Network for the Detection of Stratospheric Change

Report of the Workshop

Boulder, Colorado
March 5-7, 1986

National Aeronautics and Space Administration
National Oceanic and Atmospheric Administration
Chemical Manufacturers Association

TABLE OF CONTENTS

Attachments:
  List of Attendees
  Agenda
  Position Papers

A broad research program currently exists to understand the physics and chemistry of the Earth's upper atmosphere and its susceptibility to change due to natural and anthropogenic effects. This combined program under the auspices of NASA, NOAA, and CMA supports a wide range of investigations including field measurements (utilizing ground, aircraft, balloon, rocket, shuttle, and satellite platforms), laboratory kinetics and spectroscopy, modeling, and data analysis. The major results and understanding obtained from this decade-long effort are summarized in the recent assessment reports issued by NASA ("Present State of Knowledge of the Upper Atmosphere: Processes that Control Ozone and other Climatically Important Gases", NASA RP 1162, (1986)) and by a large international panel ("Atmospheric Ozone 1985: Assessment of our Understandng of the Processes Controlling its Present Distribution and Change", WMO Report No. 16, in press (1986)).

One particular subset of measurement activities that has not received much attention to date has been the development of a ground-based, long term measuring network that is specifically designed to provide the earliest possible detection of changes in the composition and structure of the stratosphere, and the means to understand the causes of those changes. For example, depletion of ozone by increases in stratospheric chlorine is predicted to first be evident as a loss of ozone near 40 km, long before any detectable change in the column abundance of ozone itself. In order to evaluate the feasibility of measuring such changes, as well as identifying their causes, a workshop was held in Boulder, Colorado, on March 5-7, 1986, jointly sponsored by NASA, NOAA, and CMA. This meeting brought together

chemical and dynamical modelers and experimenters with the express goals of:

1. Identifying and prioritizing the key atmospheric parameters that must be monitored in order to observe important changes in the structure of the atmosphere

2. Discussing the magnitudes of possible trends in these key species, and determining the accuracy, precision, vertical resolution and frequency of measurements required to detect these trends

3. Determining the number and locations of stations required to establish a useful network.

4. Evaluating currently available measurement techniques to determine their capability to satisfy the requirements, and identify new instrumentation required.

The agenda for the meeting is attached, as are the brief position papers presented by the speakers.

Assumptions

There are several key assumptions inherent in the limited scope of the meeting. Among them are:

1. Existing and planned satellite measurement activities will continue, e. g. SBUV measurements on the NOAA operational satellites.

2. The ALE/GAGE and NOAA GMCC networks are satisfactory for monitoring, at ground level, long-lived gases such as $CFCl_3$, CF_2Cl_2, CCl_4, CH_3CCl_3, N_2O, CH_4 and CO_2.

3. Total column ozone measurements by the Dobson network are adequate. The intercomparisons between satellite ozone measurements and Dobson column ozone are consistent.

4. Current temperature measurement systems are inadequate.

5. Virtually all other species have no systematic long term measurements.

Objectives of the Network

Long Term: The major goal of the network is a long term one; viz., to provide the earliest possible detection of changes in the stratosphere, and the means to understand them. The remainder of this report discusses that goal and its implementation.

Short Term: Although the proposed network is intended for long term trend detection, it will provide extremely valuable scientific returns in the near term as well. It will enable us to study the temporal (diurnal, monthly, seasonal, and annual) and spatial (latitudinal) variability of atmospheric composition and structure. It will also provide the basis for ground truth and complementary measurements for satellite systems such as the NASA Upper Atmosphere Research Satellite, currently scheduled for launch in the fall of 1989. With the exceptions of ozone, methane, nitrous oxide, and temperature,

no atmospheric species have been adequately measured over even a single annual cycle on either a global scale, or at a limited number of discrete stations. The most comprehensive data base for chemically active species is the seven months of global data obtained by the Nimbus 7 LIMS instrument for nitrogen dioxide, nitric acid, and water vapor. Although satellite systems represent the most promising means of obtaining extensive global data, their high cost, long lead-time, and limited lifetime, preclude their playing a major role in long term trend detection over the next decade. The data to be obtained in even the limited network envisioned here will be invaluable in more critically testing two dimensional models.

Priorities

The workshop identified the following measurements as being of the highest priority to such a network (in order of importance):

1. Column ozone

2. Vertical profile of ozone (0-70 km)

3. Temperature (0-70 km)

4. Vertical profile of ClO

5. Vertical profile of H2O

6. Vertical distribution of aerosols

7. Vertical profile or column of NO2

8. Stratospheric column of HCl

9. Vertical profiles of long-lived tracers: CH4 and N2O

10. Other species (HNO3, OH, ClONO2)

Some of the considerations that led to the above list are:

(1) Column ozone controls the penetration of solar ultraviolet radiation to the Earth's surface. Changes in column ozone may have possible consequences for human health, and terrestial and oceanic ecosystems.

(2) The vertical distribution of ozone controls the temperature structure of the stratosphere. Changes in the vertical distribution of ozone can influence the climate of Earth.

(3) The temperature of the stratosphere controls the rates of chemical reactions. Thus, it governs the catalytic efficiences of the different chemical families in controlling the abundance of ozone. In addition, the temperature structure of the stratosphere itself is controlled by the ozone distribution.

(4) The ClO radical is the chlorine species responsible for directly catalyzing the destruction of ozone. Its atmospheric concentration is predicted to be increasing at a rate of at least 5% per year due to the increasing atmospheric concentrations of chlorofluorocarbons.

(5) Water vapor plays a vital role in controlling the radiative and chemical balance of the stratosphere. It is the dominant source for the hydroxyl radical, which controls the catalytic efficiences of the HOx, NOx, and ClOx families towards ozone. The concentration of stratospheric water vapor is expected to increase due to increasing concentrations of atmospheric methane, and may alter if the Earth's climate becomes warmer and affects the exchange of water across the tropopause.

(6) While aerosols are not thought to play a major role in the chemistry of the unperturbed stratosphere, they may become important both chemically and radiatively, following major volcanic eruptions, and in the Antarctic. In addition, the presence of high levels of aerosols can influence the interpretation of some optical sensor data.

(7) NO_2 is the nitrogen species directly responsible for the catalytic control of ozone, and along with NO plays a vital role in coupling the NO_x and ClO_x families. Consequently, the atmospheric concentration of NO_2 may decrease in the future because the predicted increased concentrations of ClO will convert it into $ClONO_2$. Conversely, increases in the concentration of N_2O, the stratospheric source of NO_2, will offset some of these decreases.

(8) HCl is the key temporary reservoir species in the ClO_x family. It should be monitored in conjunction with ClO in order to see whether the partitioning of species within the chlorine family is changing with time.

(9) CH_4 and N_2O are the gases with long stratospheric lifetimes and quite simple photochemical removal mechanisms: photolysis for N_2O, and reaction with OH for CH_4. This makes them ideal tracers for studying changes in atmospheric circulation.

(10) Measurements of several other chemical species would also provide important information on changes in the composition of the stratosphere. These include $ClONO_2$, OH, HO_2NO_2, and H_2O_2. However at present, measurements of these species are thought to be of a lower priority.

Instrumentation

In order to evaluate the suitability of existing measurement systems to make the requisite measurements, review talks were presented by experimentalists having a great deal of expertise with each instrumental technique, although generally not experienced in using that instrument in a long-term observing mode. Based on the discussions generated by those talks, the following overlap of species and ground-based techniques emerged:

Species	Instrument	Status (see definitions below)
O3 column	Dobson	operating
O3 0-20 km	YAG lidar	under development, ready 1 yr
15-45 km	excimer lidar	under development, ready 1 yr
25-75 km	microwave	ready to proceed
Temperature	lidar	demonstrated
ClO 25-45 km	microwave	demonstrated
H2O 0-30 km	balloon hygrom.	operating
	microwave	proposed (>35km), demonstrated >45 km
aerosols 0-30km	lidar	demonstrated
NO2 strat col	UV/vis spectr.	demonstrated
HCl strat col	IR	demonstrated
CH4 strat col	IR	proposed
N2O 20-50 km	microwave	proposed
HNO3 strat col	IR	proposed
ClONO2 str col	IR	proposed
OH	UV fluorescence	proposed, research mode
	excimer lidar	proposed, minimum 3 yr to feasibility

Operating--currently being used in a routine observing mode; in the case of
H2O, the frost point hygrometers are launched at the rate of 1 per
month at 1 station--expansion is necessary.

Demonstrated--the technique has been used in a research mode to measure the
particular species; work is required to make the technique
network-operational.

Under development--the instruments are being developed, with demonstration
expected in the near future.

Proposed--the technique is believed to be technically sound, but the
particular measurements have not been made.

Station Considerations

For nearly all of the instruments, it is desirable to locate the monitoring
station at high elevation (>2000 meters) in order to minimize the tropospheric
water and aerosol columns. Since the goal of the network is to detect small,
long-term trends, it is necessary to conduct measurements on virtually a daily
basis for statistical reasons. This precludes the concept of timesharing,
e. g., using a single microwave instrument to monitor both ozone and ClO.
Except for the IR instrument, which obtains data for all species
simultaneously, all other instruments will be dedicated to a particular
species measurement. This will allow the buildup of a large, continuous
database which is essential for trend detection. The goal of understanding

the cause of changes, rather than just detecting them, requires that the instruments be co-located, to an extent consistent with the temporal/spatial requirements of the measurements. For instruments requiring a few hours integration time, this indicates that co-location means within about 150 km.

Network and Implementation

Since the purpose of this network is to provide an early warning system of stratospheric change, it is prudent to locate the stations with as much latitude coverage as possible given the obvious constraints of funds and resources. A minimal network, then, would require 6 stations: mid- and high latitude, northern and southern hemisphere; a tropical station; and a polar station, probably in Antarctica. While this initial network could possibly be based on funding from NASA, NOAA, and CMA, the ultimate goal would be to see the network expanded on an international scale, with numerous cosponsors co-ordinated in conjunction with the WMO or UNEP. In particular, we recognize the pre-eminent roles currently being played by the Observatoire de Haute Provence (OHP) in France, the Jungfraujoch Observatory in Switzerland, and other valuable components of a network in Europe.

In North America, major development efforts for ozone lidar systems are underway at GSFC (a mobile stratospheric lidar), NOAA's Fritz Peak Observatory (a tropospheric/lower stratospheric lidar), and JPL's Table Mountain Observatory, TMO (tropospheric and stratospheric lidars). The TMO facility could possibly serve as the first in the network, and will likely be used as a research site, with new instruments first being installed and tested at TMO, before proceeding with full scale deployment. This site may serve as a model

for the others: basing the stations at existing, observatory-type sites where many of the required facilities may already exist. The near term goal is to develop TMO and one other station within the first 2-3 years. The existing OHP site in France is a likely addition to this set. Hopefully, within the next 5 years, the network can be expanded to 6 stations.

In order for this long term effort to be successful, there are several issues that must be addressed with regard to management, personnel and quality control. It is essential that the design phase for the network involve experimentalists, theorists, data analysts, and statisticians to address the issues of measurement frequency, accuracy, and precision. Quality control must be achieved through rigorous calibration procedures and intercomparisons. The success of the ALE/GAGE network demonstrates that this is achievable in practice. It will be a difficult undertaking for traditional research groups to dedicate themselves to the sort of routine, systematic measurements that are required for trend detection, especially since there will be multiple sites involved. While skilled local talent may be used for much of the day-to-day data taking, it will be essential to have senior PI's actively involved in the measurements, at a minimum through site visits/calibrations and data analysis/checking at the home institution. Lastly, the supporting organizations and agencies must recognize that the project is a long-term commitment.

Costs

It was very roughly estimated that capital costs would be about $2-3 million per station for the instruments described earlier. Operating costs for the

full 6 station network are likely to be in the $1-2 million/year range. These costs are substantial. Given the current US budgetary situation, there is little likelihood of new money being available, so that this long term measurement program will represent a major component of the existing upper atmosphere research effort.

Conclusions

It is clearly valuable to develop a systematic measurements program in order to provide an early detection of stratospheric changes, and an understanding of the processes and perturbations causing those changes. The instrumentation and technology to accomplish the measurements are available. Although there are new difficulties in terms of management and quality control, they are not insurmountable. The costs of this program are high, and can only be met through cooperation among the interested agencies and organizations, all of whom will be required to effect a significant redirection of their resources. Although this initial impetus may come from the U. S., participation of the global community will ultimately be necessary in order to fully implement the network.

EARLY DETECTION WORKSHOP

ATTENDEES

NAME	AFFILIATION
Dr. Michael Weinreb	NOAA/NESDIS
Dr. James K. Angell	NOAA/ARL
Dr. M. T. Coffey	NCAR
Dr. William B. DeMore	JPL
Dr. M. MacFarland	Dupont/CMA-FPP
Dr. William G. Mankin	NCAR
Dr. M. Patrick McCormick	LaRC
Dr. I. S. McDermid	JPL
Dr. Thomas J. McGee	GSFC
Dr. Pauline M. Midgley	CMA
Dr. M. H. Proffitt	NOAA/Aeronomy Laboratory & CIRES
Dr. Richard B. Rood	Applied Research Corporation
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Dr. David Hofmann	University of Wyoming
Dr. Michael McElroy	Harvard
Dr. A. J. Miller	NOAA/NMC
Dr. Vernon Derr	NOAA/ERL Headquarters
Dr. Robert Mahler	NOAA/ERL Headquarters
Dr. James Peterson	NOAA/GMCC
Mr. Walt Komyhr	NOAA/GMCC
Dr. Bill Sharp	NSF

WORKSHOP ON EARLY DETECTION OF STRATOSPHERIC CHANGES
Agenda   March 5-7, 1986   Boulder, CO

Wednesday March 5

| 8:30 | Watson/Albritton | Welcome and Introduction |
| | | Format and Goals |

ANTARCTIC OZONE

8:50	Stolarski	Data: satellite and ground-based
9:15	Solomon	Theoretical interpretation/mechanism
9:30	McElroy	Theoretical interpretation/mechanism
9:45	DISCUSSION OF CHEMISTRY	
10:00	Tuck	Trajectories and polar vortex
10:15	Rood	Dynamics; effects at other latitudes
10:30	BREAK	
10:50	Watson	Strawman measurements strategy
11:00	DISCUSSION OF POSSIBLE MEASUREMENTS	
12:00	Lunch	

LONG TERM TRENDS - EARLY DETECTION OF STRATOSPHERIC CHANGES

| 1:00 | Watson | Possible network |

Theoretical Considerations

1:10	Sze	1D; critical species, predicted rates of change
1:30	Solomon	2D modifications to 1D picture: species, trends, sites
1:50	Stolarski	Uncertainity calc'n: guidance
2:10	DISCUSSION OF CHEMICAL CONSIDERATIONS	
2:30	Tuck	Dynamical considerations: species
2:50	Mahlman	Temperature
3:10	BREAK	
3:30	Prather	Sampling frequency; required network size
3:50	Angell	Guidance from past analysis efforts
4:10	DISCUSSION OF THEORETICAL CONSIDERATIONS	
5:00	End	

Thursday March 6

MEASUREMENT TECHNIQUES (15 min presentation + 5 min discussion)

Lidar 8:30-11:00

8:30	McGee	O3 (15 min)
8:45	McDermid	comment (5 min)
8:50	Megie	comment (5 min)
8:55	Discussion of lidar O3 (15 min)	

9:10	Megie	Temperature
9:30	McCormick	Aerosols (also SAGE)
9:50	Proffitt	Tropospheric lidar
10:10	McDermid	OH
10:30	DISCUSSION AND BREAK	

UV/Vis Absorption/scattering 11:00-12:30

11:00	Torr	OH (and ClO)
11:20	Miller	O3: ECC, Umkehr, SBUV, NOAA program; Temperature
11:40	Schmeltekopf	Other species
12:00	DISCUSSION	
12:30	LUNCH	

Microwave, mm, sub-mm 1:30-3:00

1:30	Solomon	O3, ClO, HO2, H2O
1:50	Waters	O3, ClO, HO2, H2O
2:10	Parrish	O3
2:30	DISCUSSION AND BREAK	

IR 3:00-5:00

3:00	Farmer	ATMOS
3:20	Farmer	Extracting stratospheric contribution from ground
3:40	Mankin	Experience from aircraft measurements
4:00	Zander	Experience from Jungfraujoch
4:20	DISCUSSION	

Friday March 7

9:30 through afternoon   DISCUSSION

We will first finish any presentations or discussions left from
the preceding days.

