Preparation, characterisation and storage of water vapour highly enriched in its ortho-H_2O nuclear spin isomer

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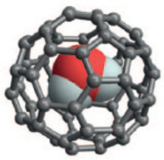
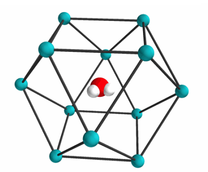
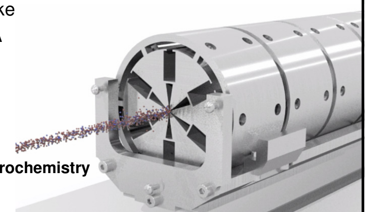
Haifa, ISRAEL

Pierre-Alexandre Turgeon, Jonathan Vermette, Patrick Ayotte
Département de chimie,
Université de Sherbrooke
Sherbrooke, CANADA







2nd Worshop on Nuclear spin effects in astrochemistry
Université Grenoble-Alpes
May 2-4, 2017

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Plan

- **Introduction and motivation**
  - Nuclear Spin Isomers (NSI)
  - Spin temperature (T_{spin}) in interstellar gas and comet
- **Separation and enrichment of NSI**
- **NSI isolation in rare gas matrix**
- **Confinement effects on NSI interconversion mechanism and rates**
- **Conclusions and perspectives**

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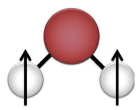
Introduction and motivation

Nuclear Spin Isomers (NSI)

Ortho



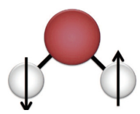
Even spin symmetry

$|1,1\rangle = |\uparrow,\uparrow\rangle$

$|1,0\rangle = \frac{1}{\sqrt{2}}[|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle]$

$|1,-1\rangle = |\downarrow,\downarrow\rangle$

Para



Odd spin symmetry

$|0,0\rangle = \frac{1}{\sqrt{2}}[|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle]$

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Introduction and motivation

Nuclear Spin Isomers (NSI)

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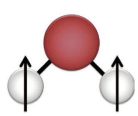

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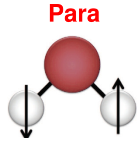
Pauli exclusion principle requires the total **wave function** to be **anti-symmetric** toward proton exchange :

$$|\Psi_{total}\rangle = |\Psi_{vib}\rangle \otimes |\Psi_{rot}\rangle \otimes |\Psi_{nucl}\rangle \otimes |\Psi_{el}\rangle$$

Para



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Introduction and motivation

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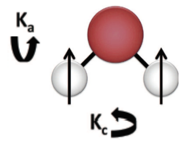

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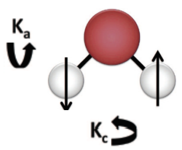
Odd rotational states

$K_a + K_c = 2n+1$

Para



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Introduction and motivation

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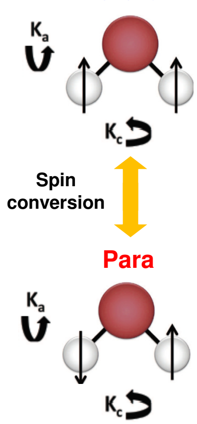

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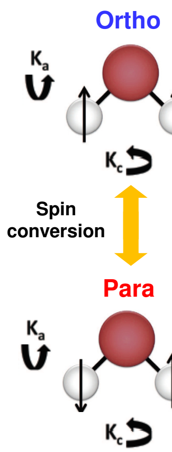
Introduction and motivation

Nuclear Spin Isomers (NSI)



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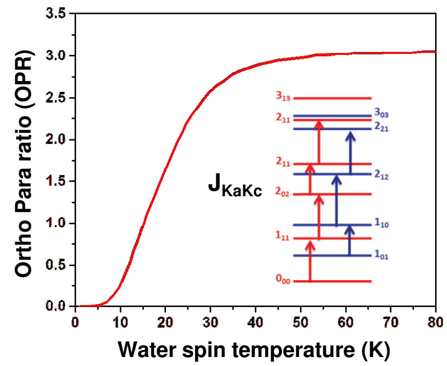

$$\mathrm{OPR} = \frac{3\sum(2J+1)\exp\left[\frac{-E_o(J_{K_a,K_c})}{k_B T_{spin}}\right]}{\sum(2J+1)\exp\left[\frac{-E_p(J_{K_a,K_c})}{k_B T_{spin}}\right]}$$

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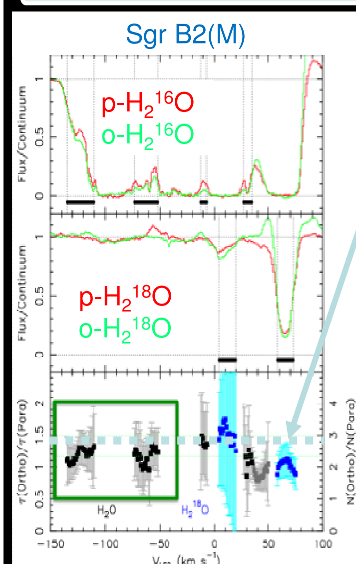
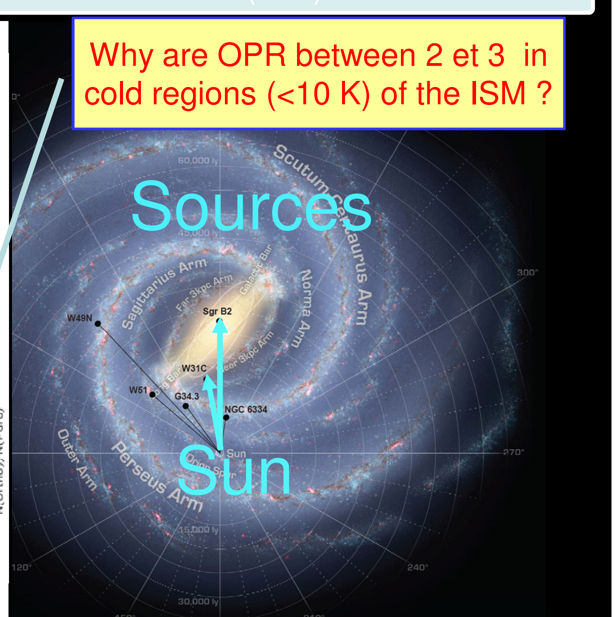
Interstellaire medium (ISM)



Lis *et al* , A&A 521 (2010)

HERSCHEL - HIFI

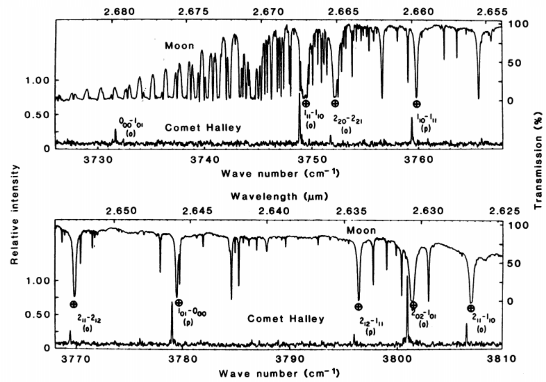


NASA/SSC

R. Monje

Detection of Water Vapor in Halley's Comet

Michael J. Mumma, Harold A. Weaver, Harold P. Larson, D. Scott Davis, Michael Williams



OPR = 2.7
T_{spin} = 32 K !

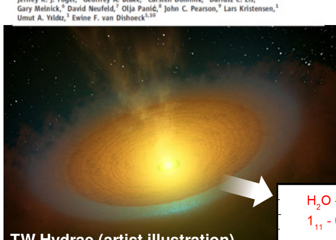
Science **232**, 1523 (1986)

Introduction and motivation

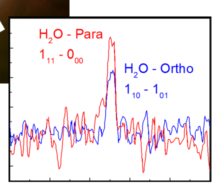
Spin temperature (T_{spin}) in interstellar gas and comet

Detection of the Water Reservoir in a Forming Planetary System

Michiel R. Hogerheijde, Edwin A. Bergin, Christian Brinch, L. Ilsedore Cleeves, Jeffrey K. J. Fogel, Geoffrey A. Blake, Carsten Dominik, Dariusz C. Lis, Gary Melnick, David Neufeld, Olja Panić, John C. Pearson, Lars Kristensen, Umut A. Yildiz, Ewine F. van Dishoeck

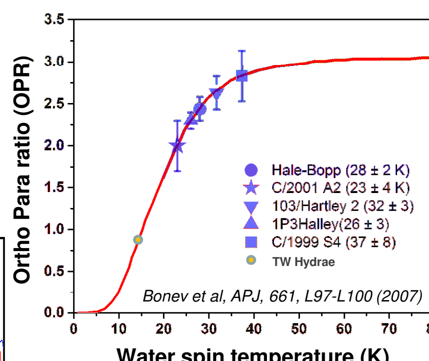


TW Hydrae (artist illustration)
Image credit: NASA



Science **334**, 338 (2011)

OPR = 0,77±0,07
T_{spin} = 13,5±0,5 K !



