Water formation and ortho para ratio

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Observational work

Lab work

Ortho Para Ratio

Nuc. Spin Conv.
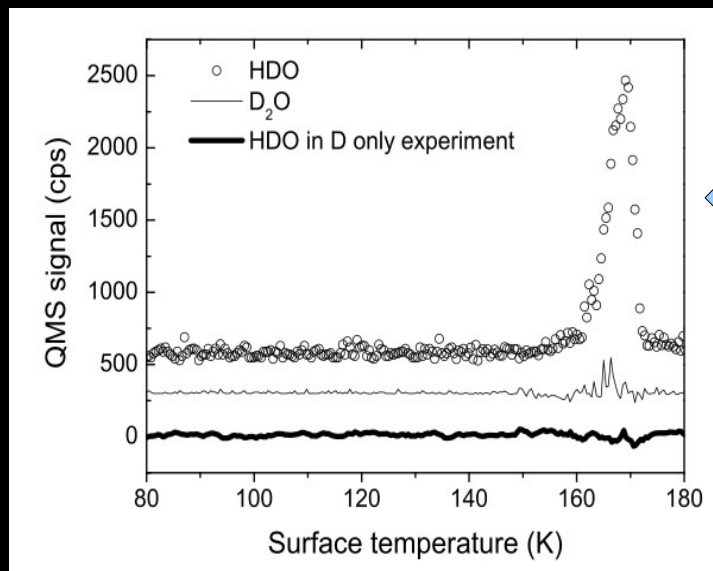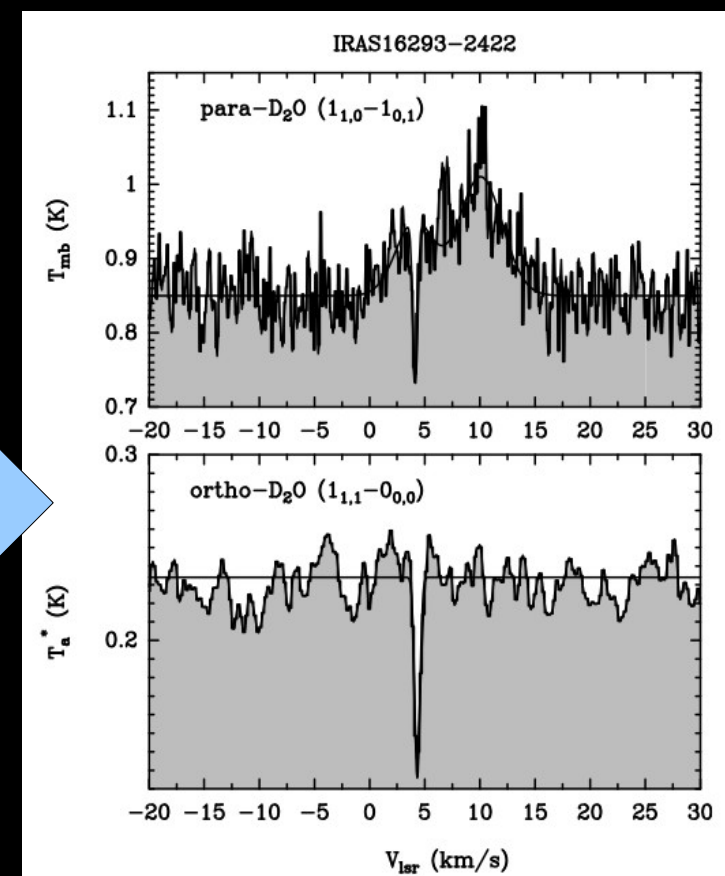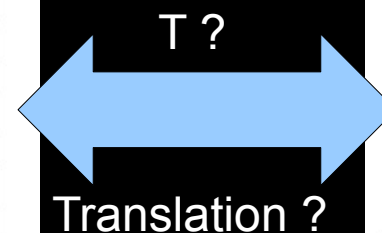
H2 NSC

H2O NSC

Spin temp.
 and desorpion

T ?

Translation ?

Dulieu et al 2010

Vastel et al 2010

Introduction

Gas vs Solid

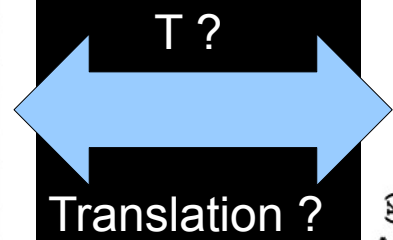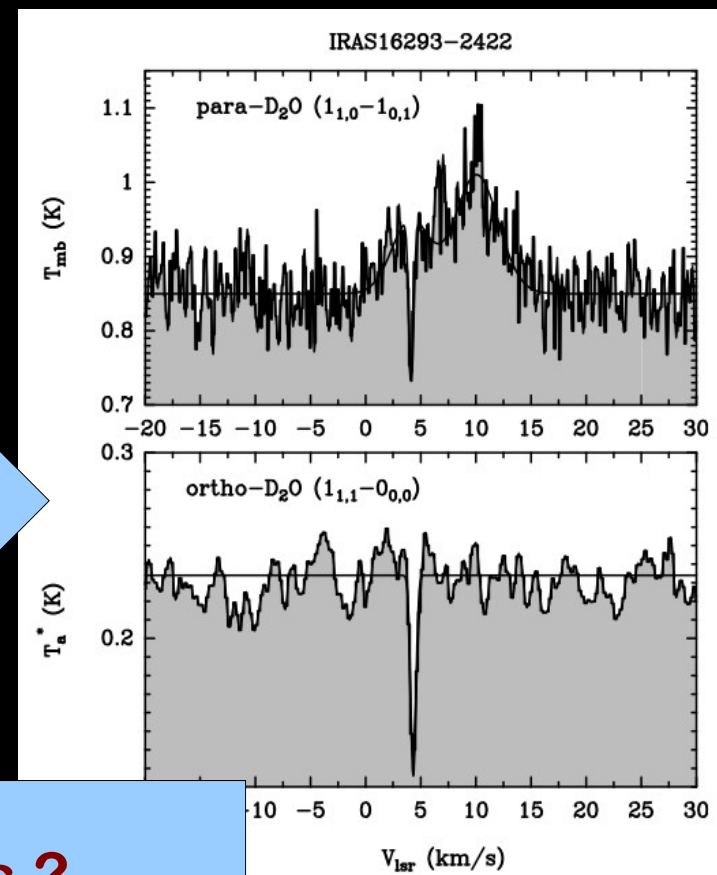Water formation

