

Column measurements of stratospheric trace species over Åre, Sweden in the winter of 1991-1992

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Abstract. Total vertical column amounts of stratospheric HCl, HF, ClONO₂ and HNO₃ are reported from high resolution infrared solar absorption spectra taken during the European Arctic Stratospheric Ozone Experiment in the winter of 1991-1992. These ground based measurements were made near Åre in North Sweden (63.4°N, 13.1°E) at an altitude of 800 m using a Fourier transform spectrometer and tunable diode laser heterodyne spectrometer. On 9th January 1992 the HCl vertical column dropped to 1.2×10^{15} molecules cm⁻² from a November average of 3.6×10^{15} molecules cm⁻². The HCl drop occurred at a time when Åre was below the polar vortex and the lower stratospheric ClO column above Åre was elevated to $\sim 2 \times 10^{15}$ molecules cm⁻² as measured by the Microwave Limb Sounder experiment on the Upper Atmosphere Research Satellite. These measurements indicate conversion of lower stratospheric chlorine from reservoir to chemically active forms.

Introduction

Infrared measurements have proved important in determining the composition of the stratosphere since many key trace species have strong absorption features in this spectral region. In previous Arctic and Antarctic campaigns spatial and temporal trends of important stratospheric gases have been derived from aircraft measurements [Mankin *et al.*, 1990] [Toon *et al.*, 1989] as well as groundbased measurements [Adrian *et al.*, 1992]. These data have provided quantitative information on the extent of stratospheric chemical processes such as chlorine activation, denitrification and denoxification.

The European Arctic Stratospheric Ozone Experiment (EASOE) was aimed at investigating the causes and extent of ozone loss in the northern hemisphere in the winter of 1991-1992. As part of the EASOE campaign the National Physical Laboratory (NPL) deployed two groundbased high resolution infrared spectrometers to study the time evolution of a number of trace species. In this paper we report the total vertical column amounts of HCl, HF, HNO₃, and ClONO₂ measured over Åre during the period November 1991-March 1992.

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Experimental Details and Data Analysis

Two transportable remote sensing instruments were located near Åre at an altitude of 800 m: a Bruker IFS 120M Fourier transform spectrometer (FTS) and a tunable diode laser heterodyne spectrometer (TDLHS) developed at NPL. Both instruments measure the infrared spectrum of solar radiation transmitted through the atmosphere. The FTS was configured with a KBr beamsplitter and an InSb detector giving coverage from 2500 cm⁻¹-4100 cm⁻¹ at a maximum unapodised resolution of 0.002cm⁻¹ (defined as 1/2L, where L is the maximum optical path difference). HCl column amounts were derived from the R(1) line at 2925.9 cm⁻¹ (Figure 1) and HF columns from the R(1) and R(2) transitions at 4001.0 cm⁻¹ and 4039.0 cm⁻¹ respectively. A single scan took approximately 1 minute to record. The TDLHS was capable of a spectral resolution of 0.0007 cm⁻¹. The TDLHS measured ClONO₂ from the Q-branch of the ν₄ band at 780.2 cm⁻¹ (Figure 2) and HNO₃ from one of the P-branch manifolds of the ν₅ band near 870 cm⁻¹. The column amounts were derived from measured spectra using a computer program originally developed at the University of Denver [R. D. Blatherwick, private communication] and extended by the authors. The current version runs on a PC computer suited to use in the field. The program consists of two major components; the ray tracing calculation, and the spectral line simulation.

In the ray tracing calculation the optical path through the atmosphere is calculated taking into account refraction and at-

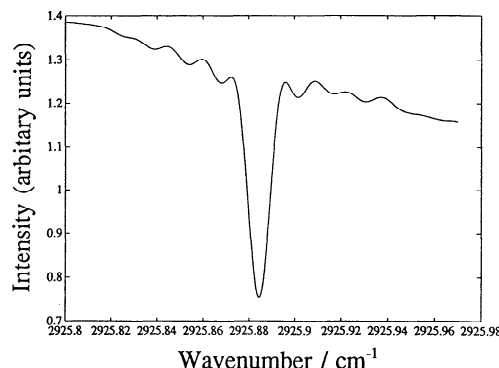


Fig. 1. Atmospheric spectrum showing HCl R(1) line. Recorded on 9th January 1992 at a solar zenith angle of 86.2°, spectral resolution is 0.0055 cm⁻¹ unapodised.

