Chemistry of the Interstellar Medium

David Neufeld
Johns Hopkins University
Outline

• Introduction: the rich chemistry of the interstellar medium
• Probing the diffuse ISM with small hydride molecules
• Determining the “oxygen budget” in the dense ISM
Astrochemistry

A rich chemistry operates in the denser, cooler regions of the interstellar medium

More than 190 interstellar molecules have been discovered over the past 80 years
Cologne Database for Molecular Spectroscopy (CDMS)

list of interstellar and circumstellar molecules

<table>
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</table>

*vibrational spectra only  **electronic spectra only  (updated Aug. 2016)
Astrochemistry

A rich chemistry operates in the denser, cooler regions of the interstellar medium.

More than 190 interstellar molecules have been discovered over the past 80 years.

Carefully interpreted, observations of interstellar molecules can provide unique information of general astrophysical interest.

Arguably, the simplest interstellar molecules show the greatest promise for advancing our understanding.
The astrochemistry game plan

Laboratory astrophysics and related theory
- Spectroscopy
- Collisional excitation rate coefficients
- Bimolecular reaction rate coefficients
- Grain surface reactions
- Photoionization and photodissociation cross-sections

Observations of astrophysical molecules
- Emission line luminosities
- Absorption line optical depths

Astrochemical modeling of ...
- Dense clouds
- Photodissociation regions
- Circumstellar outflows
- X-irradiated regions
- Excitation and radiative transfer

Information of general astrophysical interest
Collaborators

- PRISMAS Key Program Team (P.I. Maryvonne Gerin)
- HEXOS Key Program Team (P.I. Ted Bergin)
- SOFIA/GREAT team (P.I. Rolf Güsten)
- SOFIA/EXES team (P.I. Matt Richter)
- Ground-based observations: Nick Indriolo (STScI)
Outline

• Introduction: the rich chemistry of the interstellar medium
• Probing the diffuse ISM with small hydride molecules
• Determining the “oxygen budget” in the dense ISM
Recent discoveries of molecules in the diffuse ISM

Key facilities for submillimeter spectroscopy over the past 7 years

Herschel (HIFI)

APEX

SOFIA (GREAT)
Recent discoveries of molecules in the diffuse ISM

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Authors</th>
<th>Instrument</th>
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<td>OH$^+$</td>
<td>Wyrowski et al. 2010</td>
<td>APEX</td>
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<td>SH$^+$</td>
<td>Menten et al. 2011</td>
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<td>H$_2$O$^+$</td>
<td>Gerin et al. 2010</td>
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<td>de Luca et al. 2013</td>
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<td>ArH$^+$</td>
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All hydrides with high frequency rotational transitions that are unobservable from the ground or observable only from superb submillimeter sites.
Additional discoveries of small molecules in the *dense* ISM

**OD** Parise et al. 2012 SOFIA

(OD/OH probes chemistry)

**para-H_2D^+** Brünken et al. 2012 SOFIA

(ortho-H_2D^+ known previously, but ortho/para-H_2D^+ ratio serves as a molecular clock \(\rightarrow\) cloud age \(\sim\) 1Myr)

All hydrides with high frequency rotational transitions that are unobservable from the ground or observable only from superb submillimeter sites
Absorption line observations

- We can use a very luminous region of massive star formation as a background THz source.
- This allows us to search for absorption by gas in foreground material.
- A very “clean” experiment that provides robust measurements of molecular column densities.
Absorption line observations

Example

SOFIA/GREAT spectrum of SH toward the W31C star-forming region, along with IRAM 30 m observations of related molecules (H$_2$S, CS, SO)
Hydrides in the diffuse interstellar medium

First diffuse ISM detection obtained in the past seven years

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Average abundance relative to H or H₂</th>
<th>Average abundance (fraction of gas phase elemental)</th>
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<td>CH</td>
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<td>1.3 × 10⁻⁴</td>
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<td>CH₂</td>
<td>1.6 × 10⁻⁸</td>
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<td>H₂O</td>
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<td>OH⁺</td>
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<td>H₂O⁺</td>
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<tr>
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Gerin et al, ARAA 2016
Using hydride molecules as diagnostic probes

