Physics and Chemistry of the Diffuse Interstellar Medium
What is the Diffuse Interstellar Medium?

Picture from Dopita / Sutherland, “Astrophysics of the Diffuse Universe”, Springer
HII regions

- in Astronomy “HII” stands for ionized hydrogen atoms H⁺, “HI” stands for neutral hydrogen H, “FeIV” would stand for Fe³⁺, etc ...
- consequently, HII regions are characterized by all hydrogen being ionized,
- Temperatures are on the order of 10 000 K,
- HII regions are low density clouds of gas where star formation recently happened,
- too hot and violent for molecules to exist,
- Precursors are Giant Molecular Clouds -> star formation
The Cosmic Chemistry Cycle
Spectral classes of stars

<table>
<thead>
<tr>
<th>Spectral Class</th>
<th>O</th>
<th>B</th>
<th>A</th>
<th>F</th>
<th>G</th>
<th>K</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>50,000 - 28,000</td>
<td>28,000 - 10,000</td>
<td>10,000 - 7,500</td>
<td>7,500 - 6,000</td>
<td>6,000 - 4,900</td>
<td>4,900 - 3,500</td>
<td>3,500 - 2,000</td>
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<tr>
<td>Colour</td>
<td>Blue</td>
<td>Blue-white</td>
<td>White</td>
<td>White-yellow</td>
<td>Yellow</td>
<td>Orange</td>
<td>Red</td>
</tr>
</tbody>
</table>

Young, massive stars shine in the UV
HII regions and the attenuation of Extreme UV light (EUV)

Photons with $E_\gamma > 13.6$ eV directly photoionize H atoms:

$$\text{H} + \gamma \rightarrow \text{H}^+ + e^- \quad (+ \Delta E)$$

Recombination between electrons and H$^+$ can occur into any atomic level, followed by photon emission:

$$\text{H}^+ + e^- \rightarrow \text{H}(n)$$

$$\text{H}(n) \rightarrow \text{H}(n') + \gamma \quad (n' < n)$$

Except for a direct capture into $n=1$, the emitted photon has an energy of $< 13.6$ eV, insufficient to ionize neutral H, therefore the UV radiation field is weakened.
H II regions and the attenuation of Extreme UV light (EUV)

The image contains a diagram illustrating the energy levels of atomic transitions. The diagram includes:

- An electronic energy level diagram with quantized levels labeled as $n=1$, $n=2$, $n=3$, $n=4$, $n=5$, and $n=6$.
- Transitions between levels indicated with blue arrows, including:
  - $n=3 \rightarrow n=2$ at 656.3 nm, responsible for the red glow in H II regions containing ionized H atoms.

The diagram also shows:

- The Lyman series
- The Balmer series
- The Paschen series

The transitions and energy levels are labeled with corresponding wavelengths:

- Lyman $\alpha$ at 121.7 nm
- Balmer $\alpha$ at 656.3 nm

The attenuation of Extreme UV light (EUV) in H II regions is also mentioned.
Transition between HII and HI region

HII regions around young stars act as filters for EUV photons with $E > 13.6$ eV.
For completeness: the Intergalactic Medium

Very dilute, hydrogen fully ionized, very hot: $10^4$-$10^7$ K.
What is the Diffuse Interstellar Medium?

Picture from Dopita / Sutherland, “Astrophysics of the Diffuse Universe”, Springer
## Diffuse medium vs. terrestrial conditions

<table>
<thead>
<tr>
<th></th>
<th>Earth’s atmosphere</th>
<th>Interstellar Medium</th>
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</thead>
<tbody>
<tr>
<td><strong>Density</strong></td>
<td>$10^{19}$ cm$^{-3}$</td>
<td>$10^2 – 10^6$ cm$^{-3}$</td>
</tr>
<tr>
<td><strong>Collision time scale</strong></td>
<td>nanoseconds, 3-body collisions likely</td>
<td>hours – years for binary collisions, no 3-body collisions</td>
</tr>
<tr>
<td><strong>statistics</strong></td>
<td>Boltzmann</td>
<td>Often local thermodynamic equilibrium is not reached, radiative lifetimes can be much shorter than average collision times</td>
</tr>
<tr>
<td></td>
<td></td>
<td>many species in ground state, irrespective of kinetic temperature</td>
</tr>
</tbody>
</table>
Traditional Classification of the diffuse ISM

The ISM is complex in its structure, probably clumpy, therefore most sightlines probably consist of a mixture of different phases.

HIM: hot ionized medium
WIM: warm ionized medium
WNM: warm neutral medium
CNM: cold neutral medium

A SMALL CLOUD

HIM
\[ T = 4.5 \times 10^5 \text{ K} \]
\[ n = 3.5 \times 10^{-3} \text{ cm}^3 \]
\[ x = 1.0 \]

WNM
\[ T = 8,000 \text{ K} \]
\[ n = 0.37 \text{ cm}^3 \]
\[ x = 0.15 \]

WIM
\[ T = 8,000 \text{ K} \]
\[ n = 0.25 \text{ cm}^3 \]
\[ x = 0.68 \]

CNM
\[ T = 80 \text{ K} \]
\[ n = 42 \text{ cm}^3 \]
\[ x \approx 10^{-3} \]

x: ionization fraction

Modern Classification of Interstellar Cloud Types


Definitions:
Number density of species X: \( n(X) \) \([\text{cm}^{-3}]\)
Column density: \( N(X) \) \([\text{cm}^{-2}]\)
Integral of \( n(X) \) along sightline
Total nuclei number density: \( n_X \) \([\text{cm}^{-3}]\)
example: \( N_H = n(H) + 2n(H_2) \), \( n_C \approx n(C^+) + n(C) + n(CO) \)
Local fraction: \( f^n \)
example: \( f^n_{H_2} = 2n(H_2)/n_H \), \( f^n_{CO} = n(CO)/n_C \), etc ...

