Spectroscopic Measurements of Atmospheric Trace Gases at Neumayer-Station, Antarctica



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Spektroskopische Messungen atmosphärischer Spurenstoffe auf der Neumayer-Station, Antarktis

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Zusammenfassung

Diese Arbeit präsentiert die Ergebnisse von Streulichtmessungen auf der deutschen Antarktischen Forschungsstation Neumayer (70°35'S, 8°15'W) in den Jahren 1999 und 2000, basierend auf dem Prinzip der Differentiellen Optischen Absorptionsspektroskopie (DOAS). Die Messungen der atmosphärischen Spurengase Ozon, Stickstoffdioxyd (NO₂), Chlordioxyd (OClO), Bromoxyd (BrO), Jodoxyd (IO) sowie des Sauerstoff-Dimers (O₄), wurden mit Hilfe eines im Rahmen dieser Arbeit neu entwickelten UV/Vis Spektrographen durchgeführt. Das Hauptanliegen dieser Messungen in der Antarktischen Küstenregion war die Untersuchung der chemischen Zusammensetzung der Stratosphäre, wobei der Einfluss von Halogenverbindungen auf die Ozonschicht und ein verbessertes Verständnis der zum Ozonloch führenden Mechanismen im Mittelpunkt standen. Der Tages- und Jahresgang der untersuchten stratosphärischen Spurenstoffe ist in guter Übereinstimmung mit dem derzeitigen Verständnis der atmosphärischen Chemie: im polaren Winter wurden hohe OCIO-Werte beobachtet, hervorgerufen durch die heterogene Aktivierung von Chlor-Reservoirsubstanzen. Im Frühjahr verursachen reaktive Chlor- und Bromverbindungen katalytische Ozon- Abbauprozesse. Diese führten 1999 zu einem lang anhaltenden Ozonloch bis Ende Dezember. Das Minimum der Ozon-Säulendichte im Jahr 2000 betrug nur etwas mehr als 100DU. Zahlreiche stark erhöhte BrO-Säulendichten wurden jeweils im August und September 1999 und 2000 beobachtet. Sie sind auf BrO in der unteren Troposphäre zurückzuführen, das durch autokatalytische Prozesse aus angesäurten Seesalz-Oberflächen freigesetzt wird. Der gleichzeitige Rückgang der Konzentration von bodennahem Ozon wird durch katalytische Ozonzerstörung mittels reaktivem Brom verursacht. Es wurde eine detaillierte Analyse der beobachteten BrO- Erhöhungen durchgeführt. Diese beinhaltete die Messungen von bodennahem Ozon, die Daten von Ozonsondenaufstiegen sowie die Quantifizierung des Strahlungstransportes in der Troposphäre mittels der Absorption von O₄. Desweiteren wurde ein neues Verfahren zur Bestimmung der Quellregionen und der Höhenverteilung von reaktivem Brom mittels Trajektorienrechnungen in hoher Zeit- und Höhenauflösung in Kombination mit Seeiskarten entwickelt. Diese Analyse ergab, daß BrO durch Advektion von der Seeisoberfläche in Höhen von mehr als 4000m transportiert werden kann. Es ist möglich, daß diese Prozesse zu einem globalen troposphärischen BrO-Background beitragen. Im Rahmen dieser Arbeit wurde zum ersten Mal Jodoxyd in der Antarktischen marinen Grenzschicht nachgewiesen. IO ist in Mischungsverhältnissen von schätzungsweise 5-10 ppt vorhanden. Angesichts der Tatsache, daß der Ozean die Hauptquelle für reaktive Jodverbindungen in der Troposphäre ist, sind die beobachteten konstanten IO-Konzentrationen über das ganze Jahr hinweg ein überraschendes Ergebnis. Es bleibt ungeklärt, in welchem Umfang der seeisbedeckte Ozean eine Quelle für organische Vorläufersubstanzen von reaktivem Jod sein könnte.

Abstract

This thesis presents a two years record of Differential Optical Absorption Spectroscopy (DOAS) observations of zenith scattered sunlight at the German Antarctic research station Neumayer (70°35'S, 8°15'W). The measurements of the atmospheric trace gases ozone, nitrogen dioxide (NO₂), chlorine dioxide (OClO), bromine monoxide (BrO), iodine monoxide (IO) and the oxygen dimer (O_4) were performed using a new UV/Vis spectrograph, developed within the scope of this work. The main intention of DOAS measurements in the Antarctic coastal region was to investigate the chemical composition of the stratosphere, particularly the influence of halogen compounds on the ozone layer, and to improve our understanding of the mechanisms leading to the ozone hole. The diurnal and seasonal variation of the observed stratospheric trace gases is in good agreement with the current understanding of atmospheric chemistry: caused by the heterogeneous conversion of inactive reservoir species to reactive chlorine, high levels of OCIO were detected during late autumn, winter and spring. Catalytic cycles involving reactive chlorine and bromine compounds cause a severe ozone depletion during austral spring, with a persistent ozone hole until December 1999 and minimum ozone columns close to 100DU in 2000. Numerous strong and sudden enhancements of BrO were detected during August and September of both years. These events were caused by BrO located in the lower troposphere, released by well known autocatalytic processes on acidified sea salt surfaces. Simultaneously, a strong depletion of near surface ozone was observed, caused by catalytic cycles involving bromine. A detailed analysis of the observed BrO events is presented, including surface ozone measurements, ozone soundings, the quantification of the radiative transport in the troposphere using O_4 absorption and a new approach to determine the source regions and the vertical distribution of reactive bromine using trajectory calculations in high temporal and vertical resolution in combination with sea ice maps. Caused by advection processes, BrO was found to be transported from the sea ice surface to altitudes of more than 4000m. These processes possibly serve as an additional source for the recently speculated tropospheric BrO background. Within the scope of this work, the first detection of iodine oxide in the Antarctic marine boundary layer was possible. IO mixing ratios of $\approx 5-10$ ppt were estimated. In view of the fact that the ocean is the main source for reactive iodine in the troposphere, the constant IO levels observed throughout the year are a surprising finding. It remains unanswered to which extend the sea ice covered ocean can act as a source for organic iodine precursors during winter.

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Chapter 1

Introduction

The capability of ozone to absorb incoming solar short-wave radiation is of great importance for the life on our planet. The presence of ozone in our atmosphere, with a concentration maximum in altitudes between 20 and 25km, protects life from harmful UV radiation, which can affect the health of humans, animals and plants. This was already recognised in the late 19th century [Hartley, 1880] and a first theory on the photochemical formation of the ozone layer in the stratosphere was proposed by Chapman [1930]. It was soon realised that the ozone budget is influenced by numerous chemical species present in the stratosphere, such as hydrogen and nitrogen compounds [Bates and Nicolet, 1950; Crutzen, 1970; Johnston, 1971].

Used in a wide range of industrial applications, a growing amount of halogenated hydrocarbons was released into the atmosphere during the 20th century. Chloroflourocarbons (CFCs) and Halons are chemically inert compounds which are photostable, do not react with surfaces or gases in the atmosphere and have a very low water solubility. Due to these advantageous properties, CFCs and halons are ideal for the use as cooling agents in refrigerators and air-conditioning systems, as propellents, as foaming agents for plastic materials and in fire extinguishers. Due to their extremely long residence time in the atmosphere, ranging from years over decades to centuries, a part of these halogenated compounds reach the stratosphere. High energy UV radiation in higher altitudes is able to destroy these molecules, leading to a release of halogen compounds into the stratosphere.

It was first pointed out in the mid 1970's that reactive chlorine released by man-made CFCs can lead to a destruction of stratospheric ozone by catalytic cycles [Molina and Rowland, 1974; Stolarski and Cicerone, 1974]. However, the bulk of chlorine in the lower stratosphere was expected to be deactivated by chemical conversion to stable reservoir species. The persistent anthropogenic release of CFCs was predicted to lead to a global ozone reduction of 10-20% during the next 50-100 years. In view of the potential impact of human activity on the ozone layer, twenty nations agreed to the *Vienna Convention for the Protection of the Ozone Layer* in 1985. The main goal of this convention was to encourage research, cooperation among countries and exchange of information concerning the human impact on the ozone layer.

A dramatic influence of CFCs on the ozone layer was discovered in the mid 1980's, when Farman et al. [1985] found large ozone losses over Antarctica during austral spring, caused by the conversion of chlorine reservoir species to reactive chlorine on surfaces of polar stratospheric clouds [Solomon et al., 1986]. These heterogeneous processes were found to lead to the complete destruction of ozone in altitudes between 20 and 25km. In the following years, ground based and satellite borne measurements confirmed that the extent of the *ozone hole* was increasing, covering areas as large as the Antarctic continent during September and Oc-



Figure 1.1: October average of total ozone over Halley Bay, Antarctica [Farman et al., 1985; Jones and Shanklin, 1995]. Adapted from Solomon [1999].

tober. The longest existing record of total ozone measurements in Antarctica from the British Antarctic research station Halley (figure 1.1) shows that the October average of ozone column decreased dramatically from year to year since the mid 1970's.

The ozone hole phenomenon is not restricted to the southern hemisphere. Severe ozone destruction is also observed in the Arctic during spring. The Arctic ozone hole is of smaller extend compared to Antarctica and is strongly affected by dynamical influences which frequently lead to a mixing with ozone-rich air from lower latitudes due to a less stable circumpolar wind field (*polar vortex*). Ozone depletion also occurs at mid-latitudes, although on a smaller extent than in polar regions. The decline in ozone columns on the order of 5-10% observed in the 1990's cannot be explained by gas phase chemistry alone. It is very likely that heterogeneous processes on stratospheric background aerosols, involving bromine and chlorine species, are at least partly responsible for this trend in mid-latitudes.

The production and emission of halocarbons was limited by the *Montreal Protocol on Sub*stances that deplete the Ozone layer, agreed upon in 1987. The world-wide production of most ozone depleting chlorinated and brominated compounds, such as CFCs, halons and HCFCs, was limited and finally stopped by the Montreal protocol and its following amendments at London (1990), Copenhagen (1992) and Montreal (1997), which are ratified up to now by 173 countries. Due to the world-wide control of CFC production, the tropospheric concentrations of these compounds have peaked in the mid 1990's and declined afterwards. Due to the slow exchange between troposphere and stratosphere, the stratospheric chlorine abundance follows the tropospheric CFC trend with a delay of 5-10 years and a recovery of the ozone hole is predicted for the middle of the 21^{st} century.

Bromine compounds in the stratosphere are of natural as well as anthropogenic origin. They have a significant impact on the stratospheric ozone budget, although the contemporary abundances of bromine are about 200 times smaller than those of chlorine. In contrast to chlorine, which is usually present in form of inactive reservoir species, a large fraction of bromine is present as reactive compounds (Br and BrO). Bromine is therefore very effective in destroying ozone, particularly in combination with reactive chlorine. Since the atmospheric concentrations of anthropogenically released bromocarbons, particularly halons and methyl bromide, are increasing, bromine compounds are expected to have a growing impact on the chemical balance of the lower stratosphere.

Halogen species also play an important role in tropospheric chemistry. Apart from the release of bromocarbons by human activity, the ocean acts as the main source for bromine and iodine in coastal regions. Strong and sudden increases in reactive bromine were observed both in the Arctic and Antarctic marine boundary layer during spring. This *bromine explosion* is now known to be caused by autocatalytic processes on sea salt surfaces. Caused by catalytic cycles similar to the processes in the stratosphere, this phenomenon frequently leads to the complete destruction of near surface ozone, the *polar tropospheric ozone hole*. Iodine, mainly produced by the natural release of short-lived organic iodine compounds from macroalgae and phytoplancton, can have an important impact on the ozone budget even if it is only present in very small concentrations. The ability of iodine to destroy ozone is by far larger than that of bromine since most temporary iodine reservoir species are rapidly converted into reactive compounds in the presence of solar illumination.

A widely used technique for the detection of atmospheric trace gases is the *Differential Optical Absorption Spectroscopy* (DOAS). It is based on the wavelength dependent absorption of light by atmospheric constituents. Various trace gases can be identified simultaneously by their spectral signature which act as an individual 'fingerprint'. The DOAS technique has been implemented on several platforms: from ground, on aircrafts, balloons and satellites, and by using either artificial light sources, scattered sunlight or direct sun- or moonlight. Ground-based DOAS observations of scattered sunlight is very suitable for long term measurements of atmospheric constituents. Since those instruments are easy to maintain and can be designed without using any mechanical parts, they are ideal for the operation in remote regions with restricted technical infrastructure.

Within the scope of this work, a DOAS spectrograph for the observation of zenith scattered sunlight was designed. It was installed at the German Antarctic research Station, Neumayer $(70^{\circ}35$ 'S, $8^{\circ}15$ 'W), during February 1999 and operated continuously since then. The Neumayer station is located on the shelf ice in front of the Antarctic continent, in a distance of approximately 7km from the coast of the Atlantic ocean. The station is operated by the Alfred Wegener Institute for Polar and Marine Research, Bremerhaven. The Neumayer Station is very suitable for measurements of stratospheric trace gases involved in ozone chemistry: during polar winter, the Neumayer station is located below the polar vortex for a period of about 6 months, providing the ability to study the chemical and dynamical mechanisms leading to the ozone hole. The period of polar night, when the sun is always below the horizon, lasts only about 10 weeks. Due to the good light yield of the DOAS instrument, it is possible extend the detection of most trace gases over the whole winter period, although the measurements are restricted to some hours around noon, when the sun stays close enough (less than 5°) below the horizon.

The main goal of the DOAS measurements at Neumayer station was the long-term observation of stratospheric constituents. The diurnal and seasonal variation as well as the year-to-year variability of the simultaneously measured trace gases ozone, nitrogen dioxide (NO_2) , chlorine dioxide (OClO) and bromine monoxide (BrO) provides the possibility to test our understanding of stratospheric chemistry and the mechanisms leading to the ozone hole.

The primary product of a DOAS measurement is the column density of trace gases, i.e. the integrated concentration of absorbers along the light path from the top of the atmosphere to the instrument. Therefore, tropospheric constituents can also contribute significantly to the observed signal if they are present in high concentrations. Strongly enhanced BrO column densities were observed during September and October of 1999 and 2000. These events were unequivocally caused by BrO located in the lower troposphere, released by heterogeneous processes on sea salt surfaces. BrO enhancements were observed extremely frequently, so that an interpretation of the springtime measurements concerning stratospheric BrO is difficult. However, these observations provide the ability to study in detail the mechanisms leading to a bromine explosion concerning the source regions for reactive bromine, their temporal and vertical distribution and their impact on the tropospheric ozone budget.

Within the scope of this work, it was possible to detect iodine oxide for the first time in the Antarctic marine boundary layer. Although a precise quantification of iodine oxide concentrations is difficult using DOAS measurements of zenith scattered sunlight, the measurements indicate the presence of high levels of iodine oxide throughout the year, with an unexpectedly small seasonal variation.

Chapter 2 presents an overview of the present knowledge of halogen chemistry in the atmosphere. The sources and sinks of ozone in the stratosphere and remote regions of the troposphere as well as the importance of halogen compounds for the ozone budget are discussed. The instrumental setup, the properties of optics and electronics as well as the long term characterisation of the DOAS spectrograph are described in chapter 3. Chapter 4 describes the principles of DOAS spectroscopy and the modeling of radiative transport in the atmosphere. Some principle difficulties of the spectral retrieval and their consideration in the analysis procedure are discussed. The algorithms for the retrieval of ozone, NO_2 , BrO, IO and OCIO and the uncertainties of the measurements are described at the end of this chapter. After a brief overview of the meteorological conditions, chapter 5 presents the results of the DOAS observations at Neumayer station during 1999 and 2000. Finally, the major results of this thesis are summarised in chapter 6.

Chapter 2

Atmospheric Halogen Chemistry

In this chapter the chemistry of halogens and their impact on ozone chemistry in the atmosphere is discussed. The sources and sinks of ozone in the stratosphere and troposphere are described in section 2.1. Section 2.2 gives a general overview on the basic reaction schemes of atmospheric halogens. The sources and sinks of halogen compounds in the stratosphere and their impact on the ozone layer is subject of section 2.3. Section 2.4 deals with the influence of halogen compounds on the ozone budget in the remote marine boundary layer.

2.1 Atmospheric ozone

The bulk of atmospheric ozone is located in the lower stratosphere, with a concentration maximum in altitudes between 20 and 25km. Only about 10% of the total ozone column is located in the troposphere. Since the sources and sinks of stratospheric and tropospheric ozone are distinctly different, they are discussed separately in the following two sections.

2.1.1 Ozone in the stratosphere

Since ozone is responsible for the absorption of short wave radiation in the stratosphere, it is one of the most important constituents of the earth's atmosphere. The formation and destruction of ozone in the stratosphere is primarily controlled by the so-called odd-oxygen chemistry. The production of ozone is initiated by the photolysis of molecular oxygen [Chapman, 1930]:

$$O_2 + h\nu \longrightarrow 2O({}^3P) \qquad \qquad \lambda \le 240nm \qquad (2.1a)$$
$$O({}^3P) + O_2 + M \longrightarrow O_3 + M \qquad (2.1b)$$

Ozone is formed via the reaction (2.1b) of $O + O_2$ with a third body M. The following reactions result in a net sink for ozone:



Figure 2.1: Schematic diagram of the Chapman cycle.

