

STRATOSPHERIC OCIO AND NO₂ MEASURED BY GROUNDBASED UV/VIS-SPECTROSCOPY IN GREENLAND IN JAN/FEB 1990 AND 1991

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ABSTRACT

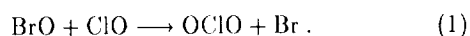
Groundbased UV/Vis-spectroscopy of zenith scattered sunlight was performed at Søndre Strømfjord (Greenland) during Jan/Feb 1990 and Jan/Feb 1991. Considerable amounts of OCIO were observed during both campaigns. Maximum OCIO vertical column densities at 92° solar zenith angle (SZA) were $7.4 \cdot 10^{13}$ molec/cm² in 1990 and $5.7 \cdot 10^{13}$ molec/cm² in 1991 (chemical enhancement is included in the calculation of the air mass factor (AMF)). A threshold seems to exist for OCIO detection: OCIO was detected on every day when the potential vorticity at the 475 K level of potential temperature was higher than $35 \cdot 10^{-6}$ Km²kg⁻¹s⁻¹.

NO₂ vertical columns lower than $1 \cdot 10^{15}$ molec/cm² were frequently observed in both winters.

1. INTRODUCTION

The UV/Vis spectra of zenith scattered sunlight contain absorptions of stratospheric constituents some of which are important in the context of polar ozone destruction. By UV/Vis spectroscopy vertical column densities of ozone and NO₂ can be obtained with appreciable accuracy. Also measurements of the halogen oxides BrO and OCIO have been reported from Antarctica [Solomon et al. 1987, Sanders et al. 1989, Wahner et al. 1989] as well as from the Arctic [Solomon et al. 1988, Schiller et al. 1990, Perner et al. 1990] in recent years.

BrO and OCIO are closely related to the ozone destroying chlorine and bromine catalytic cycles that lead to the formation of the antarctic ozone hole and are also active in the Arctic. OCIO is presumed to be formed solely in the reaction



Thus the abundance of OCIO is directly related to the concentrations of BrO and ClO, which are most important radicals in the antarctic ozone destruction cycles.

In Søndre Strømfjord/Greenland (50.7°W, 67.0°N) groundbased UV/Vis measurements were conducted in the winters 1989/90 and 1990/91. From these campaigns OCIO

and NO₂ measurements of the periods Jan. 4 – Feb. 13, 1990 and Jan. 8 – Feb. 12, 1991 are presented. Details of the experimental setup, data analysis and the spectral signatures of OCIO have been published elsewhere [Perner et al. 1990].

2. METEOROLOGICAL SITUATION

Both winters exhibit totally different meteorological conditions. The midwinter 1989/90 stratosphere is characterized as extremely cold [Naujokat et al. 1990] whereas the circulation of midwinter 1990/91 was heavily disturbed by a pronounced warming in early January [Naujokat et al. 1991]. This is reflected in the course of the 50 hPa temperatures at Søndre Strømfjord, which are shown in fig. 1 for both campaigns.

3. OCIO MEASUREMENTS

In fig.1 the days on which OCIO is identified are marked with 'x', those when no OCIO is found are marked with 'o'. Temperatures were too high in Feb. 1990 and during the whole of the campaign in 1991 for PSCs to exist at Søndre Strømfjord. The observation of OCIO and thus activated chlorine during these periods confirms the view that chlorine activation may take place somewhere in the polar region under favorable conditions (i.e. low temperatures causing PSC formation and thus chlorine activation). During transport the air can reach higher temperatures apparently without losing its state of activation.