Then, a strawman measurements strategy/implementation plan will
be presented for discussion. Some of the specific points that
need to be addressed in the discussion are:

1.   Key species to be monitored; accuracy, precision required.

2.   Instrumental techniques to be used.

3.   Number and location of stations in a network.

4.   Measurement strategies and protocols.

5.   Goals for both near (1-2 yrs) and long term (3-10 yrs).

Nimbus 7 SBUV/TOMS Measurements of the Springtime
Antarctic Ozone Hole

R. S. Stolarski

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The satellite data from the Nimbus 7 TOMS and SBUV instruments
significantly extend our view of the growing ozone minimum during the
South Polar spring and places constraints on possible mechanisms for
explaining the phenomenon. The deep minimum, or hole, has a structure
that looks much like the polar vortex. The areas of maximum decrease
are clearly confined spatially. There appears to be a smaller decrease
in the ozone maxima surrounding the polar region over the 7 years
studied. These are harder to interpret because of the strong planetary
waves in this region.

A most important mechanism constraint placed by this is that the
decrease takes place in September during twilight, not in the polar
night. During the period of polar night the parcels in the vortex are
not strictly confined to darkness but do spend a large fraction of their
time there with little exchange with air parcels outside the vortex.
The maximum rate of decrease occurs after most of the pole is sunlit.
The rate of falloff of the minimum values is about 0.6% per day extended
over 40-50 days in 1983.

Any explanation of the ozone change must be simultaneously consistent
with the year-to-year change as well as the rate of decrease through
September. These appear to be consistent with a chemical mechanism but
the problem is finding one which can affect ozone on such a short time
scale. The obvious chemicals are the halogens, bromine and chlorine.
Of these chlorine is the more likely because of the increase of its
concentration with time, although bromine may enhance the rate of ozone
loss in the lower stratosphere through its interaction with chlorine. A
crude calculation indicates that for chlorine at its 1983 concentrations
to cause the 0.6% per day decline in September would require all of the
chlorine to be in its active state, i.e. Cl and ClO with little or no
interference from NOx. Thus a mechanism must be found which removes the
chlorine from both the HCl and ClONO2 reservoirs and ties up NOx,
preferably as HNO3.

Until such a mechanism is found and demonstrated correct, it is not
clear what the implications are for global predictions of the effects of
fluorocarbons on stratospheric ozone. The magnitude of the predicted
fluorocarbon effect on ozone has been uncertain because of the
interaction among the chlorine, nitrogen and hydrogen containing species
and ozone itself. The constraint placed on a chlorine mechanism by the
data appears to require stripping away these interactions under special
conditions and observing the pure active chlorine effect on ozone. The
reactions forming this simple catalytic cycle have never been in much
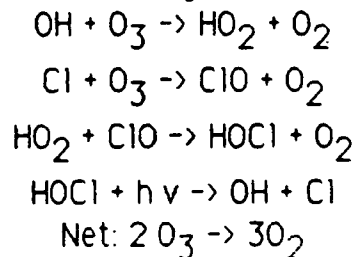doubt.

On the depletion of Antarctic ozone

Susan Solomon, NOAA Aeronomy Laboratory, Boulder, CO
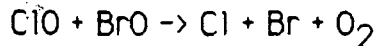NASA trends workshop, Boulder, CO, March 5-7, 1986

Farman et al. (1985) have shown that total ozone abundances in Antarctica have decreased substantially (about 30-50%) in the spring in recent years. Satellite observations (Krueger and Stolarski, 1985) have revealed similar depletions over a very extended region in general agreement with Farman et al.'s ground based data. These large depletions seem to be confined to high latitudes during Antarctic spring; no such dramatic depletions are observed in Antarctica during other seasons, nor in the Northern hemisphere.

Further information regarding the vertical profile of the ozone perturbation is essential to an understanding of the origin of the observed total column changes. Antarctic balloonsonde data are available from the Syowa (69S, 39E) ozonesonde station for several years in the late 1960's and early 1970's, and for 1982. These data show that the ozone perturbation occurs during August and September, (but not during the polar night period) and that the largest changes in the vertical profile occur near 15-20 km, where the observed percentage changes are about 30-50%. At these low altitudes, the ozone photochemical time scale is of the order of several years using presently accepted homogeneous photochemistry. If the observed depletions are the result of a chemical process, then the said process must obey the following constraints: 1) it must be essentially confined to the southern hemisphere, 2) it must be a fairly strong function of latitude, 3) it must produce an acceleration of the ozone chemical loss rate from a time scale of years to a few months near 15-20 km, and 4) it must increase with time over the past twenty years or so. Constraint 4) clearly suggests that we examine the chemistry of atmospheric chlorine.

At the low altitudes where the ozone perturbation is observed, chlorine can (in principle) destroy ozone through the process

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$HO_2 + ClO \rightarrow HOCl + O_2$$
$$HOCl + h\nu \rightarrow OH + Cl$$
$$\text{Net: } 2\,O_3 \rightarrow 3O_2$$

and by (McElroy et al., 1986):

$$ClO + BrO \rightarrow Cl + Br + O_2$$

In practice, however, these processes are not very effective near 20 km for presently accepted photochemistry since very little of the available chlorine is expected to be present in the form of ClO at these altitudes. Rather, the bulk of the available chlorine resides in the form of the reservoirs, HCl and $ClONO_2$ for presently accepted chemistry. Indeed, each of these reservoirs is predicted to be present in about 100 times greater abundance than ClO near 20 km. To appreciably enhance the density of ClO, the equilibrium between ClO and its reservoirs must be dramatically disturbed. If chlorine chemistry is the cause of the Antarctic ozone phenomenon, then the crux of the problem is the identification and validation of a process that can perturb these equilibria sufficiently to allow ClO to become the major chlorine species at 20 km. Under these circumstances (ie., ClO abundances of the order of ppbv; HCl and $ClONO_2$ greatly reduced from typical levels), the calculated ozone changes would be comparable to those observed.

It is likely that the reaction between HCl and $ClONO_2$ takes place rapidly on surfaces (Rowland, 1984):

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$$
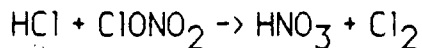
If this reaction is heterogeneous, it presumably takes place in the stratosphere only in the presence of stratospheric aerosol, and indeed, it is well known that the stratospheric aerosol surface area increases substantially in the vicinity of polar stratospheric clouds. Furthermore, these clouds are very common in the cold environment of Antarctic winter and early spring near 10-20 km, where their occurence frequency is far greater than in the warmer Northern hemisphere (McCormick, 1983), suggesting that this process should be enhanced specifically in Antarctic spring. It will be shown that this reaction can lead to ozone depletions that are similar to those observed insofar as their vertical, latitudinal, and temporal characteristics are concerned. Furthermore, the implications of this process for the behavior of NO_2 and HNO_3 are consistent with observations by McKenzie and Johnston (1984) and Williams et al. (1982), providing an independent check on inferences drawn from ozone observations. This and other mechanisms capable of producing the observed changes in ozone will be discussed and contrasted. Implications for other species in Antarctic spring will be described.

References

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McCormick, M. P., Adv. Space Res., 2, 73-86, 1983.

McElroy, M. B., Salawitch, R. J., Wofsy, S. C., and J. A. Logan, submitted to Nature, 1986.

McKenzie, R. L., and P. V. Johnston, Geophys. Res. Lett., 11, 73-75, 1984.

Rowland, F.S., paper presented at NASA meeting on the stratosphere, Feldafing, 1984.

Williams, W. J., Kosters, J. J., and D. G. Murcray, J. Geophys. Res., 87, 8976-8980, 1982.

DYNAMICS, EFFECTS AT OTHER LATITUDES
for
Session on Antarctic Ozone
Workshop on Early Detection of Stratospheric Changes
by
Richard B. Rood

If chemical processes particular to polar latitudes are important in the development of the Antarctic ozone hole, then it is likely that the dynamical configuration of the Southern Hemisphere is instrumental in maintaining the conditions necessary for the chemical processes to take place. More precisely, the strength of the southern polar vortex, coupled with the weaker planetary wave forcing in the Southern Hemisphere, inhibits the mixing of midlatitude air into the polar region during much of the winter. The Northern Hemisphere is characterized by extensive midlatitude/polar mixing particularly during stratospheric warmings. In the Southern Hemisphere during the breakdown of the vortex there is significant meridional mixing as is evidenced in satellite derived total ozone fields. If there is substantially depleted polar ozone, does the mixing during the final warming cause any significant depletion of ozone at midlatitudes or does the final warming essentially just fill up the hole?

Two numerical experiments have been performed with a three dimensional ozone transport model to determine what the effect of depleted polar ozone on midlatitude ozone might be. In the baseline experiment the redistribution of a wintertime ozone field during the growth and decay of a planetary wave is calculated. In the second experiment, an artificial ozone "hole" is placed in the initial ozone field poleward of 60°. The depletion at the pole is > 80%. The experiment is run for 60 days.

The numerical experiments are designed to isolate the effects of planetary wave transport on the preexisting ozone hole. The experiments

should give some idea of how ozone is transported during the breakdown of the polar vortex (the final warming). Since planetary wave transport is the primary mechanism of north/south transport during the winter and early spring, the amount of reduction of midlatitude ozone due to depleted polar ozone is revealed.

When compared to the baseline case, the original depletion of 80% at the pole is reduced to < 40% by day 15 between 30 and 40 km. The depletion is reduced to less than 10% by day 30. Above and below the 30-40 km layer, the reduction of the polar ozone deficit is smaller.

The initial ozone depletion is confined to latitudes poleward of 60°. By day 30, depletions relative to the baseline are computed between 30° and 60°. The magnitude of this depletion is < 10% and decreases towards lower latitude.

These experiments indicate that during the breakdown of the polar vortex, enough ozone is transported to high latitudes to largely fill in the ozone hole. The concomitant "propagation" of the ozone hole to midlatitudes during the breakdown of the polar vortex should not lead to major deficits of midlatitude ozone.

COMMENTS ON THE FEASIBILITY OF GROUND-BASED
MM-WAVE MEASUREMENTS OF ANTARCTIC CLO

Prepared by Brian Connor and R.L. de Zafra
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for NASA Workshop, Boulder,Colorado, March 5-7,1986

To accord with current modeling scenarios dealing with
the observed rapid depletion of ozone in the lower
stratosphere during spring on the eastern side of Antarctica,
there should be a marked increase in stratospheric ClO in the
same altitude range, commencing about the time of solar
return (approx. Aug. 15 at 75 degrees south, the latitude of
Halley Bay), and persisting until the breakup of the polar
vortex in mid to late November. We assume that chlorine will
be released by photolysis to equilibrium concentrations
shortly after sun-up, and that the concentration of ClO will
remain high during the entire period of catalytic ozone
destruction. From these assumptions, what are the prospects
for a successful measurement of ClO in the 15-30 km altitude
range, using the ground-based mm-wave spectrometer technique
which we have employed successfully for the measurement of
ClO over the past several years?

A. Model Predictions of ClO Signal Strength.
We have considered model profiles for vertical ClO
distribution from two sources, the Harvard model of McElroy,
et al. and the NOAA model of S.Solomon, et al. These two
models yield rather different vertical profiles for ClO, and
we have not obtained predictions from the Harvard model for
altitudes above 30 km, but in both cases the rotational
emission line intensity predicted from the mixing ratio
profiles below 30 km leads to a dramatically increased signal
strength, compared with normal mid-latitude values. Moreover,
the amount of ClO at low altitudes is sufficient,
particularly in the Harvard model, to yield an unmistakeable
contribution to the pressure broadened line shape, sufficient
to allow our line shape deconvolution techniques to get a
good measure of the vertical profile down to about 22 km, and
possibly lower.

B. Accessibility of Antarctic Sites
The best currently operating antarctic stations appear to
be the station at Halley Bay operated by the U.K. and the
U.S. station at the South Pole.Neither is easily accessible.
Halley Bay is normally supplied only by ship, during the
months of December and January.The Amundsen-Scott South Pole
station is accessed by plane, between approximately mid
November and mid February at best, via the U.S. station at
McMurdo Sound. The plane-access season at McMurdo is not much
longer in duration - generally early or mid October to the
beginning of March. McMurdo is reached by plane or ship from
New Zealand.
The normal first-access times at either Halley Bay or
the Pole are thus too late to allow adequate (or probably
any) observations to be completed before ozone has recovered

from the spring depletion cycle, especially if equipment
set-up and debugging must first be accomplished under
unfamiliar and hostile conditions.

The alternatives are (a) to set up the equipment and
leave it to winter over, counting on station personnel to
start it up and take data, after undergoing some training (or
to leave one or two dedicated volunteers to stay at the
station along with the equipment); or (b) to explore early
means of reaching Halley Bay by plane, e.g. via the
Falklands, in late September or early October.

C. Enviornmental Factors

Ground-based mm-wave observations require low water
vapor column density. It is desirable to have less than 2 mm
of precipitable water vapor overhead. This condition appears
to be met about 25% of the time at Halley Bay in spring,
according to balloon sounding profiles of water vapor
collected during 1957 and 1958. About 50% of the time,
precipitable water vapor is below 2.3mm, so that conditions
varying between adequate and quite good could be expected for
reasonable periods . Stratospheric mm-wave observations can
be carried out through cloud cover if water is in ice crystal
form (e.g. high cold cirrus). Halley Bay, as a coastal site,
is subject to substantial low cloud cover and fog, in part
associated with open water leads which may come and go,
particularly near the shore, even in the depths of winter.
The Amundsen-Scott South Pole station in mid-continent at an
elevation of 2800 meters , with a considerably colder and
drier climate year round, would be more favorable, were it
not for its remoteness and fearsomely low temperatures.

Our equipment has functioned without problems down to
about -20 C which is typical for Halley Bay in mid-spring
(October), but was not designed for the -65 C minimum
temperature encountered at the South Pole in the same season.
Some cold-proofing would have to be done and protection from
wind and wind-blown snow would be needed at either site.

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We conclude that ground-based mm-wave observations could
readily test the hypothesis that the spring depletion of
ozone in East Antarctica is due to a large enhancement in the
normal Cl_x concentration in the lower to mid stratosphere.
The problems of logistics and of adapting our equipment to
the harsh enviornment are substantial, but probably no more
so than for most other ground based experiments conducted in
Antarctica. A solution would entail extensive advanced
planning, expense, and coordination with other experimental
efforts in order to maximize cost-effectiveness and
scientific return. It would appear that no "quick in and out"
experiment is possible if the goal is to measure ClO.

The Temporal and Spatial Behavior of Trace Gases: Early Detection of Stratospheric Changes

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The concentrations of several stratospheric and tropospheric trace species are expected to show an upward trend in the next decade or so. These include CO_2 (0.5%/yr), CH_4 (1-2%/yr), N_2O (0.25%/yr), CO (2-4%/yr), and stratospheric total chlorine, ClY (~ 4%/yr). Continued monitoring of the above species is needed for early detection of stratospheric changes. The possible effects on stratospheric ozone of the above trace gases' trends are of particular interest. Although all the above species will affect stratospheric O_3 on long time scales, the detectable effect over the next decade or two may be those associated with the chlorine species. We will discuss the future trends of O_3, chlorine species (HCl, ClO), HF, and C_2H_6 (a tracer for Cl in the lower stratosphere). We will also discuss the possible effects on O_3 and other species of speculative chemistries and dynamics and suggest observational strategies by which new theories can be tested.

Ozone

The largest percent depletion of local ozone density in the near future are predicted to occur near 40 km. The calculated change in ozone at 40 km in the near future is more sensitive to trends in ClY than those of CH_4, CO_2, or N_2O. Continued monitoring of O_3 in this region appears to provide the best possibility for early direct detection of local O_3 trends. A meaningful analysis of these measurements also necessitates simultaneous observations of temperature, solar ultraviolet (UV) and chlorine species. Trend analysis of O_3 data between 40 and 50 km requires, however, the detrending of other effects affecting the ozone abundance. These effects include variations of 3 to 10 percent due to solar UV changes over an eleven-year solar cycle. Recent studies also indicate possible impact of sodium species on chlorine partitioning, inducing variation in O_3

as large as 10-15 percent near 50 km.

The hypothesized photochemical effects on O3 in the lower stratosphere (~ 20 km) could be detected in the stable region of the Antarctic polar vortex during early spring. It is, however, important to implement measurement strategies aimed at distinguishing photochemical effects from radiative-dynamical effects. The photochemical effect seems to require the existence of relatively high abundance of ClO of about 1 ppb at around 20 km during the early spring. Observation of the diurnal variation of ClO in the Antarctic region should shed additional light on the mechanisms controlling ClO and the behavior of reservoir species including OClO, ClNO3, and HOCl. The testing of the proposed radiative-dynamical mechanism involving the upward intrusion of air with low O3 content from the base of the polar vortex would require the simultaneous measurements of the behavior of other long-lived species, including aerosol, during the early spring period.

HCl

Models predict an increase of 3 to 4 percent per year in the column density of HCl above the tropopause. The above estimate depends on the assumed abundance of total chlorine and on the amount of tropospheric HCl. Continued ground-based measurements of total column HCl, tropospheric HCl, stratospheric HCl, and total chlorine are needed.

