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MEASUREMENTS OF STRATOSPHERIC ODD NITROGEN AT ARRIVAL HEIGHTS, ANTARCTICA, IN 1991

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ABSTRACT

An FTIR spectrometer was installed at Arrival Heights, Antarctica (78°S, 167°E) in February 1991 to measure the evolution of stratospheric HNO_3 during the year. In particular, it was the intention to make the first observations of HNO_3 trends during autumn, concurrently with ongoing measurements of column NO_2 made with a grating spectrometer.

The time-series of NO_2 in the Antarctic shows a rapid decline in the column amount during autumn, and a slow recovery in spring, as the photochemical conditions move the species to and from higher storage reservoirs. The new nitric acid data show for the first time that during autumn the vertical column increases from approximately 1.9 x 10^{16} molecule cm^{-2} at day 30 to approximately 3.1 x 10^{16} molecule cm^{-2} by day 100. When the sun returns in spring, it is found that the column amount has fallen to about half the value at the end of autumn. Spring amounts are variable, but as found in the data from previous years remain low inside the vortex. The autumn increase is attributed to the heterogeneous conversion of N_2O_5 to gas-phase HNO_3 on background aerosols. Low nitric acid column amounts at the start of spring suggest that the HNO_3 has moved from the gas to the condensed phase on polar stratospheric clouds with the advent of low temperatures during the polar night.

DISCUSSION

The role of heterogeneous chemistry in the stratosphere is one of the most important issues in current atmospheric studies. Of particular interest are those reactions that influence ozone depletion in polar regions, given the ability for heterogeneous chemistry to take place on aerosols in the polar night. Nitrogen compounds have a special significance because of the role they can play in moving chlorine between reactive and less reactive forms. Measurements at the New Zealand Antarctic site of Scott Base (laboratory at Arrival Heights, 78°S, 167°E) have concentrated on remote sensing of NO_2, O_3, and more recently HNO_3. A long term NO_2 and O_3 record has been built up since measurements started in 1982, using differential absorption spectroscopy techniques. A scanning spectrometer records the spectral signature from 430nm to 470nm of scattered sunlight in the zenith sky. Retrievals of NO_2 and O_3 are carried out by least squares fitting the experimental data with laboratory derived absorption cross sections [1]. Fig. 1 shows how NO_2 is removed from the atmosphere in autumn, and restored during spring. In autumn the NO_2 is believed to move into the temporary storage reservoir of N_2O_5[2]:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (1)$$
$$NO_3 + NO_2 \rightarrow N_2O_5 \quad (2)$$

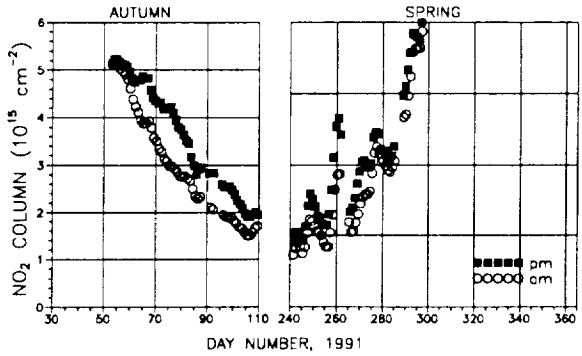

FIG. 1. Nitrogen dioxide vertical column 3-day running averages for 1991, for morning (circles) and evening (squares) when the sun is at a solar zenith angle of 90°.

As spring progresses, the NO_2 recovers through repartitioning of NOy and also through mixing with lower latitude air. The spring column shows large cyclic increases which are caused by the NO_2 depleted polar vortex moving away from the observing site[3]. When the NO_2 trends are compared with model calculations, it is found that agreement is best when a parameterisation of heterogeneous chemistry is included[4]. The implication is that in both autumn and spring the conversion of N_2O_5 to HNO_3 on aerosols is important,via the reaction

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (3)$$

In autumn the reaction is assumed to take place on background sulphate aerosols, and in spring on the surface of polar stratospheric clouds (PSC's). Actual measurements of HNO_3 at Arrival Heights over the course of a year were seen as an important test of this hypothesis, and new equipment was installed in the laboratory there in January, 1991.

Nitric acid measurements are made at the Arrival Heights laboratory using direct sunlight and a Fourier transform spectrometer (FTIR) which has a nominal resolution of 0.06 cm^{-1}. The resulting interferograms are transformed to give an absorption spectrum such as the one given in Fig. 2, which shows strong υ_5 absorption bands of HNO_3 near 870 cm^{-1} in the infrared region of the spectrum.

