Introduction
Molecular and thermochemical properties
Some illustrations of the interplay between observations and chemical mechanisms
- New analysis of the $\text{N}^+ + \text{H}_2$ reaction and its isotopic variants
- Tracers of atomic gas: $\text{OH}^+ / \text{ArH}^+$
- Tracers of molecular gas: $\text{H}_3^+$, $\text{CH}$, $\text{HF}$
Examples of (photo)chemical excitation ($\text{OH}$, $\text{H}_3\text{O}^+$, $\text{NH}_3$)
Summary
The increasing attention to hydrides

After the first detection of CH⁺, CH in absorption against bright stars ….

UV/Visible absorption spectroscopy: H₂, HD, OH, OH⁺, NH

Vibrational IR absorption spectra: H₃⁺, CH₄

Rotational submillimeter spectra:

ISO: CH⁺, CH₂, H₂O

Herschel: CH, CH⁺, OH, H₂O, OH⁺, H₂O⁺, H₃O⁺, NH, NH₂, NH₃, SH, SH⁺, H₂S, HF, HCl, HCl⁺, H₂Cl⁺, ArH⁺

Inversion spectra: NH₃, H₃O⁺

Λ doubling: OH, CH
The increasing attention to hydrides

After the first detection of CH\(^+\), CH in absorption against bright stars ....

UV/Visible absorption spectroscopy: H\(_2\), HD, OH, OH\(^+\), NH
Vibrational IR absorption spectra: H\(_3^+\), CH\(_4\)
Rotational submillimeter spectra

very luminous region of massive star formation can be used as a background THz source
Absorption by gas in foreground material
“clean experiment” allowing robust determination of molecular column densities.

Inversion spectra: NH\(_3\), H\(_3\)O\(^+\)
\(\Delta\) doubling: OH, CH
Introduction

**Molecular and thermochemical properties**
Some illustrations of the interplay between observations and chemical mechanisms
- New analysis of the N⁺ + H₂ reaction and its isotopic variants
- Tracers of atomic gas: OH⁺ / ArH⁺
- Tracers of molecular gas : H₃⁺, CH, HF

Examples of (photo)chemical excitation (OH, H₃O⁺, NH₃)

Summary
Importance of electronic structure

✓ Spectroscopy
  - UV/visible electronic transitions (talk of S. Federman)
  - Rotational/vibrational spectra pattern highly dependent on the ground electronic state property (talk of Domenech)
  - Intensity pattern / opacities (talk of Tennyson)

✓ Collisional excitation
  - PES computations
  - Collision equations and possible approximations for the different angular momenta (talks of Faure, Lique)

✓ Chemical reactivity
  - Open shell radicals are more reactive than closed electronic shells. (talks of Schneider, Alcaraz)
## Closed shell hydrides

<table>
<thead>
<tr>
<th>Diatomic</th>
<th>Triatomic</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tr>
<td>$X^{1\Sigma^+}$</td>
<td>$X^{1\Sigma^+}$</td>
<td>$X^{1A'_1}$</td>
<td>$X^{1A_1}$</td>
<td>$X^{1A_1}$</td>
</tr>
<tr>
<td>$D_{\infty h}$</td>
<td>$C_{\infty v}$</td>
<td>$C_{3v}$</td>
<td>$C_{2v}$</td>
<td>$T_d$</td>
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<tr>
<td>$H_2$</td>
<td>$H_3^+$</td>
<td>$H_2O$</td>
<td>$NH_3$</td>
<td>$CH_4$</td>
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<tr>
<td>$HF$</td>
<td>$H_2S$</td>
<td>$H_3O^+$</td>
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<tr>
<td>$HCl$</td>
<td>$H_2Cl^+$</td>
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<tr>
<td>$CH^+$</td>
<td></td>
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<tr>
<td>$ArH^+$</td>
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</table>

Detected in galactic and/or extragalactic ISM.
## Closed shell hydrides

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<tr>
<td>( X^1\Sigma^+ )</td>
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<td>( X^1\Sigma^+ )</td>
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<td>( X^1A_1 )</td>
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<tr>
<td>( \text{H}_2 )</td>
<td>( \text{LiH} )</td>
<td>( \text{H}_3^+ )</td>
<td>( \text{H}_2\text{O} )</td>
<td>( \text{NH}_3 )</td>
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<tr>
<td>( \text{HF} )</td>
<td>( \text{H}_2\text{S} )</td>
<td>( \text{H}_3\text{O}^+ )</td>
<td>( \text{H}_2\text{Cl}^+ )</td>
<td>( \text{CH}_3^+ )</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>( \text{H}_2\text{F}^+ )</td>
<td>( \text{H}_2\text{F}^+ )</td>
<td>( \text{H}_2\text{F}^+ )</td>
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<tr>
<td>( \text{CH}^+ )</td>
<td>( \text{ArH}^+ )</td>
<td>( \text{HeH}^+ )</td>
<td>( \text{SiH}^+ )</td>
<td>( \text{ArH}^+ )</td>
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</tbody>
</table>
Hydrides with non zero spin

