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

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Co-authors


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OPR of H$_2$O vs T in Ar matrix and in gas phase

Questions:
- Validity of these curves in presence of solid at low temperature
- Dynamics without proton exchange
Ortho-Para conversion dynamics with no proton exchange

OPR vs T at equilibrium for isolated molecules often used to define Spin Temperature.
Ortho-Para conversion dynamics with no proton exchange

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

Ortho-Para transition probability

\[ P(\text{O} \rightarrow \text{P}) = 2 |V_{op}|^2 \frac{\Gamma_{op}}{\omega_{op}^2 + \Gamma_{op}^2} (W_o + W_p) \]

Magnetic coupling
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$_2$CO 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 $\tau = 5$ hours for H$_2$O 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

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Lower temperature?

Cacciani et al PRA 80 (2009), PRA 85 (2012)
Second approach: cold matrices experiments

The Sample:
- polycrystalline
- low $H_2O$ concentration
- thicknesses 50 et 500 µm

Cold Finger (3-100 K)

$H_2O$: rare gas mixture

FTIR
400-4000 cm$^{-1}$ (0.03 cm$^{-1}$)

$H_2O$ and Ar gas mixture
H$_2$O in Argon Matrix

Bending vibrational band of water

Para
I=0
g$_I$=1
$J_{K,K_c}$
$2_{20}$

Ortho
I=1
g$_I$=3
$[v_1, v_2, v_3]$
$2_{21}$

$1_{11}$
$0_{00}$

$2_{12}$
$[0,1,0]$ 

$1_{10}$
$1_{01}$

$E_{\text{Energie (cm}^{-1})}$

Absorbance

Wavenumber (cm$^{-1}$)

$20$ K
H$_2$O in Argon Matrix

**Ortho**
- $I=1$
- $g_l=1$
- $[v_1,v_2,v_3]$

**Para**
- $I=0$
- $g_l=1$

Absorbance

Wavenumber (cm$^{-1}$)

Bending vibrational band of water

« Frozen » populations O/P(20 K) à 4.2 K : disequilibrium
Slow return to equilibrium after a fast cooling from 20 K

Time evolution of the rovibrational spectrum
Bending mode region $\nu_2$ of H$_2$O

- Abs (a.u.)
- Time (hours)
- Wavenumbers (cm$^{-1}$)
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 $\nu_2$ of H$_2$O
Behavior at Low Concentration

$H_2O/Ar = 1/10000$

Exponential Decay

NSC Time at 4.2 K: ~10 h
Time evolution of $x_0(t)$ for high concentration of H$_2$O in Ar matrix cannot be fitted by a simple exponential function.

NSC Time at 4.2 K: ~3 h
Results: $\text{H}_2\text{O}$ in Argon Matrix

$1/\tau$ (min$^{-1}$)

$\text{Ar/H}_2\text{O}$

T=4.2 K

Increasing contribution to conversion rate
Non Exponential Decay with Time

Inter-Molecular Magnetic Interactions
Intra-Molecular Magnetic Interactions

NSC Time: 10 h

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*  

Turgeon *et al*  

**Patrick Ayotte**  
Invited talk: *Confinement and isotopic effects*  
Nuclear Spin Effect in Astrochemistry May, 2nd, 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)
Concentration effect on NSC of H₂O in Argon Matrix

\( T = 4.2 \text{ K} \)

Rabi Oscillations

\( 1_{01} \) (ortho)

\( 0_{00} \) (Para)
Concentration effect on NSC of H$_2$O in Argon Matrix

Relaxation of the rotational energy through emission of PHONONS

$T = 4.2$ K

$0_{00}$ (Para)

$1_{01}$ (ortho)
Concentration effect on NSC of H$_2$O in Argon Matrix

- Fractional populations of \textit{ortho} molecules:

\[ x_O = \frac{n_O}{n_O + n_p} \]

- The time evolution of the number of \textit{ortho} molecules can be expressed as:

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

with

\[ k_1 = \frac{K_{INTER}^{po}}{x_o(\infty)} \]
\[ k_2 = \frac{1}{\tau_{INTRA}} - K_{INTER}^{po} \]
\[ k_3 = \frac{x_o(\infty)}{\tau_{INTRA}} \]