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Introduction and motivation

Spin temperature (T_{spin}) in interstellar gas and comet

Detection of the Water Reservoir in a Forming Planetary System

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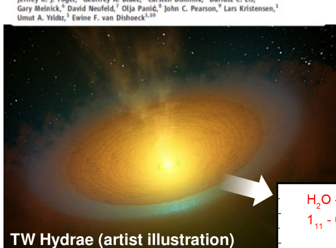
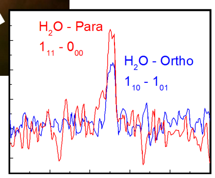


Image credit: NASA



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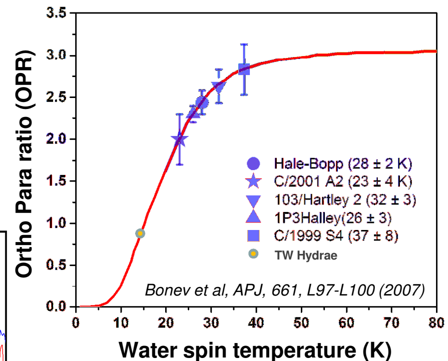

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Interstellar Ices and Comets

Water spin temperatures could be T proxies for ISM provided that:

- … there is no spin conversion in the adsorption/desorption process or in the condensed phase, the spin states are determined upon formation of H_2O and, are preserved in the ISM. $\rightarrow T_{formation}$.

- …the spin states are at equilibrium with the comae, the surface or the nucleus of the comet. $\rightarrow T_{ice}$.

A lot more work needs to be done in the lab to assert these scenarios!

Objective: Designing a methodology that will enable the preparation of sample enriched in either of the spin isomers.

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Ortho/Para Water Separation

Ortho?

Para?

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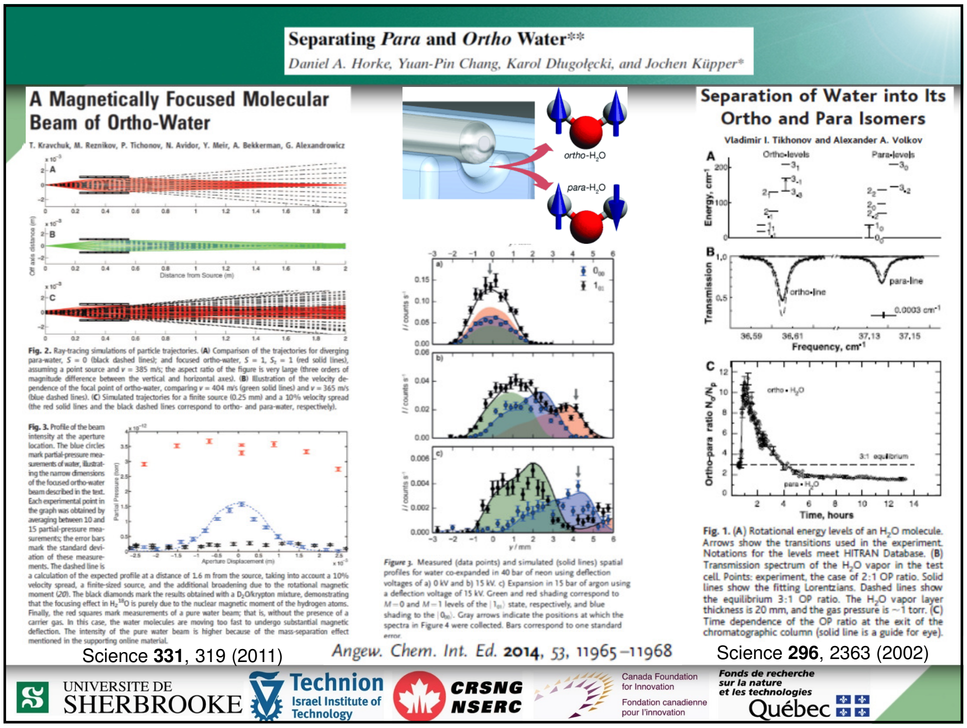
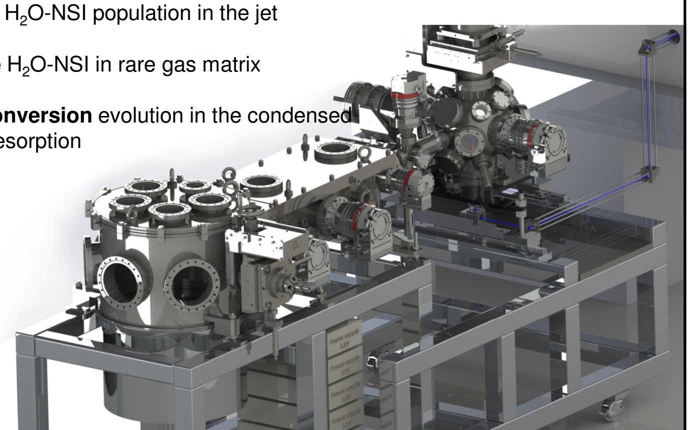


Methodology and experimental setup

Developping a setup that enables us to :

- …**separate** ortho-H_2O from para-H_2O
- …probe **gas phase** H_2O-NSI population in the jet
- …**store** and **isolate** H_2O-NSI in rare gas matrix
- …study NSI **interconversion** evolution in the condensed phase and during desorption



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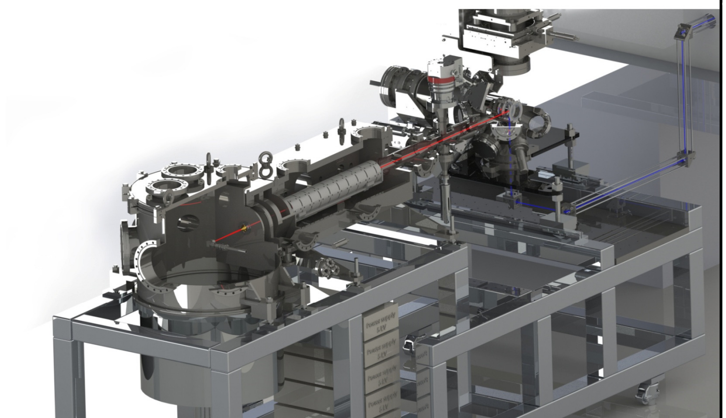
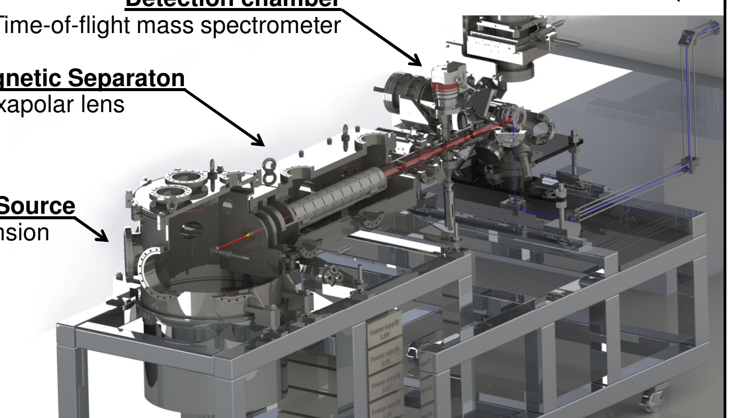
Methodology and experimental setup

