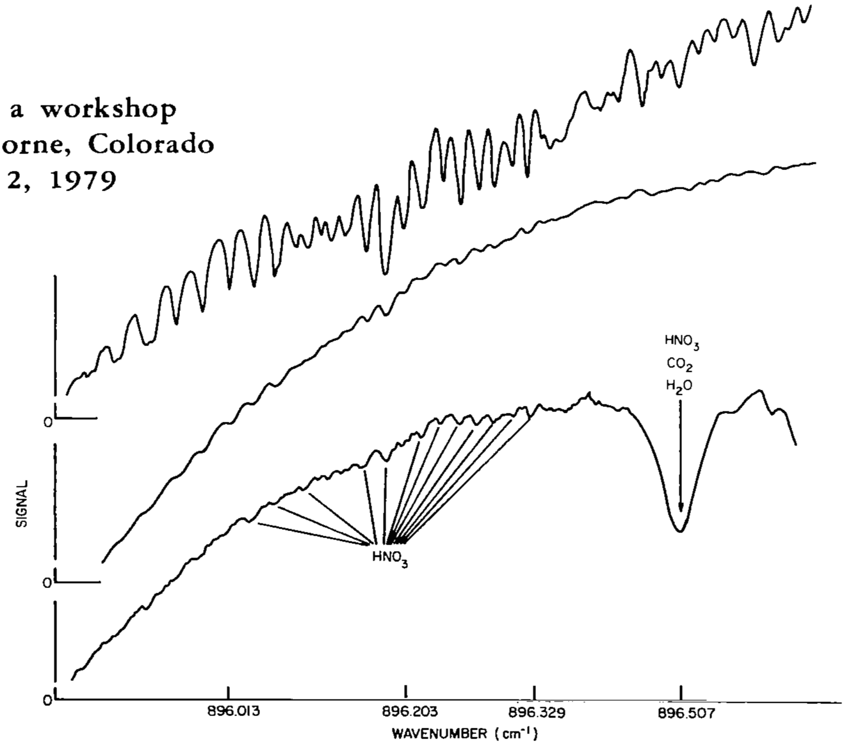
NASA Conference Publication 2134

High Resolution Infrared Spectroscopy Techniques for Upper Atmospheric Measurements

Proceedings of a workshop
held at Silverthorne, Colorado
July 31-August 2, 1979



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High Resolution Infrared Spectroscopy Techniques for Upper Atmospheric Measurements

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PREFACE

This conference publication contains the proceedings of the Workshop on High Resolution Infrared Spectroscopy Techniques for Upper Atmospheric Measurements held at Silverthorne, Colorado, July 31 to August 2, 1979. The workshop was sponsored by NASA and chaired by Dr. David G. Murcray of the University of Denver. These proceedings were edited by Dr. Murcray and by Mr. José M. Alvarez of Langley Research Center.

The major objectives of this workshop were to consider the future role of high resolution infrared techniques in performing measurements in the stratosphere and to consider the role of laser heterodyne techniques in the NASA Upper Atmospheric Research Program Plan in satellite, Space Shuttle, and balloon borne investigations. The workshop was organized into four working groups: Measurements and Data Base group, Spectral Scanning Instrumentation group, Laboratory Spectroscopy group, and Species-Specific Instrumentation group.

The findings and recommendations of each working group are presented sequentially. The general workshop discussion follows as a separate section. The Laboratory Spectroscopy working group decided to follow up on its recommendations and it met once more at Langley Research Center on October 29-30, 1979. The results of that additional session are given in appendix 4 and are published as NASA CP-2136.

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I. EXECUTIVE SUMMARY

The "Workshop on High Resolution Infrared Spectroscopy Techniques for Upper Atmospheric Measurements" held at Silverthorne, Colorado, July 31 to August 2, 1979, was convened to assess the role of high resolution techniques in measurements of trace gases in the stratosphere. The Workshop brought together scientists engaged in laboratory and upper atmosphere, high resolution infrared spectroscopy to review and determine the capabilities of proposed infrared instruments for measurements of stratospheric trace constituents, with particular emphasis on laser heterodyne techniques.

High resolution infrared heterodyne techniques offer high potential in improving the current measurement sensitivity of stratospheric constituents by extending the spectral resolution of infrared measurements to values equal to or less than the width of Doppler broadened lines in the stratosphere. In order to determine the optimum scientific investigations involving several instrument techniques from satellite, Spacelab, and balloon platforms for the NASA Upper Atmospheric Research Program (UARP), the capability of high resolution techniques ($\Delta\nu \leq 0.001$ cm^{-1}) must be assessed with the capability of moderate resolution techniques ($\Delta\nu \leq 0.02$ cm^{-1}), including interferometers, gas filter correlation radiometers, and grating spectrometers. A major criterion involved in future development of heterodyne techniques in UARP involves the broader question of the role of high resolution techniques in providing improved measurements of source, sink, and radical gas molecules in the stratosphere, beyond for example the currently projected spectral resolution of 0.02 cm^{-1} proposed for the ATMOS Spacelab experiment.

An output of the Workshop was a series of recommendations on the use of heterodyne techniques in future scientific investigations of the stratosphere. These recommendations were based upon a Measurement and Data Base strategy recommended by the report of one of the Working Groups. Stratospheric molecules were categorized by available stratospheric measurements as follows:

Priority I - Molecules predicted to be present in the upper atmosphere but not yet detected (N_2O_5, HOCl, HO_2, H_2O_2) or those with very limited detection ($ClONO_2$, OH). Careful measurements of these molecules at any time or place are of significant scientific value.

Priority II - Molecules which have been measured a few times by one or more instruments but with as-yet-unresolved interpretation problems including ClO, NO, NO_2, HNO_3, H_2O, HCl, HF, O, NO_3, and Cl. For such molecules, individual measurements were determined to be of less scientific value except as a demonstration of new technology. Therefore, crucial measurements for these molecules need to be designed to answer specific scientific questions, through carefully coordinated experiments which may consist of simultaneous measurements of other species in the same volume element at the same time, or of some unique spatial and/or temporal organization of the measurements.

Priority III - Molecules which have been well measured (or thought to be) in the upper atmosphere including O_3, N_2O, CF_2Cl_2, $CFCl_3$, and CH_4. These molecules are candidates for long term monitoring to detect trends in their concentrations and a need exists for the development of accurate measurement techniques that can be routinely operated over long periods of time.

The Workshop participants were not able to quantify the role of high resolution techniques in improving current measurements of the various classes of molecules due to the combined uncertainty of future requirements in measurement sensitivity and due to the uncertainty of proposed satellite and Spacelab instruments to achieve their experiment objectives. However, the Full Workshop was able to arrive at several recommendations:

1. Infrared heterodyne techniques should be considered primarily for Priority I molecules since they may represent a unique infrared measurement technology for this class of stratospheric molecules.

2. The laboratory data base for molecular species needs to be increased and focused toward high priority molecules proposed or currently measured by infrared instruments (i.e., ATMOS, HALOE, LHS).

3. Development of tunable semiconductor lasers from 3-30 μm to be used in LHS investigations should be continued in view of the need for measurements of stratospheric species not as yet detected or predicted by the photochemical models.

4. Scientific investigations by an LHS-type instrument should be conducted first from balloons to help obtain at least localized measurements of stratospheric source, sink, and radical species of the three major chemical families.

No general agreement of the Workshop was reached on the role of high resolution techniques in satellite investigations, but the participants emphasized that great potential scientific benefit could be obtained in collaborative investigations of LHS with ATMOS- or HALOE-type instruments. Because of this potential, the Workshop participants emphasized that LHS-type instruments proposed for space investigations should be developed for long-duration, free flyer applications. Spacelab instruments should have sufficient scientific value on their own in this field, and the value of putting an LHS with ATMOS, for example, could provide significant scientific measurements for improving interpretation of ATMOS measurements where limitations of resolution lead to questions in the interpretation of scientifically important species. However, it is conceivable that the LHS-type technology can be demonstrated successfully on aircraft or balloons, leading directly to free flyer applications.

II. INTRODUCTION

Infrared techniques have been used extensively for many years to obtain information on the physical state and composition of the Earth's atmosphere by performing measurements from satellite, aircraft, balloon, and ground-based platforms. Infrared techniques play a dominant role in atmospheric sensing of the upper atmosphere since most of the major molecules contain strong vibrational-rotational lines in the 1-30 μm region, with sharp spectral features throughout most of the stratosphere. Emission or absorption spectroscopic techniques can be used to measure the vertical profiles of stratospheric molecules using a variety of infrared instruments, including grating spectrometers, interferometers, and gas filter correlation techniques. With the current interest in the stratospheric ozone layer, increased emphasis has been placed upon obtaining information on the composition of the stratosphere, in particular with respect to the measurements of the source, sink, and radical species of the chlorine, hydrogen, nitrogen, and sulfur families. This interest is reflected in the number of satellite and Spacelab investigations which have been proposed or will be flown to obtain such data on a global basis, and in the number of balloon and aircraft investigations currently being performed to study the chemistry of the upper atmosphere.

Functionally, infrared instruments can be divided into two categories, species specific instruments and spectrally scanning survey instruments. In the first category lie such instruments as gas filter correlation radiometers, certain classes of grating spectrometers, Fabry-Perot interferometers, and laser heterodyne spectrometers. In general, for species specific instruments, the radiometric signal on the infrared detector contains information to determine the concentration of stratospheric molecules through detection of one or more spectroscopic lines of the species of interest, and to some degree, interfering lines from other gases in the atmosphere. To obtain the concentration of the target molecule, knowledge of the spectroscopic parameters of the gas molecule to be measured and interfering gases are needed in the data inversion algorithm to convert the radiometric signal-to-gas concentrations.

A second functional class of instruments are spectrally surveying instruments which generate the spectra of atmospheric molecules over a relatively broad spectral range and directly obtain spectroscopic information on a number of upper atmospheric constituents simultaneously. Instruments falling in this functional class include scanning Michelson interferometers and grating spectrometers. Development of this functional class of instruments for measuring stratospheric trace constituents historically has attempted to operate at maximum spectral resolution in order to unambiguously discriminate the spectra of tenuous gas molecules from interfering gas lines of more abundant species in the stratosphere. However, since spectral resolution is often compromised by signal-to-noise considerations, specific scientific investigations using these techniques (especially for space platforms) must properly assess scientific objectives against available signal. Due to the relatively bright radiometric signal obtained from the Sun contrasted to emission of the atmospheric limb, high resolution techniques falling in this functional class have been primarily proposed for solar occultation measurements in contrast to limb emission measurements, although recent advances in the technology of infrared detectors and cryogenic cooling of optical receivers have made possible increases in the spectral resolving power of limb emission techniques. In general, interferometric techniques in the solar occultation mode such as ATMOS currently proposed or under development for satellite and Shuttle applications have the capability to generate spectral resolutions $\leq 0.02 \text{ cm}^{-1}$, and therefore should have the capability to resolve the spectra of a large number of source and sink molecules which significantly impact the chemistry of the stratosphere. The capability of moderate resolution instruments to measure some of the radical species (e.g., ClO, HO_2) is at the present less certain.

Recent advances in the technology of tunable and fixed frequency lasers in the infrared portion of the spectrum have made possible improvements in the spectral resolution of infrared techniques by several orders of magnitude through the development of infrared heterodyne techniques in the 3 to 30 μm spectral range. The principles of heterodyne radiometry and their applications to atmospheric measurements are discussed by Menzies (ref. 1). Inherently, heterodyne detection techniques are limited by the quantum noise limit of the laser local oscillator and therefore have the potential to improve the sensitivity to measurements of tenuous gas molecules in the stratosphere having extremely narrow spectral features. These improvements in spectral resolution and sensitivity to sharp spectral features in the stratosphere appear to be important in detecting some of the radical molecules such as ClO, $ClONO_2$, HOCl, HO_2, H_2O_2 and others which are difficult to measure with moderate resolution, interferometric techniques. Recent measurements of stratospheric ClO using laser heterodyne techniques from a balloon platform have been recently reported by Menzies (ref. 2) and demonstrate the maturity of this measurement technique. These measurements were performed using a fixed transition of the $^{14}C^{12}O_2$ gas laser. Development of widely tunable semiconductor laser local oscillators in the 3 to 30 μm region has been a major NASA technology program over the past 8 years. This research has yielded the technology to build instruments which can provide measurements of a large number of important scientific gases in the stratosphere. This technology is, however, less mature for space applications, although significant measurements of the Earth's atmosphere (e.g., O_3, HNO_3, NH_3) have been reported in ground-based measurements with semiconductor laser heterodyne techniques. A major issue facing the upper atmospheric research community at the present time is the role which infrared heterodyne techniques should play in future scientific investigations of the Earth's stratosphere. In order to address this question, the Workshop on High Resolution Infrared Spectroscopy Techniques for Upper Atmospheric Measurements was sponsored by NASA and convened at Silverthorne, Colorado, July 31 to August 2, 1979, by Dr. David G. Murcray under the auspices of the University of Denver.

The major objectives of this Workshop were to consider the future role of high resolution infrared techniques in performing measurements in the stratosphere, and in particular to consider the role of laser heterodyne techniques in the NASA Upper Atmospheric Research Program Plan in satellite, Space Shuttle, and balloon borne investigations. In order to achieve meaningful discussion and recommendations from the Workshop participants, it was recognized that several aspects of the problem had to be considered simultaneously, including:

(1) The scientific requirements of the Upper Atmospheric Research Program (UARP) in the immediate future (1 to 5 years) and long range (>5 years)

(2) The requirements in spectral resolution to perform measurements of atmospheric trace constituents and the requirements and status of supporting laboratory measurements

(3) The current and projected capabilities of moderate resolution techniques in meeting major objectives of the Upper Atmospheric Research Program

(4) The current and projected capabilities of high resolution heterodyne techniques in performing measurements in the stratosphere

In order to fully consider all of these aspects, the Workshop was organized into four working groups: Measurements and Data Base working group whose chairman was Dr. R. S. Stolarski of the Goddard Space Flight Center, a Laboratory Spectroscopy working group whose chairman was Dr. A. Goldman of the University of Denver, a Spectral Scanning Instrumentation working group whose chairman was Dr. H. Buijs of BOMEN, Inc., and a Species-Specific Instrumentation working group whose chairman was Dr. R. T. Menzies of the Jet Propulsion Laboratory. The address list for the attendees and the makeup of each working group are contained in appendix 1.

During the first day of the Workshop, tutorial presentations were made by the chairman of each of the four groups. Presentations were given by Dr. Stolarski as chairman of the measurement requirements group; Dr. Goldman, chairman of the resolution group; Dr. Buijs as chairman of the conventional instrumentation group; and Dr. Menzies on Laser Heterodyne Spectrometry (LHS). In addition, presentations were given by Dr. Maki on theoretical molecular spectroscopy, Dr. Allario on tunable diode lasers for LHS applications, and finally by Dr. Boughner on the interpretation of solar occultation data in the case of rapidly varying photochemical species (such as NO). The presentation by Dr. Boughner was a summary of a paper since accepted for publication by the Journal of Geophysical Research Letters (JGRL) and the talk by Dr. Allario was first presented at the 4th International Conference on Laser Spectroscopy (FICOLS), June 1979 in Röttarch-Egern, West Germany. These papers are reprinted in appendices 2 and 3, respectively, with the kind permission of JGRL and Applied Physics.

After the first morning session, the Workshop broke into its working groups. These working groups convened as a single body twice more during the Workshop, once to present progress reports on each group, and finally in a general workshop discussion session to assess the overall workshop findings.

In what follows, the findings and recommendations of each working group are presented sequentially. The general workshop discussion follows as a separate section. One additional fact must be noted. The Laboratory Spectroscopy working group decided to follow up on its recommendations and it met once more at Langley Research Center on October 29-30, 1979. The results of that additional session are given in appendix 4, entitled "Review of Spectroscopic Data for Measurement of Stratospheric Species." (Also available as NASA CP-2136.)

Due to the limited duration of the Workshop and the highly focused approach to consideration of high resolution techniques in the infrared (1-30 μm), several significant instrument and measurement techniques were not considered in depth at this Workshop. For example, most of the Workshop discussion concentrated on solar occultation measurements because the Sun is a brighter source than the natural emission of the atmosphere, and high resolution in instruments is usually obtained at the expense of signal-to-noise ratio. However, this emphasis should not be interpreted as endorsement of solar occultation versus emission spectroscopy, although many of the considerations developed in the discussion apply to both measurement techniques.

Other instrument techniques recognized at the Workshop important to measurement in the stratosphere but not discussed in detail include microwave limb sounding techniques, far infrared, submillimeter and millimeter interferometry, and heterodyne radiometry and lidar techniques. Furthermore, the application of high resolution heterodyne techniques to stratospheric and mesospheric winds was not discussed, although this appears to be another important application of laser heterodyne spectroscopy from space platforms.

III. ACRONYMS

ATMOS	Atmospheric Trace Molecules Observed by Spectroscopy
GFC	Gas Filter Correlation
HALOE	Halogen Occultation Experiment
LHS	Laser Heterodyne Spectrometer
PMR	Pressure Modulated Radiometer
TDL	Tunable Diode Laser
UARP	Upper Atmospheric Research Program
UARS	Upper Atmospheric Research Satellite

IV. MEASUREMENTS AND DATA BASE WORKING GROUP

REPORT AND RECOMMENDATION

A. Measurement Requirements

The photochemistry of the stratosphere, particularly possible perturbations of the ozone layer by man's activities, is one of the major scientific problems which will be addressed by NASA's satellite programs in the next decade. This problem has been studied extensively in the last few years and is the subject of numerous reports including several workshops held by NASA. One of these, "Chlorofluoromethanes and the Stratosphere" (Hudson, ref. 3), summarized our current state of knowledge concerning the problem, including a listing of molecular species of interest in the photochemistry and their current measurement status. This report will be updated in the next few months to include measurements available through June 1979. A report issued by the Upper Atmospheric Research Satellite Study Group (ref. 4) addresses the measurement requirements in the mid-1980 time frame in great detail, addressing the requirements on a species by species basis. These reports group the atmospheric species into three broad categories: sources, radicals, and sinks. Measurement requirements are then addressed on the basis of category, i.e., source and sink species require global measurements while data on a global basis are not necessarily required for the radicals. The measurement requirements group of this Workshop approached the measurement criteria according to the measurement strategy first postulated by J. C. Gille, J. Anderson, and S. C. Wofsy. This strategy points out that measurement knowledge progresses through stages.

1. Molecules predicted to be present in the lower stratosphere but never before (or almost never) measured: Molecules of this type include N_2O_5, HOCl, $ClONO_2$, HO_2NO_2, H_2O_2, HO_2, and OH. In this case, any careful measurement at any time or place is of significant scientific value.

2. Molecules measured a few times by one or more instruments: Also included in this group are molecules which have been measured many times but for which there are outstanding interpretation problems. Molecules of this type include ClO, NO, NO_2, HNO_3, H_2O, HCl, HF, OH, O, NO_3, and Cl. For such molecules, individual measurements are of significantly less scientific value except as an instrument test. The crucial measurements for these molecules are those designed to answer specific outstanding questions through a carefully coordinated experiment which may consist of simultaneous measurement of other species in the same volume at the same time or of some unique spatial and/or temporal organization of the measurements.

3. Well measured molecules: Some would argue that these are nonexistent. However, the most likely candidates include O_3, N_2O, F-11, F-12, and CH_4. All of the above statements concerning carefully planned experiments apply more strongly for these molecules. In addition, these are candidates for long-term monitoring for trends due to natural and/or man-made causes and there is, therefore, a need for development of accurate measurement techniques that can be routinely operated over a long period of time (tens of years).

The measurement requirements group did not feel that it was their function to address specific accuracy and data base requirements for each species. These aspects are closely tied to the specific scientific questions to be solved and are therefore inherently dependent upon the scientific investigation. The group recommended formation of an Instrument Science Team with a major responsibility to resolve the requirements of the measurements in terms of spectral resolution, measurement accuracy, and scientific validity of the data base.

In order to select a list of potential candidate species, the measurement requirements group compared moderately high resolution instruments (of the ATMOS type) with ultrahigh resolution instruments (of the LHS type). The discussion was limited to a comparison of occultation instruments since these are the currently proposed mission investigations. However, there are some fundamental limitations associated with solar occultation measurements that should be considered which are briefly discussed in a following section. Two types of platforms were considered, balloons and Spacelab. Balloon platforms are especially useful for first time measurements of species (although ground-based, aircraft, and rockets may also be applicable). Satellite platforms, in general, are most useful for global coverage but should not be used to measure a species for the first time primarily because of funding considerations for space investigations and the long developmental lead-times involved. A balloon measurement is particularly useful for first establishing the importance of a predicted stratospheric species, or if it is even present, and for providing critical information needed to improve our theoretical modeling capability.

The complexities of stratospheric photochemistry are now fully appreciated. The emphasis in future measurement activities should be on coordinated, simultaneous measurements of several species and physical parameters (e.g., temperature, winds, etc.) to verify the photochemistry or to understand better the interaction between dynamics, radiation, and photochemistry. With these requirements, measurements of only a few species (e.g., 2) by an LHS spacelab instrument would have limited scientific justification. A possible exception to this statement would be an improved measurement of key chemical ratios, such as $ClO/ClONO_2$, that would enable photochemists to verify the important kinetic steps within the major chemical chains. In order to increase the scientific return from a given mission, the LHS instrument should be flown simultaneously with a survey type of instrument such as ATMOS. The species to be measured by LHS should be selected to complement and extend the survey instruments. To provide a guide to species choice, the measurement requirements group compared the ATMOS estimated performance (Farmer, ref. 5) with the LHS estimated performance (see appendix 3). This comparison is shown below:

ATMOS

Can measure - O_3, H_2O, N_2O, HCl, HF, F-11, F-12, CH_3Cl, CCl_4, $ClONO_2$, HNO_3, CH_4, C_2H_6, CH_2O, CO, NO, and NO_2

Can measure but spectroscopic constants not available or maybe LHS can do better - HOCl, ClO, N_2O_5, HO_2NO_2, and H_2O_2

LHS

Can measure - ClO, HO_2, $ClONO_2$, O_3, HNO_3, NO_2, H_2O_5, HOCl, H_2O_2, and H_2O

(The measurements group did not consider each molecule in detail as to whether ATMOS or LHS had higher measurement sensitivity.) A comparison of these two lists shows that the differential between LHS and ATMOS, i.e., what LHS can do better than ATMOS, reduces to the following species:

ClO, HO_2, N_2O_5, HOCl, and H_2O_2

The first two species (ClO, HO_2) fall into category 2 and would be appropriate for a Spacelab mission in conjunction with an ATMOS type instrument. The last three species (N_2O_5, HOCl, H_2O_2) have never been measured in the atmosphere (category 1) and are more appropriately measured first from a balloon platform.