<table>
<thead>
<tr>
<th>Defining Characteristic</th>
<th>Diffuse Atomic</th>
<th>Diffuse Molecular</th>
<th>Translucent</th>
<th>Dense Molecular</th>
</tr>
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<tbody>
<tr>
<td>( f^n_{H_2} &lt; 0.1 )</td>
<td>( f^n_{H_2} &gt; 0.1 ) ( f^n_{C^+} &gt; 0.5 )</td>
<td>( f^n_{C^+} &lt; 0.5 ) ( f^n_{CO} &lt; 0.9 )</td>
<td>( f^n_{CO} &gt; 0.9 )</td>
<td></td>
</tr>
<tr>
<td>A(_V) (min.)</td>
<td>0</td>
<td>( \sim 0.2 )</td>
<td>( \sim 1-2 )</td>
<td>( \sim 5-10 )</td>
</tr>
<tr>
<td>Typ. ( n_H ) (cm(^{-3}))</td>
<td>10–100</td>
<td>100–500</td>
<td>500–5000?</td>
<td>( &gt;10^4 )</td>
</tr>
<tr>
<td>Typ. T (K)</td>
<td>30–100</td>
<td>30–100</td>
<td>15–50?</td>
<td>10–50</td>
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<tr>
<td>Observational Techniques</td>
<td>UV/Vis</td>
<td>UV/Vis IR abs</td>
<td>Vis (UV?) IR abs</td>
<td>IR abs</td>
</tr>
<tr>
<td></td>
<td>H I 21-cm</td>
<td>mm abs</td>
<td>mm abs/em</td>
<td>mm em</td>
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The diffuse ISM can be explored by Visible and UV observations!
Easy to study? Still a lot of problems ...
Transition between Cloud Types

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Diffuse Atomic Clouds

- Part of the diffuse interstellar medium that is fully exposed to radiation field
- Nearly all molecules quickly destroyed by photodissociation
- Hydrogen in neutral atomic form (H)
- Elements with Ionization potential < 13.6 eV almost fully ionized (e.g. C \( \rightarrow \) C\(^+\))
• There seems to be no correlation between $N(\text{H}_2)$ and the strength of the DIB features.
• DIBS exist even when $N(\text{H}_2)$ gets very small.
• This suggests that $\text{H}_2$ is not involved when the DIB carriers are formed!

Diffuse Interstellar Bands: Dependence on $N(H)$
Diffuse Atomic Clouds

- Part of the diffuse interstellar medium that is fully exposed to radiation field
- Nearly all molecules quickly destroyed by photodissociation
- Hydrogen in neutral atomic form (H).
- Elements with Ionization potential < 13.6 eV almost fully ionized (e.g. C -> C⁺)
- Hardly any molecules, but strong Diffuse Interstellar Bands (Mystery!)
Diffuse Molecular Clouds

- Interstellar radiation field is sufficiently attenuated in the UV regime for $\text{H}_2$ to survive,
- typically surrounded by diffuse atomic gas,
- Most diffuse molecular sightlines will also cross atomic sightlines,
- densities 100-500 cm$^{-3}$,
- temperature 30-100 K,
- Almost all carbon ionized ($\text{C}^+$)
- High ionization fraction, $n(\text{C}^+) \approx n(\text{e})$
- Electron recombination dominant destruction route for many ions
Translucent Clouds

- Characterized by the transition from ionized $C^+$ to neutral C and CO
- Introduced by Van Dishoeck and Black (1989),
- Translucent regime not well understood,
- Lack of observational data,
- Chemical models do not agree in the C, Co transition regime,

- Interstellar radiation field is sufficiently attenuated at energies $<13.6$ eV that carbon becomes neutral (C) or molecular (CO)
- Typically surrounded by diffuse molecular gas,
Dense Molecular Clouds

- With increasing extinction, carbon becomes completely molecular (CO),
- No longer observable in the visible or UV regime,
- Much lower ionization fraction than diffuse medium,
- Electron recombination is much less important due to lack of electrons,
- Main source of ionization: Cosmic rays!
- Most of the detected interstellar molecules are observed in dense clouds,
- Places of star formation.
Key Species in Diffuse Molecular Clouds: \( \text{H}_2 \)

- No dipole moment, homonuclear
  - no allowed vibrational or rotational transitions
- Space-based far-UV spectrographs needed for observations

Werner bands
- \( E_\gamma > 12.3 \text{ eV} \)
- \( \lambda < 100.8 \text{ nm} \)

\[ X^1\Sigma_g^+ \rightarrow C^1\Pi_u \]

Lyman bands:
- \( E_\gamma > 11.2 \text{ eV} \)
- \( \lambda < 110.8 \text{ nm} \)

\[ X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+ \]

Electronic states of \( \text{H}_2 \), from Field, Somerville & Dressler (1966)
First Interstellar $\text{H}_2$ Absorption spectrum

- $\text{H}_2$ and H column densities comparable
H$_2$ UV observations with FUSE

Far Ultraviolet Spectroscopic Explorer

Flux ($10^{-12}$ erg s$^{-1}$ cm$^{-2}$ Å$^{-1}$)

Wavelength (Å)

H$_2$ B-X bands
HD 210839
Observed $\text{H}_2$ rotational population

Rotational excitation

Boltzmann law: $N_J \sim g_J e^{\frac{E_J}{kT}}$

Key Species in diffuse clouds: H$_2$ Formation

Direct radiative association:

\[ H + H \rightarrow H_2 + \gamma \]

Radiative transitions between the lowest states of H$_2$ forbidden, fraction of atoms in 2p states negligible

\[ \alpha < 10^{-16} \text{ cm}^3 \text{ s}^{-1} \]
\[ \alpha \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1} \]

