Astronomical and Atmospheric Spectroscopy in the SMM/THz:

Experiment, Analysis, and Catalogs

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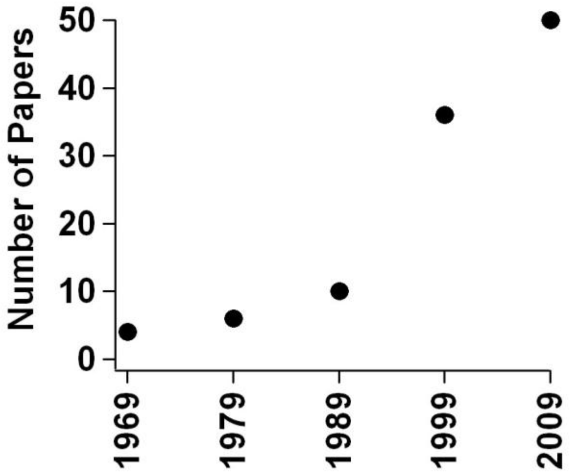
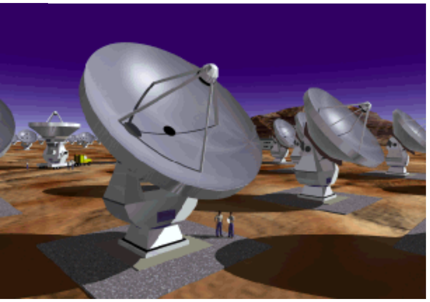
The Evolution of Submillimeter Spectroscopy



Structural Evolution

From: Single/few line spectroscopy of small molecules at high frequency

To: Confusion limited applications in molecular soups



TH02 Remijan

TH04 Gehrz

TH03 Pearson

Robust technology and computing make applications possible

The Structure of Submillimeter Rotational Spectroscopy for Air/Space Missions

SCIENTIFIC/SPECTROSCOPIC STRUCTURE

What are the frequency extent and density of states/spectra as a function of molecular size and type?

ORGANIZATIONAL STRUCTURE

How is spectroscopic structure related to remote sensing applications and what impact does it have on spectroscopy and catalogs?

DISCIPLINE STRUCTURE

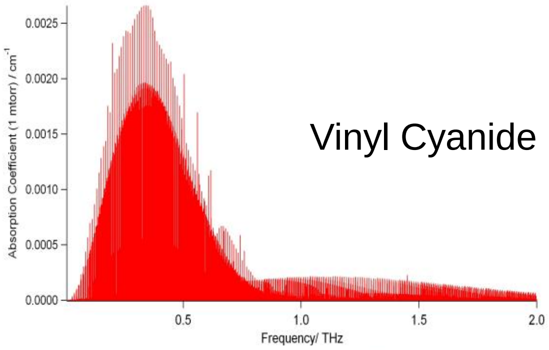
How are we spectroscopists going to respond to these new opportunities?

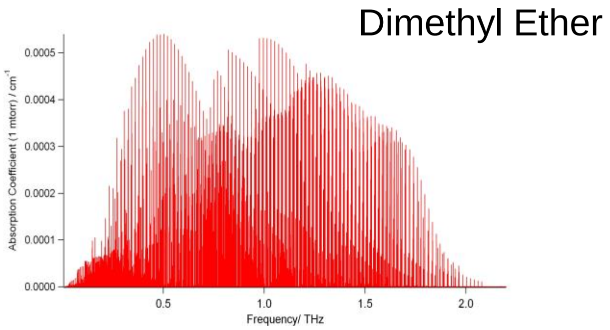
How can new people obtain the recognition needed for career development?

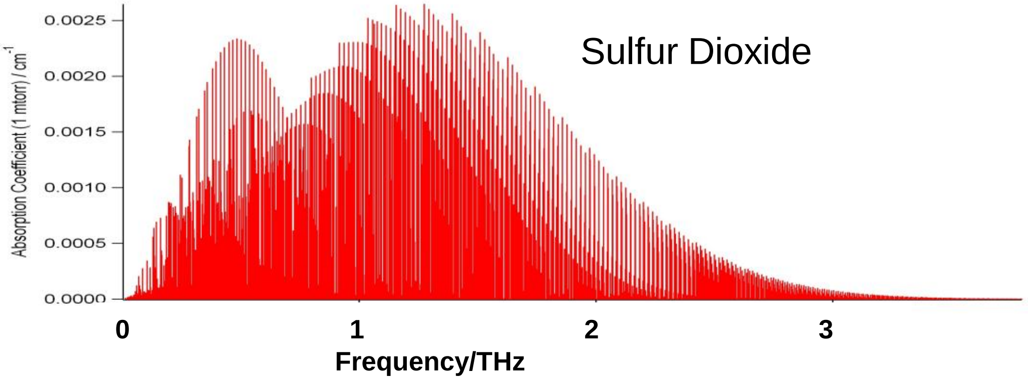
Molecular Engineering Connects Spectroscopic Science and Applications
Are we to be ‘useful servants’* or Kings?

