SOLID STATE REACTIONS II

FRANCOIS DULIEU - LERMA

SUMMER SCHOOL « ASTROCHEMISTRY FROM SPACE TO EARTH » - GRENOBLE - SEPT. 2016

francois.dulieu@obspm.fr
'SOLID STATE REACTIONS’ OUTLINE

1 - Accretion (sticking)
2 - Diffusion
3 - Energy partition
4 - Desorption
5 - Surface Reaction networks
6 - Bulk/ice reactivity (thermally induced)
7 - Energetically induced reactivity (see ME. Palumbo)
THE \([\text{O} + \text{H}]\) SYSTEM

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

first idea
Dulieu et al 2006…2010

Dulieu et al A&A 2010
THE \( [\text{O}+\text{H}] \) SYSTEM

\[ \text{O} + \text{H} \rightarrow \text{OH} \]
\[ \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} \]
\[ \text{H} + \text{H} \rightarrow \text{H}_2 \]
\[ \text{O} + \text{O} \rightarrow \text{O}_2 \]
\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]
\[ \text{O} + \text{O}_3 \rightarrow 2 \text{O}_2 \]
...

THE \( [O + H] \) SYSTEM

- \( O + H \rightarrow OH \)
- \( OH + H \rightarrow H_2O \)
- \( H + H \rightarrow H_2 \)
- \( O + O \rightarrow O_2 \)
- \( O + O_2 \rightarrow O_3 \)
- \( O + O_3 \rightarrow 2 O_2 \)
- \( H + O_2 \rightarrow HO_2 \)
- \( H + O_3 \rightarrow OH + O_2 \)
- \( H + HO_2 \rightarrow H_2O_2 \)
- \( H_2O_2 \rightarrow OH + H_2O \)
- \( OH + H_2 \rightarrow H_2O + H \)
- \( O + H_2 \rightarrow H_2O \)

SO ONE « SYSTEM » IS NOT ONE REACTION
So one « system » is not one reaction

HOW TO UNDERSTAND ?
: STUDY SUB-SYSTEMS

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

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

@ 10 K

Mokrane et al ApJL 2009

See also Romanzin et al 2011

HOW TO UNDERSTAND ?
: STUDY SUB-SYSTEMS
THE [O₃+H] SYSTEM

@ 10 K

H+O₃ —> OH+O₂
OH +H —> H₂O
H+H —> H₂
H+O₂ —> HO₂
H+HO₂ —> H₂O₂
H₂O₂ —> OH +H₂O

@ 45 K

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

@ 10 K

@ 45 K
THE \([O_3 + H]\) SYSTEM

Yes, it works, but 80\% \pm 20\% of expected water is missing!

\[H + O_3 \rightarrow OH + O_2\]

\[OH + H \rightarrow H_2O\]

\[H + HO_2 \rightarrow H_2O_2\]

Yes, it works, but 80\% \pm 20\% of expected water is missing!

\(\rightarrow \) « Chemical desorption »

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

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

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

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

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


Chemical desorption (3)

Accretion (1)

Surface diffusion (2)
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 $[\text{O}_2+\text{H}]$ SYSTEM

H$+H \rightarrow H_2$
H$+O_2 \rightarrow HO_2$
H$+HO_2 \rightarrow H_2O_2$
H$+HO_2 \rightarrow 2 \text{OH}$
OH $+ H \rightarrow H_2O$
H$+HO_2 \rightarrow H_2O_2$
H$_2$O$_2 \rightarrow \text{OH} + H_2O$

...
**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)

Many ref in Lamberts+2014 Faraday Discussion
More: work on ‘bulk surfaces’ by Ioppolo/Romanzin…Linnartz et al and Myauchi, Oba, Hama, Wanabe et al, Vidali et al for silicate surfaces 
Lamberts, Cuppen et al for modeling studies
Some Oxygen is missing.

Chemical desorption : Indirect evidence (TPD)
Some Oxygen is missing.

Chemical desorption : Indirect evidence (TPD)
Chemical desorption, effect of coverage

Exposure of 0.5 ML of O on pre-adsorbed N₂

(c) Minissale&Dulieu, JCP 2014
Physical properties ruling out the chemical desorption of $[O+O]$

<table>
<thead>
<tr>
<th></th>
<th>CD</th>
<th>O</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>498</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>$E_{binding}$</td>
<td>10</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>$N_{deg. of freedom}$</td>
<td>6</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>$\epsilon^*$ (masse)</td>
<td>0.37</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

- Type of reaction
- Exchange with the substrate (elast. coll.)

