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# Observation of unusual chlorine activation by ground-based infrared and microwave spectroscopy in the late Arctic winter 2000/01

**T. Blumenstock**[1], **G. Kopp**[1], **F. Hase**[1], **G. Hochschild**[1], **S. Mikuteit**[1], **U. Raffalski**[2], **and R. Ruhnke**[1]

[1]Institute of Meteorology and Climate Research, Forschungszentrum Karlsruhe and Univ. Karlsruhe, Karlsruhe, Germany
[2]Swedish Institute of Space Physics, Kiruna, Sweden

**Abstract.** During the Arctic winter of 2000/01, ground-based FTIR and millimetre-wave measurements revealed significant amounts of ClO over Kiruna after the final warming in February 2001. In fact, column amounts of ClO were still increased in March 2001 when temperatures were about 20 K above the PSC (Polar Stratospheric Clouds) threshold. At these temperatures, chlorine activation due to heterogeneous processes on PSCs is not possible even in the presence of strong lee wave effects. In order to discuss possible reasons of this feature, time series of other chemical species will be presented and discussed, too. Measurements of HF and $COF_2$ indicated that vortex air was still observed in mid-March 2001. Since the time series of $HNO_3$ column amounts do not give any evidence of a denitrification later than 11 February, chlorine activation persisting for several weeks after the presence of PSCs due to denitrification is rather unlikely. The photolysis of $ClONO_2$-rich air which had been formed at the end of February and beginning of March 2001 as well as chlorine activation due to the presence of an unusual aerosol layer are discussed as possible causes of the increased ClO column amounts after the final warming.

## 1 Introduction

To study ozone-depleting processes and estimate the amount of ozone loss in the Arctic, several international campaigns were performed during the last decade (e.g. Pyle et al., 1994; Von der Gathen et al., 1995; European Commission, 1997; Newman et al., 2002). These campaigns demonstrated chlorine activation whenever stratospheric temperatures were below or close to the PSC formation temperature of about 193 K. After the disappearance of PSCs, ClO is deactivated

*Correspondence to:* T. Blumenstock
(thomas.blumenstock@imk.fzk.de)

by the reaction of ClO with $NO_2$ forming $ClONO_2$ (Oelhaf et al., 1994). This was observed by many instruments, for example by ground-based FTIR spectrometers and millimetre-wave radiometers at Kiruna during the last 10 winters (Blumenstock et al., 2003; Kopp et al., 2003). The typical time scale of deactivation is about 10 days. However, column amounts of ClO were still increased in March 2001 when temperatures were about 20 K above the PSC threshold.

The winter of 2000/01 was unusual: The break-up of the vortex took a long time and allowed to observe aged vortex air several weeks after final warming. Another very interesting observation was made by aerosol lidars in the winter 2000/01. From November 2000 until February 2001, an aerosol layer in the stratosphere was detected consistently by several stations (Gerding et al., 2003). Although these observation campaigns have been made since the late eighties, such an aerosol layer has never been observed before. A possible correlation with our observations shall be discussed.

## 2 Instrument and model description

Ground-based atmospheric observations are made at the Swedish Institute of Space Physics (IRF; 67.8° N, 20.4° E, 419 m a.s.l.) in Kiruna. This site is well suited for ground-based Arctic measurements due to its high tropospheric transmission over long periods in winter and spring. Furthermore, this site is situated inside as well as outside the polar vortex in the course of the winter, which allows for the study of ozone loss and mixing processes. The polar night at this site is quite short. Consequently, FTIR measurements of solar absorption are normally interrupted for less than two months. Measurements of chlorine monoxide (ClO) using FTIR as well as microwave FTIR spectroscopy are a well-established technique (De Zafra et al., 1994; Bell et al., 1996).

## 2.1    Fourier transform infrared spectrometer (FTIR)

Within the framework of the NDSC (Network for the Detection of Stratospheric Change), infrared solar absorption spectra have been recorded routinely at Kiruna since March 1996. A Bruker 120 HR spectrometer with a maximum optical path difference of 360 cm is used, yielding a spectral resolution of up to $0.0025\,\mathrm{cm}^{-1}$. Typically, a spectral resolution of $0.005\,\mathrm{cm}^{-1}$ is applied. Spectra are coadded for up to 15 min during noon and 5 min during sunrise and sunset in order to limit the variation of the solar zenith angle to $0.2°$. The signal to noise ratio in the linefree continuum amounts to several hundreds. This results in a signal to noise ratio of several hundreds for the signatures of the constituents discussed in this paper, except for ClO. This species has far weaker signatures which are in the order of the noise level. The error bars shown in the figures represent the error due to noise in the spectrum. An NDSC side by side intercomparison was performed successfully in March 1998 (Meier et al., 2005) and the differences found were less than 3% for all compared species.

