Analytical Chemistry in the Laboratory and the Interstellar Medium

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October 6, 2011
Reno, NV

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

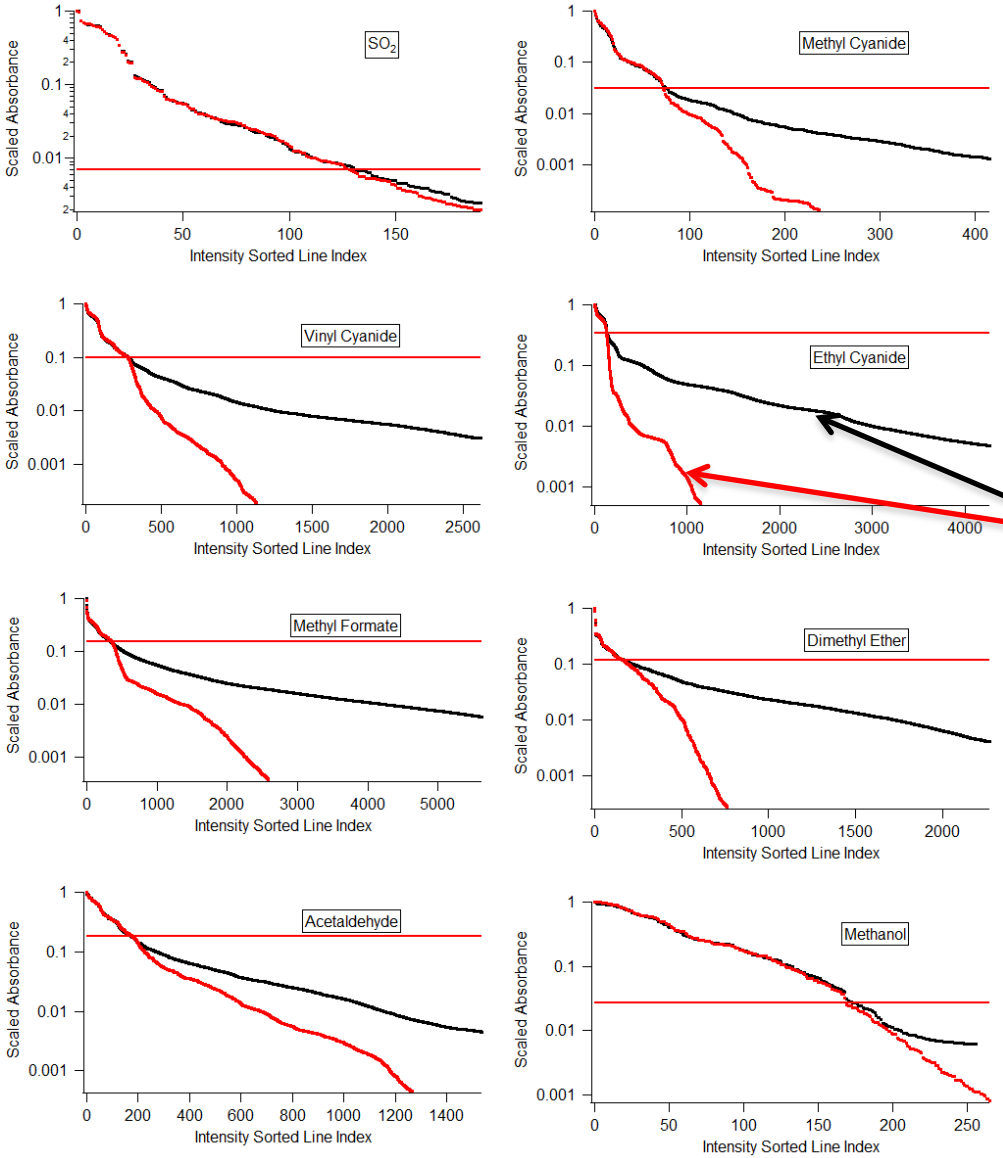
Can we use the techniques of the laboratory for the interstellar medium?

What are current astrophysical 'fit' assumptions (HEXOS)?
- LTE (heavy molecules)?

What might be necessary/possible for astrophysical fit?
- Catalog completeness

Completeness for Eight Species

[Intensity sort for experiment and catalog]



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,

Ap. J. Lett., 725, L11 (2010)

Many weak lines in catalogs
Many strong lines are not

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

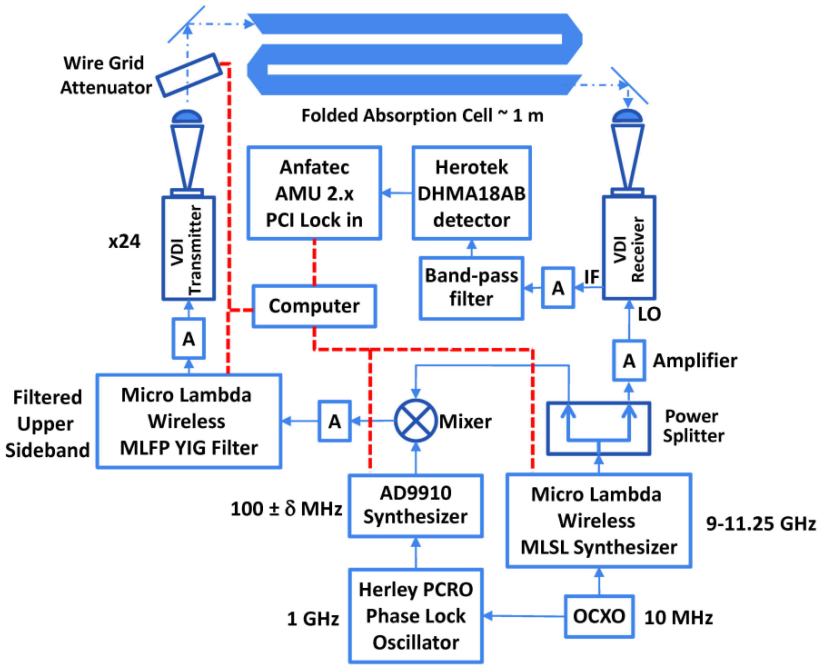
If one wants to rigorously consider intensities, one must have complete spectra.

Astrophysical spectra are incomplete even at relatively high spectral levels.

