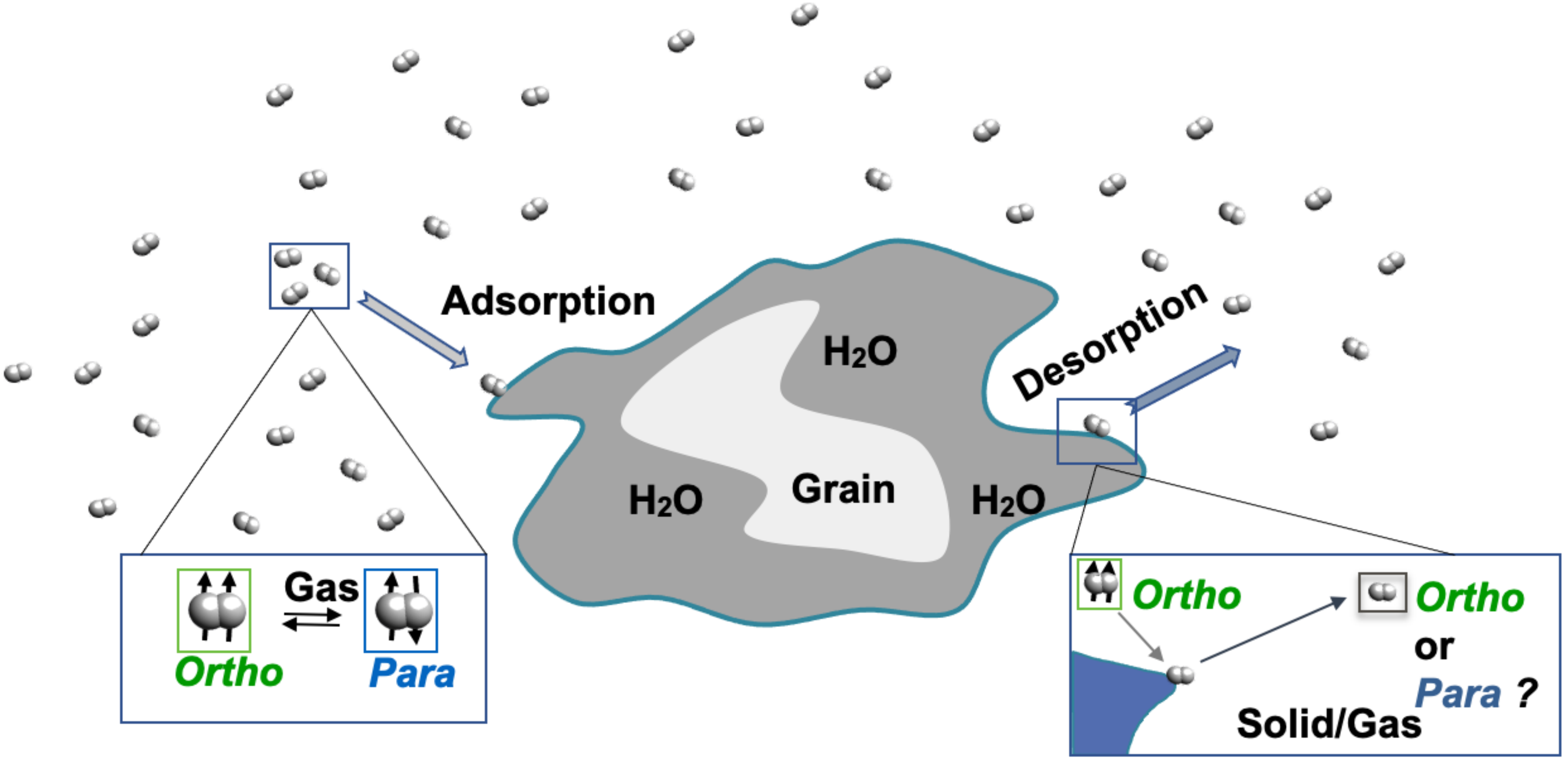
- The impact of ortho/para chemistry on water formation depends on the region studied

→ **Little impact in Orion bar but bigger impact in S140**

- In cold regions, surface grain chemistry plays a more important role than gas phase chemistry

- A new study of these regions with surface grain chemistry taking into account adsorption and desorption processes would provide a more complete model

