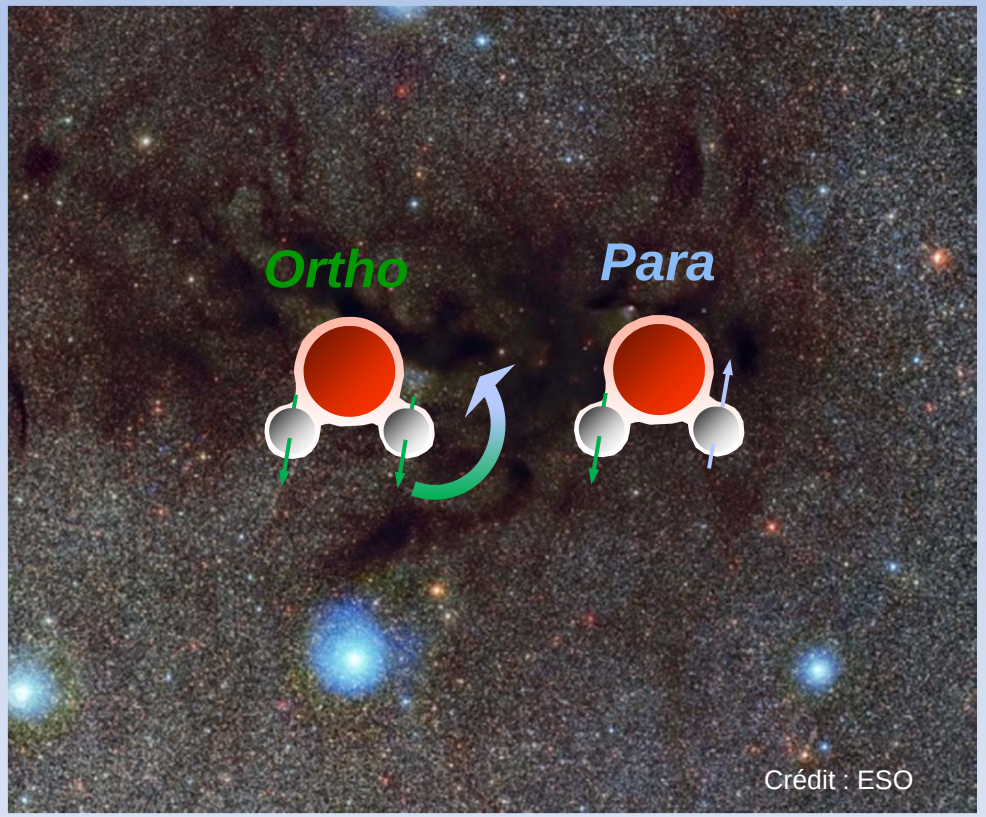
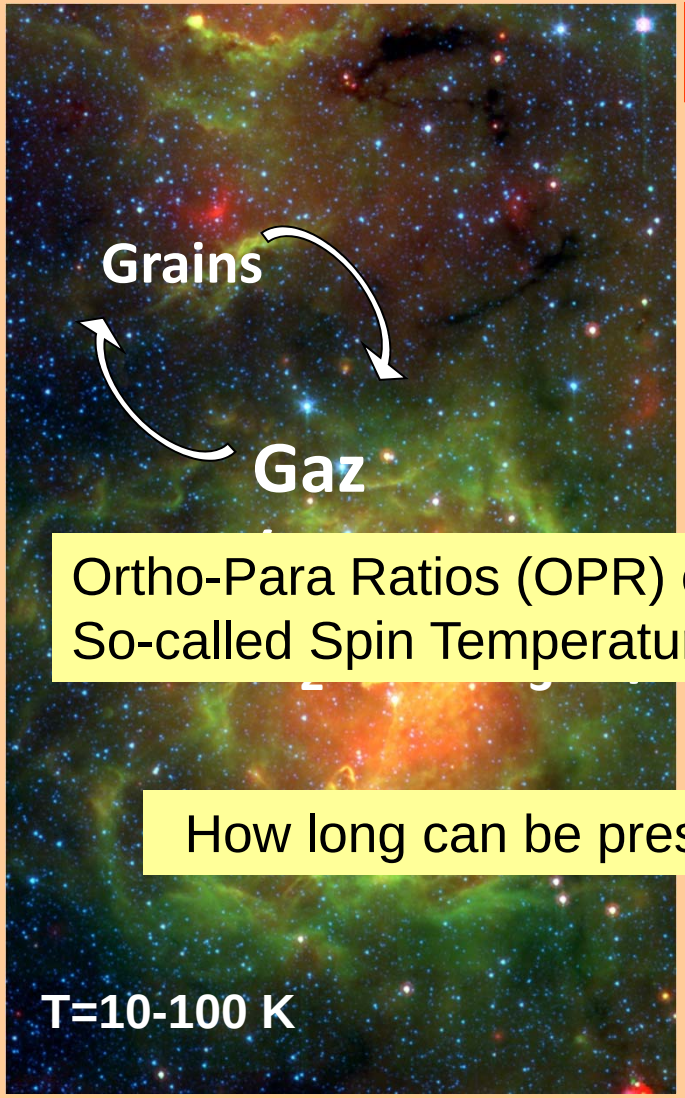
Experimental investigations on nuclear spin-states equilibration of hydrogenated molecules at low temperature gas-solid interface

X. Michaut

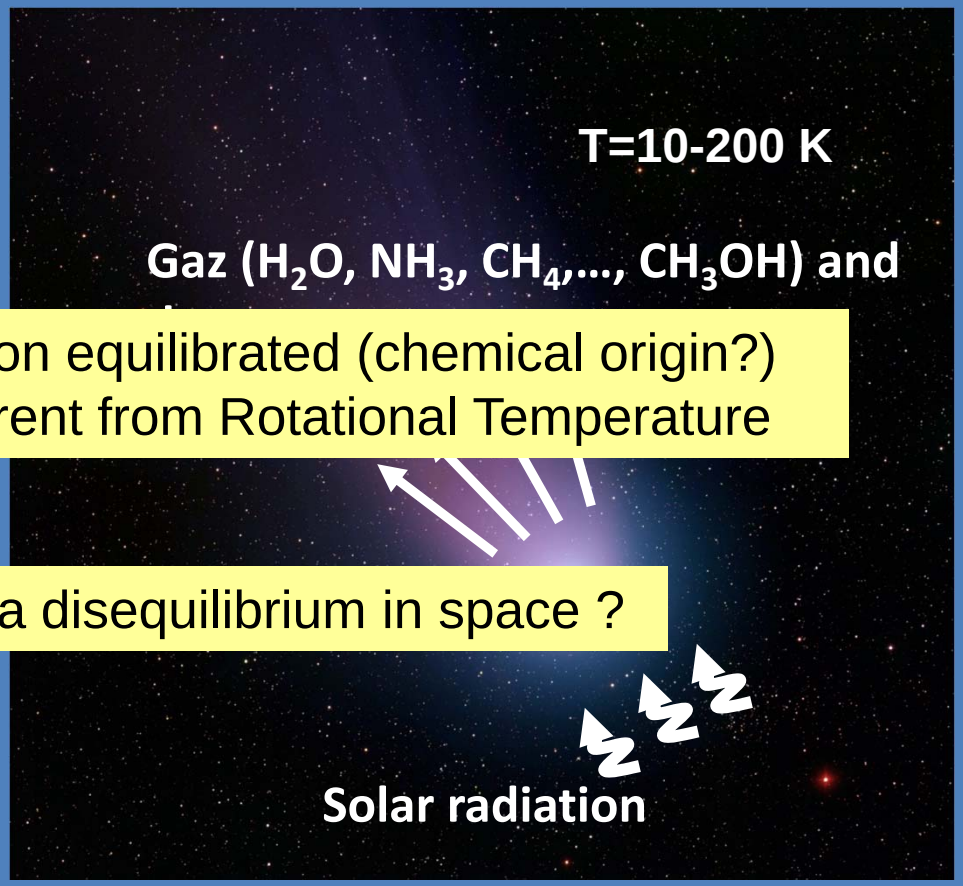


Gas & Ices



Molecular Clouds

Comets



Ortho-Para Ratios (OPR) often non equilibrated (chemical origin?)
So-called Spin Temperature different from Rotational Temperature

How long can be preserved a disequilibrium in space ?

Ortho-Para conversion dynamics in gas phase

4 typical environments (T=5-100 K, n(H_2) = 10^5 - 10^8 cm^{-3})

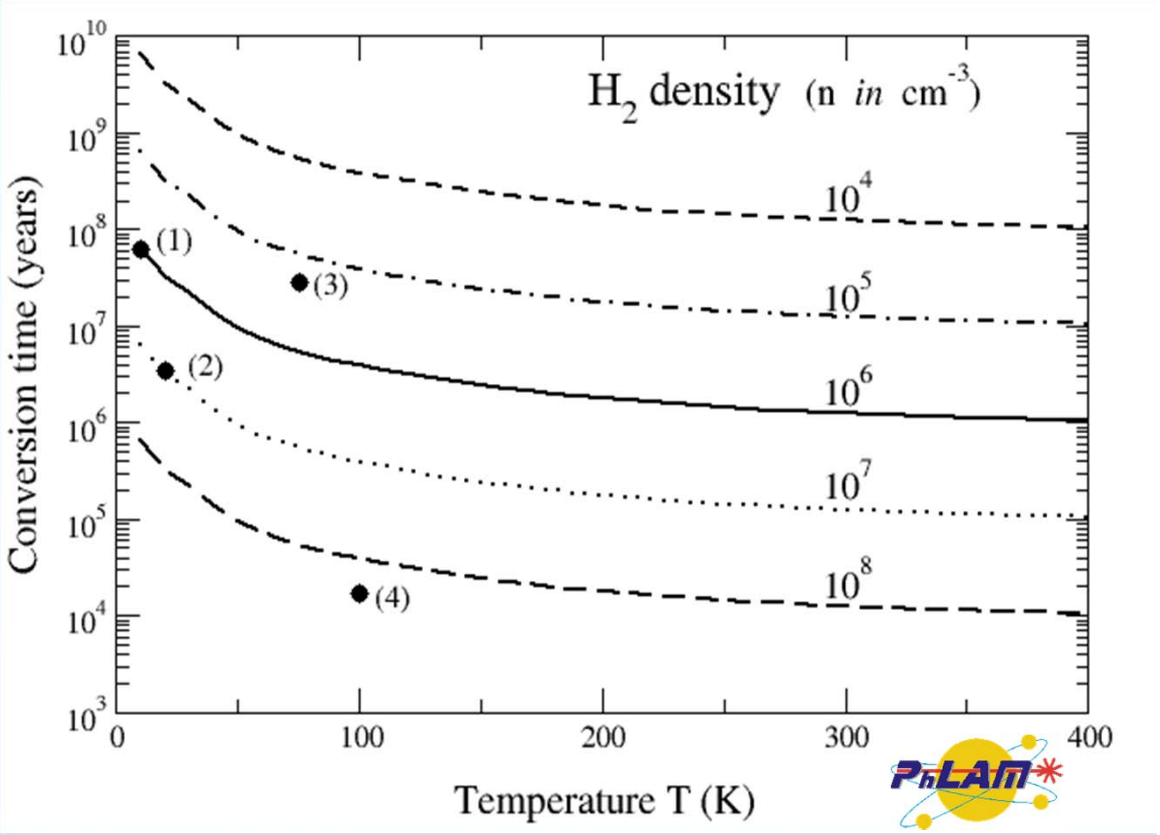
H_2CO

(1) Prestellar Core
(5-10 K, n(H_2) = 10^6 cm^{-3})

