

Microwave Spectroscopy

Nicholas Chapman
University of Kentucky

Mentors:

Frank DeLucia
The Ohio State University

Paul Helminger
University of South Alabama

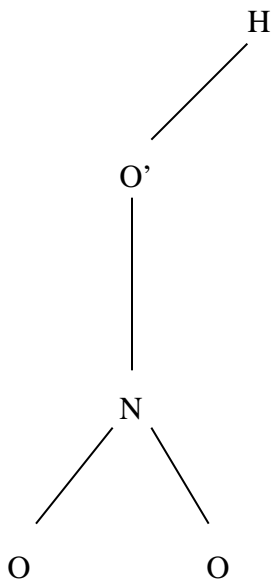
Doug Petkie
Ohio Northern University

Spectroscopy is the science of propagating electromagnetic radiation through atomic or molecular gases and observing the resultant absorption and emission spectra to learn about the species.

There are three basic types of transitions one can look at in spectroscopy: electronic, vibrational, and rotational. Electronic transitions are the basic spectroscopy that everyone sees when you look at an excited gas. These are the only transitions possible with atoms. Molecules, however, have two more degrees of freedom: vibrations and rotations. Vibrational motion can be thought of as springs connecting the atoms, allowing the molecule to stretch and bend. The final type of transition is rotations. These are simply the molecule rotating in three dimensions. To probe rotational states, which occur at small energy scales, it is necessary to use microwaves, which have energies comparable to the rotational states.

My first project was data analysis of Nitric acid (HNO_3). Nitric acid is an important in atmospheric studies because of its role in the cycle of ozone layer destruction. Thus, it is essential to have an accurate model of HNO_3 so that its spectrum can be identified when doing atmospheric studies.

I analyzed data in the frequency range of 130-180 GHz and in the three vibrational states 6, 7, 8. These three states were chosen because they are distinct and do not overlap with other states, thus making it easier to analyze the data. Below is a picture of HNO_3 and a selection of the vibrational states of Nitric acid and what they correspond to.

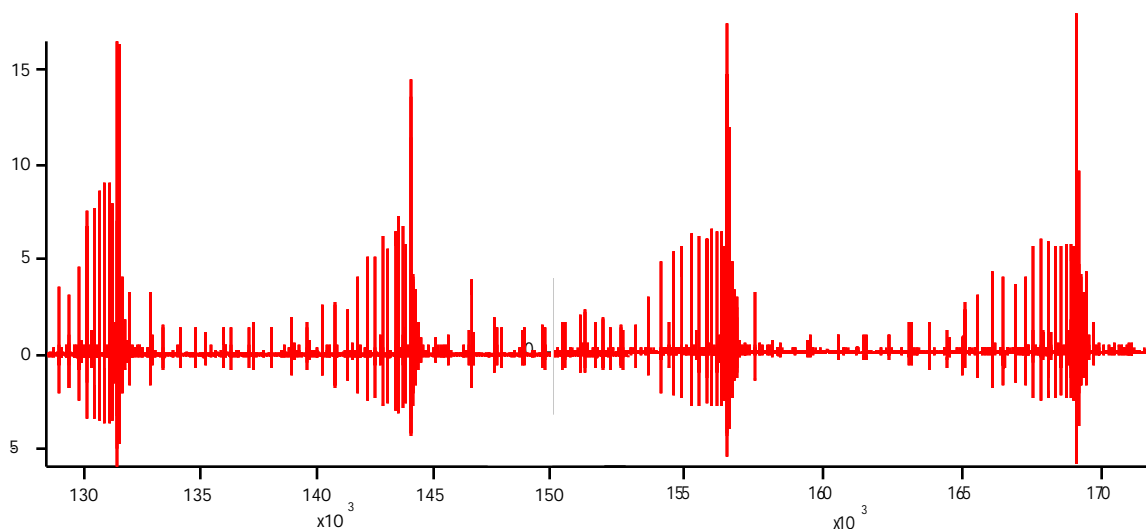


<u>State</u>	<u>Structural Motion</u>
1	O'H Stretch
2	NO antisymmetric stretch
3	HON Bend
4	NO symmetric stretch
6	NO' stretch
7	ONO' bend
8	NO ₂ out of plane

