Measurement of stratospheric trace gases by millimeter-wave spectroscopy for an annual cycle at the South Pole

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Chemistry and transport processes in the south polar stratosphere have been intensively studied since discovery of the seasonal "ozone hole" appearing over Antarctica (Farman, Gardiner, and Shanklin 1985). Nevertheless, large gaps still exist in our knowledge of the dynamical and chemical behavior of the polar winter vortex. This behavior is responsible for much of the prior processing of air, and the processing makes possible the formation of a springtime ozone hole. The work described here was intended to fill some of these gaps by frequently monitoring the behavior of several trace gases over as much of a full year cycle as possible, from a central position within the annually forming winter vortex region.

Stratospheric "trace gases" are species whose fractional mixing ratio may be a few parts per million relative to "air," as in the case of ozone (O_3), to as little as a few parts per billion or less, as in the case of several of the key species, such as nitrogen dioxide (NO_2) and chlorine monoxide (ClO), which regulate the abundance of O_3. Since no data were available on the behavior of O_3 through the winter darkness above the level reached by balloon sondes [approximately 30 kilometers (km) at most], one goal was to make frequent measurements of O_3 through the winter, combined with frequent measurements of nitrous oxide (N_2O) as an inert tracer of transport, to help differentiate changes in O_3 due to chemistry from changes due to transport. In addition, both O_3 and N_2O serve as independent tracers for downward motion during the polar night. This has been well documented to take place through the observation that by early spring, the distribution profile of N_2O shows the result of several kilometers of downward transport relative to antarctic summer profiles (e.g., Parrish et al. 1988) or to air outside the winter vortex region (e.g., Lowenstein et al. 1989). The period over which downward transport is most active, and the maximum rates involved, have not been well documented, however, despite the importance of this to the problem of correct chemical modeling.

The South Pole trace gas experiment was set up at the Amundsen–Scott Station in late January 1993. C. Trimble wintered over and operated the equipment on an almost daily basis from 5 February 1993 until 10 January 1994. The instrument used for observations was a specially developed, ultra-high-sensitivity, remote-sensing, millimeter-wave spectrometer, which records emission spectra from individual species over a bandwidth of 512 megahertz. Tuning allows emission lines from any of several species to be observed within a frequency range of approximately 268–280 gigahertz. Vertical distribution profiles for the various species are then derived from the spectra by deconvolution of the pressure-broadened line shapes. During the 49 weeks of observations, somewhat over 7,400 individual spectral scans were taken. The species covered (not all for the full duration of observations) were O_3, N_2O, NO_2, nitric acid (HNO_3), and ClO. An upper limit for hydrogen peroxide (H_2O_2) in the polar night was also determined by an unsuccessful attempt to detect it.

Millimeter-wave emission spectra of one or another stratospheric trace gas were typically taken 6 days every week for the full 11½ months of observations. Some results are summarized below.

- *O_3 and N_2O.* Both species were generally observed at 3-day intervals throughout the full 11 months. This constitutes the most complete record ever taken for either of these gases within a polar vortex region. The ozone observations are also the only record showing the behavior of ozone above balloon limits (approximately 30 km) throughout a polar night and show interesting features that are now under analysis.
- *HNO_3.* The results obtained represent the first quantitative scientific study of HNO_3 using ground-based, millimeter-wave remote sensing. We began HNO_3 observations in mid-April, when quite strong emission was observed, indicating some enhancement over summer values had already occurred. HNO_3 continued to show a slight increase until late May. We then observed a period of rapid depletion, lasting about 2 weeks, which coincided with the first appearance of polar stratospheric clouds (PSCs) detected by the University of Rome's South Pole lidar measurements. Loss of gas-phase HNO_3 is explained by rapid condensation onto PSC particles. We believe these are the first data to reveal the scope and rate of this process on a quasi-continuous basis for air confined to a well-defined area. In late June, our spectra revealed the presence of *newly created* HNO_3 in the middle stratosphere, above the range of its normal distribution. The phenomenon of increased mid-stratospheric HNO_3 during high-latitude winter was first noted in data from the LIMS satellite experiment in 1978–1979. Its cause has remained a mystery, however, and the phenomenon was not observed again until after the launching of the Upper Atmosphere Research Satellite in 1992, when it could be discerned in data from the CLAES spectrometer (Roche, Kumer, and Mergenthaler 1993). The phenomenon may be caused by conversion of nitrogen pentoxide on H_2O aerosol particles in the middle stratosphere, according to a new theoretical study by Garcia and Solomon (1994). Our own quantitative observations give a good measure of the rate and duration of HNO_3 production and are a useful test for the validity of this theory.
- *ClO.* Observations of ClO, the intermediate compound formed in the ozone-destroying catalytic chlorine cycle, were centered on the periods of antarctic sunset and sun-

