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Enclosed please find the final technical report for the Cooperative Agreement #301521 for the period April 1, 2000 to March 31, 2003.

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Title: High Resolution Spectroscopy to Support Atmospheric Measurements

Final Technical Report

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Summary of Research:

A summary of the Research activities performed during the period April 1, 2000 to March 31, 2003 under Cooperative Agreement #301521 by Dr. Malathay Devi Venkataraman (PI) is given in the following pages.

Spectroscopic parameters [such as line position, intensity, broadening and shifting coefficients and their temperature dependences, line mixing coefficients etc.] for various molecular species of atmospheric interest were determined. In order to achieve these results, infrared spectra of several molecular bands were obtained using high-resolution recording instruments such as tunable diode laser spectrometer and Fourier transform spectrometers. Using sophisticated analysis routines [Multispectrum nonlinear least squares technique] these high-resolution infrared spectra were processed to determine the various spectral line parameters that are cited above.

Spectra were taken using the McMath-Pierce Fourier transform spectrometer (FTS) at the National Solar Observatory on Kitt Peak, Arizona as well as the Bruker FTS at the Pacific Northwest National Laboratory (PNNL) at Richland, Washington.

Most of the spectra were acquired not only at room temperature, but also at several different cold temperatures. This procedure was necessary to study the variation of the spectral line parameters as a function of temperature in order to simulate the Earth’s and other planetary atmospheric environments. Depending upon the strength [or
weakness] of the various bands recorded and analyzed, the length(s) of the absorption
cells in which the gas samples under study were kept varied from a few centimeters up to
several meters and the sample temperatures varied from approximately +30°C to -63°C.
During the Cooperative Agreement [#301521] period, research on several infrared bands
of various molecular species and their isotopomers were undertaken. Those studies are
briefly described in the following pages.

**Molecules whose spectra were recorded and analyzed consisted of:**
Isotopic methane [CH₃D], Ozone [¹⁶O₃], Ozone isotopomers [¹⁶O¹⁷O¹⁶O & ¹⁶O¹⁶O¹⁷O],
carbon monoxide [CO], Carbon dioxide [CO₂] and hydrogen cyanide [H¹²C¹⁴N].

**Specific molecular bands analyzed are:** The fundamental bands ν₃, ν₅ and the ν₆ of
¹²CH₃D; the combination band ν₁+ ν₃ of ozone isotopomers ¹⁶O¹⁷O¹⁶O & ¹⁶O¹⁶O¹⁷O; the
ν₃ and the ν₁ bands of the main ozone isotopomer ¹⁶O₃; the first overtone band of the
main isotopomer of carbon monoxide [¹²C¹⁶O]; the laser bands of the main isotopomer of
carbon dioxide [¹²C¹⁶O₂] and ¹³C¹⁶O₂ isotopomer.

**A brief description of the various studies is furnished below.**
1. Lorentz self-, and nitrogen-broadening coefficients as well as self-, and nitrogen-
pressure-induced shift coefficients were measured at room temperature for over 440
transitions in the ⁰P, ⁰Q and ⁰R branches of the ν₃ (A₁) parallel band of ¹²CH₃D. The
simultaneous multispectrum nonlinear least squares fitting analysis was performed in the
1140-1440 cm⁻¹ region using 14 spectra of room temperature gas recorded with the
McMath-Pierce FTS. The measured broadening and pressure-shift coefficients were
found to vary with the rotational quantum index numbers J'' and K''. Weak line mixing
effects were observed in several high-J lines with K'' = 3 splitting and approximate values
for the off-diagonal relaxation matrix element coefficients were determined for a few
A₁A₂ split components.

Similar measurements were made for the ν₅(E) perpendicular band of ¹²CH₃D
located between 1275-1600 cm⁻¹ as well as for the ν₆(E) perpendicular band of ¹²CH₃D in
the 1035-1270 cm⁻¹ regions. These studies are important for interpretation of the infrared
spectra of the atmospheres of some of the giant planets and their moons [e.g. Titan]. Knowledge of the spectral line parameters for individual rotation-vibration lines of CH$_3$D is also important for quantitative spectroscopic analysis of industrial and research gas samples containing methane and its isotopomers.