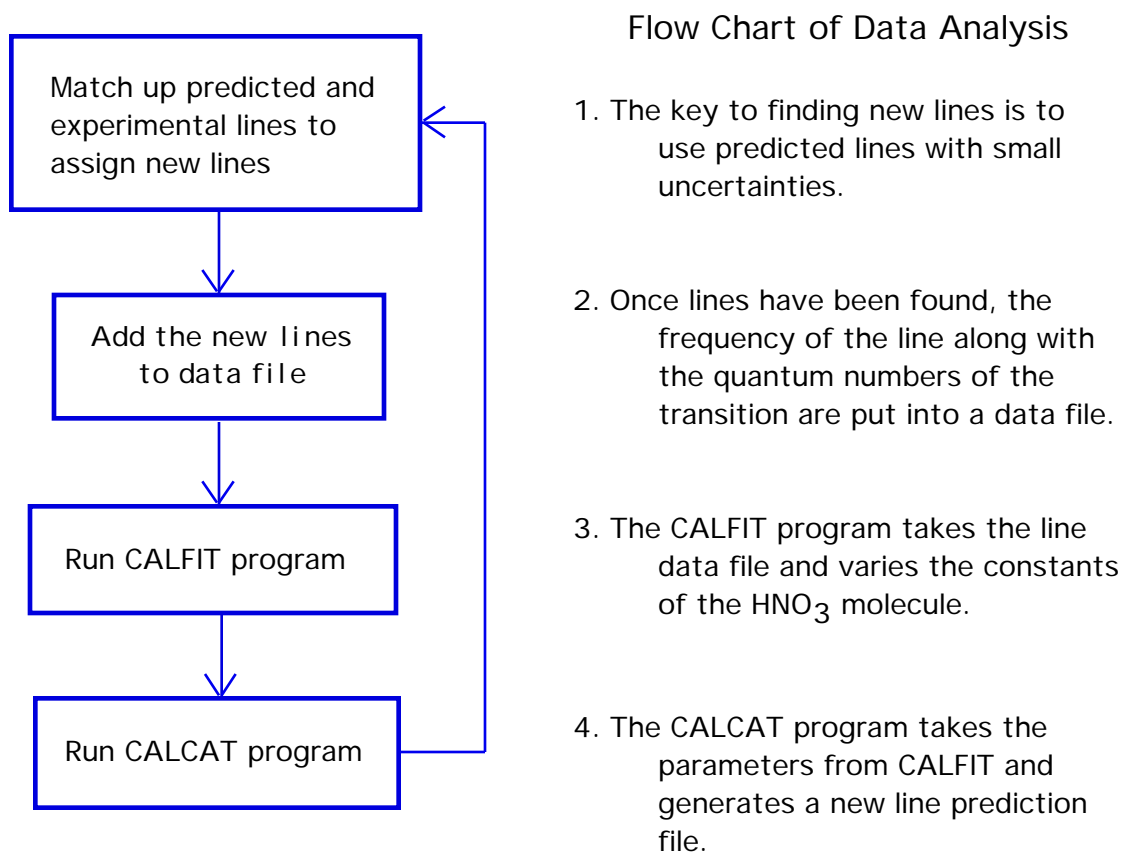
Structure of Nitric Acid

The Data analysis involves several steps. I used the line prediction files of Shaun Williams, a previous graduate student, to start my analysis. The first step is to compare the predicted lines with the actual spectrum and match up predicted and experimental lines. The spectrum of nitric acid from 130-180 GHz is shown below on a very condensed scale.

Nitric Acid spectrum from 128-175 GHz



When assigning lines, it is essential to look at lines that are well predicted to prevent assigning the wrong line to a prediction. The next step is to add the new lines to the data file and run the CALFIT program. The CALFIT program uses a least squares analysis to vary the constants for HNO_3 to find the best fit between the observed line frequencies and what is predicted by the parameters. The constants for HNO_3 describe its' angular momentum around the three principal axes of the moments of inertia and also centrifugal distortions. The final step is to run the CALCAT program to generate a new line prediction file. The flow chart below summarizes the data analysis procedure.