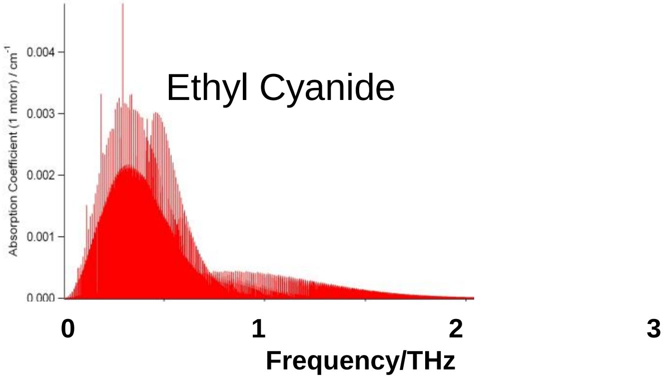
***The term ‘useful servants’ is from J.T. Hougen in Prague (2002)**

Where are the Lines (300K)?


Vinyl Cyanide


Dimethyl Ether


Sulfur Dioxide

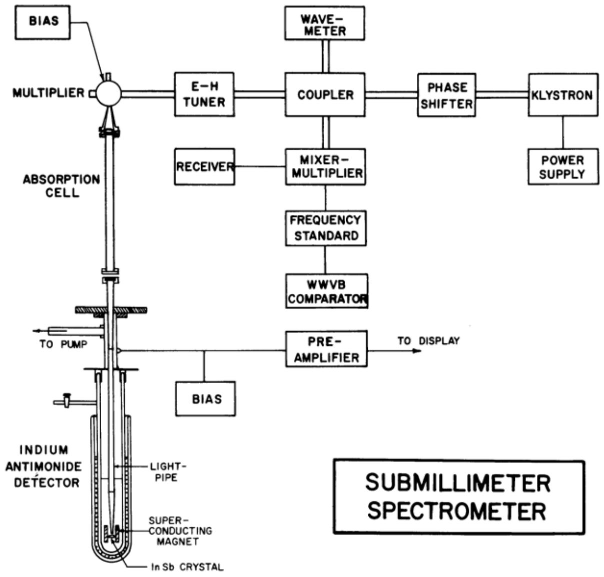

Ethyl Cyanide

Light molecules have sparse spectra throughout this region, more or less independent of temperature.

Not all that many molecules have dense spectra that exists to 2 THz, but there are important examples.

Completeness in Spectral Interval

High Resolution Analysis



SUBMILLIMETER SPECTROMETER

Long searches for sparse spectra (e.g. water)

Measure, Assign, Model and Calculate Catalog (largely ground vibrational state)

Good for Small Molecules (not all lines had to be measured; large vibrational frequencies lead to very small excited vibrational state populations)

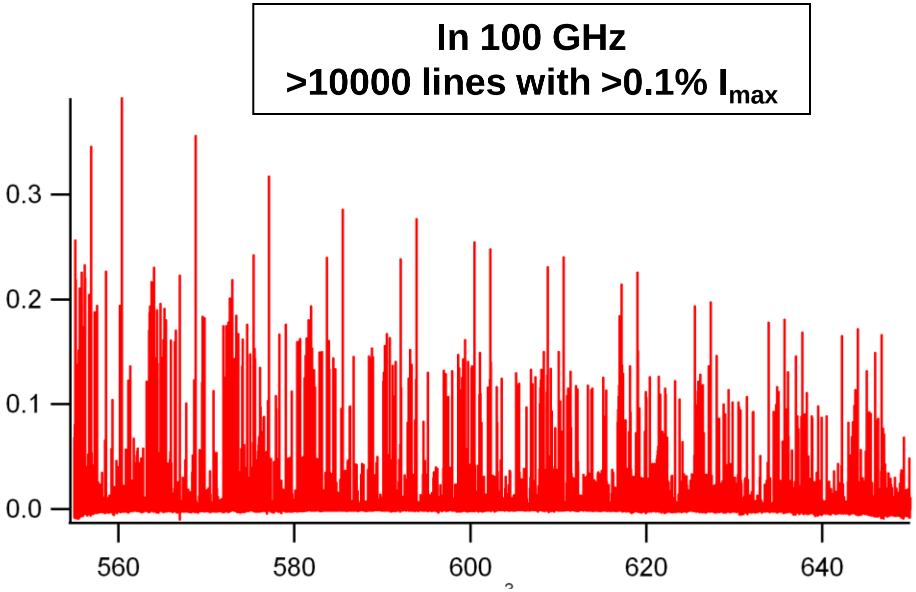
For large and complex molecules, ~lifetime job security

3D Spectroscopy

Complete in Frequency
Intensity calibrated => linestrength
Function of Temperature => E_l