NSI separation from molecular beam



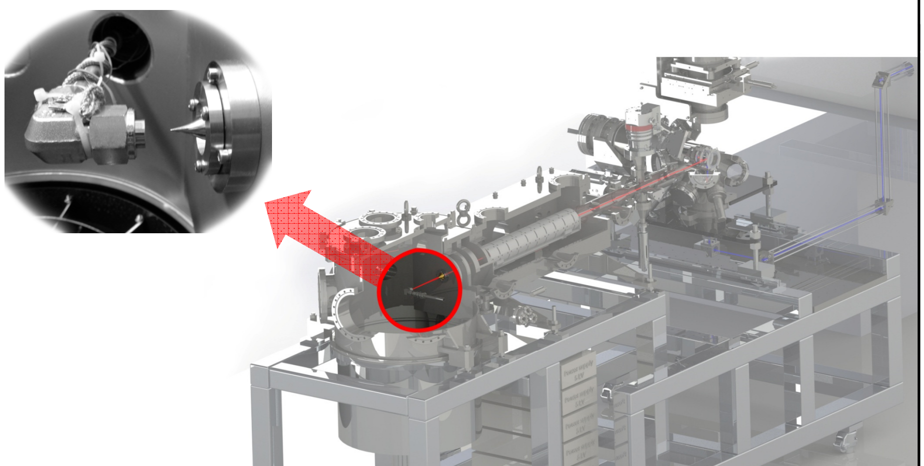
Methodology and experimental setup

NSI separation by magnetic focusing in a molecular beam



Methodology and experimental setup

Supersonic expansion: rotational cooling and seeding



Methodology and experimental setup

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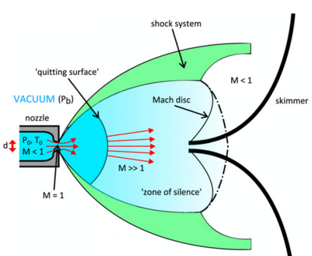
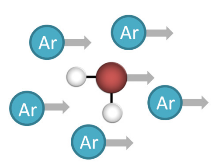
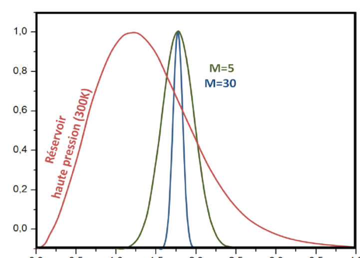


Barr et al Meas. Sci. Technol. (2012)





In the supersonic expansion :

- Mean free path **λ << d_{nozzle}**
- Po >> Pb
- Adiabatic and isentropic expansion
- **H_2O are rotationaly cooled**

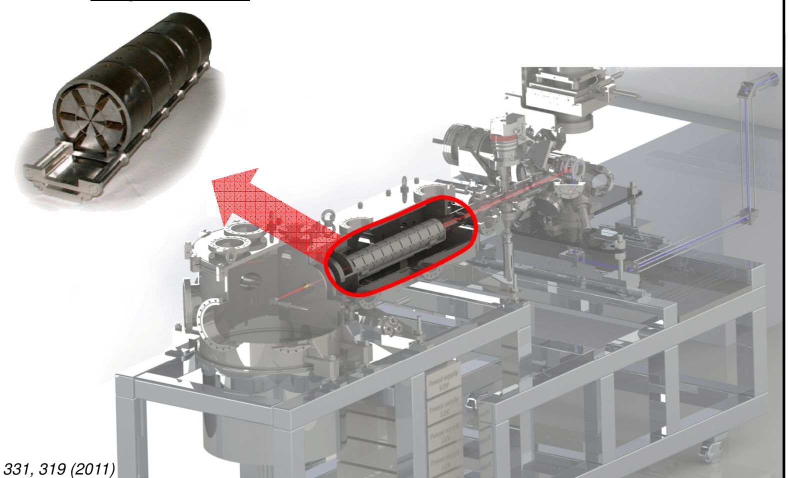
In the molecular Beam :

-1% of H_2O **seeded** in Ar/Kr
- Velocity distribution is narrower
- **H_2O are slowed by seeding in noble gas expansion**

Methodology and experimental setup

NSI separation through magnetic focussing

Magnetic lens



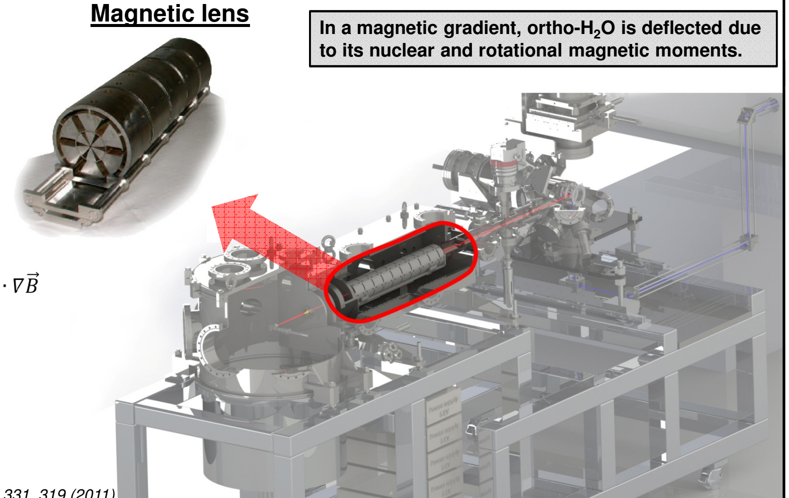
Kravchuk et al, Science 331, 319 (2011)

Methodology and experimental setup

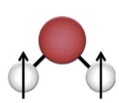
NSI separation through magnetic focussing

Magnetic lens

In a magnetic gradient, ortho-H_2O is deflected due to its nuclear and rotational magnetic moments.

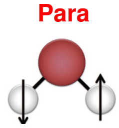


Ortho



$\vec{F} = \nabla(\vec{M} \cdot \vec{B}) = \vec{M} \cdot \nabla\vec{B}$

Para

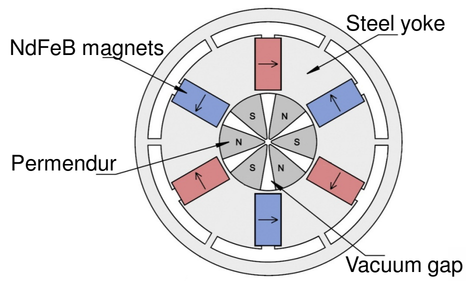


$\vec{F} = 0$

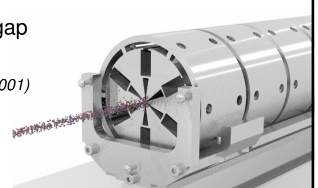
Kravchuk et al, Science 331, 319 (2011)

Methodology and experimental setup

NSI separation through magnetic focussing



Jardine et al. Rev Science Instrument, 72,3834 (2001)



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Methodology and experimental setup

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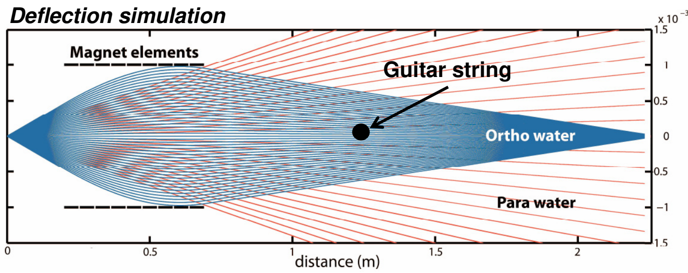
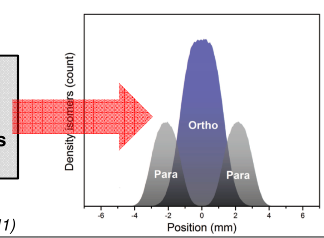


As result, ortho-water m=+1 projection is focalized in the analysis chamber while other states are blocked or defocused



Kravchuk et al, Science 331, 319 (2011)

