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PROGRESS REPORT and RESEARCH PLAN

submitted to

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

for the third year of a project

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF MOLECULES OF ATMOSPHERIC IMPORTANCE

by

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PROGRESS REPORT

In our proposal we laid out work in three areas of relevance to atmospheric science: millimeter and submillimeter spectroscopy, variable temperature pressure broadening, and band and intensity measurements in the FIR. Below we will briefly discuss our progress during the second year of this project. The technical details are contained in the publication listed below as well as in the original proposal.

In our millimeter and submillimeter (mm/submm) spectroscopic work, one of our goals has been to work towards the unification of the rotational (primarily obtained by mm/submm techniques) and rotational-vibrational (primarily obtained by infrared techniques) data sets in the context of theoretically well founded models which take advantage of the strengths of the data from each experimental technique. From the point of view of the development of the optimal data base for atmospheric observations, this is clearly a desirable goal.

During the first year of this project we did an analysis of a weighted, mixed infrared and mm/submm data set of the $n = 0$, 1, and 2 torsional states of the ground vibrational state of HOOH. The purpose of this work is to provide a unified understanding of the spectrum, which is applicable in both the rotational and rotational - vibrational regimes. We have succeed in doing this in the context of a single weighted fit which accounts for both data sets to their respective experimental uncertainty (~0.1 and 10 MHz, respectively). This work is described in more detail in one of the publications listed below. Additionally, we have now done a similar analysis on the $n = 0$ torsional state of ν_3 and begun a similar analysis on ν_6. The ν_3 analysis is complete in that it successfully predicts unobserved mm/submm lines to within the mm/submm linewidth (~ 1 MHz), but the ν_6 work is at a more preliminary state. We will return to this subject in the discussion of our plans for next year.

For several years we have been working on the mm/submm rotational spectra of the many excited vibrational states of HNO_3, again with particular emphasis on the relationships between the mm/submm and infrared spectra. During the first year of this project we were able to use mm/submm spectroscopy to fully resolve the torsional splittings in $2\nu_9$ and ν_5, establish a theoretically well founded quantitative relation between them, and show that both have their physical origin in the torsional motion of the ν_9 mode["Torsional Splitting in the $2\nu_9$ and ν_5 Vibrational Band of HNO_3," T. M. Goyette, C. D. Paulse, L. C. Oesterling, F. C. De Lucia, and P. Helminger, J. Mol. Spectrosc. 167, 365 (1994).]. This result has now been incorporated in a recent reanalysis of the infrared spectrum and has resulted in improved fits -- eliminating what was in retrospect a systematic error associated with this previously unknown effect [L. H. Coudert and A. Perrin, J. Mol. Spectrsoc. 172, 352 (1995).]. This past year we have succeeded in integrating this with the rotational energy level structure of ν_9, $2\nu_9$, and ν_5. One of the publications listed below describes our analysis of the rotational/torsional spectrum of the $2\nu_9/\nu_5$ dyad in more detail and another the analysis of ν_9.

In addition to the $2\nu_9/\nu_5$ dyad, ν_3/ν_4 is also an important for remote sensing. We have begun a project, similar to that discussed above for $2\nu_9/\nu_5$, with similar goals for ν_3/ν_4. This project is more difficult because the higher energy ν_3/ν_4 states result in a weaker pure rotational mm/submm spectrum, however, the overall sensitivity of our systems make it feasible. By means of an analysis of infrared data, we have predicted and assigned a number of mm/submm lines of the ν_3/ν_4 dyad and have begun a mixed fit similar in spirt to those discussed above for HOOH. This shows the feasibility of the overall project and provides a good starting point. We will return to this subject in the discussion of our plans for the upcoming year

During this past year we have devoted a significant effort towards the development of a new Backward Wave Oscillator (BWO) based mm/submm spectrometer. It has the important attributes of being extremely broad banded and simple in addition to those attributes ordinarily associated with phase locked mm/submm spectroscopy: high resolution, accurate frequency calibration, and good sensitivity. In the section below where we discuss our plans, we will provide additional details of this system and its use.

We have also completde and submitted for publication a study of the infrared band intensities of N_2O_5 between 250 cm^{-1} and 650 cm^{-1}. This work is being done in collaboration with Brenda and Manfred Winnewisser of Justus-Liebig Universitat, Giessen, Germany. In addition to our basic laboratory work on this species, we have provided digitized spectra of N_2O_5 (at several temperatures spread over the temperature range of the upper atmosphere) to the Harvard-Smithsonian group for direct use in their recovery of the mixing ratios for this species from atmospheric data.

