New Observational Views on the Chemistry of Diffuse Interstellar Clouds

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Collaborators:


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SOFIA telescope and mission support, insightful discussions with M. Gerin and P. Goldsmith
Overview

- Introduction: Phases of the ISM, diffuse gas characteristics, reaction kinetics.
- Diffuse gas tracers, observational techniques, quantitative analysis.
- Putting it all together: Chemical reaction networks and observed abundances.
- Towards a more realistic -and complex- picture
Phases of the ISM

Wolfire et al., 2003

Yorke, Saas-Fee Lecture 1988
# Characteristics of interstellar clouds

<table>
<thead>
<tr>
<th></th>
<th>Diffuse Atomic</th>
<th>Diffuse Molecular</th>
<th>Translucent</th>
<th>Dense Molecular</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Definition</strong></td>
<td>$f^n_{\text{H}_2} &lt; 0.1$</td>
<td>$f^n_{\text{H}_2} &gt; 0.1$</td>
<td>$f^n_{\text{C}^+} &lt; 0.5$</td>
<td>$f^n_{\text{CO}} &gt; 0.9$</td>
</tr>
<tr>
<td>$A_v &gt;$</td>
<td>0</td>
<td>~ 0.2</td>
<td>~ 1 – 2</td>
<td>~ 5 - 10</td>
</tr>
<tr>
<td>$n_{\text{H}} \sim [\text{cm}^{-3}]$</td>
<td>10 - 100</td>
<td>100 - 500</td>
<td>500 - 5000</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>$T_{\text{gas}} [\text{K}]$</td>
<td>30 - 100</td>
<td>30 - 100</td>
<td>15 – 50 ?</td>
<td>10 - 50</td>
</tr>
<tr>
<td><strong>Technique</strong></td>
<td>UV/Vis abs., HI $\lambda 21\text{cm}$</td>
<td>UV to mm abs, radio abs/em.</td>
<td>IR absorption, FIR to radio em.</td>
<td></td>
</tr>
</tbody>
</table>

Freely adapted from Snow & McCall 2006, ARA&A 44.
Characteristics of interstellar clouds

Freely adapted from Snow & McCall 2006, ARA&A 44.
### Reaction kinetics

A reaction is exothermic if it releases energy, endothermic if it absorbs energy, and weakly endothermic if it requires a small amount of energy. Endothermic reactions can sometimes be exothermic if the activation energy is low. The Kelvin equivalent of the endothermic reaction is given by $\Delta E/k_B$, where $k_B$ is the Boltzmann constant.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization potential (eV)</th>
<th>Endothermicity (Kelvin equivalent $= \Delta E/k_B$) for</th>
<th>Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.587</td>
<td>X + H₂ → XH + H</td>
<td>No reaction</td>
</tr>
<tr>
<td>C</td>
<td>11.260</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to He + H + H⁺</td>
</tr>
<tr>
<td>N</td>
<td>14.534</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>O</td>
<td>13.618</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>F</td>
<td>17.423</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>Ne</td>
<td>21.564</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>Si</td>
<td>8.152</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>P</td>
<td>10.487</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>S</td>
<td>10.360</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>Cl</td>
<td>12.968</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
<tr>
<td>Ar</td>
<td>15.760</td>
<td>X + H₂ → XH + H</td>
<td>Exothermic, but primary channel is to Ne + H + H⁺</td>
</tr>
</tbody>
</table>

Potential energy curve for an exothermic reaction with activation energy $\Delta G$:

- **Exothermic**
- **Endothermic**
- **Weakly endothermic ($\Delta E/k_B \sim 1000 \text{ K}$)**

Observational techniques:
Absorption spectroscopy towards bright background sources

Galactography from Vallée (2014)

▲ Sheffer et al. (2008), far-UV ($\text{H}_2$)/optical (CH)

■ Jensen et al. (2005), UV (OI)

Observational Techniques: UV/optical vs. FIR/submm absorption

Optical sample spectrum of CH A-X (0-0), $\lambda 4300$Å, velocity resolution 1.8 km/s (Sheffer et al. 2008)

Far-infrared sample spectrum of CH $^2\Pi_{1.2}$ $J = 3/2 \leftarrow 1/2$, $\lambda 149$ μm, velocity resolution 0.3 km/s (smoothed, Wiesemeyer et al. 2018)
UV/Optical Spectroscopy

- Restricted to local arm ± a few kpc.
- Examination of sightlines off the Galactic plane.
- Spectral resolution: FUSE: \( R \sim 10^4 \), HST-STIS: \( R \sim 6 \times 10^4 \), optical: \( R \sim 1.7 \times 10^5 \)
- Needs excitation modeling and extinction corrections.