(2) Protoplanetary disk
(20 K, 10^7 cm^{-3})

(3) PDR
(75 K, 2×10^5 cm^{-3})

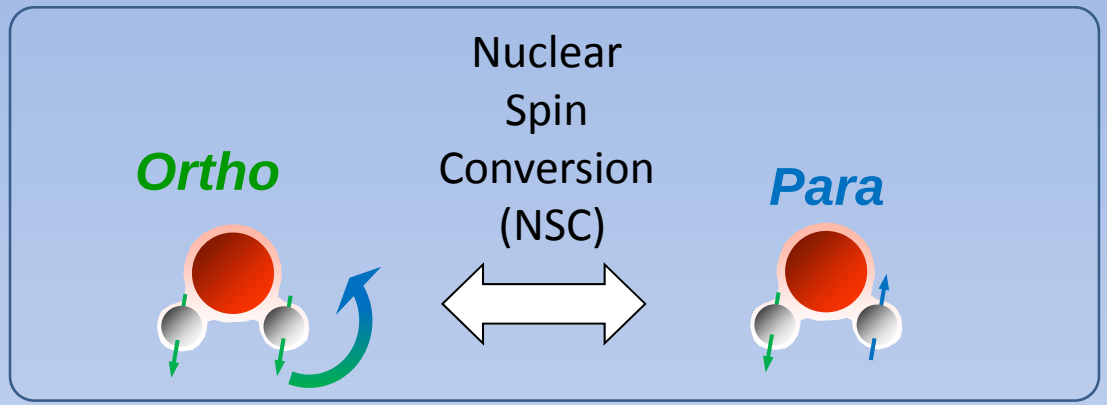
(4) Class 0 Protostar
(100 K, 3×10^8 cm^{-3})



Tudorie *et al* A&A 453 (2006)

-Very diluted medium : $\tau = 10^{+4} – 10^{+7}$ years
-Calculations do not take into account intermolecular magnetic interactions
-Do not give information about interactions with grains

Ortho-Para transition probability



Magnetic coupling

$$P(O \rightarrow P) = 2\left|V_{op}\right|^2 \frac{\Gamma_{op}}{\omega_{op}^2 + \Gamma_{op}^2}(W_o + W_p)$$

Ortho-Para energy difference

Decoherence induced by collisions

depend :

-on state of matter (solid, gas, surface interaction)

