MICROWAVE SPECTROSCOPY
AND THE
REMOTE SENSING PROBLEM

Frank C. De Lucia
Physics Department
Ohio State University

OVERVIEW

The Rotation Vibration Spectra of Molecules

Microwave and Infrared Data

Weighted Fits and the Spectral Data Base

Linewidths, Lineshapes, and the Continua

Physics and Parameterization

Experimental Issues

SPECTRAL REGIONS

HISTORICALLY:

MICROWAVE: Low J, Ground vibrational state

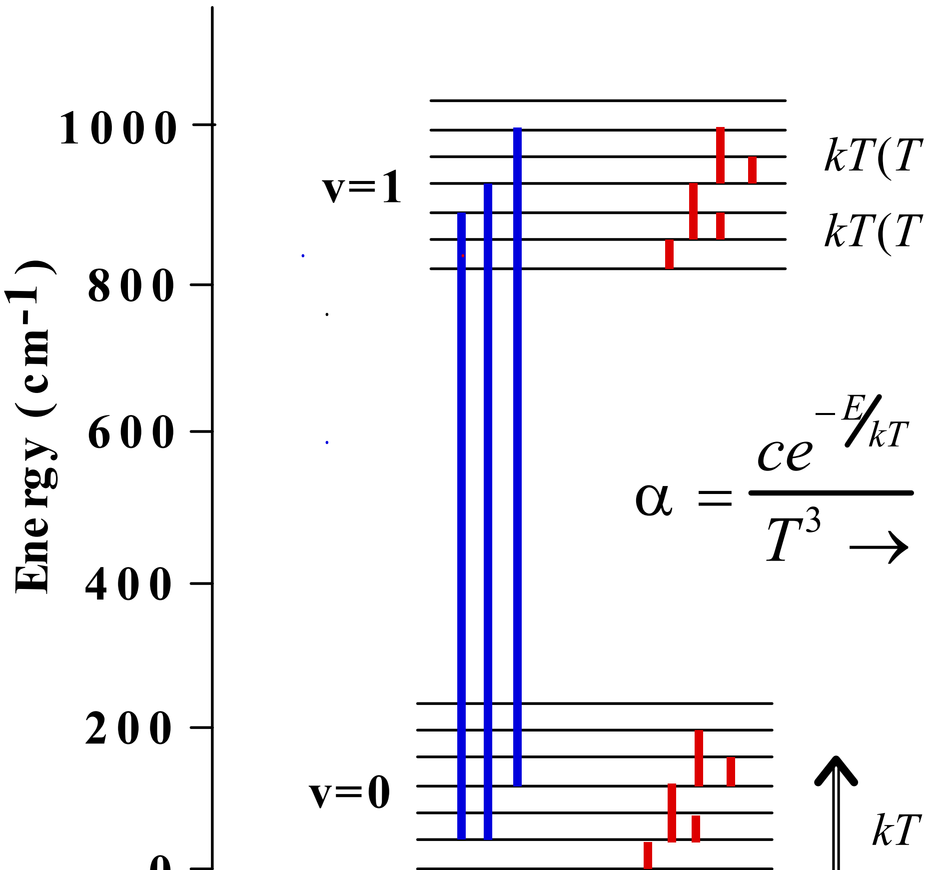
INFRARED: Vibrational bands

CURRENTLY:

