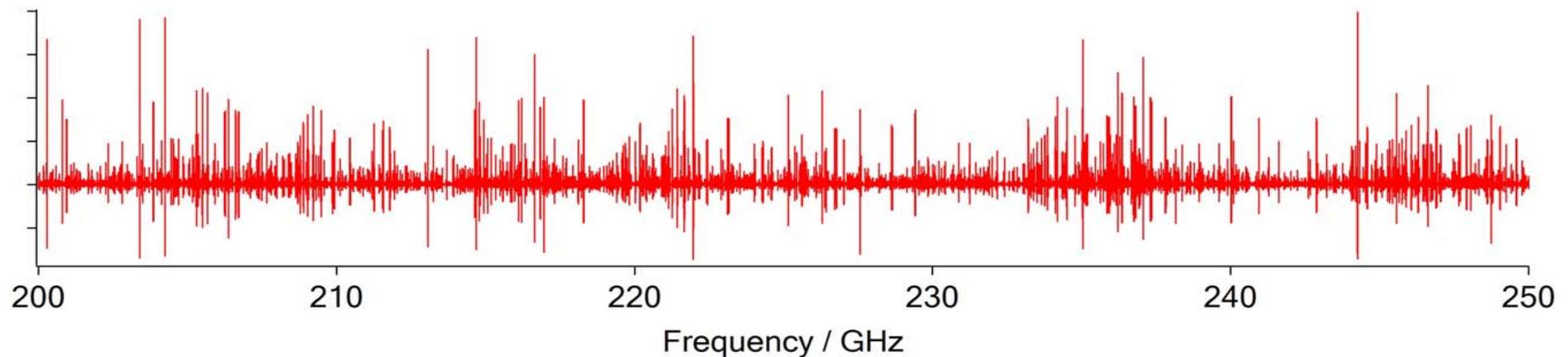




# Exterminating the Weeds in the Astronomical Garden

**Frank C. De Lucia  
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Department of Physics  
Ohio State University**



**Complex Molecules in Space: Present status and prospects with ALMA,  
Fuglsøcentret, Aarus, Denmark  
MAY 9,2006**

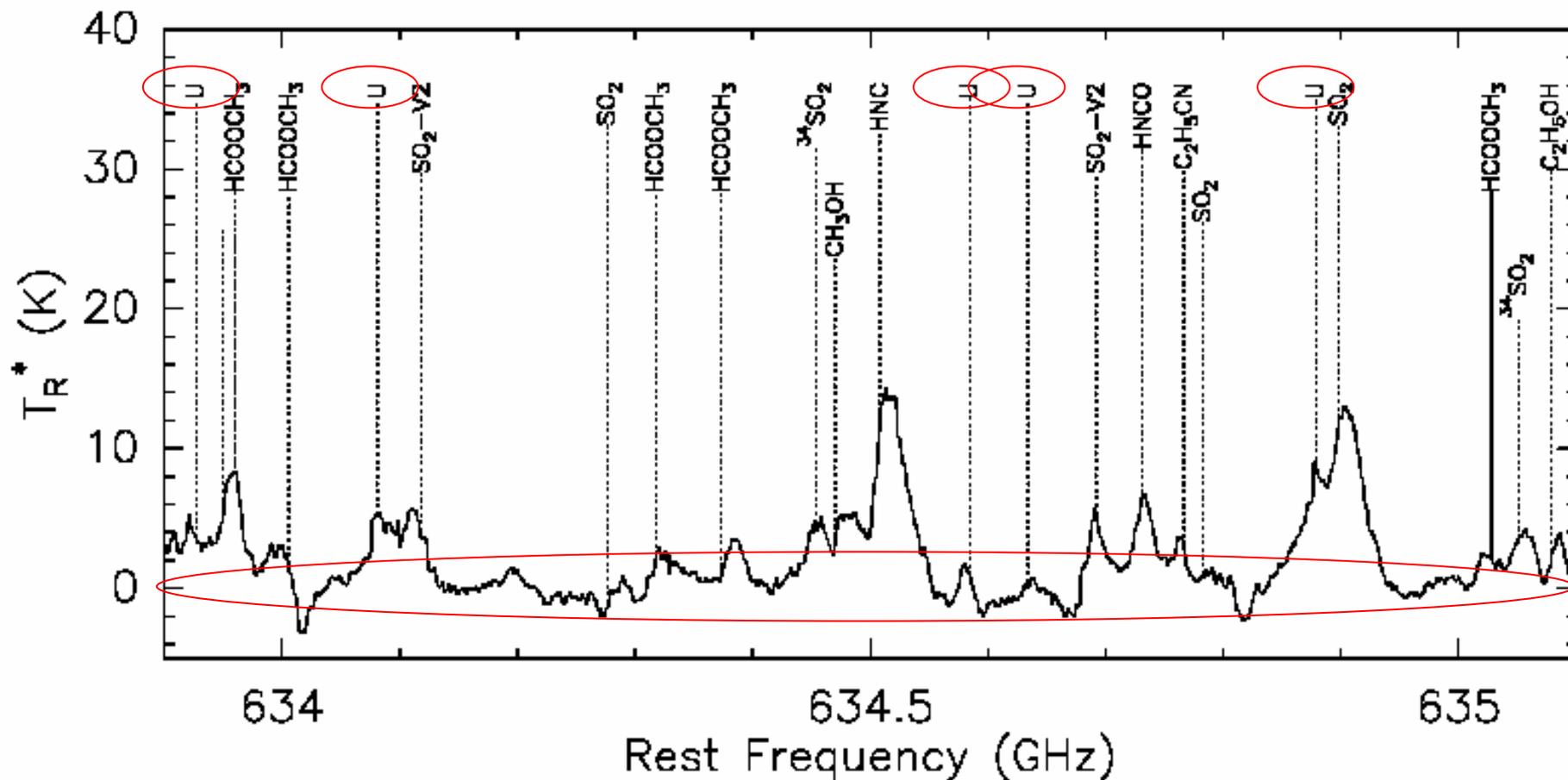


# Overview

- I. The Nature of the Problem and the Challenges along the path to its Solution**
- II. Laboratory Experimental Foundations and Developments**
- III. An Alternative Approach: Spectral Predictions without Assignment or Analysis**
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- V. A Path Forward**

