IN-46-37560
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MEASUREMENT OF HO_2 AND OTHER TRACE GASES IN THE STRATOSPHERE USING A HIGH RESOLUTION FAR-INFRARED SPECTROMETER AT 28 KM

GRANT NSG 5175

Semiannual Status Report Nos. 15, 16, 17, 18, and 19

For the period 1 July 1984 to 31 December 1986

Principal Investigators

Wesley A. Traub
Kelly V. Chance

November 1986

Prepared for

National Aeronautics and Space Administration

Greenbelt, Maryland 20771

Smithsonian Institution
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1.0 PERSONNEL WORKING ON THIS GRANT DURING THIS REPORTING PERIOD

Dr. Wesley A. Traub (Principal Investigator)

Dr. Kelly V. Chance (Principal Investigator)

Dr. Stephen C. Wofsy (Co-Investigator)

Dr. Florence J. Lin

2.0 STATUS SUMMARY

In this status report, we review the highlights of our stratospheric program over the past 2.5 years. The major efforts have been, first, the analysis of data from the BIC-2 campaign, and second, the building of new instrumentation to replace that lost at the end of BIC-2. Much of the present review has previously been presented in the "history" section of our September 1986 proposal for the continuation of the current grant. For clarity, the review will be done by topic, rather than chronologically. For reference, the overall program has been supported as follows: NASA grant NSG 7181, 1975 to 1978, construction of the initial far-infrared spectrometer (now called FIRS-1); NASA grant NSG 5175, 1977 to present, balloon flight program, laboratory measurements, and data analysis; various CMA grants, 1980 to 1986, data analysis, laboratory measurements, duplicate stabilized platform. Further support for associated activities (travel, etc.) has been supplied by the Smithsonian Institution and SAO; indirect support in the form of metal mesh filters has been provided by I. Nolt working under his own NASA grant.

2.1 Field Measurements.

The balloon-flight history of the FIRS-1 is summarized in Table 1. On the first three flights the spectrometer was mounted at the cassegrain focus of the SAO's 102 cm diameter balloon-borne telescope. This large telescope had been flown many times by G.G. Fazio at the SAO for far-infrared astronomy, and we also attempted to use it for this purpose as well as for studying the stratospheric emission spectrum. Our program was to launch during the sunset lull, ascend, spend half of the evening hours on the stratosphere and half on astronomical objects, and spend all of the dawn and daytime hours on the stratosphere.

All three of these flights were productive in the sense that we obtained useful spectroscopic data that formed the basis of several published papers on stratospheric HCl and HF, as well as a physics department Ph.D. thesis by J. Brasunas. These flights clearly demonstrated the potential of far-infrared spectroscopy of the stratosphere, but we

Table 1

Far-Infrared Spectrometer Balloon Flights

Flight	Date	NSBF No.	Altitude	Time at Float	Day/Night	Platform	Telescope	Detector
1	6/14/79	1148-P	29 km	11 hrs.	night	SAO	102 cm	bol.
2	10/16/79	1176-P	29 km	16 hrs.	night	SAO	102 cm	bol.
3	12/03/80	1231-P	29 km	13 hrs.	night	SAO	102 cm	p-c
4	1/23/83	1316-P	35 km	5 hrs.	day	JPL-4	14 cm	p-c
5	5/16/83	1321-P	(24 km)	0 hrs.	day	JPL-1	14 cm	p-c
6	6/20/83	1332-P	37 km	13 hrs.	day + night	JPL-1	14 cm	p-c

Comments, by flight number:

(1) Test flight. Good high-elevation stratospheric spectra, except for some saturation of white light point. Occasional laser failures and low-elevation pointing problems due to frozen cables.

(2) Very good stratospheric spectra. Several astronomical objects observed. Elevation angles from 30 to 2 degrees. Helium exhausted 1 hour after sunrise.

(3) Very good stratospheric spectra. Elevation angles from 30 to -2.4 degree (tangent 23 km). Azimuth pointing failure at start of flight, caused by balloon reefing sleeve entanglement. Helium exhausted before sunrise. First use of photoconductor (p-c) detectors.

(4) Test flight. BIC-I make-up. Excellent stratospheric spectra. Elevation angles from 30 to -3.9 degree (tangent 20 km). Occasional laser and telescope failures.

(5) Aborted flight. BIC-II attempt. Balloon-burst during ascent.