The FTIR spectra were analysed with the inversion program PROFFIT (PROFile FIT) (Hase, 2000; Hase et al., 2004) using the forward model KOPRA (Karlsruhe Optimized Precise Radiative transfer Algorithm) (Höpfner et al., 1998; Kuntz et al., 1998; Stiller et al., 1998). The synthetic spectra were calculated using daily pressure and temperature data of the National Centers for Environmental Prediction (NCEP) (Kanamitsu, 1989). Spectroscopic data were taken from the HITRAN 2000 database (Rothman et al., 2003). Using the inversion code PROFFIT, profiles were retrieved from the absorption line shape with the Optimal Estimation Method of Rodgers (Rodgers, 1970, 1976, 1990), the PhillipsTikhonov approach (Phillips, 1962; Tikhonov, 1963), or scaling of a-priori profiles in user-defined altitude intervals. For most of the species, profile retrievals were performed. Analysis of the averaging kernels indicated three to four independent layers from the ground up to 35 km in case of $O_3$, $HNO_3$, HCl, and HF. The instrumental line shape (ILS) needed for an accurate retrieval was derived from regular cell measurements using the LINEFIT software (Hase et al., 1999).

For $ClONO_2$, $NO_2$, $COF_2$, and ClO, scaling of the a-priori profile was performed. The retrieval strategy for ClO was adopted from Hase (2000). In case of ClO, the lower more variable peak around 20 km only was scaled by the fitting procedure, while the upper part of the profile was kept constant. For ClO, 7 microwindows (MW) were fitted simultaneously: 819 261–819 550, 822 000–822 700, 823 550–823 800, 829 150–829 400, 830 400–830 811, 831 800–832 100, and 833 200–833 600 $\mathrm{cm}^{-1}$. The ClO lines and microwindows selected were similar to those used by Bell et al. (1996) and Rinsland et al. (1992). The error bar of the FTIR data shows the error due to spectral noise and is given as 1-$\sigma$ error. While for other species this error is quite small it

is the dominant one in case of ClO. For ClO column amounts this error amounts to about 30%.

## 2.2    Millimetre-wave radiometer (MIRA)

The millimetre-wave observations were performed with the groundbased millimetre-wave radiometer MIRA-2. It was constructed at the Forschungszentrum Karlsruhe and is capable of measuring $O_3$, ClO, $HNO_3$, and $N_2O$ in the frequency range from 268 to 281 GHz. MIRA-2 measures in the emission geometry in northward direction. A Schottky diode mixer converts the signal to an intermediate frequency of 1.5–2.7 GHz. The receiver noise temperature is about 800 K. Spectral analysis is performed by an acousto-optical spectrometer with a spectral resolution of about 1.2 MHz. For balanced calibration an internal adjustable reference load is used. A detailed description of the system is given in Berg et al. (1998). The measured spectra are integrated either until the noise of the resulting spectrum is at least ten times smaller than the intensity of the signature of the desired trace gas or until the noise is significantly smaller than baseline artifacts. Integration times depend on the tropospheric conditions and typically range from 0.5 to 1 h for ozone up to 3 to 4 h for ClO.

The radiative transfer model uses spectroscopic data taken from the HITRAN 96 database (Rothman et al., 1998), except for ClO. For this species, spectroscopic data from the JPL catalogue (Pickett et al., 1998) and the JPL measurement made in 1992 for the pressure broadening coefficient were used. For the temperature dependence of the pressure broadening parameter, the measurements of Oh and Cohen (1994) were applied. The daily profiles of pressure and temperature from the National Centers for Environmental Prediction (NCEP) (Kanamitsu, 1989) were taken for the forward calculations. Retrieval was carried out using a modified Optimal Estimation Method (Rodgers, 1970, 1976, 1990), including the simultaneous retrieval of several constituents within the same inversion process (Kuntz et al., 1999), and the fit of sinusoidal undulations caused by standing waves within the inversion (Kuntz et al., 1997). With these methods, volume mixing ratio (vmr) profiles can be retrieved in the altitude range from about 17 to 55 km. Using the full width at half maximum (FWHM) of the averaging kernels as a criterion, a vertical resolution of the ClO profiles of at best 10 km can be achieved.