During this period we have also made a number of variable temperature pressure broadening measurements. Historically, there is little such data and theoretical methods for reliable calculation of these parameters are still in their infancy. Because it will be important for modeling purposes to have well founded theories, we have extended the temperature range over which these measurements are made in order to provide more stringent tests for theory. Of direct relevance to atmospheric science is our recent work on SO_2, which included direct measurements of the transition involved in the most recent observations of the Mt. Pinatubo injected species. This work is reported in one of the publications listed below. More recently we have begun a series of measurements on H_2S.

Finally, we have completed and published a chapter entitled "Rotational Energy Transfer in Small Polyatomic Molecules" for the series *Advances in Atomic Molecular and Optical Physics*. These processes underlie the calculation of pressure broadening and are important to theoretically well founded approaches to this important problem.

PLANS

We have succeeded during the second year of this project to complete a significant amount of the work proposed for the three year period, and we plan to continue to execute the proposal and to take advantage of opportunities as they arise. We will be relatively brief here and refer readers interested in more technical detail to the proposal.

We have now completed a new BWO based spectrometer system which allows us to take continuous scans over ~100 GHz ranges in the mm/submm region. Although the spectroscopic value of such continuous scans has been demonstrated in the infrared, technical difficulties and the very high resolution of mm/submm spectra have resulted in most work here being done piece by piece over relatively small spectral intervals. The basic strategy that makes this new system (which is very simple and powerful) possible is the scan of the BWO frequency at a rate (~ 10^5 linewidths/sec) which 'freezes' any frequency insatiably at subdoppler levels. Frequency calibration is then obtained interferometrically at the level of ~0.1 MHz (3×10^{-6} cm^{-1}) -- the typical measurement accuracy of spectra measured by phase lock systems in this region.

One of our first uses of this system was to record the spectrum of HNO_3. Because of the number of resolution elements, it is difficult to display the results in a fashion which fully shows the information content. Here, we have attempted to so so by displaying a series of four figures (attached) which are successive blow ups in both frequency and amplitude. In the last the frequency scale is expanded by ~ 10^4 and the amplitude by ~ 10^2 from the original. This entire spectrum was recorded in *less than 5 seconds* and, without any signal averaging, has the sensitivity to show a number of highly excited states. A large proportion of features which might at first inspection be considered as noise in the last figure are, in fact, weak lines. We plan that the first new spectroscopic work we do with this system will be the ν_3/ν_4 and ν_2 projects which we discus elsewhere. We also plan to use it in conjunction with our collisional cooling system to produce variable temperature pressure broadening measurements over large portions of the thermally populated rotational manifold of HNO_3.

Another particularly interesting project for this system will be the recording of the complete experimental spectra for several of the most important atmospheric species at a number of temperatures and to compare them with the spectra which are computed from current spectroscopic models. Although these models in general are highly accurate, they have limited accuracy beyond the bounds defined by the experimental data used as the basis for the models. Even for nitric acid, whose spectral properties make it favorable for both infrared and microwave studies, a number of additional lines are easily identifiable.

We are especially interested in the mm/submm spectra of the excited states both because it is significantly less well known than the ground state spectra and because of its close relationship with infrared spectra. Additionally, we plan to use this system to begin investigations of what in our proposal we referred to as "heavy" species: N_2O_5, $ClONO_2$, and the like. These species, which in the infrared ordinarily produce at best partially resolved bands, will be fully resolved in the mm/submm because of the reduction in Doppler width by a factor of 100. However, because of the many low lying vibrational modes and dense rotational structure, the broadband spectra which this new system will be able to produce will be essential for its analysis

Additionally, we plan to complete our work on the ν_3 and ν_6 states of HOOH and publish it. As mentioned above, we have measured and assigned a number of lines in both vibrational states and are making good progress experimentally. For the ν_3 wehave made good progress in integrating it with the infrared data base. Our goal is to be able to achieve the same kind of analysis for these states as we have done for the n = 1 and n = 0 torsional states of the ground vibrational state, an analysis which simultaneously accounts for both the mm/submm and infrared data to their experimental accuracy. This is a substantial project because of the number of interacting states and our goal is to produce a 'universal' model, good throughout the mm/submm/ir. We also plan to finish our work on the ν_3/ν_4 dyad of HNO_3 and to extend this work to higher vibrational states. As we noted in our proposal, the ν_2 is attractive because of its use in atmospheric remote sensing experiments.