After several iterations of data analysis, I had found just about all the lines possible from my data. Next, I combined my line files with those of Doug Petkie,

professor at Ohio Northern University, to produce one all-encompassing line file. Most recently, I began to analyze the new line files, attempting to produce the best fit by adding and modifying the constants and other parameters for Nitric acid. The final values of the parameters for the three states are listed below.

**Parameters for the 6
vibrational state of Nitric Acid**

const.	value(MHz)	(MHz)
C	6282.33897	0.00056
B	12057.50382	0.00072
A	13006.20264	0.00079
J	-0.00983324	0.00000061
JK	0.00792625	0.00000101
K	-0.00968474	0.00000112
J	-0.003798038	0.000000202
K	-0.00780043	0.00000045
H _J	0.407982533E-08	0.018063707E-08
H _{JK}	-0.170254674E-08	0.056539450E-08
H _{KJ}	0.712134108E-08	0.099533862E-08
H _K	0.251827949E-07	0.008103329E-07
h _J	-0.118590721E-07	0.000652941E-07
h _{JK}	0.473181060E-07	0.002901326E-07
h _K	-0.166931945E-08	0.028708920E-08

**Parameters for the 7
vibrational state of Nitric Acid**

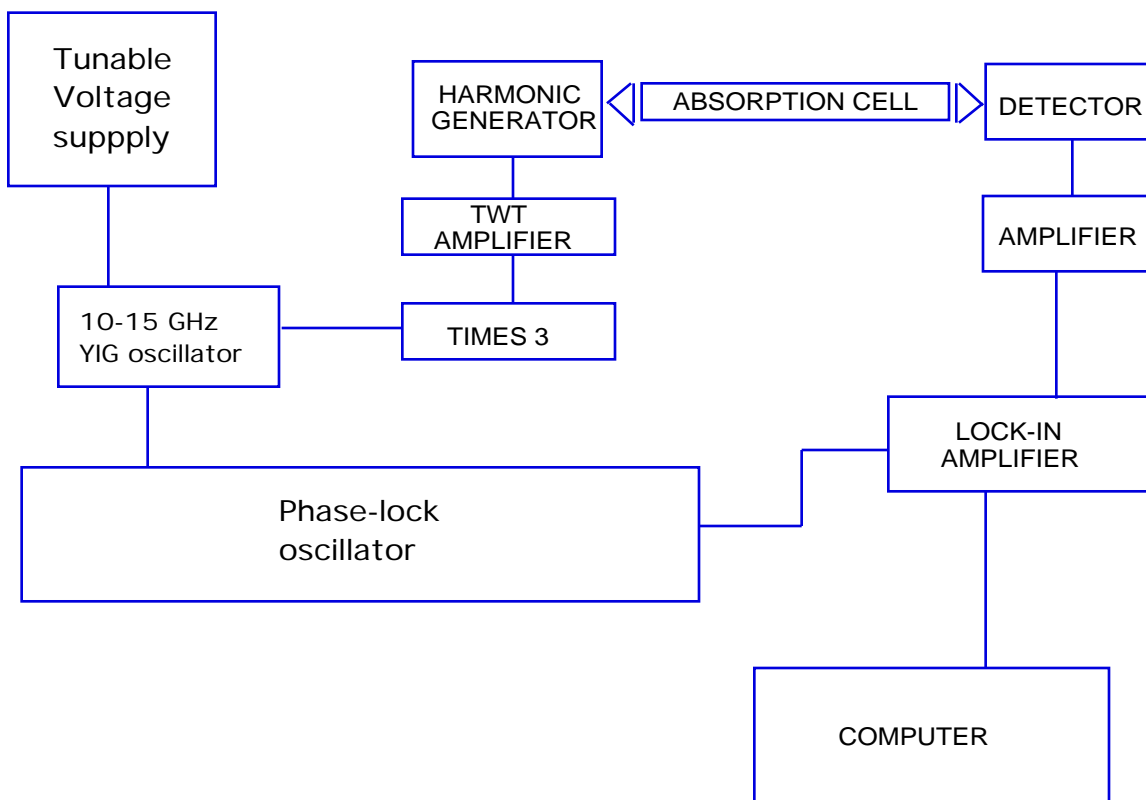
const.	value(MHz)	(MHz)
C	6201.61804	0.00067
B	12098.57039	0.00049
A	13028.97298	0.00053
J	-0.01454483	0.00000088
JK	0.02002371	0.00000248
K	-0.00598775	0.00000190
J	-0.001286024	0.000000273
K	0.0279667	0.0000058
H _J	0.224573171E-07	0.004441855E-07
H _{JK}	-0.404777861E-07	0.044949573E-07
H _{KJ}	-0.153330343E-06	0.011941894E-06
H _K	0.136638425E-06	0.007902337E-06
h _J	-0.726497584E-08	0.016905277E-08
h _{JK}	-0.138286717E-06	0.005038285E-06
h _K	0.298688283E-05	0.003112979E-05
L _{JJK}	0.521973235E-11	0.035872885E-11
L _{JK}	-0.943200500E-10	0.015237679E-10
L _{KKJ}	0.219768772E-09	0.002786252E-09
L _K	-0.129299882E-09	0.001567670E-09

