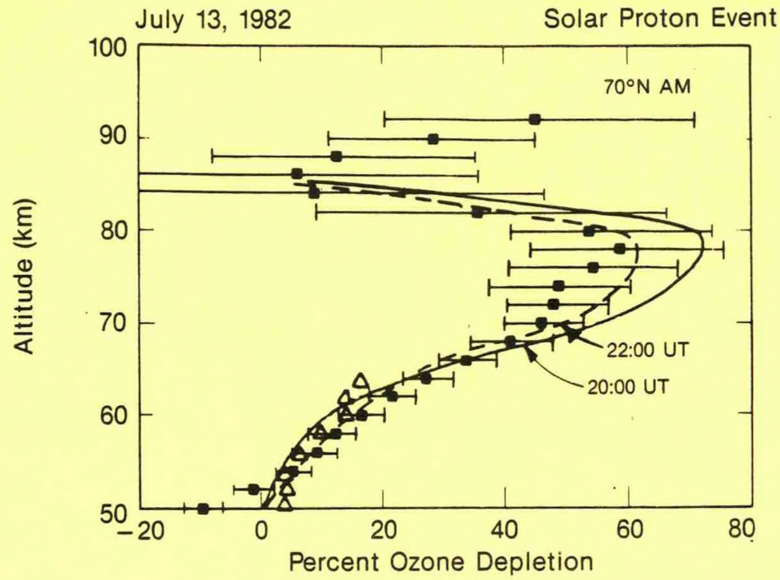
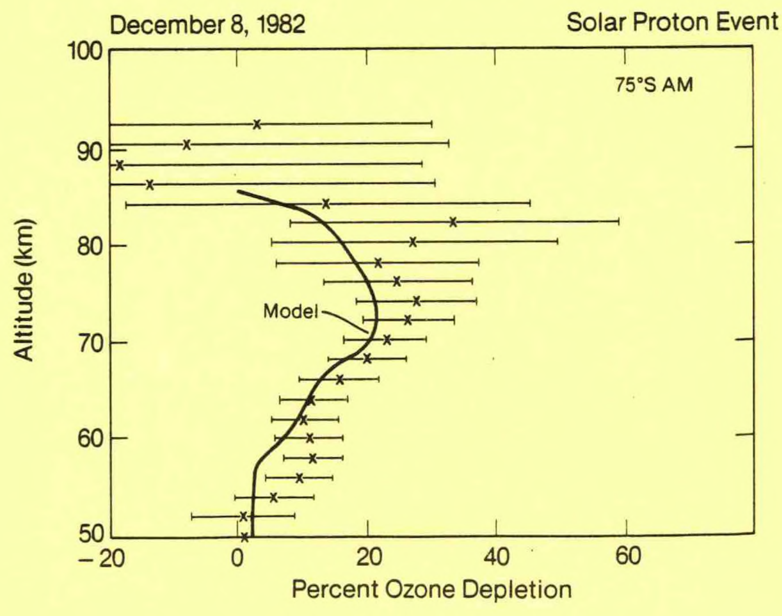
Aeronomy Laboratory

Environmental Research Laboratories

ANNUAL REPORT FY83





AERONOMY LABORATORY

ANNUAL REPORT - FISCAL YEAR 1983

October 1, 1982 - September 30, 1983

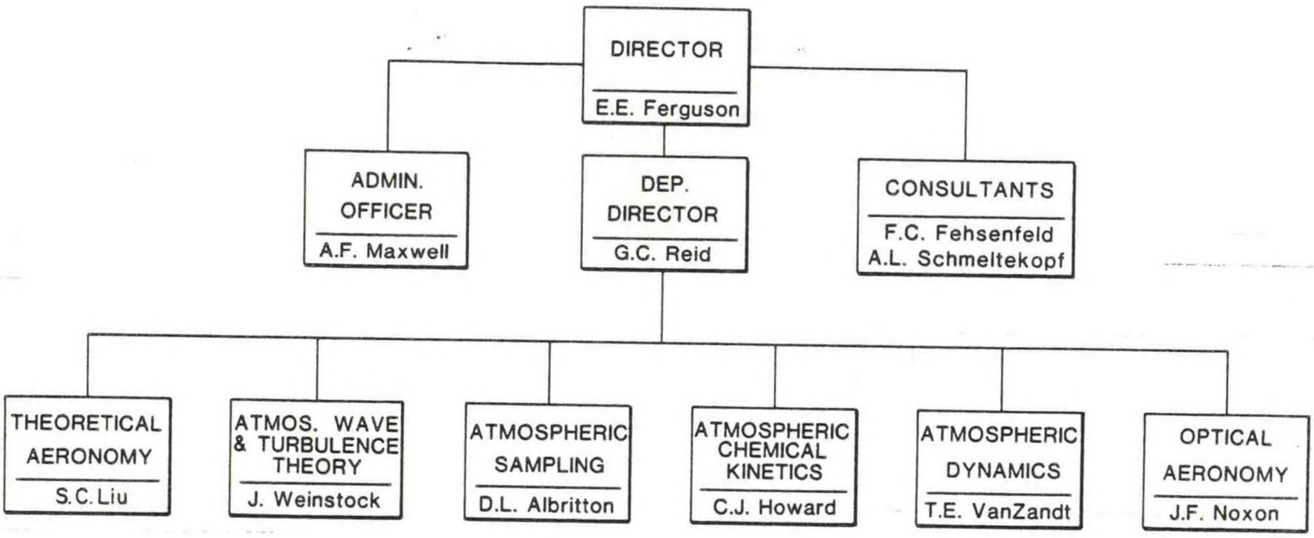
Aeronomy Laboratory
325 Broadway
Boulder, Colorado 80303
October 1983

CONTENTS

COVER

The cover figure presents a comparison between model calculations performed by members of the Theoretical Aeronomy group and observations of mesospheric ozone depletions associated with two different solar proton events as observed by the Solar Mesosphere Explorer (SME) satellite. SME is a cooperative project led principally by scientists at the University of Colorado in collaboration with researchers at the Aeronomy Laboratory and JPL. The observed changes in ozone are shown, along with error bars representing two sigma standard deviations of the monthly mean, which demonstrates that the variations observed on Dec. 8, 1982 and particularly on July 13, 1982 were well outside of the observed natural variability of O_3. The agreement between model calculations and observations as shown in both of these events indicates that the response of mesospheric ozone to a solar proton event is very similar to theoretical predictions, providing an important test of our present understanding of ozone photochemistry.

AERONOMY LABORATORY •
ORGANIZATION CHART

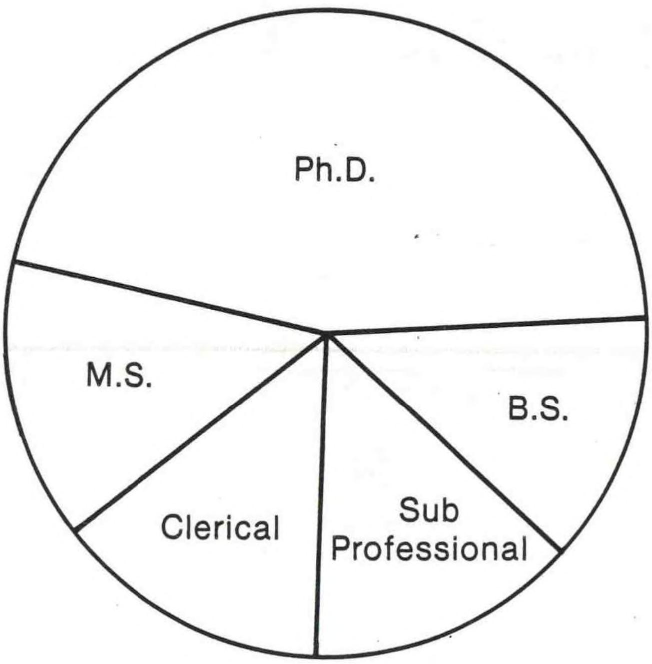


AERONOMY LABORATORY—PERSONNEL STATISTICS

FY 83 Oct. 1, 1982-Sept. 30, 1983

TOTAL FULL-TIME PERSONNEL

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



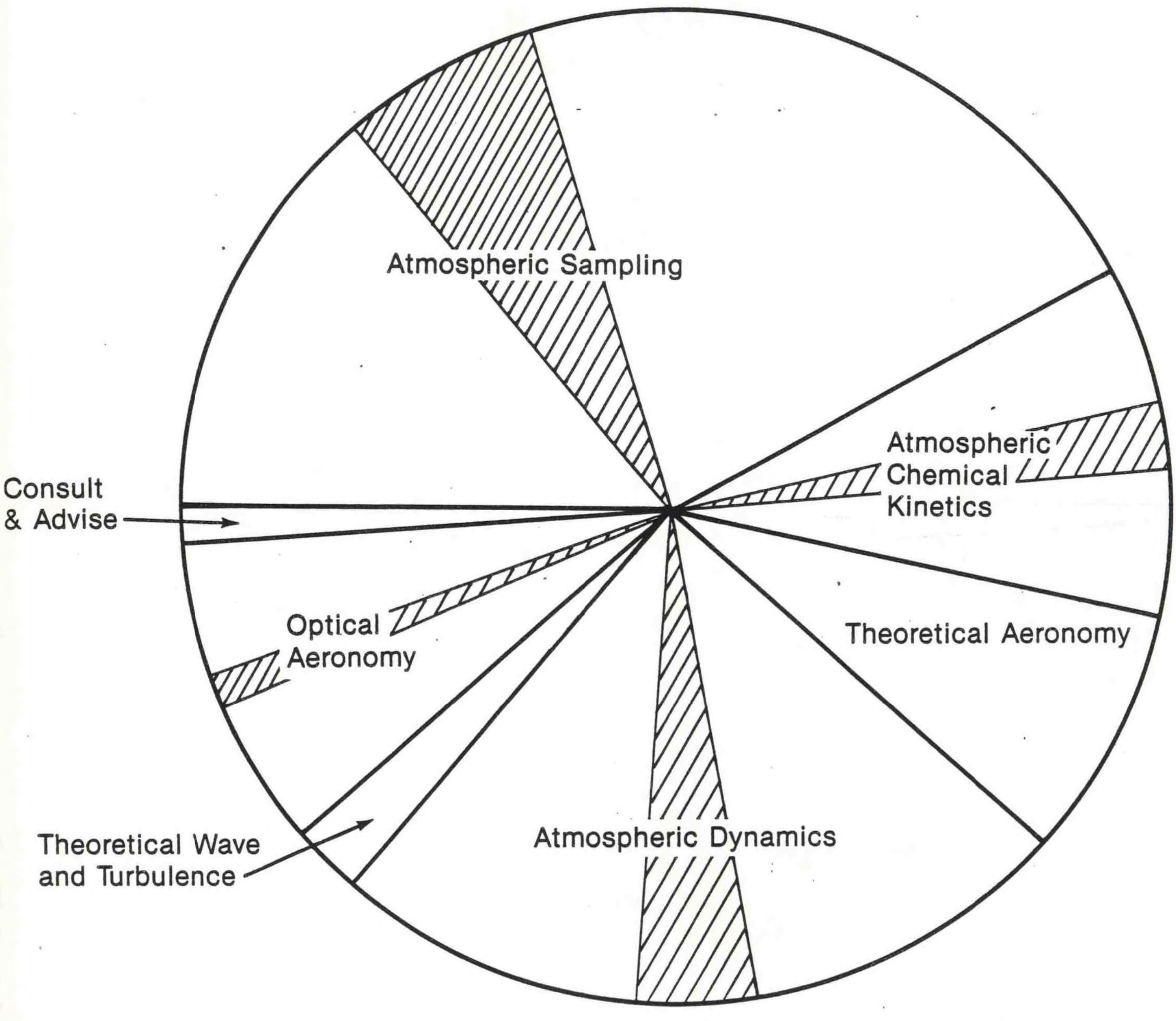
Composition of Full-Time Staff

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—1983 FUNDING

FY 83 Oct. 1, 1982-Sept. 30, 1983



OR and F	3,588,000	☐
Other Agencies	600,000	▨
Total Funding	4,188,000	

AERONOMY LABORATORY

Laboratory Director's Office

Permanent Staff

Eldon E. Ferguson	Director
George C. Reid	Deputy Director
DeeAnna Doerfler	Secretary
Alton F. Maxwell	Administrative Officer
Shirley L. Rice	Administrative Assistant

Part-time Staff

Rebecca A. Mendez	Clerk Typist
Heather L. Miller	Clerk Typist

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 extended 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 at the forefront of research.

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

The Atmospheric Sampling and the Atmospheric Chemical Kinetics Programs have evolved over a period of years out of an Atmospheric Collision Processes Program that has 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 to in-situ atmospheric composition measurements. 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. This program has been recently augmented by a very comprehensively instrumented research site in the mountains near Boulder in 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. More recently, the problem of acid rain has provided the basic motivation 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.

The following pages contain detailed descriptions of the various Programs, and listings of the Laboratory's publications in calendar years 1982 and 1983.

THEORETICAL AERONOMY PROGRAM

Permanent Technical Staff

Shaw C. Liu, Program Leader	Physicist
George C. Reid, Consultant	Physicist
Carl H. Love	Mathematician
John R. McAfee	Physicist
Susan Solomon	Chemist
DeeAnna Doerfler	Secretary

Temporary Staff

Joseph M. Coughlin	CIRES Research Assistant
Eirh-yu Hsie	CIRES Research Associate
Stuart A. McKeen	CIRES Research Associate
Michael K. Trainer	NRC Research Associate

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 middle and lower 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.

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 authropogenic 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,

$$NO_2 + OH \overset{M}{\rightarrow} HNO_3$$

$$SO_2 + OH \overset{M}{\rightarrow} HSO_3.$$

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) 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;

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

(c) Studies of the detailed photochemistry of O_3, NO_x, OH, and hydrocarbons in a 1-dimensional 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 and SO_2;

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

The gas phase oxidation mechanism of SO_2 in the atmosphere has been investigated (McKeen et al., 1984). It was shown that the SO_2 injected in the stratosphere by the El Chichon vocanic eruptions was oxidized by OH through a mechanism that recycles atmospheric OH rather than consuming it. The result predicted by our model calculation has been substantiated by the observed lifetime (about 1.5 months) of SO_2 in the stratosphere and by the observed increase in atmospheric column OH concentration following the arrival of volcanic clouds at Fritz Peak, Colorado. Verification of such an SO_2 oxidation scheme may have important implication for the linearity problem of the "source-receptor" relationship of acid deposition, since the gas-phase oxidation rate would decrease with increase in SO_2 emission if OH were consumed by SO_2. Our results show that the gas-phase oxidation rate of SO_2 is linearly proportional to SO_2 emission rate.

Previous research on vertical transport of trace gases and air pollutants has been mostly restricted to the planetary boundary layer (PBL). Exchange between the boundary layer and the free troposphere has been neglected by air quality models that concentrate on the local and urban scale air pollution problem. Recent studies in long range transport (over 1000 Km) of air pollutants such as acid deposition and global tropospheric photochemistry have shown that long range transport of air pollutants above the PBL may be more important than transport within the PBL (Liu et al., 1983). In order to quantify the vertical transport, Liu et al. (1984) analyzed the vertical distribution of radioactive tracer ^{222}Rn over the continents and derived vertical eddy diffusion coefficients for various seasons (Fig. 1). Because the radioactive decay time (3.8 days) of ^{222}Rn is similar to the atmospheric residence time of many air pollutants such as HNO_3, NO_3^-, $SO_4^=$ and some hydrocarbons, the amount of ^{222}Rn transported above the boundary layer can be used to estimate transport of these pollutants. For instance, in the summer, 25% of ^{222}Rn is transported above 2 Km (about the top of PBL) and 10% is transported above 5.5 Km (500 mb). Our results can also be used to parameterize the transport by convective clouds which is probably one of the most effective vertical transport processes in the summer. Scientists at GFDL are making a model study of the ^{222}Rn distribution and the related transport processes.

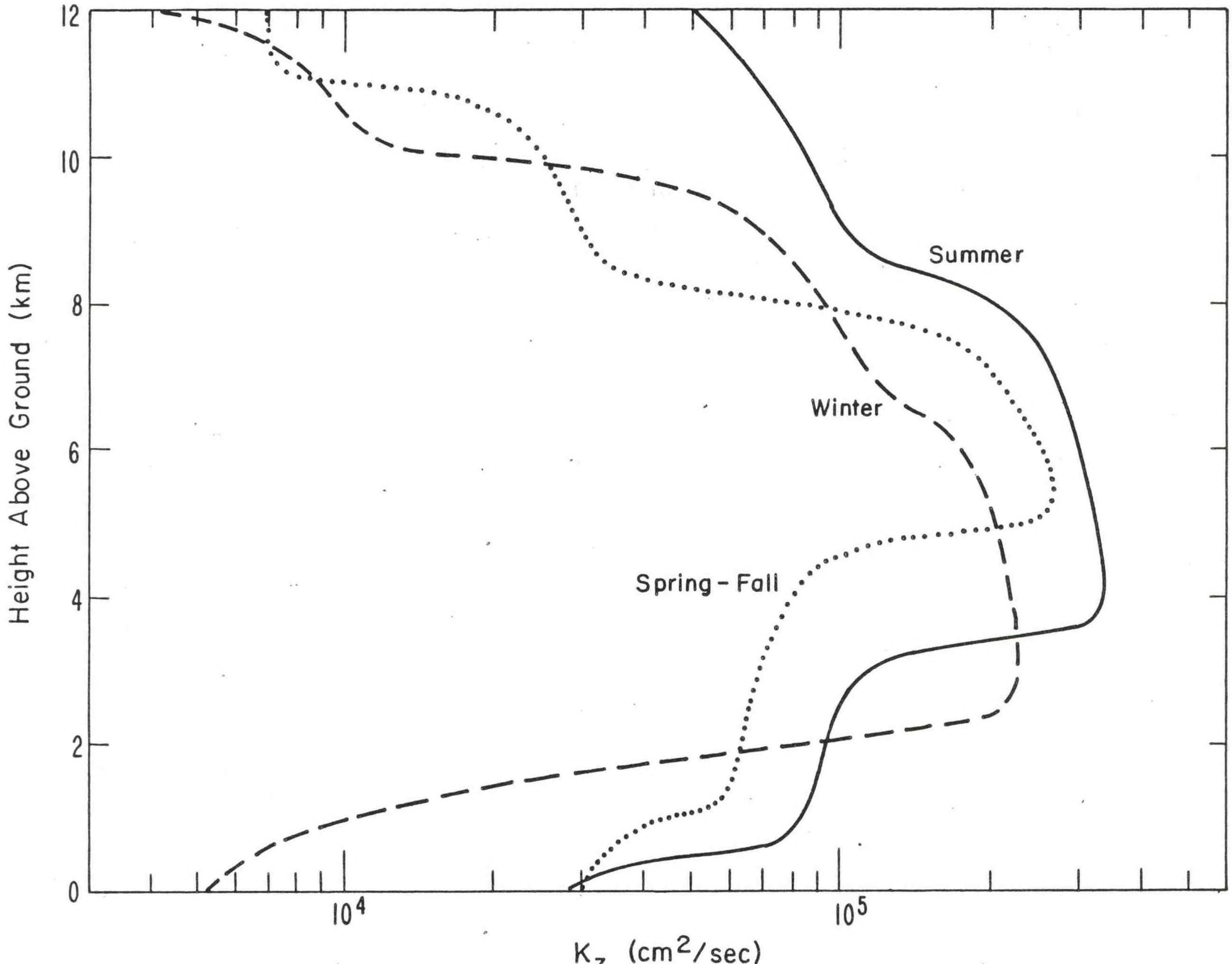


Figure 1 Vertical eddy coefficients derived from ^{222}Rn distribution.

The oxidation of NO_2 was studied by investigating the ratios of NO_2 to benzene and toluene tobenzene at Niwot Ridge measured by scientists of the Atmospheric Sampling group of our laboratory (Roberts et al., 1984). We have shown that the oxidation of NO_2 is primarily by OH in the atmosphere and that an upper limit for the concentration of OH can be derived from the aromatic hydrocarbon measurement. This is consistent with our model calculations that satisfactorily predict the photochemical production and diurnal variation of O_3 (Fehsenfeld et al., 1983). The presence of non-methane hydrocarbons increases the calculated ozone photochemical production by a factor of more than two when NO_x is greater that 2 ppb. However, the hydrocarbons have little effect on the calculated OH density because they tend to recycle OH. Production of ozone is not observed when NO_x is less than 0.5 ppb. This is consistent with the result obtained by a 3-dimensional GCM simulation of tropospheric ozone in a collaborative effort with scientists at GFDL (Levy et al. 1983).