Radiative association extremely inefficient

The H$_2^+$ pathway:

\[ H + H^+ \rightarrow H_2^+ + \gamma \]
\[ H_2^+ + H \rightarrow H_2 + H^+ \]

The 1. step is rate-limiting, renders H$_2^+$ path negligible

The H$^-$ pathway:

\[ H + e^- \rightarrow H^- + \gamma \]
\[ H^- + H \rightarrow H_2 + e^- \]

Without shielding of visible light, H$^-$ does not live long enough

\[ \text{H}^- \text{ binding energy 0.75 eV} \]

Only formation on dust grains remains
H₂ formation on grains

1. H collides with grain
2. H explores grain until either
   1. encounter with another H
   2. immobilized at enhanced binding site
3+4. second H atom collides with grain; explores surface and encounters first H atom
5. H₂ formation on surface
   H₂ ejected from surface
H$_2$ observations vs. dust grains

(NGC 6720 planetary nebula)

Fig. 1. NGC 6720 in five photometric bands. Top row from left to right: H$_2$ 2.12 $\mu$m, PACS 70 $\mu$m, PACS 160 $\mu$m. Bottom row from left to right: SPIRE 250 $\mu$m, SPIRE 350 $\mu$m, and an overlay of the Calar Alto H$_2$ contours on the PACS 70 $\mu$m image. The H$_2$ image is not flux calibrated. The maps have standard orientation (N to the top, E to the left).
Ro-vibrational excitation in HD formation detected by Resonantly Enhanced Multiphoton Ionization (REMPI)
Energy released in the Dust grain formation may contribute to the non-thermal H$_2$ distribution observed in diffuse clouds.

$\text{T_{rot}} = 368 \pm 22 \text{ K}$
$\text{H}_2$ optical pumping

B-X: Lyman system
C-X: Werner system
Observed $\text{H}_2$ rotational population

Rotational excitation of H$_2$
kinetic temperature and optical pumping

H$_2$ lines up to J = 7 detected with Copernicus + FUSE
Population distribution non-thermal, 2 temperature regimes!

Low J: excitation dominated by collisions
- sensitive to T and nH
- abundance H$^+$ large enough that ortho/para exchange rapid
  and J=1/J=0 gives T$_{\text{kin}}$

High J: energy levels lie very high (> 1000 K)
- not populated by collisions at T = 40 - 80 K
- populated by optical pumping
- process through B <- X and C <- X systems
- proportional to radiation field
- possibly contribution from dust grain formation process
**H$_2$** nuclear spin and kinetic cloud temperature

**Ortho – para exchange reactions**

1)

\[ \text{H} + \text{o-H}_2 \leftrightarrow \text{H} + \text{p-H}_2 \]

Activation barrier too high

2)

\[ \text{H}^+ + \text{o-H}_2 \leftrightarrow \text{H}^+ + \text{p-H}_2 \]

- No activation barrier
- Requires some ionized atomic H fraction

Due to high efficiency of 2), H$_2$ ortho / para fraction should reflect kinetic cloud temperature
H$_2$ destruction: possible processes

For direct photodissociation photons with $E_\gamma > 15$ eV are needed, which are already depleted by the atomic outer layers.

There is no bound state in the right energy regime for H$_2$.

Major H$_2$ destruction mechanism in the diffuse ISM.
H2 destruction by radiative dissociation through Lyman and Werner Bands

90% of the flux returns back to the electronic ground state (contributing to the observed optical pumping of rotational states)

10% of the flux leads to spontaneous dissociation
Depth dependence of various species

Note: overall density increases with depth

Van Dishoeck & Black 1986
HD observations in the diffuse medium

Can we use $N(\text{HD})$ to constrain cosmic $\text{D/H}$?

- Even most HD lines are fully saturated
- Obscured by H2 and other molecular lines
- Difficult analysis
N (HD) does not seem to represent cosmic H/D fraction (≈ 10⁻⁵). Why?