Fig.2 shows the OCIO vertical column densities measured at 92° SZA in the evening. The corresponding noon spectrum of each day is taken as the reference spectrum in the data evaluation. The column density of OCIO in the noontime spectrum is estimated from the calculation of the diurnal variation of OCIO at 50 hPa by a box model. The detection limit is estimated from the optical density of the residual structures in the spectra after correction for all known absorptions including the Ring effect. Error bars given are the sums of the 1σ -errors of the fit coefficient for OCIO and the estimated uncertainty in the estimated

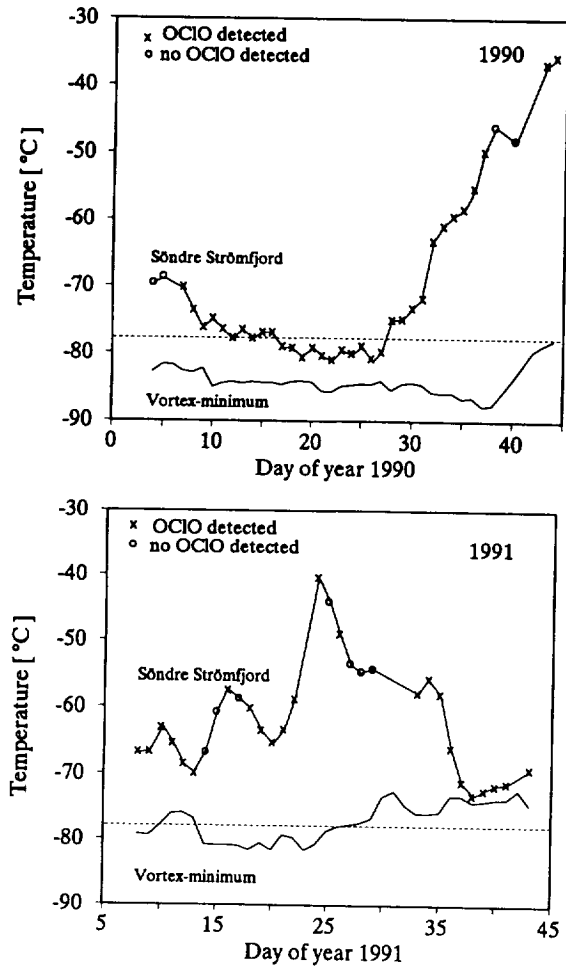


Fig.1: 50 hPa temperature above Søndre Strømfjord and absolute minimum temperature inside the vortex at 50 hPa.

OCIO content of the reference spectrum. In 1990 the highest OCIO column density is $7.4 \cdot 10^{13} \text{ molec/cm}^2$ and the average OCIO value is $3.8 \cdot 10^{13} \text{ molec/cm}^2$. In 1991 OCIO levels are 20–30% lower than in 1990. The maximum OCIO column density is $5.7 \cdot 10^{13} \text{ molec/cm}^2$ and the mean value is $3.1 \cdot 10^{13} \text{ molec/cm}^2$. The difference in the stratospheric OCIO content during the two campaigns may be a reflection of the different stratospheric temperatures. The extremely cold temperatures of 1990 may have caused a more frequent PSC-occurrence and thus a higher level of chlorine activation than in the mild winter of 1991. A contribution by a higher level of inorganic chlorine in the polar stratosphere in 1990 can not be excluded.

For the calculation of the AMF a gaussian profile of OCIO is assumed, centered at 20 km with a full width at half maximum (FWHM) of 8 km. The local SZA varies along the light path causing gradients of the OCIO photolysis rate and thus of the OCIO concentration (chemical