The expected rate of increase in the total column density of HCl could appreciably slow down if alternate heterogeneous chemical mechanisms such as $ClNO_3 + HCl \longrightarrow Cl_2 + HNO_3$ and $ClNO_3 + H_2O \longrightarrow HOCl + HNO_3$ were effective in converting various chlorine reservoirs into the more active form of chlorine. These processes, if effective, could lead to nonlinear response of O3 to stratospheric chlorine perturbations.

C2H6

The abundance of ethane above 20 km is very sensitive to the concentration of chlorine. We predict a decrease in the C_2H_6 concentration of 30 percent at 20 km and a factor of 2 at 24 km between 1985 and 2000, assuming a constant CFC emission rate

-2-

after 1980. Measurements of C2H6 in this region could be used as an early indication of anomalous increases in Cl and ClO.

HF

Models predict increases of approximately 10 percent per year, in good agreement with observation. Continued monitoring of HF will serve as a check on the expected stratospheric input of fluorocarbons (CFCl3, CF2Cl2) versus that of chlorocarbons (CCl4, CH3Cl, CH3CCl3).

Two-dimensional perspective on ozone depletion

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NASA trends workshop, Boulder, CO, March 5-7, 1986

Quantitative estimates of the effect of increasing chlorine abundances on stratospheric ozone have largely been performed with one-dimensional models. Current one-dimensional models predict a rather small steady state ozone column reduction of about 4-6%. These small values result from a balance between large depletions in the upper stratosphere and increases in the lower stratosphere (the chemical "self-healing" effect), so that the total column change is a small difference between the two. It is however, well established that lower stratospheric ozone is largely dynamically (not chemically) dominated, particularly at middle and high latitudes in winter. In particular, the chemical self-healing is likely to be much less important at high latitudes than one-dimensional model projections indicate, leading to greater total ozone column changes there. Further, latitudinal variations in long-lived species such as CH_4 are expected to produce latitudinal gradients in ClO and HCl, with associated effects on the ozone changes near 40 km. These and other two-dimensional variations in trace species related to ozone depletion projections will be explored.

Reference: Solomon, S., R. R. Garcia, and F. Stordal, J. Geophys. Res., 90, 12981-12989, 1985.

Uncertainty Calculations and Their Relationship
to the Problem of Early Detection of Ozone Change

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Laboratory measurements of rate coefficients for chemical reactions are usually input to stratospheric photochemistry models as single "best" values for each reaction. In general, a laboratory measurement is done numerous times and our best knowledge is actually a central value and a distribution about that value. We have done a Monte-Carlo calculation of uncertainty propagation through a stratospheric photochemistry model in an attempt to include the full range of information concerning chemical reaction rate coefficients. The result of such a calculation is the prediction of probability distributions for the concentrations of stratospheric species and for the changes in ozone and other species due to specified perturbations.

These probability distributions can be used in several ways to attack the problem of model-measurement intercomparison and the search for the best way to detect future changes. We have examined several possibilities for using measurements to reduce the uncertainty range of model predictions. A study of the calculated present-atmosphere ozone concentration versus altitude indicates that it has little predictive capability for changes in the ozone column induced by chlorine perturbations. This probability distribution for ozone concentration at 40 and 50 km did overlap the data with the model being generally below the data. At 30 km the model was consistently higher than the data. In none of the more than 300 cases run did the model fall within the one-sigma variability range of the data at all three altitudes. The 50 or so cases which showed the best fit with the data showed no preference for either high or low ozone depletion predictions.

The best correlations for ozone depletion predictions was with lower stratospheric parameters. It was found that sets of reaction rate coefficients which predict high ozone depletions for small chlorine injections tend to yield larger disagreements with data than do other cases. Specifically, the model predicts lower stratospheric ClO concentrations which are on the high side of measurements. Since the ambient ClO/ClX is one of the best predictors of chlorine perturbation efficiency, models with low initial ClO are favored by the data. This eliminates virtually all cases which give more than 10% ozone change for continued release of fluorocarbons at their present rate. Examination of NO and NO_2 data indicates that the model tends to yield concentrations pretty much in the center of the measurement range. The measurements thus indicate that models on both extremes of the range of odd nitrogen compounds should be discarded. This procedure eliminates a

number of low ozone depletion cases (when odd nitrogen is high) and also a number of high ozone depletion cases (many of the same cases as discarded on the basis of disagreement with ClO). When all three of these are taken together, 125 of 329 cases remain with an ozone depletion of $3\pm2\%$ for steady-state at the present fluorocarbon flux. This is contrasted with $6\pm5\%$ before screening with the measurements.

An interesting poor correlation is that of the change in ozone due to a chlorine perturbation with the lower stratospheric hydroxyl radical concentration. We have begun examining the correlations of column ozone change with a number of measured parameters and are attempting to determine a strategy for the best method of early detection of change as well as for an identification of the cause of change.

Position Paper: Dynamical Considerations in Station Location, Geographical

Representation and Variablility - Species

N91-71519

A.F. Tuck, NASA/NOAA/WMO/CMA Workshop on Early Detection of Changes in Stratospheric

Structure, Boulder 5-7 March 1986.

Introduction

Three types of changes in chemical species, particularly ozone, may be considered
for the purposes of this exercise:

1) Upper stratospheric changes, induced by photochemical chain reactions.

2) Lower stratospheric changes induced in high latitude winter and spring.

3) Changes in total column abundances induced by a combination of (1)

and (2).

It seems unlikely that detection of (3) would provide a better early warning system,
at least in principle, than (1) and (2). Accordingly, further consideration is given
mostly to these two categories. I am aware that this flies in the face of an
obvious lesson from Farman et al.

Upper Stratospheric Changes

One early warning possibility is the change in shape of the waveform of ozone
during sunlight hours under a switch from NO_x and HO_x - dominated chemistry to
Cl_x - dominated chemistry, as suggested by Pallister and Tuck (1983) and Herman
and McQuillan (1985). For ground based measurement, the requirement of 1-2 km
resolution at 40-50 km is severe. The maximum calculated amplitude of the
diurnal variation tends be in the equatorial regions. What evidence there
is suggests that the non-diurnal O_3 variance is also less there, although tidal
effects on the equatorial O_3 diurnal waveform remain unexplored. On balance, a

lidar technique near the equator would seem to be indicated by these preliminary considerations. It is obvious that for both mechanistic understanding and long term monitoring, concomitant diurnal measurements of O_3, OH, HO_2 and ClO, plus long term measurements of H_2O would add great value. A problem with the tropics is the large intervening tropospheric H_2O column; perhaps a high dry mountain site (in the Andes?) is indicated.

Lower Stratospheric Changes

There are some indications of significant changes in the ozone content of stratospheric air emerging from exposure to the cold temperatures (and possibly the concomitant Polar Stratospheric Clouds) of the Antarctic night. The requisite low temperatures for PSC formation are also intermittently found in the Arctic. Because it seems to be the case that darkness and the return of sunlight to the cold vortical air are involved there is a need to consider monitoring operations at both the preferred locations (if any) of these PSC's and also of any preferred locations for the cold air to leave the vortex. It may therefore be necessary to conduct a design study with diagnosed isentropic potential vorticity maps and/ or trajectories, before siting stations. PSC observations and synoptic intuition suggest the Hudson Bay Area, Iceland-Scandinavia and possibly the sea of Okhotsk, in addition to sites at the Centre and periphery of the Antarctic continent.

It is tempting to ask if continuous lengthy periods of darkness are essential from the chemical rather than the radiative point of view. If not, there is a possibility of effects in the lower tropical stratosphere in regions of cumulonimbus penetration, where temperatures of $-90^\circ C$ and ice crystals are also observed, but where there is an everpresent 12 hourly switching between dark and sunlit conditions.

Farman, Murgatroyd, Silnickas and Thrush (1985) point out that the decay of total ozone observed at Halley Bay and Argentine Islands during Antarctic summer (fig 1) is a combination between a photochemical sink and downward motion. The smoothness of this decay suggests that stations located inside and just outside the Antarctic

circle may be uniquely valuable for testing the photochemical loss of ozone; in particular there should be observable effects at points where, near equinox, very short periods of insolation are experienced, during which some reservoirs may be photodissociated but others may not.

The Aleutian high is another region in which isentropic potential vorticity studies suggest that air may on occasions have a long residence time in a system not subject to much dynamical fluctuation, and which may therefore be suitable for longer term ground based study of photochemical evolution. Such a proposal must be very speculative, however.

Summary

○ Upper stratospheric monitoring, possibly via diurnal cycle: best done from a high, dry tropical mountain.

○ Lower stratopheric monitoring: best at Antarctic and sub-Antarctic sites, but also possible in the Hudson Bay to Scandinavia sector in the Arctic.

○ Long shots: Aleutian high, lower tropical stratosphere at points of ingress of cumulonimbus storms. Also, consider regular flights of an aeroplane with upward pointing instruments, flying above most of the tropospheric water vapour.

WORKSHOP ON EARLY DETECTION OF STRATOSPHERIC CHANGES

March 5-7, 1986   Boulder, CO

POSITION PAPER: **Sampling Frequency & Required Network Size**

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What should be the location, size and sampling frequency for a network of stations designed to give an early warning of stratospheric changes? In lieu of providing immediate answers to this question, let us examine some of the problems which might obscure the detection of trends in the stratosphere and, therefore, some of the sampling strategies which may allow extraction of trends from the natural atmospheric variance. I will try to point to necessary research--both theoretical & observational--which is needed to answer better this primary question. I shall focus on *the middle to upper stratosphere (above 30 km)* where chemistry plays an active role on dynamical time scales, and where the photochemical perturbations to ozone are predicted to be greatest (Antarctica aside).

1. What atmospheric conditions should we expect in 10-20 years?

Chemical composition:

Extrapolation of current trends is too simple a model for atmospheric changes, but it may suffice for the next decade or so. The table below is my rough estimate of the changing atmospheric composition (loosely derived from Chapter 3, NASA Assessment). A look at the RAND assessment of halocarbon growth over the next two decades gives a similar estimate of Cl_x increases. Verification of these trends in the long-lived trace gases will come about mainly through tropospheric monitoring; trends unique to the stratosphere (HCl and C_2H_6 are discussed by Sze et al) represent important confirmation of the atmospheric models.

| | Observed trends (Chapter 3) | | | | | Rand scenario (1986) |
year	Cl_x	Br_x	CH_4	N_2O	CO_2	Cl_x
1980	2.77	28.1	1.62	296	343	2.8
1985	3.23	29.2	1.70	300	350	3.2-3.2
1990	3.85	31.2	1.79	304	357	3.6-3.9
1995	4.70	35.2	1.88	308	364	4.1-4.7
2000	5.87	42.7	1.97	311	372	4.5-5.7
2005	7.51	57.2	2.07	315	379	5.0-6.8

Climate:

We expect a detectable change in global climate within the next 2 decades (due mainly to increases in CO_2). The direct stratospheric effects of CO_2 increases are small (cooling of less than 0.5°C), but the tropospheric climate during this period is expected to undergo substantial warming (> 0.5°C). The climate change is likely to result in significant reductions of long-wave eddy kinetic energy as the pole-to-equator gradient in temperature is reduced. These planetary waves have a major impact on the forcing of the mean stratospheric circulation. This impact is a topic of current research and its effect on stratospheric monitoring strategies is unknown.

2.   What should we try to measure: O_3, T, ClO, NO, H_2O, ...?

This topic is discussed by others, and I include only the following comments: Simultaneous observation of several variables would definitely aid in the interpretation of trends. Furthermore, the observed correlations of ozone with temperature (etc.) would allow some of the atmospheric "noise" to be removed (e.g., ozone values corrected to a standard temperature), perhaps even the interannual variability & solar variability. Current photochemical models are capable of predicting such correlations.

Systematic errors or signals specific to a Cl_x perturbation:

Do the correlations of ozone with temperature change with Cl_x? Does the altitude dependence of this correlation change at high levels of Cl_x? (Can we sample so as to eliminate this atmospheric noise?)

Will elevated levels of Cl_x and CH_4 affect the diurnal cycles and therefore possibly corrupt or disguise the signal of a trend? (In 30-50 km range: no)

Can we adequately interpret solar occultation data today? (Systematic errors in the inferred abundance of $NO-NO_2$ occurs below 35 km and for O_3 above 55 km.)

Can we remove the effect of atmospheric tides which have a large diurnal amplitude in the tropics? (Systematic differences of at least 10% in ozone concentrations are predicted for the tropical stratopause.)

3.   How frequently should we sample, over what spatial scales?

High frequency variability at a fixed location is directly related to the spatial scales of inhomogeneous air parcels. We see spatial variability in the stratosphere on vertical scales of 100 m and (as inferred from ascent and descent data several hours apart) on horizontal scales of 100 km. Does a "stratospheric-trends" network need to resolve and individually average over these lamina? Or can we effectively average over them by integrating the "signal" over 1 km in altitude and half the day? This problem is unresolved.

We need to develop new types of theoretical models which are able to infer the source of the different composition of these layers and the impact of this small scale structure on average ozone concentrations (at the 5% level). Is there any hope of modelling these vertical scales in current or projected 2/3-D models? (probably not) Are the 100m lamina essential to the chemistry, or can we calculate the photochemical response of the system on the average of conditions, or will they be mixed with their environs in relatively short time scales? (probably not)

(Example: In the lower troposphere we need to resolve the spatial/temporal scales of the event/parcels which we are measuring. For example, at Cape Grim, Tasmania 'polluted' air parcels from the mainland of Australia sweep over the observing station in less than 24 hours; but at Adrigole, Ireland, events with elevated levels of CFCs typically last from 3 to 6 days. This difference is predicted by 3-D tracer models and can be identified with the relatively small extent of the Australian source region (Melbourne) as compared with that of Europe.)

Is there a measurement problem in averaging over these layers? Is a "mean" value correct? For example, when we integrate thermal emissions over a large volume, is it homogeneously weighted as in temporal averaging? Or does it disproportionately weight the hotter parcels? (It is likely that temperature will be correlated with some concentrations.)

4.   Where should we locate ground stations?

If we are limited in spatial sampling to a few fixed locations (i.e., ground stations) then the choice should be made so as (1) to enable effective spatial sampling through a time series and (2) to eliminate noise associated with natural atmospheric variability.

(1) The location should not preferentially sample air with respect to longitude. If all air parcels in a given latitude/altitude range are equally likely to pass over the station then a good time series of observations gives effective spatial sampling. (This is clearly a problem in the troposphere where we have strong longitudinal gradients associated with continental vs. oceanic sources.) At mid-latitudes the large planetary waves in the troposphere might create standing waves in the middle stratosphere, but this seems less a problem in summer than winter. A more serious problem may occur in the tropics where there is major forcing at the tropopause due to deep convection over the continents. Depending upon the zonal winds (which change seasonally and quasi-biennially), this signal may propagate through the stratosphere and create a systematic, standing disturbance in temperature which would bias the observations over one station.

(2) The location should avoid strong gradients in chemical concentrations because it would be difficult to extract chemical trends from atmospheric variability in dynamical transports. Thus 40°N is a less desirable location because of the strong, observed latitudinal gradients.

(Example: The tropospheric monitoring station at Cape Meares, Oregon sits at the edge of a large gradient in anthropogenic gases between the North American continent and the Pacific Ocean. Khalil and Rasmussen (Science, 1984) reported large seasonal variations in CO and a trend based on 3 years of nearly continuous monitoring. The large rate of increase first reported (+6%/yr) has not been confirmed by two subsequent years of observation. Although many interpretations are possible, one candidate could be the interannual variations in transport of CO near the vicinity of these large gradients.)

(added note)

5.   Correlations of trace gases in the lower stratosphere:

Following on a point emphasized by Sze, the concentration of C_2H_6 in the lower stratosphere reflects the concentration of active chlorine: atomic Cl. The profile of this species is expected to show a more rapid fall-off with height as total Cl_x increases in the next decades. The actual change in the mean profile may be difficult to observe accurately because of the small scale height. However the effect of an increase in Cl_x would be evident in the changing correlation of C_2H_6 with other gases which are mainly photolyzed ($CFCl_3$) or destroyed by reaction with OH (CH_3CCl_3, CH_4). It should be emphasized again that C_2H_6 responds not just to the total chlorine in the stratosphere, but particularly to the active form (Cl/ClO) which we predict will become increasingly important in the destruction of ozone in the lower stratosphere. If these correlative measurements are made with grab samples then it would be important also to measure H_2O simultaneously!

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WORKSHOP ON EARLY DETECTION OF STRATOSPHERIC OZONE

GUIDANCE FROM PAST ANALYSIS EFFORTS

J.K. Angell

Past analyses indicate that representative trends may be obtained from a relatively spare data network. As an example, the 63-station global radiosonde network used by Angell and Korshover has yielded temperature variations which are compatible with the variations obtained from a network of hundreds of stations. In this case it is clear that averaging in the vertical (determining the mean temperature through a layer) compensates to a large extent for the lack of large amounts of data in the horizontal. As another example, the total-ozone variations determined from the relatively sparse Dobson network have been shown to be generally compatible with the variations determined from satellite data with essentially global coverage. As a corollary, the total-ozone variations estimated from integration of layer-mean ozone changes obtained from the very sparse ozonesonde network in the north temperate zone, are in generally good agreement with the total-ozone variations estimated for this zone from the much greater number of total-ozone stations. Results obtained from a sparse network are more robust than one might think.