Small molecules, especially hydride molecules, have simple formation mechanisms

- carefully interpreted, they provide unique information of general astrophysical interest

Surrogate tracers for $\text{H}_2$
Tracers of gas heated by shocks and turbulence
Measuring the cosmic-ray ionization rate
Measuring the $\text{H}_2$ fraction

Small thermochemical differences lead to large differences in chemical behavior
Thermochemistry for different elements

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<tr>
<th>Element</th>
<th>Ionization Potential (eV)</th>
<th>Endothermicity (Kelvin equivalent $\Delta E/k_B$) for</th>
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<td>$X^+ + H_2 \rightarrow XH^+ + H$</td>
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<td>11000</td>
<td>4640</td>
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- Green: Exothermic reaction of element in its main ionization state
- Orange: Endothermic reaction of element in its main ionization state
- White: Exothermic reaction of element not in main ionization state
- Red: Endothermic reaction of element not in main ionization state

Important formation pathway

☑️ Important formation pathway
Interstellar hydrogen fluoride: a surrogate for molecular hydrogen

Fluorine chemistry is very simple

HF is rapidly produced by the exothermic reaction

HF + H₂ → HF + H

and only slowly destroyed.

It is a major reservoir of F wherever H₂ is abundant.
Hydrides in the diffuse interstellar medium

First diffuse ISM detection obtained in the past five years

<table>
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<th>Molecule</th>
<th>Average abundance relative to H or H$_2$</th>
<th>Average abundance (fraction of gas phase elemental$^6$)</th>
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<td>$3 \times 10^{-5}$</td>
</tr>
<tr>
<td>HF</td>
<td>$1.4 \times 10^{-8}$</td>
<td>$0.4$</td>
</tr>
<tr>
<td>SH</td>
<td>$1.1 \times 10^{-8}$</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$5 \times 10^{-9}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>SH$^+$</td>
<td>$1.1 \times 10^{-8}$</td>
<td>$9 \times 10^{-4}$</td>
</tr>
<tr>
<td>HCl</td>
<td>$1.5 \times 10^{-9}$</td>
<td>$0.004$</td>
</tr>
<tr>
<td>HCl$^+$</td>
<td>$8 \times 10^{-9}$</td>
<td>$0.04$</td>
</tr>
<tr>
<td>H$_2$Cl$^+$</td>
<td>$3 \times 10^{-9}$</td>
<td>$0.02$</td>
</tr>
<tr>
<td>ArH$^+$</td>
<td>$3 \times 10^{-10}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Gerin et al, ARAA 2016
Recent study by Sonnentrucker et al. 2015, ApJ

→ HF observed in 47 diffuse clouds in the disk

Remarkably, the optical depth for HF is typically larger than that for H$_2$O, even though the elemental abundance of fluorine is $10^4$ times smaller than that of oxygen

$$\tau(\text{HF}) / \tau(\text{p–H}_2\text{O}) \sim 2$$

⇒ $N(\text{HF}) / N(\text{H}_2\text{O}) \sim 0.7$
HF is present in CO-dark molecular gas

Neufeld and Wolfire (2009)
Calibrating HF using ground-based near-IR observations from VLT

- Indriolo et al. (2012) observed the $v = 1 - 0$ vibrational band of HF at 2.5 µm

- Detected in 3 sources where we have direct measurements of H$_2$ (in UV or near-IR): Elias 29, AFGL 2136, HD 154368

- Diffuse ISM abundance $\sim 1.2 \times 10^{-8}$ $\sim 40\%$ of fluorine in excellent agreement with astrochemical models
CH⁺, SH⁺ and SH as probes of “warm chemistry”

• Neither of C⁺, S⁺ nor S can react exothermically with H₂, but have reaction endothermicities of 4640K, 10⁴ K and 10⁴K respectively

