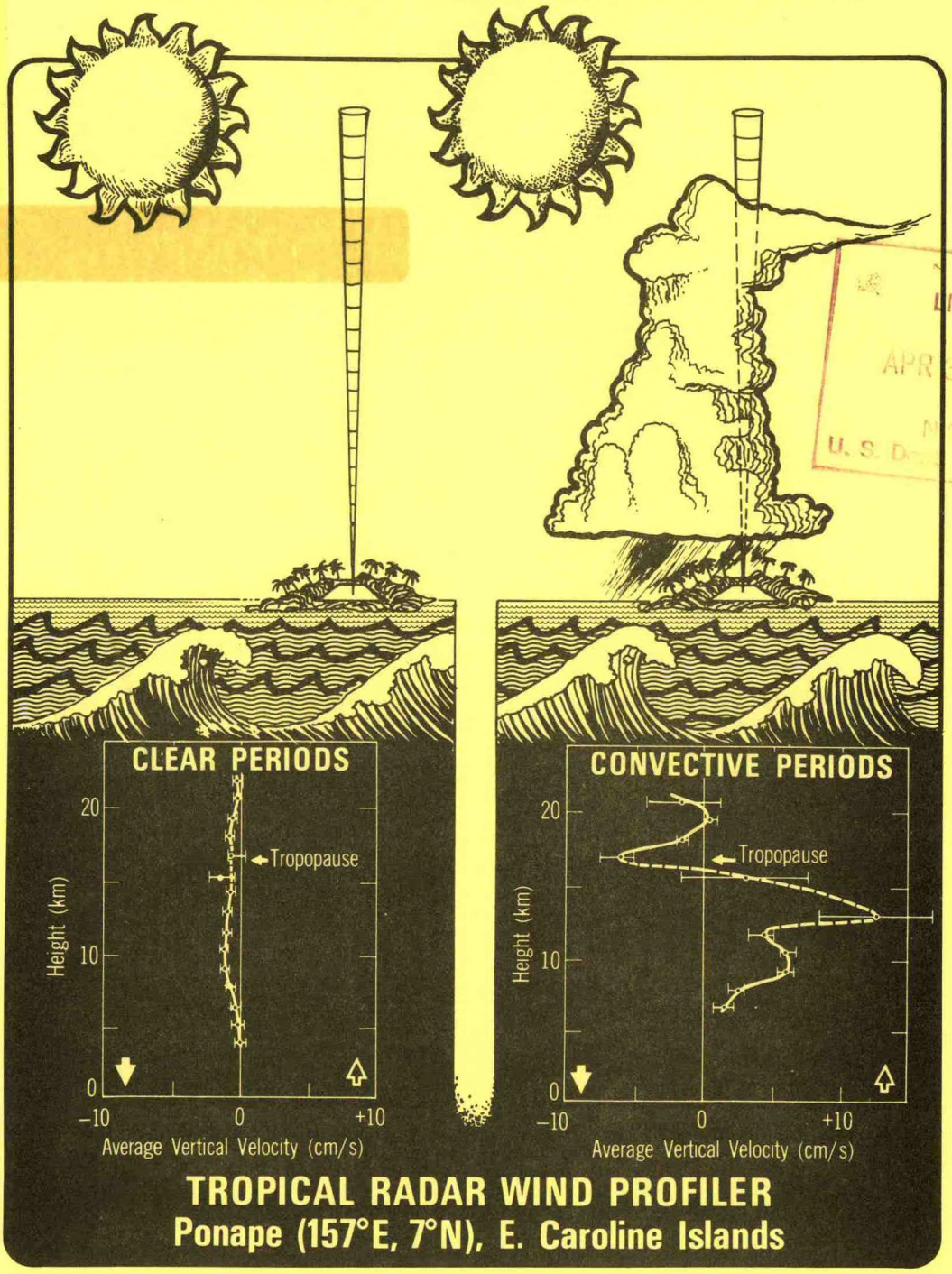
Aeronomy Laboratory

Environmental Research Laboratories

ANNUAL REPORT FY85



TROPICAL RADAR WIND PROFILER
Ponape (157°E, 7°N), E. Caroline Islands

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Environmental Research Laboratories
Aeronomy Laboratory

AERONOMY LABORATORY

ANNUAL REPORT - FISCAL YEAR 1985

October 1, 1984 - September 30, 1985

Aeronomy Laboratory
325 Broadway
Boulder, Colorado 80303

October 1985

UNITED STATES DEPARTMENT OF COMMERCE

Malcolm Baldrige, Secretary

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION

Anthony J. Calio, Administrator

Environmental Research Laboratories

Vernon E. Derr, Director

NOTICE

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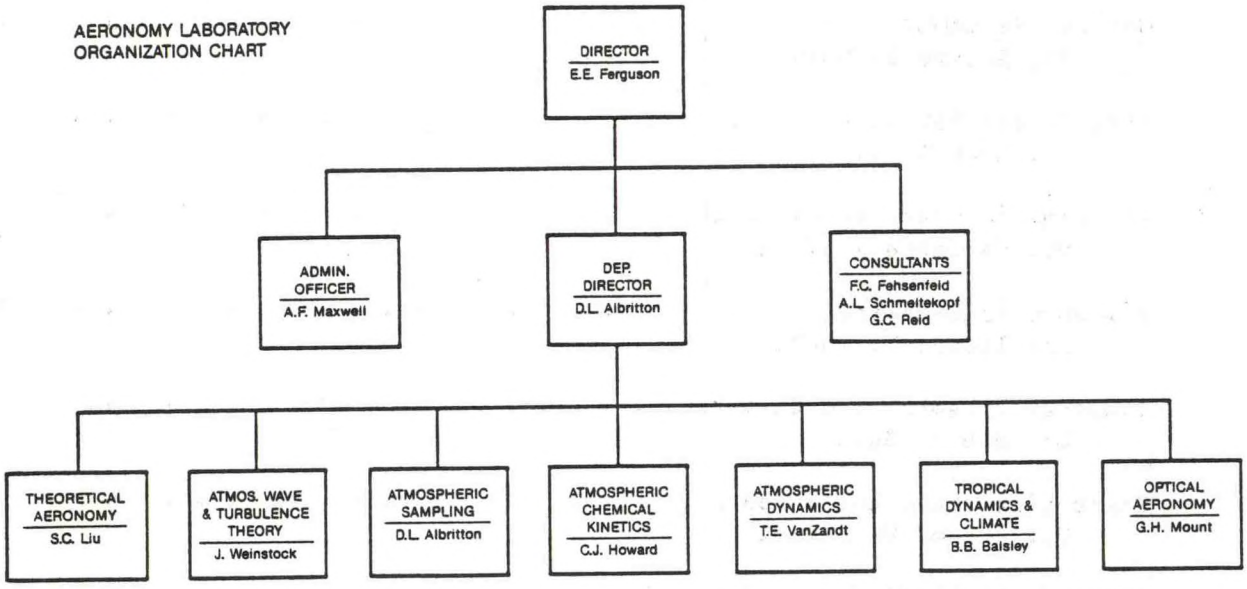
CONTENTS

COVER

The cover sketch is a schematic representation of vertical wind measurements made by AL's Radar Wind Profiler on Ponape, East Caroline Islands. The profiles depict average vertical wind values obtained over a twelve-month period under: (1) relatively clear conditions, when the observed sky cover is equal to or less than 30%, and (2) convective conditions where the spectral width of mid-tropospheric radar returns exceeds approximately 5 m/s. This second condition corresponds to periods of measurable precipitation. Horizontal bars represent the standard deviation of the mean of the sample values included in each measurement. The salient features to be noted in these profiles are the mean downward velocities throughout the troposphere during clear periods and the enhanced upward velocities during convective periods. The Ponape radar is the first of a series of such systems planned for the Equatorial Pacific that will provide continuous high-time-resolution measurements of the total wind field. These data will enable studies of the interaction between short-period, small-scale atmospheric processes and long-term, large-scale variability.

AERONOMY LABORATORY
ORGANIZATION CHART

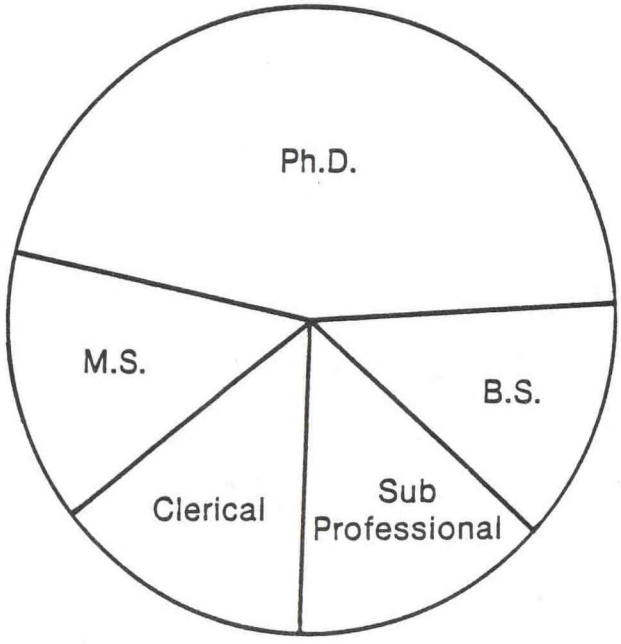


AERONOMY LABORATORY—PERSONNEL STATISTICS

FY 85 Oct. 1, 1984-Sept. 30, 1985

TOTAL FULL-TIME PERSONNEL

Professional	33
Sub Professional	6
Clerical	4
Total Full-Time Staff	43*



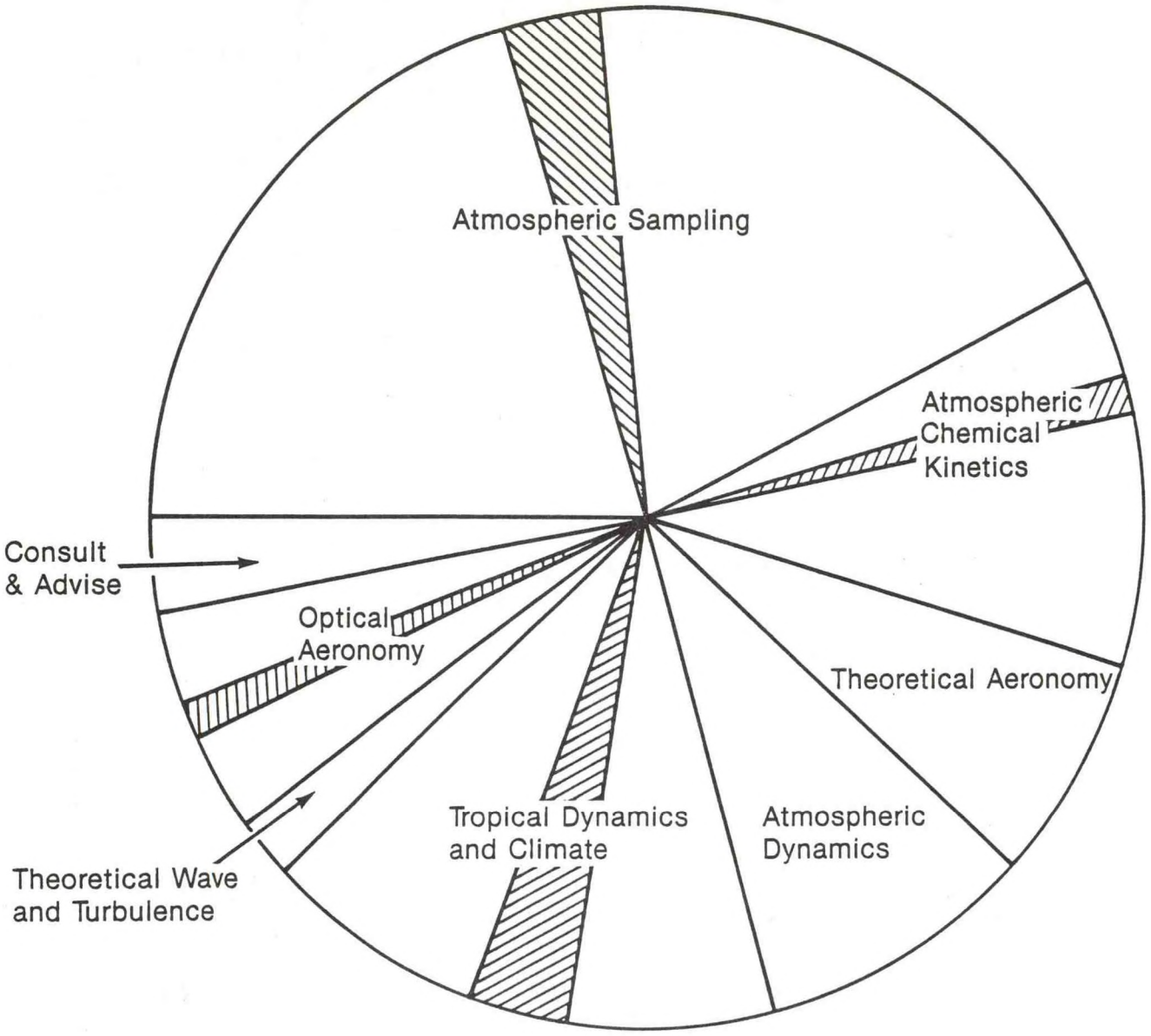
Composition of Full-Time Staff

Ph.D.	20	46%	72% of Full-Time Staff
M.S.	6	14%	
B.S.	5	12%	
Sub Professional	6	14%	28% of Full-Time Staff
(No Degree)	6	14%	

*Does not include visiting personnel

AERONOMY LABORATORY—1985 FUNDING

FY 85 Oct. 1, 1984-Sept. 30, 1985



OR and F	4,818,000
Other Agencies	439,000
Total Funding	5,257,000

AERONOMY LABORATORY

Laboratory Director's Office

Permanent Staff

Eldon E. Ferguson	Director
Daniel L. Albritton	Deputy Director
Jeanne Waters	Secretary
Alton F. Maxwell	Administrative Officer
Karen M. Layman	Clerk Typist

Temporary Staff

Carol Long	Acting Budget Assistant

Introduction

This document is an annual report on the research activities of the Aeronomy Laboratory, one of NOAA's Environmental Research Laboratories located in Boulder, Colorado. Descriptions of the various program activities are given, including some background to put the research programs into perspective, as well as discussions of recent results and plans for the near future. While there is an administrative division of personnel into Program Areas, much of the research is carried out in groups by members from various Program Areas and is not compartmentalized.

The Aeronomy Laboratory has historical antecedents extending back into the National Bureau of Standards Central Radio Propagation Laboratory. The laboratory research effort in that earlier period is best described as ionospheric physics. The mission of the Aeronomy Laboratory has changed over the years due to a combination of factors: the changing nature and mission of our parent organization in the Commerce Department (NBS → ESSA → NOAA), the changing emphasis in atmospheric research due to the normal advance of science and technology, and the ever-changing priorities for scientific knowledge in response to national needs. The program that has evolved encompasses research in several critical areas of atmospheric physics and chemistry in which the Laboratory has unique expertise through the skills and experience of its personnel.

The Laboratory's long tradition of excellence in the field of radar studies of the ionosphere has led to an extension of VHF coherent radar techniques to studies of winds, waves, and turbulence in the neutral atmosphere, from the troposphere through the stratosphere into the mesosphere. The Atmospheric Dynamics Program has played a pioneering role in this area and continues to do this at the forefront of research. A growing concern with the role played by the tropics in influencing global weather and climate patterns has led to an increased activity in this direction. To implement this research, a new program area, Tropical Dynamics and Climate, was instituted in the Aeronomy Laboratory in the past year.

The Optical Aeronomy Program is founded on the long record of leadership in the traditional areas of airglow and auroral studies. This Program has used its unique competence to develop powerful new techniques for remote measurement of important atmospheric constituents at all heights and to obtain information on high-altitude atmospheric dynamics.

The Atmospheric Sampling and Atmospheric Chemical Kinetics Programs have evolved over a period of years out of an Atmospheric Collision Processes Program that had a long tradition of international leadership in the field of laboratory reaction-rate measurements. The Atmospheric Chemical Kinetics Program represents an extension of the Laboratory's pioneering work in ionospheric ion chemistry to atmospheric neutral chemistry, and the program has reached a level of international prominence in stratospheric and tropospheric photochemistry.

The Atmospheric Sampling Program has developed as an outgrowth of the measurement expertise and experimental technology acquired in laboratory reaction studies. The program has a position of world leadership in stratospheric composition measurements using balloon technology. This has been extended by the use of the U-2 aircraft as a stratospheric and tropospheric platform and by the use of research aircraft and ships to make global tropospheric measurements. The program also includes a comprehensively instrumented research site in the mountains near Boulder at which detailed measurements are being carried out with advanced new technology developed for the purpose.

The experimental and observational Programs are supported by strong theoretical programs in both photochemistry and dynamics, employing sophisticated computer models as the principal tool. These theoretical programs also carry out wide-ranging studies of problems that are of critical importance, but lie beyond the domain of the Laboratory's field programs.

The driving force behind many of the programs in recent years has been society's concern with the ozone layer and its vulnerability to man's activities. The Aeronomy Laboratory's programs have had a major impact on our understanding of this vitally important problem of modern society. The problem of acid rain has provided one of the motivations for the tropospheric chemistry programs. The Laboratory has established a leading role in research on this problem and has provided key data and manpower to the National Acid Precipitation Assessment Program. More recently, the recognition that gases in addition to carbon dioxide may contribute to a climate warning has led to new research on the sources, trends, processes, and distributions of these species. The Aeronomy Laboratory has joined others in the Environmental Research Laboratories in the new Radiatively Important Traces Species program that is focusing on this climatic and chemical problem.

The following pages contain detailed descriptions of the various Programs and listings of the Laboratory's publications in calendar years 1984 and 1985.

ATMOSPHERIC SAMPLING PROGRAM

Full-time Staff

Daniel L. Albritton, Program Leader	Physicist
Arthur L. Schmeltekopf, Senior Scientist	Physicist
Fred C. Fehsenfeld, Senior Scientist	Physicist
Jeanne Waters	Secretary
Mary Anne Carroll	Chemist
David W. Fahey	Physicist
Paul D. Goldan	Physicist
Walter J. Harrop	Physical Science Technician
Kenneth K. Kelly	Chemist
William C. Kuster	Chemist
Richard J. McLaughlin	Mechanical Engineering Technician
Orrin A. Mills	Electronic Technician
Richard B. Norton	Physicist
Thomas L. Thompson	Electronic Engineer
Trudy Tyler	Electronic Technician
Richard H. Winkler	Electronic Engineer

Associates, Visitors, and Part-time Staff (1984 and 1985)

Stuart P. Beaton, Physicist, CIRES Summer Student (1985)
Diana L. Burn, CIRES Summer Student (1984)
Carol M. Curran, Chemist, CIRES Research Assistant
Jill A. Devendorf, Physical Science Aid (1984-1985)
Linda M. DeWitt, Secretary
Charles S. Eubank, Physicist, CIRES Research Assistant
Carole Hahn, Meteorologist, CIRES Research Associate
Gerhard Hübler, Physicist, CIRES Postdoctoral Fellow
Andrew O. Langford, Chemist, CIRES Research Associate
Daniel M. Murphy, Physicist, CIRES Research Associate
Paul C. Murphy, Chemist, CIRES Research Assistant
David D. Parrish, Chemist, Metropolitan State College and CIRES Research Associate
Dieter Perner, Physicist, Max-Planck-Institut für Chemie, Mainz, Germany (1984)
Michael H. Proffitt, Physicist, CIRES Research Associate
James M. Roberts, Chemist, CIRES Research Associate
Joseph P. Smith, Physicist, CIRES Research Assistant
Melanie J. Steinkamp, Physical Science Aid, University of Colorado
Eric J. Williams, Chemist, CIRES Research Associate

Introduction

The origins of the present Atmospheric Sampling Program lie in the recognition that man's activities may inadvertently pose a threat to the earth's stratospheric ozone layer, which serves as a protective shield from harmful solar radiation. This potential threat arose because of the possibility that the chlorofluoromethanes released from spray cans would diffuse upward into the stratosphere and would there be photolyzed into chlorine, which could then catalytically destroy ozone at these altitudes. Since the loss of even a fraction of the stratospheric ozone may produce disastrous consequences in the biosphere, this potential environmental threat attracted immediate and widespread attention. However, despite the seriousness of the possible problem, the severe economic dislocations that would follow an immediate cessation of the large chlorofluoromethane industry prohibited taking such an action on the basis of hypothesis alone.

The Atmospheric Sampling Group was formed to address this critical problem. The research effort mounted by the Group led to the first successful measurements of the chlorofluoromethanes at the altitudes in the stratosphere where these compounds are significantly photodissociated. The findings supported the predictions from theoretical models concerning the photochemistry of these compounds and, hence, the predictions of the potential adverse consequences to stratospheric ozone. Subsequent measurements by this group provided a comprehensive set of data describing the distribution of the chlorofluoromethanes in the stratosphere, which has proven useful not only in policy formation regarding these pollutants but also as tracer information for atmospheric dynamics studies.

The approach used in these stratospheric chlorofluoromethane measurements has guided the scientific efforts of the Group since that time. The problems that are selected are those that combine significant new scientific research with important national or global atmospheric environmental questions. The instruments and techniques required in the studies are generally conceived, designed, and developed within the Group and are subjected to rigorous laboratory and field validations. The subsequent field application of these instruments and techniques employ a variety of platforms: balloons, stratospheric and tropospheric aircraft, ships, vans, and semipermanent ground stations. The field campaigns are conducted by the Group's engineers and scientists who developed the instruments. These research efforts are undertaken in close collaboration with other groups in the Aeronomy Laboratory, such as Theoretical Aeronomy and Optical Aeronomy, and with other laboratories, such as the National Center for Atmospheric Research (NCAR) and the National Aeronautics and Space Administration (NASA).

The experience, skills, and interests of the Group have expanded considerably since the initial stratospheric chlorofluoromethane studies and now encompass a broad range of topics in atmospheric chemistry; e.g.:

the natural emissions that contribute to atmospheric acidity and alkalinity,

the transport, transformation, and deposition processes involved in acid deposition,

the tropospheric/stratospheric exchange processes that are factors in regulating stratospheric and tropospheric chemistry and climate, and

the tropospheric and stratospheric photochemical processes responsible for the production and destruction of global ozone.

Several key environmental issues are being addressed. All of them involve man's potential inadvertent and deleterious alteration of the earth's atmosphere: stratospheric ozone depletion, acid deposition, tropospheric ozone production, and the greenhouse effect. As such, this research figures strongly in the NOAA/ERL Long-term Climate and Air Quality Programs.

Recent investigations undertaken by the Group and its future plans are summarized below.

Recent Results

1. Intercomparison of Nitric Oxide Measurement Techniques

Over the last few years, it has been recognized that one of the most meaningful ways to increase the confidence in trace gas measurement techniques is, under field conditions, to formally intercompare the different methods that address the same species. The Atmospheric Sampling Group has been involved in several of these intercomparisons. The most recent of these has been the focus on nitric oxide, NO. This study brought together three instruments that employed two different techniques: NOAA/NCAR and the NASA Wallops Flight Center using chemiluminescence and Georgia Institute of Technology using two-photon laser-induced fluorescence. The intercomparisons were made initially at a ground site and later aboard a research aircraft, both within the boundary layer and in the free troposphere over marine and continental regions. Figure 1 shows the results from one of the ground-based tests where all three instruments sampled from a common manifold through which flowed ambient air with intermittent additions of known amounts of NO. As shown, the agreement was very good, even at these relatively low mixing ratios. Similar results were obtained from the airborne intercomparisons, with demonstrated agreement of approximately 30%. No evidence for artifacts or interferences were found at this level of uncertainty. Because the two experimental methods employed were fundamentally different in character, it has been concluded from this study that NO can be measured reliably under the range of concentrations encountered in both moderately polluted and pristine regions, which is a notable milestone in the experimental study of the chemistry of this key atmospheric species.

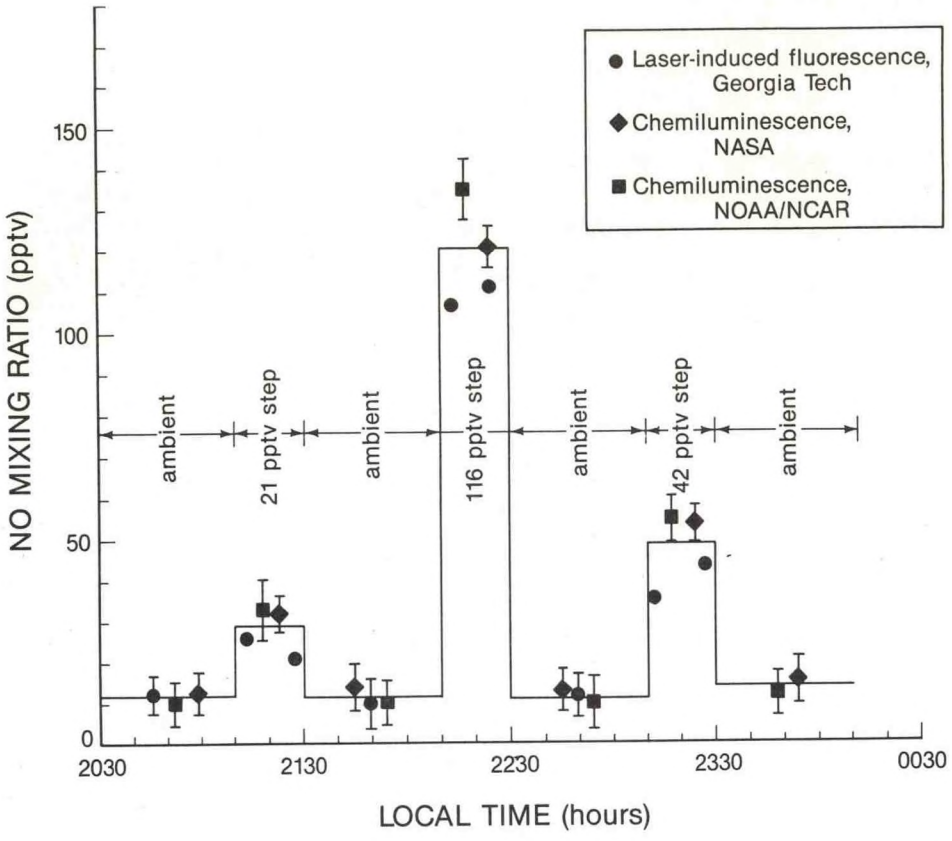


Fig. 1. Intercomparison of results from simultaneous measurements of NO by three separate instruments employing two different methods. The solid line is the mean of the three data sets and the vertical bars reflect the 1 standard deviation variance about this mean value.