For the next stage of our collaboration with the Giessen group of Brenda and Manfred Winnewisser, we have designed and built a collisionally cooled cell for their high resolution Bruker FTIR. In late winter or early spring NASA Global Change Fellow Chris Ball will take the system to Germany and oversee its installation and initial spectral runs. The costs for the trip will be borne by the Max Planck Research Prize money which was awarded jointly to us (FCD/MW) as a recognition of past work and to encourage future collaborations. Because the Giessen laboratory is a member of the ISORAC funded European atmospheric laboratory data collaboration, these collaborations have been especially efficient. We are interested in using this collisionally cooled system both to allow pressure broadening measurements at atmospheric temperatures and to obtain the spectral simplification that occurs at low temperature. For many of the relatively heavy species such as N_2O_5 this simplification is especially important for infrared studies because near ambient temperatures they are largely unresolved.

Summary of planned work:

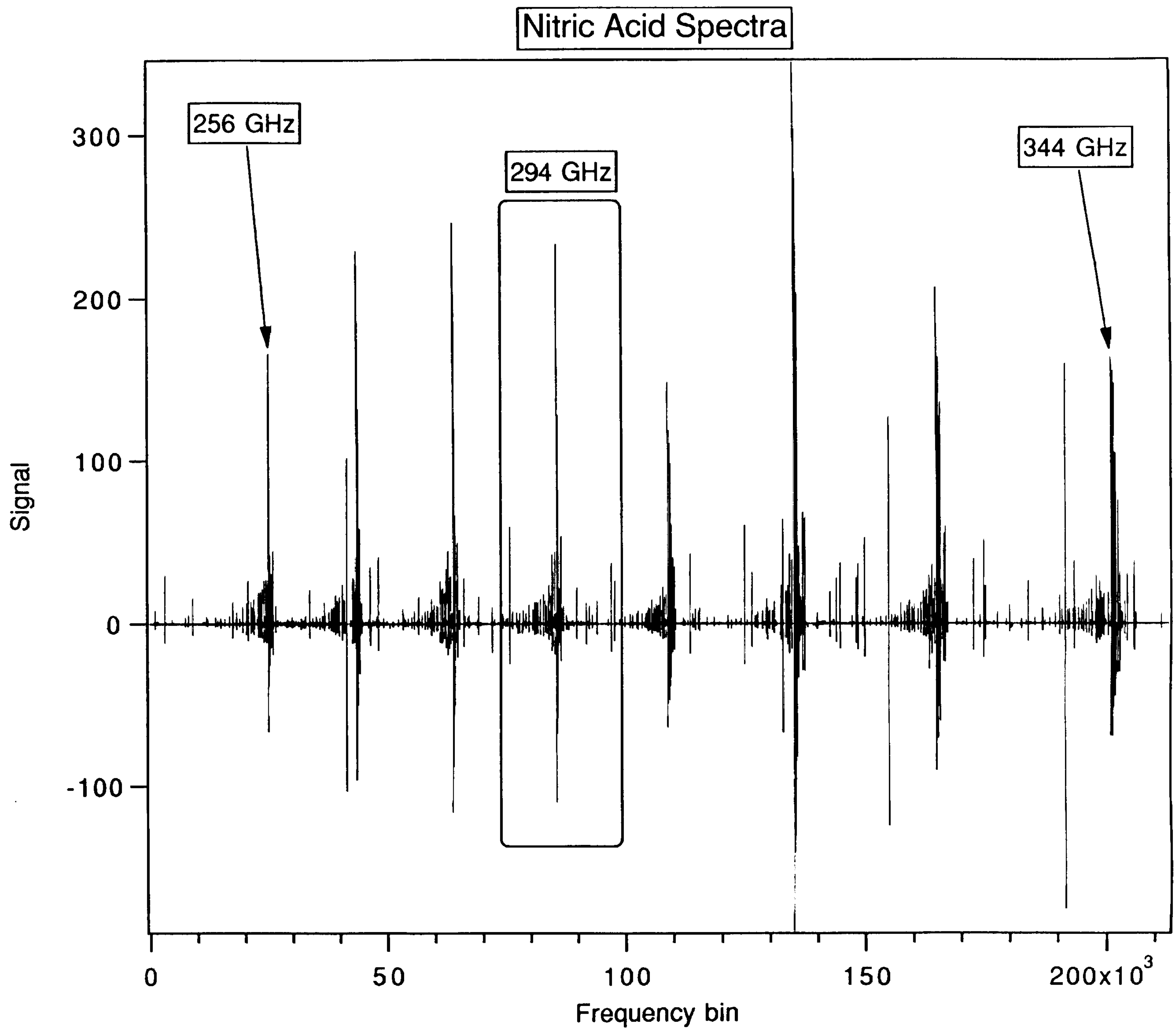
1. Pressure broadening studies of entire rotational manifolds at very high resolution via our new fast scan mm/submm spectrometer and our collisionally cooled cell for the simulation of atmospheric spectra.