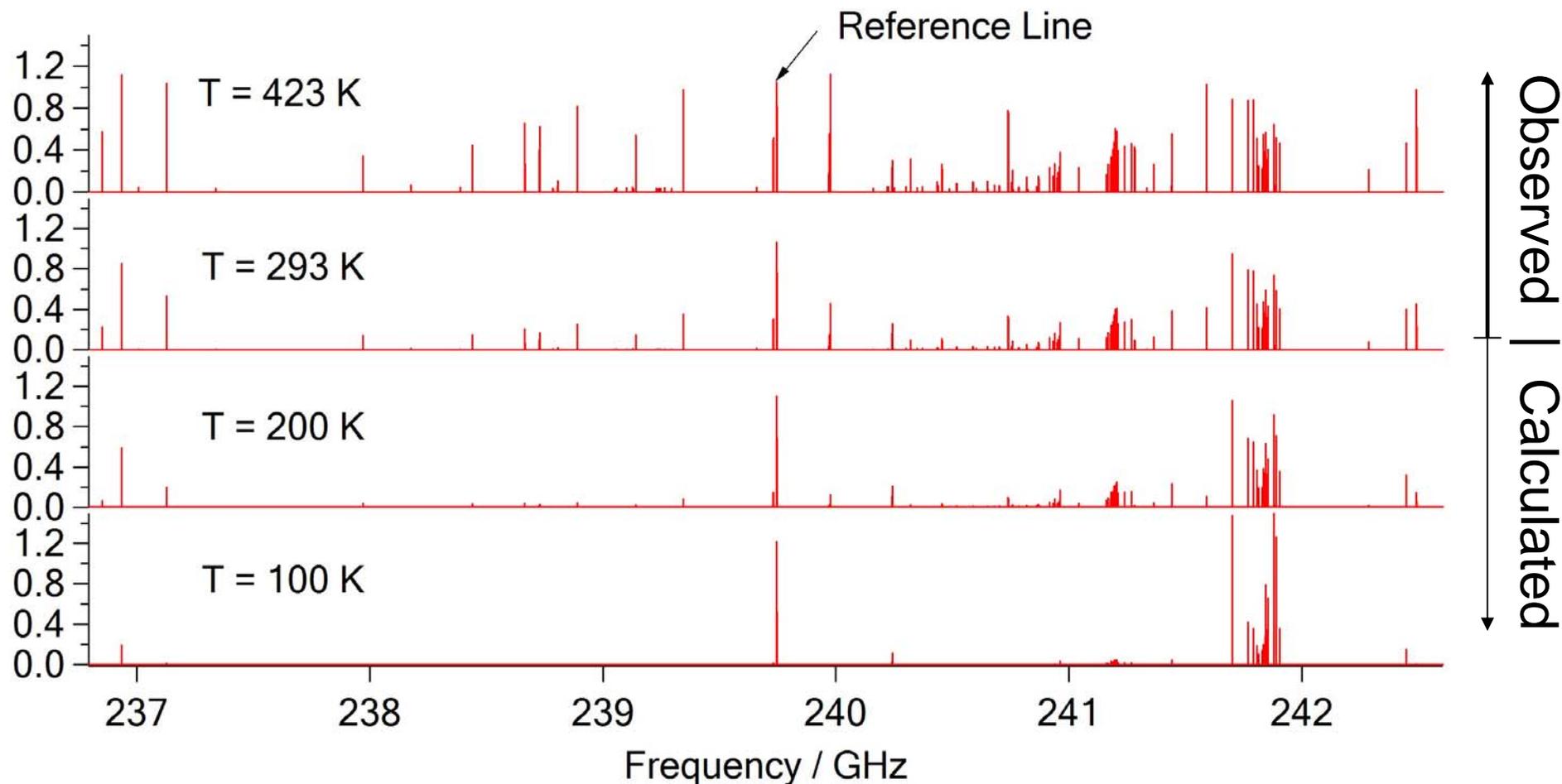
## A MOLECULAR LINE SURVEY OF ORION KL IN THE 350 MICRON BAND

*C. Comito, P. Schilke, T. G. Phillips, D. C. Lis, F. Motte, and D. Mehringer; Ap. J. S.S. 156, 127 (2005).*



1. Identify 'U' lines
2. Fit for individually identifiable 'U' lines
3. Will fits to 'complete' spectral libraries eliminate the background clutter?
4. Are there individually hidden, but collectively observable 'flowers' in the astronomical garden?

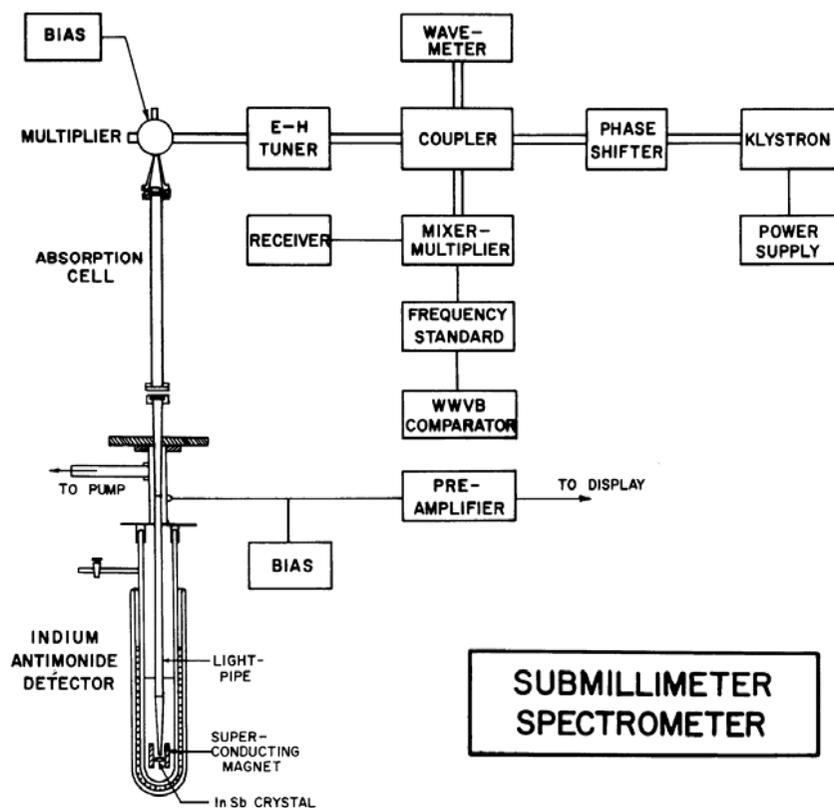
# The Effect of Temperature on the Spectrum of CH<sub>3</sub>OH



**Not just 'complete' in frequency, but also in intensity at all temperatures**

# Why Do we have the Weeds Problem?

## Narrow Band Spectrometer and Bootstrap Analysis



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



# Bootstrap Analysis of A and E Ground State Lines

THE MILLIMETER AND SUBMILLIMETER LABORATORY SPECTRUM OF METHYL FORMATE  
IN ITS GROUND SYMMETRIC TORSIONAL STATE<sup>1</sup>

