What do we know about time scales for the nuclear spin conversion in molecular ices and at the solid-gas interface?

Xavier Michaut

SPICES Group “Spins & Photons in Interaction with ICES”
Pole “Molecules in the Universe” – LERMA - PARIS

Co-authors

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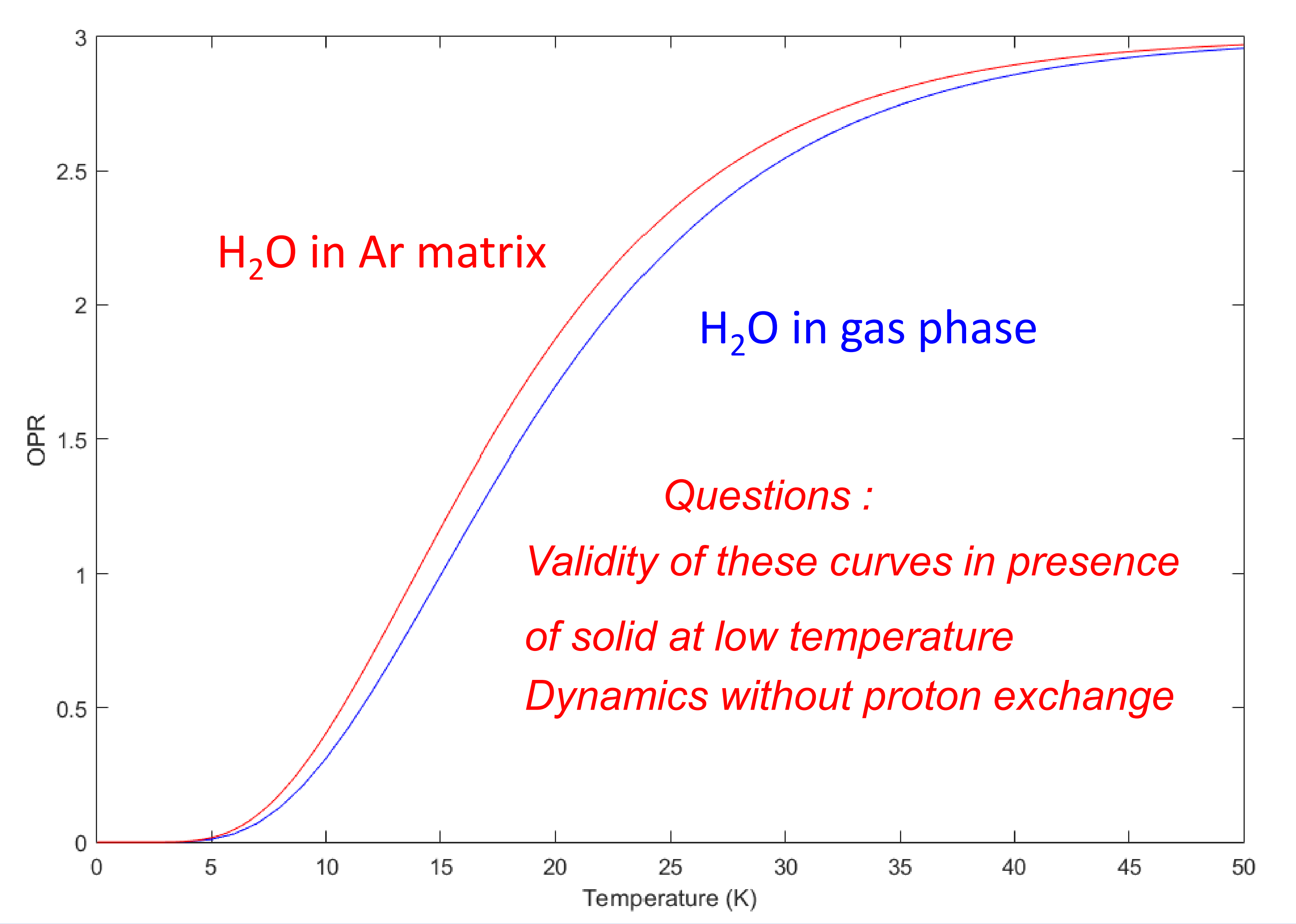
P. Cermak

C. Pardanaud

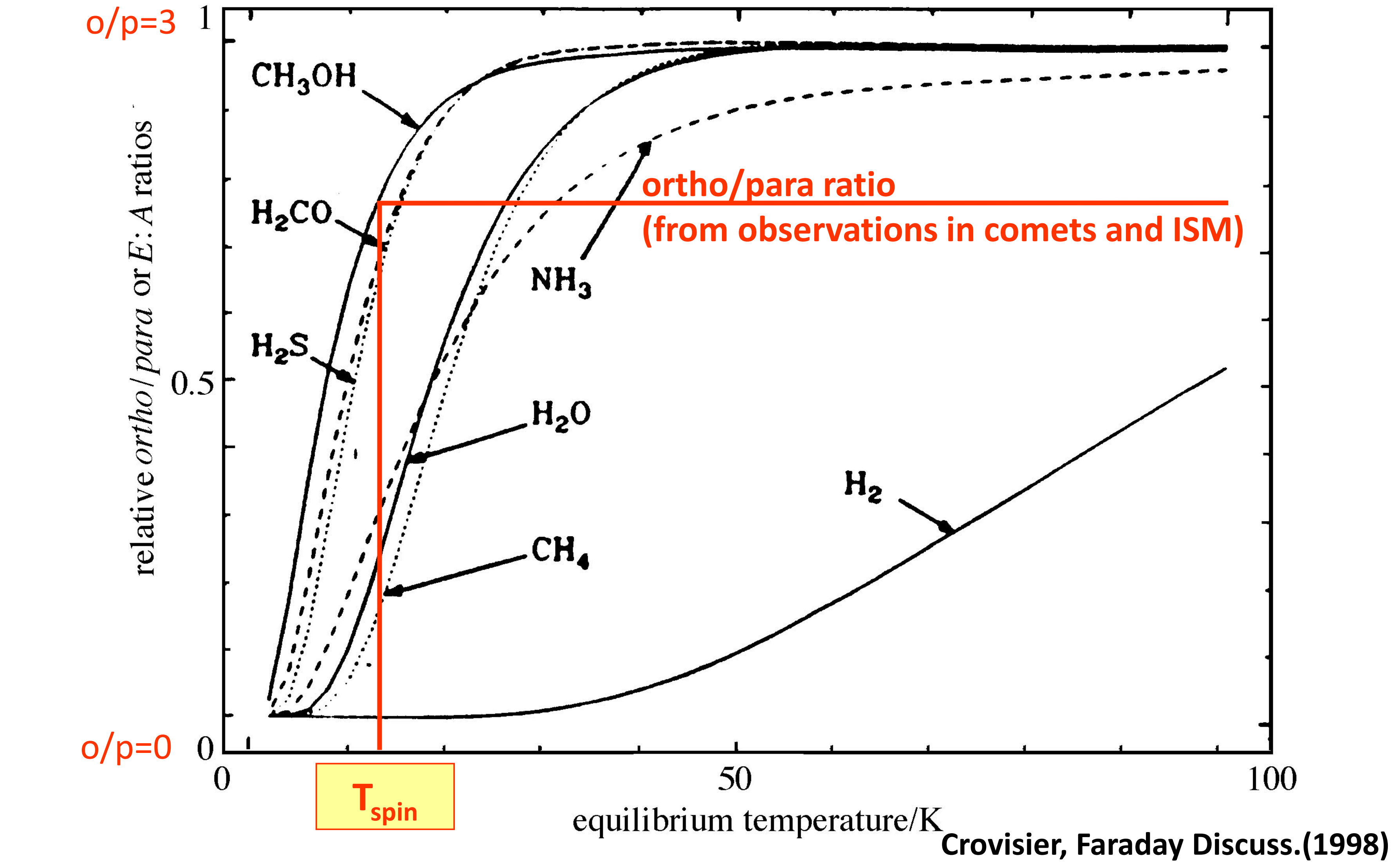
Nuclear Spin Effects in Astrochemistry2017 – Wednesday, May, 3rd , 2017

OPR of H_2O vs T in Ar matrix and in gas phase



Ortho-Para conversion dynamics with no proton exchange

OPR vs T at equilibrium for isolated molecules often used to define Spin Temperature.



Crovisier, Faraday Discuss.(1998)

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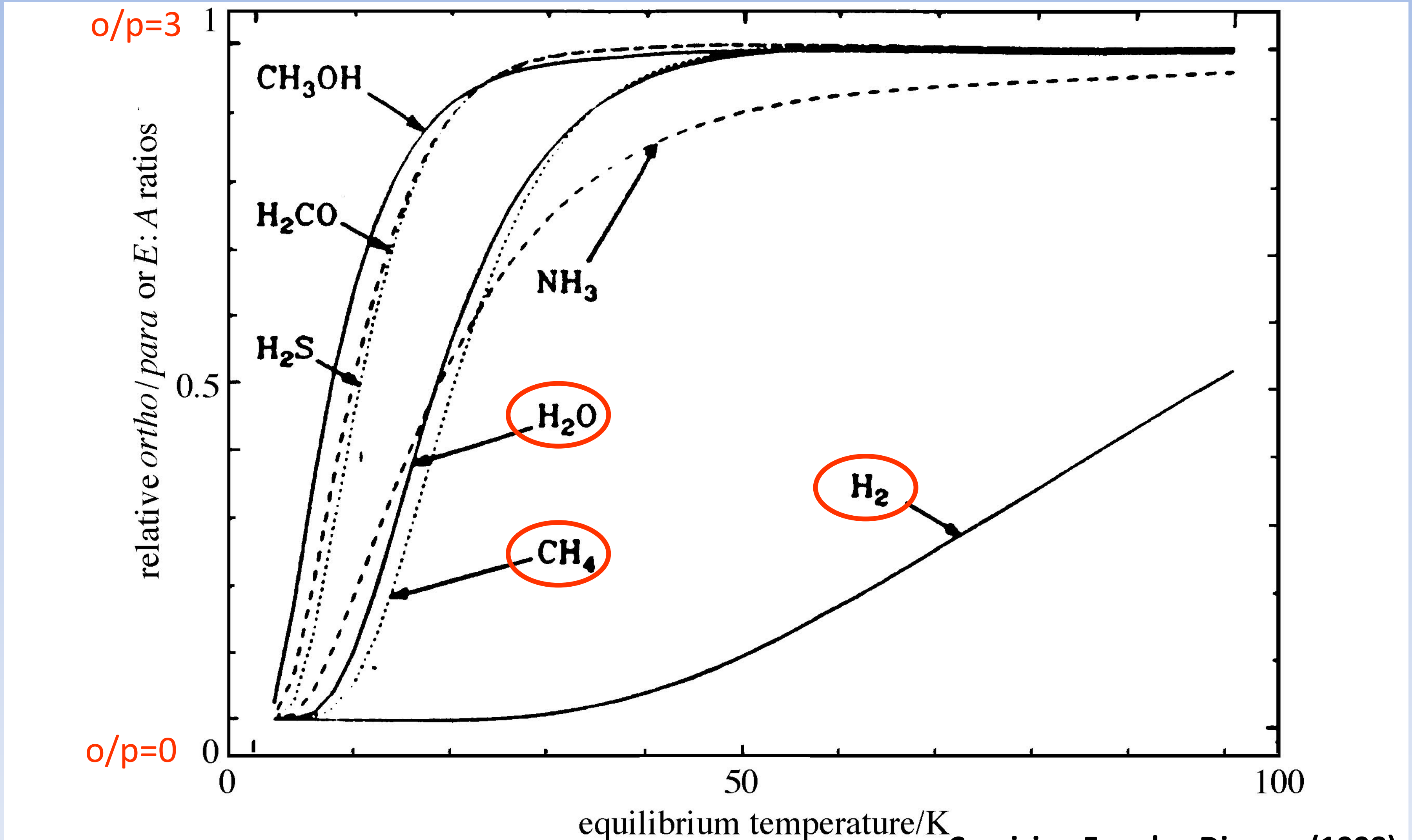
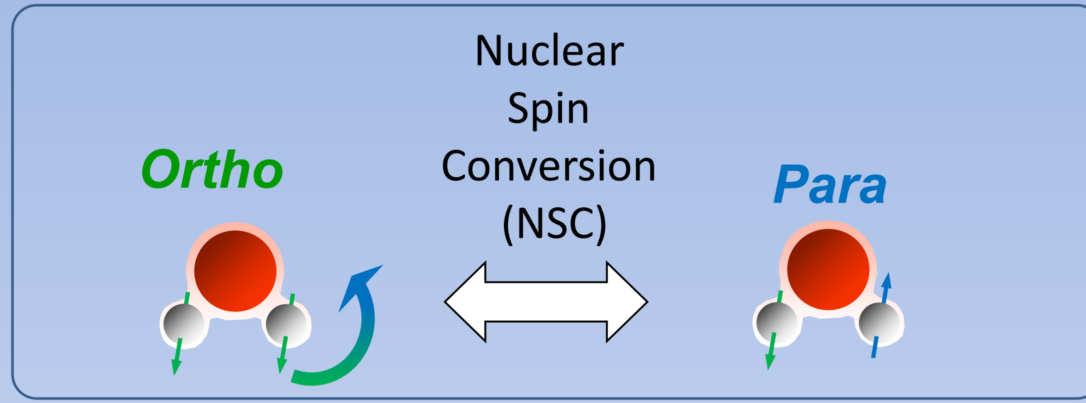


Crovisier, Faraday Discuss.(1998)

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 :

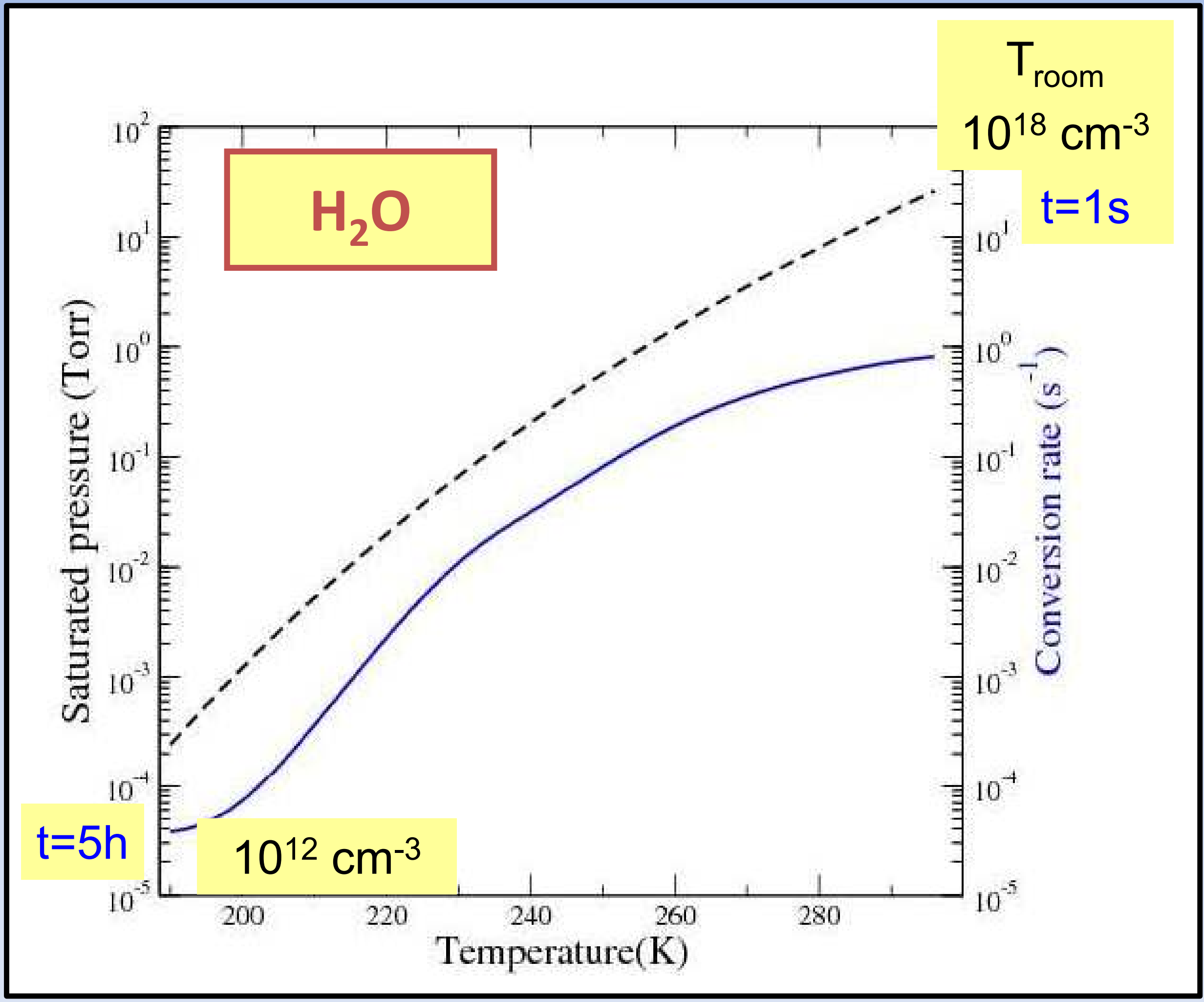
-on state of matter (solid, gas, surface interaction)