2. Using very high resolution [0.002 cm$^{-1}$] Fourier transform spectra of a $^{17}$O-enriched sample, an extensive analysis of the $v_1+v_3$ bands of the $^{16}$O$^{17}$O$^{16}$O and $^{16}$O$^{16}$O$^{17}$O isotopomers of ozone has been performed for the first time. Using a Hamiltonian matrix which took various resonance’s into account, precise vibrational energies and rotational and coupling constants were deduced, leading to a more accurate band center determination of $v_0 (v_1+v_3) = 2078.3496$ cm$^{-1}$ for $^{16}$O$^{17}$O$^{16}$O and $v_0 (v_1+v_3) = 2098.8631$ cm$^{-1}$ for $^{16}$O$^{16}$O$^{17}$O. These analyses are important because the spectral features of these isotopomers are used in remote sensing studies of ozone in the troposphere and stratosphere. The complete characterization of ozone absorption spectrum, including isotopic and hot bands, is essential to quantitative analysis of atmospheric absorption and emission spectra.

We have also identified for the first time isotopic ozone lines of $^{16}$O$^{16}$O$^{17}$O and $^{16}$O$^{17}$O$^{16}$O in the 5-$\mu$m region. These spectral features were observed in balloon-born high-resolution (0.003 cm$^{-1}$) solar absorption spectra in addition to a few lines that were also observed in the ground-based spectra. These lines are important in the analysis of atmospheric absorption spectra.

In addition to the above discussed ozone bands, we have also measured the absolute intensities of 376 lines of the fundamental $v_1$ and $v_3$ bands of the main isotopomer, $^{16}$O$_3$. These two bands fall in the 9 to 11 $\mu$m region. In this experiment, the ozone samples were contained in a glass cell having crossed IR-transmitting and UV-transmitting paths, and the UV absorption at 254 nm was used to monitor ozone concentration in the cell.

3. We made room temperature measurements of self- and hydrogen-broadening coefficients and pressure shift coefficients for the first overtone (2-0) band transitions of $^{12}$C$^{16}$O through the analysis of several high-resolution FTS spectra. This study presents the first high-resolution experimental determination of hydrogen-induced pressure
broadening and pressure-shift coefficients in the 2-0 band of $^{12}$C$^{16}$O. The results from this work should be useful for interpretation of planetary atmospheres data and also provide a useful and reliable dataset for comparison to theoretical modeling of broadening and pressure shift coefficients involving CO transitions.

4. We have made the first high-resolution measurements of pressure-broadening and pressure-induced shift coefficients due to nitrogen for a large number of rovibrational transitions in the $v_3$ band of $^{13}$C$^{16}$O$_2$. In addition, nitrogen-broadening coefficients for many transitions in the $v_3$+$v_2$-$v_2$ hot band of $^{13}$C$^{16}$O$_2$ as well as the $v_3$ band of $^{13}$C$^{16}$O$^{18}$O were also determined. These results should be valuable not only for predicting the infrared spectrum of the atmosphere due to CO$_2$ absorption or emission but also for verifying theoretical calculations of pressure broadening and pressure shift coefficients in the $v_3$ region of carbon dioxide spectra.

5. Extensive high-resolution experimental determination is also made for air- and N$_2$-broadening and air- and N$_2$ pressure-shift coefficients for the two $^{13}$C$^{16}$O$_2$ laser bands (located at 913.4 and 1076.6 cm$^{-1}$, respectively), in addition to new measurements of self-broadening and self-shift coefficients for the two $^{12}$C$^{16}$O$_2$ laser bands. By combining the spectra of $^{12}$C$^{16}$O$_2$ and $^{13}$C$^{16}$O$_2$ in the same least squares fit we were able to obtain a consistent set of line parameters for both molecules. Absolute line intensities were also determined for the two $^{12}$C$^{16}$O$_2$ laser bands ($v_3$-$v_1$ and $v_3$-2$v_2$) centered near 960.9 and 1063.7 cm$^{-1}$, respectively. Using a multispectrum fitting technique we simultaneously fit 30 spectra in these studies. These results should be included in the future updates of the HITRAN [High resolution TRANsmission] line parameters compilation.