$e = 80\%$  
$f < 5\%$

CD of $O + O \rightarrow O_2$
CD of $O_2 + O \rightarrow O_3$

(c) Minissale&Dulieu, JCP 2014
What could be the mechanism of chemical desorption?

Source of energy: Enthalpy of formation (50,000 K)

**Chemical desorption: 4 parameters?**
- Chemical energy available
- Adsorption energy of products
- Degree of freedom
- Energy transfer to the substrate (or neighbor)

Key point: how the initial energy is converted in ?
### OTHER EXPERIMENTS

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>O</th>
<th>O₂</th>
<th>O₃</th>
<th>N</th>
<th>CO</th>
<th>H₂CO</th>
<th>HCOOH</th>
<th>HNCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>O</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>✗</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>▲</td>
<td>▲</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>▲</td>
<td>▲</td>
<td></td>
</tr>
</tbody>
</table>

- Published
- To be Published
- Unpublished
### Other test experiments

Having a precise CD measurement is hard, but have an estimation is possible.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Method</th>
<th>Desorbing Product</th>
<th>Experimental CD efficiency (np-ASW, Amorphous Silicate, Oxidized HOPG)</th>
<th>Theoretical CD efficiency (Oxidized HOPG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + H</td>
<td>✓ ✓</td>
<td>O + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>O₂ + H</td>
<td>✓ ✓</td>
<td>O₂H + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>O₃ + H</td>
<td>✓ ✓</td>
<td>O₂H + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>N₂ + O</td>
<td>✓ ✓</td>
<td>N₂ + O</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>CO + H</td>
<td>✓ ✓</td>
<td>HCO + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>H₂CO + H</td>
<td>✓ ✓</td>
<td>H₂CO + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>H₂CO + H</td>
<td>✓ ✓</td>
<td>H₂CO + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>Ar + H</td>
<td>✓ ✓</td>
<td>Ar</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>NO + O/N</td>
<td>X ✓</td>
<td>many</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>CO + O</td>
<td>✓ ✓</td>
<td>HCO + O</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>H₂CO + O</td>
<td>X ✓</td>
<td>H₂CO + O</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>CH₃OH + H</td>
<td>✓ ✓</td>
<td>CH₃OH + H</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
<tr>
<td>CH₃OH + O</td>
<td>✓ ✓</td>
<td>CH₃OH + O</td>
<td>25±15 × 30±15 × &lt;70±20 × &lt;80±20</td>
<td>50±25 × 50±25 × 1.7</td>
</tr>
</tbody>
</table>
Energy transfert
Classical momentum exchange?

\[ \epsilon = \frac{(M - m)^2}{(M + m)^2} \]

M = 130 amu,
case of hyperthermal scattering of O$_2$ on graphite
see Hayes et al, 2012
Equi-partition of energy

Parameters of the reaction
\( DH_R \): Heat of reaction
\( N \): Degree of freedom of all the products

Parameters of the product
\( \epsilon \): Fraction of energy available after collision with surface
\( E_{\text{binding}} \): Binding energy

\[ CD = e^{-\frac{E_{\text{binding}}}{\epsilon \Delta H_R / N}} \]


OK FOR BARE GRAINS, STILL TO WORK FOR WATER AND OTHER SUBSTRATES
CONCLUSION ABOUT CHEMICAL DESORPTION

• Chemical desorption can be efficient but does not explain COM’s in the gas phase
• There are 4 main parameters
  - Chemical energy available
  - Adsorption energy of products
  - Degree of freedom
  - Energy transfert to the substrate (or neighbor)
• Equipartition of energy describe properly the experiments (in the limit of large experimental errors.)
• Water ice reduces strongly the CD [-20 to 500%]
• Indirect CD is not efficient

New calculations by Cuppen et al, seem to confirm the exp behavior and precise the water substrate effect (not mass dependent)
ABOUT THE IMPORTANCE OF DESORPTION

- In models desorption describe also diffusion. And diffusion is very important.

- Desorption is more complex than previously thought:
  - Can be reactions: (see later, and Theule+ ASR review 2013)
  - Can be segregation and desorption energies are affected (see CO and O$_2$, Noble+ MNRAS 2015)
  - Co-desorption with water is a wrong concept for many molecules (like NH$_2$OH, H$_2$O$_2$)
CORELLATION $O_2$ /$H_2O$

NO CORELLATION BETWEEN CO/N$_2$ AND O$_2$

O$_2$/CO desorption: Noble, Diana Dulieu MNRAS 2015
Is it possible that $O_2$ does not come from simple desorption (like $N_2/CO$)?