-density, temperature

-sources of inhomogeneous magnetic fields at the molecular scale

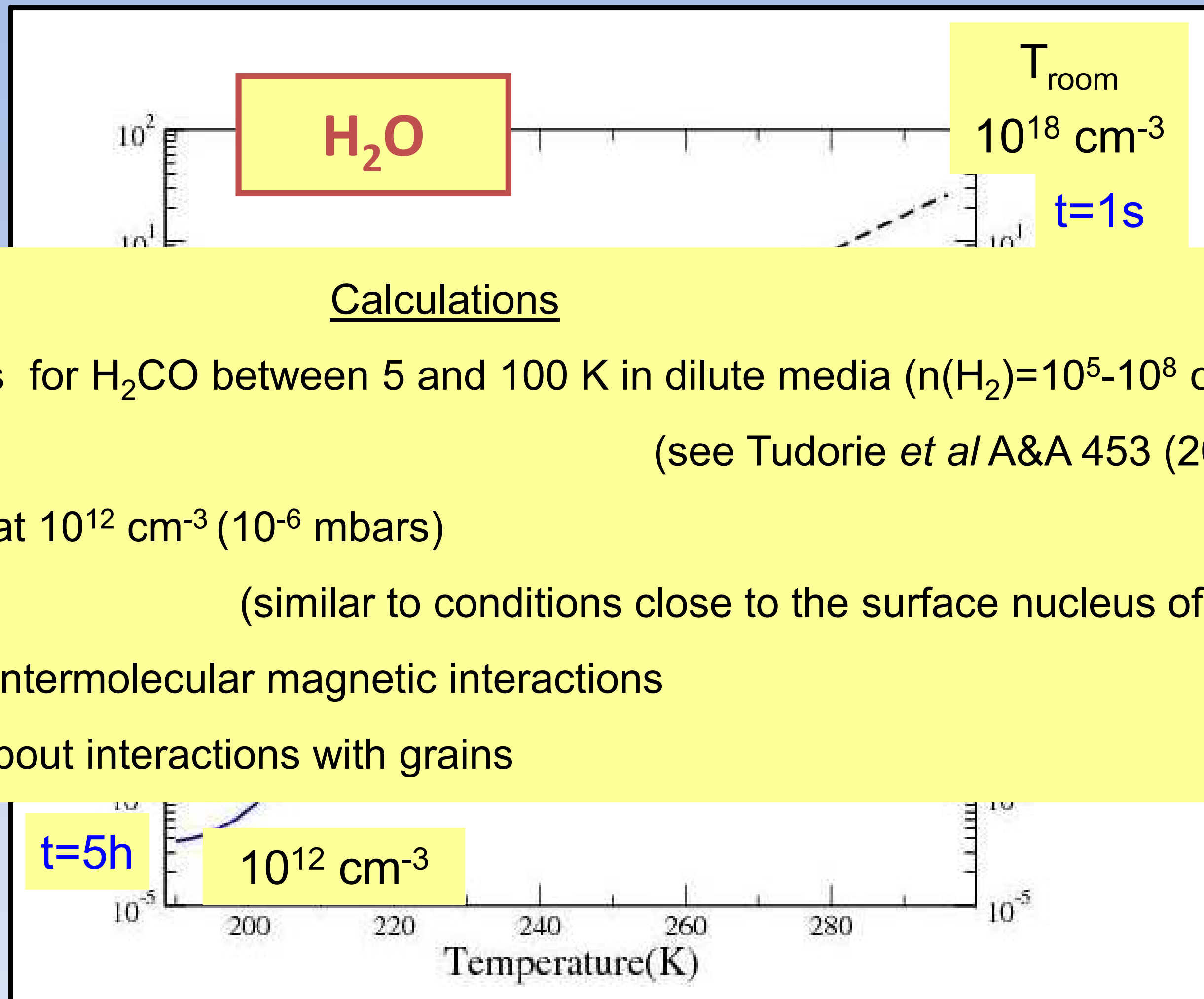
Environment can change all these parameters

One approach : calculations in gas phase



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

One approach : calculations in gas phase



Calculations

-give $\tau = 10^{+4} - 10^{+7}$ years for H_2CO between 5 and 100 K in dilute media ($n(H_2)=10^5$-10^8 cm^{-3})

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

-give τ= 5 hours for H_2O at 10^{12} cm^{-3} (10^{-6} mbars)

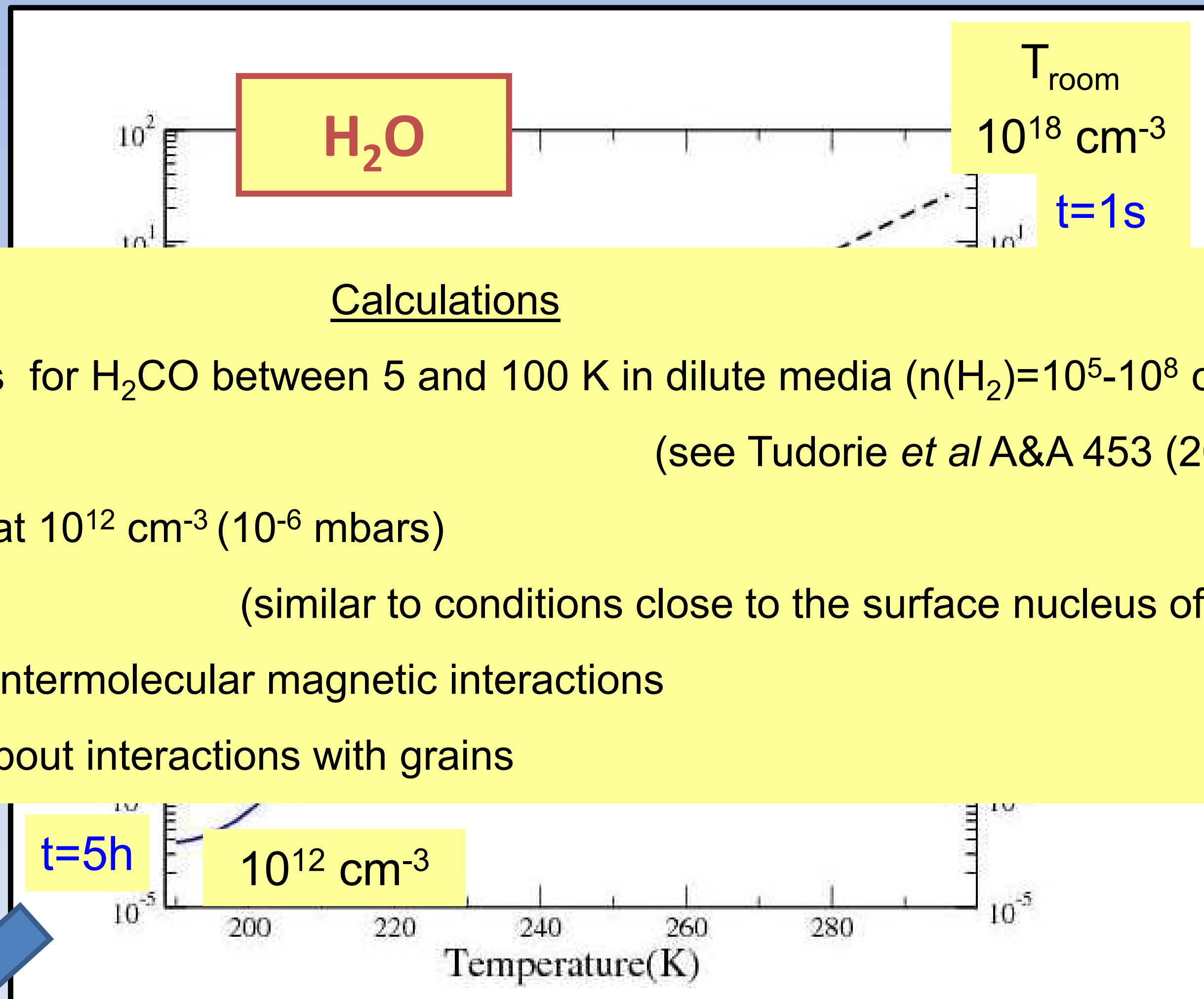
(similar to conditions close to the surface nucleus of comets)

-do not take into account intermolecular magnetic interactions

-do not give information about interactions with grains

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

One approach : calculations in gas phase



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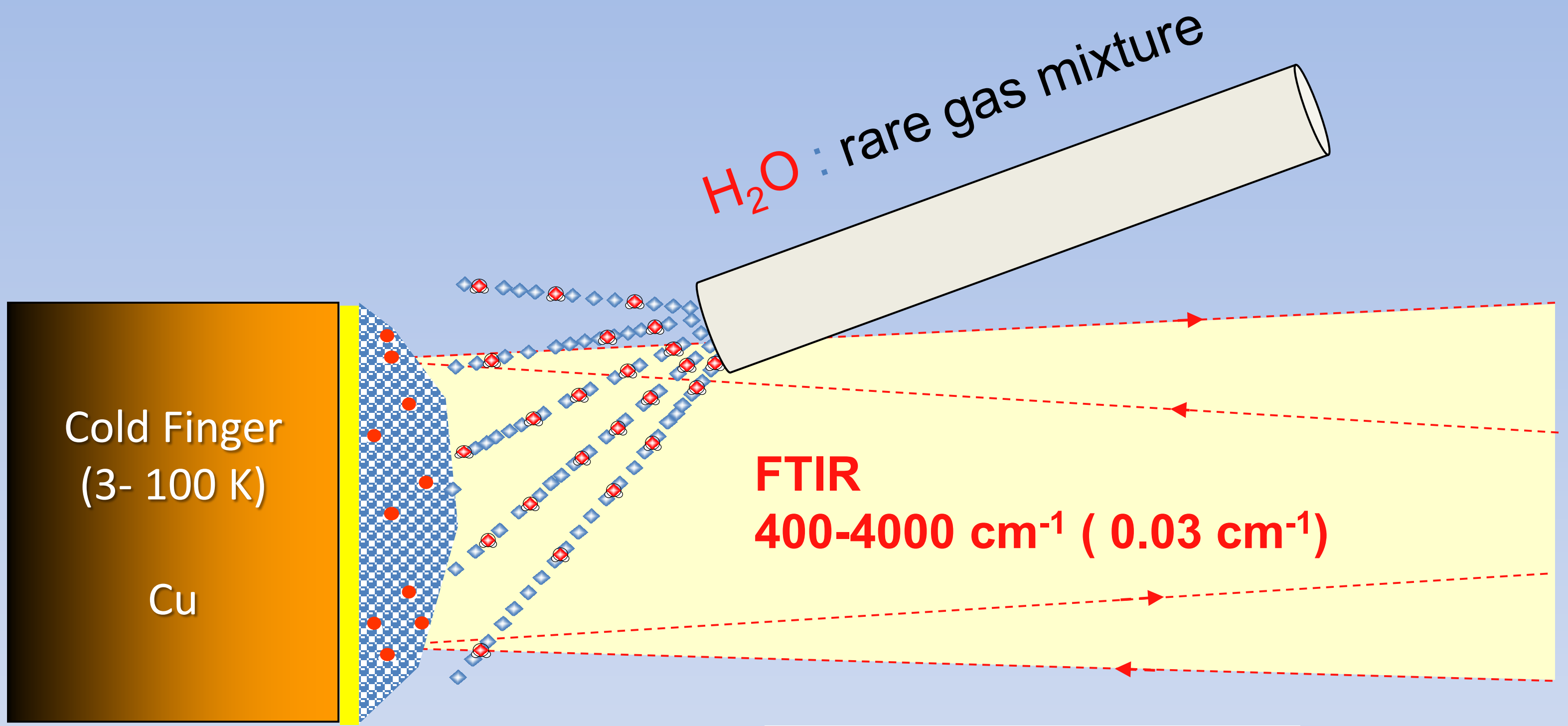
Lower temperature ?

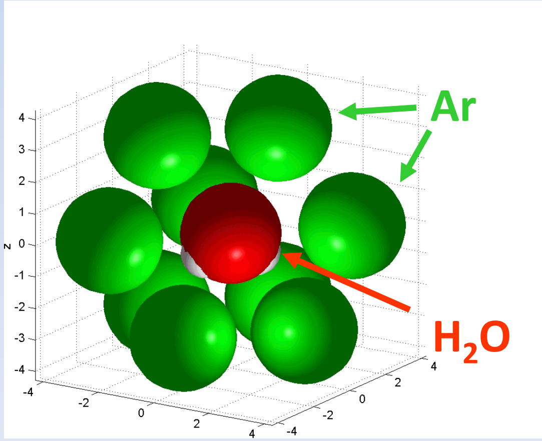
Cacciani *et al* PRA 80 (2009), PRA 85 (2012)

PhLAM

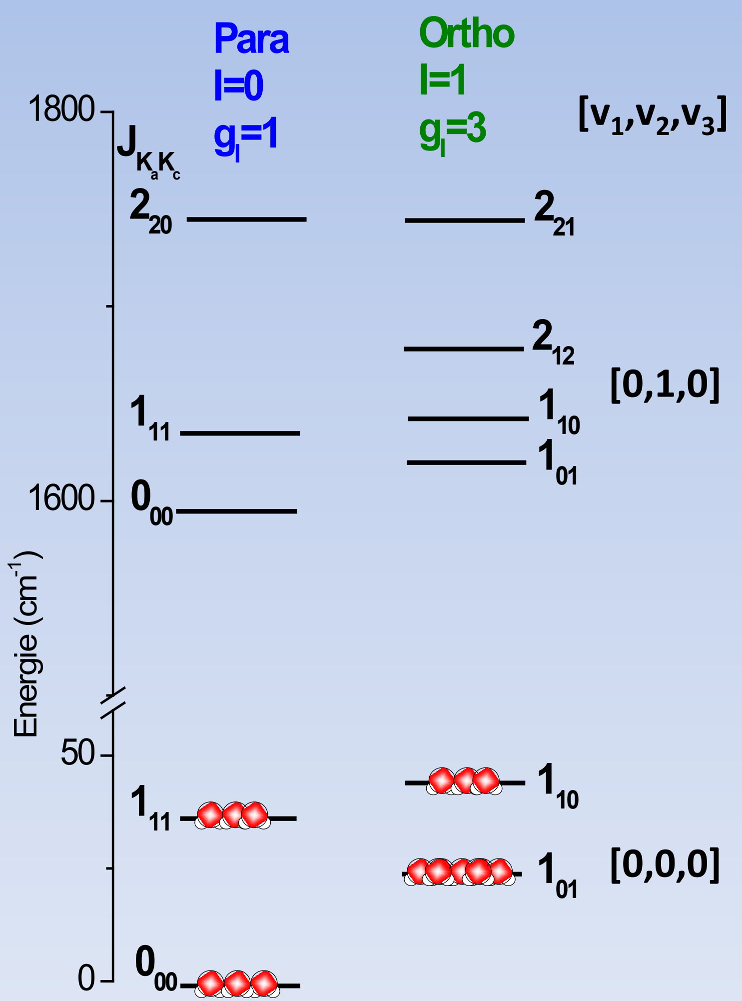
Second approach : cold matrices experiments

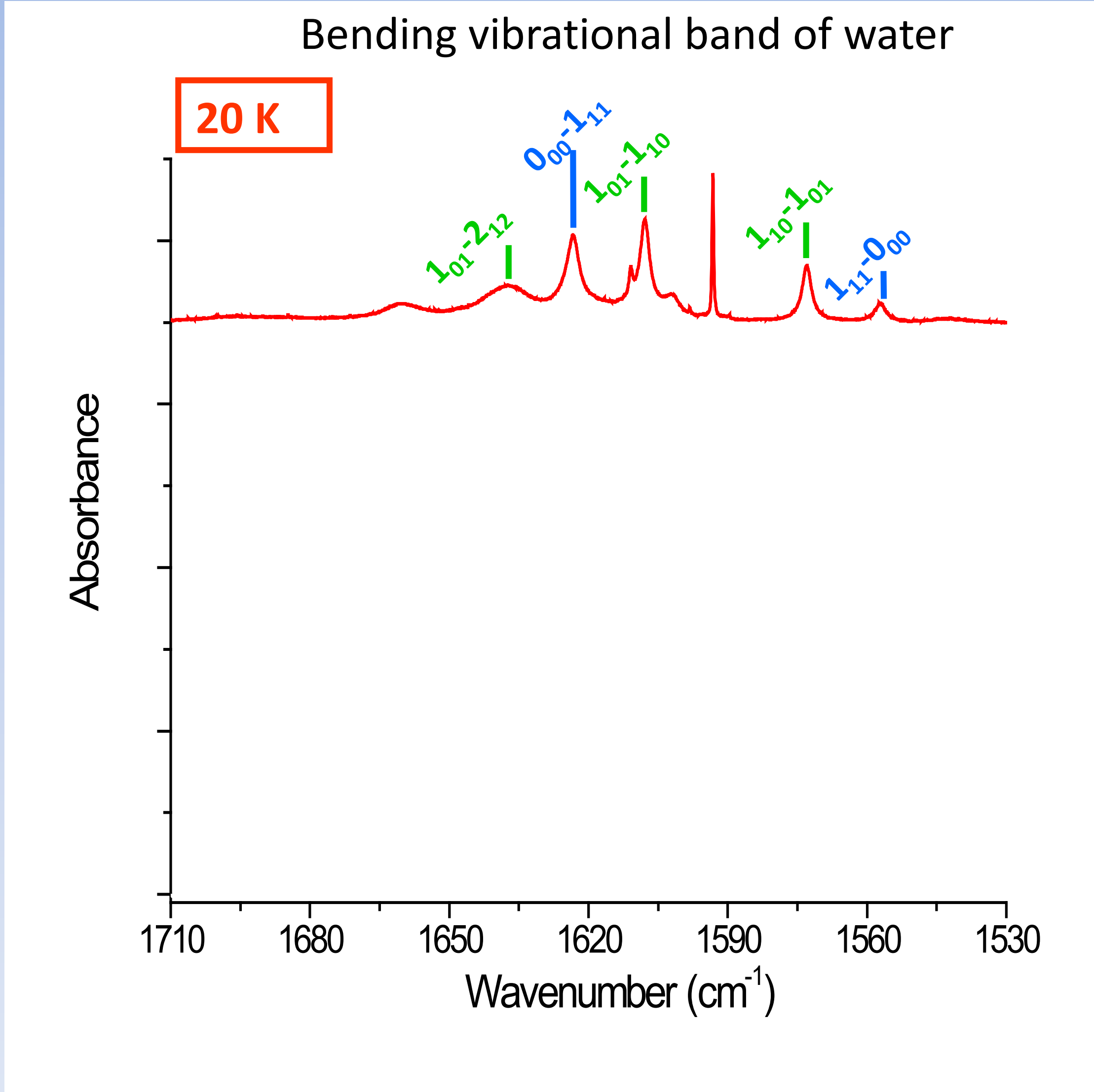


The Sample :
- **polycristalline**
- **low H_2O concentration**
- **thicknesses 50 et 500 μm**