MICROWAVE: Thermally populated rotational manifold in many vibrational states

INFRARED: Dopper limited rotation-vibration spectra

THE ROTATION-VIBRATION SPECTRUM

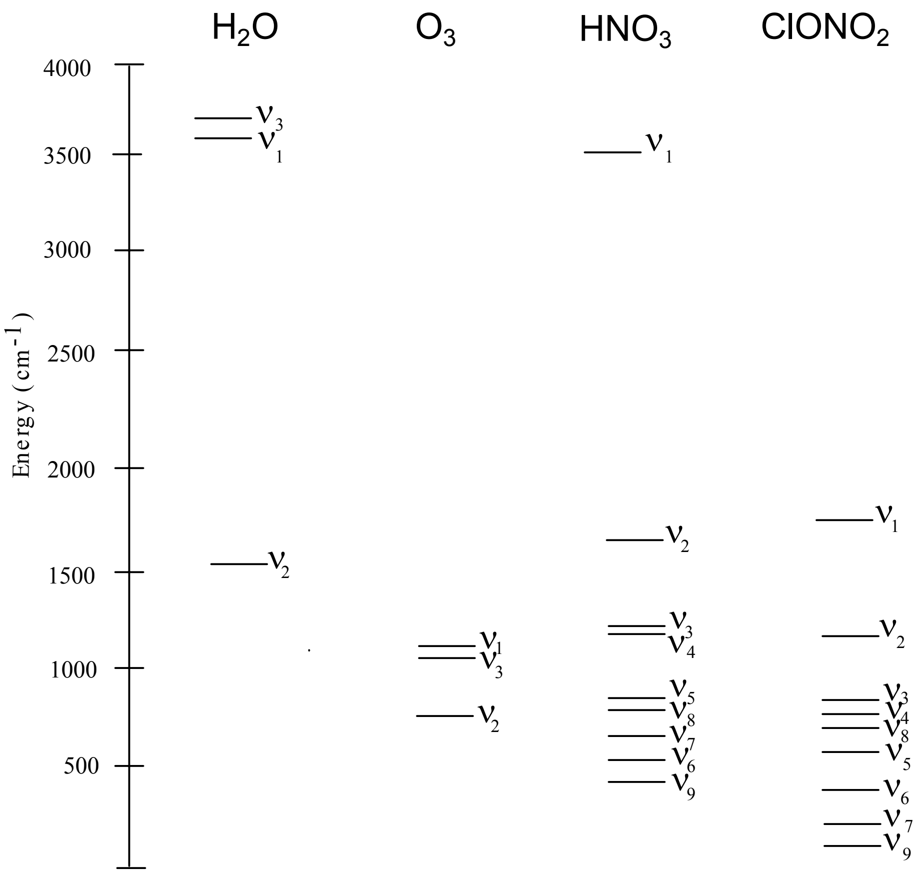


$$kT(T = 300K) = 200 \text{ cm}^{-1}$$

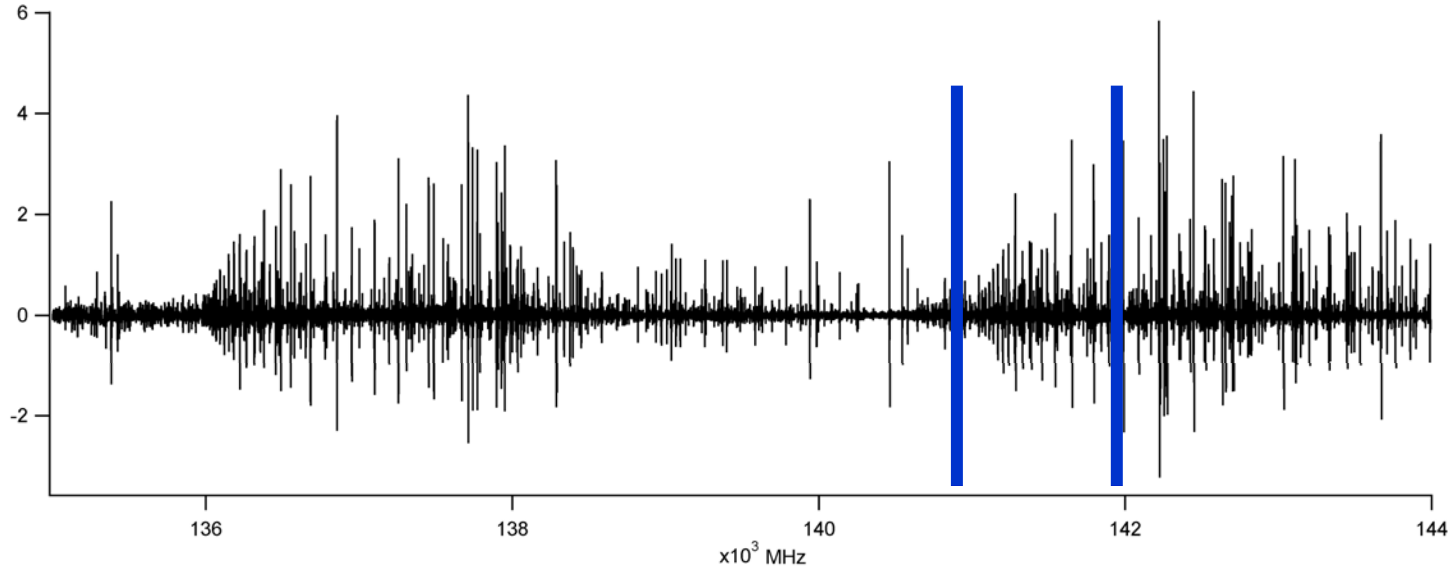
$$kT(T = 1000K) = 675 \text{ cm}^{-1}$$

$$\alpha = \frac{ce^{-E/kT}}{T^3} \rightarrow \begin{cases} \text{rotational partition function} \\ \text{linewidth} \\ \text{emission-absorption factor} \end{cases}$$

