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Measurement of Trace Stratospheric Constituents with a
Balloon Borne Laser Radar

Principal Investigator: William S. Heaps
NASA/Goddard Space Flight Center
Code 615
Greenbelt, MD 20771
(301) 286-5106

Co-Investigator Thomas J. McGee

The objective of this research has been to measure the concentration of stratospheric hydroxyl radical and related chemical species as a function of altitude, season, and time of day. Although hydroxyl plays a very important role in the chemistry controlling stratospheric ozone little is known about its behavior because it has been a difficult species to measure. The instrument employed in this program was a laser radar employing the technique of remote laser induced fluorescence. This instrument offers a number of attractive features including extreme specificity and sensitivity, a straightforward relationship between observed quantity and the desired concentration, and immunity to self-contamination.

The instrument was flown three times in the FY88-FY89 time period--June 1988, September 1988, and June, 1989. Additionally in early FY88 a modified instrument operated from the ground measuring ozone at McMurdo, Antarctica as part of the NOZE II expedition to investigate the south polar "ozone hole." All three of the flights obtained high quality measurements of the diurnal variation of hydroxyl radical and the September flight observed the transition through sunset when the concentration of hydroxyl plummets as the principal formation mechanisms for the radical cease. Analysis of the results of all three flights is continuing at present although a preliminary presentation of the data was made at the Fall 1988 meeting of the AGU. Unfortunately the instrument was lost in a freak accident during the June, 1989 flight. The instrument was overflying a severe thunderstorm and suffered a "free fall" from an altitude of roughly 105,000 feet. The mechanism for the accident is currently under investigation; lightning is implicated at the present time.

The following recent publications have arisen from this research:

John Burris, William S. Heaps, and John Cavanaugh, Ground Based Lidar Measurements of Antarctic Ozone in 1987, submitted to JGR.

William S. Heaps, James Butler, and T. J. McGee, Hydroxyl Radical Concentration Profiles in the Middle Stratosphere, in preparation.

IN SITU MEASUREMENTS OF STRATOSPHERIC OZONE

Principal Investigator: J. J. Margitan
Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Dr.
Pasadena, CA 91109

Co-Investigator: M. H. Proffitt
NOAA Aeronomy Laboratory and CIRES
325 Broadway
Boulder, CO 80303

Objective:

Under this task, the stratospheric abundance of ozone is measured using an in situ UV absorption instrument flown piggyback aboard balloon flights launched from NSBF. The dual channel UV photometer obtains ozone profiles on ascent and descent with 1-10 second time resolution (5-50 meters) with an accuracy of 3%. These measurements aid in understanding the distribution of ozone in the stratosphere, particularly the upper stratosphere near 40 km, as well as providing complementary and comparative data for other instruments.

Results:

There have been three recent flights of the UV photometer, which is shown in Figure 1. The first flight of the instrument, with its new command, timing, and data handling system was on September 13, 1988 at Palestine Texas (32°N, 96°W) aboard the gondola carrying the JPL BLISS (Balloon-borne Laser In Situ Sensor) instrument. The UV and BLISS ozone measurements are compared in Table 1.

Table 1. Comparison of BLISS and UV Ozone Mixing Ratios (ppmv)

Time (CDT)	P mb	Retro (m)	BLISS O ₃	UV O ₃
1635	11.21	100	8.24	8.25
1735	11.15	100	8.26	8.27
0045	10.37	200	8.52	8.30
0605	11.21	200	8.13	8.15
1150	6.58	200	9.03	8.55
1210	6.58	100	9.21	8.61

A second flight of the UV ozone photometer was made on May 27, 1989 aboard the BMLS (Balloon Microwave Limb Sounder) gondola, again from Palestine. In Figure 2, the UV ozone profile is compared with the (preliminary) values derived from the BMLS retrieval, the profile retrieved as a 30°N zonal average by the shuttle borne

ATMOS instrument in May 1985, and a recent model calculation by Natarajan and Callis (Geophys. Res. Lett. 16, 473, 1989) using the trace gas distributions measured by ATMOS. The agreement among observations and model in the 35-40 km range stands in sharp contrast to the situation which has existed for the last few years (both WMO 1985 and NASA 1988) where the values accepted for observed ozone (principally SBUV and LIMS) seemed to lie 30-50% higher than model calculations above 35 km.