WH04 Ivan Medvedev

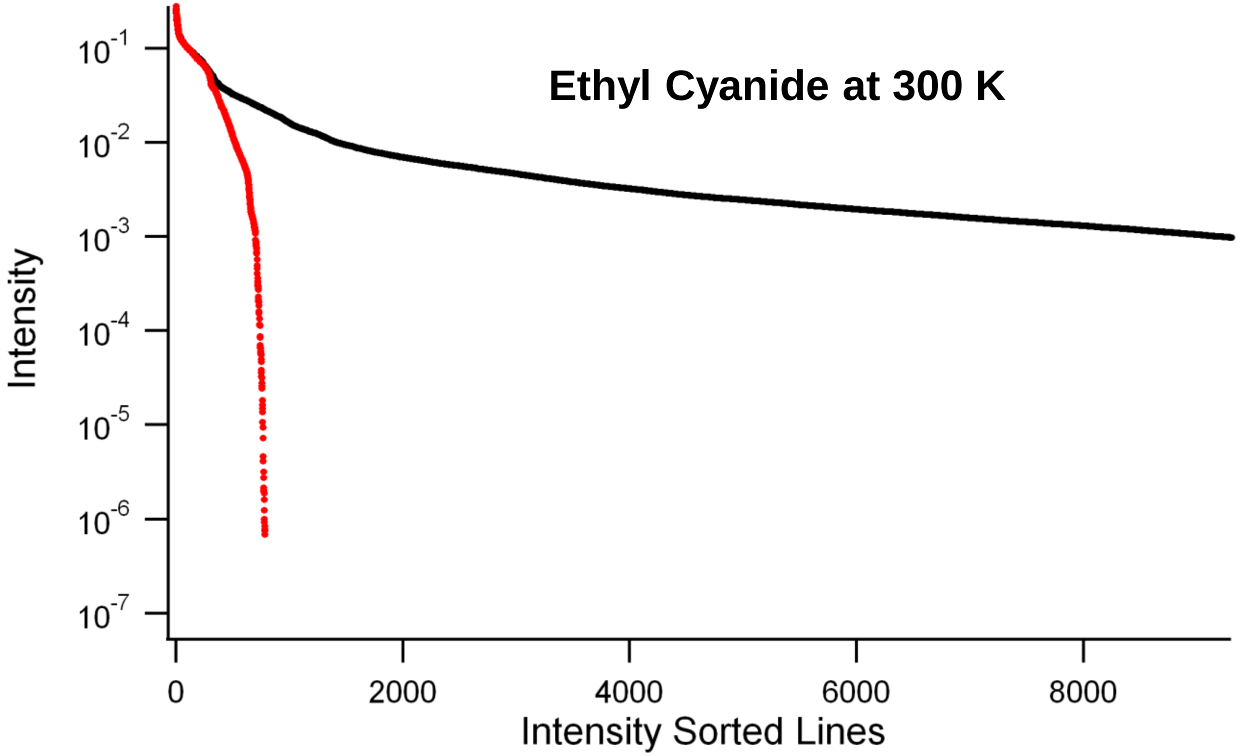
WH05 Sara Fortman



In 100 GHz
>10000 lines with >0.1% I_{max}

What is the Distribution of Line Strengths?

10 000 strongest experimental lines vs. 800 strongest ground state catalogue lines



The probability of intensity modification of assigned line by unassigned line is significant and much larger than would be inferred from catalogues.

WH05 Sara Fortman

What Do We Mean by a Clutter Limit?

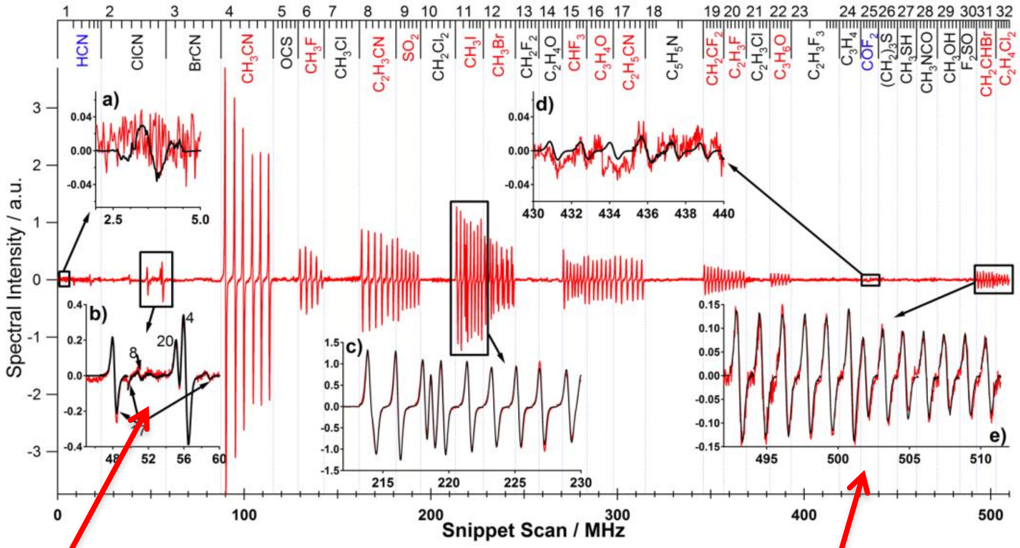
Submillimeter spectra have enormous information content:

10^6 resolution elements – 10^7 measureable frequencies + absolute intensity calibration