<table>
<thead>
<tr>
<th>Star</th>
<th>$E_{(B-V)}$</th>
<th>$f(H_2)$ (^a)</th>
<th>$N(H_1)$ ([\text{cm}^{-2}])</th>
<th>$N(H_2)$ ([\text{cm}^{-2}])</th>
<th>$N(\text{HD})$ ([\text{cm}^{-2}])</th>
<th>Ref.</th>
<th>$N(\text{HD})/2N(H_2)$</th>
<th>$N(\text{CH})$ ([\text{cm}^{-2}])</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD 27778</td>
<td>0.38</td>
<td>0.57</td>
<td>9.5(^{+0.5}_{-0.8}) (20)</td>
<td>6.2(^{+0.9}_{-0.8}) (20)</td>
<td>3.2(^{+3.2}_{-1.7}) (15)</td>
<td>1</td>
<td>2.6(^{+2.6}_{-1.4}) (-6)</td>
<td>3.0 ± 0.3 (13)</td>
<td>2</td>
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<tr>
<td>HD 73882</td>
<td>0.72</td>
<td>0.67</td>
<td>1.3(^{+0.5}_{-0.4}) (21)</td>
<td>1.3(^{+0.3}_{-0.2}) (21)</td>
<td>5.8(^{+3.7}_{-3.4}) (15)</td>
<td>1</td>
<td>2.2(^{+1.6}_{-1.3}) (-6)</td>
<td>3.5 ± 0.4 (13)</td>
<td>2</td>
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<tr>
<td>HD 110432</td>
<td>0.40</td>
<td>0.55</td>
<td>7.1(^{+2.0}_{-2.1}) (20)</td>
<td>4.4(^{+0.4}_{-0.4}) (20)</td>
<td>1.9(^{+0.7}_{-0.6}) (15)</td>
<td>1</td>
<td>2.2(^{+0.9}_{-0.7}) (-6)</td>
<td>1.5 ± 0.3 (13)</td>
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<td>HD 185418</td>
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<td>0.47</td>
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<td>5.8(^{+0.7}_{-0.6}) (20)</td>
<td>4.3(^{+1.9}_{-1.1}) (15)</td>
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<td>3.7(^{+1.7}_{-1.0}) (-6)</td>
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<td>HD 192639</td>
<td>0.66</td>
<td>0.32</td>
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<td>4.9(^{+0.6}_{-0.5}) (20)</td>
<td>1.5(^{+0.9}_{-0.7}) (15)</td>
<td>1</td>
<td>1.5(^{+1.0}_{-0.7}) (-6)</td>
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<tr>
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<td>0.42</td>
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<td>2.1(^{+1.5}_{-1.0}) (15)</td>
<td>1</td>
<td>1.4(^{+1.0}_{-0.7}) (-6)</td>
<td>3.0 ± 0.2 (13)</td>
<td>2</td>
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<tr>
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<td>0.42</td>
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<td>8.1(^{+0.8}_{-0.7}) (20)</td>
<td>5.0(^{+5.1}_{-2.4}) (15)</td>
<td>1</td>
<td>3.1(^{+3.2}_{-1.5}) (-6)</td>
<td>4.3 ± 0.2 (13)</td>
<td>2</td>
</tr>
<tr>
<td>HD 21278</td>
<td>0.10</td>
<td>0.10 (^b)</td>
<td>5.5 (20) (^b)</td>
<td>3.0(^{+2.1}_{-1.2}) (19)</td>
<td>1.5(^{+0.1}_{-0.1}) (14)</td>
<td>4</td>
<td>2.5(^{+1.7}_{-1.0}) (-6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ζ Per</td>
<td>0.30</td>
<td>0.50</td>
<td>8.0 ± 2.4 (20)</td>
<td>4.0(^{+1.6}_{-1.2}) (20)</td>
<td>3.0(^{+3.0}_{-1.5}) (15)</td>
<td>4</td>
<td>3.8(^{+4.4}_{-2.0}) (-6)</td>
<td>2.1 ± 0.2 (13)</td>
<td>5</td>
</tr>
<tr>
<td>ζ Per</td>
<td>0.33</td>
<td>0.59</td>
<td>6.4 ± 0.6 (20)</td>
<td>4.7(^{+2.4}_{-1.6}) (20)</td>
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<td>4</td>
<td>4.3(^{+5.3}_{-2.4}) (-6)</td>
<td>2.2 ± 0.2 (13)</td>
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<tr>
<td>ε Per</td>
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<td>3.3(^{+2.7}_{-1.5}) (19)</td>
<td>6(^{+2}_{-1}) (13)</td>
<td>4</td>
<td>9.1(^{+8.7}_{-4.9}) (-7)</td>
<td>&lt; 2.0 (12)</td>
<td>6</td>
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<td>α Cam</td>
<td>0.32</td>
<td>0.35</td>
<td>8.0 ± 1.6 (20)</td>
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<td>6.9 ± 1.6 (12)</td>
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<tr>
<td>139 Tau</td>
<td>0.15</td>
<td>0.12</td>
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<td>59 Cyg</td>
<td>0.18</td>
<td>0.19</td>
<td>1.8 ± 0.4 (20)</td>
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<tr>
<td>10 Lac</td>
<td>0.11</td>
<td>0.06</td>
<td>5.0 ± 1.5 (20)</td>
<td>1.7(^{+0.5}_{-0.4}) (19)</td>
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Processes that influence the HD fraction

- $\text{H}_2$ is protected by self shielding of narrow resonances
- HD self-shielding sets in much later

  $\text{H}_2$ is favored, low HD/H2 ratio

- D atoms have a lower mobility on grains, formation mechanism may be much slower
- HD has a gas-phase formation channel
  \[
  \text{H}_2 + \text{D}^+ \rightarrow \text{HD} + \text{H}^+ \quad \text{(exothermic)}
  \] (depends on ionization rate)

Too complicated to infer reliable Information on D/H.
Summary $\text{H}_2 / \text{HD}$

**$\text{H}_2$**
- Observed in the diffuse ISM through UV satellite observations,
- Formed exclusively on dust grains,
- Ortho/para ratio reflects the cloud kinetic temperature (50-100 K),
- Destroyed through radiative dissociation via Werner and Lyman bands,
- Non-thermal rotational populations in the outer layers (optical pumping),
- Increasing self-shielding with cloud depth.

**HD**
- Can also be observed in the diffuse ISM through UV satellite observations,
- Has a gas-phase formation rate,
- reduced self-shielding pushes $N(\text{HD})/(2 \times N(\text{H}_2))$ below cosmic D/H.
PAUSE
Other interesting molecules: CN and the CMB

- One of the first interstellar molecules that were discovered (McKellar PASP 1940) (actually Interstellar molecule no 2, after CH in 1937)
- Large dipole moment -> in low-collision environment, state population reflects radiation field
- Rotational temperature of (2.3 ± 0.5) K derived by McKellar in 1940 pre-discovery of the CMB
- Origin of this temperature was not understood until 1965

Anecdote:
Gerhard Herzberg, in his textbook on Diatomic Molecules 1950 noted that the 2.3 K rotational temperature of the cyanogen molecule (CN) in interstellar space is interesting, but stated that it had "only a very restricted meaning." Missed Nobel Prize in Physics?
The mysterious abundance of CH⁺

- Discovered in 1941 (Herzberg)
- First interstellar molecular ion
- Thought to be created by

\[ \text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H} \]  (endothermic by 4600K)

Where does the energy come from to overcome the reaction barrier?

