

MM/SubMM Spectroscopy: Experiments, Quantum Mechanics, Simulations, and Astronomical Comparisons

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Catalogs serve as the interface between the laboratory and observational astronomy communities. Often the catalogs are based on quantum mechanical models that simulate the mm/submm spectral lines from a much smaller set of laboratory observations. To support the rapidly growing capabilities of telescopes, the spectroscopic models have become ever more complex. At the same time the astronomical requirements have become ever more stringent. In addition to the well know issue of completeness, laboratory studies raise additional questions about the accuracies of frequencies and intensities calculated by quantum mechanical techniques. Comparisons among recent ALMA results, quantum mechanical models, and experimental observations will be presented.

**Far Infrared Workshop
October 30 2012
Atlanta, GA**

Overview

Characterization of astrophysical spectra:

How we got here

Cataloging and archiving strategies

Recent Astrophysical Results:

Simulation of ALMA Science Verification Data

Intensity Calibrated Spectroscopy

Where is spectroscopic confusion limit?

In the laboratory?

In astronomy?

Methanol: QM vs Experimental Intensities

What matters from an astronomy point of view?

Does 'curiosity driven' spectroscopy matter?

Spectroscopy in the Millimeter/Submillimeter:

How we got here

Technology was originally very narrow band and most of spectrum was white space

=> Bootstrap: QM predict, find, assign, better QM predict, . . .

=> Rotationally 'complete' (with bounds) spectrum based on measurement of relatively small subset of lines

Experimental intensities were approximate

=> Rely on QM analysis of frequencies to predict intensities

Now it is possible to obtain complete, intensity calibrated spectra (Complete Experimental Spectra – CES) in a short period of time (limit is gas handling)

CES Analysis Scheme (No QM Assignment)

[Experimental spectra at many temperatures]

General Expression for Peak Line Strength

$$A_{\text{peak}} = L\alpha_{\text{peak}}(T) = \frac{nL}{Q} \frac{8\pi^3}{3ch} (1 - e^{-h\nu_0/kT}) S_{ij} \mu^2 e^{-E_L/kT} \sqrt{\frac{\ln(2)}{\pi}} \frac{\nu_0}{\delta\nu_D}$$

Recast as Doppler Broadened Lineshape

$$\frac{A(\nu)}{nL/Q} = \frac{8\pi^3}{3ch} \sqrt{\frac{\ln(2)}{\pi}} \frac{1}{W} \frac{\left(1 - e^{-\frac{h\nu_0}{kT}}\right)}{\sqrt{T}} S_{ij} \mu^2 e^{\frac{E_L}{kT}} e^{-\frac{\ln(2)}{W^2 T} \left(1 - \frac{\nu}{\nu_0}\right)^2} = K \frac{\left(1 - e^{-\frac{h\nu_0}{kT}}\right)}{\sqrt{T}} \tilde{S}_{ij} \mu^2 e^{-\frac{\tilde{E}(\nu)}{kT}}$$

With

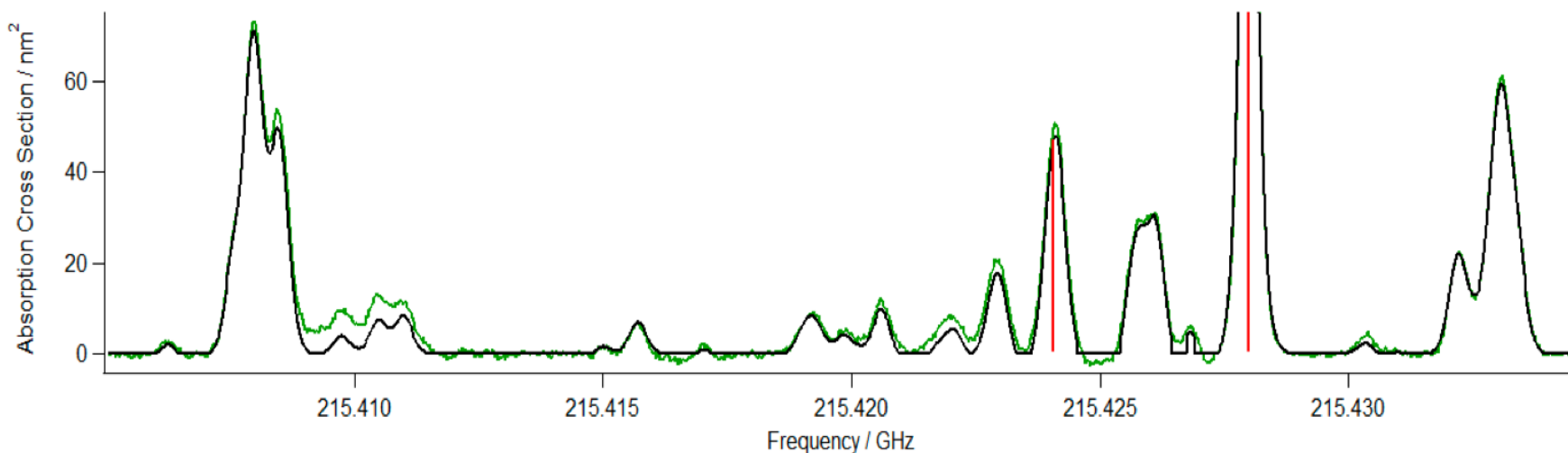
$$\delta\nu_D = \sqrt{\frac{2N_a k \ln(2)}{Mc^2}} \sqrt{T} \nu_0 = W \sqrt{T} \nu_0 \quad \tilde{E}(\nu) = E_L + k \frac{\ln(2)}{W^2} \left(1 - \frac{\nu}{\nu_0}\right)^2$$

Fit ~ 100 known QM assigned lines at ~1000 temperatures to get nL/Q and T

With known nL/Q and T , fit each of ~ 2×10^6 spectral points at ~1000 temperatures to get \tilde{E} and \tilde{S}_{ij} for each point

Invert to simulated spectrum at arbitrary temperature and column density

Simulation from Point-by-Point Analyses



Red Sticks: QM Catalog Spectra

Green: Small segment of one of ~ 15 second ~ 1000 spectral scans

Black: Point-by-point (each 0.025 MHz) simulation from analysis of spectral scans at ~ 1000 temperatures

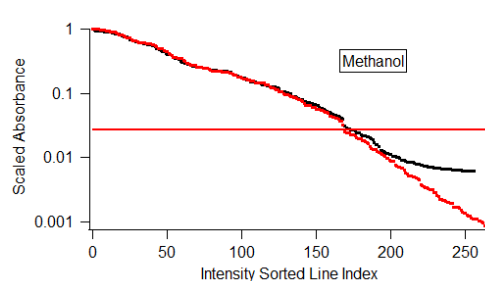
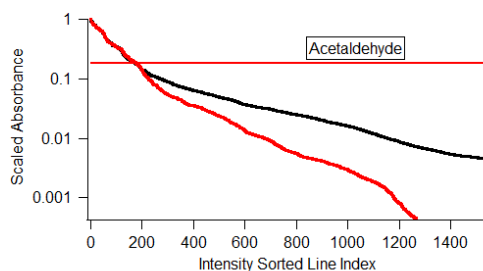
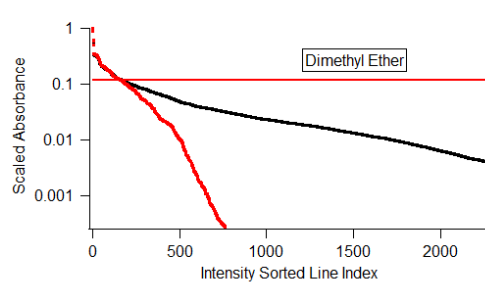
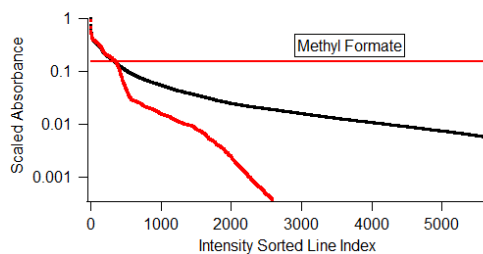
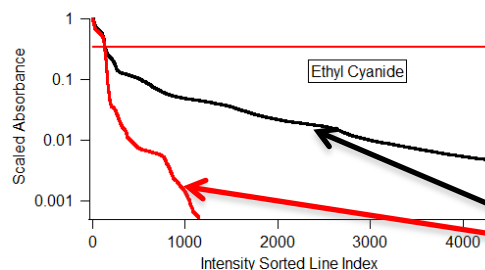
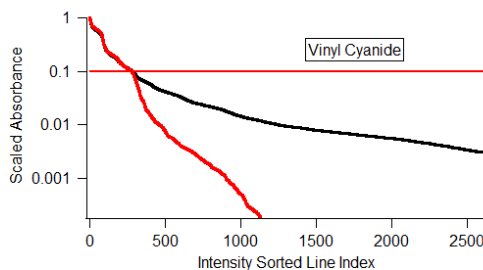
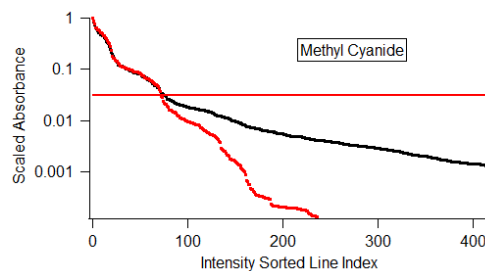
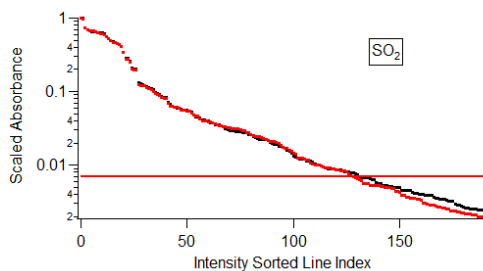
Accurately characterizes regions of complex blends