Chem. network

Ortho Para Ratio

Nuc. Spin Conv.

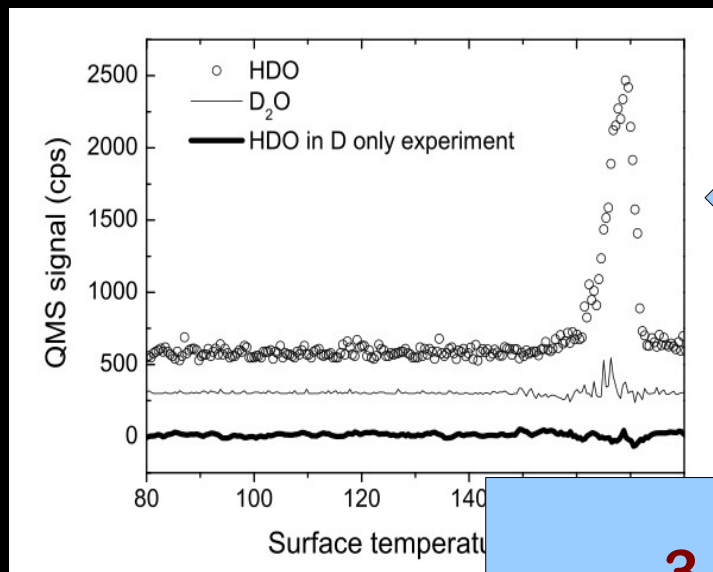H2 NSC

H2O NSC

Spin temp.
 and desorpion

Observational work

Lab work

T ?

Translation ?

3 main ideas ?

Dulieu et al 2010

Vastel et al 2010

F- Dulieu – LERMA - IAU symposium 280– Toledo - 2011

Water and surface chemistry

The magic box ?
" Chemistry on dust grains is supposed to work when gas phase do not ! "

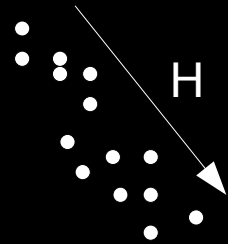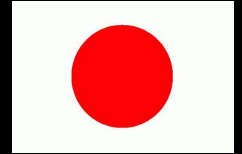### Gas phase

$$OH + H \rightarrow OH + H$$
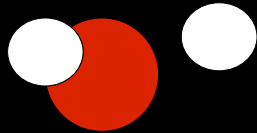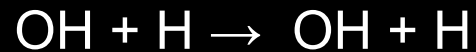
One collision every day

Solid phase

?
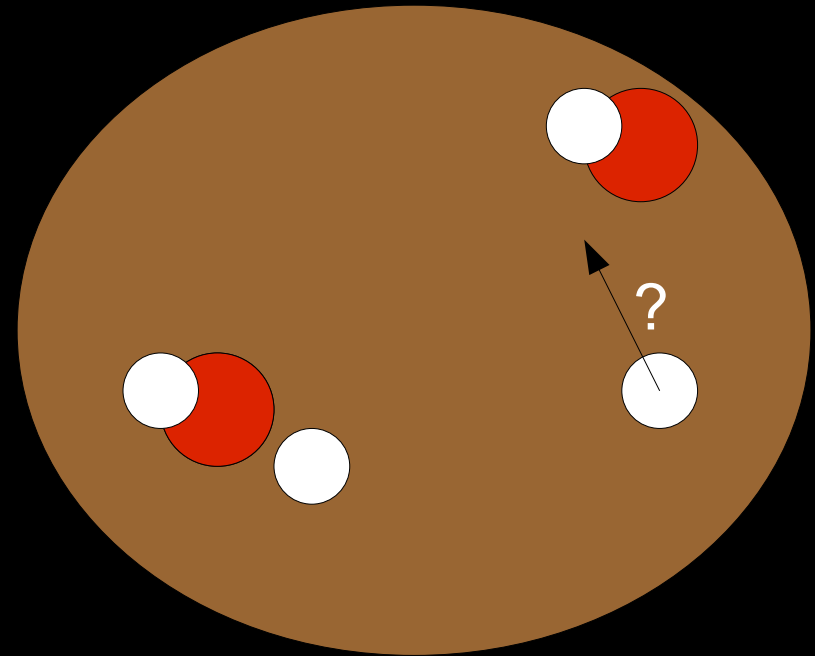
One collision every picosecond

O2 + H (1)