(6) Excellent stratospheric spectra. BIC-II flight. Elevation angles from 30 to -4.9 degree (tangent 13 km). Additional spectra on ascent. All instruments functioned perfectly during entire flight. Instruments destroyed in free-fall after termination.

were hampered by a number of problems which were a direct result of being mounted on the large telescope platform: the platform was quite heavy, limiting our altitude range; there was no way to point accurately in absolute elevation for atmospheric limb-sounding; the spectrometer was exposed to the cold air and mounted in a cramped space; and instrument rotation at the cassegrain focus caused excessive cryogen boil-off when the horizon was viewed. In response to these difficulties, we proposed in 1981 to build a small, dedicated telescope for the FIRS-1. In addition, we accepted the offer of a JPL flight platform and support. The results of these flights are discussed next.

Our last three flights all took place in 1983. The January test flight was quite successful, yielding many excellent atmospheric spectra down to a tangent height of 20 km, and also uncovering several engineering problems which were solved before the next flight. The new telescope worked quite well. The spectrometer ran better than ever before, producing spectra free of sidebands (spectral line ghosts) for the first time, due to a change in the internal optics (which change has also been included in the FIRS-2). In addition, this was the first flight on which we had a calibrated black-body reference source, a completely baffled beam out onto the sky, and a very well calibrated elevation read-out. All this, plus the fact that we were observing in the afternoon, led to extremely good spectra in which we were able to locate easily 12 lines of OH, thus extending previous sub-mm detections of OH by Kendall and Clark, and by Carli and Bonetti.

The fifth flight was aborted during ascent because the balloon burst. After a hard landing, which damaged the gondola but not our spectrometer or telescope, we refurbished the instruments and returned for another attempt.

The sixth flight was part of the last BIC-2 campaign, and it was a scientific success. We enjoyed our highest flight altitude and longest time at float during this afternoon/sunset/evening flight. Furthermore, all of our instruments worked flawlessly the entire time. We also took advantage of the azimuth-stabilized gondola to take ascent spectra at constant elevation angle. Operations were continued downrange, but at much lower efficiency, due to our limited command and monitoring capabilities in this mode. In total, over 1600 spectra were obtained, all free of sidebands. Since these spectra cover nearly one-half of a diurnal cycle, divided between day and night, they give an especially good view of the OH variation. At the end of the flight all instruments were unfortunately destroyed when the gondola free-fell from about 33 km.

2.2 Laboratory Measurements.

Our initial laboratory experiments with the FIRS-1 were to calibrate the instrument's wavenumber scale, by measuring the emission spectrum of H_2O and HCl. To increase our experience with the technique, we measured the spectra of a number of gases. In several cases, we shared this data with other groups; for example NH_3 spectra were sent to R. Poynter at JPL, and H_2O_2 spectra were sent to F. De Lucia at Duke

University. Three species were specifically examined to aid us in searching for their signatures in stratospheric spectra: H_2O_2, $ClNO_3$, and HOCl. The hydrogen peroxide spectra were very useful in helping us identify prominent Q-branches which stand out from the forest of lines seen in this molecule, and played a leading role in our recent papers on an upper limit and detection, respectively (cf. Scientific Results section, below). The spectrum of chlorine nitrate was measured, torsional transitions identified, potential constants determined, and the torsional partition function calculated as a function of temperature; the strengths of far-infrared features were found to be about a factor of ten below our detection threshold at the time this work was done, but may be within our range in future flights. Finally, we measured the rotational spectrum of HOCl, and identified prominent Q branches which are useful in searching for this molecule in stratospheric spectra. Other experiments on line broadening were undertaken as collaborative projects with colleagues at IROE in Florence (HCl and HF), and NBS in Boulder (OH and others), but these were supported by the CMA and will not be discussed further here.

2.3 Spectral Analysis Capabilities.

We have at hand a substantial body of software for the reduction and analysis of far-infrared spectra. All of these programs were originally written for use with the FIRS-1 spectrometer. We have begun to make the modifications necessary to reduce data from the FIRS-2, principally in the areas of different data formats from the telemetry stream, and eight-times larger data arrays. We use both the central computing facilities at the CFA (a pair of VAX 11/780s) and our own microVAX (with its recent 8 MB memory extension). All programs can be run on both machines interchangeably, and via either machine through the local network; however hard-copy must be done on the CFA VAX because we have no FIRS printer or plotter.

