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Infrared measurements of column amounts of stratospheric constituents in the Antarctic winter, 1987

by

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The discovery by Farman *et al.* (1985) of recent large depletions of ozone in the Antarctic stratosphere in the austral spring has aroused great interest because of its serious potential consequences, as well as its surprising nature. An airborne expedition, including 21 experiments on two aircraft, was mounted from Punta Arenas, Chile, in August and September, 1987, to gather a wide range of data to understand the origins and implications of this phenomenon, known as the "ozone hole". As a part of this expedition, we flew a high resolution Fourier transform spectrometer on the DC-8, measuring the column amount of a number of trace gases above the flight altitude.

Infrared spectroscopy is a valuable technique for studying the chemistry of the stratosphere. It is a remote sensing technique, capable of operation on aircraft with ceilings below the region to be observed. Using the sun as a source for absorption spectroscopy allows high resolution and signal-to-noise, permitting detection of species at sub-ppb levels. The inherent spatial averaging of the technique focuses on large scale phenomena rather than small fluctuations. Perhaps its most valuable attribute is the ability to measure a number of species simultaneously, allowing study of the relationships of members of a family of chemical species. The principal disadvantages are the inability to measure some important species, especially free radicals, because of their low concentration, the limited ability to determine the vertical profile of concentration, and the sensitivity of retrieved columns to assumptions of the distribution of temperature and relative concentration.

Our instrument consists of an infrared window for admitting infrared radiation from the sun, a suntracker for directing the radiation into the spectrometer, a Michelson interferometer for separating the wavelengths and measuring the intensity, and a computer for collecting the data and storing it for analysis. The window is a disk of ZnSe 20 cm in diameter and 1.5 cm thick; it allows us to observe the sun over a range of zenith angles of 75 to 93° and azimuths of 80 to 100° relative to the aircraft heading. The suntracker has two axis control, frequency response from d.c. to about 10 Hz, and automatic gain control to correct for varying solar brightness as the sun sets or we encounter thin clouds. It maintains the solar image stable to about an arcmin even in the presence of moderate turbulence or clouds with visible optical depth less than 2.

The spectrometer is based on a commercial modulator. It uses plane mirrors and an air bearing for motion of the moving mirror. The maximum optical path difference is 16 cm, yielding an apodized resolution (FWHM) of 0.06 cm^{-1} . The output beam is focused on a field stop with diameter about 15 arcmin. This reduces the effect of any modulation of the signal by tracking errors. A bandpass filter selects the spectral region to be observed. A dual element "sandwich" detector measures the intensity; the elements are InSb for wavenumbers greater than 1900 cm^{-1} , and HgCdTe for lower

frequencies. The spectral region covered is 700-5000 cm^{-1} in several bands. A single spectrum requires 6 seconds to record. Typically 10 successive spectra are averaged for analysis.

A PDP-11/23+ computer controls the operation of the instrument and records the interferograms, housekeeping data, and the output of the aircraft navigation data system on magnetic tape. It includes a high speed array processor which allows transformation of interferograms to produce spectra allowing analysis and determination of column amounts of several species during the flight. This proved to be useful in determining when the observations were inside the region of reduced ozone in almost real time.

We made observations on two test flights from Ames Research Center, on ferry flights to and from Punta Arenas, and on ten flights over Antarctica. Three other flights, including one from Punta Arenas to Christchurch, N.Z., were made entirely in the dark. Most of the observation flights had one or more periods of typically half hour duration when the heading of the aircraft was selected to permit solar observations. In the course of the experiment, we obtained approximately 6440 spectra. These are distributed among the filters as shown in Table I.

Table I

Filter	Spectral Region	Number of Spectra	Molecules Measured
1	1900-3900 cm^{-1}	470	none
2	700-1850 cm^{-1}	660	$\text{O}_3, \text{CH}_4, \text{HNO}_3$
3	700-1340 cm^{-1}	1800	$\text{O}_3, \text{HNO}_3, \text{N}_2\text{O}, \text{CH}_4, \text{ClONO}_2$
4	2850-3100 cm^{-1}	1170	HCl, CH_4
5	1970-2420 cm^{-1}	540	$\text{CO}, \text{OCS}, \text{O}_3$
6	1500-1650 cm^{-1}	870	$\text{H}_2\text{O}, \text{NO}_2$
7	790-1070 cm^{-1}	30	none
8	4000-4500 cm^{-1}	610	HF
9	1760-1980 cm^{-1}	290	NO

For each molecule and spectral region used, a spectral line or group of lines was selected for analysis, based on strength and freedom from interference. For molecules such as HCl where the suitable lines are few and far apart, we used an equivalent width method of analysis (Coffey *et al.*, 1981), whereas for molecules such as ozone where there are many suitable lines, including spectral regions where the target molecule dominates the atmospheric absorption, the process of nonlinear least squares fitting of a calculated spectrum to the observed spectrum was employed (Niple *et al.*, 1980). The latter process is more laborious and computer intensive, but improves the precision by using more lines, including overlapping lines. Details of the analysis procedure will be published elsewhere. The spectroscopic parameters for the selected lines were taken from the AFGL compilation (Rothman *et al.*, 1987)