H

"thick" O2 layer

Gold or Al substrate 10 K

H2O2 and H2O are formed

Myauchi et al 2008
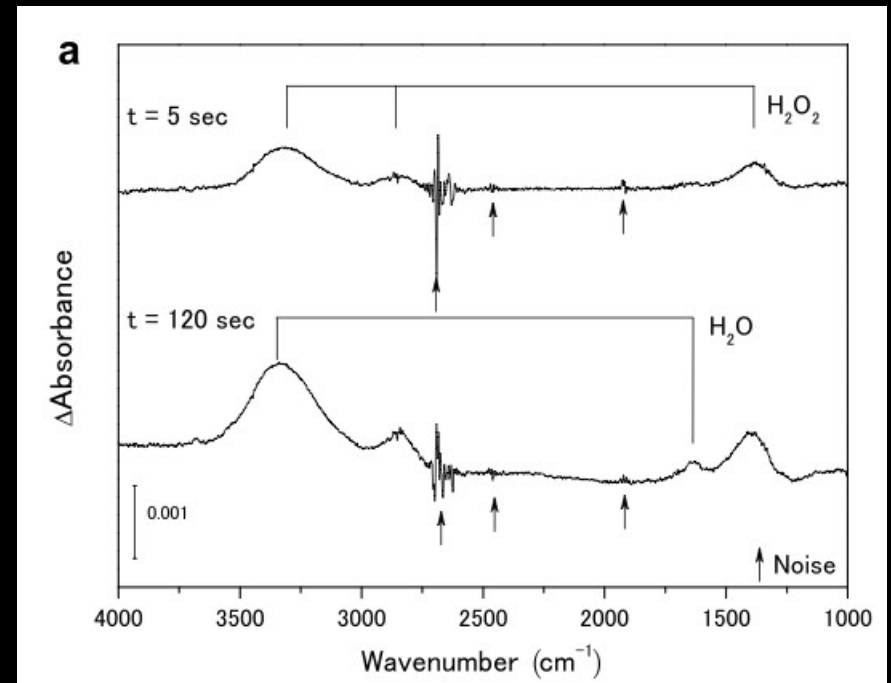
O2 + H (2…)

H

O2

Gold substrate **10 - 25K**
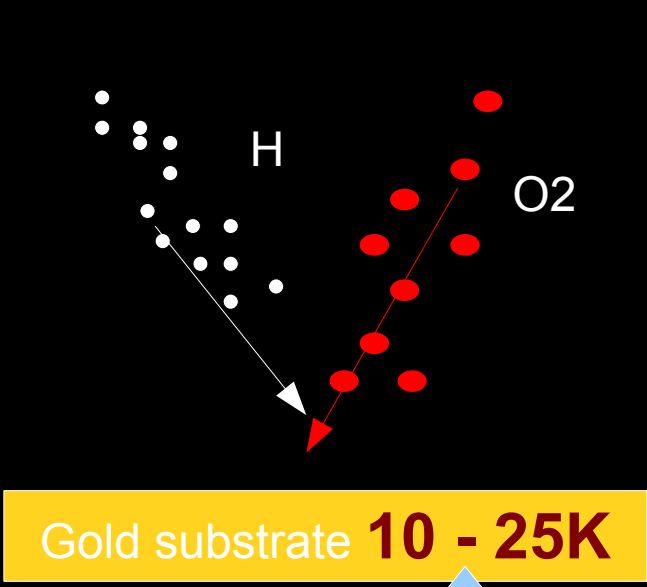
H2O2 and H2O and O3, OH
O2H … are formed
Ioppollo et al 2008, 2010 ...
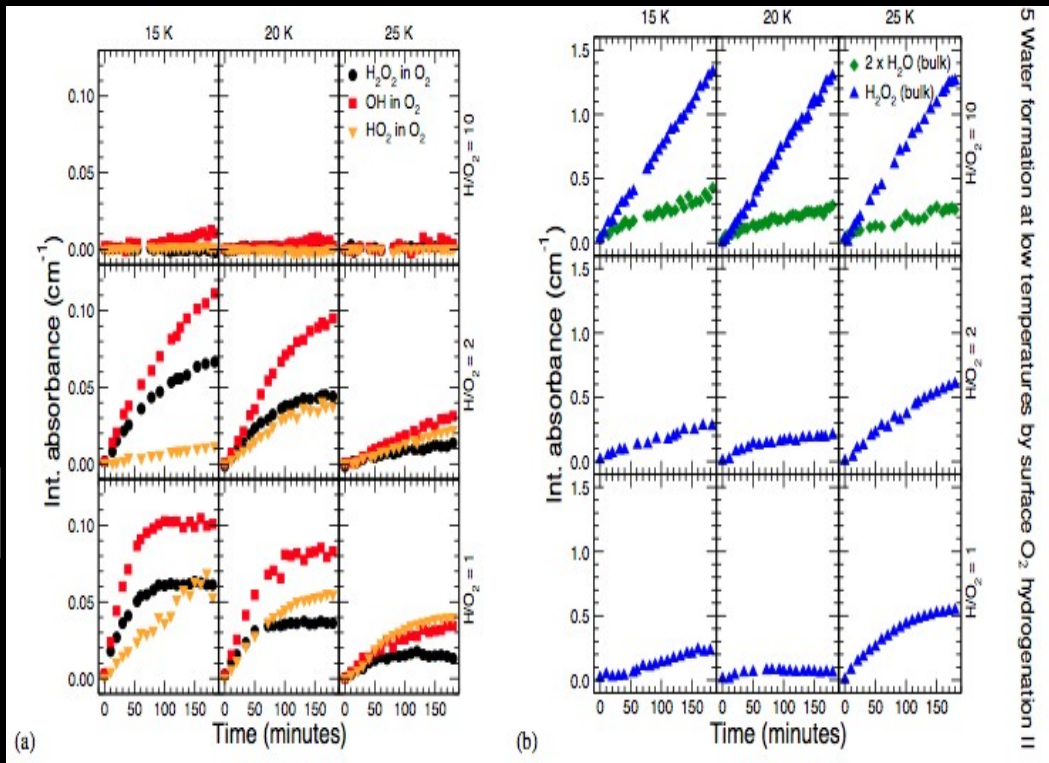
Ioppollo thesis

Water from a combination of O and H

Water is easy to form experimentally !