A third flight of the instrument was made from Palestine on August 29, 1989 aboard the UV spectrometer of the University of Liege which was measuring OH via UV solar absorption.

Publications:

J. J. Margitan, G. A. Brothers, E. V. Browell, D. Cariolle, M. T. Coffey, J. C. Farman, C. B. Farmer, G. L. Gregory, J. W. Harder, D. J. Hofmann, W. Hypes, S. Ismail, R. O. Jakoubek, W. Komhyr, S. Kooi, A. J. Krueger, J. C. Larsen, W. Mankin, M. P. McCormick, G. H. Mount, M. H. Proffitt, A. R. Ravishankara, A. L. Schmeltekopf, W. L. Starr, G. C. Toon, A. Torres, A. F. Tuck, A. Wahner and I. Watterson, "Intercomparison of Ozone Measurements Over Antarctica", J. Geophys. Res. **94**, in press, AAOE Special Issue, 1989

M. H. Proffitt, J. A. Powell, A. F. Tuck, D. W. Fahey, K. K. Kelly, A. J. Krueger, M. R. Schoeberl, B. L. Gary, J. J. Margitan, K. R. Chan, M. Loewenstein and J. R. Podolske, "A Chemical Definition of the Boundary of the Antarctic Ozone Hole", J. Geophys. Res. **94**, in press, AAOE Special Issue, 1989

A. F. Tuck, R. T. Watson, E. P. Condon, J. J. Margitan and O. B. Toon, "The Planning and Execution of ER-2 and DC-8 Aircraft Flights Over Antarctica, August and September 1987", J. Geophys. Res. **94**, in press, AAOE Special Issue, 1989

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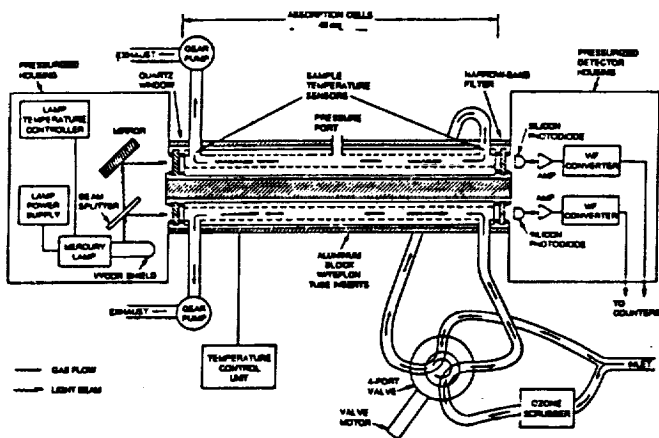
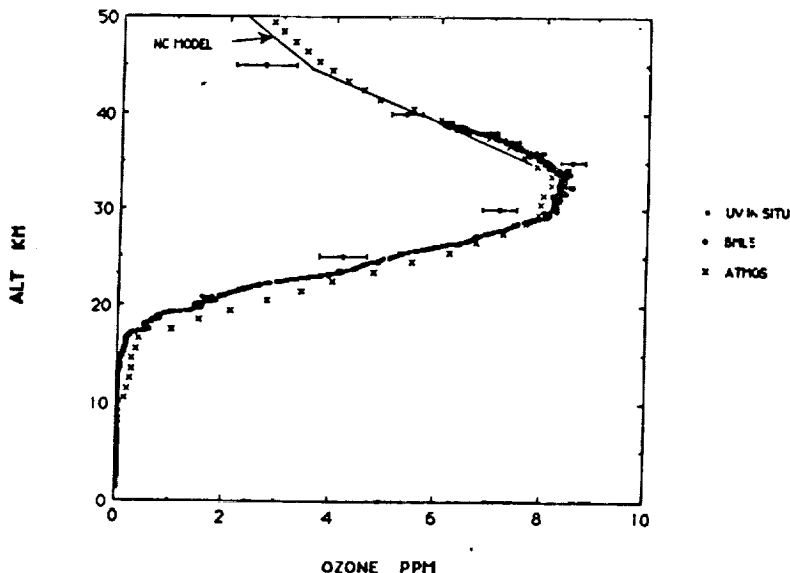


Figure 1. Schematic diagram of the ATMOS.

