Electron impact fragmentation of molecular ions

Light Element Atom, Molecule and Radical Behaviour in Divertor and Edge Plasma Regions
IAEA, 23-25 May 2011

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Electron induced fragmentation of molecules proceeds via dissociation reactions producing neutral and ionic fragments:

- **Dissociative Recombination (RD)**
  \[ AB^+ + e^- \rightarrow A + B \]
  in the very low energy range (<10 eV)

- **Dissociative Excitation (DE)**
  \[ AB^+ + e^- \rightarrow A^+ + B + e^- \]
  \[ \rightarrow A + B^+ + e^- \]
  above 10 eV

- **Single Ionization (SI)**
  \[ AB^+ + e^- \rightarrow AB^{++} + 2 e^- \]
  above 20 eV

- **Dissociative Ionization (DI)**
  \[ AB^+ + e^- \rightarrow A^+ + B^+ + 2 e^- \]

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Only ionic fragments are collected in present experiments

Schematic potential curves associated with the dissociation processes for a diatomic molecular ion
The animated crossed beams method is applied to measure:

- Absolute inclusive cross sections for electron impact dissociation to individual ionic fragments from the threshold up to 2.5 keV.

- The contributions from the different reaction channels are separated: single ionization (SI), dissociative excitation (DE) and dissociative ionization (DI)

- Kinetic energy release distributions (KERD) of the fragment ions are determined at selected incident electron energies.

- Energy threshold determination allows identification of target initial ground and excited states
Light ions:
- $H_2^+$, $D_2^+$
- $D_3^+$, $D_2H^+$

Hydride ions:
- $HeH^+$ (unpublished)
- NeD$^+$
- $OH^+$, $OH_2^+$, $OH_3^+$ and isotopologues (unpublished)

Hydro(deutero)-carbon ions:
- CH$^+_n$ or CD$^+_n$ (n=1–4)
- $C_2D^+$; $C_2D_2^+$,
- $C_2D_3^+$, $C_2D_4^+$ and isotopologues $C_2D_3H^+$ and $C_2D_2H_2^+$ (unpublished)

Others
- CO$^+$, CO$_2^+$, O$_2^+$
- C$_2^+$ (unpublished)

Nitrogen:
- N$_2^+$
- NH$^+$, ND$^+$

A comprehensive understanding of the plasma requires the knowledge of the various mechanisms governing the destruction of these species.
• For the light ions:

\[ \text{H}_2^+, \text{D}_2^+, \]


Particular importance of the internal energy: vibrational population

\[ \text{H}_3^+, \text{D}_3^+ \]


\[ \text{D}_2\text{H}^+ \]

Detected fragments: \text{H}^+, \text{D}^+, \text{HD}^+, \text{D}_2^+


Isotope effects in the fragmentation
Results: $D_2H^+$

$D_2H^+ + e^- \rightarrow X^+ + ...$

H$^+$ (○), D$^+$ (●), HD$^+$ (□) and D$_2$$^+$ (■)

For clarity reasons, error bar are not presented in the figure.
Results: $D_2H^+$

$D_2H^+ + e^- \rightarrow H^+ + ...$
$D^+ + ...$

(■) : $H^+$ (a) and $D^+$ (b)
(x) : dissociative excitation (DE) contributions.
The solid lines are a guide to the eye to help visualize DE contributions.
Results: $D_2H^+$

$$D_2H^+ + e^- \rightarrow DH^+ + \ldots$$
$$D_2^+ + \ldots$$

Graphs (c) and (d) show the cross-section for $D_2H^+$ and $D_2^+$ production. The solid lines are a guide to the eye to help visualize dissociative excitation (DE) contributions.

- ■: $DH^+$ (a) and $D_2^+$ (b),
- (x) : dissociative excitation (DE) contributions.