Candidates:
Shocks? Magnetohydrodynamic waves?
Alv’en waves? Turbulence?

Why do these mechanisms not enrich other endothermic species?

Presently no answer.
The mysterious abundance of CH$^+$

In equilibrium the formation and destruction processes will determine the abundance of CH$^+$

New experiment (2011): \[ \text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2 \]

The rate coefficient for the reaction \[ \text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2 \] is a factor of 50 smaller than the classical Langevin value at low energy

H$_3^+$: the Engine of Interstellar Chemistry

Molecular clouds:
It’s cold and (relatively empty)

- temperatures: 10-100 K
- density: $10^2 - 10^4$ cm$^{-3}$

Key for active low-temp chemistry:
Ion-neutral Reactions!

- No endothermic reactions
- No 3-body collisions
- No reactions with barriers

McCall, PhD thesis, Chicago 2001
First quantitative cloud model

(Herbst & Klemperer 1973)

THE FORMATION AND DEPLETION OF MOLECULES IN DENSE INTERSTELLAR CLOUDS*
ERIC HERBST† AND WILLIAM KLEMPERER
Department of Chemistry, Harvard University
Received 1973 April 9; revised 1973 May 24

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<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k(10^{-9} \text{ cm}^3 \text{s}^{-1})$</th>
<th>Reference/Remarks</th>
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<tbody>
<tr>
<td>4. $H_2^+ + H_2 \rightarrow H_2^+ + H$</td>
<td>$2.1$</td>
<td>Bowers et al. 1969</td>
</tr>
<tr>
<td>5. $CO^+ + H_2 \rightarrow HCO^+ + H$</td>
<td>$2.0$</td>
<td>Fehsenfeld et al. 1967</td>
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<td>6. $N_2^+ + H_2 \rightarrow N_2^+ + H$</td>
<td>$1.5$</td>
<td>Fehsenfeld et al. 1967</td>
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<tr>
<td>7. $He^+ + H_2 \rightarrow \text{products}$</td>
<td>$&lt; 10^{-4}$</td>
<td>Fehsenfeld et al. 1967b</td>
</tr>
<tr>
<td>8. $O^+ + H_2 \rightarrow OH^+ + H$</td>
<td>$2.0$</td>
<td>Fehsenfeld et al. 1967</td>
</tr>
<tr>
<td>9. $N^+ + H_2 \rightarrow NH^+ + H$</td>
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<td>Fehsenfeld et al. 1967</td>
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<tr>
<td>10. $OH^+ + H_2 \rightarrow OH^+ + H$</td>
<td>$0.6$</td>
<td>Ferguson 1973</td>
</tr>
<tr>
<td>11. $NH^+ + H_2 \rightarrow NH_2^+ + H$</td>
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<td>Fehsenfeld et al. 1967</td>
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<tr>
<td>12. $OH_2^+ + H_3 \rightarrow OH_2^+ + H$</td>
<td>$0.23$</td>
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<tr>
<td>13. $NH_2^+ + H_3 \rightarrow NH_2^+ + H$</td>
<td>$5 \times 10^{-4}$</td>
<td>Ferguson 1973</td>
</tr>
<tr>
<td>14. $NH^+ + H_3 \rightarrow \text{products}$</td>
<td>$&lt; 10^{-9}$</td>
<td>Fehsenfeld et al. 1967</td>
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<tr>
<td>15. $CH^+ + H_2 \rightarrow CH_2^+ + H$</td>
<td>$10^{-9}$</td>
<td>Fehsenfeld et al. 1967</td>
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<td>16. $CH_2^+ + H_3 \rightarrow CH_2^+ + H$</td>
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<td>17. $HCN^+ + H_2 \rightarrow H_2CN^+ + H$</td>
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<td>18. $He^+ + CO \rightarrow C^+ + O + He$</td>
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<td>Fehsenfeld et al. 1967</td>
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<tr>
<td>19. $He^+ + N_2 \rightarrow N^+ + N + He$</td>
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<td>Fehsenfeld et al. 1967</td>
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<td>20. $He^+ + O_2 \rightarrow O^+ + O + He$</td>
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<td>Fehsenfeld et al. 1967</td>
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<td>21. $He^+ + CN \rightarrow C^+ + N + He$</td>
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<td>Fehsenfeld et al. 1967</td>
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<td>Burt et al. 1970</td>
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<td>Burt et al. 1970</td>
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<td>55. $H_2^+ + C \rightarrow CO + H_2$</td>
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<td>Burt et al. 1970</td>
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<tr>
<td>56. $H_2^O^{-} + C \rightarrow HCO^{-} + H_2$</td>
<td>$2.0$</td>
<td>Burt et al. 1970</td>
</tr>
</tbody>
</table>
Extraterrestrial $\text{H}_3^+$

Dense clouds


Diffuse clouds

McCall et al., Science 279, 1910 (1998)

Plus:

- detection in the atmosphere of Uranus
- detection in Saturn’s atmosphere
- high abundance towards the galactic center
- extragalactic detection in IRAS 08572+3915NW

Connerney et al., Science 262, 1035 (1993)
Extraterrestrial $\text{H}_3^+$

$\text{H}_3^+$ auroral emission from the Jovian atmosphere


Plus:
- detection in the atmosphere of Uranus,
- detection in Saturn’s atmosphere,
- high abundance towards the galactic center.