The centerpiece of our data analysis programs is a large, least-squares fitting program which compares a segment of the observed spectrum with a theoretical spectrum, and iterates selectable concentrations and other parameters until the spectral differences are minimized. The theoretical spectrum is calculated by first generating a high-resolution model spectrum from an arbitrarily layered spherical model atmosphere. We use a precision radiative transfer program which includes the effects of Doppler and pressure broadening of lines, absorption and emission from near and far neighbor lines, absorption and emission from continuum opacity sources, and possible contributions from local contaminants. A number of special devices are employed to make this calculation as fast as possible without significant loss of precision. The spectra are smeared by a selectable instrument function. Atmospheric parameters are contained in separate files specifying the temperature, pressure, abundances, etc. as a function of altitude. Molecular parameters such as the AFGL catalog data and our own analogous data for non-AFGL species are contained in other files. A typical iteration cycle is done interactively with graphic output display on the terminal screen, and takes less than one minute. Hard copy of graphs and fitting results is available on command.

Many other utility programs have been developed. For example, we routinely screen each interferogram for data dropouts or glitches. Spectra are also screened by calculating the noise level in designated segments. Spectra can be co-added, and statistics generated to give the scan-to-scan rms variation at each point in the spectrum, to be later compared to the point-to-point rms variation of residuals from the difference of the co-added and calculated spectra. A different fitting program allows broadening parameters to be determined from laboratory spectra.

2.4 Instrumentation.

Since the loss of FIRS-1, we have invested a considerable effort in re-building and simultaneously improving our spectrometer and telescope instrumentation. As of this writing, we have completed the re-build; we have gone through one iteration of improving the moving mirror drive system; we have tested the dewar and its detectors away from the spectrometer, but coupled to the full pre-amp circuits; we have tested the stabilized platform under static and dynamic conditions (and have completed a duplicate of this device for use by IROE); and we have completed nearly all of the programming of the instrument control computer. Remaining tasks are to complete the internal optical alignment of the spectrometer, integrate the dewar to the FIRS vacuum tank, systems-test the entire unit, mount and align the telescope and stabilized platform, environmental test the complete package, and run laboratory tests to further shake down the system.

The improvements to the system are mainly as follows. The spectral resolution has been increased by a factor of eight by making a corresponding increase in the length of travel of the moving mirror, now 62.5 cm from the white-light point, giving a single-sided interferogram with a path difference of 125 cm, and an (unapodized) spectral resolution of 0.004 cm^{-1}. The diameter of the internal optics was also increased by a factor of eight, so that the etendue (product of area and solid angle) of FIRS-2 is the same as that of FIRS-1, meaning also that the total radiation from the atmosphere falling on the detector will be the same. The moving mirror is now a hollow corner-cube, instead of a parabola-flat cats-eye combination, to simplify alignment and to save space. The detectors have been increased from two to four, by using a metal mesh diplexer (cold mirror) in one beam and a mirror with a central hole in the other beam; this allows us to use filters to isolate OH and $ClNO_3$ features, and thereby achieve increased signal-to-noise. The stabilized platform has been modified so that it can use a readily available, moderate-drift gyro (instead of the very low drift Skylab surplus gyro used with FIRS-1), and it has at the same time been improved so that its internal offset error will be smaller than before. The telescope is now an off-axis spherical primary with flat folding mirrors, which eliminates the large thermal radiation from the central hole and secondary support spider in the original instrument. The on-board electronics now has the capability to store and recall complex command sequences, including entire limb-scan procedures, thus saving us from having to manually type in each command in real time during the flight, and also allowing us the ability to pre-program the entire instrument so that it will be able to continue gathering data long after we lose direct telemetry contact with the payload.

These improvements to the system will undoubtedly result in higher signal-to-noise spectra in a given amount of observing time, and will also result in more efficient use of our time at float, altogether giving us markedly improved data. In the current context, it is perhaps worth commenting that the rebuilding effort has taken more time and effort than we originally expected. The improvements to the spectrometer were in several cases explorations into unknown engineering territory. As a result, our schedule has stretched out, and we have not been able to do all the data analysis that we had hoped to do by this time. However a great amount has indeed been accomplished in the time available, and we believe that the improvements to the instrumentation are so significant that we view the extra time required as being a good investment.