O3 PROFILES MAY 32 N



UV and BMLS measurements of ozone on the flight of May 27, 1989, compared to the ATMOS 30 N zonal average measured in May 1985, and a recent model calculation by Natarajan and Callis.

A. Neutral Constituent Measurement in the Stratosphere

B. Principal Investigator: Konrad Mauersberger
School of Physics and Astronomy
University of Minnesota
Minneapolis, MN 55455

C. Abstract of Research Objectives:

The research objectives are: Measurements of major and minor neutral constituents in the middle and upper stratosphere using a mass spectrometer or sample collection system. Laboratory studies of ozone's chemical and physical properties, the enhancements of ozone's heavy isotopes. Calibration of instruments using an absolute ozone calibration system. Laboratory studies simulating polar stratospheric cloud particles, condensation of nitric acid trihydrates (NAT), solubility of HCL in ice and NAT's.

D. Summary of Progress and Results:

The observed unusual enhancement in the heavy isotopes of stratospheric ozone found by mass spectrometer and infrared instrument measurements has been studied in a variety of laboratory experiments using mass spectrometers and tunable diode lasers. Enhancements at mass 50 of about 15% have been repeatedly measured. In a unique experiment all isotopes of ozone were formed (48 through 54) and the enhancements measured: A clear dependence on the symmetry of the ozone molecule was found. Ozone of mass 51 ($^{16}\text{O}^{17}\text{O}^{18}\text{O}$), representing a complete asymmetric molecule, showed an enhancement of 20%. A number of theories to explain the ozone isotopic results have been tested in those laboratory studies. So far, results have shown that during the ozone formation process $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ the isotopic fractionation occurs. An understanding of the isotope enrichment process will provide information on the formation of the ozone molecule.

Extensive laboratory studies have been conducted to experimentally test the formation and composition of polar stratospheric cloud particles which play an important role in the large ozone reduction observed during Spring. For the first time, we measured in a lab simulation experiment the temperature of formation and the composition of the cloud particles: HNO_3 and H_2O condense above ice temperature to form nitric acid trihydrates (NATs) which may be diluted by additional ice condensation as the temperature drops below the ice point. In addition the solubility of HCL in ice and NAT's was investigated and it was found that the solubility of HCL in ice is low, it is, however,

much higher in NATs. Surface effects on cloud particles may play a major role in the heterogeneous chemistry.

A new collection system has been designed and flown on board a balloon gondola to obtain, besides others, ozone samples in the stratosphere. Samples are returned to the laboratory for precision analysis of ozone isotopes, including the isotopic ratio for mass 49. The first flight was successful and provided isotopic ratios showing an enhancement similar to those found with other techniques. Data from a second successful flight are being analyzed at the present time.

E. Journal Publications:

1. "Vapor Pressures of HNO₃/H₂O at Low Temperatures," D. Hanson and K. Mauersberger, *J. Phys. Chem.* **92**, 6167 (1988).
2. "Laboratory Studies of the Nitric Acid Trihydrate: Implications for the South Polar Stratosphere," D. Hanson and K. Mauersberger, *Geophys. Res. Lett.* **15**, 855-858 (1988).
3. "Solubility and Equilibrium Vapor Pressures of HCL Dissolved in Polar Stratospheric Cloud Materials: Ice and the Trihydrate of Nitric Acid", D. Hanson and K. Mauersberger, *Geophys. Res. Lett.* **15**, 1507-1510 (1988).
4. "Laboratory Studies of Heavy Ozone," J. Barnes, B. Schueler, J. Morton, and K. Mauersberger, accepted for publication, *JGR* (1989).
5. "Oxygen Fractionation of Ozone Isotopes ⁴⁸O₃ Through ⁵⁴O₃", J. Morton, B. Schueler, and K. Mauersberger, *Chem. Phys. Lett.* **154**, 143-145 (1989).
6. "Laboratory Measurements of Ozone Isotopomers by Tunable Diode Laser Absorption Spectroscopy", S.M. Anderson, J. Morton, and K. Mauersberger, *Chem. Phys. Lett.* **156**, 175-180 (1989).
7. "HCL/H₂O Solid Phase Vapor Pressures and HCL Solubility in Ice", D. Hanson and K. Mauersberger, submitted to *J. Phys. Chem.* (1989).