2. Comparisons between synthetic spectra calculated from existing spectral data bases and the results of our broad spectral scans.

3. Integration of the infrared and mm/submm spectra for the ν_3/ν_4 dyad and possibly the ν_2 of HNO_3

4. Integration of the infrared and mm/submm spectra for the ν_3 and ν_6 of HOOH.

5. Installation and preliminary measurements of a collisionally cooled spectroscopic cell on the Bruker FTIR system at Giessen for use in collaboration with their ISORAC sponsored research.


Nitric Acid Spectra
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294 GHz
344 GHz
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200
100
0
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Signal
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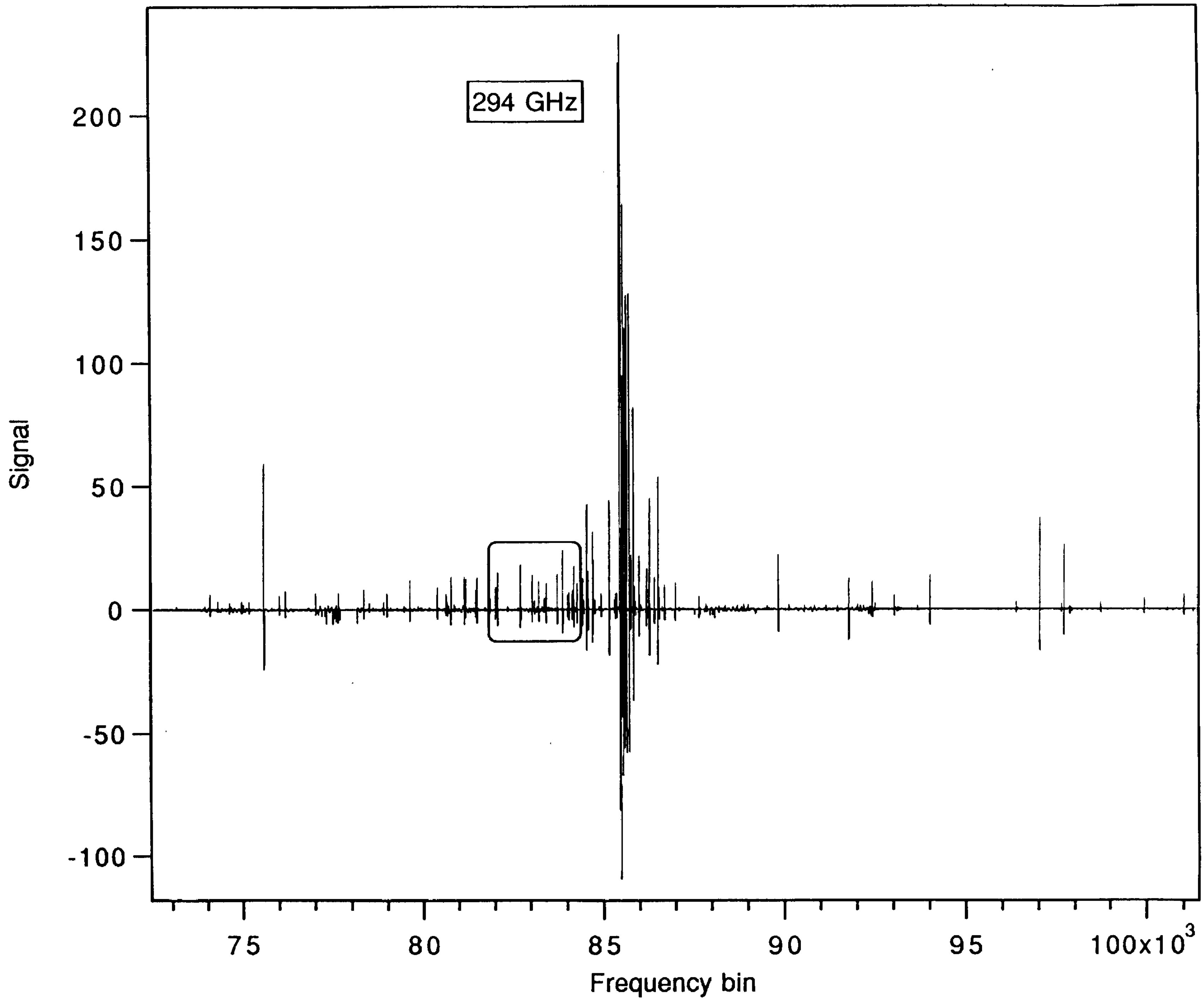