2. Studies of the Nitrogen Chemistry at Niwot Ridge

The Niwot Ridge research site is located in the Colorado mountains at 3000 m elevation west of the Denver metropolitan area and near the Continental Divide. The air quality at the site varies from clean, when the winds are from the unpopulated regions to the west, to moderately polluted, when the winds are from the Denver metropolitan area to the east. This wide variation is ideal for testing the understanding of chemical processes by questioning whether theory and experiment agree over such decades of concentration variation. A focus at the research site has been the processes that involve the reactive nitrogen species, since these constituents play key roles in tropospheric chemistry and climate. During the summer and fall of 1984, an intensive investigation of several facets of this nitrogen chemistry was conducted:

(a) Total reactive odd-nitrogen measurements

During these campaigns, a measurement of the sum of the reactive odd-nitrogen species, NO_y, was made at the site during a summer and fall season. NO_y was detected by utilizing a new method developed by the Group, namely, the reduction of the higher nitrogen oxides to NO on the surface of a heated gold catalyst in reaction with CO reagent gas. The NO produced was subsequently detected with a chemiluminescence detector. Correlations of NO_y with NO; nitrogen dioxide, NO_2; peroxyacetyl nitrate, PAN; nitric acid, HNO_3; and particulate nitrate, NO_3^-, show the influence of chemistry and transport on the abundance of these component species at the site. The seasonal variations in the data reflect the change in average photochemical activity in the sampled air masses that results from changes in solar UV flux, temperature, and humidity. These NO_y measurements serve as an important step in the overall validation of this new technique. The global and regional measurements of reactive odd-nitrogen that can be afforded by this new technique will address one of the pressing uncertainties in tropospheric chemistry.

(b) Composition of NO_y

The measurements at Niwot Ridge of NO_y and the individual nitrogen oxide species were combined to examine the composition of NO_y in the sampled air masses. Measurements of NO_y, NO_x (= NO + NO_2), HNO_3, and NO_3^- were provided by the Group's instruments, while levels of PAN were provided by SRI International and NCAR. The mixing-ratio sum of NO_x, HNO_3, NO_3^-, and PAN is designated as $\Sigma(NO_y)_i$. The results are shown in Fig. 2. In the summer, the mean value of the ratio $\Sigma(NO_y)_i/NO_y$ was 0.55 for measurements made over a wide range of NO_y values. In the fall, the mean value increased to 0.88. The difference between measured NO_y and the component species, $NO_y - \Sigma(NO_y)_i$, is termed the shortfall in the composition of NO_y. The shortfall in the fall season is small and within the accuracy of the measurements. In the summer, the large shortfall is thought to result from the higher levels of photochemical activity that promote the formation of other unidentified nitrogen oxide species. Organic nitrate species other than PAN are candidates for the shortfall species. Further measurements of the shortfall and pursuit of its identity promise to be a fruitful course of continued investigation.

(c) Ratio of PAN to NO_x

PAN proved to be comparable to NO_x, an important fact established here for the first time for a rural site, since measurements of PAN and NO_x had not been made simultaneously by instruments comparable to those used by SRI International and NCAR here for PAN and by NOAA for NO_x. These results confirm a highly significant role for PAN in the nitrogen photochemistry of non-urban areas and in the transport of reactive nitrogen to remote regions. In addition, PAN is likely to be an important source of radical species that play roles in gas- and liquid-phase oxidation of pollutant and natural emissions.

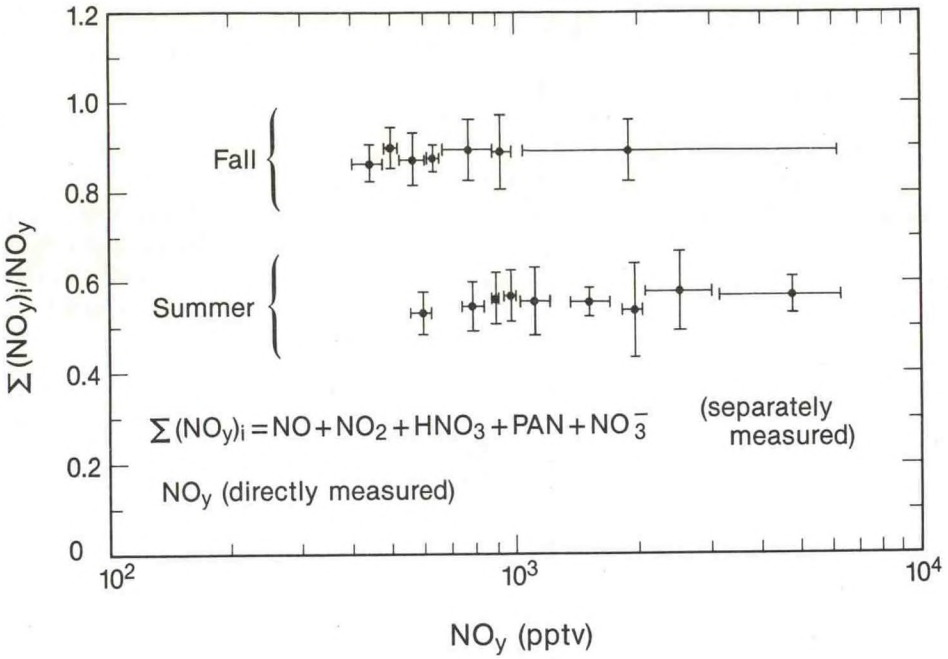


Fig. 2. Ratio of the sum of the individually measured reactive nitrogen species to the measured total reactive nitrogen, NO_y. The data were taken at Niwot Ridge, Colorado, in the summer and fall of 1984. The horizontal bars encompass the range of NO_y values that were averaged to yield each datum, and the vertical bars reflect the 1 standard deviation variance about that mean.

3. Measurements of HNO_3 and NO_3^-

The measurements made during the summer and fall of 1984 supplemented a data set for several nitrogen species that has been accumulating over the years that Niwot Ridge has been operating as a research site. The diurnal and seasonal behavior of numerous species has now been established from these time series. For example, HNO_3 and NO_x have been measured now at all times of the day during all seasons. The ratio of HNO_3 to NO_x concentrations is observed to rise during the day and to decrease at night. For each season, this diurnal pattern can be fitted very well by modeling the production of HNO_3 from NO_2 by combination with hydroxyl radicals and the heterogeneous removal of HNO_3. The conclusion is that HNO_3 has a very short lifetime in the troposphere (approximately 12 h in summer and 24 h in winter) and that surface deposition is the primary removal process. Other Niwot Ridge studies indicate that HNO_3 is a relatively small (generally less than about 15%) component of the atmospheric reactive nitrogen present in the summer. HNO_3 has been a major focus of the National Acid Precipitation Assessment Program, since it had been believed to be the major precursor for deposited nitrate. Hence, the present observation that other nitrogen species need more emphasis is highly significant to the research directions of that program.

4. Photochemical Production of Ozone

Ozone is perhaps the single most important trace species in the atmosphere: its photolysis initiates atmospheric photochemistry, it influences climate by absorbing infrared radiation, and it is toxic in elevated concentrations. Ozone has both natural and man-made sources, and many scientists believe that, in the northern hemisphere, man has wrested control from nature of the ambient ozone levels. Hence, it is important to establish the natural ozone levels and to quantify the production of ozone from man-made precursors, NO_x and nonmethane hydrocarbons. The Niwot Ridge data gathered over the last few years allow those questions to be addressed. The correlation of the O_3 and NO_x mixing ratios measured at Niwot Ridge have been examined for seasonal trends that would reflect the role of photochemistry. Figure 3 shows the results. The wintertime O_3 levels are independent of the NO_x mixing ratio. This result, when coupled with the observation that the NO_x levels in the winter are no larger than those predicted for natural sources alone, leads to the conclusion that these data are likely reflecting the natural background of O_3 at this site.

During the summer, the O_3 levels are found to depend on the NO_x mixing ratio. These data yield an O_3 production rate of 17 ppbv of O_3 per day per ppbv of NO_x, which is in good agreement with a theoretical estimate from a model of the constituents and chemistry at Niwot Ridge. These results have shown that O_3/NO_x correlations can establish the background levels of O_3 at given sites and can reveal the perturbations due to ozone precursors. It is an example of the types of investigations that can lead to a global budget for ozone in the troposphere.

5. Free-Tropospheric NO_x Measurements

In-situ measurements of NO, (fall 1983 and spring 1984) and NO_2 (spring 1984) were made during aircraft flights at altitudes ranging from 500 to 33,000 ft over the Pacific Ocean. These studies were in collaboration with NCAR and were conducted with a NASA aircraft. During the fall series of flights, NO values in the marine boundary layer and the free troposphere were observed to be extremely low, with values ranging from 0 to 10 and 0 to 50 pptv, respectively. Altitude profiles within a single clean air mass were constructed from measurements made during constant-altitude flight legs, and a positive gradient with altitude was typically observed for NO. Typical free tropospheric NO_x values ranged from 10 to 100 pptv, with NO_2/NO ratios exceeding by an average factor of 2.5 those that would be expected during conditions of photochemical steady state. During the fall flights, elevated NO values were observed in the free troposphere during periods of subsiding upper-tropospheric or stratospheric air. Furthermore, evidence for the production of NO in electrically active clouds was also observed, and enhanced NO_x levels were observed in the vicinity of a tropopause fold in the spring of 1984 flights. These 1983 and 1984 aircraft campaigns have provided the most extensive look thus far at the budget of NO and NO_2 in the remote global troposphere.

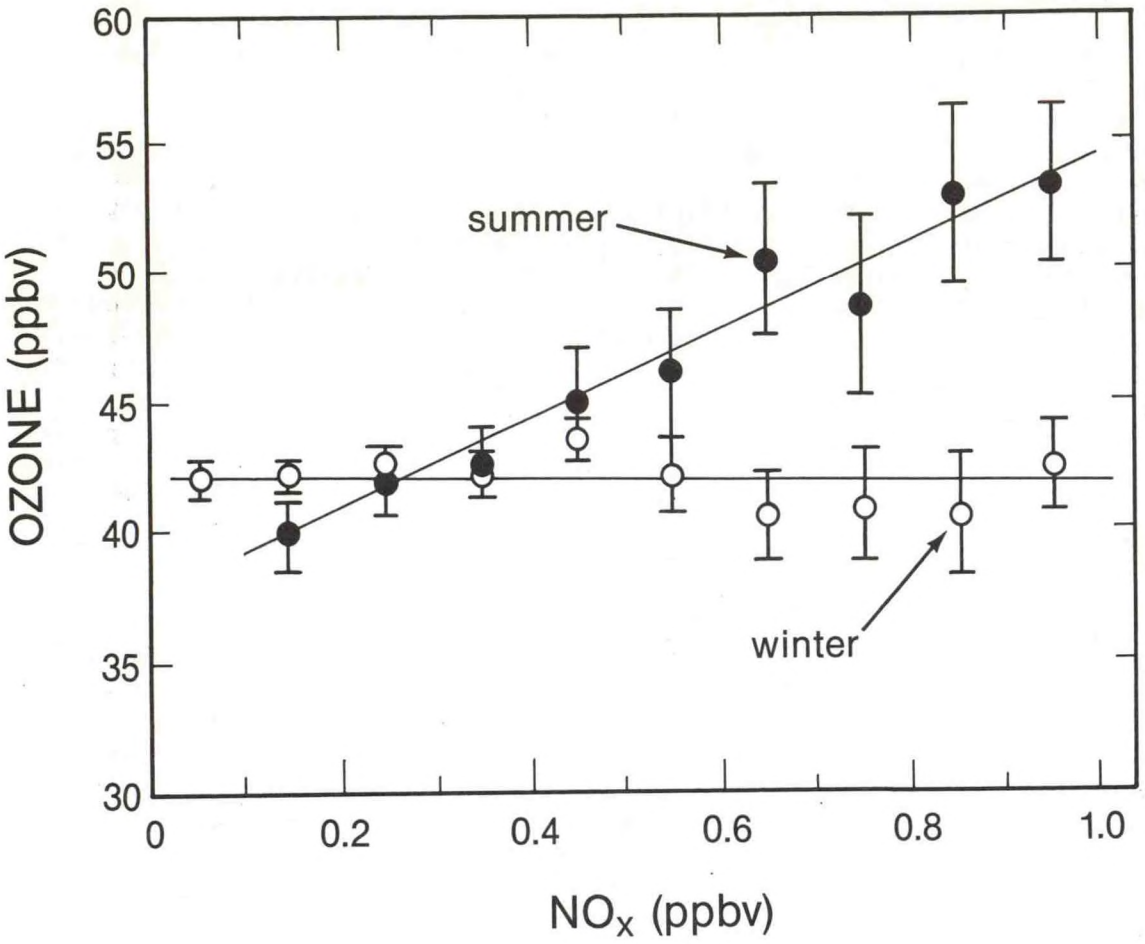


Fig. 3. Ozone mixing ratios as a function of NO_x in the afternoons in summer and winter at Niwot Ridge, Colorado. Each point is an average of all O_3 values in an 0.1-ppbv NO_x interval, based on three years of nearly continuous data. The vertical bars represent 95% confidence limits for the averages shown. The lines are linear least-squares fits to the averages.

6. Long-path Absorption Measurements of Tropospheric Nitrogen Species

A state-of-the-art diode-array spectrometer has been incorporated into a spectrometer/computer absorption spectroscopy apparatus. The device has been used to obtain spectra of stratospheric NO_2 and tropospheric NO_3 of heretofore unobtainable sensitivity. A key part of the method is a least-squares data reduction procedure that employs standard spectral relative intensities obtained from laboratory measurements. The system obtained total-column NO_2 data when it accompanied the stratospheric NO/NO_2 experiment into the field. Now, the system is at the Fritz Peak Observatory in Colorado as part of a long-path (approximately 10 km)

absorption experiment to examine the photochemistry of several tropospheric species. The initial measurements focused on the $N_2O_5 \rightleftarrows NO_3 + NO_2$ equilibrium in a collaborative laboratory/field experiment with NCAR and the University of California at Berkeley. The laboratory component was carried out at NCAR and the field component at Fritz Peak. From the observed rate of increase of NO_3 after sunset, the equilibrium constant, K_{eq}, for the above reactions and the concentrations of N_2O_5 were estimated. Since the ambient pressures and temperatures encountered in this field determination of K_{eq} were substantially different than those of the laboratory component of the experiment, the resulting two data sets are complementary, as the Arrhenius plot in Fig. 4 shows. These data from the equilibrium constant and the observed concentrations of NO_3 and NO_2 in the remote troposphere show that a significant fraction of the reactive nitrogen can be in the N_2O_5 form at low temperatures. The possibility exists, therefore, for the direct impact of N_2O_5 on living matter in remote areas under those conditions.

7. Development of Methods for Measuring NO_x Flux from Soils

While man-made emissions of the nitrogen oxides that control oxidant formation and lead to nitric acid have been estimated with reasonable accuracy, the natural source strengths are poorly known at present. Yet it is understood that such sources exist. Among these natural sources, biogenic emission from the soils is presently considered one of the most important. To reduce the uncertainties, a research program has been started that will (a) use sensitive chemiluminescence instruments to develop flux-measurement methods, (b) critically assess the techniques available for determining NO_x flux from soils, (c) measure the soil emission flux of NO_x at representative sites in North America, and (d) provide a national inventory of NO_x emissions from soils.

The techniques that are presently being used to measure flux are principally the enclosure, gradient, and eddy correlation methods. The enclosure technique measures the NO_x flux from a small, enclosed sample of soil (typically approximately one square meter), while the gradient and eddy correlation methods are used to infer the average NO_x flux from larger areas (typically thousands of square meters). The present study is aimed at intercomparing the results obtained using the enclosure and gradient methods to determine NO_x flux from soils during the nighttime hours. Measurements were carried out on grassland in Colorado during August and September, 1985. The NO_x flux during this period of intercomparison ranged from 0.3 ng N m^{-2} s^{-1} to 25 ng N m^{-2} s^{-1}. There was general agreement in the results from these techniques over this range, thereby increasing the confidence in both methods and allowing the planning of more extensive survey studies of NO_x emissions from a variety of soil conditions.

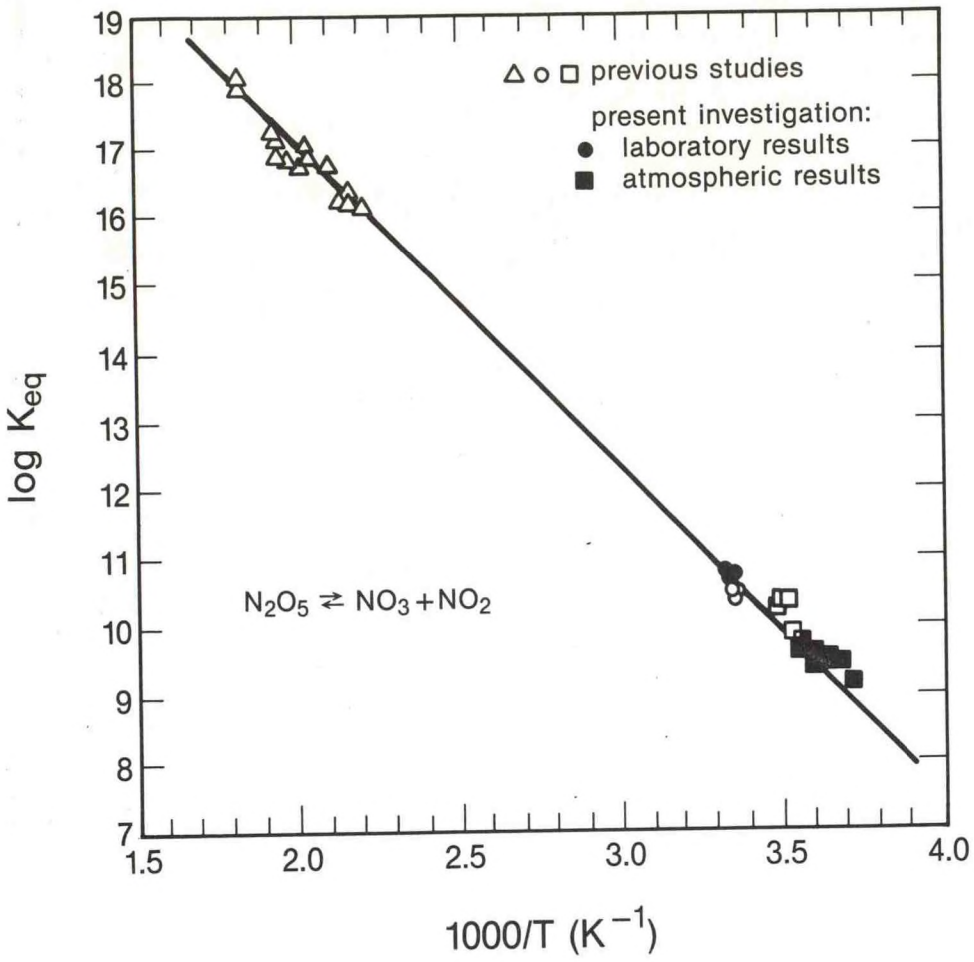


Fig. 4. Arrhenius plot of direct experimental estimates of the equilibrium constant, K_{eq}, of the reactions coupling N_2O_5 to NO_2 and NO_3.

8. Development of Methods for Measuring Atmospheric Ammonia

Ammonia is an important constituent in the atmospheric nitrogen cycle because of its chemical basicity and because atmospheric reactions of NH_3 may yield a net source or sink of NO_x. There are major uncertainties in the magnitude and occurrence of the natural sources of NH_3. The primary natural continental sources of NH_3 are thought to be biological processes in soils and plants and decay of plant and animal wastes. It is desirable to have a relatively fast (10-15 min) and sensitive (detection limit less than 10 pptv) technique for the measurement of ambient concentrations and emissions of NH_3.

The technique applied by the Group uses the tungsten oxide diffusion-denuder tube, which relies on the selective collection of NH_3 on a tungsten oxide surface. The adsorbed NH_3 is subsequently desorbed and converted to NO, which is detected by chemiluminescence. Ammonia is

separated from HNO_3 (and other oxidized nitrogen species that are also collected) by temperature programmed thermal desorption. The desorption behavior of NH_3 is found to critically depend on the preparation and subsequent treatment of the tungsten oxide surface. The collection and recovery of NH_3 in the tungsten oxide system is found to be quantitative (100 ± 5%) in laboratory experiments. The complete conversion of NH_3 to NO is accomplished using a CO-doped gold catalyst operated at 725°C. This conversion is also used to standardize NH_3 permeation devices with accurate NO standards. Alkyl amines are found to partially interfere with the ammonia measurement, but show a different desorption profile, which may permit the presence of alkyl amines to be determined in ambient samples. Field tests of this ammonia technique have been made at several sites.

9. Development of Methods for Measuring Biogenic Sulfur Fluxes

In the attempts to quantify atmospheric concentrations and distributed source strengths of naturally-occurring sulfur species, several conventional analytical techniques have been used to measure concentrations sufficiently low that the accuracy and/or lack of interference has not been demonstrated. Because of the reactive and labile nature of many of the sulfur species of interest, sample acquisition and instrument calibration become especially difficult when mixing ratios of species are below 1 ppbv. The Group has undertaken a critical assessment of the use of: permeation tube sources for calibration standards, enclosures for the determination of source strengths, and potential difficulties associated with cryogenic sample enrichment.

An intercomparison of standards generated at the ppbv level for carbon disulfide, CS_2; sulfur dioxide, SO_2; hydrogen sulfide, H_2S; and methylmercaptan, CH_3SH from two completely independent approaches has been completed. Gravimetrically calibrated permeation tube sources have been compared to sources calibrated by the Department of Chemistry at the University of Idaho using conventional liquid standards and a flash vaporization technique. Agreement was generally at the 10% level for CS_2, SO_2, and CH_3SH and at the 25% level for H_2S.

The use of several different enclosure materials for source strength determinations was examined. Surface adsorption and irreversible losses for both dry and moist (approximately 50% relative humidity) calibration mixtures at the 200 ppt level were examined for several sulfur species. Although some of these, such as COS and CS_2, passed through all the enclosures, many were significantly diminished. Significant humidity effects were observed for these species even for nominally hydrophobic Teflon surfaces.

The role of O_3 in loss of species during cryogenic sample enrichment and subsequent re-evaporation for analysis has been examined. Very significant apparent losses for some species have been observed at O_3 mixing ratios in the 10 to 100 ppbv range.

The results of these studies have been used to improve the techniques that were employed in the summer of 1985 to re-investigate the flux of natural sulfur-containing species from several southeastern-U.S. sites.

10. Organic Acids in Precipitation and Aerosols

Formate and acetate, as well as other organic and inorganic anions, have been measured in precipitation collected at Niwot Ridge (a remote site) and Boulder (an urban site). A protocol was developed to collect the samples free of interfering organic contamination and preserve the samples until analysis using ion chromatography. Figure 5 shows a plot of formate against nitrate ions measured in precipitation collected during the spring and summer of 1984. The diagonal lines are linear correlations, with formate being the indicated percentage of nitrate. At both

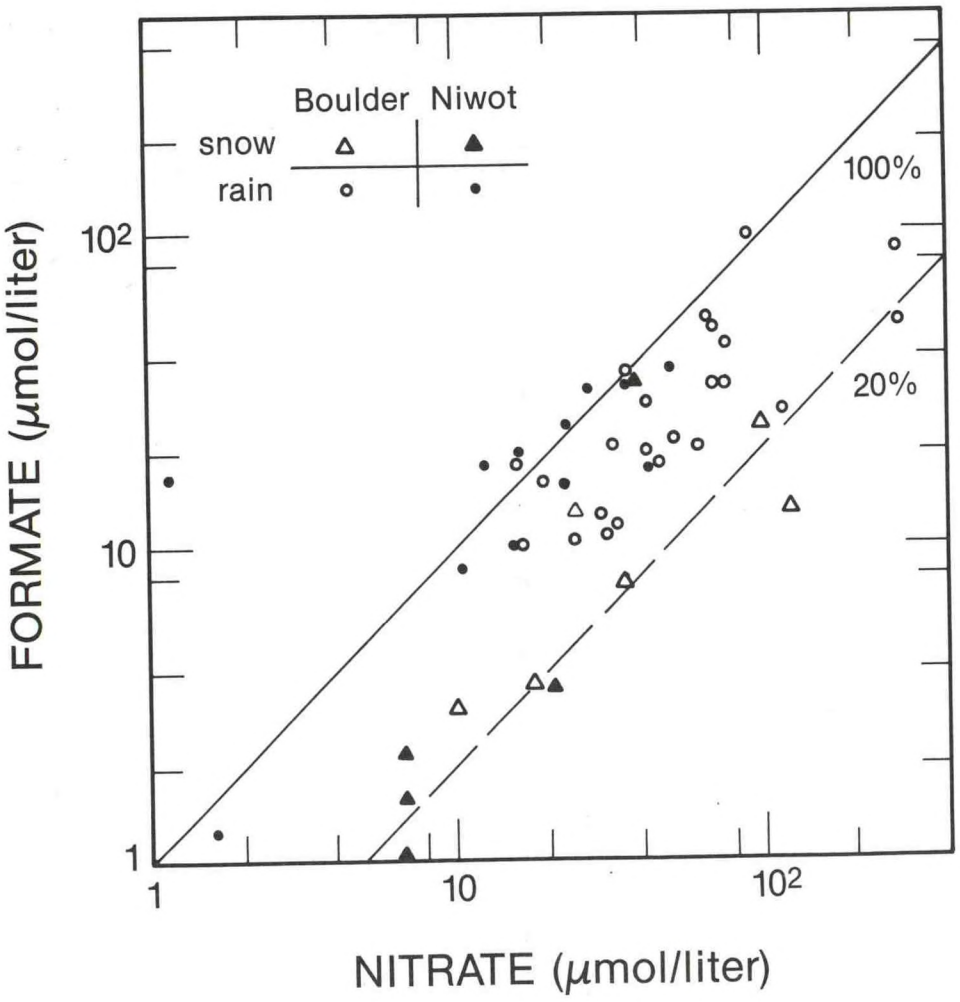


Fig. 5. Observed concentrations of formate relative to those of nitrate at remote (Niwot) and urban (Boulder) sites in the spring and summer.

locations, the organic anion concentration is usually 20% of the nitrate concentration and occasionally exceeds the nitrate. Formate is the dominant organic anion measured, with concentrations as large as 9×10^{-5} M occurring in summer rain showers. A variety of dicarboxylic anions are observed, but their concentration is generally much less than formate. The present observations show that the organic acids can be significant contributions to the acidity in urban and rural continental areas. Organic anions also make a significant contribution to the chemical composition of aerosols, again with formate the dominant organic anion.

