Analytical Chemistry in the Laboratory and the Interstellar Medium

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Sensors vs the Interstellar Medium

CURRENT PRACTICE

Fit to unassigned, but intensity calibrated library spectra.
Quantitative measure of concentration and statistical uncertainty.

Fit to spectral catalog on line by line basis (unassigned lines make ‘fit’ challenging).
Empirical questions in the literature: “How many lines required for an identification?”

DIFFERENCES and SIMILARITIES

Chemical Mixture
Homogeneous
Single, well defined temperature

Chemical mixture
Inhomogeneous
Variable temperature (LTE?)

QUESTIONS

Can we use the techniques of the laboratory for the interstellar medium?

What are current astrophysical ‘fit’ assumptions (HEXOS)?
   LTE (heavy molecules)?

What might be necessary/possible for astrophysical fit?
   Catalog completeness
How complete are astrophysical catalogs for the millimeter and submillimeter spectral region?

S. M. Fortman, I. R. Medvedev, C. F. Neese, F. C. De Lucia,


Many weak lines in catalogs
Many strong lines are not

If one’s goal is to do analytical fits, one must have ‘complete’ spectra.

If one wants to rigorously consider intensities, one must have complete spectra.

Astrophysical spectra are incomplete even at relatively high spectral levels.
Self-Contained Gas Sensor
An Implementation as a Point in Trade Space

Goals:
1 Cubic Foot Box
<10^{-4} PFA on >30 gas mixture
<100 ppt on one gas

‘absolute’ specificity on mixture of 32

2 ppt sensitivity demonstrated on one gas

Synthesized snippets to optimize photon use
For each of the 32 gases, six small ‘snippets’ of ~ 2 MHz scanned for each line in order of expected line strength and displayed here in this order.

Notice the importance of the intensity calibration to quality of fit.
Intensity Calibration

Subtraction of spectra due to four other species in ClCN snippets

Requires overlapping gases be in library

CH₂CHBr / C₂H₄Cl₂ Snippets

CICN Snippets
Numerical Analysis Provides Quantitative Concentrations and Statistical Measure of Presence

<table>
<thead>
<tr>
<th>Name</th>
<th>Partial Pressure</th>
<th>Uncertainty</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Cyanide (HCN)</td>
<td>0.00005887</td>
<td>0.00001177</td>
<td>5.0</td>
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<tr>
<td>Cyanogen Chloride (CICN)</td>
<td>0.00000373</td>
<td>0.00000863</td>
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<tr>
<td>Cyanogen Bromide (BrCN)</td>
<td>0.00001529</td>
<td>0.00001190</td>
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<tr>
<td>Acetonitrile (CH₃CN)</td>
<td>0.06179212</td>
<td>0.00010329</td>
<td>598.2</td>
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<tr>
<td>Carbonyl Sulfide (OCS)</td>
<td>-0.00002180</td>
<td>0.00004785</td>
<td>0.5</td>
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<tr>
<td>Methyl Fluoride (CH₃F)</td>
<td>0.02696802</td>
<td>0.00008850</td>
<td>304.7</td>
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<tr>
<td>Methyl Chloride (CH₃Cl)</td>
<td>0.00000402</td>
<td>0.00006642</td>
<td>0.1</td>
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<tr>
<td>Acrylonitrile (C₂H₃CN)</td>
<td>0.06608506</td>
<td>0.00015278</td>
<td>432.5</td>
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<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>0.05412899</td>
<td>0.00016715</td>
<td>323.8</td>
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<tr>
<td>Dichloromethane (CH₂Cl₂)</td>
<td>0.00011741</td>
<td>0.00009668</td>
<td>1.2</td>
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<tr>
<td>Methyl Iodide (CH₃I)</td>
<td>0.13009995</td>
<td>0.00032185</td>
<td>404.2</td>
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<tr>
<td>Methyl Bromide (CH₂Br)</td>
<td>0.08504046</td>
<td>0.00021784</td>
<td>390.4</td>
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<tr>
<td>Difluoromethane (CH₂F₂)</td>
<td>0.00015923</td>
<td>0.00015236</td>
<td>1.0</td>
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<tr>
<td>Ethylene Oxide (C₂H₄O)</td>
<td>-0.00002183</td>
<td>0.00016894</td>
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<tr>
<td>Trifluoromethane (CHF₃)</td>
<td>0.07005161</td>
<td>0.00025661</td>
<td>273.0</td>
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<tr>
<td>Acrolein (C₃H₄O)</td>
<td>0.05893068</td>
<td>0.00020953</td>
<td>281.2</td>
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<tr>
<td>Propionitrile (C₃H₄CN)</td>
<td>0.06061219</td>
<td>0.00018844</td>
<td>321.7</td>
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<tr>
<td>Pyridine (C₅H₅N)</td>
<td>-0.00011725</td>
<td>0.00014392</td>
<td>0.8</td>
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<tr>
<td>1,1 Difluoroethane (CH₂CF₂)</td>
<td>0.05567078</td>
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<td>192.8</td>
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<tr>
<td>Vinyl Fluoride (C₂H₃F)</td>
<td>0.04030862</td>
<td>0.00024987</td>
<td>161.3</td>
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<tr>
<td>Vinyl Chloride (C₂H₃Cl)</td>
<td>-0.00055029</td>
<td>0.00027035</td>
<td>2.0</td>
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<tr>
<td>Oxetane (C₃H₆O)</td>
<td>0.03009420</td>
<td>0.00032445</td>
<td>92.8</td>
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<td>1,1,1 Trifluoroethane (C₃H₃F₃)</td>
<td>-0.00007049</td>
<td>0.00021531</td>
<td>0.3</td>
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<tr>
<td>Propyne (C₃H₄)</td>
<td>-0.00016353</td>
<td>0.00034151</td>
<td>0.5</td>
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<tr>
<td>Carbonyl Fluoride (COF₂)</td>
<td>0.00467462</td>
<td>0.00048952</td>
<td>9.5</td>
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<tr>
<td>Thietane ((CH₂)₂S)</td>
<td>-0.00089690</td>
<td>0.00049489</td>
<td>1.8</td>
</tr>
<tr>
<td>Methyl mercaptan (CH₃SH)</td>
<td>0.00009574</td>
<td>0.00060512</td>
<td>0.2</td>
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<tr>
<td>Methyl isocyanate (CH₃NCO)</td>
<td>0.00080489</td>
<td>0.00052955</td>
<td>1.5</td>
</tr>
<tr>
<td>Methanol (CH₃OH)</td>
<td>0.00026869</td>
<td>0.00046662</td>
<td>0.6</td>
</tr>
<tr>
<td>Thionyl fluoride (F₃SO)</td>
<td>-0.00063312</td>
<td>0.00058645</td>
<td>1.1</td>
</tr>
<tr>
<td>Vinyl bromide (CH₂CHBr)</td>
<td>0.07177855</td>
<td>0.00058255</td>
<td>123.2</td>
</tr>
<tr>
<td>1,2 dichloroethane (C₃H₇Cl₂)</td>
<td>0.07311919</td>
<td>0.00088521</td>
<td>82.6</td>
</tr>
</tbody>
</table>