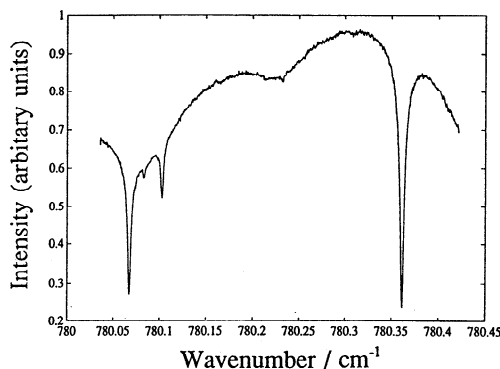


Fig. 2. Atmospheric spectrum in the region spanning the ν_4 Q-branch of ClONO₂ at 780.22 cm⁻¹. Spectral resolution is ~ 0.001 cm⁻¹. Recorded on 24th January 1992. Solar zenith angle is 85.6°.

atmospheric curvature in order that the measured slant columns can be converted into vertical columns. In the model the atmosphere is divided into eight layers with layer boundaries set by the user. Density weighted mean pressure and temperature values are calculated for each of the layers (derived from local radiosonde measurements, US standard atmosphere latitudinal monthly means were used above 30mb). Initial trial volume mixing ratio (VMR) profiles, taken from WMO [WMO, 1985] for HNO₃, and Smith [Smith, 1982] for HF and HCl, are scaled in a least squares fit to calculate slant and total columns. ClONO₂ columns were derived from residual spectra, generated by subtracting interfering absorptions due to O₃ and CO₂ in the 780.0-780.5 cm⁻¹ region, using the absorption coefficients of Ballard [Ballard et al., 1988].

The slant columns and effective pressures and temperatures in each of the eight layers are used as input to the line simulation. Voigt profiles are generated using a method suggested by Drayson [Drayson, 1976] with parameters from the HITRAN data base [Rothman et al., 1987] except for the HNO₃ parameters in the 860-880 cm⁻¹ spectral region [A. Goldman, private communication]. The experimental transmission spectra are converted into absorbances (optical depth) by generating a local background using a spline fit. Two approaches were adopted in deriving total columns. In the first, the eight layer contributions to the lineshape were allowed to vary independently in the least squares fit to the data. For the best spectra taken only five of the eight independent lineshapes were required to achieve the best fit to the data. This may indicate a fundamental limit to the amount of altitude information recoverable from high resolution FTS measurements. In the second the eight layer contributions were scaled by a single factor in the least squares fit. In this later approach the shape of the initial guess VMR profile is preserved. Typically 3-4 spectra were analysed for each day. A number of fits were obtained for each spectrum by changing the local continuum, atmospheric layering in the model and the assumed instrument profile. The column amounts given are the mean values derived from the range of fits to the spectra (~ 20 per spectrum). The quoted uncertainties are the standard deviations from the mean. There was found to be no significant systematic difference between columns obtained using the constrained VMR profile and unconstrained VMR profile methods outlined above. The quoted 1σ uncertainties are dominated by scatter in the derived columns as a result of changing a number of factors in

the fitting procedure, most significantly: atmospheric layering; choice of local continuum; zero transmission level and the nature of the instrument function. In addition to the quoted uncertainty there remains an uncertainty associated with the assumed tropospheric contribution which may be as much as $\pm 10\%$. In our fitting procedure the tropospheric contribution is determined by the choice of the local background.

Results and Discussion

Table 1 gives a summary of the results obtained during the EASOE campaign for all the target reservoir species detected. Figure 3 shows the time series of total column amounts of HCl and HF obtained from 10th November 1991 to 24th March 1992. It can be clearly seen that the HCl column declines from a value of 3.9×10^{15} molecules cm⁻² on 17th November to 1.2×10^{15} molecules cm⁻² on 9th January 1992 before showing a partial recovery. This is consistent with previous studies where very low values of HCl have been measured within the polar vortex of the Arctic stratosphere during the winter of 1989 [Toon et al., 1992] [Mankin et al., 1990]. The low HCl column for 9th January represents a mean value derived from a number of analyses of three spectra taken at zenith angles of 85.8°, 86.2° and 87.0°. The outlying values from all analyses of these spectra were 0.85 and 1.6×10^{15} molecules cm⁻². Effects such as noise, line asymmetry and irregular modulation in high resolution infrared spectra make it difficult to distinguish between stratospheric and tropospheric contributions to the total column. However, the earlier November spectra indicate the tropospheric contribution lies in the range 15-25% (approximately $0.5-0.9 \times 10^{15}$ molecules cm⁻²). Assuming this tropospheric contribution is unaffected by chemical process-

TABLE 1. Column amounts over Åre, Sweden during winter 1991-1992.