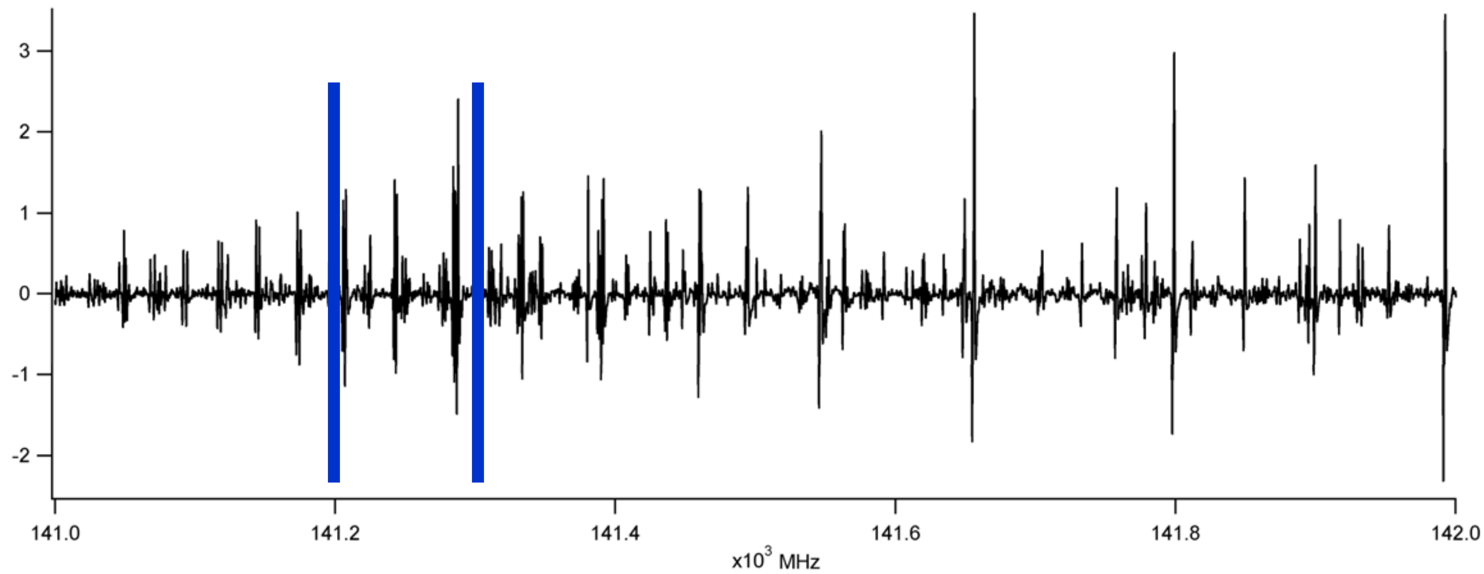
SPECTRAL DENSITY



FASSST SPECTRUM OF $ClONO_2$

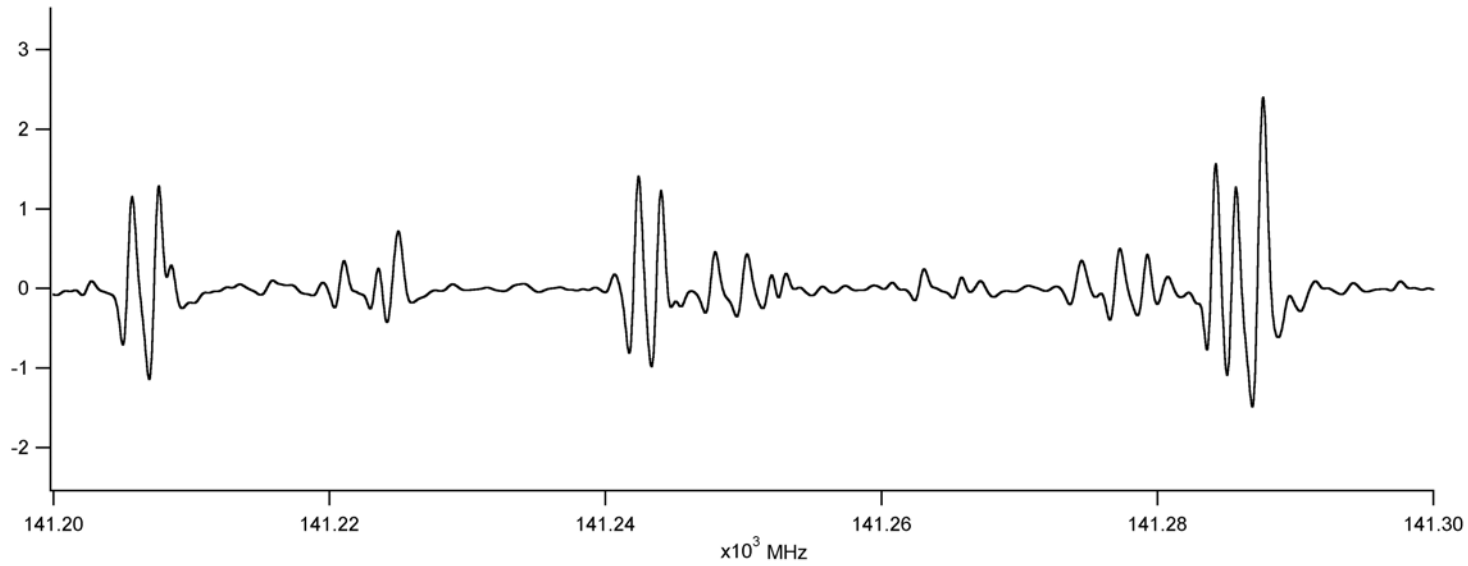


EXPANDED FASSST SPECTRUM OF $ClONO_2$

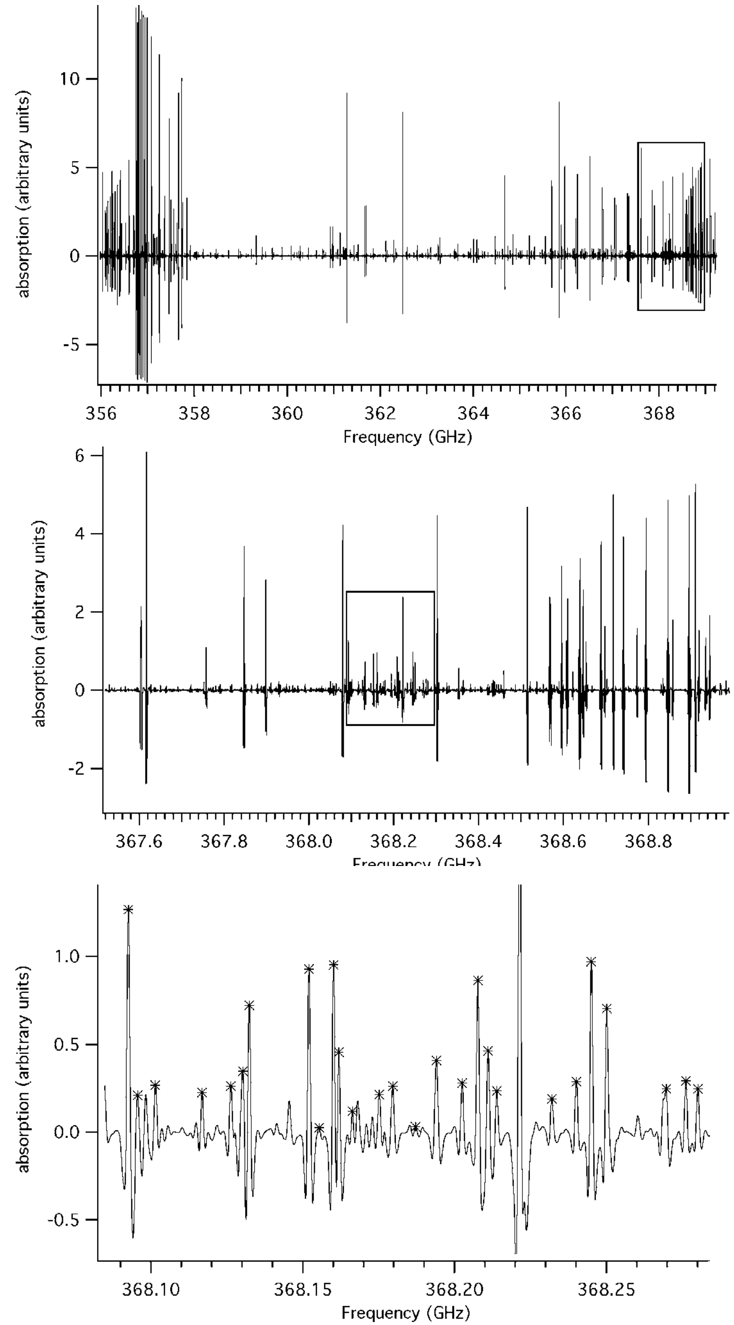


