TITLE OF RESEARCH TASK: Collecting, Analyzing and Archiving of Ground Based Infrared Solar Spectra Obtained from Several Locations.

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ABSTRACT OF RESEARCH OBJECTIVES:

The infrared solar spectrum as observed from the ground under high resolution contains thousands of absorption lines. The majority of these lines are due to compounds that are present in the Earth's atmosphere. Ground based infrared solar spectra therefore contain information concerning the composition of the atmosphere at the time the spectra were obtained. The objective of this program is to record solar spectra from various ground locations, and to analyze and archive these spectra. The analysis consists of determining, for as many of the absorption lines as possible, the molecular species responsible for the absorption, and to verify that current models of infrared transmission match the observed spectra. Archiving is an important part of the program since a number of the features in the spectra have not been identified. At some later time, when the features are identified, it will be possible to determine the amount of that compound that was present in the atmosphere at the time the spectrum was taken.

SUMMARY OF PROGRESS AND RESULTS:

Our high resolution (0.01 cm⁻¹) interferometer system was used during NOZE-2 (Sept. and Oct. 1987) to measure HNO₃, HCl and other stratospheric gases from McMurdo, Antarctica. It was operated again in the austral spring of 1988 and 1989 in cooperation with investigators from the New Zealand DSIR. Results from the first two years are very similar, with variable HNO₃, and a steady increase in HCl from a very low value.

On its way to and from Antarctica, the instrument has been set up and operated from the DSIR station at Lauder, New Zealand. Observing periods there include August 1988, Dec. 1988 and Jan. 1989, and August 1989. The set of HNO₃ observations from Lauder extends back to 1985, and indicates either a significant annual cycle, a significant long-term increase, or both.

Much of the work with our very high resolution (0.002 cm⁻¹) system has been directed toward development of instrumentation for the Network for the
Detection of Stratospheric Change. We have operated the instrument on the ground for several days in preparation for balloon flights, and those data are being analyzed and stored for the development of retrieval algorithms for the Network.

PUBLICATIONS:


MEASUREMENT OF STRATOSPHERIC CHLORINE MONOXIDE AND OTHER TRACE CONSTITUENTS FROM A PORTABLE GROUND-BASED MM-WAVE SYSTEM

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Research Objectives:

A.) To reduce, analyze, and prepare for publication the results of field observations conducted during September and October, 1987, at McMurdo Station, Antarctica;
B.) To continue the measuring and monitoring of ClO in the stratosphere over Mauna Kea, Hawaii (20 N latitude), with particular attention to the determination of long term changes (years to decade time span) and to improve the measurement of its diurnal variation;
C.) To measure O₃, N₂O, and HCN with emphasis on vertical profile recovery and short-term (e.g., seasonal) variations, related to variability in transport and production.

Summary of Progress and Results:

Data Analysis of Antarctic Field Observations: This work consumed considerable time during 1988 and led to three papers discussing our findings. Despite generally much poorer (weather-related) observing conditions at McMurdo during the fall of 1987, a good block of data was obtained, with twice the spectral bandwidth used for our initial discovery of anomalous low-altitude Antarctic ClO in 1986. This new data, with its greater spectral coverage, allowed a reasonably accurate profile recovery to be made for the mixing ratio of ClO down to about 17 km, and also the determination of the altitude (19.5±1 km) at which the mixing ratio reached its maximum value (1.6±0.4 ppb), as well as a good measure of diurnal variation of the low-altitude ClO layer found in Antarctica during the period of seasonal ozone depletion.