The group also discussed whether LHS was better suited to measure $ClONO_2$ but could not reach any definite conclusions due to the inadequacy of present spectroscopic data. Based on present knowledge, it was not clear that the enhanced spectral resolution capability of LHS would yield significantly better results than could be obtained from the moderate resolution capability of ATMOS. The group felt that higher resolution measurements on $ClONO_2$ were needed to resolve this question.

B. Limitations of a Spacelab Instrument

The measurement requirements group also briefly considered some of the limitations associated with Spacelab occultation measurements which may influence its selection. The major objections were:

1. Limited coverage, especially the inability to obtain nighttime measurements such as in the polar night

2. Difficulty in interpretation of the measurements for species which change rapidly at sunrise or sunset (see appendix 2). On the positive side, inversions are generally easier for occultation measurements than for emission measurements.

3. Severe scientific limitations due to the short time frame of a Spacelab mission, particularly with regard to answering questions concerning the interaction between dynamics and chemistry. The group felt that Spacelab should only be considered a test platform for a free-flyer experiment.

C. Possible Mesospheric Applications

Most of the above considerations have been oriented toward stratospheric applications. There are also interesting mesospheric problems, requiring focus on a somewhat different set of atoms and molecules which can best (or only) be obtained by an LHS instrument with its high spectral resolution. These include NO, O_3, H_2O, OH, HO_2, Cl, O, N, HF, HCl, CH_4, H_2, H, CO_2, CO, NO^+, and OH ($\nu > 0$). Problems that might be studied include the odd nitrogen budget, determination of K_z profiles, ozone-hydrogen chemistry at and above the stratopause, the total Cl and F family concentrations, and the flux of NO into the stratosphere.

V. LABORATORY SPECTROSCOPY WORKING GROUP REPORT AND RECOMMENDATIONS

A. Role of Resolution in Constituent Measurements

In order to use infrared techniques to obtain information concerning the distribution of a constituent in the atmosphere, it is necessary that the technique give rise to an observable signal uniquely associated with that constituent. In the case of spectral data, it is evident that spectral resolution is an important characteristic in determining whether a constituent is giving rise to an observable signal. Thus, the infrared solar spectrum given in figure 1, obtained at a resolution of $\approx 10\ \text{cm}^{-1}$, contains absorption features due to a number of constituents; however, only a few of the species contributing to this spectrum could be measured from such data. Figure 2 shows a portion of an infrared solar spectrum obtained from the ground at a resolution of $\approx 0.06\ \text{cm}^{-1}$. Absorption features due to HNO_3, F-11, and NH_3 are all identifiable in the spectrum. None of these species could be measured from the spectrum given in figure 1. Figure 3 illustrates that even higher spectral resolution may be needed to identify some absorption features. The HNO_3 features shown in this figure were obtained from a ground-based heterodyne radiometer (ref. 6) having

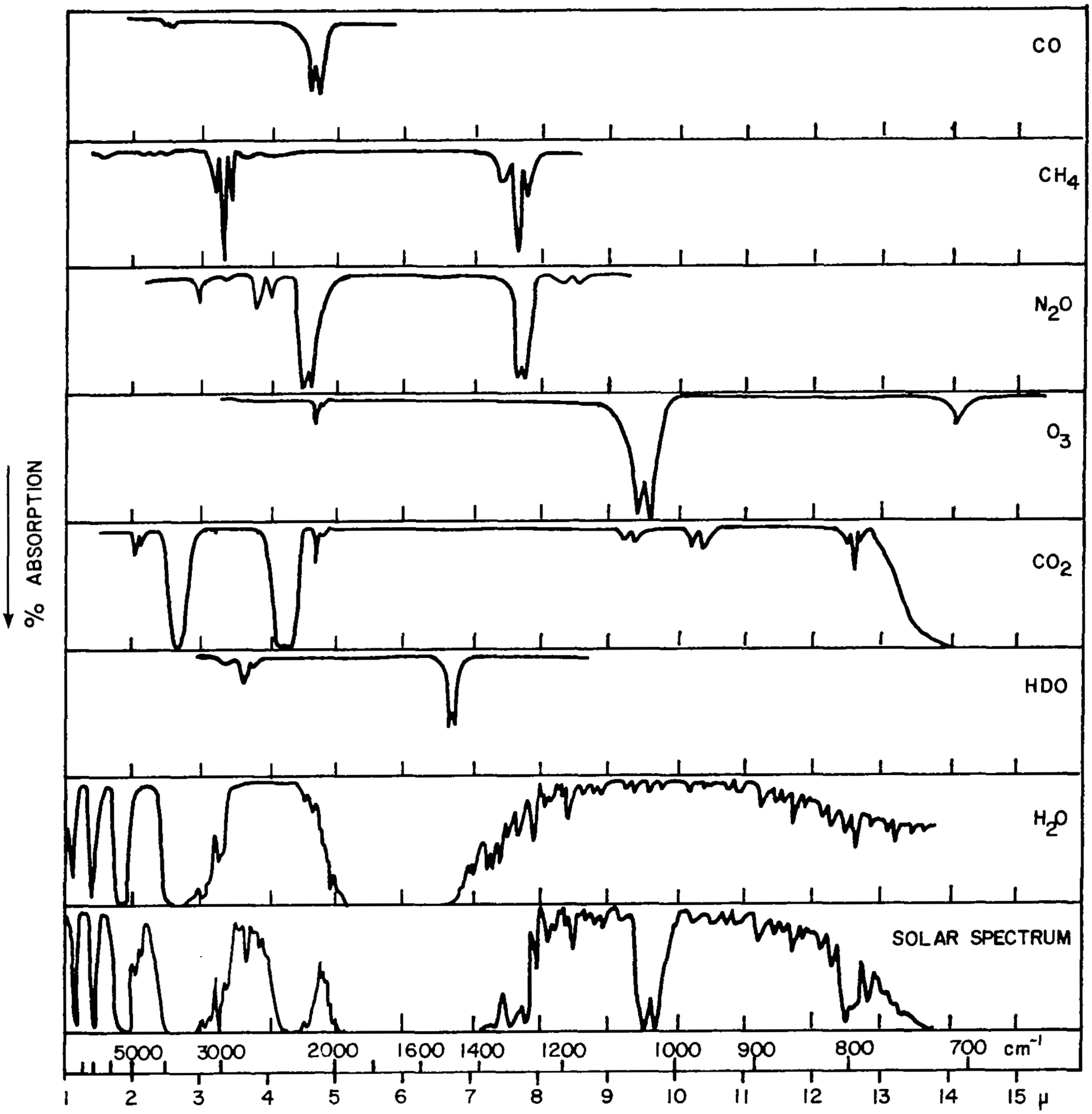

Figure 1.- Near-infrared solar spectrum (bottom curve). Other curves are laboratory spectra of molecules indicated.

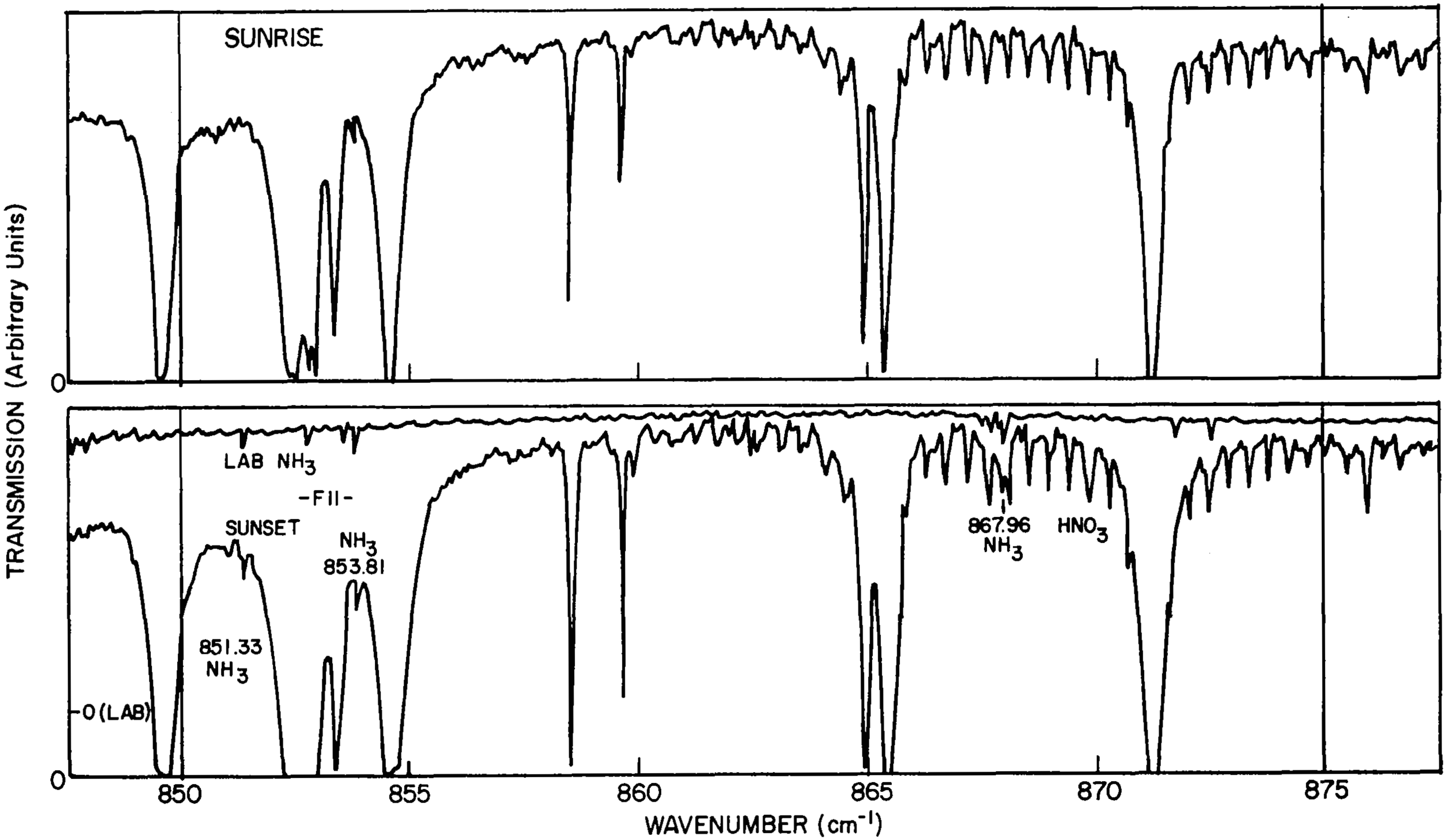

Figure 2.- Identification of ν_2 NH_3 band in ground-based solar spectra obtained during sunrise and sunset from Denver, Colorado, Feb. 24, 1978. Optical paths are 15.2 and 15.9 air-masses for sunrise and sunset spectra, respectively. The NH_3 laboratory spectrum was obtained with cell length of 10 cm at a pressure of 0.5 mm Hg. The zero level of the NH_3 spectrum is shifted for clarity.

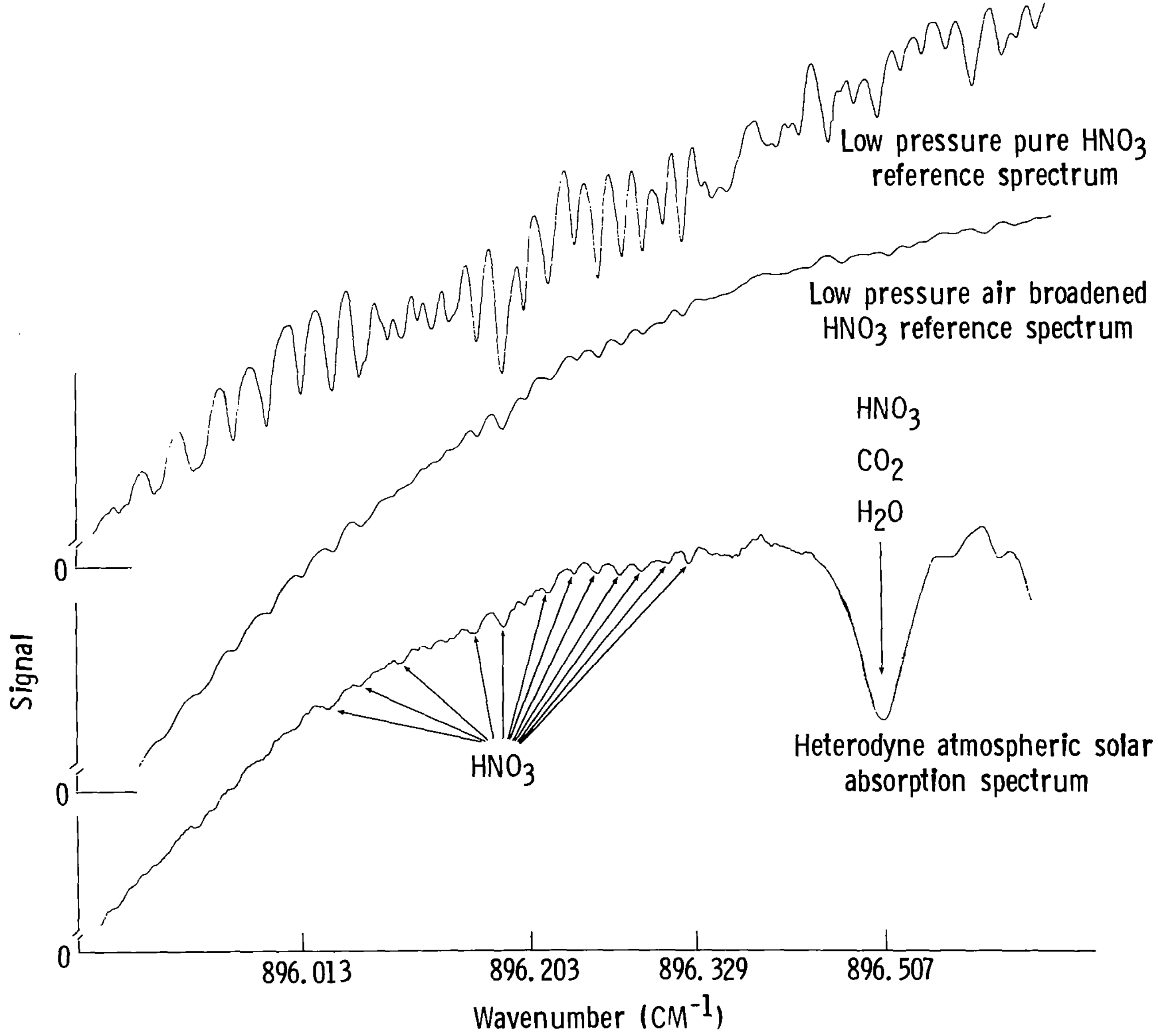

Figure 3.- High resolution (0.007 cm^{-1}) HNO_3 spectrum obtained by laser heterodyne radiometer.

a spectral resolution of ≈0.007 cm^{-1}. In addition to the advantage that increased resolution gives in the identification of absorption features is the advantage it gives in separating features due to two different absorbers. This is illustrated in figure 4, which shows various HCl lines as observed in sunset solar spectra at a resolution of ≈0.20 cm^{-1} (ref. 5) versus a resolution of 0.02 cm^{-1} by Henry Buijs. Note particularly the separation of the 2942.74 cm^{-1} line from the interfering CH_4 lines. This separation results in greater ease in removing the effects of the CH_4 when analyzing the spectra to determine HCl amounts.

While resolution is certainly advantageous, it does not follow that increased resolution necessarily results in more accurate measurements of molecular concentrations. Increased resolution is generally achieved at the expense of some other parameter, i.e., signal-to-noise ratio, spectral coverage, etc. In addition, the absorption lines which are of interest in the atmosphere are not infinitely narrow, but rather have widths that are determined to a large degree by their environment. In the lower stratosphere the line width can become wide enough that increased resolution in the measurement may not increase the information available regarding the absorption feature. These constraints on the advantages of increased resolution along with the cost of achieving increased resolution require detailed examination of the role of spectral resolution in measurements of stratospheric constituents. Thus, one seeks answers to questions such as:

(1) What minimum resolution is required to detect a constituent predicted to be present at a particular concentration at a certain altitude?

(2) What increase in absolute accuracy of the measurement of a constituent will result if the measurement is made at a resolution of 0.001 cm^{-1} rather than 0.01 cm^{-1} or even 0.1 cm^{-1}?

(3) What are the interfering species and what spectral region and resolution is needed to minimize their effects?

In principle it should be possible to answer these questions theoretically by calculating spectra which simulate the conditions of observation and varying (a) the resolution and (b) the amount of constituent of interest for each instrument. In practice it is often not possible to perform such calculations for many trace species with any confidence in the results. This is due to the current incomplete knowledge of the spectral line parameters for constituents of atmospheric interest. A great deal of discussion at the Workshop concerned such questions and calculations. The details of the discussion are as follows.

Calculations of high resolution atmospheric spectra are not a trivial operation. The calculations involve thousands of spectral lines and are complicated in the case of slant paths by the fact that the absorption depends on pressure and temperature, both of which vary along the path. Computer programs for performing such calculations have been developed by several groups in the U.S. and abroad. The heart of any such calculation is the input data concerning the various absorption spectral parameters of atmospheric gases. During the 1960's and early 1970's, a group of investigators with the support and collaboration of several scientists at the Air Force Cambridge Research Laboratories (now

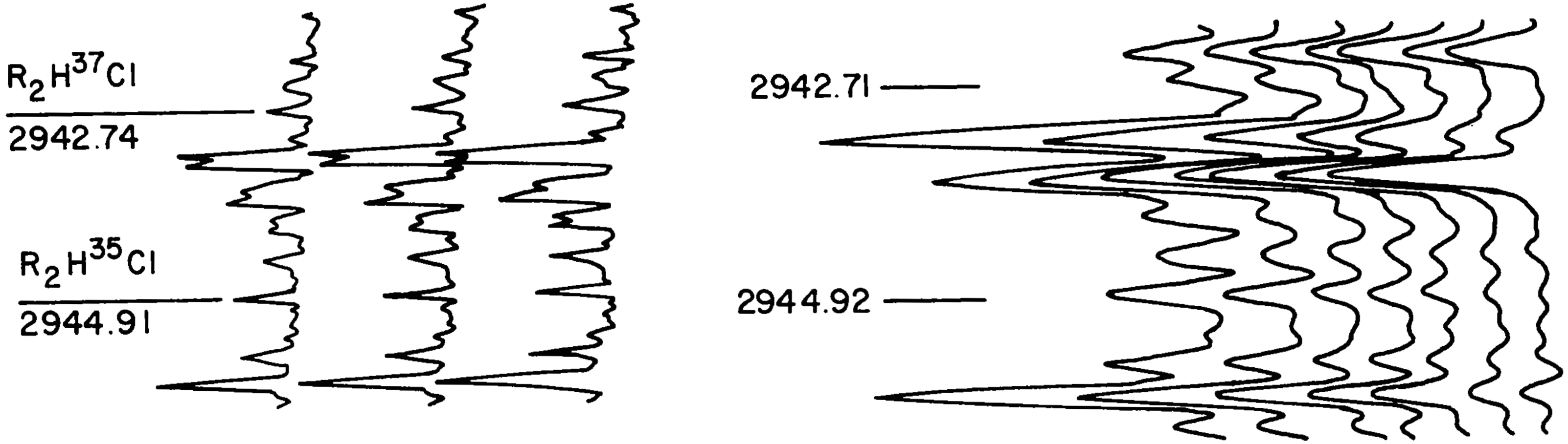

Figure 4.- Spectra of various HCl lines observed at a resolution of 0.2 cm^{-1} and 0.02 cm^{-1}.

Air Force Geophysics Laboratory) compiled a data base containing spectroscopic parameters for many atmospheric spaces. This data base, often referred to as the AFGL Tape, has become the source for most synthetic spectral calculations. While the Air Force has maintained an interest in this data base, there currently is no extensive effort at any single facility to upgrade the data on the tape and provide interested scientists with an up-to-date version. Thus, as the state of the art advances, the tape has become deficient for performing many of the calculations required today. As part of their current research, various groups kept updating the tape for their own use. Updating the tape is expensive, mainly because most new laboratory data becoming available for additions and corrections are not in the form required for inclusion on the tape and, therefore, require additional analysis. A more difficult problem is the evaluation of new laboratory results that differ significantly from the results of previous investigators. It is here that the comparison between the field results and theoretical results becomes essential since in many cases the field data can be used to determine which of the conflicting results are correct.

Current status of atmospheric spectral parameters is evident by considering recent high resolution infrared solar spectra. The complexity of the spectrum is obvious and will increase as the resolution increases. Identification of the absorption features starts by examining the listings of available line positions, identifications, and strengths. Three major deficiencies in the current line listings are:

(1) The inaccuracy in many line positions exceeds one or more resolution elements of present instruments. Thus, a close doublet may be completely misidentified on the basis of the reference line positions. It is important that line positions be known to better than ≈0.1 of resolution. This is feasible for numerous lines.

(2) Numerous medium and weak lines of already known atmospheric molecules, which appear as background absorptions, are not included in the compilations. Thus, a newly observed line in long path solar absorption measurements could be just another line of a known molecule, not yet cataloged.

(3) Intensities and line-shape data are only approximate in many cases, and their temperature dependence is not always available. It is expected that this type of data for selected lines can be measured in the laboratory to better than ≈0.5 percent. The experimental data coupled with theoretical calculations of the corresponding parameters should result in an overall accuracy of ≈5 percent for a wide spectral region.

It should be noted that even for simple molecules, say CO_2, which has been studied extensively, recent laboratory results have shown that many of the weak lines differ by more than 0.05 cm^{-1} from the predicted positions. For H_2O, deviations of 0.1 cm^{-1} in line positions are quite common. No estimate of the precision of the intensities of widths are usually available.

The importance of accurate line positions is apparent in the identification of single absorption lines in the stratosphere, which relies heavily on the exact line position. However, without a comparable spectrum of potential interferences, one cannot conclude that the molecule claimed is the major contributor to the observed line.

As indicated in the discussion above, a major part of our knowledge in atmospheric spectroscopy is contained in the data which are incorporated in the molecular parameters compilations. Much additional research is required to increase the amount and absolute accuracy of the molecular line parameters.

It should be realized that, as higher resolution field data become available, identification of the increased number of lines present in the spectra will require a significant amount of dedicated effort. Identification of the "unidentified" features in current spectra requires that, as laboratory data become available for "candidate" species (i.e., those known or thought to be present in the atmosphere), they be compared with the field data in an attempt to identify these features. Once the identification of new atmospheric molecular bands has been established, further laboratory and theoretical programs will be required for the generation of the proper spectral parameters.