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<tr>
<td>$X^2\Sigma^+<em>{C</em>{\infty}}$</td>
<td>$X^2\Pi_{C_{\infty}}$</td>
<td>$X^3\Sigma^-<em>{C</em>{\infty}}$</td>
</tr>
<tr>
<td>CH</td>
<td>NH</td>
<td>NH$_2$</td>
</tr>
<tr>
<td>OH</td>
<td>OH$^+$</td>
<td></td>
</tr>
<tr>
<td>SH</td>
<td>SH$^+$</td>
<td></td>
</tr>
<tr>
<td>HCl$^+$</td>
<td></td>
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*detected in the ISM*
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<tr>
<td>$X^2\Sigma^+_{\infty V}$</td>
<td>$X^2\Pi_{\infty V}$</td>
<td>$X^3\Sigma^-_{\infty V}$</td>
</tr>
<tr>
<td>$H_2^+$</td>
<td>CH</td>
<td>NH</td>
</tr>
<tr>
<td>LiH$^+$</td>
<td>OH</td>
<td>OH$^+$</td>
</tr>
<tr>
<td>BeH</td>
<td>SH</td>
<td>SH$^+$</td>
</tr>
<tr>
<td>MgH</td>
<td>HCl$^+$</td>
<td></td>
</tr>
<tr>
<td>CaH</td>
<td>NH$^+$</td>
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<tr>
<td>+ FeH : $X^4\Delta$</td>
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</table>
## Isotopically substituted ISM hydrides

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<td>$X \ ^1\Sigma^+$</td>
<td>$X \ ^2\Pi$</td>
<td>$X \ ^3\Sigma^-$</td>
<td>$X \ ^1\text{A}_1$</td>
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<tr>
<td>HD</td>
<td>OD</td>
<td>ND</td>
<td>H$_2$D$^+$</td>
</tr>
<tr>
<td>$^{13}\text{CH}^+$</td>
<td></td>
<td></td>
<td>D$_2$H$^+$</td>
</tr>
<tr>
<td>$^{38}\text{ArH}^+$</td>
<td></td>
<td></td>
<td>HDO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>D$_2$O</td>
</tr>
<tr>
<td></td>
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</tbody>
</table>

* tentative

See talk of P. Caselli
Thermodynamical properties (1)

\[ \text{X} + \text{H}_2 \rightarrow \text{XH} + \text{H} \]

possibility of activation barriers

<table>
<thead>
<tr>
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<td><strong>exothermic</strong></td>
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<td>3</td>
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<td>1</td>
<td></td>
<td>4</td>
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<td>2</td>
<td>1</td>
<td></td>
<td>4</td>
<td>3</td>
<td>2</td>
<td>1</td>
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<tr>
<td><strong>endothermic</strong></td>
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</tr>
</tbody>
</table>

- carbon
- oxygen
- nitrogen
- sulfur
- halogen
Thermodynamical properties (2)

\[ X^+ + H_2 \rightarrow XH^+ + H \]

Ionization source: photons, cosmic rays
Thermodynamical properties (3)

\[ X + H_3^+ \rightarrow XH^+ + H_2 \]

- Endothermic
- Exothermic

Proton affinity diagram
Chemical gas phase scenarii

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization potential (eV)</th>
<th>Endothermicity (Kelvin equivalent = (\Delta E/k_B)) for (X + H_2 \rightarrow XH + H)</th>
<th>Endothermicity (Kelvin equivalent = (\Delta E/k_B)) for (X^+ + H_2 \rightarrow XH^+ + H)</th>
<th>Endothermicity (Kelvin equivalent = (\Delta E/k_B)) for (X + H_3^+ \rightarrow XH^+ + H_2)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.587</td>
<td>No reaction</td>
<td>Exothermic, but primary channel is to (He + H + H^+)</td>
<td>29,000</td>
<td>unstable ground state of HeH</td>
</tr>
<tr>
<td>C</td>
<td>11.260</td>
<td>11,000</td>
<td>4,300</td>
<td>²</td>
<td>energy input required w C⁺</td>
</tr>
<tr>
<td>N</td>
<td>14.534</td>
<td>15,000</td>
<td>??</td>
<td>10,000</td>
<td>state to state chemistry (o/p)</td>
</tr>
<tr>
<td>O</td>
<td>13.618</td>
<td>920</td>
<td>²</td>
<td>²</td>
<td>CRs / warm neutral chemistry</td>
</tr>
<tr>
<td>F</td>
<td>17.423</td>
<td>²</td>
<td>²</td>
<td>10,000</td>
<td>neutral chemistry</td>
</tr>
<tr>
<td>Ne</td>
<td>21.564</td>
<td>No reaction</td>
<td>Exothermic, but primary channel is to (Ne + H + H^+)</td>
<td>27,000</td>
<td>Poorly known NeH⁺ spectro</td>
</tr>
<tr>
<td>Si</td>
<td>8.152</td>
<td>17,000</td>
<td>15,000</td>
<td>²</td>
<td>energy input required w Si⁺</td>
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<tr>
<td>P</td>
<td>10.487</td>
<td>19,000</td>
<td>13,000</td>
<td>²</td>
<td>energy input required w P⁺</td>
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<tr>
<td>S</td>
<td>10.360</td>
<td>10,000</td>
<td>10,000</td>
<td>²</td>
<td>energy input required w S⁺</td>
</tr>
<tr>
<td>Cl</td>
<td>12.968</td>
<td>515</td>
<td>²</td>
<td>²</td>
<td>sensitivity to threshold photons</td>
</tr>
<tr>
<td>Ar</td>
<td>15.760</td>
<td>No reaction</td>
<td>²</td>
<td>6,400</td>
<td>Cosmic rays / small (f_{H_2})</td>
</tr>
</tbody>
</table>