Another question involves the relative merits of a few good stations and a larger number of fair stations. This problem is about to arise with regard to the 7-station automated Dobson network. Will more representative results be obtained by using only this network to estimate ozone variations in the stratosphere by means of the Umkehr technique, or will more representative results be obtained by integrating these good stations with frequent observations together with the fair stations with infrequent observations, i.e., how does one balance increased spatial coverage with increased coverage in time? Probably as

a surprise to some, our impression has been the more the merrier, that is, it is better to include all the stations even though the records of some stations are not very good. Errors at such stations tend to be random and "come out in the wash".

Ozone variations are once more a matter of concern. Not only is there the startling ozone decrease indicated for Antarctica, but there is the observation that global total ozone was as low in 1985 as during early 1983, and without the excuse of El Chichon and El Nino. In the north temperate zone in 16-24 and 24-32 km layers the ozone amount is even lower in 1985 than in early 1983. Something appears to be going on, and it behooves us to get cracking on the envisaged multi-instrumented network so that we may understand what this something is. The stations of the automated Dobson network should be considered for this multi-instrumented network.

DIFFERENTIAL ABSORPTION LIDAR (DIAL) MEASUREMENTS OF STRATOSPHERIC OZONE

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Differential Absorption Lidar (DIAL) measurements of ozone have been made for a number of years, but the recent development of high powered lasers in the ultraviolet now allow for ground based measurements in the 40-45 kilometer regime. Tunable XeCl lasers with low divergence and high output powers are now commercially available and are the main laser systems proposed for strato-spheric O_3 measurements from the ground or from space.

A DIAL instrument consists of a transmitter, which emits two wavelengths ("on-line" and "off-line") into the atmosphere, and a receiver, comprising a telescope, wavelength separator, and detectors. The scattering medium can be a topographic target or atmospheric scattering (Mie or Rayleigh). If atmo-spheric scattering is used, range resolution is achieved by time gating the detector electronics relative to the transmitted laser pulse. The attenuation due to ozone (and therefore its number density) can be extracted from a com-parison of adjacent range cells.

The lidar equation for the absorption of backscattered radiation can be written:

$$C_{\lambda Z} = I_\lambda \epsilon_\lambda \frac{A}{4\pi} \int_{Z_1}^{Z_2} N(Z)\ \sigma_{s\lambda} \frac{e^{-\alpha Z}}{Z^2}\ dZ \tag{1}$$

where

$C_{\lambda Z}$ = the number of counts received at wavelength λ from a distance Z.

I_0 = the number of photons emitted at λ.

ϵ_λ = the total detector efficiency at wavelength λ.

A = the area of the receiver telescope.

$N(Z)$ = the number of scatterers as a function of Z within the range

cell.

$\sigma_{s\lambda}$ = the scattering cross section at wavelength λ.

$\alpha = 2[n_{O_3}\sigma_{O_3\lambda} + n_s(Z)\sigma_{s\lambda}]$ where n_{O_3} and n_s are the number densities of ozone and atmospheric scatterers respectively.

Z = the range from the detector.

Ratioing the returns from adjacent range cells for both the on-line and off-line wavelengths and rearranging we can arrive at:

$$\ln \frac{C_{11}C_{22}}{C_{12}C_{21}} = (\alpha_1 - \alpha_2) \, \Delta Z \qquad (2)$$

where the first subscript refers to the wavelength (1 = on-line, 2 = off-line) and the second subscript refers to the range cell. It is apparent from equation (2) that all the instrumental parameters have dropped out of the expression.

Measurements of stratospheric ozone using the DIAL technique have been performed by a number of different groups. Heaps, et al.[1] measure ozone from a balloon-borne package using a frequency doubled dye laser tuned to an OH absorption line. The purpose of these measurements is to provide a correction to the atmospheric transmission at the OH absorption frequency.

Uchino, et al.,[2] Pelon and Megie,[3] and Werner, et al.[4] have all made measurements of stratospheric ozone from the ground using XeCℓ based lidar systems. The French group have also made O_3 measurements with a dye laser lidar.

Werner, et al. have made measurements up to 50 km in and claim that the statistical error in their measurements is less than 1%. All night integration is required to achieve this accuracy above 40 km. The reference wavelength at 338 nm, was generated by Stimulated Raman Scattering in methane. The instrument was situated at the summit of the Zugspitze.

Pelon and Megie have reported measurements from the Observatoire de Haute-Provence also using XeCℓ for the on-line frequency. This group used a tripled Nd-YAG (355 nm) for the reference wavelength. Ozone was measured between 25 and 50 km. Error bars above 40 km were greater than 15-20% and increased rapidly with altitude.

Uchino, et al. have also published results based on a low energy, low rep-rate XeCℓ laser up to an altitude of 30 km with error bars of approximately 50%. They indicated that later measurements would be made using a more powerful laser system.

In addition to these groups there are two others, one at JPL and one at GSFC, which are preparing to make measurements of stratospheric ozone from the ground with XeCℓ lidars.

Beyond the ground based systems a XeCℓ lidar system has been discussed for the EOS platform. This system would be capable of measuring ozone profiles down to the ground.

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LIDAR MEASUREMENTS OF STRATOSPHERIC TEMPERATURE

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The radiative budget of the stratosphere and mesosphere is mainly influenced by ozone and carbon dioxide and thus directly sensitive to the variations of these trace species which can be induced by anthropogenic activities. Temperature distribution will thus vary at various temporal and spatial scales related to dynamical processes such as planetary waves activity or radiative effects induced by trace species or aerosols fluctuations. Long term variations or trends either related to solar variability or to anthropogenic perturbations have not yet been detected and will constitute part of the rationale to implement a monitoring programme. Furthermore, systematic observations of the temperature profile will provide a data base of particular value for the establisment of Reference Model of the Middle Atmosphere. Use of ground based systems which can provide a high accuracy and vertical resolution is also important for the validation of satellite data including temperature measurements and trace species concentration retrievals from IR and microwave passive sensors.

Rayleigh backscattering of a laser beam by atmospheric molecules has been observed by most of the first lidar researchers but the first tentative determination of stratospheric temperature was only performed in the late 1970s. In 1980 a lidar system devoted to that type of measurements has been set up at the Observatoire de Haute Provence and operated on a quasiroutine basis from this time (Hauchecorne and Chanin, 1983). Several systems are presently under development in various countries (RFA, USA, UK, France,....) which might provide the basis of a future global network.

When a monochromatic laser beam, at a wavelength which does not coincide with any absorption or resonant feature of atmospheric species, is sent in the atmosphere, two processes can provide a backscattered signal : Rayleigh scattering by atmospheric molecules and Mie scattering by aerosol particles. At the height above 30 to 35 km where the aerosol content is very low, if any, the atmosphere can be considered as purely molecular and the lidar backscattered signal is proportional to the

atmospheric density. The temperature profile can then be computed from the density profile assuming that the atmosphere obeys the perfect gas law and is in hydrostatic equilibrium. This second assumption implies that atmospheric turbulence does not affect the mean air density, which is the case considering the temporal and spatial resolutions of the lidar data. The constant mixing ratio of the major atmospheric constituents (N_2, O_2 and Ar) and the negligible value of the H_2O mixing ratio justify the choice of a constant value for the air mean molecular weight. Details of the analysis are given in Annex. It should be pointed out that the only assumption to be made to compute the temperature profile is that of a pressure boundary at the top of the atmosphere, the accuracy of which can be evaluated to be of the order of 15 %. Its contribution to the temperature uncertainty decreases rapidly with altitude and is smaller than 2 % at 15 km from the top, and smaller than 1 %, 5 km lower. It is important to note that only the ratio of experimental density values is taken into account and that consequently any constant of normalization in the return signal disappears. The temperature determination can then be considered as absolute as soon as one can neglect the term due to the pressure at the top, even though the density is only measured on a relative way.

The characteristics of the "Rayleigh" lidar in operational use at the Observatoire de Haute Provence are given in the Appendix. Such a system will include a powerful Nd Yag laser emitting at the second harmonic wavelength (532 nm). The choice of the emitter is obviously a function of the state of the art of laser development and particular attention should be brought to the new sources such as exciplex lasers (XeF) at 355 nm. The receiver is a large diameter (— 1 m) telescope required for high altitude measurements. Due to the large dynamics of the signal two acquisition modes are used, i.e. analogical time sampling for the lower attitude ranges and photon counting in the upper levels. All the experiment is computer controlled and can be run efficiently for many hours without an operator assistance. Typical accuracy on the measurements can be quoted as follows for the OHP system :

- $\Delta T = $; 1 K at 40 km for a 1 hour integration time and 1 km height
    resolution

- $\Delta T = $; 5 K at 70 km for a 3 hours integration and a 0.5 km height
    resolution.

With the performances already available, the advantages of a Rayleigh lidar, in terms of atmospheric needs, are mainly due to three characeristics :

- The possibility of making absolute temperature determination without requiring an external calibration, and this with an accuracy better than a few K in the stratosphere.

- The availability of good vertical resolution (— 1 km)

- The continuity of the survey in altitude, from 30 to 80 km, and in time. The observations are only limited by meteorological conditions which implies a good choice of the site and at the present time restricted to nighttime.

These three characteristics make the Rayleigh lidar a powerful tool mostly for two types of studies based either on the knowledge of the absolute temperature and its eventual evolution, or on the description of the temporal and spatial fine structure of both density and temperature. For both approaches it is a necessary complement of satellite observations.

CHARACTERISTICS OF THE RAYLEIGH LIDAR

IN OPERATIONAL USE AT THE OBSERVATOIRE DE HAUTE PROVENCE

Laser

type	Neodymium - Yag (Quantel Model 408)
Energy per pulse	400 mj at 532 nm
	(150 mj at 355 nm)
Repetition rate	10 Hz
Pulse width	15 ns
Divergence	4.10^{-4} rad
Divergence	10^{-4} rad (with a beam expander)

Receiver

Telescope diameter	80 cm
Telescope area	0.5 m^2
Field of view	10^{-3} to 10^{-4} rad
Band pass filter	0.8 nm (FWHM)
P.F. interferometer	20 pm (FWHM)
Gate width	4 μm (0.6 km)

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HAUCHECORNE, A. and M.L. CHANIN (1983) : Mid latitude lidar observations of planetary waves in the middle atmosphere during the winter of 1981-1982
J. Geophys. Res. 88, 3843-3849.

CHANIN M.L. and A. HAUCHECORNE (1984) : Lidar studies of temperature and density using Rayleigh scattering
MAP Handbook n° 13, 87-99.

APPENDIX

MEASUREMENTS OF THE TEMPERATURE PROFILE

IN THE STRATOSPHERE

from

CHANIN, HAUCHECORNE
MAP Handbook n° 13, 87-99 (1984)

If the backscattered light is only due to Rayleigh and Mie scattering, the lidar equation can be written :

$$N(z_i) = \frac{N_0 A\, K\, R_q\, T^2(z_0, z_i)}{4\pi (z_i - z_0)^2} \cdot [n_r(z_i)\, \beta_r + n_m(z_i)\, \beta_m(z_i)]\, \Delta z \qquad (1)$$

$N(z_i)$ is the number of detected photons for one laser pulse, from a layer of thickness Δz centered at the height z_i

N_0 is the number of photons emitted for each laser pulse

A the telescope area

K the optical efficiency of the lidar system (including the optical transmission through the transmitter and receiver)

R_q the quantum efficiency of the photomultiplier

$T(z_0, z_i)$ the atmospheric transmission between the altitude of the lidar site and the height of the emitting layer z_i

n_r and $n_m(z_i)$ the air molecules and aerosols concentrations

β_r and $\beta_m(z_i)$ the Rayleigh and Mie backscattering cross-sections.

In the height range when the Mie contribution is negligible (i.e. between 35 and 80 km) the atmospheric density is given by the expression :

$$\rho(z) = C\, [S_L(z) - B(z)]\, /\, T^2(z, \infty) \qquad (2)$$

$S_L(z)$ is the signal coming from the altitude z, in a constant solid angle (i.e. multiplied by $(z - z_0)^2$) and eventually corrected for the non linearity of the photomultiplier if this one is close to saturation

B (z)   is the background signal due to dark current and sky background, extrapolated linearly for the altitude z^*

T (z, ∞) is the atmospheric transmission between z and the top of the atmosphere, evaluated at the laser wavelength, taking into account ozone and Rayleigh attenuation.

C   a normalisation constant, depends upon N_0, K, R_a and T (z_0, z_i) as defined above and may vary with time (mainly under the influence of fluctuations in the laser energy output and the atmospheric transmission). For each period of measurement C is evaluated by fitting the density measured either with a model (CIRA 1972) between 30 and 35 km, or with radio-sonde data at 30 km obtained from the nearest meteorological site.

The relative uncertainty on the density determination is given by :

$$\frac{\Delta \rho}{\rho} = \frac{\Delta S_L (z)}{S_L (z) - B (z)} \qquad (3)$$

TEMPERATURE DETERMINATION

The temperature profile is computed from the density profile assuming that the atmosphere obeys the perfect gas law and is in hydrostatic equilibrium. This second assumption implies that atmospheric turbulence does not affect the mean air density, which is the case considering the temporal and spatial resolutions of the lidar data. The constant mixing ratio of the major atmospheric constituents (N_2, O_2 and Ar) and the negligible value of the H_2O mixing ratio justify the choice of a constant value M for the air mean molecular weight. The air pressure P (z), density $\rho(z)$ and temperature T (z) are then related by :

$$P (z) = \frac{R \rho (z) T (z)}{M} \qquad (4)$$

$$dP (z) = - \rho (z) g (z) dz \qquad (5)$$

where R is the universal gas constant and g (z) the acceleration of gravity. The combination of Eq. (4) and Eq. (5) leads to :

$$\frac{dP (z)}{P (z)} = \frac{M g (z)}{R T (z)} dz = d (Log P (z)) \qquad (6)$$

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*   *The recovery time of a photomultiplier exposed to a high level of light may be a source of error in estimating the background coming from the dark current. To reduce such a source of error, a shutter should be used during the return of the low altitude echo ; both mechanical and electronic shutter have been used successfully.*

If the acceleration of gravity and the temperature are assumed to be constant in the ith layer, the pressure at the bottom and top of the layer are related by :

$$\frac{P(z_i - \Delta z/2)}{P(z_i + \Delta z/2)} = \exp \frac{M g(z_i)}{R T(z_i)} \Delta z \qquad (7)$$

and the temperature is expressed as :

$$T(z_i) = \frac{M g(z_i) \Delta z}{R \operatorname{Log} [P(z_i - \Delta z/2) / P(z_i + \Delta z/2)]} \qquad (8)$$

The density profile is measured up to the nth layer (about 80 km). The pressure at the top of this layer is fitted with the pressure of the CIRA 1972 model, $P_m(z_n + \Delta z/2)$, for the corresponding month and latitude. The top and bottom pressures of the ith layer are then :

$$P(z_i + \Delta z/2) = \sum_{j=i+1}^{n} \rho(z_j) g(z_j) \Delta z + P_m(z_n + \Delta z/2) \qquad (9)$$

$$P(z_i - \Delta z/2) = P(z_i + \Delta z/2) + \rho(z_i) g(z_i) \Delta z \qquad (10)$$

Let X be :

$$X = \frac{\rho(z_i) g(z_i) \Delta z}{P(z_i + \Delta z/2)} \qquad (11)$$

The temperature is then :

$$T(z_i) = \frac{M g(z_i) \Delta z}{R \operatorname{Log}(1 + X)} \qquad (12)$$

The statistical standard error on the temperature is :

$$\frac{\delta T(z_i)}{T(z_i)} = \frac{\delta \operatorname{Log}(1 + X)}{\operatorname{Log}(1 + X)} = \frac{\delta X}{(1 + X) \operatorname{Log}(1 + X)} \qquad (13)$$

with

$$\left(\frac{\delta X}{X}\right) = \left|\frac{\delta\rho(z_i)}{\rho(z_i)}\right|^2 + \left|\frac{\delta P(z_i + \Delta z/2)}{P(z_i + \Delta z/2)}\right|^2 \qquad (14)$$

$$\delta P(z_i + \Delta z/2)^2 = \sum_{j=i+1}^{n}(g(z_j)\,\delta\rho(z_j)\,\Delta z)^2 + (\delta P_m(z_n + \Delta z/2))^2 \qquad (15)$$

The uncertainty on the extrapolated pressure at the top at the profile is evaluated to be 15 %. Its contribution to the temperature uncertainty decreases rapidly with altitude and is smaller than 2 %, at 15 km from the top, and smaller than 1 %, 5 km lower. It is important to notice that the term X represents a ratio of experimental density values and consequently the constant of normalisation disappears. The temperature determination is then absolute as soon as one can neglect the term due to the pressure at the top, even though the density is only measured on a relative way.