-density, temperature

-sources of inhomogeneous magnetic fields at the molecular scale

Environment can change all these parameters

Ortho-Para conversion dynamics with no proton exchange

ANR Project

GAS SPIN

2009-2014

LPMAA

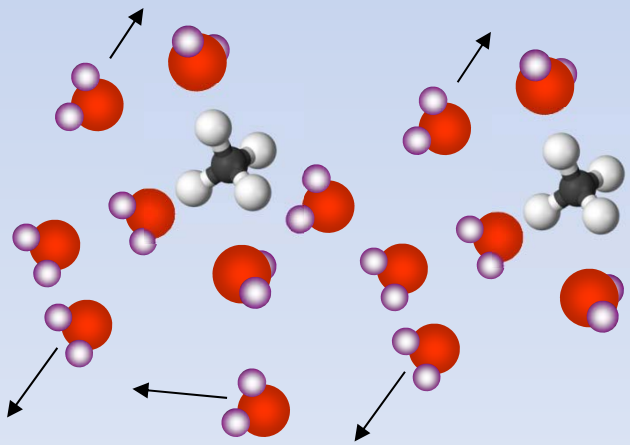
LERMA

PhLAM

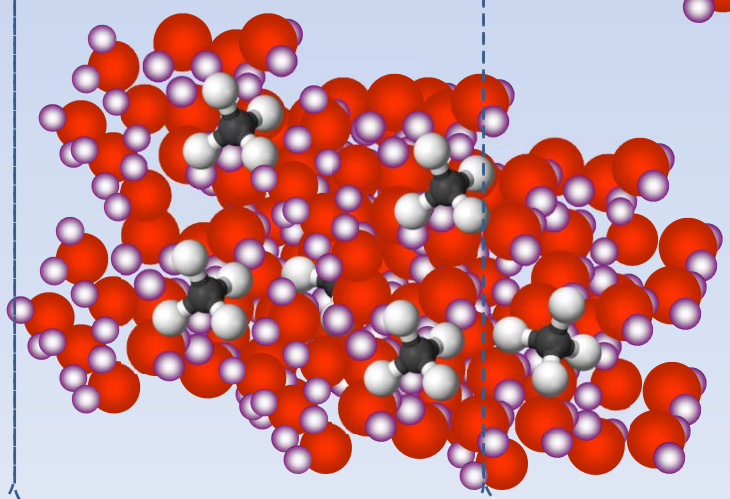
PIIM

Physique des Interactions Ioniques et Moléculaires

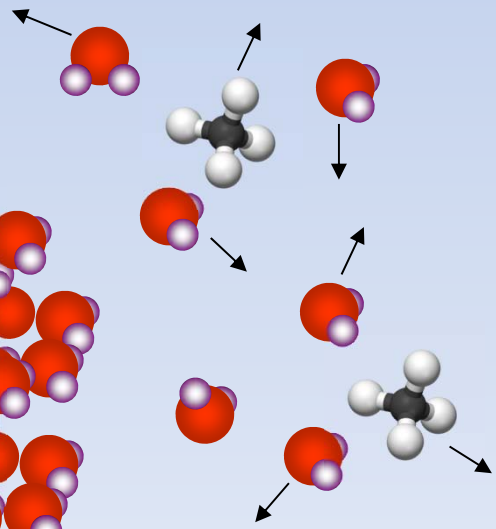
In the Gas-Phase



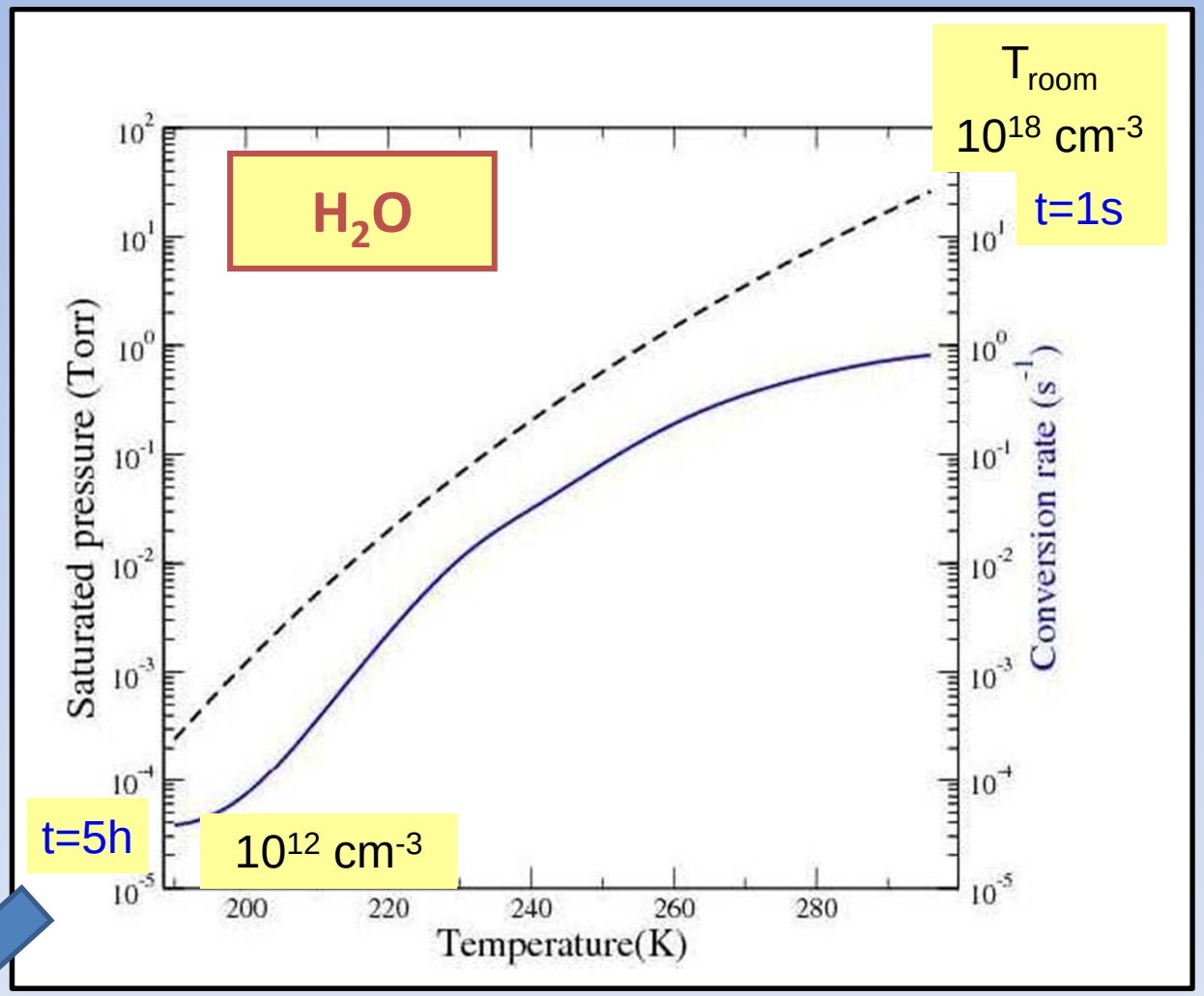
In the solid



At Gas-Solid interface



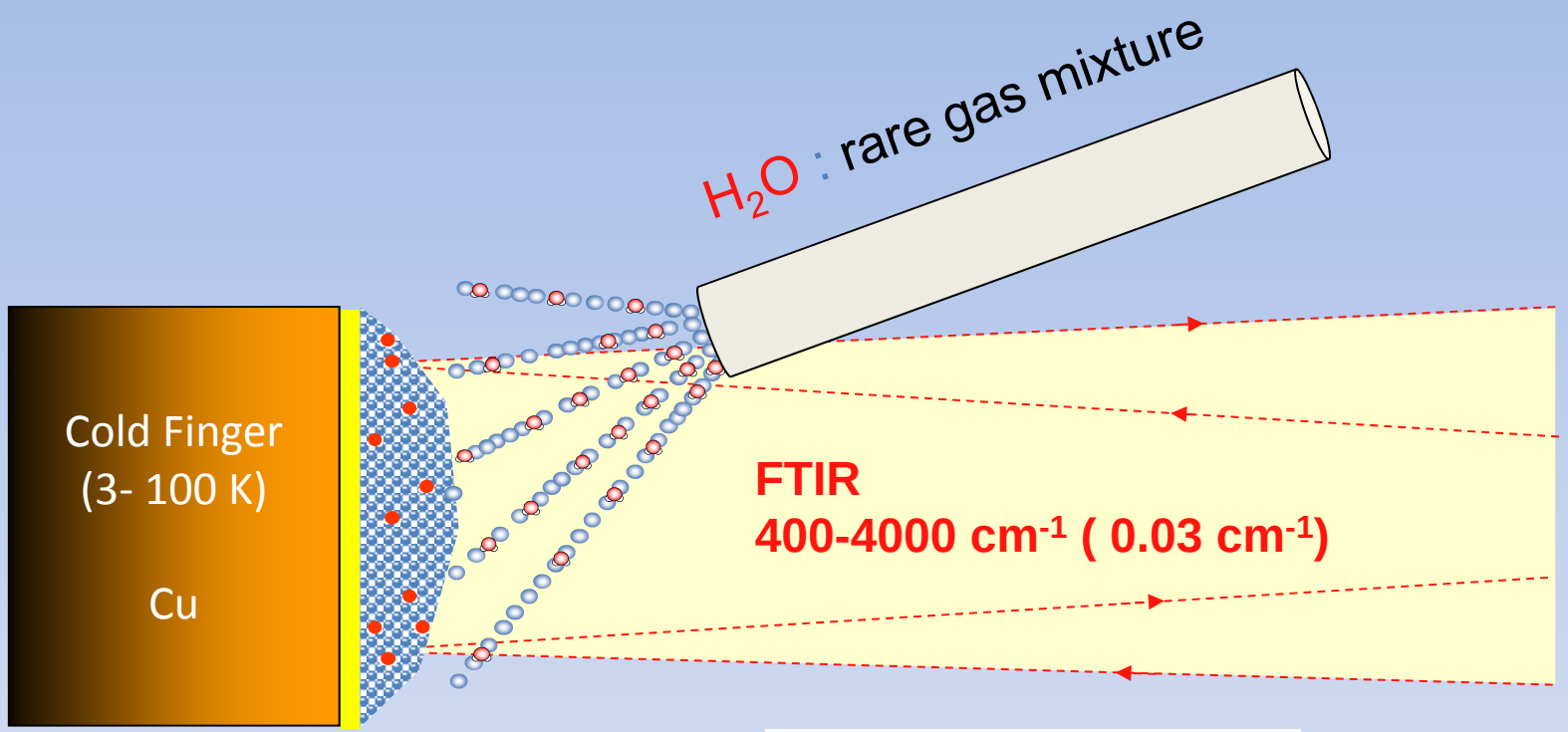
One approach : calculations in gas phase



Lower temperature ?

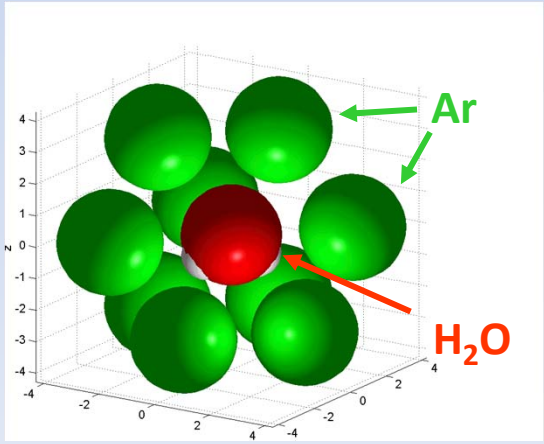
Cacciani *et al* PRA 80 (2009), PRA 85 (2012)

Second approach : cold matrices experiments

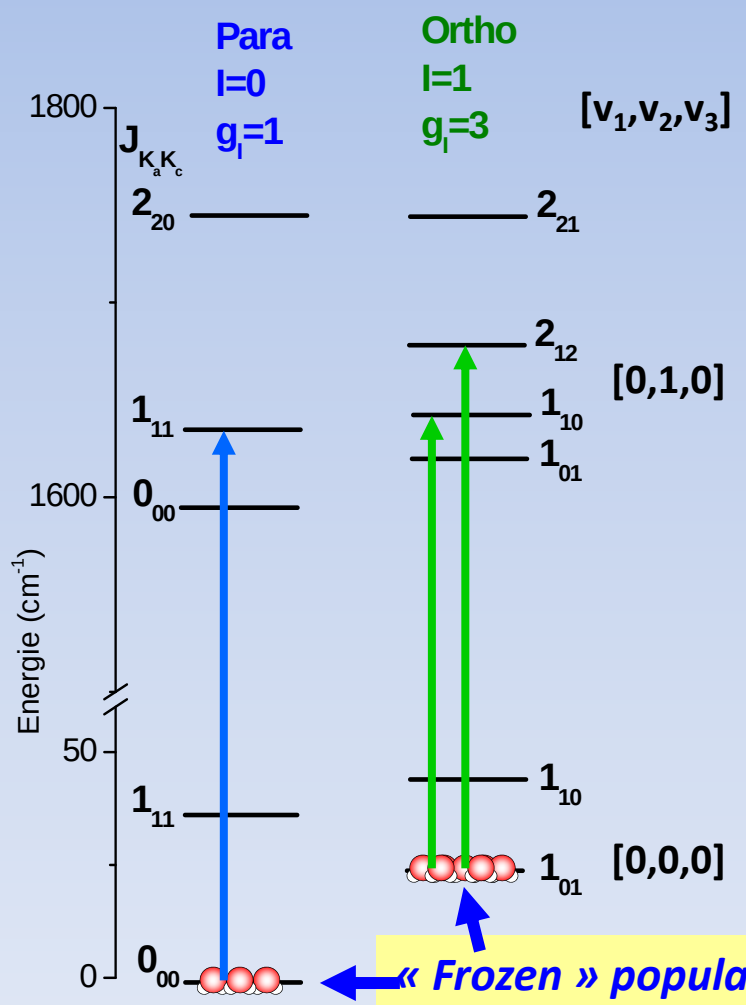


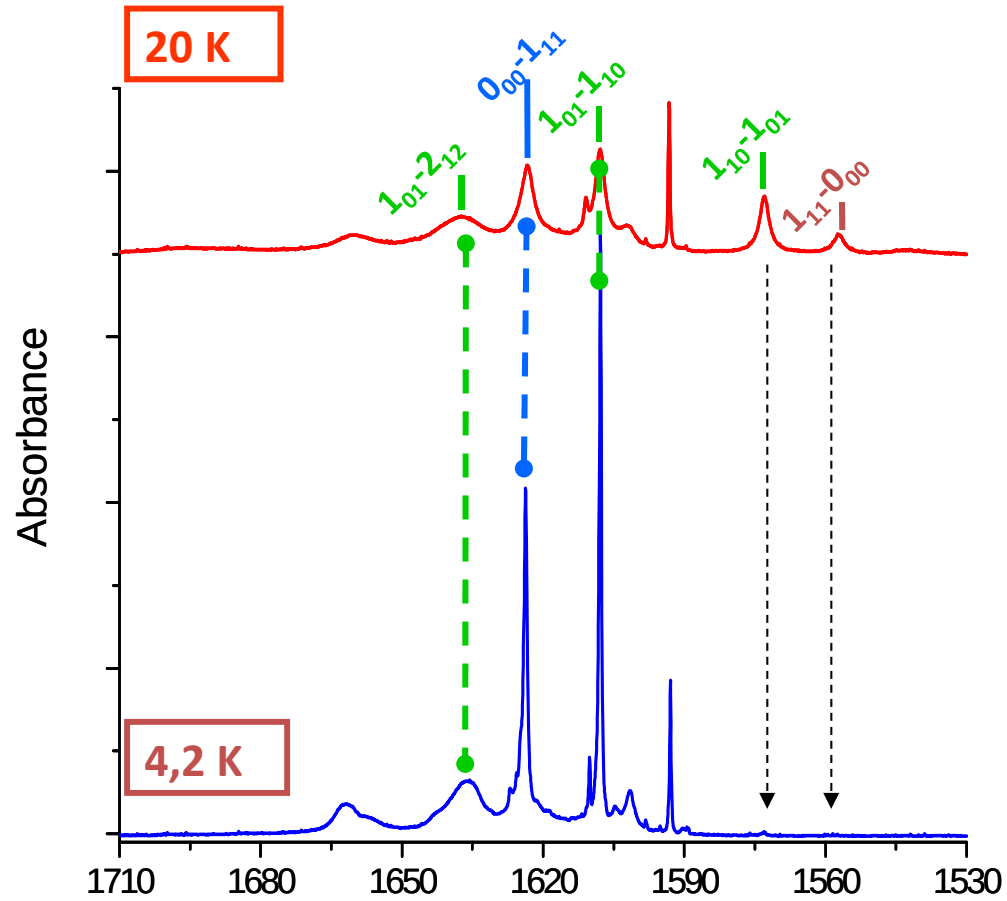
The Sample :

- **polycristalline**
- **low H_2O concentration**
- **thicknesses 50 et 500 μm**