**But this is only about 10% of lines**

AND

GEOFFREY A. BLAKE

Department of Chemistry, California Institute of Technology

*Received 1983 December 27; accepted 1984 February 17*

**But this is a spectroscopic opportunity**

THE LABORATORY MILLIMETER-WAVE SPECTRUM OF METHYL FORMATE  
IN ITS GROUND TORSIONAL *E* STATE

GRANT M. PLUMMER, ERIC HERBST, AND FRANK C. DE LUCIA

*Department of Physics, Duke University*

**2 Papers/0.1 of lines = 20 Future Publications**

Department of Chemistry, California Institute of Technology

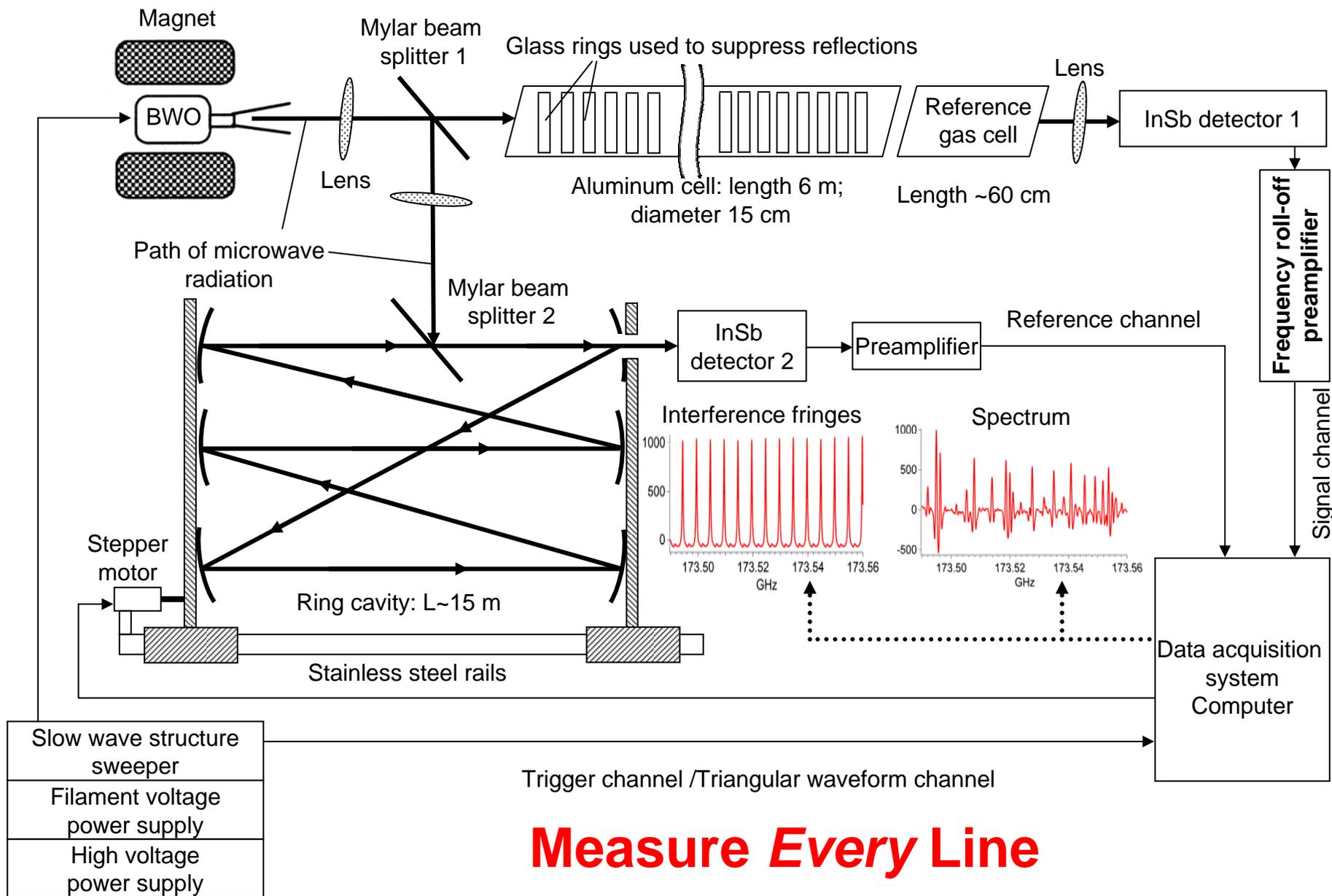
*Received 1985 September 25; accepted 1985 December 5*



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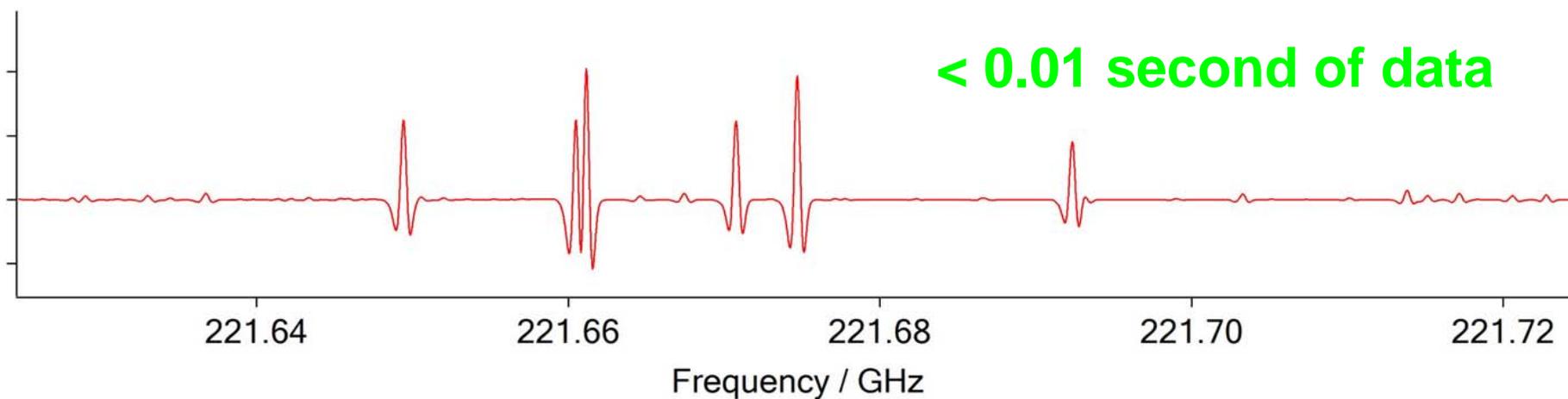
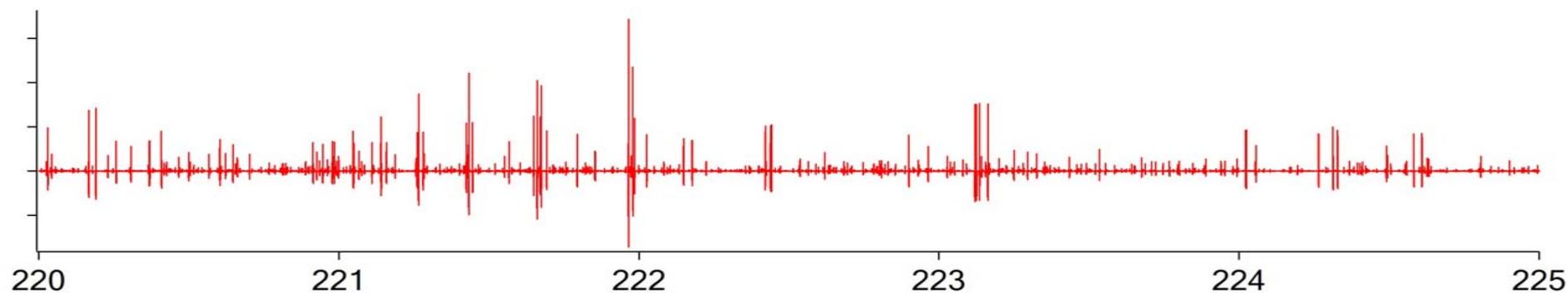
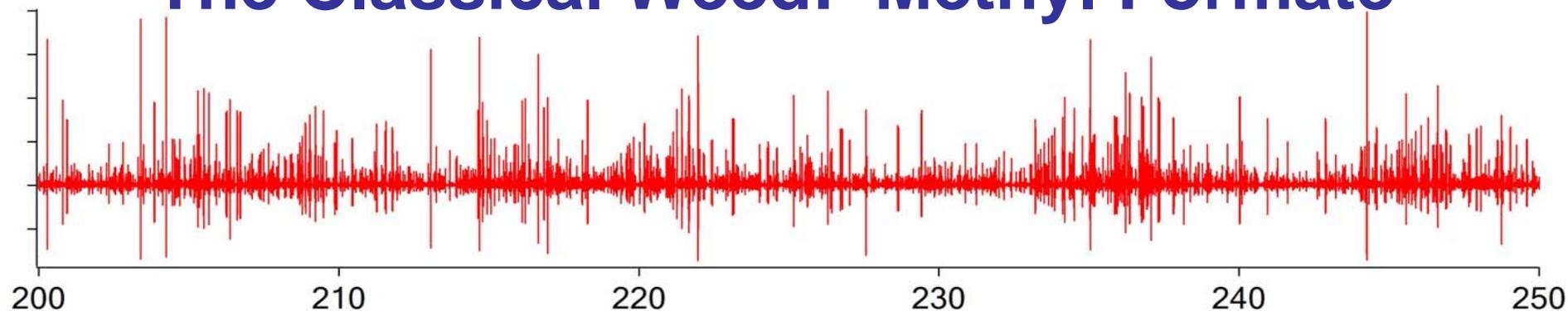
# FAST Scan Submillimeter Spectroscopic Technique (FASSST) spectrometer