DEVELOPMENT OF TROPOSPHERIC OZONE LIDAR

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Introduction

Ozone is considered to be the single most important trace species in the atmosphere. It initiates photochemistry, it is a key non-CO_2 "greenhouse" molecule, and it can damage vegetation and human health. There are indications that ozone is increasing in the global troposphere, perhaps 20% over the past two decades. However, the data sets available for this period are too limited in global and temporal coverage and their long-term relative accuracy has been seriously questioned. Ozone measurements are also of value as a tracer in the dynamical processes of exchange between the stratosphere and troposphere. A high resolution ground-based instrument with a short measurement time and reliable long-term precision would help fill some of these needs. To this end, the lidar technique seems particularly well suited.

Objective

Our goal in the NOAA Aeronomy Lab is to optimize the differential absorption lidar (DIAL) technique for rural tropospheric ozone measurements. Although the prototype version is being built as a research instrument with maximum flexibility, it will be used to determine a suitable design for a long-term tropospheric ozone monitoring network. We anticipate that the prototype lidar will be capable of providing an ozone profile up to 12 km once every 60 seconds with an altitude resolution of 1 km or less. Better resolution and higher altitudes will result from longer integration times. The wavelength range that we have chosen will minimize solar interference, thereby allowing 24 hours-per-day observations in clear skies. When clouds are present, measurements can be made in those portions of the sky that are clear for the 60-second integration time required. The precision of the measurements should be 5% and their accuracy 10%.

Approach

From previous work of J. Pelon and G. Megie (J. Geophys. Res., 87, 4947, 1982), the wavelength range of 280 to 300 nm was chosen for the tropospheric ozone measurements. This optimized the sensitivity of the DIAL measurement for the rather low tropospheric ozone concentrations and allowed for the 24 hours-per-day observations. A careful survey of possible molecular interferents for both the rural boundary layer and the free troposphere (searching for worst-case differential cross sections and abundances) yielded the result that SO_2, NO_2, and formaldehyde could, under adverse conditions, contribute a few percent to the uncertainty of the ozone measurements. Therefore, it was decided that a scanning of the wavelengths was necessary to search for the interfering species. Computer modeling of

the important atmospheric parameters indicated that the uncertainty in the aerosol scattering could introduce unacceptable errors in the ozone calculation. Therefore, aerosols will be monitored simultaneously with ozone using the longer-wavelength aerosol lidar technique. With these requirements, we decided that two identical laser systems consisting of a doubled Nd/YAG laser pumping a dye laser, which is again doubled, would provide the necessary wavelengths (280-300 nm, 560-600 nm, 532 nm, and 1.06 micron) and the necessary power (1 watt from 280-300 nm) for the experiment. With experience, we should be able to select the optimal fixed wavelengths for a simpler laser system.

Progress

After completing the search for molecular interferents, an atmospheric model was made to predict the uncertainties that we would likely encounter in ozone calculations using this DIAL lidar technique. It was concluded that the two laser systems described above would fulfill our requirements. The laser systems have been purchased and are now installed at the Aeronomy Lab's mountain observatory at Fritz Peak, west of Boulder. Although these are not off-the-shelf laser systems, their components are. Our initial testing has shown that the energy and wavelength requirements have all been met. We are continuing with other tests and expect these systems to be quite satisfactory. We anticipate that our model predictions for photon returns (detected signal) will be verified in the next few months. Then other critical components can be selected and ordered or, if necessary, built. Critical to the success of the experiment is a proper match between the different components. In particular, the detector and the waveform digitizer must be suitable for the wide dynamic range of signal intensity expected. Also a computer will be interfaced for control of the experiment and for real-time data analysis.

THE FEASIBILITY OF GROUND BASED LIDAR MEASUREMENTS OF STRATOSPHERIC HYDROXYL

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Currently much effort is being expended to develop ground based lidars
for the routine monitoring of stratospheric ozone. These lidars operate
at a fundamental wavelength near 308 nm and typically employ xenon
chloride excimer lasers. When these systems have been shown to be
successful the potential for using similar systems to monitor stratos-
pheric hydroxyl by laser induced fluorescence excited in the A-X, 0-0
band, also near 308 nm, should be considered.

A program to study the kinetics and spectroscopy of 0-0 excitation of OH
and to develop a tunable XeCl excimer laser has been completed at JPL.
The XeCl laser can be tuned, with narrow spectral bandwidth, over the
region from 307.5 - 308.5 nm which covers a number of OH absorption
features, including the Q(1) bandhead. Many detailed spectroscopic
excitation and detection schemes have been considered. In summary, the
Q(21)1 absorption line at 307.847 nm is chosen for the excitation line
and the overlapped Q(2)2, Q(12)2, Q(2)3 and Q(12)3 lines at 308.986 nm
would be used for the fluorescence detection. By using a detector with
a narrow spectral bandpass, matched to the fluorescence bandwidth of this
this group of overlapped lines, the solar background can be reduced to
an insignificant level. The type of filter appropriate to this scheme
is the Fabry-Perot filter as developed for Doppler wind measurements,
by Rees and Hays, and flown on Dynamics Explorer and UARS. Further
details of the experimental arrangement will be given at the workshop.

The OH profile from "The Stratosphere 1981" together with the U.S.
Standard Atmosphere data have been used to model the anticipated lidar
returns. The lidar system parameters were based on the ozone systems
as was the atmospheric transmission for the UV wavelengths. The
results of this model show that a repeatability (or precision) of 1%
could be achieved with an integration time of one hour, with a laser
operating at 1 J/pulse and 30 Hz, over the altitude range from 25 to
75 km. The accuracy of the measurement is significantly poorer since
the lidar inversion depends on the accurate knowledge of various
state-to-state rate constants in the excited A state of OH. These
data are only just becoming available and the accuracy is as yet
undetermined. At best it is estimated that the overall accuracy
would be about 10%. However, since the precision is high, statistical
trend analyses could be performed with high confidence.

Position Paper On

Groundbased Measurements of Stratospheric Trace Constituents as a Function of Height by High Resolution UV Spectroscopy

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With recent advances in optical design techniques and detector technology, it has become possible to observe atmospheric emissions in the daytime in the presence of the large Rayleigh scattered daylight background. Using high resolution spectroscopy techniques we have obtained spectral images of the near-UV dayglow in the range 2,950-3,000 $\overset{o}{A}$. These data have revealed the presence of a spectrum which is rich in its spectral detail. In particular, it has been possible to clearly identify rotational lines of the OH ($A^2\Sigma \rightarrow X^2\pi$) 0,0 band which is generated by resonance fluorescent scattering of near UV sunlight. In addition, absorption features have been observed at wavelengths which coincide with absorption features of the ($A^2\pi \leftarrow X^2\pi$) 2,0 band of ClO. The value of information on these constituents to stratospheric photochemistry is well known.

There are certain advantages to being able to observe in emission, the primary one being that in the presence of both absorption by O_3 and self absorption, the brightness observed shows a strong dependence on the angle of elevation of the line-

1

of-sight, as well as on the solar zenith angle. At very small
elevation angles, emissions from the stratosphere are
effectively obscured, owing to O_3 absorption. Also, the impact
of the presence of OH on the observed spectrum is in absorption,
because of strong quenching at tropospheric heights. As the
elevation angle is increased, the region sampled also increases in
altitude, and the OH signature on the observed brightness profile
changes from one of absorption around $\sim 40^{o}$ elevation angle to an
emission signature.

We have calculated OH contribution functions as a function
of altitude for different viewing geometries and have established
that, at least in principle, the potential information content of
the data that could be acquired should allow the data to be
inverted to profiles of concentration vs. altitude from the
troposphere to the stratosphere. There are many problems that
still have to be resolved, however, particularly with regard to
the transmission of light through the troposphere.

In order to estimate the statistical noise limitations of the
large background emission on the measurements, we have computed
the signal to noise ratio for OH emissions which arise from
spherical shells, 1 km in thickness. These calculations have lead
us to be optimistic about the viability of inverting the data.
Signal to noise ratios in excess of 1000 are plausible.

We have been actively involved for the last 7 years in the
development of techniques for the inversion of intensity
measurements made from balloons and satellites in the presence of
large scattered background emission and ozone absorption. Our

2

knowledge in this area has now developed to a level of maturity
where we believe we can provide a quantitative assessment of the
uniqueness (or validity) of the results obtained.

In addition to the advances in data reduction techniques
that have been made, we are actively involved in the development
of improved as well as new and more powerful measurement
techniques.

In conclusion, we believe that high resolution ground-based
UV spectroscopy offers a powerful new technique for obtaining
measurements of key trace constituents in the stratosphere and
troposphere.

Position Paper on Ozone: ECC, Umkehr, SBUV Measurements
and the NOAA Program
by
Alvin J. Miller

Given the very broad topic and the limitation on space, we will briefly discuss 3 seperate issues:

1. Comparison of SBUV ozone profiles with other measurement systems
2. The NOAA program of stratospheric ozone monitoring
3. The combined trend detection capability

1. Comparison of SBUV ozone profiles with other measurement systems

The basic comparisons of SBUV data with Umkehr and balloon ozonesondes have been presented by Bhartia et al (1984) and, more recently, have been updated to include the new Bass and Paur ozone absorption coefficients in the SBUV measurements. The new absorption coefficients have not yet been adopted for the Umkehr measurements. Preliminary results, summarized by Umkehr layer, are depicted in Figure 1, where the variations in time have been taken into consideration and the numbers reflect the difference at Nimbus launch. We see that an overall "S" shape appears in the comparisons with the tendency for near zero bias in layers 9 and 7 with a positive bias in layer 8, a negative bias in layers 6 and 5 of 5-10 %, although a large difference occurs between Umkehr and balloons in layer 6, a positive bias in layer 3 of 10-15 % and a return to zero bias in the lower layers. This pattern is consistent with the SBUV, LIMS and SAGE comparisons depicted in the NASA/WMO Assessment Document, Chapter 8, and the recent results of the balloon photometer intercomparisons.

2.NOAA Ozone Trend Evaluation Program

The trend evaluation program is comprised of the SBUV/2 instrument on-board the NOAA operational satellite series plus a validation program outlined in Table 1. As depicted in Table 1, the validation measurements were selected to complement each other as much as possible providing maximum information for the least cost. Two weaknesses appear, though, that should be addressed directly. First, the routine validation measurements extend only up to 1 mbar although the SBUV/2 profiles extend to about 0.4 mbar. Second below about 30 mbar the SBUV/2 retrievals are not independant of the total ozone retrievals such that in the lower stratosphere we are still very dependant on the limited ground-based data for trend detection.

3.Trend Detection Capability

The combined trend detection capability of the SBUV/2 validation program is summarized in Figure 2 which depicts the 95% confidence limits of decadal trend detection as a function of the standard deviation of instrument calibration. That is, over a decade, 5 satellite instruments will be launched with an error in their calibration, S. Within the computations presented, we have assumed that the SBUV/2 instrument is well characterized by the on-board Hg lamp. If this is not the case, different scenarios can be

presented that are beyond the brief description presented here.

Within Figure 2, the solid line at 3% per decade represents the approximate level of decadal trend depicted by one–dimensional models for a 5 km layer at about Umkehr layer 8. Above this line, we see the values of trend detection for SBUV/2 validated by the Umkehr and balloonsonde measurements. It is stressed, however, that if the measurements are continued over a 15 year period, the values are decreased to about 2.3 and 1.9 % per decade, respectively. Looking at the SBUV/2, by itself, if the instrument satisfies it specifications (S = 0.93) we can detect a trend of about 2.8% per decade if we do nothing and this can be reduced to about 2.2% per decade if we include knowledge of when the instrument changes occurred and include this in the statistical analysis. Finally, if we include overlap between instruments such that we know the instrument- to - differences to the 0.5% level, the trend detection capability increases to 1.5 % per decade.

As stated, above, these results are for a well characterized system. If this is not true, ie if the Hg lamp fails and we can not determine the instrument drift internally, then we must utilize the NASA space shuttle SBUV (SSBUV) which brings the precision estimates to the 3% per decade level.

In summary, the combined program of SBUV/2 and its validation program should provide trend estimates in the middle stratosphere capable of detecting ozone changes at the level currently depicted by one–dimensional models.
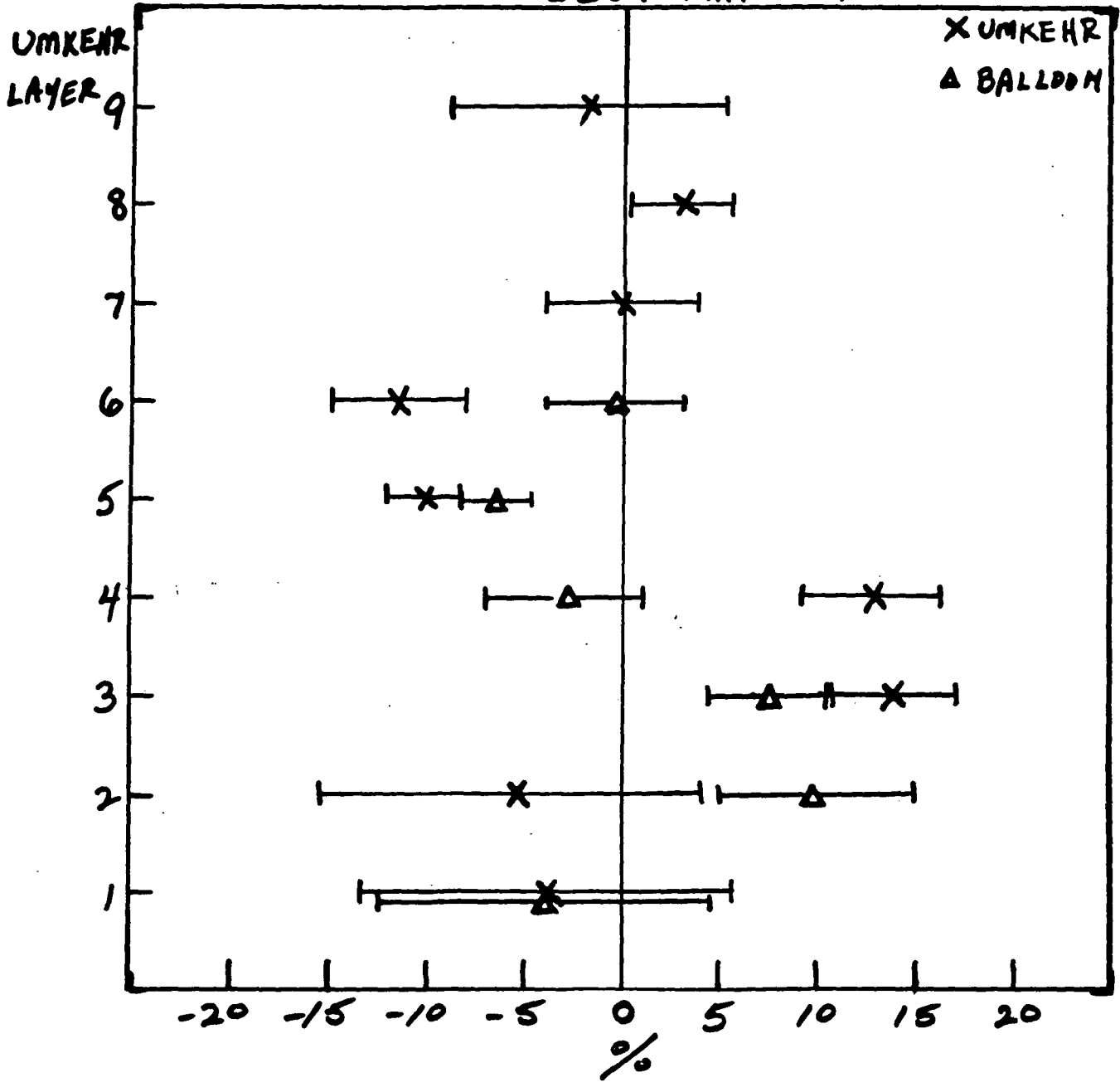
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Table 1.   NOAA SATELLITE OZONE

VALIDATION PROGRAM

- ~16 PRIMARY DOBSON STATIONS - TRIENNIAL CALIBRATION
  AGAINST BOULDER STANDARD INSTRUMENT

- OTHER DOBSON AND M-83 SITES WITH OVERSIGHT VIA
  SATELLITE CONSISTENCY, WMO, U.S. AND AES CALIBRATION
  PROGRAMS

- ~16 PRIMARY UMKEHR SITES - INCLUDES 7 AUTOMATED
  INSTRUMENTS

- OTHER UMKEHR SITES AS AVAILABLE

- AEROSOL IMPACT EVALUATION BY GMCC

- BALLOONSONDE MEASUREMENTS MONITORED BY GMCC AT 3 SITES
  ON A ONCE-PER-WEEK SCHEDULE

- OTHER BALLOONSONDES AS AVAILABLE

- SSBUV

- OTHER SOURCES AS AVAILABLE:
  OZONE ROCKETSONDES
  SOLAR OBSERVATIONS

SBUV minus X

X UMKEHR
△ BALLOON

UMKEHR
LAYER

%

Figuret

% PER DECADE

95% CONF. TREND DETECTION

Y-axis labels: 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5

SBUV2/UMKEHR

SBUV2/BALLOON

SBUV2 - NO OVERLAP? STAT INT.