Middle Atmosphere

Chemical-dynamical model studies of the middle atmosphere have continued, with an increased focus on the photochemistry of ozone and NO_2 in the stratosphere. These studies have been performed in collaboration with Rolando Garcia of the National Center for Atmospheric Research, using a two dimensional residual Eulerian model which extends from 16 to 116 km altitude, from pole to pole. The advantage of the residual Eulerian framework can be summarized as follows: it can be shown that when the classical Eulerian mean and eddy transports are computed self-consistently, a large cancellation occurs such that the remaining net transport in the stratosphere is a small residual. Problems arise in many photochemical models because neither of the two terms is computed at all; rather the eddy transports are parameterized by eddy diffusion coefficients and the mean circulation is taken from a dynamical model study. Thus the eddy coefficients may not be consistent with the adopted mean circulation. Recent dynamical studies have shown that many of these problems can be avoided by using the residual Eulérian circulation, which represents the desired net residual directly. Although certain assumptions are inherent in the residual Eulerian approach as well, at least the correct qualitative sense of the transport should result from such a formulation. Garcia and Solomon (1983) present a detailed description of the present model.

A stratospheric species which is strongly influenced by transport processes is NO_2. We have found that the use of the residual Eulerian circulation has important effects on the computed NO_2 distribution. We have also employed new temperature dependent absorption cross sections for N_2O_5. It has been shown that the present study is in good agreement with many of the observed features of the behavior of stratospheric NO_2 (Solomon and Garcia, 1983a). During winter at high latitude, extremely sharp gradients in the total column of NO_2 are sometimes observed, and this is sometimes referred to as a Noxon "cliff", first observed by John Noxon of the Optical Aeronomy group in 1977. We have conducted a theoretical study of the phenomenon, and have shown that it is probably due in large part to the conversion of NO_2 to N_2O_5 in the polar night region. In particular, we have shown that the complete dynamical-chemical history of the air parcels under observation must be considered, expecially in high latitude winter where the presence of planetary waves leads to unusually rapid meridional flow, transporting air parcels out of the polar night, where NO_2 has been converted to N_2O_5, to lower latitudes. The observed and calculated abundance of NO_2 in such parcels is then found to be unusually low. Figure 2 presents a comparison of total column observations by Noxon in February, 1977, with model calculations including these effects. Many of the previously unexplained features of the "cliff" phenomenon are clearly consistent with the present study (Solomon and Garcia, 1983b).

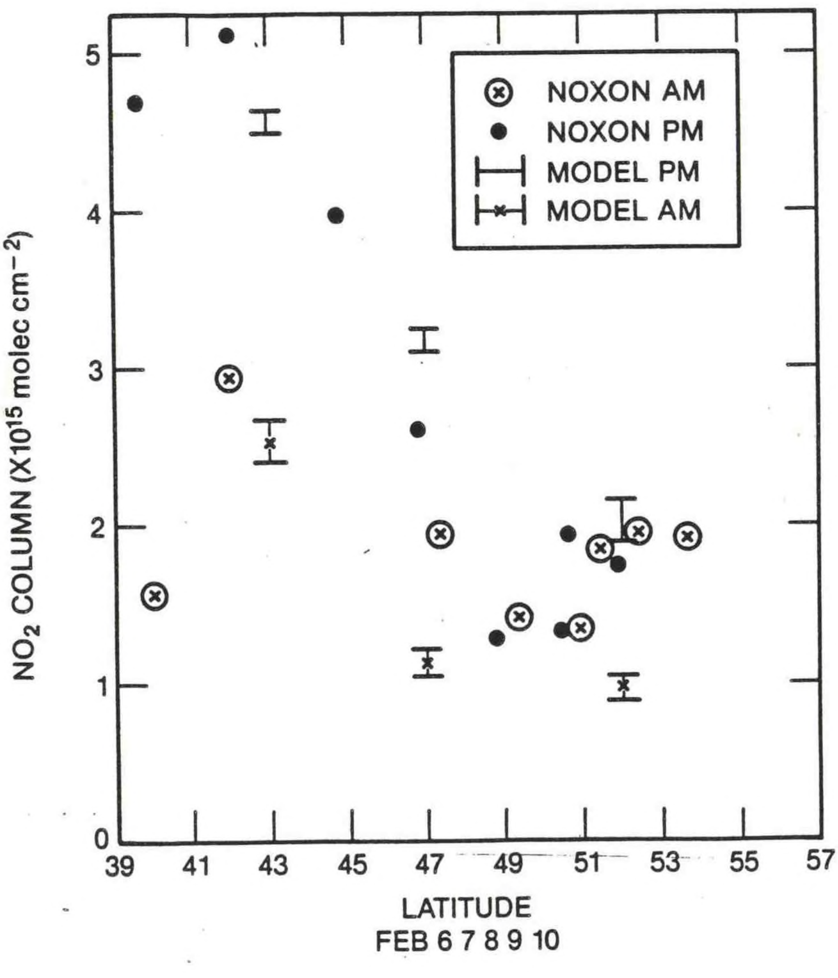


Figure 2. Total NO_2 column - observations and theory.

We have also conducted a study of the 11-year solar cycle using this model. Likely variations in auroral particle precipitation, extreme ultraviolet, middle ultraviolet, and visible radiation, have been considered. We have then examined the photochemical and dynamical responses to these perturbations (Garcia et al., 1983). A most interesting result of this study was that the increased auroral particle and EUV flux changes led to greatly enhance thermospheric NO densities. In the polar night region, NO was found to flow down to the upper stratosphere, resulting in a decrease in high latitude upper stratospheric ozone abundances in the theoretical model, particularly at solar maximum. An analysis of available satellite ozone data exhibits several features which support this conclusion (Solomon and Garcia, 1983c), suggesting that coupling between the thermosphere and stratosphere may have interesting consequences for stratospheric ozone at high latitudes.

Collaborative work with scientists at the University of Colorado on the Solar Mesosphere Explorer (SME) satellite has continued. A comparative study of the calculated and observed ozone abundances in the mesosphere during quiet conditions has been performed (Solomon et al., 1983a). On July 13, 1982 an extremely intense solar proton event occurred. Such events are expected to produce large amounts of odd hydrogen in the mesosphere, a species which catalytically destroys ozone there. Therefore, significant ozone changes are expected to occur in the mesosphere under these conditions. Observations of these changes provide an important test of the present understanding of ozone photochemistry, both in the mesosphere and in the stratosphere. The front cover of this document displays a comparison of the ozone changes observed by SME versus those calculated with our theoretical model. The good agreement obtained in this study (Solomon et al., 1983b) indicates that the response of mesospheric ozone to an impulsive injection of odd hydrogen is similar to theoretical predictions.

Atmospheric Dynamics and Climate

Work on the interannual variability of the height of the tropopause in the western equatorial Pacific Ocean has continued using a data base of radiosonde profiles obtained from the National Climatic Data Center. This work is carried out jointly with the Atmospheric Dynamics program. The main emphasis has been on examining the global nature of the interannual variation by comparing the western Pacific data with data from other tropical locations and on searching for significant periodicities. Three stations with long data bases have been used - Yap (10°N, 138°E), Curacao (12°N, 69°W), and Ascension (8°S, 14°W). The principal results are:

(1) the tropopause over Yap is almost always higher and colder than that over the other stations;
(2) the interannual variations are extremely well correlated over the entire period examined (29 years at Yap, 27 years at Curacao, 13 years at Ascension);
(3) the principal periods are close to 2 and 4 years.

The significance of each of these results is as follows:

(1) the adiabatic ascent of upper tropospheric and lower stratospheric air forming the rising branch of the Hadley cell is more intense in the western Pacific than in the eastern or western tropical Atlantic, probably reflecting warmer sea-surface temperatures and enhanced convective activity;

(2) the interannual variations are a manifestation of a truly global phenomenon Yap and Ascension are separated by 23000 kilometers, and are in separate oceans and different hemispheres;

(3) the periods are close to those of the stratospheric quasi-biennial oscillation and the tropospheric Southern Oscillation respectively, suggesting a physical link between these mysterious features of the tropical atmosphere.

A separate study has been made of the response of the tropical Pacific tropopause to the injection of stratospheric aerosols by the El Chichon volcanic explosion in the spring of 1982. Preliminary results have indicated that the increase in temperature in the lower stratosphere caused by the absorption of solar radiation by the volcanic material was largely compensated by increased adiabatic cooling due to the enhanced tropospheric convective activity associated with the great oceanic warming event (El Nino) of 1982-83. If the two phenomena were in fact unrelated, this conspiracy between El Chichon and El Nino must rank as one of the most curious climatic coincidences of recent times.

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. 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 will consist of a mesoscale meteorological model and a photochemical model. It is clear that such a model can be readily applied to study regional oxidant probles such as that of rural O_3. This model will be developed in collaboration with scientists at NCAR.

Middle Atmosphere

The interaction of dynamics and chemistry in the middle atmosphere represents an important part of our understanding of aeronomy, particularly under the influence of chlorofluorocarbons or other external perturbations. We plan to continue to develop our dynamical-chemical model in order to study both the natural and the perturbed stratosphere. Chlorocarbon chemistry is being incorportated into the model, and we are also studying the effects of turbulence produced by breaking planetary and gravity waves. The continued refinement of these and other aspects of the physics and chemistry of the model is expected to lead to a more detailed understanding of the stratosphere and mesosphere.

Atmospheric Dynamics and Climate

Cooperative work with the Atmospheric Dynamics program on the variability of the tropical tropopause will continue, with emphasis on some aspects that have not been adequately considered in the past. These include the relationship between the height of the tropical tropopause and the global angular momentum of the atmosphere, an analysis of the physical mechanisms underlying tropopause formation, and a study of the implications of a varying tropopause height and temperature for stratospheric composition and for the earth's radiation budget.

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M. J. Bollinger, S. C. Liu, D. D. Parrish, M. McFarland, F. C. Fehsenfeld, M. Trainer, D. Kley, P. C. Murphy, D. L. Albritton, and D. H. Lenchow, A study of ozone in the Colorado mountains, J. Atmos. Chem., 1983.

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ATMOSPHERIC WAVE AND TURBULENCE THEORY PROGRAM

Permanent Technical Staff

Jerome Weinstock, Program Leader	Physicist
DeeAnna Doerfler	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 resonse 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 ionsphere, 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 non-linear 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 is being 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.

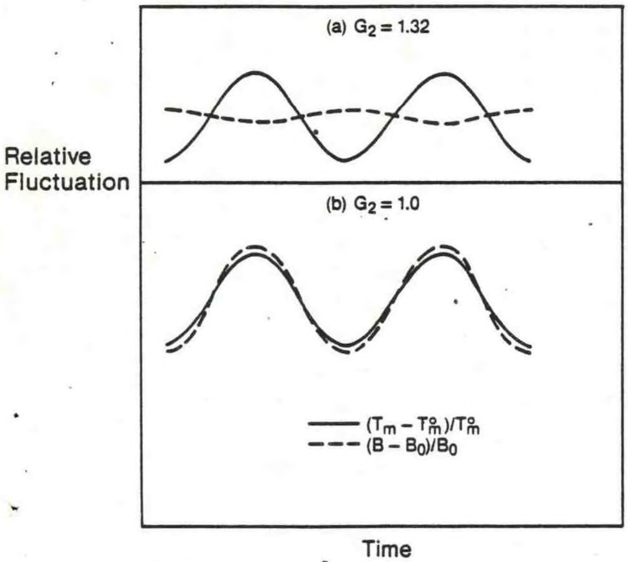

Figure 1. Theoretical ratio of $O_2(^1\Sigma)$ brightness fluctuations $B - B_0$ to temperature fluctuations $T_m - T_m^o$ for (a) large amplitude gravity waves and (b) small amplitude gravity waves. Both kinds of ratios are observed (Noxon, 1978).

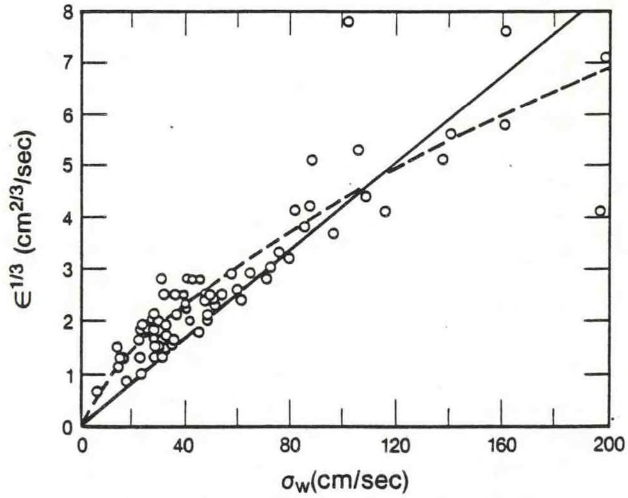

Figure 2. Turbulence dissipation rate ε versus vertical RMS velocity σ_w. A preliminary theory is given by the dashed line -----. The observations in the stratosphere are given by circles O.

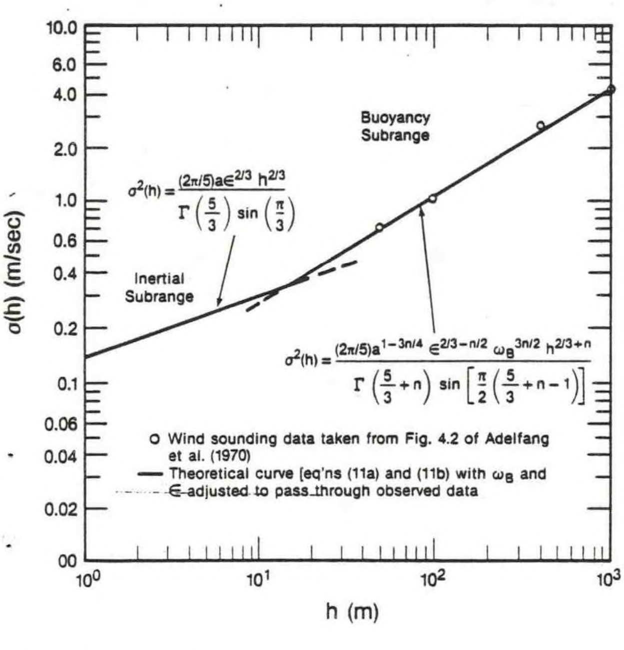

Figure 3. Turbulence RMS energy $\sigma(h)$ versus layer thickness h. Our theoretical prediction is given by the solid lines ——, and the observations from rockets and balloons are given by the circles O. Layer thickness less than 50m are not adequately resolved by balloons or rockets, and their turbulence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

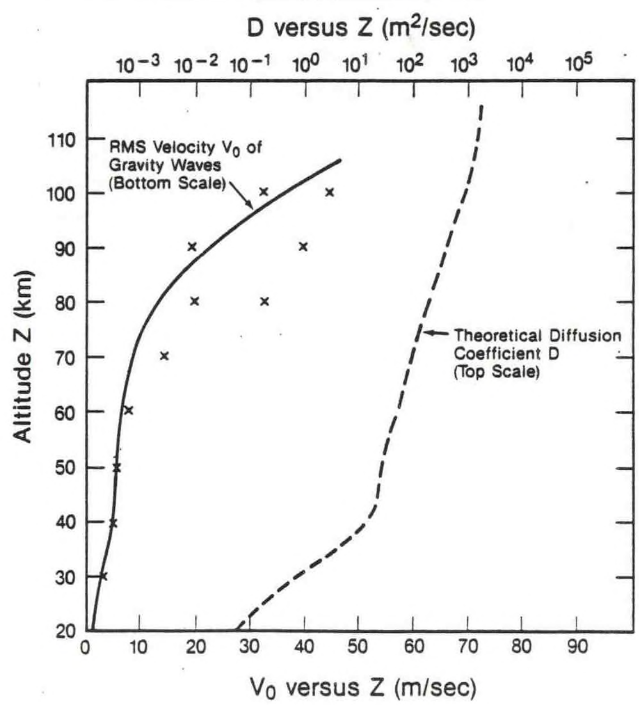

Figure 4. Theoretical curves of RMS gravity wave velocity V_o and diffusion coefficient D versus altitude Z. The small crosses are observed values of V_o.

(8) A theoretical determination was made of the turbulent diffusivity in neutral as well as stable layers of oceans (moderate as well as large Cox number). This calculation was made to explain recent measurements in the oceans by Caldwell et al. (J. Geophys. Res., 1980).

(9) 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 develpment of turbulence along the direction of the main flow, a result that was unexpected and that could explain some observations by Wyngaard (1979).

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, with practical applications, which are included 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 will continue 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 shear instabilities.

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

(d) Deduction of the turbulence state in the lower atmosphere from Sunset 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 theormosphere.

(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 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) 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 flucturations 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 circulation;

(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 conditions. 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.

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ATMOSPHERIC SAMPLING PROGRAM

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ATMOSPHERIC SAMPLING

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 to policy formation regarding these pollutants but also to serve 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, in particular, Theoretical Aeronomy and Optical Aeronomy.

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 a factor in regulating stratospheric and tropospheric chemistry and climate, and

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

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

Recent investigations undertaken by the Group are summarized below.

Stratospheric Studies

The temperature increases with altitude in the stratosphere because of ozone photochemistry. As a result of this temperature inversion, there is very slow vertical mixing. In addition, the stratosphere is very dry and cloud free, and rain, a significant cleansing agent in the troposphere, is absent. Consequently, compounds are only slowly transported to the stratosphere, but, once there, they can remain so for a very long time. Thus, there is great importance attached to the understanding of the photochemical fate of the chemicals that are transported to the stratosphere. This has been a very active area of atmospheric research over the last decade. The Group's research emphasis in this regard has been the detection of trace constituents that play key roles in stratospheric photochemistry and the use of these data to test and further develop the understanding of these processes. Examples are given in the following sections.

1. Water vapor measurements. Stratospheric H_2O concentrations figure directly into the photochemistry of this region. Water vapor is the source of the reactive odd-hydrogen species in this region. Furthermore, water vapor is formed by the oxidation of methane in the stratosphere. Hence, water vapor measurements can reveal several aspects of stratospheric photochemistry.

With the goal of using H_2O as a window into these photochemical processes, a balloon-borne, fast-response, self-calibrating instrument for the *in-situ* measurement of stratospheric H_2O was designed, developed, and flown. The technique employs ultraviolet photodissociation of H_2O to form an excited OH product, whose de-exciting radiation is detected. The detection limit is twenty times greater than minimum stratospheric H_2O concentrations; therefore, the measurement precision is extremely good. The rapid response time yields an unequaled altitude resolution of 50 m. Since 1978, there have been numerous successful flights from Wyoming, Texas, and Brazil, the results of which have already contributed significantly toward the understanding of stratospheric photochemistry.

Almost all of the flights have found that the stratospheric H_2O concentrations have a minimum just above the tropopause and increase with increasing altitude. Moreover, a comparison of the Wyoming flights with the Brazil flight suggests that stratospheric H_2O increases meridionally from the tropics to midlatitudes. Both of these observed vertical and meridional increases are consistent with a stratospheric source of H_2O, such as the oxidation of methane.

The fast response of the instrument has revealed a rich structure in the H_2O profile, which is reproduced from ascent to descent. This indicates that the structure is relatively long lived in both time and space. These data, with accompanying fast-response ozone measurements, are providing considerable insight into atmospheric microdynamics.

2. <u>NO and NO_2 measurements</u>. Stratospheric NO plays a key photochemical role in establishing the ambient ozone levels in this region. Furthermore, NO_2 is also a major intermediate species in this photochemistry. Simultaneous in-situ NO and NO_2 measurements can provide tests of our understanding of the photochemistry.

The first of such measurements have been made by the Group in collaboration with the National Center for Atmospheric Research, using a balloon instrument that employs chemiluminescent/photolytic detection of NO and NO_2. Simultaneous measurements of ozone concentrations were made on the same gondola using a UV-absorption instrument.

The experiment has been flown four times. NO and NO_2 mixing ratios were measured during flights from Palestine, Texas (Nov., 1981; July, 1982) and Gimli, Manitoba, Canada (Aug., 1982). Only mixing ratios for NO were obtained from the flight launched from Gimli in December, 1982. These flights produced the first in-situ measurements of NO_2 mixing ratios in the stratosphere. Ozone concentration profiles were also measured during all of these flights.