**Measure Every Line**



# The Classical Weed: Methyl Formate





## FASSST Attributes

1. Can record 10000-100000 resolution elements/sec  
**Freezes Source Frequency Drift**
2. Can record entire spectrum in a few seconds  
**Freezes Chemistry Changes**
3. 'Locally' intensity measurement is flat to ~1%  
**A basis for intensity measurement**

**But to be astronomically 'complete,' we need intensities at other, typically lower temperatures**



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# Absorption Coefficients

## What You Need to Know to Simulate Spectra at an Arbitrary Temperature $T_3$ without Spectral Assignment

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

The total number density (chemistry and pressure issues).

But, for an unassigned line, one does not know

- The matrix element
- The lower state energy
- The partition function

# Consider two lines, one assigned and one unknown at two temperatures $T_1$ and $T_2$

$$\frac{\alpha_{l \rightarrow u}(T_1)}{\alpha_{l \rightarrow u}(T_2)} = \frac{n(T_1) / \sum_{n=0}^{\infty} g_n e^{-E_n/kT_1}}{n(T_2) / \sum_{n=0}^{\infty} g_n e^{-E_n/kT_2}} \frac{1 - e^{-h\nu/kT_1}}{1 - e^{-h\nu/kT_2}} e^{-E_l/k(1/T_1 - 1/T_2)}$$

Eqn. 1

*Step 1:* With Eqn. 1 for both the known and unknown line, we have two equations and two unknowns:

1. The number density and partition function ratio for the  $T_1$  and  $T_2$  lab measurements
2. The lower state energy of the unassigned line

*Step 2:* Solve for the lower state energy of unassigned line

$$E_{l,usgn} = -\frac{k}{(1/T_1 - 1/T_2)} \ln \left( \frac{1}{C} \frac{\alpha_{l \rightarrow u,n}(T_1)}{\alpha_{l \rightarrow u,n}(T_2)} \right) = E_{l,asgn} - \frac{k}{(1/T_1 - 1/T_2)} \ln \left( \frac{\frac{\alpha_{l \rightarrow u,usgn}(T_1)}{\alpha_{l \rightarrow u,usgn}(T_2)}}{\frac{\alpha_{l \rightarrow u,asgn}(T_1)}{\alpha_{l \rightarrow u,asgn}(T_2)}} \right)$$

Eqn. 2

*Step 3:* Form a ratio between the observed intensities of an assigned and unassigned line at  $T_1$

$$\frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_1)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_1)} = \frac{\nu_{u \text{ sgn}} (1 - e^{-h\nu_{u \text{ sgn}} / kT_1})}{\nu_{a \text{ sgn}} (1 - e^{-h\nu_{a \text{ sgn}} / kT_1})} \frac{|\mu_{u \text{ sgn}, l \rightarrow u}|^2 g_{l, u \text{ sgn}}}{|\mu_{a \text{ sgn}, l \rightarrow u}|^2 g_{l, a \text{ sgn}}} e^{-(E_{l, u \text{ sgn}} - E_{l, a \text{ sgn}}) / kT_1} \quad \text{Eqn. 3}$$

*Step 4:* Combining with the lower state energy for the unassigned line from the previous Eqn. 2, provides the matrix element of the unassigned line

*Step 5:* To predict ratios at  $T_3$  of the known (assigned) reference line and unassigned line in the molecular cloud

$$\frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_3)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_3)} = \frac{\nu_{u \text{ sgn}} (1 - e^{-h\nu_{u \text{ sgn}} / kT_3})}{\nu_{a \text{ sgn}} (1 - e^{-h\nu_{a \text{ sgn}} / kT_3})} \frac{|\mu_{u \text{ sgn}, l \rightarrow u}|^2 g_{l, u \text{ sgn}}}{|\mu_{a \text{ sgn}, l \rightarrow u}|^2 g_{l, a \text{ sgn}}} e^{-(E_{l, u \text{ sgn}} - E_{l, a \text{ sgn}}) / kT_3} \quad \text{Eqn. 4}$$

# The Combined Equation

$$\frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_3)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_3)} = \frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_1)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_1)} \left( \frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_2)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_1)} \right)^{\frac{1/T_3 - 1/T_1}{1/T_1 - 1/T_2}}$$