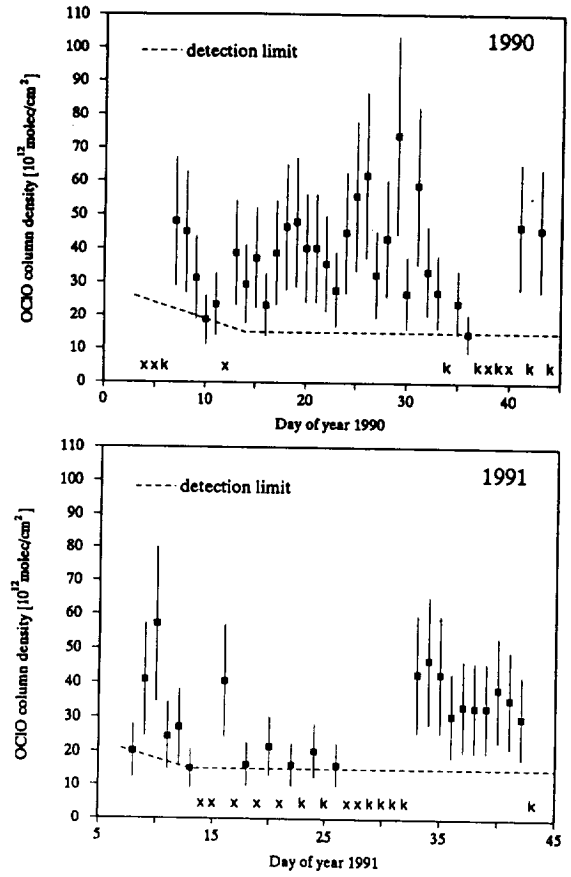


Fig.2: Vertical OCIO-column density at 92° SZA in the evening. x = OCIO below detection limit, which is indicated by the broken line. k= no measurements.

enhancement). This has to be considered in the AMF calculation. The amplitude of the OCIO profile is assumed to change with SZA according to the variation of the OCIO concentration at 50 hPa as calculated by the box model. The OCIO concentration at the place of observation is higher than it's average along the light path. For example at 92° SZA the AMF for OCIO measured at 378 nm is reduced by a factor of about 3.6 when chemical enhancement is properly considered. In order to perform a comparison of our results with published data we correct the latter for chemical enhancement. Table 1 shows that the OCIO column densities in the Arctic in 1989 reported by Schiller et al. were significantly lower than those in this work for 1990 and comparable to those found in 1991. OCIO amounts in the Arctic are generally lower than in Antarctica. This comparison has to be regarded in a qualitative way. In order to quantitatively compare the data the different situations in meteorology, vertical OCIO distribution, chemical composition (inducing different dependencies of OCIO columns on SZA) during the campaigns must be considered as well.

Table 1: OCIO-measurements at 92° SZA in polar regions. AA = Antarctica, A = Arctic. Correction for chemical enhancement is applied to all data.

	mean	maximum	reference
AA 1986	$4.3 \cdot 10^{13}$	$8.6 \cdot 10^{13}$	[Solomon et al. 1987]
AA 1987	20 - 30% more than AA 1986		[Sanders et al. 1989]
A 1989	$2.2 - 3.6 \cdot 10^{13}$		[Schiller et al. 1990]
A 1990	$3.8 \cdot 10^{13}$	$7.4 \cdot 10^{13}$	this work
A 1991	$3.1 \cdot 10^{13}$	$5.7 \cdot 10^{13}$	this work

From fig. 3 it appears that there exists a threshold for the appearance of OCIO. OCIO was detected whenever the potential vorticity in the 475 K level of potential temperature was larger than about $35 \cdot 10^{-6} \text{ Km}^2 \text{ kg}^{-1} \text{ s}^{-1}$. On a few occasions OCIO was positively identified when the potential vorticity was low at the 475 K and adjacent levels. So it appears that OCIO was detected well outside the vortex on a few occasions.

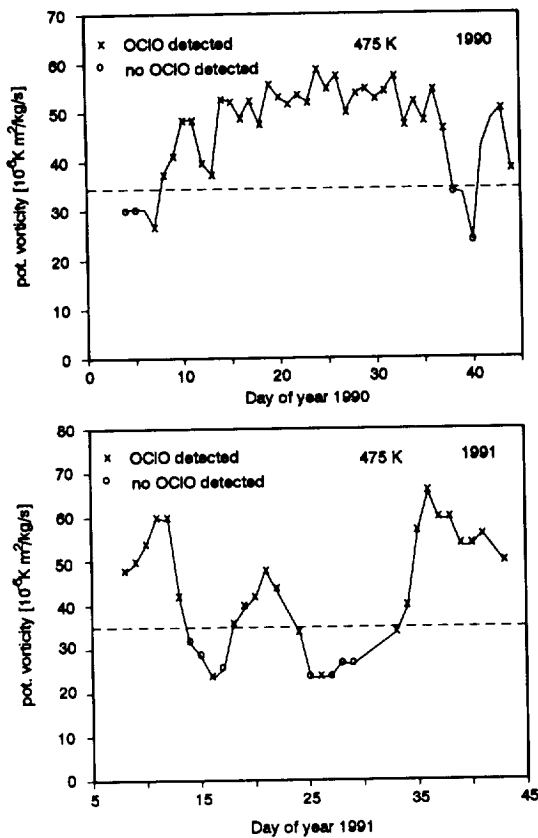


Fig.3: Plot of occasions when OCIO was positively identified against potential vorticity at the 475 K level of potential temperature. OCIO is found on every day when PV is higher than the threshold value.