**BALLOON-BORNE LASER IN-SITU SENSOR (BLISS)
AIRCRAFT LASER INFRARED ABSORPTION SPECTROMETER (ALIAS)**

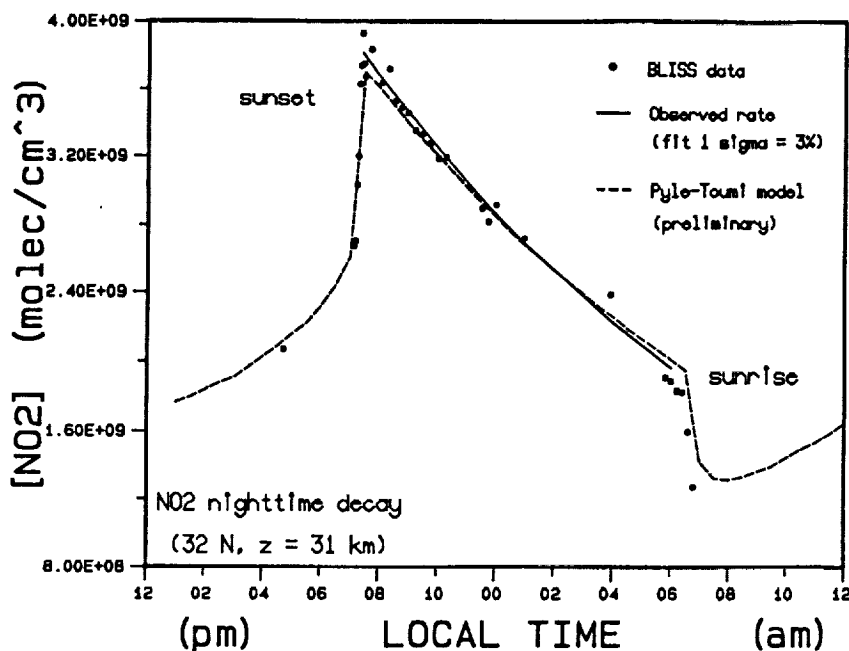
Principal Investigator: Dr. Christopher R. Webster
Co-Investigator: Dr. Randy D. May
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

Abstract of Research Objectives

The Balloon-borne Laser In-Situ Sensor (BLISS) and the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) programs have as their primary objective the collection of reliable data on the concentrations, distributions, and variabilities of the minor and trace species in the stratosphere. The BLISS instrument uses tunable diode lasers in the 4 to 20- μ m wavelength region to measure the absorption due to selected species between the balloon gondola and a lowered retroreflector which defines a path of up to 1 km. The current measurement capability for a single flight includes: NO, NO₂, O₃, HNO₃, CH₄, HCl, H₂O, N₂O, CO₂, and jNO₂ (Stedman), with capability for more species.

Summary of Progress and Results

The BLISS instrument was successfully flown twice in 1988 from Palestine, Texas. Simultaneous in-situ measurements of [NO], [NO₂], [HNO₃], [O₃], [CH₄], [N₂O], jNO₂, pressure, and temperature at 30 km were made on Sept. 13, 1988 with BLISS carrying piggy-back two other instruments: a NOAA dual-channel balloon UV Ozone Spectrometer, and the U. of Denver upward- and downward-looking radiometers for measurement of jNO₂. Using tunable diode laser absorption spectroscopy over a long pathlength, measurements were made of daytime [NO], [NO₂], [O₃], with supporting jNO₂, and of the diurnal variation in [NO₂]. Measurements of [NO₂], made every half-minute throughout much of the night, show the NO₂ mixing-ratio falling from a sunset value of 10.5 ppbv to about 5 ppbv at night's end. According to the simple identity $(d/dt)[NO_2] = -2k[NO_2][O_3]$ for the rate of decay of [NO₂], where k is the rate constant for the reaction between NO₂ and O₃, an exponential fit to the observed decay agrees with the decay rate calculated using in-flight measured O₃ concentrations and the laboratory-measured rate constant to about 7%, with a one-sigma standard deviation of the fit of only $\pm 3\%$. Photochemical model calculations constrained to the measured temperature and ozone values, and incorporating both N₂O₅ and ClONO₂ chemistry, predict in detail the observed NO₂ diurnal behavior. From the sunset/sunrise difference in the volume mixing ratio of NO₂ is derived a value of 2.75 ppbv for the sunrise N₂O₅ mixing-ratio,



