Influence of nuclear spin conversion of H$_2$ molecules on the chemistry of the interstellar medium - Experiment and modelling

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Why look at the OPR in the ISM?

- Parameter tracer such as the temperature of the medium?
- Impact on the chemistry of the ISM?

**Ortho to Para Ratio (OPR) in the Interstellar Medium (ISM)**

One of the lowest OPR values reported in the ISM:

**Hartley 2 Comet**

OPR = 2.59 ± 0.13

**Molecular Cloud W 51**

OPR = 3.2 ± 0.1

**Orion Bar**

OPR = 0.2 - 0.5
PDR CODE:

- Computes the atomic and molecular structure of interstellar clouds.
- Analysis of physical and chemical processes

MAIN PARAMETERS:

- \( G_0 \) (UV intensity radiation field), stellar spectrum
- Density, pressure, user profile density: clumps
- Metallicity and elemental abundances
- Cosmic ray ionisation rate
- Grain properties

**Radiative transfer**

- Photo-reactions
- Photo-electric effect

**Chemistry**

- Gas phase
- Surfaces

**Thermal Balance**

- Heating
- Cooling

**MEUDON PDR CODE (Photo Dissociated Region)**

- Abundances of hundreds species
- Excitation in levels
- Gas & grains temperatures
- Intensities (\( H_2 \), CO, H\(_2\)O, ...)
- Column densities of species
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Why the study of $\text{H}_2$ is so important for the interstellar medium?

- $\text{H}_2$ is the most abundant molecule in the interstellar medium
- For a given reaction, the reaction rate may be different depending on whether $\text{H}_2$ is ortho or para (Dislaire et al A&A 537, A20 (2012))

$\implies$ The OPR of $\text{H}_2$ may have a great impact on the chemistry
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E. F. van Dishoeck and al. Chem. Rev. 2013, 113, 12, 9043–9085
H$_2$ IN THE CHEMICAL CHAIN REACTION OF WATER FORMATION

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(i) Chemistry

Modification of reaction rates depending on the ortho/para character of the species

\[ H_2O^+ + e^- \rightarrow H_2O + H \quad k \]

\[ H_3O^+ - o + e^- \rightarrow H_2O - o + H \quad k_1 = k \]

\[ H_3O^+ - p + e^- \rightarrow H_2O - p + H \quad k_2 = k/2 \]

\[ H_3O^+ - p + e^- \rightarrow H_2O - o + H \quad k_3 = k/2 \]

(ii) Excitation

Different processes that populate and depopulate an i-level for a given species:

- Radiative processes
- Collisional processes
- Formation processes
- Destruction processes

- The excitation is calculated for 4 ortho/para species: H_2, H_2O, H_2^{18}O, and H_3^+
- X-o and X-p are not chemical species in the PDR code
- The excitation computation in quantum states is only made for the X species while taking into account the ortho/para reactions of the X species

The population X-o and X-p are finally deduced from this computation

Between 300-400 more reactions with OP chemistry than without
Observations  
Putaud 2019  

$I$ [erg cm$^{-2}$ s$^{-1}$ sr$^{-1}$]  

Rotational lines  
$H_2O$ levels  

H$_2$O lines  

Para  
Ortho  

T. Putaud et al. A&A 2019
Ortho/para chemistry has little impact compared to other excitation processes.
PS05 : Poelman & Spaans A&A 2005
Ortho/para chemistry has a greater impact compared to other excitation processes

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Modelisation:

- Chemistry is in competition with other processes such as collisional and radiative processes.

- The impact of ortho/para chemistry on water formation depends on the region studied.

Little impact in Orion bar but bigger impact in S140

- In cold regions, surface grain chemistry plays a more important role than gas phase chemistry.

- A new study of these regions with surface grain chemistry taking into account adsorption and desorption processes would provide a more complete model.
Behaviour of the nuclear spin isomers at the solid-gas interface?
Molecular hydrogen on Amorphous Solid Water (ASW)

At 10K

<table>
<thead>
<tr>
<th></th>
<th>(SPICES) LERMA In situ</th>
<th>FORMALISM (1) After desorption</th>
<th>Sugimoto (2) After desorption</th>
<th>Ueta (3) After desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (min)</td>
<td>H$_2$ : 220 (17)</td>
<td>H$_2$ : &gt;300</td>
<td>H$_2$ : 8 (2)</td>
<td>H$_2$ : 52 (5)</td>
</tr>
<tr>
<td>H$_2$ coverage</td>
<td>1ML</td>
<td>0.3 - 0.75 ML</td>
<td>1 - 2 ML</td>
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(1) Chehrouri, Fillion et al. PCCP 2011
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(3) Ueta, Watanabe, Hama, Kouchi. PRL 2016
IMPLEMENTATION OF A CHEMICAL NETWORK

TEST OF A CHEMICAL NETWORK ON A DIFFUSE CLOUD

DIFFERENCE BETWEEN TWO MODELS WITH AND WITHOUT ORTHO PARA CHEMISTRY

COSPINU2

Sample holder
6K < T < 300K

QMS
(Gas phase detection)

Detector

Ultrahigh Vacuum chamber \( P \sim 10^{-10}\text{mbar} \)

Ice growth system

Bayard Alpert pressure gauge
Use of a special deposition technique to produce thick ices without breaking the background vacuum. Allows to avoid redeposition during the experiment.