Is it possible that $O_2$ is produced during water desorption?

We know that water is formed and should include a fraction of $H_2O_2$.

What about $H_2O_2$ dismutation?

At room temperature $H_2O_2$ evaporate in $H_2O$ and $O_2$.

Bieler et al. Nature 2015
Desorption of mixed H$_2$O/H$_2$O$_2$ layer

H$_2$O/H$_2$O$_2$ mixture (50/50 %) made from [O$_2$+D] experiments

Thin layer (<1ML) on silicate

2 H$_2$O$_2$ $\rightarrow$ 2 H$_2$O + O$_2$.

Yes, dismutation occurs at 180 K, but incomplete

ratio & stochiometry efficiency 25-50%
H₂O/D₂O₂ mixture (95/5%) made from [O₂+D] on H₂O layers

Desorption of mixed H₂O/H₂O₂ layers

Yes, dismutation occurs at 155 K, and complete*

D₂O₂/D₂O
H₂O
silicates

2 H₂O₂ → 2 H₂O + O₂.
DESORPTION OF MIXED $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ LAYERS

Yes, dismutation occurs, and is complete at the very end of water desorption.

It is possible that 7% of initial $\text{H}_2\text{O}_2$ release 3.5% of $\text{O}_2$ just after the final desorption of water ice.
O₂ IN THE ISM?

O₂ and H₂O₂ is/was over predicted
O₂ and H₂O₂ are sparsely detected

H₂O₂ only detected where O₂ is detected (see Parise et al 2014)

denoted Peak A, the Western Clump, or MF4. The mass of this source is ∼10 \( M_\odot \) and the dust temperature is \( \geq 150 \) K. Our preferred explanation of the enhanced O₂ abundance is that dust grains in this region are sufficiently warm (\( T \geq 100 \) K) to desorb water ice and thus keep a significant fraction of elemental oxygen in the gas phase, with a significant fraction as O₂. For this small source, the line ratios require a temperature \( \geq 180 \) K. The inferred
Competition between $O_2/O_3$ and $CO_2$ formation
Faible production de CO$_2$: 
**Barrière** $E_{\text{CO}+\text{O}} \in [480K - 750 K]$

Voir aussi CO+OH $\rightarrow$ CO$_2$ + H, Noble et al MNRAS 2012
C/O/H

[CO + H] ... METHANOL, ALREADY STUDIED (HIRAOKA ET AL, WATANABE ET AL, FUCHS ET AL, PIRIM ET AL ...) BUT IN MULTILAYERS
CO + H et H₂CO + H thin layers

No methanol formation in [CO+H] experiments
Formation of methanol and CO in [H₂CO+H] exp.

(c) Minissale + MNRAS 2016
CO + H et H_{2}CO + H thin layers

Mesure retour phase gaz, pendant irradiation
Hydrogenation of CO on surfaces

Need more H than previously thought
CO is desorbing back in many cases
Validation of the H$_2$ formation mechanism proposed by Tielens & Hagen

See also confirmation by Chuang + A&A 2015
Difference with other groups: sub-monolayers
O SENT ON A PRECOVERED H2CO SUBSTRATE

• H2CO is easily detectable in the IR

• H2CO is evaporating at $T > 100$ K (Noble et al A&A 2012)

• $\text{H2CO} + \text{O} \rightarrow \text{CO2} + \text{H2} (90\%) \ / \ \text{CO} + \text{H2O} (10\%)$ (Minissale et al A&A 2015)
\[ \text{H}_2\text{CO} + \text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

At low T, O atoms lands and form \( \text{O}_3 \): low \( \text{CO}_2 \) formation

At high T, O atoms lands and form only \( \text{CO}_2 \) formation
Excellent match for a combination of linked parameter
O diffusion of about 750 K, and reaction barrier of about 300 K

O diffusion in the thermal regime: [600 - 900 K]
<table>
<thead>
<tr>
<th>Réaction</th>
<th>Barrier</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + OH</td>
<td>yes</td>
<td>CO</td>
</tr>
<tr>
<td>CO + O</td>
<td>~ 7</td>
<td>CO</td>
</tr>
<tr>
<td>H</td>
<td>~</td>
<td>CO</td>
</tr>
<tr>
<td>H</td>
<td>~</td>
<td>CO, CH</td>
</tr>
<tr>
<td>HCOOH + H</td>
<td>yes</td>
<td>H</td>
</tr>
<tr>
<td>HCOOH + O</td>
<td>yes</td>
<td>CO</td>
</tr>
<tr>
<td>CH</td>
<td>Too large</td>
<td>-</td>
</tr>
<tr>
<td>CH</td>
<td>Too large</td>
<td>-</td>
</tr>
</tbody>
</table>
H/C/O