**Parameters for the 8
vibrational state of Nitric Acid**

const.	value(MHz)	(MHz)
C	6260.81195	0.00071
B	12005.52821	0.00107
A	12998.02142	0.00115
J	-0.00889984	0.00000103
JK	0.00374633	0.00000218
K	-0.00635547	0.00000312
J	-0.00377796	0.00000044
K	-0.00680833	0.00000090
H _J	0.127688449E-07	0.004172389E-07
H _{JK}	-0.570800252E-07	0.014171774E-07
H _{KJ}	0.887546480E-07	0.046285603E-07
H _K	-0.175022365E-07	0.054762448E-07
h _J	0.657700164E-08	0.017125579E-08
h _{JK}	0.187834189E-08	0.070260956E-08
h _K	0.221856421E-07	0.012693125E-07

My second project has been working with the Broadband Spectrometer. The essential components of this system are the YIG (Yttrium-Iron-Garnet) oscillator that produces frequencies from 10-15 GHz, an absorption cell, where the molecule being studied is placed, and the detector, which observes the absorption lines.

Schematic of Broadband Spectrometer



This device has been around for years, and was in need of rebuilding several components. My project was to build the tunable voltage supply to the YIG oscillator.

The voltage supply had to be able to do many different things. First, it had to supply a DC voltage between 0-10 Volts. Also, it needed to optionally add a sweep to the DC voltage. For example, instead of supplying 8 volts, it might need to be able to

continuously sweep from 7.9-8.1 volts. Finally, besides doing all this manually, it needed to be able to accept an input voltage and sweep from a computer.

The voltage supply outputs a signal from 0-10 volts. The YIG oscillator takes this voltage and oscillates at a frequency of 10-15 GHz. Next, this signal is multiplied by three to produce a frequency from 30-45 GHz. The amplifier boosts the power of the signal so that useful measurements can be done. The phase-lock oscillator and lock-in amplifier allow much weaker absorption lines to be observed.

Actually constructing the voltage supply was not too difficult, but before beginning work, I had to learn a lot about circuits, especially voltage dividers, impedance and reactance, and high and low pass filters.

Both of my projects went fairly well. I analyzed three vibrational states for Nitric acid (6, 7, 8). I also got a more hands-on approach with electronics, building a tunable voltage supply for the Broadband Spectrometer. My data analysis went very well, though I had trouble adding new parameters to form a better fit for HNO_3 . This is not the type of thing to complain about, though! The voltage supply also works well. I did not get a chance to hook it up to the Broadband system, since another student is upgrading a separate part of the system. Just as important as the research itself is the experience I gained in doing research first-hand; the knowledge of just what research is, and what one does when “doing research”.

References

Booker, Randy, Ph.D. Thesis, Duke University, (1986).

Gordy, W. and R. L. Cook, Microwave Molecular Spectra (Wiley-Interscience, New York, 1984)