Self-Contained Gas Sensor

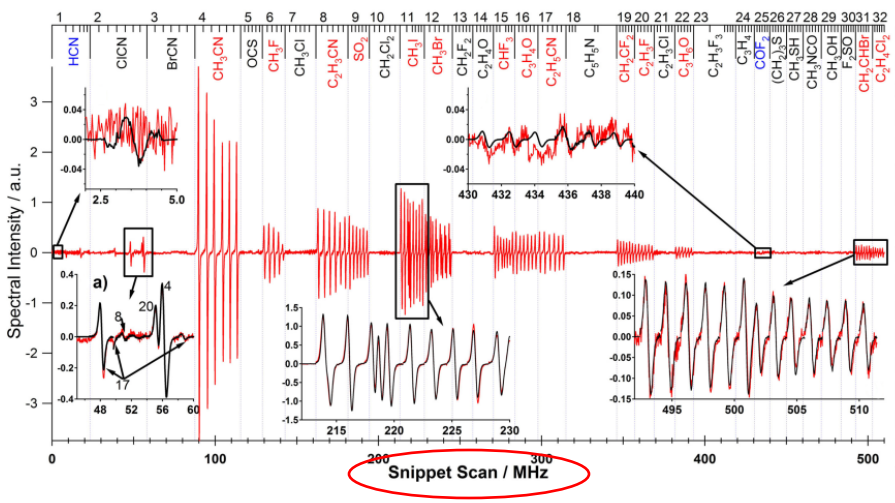
An Implementation as a Point in Trade Space

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



Synthesized snippets to optimize photon use

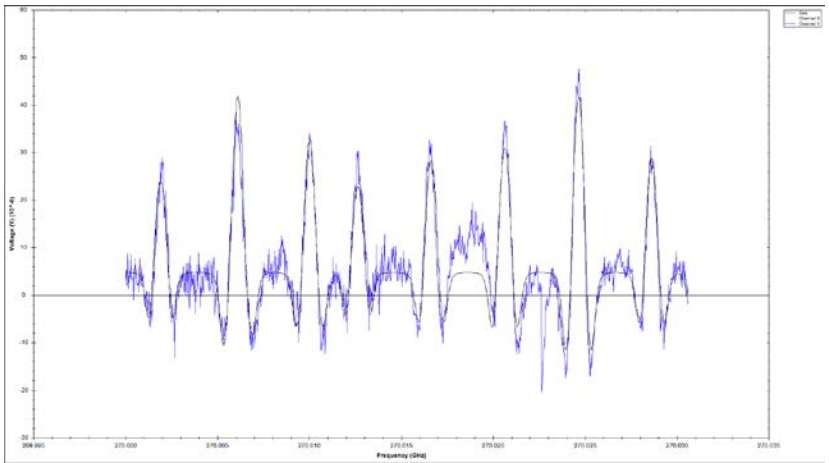
'absolute' specificity on mixture of 32

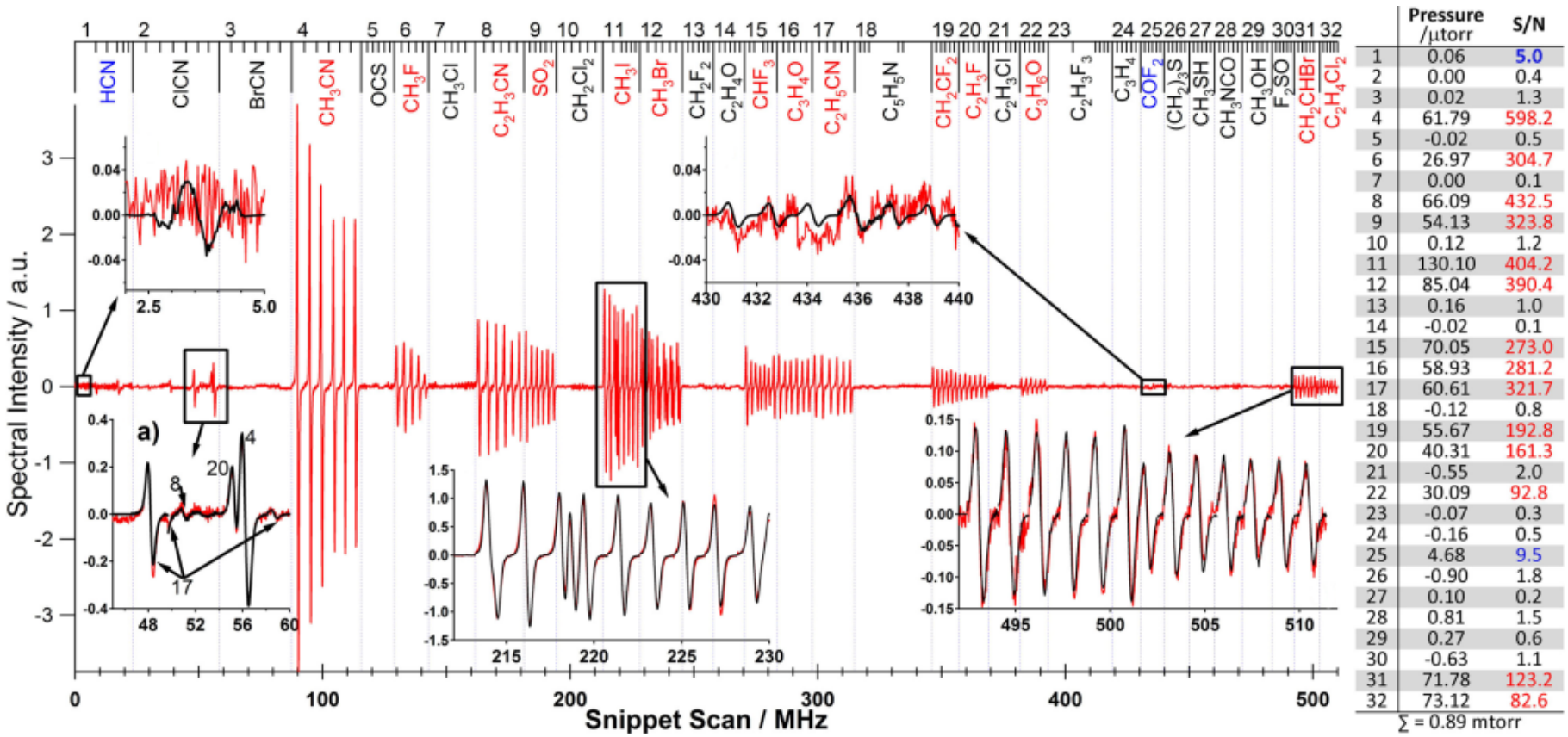


	Pressure /μtorr	S/N
1	0.06	5.0
2	0.00	0.4
3	0.02	1.3
4	61.79	598.2
5	-0.02	0.5
6	26.97	304.7
7	0.00	0.1
8	66.09	432.5
9	54.13	323.8
10	0.12	1.2
11	130.10	404.2
12	85.04	390.4
13	0.16	1.0
14	-0.02	0.1
15	70.05	273.0
16	58.93	281.2
17	60.61	321.7
18	-0.12	0.8
19	55.67	192.8
20	40.31	161.3
21	-0.55	2.0
22	30.09	92.8
23	-0.07	0.3
24	-0.16	0.5
25	4.68	9.5
26	-0.90	1.8
27	0.10	0.2
28	0.81	1.5
29	0.27	0.6
30	-0.63	1.1
31	71.78	123.2
32	73.12	82.6