The table uses color coding to indicate the type of reaction and its significance:
- Green: Exothermic reaction of element in its main ionization state
- Red: Endothermic reaction of element in its main ionization state
- Gray: Exothermic reaction of element not in main ionization state
- Orange: Endothermic reaction of element not in main ionization state

Adapted from Gerin et al. 2016, ARAA 54, 181 and Neufeld 2016, SOFIA conference
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- Tracers of molecular gas: $\text{H}_3^+$, CH, HF

Examples of (photo)chemical excitation ($\text{OH}$, $\text{H}_3\text{O}^+$, $\text{NH}_3$)

Summary
Revisiting the $N^+ (^3P_j) + H_2 (J) \rightarrow NH^+ + H$ reaction (1)

Almost thermo-neutral reaction
Fine structure channels mixed to reactive channels
Highly perturbed structure of NH+

Electronic states correlation diagram for $C_{2v}$ and $D_{\infty h}$ symmetries
Gonzalez et al. 1986, Chem.Phys. 104, 57
Russel & Manolopoulos 1999, JCP110, 177

Hubers et al. 2009, JCP131, 4311
Revisiting the $\text{N}^+ (3P_j) + \text{H}_2 (J) \rightarrow \text{NH}^+ + \text{H}$ reaction (1)

Almost thermo-neutral reaction
Fine structure channels mixed to reactive channels
Highly perturbed structure of $\text{NH}^+$

Electronic states correlation diagram for $C_{2v}$ and $D_{\infty h}$ symmetries including fine structure of $\text{N}^+$

Hubers et al. 2009, JCP 131, 4311
Revisiting the $N^+(^3P_j) + H_2 (J) \rightarrow NH^+ + H$ reaction (2)

Use of statistical theory of reactive collisions where the energies of the fine structure states ($j=0, 1, 2$) of the $N^+$ ions are treated on an equal footing with other energies of internal rotation motions.

Critical parameter: $\Delta E_e$: equilibrium ergicity (vibrationless energy variation)

$$N^+ + H_2$$
$$\Delta E_e = D_e(H_2) - D_e(NH^+) = \Delta E_0 + E_{00}(H_2) - E_{00}(NH^+)$$
$$\Delta E_0 = D_0(H_2) - D_0(NH^+)$$

$$N^+ + HD$$
$$NH^+ channel$$
$$\Delta E_e = D_e(HD) - D_e(NH^+) = \Delta E_0^1 + E_{00}(HD) - E_{00}(NH^+)$$
$$\Delta E_0^1 = D_0(HD) - D_0(NH^+)$$

$$ND^+ channel$$
$$\Delta E_e = D_e(HD) - D_e(ND^+) = \Delta E_0^2 + E_{00}(HD) - E_{00}(ND^+)$$
$$\Delta E_0^2 = D_0(HD) - D_0(ND^+)$$

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$$N^+ + HD$$
$$NH^+ channel$$
$$\Delta E_e = D_e(HD) - D_e(NH^+) = \Delta E_0^1 + E_{00}(HD) - E_{00}(NH^+)$$
$$\Delta E_0^1 = D_0(HD) - D_0(NH^+)$$

$$ND^+ channel$$
$$\Delta E_e = D_e(HD) - D_e(ND^+) = \Delta E_0^2 + E_{00}(HD) - E_{00}(ND^+)$$
$$\Delta E_0^2 = D_0(HD) - D_0(ND^+)$$

Grozdanov & McCarroll 2015, JPCA119, 5988

interprete the collision cross sections measurements of Sunderlin & Armentrout 1994, JCP 100, 5639 of the $N^+ + H_2 (HD, D_2)$ reactions

$101 \leq \Delta E_e \leq 106$ meV
Revisiting the $N^+ (^3P_j) + H_2 (J) \rightarrow NH^+ + H$ reaction (3)

Constraining the critical parameter $\Delta E_e$ by comparison with low temperature measurements of reaction rate constants

$\Delta E_e = 101$ meV

- Experimental results of Marquette et al. 1988, JCP 89
- New statistical model with best choice of $\Delta E_e$
  Dislaire et al. 2012, A&A 537, A20 fits of Marquette et al. experiment (JCP89, 2041)