rise. ClO, particularly in the lower stratosphere where it is responsible for rapid, massive destruction of ozone, has a very strong diurnal cycle, with concentration dropping dramatically in a 2–4-hour period around sunset and increasing even more rapidly at sunrise. ClO observations were started during the March sunset period to establish the altitude range of the "normal" upper stratospheric layer (which is a persistent global feature), before the onset of wintertime downward air transport. There was no evidence of a lower stratospheric ClO layer at this time. We continued to track the "normal" ClO layer, after realizing that it remained weakly visible many days after sunset, and detected it again beginning to appear significantly before polar sunrise. It proves, therefore, to be an additional useful tracer of lateral transport from regions receiving sunlight. During the spring sunrise period, we also made continuous observations at McMurdo, as well as South Pole observations of ClO every third or fourth day.

- *NO_2*. The millimeter-wave emission lines from this molecule are numerous but very weak in the normal stratosphere and have never before been observed with millimeter-wave equipment. We accidentally discovered the presence of several NO_2 emission lines which fall within the spectral ranges used for ClO and HNO_3 observations, when observing the latter species. These lines began to appear late in May and lasted into July. Their extreme narrowness reveals an origin no lower than approximately 50 km. Due to the weakness and high altitude of these lines, our observations give a measure of the total column amount only. The increase of mesospheric NO_2 revealed in these and other recent observations is regarded to be a result of poleward and downward transport from lower latitudes and higher altitudes (e.g., Fisher, O'Neill, and Sutton 1993). We believe that the present record may be the most complete set of observations of the time duration and variation of this process yet obtained.
- *H_2O_2*. This species has not been observed before with ground-based millimeter-wave equipment, although an earlier attempt by us resulted in a useful upper limit being set (de Zafra et al. 1985). The mixing ratio is quite small, and the emission intensity will be extremely weak. Since *no* observational data at polar latitudes was available on this important species, whose concentration might increase in the winter vortex night, we made a brief but unsuccessful attempt to find emission. An upper limit was set on mixing ratio similar to that of our earlier midlatitude attempt.

R.L. de Zafra, D.T. Shindell, and C. Trimble all participated in setting up the equipment and debugging it at the Amundsen–Scott Station. C. Trimble remained to maintain the equipment and conduct all observations through the following year.

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Ultraviolet radiation in the southern seas in early spring 1993

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The National Science Foundation research vessel *Nathaniel B. Palmer* carried out a cruise to Antarctica in early spring of 1993. It left Punta Arenas, Chile, close to the tip of South America on 11 August 1993, sailed south for 3 days to the tip of the Antarctic Peninsula, stopping at O'Higgins and Palmer Stations, and from there went southwest and into the Bellingshausen Sea. On 10 September, it reached the most southerly position, 71°S, some distance north of the Thurston Island. From there, it went as far as 110°W before returning to Punta Arenas. The main purpose of the cruise was to investigate the snow- and sea-ice thickness, properties, and structures in this part of the southern oceans (Jeffries 1994). It also allowed us to carry out continuous radiation measurements. We measured the following fluxes: global radiation (Eppley PSP), infrared