$O + H$	**Dulieu et al 2010**
$O_2 + H$	**Miyauchi et al 2008, Ioppolo et al 2008 Matar et al 2008, Oba et al 2009, Ioppolo et al 2010, Cuppen et al 2010**
$O_3 + H$	**Mokrane et al 2009, Romanzin et al 2011**
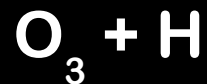
Water is one of the compound _easily_ formed on cold surfaces (10 - 50K)

Water formation rate >> CO + H ; CO+OH …

> H + H

Water is amorphous and compact (Oba et al 2009, Accolla thesis)

Chemical network...
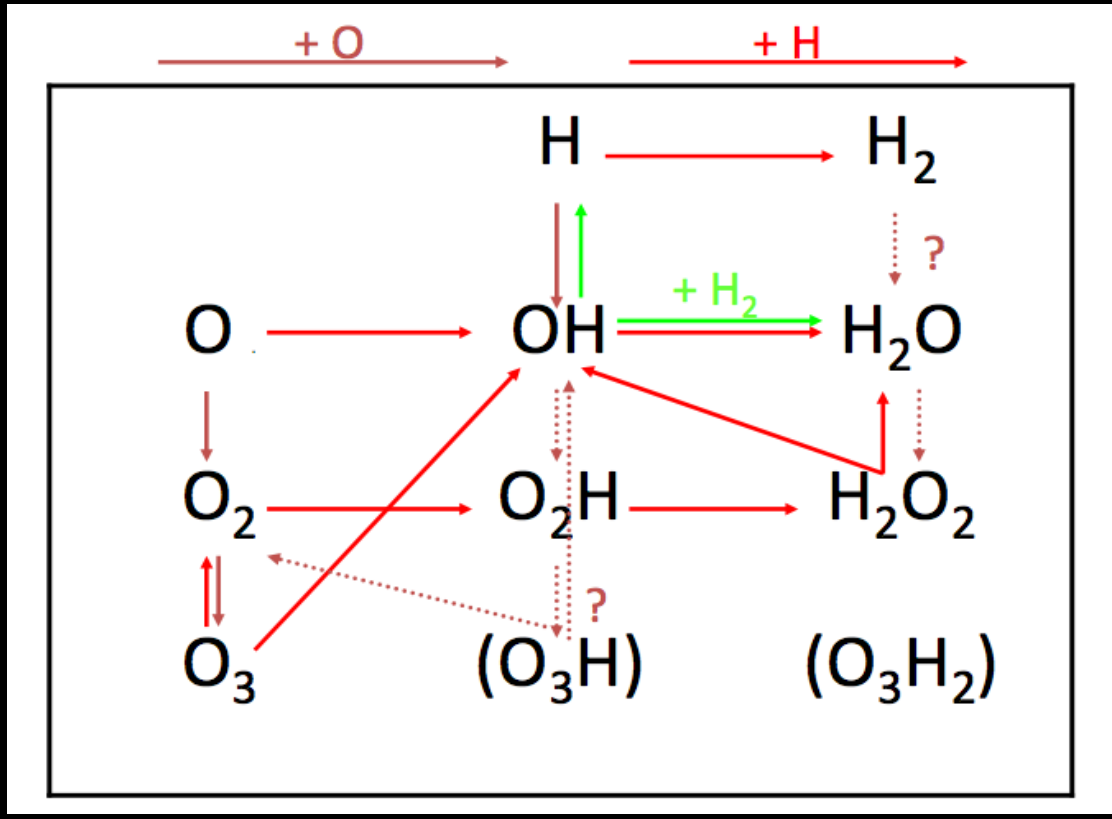
About 20 reactions...
 + different experimental conditions and methods

Experimental agreement ?

Reaction	#	No Barrier	Barrier	No reaction
$O + O \longrightarrow O_2$	1	** ††		
$O_2 + O \longrightarrow O_3$	2	***	†† oo	
$O + H \longrightarrow OH$	3	** †† o		
$O_2 + H \longrightarrow HO_2$	4	*** †† ooo		
$O_3 + H \longrightarrow O_2 + OH$	5	** ††† ooo		
$HO_2 + H \longrightarrow H_2O_2$	6	*** †ooo		
$HO_2 + H \longrightarrow OH + OH$	7	*†ooo		
$HO_2 + H \longrightarrow H_2O + O$	8	†ooo		
$OH + H \longrightarrow H_2O$	9	**†† oo		
$OH + OH \longrightarrow H_2O_2$	12	***† ooo		
$OH + OH \longrightarrow H_2O + O$	13	***†	†	
$H_2O_2 + H \longrightarrow H_2O + OH$	14		***††ooo	
$O + H_2 \longrightarrow H_2O$	15			***††
$O_2 + H_2 \longrightarrow H_2O + OH$	16			***†††ooo
$OH + H_2 \longrightarrow H_2O + H$	17		**oo	††
$O_3 + H_2 \longrightarrow H_2O + O_2$	18			††† ooo

3 items
No doubt

2 items
strong evidences

1 item
weak evidence

No item
?
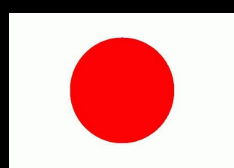
Water formation

The magic box ?
" Chemistry on dust grains is supposed
to work when gas phase do not ! "

Yes, for the case of water !