Day	HCl	HF	ClONO ₂	HNO ₃	position rel. to vortex [†]
10/11/91	3.27(7)	-	-	-	out
17/11/91	3.95(6)	1.52(4)	-	-	edge
18/11/91	3.95(9)	1.56(5)	-	-	in
19/11/91	3.18(9)	1.33(4)	-	-	edge
9/12/91	2.68(19)	0.76(2)	-	-	out
9/1/92	1.20(20)	0.94(5)	-	-	in
22/1/92	2.57(9)	0.84(2)	-	-	out
24/1/92	3.23(25)	0.63(2)	1.15(35)	-	out
25/1/92	-	-	0.95(29)	-	out
1/2/92	3.10(18)	-	-	-	out
9/2/92	2.57(5)	1.07(3)	-	-	out
11/2/92	-	-	-	2.1(3)	out
14/2/92	-	-	-	2.2(3)	out
9/3/92	-	-	-	1.9(3)	out
11/3/92	3.65(12)	1.20(5)	-	-	out
17/3/92	2.89(16)	0.91(7)	-	-	out
20/3/92	3.33(11)	1.10(2)	-	-	out
24/3/92	3.12(17)	1.20(3)	-	2.6(3)	out

note: all vertical columns are in units of 10^{15} molecules cm⁻². [†] in is defined here as potential vorticities at the 475K potential temperature level over Åre $> 42 \times 10^{-6}$ Km²/kgs, out as $< 36 \times 10^{-6}$ Km²/kgs and edge as between these two values. Potential vorticity values were taken from ECMWF analyses.

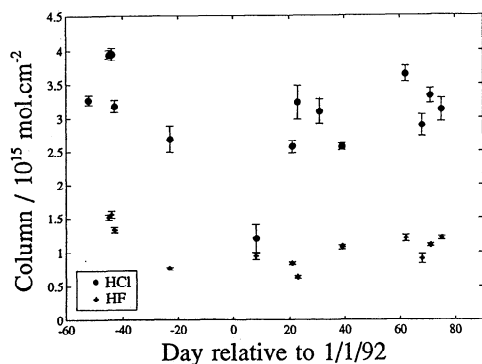


Fig. 3. HCl and HF total column time series during the EASOE campaign.

ing, the HCl column for 9th January suggests a total stratospheric column decrease of at least 65% from its November value. It is conceivable that such large changes in the HCl column could be brought about by an upwards displacement of the stratospheric HCl profile. This could be caused by tropospheric disturbances which elevate the tropopause. In order for this mechanism to explain the observed change in the HCl column around the 9th January it would be necessary for the HCl profile to be displaced upwards by ~ 7 km. It is clear from sonde data from three stations in central Scandinavia (67.3°N , 14.4°E ; 60.2°N , 11.1°E and 62.5°N , 17.5°E) that no such displacement took place on 9th January.

The HF columns measured over the observation period were consistent (within estimated uncertainties) with previous measurements at northern latitude sites, [Mankin et al., 1990] [Adrian et al., 1992]. HF is unreactive once it is formed in the stratosphere due to its extremely strong bond energy and its eventual fate is rain-out [Thrush, 1988]. However, there is also the suggestion that HF may be produced by the heterogeneous destruction of COF_2 and removed by interaction with ice particles [Wofsy et al., 1990] in polar regions but these contributions are as yet not well understood. Recent laboratory studies have shown that in stratospheric conditions the sticking coeffi-



Fig. 4. ECMWF analysis of potential vorticity on the 475K potential temperature surface for 9th January 1992. The hatched area marks the edge of the vortex, defined here as $36\text{--}42 \times 10^{-6} \text{ Km}^2/\text{kgs}$. Latitude circles in 10° increments from the pole. The location of Åre is shown.