~ 5 - 6 µm of H₂O amorphous and porous water

Cu polycristallin, T = 9-10 K
Surface (interface $\text{H}_2\text{O} – \text{vacuum}$) saturated with $\text{H}_2$

$\sim 5 - 6 \text{ µm of } \text{H}_2\text{O}$

amorphous and porous water

Cu polycristallin, $T = 9\text{-}10 \text{ K}$
Surface (interface $\text{H}_2\text{O} - \text{vacuum}$) saturated with $\text{H}_2$

$\sim 5 - 6 \mu\text{m}$ of $\text{H}_2\text{O}$

amorphous and porous water

Cu polycristallin, $T = 9-10 \text{ K}$
~ 5 - 6 µm amorphous and porous H₂O saturated with H₂. IR spectra in the range 4050-4200 cm⁻¹ obtained with COSPINU2 and time evolution of the two spin isomers.
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\[
\text{Para } H_2 \overset{\nu = 1, J = 0}{\longrightarrow} \overset{\nu = 0, J = 0}{\text{Ortho } H_2}
\]

\[
\overset{\nu = 1, J = 1}{\text{Ortho } H_2} \overset{\nu = 0, J = 1}{\longrightarrow} \overset{\nu = 1, J = 0}{\text{Ortho } H_2}
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Characteristic time: 
351 ± 6 min
**IMPLEMENTATION OF A CHEMICAL NETWORK**

**TEST OF A CHEMICAL NETWORK ON A DIFFUSE CLOUD**

**DIFFERENCE BETWEEN TWO MODELS WITH AND WITHOUT ORTHO PARA CHEMISTRY**

**NSC ON ASW USING IR SPECTROSCOPY**

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<tr>
<th>(SPICES) LERMA In situ</th>
<th>FORMOLISM (1) After desorption</th>
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<th>COSPINU2 (~ 3.5 µm H₂O) in situ</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (min)</td>
<td>H₂ : 220 (17)</td>
<td>H₂ : &gt;300</td>
<td>H₂ : 8 (2)</td>
<td>H₂ : 376 (25)</td>
<td>H₂ : 273 (15)</td>
</tr>
</tbody>
</table>

| H₂ coverage            | 1ML                            | 0.3 - 0.75 ML                 | 1 - 2 ML                  | 0.3 - 1 ML                   | 1ML                            | 1ML                            |

**Big discrepancies in the data set between the different experiments**

- O₂ molecules have a **high magnetic moment**, and O₂ impurities in the system may significantly decrease the conversion time.
CONCLUSIONS

Experiment:

• The NSC of H\textsubscript{2} on ASW has been studied with different techniques.
  The measurements carried out with FORMOLISM and COSPINU2 give similar characteristic times.
  There is a large discrepancy with the data collected in the literature.

• Measurements with COSPINU2 will be done on a large time scale to investigate the temporal dynamics and the temperature dependence of the NSC.

• Developments are in progress to investigate the link between \textit{in situ} OPR of H\textsubscript{2} and the OPR after thermal and non thermal desorption.
Thank you for your attention!
Processes that govern the ortho to para ratio in the PDR code and $H_2O$ chemistry

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_2$</th>
<th>$H_2O$</th>
<th>$H_2^+$</th>
<th>$H_3^+$</th>
<th>$H_2O^+$</th>
<th>$H_3O^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation</td>
<td>✔</td>
<td>✔</td>
<td>✗</td>
<td>✔</td>
<td>✗</td>
<td>✗</td>
</tr>
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</table>

Reaction chain for the $H_2O$ formation:

$$OH + H_2 \rightarrow H_2O + H$$
$$O^+ + H_2 \rightarrow OH^+ + H$$
$$OH^+ + H_2 \rightarrow H_2O^+ + H$$
$$H_2O^+ + H_2 \rightarrow H_3O^+ + H$$
$$H_3O^+ + e^- \rightarrow H_2O + H$$

Duplication with ortho/para forms of the 5 $H_2O$-forming reactions and all reactions where $H_2^+$, $H_2O^+$ and $H_3O^+$ appear.

Between 300-400 more reactions than without OP chemistry.

Use of UGAN, Rist+ 2013, Oka 2004, Sipilä+ 2015
- Branching ratios more efficient for ortho molecules
- High temperature 3/4 ortho $H_2$ and 1/4 para $H_2$
### Table: Chemical Network Test

<table>
<thead>
<tr>
<th>O₂</th>
<th>t (min) IR Vib (SPICES) LERMA</th>
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<tbody>
<tr>
<td>0.2 %</td>
<td></td>
<td>H₂ : 3.7 (1) 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) D₂ : 49 (38)</td>
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