Final Report

HALOE Science Investigation
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I. Introduction

This cooperative agreement has investigated a number of spectroscopic problems of interest to the Halogen Occultation Experiment (HALOE). The types of studies performed are in two parts, namely, those that involve the testing and characterization of correlation spectrometers and those that provide basic molecular spectroscopic information. In addition, some solar studies were performed with the calibration data returned by HALOE from orbit.

II. Instrumental Studies

Analysis of data from a gas correlation spectrometer requires considerable knowledge of the characteristics of the spectrometer. All calculations must be performed monochromatically, then the total signal integrated. This ability is required also for some of the testing of the instrument prior to launch. In order to accomplish this a software package was written as part of this cooperative agreement. The HALOE spectroscopic instrument package is a general purpose code that is not designed for sufficient efficiency for final analysis from a gas correlation spectrometer, but provides flexibility for instrumental studies which is far wider than the more efficiently written retrieval software.

The HALOE spectroscopic instrument package was used in various tests of the HALOE flight instrument. These included the spectral response test, the early stages of the gas response test and various spectral response tests of the detectors and optical elements of the instruments.

Considerable effort was also expended upon the proper laboratory setup for many of the prelaunch tests of the HALOE flight instrument, including the spectral response test and the gas response test. These tests provided the calibration and the assurance that the calibration was performed correctly.
III. Spectroscopic Studies

Numerous spectroscopic studies were performed under this cooperative agreement. These studies are documented in the publications listed in section V. Two of the studies are ongoing and these will be published in more detail as they are completed. The studies have all been included or will be included, if appropriate, in the United States Air Force’s HITRAN database of spectroscopic line parameters.

Techniques of analysis of experimental spectroscopic data have been given high priority in these studies. The standard least squares spectrum fitting technique was expanded to much larger cases than had ever been tried before and the technique was expanded to the simultaneous analysis of many spectra acquired under different physical conditions and even with different spectrometers. These new techniques are orders of magnitude more rapid than the former techniques and with the rapid increase in speed of computers during this time, projects that were once unimaginable are now routine. In addition, the multispectrum technique makes the detection and measurement of parameters such as line mixing relaxation matrix elements possible for the first time from experimental data.

A very large, detailed study of the carbon dioxide molecule was successfully undertaken. The largest studies were undertaken in the spectral regions of the HALOE NO and CO₂ channels, but the regions studied actually were much broader than these channels. This large number of spectral line identifications, positions and intensities made it possible for Richard Wattson to improve the theoretical model of this molecule. The result has been a large improvement in the CO₂ spectroscopic line parameters available to HALOE in all spectral regions. The study in the region of the HALOE CO₂ channel and the studies of minor isotopomers are ongoing.
The methane molecule was also targeted as one that required better understanding in order to retrieve mixing ratios by way of the HALOE orbital data. Here, the theory upon which the experimental data could be analyzed was much less complete. During the time of this cooperative agreement, there was considerable improvement in the ability to theoretically predict positions and intensities of methane spectral lines by a French group. This enabled us to experimentally measure these same quantities as well as the widths and shifts (and their temperature dependencies) of these spectral lines which have proven too difficult to calculate from theory. The resulting spectral line parameters were disappointing in their ability to reproduce the experimental spectra from which they were derived. Application of Dicke line narrowing to the spectral lines was of no help. Application of line mixing in the Rosenkrantz approximation showed great promise, but further analysis showed that this approximation is not expected to be very accurate in the case of methane in the spectral region of the HALOE HCl and methane channels. A simple theory was applied to calculate the relaxation matrix elements and then exact line mixing theory applied to the calculation of the spectrum. The success of this technique was spectacular when only spectra from a single broadener at a single temperature were included. This theory was used to derive new spectral line parameters for both air and self broadening including temperature dependence for the air broadening. These parameters are the best now available for methane in this spectral region and were incorporated into the version 19 HALOE retrievals.