2.5 Scientific Results.

In order to generate a rough measure of scientific output, we simply counted the number of publications and presentations associated with this program since its inception. We have a total of 27 published papers from FIRS-1, including papers appearing in refereed journals, papers appearing in published conference proceedings, a Ph.D. thesis, and papers which have either been accepted for publication or are completely written and only need to be submitted (i.e. BIC results). The titles and abstracts of these papers are given in an appendix. At the same time, there have been a total of 16 oral presentations at professional meetings, including several invited talks, but excluding of course numerous other talks at, for example, local seminars, BIC meetings, and ozone assessment meetings. Most of these papers and presentations (63 percent) have appeared since 1983, in part reflecting the fact that the BIC campaign was very successful for us.

The collection of FIRS-1 papers resulting from our participation in the BIC-2 campaign is of interest. We measured H_2O, HCl, HF, and O_3 as prime intercomparison species. Details of these measurements will not be discussed here, as they can be found in the individual papers. The key general result is that our abundance determinations agree quite well with the average or "best" profiles from the BIC group as a whole, and the agreement extends over the full altitude range of roughly 20 to 45 km Much of the uncertainty that we estimated for FIRS-1 is expected to be reduced in FIRS-2, due to increased spectral resolution, decreased detector loading, background radiation reduction, better intensity calibration, and improved knowledge of line broadening parameters. In some cases, our measurements appear to be yield systematically slightly higher abundances than the average, possibly due to errors in the adopted line parameters. Generally, however, our abundance profiles for BIC-2 were in very good agreement with the average, and we expect to do better in the future.

We have measured H_2O_2 in both winter and summer in 1983, finding in the first case an upper limit and in the second case a probable detection. The upper limit is the lowest such limit to date, and is essentially in agreement with the model calculations for that time of year. The summer measurements are another situation however, since they do not agree with model results in two ways. First, we see a larger amount of H_2O_2 above the balloon (about 35 km) than expected. Second, we see very little H_2O_2 below the balloon, certainly less than expected from models. If our results are correct, there is a strong discrepancy with theory that must be explained. One of the key priorities in our next flight will be to remeasure H_2O_2, including the $^RQ_5$ branch as well as other Q branches which should be measurable with the higher resolution and improved sensitivity of FIRS-2.

We have used the atomic oxygen $O(^3P)$ emission line in our spectra to estimate the overhead column of O atoms. Since essentially all of this line arises from the region around and above the boundary between the mesosphere and the thermosphere, we used the leverage from observations at two elevation angles to help pin down the vertical column. The problem is further complicated by the extremely large optical depths found in this line, leading to a complex interplay of absorption and emission as a function of altitude (hence temperature and pressure). The result is that it is certainly within reason to use the data to put constraints on the profile, although it is not possible to make a unique and independent determination of a vertical profile. Thus, our approach was to assume a profile shape from existing measurements and calculations, and to determine an overall scaling factor for the profile from our measurements.

A number of other results are currently in progress, including work on OH, the far-infrared continuum spectrum, the measurements of contamination from balloon-borne water, our measurements of isotopic fractionation of stratospheric water molecules, and work to date on the search for HO_2 in our spectra.

APPENDIX A

Stratospheric Publications

Stratospheric Publications

1975 Balloon-Borne Fourier Transform Spectroscopy, W. A. Traub, in *Far-Infrared Astronomy,* ed. M. Rowan-Robinson, 1-10, Pergamon Press.

1976 Theoretical Atmospheric Transmission in the Mid- and Far-Infrared at Four Altitudes, W. A. Traub and M. T. Stier, *Applied Optics l5,* 364.

1980 Far Infrared Measurability of HCl, OH, H_2O_2, HO_2 and HOCl, K. V. Chance and W. A. Traub, *OSA Topical Meeting on Spectroscopy in Support of Atmospheric Measurements, Technical Digest,* TuP2.

1980 Far Infrared Measurement of Stratospheric HCl, K. V. Chance, J. C. Brasunas, and W. A. Traub, *Geophysical Research Letters 7,* 704.

1981 Stratospheric HF and HCl Observations, W. A. Traub and K. V. Chance, *Geophysical Research Letters 8,* 1075.

1981 *Far-Infrared Spectrsocopy of Gaseous Nebulae,* J. C. Brasunas, Ph. D. Dissertation, Harvard University.