FIR Spectroscopy

- Does not suffer from extinction (but absorption may saturate).
- Restricted to FIR-bright targets (hot dust from star forming regions)
- Spectral resolution: \( R \sim 10^7 \) (upGREAT, LFA)
- Ground state transitions, no extinction corrections needed:

\[
\tau_{ij,\nu} = \sqrt{\frac{\ln 2}{\pi}} \frac{A_{E,j} c^3}{4 \pi \Delta v_i \nu_j^3 g_{i,j}} \frac{g_{u,j}}{g_{i,j}} N_{w_j} \exp\left(-4 \ln 2 \left(\frac{\nu - \nu_{0,ij}}{\Delta v_i}\right)^2\right).
\]
### Quantitative Analysis: Surrogates for H$_2$

#### Primary tracers:
- FIR ground-state lines of HF, OH, CH, H$_2$O
- HF, OH and H$_2$O saturate frequently.
- CH and OH do not necessarily trace the same environment, but are correlated.
- The $\lambda$63 $\mu$m fine structure line of [OI] traces the hydrogen reservoir 2N(H$_2$)+N(HI)

#### Secondary tracers:
- Radio lines of OH and CH.
- HCO$^+$ J = 1 $\leftarrow$ 0 (correlates with OH, Liszt & Lucas 1996),
- Some hyperfine components of OH and CH appear in emission and absorption.
- Also probe physical conditions (n, T), not just column density, but collisional rates uncertain.

Wiesemeyer et al. (2016)
Quantitative analysis: Devonvolution from hyperfine structure and component separation

- The blend between hyperfine structure and overlapping velocity components requires a deconvolution strategy, like
- “Shift and subtract” (e.g., Gerin et al. 2010),
- principal component analysis (e.g., Neufeld et al. 2015 → et al. 2018 in prep.),
- Wiener-filter deconvolution (Jacob et al. 2018 in preparation),
- merit function minimization, e.g., Levenberg-Marquardt optimization (Schilke et al. 2001), simulated annealing (e.g., Wiesemeyer et al. 2016, 2018).

Left: observed \(^{1}^{2}\Pi_{1.2} J = 3/2 \leftarrow 1/2\) spectrum,

Right: Deduced column density profile.
Correlations

N(OI) vs. 2N(H$_2$)+N(HI)
Wiesemeyer et al. 2016

N(OH)/N(OH$^+$) vs. f$_{N_{H_2}}$
Wiesemeyer et al. 2016

Left: CH vs OH
Wiesemeyer et al. 2018
Liszt & Lucas 2002

Right: HCO$^+$ vs OH
Lucas & Liszt 1996
### Dissociative recombinations

$\alpha [10^{-10} \text{ s}^{-1}]$ for $T = 100 \text{ K}$, $n_e^{-} = 10^{-2} \text{ cm}^{-3}$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OH}^{+} + e^{-} \rightarrow \text{H} + \text{O}$</td>
<td>1.1</td>
</tr>
<tr>
<td>$\text{H}_{2}\text{O}^{+} + e^{-} \rightarrow \text{H} + \text{H} + \text{O}$</td>
<td>52.8</td>
</tr>
<tr>
<td>$\rightarrow \text{H} + \text{OH}$</td>
<td>14.9</td>
</tr>
<tr>
<td>$\rightarrow \text{O} + \text{H}_{2}$</td>
<td>6.8</td>
</tr>
<tr>
<td>$\text{H}_{3}\text{O}^{+} + e^{-} \rightarrow \text{H} + \text{H} + \text{OH}$</td>
<td>45.0</td>
</tr>
<tr>
<td>$\rightarrow \text{H} + \text{H}_{2} \text{O}$</td>
<td>19.1</td>
</tr>
<tr>
<td>$\rightarrow \text{H}_{2} + \text{OH}$</td>
<td>10.4</td>
</tr>
<tr>
<td>$\rightarrow \text{H} + \text{O} + \text{H}_{2}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Photodissociation

$\alpha [10^{-10} \text{ s}^{-1}]$ for $A_v = 0.2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OH}^{+} + \nu \rightarrow \text{H}^{+} + \text{O}$</td>
<td>0.05</td>
</tr>
<tr>
<td>$\text{OH} + \nu \rightarrow \text{H} + \text{O}$</td>
<td>2.49</td>
</tr>
<tr>
<td>$\quad \rightarrow \text{e}^{-} + \text{OH}^{+}$</td>
<td>0.01</td>
</tr>
<tr>
<td>$\text{H}_{2}\text{O} + \nu \rightarrow \text{H} + \text{OH}$</td>
<td>5.15</td>
</tr>
<tr>
<td>$\quad \rightarrow \text{e}^{-} + \text{H}_{2}\text{O}^{+}$</td>
<td>0.14</td>
</tr>
</tbody>
</table>

### Endothermic reactions & slow radiative association

- $\text{O} + \text{H} \rightarrow \gamma + \text{OH} \quad < ~ 10^{-6}$
- $\text{O} + \text{H}_{2} \rightarrow \text{H} + \text{OH} \quad 6.34 \text{ s}^{-1} \exp(-4000/\text{T[K]})$
- $\text{O(1D)} + \text{H}_{2} \rightarrow \text{H} + \text{OH} \quad 103.$
- $\text{OH} + \text{H} \rightarrow \text{H}_{2} + \text{O} \quad < ~ 0.001 \text{ s}^{-1} \exp(-1950/\text{T[K]})$
- $\text{OH} + \text{H} \rightarrow \gamma + \text{H}_{2}\text{O} \quad < ~ 10^{-5}$
- $\text{OH} + \text{H}_{2} \rightarrow \text{H} + \text{H}_{2}\text{O} \quad 7.7 \text{ s}^{-1} \exp(-2100/\text{T[K]})$

