Nuclear spin symmetry conservation in H$_2$O investigated by direct absorption FTIR spectroscopy of water vapor cooled down in supersonic expansion


(To be published in JPCA 2017)

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Introduction

- Nuclear spin conversion of water in the gas phase is still an open question.

- Intramolecular processes in an individual water molecule can not lead to spin conversion.

- However an interaction between a water molecule and a water cluster has been evoked as a possible route towards ortho-para conversion (Manca Tanner et al 2013).

- Water clusters can be formed in an adiabatic expansion. However, ortho-para conversion in condensed phase occurs on a timescale of milliseconds (Limbach et al 2006; Abouaf-Marguin et al 2007; Sliter et al 2011). Is the “interaction time” long enough in a supersonic expansion to lead to nuclear spin conversion?
Previous work done by Manca Tanner et al. JPCA 2013

- CRDS + Slit jet expansion
- 2OH stretching range
- 3 rovibrational lines are observed
- Detection of water clusters not possible

$R(1_{1,0})$
- ortho

$R(1_{1,1})$
- para

$R(2_{1,2})$
- ortho

No conversion
(weak clustering)

Conversion!
(strong clustering)
Our objectives

- Is the experiment performed by Manca Tanner et al. reproducible?

- The **number of observed water transitions** has to be increased in order to get a reliable conclusion and to confirm (or to infirm) the results obtained by Manca Tanner et al.

- Is it possible to detect **water clustering** which is supposed to play a major role in the nuclear spin conversion? What is the proportion of water molecules condensing in the jet?

- Can we characterize the flow expansion accurately?
Rotational states associated to para- and ortho-H$_2$O

The Pauli exclusion principle states that the total wave function of H$_2$O must be antisymmetric under hydrogen atoms (fermions) exchange

$\Rightarrow$ Ortho- and para- molecules have different Rotational states

In the present study:
- Ground electronic state (symmetric wave function)
- Ground vibrationnel state (symmetric wave function)

The symmetry of $\psi_{Tot}$ depends on the symmetry of $\psi_{rot}$ et $\psi_{ns}$.
Rotational states associated to para- and ortho-$H_2O$

A symmetric rotational wave function $[A^+/e,e$ or $A^-/o,o]$ must correspond to an antisymmetric nuclear spin wave function $[B^+]$, that is to say to para-$H_2O$ with a statistical weight $g_{NS} = 1$.

An antisymmetric rotational wave function $[B^+/o,e$ or $B^-/e,o]$ must correspond to a symmetric nuclear spin wave function $[A^+]$, that is to say to ortho-$H_2O$ with a statistical weight $g_{NS} = 3$. 
Rotational states associated to para- and ortho-$\text{H}_2\text{O}$

From Manca Tanner et al. JPCA 2013
Ortho-to-Para Ratio (OPR)

\[ OPR(T) = \frac{\sum g_{NS}(\text{ortho})g_J(\text{ortho}) \exp\left(-\frac{\hbar c E_{\text{ortho}}}{kT}\right)}{\sum g_{NS}(\text{para})g_J(\text{para}) \exp\left(-\frac{\hbar c E_{\text{para}}}{kT}\right)}. \]

From Crovisier Faraday Discuss., 109, 437 (1998)

High temperature limit
OPR = 3

Low temperature limit (0 K)
OPR = 0
The two limiting cases in a supersonic expansion

1. Instantaneous nuclear spin conversion (equilibrium)
   The OPR adapts instantly to the equilibrium curve as the temperature of the gas expansion evolves
   \[
   OPR(T) = \frac{3 \sum g_J(\text{ortho}) \exp\left(-\frac{\hbar c E_{\text{ortho}}}{kT}\right)}{\sum g_J(\text{para}) \exp\left(-\frac{\hbar c E_{\text{para}}}{kT}\right)}.
   \]

2. Absence of nuclear spin conversion
   The number of ortho- and para- molecules remains what it was initially in the room temperature reservoir (OPR is fixed to 3)
   \[
   OPR(T) = \left(\frac{g_{\text{NS(ortho)}}}{g_{\text{NS(para)}}}\right)_{\text{Slow}} \frac{\sum g_J(\text{ortho}) \exp\left(-\frac{\hbar c E_{\text{ortho}}}{kT}\right)}{\sum g_J(\text{para}) \exp\left(-\frac{\hbar c E_{\text{para}}}{kT}\right)} = 3
   \]
   In that case, we have to consider an effective nuclear spin statistical weight
   \[
   \left(\frac{g_{\text{NS(ortho)}}}{g_{\text{NS(para)}}}\right)_{\text{Slow}} = \frac{3}{\left(\frac{\sum g_J(\text{ortho}) \exp\left(-\frac{\hbar c E_{\text{ortho}}}{kT}\right)}{\sum g_J(\text{para}) \exp\left(-\frac{\hbar c E_{\text{para}}}{kT}\right)}\right)}
   \]
How to access to the number of nuclear spin isomers?