Σ = 0.89 mtorr

2 ppt sensitivity demonstrated on one gas





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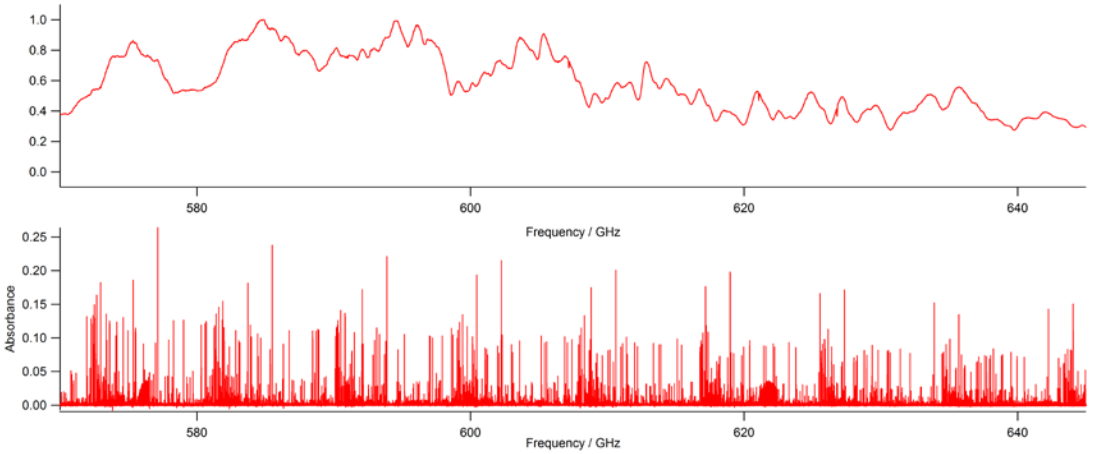
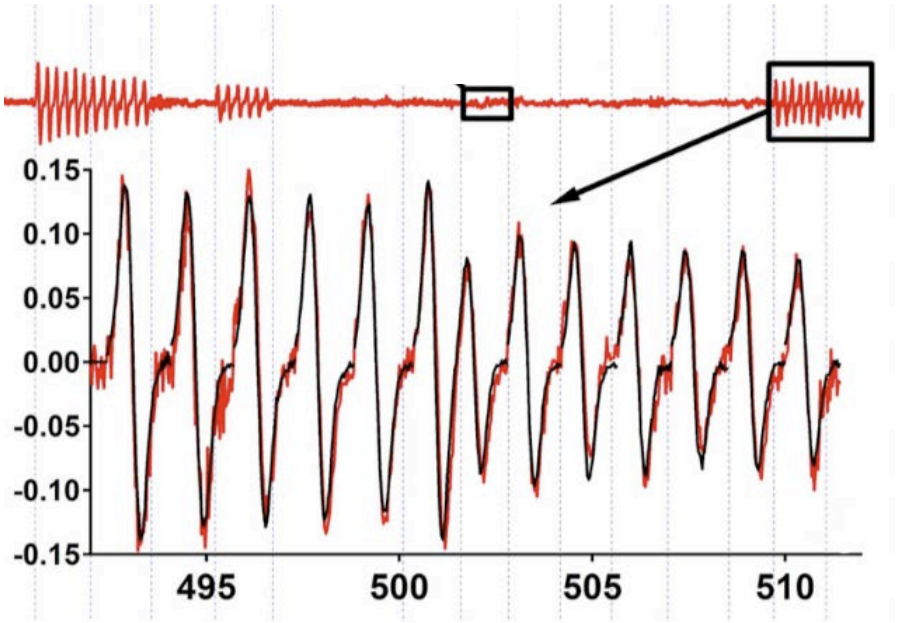
	∑ = 0.89 mtorr	

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

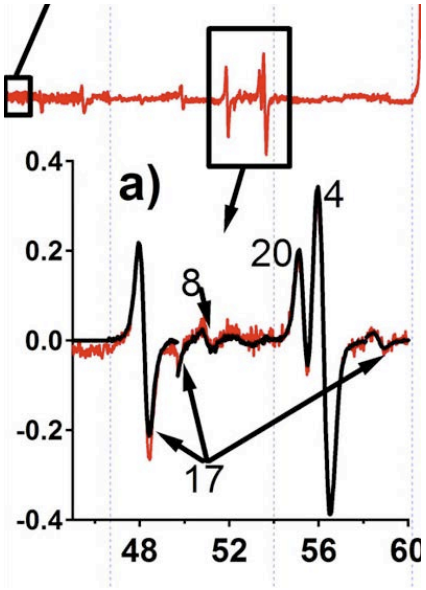




CH_2CHBr / $C_2H_4Cl_2$ Snippets

Subtraction of spectra due to four other species in ClCN snippets

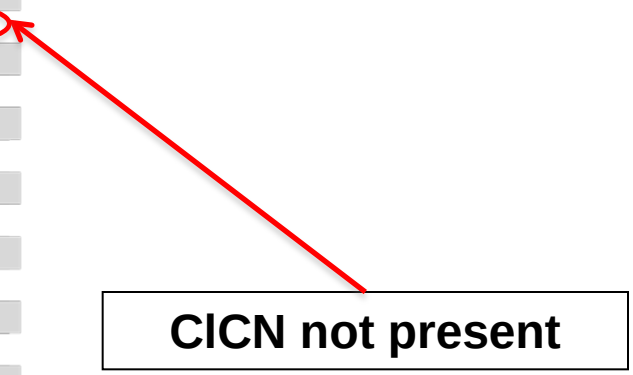
Requires overlapping gases be in library



ClCN Snippets

Numerical Analysis Provides Quantitative Concentrations *and* Statistical Measure of Presence