 $O_3 + h\nu \longrightarrow O_2 + O(^1D)$ $\lambda \leq 320 nm$ (2.2a)

$$O(^{1}D) + M \longrightarrow O(^{3}P) + M$$
 (2.2b)

 $O_3 + h\nu \longrightarrow O_2 + O({}^3P)$ $2O({}^3P) + M \longrightarrow O_2 + M$ $\lambda \leq 1180 nm$ (2.2c)

$$2O(^{3}P) + M \longrightarrow O_{2} + M \tag{2.2d}$$

$$O(^{3}P) + O_{3} \longrightarrow 2O_{2}$$
 (2.2e)

Reactions (2.2d) and (2.2e) which produce molecular oxygen are by far slower than reaction (2.1b). Thus only a very small fraction of oxygen is reconverted to molecular oxygen. On the other hand, ozone and atomic oxygen cycle very rapidly between each other. Since ozone and molecular oxygen are linked by relatively slow reactions, it is useful to distinguish between the odd oxygen (O and O_3) and the much longer-lived even oxygen (O_2). The situation is sketched in figure 2.1

Soon it became clear that the observed ozone profiles cannot be explained solely by the Chapman cycle, but that other ozone destroying mechanisms must exist. Model calculations including only oxygen chemistry strongly overestimated the stratospheric ozone abundance by more than a factor of two. Therefore additional sinks for ozone must exist. A set of ozone destroying reaction cycles, involving hydrogen oxides, was first proposed by Bates [1950]:

$$O + OH \longrightarrow O_2 + H$$
 (2.3a)

$$H + O_2 + M \longrightarrow HO_2 + M$$
 (2.3b)

$$O + HO_2 \longrightarrow O_2 + OH$$
 (2.3c)

 $2O \longrightarrow O_2$ net:

$$O + OH \longrightarrow O_2 + H$$
 (2.4a)

$$H + O_3 + M \longrightarrow OH + O_2 + M \tag{2.4b}$$

 $O + O_3 \longrightarrow 2O_2$ net:

$$O_3 + OH \longrightarrow O_2 + HO_2$$
 (2.5a)

$$O + HO_2 \longrightarrow OH + O_2$$
 (2.5b)

net:
$$O + O_3 \longrightarrow 2O_2$$

OH is produced in the stratosphere by the reaction of water vapour with oxygen atoms. The cold tropopause prevents tropospheric water vapour from entering the stratosphere. Instead, water vapour is produced in the stratosphere by the oxidation of methane (CH₄):

$$CH_4 + O(^1D) \longrightarrow OH + CH_3$$
 (2.6a)

$$CH_4 + OH \longrightarrow H_2O + CH_3$$
 (2.6b)

$$O(^{1}D) + H_{2}O \longrightarrow 2OH$$
 (2.6c)

The reaction chains (2.3) to (2.5) were the first of numerous catalytic reaction cycles proposed for the destruction of ozone: the compound responsible for the conversion of ozone to molecular oxygen (OH) is restored after one cycle and therefore remains available for the decomposition of ozone unless it is removed by other sinks. Thus such catalysts have a strong impact on the ozone budged even if their concentration is by far smaller than that of ozone. The class of odd hydrogen compounds, i.e. OH and HO_2 , are summarised as HO_x . They are particularly important for the ozone budget in the lower stratosphere (10-15km altitude), where the catalytic cycles (2.3)-(2.5) are responsible for about 80% of the total ozone loss processes.

Further catalytic ozone destruction cycles involve nitrogen oxides [Crutzen, 1970; Johnston, 1971]:

$$O_3 + NO \longrightarrow O_2 + NO_2$$
 (2.7a)

$$O + NO_2 \longrightarrow NO + O_2$$
 (2.7b)

net: $O + O_3 \longrightarrow 2O_2$

$$O_3 + NO \longrightarrow O_2 + NO_2$$
 (2.8a)

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
 (2.8b)

$$NO_3 + h\nu \longrightarrow NO_2 + O$$
 (2.8c)

net: $2O_3 + h\nu \longrightarrow 3O_2$

Nitrogen oxides are produced in the stratosphere mainly by oxidation of N_2O :

$$N_2 O + O(^1 D) \to 2NO \tag{2.9}$$

The NO_x cycles (2.7) and (2.8) particularly important for the ozone budged in the middle stratosphere (30-40km altitude), where they are responsible for 60-70% of the odd oxygen loss.



Figure 2.2: Comparison between observed and modeled stratospheric ozone mixing ratio, if only the Chapman cycle is taken into account and by taking HO_x , NO_x and ClO_x chemistry into account. Adapted from Röth [1994].

Human activity has an impact on the nitrogen oxide contents of the stratosphere by increasing the atmospheric abundance of the source gas N_2O , but also by direct emissions of nitrogen oxides in the stratosphere from supersonic aircrafts. NO_x denotes the family of the reactive nitrogen compounds NO, NO_2 and NO_3 , while all inorganic nitrogen species are summarised as NO_y .

Together with catalytic cycles involving chlorine and bromine chemistry, which will be discussed in section 2.3, the consideration of the catalytic cycles described above leads to an ozone budget in the stratosphere which is consistent with the observations (see figure 2.2).

2.1.2 Ozone in the remote marine boundary layer

Only about 50% of the tropospheric ozone has its origin in the stratosphere and is transported through the tropopause. The production of ozone by the Chapman cycle is not possible in the troposphere, since short wave UV radiation is a necessary prerequisite for the production of atomic oxygen. Instead, the production of ozone in the troposphere is driven by NO_x chemistry and reactions involving methane or higher hydrocarbons.

Of importance for the formation and destruction of tropospheric ozone are reactions involving NO_x :

$$NO_2 + h\nu \longrightarrow NO + O({}^3P) \qquad \lambda \le 420nm \qquad (2.10a)$$

$$O(^{3}P) + O_{2} + M \longrightarrow NO + O_{3} + M$$
 $k_{1} = 1.5 \cdot 10^{-14}$ (2.10b)

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 $k_2 = 1.8 \cdot 10^{-12}$ (2.10c)

with the rate constants given in units of $cm^3 molec^{-1} sec^{-1}$. The ozone concentration

is then determined by the photostationary steady state of reactions (2.10), which can be expressed by the *Leighton ratio L*:

$$L \equiv \frac{[NO]}{[NO_2]} = \frac{J(NO_2)}{[O_3] \cdot k_2}$$
(2.11)

Remote regions are, in contrast to areas with anthropogenic influence, generally characterised by low NO_x with typical mixing ratios of 5-10ppt in the marine boundary layer [Jones et al., 1999]. Under these conditions, nitrogen and hydrogen oxides are able to produce ozone together with methane or higher hydrocarbons by the following reaction sequence [Johnston and Podolske, 1978]:

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$
 (2.12a)

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2$$

$$(2.12d)$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$$
 (2.12c)

$$CH_3O + O_2 \longrightarrow CH_2O + HO_2 \tag{2.12d}$$
$$CH_2O + h_{U} \longrightarrow COH + H \tag{2.12e}$$

$$CH_2O + h\nu \longrightarrow COH + H$$

$$(2.12e)$$

$$COH + O_2 + M \longrightarrow CO + HO_2 + M$$

$$(2.12f)$$

$$H + O2 + M \longrightarrow CO + HO_2 + M$$

$$(2.121)$$

$$H + O2 + M \longrightarrow HO_2 + M$$

$$(2.12g)$$

$$2HO_2 + 2NO \longrightarrow 2OH + 2NO_2 \qquad (2.12b)$$

$$HO_2 + OH \longrightarrow H_2O + O_2 \tag{2.12i}$$

$$3(NO_2 + h\nu) \longrightarrow 3(NO + O)$$
 (2.12j)

$$3(O+O_2+M) \longrightarrow 3(O_3+M) \tag{2.12k}$$

net:
$$CH_4 + 6O_2 \longrightarrow CO + 2H_2O + 3O_3$$

Ozone producing reaction schemes similar to (2.12) can also involve higher hydrocarbons. Other the production of ozone, this reaction cycle is an important source of carbon monoxide (CO) in the troposphere.

Carbon monoxide is able to produce ozone according to the following cycle [Crutzen and Giedel, 1983]:

$$CO + OH \longrightarrow CO_2 + H$$
 (2.13a)

$$H + O2 + M \longrightarrow HO_2 + M$$
 (2.13b)

$$HO_2 + NO \longrightarrow OH + NO_2$$
 (2.13c)

$$NO_2 + h\nu \longrightarrow NO + O$$
 (2.13d)

$$O_2 + O + M \longrightarrow O_3 + M$$
 (2.13e)

net:
$$CO + 2O_2 \longrightarrow CO_2 + O_3$$

Carbon monoxide is, however, only producing ozone if the NO_x concentrations are sufficiently high. This is not the case for low NO_x conditions of remote areas, such as Antarctica, with typical background conditions of less than 10ppt [Jones et al., 1999]. Instead, CO leads to a destruction of ozone under low NO_x conditions:



Figure 2.3: Upper panel: seasonal variation of the ozone partial pressure in the troposphere above the Neumayer station as a function of altitude and time, determined using the ozone sounding data. Lower panel: Ozone mixing ratio at the ground, measured by the ozone monitor in the Neumayer trace gas observatory. Data kindly provided by G. König- Langlo.

$$CO + OH \longrightarrow CO_2 + H$$
 (2.14a)

$$H + O_2 + M \longrightarrow HO_2 + M$$
 (2.14b)

$$HO_2 + O_3 \longrightarrow OH + 2O_2$$
 (2.14c)

net: $CO + O_3 \longrightarrow CO_2 + O_2$

The ozone mixing ratios in the unpolluted Antarctic marine boundary range from ≈ 12 ppb during summer to ≈ 30 ppb during mid-winter. This pronounced seasonal variation of ozone is partly controlled by the availability of OH radicals, which depends on the solar illumination. OH is generated by the photolysis of O₃ to O(¹D), followed by its reaction with water vapour:

$$O_3 + h\nu \longrightarrow O_2 + O(^1D)$$
 $\lambda \le 320nm$ (2.15a)

$$O(^{1}D) + H_{2}O \longrightarrow 2OH$$
 (2.15b)

The removal of OH occurs via the reaction with CH_4 (reactions (2.12a) and (2.12b)) and with CO (reactions (2.13a) and (2.14a)).

Figure 2.3 shows the seasonal variation of tropospheric ozone above Neumayer, measured by ozone soundings and by the ozone monitor operating in the Neumayer trace gas observatory. Apart from influence of the OH and NO_x chemistry on ozone described above, dynamical influences are most likely responsible for the pronounced seasonal variability with a maximum during winter. A possible source of ozone during winter is the downward transport of ozonerich air masses from the stratosphere into the troposphere caused by gravity waves [Shaw, 1988]. Another process responsible for the winter maximum is the large-scale transport of ozone-rich air from mid-latitudes to the polar region in the middle troposphere, followed by the descent of air over the cold Antarctic continent and an air flow in northern direction [Ito, 1989; Murayama et al., 1992].

During polar spring, the ozone budget in the polar marine boundary layer is strongly influenced by halogen chemistry. The mechanisms leading to the almost complete depletion of ozone during such periods, the *tropospheric ozone hole*, are described in section 2.4.

2.2 Reaction schemes of reactive halogens in the atmosphere

Apart from the reactions described above, involving hydrogen and nitrogen compounds, the destruction of ozone in the atmosphere can be triggered by halogen species. The typical reaction scheme for catalytic cycles involving inorganic halogen species is

$$X + O_3 \longrightarrow XO + O_2$$
 (2.16a)

$$Y + O_3 \longrightarrow YO + O_2$$
 (2.16b)

$$XO + YO \longrightarrow X + Y + O_2$$
 (2.16c)

$$\longrightarrow XY + O_2$$
 (2.16d)

$$\longrightarrow OXO + Y$$
 (2.16e)

net:
$$2O_3 \longrightarrow 3O_2$$

Here, X and Y denote halogen atoms (Cl, Br, or I). An important loss channel for the halogen oxide formed in reaction (2.16a) is its photolysis and the reaction with NO:

$$XO + h\nu \longrightarrow X + O$$
 (2.16f)

$$XO + NO \longrightarrow X + NO_2$$
 (2.16g)

The XY molecule formed in reaction (2.16d) is rapidly photolysed in the sunlit atmosphere:

$$XY + h\nu \longrightarrow X + Y$$
 (2.16h)

Reaction (2.16e) does not lead to a net destruction of ozone, since its photo dissociation leads to the formation of atomic oxygen and subsequently to the reformation of ozone:

$$OXO + h\nu \longrightarrow XO + O$$
 (2.16i)

$$O + O_2 \longrightarrow O_3$$
 (2.16j)

In case of X=I, however, the photo-dissociation of OIO possibly yields I and O₂, leading to a net ozone destruction [Hebestreit, 2001]. This will be discussed in section 2.4.2.

The reaction of XO with YO ((2.16c) and (2.16d)) is the rate limiting step of the reaction chain. The self reactions (X=Y=Br or X=Y=Cl) are usually slower than the mixed reactions (X=Br and Y=Cl). Particularly reactions involving iodine (X=I, Y=Br or Cl) are very effective in destroying ozone. Both in the stratosphere and in the troposphere, catalytic cycles involving hydrogen and nitrogen radicals are of importance:

$$X + O_3 \longrightarrow XO + O_2$$
 (2.17a)

$$OH + O_3 \longrightarrow HO_2 + O_2$$
 (2.17b)

$$XO + HO_2 \longrightarrow HOX + O_2$$
 (2.17c)

$$HOX + h\nu \longrightarrow OH + X$$
 (2.17d)

net:
$$2O_3 + h\nu \longrightarrow 3O_2$$

and

$$X + O_3 \longrightarrow XO + O_2 \tag{2.18a}$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{2.18b}$$
$$XO + NO_2 \longrightarrow XONO_2 \tag{2.18c}$$

$$XO + NO_2 \longrightarrow XONO_2$$

$$(2.18c)$$

$$XONO_2 + h\nu \longrightarrow NO_2 + X$$

$$(2.18d)$$

$$NO_2 + n\nu \longrightarrow NO_3 + X$$
 (2.16d)
$$\longrightarrow NO_2 + XO$$
 (2.18e)

$$NO_3 + h\nu \longrightarrow NO + O_2$$
 (2.18f)

net:
$$2O_3 + 2h\nu \longrightarrow 3O_2$$

The efficiency of cycle (2.18) is controlled by the branching ratio of reactions (2.18d) and (2.18e), where the latter one leads to a null cycle without ozone destruction.

The efficiency of the catalytic cycles, described above, involving halogen radicals strongly depends on the availability of the reactive compounds X and XO. When going through the family of halogens from fluorine over chlorine and bromine to iodine, the halogen reservoir species formed in the atmosphere are less tightly bound:

- Fluorine reacts immediately with HO_2 or CH_4 to form HF after its release in the stratosphere from CFCs. Since HF is inert against photolysis or reaction with OH, it will remain in this deactivated form and therefore has a negligible impact on ozone [Rowland and Molina, 1975; Stolarski and Rundel, 1975].
- *Chlorine* is mainly abundant in its inactivated form (ClONO₂ and HCl) in the lower stratosphere and troposphere, although it is converted to its active form under special circumstances described in section 2.3.
- The reservoir species of *bromine* are less stable than their chlorine counterparts. Therefore a large fraction ($\approx 30 - 50\%$) of bromine is present in its activated form (Br, BrO) by photolysis of the reservoir species or their reaction with OH.
- *Iodine* compounds are in general rapidly photolysed. Therefore a large fraction of iodine is in the form of I and IO.

The catalytic cycles involving bromine and in particular iodine, are very effective in destroying ozone since (1) the reactions are faster and (2) the number of cycles a halogen atom is passing through before it is converted to a deactivated form is increasing from chlorine over bromine to iodine.

Species Formula		Life time [years]		Mix. ratio [ppt]		EESC^{a} [ppb]	
		trop.	strat.	1999	1999-98	1999	1999-98
CFC							
-11	CCl_3F	∞	55	260.2	-1.07	0.625	-0.0020
-12	CCl_2F_2	∞	116	537.1	+2.85	0.516	+0.0030
-113	CCl_2FCClF_2	∞	640	82.3	-0.23	0.148	-0.0010
-114	$CClF_2CClF_2$	∞	220	17.4	+0.15	0.010	0.0000
CFC chlorine				2144.5	+2.24	1.301	0.0000
HCFC							
-22	$CHClF_2$	17	240	128.2	+4.70	0.036	+0.0013
-141b	CH_3CCl_2F	76	13	9.3	+1.87	0.011	+0.0022
-142b	CH_3CClF_2	25	215	10.1	+1.08	0.003	+0.0003
HCFC chlorin	e			156.8	+9.52	0.050	+0.0040
Halons							
H-1211	CF_2ClBr	2.3	11	4.3	+0.18	0.191	+0.0080
H-1301	CF_3Br	∞	77	2.3	+0.11	0.073	+0.0040
H-2402	CF_2BrCF_2Br	3.4	20	0.45	0.00	0.032	0.0000
H-1202	CF_2Br_2	3.3		0.05			
halon bromine				7.6	+0.29	0.296	+0.0120
other halocarbons							
methyl							
chloroform	CH_3CCl_3	7	6	53.9	-9.43	0.140	-0.0240
carbon							
tetrachloride	CCl_4	∞	47	96.1	-0.95	0.326	-0.0030
chlorine from	other halocarbon	s		545.9	-32.09	0.466	-0.0270
Total EESC						2.113	-0.0110

 a The Equivalent Effective Stratospheric Chlorine (EESC) is an indicator for the potential of the source gases to destroy stratospheric ozone, in terms of reactive chlorine [Daniel et al., 1995].

Table 2.1: Abundances and trends of halocarbons measured at Cape Grim, Tasmania [Fraser et al., 2000]. The halcarbon lifetimes were adapted from Schauffler et al. [1993] and Wamsley et al. [1998].

