CHEMISTRY AT THE SURFACE OF COLD GRAINS

FRANCOIS DULIEU - LERMA

MICHEM SYMPOSIUM - PARIS- JUNE 15
AND THE SOLID PHASE IS (MOSTLY) DUST GRAINS...

BEAUTY OF NEBULAE IS DUE TO THE DIFFUSION OF LIGHT BY THE SOLID PHASE.

*Image credit: J. Freitag and S. Messenger*
Dark interstellar clouds

- Dust obscures the line of sight
- Cold (10K), and « dense » (>10⁴/cm³)
- But active : star formation regions

Zoom and shift in frequency :

visible —> FIR

Source : Spitzer Space Telescope - NASA Caltech
BEAUTY OF NEBULAE IS DUE TO THE DIFFUSION OF LIGHT BY THE SOLID PHASE

Real image by ALMA nov 14

« Dust emission »
in proto planetary disc

AND THE SOLID PHASE IS (MOSTLY) DUST GRAINS...
And molecules are the best probes of physical conditions. But most of the (molecular) information is carried by the gas phase. Pressure (density), temperature, chemistry is the clock.
MOLECULAR RICHNESS AND THE SOLID PHASE

- Accretion and catalysis
- Third body effect, and long residence time
- Source of chemical richness - observed in meteorites
- But obscure phase, no rotation
SOLID STATE CHEMISTRY IS MAINLY RULED BY ACCRETION AND DIFFUSION RATES

BUT THE RETURN TO THE GAS PHASE IS A REQUIREMENT FOR A BETTER OBSERVATION

LABORATORY ASTROPHYSICS IS NEEDED TO FILL THE GAP
Cergy’s team purpose:

**HOW FAR CAN MOLECULAR COMPLEXITY GROW?**

- starting from atoms or small radicals
- without external energy
- **on** surfaces
- Understand processes, like the return in the gas phase, or the diffusion
OUTLINE

(INTRODUCTION)

EXPERIMENTAL CONTEXT

CHEMISTRY - THE CASE OF [O+H]

OTHERS TOPICS - MICHEM PROJECT
From **concept** to reality...

- On cold surfaces
- Put on atoms
- Observe the result
From concept to reality...

- on cold surfaces, silicates, graphite or ices
  - Put on atoms
  - Observe the result

Thermal control 6.5 - 400K
Balance between He cryocooler (close cycle) and resistive heater + thermic background
From concept to reality...

- on cold surfaces, silicates, graphite or ices

- Put on atoms

(c) Crystalline water ice (Surface)  (d) Amorphous solid water (Surface)
From concept to reality…

- on cold surfaces, silicates, graphite or ices

- Put on atoms

- Physisorption is the dominant interaction
- Surface model: « egg box, or grid »
- One « Monolayer » = 100% occupation
- One « Monolayer » = $10^{15}$ sites/cm$^2$
- UHV (unless 1 ML growing in 5 minutes @ $10^{-8}$ mbar)
From concept to reality...

- on cold surfaces,

<table>
<thead>
<tr>
<th>TYPICAL BINDING ENERGIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200 K*</td>
</tr>
<tr>
<td>100 MEV</td>
</tr>
<tr>
<td>10 KJ/MOL</td>
</tr>
<tr>
<td>2.4 KCAL/MOL</td>
</tr>
<tr>
<td>834 CM$^{-1}$</td>
</tr>
</tbody>
</table>

- Put on atoms

<table>
<thead>
<tr>
<th>TYPICAL AMOUNT OF SPECIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAX : $10^{14}$ MOLECULES</td>
</tr>
<tr>
<td>&gt; 1 NANO-MOLE</td>
</tr>
</tbody>
</table>

- Physisorption is the dominant interaction
- Surface model: « egg box, or grid »
- One « Monolayer » = 100% occupation
- One « Monolayer » = $10^{15}$ sites/cm$^2$
- UHV (unless 1 ML growing in 5 minutes @ $10^{-8}$ mbar)
From concept to reality…

- on cold surfaces, silicates, graphite or ices

- Put on atoms

- En mesurer le résultat
From concept to reality…

- Sur une surface froide, silicates, graphite ou glace

- **Put on atoms**

- Flux 0.003 ML/s
- 300 s to achieve one ML
- O and H atoms in ground state
From concept to reality...

- Sur une surface froide, silicates, graphite ou glace
- Déposer des atomes

**Observe the result**

**Reflection Absorption Infra Red Spectroscopy (RAIRS)**

(c) Minissale
Mass spectroscopy (4 folds)

- By induced desorption (TPD)
- Spontaneous desorption (DED)
- Beam interception
- Possibility to have information about internal energy

- Detection efficiency down to 0.01 ML
FROM CONCEPT TO REALITY...

- on cold surfaces, silicates, graphite or ices

- Put on atoms

(c) Minissale
THE \([O+H]\) SYSTEM

\[ \text{O} + \text{H} \rightarrow \text{OH} \]
\[ \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} \]
\[ (\text{H}+\text{H} \rightarrow \text{H}_2) \]

Dulieu et al 2006…2010

first idea

Dulieu et al A&A 2010
THE [O+H] SYSTEM

O+H → OH
OH +H → H₂O
H+H → H₂
O+O → O₂
O+O₂ → O₃
O+O₃ → 2 O₂
...