SBUV2 NO OVERLAP
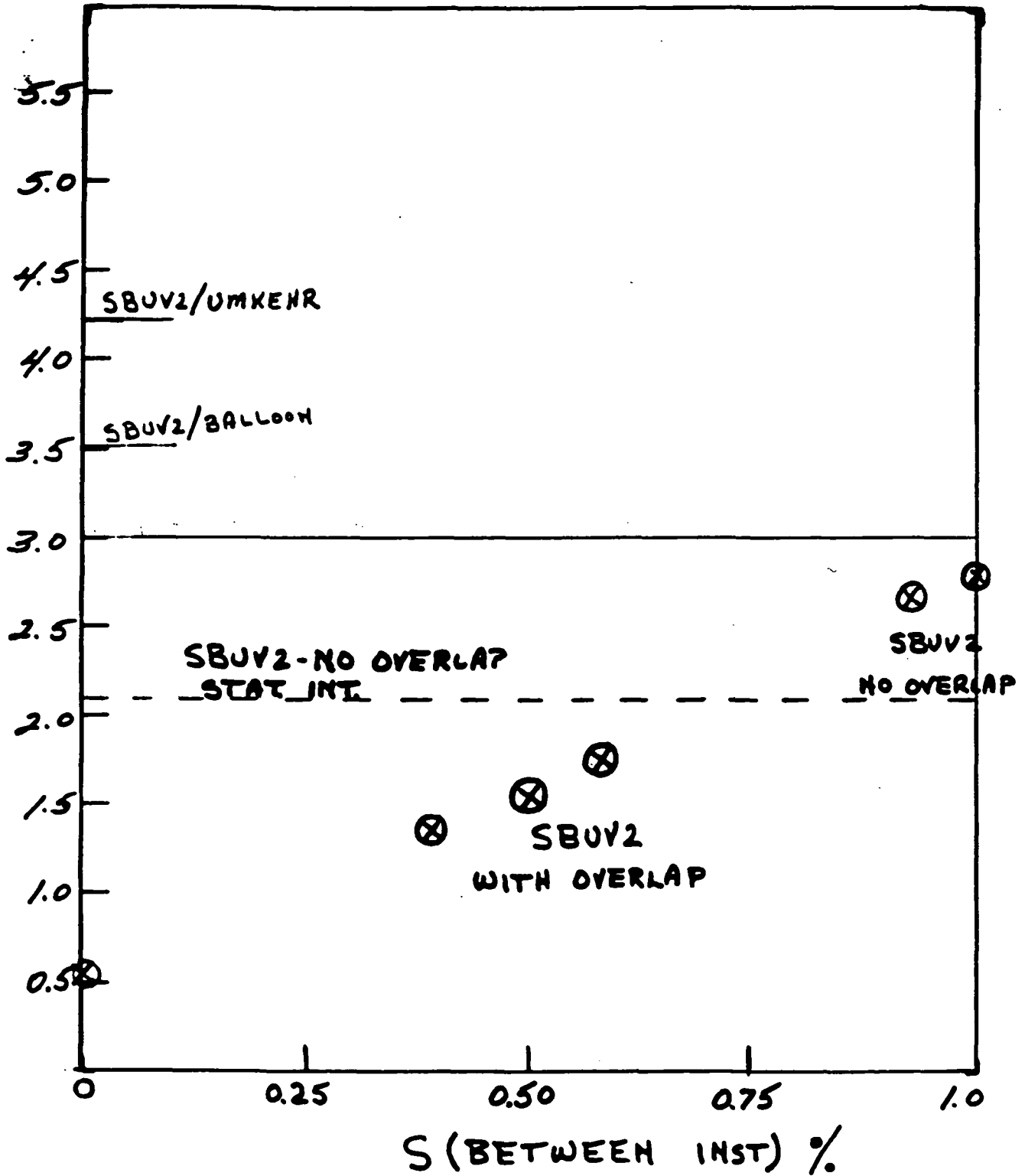
SBUV2 WITH OVERLAP

X-axis: 0, 0.25, 0.50, 0.75, 1.0

S (BETWEEN INST) %

Figure 2

Position Paper on NOAA Operational Stratospheric Temperature Measurements

Alvin J. Miller

The basic retrieval technique currently utilized by the NESDIS for operational temperature profiles is outlined in Table 1 for the three distinct layers 1000-100 mbar, 70-10 mbar and 5-0.4 mbar. This layered structure is, essentially, dictated by the available rawinsonde information up to 10 mbar and the more limited rocketsonde data above that level. The points we wish to stress are three-fold:

1. The TOVS system is comprised of 3 seperate instruments; MSU,HIRS-2 and SSU, with seperate channels within each instrument. Thus, a failure mode can occur that will reduce the available information, but will not be catastrophic. Retrievals can be produced that will have inherently different properties.

2. For 10 mbar and below, the updated regressional retrievals are self-healing in that changes in the system, either due to a failure mode or to launch of a new instrument, are adjusted within a few weeks.

3. Above 10 mbar this self- healing process is not possible as the rocketsonde data are much more limited both in time and space. Hence, a collective is made after the fact and a series of analysis- rocketsonde comparisons published.

To indicate the magnitude of the problem, we present in Figure 1 the average values of the analysis minus rocketsonde matchups for 4 periods from October '80 to February '85. We see that the range of adjustments is about 4-6 degrees and that unless these are taken into consideration we would have little hope of being able to detect a trend of about 1.5 degrees per decade.

Finally, in Figure 2 we present the analysis minus rocketsonde comparisons at 1- and 2- mbar for the period September '81 to October '83, plotted by station as function of latitude. We note that at the time of preparation of this figure the data from the Eastern Test Range (Cape Kennedy, Antigua, Ascension Island) and Shemya were not available. They have since become available and are consistent with the presented values. For both levels, it is clear that the values at Primrose Lake are the major departure from average. The question is whether they are part of a pattern of satellite bias with latitude (or air mass) or are merely a reflection of some difficulty at site. Also, there are no data beyond 8 degrees south in the Southern Hemisphere.

In summary, we have indicated that the requirement exists for a high quality, independent stratospheric temperature measurement system with which to verify the satellite instrument to instrument consistency. Such a system does not exist.

Table 1.

TIROS OPERATIONAL VERTICAL SOUNDINGS (TOVS)

LAYER MEAN TEMPERATURES BETWEEN STANDARD PRESSURE LEVELS

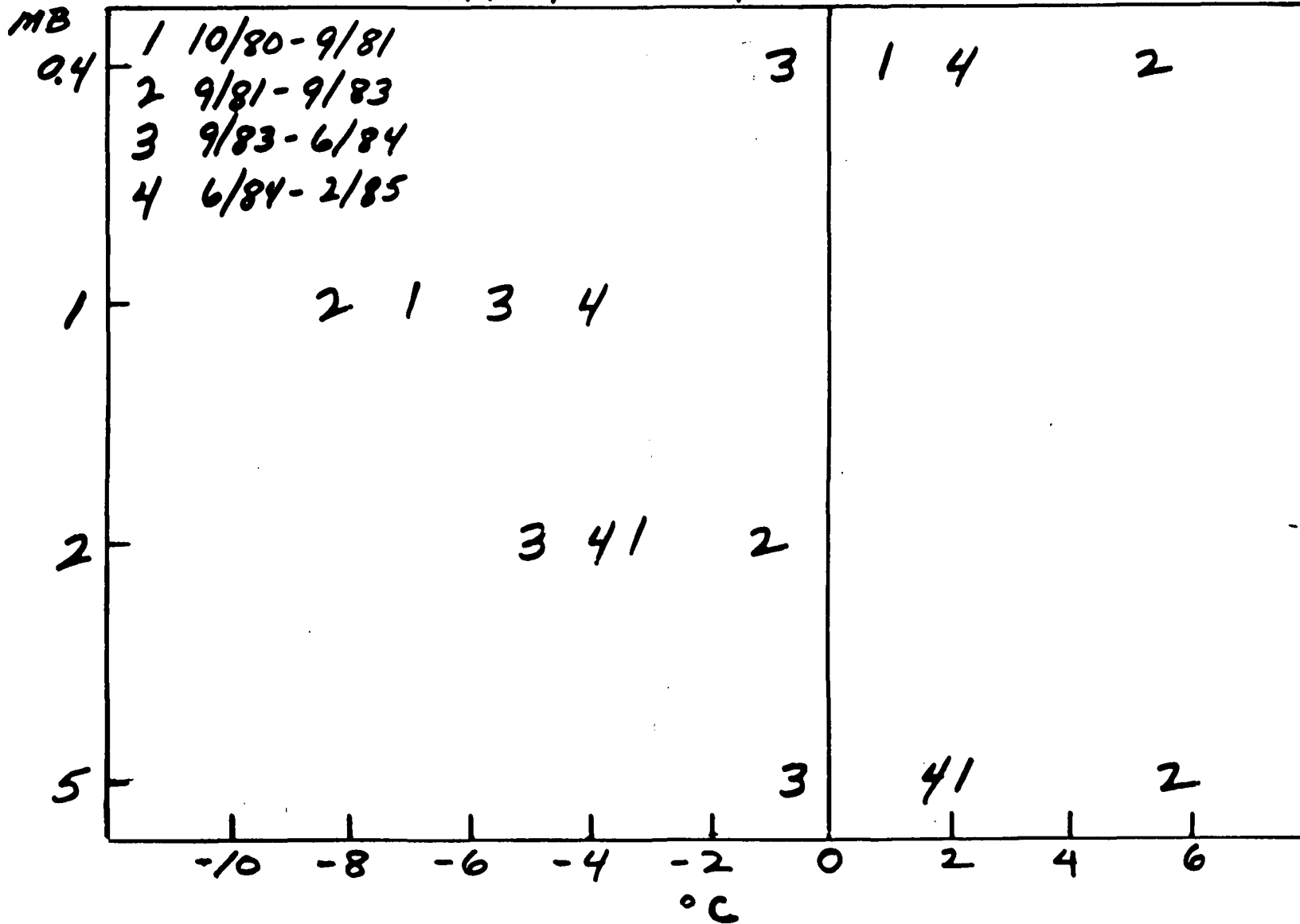| Level	Description
0.4 1 2 5	MULTIPLE LINEAR REGRESSION OF 9 MEASURED RADIANCES FROM STRATO-SPHERIC CHANNELS OF SSU, HIRS AND MSU TO OBTAIN TEMPERATURES AT LEVELS FROM 5 TO 0.4 MB. REGRESSION COEFFICIENTS DERIVED BY REGRESSING RADIANCES SIMULATED FROM CLIMATOLOGICAL SAMPLE OF 1200 ROCKETSONDES-RADIOSONDES AGAINST TEMPERATURE FROM THAT CLIMATOLOGICAL SAMPLE. COEFFICIENTS ARE NOT UPDATED.
10 30 50 70	MULTIPLE LINEAR REGRESSION OF TOVS MEASURED RADIANCES TO OBTAIN TEMPERATURES AT LEVELS FROM 70 to 10 MB. REGRESSION COEFFICIENTS DERIVED BY REGRESSING MEASURED RADIANCES AGAINST NEARLY COINCIDENT RADIOSONDE DATA FOR RECENT PERIOD. COEFFICIENTS UPDATED EVERY 1 TO 2 WEEKS, STRATIFIED IN 5 LATITUDE BANDS (90-60S, 60-30S, 30S-30N, 30-60N, 60-90N).
100 1000	TROPOSPHERIC RETRIEVALS DERIVED BY EIGENVECTOR (STATISTICAL) TECHNIQUE (SMITH AND WOOLF). COEFFICIENTS UPDATED EVERY WEEK.

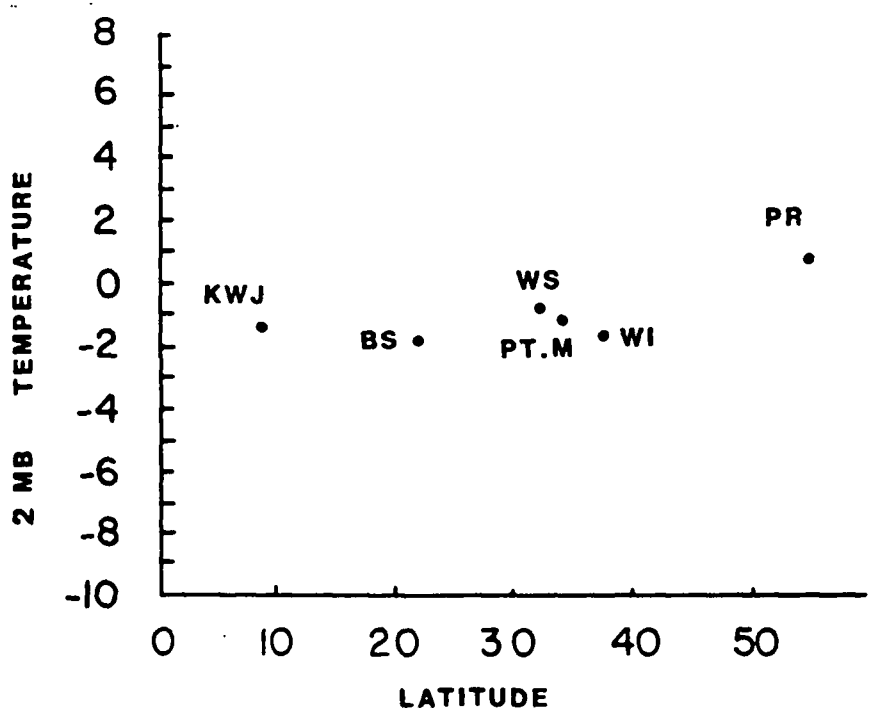Figure 1

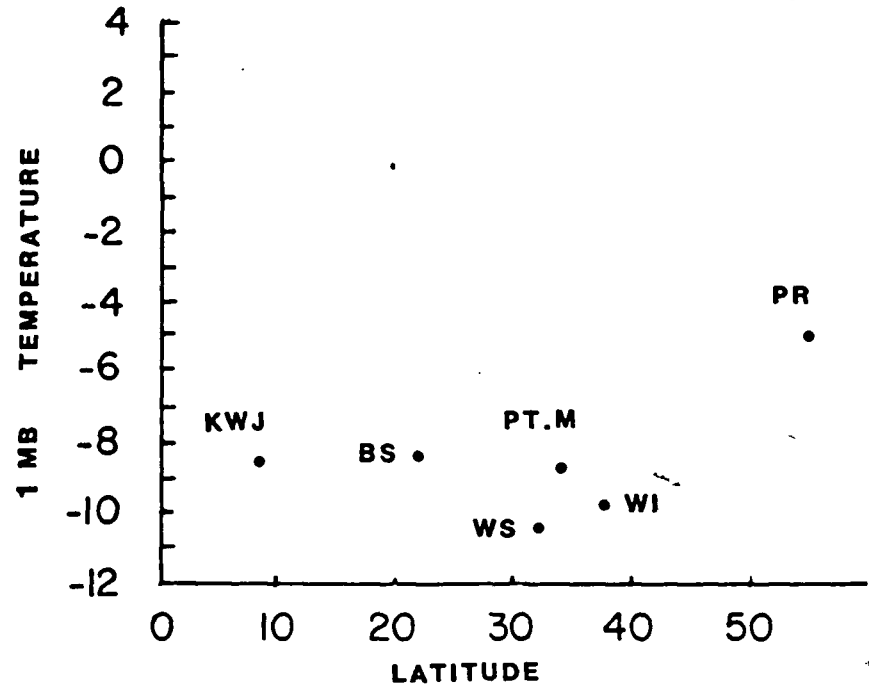ANALYSIS MINUS ROCKET   SEPT. 81 — OCT. 83

Fig. 24

A SHORT DISCUSSION OF UV/VIS ABSORPTION BY OTHER SPECIES
A. L. SCHMELTEKOPF

I WILL DISCUSS THE SPECTROMETERS WE HAVE BUILT USING THE RETICON
RL1024S DIODE ARRAY CHIPS. THESE CHIPS HAVE DIODES THAT ARE 24 MICRONS
WIDE AND 2.5 MM HIGH. THIS GIVES A VERY GOOD ASPECT RATIO FOR USE AS THE
EXIT SLIT OF A SPECTOMETER. EACH DIODE HAS 2 PICOFARADS OF CAPACITANCE AND
IS CHARGED TO 5 VOLTS THAT MEANS THAT EACH DIODE HAS IN ACCESS OF 64
MILLION ELECTRONS STORED ON IT WHEN IT IS READY TO BE EXPOSED TO LIGHT.
THUS SINCE THE DIODES HAVE 30 TO 85 PERCENT QUANTUM EFFICIENCY (AROUND .80
THROUGHOUT THE VISIABLE) WE CAN SAY THAT EACH DIODE IS CAPIABLE OF
INTEGRATING 64 MILLION PHOTONS. THUS THE NOISE ON EACH DIODE DUE TO SHOT
NOISE ALONE IS 8000 PHOTONS YIELDING A BEST SIGNAL TO NOISE FOR A DIODE OF
8000 WITH A SINGLE INTEGRATION. WE OFTEN INTEGRATE FOR 64 CYCLES AND THUS
WE COMMONLY HAVE A SIGNAL TO NOISE OF 64000 PER DIODE.