\[ \Sigma = 0.888408 \]

**CICN not present**
Sensitivity Comparisons\textsuperscript{1,2}

- For variety of Op/IR experiments
  (Optical Comb in Nature/Science Specific)
- Similar in terms of ppx sensitivity with wide variation according to choice of molecule, critical for IR sensor (very widely spaced spectra)
- Generality
- Specificity
- Clutter limits in IR due to CO\textsubscript{2}, H\textsubscript{2}O, \ldots
- Technical implementations

- Because the optimum pressure is proportional to Doppler width

- 100 – 1000 less sample smaller sample in the SMM
- \textasciitilde 10^{-14} moles for HCN, \textasciitilde 5 \times 10^{-14} moles for CH\textsubscript{3}CN, and 10^{-12} moles for C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2}

\textsuperscript{1.} Without sorbant collector
Summary: Submillimeter Sensors of Static Samples

- Dominates a significant portion of spectroscopic sensor space
- Absolute specificity
- Extremely small samples with good sensitivity
- Low atmospheric clutter limits (1 ppt)
- Favorable trades of sensitivity for speed (agility of electronic synthesis)

- Clear path to small and inexpensive implementations
  - Wireless technology and CMOS
  - Electronic synthesis provides size independent resolution
  - Small sample requirements allow less elaborate vacuum systems

- Challenges and opportunities
  - Limits on applicability to larger molecules – unclear bounds – not as general as MS or GC
  - Vacuum requirements
    - Significant up side potential – fundamental limits very favorable – infant development
Experimental and Quantum Mechanical Catalogs for Astrophysical Application

• Analytical Catalogs Require Completeness and are **Typically Experimental** in the IR (and now in the Submillimeter as well).

• Astrophysical Catalogs are **Typically QM** in the Submillimeter (and grew up with identifications of small molecules with sparse spectra).
How do we deal with this?

