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Time Series of HNO₃ Column Amounts Measured by Ground-Based FTIR Spectroscopy at Kiruna (Sweden) in Winter 1995/96 and 1996/97

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INTRODUCTION

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 1993/94 until winter 1995/96 at Esrange, a Bruker 120 HR is in operation at the Institute of Space Physics (IRF) since March 1996. The latter one is operated continuously and is part of the ILAS validation experiment (Improved Limb Atmospheric Spectrometer onboard of the Japanese Advanced Earth Observing Satellite). Zenith column amounts (ZCA) of several trace gases like O₃, H₂O, HDO, N₂O, CH₄, HF, HCl, ClONO₂, NO, NO₂, and HNO₃ have been retrieved from these spectra. HNO₃ will be discussed along with other nitrogen compounds like ClONO₂, and NO₂.

EXPERIMENTAL

In winter 1996 infrared absorption spectra were recorded from Feb. 6 until March 30 at Esrange near Kiruna (67.9°N, 21.1°E, 470 m a.s.l.). In winter 1997 observations were made at the IRF, Kiruna (67.8°N, 20.4°E, 420 m a.s.l.). Data covering the period from Jan. 23 until March 30, 1997 are included in this paper. While at Esrange a Bruker 120 M was used as FTIR instrument, a Bruker 120 HR is operated at the IRF. The optical path difference (OPD) is 250 cm for the 120 M and 360 cm for the HR yielding a spectral resolution of 0.003 cm⁻¹ and 0.002 cm⁻¹, respectively. In both instruments 2 detectors (MCT and InSb) and several optical filters are used, covering the spectral range of 700 - 5000 cm⁻¹. Solar absorption spectra were recorded, while coadding up to 15 min.

DATA ANALYSIS AND ERRORS

For the analysis of the spectra synthetic spectra were calculated with SCAIS (Simulation Code for Atmospheric Infrared Spectra) using daily ozone sonde and ECMWF data for O₃, p, T, and H₂O. Spectroscopic data were taken from HITRAN 96 data base. The synthetic spectra were fitted to the measured ones by the non-linear least-squares-fitting algorithm RAT (Retrieval of Atmospheric Trace Gases) [1]. The errors of the ZCA were estimated taking into account several sources of error like spectral noise, uncertainties of the observation angle, of the temperature, errors of the shape of the initial volume mixing ratio profile, and errors due to interfering gases.

	HNO ₃	ClONO ₂	NO ₂	HF
Precision (1σ) [%]	4	8	10	3
Accuracy (1σ) [%]	11	14	11	6

Table 1: Typical errors in % of the zenith column amounts.