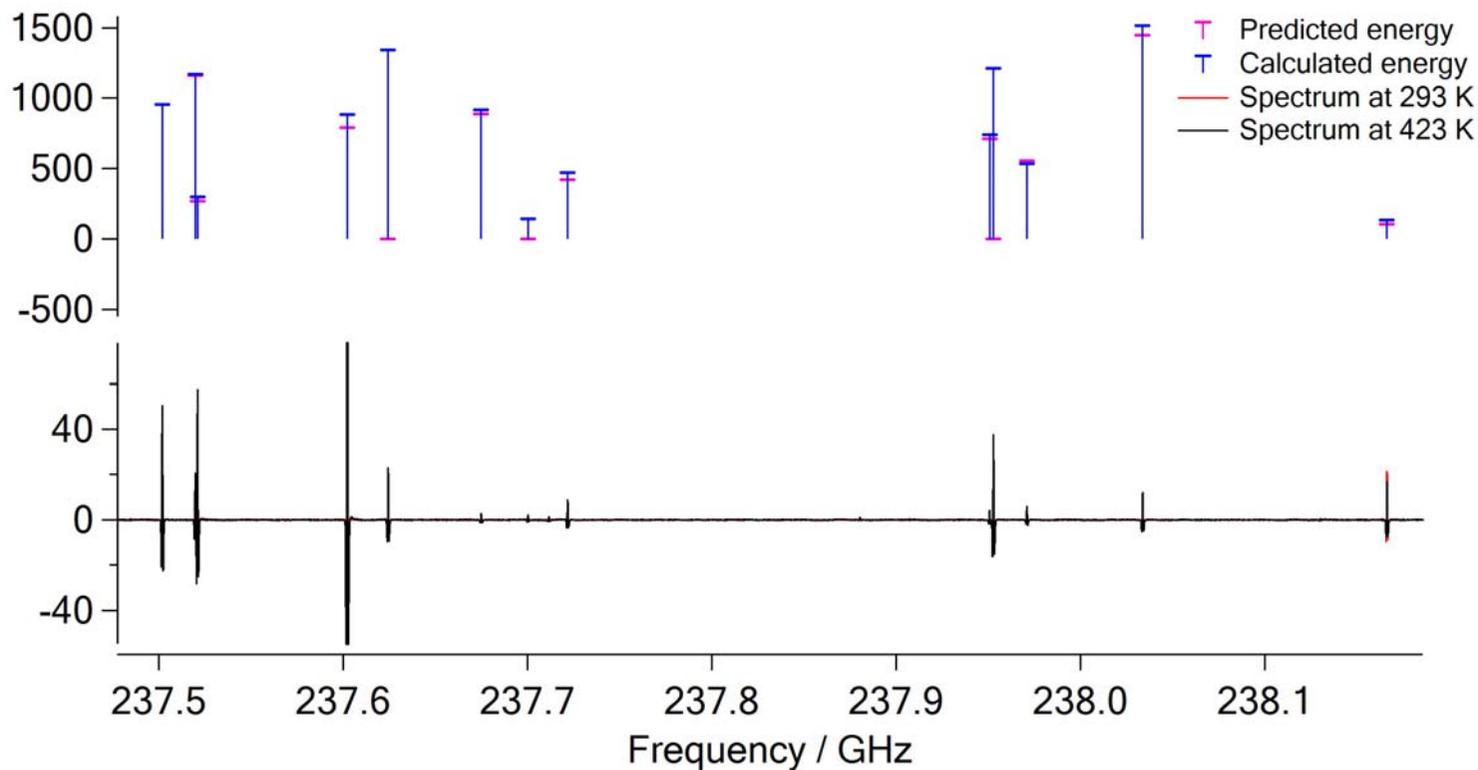


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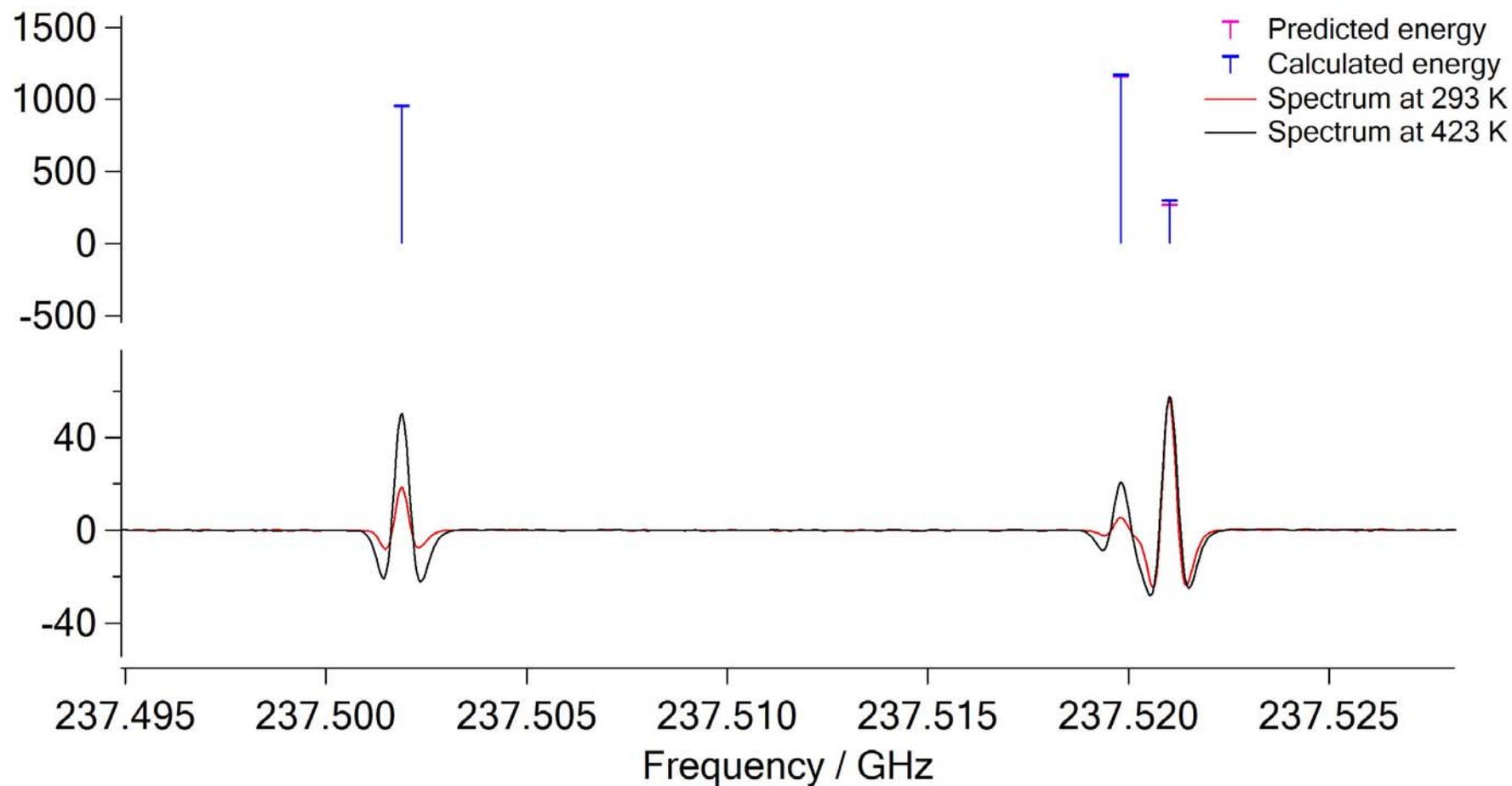
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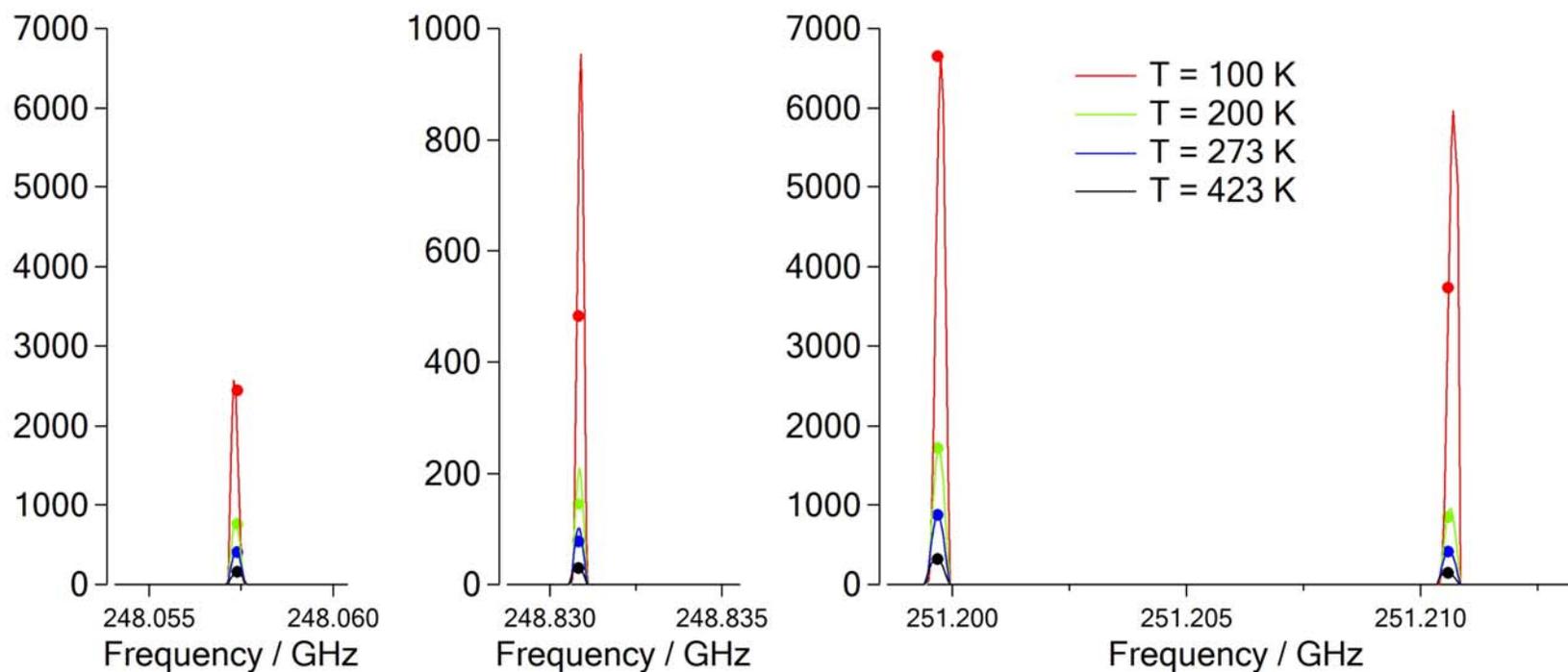
# Comparison of Energy Levels Calculated from Experimental and Quantum Calculations for SO<sub>2</sub>