H_2O in Argon Matrix





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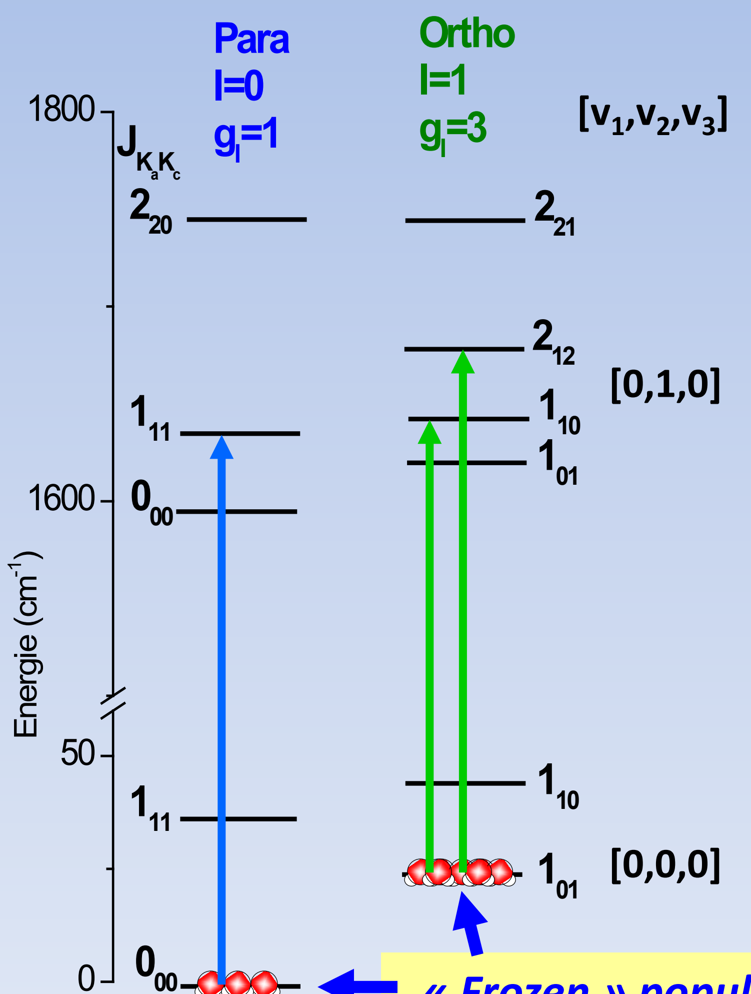
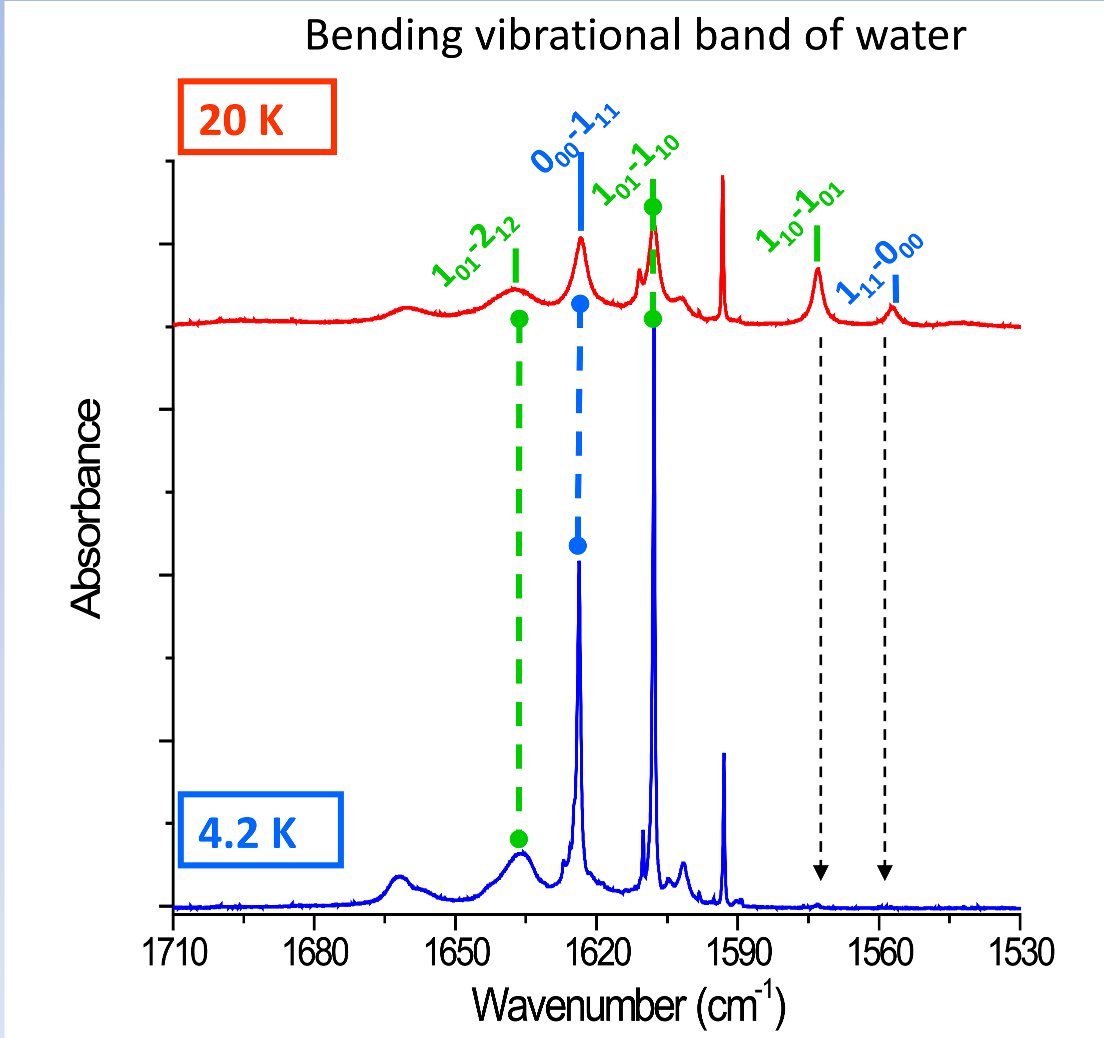
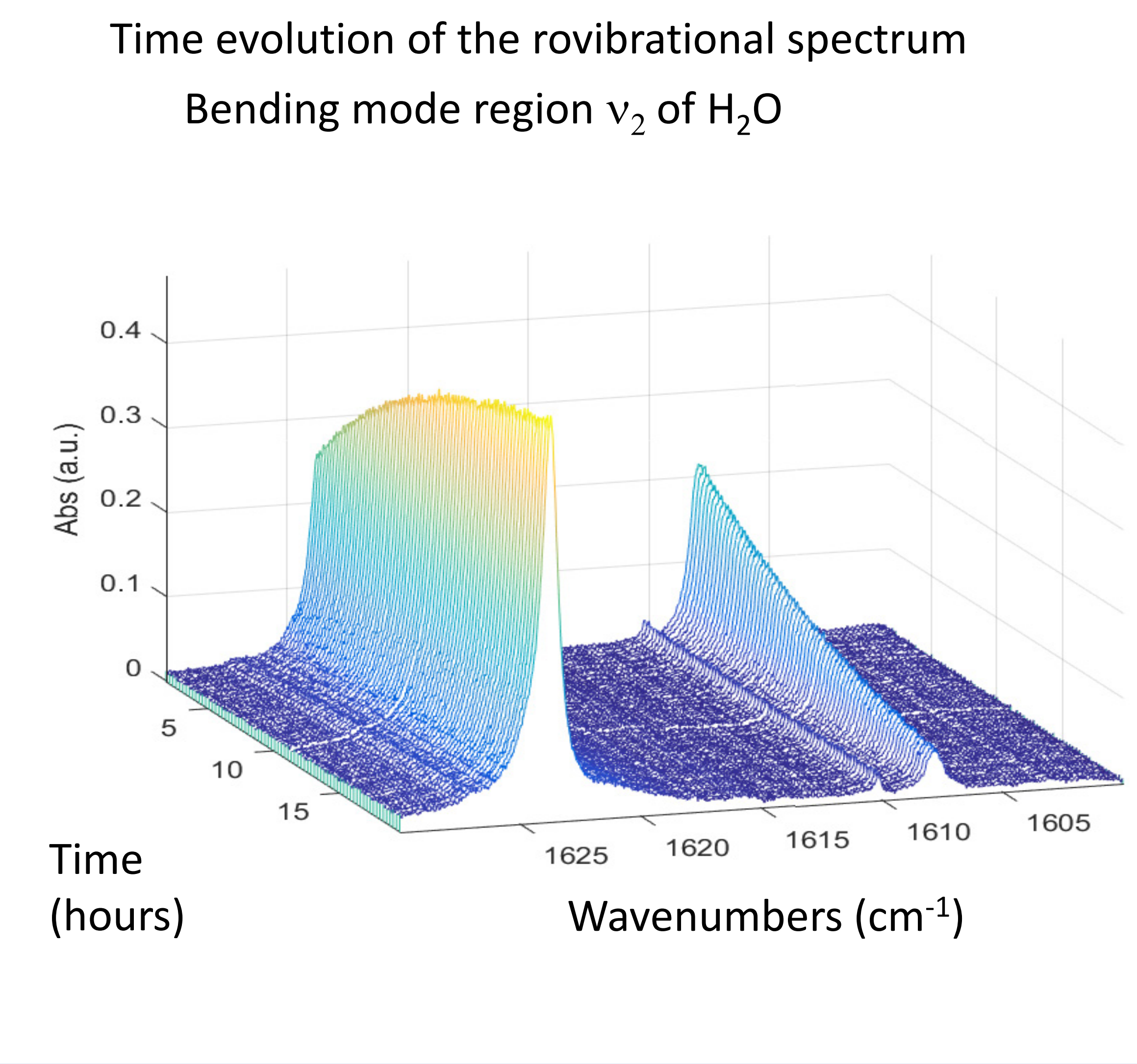