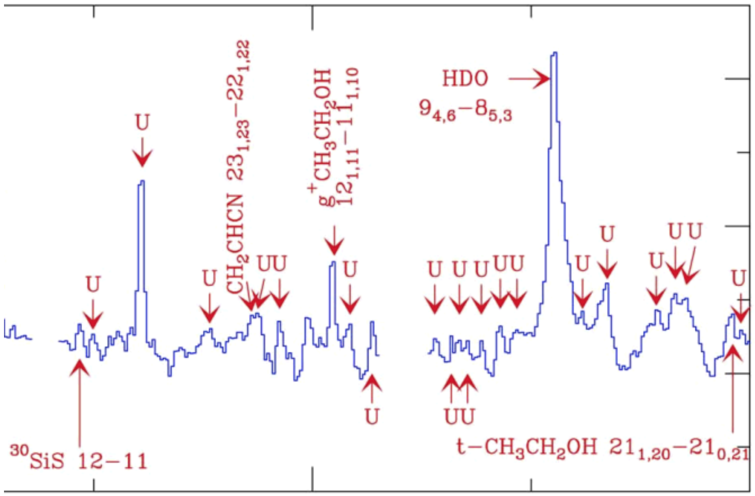
But, Submillimeter spectra *can be* very dense

Cannot deconvolve molecular presence vs No empty white space

Doppler Limited Spectra in Thermal Equilibrium



Astrophysical Spectra



Fits add target line strengths lines together

Intensity calibration subtracts overlap to accuracy of intensity

But Astrophysics is much harder

- **Inhomogeneity**
- **Incomplete catalogues**

TI10 – Christopher Neese

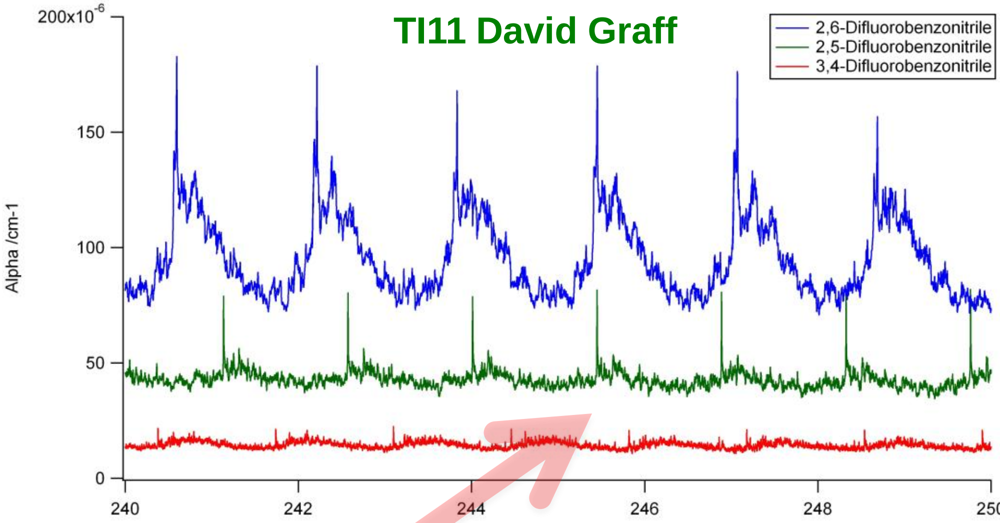
Is there an Ultimate Clutter limit?

As we showed above, the density of lines grows rapidly with increasing sensitivity. Are we doomed to reach a clutter limit?

Yes

Does it matter, will it limit us?

Probably not as much as we might think



When 'many' small clutter lines (the weak lines of the weed molecules) merge into a continuum, they average like noise and their signal power will be much greater than their noise power. The few stronger lines of large flowers can still stand out against this floor.

This is driven by the statistical distribution of line strengths, which can vary substantially by molecular type. The spectroscopic engineering is complicated.

Where are the Photons?

Rotational Partition Functions

$$ {}^{S}\!/_{N} \propto \frac{1}{Q_{ast}} \propto \sqrt{ABC} $$

$$ {}^{S}\!/_{N} \propto \frac{1}{Q_{st}} \propto \sqrt{AB^{2}} $$

$$ {}^{S}\!/_{N} \propto \frac{1}{Q} \propto \sqrt{R^{3}} \quad \boxed{\propto {}^{1}\!/_{M^{5/2}}} $$

At a given observational frequency:

the distance between band heads is

$$ \Delta_{BH} \sim 2R $$

the number of K-levels associated with each band head is:

$$ N_{K} \propto \frac{1}{R} $$

the number of M_J levels associated with each K - line is:

$$ N_{M_J} \propto \frac{1}{R} $$

Sum of line strengths/frequency interval - the number of spectral photons available to a multi-channel telescope

$$ \alpha / MHz \propto \frac{N_{K} N_{m_J}}{Q_{r} \Delta_{BH}} \propto \frac{1}{R^{3/2}} $$

Because the spectral space occupied by these lines grows as R^2 (the M_J factor above adds intensity, but not spectral space)