6. The infrared spectrum of HCN in the region between 3150 and 3450 cm$^{-1}$ has been recorded at 0.005 and 0.008 cm$^{-1}$ resolution using two different Fourier transform spectrometers, the McMath–Pierce Fourier transform spectrometer located at the National Solar Observatory (on Kitt Peak) and the Bruker–120HR Fourier transform spectrometer situated at the Pacific Northwest National Laboratory at Richland, Washington. Room temperature measurements were made of positions, absolute
intensities, self-broadening and self shift coefficients for individual lines belonging to the HCN $v_1$ band centered near 3311 cm$^{-1}$. These are to our knowledge the first extensive set of self-broadening and self shift measurements in the band. In addition, intensities, self broadening and self shift coefficients for several lines of the $v_1 + v_2^1 - v_2^1$ hot band and several intensities for lines in the $H^{13}C^{14}N$ and $H^{12}C^{15}N$ isotopomers were also determined. A multispectrum nonlinear least squares fitting algorithm was used to fit the entire spectral region covering the 3200 to 3400 cm$^{-1}$ region of up to 27 spectra simultaneously.

In addition to intensities, air- and $N_2$-broadening, air- and $N_2$-pressure-induced shift coefficients and the temperature dependence exponent of the broadening coefficients and the temperature dependent coefficient of pressure-induced shifts have been determined for transitions of the $v_1$ band of $H^{12}C^{14}N$ from 39 laboratory absorption spectra recorded at 0.005 and 0.008 cm$^{-1}$ resolutions. Two articles have been submitted to the special issue of J. Quant. Spectrosc. Radiat. Transfer that is expected to be out in the fall of 2003.
The following Journal articles and Oral Presentations resulted from the 3-year Cooperative Agreement period.

**Journal Articles:**

1. Measurements of air-broadening, pressure shifting and off-diagonal relaxation-matrix coefficients in the \( v_3 \) band of \( ^{12}\text{CH}_3\text{D} \).

2. Measurements of air broadened width and air-induced shift coefficients and line mixing in the \( v_6 \) band of \( ^{12}\text{CH}_3\text{D} \).

3. Measurements of air broadened width and air-induced shift coefficients and line mixing in the \( v_5 \) band of \( ^{12}\text{CH}_3\text{D} \).

4. Absolute intensities of \( 0_3 \) lines in the 9-11 \( \mu \)m region.

5. The \( v_1+v_3 \) bands of the \( ^{16}\text{O}^{17}\text{O}^{16}\text{O} \) and \( ^{16}\text{O}^{16}\text{O}^{17}\text{O} \) isotopomers of ozone.
   A. Perrin, J.-M. Flaud, F. Keller, M. A. H. Smith, C. P. Rinsland, V. Malathy Devi,
   D. Chris Benner, T. M. Stephen and A. Goldman.

6. Multispectrum analysis of self- and \( \text{N}_2 \)-broadening, shifting and line mixing coefficients in the \( v_6 \) band of \( ^{12}\text{CH}_3\text{D} \).
   V. Malathy Devi, D. Chris Benner, Linda R. Brown, Mary Ann H. Smith, Curtis P.
   Rinsland, Robert L. Sams, Steven W. Sharpe.