	Name	Partial Pressure	Uncertainty	σ
1	Hydrogen Cyanide (HCN)	0.00005887	0.00001177	5.0
2	Cyanogen Chloride (ClCN)	0.00000373	0.00000863	0.4
3	Cyanogen Bromide (BrCN)	0.00001529	0.00001190	1.3
4	Acetonitrile (CH_3CN)	0.06179212	0.00010329	598.2
5	Carbonyl Sulfide (OCS)	-0.00002180	0.00004785	0.5
6	Methyl Fluoride (CH_3F)	0.02696802	0.00008850	304.7
7	Methyl Chloride (CH_3Cl)	0.00000402	0.00006642	0.1
8	Acrylonitrile (C_2H_3CN)	0.06608506	0.00015278	432.5
9	Sulfur Dioxide (SO_2)	0.05412899	0.00016715	323.8
10	Dichloromethane (CH_2Cl_2)	0.00011741	0.00009868	1.2
11	Methyl Iodide (CH_3I)	0.13009995	0.00032185	404.2
12	Methyl Bromide (CH_3Br)	0.08504046	0.00021784	390.4
13	Difluoromethane (CH_2F_2)	0.00015923	0.00015236	1.0
14	Ethylene Oxide (C_2H_4O)	-0.00002183	0.00016894	0.1
15	Trifluoromethane (CHF_3)	0.07005161	0.00025661	273.0
16	Acrolein (C_3H_4O)	0.05893068	0.00020953	281.2
17	Propionitrile (C_2H_5CN)	0.06061219	0.00018844	321.7
18	Pyridine (C_5H_5N)	-0.00011725	0.00014392	0.8
19	1,1 Difluoroethene (CH_2CF_2)	0.05567078	0.00028872	192.8
20	Vinyl Fluoride (C_2H_3F)	0.04030862	0.00024987	161.3
21	Vinyl Chloride (C_2H_3Cl)	-0.00055029	0.00027035	2.0
22	Oxetane (C_3H_6O)	0.03009420	0.00032445	92.8
23	1,1,1 Trifluoroethane ($C_2H_3F_3$)	-0.00007049	0.00021531	0.3
24	Propyne (C_3H_4)	-0.00016353	0.00034151	0.5
25	Carbonyl Fluoride (COF_2)	0.00467462	0.00048952	9.5
26	Thietane ($(CH_2)_3S$)	-0.00089690	0.00049489	1.8
27	Methyl mercaptan (CH_3SH)	0.00009574	0.00060512	0.2
28	Methyl isocyanate (CH_3NCO)	0.00080489	0.00052955	1.5
29	Methanol (CH_3OH)	0.00026869	0.00046662	0.6
30	Thionyl fluoride (F_2SO)	-0.00063312	0.00058645	1.1
31	Vinyl bromide (CH_2CHBr)	0.07177855	0.00058255	123.2
32	1,2 dichloroethane ($C_2H_4Cl_2$)	0.07311919	0.00088521	82.6
		∑ = 0.888408		



Sensitivity Comparisons[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_2, H_2O, . . .**
- **Technical implementations**

- **Because the optimum pressure is proportional to Doppler width**

- **100 – 1000 less sample smaller sample in the SMM**
- **~10^{-14} moles for HCN, ~ 5 x 10^{-14} moles for CH_3CN, and 10^{-12} moles for $C_2H_4Cl_2$**

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1. Without sorbant collector
2. "Submillimeter spectroscopy for chemical analysis with absolute specificity," Ivan R. Medvedev, Christopher F. Neese, Grant M. Plummer, and Frank C. De Lucia, Opt. Lett. 35, 1533 (2010).

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
=> Complete Experimental Spectra/Catalogs

Unassigned Line (1)

$$\alpha_{l\to u} = \nu\, n\, (1-e^{-h\nu/kT})\frac{8\pi^3}{3ch}\sum_{i=x,y,z}\left|\mu_{i,l\to u}\right|^2 \frac{g_l\, e^{-E_l/kT}}{\sum_{n=0}^{\infty} g_n\, e^{-E_n/kT}}$$

Divide:

QM Catalog Line (2)

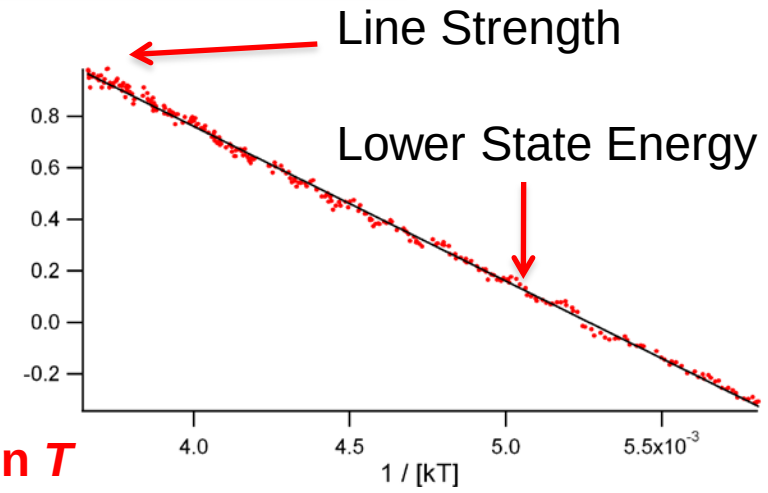
$$\alpha_{l\to u} = \nu\, n\, (1-e^{-h\nu/kT})\frac{8\pi^3}{3ch}\sum_{i=x,y,z}\left|\mu_{i,l\to u}\right|^2 \frac{g_l\, e^{-E_l/kT}}{\sum_{n=0}^{\infty} g_n\, e^{-E_n/kT}}$$