Water ice formed is compact.

Remaining questions :
- Fraction of water desorbing during the reaction
- OH + H2 ?

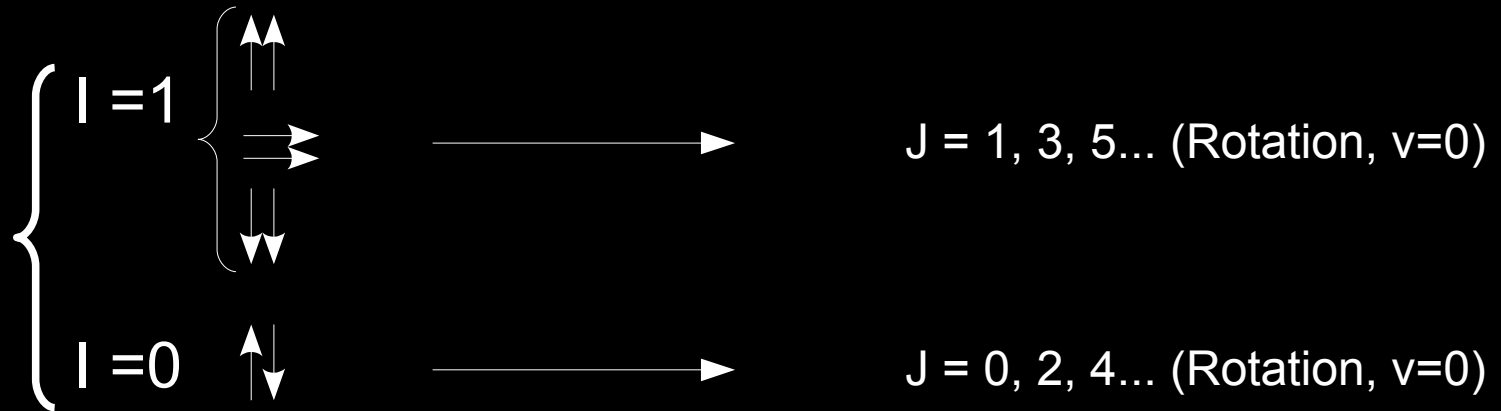# Ortho and para states

X
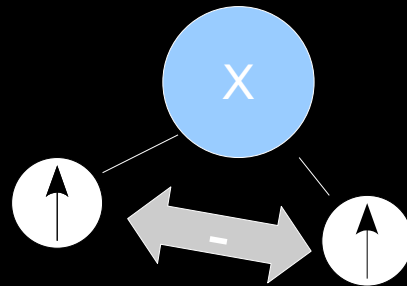
Total wave function must be
antisymetric by proton exchange
Including nuclear spin (NS)

-

For H2 (or H2O) **In Gas Phase**

$I = 1$

$J = 1, 3, 5...$ (Rotation, v=0)

$I = 0$

$J = 0, 2, 4...$ (Rotation, v=0)

Nuclear spin conversion (NSC) H2

Gas phase

30 K

300 K

j=4

j=3

j=2

j=1

j=0

One population

Ortho pop.

para pop.

NSC of H2 on water ice

Expose to H2 (1:3)
Or D2 (2:1)

Probe J with laser

Porous water substrate
10 K

Wait (t)