7. Multispectrum analysis of self- and nitrogen-broadening, pressure shifting and line mixing in the \( v_3 \) parallel band of \( ^{12}\text{CH}_3\text{D} \).
   V. Malathy Devi, D. Chris Benner, Mary Ann H. Smith, Curtis P. Rinsland, Linda R.
   Brown.
8. Self- and N2-broadening, pressure induced shift and line mixing in the v5 band of $^{12}$CH$_3$D using a multispectrum fitting technique.

9. Determination of self- and H$_2$-broadening and shift coefficients in the 2-0 band of $^{12}$C$^{16}$O using a multispectrum fitting procedure.

10. Weak ozone isotopic absorption in the 5 mm region from high resolution FTIR solar spectra.

11. Nitrogen broadening and shift coefficients in the 4.2 to 5.5-μm bands of CO$_2$.

12. Absolute intensity measurements of the $^{12}$C$^{16}$O$_2$ laser bands near 10μm.

13. Multispectrum analysis of pressure broadening and pressure shift coefficients in the $^{12}$C$^{16}$O$_2$ and $^{13}$C$^{16}$O$_2$ laser bands.

15. A multispectrum analysis of the $v_1$ band of $^{12}C^{14}N$: II. Air- and N$_2$-broadening, shifts and their temperature dependences. 


Oral Presentations:


Aoaeh, B.; Kolodziejski, N.; Mantz, A.W.; Benner, D.C.; Malathy Devi, V.; Smith, M.A.H.; Ball, C.D.; and De Lucia, F.C.: Measurements of the 1-0 band of carbon monoxide at temperatures between 11 and 296 Kelvins. Presented at the 55th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 12-16, 2000 (Paper ME07, p. 77)


Malathy Devi, V.; Benner, D.C.; Smith, M.A.H.; Rinsland, C.P.; Brown, L.R.; and Sams, R.L.: Nitrogen broadening and shift coefficients in the $v_5$ and $v_6$ fundamental bands of $^{12}$CH$_3$D. Presented at the 55th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 12-16, 2000 (Paper WG10, p.170).

Brown, L.R.; Malathy Devi, V.; Benner, D.C.; Smith, M.A.H.; Rinsland, C.P.; and Sams, R.L.: Analysis of self-broadened spectra in the $v_5$ and $v_6$ fundamental bands of $^{12}$CH$_3$D. Presented at the 55th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 12-16, 2000 (Paper WG11, p. 171).

Smith, M.A.H.; Rinsland, C.P.; Malathy Devi, V.; Benner, D.C.; and Brown, L.R.: Nitrogen- and self-broadening and shift coefficients in the $v_3$ fundamental band of $^{12}$CH$_3$D. Presented at the 55th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 12-16, 2000 (Paper WG12, p.171).

Benner, D.C.; Malathy Devi, V.; Brown, L.R.; Smith, M.A.H.; and Rinsland, C.P.: Line mixing in the triad of $^{12}$CH$_3$D. Presented at the 55th Ohio State University

Smith, M.A.H.; Malathy Devi, V.; Benner, D.C.; Brown, L.R.; and Sams, R.L.: Air-, N_2- and self-broadening and shift coefficients and line mixing in the \nu_3, \nu_5 and \nu_6 bands of \textsuperscript{12}CH_3D. Presented at the Sixth Biennial HITRAN Conference, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, June 19-21, 2000 (Paper P21, p. 37).

Nikitin, A.; Champion, J.P.; Brown, L.R.; Malathy Devi, V.; Benner, D.C.; Smith, M.A.H.; and Tyuterev, V.G.: Line strengths of CH_3D in the region 900 - 3500 cm\textsuperscript{-1}. Presented at PRAHA2000, the 16th International Conference on High Resolution Molecular Spectroscopy, Prague, Czech Republic, September 3-7, 2000 (Paper D11).


Smith, M.A.H., Rinsland, C.P., Benner, D.C., Malathy Devi, V., and Dulick, M.: Broadening and shift coefficients in the 3 µm bands of HCN. Presented at the
57th International Symposium on Molecular Spectroscopy, Ohio State University, June 17-21, 2002 (Paper MH05).

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