Barrier to oxidation seems to be lower. CO$_2$ more stable than CH$_3$OH. Compatible with observations of ISM?
DIMERS ARE EASILY FORMED
OXIDATION AND HYDROGÉNATION EASY

Congiu et al 2012, ApjL
Congiu et al 2012, JCP
Ioppolo et al 2012, JCP
Minissale et al 2013, CPL
Minissale et al 2014, PCCP
Ioppolo et al 2014, PCCP
Hydrogenation at low temperatures does not always lead to saturation: the case of HNCO.

J. A. Noble, P. Theule, E. Congiu, F. Dulieu, M. Bonnin, A. Bassas, F. Duvernay, G. Danger, and T. Chiavassa

a Laboratoire Physique des Interactions Ioniques et Moléculaires, UMR 7345-CNRS, Aix-Marseille Université, 13097 Marseille Cedex 20, France
b LERMA-LAMAp, Université de Cergy-Pontoise, Observatoire de Paris, ENS, UPMC, UMR 8112 du CNRS, 5 mail Gay Lussac, 95000 Cergy Pontoise Cedex, France
e-mail: jennifer.noble@univ-amu.fr
1) Determine the ML
2) Measure the binding energies
HNCO + H / + D

HNCO + H (2ML) → Almost nothing, small reduction
HNCO + D (2ML) → Fast (large) reduction

HNCO avant réaction
HNCO après réaction

HNCO + D (2ML) → DNCO
HNCO + H (long exposure) => HNCO loss

Table 2. The results of experiments carried out on (sub)monolayer quantities of HNCO.

<table>
<thead>
<tr>
<th>Initial HNCO (ML)</th>
<th>Exposed to</th>
<th>Temperature (K)</th>
<th>HNCO reduction (%)</th>
<th>DNCO produced (%)</th>
<th>Loss (to CD) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.7 ML D</td>
<td>10</td>
<td>34 ± 5</td>
<td>36 ± 5</td>
<td>-2 ± 5</td>
</tr>
<tr>
<td>1.0</td>
<td>10 ML H</td>
<td>7</td>
<td>11 ± 5</td>
<td>none</td>
<td>11 ± 5</td>
</tr>
<tr>
<td>1.0</td>
<td>25 ML D</td>
<td>15</td>
<td>57 ± 5</td>
<td>22 ± 5</td>
<td>35 ± 5</td>
</tr>
</tbody>
</table>

Fig. 8. Proposed reaction scheme for HNCO with H.

No hydrogenation and efficient chemical desorption (env 10%)
• O and H can increase the molecular complexity, but they can also reduce it! (i.e. $\text{H}_2\text{CO} + \text{O} \rightarrow \text{CO}_2 + \text{H}_2$)

• Many new molecules have been synthesized at low T on amorphous surfaces (Glyco-aldehyde, Ethylene glycol, Formamide…)

• Complex organic molecules can be form, but **how** and **how much** is the current problem

• Reaction networks are looping, and an experiment is only the measure of a chemical equilibrium

• **Ongoing efforts** to couple reasonable models to experimental facts

• Desorption is more complex than previously thought

• Isotopic effects, nuclear spin conversion (OPR), also happen in the solid phase …
OUR LAB IS HERE! (50km...)

Communauté d’agglomération de Cergy-Pontoise / photo : Guy Demesme ©
BEAM DISSOCIATION EFFICIENCY

The graph shows the mass 32 signal with discharge on and off states, and a flag on at a certain power level.
BEAM INTERNAL ENERGY OF O AND N DISCHARGES
During Exposure Detection (DED)

Case of D, sent on 0.5 ML of O₂

D₂O detected!

(D₂O₂ not detected)

Limits of DED
- Weak signals
- Hard to calibrate
- Possibility of multiple assignation

But direct!