The NO and NO_2 mixing ratios agree reasonably well, given normal atmospheric variability, with previous determinations of NO (in-situ) and NO_2 (long-path) in the stratosphere (c.f. "Stratosphere 1981: Theory and Measurements", WMO Rept. #11, Stratospheric Physics and Chemistry Branch, Code 963, NASA Goddard Space Flight Center, Greenbelt, MD 20771). In addition, the measured $[NO_2]/[NO]$ ratio altitude profiles for the Palestine (Nov., 1981) and Gimli (Aug., 1982) flights agree with theoretical predictions of those ratios. However, the measured $[NO_2]/[NO]$ ratio altitude profile from Palestine (July, 1982) is smaller than theoretical predictions of this ratio above 30 km and larger than theory below 21 km. We presently speculate that enhanced stratospheric aerosols concentration, produced by the El Chichon eruption, caused significant UV scattering, increasing NO_2 photodissociation above 30 km and reducing the NO_2 photodissociation below 21 km relative to normal expectations. Finally, the NO mixing ratio profile measured from Gimli (Dec., 1982) indicated that the NO mixing ratio increased sharply between 25 and 30 km. This observation supports the Solomon-Garcia model for the Noxon NO_2 "cliff" (c.f. Solomon and Garcia, JGR, 88, 5497, 1983; Noxon, JGR, 84, 5067, 1979; Noxon, GRL, 5, 11021, 1978) that predicts such strong photochemistry and transport induced gradients of the concentrations of NO and NO_2 in northern latitudes at these altitudes during the winter.

Tropospheric Studies

In recent years, the effort of the Group has been drawn to studies of tropospheric chemistry and ozone has been a focal point. This constituent is a principal oxidant and, as a precursor to the hydroxyl radical OH in the rural and remote troposphere, it is a controlling factor in tropospheric chemistry. Furthermore, ozone is a "greenhouse" molecule in the troposphere and, like that of CO_2, its global budget influences the temperature at the earth's surface. Lastly, ozone is an important secondary pollutant, harmful to both plants and animals.

Although the origin of ozone in the troposphere is currently a subject of considerable debate, there is general agreement that the oxides of nitrogen play a key role in the production of ozone in this region. In addition, the oxides of nitrogen are precursors to nitric acid, which is one of the two principal acids in acid deposition. Over the past years, the Group has developed a unique capacity to measure the oxides of nitrogen at very low concentrations. These, along with other sensitive techniques, are being applied to several pressing questions in tropospheric chemistry. A few examples are summarized here.

1. Niwot Ridge research site. The Group maintains and operates a permanent field station at a remote site at the 10,000 ft level on Niwot Ridge, near the Continental Divide, in a biopreserve administered by the Arctic and Alpine Research Institute of the University of Colorado. The location has the valuable feature that, depending on wind direction, the site can be used to examine the photochemistry of clean continental air, or it can offer the opportunity to study the chemistry of relatively polluted air.

Because of the unique facilities and location of the Niwot Ridge site, it has been designated by the National Acid Precipitation Assessment Program as one of their three acid precipitation research sites, where research is conducted on measurement methodologies and special regional and local acid rain problems. The goals of the Niwot Ridge site are:

(a) To determine the likely origins of the acidity observed in the rainfall in the remote mountain areas of the Colorado Front Range, a point of current controversy.

(b) To identify and quantify the significant contributions to the acidity in precipitation at Niwot Ridge and their gas-phase precursors.

(c) To establish the diurnal and seasonal variations of the above constituents.

(d) To maintain a year-round-accessible field-laboratory site that is sufficiently equipped and supplied to conduct instrument and technique development as required and to carry out other special monitoring research.

Several of the tropospheric studies and instrument development described below employed the Niwot Ridge research site.

2. Tropospheric ozone studies. The seasonal and diurnal variations of ozone mixing ratios have been measured at Niwot Ridge. These data have been correlated with the NO_x ($NO + NO_2$) mixing ratios measured concurrently at the site. The seasonal and diurnal variations in O_3 can be reasonably well understood by considering photochemistry and transport. In the winter there is no apparent systematic diurnal variation in the O_3 mixing ratio because there is little diurnal change of transport and there is a slow photochemistry. In the summer the O_3 levels at the site are suppressed at night due to the presence of a nocturnal inversion layer that isolates ozone near the surface, where it is destroyed. Ozone is observed to increase in the summer during the day. The increases in ozone correlate with increasing NO_x levels, as well as with the levels of other compounds of anthropogenic origin. This correlation is interpreted as *in-situ* or in-transit photochemical production of ozone from these precursors that are transported to the site. The levels of ozone recorded approach 100 ppbv at NO_x mixing ratios of approximately 3 ppbv. Calculations made using a simple clean-tropospheric chemical model are consistent with the NO_x-related trend observed for the daytime ozone mixing ratio. However, the chemistry, which does not include non-methane hydrocarbon photochemistry, underestimates the observed ozone production. These statements are illustrated in Figure 1, in which the ozone concentration observed during the peak period in ozone production, 1600 hours to 1900 hours during the summer, is given as a function of the NO_x ($NO + NO_2$) concentration. The symbols, X, represent 2 min. averages of the measured ozone concentration, while the hatched area represents the O_3 mixing ratios calculated by the Liu model (c.f. Liu et al., JGR, 85, 7546, 1980) that neglects non-methane hydrocarbons.

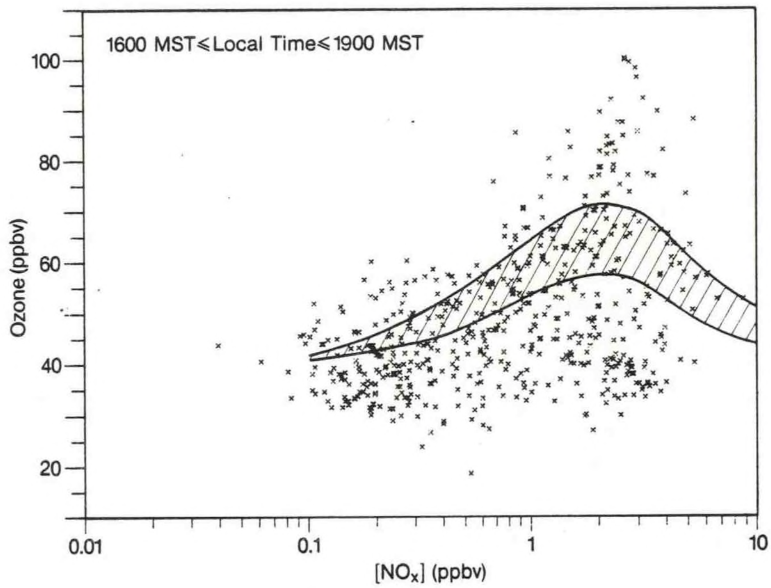

Fig. 1. Plot of ozone mixing ratio vs NO_x mixing ratio observed between 1600 and 1900 MST and between May 1 and August 31, 1981. Each symbol represents a 2-min average of the ozone mixing ratio made at the time of an NO_x determination. For comparison, the O_3 mixing ratios calculated by a model (c.f. Liu et al., JGR, <u>85</u>, 7546, 1980) that neglects non-methane hydrocarbons are shown as the shaded area.

3. <u>Systematics of aromatic hydrocarbon concentrations</u>. Measurements of the aromatic hydrocarbons -- benzene, toluene, ethylbenzene and ortho-xylene -- at Niwot Ridge have shown distinct correlations between the ratios of the concentrations of these compounds and the degree of direct urban influence, as indicated by NO_x ($NO + NO_2$) concentration. Reported measurements of aromatic compounds in urban areas of North America have yielded surprisingly consistent ratios of aromatic hydrocarbons. The major homogeneous atmospheric removal mechanism of aromatic hydrocarbons is reaction with the hydroxyl radical, OH. This allows the decrease in the ratios of aromatic hydrocarbon concentrations, which are independent of dilution, to be related to the transport time and average OH number density of an air mass, if it is assumed that free tropospheric concentrations of aromatic compounds are negligible and there exist no significant heterogeneous removal mechanisms. Measured ratios of aromatic compounds at this site, along with ratios reported for several cities in the western United States, and estimates of transport times from these cities were used to calculate temporally and spatially averaged OH number densities. Air mass trajectories were calculated to obtain transport times of urban air parcels from the west coast of North America to the

sampling site. Hydroxyl radical number density estimates using toluene-, ethylbenzene-, and ortho-xylene-to-benzene ratio yield diurnally averaged values of about 10^6 molecules/cm^3:

toluene/benzene	$(1.0 \pm 0.6) \times 10^6$
ethylbenzene/benzene	$(1.0 \pm 0.8) \times 10^6$
orthoxylene/benzene	$(0.45 \pm 0.8) \times 10^6$

This approach offers a technique to understand the photochemistry and/or sources of atmospherically important non-aromatic hydrocarbons as well. For example, the ratio of NO_x-to-benzene was found to yield no correlation with toluene-to-benzene ratio for periods of westerly air movements, but was well correlated with toluene-to-benzene ratio during periods of direct urban impact on the site (upslope easterly winds). The correlation of these ratios in urban plume air masses was consistent with $NO_2 + OH + M$ being the major daytime removal mechanism of NO_x in the summertime.

4. Oxalate observations. The precipitation samples and the aerosols collected with filters at the Niwot Ridge site have been examined for acids other than sulfate and nitrate. The existence of oxalate, $(COO)_2^{=}$, in both types of samples has been demonstrated using ion chromatography. Mixing ratios have been observed up to 50 pptv in air samples and 0.3 ppm in precipitation. This is apparently the first identification of tropospheric oxalate. Correlation of airborne oxalate with airborne nitrate suggests a pollution source.

5. Global nitrate deposition from lightning. Lightning has been long-recognized to be a natural source of NO_x. The current source-strength values are calculated from estimated nitrogen production per stroke, stroke frequency, and spatial distribution, which are difficult to quantify accurately. The predictions of these lightning/nitrogen models have been assessed in the following way. The nitrate deposition fluxes predicted by the lightning model are compared to measurements of (a) the current nitrate deposition occurring in remote areas and (b) the preindustrial nitrate deposition.

The remote-area data include those measured at Samoa, deduced from Hawaii and Amsterdam Island precipitation, obtained from South Pole ice cores, and inferred from our own South Pacific studies. The preindustrial data are from pre-1900 levels in South Pole and Greenland ice cores.

The resulting global distribution of nitrate fluxes agrees well with that predicted by the lightning model. Furthermore, the observed seasonal variations are consistent with the maximum lightning occurrence in the summertime. This agreement points to lightning as probably the major source of nitrate in remote areas and permits a meaningful estimate of the lightning contribution to nitrate deposition over North America: 5 to 10% of the anthropogenic NO_x emissions, with a current uncertainty of a factor of 3.

Tropospheric/Stratospheric Exchange Studies

The chlorofluorocarbon threat to the stratosphere demonstrated that compounds generated in the troposphere can have potentially great impact on the stratosphere. The reverse is also true. The oxides of nitrogen produced in the stratosphere appear to be responsible for the generation of a significant fraction of the tropospheric ozone in remote areas. The details of this coupling between the two regions of the atmosphere are poorly understood at present. Yet, an understanding of this phenomenon is important for a clearer picture of global photochemistry and climate. Therefore, tropospheric/stratospheric exchange studies have taken on a special importance in the Group's activities.

1. Water vapor tracer studies. Water vapor serves as an excellent tracer of tropospheric/stratospheric exchange and transport processes. The reason for this is that the vapor pressure of H_2O at the tropopause is established by the tropopause temperature. Thus, a given stratospheric H_2O concentration reflects the temperature of the tropopause through which this H_2O entered the stratosphere. Furthermore, since the tropopause temperature varies with latitude, the stratospheric H_2O concentration at a given latitude identifies the location where this water vapor entered the stratosphere; hence, H_2O measurements can reveal global transport paths.

The H_2O detector has been redesigned to operate in the daytime. The first application of this new design has been built into an instrument that is carried aboard NASA's U2 aircraft, which flies up to 21 km. This research platform offers several hours flight time at many global locations. The first application was in Panama in the late summer of 1980. This mission explored tropical tropospheric/stratospheric exchange processes.

Some of the results of the ten Panama flights are given in Figure 2. The x's are the H_2O mixing ratios measured during the descents of the U2 aircraft from 21 km to 12 km. All of these data reflect the background H_2O levels, since none of the descents penetrated clouds. The solid lines give the temperature profile observed on the descents. The tropopause can be identified at 15 km.

Two features of the average H_2O profile are noteworthy. The first is the "bulge" in the mixing ratios that occur at 17 km, just above the tropopause. The mixing ratio in the bulge is about 7 ppmv, which is the equilibrium mixing ratio of vapor over ice at the observed minimum temperature. Therefore, the bulge is interpreted as evaporation of ice crystals brought to these altitudes by tropopause-overshooting cumulonimbus clouds. Hence, such clouds appear to be able to hydrate the lower stratosphere.

The second feature that draws attention is the minimum observed in the H_2O mixing ratio at 18-19 km. A mechanism that can cause such a minimum has been proposed and is the following. Hydrating clouds can reach

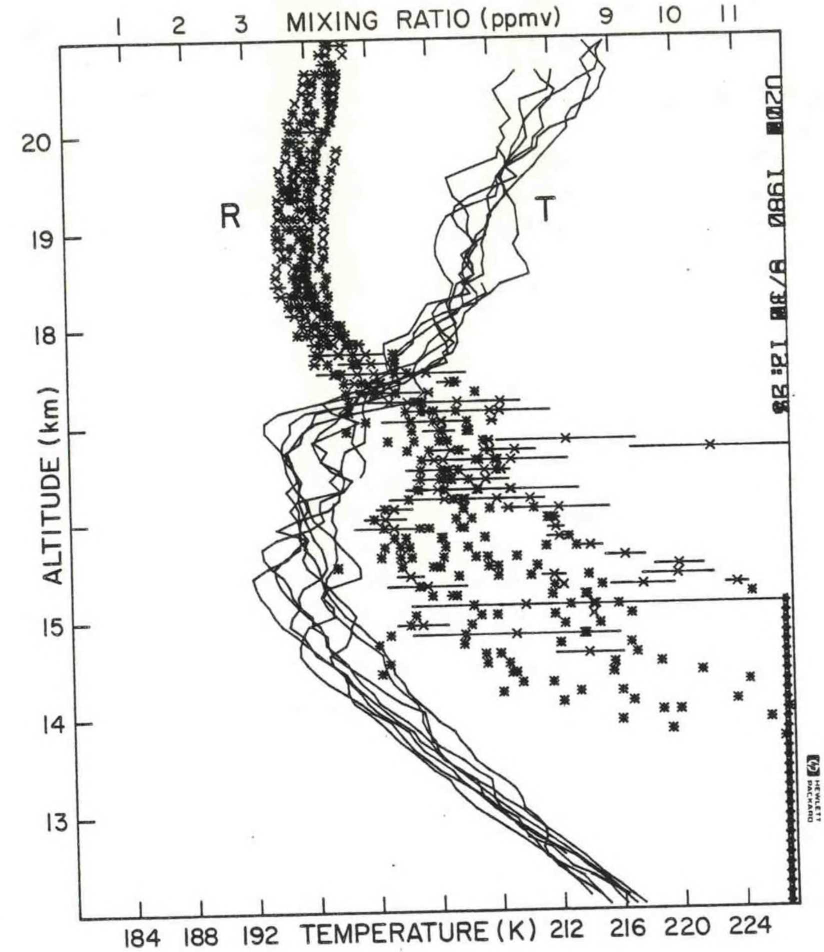

Fig. 2. H_2O mixing ratios (x) and temperatures (solid line) obtained during the descents of the U2 research aircraft over Panama in late summer, 1980. From Kley, Schmeltekopf, Kelly, Winkler, Thompson, and McFarland (1982).

different heights over different areas of the tropical zone. Different heights imply different temperatures at the heights of the cloud tops: the higher the clouds go, the lower will be the temperature of the air mixture, and, therefore, the saturation mixing ratios will be lower as well. The conjecture is that the negative water gradient and the minimum observed over Brazil and Panama are the results of injections of water at very low saturation mixing ratios somewhere else. Since the lower stratospheric flow is mainly zonal, a water profile taken over Panama will show large mixing ratios from local and regional hydration above, but close to, 17 km. Higher up, the zonal flow will provide air with lower mixing ratios from injections at higher altitudes in other areas. A negative gradient will result. Clouds apparently can reach 19 km over Micronesia and this has been identified as the likely source of the low mixing ratios observed over Panama. This mechanism has generated considerable interest and field programs that could test it are being designed.

Instrument Development

At the heart of all the field studies summarized above is a state-of-the-art detection system. The development of the new instrumentation that can address such trace-gas measurements with the required accuracy and precision has been a hallmark of the Group's activities. The initial focus of this development was chromatographic techniques that could detect sub-ppbv levels of chlorofluoromethanes in stratospheric air samples. Later, balloon- and aircraft-borne detectors for water vapor and NO and NO_2 were developed. The growing interest in tropospheric chemistry led to the need to measure trace levels of nitric acid, ammonia, nitrates, sulfates, sulfur compounds, and radicals. Spectroscopic, laser-induced emission, filter-collector, chromatographic, and other methods are currently being applied to these needs. Summaries are given here of a few of these development programs.

1. Aircraft NO instrument. A new-generation chemiluminescence NO instrument is being developed in collaboration with the National Center for Atmospheric Research. This aircraft instrument is designed for rapid-response NO measurements at the parts-per-trillion level in the boundary layer, in clouds, and in the free troposphere. Recently, the instrument was intercompared with another chemiluminescence instrument and a laser-induced-fluorescence technique at Wallops Island, Virginia. This rigorous, triple-blind intercomparison, sponsored by NASA, showed that the three instruments could obtain NO data that agreed within ± 20% over a wide range of concentrations. The excellent comparison between the laser-induced-fluorescence and chemiluminescence methods, done there for the first time, is particularly valuable, since it strongly suggests that the markedly different methods are free from artifacts and/or interferences. The aircraft NO instrument is presently being installed in NASA's CV-990 aircraft to take part in their Global Tropospheric Experiment.

2. Total odd-nitrogen detector. A new technique has been developed for the real-time, quantitative conversion of the sum of the atmospheric odd-nitrogen species, NO_y, to NO. The technique utilizes the reduction of these compounds by CO at a heated gold catalyst to yield NO. This product is then detected by the sensitive chemiluminescence detectors for NO developed in this laboratory. The technique has been demonstrated to convert NO_2, HNO_3, and n-propyl nitrate quantitatively to NO for mixing ratios in the range of 1-120 ppbv in synthetic air at atmospheric pressure. Conversion results were obtained for CO mixing ratios in the range of 0.2-1000 ppmv and for temperatures in the range of 20-600°C.

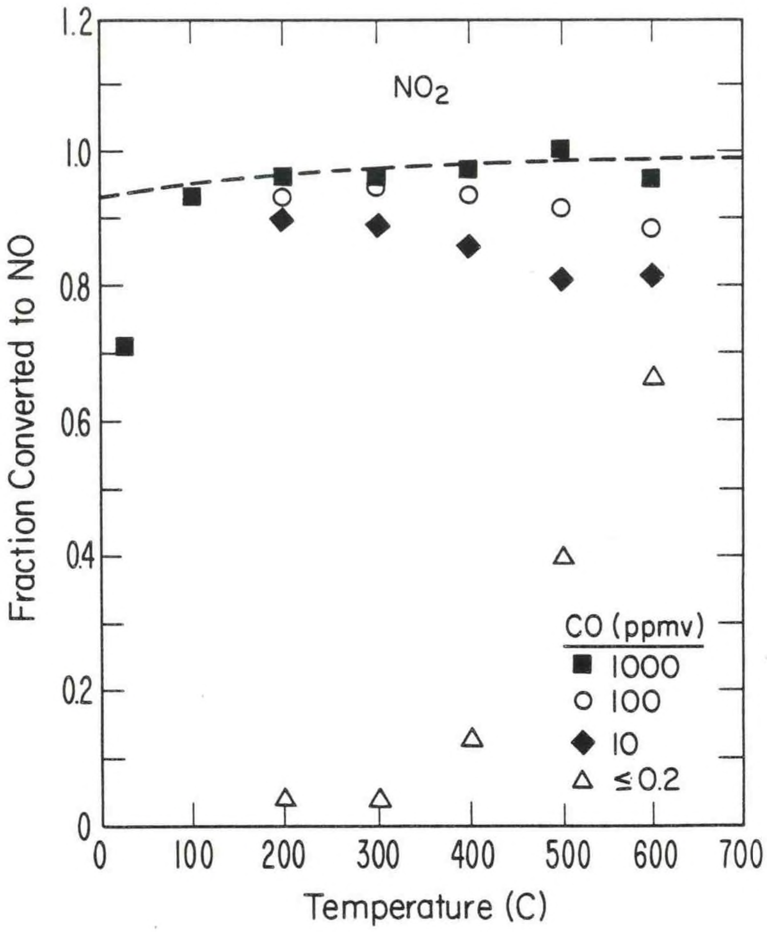

Fig. 3. Fraction of NO_2 converted to NO as a function of temperature in the Au-coated converter tube. Symbols correspond to the CO concentration in an air sample flow of 1 slpm. The fractions calculated with the Gormley-Kennedy equation are given by the dashed line.