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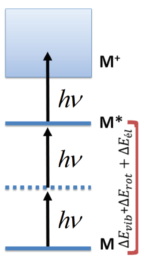
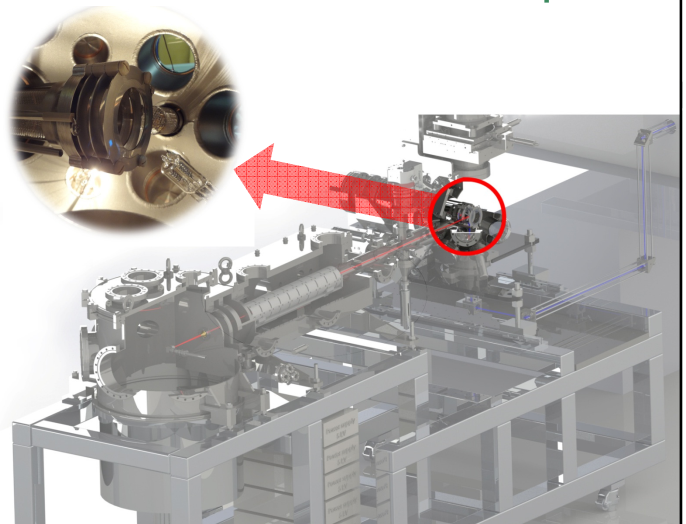
Methodology and experimental setup

Gas phase NSI detection with REMPI-TOF technique

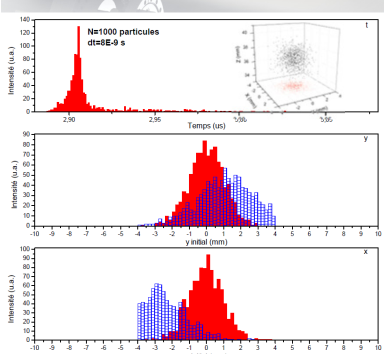
Resonance
Enhanced
Multi-
Photon
Ionization

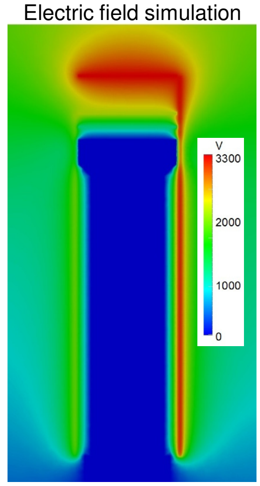


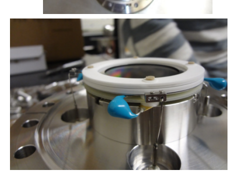


Methodology and experimental setup

Gas phase NSI detection with REMPI-TOF technique

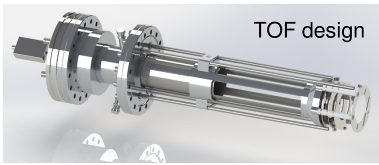


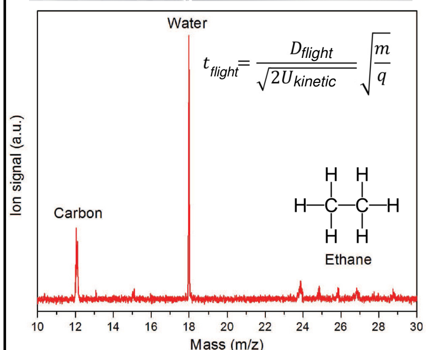




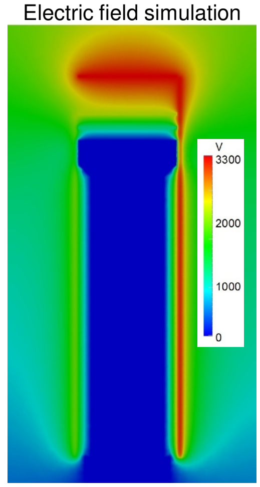
Methodology and experimental setup

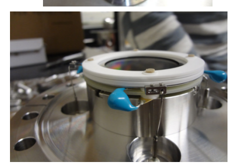
Gas phase NSI detection with REMPI-TOF technique





Electric field simulation



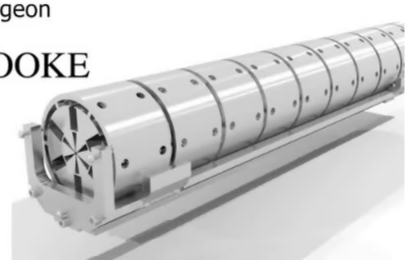


FOCALISATION MAGNÉTIQUE DES ISOMÈRES DE SPIN DE L'EAU ET DÉTECTION PAR REMPI (2+1)

MAGNETIC FOCUSSING OF THE SPIN ISOMERS OF WATER AND DETECTION WITH REMPI (2+1)

Animation:
Pierre-Alexandre Turgeon

UNIVERSITÉ DE SHERBROOKE



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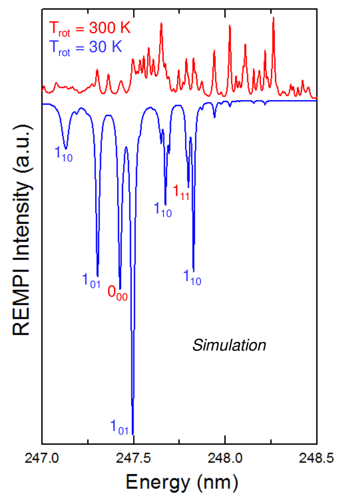

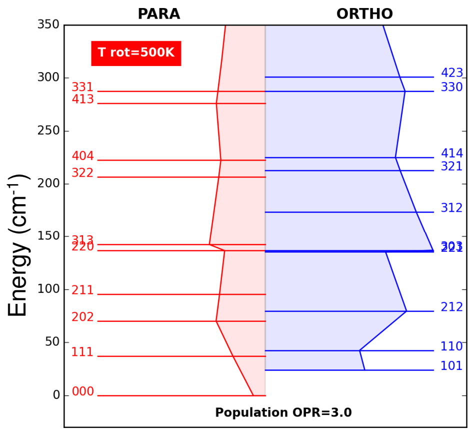

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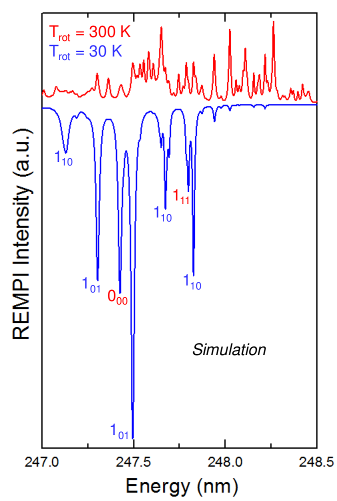

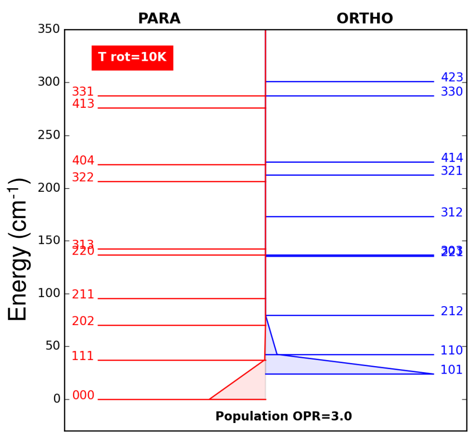

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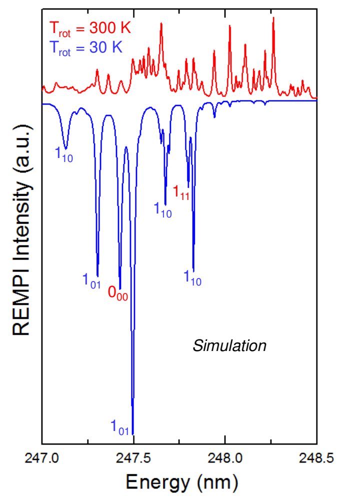

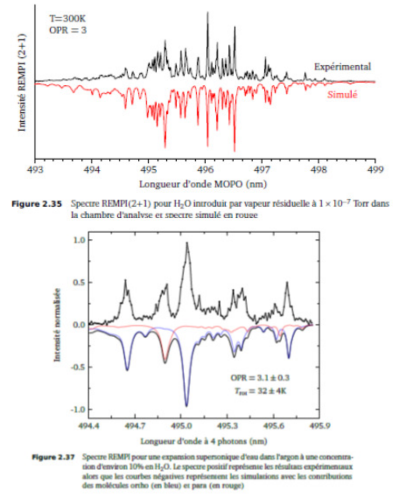

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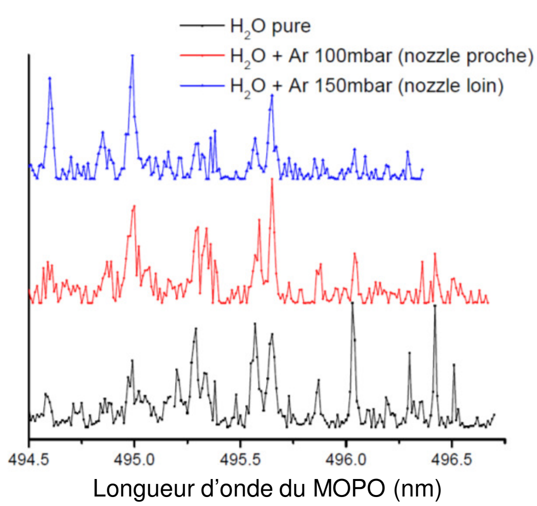
Methodology and experimental setup



Varying source conditions affect rotational temperature (30K<T<150K).