• Observed CH⁺, SH⁺ and SH abundances are much greater than what would be expected at the average temperature of the diffuse ISM (Godard et al. 2012; Neufeld et al. 2015)

→ Evidence for ion-neutral drift or elevated temperatures in material affected by shocks or the dissipation of turbulence.
# Thermochemistry for different elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionization Potential (eV)</th>
<th>Exothermic reaction of element in its main ionization state</th>
<th>Endothermic reaction of element in its main ionization state</th>
<th>Exothermic reaction of element not in main ionization state</th>
<th>Endothermic reaction of element not in main ionization state</th>
<th>Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>11.260</td>
<td><img src="image" alt="11000" /></td>
<td><img src="image" alt="4640" /></td>
<td><img src="image" alt="6" /></td>
<td><img src="image" alt="6" /></td>
<td>Warm gas</td>
</tr>
<tr>
<td>N</td>
<td>14.534</td>
<td><img src="image" alt="15000" /></td>
<td><img src="image" alt="230" /></td>
<td><img src="image" alt="10000" /></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>O</td>
<td>13.618</td>
<td><img src="image" alt="940" /></td>
<td><img src="image" alt="6" /></td>
<td><img src="image" alt="6" /></td>
<td><img src="image" alt="6" /></td>
<td>Warm gas or cosmic rays</td>
</tr>
<tr>
<td>F</td>
<td>17.423</td>
<td><img src="image" alt="6" /></td>
<td><img src="image" alt="10000" /></td>
<td></td>
<td></td>
<td>None needed</td>
</tr>
<tr>
<td>Ne</td>
<td>21.564</td>
<td><img src="image" alt="No reaction" /></td>
<td>Exothermic, but primary channel is to Ne + H + H'</td>
<td><img src="image" alt="27000" /></td>
<td></td>
<td>27000</td>
</tr>
<tr>
<td>Si</td>
<td>8.152</td>
<td><img src="image" alt="17000" /></td>
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</tr>
<tr>
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<td></td>
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</tr>
<tr>
<td>S</td>
<td>10.360</td>
<td><img src="image" alt="10000" /></td>
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<td></td>
<td></td>
<td>Warm gas</td>
</tr>
<tr>
<td>Cl</td>
<td>12.968</td>
<td><img src="image" alt="450" /></td>
<td></td>
<td></td>
<td>UV with $h\nu &gt; 12.97 \text{ eV}$</td>
<td>6400</td>
</tr>
<tr>
<td>Ar</td>
<td>15.760</td>
<td><img src="image" alt="No reaction" /></td>
<td></td>
<td></td>
<td></td>
<td>Cosmic rays</td>
</tr>
</tbody>
</table>

- **Important formation pathway**

- Green triangle indicates important formation pathway.
CH\(^+\), SH\(^+\) and SH as probes of “warm chemistry”

• Neither of C\(^+\), S\(^+\) nor S can react exothermically with H\(_2\), but have reaction endothermicities of 4640, \(10^4\) and \(10^4\)K respectively.

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→ Evidence for ion-neutral drift or elevated temperatures in material affected by shocks or the dissipation of turbulence.
CH⁺, SH⁺ and SH as probes of “warm chemistry”

The abundance of CH⁺ has long been recognized as anomalous, but recent observations of SH⁺ and SH corroborate the presence of a ubiquitous “warm chemistry.”

CH⁺ prediction
CH$^+$, SH$^+$ and SH as probes of “warm chemistry”

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Measuring the cosmic-ray ionization rate with OH\(^+\) and H\(_2\)O\(^+\)

Unlike C\(^+\) and S\(^+\), O\(^+\) does react with H\(_2\) at low temperature. But O is not ionized by UV radiation longward of the Lyman limit, so OH\(^+\) and H\(_2\)O\(^+\) formation must be initiated by cosmic ray ionization.
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- **Green**: Endothermic reaction of element in its main ionization state
- **Orange**: Endothermic reaction of element not in main ionization state
- **Yellow**: Exothermic reaction of element not in main ionization state
- **Red**: Exothermic reaction of element in its main ionization state