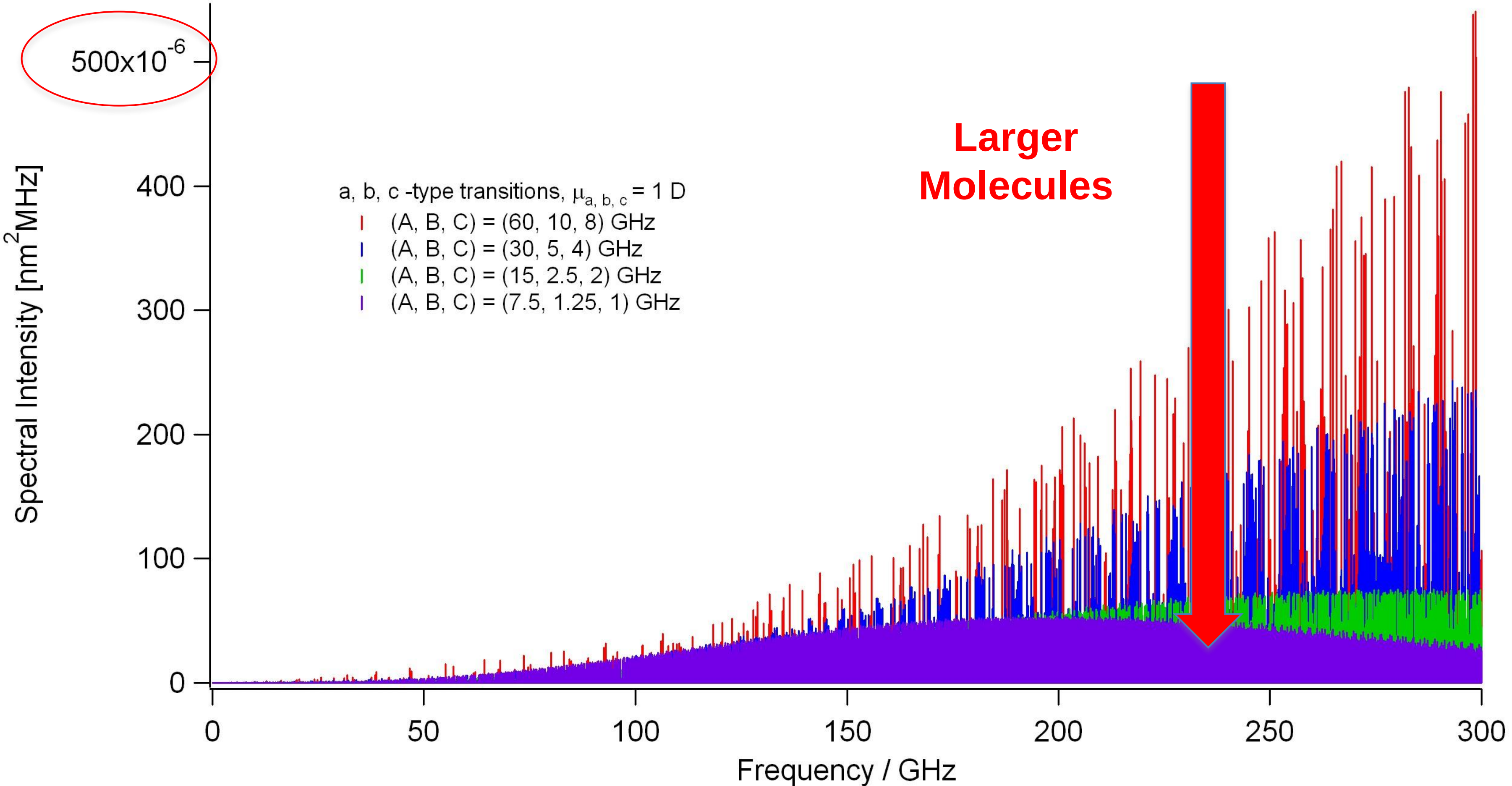
$$ {}^{S}\!/_{N} \propto \frac{1}{\sqrt{R}} $$

For a spherical molecule, $R \propto 1/M^{5/3}$

$$ \boxed{{}^{S}\!/_{N} \propto M^{5/6}} $$

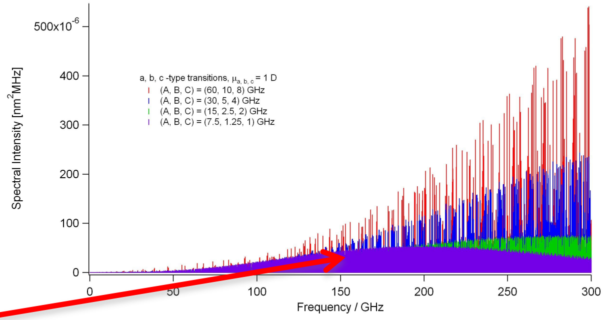
Conventional Wisdom about Large Molecules
Are Detections Doomed?

Lines get weaker as molecule gets larger for asymmetric rotor
This is the right question for a laboratory spectrometer,
but the wrong question for a multiplex telescope