This data (de Zafra, et al., 1989) provides a substantial improvement over our profile determinations from 1986 data, but served to confirm and strengthen, rather than alter, the conclusions reached from the previous year's discovery. The present data, with a reasonably detailed measurement of the ClO mixing ratio as a function of altitude over the stratospheric layer in which ozone is being destroyed, allowed us to evaluate the rate at which the ClO dimer formation mechanism can act to return free chlorine to continue the catalytic ozone destruction cycle. The probability of ClO dimer formation depends upon the product of background air pressure and the square of ClO concentration, and thus varies very strongly over the altitude range in which the low-level ClO exists. From this analysis, an estimate of the rate of ozone destruction can be made as a function of altitude. We compared this rate with the observed rate of ozone loss at various altitudes as measured by direct balloon sounding, and found very good agreement (Barrett, et al., 1988), suggesting that the dimer mechanism is capable of closing the chlorine-ozone catalysis cycle with an efficiency high enough to explain the rapid loss of ozone now being observed.

We have also analyzed measurements of HCN taken at McMurdo in both 1986 and 1987, and shown that these tend to indicate that a substantial subsidence of stratospheric air has occurred over Antarctica by the end of the winter period, as previously indicated by our measurements of anomalously small amounts of the 'stable' tracer N₂O in 1986. A complicating factor in the case of HCN arises from evidence that the tropical or mid-latitude profile of this species is not in agreement with current theory (Jaramillo, et al., 1989), so that our analysis had to be based on a comparison of Antarctic with tropical
measurements, and does not take into account chemical or photo-processing which may modify the HCL profile during transport from low-latitude sources to Antarctica.

At the end of the summer (1988) the equipment was returned to Mauna Kea for the first time since June 1986, after it was checked and minor repairs were made at Stony Brook. Partly as a result of poor weather and partly because of technical problems and a short time allocated for this trial run, no good-quality emission data was collected. A second run was carried out in November 1988, with the intention of carefully analyzing and improving some questionable performance noted in the first run. Again the weather was unusually poor (frequent storms, nearly continuous high humidity), but considerable progress was made in improving the equipment performance, and some useful data was taken on N$_2$O and HNO$_3$ during one moderately good break in the weather.

A significant modification was made on part of the equipment at Stony Brook during the early spring, to improve the broad-band baseline flatness, and a third run was made in late May-early June, 1989. A substantial improvement in baseline flatness over the full 512 MHz passband of the present equipment was noted. Again the weather was uncooperative, and only N$_2$O data was obtained. (The entire period from the late summer of 1988 through the late spring of 1989 was one of unusually frequent storms, cloud overcast, and unusually high humidity at Mauna Kea - the worst period in our experience. Much of the astronomical program at the observatory was crippled, as well as our own work. There is some belief that this problem is associated with a current "anti-El Nino" cycle in the Pacific, and should soon end.)

Journal Publications During This Period.


A. Title of Research Project: Global Atmospheric Gases Experiment: Calibration, Oregon Station and Samoa Station

B. Investigators: R.A.Rasmussen & M.A.K.Khalil, Institute of Atmospheric Sciences, Oregon Graduate Center, Beaverton, Oregon 97006, U.S.A.

C. Research Objectives: The research had 6 objectives:

1. To continue systematic, in-situ, high precision measurements of F-11, F-12, CH3CCl3, CC14, N2O, CH4 and F-113 at Samoa and Oregon stations (similar experiments were done at Barbados and Tasmania by other members of the GAGE team).

2. Improving the calibration standards to ensure the long-term stability and accuracy for measuring the halocarbons, CH4 and N2O.

3. Use flask samples to corroborate the real-time measurements.

4. Maintain and increase the air stored for future analyses (air bank) of new species.

5. Collate, manage and enter the data on our computer systems and prepare it for analysis.

6. Analyze the data for trends, lifetimes and mass balances of the gases measured.


During 1988-1989, concentrations of F-11, F-12, F-113, CHCl3, CH3CCl3, CC14, N2O and CH4 were measured at Samoa and Oregon and are now a part of the long-term GAGE data base. The other tasks listed above were also successfully completed.