Figure 3 illustrates the operation of the device. In this figure, the fraction of NO_2 converted to NO for various CO concentrations, denoted by the various symbols, are plotted as a function of temperature. The dashed line indicates the predicted behavior for a converter of this geometry assuming each NO_2 molecule that contacts the tube wall (diffusion limited) is converted. It is clear that, for large CO concentrations, the conversion of NO_2 to NO occurs at high efficiency, even at low temperatures. As the concentration of the CO, used as the reducing agent, is decreased, the conversion efficiency rapidly drops (most noticeably at low temperatures). Similar results were obtained for HNO_3 and n-propyl nitrate. Surfaces, other than gold, were found to be far less effective.

The capability to detect a variety of NO_y compounds (NO_2, HNO_3, N_2O_5, NO_3, PAN) in this way opens up attractive prospects for determining tropospheric and stratospheric odd-nitrogen budgets and provides an additional tool to investigate tropospheric/stratospheric exchange mechanisms.

3. Stratospheric ozone instrument. A new dual-beam UV-absorption instrument for balloon-borne measurements of atmospheric ozone has been developed. It has two identical absorption chambers, each alternating between reference mode (ozone free) and sample mode by means of a four-port valve and ozone scrubber. The ratio of the absorption signals, along with the known lengths and ozone absorption cross section, yield the ozone concentration. The dual-beam feature cancels the effects of lamp intensity fluctuations, while the mode alternation compensates for mechanical changes and also provides continuous measurements. The absorption measurement requires no calibration and hence is independent of gas flow rate. The response time is 1 s and, for this measurement duration, the minimum ozone concentration detectable by this instrument (one standard deviation) is 1.5×10^{10} molecules/cm^3 (0.6 ppbv at STP). The overall uncertainty of a 1 s measurement at the ozone maximum (22 km) is 3.6%, where 2% of this is the accuracy of the ozone cross section. The size and weight are suitable for launch by small balloons.

The instrument has been flown six times, accompanying the Group's H_2O and NO/NO_2 experiments. A sample of the ozone height profile obtained on one of these flights is shown in Figure 4. The solid line depicted has been drawn from point to point through the approximately 6500 separate measurements made on the 2-h ascent to reach float. Considerable ozone structure is revealed. In addition to providing ozone data to use in these stratospheric photochemistry and dynamics experiments, the structure in these profile data also gives a good indication of the instrument's very rapid response time. For example, the extremely sharp increase in ozone at 11 km (more than a 200% increase within 90 m) is defined by 20 separate measurements. All of the major variations shown are atmospheric ozone changes, not noise. This response time allows covariation studies to be done in concert with other fast-response instruments to examine atmospheric dynamics.

4. Quantification of nitric acid measurements. A small portable HNO_3 calibration system utilizing a nitric acid permeation tube has been built. The emission from the permeation tube is corrected for a significant amount of NO_2 that appears to be unavoidable as an impurity. The calibration system has been employed to field test the Nylon filter used to collect gas-phase acids. These tests indicate that there are no major analytical problems with the collection, extraction, and analysis procedure we use to measure HNO_3 and that such measurements are a true indication of the HNO_3 loading within +0.1, -0.4 μg at the 60% confidence level. This corresponds to an uncertainty in nitric acid concentration of +5, -20 pptv for a one-hour collection period at a sample flow rate of 120 liters/min. The Group is using these results to guide our measurement strategy and to place appropriate uncertainties on clean-air HNO_3 measurements.

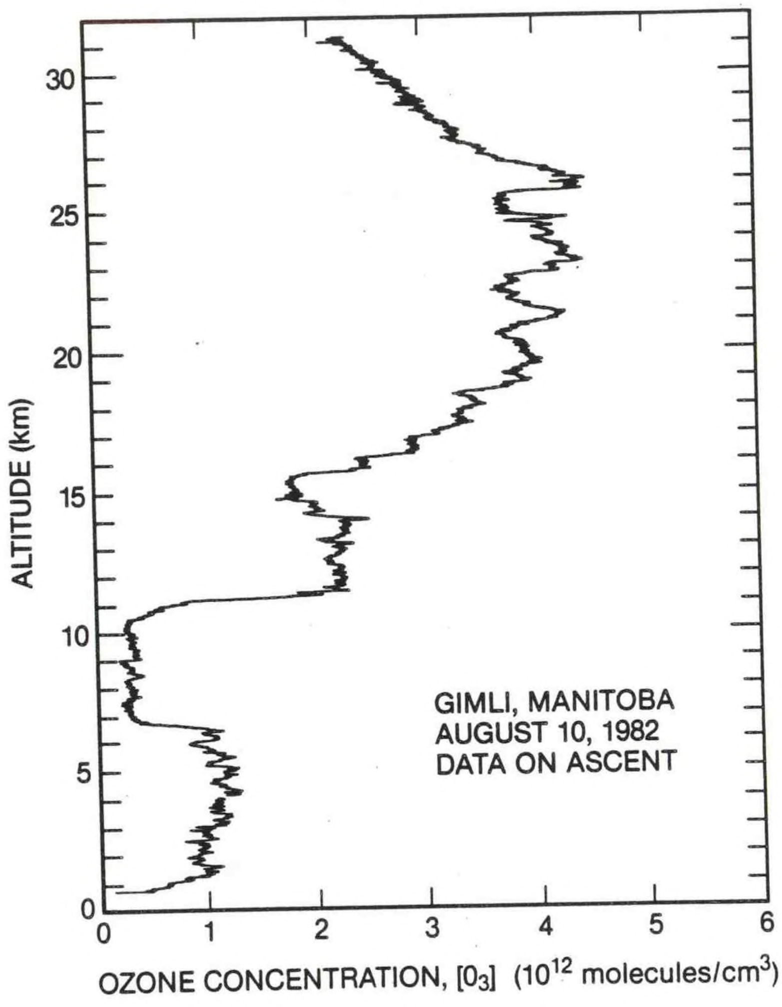

Fig. 4. Ozone height profile on a 2-h ascent taken at a 1-s data rate. The solid line depicted has been drawn from point to point through the approximately 6500 measurements.

Experiments-in-Progress and Future Plans

1. Balloon-borne and U2 H_2O instruments. NASA will sponsor the second intercomparison of stratospheric H_2O instruments in October, 1983, at the National Scientific Balloon Facility in Palestine, Texas. Both of the Atmospheric Sampling Program's H_2O instruments will take part. The agreement among water-vapor measurement techniques on the first flight series in May, 1981, was within ± 30%, but the systematics of the differences prompted laboratory reevaluation of many aspects of the instruments. The Group's Lyman-alpha photofragment fluorescence instrument had

used a published cross section in its analysis. As part of the intercomparison, this cross section was measured. The new value is similar to the earlier datum, but the precision and accuracy is better, thereby improving the data of the instrument.

2. N_2O, $CFCl_3$, and CF_2Cl_2 grab-sampling package. NASA will also sponsor an intercomparison of four techniques for measuring stratospheric N_2O, $CFCl_3$, and CF_2Cl_2 concentrations. These balloon-borne instruments will be launched simultaneously from the National Scientific Balloon Facility in Palestine, Texas in Spring 1984. The Group's grab sampler will be one of the instruments involved.

3. Gas chromatographic detection of sulfur compounds. A cryogenic-trapping/flame-ionization gas-chromatographic system is being developed for the atmospheric sulfur compounds. The laboratory tests are complete and the first field trials are underway at the Niwot Ridge site. The initial aim of this study is to assess the clean-air and polluted levels of gas-phase sulfur in relation to that in precipitation in the mountain area. Intercomparison of calibration standards is underway with the University of Idaho.

4. Diode array spectrometer. 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 of heretofore unobtainable quality. A key part of the procedure is a least-squares data reduction procedure that employs standard spectral relative intensities obtained from laboratory measurements. The system has obtained total-column NO_2 data when it accompanied the stratospheric NO/NO_2 experiment into the field. Now, the system is at Fritz Peak Observatory and will use long-path (approximately 10 km) absorption techniques to examine the photochemistry of several tropospheric species.

5. Ultraviolet ozone instrument. The Group's UV ozone instrument took part in the first flight of the NASA-sponsored Balloon Ozone Intercomparison in the summer of 1983. These data are being assessed for instrument performance characteristics. The second flight of this series is scheduled for October, 1983.

6. H_2O_2 instrument development. An ultraviolet excimer laser is being explored as a detection scheme for hydrogen peroxide, using photofragment fluorescence. Hydrogen peroxide is thought to be a major oxidant of SO_2. Currently, there is no way to reliably detect H_2O_2 in the gas phase.

7. NO flux measurements. The sensitive chemiluminescence detectors for NO available in this laboratory will be used to develop accurate methods to determine the concentrations and fluxes of natural nitrogen compounds and, thereby, to provide the data necessary to estimate contribution of natural sources to the NO/NO_2 budgets.

8. Tungstic acid denuder tube. Work is in progress to evaluate and develop the tungstic acid denuder tube method as a fast-response technique for measuring HNO_3 and NH_3.

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ATMOSPHERIC DYNAMICS PROGRAM

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Introduction

The experimental research of the Atmospheric Dynamics Program is based on the study of the atmosphere by analysis of radar echoes from irregularities in the atmosphere. Backscattered radio waves are preferentially 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 (Balsley and Gage, 1980). 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, and the width of the spectrum is determined partly by the spectrum of turbulent velocities in the volume. Also, the radar reflectivity is proportional to the amplitude of the spectrum of turbulent irregularities of radio refractive index. An example of the echo power 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 make measurements about 1000 times more frequently than routine balloon or rocket observations in the same altitude range. Their much faster cadence of measurement together with their great altitude range make Doppler radar uniquely suited for studying phenomena that vary rapidly in time, such as buoyancy waves (internal gravity waves) and turbulence. They can, of course, also study slowly varying phenomena such as planetary waves and tides.

These capabilities 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.

In order to exploit the capabilities of the MST radar technique, the Program has been pursuing several lines of experimental research: First, in 1973 we started construction of the Sunset VHF pulsed Doppler ST radar near Boulder. This was the first VHF radar designed and constructed specifically for MST radar studies. It continues to be a very useful tool for study of the dynamics of the atmosphere because it is more flexible than our other systems. It has been modified from time to time to keep it in the forefront of radar capabilities.

Second, in 1976 we began exploring the limits of the MST radar technique by using a wide variety of radars with a wide range of frequencies (from 40 to 1300 MHz), geographical locations (from near the equator to the arctic), sensitivities, and configurations. These studies demonstrated that the MST radar technique works throughout this frequency range, at all locations, and that, with a sufficiently powerful radar operating below about 70 MHz, measurements can be made at all heights from near the ground up to about 100 km.

Third, we have designed and constructed the very large Poker Flat MST radar near Fairbanks, Alaska. The configuration of the radar is shown in Fig. 2. Because of its unique design it has been possible to operate it almost continuously since construction began in February 1979. In its completed con-

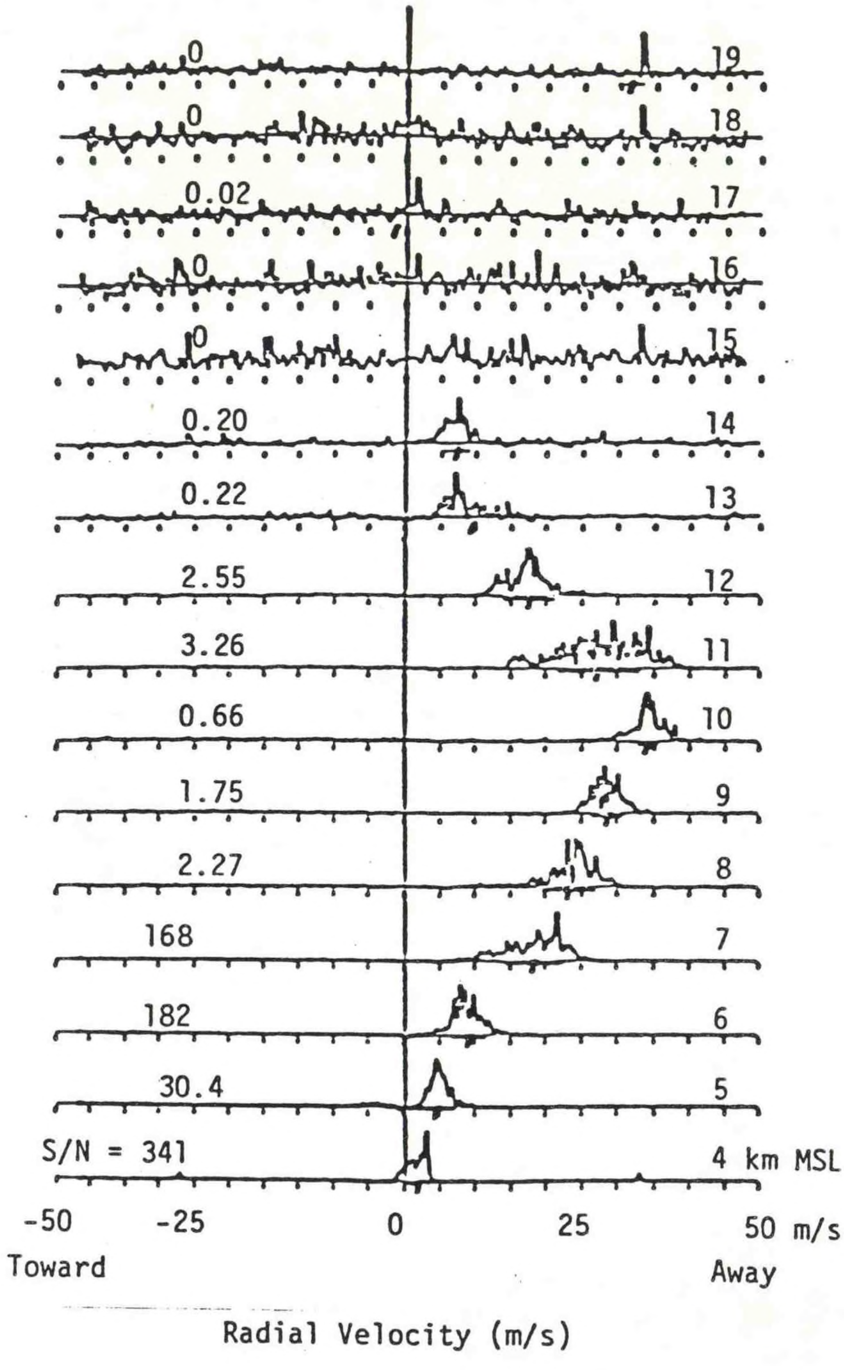


Figure 1. An example of Doppler spectra measured by the Sunset ST radar at 76/04/15 1548.21 75°W time. Each spectrum is a 50-second average over a 1-km height range centered at the height given at the right. These spectra were observed looking 30°N of the zenith. The corresponding horizontal velocities 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)

figuration, when the system goes to full average power, the Poker Flat MST radar will be able to obtain echoes and measure the complete wind and turbulence fields from about 3 km up to about 100 km.

Fourth, in order to increase further our experimental capabilities we cooperated with the Wave Propagation Laboratory to refurbish the Platteville ST radar (originally built by the Aeronomy Laboratory to test the design of the Poker Flat MST radar). Finally, we have developed a portable ST radar system that makes possible campaigns in remote locations to study particular atmospheric phenomena.

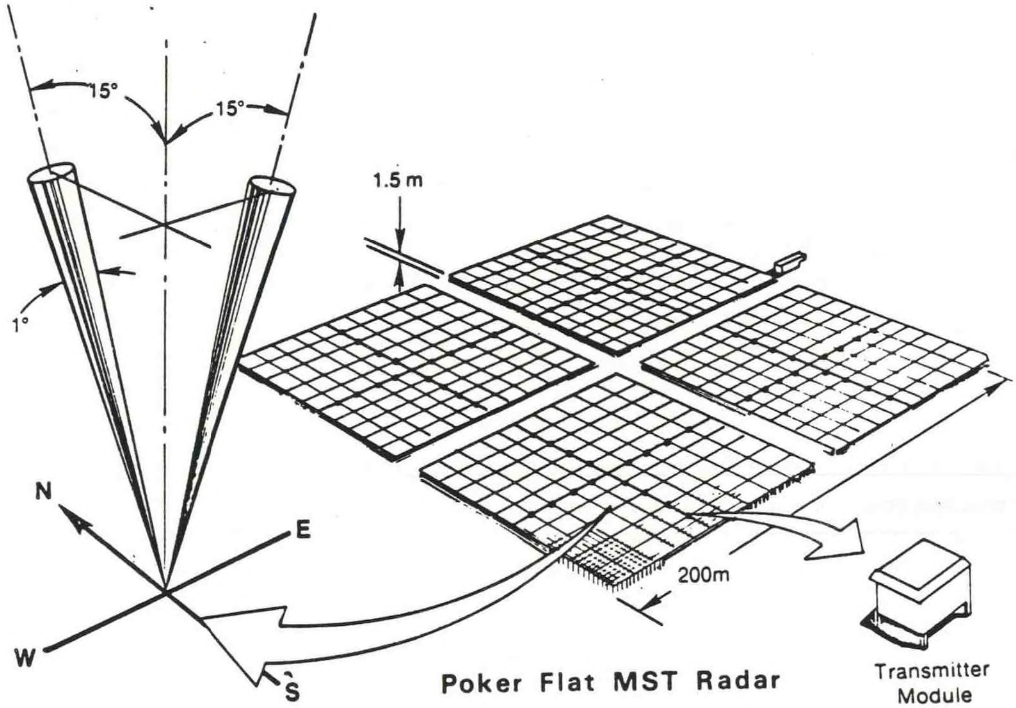


Figure 2. Artist's sketch of the Poker Flat system. (After Balsley et al., 1981)

Recent Results

MST Radar Studies

1. Atmospheric Turbulence. Parameters of turbulence can be inferred from MST radar observations in two ways.

(a) The variance of the Doppler spectrum involves the variance of the turbulence velocity fluctuations, which is directly related to the turbulence energy dissipation rate ε. ε is the most important parameter of turbulence, since it is proportional to the intensity of turbulence and since it plays an important role in atmospheric dynamics. Unfortunately, because of instrumental and geophysical limitations, thus far it has been impossible to infer ε from spectral widths except when ε and the spectral width are unusually large.

(b) 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.

Radar reflectivity measurements by the Sunset ST radar have recently been improved by the incorporation of daily absolute calibration and by antenna beam steering. Absolute calibration, instead of the usual calibration with cosmic noise, improves the accuracy and consistency of the reflectivity measurements. Antenna beam steering improves the accuracy of the determination of the radar reflectivity by permitting an average over up to eight different atmospheric volumes.

The validity and accuracy of C_n^2 inferred from radar reflectivities was Sunset during June 1983 by comparison between C_n^2 profiles measured by the ST radar and simultaneous profiles of C_n^2 inferred from the scintillation of stars. The optical experiment was developed by Dr. J. Vernin of the University of Nice, France. Preliminary comparisons show excellent agreement between the two experiments at most heights and times where humidity, which affects only the radar C_n^2, is negligible.

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 $\overline{C_n^2}$ and $\overline{\varepsilon}$ 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 buoyancy waves in the troposphere and lower stratosphere (see the section on Buoyancy Waves).

large set of carefully calibrated radar data was taken by the Sunset ST radar in order to test the statistical model. The data set included radar and balloon observations over a wide range of meteorological conditions and in all four seasons. The radar reflectivity was compared with model calculations of radar reflectivity. Preliminary results of this study show good statistical agreement when the observations and the model are averaged over at least several days. But because of the statistical nature of the model, agreement with individual profiles is often relatively poor.