C_1

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

or

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

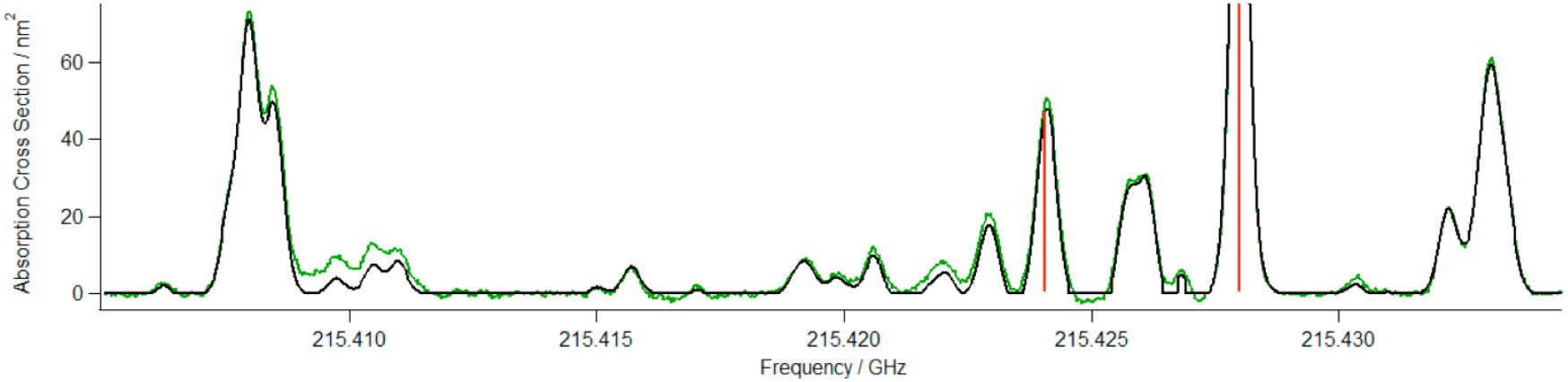


Catalog C_1 and C_2 to characterized spectra as fcn *T*

Characterization of the Spectroscopy

	Quantum Mechanical Catalogs	Experimental Spectra
Frequency	Model redundancy Model extrapolation error	Directly measured
Lower state energy	Very accurate from model	accurate enough to give ~1% intensity error
Completeness	Only for analyzed vibrational states and for rotational states within cutoffs	Currently down to ~10^{-3} – 10^{-4} of strongest line for species
Quantum Numbers	known	unknown

Blends and Uncataloged Lines: Point-by-Point Analyses



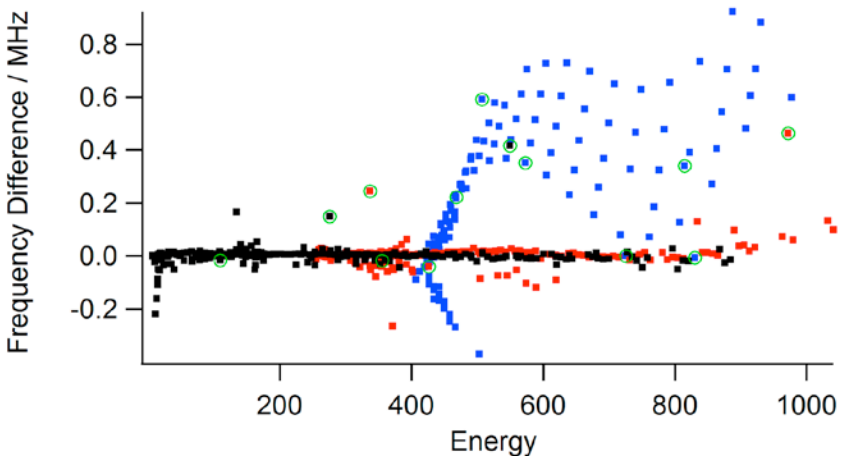
Red Sticks: QM Catalog Spectra

Green: Small segment of <u>one</u> of ~400 spectral scans

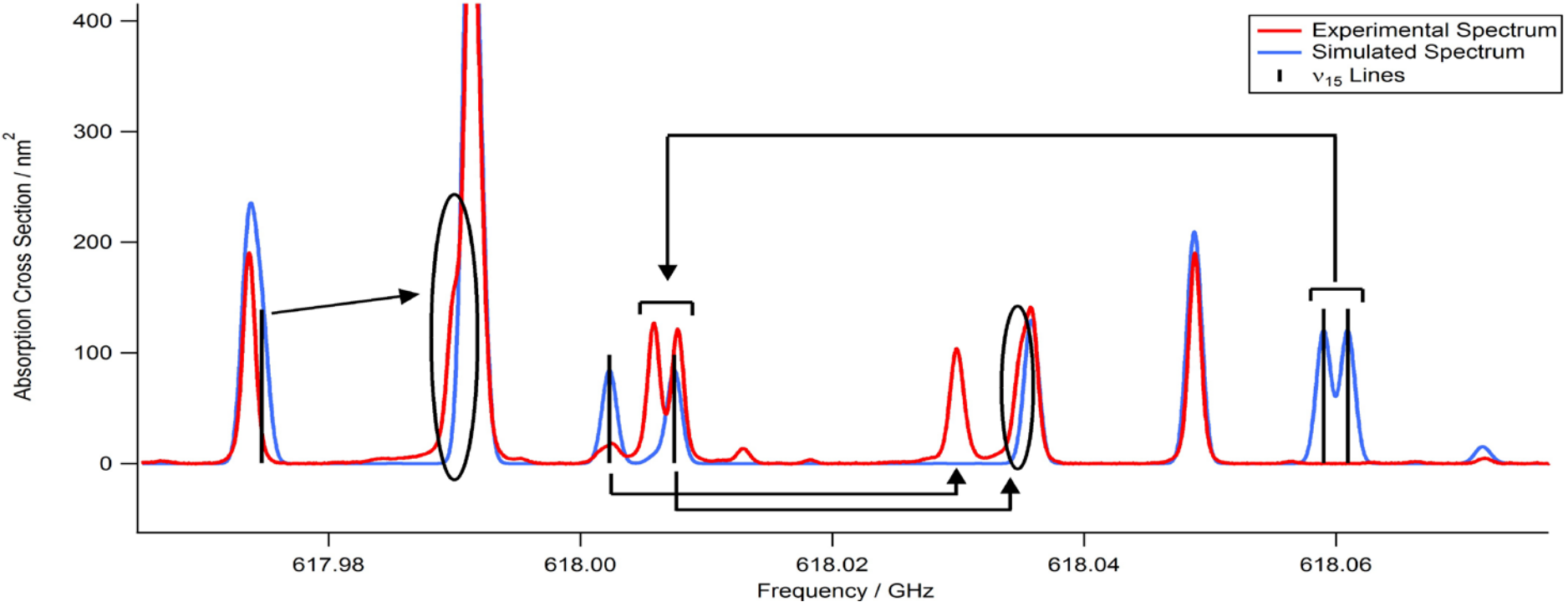
Black: Point-by-point (each 0.025 MHz) simulation from analysis of spectral scans at 400$^+$ temperatures