The enigma related to interstellar $\text{H}_3^+$

Dense clouds: formation
\[ H_2 + \text{c.r.} \rightarrow H_2^+ \]
\[ H_2^+ + H_2 \rightarrow H_3^+ + H \]

Destruction
\[ H_3^+ + \text{CO} \rightarrow \text{HCO}^+ + H_2 \]

Observed column density: $6 \times 10^{14} \text{ cm}^{-2}$

Diffuse clouds: formation
\[ H_2 + \text{c.r.} \rightarrow H_2^+ \]
\[ H_2^+ + H_2 \rightarrow H_3^+ + H \]

Destruction
\[ H_3^+ + e^- \rightarrow H_2 + H / H + H + H \]

Observed column density: $4 \times 10^{14} \text{ cm}^{-2}$

Dissociative Recombination DR

2-3 orders of magnitude too much $\text{H}_3^+$ in diffuse clouds!
The Problem with $\text{H}_3^+$ Electron Recombination

Help!!! Theory for $\text{H}_3^+$ Recombination Badly Needed

TAKESHI OKA
Department of Chemistry, and Department of Astronomy and Astrophysics, the Enrico Fermi Institute,
The University of Chicago

1. INTRODUCTION
The Enigma of $\text{H}_3^+$ in Diffuse Clouds

Steady State:

$$\left[ \text{H}_3^+ \right] = \frac{\zeta}{k_e} \frac{[\text{H}_2]}{[e^-]}$$

Fast DR rate coefficient
$(10^{-7} \text{ cm}^3 \text{ s}^{-1})$

Cosmic ray ionization rate
$(10^{-17} \text{ s}^{-1})$

Inverse ionization fraction
$(1/10^{-4})$

$N(\text{H}_3^+) = 10^{-6} \text{ cm}^{-3}$

With the canonical value for the Cosmic Ray Ionization Rate
Of $\zeta \approx 10^{-17} \text{ s}^{-1}$ and a fast DR process,
$\text{H}_3^+$ should not be observable in the diffuse ISM!
Why $H_3^+$ observations are so useful

- $H_3^+$ density $n(H_3^+)$ is constant with two phases in diffuse and dense sightlines
- By measuring the column density, the length of the cloud $L$ along the line of sight can be calculated:

$$L = \frac{N(H_3^+)}{n(H_3^+)}$$
Advantages

• radiative relaxation (rotations, vibrations)
• direct measurement
• 100% detection efficiency
• high resolution

Problem

$H_3^+$

vibrational excitation?
**H$_3^+$ Vibrational Cooling**

Metastable rotational states


Kreckel et al., PRA 66, 052509 (2002)
Rotationally “cold” Ion Sources

Supersonic expansion

CRYRING Stockholm

Solenoid valve

-900 V ring electrode

H₂

Gas inlet 2 atm

H₂

H₃⁺

Cryogenic 22-pole ion trap

TSR Heidelberg

H$_3^+$ DR Spectrum High Resolution

**MOLECULAR PHYSICS**

Recombination cool and fast


Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

**FRONTIERS ARTICLE**

The dissociative recombination of H$_3^+$ - a saga coming to an end?

M. Larsson$^a$, B.J. McCall$^b$, A.E. Orel$^c$

$^a$ Department of Physics, AlbaNova University Centre, Stockholm University, SE-106 91 Stockholm, Sweden
$^b$ Department of Chemistry and Astronomy, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
$^c$ Department of Applied Science, University of California Davis, Davis, CA 95616, USA

Energy can be lost only by emitting a photon, a slow process that seldom happens during the short time a collision takes. In most such collisions, the ion and electron fly away from each other again. If $X^+$ is a molecular ion, however, there is a much more efficient option: the molecule can break apart following recombination with the electron, and the resulting neutral fragments can carry away kinetic energy. This is the

**Figure 1** Cosmic mystery. When an electron and a positively charged H$_3^+$ ion meet, three separate neutral hydrogen atoms are formed in a process known as dissociative recombination. The image is overlaid on a wide-field image of the Perseus region: the bright stars at bottom left are the Pleiades, or Seven Sisters, and the red region to the right is the California nebula. The bright star at the arrow’s head is η Persei, where H$_3^+$ has been observed in unexpectedly high abundance. The results of Krekel et al.$^b$

Steady State:

\[
[H_3^+] = \frac{\zeta [H_2]}{k_e [e^-]}
\]

High observed $H_3^+$ column densities

High Cosmic ray ionization rate

Fast DR rate coefficient

$H_3^+$ Laboratory Astrophysics Research leads to a revised Cosmic ray ionization rate in the Diffuse ISM
Nuclear Spin equilibrium in the diffuse ISM

Solution:

\[ \text{H}_3^+ + \text{H}_2 \rightarrow (\text{H}_5^+)^* \rightarrow \text{H}_3^+ + \text{H}_2 \]

or

\[ \text{H}_3^+ + \text{e}^- \]

\( \text{T}(\text{H}_3^+) \sim 30 \text{ K} \)

\( \text{T}(\text{H}_2) \sim 60 \text{ K} \)

\( \text{H}_3^+ \) colder than \( \text{H}_2 \)!

Too much para-\( \text{H}_3^+ \)