Greatly increased sensitivity due to average over ~1000 spectra

Significantly improved baseline due to average over ~1000 standing wave patterns

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)

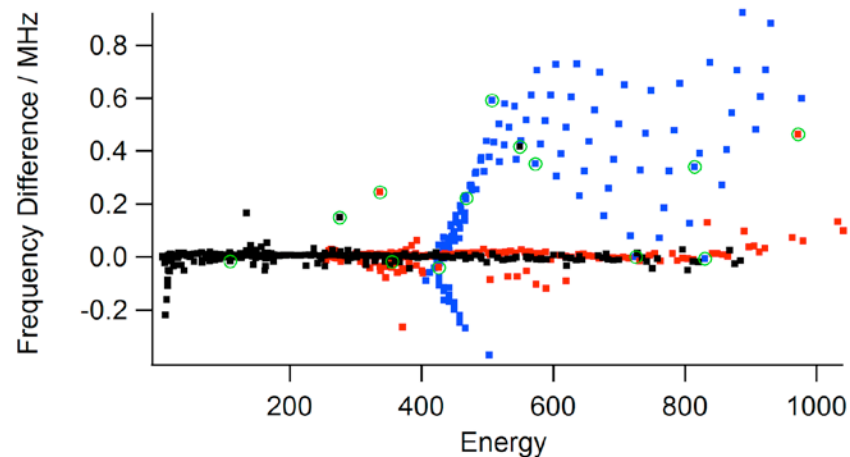
Many weak lines in catalogs
Many strong lines are not

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

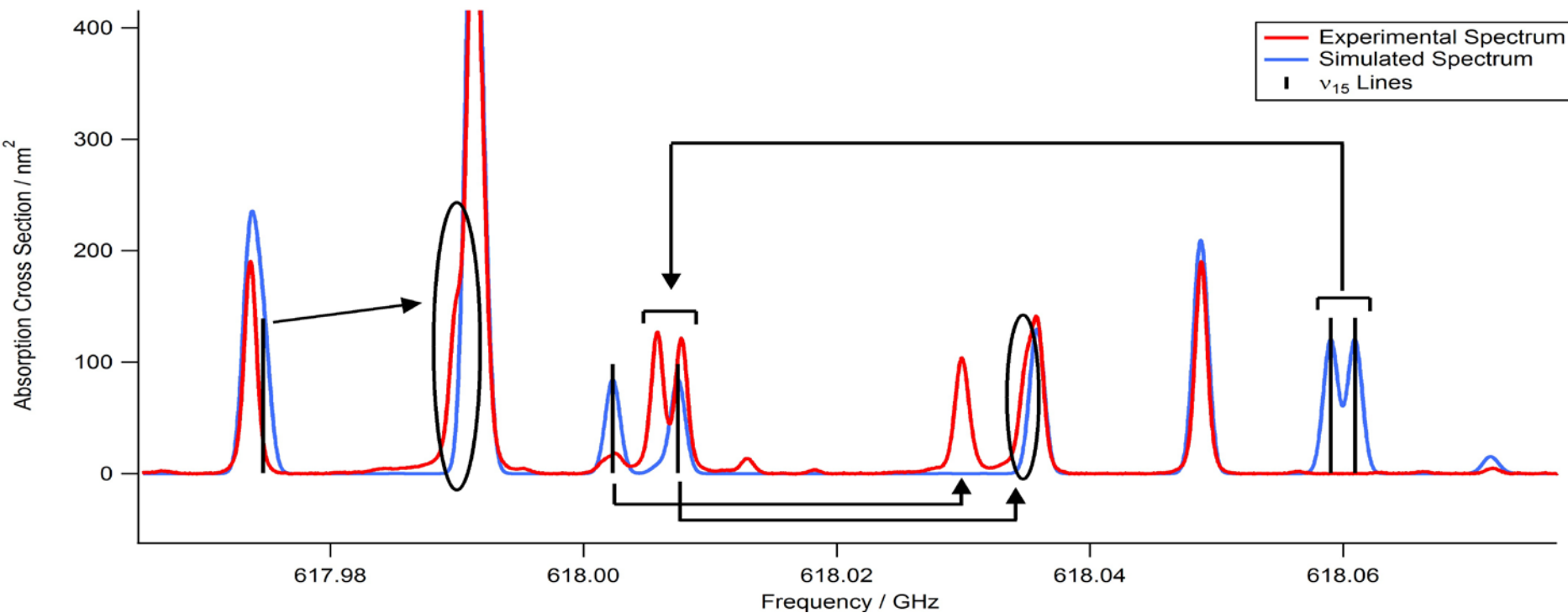
If one wants to rigorously consider intensities, one must have complete spectra.

Astrophysical spectra are incomplete even at relatively high spectral levels.

Frequency Shifts in Calculated Spectrum of Vinyl Cyanide



Plot of 210 – 270 GHz differences



618 GHz Experimental vs QM Simulation

Cataloging: Quote 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 identified.

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

Bottom lines:

Data and analyses should be traceable via the refereed literature

How do you achieve this for intensity calibrated spectra?

5% goal became 1%, scrub deeper for impurities, . . .

Deposit all 1000 scans of raw data in archival journals, can then add more T, etc.

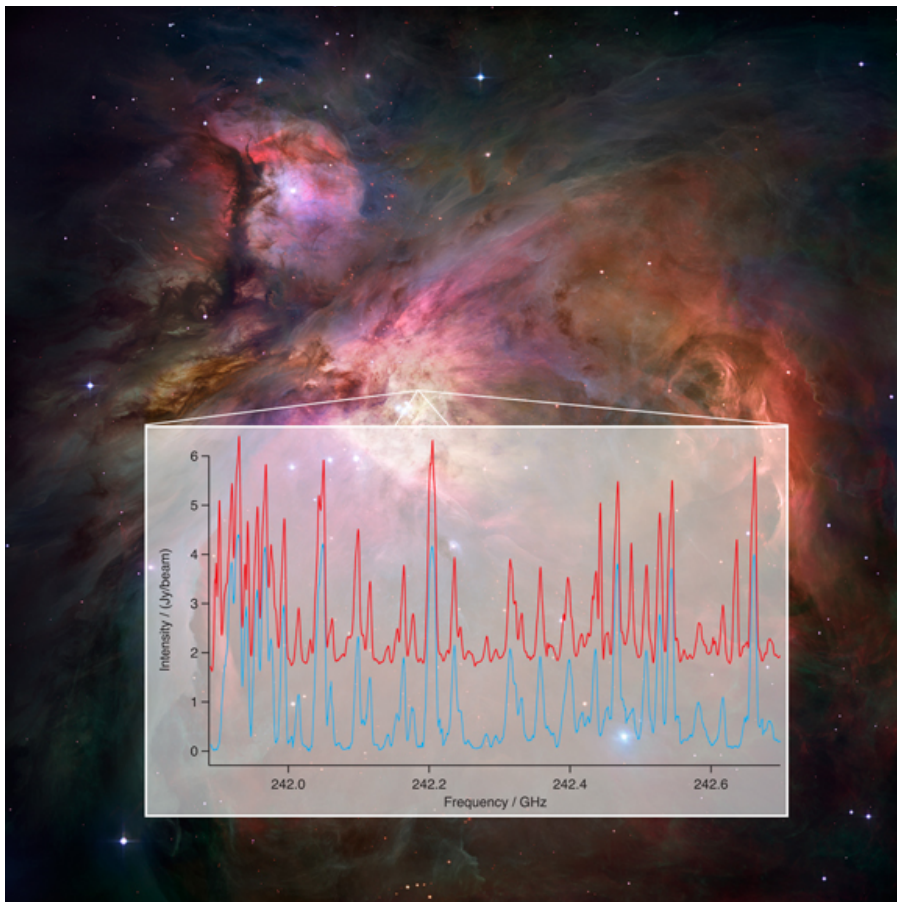
We have no proprietary data, but are perhaps being too persnickety before putting it into the archival literature

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 $\sim 10^{-3}$ – 10^{-4} of strongest line for species
Quantum Numbers	known	unknown

Measured line frequencies are easy to archive; QM analyses are extensible.

Results Based on ALMA Science Verification Data*



This is beautiful from an astronomical and spectroscopic point of view, but the questions I want to ask include:

“What matters from an astronomy point of view?”

