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Final Research Summary for Grant NAGW-2182, "Stratospheric and Mesospheric Trace Gas Studies Using Ground-Based mm-Wave Receivers" (Jan 1994–Dec 1997).

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Summary: The research covered here involved field measurements of stratospheric trace gases important in the polar and global stratosphere, and subsequent analysis of these measurements. It represents the continuation of a cycle of Antarctic and Arctic measurements begun in the spring of 1992 with a ground-based mm-wave spectrometer of greatly improved sensitivity relative to that which we had previously used. During a significant part of the present grant, we have in fact had two portable mm-wave spectrometers (one older, plus the improved version referred to above) in action in Antarctica. Both were at McMurdo Station from late August to early October, 1994, allowing simultaneous measurements of several stratospheric trace gases during an ozone hole event, and one of these was then moved to the South Pole for an 11 month period of measurements beginning in January of 1995, under partial funding from the NSF, and with collaboration from the Center for Astrophysical Research in Antarctica. The other, more sensitive, spectrometer was again used at McMurdo Station during the spring ozone hole seasons, from late August until early October, 1995, and 1997. We requested and received a 12 month extension on the original grant period to allow application of some residual funds to upgrading of equipmnent, when suppliers could not meet the initial grant termination date due to manufacturing problems. In 1997 we weer finally able to begin upgrading our older receiver to increase its sensitivity at least 4-fold and ready it for a new cycle of observations at the South Pole research station, to begin in 1998-99. A grant from the NSF will furnish logistical and some personnel support, plus a small amount of funding for this effort, which will also be aided by a collaboration with the Antarctic Submillimeter Telescope and Remote Observatory (AST/RO) group at the South Pole.

In early 1996, logistical support was applied for and received from the European Community to allow us to participate in an intercomparison campaign involving new ClO-measuring instruments from Germany and Japan during the Arctic spring of 1997. (Antarctic field work was consequently suspended for the austral spring of 1996, due to the time scale needed to send our equipment by ship to the Arctic). The intercomparison was carried out at Ny Ålesund on the island of Spitzbergen, where we made observations from the end of January until early March, 1997.

Through our development of an in-house photochemical model and its application to our observations, new insights have been gained concerning the accuracy of current knowledge about the diurnal chlorine dimer cycle (the primary chlorine cycle destroying lower stratospheric ozone in the Antarctic spring). Separate from these model studies, analysis of results from McMurdo and from the Pole have given new information about the O_3/N_2O ratio over Antarctica as a function of altitude and season, and its validity as a proxy indicator of chlorine-induced ozone depletion. We have also added to knowledge about the long-term build-up of active chlorine in the Antarctic stratosphere, about the timing, degree, and altitude range in which nitric acid (HNO_3) is removed from the stratosphere by polar stratospheric cloud formation; about the rate and time span of downward transport in the

polar winter stratosphere, and about intrusion of mesospheric air into the polar winter stratosphere. Through participation in the UARS/MLS validation effort, and in on-going intercomparisons with European, Japanese, and NDSC mm-wave spectroscopy instruments, we are helping to establish uniform and tested methods of instrument calibration, observational techniques, and data reduction.

Antarctic field campaigns have been carried out under direct arrangements in the form of both nominal (no funding) and funded grants from the National Science Foundation's Division of Polar Programs, which oversees operations and logistics for all U.S. science carried out on the Antarctic continent and which must formally grant approval for all research carried out there. NASA funding has been vital for all other phases of this research.

Detail of Progress and Results

Field Work: In the austral spring of 1994, we were able to set up both of our ground-based mm-wave spectrometers at McMurdo to make simultaneous measurements of several stratospheric trace gases during the formation of the 1994 Antarctic ozone hole. One of these instruments, employing an older and less sensitive receiver, had been used in a very successful pioneering experiment to carry out an 11-month cycle of stratospheric trace measurements over the South Pole during 1993. We operated it in tandem with our more sensitive superconducting receiver system. The latter was used to make difficult chlorine monoxide (ClO) measurements requiring the utmost sensitivity, while the older spectrometer was used for daily measurements of nitrous oxide (N_2O) and nitric acid (HNO_3). N_2O is a useful tracer of transport, and helps distinguish air that has been within the vortex for a considerable period (thus subject to vertical subsidence) from air which may have recently entered across the vortex boundary. Measurements of strongly depleted HNO_3 are a good indicator of air that has been exposed to very cold temperatures within the vortex, and is chemically primed, via the removal of nitrogen oxides, for catalytic ozone destruction by chlorine. ClO is the intermediary product in the catalytic destruction of ozone by chlorine. This is the first time that vertical profiles for all three species have been measured using ground-based equipment during an ozone hole event. Our results and analysis have recently been published (Klein, et al., 1996).