- **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**

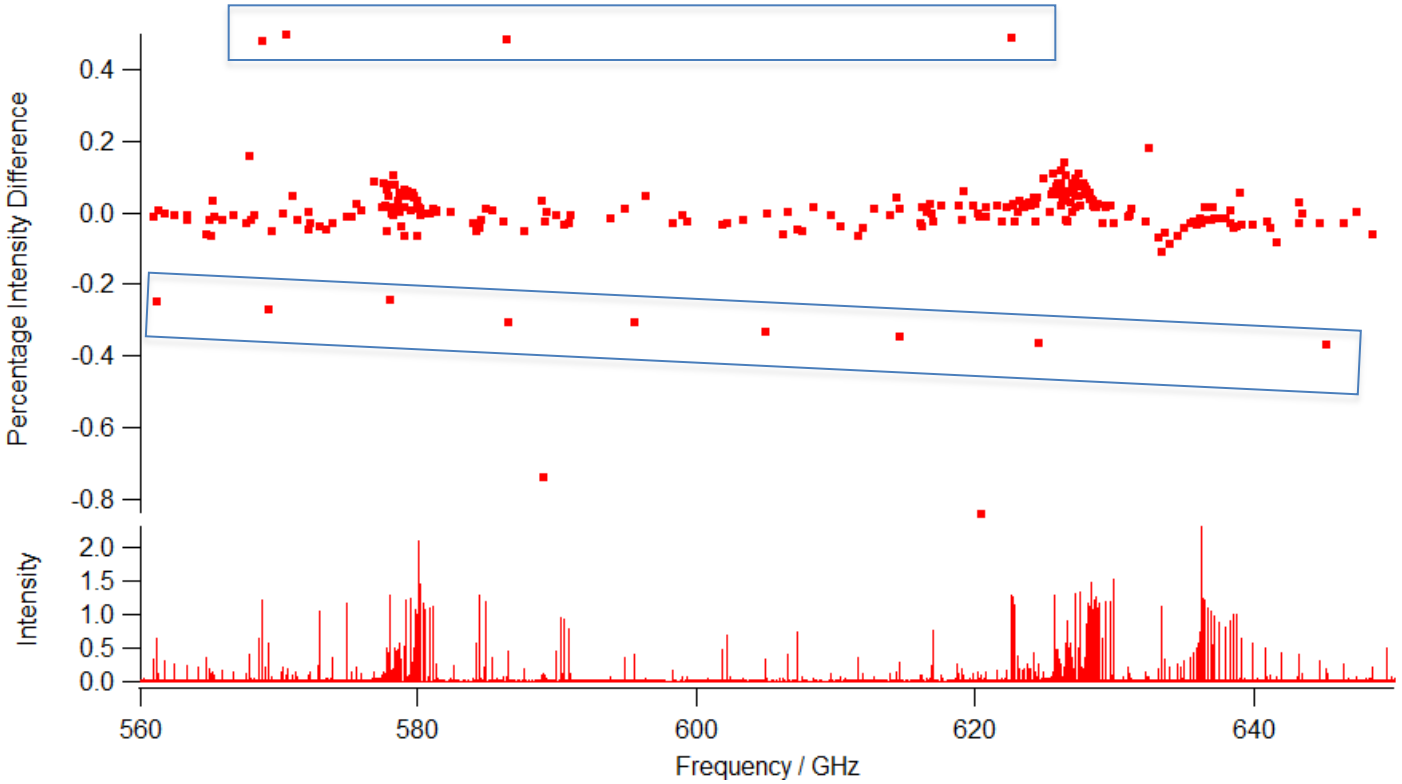
Frequency Shifts in Calculated Spectrum of Vinyl Cyanide



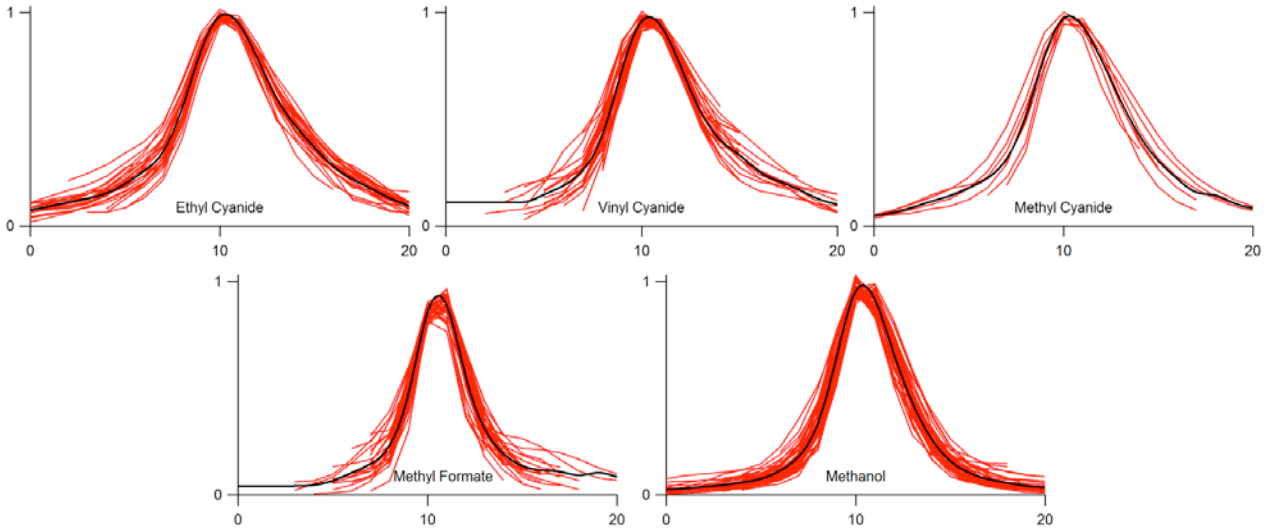
Plot of 210 – 270 GHz differences



Intensity Calculations in Methanol?