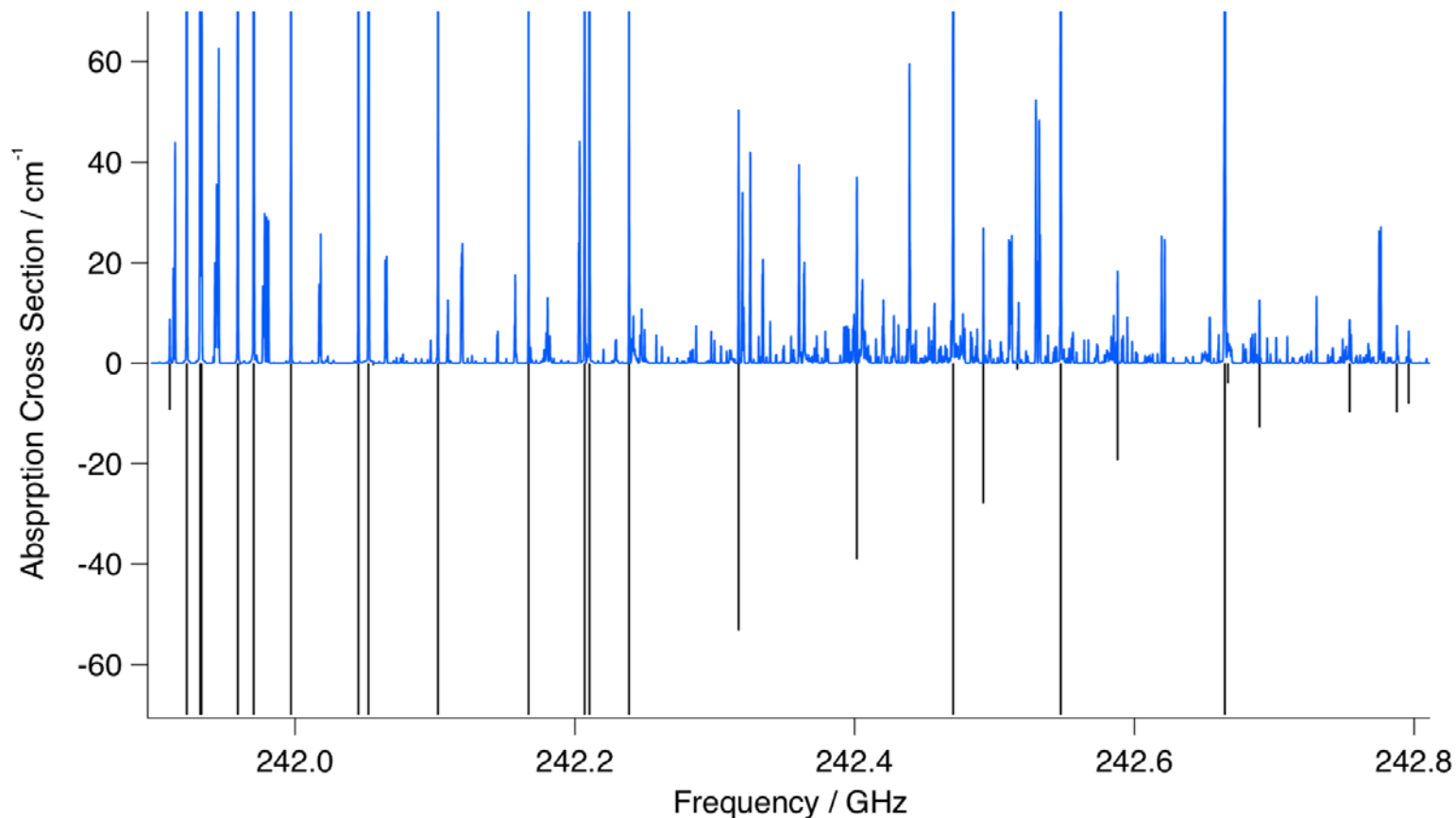
“What matters from a spectroscopy point of view?”

“Is there a place for ‘curiosity driven’ spectroscopic investigations in the context of astronomy?”

*Sarah M. Fortman, James P. McMillan, Christopher F. Neese, Suzanna K. Randall, Anthony J. Remijan, T.L. Wilson, Frank C. De Lucia, “An analysis of a preliminary ALMA Orion KL spectrum via the use of complete experimental spectra from the laboratory,” J. Mol. Spectrosc., In Press, Available online 14 August 2012

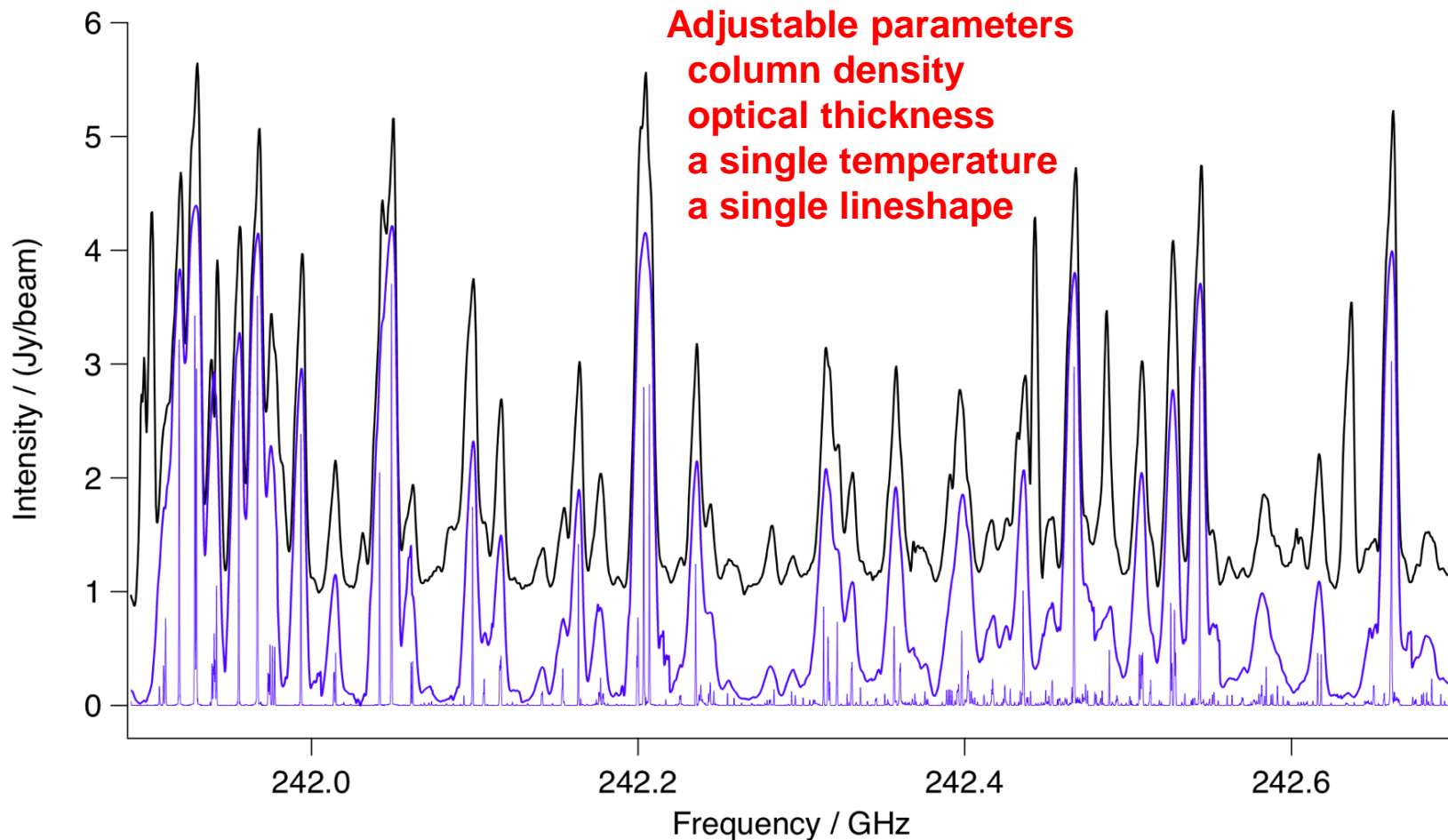
** Image from www.nsf.gov, based on NRAO press release organized by Tony Remijan