B. Recommendations

From the above discussion the following recommendations are made:

(1) Additional and improved measurements of frequency, intensity, line shape, temperature, and pressure effects are needed on many spectral lines of many atmospheric species. These measurements should improve the measurement accuracy of many infrared instruments being used for constituent measurements of the upper atmosphere.

(2) A method of setting priorities for future work in spectroscopy is needed. This includes the specification of molecular bands of atmospheric interest and their feasible quantitative analysis for spectral parameters. It should be noted that although a knowledge of abundances of some trace gases to ±50 percent is adequate today, ±5 percent will be required eventually.

(3) Improved means of archiving and disseminating spectroscopic information on a national and international level is needed.

(4) Greater coordination of efforts in various laboratories is needed in order to ensure that appropriate priorities are observed and to minimize duplication of efforts.

(5) Interaction between instrument builders and laboratory spectroscopists should be encouraged and improved wherever possible.

For the support of these recommendations, it is recommended that a study group consisting of users and generators of the required data be convened to formulate a program (possibly at a NASA center or a University) to consolidate existing information, to disseminate it to interested users, to identify additional information needed, and to coordinate experimental and theoretical programs to provide the necessary data.

VI. INSTRUMENTATION ASPECTS OF VERY HIGH RESOLUTION SPECTROSCOPY IN THE UPPER ATMOSPHERE

A large amount of effort has been expended to develop spectrometers for use in atmospheric solar absorption measurements. This development is responsible for instrumentation achieving a very wide range of operational characteristics such as resolution and spectral coverage. It is useful to characterize these instruments and place them into different classes in order to compare them and determine where the strengths and weaknesses of each class lie. This comparison, however, is restricted to instruments which obtain spectral intensities as a function of wavelength in such a way that composition is deduced from specific variation in intensity.

Atmospheric measurement via solar absorption has yielded higher sensitivity than measurement via thermal emission. This arises from the large difference in available signal strength over a wide spectral band despite the limitation of observation time in solar occultation. Comparison is made between various instrument classes both for solar occultation as well as for thermal emission (see tables 1 and 2, respectively). Aspects of instrumentation for solar occultation are emphasized, however.

The instruments under discussion can be placed in three classes of spectroscopic devices: (1) spectroscopic devices where individual spectral elements are registered on the detector, (2) devices where spectral information is multiplexed on the detector, and (3) heterodyne devices. The first class of devices is comprised of grating spectrometers and Fabry-Perot interferometers. The second class includes Fourier and Hadamard spectrometers, and the third class is comprised of laser heterodyne radiometers and spectrometers.

The comparison is performed by identifying a series of attributes and then determining a numerical value for that attribute or how well that class fulfills that attribute. A comparison of the list of attributes permits an objective evaluation of merit of each class of instrumentation even though the list is probably incomplete. The comparison is given in table 1. The following are remarks regarding table 1:

(a) Wavelength Coverage

Class 1: Grating instruments operate over a wide wavelength range because no transmitting elements such as prisms are needed. By appropriate selection of line spacing, very effective operation can be achieved in the UV and VUV as well as in the IR. However, since second-order diffraction occurs at one-half the first-order wavelength, order separation becomes increasingly difficult at longer wavelengths.

TABLE 1.- COMPARISON OF THREE CLASSES OF INSTRUMENTATION FOR ATMOSPHERIC MEASUREMENT VIA SOLAR OCCULTATION

Attribute	Class 1	Class 2	Class 3
Wavelength (frequency) coverage	Grating (10 - 10,000 cm^{-1}) Fabry-Perot (1 - 20 μm, >50 μm)	(10 - 10,000 cm^{-1})	Current: 7.0 - 13.0 μm Possible: 3 - 30 μm Development R'QT: >30 μm
Wavelength (frequencies) per setup	(1 cm^{-1} to 1000 cm^{-1})	(50 - 5000 cm^{-1}) Generally large	(0.05 cm^{-1})
Limiting resolution	0.01 cm^{-1}	0.01 cm^{-1} at present >0.001 cm^{-1} (Near term dev.)	0.0001 cm^{-1} (5 MHz)
Noise Equivalent-Equivalent Width - (NEEW)	10^{-4} to 10^{-5} cm^{-1}	10^{-4} cm^{-1} (obs.) 10^{-5} cm^{-1} (poss.)	10^{-6} to 10^{-7} cm^{-1} (Observed when applicable)
Number of features per sec obs. per detector	F.P. 10^3 GR. 100 to 1000	$3 \times 10^3 - 3 \times 10^4$	<100
Multidetector array implementation	Very good	Fair	Fair
Frequency accuracy	0.1 to 0.01 cm^{-1}	$\pm 10^{-4}$ cm^{-1}	$CO_2 < 10^{-5}$ cm^{-1} TDL $\sim 2 \times 10^{-4}$ cm^{-1}
Instrument Line Width Function (ILWF)	Fair	Good	Excellent
Relative photometric precision	10^{-3}	10^{-2} to 10^{-3}	10^{-3}

TABLE 1.- Concluded

Attribute	Class 1	Class 2	Class 3
Throughput $A\Omega$ @ resolution (for $R = 10^5$ at 10 μm)	GR. $A\ell$ #/R ($\cong 10^{-4}$ cm^2 sterad.) F.P. $A\pi/R$ ($\cong 10^{-3}$ cm^2 sterad.)	$A\pi/R$ ($\sim 10^{-3}$ cm^2 sterad.)	λ^2 (10^{-6} cm^2 sterad.)
Physical size of system	GR. large F.P. compact	Compact to 0.01 cm^{-1} resolution, large to 0.001 cm^{-1} resolution	Compact; depends on local oscillator size
Complexity	Simple	Average	Depends on l.o.
Reliability	Excellent	Limited life laser and mirror slide	Depends on l.o. reliability
Cost	Moderate	Mod. high	Mod. high
Data manipulation complexity	Simple	High volume	Simple
Data interpretation complexity	Calibration depends on mechanical configuration	Good basic spectral quality	Direct/simple
Problems best suited to class	Multispecies specific (multiline)	Scanning (survey-multiple species)	Multispecies specific (single-line)
Problem areas in technique	Very large gratings Many detectors Curved slit geometry Calibration requirement	High technology in mirror servos High technology for data processing Reference laser	L.o. technology beam missing Speed and efficiency of detectors Prior spectroscopy requirement

TABLE 2.- COMPARISON OF INSTRUMENT PERFORMANCE IN SOLAR OCCULTATION AND THERMAL EMISSION APPLICATION

Attributes	Emission	Occultation
Observation time	<100 sec	≈1 to 2 sec
Resolution	≈0.1 cm^{-1} present 0.01 cm^{-1} future 0.001 cm^{-1} LHS with arrays	Very high
Cryogenic requirements	Limited to "short" missions	None
Spatial coverage/time	15 times faster	1
Spectral coverage	>4 µm	Not restricted
Spectral coverage/scan	Depends on sensitivity required; must exclude regions of strong emission	See table 1
Complexity	All optical components seen by detector must be maintained at low temperature	High information density because of brief observation time with very intense source
	Inversion process to obtain density profile is more difficult and less reliable than in occultation	Needs very accurate pointing optics especially at high altitude
Sensitivity (NEEW)	Depends NESR $[10^{8} - 10^{-9}$ watts/ cm^{2} ster. $(cm^{-1})]$ 0.1 cm^{-1} @ 5 µm 10^{-4} cm^{-1} @ 10 µm	See table 1

The Fabry-Perot depends on very precisely figured transmitting elements and efficient high reflection coatings. Both these requirements restrict the usable wavelength range of this device.

Class 2: The Fourier transform spectrometer requires an optically flat beam splitter that must transmit radiation of interest. By selection of substrate material and partial reflection coatings operation has been achieved from UV to FIR.

The Hadamard spectrometer is basically a grating spectrometer subject to the same restrictions as stated above.

Class 3: The principle of IR heterodyne spectroscopy is applicable from about 300 to 3000 cm^{-1} by virtue of diode laser local oscillator availability. These diode lasers are currently under development. Operational airborne instruments to date have used CO_2 lasers, which are in the 800 to 1100 cm^{-1} region. High-speed photomixers can be found over the 700 to 3000 cm^{-1} region.

(b) Wavelength Coverage for a Single Instrument Setup

Class 1: Because of simple sequential scanning of wavelength, gratings are highly flexible in selection of wavelength coverage and are only restricted to order-overlap considerations. It must be kept in mind that there is a direct trade-off between spectral element observation time and spectral coverage, except for instruments having detector arrays.

The Fabry-Perot is restricted to a frequency coverage of about 100 times the resolution (Finesse). When the Fabry-Perot is used in conjunction with a synchronously scanned monochromator, the frequency coverage is vastly extended.

Class 2: For the Fourier Transform Spectrometer (FTS) the wavelength coverage is fixed once the instrument is set up because of scanning in the Fourier domain. The FTS handles large wavelength intervals most efficiently since spectral components are multiplexed. The multiplex feature may not be advantageous in a source noise limited situation and optical bandwidth limiting may be employed to improve the signal-to-noise ratio.

Class 3: The only practical option to date appears to be to use the local oscillator to generate a fixed frequency. This limits the frequency coverage to the bandwidth of the photomixer. This is currently about 0.05 cm^{-1}. Generally such an interval implies observation of one spectral line only. However, more than one spectral line may be studied by utilizing the double side band nature of the receiver.

(c) Resolution Limits

Class 1: The Fabry-Perot achieves a 0.01 cm^{-1} resolution relatively easily. A grating can also achieve this resolution but the grating must be greater than 50 cm wide and must be operated at a large angle. Furthermore, the input and output optics must be of high quality.

Class 2: Fourier transform spectrometers routinely achieve 0.01 cm^{-1} resolution even in balloon and aircraft environments. It is technologically feasible to achieve 0.001 cm^{-1} resolution but a relatively bulky instrument will be required.

Class 3: The resolution in heterodyne spectroscopy is limited to the stability of the local oscillator which is about 0.00017 cm^{-1} (5 MHz).

(d) Noise Equivalent-Equivalent Width (NEEW)

This attribute is a measure of simultaneous spectral signal-to-noise ratio and resolution. This is also a useful scientific attribute since it translates directly to minimum measurable column density of a given molecule via the line strength of the spectral feature.

The given value of this attribute is degraded by a factor equal to the true line width to resolution ratio when the actual line width is greater than the resolution line width (i.e., too high resolution is not an inherent advantage).

Class 1: At the stated limiting resolution of 0.01 cm^{-1}, a spectral signal-to-noise ratio of 100 to 1000 is required to achieve the stated NEEW. *To achieve this in short observation times, such as occur in solar occultation,* the wavelength coverage may have to be limited considerably in class 1 instruments.

Class 2: Because of the multiplex feature, NEEW of 10^{-4} to 10^{-5} cm^{-1} can be achieved over a wider frequency interval than is possible with class 1 instruments.

Class 3: Source photon statistics is the predominant listing factor in signal-to-noise ratio achievement. In solar occultation, this leads to achievable NEEW of 10^{-6} to 10^{-7} cm^{-1} even for relatively short observation time. Photomixer efficiency is, however, a sensitive factor in achieving low NEEW. Furthermore, the NEEW is low in heterodyne spectroscopy by virtue of the high resolving power. NEEW can therefore be rapidly degraded when the line width is greater than resolution width. Hence, use of the technique in lower stratospheric measurement may not be as advantageous as suggested by NEEW attribute because of pressure broadening of spectral lines in the lower atmosphere.

(e) Number of Features Per Second Observation Time for One Detector

This attribute is intended to reflect the rate of information gathering for each class of instrument. This may be the frequency at which a single feature can be uniquely remeasured or the rate at which new features can be recorded.

Class 1: These devices are relatively flexible with respect to selection of repeated short scans or infrequency long scans.

Class 2: The FTS by virtue of scanning in the Fourier domain is essentially restricted to measuring many features in a relatively long observation time.

Class 3: The LHS is restricted to frequent measurements of few resolution elements essentially covering one spectral line.

(f) Frequency Accuracy

Class 1: The value given to this attribute reflects the inherent frequency accuracy of these devices independent of the spectral content of the measurement. Hence, it relates to the accuracy of grating angle settings, etc.

Class 2: The inherent frequency accuracy in the FTS is given by the monochromatic reference source and is nearly independent of mechanical tolerances.

Class 3: The frequency accuracy is related to the ability to select the local oscillator frequency and its subsequent stability.

(g) Instrument Line Width Function

This is a measure of how well the intensity response at the level of one resolution element can be established.

Class 1: For this class of instruments the instrument line shape function is affected by mechanical tolerances such as slits for a grating and achievable Finesse for a Fabry-Perot.

Class 2: For the FTS, the instrument line shape function is to first order not dependent on mechanical tolerances. The instrument line shape function is principally determined by the constancy of source intensity and spectral distribution, and by the constancy of the response of the interferometer (i.e., alignment variation with scale affects line shape function).

Class 3: The instrument line shape function is determined by the frequency response of the photomixer and the subsequent discrimination electronics.

(h) Relative Photometric Precision

Class 1: Relative photometric precision is only affected by variation in stray light and ghost features, both of which can be held relatively small.

Class 2: The photometric precision in Fourier transform spectroscopy is a sensitive function of very few critical measurements near zero retardation in the Fourier domain and the ability to precisely symmetrize interferograms.

Class 3: Relative photometric precision is related to intensity stability of the local oscillator and beam alignment between local oscillator and source.

(i) Throughput at Resolution ($A\Omega$)

Class 1: The grating has a dispersion of approximately $1/\lambda$. Hence, the angle subtended by the slit width at the collimator is about $1/R$ (the inverse of resolving power $\lambda/\Delta\lambda$). The slit height is expressed as the ratio of height to collimator focal length ($\ell\#$). The solid angle subtended by the slit is

$\ell\#/R$. The throughput is then given by the projected grating area Ag multiplied by $\ell\#/R$, and Throughput = $Ag\ell\#/R$ (best value of $\ell\# \cong 1/30$, i.e., $\theta = Ag/30R$).

Interferometric devices have a throughput limited by the optics cross section and the solid angle subtended by the smallest central fringe. This is $A_{optics}(\pi/R)$. It is seen that at high resolving power, the grating cannot match the throughput of an interferometer even with the difficulty of handling large slit aspect and very large gratings.

A. Summary

(1) Reduced NEEW implies increased sensitivity.

(2) When lowest achievable NEEW of conventional techniques is insufficient, it is useful to go to laser heterodyne techniques to pick up another factor of 100 but only when observed line width is less than or equal to resolution.

B. Applications of Heterodyne Technique

(1) Extension of profiles beyond 40 km of selected species

(2) Improvement in accuracy of currently measured species which is needed in cases where current measurements are tenuous, or to establish accurate concentration ratios which have significance in the understanding of chemical mechanisms controlling the measured species

(3) Detection of new species when these are proposed and when lab spectra are established

NEEW is a measure of the performance of a spectroscopic device which includes simultaneously signal-to-noise ratio and resolution. NEEW also is directly proportional to minimum detectable number of molecules in the path of the radiation.

The sensitivity of an instrument with low NEEW is fully realized for molecules having sharp spectral features in the stratosphere. These may be lines of simple diatomic molecules like ClO or a multiplicity of lines, i.e., a complex molecule like $ClONO_2$. However, the importance of prior lab spectroscopy for complex molecules must be emphasized in order to select the most appropriate features in the best wavelength region.

The application of heterodyne techniques also requires careful prior laboratory spectroscopy[1] in restrictive wavelength regions in order to qualify interferences, if any, due to other molecules present in the stratosphere. This is an important aspect in the process of selecting the most suitable wavelength

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[1] Prior laboratory spectroscopy means measurement of spectra and parameterization of molecular bands in sufficient detail to characterize fully the spectral features used in the field experiments.

region for field measurements. Furthermore, balloon measurements with simultaneous Class II and III instruments to identify potential interferences in the real atmosphere may be required prior to a dedicated Spacelab mission.

C. Recommendations

(1) Utilize Class III instruments to extend profiles to higher altitudes than currently achievable with Class I and II instruments. Caveat: Spacelab required to extend balloon measurements beyond 40 km.

(2) Utilize Class III instruments to detect atmospheric molecules previously undetected.

(3) Interferometer - LHS balloon investigation is required to identify interferences from atmospheric molecules and identify spectra of molecules under stratospheric conditions.

(4) Formation of Science Team to address the following tasks:

(a) Examine suspected increases in accuracy and precision of vertical profiles over Class I and II instruments for currently proposed stratospheric payloads (i.e., ATMOS/HALOE) to identify improved measurement sensitivity for feedback to requirement of upper atmospheric models. Relatively large improvements in vertical profile accuracy (i.e., 100 percent to 25 percent) may provide significant scientific payoff. Relatively low improvements (i.e., 25 percent to 10 percent) may provide marginal payoff.

(b) Examine improvements in chemical ratios (e.g., $ClO/ClONO_2$) or other significant ratios for studying chemical mechanisms in models. Here relatively small improvements (factor of 2) may provide significant scientific payoff.

(5) Perform high resolution broadband solar spectroscopy in support of LHS applications with current resolution of 0.0001 cm^{-1} in order to identify potential interferences in solar spectra.

VII. SPECIES-SPECIFIC INSTRUMENTATION WORKING GROUP

REPORT AND RECOMMENDATION

The Species-Specific Instrumentation Group focused its activities also on capabilities of heterodyne techniques and its potential contributions to stratospheric measurements in view of the other instruments of the Class II category. Several methods of comparing the performance of Class II and Class III instruments were discussed; however, because most of the comparison details have been highlighted in the previous Working Group report, they will not be covered again here. A comparison of heterodyne radiometer and scanning Michelson interferometer spectrometer capabilities is also discussed by Menzies (ref. 1). A conclusion of this group was that species specific instruments should have a spectral resolution which is less than the Doppler line widths of the species, permitting the ultimate in sensitivity and specificity for remote sensing of these species in the stratosphere. Heterodyne techniques normally used in the occultation mode measure small, carefully selected portions of the spectra which contain absorption features of the species of interest.

One important criterion applied to the spectral regions chosen for observation is that they be free from blending or interference by lines of other atmospheric species which could cause interpretational problems. Using the equivalent width concept to describe weak atmospheric absorption lines, the minimum detectable width for a laser heterodyne radiometer in the 7 t0 14 µm wavelength region is about 50 times smaller than that for ATMOS. The species specific GFC and PMR types of instruments are efficient in maximizing response to a spectral band of a gas, since the totality of the spectral lines in that band produces a signal. However, interpretational problems are sometimes encountered when severe blending occurs in regions of the spectral band which are being observed. The different temperature dependences of the various lines in a band might also limit the usefulness of this technique in obtaining accurate vertical concentration profiles with high vertical resolution. Many reactive species, such as the free radicals, cannot be confined in the sealed cells which are a part of these instruments. These drawbacks limit the usefulness of the correlation techniques to a few species; however, for these species, this technique is very efficient.

The active laser system has the advantage of day/night operation, and, with two-satellite operation, it can have a sensitivity equal to any of the other techniques considered at this Workshop. However, our main interest at this time is to compare the passive sensors (active laser systems do require more satellite power, generally).

The laser heterodyne spectrometer approach permits high resolution and high sensitivity without the disadvantages mentioned above for the PMR and GFC. Specific species which are under consideration for remote sensing using LHS are listed in table 3, along with a rough indication of the status of knowledge about the important line parameters relevant to this measurement technique.

These species have different levels of importance for understanding stratospheric chemistry. They also have different degrees of detectability using the LHS technique. In general, the ability to make a scientifically meaningful measurement depends on several factors:

(1) High resolution spectroscopic data (table 3) (knowledge of spectroscopic line parameters <u>and</u> interferences)

(2) Suitable local-oscillator laser (wavelength, power, mode structure, and stability)

(3) Suitable infrared detector (wavelength, speed, and efficiency)

(4) Appropriate spectral line(s) of species (strong, with little interference)

TABLE 3.- STATUS OF SPECTRAL KNOWLEDGE ABOUT CERTAIN SPECIES

Species	Line center positions	Line strengths	Air broadening coefficients	Line center pressure shifters	Air broadening coefficients versus temperature	Line shapes in "Voight" regime
HO_2	(1)	(3)	(3)	(3)	(3)	(3)
H_2O_2	(1)	(3)	(3)	(3)	(3)	(3)
HOCl	(2)	(3)	(3)	(3)	(3)	(3)
ClO	(1)	(1)	(2)	(3)	(2)	(2)
CH_3Cl	(1)	(1)	(2)	(3)	(2)	(2)
$ClONO_2$	(1)	(1)	(2)	(3)	(3)	(2)
NH_3	(1)	(1)	(1)	(3)	(3)	(2)
N_2O_5	(3)	(3)	(3)	(3)	(3)	(3)
OCS	(1)	(2)	(2)	(2)	(2)	(2)
CO	(1)	(1)	(1)	(1)	(1)	(1)

Legend for table 3:

[1] Good measurements available for LHS measurement.
[2] Few measurements available.
[3] Essentially no measurements made.

(5) Understanding of diurnal variability and its effect on measurement

The laser heterodyne spectrometer can be used to measure some of these species (e.g., ClO, $ClONO_2$, NH_3, and CH_3Cl) with instruments which are now operational. At the present time, the ability of the laser heterodyne spectrometer to accurately measure vertical profiles of stratospheric ClO and HO_2 is unique among infrared instruments. For other species (e.g., HO_2), the technology exists to make the measurement, but spectral line strength measurements must be completed in order to quantify the measurement for a desired accuracy.

VIII. GENERAL WORKSHOP DISCUSSION

A. Role of Increased Spectral Resolution in Stratospheric Measurements

One of the first issues discussed by the Full Workshop participants was the role of increased spectral resolution upon detection and measurement of upper atmospheric constituents. For purposes of discussion, moderate resolution was defined to be of the order of 0.02 cm^{-1}, representative of current capabilities of field-type, interferometric techniques; high resolution was defined to be ≤ 0.001 cm^{-1}, representative of heterodyne technology. A major objective of the discussion was to determine quantitatively advantages in increased spectral resolution of current interferometric techniques and/or advantages in utilizing the inherent high spectral resolution of heterodyne techniques.

The general Workshop agreed in general with the report of Working Group II that increased spectral resolution was required to improve the detection capability of certain species but not of others since the current capability appears to be adequate for some of the major species. In general, it was difficult to quantify the optimum spectral resolution pertaining to all stratospheric molecules, but it was agreed that the optimum spectral resolution must be established on a molecule by molecule basis, and must be determined by objectives of the scientific investigation. However, several general conclusions were drawn:

1. For relatively simple molecules with sharp spectral features in the stratosphere (e.g., ClO, HO_2), the high resolution capability of heterodyne techniques may be <u>necessary</u> for detection and measurement in the stratosphere.