- Experimental results of o-$H_2$ from Marquette et al. reproduced satisfactorily.
- p-$H_2$ less satisfactory
- State to state reaction rates including fine structure states of $N^+$ and $H_2 (J=0,1)$
**Endothermicities computed with the assumption that $\Delta E_e = 101$ meV.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E_0$ (meV)</th>
<th>$\Delta E_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N^+ (^3P_0) + H_2 (J = 0)$ $\rightarrow$ $NH^+ + H$</td>
<td>18.53</td>
<td>215.0</td>
</tr>
<tr>
<td>$N^+ (^3P_0) + H_2 (J = 1)$ $\rightarrow$ $NH^+ + H$</td>
<td>3.84</td>
<td>44.6</td>
</tr>
<tr>
<td>$N^+ (^3P_1) + H_2 (J = 0)$ $\rightarrow$ $NH^+ + H$</td>
<td>12.49</td>
<td>144.9</td>
</tr>
<tr>
<td>$N^+ (^3P_1) + H_2 (J = 1)$ $\rightarrow$ $NH^+ + H$</td>
<td>-2.20</td>
<td></td>
</tr>
<tr>
<td>$N^+ (^3P_2) + H_2 (J = 0)$ $\rightarrow$ $NH^+ + H$</td>
<td>2.31</td>
<td>26.8</td>
</tr>
<tr>
<td>$N^+ (^3P_2) + H_2 (J = 1)$ $\rightarrow$ $NH^+ + H$</td>
<td>-12.38</td>
<td></td>
</tr>
<tr>
<td>$N^+ (^3P_0) + HD (J = 0)$ $\rightarrow$ $ND^+ + H$</td>
<td>4.21</td>
<td>48.9</td>
</tr>
<tr>
<td>$N^+ (^3P_0) + HD (J = 0)$ $\rightarrow$ $NH^+ + D$</td>
<td>54.06</td>
<td>627.3</td>
</tr>
<tr>
<td>$N^+ (^3P_1) + HD (J = 0)$ $\rightarrow$ $ND^+ + H$</td>
<td>-1.83</td>
<td></td>
</tr>
<tr>
<td>$N^+ (^3P_1) + HD (J = 0)$ $\rightarrow$ $NH^+ + D$</td>
<td>48.02</td>
<td></td>
</tr>
<tr>
<td>$^{15}N^+ (^3P_0) + H_2 (J = 0)$ $\rightarrow$ $NH^+ + H$</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td>$^{15}N^+ (^3P_0) + H_2 (J = 1)$ $\rightarrow$ $NH^+ + H$</td>
<td>3.51</td>
<td></td>
</tr>
<tr>
<td>$^{15}N^+ (^3P_0) + HD (J = 0)$ $\rightarrow$ $^{15}ND^+ + H$</td>
<td>3.74</td>
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</table>

The measured reaction rate coefficient of $N^+ + o-H_2 + HD$ is larger than that of $N^+ + o-H_2$, despite a larger endothermicity!

Reaction rate coefficients of Marquette et al. 1988, JCP 89, 20411

<table>
<thead>
<tr>
<th>Reaction</th>
<th>8 K</th>
<th>20 K</th>
<th>27 K</th>
<th>45 K</th>
<th>68 K</th>
<th>163 K</th>
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</thead>
<tbody>
<tr>
<td>$N^+ + nH_2$ (1)</td>
<td>2.3(-12)</td>
<td>4.0(-11)</td>
<td>1.0(-10)</td>
<td>1.6(-10)</td>
<td>2.2(-10)</td>
<td>3.5(-10)</td>
</tr>
<tr>
<td>$N^+ + pH_2$ (6)</td>
<td>...</td>
<td>...</td>
<td>2.7(-11)</td>
<td>2.0(-11)</td>
<td>6.6(-11)</td>
<td>3.0(-10)</td>
</tr>
<tr>
<td>$N^+ + HD$ (4)</td>
<td>...</td>
<td>...</td>
<td>1.4(-10)</td>
<td>...</td>
<td>3.3(-12)</td>
<td>1.0(-11)</td>
</tr>
</tbody>
</table>

$k(n-H_2) \sim \frac{3}{4} k(o-H_2)$ at 20K

$k(o-H_2) \approx 5.3 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$ at 20K
Endothermicities computed with the assumption that $\Delta E_e = 101$ meV.

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<td></td>
</tr>
<tr>
<td>$N^+ (^3P_0) + HD (J = 0)$ → $ND^+ + H$</td>
<td>48.02</td>
<td>557.2</td>
</tr>
<tr>
<td>$^{15}N^+ (^3P_0) + H_2 (J = 0)$ → $NH^+ + H$</td>
<td>18.2</td>
<td>211.2</td>
</tr>
<tr>
<td>$^{15}N^+ (^3P_0) + H_2 (J = 1)$ → $NH^+ + H$</td>
<td>3.51</td>
<td>40.7</td>
</tr>
<tr>
<td>$^{15}N^+ (^3P_0) + HD (J = 0)$ → $^{15}ND^+ + H$</td>
<td>3.74</td>
<td>43.4</td>
</tr>
</tbody>
</table>

Reaction rate coefficients of Marquette et al. 1988, JCP 89, 2041.

\[
\frac{k(n - H_2)}{k(o - H_2)} \approx \frac{3}{4}
\]

\[
k(o-H_2) \approx 5.3 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}
\]


Theoretical statistical model calculations based on computed endothermicities

State to state reaction rate coefficients for $N^+ (J) + H_2 (J), HD(J)$ and $^{15}N^+ (J) + H_2 (J), HD(J)$.
Endothermicities computed with the assumption that $\Delta E_e = 101$ meV.