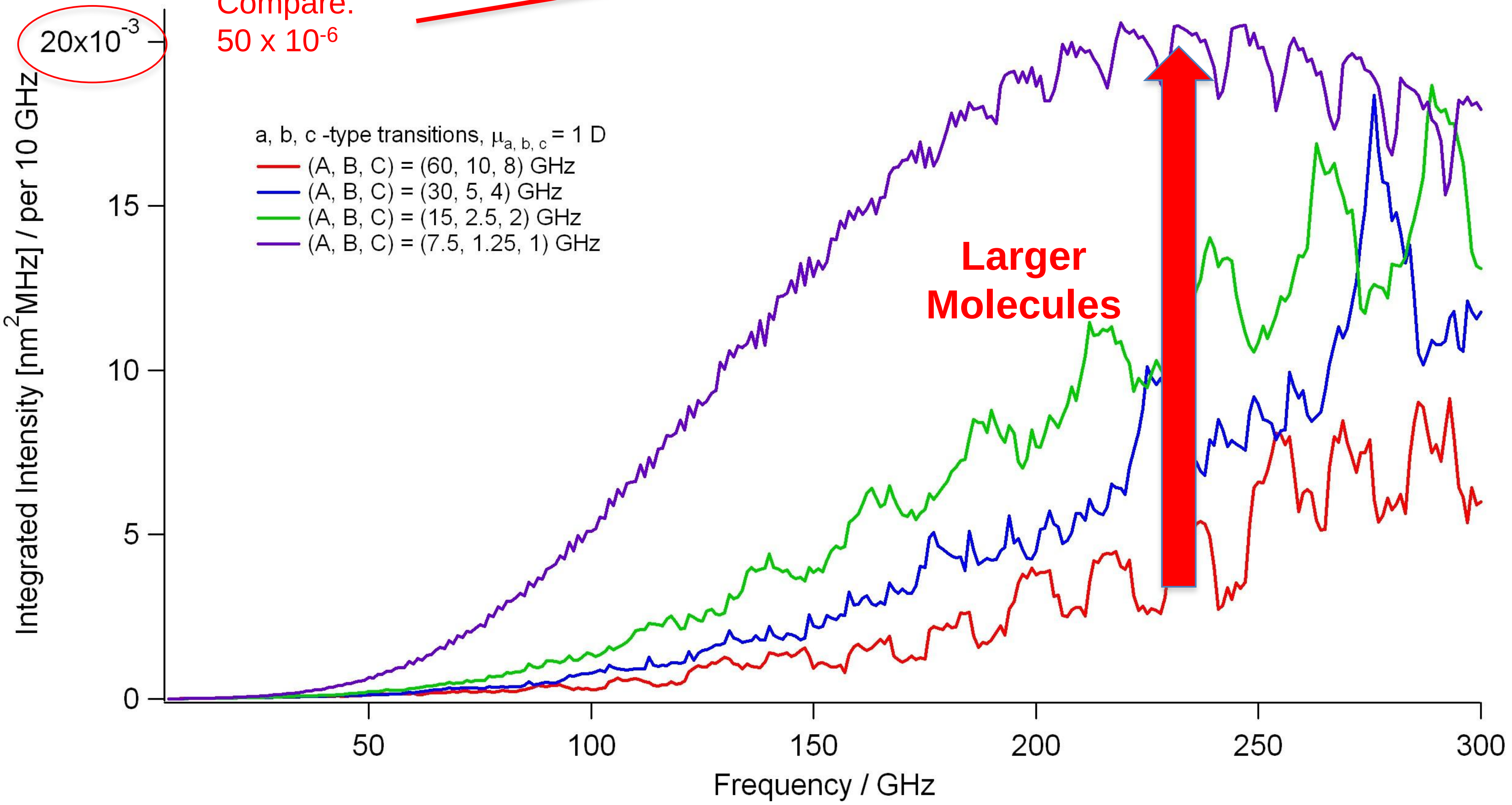


Detailed Line-by-line Calculation

Integrated absorption goes up as molecule gets larger



Compare:
50 x 10^{-6}



Larger Molecules

What Do We Conclude?

1. **Both the rotational and vibrational density of states and spectral congestion grow rapidly with molecular size. Low temperature is a significant advantage, but many astronomical sources are warm.**

2. **Spectra based on calculations can be significantly different from experiment both in density and in distribution of line strengths**

3. **In single line spectrometers, line strengths grow correspondingly weaker with larger molecules.**

4. **But In multiplex instruments integrated spectral intensity grows.**

5. **Collective analysis of spectra becomes more important.**

6. **This is much harder in astrophysics because of the inhomogenity of the sample, but the higher spatial resolution of systems like ALMA should help.**

Catalogs and Data

In the beginning **line frequencies were easier to model/predict than to measure**

Small, easy to model species - measure a few well selected transitions, predict the rest

As an important by-product, these models gave astronomers intensities

As an additional by-product, this led naturally to catalogues based on these models

Now **it is often easier to measure spectra than to predict them**

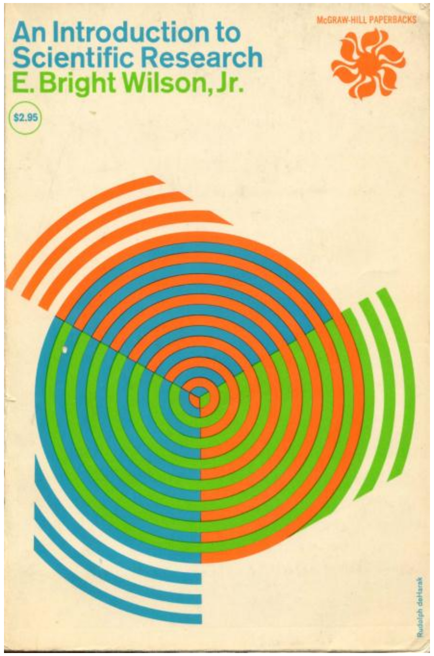
Orders of magnitude increase in the difficulty of modeling (large molecules/perturbations)