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

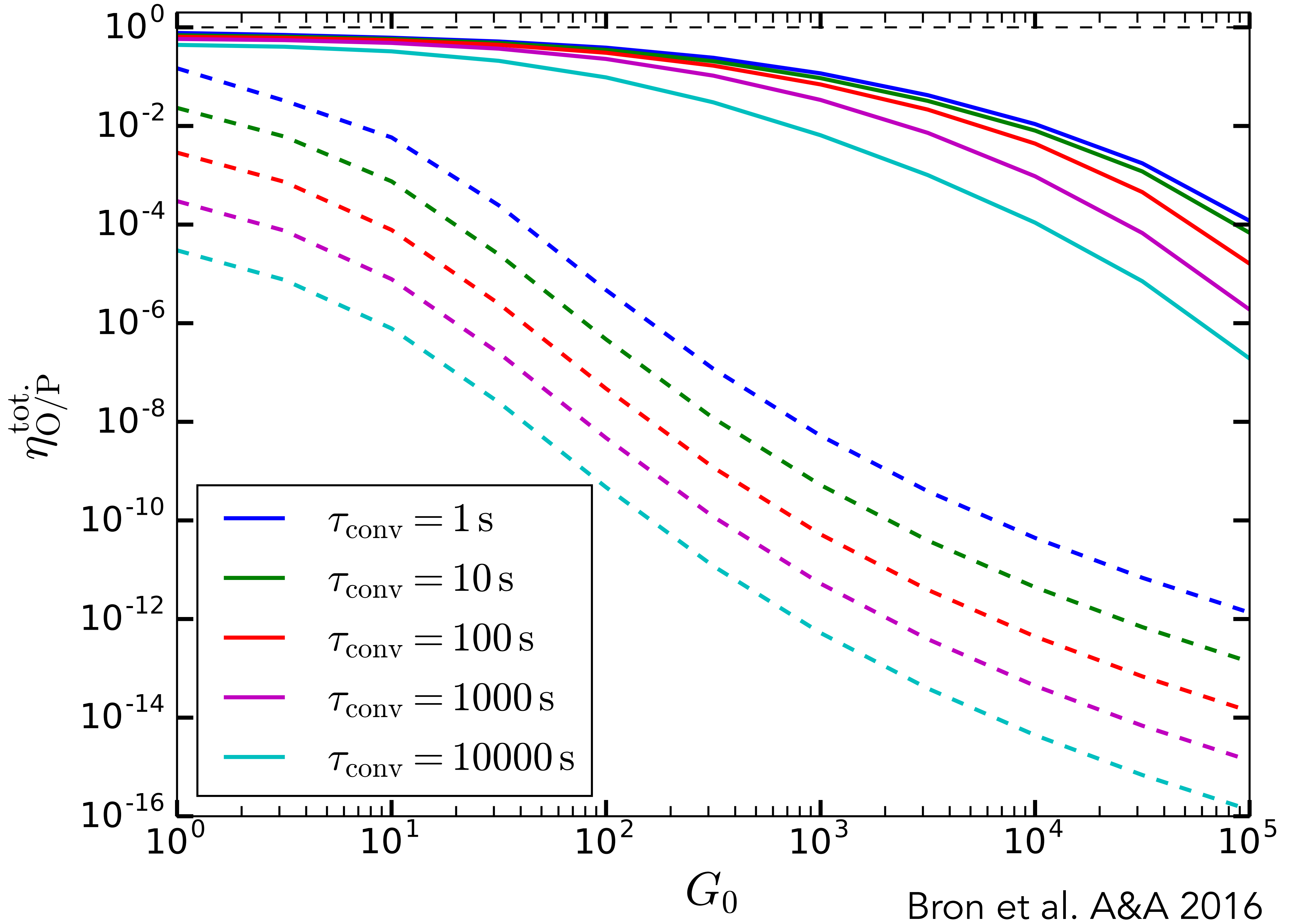


Molecular hydrogen on Amorphous Solid Water (ASW)

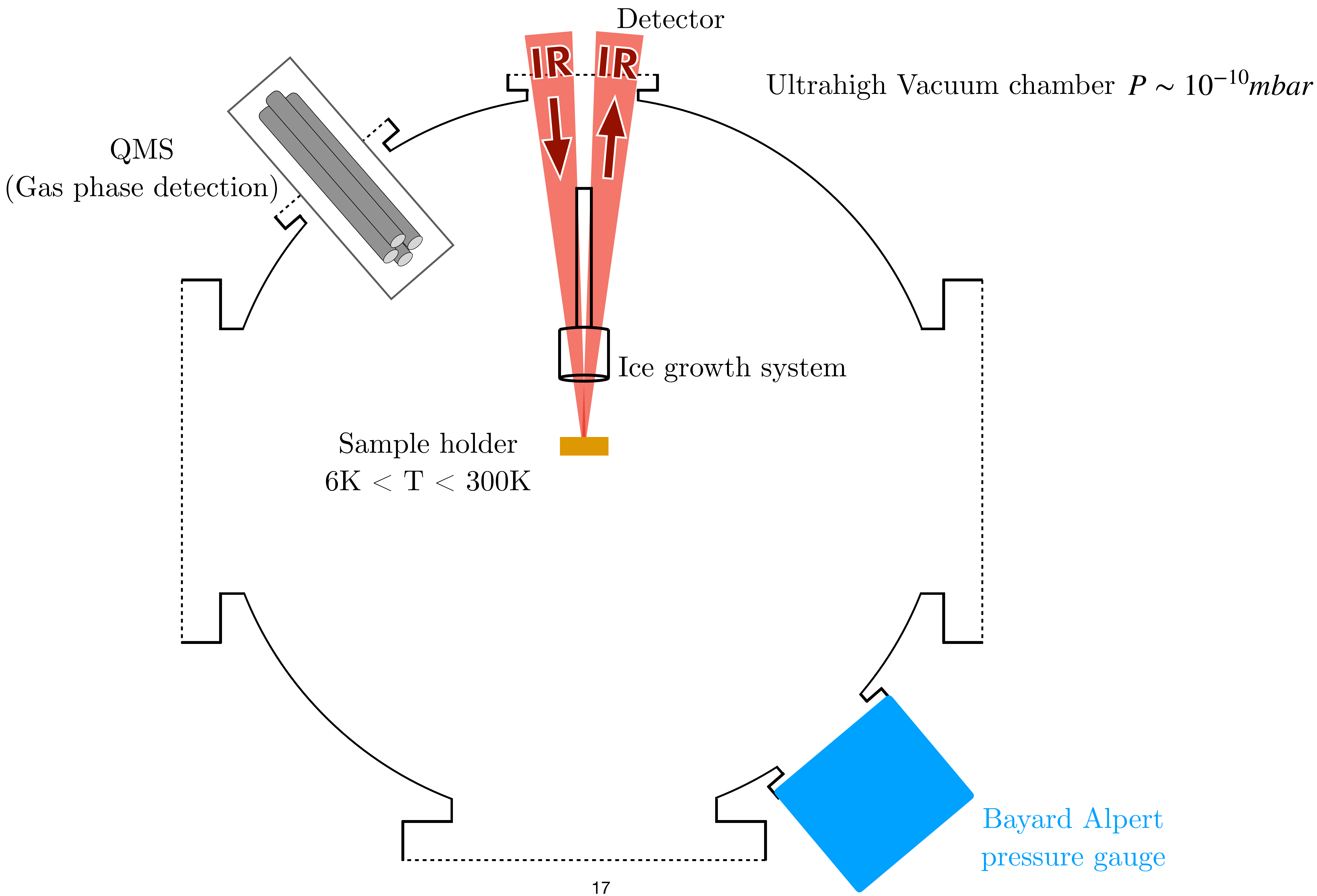
At 10K

	(SPICES) LERMA In situ	*FORMOLISM* (1) After desorption	*Sugimoto* (2) After desorption	*Ueta* (3) After desorption
t (min)	H_2 : 220 (17)	H_2 : >300	H_2 : 8 (2) D_2 : 49 (38)	H_2 : 52 (5)
H_2 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