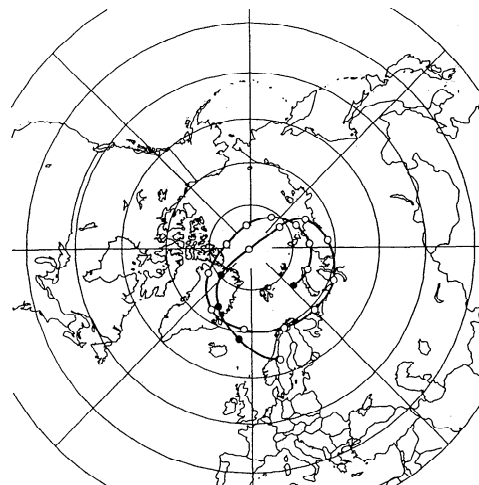


Fig. 5. ECMWF trajectory plot on 475K surface showing the 10 day history of air over Åre on 9th January 1992. Full circles indicate temperatures below Type-I PSC threshold temperature.

icients are too low for significant processing of COF_2 on either sulphuric acid aerosols or on particles of ice or nitric acid trihydrate [Turco and Hamill, 1992]. It is therefore reasonable to use HF as a dynamical tracer to reflect vertical air motion in the lower stratosphere. Furthermore, as HCl and HF have similar vertical distributions in the stratosphere the HCl/HF ratio is expected to remain approximately constant in the absence of any chemical destruction of HCl since dynamics will have a similar effect on both species. It is clear from an inspection of Table 1 that the fall in the HCl/HF ratio from 2.6 on 17th November to 1.3 on 9th January suggests that chemical depletion is a major contributor to the reduction in the total HCl column. A potential vorticity (PV) plot for this day is given in Figure 4 which shows that Åre is within the polar vortex (the edge of the vortex is defined by the shaded area). On 9th January the polar vortex is characterised by low enough temperatures for Type-I polar stratospheric clouds (PSCs) to be formed. In addition, a ten-day European Centre for Medium Range Weather Forecasting (ECMWF) back trajectory calculation plot (Figure 5) shows that the air parcels are all derived from within the cold polar vortex. Under these conditions HCl can be removed by heterogeneous reaction with ClONO_2 on PSCs to form Cl_2

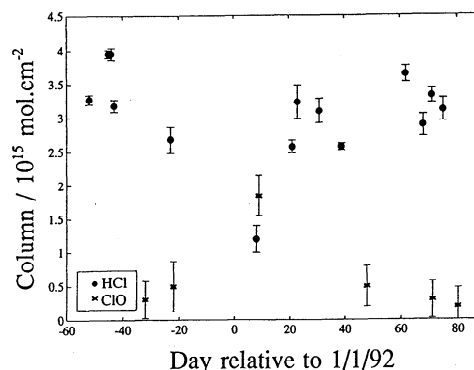


Fig. 6. HCl and ClO column time series over Åre during EASOE. ClO columns were derived from MLS measurements above 100mb (~ 15 km).

which would be expected to lead to high levels of ClO. This is confirmed by measurements of ClO obtained from the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS) which began global measurements of stratospheric ClO in September 1991 [Waters, 1992]. Preliminary ClO stratospheric columns (integrated column above 100 mb) over Åre are presented as a time series together with HCl in Figure 6. The strong anticorrelation between HCl and ClO columns indicates chemical conversion of stratospheric chlorine from the inactive HCl reservoir into the active ClO radical.

The observed recovery of HCl from late January to March is in agreement with aircraft borne HCl measurements over northern Scandinavia made by the Bremen group using a submillimetre wave sounder (H.Nett, private communication).

The chlorine nitrate columns for 24th and 25th January are from a period when the HCl column is showing a partial recovery towards the 10th November value. The vortex is no longer over Åre and the ClONO₂ columns are close to those found at mid-latitudes [Toon et al., 1992]. It is not yet clear whether the abundance of NO₂ is sufficiently high for substantial amounts of ClONO₂ to be formed close to the vortex edge.

The preliminary total HNO₃ columns are all from outside the vortex and show an enhancement over typical mid-latitude values [Rinsland et al., 1991] with the highest recorded value of 2.6×10^{16} molecules cm⁻² on 24th March. The high values presumably originate from the efficient heterogeneous conversion of N₂O₅ with water into HNO₃ on sulphuric acid aerosols which can take place at high temperatures [Wolff et al., 1991].

Conclusion

It is clear from the results presented here that for the winter of 1991-1992 there is strong evidence for a large chemical contribution to the removal of stratospheric HCl on or before 9th January 1992. This is highlighted by the drop in the HCl/HF ratio to 1.2 on this day followed by a recovery. The depletion is also correlated with the location of the polar vortex, as defined by the gradient of PV, where cold temperatures allow heterogeneous destruction of HCl on PSCs to occur. This conclusion is further supported by MLS measurements of enhanced levels of ClO in the lower stratosphere. The observed columns of HNO₃ reach high levels outside the vortex and may point to heterogeneous removal of N₂O₅.

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