This information is extracted from the absorption line intensities (absorbances)

\[
\frac{A_{f_i}}{A_{f'_{i'}}} = \frac{F_{f_i}^N}{F_{f'_{i'}}^N} \times \frac{n_i}{n_{i'}} = \frac{F_{f_i}^N}{F_{f'_{i'}}^N} \times \frac{g_i}{g_{i'}} \exp \left( -\frac{h\nu (E_i - E_{i'})}{kT} \right)
\]

Absorbance (integrated line area)

Line strength

Fractional population in the initial state

\[ g_i = g_{NSGJ} \]
Direct absorption FTIR spectroscopy
Jet-AILES apparatus

- Bellows
- M₁, M₂
- Pumping
- Polypropylene windows
- M₃, M₄
- MCT Detector
- Modulated IR parallel beam from FTS
- Optical compartment
- Slit nozzle
- Expansion chamber
Supersonic slit-jet expansion (characterized by Pitot probe)

Slit dimension
Width either 18 or 36 μm
Length 60 mm

Hydrodynamic time
between 3 (He) and 9 (Ar) μs

The gas concentration can be easily estimated from these measurements
Tuning of the temperature

Temperature is tuned by:
- condensing a fraction of the water vapor in the expansion
- changing the specific heat ratio of the carrier gas
- changing the rotational relaxation efficiency of the carrier gas
Few spectra (OH stretching region)

$\chi = 6.47\%$
$T_{rot} = 32.1 \pm 0.4 K$

$\chi = 1.23\%$
$T_{rot} = 13.3 \pm 0.2 K$

$\chi = 0.41\%$
$T_{rot} = 9.8 \pm 1.5 K$

Wavenumber / cm$^{-1}$
Few spectra (OH stretching region)

Instrumental resolution: 0.002 cm$^{-1}$
Rotational temperature

- Example of "Boltzmann plot" used to extract the rotational temperature from the absorbance spectra
- Ortho and para lines are treated separately
- The low temperature is corrected from the warm gas contribution

\[ n_J(2J+1) \text{ (molecule/cm}^2) \]

Rotational Energy (K)

- \( T_{\text{hot}} = 251 \pm 11 \text{ K} \)
- \( T_{\text{ortho}} = 32.3 \pm 0.4 \text{ K} \)
- \( T_{\text{para}} = 31.9 \pm 0.4 \text{ K} \)
<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>( \text{H}_2\text{O} )</th>
<th>( P_{\text{H}_2\text{O}} )</th>
<th>( P_0^b )</th>
<th>( P_{ch}^c )</th>
<th>( d^{i/d} )</th>
<th>( T_{\text{rot}(O/P)}^z )</th>
<th>( N L_{\text{cold}}^{j} )</th>
<th>( T_{\text{rot}}^g )</th>
<th>( N L_{\text{hot}}^{f} )</th>
<th>( \tau_{\text{hyd}}^h )</th>
<th>( x_{\text{cond}}^i )</th>
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<tr>
<td>slm</td>
<td>g/h</td>
<td>slm</td>
<td>( \text{mol}% )</td>
<td>hPa</td>
<td>hPa</td>
<td>( \mu\text{m} )</td>
<td>K</td>
<td>molec/cm(^2)</td>
<td>K</td>
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<td>Ar</td>
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<td>1.73</td>
<td>843</td>
<td>0.71</td>
<td>36</td>
<td>10.7±1.6 / -</td>
<td>1.1±0.3</td>
<td>-</td>
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<tr>
<td>He</td>
<td>20</td>
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<td>He</td>
<td>20</td>
<td>8</td>
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<td>0.82</td>
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<td>0.71</td>
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<td>11.6±0.3 / 13.4±2.7</td>
<td>4.3±0.3</td>
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<td>O(_2)</td>
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<tr>
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<td>0.41</td>
<td>8.25</td>
<td>2013</td>
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<td>36</td>
<td>41.8±3 / 39.7±4</td>
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</tbody>
</table>

\(^a\) water vapor/carryer gas molar ratio; \(^b\) stagnation pressure; \(^c\) residual pressure in the expansion chamber; \(^d\) nozzle width (the slit length is 60 mm); \(^e\) rotational temperature extracted from ortho (O) or para rovibrational lines (P); \(^f\) column densities for hot and cold gases (see text for details); \(^g\) rotational temperature of the warm residual gas in shear layers; \(^h\) hydrodynamic time; \(^i\) fraction of condensed water vapor.
Water clusters signature
Water clustering

Intrum. Resolution
1 cm\(^{-1}\)
**Water condensation**

- Water vapor condenses all the more as its partial pressure is high.
- A maximum of 83% of condensation is achieved in argon.
- Condensation is responsible for a significant rise in temperature.

![Graph showing water expanded in argon](image)
No nuclear spin conversion was observed...
Conclusion

Unlike Manca Tanner’s study, no nuclear spin conversion was observed in our supersonic expansion, despite:

- Similar jet conditions
- A very good signal-to-noise ratio
- A direct observation of water clusters
- A larger covered temperature range (10 – 42 K)
- A larger range of water mole fraction (0.2 – 6.5%)
Use of de Laval nozzle uniform flows instead of free-jet expansions

- Interaction time increased from few $\mu$s to $\sim 1$ ms
- Intense clustering
- Equilibrated translational and rotational temperatures