A number of other studies were undertaken for other reasons. These ranged from assistance in a larger study of ozone which has a large impact upon the HALOE ozone and HCl channels, a study of the temperature dependence of the halfwidths and shifts of methane spectral lines in the spectral region of the HALOE HF channel and various studies of minor isotopomers or spectral regions not used by HALOE which have lesser or no effect on the HALOE retrievals. These latter studies contribute to the overall theory of the molecules in question and improvement in this theory produces improved spectral lines where HALOE needs them.

Spectroscopic efforts under this study also included keeping the HALOE project abreast of relevant studies by other groups concerning newly measured or predicted spectral line parameters.
IV. Solar Studies

Philip Spickler used the HALOE solar scan data to study the surface of the sun for his Ph.D. dissertation. The center to limb brightness function of the quiet sun was measured in the 2.5 to 10 micrometer spectral region to much greater precision than ever before. The relative brightness over the surface of the sun was measured to better than 0.1%. The results of this study along with comparisons to what is predicted by solar atmospheric models is reported in a 1996 Solar Physics article (see section V). The center to limb intensity functions were quite different from those predicted by earlier studies, but that observed was consistent with the current temperature models of the sun.

These solar studies have also been supplemented with similar studies of some sunspots. The results show a considerable variation in the temperature structure of sunspots. This work appears in part in the dissertation and is an ongoing study.
V. Publications

D. C. Benner, C. P. Rinsland, D. J. Richardson, T.-H. Soo and M. A. H. Smith

Absolute Intensity Measurements of the (111O)\_\text{\textsubscript{\textit{II}}} - OOOO Band of \textsuperscript{12}C\textsuperscript{16}O\textsubscript{2} at 5.2 \textmu m.
Curtis P. Rinsland, D. Chris Benner, Donald J. Richardson and R. A. Toth


Curtis P. Rinsland, D. Chris Benner, V. Malathy Devi, Penelope S. Ferry, Carolyn H. Sutton and
Donald J. Richardson

Absolute Intensity Measurements of CO\textsubscript{2} Bands in the 2395-2680-cm\textsuperscript{-1} Region.
V. Malathy Devi, Curtis P. Rinsland, and D. Chris Benner

Absolute Intensities of Spectral Lines in Carbon Dioxide Bands Near 2050 cm\textsuperscript{-1}.
Curtis P. Rinsland and D. Chris Benner

Identification and Intensities of the "Forbidden" \textit{3v}\textsubscript{3} Band of \textsuperscript{12}C\textsuperscript{16}O\textsubscript{2}.
D. Chris Benner and Curtis P. Rinsland

Measurements of Absolute Line Intensities in Carbon Dioxide Bands Near 5.2 \textmu m.
Curtis P. Rinsland, D. Chris Benner and V. Malathy Devi

Measurements of \textsuperscript{12}CH\textsubscript{4} \textit{v}\textsubscript{4} Band Halfwidths Using a Tunable Diode Laser System and a Fourier
Transform Spectrometer.
V. Malathy Devi, Curtis P. Rinsland, Mary Ann H. Smith and D. Chris Benner
Tunable Diode Laser Measurements of Widths of Air- and Nitrogen-broadened Lines in the $v_4$ Band of $^{13}$CH$_4$.
V. Malathy Devi, Curtis P. Rinsland, Mary Ann H. Smith and D. Chris Benner

Tunable Diode Laser Measurements of Air- and N$_2$-broadened Halfwidths in the $v_2$ Band of D$_2$O.
V. Malathy Devi, C. P. Rinsland, D. Chris Benner and M. A. H. Smith

Absolute Intensities and Self-, N$_2$-, and Air-broadened Lorentz Halfwidths for Selected Lines in the $v_3$ Band of $^{12}$CH$_3$D from Measurements with a Tunable Diode Laser Spectrometer.
V. Malathy Devi, Curtis P. Rinsland, D. Chris Benner, Mary Ann H. Smith and K. B. Thakur

Diode Laser Measurements of Air and Nitrogen Broadening in the $v_2$ Bands of HDO, H$_2$O and H$_2$H$_2$O.