*Important formation pathway*
Measuring the cosmic-ray ionization rate with OH$^+$ and H$_2$O$^+$

Unlike C$^+$ and S$^+$, O$^+$ does react with H$_2$ at low temperature. But O is not ionized by UV radiation longward of the Lyman limit, so OH$^+$ and H$_2$O$^+$ formation must be initiated by cosmic ray ionization.

\[
\begin{align*}
\text{O} & \xrightarrow{\text{H}} \text{O}^+ \xrightarrow{\text{H}_2} \text{OH}^+ \xrightarrow{\text{H}_2} \text{H}_2\text{O}^+ \xrightarrow{\text{H}_2} \text{H}_3\text{O}^+
\end{align*}
\]
Measuring the cosmic-ray ionization rate with OH$^+$ and H$_2$O$^+$

OH$^+$ and H$_2$O$^+$ abundances measured by Herschel/HIFI allow the CR ionization rate to be measured. Indriolo et al. (2015) surveyed OH$^+$ and H$_2$O$^+$ in ~ 100 diffuse clouds

Confirm typical ionization rates ~ 2 x 10^{-16} s$^{-1}$ inferred from recent H$_3^+$ observations (which are ~ 10 times the "canonical value" assumed previously)
Determining the molecular fraction in the diffuse ISM

The OH$^+$/H$_2$O$^+$ ratio reflects a competition between reaction of OH$^+$ with H$_2$ and reaction with electrons.

Observed OH$^+$/H$_2$O$^+$ ratios ~ 3 to 15 imply that only 2 – 10% of the H is typically in H$_2$. 
Argonium: the first known interstellar molecule containing a noble gas atom
Other molecules provide additional probes of the H$_2$ fraction

Argonium (ArH$^+$) has been widely observed in the diffuse ISM through its 617 GHz $J = 1 – 0$ absorption line (identified by Barlow et al. 2013 only several years after it was first detected)

It is rapidly destroyed by H$_2$ in the reaction

$$\text{ArH}^+ + \text{H}_2 \rightarrow \text{Ar} + \text{H}_3^+$$

and attains its maximum abundance when

$$f_{\text{H}_2} = \frac{2n(\text{H}_2)}{[2n(\text{H}_2) + n(\text{H})]} \sim 10^{-4}$$

A molecular tracer of almost purely atomic gas
Argon chemistry

- If $n(H_2)/n_H > 10^{-5}$, almost every ionization of Ar leads to ArH$^+$
- Destruction of ArH$^+$ is usually dominated by reaction with O or $H_2$
Diffuse cloud model results 
(with Mark Wolfire)

\[ \zeta_\nu(n) = 2 \times 10^{-16} \text{ s}^{-1} \text{, } n_H = 50 \text{ cm}^{-3} \text{, } \chi_{uv} = 1 \text{, } A_\nu(\text{tot}) = 0.3 \]

**Abundances**

- \( \text{Ar}^+ \)
- \( \text{ArH}^+ \)

(Solar elemental abundance of argon = \(3.2 \times 10^{-6}\))

**Molecular fraction**

**Ar\(^+\) balance**

**ArH\(^+\) balance**
Diffuse cloud model results
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Abundances

(Solar elemental abundance of argon = $3.2 \times 10^{-6}$)

Ar$^+$ balance

ArH$^+$ balance

Molecular fraction

Observed range
A combination of molecular ions could constrain the distribution function for $f_{\text{H}_2}$

Model predictions

$\xi_p(H) = 2.0 \times 10^{-16} \text{ s}^{-1}$, $n_H = 50 \text{ cm}^{-3}$, $\chi_{\text{UV}} = 1$, $A_V(\text{tot}) = 1.0$
Summary: what we’ve learned from recent molecular observations of the diffuse ISM

- A substantial component of the diffuse ISM has a small H$_2$ fraction (few % or less)
- “Warm chemistry” (e.g. due to turbulent dissipation in shocks) is ubiquitous (and must be warm enough to produce SH and SH$^+$)
- The cosmic-ray ionization rate is confirmed to have a typical value of $2 \times 10^{-16} \text{ s}^{-1}$ in the diffuse ISM, an order of magnitude larger than was believed a decade ago
The diffuse ISM: future directions

Herschel’s helium ran out in April 2013. What’s next for spectroscopic studies of the neutral diffuse ISM?