11. Water Vapor Measurements in the Vicinity of a Tropopause Fold

The exchange (i.e., irreversible transfer) of mass, trace gases, and aerosols between the stratosphere and the troposphere varies with latitude, longitude, and season and is one of the key dynamical processes that effect atmospheric chemistry. The outflow from the stratosphere occurs predominately in tropopause folding events associated with the extratropical jet stream at midlatitudes. In April of 1984, the Group was involved in a NASA-sponsored experiment to study the details of a folding event with a coordinated group of sensors aboard a U-2 aircraft. In particular, the flights were designed to transect the tropopause fold above the axis of the extratropical jet stream and to span the potential vorticity gradients in this part of the lower stratosphere.

In such events, the mean potential vorticity gradients are folded across the jet axis in the lower stratosphere and across the mean tropopause into the troposphere. The mean distributions of trace constituents that are correlated with potential vorticity are also folded, thereby creating laminar distributions from smooth monotonic gradients maintaining the previous correlations and hence permitting source identification. On these flights, the Group's fast-response water vapor sensor provided data with which such correlations could be explored.

Figure 6 shows the flight legs and the distribution of the water vapor that was deduced from these observations. The water vapor mixing ratios clearly identify the wet troposphere, the dry stratosphere, and the transition zone in between, where the folded mean tropopause extends downward and poleward. The water vapor mixing ratios decreased sharply upward and poleward in the transition zone. At the higher elevations in the dry stratosphere, the mixing ratios increased upward and poleward. The detailed comparisons of water vapor and ozone (the latter measured by NASA) are consistent with the known sources of these species.

In the transition zone, the covariation in the mixing ratios is negative, which is in accord with the source of ozone being in the stratosphere above and the major source of water being in the troposphere below. At higher elevations in the dry stratosphere, the covariation is positive, as the example in Fig. 7 shows. This is consistent with both sources being in the stratosphere: the oxidation of methane producing water vapor and the photochemical production of ozone. These data and the others obtained in this campaign demonstrate that potential vorticity and trace

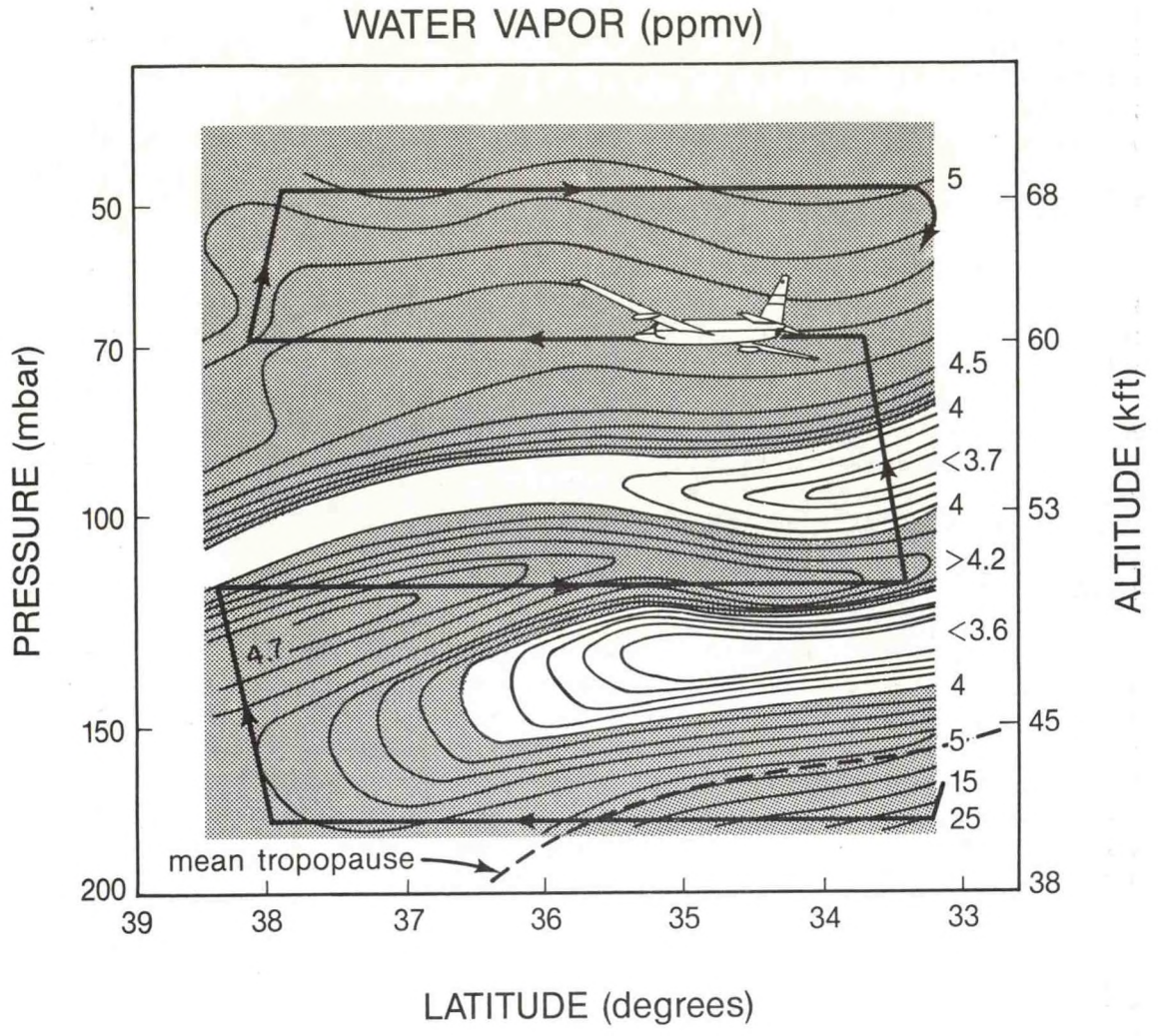


Fig. 6. Water vapor distribution determined on the indicated flight path of a U-2 research aircraft on 20 April 1984.

gas distributions are multiply folded by differential advection, maintaining their respective correlations during the transport. Evidence of irreversible mixing by small-scale turbulence is implicit in the observed tendency for negatively correlated tracers to become uncorrelated on the smallest spatial scales. These observations have strongly guided the design of the future stratospheric/tropospheric exchange studies in which the Group will participate.

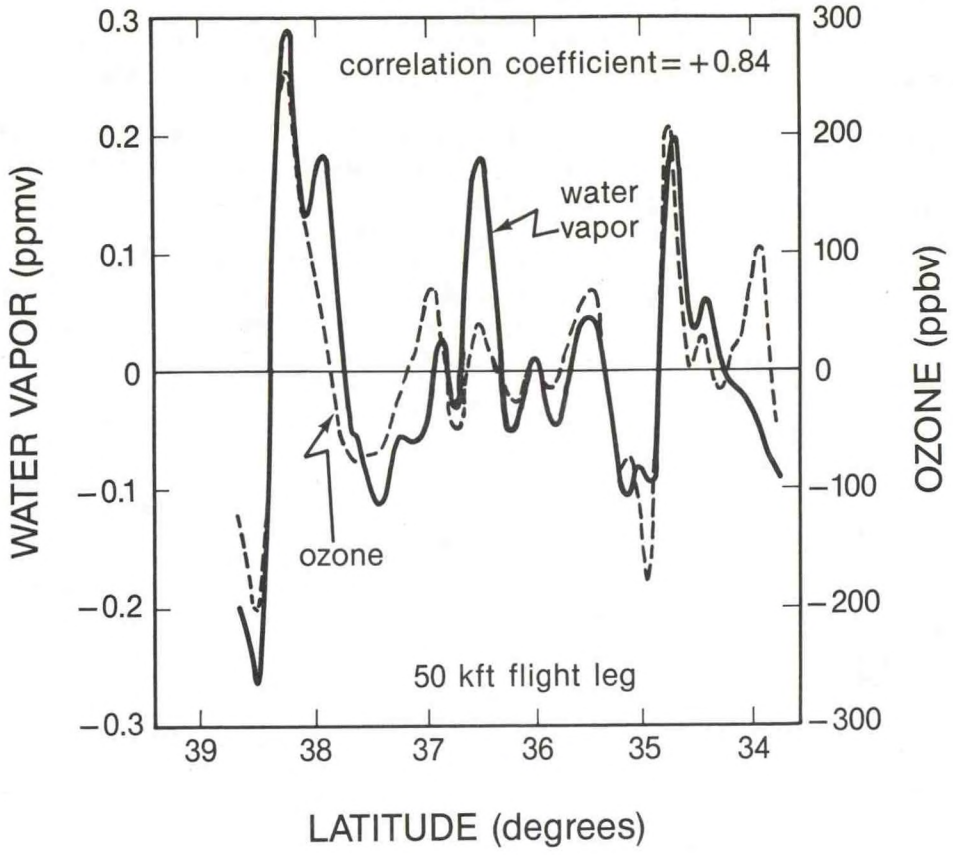


Fig. 7. The variation of water vapor and ozone mixing ratios about their respective means over the 50 kft flight leg in the dry stratosphere. The raw data for both sets have been smoothed on a spatial scale that is very small compared to the length of the flight leg.

Experiments-in-Progress and Future Plans

1. Studies of the Nitrogen Chemistry at a Clean Coastal Site

A newly instrumented research van has been used to explore further the aspects of tropospheric nitrogen chemistry. Namely, the Niwot Ridge study of 1984 has been repeated in April and May of 1985 at Point Arena, California. This site is located north of San Francisco and typically receives inflow of marine air during this time period. Therefore, both Niwot Ridge and Point Arena represent relatively clean sites, but the latter provides a marine contrast. These data are being analyzed and should provide a unique opportunity to test the models of the chemistry of marine air, a system where only a few fundamental processes are thought to dominate.

2. Free-Tropospheric NO, NO_2, and NO_y Flights

The NO_y technique will be added to the airborne NO and NO_2 instruments and used, in collaboration with NCAR, on a series of aircraft flights in the summer of 1986. A NASA aircraft will carry a suite of instruments that will focus on the reactive nitrogen chemistry of the troposphere: the distributions, reactions, and instrument reliability. The reactive nitrogen species to be addressed are NO, NO_2, HNO_3, PAN, and NO_y. In addition, measurements of O_3, NH_3, CO, nonmethane hydrocarbons, and solar flux will be made, as well as aircraft and meteorological parameters. For most of these reactive nitrogen species, two to four instruments employing different methods will be aboard. Thus, in addition to providing the most detailed examination to date of the reactive nitrogen species in the free troposphere, this study will be able to critically evaluate, via intercomparison, the reliability with which NO_2, HNO_3, PAN, and NO_y measurements can be made.

3. Investigation of NO_x Emissions from Soils

In the technique-evaluation and pilot measurement studies made in the late summer of 1985 for NO_x emissions from soils in Colorado, the observed NO_x flux ranged between 0.3 ng N m^{-2} s^{-1} and 40 ng N m^{-2} s^{-1}. The NO_x flux was found to depend strongly on soil temperature, increasing rapidly with increasing soil temperature. In addition, this sampling was marked by an extended dry period during August, followed by a period of wetter conditions in early September. For similar soil temperatures, the NO_x flux was lowest toward the end of the dry period and increased sharply with the onset of precipitation. At the end of the extended dry period, NO_2 was observed to be present in the effluent from the sampling enclosure, but was not present after the onset of precipitation. This measurement series, therefore, not only supported the validity of the methods involved, but also laid the groundwork for the next stage of research. The future plans include the deployment of the flux measurement techniques of choice to measure NO_x flux from representative soils at selected field sites in the U.S. in 1986. Later work will focus on the development of fast-response NO_x detectors to be used in conjunction with eddy-correlation methods for NO_x flux determination.

4. Measurements of Ambient Ammonia Concentrations

Ambient measurements of NH_3 were made at Niwot Ridge, Colorado, and Point Arena, California. Measurements at Niwot Ridge were made in October and November, 1984, when the ground was mostly covered with snow. The mean NH_3 mixing ratio was 175 pptv at Niwot Ridge with some evidence of local, possibly biogenic, sources. The measurements at Point Arena were made in April and May, 1985. The mean NH_3 mixing ratio was 325 pptv and the values ranged from 140 pptv to 1.1 ppbv. The surface winds were virtually always blowing from out over the ocean, but detailed studies of the air mass trajectories are still underway. Small variable oceanic sources of NH_3 are possible explanations for the relatively high levels of NH_3 observed. Future work will involve the comparison of the tungsten oxide technique with treated-filter and citric-acid denuder-tube sampling methods, combined with ion chromatographic analysis. The enclosure method

for soil and plant flux measurements will be explored using Teflon film-lined boxes. The longer-term goal is an inventory of mean ammonia concentrations from natural sources for the major regions of the U.S., which is input required in the understanding of the acid deposition phenomenon.

5. Measurements of Biogenic Sulfur Fluxes

An assessment of the significance of natural biogenic sulfur sources compared to anthropogenic sources as potential contributors to the acidification of rainfall requires the measurement of flux at or below 10^{-8} g S m^{-2} min^{-1} over large geographic areas. To date, such an assessment has rested almost entirely on one study completed in 1979. In view of the importance attached to these measurements, the analytical difficulties recognized by these investigators, and recent improvements and advances in measurement techniques for trace sulfur species, a reassessment of the strengths of natural sulfur flux was deemed desirable. The laboratory development and testing of new methods for sulfur flux measurements has been completed, as well as laboratory intercomparisons of the new methods and those used in the earlier field studies. For the second phase of this reassessment, simultaneous measurements at three previously-measured sites were undertaken jointly by NOAA, Washington State University, and the University of Idaho in July and August, 1985. These results are currently being analyzed and evaluated. They will be used over the coming year to help construct an inventory of biogenic emissions of sulfur compounds that contribute to the acidity of atmospheric deposition.

6. Studies of Organic Acids and Bases

The study of organic acids and bases that have been observed in different regions will be continued. To date, the studies have concentrated on liquid and aerosol phase; however, these investigations are being extended to include gas-phase measurements. Preliminary results indicate concentrations of formic acid up to nearly 1 ppbv and smaller concentrations of other gas-phase organic acids. A program to measure aldehydes, which are possible precursors of the organic acids, has been initiated also.

7. Development of a Tropospheric Ozone Lidar Instrument

The differential absorption lidar technique will be developed as a means for measuring ozone in the free troposphere. There is currently no fully acceptable method to do such, despite the need to assess man's potential alteration of this important climatic and chemical species. Two lasers will be used for the differential absorption method, one providing the wavelength that is absorbed strongly by ozone and the other providing the wavelength that is not. Tunability will be used to generate a signature that will verify that the absorption is due to ozone alone. Aerosol densities, which could cause an artifact absorption, will be monitored with a separate wavelength. Range scanning of the lidar will define the altitude variation. The optical and chemical properties of the troposphere were modeled to test the performance of possible designs. The conclusion was that an identical pair of pulsed lasers (Nd:YAG and doubled

dye, 1 W) would give the required wavelengths (1064, 532, 560-610, and 280-305 nm) for both the ozone and aerosol measurements. It is expected that a profile up to 12 km can be obtained in minutes with a precision of 5% and an accuracy better than 10%. Assessments with theoretical models at the Aeronomy Laboratory and the Geophysical Fluid Dynamics Laboratory indicate that this will be adequate to define the ozone variance in the troposphere. The two laser systems have been ordered. The site for the lidar development will be at the Fritz Peak Observatory, a mountain location west of Boulder and above metropolitan Denver's aerosol layer. The remaining components of the lidar system (laser coolers, telescope, optics, detectors, and electronics) will be specified and ordered. The room at Fritz Peak Observatory will be readied. Preliminary optical tests could begin mid-1986 and initial atmospheric tests by 1987. Intercomparisons with high-accuracy balloon-borne ozone instruments are planned and then regular measurements would follow.

8. Stratospheric/Tropospheric Exchange Investigation

In addition to transfer of constituents between the stratosphere and troposphere in the extratropics by tropopause folds associated with jets, there is also considerable transfer occurring in the tropics. The most intriguing of these are by large cumulonimbus clouds and/or thermally forced mean circulations. The stratosphere/troposphere exchange program in which the Group is involved is addressing all of these, the tropopause fold study conducted with the U-2 aircraft in the spring of 1984 being the initial campaign. The later studies will be made with the ER-2, a more advanced stratospheric research aircraft, and more sophisticated sensors. The Group is developing four of those: water vapor, water vapor and ice, ozone, and total reactive nitrogen, NO_y. The test flights for the first three of these, the accompanying computers and data storage devices, and the gas/particle inertial separator have just been completed in the late summer and early fall of 1985.

Extratropical flights will start in 1986 and the NO_y instrument will join the set during that year. The flights in the early part of 1987 will focus on cloud processes north of Australia. The goal will be to better characterize both the rapid vertical transport by large cumulonimbus clouds, which form their anvils in the lower stratosphere, and the slower, larger-scale transport attributed to mean circulation.

9. Temperature Dependence of the NO_3 Cross Section

The diode-array spectrometer will be used, in collaboration with the Atmospheric Chemical Kinetics Group, to establish the temperature dependence of the NO_3 absorption cross section. Two tandem flow tubes and two diode-array spectrometers will be used to identify the relative change in the cross section with temperature. Atmospheric concentrations of NO_3 are most often deduced using the cross section in the 662 nm regions, and it has been assumed that there is no temperature dependence. However, recent preliminary observations have suggested that this assumption may not be correct and hence the need for this re-investigation.

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OPTICAL AERONOMY PROGRAM

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Introduction

This program utilizes optical measurements of the atmosphere as a tool for studying fundamental atmospheric processes such as energy balance, composition and dynamics. The center for the observational program continues to be the Fritz Peak Observatory in the mountains west of Boulder. For more than a decade after its establishment the observational program was concentrated on measurements of light emitted in the upper atmosphere (> 70 km) either from chemiluminescent airglow reactions or the aurora. This was at a time when the Commerce Laboratories in Boulder were principally concerned with ionospheric radio propagation and so with the physical state of this same high region of the atmosphere.

The major thrust of the program is currently studies of the lower atmosphere including both the stratosphere and troposphere. The composition and chemistry of the lower atmosphere had begun to receive major attention as the fragility of the ozone layer and problems of pollution became apparent. The lower atmospheric studies have generally utilized measurements of absorption by molecules. But, almost all of the expertise and optical equipment previously developed has been immediately applied to these new areas and so the program has moved swiftly and efficiently into a leading role in them. In so doing we have exploited the extraordinary sensitivity of optical absorption for the detection and quantitative measurement of minute quantities of chemically important species in both the stratosphere and the troposphere. The location of the Fritz Peak Observatory has proven to be a very favorable one in the new program, particularly for troposphere studies, since the wind patterns allow us to both study the occasional downwind pollution from Denver as well as the extremely clean air experienced during the normally westerly wind flow. We have also carried out measurements at a large number of other locations using platforms ranging from vans, ships, and aircraft to the presently operational Solar Mesosphere Explorer satellite built and operated by the University of Colorado in Boulder. In all of this work, we have taken

advantage of the flexibility of a small group to quickly adapt broad and powerful optical techniques to new problems in the atmosphere as they arise.

The group notes with great regret the death of John Noxon in January 1985.

Major Areas of Investigation

Stratospheric and Tropospheric Composition

The techniques developed at the Lab for separately determining the stratospheric and tropospheric abundances of NO_2 using ground based absorption spectroscopy continue to be applied with changes in abundance and altitude distribution of NO_2 in the stratosphere being followed on a routine basis. Stratospheric NO_x ($NO+NO_2$) is critically important in controlling ozone abundance.

Major perturbations in the structure of stratospheric NO_2 are associated with changes in the large-scale stratospheric circulation pattern accompanying stratospheric warmings. The interpretation of these large changes has been attributed by Solomon and Noxon as being due to southward movement of NO_2-poor polar air in which NO_2 has been converted to N_2O_5 during polar night. The temperature dependent photodissociation rate of N_2O_5 during the day inhibits breakup of N_2O_5 to NO_2 in the extremely cold polar air and slows down conversion to NO_2. Thus, NO_2 column measurements can be a tracer of the excursion of polar air into mid-latitudes. The Noxon cliff has been identified in SME data and application of photochemical modeling to approximate air trajectories indicates the correctness of the N_2O_5 interpretation.

A method has been developed for measuring NO_2, in the free troposphere from mountain tops and aircraft. Results from Mauna Loa, Hawaii indicate extremely low NO_2 column in this clean background air.

The total column abundance of NO_3 in the stratosphere at night has been measured for five years at 40°N with additional observations at 19°N, 31°N, 51°N, and 64°N. At low latitude the mean abundance is about 8×10^{13} cm^{-2}; it varies little with season and appears to be in general agreement with a model based upon simple NO_x chemistry except, perhaps, in spring. At mid latitude the variation in abundance exceeds prediction and the abundance exhibits a close relation to the highest latitude experienced by stratospheric air prior to its arrival at mid latitude; the higher the latitude the lower is the NO_3 abundance. At 64°N the upper limit in April and November is 1.5×10^{13} cm^{-2}; in April this is far below what is predicted. These observations suggest that a scavenger of NO_3 is continually produced in the stratosphere at high latitude and that when there is strong equatorward flow the scavenger can at least reach mid latitude. The identity of the scavenger remains unknown as does the importance of its role as a sink for NO_x in the stratosphere.

A new series of observations has begun of stratospheric NO_3 with the diode array spectrograph. For studies of tropospheric NO_3, a powerful light source has been installed 10 km from Fritz Peak and studies have begun of NO_3 once again utilizing the array spectrograph. We expect to replace the light source with a retroreflector in order to eliminate problems in monitoring light intensity and to increase the path to 20-km length.

The PEPSIOS interferometer located at the peak continues to successfully measure stratospheric OH. Thus, this long series of observations continues to be taken on a regular basis. Measurements were made during the partial solar eclips of 30 May 1984 and a large amplitude oscillation in the vertical column was detected. An initial OH reduction during the eclipse was followed by an underdamped oscillation having a period of about one hour. The OH abundance returned to normal values two hours after the eclipse termination. This is believed to be the first observation of a ringing response of any atmospheric constituent to a solar eclipse. The photochemistry of this observation is not understood.

Global measurements of NO_2 by SME continue to be analyzed by the group. Following extensive analysis of the pre-El Chichon NO_2 data, attention has shifted to interpretation of nadir data. Clear NO_2 enhancements are present over tropical oceanic regions due to lightning. Analysis shows that a large contribution to the tropospheric NO_x budget is made by lightning. In addition to natural NO_2, we have found that man made NO_2 is easily traced from centers of its creation in cities, and the paths of commercial jetliner traffic are clearly present in the data.

The eruption of the El Chichon volcano in Mexico drastically altered the aerosal composition of the stratosphere. A remarkably large decrease in stratospheric NO_2 is associated with certain regions of the cloud as the cloud comes and goes over Fritz Peak. Portable measurements made as far south as Soccorro, N.M. confirm this result. No explanation for this effect exists. Whenever NO_2 is reduced there is a corresponding small increase in the total column of stratospheric ozone. Stratospheric OH was also significantly affected by El Chichon.

Mesospheric and Thermospheric Studies

1. Dynamics and Thermal Structure in the Thermosphere.

High resolution interferometric techniques have been applied to the study of atmospheric emission lines at Fritz Peak Observatory in order to determine both temperature and wind fields in the thermosphere. These are fundamental quantities which cannot be directly determined by other means. The observational program, coupled with theoretical modeling, provides insights on the dynamics and thermal structure of the atmosphere above ~ 70 km.