FASSST SPECTRUM OF $ClONO_2$

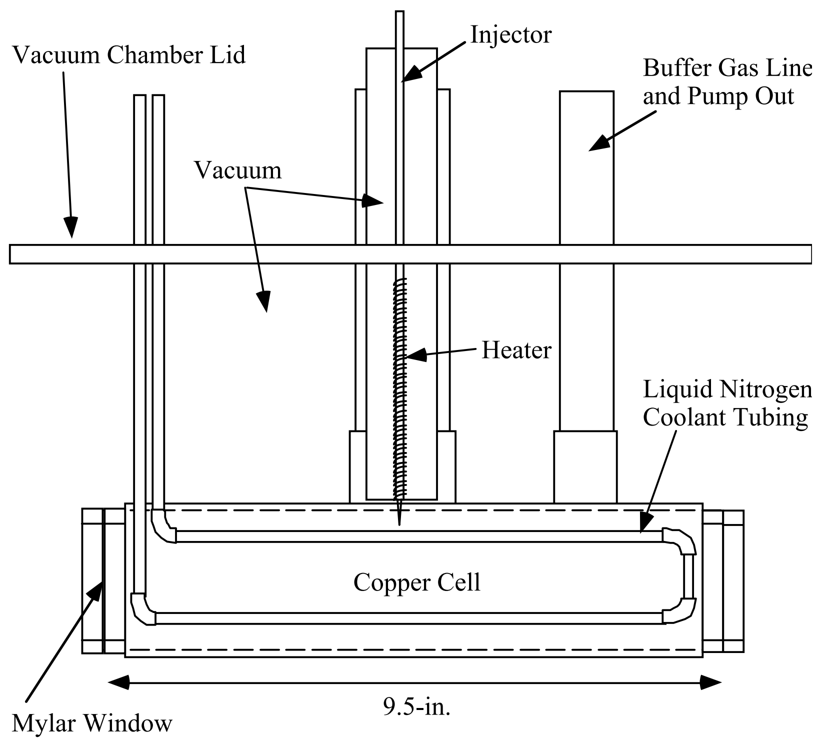
- 0.02 Second Measurement Time

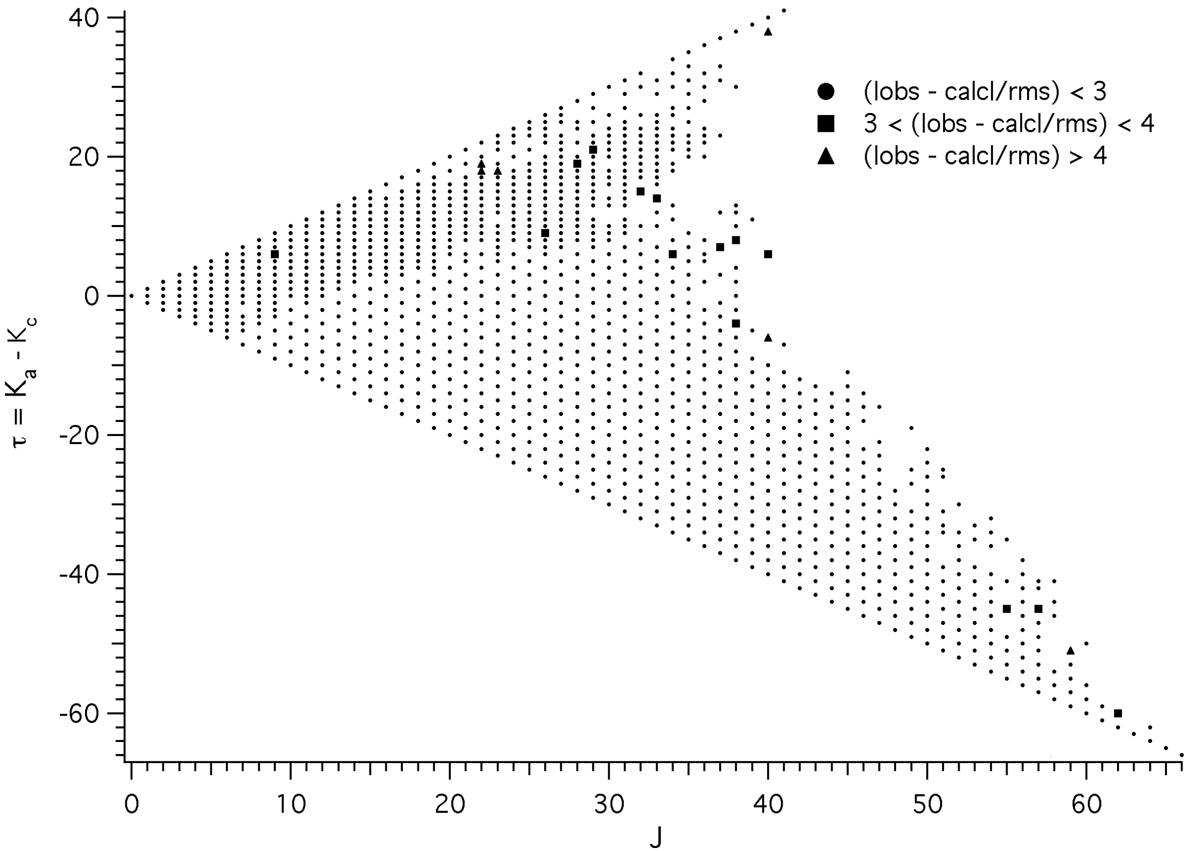


Series of expansions of a spectrum of HNO_3 recorded by the FASSST spectrometer. The last expansion displayed shows 23 lines of the pure rotational spectrum of ν_5 and required 0.02 seconds to record. These lines are about 150 times weaker than lines in the ground vibrational state.

