MEASUREMENT OF HO_2 AND OTHER TRACE GASES IN THE STRATOSPHERE USING A HIGH RESOLUTION FAR-INFRARED SPECTROMETER

NASA GRANT NSG 5175

Final Report

For the period 1 April 1998 to 31 March 1999

Principal Investigators

Wesley A. Traub
Kelly V. Chance

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Greenbelt, Maryland 20771

Smithsonian Institution
Astrophysical Observatory
Cambridge, Massachusetts 02138

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The NASA Technical officer for this grant is Dr. John Burris, Code 916, Atmospheric Experiments Branch, Goddard Space Flight Center, Greenbelt, Maryland 20771

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1. Personnel Working Under this Grant During this Reporting Period

Dr. Wesley A. Traub (Principal Investigator)

Dr. Kelly V. Chance (Principal Investigator)

Dr. David G. Johnson (Co-Investigator)

Dr. Kenneth W. Jucks (Co-Investigator)

Dr. Ross J. Salawitch (Co-Investigator)

2. Status Summary

This report covers the time period 1 April 1998 to 31 March 1999. During this period we continued analyzing data from past flights, exploring issues such as radical partitioning, stratospheric transport, and the ozone budget.

3. Instrument and Software Development

We have completed an on-board data recorder, partially funded by the Smithsonian Institution (SI), so that we can reduce our reliance on high-quality telemetry during balloon flights. The system holds almost 150 hours of data and also enables control of the instrument over the Internet, allowing remote ground-based observing.

We have also completed a gas cell for lab measurements, partially funded by SI, so that we can check the accuracy of spectroscopic parameters used in our retrievals.

We are making excellent progress towards porting our data reduction software from the OpenVMS operating system to Unix. Once the migration is complete we will finally retire our obsolete Vaxcluster and perform future data reduction and analysis tasks on modern Sun Ultra 5 workstations.

4. Data Interpretation

Understanding the stratospheric ozone budget requires accurate modeling of the HO_x, NO_y, and Cl_y families. FIRS-2 has the unique ability to make simultaneous measurements of most members of these chemical families throughout the middle stratosphere, during both day and, for those species which do not disappear, at night. During this reporting period we continued our studies of chemical partitioning, with one paper on HO_x appearing in print; a paper on HNO_3/NO_y has been accepted by JGR, and a paper on on HCl/Cl_y has been submitted.

We find that our measurements of HCl/Cl_y for the period 1989–1997 are in good agreement with model calculations, in contrast with the conclusions of recent studies of in-situ measurements, and that much of the variability we see in this ratio is driven by changes in $[CH_4]/[O_3]^2$. Reactions on sulfate aerosols are not important except under conditions of high aerosol surface area density and unusually low temperatures.

We conclude from our studies of HNO_3/NO_y that recently recommended changes in the rates of the $OH + NO_2$ and $OH + HNO_3$ reactions produce improved agreement between photochemical model calculations and stratospheric observations, but significant discrepancies remain, especially in the middle and upper stratosphere.

We have been examining the isotopic composition of stratospheric ozone using FIRS-2 measurements of symmetric and asymmetric $^{49}O_3$ and $^{50}O_3$. We find that our measurements of the enhancement in heavy isotopes are in excellent agreement both with recently published results and with calculations based on measured rate constants for isotopic variants of the Chapman reactions. FIRS-2 measurements may shed new light on the mechanism producing enhancements by providing the first high-precision measurements of both symmetric and asymmetric forms.

Understanding the effect of anthropogenic activities on stratospheric ozone requires understanding both photochemistry and transport, and to this end we have continued our work on transport issues. At present we are exploring troposphere-stratosphere transport and stratospheric age spectra.

Water vapor provides a unique tracer of troposphere-stratosphere transport because the water vapor mixing ratio is determined by the lowest temperature encountered by an air parcel. The minimum temperature typically occurs at the tropopause, and it has long been noted that the tropics is the only region with low enough tropopause temperatures to explain the extreme dryness of the stratosphere. Because δD and δ^{18}O are also affected by condensation, measurements of the isotopic composition of water vapor can further constrain models of stratospheric dehydration and transport. In work still in progress, we find that FIRS-2 measurements of δD and δ^{18}O are best explained by allowing mixing between roughly 100 and 200 mb, which suggests that the mass flux across the tropical tropopause is not dominated by direct injection of convected air into the stratosphere but by slow heating and uplift in the uppermost tropical troposphere, as suggested by some current transport models.

In a paper now in press at JGR, we use our measurements of H_2O, together with measurements made by the JPL MkIV interferometer, to correct for systematic biases in the SAGE II and HALOE instruments. We then combine the data sets to produce a global record of stratospheric H_2O covering 1986–present. By comparing the time variation in $H_2O + 2(CH_4)$ at different altitudes and latitudes with the record at the tropical tropopause, we are able to estimate the age spectrum of stratospheric air as a function of altitude and latitude. While the resulting estimates have relatively low precision, we believe that the technique shows great promise and that estimates will improve as the satellite record continues to grow in time.

In collaboration with colleagues at NIES in Japan we have continued our work on calibrating and validating data from the ILAS sensor on board the ADEOS satellite. We have compared FIRS-2 observations from 30 April 1997 with ILAS version 4.0 data, and believe the results confirm the drift in the ILAS slit function proposed by ILAS project scientists. We presented these comparisons, along with scientific interpretations of both FIRS-2 and ILAS data, at the ILAS science team meeting in Nara, Japan during March 1999.

5. Publications and Presentations

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Jucks, K. W., D. G. Johnson, W. A. Traub, K. V. Chance, G. C. Toon, J.-F. Blavier, B. Sen, G. B. Osterman, and R. J. Salawitch, Mid-latitude HCl in the lower stratosphere: Balloon observations before during and after Pinatubo, *J. Geophys. Res.*, submitted, 1999.

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Jucks, K. W., D. G. Johnson, W. A. Traub, K. V. Chance, G. C. Toon, R. A. Stachnik, R. J. Salawitch, and G. B. Osterman, Photochemical partitioning of HO_x, Cl_y, and NO_y in the middle and upper stratosphere, poster presented at the meeting of the American Geophysical Union, Boston, May 1998, and the OMS/POLARIS/STRAT science team meeting, Snowmass, June 1998.

Johnson, D. G., K. W. Jucks, W. A. Traub, K. V. Chance, FIRS-2 observations of $H_2{}^{16}O$, $H_2{}^{18}O$, and HDO: Constraints on the stratospheric dehydration mechanism, presented at the meeting of the American Geophysical Union, Boston, May 1998.

Johnson, D. G., K. W. Jucks, W. A. Traub, K. V. Chance, FIRS-2 observations of the abundance and isotopic composition of H_2O in the stratosphere: Implications for transport, poster presented at OMS/POLARIS/STRAT science team meeting, Snowmass, June 1998.

Johnson, D. G., K. W. Jucks, W. A. Traub, K. V. Chance, FIRS-2 measurements of the isotopic composition of water vapor and ozone, presented at the meeting of the American Geophysical Union, San Francisco, December, 1998.

Jucks, K. W., D. G. Johnson, W. A. Traub, K. V. Chance, R. J. Salawitch, and G. B. Osterman, Photochemical Partitioning of NO_y and HO_x in the Middle and Upper Stratosphere at Mid and High Latitudes,presented at the meeting of the American Geophysical Union, San Francisco, December, 1998.