The typical uncertainty is about 0.5 ppbv, caused by errors due to thermal noise, standing waves, and systematic errors (Kopp, 2000). In addition, day–night difference spectra were calculated and analysed when available. An error estimate for these profiles shows a systematic error of about 0.08 ppbv and a random error of about 0.02 ppbv and a total error of about 0.1 ppbv. The systematic error includes errors of pointing, calibration, temperature and spectroscopic data. Since some error sources like standing waves nearly cancel out the error is reduced significantly.
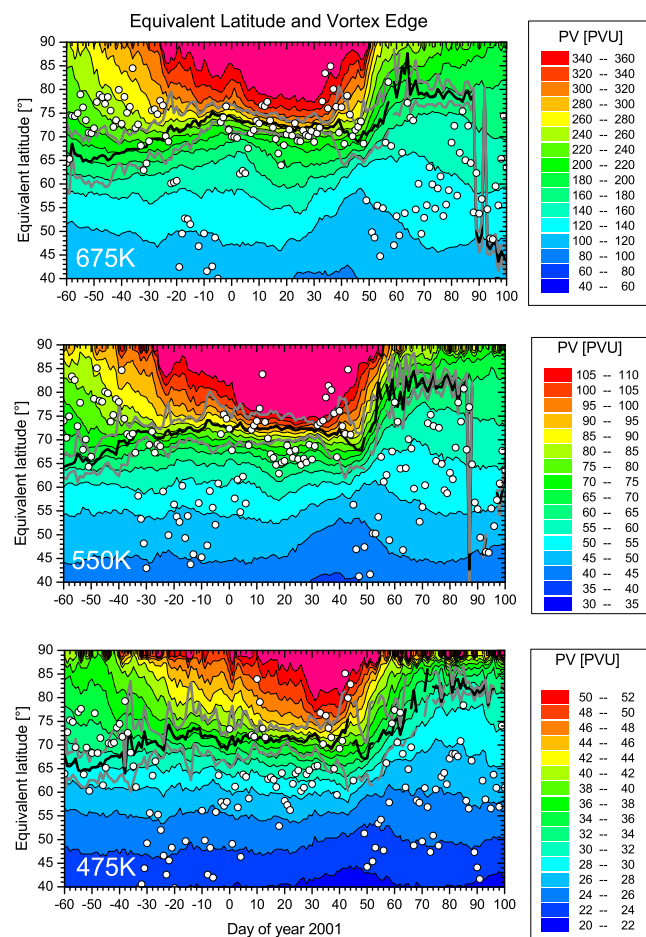
**Fig. 1.** The evolution of the polar vortex in equivalent latitudes during the Arctic winter 2000/01 on the 675, 550, and 475 K isentropic level (based on ECMWF T213 data). The grey lines indicate the inner and outer edge of the vortex, respectively, while the black line describes the mean vortex edge. The colour coding shows the strength of the vortex in PVU ($10^{-6}$ km$^2$/kgs). The open circles depict the PV over Kiruna, showing its position relative to the vortex.



**Fig. 2.** Time series of HF column amounts and of COF$_2$ to HF column ratios as measured by FTIR along with temperature and potential vorticity (ECMWF data) on the 475 K level above Kiruna in the winter of 2000/01.

MIRA data, the model output for 12:00 UT each day during the simulation was used.

## 3 The Arctic vortex in the winter of 2000/01

Figure 1 shows the evolution of the Arctic vortex in the winter of 2000/01 on different isentropic levels using the equivalent latitude method as suggested by Nash et al. (1996). The equivalent latitude is a measure of the area enclosed by a given value of the potential vorticity (PV) of the polar vortex ideally centered on the pole. The colour index of the graphs gives the PV of the idealised vortex at the corresponding equivalent latitude. The grey lines are the inner and outer vortex edge and describe the strongest curvature of the PV plotted versus the equivalent latitude on the respective day. The black line is the mean vortex edge and given by the steepest gradient in the plot of the PV versus equivalent latitude on the respective day. The open circles depict the position of Kiruna relative to the polar vortex, the colour index below the circles corresponds to the PV over Kiruna on the respective day and isentropic level. ECMWF T213 data were used for these calculations.

From early December to mid–February, there was an Arctic vortex with well-defined vortex edges, especially at higher altitudes (Fig. 1). In comparison to other Arctic winters when the mean vortex edge reached equivalent latitudes of about 60°, the vortex of the 2000/01 Arctic winter was smaller and weaker. In February 2001, vortex break-up during the final warming led to a drastic loss of area of the polar vortex. Later on, the criteria for the determination of the vortex edges did not yield any unique solution resulting in oscillations of the vortex boundary or failed completely.