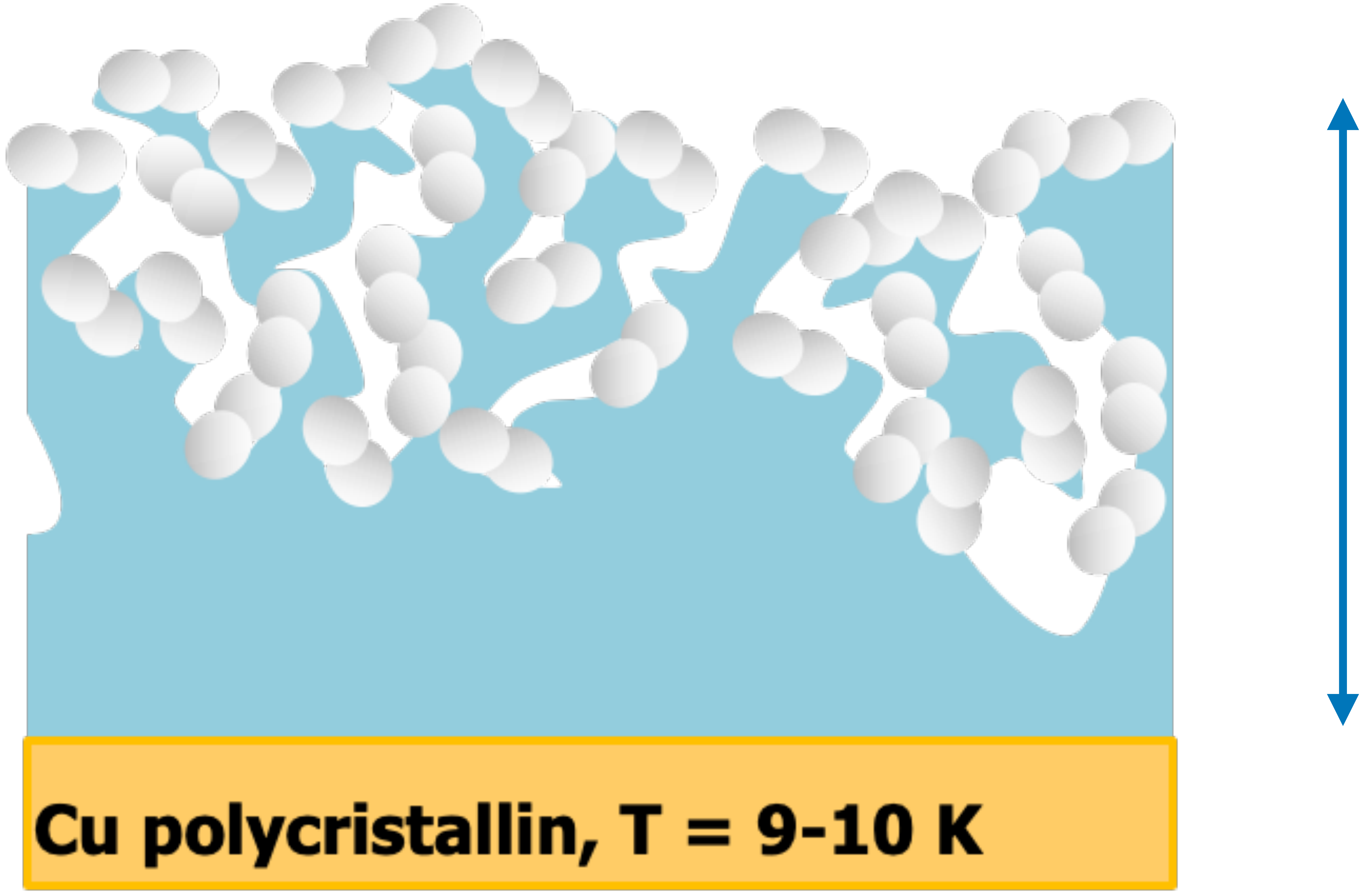
Bron et al. A&A 2016


Detector
IR
IR
Ultrahigh Vacuum chamber $P \sim 10^{-10} mbar$
QMS
(Gas phase detection)
Ice growth system
Sample holder
6K < T < 300K
Bayard Alpert
pressure gauge