For more than a decade, we have taken systematic, in situ, global measurements of F-11, F-12, F-113, CHCl3, CH3CCl3, CC14, N2O and CH4 as an integral part of the Atmospheric Lifetime Experiment (ALE) and for the Global Atmospheric Gases Experiment (GAGE) using automated instruments. Recently continuous measurements of CH4 and F-113 were also added. During the last year we have evaluated the usefulness of such intensive automated measurements compared to collection of air in flask samples that are sent to our laboratory for detailed analysis. We have concluded that the automated sampling and analysis used in the ALE/GAGE program has substantial benefits if confined to 1-3 years to establish the climatology of these long-lived gases. After that time the process of continuous monitoring brings diminishing returns and is inferior to regular flask sampling.

In summary, the benefits of flask sampling compared to continuous monitoring are:

1. It is practical to increase sampling frequency for short periods to equal that of continuous monitoring. Any information requiring intensive measurements can be obtained also by flask sampling schedules.

2. Many more trace gases can be measured simultaneously instead
of just a few with continuous monitoring. In particular there are a number of environmentally important trace gases for which continuous automated measurements are not yet possible or practical. These include non-methane hydrocarbons, F-22 and man-made bromine containing gases such as CF3Br and CF2BrCl and the CFC replacements compounds HCFC-123 and HCFC-134a.

(3) The overall costs of measurements by flask sampling are only a small fraction of the costs of continuous monitoring.

(4) Flask samples provide an opportunity to verify measurements that appear unusual.

(5) Flask samples provide a means to archive air for future analyses and verification of data and absolute calibration.

(6) Most importantly, with flask sampling, stable primary laboratory calibration standards can be maintained for decades. There are proven methods to make and keep stable calibration standards for a decade or more. For continuous field measurements many secondary calibration standards have to be prepared and used over the years. The ALE-GAGE program has consumed over 300 secondary standards. These secondary standards, no matter how carefully prepared, introduce uncertainties that grow in time causing the long-term data to be less reliable than flask sampling data based on a single or several primary standards. In the ALE/GAGE program the flask samples were often used to correct the absolute concentrations as the continuous measurements drifted or were affected by variations of secondary standards.

(7) Over the years we have maintained an independent flask sampling network that has produced all the results obtained from the ALE/GAGE program and have established the importance and usefulness of flask sampling techniques. Many results from the network have been published. In some cases the work based on flask samples has turned out to be more reliable than from continuous monitoring. In general we have found that weekly flask samples provide the same information on trends and lifetimes of the trace gases measured in the ALE/GAGE program as the continuous measurements.

At present we are using the data obtained from the ALE/GAGE program to arrive at the best flask sampling strategies for long-term measurements of long-lived and moderate-lived trace gases.


The primary goal of this project is the understanding of the global sources, sinks, and distribution of volatile gaseous trace species. The basic experimental input for these studies is the measurement of the atmospheric mixing ratios of numerous halocarbons (CFCs, especially CHF3, CH2F2, and CH2FCCl2F; CH3CCl3, CCl4, CCl2-CCl2, and others), hydrocarbons (CH4, alkanes to C6H14, C2H2, several olefins), and carbon monoxide every three months on a regular grid from 71°N (Barrow, Alaska) to 47°S (New Zealand). The air samples are collected at ground level in remote locations, away from sources of these compounds, and then returned to the home laboratory for analysis by gas chromatography. The measurements provide information about the growth in atmospheric mixing ratios of the longer lived species (e.g. CH4, CFCs, CCl4, CH3CCl3). They also demonstrate the pronounced seasonal and latitudinal mixing ratio differences found for molecules such as CO, CH2H6, and CH3H8 which have atmospheric lifetimes of less than a year. Correlation among the mixing ratios of different compounds provide details about source and sink relationships. Global average mixing ratios are calculated for the longer-lived molecules from the average concentrations in 16 equal area latitudinal bands.

Our measurements of the average global mixing ratios of methane have shown a monotonic increase from 1.52 ppmv in January 1978 to 1.70 ppmv in June 1989, for an average yearly increase of 16 ppbv over 11.5 years. The best fit to this data series indicates a gradual slowing in the yearly rate of increase in methane concentrations, but the non-linearity is not large and is only marginally significant statistically. No substantial deviations for isolated geophysical events (e.g. eruption of El Chichon volcano) have been found, with a one-sigma standard error of only 0.003 ppmv for deviation from a linear fit for 27 data periods over 11.5 years.

