Ground Based FTIR Measurements of O_3, HF, HCl, $ClONO_2$, and HNO_3 at Kiruna (Sweden) since Winter 1993/94

T. Blumenstock, F. Hase, H. Fischer, R. Ruhnke, G.P. Stiller

Institute of Meteorology and Climate Research (IMK), Forschungszentrum Karlsruhe and University Karlsruhe, P.O. Box 3640, D-76021 Karlsruhe, Germany, e-mail: thomas.blumenstock@imk.fzk.de

D. Yashcov, A. Meier[1], A. Steen

Swedish Institute of Space Physics (IRF), P.O. Box 812, S-98128 Kiruna, Sweden

Y. Kondo

Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo 153-8904, Japan

Abstract. Zenith column amounts of O_3, HF, HCl, $ClONO_2$, and HNO_3 have been measured at Kiruna within the polar vortex. Chlorine activation has been detected during all winters since 1993/94, except of 1998/99. Low HNO_3 to HF ratios as observed in February 1995 and 1996 indicate denitrification.

Introduction

Zenith column amounts (ZCA) of several trace gases like O_3, HF, HCl, $ClONO_2$, and HNO_3 have been derived from FTIR spectra. This paper will focus on chlorine and nitrogen compounds which are relevant for atmospheric ozone.

In order to reduce dynamic effects the ZCAs of O_3, HCl, $ClONO_2$, and HNO_3 will be related to the ZCA of HF. The corresponding ratios will be discussed for winters 1993/94 (marked as 1994) to 1998/99 (marked as 1999). While stratospheric temperatures below PSC threshold temperature of about 193 K occurred rather seldom in 1994 or never in 1999, this was quite often the case in other winters.

Experimental

Atmospheric absorption spectra using the sun as the source of radiation were recorded by ground based FTIR (Fourier Transform InfraRed) spectrometers at Kiruna (Sweden, 68°N, 20°E) during winter and early spring since winter 1990. While a Bruker 120 M was used from winter 1994 until winter 1996 at Esrange near Kiruna, a Bruker 120 HR is in operation at the IRF since March 1996. The latter one is operated permanently and is part of NDSC (Network for the Detection of Stratospheric Change). An NDSC side by side intercomparison has been performed successfully in March 1998.

Data Analysis

Spectra recorded before 1998 were analyzed with RAT (Retrieval of Atmospheric Trace Gases) [*von Clarmann*, 1994]. Spectra recorded in 1998 were analyzed with PROFFIT (PROFile FIT); it includes the forward model KOPRA (Karlsruher Optimized Precise Radiative-transfer Algorithm) [*Stiller et al.*, 1998] and the retrieval code is based on the Phillipps-Tikhonov and Optimal Estimation approach. Spectra from 1999 have been analyzed with SFIT-1 (C.P. Rinsland, NASA). Results of different codes have been compared within NDSC exercises and are in good agreement. A data analysis with PROFFIT for all these winters is envisaged.

The errors of the ZCA are typically 4% (O_3), 4% (HCl), 10% ($ClONO_2$), 4% (HNO_3), and 3% (HF). Herein errors of auxiliary data like temperature and initial vmr profiles, of solar observation angle, interfering gases and noise are taken into account.

Discussion

Since differences of column abundances of trace gases like O_3, HF, HCl, $ClONO_2$, and HNO_3 measured inside and outside the polar vortex have been discussed already [*Blumenstock et al.*, 1996], this paper will focus on observations made within the polar vortex or at its edge. Therefore, the following figures contain only data of days of observation when the potential vorticity (PV) exceeded 36 PVU on the potential temperature level of 475 K.

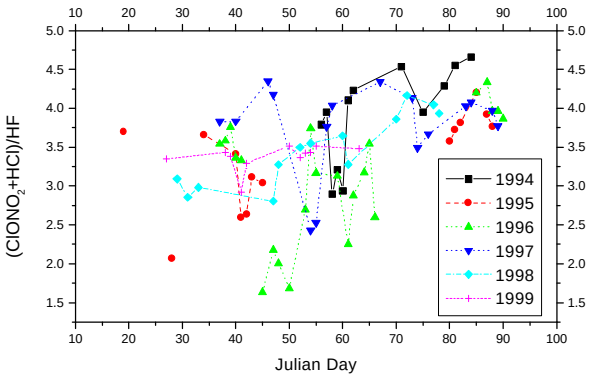

Figure 1. Ratios of the sum of HCl and $ClONO_2$ to HF during winters 1994 to 1999. Only observations made when the site was located inside the polar vortex (PV > 36 PVU on the 475 K level) are included.