2. For molecules with relatively complex spectral structure and broad spectral features (i.e., HNO_3 or $ClONO_2$), current or proposed measurements are probably adequate with moderate resolution instruments, based upon measurement requirements reported by Working Group I. For such molecules, therefore, high resolution measurements should be assessed on the basis of substantial improvement in measurement sensitivity through reduction of spectral interferences and improved signal-to-noise ratios. For example, heterodyne techniques should be considered for those molecules where current measurement uncertainty is high (50 to 100 percent), and improvements by factors of 5 to 10 improve scientific interpretation. Heterodyne techniques should also be considered when improvements in factors of 1.5 to 2.0 can be achieved in improving the measurements of important chemical ratios (i.e., $ClO/ClONO_2$).

The Workshop participants, recognizing that scientific benefits could be obtained by increasing the spectral resolution of infrared instruments to better than 0.02 cm^{-1} for certain species, subsequently attempted to quantify this improvement for at least the molecules with relatively sharp spectral features in the upper stratosphere. Based upon the report of Working Group III, the detectability of a constituent in the stratosphere depends upon the ratio of A_m/S, where A_m is defined as the minimum detectable absorption of a spectral feature measured with an infrared receiver, and S is the strength of the absorption feature detected. This parameter, defined as the Noise Equivalent-Equivalent Width (NEEW), is a figure of merit which should be minimized for optimum detection capability of high resolution instruments. For heterodyne techniques, NEEW was estimated to be one to two orders of magnitude smaller than interferometric techniques, thereby increasing the potential detection capability by comparable amounts.

Based upon this estimate of sensitivity and the reduction in spectral interferences with high resolution capability, the Workshop participants agreed that heterodyne techniques may be necessary for the detection of atmospheric molecules previously unobserved but predicted in the stratosphere (Priority I molecules), or for those molecules for which current measurements lead to interpretation problems in the photochemical models (Priority II molecules).

Based upon this series of discussions, a recommendation of the Workshop was that infrared heterodyne techniques be considered primarily for Priority I molecules since they may represent a unique infrared (3 to 30 μm) measurement technology for this class of stratospheric molecules. Furthermore, cost considerations led the Workshop to an additional conclusion: the search for Priority I molecules is best accomplished initially by balloon platforms. LHS flights aboard Shuttle were viewed as probably being needed for no firm conviction was evident. Therefore, the resulting Workshop recommendation was that LHS investigations be conducted at least from balloons to obtain measurements of stratospheric sonic, sink, and radical gas molecules.

Also, based upon this series of discussions involving the role of high resolution in measurements of stratospheric species, the Workshop recommended that the laboratory data base for molecular species be increased and focused toward high priority molecules proposed or currently measured by infrared instruments (i.e., ATMOS, HALOE, and LHS).

B. Fixed-Frequency and Tunable Semiconductor Local Oscillators

The Full Workshop participants also addressed the issue of the importance of continued development of widely tunable local oscillators (3 to 30 μm) for obtaining scientific measurements of trace gases in the stratosphere, particularly for Priority I molecules. Based upon the report of Working Group IV, fixed frequency CO_2 lasers currently have the capability to detect stratospheric ClO and HO_2 in heterodyne measurements. The vertical profile of ClO in the stratosphere has been measured and reported from a balloon platform with an LHS technique using the $^{14}CO_2{}^{12}$ isotope of a CO_2 laser. Current estimates of CO_2 laser transitions and HO_2 line positions lead one to expect that a similar measurement is possible for HO_2. However, spectroscopic data for HO_2 is currently incomplete (appendix 4) so that minimum measurement sensitivities for HO_2 can only be speculative, with the current status of high resolution spectroscopy of HO_2.

Tunable semiconductor lasers with wavelength tunability from 3 to 30 μm overlap absorption bands of all infrared active gases of Priority I, II, and III molecules. However, due to the fact that semiconductor lasers are tunable and that the technology of the semiconductor lasers is not as mature as CO_2 laser technology, development of an LHS Tunable Diode Laser (TDL) instrument for balloon or space applications requires a higher degree of complexity in the optical receiver and related subsystems (appendix 3). Furthermore, due to the lack of high resolution spectroscopic data on stratospheric molecules, it is difficult to assess the magnitude of improvements in sensitivity of a tunable local oscillator over a fixed frequency local oscillator, although improvements are expected in reduction of spectral interference and increased sensitivity.

Because of the immediate importance to increase measurements of ClO and HO_2 in the stratosphere for interpretation and validation of photochemical models, the Full Workshop encouraged continued measurements and laboratory spectroscopy in support of the LHS investigations. Further, the Full Workshop recognized that the current complement of Priority I gases reported by Working Group I is incomplete, and that the future requirements to measure other molecules on a Priority I basis will arise (i.e., HOCl, HONO, bromines, iodines, etc.).

Therefore, the Full Workshop recommended that in view of the need for techniques to measure a number of stratospheric species not as yet detected, the development of tunable semiconductor lasers to be used in LHS investigations be continued.

C. Role of High Resolution Heterodyne Techniques in Satellite Investigations

The Full Workshop also considered the role of high resolution techniques (e.g., LHS) in performing scientific investigations from satellites and Spacelab. Again, adopting the measurement strategy reported by Working Group I, with the assumptions that the ATMOS instrument will fulfill requirements for the gases proposed, high resolution techniques should be restricted to Priority I and/or II molecules. Furthermore, scientific investigations from satellites (e.g., UARS) with long duration mission capability (12 to 18 months) should be focused toward studies of transport and radiative balance as opposed to photochemistry since the photochemistry of the stratosphere should be adequately understood from currently planned balloon and Spacelab investigations.

However, some of the Workshop participants adopted the view that measurement requirements for radical species currently insufficiently measured in the stratosphere (i.e., ClO, $ClONO_2$, HOCl, HO_2, H_2O_2, N_2O_5, etc.) or undefined (bromines, iodines, etc.) will place future measurement requirements on infrared instruments which are currently unforeseen and may require global measurements. Furthermore, current scientific requirements for molecules with a poor data base will probably increase as new stratospheric measurements become available, requiring higher accuracy and precision than currently perceived in molecules previously measured. High resolution techniques, through improved detectability at higher altitudes (A_m/S), could also represent an important contribution in measuring stratospheric molecules at higher altitudes than balloon platforms (>40 km). Therefore, although no general agreement of the Workshop was obtained on the role of high resolution heterodyne techniques in satellite investigations, the Workshop participants encouraged development of tunable semiconductor lasers for space investigations, and emphasized the potential scientific benefit in the future of collaborative investigations of LHS with ATMOS- or HALOE-type instruments. Further, LHS-type instruments should be developed for long-duration, free flyer applications with Spacelab investigations serving as an intermediate step to provide correlative measurements for satellites (i.e., UARS) or to provide complementary measurements of radical gas species through corroborative orbital flights if these measurements are not available from satellite-borne instruments.

The inability of the Workshop to resolve the issue of the role of increased spectral resolution in improving measurements of constituents in the stratosphere concerned the question of measurement accuracy. It is apparent that in many cases where a constituent can be measured by moderate resolution techniques, a significant improvement in the absolute accuracy of the measurement can be achieved by using higher resolution techniques. A number of participants felt that the improvement in accuracy would warrant development of semiconductor lasers so that LHS techniques could be used for measuring Priority I, II, and III molecules. Again, since the accuracy required could not be specified, no concensus was reached on the need to develop LHS techniques for improved measurement accuracy. In many respects, the differences in opinion on the role high resolution would play in constituent measurements depended upon the optimism of the participant with regard to the capability of other instruments to achieve their measurement objectives. The increased detection and measurement sensitivity which would be available with a fully developed LHS capability could be important in the event other systems do not prove adequate to meet stratospheric measurement requirements. Comparison of moderate and high resolution balloon data of stratospheric spectra appears invaluable in addressing the quantitative advantages of increased spectral resolution through the use of LHS-type techniques.

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APPENDIX 1

HIGH RESOLUTION INFRARED TECHNIQUES FOR ATMOSPHERIC REMOTE SENSING WORKSHOP

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APPENDIX 2

THE INFLUENCE OF NO AND CℓO VARIATIONS AT TWILIGHT ON THE INTERPRETATION OF SOLAR OCCULTATION MEASUREMENTS

BY R. BOUGHNER, J. C. LARSEN, M. NATARAJAN

THE INFLUENCE OF NO AND CℓO VARIATIONS AT TWILIGHT ON THE INTERPRETATION OF SOLAR OCCULTATION MEASUREMENTS

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ABSTRACT

Measurement of short-lived photo-chemically produced species in the stratosphere by solar occultation is difficult because the rapid variation of such species near the terminator introduces ambiguities in interpreting the measured absorption in terms of meaningful atmospheric abundances. These variations produce tangent path concentrations that are asymmetric relative to the tangent point, as opposed to the symmetrical distribution usually assumed in most inversion algorithms. Neglect of this asymmetry may yield an inverted profile that deviates significantly from the true sunset/sunrise profile. In the present paper, the influence of this effect on solar occultation measurements of CℓO and NO is examined. Time varying altitude profiles of CℓO and NO were calculated with a time-dependent photochemical model to simulate the distribution of these species during a solar occultation measurement. These distributions were subsequently used to calculate simulated radiances for various tangent paths from which mixing ratios were inferred with a conventional technique that assumes spherical symmetry. These results show that neglecting the variation of CℓO in the retrieval process produces less than a 10 percent error between the true and inverted profile for both sunrise and sunset above 18 km. For NO, errors are less than 10 percent for tangent altitudes above about 35 km for sunrise and sunset; at lower altitudes, the error increases, approaching 100 percent at altitudes near 25 km. The results also show that average inhomogeneity factors, which measure the concentration variation along the tangent path and which can be calculated from a photochemical model, can indicate which species require more careful data analysis.

Determination of stratospheric abundances of trace species from solar occultation measurements is a technique particularly useful for measurements of more tenuous gases because of the long absorption path involved. It has been successfully applied, for example, to measurements of HCL, HNO_3, NO_2, CH_4

(see summary given in Hudson, 1977), CℓO (Menzies, 1979), and to place upper limits on the abundance of N_2O_5 (King et al., 1976) based on balloon borne solar IR measurements (Murcray et al., 1969). Measurement of short-lived photochemically produced species is more difficult because rapid variation of such species near the terminator introduces ambiguities interpreting the measured absorption in terms of meaningful atmospheric abundances. For balloon measurements, this problem was addressed by Kerr et al. (1977), who found a small effect for NO_2, and by Goldman et al. (1978), who concluded that serious errors would arise for NO in the lower stratosphere. The present paper reports on a similar study that uses results of a time-dependent photochemical model in conjunction with a radiance simulation and inversion algorithm to establish quantitatively the impact of concentration variations near the terminator on the interpretation of sunrise/sunset occultation measurements of CℓO and NO from a space platform.

Occultation Geometry

Figure 1 illustrates schematically the occultation geometry. Solar radiance I_ν of frequency ν received at the instrument for a given tangent path is given by Beer's law as

$$I_\nu = I_{s,\nu} \, T_\nu = I_{s,\nu} \cdot \exp(-\tau_\nu) \qquad (1)$$

The optical thickness, τ_ν, depends on the target gas density, ρ, as follows

$$\tau_\nu = \int_{-\infty}^{\infty} \rho(s') \chi_\nu(s') ds' \qquad (2)$$

where χ_ν is the mass absorption coefficient, a function of temperature and pressure, and ds' is the incremental pathlength along the limb measured relative to the tangent point ($s' = 0$). Equation (2) can also be expressed as

$$\tau_\nu = 2 \int_{Z_T}^{\infty} \rho_n(z) \ \chi_\nu(z) \ \sec\theta(z) \ R(z, \theta) \ dz \qquad (3)$$

where

$$R(z,\theta) = 1/2[\rho(z,\theta) + \rho(z,\pi - \theta)]/\rho_n(z) \qquad (4)$$

z and θ are defined in Figure 1, and Z_T is the tangent altitude. The term $\rho_n(z) = \rho(z,\pi/2)$, the tangent point density at altitude z, is the value to be inferred.

The assumption of spherical symmetry is equivalent to taking $R(z,\theta) = 1$ in equation (3). Consequently, $R(z,\theta)$ can be thought of as an inhomogeneity factor because the magnitude of its deviation from unity indicates the degree to which the concentration varies along the limb. Equation (3) also shows that if the concentration varies so that $R \doteq 1$, then one should be able to retrieve a concentration profile that is close to $\rho_n(z)$. The factor R may diverge substantially from one in a given region but have little overall significance since the incremental contribution from that region to the total optical thickness is small. In order to account for this, we define a mean factor for a tangent path, $R(Z_T)$, as the ratio of the actual column density along the absorption path to the column density that would be present, assuming spherical symmetry, with distribution $\rho_n(z)$. Since most inversion algorithms assume spherical symmetry, equation (3) implies that if $\bar{R} < 1$ (>1), the inferred concentration is smaller (larger) than the desired value $\rho_n(z)$. The quantities $R(z,\theta)$ and $\bar{R}$ can be obtained from a time-dependent photochemical calculation as described in the next section.

Photochemical Model

The concentration variation, $\rho(z,\theta)$, of the target gas along a given tangent path was calculated with a time-dependent photochemical model using a two step process as indicated below. The chemical scheme used (Boughner and Nealy, 1979) includes all the important reactions involving the major elements within the oxygen, nitrogen, hydrogen, and chlorine families. Altitude profiles of the long-lived species and chemical families (O_3, H_2O, CH_4, N_2O, NO_x, $C\ell_x$) were held fixed in the time varying calculations. These distributions and the initial profiles of the remaining species were computed from 16 to 55 km at 1.5 km increments from a steady-state photo-chemical model that incorporates correction factors for diurnal effects (Boughner and Nealy, 1979). Temperature and total molecular number density distributions from the U. S. Standard Atmosphere (1976) were used in the photochemical model and in the simulation-retrieval calculations. The results presented below correspond to a $C\ell_x$ mixing ratio which becomes asymptotic to 4.8 ppbv in the upper stratosphere. This concentration was used in order to obtain sufficient $C\ell O$ concentrations for the retrievals and to emphasize its diurnal variability. Other calculations, not reported here, indicate the conclusions are unaffected if a $C\ell_x$ concentration closer to that which is thought to exist presently in the stratosphere is used.

Because the short-lived species are driven primarily by photodissociation processes, photolysis rates were calculated for a spherical atmosphere at the equinox and a latitude of 45° with molecular scattering and reflection from the lower atmosphere and surface included. Due to the inherent difficulties associated with making multiple scattering calculations in a spherical atmosphere for grazing sun angles, only the single scattering approximation was used. However, comparisons with detailed multiple scattering calculations (Luther et al., 1978) at zenith angles where the plane-parallel approximation is valid indicate that our single scattering results account for about 70 to 80 percent of the effects of scattering on the photolysis rates. Back reflection from the lower atmosphere/surface system, which embodies the influence of cloud and aerosol scattering, was treated very simply as a Lambertian surface with reflectivity 0.25. With the Lambertian assumption, the photolysis rates are independent of the assumed surface reflectivity for high solar zenith angles.

Figures 2 and 3 illustrate the variations of $C\ell O$ and NO, respectively, at sunset as a function of local zenith angle along the absorption path for tangent altitudes of 19 km and 34 km, computed as described above. The variation with zenith angle represents both altitudinal and diurnal variations.

Simulation-Retrieval Calculations

A simulated radiance was calculated for 32 tangent altitudes between 16 and 55 km using equations (1) and (3) combined with the time varying densities, $\rho(z,\theta)$, from the photochemical model calculations. The mass absorption coefficient was modeled with a Lorentz or Voight line shape depending on altitude and frequency. Line strengths and half-widths for $C\ell O$ (Rogowski et al., 1978) and NO (Abels and Shaw, 1966) complete the information needed to specify χ_ν. The retrieval algorithm is an onion peel method (Tallamaraju, 1975) adapted for use with a high spectral resolution laser heterodyne radiometer (Menzies, 1979;

Peyton et al., 1975). Interference from other atmospheric gases with nearby absorption lines was included in the calculation of χ_ν based on the AFCRL compilation (McClatchey, 1973), but in all cases the effect was negligible on the inferred concentration. Most onion-peel retrievals use the assumption of spherical symmetry to reduce the number of unknown densities along the absorption path to the density at the tangent point. After this density is obtained, it becomes available for use at lower tangent altitudes. If $R(z,\theta) = 1$, the assumption of spherical symmetry holds, and the retrieval process will reproduce the vertical concentration profile. Those species for which $R(z,\theta)$ differs greatly from 1 are subject to error because the average density $[0.5\{\rho(z,\theta) + \rho(z,\pi - \theta)\}]$ at altitude z along the absorption path will no longer match the previously inferred density at the tangent point $\rho_n(z)$. The inability of the retrieval to detect this deviation from spherical symmetry will lead to errors in the retrieved profile as illustrated in Figures 4 and 5. Here, the inverted profiles for CℓO and NO are displayed at sunset along with the inverted local sunset profile $\rho_n(z)$.

DISCUSSION

The asymmetrical distributions displayed in Figures 2 and 3 are indications of the chemical conversions taking place along the limb in response to variations in the amount of transmitted sunlight. For NO, the symmetry is particularly pronounced at low stratospheric altitudes where NO is rapidly converted to NO_2 via reaction with O_3 as sunlight in the wavelength region of NO_2 photolysis rapidly diminishes for $\theta > 90^\circ$. The asymmetry is smaller for CℓO because its major loss at "night" is conversion to $C\ell ONO_2$ by reaction with NO_2 which occurs on a longer time scale in comparison with the NO to NO_2 conversion. At 19 km, the skewed distribution for NO results in approximately 75 percent of the total optical depth in the tangent path occurring on the sun side of the tangent point, which contrasts sharply with the 50-50 split assumed for spherical symmetry. In addition, the inhomogeneity factors are substantially smaller than 1. This fact is reflected in the $\bar{R}$ variation shown in Figure 6 as a function of tangent height. Since $\bar{R} < 1$, the retrieved profile will fall progressively below the desired profile $\rho_n(z)$ as the tangent altitude decreases, a fact confirmed by the simulated retrieval shown in Figure 5. For CℓO, the parameter

$\bar{R}$ deviates from unity by less than 10 percent for altitudes above 16 km so that the retrieved profile is close to $\rho_n(z)$, as shown in Figure 4. Results for CℓO and NO at sunrise are similar to those displayed in Figures 4 and 5 except the altitude at which the retrieved profile begins to deviate from $\rho_n(z)$ is moved upward by approximately 4 km for both CℓO and NO. Although these results were obtained with one specific retrieval technique, any occultation absorption technique that assumes spherical symmetry and attempts to infer a vertical concentration profile from the diurnal variation used in this paper will reproduce the overall trend of Figures 5 and 6.

In summary, neglect of the twilight variation of CℓO results in less than 10 percent differences between the inverted profile and the true profile above 18 km. For NO, however, these variations must be included for altitudes below approximately 30 to 35 km. Otherwise, the inverted profile becomes substantially smaller than the true 90° profile. Time-dependent photochemical calculations, such as those summarized here, are one way to incorporate these effects into the inversion process. However, the influence of various model input parameters and assumptions on the inverted profiles must be carefully studied in order to establish the feasibility of this approach.

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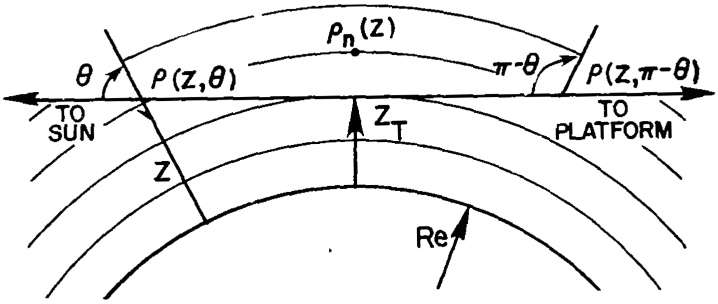

Figure 1.- Occultation geometry.

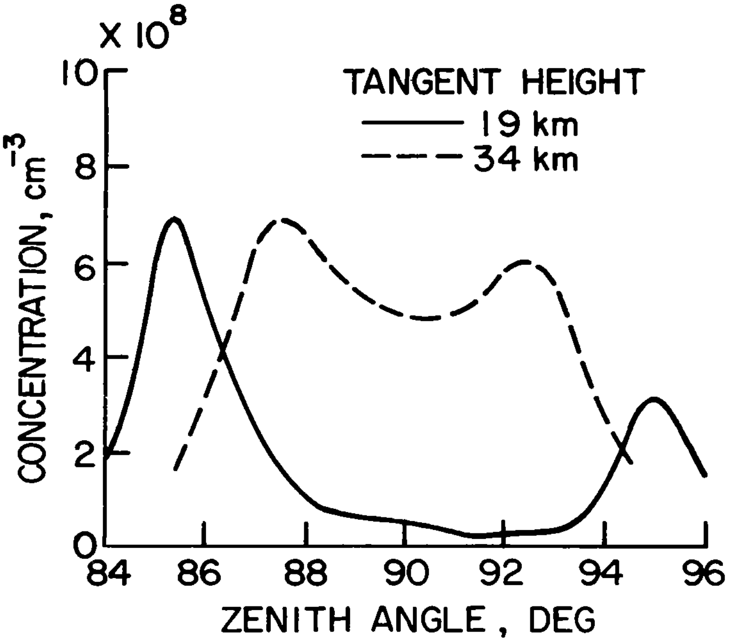

Figure 2.- Sunset variation of CℓO concentration as a function of local zenith angle along absorption path for tangent heights of 19 and 34 km.