The quite large value reported for $N^+ + HD$ rate coefficient is somewhat puzzling.

The proposed fit of Marquette et al., $k=3.17 \times 10^{-10} \exp(-16.3/T)$, is based on this single point and the measurement of Adams & Smith 1985, CPL117, 67 at 300K.
Revisiting the $\text{N}^+ \left(^3\text{P}_j\right) + \text{H}_2 (J) \rightarrow \text{NH}^+ + \text{H}$ reaction (4)

Suggested fits for the various isotopics variants (Grozdanov et al, 2016)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k \text{ (cm}^3\text{ s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}^+ + \text{p} - \text{H}_2$ $\rightarrow$ $\text{NH}^+ + \text{H}$</td>
<td>$3.17 \times 10^{-10} \times \exp(-213.8/T)$</td>
</tr>
<tr>
<td>$\text{N}^+ + \text{o} - \text{H}_2$ $\rightarrow$ $\text{NH}^+ + \text{H}$</td>
<td>$4.86 \times 10^{-10} \times \exp(-41.1/T)$</td>
</tr>
<tr>
<td>$^{15}\text{N}^+ + \text{p} - \text{H}_2$ $\rightarrow$ $^{15}\text{NH}^+ + \text{H}$</td>
<td>$3.19 \times 10^{-10} \exp(-208.3/T)$</td>
</tr>
<tr>
<td>$^{15}\text{N}^+ + \text{o} - \text{H}_2$ $\rightarrow$ $^{15}\text{NH}^+ + \text{H}$</td>
<td>$5.35 \times 10^{-10} \exp(-37.0/T)$</td>
</tr>
<tr>
<td>$\text{N}^+ + \text{HD}$ $\rightarrow$ $\text{ND}^+ + \text{H}$</td>
<td>$4.77 \times 10^{-10} \exp(-50.1/T)$</td>
</tr>
<tr>
<td>$^{15}\text{N}^+ + \text{HD}$ $\rightarrow$ $^{15}\text{ND}^+ + \text{H}$</td>
<td>$4.92 \times 10^{-10} \exp(-47.2/T)$</td>
</tr>
</tbody>
</table>

- Minor effect on NH/ND model predictions as NH(ND) principally produced from DR of $\text{N}_2\text{H}^+$ ($\text{N}_2\text{D}^+$)
- Similar NH$_3$ gas phase abundance (coming specifically from $\text{N}^+ + \text{o-H}_2$)
- Reduction of deuterated ammonia
- **New experiments on $\text{N}^+ + \text{HD}$ welcome!**
- Full theoretical treatment still to be done (introduction of the fine and electronic structure of NH$^+$)
Introduction

Molecular and thermochemical properties

Some illustrations of the interplay between observations and chemical mechanisms

- New analysis of the N$^+$ + H$_2$ reaction and its isotopic variants
- Tracers of atomic gas: OH$^+$ / ArH$^+$
- Tracers of molecular gas: H$_3^+$, CH, HF

Examples of (photo)chemical excitation (OH, H$_3$O$^+$, NH$_3$)

Summary

Paris, December 12, 2016
Ion molecule chemistry at work: a measure of the cosmic ionization rate and molecular fraction

**Oxygen chemistry**

2 channels, 3 successive possible steps

Gerin et al. 2010, AA 518, L110
Neufeld et al. 2010, AA 521, L10
Indriolo et al. 2015, ApJ 800, 40

**ArH⁺ chemistry**

2 channels, one single step

Schilke et al. 2014, AA 566, A29

Well studied chemistry (see Indriolo et al. 2012) apart photodissociation of OH⁺

badly known:
RR of Ar⁺ (≠ collisional radiative recombination)
DR of ArH⁺ (only upper limit)
### Simplified chemical network

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Differential Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 + CR \rightarrow H_2^+ + e$</td>
<td>$\zeta_2$</td>
<td>$dn(H_2^+)/dt = \zeta_2 n(H_2)$</td>
<td></td>
</tr>
<tr>
<td>$H_2^+ + H_2 \rightarrow H_3^+ + e$</td>
<td>$k(H_2^+</td>
<td>H_2)$</td>
<td>$dn(H_3^+)/dt = k(H_2^+</td>
</tr>
<tr>
<td>$H_3^+ + e \rightarrow $ products</td>
<td>$k_e(H_3^+)$</td>
<td>$dn(H_3^+)/dt = -k_e(H_3^+) n(H_3^+) n_e$</td>
<td></td>
</tr>
<tr>
<td>$H + CR \rightarrow H^+ + e$</td>
<td>$\zeta_H$</td>
<td>$dn(H^+)/dt = \zeta_H n(H)$</td>
<td></td>
</tr>
<tr>
<td>$O + H^+ \rightarrow O^+ + H$</td>
<td>$k(O</td>
<td>H^+)$</td>
<td>$dn(O^+)/dt = k(O</td>
</tr>
<tr>
<td>$O^+ + H_2 \rightarrow OH^+ + H$</td>
<td>$k(O^+</td>
<td>H_2)$</td>
<td>$dn(OH^+)/dt = k(O^+</td>
</tr>
<tr>
<td>$OH^+ + H_2 \rightarrow H_2O^+ + H$</td>
<td>$k(OH^+</td>
<td>H_2)$</td>
<td>$dn(H_2O^+)/dt = k(OH^+</td>
</tr>
<tr>
<td>$H_2O^+ + H_2 \rightarrow H_3O^+ + H$</td>
<td>$k(H_2O^+</td>
<td>H_2)$</td>
<td>$dn(H_3O^+)/dt = k(H_2O^+</td>
</tr>
<tr>
<td>$OH^+ + e \rightarrow O + H$</td>
<td>$k_e(OH^+)$</td>
<td>$dn(OH^+)/dt = -k_e(OH^+) n(OH^+) n(e)$</td>
<td></td>
</tr>
<tr>
<td>$H_2O^+ + e \rightarrow $ products</td>
<td>$k_e(H_2O^+)$</td>
<td>$dn(H_2O^+)/dt = -k_e(H_2O^+) n(H_2O^+) n(e)$</td>
<td></td>
</tr>
<tr>
<td>$H_3O^+ + e \rightarrow $ products</td>
<td>$k_e(H_3O^+)$</td>
<td>$dn(H_3O^+)/dt = -k_e(H_3O^+) n(H_3O^+) n(e)$</td>
<td></td>
</tr>
</tbody>
</table>
Ion molecule chemistry at work: a measure of the cosmic ionization rate and molecular fraction