Spectroscopic Basis of Simulation on Previous Slide



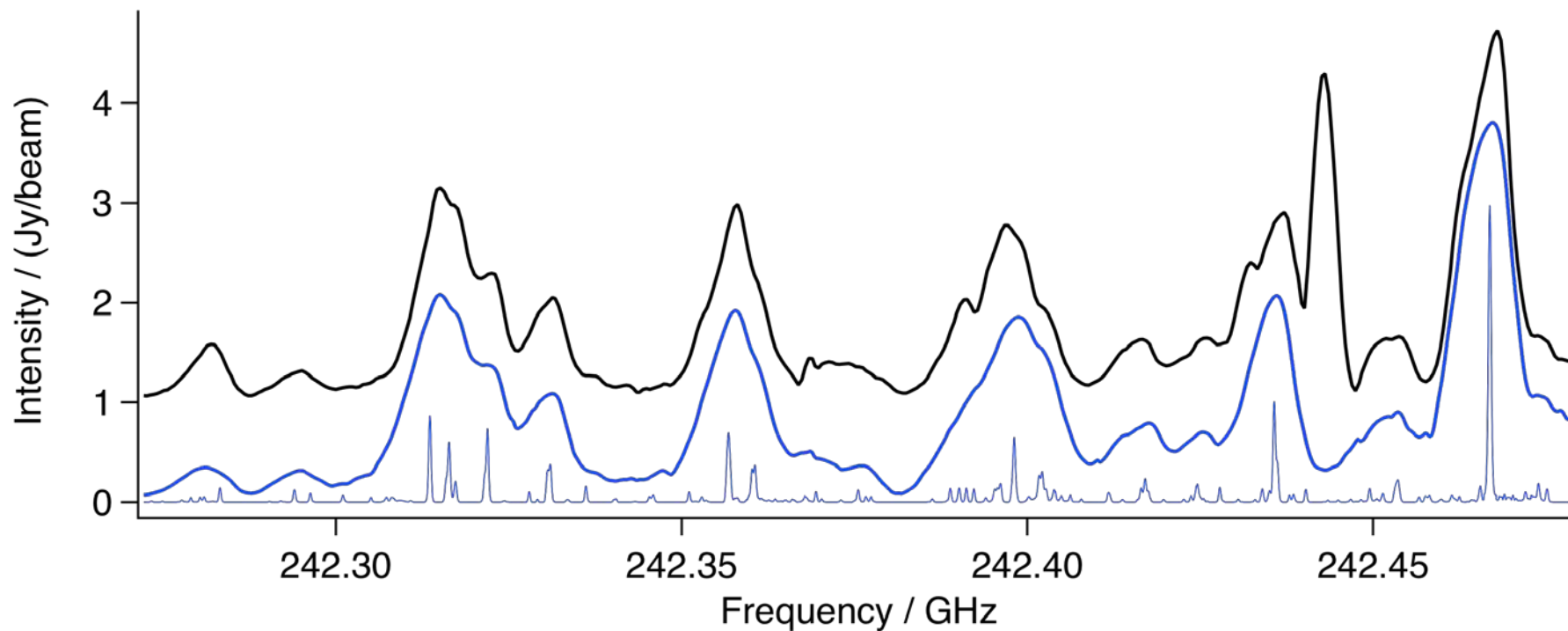
**Complete Experimental Spectra (blue, upward going)
QM catalog (black, downward going).**

Convolve with Astrophysical Lineshape



The ALMA spectrum: upper black trace
Simulation: lower blue trace.
Stick spectrum: CES at laboratory resolution.

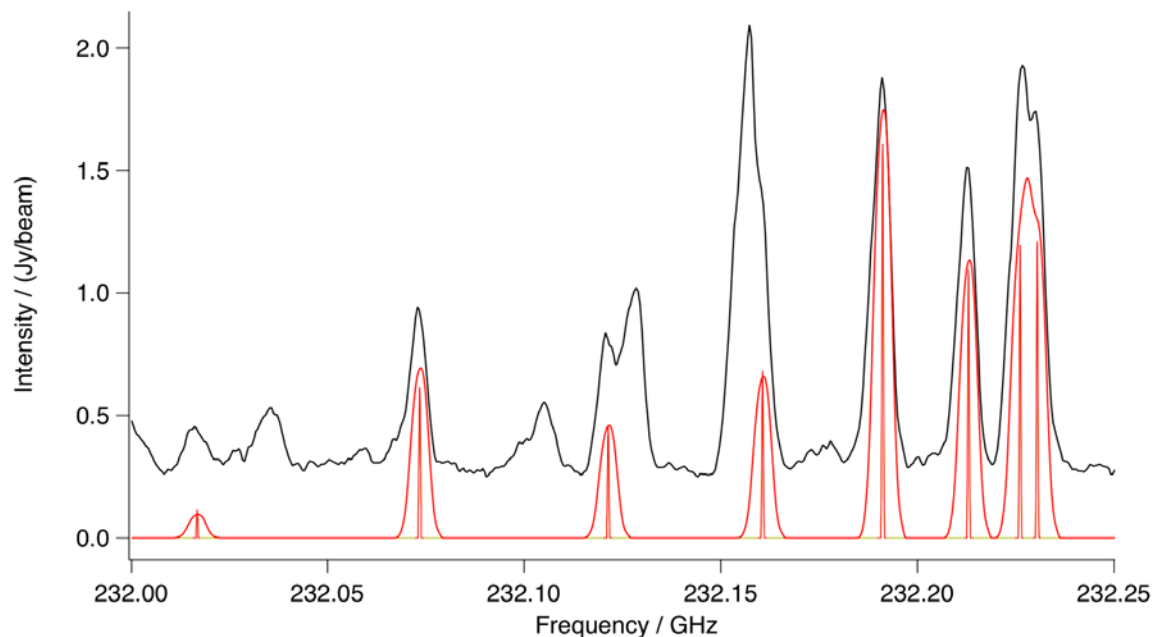
Detail



All the little lines add up to have major impact on simulation accuracy

The convolved astronomical linewidth is slightly too large

Isotopologues

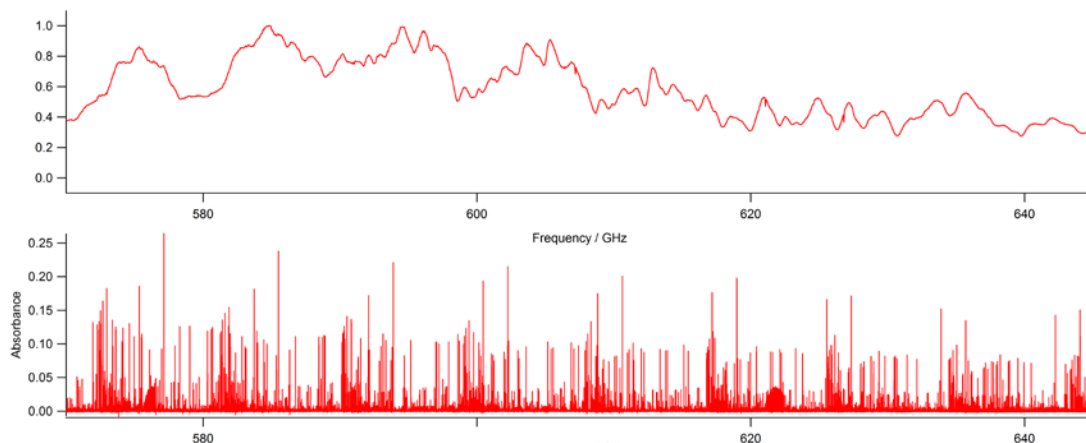


Spectral comparison in the region of a methyl cyanide ground vibrational state, ^{13}C methyl group bandhead. The upper black trace is ALMA and the lower red trace a CES LTE simulation at 190 K. To account for the differences in interstellar and terrestrial abundances, the intensity of the simulation has been increased by a factor of 2.5.

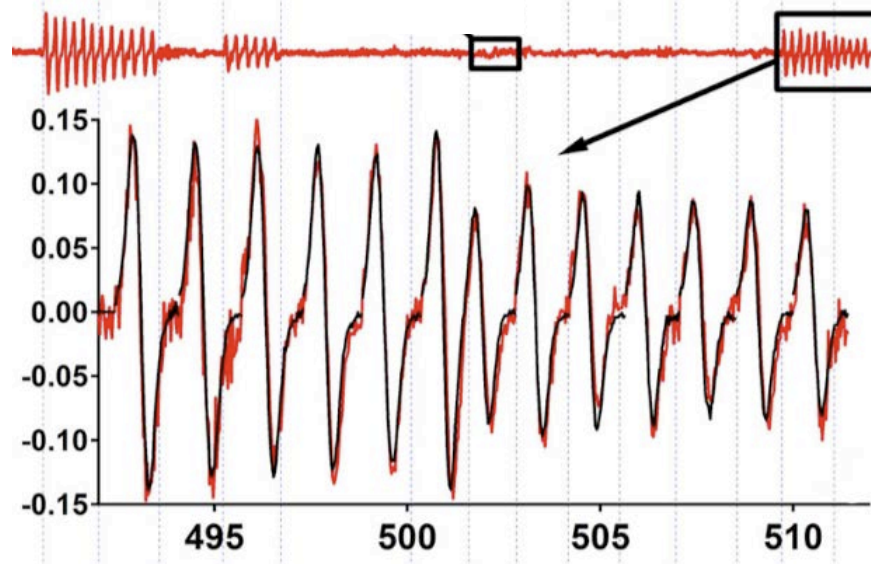
The ground state isotopologues are in general much easier to analyze than perturbed excited vibrational states (which are often more abundant)

Subtraction in Lab via Intensity Calibration

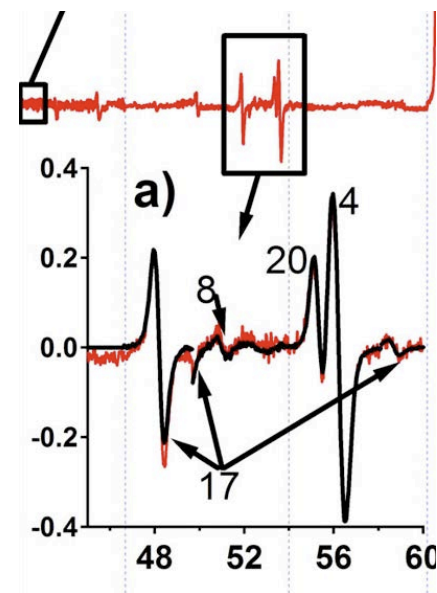
Will this work *at any level* astrophysically?