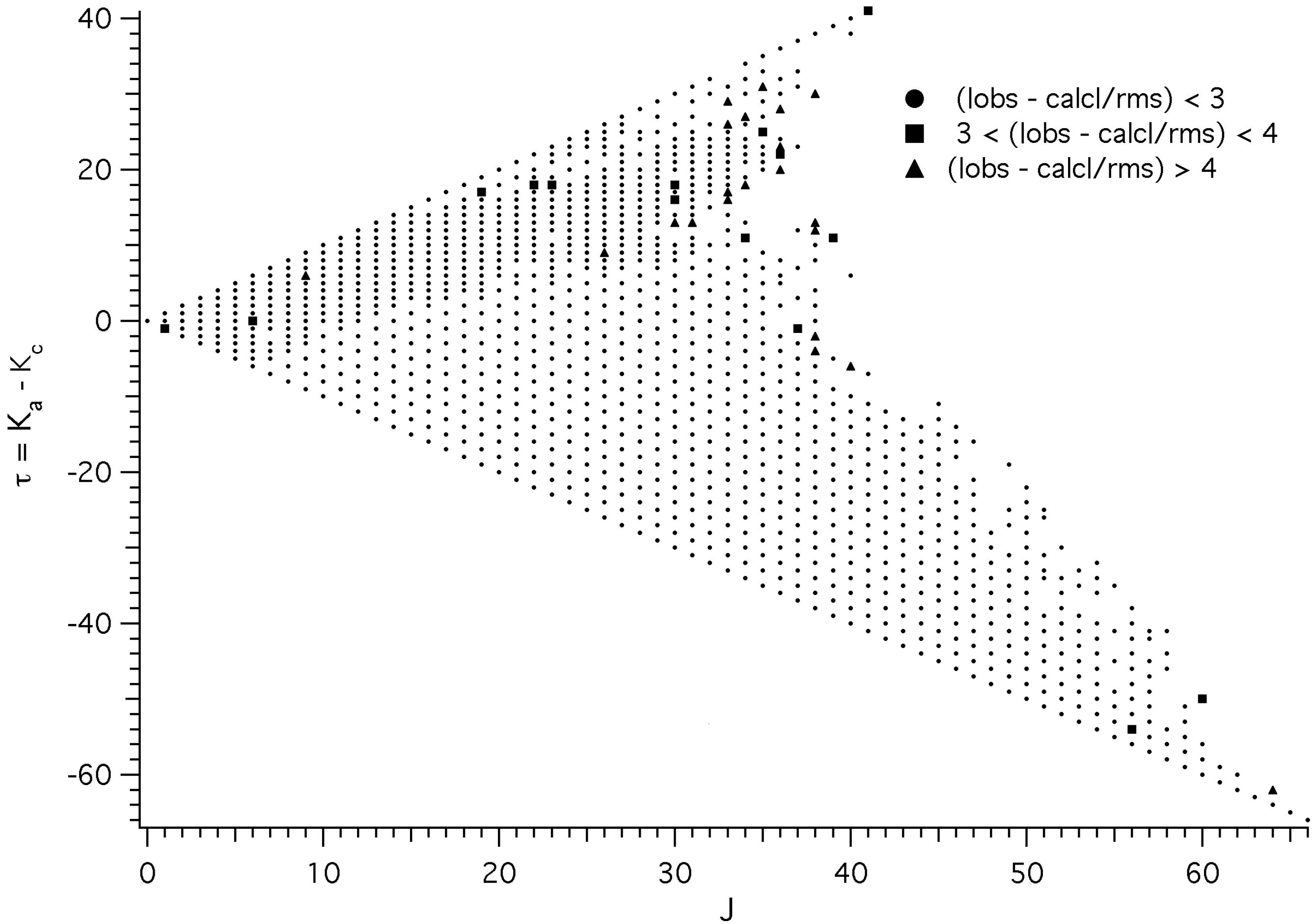


SEPARATION OF ROTATIONAL AND VIBRATIONAL TEMPERATURES





Distribution of differences for a fit to the experimental infrared energy levels of ν_5 of HNO_3.



Distribution of differences between the experimental infrared energy levels of ν_5 and levels *predicted* from the microwave analysis.

SPECIES OBSERVED BY IR SENSING BETWEEN 700 TO 1300 CM^{-1}

1. H_20, CO_2, O_3, N_2O, CH_4, OCS, NH_3, C_2H_6
2. HNO_3, SF_6, C_2H_6, COF_2, HCOOH, CF_4
3. CCl_2F_2 (CFC-12), $CHClF_2$ (CFC-22), CCl_3F (CFC-11), CCl_4
4. $ClONO_2$, HO_2NO_2, N_2O_5

Adapted from Brown, Farmer, Rinsland, and Zander

THE ROTATION-VIBRATION DATA BASE

WEIGHTED FITS OF MICROWAVE AND INFRARED DATA

Many infrared data points

Starting to be many microwave data points

Fits need to be at level of data, not derived levels

Fits need to include all relevant data

LINEWIDTHS: EXPERIMENT AND THEORY

No ‘Spectroscopy-like’ Fitting Theory
--> accuracy?

Gamache, Hartmann, Rosenmann Survey

JPL/OSU HNO_3 Intercomparison

IR and MW LINEWIDTHS

Function of J?	light (H_2O):	yes
	medium (HNO_3):	self - yes
	heavy (CFC's):	?

Function of v? ?

A combined MW/IR broadening data base?
For which molecules?
For which states?