THE SPECTROMETERS WE HAVE BEEN USING ARE 26 CM CROSSED ASYMETRIC
CZERNY-TURNERS THAT HAVE 0.05 NM/DIODE DISPERSION IN 3RD ORDER AND 0.075
NM/DIODE DISPERSION IN THE 2ND ORDER. THE SPECTROMETERS HAVE BEEN DESIGNED
TO BE USED FOR NO2 FROM 400 TO 450 NM IN THE 3RD ORDER AND FOR NO3 FROM 600
TO 675 NM IN 2ND ORDER. WE HAVE A CAREFULLY SELECTED SET OF FILTERS TO
SEPERATE THE 2ND AND 3RD ORDERS SO THAT, BY CHANGING FILTERS UNDER COMPUTER
CONTROL, ONE CAN LOOK AT NO2 OR NO3. BY CAREFULLY LOOKING AT THE BAND
WIDTHS OF NO2 AND NO3 WE HAVE SELECTED THE ENTRANCE SLIT WIDTH TO BE 250
MICRONS THUS (TAKING INTO ACCOUNT THE ASYMETRY OF THE SPECTROMETER)
CORRESPONDING TO A RESOLUTION OF 12 DIODES OR 0.6 NM IN THE 3RD ORDER AND
0.9 NM IN 2ND ORDER

WE HAVE USED THESE SYSTEMS TO LOOK AT NO2 USING THE SUN, THE SKY AND
THE MOON AS LIGHT SOURCES AND HAVE LOOKED AT NO3 USING THE MOON AS THE
LIGHT SOURCE. FROM ANY OF THESE SOURCES YOU CAN GET A LITTLE INFORMATION
ABOUT THE ALTITUDE OF THE ABSORBING LAYER BUT ONLY IN A GROSS SENSE.
HOWEVER, WE CAN GET VERY HIGH SENSITIVITY. IT IS EASY TO RESOLVE 0.01%
ABSORPTION IN THAT CASE YOU CAN SEE 3.0(14)/CM**2 FOR NO2 AND 6.0(12)/CM**2
FOR NO3. THIS SENSITIVITY IS VERY EASY TO OBTAIN EVEN IF YOU DO NOT HAVE A
VERY GOOD KNOWLEDGE OF THE OTHER SPECIES IN YOUR SPECTRAL RANGE. IF YOU
HAVE A GOOD QUALITY FRONHOFFER SPECTRUM OF THE SUN WITH NO, OR LITTLE,
INTERVENING ATMOSPHERE AND AN UNDERSTAND THE RING EFFECT THEN IF THE
ATMOSPHERE IS NOT TOO WET YOU CAN DO NO2 ABOUT 50 TIMES BETTER THAN STATED
ABOVE (TO ABOUT 6.0(12)/CM**2). TO IMPROVE NO3 SENSITIVITY YOU NEED TO
KNOW SEVERAL OTHER THINGS AS WELL; YOU NEED TO KNOW THE CROSSECTIONS FOR
H2O, O2 AND O4. THEN YOU COULD GET DOWN TO ABOUT 2.0(11)/CM**2. THIS
LOOKS TO BE MUCH BETTER THAN THE SIGNAL TO NOISE THAT WAS STATED ABOVE, BUT
YOU GAIN FROM TWO SOURCES; YOU HAVE DONE AN AVERAGING TO FORM AND EFFECTIVE
EXIT SLIT AND YOU USE ALL THE DIODES IN THE SPECTRUM IN A LEAST-SQUARES
ROUTINE TO FIT THE SPECTRUM. THE AMOUNT YOU GAIN FROM THE LEAST-SQUARES
DEPENDS ON THE SPECTRAL SIGINATURE OF THE GAS OF INTREST (LOTS OF WIGGLES;
BIG GAIN, FEW WIGGLES; SMALL GAIN).

WE HAVE A YEARS WORTH OF ZENITH SKY DATA FOR NO2 TAKEN AT FRITZ PEAK IN
1985 AND A YEARS WORTH OF NO3 DATA TAKEN AT FRITZ PEAK USING THE MOON AS A
LIGHT SOURCE BY JOHN NOXON IN 1984. THE NO2 DATA IS BEING REDUCED AND
NOXON HAD REDUCED SOME OF HIS NO3 DATA BY HAND. HOPEFULLY THAT DATA
REDUCTION WILL BE COMPLETED SOMEDAY.

WE ORIGINALY DESIGNED THESE SPECTROMETERS TO BE CONTROLLED BY A HOME
BUILT COMPUTER WHICH IS TOO SMALL TO ADEQUATLY CONTROL THE SPECTROMETER AND
DIODE ARRAY. THE DIODE ARRAY ELECTRONICS IS SLIGHTLY NOISIER THAN WE WOULD
LIKE AND IS NOT AS FLEXIBLE AS WE WOULD LIKE. AS A RESULT WE ARE NOW
REDESIGNING THE ELECTRONICS TO WORK WITH A NEW COMPUTER AND WE HOPE TO HAVE

THAT COMPLETED BY THE END OF THE YEAR. WE PLAN TO USE THE SYSTEMS MOSTLY
TO DO TROPOSPHERIC MEASURMENTS OF NO2, NO3, H2O, O4 (TO GET AT
TEMPERATURE), OH, SO2, O3 AND A NUMBER OR OTHER SPECIES. THIS SYSTEM WILL
USE A RETRO REFLECTOR 10 KM ACROSS A VALLEY FROM FRITZ PEAK AND USE EITHER
A QUARTZ IODINE OR HIGH PRESSURE XENON LIGHT SOURCE. IN THE RESIDUALS OF
THE DATA THAT WE HAVE TAKEN TO DATE THERE ARE A NUMBER OF SPECTRAL FEATURES
THAT WE HAVE NOT BEEN ABLE TO IDENTIFY AND SOME OF THEM HAVE VERY
INTRESTING DIURNAL CHARACTERISTICS. WE HOPE TO BE ABLE TO MEASURE SOME OF
THE CROSSECTIONS THAT WE NEED IN THE LAB AND THEN USE THEM TO REDUCE OUR
RESIDUALS. I BELIEVE THAT IF SHOT NOISE WERE THE ONLY NOISE SOURCE THAT WE
WOULD EASILY BE ABLE TO HAVE 1(6) AS AN EFFECTIVE SIGNAL TO NOISE. THESE
DIODE ARRAYS WORK FROM BELOW 250 NM TO 1100 NM, THEY HAVE A HIGHER QUANTUM
EFFICIENCY THAN ANY PHOTOMULTIPLIER AND THE HAVE THE MULTIPLEX ADVANTAGE OF
TAKING ALL OF THE SPECTRUM AT ONCE, FOR THOSE REASONS I BELIEVE THAT THEY
WILL BE INCREASINGLY USED IN ATMOSPHERIC ABSORPTION MEASUREMENTS. THE ONLY
DISADVANTAGE IS THE FACT THAT YOU CANNOT MAKE AN AMPLIFIER THAT HAS A NOISE
LEVEL BELOW 450 ELECTRONS (BECAUSE OF THE VIDIO LINE CAPACITANCE ON THIS
ARRAY) AND THUS A DIODE ARRAY ONLY EXIBITS ITS SUPERIORITY OVER THE
PHOTOMULTIPLIER FOR LARGE SIGNALS.

MICROWAVE, MM, AND SUB-MM MEASUREMENT CAPABILITY

Position Paper for Workshop on Early Detection of Stratospheric Changes
Boulder, CO   5-7 March 1986

J.W. Waters,   Jet Propulsion Laboratory

The microwave, millimeter, and sub-millimeter spectral range covers wavelengths between about 10 mm and 0.1 mm and contains spectral lines due to rotational transitions of many molecules of interest to upper atmospheric research. These spectral lines can be measured, either in thermal emission or in absorption, to remotely determine the abundances of certain molecules. Temperature and pressure can also be determined. Measurements in this spectral region have been performed from ground, aircraft, balloon, and are now being developed for Earth orbit. Most measurements have been made of thermal emission due to the sensitivity of the technique and the desire to obtain data over all portions of the diurnal cycle.

At wavelengths longer than about 1 mm measurements are generally performed using coherent microwave (superheterodyne) techniques. At wavelengths shorter than about 1mm measurements are generally performed using incoherent (filter, interferometric) techniques, although coherent techniques are rapidly being pushed to the shorter wavelengths. Coherent techniques have the advantage of greater sensitivity and spectral resolution than incoherent techniques; this spectral resolution can be used to infer vertical profiles from the measured line shape of pressure-broadened lines. Incoherent techniques have the advantage of more easily covering a wider spectral range than coherent techniques and, because they now operate at shorter wavelengths, can measure the important species of OH and atomic O which do not have measurable lines at longer wavelengths. However, the sensitivity to other radicals such as ClO, HO2, and NO2 appears to be about 10x worse for incoherent techniques than for coherent techniques even though the incoherent techniques operate in a region of larger line strengths.

The spectroscopy in this spectral region is relatively well-known and spectroscopic uncertainties appear not to be a limitation in either planning or interpreting measurements. Line strengths in this region can be reliably calculated from the molecular dipole moment which is measured very accurately from Stark or Zeeman effects.

Figure 1 shows the calculated stratospheric spectrum for balloon measurements of a layer around 30 km using expected stratospheric abundances. This figure, which covers a wavelength range of only 1.5mm to 1.0mm, illustrates the many lines which are available for measurement; it also illustrates the care which must be taken to avoid interference from unwanted lines. The vertical scale in the figure is the logarithm of the optical depth (for weak lines the optical depth is

proportional to the strength of the emission). The heavy horizontal line represents rms noise for a liquid nitrogen cooled radiometer with a few minutes integration; anticipated technological developments, e.g. SIS-based radiometers, could improve sensitivity 10x. Many of the lines in Figure 1 can be measured from ground; Figure 2 compares vertical resolution of balloon-based and ground-based measurements.

Our program at JPL has involved measurements with a balloon-borne microwave limb sounder which is tuned to lines of CLO, O3, and H2O2 near 205 GHz and is now operational. A similar instrument is now being developed for the Upper Atmosphere Research Satellite, which has additional measurements of H2O and pressure. W. Wilson at JPL and collaborators have recently performed ground-based measurements of mesospheric H2O using a borrowed radiometer which is no longer available; there is interest in continuing these measurements, but an instrument needs to be constructed. Wilson and D.Muhlemann at Caltech now have a developmental model of a 233 GHz radiometer for a Mars mission; tentative plans are to test that instrument with ground-based measurements of stratospheric and mesospheric O3 and mesospheric CO. H.Pickett and collaborators at JPL are also developing an incoherent balloon instrument operating at 0.1mm wavelength for measurements of OH and possibly other species.

Table 1 indicates the general capability of measurements which could be performed from balloon at millimeter wavelengths where heterodyne radiometers can be constructed using existing technology.

Table 1. Some millimeter-wavelength spectral lines of stratospheric molecules and approximate measurement sensitivities for balloon-based measurements. The lines given here are expected to be substantially free from other interfering lines based on the JPL catalog. The approximate sensitivity is the volume mixing ratio required to produce an emission brightness temperature of approximately 0.05 Kelvin for a balloon-based measurement of a 3 km thick layer at 30 km height; this signal corresponds to the rms noise for a liquid-nitrogen cooled radiometer (system noise temperature of 1500 Kelvin) with square-wave switching, spectral resolution of 30 MHz (approximate width of the lines at 30 km), and integration time of 2 minutes. Many of these lines can also be measured from the ground.

Molecule	Line Frequency (GHz)	Approximate Sensitivity (vmr)	Note
O3	206.13	3 E-09	1
O3(16-17-16)	283.42	2 E-10	
O3(16-16-17)	266.92	6 E-10	
O3(16-18-16)	278.45	3 E-10	
O3(16-16-18)	277.93	4 E-10	
H2O	183.31	2 E-10	2,3
HDO	255.05	8 E-11	
H2O2	204.57	1 E-10	
HO2	265.77	3 E-11	3
N2O	276.33	2 E-10	
NO	250.44	1 E-09	3
NO2	265.56	3 E-09	3
HNO3	269.2	2 E-11	
CL-35-O	204.35	2 E-11	4
CL-37-O	237.42	1 E-11	
HOCL-35	227.60	5 E-11	
HOCL-37	297.01	3 E-11	
BR-79-O	320.48	3 E-12	
BR-81-O	395.65	2 E-12	
CO	230.54	6 E-10	3
HCN	265.89	5 E-13	
H2CO	225.70	8 E-12	
SO2	221.97	4 E-11	
OCS	267.53	2 E-11	

Notes:

1. This line is given because of the insensitivity of its emission strength to stratospheric temperature variations. Other O3 lines exist which are ten times stronger.

2. Not observable from ground, but the 22.23 GHz H2O line can be used from ground to measure mesospheric H2O with a sensitivity of approximately 5 E-07 volume mixing ratio.

3. An additional mesospheric contribution must be accounted for.

4. CLO line at 278.63 GHz is approximately 3x stronger.

Fig. 1. Atmospheric spectral lines in the 200–300 GHz range. The vertical scale is the logarithm of the calculated optical depth for a limb sounding path through the middle stratosphere. The calculations are for a temperature of 225 K and the species abundances in Table 1a.The heavy horizontal line is the approximate noise level for emission measurements using a state-of-the-art radiometer with a few minutes integration and spectral resolution to resolve the stratospheric lines.

Table 1. The stratospheric species abundances used for calculations shown in Fig. 1. Abundances here are relative to the total number density by volume. Species are listed in order of increasing mass.

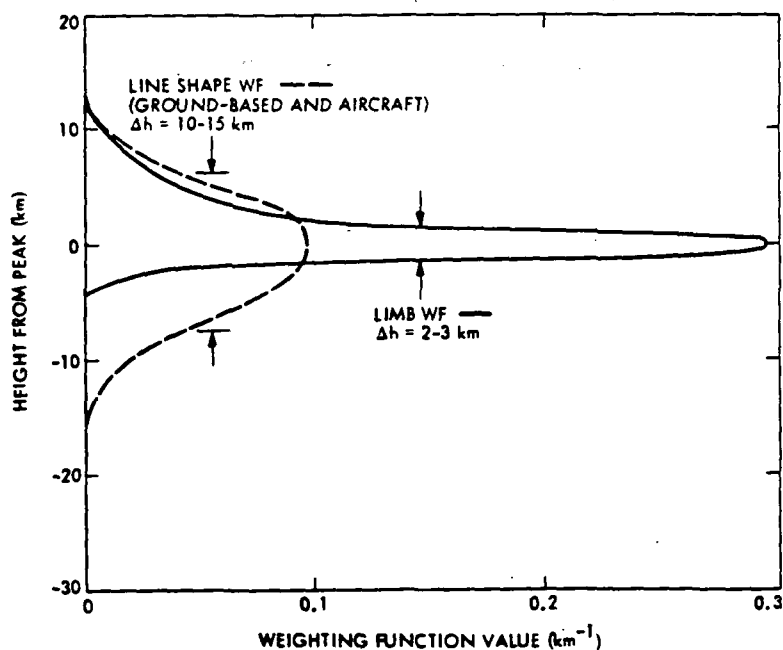| SPECIES	LOG (ABUNDANCE)	SPECIES	LOG (ABUNDANCE)
H_2O	-5.3	$^{16}O^{17}O^{18}O$	-8.7
HDO	-9.1	$^{16}O^{16}O^{17}O$	-8.3
HCN	-9.8	$^{16}O^{18}O^{16}O$	-7.8
CO	-7.0	$^{16}O^{16}O^{18}O$	-7.5
H_2CO	-10.0	ClO	-9.4
NO	-8.0	$HOCl$	-9.8
O_2	-0.7	^{37}ClO	-9.9
HO_2	-9.7	$HO^{37}Cl$	-10.3
$^{16}O^{18}O$	-3.1	OCS	-10.7
H_2O_2	-9.5	HNO_3	-8.7
N_2O	-7.0	SO_2	-11.0
NO_2	-8.0	^{79}BrO	-11.1
O_3	-5.2	^{81}BrO	-11.1

Fig. 2. Weighting functions for limb and spectral line shape microwave measurements. These functions describe the vertical resolution of the technique; the measured signal is proportional to the integral, through the observed atmospheric path, of the product of this function and the mixing ratio of the species being measured. The curves shown here have been normalized to unity area. The limb curve includes smearing by the BMLS antenna when pointed at 15 km tangent height from a float height of 40 km; for higher tangent heights this curve is narrower. The line shape curve is calculated for infinitesimally spaced spectral channels with infinitesimal resolution.