Diurnal variation of $[NO_2]$ at 30 km and 32°N measured by BLISS instrument.

Derived N_2O_5 vmr = 2.75 ppbv

in excellent agreement with the model prediction of 2.78 ppbv at this latitude. Simultaneous measurements of the mixing ratios of HNO_3 and post-sunset NO_2 , allow an estimate of total odd nitrogen, approximated by $[NO_2] + [HNO_3] + 2[N_2O_5]$, of 15.8 ± 0.7 ppbv at 30 km. The OH concentration derived from the measured $[NO_2]/[HNO_3]$ ratio is compared with previous direct measurements.

In the May 1988 flight, in addition to studies of odd-nitrogen photochemistry, an intercomparison of BLISS-measured HCl was made with R. Zander's U. of Liege instrument, on another balloon at the same time (see ref. 1).

The build of the Aircraft Laser Infrared Absorption Spectrometer (ALIAS) experiment for the ER-2 began in October 1988, with BLISS balloon flights suspended for one year. This instrument will measure NO_2 , HNO_3 , HCl, CH_4 , O_3 , and H_2O on future polar missions. The design is completed, and the build underway, with plans to integrate the instrument at NASA Ames in July 1990.

E. Journal Publications

1. "In-situ Stratospheric Measurements of HNO_3 and HCl near 30 km using the BLISS Tunable Diode Laser Absorption Spectrometer", R. D. May and C. R. Webster, accepted for publication, *Geophys. Res. Letters*, 1989.
2. "Simultaneous In-situ Measurements of NO, NO_2 , HNO_3 , O_3 , N_2O , and jNO_2 using the BLISS Diode Laser Spectrometer: the Daytime NO_2/NO Ratio, the Nighttime Decay of NO_2 , Derived N_2O_5 and OH, and Estimate of NO_y at 30 km", C. R. Webster, R. D. May, R. Toumi, J. Pyle, and D. Stedman, prepared for submission to *JGR*, 1989.
3. "Stratospheric Measurements of Isotopic CH_4 , N_2O , and CO_2 using the BLISS Tunable Diode Laser Spectrometer", C. R. Webster and R. D. May, in preparation for *Geophys. Res. Letters*, 1989.

A. Balloon-Borne and Aircraft-Borne, In Situ Measurements of Stratospheric Free Radicals
B. James G. Anderson, Harvard University

C. Abstract. Free radicals from the chlorine, bromine, hydrogen, oxygen and nitrogen families constitute the catalytic chain sustaining species which dictate chemical transformation rates in the stratosphere and troposphere. This research is directed toward *in situ* detection of OH, HO₂, Cl, ClO, BrO, O₃ and H₂O from balloons and from the ER-2 aircraft. The scope of the work embraces balloon and aircraft field programs, instrument development, data analysis, and interpretation based on photochemical calculations. Isolating and quantifying ozone destruction mechanisms in the midlatitude and polar stratospheres is the abiding objective.

D. Progress and Results

1. *Detection of OH and HO₂ using the high repetition rate copper vapor laser.* We report on three flights of the copper vapor laser system: 15 July 1987, 6 July 1988, and 25 August 1989. Figure 1 displays the results of the first two flights which define for the first time the hydroxyl radical concentration in the most critical region of the stratosphere, 22-40 km altitude. Figure 2 displays the high time resolution OH and HO₂ data in the lower-middle stratosphere, obtained on 25 August 1989, representing the first simultaneous, *in situ* spectroscopic measurements of OH and HO₂ in the critical altitude region. While these results are discussed in detail in the manuscripts listed under E, it is clear that the observed OH distribution occupies the lower boundary of the OH distribution predicted by current models, indicating that OH is controlled at and below 30 km by HONO₂ and HO₂NO₂.