...
THE [O + H] SYSTEM

O + H → OH
OH + H → H₂O
H + H → H₂
O + O → O₂
O + O₂ → O₃
O + O₃ → 2 O₂
H + O₂ → HO₂
H + O₃ → OH + O₂
H + HO₂ → H₂O₂
H₂O₂ → OH + H₂O
OH + H₂ → H₂O + H
O + H₂ → H₂O

SO ONE « SYSTEM » IS NOT ONE REACTION...
THE [O+H] SYSTEM

O+H → OH
OH +H → H₂O
H+H → H₂
O+O → O₂
O+O₂ → O₃
O+O₃ → 2 O₂
H+O₂ → HO₂
H+O₃ → OH+O₂
H+HO₂ → H₂O₂
H₂O₂ → OH +H₂O
OH + H₂ → H₂O+H
+ H₂ → H₂O

HOW TO UNDERSTAND ?
: STUDY SUB-SYSTEMS

So one « system » is not one reaction...
THE \([\text{O}_3+\text{H}]\) SYSTEM

\[
\begin{align*}
\text{H}+\text{O}_3 & \rightarrow \text{OH}+\text{O}_2 \\
\text{OH}+\text{H} & \rightarrow \text{H}_2\text{O} \\
\text{H}+\text{H} & \rightarrow \text{H}_2 \\
\text{H}+\text{O}_2 & \rightarrow \text{HO}_2 \\
\text{H}+\text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 & \rightarrow \text{OH}+\text{H}_2\text{O}
\end{align*}
\]

HOW TO UNDERSTAND? : STUDY SUB-SYSTEMS

Mokrane et al ApJL 2009
THE \([O_3+H]\) SYSTEM

\[ \begin{align*}
H + O_3 & \rightarrow OH + O_2 \\
OH + H & \rightarrow H_2O \\
H + H & \rightarrow H_2 \\
H + O_2 & \rightarrow HO_2 \\
H + HO_2 & \rightarrow H_2O_2 \\
H_2O_2 & \rightarrow OH + H_2O
\end{align*} \]

How to understand? : Study sub-systems at different surface temperatures
THE [O₃+H] SYSTEM

Yes, it works, but 80% +/-20% of expected water is missing!

→ «Chemical desorption»

*Chemical desorption*


How to understand?

: Study sub-systems at different surface temperatures

$\text{H}^+$ + O₃ $\rightarrow$ OH + O₂

OH + H $\rightarrow$ H₂O₂

H₂O₂ $\rightarrow$ OH + H₂O

@ 10 K

@ 45 K
THE \([\text{O}_3+\text{H}]\) SYSTEM

Yes, it works, but 80\% +/- 20\% of expected water is missing!  

\[ \text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 \]  
\[ \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} \]  
\[ \text{H} + \text{H} \rightarrow \text{H}_2 \]  
\[ \text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 \]  
\[ \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{O} \]

HOW TO UNDERSTAND?  
: STUDY SUB-SYSTEMS  
AT DIFFERENT SURFACE TEMPERATURES  

– « Chemical desorption »

During Exposure Detection (DED)

Case of D, sent on 0.5 ML of O₂

D₂O detected!

\[ \text{O}_2 + \text{D} \rightarrow \text{D}_2\text{O} \]
THE $[O_2+H]$ SYSTEM

H$+H$ → H$_2$
H$+O_2$ → HO$_2$
H$+HO_2$ → H$_2$O$_2$
H$+HO_2$ → 2 OH
OH $+ H$ → H$_2$O
H$+HO_2$ → H$_2$O$_2$
H$_2$O$_2$ → OH $+ H$_2$O$

DIFFERENCE WITH LEIDEN, SAPPORO, PARIS
SUB-MONOLAYER REGIME

(c) Chaabouni et al JCP 2012
WATER FORMATION

- Water is easily formed by many ways (minimum energy principle ?)
- Mostly water is formed (not $\text{H}_2\text{O}_2$) on surface
- Chemical desorption is important
- Apparent differences in experiments are due to surface vs matrix effects
- Water formed is compact, and not porous even made at 10K (Accolla et al, *MNRAS* 2013)
MORE ON CHEMISTRY

23 molecules formed (+ isotopes)
MORE ON CHEMISTRY
+ non reactive species...

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>O</th>
<th>O</th>
<th>O</th>
<th>O</th>
<th>N</th>
<th>CO</th>
<th>H</th>
<th>HCOOH</th>
<th>HNCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>«OH»</td>
<td>NO AND O₂ ARE REACTIVE ON ICE! ATMOSPHERIC IMPLICATION SEE M. MINISSALE’S POSTER</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>«OH»</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>«OH»</td>
<td>«OH»</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>NO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

23 molecules formed (+ isotopes)

(c) Minissale et al CPL 2013
\textbf{N/O/H NETWORK}

Congiu et al. 2012, \textit{ApjL}
Congiu et al. 2012, \textit{JCP}
Ioppolo et al. 2012, \textit{JCP}
Minissale et al. 2013, \textit{CPL}
Minissale et al. 2014, \textit{PCCP}
Ioppolo et al. 2014, \textit{PCCP}

Go easily to « dimers »
Fast oxydation and hydrogenation
Chemical origin of $N_2$ and CO differential depletion in prestellar cores: observations and laboratory investigations.

Acronym: Depletion In pre-Stellar Cores (DISC)
OTHER FIELDS OF INTEREST

- Quantum tunneling
- Diffusion and chemical desorption
- Sticking coefficients
- Desorption rates; Desorption processes; role of substrate
- Morphology of water
- Isotopic exchange/ effects
- o-p ratio, nuclear spin conversion (H₂)
- H₂ formation
OTHER FIELDS OF INTEREST

POSSIBLE THEMATIC CONNECTIONS IN MICHEM?

H₂ STORAGE
ATMOSPHERIC CHEMISTRY
SURFACE MORPHOLOGY DETERMINATION
SURFACE OXYDATION / REDUCTION

- Isotopic exchange/ effects
- o-p ratio, nuclear spin conversion (H₂)
- H₂ formation
OUR LAB IS HERE! (50km...
OUR LAB IS HERE! (50km...)

Famous?
THANK YOU!


FP 7 ITN LASSIE