2.3 Stratospheric halogen chemistry

2.3.1 Source gases for stratospheric halogen compounds

The fact that industrially produced halogen compounds with a very long residence time in the atmosphere, namely chloroflourocarbons (CFCs), have a potential impact on the stratospheric ozone chemistry, was first pointed out in the mid 70's of the last century [Molina and Rowland, 1974; Rowland and Molina, 1975]. CFCs are chemically inert compounds which are photostable, do not react with surfaces or gases in the atmosphere and have a low water solubility. Therefore CFCs have a very long residence time in the troposphere, varying from years to decades and centuries (see table 2.1), which leads to an almost uniform distribution of these gases throughout the whole troposphere. Due to their long tropospheric residence time, a fraction of the CFCs is, mainly in the tropics, transported into the stratosphere. The stratospheric large scale circulation cell (Brewer-Dobson circulation) leads to slow upward and poleward transport of the air masses [Dobson, 1930; Brewer, 1949] and a downward movement over the polar regions. The high energy UV radiance in the middle and upper stratosphere leads to the destruction of CFCs by photolysis or reaction with atomic oxygen. The inorganic chlorine compounds released by the destruction of these precursors are key reactants for the destruction of stratospheric ozone.

In addition to CFCs, a number of halocarbons of both natural and anthropogenic origin are emitted into the atmosphere (e.g. CH_3Br , CH_2Br_2 , $CH_2BrCl,...$). Most of them have a short lifetime compared to CFCs, but species like methyl bromide (CH_3Br) and methyl chloroform (CH_3CCl_3) (with a lifetime of 1.6 and 7 years, respectively) are relatively stable in the troposphere and can therefore contribute significantly to the stratospheric halogen budget. Organic iodine compounds generally have a very short lifetime between hours and days. It is therefore unlikely that large amounts of iodine reach the stratosphere. However, already small concentrations of reactive iodine in the lower stratosphere would have a large impact on the ozone budget due to its large ozone depletion potential [Solomon et al., 1994; Solomon et al., 1997]. The sources of short- lived halocarbons, which are of importance for the atmospheric chemistry of the marine boundary layer, are described in section 2.4.1.

Table 2.1 summarises the lifetimes and tropospheric and stratospheric abundances of several halogenated hydrocarbons. The Equivalent Effective Stratospheric Chlorine (EESC) listed in table 2.1 illustrates that the ability of the individual halocarbons to destroy ozone depends on their tropospheric lifetime (which determines the probability to enter the stratosphere), their stratospheric lifetime (which determines the rate of release of reactive halogen compounds), the number of halogen atoms per halocarbon molecule and on the ozone depletion potential of the different halogen species (bromine and chlorine).

Since the time scale for a Brewer-Dobson circulation cycle is approximately 5 years, CFC-11 with its lifetime of 55 years circulates about 10 times through the stratosphere before it is completely removed by photo dissociation. The worldwide production of CFCs was limited and finally stopped after the Montreal protocol (1987) and the amendments of Copenhagen (1990), London (1992) and Montreal (1997). Figure 2.4 shows that the chlorine loading of the stratosphere has peaked in the early 90's and is now expected to decline due to the global prohibition of CFC production. Due to the relatively slow troposphere/stratosphere exchange, the stratospheric chlorine abundance follows the tropospheric CFC trend with a delay of about 10 years (compare the tropospheric abundance of halocarbons in figure 2.4 with the lower stratospheric Cl_y loading in figure 2.5). The critical chlorine level of 2ppb, below which a recovery of the ozone hole is expected to occur, is predicted for the middle of this century. However, a possible radiative cooling of the stratosphere due to the coupling to a possible global warming could delay the recovery of the ozone hole [Shindell et al., 1998].

2.3.2 Stratospheric gas phase nitrogen chemistry

This section briefly describes the stratospheric gas phase nitrogen chemistry. The heterogeneous processes involving nitrogen species are described in section 2.3.4.

The most abundant nitrogen species during day are NO and NO_2 . Their partitioning is controlled via the reaction of NO with ozone and the photolysis of NO_2 :

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (2.19)

$$NO_2 + h\nu \longrightarrow NO + O$$
 (2.20)



Figure 2.4: EESC from CFCs, solvents (CH₃CCl₃ and CCl₄), halons and HCFCs based on measurements at Cape Grim, Tasmania (solid lines) compared to the Montreal Protocol scenario [Madronich and Velders, 1999] (dashed lines). Adapted from Fraser et al. [2000].

In absence of sunlight, N_2O_5 is formed via the reactions

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
 (2.21)

$$NO_2 + NO_3 + M \longleftrightarrow N_2O_5 + M$$
 (2.22)

NO₃ is not present in the sunlit atmosphere since it is rapidly destroyed by photolysis $(J(NO_3) = 0.36 \text{ sec}^{-1})^1$. The photolysis of N₂O₅ proceeds some orders of magnitude slower than the photolysis of NO₂ $(J_{NO_2} \approx 1.4 \cdot 10^{-2} \text{ sec}^{-1}, J_{N_2O_5} \approx 3 \cdot 10^{-5} \text{ sec}^{-1})$. Therefore a decrease in the NO₂ concentration is observed at sunrise, until a photochemical steady state between NO₂ and NO is established. Accordingly, the NO₂ concentration increases in the evening due to its reduced photolysis and the reaction of NO with O₃. The slow photolysis of N₂O₅ leads to an increase of NO₂ during day and therefore to higher NO₂ concentrations in the evening than in the morning. These processes (and the heterogeneous conversion of N₂O₅ to HNO₃ described in section 2.3.4) lead to a pronounced seasonal variation of NO₂. NO₂ is almost completely converted to the reservoir species N₂O₅ and HNO₃ during the long winter nights. Also, the equilibrium of reaction (2.22) depends strongly on the temperature with N₂O₅ being more stable under cold conditions. The abundance of NO₂ therefore decreases strongly during winter (*denoxification*).

Heterogeneous reactions on particles have a strong impact on the partitioning of stratospheric nitrogen compounds via the conversion of N_2O_5 to HNO_3 , and in turn on the par-

¹Photolysis rates are given for a solar zenith angle of $\Theta = 0^{\circ}$.



Figure 2.5: Predicted temporal evolution of CFCs and chlorine loading in the lower stratosphere according to the Montreal protocol and the Copenhagen amendments. Also shown are the emission trends for the greenhouse gases CO_2 , CH_4 and N_2O , which are thought to delay the recovery of the ozone hole for up to 20 years due to radiative cooling of the stratosphere. Adapted from Shindell et al. [1998].

titioning of halogen species due to the reduced formation of halogen nitrates during polar winter. Processes on aerosol and cloud surfaces involving halogen and nitrogen compounds are therefore closely linked. The heterogeneous chemistry and its impact on the partitioning of nitrogen species is described in section 2.3.4.

2.3.3 Stratospheric gas phase halogen chemistry

Due to the anthropogenic release of halocarbons, chlorine is the most abundant halogen species in the stratosphere with Cl_y mixing ratios of about 3-3.5ppb [Stachnik et al., 1999]. In the lower stratosphere, most of the chlorine is present in its inactivated form due to the reaction with NO₂, HO_x or CH₄:

$$ClO + NO_2 + M \longrightarrow ClONO_2 + M$$
 (2.23)

$$ClO + OH \longrightarrow HCl + O_2$$
 (2.24)

$$Cl + HO_2 \longrightarrow HCl + O_2$$
 (2.25)

$$Cl + CH_4 \longrightarrow HCl + CH_3$$
 (2.26)

The re-conversion of HCl and ClONO₂ in the gas phase,

$$ClONO_2 + h\nu \longrightarrow ClO + NO_2$$
 (2.27)

$$HCl + OH \longrightarrow Cl + H_2O$$
 (2.28)



Figure 2.6: Observations of chlorine partitioning as a function of altitude from an instrument on board the space shuttle [Zander et al., 1996; Solomon, 1999].

occurs only in the upper stratosphere between 30 and 50km (see figure 2.6), since it requires high energy UV radiation and the availability of OH. Chlorine can, however, be effectively activated in the lower stratosphere by heterogeneous processes. This will be discussed in detail in section 2.3.4.

Under 'normal' (non-ozone hole) conditions, chlorine is mainly present in its inactivated form in the lower stratosphere since the chlorine partitioning is controlled by the above gas phase reactions. In this case, the following catalytic cycles are mainly important for the ozone budget in the upper stratosphere (above 30km), where a fraction of about 10% of inorganic chlorine is available in its activated forms Cl, ClO and Cl_2O_2 (= Cl_x):

1. ClO_x cycle:

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{2.29a}$$

$$ClO + O \longrightarrow Cl + O_2$$
 (2.29b)

net: $O_3 + O \longrightarrow 2O_2$

2. ClO dimer cycle:

$$2Cl + 2O_3 \longrightarrow 2ClO + 2O_2$$
 (2.30a)

$$2ClO \longrightarrow Cl_2O_2 \tag{2.30b}$$

$$Cl_2O_2 + h\nu \longrightarrow ClOO + Cl \qquad (2.30c)$$

$$ClOO + M \longrightarrow Cl + O_2 + M$$
 (2.30d)

net:
$$2O_3 + h\nu \longrightarrow 3O_2$$

3. ClO/HO_2 cycle:

- $Cl + O_3 \longrightarrow ClO + O_2$ (2.31a)
- $OH + O_3 \longrightarrow HO_2 + O_2$ (2.31b)
- $ClO + HO_2 \longrightarrow HOCl + O_2$ (2.31c)
- $HOCl + h\nu \longrightarrow Cl + OH$ (2.31d)

net:
$$2O_3 + h\nu \longrightarrow 3O_2$$

4. ClO/NO_2 cycle:

 $Cl + O_3 \longrightarrow ClO + O_2$ (2.32a)

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (2.32b)

$$ClO + NO_2 \longrightarrow ClONO_2$$
 (2.32c)

$$ClONO_2 + h\nu \longrightarrow ClO + NO_3$$
 (2.32d)

$$NO_3 + h\nu \longrightarrow NO + O_2$$
 (2.32e)

net: $2O_3 + h\nu \longrightarrow 3O_2$

The bromine reservoir species are in general less tightly bound compared to their chlorine counterparts. Bromine nitrate (BrONO₂) has a photolytic lifetime of a few minutes throughout the sunlit stratosphere compared to ClONO₂ with a lifetime of about 5 hours. BrONO₂ can therefore be expected to be close to photochemical steady state with BrO and NO₂ during day; HBr is the bromine reservoir species with the longest photolytic lifetime of about one day. The formation of the reservoir species occurs via

$$BrO + NO_2 + M \longrightarrow BrONO_2 + M$$
 (2.33)

$$Br + HO_2 \longrightarrow HBr + O_2$$
 (2.34)

$$Br + HCHO \longrightarrow HBr + CHO$$
 (2.35)

The rate constants for HBr formation at 220K are $k = 9.6 \cdot 10^{-13}$ cm³ molec⁻¹ sec⁻¹ and $k = 4.5 \cdot 10^{-13}$ cm³ molec⁻¹ sec⁻¹ for reactions (2.34) and (2.35), respectively, compared to $k = 1.2 \cdot 10^{-11}$ cm³ molec⁻¹ sec⁻¹ and $k = 3.9 \cdot 10^{-11}$ cm³ molec⁻¹ sec⁻¹ for the corresponding chlorine reactions (2.24) and (2.25). Due to the about one hundred times slower formation of HBr and its faster reaction with OH compared to HCl, the maximum contribution of HBr to



Figure 2.7: Modeled Br_y partitioning in the stratosphere for local noon at equinox in the mid-latitudes. Only gas-phase reactions are assumed. Adapted from Lary [1996].

the total inorganic bromine is at most a few percent [Lary, 1996]. The bromine reservoirs are destroyed by the following reactions:

$$BrONO_2 + h\nu \longrightarrow BrO + NO_2$$
 (2.36)

$$HBr + OH \longrightarrow Br + H_2O$$
 (2.37)

$$HBr + O(^{3}P) \longrightarrow Br + OH$$
(2.38)

Due to the relatively short lifetime of BrONO₂ and HBr, a large fraction of inorganic bromine ($\approx 30-50\%$) is present in the form of BrO in the lower stratosphere (see Figure 2.7).

Catalytic cycles involving bromine are:

1. BrO_x cycle:

$$Br + O_3 \longrightarrow BrO + O_2$$
 (2.39a)

$$BrO + O \longrightarrow Br + O_2$$
 (2.39b)

net:
$$O_3 + O \longrightarrow 2O_2$$

2. BrO/HO_2 cycle:

$$Br + O_3 \longrightarrow BrO + O_2$$
 (2.40a)

$$OH + O_3 \longrightarrow HO_2 + O_2$$
 (2.40b)

 $BrO + HO_2 \longrightarrow HOBr + O_2$ (2.40c)

$$HOBr + h\nu \longrightarrow Br + OH$$
 (2.40d)

net:
$$2O_3 + h\nu \longrightarrow 3O_2$$



Figure 2.8: Schematic diagram of the stratospheric gas phase halogen chemistry.

3. BrO/NO_2 cycle:

 $Br + O_3 \longrightarrow BrO + O_2$ (2.41a)

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (2.41b)

$$BrO + NO_2 \longrightarrow BrONO_2 \tag{2.41c}$$

$$BrONO_2 + h\nu \longrightarrow BrO + NO_3$$
 (2.41d)

$$NO_3 + h\nu \longrightarrow NO + O_2$$
 (2.41e)

net: $2O_3 + h\nu \longrightarrow 3O_2$

While reactions (2.40) and (2.41) are important ozone loss processes in the lower stratosphere, reactions (2.39) are of minor importance at low altitudes, but due to the availability of atomic oxygen the dominant catalytic bromine cycle above 30km.

Particularly in the chlorine activated polar vortex, the following BrO/ClO cycle is a very important catalytic process for the destruction of ozone [McElroy et al., 1986]:

$$Br + O_3 \longrightarrow BrO + O_2$$
 (2.42a)

$$Cl + O_3 \longrightarrow ClO + O_2$$
 (2.42b)

$$BrO + ClO \longrightarrow BrCl + O_2 \qquad (\approx 7\%) \qquad (2.42c)$$

$$\longrightarrow Br + ClO_2$$
 ($\approx 38\%$) (2.42d)

$$BrCl + h\nu \longrightarrow Br + Cl$$
 (2.42e)

$$ClO_2 + M \longrightarrow Cl + O_2 + M$$
 (2.42f)

net: $2O_3 + h\nu \longrightarrow 3O_2$

with branching ratios of the reaction of BrO with ClO given for T = 210K. The reaction channel (2.42d) involving the formation of ClO₂ is about one order of magnitude more effective

Cycle	Reaction(s)	Approx. chain length
HO_x	(2.3)- (2.5)	1,000,000
NO_x	(2.7), (2.8)	300
ClO_x	(2.29), (2.30)	50
ClO/HO_2	(2.31)	20
ClO/NO_2	(2.32)	8
BrO_x	(2.39)	5000
BrO/HO_2	(2.40)	10,000
BrO/NO_2	(2.41)	10,000
BrO/ClO	(2.42)	10,000

Table 2.2: Chain length of ozone destroying catalytic cycles in the mid-latitude lower stratosphere. Adapted from Lary [1996].

in destroying ozone than the cycle involving BrCl (reaction (2.42c)). The reaction of BrO with ClO has a third reaction channel:

$$BrO + ClO \longrightarrow Br + OClO$$
 ($\approx 55\%$) (2.42g)

The formation of OClO leads to a null cycle, since OClO photolyses to produce ClO and atomic oxygen:

$$OClO + h\nu \longrightarrow ClO + O$$
 (2.43)

The photolysis of OClO is very fast, which prevents the formation of significant amounts of OClO in the sunlit stratosphere. However, OClO is of importance since it can be detected by spectroscopic measurements using its absorption bands in the UV. Observations of OClO during twilight can therefore act as an (at least qualitative) indicator of chlorine activation [Solomon et al., 1987a; Schiller et al., 1990; Pommereau and Piquard, 1994; Erle et al., 1998b; Frieß, 1997].

The importance of the various catalytic destruction cycles can be quantified by the *chain* length L_C , which is defined as the rate constant k_{limit} of the rate limiting step in the reaction sequence (the XO + YO reaction) divided by the rate k_{dest} of conversion of the involved reactive compound (i.e. NO_x, HO_x, Cl_x, Br_x) into its reservoir species:

$$L_C = \frac{k_{limit}}{k_{dest}} \tag{2.44}$$

 L_C determines the number of cycles a reactive compound passes before it is converted into inactive species, as determined by the speed of the catalytic cycle and the stability of the reservoir species. The chain length of the above described catalytic cycles for midlatitudes is listed in table 2.2. The variation of L_C of 6 orders of magnitudes for the different catalytic cycles reflects their potential do destroy ozone. Reactive bromine is about three orders of magnitude more effective than reactive chlorine in destroying ozone on a per atom basis. Therefore reactive bromine is of great importance for the ozone budget in the lower stratosphere, although the abundances of total stratospheric bromine are about 2000 times smaller than those of chlorine [Schauffler et al., 1993; Wamsley et al., 1998]. However, the chain length of the chlorine cycles, particularly the ClO dimer and BrO/ClO cycles, can be dramatically increased if heterogeneous processes lead to a release of reactive chlorine, as discussed in the next section.

2.3.4 Stratospheric heterogeneous halogen chemistry -The Antarctic ozone hole

The discovery of the ozone hole in the mid 1980's [Farman et al., 1985] came unexpected, since a drop in the ozone total column far below 200 Dobson units² (DU) was not predictable by gas phase chemistry only. As discussed in section 2.3.3, a large fraction of the stratospheric chlorine is present in form of inactive reservoir species (HCl, ClONO₂) when only considering gas phase chemistry. It is now known that heterogeneous processes on particle surfaces have a strong influence on the partitioning of the halogen (and nitrogen) species and lead to an activation of reactive chlorine. Available surface areas for the heterogeneous reactions in the lower stratosphere are believed to be provided by sulfate aerosols at low temperatures (< 220K) and, in the cold polar vortex, by polar stratospheric clouds (PSCs).

The lack of solar radiation leads to very cold temperatures over the polar regions during winter. The large scale descent of stratospheric air masses and the Coriolis force generate a circumpolar wind field, the *polar vortex*. The strong gradient in the potential vorticity³ (PV) at the edge of the polar vortex prevents inner and outer vortex air from mixing.