H_2O in Argon Matrix





« Frozen » population O/P(20 K) à 4,2 K : desequilibrium

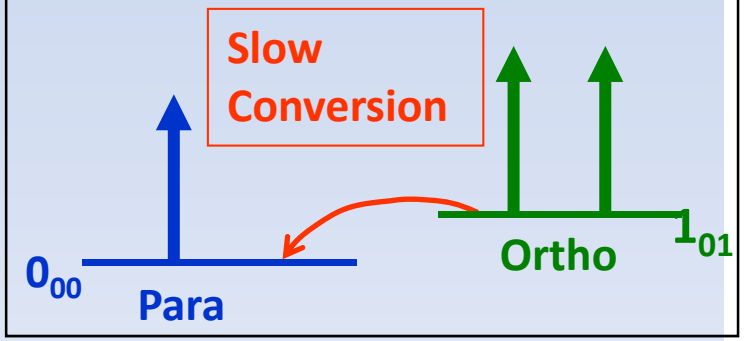
H_2O in Argon Matrix

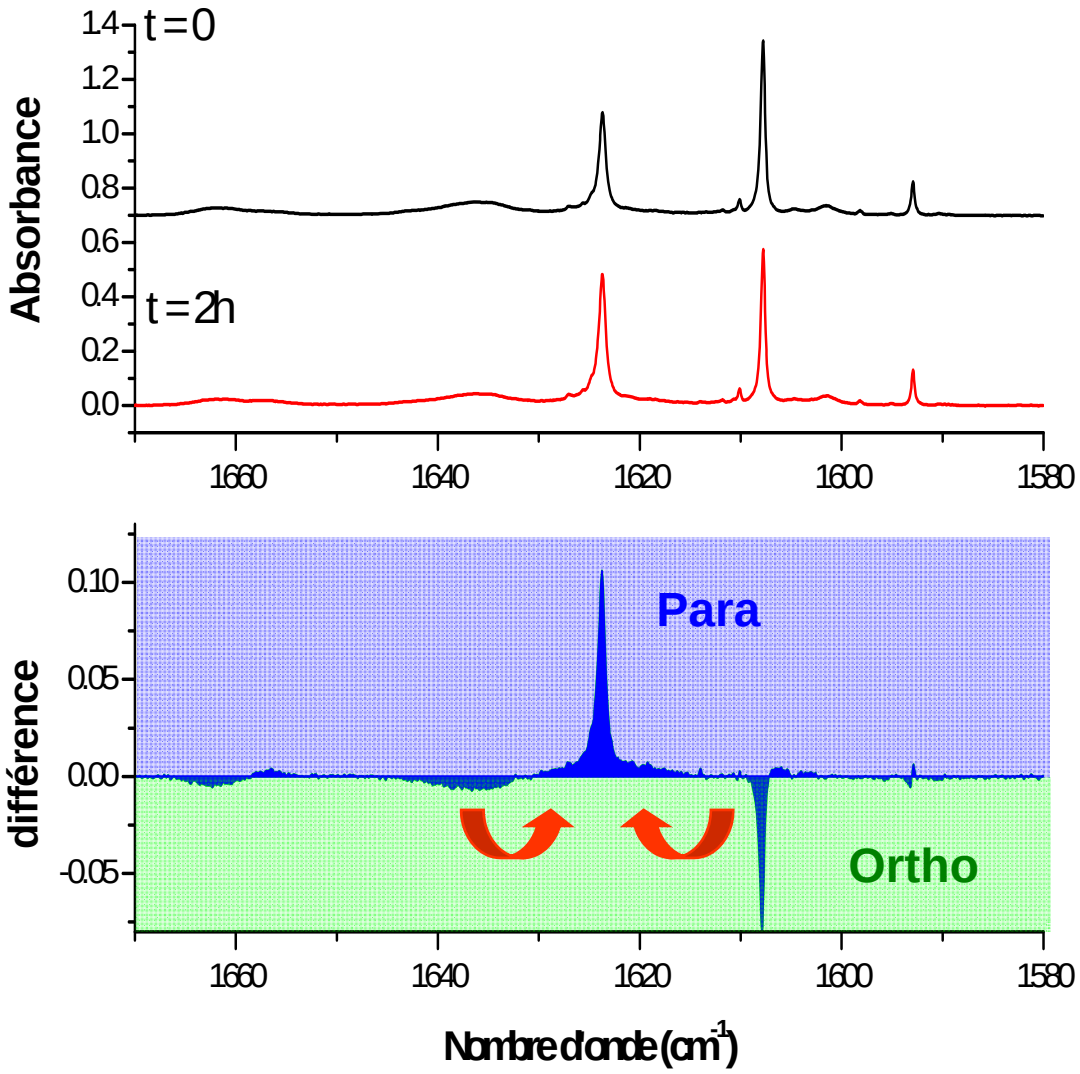
Slow return to equilibrium after

a rapid thermal induced desequilibrium

NSC

ortho/para time evolution

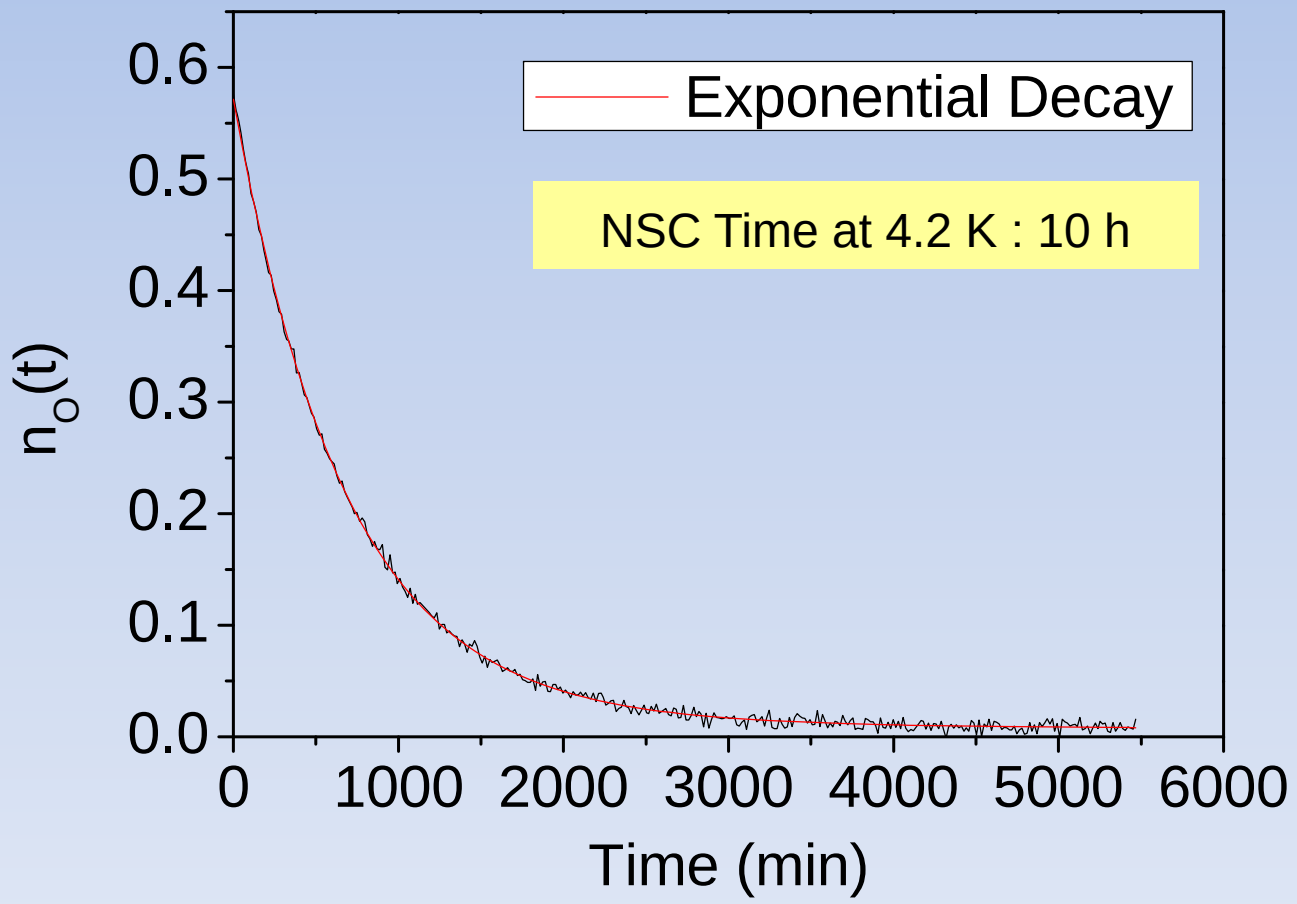




H_2O in Argon Matrix

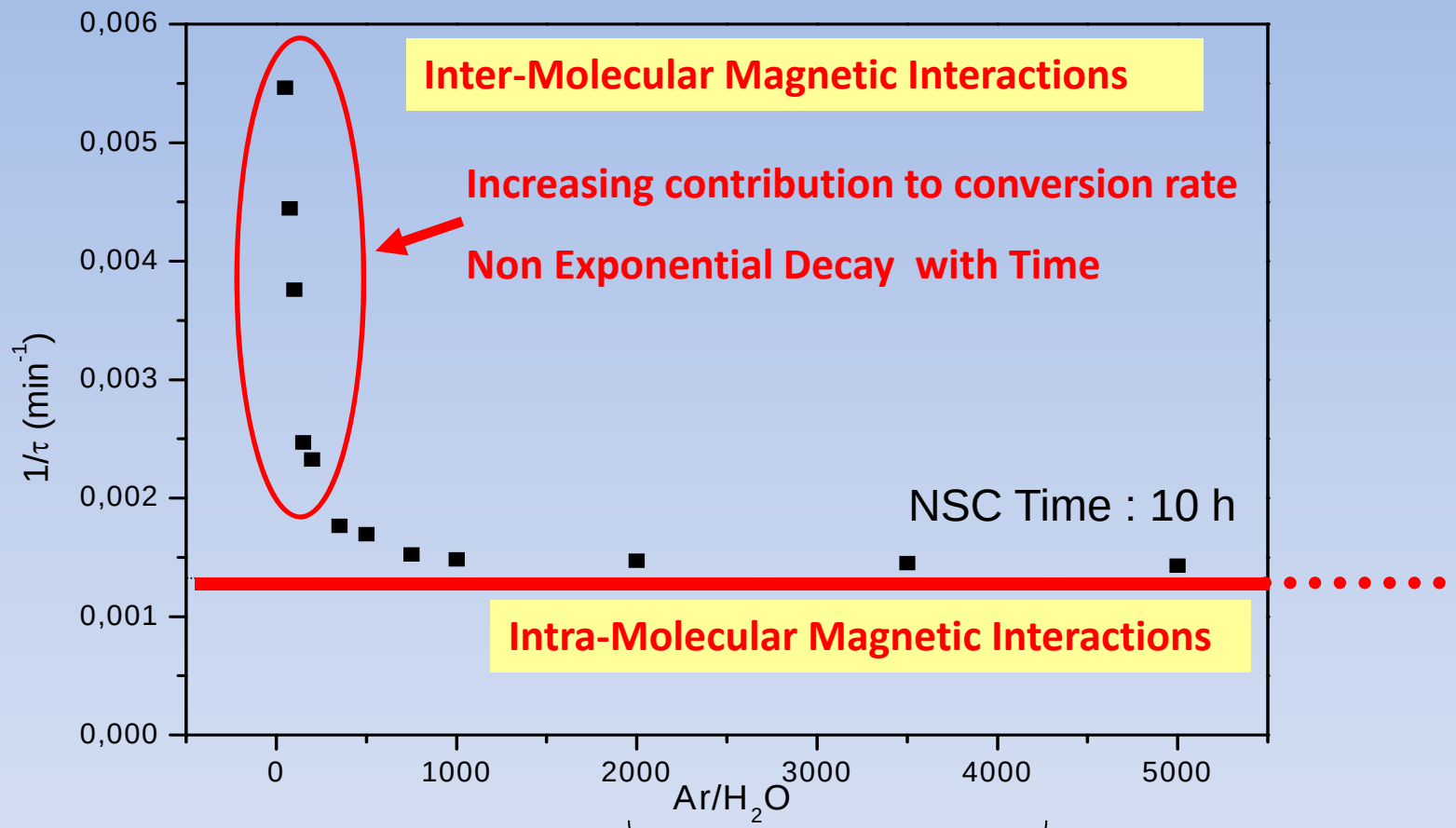
Behavior at Low Concentration

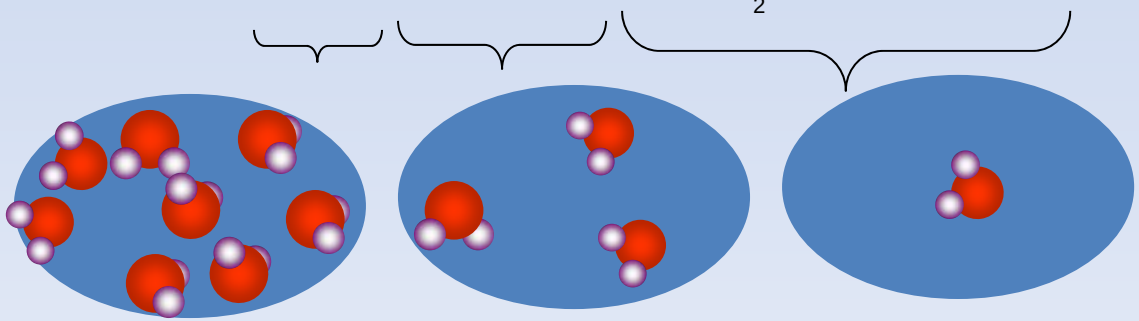