« Frozen » populations O/P(20 K) à 4.2 K : disequilibrium

H_2O en matrice d'argon

Slow return to equilibrium after a fast cooling from 20 K

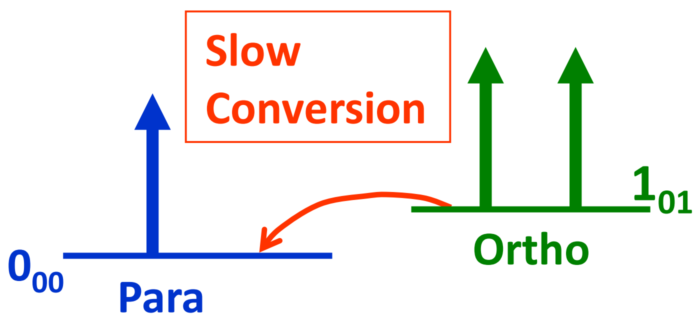


H_2O en matrice d'argon

Slow return to equilibrium after a fast cooling from 20 K

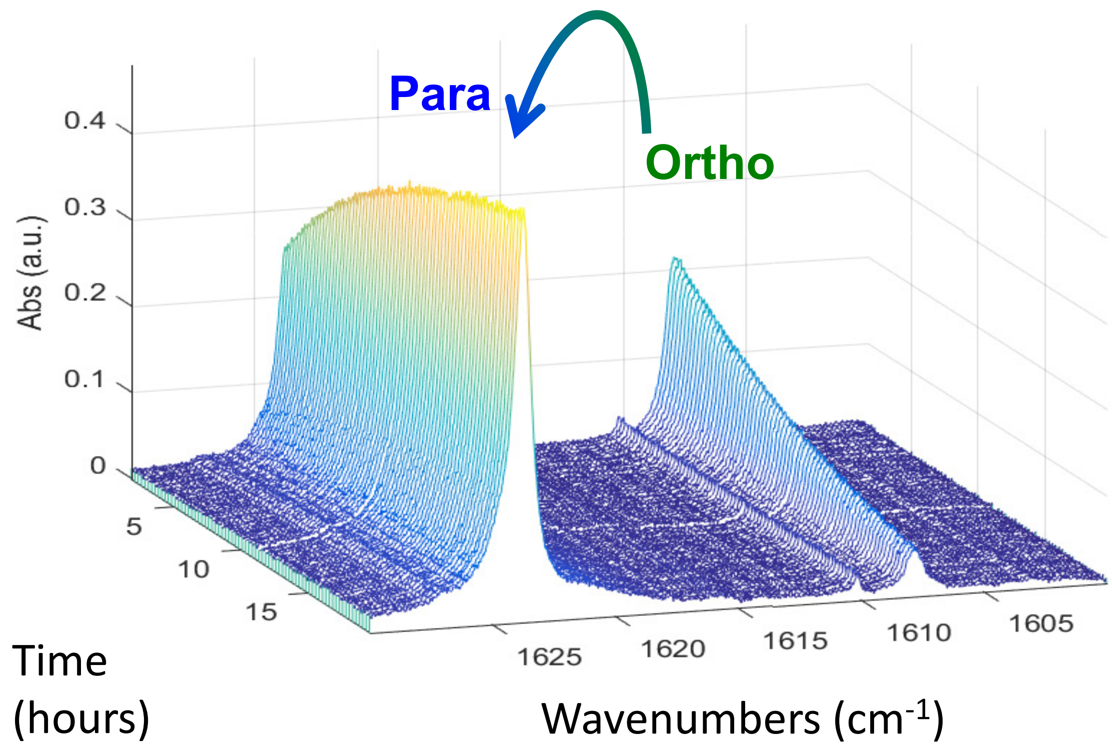
Nuclear Spin Conversion

Time evolution of *ortho/para pop.*



Time evolution of the rovibrational spectrum

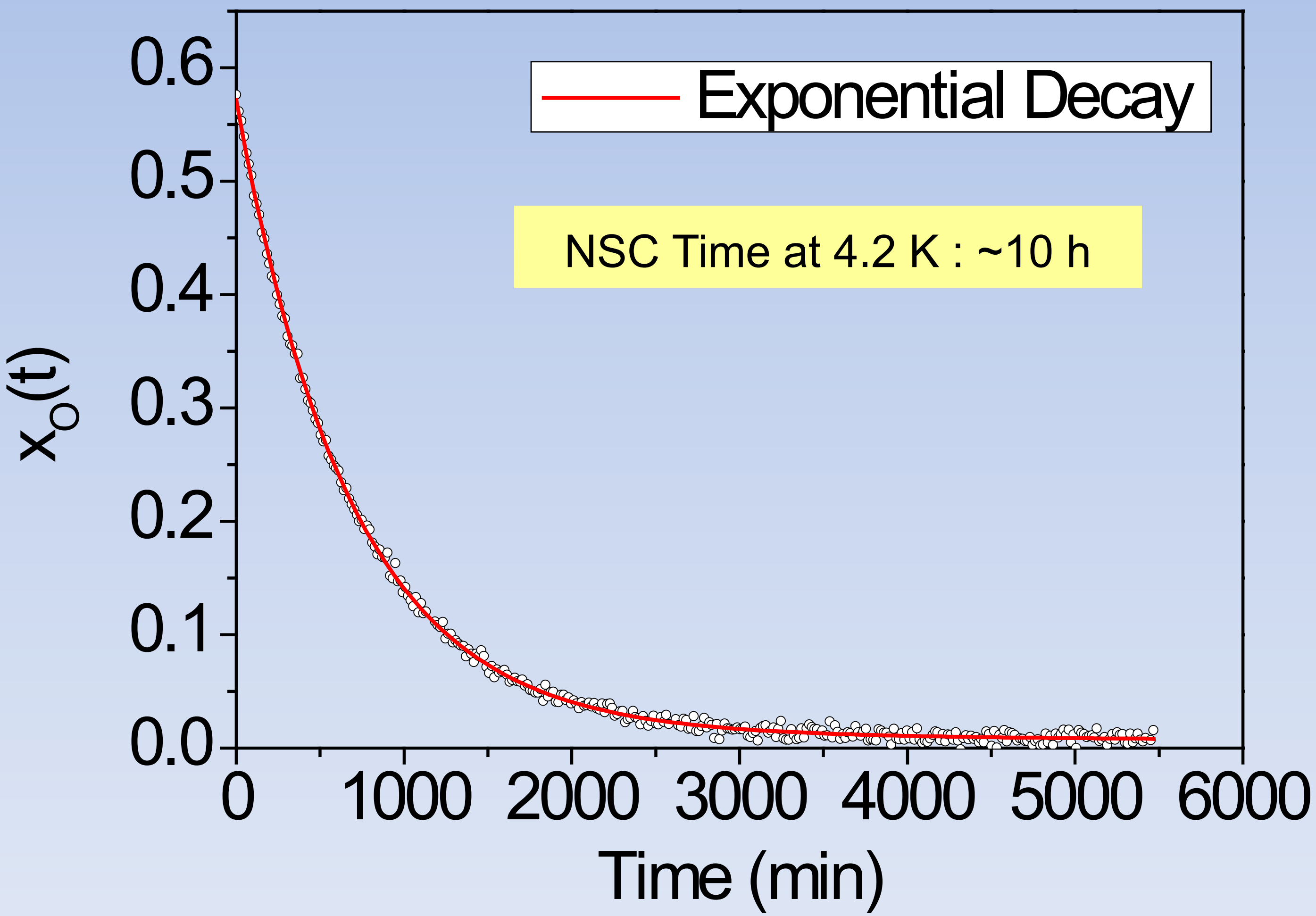
Bending mode region ν_2 of H_2O



H_2O in Argon Matrix

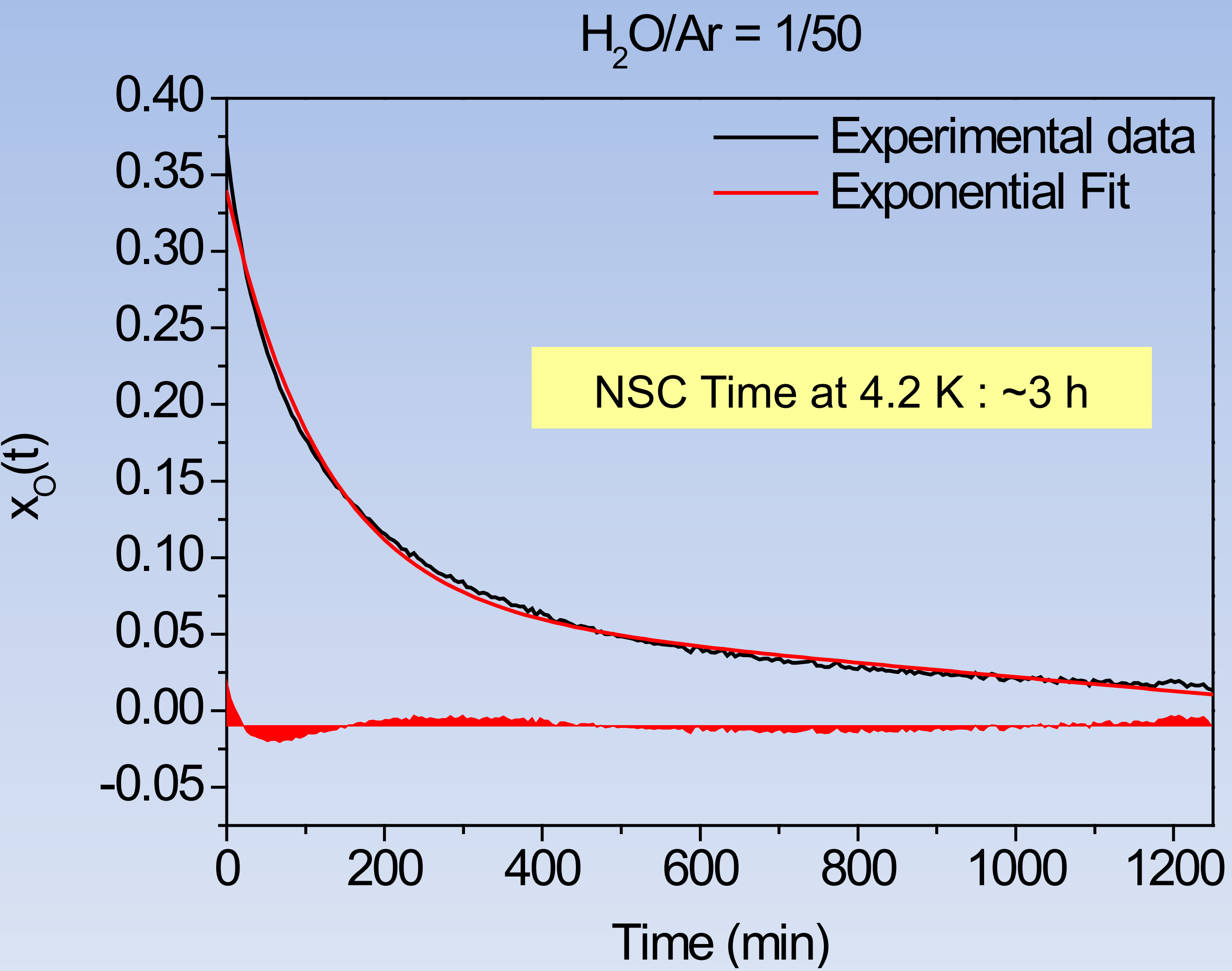
Behavior at Low Concentration

$H_2O/Ar = 1/10000$



Concentration effect on NSC of H_2O in Argon Matrix

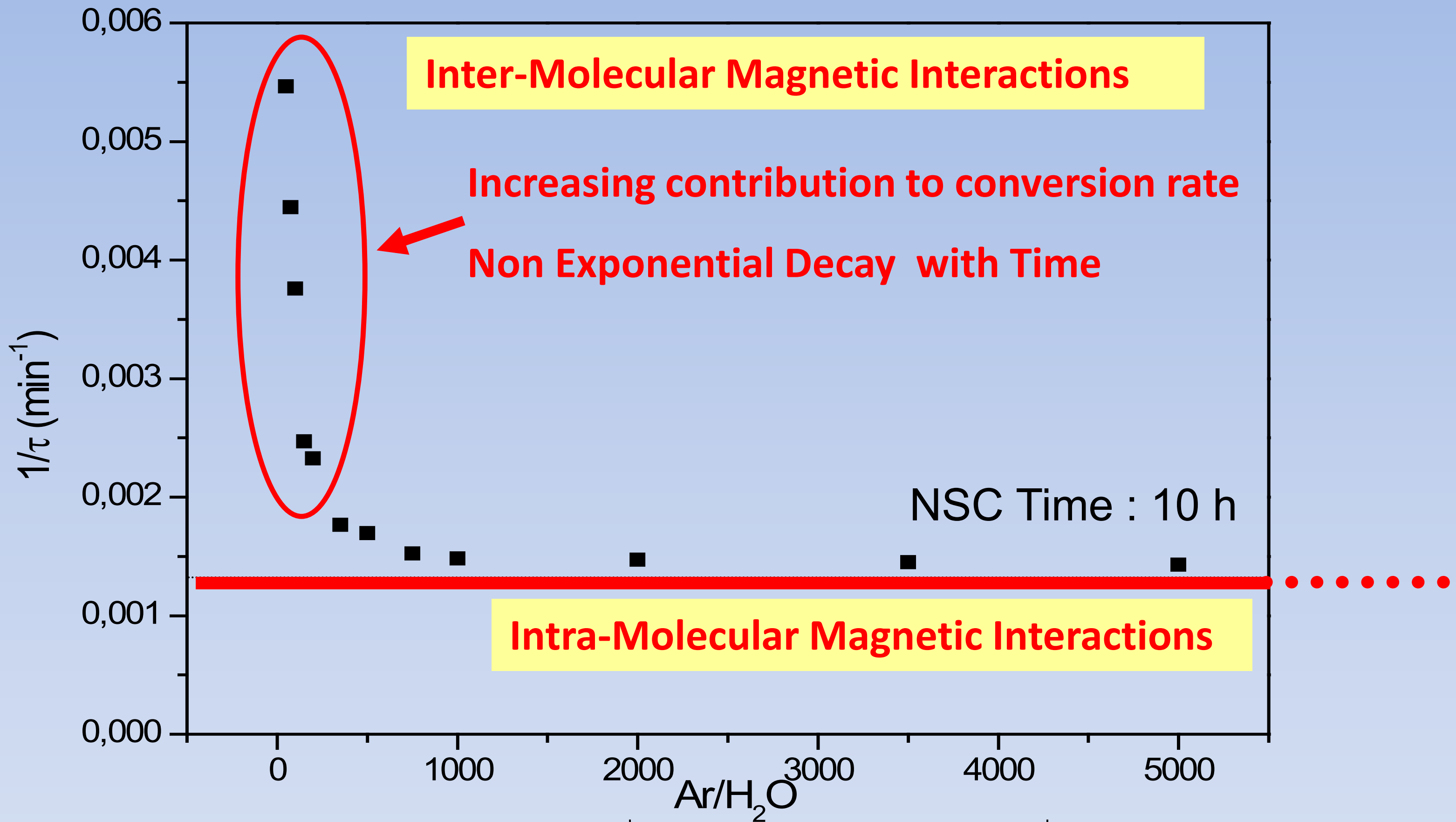
Behavior at High Concentration

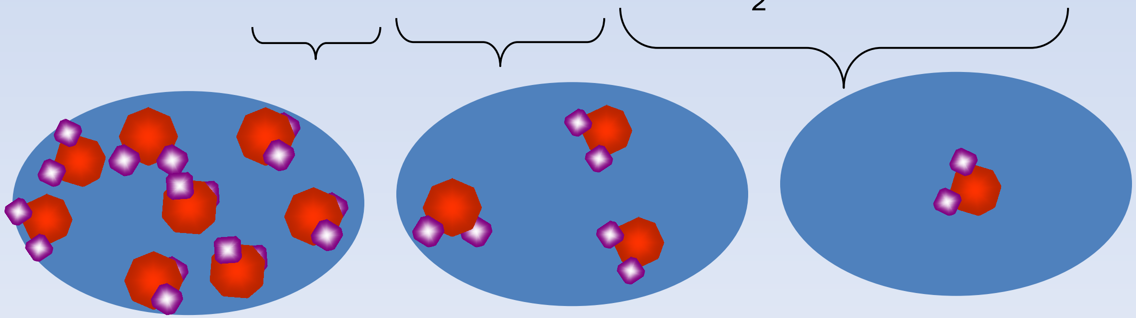


Time evolution of $x_o(t)$ for high concentration of H_2O in Ar matrix can not be fitted by a simple exponential function.

Results : H_2O in Argon Matrix

T=4.2 K



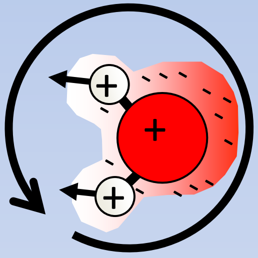


C. Pardanaud PhD Thesis
Fillion et al ECLA 2012
Michaut *et al.*
(to be submitted)

Origin of the magnetic coupling between Ortho and Para states

INTRAMOLECULAR
Interactions

Spin-Rotation coupling



Cacciani *et al*
Phys Rev A 80 (2009) & Phys Rev A 85 (2012)

Turgeon *et al*
J. Phs. Chem. A 121 (2017)

PhLAM

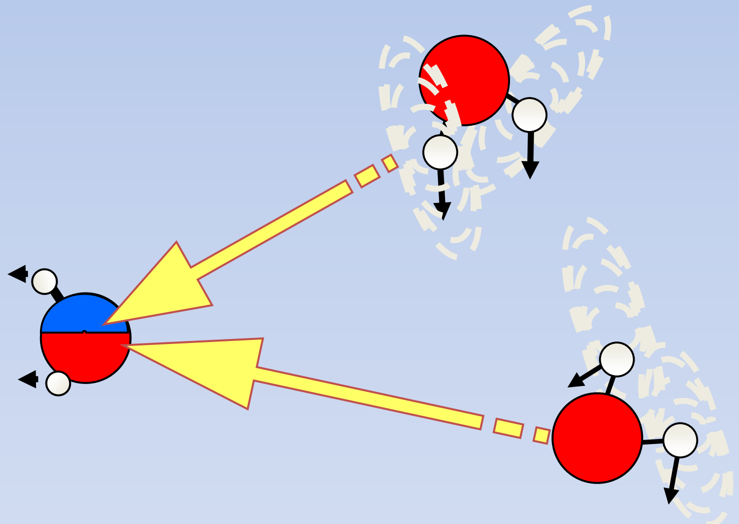
LERMA

Patrick Ayotte
Invited talk : *Confinement and isotopic effects*
Nuclear Spin Effect in Astrochemistry May, 2^{nd} , 2017

Origin of the magnetic coupling between Ortho and Para states

INTERMOLECULAR
Interactions

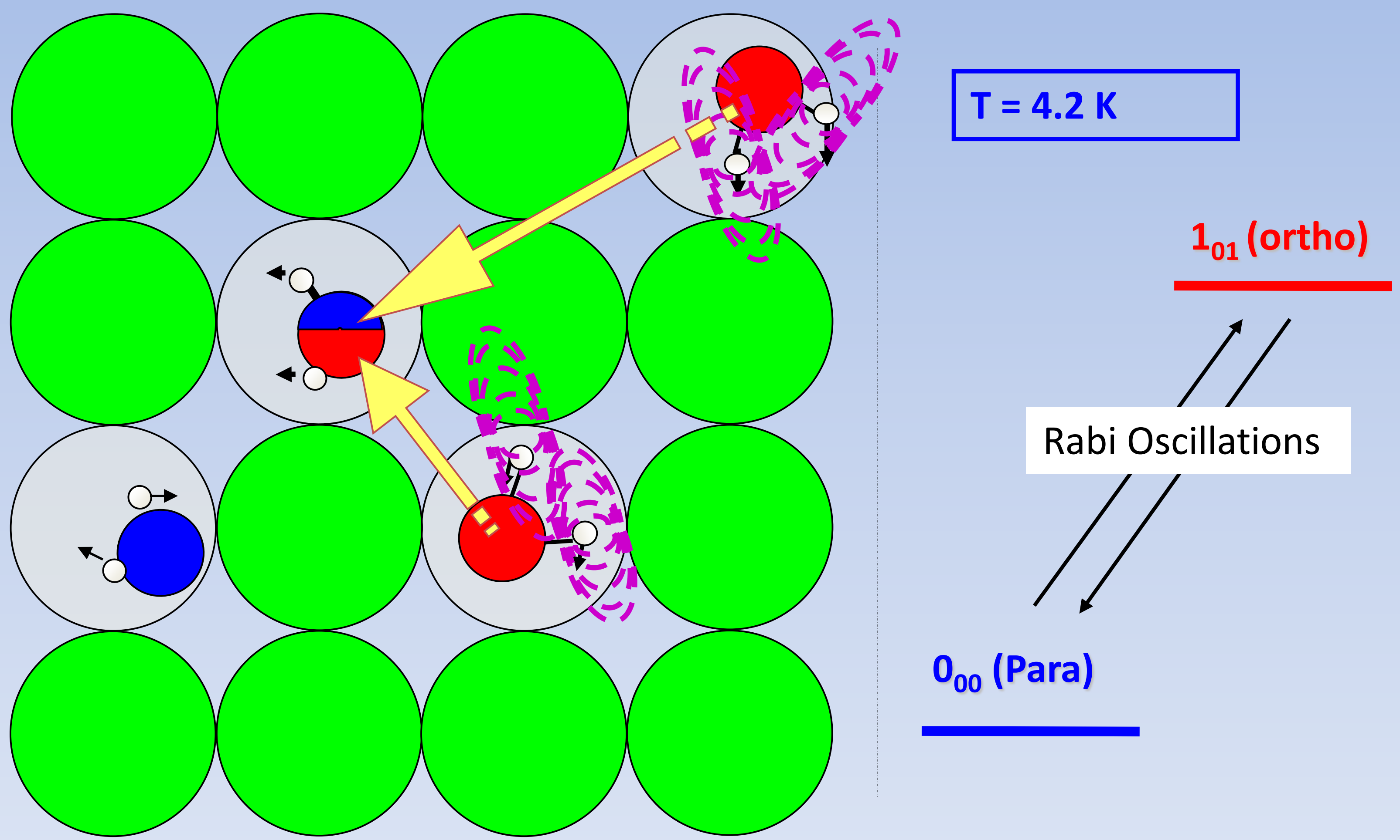
Spin-spin coupling



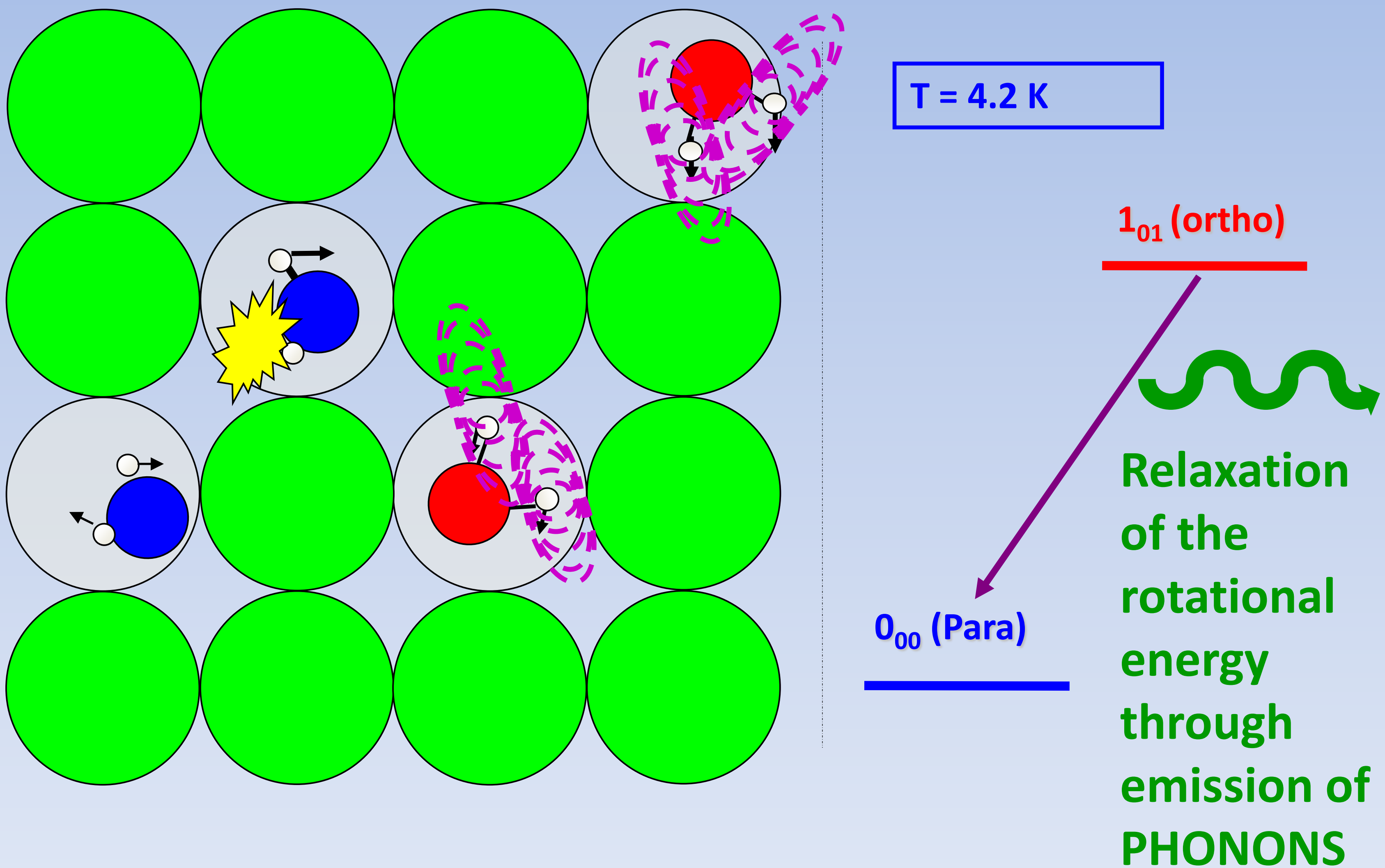
Fillion et al, ECLA proc.
EAS Publications Series, 58 (2012)
C. Pardanaud PhD thesis 2007
Michaut *et al* (to be submitted)