Subtraction of spectra due to four other species in CICN snippets



CH₂CHBr / C₂H₄Cl₂ Snippets

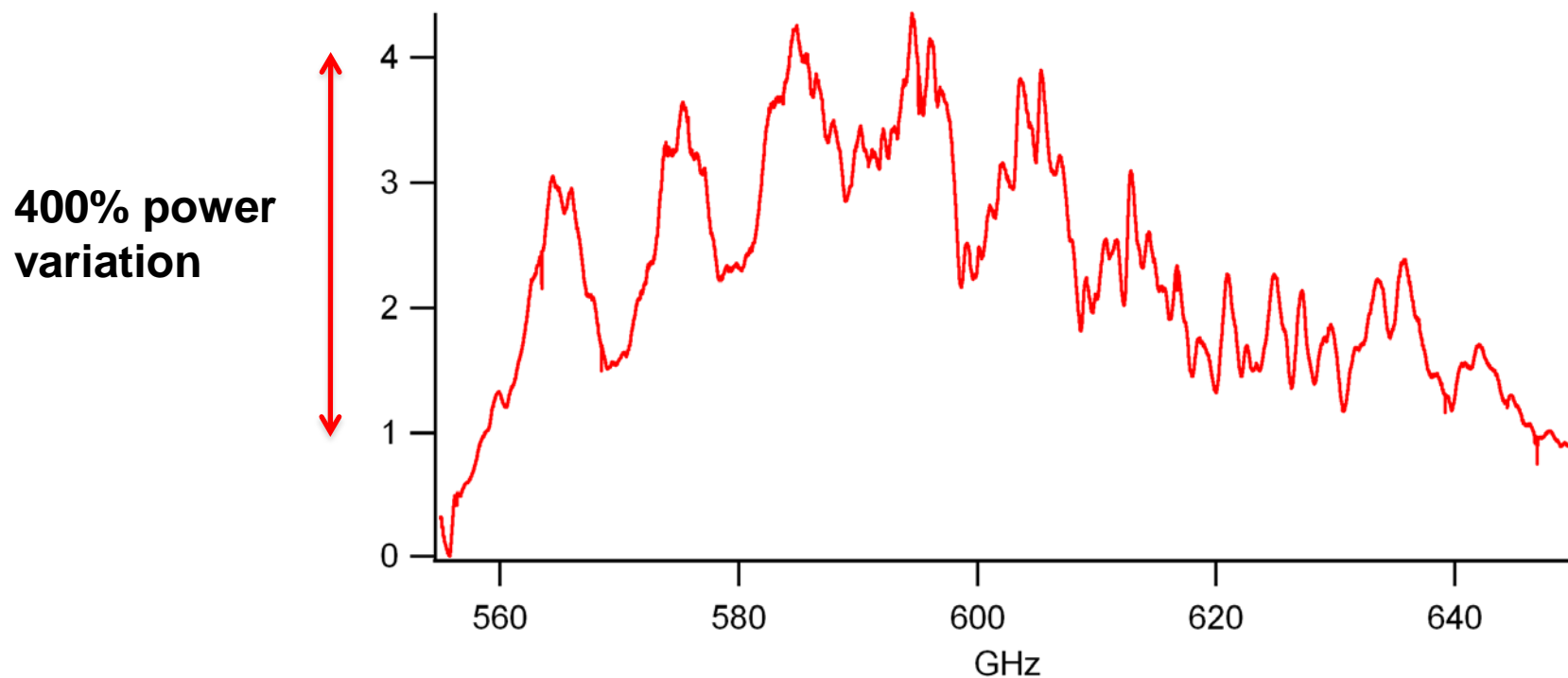


CICN Snippets



Intensity Calibration

Absolute System Power



We seek 1% intensity calibration

Intensity Calibration Challenges

System linearity, saturation, dynamic range

Integrated vs peak intensities (lineshapes and widths)

Molecular saturation

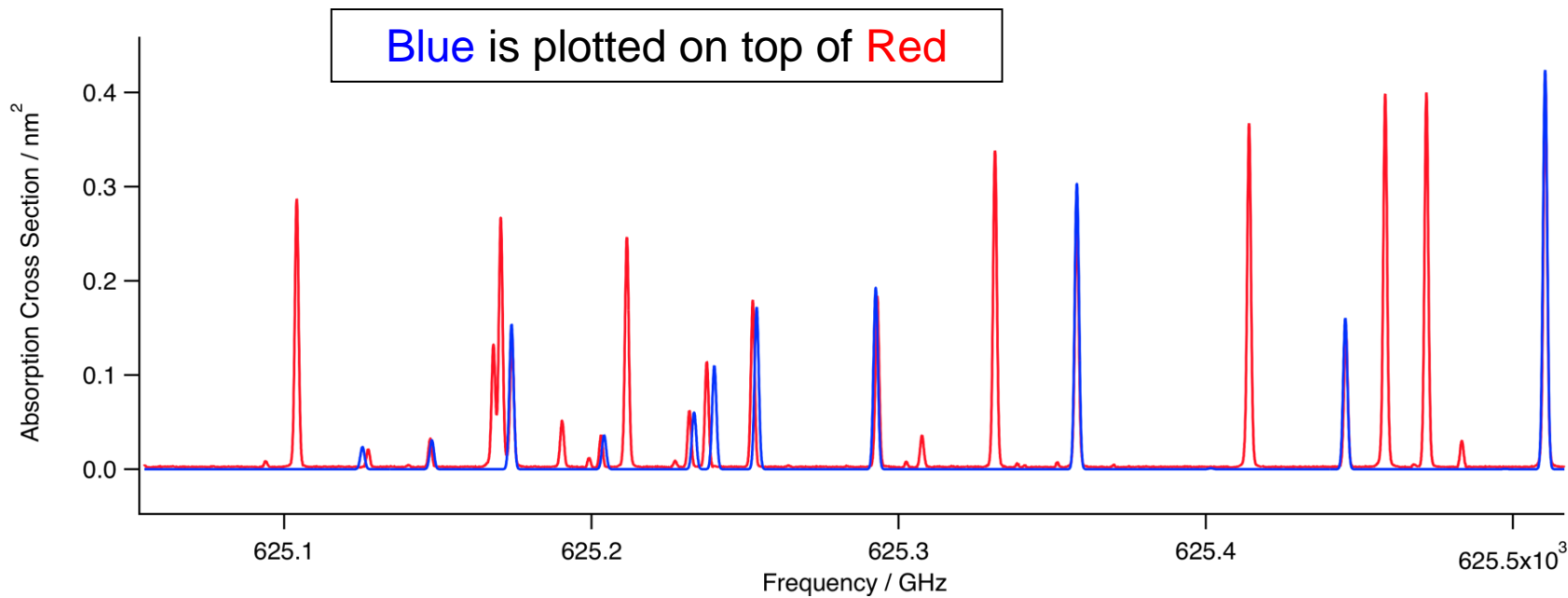
Especially for low pressure Doppler limited lines

Power is not constant in cell

Our solution: just sacrifice sensitivity both in probe power and in sample pressure

Do lots of temperatures on the fly

Methanol



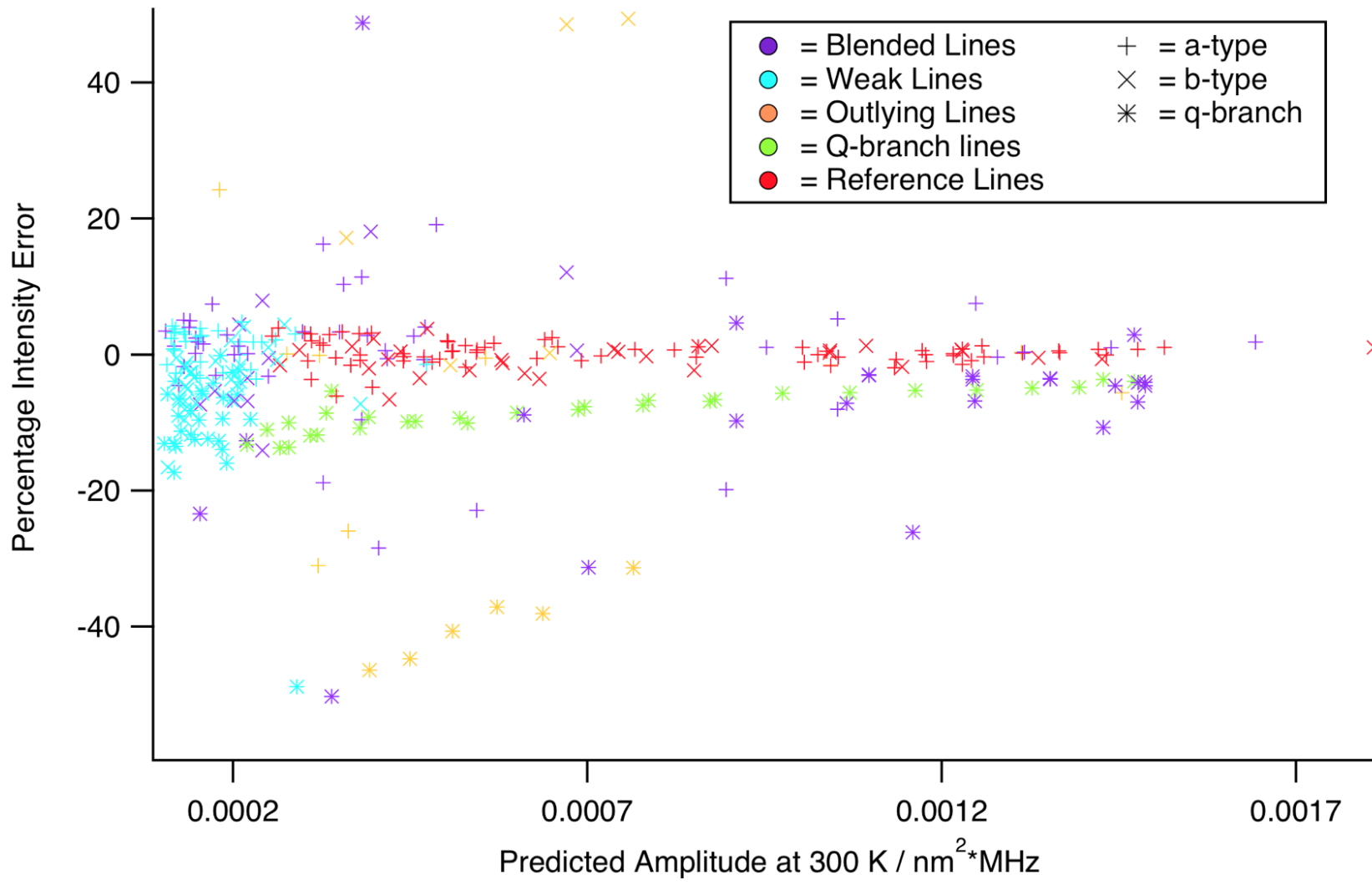
Blue trace: Spectrum simulated from the QM catalog