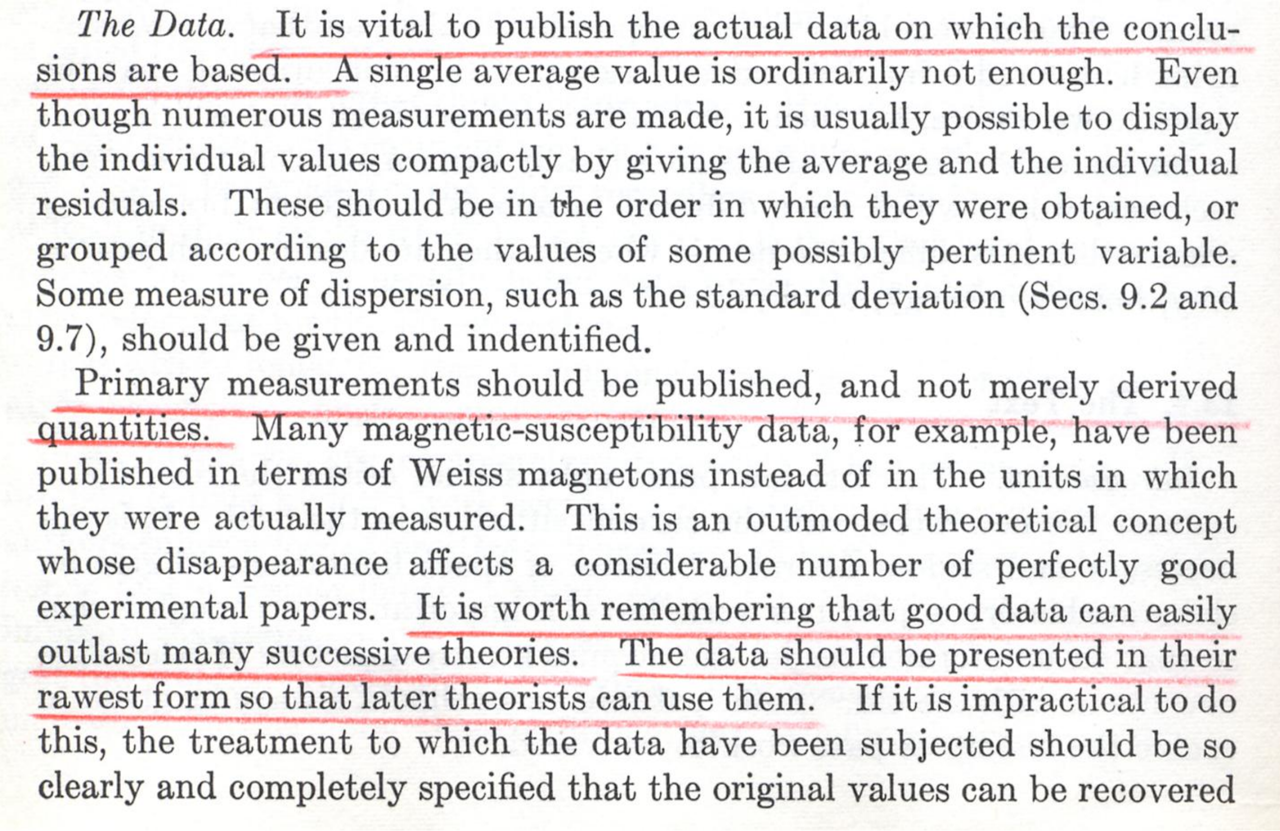
Robustness of experimental approaches

Catalogues have become very incomplete in unpredictable ways

But **even with experimentally measured spectral frequencies, we have to deal with the intensity/temperature problem**

Start by Quoting an Authority





The Data. It is vital to publish the actual data on which the conclusions are based. A single average value is ordinarily not enough. Even though numerous measurements are made, it is usually possible to display the individual values compactly by giving the average and the individual residuals. These should be in the order in which they were obtained, or grouped according to the values of some possibly pertinent variable. Some measure of dispersion, such as the standard deviation (Secs. 9.2 and 9.7), should be given and indentified.

Primary measurements should be published, and not merely derived quantities. Many magnetic-susceptibility data, for example, have been published in terms of Weiss magnetons instead of in the units in which they were actually measured. This is an outmoded theoretical concept whose disappearance affects a considerable number of perfectly good experimental papers. It is worth remembering that good data can easily outlast many successive theories. The data should be presented in their rawest form so that later theorists can use them. If it is impractical to do this, the treatment to which the data have been subjected should be so clearly and completely specified that the original values can be recovered

A bottom line: Data and analyses must be traceable via the refereed literature

An Extensible and Sustainable Approach

Spectroscopic analyses use good data from decades ago
Incremental extensions and improvements are the norm
This supports the attractiveness and power of calculated catalogues