LERMA

Concentration effect on NSC of H_2O in Argon Matrix



Concentration effect on NSC of H_2O in Argon Matrix



Concentration effect on NSC of H_2O in Argon Matrix

- Fractional populations of *ortho* molecules: $x_O = \dfrac{n_O}{n_O + n_p}$
- The time evolution of the number of *ortho* molecules can be expressed as:

$$\frac{dx_o}{dt} = -k_1 x_o^2 - k_2 x_o - k_3$$

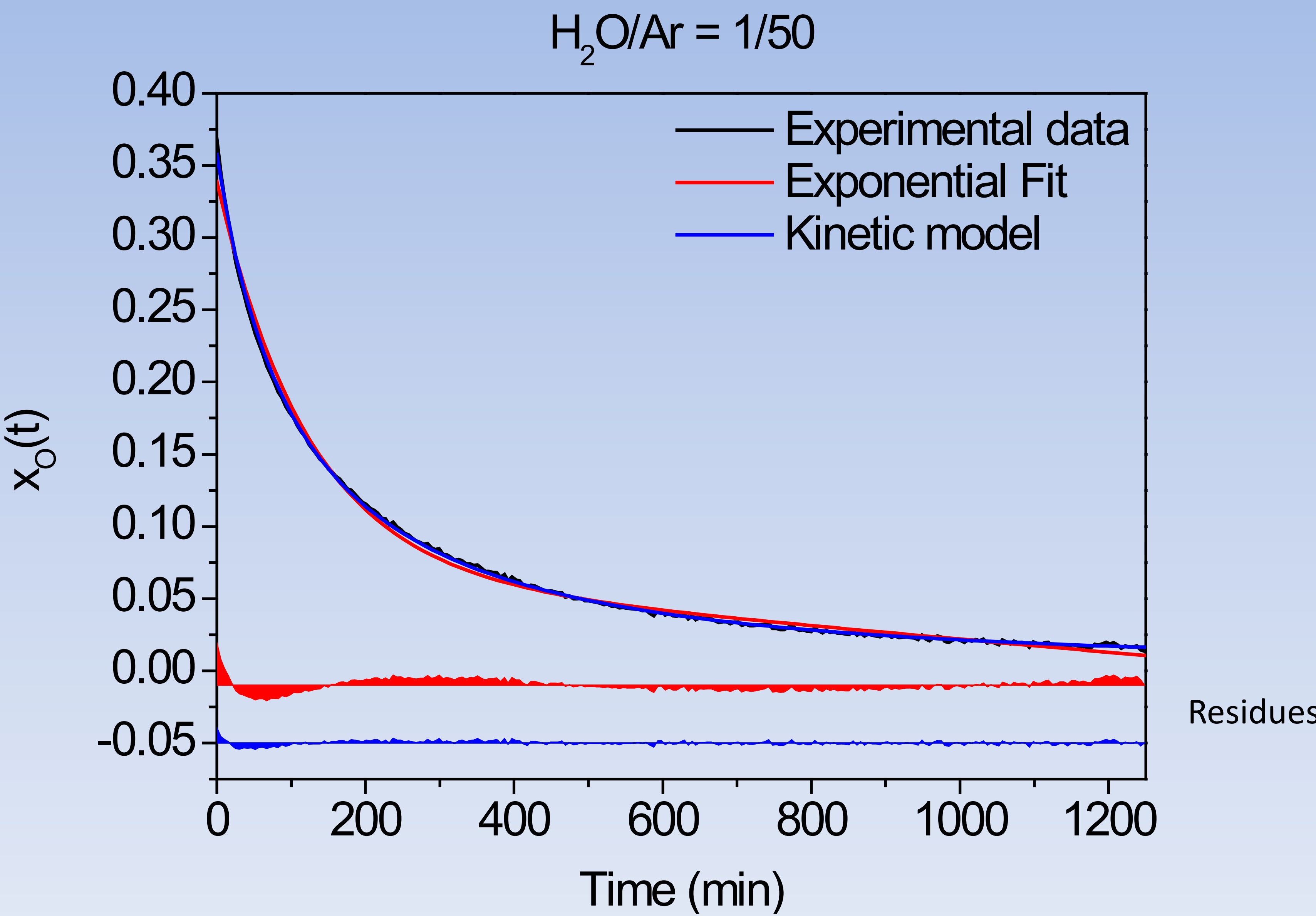
with $k_1 = \dfrac{K_{INTER}^{po}}{x_o(\infty)}$ $\quad k_2 = \dfrac{1}{\tau_{INTRA}} - K_{INTER}^{po}$ $\quad k_3 = \dfrac{x_o(\infty)}{\tau_{INTRA}}$

- The solution can be expressed as :

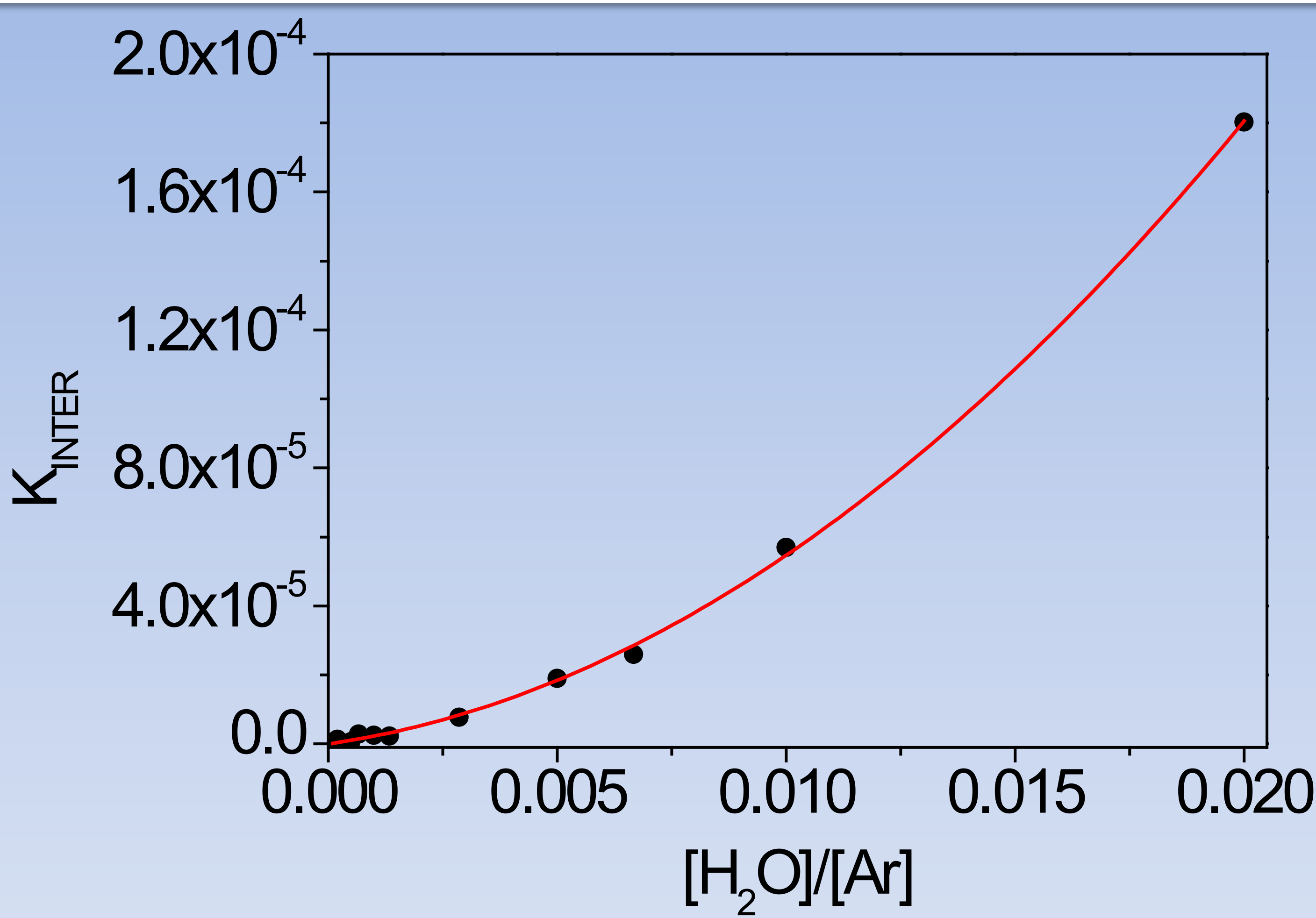
$$x_o(t) = \frac{x_+ - x_- \varepsilon \exp\left(-k_1\sqrt{\beta^2 + 4\gamma t}\right)}{1 - \varepsilon \exp\left(-k_1\sqrt{\beta^2 + 4\gamma t}\right)}$$

- Only one parameter to be adjusted K_{INTER}^{po}

Concentration effect on NSC of H_2O in Argon Matrix



Concentration effect on NSC of H_2O in Argon Matrix

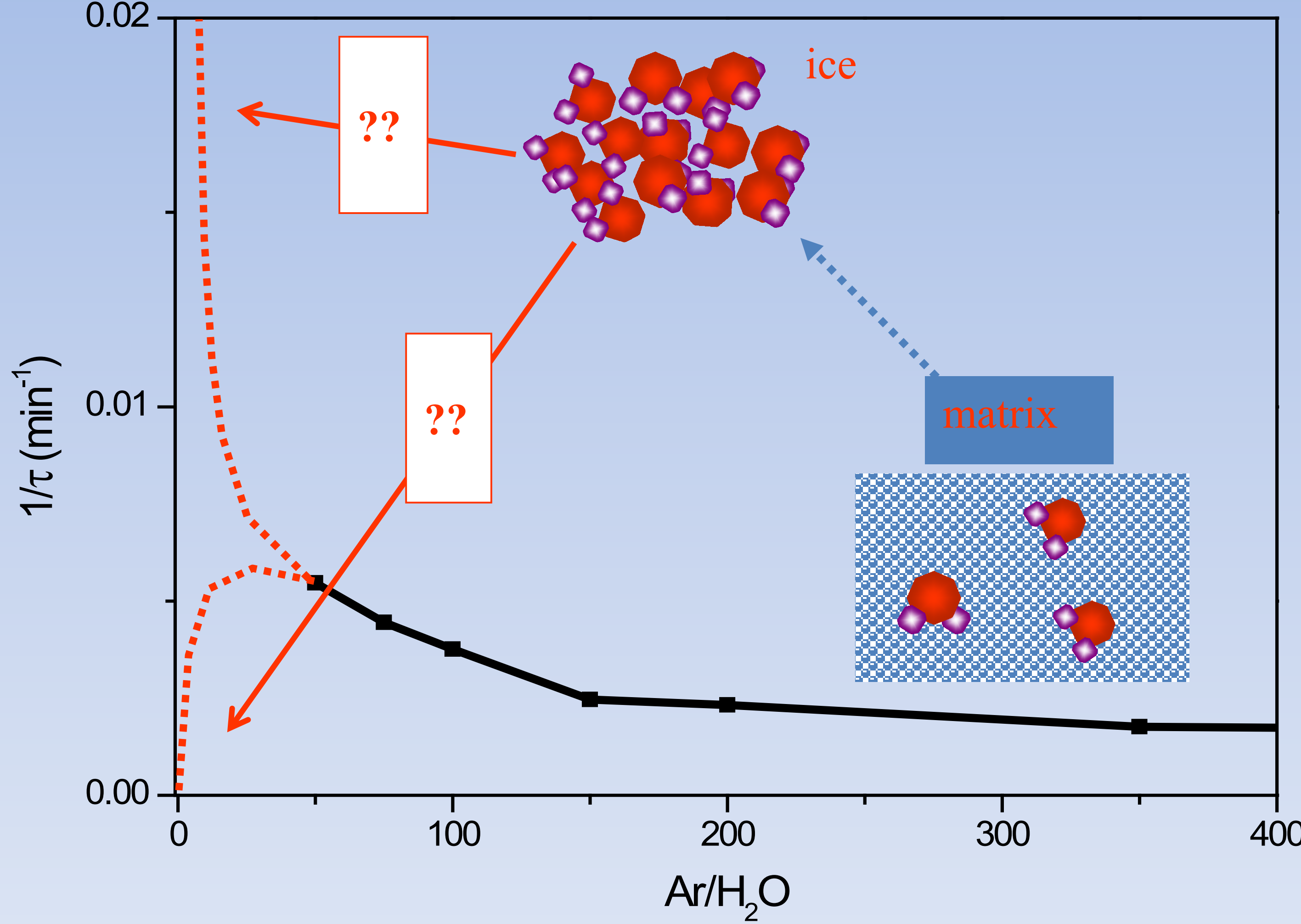


Quadratic dependence of $\boxed{K_{INTER}^{po}}$ with C_{H_2O} presumably due to dependence of rotational relaxation on water concentration C_{H_2O}

Michaut *et al* (to be submitted)

Extrapolation to ices

T=4.2 K



Can we extrapolate results in rare gas matrix to icy environment ?

Intermolecular Magnetic Interactions In Ices

Calculations estimate the NSC to be few ms (Buntkowsky *et al* Z. Phys. Chem. 2008)

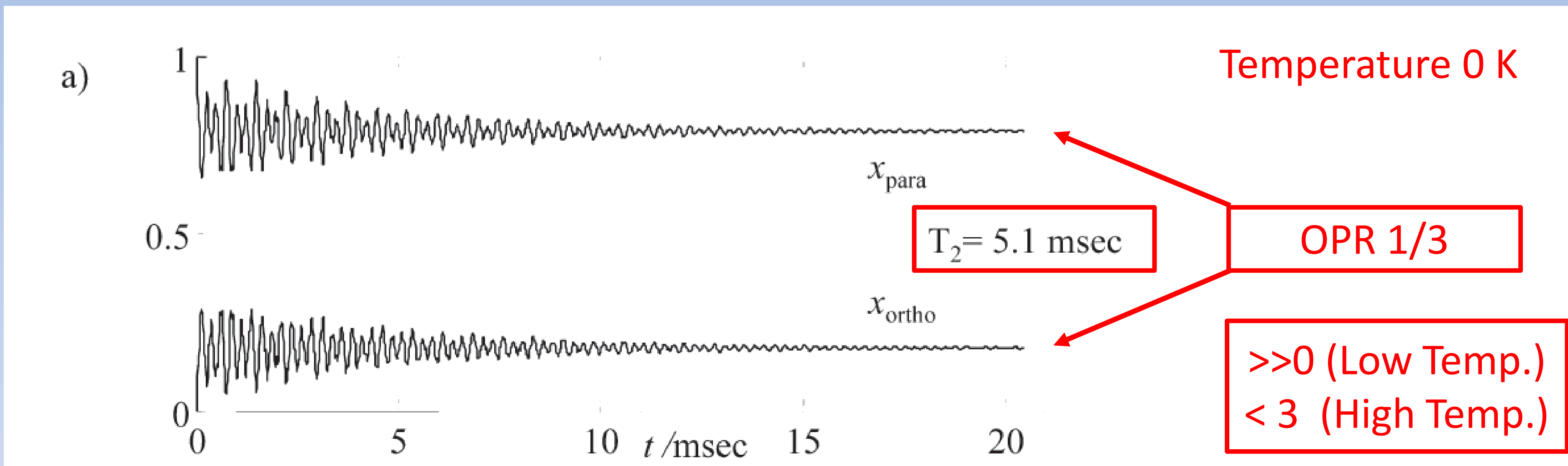
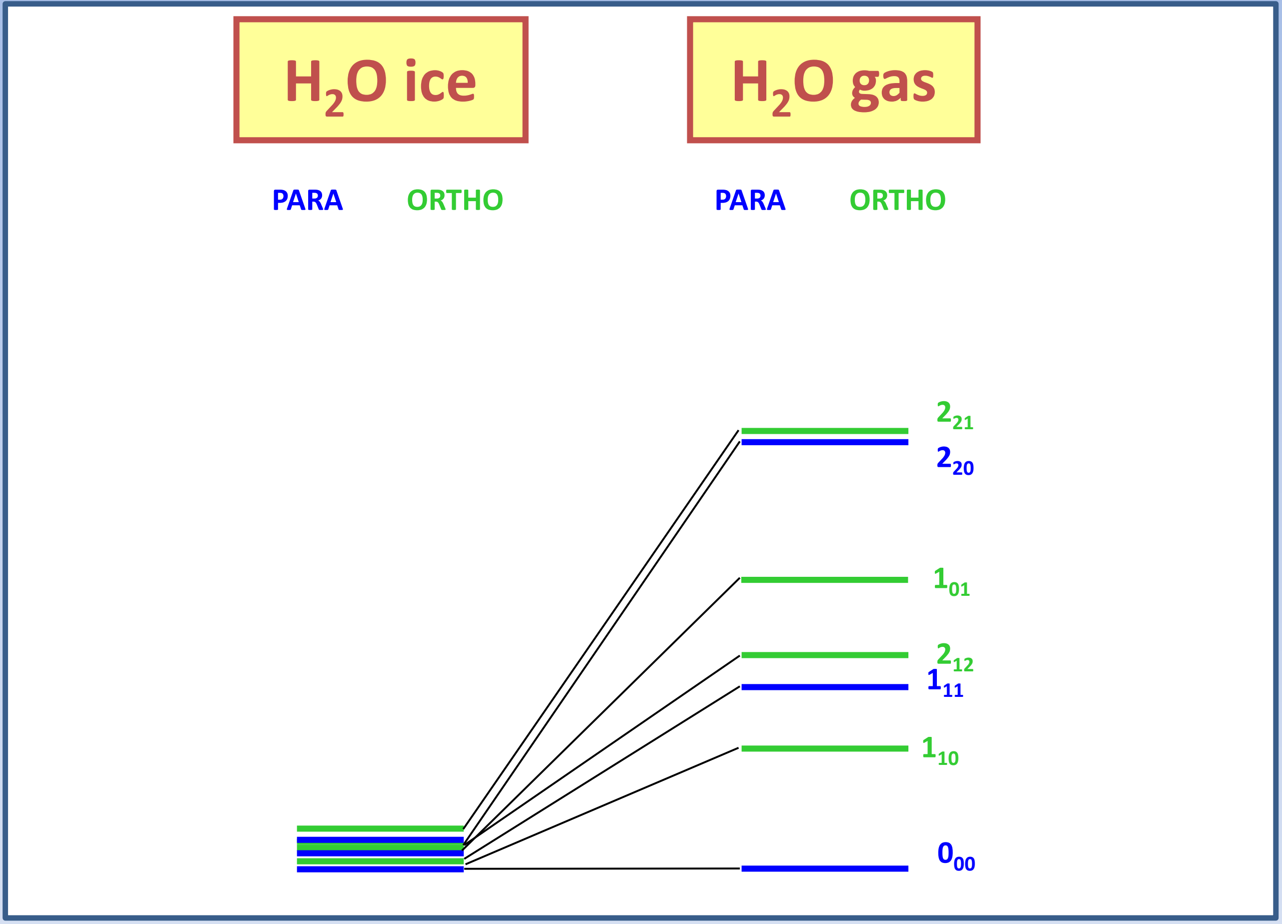