The cold and dark conditions inside the polar vortex lead to a formation of PSCs, which play a key role in the development of the Antarctic ozone hole. The formation of PSCs occurs at very cold temperatures through the condensation of nitric acid and water. The composition of the PSC particles is important since it determines their formation temperature and the rate of reactions which occur on their surfaces. The various types of PSCs are classified as follows:

- Type 1 PSCs are formed above the frost point below a temperature of about 195K. It was originally suggested that type 1 PSCs were composed of nitric acid trihydrate (NAT) which is stable under stratospheric conditions. However, some type 1 PSCs were observed at high supersaturations with respect to NAT. In situ measurements showed that type 1 PSCs are most likely composed of liquid supercooled ternary solutions (STS; HNO₃/H₂SO₄/H₂O) [Tabazadeh et al., 1994; Carslaw et al., 1994; Carslaw et al., 1995]. The type 1 PSCs are subdivided into two types according to their depolarisation characteristics:
 - Type 1a PSCs are depolarising as expected for aspherical solid particles. At least a part of these particles are most likely composed of NAT.
 - Type 1b PSCs are non-depolarising particles, suggesting liquid rather than solid particles. Various measurements are consistent with the description of type 1b particles as being composed of STS.
- *Type 2 PSCs* are composed of water ice particles and form below a temperature of about 188K. Since they can rapidly grow by further condensation of water vapour, they can be irreversibly removed from the stratosphere by sedimentation (dehydration).

²One Dobson unit is defined as the hundredths part of an ozone column of one millimetre height at standard pressure and temperature: $1\text{DU} \approx 2.7 \cdot 10^{16} \text{ molec/cm}^2$.

³The potential vorticity is defined as $PV = \frac{\eta}{\rho} \cdot \frac{d\theta}{dz}$ with the vorticity $\eta = 2\Omega \sin \phi + (\vec{\nabla} x \vec{v})_z$ (Ω : angular velocity of the earth rotation, ϕ : latitude, v: velocity of the air parcel), the air density ρ , the potential temperature θ and the altitude z. The potential vorticity is conserved along trajectories of air parcels and is an indicator for the vortex strength.


Figure 2.9: Schematic illustration of the PSC composition and possible phase transitions between liquid and solid particles. Liquid phases ar symbolised by circles, solid phases by boxes. NAT is indicated by $\backslash\$ hatching, ice by /// hatching and SAT by gray box shading. Adapted from Larsen [1999].

The various phase transitions which occur between the different types of PSCs are of importance since their chemical composition and physical properties determines the heterogeneous reaction rates. An overview on the composition and phase transitions between the different PSC types is provided by figure 2.9.

The following heterogeneous reactions occur on/in polar stratospheric cloud particles and sulphate aerosols:

$$N_2O_5 + H_2O(s) \longrightarrow 2HNO_3(s) \tag{2.45}$$

$$N_2O_5 + HCl(s) \longrightarrow ClNO_2 + HNO_3(s) \tag{2.46}$$

$$ClONO_2 + H_2O(s) \longrightarrow HOCl + HNO_3(s)$$
 (2.47)

$$ClONO_2 + HCl(s) \longrightarrow Cl_2 + HNO_3(s)$$
 (2.48)

$$HOCl + HCl(s) \longrightarrow Cl_2 + H_2O(s)$$
 (2.49)

$$BrONO_2 + H_2O(s) \longrightarrow HOBr + HNO_3(s)$$
 (2.50)

$$BrONO_2 + HCl(s) \longrightarrow BrCl + HNO_3(s)$$
 (2.51)

 $HOBr + HCl(s) \longrightarrow BrCl + H_2O(s)$ (2.52)

Here, (s) denotes the liquid or solid phase. These heterogeneous reactions have important implications on the partitioning of the stratospheric halogen and nitrogen species:



Figure 2.10: Modeled seasonal variation of the chlorine (left) and bromine (right) partitioning at 75°S and 50mbar including heterogeneous chemistry on PSCs and sulphate aerosol. Note the different time scales on the x-axis. Adapted from Danilin and McConnell [1994].

- N_2O_5 is converted to HNO_3 , which remains in the particles. Sedimentation of PSCs can irreversibly remove inorganic nitrogen from the stratosphere (*denitrification*), leading to a more pronounced chlorine activation due to the reduced formation of chlorine nitrate.
- The halogen reservoir species ClONO₂, HCl, BrONO₂ and HBr are efficiently converted into the less photostable compounds Cl₂, HOCl, BrCl and HOBr.
- Photolysis leads to the rapid conversion of Cl₂, HOCl, BrCl and HOBr to Cl, ClO, Br and BrO after polar sunrise. These halogen radicals initiate an almost complete destruction of ozone in the lower stratosphere during polar spring by catalytic cycles described in section 2.3.3. Since the efficiency of the ClO dimer cycle (2.30) is proportional to the square of the ClO concentration, it becomes the most important catalytic ozone destruction cycle in chlorine activated air masses. The ClO dimer cycle is responsible for about 75% of the ozone destruction in Antarctic spring. Also the chain length of the BrO/ClO cycle (2.42), which is already in the order of 10⁴ under undisturbed conditions, is strongly increased due to heterogeneous chlorine release.

Figure 2.10 illustrates the seasonal cycle of the chlorine and bromine compounds at 75°S, as determined by model calculations. Since the formation of BrONO₂ is reduced due to denoxification, the BrO mixing ratio increases during winter. During late winter, HCl is completely converted into reactive chlorine compounds (Cl, Cl₂, ClO, and HOCl) by heterogeneous processes. Another important chlorine compound formed during late formed by reaction (2.30b), the chlorine monoxide dimer Cl_2O_2 [Molina and Molina, 1987], is not shown in figure 2.10. Due to the heterogeneous conversion of HOBr and BrONO₂ (reactions (2.51) and (2.52)), BrCl is the most abundant bromine reservoir species before sunrise during mid-winter. Reactive halogen species are rapidly formed by these compounds under solar illumination. Therefore, ozone immediately starts to decline after polar sunrise. The depletion lasts until the chlorine species are completely re-converted into HCl and ClONO₂.

Figure 2.11 shows strikingly the impact of halogen activation on ozone in the lower stratosphere: while the ozone mixing ratio typically ranges between 4 and 6ppm under undisturbed conditions, it is completely destroyed in altitudes between 14 and 21km during Austral spring. This leads to ozone column densities of less than 120DU for the example shown in figure 2.11.



Figure 2.11: Ozone profiles at Neumayer during late winter, spring and early summer of 1999. The data is kindly provided by G. König-Langlo, AWI.

2.3.5 Dynamical aspects of ozone depletion

An important prerequisite for the formation of an ozone hole is the effective isolation of inner vortex air masses from ozone-rich mid-latitude air. Due to the symmetry of the Antarctic continent and the lack of land masses around, a stable and persistent polar vortex is established each winter over Antarctica. In contrast, the northern polar region is surrounded by inhomogeneous land masses with mountains as topographic barriers, leading to a higher planetary wave activity compared to the south. Therefore a stable and persistent vortex as observed in Antarctica is usually not observed over the Arctic. This leads to a higher mixing between inner-vortex and mid-latitude air and higher temperatures inside the polar vortex. Only relatively small areas in the Arctic are sufficiently cold to form PSCs which trigger the release of reactive chlorine, while temperatures below the PSC threshold are found in winter over the whole Antarctic continent. It therefore depends strongly on the current meteorology if significant chlorine activation can occur in the Arctic stratosphere.

Figure 2.12 illustrates that ozone loss in the Arctic is subject to a large year-to-year variability: ozone loss occurs whenever the temperature drops below the PSC threshold value and polar stratospheric clouds are likely to occur. While ozone loss rates of more than 40ppb/day are determined during cold years (such as 1995 and 1997), the winter of 1998 was too warm for PSC formation and almost no ozone depletion was observed.

The difference in the amount of ozone destruction between both hemispheres is shown in figure 2.13. Both measurements and model predictions show that the minimum ozone column density during spring in the northern hemisphere is larger on average and has a much higher year to year variability than in the southern hemisphere. Since small negative temperature trends would already have a strong impact on the PSC incidence and therefore on the chlorine activation, a possible radiative cooling of the stratosphere due to global warming is expected to have a much stronger impact on the ozone depletion of the northern than on the southern



Figure 2.12: Results from the Match campaign: Ozone loss in the Arctic (left-hand scale, symbols) and area of possible PSC incidence (right-hand scale, gray areas) [Becker et al., 1998; Rex et al., 1999; Schulz et al., 2000].



Figure 2.13: Measured (filled symbols) and predicted (open symbols) total column ozone minima in the polar regions during spring, averaged over the last three days of September (southern hemisphere) and March (northern hemisphere). Adapted from Shindell et al. [1998].

2.4. TROPOSPHERIC HALOGEN CHEMISTRY

Compound	Laminaria	Desmarestia	Fucus
	saccarina	a culeata	distichus
CH_2Br_2	8.2	0.9	8.1
$CHBr_3$	71.5	3.4	17.4
CHBrCl_2	0.07	0.02	0.07
$\mathrm{CHBr}_{2}\mathrm{Cl}$	1.8	0.2	0.5
OTT T			
CH_3I	0.2	0.14	0.8
CH_2I_2	4.1	1.6	0.08
CH_2CII	0.2	0.04	0.16
$CH_3CH_2CH_2I$	0.0	0.02	0.15
CH_3CHICH_3	0.0	0.14	0.8
CH_3I	0.2	0.14	0.8

Table 2.3: Releasing rates of iodinated and brominated substances by different polar macroalgae. All releasing rates are given in ng per g of wet weight alga and day.

hemisphere [Shindell et al., 1998].

2.4 Tropospheric halogen chemistry

2.4.1 Source gases for tropospheric halogen compounds

Since the high energy UV radiation is effectively absorbed by ozone in the lower stratosphere, the man-made CFCs are too stable to be photolysed and to release any halogen compounds in the troposphere. However, halocarbons emitted from natural sources are potential precursors for reactive halogen compounds in the remote Antarctic boundary layer. Besides, methyl bromide (CH₃Br) has also anthropogenic sources like fumigation of soils, burning of leaded gasoline and biomass burning.

Macroalgae and phytoplankton are responsible for a part of the total production of volatile iodinated and brominated organic substances in the polar coastal seawater and therefore for their corresponding atmospheric abundance. The production of halocarbons by different types of macroalgae in the south polar sea was investigated by Schall et al. [1994]. The production rates are listed in table 2.3. If the ocean becomes supersaturated of these compounds, the ocean acts as a source for hydrocarbons. This is in particular the case for iodinated hydrocarbons with mean sea water concentrations of 2.5 ng/l for methyl iodide (CH₃I) and 0.15 ng/l for chloroiodomethane (CH₂CII) in the south polar sea [Reifenhäuser and Heumann, 1992].

There is only limited knowledge about the primary production of biomass related to algaes and phytoplankton and about the related release of brominated and iodinated compounds into the atmosphere [Lønne, 1999]. The primary production of biomass in the Southern Ocean per area and year is estimated to 645 gCm⁻²y⁻¹, compared to only 282 gCm⁻²y⁻¹ on average for all oceans [Longhurst et al., 1995]. Only rough estimates exist on the biomass production of the sea ice covered Antarctic ocean during winter. The total primary biological production associated with Antarctic sea is is estimated to $2.14 \cdot 10^{14}$ gCy⁻¹ [Legendre et al., 1992]. Thus 33% of the total primary production takes place below, in, or on the surface of the sea ice, with the majority $(1.41 \cdot 10^{14} \text{ gC/y}^{-1})$ being produced in the water column in ice edge blooms. While the biological activity is more uniformly distributed over the whole water column during summer, it is concentrated on the surface in the ice covered ocean. This makes it likely that

Compound	Approx. lifetime	Mixing ratio [ppt]
CH_3Br	8 months^a	10^{a}
$\mathrm{CH}_{2}\mathrm{Br}_{2}$	4 months^b	$< 1.5^{c}$
CH_2BrCl	5 months^d	$< 0.5^{c}$
$\mathrm{CHBr}_{2}\mathrm{Cl}$	1.2 months^d	$< 0.5^{c}$
CHBr_3	1.2 months^e	$< 2.0^{c}$
CHBrCl_2	1.2 months^d	$< 0.5^{c}$
$CH_{3}I$	5 days^f	2.4^{g}
C_3H_7I	40 hours^{f}	0.43^{h}
CH_2CII	5 hours^f	$\mathrm{n.d.}^h$
$\mathrm{CH}_{2}\mathrm{I}_{2}$	5 minutes^f	0.5^{h}

^a[Butler and Rodriguez, 1996]

^b[Mellouki et al., 1992]

^c[Schall and Heumann, 1993]

d[Bilde et al., 1998]

 e [Moortgat et al., 1993]

f[Vogt et al., 1999]

^g[Reifenhäuser and Heumann, 1992]

 h [Carpenter et al., 1999]

Table 2.4: Lifetime and typical tropospheric mixing ratio of brominated and iodinated substances. Adapted from Schauffler et al. [1999], Carpenter et al. [1999] and Vogt et al. [1999]. 'n.d.' = not detected.

the emission of halocarbons to the atmosphere per weight of algaes is strongly increased during winter, although the total biomass production is decreased.

The lifetime of biogenic organoiodine and organobromine compounds ranges from about one year to a few minutes (see table 2.4). Bromocarbons are generally more stable compared iodocarbons. Methyl bromide (CH₃Br), the by far most abundant bromocarbon in the troposphere, has a lifetime of approximately 8 months. Apart from the fact that methyl bromide is one of the most important source gases for reactive bromine in the lower stratosphere, its decomposition at lower altitudes possibly contributes to a global BrO background in the free troposphere [Frieß et al., 1999; Fitzenberger et al., 2000]. Iodocarbons are rapidly destroyed by photolysis or degradation with OH, with lifetimes between 5 days for methyl iodide (CH₃I) and only 5 minutes for diiodomethane (CH₂I₂). Therefore organic iodine compounds are rapidly destroyed to form reactive iodine (I, IO) which has a large potential impact on the boundary layer ozone chemistry.

In addition to the emission and photolysis of short lived halocarbons, the release of reactive halogens from sea salt aerosols can have an important impact on the ozone chemistry in the marine boundary layer. Under particular circumstances, large amounts of bromine can be released from sea salt aerosols by autocatalytic processes. These processes will be described in section 2.4.2.

2.4.2 Reactive halogens in the troposphere

Significant amounts of BrO and IO were recently found in the marine boundary layer (MBL) of various coastal areas. Strong and sudden increases in the BrO mixing ratio during spring were found both in the Arctic [Hausmann and Platt, 1994; Tuckermann et al., 1997] and in the



Figure 2.14: GOME satellite picture showing clouds of enhanced BrO on the sea ice around the Antarctic continent. Kindly provided by M. Wenig and J. Hollwedel.



Figure 2.15: Ozone, filterable bromine and BrO mixing ratios observed at Ny Alesund, Spitsbergen during the ARCTOC campaign 1996. Adapted from Langendörfer et al. [1999].

Antarctic [Kreher et al., 1997; Frieß, 1997]. Enhanced concentrations of water soluble bromine species in sea salt aerosols that can be collected by aerosol filters were found simultaneous to elevated levels of BrO [Langendörfer et al., 1999; Lehrer, 1999] (see figure 2.15). Huge clouds of highly elevated BrO amounts over the polar sea ice of both hemispheres, with areas of several thousand km², were observed from satellite [Wagner and Platt, 1998; Richter et al., 1997; Hegels et al., 1998]. Thse events of highly elevated BrO in polar regions, with levels of up to 30ppt, were always coincident with the destruction of MBL ozone, indicating that reactive bromine is responsible for its catalytic destruction. Enhanced BrO in the boundary layer associated with ozone destruction was also detected over the Caspian Sea [Leue et al., 2000] and in the Dead Sea basin [Hebestreit et al., 1999].

Iodine oxide was found at various marine sites with mixing ratios of several ppt: at coastal



Figure 2.16: Simplified scheme of the tropospheric halogen chemistry. Source gases are shown in brown, red arrows indicate ozone depleting catalytic reaction cycles, and blue arrows indicate heterogeneous autocatalytic halogen release mechanisms. Adapted from Platt and Janssen [1997] and Vogt et al. [1999].

sites in Ireland [Alicke et al., 1999], at the Canarian Islands [Allan et al., 2000], and in the high Arctic [Wittrock et al., 2000]. First observations of iodine oxide in the Antarctic marine boundary layer are reported in this thesis.