The solid lines are a guide to the eye to help visualize DE contributions.
Dissociative ionization (DI): □, HD$^+$+D$^+$ channel ; ○, D$_2$$^+$+H$^+$ channel

Results: D$_2$H$^+$

\[ D_2H^+ + e^- \rightarrow X^+ + Y^+ + 2e^- \]
### Results: $D_2H^+$

<table>
<thead>
<tr>
<th>Dissociation process</th>
<th>$H_3^+$</th>
<th>Experimental (eV)</th>
<th>Predicted (eV)</th>
<th>$D_2H^+$</th>
<th>Experimental (eV)</th>
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<td>RDE</td>
<td>$H^++H_2$</td>
<td>4.5 ± 0.5</td>
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<td></td>
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<td>$D^++HD$</td>
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<td>$H^++H+H^-$</td>
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<td>DE</td>
<td>$H^++H+H$</td>
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<td>$H^++D+D$</td>
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<td>14 ± 1</td>
<td>14.75 ($1^3E'$)</td>
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<tr>
<td>RIP</td>
<td>$H_2^++H^-$</td>
<td>5.8</td>
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<td>DE</td>
<td>$H_2^++H$</td>
<td>6.0 ± 0.5</td>
<td>6.2</td>
<td>$HD^++D$</td>
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<td>$D_2^++H$</td>
<td>8.5 ± 0.5</td>
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<td>DI</td>
<td>$H^++H_2^+$</td>
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<td>$H^++D_2^+$</td>
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<td>12.0 ± 0.5</td>
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<td>DI</td>
<td>$H^++H^++H$</td>
<td>22.5</td>
<td>33.47 (FC) 4</td>
<td>$D^++HD^+$</td>
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<td>$D^++H^++D$</td>
<td>35 ± 1 (HD$^+$)</td>
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<td>35 ± 1 ($D_2^+$)</td>
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Threshold energies (eV) for the dissociation of $D_3^+$ and of $D_2H^+$.

1 [10] 2 [23], 3 [13], 4 [20]

**Note:** RIP (Resonant-Ion-Pair formation) and FC (Franck-Condon)
Isotopes (H, D) are equivalent with respect to the electronic energy of the molecular system, but they are not equivalent with respect to the dynamics. In a classical potential $U(r)$ scattering description, the total energy of a particle is:

$$E = \frac{1}{2} m \left( \frac{dr}{dt} \right)^2 + U(r) + \frac{L^2}{2mr^2}$$

$L^2/2mr^2$ corresponds to the centrifugal potential barrier. Integration of this expression gives:

$$t = \sqrt{\frac{m}{2}} \int \frac{dr}{\sqrt{E - U(r) + L^2/2mr^2}}$$

For two isotope (mass $m_1$ and $m_2$) along the same path in the potential:

$$\frac{t_2}{t_1} = \sqrt{\frac{m_2}{m_1}}$$

Among isotopic species in the same kinematical conditions, the light particle should be ejected more rapidly than the heavy one, so that its production should be favored.

This tendency is confirmed for RDE: the signal is observed for $H^+$ only, not for $D^+$, $HD^+$, $D_2^+$

Estimation of the cross section ratios for DE:

$$2 \left[ H^+ + D_2 \right] / \left[ D^+ + DH \right]$$

and for DI:

$$2 \left[ D_2^+ + H \right] / \left[ HD^+ + D \right]$$

$$2 \left[ D_2^+ + H^+ \right] / \left[ HD^+ + D^+ \right]$$
Search for isotope effects: DE and DI

Results: $\text{D}_2\text{H}^+$

Cross section ratios for DE: (●) $2[H^++D_2]/[D^++HD]$; (×): $2[D_2^++H]/[HD^++D]$; for DI: (○): $2[D_2^++H^+]/[HD^++D^+]$

The tendency is not confirmed for DE production of $H^+$ versus $D^+$, The tendency is confirmed for DE production of $HD^+$ versus $D_2^+$ and for DI.
Search for isotope effects: $D_2H^+$ versus $D_3^+$