Fig. 3. Time dependence of the relative *para-* and *ortho*-H_2O concentrations for completely quenched tunnel splitting (J_{H_2O}=0 Hz). (a) Long time behavior. Oscillations are initially damped with a time constant T_2. (b) Initial part of the oscillations. Note that already after ca 100 μsec an efficient conversion has occurred.

Open Question

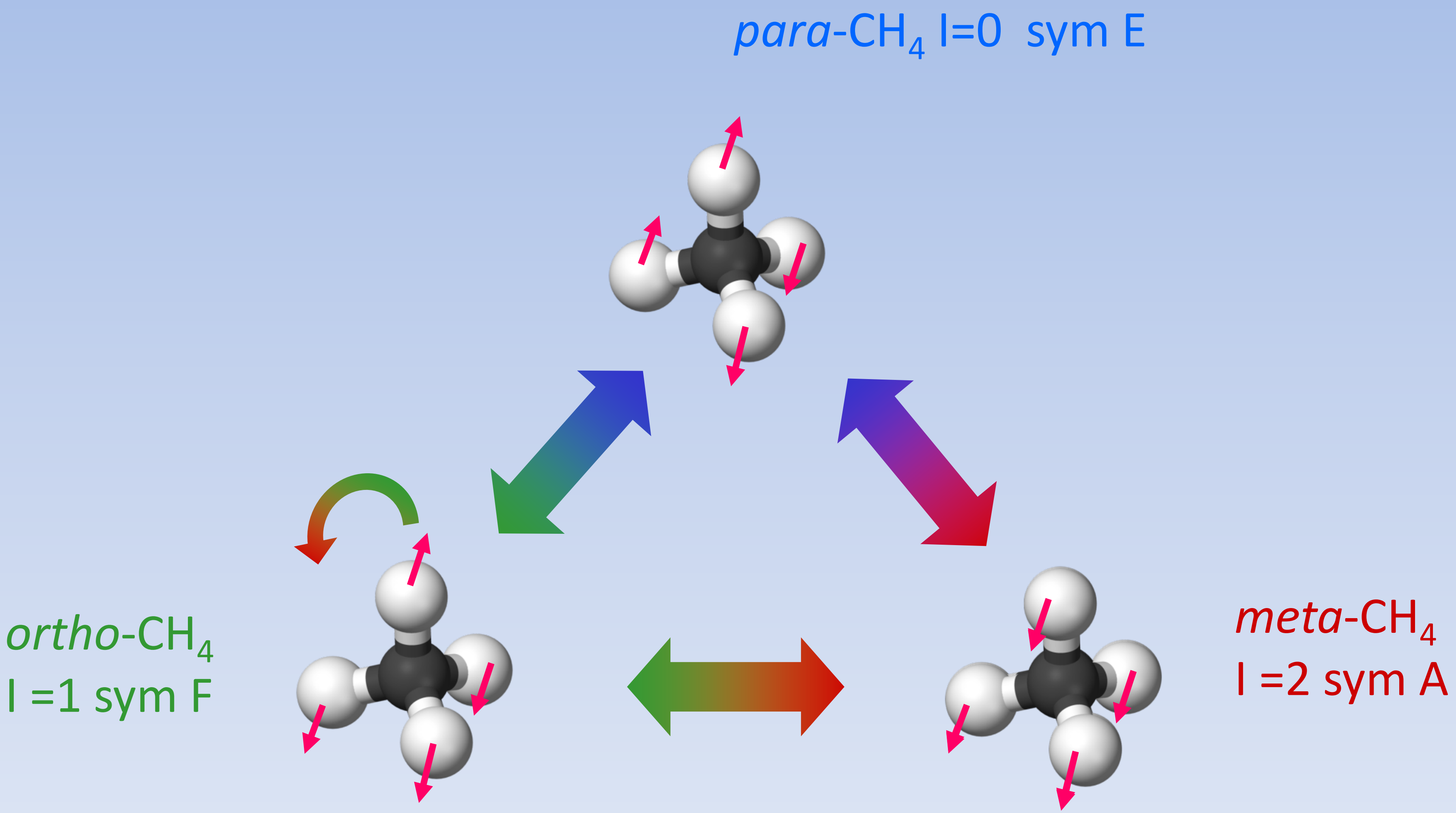
behavior at very low temperatures in the ice?



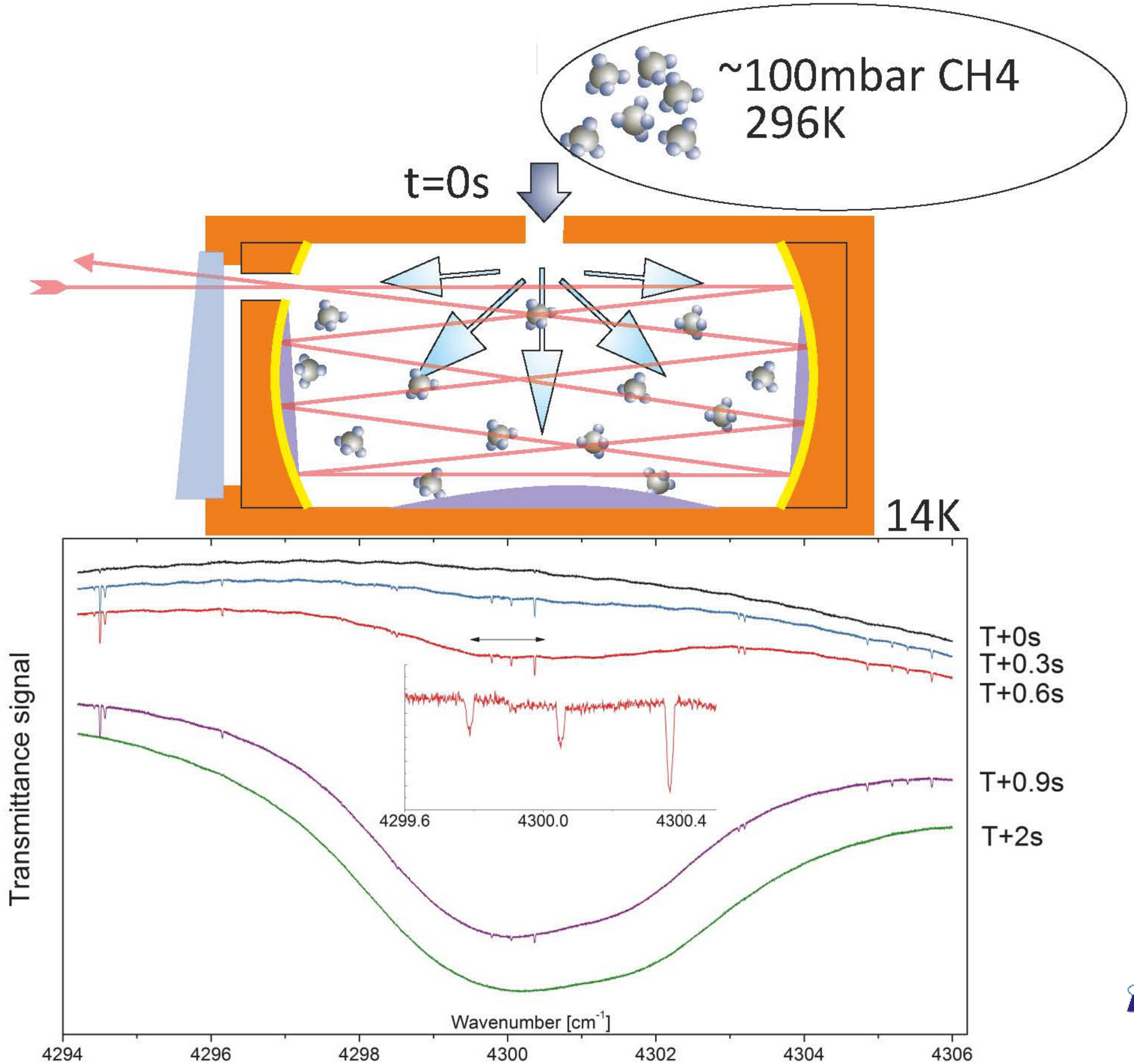
Experiments in molecular beams claim that conversion proceeds in few μs in the water aggregates (Manca et al JPC 2013) : not confirmed by experiments performed with Jet-Ailes Team (IPR-LADIR-PhLAM-SOLEIL-Ailes beamline consortium)

See Robert Georges' talk

METHANE



Nuclear Spin Conservation during Solid formation

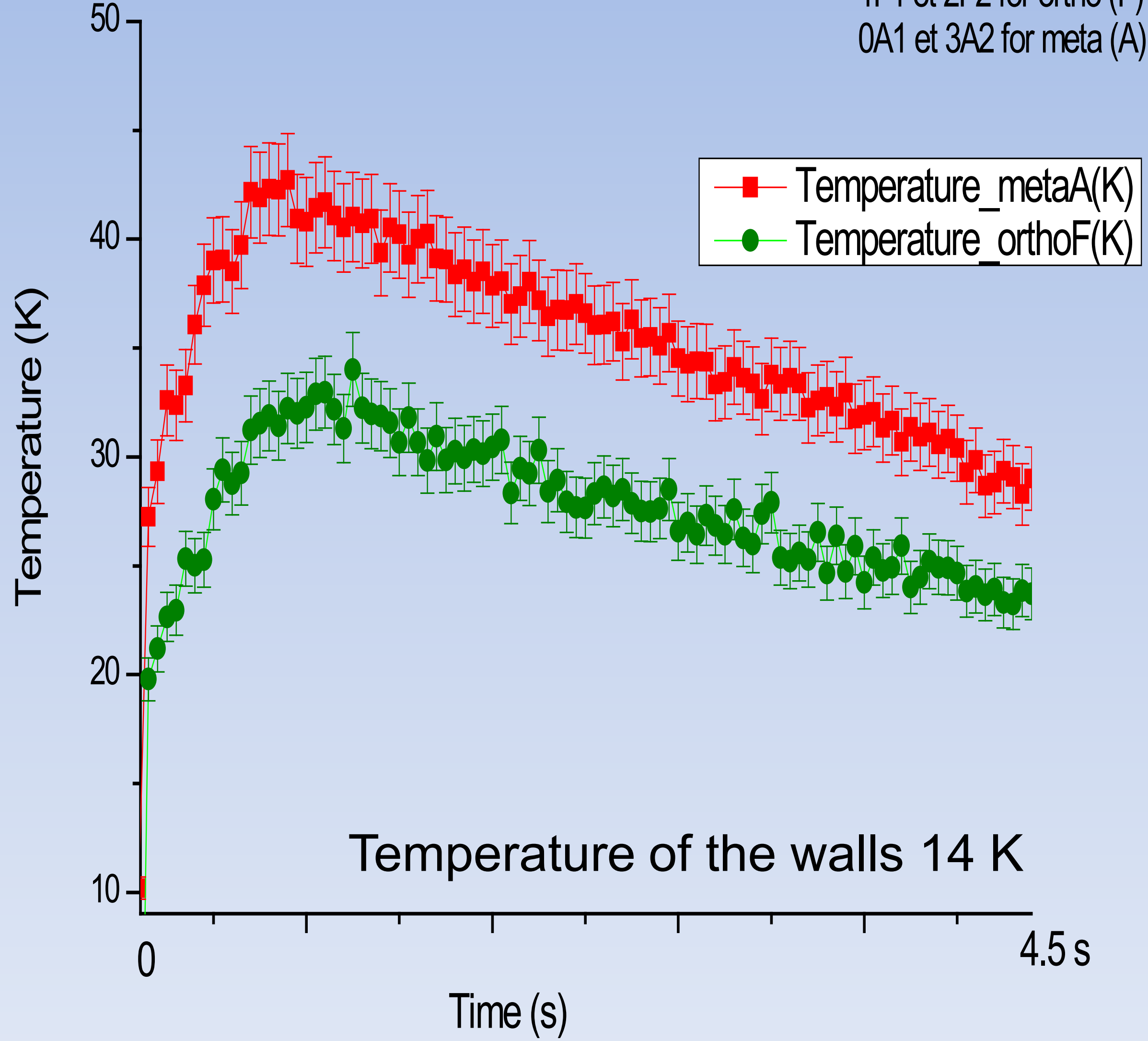


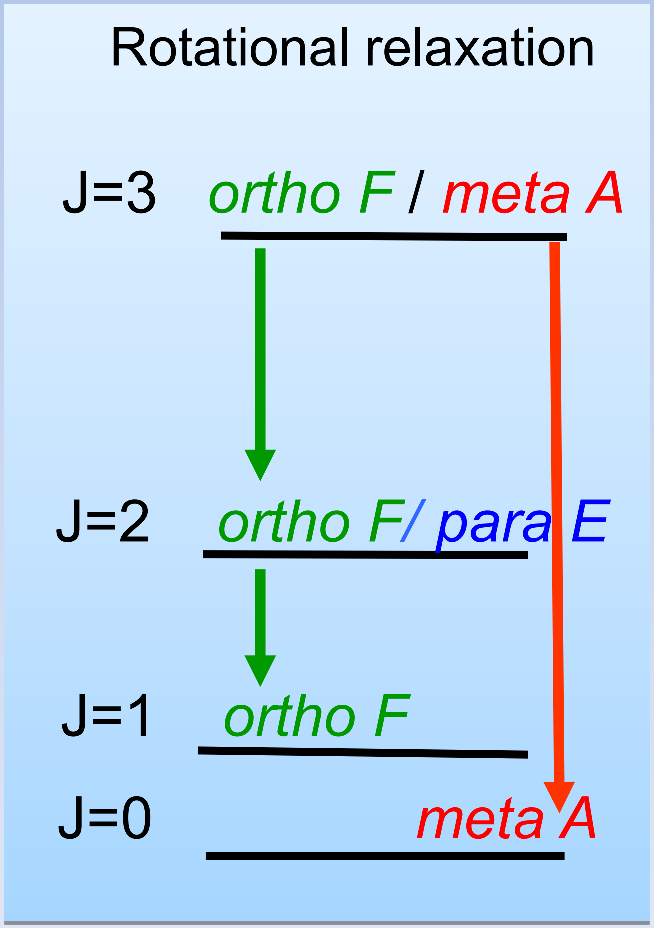
Temperature cooling of the gas during Solid formation

Temperatures measured from intensities of line transition starting from energy levels