Red trace: Simulation based on the CES

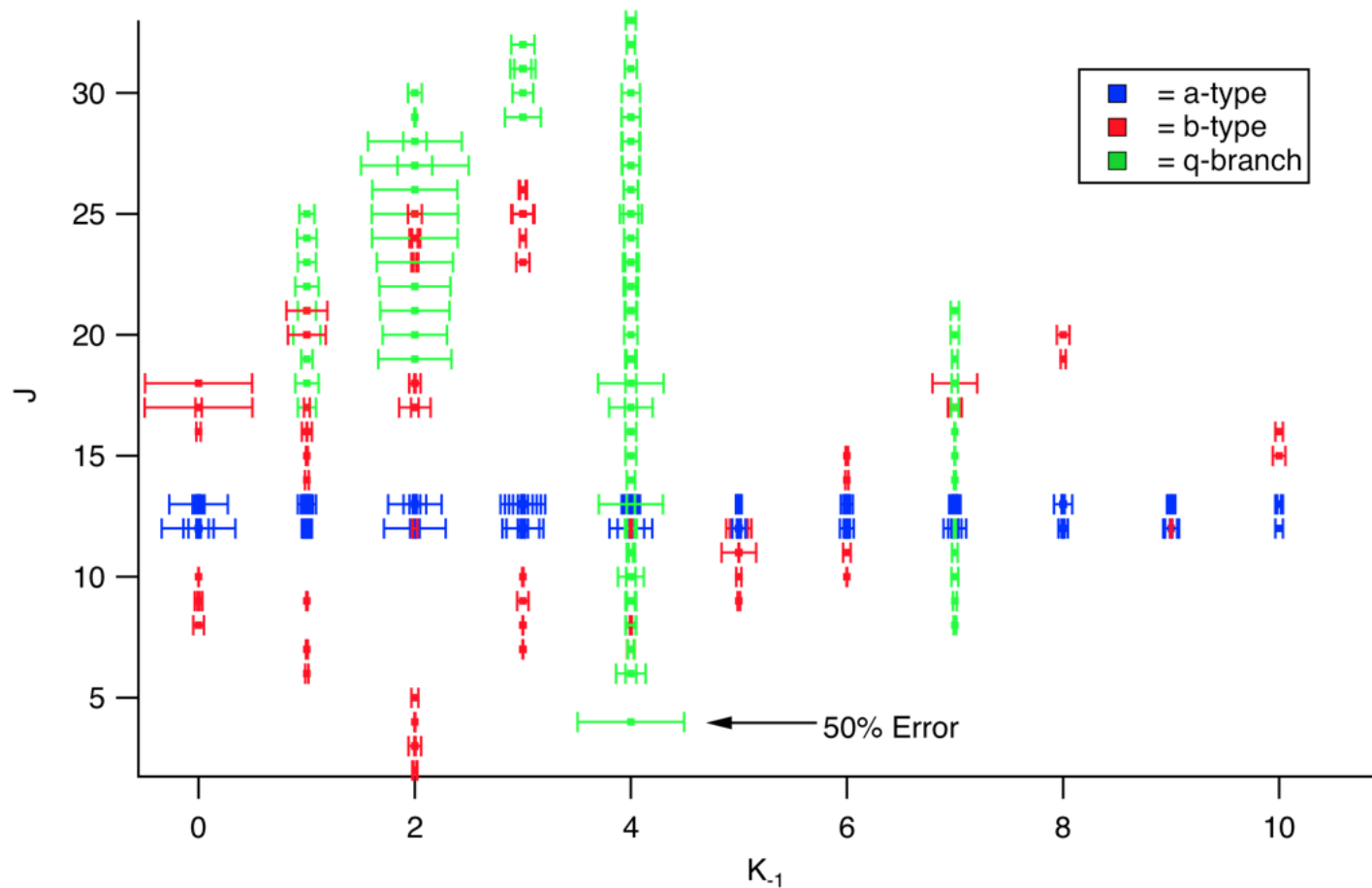
QM simulation frequency errors ≤ 1 MHz



Intensity Error from Calibration nL/Q and T Fit

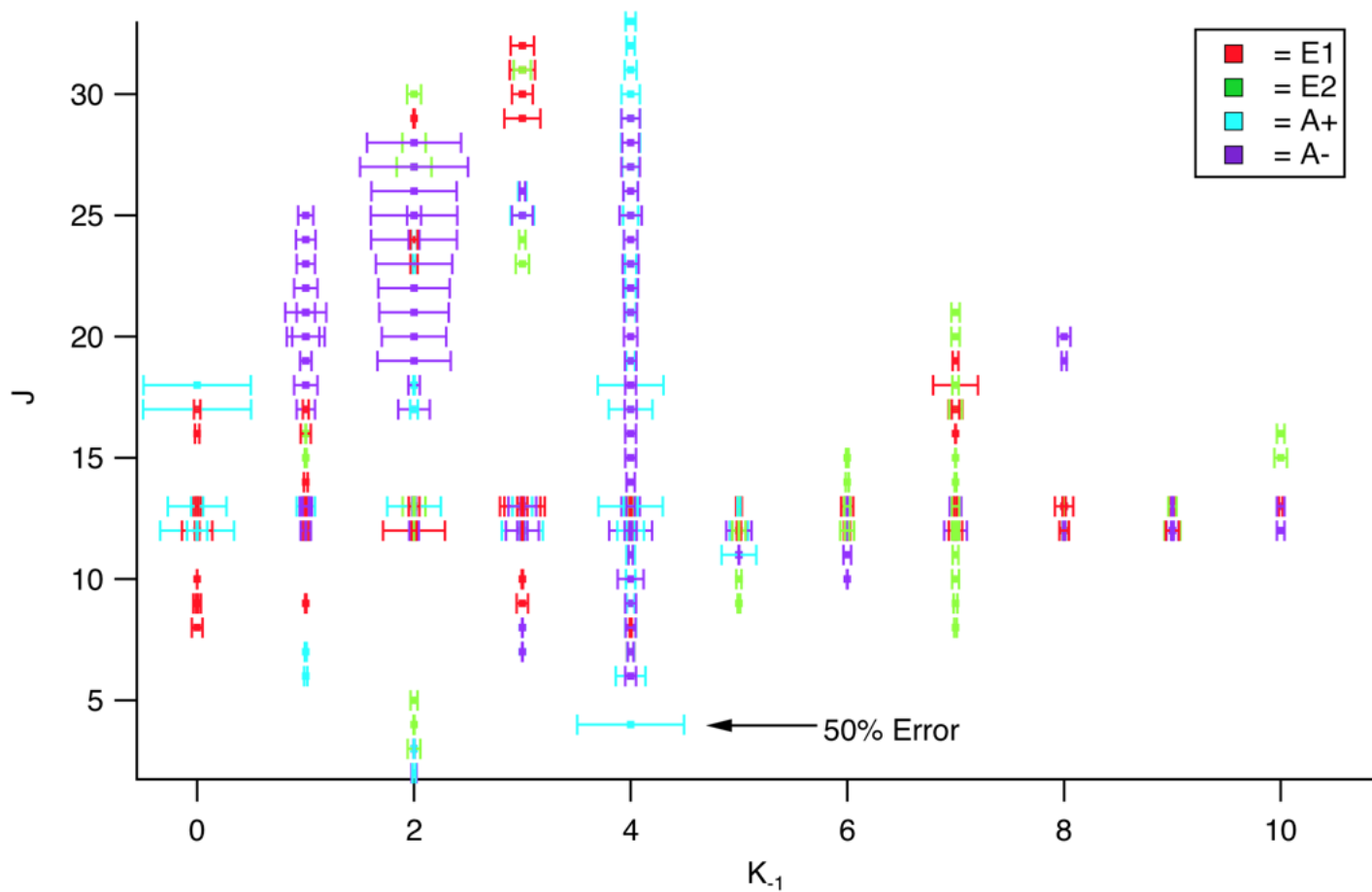


Intensity Error Sorted According to Quantum Number



Intensity error as a function of J and K_1 and transition type. The horizontal error bars are proportional to the size of the error, with one 50% error identified for normalization.