(a) Solar minimum

The geomagnetically quiet behavior of the thermosphere during solar minimum has been determined, and the results show the existence of strong equatorward winds during the summer which decrease to fairly weak winds, sometimes poleward, during the winter. The temperatures show lower values in the winter than in the summer. These results are in general agreement with the predictions of a General Circulation Model (GCM) where the winds are primarily driven by global pressure gradients established by solar heating and high-latitude heat and momentum sources at a large distance from Fritz Peak Observatory. The present observations showed the necessity to include the high-latitude forcing as a permanent feature of the global circulation, in particular during quiet periods.

The geomagnetically disturbed behavior of the thermosphere shows enhanced temperature and wind gradients with latitude. The wind structure during disturbed periods tends to have a very strong equatorward component reaching speeds of 640 m/s. Large scale thermospheric waves have been observed during some of these geomagnetic storms. The high latitude energy source required to explain the observations has been successfully parameterized using the auroral electrojet index AE.

b) Solar maximum

The response of the atmosphere to geomagnetic storms during solar maximum is quite complex, showing strong convergences lasting for several hours, as well as elevated temperatures of the order of 2000 K. This has been interpreted again in terms of the expanded magnetospheric pattern reaching the neighborhood of Fritz Peak, thus placing Fritz Peak at the boundary of two circulation patterns during part of the storm. Further measurements at other latitudes are now in progress, or being planned, in order to further understand this thermospheric behavior.

The need for wider latitudinal coverage of atmospheric circulation has been partially fulfilled by making observations at high latitudes near Fairbanks, AL (64° N), in collaboration with the Geophysical Institute of the University of Alaska, and at the University of Michigan field site at Calgary, Alberta (51° N). The observations show considerable meridional divergencies in the winds over the length of the chain of these stations, in keeping with the localized heating effects at high latitudes. Some of the recently initiated investigations at high latitude have revealed the presence of large vertical winds in both the lower and upper thermosphere. These vertical motions appear both as short-term (minutes) and long-term effects (hours). The short-term effects are interpreted as being caused by the localized heating at those latitudes but the long term effects require further observations.

Investigations of the upper thermospheric temperature at 40°N latitude over a 12-year period have provided the ability to study solar, geomagnetic and long-term effects on the thermosphere. An unexpected finding is the existence of a semi-annual variation of the temperature in addition to the known semi-annual density variation. The present (one

station) results do not provide confirmation for the hypothesis of a semi-annual Joule heating effect or of planetary wave energy leakage into the upper atmosphere that are normally invoked to explain the semi-annual variation in the densities.

Global studies of the dynamical and thermal behavior of the atmosphere by means of high resolution optical techniques are to be undertaken using the Space Shuttle as a platform. These studies will be carried out in collaboration with colleagues at the University of Michigan, University College (London), York University, and the National Center for Atmospheric Research.

Measurements of vertical motions of the atmosphere have been made with the prototype high luminosity TESS device. The results show large amplitude (~ 40 m/s) oscillations with a periodicity of about 40 minutes, coupled with small emission rate changes. This has been interpreted to be the atmosphere's response to the passage of gravity waves since the observed periodicity is within the narrow range of periodicities possible at that atmospheric height, and the observed ratio of horizontal to vertical velocities is that expected for gravity waves. The measured vertical winds also show that individual (high-time-resolution) zenith measurements of neutral winds cannot be used as (zero) reference winds with any degree of certainty.

2. Twilight Airglow

In line with our policy of continuing a few selected studies of the upper atmosphere we continue to observe infrared molecular oxygen emission at twilight which permits a measurement of ozone at altitudes where it cannot otherwise be determined. The dramatic seasonal and short term changes observed indicate a corresponding change in the upflow of hydrogen compounds from the underlying stratosphere. In effect, this permits a study of the upper boundary conditions on the stratosphere which are necessary for realistic modelling of its behavior.

Another twilight program involves measurement of emission from O^+ ions in the upper thermosphere created by the absorption of solar ultraviolet light by O atoms. We can thus determine directly the density of the atmosphere at high altitudes where the majority of satellite instruments can no longer make in-situ observations. It is thus possible to follow the changes in upper thermospheric composition with season and geomagnetic activity.

3. Mesospheric Gravity Waves

Both the O_2 and OH emission in the nightglow can be analyzed to yield a relatively direct measurement of the atmospheric temperature at 95 and 85 km respectively. The most important discovery has been that large periodic fluctuations exist at both altitudes and show a phase coherence similar to that expected from internal gravity waves originating in the troposphere as

well as in the high latitude auroral mesosphere. An instrument to monitor mesospheric gravity waves is now in automatic operation. When analyzed in conjunction with the nonlinear theory of gravity waves developed by Weinstock these observations permit a study of the deposition of heat and turbulent energy in the lower thermosphere by internal gravity waves. Correlations are evident between these waves and other mesospheric quantities, such as ozone.

Future Plans

The outline of our current areas of study is intended to indicate our concern with using optical methods to open up new areas in atmospheric studies and to pursue them as long as important results continue to emerge or until a clear pattern of change with time is evident in the species measured. Major emphasis will of course remain upon studies of the troposphere and stratosphere, their composition, and the exchange between them. The stratosphere is both a source and sink for minor species in the troposphere and so one must consider both regions jointly in many cases.

Several significant new programs are starting up at Fritz Peak. Instrumentation to begin measurement of tropospheric OH is in the final design phase. The light source located 10 km from the Peak is being replaced by a retroreflector mosaic of corner cubes and will remove problems involved in monitoring the intensity of the light output. The OH instrumentation will consist of a high power excimer laser and a very high resolution double pass spectrograph. The spectrograph is also being designed to be used to study very low concentrations of atmospheric trace species both in Rayleigh scattered sunlight and using a light source and long path absorption.

Recent theoretical analysis has demonstrated the importance of multiple scattering in the interpretation of daytime photochemistry. An accurate knowledge of the tropospheric and stratospheric radiation field is essential to verification of the theory and could potentially have a significant effect on tropospheric and stratosphere photochemistry. A three year program will begin to build instrumentation to accurately measure the seasonal radiation field at Fritz Peak. The series of U-2 research aircraft flights will be made over regions of known albedo into the lower stratosphere to measure the field as a function of altitude.

Current programs in NO_2 and NO_3 will continue as will the long series of stratospheric OH.

A new shuttle based instrument is being constructed in collaboration with the Naval Research Laboratory to measure OH in the upper stratosphere and mesosphere.

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THEORETICAL AERONOMY PROGRAM

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Introduction

The objective of the Theoretical Aeronomy Program is to undertake theoretical studies of important atmospheric problems, to construct and utilize computer models of the chemistry and dynamics of the atmosphere, and to analyze atmospheric data collected within the laboratory or by collaborative experiments. In recent years the principal concern has been with problems related to the minor-constituent composition of the stratosphere and mesosphere (the middle atmosphere), deriving largely from the widespread practical interest in stratospheric ozone and its potential depletion by artificial pollutants. Recently, however, the interests of the group have expanded both downward in altitude to the complexities of tropospheric chemistry and outward in discipline toward the problems of radiative effects in the atmosphere and of the dynamics of climate. Future years should show a further expansion of these new and exciting areas.

Although the chief concern is with the lower and middle atmosphere, there is some continuing interest in the unsolved problems of the thermosphere. The ultimate goal of the program as a whole can best be described as that of attaining a sufficiently detailed understanding of the composition and energy budget of the atmosphere that accurate predictions of future trends can be made. Many aspects of the thermosphere are better understood than the corresponding aspects of the lower regions of the atmosphere since they have been explored on a global basis by such satellite missions as the Atmosphere Explorer series. To the extent that important

problems of thermospheric composition or energy budget remain unsolved, and are of potential importance to the atmosphere as a whole, a continuing involvement is expected. A similar philosophy applies to problems of the atmospheres of other planets and to problems connected with the evolution of the earth's atmosphere, since studies of these topics can yield important insight into the processes operating in our own atmosphere.

The biosphere-atmosphere interaction plays a critical role in the budget of many important trace gases. The biospheric response to changes in atmospheric trace gases and in climate probably has significant feedback effect on the atmosphere. This area of research will be a new addition to our tropospheric modeling effort.

In addition to these internal studies, an important function is that of providing assistance to other Laboratory programs on problems that require advanced computer programming techniques. In addition to this direct service function, strong scientific coupling exists in several areas, and the objectives of the Program are continually developed and approached in collaboration and consultation with the experimental and observational Programs.

Recent Results

Troposphere

Research in the tropospheric photochemistry centers around two major subjects: acid deposition and tropospheric ozone.

Acid deposition is a serious problem in the north-eastern U.S. and eastern Canada. Precipitation with pH in the range of 4.0 to 4.5 is quite common in these areas downwind of the mid-western heavy industrial states. Most of the anions contributing to the high acidity are $SO_4^=$ and NO_3.

Tropospheric ozone has been one of the major research subjects of this laboratory in recent years. Ozone plays a central role in the photochemistry that controls the abundance and interaction of most of the important trace species (e.g. CO, CH_4, H_2S, NO_2 and SO_2) in the troposphere. There is increasing evidence that tropospheric ozone may have been perturbed by the anthropogenic emissions of hydrocarbons and NO_x ($NO + NO_2$). Perturbation of tropospheric ozone may cause a chain reaction that could change the distributions of the above mentioned trace gases. Since ozone and some of these trace gases absorb IR radiation in the window of CO_2 and H_2O absorption, the radiation budget in the troposphere and thus the climate may be altered. In addition, high surface ozone may damage plants and may be a health hazard.

The photochemistry and transport of acid material and ozone are closely related. For instance, the hydroxyl radical OH is produced by photolysis of O_3

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

followed by

$$O(^1D) + H_2O \rightarrow 2\ OH.$$

The gas phase oxidation of NO_2 and SO_2 are both initiated by OH,

$$NO_2 + OH \xrightarrow{M} HNO_3$$

$$SO_2 + OH \xrightarrow{M} HSO_3.$$

The OH radical is quickly converted to HO_2 by reaction with CO and hydrocarbons. In turn, HO_2 produces H_2O_2 which is the major oxidant for SO_2 in the aqueous phase reactions. Furthermore, OH, HO_2, and NO_x are catalysts that control the photochemical production of ozone.

The Theoretical Aeronomy group is involved in several topics of research in the areas of tropospheric ozone and acid deposition:

(a) development of a fine resolution planetary boundary layer model to simulate the transport and photochemistry of O_3, NO_x, and hydrocarbon species, especially near the surface layer.

(b) collaboration with the Atmospheric Sampling group on planning and interpreting measurements of NO_x, O_3, HNO_3, SO_2, particulate NO_3 and $SO_4^=$, with emphasis on measurements made at Niwot Ridge, Colorado;

(c) collaboration with scientists at GFDL on modeling the tropospheric ozone and NO_x distributions with a 3-dimensional general circulation model;

(d) collaboration with scientists at NCAR on developing a mesoscale air quality model for the Colorado Front Range;

(e) development of a combined liquid phase and gas phase photochemical model to study the oxidation of NO_x amd SO_2;

(f) model studies of the distribution of NO_x, natural hydrocarbons, and SO_2 that are produced from natural sources.

The fine resolution planetary boundary layer model has been used to evaluate the distribution and the photochemistry of naturally emitted hydrocarbons (isoprene and monoterpenes). Several important findings have resulted from this study. It is found that natural hydrocarbons at typical observed values affect the ambient photochemistry significantly (Liu et al., 1985). The peroxyl radicals (HO_2 + RO_2) increase by more than a factor of 2. On the other hand, the OH radical decreases by about 50% when natural hydrocarbons are included. Furthermore, the model predicts that isoprene and monoterpenes mixing ratios decrease quickly with height in the surface layer. This is the result of the short chemical lifetime of these natural hydrocarbons and the highly stable conditions in the surface layer.

Because of the high concentration of natural hydrocarbons in the surface layer, RO_2 and HO_2 may be high enough to account for the missing

oxidant observed at Niwot Ridge (Parrish et al., 1985a). In turn, the O_3 formation rate in the surface layer will be increased proportionally. However, because of the long lifetime of O_3 its diurnal behavior is controlled by the photochemistry in the entire planetary boundary layer where the concentrations of natural hydrocarbon are much lower. It shows that measurements made near the surface need to be interpreted carefully.

The summer O_3 production efficiency per unit NO_x at Niwot Ridge has been compared to 8 other rural stations in the central and eastern US. With only one exception, the daily O_3 production rate for these stations all lie within the range of 6 to 12 ppb per ppb of NO_x, a remarkable agreement considering the wide range of geographical locations. Model calculated efficiency agrees with observed values when NO_x is greater than 1 ppb. The consistency of the summer O_3 production efficiency suggests that the average daily O_3 production at a rural station may be predicted if NO_x is known. The dependence of O_3 production rate on NO_x also allows a crude estimate of the total O_3 production in the summer season for anthropogenically emitted NO_x and NMHC. For the eastern United States, we estimate an average summer column O_3 production of 6.4×10^{11} $cm^{-2}s^{-1}$, about 13 times the average cross tropopause O_3 flux (Liu et al., 1985).

Seasonal variation of ozone at Niwot Ridge has been found to be a very sensitive function of NO_x (Parrish et al., 1985b). At NO_x level less than 0.2 ppb, the O_3 seasonal variation agrees with results from general circulation model calculations that exclude photochemistry (Levy et al., 1984). When NO_x is greater than 0.3 ppb, there is a clear summer maximum due to photochemical production of ozone. The difference between the O_3 concentration for NO_x less than 0.2 ppb and the average O_3 concentration gives the lower limit estimate of the anthropogenic impact on the O_3 distribution at the site.

PAN and other organic nitrate have been shown to be major odd nitrogen species in the rural atmosphere (Singh et al., 1985). They may be the major carrier of NO_x to the free troposphere and remote areas. In the summer, PAN correlates with O_3 and NO_x very well in the afternoon. This is consistent with the photochemistry of PAN. The peroxyacetyl radical and the equivalent acetyldehyde calculated from the observed PAN level provide valuable information on the total reactive non-methane hydrocarbon abundance at the measurement site. Organic nitrates may contribute substantially to the total odd nitrogen observed at Niwot Ridge (Fahey et al.,1985).

The mesoscale model development has progressed as planned. A vertical diffusion based on Blackadar's scheme is added to the bulk planetary boundary layer. Some modifications to the Deardorff's scheme are made to improve the vertical mixing of momentum during calm wind conditions. At the interface between coarse-mesh and fine-mesh domains, the smoother-desmoother scheme used in the model generates noise near the interface. A new scheme similar to Newtonian relaxation is applied to the interface. It has improved the transition from the coarse-mesh domain to the fine-mesh domain. The predicted wind fields of nested grid and uniform grid have been compared to observed values. It is concluded that the nested grid with two-way interaction gives the best results.

Middle Atmosphere

Chemical-dynamical modeling studies of the middle atmosphere have continued to be carried out, in collaboration with Rolando Garcia of the National Center for Atmospheric Research. Current research has focussed on transport effects on possible future ozone depletions due to chlorofluorocarbons, and on a more complete understanding of transport in the mesosphere.

Quantitative estimates of the effects of increasing chlorofluorocarbon abundances on stratospheric ozone have largely been performed with one-dimensional models. Current (1985) one-dimensional models predict a rather small steady state ozone column reduction of about 4-6%. These small values result from a balance between large depletions in the upper stratosphere that are compensated to a substantial degree by increases in the lower stratosphere (the chemical "self-healing" effect), so that the total ozone column change is a small difference between the two.

It is, however, well established that lower stratospheric ozone is dynamically rather than chemically dominated, particularly at middle and high latitudes in the winter season, so that one-dimensional models may not be the most appropriate tool for evaluation of these effects at those latitudes and seasons. In particular, the lower stratospheric self-healing effect is likely to be significantly less important at high latitudes than one-dimensional model projections indicate. Solomon et al., (1985a) presented a two-dimensional residual Eulerian model calculation of the ozone response to projected chlorofluorocarbon increases to examine these effects quantitatively. We find that the predicted ozone reductions during winter and spring in high latitudes are likely to be substantially greater than one-dimensional model predictions, in agreement with some other multi-dimensional model studies (see Solomon et al., 1985a and references therein). This occurs because ozone is largely dynamically controlled at these latitudes and seasons, and because the net transport is downward directed from higher altitudes where large ozone depletions are predicted to occur due to chlorine increases. The observed spring maximum in the annual cycle of total ozone is a direct result of the same downward transport phenomenon, strongly suggesting that a maximum in ozone depletion must be expected to occur during that season as well. This behavior is readily seen when ozone chemistry and transport are examined in a coupled chemical-dynamical model like that used in Solomon et al., (1985a).

The behavior of mesospheric ozone also exhibits important variations that are likely to be due to transport processes, and can be used to test our understanding of mesospheric dynamics. In particular, ozone observations from the Solar Mesosphere Explorer (SME) satellite exhibit a pronounced equinox maximum at about 80 km which is not explained by photochemical theory. Recent work has suggested that breaking small scale gravity waves play an important role in the dynamics of the mesosphere. We have incorporated a parameterization of the propagation and dissipation of gravity waves into our dynamical chemical model. The parameterization enables us to compute both the momentum forcing and turbulent diffusion induced by the waves at mesospheric altitudes, providing a physically based description of the variations in transport of photochemical constituents as

a function of latitude and season. The seasonal variations in the computed eddy diffusion coefficient are consistent with the large seasonal changes in MST radar echoes at Poker Flat, Alaska observed by the Aeronomy Laboratory's atmospheric dynamics group. The computed variations in eddy diffusion have important effects on the transport of chemical species in the mesosphere, particularly atomic oxygen and water vapor. Changes in water vapor densities near 80 km have been shown to induce a seasonal variation in ozone that closely resembles that observed by SME. The consistency between the model simulation of both chemical and dynamical observables strongly supports the suggestion that gravity waves play a very important role in determining the structure of the mesosphere and lower thermosphere. This study is described in detail in Garcia and Solomon (1985).

Another chemical tracer of interest at mesospheric altitudes is carbon monoxide. Carbon monoxide is produced very rapidly in the lower thermosphere through photodissociation of carbon dioxide. In the mesosphere, carbon monoxide is destroyed through reaction with OH. Therefore, the vertical profile of carbon monoxide generally decreases from the source region at about 100 km to the sink region near 50-70 km. The vertical structure depends strongly on the rate of transport between the thermosphere and the mesosophere, and on the abundance of mesospheric OH. OH is produced predominantly by water vapor photolysis at altitudes above about 65 km, and it is therefore present in larger quantities in summer, when the solar zenith angle is smaller, than it is in winter. In the polar night region, OH is not produced at all, and the large CO abundances obtained in the thermosphere may be transported down into the mesosphere without encountering the loss process with OH that exists in the sunlit atmosphere. Therefore, CO represents an excellent tracer for mesospheric transport, particularly inside the polar night region. We have presented a two-dimensional chemical-dynamical model study of CO to examine this behavior quantitatively. Comparison with several ground-based microwave observations of CO have been used to show the utility of CO for tracer studies (Solomon et al., 1985b).

Future Plans

Troposphere

Tropospheric ozone and its possible perturbation by anthropogenic activities will continue to be one of the major subjects of our research. Important problems in this area are the photochemical production and destruction of O_3, transport of O_3, the distribution of tropospheric NO_x, OH, and RO_2 radicals, and the effects of nonmethane hydrocarbons. The role of natural hydrocarbons, in particular, will be examined in view of their large emission rate and their high reactivity toward both O_3 and OH radicals. We will continue to study these problems by working closely with the Atmospheric Sampling group and the Atmospheric Chemical Kinetics group. Collaboration with scientists at GFDL on 3-dimensional modeling will be strengthened in both stratospheric and tropospheric modeling.

Studies of the acid deposition problem will be expanded. Emphasis will be on atmospheric transformations of SO_2 and NO_x, heterogeneous processes, and natural emissions of sulfur and nitrogen compounds. Developing a regional acid deposition model for the Colorado Front Range is a long-range goal for this group. The model will be very useful for interpreting the data at Niwot Ridge and for designing other measurement strategies. It is clear that such a model can be readily applied to study regional oxidant problems such as that of rural O_3. This model will be developed in collaboration with scientists at NCAR.

The interaction of the atmosphere and the biosphere is an important and fascinating research subject. Biogenic emissions of hydrocarbons, reactive nitrogen species, NH_3, and reduced sulfur species may have significant impact on the tropospheric O_3 and acid deposition. Our interest in this area of research has been growing in the past few years. In the future, atmospheric chemical models may need to include the important feedback processes involving the biosphere.

Middle Atmosphere

The interaction of dynamics and chemistry in the middle atmosphere represents an important element in our understanding of aeronomy. We plan to continue to pursue our studies of the natural and perturbed stratosphere and mesosphere. We will couple a detailed treatment of infrared radiation, as well as a linear planetary wave model, into our chemical/dynamical model. With these tools, the zonally averaged radiative/chemical/dynamical behavior of the stratosphere can be investigated, and the role of chemical transport by planetary waves can be examined.

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Introduction

The major goal of the Atmospheric Chemical Kinetics program is to develop and apply laboratory techniques for the study of important atmospheric chemical processes. The products of these studies include reaction rate coefficients, reaction product identities, photochemical parameters, and thermochemical data. The information obtained is used to develop an understanding of how natural and man-made chemicals released into the atmosphere affect our environment. The evaluation of current environmental issues, such as stratospheric ozone depletion, photochemical air pollution, and acid rain require an understanding of the basic chemical reactions that occur in the atmosphere.

The Atmospheric Chemical Kinetics program has evolved from the Atmospheric Collision Processes program which was dedicated to the study of ion-molecule reactions which dominate the chemistry of the upper regions of the atmosphere. The laboratory continues to play a minor role in atmospheric ion chemistry measurements. These measurements have important applications in communication and in atmosphere composition studies.

In the Aeronomy Laboratory, two principal experimental methods have been developed to study ion chemistry. The first is the flowing afterglow technique, which has now been reproduced in numerous laboratories around the world and which has become the standard technique for studying ion-molecule reactions at near-thermal energies. Its success is due, in part, to the unique capability of studying the reactions of an enormous variety of ion and neutral chemical species. The second device is the flow-drift tube which combines the chemical versatility of a flowing afterglow with the energy variability of a drift tube. This combination permits the study of the kinetic energy dependence of an extensive variety of ion-neutral reactions, ground state or excited state ions with stable or unstable neutrals. The accessible kinetic energy range is from 0.03 to several electron volts, a range that bridges the experimentally difficult gap between room temperature and beam energies.

With these techniques, the Aeronomy Laboratory has provided a large fraction of the available data on the ion-neutral reactions that control the ion composition in the earth's atmosphere. Some examples include the development of a detailed D-region negative ion reaction scheme that correctly predicted the dominant ion species before composition measurements were available, the development of a positive ion reaction mechanism to explain rocket observations of water vapor ions, and the discovery of associative detachment reactions, a new class of ion-neutral interaction with important physical and atmospheric applications.

Recent interest in atmospheric ion chemistry has concentrated on the application of ion-chemistry as a sensitive analytical tool for the determination of critical trace atmospheric species, on the role of ion chemistry in the production and destruction of critical atmospheric species in the troposphere and the stratosphere, and on the production and reactions of vibrationally excited ions. For example, the first stratospheric measurements of sulfuric acid vapor have been obtained from the combination of ion kinetic data from the AL and in situ negative ion composition measurements by a research group in Germany. The latest analytical application of the flowing afterglow experiment has been to use it as a reactor and detector for chemical ionization detection of reactants and products of neutral reactions. Ions, noble gas metastables, and UV photons have been used to achieve the sensitive detection of trace gases at concentrations down to about 10^9 molecule cm^{-3} in a flow tube experiment.

In the 1970's the laboratory extended its research in reaction kinetics to neutral processes which dominate the chemistry of the lower regions of the atmosphere. This shift was in response to the increasing interest of the atmospheric science community in environmental issues.

The laboratory was the first to adapt the technique of laser magnetic resonance (LMR) for kinetic studies of the reactions of atmospheric radicals. LMR was invented in the Boulder National Bureau of Standards Laboratories for the study of the Zeeman spectroscopy of radicals. In an early study it was used to make a thorough investigation of the reactions of man-made chlorocarbons with

atmospheric OH radicals. Subsequent legislation and regulations on the uses and emissions of these materials were based in part on these data. Using the LMR apparatus the laboratory has made measurements that have led to major revisions in the kinetic data base for HO_2 radical reactions. These new data have resulted in major changes in the predictions of stratospheric ozone depletion by man-made nitrogen oxides and chlorocarbons. These studies have also provided evidence that new chemical species such as HOCl and HO_2NO_2 must be included in stratospheric models. The LMR technique has been improved in collaboration with NBS scientists. The current instrumentation permits a larger variety of radical molecules to be detected and, therefore, more complex reactions to be studied. These studies not only improve our knowledge of environmental chemistry, but their unusual and unpredicted temperature and pressure behavior has generated interest and attention beyond the atmospheric science community.

In recent years the research emphasis of the laboratory has shifted towards tropospheric chemistry. A large fraction of the chemical processes that take place in the troposphere are sensitive to pressure. Therefore, a program aimed at carrying out experimental investigations at atmospheric pressure has been initiated. Pulsed laser and flash lamp photolysis are used to create free radicals and optical spectroscopic techniques such as resonance fluorescence, laser induced fluorescence and long path absorption are used to monitor the radicals.

Much of the research in this program is carried out with collaboration and support from other organizations. NBS physicists from the Time and Frequency Division provide a valuable service as consultants in the area of laser technology. The program provides opportunities for young scientists to be trained in atmospheric and environmental chemistry. This includes both Postdoctoral Research Associates from CIRES and the National Research Council and graduate students from the University of Colorado, Department of Chemistry and CIRES. Substantial financial support has been obtained through research contracts with the Chemical Manufacturers Association, the Defense Nuclear Agency, National Aeronautics and Space Administration, and the Federal Aviation Administration.