In the winter of 2000/01, the stratospheric conditions were divided into 2 phases: until mid-February, there was

## 2.3 The Karlsruhe simulation model of the middle atmosphere (KASIMA)

The 3D CTM KASIMA (KArlsruhe SImulation model of the Middle Atmosphere) used in this study has a unique model architecture, as it couples a mechanistic model with an off-line model forced by meteorological analyses (Kouker et al., 1999). The distribution of chemical species in this model run was initialised on 11 March , 1999, with 2-D model data of the MPI for Chemistry in Mainz. The meteorology was based on operational ECMWF analyses up to 1 hPa and the prognostic model on top. The horizontal resolution is approximately 5.6×5.6 degrees (T21). In the vertical regime, 63 levels between 10 and 120 km pressure altitude and a 0.75 km spacing from 10 up to 22 km with an exponential increase above were used. For comparison with FTIR and
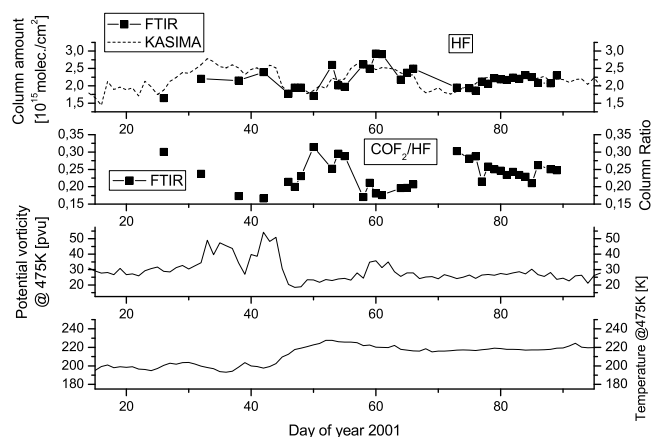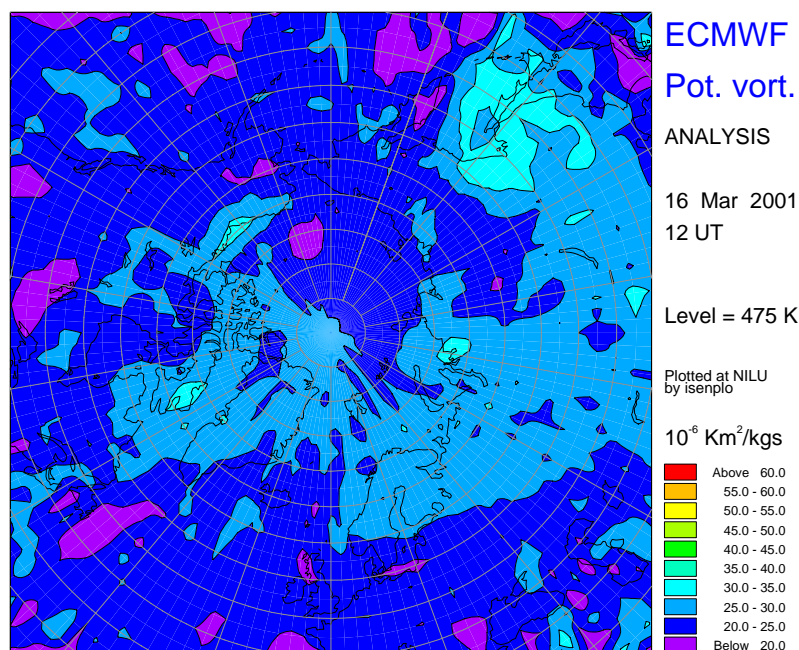
**Fig. 3.** Contour plot of the polar vortex for the 475 K level on 16 March, 2001.

a well-defined polar vortex and the temperatures were occasionally below PSC temperature. After major warming in mid-February, temperatures increased and the vorticity decreased strongly (Fig. 2). During March, the vortex dissolved over a long period; a vorticity contour plot from 16 March 2001 that is typical of almost the entire March 2001 is shown in Fig. 3.

Since HF has a long life time, it is used as a dynamic tracer. In other winters, HF column amounts correlate well with potential vorticity. In this case, column amounts of HF add up to about $1.5 \times 10^{15}$ molec cm$^{-2}$ outside and about $2.5 \times 10^{15}$ molec cm$^{-2}$ inside the vortex. In March 2001, however, the column amounts of HF were still larger than $2 \times 10^{15}$ molec cm$^{-2}$. This indicates that subsided air masses were still observed, although the potential vorticity was lower than 30 PVU ($10^{-6}$ km$^2$/kgs) on the 475 K level (Fig. 2).

Another quite sensitive indicator for vortex air is the ratio of COF$_2$ to HF. Since COF$_2$ is released first by photolysis of CFCs and its life time is about half a year before it is converted to HF, the ratio of these species is an indicator for the age of the air. This means that low ratios indicate "old" air masses or, in other words, old polar vortex air. This was observed around days 40 and 60 and in mid-March (Fig. 2).