$H_2O/Ar = 1/10000$



Results : H_2O in Argon Matrix

T=4.2 K



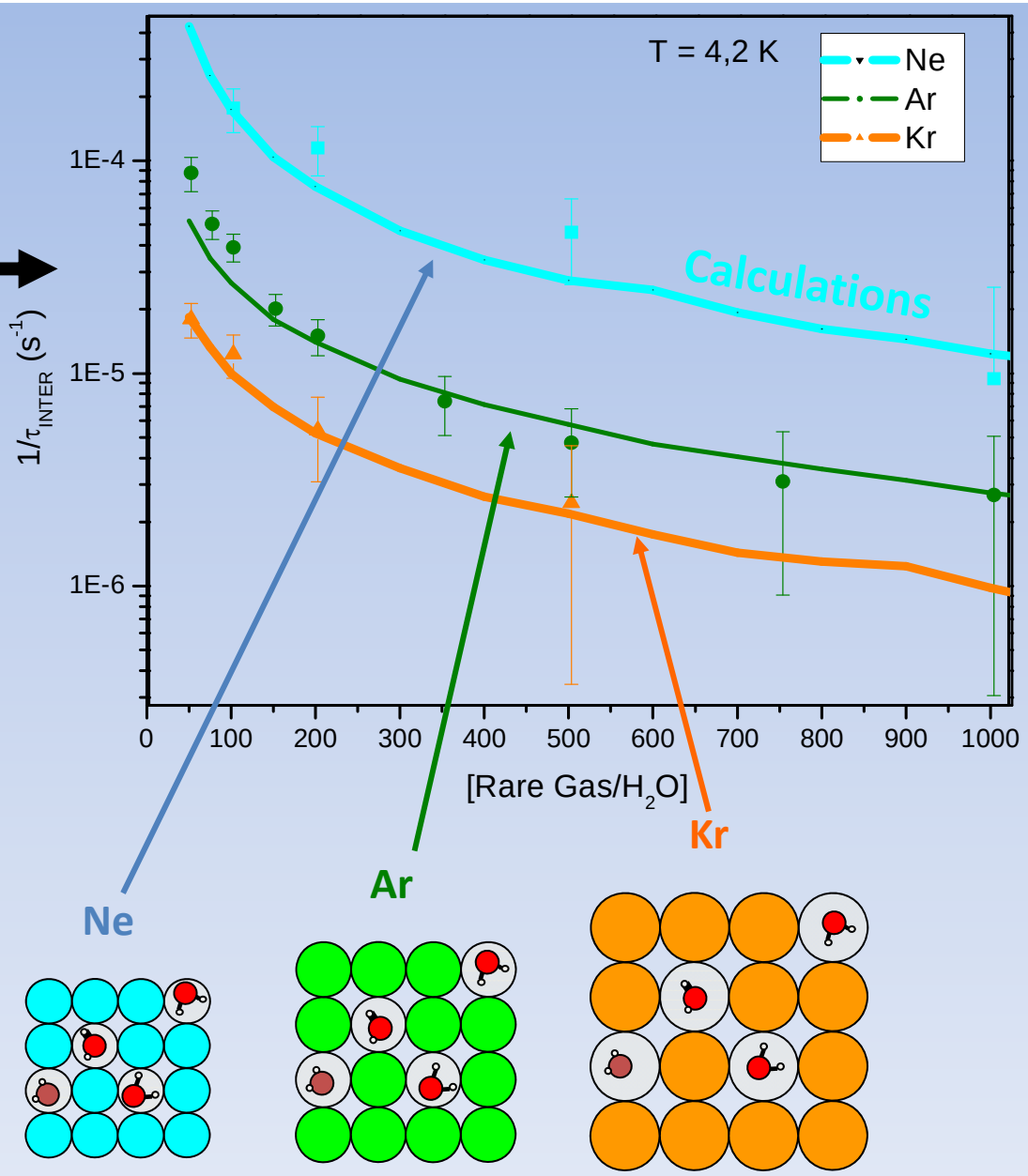


C. Pardanaud PhD Thesis
Michaut *et al.*
(to be submitted)

Intermolecular Magnetic Interactions Model at 4.2 K

«Concentrated» samples

$$\frac{1}{\tau_{INTER}} = \frac{1}{\tau} - \frac{1}{\tau_{\infty}}$$



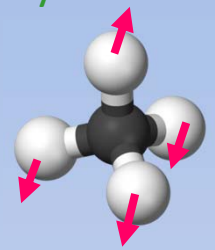
Average distance effect

↕

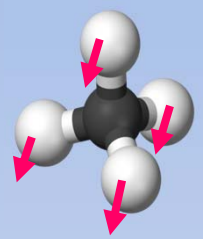
Different Lattice Parameter

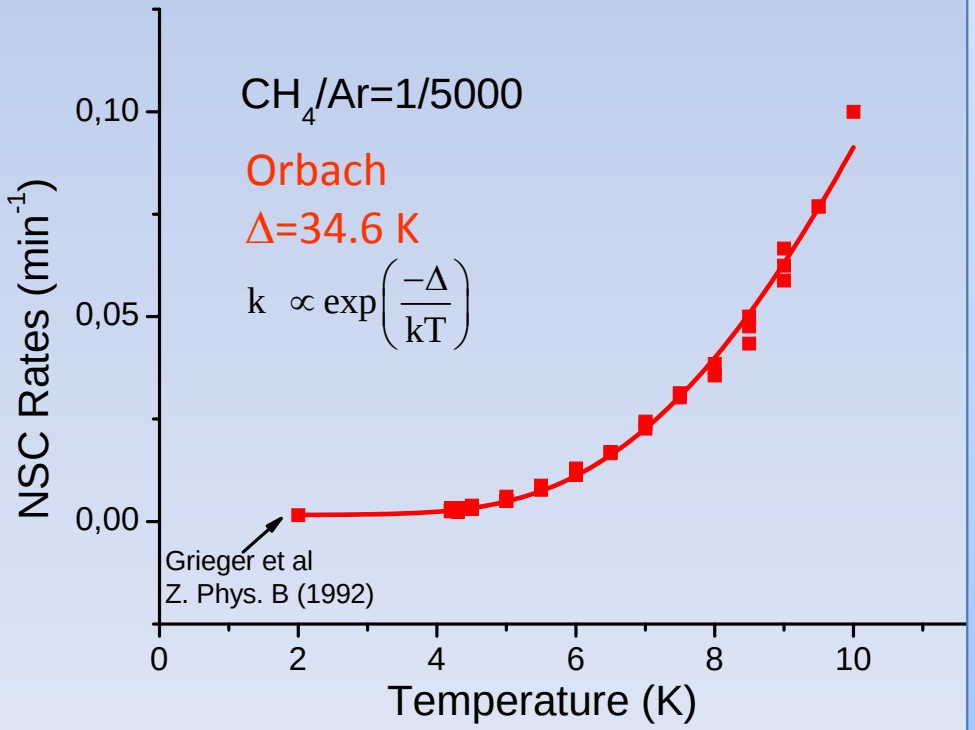