Our data for CH2FCCl2F (CFC-113) continue to display a rapidly increasing atmospheric mixing ratio, having risen from about 15 pptv in the northern hemisphere in 1977 to about 75 pptv in mid-1989. The tonnage of CH2FCCl2F emitted to the atmosphere yearly is almost as large as for CHClF (CFC-11). Urban air samples in major U.S. and Japanese cities often exhibit CH2FCCl2F as the most prominent halocarbon added by local emission, although 28 more halocarbons with no more than two carbon atoms have been readily identified in our analyses.

The strong seasonal variation in CH2H6 mixing ratios continues, consistent with a source almost entirely in the northern hemisphere land masses and reaction with hydroxyl radical as the only major sink. The seasonal variation for CH2H6 is about a factor of 2.5 in each hemisphere, with maximum mixing ratios in the winter. The northern winter concentrations are in the 2 to 3 ppbv range, while the southern summer values generally fall between 0.1 and 0.2 ppbv. Although not yet measured on a global basis, hydroxyl radical concentrations are much lower in the larger winter solar with zenith angles and colder temperatures, allowing the build-up of CH2H6 mixing ratios. On the basis of more than 3 years of CO measurements, the northern hemispheric mixing ratios peak at
about 150 ppbv in temperate latitudes, and drop to 80 ppbv in the summer. The southern hemispheric seasonal variations are less, ranging only between about 40 and 55 ppbv. The mixing ratios of CO in the southern hemisphere are consistent with the oxidation of CH$_4$ by HO as the predominant carbon source. Because the CH$_4$ north/south mixing ratio is only about 1.1, the major source of the much more abundant northern hemisphere CO is not CH$_4$, but a combination of direct CO emission and atmospheric oxidation of various non-methane hydrocarbons (NMHC).

Our current detailed analyses have been extended to enough rapidly-reacting molecules that large mixing ratio variations are often encountered, and occasional data are indicative of a major source in close proximity to the location of the air sampling, e.g. isoprene in the vicinity of the jungles of the Solomon Islands.


A. **Ground-based Observations and Theoretical Studies of the Vertical Column Abundance of Atmospheric Hydroxyl**

B. **Co-investigators:**

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C. **Abstract of Research Objectives:**

The hydroxyl molecule (OH) is a free radical of considerable importance in the photochemistry of the earth's atmosphere. Studies of the middle atmosphere require experimental data on hydroxyl concentration and behaviors for the constraint of theoretical models and for the prediction of future ozone response to stratospheric pollution resulting from man's activities. The experimental work yields measurements of the vertical column abundance of hydroxyl by spectroscopic observations of the absorption of sunlight. The observations include a continuation of the baseline OH measurements, begun in 1976, at the NOAA Fritz Peak Observatory, Colorado (40°N). A second instrument is used to obtain a 2-year series of OH measurements in the tropics (7°N); this instrument is then to be shipped to New Zealand (45°S) for the first southern hemisphere measurements of hydroxyl. A theoretical study of geographic differences and chronological changes in OH behavior will be made in order to gain an improved understanding of processes relating to the global problem of atmospheric ozone.

D. **Summary of Progress and Results:**

The vertical column abundance of atmospheric OH was monitored at Fritz Peak Observatory, Colorado at times of good atmospheric observing conditions during 1987-1989 except during February and April of 1989. Observations with a second instrument located at the National Weather Service Office on Truk, Federated States of Micronesia were also made during the periods: January-February 1987, June-July 1987, September-October 1987, February-March 1988, September-October 1988, and April 1989.

The total number of independent measurements at Fritz Peak Observatory from January 1, 1988 to July 31, 1989 was 1760. Similarly, 384 independent measurements were made at Truk for the 1987-1989 series. These were approximately 20 minute observation periods with about 15% uncertainty. The Truk instrument was returned to Fritz Peak Observatory on April 30, 1989 for performance check prior to shipping to Lauder, New Zealand for a future 2-year observation series.