The older spectrometer system was up-dated with new and faster computers, improved operating and analysis software, and minor mechanical improvements, and reshipped to the Pole in January of 1995, to follow another annual cycle of trace gas measurements (O_3, N_2O, HNO_3, and NO_2). This time, operations were carried out by cooperative arrangement with Dr. Richard Chamberlin, a winter-over astronomer for the AST/RO effort. Dr. Chamberlin was simultaneously carrying out a program of tests and observation with a new mm-wave astronomical telescope, and this resulted in fewer measurements, with some longer breaks between, than we had obtained with our own dedicated observer in 1993. Nevertheless, this allowed us to make important comparisons and confirmations of the behavior of various trace gases observed during the 1993 cycle (see publications list below). The first in a projected series of papers resulting from the 1995 observations has been accepted for publication (Cheng et al, 1997). The 1995 observations essentially confirm the patterns of trace gas behavior noted in 1993.

Our observations of ClO continued at McMurdo during August-October, 1995, and again in 1997. The consecutive 4-year record established between 1992 and 1995 showed an interesting two-year cycle in the average September amount of ClO, reminiscent of 2-year cycles noted earlier in other Antarctic ozone-depletion parameters, but now harder to trace, presumably due to saturation effects as the hole grew larger. No attempts so far (including ours) to tie strong or weak years of Antarctic ozone depletion to the well known tropical quasi-biennial oscillation cycle have succeeded in demonstration a consistent, long term relation between the easterly or westerly equatorial wind direction and lesser versus greater ozone depletion, however.

Data Analysis and Chemical Modeling: A considerable amount of time and effort was put into analysis of the large amount of data flowing from the two annual cycles of observations at the South Pole (1993, 1995). The data collected are extremely interesting, as well as rare or unique in several aspects (length of coverage, altitude range covered, species observed, near simultaneity of data for various species). The analysis of two years of data has given us a good basis for confidence in the rate of downward transport derived for the fall and winter polar stratosphere from NO_2 and O_3 observations; in the timing, degree, altitude range, and severity of HNO_3 condensation into polar stratospheric clouds near the beginning of polar winter; in the generation of new HNO_3 in the middle stratosphere during polar winter; in the timing, duration, and degree of intrusion of mesospheric and thermospheric NO_2 into the middle to upper stratosphere during winter; and the transport of lower latitude air into the center of the vortex at higher altitudes well before it is brought in at lower altitudes (see publications list below).

During 1994-95, we developed and applied an in-house photochemical model of the stratosphere, to enable us to analyze in detail our own McMurdo measurements of the diurnal cycle of lower stratospheric ClO during an ozone hole event (essentially the only such measurements existing). The model pays particular attention to accurate simulation of radiative transfer through the atmosphere at high solar zenith angles, a feature often treated less accurately in general photochemical models for the sake of computational efficiency, This work was the Ph.D. thesis of D.T. Shindell, who showed that the recommended 1994 JPL photochemical reaction rates for the key reactions governing the ClO dimer cycle are in very good agreement with observations, and that uncertainty in some recommended values can indeed be narrowed on the basis of the observed diurnal behavior (Shindell et al., 1995, Shindell and de Zafra, 1996, 1997). In work done for a Master's thesis, V. Chan developed a very useful and flexible constrained matrix inversion package for retrieval of vertical profiles when several emission lines are present in one spectrum, which we are now using for analysis of the multiplet of lines observed in the spectrum of HNO_3, and as an alternative to the Chahine-Twomey inversion technique we normally use for other emission lines.

