# Summary of Research

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# Theoretical Studies of Molecular Spectra

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# Spectroscopy

The Ames program of the analysis of high dispersion molecular spectra has produced data that is useful to modelers of the earth's and other planetary atmospheres, and also advances the field of spectroscopy in general by improving the base of experimental data that is used to compare theoretical predictions with experiment. The majority of the data comes either from the FTS (Fourier Transform Spectrometer) instrument at the Kitt Peak Solar Telescope, or the Bomem spectrograph at Ames. Ames scientists also collaborate with other institutions such as the Pacific Northwest Laboratories in order to make use of specialized instruments available at other institutions.

I have helped to develop the software that Ames scientists use to analyze the line spectra. I improved the non-linear least squares procedure to fit the line profiles and made other changes that facilitate the derivation of line parameters [position, intensity, pressure broadening, line shape] from the spectra. I also modified and expanded the program to include other capabilities. This has included other types of line profiles which include velocity [Dicke] narrowing. Currently, the program is operating on a Linux workstation and can read many different types of data formats and produce results in the form of tables and plots. This program was migrated from an earlier version that ran on a Sun workstation.

### Oxygen broadening of NO [Nitric Oxide]

Data taken with the Kitt Peak FTS was transferred to Ames for analysis. Because of the high resolution of the current data, all the information about the individual hyperfine components of the NO lines is included in the fit. The resolution of the instrument is high enough to see the influence of the individual hyperfine components, and to resolve the splittings due to the unpaired electron in NO [lambda doubling]. The instrument function was checked by examining sharp $N_2O$ lines. A project on $O_2$ broadening of NO was completed and a paper published [Marley, Mark S.; Seager, S.; Saumon, D.; Lodders, Katharina; Ackerman, Andrew S.; Freedman, Richard S.; Fan, Xiaohui. Clouds and Chemistry: Ultracool Dwarf Atmospheric Properties from Optical and Infrared Colors, *Astrophysical Journal* **568**, 335M (2002)]. This is the first reported measurement of $O_2$ broadening of NO and results were reported for both the Omega = 1/2 (e and f) and the Omega = 3/2 levels.

### Analysis of $CO_2$ spectra

Weak bands of $CO_2$ that arise from excited levels are of great interest in certain astronomical objects such as Venus that have a thick, hot $CO_2$ atmosphere. These bands are usually too weak to measure at room temperature so a very long path length is required. The new measurements will be reported in an upcoming publication and will be compared to theoretical calculations made by Richard Wattson and Lawrence Rothman.

### Analysis of $HNO_3$ spectra

Nitric acid is an important trace constituent in the earth's atmosphere particularly as it influences certain chemical reactions that are important in the stratosphere. Work is under way to measure line strengths for a series of important transitions. Data on $HNO_3$ (Nitric Acid) was analyzed in an attempt to determine the lines strengths for some transitions that are commonly used to determine the abundance in the earth's atmosphere.

This work is complicated by the fact that $HNO_3$ is highly reactive and as the measurements are taking place new compounds are forming in the cell and thus the actual number of molecules of $HNO_3$ is a function of time. This has complicated the efforts to measure the actual line strengths because it is not clear at any given time how much $HNO_3$ is actually in the cell. As the experiment progresses, the original concentration of $HNO_3$ is changing and other molecules such as NO, $NO_2$, $N_2O$, CO, $CO_2$ are being formed along with $H_2O$. It is possible that a new analysis will have to be conducted using data obtained at the Batelle Pacific Northwest Laboratories before this problem can be fully resolved. This newer data was obtained recently in a specially designed call that was gold plated and was taken under conditions that will minimize the problems with the chemical reactions.

**Analysis of CO spectra**

Work is underway on a study to remeasure line strengths in the 1-0 2-0 and 3-0 bands of CO. The results are being used to redetermine the dipole moment function for CO in this region, and thus to predict the line intensities from high J (rotational) levels that only appear at higher temperatures. This project makes use of a number of computer programs that have been obtained from Prof. Robert J. LeRoy for the generation of wavefunctions and RKR (Rydberg-Klein-Reese) potentials for diatomic molecules. Early results have been obtained on the dipole moment function, line intensities and Herman-Wallis factors.