NSC dynamics versus Temperature

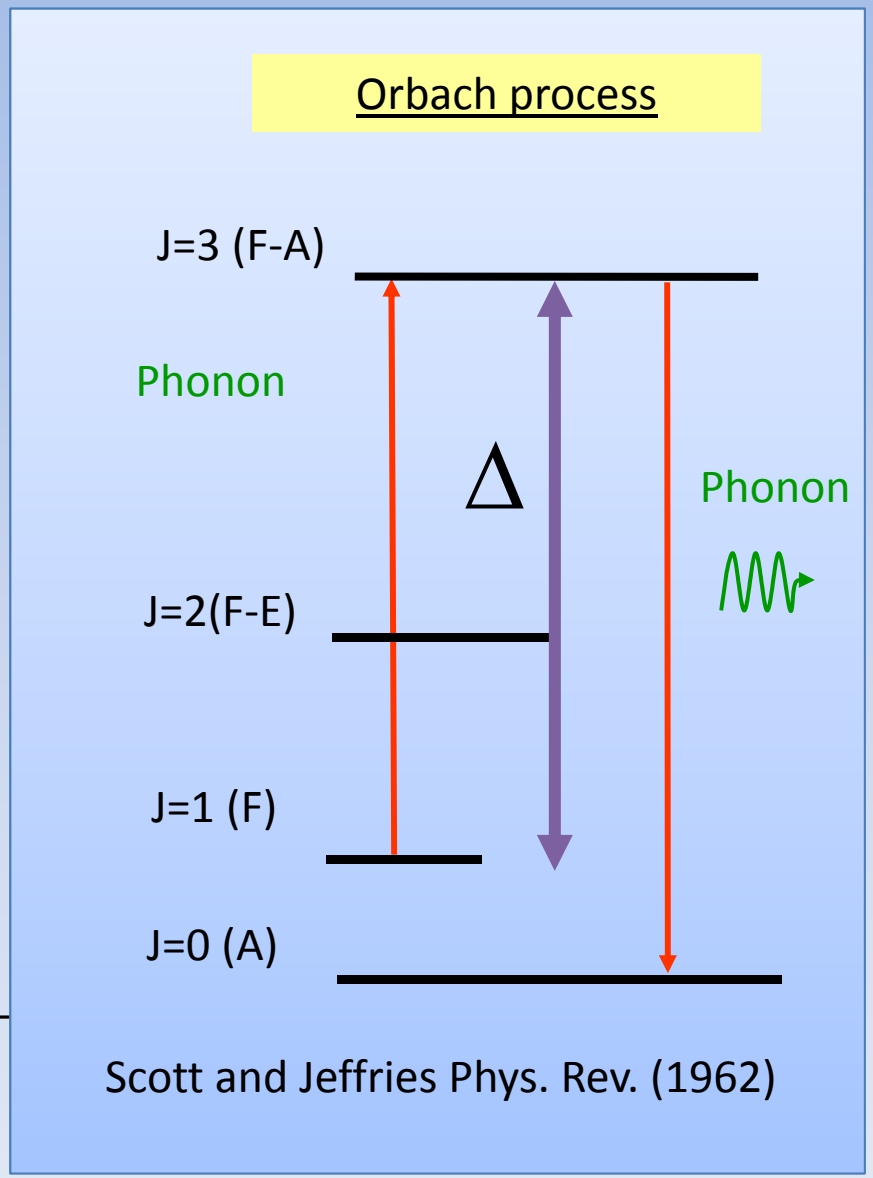
ortho-CH_4
I =1 sym F



meta-CH_4
I =2 sym A

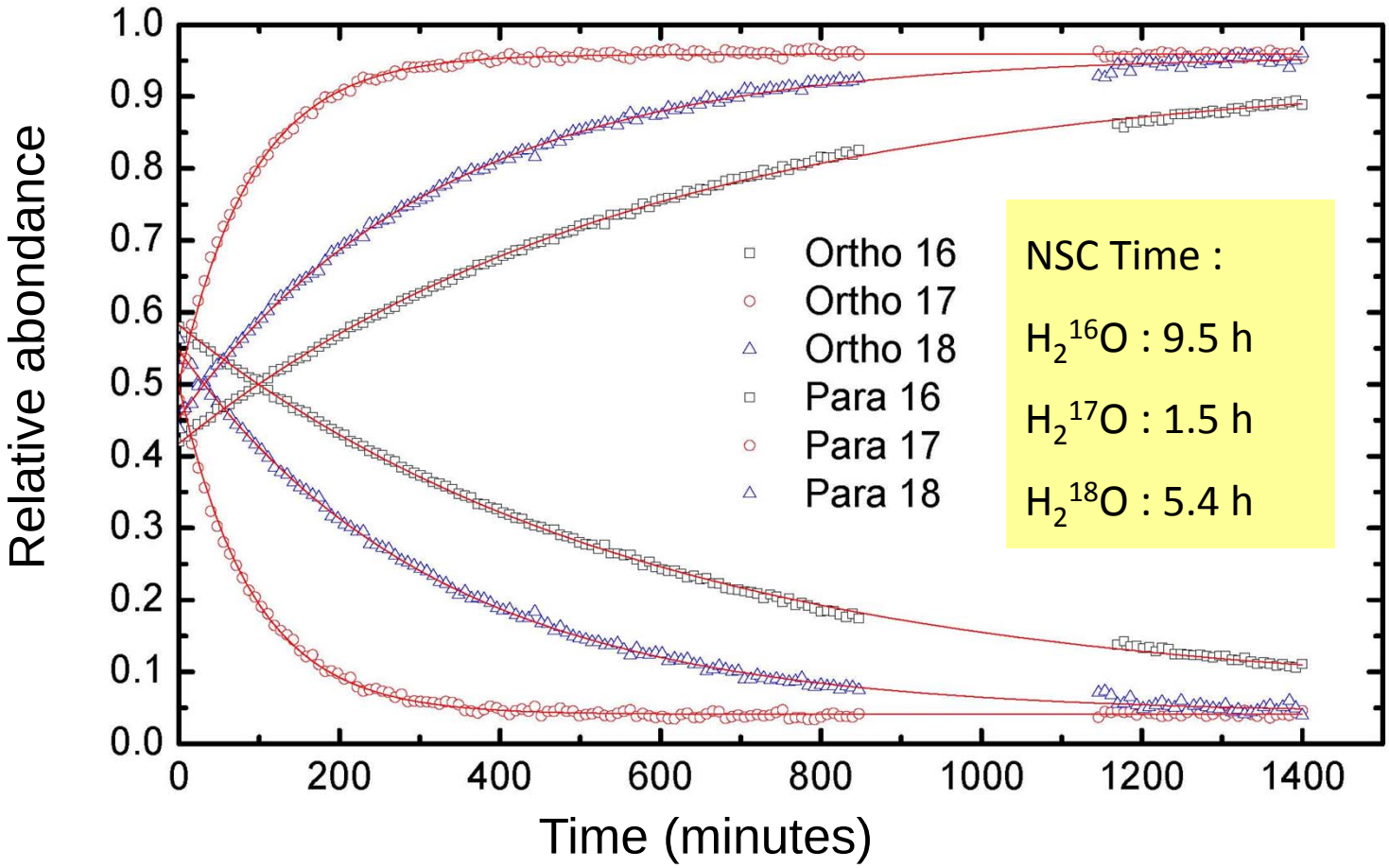






A. Lekic PhD Thesis, 2011

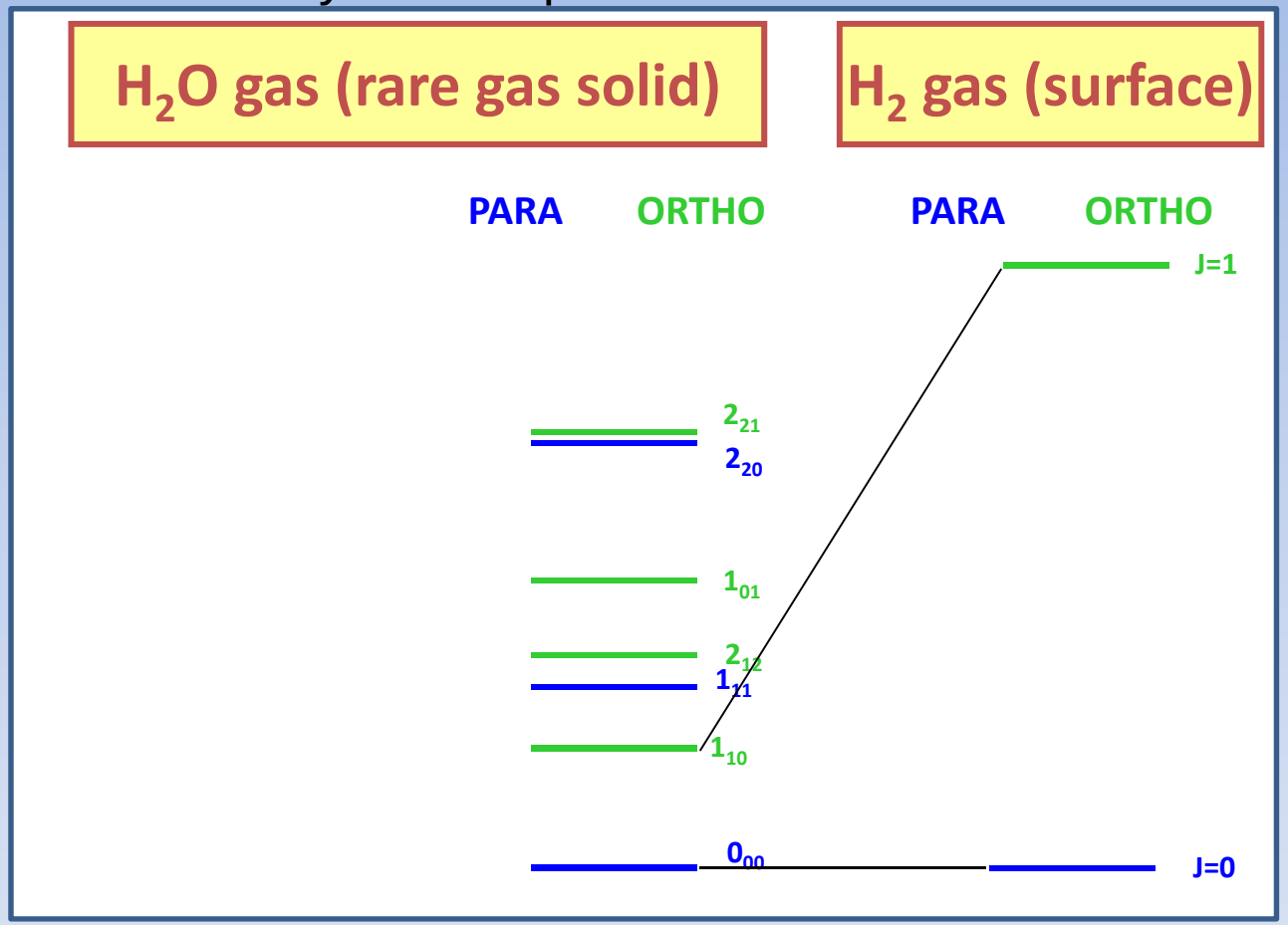
Isotopic Effect in Water



Collaboration: J. Campéri, PA Turgeon, J. Vermette, and P. Ayotte
Université de Sherbrooke - Canada

NSC during interaction with cold surface

behavior at very low temperatures on the iced surface?