## 4  Observation of unusual chlorine activation

The time series of ClO column amounts over Kiruna as measured by FTIR and MIRA in the Arctic winter of 2000/01 and calculated by KASIMA together with possible PSC con-

tact hours and minimum temperatures at 30 hPa are shown in Fig. 4. Before mid-February, increased amounts of ClO were observed periodically due to chlorine activation on PSCs, correlating well with low stratospheric temperatures and possible PSC contact times. Similar observations had been made in earlier winters, for example in the winter of 1999/2000 (e.g. Kopp et al., 2003).

In mid-February, the final warming occurred and stratospheric temperatures strongly increased. Enhanced amounts of ClO, however, were still observed in March 2001, 4 weeks after the final warming. This behaviour differed from previous winters when low stratospheric temperatures and contact to PSCs had been a precondition of enhanced ClO columns (European Commission, 1997). MIRA detected significantly increased ClO amounts on 16 and 17 March. This is the most striking finding of the time series of stratospheric compounds presented in this paper (Fig. 4).

Difference microwave spectra (day–night) were calculated for observation days with sufficiently stable tropospheric conditions (Fig. 5). Signatures of interfering species without diurnal variation are mostly diminished in these difference spectra, whereas signatures of ClO remain and are visible in the difference spectra of 6 February and 17 March. In contrast to this, ClO is hardly visible in the spectrum of 16 February. The profiles retrieved from these difference spectra are presented in Fig. 6 and also show enhanced volume mixing ratios of ClO in the lower stratosphere on 6 February and 17 March. However, the maximum concentration in the profile of 17 March is found in an altitude which is about 3 km lower than that of the spectrum of 6 February. Some ClO is also found in the middle stratosphere which is probably due
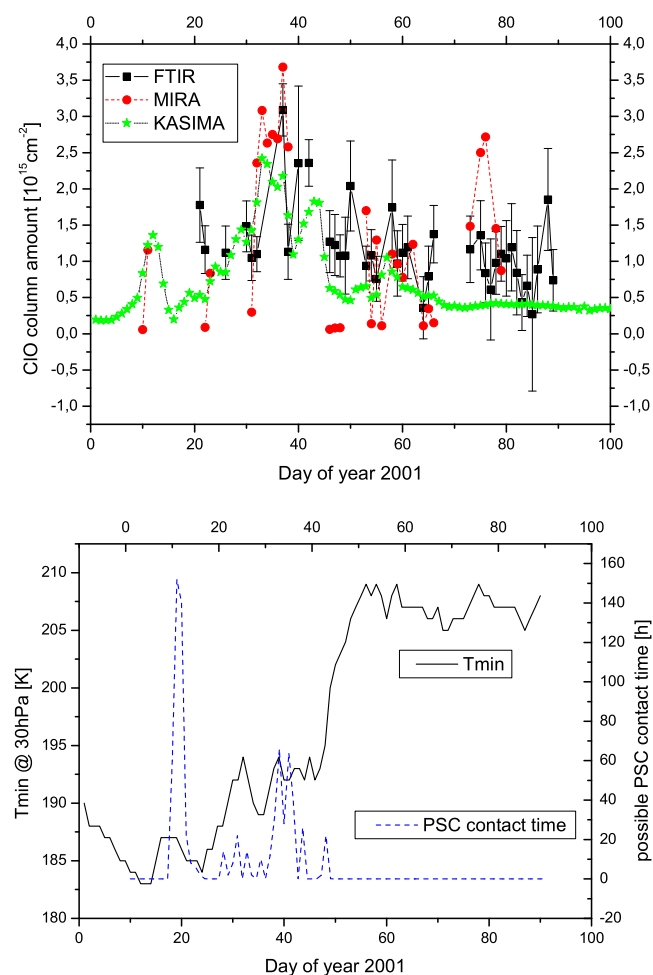
**Fig. 4.** Time series of column amounts of ClO as measured by FTIR and MIRA and calculated by KASIMA together with possible contact hours with PSCs and the minimum stratospheric temperature (ECMWF data).



**Fig. 5.** Difference microwave spectra (day- night) for some days of observation. The spectrum of 6 February has been shifted by 0.2 K for clarity. Difference spectra from 16 February and 17 March, 2001, clearly show a signature of ClO.

to the photolysis of $ClONO_2$. Furthermore, the day–night difference spectrum of 6 February shows an unusual shape which is different from the typical shape in the case of chlorine activation by PSCs. This corresponds to ClO in altitudes above 25 km, higher than the usual PSC occurrence.