CONTINUA

Dimers and/or Polymers

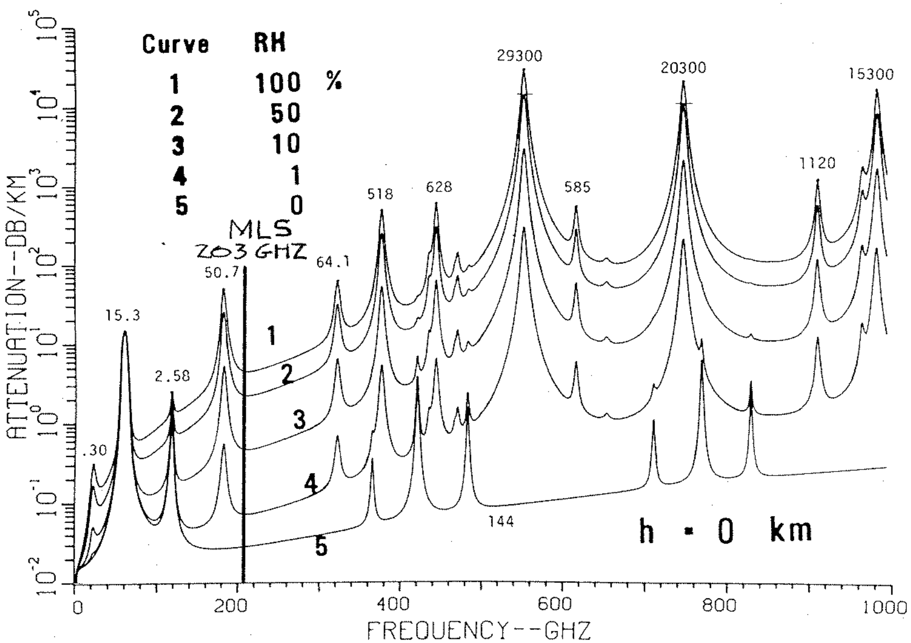
Nearest Neighbor Lineshape Effects

Far Wing Lineshape Effects

Anomalous Absorption

Collision Induced Absorption

I. OVERVIEW



MLS Function $\beta = Ap^2\left(\frac{300}{T}\right)^B$

Dry Air
$A = 7.30 \bullet 10^{-9}\, km^{-1} hPa^{-2}$
$B = 2.79$

Moist Air
$A = 5.67 \bullet 10^{-5}\, km^{-1} hPa^{-2}$
$B = 3.59$

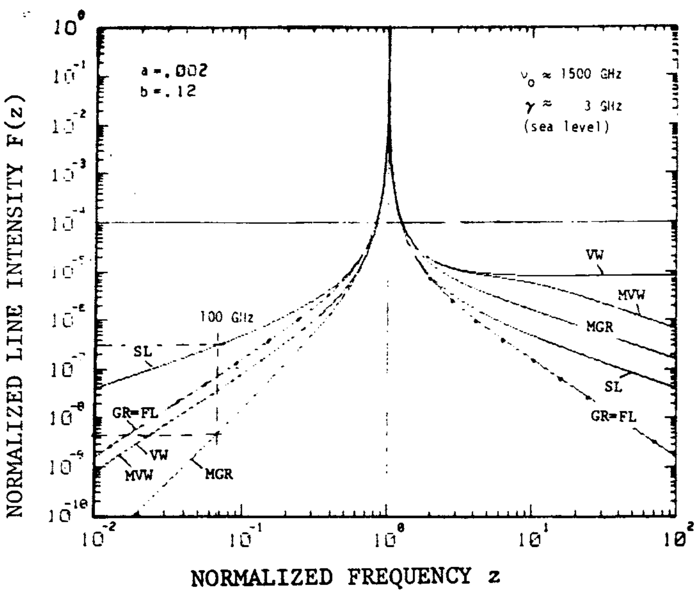
Liebe Function

Dry Air $\alpha(db/km) = 2.5 \bullet 10^{-11} f^2 p^2 \left(\frac{300}{T}\right)^{4.5}$

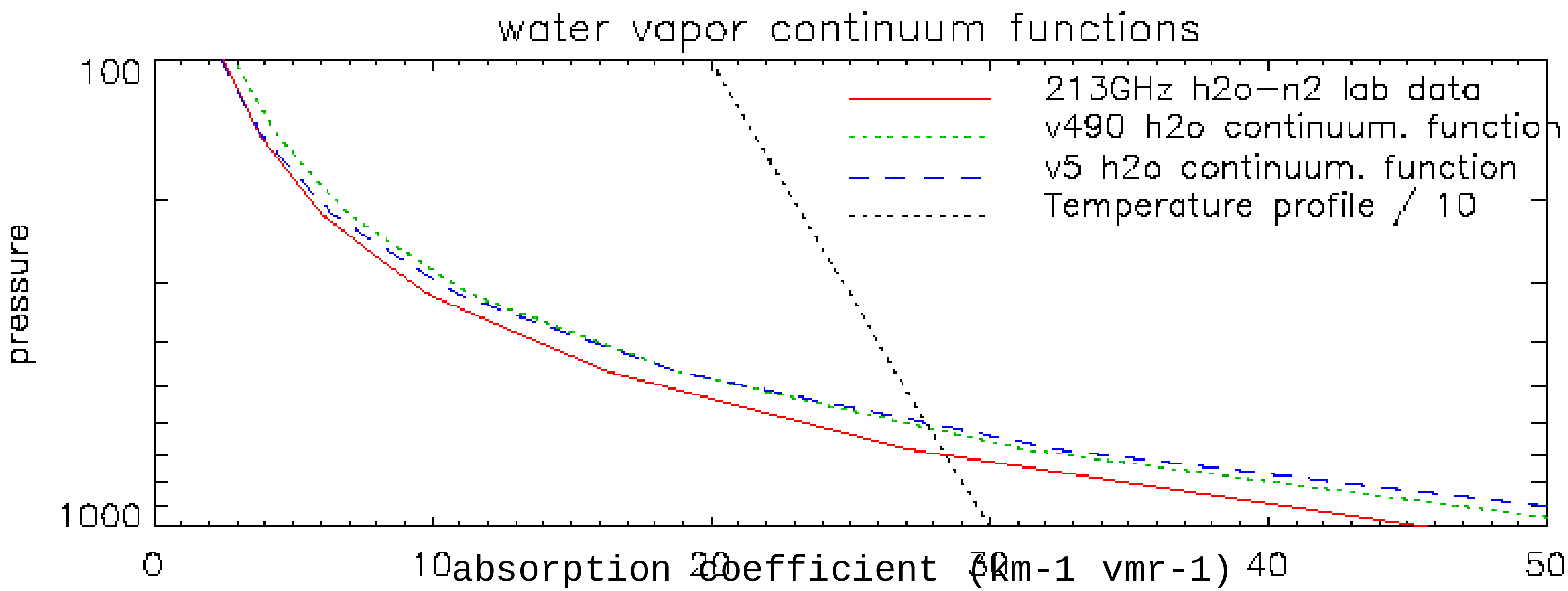
Moist Air $\alpha(db/km) = 2.5 \bullet 10^{-7} pef^2 \left(\frac{300}{T}\right)^{2.5} + 9.7 \bullet 10^{-6} e^2 f^2 \left(\frac{300}{T}\right)^{5.5}$