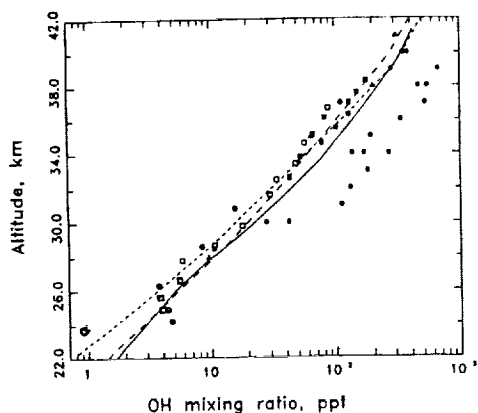


Figure 1

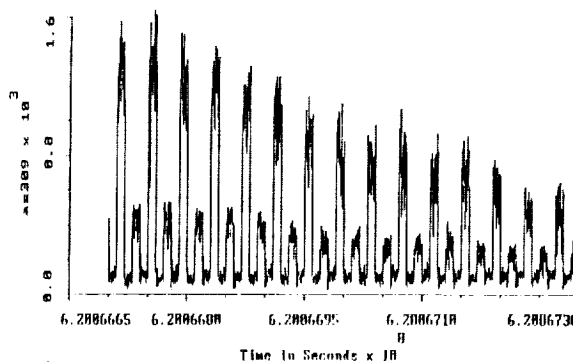


Figure 2

2. *Simultaneous detection of OH, HO₂, H₂O, and O₃ from the multisensor balloon package.* Figure 3 notes the geometry of the balloon gondola, and Figure 4 reviews the simultaneously observed profiles of OH, H₂O, and O₃ obtained from the instrument array on 6 July 1988.

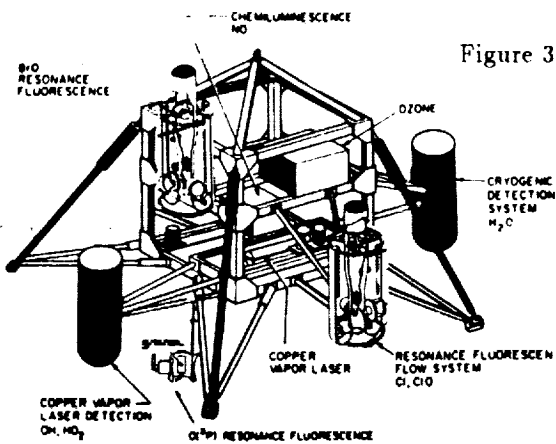


Figure 3

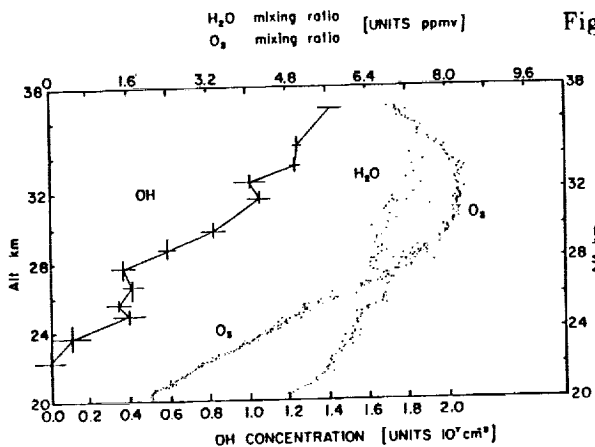


Figure 4

3. *ClO and BrO detection from the ER-2 aircraft within the Antarctic and Arctic vortices.* A significant fraction of our field efforts turned toward aircraft missions into the polar regions; specifically the AAOE and AASE projects that demonstrated that CFCs were responsible for the Antarctic ozone hole. Figures 5 and 6 trace the development of ClO-O₃ anticorrelation from the initial conditions on 23 August 1987 to 16 September 1987 within the Antarctic vortex. A detailed analysis of the kinetics of ozone destruction by ClO and BrO, both observed *in situ* simultaneously with

O₃, demonstrates that a major fraction of the observed rate of O₃ loss can be accounted for by currently proposed mechanisms, but that there may be other contributions.