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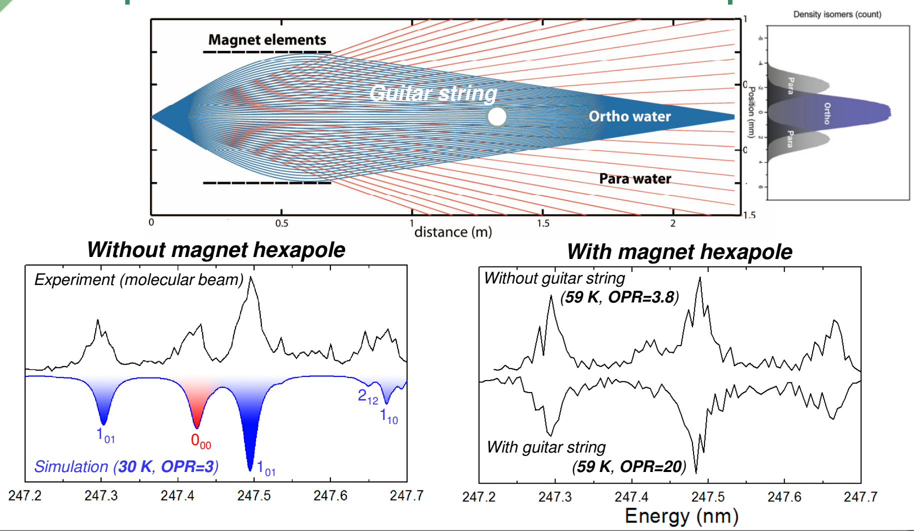

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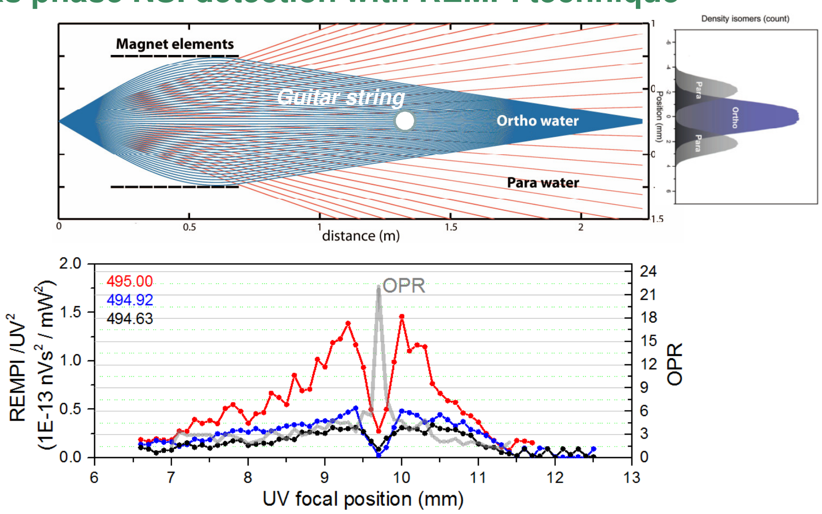

Plan

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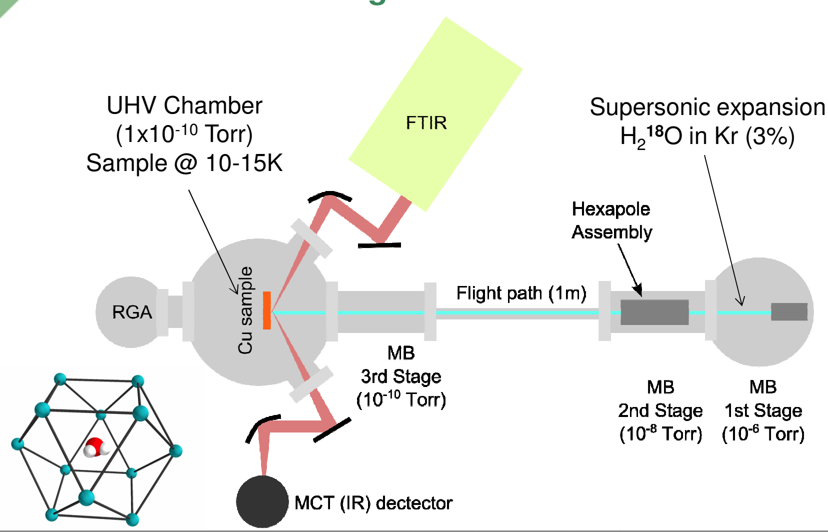
Methodology and experimental setup

NSI isolation in rare gas matrix and characterisation



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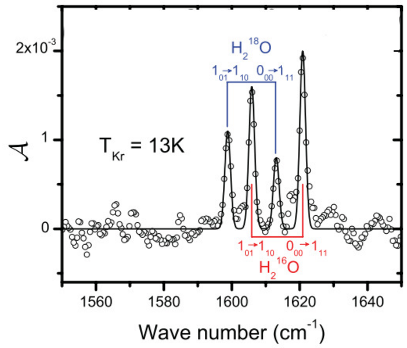
Methodology and experimental setup

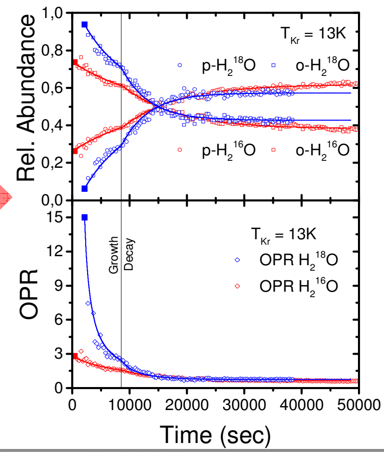
NSI isolation in rare gas matrix and characterisation

Ortho-enriched $H_2{}^{18}O$ from the magnetically focused beam is condensed, along with normal $H_2{}^{16}O$ from the background, into a Kr matrix at 13K.



Turgeon et al PRA (2012)

Enrichment in o-H_2O decays with $t_{½}$ ~2h!



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Some theory

NSI interconversion mechanism

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 46, NUMBER 8 15 APRIL 1967

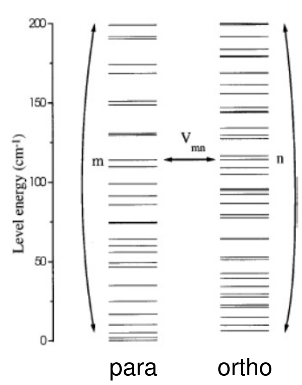
Nuclear Spin State Equilibration through Nonmagnetic Collisions*

R. F. Curl, Jr., Jerome V. V. Kasper,† and Kenneth S. Pitzer
Department of Chemistry, Rice University, Houston, Texas

$$\underbrace{\langle ortho|}\, W \,\underbrace{|para\rangle} \neq 0?$$

$$|1,1\rangle = |{+}{+}\rangle$$
$$|1,0\rangle = \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle + |{-}{+}\rangle\right)$$
$$|1,-1\rangle = |{-}{-}\rangle$$

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle - |{-}{+}\rangle\right)$$



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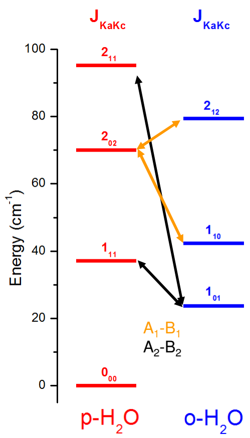
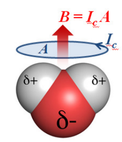