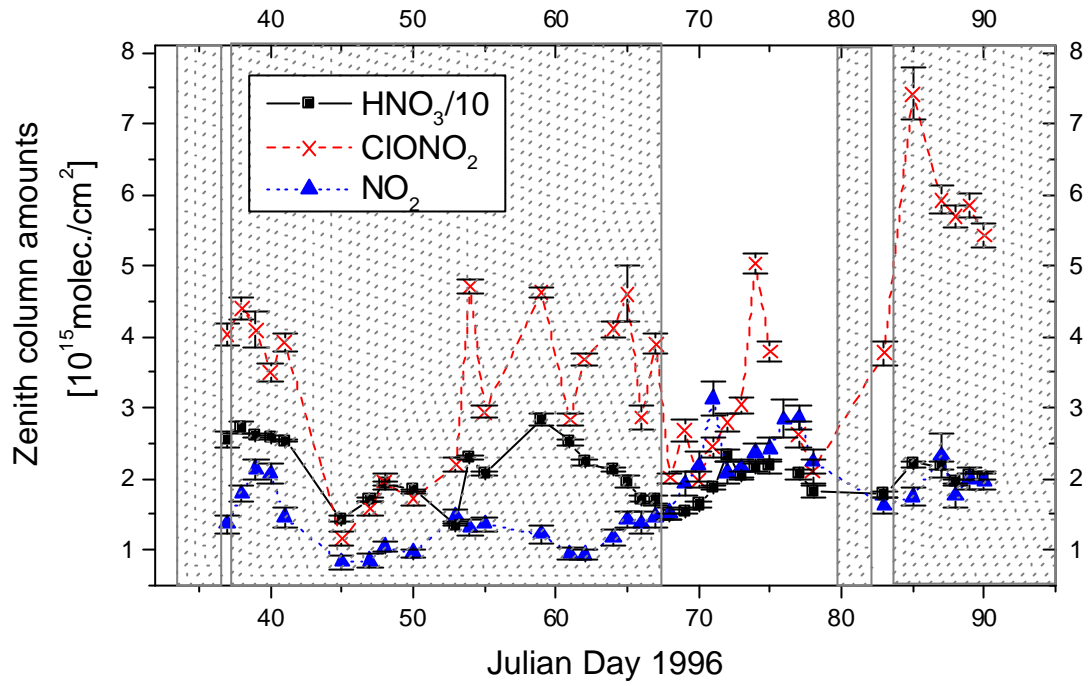


Fig. 1: ZCA of HNO_3 , ClONO_2 and NO_2 in Kiruna during winter 1996. The shaded areas mark observations inside the polar vortex or at its edge ($\text{PV} > 36 \times 10^{-6} \text{ Km}^2 \text{ kg}^{-1} \text{ s}^{-1}$ (pvu) on 475 K level).

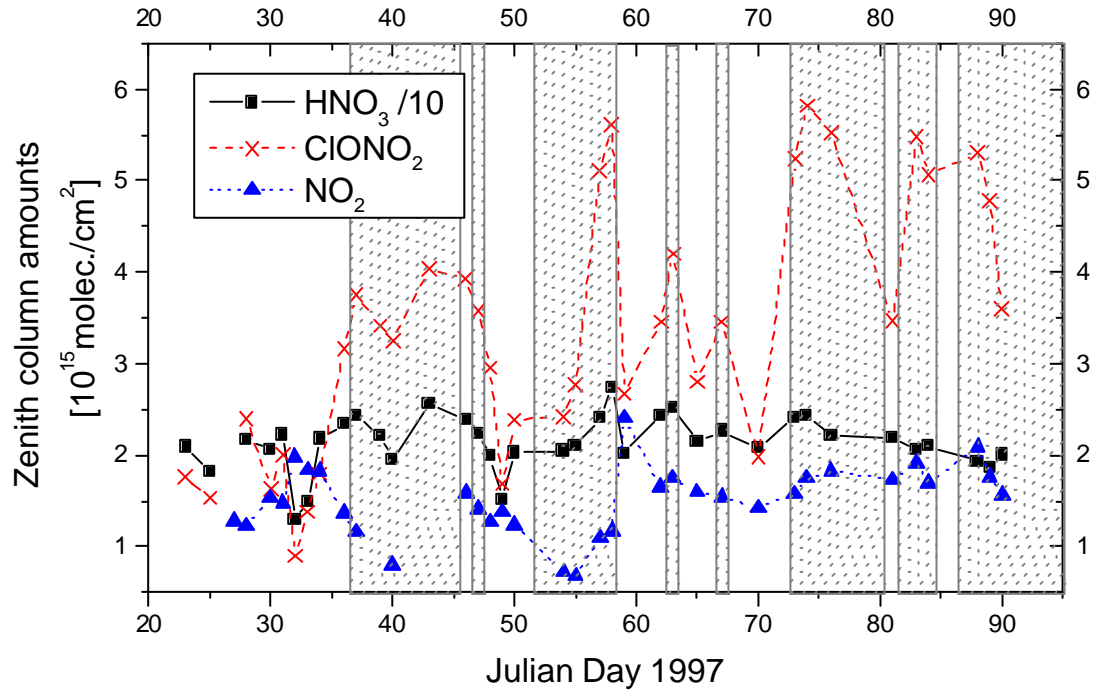


Fig. 2: ZCA of HNO_3 , ClONO_2 and NO_2 in Kiruna during winter 1997. The shaded areas mark observations inside the polar vortex or at its edge ($\text{PV} > 36 \text{ pvu}$ on 475 K level).

