Kinetics of Neutrals & Ions in Cold Molecular Plasmas
Gas and Surface Processes

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1.- Diagnostic and Modelling of Cold Plasmas

( \( T_e >> T_{gas} \) )

*Plasmas considered in this work (rich in \( H_2 \)):

\( H_2, H_2 + D_2, H_2 + N_2, H_2 + O_2, H_2 + Ar \)

2.- Stability of hydrogenated amorphous carbon deposits (taken as dust analogs) versus UV irradiation and electron bombardment
Interest of cold plasmas with high H$_2$ content

• Surface Engineering (Microelectronics, Optics, Solar cells...)
• Plasma-Wall Interaction in Nuclear Fusion Reactors
• Chemistry of Interstellar Media & Planet Atmospheres...

• Some kinetic mechanisms common to plasmas and ISM
• Spectroscopy of transient species of interest in Astrophysics
Cold $H_2$ rich lab. plasmas vs. ISM Molecular Clouds

**Similarities**

- Gas-phase dominated by $H_2$
- Low ionization degree
- Low density ⇒ only binary collisions
- Extensive ion-molecule chemistry (large $k \neq f(T_{\text{gas}})$)
- Surface chemistry explains the formation of molecules like $H_2$
Cold H$_2$ rich lab plasmas vs. ISM Molecular Clouds

**Differences**

- **Ionization mechanisms:**
  - Lab: electron impact
  - Mol. Clouds: cosmic rays

- **Neutralizations of ions:**
  - Lab: neutralization in the wall
  - Mol. Clouds: mainly dissociative electron attachment...

- **Surface chemistry among neutral particles:**
  - Different relevance of the different possible processes, such as Langmuir-Hinshelwood, Eley-Rideal...
The plasmas have been generated in Hollow Cathode DC Discharges

- Very stable and homogeneous plasmas confined in the negative glow, where $E = 0$, and neutrals & ions diffuse at low energies.

- Potential fall in the cathode sheath $\sim V_{DC}$, where ions, maintaining the distributions acquired in the negative glow, are accelerated towards the cathode and neutralized in the wall.

- Reactor designs adaptable to different aims and diagnostic techniques.
Experimental details

- Low Pressure $\sim 0.7 - 8 \text{ Pa}$
- Low ionization degree $\sim 10^{-4} - 10^{-5}$
- $T_e \sim 20.000 - 90.000 \text{ K} (2 - 8 \text{ eV})$
- $T_{\text{gas}}$ (neutrals & ions) $\sim 300 - 400 \text{ K}$

Diagnostics

- Spectrometric techniques (emission, MS of ions & neutrals)
- Langmuir probes

*Tanarro et al., J.P. C. A 111, 9003 (2007)*
*Jiménez-Redondo et al., PSST, 22, 25022(2013)*
Kinetic Models

Main Processes Considered:

- Ionization + dissociation by electron impact in the glow.
- Gas phase ion-molecule reactions.
- Surface recombination of neutrals and neutralization of ions.

Methodology

- Zero order models (two volumes: negative glow + sheath).
- Set of time dependent differential equations,
  from the ignition of the discharge to the steady-state.
- Maxwellian electron energy distributions.
**H₂ plasmas**

**NEUTRALS:** \([H] / [H₂] \sim 10-15 \%\)

\(H₂\) Dissociation \(\Rightarrow\) H + H Surface Recombination

**IONS:** Inversion of Major Ion from \(H₂^+\) to \(H₃^+\) with \(P_{gas} \uparrow\)

\(H₂\) Ionization \(\Rightarrow\) \(H₂^+ + H₂ \rightarrow H₃^+ + H\)

![Graphs and images showing relative concentration and reaction rates](image)

Méndez et al, JCP A 110, 6060 (2006)
In pure \( \text{H}_2 \) discharges, the \( \text{H}_2 \) “precursor”, renewed continuously by the gas flow, can’t be distinguished experimentally from the \( \text{H}_2 \) produced by dissociation + recombination in the wall (SS).

\( \text{H}_2 + \text{D}_2 \) discharges would help to clarify the relevance of the heterogeneous recycling!
**NEUTRALS:**

$H_2$, $D_2$ precursors & HD product found in comparable amounts $\Rightarrow$ Extensive dissociation and wall recycling!

**IONS:**

$P \uparrow \Rightarrow T_e \downarrow$ and triatomic ions prevail, due to protonation reactions.

*Statistical ion isotopic composition: $T_{gas} \approx 300 - 400$ K $\Rightarrow D$ enrichment through zero point effect unnoticeable*

*Jiménez-Redondo et al, PCCP 13, 9655 (2011)*
Wall recycling in H₂ + D₂ plasmas

Langmuir-Hinshelwood processes, crucial in the interstellar media, would be relevant in our discharges only for low activation energies (< 0.6 eV) but would lead to serious discrepancies with experimental observations.