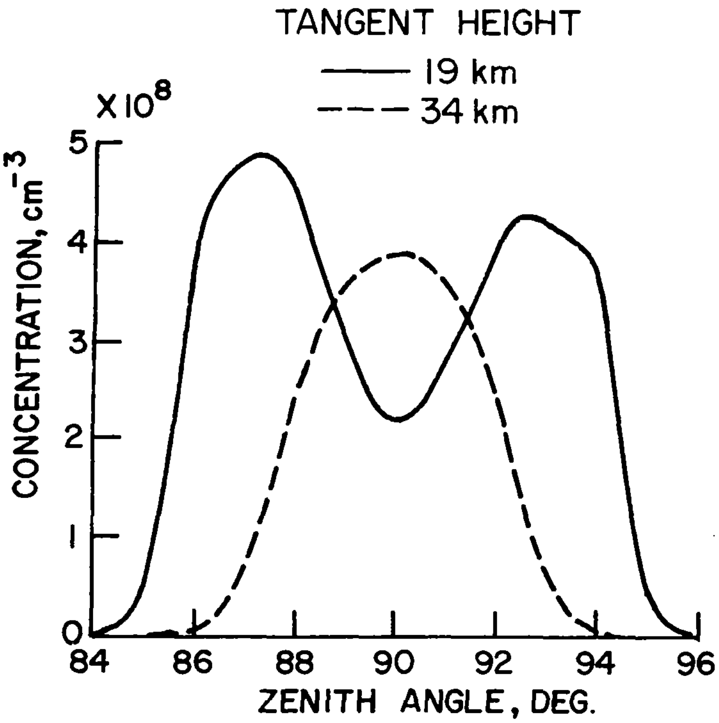

Figure 3.- Sunset variation of NO concentration as a function of local zenith angle along absorption path for tangent heights of 19 and 34 km.

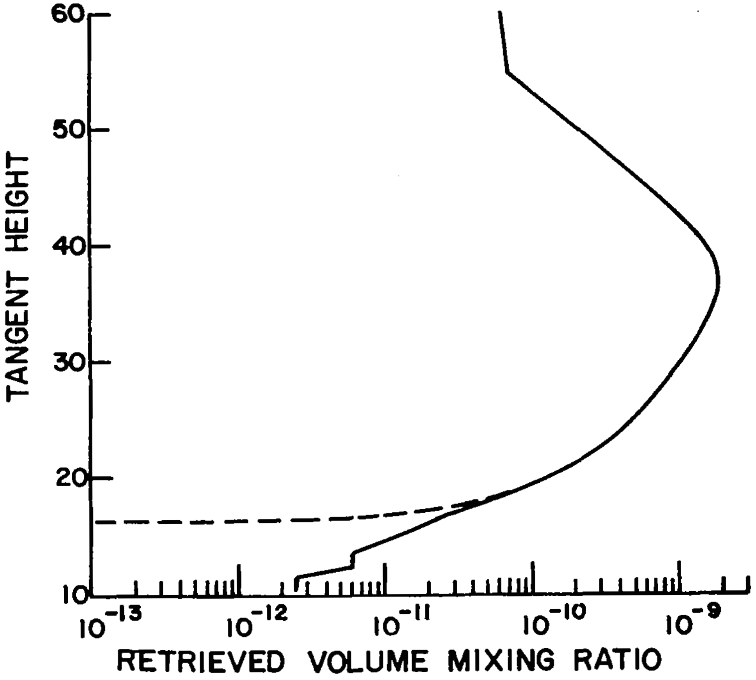

Figure 4.- Retrieved CℓO sunset profiles based on two simulated radiance data sets with $R(z,\theta) \neq 1$ (dashed line) and $R(z,\theta) = 1$ (solid line) in equation (3). For both cases, the retrieval algorithm assumes $R(z,\theta) = 1$. Solid line agrees closely with actual tangent height distribution $\rho_n(z)$ (not shown).

APPENDIX 3

AN EXPERIMENT CONCEPT TO MEASURE STRATOSPHERIC TRACE CONSTITUENTS BY LASER HETERODYNE SPECTROSCOPY

By Frank Allario, James M. Hoell, Steven J. Katzberg,
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AN EXPERIMENT CONCEPT TO MEASURE STRATOSPHERIC TRACE CONSTITUENTS BY LASER HETERODYNE SPECTROSCOPY

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ABSTRACT

Laser Heterodyne Spectroscopy (LHS) techniques with semiconductor laser local oscillators (LO) in the 3-30 μm range have the potential to measure radical gas species in the stratosphere. The goal of this experiment is to measure radical gases from Spacelab, including $C\ell O$, $C\ell ONO_2$, HO_2, H_2O_2, N_2O_5, and $HOC\ell$ in solar occultation with vertical resolution $\leq$ 2 km and vertical range from 10 to 70 km. Sensitivity analyses have been performed on $C\ell O$ and O_3 to determine design criteria for the LHS instrument. Results show that O_3 and $C\ell O$ vertical profiles can be measured with an accuracy $\geq$ 95 percent and $\geq$ 80 percent, respectively, over the total profile. These accuracies require the LO to maintain the following characteristics: frequency stability ($\Delta f_W \leq 20$ MHz), single mode power ($P_{LO} \geq 500$ μW), and minimum frequency drift (≤ 5 MHz). Laboratory heterodyne measurements performed with semiconductor lasers generated the same shot-noise photocurrent as CO_2 lasers for comparable single mode power. "Excess-noise" regions were identified, but could be wavelength controlled by fine control of operating temperature and injection current. Doppler shift effects and limited solar occultation measurement times due to Spacelab orbits should pose minimum mission constraints on the experiment.

I. INTRODUCTION

The possibility that anthropogenic activity might affect the delicate balance of stratospheric ozone became apparent in 1971 with the potential that injection of oxides of nitrogen [1,2] would increase the rate of catalytic destruction of O_3. Since then, other effects on the chemistry of the upper atmosphere have been identified including chlorine from chlorofluorocarbons [3], bromine compounds [4], and perturbations to the global nitrogen cycle and atmospheric N_2O [5,6]. Since that time a number of scientific measurements of the upper atmosphere have been performed from ground-based, aircraft and balloon platforms and compared to photochemical models of the stratosphere [7]. Recently, a satellite investigation of the stratosphere (Nimbus-7) was launched to measure aerosols and several molecular species of the nitrogen oxide chemical family [8].

In 1977, a science working group was sponsored by the National Aeronautics and Space Administration to develop a satellite program to perform research on the chemistry, dynamics, and energy balance of the upper atmosphere [9]. A major recommendation of the working group was that measurements of several families of stratospheric constituents including oxygen, nitrogen, hydrogen, and chlorine should be conducted to understand the interaction of these basic families and their effects on the global budget of stratospheric O_3. These chemical families are similar since they contain three basic types of species: source molecules which are relatively stable compounds, radicals that are short-lived derivatives of source molecules, and sink molecules that are chemically evolved forms of the radicals. Infrared measurements of source, sink, and radical species represent an important technique for stratospheric observations, since most of the important species contain vibrational-rotational spectra from 3.0 to 30.0 μm. Two types of measurements available for stratospheric observations are solar occultation and limb emission [10] for which several generic classes of instruments can be used, including gas filter correlation radiometry [11], interferometry, [10] grating spectrometry, and laser heterodyne spectroscopy [12].

For performing measurements of most of the major source and sink gases in the stratosphere, gas filter correlation radiometry and interferometry are scheduled for satellite and Spacelab investigations. For performing initial detection and measurement of some of the radical gas species (e.g. $C\ell O$, HO_2, $HOC\ell$, H_2O_2, N_2O_5,...), laser heterodyne spectroscopy may be required due to the inherent high spectral resolving power ($\Delta\nu \leq 0.001$ cm^{-1}) and the potential gain in signal to noise of the heterodyne detection system. A recent measurement of stratospheric $C\ell O$ with heterodyne detection from a balloon platform using a $C^{14}O_2^{12}$ laser transition as the local oscillator has been reported [13]. Excellent reviews of the theory of heterodyne receivers for the infrared have been published [12,14], and atmospheric measurements of transmissivity [15], stratospheric O_3 [16,17] and tropospheric NH_3 [18] have been reported with CO_2 lasers as local oscillators. The use of CO_2 lasers as local oscillators, however, limits the species which can be measured since the overlap of CO_2 laser transitions with molecular absorption lines involves a limited number of atmospheric molecules. Tunable Pb-salt semiconductor lasers provide the ability to measure a variety of stratospheric molecules, while also optimizing molecular line strengths and atmospheric windows in the atmosphere [19]. Measurements of stratospheric O_3 [20] and HNO_3 [21] have been reported from ground-based solar occultation systems using infrared semiconductor lasers and demonstrate the importance of high resolution in resolving molecular absorption spectra in the stratosphere.

In this paper, an experiment concept and analysis of a Laser Heterodyne Spectrometer (LHS) experiment from a Spacelab platform for measuring the vertical profiles of several stratospheric trace gases will be described. The goal of this experiment is to develop a multiple gas, laser heterodyne receiver with the capability to measure 2 to 4 gases simultaneously from Spacelab and ultimately free-flyer platforms. Specific target gases for this experiment will be determined after collaborative experiments with interferometric and gas filter correlation radiometers have been analyzed. Sensitivity analyses are currently being performed for tenuous molecules such as $C\ell O$, $C\ell ONO_2$, $HOC\ell$, HO_2, H_2O_2, and N_2O_5, although the capability exists with LHS to measure more abundant gases such as O_3, HNO_3, N_2O, NO_2, CH_4, and others. The experiment operates in a solar occultation mode, measuring vertical profiles from 10 to 70 km, with vertical resolution $\leq$ 2 km. In the analysis of the experiment concept, tunable semiconductor lasers are considered as local oscillators from 7.5 to 13.0 μm. Laboratory measurements of some performance characteristics of the local oscillator and heterodyne detector are used in sensitivity studies of the experiment. These results provide the basic design criteria for development of an LHS instrument for performing a number of scientific investigations from Spacelab in the upper atmosphere.

II. EXPERIMENT CONCEPT

The experiment concept for the LHS experiment is shown in Figure 1. A detailed description of the solar occultation technique for measuring the vertical profile of molecular gases has been presented for radiometric sensors, including details of the onion-peeling technique [11,22]. The major difference of the LHS experiment over other techniques is in the use of heterodyne detection, with high spectral resolving power of the optical receiver, and shot-noise limited detection of the heterodyne process. In formulating a scientific investigation for the LHS experiment, scientific gases must be chosen which significantly add to measurements of the stratosphere currently proposed by other techniques, either through new measurements, in significantly improving the accuracy of previously measured gases, or in significantly improving specific scientific measurements of stratospheric chemistry, such as ratios of $C\ell O/C\ell ONO_2$. Candidate gases which fall in these categories include most radical gas species, such as $C\ell O$, $C\ell ONO_2$, HO_2, H_2O_2, $HOC\ell$, and N_2O_5. Therefore, in the definition of the LHS experiment, it is important to determine estimates of the ability of the experiment to generate the vertical profiles of these gases with high precision and accuracy. Also, since most of these radical gas species are diurnally varying, it is important to address the question of interpretation of solar occultation data in photochemical models. A discussion of the latter has been presented [23] and currently does not appear to significantly impact the measurement of LHS target molecules.

A single gas LHS instrument is shown in Figure 2. A conventional heterodyne front-end receiver collects the radiometric solar signal which serves as a blackbody continuum source, attenuated by individual vibrational-rotational absorption lines of stratospheric molecules. A semiconductor laser tuned to the absorption maximum of a vibrational line serves as the local oscillator, simultaneously irradiating the surface of a mercury-cadmium-telluride (Hg-Cd-Te) photomixer with the solar signal. Phase fronts of the incoming radiometric signal and local oscillator must be matched at the photomixer to obtain maximum mixing efficiency. In the photomixing process, a range of intermediate frequencies (IF) in both upper and lower sidebands are generated, with the upper limit of this range determined by the frequency response of the photomixer and preamplifier system. The two sidebands are folded at the IF so that a given radio frequency (RF) filter contains contributions from both upper and lower sidebands. A multiplex advantage is gained by simultaneously sampling the IF range with a set of consecutive RF filters, and a maximum two-fold increase in signal is obtained by tuning the local oscillator to an absorption peak. For photovoltaic Hg-Cd-Te detectors, frequency responses > 1.5 GHz at the 3 dB roll-off point, with 25% quantum efficiency, have been reported [24], although significantly higher quantum efficiencies with research photomixers have been measured in our laboratory.

The channelized IF signals are proportional to the atmospheric transmissivity at a particular spectral location within the absorption line, and are a measure of the distribution of spectral absorption of a molecular transition. The IF signals are subsequently converted to a molecular gas concentration at the tangent altitude by an inversion algorithm utilizing Beer's law. Vertical profiles of gas concentrations in the stratosphere are obtained by locking the instrument pointing system to a fixed location on the solar disc and using the orbital motion of the spacecraft to generate various slant path angles through the atmosphere. The lower altitude limit is determined by cloud cover. The vertical resolution of the measurement is determined essentially by two parameters: (1) the field of view (≤ 0.25 mrad), and (2) the post detection integration time (τ) to achieve signal-to-noise ratios defined by the desired sensitivity of the measurement. In the simulation studies to be discussed subsequently, integration times of 100 to 500 ms provide sufficient sensitivity for most of the stratospheric gases analyzed, with a vertical resolution ≤ 2 km.

A major subsystem not shown in Figure 2 but crucial to the LHS experiment concept is the wavelength identification and control system for identifying the local oscillator wavelength and controlling it to a specified precision required by the scientific measurement and to account for Doppler shifts. Sensitivity studies performed for some of the LHS target gases indicate that a 5 MHz precision in wavelength is required to generate vertical profiles with an rms uncertainty $\leq 5\%$. For larger rms uncertainties in the retrieved profiles, rms uncertainties of 20 to 30 MHz are acceptable. To meet these scientific requirements a combination of low pressure gas cells with appropriate reference gases (i.e. SO_2, NH_3) and a Fabry-Perot etalon should be adequate for final design of the LHS optical receiver.

III. SENSITIVITY ANALYSIS

The sensitivity analysis performed for the LHS experiment consisted of three basic codes: (1) a line-by-line radiative transfer code to calculate transmission through the upper atmosphere in narrow spectral ranges, spanning the 2.0 to 15.0 μm range; (2) an instrument transfer code to simulate the instrument response function, converting solar irradiance to digitized voltages vs. altitude, and (3) an inversion algorithm to convert the digitized voltages to vertical profiles.

In the radiative transfer code, transmittance of the solar signal through the atmosphere is governed by Beer's law, and a spherically symmetric atmosphere is assumed consisting of 100 shells with density ρ_g and absorption cross section k_g defined in each shell for the target gas and interfering gas lines. The altitude dependence of k_g is governed by the temperature dependence of the line strength, and the pressure and temperature dependence of the half widths of the lines. Line strengths, Lorentz half widths, and lower state energies are taken from the AFCRL compilation [25] and supplemented with measurements using semiconductor lasers [26,27,28].

The model for the instrument transfer code is shown in Fig. 3. In the heterodyne conversion process, the receiver integrates over the solid angle field of view (Ω), detector area (A) and intermediate frequency channel bandwidth (B_{IF}) to generate an IF current in each channel, proportional to the input radiance at each tangent altitude. Integration over the field of view and detector area is calculated according to Siegman's antenna theorem [29] as

$$P(\nu,H_T) = \int_A \int_\Omega B(\nu,H_T)\, d\Omega dA \sim B(\nu,H_T) A\Omega \simeq B(\nu,H_T)\lambda^2 \qquad (1)$$

where $P(\nu,H_T)$ = spectral power at the photomixer (ergs/sec-cm^{-1}); $B(\nu,H_T)$ = solar radiance attenuated by the atmosphere (ergs/sec-cm^{-1}-sr-cm^2); Ω = solid angle field of view (sr); A = photomixer area (cm^2); λ = wavelength (cm). The expression for the dc current signal generated in each channel i, is given by

$$I_i(H_T) = \frac{2e^2 q P_{LO}}{h^2 \nu^2} \int_{B_{IF}} P(\nu,H_T)\, |H_O(IF)|^2 |H_{PA}(IF)|^2 \, df \qquad (2)$$

where e = electronic charge; q = effective detector quantum efficiency; P_{LO} = local oscillator power (watts); h = Planck's constant; ν = wavenumber. $|H_O(IF)|^2$; $|H_{PA}(IF)|^2$ = power spectral density transfer function of the photomixer and preamplifier, respectively. The dc signal currents are then assumed to be digitized with a digitization error of $\pm 0.1\%$, and are subsequently utilized with the inversion algorithm to obtain the retrieved gas concentration as a function of altitude.

The instrument transfer code has been developed to allow parametric studies of various noise effects induced by the optical, electronic, and local oscillator subsystems. Variable parameters in the model include local oscillator power, effective detector quantum efficiency, detector half power frequency, low pass bandwidth, and optical power losses. Noise sources of the detector include shot noise of the local oscillator, broadband shot noise induced by the signal, leakage current of the detector, Johnson noise of the detector and preamplifier, and noise induced by photomixing the local oscillator and the solar signal. The overall optical efficiency due to the beamsplitter, optical chopper, and polarization effects are assumed to be 0.125 for the sensitivity analysis.

The inversion algorithm uses the standard "onion peeling" technique illustrated in Figure 1 and discussed in reference [22] to convert the digitized voltages to molecular concentrations. An important advantage of the LHS technique in reducing the radiance data is the ability of LHS to view a relatively clear channel in the stratosphere (reference channel) with proper selection of the laser local oscillator wavelength and the location of the outermost RF channel. Therefore, changes in the solar intensity and/or background continuum absorption can be minimized by ratioing the reference channel to each signal channel. In the Spacelab experiment, exoatmospheric intensity weighted by the detector roll-off and averaged over each channel bandwidth can also be obtained. In the sensitivity analysis for the experiment, a transmittance ($\bar{\tau}_i$) is defined for each channel as

$$\bar{\tau}_i \equiv \frac{I_i(H_T)}{I_i(EXO)} \tag{3}$$

where $I_i(EXO)$ is the signal current in each channel for the exoatmospheric measurement, and $I_i(H_T)$ is the signal current at an altitude corresponding to tangent altitude, H_T. This ratio minimizes dc biases in the electronic gain of each channel. Subsequently, the transmission ratio is formed from equation (3) for channels i and j.

$$TR(H_T) = \frac{\bar{\tau}_i}{\bar{\tau}_j} \tag{4}$$

Typically, j is the least absorbing signal channel, and i is the ith signal channel within the molecular absorption line. This transmission ratio is used in the standard "onion peeling" technique to generate vertical profiles of molecular constituents.

IV. SIMULATION RESULTS

Figure 4 shows results of the LHS sensitivity studies for measuring stratospheric O_3 from Spacelab altitudes. For this simulation, a local oscillator (LO) wavelength at 1129.4420 cm^{-1} was selected to correspond to the peak of a relatively intense O_3 molecular transition lying within an atmospheric window. Five IF channels were selected to detect radiances within the O_3 line in order to optimize the sensitivity of the measurement over the entire altitude range. The position of the IF channel centers relative to the LO wavelength are listed as DNU (cm^{-1}); the bandpass of each channel is listed as BETA (MHz). An integration time, TAU (sec), of 100 ms is used for each channel. For each tangent altitude, two channels are used to invert the radiance data. One channel lies within the O_3 absorption line, and the other channel lies outside the absorption line to account for fluctuations in the background radiance and for continuum absorption effects. For upper altitudes where O_3 attenuation is relatively low, channels near the center of the line are used; for lower altitudes where O_3 attenuation is high, channels in the wing of the O_3 line are used. The channels selected for various altitudes are listed to the right of Fig. 4.

In Fig. 4, the two solid profiles represent the initial and mean retrieved O_3 profiles. Error bars indicate standard deviation of 20 sample retrievals generated by perturbing the simulated instrument current profile(from (2)) with a random Gaussian noise source to simulate random instrument errors. The error bars are an estimate of the uncertainty in the LHS measurement of ozone at various tangent altitudes. Figure 5 shows the fractional error of the mean mixing ratio for the simulated measurements as a function of altitude for the profile in Fig. 4. Measurement uncertainties $\leq$ 5% can be achieved for altitudes $\geq$ 20 km. For altitudes below 20 km, the fractional error increases due to the relatively small O_3 concentrations in this altitude range and the large attenuation by O_3 in the outer shells. To obtain a fractional error of the mean $\leq$ 5% below 20 km requires the use of a second local oscillator tuned to a weaker O_3 transition in order to increase the solar radiance incident upon the Hg-Cd-Te photomixer. Use of two LO's for the ozone measurement provide measurement uncertainties $\leq$ 5% over the total profile.

Figures 6 and 7 show similar results for $C\ell O$ for an LO wavelength of 856.499 cm^{-1}. For $C\ell O$, the fractional error in the mean mixing ratio from 20 to 42 km was approximately 20%. Larger uncertainties for $C\ell O$ arise due to the smaller differential absorption signal of the reference and signal channels. For these simulations, it has been assumed that atmospheric pressure at the tangent altitude can be measured to an accuracy of ± 3% [30] and the temperature profile is determined to an accuracy of $\pm 3^{o}K$. Sensitivity studies performed on O_3 and $C\ell O$ to determine effects of frequency instability (Δf_w), single mode power ($P_{\ell o}$), and minimum frequency drift ($f_{\ell o}$) of the LO on the retrieved profiles were established as: $\Delta f_w \leq 20$ MHz; $P_{\ell o} \geq 500$ μW; $f_{\ell o} \leq 5$ MHz. These parameters are within current capability of semiconductor laser technology. It should be pointed out that these sensitivity studies have not taken advantage of any smoothing techniques to improve measurement uncertainties [31], nor have they considered optimization of post-detection integration times for individual altitude measurements in the various channels. These studies are currently in progress and could provide improvements by factors of 2 in the retrieved profiles.

A major uncertainty in the accuracy of the retrieved profiles for LHS arises from current uncertainties in line intensity, position, and half width of the target gases. Small uncertainties in these parameters result in large uncertainties in the retrieved profiles. The AFCRL compilation [25] has been found to be inadequate in some cases for the LHS experiment, and future laboratory data on HO_2, $C\ell ONO_2$, N_2O_5 are required. Sensitivity studies are currently in progress for $HOC\ell$* and H_2O_2*.

V. LABORATORY HETERODYNE MEASUREMENTS

In order to provide input parameters to the sensitivity analysis of the LHS experiment, laboratory measurements have been performed to compare signal-to-noise ratios with selected semiconductor lasers and highly stable CO_2 laser

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*$HOC\ell$ data obtained from Dr. Arthur Maki; National Bureau of Standards. H_2O_2 data obtained from Dr. Aaron Goldman; University of Denver.

local oscillators. The laboratory system used to perform the experiments was similar to one reported previously by Ku and Spears [32] in which three radiation sources were used including a 1273°K blackbody, a stabilized CO_2 laser, and 10.6 μm semiconductor laser. Two photomixers were used with quantum efficiency of 12% from 3 to 115 MHz, and 38%† from 5 to 400 MHz, and a preamplifier noise figure of 2 dB. Figure 7 shows comparative results of the signal-to-noise measurements with CO_2 lasers (solid lines) and a semiconductor laser (squares). The measured signals for the CO_2 laser measurements were compared to a theoretical curve for a 1273°K blackbody, with appropriate optical losses included. Comparison between theory and experiment is shown on the figure for the two photomixers. The experiments performed with the semiconductor laser generated a maximum detector photocurrent of several hundred microamperes, with single mode operation over the tuning range. Higher signal-to-noise ratios for the semiconductor laser resulted from minor alignment differences and experimental scatter. The important point of these results is the ability of semiconductor lasers to generate the same shot-noise photocurrent as CO_2 lasers for comparable power and single mode operation. Using measured values at 1273°K, the experimental semiconductor laser curve was extrapolated to a solar temperature of 5500°K, for an effective heterodyne quantum efficiency of 25%, and other parameters listed on Figure 8. This result demonstrated that signal-to-noise ratios in excess of 1000 can be achieved at relatively low values of photocurrent corresponding to local oscillator power levels on the order of 500 to 700 μwatts.