Intensity Error Sorted According to Quantum Number



Intensity error as a function of J and K_1 and transition type. The horizontal error bars are proportional to the size of the error, with one 50% error identified for normalization.

Observations, Questions, and Speculations

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

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

Can we subtract weeds? We do not have to gain a factor of 100 into clutter to be successful – a factor of 2 is worthwhile

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

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

ALMA and SMM/FIR telescopes will look at much smaller, more homogeneous regions.

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

Bigger Lab Astrophysics Questions

What Matters Astrophysically (now?)?

What has long lasting value (the future)?

Spectroscopic work for QM catalogs has had very long lasting value

How do we keep track?

Frequencies of assigned spectral lines relatively straightforward

Does ‘Curiosity Driven’ astrophysical spectroscopy have astrophysical importance?

As a spectroscopist I’m curious how well we can fit the nuances of the astrophysical spectra and what the strategies related to non-LTE, non-terrestrial isotopic abundances, etc. might be



Experimental Measurements of Collisional Cross Sections and Rates at Astrophysical and Quantum Collisional Temperatures

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

**Leiden Center on Herschel Preparatory Science
Leiden
December 5 - 7, 2006**

An Experimentalist's History and Perspective

Pioneering Theory of Green and Thaddeus

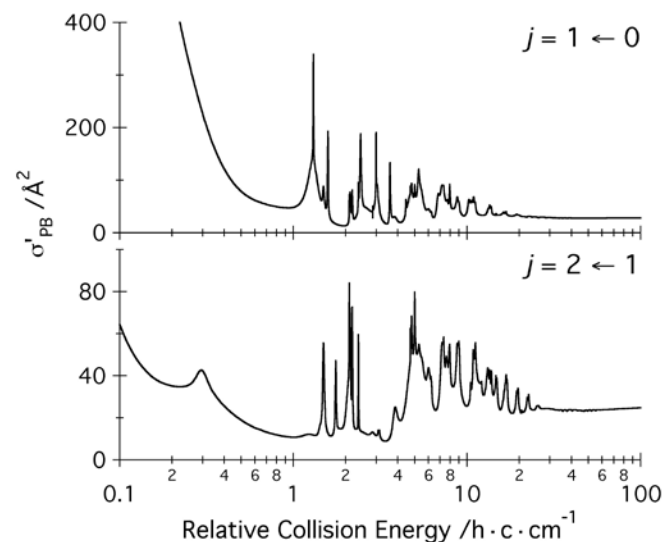
Calculation of pressure broadening parameters for the CO-He system at low temperatures

Sheldon Green

NASA Goddard Space Flight Center, Institute for Space Studies, New York, New York 10025

(Received 27 November 1984; accepted 8 February 1985)

Theoretical pressure broadening parameters were computed for the 0-1 and 1-2 rotational transitions of CO in He at very low temperatures and compared with the recent experimental measurements at 4.2 K. The interaction potential was taken from extensive SCF-CI calculations, molecular collision dynamics were described by essentially exact converged close coupling calculations, and pressure broadening cross sections were obtained from the collisional S matrices within the accurate Fano-Ben Reuven framework. Resonances at low collision energies give rise to an increase in the thermally averaged cross sections at low temperatures. Although previous calculations for this system at higher temperatures (77-300 K) were in good accord with experiment, at 4.2 K predicted values are about two times larger than experiment; possible sources of this discrepancy are discussed.



Explore New Experimental Regimes

What is the physics in the regime where $kT \sim hv_r \sim V_{well}$?

VOLUME 53, NUMBER 27

PHYSICAL REVIEW LETTERS

31 DECEMBER 1984

Measurement of Pressure-Broadening Parameters for the CO-He System at 4 K

J. K. Messer^(a) and Frank C. De Lucia

Department of Physics, Duke University, Durham, North Carolina 27706

VOLUME 75, NUMBER 16

PHYSICAL REVIEW LETTERS

16 OCTOBER 1995

Pressure Broadening of Gas Phase Molecular Ions at Very Low Temperature

J. C. Pearson,* L. C. Oesterling, Eric Herbst,† and F. C. De Lucia

Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210-1106

VOLUME 81, NUMBER 2

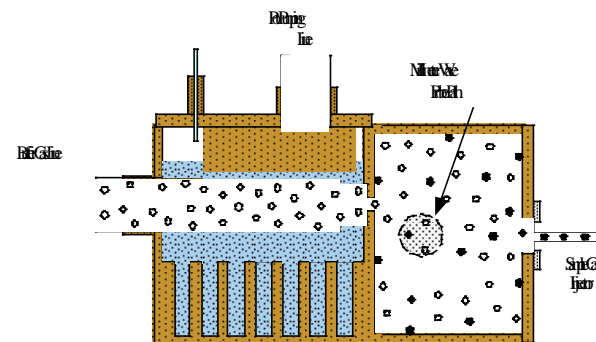
PHYSICAL REVIEW LETTERS

13 JULY 1998

Direct Measurement of Rotationally Inelastic Cross Sections at Astrophysical and Quantum Collisional Temperatures

Christopher D. Ball and Frank C. De Lucia

Department of Physics, The Ohio State University, Columbus, Ohio 43210



Other Systems

VOLUME 75, NUMBER 16

PHYSICAL REVIEW LETTERS

16 OCTOBER 1995

Pressure Broadening of Gas Phase Molecular Ions at Very Low Temperature

J. C. Pearson,* L. C. Oesterling, Eric Herbst,[†] and F. C. De Lucia

Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210-1106

(Received 5 July 1995)

A novel apparatus has been developed to produce large quantities of thermal molecular ions at temperatures well below the freezing points of their precursor neutrals. This apparatus has been used to study the pressure broadening of the $J = 3-2$ rotational transition of HCO^+ in H_2 gas at temperatures in the range 11–30 K.

PACS numbers: 34.20.Gj

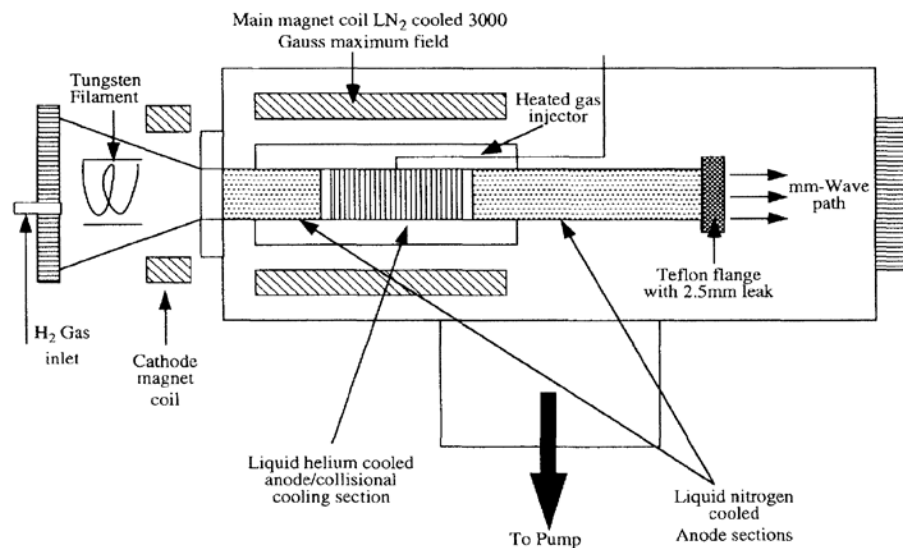


FIG. 1. The experimental apparatus, combining magnetic enhancement of ion concentrations, collisional cooling, and an electron gun ionization source.

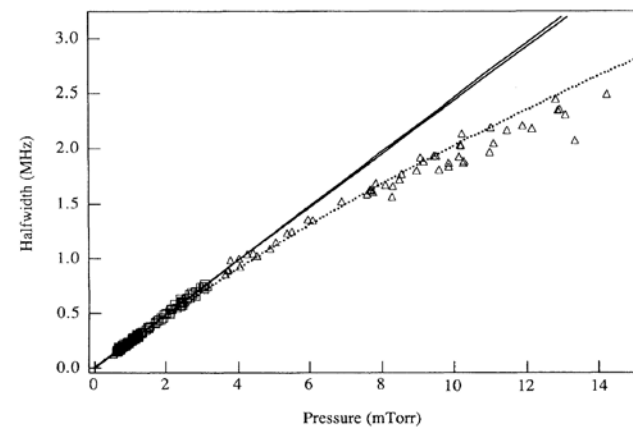


FIG. 2. Observed half-width for HCO^+ ($J = 3-2$) in collision with H_2 as a function of pressure at 11.2 K and 8 mA electron beam current. The two solid lines represent fits to the linear portion of the data and the dotted line the prediction of the electron beam heating model. The high pressure data clearly show the effects of electron beam heating.