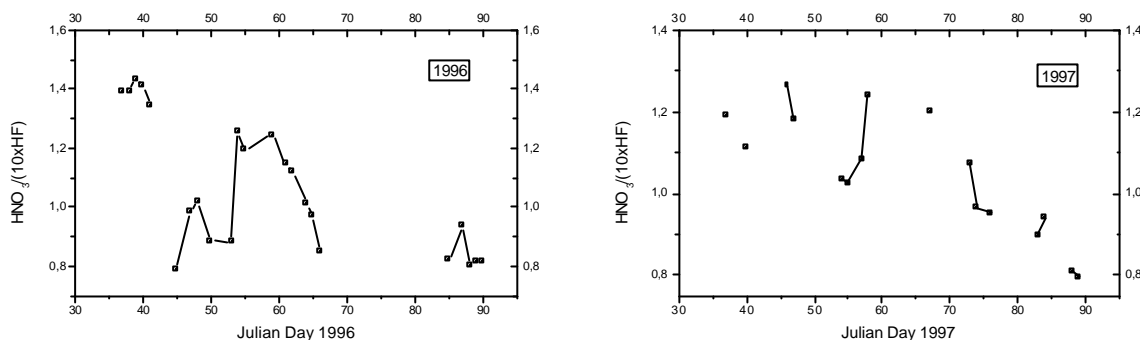


Fig. 3: Ratios of ZCA of HNO_3 to the ZCA of HF during winters 1996 and 1997. Only days of observation with PV > 36 pvu on the 475 K level are shown.

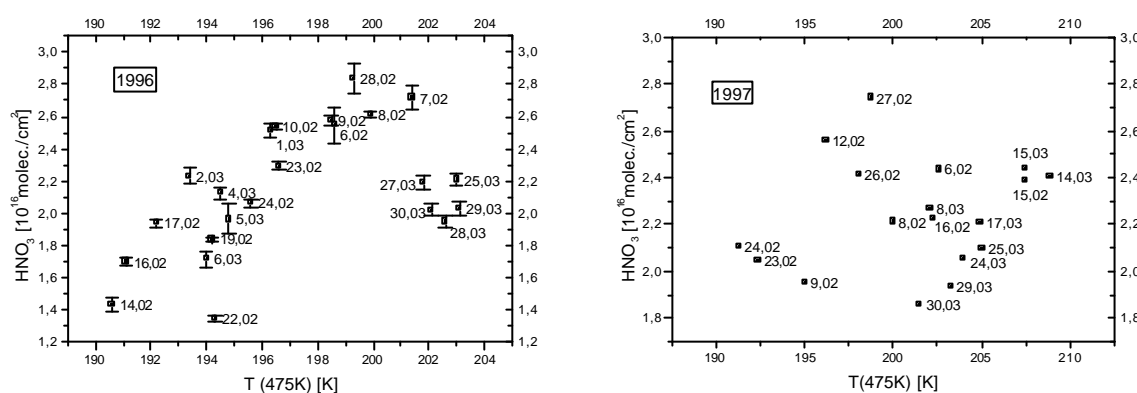


Fig. 4: The ZCA of HNO_3 plotted versus temperature on the 475 K level. Only days of observation with PV > 36 pvu on the 475 K level are shown; the date of observation is marked at each data point.