A mechanism suggested to cause the observed sudden BrO enhancements in the MBL is the autocatalytic release of BrO involving heterogeneous reactions on sea salt surfaces [Fan and Jacob, 1992; Tang and McConnel, 1996; Vogt et al., 1996]. The release of reactive halogens from acidic sea salt surfaces occurs via the uptake of gaseous HOX (in the following, X and Y denote halogen atoms: X,Y = Cl, Br, or I):

$$X + O_3 \longrightarrow XO + O_2$$
 (2.53a)

$$OH + O_3 \longrightarrow HO_2 + O_2$$
 (2.53b)

$$XO + HO_2 \longrightarrow HOX + O_2$$
 (2.53c)

$$HOX + (Y^{-})_{aq} + (H^{+})_{aq} \longrightarrow XY + (H_2O)_{aq}$$

$$(2.53d)$$

$$XY + h\nu \longrightarrow X + Y$$
 (2.53e)

net:
$$X + OH + (Y^{-})_{aq} + (H^{+})_{aq} + 2O_3 + h\nu \longrightarrow X + Y + (H_2O)_{aq} + 3O_2$$

Here, (aq) denotes the aqueous phase, i.e. reactions on sea salt aerosol surfaces. This

halogen release mechanism is also illustrated in figure 2.16 when following the blue arrows. The oxidation of Y^- to Y by O₃ leads to the release of two halogen atoms for each halogen atom scavenged by the sea salt surface as HOX. In case of X = Y = Br, this mechanism can lead under particular circumstances to an exponential growth of gaseous reactive bromine, the *bromine explosion* [Platt and Lehrer, 1997]. The release of Br₂ is preferred to BrCl, even if Br is much less abundant in a sea salt solution [Fickert et al., 1999]. The following prerequisites are necessary for the formation of a bromine explosion:

- 1. The bromine release from sea salt only occurs for pH < 6.5. A high acidity of the aerosol could by caused by the uptake of strong acids, such as HNO₃ and H₂SO₄ [Lehrer, 1999].
- 2. The heterogeneous processes only lead to an exponential increase in gaseous reactive halogen compounds if more than one halogen atom is produced for each scavenged XOBr molecule. This is the case for X = Y = Br in cycle (2.53). An analogous 'chlorine explosion' mechanism does not exist because the gas-phase conversion of Cl to HOCl is too inefficient. An 'iodine explosion' is not expected to occur since the concentration of particulate iodine is too small. The bromide to chloride ratio in sea water is about 1:700, the corresponding ratio for iodide is 1:40,000. However, strong enrichments in particulate iodine were found in Antarctic aerosol samples [Gäbler and Heumann, 1993]. If reactive iodine is abundant in the atmosphere, it can have the effect of accelerating photochemical release of Br and Cl from the sea salt [Vogt et al., 1999].
- 3. To keep the concentrations of the bromine reactants high, the meteorological conditions must prevent boundary layer air from mixing with air from the free troposphere. During late winter and early spring, strong inversion layers in the lowermost 1000m of the atmosphere effectively confine the boundary layer in the polar regions.
- 4. Aerosols and sea ice surfaces strongly enriched in sea salt can be provided by brine (a liquid layer with a high salinity on the frozen sea ice) and frost flowers.
- 5. The autocatalytic bromine release and the subsequent destruction of ozone requires light, which is provided after polar sunrise.
- 6. Any initial reactive bromine can now start the heterogeneous bromine release on these sea salt surfaces.
- 7. The released bromine causes the destruction of ozone in the marine boundary layer. When all ozone is consumed, reactive Br is converted HBr and scavenged by the aerosol as bromide (Br⁻).
- 8. After the reconversion of reactive bromine into inactive compounds, ozone can recover due to mixing processes.
- 9. This cycle can be passed several times during polar spring.

Because of the prerequisites listed above, episodes of bromine explosion events and boundary layer ozone depletion in polar regions are only observed during spring.

While the major source for reactive bromine in the MBL is thought to be the above described autocatalytic release on sea salt surfaces, the main source for reactive iodine in coastal regions are iodocarbons emitted from the sea surfaces and their subsequent photolysis or degradation by OH. However, catalytic processes corresponding to reactions (2.53) involving

HOI can lead to an additional release of reactive halogens from aerosols and sea ice surfaces. Thus the presence of reactive iodine in the MBL is expected to have no 'event-like' character as it is the case for bromine. Instead, the abundance of inorganic iodine is mainly linked to the biogenic activity in the ocean and to the distance of the open sea as the source region for iodocarbons.

Reactive halogen compounds in the troposphere can destroy ozone by the following reaction cycles:

$$X + O_3 \longrightarrow XO + O_2 \tag{2.54a}$$

$$Y + O_3 \longrightarrow YO + O_2 \tag{2.54b}$$

$$XO + YO \longrightarrow X + Y + O_2$$
 (2.54c)

 $\longrightarrow XY + O_2 \tag{2.54d}$

$$\longrightarrow OXO + Y$$
 (2.54e)

net:
$$2O_3 \longrightarrow 3O_2$$

- $X + O_3 \longrightarrow XO + O_2 \tag{2.55a}$
- $OH + O_3 \longrightarrow HO_2 + O_2$ (2.55b)
- $XO + HO_2 \longrightarrow HOX + O_2$ (2.55c)
- $HOX + h\nu \longrightarrow OH + X$ (2.55d)

net:
$$2O_3 + h\nu \longrightarrow 3O_2$$

with X, Y = Cl, Br, I. In case of X=Y=Br, these cycles lead to the complete destruction of boundary layer ozone during bromine explosion events described above. In case of X=I, cycle (2.55) involving OH radicals is very effective in destroying ozone. Model calculations have shown that the IO/HO_x cycle accounts for up to 50% of the ozone destruction if only 3-4ppt of organic iodine are abundant in the MBL [Vogt et al., 1999] (see figure 2.17). The importance of reactive iodine on the tropospheric ozone budget is thus comparable to the odd oxygen ozone loss processes if only a few ppt of reactive iodine is present.

Not only the source mechanisms, but also the sinks of reactive bromine and iodine are distinctly different. The most important sink for reactive bromine is the formation of HBr by its reaction with HO_2 , formaldehyde (HCHO) or alkenes and its subsequent uptake on aerosols [Bedjanian et al., 1998]:

$$Br + HO_2 \longrightarrow HBr + O_2$$
 (2.56a)

$$Br + HCHO \longrightarrow HBr + CHO$$
 (2.56b)

A recycling of HBr to reactive bromine is possible via the gas phase reaction of HBr with OH [Cox et al., 1999]:

$$HBr + OH \longrightarrow Br + H_2O$$
 (2.57)



Figure 2.17: Ozone destruction rates of the different catalytic reaction cycles, based on a model study of iodine chemistry in the MBL. Adapted from Vogt et al. [1999].

However, the lifetime of HBr controlled by reaction (2.57) is on the order of half a day. Therefore the destruction of HBr by OH is too slow to be an effective recycling mechanism for reactive bromine.

In contrast, I atoms do not react with hydrocarbons to form HI. However, the reaction of iodine with HO_2 ,

$$I + HO_2 \longrightarrow HI + O_2 \tag{2.58}$$

is a reaction path which leads to the formation of HI. The rate constant for the HI decomposition reaction

$$HI + OH \longrightarrow I + H_2O$$
 (2.59)

 $(k = 7 \cdot 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$ is a factor of seven larger than the rate constant of the corresponding HBr decomposition reaction (2.57) $(k = 1.1 \cdot 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$, the lifetime of HI is accordingly shorter (at most some hours). Also, the iodine compounds IONO₂, I_2O_2 and INO₂ with photolytic lifetimes of only a few minutes act only as temporary reservoir species and not as a sink for reactive iodine. Vogt et al. [1999] have suggested the uptake of the IO dimer on aqueous aerosol surfaces or the self- reaction of IO in the aqueous phase, followed by a hydrolysis reaction:

$$IO + IO \longrightarrow I_2O_2$$
 (2.60a)

$$I_2O_2 + (H_2O)_{aq} \longrightarrow (HOI)_{aq} + (IO_2)^-_{aq} + (H^+)_{aq}$$
 (2.60b)

$$IO + IO + (H_2O)_{aq} \longrightarrow (HOI)_{aq} + (IO_2)^-_{aq} + (H^+)_{aq}$$
 (2.60c)

$$(IO_2)_{aq}^- + (H_2O_2)_{aq} \longrightarrow (IO_3)_{aq}^- + (H_2O)_{aq}$$
 (2.60d)

The formation of iodate (IO_3^-) is a possible loss process for reactive iodine since reactions (2.60) lead to an accumulation of this compound in the aerosol. Another possible sink is the formation of OIO:

$$IO + YO \longrightarrow OIO + Y$$
 (2.61)

with Y = Br, I. In contrast to OClO and OBrO, computational studies suggest that OIO may be photolytically stable since the calculated threshold wavelength for its photo dissociation via

$$OIO + h\nu \longrightarrow IO + O(^{3}P)$$
 (2.62)

is 418nm [Misra and Marshall, 1998], while the visible absorption spectrum of OIO covers the wavelength region between 480 and 660nm [Cox et al., 1999]. The mechanisms to reactivate OIO are still uncertain. The following reactions with OH and NO possibly lead to a reconversion of OIO into reactive iodine:

$$OIO + NO \longrightarrow IO + NO_2$$
 (2.63a)

$$OIO + OH \longrightarrow IO + HO_2$$
 (2.63b)

Measurements from Hebestreit [2001], who observed OIO for the first time in the boundary layer, suggest that the reaction with NO (2.63a) is the most important loss process for OIO. He has estimated a lifetime of OIO of approximately 20 minutes. However, the NO mixing ratios during these measurements performed at Mace Head, Ireland, were 0.25-1ppb, while typical values for the NO mixing ratio in the Antarctic MBL are 5-10ppt, a factor of 100 smaller than during the Mace Head measurements. Thus the formation of OIO can be an important sink for reactive iodine, particularly under the low NO_x conditions in the Antarctic MBL.

Figure 2.18 shows the diurnal cycle of different inorganic iodine species, as calculated by a model study [Vogt et al., 1999]. Formed by reaction (2.55c), HOI is the most abundant iodine species during. Due to the scavenging of HOI by aerosols, the HOI mixing ratio drops during nighttime. This subsequently leads to the release of ICl and IBr by the heterogeneous reactions (2.53). ICl and IBr accumulate in the gaseous phase in absence of sunlight. The iodine radicals I and IO are almost immediately formed at sunrise by the photolysis of IBr and ICl and rapidly vanish at sunrise due to their conversion into reservoir species (note the logarithmic scale of the y-axis in figure 2.18). The mixing ratios of I and IO are almost constant during day, which reflects that they are in photochemical steady state. The iodine oxide dimer (I₂O₂) formed by the IO self reaction (2.60a) shows a pronounced diurnal cycle. I₂O₂ has a photolytic lifetime in the order of five minutes. Due to the reduced photolysis, the



Figure 2.18: Diurnal variation of iodine compounds for equinox at mid-latitudes, adapted from the model study of Vogt et al. [1999]. The formation of OIO is not included in the model.

highest I_2O_2 mixing ratios occur just after sunrise and before sunset and a local minimum occurs around noon. The concentration of I_2O_2 decreases during night with a rate in the order of $30s^{-1}$ due to its thermal decomposition.

Chapter 3

Instrumental Setup

An instrument designed for long-term measurements in remote areas such as Antarctica needs to meet several requirements:

- 1. Since any changes in the optical adjustment can affect the spectral retrieval, high mechanical and thermal stability is required.
- 2. Due to the restricted technical infrastructure, the instrument should be easy to maintain.
- 3. It should be avoided to use any movable parts which could be damaged due to wear and tear.



Figure 3.1: Sketch draw of the instrument setup

- 4. The instrument should cover a large wavelength range with a suitable spectral resolution in order to detect the desired atmospheric compounds.
- 5. Any additional optical components (e.g., mirrors or quartz windows in front of the detectors) which could cause intensity losses or disturbing interference effects should be avoided.

The spectrograph recently developed at the Institut für Umweltphysik for balloon borne direct sunlight measurements [Ferlemann et al., 2000] was found to match the above requirements, but some modifications of the detector cooling, thermal stabilisation and a new design of the entrance optics were necessary.

An outline of the instrumental setup is shown in figure 3.1. Zenith scattered sunlight is collected using a small telescope as described in section 3.2. The light is fed into the spectrograph using two depolarising fiber bundles, each consisting of 14 individual quartz fibers of $120\mu m$ diameter. The instrument consists of two separate spectrograph units for the UV (320 nm to 420 nm) and visible (400 nm to 650 nm) wavelength regions as described in chapter 3.3. The incoming light is dispersed with two holographic gratings and it is detected by two 1024 channel photodiode arrays (PDAs). To minimise the detector dark current and signal noise, the detectors are thermostabilised at -35° C using water pre-cooled two-stage Peltier cascades. The whole optical set-up is located inside a vacuum sealed aluminium housing which is filled with dry argon.

The PDA signals are preamplified and digitalised using 16-bit analog/digital converters. A commercial DOAS controller unit, manufactured by Hoffmann Messtechnik, controls the measurements and the temperature stabilisation of the PDA cooling. The data is transferred to a personal computer where the spectra are stored on harddisk.

3.1 The measurement site

The German Antarctic research station Neumayer is located on the Antarctic Ekström Shelf Ice (70°39'S, 8°15'W), in a distance of approximately 7km to the Weddell Sea. It is operated by the Alfred Wegener Institute (AWI) for polar and marine research, Bremerhaven. The predecessor of the Neumayer station, the Georg von Neumayer station, was established in 1981 on the Ekström Shelf Ice as a research observatory for geophysical, meteorological and air chemistry measurements, as well as a logistics base for summer expeditions. Due to ice movements and heavy snow deposits, the construction of a new station building in the early 1990s was necessary. The new Neumayer station was completed in 1992 in a distance of about 10km to the old station. The Neumayer station houses meteorological, geophysical and air chemistry observatories. The station is also used as a base for research on sea ice in the Atka Bay located northeast of Neumayer.

The DOAS instrument is installed at the air chemistry observatory at Neumayer. The first air chemistry observatory was initiated 1982 by the Institut für Umweltphysik, University of Heidelberg. Following almost 13 years of operation, the technical equipment and the data acquisition facilities had to be modernised. The new observatory was designed as a container building placed on a platform some metres above the snow. Figure 3.3 shows the Neumayer air chemistry observatory.

The atmosphere above Antarctica is the cleanest part of the earth's troposphere and can be employed as a large clean air laboratory to study natural conditions comparable to atmospheric



Figure 3.2: Map of Antarctica with the position of the Neumayer station.



Figure 3.3: The Neumayer trace gas observatory.

processes prevailed elsewhere in preindustrial times. Furthermore, with the exception of some rocky coastal sites, the Antarctic continent is largely free of aerosol and trace gas sources, so that the main part of atmospheric trace compounds have to be advected by long range transport to Antarctica or has its source region in the surrounding Southern Ocean. Thus local pollution by vehicles and the base itself is a potential problem for many measurements concerning the background status of the Antarctic troposphere. Consequently, a central aspect of the technical concept lies in the possibility of contamination-free sampling of aerosols and trace gases. The Air Chemistry Observatory is situated in a clean air facility approximately 1.5 km south of Neumayer. Due to the fact that northern wind directions are very rare, contamination from the base can be excluded most of the time. The power supply is provided by cable from the main station, thus no fuel driven generator is operated in the vicinity. Contamination free sampling is controlled by the permanently recorded wind velocity, wind direction and by condensation nuclei concentration.

3.2 The entrance optics

The entrance optics consist of a small telescope which focuses parallel light scattered in the zenith to the entrance of both quartz fiber bundles. The telescope setup is sketched in figure 3.4 (see also the construction plans in appendix A.4). The telescope is located inside a stainless steel housing mounted on the roof of the trace gas observatory. Heat resistors (100W) prevent ice and water condensation and freezing on the optical parts. The temperature inside the telescope is monitored using a PT100 sensor.

Zenith scattered sunlight enters through a 45° slanted quartz glass window and is focused on the entrances of both fiber bundles by two quartz glass lenses with f = 50mm focal length. The aperture ratio is adjusted to the grating specifications using appropriate apertures. The instrument's field of view is given by

$$\alpha = 2 \arcsin\left(\frac{d}{2f}\right) \approx 0.86^{\circ} \tag{3.1}$$

with the focal length f = 50mm and the diameter of the fiber entrance $d \approx 0.75mm$ (14 individual fibers with $\approx 150\mu m$ diameter in a circular arrangement).

Both a halogen and a mercury lamp are mounted inside the telescope housing. Their light can be focused on the fiber entrance of each spectrograph without using any mechanical parts, such as movable mirrors, which could easily fail in the cold and stormy environment. For this purpose, the light emitted by both lamps is splitted using a beam splitter cube. A mirror system leads the light horizontally to the entrance window where it is partially reflected on the entrance lenses. Therefore, background spectra (offset, dark current, mercury lamp and halogen lamp) can be recorded automatically each night. During summer, when there is permanent daylight, these measurements are performed manually once per week after covering the entrance window of the telescope to prevent that light enters the instrument. These regularly performed calibration measurements give the ability to characterise the long term stability of the instrument (see section 3.12).

The telescope controller unit contains the power supplies for the telescope heater and the halogen and mercury lamps, which can be switched by software using the analog output ports of the DOAS controller.



Figure 3.4: Sketch draw of the telescope setup



Figure 3.5: The inner parts of the telescope.

3.3. THE SPECTROGRAPH



Figure 3.6: The telescope mounted on the roof of the trace gas observatory at Neumayer Station

	UV	Visible
Manufacturer	Yobin Yvon	American Holographics
Diameter [mm]	70	85
Focal length [mm]	210	160
Aperture ratio	f/3.2	f/2
Grooves/mm	1200	510
Diffraction order	-1	1
Wavelength range [nm]	320 - 420	400 - 650
Average resolution (FWHM) [nm/channel]	0.5/5.0	1.8/7.2

Table 3.1: Grating specifications

3.3 The spectrograph

The instrument consists of two separate spectrograph/detector units for the UV and visible (Vis) wavelength range, located in a single aluminium housing (see also the construction plans in Appendix A.1). Aluminium was chosen to avoid temperature gradients and to ensure a good thermal stability of the instrument. The optical parts of the spectrograph are mounted in a 'sandwich' design between 3 and 5mm thick stainless steel plates which ensure a high mechanical stability. All inner parts are blackened using Teflon coating. The housing is evacuated ($p < 10^{-5}$ mBar) and filled with dry argon under slight over-pressure to avoid any freezing or condensation of water onto the cooled detector surfaces. At the the fiber bundles exit, the 14 quartz fibers are arranged as columns, serving as entrance slits. The light is dispersed in each spectrograph using concave holographic gratings and is detected with photo diode arrays. The characteristics of both gratings are listed in table 3.1.

To avoid any changes in the optical adjustments and to improve the detector cooling, the housing is held on a stable temperature of -10° C using a commercial water cooling device with an heat exchanger mounted on top of the flange. The water cooling simultaneously removes the heat of the Peltier elements. The whole instrument is mounted inside a box with a styrofoam insulation of 80mm thickness.

