STRATOSPHERIC OC\textsubscript{10} AND NO\textsubscript{2} 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 OC\textsubscript{10} were observed during both campaigns. Maximum OC\textsubscript{10} vertical column densities at 92° solar zenith angle (SZA) were 7.4-10\textsuperscript{13} molec/cm\textsuperscript{2} in 1990 and 5.7-10\textsuperscript{13} molec/cm\textsuperscript{2} in 1991 (chemical enhancement is included in the calculation of the air mass factor (AMF)). A threshold seems to exist for OC\textsubscript{10} detection: OC\textsubscript{10} was detected on every day when the potential vorticity at the 475 K level of potential temperature was higher than 35-10\textsuperscript{-6}Km\textsuperscript{2}kg\textsuperscript{-1}s\textsuperscript{-1}.

NO\textsubscript{2} vertical columns lower than 1-10\textsuperscript{13} molec/cm\textsuperscript{2} 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 NO\textsubscript{2} can be obtained with appreciable accuracy. Also measurements of the halogen oxides BrO and OC\textsubscript{10} 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 OC\textsubscript{10} 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. OC\textsubscript{10} is presumed to be formed solely in the reaction

\[ \text{BrO} + \text{ClO} \rightarrow \text{OCIO} + \text{Br} . \]

Thus the abundance of OC\textsubscript{10} 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 OC\textsubscript{10} and NO\textsubscript{2} 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 OC\textsubscript{10} 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. OC\textsubscript{10} MEASUREMENTS

In fig.1 the days on which OC\textsubscript{10} is identified are marked with 'x', those when no OC\textsubscript{10} 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 OC\textsubscript{10} and thus activated chlorine during these periods confirms the view that chlorine activation may take place somewhere in the polar region under unfavorable 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 OC\textsubscript{10} 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 OC\textsubscript{10} in the noontime spectrum is estimated from the calculation of the diurnal variation of OC\textsubscript{10} 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 OC\textsubscript{10} and the estimated uncertainty in the estimated...
OCIO content of the reference spectrum. In 1990 the highest OCIO column density is $7.4 \times 10^{13}$molec/cm$^2$ and the average OCIO value is $3.8 \times 10^{13}$molec/cm$^2$. In 1991 OCIO levels are 20–30% lower than in 1990. The maximum OCIO column density is $5.7 \times 10^{13}$molec/cm$^2$ and the mean value is $3.1 \times 10^{13}$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 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 its 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: OClO—measurements at 92° SZA in polar regions. AA = Antarctica, A = Arctic. Correction for chemical enhancement is applied to all data.

<table>
<thead>
<tr>
<th></th>
<th>mean</th>
<th>maximum</th>
<th>reference</th>
</tr>
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<tbody>
<tr>
<td>AA 1986</td>
<td>4.3 \times 10^{13}</td>
<td>8.6 \times 10^{13}</td>
<td>Solomon et al. 1987</td>
</tr>
<tr>
<td>AA 1987</td>
<td>20 – 30% more than AA 1986</td>
<td>Schiller et al. 1990</td>
<td></td>
</tr>
<tr>
<td>A 1989</td>
<td>2.2 – 3.6 \times 10^{13}</td>
<td>this work</td>
<td></td>
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<tr>
<td>A 1990</td>
<td>3.8 – 10^{13}</td>
<td>7.4 – 10^{13}</td>
<td></td>
</tr>
<tr>
<td>A 1991</td>
<td>3.1 – 10^{13}</td>
<td>5.7 – 10^{13}</td>
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From fig. 3 it appears that there exists a threshold for the appearance of OClO. OClO was detected whenever the potential vorticity in the 475 K level of potential temperature was larger than about 35 \times 10^{-6} \text{Km}^2\text{kg}^{-1}\text{s}^{-1}. On a few occasions OClO was positively identified when the potential vorticity was low at the 475 K and adjacent levels. So it appears that OClO was detected well outside the vortex on a few occasions.

Fig. 3: Plot of occasions when OClO was positively identified against potential vorticity at the 475 K level of potential temperature. OClO 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 \times 10^{18} \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...
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 NOx 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 build-up 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 Sondre Strømfjord is shown for 1990. Maximum latitude is 67° (Sondre 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 NOx 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 NOy-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

\[
\text{NO}_2 + \text{O}_3 \xrightarrow{k_2} \text{NO}_3 + \text{O}_2 \quad (2)
\]

followed by

\[
\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}. \quad (3)
\]

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 NO3 values are strongly influenced by the stratospheric temperature.

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REFERENCES