Astrophysical Comparisons - Lineshapes

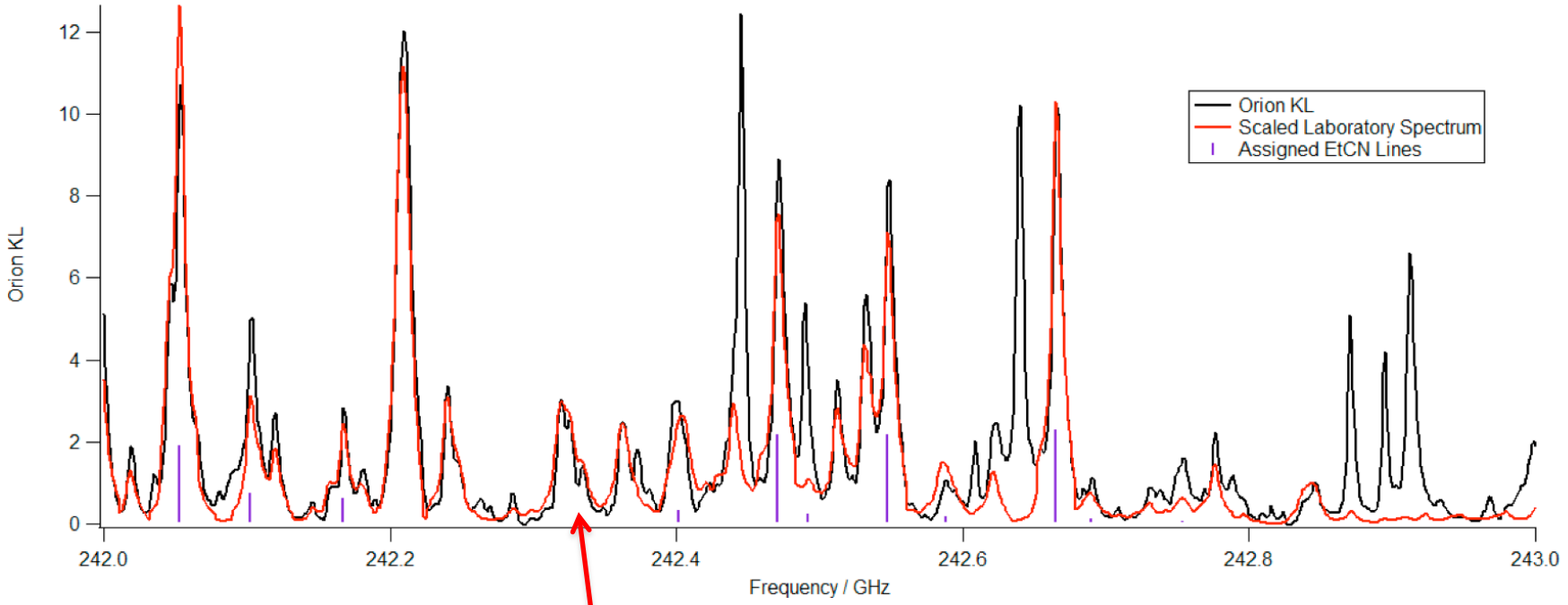


Astrophysically derived lineshapes for five species

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

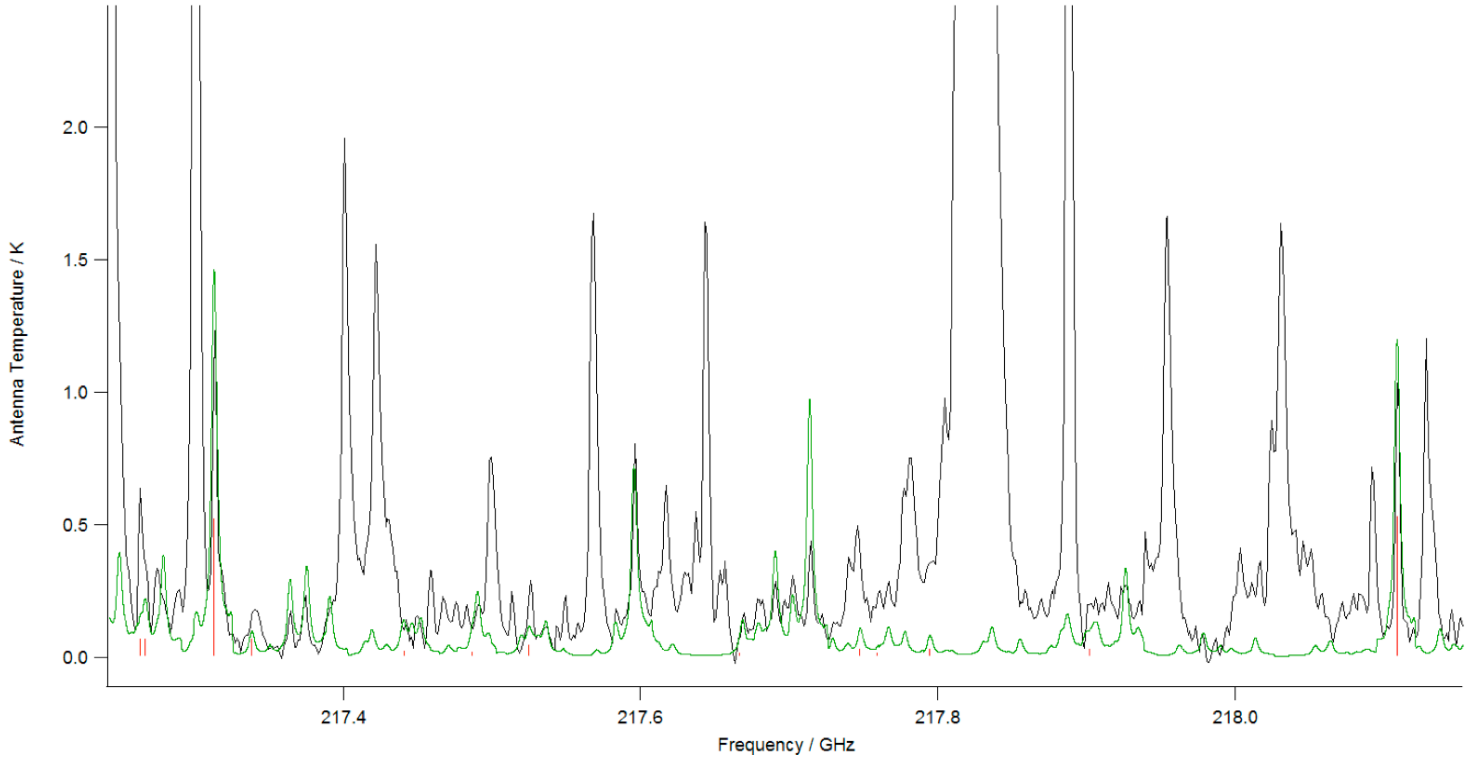
Fifteen additional lines accounted for by experimental simulation