During the course of these measurements, it was observed that semiconductor lasers exhibited regions over their tuning range in which "excess noise" was generated, degrading the heterodyne signal [32]. Excess noise regions were observed to occur in narrow tuning ranges, varying with different lasers. For individual lasers, regions of "excess noise" were reproducible for the same temperature and current settings, if the lasers did not undergo temperature cycling. Temperature cycling from room temperature to operating temperatures (15-20°K) caused slight shifts in the "excess-noise" regions. For an uncycled laser, "excess noise" regions could be controlled with minor changes in temperature and injection current.

In Fig. 9, results are shown of an experiment performed to identify whether an individual semiconductor laser exhibiting "excess noise" in the spectral range of NH_3

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†The research photomixer was provided by the MIT Lincoln Laboratories, D. L. Spears.

absorption lines could be temperature tuned to reduce the magnitude of the noise. The bottom trace on the oscilloscope photograph identifies two ammonia absorption lines obtained in a direct absorption measurement with the semiconductor laser. The top trace shows a simultaneous measurement of the photomixer output where a portion of the semiconductor laser was used as a local oscillator signal. These results demonstrate that in some cases, the region of "excess noise" can be shifted in wavelength through small changes in operating point to provide nearly shot noise limited operation over the absorption line of interest. Although these results cannot be assumed to apply for all semiconductor lasers over all tuning ranges, they are important since they demonstrate the importance of a selection process for semiconductor lasers as local oscillators and point to the flexibility possible when using the local oscillator with a cryogenic system with fine temperature control. Measurements are currently in progress to relate the onset of "excess noise" regions with other parameters of the laser including laser mode competition, far field diffraction patterns, and laser feedback mechanisms [33]. Preliminary results indicate that "excess-noise" effects are in some cases due to laser feedback mechanisms from system optics and can be eliminated. In some cases, "excess noise" effects are due to inherent laser instabilities caused by amplitude oscillations induced by competing longitudinal modes.

VI. SPACELAB MISSION CONSIDERATIONS

In defining this experiment for Spacelab or satellite measurements, several mission related considerations have been evaluated, including the Doppler shift of the absorption lines due to the instantaneous velocity of the spacecraft with respect to the tangent point in the stratosphere, and the available measurement time for the experiment. An analysis of the Doppler shift and measurement time for a typical Spacelab mission has been performed for various altitudes, orbital inclinations, and times of launch [34]. Depending upon these mission parameters, the Doppler shift ranges from a minimum of ±100 MHz to a maximum of ±800 MHz over the duration of the mission, and up to 5 MHz during the solar occultation measurement period. Since the Doppler shift increases during sunrise measurements and decreases the same amount during sunset, the heterodyne detector may require bandwidths up to 1.6 GHz under worst case conditions. With semiconductor lasers as local oscillators, the Doppler shift can be compensated by frequency shifting the local oscillator through a servo loop controlled by Shuttle ephemeris data. Therefore, orbital mission constraints do not degrade the spectral resolution of the LHS experiment since wavelength control and tracking can be achieved through the wavelength identification and control subsystem. Measurement times for sunrise and sunset measurements have also been calculated for a Spacelab pointing system in which the pointing system is fixed within the solar disc, and the tangent altitude in the atmosphere is swept by the orbital motion of the spacecraft. Total measurement times for the experiment range from 10s to >100s, again depending upon mission parameters. Dwell times for 2 km vertical resolution for a field of view of 0.25 mrad are no less than 600 msec under the most severe mission constraints. Therefore, the 100 msec integration times assumed for the sensitivity analysis are conservative and should account for the most severe orbital constraints, although larger integration times (>1 sec) should be available for typical Spacelab orbital parameters to obtain a geometrical vertical resolution $\leq$ 2 km.

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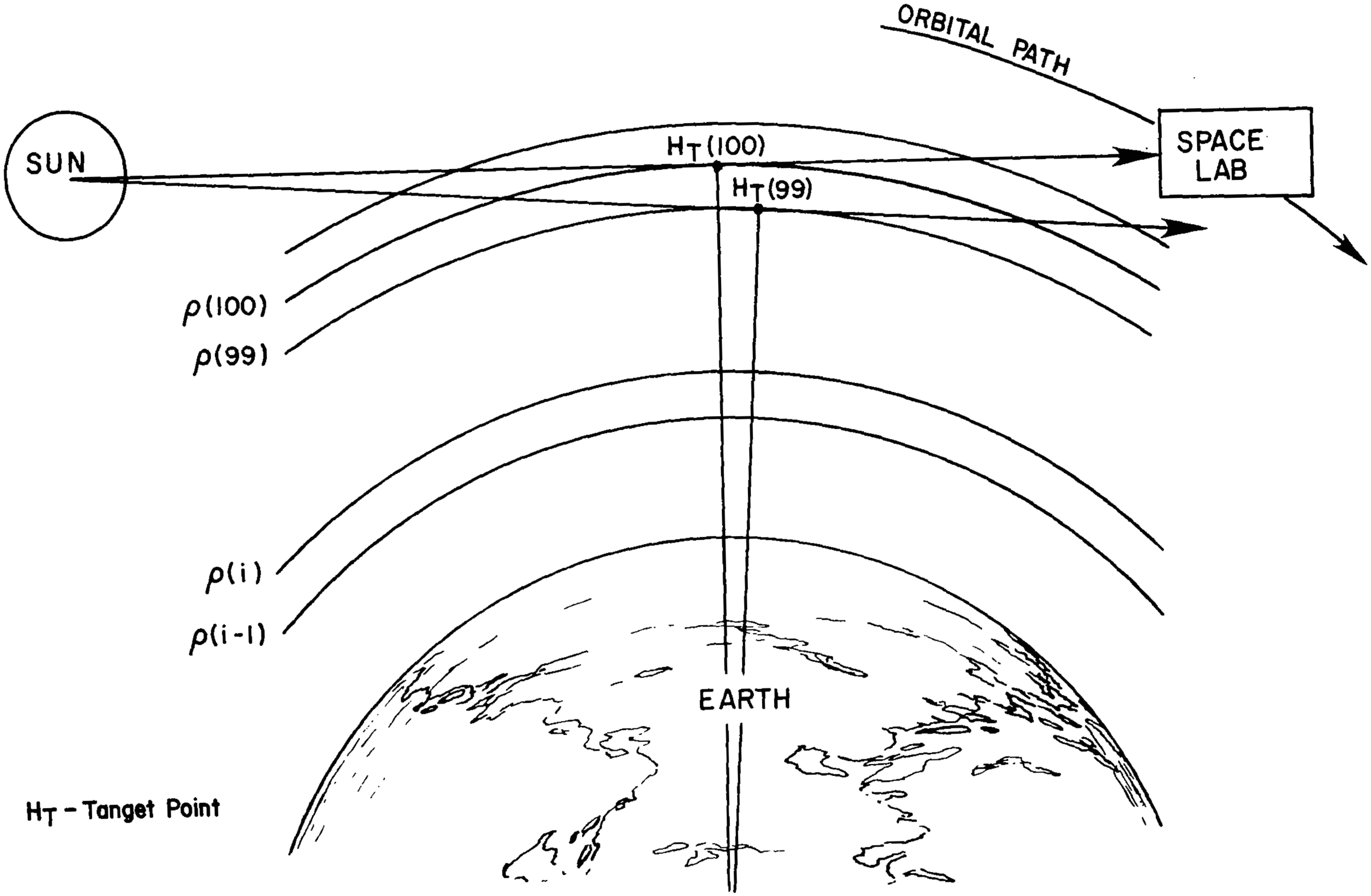

Figure 1.- Laser Heterodyne Spectrometer (LHS) experiment concept.

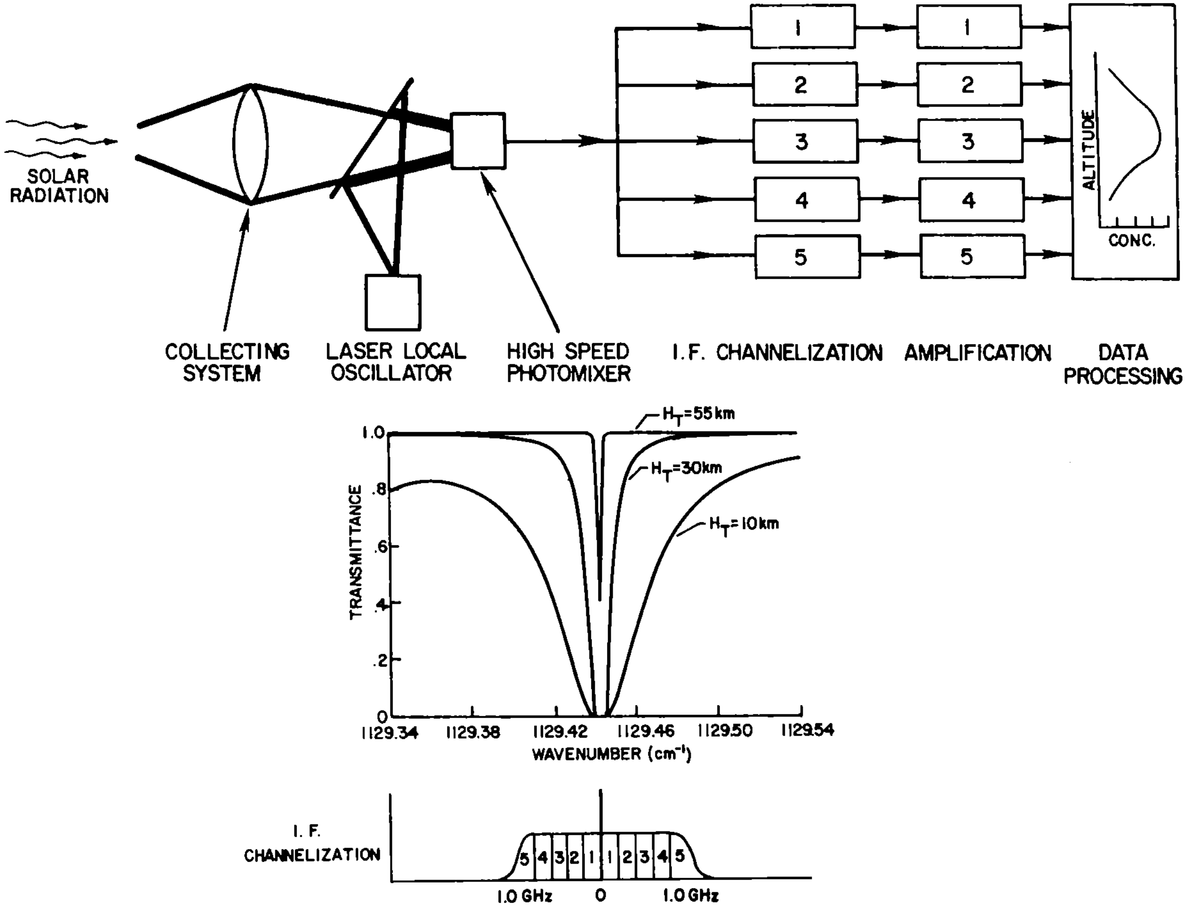

Figure 2.- Laser Heterodyne Spectrometer (LHS) instrument concept.

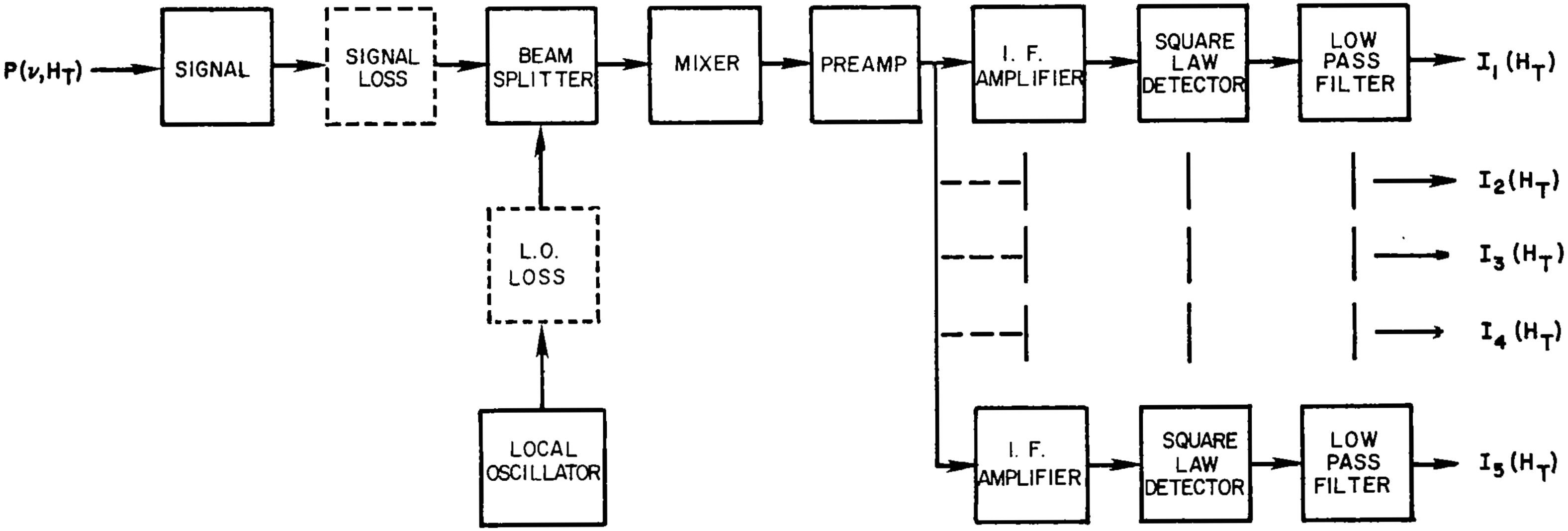

Figure 3.- Model for the LHS Instrument Transfer Function (ITF).

CHANNEL	V(CM-1)	DNU(CM-1)	BETA(MHZ)	TAU(SEC)
1	1129.4420	.0267	400.0	.100
2	1129.4420	.0158	250.0	.100
3	1129.4420	.0083	200.0	.100
4	1129.4420	.0033	100.0	.100
5	1129.4420	.0010	40.0	.100

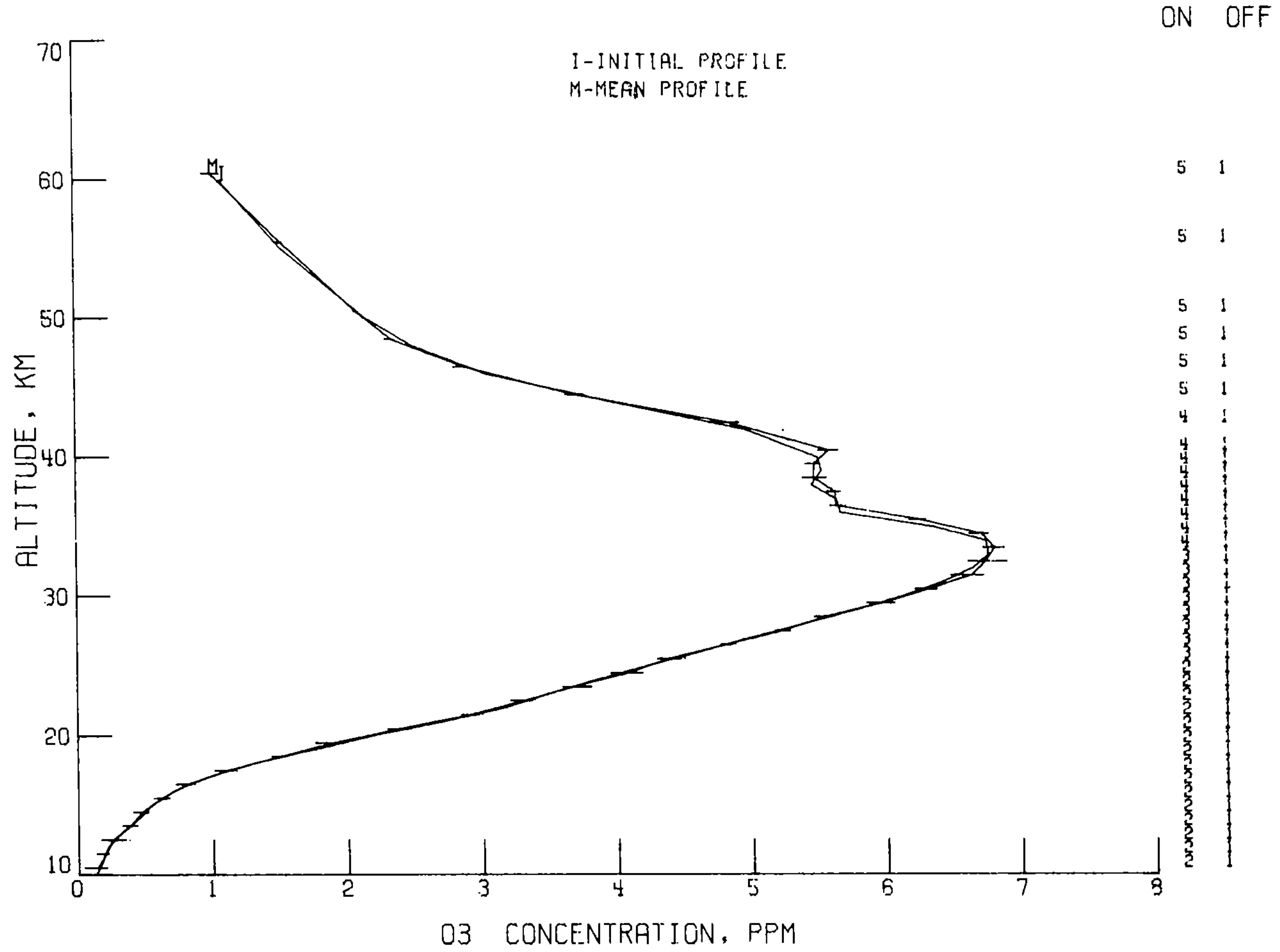

Figure 4.- LHS sensitivity results for stratospheric O_3.

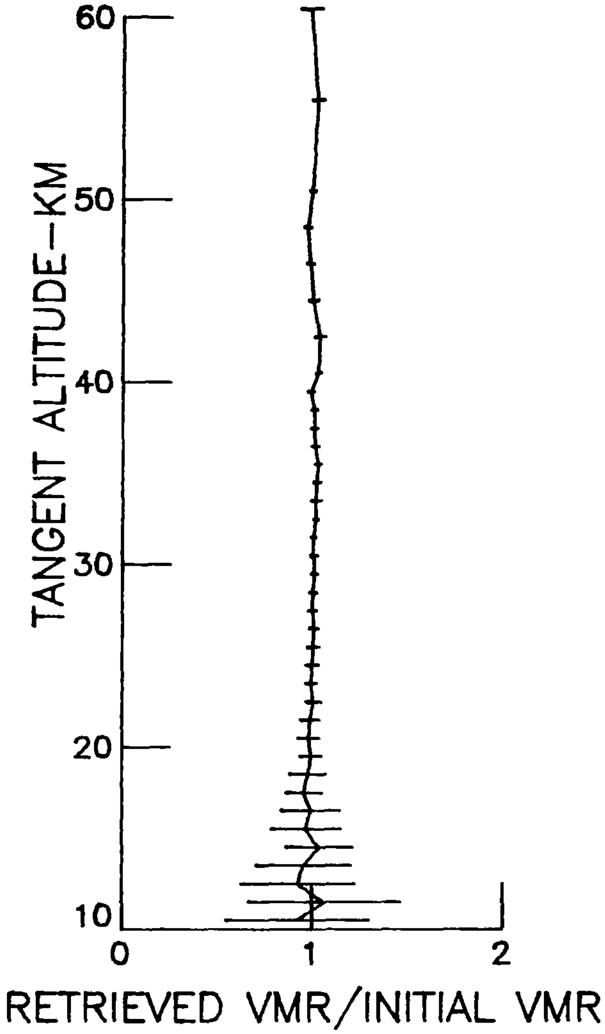

Figure 5.- Fractional error of the mean mixing ratio for stratospheric O_3. Error bars $\pm 1\sigma$ deviation.

	CHANNEL	DNUcm−1	BETAmhz	TAUsec
	1	.0267	400.0	.100
WAVELO	2	.0158	250.0	.100
856.4990	3	.0083	200.0	.100
	4	.0033	100.0	.100
	5	.0010	40.0	.100

ERROR BARS ±1σ DEVIATION

I−INITIAL PROFILE
M−MEAN PROFILE

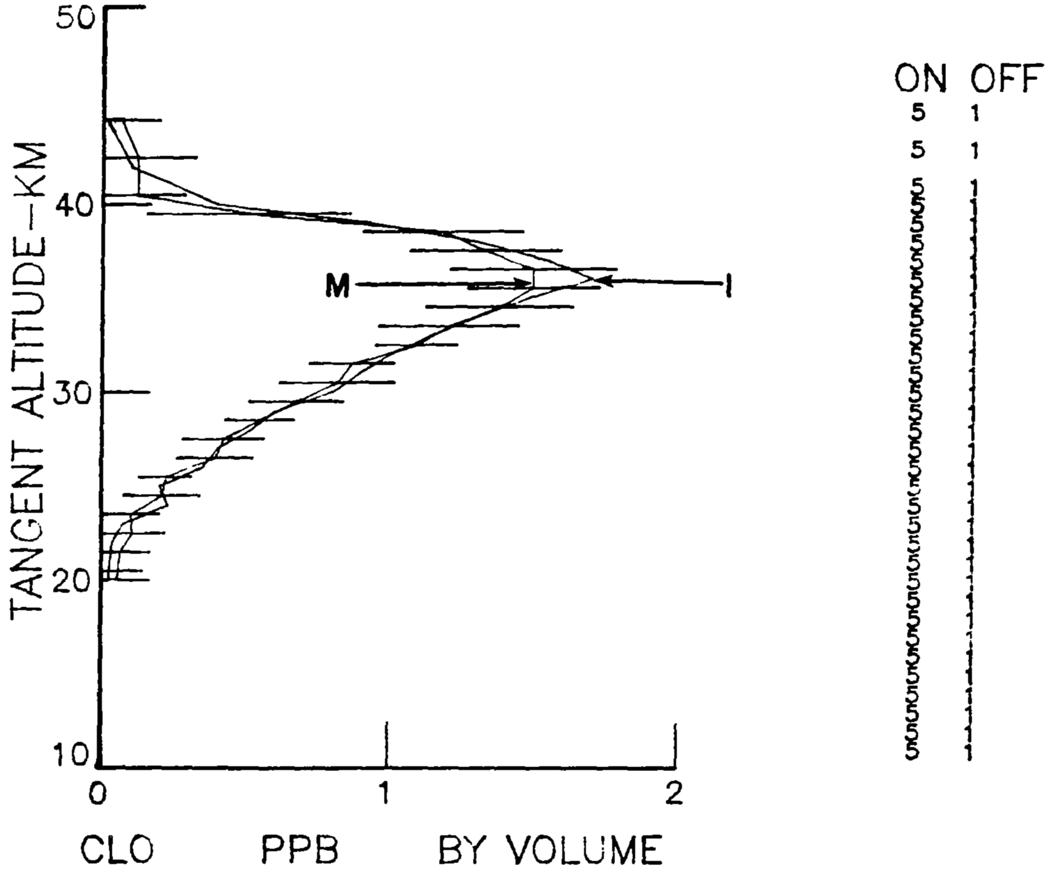

Figure 6.- LHS sensitivity results for stratospheric CℓO.