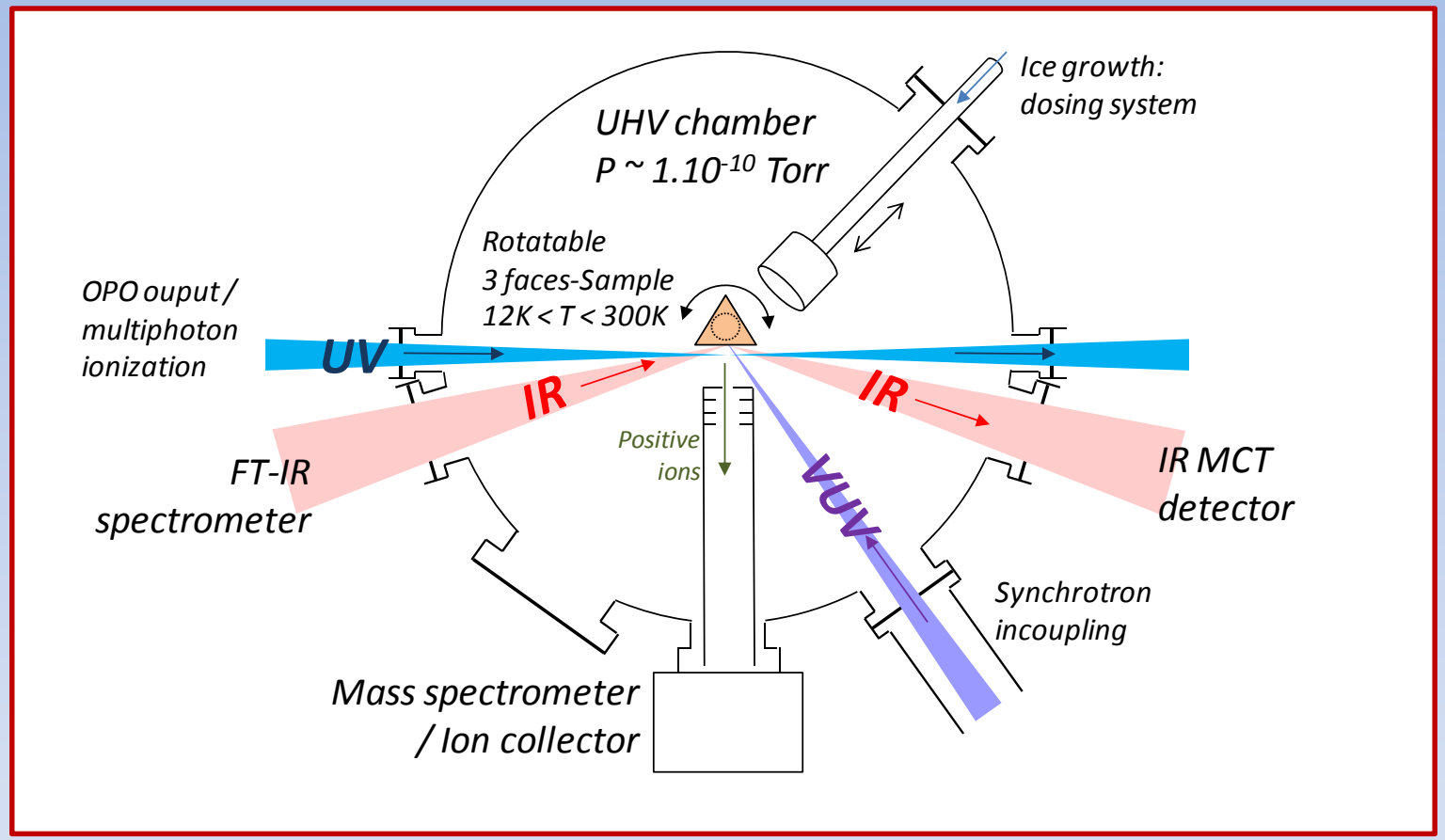
Experiments [1,2] using REMPI spectroscopy to investigate released gas after desorption showed fast NSC in H_2 molecules trapped on cold Amorphous Solid Water (ASW).

(1) Chehrouri, Fillion *et al* PCCP 2011

(2) Sugimoto & Fukutani Nature Physics 2011

Nuclear Spin Conversion Dynamics on Surfaces

Probing the Molecular hydrogen on ASW using FTIR spectroscopy

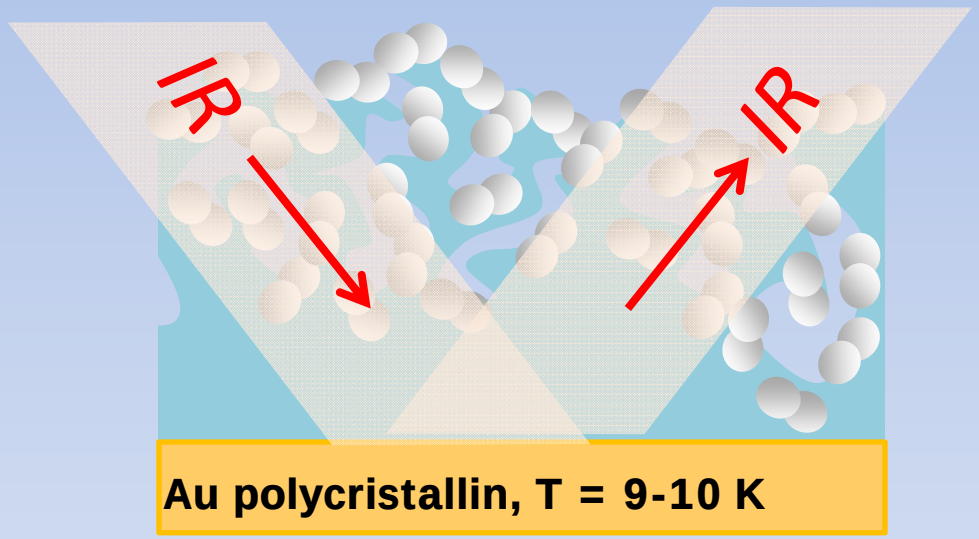


Surfaces Processes & Ices (SPICES set-up)

H_2 adsorbed on ASW

Reflection Absorption InfraRed Spectrosopy (RAIRS)

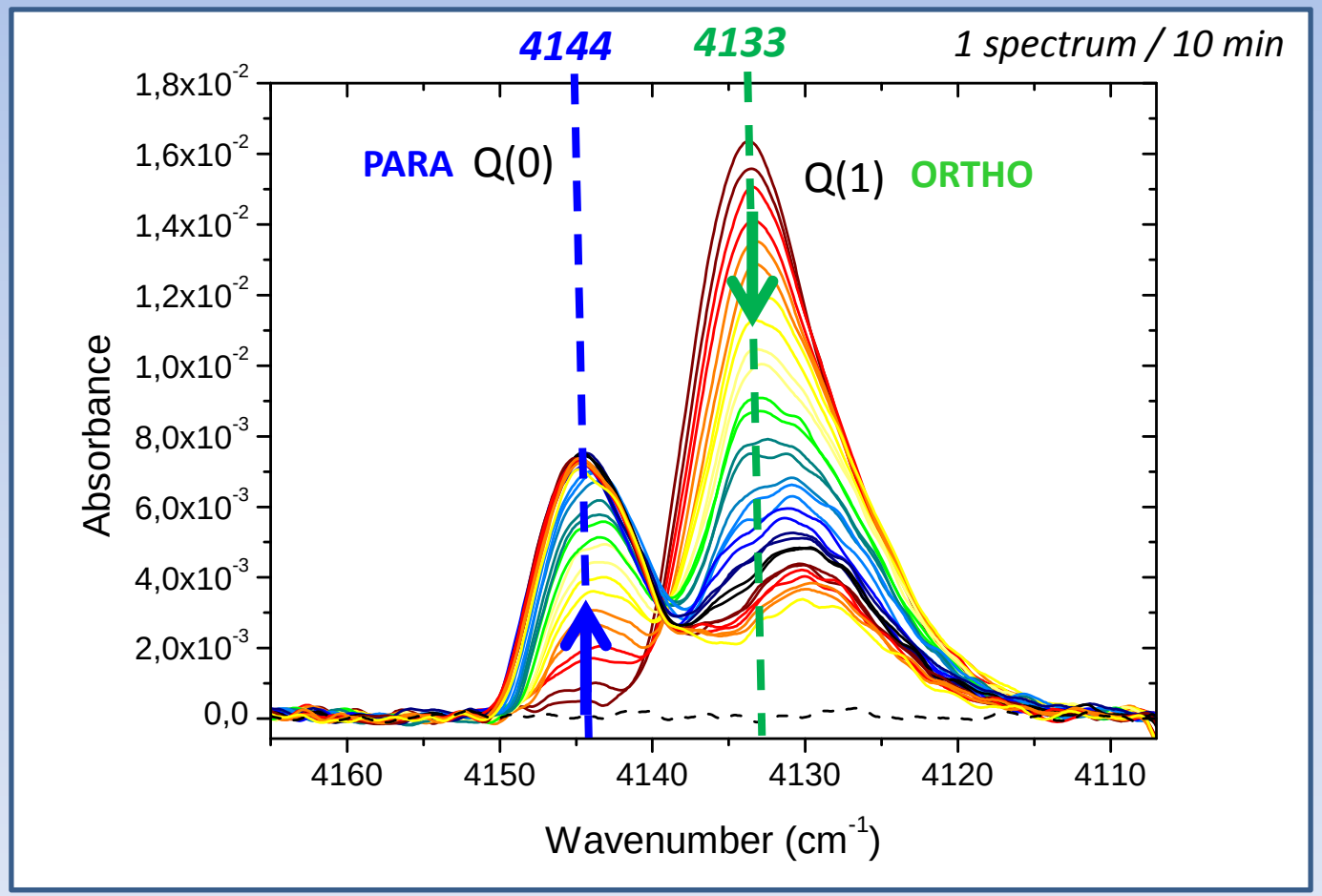
Porous Amorphous Solid Water (ASW)