Porous water substrate
Heat to 30 K

No added O2

3/10000 added O2

3/1000 O2

3/1000 O2
3 x more D2
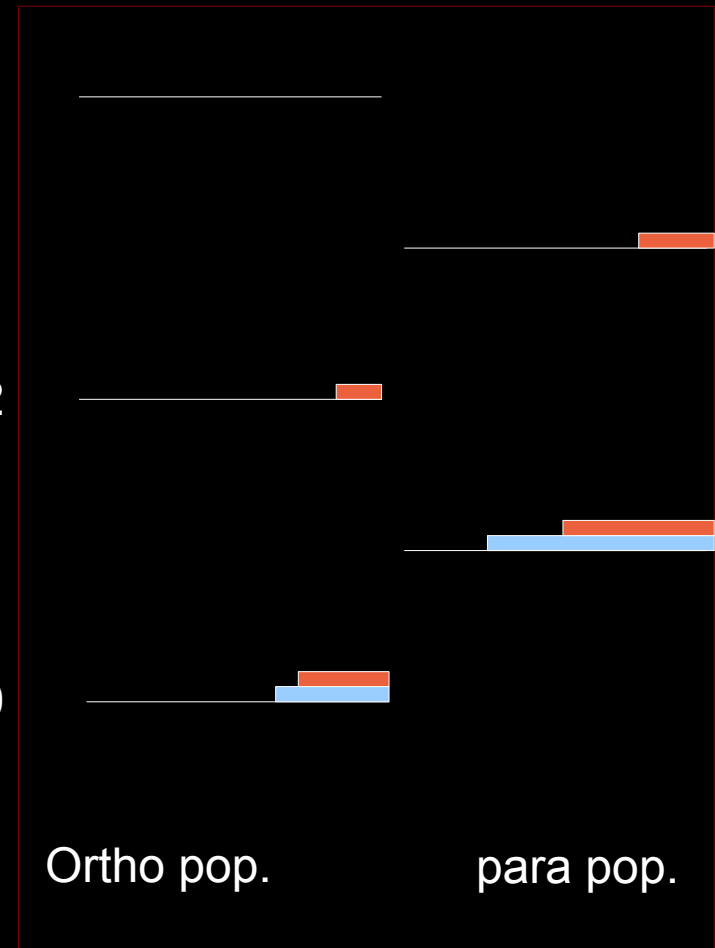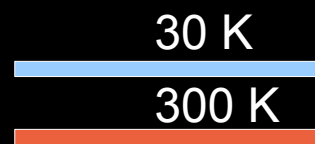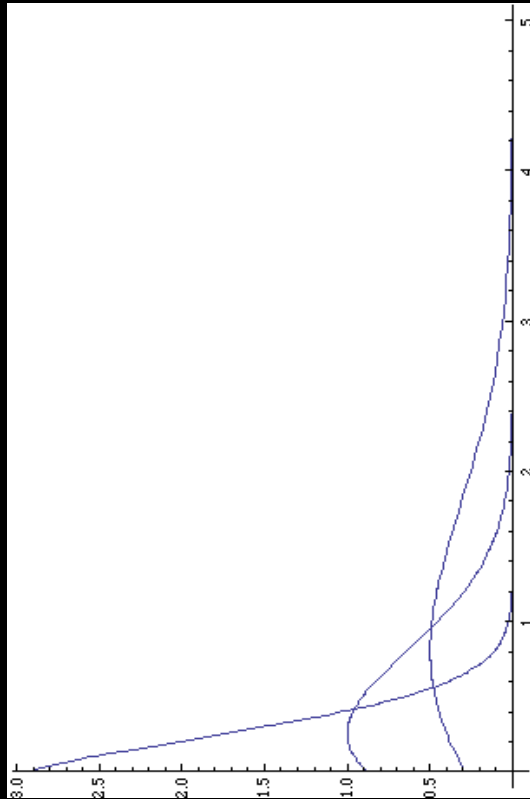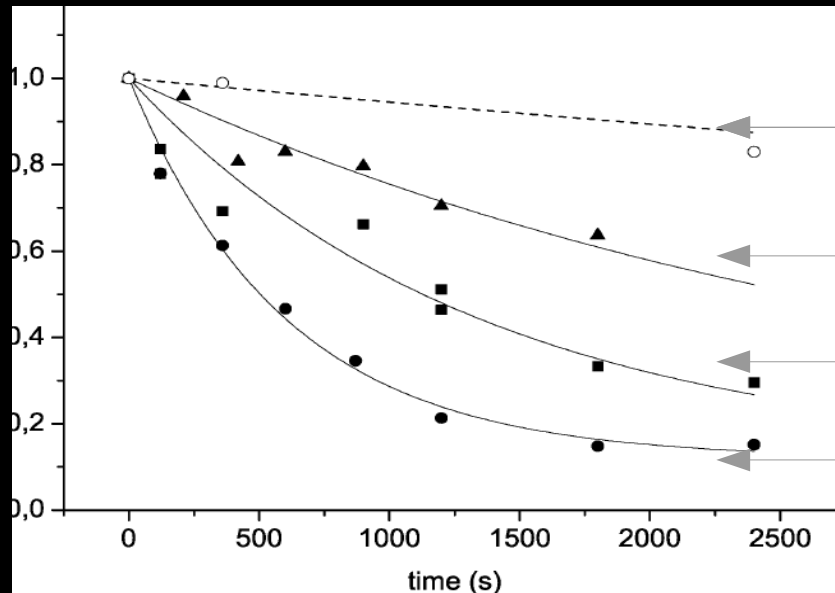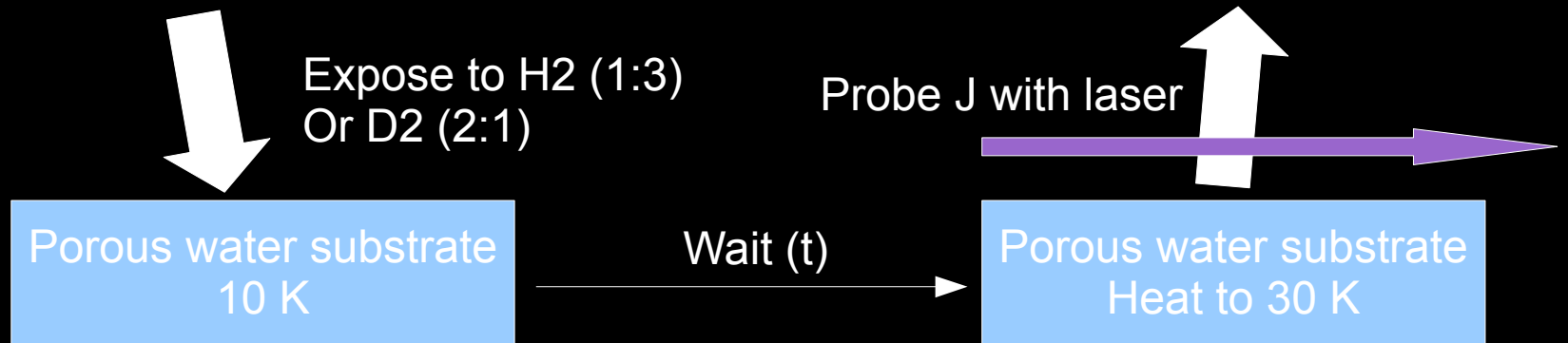
Chehrouri, Fillion et al 2011

A tiny fraction of paramagnetic species induces NCC in solid phase

NSC of water in matrix (I)