The climatology of C_n^2 has been investigated using the accumulating data sets from the Poker Flat MST radar. Significant variability has been found both seasonally and from day to day (Nastrom et al., 1981, 1982). The day-to-day variations in C_n^2 show an unexpected correlation with wind speed near the tropopause. Since wave activity also shows a similar correlation with wind speed, there is probably a causal link between the wave activity and intensity of turbulence.

2. Fresnel Reflectivity and Atmospheric Stability. When a radar operating at lower VHF frequencies is pointed toward the zenith the reflectivity is greatly enhanced in stable regions of the atmosphere. This enhancement is attributed to partial specular or Fresnel reflection from horizontal stratification of the radar refractive index.

We have developed a model, called the Fresnel scattering model, that predicts the profile of Fresnel reflectivity as a function of the atmospheric lapse rate (dT/dz) (Gage et al., 1981). The model parameterizes the scattering from the half-wavelength Fourier component of the horizontally stratified refractivity (Gage and Balsley, 1980). An adjustable constant in the model was determined by normalization to data from the Sunset ST radar. But it is found that the model calculations also agree very well with observations from the Poker Flat MST radar.

There has been controversy over the dependence of the Fresnel reflectivity on the length of the radar range gates. Careful measurements of the range gate dependence were made by the Sunset ST and Poker Flat MST radars. The result was that in most cases the reflectivity was linearly proportional to the length of the range gate 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 range gate length.

The Fresnel scattering model explains the echo strength given the horizontal stratification of refractivity, but it does not attempt to explain the origin of such structure. VanZandt and Vincent (1983) showed that the required structure could be due to oblique displacements by buoyancy (internal gravity) waves (see the section on Buoyancy Waves) acting on the background gradient of refractive index. Their model is not inconsistent with any of the observed features of Fresnel reflectivity. Moreover, their model is subject to test by further appropriately designed experiments.

The Fresnel scattering model leads naturally to an objective method for determining the tropopause height from radar observations of the Fresnel reflectivity (Gage and Green, 1982b). The model is used to construct a profile of Fresnel reflectivity for the minimum stratospheric lapse rate (2K/km). The tropopause is determined as the height where the observed reflectivity first exceeds the model reflectivity. Time series of radar and radiosonde tropopause heights are compared in Fig. 3.

The existence of a quantitative relationship between the atmospheric lapse rate and the magnitude of the Fresnel reflectivity observed by VHF radar permits the determination of temperature gradients in stable regions of the atmosphere (Gage and Green, 1980). The significance of this development is that if the temperature is known at some reference level, a temperature profile can be constructed from the inferred gradients through the stable region. Also, radar determinations of tropopause heights or large temperature gradients can be used to improve the retrieval of temperature profiles from satellite or ground-based radiometer measurements (Westwater et al., 1983), by as much as 1 K rms.

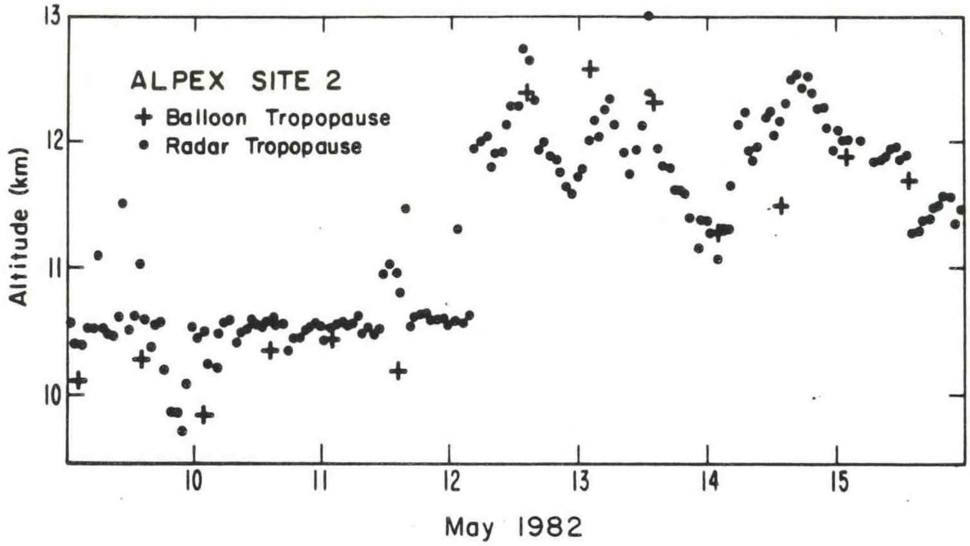


Figure 3. Comparison of radar derived tropopause heights (•) with tropopause heights derived from routine balloons launched from Nimes, France, 85 km NW of the radar site (+). (After Riddle et al., 1983)

3. Buoyancy (Internal Gravity) Waves. The MST radar technique is particularly well suited for the study of rapid variations of wind, such as buoyancy waves. The observations of buoyancy waves tend to be of two kinds: observations of discrete, nearly monochromatic, wave trains or observations of wind fluctuations that are due to a more or less random superposition of buoyancy waves.

Observations of discrete waves are essential for understanding the generation and propagation of buoyancy waves. But discrete waves are rather rare, certainly not occurring more than 5% of the time at a given height. A random superposition of buoyancy waves, on the other hand, appears to be nearly ubiquitous, so that the average effects of buoyancy waves in the atmosphere, such as the rates of transport of energy and momentum, are dominated by the latter. Superpositions of waves are usually studied by means of spectral analysis.

An example of power spectra calculated from Poker Flat radar data is shown in Fig. 4 for 8.1 km. The spectra at other heights are similar in shape. The power between the buoyancy or Brunt-Väisälä period at about 10 min and the inertial period, 13.2h at the latitude of Poker Flat, can be attributed to buoyancy waves. In this range the energy per unit mass is about 200 times larger in the mesosphere (86 km) than in the troposphere (8.1 km), but the energy per unit volume is about 300 times smaller.

Such spectra tend to have a universal shape, in this case a power law with a power of about -5/3. VanZandt (1982) pointed out that the spectra of horizontal wind versus frequency and versus horizontal and vertical wave number can be fitted by a slight modification of the Garrett and Munk (1975) universal spectrum of oceanic buoyancy waves. With this interpretation, the universal shape of the spectrum is maintained by a cascade of resonant wave interactions, with the energy source at large scales and loss to turbulence at small scales. Gage (1979), on the other hand, suggested that the wind fluctuations were due to

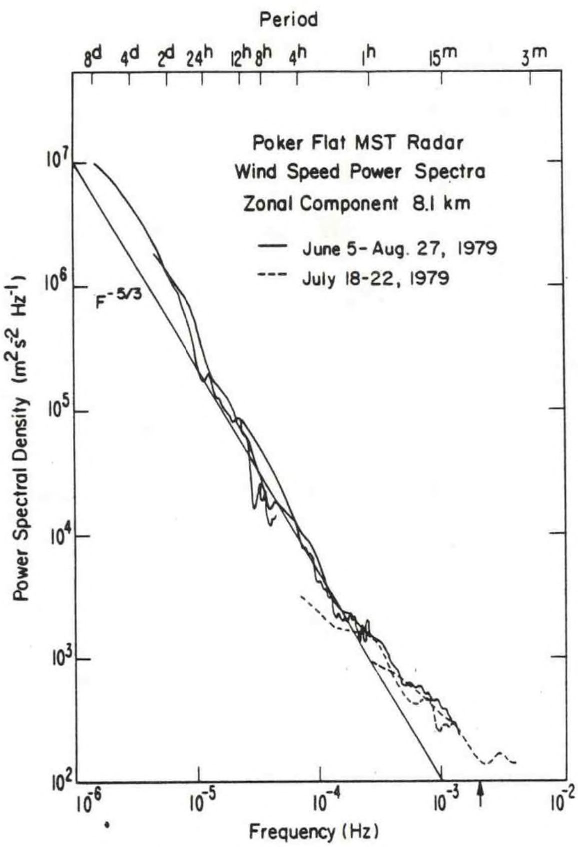


Figure 4. Power spectrum of the zonal wind fluctuations at 8.1 km obtained using the Poker Flat MST radar in Alaska. This composite spectrum represents summertime conditions from mid-June to the end of August 1979. The arrow marks the nominal value of the buoyancy frequency (9.75^m). The straight line represents a power law slope of $f^{-5/3}$. (After Balsley and Carter, 1982)

two-dimensional turbulence, with an energy source at small scales and loss at intermediate scales. These ideas have stimulated considerable theoretical and experimental research. In particular, the universal spectrum of buoyancy waves predicts the spectra of vertical velocity and vertical displacement and the coherence functions versus horizontal and vertical displacement, and we have devised experiments to test these predictions.

Buoyancy 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 buoyancy waves are generated by shear instability (VanZandt et al., 1979).

We have also observed wave trains associated with convective storms. In Fig. 5 the large, quasi-sinusoidal wave train between 17 and 24h is thought to

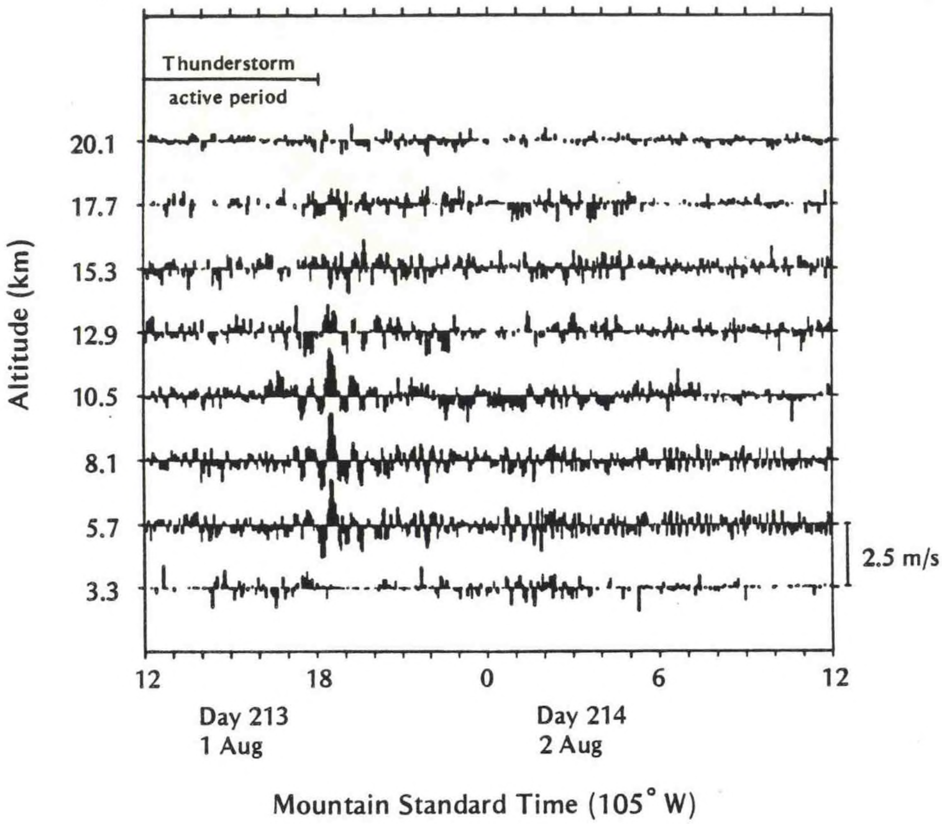


Figure 5. Buoyancy waves associated with thunderstorm activity. (After Lu et al., 1984)

be associated with a large thunderstorm that was active from 15 to 18h about 100 to 200 km from the Platteville ST radar (Lu et al., 1984). In In addition to such discrete wave trains, 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.

Because these observations were made by only a single radar, the wavelengths or phase velocities that are essential for a complete understanding of wave dynamics could be determined only by the use of simultaneous microbarograph observations, which are not always available.

In order to remedy this deficiency we have been the first group to utilize arrays of ST radars. In April and May 1982 we deployed three portable ST radars in an ∿ 5 km triangle in southern France, in cooperation with M. Crochet of the Laboratoire de Sondages Électromagnetiques de l'Environment Terrestre (LSEET) of Toulon, France, as part of ALPine EXperiment (ALPEX) of the Global Atmospheric Research Program (GARP). The radars obtained continuous vertical wind data during nearly two months of operation (Balsley, Crochet et al., 1983).

The data are being analyzed in several ways. Typical frequency spectra are shown in Fig. 6. When the wind was light (Quiet Days) the spectra are nearly

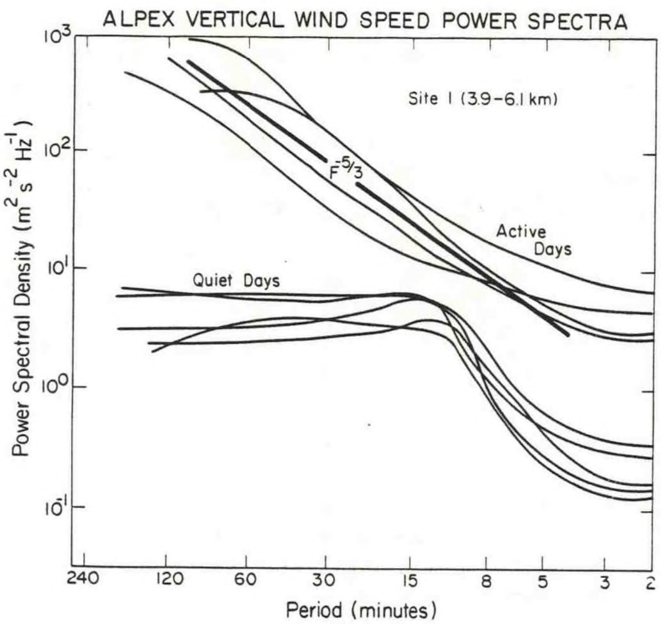


Figure 6. Representative spectra of the vertical wind fluctuations for active and quiet periods. (After Balsley, Crochet et al., 1983)

flat at longer periods, rise to a weak maximum at the Brunt-Väisälä period, and decrease rapidly at shorter periods. During Active Days the spectra are greatly enhanced and tend to have the shape of the horizontal spectra (Fig. 4). The Quiet Day spectra are consistent with the universal spectrum, which predicts a flat or slowly rising spectrum of vertical velocity. Further analysis accounts for the peak near the Brunt-Väisälä frequency in terms of the behavior of buoyancy waves near their turning point (Desaubies, 1975). The departure from the universal spectrum on Active Days is attributed to Doppler smearing, tilted isentropic surfaces, and slowly varying mountain lee waves.

These data are also being analyzed by cross-spectral analysis to obtain the wave phase velocity as a function of wave period.

In July and August 1983 an array of three existing ST radars in an ∿ 60 km triangle in Colorado together with over 20 barographs was used to observe further the buoyancy wave activity associated with thunderstorms. These observations were made in cooperation with PROFS and the Wave Propagation Laboratory of NOAA. The data will be analyzed during 1984 in collaboration with Prof. F. Einaudi of the Georgia Institute of Technology.

4. <u>Vertical Velocity</u>. Vertical velocity plays an important role in the dynamics of atmospheric circulation systems on all scales. However, until very recently there has been no technique capable of measuring the vertical wind directly, and as a result our present knowledge of the role of vertical velocity in wind fields is based upon inferences from routine radiosonde data. These analyses provide insight into the synoptic-scale features of vertical velocity but give us no information about the variability of vertical velocity at any

particular location. The local vertical velocities can be expected to contain contributions from convection, buoyancy waves (including stationary lee waves) and turbulence, in addition to the much smaller, synoptic-scale vertical wind.

A 34-day record of hourly averaged vertical velocities seen by the Poker Flat MST radar is shown in Fig. 7 (Ecklund et al., 1981). The most striking feature of this display is the large variation in the amplitude of the vertical wind fluctuations, with "active" periods recurring at 5 to 8 day intervals. An active day and a quiet day of 1.5 min resolution winds are shown in Figs. 8a and 8b. On the active day there is some evidence of sinusoidal oscillation in the vertical wind, however, most of the variations have no apparent dominant period. Occasionally, the vertical wind can be in one direction for several hours with significant velocities. The quiet day also shows vertical wind fluctuations, but of higher frequency and greatly reduced amplitude.

A statistical analysis has been made of three years of vertical velocity observations by the Poker Flat radar (Nastrom and Gage, 1983). Statistical distributions of vertical velocity reveal a bi-modal character related to the active and quiet periods described above. The standard deviation of the vertical velocity distribution varies from day to day in concert with the magnitude of the mean wind. Surprisingly, the standard deviation correlates best with the winds at the 700 mb (3 km) level.

5. Mesospheric Studies. The theory of nonlinear wave breaking in the mesosphere was refined, in collaboration with Prof. D. C. Fritts of the University of Alaska, to explain the strong seasonal variability of the mesospheric echo structure observed at Poker Flat (Balsley et al., 1984).

In June 1983 the Air Force Geophysical Laboratory launched a series of rockets concurrently with Poker Flat MST radar observations in order to examine the fine scale mesospheric structure responsible for the strong radar echoes observed at Poker Flat. The rockets, instrumented to measure mesospheric temperature, turbulence intensity, winds, electron densities, and chemical composition, were launched during periods of strong echoes as determined by the radar. Preliminary results show a surprising amount of structure in the electron density profile, which appears to correspond to regions of strong radar echoes. Subsequent studies of these and the other rocket-measured parameters, when they become available, will be uniquely useful in fixing the causal mechanism(s) for the echoes.

Dr. L. Coy, an NRC Resident Research Associate, began making a time lapse movie of the high-resolution radar data obtained concurrently with the foregoing rocket experiments, using the graphics capability of NCAR's CRAY computer facility. This movie will show the complex temporal variability of the Doppler shift and intensity of the radar echoes. We have already noted a series of "satellite" spectral returns that could arise from the breakup of the long period waves responsible for the echoes.

The capability of the Poker Flat MST radar as a meteor radar has been further examined by Dr. S. K. Avery of CIRES. This work, which was initiated several years ago through a NOAA Grant, has yielded atmospheric tidal amplitudes and phases and mean zonal and meridional winds as a function of season.