- 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$_2$O in Argon Matrix

$H_2O/Ar = 1/50$

$x_O(t)$

- Experimental data
- Exponential Fit
- Kinetic model

Residues
Concentration effect on NSC of $\text{H}_2\text{O}$ in Argon Matrix

Quadratic dependence of $K_{\text{INTER}}^{po}$ with $C_{\text{H}_2\text{O}}$ presumably due to dependence of rotational relaxation on water concentration $C_{\text{H}_2\text{O}}$

Michaut et al (to be submitted)
Can we extrapolate results in rare gas matrix to icy environment?
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$_2$O 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
para-CH₄ l=0  sym E

ortho-CH₄
l =1 sym F

meta-CH₄
l =2 sym A
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)

Temperature of the walls 14 K

Rotational relaxation:
- J=3: \textit{ortho F / meta A}
- J=2: \textit{ortho F / para E}
- J=1: \textit{ortho F}
- J=0: \textit{meta A}
OPR evolution in the gas during Solid formation

fractional population

Room Temperature Ratios

9/16

5/16

2/16

ortho F

meta A

para E

Time (s)
- 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 \( \text{H}_2 \) molecules trapped on cold Amorphous Solid Water (ASW).

(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)
Reflection Absorption InfraRed Spectroscopy (RAIRS)

Porous Amorphous Solid Water (ASW)

$H_2$ adsorbed on ASW

Solution

- 1000 ML Equivalent
- Saturation of $H_2$
Time evolution of the RAIRS spectrum of H₂/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**

<table>
<thead>
<tr>
<th>$O_2$</th>
<th>$t$(min)</th>
<th>IR Vib</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 %</td>
<td>H$_2$: 30 (2)</td>
<td></td>
</tr>
<tr>
<td>0.02 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 %</td>
<td>H$_2$: 220 (17)</td>
<td></td>
</tr>
<tr>
<td>Coverage</td>
<td>1 ML</td>
<td></td>
</tr>
</tbody>
</table>

(1) Chehrouri, Fillion et al PCCP 2011
(2) Sugimoto & Fukutani Nature Physics 2011
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Nuclear Spin Conversion Dynamics on Surfaces

Molecular hydrogen on ASW

**NSC in the presence of O₂ traces**

Molecular Hydrogen Diffusion

Temperature 10 K

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<tr>
<th>O₂</th>
<th>t(min) IR Vib</th>
<th>t(min) Laser FORMOLISM&lt;sup&gt;(1)&lt;/sup&gt;</th>
<th>t(min) Laser Sugimoto&lt;sup&gt;(2)&lt;/sup&gt;</th>
<th>T (min) Laser Ueta&lt;sup&gt;(3)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 %</td>
<td></td>
<td>H₂ : 3.7 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>D₂ : 11 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 %</td>
<td>H₂ : 30 (2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02 %</td>
<td></td>
<td>D₂ : 51 (4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 %</td>
<td>H₂ : 220 (17)</td>
<td>H₂ : &gt; 300</td>
<td>H₂ : 8 (2)</td>
<td>H₂ : 26 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D₂ : 49 (38)</td>
<td></td>
</tr>
</tbody>
</table>

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 H₂ at 4 K : 1.5 days
Gas H₂ (2 bars, 293K) : 12.8 days (DG)
CONCLUSIONS

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

Calculations in gas phase
- NSC strongly dependent on density and temperature
  $10^4 - 10^7$ years for H$_2$CO 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

Solid-gas Interface

Suggest a fast NSC in the solid state

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

Open question
PROSPECTS

- New Approaches: desorption studies

Ice sample preparation
Enriched in ortho H₂O
Coll. Univ. Sherbrooke

Ice

substrate T<20 K

thermal desorption

UV desorption (non thermal)

VUV radiation

Orion Nebula

Crédit : Spitzer-Nasa

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) Para-$H_2O$ and ortho-$H_2O$

Energy levels:
- Vibrational state
- Antisymmetric stretching

3756 cm$^{-1}$

(b) Graph showing OPR over time and quantum numbers.

OPR=3 high temperature limit

OPR=0.7 after irradiation at 4.3 K

Natural OPR=0.003 to 4.3 K

Thomas Putaud, PhD thesis, 2016-
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