Understanding the $\text{H}_3^+ - \text{H}_2$ collision system

Measure with thermal p-$\text{H}_2$ samples in 10k steps
# Detected Molecules

## Table 2: Molecules detected in diffuse molecular clouds

<table>
<thead>
<tr>
<th>Weight</th>
<th>Species</th>
<th>Method</th>
<th>Target</th>
<th>$N(X)/N_H$</th>
<th>Reference</th>
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<tr>
<td>2</td>
<td>$\text{H}_2$</td>
<td>UV</td>
<td>ζ Oph</td>
<td>0.56</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>HD</td>
<td>UV</td>
<td>ζ Oph</td>
<td>4.5 (−7)</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>$\text{H}_3^+$</td>
<td>IR</td>
<td>ζ Per</td>
<td>5.1 (−8)</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td>CH</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>1.5 (−9)</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>CH$^+$</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>2.4 (−8)</td>
<td>5</td>
</tr>
<tr>
<td>14</td>
<td>$^{13}\text{CH}_2^+$</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>3.5 (−10)</td>
<td>6</td>
</tr>
<tr>
<td>15</td>
<td>NH</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>6.2 (−10)</td>
<td>7</td>
</tr>
<tr>
<td>17</td>
<td>OH</td>
<td>UV</td>
<td>ζ Oph</td>
<td>3.3 (−8)</td>
<td>8</td>
</tr>
<tr>
<td>24</td>
<td>C$_2$</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>1.3 (−8)</td>
<td>9</td>
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<tr>
<td>25</td>
<td>C$_2$H</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>1.8 (−8)</td>
<td>10</td>
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<tr>
<td>26</td>
<td>CN</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>1.9 (−9)</td>
<td>11</td>
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<tr>
<td>27</td>
<td>HCN</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>2.6 (−9)</td>
<td>12</td>
</tr>
<tr>
<td>27</td>
<td>HNC</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>4.4 (−10)</td>
<td>12</td>
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<tr>
<td>28</td>
<td>N$_2$</td>
<td>UV</td>
<td>HD 124314</td>
<td>3.1 (−8)</td>
<td>13</td>
</tr>
<tr>
<td>28</td>
<td>CO</td>
<td>UV</td>
<td>X Per</td>
<td>6.4 (−6)</td>
<td>14</td>
</tr>
<tr>
<td>29</td>
<td>HCO$^+$</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>1.5 (−9)</td>
<td>15</td>
</tr>
<tr>
<td>29</td>
<td>HOC$^+$</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>2.2 (−11)</td>
<td>15</td>
</tr>
<tr>
<td>29</td>
<td>$^{13}\text{CO}$</td>
<td>UV</td>
<td>X Per</td>
<td>8.9 (−8)</td>
<td>16</td>
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<tr>
<td>29</td>
<td>C$^{17}$O</td>
<td>UV</td>
<td>X Per</td>
<td>7.4 (−10);</td>
<td>16</td>
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<tr>
<td>30</td>
<td>C$^{18}$O</td>
<td>UV</td>
<td>X Per</td>
<td>2.1 (−9);</td>
<td>16</td>
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<tr>
<td>30</td>
<td>H$_2$CO</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>3.7 (−9)</td>
<td>17</td>
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<tr>
<td>36</td>
<td>C$_3$</td>
<td>Optical</td>
<td>ζ Oph</td>
<td>1.1 (−9)</td>
<td>18</td>
</tr>
<tr>
<td>36</td>
<td>HCl</td>
<td>UV</td>
<td>ζ Oph</td>
<td>1.9 (−10)</td>
<td>19</td>
</tr>
<tr>
<td>38</td>
<td>C$_3$H$_2$</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>6.4 (−10)</td>
<td>10</td>
</tr>
<tr>
<td>44</td>
<td>CS</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>1.6 (−9)</td>
<td>20</td>
</tr>
<tr>
<td>64</td>
<td>SO$_2$</td>
<td>mmn abs.</td>
<td>BL Lac</td>
<td>$\leq 8.2$ (−10)</td>
<td>20</td>
</tr>
</tbody>
</table>
Processes in Diffuse Clouds

- **Formation of bonds**
  - Radiative association:
  - Grain surface:

- **Destruction of bonds**
  - Photo-dissociation:
  - Dissociative recombination:

- **Rearrangement of bonds**
  - Ion-molecule reactions:
  - Neutral-neutral reactions:

\[ k \ (\text{cm}^3 \ \text{s}^{-1}) \]

- \( \sim 10^{-17} - 10^{-14} \)
- \( \sim 10^{-17} \)
- \( \sim 10^{-10} - 10^{-8} \ \text{s}^{-1} \)
- \( \sim 10^{-7} - 10^{-6} \)
- \( \sim 10^{-9} - 10^{-8} \)
- \( \sim 10^{-10} - 10^{-9} \)

Hydrogen is dominant element \( \Rightarrow \) if species can react with H or H\(_2\), it will be the dominant route
Carbon / Oxygen Network
Carbon / Nitrogen Network
Figure 5 A comparison of the gas-phase abundances, \([X/H] = \log(X/H) - \log(X/H)_\odot\), in the cool and warm diffuse clouds toward \(\xi\) Oph at heliocentric velocities of \(-15\) km s\(^{-1}\) and \(-27\) km s\(^{-1}\), respectively. The elements are arranged in order of decreasing gas-phase abundance (which is approximately one of increasing condensation temperature). The dashed line indicates the column density-weighted sight-line average abundances. There is a general progression in abundance differences as a function of elemental depletion (see text). The data used to construct this plot are listed in Table 5.
Elemental Depletion

\[ D_x = \log \left( \frac{N(x)}{N(H)} \right) - \log \left( \frac{N(x)}{N(H)} \right)_\odot \]

Timescale for depletion:

\[ \tau_d = \frac{1}{\varepsilon f(X) v(X) n} \]

- \( \varepsilon \) Grain surface per H atom cm\(^{-3} \)
- \( f(X) \) Sticking probability for species \( X \)
- \( v(X) \) velocity of species \( X \)
- \( n \) cloud density

<table>
<thead>
<tr>
<th>M (a.m.u.)</th>
<th>( \tau_d ) (Diffuse cloud, ( n = 10^2 \text{ cm}^{-3}, T = 100 \text{ K} ))</th>
<th>( \tau_d ) (Dark cloud, ( n = 2 \times 10^4 \text{ cm}^{-3}, T = 30 \text{ K} ))</th>
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</thead>
<tbody>
<tr>
<td>10</td>
<td>( 1.0 \times 10^{14} \text{ s} )</td>
<td>( 9.4 \times 10^{11} \text{ s} )</td>
</tr>
<tr>
<td>50</td>
<td>( 2.3 \times 10^{14} \text{ s} )</td>
<td>( 2.1 \times 10^{12} \text{ s} )</td>
</tr>
<tr>
<td>100</td>
<td>( 3.3 \times 10^{14} \text{ s} )</td>
<td>( 3.0 \times 10^{12} \text{ s} )</td>
</tr>
</tbody>
</table>