Recent Results

Two experiments, a laser magnetic resonance spectrometer (LMR) and a chemical ionization flowing afterglow (CI-FA), have been used to study the mechanism by which sulfur dioxide, SO_2, is converted to sulfuric acid, H_2SO_4, in the atmosphere. This process is a major source of uncertainty in modelling acid precipation chemistry. The central issue is whether odd hydrogen radicals, OH and HO_2, are consumed in the conversion process. If radicals are consumed, a reduction in SO_2 emissions would not necessarily produce a proportionate reduction in the amount of H_2SO_4 deposited in critical areas. This follows because the present rate of H_2SO_4 production may be limited by the number of odd hydrogen radicals produced and not by the amount of SO_2 released into the atmosphere. Recent experiments in other laboratories have provided indirect evidence that the gas phase SO_2 oxidation process does not consume radicals. Our direct LMR study confirms these experiments and shows that the OH radical which reacts with SO_2 to form $HOSO_2$ in the primary process is regenerated as an HO_2 radical, when oxygen is present. The rate coefficient for the reaction of $HOSO_2$ with O_2 was determined from measurements of the rate of formation of the HO_2 product. The yield of HO_2 product was found to be $> 70\%$ of the initial OH concentration in the LMR experiment.

The CI-FA experiment has been used to detect both the $HOSO_2$ reactant and the SO_3 product in the reaction of $HOSO_2$ with O_2. Cl^- ions were used to detect $HOSO_2$ as SO_3^- and SO_3 as SO_3Cl^-. Figure 1 shows data for a rate coefficient measurement. At 298K the rate coefficient for this reaction was found to be $(4.4 \pm 0.9) \times 10^{-13}$ cm^3 $molecule^{-1}s^{-1}$. This preliminary result agrees well with the value we obtain from the LMR experiment and a published measurement using an indirect technique.

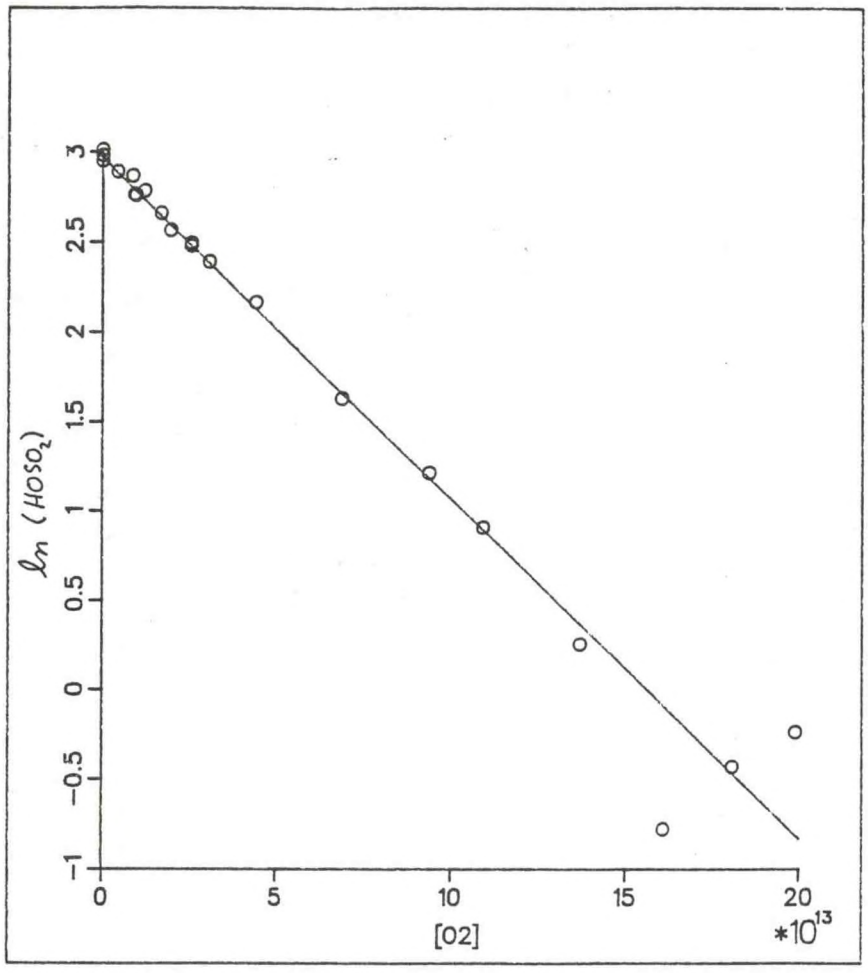

Figure 1. Data for the reaction $HOSO_2 + O_2$ using chemical ionization detection of $HOSO_2$ in a flowing afterglow apparatus. The experimental conditions were P = 4.07 torr, $\bar{v}$ = 824 cm s^{-1}, T = 296K, and reaction time = 43.7 ms.

The proposed mechanism is described by the following scheme:

$$OH + SO_2 + M \rightarrow HOSO_2 + M$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

The SO_3 product is probably rapidly converted to H_2SO_4 by water on the surface of droplets and aerosols. In this mechanism the odd hydrogen radicals are oxidized from OH to HO_2, but OH is rapidly regenerated from HO_2 in the atmosphere by reactions with NO and ozone. The overall effect is that the radicals act to catalytically oxidize SO_2 to SO_3 so that one may expect a nearly linear relationship between SO_2 emission rates and H_2SO_4 deposition rates for the gas phase conversion process. Also the production of SO_3 in this mechanism indicates that the chemistry of this molecule must be investigated. Previously it was believed that there was no significant atmospheric source of this molecule.

The reaction of nitrate radicals, NO_3, with nitric oxide has been studied

$$NO_3 + NO \rightarrow 2NO_2$$

using laser induced fluorescence detection of NO_3. This reaction is used for laboratory calibrations of NO_3 concentrations and is important in nighttime urban chemistry. The rate coefficient has been measured as a function of temperature from 209 to 414K. These data are shown in Figure 2. Below room temperature the rate coefficient increases with decreasing temperature

$$k(T) = (1.55 \pm 0.23) \times 10^{-11} \exp [(195 \pm 39)/T] \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$$

while above room temperature the rate coefficient is approximately constant

$$k = (2.95 \pm 0.4) \times 10^{-11} .$$

The curvature in this plot is similar to what we have seen in other radical-radical reaction data. The value at room temperature is about 50% larger than the published result from a less direct study.

The kinetics and transport properties of gaseous sodium, Na, have been studied in a fast-flow reactor with resonant fluorescence detection of Na. Sodium is deposited in the upper atmosphere by meteors. It was recently proposed that the presence of Na in the stratosphere could modify the chemistry of chlorine species which have been shown to be effective ozone destruction catalysts. The diffusion coefficients of Na in He, Ne, Ar, N_2, and CO_2 have been measured at room temperature. Some of these results have been compared with data on intermolecular parameters using Chapman-Enskog theory. The theoretical analysis give good agreement between the two data sets.

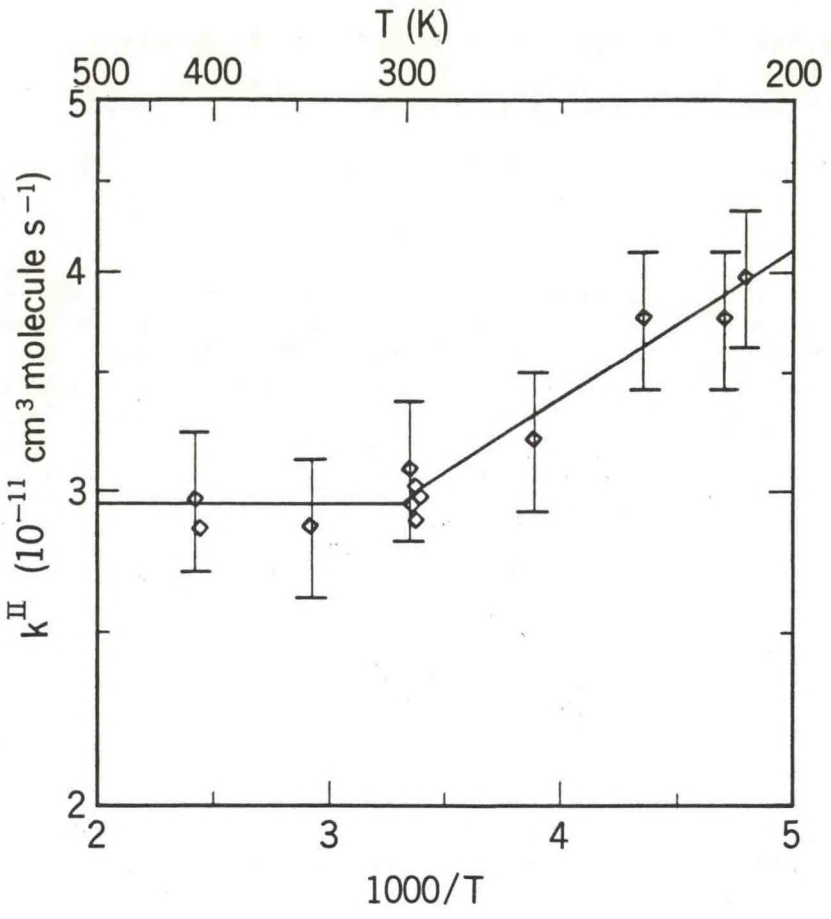

Figure 2. Arrhenius plot for $NO_3 + NO \rightarrow 2NO_2$ reaction.

The reaction of Na with N_2O was found to be slow k = (8.2 ± 1.5) x 10^{-13} cm^3 $molecule^{-1}s^{-1}$, but it is an excellent kinetic source of NaO molecules. Using this source the reactions of NaO with H_2, H_2O, CH_4, and NO were studied. All react quite rapidly except CH_4. One surprising result is that the NaO + H_2 reaction regenerates Na on about 30% of the collisions. This mechanism indicates an unusual amount of rearrangement for an elementary reaction, but is similar to the reaction $O^- + H_2$, which also gives H_2O as a product. The rapid reaction of NaO with H_2O to give NaOH and OH products provides a rapid route to NaOH for NaO in the atmosphere.

The mechanism for the atmospheric oxidation of hydrogen sulfide, H_2S, is being investigated. The objective of this study is to determine the extent to which this compound of natural origin can contribute to the production of sulfuric acid, H_2SO_4. The first step in the mechanism is the reaction of OH with H_2S and has been well characterised by studies in several different laboratories. However, the subsequent chemistry of the HS product is not established.

Using a far infrared laser magnetic resonance (LMR) apparatus with a discharge flow reactor the kinetics of HS is being examined. The first step in this process is to develop kinetics sources for HS. Two methods have been established:

$$H_2S + F \rightarrow HS + HF$$

and

$$H + \underset{\diagdown\ \diagup}{\overset{S}{CH_2 - CH_2}} \rightarrow HS + C_2H_4 \quad .$$

The first reaction of HS to be studied is the one with NO_2. Sample data for this reaction are shown in Figure 3. The rate coefficient measured at room temperature is $(6.7 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1}s^{-1}. This value is about a factor of two larger than that reported by two other labs. We believe that the discrepancy is due to secondary chemistry in the earlier work. The HSO radical has been observed as a primary product of the HS + NO_2 reaction using LMR detection. A scan of the strongest HSO lines observed is shown in Figure 4 with a sample of the HS lines used in our kinetics study. It is a fortunate coincidence that both HS and HSO can be detected using the same laser line.

The high resolution Fourier transform spectrometer has been used to analyze the products of the OH + NO_2 + M reaction. This reaction is important in the atmosphere as the major source of nitric acid, HNO_3. It is also the major removal mechanism for nitrogen oxides and a critical factor in controlling atmospheric OH concentrations. Our study was undertaken to test the hypothesis that peroxynitrous acid, HOONO, an isomer of nitric acid, could be formed in this reaction. The formation of the isomer could be significant in the atmosphere because it is expected to have completely different chemical properties than nitric acid. A search for HOONO was made in the infrared region over the range 1850 to 3850 cm^{-1} using a 100 m optical path in a 1.6 m absorption cell. Several independent methods of forming HOONO were also tested. No features were observed which could be assigned to HOONO in any of these experiments. As a final test, quantitative measurements were made of the HNO_3 yield from the OH + NO_2 + M reaction. The OH reactant was formed by the reaction

$$H + NO_2 \rightarrow OH + NO \quad .$$

Thus one NO molecule is formed for each OH. By comparing the amounts of NO and HNO_3 one can determine the fraction of the OH which yield HNO_3. A summary of these data is given in Figure 5. Measurements were made over a wide range of pressures (3 to 850 torr) and temperatures (248 to 298 K). No evidence of HOONO isomer formation was found and it was concluded that the yield of nitric acid from the reaction is $\geq 80\%$.

In a separate study, a search for the HO_2 radical was made with the FTS apparatus. HO_2 radicals were formed in a discharge flow reactor and injected into the FTS absorption cell. All three of the IR absorption bands were observed. Figure 6 shows the ν_2 band spectrum. These data were taken at a resolution of 0.01 cm^{-1}. About 850 lines have been identified in this spectrum. Since spectroscopy is a powerful tool for detecting and identifying chemical species, these data have application to both laboratory and field experiments.

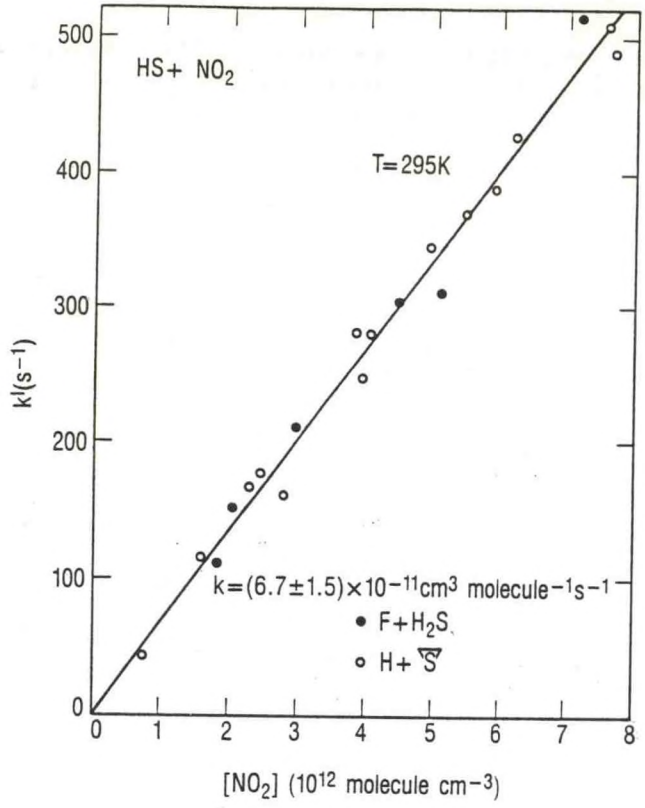

Figure 3. Summary of kinetic data on the reaction HS + NO_2. The different symbols represent two different kinetic sources. The slope of the line is the bimolecular rate coefficient at 295K.

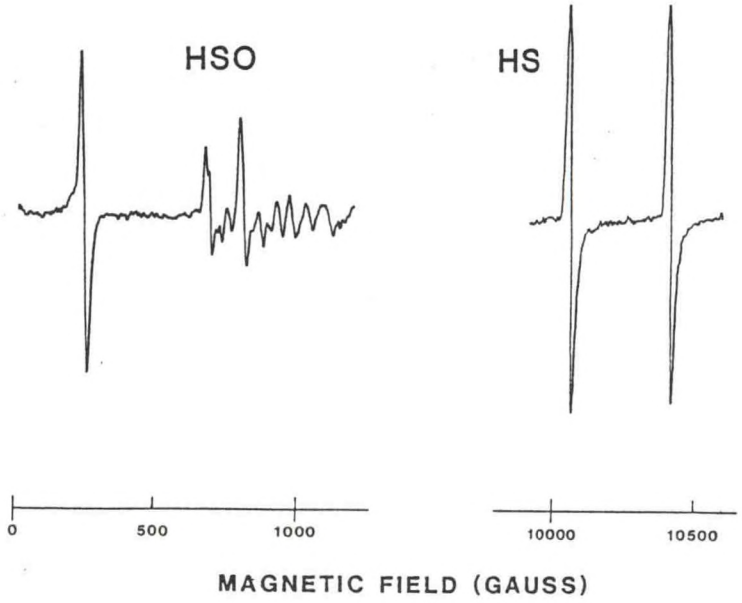

Figure 4. Laser magnetic resonance spectrometer scans of HSO and HS lines used in kinetics studies. Spectra were taken with the 216 μm wavelength line of CH_3OD in σ polarization. The spectra are shown as first derivatives of the absorption line because magnetic modulation was used to enhance the signal.

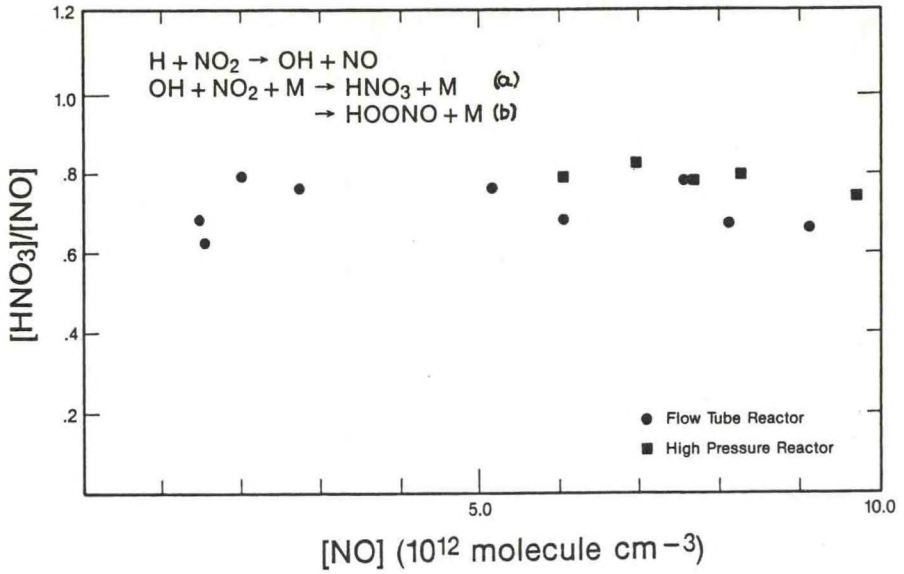

Figure 5. Summary of data for OH + NO_2 + M reaction product study. The yields of HNO_3 relative to NO are shown on the vertical scale versus [NO]. It was concluded that the yield of HNO_3 from this reaction is $\geq$ 80%.

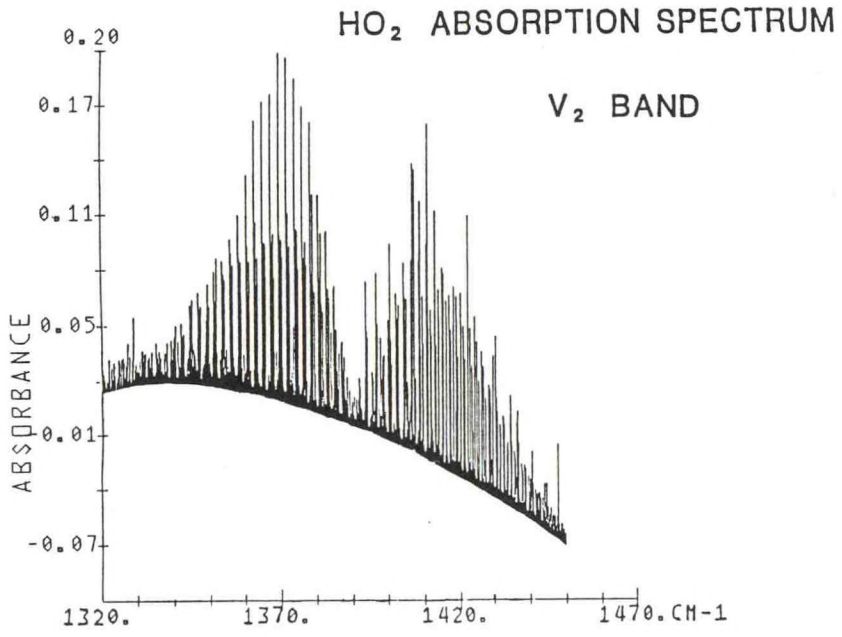

Figure 6. High resolution spectrum of the HO_2 ν_2 band taken with Fourier transform spectrometer. The HO_2 concentration in the absorption cell was about 5 x 10^{12} molecule cm^{-3}, the optional path length was about 100 m, and the residence time in the cell was about 70 ms.

The reaction of HO_2 radicals with ozone is very important in stratospheric and tropospheric chemistry as an ozone destruction mechanism.

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

In the atmosphere it is coupled with the reaction of OH with ozone,

$$OH + O_3 \rightarrow HO_2 + O_2$$

and these two reactions taken together demonstrate how the odd hydrogen radicals, OH and HO_2, can catalytically destroy ozone. There has been only one direct study of the $HO_2 + O_3$ reaction and that was done in the Aeronomy Lab about five years ago. The difficulty in studying this reaction is that the $OH + O_3$ reaction is much faster and regenerates the HO_2 reactant. In the earlier study this problem was overcome by using a chemical scavenger to remove the OH radicals to prevent HO_2 regeneration. The new approach to this problem is to use isotopically labelled HO_2 molecules which cannot be regenerated. The ^{16}O in natural HO_2 has been replaced with ^{18}O. Preliminary results at room temperature are in good agreement with the previous study.

Collisional quenching of vibrationally excited NO^+ ions by a number of atmospheric and other neutral molecules has been carried out in a collaboration with former Aeronomy Laboratory Guest Workers at the University of Innsbruck. A technique that was developed in the Aeronomy Laboratory was employed in these studies. NO^+ is a dominant ion in certain regions of the ionosphere ($\sim$100 km), where it is formed in the reactions of O^+ with N_2, N^+ with O_2, and N_2^+ with O. Vibrationally excited NO^+ is an infrared emitter so that its concentration is of concern in atmospheric spectroscopy. It is found that NO^+ is rapidly quenched in the atmosphere by N_2,

$$NO^+(v=1) + N_2 \rightarrow NO^+(v=0) + N_2, \; k = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \text{ at } 300 \text{ K}.$$

The rate coefficient decreases very slightly with increased temperature. Although ground state O_2 does not relax vibrationally excited NO^+ efficiently, electronically excited O_2 in the ($a^1\Delta_g$) state does, $k = (3 \pm 2) \times 10^{-10}$ cm^3 molecule^{-1}s^{-1}. A theoretical model has been developed which explains these observations. The model involves complex formation followed by vibrational predissociation. It also satisfactorily explains most of the vibrationally excited O_2^+ and other NO^+ quenching measurements. This work is the first systematic and detailed study of vibrational relaxation in ions that has been made to date. The first measurements of vibrational energy transfer rates from excited neutral molecules to molecular ions at thermal energies were carried out in collaboration with colleagues in the Department of Space Science at Birmingham University in England. These results provide a very important insight into the molecular interaction process and show that vibrationally excited N_2 in disturbed atmosphere conditions does not pump NO^+.

In collaboration with colleagues at the University of Colorado; Birmingham, England; and Meudon, France the reaction $O_2^+ + CH_4 \rightarrow H_2COOH^+ + H$ has been analyzed using several different experimental techniques and a wide range of experimental conditions. This work constitutes the most thorough study of an ion-molecule reaction of this complexity. The data collected on this reaction has made it possible to establish a detailed mechanism for the process as it proceeds from reactants to products.

Future Plans

New experiments to study gas phase reactions at atmospheric pressure have been initiated. Free radicals for these studies are generated by pulsed laser photolysis of stable molecules. Radical detection is achieved using resonant fluorescence, laser induced fluorescence, or long path absorption techniques. These experiments are directed toward investigating reactions which are thought to exhibit a pressure dependence and which are related to the formation of acid species in the troposphere.

Experiments are being developed to study the products of atmospheric photochemical processes. Although a great deal is known regarding the rates of such reactions, there is often a major uncertainty associated with the product yields. The product identities are critically important in determining the role of a reaction in the atmosphere. The objectives of these experiments will be to quantitatively evaluate the products of photochemical processes such as the photolysis of NO_3, N_2O_5, and N_2O and the reactions of species such as OH with many species. Various optical techniques and mass spectrometry are used to measure the product yields. In addition, a pulsed photolysis - long path (pulsed) light absorption system utilizing a diode array spectrometer is being constructed to study reaction intermediates, especially those formed by association of a free radical with a molecule.

At night N_2O_5 is a major odd nitrogen reservoir in both the stratosphere and the troposphere. During sunlit hours N_2O_5 is photolyzed to release the active NO_x species (NO_3, NO_2, and NO). The products of N_2O_5 photolysis are uncertain. NO_3 and $O(^3P)$ have been identified as products and their quantum yields measured in the wavelength range 248-305 nm. To completely understand the photolysis process, the quantum yields for NO as a function of wavelength are needed. The NO quantum yields will be measured by laser induced fluorescence following N_2O_5 photolysis by an excimer laser or a Nd:YAG laser pumped dye laser system. The wavelength range of 248 to 305 nm will be covered.

In the methane oxidation cycle a major uncertainty is the chemistry of CH_3OOH. The rate coefficient for the reaction of OH with CH_3OOH, one of the CH_3OOH removal mechanisms, will be measured as a function of temperature. A pulsed Xe lamp will be used for photolytic production of OH. Pulsed laser induced fluorescence will be used to follow the OH concentration during the reaction. Information regarding the products of the reaction will be obtained by isotope labelling the reactants. The quantum yield for the production of OH in the photolysis of CH_3OOH will also be measured using the same experimental technique.