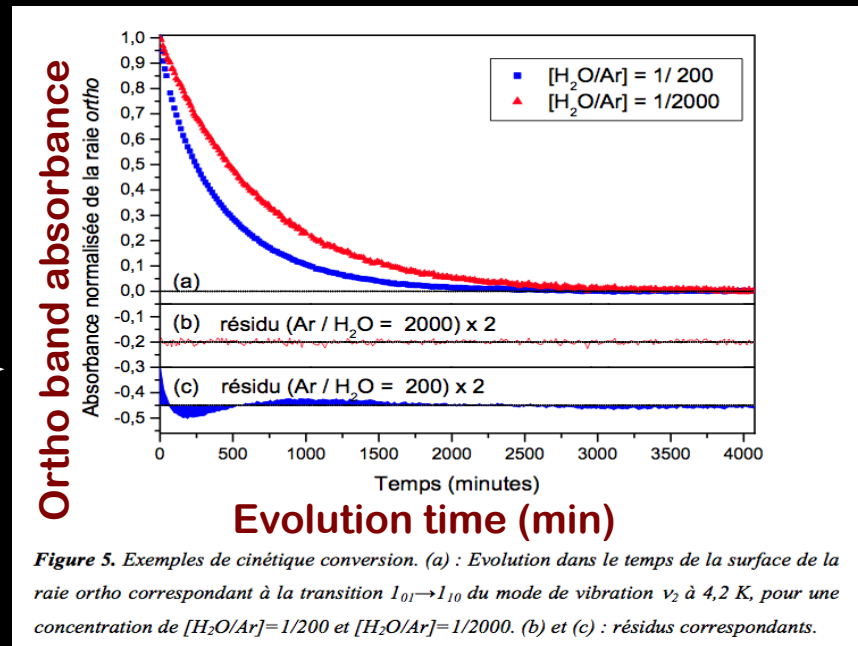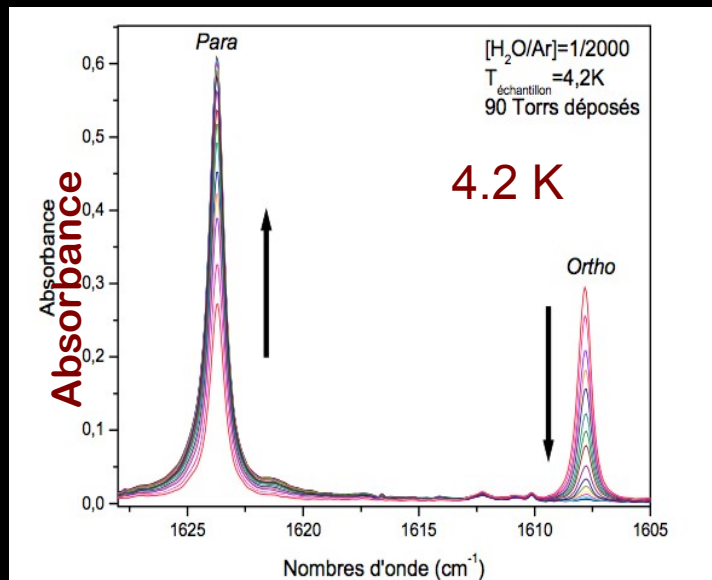Water in rare gas matrix --> pseudo gas phase behaviour

Follow in time IR bands (ortho and para)

LPMAA, Michaut, Fillion et al

Pardanaud thesis 2007

Figure 5. *Exemples de cinétique conversion. (a) : Evolution dans le temps de la surface de la raie ortho correspondant à la transition $1_{01} \rightarrow 1_{10}$ du mode de vibration v_2 à 4,2 K, pour une concentration de [H₂O/Ar]=1/200 et [H₂O/Ar]=1/2000. (b) et (c) : résidus correspondants.*

➡ **Experimental measurement of NSC time**

NSC of water in matrix (II)

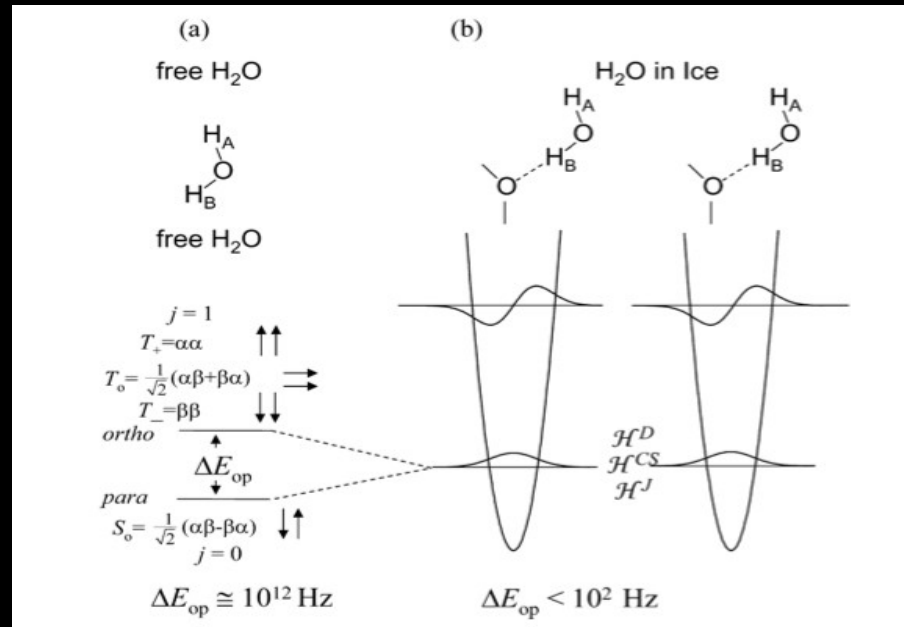**LPMAA, Michaut, Fillion et al**   **Pardanaud thesis 2007**