APEX → ALMA: vastly improved sensitivity, that will facilitate observations of hydrides at high-z (including those that cannot be observed from the ground at z = 0)

Example (right): H$_2$Cl$^+$ at z = 0.89 with ALMA (Muller et al. 2014, A&A)

Measured $^{35}$Cl/$^{37}$Cl (found to be the same as in the solar system), a probe of stellar nucleosynthesis
SOFIA: heterodyne spectroscopy at frequencies inaccessible with Herschel

Future instrumentation may allow access to frequencies below 1.25 THz that were previously covered by HIFI but are unobservable from the ground
Outline

• Introduction: the rich chemistry of the interstellar medium
• Probing the diffuse ISM with small hydride molecules
• Determining the “oxygen budget” in the dense ISM
Water around deeply-embedded massive protostars

- Water ice is the major constituent of icy grain mantles, accounting for almost 10% of interstellar oxygen nuclei in cold dense clouds.

- Close enough to massive protostars, the dust temperature exceeds ~100 K, and water ice is vaporized.
Water vapor was detected by ISO in absorption toward many massive protostars

- Observations of the 6 $\mu$m $\nu_2$ bending mode yielded clear detections of water vapor in 7 of 11 sources observed
- Inferred gas temperatures were 250 – 500 K
- Significant limitation of these observations: spectral resolving power $\lambda/\Delta\lambda \sim 1500$ was insufficient to fully resolve rotational structure

Water vapor was detected at higher spectral resolution from the ground toward AFGL 2136

- Observations near 2.5 µm (in a search for HF) led to the fortuitous detection of 47 rovibrational lines in the $\nu_1$ and $\nu_3$ bands
- Resolving power $\lambda/\Delta\lambda \sim 10^5$ ➔ rotational structure fully resolved
- Rotational diagram implies $T = 506 \pm 25$ K and $N(\text{H}_2\text{O}) = (1.02 \pm 0.02) \times 10^{19}$ cm$^{-2}$ (7 times the value inferred from the low resolution ISO spectrum)
- Significant limitation of these observations: atmosphere blocks access to states with $E_L/k < 470$ K

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  (7 times the value inferred from the low resolution ISO spectrum)
- Significant limitation of these observations: atmosphere blocks access to states with $E_L/k < 470$ K
  \( \Rightarrow \) no information about water in cold component seen in CO

SOFIA/EXES observations of AFGL 2591

- Observations of the 6.3 \( \mu \text{m} \) band are possible from 43,000 ft, and allow even the ground rotational state to be observed.
- This capability was demonstrated in commissioning phase observations.

SOFIA/EXES observations of AFGL 2591

- Observations of the 6.3 μm band are possible from 43,000 ft, and allow even the *ground rotational state* to be observed.
- This capability was demonstrated in commissioning phase observations.

![Graph showing observations of AFGL 2591](image)
SOFIA/EXES observations of AFGL 2591

- No evidence for cold water component

- In hot component,
  \[ \frac{N(\text{H}_2\text{O})}{N(^{13}\text{CO})} = 35 \]
  \[ \Rightarrow \frac{N(\text{H}_2\text{O})}{N(^{12}\text{CO})} = 0.58 \]

- Similar to result obtained for AFGL 2136
  \[ \frac{N(\text{H}_2\text{O})}{N(^{13}\text{CO})} = 40 \]
  \[ \Rightarrow \frac{N(\text{H}_2\text{O})}{N(^{12}\text{CO})} = 0.67 \]

- \( N(\text{H}_2\text{O}) \) is 3 – 4 orders of magnitude larger than that inferred from submm/far-IR Herschel observations
  \[ \Rightarrow \text{probing gas much closer to the protostar} \]
Oxygen budget for cold dense ISM
(ices from Boogert et al. 2015 ARAA)