Frequency bin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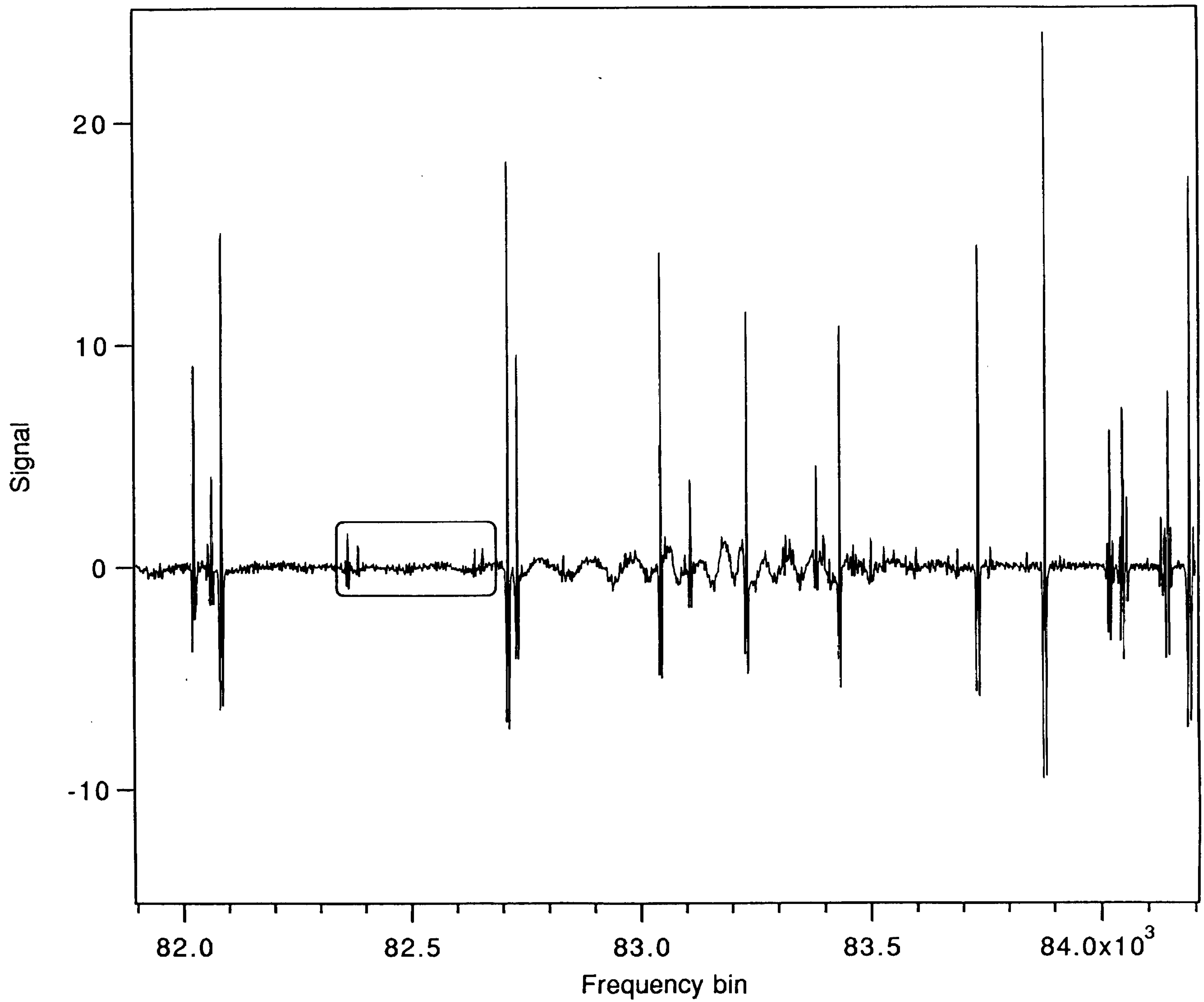
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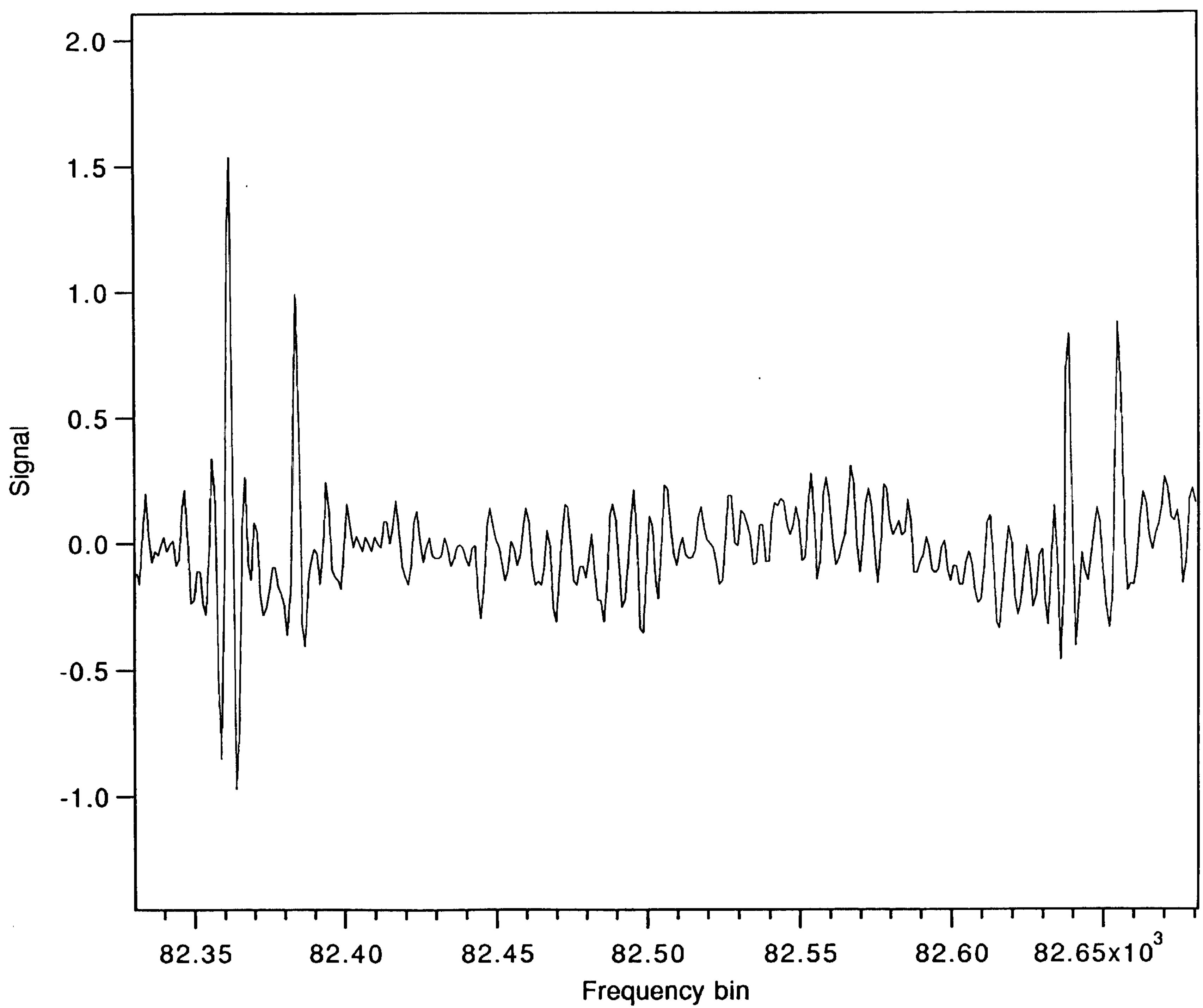
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0.0
-0.5
-1.0
Signal
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82.40
82.45
82.50
82.55
82.60
82.65x10^3
Frequency bin