~ 5 - 6 µm of H_2O amorphous and porous water

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

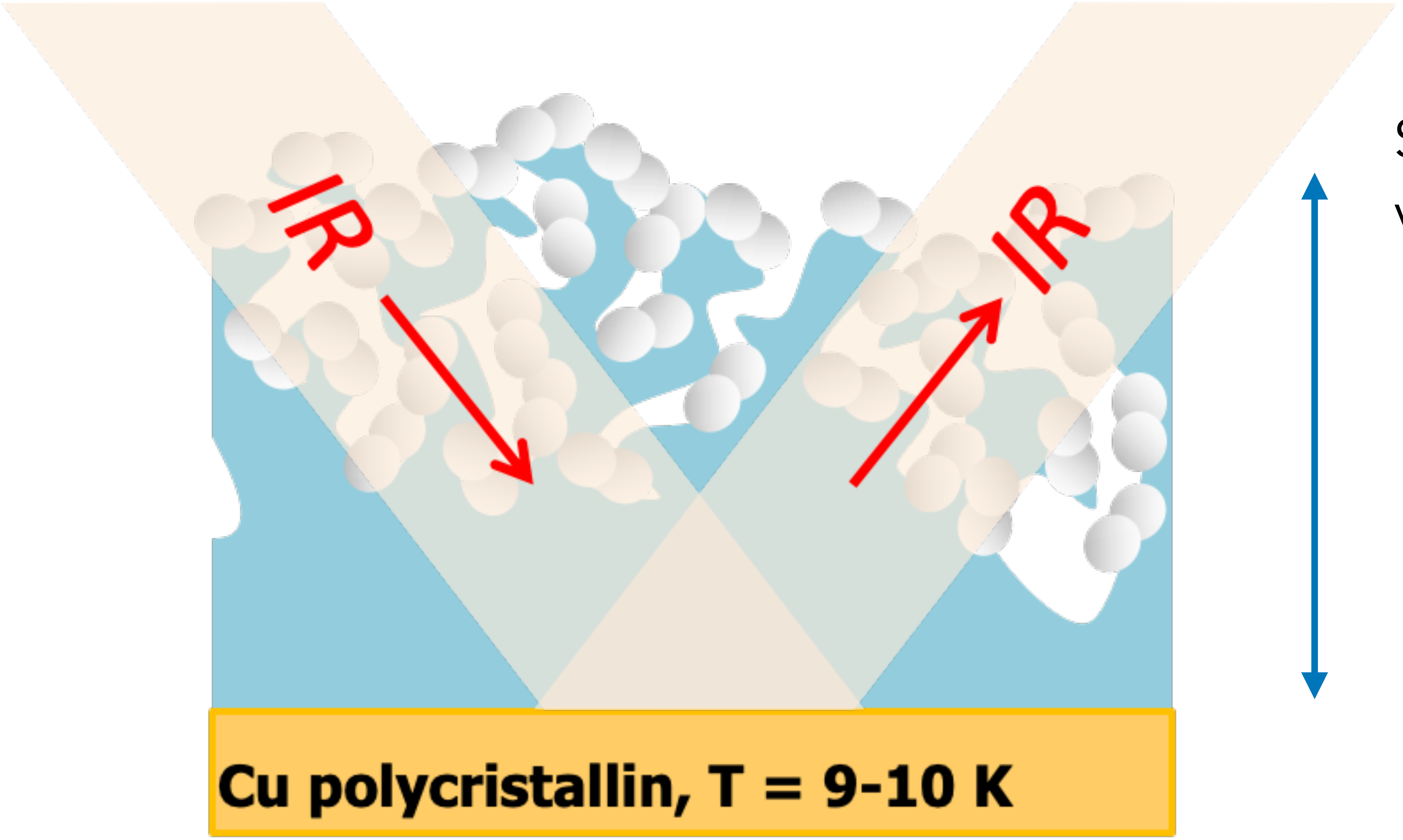
NSC ON ASW USING IR SPECTROSCOPY



Surface (interface H_2O – vacuum) saturated with H_2

~ 5 - 6 µm of H_2O amorphous and porous water

Fourier Transform IR spectroscopy



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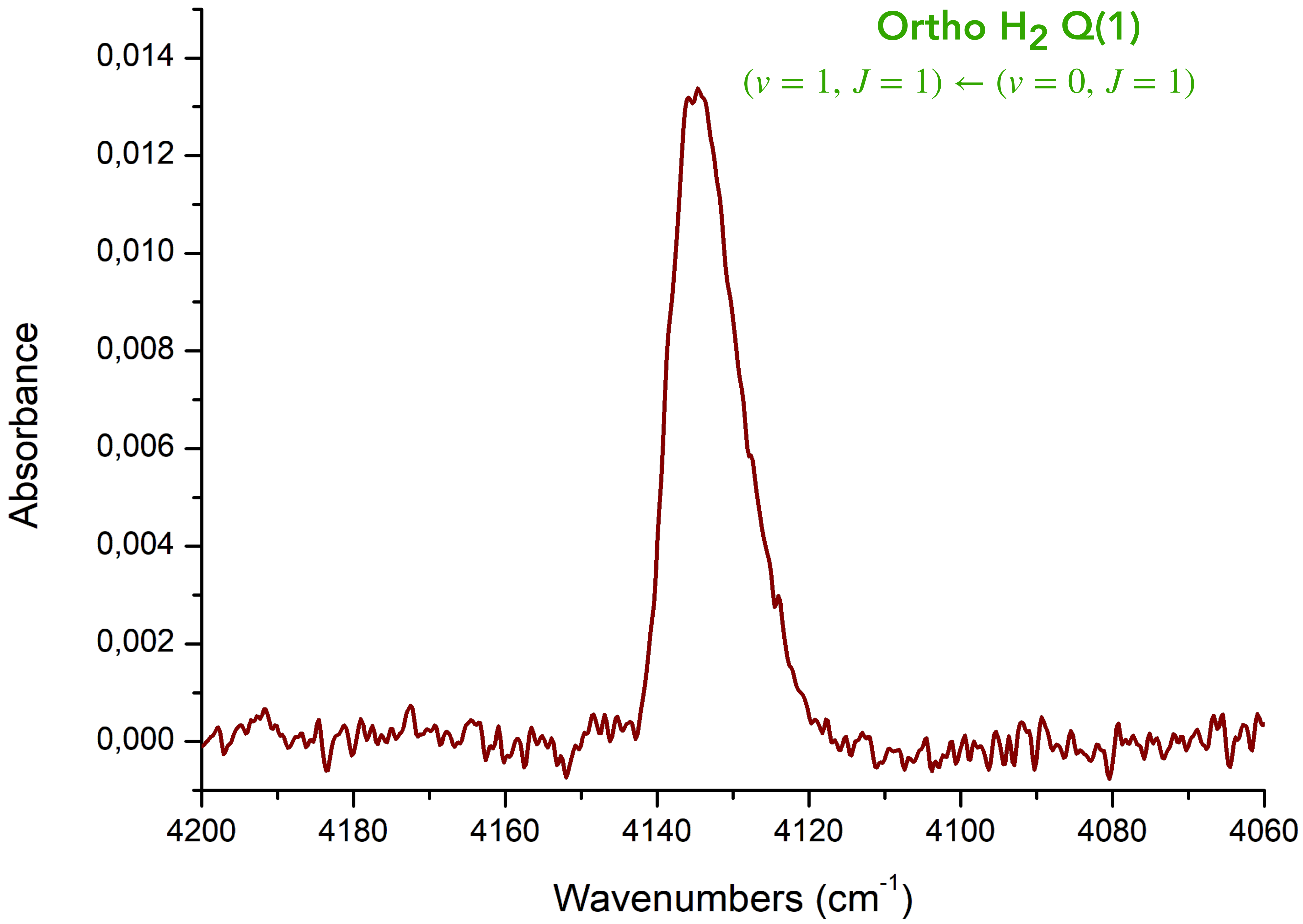
NSC ON ASW USING IR SPECTROSCOPY

~ 5 - 6 µm amorphous and porous H_2O saturated with H_2. IR spectra in the range 4050-4200 cm^{-1} obtained with COSPINU2 and time evolution of the two spin isomers