Details of blends predicted

Many similar spectral intervals

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

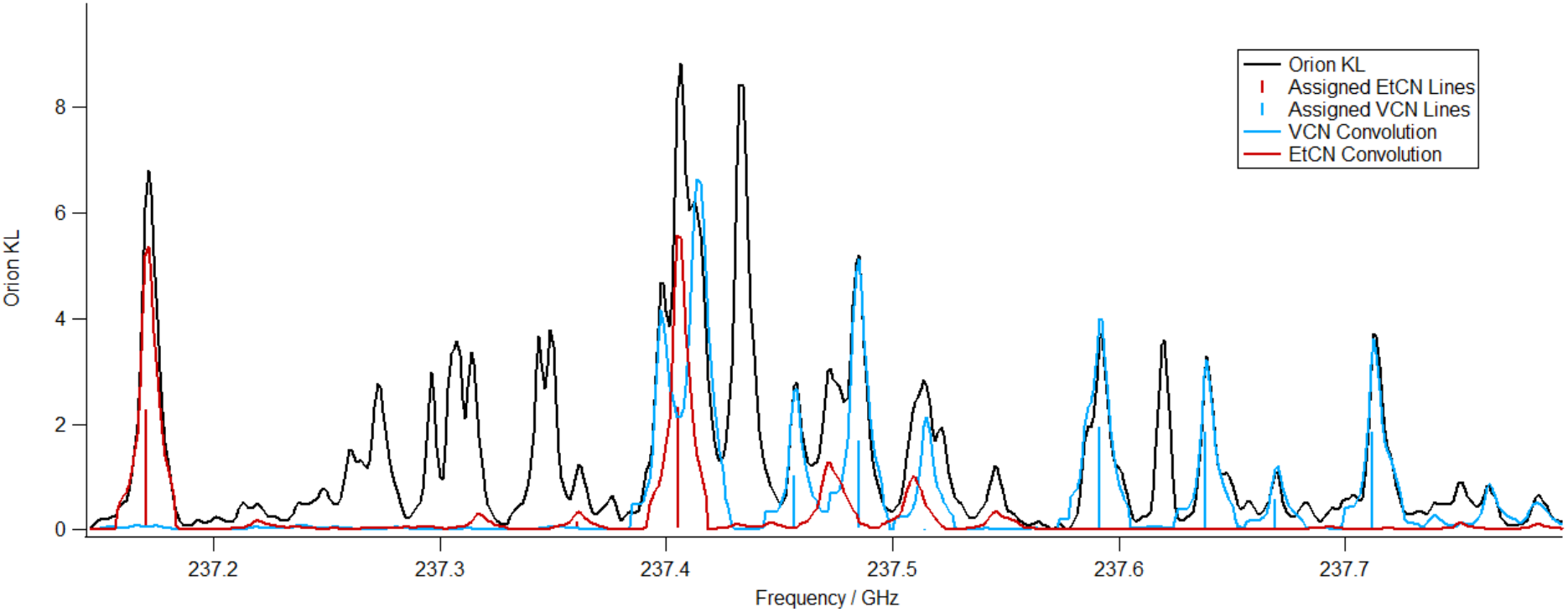
Comparison of 190 K Catalog Predictions, Simulation of Methyl Formate, and Orion KL



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.

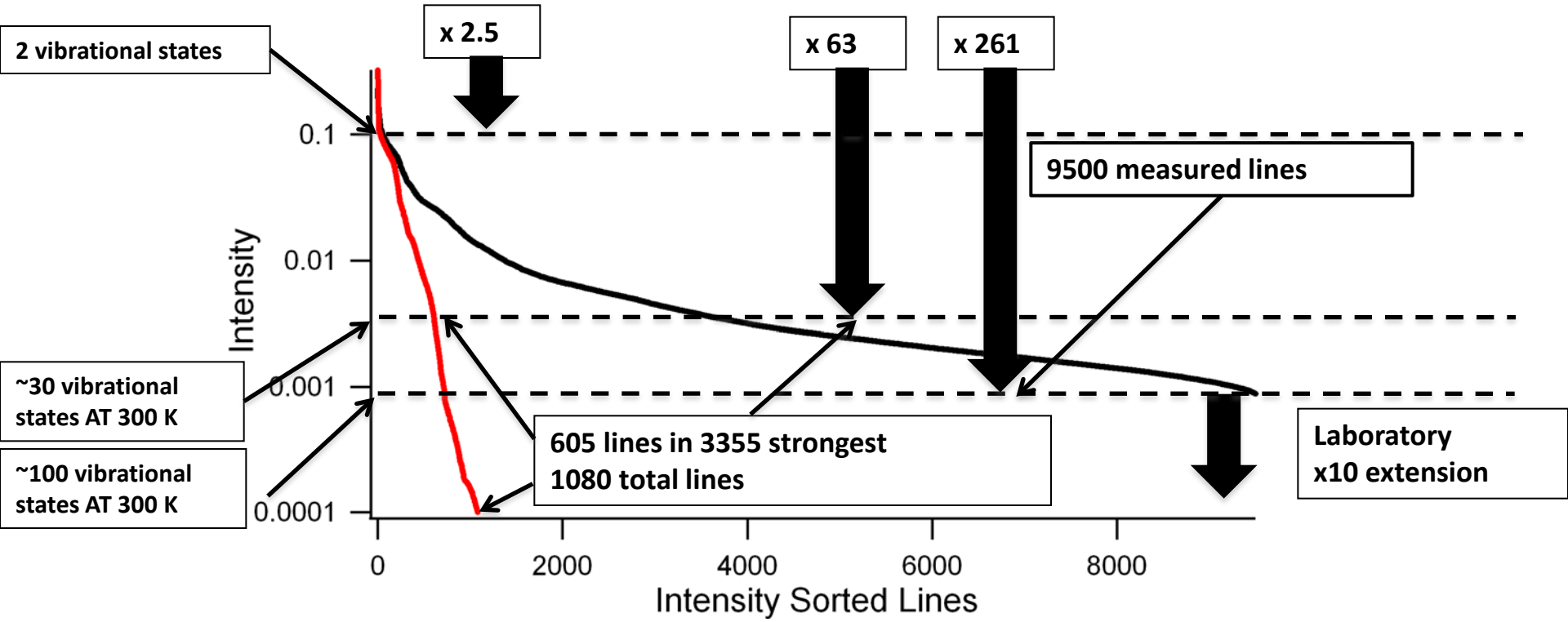
The answers to many of these questions lie in the exploration of the increasingly detailed astrophysical data with complete spectroscopic data.

=> 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