Equipment improvements and future planning: Some improvements were made to the existing superconducting mm-wave receiver during the latter part of 1996, in preparation for its deployment to the European research station at Ny Ålesund on the Arctic islands of Spitzbergen, prior to its use during the Arctic spring of 1997 in an intercomparison campaign of ClO measurements with newly built German and Japanese instruments

We are replacing the solid-state Schottky diode receiver in our older spectrometer system with an ultra-sensitive superconducting receiver. Using residual funds carried into 1997, a new, very broadband SIS mixer was purchased from the National Radio Astronomy Observatory for this purpose. This device will act as the primary receiving element, and will allow observations over a very broad spectral range (220-280 GHz) with a noise improvement of a factor of 4 or better relative to the Schottky receiver, and will require no tuning. A factor of 4 in receiver noise translates to shortening the required observing time by a factor of nearly 16 under South Pole observing conditions. We are also making other improvements to increase the reliability of the equipment for prolonged field use at the South Pole. Using residual funds carried into 1997, we have also purchased a new closed-cycle helium refrigerator to produce the required superconducting operating temperature for this new receiver. The refrigerator is a new design, with good power efficiency and low maintenance requirements, as needed for operation at the South Pole station.

A proposal has been funded by NSF for the installation of this upgraded spectrometer at the South Pole starting in the austral summer of 1998-99, for at least a one-year cycle of quasi-continuous trace-gas measurements that would complete the series begun in 1993 and 1995, as well as add new and more sensitive measurements of hard-to-detect species. A separate proposal covering logistical and other incidental support for continued field work at McMurdo Station during 1997-1998 has also been funded, as well as a new NASA proposal to continue major funding for additional field work and analysis over the next 3 years.

Publications in refereed journals resulting from work completed in part or in whole during the period 1994-1997:

1. "Arctic Chlorine Monoxide Observations During Spring 1993 over Thule, Greenland and Implications for Ozone Depletion, D.T. Shindell, J.M. Reeves, L.K. Emmons, and R.L. de Zafra, *J. Geophys. Res.*, *99*, 25697-25704, 1994.
2. "Stratospheric ClO Profiles from McMurdo Station, Antarctica, Spring 1992", L.K. Emmons, J.M. Reeves, D.T. Shindell, and R.L. de Zafra, *Journ. of Geophys. Res.*, **100**, 3049-3055, 1995.
3. "Chlorine Monoxide in the Antarctic Spring Vortex over McMurdo Station, 1993, 1: Evolution of Midday Vertical Profiles", R.L. de Zafra, J.M. Reeves, and D.T. Shindell, *Journ. of Geophys. Res.*, **100**, 13,999-14,007, 1995.
4. "The chlorine budget of the lower polar stratosphere: Upper limits on ClO, and implications of new Cl_2O_2 photolysis cross sections", D.T. Shindell and R.L. de Zafra, *Geophys. Res. Letters*, **22**, 3215-3218, 1995.
5. "Chlorine Monoxide in the Antarctic Spring Vortex, 2: A Comparison of Measured and Modeled Diurnal Cycling over McMurdo Station, 1993", D.T. Shindell and R.L. de Zafra, *J. Geophys. Res.*, **101**, 1475-1487, 1996.
6. "Correlated millimeter-wave measurements of ClO, N_2O, and HNO_3 from McMurdo, Antarctica, during polar spring, 1994", U. Klein, S. Crewell, and R.L. de Zafra, *J. Geophys. Res.*, **101**, *J. Geophys. Res. 101,* 20,925-20,932, 1996.
7. "Limits on heterogeneous processing in the Antarctic spring vortex from a comparison of measured and modeled chlorine", D.T. Shindell and R.L. de Zafra, to be published in *J. Geophys. Res.* **102** (Special issue on stratospheric ozone), Feb. 1997.
8. "Millimeter-wave Spectroscopic Measurements over the South Pole, 1: A study of stratospheric dynamics using N_2O observations", S. Crewell, D. Cheng, R.L. de Zafra, and C. Trimble, *J. Geophys. Res.*, **100**, 20,839-20,844, 1995.
9. "Millimeter-wave Spectroscopic Measurements over the South Pole, 2: An 11-month cycle of stratospheric ozone observations during 1993-94", D. Cheng, R.L. de Zafra, and C. Trimble, *J. Geophys. Res.*, **101**, 6781-6793, 1996.