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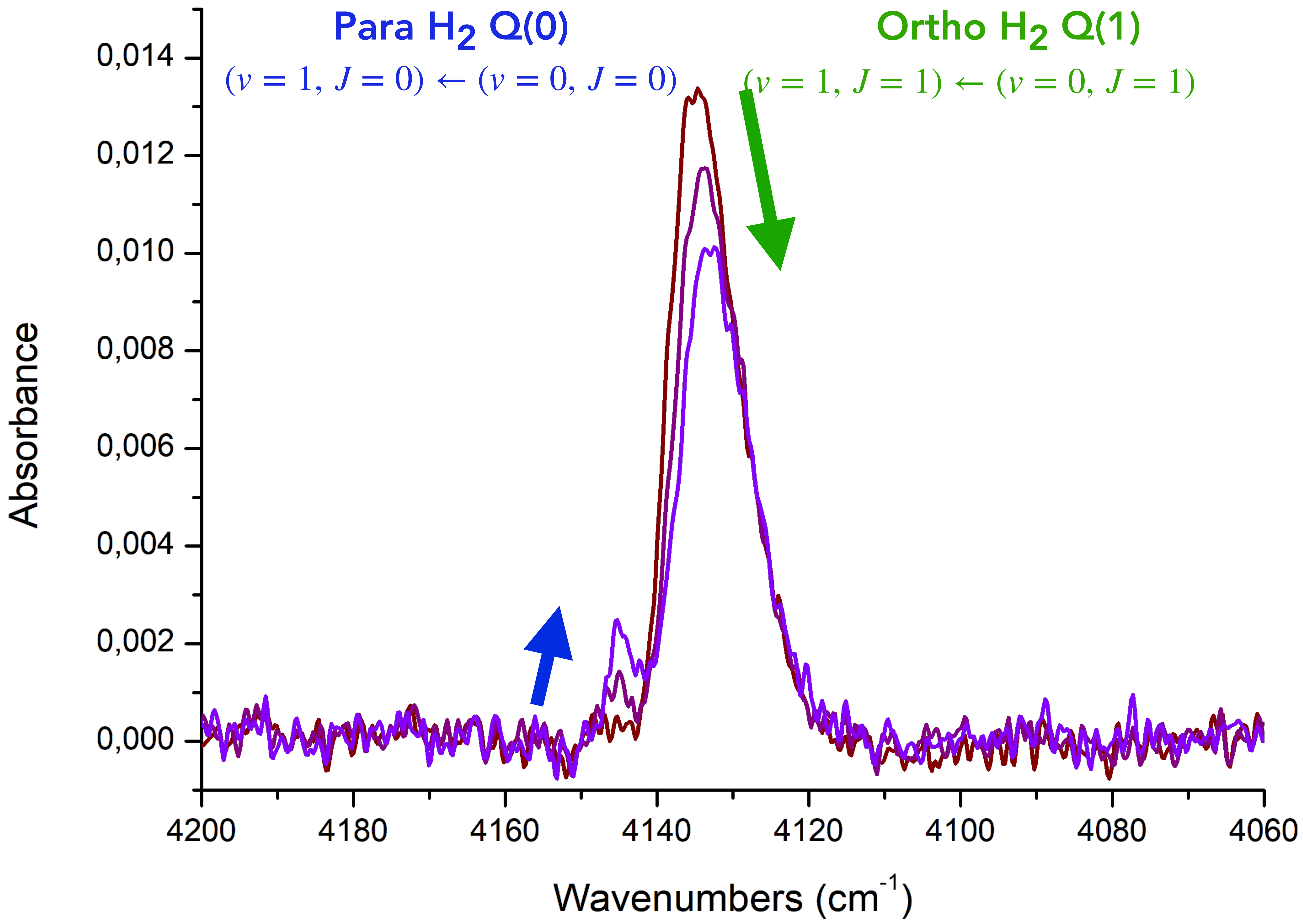

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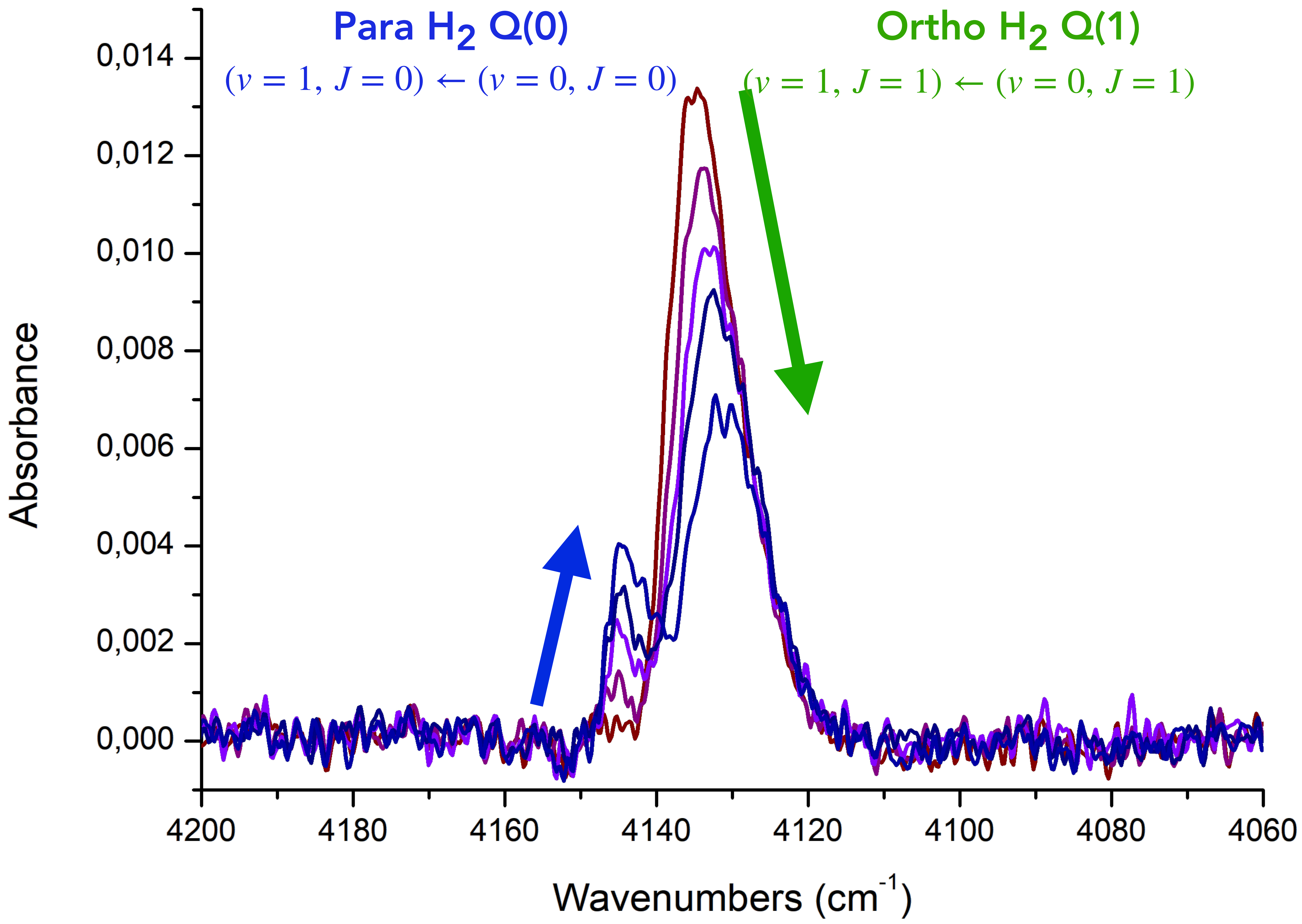