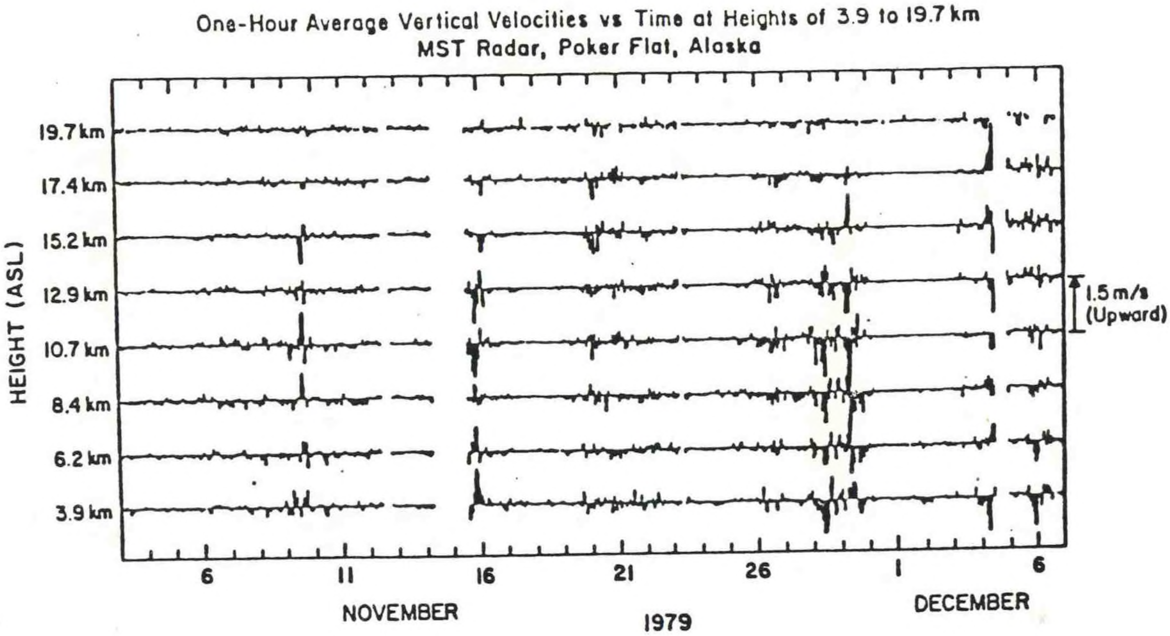


Figure 7. 34-day record of hourly averaged vertical wind velocities at heights of 3.9 to 19.7 km. The vertical velocity scale is shown on the right margin. (After Ecklund, Gage, and Riddle, 1981)

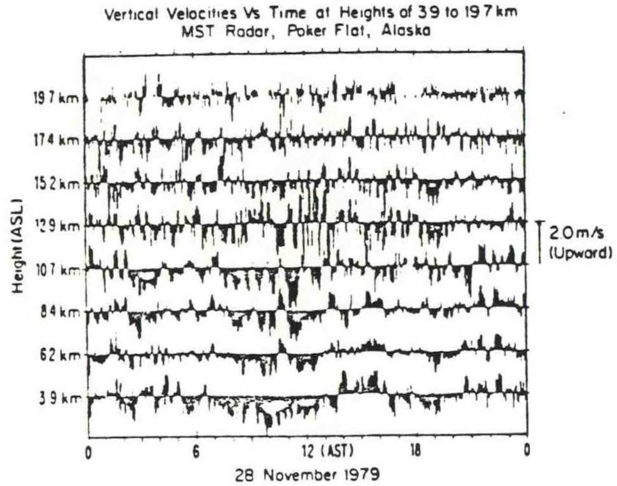
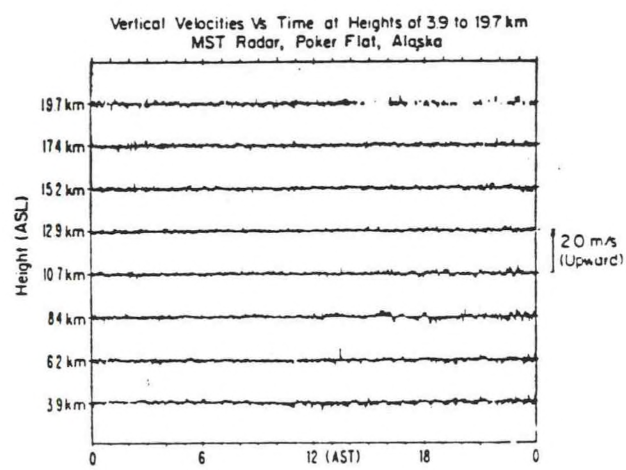


Figure 8. (a) Vertical velocities at heights of 3.9 to 19.7 km on an active day (28 Nov. 1979).



(b) Vertical velocities on a quiet day (24 Nov. 1979). The vertical velocity scale is shown on the right margin. (After Ecklund, Gage, and Riddle, 1981)

Dr. A. C. Riddle of CIRES has studied the long term variability of the mesospheric wind field, including the vertical wind component, using both turbulent and meteor echoes. The resulting mean horizontal flow is in agreement with our current knowledge of the global horizontal circulation pattern. However the vertical motion appears to be almost an order of magnitude larger than, and in opposite direction to, that expected on theoretical grounds. Efforts are currently underway to examine further this surprising feature of the arctic mesospheric mean circulation pattern.

The dependence on magnetic activity of the summer mesospheric zonal winds at Poker Flat have been investigated by Dr. J. G. Luhmann and R. Johnson of UCLA in order to verify the results of an earlier AL investigation. Results of this investigation are shown in Fig. 9, which compares the distribution of mesospheric zonal velocities during magnetically quiet and active periods. The difference between these histograms indicates a magnetic activity effect on mesospheric winds at 86 km.

6. Momentum Transport in the Troposphere, Stratosphere and Mesosphere. One of the major unknown areas in middle atmospheric dynamics lies in the coupling of energy and momentum between the troposphere, stratosphere and mesosphere, as well as between low and high latitudes. Such coupling not only must occur, but in some instances it is the controlling factor in ultimately determining the global atmospheric circulation pattern. The process involves the breakup and resulting deposition of buoyancy wave energy in a region of the atmosphere far removed from the buoyancy wave source. Two examples that illustrate the importance of coupling are: 1) mesospheric circulation models require large buoyancy wave momentum depositions to limit the meridional wind magnitude to reasonable (i.e., measured) values, and 2) buoyancy wave "drag" processes are apparently necessary to understand the circulation in the winter polar stratosphere.

The problem of vertical momentum transport is being studied in several different ways. First, the distribution of gravity wave energy as a function of frequency and horizontal and vertical wavelength, geographical location, altitude, season, etc. are being studied, as described in the section on Buoyancy Waves. Second, the vertical flux of horizontal momentum as a function of height is being measured by an adaptation of the technique introduced by R. A. Vincent. Third, the rate of deposition of wave energy is being assessed by studying the variation with height of wave energy as a function of frequency.

Climate Variability and Solar Radiation

We have continued a major effort in the description and modelling of seasonal and secular changes in the height of the tropical tropopause (Reid and Gage, 1981; Gage and Reid, 1982a,b). This work is a cooperative effort with the Theoretical Aeronomy Program, and a detailed description of it will be found in that chapter of this Annual Report.

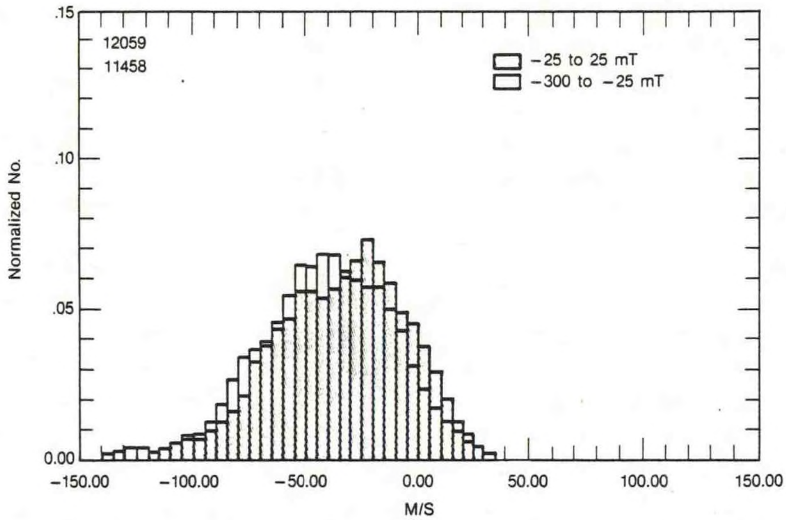


Figure 9. Histograms of occurrence of summer zonal winds at Poker Flat for magnetic activity indices between 25 mT and -25 mT and between -25 mT and -300 mT.

Future Plans

MST Radar Studies

1. Atmospheric Turbulence. Our research on turbulence has two objectives: first, to describe the statistics of occurrence of turbulence and, second, to develop physical understanding that permits us to construct a model for its occurrence. A description and a model for the morphology of occurrence of turbulence are important to the design of radio and optical propagation systems. Also, turbulence is the principal dynamical sink of energy in the free atmosphere. The statistics of its occurrence can be incorporated into general circulation models.

The dependence of the occurrence of turbulence on geographical location including latitude, topography, etc., season, time of day, synoptic weather, thunderstorm activity, buoyancy wave activity, etc., will continue to be studied with existing radars, including our portable systems. But because of the enormous observational effort that would be required to describe fully the statistical dependence on all of these variables, a physical understanding that permits construction of a model for the occurrence of turbulence is essential. A simple understanding has led to our present model, which can be used to predict the occurrence of turbulence from background parameters. More detailed observations as described above will be used to improve the model to extend its reliable application to a wider range of atmospheric conditions. The connection between this model and the universal spectrum of buoyancy waves, which is basic to the success of the model, will be further strengthened and its implications explored.

The comparisons of simultaneous measurements of C_n^2 made during June 1983 by the Sunset ST radar and Vernin's stellar scintillometer will be repeated during October and November 1983. The new measurements will be improved in several respects. First, the design of the experiment will be optimized, based on what we learned from the June 1983 observations. Second, the optical observing conditions during the autumn should be much better than during spring. Third, additional independent measurements of C_n^2 profiles will be made by another kind of stellar scintillometer, designed by Dr. G. R. Ochs of the Wave Propagation Laboratory and furnished by the Air Force Geophysical Laboratory.

2. Fresnel Reflection and Atmospheric Stability. Our previous research has shown that the Fresnel reflectivity has a definite relation to the gradient of temperature, so that from observations of the reflectivity the buoyancy frequency and temperature profiles can be inferred. We will continue to explore and develop this technique, both for the determination of tropopause heights and for the retrieval of temperature profiles as a part of a combined radar/microwave radiometer profiler system.

Further development of this technique depends in part upon a better understanding of the morphology of the irregularities of refractive index from which the reflection occurs and of their dynamical origin, which is at present the subject of speculation. The morphology will be studied in more detail by the Sunset radar, taking advantage of its good height resolution (down to 150m) and steerability. The model of VanZandt and Vincent for the origin of the irregularities will be studied by performing critical experiments to test the predictions of the model.

3. Buoyancy (Internal Gravity) Waves. The MST radar technique has unique capabilities for the study of rapidly varying phenomena in the free atmosphere, such as buoyancy waves. This is fortunate, because buoyancy waves play an important role in atmospheric dynamics: they efficiently transport energy and momentum, both vertically and horizontally, and their breakdown into turbulence at small vertical scales results in a major energy sink in the free atmosphere.

As was said in the Recent Results section on Buoyancy Waves, radar studies of buoyancy waves are of two kinds: observations of discrete waves in order to study their generation and propagation, and observations of spectral properties in order to study their statistical properties.

To improve our observations of discrete waves, a four-station microbarograph array will be installed in conjunction with the Sunset radar. Also, further observations will be made with three-radar arrays such as that used in the ALPEX experiment and the 1983 thunderstorm experiment. These observations will be analyzed to obtain periods, horizontal and vertical wavelengths and phase velocities, in order to study modal structure, vertical propagation, interaction of waves with critical levels, etc. Most of these studies can be accomplished only by using the MST radar technique.

The Poker Flat radar does not have the capability of measuring horizontal wavelength and phase velocity, but because of its great altitude range, it can be used to study the propagation of discrete waves from one atmospheric region to another. It will also continue to be used to study buoyancy waves in the mesosphere and their effects. The continuous operation of the Poker Flat radar makes it particularly useful for observing rare but important wave events.

The steerability of the Sunset radar makes it very useful for studying mountain lee waves and the conditions in the free atmosphere associated with downslope wind storms. By scanning the radar in the east-west vertical plane, we will be able to measure the radial component of wind and the spatial distribution of turbulence. These observations will be compared with theoretical models of lee waves and downslope wind storms.

Power spectra of wind fluctuations versus period, vertical wavenumber, and horizontal wavenumber (when possible) will be observed under as wide a variety of conditions as possible: geographical location, altitude, season, weather conditions, etc., in order to study the degree of universality of spectral shape and amplitude. Departures from universality will be studied particularly closely, since these may indicate proximity to sources of spectral energy. The variation of the amplitude of the spectrum with altitude will be analyzed to determine the loss of energy versus altitude and its relation to the background wind profile.

These spectra will also be used to study the relative contributions of different dynamical processes, particularly buoyancy waves and two-dimensional turbulence.

The dissipation of buoyancy waves by dynamical instability to generate three-dimensional turbulence will be studied. This is important as the principal loss of buoyancy wave energy in the atmosphere and as the principal source of turbulence under non-convective conditions. The relation between the buoyancy wave spectrum and our model for the occurrence of turbulence will be further refined.

4. Vertical Velocity. We shall continue our observations of vertical velocity and their interpretation. We shall continue to study the connection between the day-to-day variations in the magnitude of short-period vertical wind fluctuations and large-scale wind fields. In particular, we shall attempt to determine more precisely the nature of the small-scale vertical velocity fluctuations. Experience with radars in different locations and closely-spaced networks of radars should elucidate this subject.

In addition, we will further explore the direct measurement of synoptic scale vertical velocities. Since these velocities have never been directly measured, it will be important to determine the potential impact of this kind of data on weather forecasting.

5. Mesospheric Studies. The continuous data set already obtained from the Poker Flat MST radar over the past 4-1/2 years is proving to be invaluable in studying a variety of mesospheric phenomena: zonal and meridional tidal variations; energy coupling processes between the mesosphere and the lower atmosphere; the generation and propagation of atmospheric waves; sun-weather relationships; atmospheric turbulence, etc. The data obtained using the complete system serves as a data base for a number of ongoing cooperative studies with the university community and other agencies. Cooperative programs using Poker Flat data are underway with the University of Alaska (several groups), Boston College, UCLA, the University of Colorado (LASP and CIRES) Cornell University, the University of Illinois, the University of Washington, the Air Force Geophysical Laboratory, and NOAA's Geophysical Fluid Dynamics Laboratory.

Continuing analysis of the simultaneous Poker Flat MST radar and rocket data taken during June 1983 will provide a number of new insights into mesospheric dynamics in the coming year. Similar high spatial resolution data will be gathered during the winter, when the causal mechanism for the observed turbulence is thought to be quite different.

6. Momentum Transport in the Troposphere, Stratosphere and Mesosphere. A concerted effort will take place in the coming few months to examine wave momentum fluxes and energy deposition as a function of height and season. The technique discussed under Recent Results will be used to obtain a more complete picture of these important processes and their effects on energy and momentum deposition in the atmosphere.

7. Development of an Equatorial MST Radar. It has been increasingly apparent over the past few years that both midlatitude weather patterns and climate variability are greatly influenced by climate variability in tropical latitudes. Improved knowledge of equatorial atmospheric dynamics would therefore be of great value in furthering our understanding of both climate and weather variability. Few tropical and/or equatorial observations exist. The Workshop on Equatorial Middle Atmospheric Measurements and Middle Atmospheric Radars held in Estes Park, Colorado, in May 1982 stressed the need for MST/ST radars near the equator. Since then a Study Group on the Scientific Aspects of an International Equatorial Observatory has been established by the Middle Atmospheric Program (MAP).

Within the Aeronomy Laboratory, consideration is being given to the establishment of one or two ST radars at tropical and/or equatorial locations. Such systems would be useful in several studies. Two examples include 1) the measurement of the vertical motion of the tropical atmosphere on scales ranging between a few minutes and many months (such information would impact strongly on studies of water vapor injection into the stratosphere), and 2) long-term high time-resolution studies of atmospheric wave processes, including studies of Kelvin waves and mixed Rossby-gravity waves. Toward this end, the Aeronomy Laboratory requested and received an increment in funding last year to establish a temporary ST radar site in the western equatorial Pacific to obtain preliminary data on vertical winds aloft in that region.

In addition, the Aeronomy Laboratory is proposing to become involved in the TOGA (Tropical Oceans and Global Atmosphere) experiment by installing one or more relatively permanent ST systems in the equatorial Pacific. The resulting data base will provide the winds aloft information necessary to TOGA. It will also furnish a continuous data set similar to that at Poker Flat for use in studying short period dynamics in the equatorial atmosphere, where data are virtually nonexistent.

Ionosphere and Lower Thermosphere

Auroral Ionosphere. We will continue studying the relationship between heating in the lower auroral ionosphere during magnetically active periods and upper mesospheric winds. This study will use mesospheric data from the Poker Flat MST radar and ionospheric data from the NOAA operated VHF radar-auroral radar at Elmendorf AFB in Anchorage, AK. The existing data base from the Chatanika incoherent scatter radar will also be incorporated into these studies.

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ATMOSPHERIC CHEMICAL KINETICS

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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 reactions. The products of these studies include reaction rate coefficients, reaction product identities, 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 ionosphere, i.e., the upper regions of the atmosphere. The laboratory continues to play a role in atmospheric ion chemistry measurements. These measurements have important applications in radio 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 laboratories world-wide 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 energy range is from 300 K 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 implications.

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 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 AL and *in situ* negative ion composition measurements by a research group in Germany.

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 sciences 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 certain critical atmospheric radicals such as OH, HO_2, and ClO. 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 providing estimates of the expected atmospheric lifetimes of these molecules. Subsequent legislation and regulations on the allowed uses and emissions of these materials were based in part on these data.

Using the LMR apparatus the laboratory has made measurements that have lead 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 latest instrumentation permits a larger variety of radical molecules to be detected and, therefore, more complex reactions to be studied. For example, recent work has concentrated on measuring rate constants for reactions involving two unstable radicals. These studies not only improve our knowledge of the chemistry of the stratosphere, but their unusual and unpredicted temperature and pressure behavior has generated interest and attention beyond the atmospheric science community.

A new instrument, a tunable diode laser, has been put into operation. The first study was a measurement of the N_2O concentration in the air. This work has resolved a significant discrepancy in the previous measurements of atmospheric N_2O.

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

1. The deactivation of vibrationally excited O_2^+ ions has been investigated in a selected ion flow-drift apparatus. Ions in the v=1, 2, and >2 vibrational levels were selectively detected by their enhanced reactions with Xe, SO_2, and H_2O, respectively. Rate coefficients for relaxation of $O_2^+(v>0)$ by Ne, Ar, Kr, H_2, D_2, N_2, CO, CO_2, H_2O, CH_4, SO_2, SF_6, and O_2 were measured. The quenching rate coefficients for v=2 were found to be about a factor of two larger than for v=1. The rate coefficients were found to be correlated with the energy of the ion-quenching neutral bond. These data are shown in Figure 1. The dependence of some of the rate coefficients on collision energy was also investigated. A major conclusion of this study is that the relaxation occurs through the formation of a collision complex in which the vibrational excitation is transferred into the weak complex bond resulting in dissociation, analogous to vibrational predissociation in van der Waals complexes. These results have important applications to the relaxation processes in ionized environments such as the earth's upper atmosphere and electrical discharges.

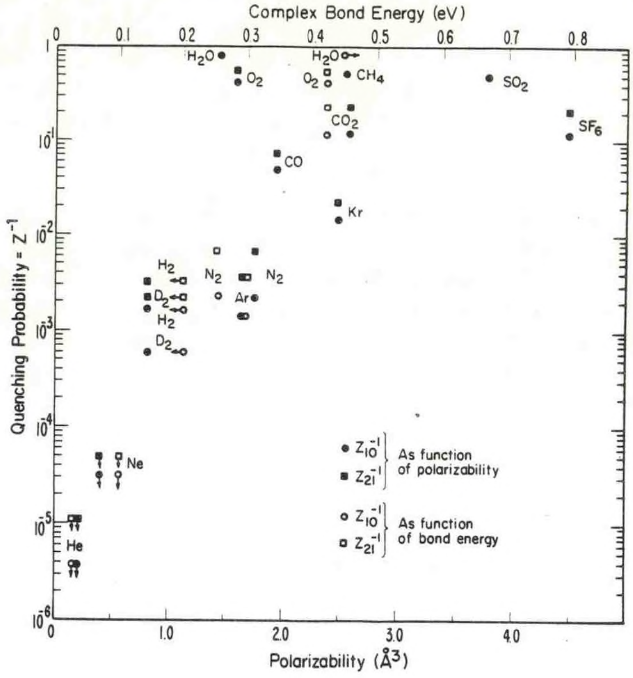

Fig. 1. Plot of the quenching probabilities, Z_{10}^{-1} for $O_2^+(v=1)$ and Z_{21}^{-1} for $O_2^+(v=2)$, as a function of the polarizabilities of the neutral quencher or ion-neutral bond energy, when the latter is known. The arrows indicate values that are upper or lower limits.

2. In ion transport theory, the effect of inelastic collisions has not been treated in detail due to the complexity of the problem and the lack of experimental data. The first measurements have been made of the quantity ξ, the ratio of the collision integral for inelastic loss to that for momentum transfer in the ion-molecule collision systems of Cl^-, NO_2^-, NO_3^-, and NO^+ with N_2. ξ is derived from the "mobility difference" observed between mobility measurements made in the NOAA flow-drift tube apparatus as a function of E/N (electric field/number density) and measurements made in a high-pressure drift-tube mass spectrometer as a function of gas temperature. The difference is found when the mobility data sets are plotted as a function of effective collision temperature T_{eff} as shown in Figure 2 for NO^+ in N_2. The mobility difference can be understood qualitatively as the propensity for energy to distribute into all degrees of freedom of an ion-molecule collision system. For a given T_{eff}, this results in an ion undergoing collisions at high E/N and low-gas temperature to lose more momentum on the average and, hence, mobility, than an ion undergoing collisions at low E/N and high gas temperatures.