Solution

- 1000 ML Equivalent
- Saturation of H_2

Time evolution of the RAIRS spectrum of H_2 /ASW

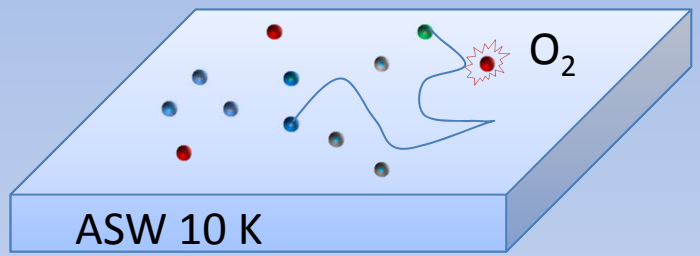


Nuclear Spin Conversion Dynamics on Surfaces

Molecular hydrogen on ASW

- NSC in the presence of O_2 traces

Molecular Hydrogen Diffusion



O_2	t(min) IR Vib	t(min) Laser *FORMOLISM*[1]	t(min) Laser *Sugimoto*[2]
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)

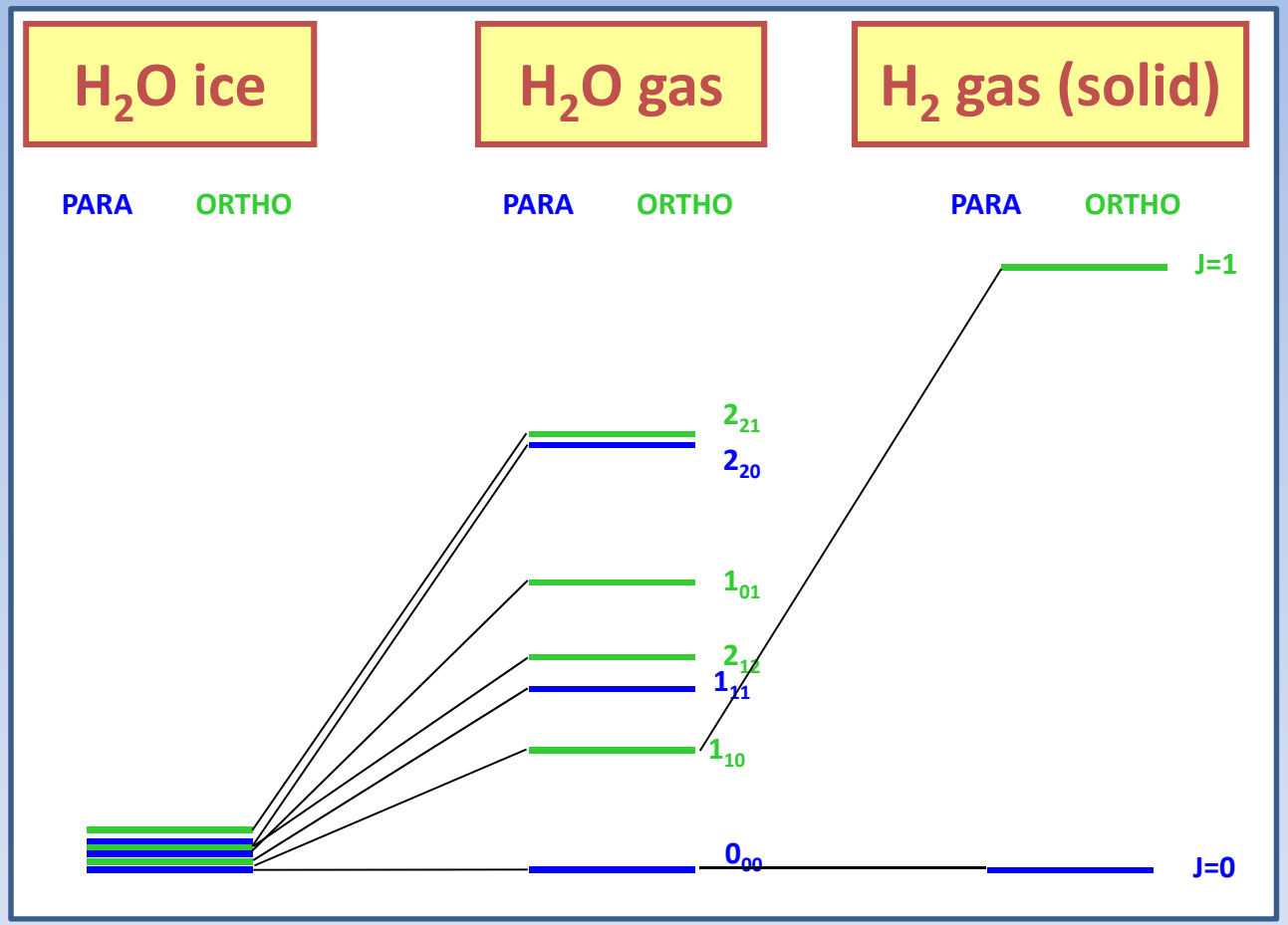
(1) Chehrouri, Fillion *et al* PCCP 2011

(2) Sugimoto & Fukutani Nature Physics 2011

« *Electric –Field-induced nuclear-spin flips mediated by enhanced spin-orbit coupling* »

Open Question

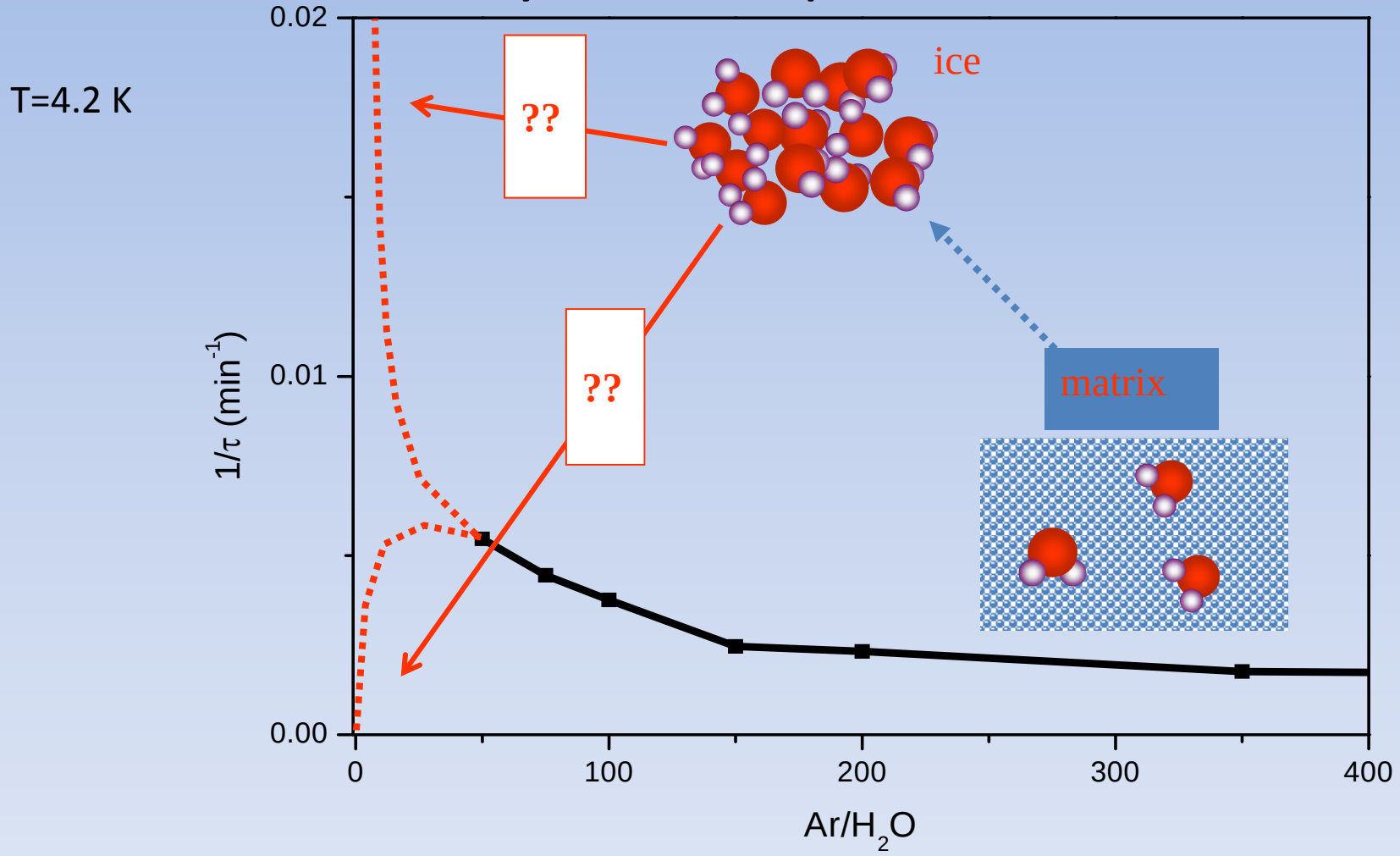
behavior at very low temperatures in the ice?



Calculations estimate the NSC to be few ms (Buntkowsky *et al* Z. Phys. Chem. 2008)
Experiments in molecular beams claim that conversion proceeds in few μs in the water aggregates (Manca et al JPC 2013) : not confirmed by experiments performed with Jet-Ailes Team (IPR-LADIR-PhLAM-SOLEIL-Ailes beamline consortium)

Open Question

behavior at very low temperatures in the ice?



Can we extrapolate to iced environment ?

CONCLUSIONS

❑ Calculations in gas phase
-NSC strongly dependent on density and temperature

Suggest very slow NSC in a very diluted gas at low temperature

❑ Matrices Experiments
- well controled environnement : reveal magnetic inter- and intra- molecular interactions
- importance of rotational structure
- importance of rotational relaxation

Suggest a fast NSC in the solid state

❑ H_2 physisorbed / ASW
- long time (lab.) / short time (astro.)
- O_2 paramagnetic catalysis

Suggest a fast NSC on a cold surface

PERSPECTIVES

❑ New Approaches :
-Development of studies at gas-ice equilibrium in cold gas cell. (See poster Pardanaud *et al*)
-Development for SPICES 2 set-up for photodesorption studies. (See poster Bertin *et al*)

Acknowledgments

M. Bertin

J.-H. Fillion

A. Lekic

A. Moudens

P. Jeseck

C. Romanzin

E. Fayolle

Thank you !!

C. Bouriser

J. Rakovsky

L. Philippe

P. Cacciani

P. Cermak

J. Cosléou

M. Khelkhal

C. Pardanaud

C. Martin

S. Coussan

J. Noble

Fundings