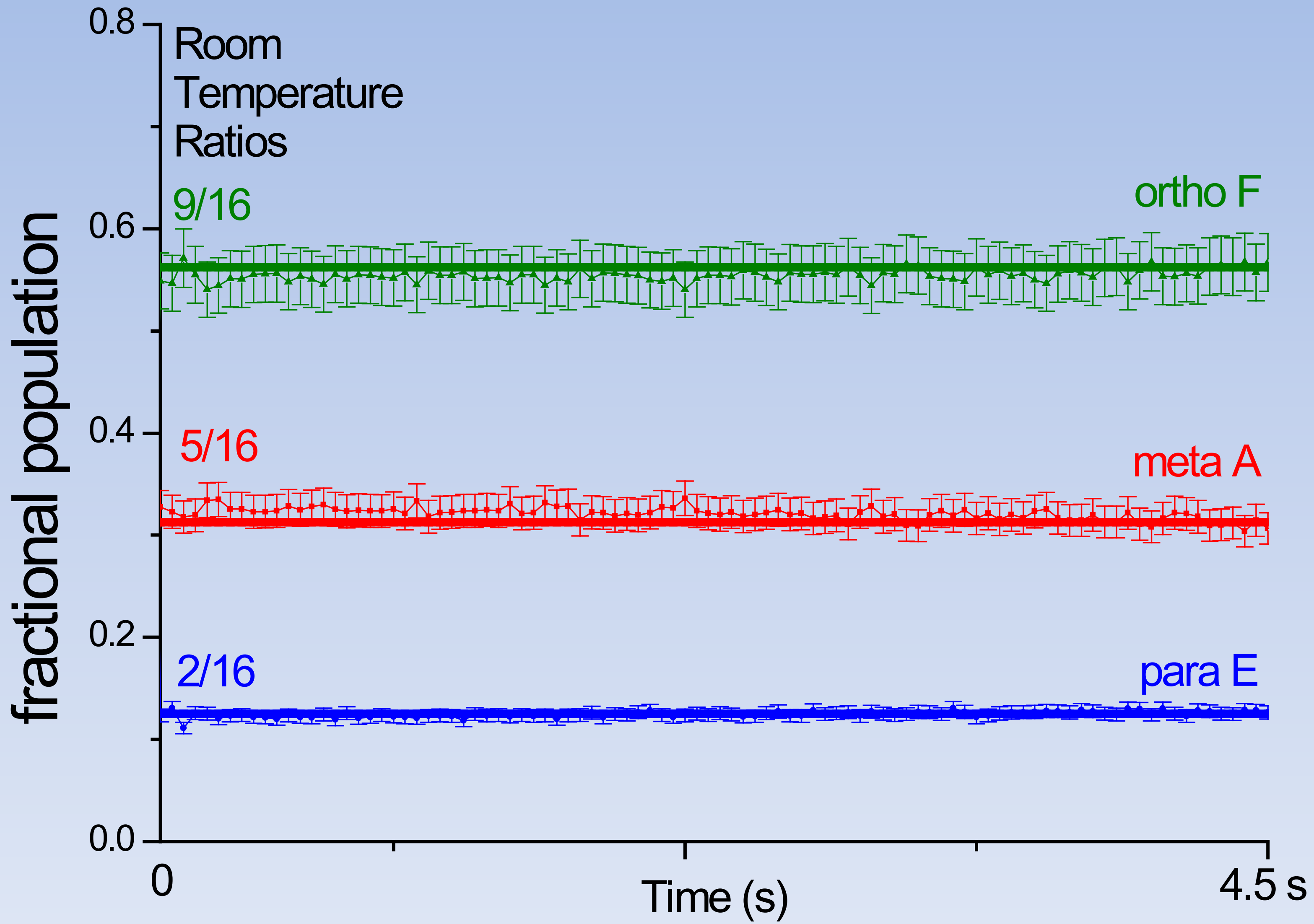
1F1 et 2F2 for ortho (F)

0A1 et 3A2 for meta (A)

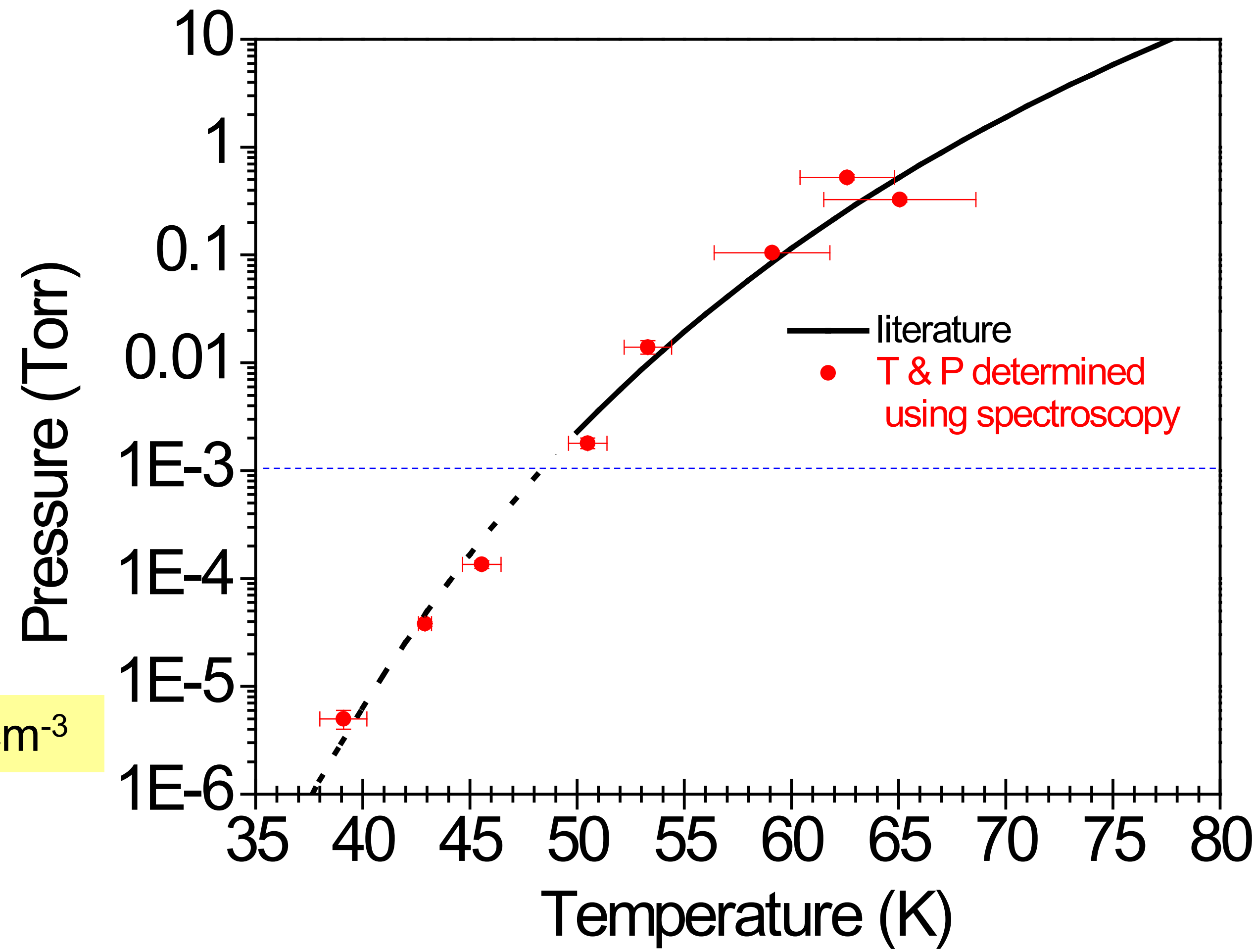




OPR evolution in the gas during Solid formation



Measurement of OPR at solid-gas interface

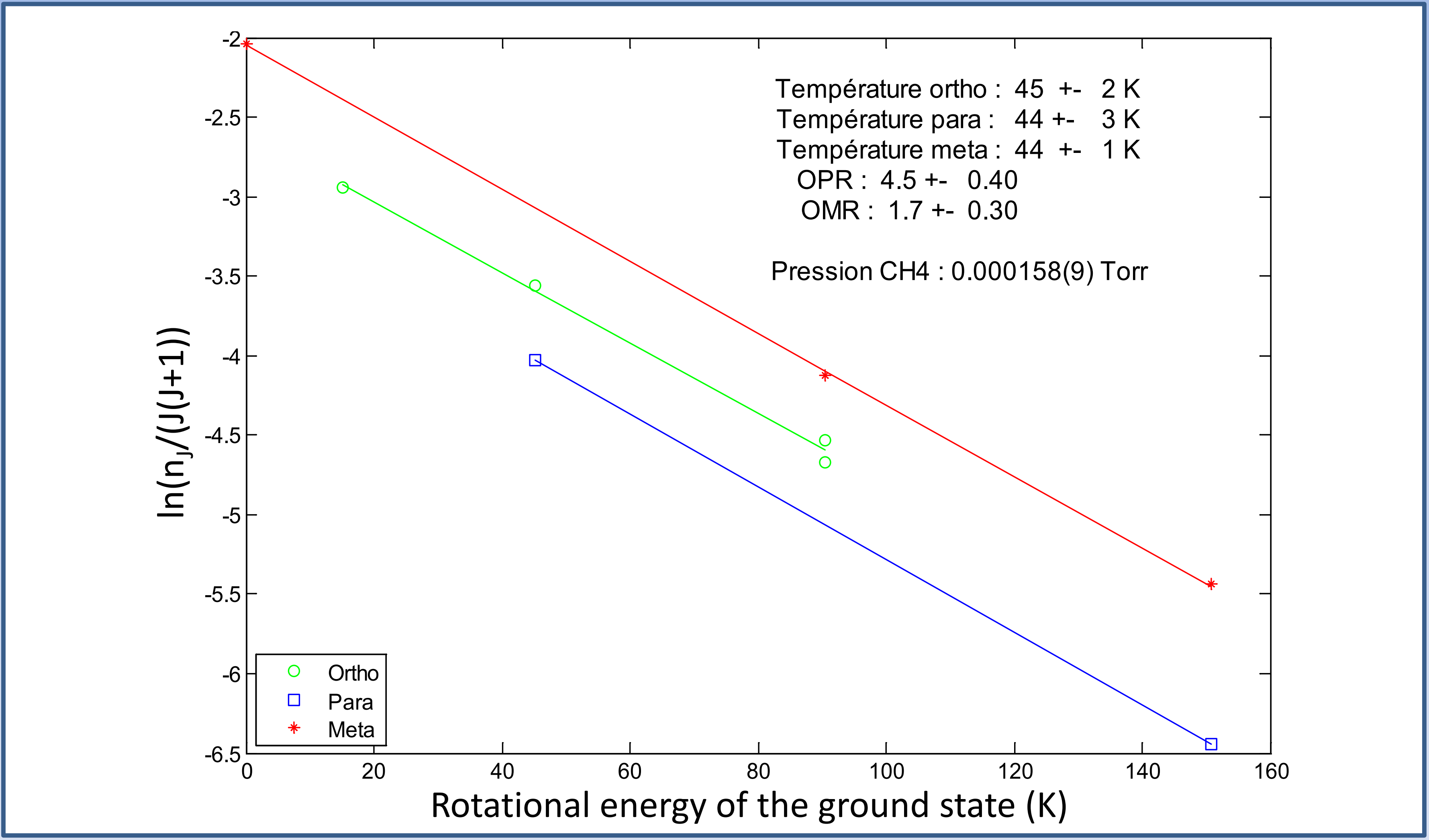


10^{12} cm^{-3}

- ❑ Vapor pressure measured between 40 and 70 K
- ❑ Evolution of the pressure over 6 orders of magnitude

C. Pardanaud (in prep.)

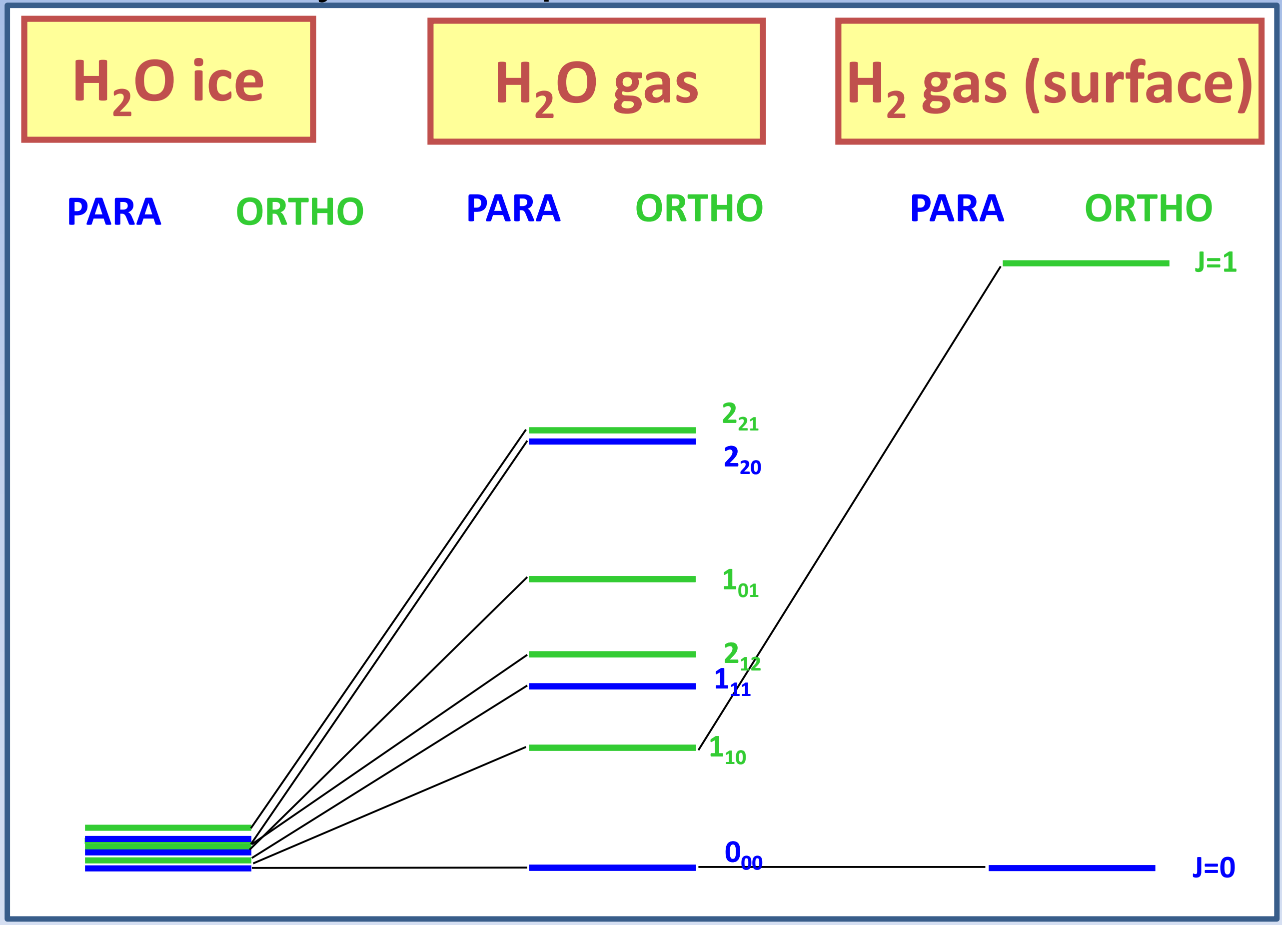
Measurement of OPR at solid-gas interface



- Measurement of OPR and OMR between 43 and 70 K
- *OPR* and *OMR* equals to the expected values at equilibrium in gaseous phase *(value close to the high limit value)*

NSC during interaction with cold surface

behavior at very low temperatures on the iced surface?

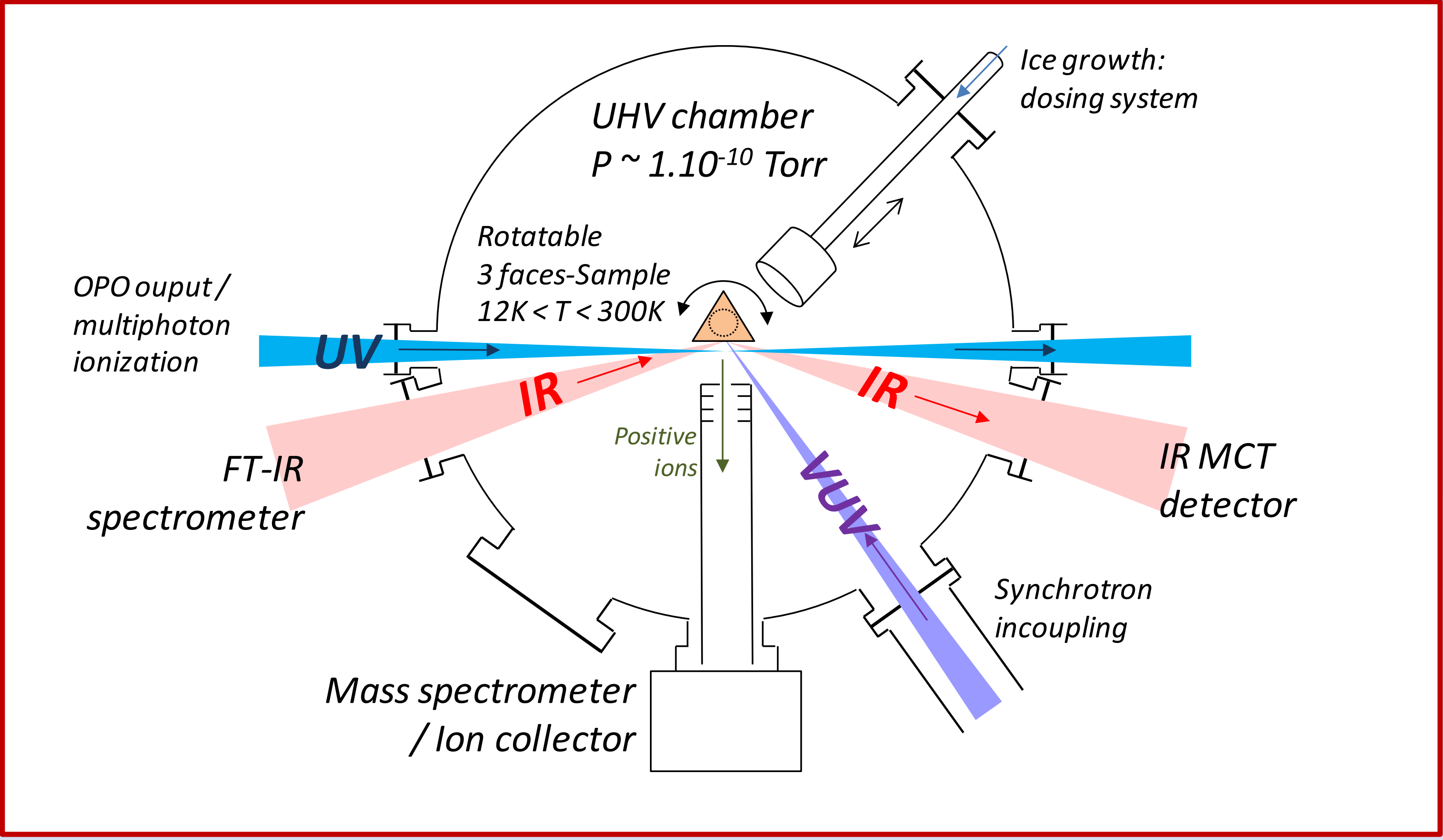


Experiments [1,2,3] using REMPI spectroscopy to investigate released gas after desorption showed fast NSC in H_2 molecules trapped on cold Amorphous Solid Water (ASW).