3. A flowing afterglow apparatus has been modified for use as a chemical ionization detector for atmospheric free radicals. A small glass flow tube reactor where neutral radical reactions will be carried out has been installed on the side of the flowing afterglow flow tube. All of the gas from the radical reactor flows into the ion reactor. The idea of the experiment is to detect radicals by converting them to ions and observing the ion product using the ion detection section of the flowing afterglow.

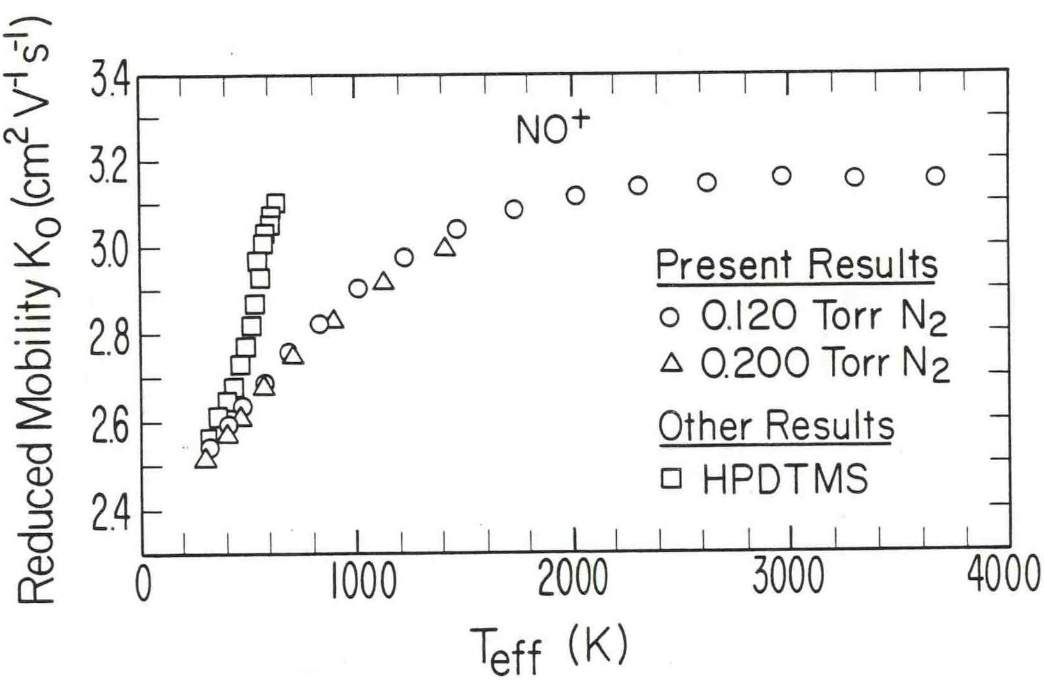

Fig. 2. Reduced mobility, K_o, as a function of the effective collision temperature, T_{eff}, for NO^+ ions in N_2. The results are from the NOAA flow-drift tube apparatus and the other results are from the high-pressure drift-tube mass spectrometer (HPDTMS) at the Georgia Institute of Technology.

The ionization process is efficient because reactions between neutrals and ions tend to be very rapid and because radicals form very stable ions. Preliminary results show that stable radicals such as NO and NO_2 have detection limits in the range 10^9 to 10^{10} molecules cm^{-3} for chemical ionization and Penning ionization methods.

4. The temperature dependence of the disproportionation reaction of HO_2 radicals has been studied at low pressures using laser magnetic resonance detection with a flow tube kinetic system. The rate constant for

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

has been measured at temperatures between 253 and 390 K. The results are summarized in Figure 3. The reaction is found to have a large negative temperature dependence, $k = (2.0 \pm 0.6) \times 10^{-13} \exp\{(595 \pm 120)/T\}$ cm^3 $molecule^{-1}$ s^{-1}. A similar negative temperature dependence has been observed in other studies of radical-radical reactions. This reaction is very important in the atmosphere because it is the source of gaseous hydrogen peroxide. The hydrogen peroxide is thought to be taken up by water droplets and aerosol particles where it oxidizes SO_2 to sulfuric acid.

5. The rate coefficient for the radical-radical reaction

$$OH + ClO \rightarrow HO_2 + Cl$$

has been measured. This reaction is of minor importance in the stratosphere but its rate coefficient has an important application to the heat of

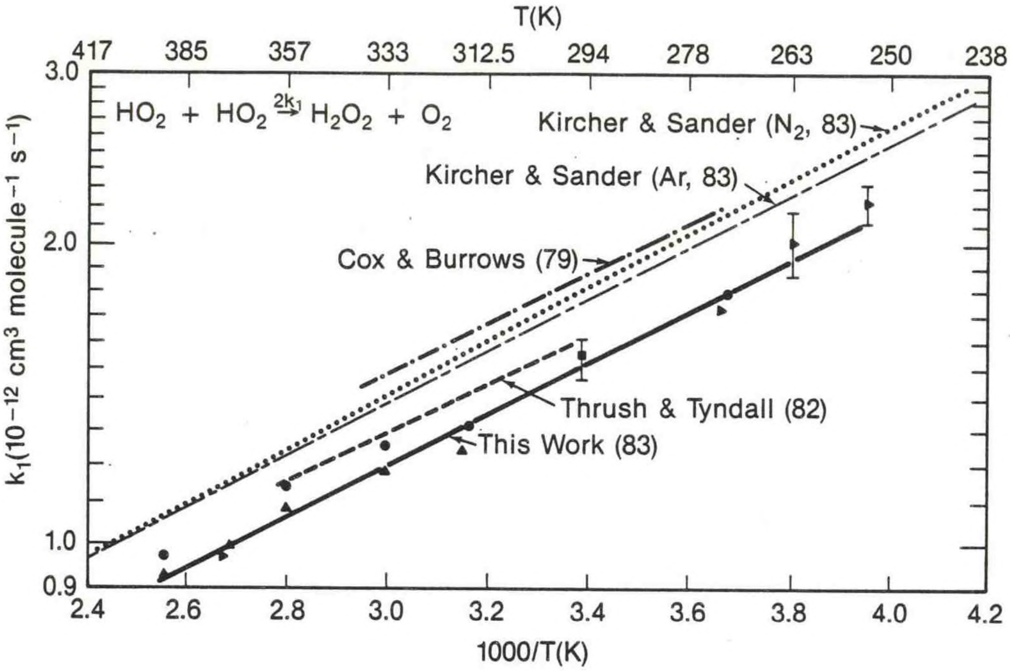

Fig. 3. Plot of bimolecular rate constant for the $HO_2 + HO_2$ reaction versus 1/T. Data for one previous study (Cox and Burrows) and two current studies (Thrush and Tyndal) and (Kircher and Sander) are also shown. All measurements are in excellent agreement.

formation of the HO_2 radical. Two previous studies of the reaction gave results that indicated an inconsistency in the data for the heat of formation and the reverse rate constant, both of which were measured independently in our laboratory. The present measurement finds the two previous studies to be in error. The preliminary value of the heat of formation of HO_2 obtained from this measurement is $\Delta H°_{f_{298}}(HO_2) = 2.9 \pm 0.5$ kcal mol^{-12}, which is somewhat higher but consistent with our earlier work. The reaction is found to have a negative temperature dependence.

6. Some preliminary results have been obtained on the kinetics of atomic sodium. A flow system with two movable inlets and a resonant fluorescence detection system for Na has been constructed. One inlet is attached to an oven containing Na by means of a heated tube which delivers the Na vapor to the flow tube. The second inlet provides a movable source of O_3 reactant. Two types of measurements have been made: (1) with the O_3 off, moving the Na source permits the measurement of the diffusion coefficient of Na in the carrier gas and (2) with the Na source fixed and O_3 added through the reactant inlet permits the measurement of the rate coefficient for the reaction

$$Na + O_3 \rightarrow NaO + O_2.$$

At about 290 K the diffusion coefficient of Na in He is approximately 300 cm^2 torr s^{-1} and the rate coefficient is about 2×10^{-10} cm^3 $molecule^{-1}$ s^{-1}. The measurement of Na rate data is aimed at clarifying the role of Na in stratospheric ozone chemistry.

Future Plans

1. Studies of the kinetics of vibrationally excited ions will be continued. Further measurements of the rate constants for deactivation of atmospheric ions will be made using the SIFT-DRIFT experiment. Data on the vibrational relaxation of ions by neutrals will be analyzed with the objective of developing a comprehensive theory to describe the quenching process. Such a theory would be very useful for predicting the relaxation rates for ions for which no laboratory measurements are available.

2. Development of the chemical ionization detection method for free radicals will continue. The results obtained so far indicate that positive ion, negative ion, and Penning ionization by argon metastables all appear to be very promising. Current work is pursuing negative ion chemical ionization detection of $HOSO_2$ racicals which are very important in acid rain research. The major problem being confronted is to find a suitable negative ion species that can be used to ionize the $HOSO_2$ radicals. This problem results from the lack of thermochemical data on the $HOSO_2$ radical and its ion and the presence of electronegative compounds such as SO_2 and NO_2 in the gas mixture containing $HOSO_2$.

3. An experiment is being developed to test some new methods for generating atmospheric radicals using hot metal surfaces. Research in other laboratories has produced evidence that some metal surfaces will generate radicals when certain gases are passed over them. For example, hot platinum wires have been used to generate OH radicals from water vapor for some spectroscopic studies. A sketch of the proposed experiment is shown in Figure 4. The experiment consists of a small flow tube with

HOT WIRE RADICAL SOURCE

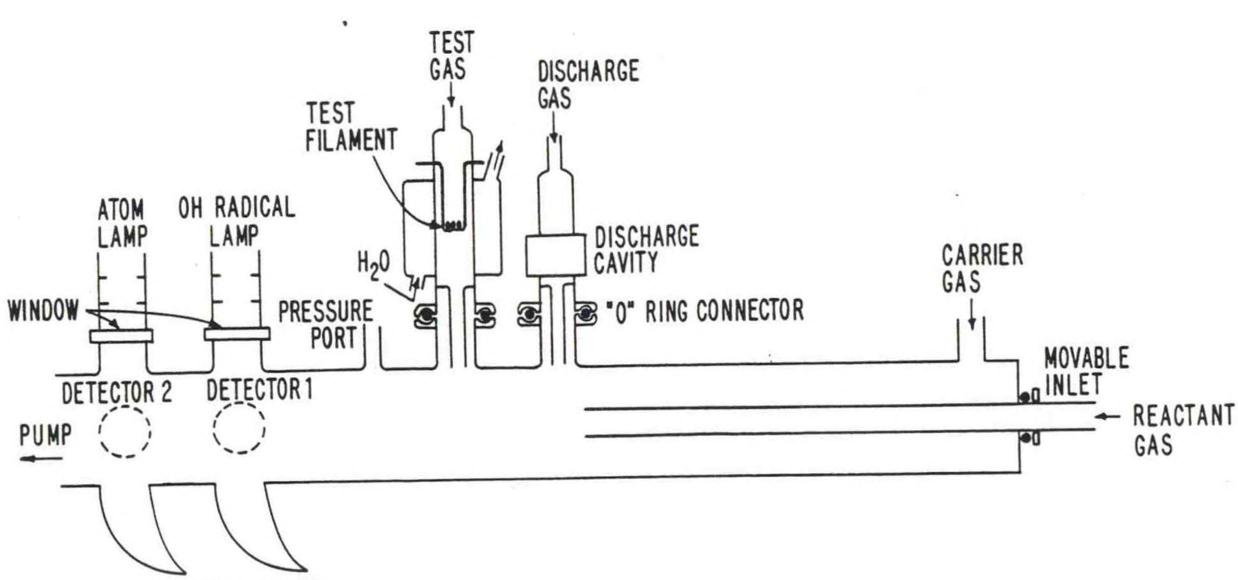

Fig. 4. A schematic of the experiment to be used to evaluate hot wires as potential radical sources.

a test filament source and a microwave discharge source. The microwave discharge will be used as a standard for calibrating the resonant fluorescence detectors for OH (detector 1) and atoms such as H, O, and Cl (detector 2). For a source to work well, it must produce OH at concentrations of about 3×10^{11} molecule cm^{-3} with less than 1% H or O. New methods of generating H, O, Cl, and Br will also be tested. The development of these new radical sources is very important to kinetic studies because the present methods of generating radicals are not direct or introduce reactive impurities.

4. Current projects on NO_3 and Na kinetics will be continued. NO_3 reactions with NO and NO_2 which are very important in the atmosphere will be studied. The reaction of Na with O_3 will be completed and some other reactions of Na will be studied. The temperature and pressure effects in the reactions of both NO_3 and Na will also be investigated.

5. The Fourier Transform spectrometer (FTS) which was purchased recently will be put into operation. There are experiments with two unstable atmospheric molecules which will be undertaken. One experiment concerns HO_2NO_2, peroxynitric acid. High resolution infrared spectra of HO_2NO_2 will be taken. These will be used by scientists in other laboratories to evaluate high resolution spectra taken in the atmosphere to determine if detectable amounts of HO_2NO_2 are present. This evaluation will be a valuable use of models of atmospheric chemistry. The second molecule to be studied is HO_2NO, peroxynitrous acid. This molecule has never been detected in a gas phase system. It is proposed that HO_2NO may be formed in the reaction:

$$OH + NO_2 + M \rightarrow HONO_2 + M \quad (a)$$

$$\rightarrow HOONO + M , \quad (b)$$

via (b). If this is found to be true it will have a very important effect on our understanding of the chemistry of nitrogen oxides in the atmosphere. At present this reaction is the main removal mechanism for nitrogen oxides and the major source of atmospheric nitric acid.

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OPTICAL AERONOMY PROGRAM

Permanent Technical Staff

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Gonzalo Hernandez	Physicist
Edward Marovich	Physicist
Orrin A. Mills	Electronic Technician
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Introduction

This program utilizes optical measurements on 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. With time the program moved towards more current concerns such as the upper portion of the ozone layer and the temperature and winds in the upper atmosphere, the latter being of importance to the perturbation of satellite orbits.

The major change in the program has been an expansion into studies of the lower atmosphere to include 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 rather than the measurements of emission formerly employed for upper atmospheric studies. But almost all of the expertise and optical equipment previously developed could be immediately applied to these new areas and so the program was able to move swiftly 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 clear 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 atmospheric as they arise.

Major Areas of Investigation

Stratospheric and Tropospheric Composition

A technique was developed for separately determining the stratospheric and tropospheric abundance of NO_2 using ground based absorption spectroscopy. Changes in the abundance and altitude distribution of NO_2 in the stratosphere can be followed on a routine basis; at the same time the variations in tropospheric NO_2 with changing weather patterns can be studied. In the stratosphere NO_x ($NO + NO_2$) is the principal naturally occurring species controlling the ozone abundance. In the troposphere it plays a similar important role.

The natural clean air background of NO_2 has been found to be very much lower than previously reported and a major enhancement was discovered in thunderstorms. A method has been developed for measuring NO_2 in the free troposphere from mountain tops or aircraft. The results from Mauna Loa, Hawaii, confirm that NO_x is extremely low in mid-Pacific air. Measurements made on board a jet aircraft have revealed a large and unexpected decrease in stratospheric NO_2 at high latitude in winter with a return to high values in the summer. Only now is the interpretation of this beginning to emerge, largely as a consequence of studies by S. Solomon of the Aeronomy Laboratory and her collaborators. Major perturbations in the structure of stratospheric NO_2 accompany the formation of a jet stream and others have been shown to be associated with a change in the large-scale stratospheric circulation pattern which accompanies a stratospheric warming.

Efforts to understand these new observations are proving to be of value in the larger problem of the effect of nitrogen oxides in controlling the ozone layer. Automated instruments for monitoring NO_2 by this technique were installed at a number of NOAA GMCC stations at both high and low latitude. The results from Barrow, Alaska, confirm earlier airborne observations at high latitude and show changes at stratospheric warmings. These changes have been identified with major alterations in the quasi-horizontal flow patterns in the stratosphere. Under certain circumstances the bahavior of NO_2 can thus be used to study stratospheric circulation patterns (See Figure 1).

The technique for NO_2 was extended to give the first measurements of NO_3 in the atmosphere; NO_3 is an important intermediate in the nitrogen chemical cycle. The method distinguishes between stratospheric and tropospheric NO_3 when the moon is used as the light source. We have also studied NO_3 in the troposphere over a horizontal 15 km path. The NO_3 behavior exhibits a number of unexpected facets. In the stratosphere it maximizes in the spring, contrary to theoretical expectation. In the troposphere NO_3 is considerably below the amount expected and the evidence is strong that the molecule is attached by an as yet unknown scavenger. The unraveling of the NO_3 anomalies is likely to lead to changes in our understanding of atmospheric odd nitrogen.

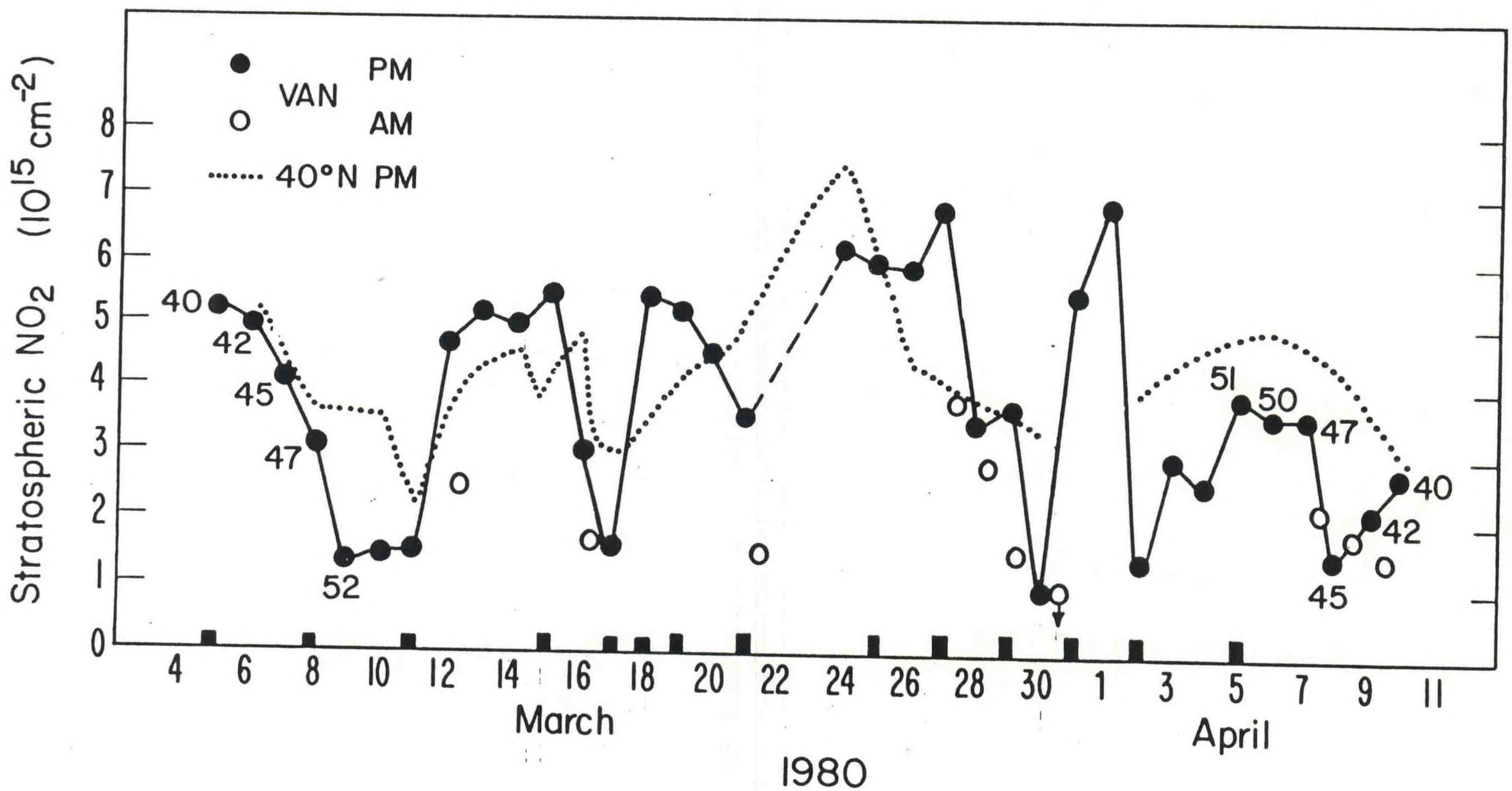

Fig. 1. NO_2 at 40°N and 51°N in the spring of 1980. There is a large scale correlation between the two locations and the ups and downs in NO_2 result from an alternation of northward and southward motion in the stratosphere; this shows how NO_2 may be used as a tracer of such motion.