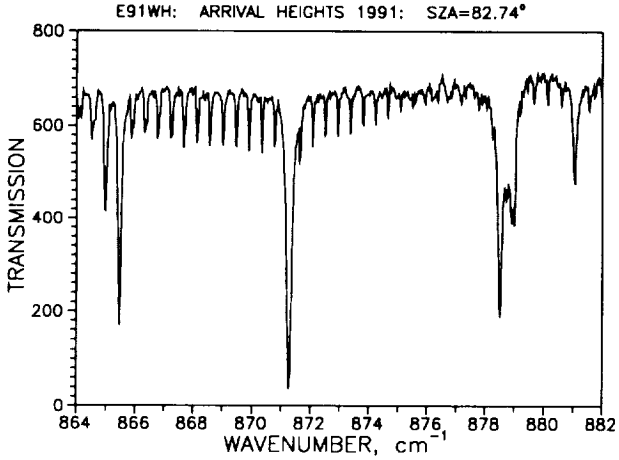

FIG. 2. Infrared spectrum recorded at Arrival Heights, Antarctica, showing strong absorption bands that are due to nitric acid in the stratosphere. The bands measured are those in the 866-871 cm^{-1} region.

The Antarctic spectra are of very good quality, and compared with data from lower latitudes are relatively unaffected in this region of the spectrum by other absorbers such as NH_3 and H_2O. Column amounts of the absorber(s) are generated in a conventional manner by fitting the experimental spectrum to a synthetic spectrum derived from theoretical absorber line strengths, and considering a multi-layered atmosphere. For our autumn retrievals we have assumed the HNO_3 vertical profile for May at 65°S obtained from the LIMS satellite[5], and stratospheric temperatures from the 80°S zonal mean climatology of Barnett and Corney[6]. Temperatures for spring were taken from the sonde flights of Johnson et. al[7]. Sensitivity tests show that day to day temperature changes and movements of the nitric acid layer peak by a few km will only affect the retrieved HNO_3 vertical column by a few percent. In spring, however, it is likely that there are substantial changes to the unperturbed profile[8], and to test the significance of this on the retrievals a profile has been assumed where all the nitric acid is removed between 15 and 20km. This results in an underestimate of the column amount by about 17 percent, so that discrepancies of this order may result when extreme changes to a normal profile take place and are not accounted for. Trends such as that observed in autumn will not be substantially affected.

The resulting nitric acid vertical column amounts at Arrival Heights are shown in Fig.3. There is a steady increase in the column amounts during autumn that is attributed to the heterogeneous conversion of N_2O_5 to HNO_3 on background aerosols. Gas phase models, by contrast, predict no substantial increase over this autumn period (Susan Solomon, private communication). When measurements resume with the return of the sun in spring it can be seen that the HNO_3 column amount has fallen to about half the late autumn value. The decrease is believed to be due to the conversion of gas phase HNO_3 to the solid phase on the surface of polar stratospheric clouds as temperatures fall below the threshold temperature of approximately 196K to form the nitric acid trihydrate:

$$HNO_3(g)+H_2O(g)\rightarrow HNO_3.3H_2O(s) \qquad (4)$$

This is the second step, then, in the "denoxification" of the atmosphere that is a necessary condition for ozone depletion.

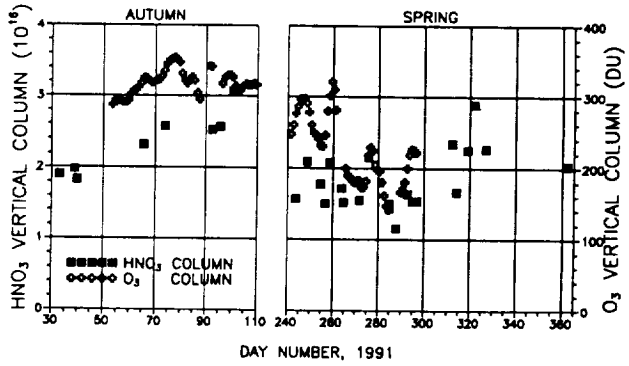

FIG. 3. Nitric acid vertical column amounts (squares) derived from direct sun FTIR observations, and the approximate ozone column obtained from scattered sunlight measurements at twilight (crosses). The steady increase in nitric acid during autumn and the reduction over winter are attributed to the effects of heterogeneous chemistry. Wave-driven variations in the ozone column in spring can be seen to correlate with those in the HNO_3 data.

Fig.3 also shows the ozone vertical column amount as derived from the scattered light measurements. Cyclic variations in the HNO_3 column during spring reflect planetary wave driven excursions of the polar vortex. They are in phase with those seen in the O_3 and NO_2 retrievals, and show that column amounts of all three species are low inside the vortex. The minimum ozone value at day 283 is approximately 140 Dobson units, and at the same time the HNO_3 column reaches its lowest value of 1.2×10^{16}. The values in the vortex are comparable with those measured in spring 1987 [9].

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