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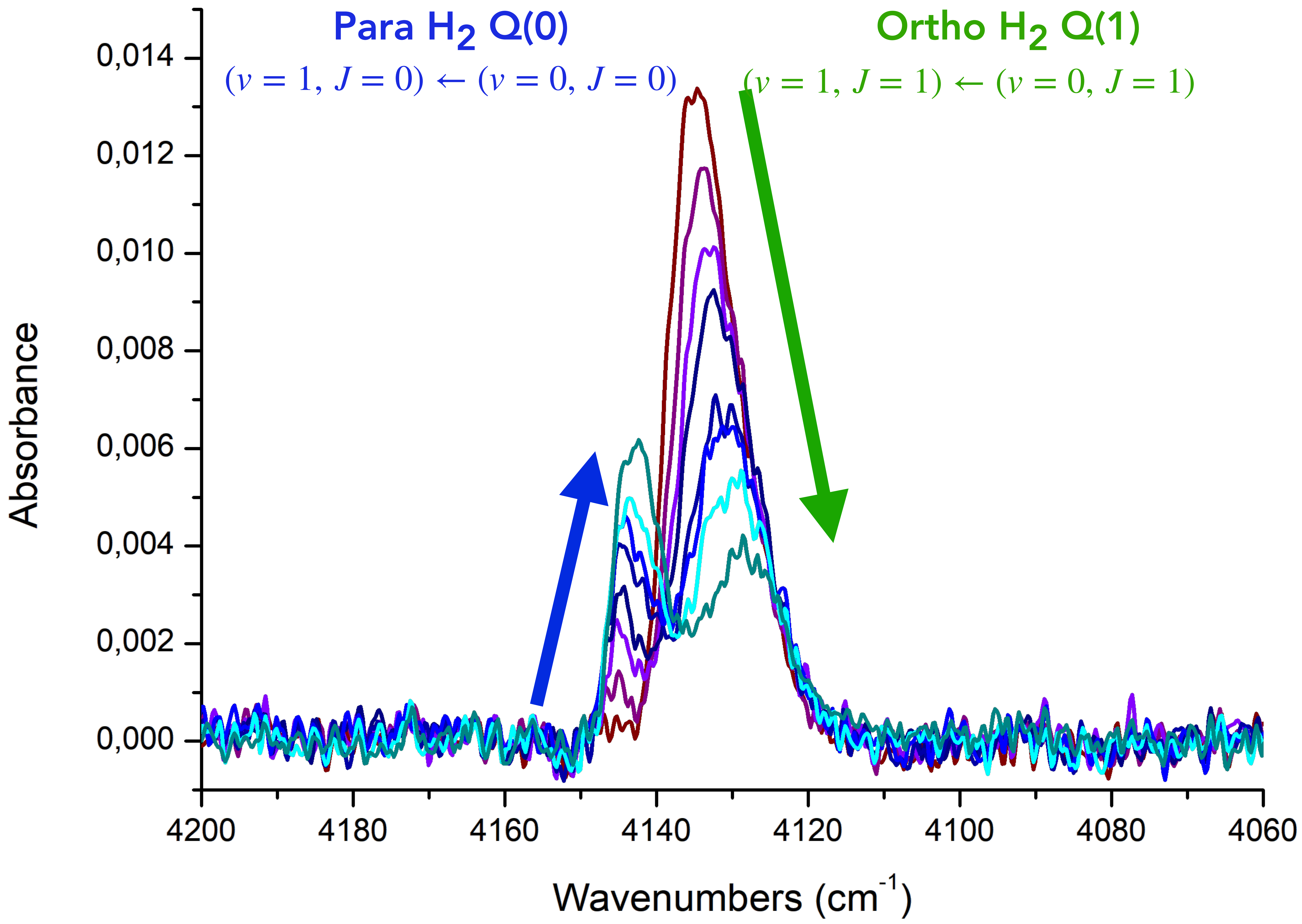