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

Nuclear Spin Conversion Dynamics on Surfaces

Probing the Molecular hydrogen on ASW using FTIR spectroscopy

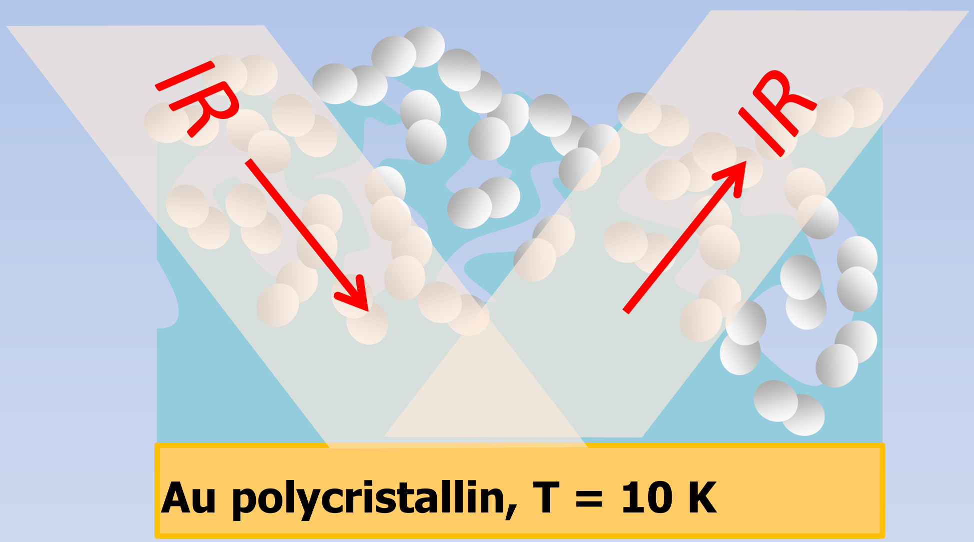


Surfaces Processes & Ices (SPICES set-up)

H_2 adsorbed on ASW

Reflection Absorption InfraRed Spectrosopy (RAIRS)

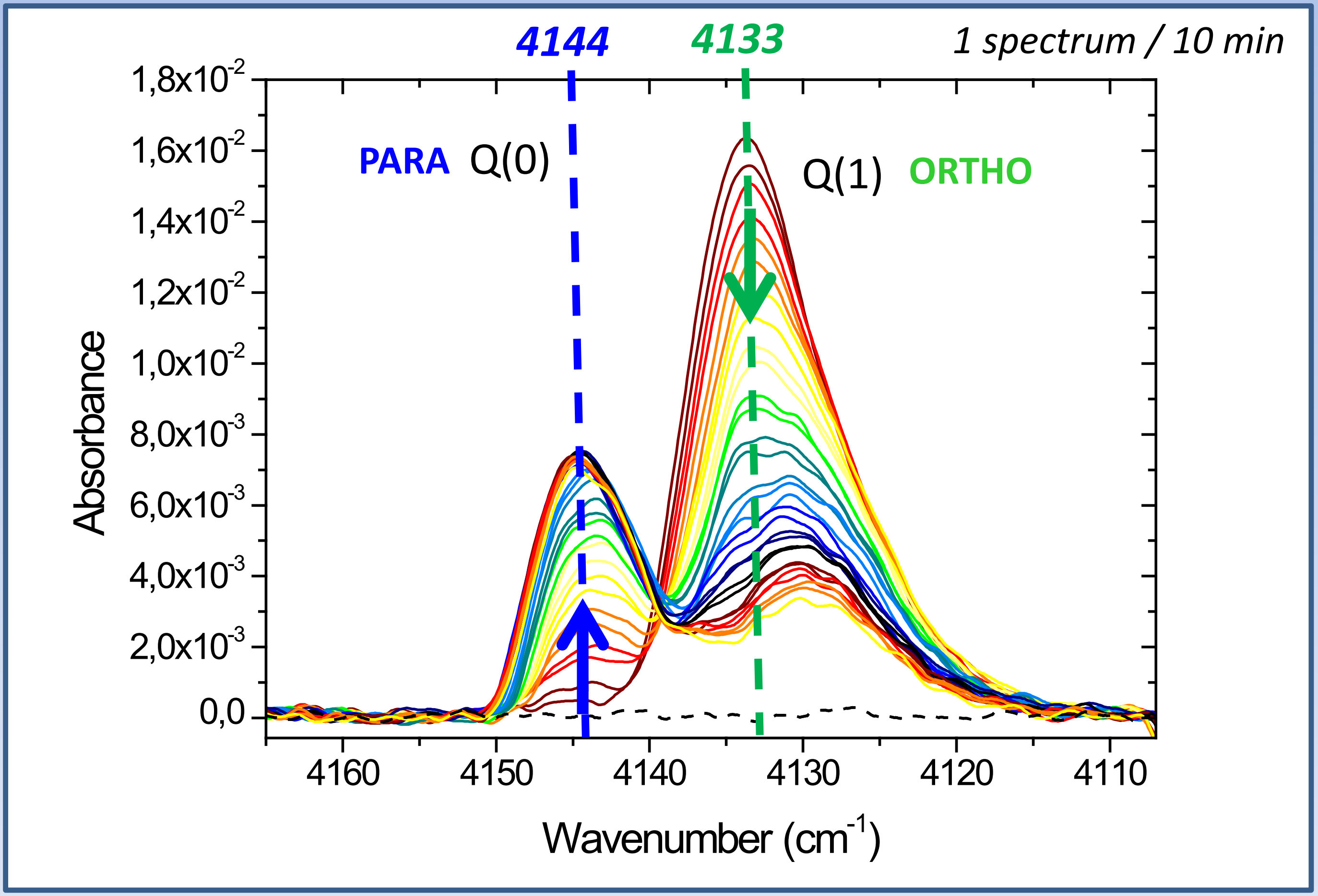
Porous Amorphous Solid Water (ASW)



Solution

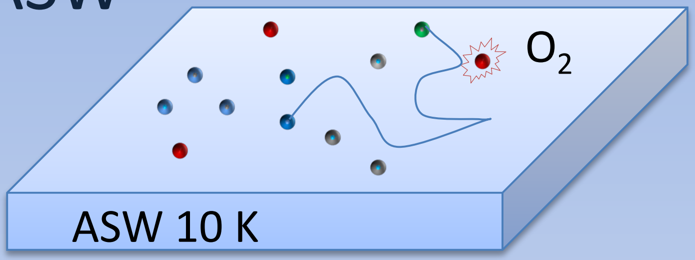
- ❑ 1000 ML Equivalent
- ❑ Saturation of H_2

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

Temperature 10 K

O_2	t(min) IR Vib
0.2 %	
0.1 %	H_2 : 30 (2)
0.02 %	
0 %	H_2 : 220 (17)
Coverage	1 ML

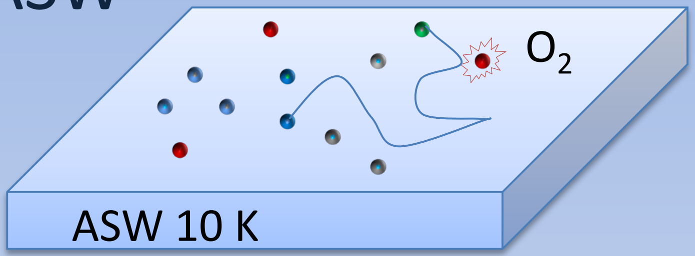
(1) Chehrouri, Fillion *et al* PCCP 2011
(2) Sugimoto & Fukutani Nature Physics 2011
(3) Ueta, Watanabe, Hama, Kouchi PRL 2016

Nuclear Spin Conversion Dynamics on Surfaces

Molecular hydrogen on ASW

- NSC in the presence of O_2 traces

Molecular Hydrogen Diffusion



Temperature 10 K

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 : 26 (5)
Coverage	1 ML	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)

CONCLUSIONS

Astronomical clock

- **Matrices Experiments**
  - well controlled environnement : reveals role of magnetic inter- and intra- molecular interactions
  - importance of rotational structure
  - importance of rotational relaxation

Suggest a fast NSC in the solid state

- **Calculations in gas phase**

-NSC strongly dependent on density and temperature

$10^{+4} - 10^{+7}$ years for H_2CO between 5 and 100 K in dilute media ($n(H_2)=10^5$-10^8 cm^{-3})

5 hours close to surface nucleus of comets

Suggest a very slow NSC in a very diluted gas at low temperature Comparable to proton exchange ?

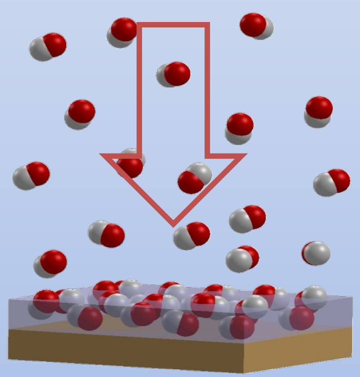
- **Solid-gas Interface**

Open question

PROSPECTS

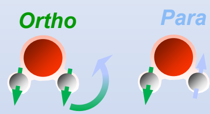
- New Approaches : desorption studies

Ice sample preparation
Enriched in ortho H_2O
Coll. Univ. Sherbrooke

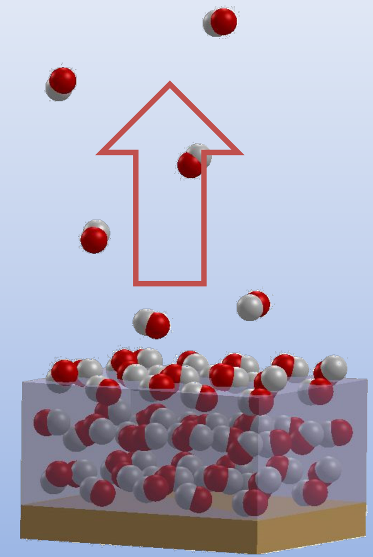


ice

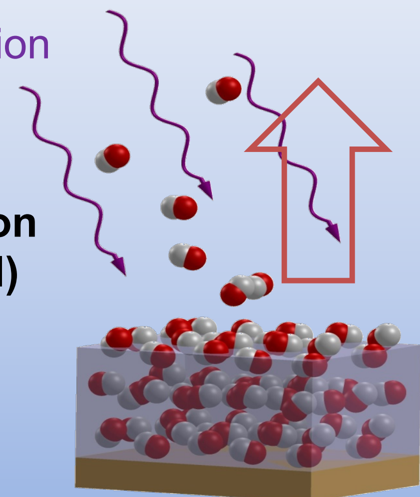
substrate T<20 K



thermal desorption

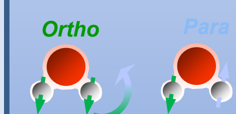


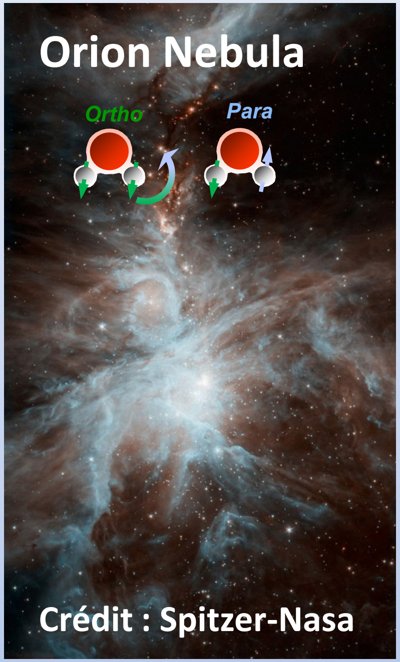
VUV radiation



UV desorption (non thermal)

SPICES 2





X. Michaut
P. Ayotte
D. Lis
M. Gerin
J. Goicoechea ICCM

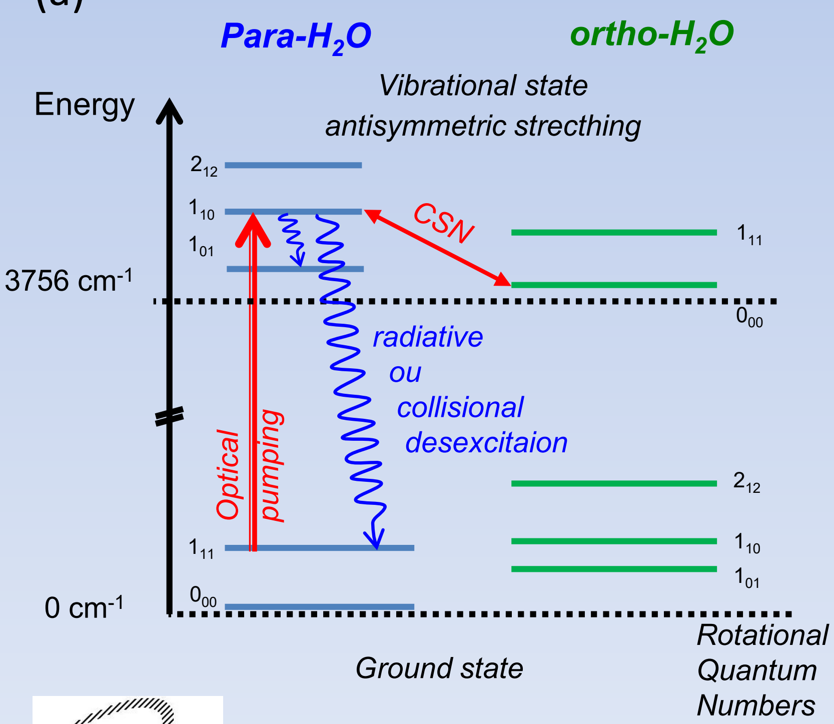
PROSPECTS

- ❑ New Approaches : Enrichment techniques
- ❑ Magnetic lensing

Patrick Ayotte Invited talk
Nuclear Spin Effect in Astrochemistry May, 2nd , 2017

- ❑ Optical techniques

(a)



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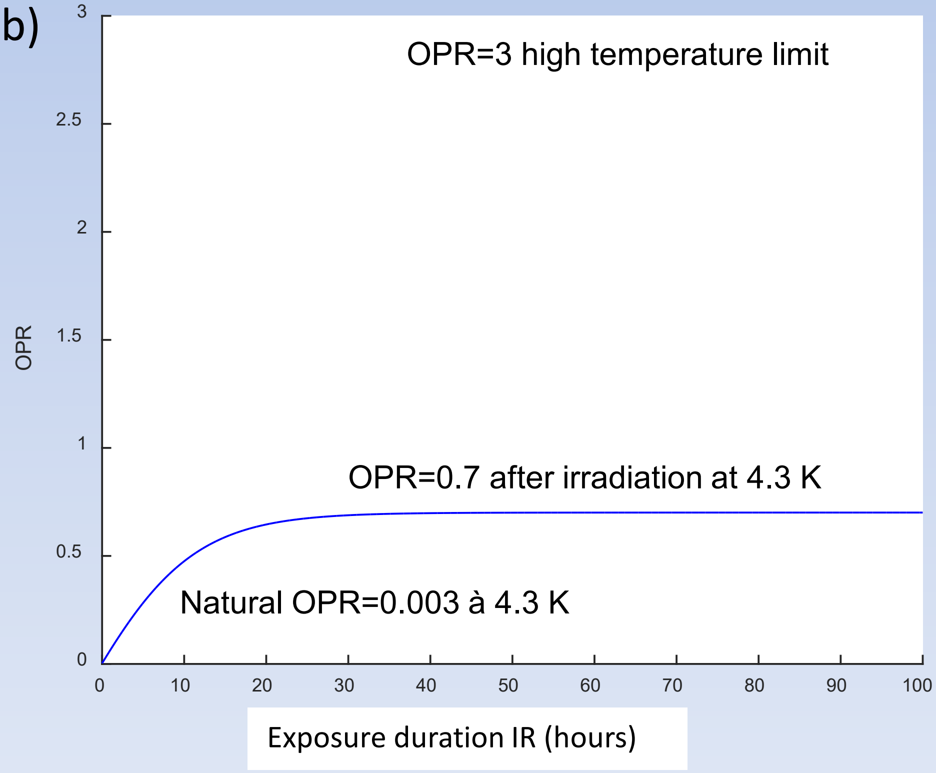

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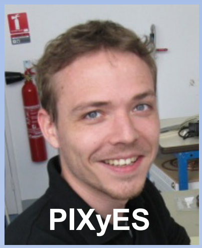

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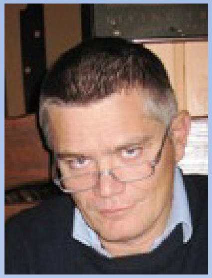

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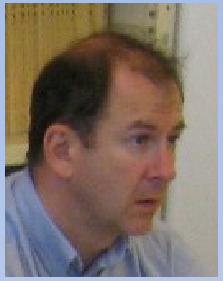

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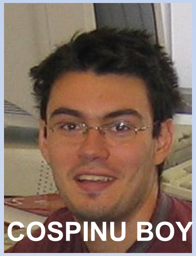

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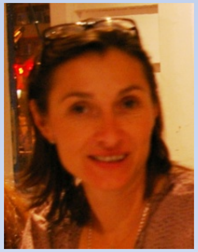

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Thank you for your attention!!