Intensity and Temperature Calibrated Spectra

$\Rightarrow$ Complete Experimental Spectra/Catalogs

Unassigned Line (1)

$\alpha_{1\rightarrow u} = v n \left(1 - e^{-\hbar v / kT}\right) \frac{8 \pi^3}{3 ch} \sum_{i=x,y,z} |\mu_{i,1\rightarrow u}|^2 \frac{g_i}{ \sum_{n=0}^{\infty} g_n e^{-E_n / kT} }$

Divide:

QM Catalog Line (2)

$\alpha_{1\rightarrow u} = v n \left(1 - e^{-\hbar v / kT}\right) \frac{8 \pi^3}{3 ch} \sum_{i=x,y,z} |\mu_{i,1\rightarrow u}|^2 \frac{g_i}{ \sum_{n=0}^{\infty} g_n e^{-E_n / kT} }$

$C_1$

Line Strength

Lower State Energy

$\alpha_1(T)/\alpha_2(T) = C_1 e^{-\left(E_1 - E_2\right) / kT}$

or

$\ln[\alpha_1(T)/\alpha_2(T)] = C_2 - \left(E_1 - E_2\right) / kT$

Catalog $C_1$ and $C_2$ to characterized spectra as fcn $T$
## Characterization of the Spectroscopy

<table>
<thead>
<tr>
<th></th>
<th>Quantum Mechanical Catalogs</th>
<th>Experimental Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frequency</strong></td>
<td>Model redundancy</td>
<td>Directly measured</td>
</tr>
<tr>
<td></td>
<td>Model extrapolation error</td>
<td></td>
</tr>
<tr>
<td><strong>Lower state energy</strong></td>
<td>Very accurate from model</td>
<td>accurate enough to give ~1% intensity error</td>
</tr>
<tr>
<td><strong>Completeness</strong></td>
<td>Only for analyzed vibrational states and for rotational states within cutoffs</td>
<td>Currently down to $\sim 10^{-3} - 10^{-4}$ of strongest line for species</td>
</tr>
<tr>
<td><strong>Quantum Numbers</strong></td>
<td>known</td>
<td>unknown</td>
</tr>
</tbody>
</table>
Blends and Uncataloged Lines: Point-by-Point Analyses

Red Sticks: QM Catalog Spectra
Green: Small segment of one of ~400 spectral scans
Black: Point-by-point (each 0.025 MHz) simulation from analysis of spectral scans at 400+ temperatures
  Accurately characterizes regions of complex blends
  Greatly increased sensitivity due to average over 400+ spectra
  Significantly improved baseline due to average over 400+ standing wave patterns
Frequency Shifts in Calculated Spectrum of Vinyl Cyanide

Plot of 210 – 270 GHz differences
Intensity Calculations in Methanol?
Astrophysical Comparisons - Lineshapes

Astrophysically derived lineshapes for five species

Variation ~ bin resolution of astrophysical data

Convolve with laboratory based simulations for astrophysical analysis
Comparison of 190 K Catalog Predictions, Simulation of Ethyl Cyanide, and Orion KL

Only free variable in fit was a single concentration

Six features can be attributed to QM catalog lines

Fifteen additional lines accounted for by experimental simulation

Details of blends predicted

Many similar spectral intervals

Astrophysical data from IRAM, courtesy of Jose Cernicharo and Belen Tercero
Comparison of 190 K Catalog Predictions, Simulation of Methyl Formate, and Orion KL

Much more complex spectral region
Many additional assignments from experimental spectrum
Still need to consider intensities in more detail

Astrophysical data from IRAM, courtesy of Jose Cernicharo and Belen Tercero
Vinyl Cyanide and Ethyl Cyanide fits to Orion KL Spectrum

190 K simulations provide good detailed fit to Orion KL Spectrum

Astrophysical data from IRAM, courtesy of Jose Cernicharo and Belen Tercero
Observations, Questions, and Speculations

If the experimental simulation goes down $10^{-3} - 10^{-4}$ and is complete, how do we interpret remaining ‘U’ lines?

=> ‘U’ lines become a better focus on ‘interesting’ physics and chemistry

Heavier molecules are probably the closest to LTE. If not LTE, a vibrational temperature?

a two temperature or temperature gradient model (Herschel HEXOS)?

We do not have to gain a factor of 100 into clutter to be successful – a factor of 2 is worthwhile.

ALMA will look at much smaller region, more homogeneous regions.

The answers to many of these questions lie in the exploration of the increasingly detailed astrophysical data with complete spectroscopic data.

=> Analytical Fits with ‘complete’ spectral data base are the future.
Why Should We Care About Alternative Catalogs?

Completeness of QM Calculations (‘U’ – Lines)

A Statistical View of Ethyl Cyanide Spectrum

- Intensity calibrated experimental spectrum used for comparison
- Of 9500 strongest lines in 210 – 270 GHz region, only about 700 are in QM catalogs
- Strongest of these start at intensity of 40% of strongest lines
- The density of vibrational states grows very rapidly with system sensitivity