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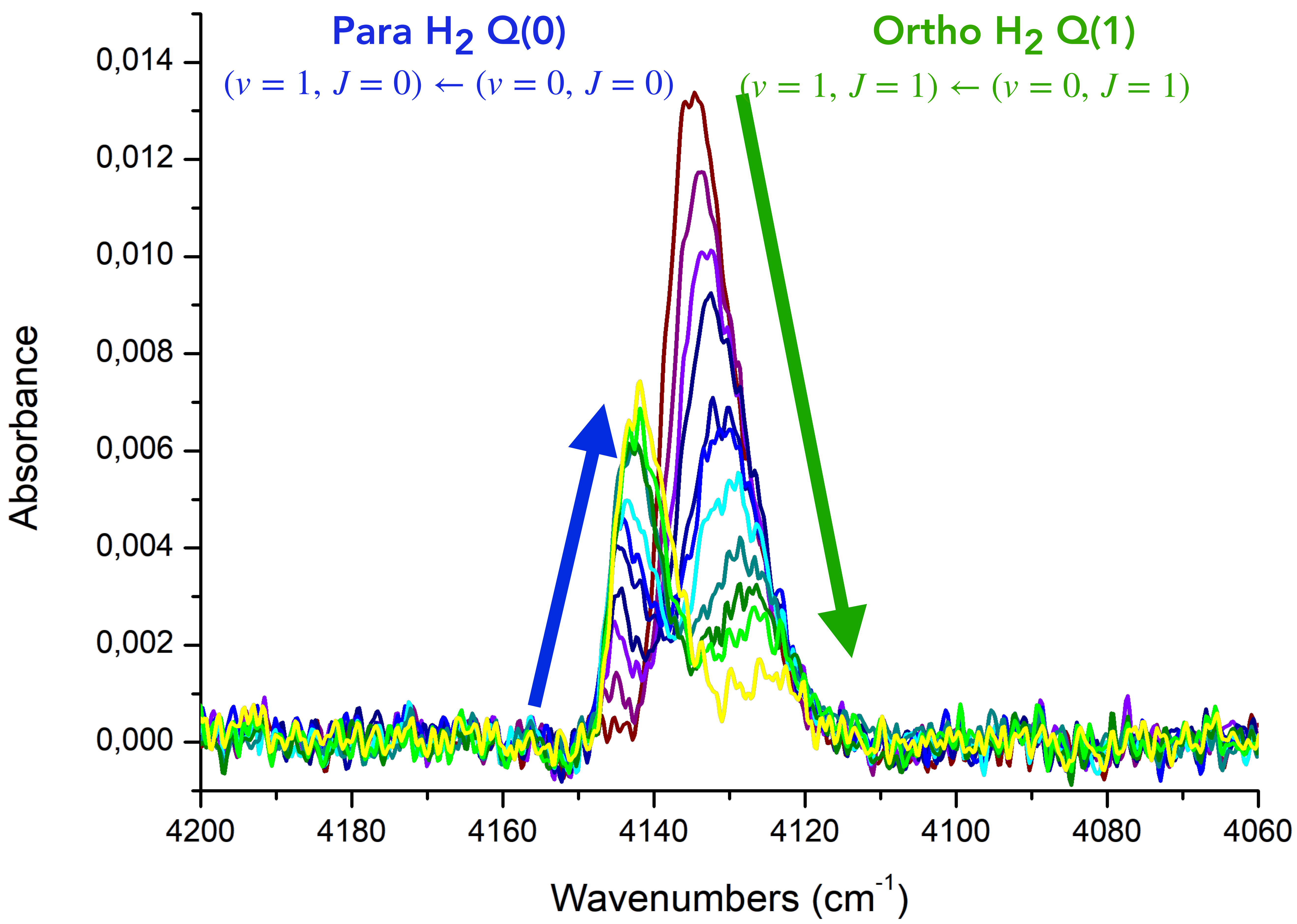

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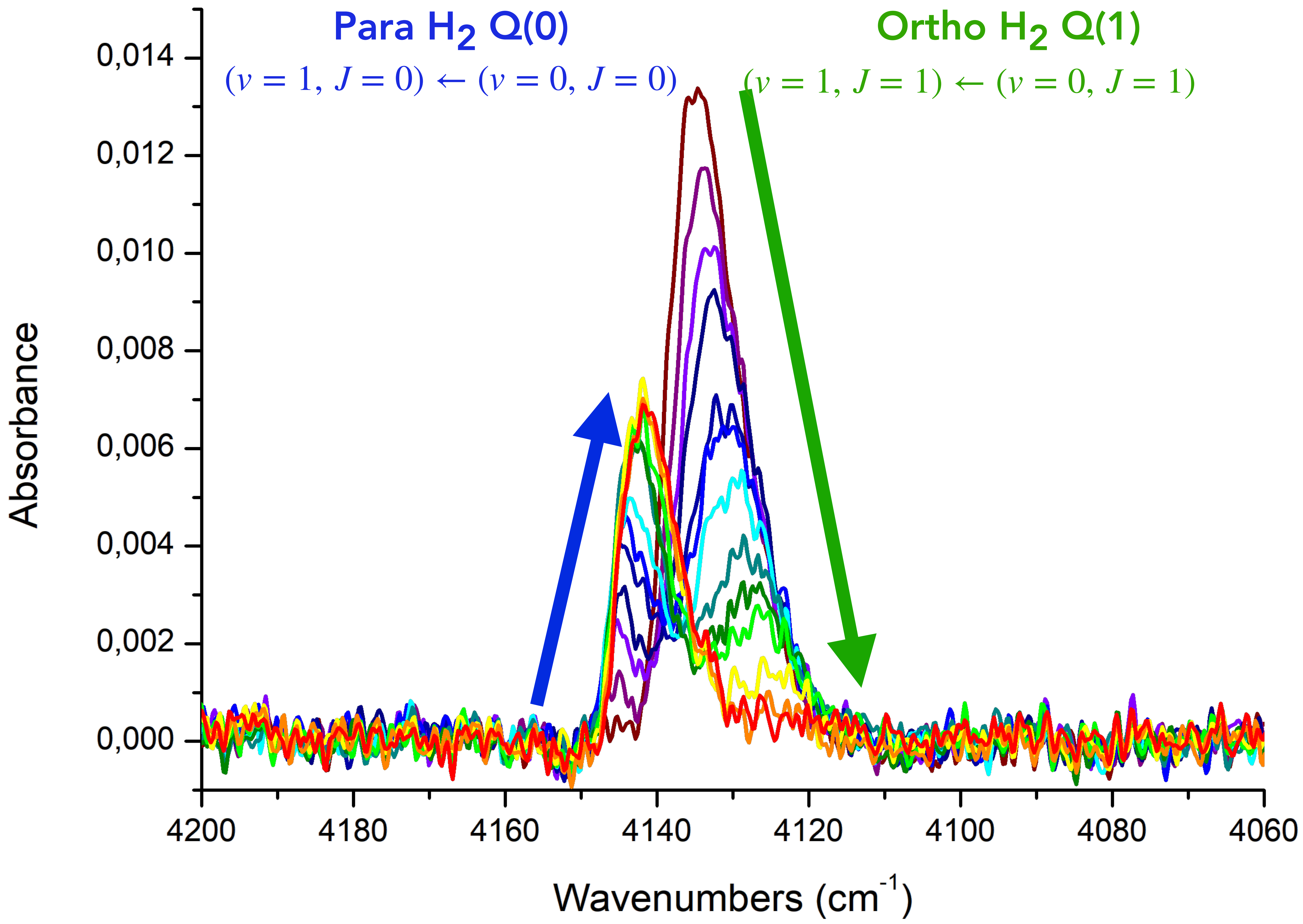

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NSC ON ASW USING IR SPECTROSCOPY

	(SPICES) LERMA In situ	*FORMOLISM* (1) After desorption	*Sugimoto* (2) After desorption	*Ueta* (3) After desorption	COSPINU2 (5 - 6 µm H_2O) in situ	COSPINU2 (~ 3.5 µm H_2O) in situ
t (min)	H_2 : 220 (17)	H_2 : >300	H_2 : 8 (2)	H_2 : 52 (5)	H_2 : 376 (25)	H_2 : 273 (15)
H_2 coverage	1ML	0.3 - 0.75 ML	1 - 2 ML	0.3 - 1 ML	1ML	1ML

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Big discrepancies in the data set between the different experiments

- O_2 molecules have a **high magnetic moment**, and O_2 impurities in the system may significantly decrease the conversion time.