Spin Rotation Coupling

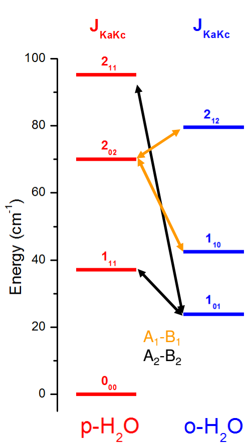
$$H_{SR} = \mathbf{I}_K \cdot C_K \cdot \mathbf{J} \;\rightarrow\; \langle \psi_{para} | H_{SR} | \psi_{ortho} \rangle \neq 0$$



$$\left\langle J^o_{K_aK_c} I^o \middle| H_{SR} \middle| J^p_{K_aK_c} I^p \right\rangle = \sum_{k_o} \sum_{k_p} A^o_{J_o k_o m_o} A^p_{J_p k_p m_p} \left[(-1)^{2J_p+J_o+k_o+1}\right] \times \{15\,[J_p(J_p+1)(2J_o+1)]\}^{\frac{1}{2}} (2J_p+1) \times \begin{Bmatrix} J_p & 1 & J_o \\ 1 & J_p & 0 \end{Bmatrix} \begin{Bmatrix} J_o & J_p & 2 \\ 1 & 1 & J_p \end{Bmatrix} \begin{Bmatrix} J_o & 2 & J_p \\ -k_o & 1 & k_p \end{Bmatrix} C_{ab}$$

Some theory

NSI interconversion mechanism



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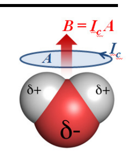
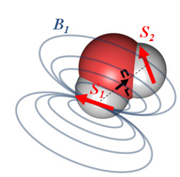


$$\left\langle J^o_{K_aK_c} I^o \middle| H_{SR} \middle| J^p_{K_aK_c} I^p \right\rangle = \sum_{k_o} \sum_{k_p} A^o_{J_o k_o m_o} A^p_{J_p k_p m_p} \left[(-1)^{2J_p+J_o+k_o+1}\right] \times \{15\,[J_p(J_p+1)(2J_o+1)]\}^{\frac{1}{2}} (2J_p+1) \times \begin{Bmatrix} J_p & 1 & J_o \\ 1 & J_p & 0 \end{Bmatrix} \begin{Bmatrix} J_o & J_p & 2 \\ 1 & 1 & J_p \end{Bmatrix} \begin{Bmatrix} J_o & 2 & J_p \\ -k_o & 1 & k_p \end{Bmatrix} C_{ab}$$

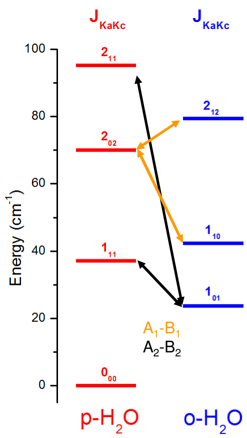
Nuclear magnetic dipole-dipole coupling

$$H^{HH}_{SS} = \mathbf{S}_{H1} \cdot D^{HH} \cdot \mathbf{S}_{H2} \;\rightarrow\; \langle \psi_{para} | H^{HH}_{SS} | \psi_{ortho} \rangle = 0$$



Some theory

NSI interconversion mechanism



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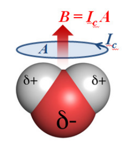

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$$\times \left\{15 \left[J_p (J_p+1)(2J_o+1)\right]\right\}^{\frac{1}{2}} (2J_p+1)$$
$$\times \begin{Bmatrix} J_p & 1 & J_o \\ 1 & J_p & 0 \end{Bmatrix} \begin{Bmatrix} J_o & J_p & 2 \\ 1 & 1 & J_p \end{Bmatrix} \begin{pmatrix} J_o & 2 & J_p \\ -k_o & 1 & k_p \end{pmatrix} C_{ab}$$

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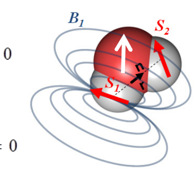
$$H^{OH}_{SS} = \mathbf{I}_{O17} \cdot D^{O17H} \cdot \underbrace{(\mathbf{S}_1 + \mathbf{S}_2)}_{\mathbf{I}_H} \;\rightarrow\; \langle \psi_{para} | H^{OH}_{SS} | \psi_{ortho} \rangle \neq 0$$

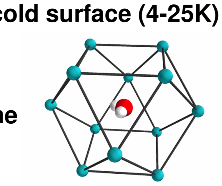


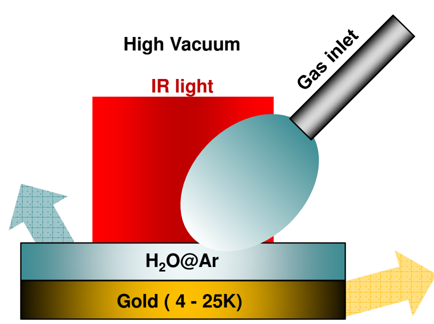
Methodology and experiments

NSI isolation in rare gas matrix

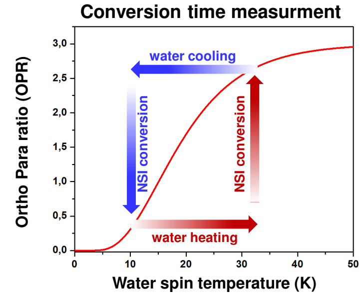
By condensing « normal » H_2O/Ar (1/1000) on a cold surface (4-25K):

- H_2O is **trapped** in argon matrix
- **In matrix**, H_2O is a near-**free rotor**
- **Spin isomer** populations can be probed **over time**





Conversion time measurment



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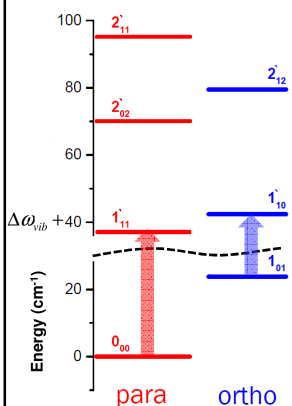

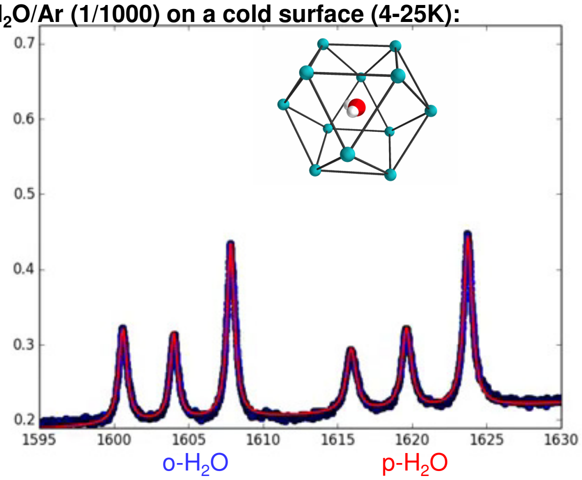

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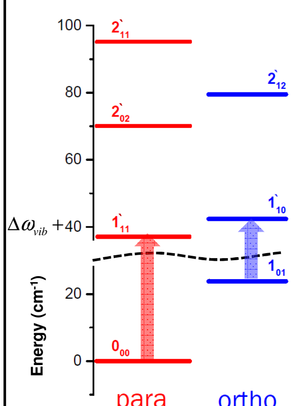
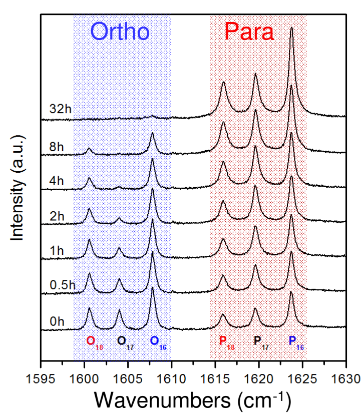
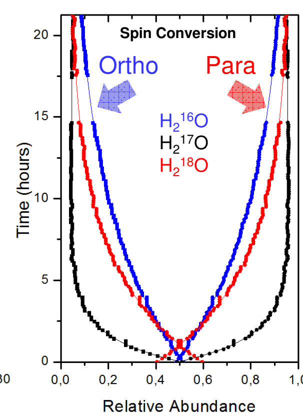
Methodology and experiments