To further improve the ability to study chemically important tropospheric gases, such an NO_2 and NO_3, a powerful well collimated light source has been installed 10 km from the Observatory. We expect this long path absorption facility to become one of our principal centers of activity in the next few years with the use of new instrumentation such as the sensitive diode-array spectrograph developed in the Aeronomy Laboratory by Dr. Schmeltekopf.

The Florida Atlantic University "PEPSIOS" interferometer has been used successfully to measure stratospheric OH. This important and highly reactive species has now been studied for several years by the Burnetts at Fritz Peak and their work continues to yield almost all of the information presently available on its behavior (See Figure 2).

The Solar Mesosphere Explorer Satellite was launched successfully in October 1981 and is now returning data on stratospheric ozone and a number of other species important in its creation and destruction. As a result of our suggestion in the planning stages the satellite measures stratospheric NO_2 on a global scale, (see figure 3). We are actively participating in the analysis of these measurements as are others from the Aeronomy Laboratory. The results for NO_2 confirm the global picture obtained earlier by us but will naturally lead to a far better and more detailed one than previously possible. One of the most interesting aspects is the ability to study global circulation patterns in the stratosphere using NO_2 as a tracer of the motion. The satellite is also used to measure tropospheric NO_2 by observing the light backscattered from the earth's surface. This permits observation of pollution, and its dispersal, from space on a global scale. This unplanned extra output from SME is being actively pursued and has already revealed a large contribution from lightning to the tropospheric NO_x budget.

The eruption of the El Chichon volcano in Mexico drastically altered the aerosol composition of the stratosphere. The dust cloud was observed by the SME satellite and we have studied the unexpected effects of the aerosol upon stratospheric NO_2. To do so we had to revert to the older ground based methods since the dust itself temporarily rendered SME incapable of detecting NO_2 itself. A remarkably large decrease in stratospheric NO_2 is associated with certain regions of the cloud; no explanation for this yet exists. Whenever the NO_2 is reduced there is a corresponding small increase in the total column abundance of stratospheric ozone. This appears to be the first direct evidence that the total column of ozone does exhibit the theoretically expected dependence upon a measurable change in NO_2 in the stratosphere. The Burnetts have also discovered a sizable effect of the dust cloud upon stratospheric OH.

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, 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.

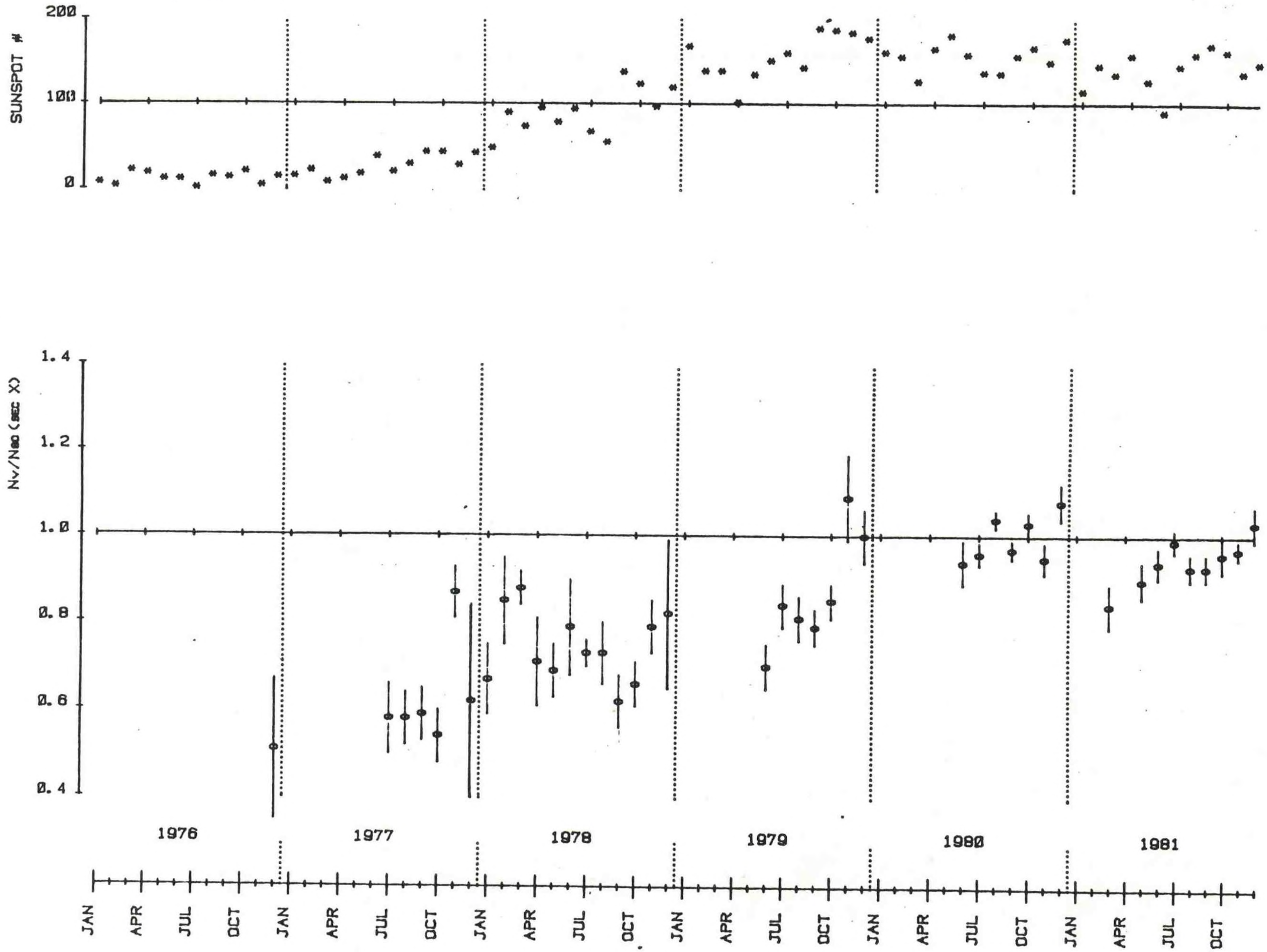

Figure 2. Normalized monthly stratospheric OH abundance and sunspot numbers: 1976 - 1981. The similarity of the long-term trends of the OH abundances and sunspot numbers is apparent.

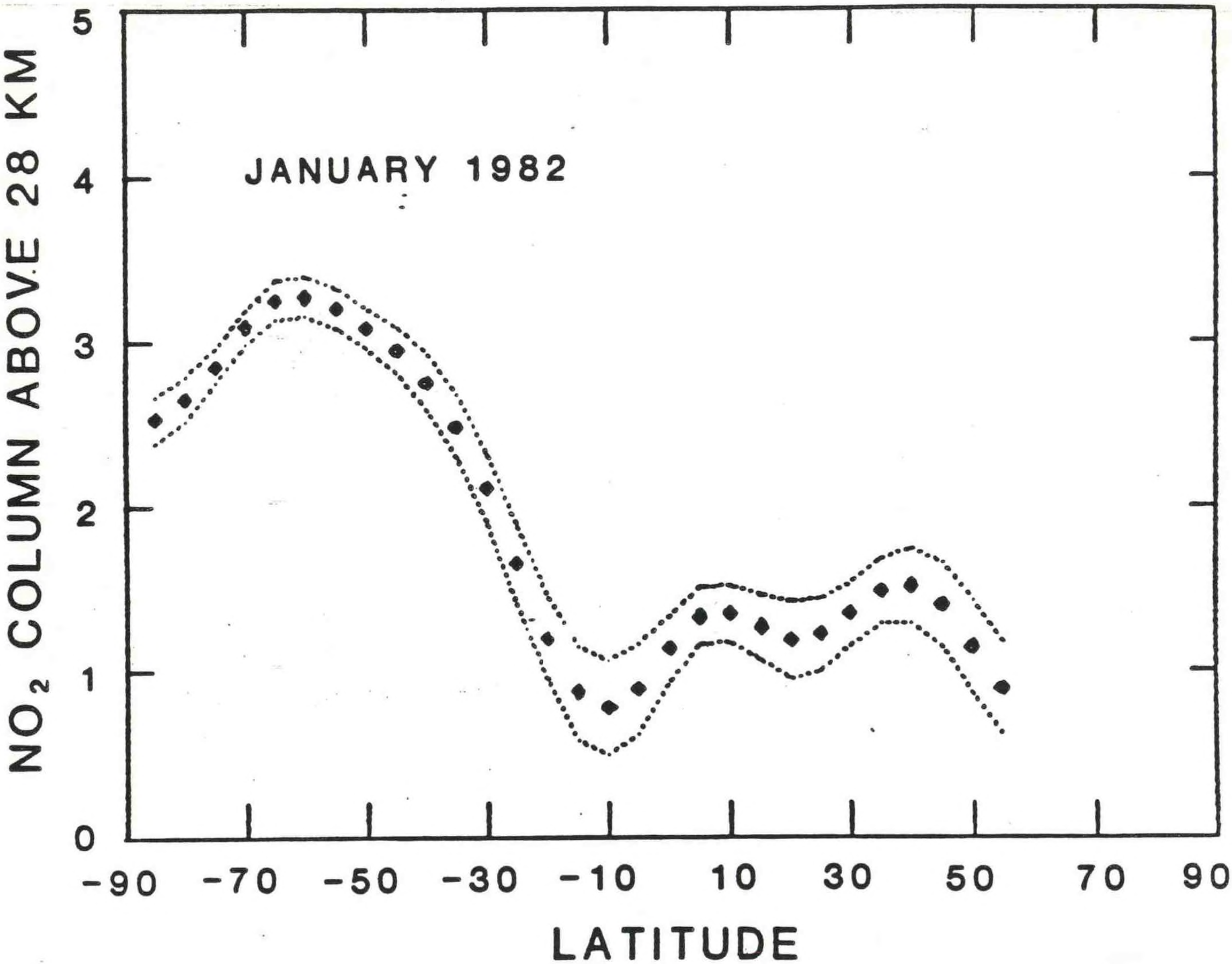

Figure 3. Solar Mesospheric Explorer column abundances of NO_2 ($\times 10^{15}$ cm^{-2}) for January 1982 above 28 km over the sunlit Earth averaged for longitudes between 40^{o}W and 130^{o}W. The dashed lines show the $\pm 1\sigma$ standard deviation of the data at each latitude, including both geophysical "noise" and instrumental noise.

a) Solar minimum

The geomagnetically quiet behavior of the thermosphere during solar minimum has been determined, and the results show the existence of strong equatorwards 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. (See Figure 4).

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 Fritz Peak as well as 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, AK (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 divergences 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 an 8-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.

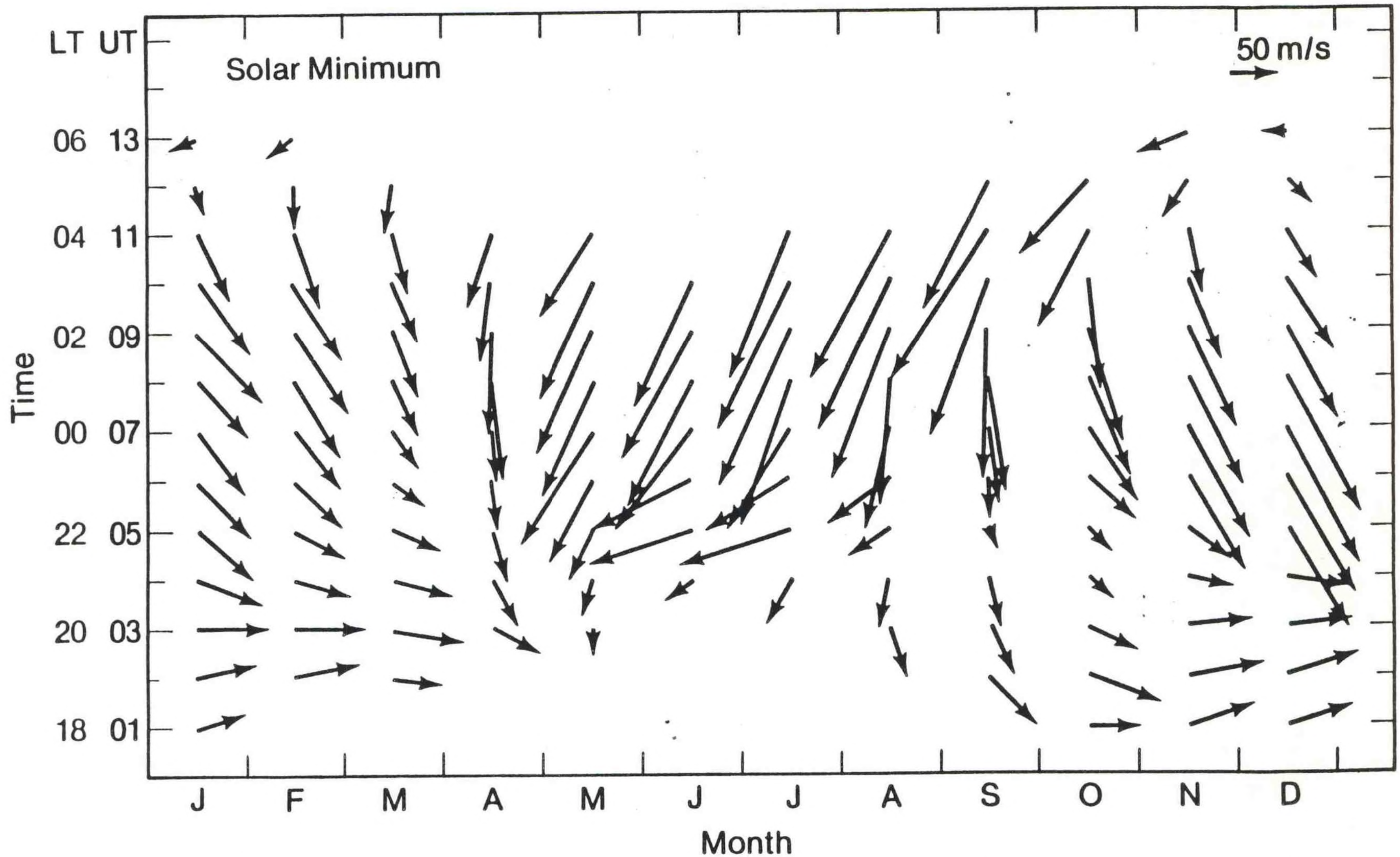

Figure 4. Wind vector variation at ~300 km during the year over Fritz Peak Observatory for solar minimum. Direction is upward to the north, rotating clockwise to the east, south and west.

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 resonse 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 observe infrared molecular oxygen emission at twilight which permit 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.

Spectroscopic Instrumentation

A theoretical study of high resolution spectrometers shows that the ultimate precision and accuracy of measurements is limited by the characteristic noise spectrum of the nearly incoherent radiation sources under measurement, the instrumental spectrum, as well as the noise spectrum of unwanted radiation. The results of this study are applicable to any instrument which depends on the interference of light for its operation.

The conventional high-resolution Fabry-Perot spectrometer is light-limited in its operation. This limitation exists because only one interference ring is utilized out of the 50,000 or more available. Recently we have broken this barrier and we find we are able to use (theoretically) all the available light from this instrument. A practical version of this multiplexed Fabry-Perot spectrometer has been built where we find that gains of 100 in the throughput of the instrument are easily attainable. This high luminosity and high resolution spectrometer has been dubbed TESS, which is the acronym for a Twin Etalon Scanned Spectrometer.

The observations of atmospheric emissions in the auroral zone have, because of the large changes in the source irradiance over short periods of time, led into a new method of measurement. This method is called an equal noise technique, because the measurements are limited to a fixed signal to noise ratio. The basic method consists of measuring for each spectral element only long enough to reach a preset signal to noise ratio, recording this time and then moving on to the next spectral element and so on. This new method is of general applicability to spectroscopic problems, such as hyperfine structure investigatious, since the signal-to-noise ratio is fixed for all features present in the spectrum, regardless of their intensity.

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 exhange 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.

Optical methods lend themselves well to many remote sensing problems, particularly those involving the measurement of minor but chemically important species in both the troposphere and stratosphere. The long path absorption facility at Fritz Peak has only begun to be exploited and we expect the coming years to see a program develop in which a number of important tropospheric species can be studied. One great advantage of the long path absorption technique is that it provides an unambiguous quantitative spectral identification without perturbing the atmosphere itself.

While the great outflow of data from satellites, in particular the Solar Mesosphere Explorer, will receive our active study the recent experience with the volcanic dust cloud shows once again that carefully planned ground based studies of the stratosphere must continue to be carried through. Thus we shall maintain a strong activity in such studies.

The upper atmosphere remains of concern both as the effective upper boundary region for the stratosphere and of course for its role as the environment in which satellites must operate. We therefore expect to maintain activity in this area, concentrating on important problems which can be efficiently studied from ground level.

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AERONOMY LABORATORY SEMINARS

1982 - 1983

October 13, 1982	Satellite Observations of the El Chichon Volcanic Aerosol in the Stratosphere, Gary E. Thomas, Laboratory for Atmospheric and Space Physics and Department of Astro-Geophysics, University of Colorado, Boulder, Colorado
November 3, 1982	VHF Doppler Radar Observations of Buoyancy Waves Induced by Thunderstorms, Daren Lu, Institute of Atmospheric Physics, Beijing, People's Republic of China
November 17, 1982	Recent Results from in situ Measurements of Atmospheric Ions, Al Viggiano, Max-Planck-Institut, Heidelberg
January 5, 1983	Laboratory Chemistry of Atmospheric Cluster Ions, Dr. Hans Boehringer, Aeronomy Laboratory Visitor
January 19, 1983	Electron Spin Resonance Spectroscopy at Matrix Isolated Radicals, Dr. Michael Trainer, NRC Fellow, Boulder, Colorado
February 16, 1983	An Experimental Study of the Fluxes of OCS and H_2S from a Saltwater Marsh, Mary Anne Carroll, NCAR graduate assistant, Atmospheric Chemistry and Aeronomy Division, Boulder, Colorado
March 2, 1983	Radar Studies of Atmospheric Gravity Waves, Dr. R. A. Vincent, Physics Department, University of Adelaide, Adelaide, South Australia
March 16, 1983	Aerosol Chemistry in Trace Vapor Environments, Brian Heikes, NCAR Visitor, Boulder, Colorado
March 30, 1983	Cloud Transport and the Cycles of Sulfur and Carbon in the Clean Pacific Atmosphere, Dr. Robert Chatfield, NCAR, Boulder, Colorado
April 13, 1983	Polar Glaciochemistry: NO_3^- and $SO_4^=$ Deposition, Dr. Michael M. Herron, Schlumberger-Doll Research, Ridgefield, CONN
May 11, 1983	Hydrocarbons at Niwot Ridge (revisited), Dr. J. M. Roberts, NRC Postdoctoral Fellow, Aeronomy Laboratory, Boulder, Colorado

May 25, 1983	Interpretations of Niwot Ridge Results, Dr. David Parrish, Aeronomy Laboratory and Metropolitan State College
June 10, 1983	Measured Fine Scale Structures in the Lower Ionosphere and Their Relation to Mesospheric Turbulence, Dr. Eivind Thrane, Norwegian Defense Research Establishment, Ullestrom, Norway
July 20, 1983	On the Temporal Variations of Stratospheric Trace Gas Concentrations, Dr. Dieter Ehhalt, Institute for Atmospheric Chemistry, Juelich, West Germany
August 3, 1983	Dynamical Control of the D-Region, Dr. Guy Brasseur, Institut D'Aeronomie, Brussels, Belgium
August 10, 1983	Halocarbons in the Troposphere and Stratosphere, Dr. Peter Fabian, Max Planck Institute, Lindau, West Germany
September 14, 1983	Gravity Wave Breaking and Eddy Diffusion in the Mid-Atmosphere, Dr. Jerry Weinstock, Aeronomy Laboratory, NOAA, Boulder, Colorado
September 28, 1983	Studies of the Chemical Composition of Stratiform Clouds, Peter Daum, Environmental Chemistry Division of Brookhaven National Laboratories