(D₂O not detected)
Chemical desorption of water

3 kind of substrates: ASW is reducing CD

During irradiation, D$_2$O is detected, not D$_2$O$_2$
Chemical desorption studied through DED method

![Diagram showing desorbing molecules and particles from the beams.](image_url)

![Graph showing cps vs. time for m32 (O on H2O) and m32 (O on graphite).](image_url)

![Bar chart comparing O2 chemical desorption and Undissociated beam.](image_url)
CD is dependent on the type of substrate

CD close to 0 for ices
CD variable but similar behavior for silicates and O-graphite
TPD areas, representation O3vsO2

Missing amount identical for Ts variable

==> Only depends on coverage
CD is decreasing with the coverage
3 unknowns? use a as parameter

\[ e \text{ CD}, \ O + O \rightarrow O_2 \]
\[ f \text{ CD}, \ O_2 + O \rightarrow O_3 \]

**conclusion** \( e \gg f \)

Minissale & Dulieu 2014
Chemical desorption, effect of coverage

Exposure of 0.5 ML of O on pre-adsorbed N\textsubscript{2}
O ON OX-GRAPHITE

CD + ONE DIFFUSION K

![Graph showing TPD yields and exposure time]
CORELLATION O$_2$ / H$_2$O
NO CORELLATION BETWEEN CO/N$_2$ AND O$_2$

O$_2$/CO desorption: Noble, Diana Dulieu MNRAS 2015
• Is it possible that O2 does not come from simple desorption (like N2/CO)?

• Is it possible that O2 is produced during water desorption?

• We know that water is formed and should include a fraction of H2O2

• What about H2O2 dismutation?

• At room temperature H2O2 evaporate in H2O and O2.

Bieler et al Nature 2015

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H$_2$O/H$_2$O$_2$ mixture (50/50 %) made from [O$_2$+D] experiments

Desorption of mixed H$_2$O/H$_2$O$_2$ layer

Thin layer (<1ML) on silicate

2 H$_2$O$_2$ $\rightarrow$ 2 H$_2$O + O$_2$.

Yes, dismutation occurs at 180 K, but incomplete.

Ratio & stochiometry efficiency 25-50%
**Desorption of Mixed H₂O/H₂O₂ Layers**

H₂O/D₂O₂ mixture (95/5%) made from [O₂+D] on H₂O layers.

Yes, dismutation occurs at 155 K, and complete.*

**Equation:**

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2. \]

**Graph:**

Temperature-programmed desorption (TPD) yields for O₂, D₂O₂, and H₂O. 

*HDO refers to heavy water oxide.*
It is possible that 7% of initial H$_2$O$_2$ release 3.5% of O$_2$ just after the final desorption of water ice.
\textbf{O}_2 \textbf{IN THE ISM ?}

O$_2$ and H$_2$O$_2$ is/was over predicted
O$_2$ and H$_2$O$_2$ are sparsely detected

H$_2$O$_2$ only detected where O$_2$ is detected (see Parise et al 2014)

\textbf{Goldsmith et al 2011}

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\textbf{HERSCHEL* MEASUREMENTS OF MOLECULAR OXYGEN IN ORION}

denoted Peak A, the Western Clump, or MF4. The mass of this source is $\sim 10\, M_\odot$ and the dust temperature is $\geq 150\, \text{K}$. Our preferred explanation of the enhanced O$_2$ abundance is that dust grains in this region are sufficiently warm ($T \geq 100\, \text{K}$) to desorb water ice and thus keep a significant fraction of elemental oxygen in the gas phase, with a significant fraction as O$_2$. For this small source, the line ratios require a temperature $\geq 180\, \text{K}$. The inferred
• Many new molecules have been synthesized at low T on amorphous surfaces

• Reaction networks are looping, and an experiment is only the measure of a chemical equilibrium

• Complex organic molecules can be form, but how and how much is the current problem

• **Ongoing efforts** to couple reasonable models to experimental facts

• Desorption is more complex than previously thought

• Isotopic effects, nuclear spin conversion (OPR), also happen in the solid phase ...
D$_2$ TPD: A VERY SENSITIVE TOOL TO PROBE THE WATER ICE MORPHOLOGY

One over-layer of «porous ice» is enough to get energetical properties of «thick» porous ice.

5 layers required to «hide» the ice substrate properties.
POROSITY REDUCTION DUE TO D RECOMBINATION

Experiments: overlayer of porous ice is exposed to D (or H)
O$_2$ calibration

Calibration of O$_2$ beam

- **O$_2$ Exposure time**
  - 35 s
  - 60 s
  - 120 s
  - 180 s
  - 240 s
  - 360 s
  - 480 s
  - 600 s

- **100ML np-ASW**

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**O$_2$ signal (cps)**

**Temperature (K)**