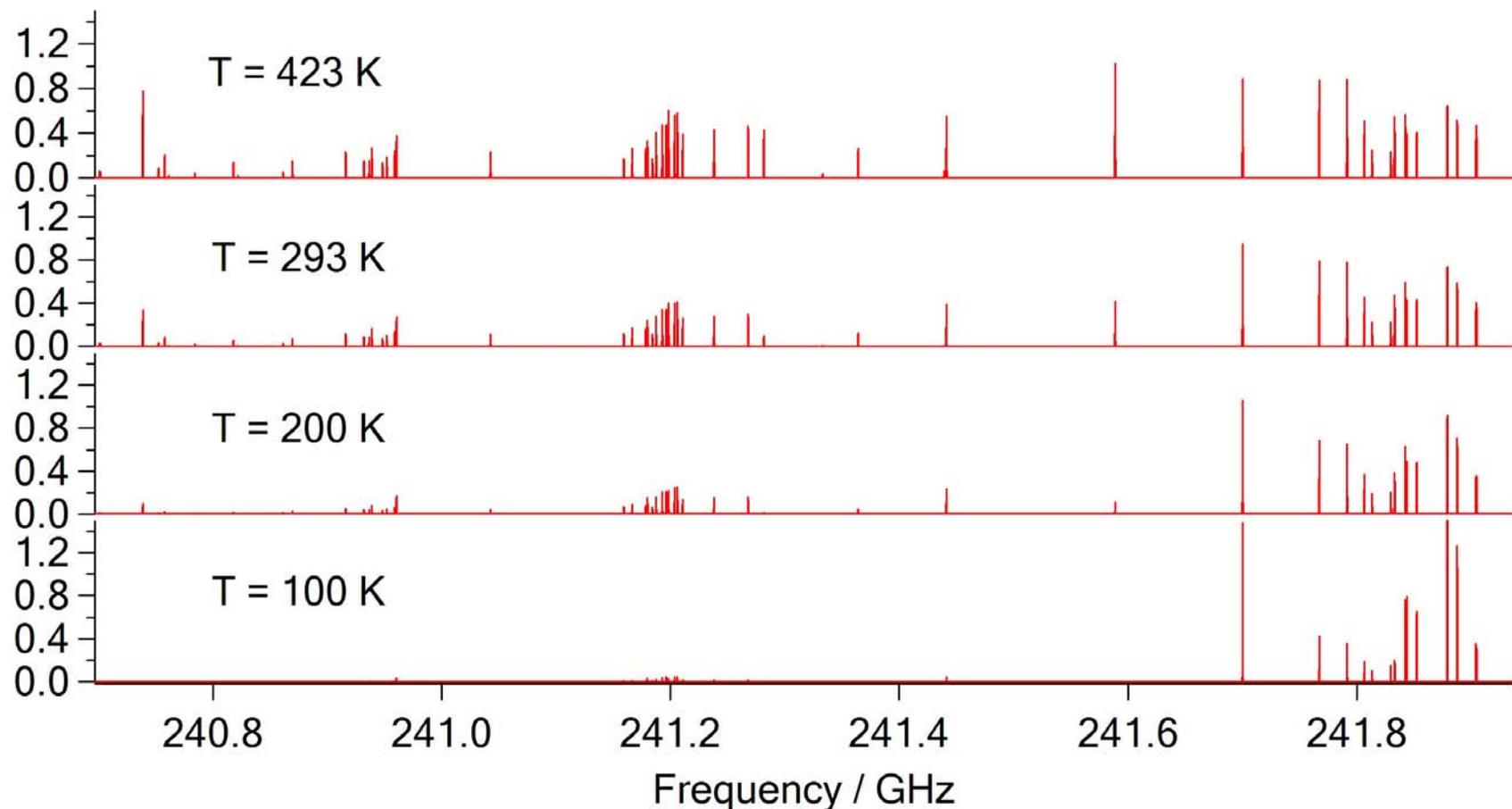
# Comparison of Energy Levels Calculated from Experimental and Quantum Calculations for $\text{SO}_2$



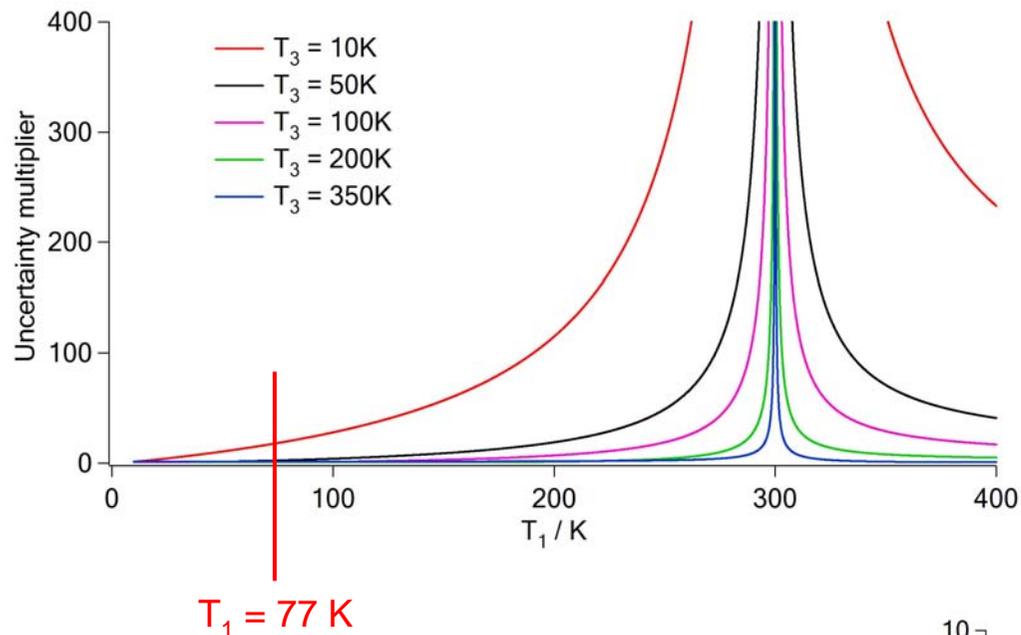
# Comparison of Intensities Calculated from Experimental and Quantum Calculations for $\text{SO}_2$