NSI isolation in rare gas matrix

-**Rovibrational** transition **intensity** is a probe for **spin** isomers population
-**Time** for NSI to reach **temperature equillibrium** reveals **conversion rate**
-**Differents** water **isotopomers** ($H_2{}^{16}O$, $H_2{}^{17}O$ and $H_2{}^{18}O$) are under study







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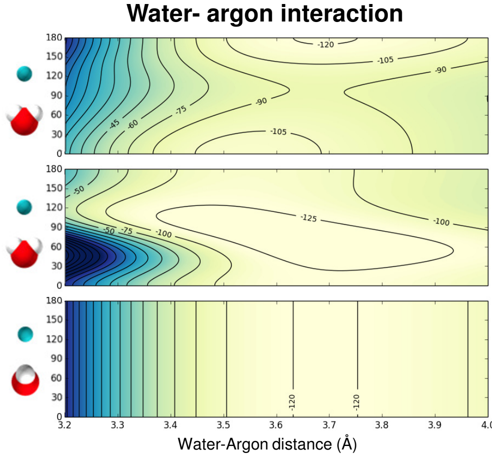
NSI isolation in rare gas matrix

Water- argon interaction



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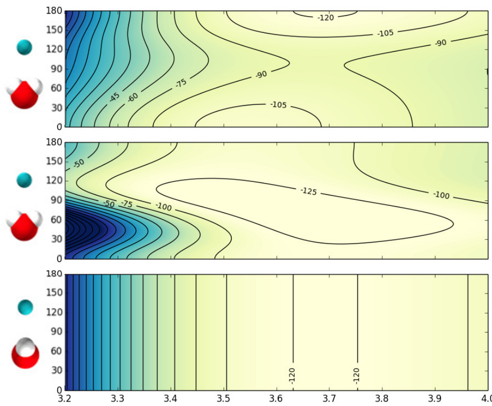
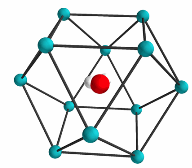
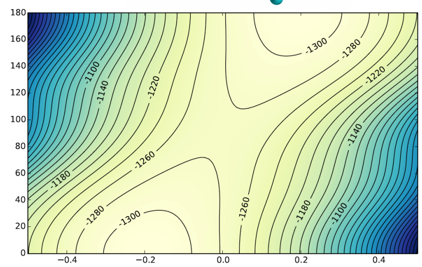


Water in argon matrix





From Ar-H_2O pair potential : Makarewicz, J.Chem.Phys. 129, 184310 (2008); Cohen and Saykally, JCP 95, 7891 (1991).

Methodology and experiments

NSI isolation in rare gas matrix

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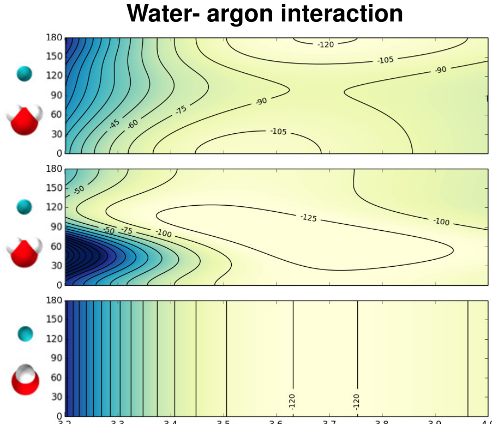

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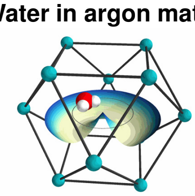

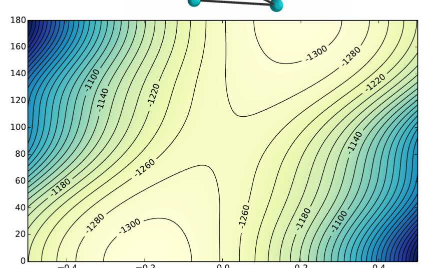

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Methodology and experiments

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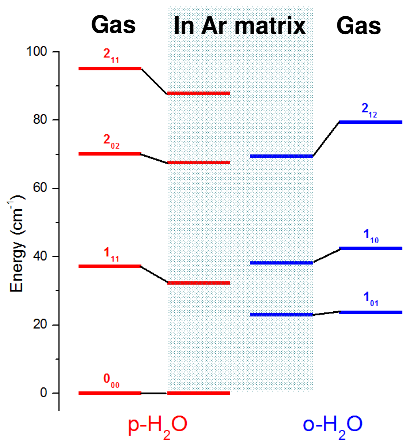
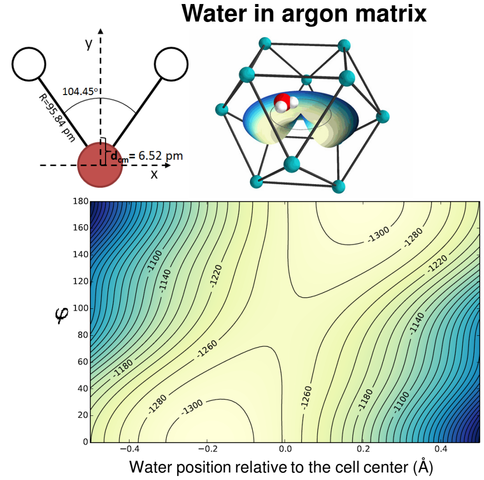


Water in argon matrix



Friedmann and Kimel, J.Chem.Phys. 47 (3589 1967); Ceponkus et al, JCP 138 244305 (2013)

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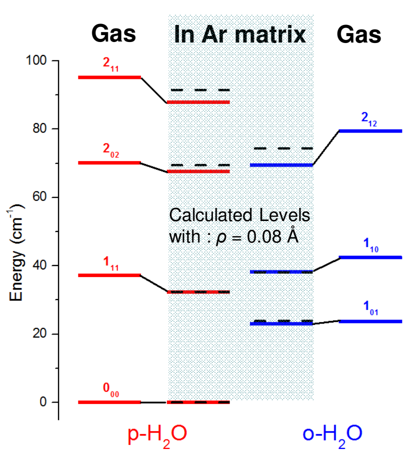
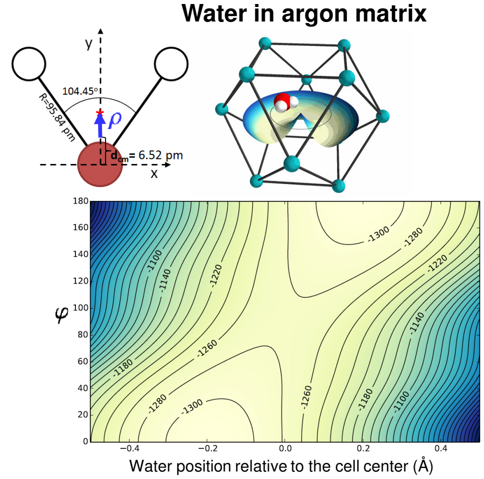