The analysis of the CO 2-0 and 3-0 bands has been almost completed. A paper on some of the results is being readied for publication. Analysis of the 2-0 band is continuing because the very high quality of the data allows us to push the analysis to new limits that have not been possible before. We are deriving improved values for the band and line strengths, and getting values for the line narrowing coefficients. This will eventually lead to a better value for the line broadening and line narrowing coefficients, and to an improved value for the dipole moment function of the ground electronic state of CO. We are also planning to include the effects of velocity dependent line narrowing in our analysis.

## Management of Molecular Databases

I collaborated with Dr. Larry Giver to verify the water lines in the Hitran database. He has published a list of corrections to a list of water lines that he discovered were entered in the database with incorrect line strengths. These have now been incorporated into the Hitran database. I am also collaborating with Dr. Giver and Dr. Peter Pilewskie in their use of an airborne instrument in the lab to calibrate the strength of several water bands that are widely used for remote sensing applications in the earth's atmosphere. This has involved the simulation of numerous water spectra and a comparison with laboratory data that I have reduced from the instrumental data. Water data taken in the Ames Bomem spectrometer is reduced and simulated using programs developed to calculate absorption coefficients and transmissions.

## Generation of Spectral Line Profiles and Opacity Data.

Computer simulations of brown dwarves and extra solar planets were constructed and used to model their emergent radiation [spectra and luminosity] and thus to study their physical properties.

Because of the continuing improvement in the observational data, significant progress has been made in advancing the understanding of these objects. Brown dwarfs are objects that are presumably formed in a similar way to stars, but whose mass is too low to support fusion in the central core. These objects then cool off over time, and as they move along their evolutionary tracks they will mimic first cool, dwarf stars, then they will appear to be sub-stellar objects until finally they fade from view as they become too cool to detect.

The extra solar planet work overlaps with the brown dwarf studies as the techniques used to study these objects are quite similar in nature. The planets may not be formed by the same processes as the brown dwarfs but their atmospheres appear quite similar in their overall structure. The large number of new extra solar planets being discovered means that there is a great deal of interest in studying their overall structure and spectra.

The following topics were addressed in the course of this research: (1) the collection and evaluation of spectroscopic data on a large number of molecules and atoms whose opacities are important in determining the structure of the atmospheres of these objects; (2) the understanding of the broadening mechanisms of the spectral lines [mainly due to molecular hydrogen]; (3) the collection of data on bands which are excited at elevated temperatures [hot bands] even though they are difficult to observe and measure at room temperatures. In order to collect this data I have made use of calculations done by others and by myself to supplement the currently available spectroscopic line lists. My opacity generating program also has the ability to use different types of line shapes and line broadening in order to provide the best match to the physical conditions in these objects.

Collaborators who model brown dwarfs and cool stellar and sub-stellar objects have been concentrating on chemistry problems in the past year. It is important to understand all the chemical processes taking place in the atmospheres of these objects in order to properly predict the relative abundances of a wide variety of gases and solids [minerals] that could be present. Improving the chemical abundance data in our models [as supplied by Katharina Lodders of Washington University, St. Louis] and in incorporating the effects of clouds [formed by molecules such as water, and by solid condensates] into our models took up much of my time this past year. Using new chemical abundance tables from Lodders, I instituted a complete recalculation of various molecular opacities [due to a total of 10 species at present: $H_2O$, $CH_4$, CO, $NH_3$, $H_2S$, $PH_3$, CO, TiO, VO, and FeH] which are now being incorporated into the latest models.

The data for methane [CH4] was upgraded using the latest available predictions from the Dijon group. This allowed better fits in the 1.5 micron region. I have also been collaborating with several other researchers in an attempt to improve the quality of the data available for various molecules such as CrH and VO. As newer data becomes available I incorporate that into my calculations.

I also used the opacities that were calculated for the brown dwarf work to construct tables of Rosseland mean opacities. Preliminary results of this work and its relation to the structure [the adiabatic gradient] of the atmosphere of Jupiter were presented as a poster in collaboration with [and by] Tristan Guillot of the Observatoire de la Cote d'Azur [Nice, France] at a meeting in July 2001.

# Appendix

## Subject Inventions Certification

There were no subject inventions required to be disclosed to NASA which resulted from this work. There were no subcontracts awarded under this Cooperative Agreement.