Eley-Rideal must be the origin of H₂ + D₂ recycling and HD formation, in “high surface coverage” plasmas!
H₂ + N₂ plasmas

**Neutrals:**
- NH₃ formation by multistep wall reactions involving H, N, NH, NH₂.
- E-R & L-H processes necessary.
- NH₃ is always the minor species (≤ 2%).

**Ions:**
- Prevalence of protonated ions over the parent ones: H₃⁺, N₂H⁺ & specially NH₄⁺, which does not further react in gas phase.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Proton affinity</th>
<th>Protonated ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>854 kJ mol</td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>N₂</td>
<td>494</td>
<td>N₂H⁺</td>
</tr>
<tr>
<td>H₂</td>
<td>422</td>
<td>H₃⁺</td>
</tr>
</tbody>
</table>

*Carrasco et al, PCCP 13, 19561 (2011)*
**H₂ + N₂: Time resolved predictions**

**Neutrals:**

Slow formation of NH₃ in the surfaces ($t > 0.1$ s)

**Ions:**

Initial transfer $H₂^+$ to $H₃^+$ ($t < 0.1 \mu$s), then from $H₃^+$ to $N₂H^+$ ($t < 10 \mu$s), and $NH₄^+$ prevails when NH₃ appears.

E. Carrasco et al. PCCP, **15**, 1699 (2013)
**H₂ + O₂ plasmas**

**Neutrals:**
H₂O, formed at the walls, more abundant than the O₂ precursor. Less steps than in the case of NH₃.

**Ions:**
H₃O⁺ always dominant. Contrary to N₂H⁺ in H₂+ N₂ discharges, hardly any O₂H⁺ is detected (<1%).

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<tr>
<td>H₂O</td>
<td>691</td>
<td>H₃O⁺</td>
</tr>
<tr>
<td>H₂</td>
<td>422</td>
<td>H₃⁺</td>
</tr>
<tr>
<td>O₂</td>
<td>421</td>
<td>HO₂⁺</td>
</tr>
</tbody>
</table>
**H₂ + Ar plasmas**

**IONS:** Drastic change in ArH⁺ distributions with P: $T_e$ changes and $(H_3^+)^*$ influences the balance of $H_3^+ + Ar \rightleftharpoons ArH^+ + H_2$


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<tr>
<td>H₂</td>
<td>422</td>
<td>$H_3^+$</td>
</tr>
<tr>
<td>Ar</td>
<td>371</td>
<td>ArH⁺</td>
</tr>
</tbody>
</table>
Conclusions - Part 1

• Neutral products like HD, NH₃ or H₂O are efficiently formed in the surfaces of the plasmas studied, mainly through Eley-Rideal processes.

• The ion chemistry is very sensitive to electron temperatures and is dominated by protonation reactions. Internal excitation can also be relevant.

• The preponderance of a given ion is largely given by the proton affinity of its neutral precursor.
2\textsuperscript{nd} Part:
Stability of hydrogenated amorphous carbon (HAC) deposits (taken as dust analogs) versus UV irradiation and electron bombardment
HAC film deposition in CH$_4$/He plasma

- CH$_4$(40%)/He, 0.3 mbar
- 40 W, 13.56 MHz, 1 h

*Inductively coupled RF discharge*

outside the coil  
inside the coil
IR spectra of the deposits

- **CH asymm stretch**
  - CH₃ CH₂ CH₃
  - 3.4 µm

- **C= C stretch**
  - 6.9 µm
  - 6.2 µm

- **CHₓ bend**
  - 7.2 µm
  - 11.3 µm

- **Aromatics**
- **Aliphatics**

- Outside the coil
- Inside the coil x5

Absorbance vs. wavenumber / cm⁻¹

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INSTITUTO DE ESTRUCTURA DE LA MATERIA

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS

IEM

CSIC
Two kinds of energetic processing: UV and $e^-$

- 160 nm, 7.6 eV
  - UV photons
  - $D_2$ lamp
  - Flow: $4.0 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$

- 2 keV
  - electrons
  - electron gun
  - Flow: $2.66 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$

Diffuse cloud $\sim 3 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$
2 keV e- are noticeably less efficient than UV photons.

HAC deposits from different precursors

Different absorption structures

methane (35%) + He, 0.31 mbar, 120 min
bencene (35%) + He, 0.21 mbar, 10 min

RF 40 W
Conclusions Part 2

• Hydrogenated amorphous carbon deposits formed in a CH₄ + He RF discharge are relatively stable under UV light and electron bombardment.

• UV photons (160 nm, 7.6 eV) induce a certain dehydrogenation of the structure, probably increasing the chain length.

• Bombardment with 2 keV electrons is energetically less efficient. It does not seem to change the structure, but produces a layer by layer erosion of the films.
Thank you!