Inclusive cross sections (DE+DI)
(a) for $D^+/D_3^+$ (■) and for $(H^++D^+)/D_2H^+$ (∗)
(b) for $D_2^+/D_3^+$ (■) and for $(HD^++D_2^+)/D_2H^+$ (∗)
The solid line is a guide to the eye to help visualize DE contribution.
Absolute cross sections versus the electron energy for
(a) DE for $D^+/D_3^+$ (■) and for $(H^++D^+)/D_2H^+$ (×),
(b) DE $D_2^+/D_3^+$ (■) and for (×), $(HD^++D_2^+)/D_2H^+$
Search for isotope effects: $\text{D}_2\text{H}^+$ versus $\text{D}_3^+$

(c) DI for $\text{D}_2^+/\text{D}_3^+$ (■) and for, (HD$^+$+D$_2^+$)/D$_2$H$^+$ (×)

Results: $\text{D}_2\text{H}^+$, $\text{D}_3^+$
Search for isotope effects: $D_2H^+$ versus $D_3^+$

Cross section ratio $\{X^+/D_3^+\}/\{Y^+/D_2H^+\}$ for the dissociative contributions:

$[D^+]/[H^++D^+]$ (DE, ●), $[D_2^+]/[HD^++D_2^+]$ (DE, ×) and $[D_2^+]/[HD^++D_2^+]$ (DI, ○).
• Hydride ions:

\textbf{HeH}^+

Detected fragments: He$^+$, He$^{2+}$
Analysis of the vibrational population: in progress

\textbf{Others targets: OH}^+, \textbf{OH}_2^+, \textbf{OH}_3^+ and isotopologues

Unpublished, analysis in progress

For dissociative ionization of HDO$^+$, the results are analysed in the Born approximation, including the molecular dynamics treatment of the doubly charged target
Present cross results: inclusive ($\sigma_{1,3}$, ○), DE ($\sigma_1$, ●) and DI ($\sigma_3$, ▼).
Experimental DE ($\times$—$\times$) (Stromholm et al, 1996).
Theoretical total excitation cross sections, (—) (Orel et al, 1991).

Results: hydride ions

$e^- + HeH^+ \rightarrow He^+ + ...$
Total kinetic energy release distributions for He$^+$ at:
(a) 21 eV, (b) 45 eV, (c) 95 eV and (d) 295 eV.
• **Hydro(deutero)-carbon ions:**

\[ \text{C}_2\text{D}_3^+ , \text{C}_2\text{D}_4^+ \text{ and isotopologues } \text{C}_2\text{D}_3\text{H}^+ \text{ and } \text{C}_2\text{D}_2\text{H}_2^+ \text{ (unpublished)} \]

• **Others**

\[ \text{C}_2^+ \text{ (unpublished)} \]
Results: hydrocarbons

Experimental results to be analysed

Work in progress
Results: $C_2^+$
Theory: ionization cross sections are estimated by:

- Binary-Encounter-Bethe, BEB, Kim *et al*
- **Deutsch-Märk** Formalism, DM, Deutsch *et al*
- *Semi-empirical model of* R.K. Janev and D. Reiter for dissociative excitation (DE) and for dissociative ionization (DI)
- Plane-Wave-Born calculations by C. Dal Capello, P.A. Hervieux and E. Giglio allow the detailed analysis of the fragmentation pattern by means of the molecular dynamics description of the target in the final state. This includes temperature effects.

Results are: partial cross sections for each fragment and associated branching ratios or isotope effects and *KER distributions*. 
Absolute cross sections for electron impact fragmentation of molecular ions are measured from the respective thresholds up to 2.5 keV for molecular ions.

- contributions from different reaction channels: single ionization (SI), dissociative excitation (DE) and dissociative ionization (DI)

- kinetic energy release distributions are determined (KERD) for the fragment ions.

Isotope effects are seen to play an important role in the fragmentation via RDE, DE and DI.

For dissociative ionization, the Born approximation, combined with a molecular dynamics treatment allows the detailed description of the fragmentation pattern.
Nitrogen hydrides: dissociation of NH$^+$ and ND$^+$

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2nd research coordination meeting
"Light element atom, molecule and radical behaviour in the divertor and edge plasma regions"
IAEA – May 2011

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Why?