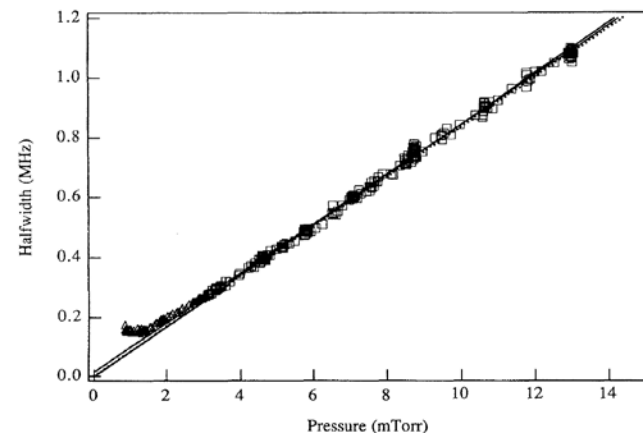
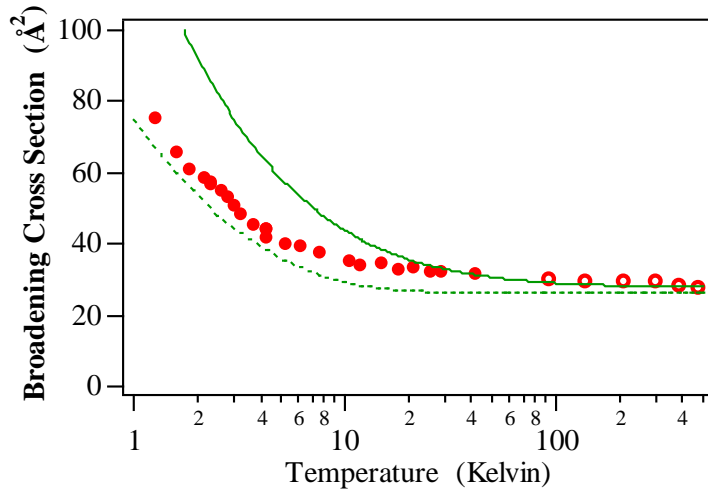


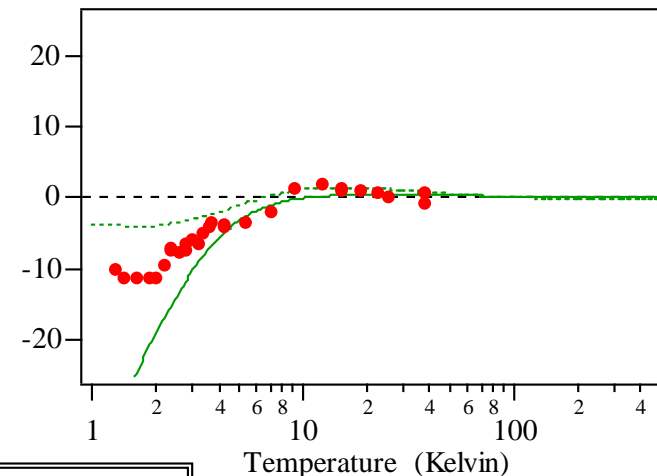
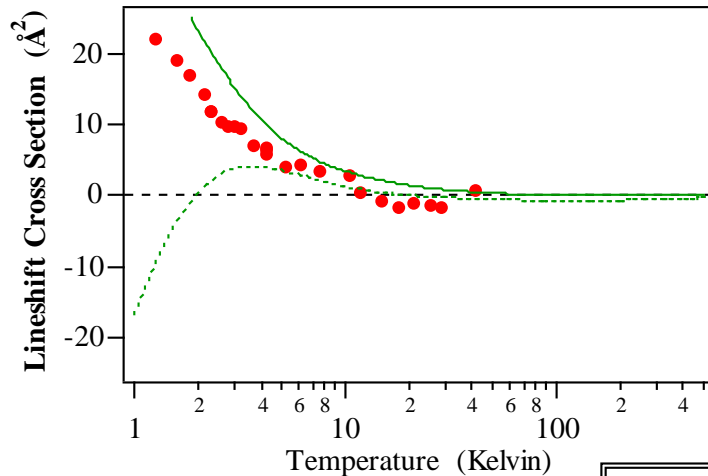
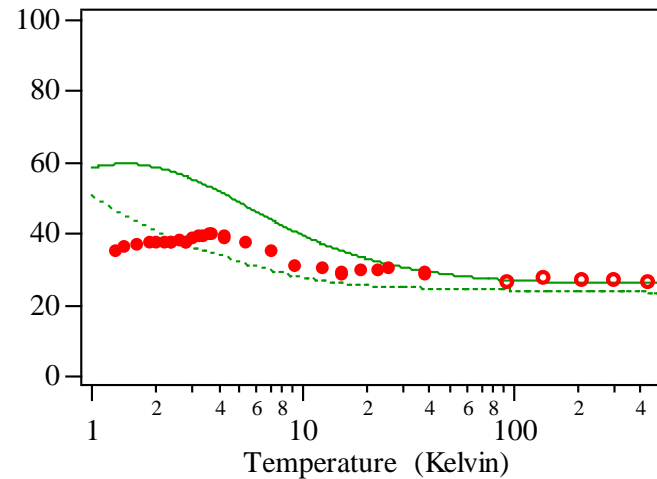
FIG. 3. Observed half-width for HCO^+ ($J = 3-2$) in collision with H_2 as a function of pressure at 28 K and 10 mA electron beam current. The two solid lines represent fits to the linear portion of the data and the dotted line the prediction of the electron beam heating model. The low pressure show the "hook" from the loss of cooling while the high pressure data show little effect from electron beam heating.

CO-He CROSS SECTIONS

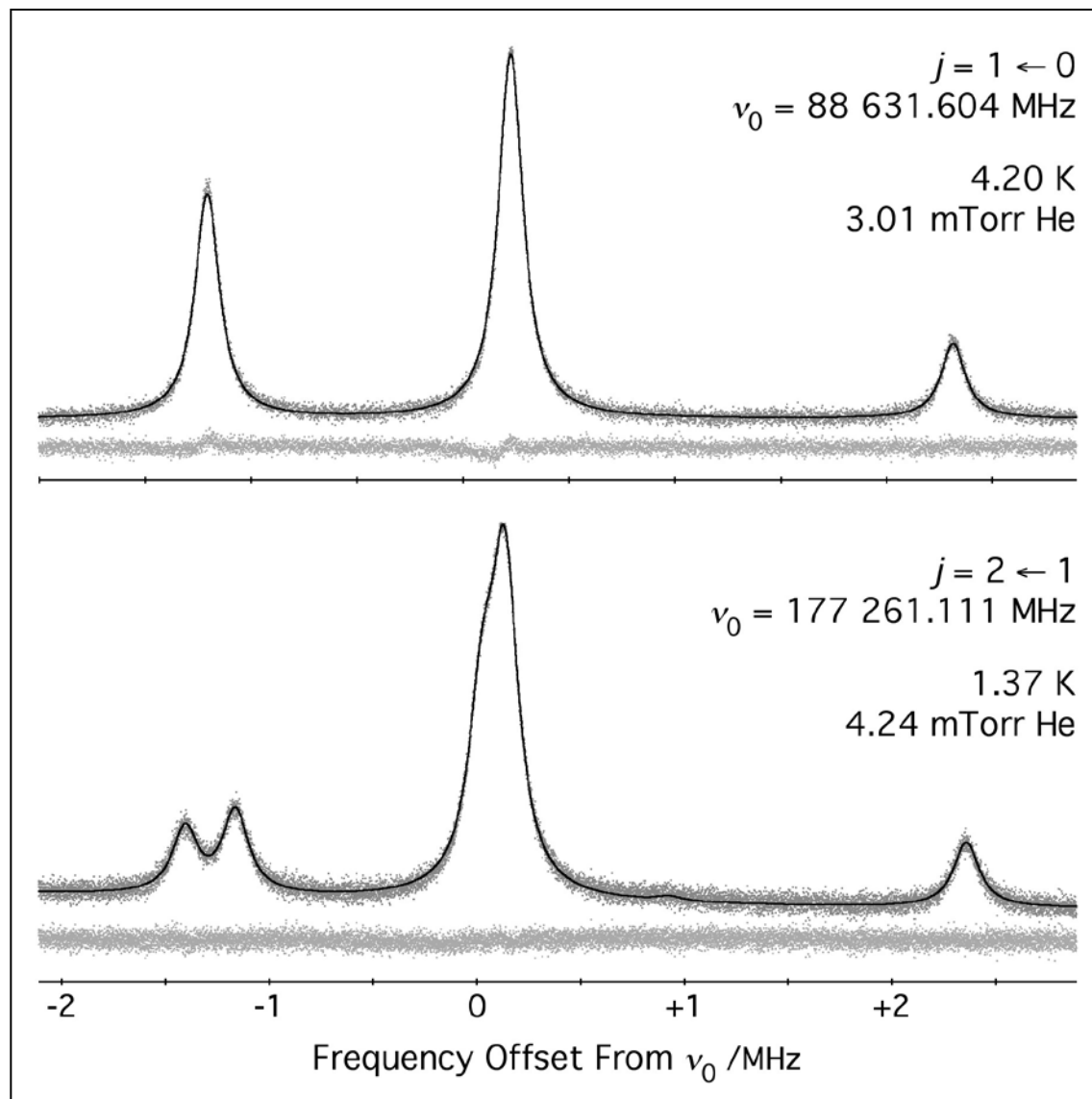
$J = 1 \leftarrow 0$



$J = 2 \leftarrow 1$



Typical Spectra - HCN



Spectroscopic Engineers: Kings or Useful Servants