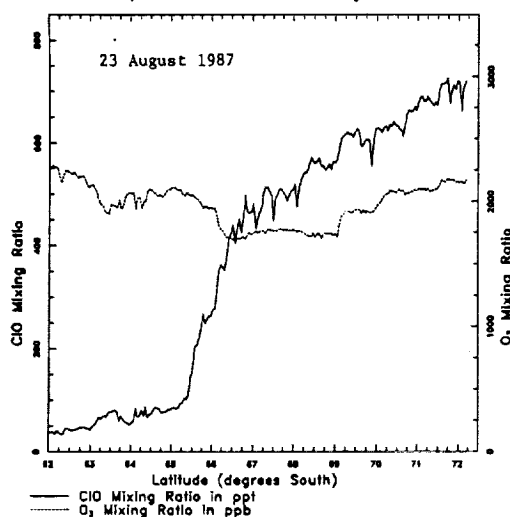


Figure 5

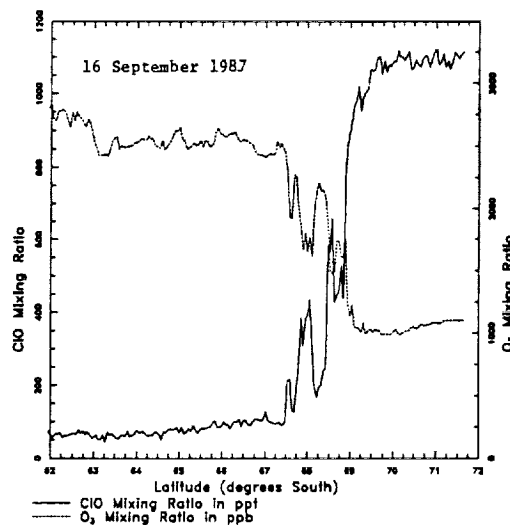


Figure 6

Finally, two flight series were made into the Arctic, the first a single flight to the edge of the Arctic vortex in February, 1988, and the second an extensive series as part of the AASE mission to Stavanger, Norway in January–February, 1989. As was the case for the Antarctic, extremely high CIO concentrations were observed, as shown in Figure 7.