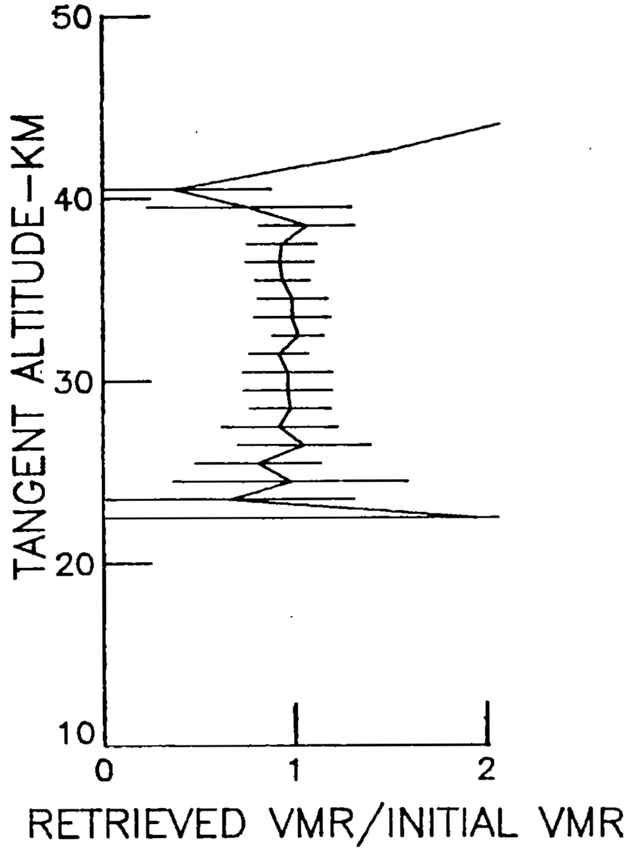

Figure 7.- Fractional error of the mean mixing ratio for stratospheric $C\ell O$. Error bars $\pm 1\sigma$ deviation.

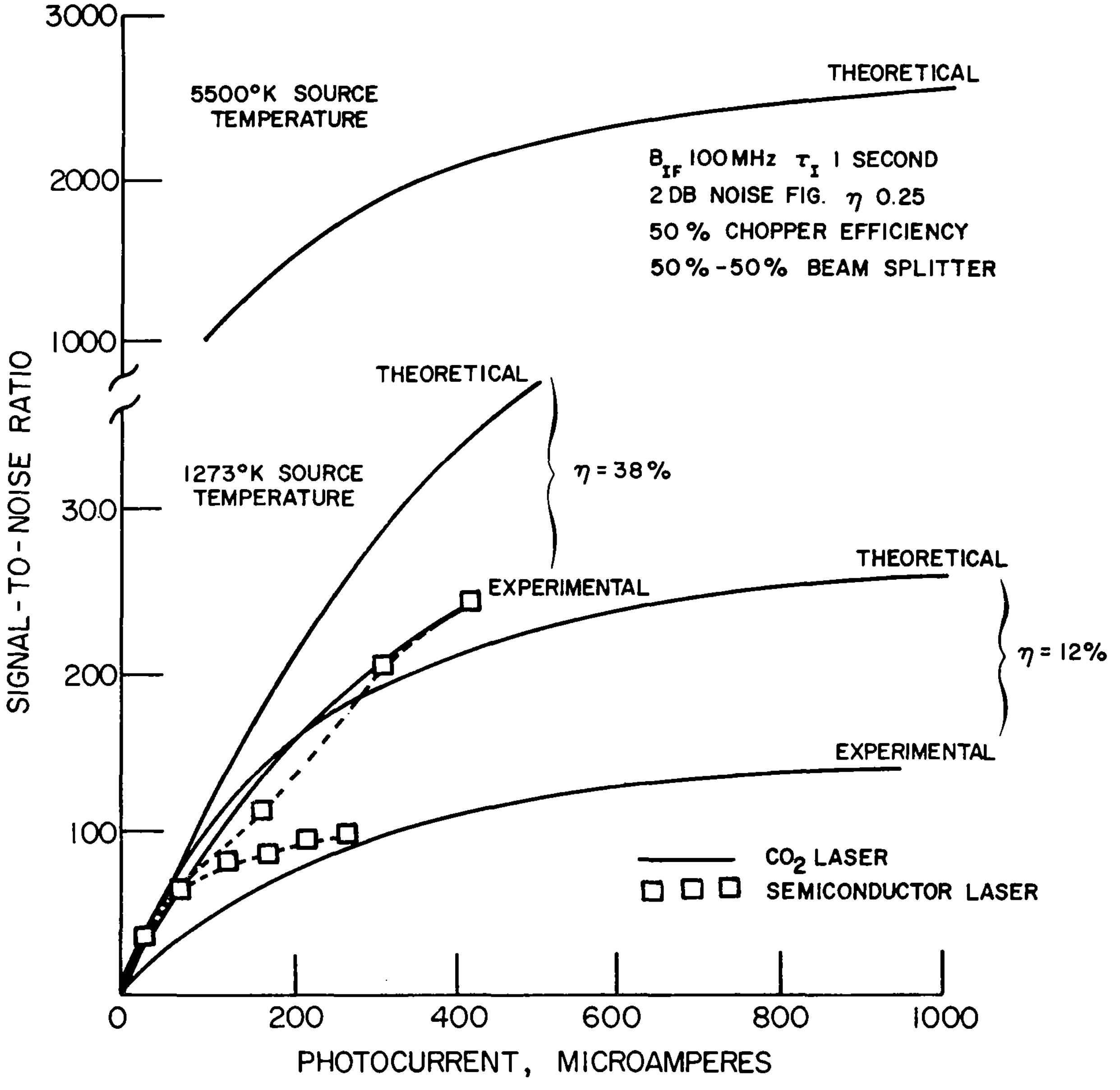

Figure 8.- Comparative results of LHS signal-to-noise ratios for CO_2 and semiconductor LO's.

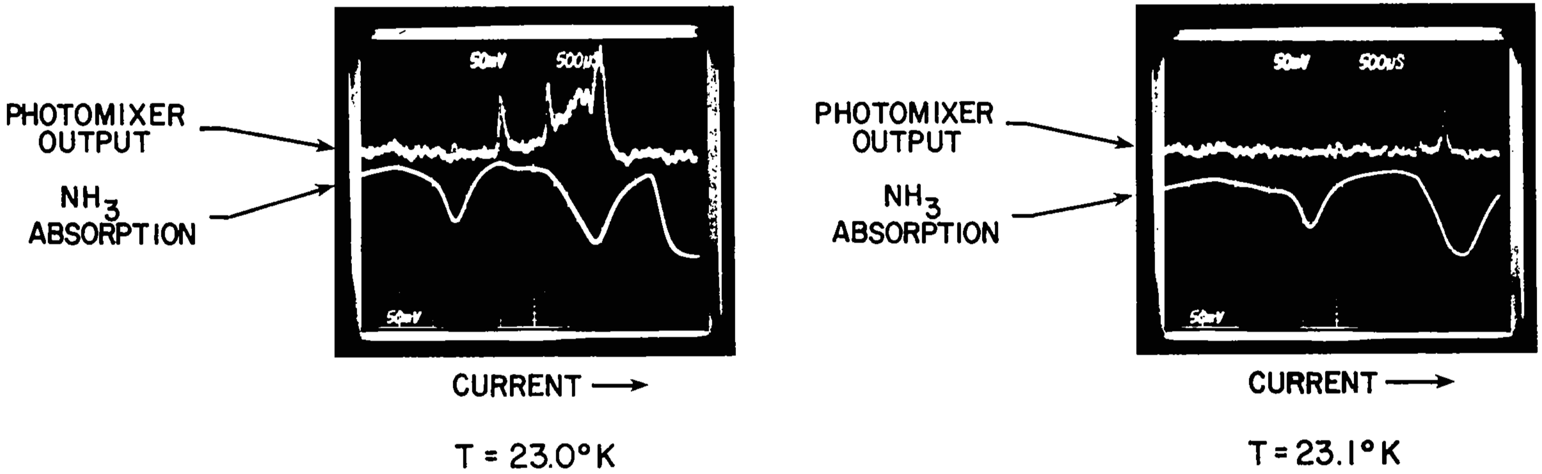

Figure 9.- Measurements of "Excess-Noise" effects in heterodyne semiconductor laser experiments.

APPENDIX 4

REVIEW OF SPECTROSCOPIC DATA FOR MEASUREMENT OF STRATOSPHERIC SPECIES

Editors: Aaron Goldman, University of Denver
James Hoell, Langley Research Center

INTRODUCTION

Background

Under NASA's Upper Atmospheric Research Program (UARP) a wide range of infrared instruments have been developed or are in various states of development for atmospheric research from Shuttle or free flyer platforms. These instruments encompass a range of spectral resolution (i.e., from 0.1 cm^{-1} to less than 0.001 cm^{-1}) and spectral coverage (i.e., from several hundred cm^{-1} to less than 0.001 cm^{-1}). The "Workshop on High Resolution Infrared Spectroscopy Techniques for Upper Atmospheric Measurements" held in Silverthorne, Colorado, July 31 to August 2, 1979, was convened to assess the role of various infrared techniques in measurements of trace gases in the stratosphere. The Workshop placed particular emphasis on the role of instruments exhibiting ultrahigh resolution (i.e., $\lesssim 0.001$ cm^{-1}) such as laser heterodyne spectrometers. The Workshop brought together scientists engaged in laboratory and upper atmosphere high resolution infrared spectroscopy. The participants were organized into four working groups, one of which considered the status of infrared spectroscopic data. The spectroscopic workshop, which will be discussed below, is a direct result of the general discussions held at Silverthorne and specific recommendations from the spectroscopic working group at Silverthorne.

At the Silverthorne Workshop, it was generally recognized that current and future stratospheric measurements as well as evaluation of the relative merits of the various instruments depends heavily upon the availability and accuracy of infrared spectroscopic data for all stratospheric species. The Workshop noted that a large body of spectroscopic data is currently available, particularly for the more abundant atmospheric species (i.e., CO_2, O_3, CH_4, N_2O, and H_2O). However, for many trace species currently of interest (ClO, $ClONO_2$, HO_2, H_2O_2, etc.) little, if any, data are available. Furthermore, it was noted that additional experimental and theoretical research is needed for virtually all species to support the high resolution instruments becoming available. The Silverthorne Workshop also noted the limitation of the spectroscopic data base which is widely used by many groups (i.e., A.F. Geophysics Laboratory (AFGL) tape). This tape, while extremely useful, is inadequate for many high resolution applications. Because of this, many laboratories in the United States and foreign countries have, or are in the process of, improving the spectral data on the AFGL tape; however, the availability and format of this data is such that it is not readily available to the community.

From these general observations, the Silverthorne spectroscopic working group recommended that a detailed review of the current spectroscopic data base be conducted and that a formalized mechanism be established to facilitate dissemination of existing and future spectroscopic data to the appropriate users. To this end, the spectroscopic working group from Silverthorne was reconvened at the Langley Research Center as an informal workshop with wider representation from various U.S. and foreign spectroscopic laboratories.

Scope of Spectroscopic Workshop

The first meeting was held October 29-30, 1979, at Langley Research Center, Hampton, Virginia, with Dr. Aaron Goldman (University of Denver) and Mr. James M. Hoell (Langley) acting as co-chairmen. A list of attendees is given in table I. The specific objectives of the Workshop were: (1) to review in detail the current status of experimental and theoretical spectroscopic data on atmospheric species, (2) to explore methods for disseminating new data in a format readily available for applications, and (3) to discuss formalization of the Workshop in order to support objectives (1) and (2) on a long term basis.

A major portion of the Workshop was devoted to discussing the status (i.e., accuracy and availability) of spectroscopic data currently available on stratospheric species. Table II lists the molecules that were considered. While this list is extensive, it is not meant to be complete. Table III is a summary of information assembled by the Workshop attendees related to research completed (C), underway (U), or planned (P) at a number of U.S. or foreign laboratories. Here again, the table is not complete, but provides a good review of the current status of the spectroscopic data available to the user community.

During the status review, the initial emphasis was placed on the spectral data available on the more abundant species (H_2O, O_3, CO_2, CH_4, and N_2O). This approach was selected since a large body of spectral data already exists for these molecules, and interfering effects from these species often represent the limiting factor on our ability to identify and quantify many of the less abundant species. It should be noted that this Workshop report does not explicitly enumerate the requirements imposed on spectral data by the various instruments or science missions. However, throughout the review process, instrument requirements and scientific goals were considered.

Specific recommendations for additional experimental and theoretical research are given below. In general, the recommendations reflect the feeling of the Workshop attendees that additional quantitative spectral data are needed on the species which have been detected and require more accurate atmospheric measurements, while only qualitative spectral data (i.e., location of absorption features) are needed for the extremely tenuous species which have not yet been detected in the stratosphere.

The discussions related to objective (2) centered around the continued use of the AFGL format for compiling spectroscopic parameters. Dr. L. Rothman, from AFGL, reviewed his current efforts and limitations for updating and expanding the AFGL line parameter tape. In summary, this is a continuing effort at AFGL, but is limited by the availability of data suitable for inclusion on the tape as well as manpower to evaluate, select, and format the data.

The recommendations relative to objectives (2) and (3) tend to be less specific than those associated with objective (1). This is due to the uncertainty in the degree of long range support that might eventually be available.

RECOMMENDATIONS

General

(1) Future meetings of the Workshop should be convened with representatives from other organizations and specialists on specific molecules.

(2) A newsletter should be established and mailed periodically to update and improve the data contained in table III and to solicit data for the AFGL compilation. The goal of the current Workshop should be expanded to provide a forum to aid in obtaining and reviewing spectroscopic data for the AFGL tape. However, such activities will require support from one or more government agencies.

(3) Most molecules require additional studies for more accurate determination of the effects of temperature and foreign gas broadening on spectral line widths along with high resolution measurements to determine far wing line shapes.

(4) For the major atmospheric species (i.e., CH_4, H_2O, CO_2, O_3, and N_2O) long path absorption measurements are needed to identify weak transitions.

SPECIFIC RECOMMENDATIONS

CH_4

(a) Since a sizeable body of experimental data is currently available for CH_4, a quantum mechanical analysis of CH_4 should be performed using the current data base.

(b) Additional long path absorption data are required for identification of weak lines (i.e., $\leqq 10^{-26}$ cm per molecule).

(c) Experimental and analytical studies are required on the ν_4 band of the isotopic species of CH_4.

O_3

(a) Analysis of isotopic ozone is needed. The ν_3 isotopic band is particularly important because of its potential interfering effects.

(b) Line strengths for the $3\nu_3$, and $\nu_1 + \nu_2 + \nu_3$ are needed for the normal isotope of O_3.

N_2O

Measurements of the line intensities for the perpendicular bands are needed, as well as analysis of long path absorption data.

$\underline{CO}$

Revised analysis of solar CO transitions is needed for the $\Delta V = 1$ and $\Delta V = 2$ bands.

$\underline{H_2O}$

(a) Laboratory measurements for the ν_1, $2\nu_2$, and ν_2 band of HDO are needed.

(b) Measurements of line strengths for the high J transition are needed.

$\underline{CO_2}$

(a) Additional CO_2 line position measurements are needed for vibrational energy levels above 2000 cm^{-1}.

(b) Analysis of long path absorption data is needed for identification of weak absorption lines.

(c) Additional laboratory studies are needed on line intensities in the 15 μm spectral region.

(d) Additional experimental and analytical work is needed on the 5 μm isotopic CO_2 band.

$\underline{HCl}$

Experimental studies of half width versus temperature.

$\underline{ClO}$

Experimental studies of half width versus temperature.

$\underline{HF}$

Measurements of line intensities are needed at room temperature to verify extrapolated values obtained at 400 K.

$\underline{HBr}$

Experimental values of half width are not available; however, current estimates are probably sufficient to support current atmospheric measurements.

$\underline{HNO_3}$

Analysis of high resolution diode laser data and lower resolution spectra has provided line intensities, half width, and quantum assignments of the ν_5 band. However, additional diode laser measurements are needed in the 870 to 865 cm^{-1} region to check extrapolation of this analysis. Additional work is also needed for the R-region of the $2\nu_9$ band. Analysis of available high resolution data of the ν_3 and ν_4 region is needed. The ν_2 region analysis needs to be extended to the wings of the band.

HOCl

Pressure and temperature effects on half width will be needed if HOCl is to be observed in the atmosphere.

Freon-12

Analysis of currently available diode laser spectra of the ν_6 (1161 cm^{-1}) and ν_8 (923 cm^{-1}) bands should be pursued.

CF_4

Line parameters are needed for the ν_3 region.

NO_2

Line parameters are needed for the wings of the ν_3 and $\nu_3 + \nu_2 - \nu_2$ band.

$ClONO_2$

Analysis of currently available diode laser spectra should be pursued.

H_2O_2

Line intensities and assignments are needed for ν_6 band of H_2O_2.

HO_2

Line position and intensity data are needed.

CH_3Cl

Line parameters are needed for the 3 µm region.

NH_3

An extensive data base is currently available; however, a critical comparison of the various experimental and theoretical results is needed.

SUMMARY

As a result of the Workshop recommendations, plans are underway for establishing a periodic newsletter and holding at least one additional meeting of the Spectrascopic Workshop. The format for the newsletter is shown in table IV. It is anticipated that this will be mailed from AFGL at least once a year and will encourage more rapid inclusion of new data on the AFGL compilation tape. Planning is underway to hold the next Workshop during the Ohio State Spectroscopic Conference in June 1980, with Dr. John Shaw as the host chairman.

The review undertaken at the Langley Workshop and the resulting recommendations, while certainly not complete, have identified important areas of future research. Moreover, the recommendations of both the Silverthorne and this Workshop have identified the desirability of supporting periodic workshops to maintain an up-to-date review as well as to assist in the timely dissemination of new spectral data.

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TABLE II.- ATMOSPHERIC SPECIES

CH_4

N_2O

NO_2

HO_2NO_2

NO_3

N_2O_5

NH_3

CCl_3F

CCl_2F_2

O_3

HNO_3

ClO

$ClONO_2$

HOCl

HO_2

H_2O_2

NO

H_2O

OH

CH_3Cl

OCS

CO

HF

HCl

CO_2

CH_3F

H_2CO

HDO

CFClO

CF_2O

HONO

HB_r

CF_4

TABLE III.- SUMMARY OF MOLECULAR SPECTROSCOPIC PARAMETERS

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
CCl_2F_2 (Freon-12)	840-940 1080-1180 1070-1250	EOCOM @ 60 mK	Laboratory spectra	C		University of Denver (Goldman)
CCl_2F_2 (Freon-12)	1150-1173	Diode laser @ 1 mK	Laboratory spectra Absorption coefficient vs. T & P	C C	1 mK	Langley Research Center (Hoell)
CF_2	850-1100	Diode laser @ ~3 mK	Position Assignment	C U	~1 mK	Physical chemistry Univ. of Cambridge
CF_3	850-1100	Diode laser @ ~3 mK	Position Assignment	C U	~1 mK	Physical chemistry Univ. of Cambridge
CF_4	1200-1300	EOCOM @ 60 mK BOMEN @ 20 mK	Laboratory spectra	C		University of Denver (Goldman)
CF_3Cl (Freon-13)	1070-1250	EOCOM @ 60 mK	Laboratory spectra	C		University of Denver (Goldman)
CF_3Cl (Freon-13)	1235-1265 (Selected regions)	Diode laser	Laboratory spectra Analysis	C U	1 mK	Goddard Space Flight Center (Hillman)
$CFCl_3$ (Freon-11)	8-12 μm		Temperature dependence of 8-12 μm band	C		Ames Research Center (Silvaggiv)
$CFCl_3$ (Freon-11)	810-890 1060-6160	EOCOM @ 60 mK	Laboratory spectra	C		University of Denver (Goldman)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
$^{12}CH_4$	1200-2400	FTS @ 15 mK	Position Position $\nu_2+\nu_4-\nu_2$	C C P		JPL (Margolis)
$^{12}CH_4{}^b$	ν_2,ν_4	Calculation	Position Strength	C C		Orton/Rohrette
$^{12}CH_4$	2400-3200	FTS @ 15 mK	Compilation of 9000 lines Position Strength Assignment	 90% C 90% C 70% C		JPL (Toth/Brown)
$^{12}CH_4$	3900-4700 ($\nu_3+\nu_4$)	FTS @ 15 mK	Position Assignment	C C		JPL (Toth/Brown)
$^{12}CH_4$	1200-1280	Diode laser @ 0.5 mK	Position Strength	C U	1 mK 1-2%	Goddard Space Flight Center (Hillman)
$^{12}CH_4$	1100-1800	EOCOM @ 60 mK BOMEN @ 20 mK	Spectral atlas Spectral atlas	C P		University of Denver (Goldman) Ames (Boese)
$^{12}CH_4$	2940-2990	Diode laser (Doppler resolution)	Line broadening (0.1 - 0.5 torr) Intensities	U U	±0.7 mK	JRC - ISPRA (Restelli)

[a] C = Complete; U = Underway; P = in Progress.

[b] Available for next version of AFGL Atmospheric Absorption Line Parameters Compilation (from Glenn Orton).