In general, the agreement of MIRA and FTIR is quite good (Fig. 4). Time series of ClO from previous winters also showed a good agreement of MIRA and FTIR (Kopp et al., 2003). On 6 February, in particular, both instruments clearly detected increased amounts of ClO. On 16 and 17 March, FTIR measured slightly increased amounts of ClO, but lower amounts as compared to MIRA. However, it must be considered that errors in ClO measurements by FTIR are quite large and that the instruments are looking in opposite azimuthal directions. This may cause some difference, especially if there are some inhomogeneities in the vortex. Unfortunately, due to the lack of night time measurements, day-night differences of FTIR spectra cannot be calculated.
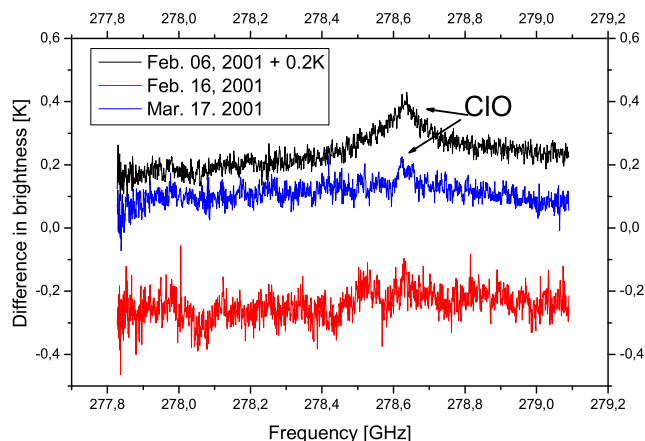
The mean column amount and standard deviation of the data from 14 March to 20 March is $(1.81+/-0.78)\times10^{15}$ molec $cm^{-2}$ for MIRA results, $(1.01+/-0.26)\times10^{15}$ molec $cm^{-2}$ for FTIR, and $(0.40+/-0.02)\times10^{15}$ molec $cm^{-2}$ for KASIMA, respectively. From 14 to 20 March ClO column amounts obtained from MIRA are about a factor of 5 increased as compared to model data. During this period MIRA results are about a factor of 10 larger as compared to periods with no chlorine activation (Fig. 4).

To our knowledge, increased ClO levels in the late Arctic winter 2000/01 were not observed and reported by other instruments. This might be due to the absence of extended field campaigns during this winter. Moreover, most balloon and aircraft missions were conducted in January during the cold period of this winter. In mid-March 2001, no enhanced levels of OClO were observed by GOME (Wilms-Grabe et al., 2003).

Very few observations of chlorine activation outside the vortex are reported in literature: OClO formation on stratospheric sulphate aerosols, whose number density was increased due to the eruption of Pinatubo (Solomon et al., 1993; Perner et al., 1994). Enhanced levels of OClO and BrO outside the vortex were observed by Erle et al. (1998) in 1994 when sulphate aerosol loading was close to background levels. They suggested a heterogeneous activation of $BrONO_2$ on sulphuric acid aerosols at temperatures of about 200 to 210 K. Enhanced ClO mixing ratios were detected by Raffalski et al. (1998) in April 1997.

While KASIMA agrees quite well with the observations prior to the final warming, KASIMA does not reproduce increased amounts of ClO in March. Other models like SLIM-CAT or REPROBUS do not show enhanced amounts of ClO in March either (Harris, 2001). This demonstrates that cur-
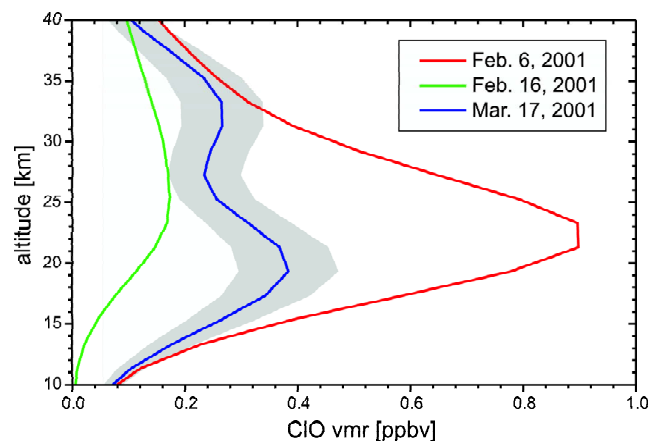
**Fig. 6.** Profiles retrieved from difference microwave spectra (day-night) for some days of observation. Shaded area show random and systematic error.

rent knowledge cannot describe the chlorine activation observed by the two independent techniques.