The ratios of the sum of the chlorine reservoir gases HCl and $ClONO_2$ to HF are shown in Fig. 1. While this ratio is about 4 in unperturbed conditions, it drops to 3 or less during periods of chlorine activation. During winter 1999

[1] Now at University of Wollongong, Australia

which might be used as reference for a winter with warm stratosphere chlorine activation can be detected at most on 1 day of observation (day 41). All other winters show significant chlorine activation, most pronounced during winter 1996.

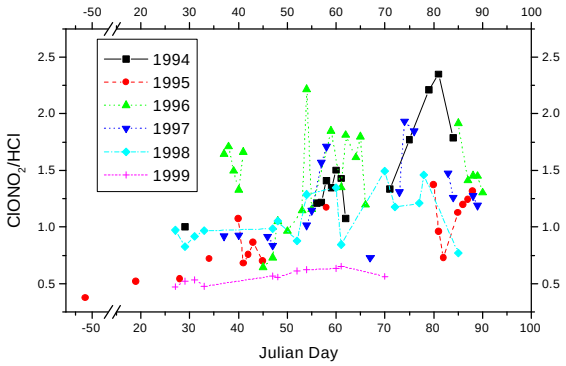

Figure 2. Ratios of $ClONO_2$ to HCl during winters 1994 to 1999. Only observations made when the site was located inside the polar vortex (PV > 36 PVU on the 475 K) level are shown.

Normally the ratio of $ClONO_2$ to HCl is less than 1. Such a ratio is observed during the 'reference warm' winter 1999. While chlorine activation effects both reservoir gases, the partitioning of chlorine reservoir gases is changed strongly during the recovery phase. In the Arctic the $ClONO_2$ to HCl ratio increases strongly at the end of the winter due to the fast reaction of ClO with NO_2 to $ClONO_2$. This is observed in all winters (Fig. 2), except in winter 1999.

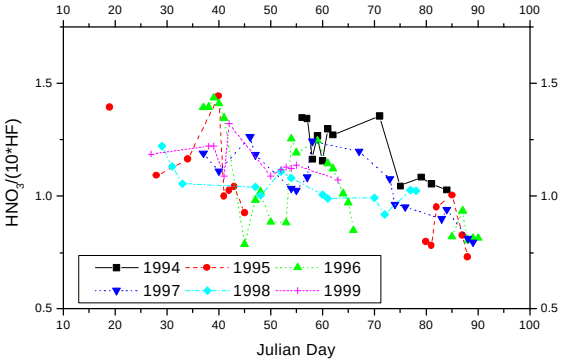

Figure 3. Ratios of HNO_3 to HF during winters 1994 to 1999. Only observations made when the site was located inside the polar vortex (PV > 36 PVU on the 475 K level) are included.

The ratio of HNO_3 to HF is decreasing towards the end of the winter due to photolysis of HNO_3 (Fig. 3). In 1995 and 1996 low HNO_3 to HF ratios have been observed already in February indicating denitrification inside the polar vortex.

The ratio of O_3 to HF is plotted in Fig. 4 to detect the depletion of ozone inside the polar vortex. Low O_3 to HF ratios are observed during winters 1995 and 1996. In winter 1998 an ozone depletion is observed until day 48. During winter 1999 no significant O_3 loss is detected. These observations are consistent with the degree and duration of chlorine activation as described above.

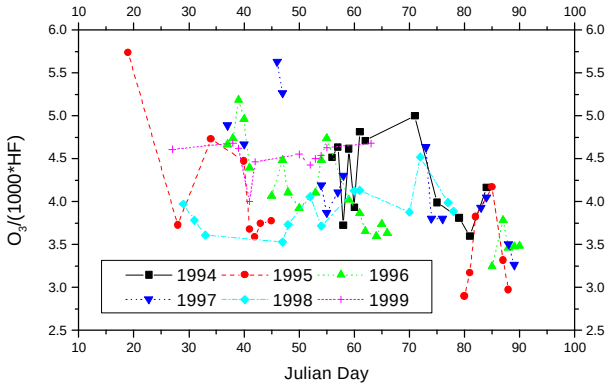

Figure 4. Ratios of O_3 to HF during winters 1994 to 1999. Only observations made when the site was located inside the polar vortex (PV > 36 PVU on the 475 K level) are shown.

Furthermore, the retrieval of profiles of O_3, HNO_3, HCl, HF from FTIR spectra recorded during winter 1997/98 show that useful height information can be obtained up to about 35 km. Comparisons with model calculations made with KASIMA (Karlsruhe SImulation model of the Middle Atmosphere) [*Ruhnke et al.*, 1999] show good agreement.

Conclusion

Numerous observations have been made within the polar vortex at Kiruna during the last winters. They indicate denitrification in February 1995 and 1996. Chlorine activation has been observed during all winters since 1993/94 except 1998/99. This is consistent with low O_3 to HF ratios observed in the winters 1994/95, 1995/96, and February 1998.

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