Both analysis methods require the calculation of the expected spectrum with a particular amount of the target gas, for comparison with the observed spectrum. The spectra are calculated by the Fourier technique of Mankin (1979). The calculations

require knowledge or assumption of the vertical distribution of the temperature, pressure, and absorber mixing ratio. This information is used at two stages: first, for the calculation of the absorption corresponding to a given amount of absorber along the line of sight, and second, for the conversion of the line of sight amount to a vertical column. While in the past, we have taken the shape of the mixing ratio curves from published vertical profiles (Coffey *et al.*, 1981), in the highly perturbed chemical region of Antarctica, the profiles are expected to be quite different than standard midlatitude profiles. For ozone, there are ozonesonde data from several stations which serve as a guide, but for the trace species, there is little information. Some information can be gained from the spectra if observations are made through the same air mass at different solar elevations. This experiment was, in fact, performed on September 24, when three sun runs were made in the vicinity of 80°S., 111°W. at sun angles around 0.75°, 2.84°, and 6.03°. We have used these data to adjust the mixing ratio profiles, and have used these profiles to reduce other observations within the vortex. The greatest uncertainty from this source occurs near the vortex boundary.

The precision of the results is good, particularly from the flights later in the mission after certain improvements in the operation were made. During the flight of September 21, a series of 40 successive spectra were recorded near 82°S. These were divided into groups of 10, averaged, and analyzed. The standard deviation in the ozone column retrieved from the four groups was less than 1% of the mean. The comparison of our ozone columns with those of TOMS and the JPL interferometer was also good (Margitan, this volume). The absolute accuracy is harder to estimate. The principal errors come from errors in the line parameters, errors in the assumed distribution of temperature and mixing ratio, and approximations made in the calculation of the synthetic spectra. These errors are estimated at 10% for ozone and somewhat greater for the trace gases.

In this paper, we present column results only from the flight of September 21; results from other flights are included in the accompanying paper. Figure 1 shows the deduced columns for ozone, HCl, and NO₂ deduced from the spectra, plotted as a function of latitude. It should be noted that there are many other factors varying as well as the latitude, but latitude seems to be the variable which most clearly provides a passage across the vortex boundary. It can be seen that south of 76°S., the column of ozone, HCl, and NO₂ all decrease markedly. The ratio of HCl to HF, normally about 5:1 in midlatitudes, approaches unity. Clearly the chemistry of chlorine and nitrogen are disturbed in the region of low ozone. While dynamical theories could perhaps explain a reduction of these three gases in the same region, since all are of stratospheric origin, it is difficult to see how any purely dynamical mechanism could produce the observed HCl:HF ratio, since the two gases have similar origins. A close look at other species to be reported as well as the correlation with other measurements, such as ClO (J. Anderson, private comm.) supports the conclusion that the ozone depletion is a result of chemical processes which deplete HCl and NO_x relative to the midlatitude situation.

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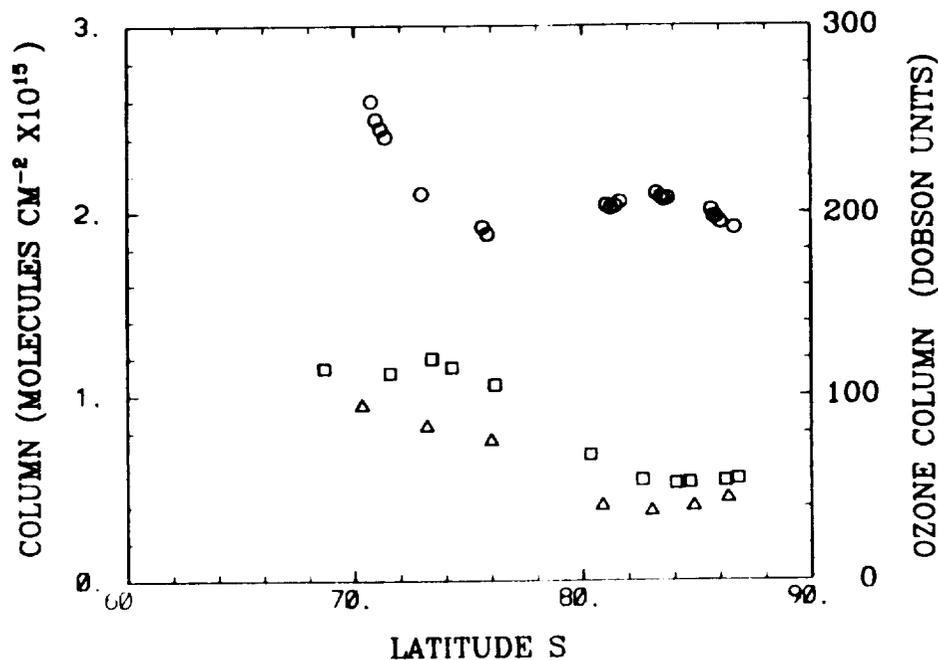


Figure 1. Latitudinal variation of observed columns of ozone, HCl, and NO_2 on September 21, 1987. The ordinate scale on the right refers to ozone, while the scale on the left refers to the other two molecules. \circ : ozone; \square : HCl; \triangle : NO_2 .

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