Steady state analysis (Indriolo et al. 2015)

- From H$_3^+$ chemistry: $\zeta_2 = x_e \, k_e(H_3^+) \, n_H \, \frac{n(H_3^+)}{n(H_2)}$ with $x_e = \frac{n(e)}{n_H}$ and $\zeta_2$ CR ionization of H$_2$

- From OH$^+$, H$_2$O$^+$ chemistry:
  
  $f_{H_2} = \frac{2x_e k_e(H_2O^+)/k(OH^+ \mid H_2)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2)}$

where $f_{H_2} = \frac{2 \times n(H_2)}{n(H) + 2 \times n(H_2)} = \frac{2 \times n(H_2)}{n_H}$

Defining $\epsilon$ as the ratio of the OH$^+$ production rate to the cosmic ray ionization rate

$\epsilon \zeta_H = \frac{N(OH^+)}{N(H)} \frac{n_H}{n_H} \left[ \frac{f_{H_2}}{2} k(OH^+ \mid H_2) + x_e k_e(OH^+) \right]$  

$\epsilon$ accounts for the fact that not every instance of hydrogen ionization results in the formation of OH$^+$ due to O$^+$ + H → O$^+$H$^+$ and H$^+$ recombination (Neufeld et al. 2010)

Assuming $\zeta_2 \approx 2 \times \zeta_H$

$\epsilon \zeta_2 = \frac{N(OH^+)}{N(H)} 2 \times n_H \times x_e \left[ k_e(H_2O^+) \frac{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2) + k_e(OH^+)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2) + k_e(OH^+)} \right]$

Analysis requires estimates of $x_e$, $\epsilon$, $T$, $n_H$, + observations of OH$^+$, H$_2$O$^+$, H (see talk of N. Indriolo)
Example of W51 (1)


CGS4 + Phenix

H$_3^+$, R(1,0)

H$_2$O$^+$

OH$^+$

CO

Indriolo et al. 2015, ApJ 800, 40

HFI

Sonnentrucker et al. 2015, ApJ 806, 49

HF $J=1-0$ ($\nu=1232.4762$ GHz)

p-H$_2$O $^{1}\nu=1113.3430$ GHz

HF $J=1-0$ $^{1}\nu$
1. Diagnostics of the cosmic ionization rate

<table>
<thead>
<tr>
<th>Species</th>
<th>N(X)</th>
<th>$v_{\text{LSR}}$ (km s$^{-1}$)</th>
<th>FWHM (km s$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$(1.39 \pm 0.3) \times 10^{21}$</td>
<td>6.2</td>
<td>5.6</td>
<td>1</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$(1.06 \pm 0.52) \times 10^{21}$</td>
<td>3–10</td>
<td>...</td>
<td>2</td>
</tr>
<tr>
<td>H$_3^+$</td>
<td>$(2.89 \pm 0.37) \times 10^{14}$</td>
<td>5.0</td>
<td>10.5</td>
<td>3</td>
</tr>
<tr>
<td>OH$^+$</td>
<td>$(2.97 \pm 0.13) \times 10^{13}$</td>
<td>0–11</td>
<td>...</td>
<td>3</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>$(6.09 \pm 0.96) \times 10^{12}$</td>
<td>0–11</td>
<td>...</td>
<td>4</td>
</tr>
<tr>
<td>C$^+$</td>
<td>$(4.0 \pm 0.4) \times 10^{17}$</td>
<td>0–11</td>
<td>...</td>
<td>4</td>
</tr>
<tr>
<td>CH</td>
<td>$(3.7 \pm 0.2) \times 10^{13}$</td>
<td>3–10</td>
<td>...</td>
<td>5</td>
</tr>
<tr>
<td>CO</td>
<td>$(2.81 \pm 0.21) \times 10^{15}$</td>
<td>4.8</td>
<td>9.6</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4: Molecular and Atomic Abundances in the Diffuse Cloud toward W51