Since stratospheric temperatures were about 20 K above the PSC threshold, chlorine activation on PSCs was not possible even in the presence of strong lee wave effects. Therefore, the following explanations were considered:

1. Long-lasting activation due to denitrification.

2. Photolysis of ClONO$_2$ in deactivated air masses within the dissolving vortex.

3. Chlorine activation on non-PSC aerosols.

### 4.1  Long-lasting chlorine activation due to denitrification?

For the chlorine activation to persist over several weeks after the presence of PSCs, denitrification is needed. In order to investigate denitrification processes in the winter 2000/01, HNO$_3$ and NO$_2$ are shown in Fig. 7. The time series of HNO$_3$ columns as well as the ratio to HF do not reveal any significant denitrification in March 2001. When comparing the HNO$_3$ to HF ratio with that of previous winters and considering the decrease towards the end of the winter by photolysis of HNO$_3$, it may well be assumed that there might have been some dentrification on day 42 or in January only.

Due to the photolysis of HNO$_3$, NO$_2$ increased towards the end of the winter. This had been observed in many previous winters. Therefore, the NO$_2$ in the stratosphere was expected to be sufficient to recombine ClO to ClONO$_2$. This was also calculated with KASIMA. Furthermore, the increase of NO$_2$ in March 2001 supports the statement that denitrification did not occur and affect the stratosphere at that time. So, chlorine activation lasting since mid-February is quite unlikely to be the reason of enhanced levels of ClO in March 2001.
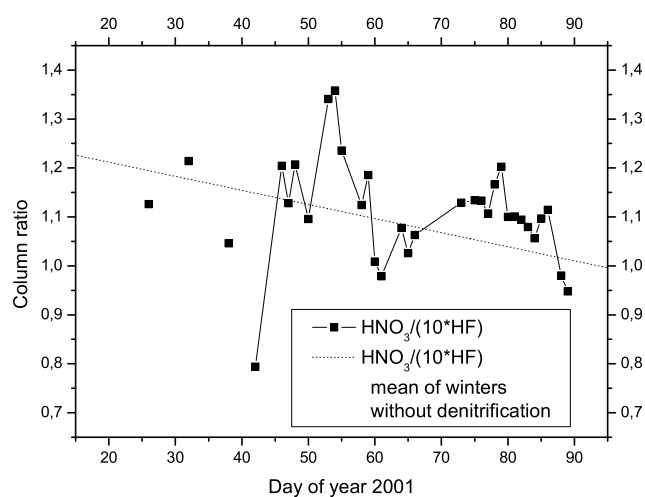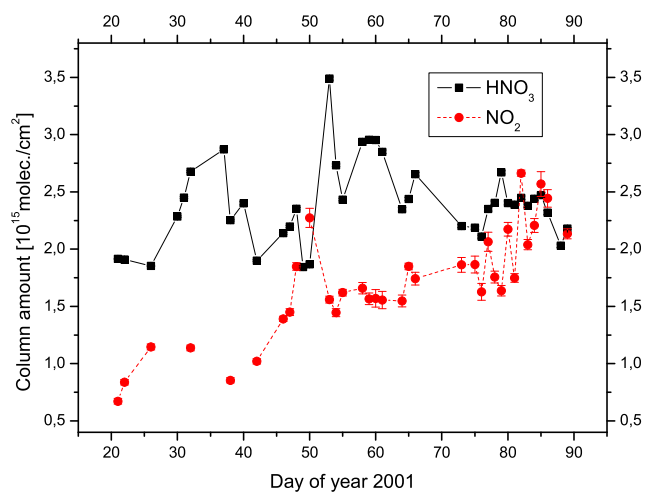


**Fig. 7.** Time series of column abundances of HNO$_3$ and NO$_2$ and of column ratios of HNO$_3$ to HF as measured by FTIR in the winter of 2000/01.