4. NO₂ MEASUREMENTS

Fig. 4 shows morning and evening NO₂ column densities in 1990 and 1991 at 90° SZA. For the calculation of the corresponding AMF a gaussian NO₂ profile (peak = 30 km, FWHM = 20 km) is assumed and chemical enhancement is included. In both years NO₂ column densities were below $1 \cdot 10^{15} \text{ molec/cm}^2$ for several days exhibiting a reduction compared to the values found at low latitude or at high latitude in summer [Noxon, Whipple and Hyde, 1979] or [McKenzie and Johnston, 1982]. This reduction reflects

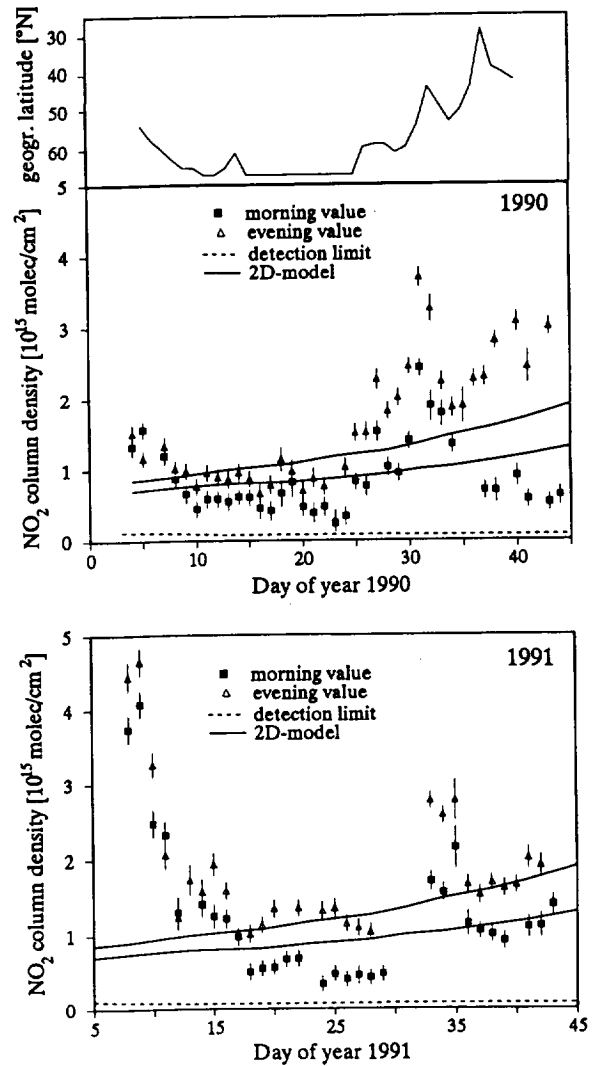


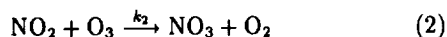
Fig.4: NO₂-column densities above Søndre Strømfjord at 90° SZA. Solid lines show 2D-model results of homogeneous chemistry from Solomon and Garcia [1983] (lower line: morning values; upper line: evening values). On top of the figure for 1990 the lowest latitude of the 20 hPa-trajectories within the last 5 days before arriving at Søndre Strømfjord is given.