The Colorado data base from 1977 through 1988 has revealed significant annual and semi-annual cycles which are amplitude modulated over the 12-year data base. This modulation of the OH seasonal behavior is in phase with solar
activity as described by the sunspot number index. No mechanism for the observed covariance of the OH seasonal behavior with solar activity has yet been identified. These results have been reported to the American Geophysical Union and the American Meteorological Society and have been submitted for publication in Geophysical Research Letters.

The OH observations from Truk are the first column measurements reported for the tropics. These have been examined for possible correlation with the observed tropical middle atmosphere circulations of the quasi-biennial oscillation (QBO) and the semi-annual oscillation (SAO), and for possible effects of heterogeneous reactions which are expected to depend on the tropical tropopause temperatures. The average solar zenith angle dependence of the tropical OH varied approximately as for the Colorado data. The normalized abundances, which eliminate most of the solar zenith angle dependence, exhibited long term variations with the winter-spring abundances significantly above those for summer-fall. The data do not show any clear correlation with tropical circulations. While the observed annual cycle is similar to the Colorado annual cycle, the large abundances are seen to occur at the time of minimum tropopause temperature (−83°C) which also suggest a possible heterogeneous source for OH. A manuscript detailing the Truk results is in preparation.

A theoretical study of a possible mesospheric source for the high-sun enhancement of the Colorado OH data from 1980-1988 has been completed. Results demonstrate that conventional mesospheric photochemistry along with reasonable changes in mesospheric constituents such as ozone and water vapor, temperature, and radiation do not reproduce the observed OH behavior. This study is the subject of a Master's Thesis at Florida Atlantic University by Ms. Yan Liu, and a journal article is in preparation.

E. Journal Publications:

A. DIAL SYSTEM FOR STRATOSPHERIC OZONE

B. Principal Investigator: Dr. I. Stuart McDermid

Table Mountain Facility
Jet Propulsion Laboratory
California Institute of Technology
Wrightwood
California 92397-0367

C. Research Objectives

The object of this project has been the establishment of a facility at the JPL-Table Mountain Facility, Wrightwood, California, from which to make long-term atmospheric measurements. The laser remote sensing technique of differential absorption lidar (DIAL) is being used to derive atmospheric ozone concentration profiles. Data will be collected over a long term in order to aid in the detection of trends and changes in the ozone concentration and its vertical distribution. It is anticipated that the JPL-TMF facility could become part of a global network of atmospheric monitoring stations making similar observations. It is also expected that this facility will play an important role in the correlative measurements program related to the Upper Atmosphere Research Satellite (UARS).

D. Progress and Results

Two separate systems are required to obtain the full profile from the ground to 50 km. For the tropospheric part of the profile the lidar system is at the stage of making preliminary test measurements. For the stratosphere, ozone profiles have been obtained on a routine basis since January 1988. During 1988 profiles were measured on 111 separate days. For 1989, 100 profiles have been measured by the end of July. Two extensive inter-comparison campaigns involving a number of ozone measuring systems and techniques have been carried out at the TMF location. Also, a longer term comparison with results from the SAGE II instrument from all of 1988 have been undertaken. The results from these inter-comparisons confirm the ability of the lidar instrument to make precise and accurate measurements of the ozone concentration profile on a regular basis.

E. Publications

I. S. McDermid and S. M. Godin.
Stratospheric Ozone Measurements Using a Ground-Based, High-Power Lidar.
Ground-Based Laser DIAL System for Long-Term Measurements of Stratospheric Ozone.

D. A. Haner and I. S. McDermid.
Stimulated Raman Shifting of Nd:YAG Fourth Harmonic (266 nm) in H₂, HD and D₂.

Variations in the Stratospheric Ozone Profile During 1988 at 34° N Measured by Lidar and SAGE II.


Lidar Observations of Ozone Changes Induced by Sub-Polar Airmass Motion Over Table Mountain, 34° N.