- Unidentified: 43%
- Silicates and oxides: 30% (Whittet et al. 2007)
- Water ice: 9%
- CO ice: 9%
- CO$_2$ ice: 6%
- CO gas: 3%
- H$_2$O$_{gas}$/CO$_{gas}$ << 1
Expected budget near protostar
(after vaporization of ices)

- Unidentified: 43%
- Silicates and oxides: 30% (Whittet et al. 2007)
- CO gas: 12%
- CO₂ gas: 9%
- Water gas: 6%

\[
\frac{\text{H}_2\text{O}_{\text{gas}}}{\text{CO}_{\text{gas}}} \approx 0.72
\]
Expected budget near protostar
(after vaporization of ices and CO$_2$ destruction)

- Unidentified: 43%
- Silicates and oxides: 30% (Whittet et al. 2007)
- CO gas: 15%
- Water gas: 12%

Result of CO$_2$ + H$_2$ → CO + H$_2$O
Key conclusions

• The observed column densities of warm water (with $N(\text{H}_2\text{O})/N(^{12}\text{CO}) = 0.6 – 0.7$) are consistent with the hypothesis that the water vapor originates from the vaporization of H$_2$O ice.

• Because atomic oxygen reacts rapidly with H$_2$ to form water, the observed column densities of warm water argue against a significant fraction of the “missing oxygen” in dense gas being atomic oxygen or any other material (e.g. O$_2$ ice) that could be processed rapidly at high temperature to form water vapor.


*UDO = unidentified depleted oxygen
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The dense ISM: future directions

• SOFIA/EXES provides a unique probe of water vapor
  Advantages:
  – can probe water in rotational states all the way down to the ground state
  – spectral resolution allows the rotational structure to be resolved
  – levels of widely varying excitation observed at nearly the same wavelength
  – Individual absorption lines resolved → kinematic information

• Ice abundances are variable ➔ need water vapor observations toward a larger sample of protostars to draw stronger conclusions about the oxygen budget

• Many other molecules have vibrational modes in the range accessible to EXES: Adwin Boogert will discuss $\text{CH}_4$ and $\text{SO}_2$
The dense ISM: future directions

- SOFIA/HIRMES will bridge the gap between the two current high-resolution SOFIA instruments.
The dense ISM: future directions

- SOFIA/HIRMES will bridge the gap between the two current high-resolution SOFIA instruments
- Access to many rotational emission lines of water, CO, H$_2$O, OH, and HD that are excited in warm dense gas.
- Primary science driver is the chemistry of protostellar disks, but will provide valuable constraints on interstellar chemistry as well.
- Gordon Stacey will talk about this on Thursday
Extra slides
Principal component analysis

The optical depth spectra, shown by the black histograms on the right, are written as a linear combination of the six principal components shown at left. These six components are mutually orthogonal (uncorrelated) and listed in decreasing order of their contribution. The first two components are sufficient to yield a good fit to the data (red histogram on right).

\[ \tau_i(v) = a_i + b_i \sum_{j=1}^{6} C_{ij} S_j(v) \]

6 terms in \( \Sigma \) → black
Gives an exact fit

\[ \tau_i(v) = a_i + b_i \sum_{j=1}^{2} C_{ij} S_j(v) \]

2 terms in \( \Sigma \) → red
Good approximation
Principal component analysis

A plot of the first two coefficients, $C_{i1}$ and $C_{i2}$, for each absorption line shows the similarities and differences graphically.

NOTES

(1) Except for ArH$^+$, all points lie close to unit circle, indicating that the first two components account for most of what is observed

$\Rightarrow$ the correlation coefficient is roughly the cosine of the angle between any two vectors

(2) The position of the neutral sulphur-bearing molecules relative to H, CH and the other species may suggest that they are present mainly in material with a large molecular fraction (since HI traces atomic gas and CH traces $H_2$ in partially- or fully-molecular gas)