the frequently observed Noxon cliff [Noxon 1979, Ridley et al. 1987, Wahner et al. 1990]. The Noxon cliff is due to a different partitioning of stratospheric NO_x in winter at high latitudes compared to the sunlit stratosphere. Because of the reduced photolysis and due to the lower stratospheric temperatures in winter at high latitude the buildup of reservoir substances such as HNO₃ or N₂O₅ is favoured, lowering the amount of NO and NO₂. An estimate of the average expected NO₂ levels can be derived from 2D model results [Solomon and Garcia, 1983], which are also shown in fig. 4. On an average the measured values are in agreement with the model expectations. The variability of measured NO₂ vertical column densities is due to the local temperature changes and stratospheric transport. High evening-levels of NO₂ correspond to advection of air from lower latitudes as can be seen from trajectory calculations performed by Petzold [1992]. In fig. 4 the southernmost latitude encountered by the 20hPa trajectory during the last 5 days before reaching Søndre Strømfjord is shown for 1990. Maximum latitude is 67° (Søndre Strømfjord). There is good correlation with the amounts of NO₂ in the evening. NO₂ column densities in the morning are determined by the nighttime partitioning of NO_x which is strongly influenced by temperature as will be discussed below.

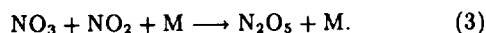
5. DIURNAL VARIATION OF NO₂

From fig. 4 a general increase of NO₂ during the day can clearly be identified. This NO₂ increase is explained by N₂O₅ photolysis. In comparison with N₂O₅ the NO_y-reservoir HNO₃ photolyses about 2 orders of magnitude more slowly and therefore does not contribute to the NO₂ diurnal variation. So the increase of NO₂ during the day is coupled to the N₂O₅ reservoir. The average ratio of NO₂ column densities for evening and morning is 2.1 in 1990 and 1.9 in the year 1991 which is consistent with measurements of Ridley et al. [Ridley et al. 1984, Ridley et al. 1987]. This is in contrast to the findings of several other authors [Noxon 1979, Pirre et al. 1990, Mount et al. 1987, Sanders et al. 1989] who report a negligible or a small increase of NO₂ during the day.

Assuming stationary state conditions the NO₂ produced during daylight by N₂O₅ photolysis returns to the reservoir N₂O₅ at night via



followed by



Because k_2 is temperature dependent, the rate of NO₃ formation and thus NO₂ depletion at night is a function of temperature. Thus the morning NO₂ values are strongly influenced by the stratospheric temperature.

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REFERENCES

- McKenzie R.L. and P.V. Johnston, *Geophys. Res. Lett.* **9**, 1255-1258, 1982.
- Mount G.H. et al., *J. Geophys. Res.* **92**, D7, 8320-8328, 1987.
- Naujokat, B. et al., *Beilage zur Berliner Wetterkarte*, SO 12/90, 1990.
- Naujokat, B. et al., *Beilage zur Berliner Wetterkarte*, SO 13/91, 1991.
- Noxon J.F., E.C. Whipple and R.S. Hyde, *J. Geophys. Res.* **84**, C8, 5047-5065, 1979.
- Noxon J.F., *J. Geophys. Res.* **84**, 5067-5076, 1979.
- Perner D. et al., *Geophys. Res. Lett.*, **18**, 787, 1990.
- Petzold K., private comm., 1992.
- Pirre M. et al, *Proc. First European Workshop on Polar Stratospheric Ozone Research Schliersee*, October 1990.
- Ridley B.A. et al., *J. Geophys. Res.* **89**, D3, 4794-4820, 1984.
- Ridley B.A. et al., *J. Geophys. Res.* **92**, D10, 11919 - 11929, 1987.
- Sanders R.W. et al., *J. Geophys. Res.* **94**, 11381 - 11391, 1989.
- Schiller C. et al., *Geophys. Res. Lett.* **17**, 4, 501-504, 1990.
- Solomon S. and R.R. Garcia, *J. Geophys. Res.* **88**, C9, 5229-5239, 1983.
- Solomon S. et al., *J. Geophys. Res.*, **92**, 8329, 1987.
- Solomon S. et al., *Science* **242**, 550-555 1988.
- Wahner A. et al., *J. Geophys. Res.*, **94**, 11405, 1989.
- Wahner A. et al., *Geophys. Res. Lett.* **17**, 497-500, 1990.