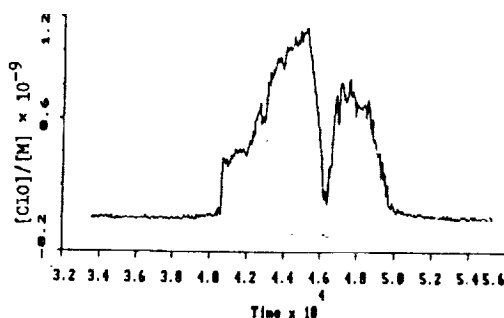


Figure 7

E. Journal Publications

- Anderson, J. G., "Free radicals in the Earth's atmosphere: Their measurement and interpretation," *Ann. Rev. Phys. Chem.* **38**, 489–520, 1987.
- Brune, W. H., E. M. Weinstock, and J. G. Anderson, "Midlatitude CIO below 22 km altitude: measurements with a new aircraft-borne instrument," *Geophys. Res. Lett.* **15**(2), 144–147, 1988.
- Brune, W. H., D. W. Toohey, J. G. Anderson, W. L. Starr, J. F. Vedder, and E. F. Danielsen, "In situ observations of CIO and O₃ in the wintertime lower stratosphere between 37°N and 61°N latitude," *Science* **242**, 558–562, 1988.
- Stimpfle, R. M., and J. G. Anderson, "In situ detection of OH in the lower stratosphere with a balloon borne high repetition rate laser system," *Geophys. Res. Lett.* **15**(13), 1503–1506, 1988.
- Anderson, J. G., W. H. Brune, S. A. Lloyd, D. W. Toohey, S. P. Sander, W. L. Starr, M. Loewenstein, and J. R. Podolske, "Kinetics of O₃ destruction by CIO and BrO within the Antarctic vortex: An analysis based on *in situ* ER-2 data," *J. Geophys. Res.*, in press, 1989.
- Anderson, J. G., W. H. Brune, and M. H. Proffitt, "Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of CIO–O₃ anticorrelation based on *in situ* ER-2 data," *J. Geophys. Res.*, in press, 1989.
- Brune, W. H., J. G. Anderson, and K. R. Chan, "In situ observations of CIO in the Antarctic: ER-2 aircraft results from 54°S to 72°S latitude," *J. Geophys. Res.*, in press, 1989.
- Brune, W. H., J. G. Anderson, and K. R. Chan, "In situ observations of BrO over Antarctica: ER-2 aircraft results from 54°S to 72°S latitude," *J. Geophys. Res.*, in press, 1989.
- Stimpfle, R. M., L. B. Lapon, and J. G. Anderson, "Balloon borne *in situ* detection of OH in the stratosphere from 37 to 23 km," *Geophys. Res. Lett.*, in press, 1989.

Measurements of Nitric Oxide and Total Odd Nitrogen in the Stratosphere

A.J. Weinheimer, J.D. Shetter, J. Walega, F. Grahek, B.A. Ridley
National Center for Atmospheric Research, Boulder, CO 80307 *

Objectives

The nitric oxide instrument is designed for flight on the Harvard University (Professor J. G. Anderson) gondola. The NO measurement accompanies a suite of other measurements of radical species (HO, HO₂, Cl, ClO, O) that are believed to control the abundance of stratospheric ozone. By measuring these species simultaneously, theoretical predictions of stratospheric photochemistry may be tested.

The total odd nitrogen instrument is a stand-alone experiment designed to provide critical information concerning the modelled impact of future anthropogenic emissions of chlorine-containing species upon stratospheric ozone. Current estimates of total odd nitrogen rely upon summing measurements— along with all the associated uncertainties— of individual species. This experiment should provide data of sufficient accuracy to narrowly restrict models of the stratospheric odd nitrogen budget.

Progress

The nitric oxide instrument has undergone further testing, modification, and calibration. An ultraviolet absorption cell has been added for monitoring the ozone used to produce chemiluminescence in the measurement of NO. The instrument was tested in a high-altitude chamber, where it functioned extremely well, except for a design flaw in the mass flow controllers that was discovered as a result of these tests. The controllers exhibit a marked variation in sensed (and hence controlled) flow with a variation in ambient pressure, in violation of the manufacturer's specifications. This was overcome by housing the controllers in a pressure-tight box. The instrument was flown on the Harvard gondola on July 28, 1989. Unfortunately, the instrument's data acquisition system failed during the flight, resulting in the acquisition of virtually no scientific data. This was not as tragic as it might have been, for the Harvard gondola failed to acquire the desired data on OH and HO₂. Fortunately, some useful information on the instrument's performance in the stratospheric environment has been obtained from the housekeeping signals, and this will lead to improvements prior to the next flight.

* The National Center for Atmospheric Research is sponsored by the National Science Foundation.

The total odd nitrogen instrument utilizes an inlet converter on the nitric oxide instrument to reduce NO_2 , HNO_3 , N_2O_5 , ClONO_2 , etc., to NO . The inlet converter has been thoroughly bench-tested to characterize the pressure, temperature, humidity, reducing reagent (H_2 or CO), and O_3 effects on the conversion of NO_2 , HNO_3 , and NH_3 to NO . The most notable operational difference between ground- and aircraft-based converters and the balloon-based converter is the need to operate the balloon device at constant pressure. This means the converter will be mounted downstream of the existing inlet valve and the inlet valve will need to be tested to determine its ability to pass the various components of NO_y . No difficulties are anticipated. The existing payload needs to be modified to accommodate the additional hardware required for NO_y measurement. This includes the CO cylinder, regulator, and flow controller; the NO_y calibration source; as well as the batteries and temperature controller for the converter.

B. BALLOON-BORNE REMOTE MEASUREMENTS

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