Carbonyl sulfide, COS, is believed to be quite inert in the troposphere. But it is possible that its reaction with OH is enhanced by the presence of O_2, just as the analogous reaction of CS_2 with OH is much faster when O_2 is present at high pressures. This possibility will be investigated using the same apparatus and methodology as those used in the study of OH + CH_3OOH reaction.

NO_3 is known to be an important intermediate in the troposphere as well as in the stratosphere. Its atmospheric concentration is usually measured using long path absorption at 662 nm wavelength. To calculate concentrations from measured absorbances, the value of the absorption cross section at the atmospheric temperature is needed. Preliminary investigations have shown that the absorption cross section of NO_3 in the 662 nm band is temperature dependent,

contrary to previous beliefs. Therefore, the temperature dependence of the entire NO_3 spectrum will be investigated. Two flowtubes will be used in tandem in conjunction with two diode array spectrometers. By this method the relative changes in cross sections with temperature will be measured. N_2O_5 thermolysis will be used to produce NO_3 and titration with NO will provide the absolute NO_3 concentration.

The major source of odd nitrogen in the stratosphere is the reaction of $O(^1D)$ with N_2O. The major loss process for N_2O in the stratosphere is photolysis in the 190-210 nm wavelength region. Experimental investigations will be carried out to assess the possibility of NO production directly from N_2O photolysis, and to accurately measure the NO production rate from the $O(^1D)$ reaction with N_2O under stratospheric conditions. Laser induced fluorescence detection will be used to measure NO.

Further studies will be carried out on the SO_2 oxidation mechanism. First the temperature dependence of the $HOSO_2 + O_2$ reaction will be evaluated. Then an effort will be made to measure the efficiency of the conversion of $HOSO_2$ to SO_3. A study of SO_3 kinetics will be initiated using chemical ionization detection to see if the gas phase reaction with water proceeds with a significant rate. Other methods for detection of SO_3 will also be pursued to carryout SO_3 reaction studies at atmospheric pressures.

A new experiment utilizing vacuum UV photoionization mass spectrometric detection of free radicals will be developed. A prototype hydrogen Lyman alpha light source has been tested and has demonstrated a detection limit of about 10^8 molecule cm^{-3} for nitric oxide. As a first test of this experiment, the products of the $NO_2 + O_3$ reaction will be examined. The long term objective of this experiment is to study the mechanisms for atmospheric hydrocarbon oxidation. These reactions are a central part of tropospheric chemistry since they play a role in oxidant production and they involve all major free radical families.

The studies of NO_3 radical kinetics will be continued. The next reactions to be examined are the reactions of NO_3 with reduced sulfur compounds such as hydrogen sulfide and dimethylsulfide. Since NO_3 is a nighttime radical reactant, these studies will examine the possibility that there may be nighttime radical chemistry involving sulfur species. If there are significant reactions among these chemicals, there is a possibility that other reactive radicals may be produced and that other aspects of nighttime chemistry should be examined.

The kinetics of Na and its compounds will be extended to include studies of the temperature dependence of some selected processes. First the temperature dependence of some Na diffusion coefficients will be measured. These results will be compared with the predictions of the Chapman-Enskog model using published data on Na-inert gas potentials. The temperature dependence of some Na and NaO reactions will also be examined. Some reactions of NaO with organic compounds will be studied to determine how NaO reaction mechanisms parallel other reactants.

The analysis of the H_2S oxidation mechanism will be continued. First the temperature dependence and product analysis of the $HS + NO_2$ reaction will be

completed. Then the kinetics of the HS + O_3 reaction will be examined. A study of HSO kinetics has been initiated. Some details of the kinetic sources of HSO still need to be established. The first studies of the chemistry of this radical will include the reactions of HSO with O_2, NO_2 and O_3.

The Fourier transform spectrometer will be used to examine the high resolution spectrum of gaseous molecules. First, searches will be made for the transient species $HOSO_2$ and HSO. Both of these radicals are important intermediates in acid precipitation chemistry. Next, the reaction of HO_2 radicals with NO_2 will be studied to determine the relative yields of HONO and $HOONO_2$ products. The formation of significant amounts of HONO in this reaction would be an important finding because this molecule is rapidly photolyzed to produce highly reactive OH and NO radicals. The $HOONO_2$ molecule, on the other hand, has much different atmospheric effects. The high resolution spectrum of $HOONO_2$ will be examined for the purpose of providing data which can be used to make quantitative measurements of $HOONO_2$ in the atmosphere using infrared spectroscopy.

The kinetics study of the HO_2 + O_3 reaction using isotope labelled HO_2 radicals will be completed. The mechanism of the reaction will be examined by measuring the yield of isotope labelled OH product. A few other atmospheric reaction mechanisms will be studied using similar isotope labelling techniqiues.

The Aeronomy Laboratory ion chemistry program has been terminated except as an adjunct to the neutral atmospheric kinetics program. The ion-molecule studies are now being continued in collaborative efforts at Innsbruck, Birmingham, and Meudon. There are also collaborations with groups at Heidelberg and Dallas on the interpretation of _in situ_ atmospheric ion composition measurements.

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ATMOSPHERIC DYNAMICS PROGRAM

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Introduction

The objective of the Atmospheric Dynamics Program Area is to further our understanding of the dynamics of the atmosphere, particularly mesoscale and small-scale dynamics of the free atmosphere. Thus, we devote most of our research to the study of internal gravity waves (also called buoyancy waves), turbulence, etc. These mesoscale and small-scale processes are important for several reasons. First, they are important problems in atmospheric and, more generally, geophysical fluid dynamics. Second, they are the meteorological background noise against which synoptic scale measurements are made. Third, gravity waves transport energy and momentum upwards from sources in the lower atmosphere to sinks in the upper atmosphere. Fourth, gravity waves are thought to be the source of all of the turbulence in the free atmosphere. Finally, turbulence is the cause of most of the energy dissipation in the free atmosphere and part of the vertical mixing and transport of trace species. The study of mesoscale and small-scale processes takes advantage of the unique experimental and analytical capabilities of the group.

The experimental research of the Program is based largely on the study of the atmosphere by analysis of radar echoes from irregularities in the atmosphere. Backscattered radio waves are Bragg scattered by radio refractive index irregularities whose scale is half the radar wavelength. In the ionosphere the scatter is by irregularities in electron density; in the troposphere and stratosphere, by irregularities in the atmospheric density or humidity. The frequency spectrum of the radar echoes can be interpreted

as the Doppler spectrum of the motions of the irregularities in the volume observed by the radar. Since below about 90 km the irregularities are carried by the atmosphere, the mean Doppler shift is proportional to the mean motion, or wind, in the sampled volume. Also, the radar reflectivity is proportional to the amplitude of turbulent irregularities of radio refractive index.

An example of the Doppler velocity spectra is shown in Fig. 1. The variation with altitude of the horizontal wind is clearly visible. Many comparisons with balloon wind profiles have shown that the mean Doppler shift is indeed a good measure of the wind (Gage and Balsley, 1978). Other, more sensitive, Doppler radars can measure over a much larger altitude range, including the troposphere, at least the lower half of the stratosphere, and, in the daytime, the mesosphere.

Doppler radars can routinely measure wind profiles about 1000 times more frequently than routine balloon or rocket observations in the same altitude range. Their much faster cadence of profiling make Doppler radars uniquely suited for studying phenomena that vary rapidly in time, such as gravity waves and turbulence. They can, of course, also study slowly varying phenomena, such as the background wind, planetary waves, and tides. Indeed, because of their rapid cadence, they can make more representative measurements of these phenomena than can other techniques, such as balloon measurements.

The capabilities of the technique can be realized, however, only by very sensitive coherent radars with on-line computer analysis of the received data. Because the Doppler radar technique and the radar systems that make it possible are so different from conventional meteorological radars (which depend on echoes from hydrometeors and/or do not do spectral analysis of the echoes), it is convenient to have a concise term to describe this technique. It has been generally agreed to call it the "MST radar technique", for "Mesosphere-Stratosphere-Troposphere". Radars that are sensitive enough to make measurements in all three regions are called "MST radars"; those that can observe only in the troposphere and lower stratosphere are called "ST radars", even though they use the MST radar technique. ST radars developed for operational wind profiling are often called "wind profilers".

In order to exploit the capabilities of the MST radar technique, in 1973 the Program started construction of the Sunset ST radar near Boulder. This was the first VHF radar designed and constructed specifically for MST radar studies (Green et al., 1975). Some of the pioneering contributions that we have made using this radar are: measurement of all three components of wind velocity; comparison of velocity measured by ST radar and balloons; observation of mountain lee wave effects; observation of VHF ST radar echoes from hydrometeors; simultaneous measurement of the fall velocity of hydrometeors and the vertical wind velocity; demonstration that oblique VHF ST radar echoes are from turbulent irregularities; development of a model for the occurrence of turbulence; identification of specular echoes (Fresnel reflection) and radar measurement of the height of the tropopause; comparison of Doppler spectral width and turbulence encountered by aircraft

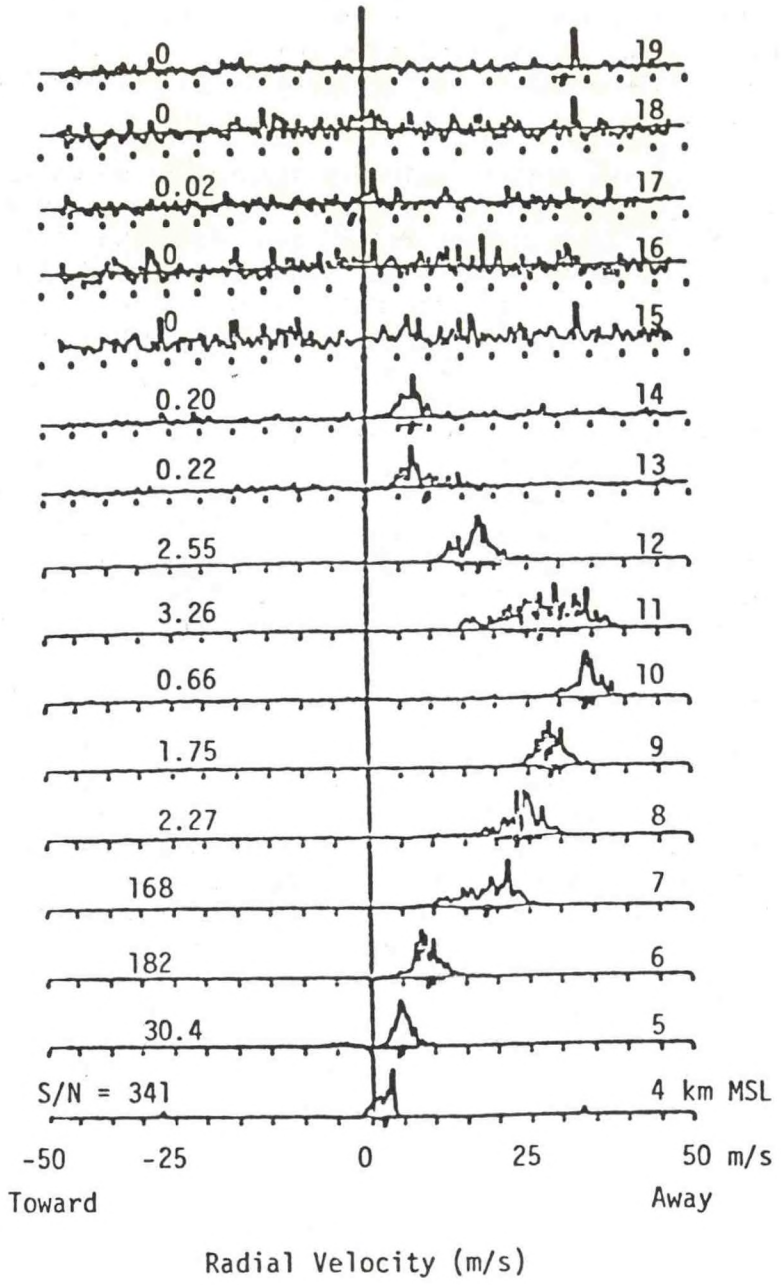

Figure 1. An example of Doppler spectra measured by the Sunset ST radar at 76/04/15 1548.21 75°W time. Each spectrum is a 50-second average over a 1-km height range centered at the height given at the right. These spectra were observed looking 30°N of the zenith. The corresponding horizontal velocities are approximately equal to the radial velocities times 1/sin 30° = 2. The spectra are normalized. The actual signal-to-noise ratio S/N is given on the left. (After VanZandt et al., 1978)

observation of turbulence in the stratosphere above thunderstorms; comparison of radar reflectivity with integrated laser scintillation and double-star scintillation. These contributions have had a major impact on the development and utilization of the MST radar technique throughout the world. The Sunset radar continues to be a very useful tool for the study of the dynamics of the atmosphere since it has been modified from time to time to keep it in the forefront of ST radar capabilities.

Recent Results

1. Internal gravity waves.

The Program is engaged in an intensive program of experimental and theoretical research on gravity waves with two broad objectives: first, to describe the gravity wave field so that it can be used in the foregoing applications, and, second, to develop the full potential of the MST radar technique for the study of gravity waves.

1.1 The atmosphere varies rapidly versus time and space when it is observed on fine scales. When these variations are nearly sinusoidal they are almost certainly due to gravity waves. But such monochromatic waves are observed only occasionally, not more than 5% of the time at a given height. During the rest of the time the velocity is observed to fluctuate almost randomly.

Two quite different mechanisms have been proposed to explain these fluctuations and their power spectra. Gage (1979) suggested that they are due to the energy cascade toward larger scales in two-dimensional turbulence. VanZandt (1982), on the other hand, showed that the spectra as functions of frequency and horizontal and vertical wavenumber are consistent with the gravity wave dispersion relation. His analysis followed the analysis of very similar spectra of fluctuations in the ocean by Garrett and Munk (1972, 1975). Such gravity wave spectra are thought to be maintained by a wave-wave interaction cascade toward lower frequencies and smaller scales. The direction of energy cascade -- whether upscale or downscale -- has important implications for the predictability of the atmosphere.

As mentioned in the Introduction, the MST radar technique is uniquely suited for the study of gravity waves because of its rapid cadence of observations together with good height resolution. The technique measures the radial velocity versus time and radial range, leading to spectra of radial velocity versus frequency and radial wavenumber. On the other hand, model gravity wave spectra are expressed in terms of vertical and horizontal velocities as a function of vertical and horizontal wavenumbers. In order to interpret MST radar spectra, VanZandt (1985a) derived model radial spectra from a formalism developed by Pinkel (1981) for the interpretation of oceanic Doppler sonar spectra. Smith et al. (1985) then compared VanZandt's model with observations of radial wavenumber spectra in the summer mesosphere taken by the Poker Flat MST radar. An example of the comparisons is shown in Fig. 2. Since the agreement is rather good, it was concluded that the observed spectra were dominated by gravity waves. Similar results were obtained by Scheffler and Liu (1985).

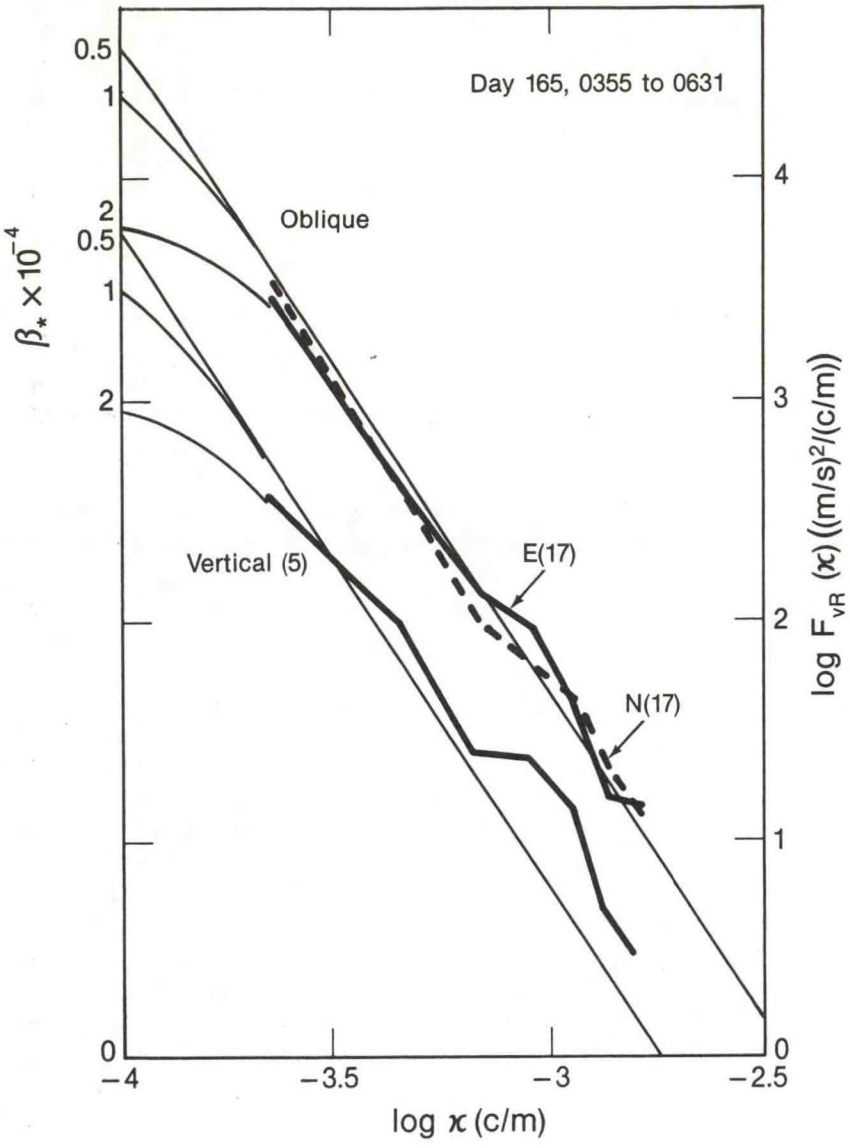

Figure 2. Power spectra of radial velocity versus radial wavenumber in the mesosphere on Day 165 (14 June) 1983. The oblique spectra labeled E and N are in the azimuths 64° and 334°, respectively, clockwise from true north, at a zenith angle of 15°. The solid lines are model radial gravity wave spectra from VanZandt (1985a).

VanZandt and D.C. Fritts (University of Alaska) are also addressing the important problem of the Doppler shifting of gravity wave frequency spectra by the background wind. The usual models of gravity wave spectra and the fluid dynamical theories that support them apply to intrinsic spectra, that is, spectra in a reference frame moving with the background wind. Radars, on the other hand, observe in a fixed reference frame, so that they observe a Doppler-shifted intrinsic spectrum. In order to gain insight into the meaning of the observed spectra, VanZandt and Fritts are developing a model for the calculation of Doppler-shifted spectra from intrinsic spectra.

1.2 The dissipation of gravity waves in the mesosphere is thought to decelerate the wind, thereby transfering the momentum carried by the gravity waves to the mean flow. Such a deceleration is necessary in order to bring the zonal wind in global circulation models into agreement with the observed zonal winds. The effect may also cause a small, but significant, acceleration in the stratosphere. While this model has been quite successful in a general sense, much more observational and theoretical work is needed before the process can be considered to be understood.

The vertical flux of horizontal momentum in the stratosphere can be directly measured by ST radars using the technique of Vincent and Reid (1983). G.D. Nastrom (Control Data Corporation) has done a preliminary analysis of momentum flux using data from the Sunset radar.

VanZandt (1985b) showed that although the energy in gravity wave frequency spectra increases by a factor of several hundred from the troposphere to the mesosphere, the energy in vertical wavenumber spectra does not increase significantly. This anomaly has been explained by Fritts, VanZandt, and S.A. Smith (CIRES) in terms of a model for the saturation of gravity wave spectra as they propagate upwards through the atmosphere.

1.3 Gravity waves can be generated by various processes, including jet streams, convective storms, flow over mountains, etc. But because wave motions oscillate rapidly (except for mountain lee waves), the generation processes have been very difficult to study. With the advent of the MST radar technique we were able to show, by comparison of detailed observations of discrete wave trains with a theoretical model, that in a jet stream the gravity waves are generated by shear instability (VanZandt et al., 1979).

We have also studied the generation of gravity waves by thunderstorms, or, more generally, the relation between gravity waves and thunderstorms. In an earlier study (Lu et al., 1984) we found that the amplitude of the wave spectra was about an order of magnitude larger during periods of thunderstorm activity than during quiet periods. More recently, we used an array of existing ST radars together with a network of 22 microbarographs in northeastern Colorado to study the relation between thunderstorms and convection (see Fig. 3). These observations were made in cooperation with PROFS and the Wave Propagation Laboratory of NOAA, and they are being analyzed in collaboration with F. Einaudi (Georgia Institute of Technology), and D. Fuá (Istituto di Fisica dell' Atmosphera, Rome, Italy). We find that on some occasions the gravity waves and the convective cells (thunderstorms) move together, suggesting that the gravity waves initiate

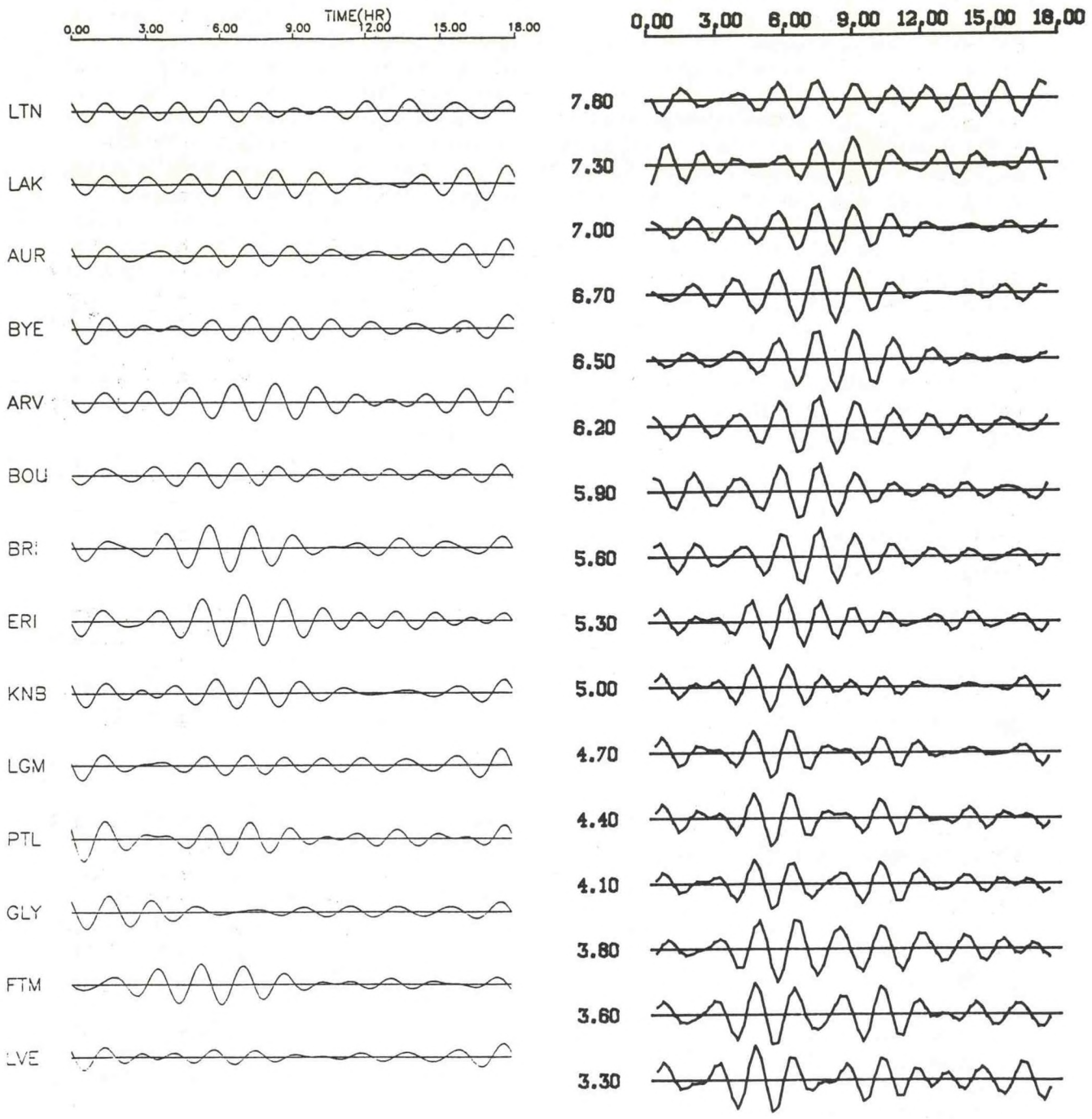

Figure 3. Simultaneous time series showing gravity waves in the surface pressure at 14 microbarograph stations in northeastern Colorado (left) and radial velocity from 3.30 to 7.60 km above Denver (right), during a period of strong convective activity. The time series have been filtered with a pass band between 1.3 and 2.1 hr.

the convection and that perhaps the convection reinforces the gravity waves. On other occasions the two phenomena move differently, suggesting that the convection is independent of the gravity waves.

2. Atmospheric Turbulence. The radar reflectivity, which can be inferred from the observed signal-to-noise ratio, is usually proportional to the turbulence structure constant C_n^2 of the radio refractive index. This quantity is very important in electromagnetic wave propagation in the atmosphere.