Absolute Line Intensity Measurements in the $v_2$ Bands of HDO and D$_2$O Using a Tunable Diode Laser Spectrometer.
K. B. Thakur, C. P. Rinsland, M. A. H. Smith, D. Chris Benner and V. Malathy Devi
Journal of Molecular Spectroscopy 120, 239 (1986).

Diode Laser Measurements of Intensities and Halfwidths in the $v_6$ Band of $^{12}$CH$_3$D.
V. Malathy Devi, D. Chris Benner, Curtis P. Rinsland, Mary Ann H. Smith and K. B. Thakur

Measurements of Air-Broadened and Nitrogen-Broadened Lorentz Width Coefficients and Pressure Shift Coefficients in the $v_4$ and $v_3$ Bands of $^{12}$CH$_4$
Curtis P. Rinsland, V. Malathy Devi, Mary Ann H. Smith and D. Chris Benner

Air-Broadened Lorentz Halfwidths and Pressure-Induced Line Shifts in the $v_4$ Band of $^{13}$CH$_4$
V. Malathy Devi, Curtis P. Rinsland, Mary Ann H. Smith and D. Chris Benner

Measurements of Air-Broadened and Nitrogen-Broadened Halfwidths and Shifts of Ozone Lines Near 9 $\mu$m.
Absolute Intensities of CO$_2$ Lines in the 3140 to 3410 cm$^{-1}$ Spectral Region
D. Chris Benner, V. Malathy Devi, Curtis P. Rinsland and Penelope S. Ferry-Leeper

Measurements of Argon-broadened Lorentz Width and Pressure Induced Line Shift Coefficients in the $v_4$ band of $^{12}$CH$_4$.
C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. C. Benner

Measurements of Air-, N$_2$-, and O$_2$-Broadened Halfwidths and Pressure-Induced Line Shifts in the $v_3$ Band of $^{13}$CH$_4$
V. Malathy Devi, D. Chris Benner, Mary Ann Smith and Curtis P. Rinsland

Measurements of Lorentz Broadening Coefficients and Pressure Induced Line Shift Coefficients in the $v_3$ Band of D$_2$O
Curtis P. Rinsland, Mary Ann H. Smith, V. Malathy Devi and D. Chris Benner

Measurements of Lorentz Broadening Coefficients and Pressure Induced Line Shift Coefficients in the $v_2$ Band of HD$^{16}$O
C. P. Rinsland, M. A. H. Smith, V. Malathy Devi and D. Chris Benner

Measurements of Pressure Broadening and Pressure Shifting by Nitrogen in the 4.3 μm Band of $^{12}$C$^{16}$O$_2$
V. Malathy Devi, D. Chris Benner, Curtis P. Rinsland and Mary Ann H. Smith

Methane and Its Isotopes: Current Status and Prospects for Improvement

The HITRAN Molecular Database: Editions of 1991 and 1992

Temperature Dependence of Broadening and Shifts of Methane Lines in the $v_4$ Band
M. A. H. Smith, C. P. Rinsland, V. Malathy Devi and D. Chris Benner
Measurements of Pressure Broadening and Pressure Shifting by Nitrogen in the \( v_1 \) and \( v_3 \) Bands of \( \text{H}_2^{16}\text{O} \)
V. Malathy Devi, D. Chris Benner, Mary Ann H. Smith and Curtis P. Rinsland

Measurements of Lorentz-Broadening Coefficients and Pressure-Induced Line Shift Coefficients in the \( v_1 \) Band of HD\(^{16}\text{O} \) and the \( v_3 \) Band of D\(_2^{16}\text{O} \)
Curtis P. Rinsland, Mary Ann H. Smith, V. Malathy Devi and D. Chris Benner