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
$^{12}CH_4$	1305-1327	Diode laser @ 4 mK	10 lines measured Relative intensity Absolute intensity	 C C	 5% 5%	JRC - ISPRA (Restelli)
$^{12}CH_4$	1243.34-1377.83	0.1 mK	Absolute line intensities	C		University of Tennessee (Fox) from Ames Newsletter
$^{13}CH_4$	1200-2000	FTS @ 15 mK	Position Some ν_4 assignments	C ---		JPL (Toth/Brown)
$^{13}CH_4$	2400-3200 ($2\nu_4, \nu_2+\nu_4, \nu_3$)		Position Assignments	C C		JPL (Toth/Brown)
$^{13}CH_4$	3900-4700		Position Some $\nu_3+\nu_4$ assignments	C ---		JPL (Toth/Brown)
$^{13}CH_4$	1200-1270	Diode laser @ 0.1 mK	Position Strength	U U		Goddard Space Flight Center (Hillman)
CH_4	1213-1380	60 mK	Position Intensities Assignment	U U U	4 mK	ONERA (Battineau)
CH_4	2404-2730		Position Assignment Intensities	C C		Dijon Lab

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
CH_4	2700-3000		Position Assignment Intensities	C C		Dijon Lab & JPL
CH_4	1100-1800	60 mK	Position Assignment	C C		Dijon Lab & LUTZ
CH_4	5600-7100	12 mK	Position Assignment	C C	1 mK	Dijon Lab (J. P. Maillard)
CH_4	2700-3500	7 mK	Position Assignment	C C	1 mK	Dijon Lab
CH_4	6057-4700	5 mK	Position Assignment	C C	1 mK	Dijon Lab
CH_4	1213-1386	50 mK	Position Assignment	C C	5 mK	Dijon Lab
CH_4	7000-9300	12 mK	Position Assignment	C C	1 mK	Dijon Lab (J. P. Maillard)
CH_4	7000-9200	12 mK	Position Assignment Intensities	C C C		Dijon Lab (J. P. Maillard)
CH_4	3686-6386	5 mK	Position Assignment	C C	1 mK	Dijon Lab (J. P. Maillard)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
CH_4	2858-4394	5.5 mK	Position Assignment	C C	1 mK	Dijon Lab
CH_4	5500-7000 ($2\nu_3$)	10 mK	Position Assignment	C C	0.5 mK	Observatoire de Meudon (J. O. Maillard)
CH_4	3700-11000	FTS @ 420 mK	Laboratory spectra	C		University of Arizona (U. Fink) from Ames Newsletter
CH_4	1.1 μm	1 m grating Spectrometer @ 160-300 mK	Laboratory spectra Analysis	C U		Ames Research Center (Giver) from Ames Newsletter
CH_4	2600-3200	10 - 20 mK	Position Strength Assignment	C C U		Florida State University (Hunt) from Ames Newsletter
$^{13}CH_3D$ $^{12}CH_3D$	1750-2400 ν_2	FTS @ 5.5 mK	Position Strengths	C C	0.3 mK ±5%	Ames Research Center (Chackerian) L. Infrarouge (Guelochvili)
CH_3D	1200-2000	FTS @ 15 mK	Line list	C		JPL (Toth/Brown)
CH_3D	2400-3200	FTS @ 15 mK	Spectrum	C		JPL (Toth/Brown)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
CH_3D	1033-1270 1270-1420	40 mK	Position Assignment Relative Strength	C C C		Ohio State (Rao) Orsay (Tarrago)
CH_3F	2400-3200	FTS @ 10 mK	Laboratory spectrum	C		JPL (Margolis)
CH_3Br	1200-3200	FTS @ 10 mK	Laboratory spectrum Analysis	C P		JPL (Toth/Brown)
CH_3Cl	670-770 950-1110 1300-1600	EOCOM @ 60 mK	Laboratory spectra	C		University of Denver (Goldman)
CH_3Cl	2400-3200	FTS	Position	C		JPL (Margolis)
CH_2Cl_2	1200-3200	FTS @ 10 mK	Laboratory spectrum Analysis	C P		JPL (Toth/Brown)
CH_2Cl_2	720-800 1240-1300	EOCOM @ 60 mK	Laboratory spectrum	C		University of Denver (Goldman)
ClO[b]	849.63-858.74 871.70-874.40	Diode laser @ 1 mK	Position Strength Assignment	C C C	10-50 mK 20%	Langley Research Center (R. Rogowski)
ClO[b]	796-880	Diode laser	Position Strength Assignment	C		JPL (Menzies)

[a] C = Complete; U = Underway; P = in Progress.

[b] Available for next version of AFGL Atmospheric Absorption Line Parameters Compilation (from Glenn Orton).

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
$ClONO_2$	1250-1330	60 mK	Position Intensity (curve of growth of Q branch @ 1292 cm^{-1})	C C		ONERA (Louisnard)
$ClONO_2$	1250-1350	EOCOM @ 60 mK BOMEN @ 20 mK	Laboratory spectrum	C		University of Denver (Goldman)
$ClONO_2$	776-793	Diode laser @ 1 mK	Position Intensity Halfwidth Assignment	U U U	±50 mK	Langley Research Center (Rogowski)
CO			Intensities of CO overtone up to 15th vibrational level Isotopic data	C		Ames (Chackerian)
CO	Pure rotation, fundamentals, and overtones AFGL data being updated Canadians have new data Goldman has data for $\Delta V = 1$ solar CO lines D. Williams - self- and foreign-gas broadening					

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
CO_2	1600-2400	FTS @ 6 mK	Position Strength	C U	2 mK	AFGL and U. Mass. (H. Sakai)
$^{13}CO_2$	2170-2335	30 mK	Position	C		Ohio State (Rao)
$^{13}CO_2$	4.3 μm	30 mK	Strength	C		Ohio State (Rao)
CO_2	800-4000	FTS @ 50 mK	Long path absorption spectral - analysis underway	U	1 mK	Ohio State (Shaw)
$^{12}CO_2$ $^{13}CO_2$	3700-7000	9 mK	Position Assignment	C C	0.2 mK	Télescope IR Obs. de Meudon (J. P. Maillard)
$^{12}CO_2$ $^{13}CO_2$	3400-8150	100 mK	Position Assignment	C C	80 mK	National Research Council (C. Courtey)
COF_2	730-830 1180-1280	EOCOM @ 60 mK	Laboratory spectrum	C		University of Denver (Goldman)
COF_2	1200-2200	FTS @ 10 mK	Laboratory spectrum Analysis	C P		JPL (Toth/Brown)
HF	HF, HCl, HI, and HB_r available from R. Tipping, University of Nebraska, and are being incorporated onto the AFGL Trace Gas Compilation.					
HBr	2500-2600		Position Intensity	C C	15%	University of Denver (Goldman)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
HCl	2770-3000	24 mK	Position Assignment	C C		Départment de Physique Atomique & Moléculaire Universite of Rennes (J. P. Haudeau)
HCl	2700-3000	24 mK	Position Assignment	C C		Universite de Rennes
H_2CO	1200-2700	FTS @ 10 mK	Laboratory spectrum	C		JPL (Toth/Brown)
H_2CO	1 - 15	MMW spectrometer @ Doppler limit	Position	C	5×10^{-7} cm^{-1}	Physikalisch Chemisches Institute Justus Liebig - Universität
HCHO	1760-1780	60 mK	Position Intensity (curve of growth @ 1764.96 cm^{-1})	C C		ONERA (Louisnard)
HNO_3	865-885	110 mK	Position Assignment Intensities	C C C		Spectroscopie Moleculaire (Lado-Bordawyky)
HNO_3	860-907	50 mK	Position Assignment	C	7 mK	ONERA/LPMOA (Giraudet-Chevillard)
HNO_3	1270-1370	60 mK	Position Intensities	C	3 mK	ONERA (Giraudet)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
HNO_3	1200-1350 1600-1800	BOMEN @ 20 mK	Laboratory spectra	C		University of Denver (Goldman)
HNO_3	840-940	EOCOM @ 60 mK	Laboratory spectra	C		University of Denver (Goldman)
HNO_3	850-870	Diode laser	Position Intensity	U U	±0.4 mK	National Bureau of Standards (Maki)
HNO_3	1670-1726	Diode laser	Position Intensity	C	±0.4 mK	National Bureau of Standards (Maki)
HNO_3[b]	1718.97-1729.57	Diode laser @ 1 mK	Position Intensity Halfwidth	C	10 mK	Langley Research Center (Bair)
HNO_3	891.25-898.77	Diode laser @ 1 mK	Position Intensity Halfwidth	C	5 mK	Langley Research Center (Bair)
HNO_2	1685-1727	Diode laser	Position Assignment Relative intensity	C C C	±4 mK	National Bureau of Standards (Maki)
HNO_3	700-1900	60 mK	Line intensities N_2 broadening	C C		U. Maryland (Wilkerson) Ames (Giver)

[a] C = Complete; U = Underway; P = in Progress.

[b] Available for next version of AFGL Atmospheric Absorption Line Parameters Compilation (from Glenn Orton).

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
HDO	2900-4000	FTS @ 15 mK	Position Strength	U		JPL (Toth)
HO_2	850-1100	Diode laser @ ~3 mK	Position Assignment	C	~1 mK	Physical Chemistry Univ. of Cambridge
HO_2	1100 cm^{-1} region	Laser	Intensity (few lines)	U		JPL (Toth/Brown)
$H_2{}^{16}O$ AFGL update	1600-2650 $\nu_2, 2\nu_2-\nu_2, \nu_1-\nu_2, \nu_3-\nu_2$	5 mK	Position Relative intensity Absolute intensity Assignment	C C C C	5 mK 10% 10%	LPMOA (Camy-Peyret, Flaud)
$H_2{}^{16}O$ AFGL update	2620-4500 $\nu_1, 2\nu_2, \nu_3$	5 mK	Position Assignment	C C	1 mK	LPMOA (Flaud, Camy-Peyret)
$H_2{}^{16}O$	4200-5000	70 mK	Position Relative intensity Absolute intensity Assignment	C C C C	5 mK 10% 15%	LPMOA (Camy-Peyret, Flaud)
$H_2{}^{16}O$	5000-6000	25 mK	Position Relative intensity Absolute intensity Assignment	C C C C	3 mK 8% 10%	LPMOA (Flaud, Camy-Peyret) JPL (Toth)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
$H_2{}^{16}O$	6000-78000	5 mK	Position Assignment	C C		LPMOA (Camy-Peyret, Flaud)
$H_2{}^{16}O$	7800-9400	70 mK	Position Assignment	C C		LPMOA (Flaud, Camy-Peyret, Rao)
$H_2{}^{16}O$	1580-2370 $\nu_2, 2\nu_2 - \nu_2$	6 mK	Position Assignments Relative intensity	C P P	2 mK	AFGL (H. Sakai)
$H_2{}^{16}O$	7800-9400	70 mK	Position Assignments	C C		LPMOA (Flaud) Ohio State (Rao)
H_2O	13666-13987	50 mK	Line intensities N_2 broadening	C C		U. Maryland (Wilkerson) Ames (Giver)
H_2O	10407-10727	46 mK	Line intensities N_2 broadening	C C		Ames (Giver) U. Maryland (Wilkerson)
$H_2{}^{18}O$	2950-4200	FTS @ 10 mK	Position Strength	C C		JPL (Toth/Brown)
$H_2{}^{17}O$	2950-4200	FTS @ 10 mK	Position Strength	C C		JPL (Toth/Brown)
H_2O	800-4000	FTS @ 50 mK	Long path absorption spectra: Position Intensity Halfwidth	 U U U	10 mK	Ohio State (Shaw)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
H_2O	1500-2000	BOMEN @ 20 mK	Laboratory spectra	C		University of Denver (Goldman)
$H_2{}^{17}O$ $H_2{}^{18}O$	6974-7387	70 mK	Position	C	5 mK	LPMOA (Flaud, Camy-Peyret)
			Assignment	C		JPL (Toth)
$H_2{}^{17}O$ $H_2{}^{18}O$	5030-5640	50 mK	Position	C	5 mK	LPMOA (Flaud, Camy-Peyret)
			Assignment			
			Relative intensity	C	8%	JPL (Toth)
			Absolute intensity	C	10%	
H_2O_2	1220-1277	Diode laser	Position	C	±1 mK	Goddard Space Flight Center (Hillman)
H_2O_2	3 µm region		Position Assignment	U U		Florida State Univ. (Brenda Young)
H_2O_2	1150-1350	BOMEN @ 20 mK	Laboratory spectrum	C		University of Denver (Goldman)
H_2O_2	1100-1400	60 mK	Intensities N_2 broadening $278 \leq T \leq 295$ K	P P		Ames (Valero)
HOCl	3250-3875	Grating	Position Intensity	C C		NBS (Wells)
HOCl	1200-1300	Diode Laser/ Grating	Position Relative intensity	C C		NBS (Sams)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
NF_2	850-1100	Diode laser @ ~3 mK	Position Assignment	C U	~1 mK	Physical Chemistry
NH_3	1200-2700	FTS @ 10 mK	Laboratory spectrum	C		JPL (Toth/Brown)
NH_3	750-950 1070-1210	EOCOM @ 60 mK	Laboratory spectrum	C		University of Denver (Goldman)
NH_2	11 μm region	CO_2 heterodyne technique	Position of 20 lines	C	1 mK	Goddard Space Flight Center (Hillman)
$^{14}N^{15}NO$	1800-6000	5 mK	Position Assignment	C C	1 mK	LPMOA (C. Amiot)
$^{15}N^{14}NO$	1800-6000	5 mK	Position Assignment	C C	1 mK	LPMOA (C. Amiot)
$^{14}N^{15}N^{16}O$	2100-2300	30 mK	Position	C	2 mK	Laboratory of Molecular Spectroscopy. NUMUR, Belgium (Courtoy/Blanquet)
$^{14}N^{14}N^{18}O$	2850-2950	30 mK	Assignment	C		
N_2O	522-627 1115-1300	Diode laser	Position Relative intensity Absolute intensity Halfwidth vs. pressure for few lines	C C U U	±10 mK	National Bureau of Standards (Maki)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
$^{14}N_2{}^{16}O$	1800-8090	5 mK	Position Assignment	C C	1 mK	LPMOA (C. Amiot)
$^{15}N_2{}^{16}O$	1800-6000	5 mK	Position Assignment	C	1 mK	LPMOA (C. Amiot)
$^{14}N_2{}^{18}O$	1800-3100	5 mK	Position Assignment	C	1 mK	LPMOA (C. Amiot)
N_2O	2400-3000		Position Line strength	C C		JPL (Toth/Brown)
N_2O	4000-4600		Pressure broadening @ RT	C		JPL (Toth/Brown)
N_2O	800-4000	FTS @ 50 mK	Long path Absorption spectra: Analysis { Position Intensities Half width	U	1 mK	Ohio State (Shaw)
N_2O	522-627	Diode laser	Position Relative intensities Absolute intensity Line widths vs. pressure	C C U U	±10 to 1 mK	National Bureau of Standards (Maki)
NO_2	1500-1700	BOMEN @ 20 mK	Laboratory spectra	C		University of Denver (Goldman)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
NO_2	2862-2940	FTS @ 10 mK	Strength Spin splitting	C C		JPL (Toth/Hunt)
NO_2	4680-4777	5 mK	Position Assignment	U U	1 mK	Spectroscopie Moléculaire (Dana)
NO_2	4120-4200	5 mK	Position Assignment	U U	1 mK	Spectroscopie Moléculaire (Dana)
NO_2	1588-1629	60 mK	Position Assignment Intensities	C C C	4 mK ±10%	ONERA - LPMOA (Fontanella-Dana)
NO_2	2900-2950	FTS @ 3 mK	Position Intensity	C U		Observatoire de Meudon (Maillard and Dana)
N_2O_4	1750	BOMEN	Band envelope	C	20 mk	University of Denver (Goldman)
N_2O_5	500-2000	FTS (Nicolet)	Band intensities	C	±10-20%	Ames Research Center (Lovejoy)
N_2O_5	1220-1270	EOCOM @ 60 mK BOMEN @ 20 mK	Laboratory spectrum	C		University of Denver (Goldman)
NO	1800-1960	EOCOM @ 60 mK	Laboratory spectra	C		University of Denver (Goldman)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
NO	1700-2000	BOMEN @ 20 mK	Laboratory spectra	C		University of Denver (Goldman)
NO	1800-1900	24 mK	Position Assignment	U U		Universite de Rennes
$^{14}N^{16}O$ $^{15}N^{16}O$	1700-2200	2.7 mK	Position Relative intensities Assignment	C C C	1 mK	LPMOA (Amiot)
NO_2	1600-2200 3500-3800	70 mK	Position Relative intensities	U U		Universite de Rennes
O_3	700 (ν_2)		Position Relative intensity	C		Laboratoire de Physique Moléculaire-Reims (Barbe & Lille & Rao)
O_3	948-1215 $(\nu_3, \nu_2+\nu_3-\nu_2, \nu_1+\nu_2-\nu_2, 2\nu_3-\nu_3, \nu_1+\nu_3-\nu_1)$	10 mK	Position Intensity Assignment	C C C	2 mK 1%	Laboratoire de Physique Moléculaire-Reims (Barbe)
O_3	966-1234 (ν_1)	25 mK	Position Assignment	C C	4 mK	Laboratoire de Physique Moléculaire-Reims (Barbe)

[a] C = Complete; U = Underway; P = in Progress.

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
O_3	2900-3122	25 mK	Position Intensity Assignment	C U U	5 mK	Laboratoire de Physique Molécularie-Reims (Barbe)
O_3	2710-2804 $(\nu_1+\nu_2+\nu_3)$	25 mK	Position Intensities Assignment	C U U	5 mK 20% (absolute)	Laboratoire de Physique Moléculaire-Reims (Barbe)
O_3	1700-1850 $(\nu_2+\nu_3, \nu_1+\nu_2)$	15 mK	Position Assignment	C C	3 mK	Laboratoire de Physique Moléculaire-Reims (Barbe & LPMOA)
O_3[b]	948-1240 $\nu_3, \nu_1, \nu_2+\nu_3-\nu_2, \nu_2+\nu_1-\nu_2, 2\nu_3-\nu_3$ $\nu_1+\nu_3-\nu_1$	Calculation ≃3 mK	Position Assignment Intensity	C C C	3 mK 5-25%	LPMOA (Flaud, Camy-Peyret)
O_3	700 $\nu_2, 2\nu_2-\nu_2$	Diode laser @ 1 mK	Position Assignment	C C	2 mK	Rao, Flaud, Camy-Peyret
O_3[b]	1900-2250 $(2\nu_1, 2\nu_3, \nu_1+\nu_3)$	20 mK	Position Intensities Assignment	C C C	3 mK	Laboratoire de Physique Móleculaire-Reims (Barbe) LPMOA (Flaud, Camy-Peyret)
O_3	1038-1054 $(\nu_3, \nu_2+\nu_3-\nu_2)$	Heterodyne radiometer 5 MHz & 25 MHz	Position Relative strength	C U		Goddard Space Flight Center (Hillman)

[a] C = Complete; U = Underway; P = in Progress.

[b] Available for next version of AFGL Atmospheric Absorption Line Parameters Compilation (from Glenn Orton).

TABLE III.- Continued

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
O_3	800-4000	FTS @ 50 mK	Long path (100-1000 m) Absorption spectra: Analysis	U	1 mK	Ohio State (Shaw)
O_3	1040-1049	Diode laser @ 1 mK	Position Relative intensities	C C	5 mK 10%	Langley Research Center (C. Bair)
O_3	3-40	50 mK	Position Intensities Assignment	C C C	±10 mK 1%	National Physical Labs. (George Chantry)
OCS	1020-1080 825-885 1655-1737	Diode laser; grating; heterodyne	Position Absolute intensity near 10 μm Relative intensity	C[b] C[b] C[b]	0.2-4 mK 10%	National Bureau of Standards (Maki) Harry Diamond Ordnance Laboratory
OCS	1000-2500	60 mK	Position Strength Halfwidth	C U U	10 mK <15%	NCAR (Drayson)
OCS	10 cm^{-1} - 20 cm^{-1}	MMW spectrometer @ Doppler limited	Position Assignment	C C	5 × 10^{-7} cm^{-1}	Physikulisch Chemisches Institut Justus Liehig - Universitüt Heirrich

[a] C = Complete; U = Underway; P = in Progress.
[b] Additional work in progress.

TABLE III.- Concluded

Molecule	Spectral coverage (cm^{-1})	Instrument and resolution	Type of data	Status (a)	Accuracy	Source
$^{16}O^{12}C^{34}S$ $^{16}O^{13}C^{34}S$	1950-2100	30 mK	Position Assignment	C C	2 mK	Spectroscopie Moléculaire NAMUR BELGIUM (Fayt)
SO_2	1123-1226	60 mK	Position Assignment	C C	4 mK	ONERA/LPMOA (Dana)
SO_2	1150-1172.5	Diode laser @ 0.1 mK	Position Assignment	C U		Langley Research Center (Hoell)

[a] C = Complete; U = Underway; P = in Progress.

TABLE IV.- HIGH RESOLUTION MOLECULAR SPECTROSCOPY RELEVANT TO ABSORPTION LINE PARAMETER COMPILATIONS

NAME(S):

AFFILIATION:

ADDRESS:

TELEPHONE: DATE:

MOLECULE:

WAVENUMBER RANGE:

INSTRUMENT:

RESOLUTION:

EXPERIMENTAL CONDITIONS

TEMPERATURE(S): PRESSURE(S):

PATHLENGTH: BROADENING GAS(ES):

DATA FORMAT STATUS (Indicate "Yes" or "No" in the blanks)

LINE POSITIONS: ______ ACCURACY:

RELATIVE INTENSITIES: ______

ABSOLUTE INTENSITIES: ______ ACCURACY:

HALFWIDTHS: ______

LINE ASSIGNMENTS: ______

AFGL FORMAT: ______ OTHER (SPECIFY):

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16. Abstract

High resolution heterodyne techniques offer high potential for improving the sensitivity of remote measurements of stratospheric constituents. This workshop was convened to help define the role which these techniques will play in the future. The workshop conclusions were the following:

1. Infrared heterodyne techniques should be considered primarily for detecting molecules predicted to be present but not yet detected in the upper atmosphere. Infrared heterodyne technology may be unique in being able to provide such a measurement.

2. The molecular species laboratory data base needs to be increased and focused toward species currently being measured or being proposed for measurement.

3. Development of tunable infrared semiconductor lasers should be continued in light of conclusion 1.

4. Scientific investigations by laser heterodyne spectrometer type instruments should be first conducted from balloons.

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