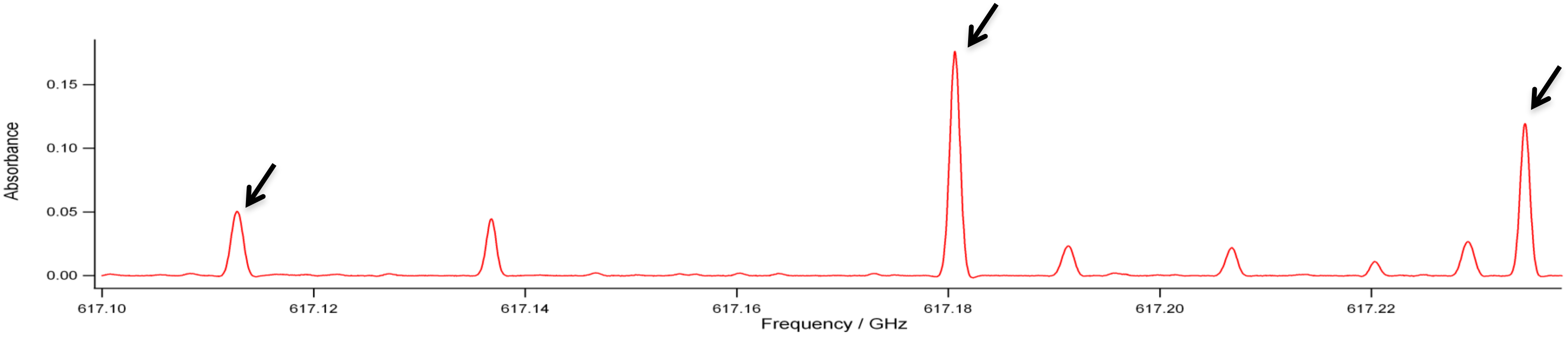
How can 3D spectroscopy be extensible, for:
- **A new temperature range?**
- **More sensitivity?**
- **More accuracy?**

For both, we have to have access to the data so that we can refit

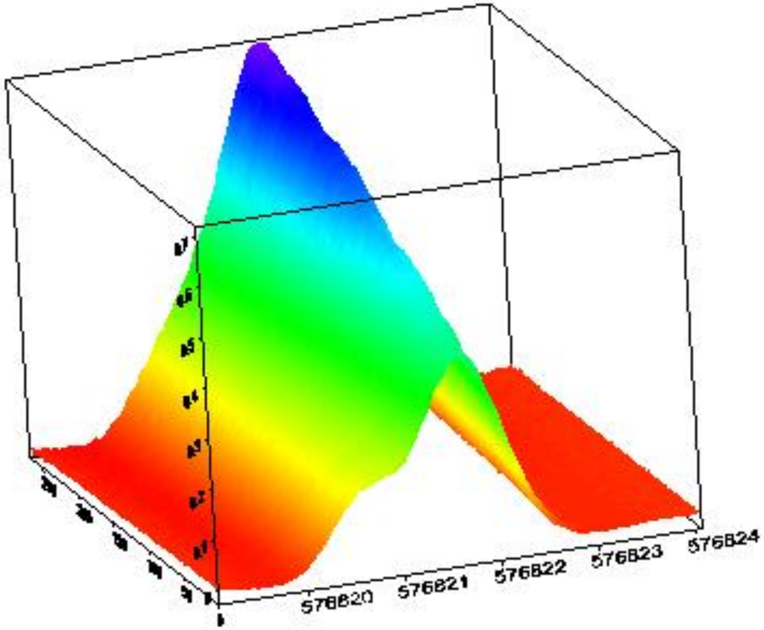
How much data is there?
How might it be archived?
Is there an intermediate level for the user?

Approach 1:
What Might a Hybrid Catalog Look Like?

Frequency (MHz)	Catalog Energy	Measured Energy (error)	Catalog Strength	Measured Strength (error)		J'	K-1"	K+1"	J'	K-1'	K+1'
617112.6524		990.39 (13)		1945.52 (123)							
617136.7024	1008.18	1033.32 (13)	883.961	2025.2 (129)		69	20	49	68	20	48
617136.7024	1008.18		883.961			69	20	50	68	20	49
617179.8714	743.418	744.749 (13)	104.694	2041.2 (129)		72	1	71	71	2	70
617180.4969	743.418		1004.2			72	2	71	71	2	70
617180.6625	743.418		1004.43			72	1	71	71	1	70
617181.288	743.418		104.693			72	2	71	71	1	70
617191.1912		1131.4 (13)		1738.31 (108)							
617206.6472		1157.92 (13)		1799.48 (113)							
617220.2302		1262.54 (13)		1526.24 (98)							
617228.9983		1114.93 (13)		1865.35 (118)							
617234.3798	811.78	800.536 (13)	935.908	1803.8 (115)		69	12	58	68	12	57
617234.4387	811.78		935.907			69	12	57	68	12	56



Approach 2:
A Normalized Complete Spectral Alternative



4 x 10^6 pts/100 GHz

for

Hundreds of temperatures?

A few polynomial parameters?

There are many blended lines that are revealed by the variable temperature spectra. For catalogue purposes, these can be fitted with simple polynomials.

WH04 Ivan Medvedev

Summary

The integrated development of science and technology in the submillimeter has aided the explosive growth of the field and influences how we do science.

Spectroscopic engineering is the interface with the applications community.

The structure of submillimeter spectroscopy is at the heart of this spectroscopic engineering.

- **How we run experiments and what we measure.**
- **How we handle our results and what kinds of information we provide.**
- **How we interface with other communities.**
- **How we transfer and archive our results.**

What happens to spectroscopic engineers is up to us - our behavior and ambition:

Sometimes we are useful servants, sometimes we become kings

Spectroscopic Engineers:

Kings or Useful Servants