Measurements of Air Broadening and Pressure Shifting of Methane Lines in the 2.3 \( \mu \)m Region
V. Malathy Devi, D. Chris Benner, Mary Ann H. Smith and Curtis P. Rinsland

The Fundamental Bands of \( \text{H}^{35}\text{Cl} \) and \( \text{H}^{37}\text{Cl} \: \) Line Positions from High-Resolution Laboratory Data
C. P. Rinsland, M. A. H. Smith, A. Goldman, V. Malathy Devi and D. Chris Benner

Air-, \( \text{N}_2 \)-, and \( \text{O}_2 \)-Broadening and Shift Coefficients in the \( v_1 \) Spectral Region of \( {^{12}\text{CH}_4} \).
D. Chris Benner, V. Malathy Devi, Mary Ann H. Smith and Curtis P. Rinsland

Temperature Dependence of Lorentz Air-broadening and Pressure-shift Coefficients of \( {^{12}\text{CH}_4} \) Lines
in the 2.3-\( \mu \)m Spectral Region
V. Malathy Devi, D. Chris Benner, M. A. H. Smith and C. P. Rinsland

A Multispectrum Nonlinear Least Squares Fitting Technique
D. Chris Benner, Curtis P. Rinsland, V. Malathy Devi, Mary Ann H. Smith and David Atkins

Solar Center to Limb Infrared Intensity from the Halogen Occultation Experiment
Philip T. Spickler, D. Chris Benner and James M. Russell, III

Validation of HALOE \( \text{CH}_4 \) Measurements from the UARS
Infrared Spectroscopy of the CO\textsubscript{2} Molecule
V. Malathy Devi, D. Chris Benner, C. P. Rinsland, M. A. H. Smith and D. S. Parmar

Solar Infrared Relative Intensity Data From the Halogen Occultation Experiment
Philip T. Spickler

Air-Broadening and Shift Coefficients of O\textsubscript{3} Lines in the v\textsubscript{2} Band and their Temperature Dependence
V. Malathy Devi, D. Chris Benner, M. A. H. Smith and C. P. Rinsland
Journal of Molecular Spectroscopy 182, 221-238 (1997)

Temperature Dependence of Air-Broadening and Shift Coefficients of O\textsubscript{3} Lines in the v\textsubscript{1} Band
M. A. H. Smith, V. Malathy Devi, D. Chris Benner and C. P. Rinsland

Air- and N\textsubscript{2}-broadening Coefficients and Pressure-Shift Coefficients in the \textsuperscript{12}C\textsuperscript{16}O\textsubscript{2} Laser Bands
V. Malathy Devi, D. Chris Benner, Mary Ann H. Smith and Curtis P. Rinsland

Pressure Broadening and Pressure Shift Coefficients in the 2v\textsubscript{2}\textsuperscript{0} and v\textsubscript{1} Bands of \textsuperscript{16}O\textsuperscript{13}C\textsuperscript{18}O
V. Malathy Devi, D. Chris Benner, Mary Ann H. Smith and Curtis P. Rinsland

Spectroscopic Parameters for Ozone and Its Isotopes: Current Status, Prospects for Improvement,
and the Identification of \textsuperscript{16}O\textsuperscript{16}O\textsuperscript{17}O and \textsuperscript{16}O\textsuperscript{17}O\textsuperscript{16}O Lines in Infrared Ground-based and Stratospheric Solar Absorption Spectra

Self-Broadening and Self-Shift Coefficients in the Fundamental Band of \textsuperscript{12}C\textsuperscript{16}O
V. Malathy Devi, D. Chris Benner, Mary Ann H. Smith and Curtis P. Rinsland

Absolute Rovibrational Intensities of \textsuperscript{12}C\textsuperscript{16}O\textsubscript{2} Absorption Bands in the 3090 to 3900-cm\textsuperscript{-1} Spectral Region
V. Malathy Devi, D. Chris Benner, Curtis P. Rinsland and Mary Ann H. Smith