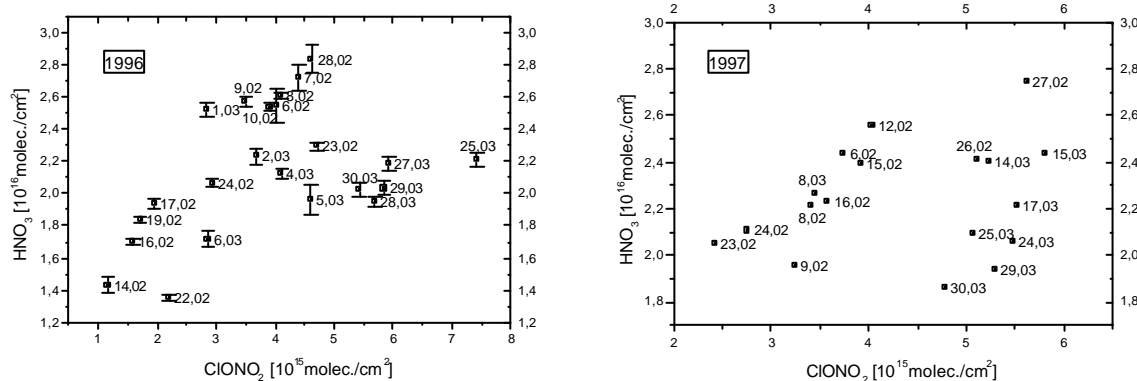


Fig. 5: The ZCA of HNO_3 plotted versus the ZCA of ClONO_2 . Only days of observation with PV > 36 pvu on the 475 K level are shown; the date of observation is marked at each data point.

RESULTS AND DISCUSSION

In Figs. 1 and 2 the time series of ZCA of HNO_3 , ClONO_2 and NO_2 during winters 1996 and 1997 are shown. The ZCA of HNO_3 and ClONO_2 are rather small from day 45 until 53, 1996, indicating

sequestration in PSC (Polar Stratospheric Clouds) (HNO_3) and chlorine activation (ClONO_2). Inside the vortex (marked by shaded areas) ClONO_2 varies strongly, but is mostly large (except for that period) indicating ClONO_2 production. During winter 1997 the ZCA of NO_2 is rather low from day 53 until 58, while ClONO_2 is strongly increasing, indicating production of ClONO_2 from ClO and NO_2 .

In order to reduce dynamic effects the ratios of the ZCA of HNO_3 to that of HF are shown in Fig.3. Days of observation with potential vorticity less than 36 pvu on the 475K level are omitted in Figs. 3-5. In winter 1997 HNO_3/HF is decreasing towards the end of the winter, probably due to photolysis. In winter 1996 HNO_3/HF is rather small also for the days 45 to 53, 1996, suggesting sequestration into PSCs.

Fig. 4 shows the ZCA of HNO_3 versus the temperature on the 475 K level. For winter 1996 the columns of HNO_3 correlate rather well with the stratospheric temperature, except from March 25 until March 30. These data with small columns of HNO_3 correspond to large columns of ClONO_2 (Fig. 1) indicating that NO_2 was released by photolysis of HNO_3 reacting with ClO to ClONO_2 . From February 6 until March 6, 1996 the columns of HNO_3 are controlled by the stratospheric temperature, indicating that heterogeneous processes play a major role. In winter 1997 the stratospheric temperatures above Kiruna were higher as compared to winter 1996, and a temperature dependence of HNO_3 is less obvious.

In Fig. 5 the ZCA of HNO_3 are plotted versus the ZCA of ClONO_2 . For both winters the plots show 2 types of data with different behavior. Up to a column amount of ClONO_2 of about 4×10^{15} molec./cm², HNO_3 correlates well with ClONO_2 . For larger columns of ClONO_2 , HNO_3 is lower as compared to the first case and depends less on ClONO_2 (end of March). These 2 types of behavior may correspond to the 2 different sources of NO_2 necessary to produce ClONO_2 , i. e. in-situ production out of HNO_3 or mixing at the vortex boundary. The first type (increase of HNO_3 with increasing ClONO_2) indicates transport of NO_2 into the vortex at its edge. The other type with reduced columns of HNO_3 represents in-situ production of NO_2 from HNO_3 . The data from March 4 and 5, 1996 as well as those from February 26 to March 15, 1997 cannot be associated with one of these types, they might represent a combination of both processes. A model study performed by Chipperfield et al. [2] concludes that in-situ production of NO_2 is more important than mixing. This is in agreement with our data for columns of ClONO_2 greater than 4×10^{15} molec./cm², but not for smaller column amounts of ClONO_2 .

CONCLUSION

The ZCA of HNO_3 behave differently in winter 1996 and 1997. While in 1997 HNO_3 is mainly controlled by photolysis, a temperature dependence can be found in 1996, indicating that HNO_3 is controlled by heterogeneous processes. In 1996, the ZCA of HNO_3 and ClONO_2 correlate well up to a column of 4×10^{15} molec./cm² of ClONO_2 . During periods with greater ZCA of ClONO_2 a decrease of HNO_3 is observed indicating photolysis of HNO_3 .

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