OZONE MEASURING CAPABILITY OF GROUND-BASED, MILLIMETER WAVE SPECTROSCOPY

Millimeter wave spectroscopy of the rotational transitions of ozone is a powerful technique for measuring the stratospheric ozone distribution. This technique has the following characteristics:

1) The altitudes near 40 km where ozone depletion is first expected to manifest itself are those at which the technique works best. The altitude coverage of the technique is from approximately 23 to 67 km.

2) The calibration standards used in this technique are black body sources at known temperatures. These can be made to be highly reproducable as temperature is an easily maintained standard.

3) The millimeter wave data are not affected by the stratospheric aerosols which can make the results from scattered ultraviolet techniques such as Dobson/UMKEHR uncertain.

4) Millimeter wave emission observations can be carried out at any time of the day or night. This can, for example, facilitate intercomparison of the data with data from a satellite passing over the observing site.

5) The millimeter wave observations can be carried out at a sufficient variety of sites that full latitude coverage can be obtained.

6) The ozone altitude distribution is obtained from the spectral line profile by an inversion procedure that makes use of the pressure broadened nature of the spectral line. The pressure broadening coefficient has been well measured in the laboratory.

7) The instrument can be readily operated by a technician at a field location.

The power of the technique is best suggested by its application by the research group at the State University of New York to measurements of stratospheric trace constituents such as ClO and HO_2. These constituents produce spectral lines that are two orders of magnitude weaker than typical ozone lines. (See, for example, Parrish, et. al. Science, 211, 1158, 1981; deZafra, et. al., J. Geophys. Res., 89, 1321, 1984; and Solomon et. al., Science, 224, 1210, 1984.)

At Millitech, we have carried out an analysis of the millimeter wave ozone measurement technique and particularly the problem of recovering the altitude distribution from the spectral line profile. The results of this analysis are that the following specifications for stratospheric ozone measurements should be achievable using current millimeter wave technology:

Achievable Specifications for Measurements of Stratospheric Ozone

Time Requirement for Individual Observation: 20^m (for, e.g., line at 110.835 GHz.)[1]

Altitude Coverage   23 to 67 km.

Error in Determination of Altitude
    of Mixing Ratio Maximum:[2]   2 km.

Altitude Resolution: Full Width at
    Half Maximum if Hypothetical
    Stratosphere was Single Thin Layer   5 km.

Formal Altitude Resolution (Resolution
    of Two Thin Layers):[3]   8 km.

Measurement Precision:[4]   2%

Overall Absolute Calibration Accuracy   4%

Notes: 1) For a site with 2 mm precipitable water vapor.

     2) For a typical ozone distribution similar to that in the U. S. Standard Atmosphere.

     3) Defined as the minimum spacing between two infinitesimally thick layers of ozone for which the recovered altitude distribution will distinguish the presence of the two individual layers. This result is for a hypothetical distribution having these two layers only.

     4) For an individual 20 minute observation with 5 km altitude bins.

The statistics developed by Frederick (Proceedings of the Ozone Correlative Measurements Workshop, Greenbelt, MD, 1983, NASA Conference Publication #2362) indicate that the 2% precision quoted above is more than adequate to detect an ozone trend of -0.1% per year if 200 measurements are made per year over a ten year span.

The resolution capabilities quoted above are set by the weighting functions for the ground based geometry. The resolution is adequate for direct intercomparison with the data from most other remote sensing techniques such as SBUV or for comparison with the results of theoretical models.

Millimeter wave spectroscopy is thus seen to be a feasible technique for detecting small trends in stratospheric ozone and is also one that is not affected by the calibration uncertainities that affect the scattered ultraviolet techniques that have been historically relied upon to obtain global ozone data.

Submitted by:
Dr. Alan Parrish
February 12, 1986

Workshop on Early Detection of Stratospheric Changes.
March 5 - 7, 1986

SUMMARY OF THE RESULTS FROM ATMOS
C.B. Farmer

The ATMOS experiment was flown for the first time in April, 1985, as part
of the Spacelab 3 payload. The instrument is a Michelson interferometer
operating in the absorption (solar occultation) mode, covering the 2 to 16
microns wavelength range (600 to 4500 cm^{-1}) at a resolution of 0.01 cm^{-1}.
During the Spacelab 3 mission ATMOS recorded 12 sunset and 4 sunrise occul-
tations, on April 30th, and May 1st and 2nd. The sunsets occurred at
latitudes between 25 and 33° N and the sunrises between 47 and 49° S.

The reduction and analysis of the data has been carried out with the ATMOS
computer system, a dedicated facility at JPL with remote terminals at
several coinvestigator sites in the US and in Europe. The analysis is
currently proceeding towards the final determination of vertical profiles of:

1. Density, temperature and pressure;
2. Concentration of:
   (i)   minor gases
   (ii)   nitrogen trace species
   (iii)   halogen source gases
   (iv)   halogen products
   (v)   other trace gases;
3. Winds in the mesosphere and lower thermosphere;
4. Isotopic abundances.

In addition to these, useful upper limits (i.e. at or below the concentration
levels predicted by current photochemical models) are being determined for
other key species such as ClO, HOCl, HO_2, and H_2O_2.

An atlas of high signal-to-noise coadded spectra of the sun and of the upper
atmosphere, at tangent altitude intervals of approximately two scale heights,
is being prepared for publication later this year.

The Table summarises the altitude ranges over which the profiles of concen-
tration can be retrieved for each of the molecular constituents identified
in the ATMOS spectra thus far. In general, the precision of the retrieved
values of mixing ratio is about 10%, and can be better than 5% for con-
stituents which show a large number of spectral features (for example, O_3,
CO_2, N_2O, HCl, HNO_3 etc.). The systematic uncertainties (excluding molecular
spectral parameters) are estimated to be between 10 and 20%, depending on
the spectral region involved. It is expected that these uncertainties will
be reduced considerably as the refinement of the analyses proceeds. Never-
theless, the precision achieved at the present time is sufficient to reveal
longitudinal variability (e.g. H_2O, O_3), hemispheric (or diurnal) differences,
and vertical structure.

The analysis of the first data set has necessitated a careful verification
and redefinition of the microwindows assigned to the species retrievals.
In turn the ATMOS spectra are proving to be of great value in clarifying
deficiencies in the basic molecular spectral parameters.

TABLE 1 MOLECULAR SPECIES IDENTIFIED IN THE ATMOS SPECTRA

Constituent	Altitude Range (km)	Comments/Isotopes
N_2	< 18 – 35	Pressure at the tangent altitude
CO_2	5 – 140	T,P,ρ; C12, C13, 016, 017, 018
CO	5 – 120	C12, C13, 016, 017, 018
H_2O	5 – 85	HDO between 5 and 35 km
O_3	< 10 – 90	O_3(16,16,18) < 20 to 42 km
N_2O	5 – 65	
CH_4	5 – 80	C12, C13
NO	< 18 – 140	
NO_2	< 18 – 50	
N_2O_5	20 – 38	Max. 1.6×10^{-9} at 32 km (sunrise)
HNO_3	18 – 50	
HNO_4	18 – 40	Max. 3×10^{-10} at 28 km (sunset)
CF_4	5 – 40	
CCl_4	5 – 20	
F11, 12, 22	5 – ~ 35	Several bands observed
CH_3Cl	18 – 35	Several Q branches
CH_3CCl_3		
HCl	12 – 60	3×10^{-9} above 45 km
HF	< 15 – 55	6×10^{-10} above 45 km
COF_2	18 – 40	2 bands; max. ~ 1.3×10^{-10} near 32 km
$ClONO_2$	18 – 35	5 bands; max. ~ 1.5×10^{-9} near 30 km
OCS	< 18 – 20	2 bands observed
HCN	< 18 – 30	
C_2H_2	5 – 14	
C_2H_6	5 – 10	

February 1986

Position paper for Workshop on Early Detection of Stratospheric Changes

Airborne Infrared Spectroscopic Measurements
William G. Mankin and M. T. Coffey
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Infrared spectroscopy is one of the most powerful methods of remote sensing of atmospheric composition. For measurements of the composition of the stratosphere, the use of a Fourier transform spectrometer on an aircraft platform provides some unique advantages, as well as some disadvantages. The advantages of Fourier transform infrared spectroscopy include the ability to achieve high resolution in a compact instrument, high signal to noise spectra due in part to the multiplex and throughput advantages, rapid recording of spectra from broad spectral regions, and a well understood instrument line shape. Since such an instrument generally records a broad spectral region, many constituents may be measured simultaneously and the spectra may be searched later for species which were not expected at the time of observation.

The principal advantage of aircraft as observing platforms is their mobility. It is possible with long range jet aircraft to reach any spot on the globe (which is politically accessible). Even a plane with comparatively short range, such as the NCAR Sabreliner, is able to cover a large geographical range with a number of flights. It is readily feasible, for instance, to cover latitude continuously from 70°N. to 55°S. This situation contrasts with the ability to launch large scientific balloons from only a few sites worldwide. Furthermore, almost any day has satisfactory conditions for an aircraft flight, whereas balloon launches may wait weeks for suitable launch and float conditions. The ability of the aircraft to go when and where observations are needed makes it very valuable for observing targets of opportunity such as volcanic eruptions or solar eclipses.

The cost of a single flight on aircraft is relatively small, so it is practical to make more flights than with balloons. This is important when looking for geographical or temporal change. Jet aircraft can reach the upper troposphere or lower stratosphere depending upon the latitude, and thus are above most of the water vapor that prevents observation from the ground at many wavelengths. Furthermore, the stratospheric column of the compound of interest is not obscured by the tropospheric contribution.

Another advantage that is frequently overlooked is the ability of the experimenter to accompany the instrument in an aircraft. This allows more complex adjustments of the instrument or observing plans during operations than is practical with a balloon experiment. Problems can be diagnosed and frequently solved. If it is necessary to cancel observations, it is usually possible to fly again in a short time period.

The chief disadvantage of aircraft as observing platforms is their inability to reach the altitudes of greatest interest for stratospheric chemistry. By observing

from below the stratosphere, we can measure the total stratospheric column of many species of interest, but are not able to obtain the vertical profile in the stratosphere. Some limited height information exists in the variation of line-of-sight amount with zenith angle, or in the determination of mean pressure from pressure broadened line widths, but unless one has sufficient spectral resolution (as with microwave or laser heterodyne spectroscopy) to resolve the line shape, or uses range resolved methods (such as differential absorption lidar), one cannot obtain a true profile of stratospheric constituents from aircraft (or ground based) measurements.

Other disadvantages include the requirement of a window between the instrument and the atmosphere, and the vibration level which can cause noise problems. Solar absorption measurements are generally more sensitive for measuring trace gases, particularly in busy spectral regions, because of the higher resolution and higher signal-to-noise ratio associated with a brighter source. These have the disadvantage of being possible only near sunrise and sunset, which eliminates some very important observations such as measurements of the diurnal cycle or measurements in the polar night.

A number of groups have used infrared absorption or emission spectroscopy from aircraft for study of the stratosphere, although far fewer than have made observations from balloons. Groups that have flown spectrometers include those of Murcray at Denver University, Girard at O.N.E.R.A., and our group at NCAR. Aircraft observations have also been made in the far infrared, although there have been no such measurements recently. Girard *et al.* have made latitudinal measurements from 60°S. to 62°N. We have made a number of series of flights primarily in the Northern Hemisphere, between 1976 and 1985. Our data base contains over 12,000 individual spectra, taken from 23°S. to 72°N. in different seasons and at both sunrise and sunset. Most of the data were taken at an altitude of 12 km with solar zenith angles of 86-92°.

From this data base, we have published column amounts of NO, NO_2, HNO_3, HCl, HF, OCS, HCN, HDO, and C_2H_6. We also have data on N_2O, CH_4, O_3, H_2O, CO, and CO_2. For most of the species, we have latitudinal distributions, and seasonal, diurnal, and secular trends for some. We see, for instance, a secular trend of 4-5% per year for HCl and 12-14% per year for HF over seven years.

The perturbation of the stratospheric chemistry by the eruption of El Chichon provides an interesting example of the ability of aircraft observations to provide data on localized events. Some six months after the eruptions, the cloud of debris had extended to about 30°N., as indicated by lidar. Balloons launched at Palestine, Texas, were near the edge of the cloud. We flew under the cloud as far as 20°N. and saw several modifications to the stratospheric composition. HCl was increased, presumably due to the injection of chlorine by the volcano. NO_x was decreased. SO_2 was undetectable in the gas phase by the time of observation.

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Ground-Based Infrared Solar Observations
for Early Detection of Stratospheric Changes

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Over the last decades, spectroscopic ground-based observations in the infrared, using the sun as the source of radiation, have provided a large amount of information about the composition and structure of the Earth's atmosphere. Recognition of many advantages of that infrared absorption spectroscopy technique for remote sensing of specific layers in the atmosphere led to subsequent investigations from on-board flying aircraft, balloons, satellites and more recently from the shuttle platform. These various "sites" of observation show obvious relative advantages, also constraints and limitations; within the context of telluric researches encompassing wide time and space spans, none of these "sites" has proven obsolete yet. Worth recalling here is the fact that the absorption spectroscopy technique for remote sensing is as good as the tools involved in both the observation and the analysis phases: grating – and Fourier transform spectrometers, heterodyne systems,...., associated to cryogenically cooled detectors have reached some state-of-the-art operation (providing high resolution and signal-to-noise ratios) and line parameters compilations have been supplemented significantly over the last years (major improvements are anticipated for OH, HO_2, H_2O_2 and some HNO_3 bands).

Ground-based stations located favorably on high mountains and equipped with high performance instruments offer routine possibilities to:

(1) measure <u>integrated column densities</u> for a large number of atmospheric constituents (e.g. N_2, H_2O, CO_2, N_2O, CH_4, CO, O_3, NO, NO_2, HNO_3, HF, HCl, HCN, OCS, H_2CO, $HCOOH$, C_2H_2, C_2H_6, $CFCl_3$, CF_2Cl_2, CHF_2Cl,...), among which are all those gases playing an important role in the radiation budget of the Earth's atmosphere and therefore of key importance in climatology related studies.

(2) provide information on <u>diurnal variations</u> (e.g. NO, NO_2...), establish <u>seasonal changes</u> and <u>secular trends</u> (e.g. HCl, HF, CH_4, CO_2,...)

For most of the measurements related to points (1) and (2) above, the precision is very important. Using high quality solar spectra recorded at the Jungfraujoch station (Switzerland, 3580m altitude, 46.5°N, 8°E) with an FTS (resolution 0.005 cm^{-1}; S/N > 1000), we have established that moderately strong absorption lines with central depths between 10 and 50% can be measured to better than $\pm$ 2%; for this, use was made of solar lines as well as temperature-independent lines of N_2, CO_2 and N_2O.

Further to the determination of integrated column densities, ground observations carried out with spectral resolutions of 0.005 cm^{-1} or better and S/N ratios in excess of 1000 allow to extract information about the concentration versus altitude, by fitting precisely the contours of series of lines having various strengths and temperature dependences, recorded over large zenith angle changes; such retrievals are relatively time consuming and not always unambiguous (they require a good knowledge of the temperature profile prevailing during the observations).

Investigations are being carried out at the Jungfraujoch station to assess the detectability limits of $ClONO_2$, HO_2NO_2 and ClO.

POSITION PAPERS

Authors	Titles
Stolarski	Nimbus 7 SBUV/TOMS Measurements of the Springtime Antarctic Ozone Hole
Solomon	On the depletion of Antarctic Ozone
Rood	Dynamics, Effects at Other Latitudes
Connor & deZafra	Comments on the Feasibility of Ground-Based MM-Wave Measurements of Antarctic ClO
Sze et al.	The Temporal and Spatial Behavior of Trace Gases: Early Detection of Stratospheric Changes
Solomon	Two-dimensional Perspective on Ozone Depletion
Stolarski & Douglass	Uncertainty Calculations and their Relationship to the Problem of Early Detection of Ozone Change
Tuck	Dynamical Consideration in Station Location, Geographical Representation and Variability - Species
Prather	Sampling Frequency & Required Network Size
Angell	Guidance from Past Analysis Efforts
McGee	Differential Absorption Lidar (DIAL) Measurements of Stratospheric Ozone
Megie	Lidar Measurements of Stratospheric Temperature
Proffitt	Development of Tropospheric Ozone Lidar
McDermid	The Feasibility of Ground Based Lidar Measurements of Stratospheric Hydroxyl
Torr et al.	Groundbased Measurements of Stratospheric Trace Constituents as a Function of Height by High Resolution UV Spectroscopy