Publications and presentations for second year of project:

"Millimeter/Submillimeter-Wave Spectrum of the First Excited Torsional State of HOOH," D. T. Petkie, T. M. Goyette, J. J. Holton, F. C. De Lucia, and P. Helminger, J. Mol. Spectrsoc. 171, 145 (1994).

"Rotational Energy Transfer in Small Polyatomic Molecules," H. O. Everitt and F. C. De Lucia, in *Advances in Atomic Molecular and Optical Physics*, Academic Press, San Diego (1995).

"Determination of the Absorbance Cross Sections for N_2O_5 Band Systems in the Region 250-650 cm^{-1}," J. W. G. Seibert, B. P. Winnewisser, M. Winnewisser, F. C. De Lucia, P. Helminger, and G. Pawelke, J. Mol. Spectrosc., submitted.

"Torsional Splitting in the ν_9 Band of Nitric Acid," C. D. Paulse, L. H. Coudert, T. M. Goyette, R. L. Crownover, P. Helminger, and F. C. De Lucia, J. Mol. Spectrsoc., in press.

"Rotational Spectrum of HNO_3 in the ν_5 and $2\nu_9$ Vibrational States," T. M. Goyette, L. C. Oesterling, D. T. Petkie, R. A. Booker, P. Helminger, and F. C. De Lucia, J. Mol. Spectrsoc, in press.

"The Pressure Broadening of SO_2 by N_2, O_2, He, and H_2 between 90 and 500 K," C. D. Ball, J. M. Dutta, T. M. Goyette, P. Helminger, and F. C. De Lucia, J. Mol. Spectrosc., in press.

"Torsional Splitting in the Microwave Spectrum of Nitric Acid; the ν_9 State," C. D. Paulse, L. H. Coudert, T. M. Goyette, P. Helminger, and F. C. De Lucia, 50^{th} Symposium on Molecular Spectroscopy, Columbus, 141 (1995).

"Experimental Techniques using Backward Wave Oscillators," D. T. Petkie, T. M. Goyette, and F. C. De Lucia, 50^{th} Symposium on Molecular Spectroscopy, Columbus, 335 (1995).

1 March 1996 - 28 February 1997	NASA	OSU	Total
1. Salaries and Wages			
Frank C. De Lucia (Professor, The Ohio State University)			
Graduate Research Assistant[1] -- 6 months	7600		7600
Tom Goyette (Research Associate) -- 6 months	18000		18000
Paul Helminger (Prof., University of South Alabama)[2]	26700		26700
2. Capital equipment			
Stabilizer	3150	1350	4500
Oscilloscope	2800	1200	4000
mm/submm components	4200	1800	6000
Klystron/mm source	4200	1800	6000
Data acquisition components	2975	1275	4250
3. Expendable Supplies and Material			
Stock Supplies(electronic components, helium,etc.)	4000		4000
Instrument Shop (200 hr @ $5/hr)	2000		2000
Miscellaneous Electronics	3000		3000
Office Supplies	500		500
Communications and Shipping	1000		1000
4. Travel			
2 trips Mobile / Columbus @$700	1400		1400
1 trips NASA @$970	970		970
5. Employee Benefits			
(Research Associate 15.4%)	2772		2772
(Graduate Research Assistant 1.2%)	91		91
6. Sum of 1, 3, 4, 5, 6 which is subject to overhead[3]	41333		41333
7. Portion of 1 which is not subject to overhead	26700		26700
8. Indirect Costs			
46% of 6	19013		19013
Totals	104371	7425	111796

[1] Stipend only, OSU provides a tuition and fee waiver for graduate students.

[2] Based on the academic summer salary calculation and derived from PAH's nine month salary at the University of South Alabama to provide $356/day for 75 days.

[3] First $25000 of personnel subcontract subject to overhead, cap used in years one and two.