The data from various temperature sensors provide the ability to characterise the long



Figure 3.7: Sketch of the dual channel spectrograph arrangement.



Figure 3.8: The spectrograph inside the insulation box.

term stability of the instrument (see section 3.12.1). Temperature sensors are mounted at the following positions:

- at the photo diode arrays
- at the warm side of the Peltier elements
- at the top of the flange, near the heat exchanger
- inside the insulation box, below the instrument housing
- inside the telescope housing

The temperature data is transferred to the computer and stored in a text file each 15 minutes.

3.4 The detectors

The light dispersed by the holographic gratings is detected using photo diode arrays (PDAs) manufactured by Hamamatsu (type ST3904-1024). They consist of 1024 individual Si CMOS photo diodes of 2.5mm height and $25\mu m$ width. To protect the sensitive detector surface, photo diode arrays are often equipped with a quartz window. This can lead to Fabry-Perot etalon structures caused by interference effects on the glass surfaces [Stutz, 1991]. If these structures vary with time due to condensation of water vapour, they can strongly affect the spectral retrieval. To avoid Fabry-Perot etalon structures, the PDAs are operated without quartz glass windows.



Figure 3.9: Screen-shot of the measurement program.

A voltage of 2.06V is applied to the photo diodes during operation, leading to a depletion layer at the n-p junctions. Excitement of electrons by incoming photons leads to a electron/hole recombination. This leads to a dischargement proportional to the light intensity. The charge that is necessary to restore the voltage of 2.06V at the end of a scan (read-out) is therefore proportional to the number of incoming photons. The individual photo diodes have a capacity of 10pF, which yields a saturation charge of $\approx 10^8$ photo electrons.

The spectral response of the photo diodes has is maximum at 600nm with a photo sensitivity (photo current per light intensity) of 600mA/W. The photo sensitivity at the lower end of the UV spectral region (320nm) is by far smaller (≈ 50 mA/W).

Due to thermal excitement of electrons, a dischargement of the photo diodes also takes place if the PDA is not exposed to light. This *dark current* will be discussed in section 3.6. The dark current can be minimised by reducing the temperature of the detectors since the number of thermally excited electrons follows a Boltzmann factor: $I_{DC} \propto e^{-\frac{\Delta E}{kT}}$.

After the read-out, the signal is amplified and a constant electronic offset is added to avoid negative signals which cannot be processed by the analog/digital converter (see section 3.7). The signal is digitised using a 16 bit A/D converter, i.e. $2^{16} - 1 = 65535$ binary units (b.u.) correspond to a fully saturated photo diode. Several spectra can be subsequently added to reduce the spectral noise, which will be discussed in section 3.8.

3.5 The measurement program

The DOAS controller unit is equipped with two separate CPU units witch independently control the measurements of both PDA detectors. This set-up allows to operate both detectors simultaneously. Both CPU units are connected to a personal computer by a common serial port. It is possible to switch between both units by software to initiate measurements and to transfer the spectra to the personal computer. Unfortunately, the existing controller software MFC [Gomer et al., 1995] does not support the simultaneous operation of two CPU units. It was therefore necessary to develop a new software which is able to simultaneously control the measurements of both detectors.

A screen-shot of the measurement program is shown in figure 3.9. It performs the following tasks:

- Initiating measurements and read-out of the spectra: It is important to keep the saturation $S = I/I_{max}$ of the spectra on an appropriate level (between 70 and 90%). Spectra with too low saturation have a poor signal to noise ratio and and over-saturation (signal > 2¹⁶ binary units) has to be avoided. The integration time t_k of the current measurement is determined using the light intensity I_{k-1} of the last spectrum: $t_k = t_{k-1} \cdot S \cdot (I_{max}/I_{k-1})$ with $I_{max} = 2^{16} 1$. To reduce spectral noise, N_k subsequently measured spectra are added. N_k is determined by a given maximum time T_{max} for the total integration time: $N_k \leq T_{max}/t_k \leq N_k + 1$. To account for the lower light intensity during twilight, the integration time T_{max} is set to 600 seconds for $\Theta \leq 92^{\circ}$ and to 800 seconds for $92^{\circ} < \Theta \leq 97^{\circ}$. Although the measurements are performed with a high time resolution of 5 minutes, a good signal to noise ratio is achieved (see section 3.8). This allows to observe short term variations of trace gas abundances, which is particularly of interest for tropospheric absorbers. The spectra are graphically displayed and finally stored on harddisk after transfer to the personal computer.
- *Measurement of background spectra*: The program controls the measurement of a set of background spectra (dark current, offset, halogen and mercury lamp spectra) which is automatically performed each night.
- Readout of temperature data: Temperature sensors are mounted at the spectrograph housing, the PDA detectors and inside the telescope housing. The temperature data is transferred from the controller to the personal computer each 3 minutes and stored in a text-file each 15 minutes. The temperature history for the last 12 hours is graphically displayed. Error messages are displayed and written in a log-file if the PDA temperature deviates for more than $\pm 0.15^{\circ}$ C from -35° C. To avoid damaging of the thermoelectric cooling, it is turned off if the temperature at the warm side of the Peltier elements exceeds $+40^{\circ}$ C.

3.6 The dark current

During a measurement, each individual photo diode acts as a capacity with a discharge proportional to the number of incoming photons. In addition, a self dischargement occurs due to thermal excitement even if the detector is not exposed to light. This dark current I_{DC} is proportional to a Boltzmann factor: $I_{DC} \propto e^{-\Delta E/kT}$. Thus a cooling of the photo diode array can effectively reduce the dark current signal. In a first approximation, one can assume that the dark current is constant with time and the dark current signal Q_{DC} is therefore proportional to the integration time of the measurement:

$$Q_{DC}(t) = I_{DC} \cdot t \tag{3.2}$$

Equation (3.2) is only valid under the assumption that both the charge and the capacity of the photo diode is constant with time, i.e. if the saturation of the photo diode is small. A more realistic description of the physical processes leads to a nonlinear behaviour of the dark current, which is a function of both the incident light intensity I_L and the charge of the photo diode Q [Stutz, 1991]. This can be described by the following differential equation:



Figure 3.10: Dark current signal of the Vis (upper panel) and UV (lower panel) photo diode array for a detector temperature of $-35^{\circ}C$ and an integration time of ≈ 30 hours.

$$\frac{dQ_{DC}(t)}{dt} = aQ^2(t) + bQ(t) + I_L + c$$
(3.3)

The constants a, b and c can be estimated empirically using measurements of the dark current at different signal levels and thus diode charges Q.

The dark current signal of both detectors cooled to -35° C is shown in figure 3.10. The structure in the dark current of the detector of the Vis spectrograph around channel 410 is most likely caused by a dust particle on the PDA surface. The dark current signal as a function of the detector saturation shown in figure 3.11 decreases for both detectors, indicating the expected nonlinear behaviour of the dark current.

The average dark current for both detectors of around 0.2 counts/sec is small but may, however, have a significant impact on the spectral retrieval during twilight when the light intensity is small. Figure 3.12 illustrates the influence of the dark current on twilight measurements under clear sky conditions. The intensities shown in this figure are a lower limit since they usually increase if clouds or snow drift is present along the light path. While the dark current is very small compared to the signal during daytime (< 0.3% for Θ < 90°), it contributes significantly to the observed intensity during twilight ($\Theta > 92^{\circ}$), reaching values of 1 - 10% in the UV region. It therefore an accurate dark current correction of twilight spectra is important for the spectral retrieval. In particular, the nonlinear and intensity dependent behaviour of the dark current signal may have an influence on strong absorption lines. The solar spectrum (Fraunhofer spectrum) is highly structured due to absorption in the solar photosphere. These strong absorption lines (Fraunhofer lines) are removed in the spectral retrieval by dividing two spectra measured under different light intensity conditions (usually at noon and during twilight). The optical density of Fraunhofer lines can be modified if the dark current is not removed properly since the saturation of the photo diodes and thus the dark current vary with wavelength. This effect can lead to remaining residual structures.



Figure 3.11: Average dark current of the Vis (squares) and UV (circles) photo diode array as a function of the detector signal for a detector temperature of $-35^{\circ}C$.



Figure 3.12: Upper panels: Observed intensity as a function of SZA. Lower panels: Contribution of the dark current to the total signal. The observations were made under clear sky conditions on April 23, 2000.



Figure 3.13: Influence of the dark current correction on the spectral retrieval during twilight. Left panels: IO retrieval in the Vis spectral region between 415 and 461.5 nm for October 30, 1999. Right panels: BrO retrieval in the UV spectral region between 346 and 358.5 nm for September 1, 2000. Upper panels: Change of the retrieved slant column density if the dark current correction is not applied. Lower panels: RMS residual for the retrieval with (solid lines) and without (dashed lines) dark current correction.

Unfortunately, the WINDOAS¹ program used to perform the spectral retrieval does not support the above mentioned nonlinear dark current correction. Therefore, only a linear dark current correction according to equation (3.2) was applied. Figure 3.13 illustrates the influence of the dark current correction on the spectral retrieval during twilight for IO and BrO in the Vis and UV spectral region, respectively. When omitting the dark current correction, the change of both the retrieved column density and the residual structure of IO is very small (< 1.5% for solar zenith angles Θ < 95°). Due to the lower light intensity in the UV region, the retrieval of BrO is very sensitive on the accuracy of dark current correction: the BO column density changes strongly with increasing SZA and the residual structures are much larger if the dark current correction is not applied.

3.7 The electronic offset

The analog PDA signal is converted into a digital signal using a 16 bit D/A converter. Negative signals from the PDA, which may occur due to detector noise, cannot be interpreted by the D/A converter. To avoid this, an artificial signal is added to each measurement. This electronic offset must be subtracted from each recorded spectrum prior to the analysis.

The offset spectra for both detectors are shown in figure 3.14. The average offset signals amount to 672 ± 2 and 709 ± 1 counts per scan for the Vis and UV detector, respectively. Although both detectors are operated with identical electronics, the standard deviation of the Vis offset signal is twice as large as for the UV detector. The reason for this difference is unknown.

¹The WINDOAS spectral analysis program is kindly provided by C. Fayt and M. van Roozendael, IASB, Brussels.



Figure 3.14: Offset signal for the Vis (upper panel) and UV (lower panel) detector. The spectra were recorded by averaging 1000 spectra with an integration time of 0.06 seconds.

3.8 Instrument noise

The instrument noise determines the theoretical detection limit of the spectral retrieval. It is caused by two independent sources [Stutz, 1991]:

• The photo electron noise σ_{ph} is caused by the statistical distribution of the number of detected photo electrons. This noise source cannot be reduced and defines the physical detection limit. Since the photo electron noise is Poisson distributed, it is proportional to the square root of the number of observed photo electrons and thus to the PDA signal N:

$$\sigma_{ph} \propto \sqrt{N} \tag{3.4}$$

The photo electron noise was investigated using a halogen lamp as light source. Two spectra with identical integration time and light intensity were subsequently measured and the root mean square of their difference was calculated. The integration time was varied to obtain the photo electron noise as a function of the PDA signal. As shown in figure 3.15, the photo electron noise increases linearly with the square root of the PDA signal as expected from equation (3.4). The intercept of the lines is not zero since also the detector noise contributes to the measured signal (see below). According to equation (3.4), the photo electron noise is given by the slope of both graphs:

$$\sigma_{ph}(I) = 0.04197 \cdot \sqrt{N}$$
 (Vis) (3.5a)

$$\sigma_{ph}(I) = 0.06711 \cdot \sqrt{N}$$
 (UV) (3.5b)

with the PDA signal I given in binary units.



Figure 3.15: Photo electron noise σ_{ph} as a function of the square root of the average PDA signal \overline{N} (given in binary units) for the Vis (upper panel) and UV (lower panel) detector.

• The detector noise σ_{det} is caused by the electronics. The detector is designed to minimise the noise sources so that the photo electron noise dominates all other sources. Several effects contribute to the detector noise which are discussed in detail in [Stutz, 1991]: the statistical fluctuation of the dark current signal, the noise of the preamplifier and the analog digital converter and the readout noise. With exception of the temperature and integration time dependent dark current noise, these noise sources are proportional to the square root of the number of subsequently added spectra (scans) j:

$$\sigma_{det} \propto \sqrt{j} \tag{3.6}$$

The detector noise was investigated by subsequently measuring two offset spectra with the shortest possible integration time of 0.06 seconds and by calculating the root mean square of their difference as a function of scan number j (see figure 3.16):

$$\sigma_{det}(j) = 2.76 \cdot \sqrt{j} \qquad \text{(Vis)} \tag{3.7a}$$

$$\sigma_{det}(j) = 2.63 \cdot \sqrt{j} \qquad (\text{UV}) \tag{3.7b}$$

The total noise of a measurement depending on the PDA signal N and the scan number j is given by the square sum of the detector and photo electron noise:

$$\sigma_{tot}(N,j) = \sqrt{\sigma_{ph}^2(N) + \sigma_{det}^2(j)}$$
(3.8)

Equation (3.8) can be used to estimate relative noise of the retrieval for twilight measurements, which determines the detection limit of the instrument. The detection of trace gas



Figure 3.16: Detector noise σ_{det} as a function of the square root of the number of scans *j*.



Figure 3.17: Theoretical noise level of the spectral retrieval under cloud free conditions (September 1, 2000) when using a reference spectrum I_0 observed at noon. The values are calculated using equation (3.10).

absorption is based on the determination of the optical density τ , which is the logarithmic ratio of two intensities I and I_0 , which are proportional to the according detector signal Nand N_0 (see section 3.9):

$$\tau = -ln\left(\frac{I}{I_0}\right) = -ln\left(\frac{N}{N_0}\right) \tag{3.9}$$

where I_0 is usually a spectrum measured at noon and the spectra I are observed during twilight. It follows that the noise of the optical density is

$$\sigma_{\tau} = \sqrt{\left(\frac{\sigma_N}{N}\right)^2 + \left(\frac{\sigma_{N_0}}{N_0}\right)^2} \tag{3.10}$$

with σ_N and σ_{N_0} being the total noise of the detector signals N and N_0 according to equation (3.8). The theoretical noise level $\sigma_{\tau}(\Theta)$ of the spectral retrieval as a function of solar zenith angle Θ is shown in figure 3.17. It is inferred from the diurnal variation of the average PDA signal $N(\Theta)$ and the number of scans $j(\Theta)$ under cloud free conditions by combining equations (3.8) and (3.10). The higher noise level in the UV region ($\approx 0.5 \cdot 10^{-3}$ for $\Theta = 90^{\circ}$) compared to the Vis region ($\approx 0.08 \cdot 10^{-3}$ for $\Theta = 90^{\circ}$) is caused by the smaller PDA signal at shorter wavelengths. The residual root mean squares (RMS) of the spectral retrieval are very close to this physical limit (see sections 4.9-4.13). This indicates that systematic retrieval errors, e.g due to improperly prepared reference spectra, are small.

3.9 Detector linearity

For a good quality of the spectral retrieval, it is essential that the detector signal N is strictly proportional to both the observed intensity and the integration time. When measuring a constant light intensity, the following equation should be fulfilled:

$$N(I,t) = k \cdot I \cdot t$$
 with $k \equiv const.$ (3.11)

The linearity of the instrument can be tested in two different ways:

- 1. by measuring the detector signal N as a function of the intensity I with constant integration time t. these measurements are difficult to realise since they require a variation of the intensity in a controlled way, e.g. by using gray filters which decrease the intensity constantly over the whole wavelength range of the spectrograph.
- 2. by keeping the intensity I constant and measuring the detector signal N as a function of the integration time t.
- 3. by determining the amplitude of the etalon structure as a function of the intensity I.

The detector linearity was tested using the second method, with the a halogen lamp as light source. Figure 3.18 shows the observed intensity I(t) = N(t)/t as a function of the detector signal N. The observed intensity remains constants for all saturation levels, except for very small intensities in the Vis region (N < 2500 b.u.), where the observed intensity differs about 4% from the average of the measurements. these deviations are possibly caused by an improper correction of the dark current signal.



Figure 3.18: Observed intensity I(t) = N(t)/t as a function of the PDA signal N (given in binary units) for the Vis (upper panel) and UV (lower panel) detector, observed using the light from a halogen lamp.

3.10 Instrumental stray light

Instrumental stray light can be caused by the reflection of light at the inner parts of the spectrograph, e.g. from higher diffraction orders. When reaching the diode array, this stray light may cause an additional artificial offset to the signal which disturbs the measurement and decreases the quality of the spectral retrieval. A possible instrumental stray light background was investigated using high pass colour glass filter which block any light below a given wavelength. A transmission of zero should be observed below this threshold wavelength if there is no stray light. The transmission coefficients for several high-pass filters measured with the instrument are shown in figure 3.19. They are obtained by dividing two subsequently measured zenith sky spectra with and without filter under clear sky conditions.

It is noteworthy that the threshold wavelengths from the measurements and from the data sheets of the manufacturer (Schott) shown in figure 3.19 differ strongly. However, the signal below the threshold wavelengths in the UV region was found to be in the order of the instrument's noise level ($\approx 10^{-4}$). It therefore can be assumed that the influence of instrumental stray light on the measurements in the UV region is small. There is a significant instrumental stray light signal in the Vis region (left panel of figure 3.19, where a signal in the order of $10^{-4} - 10^{-3}$ is found for $\lambda > 550$ nm.

The possible influence of the instrumental stray light signal in the Vis region was tested as follows: A 4^{th} order polynomial was fitted to the RG665 filter transmission graph shown in figure 3.19. The stray light signal modeled by this polynomial was added to the spectra from September 1, 2000 and a spectral retrieval was performed both in the fit region of iodine oxide (415 - 461.5nm) and ozone (490 - 555nm). No changes were found both in the residual noise



Figure 3.19: Transmission coefficient for several Schott high pass colour glass filters in the Vis (left panel) and UV (right panel) region. Solid lines: apparent transmission coefficients measured with the DOAS instrument. Dotted lines: transmission coefficients from Schott data sheets.

of the fit and the retrieved trace gas column densities. It can therefore be expected that the observed stray light signal in the Vis region has only a small impact on the quality of spectral retrieval.