- Nitrogen is a natural impurity in plasma experiments after the vessel’s exposure to air.
- Nitrogen is also sometimes deliberately introduced as a radiating impurity to cool the edge of the plasma.
- The formation of hydrides XH and XH⁺ (X = Li, Be, B, C, N, O…) is not adequately understood

\[
\text{NH}^+ + e^- \rightarrow \text{NH}^{2+} + 2e^- \quad \text{(SI) not observed}
\]
\[
\rightarrow \text{N}^+ + \text{H}^+ + 2e^- \quad \text{(DI)}
\]
\[
\rightarrow \text{N}^{2+} + \text{H} + 2e^- \quad \text{(ADI)}
\]
\[
\text{NH}^+ + e^- \rightarrow \text{N}^+ + \text{H} + e^- \quad \text{(DE)}
\]
\[
\text{ND}^+ + e^- \rightarrow \text{N} + \text{D}^+ + e^- \quad \text{(DE)}
\]

Absolute cross sections

for the N⁺ production
versus the electron energy.

- Total cross sections (▲)
- Dissociative Excitation (×)
- Dissociative Ionization (□)

The solid curve results from a fitting procedure of the present experimental data to help distinguish the dissociative excitation channel.

Total absolute cross sections (▲):

\[ \sigma_N = \sigma_{DE} + \sigma_{DI} \]

The maximum total cross section for N⁺ is observed to be \(15.7 \times 10^{-17}\) cm².
Potential Energy Curves

<table>
<thead>
<tr>
<th>State</th>
<th>VEE (eV)</th>
<th>Dissociation limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>X^2Π</td>
<td>0.00</td>
<td>N(^3P)+H(^2S)</td>
</tr>
<tr>
<td>a^4Σ^-</td>
<td>0.00</td>
<td>N(^4S)+H^+(^1S)</td>
</tr>
<tr>
<td>A^2Σ^-</td>
<td>3.11</td>
<td>N(^3P)+H(^2S)</td>
</tr>
<tr>
<td>B^2Δ</td>
<td>3.11</td>
<td>N(^2D)+H^+(^1S)</td>
</tr>
<tr>
<td>C^2Σ^+</td>
<td>4.54</td>
<td>N(^1D)+H(^2S)</td>
</tr>
<tr>
<td>2^2Π</td>
<td>7.83</td>
<td>N(^2D)+H^+(^1S)</td>
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<tr>
<td>2^4Σ^-</td>
<td>10.48</td>
<td>N(^3P)+H(^2S)</td>
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<tr>
<td>1^4Π</td>
<td>12.43</td>
<td>N(^3P)+H(^2S)</td>
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<td>2^2Σ^+</td>
<td>12.81</td>
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<td>N(^1S)+H(^2S)</td>
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<td>3^4Σ^-</td>
<td>16.52</td>
<td>N(^5S)+H(^2S)</td>
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<tr>
<td>1^6Σ^-</td>
<td>19.40</td>
<td>N(^5S)+H(^2S)</td>
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<tr>
<td>2^5Σ^-</td>
<td>25.73</td>
<td>N(^4S)+H^+(^1S)</td>
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</tbody>
</table>

Vertical excitation energies (VEE) of the states that correlate to the lowest dissociation limits of NH^+ at r_e(X^2Π).
The N⁺ appearance energy is 2.5 eV.

Around the maximum, $\sigma_{DE}$ is $8.1 \times 10^{-17}$ cm².

Indirect dissociative excitation (IDE) is observed below the threshold of direct dissociative excitation (DDE) at 8.0 eV.
Vibrationally excited states of NH\(^+ (v)\) are populated in the ion beam. Two mechanisms can produce these levels:

a) the endothermic reaction \(H_2^+(v') + N\)

b) the ion–molecule reaction \(H_2(v'') + N^+\)

The three lowest states are bound and non-dissociative. They should not contribute to the \(N^+\) formation if no vibrational population is involved.