Steady state formulae + guessed $x_e$ from C$^+$ : C$^+$ / $n_H$ $\approx$ $x_e$

from H$_3^+$

Indriolo et al. 2012:
$\zeta_2 \approx (4.8 \pm 3.4) \times 10^{-16}$ s$^{-1}$

from OH$^+$

Indriolo et al. 2015:
$\varepsilon \approx 0.07$
$\zeta_2 \approx (5.6 \pm 1.0) \times 10^{-16}$ s$^{-1}$ in the (4, +11 km/s) VLSR range
Different $\zeta_2$ for different velocity ranges

mean value of the cosmic ionization rate outside the Galactic center $\zeta_2 \approx 3.6 \times 10^{-16}$ s$^{-1}$ (Indriolo et al. 2015)

$\zeta_2$ significantly larger than previously thought

Hartquist, Black & Dalgarno 1978 (MNRAS 185, 643) derived $\zeta_2 \approx 5 \times 10^{-17}$ s$^{-1}$ from OH and HD in diffuse clouds

+ N(HF) $(1.63 \pm 0.12) \times 10^{13}$ cm$^{-2}$
Sonnentrucker et al. 2015

Example of W51 (2)
Example of W51 (3)

2. Diagnostics of the molecular fraction

Steady state formulae + guessed $x_e$:

$$f_{H_2} = \frac{2x_e k_e (H_2O^+)/k(OH^+ | H_2)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ | H_2)/k(OH^+ | H_2)}$$

$$f_{H_2} = 0.04 \pm 0.01 \text{ from } OH^+, H_2O^+ \text{ towards W51}$$

The derivation of the molecular fraction from $OH^+/H_2O^+$ is a signature of its value at the formation peak.

$n_H=50 \text{ cm}^{-3}$, $\zeta_2 = 5 \times 10^{-16} \text{ s}^{-1}$, $\chi = 1$, $A_{\text{v, tot}} = 2$

Meudon PDR code model
Example of W51 (4)

Diagnostics of the molecular fraction

Steady state formulae + guessed $x_e$:

\[
f_{H_2} = 0.04 \pm 0.01 \text{ from } OH^+, H_2O^+ \text{ towards W51}
\]

From the observations of HI 21cm and proxies of $H_2$: CH, HF

N(CH)/N($H_2$) = 3.6 10^{-8} (Sheffer+ 2008, ApJ 687, 1075)


<table>
<thead>
<tr>
<th>N(H) (cm^{-2})</th>
<th>1.4 10^{21}</th>
<th>N($H_2$) (cm^{-2})</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(CH) (cm^{-2})</td>
<td>3.7 10^{13}</td>
<td>1.0 10^{21}</td>
<td>0.6</td>
</tr>
<tr>
<td>N(HF) (cm^{-2})</td>
<td>1.6 10^{13}</td>
<td>1.3 10^{21}</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Diagnostics of the molecular fraction

Steady state formulae + guessed $x_e$:

$$f_{H_2} = 0.04 \pm 0.01 \text{ from } OH^+, H_2O^+ \text{ towards } W51$$

From the observations of HI 21cm and proxies of $H_2$: CH, CF

$$f_{H_2} \sim 0.6 - 0.7$$

The molecular fraction obtained from observations of $H$ and proxies of $H_2$ involves the integration over the cloud

see also discussion in Le Petit et al. 2016, AA585, A105
ArH$^+$ chemistry (1)

**Surprise!** First rare gas containing molecule
Schilke et al. 2014, AA566, A29

$^{36}$ArH$^+$ and $^{38}$ArH$^+$ isotopes detected also at $z=0.89$ in absorption toward PKS1830-211
(Müller et al. 2015, A&A582, L4)

Transition shifted towards 350GHz
Detectable then from ground with ALMA.

Extensive grid of diffuse cloud models reported in Neufed + Wolfire 2016,

ArH$^+$ essentially present in atomic gas

No single set of cloud parameters provides an acceptable fit to the observed abundances of ArH$^+$, OH$^+$, H$_2$O$^+$

2 components model may be appropriate (cf talk of M. Wolfire)
→ Even simpler reaction schema (Ar, Ar\(^+\), H\(_2\), H\(_2\)^+, O, C)

Slow photodissociation (Alekseev+2007, Roueff+2014)

H\(?\), He\(^+\)? Exothermic charge exchange not included in the chemistry of Schilke+ 2014

Recombination of Ar\(^+\) (formula of Shull and van Steenberg based on formulae extrapolation). Not available from Badnell recent data base.