3.11 Wavelength calibration

A precise wavelength calibration of the instrument is necessary since this calibration determines the alignment of the reference cross sections, if they are adapted from the literature. In this section, several methods to determine the *dispersion relation* $\lambda = \lambda(k)$ which describes the relationship between the wavelength λ and the cannel number k are presented.

The first method is the wavelength calibration by measuring the positions of atomic emission lines of known wavelengths. The line widths of atomic emission lines are usually negligible compared to the resolution of the instrument and can therefore be treated as delta functions. Since the spectrograph has a limited resolution, the image of a spectral line on the detector has a finite width. This image of a spectral line of indefinite width, as observed with the instrument, is referred to as *instrument function* $T(\lambda)$ (see also section 4.5). The spectral resolution of the instrument is determined by the width of the instrument function ΔT , which is commonly expressed at the *Full Width at Half Maximum* (FWHM), i.e. the line width at wavelengths where the intensity of the instrument function has decreased to half of the maximum value.

A Gaussian function is fitted to the individual emission lines to determine the centre position k_j of the jth emission line with wavelength λ_j . Then a polynomial P(k) is least squares fitted to the data points $(x, y) = (k_j, \lambda_j)$ to determine the dispersion relation $\lambda(k) = P(k)$. The spectral resolution of the instrument can be determined simultaneously by the width of the Gaussian function.

The spectra observed with a mercury lamp and the shape of the individual lines are shown in figure 3.20 and 3.21, respectively. While the UV lines have a very symmetric shape, the line shapes of the Vis instrument are broader than the theoretical line width of 4.8 channels $(120\mu m \text{ entrance slit width compared to } 25\mu m \text{ pixel size})$ and have an asymmetric shape. The



Figure 3.20: Mercury emission line spectra measured in the Vis (upper panel) and UV (lower panel) spectral region.

UV		Vis					
Pos	λ_{vac}	FWHM	FWHM	Pos	λ_{vac}	FWHM	FWHM
[chan]	[nm]	[chan]	[nm]	[chan]	[nm]	[chan]	[nm]
138.3	334.2	4.15	0.41	26.5	404.8	5.95	1.53
447.2	365.6	5.46	0.54	141.8	436.0	5.76	1.48
459.5	366.4	4.39	0.44	415.2	507.4	7.17	1.85
846.7	404.8			569.0	546.2	6.38	1.64
878.5	407.9			694.4	577.1	6.36	1.64
				703.2	579.2	7.28	1.87

Table 3.2: Channel position, wavelength and line width of mercury emission lines. All wavelengths are in vacuum.



Figure 3.21: Line shapes as observed by a mercury lamp for the Vis (left panel) and UV (right panel) region.

position and width of the individual lines are listed in table 3.2. The determination of the dispersion using atomic emission lines has some disadvantages:

- Only a limited number of data points is available for the determination of the dispersion relation. This number can, of course, be increased by using emission lines from other elements (e.g. cadmium or neon) and absorption bands (e.g. NO₂ and ozone). However, interpolation and extrapolation errors remain, particularly if there are no lines available at the outer margins of the spectrum.
- The centre wavelength of the individual emission lines cannot always be determined precisely, particularly if their line shape is asymmetric or if neighbouring lines are not resolved by the instrument.
- During long term measurements, emission line spectra are not always available for calibration purposes.

A more precise dispersion relation can be derived by performing a *continuous* wavelength calibration over the whole wavelength range of the instrument. This procedure takes advantage of the strong absorption lines (Fraunhofer lines) in the solar spectrum (Fraunhofer spectrum), caused by absorption in the solar photosphere. The WINDOAS evaluation program provides the ability to align observed zenith sky spectra to a high resolution Fraunhofer spectrum with a precise wavelength calibration using a nonlinear least- square fit algorithm. Since the retrieval algorithm is discussed in detail in section 4.3, only a brief explanation is given here:

- 1. The dispersion relation $\lambda = \lambda(k)$ of the instrument must be known approximately, e.g. by measuring the position of atomic emission lines as described above.
- 2. The instrument's wavelength range is subdivided into N sub-intervals of equal width $\Delta \lambda$: $I_n = [\lambda_0 + n \Delta \lambda, \lambda_0 + (n+1) \Delta \lambda], n = 0 \dots N 1.$
- 3. For each wavelength interval I_n , a least squares algorithm according to equation 4.12 is performed in order to align the measured spectrum I to a high resolution Fraunhofer spectrum $I_0(\lambda)$. I_0 is taken from the literature [Kurucz et al., 1984]. The least squares fit is performed with the following additional nonlinear parameters:
3.11. WAVELENGTH CALIBRATION

- (a) Shape of the instrument function: The observed sky light spectrum is the convolution of the 'true' high resolution Fraunhofer spectrum $I_0(\lambda)$ with the instrument function $T(\lambda)$: $I(\lambda) = (I_0 \circ T)(\lambda)$. The shape of the instrument function is modeled by a number of nonlinear parameters $w_{0,n}, w_{1,n}, \ldots$. Several built- in instrument functions are provided by the WINDOAS program, such as Gaussian functions with a single parameter $w_{0,n}$ being the FWHM² of the instrument function or a Voigt function with two parameters $w_{1,n}$ and $w_{2,n}$ describing the line width and asymmetry of the instrument function. These parameters are determined by a nonlinear fit of the Fourier transformed spectra $\mathcal{F}[I]$, using the relationship $\mathcal{F}[I_0 \circ T] = \mathcal{F}[I_0] \cdot \mathcal{F}[T]$.
- (b) Wavelength calibration: To determine the precise dispersion relation, the measured spectrum is allowed to shift (and, if necessary, to squeeze) in wavelength relative to I_0 according to equation 4.15. The wavelength shift of each wavelength interval n is described by the nonlinear parameters s_n .
- 4. Finally, a polynomial $S(\lambda)$ is fitted to the derived set of wavelength shift parameters $s_1 \dots s_N$ to calculate the new dispersion relation: $\lambda(k) \longrightarrow \lambda(k) + S(\lambda(k))$.

Figure 3.22 shows an example for the wavelength alignment using the nonlinear algorithm of the WINDOAS program. The convoluted high resolution Fraunhofer spectra fits well to the aligned sky light spectra, with an residual RMS of $1.7 \cdot 10^{-3}$ and $8.2 \cdot 10^{-3}$ for Vis and UV, respectively. The instrument resolution determined by the fit algorithm is in very good agreement with the values determined by the measurement of mercury emission lines listed in table 3.2, except for the fit window around 590nm in the Vis region, where the line width is strongly overestimated. This is possible due to the lack of Fraunhofer lines and the unstructured spectral signature in this wavelength region.

A comparison between both methods of wavelength calibration is shown in figure 3.23. The upper panels show the channel positions of the mercury emission lines and the fitted polynomials of 3^{rd} degree. In the lower panels, this polynomial is compared to the dispersion relation derived using the Fraunhofer alignment algorithm of the WINDOAS program. The positions of the mercury lines fit very well both for UV and Vis, with exception of the neighbouring mercury lines at 365.6 and 366.4nm, which are not fully resolved by the UV spectrograph (see figures 3.20 and 3.21) and therefore cannot be located precisely. Also, the line width determined by the Fraunhofer alignment agrees well with the with of the mercury lines (compare panel D in figure 3.22 with the with of the mercury lines listed in table 3.2). This good agreement between both methods gives confidence that the Fraunhofer alignment is a very precise method for the wavelength calibration. However, there is a large difference of up to 1nm between the dispersion relations derived using the mercury lines and the Fraunhofer alignment, particularly at both ends of the wavelength windows. This is caused by interpolation and extrapolation errors when fitting a polynomial using the positions of only a few mercury lines, compared to the continuous alignment using the high resolution Fraunhofer spectrum.

The advantages of the Fraunhofer wavelength alignment compared to the alignment using atomic emission lines can be summarised as follows:

• Since the Fraunhofer alignment is performed continuously over the whole wavelength

 $^{^{2}\}mathrm{The}$ Full Width at Half Maximum (FWHM) is defined as the width of the instrument function at half the maximum intensity.



Figure 3.22: Example for the wavelength calibration using the nonlinear fit algorithm of the WINDOAS program in the Vis (left figure) and UV (right figure) region. The wavelength range is divided into 10 fit windows between 400 and 625 nm (Vis) and 330 and 410 nm (UV). Panel A: Convoluted high resolution Fraunhofer spectrum (thick line) and aligned sky light spectrum (thin line). Panel B: Residual structure. Panel C: Wavelength shifts for each fit window (dots) relative to the dispersion relation determined by mercury emission lines, and fitted 3rd order polynomial. Panel D: Width of the Gaussian instrument function for each fit window (dots) and fitted 3rd order polynomial. The sky light spectra were measured at noon of February 20, 1999.



Figure 3.23: Dispersion relation for the Vis (upper figure) and UV (lower figure) region. Upper panels: Wavelength positions of the mercury emission lines (open squares) and fitted polynomials P(k) (lines). The polynomial coefficients for the alignment using the mercury lines ($P_{hg}(k)$) and the Fraunhofer alignment ($P_{fraunh}(k)$) are denoted in the legend. Lower panels: Difference between the position of the mercury lines and the corresponding wavelengths determined by the Fraunhofer alignment as given in figure 3.22 (open squares) and wavelength difference $P_{fraunh}(k) - P_{hg}(k)$ between the dispersion as determined by the position of the mercury lines and by the Fraunhofer alignment (lines).

interval, no interpolation or extrapolation errors can occur. It is therefore a very precise tool to determine the instrument's dispersion relation.

- The Fraunhofer alignment algorithm simultaneously determines the shape and width of the instrument function in each fit window.
- The Fraunhofer alignment can be performed on any sky light spectrum, giving the ability to determine short- and long term changes of the instrument properties.
- The Fraunhofer alignment can in principle also be used to compensate for changes in the wavelength calibration and instrument resolution by performing a cross convolution of the spectra and cross sections prior to the spectral analysis.

3.12 Long term characterisation of the instrument

In order to analyse long term measurements using a single Fraunhofer reference spectrum, it is important to keep the instrument conditions as stable as possible. Since the dark current signal depends strongly on the detector temperature, it needs to be kept constant within tenths of degrees. Changes in the wavelength alignment and the instrument's resolution caused by variations of the spectrograph temperature can strongly affect the spectral analysis.

In the following, changes in the instrument properties are scrutinised using information gained from

- 1. the temperature sensor data
- 2. the regularly performed set of offset, dark current and halogen lamp measurements (background spectra)
- 3. the analysis of the regularly measured mercury lamp spectra
- 4. the Fraunhofer alignment algorithm

3.12.1 Temperature data

As described in section 3.3, the data of various temperature sensors is stored in a text file each 15 minutes. These data can be used to characterise the long term stability of the instrument.

Figure 3.24 shows the daily average, maximum and minimum temperatures during 1999 and 2000. Until February 2, 2000, the temperatures of the instrument housing (flange and insulation box) are characterised by relatively high variability, because the temperature of the cooling agent was thermostabilized using a sensor mounted at the reservoir vessel of the water cooling device and not at the heat exchanger. The temperature of the heat exchanger was therefore strongly coupled to the highly variable room temperature of the trace gas observatory.

The temperature controller of the cooling device failed on February 2, 2000. Therefore the water cooling device operated continuously under full power until a new temperature controller was installed on April 8, 2000. This caused a decrease in the temperature of the instrument housing of about 15°K during this period and a disalignment of the optical setup as discussed in section 3.12.3.







Figure 3.25: Temperature inside the telescope housing during 1999 and 2000. Thick line: daily average; thin lines: daily maximum and minimum temperatures.

On July 30, 2000, the temperature sensor of the water cooling device was moved from the reservoir vessel of the cooling device to the heat exchanger on top of the spectrograph housing. Much better stability of the spectrograph temperature was achieved afterwards. However, the stronger coupling of the spectrograph temperature to the oscillating temperature of the cooling liquid caused increased fluctuations of the PDA temperature of $\pm 0.1^{\circ}$ K compared to $\pm 0.06^{\circ}$ K during 1999. The sudden increases of the PDA temperatures during the whole period were caused by frequent power failures at Neumayer Station.

The air temperature inside the telescope housing during 1999 and 2000 is shown in figure 3.25. Unfortunately, the telescope heater failed during the winter of 2000. However, due to the low air humidity at the measurement site, a freezing or steaming up of the entrance optics or the telescope window was rarely observed and no disadvantageous effects on the measurements were found.

3.12.2 Background spectra

A set of background spectra, consisting of offset, dark current, halogen lamp and mercury lamp measurements (see table 3.3) is automatically measured at midnight for solar zenith angles $\Theta > 97^{\circ}$. During summer, when the sun is not below the horizon during night, the background spectra are measured manually once per week after covering the entrance window of the telescope to avoid sun light disturbing the measurement.

The background measurements can be used to characterise the stability of the instrument:

• Changes in the offset signal are related to the stability of the electronics, particularly of the PDA preamplifier. Furthermore, the offset can be used to determine changes of the detector noise (see section 3.8).

	UV		Vis	
	T_{int} [sec]	scans	T_{int} [sec]	scans
Offset	0.06	5000	0.06	5000
Dark current	1000	1	1000	1
Halogen lamp	25	4	10	10
Mercury lamp	300	1	10	30

Table 3.3: Integration time and number of scans of background spectra.

- The dark current signal depends on the detector temperature, but changes can also be a hint for a degradation of the PDA.
- Due to ageing of the halogen lamp, a constant light intensity over long time ranges cannot be expected. The Fabry Perot etalon effect can cause variations of the broad band structure of the halogen spectra due to freezing of vater vapour on the PDA surface. Furthermore, the long term behaviour of the instrument noise can be characterised using halogen lamp spectra.
- The position and width of the mercury lines is useful to characterise changes in the spectral calibration. This is discussed in detail in section 3.12.3.

The instrument properties derived from background measurements are shown in figure 3.26. The UV dark current signal $(0.94 \pm 0.03 \text{ counts/scan})$ remains constant over the whole measurement period, but the Vis dark current signal is strongly increased each 28 days. This finding is clearly related to the moon phase: the instrument is sensitive to the (very small) sky light intensity during full moon. An increased Vis dark current signal is also found during summer, since it was not possible to avoid that some light enters the telescope. Both detectors show a small but significant decrease in the offset signal (UV: $\approx -4\%$ per year, Vis: $\approx -6\%$ per year), which is most likely caused by the ageing of the preamplifier electronics.

As discussed in section 3.8, the physical limit of the signal to noise ratio of the spectral retrieval is given by the detector and instrument noise. The time series of the detector noise shown in figure 3.26 were calculated are calculated according to equation (3.6). Each off-set spectrum was subtracted from a fixed offset spectrum recorded at the beginning of the measurement period (January 20, 1999). Therefore the data shown here provide an estimate for the expected noise level of the spectral retrieval when using a single Fraunhofer reference spectrum for the spectral analysis of the whole period. Since the broad band structure of the offset spectra changed slightly with time, a high pass filter was applied to the difference prior to the calculation of the root mean square. A constant detector noise relative to the measurement on January 20, 1999 is achieved for the UV instrument, while the detector noise of the Vis instrument is highly variable. The reason for this variability in the Vis region is unknown. It is possibly caused by some residual light entering the telescope.

The instrument noise, i.e. the sum of detector and photon noise, is calculated in the same way as the detector noise, but with the PDAs exposed to light from the halogen lamp. Again, no temporal changes of the noise with time is found for the UV instrument, while the noise of the Vis instrument is highly variable.

The halogen lamp spectra recorded during 1999 and 2000 (see figure 3.27) show no changes with time in their structure, indicating that the instrument is free of any interference effects (Fabry Perot etalon structures), which could for example be caused by freezing of water vapour on the photosensitive surface of the PDA. The broad band structure of the Vis spectra is not



Figure 3.26: Instrument properties derived using the regularly performed background measurements. Upper panels: Dark current and offset signal. Lower panels: Detector and instrument noise relative to the measurements of February 20, 1999.



Figure 3.27: Some halogen lamp spectra observed during 1999 and 2000 for UV (upper Panel) and Vis (lower Panel).

caused by interference effects but by the transmission curve of the UG5 colour glass filter mounted in front of the Vis light entrance.

3.12.3 Stability of the spectral calibration

While possible changes of the wavelength alignment can be compensated in the spectral analysis by allowing for a wavelength shift, the quality of the spectral retrieval is very sensitive to any changes of the instrument's resolution. Both parameters can be determined using the position and line width of the regularly recorded mercury lamp spectra as well as by performing the Fraunhofer calibration algorithm described in section 3.11.

Changes in the position and width of the mercury lines were determined by performing a nonlinear fit (see section 4.3.2) of the individual emission lines to a reference mercury lamp spectrum recorded on March 9, 1999. The shift and squeeze parameters derived by this fit are a measure for changes in the wavelength alignment and the width of the instrument function. The Fraunhofer calibration was performed as discussed in section 3.11, using daily noon spectra.

The results are shown in figure 3.28. The data determined using the mercury lines and the Fraunhofer calibration agree well, except for the period where the temperature controller of the liquid cooling device failed (February 2 to April 8, 2000). However, the shift and squeeze parameters derived using the mercury lines show a much higher day to day variability than the fitting parameters derived by the Fraunhofer alignment. This shows again that the Fraunhofer alignment procedure produces more precise calibration parameters than the measurement of spectral lines. One exception is the fit window #9 of the Vis region (580 - 605nm), where the high variability of the fit parameters is most likely caused by the lack of Fraunhofer structure in the spectra.