Figure 7. *Evolution de la constante de conversion de spin nucléaire de H_2O isolée en matrice d'argon d'origine intermoléculaire, en fonction de la dilution en eau.*
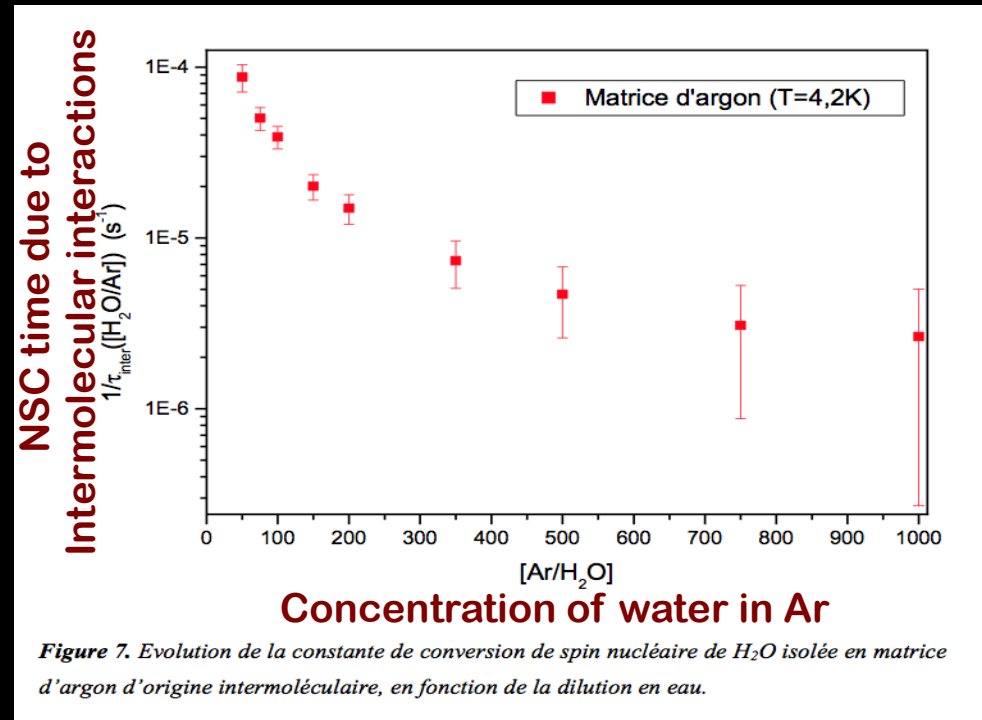
NSC time decreases with:
- the intermolecular interaction (increase)
==> frustrated rotation?
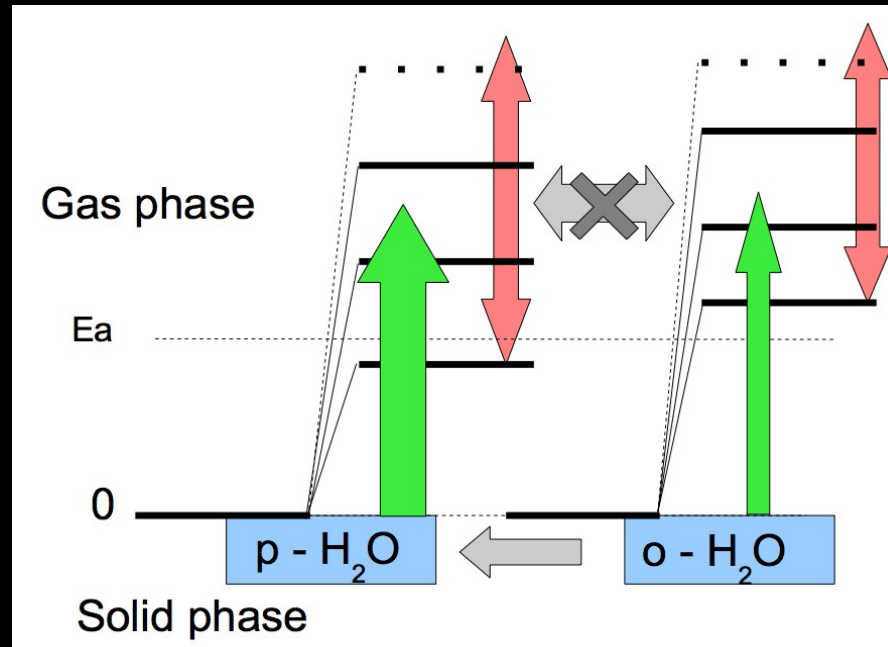
Dipolar NSC of water ice

Buntkowsky et al 2008

Frustration of rotation induces a reduction of energy difference

NSC in water ice it expected to occur in the ms time scale

Differential water desorption from ice

Dulieu, Fillion et al in prep

Desorption time scale << NSC time scale
Due to rotationnal energy the desorption energy of o-H2O is higher
p-H2O desorption is favoured

OPR ~ 2.4 could be a signature of water thermal desorption

Ortho and para ... conclusions

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H2 NSC

H2O NSC

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 and desorpion

Ortho and para states are well defined for gas states

Adsorption of H2 on ice shows a NSC in presence of traces of O2

Intermolecular interactions of H2O in matrix induce NSC

Calculations of dipolar H2O-H2O interaction predict a rapid NSC

Thermal differential desorption from water ice should lead to OPR around 2.4

Experiments more than never needed (project in Lille and Paris)
       to understand OPR from solid to gas phase.

For lab astrophysicists and others

26th - 30th September 2011, Paris

Early registration: up to end of week

Abstracts: 15th of june

For lab astrophysicists and others

Thank you !

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