The availability of radar profiles of C_n^2 has enabled us to develop a statistical model for the occurrence of turbulence that permits the calculation of profiles of C_n^2 and ε from measurements of the background wind and temperature (VanZandt et al., 1981). The model depends upon the probability distribution functions for the unobservable, fine-structure fluctuations of vertical shear and stability, which are derived from our model of the spectrum of gravity waves in the troposphere and lower stratosphere (VanZandt, 1982). The turbulence model has been widely used to calculate the optical seeing in the atmosphere, for example, to assist in siting optical devices such as lasers and large telescopes. Because of this broad interest, a NOAA Technical Report (Warnock and VanZandt, 1985) has been prepared that describes its implementation, including listings and descriptions of programs.

3. Fresnel Reflectivity and Atmospheric Stability. As the antenna pointing direction of a radar operating at lower VHF frequencies is moved from an oblique angle to the zenith, the reflectivity is often greatly enhanced (Gage and Green, 1978). This enhancement is attributed to partial specular or Fresnel reflection from horizontal stratification of the radio refractive index. The fact that Fresnel reflectivity increases with increasing stability of the atmosphere has been used to infer the height of the tropopause from altitude profiles of reflectivity (Gage and Green, 1982).

However, there has been controversy over the dependence of the Fresnel reflectivity on the radar range resolution. Careful measurements of this dependence were made with the Sunset radar (Green and Gage, 1985). To interpret these experiments, the effective length of the radar range resolution was defined geometrically and a method for its calculation from radar parameters was devised. The result was that in most cases the reflectivity from stable layers was linearly proportional to the effective length as is predicted by simple theory, while in a small fraction of cases the reflectivity varied as a larger power (up to 2) of the effective length.

4. Participation in FAA aircraft safety studies. During the period 23 January - 10 February 1984 and again in the period 23 January - 1 March 1985 the Sunset Radar was used to measure the wind, particularly the vertical component, over the Front Range of Colorado in an FAA sponsored experiment to assess the reliability of aircraft altimeters over mountains. As part of this experiment, many other meteorological sensors were operated by the FAA, NCAR, WPL, and NWS. This data base should be the best ever taken for the study of mountain lee waves and associated phenomena, such as downslope winds and turbulence.

5. Further development of wind measurement using the MST radar technique. As was mentioned above, the rapid, ground-based measurement of wind velocity profiles is an important meteorological capability of ST radars. The Sunset radar was used to test the consistency of ST radar wind measurements by comparing horizontal vectors calculated in several ways from the radial velocities measured with five antenna beam positions (see Fig. 4) (Clark et al., 1985). It was found that the inclusion of the measured vertical velocity in the calculation of the horizontal wind vector velocity results in a significant improvement in the estimation of the horizontal wind velocities (see Fig. 5), and that the use of redundant slant beam positions can indicate times when the implicit uniform flow assumption causes significant error in the estimation of background wind.

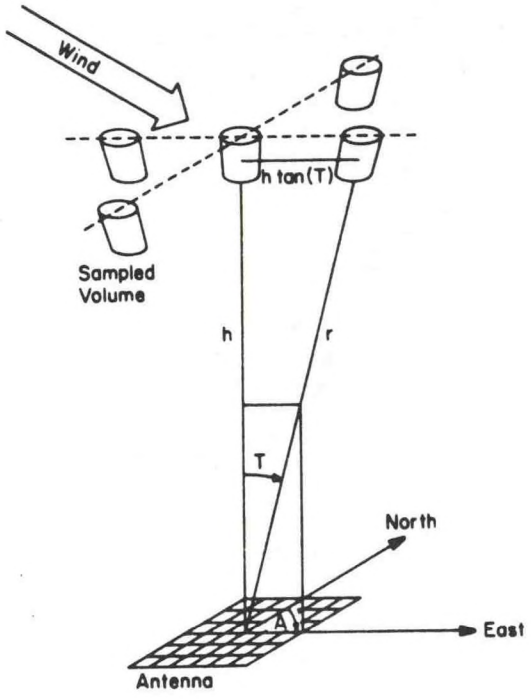

Figure 4. Geometry of the Sunset radar wind measurements. During these experiments T was 15°.

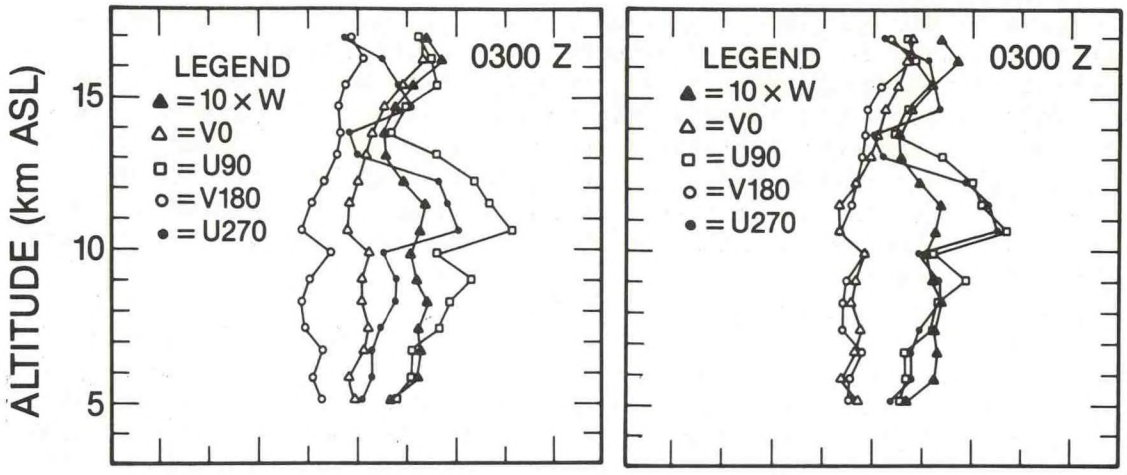

Figure 5. Left: Wind profiles derived neglecting the contribution of vertical winds to the radial velocity. Right: Including the contribution of vertical winds. W denotes the vertical velocity and V0, U90, V180, and U270 denote the inferred horizontal wind components in the indicated azimuths.

The measurement of the vertical component of wind velocity is an almost unique capability of the ST radar technique. For several years there has been a question as to the validity of the measurement of vertical velocity in stable layers, such as the tropopause, that provide Fresnel rather than turbulence scattering (Gage and Green, 1978). The same five antenna beam arrangement, described above, was used so that a vertical component of velocity derived from the radial velocities measured with the slant antenna beams (known to be from turbulence scattering (VanZandt et al., 1978)) could be compared with the velocities measured with the vertical beam. The result of this comparison was that the vertical velocities measured by these two methods and with these two scattering mechanisms were found to agree within experimental error.

The editing of radar records to eliminate spurious data points is a necessary but often times consuming task. To increase the reliability of ST radar data and to reduce the labor, we have devised and installed an improved transmit-receive switch in the Sunset that eliminates an important class of spurious radar echoes, and we are developing a new automatic, self-editing computer program for scaling the radar data tapes. As the problem of spurious echoes and the expense of editing records are common to all ST radars, these improvements should find wide application.

Future Plans

We will continue to study the gravity wave field and its effects. In particular, the model for radial velocity spectra will be generalized to include wave fields that are azimuthally anisotropic. The parameters of the anisotropic spectra will then be determined by comparing the model with observations using the Arecibo radar in Puerto Rico and the MU radar in Japan. These anisotropic spectra will be used later to examine gravity wave propagation (and subsequent transfer of horizontal momentum) from the troposphere through the stratosphere into the mesosphere. The model study of Doppler shifting of intrinsic spectra will be completed. Studies of the vertical flux of horizontal momentum will be extended, using data from the Sunset radar and other radars.

We will also continue to study methods of deriving the total wind vector from radial velocity measurements. This study is particularly timely because of the development of ST radars or wind profilers for operational wind sounding and their use in major experiments such as the STORM-Central phase of the National STORM Program, which will deploy up to 70 ST radars.

Most existing middle and high latitude ST radars are in or near regions of strong relief, which generate lee waves and turbulence that often vitiate the interpretation of the data. In order for the nation to have available a radar in a location free from this effect, we have proposed to the National Science Foundation to construct and operate a state-of-the art ST radar in very flat terrain near Urbana, Illinois. University atmospheric science groups will collaborate, both in experiments and in the analysis of data. Although this "Flatland" radar was motivated by the need to measure the small vertical velocities accompanying synoptic scale weather systems, the absence of terrain effects will also make the data uniquely valuable for studying gravity waves, turbulence, Fresnel reflection, etc. in the lower atmosphere. Extensive design studies have been conducted using existing radar data to determine the optimum system configuration for the proposed experiments. Innovations resulting from these studies are being tested with the Sunset radar. If funded, the Flatland radar will constitute a major new direction for the program.

The Program Leader (Thomas E. VanZandt) will be on extended travel in Japan and Australia from March 1986. He will conduct research using the MU radar near Kyoto, Japan, which is the most flexible ST radar in the world and the Buckland Peak radars near Adelaide, Australia. This travel will be funded by other agencies.

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TROPICAL DYNAMICS AND CLIMATE PROGRAM

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Introduction

A growing awareness of the profound role played by the tropics in influencing our global weather and climate patterns has resulted in the formation within the Aeronomy Laboratory of the Tropical Dynamics and Climate Program Area.

Current understanding of the dynamical processes that operate in the tropical atmosphere is quite limited. This is primarily due to the paucity of existing observational data. The creation and use of comprehensive, large-scale atmospheric and oceanic data sets has been undertaken only recently by a number of major scientific initiatives. Examples include such programs as EPOCS (Equatorial Pacific Ocean Climate Study), TOGA (Tropical Oceans Global Atmosphere), and STEP (Stratosphere-Troposphere Exchange Processes).

The newly-formed Tropical Dynamics and Climate Program Area can contribute uniquely to such programs by making use of its extensive expertise in developing and using wind profiling radar systems. A brief listing of this laboratory's background in the wind profiling radar technique includes:

- Wind profilers, which can continuously monitor the total wind field and associated parameters in the troposphere and lower stratosphere, were developed originally by Aeronomy Lab scientists as an outgrowth of initial studies at Peru's Jicamarca Radar Observatory, itself a former Aeronomy Lab project.

- Over the past twelve years, Aeronomy Lab scientists and engineers have published well over two hundred papers on various aspects of wind profiling systems, including system design, scattering theories, and related topics in atmospheric dynamics. These efforts have established this laboratory as a world leader in the use of this technique.

- The Sunset radar (begun in 1973) and the Platteville radar (begun in 1977) comprise two of the earliest Aeronomy Lab systems that continue to produce significant results. Indeed, the Platteville radar, currently being operated jointly with NOAA's Wave Propagation Laboratory, has served as a prototype system for WPL's current program to establish a mesoscale network of similar systems throughout the Midwest that will provide high resolution wind profiles for the National Weather Service.

- The Aeronomy Lab's large MST (Mesosphere, Stratosphere, Troposphere) radar at Poker Flat, Alaska has provided essentially continuous information on winds, waves, and turbulence for the past six years. Analyses of these data have already yielded over ninety research papers, five PhD and two MSc. dissertations. Technological spin-offs from Poker Flat have resulted in the formation of at least one small business in Boulder's private sector.

- The Aeronomy Lab has recently established profilers in the tropics at Ponape (E. Caroline Islands) and Christmas Island (Republic of Kiribati). These systems will provide preliminary data on small-scale atmospheric processes in the Equatorial Pacific.

Wind profilers are capable of providing height profiles of the total wind vector, atmospheric waves and turbulence, spectral kinetic energy density, and gravity wave momentum flux. They can also provide a continuous measurement of the tropopause height. In addition to their ability to obtain continuous data, another major advantage of profilers over more conventional balloon-borne systems is that profilers measure the vertical wind. Although this parameter is considered to be a major factor in a variety of atmospheric processes, it is virtually unmeasurable on a continuous basis by any other technique. In addition, profiler operation is continuous, relatively inexpensive, and essentially unattended.

A program of long-term, continuous observations of the above-listed variables in the Tropics will yield, for the first time, a tropical climatology of small- and meso-scale atmospheric processes. This climatology, in conjunction with existing rawinsonde and satellite data bases, will permit studies relating to the importance of small- and meso-scale tropical atmospheric processes in controlling global circulation, climate, latitudinal and vertical energy exchange, large-scale vertical circulation systems (Walker and Hadley cells), and large-scale wave activity. To properly study the scale interactions, our long-term goal is to establish and operate a chain of radars, initially spanning the Equatorial Pacific Basin. Such wind observations can also be incorporated into the Global Telecommunication System (GTS) for worldwide distribution. Since these data

will come from climatologically important but data-sparse regions, we anticipate their inclusion into numerical forecast models will lead to improved weather forecasts around the world.

In general terms, the research thrust within this program area is to study, by radar techniques and ancillary data bases, the effects of small- and meso-scale dynamic processes (including convection) in the tropical atmosphere on worldwide climate. Associated tasks include, of course, studies of relatively short-term climatic variations, exemplified by the recent El Niño event, which caused disastrous effects over a significant portion of the entire globe.

Recent Results

I. Poker Flat MST Radar

The Aeronomy Laboratory's Poker Flat MST Radar in Alaska ceased normal operation in April 1985, following more than six years of almost continuous data taking. During this period, the radar produced data on atmospheric winds and related parameters in the troposphere, lower stratosphere, and mesosphere.

The radar, which was funded primarily by the National Science Foundation, is now being configured to measure gravity wave momentum flux (GWMF) over the same height range. Determination of a climatology of GWMF is considered to be a crucial factor in our eventual understanding of atmospheric circulation, since gravity waves are thought to provide the vertical coupling between lower and middle atmosphere. This project has been jointly funded by NSF, NASA, and AFOSR and will terminate in December 1986. At present, the radar can operate in the new mode using only one-quarter of the full (200 mx 200 m) antenna array. Complete modification is expected by December 1985.

II. Equatorial Dynamics and Climate

Ponape Radar

In 1983 we received funding to install the first wind profiling Doppler radar in the tropical Pacific. The site chosen for this radar was Ponape, Federated States of Micronesia. This radar, operating in a vertical mode, began operation in May 1984, obtaining vertical velocities only. The system has operated essentially continuously and virtually unattended since then. During this period, it has provided a wealth of design data for future tropical systems and has revealed several new dynamical features of the tropical atmosphere. For example, our preliminary results show that intervals of large vertical velocities are well correlated with periods of precipitation and associated convection. Furthermore, a preliminary analysis of mean vertical motion shows an average upward motion in the troposphere during convective episodes and a weak downward motion at times of little or no convective activity. Spectral analysis of these quiet periods between convective episodes reveals a power spectrum very similar to the Garrett-Munk spectrum of internal waves in the ocean. The spectrum is quite flat with a pronounced peak near the Brunt-Vaisala period and a rapid

falloff evident at shorter periods. This spectrum appears similar to other vertical velocity spectra obtained during undisturbed conditions at diverse geographical locations, and provides evidence of a nearly universal background spectrum of internal waves in the atmosphere similar to that found in the ocean.

Christmas Island Radar

We have essentially completed the installation of an additional wind profiling Doppler radar located on Christmas Island, Republic of Kirabati with funding from the Tropical Ocean Global Atmosphere (TOGA) program. Unlike the Ponape radar, the Christmas Island radar has been constructed to look obliquely, as well as vertically, so that it will provide profiles of horizontal as well as vertical velocities. The Christmas Island site is the most hostile environment to date in which a wind profiler has been located. A self-contained power generating facility will be required for the first time to assure a reliable and continuous source of power. Data from the Christmas Island radar will be telemetered four times daily via GOES satellite data collection system and transferred automatically onto the Global Telecommunication System (GTS) for worldwide distribution.

The Christmas Island facility is located in a data-sparse region of great importance to regional and global climate. Establishment of a remote wind profiler on Christmas Island represents a major milestone in remotely monitoring winds from remote locations.

Tropical Tropopause-Angular Momentum Correlations

A relationship between tropical tropopause heights and the global angular momentum of the atmosphere found earlier, using monthly mean data, has been extended using atmospheric angular momentum data at 3-day intervals from 46 equal-area latitude belts during 1976-82 (provided by R.D. Rosen and D.A. Salstein of Atmospheric and Environmental Research, Inc., Cambridge, MA). Preliminary results show that the correlation takes place mainly within the tropics, i.e., there is a highly significant correlation between tropopause height variations in the western tropical Pacific and variations in the height-integrated, zonally-integrated winds in the ± 15° latitude belt. While this correlation is pronounced on the annual time scale, it is also highly significant at time scales of 30 to 60 days. This is the first time, to our knowledge, that significant variability in tropical tropopause height has been shown to exist in the 30 to 60 day range of periods. Within this latter range of periods, maximum coherence occurs with angular momentum at about 10° N and with a period of about 38 days in the Northern winter half of the year, and at about 5° S with a period of about 51 days in the Northern summer. The interpretation of these results is not yet complete, but they clearly show the key role of tropical convective activity in the global-scale dynamics of the atmosphere.

Interannual Variations of the Tropical Tropopause and Global Climate

A study of the interannual variability of tropopause heights over a wide range of tropical longitudes from the western Pacific to the eastern Atlantic has been completed. The height of the tropopause was found to vary

coherently over this spatial range on interannual time scales, and to be related to both the quasi-biennial oscillation in tropical stratospheric winds and to the phase of the Southern Oscillation. The time-averaged height of the tropopause appears to be determined by the combined effect of the intensity of deep tropospheric convective activity and the cooling of the lower stratosphere associated with the Hadley and Walker circulations, and with the vertical motions needed to maintain geostrophic balance in the quasi-biennial wind anomalies.

Small-Scale Turbulence

Small-scale, three-dimensional turbulence is a fundamental atmospheric process whose dynamics and climatology is poorly established in the free atmosphere. Under some conditions, turbulence can be quantified, using Doppler radar observations of the variance of velocity fluctuations. The magnitude of turbulence parameters can also be inferred from measurements of the observed signal-to-noise ratio, which is proportional to the turbulence structure constant C_n^2 of the radio refractive index. In collaboration with G.D. Nastrom (C.D.C. Minneapolis), we have examined long-term observations of radar reflectivities from Poker Flat, AK and Platteville, CO to study the climatology of C_n^2. This quantity is very important in electromagnetic wave propagation in the atmosphere, as well as a useful proxy indicator of eddy dissipation rate. The climatological studies have revealed that C_n^2 is log-normally distributed and has significant seasonal and diurnal variations. The frequency spectrum of log C_n^2 variability shows an unexpected power law dependence. At periods greater than 1 to 2 hours, the spectrum follows a -5/3 power law. At shorter periods, the spectrum follows a power law close to -1.

Mesoscale Spectrum of Winds and Temperatures

Earlier studies of the frequency spectrum of radar-observed winds revealed a mesoscale spectrum of fairly universal shape. At scales longer than one hour, spectral slope was found to be close to -5/3. Those observations have led to consideration of the relative contributions of internal waves and quasi-two-dimensional turbulence to the observed spectrum. In collaboration with G.D. Nastrom, we have recently completed a climatological study of wavenumber spectra of winds and temperatures measured by commercial aircraft during routine flights. Scale sizes ranging from a few kilometers to 5,000 km are resolved in the analysis, which has revealed the remarkable result of a nearly universal spectrum for both wind and temperature. Moreover, wind and temperature spectra have the same shape: for scales larger than 500 km or so, they conform to a k^{-3} power law; and for scales less than about 500 km, they conform to an approximate $k^{-5/3}$ power law. This spectral behavior is consistent with a simple model of quasi-two-dimensional turbulence.

Vertical Profiles of Kinetic Energy Density in the Troposphere, Stratosphere, and Mesosphere

Height profiles of the average kinetic energy (K.E.) density can be obtained by multiplying height profiles of the mean square wind velocity by one-half the height-dependent atmospheric density. Such profiles have been

extracted from the Poker Flat MST Radar data base. The results are consistent with the idea that atmospheric gravity waves, which are generated in the troposphere, grow in amplitude as they propagate upward into the more rarified atmosphere. This growth is limited by wave saturation, with the excess wave energy being eventually deposited into in situ turbulence or modifying the local mean flow. The emerging picture from this and similar studies is one in which large (vertical) regions of the atmosphere between 1 and 100 km contain a fully saturated spectrum of waves. In other height ranges, specifically in the lower stratosphere, wave saturation is less pronounced because the upward propagating waves are being modified by other processes (e.g., wave damping, reflection, or changes in the wave kinetic energy as they pass through regions of vertical wind shears).

The Universality of the Spectrum of Vertical Velocity Fluctuations

Frequency spectra of vertical velocity fluctuations in the troposphere and lower stratosphere contain important information on the energy distribution of gravity waves and similar phenomena. Such spectra can be obtained on a continuous basis only by the wind profiler technique. Sample vertical velocity spectra have been obtained from a variety of geographical locations over the past few years. Comparisons between spectra taken under similar background wind conditions at dissimilar locations, from the Arctic to the equator and from the central plains to the middle of the ocean, show remarkable similarities and some significant differences.

Influence of El Chichón Eruption on Tropical Tropopause and High Latitude Wind Fields

The effect on tropopause heights of the stratospheric aerosol cloud generated by the eruption of the El Chichón volcano in April 1982 was investigated, using rawinsonde data from the western tropical Pacific. The behavior of tropopause heights and potential temperatures led to the conclusion that the influence of El Chichón was largely cancelled out by the opposing influence of the great ENSO (El Niño Southern Oscillations) event during the latter half of 1982. Data from 1983-84 has now become available, and the study will be extended to include the more intense portion of the ENSO event in early 1983 and the post-ENSO period of 1984.

Using the long-term data base of tropospheric, stratospheric, and mesospheric wind available from Poker Flat, AK, we have also investigated possible changes in velocity fluctuation statistics following El Chichón. In the lower atmosphere, the variance of horizontal winds was found to be significantly lower in early 1983 compared to 1982 and 1984. At mesospheric altitudes, an increase in tidal energy was found. This increase would be expected to follow enhanced heating in the lower stratosphere.

IV. Innovative Developments

Measurement of Vertical Motions and Their Variability

Mean vertical motions play an important role in atmospheric dynamics and in the creation of weather. Yet, until wind profiling Doppler radars

were used for this purpose, there had been no method of measuring the vertical velocity continuously.

Working in collaboration with G.D. Nastrom, we have considered the possibility of direct measurement of large-scale vertical motion by averaging vertical velocities measured by a wind profiler at a single station. One difficulty in accomplishing this is that large-scale vertical velocities are so small they can be lost in the geophysical noise of small-scale vertical wind variability. Even under ideal conditions, it is necessary to average vertical velocities for several hours to reduce the vertical velocity variance to a level where the large-scale vertical motions can be detected. Under these circumstances, it has been demonstrated that directly measured vertical velocities are comparable to vertical velocities inferred from NMC analyses. In a related case study, vertical motions observed by the Platteville radar were shown to be well correlated with rainfall rates observed nearby during an upslope storm.

The mean vertical velocity also plays an important role in the mesosphere. Mean vertical motions observed by radar at mesospheric altitudes are an order of magnitude larger and of the opposite sense to the vertical velocities predicted by current theoretical models. A preliminary study of the possible role of Stokes drift at these altitudes, suggests that the mean vertical motions observed by the radar are influenced by Stokes drift and may be more directly related to vertical wave energy fluxes than to mean meridional circulations.

Fluctuating vertical motions also appear to be a good indicator of gravity wave activity. Using a single station only, statistics of the gravity wave fluctuations can be determined. Our first use of an array of three vertically directed Doppler radars demonstrated that, by cross-spectral analysis, it was possible to determine wavelength, direction of propagation, and phase speed of individual waves. Using the 5 km baseline array established in Southern France during ALPEX (ALPine EXperiment), waves of period 15 to 90 min, of horizontal wavelength 7 to 40 km, and phase speed 5 to 20 m/s were detected.

Rocket Experiments at the Poker Flat MST Radar Site

Two separate rocket experiments have been made in conjunction with the Poker Flat radar program. A number of results from the first of these launches (R. Philbrick of AFGL) are contained in a recent PhD thesis by S. Smith from the University of Alaska's Geophysical Institute. In this work, the major characteristics of atmospheric gravity waves in the summertime high-latitude mesosphere are determined and the conditions for wave breaking are established experimentally. In the second rocket experiment (R. Goldberg of NASA), which occurred this March, data were obtained to study the wintertime mesospheric echoing region, in particular, and the relationship between the radar echo strength and the flux of high-energy particles impinging on the polar mesosphere from space. Analysis of this data is underway.

Tropopause Height Determination, Fresnel Scattering, and Atmospheric Stability

A vertically-looking VHF radar observes significantly enhanced backscattered power from stable regions of the atmosphere. This enhancement is attributed to Fresnel scattering from stable laminae of radio refractive index. A Fresnel scattering model has been developed that predicts the magnitude of backscattered power as a function of the atmospheric lapse rate (dT/dz). The model has been shown to agree well with observations from the Sunset, CO and Poker Flat, AK radars.

The Fresnel scattering model leads naturally to an objective method for determining tropopause height from radar observations of backscattered power. It has been recently demonstrated that tropopause heights can be determined routinely in this way with an r.m.s error of a few hundred meters, using a probing pulse with a one kilometer pulse length. A radar determination of the tropopause with this accuracy would be more than adequate to aid the retrieval of temperature profiles, using satellite and ground-based radiometry. This is particularly true, since the radar can measure the tropopause height every few minutes in contrast to 12-hour radiosonde determinations.

Cooperation with the PRESTORM Program

During May-June 1985, the radar profiler scheduled for Christmas Island was installed and operated at a site in Northern Oklahoma. This was part of a cooperative effort with ERL's PRESTORM Experiment, a program designed to obtain preliminary atmospheric data on convective activity in the Oklahoma-Kansas area. The Christmas Island profiler provided two months of almost continuous data for PRESTORM before being shipped to its Pacific location in early July. These data contain information on the wind, wave, and turbulent activity during a number of significant convective periods. Analysis by the PRESTORM group is underway.