10. "Millimeter-wave Spectroscopic Measurements over the South Pole, 3: The behavior of stratospheric nitric acid through polar fall, winter, and spring", *J. Geophysical Res.*, **102**, 1399-1410, 1997.
11. "Millimeter-wave Spectroscopic Measurements over the South Pole, 4: O_3 and N_2O during 1995 and their correlations for two quasi-annual cycles", D. Cheng, S.Crewell, U. Klein, R.L. de Zafra, and R.A. Chamberlin, *J. Geophys. Res.* **102**, *,6109-6116,* 1997.
12. "Millimeter-wave Spectroscopic Measurements over the South Pole, 5: Observed NO_2 enhancement in the mesosphere/upper stratosphere over the South Pole in winter" R.L. de Zafra, D. Cheng, J.M. Reeves, and C. Trimble, and R. Chamberlin (*In manuscript: to be submitted to J. Geophys. Res*).

Book Chapter:

"The ground-based measurement of stratospheric trace gases using quantitative millimeter wave emission spectroscopy", R.L. de Zafra, pp23-54, *Diagnostic Tools in Atmospherics*, Course CXXIV, Proceedings of the International School of Physics "Enrico Fermi", editors G. Fiocco and G. Visconti, IOS Press, Amsterdam, 1995.

Conference presentations in published form (2-4 pages):

1. Accuracy of Profile Retrievals from mm-Wave Spectra of ClO and N_2O", Vol. III, pp.1684-1686, *Proceedings of the Internat. Geoscience and Remote Sensing Symp., Pasadena, CA. Aug. 1994*, IEEE Cat. No. 94CH3378-7, Inst. of Electrical and Electronics Engineers, Piscataway, N.J., (1994).
2. "mm Wave Spectroscopy of Stratospheric Trace Gases at the South Pole over an 11-Month Cycle: O_3, N_2O, HNO_3, NO_2, and ClO", R.L. de Zafra, C. Trimble, J.M. Reeves, D. Cheng, and D. Shindell, Vol. III, pp. 1678-1680, *Proceedings of the Internat. Geoscience and Remote Sensing Symp., Pasadena, CA. Aug. 1994*, IEEE Cat. No. 94CH3378-7, Inst. of Electrical and Electronics Engineers, Piscataway, N.J., (1994).
3. "Interpretation of a Unique Record of Ozone Profiles from 16-55 km Measured over an Annual Cycle at the South Pole by mm-Wave Spectroscopy", D. Cheng, R.L. de Zafra, and C. Trimble, in *Proceedings of the International Conference on Ozone in the Lower Stratosphere*, Halkidiki, Greece, May, 1995.
4. "A Nine-Month Record of HNO_3 Profiles Over the South Pole: Implications for PSC Formation and NOx Removal in the Antarctic Stratosphere", R.L. de Zafra, V. Chan, and C Trimble, in *Proceedings of the International Conference on Ozone in the Lower Stratosphere*, Halkidiki, Greece, May, 1995.
5. "Diurnal Chlorine Monoxide Measurements in the Antarctic Spring Stratosphere over McMurdo Station: A Critical Test of Current Chemical Understanding of the Dimer Catalytic Cycle", D.T. Shindell and R.L. de Zafra, in *Proceedings of the International Conference on Ozone in the Lower Stratosphere*, Halkidiki, Greece, May, 1995.
6. "A review of results from a decade of ground-based ClO observations in the Antarctic springtime" R.L. de Zafra, D.T. Shindell, S. Crewell, U. Klein, and D. Cheng, to be published in the Proceedings of the XVIII Quadrennial Ozone Symposium, L'Aquilla, 1996.
7. " Long-term trends in springtime peak mixing ratio and total column ClO at McMurdo Station, Antarctica, from 1987 to 1995", U. Klein, D. Cheng, S. Crewell, and R.L de

Zafra, to be published in the Proceedings of the XVIII Quadrennial Ozone Symposium, L'Aquilla, 1996.

Theses and degrees, 1994-1997, with support from NAGW-2182:

Louisa K. Emmons, "Measurement and Analysis of Polar Stratospheric ClO and N_2O by Ground-Based mm-Wave Spectroscopy", Ph.D. degree, May 1994.

Victor Chan, "Retrieval of Stratospheric Trace Gas Profiles by a Constrained Matrix Inversion Method", M.S. degree, September, 1995.

Drew T. Shindell, "Model/Measurement Comparisons of Ozone Depleting Chlorine Chemistry in the Polar Stratosphere", Ph.D. degree, September, 1995.

Dongjie Cheng, "Analysis of Ground-Based mm-Wave Observations of Ozone at the South Pole Through Two Quasi-Annual Cycles", Ph.D. degree, September, 1996.

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