### Connection to C network

$\text{OH} + \text{C}^{+} \rightarrow \text{H} + \text{CO}^{+}$

**Source:**
KIDA Database
Wakelam et al. 2012
/kida.obs.u-bordeaux1.fr
Meudon PDR Code Employed to Evaluate OH Abundance Under Different Conditions (credits to Paul Goldsmith)

• All runs have total extinction equal to 10 mag
• ISRF is standard Habing field ($G_0 = 1$) or 10x standard ($G_0 = 10$)
• Hydrogen nucleus density, $n_H$, is 50 cm$^{-3}$ or 200 cm$^{-3}$
• Standard cosmic ray rates throughout; no enhanced rate at cloud edges as indicated by e.g. $H_3^+$ and other chemical tracers
• Standard grain properties
• Depleted sulfur abundance in accordance with most modeling
Key Aspects of Code Output

For standard ISRF, H-H$_2$ transition occurs at $A_v \sim 0.1$ mag:

- Hydrogen is largely atomic throughout $T_k \sim 25$ K for $A_v > 1$ mag (a little low) but rises to 200 K at cloud edge.

- C$^+$ is dominant form of carbon for $A_v < 2$ mag.

- $X$(CO) = $1.6 \times 10^{-4}$ in interior of cloud but drops precipitously to $\sim 8 \times 10^{-8}$ for $A_v < 1$ mag.

- OH abundance relatively constant at $1.2 \times 10^{-8}$ throughout $0.05$ mag < $A_v$ < 3 mag.

OH is a more unbiased tracer than CO throughout the region with $A_v < 3$ mag.
OH is a remarkably resilient tracer of total hydrogen nucleus density throughout the range $0 < A_V < 3$ mag, according to chemical modeling.

Larger $G_0$ heats cloud edge, thus increases OH formation rate but also increases the photodestruction rate.

No substantial variation, unlike CO which depends on self-shielding for protection against line photodissociation, and $C^+$ which disappears when CO builds up.

Higher density pushes $H^0/H_2$ transition to lower $A_V$, compensating the effect of higher $G_0$. 

16/20
The case of CH – environmental diversity?

Top left: Sheffer et al. (2008, opt./UV), N(CH)/N(H₂) = 3.5 x 10⁻⁸

Top right: SOFIA/GREAT (Wiesemeyer et al. 2018) & PRISMAS (Gerin et al. 2012, Sonnentrucker et al 2015), four lines of sight & stacking analysis, overabundance of factor ~3 w.r.t. Sheffer et al. (2008)

Bottom left: Liszt & Lucas (2002)
Warm neutral-neutral chemistry

- The over-abundance of CH$^+$ (e.g., Elitzur & Watson 1978) is puzzling, due to the endothermicity of the key reaction C$^+$(H$_2$,H)CH$^+$ (4640 K).

- The dissipation of turbulence, C-type shocks, or ion-neutral friction can supply the activation energy (Godard ea 2014).

- This yields to an increased abundance of CH thanks to fast hydrogen abstraction reactions of CH$^+$ and the subsequent dissociative recombination of CH$_3^+$.

- OH and CH behave differently in quiescent and turbulent gas.

Phase diagrams of the TDR model (Godard et al. 2014)

Left: $n_H = 50$ cm$^{-3}$, $A_v = 0.1 - 1.0$ mag
Right: $A_v = 0.4$ mag, $n_H = 20 - 300$ cm$^{-3}$
Towards more complexity – and reality?

TDR model: Chemical enrichment due to endothermic reaction pathways only on a fraction of the sightline (Godard et al. 2014, Fig. 2) →

MHD simulations (Valdivia et al. 2017a,b) ↓

- Highly anisotropic $A_V$
- Transport of $\text{H}_2$ formed in UV shielded regions towards warmer regions where it triggers a warm chemistry.
- Magnetic fields slow down formation of denser structures, but also lead to more complexity.
Summary

The chemistry of the cold neutral medium, i.e., precursors of molecular clouds, is reasonably well understood.

Far-infrared spectroscopy with HIFI and SOFIA, completed with radio data, suggests that OH and CH are reliable surrogates for $H_2$ in CO-dark diffuse gas.

However, at low column densities CH tends to be over-abundant, presumably thanks to the endothermic production path of CH$^+$. This observational evidence is confirmed by recent theoretical studies with a remarkable degree of complexity, assisted by experimental determinations of reaction rates at a relevant range of temperatures.

Caveat: Spectral features, even at the velocity of a single spiral arm crossing, do not necessarily represent a single cloud entity, but rather a weighted average of a complex medium.