Initial capture of the incoming electron into a doubly excited electronic state of NH:

\[
e^- + NH^+(v) \rightarrow (NH)^{**}
\]

\[
\rightarrow (NH^+)^* + e^-
\]

\[
\rightarrow N^+ + H + e^-
\]

\[
\rightarrow N + H^+ + e^-
\]

In the energy range starting above a few eV, the Rydberg series that converge to excited electronic states of the ion become accessible.
**IDE**: peaked on 5 eV and it exhibits a cross section of $3.6 \times 10^{-17}$ cm$^2$

**DDE**: peaked on 21 eV and it exhibits a cross section of $7.6 \times 10^{-17}$ cm$^2$

DDE occurs via transition to a repulsive excited electronic state with enough internal energy to induce fragmentation.

- First dissociative state ($N^+(3P)+H(2S)$) is the $2^4\Sigma^−$ at 10.48 eV.
- Second dissociative state is the $1^4\Pi$ at 12.43 eV.

One needs to take into consideration the effect of the NH$^*$ vibrational population.

The third and last contribution starts from about 35 eV: broad with a maximum of $2.3 \times 10^{-17}$ cm$^2$ (@ 250 eV)

Many electronic states, the vertical excitation energies of which are included in the 20–40 eV range, can contribute to the DE signal.
**Ionization**

\[ \text{NH}^+ + e^- \rightarrow \text{N}^+ + \text{H}^+ + 2e^- \]
\[ \rightarrow \text{N}^{2+} + \text{H} + 2e^- \]

**Legend:**
- □: Dissociative Ionization \((\sigma_{\text{DI}})\)
- ●: Asymmetric DI \((\sigma_{\text{ADI}}) \times 10\)

- **Dissociative Ionization:**
  Threshold at 20.0 eV and max of \(12.1 \times 10^{-17} \text{ cm}^2\) (50% higher than DE).
  Direct vertical ionization in the 25–27 eV range, high-lying sextet states of NH\(^+\) cross the \(X^1\Sigma^+\) state of NH\(^2+\) such that autoionization occurs.

- **Asymmetric DI:**
  Threshold at 31.5 eV and max of \(11.1 \times 10^{-18} \text{ cm}^2\).
\[ \text{NH}^+ + \text{e}^- \rightarrow \text{N}^+ + \text{H}^+ + 2\text{e}^- \]
\[ \rightarrow \text{N}^{2+} + \text{H} + 2\text{e}^- \]

**Bethe-plot** of present ionization cross sections.

Energy dependence of the electron-impact ionization cross sections \( \sigma_i \)

\[
\sigma_i = \frac{a}{E I_i} \left[ \ln \left( \frac{E}{I_i} \right) + b \right]
\]

Experimental data for N\(^+\)+H\(^+\) (DI) and for N\(^{2+}\)+H (ADI) are well adjusted along straight lines from above 40eV.
Comparison of absolute cross sections for the formation of D⁺ (×) and of N⁺ (▲), versus the electron energy.

The curves result from fitting procedure of the present experimental data obtained for D⁺ and for N⁺.

Full lines (—) are for the total cross sections and dashed lines (−−) are for the DE contributions.
**Absolute cross sections**

for the **D⁺ production**

versus the electron energy.

- Total cross sections (×)
- Dissociative Excitation (●)
- Dissociative Ionization (○)

The maximum total cross section for D⁺ is observed to be 16.8×10⁻¹⁷ cm².

At the maximum, the absolute cross section for dissociative excitation is found to be 13.9×10⁻¹⁷ cm² and the appearance energy is measured to be 4.0 eV.

DE clearly dominates below 20 eV.
### Potential Energy Curves

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Vertical excitation energies (VEE) of the states that correlate to the lowest dissociation limits of \(NH^+\) at \(r_e(X^2\Pi)\).
Absolute cross sections for the dissociative excitation channel (N+D\(^+\)), versus the electron energy (●), together with the excited electronic states that correlate to the lowest dissociation limits yielding to the D\(^+\) production.