Future Plans

I. Poker Flat

As mentioned earlier in this section, the Poker Flat MST Radar is being modified for a beam-steering capability in order to measure gravity wave momentum flux and associated phenomena. Thus, our efforts at Poker Flat during the coming year will involve completing this modification (we anticipate that full capability will be available by Dec. 1985) and then gathering a complete data set during the ensuing twelve-month period. A contingency data set, using only the available one-quarter antenna array, will be gathered during the modification period.

An additional effort is to prepare an archive of the existing six-year Poker Flat data set. It appears likely that NSF funds will be made available for this purpose. The archive, when complete, will be transferred to the National Center for Atmospheric Research (NCAR) for use by the scientific community.

II. Equatorial Dynamics and Climate

Profiler Sites in the Tropical Pacific

The vertically-directed radar profiler at Ponape, which has produced a continuous set of vertical wind data during the last sixteen months, will be reconfigured into a beam-steerable configuration for gravity wave momentum flux measurements. Funding for this modification has been received, and the modification hardware has been constructed. Current plans are to make the modification in November and to begin the observation program at that time. These measurements will provide an exciting first look at the vertical distribution and character of the gravity wave momentum flux in the tropics.

Operation of the Christmas Island profiler will begin in the next month or so, following the installation of a diesel generator to provide continuous power to the station. Inclusion of the Christmas Island data set with our existing Ponape data set will initiate a number of preliminary studies of the short-term dynamics of the tropical atmosphere.

In addition to our activities at Ponape and Christmas Island, we will continue to examine other sites to complete our tropical Pacific chain. In general, the most crucial tropical regions that should be included lie in the western-most extent of the Pacific Basin (i.e., near Indonesia and Malaysia) and the region containing the Galapagos Islands and the Equadorian/Peruvian coast. Preliminary site surveys have been made in both regions.

Tropical Studies Using Other Data Bases

The study of the tropical tropopause region, using radiosonde data, will continue. Emphasis will be on (1) completing the study of the relationship between tropopause heights and atmospheric angular momentum, (2) studying the effects of the ENSO event of 1982-83 on the tropical tropopause region, (3) investigating the relationship between anomalies in Pacific sea surface temperatures and in atmospheric temperatures in the tropical upper troposphere and lower stratosphere, and (4) developing a conceptual picture of the mechanism of troposphere-stratosphere exchange in the tropics.

III. Climatological Studies

Poker Flat

The existing six-year Poker Flat radar data set will continue to be studied to establish long-term trends in gravity wave and turbulence activity, and the seasonal characteristics of the height distribution of these parameters.

The Tropics

We will begin an intensive study of the climatology of convective dynamics by combining the existing sixteen-month data set from the Ponape radar with additional data sets from satellites and rawinsondes. Also,

using data acquired from the Ponape and Christmas Island wind profilers, we will examine long-term average vertical motion for evidence of Hadley and Walker circulations. If we can identify long-term mean vertical motions associated with these large-scale circulations, we will begin to explore the variability of these circulations within the context of the broad-scale features of tropical dynamics being explored by TOGA.

IV. Innovative Developments

It has become apparent during the course of the last two years that one of the major limitations to the existing profiler technology is that the lowest observable height is typically in the vicinity of one or two kilometers. In order to improve this lower limit and to provide higher resolution in the first 2 to 3 km of the atmosphere, we are designing a "Boundary Layer" radar system. The work is being funded under TOGA and should yield an inexpensive, low power radar that will operate at much higher frequencies and be capable of observing the region between about 300 m and 2 to 3 km altitude. This system will supplement our existing VHF system on Christmas Island.

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THEORETICAL WAVE AND TURBULENCE PROGRAM

Permanent Technical Staff

Jerome Weinstock, Program Leader	Physicist
Lurania Topakas	Secretary

Introduction

This program is devoted to theoretical studies of turbulence, waves, and transport in the atmosphere, with an emphasis on flexibility and with a direction toward problems that are challenging and timely. Although small in terms of staff and funding, the program has had a very high output, and as a result it has attracted a number of visiting scientists and post-doctoral research associates over the years.

The program grew out of an earlier program aimed at understanding and predicting turbulence and wave fluctuations in the plasma environment of the earth's ionosphere and upper atmosphere. This original program was developed in response to the mission of the Aeronomy Laboratory as part of the Central Radio Propagation Laboratory of NBS, and was designed to provide the necessary theoretical background for understanding and predicting the behavior of the ionosphere, and its influence on radio propagation. The more recent development of the program has taken place in response to the changing mission of the Laboratory as part of NOAA, and the basic theme has been the application of the theoretical expertise and techniques developed in the studies of plasma turbulence to the problems of turbulence and wave fluctuations in the lower and middle atmosphere.

Turbulence is widespread in geophysical fluids, and it often has a dominating influence on transport. The conceptual and mathematical difficulties associated with turbulence theory, however, are notorious, and until recently there have been no satisfactory theories available to determine the strength of the fluctuations produced by nonlinear wave interaction and turbulence. In the case of the ionosphere, this program provided the first, and often the only, formulas for predicting the strengths of irregularities in plasma density, temperature, electric field, and other important parameters. Confirmation of the theory has been provided in many cases by optical and radar measurements and by direct rocket observations.

Specific accomplishments of the original ionospheric turbulence program included the development of the Dupree-Weinstock theory of strong plasma turbulence, and of a theory of strong turbulence in fully ionized gases in a magnetic field that is valid at all frequencies. Theories were developed to allow the prediction of the strength of irregularities produced by plasma instabilities in the ionosphere and of the modification of the ionosphere by

strong radio transmitters. Contributions were also made to the theory of laser heating of laboratory plasmas.

As mentioned above, the program in recent years has been devoted to the investigation of turbulence and waves in the neutral atmosphere, applying the novel approaches that were so successful in the area of plasma turbulence. Among the accomplishments have been the development of a comprehensive nonlinear theory of atmospheric gravity waves, which are important contributors to transport and dynamics throughout the atmosphere, a theory of turbulence in the buoyancy subrange of stably stratified shear flow, and a theory of the influence of gravity waves on airglow emission from the atmosphere. Observations made by the Optical Aeronomy program confirmed the theoretically predicted oscillations in the $O_2(^1\Sigma)$ airglow, showing that gravity waves were indeed responsible through the oscillations in temperature that they produce (See Figure 1). The theory can now be extended to other airglow emission, such as those of OH and O.

Other major investigations have included studies of the vertical propagation of a broad spectrum of gravity waves from the troposphere to the mesosphere, the development of a relationship between turbulence energy dissipation rate and turbulent diffusivity under conditions of stable stratification, and development of a theory that relates radar measurements of the refractive index structure constant C_n^2 to the energy dissipation rate (See Figure 2). The observed correlation between wind shears and turbulence layers was also explained quantatively (See Figure 3).

Recent Results

The following are the principal recent results of the program:

(1) It has been proven that diffusion, friction, momentum deposition, and heat flux are all interrelated in a simple way. All of these transport parameters are needed for dynamical models of the middle atmosphere.

(2) A simple algorithm for nonlinear gravity waves has been developed for use by non-experts.

(3) A theoretical calculation of the pressure-strain relationship in shear flows has been made for the first time. The theory is fundamental in modeling the planetary boundary layer.

(4) Diffusion due to gravity waves in the 30-100 km height range was modeled, tending to establish that gravity waves are the major cause of diffusion in the mesosphere (See Figure 4).

(5) Theory of the interaction of gravity waves with turbulence in the ocean and atmosphere was developed. The theory explains the observations of a numerical experiment carried out recently at GFDL to study this interaction.

(6) A theoretical calculation was made of the heat flux caused by nonlinear gravity waves in the middle atmosphere. This flux was shown to actually cause cooling, and has potentially important implications for the circulation of the middle atmosphere.

(7) A theoretical formula was developed to predict the kinetic energy of clear-air turbulence (CAT) from a knowledge of dissipation rates, which can be obtained from radar measurements.

(8) The major program to develop turbulence models of the planetary boundary layer has been strengthened and extended by financial support from and personal collaboration with the Naval Environmental Prediction Research Facility (NEPRF) at Monterey, California. Use of their boundary layer model codes and of their computing facilities is allowed under this arrangement.

Recent research progress was aimed at determining the influence of pressure correlations on the mean flow. It was discovered that such correlations could decrease the development of turbulence along the direction of the main flow, a result that was unexpected and that could explain some observations by Wyngaard (1979)

(9) Proved that gravity waves "break" in a manner resembling the surfing of ocean waves, and that this "breaking" is the principal process by which waves cause transport in the atmosphere.

(10) Determined the buoyancy subrange spectrum of temperature fluctuations in atmosphere and oceans, and corrected a commonly quoted twenty year-old error in the literature concerning such spectra.

(11) Proved that "return to isotropy" -- the principal hypothesis of turbulence model -- is invalid and developed a theory to determine realistic deviations from isotropy.

(12) Theoretically determined how observed height variations of gravity wave amplitudes can be used to infer eddy diffusivities in the middle atmosphere.

(13) Explained why vertically towed grid turbulence experiments differ from horizontally towed experiments, and how each are related to atmospheric turbulence phenomena.

(14) Discovered a new mechanism by which gravity waves generate thin layers of turbulence observed in oceans and atmosphere, namely a dynamical instability cuased by nonlinearly steepened wave shear. This mechanism might provide the widely sought-after "sink" of fluctuation energy in oceans.

(15) It was shown that observed radar spectra in the middle atmosphere may be caused by strongly interacting gravity waves rather than by the generally assumed weakly interacting waves. This distinction has an implication for modeling transport.

(16) Influence of stratification on the Pressure-Strain term was determined. That term is crucial for predictive modeling of the atmospheric boundary layer.

(17) Progress was made on an exact analytical calculation of a breaking internal gravity wave.

Future Plans

Future plans are divided into two major program areas: (1) theory of turbulence, wave enhanced diffusion, friction, and heat transport in the troposphere, stratosphere and mesosphere; and (2) a rigorous theoretical model of the atmospheric boundary layer; this also has important, practical engineering applications because of the great present need of reliable turbulence models in so many areas of our industrial complex.

Future research goals of these programs areas are as follows:

1. Theoretical investigations on fluid turbulence, waves, and enhanced transport in the atmosphere. Research activities (not in order of priority) will be

(a) Development of a comprehensive theory of turbulence in stably stratified flows, with relevance to both the atmosphere and the oceans. A goal is to explain the velocity spectra observed in the oceans and atmosphere.

(b) Development of a nonlinear theory of wave breaking in atmosphere and oceans.

(c) Studies of turbulent and wave diffusion in the stratosphere and troposphere.

(d) Deduction of the turbulence state in the lower atmosphere from radar measurements and from measurements of temperature fluctuations.

(e) Determination of the role of tidal waves in atmospheric eddy diffusion. Derivations of a nonlinear theory of tidal waves for this purpose.

(f) Determination of the contribution of gravity waves to atmospheric diffusion from 20 km to 100 km and modeling of the upward propagation of gravity waves from the stratosphere to the thermosphere.

(g) Modeling the profile of momentum flux and friction needed to predict the mean circulation in the middle atmosphere. Determine if the Rayleigh friction assumed by mean circulation models is theoretically justifiable.

(h) Fundamental study of inertial range turbulence in incompressible fluids (Kolmogoroff turbulence). The recently developed Three-Point Method will be used to obtain a rigorous self-contained Test Field Model.

(i) Modeling the cooling of part of the middle atmosphere by gravity waves.

(j) Explanation of the universal vertical spectra of velocity and temperature found in atmospheres and oceans.

(k) Determine the formation of steady winds by gravity waves.

(l) Critical evaluation of conflicting viewpoints of the basis for wave induced transport in the atmosphere.

(m) A study of gravity waves and transport in the mesosphere and thermosphere based on Noxon's observations of OH and $O_2(^1\Sigma)$ airglow--see Figure 1 for example of previous work.

2. Major comprehensive program to develop a theoretical model of the earth's boundary layer (BL) (this model also has industrial applications). Until now boundary layer models have relied on ad hoc, heuristic considerations to determine the influence of pressure fluctuations and turbulent diffusion on boundary layer flows. These models are often not satisfactory, and there is no way of knowing when their forecast will be accurate or not. The theoretical model will determine the influence of fluctuations of pressure, temperature, and humidity from first principles, and the resulting forecasts are expected to be more accurate and reliable than existing models. This research is a new direction in modeling. It is based on contemporary methods of statistical physics and turbulence theory. Our goal is to supply the theory needed to make turbulence modeling succeed.

Specific research goals are:

(a) To model the pressure-strain rate in the neutral boundary layer, correct the Rotta model, and to calculate the influence of terms nonlinear in the velocity shear;

(b) To extend the pressure-strain rate theory (developed last year) to stable and unstable atmospheric conditions. This means including the effects of buoyancy on the pressure-strain terms needed for modeling. A theory of pressure fluctuations (the pressure-strain rate) is vital for modeling because such fluctuations cannot be measured directly (except near a wall) and yet have a profound influence on the mean flow circulations;

(c) To theoretically model buoyancy (heat) flux, kinetic energy flux, pressure flux, momentum flux, humidity flux, mechanical energy dissipation, and heat dissipation from first principles -- for neutral, stable and unstable conditioins. These flux and dissipation quantities are all required for a model of the boundary layer, although, as of now, they are not known in other than an ad hoc, unsatisfactory, empirical way -- analogous to eddy transport terms.

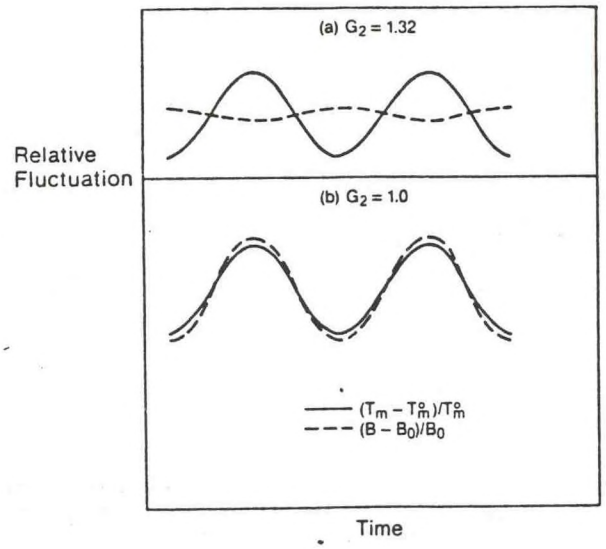

Figure 1. Theoretical ratio of $O_2(^1\Sigma)$ brightness fluctuations $B - B_0$ to temperature fluctuations $T_m - T_m^o$ for (a) large amplitude gravity waves and (b) small amplitude gravity waves. Both kinds of ratios are observed (Noxon, 1978).

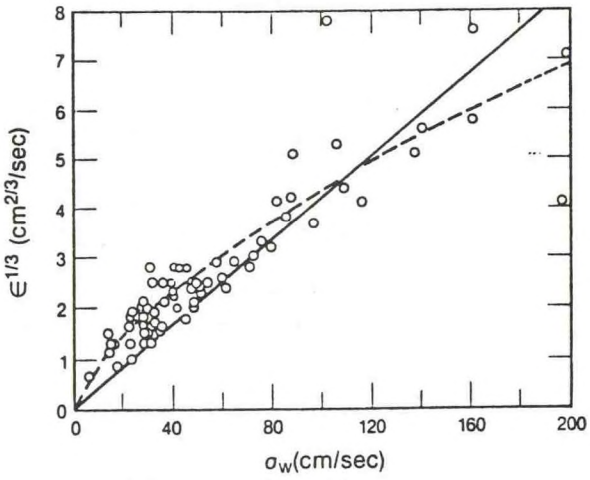

Figure 2. Turbulence dissipation rate ϵ versus vertical RMS velocity σ_w. A preliminary theory is given by the dashed line -----. The observations in the stratosphere are given by circles O.

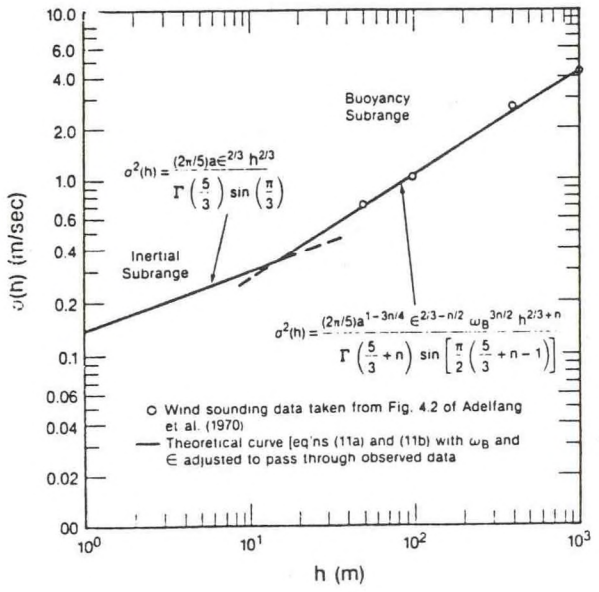

Figure 3. Turbulence RMS energy $\sigma(h)$ versus layer thickness h. Our theoretical prediction is given by the solid lines ——, and the observations from rockets and balloons are given by the circles O. Layer thickness less than 50m are not adequately resolved by balloons or rockets, and their turbulence properties must be determined by theory (i.e., theoretical extrapolation).

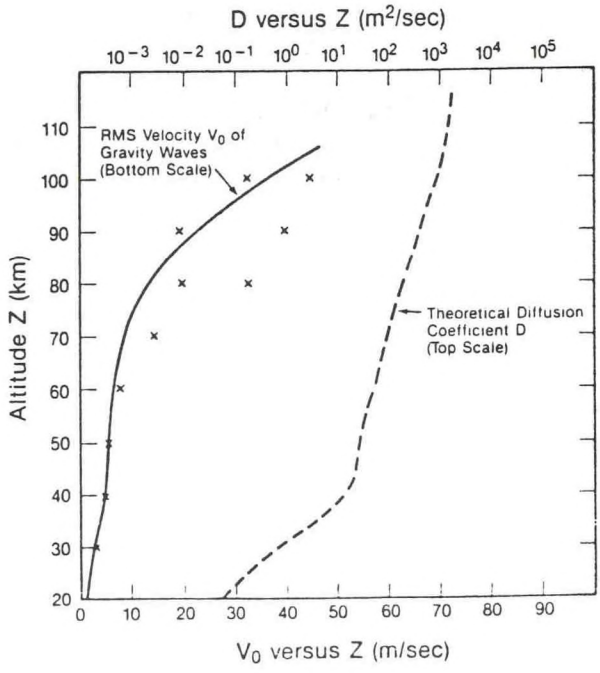

Figure 4. Theoretical curves of RMS gravity wave velocity V_o and diffusion coefficient D versus altitude Z. The small crosses are observed values of V_o.

PUBLICATIONS 1984

Weinstock, J., Effects of Gravity Waves on Turbulence Decay in Stratified Fluids, J. Fluid Mech., 140, 11-26, 1984.

Weinstock, J., Simplified Derivation of an Algorithm for Nonlinear Gravity Waves, J. Geophys. Res., 89, 345-350, 1984.

Weinstock, J., Gravity Wave Saturation and Eddy Diffusion in the Middle Atmosphere, J. Atm. Terr. Phys., 46, 1069-1082, 1984.

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Weinstock, J., and S. Burk, Theoretical Pressure-Strain Term, Experimental Comparison and Resistance to Large Anisotropy, J. Fluid Mech., 154, 429-443, 1985.

Weinstock, J., On the Theory of Temperature Spectra in a Stably Stratified Fluid, J. Physical Ocean., 15, 475-477, 1985.

Weinstock, J., Theoretical Gravity Wave Spectrum in the Atmosphere: Strong and Weak Wave Interactions, Radio Science

Weinstock, J. and S. Burk, Theoretical Pressure Strain Term: Resistance to Large Anisotropics of Stress and Dissipation, Turbulent Shear Flows, Vol. 5, edited by Durst, Schmidt, Launder, and Whitelow, Cornell University, 1985.

Weinstock, J., Finite Amplitude Gravity Waves: Harmonics, Advective Steepening, Breaking and Saturation, Proceedings, IUTAM Symposium on Mixing in Stratified Fluids, Edited by J. Imberger, University of Western Australia, Perth, August, 1985.

AERONOMY LABORATORY SEMINARS

1984 - 1985

June 27, 1984	On the Interaction of Gravity Waves and Convective Storms, Prof. Franco Einaudi, School of Geophysical Sciences, Georgia Institute of Technology, Atlanta, Georgia
July 18, 1984	Using Radioactive Nuclei to Study Boundary Layer Free Atmosphere Exchange, Dr. Mark Kritz, NASA/AMES Research Center, Moffitt Field, California
August 1, 1984	MASS Transfer of Trace Gases to Cloud and Rain Drops, Dr. Chris J. Walcek, Acid Deposition Modeling Project, National Center for Atmospheric Research, Boulder, Colorado
August 15, 1984	Measurements of Hydroxyl Radicals by Long Path Absorption Spectroscopy, Dr. Gerhard Hübler* and Dr. Uli Platt, Kernforschungsanlage, Jülich, FRG * Present Affiliation: CIRES, University of Colorado
September 19, 1984	The Tropical Tropopause and Global Climate, Dr. George Reid, NOAA, Aeronomy Laboratory, Boulder, Colorado
September 26, 1984	A Theoretical and Experimental Study of a Universal Gravity Wave Spectrum in the Atmosphere, Dr. Edmund M. Dewan, Air Force Geophysics Laboratory, Hanscom AFB, MA
October 10, 1984	Trace Gas Trends and Their Potential Role in Climate Change, Dr. V. Ramanathan, NCAR, Boulder, Colorado

October 24, 1984	A Two-Dimensional Study of Chlorine Compounds and Stratospheric Ozone, Dr. Susan Solomon, NOAA, Aeronomy Laboratory, Boulder, Colorado
November 7, 1984	Stokes Drift and Internal Waves in the Middle Atmosphere, Dr. Larry Coy, NOAA, Aeronomy Laboratory, Boulder, Colorado
November 28, 1984	Measurements of NO_y in the Troposphere, David W. Fahey, NOAA, Aeronomy Laboratory, Boulder, Colorado
December 12, 1984	Stratospheric Water Vapor, Dr. Dieter Kley, NOAA, Aeronomy Laboratory, Boulder, Colorado
January 7, 1985	Photofragment Emissions for Optical Detection of Atmospheric Species, Prof. Long C. Lee, San Diego State University, San Diego, California
January 9, 1985	Cloud Chemistry, Prof. William Chameides, Georgia Institute of Technology, Atlanta, Georgia
January 14, 1985	Observations of Heterogeneous Aerosol Formation in Urban Plumes and Hazes, Prof. James C. Wilson, University of Minnesota, Minneapolis, Minnesota
January 29, 1985	Biogenic Hydrocarbon Emissions in the Continental U.S., Prof. Brian Lamb, Washington State University, Pullman, Washington
February 6, 1985	Review of Atmospheric Chemical Kinetics Program, Dr. Carl Howard, Aeronomy Laboratory, Boulder, Colorado
February 20, 1985	Acid Rain: Theory and Observation of a Natural Background, Prof. Robert Charlson, University of Washington, Seattle, Washington

March 6, 1985	Chemical Mechanisms for Regional Acid Deposition Models, Dr. Bill Stockwell, NCAR, Boulder, Colorado
March 13, 1985	Volatile Organics in and Over the Open Ocean, Dr. George Harvey, NOAA Atlantic Oceanic and Metorological Laboratory, Miami, Florida
April 5, 1985	Recent Studies of NO_3 and $ClNO_3$ Kinetics and Photochemistry, Dr. Stanley P. Sander, Jet Propulsion Laboratory, Pasadena, California
April 10, 1985	The Latest Results from Satellite Measurements of the Earth's Radiation Budget, Prof. Thomas Vonder Haar, Colorado State University, Fort Collins, Colorado
April 17, 1985	Model Simulation of an April, 1981, Acid Precipitation Event, Dr. Julius S. Chang, Director, Acid Deposition Modeling Project, NCAR
April 22, 1985	Gravity Waves in the Mesosphere, Dr. Ian Reid, University of Saskatchewan, Saskatoon, Saskatchewan, Canada
April 26, 1985	Optical Modeling of Stratospheric Aerosols: Present Status, Dr. James M. Rosen, Department of Physics and Astronomy, University of Wyoming, Laramie, Wyoming
April 29, 1985	The Seasonal Evolution of the Stratosphere and Implications for the Transport of Tracers, Dr. Alan O'Neill, Meteorological Office, Bracknell, United Kingdom
May 15, 1985	Meridional Circulations Associated with the Cycle of El Niño/ Southern Oscillation, Dr. Colin Ramage, CIRES/University of Colorado, Boulder, Colorado

May 22, 1985	The Southern Oscillation and Related Atmospheric Circulations and Precipitation Anomalies, Dr. Vernon E. Kousky, NOAA/Climate Analysis Center, Washington, D.C.
June 3, 1985	Photochemistry Along Quasi-Isentropic Trajectories in the Stratosphere in Early 1979, Dr. Adrian F. Tuck, British Meteorological Office, Bracknell, Berk., England
July 24, 1985	On the Photostationary State of NO_x, Dr. John W. Drummond, Institut für Chemie 3: Atmosphärische Chemie, Kernforschungsanlage Jülich, Federal Republic of Germany
August 12, 1985	Atmospheric Chlorine: Problems and Solutions, Dr. William Brune, Harvard University, Cambridge, Massachusetts
September 18, 1985	Aeronomy Laboratory Acid Rain related Research: An Overview, Dr. Dan Albritton, NOAA, Aeronomy Laboratory, Boulder, Colorado