# Spectra Calculated at 100 K and 200 K from Measurements at 423 K and 293 K

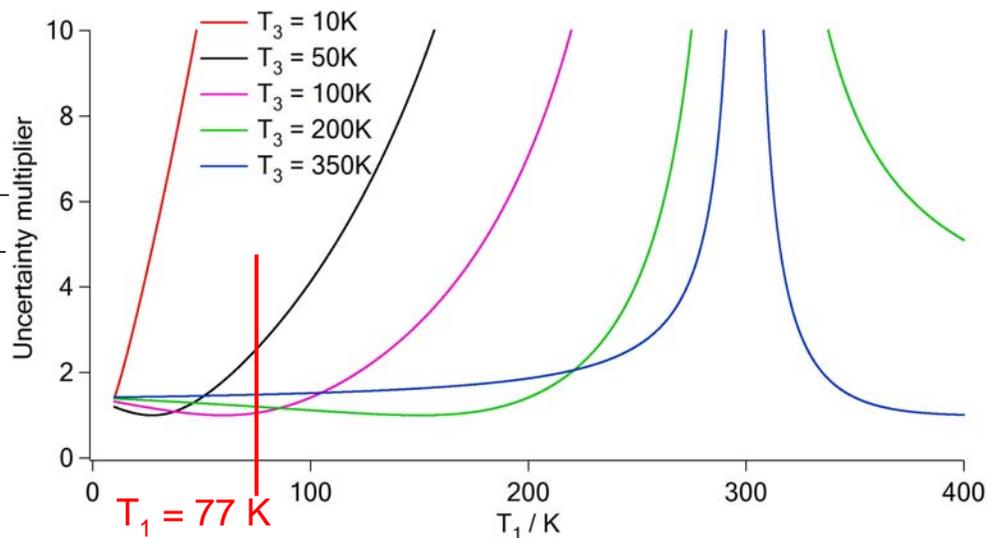


# Propagation of Uncertainty ( $T_2 = 300$ K)



$$\frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_3)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_3)} = \frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_1)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_1)} \left( \frac{\alpha_{l \rightarrow u, u \text{ sgn}}(T_2)}{\alpha_{l \rightarrow u, u \text{ sgn}}(T_1)} \right)^{\frac{1/T_3 - 1/T_1}{1/T_1 - 1/T_2}} \left( \frac{\alpha_{l \rightarrow u, a \text{ sgn}}(T_2)}{\alpha_{l \rightarrow u, a \text{ sgn}}(T_1)} \right)^{\frac{1/T_3 - 1/T_1}{1/T_1 - 1/T_2}}$$

$$\frac{\delta \left( \frac{\alpha_{l \rightarrow u, 2}(T_3)}{\alpha_{l \rightarrow u, 1}(T_3)} \right)}{\left( \frac{\alpha_{l \rightarrow u, 2}(T_3)}{\alpha_{l \rightarrow u, 1}(T_3)} \right)} = \frac{\delta \alpha_{l \rightarrow u}}{\alpha_{l \rightarrow u}} \sqrt{2} \sqrt{\frac{(1/T_3 - 1/T_2)^2 + (1/T_3 - 1/T_1)^2}{(1/T_1 - 1/T_2)^2}}$$

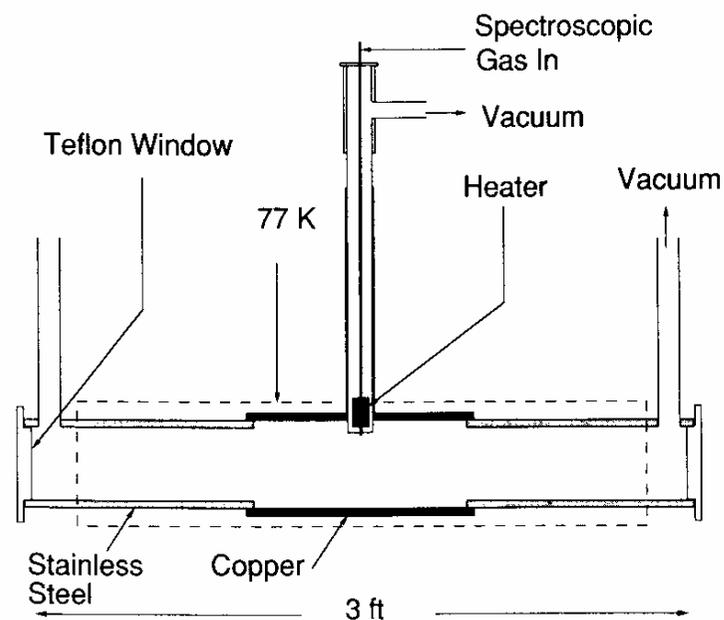
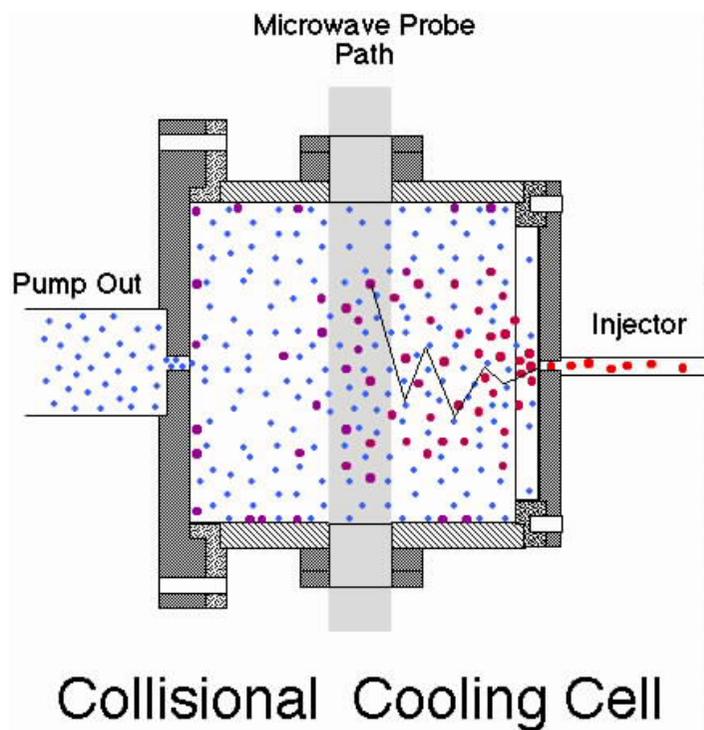