CONCLUSIONS

Experiment :

- The NSC of H_2 on ASW has been studied with different techniques.

  The measurements carried out with FORMOLISM and COSPINU2 give similar characteristic times.

  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

- Developments are in progress to investigate the link between *in situ* OPR of H_2 and the OPR after thermal and non thermal desorption.

Thank you for your attention !

PROCESSES THAT GOVERN THE ORTHO TO PARA RATIO IN THE PDR CODE AND H_2O CHEMISTRY

Species	H_2	H_2O	H_2^+	H_3^+	H_2O^+	H_3O^+
Excitation	✓	✓	✗	✓	✗	✗

Reaction chain for the H_2O formation :

$$OH + H_2 \longrightarrow H_2O + H$$
$$O^+ + H_2 \longrightarrow OH^+ + H$$
$$OH^+ + H_2 \longrightarrow H_2O^+ + H$$
$$H_2O^+ + H_2 \longrightarrow H_3O^+ + H$$
$$H_3O^+ + e^- \longrightarrow H_2O + H$$

⇨ Duplication with ortho/para forms of the 5 H_2O-forming reactions and all reactions where H_2^+, H_2O^+ and H_3O^+ appear.
Use of UGAN, Rist+ 2013, Oka 2004, Sipilä+ 2015

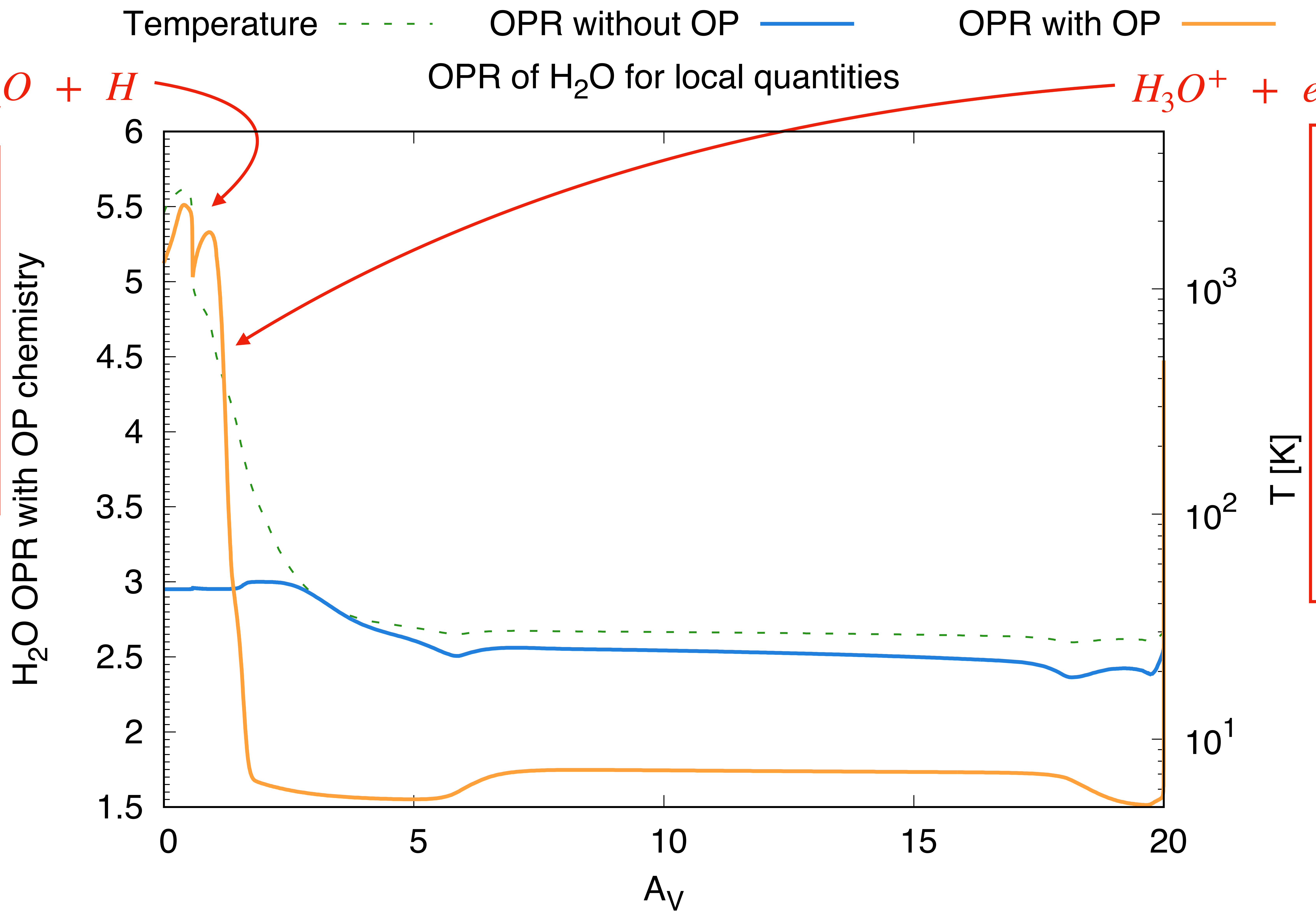
Between 300-400 more reactions than without OP chemistry

ORION BAR : H_2O CHEMISTRY

$H_2 + OH \longrightarrow H_2O + H$

- Branching ratios more efficient for ortho molecules
- High temperature 3/4 ortho H_2 and 1/4 para H_2

$H_3O^+ + e^- \longrightarrow H_2O + H$



- H_3O^+ mainly created by $H_2O^+ + H_2$ and H_2O^+ mainly created by $OH^+ + H_2$
- H_2 OPR drops drastically

NSC ON ASW USING IR SPECTROSCOPY

O_2	t (min) IR Vib (SPICES) LERMA	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

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