Dissociative recombination: upper limit available only from experiments Mitchell et al. 2005, J. Phys. B 38, challenge for theorists; no favorable crossing for recombination
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- Tracers of atomic gas: OH\(^+\) / ArH\(^+\)
- Tracers of molecular gas: H\(_3^+\), CH, HF

Examples of (photo)chemical excitation (OH, H\(_3\)O\(^+\), NH\(_3\))

Summary
Suprathermal excitation of OH in the HH 211 outflow (1)

SPITZER Space Telescope observations
OH and H$_2$O emission present in the terminal shock region

Pure rotational: H$_2$, HD, H$_2$O
Highly excited levels of OH $E_{up} \approx 28200$K above ground state
OH also populated at lower excitation as shown by intersystem transitions; no convincingly vibrationally excited transition detected.
Suprathermal excitation of OH in the HH 211 outflow (2)

IRS spectrum of the terminal shock
Tappe et al. 2012

Higher possibly present excited transitions below 10µ
not available in the IRS spectrum

>Selective non thermal excitation of OH
A Einstein coefficient of high J transitions ≈ 10 - 400 s^{-1} compared to H_2O
A values of a few × 10^{-3} s^{-1} and H_2. A values of 3 × 10^{-11} – 3 × 10^{-7} s^{-1}
too large critical densities for OH

Shock chemistry?
≈ 29000 K endothermicity required to populate OH (J=63) : much larger than typical neutral fluid temperature
Suprathermal excitation of OH in the HH 211 outflow (3)

Experiments:
- weak featureless band at 7.4 eV + structured emission at 9.5 eV (Cheng et al. 2011 JCP134, 06431)

Theory:
The photodissociation of H$_2$O in its B band is a prototype for nonadiabatic reaction dynamics.

In addition to dissociation via the adiabatic pathway to the OH(Å^2Σ+) + H fragments, it also produces the OH (X^2Π) + H fragments through two nonadiabatic pathways:
- the B → X transition via two conical intersections (CI) and the
- B → Å transition via a Renner - Teller (RT) pair.

Possible role of H$_2$O photodissociation:
- photodissociation of H$_2$O through photons with E>9eV leads to ground state OH with high rotational excitation.

Guo & Yarkony 2016, PCCP 18, 26335
Proposed scenario:

UV-induced photodesorption of water ice from grain mantles and photodissociation of \( \text{H}_2\text{O} \) either in the gas phase or directly in the grain ice mantles are the primary sources of OH and \( \text{H}_2\text{O} \).

Ly\( \alpha \)-dominated FUV radiation coming from a radiative shock; assumed x-section: \( 8 \times 10^{-18} \text{ cm}^2 \), photodesorption yield of \( 3-5 \times 10^{-3} \).

Include other molecular emissions (\( \text{HCO}^+ \), HCN, (\( v=1-0 \)) CO, …)

A nice challenge for future model

Other sources with high J excited OH: TW Hya, other outflows (Tappe et al. 2012)

Similar mechanism invoked in the observed prompt visible A-X emission of OH in comet Hyakutake (A Hearn et al. 2015, ApJ 150:5)
Inversion transitions; A values between a few $\times 10^{-2}$ and $10^{-1} \text{ s}^{-1}$

**Galactic Center**: highly excited NH$_3$ also detected presence of warm gas

**W31C**: quiescent environment

chemical pumping scenario formation:

$\text{H}_2 + \text{H}_2\text{O}^+ \rightarrow \text{H}_3\text{O}^+ + \text{H} \quad \Delta E \approx 1.7 \text{eV}$

wich fraction into internal energy?

Highly excited non metastable levels relax rapidly to metastable levels (lower $J=K$) by spontaneous emission. Populations partially redistributed by inelastic collisions and background IR continuum radiation.

**Destruction** rapid through DR: $k_e \approx 10^{-6} n_e$
Widespread rotationally hot $\text{H}_3\text{O}^+$ in the Galactic ISM

Collision rates not available for highly excited $\text{NH}_3$ (possible proxy of $\text{H}_3\text{O}^+$) nor for $\text{H}_3\text{O}^+$

Difference between reported energies of highly excited $\text{NH}_3$ and $\text{H}_3\text{O}^+$ sensitivity coefficients for probing a variable proton to electron mass ratio (Owens et al. 2016, PRA93, 052506; 2015, MNRAS 454, 22920)

Radiative cooling of $\text{H}_3\text{O}^+$ (Melnikov et al. 2016, PCCP 18, 26268)

Destruction rapid through DR: $k_e \approx 10^{-6} n_e$

basic thermochemical properties provide the general frame of the chemical processes at work

Hydride families, supposedly involving simple formation reactions (with H$_2$), are very diverse and allow to address different aspects
  atomic gas
  molecular proxy
  warm environments
  probe of ionization sources
  photochemistry
  anomalous excitation resulting from photo-chemical mechanisms

dedicated studies of elementary reactions
  the case of N$^+$ + H$_2$: a nice example of state to state chemistry
  not yet fully understood

full understanding requires complementary information from other molecules
| Density diagnostics: atomic / molecular | HI, OH⁺, ArH⁺/ CH, HF |
| Warm environments                      | endothermic reactions |
| shocks                                 | OH, H₂O, CH⁺, SH⁺     |
| turbulent                              | C, S, Cl chemistries / |
| Photons / X rays                       | H₃⁺, OH⁺, H₂O⁺, ArH⁺  |
| Source of ionization: UV / CR / Xrays  | Role of internal energy |
| coupling to magnetic field             | H₂, H₂O, H₂O⁺, NH₂    |
| State to state chemistry:              | Nuclear spin dynamics in water |
| ortho/para                             | ice                    |
| Role of surface processes              | H₂O                    |
|                                       | Sulfur chemistry       |
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