p = partial pressure of dry air (kPa)
e = partial pressure of water (kPa)
f = frequency (GHz)

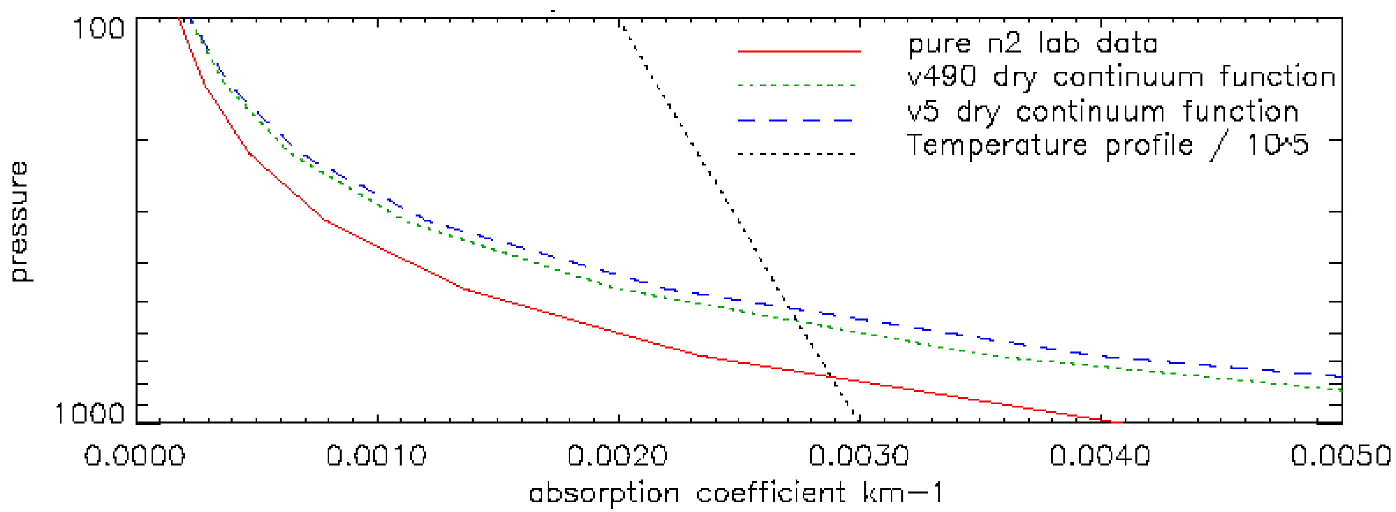
Lineshapes


a = .002
b = .12
$\nu_0 \approx$ 1500 GHz
$\gamma \approx$ 3 GHz
(sea level)
100 GHz
SL
GR=FL
VW
MVW
MGR
NORMALIZED LINE INTENSITY F(z)
NORMALIZED FREQUENCY z

Comparison of ‘laboratory’ and field measurements of the moist air continuum (from Read et al.)



Comparison of ‘laboratory’ and field measurements of the dry air continuum (from Read et al.)



II. THE PHYSICS

Moist Air

Observed excess in atmospheric windows over simple Lorentzian

Lineshape from nearby lines?

Far wings of very strong lines at higher frequencies?

Stable species (e. g. dimers)?

Metastable states, non-equilibrium physics?

More exotic physics?

Dry Air

Collision induced due to O_2 and/or N_2

III. THE EXPERIMENTAL ISSUES

Moist Air Continuum:

What is in the cell?

Monomers, clusters, nonequilibrium species

(What is in the atmosphere?)

Dry Air Continuum:

Small effect in the laboratory

What is in the cell?

Contamination from Moist Air Continuum

IV. THE EXPERIMENT

10 m Fabry-Perot Cavity

Q ~ 10^7, $\Delta\nu$ = 20 kHz, EPL 1 - 10 km

Stainless Vacuum/Pressure Chamber

(10^{-9} - 10 atm)

FASSST Scanning with skip-lock frequency stabilization

Continuous Scan: ~1000 s, duty cycle ~10^{-3}

Skip-lock Scan: adjustable scan time, duty cycle ~1

SUMMARY

Due to advances in sensors and analysis

Significant Advances in IR and MW Field Data

Significant Advances in IR and MW Laboratory Data

We should pay careful attention to the

Integration of MW/IR data base

Transition between lineshape and continua