Initial capture of the incoming electron into a doubly excited state of ND:
\[
e^{-} + \text{ND}^{+}(\nu) \rightarrow (\text{ND})^{**} \\
\rightarrow (\text{ND}^{+})^{*} + \text{e}^{-} \\
\rightarrow \text{N}^{+} + \text{D} + \text{e}^{-} \\
\rightarrow \text{N} + \text{D}^{+} + \text{e}^{-}
\]
At low incident electron energies (e.g. 15 eV), the present KERDs are mainly due to dissociative excitation, whereas ionization is the dominant contribution for the KERDs measured at the highest incident energies (e.g. 295 eV).

It appears than the expected kinetic energies for excitation ($N^+ + H$) are expected to be included in the 5.7–9.2 eV range.

<table>
<thead>
<tr>
<th>State</th>
<th>Dissociation limit</th>
<th>$E_{KER}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^2\Pi$</td>
<td>$N^+(3P)+H(2S)$</td>
<td>-</td>
</tr>
<tr>
<td>$A^2\Sigma^-$</td>
<td>$N^+(3P)+H(2S)$</td>
<td>-</td>
</tr>
<tr>
<td>$C^2\Sigma^+$</td>
<td>$N^+(1D)+H(2S)$</td>
<td>-</td>
</tr>
<tr>
<td>$2^4\Sigma^-$</td>
<td>$N^+(3P)+H(2S)$</td>
<td>5.7</td>
</tr>
<tr>
<td>$1^4\Pi$</td>
<td>$N^+(3P)+H(2S)$</td>
<td>7.7</td>
</tr>
<tr>
<td>$3^2\Pi$</td>
<td>$N^+(1D)+H(2S)$</td>
<td>7.5</td>
</tr>
<tr>
<td>$2^2\Delta$</td>
<td>$N^+(1D)+H(2S)$</td>
<td>7.9</td>
</tr>
<tr>
<td>$3^2\Sigma^+$</td>
<td>$N^+(1S)+H(2S)$</td>
<td>7.5</td>
</tr>
<tr>
<td>$3^4\Sigma^-$</td>
<td>$N^+(5S)+H(2S)$</td>
<td>6.3</td>
</tr>
<tr>
<td>$1^6\Sigma^-$</td>
<td>$N^+(5S)+H(2S)$</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Three types of molecular activated processes coexist: dissociative recombination (MAR), dissociative excitation (MAD) and dissociative ionization (MAI).

**Molecular activated recombination (MAR):**
\[ \text{H}_2(v) + e^- \rightarrow \text{H} + \text{H}^- \text{ (dissociative attachment)} \]
followed by \[ X^+ + H^- \rightarrow X + H \text{ (charge exchange neutralization)} \]
and \[ \text{H}_2(v) + X^+ \rightarrow \text{H} + \text{XH}^+ \text{ (ion conversion)} \]
followed by \[ \text{XH}^+ + e^- \rightarrow X + \text{H} \text{ (dissociative recombination)} \]

**Molecular activated dissociation (MAD):**
\[ \text{H}_2(v) + X^+ \rightarrow \text{H} + \text{XH}^+ \text{ (ion conversion)} \]
followed by \[ \text{XH}^+ + e^- \rightarrow X^+ + \text{H} + e^- \text{ or } X + \text{H}^+ + e^- \text{ (dissociative excitation)} \]

**Molecular activated ionization (MAI):**
\[ \text{H}_2(v) + X^+ \rightarrow \text{H} + \text{XH}^+ \text{ (ion conversion)} \]
followed by \[ \text{XH}^+ + e^- \rightarrow X^+ + \text{H}^+ + 2e^- \text{ (dissociative ionization)} \]

X is either an existing impurity or an atom injected in the plasma (N, Ne, Ar...). Better knowledge of such reaction chain is important for an understanding of the overall plasma chemistry.
Thanks for your attention