Typical cloud lifetime: \( 3 \times 10^{14} \text{ s} \)
Non-detections

Table 3  Molecules not detected in diffuse molecular clouds

<table>
<thead>
<tr>
<th>Weight</th>
<th>Species</th>
<th>Method</th>
<th>Target</th>
<th>N(X)/N_H</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>14</td>
<td>CH_2</td>
<td>UV</td>
<td>ζ Oph</td>
<td>≤2.4 (-8)</td>
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</tr>
<tr>
<td>15</td>
<td>NH^+</td>
<td>UV</td>
<td>ζ Oph</td>
<td>&lt;8.7 (-10)^a</td>
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<tr>
<td>18</td>
<td>H_2O</td>
<td>UV</td>
<td>HD 154368</td>
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<tr>
<td>24</td>
<td>NaH</td>
<td>UV</td>
<td>ζ Oph</td>
<td>&lt;1.2 (-9)</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>MgH</td>
<td>UV</td>
<td>ζ Oph</td>
<td>&lt;3.0 (-8)</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>MgH^+</td>
<td>UV</td>
<td>ζ Per</td>
<td>&lt;1.0 (-10)^a</td>
<td>2</td>
</tr>
<tr>
<td>26</td>
<td>CN^+</td>
<td>UV</td>
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</tr>
<tr>
<td>28</td>
<td>CO^+</td>
<td>UV</td>
<td>ζ Oph</td>
<td>&lt;4.1 (-9)</td>
<td>2</td>
</tr>
<tr>
<td>28</td>
<td>AlH</td>
<td>UV</td>
<td>ζ Oph</td>
<td>&lt;1.3 (-10)^a</td>
<td>2</td>
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<tr>
<td>29</td>
<td>SiH</td>
<td>UV</td>
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<td>29</td>
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<tr>
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<td>&lt;1.2 (-6)</td>
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</tr>
<tr>
<td>30</td>
<td>NO^+</td>
<td>UV</td>
<td>ζ Oph</td>
<td>&lt;5.9 (-8)</td>
<td>5</td>
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<tr>
<td>32</td>
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<td>UV</td>
<td>o Per</td>
<td>&lt;1.8 (-10)^a</td>
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</tr>
<tr>
<td>33</td>
<td>SH</td>
<td>UV</td>
<td>o Per</td>
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</tr>
<tr>
<td>37</td>
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<td>various</td>
<td>_</td>
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<tr>
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<tr>
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<tr>
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<td>12</td>
</tr>
</tbody>
</table>

(Continued)
Some notable reaction chains

**H$_3^+$ formation and destruction**

\[ \text{H}_2 \xrightarrow{\text{cosmic ray}} \text{H}_2^+ \xrightarrow{} \text{H}_3^+ \xrightarrow{\text{e}^-} \text{H}_2 + \text{H} \]

\[ \text{H} + \text{H} + \text{H} \]

**Water formation**

\[ \text{O} \xrightarrow{\text{H}_3^+} \text{OH}^+ \xrightarrow{} \text{OH}_2^+ \xrightarrow{} \text{OH}_3^+ \xrightarrow{\text{e}^-} \text{OH} + \text{H}_2 \]

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

**Carbon chemistry**

\[ \text{C}^+ \xrightarrow{\text{OH}} \text{CO}^+ \xrightarrow{} \text{HCO}^+ \xrightarrow{\text{e}^-} \text{H} + \text{CO} \]
Herschel surprisingly finds a lot of $\text{H}_2\text{O}^+$

Regions with low $\text{H}_2$ density?

Water formation:

\[
\begin{align*}
\text{O} & \xrightarrow{\text{H}_3^+} \text{OH}^+ & \xrightarrow{\text{H}_2} \text{OH}_2^+ & \xrightarrow{\text{H}_2} \text{OH}_3^+ & \xrightarrow{\text{e}^-} \text{OH} + \text{H}_2 \\
& \quad \text{H}_2\text{O} + \text{H} 
\end{align*}
\]

Benz, Bruderer et al. 2010

Also: Gerin et al. 2010, Ossenkopf et al. 2010, Wyrowski et al. 2010, ...
Or: maybe it’s more complicated

Summary

• The diffuse interstellar medium can be classified into 3 phases:
  1. diffuse atomic clouds (hydrogen atomic H)
  2. diffuse molecular clouds (hydrogen molecular H\(_2\), carbon ionized C\(^+\))
  3. translucent clouds (hydrogen molecular H\(_2\), carbon neutral C)

• Active Ion-neutral collisions build up larger molecules,
• High electron fraction \(\rightarrow\) Electron recombination important,
• H\(_2\) becomes self-shielding,
• H\(_2\) ortho/para excitation temp. reflects the temperature of the cloud (10-100 K),
• HD can be observed easily, exact abundance difficult to predict,

Mysteries Remain:
• Formation of CH\(^+\)
• H\(_3^+\) column densities imply higher cosmic ray ionization rate, enigma solved?
• Why so much H\(_2\)O\(^+\)?
• Why is H\(_3^+\) colder than H\(_2\)?
Literature

Snow & McCall,
“Diffuse Atomic and Molecular Clouds”

Tielens, A.G.G.M.
“The physics and chemistry of the interstellar medium”
Cambridge University Press