1982 Use of a Fourier Transform Spectrometer on a Balloon-Borne Telescope and at the MMT, W. A. Traub, K. V. Chance, J. C. Brasunas, J. M. Vrtilek, and N. P. Carleton, *Proc. S.P.I.E., Instrumentation in Astronomy IV, 331,* 208.

1982 The Torsional Spectrum of Chlorine Nitrate, K. V. Chance and W. A. Traub, *Journal of Molecular Spectroscopy 95,* 306.

1982 Q Branches in the Rotational Spectrum of HOCl, K. V. Chance and W. A. Traub, *Journal of Quantitative Spectroscopy and Radiative Transfer, 29,* 81.

1983 Far Infrared Spectroscopy, K. V. Chance, *Proc. CMA/NBS Workshop on Atmospheric Spectra,* IIA53.

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1984 An Upper Limit for Stratospheric Hydrogen Peroxide, K. V. Chance and W. A. Traub, *Journal of Geophysical Research D. 89,* 11,655-11,660; erratum *Journal of Geophysical Research D. 90,* 10,756 (1985).

1985 Ozone Intercomparisons from the Balloon Intercomparison Campaign, D. Robbins, W. Evans, N. Louisnard, S. Pollitt, W. Traub, K. Chance, and J. Waters, *Proc. Quadrennial Ozone Symposium,* ed. C. S. Zerefos and A. Ghazi, 454-459, D. Reidel, Hingham, MA.

1985 Intercomparison of Stratospheric Water Vapor Profiles Obtained During the Balloon Intercomparison Campaign, D. G. Murcray, A. Goldman, J. Kosters, R. Zander, W. Evans, N. Louisnard, C. Alamichel, M. Bangham, S. Pollitt, B. Carli, B. Dinelli, S. Piccioli, A. Volboni, W. Traub, and K. Chance, *Proc. Quadrennial Ozone Symposium,* ed. C. S. Zerefos and A. Ghazi, 144-148, D. Reidel, Hingham, MA.

1985 Far-Infrared Measurements of Stratospheric Trace Species, K. V. Chance, F. J. Lin, and W. A. Traub, *OSA Topical Meeting on Optical Remote Sensing of the Atmosphere, Technical Digest,* TuC7.

1985 Far-Infrared Measurements of Stratospheric Trace Gases, K. V. Chance, F. J. Lin, and W. A. Traub, *Proc. Seventeenth International Symposium on Free Radicals,* 166.

1985 Far-Infrared Spectroscopy of the Earth's Stratosphere, K. V. Chance, W. A. Traub, B. Carli, I. G. Nolt, and J. V. Radostitz, *Proc. AIAA/NASA Earth Observing System Conference,* AIAA-85-3006.

1985 Far-Infrared Radiometer to Map OH in the Middle Atmosphere, I. G. Nolt, J. V. Radostitz, K. V. Chance, W. A. Traub, P. A. R. Ade, and B. Carli, *Proc. AIAA/NASA Earth Observing System Conference,* AIAA-85-3007.

1985 Far-Infrared Filter Radiometry of Stratospheric Trace Gases, I. G. Nolt, J. V. Radostitz, K. V. Chance, W. A. Traub, B. Carli, and P. A. R. Ade, *10th International Conference on Infrared and Millimeter Waves, Technical Digest.*

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1986 Performance of a Single-Axis Platform for Balloon-Borne Remote Sensing, W.A. Traub, K.V. Chance, and L.M. Coyle, *Review of Scientific Instruments,57,* 2519.

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1987 Evidence for Stratospheric Hydrogen Peroxide, K. V. Chance and W. A. Traub, to appear in *Journal of Geophysical Research.*

1987 Ozone Measurements During the Balloon Intercomparison Campaign, D. Robbins, J. Waters, P. Zimmerman, R. Jarnot, J. Hardy, H. Pickett, S. Pollitt, W. A. Traub, K. Chance, N. Louisnard, W. Evans, and J. Kerr, to be submitted to *Journal of Geophysical Research.*

1987 Intercomparison of Measurements of Stratospheric Hydrogen Fluoride, W. G. Mankin, M. T. Coffey, K. V. Chance, W. A. Traub, B. Carli, A. Bonetti, I. G. Nolt, R. Zander, D. W. Johnson, G. Stokes, C. B. Farmer, and R. K. Seals, to be submitted to *Journal of Geophysical Research.*

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1987 BIC HCl.