Water in argon matrix



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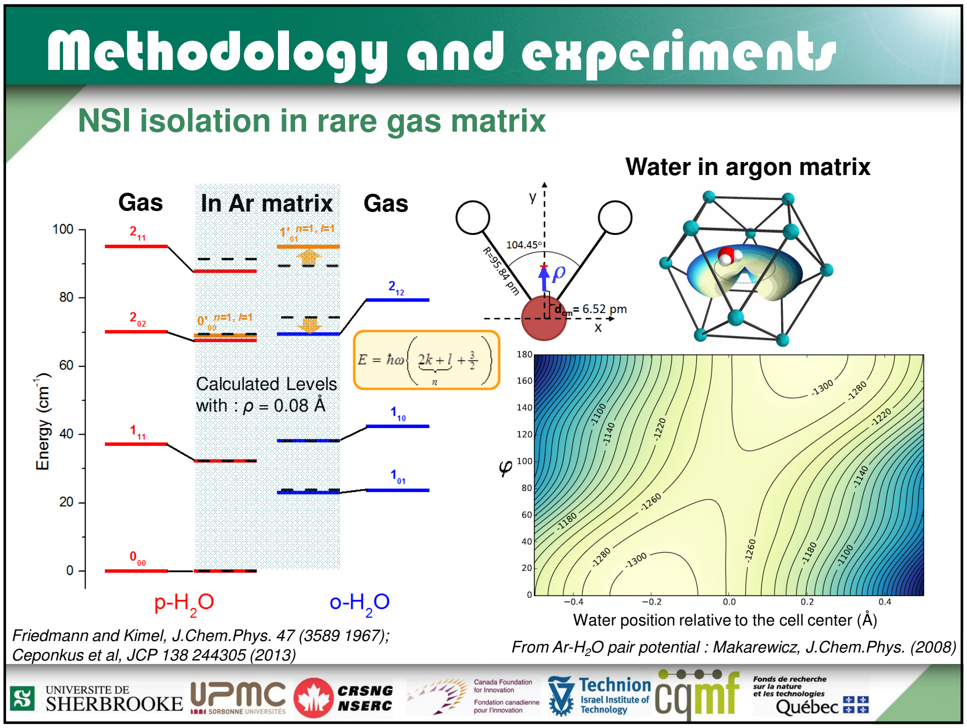
Methodology and experiments
NSI isolation in rare gas matrix
Water in argon matrix
Gas
In Ar matrix
Gas
Energy (cm⁻¹)
Calculated Levels
with : ρ = 0.08 Å
p-H2O
o-H2O
104.45°
R=95.84 pm
dcm = 6.52 pm
Water position relative to the cell center (Å)
Friedmann and Kimel, J.Chem.Phys. 47 (3589 1967);
Ceponkus et al, JCP 138 244305 (2013)
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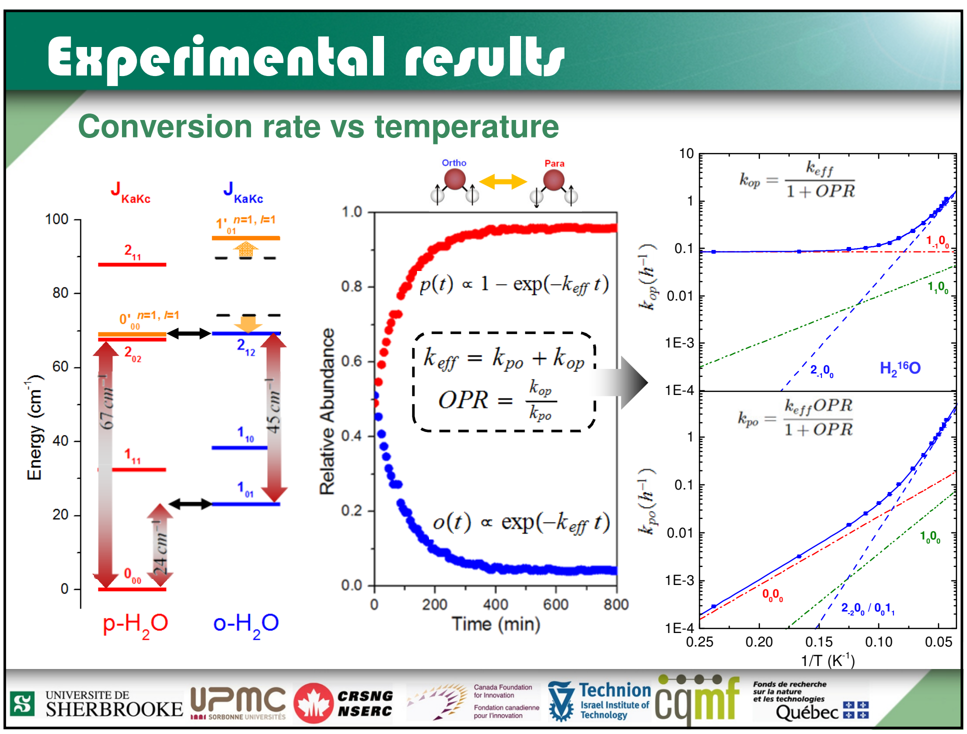
Experimental results
Conversion rate vs temperature
JKaKc
Energy (cm⁻¹)
67 cm⁻¹
45 cm⁻¹
24 cm⁻¹
p-H2O
o-H2O
Ortho
Para
Relative Abundance
Time (min)
p(t) ∝ 1 − exp(−keff t)
keff = kpo + kop
OPR = kop / kpo
o(t) ∝ exp(−keff t)
kop = keff / (1 + OPR)
kpo = keff OPR / (1 + OPR)
H2¹⁶O
1/T (K⁻¹)
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Plan

- Introduction and motivation
  - Nuclear Spin Isomers (NSI)
  - Spin temperature (T_{spin}) in interstellar gas and comet
- Separation and enrichment of NSI
- NSI isolation in rare gas matrix
- Confinement effects on NSI interconversion mechanism and rates
- **Conclusions and perspectives**

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Coda

Conclusions

- Magnetic focussing provides an efficient method to prepare water highly enriched in o-H_2O.
- Enriched sample can be transferred to the condensed phase (i.e., RG matrix)
  $\rightarrow$ Could spin polarisation also be transferred to surfaces? Inert matrices? Ice?
- NSI interconversion is enhanced in confinement due to rotation-translation coupling and is triggered by phonon scattering.

Perspectives

- Exploration of confinement effects $\rightarrow$ $H_2O@C_{60}$, H_2O@inert matrix (including p-H_2), H_2O@beryl as a function of temperature for different isotopologues.
- Heterogeneous reactive scattering: o-$H_2O_{(ads)}$+$CaC_{2(s)}$ $\rightarrow$ o/p-$HCCH_{(g)}$+$CaO_{(s)}$ and o-$H_2O_{(ads)}$+$H_2CO_{(ads)}$ $\rightarrow$ o/p-$H_2C(OH)_{2\ (ads/g)}$ or o-$H_2O_{(ads)}$+$F_3CHO_{(ads)}$ $\rightarrow$ $F_3CH(OH)_{2\ (ads/g)}$.
- Application of water vapour enriched in o-H_2O to enhance sensitivity in NMR spectroscopy/imaging.
- H_2O nuclear spin isomers interconversion dynamics upon scattering/adsorption/desorption on ice, mineral and paramagnetic substrates.

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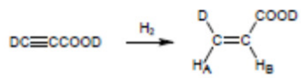
Nuclear Magnetic Resonance

Spin polarized H_2O has enormous potential to enhance sensitivity in NMR (PHIP, PASADENA & ALTADENA)!



Bowers and Weitekamp, **PRL** 57, 2645 (1986).

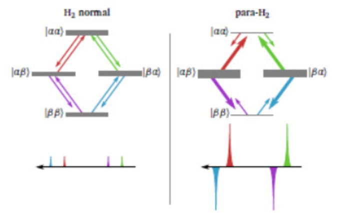
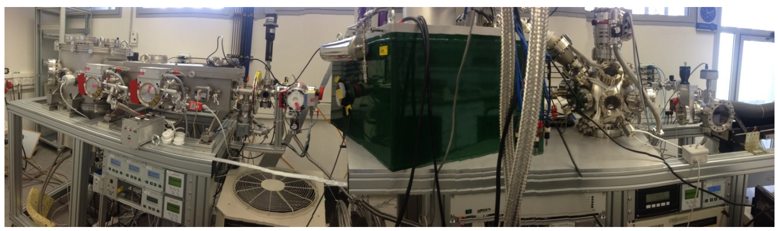


Figure I.4 Niveaux d'énergie pour un système à deux spins de type AX. Le panneau de gauche représente la spectroscopie RMN conventionnelle alors que le panneau de droite représente la spectroscopie RMN après une réaction d'hydrogénation au parahydrogène, ce qui mène à une hyperpolarisation des niveaux $|\alpha\beta\rangle$ et $|\beta\alpha\rangle$.



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Thanks, Merci, Toda

Team Sherbrooke

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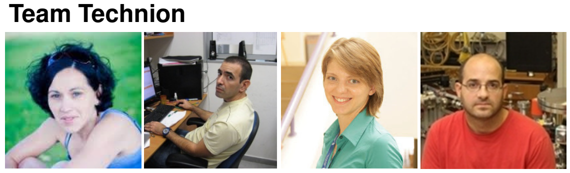
Team Technion



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