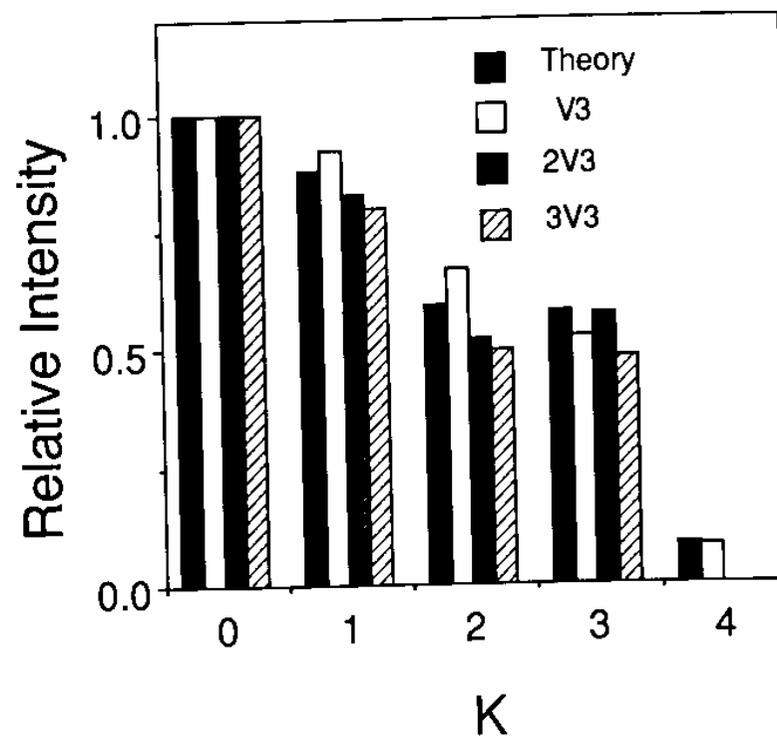
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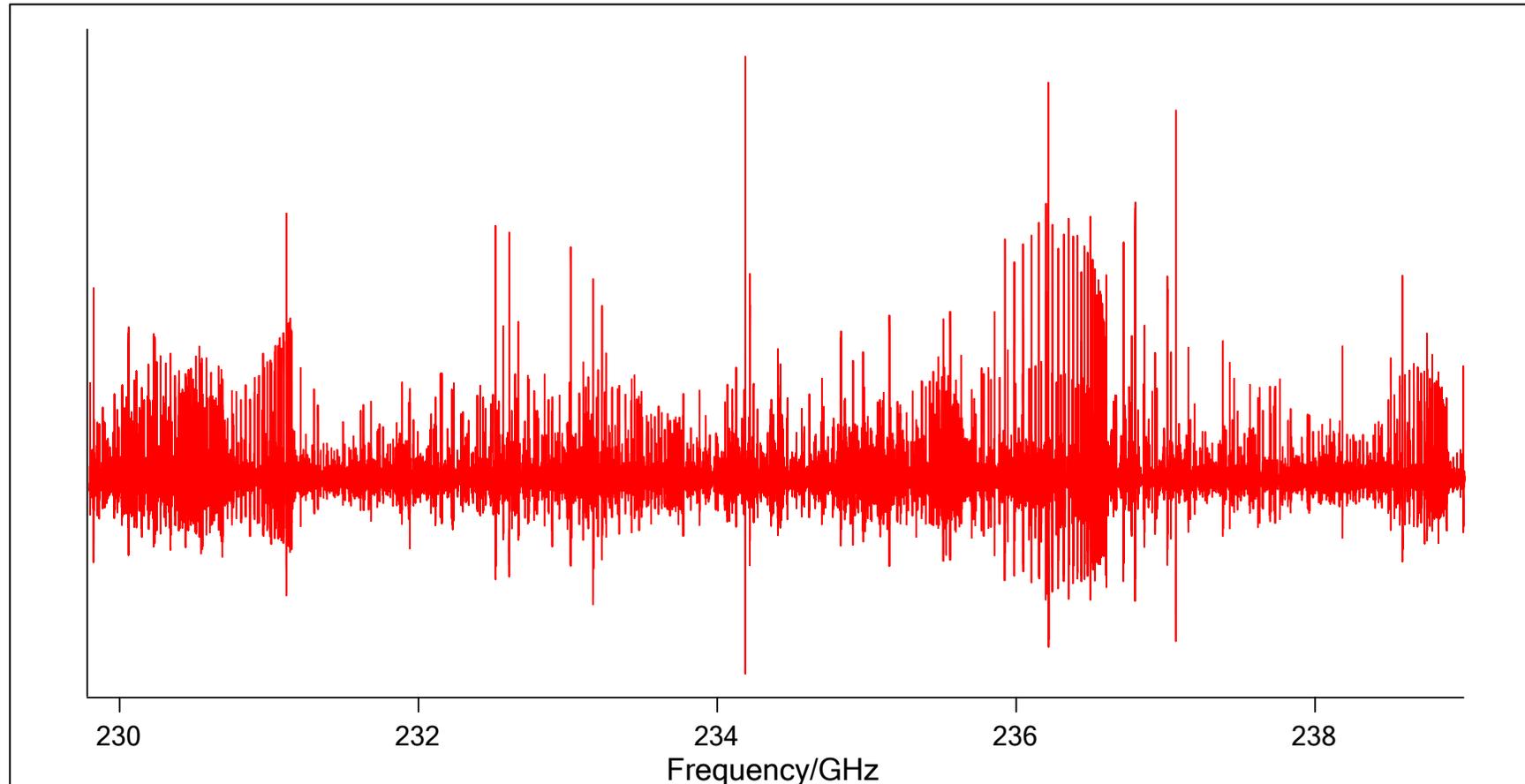
# Collisional Cooling for low $T_2$



# CH<sub>3</sub>F 77 K Rotational Temperatures in a Collisional Cooling Cell as a function of K-state: Experiment vs. Theory



# A Denser Spectrum: Diethyl Ether



**Ramp temperature** too, then direct *fits* to the  $\sim 10^6$  data points of each recorded spectra provide a **3-D spectrum**



# Considerations

**Operationally:** Rather than single reference, **fit for all assigned lines.**

For laboratory resolved spectra, results can be **tabularized** in exactly same form as the results from quantum mechanical models.

Method **provides accurate frequency measurements** for all lines, there is no model extrapolation uncertainty.

But, one **loses the redundancy of the intensities** calculated with quantum mechanical models.

Need **redundancy of multiple temperatures** and perhaps of multiple spectrometers.

# Summary and Conclusions

From experimental measurements at two temperatures  $T_1$  and  $T_2$ , it is possible to calculate spectrum (**with intensities**) at an arbitrary  $T_3$ .

For low  $T_3$ , a relatively **low  $T_2$  improves the accuracy** of the calculated spectrum.

**Collisional cooling provides a general method for achieving this low  $T_2$** , with 77 K convenient and suitable for all but the lowest temperatures.

**FASSST** is a means of obtaining the needed data **rapidly** and with **chemical concentrations constant** over the data collection period.

It is realistic in a finite time to produce **catalogs complete enough** to account even for the quasi-continua that sets **the confusion limit**.

In the **limit of 'complete' spectroscopic** knowledge, the confusion limit will probably be set by the unknowns associated with the complexity of the astrophysical conditions, but the high spatial resolution of ALMA should reduce this complexity.

- You've carefully thought out all the angles.
- You've done it a thousand times.
- It comes naturally to you.
- You know what you're doing, its what you've been trained to do your whole life.
- Nothing could possibly go wrong, right ?

Think Again.