### 4.2  Photolysis of chlorine nitrate (ClONO$_2$)

Another explanation considered was the photolysis of ClONO$_2$. The time series of ClONO$_2$ had a maximum on 1 and 2 March, 2001 (Fig. 8). An increase of ClONO$_2$ in the late polar vortex, in particular in the vortex edge region, had been observed in most of the previous winters (European Commission, 1997). If ClONO$_2$ was the source of enhanced levels of ClO in mid-March, the amount of ClONO$_2$ should decrease on a slower time scale than observed. And in this case it should be a feature of the dissolving vortex and be observable in other late winters, too. KASIMA model runs also suggest that the amount of ClONO$_2$ is reduced quickly and enhanced levels of ClONO$_2$ are not calculated after the final warming. While Fig. 8 shows KASIMA results for Kiruna only, enhanced levels of ClONO$_2$ are not calculated anywhere else in March 2001. Based on the current knowledge,
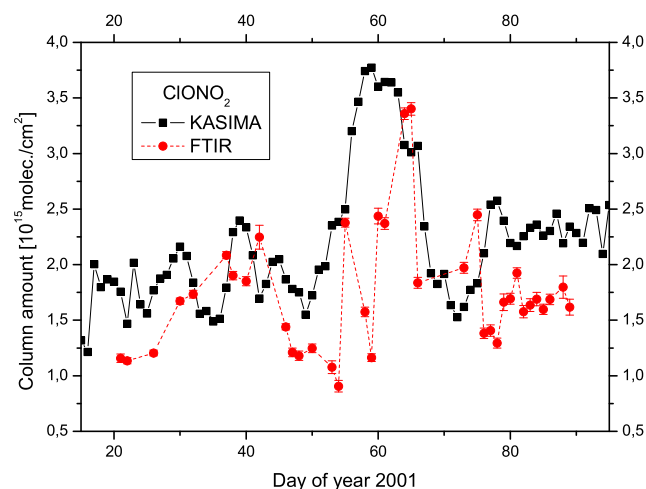
**Fig. 8.** Time series of column abundances of ClONO$_2$ as measured by FTIR and calculated by KASIMA.

heterogeneous processes and, hence, particles are necessary to activate chlorine.

### 4.3 Chlorine activation on non-PSC aerosols

Gerding et al. (2003) observed an unusual aerosol layer in the middle stratosphere at four different Arctic lidar stations in winter 2000/01. These stations are Ny-Ålesund (79° N,12° E), Søndre Strømfjord (67° N, 51° W), Andenes (69° N, 16° E), and Kiruna (68° N, 20° E). The layer had a thickness of about 3 km and descended from 38 km on 16 November 2000, to 26 km on 12 February 2001. Gerding et al. (2003) reported a sedimentation rate of 155 m/d. If sedimentation would have continued until March, an altitude of about 22 km would have resulted. As shown in Fig. 6, the increase of ClO in March occurred at altitudes between 19.5 km and 22.5 km. In February part of the chlorine activation might be due to PSCs which form at altitudes well below the unusual aerosol layer during that time. But as discussed above significant values of ClO were found above the typical height of PSCs which is consistent with the altitude of the aerosol layer in February. The lower altitude of the ClO maximum in the March measurement is also consistent to a further sedimentation of the aerosol layer.

The lidar measurements revealed that the particle size was between 30 and 50 nm and that the particles were solid. The authors suggested that the particles consisted of soot, Al$_2$O$_3$, SiO$_2$, or iron particles. Such particles might have been injected by rocket exhaust or meteoric dust. The total mass of the layer was roughly estimated to be 200 to 2000 kg. Various investigations were published about heterogeneous chemical reactions on rocket exhaust particles (e.g. Jones et al., 1995; Jackman et al., 1998). A more recent study shows that meteoritic dust particles entering the Earth's atmosphere might be larger than expected (Klekociuk et al., 2005). Thus, one

possible explanation of the enhanced ClO values measured in March might be chlorine activation on the aerosols of the unusual aerosol layer observed by the lidar instruments.

After mid-December, the entire vortex area was filled with the aerosol, but no sign of the aerosol layer could be detected outside the vortex. This layer was observed until 12 February 2001. No observations of this layer were made after the vortex break-up. However, it is reasonable that the particles were still in the stratosphere, but thinned out by mixing processes. In fact, the FTIR measurements of HF and COF$_2$ indicate that residuals of vortex air masses were over Kiruna on the respective days and it is plausible to assume that residuals of the aerosol layer were over Kiruna on these days.

## 5 Conclusions

Enhanced levels of ClO were observed above Kiruna in March 2001. Since stratospheric temperatures were about 20 K above the PSC threshold, chlorine activation due to heterogeneous processes on PSCs was impossible even in the presence of strong lee wave effects. As no signs of denitrification were seen later than 11 February, chlorine activation persisting over several weeks after the presence of PSCs due to denitrification was rather unlikely. Another source of ClO discussed in this paper is the photolysis of ClONO$_2$-rich air which had formed at the end of February and beginning of March 2001. However, such processes had not been observed in other winters.

Another possibility is chlorine activation on the surface of particles of an unusual aerosol layer consisting of rocket exhaust or meteoric dust, which was observed inside the Arctic vortex by several lidars between November 2000 and February 2001. Later on, no aerosol lidar observations were made at Kiruna. Therefore, a clear correlation cannot be proven. However, such an aerosol layer had not been observed in previous winters, although lidar observations have been made since the late eighties. This means that two unusual observations coincided in winter 2000/01, which both were unique in their corresponding 10-years time series.

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