Except for the period between February 2 to April 8, 2000, when the temperature of the spectrograph decreased for about 15°K (see figure 3.24), the wavelength alignment remains fairly constant. However, until July 30, 2000, a higher variability is found when the temper-





possible to evaluate the spectra recorded during this period, except for ozone.

a wavelength shift but also a strong change of the spectral resolution. It was therefore not

Chapter 4

Absorption Spectroscopy of Atmospheric Trace Gases

The differential optical absorption spectroscopy (DOAS) is a widely used measurement technique for the detection of various atmospheric trace gas species [Perner and Platt, 1979; Platt, 1994]. It is based on the wavelength dependent absorption of light through matter using artificial or extraterrestrial light sources as described in section 4.1. The DOAS technique can be used on various platforms and with different observation geometries:

- using *artificial light sources* (long path DOAS, multiple reflection cells) gain information about the atmospheric composition in the lowermost troposphere, e.g. to investigate urban pollution or natural phenomenons such as ozone depletion in the marine boundary layer.
- ground- based observations of scattered sunlight, the measurement technique on which this work is based, provide information on the integrated concentration of atmospheric trace gases above a specific measurement location. Since those instruments are easy to maintain, they can be used for long-term measurements even in very remote locations. This gives the ability to study the diurnal and seasonal variation of trace gases both in the stratosphere and in the troposphere. Depending on the viewing geometry (zenithsky and/or off-axis) the sensibility on trace gases located in specific altitudes can be increased in order to gain information on their altitude distribution.
- satellite borne DOAS measurements can provide a global picture of the spatial distribution of atmospheric trace gases. Nadir-viewing instruments (such as the GOME spectrograph on the ERS-2 satellite) are able to detect integrated trace gas concentrations below the instrument. Profiles of atmospheric trace gases can be determined using limb viewing geometry by observing direct or scattered sunlight passing through different altitude ranges of the atmosphere.
- *balloon borne DOAS measurements* using direct sunlight give the ability to derive altitude profiles of atmospheric trace gases.
- *airborne DOAS measurements* provide the ability to observe stratospheric trace gases along a flight track of an aircraft. Information on the vertical distribution of atmospheric absorbers can be gained by varying the viewing direction of a DOAS spectrograph aboard an airplane.

• two- and three dimensional concentration fields of atmospheric trace gases can be derived by simultaneously observing different light pathes (e.g. *DOAS tomography* and *multiaxis DOAS*).

4.1 The Lambert-Beer law

The absorption of radiation of a given wavelength λ passing through an infinitesimally small volume with the thickness ds at the location \vec{s} (see figure 4.1) is given as:

$$dI(\lambda, \vec{s}) = -I(\lambda, \vec{s}) \cdot \sum_{l} \rho_l(\vec{s}) \sigma_l(\lambda, \vec{s}) \ ds$$
(4.1)

where $\sigma_l(\lambda, \vec{s}) \equiv \sigma_l(\lambda, T(\vec{s}), p(\vec{s}))$ is the wavelength, temperature and pressure dependent absorption cross section and $\rho_l(\vec{s})$ is the concentration field of the lth absorbing species. The intensity $I(\lambda)$ is the energy flux at wavelength λ in direction of the beam, given in units of $W/(nm \cdot cm^2)$.



Figure 4.1: The absorption of radiation through an infinitesimally small air parcel

Integrating equation (4.1) leads to the well known Lambert Beer law:

$$I(\lambda) = I_0(\lambda) \cdot \exp\left(-\sum_l \int_0^L \rho_l(\vec{\gamma}(s))\sigma_l(\lambda, \vec{\gamma}(s)) \ ds\right)$$
(4.2)

which is written here in a generalised form along a light path parameterised by the function $\vec{\gamma}(s)$, with s being the arc length of curve (which implies that $|d\vec{\gamma}/ds| \equiv 1$). This parameterisation is chosen since, due to refraction and scattering, the light passes the absorber not necessarily on a straight line. Equation (4.2) describes the relationship between the incident light intensity $I_0(\lambda) = I(\lambda, \vec{\gamma}(0))$ and the transmitted intensity $I = I(\lambda, \vec{\gamma}(L))$ at the location $\vec{\gamma}(L)$.

Furthermore, the *optical density* τ is defined as the logarithm of the ratio of transmitted and incident intensity:

$$\tau(\lambda) := \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sum_l \int_0^L \rho_l(\vec{\gamma}(s))\sigma_l(\lambda, \vec{\gamma}(s)) \, ds \tag{4.3}$$

If the temperature and pressure dependency of the absorption cross sections σ_l are negligible (or temperature and pressure are constant along the light path), equation (4.3) can be written as:

$$\tau(\lambda) = \sum_{l} \sigma_{l}(\lambda) \cdot \int_{0}^{L} \rho_{l}(\vec{\gamma}(s)) \, ds =: \sum_{l} \sigma_{l}(\lambda) \cdot S_{l} = \sum_{l} \tau_{l}(\lambda) \tag{4.4}$$

The *slant column density* (SCD) S of an absorber, given in units of molecules per area, is the integrated concentration along a given light path through the atmosphere:

$$S_l = \int_0^L \rho_l(\vec{\gamma}(s)) \, ds = \frac{\tau_l(\lambda)}{\sigma_l(\lambda)} \tag{4.5}$$

4.2 Differential optical absorption spectroscopy

Equation (4.4) implies that the estimation of the slant column density requires the knowledge of the incident and transmitted light intensities $I_0(\lambda)$ and $I(\lambda)$. In case of ground-based DOAS measurements, the solar radiation outside the atmosphere $I_0(\lambda)$ cannot be determined directly. Furthermore, broad-banded spectral features caused by Rayleigh and Mie scattering are overlaid to the absorption structures. They depend strongly on the actual observing parameters (e.g. solar zenith angle, aerosol loading and ground albedo). These restrictions can be avoided by introducing differential quantities: the *differential cross section* σ' is derived by separating the high and low frequency parts of the cross section:

$$\sigma(\lambda) = \sigma'(\lambda) + \sigma^b(\lambda) \tag{4.6}$$

 σ^b is a function that varies slowly with wavelength. It describes the broad-banded structure of the cross section (see example in figure 4.2). It can be derived by interpolating a polynomial or by iteratively applying triangular smoothing (e.g. 1000 times) to the cross section.

Applying equation (4.6) to equation (4.4) leads to the corresponding definition of the differential optical density τ' :

$$\tau_l(\lambda) = \sigma'_l(\lambda) \cdot S_l + \sigma^b_l(\lambda) \cdot S_l =: \tau'_l(\lambda) + \tau^b_l(\lambda)$$
(4.7)

Equation (4.2) can now be written as:

$$I(\lambda) = I_0(\lambda) \cdot \exp\left(-\sum_l (\tau_l'(\lambda) + \tau_l^b(\lambda))\right) = I_0'(\lambda) \cdot \exp\left(-\sum_l \tau_l'(\lambda)\right)$$
(4.8)

Hence, the slant column densities of the individual absorbers can be estimated by merely observing differential quantities and the knowledge of the 'true' I_0 is not necessary:

$$S_l = \frac{\tau_l(\lambda)}{\sigma_l(\lambda)} = \frac{\tau_l'(\lambda)}{\sigma_l'(\lambda)}$$
(4.9)

4.3 The spectral retrieval

The numerical analysis of DOAS sky light observations should take into account the important aspects of both the measurement conditions and the instrument properties. The situation is sketched in figure 4.3 and can be summarised as follows:



Figure 4.2: Example for the separation of the cross section into its differential and broadbanded parts using an NO₂ cross section. Panel A: Cross section σ (solid line) and broadbanded structure σ^b (dashed line), derived by interpolating a polynomial of 3^{rd} degree. Panel B: Differential cross section σ' .

- The main goal of the spectral retrieval discussed in this section is the determination of the slant column density of individual absorbers. In particular for strong absorbers (ozone in the UV spectral region), the absorption process is coupled to the radiative transport (which is discussed in detail in section 4.6) since not only the amount of absorption is determined by the light path, but in turn strong absorbers may also have an significant impact on the radiative transport.
- When entering the instrument, the field of view given by the entrance optics of the instrument determines the angular range of the collected skylight.
- Both the width of the entrance slit and the properties of the grating determine the resolution of the spectrograph. This can be described by a convolution of the high resolution Fraunhofer spectrum with the instrument function. Thus the high resolution cross sections used for the spectral retrieval need to be transformed to the instrument's resolution prior to the analysis. The impact of the finite resolution on the spectral analysis is discussed in sections 4.4 and 4.5.
- The light dispersed by the gratings is detected using photo diode arrays (PDAs). Each photo diode integrates the intensity over a discrete wavelength interval.
- In addition to the PDA signal caused by the incident light, the self discharge of the photo diodes causes a dark current signal . In addition, an artificial signal is added to each PDA signal. As already described in sections 3.6 and 3.7, it is necessary to corrected for these effects prior to the spectral analysis.



Figure 4.3: Sketch of the observation conditions for DOAS sky light measurements

4.3.1 The linear fitting procedure

When measuring the incident and transmitted light intensity through a mixture of absorbers, the integrated concentration along a defined light path can be determined by applying a least squares fit to equations (4.3) and (4.4):

$$\chi^2 := \int_{\lambda_1}^{\lambda_2} \left(\ln(I(\lambda)) - \ln(I_0(\lambda)) + \sum_l \sigma_l(\lambda) S_l \right)^2 \, d\lambda \stackrel{!}{\longrightarrow} \min$$
(4.10)

where the S_l are free parameters of the fit and $[\lambda_1, \lambda_2]$ is an appropriate wavelength interval which should be chosen to optimise the retrieval of individual slant column densities S_l .

Equation (4.10) is only valid under idealised measurement conditions. In practice, the situation is complicated due to several reasons:

• The continuous spectrum $I(\lambda)$ is sampled on a discrete wavelength grid determined by the pixel size of the photo diode array. This leads to a replacement of the integral over the wavelength by a sum over a discrete wavelength grid:

$$I(\lambda) \longrightarrow I(\lambda_k) := \int_{\lambda_k - \Delta\lambda_k/2}^{\lambda_k + \Delta\lambda_k/2} \eta_k(\lambda_k - \lambda)\tau(\lambda)I(\lambda) \ d\lambda$$
(4.11)

where λ_k is the centre wavelength and $\Delta \lambda_k$ is the wavelength interval covered by the kth photo diode. The normalised function $\eta_k(\lambda)$ ($\int \eta_k(\lambda) d\lambda = 1$) reflects the sensibility of each individual photo diode as a function of space. $\tau(\lambda)$ is the quantum efficiency of the photo diode array as a function of wavelength.

• When observing scattered radiation, Rayleigh and Mie scattering lead to a modulation of the observed optical density. these broad-banded spectral features can be approximated using a polynomial $P(\lambda) = \sum_{n} c_n \lambda^n$ of an appropriate degree.

Therefore, the integral over the wavelength region in equation (4.10) can be replaced by a sum over discrete data points:

$$\chi^2 := \sum_k \left(\ln(I(\lambda_k)) - \ln(I_0(\lambda_k)) + \sum_i \sigma_i(\lambda_k) S_i + \sum_n c_n \lambda_k^n \right)^2 \xrightarrow{!} \min$$
(4.12)

which can be solved analytically by calculating the partial derivations of χ^2 concerning the free parameters:

$$\frac{\partial \chi^2}{\partial S_i} \xrightarrow{!} 0 \quad \text{and} \quad \frac{\partial \chi^2}{\partial c_n} \xrightarrow{!} 0 \quad (4.13)$$

Equations (4.13) are equivalent to a linear equation system which can be solved using well known matrix inversion algorithms, e.g. the *single value decomposition* (SVD) method [Press et al., 1988].

The residual of a spectral retrieval is defined as the difference between the optical density of the measured and modeled spectrum:

$$R_k = \ln(I(\lambda_k)) - \ln(I_0(\lambda_k)) + \sum_l \sigma_l(\lambda_k) S_l + \sum_n c_n \lambda_k^n$$
(4.14)

For an ideal measurement, R would consist only of noise. Possible systematic structures in the residual spectra can be caused by improperly prepared cross sections, wavelength disalignments or any absorbers not considered in the spectral retrieval. A measure for the overall quality of the fit is given by the root mean square (RMS) of the residual, which is given by χ (see equation (4.12)).

4.3.2 The nonlinear fitting procedure

The spectral analysis according to equation (4.12) cannot account for nonlinear effects caused by changes of the wavelength calibration, a variable spectral resolution, instrumental stray light or a nonlinear relationship between light intensity and detector signal.

The spectral retrieval of trace gases with small optical density is very sensitive on changes in the wavelength calibration. Wavelength shifts already in the order of a few percent of a pixel can cause strong artificial structures in the residual spectra. Possible changes in the spectral calibration can be taken into account by allowing for a shift and squeeze of the spectra:

$$I(\lambda_k) \longrightarrow I(\lambda'_k)$$
 with $\lambda'_k = \lambda_k + s_0 + s_1(\lambda_k - \lambda_c) + s_2(\lambda_k - \lambda_c)^2$ (4.15)

 λ_c is usually set to the centre wavelength of the fitting window ($\lambda_c = (\lambda_2 - \lambda_1)/2$, see equation (4.10)). The shift- and squeeze- parameters $s_0 \dots s_2$ are nonlinear, which means that they cannot be determined analytically by setting $\partial \chi^2 / \partial s_i$ to zero. Other numerical methods such as the Levenberg- Marquardt- algorithm [Levenberg, 1944; Marquardt, 1963] are necessary in order to minimise χ^2 concerning these parameters. The intensity at the new grid points λ'_k is determined by a spline interpolation. This procedure leads to interpolation errors, which are discussed in section 4.4.

Furthermore, the spectral retrieval can be affected by artificial offset signals, which add to the observed intensity. This intensity offset can be caused by several effects:

- an improper offset and/or dark current correction, caused by instabilities of the PDA temperature or a nonlinear relationship between exposure time and dark current signal
- stray light, caused by reflection of light inside the spectrograph housing
- a nonlinear relationship between the PDA signal and the incident light intensity

If this offset signal varies only slowly with wavelength, adding a polynomial to the intensity (not to be confused with the polynomial $P(\lambda)$ in equation (4.12), which adds to the *logarithm* of the spectrum) can compensate those effects:

$$I(\lambda_k) \longrightarrow I'(\lambda) = I(\lambda) + q_0 + q_1(\lambda_k - \lambda_c) + q_2(\lambda_k - \lambda_c)^2$$
(4.16)

Again, the offset parameters $q_0 \ldots q_2$ can be determined using a nonlinear algorithm in order to minimise χ^2 .

It sometimes can be useful to scale a cross section by multiplying it with a polynomial according to

$$\sigma(\lambda) \longrightarrow \sigma'(\lambda) = \sigma(\lambda) \cdot (r_1(\lambda - \lambda_c) + r_2(\lambda - \lambda_c)^2)$$
(4.17)

with the nonlinear parameters r_1, r_2 . these parameters are not used for the spectral retrieval within this work, but can be applied if the light path through the atmosphere, and hence the slant column density, varies with wavelength within the fitting window (e.g. for the strong ozone absorption bands in the wavelength region below 330 nm). However, this requires that the variation of the slant column density with wavelength can be approximated with a polynomial of third degree, which is not necessarily the case.

4.4 Spectral oversampling

As described in section 4.3.2, changes in the wavelength alignment of the instrument can be compensated by shifting and squeezing the spectrum according to equation (4.15). This algorithm, however, leads to interpolation errors since the spectrum is sampled on a discrete wavelength grid [Roscoe et al., 1996]. This error strongly depends on the *sampling ratio* which is defined as:

$$R_k := \frac{\Delta T(\lambda_k)}{\lambda_k - \lambda_{k-1}} \tag{4.18}$$

where $\Delta T(\lambda_k)$ is the width of the instrument function $T(\lambda)$ (FWHM) at channel k, and $\lambda_k - \lambda_{k-1}$ is the wavelength difference between two neighbouring channels.

The transformation of a 'true' spectrum (which would be observed when using an instrument with infinitely high resolution and sampling ratio) to the spectrum observed with an instrument of finite resolution can be derived under consideration that an spectral line of indefinitely small width (delta function) is transformed by the spectrograph to the instrument function $T(\lambda)$:

$$\delta(\lambda) \longrightarrow T(\lambda) \tag{4.19}$$

Hence the observed intensity can be written as a convolution of a high resolution spectrum with the instrument function:

$$I(\lambda_k) = \int I(\lambda')\delta(\lambda_k - \lambda') \ d\lambda' \longrightarrow \int I(\lambda')T(\lambda_k - \lambda') \ d\lambda' \equiv (I \circ T)(\lambda_k)$$
(4.20)

A wavelength shift of a spectrum is a transformation from a wavelength grid λ_k on a new wavelength grid λ'_k , which can be described by an operator **S**:

$$\mathbf{S}_{\Delta\lambda}[I]: \quad I(\lambda_k) \longrightarrow I(\lambda'_k) \quad \text{with} \quad \lambda'_k = \lambda_k + \Delta\lambda$$

$$(4.21)$$

The compensation of a wavelength shift is usually performed using a spline interpolation between the data points $(x_k, y_k) = (\lambda_k, I(\lambda_k))$. A wavelength shift leads to interpolation errors since the convolution and the wavelength shift are not commutative:

$$\mathbf{S}_{\Delta\lambda}[I \circ T](\lambda_k) \neq [\mathbf{S}_{\Delta\lambda}[I] \circ T](\lambda_k) \tag{4.22}$$



Figure 4.4: Two Gaussian functions with 1.5 channel FWHM sampled on different grids. Squares and solid line (a): Sampled on a whole numbered grid (lower x-axis) and its splineinterpolation; Circles and dotted line (b): Sampled on a grid shifted by 0.5 channels (upper x-axis) and its spline-interpolation.



Figure 4.5: Measured instrument function (blue lines) depending on the position of the emission line on the PDA (red lines) at low instrumental resolution (FWHM = 2 channel). The x-axis denotes the pixel number. Panel A: Maximum of the instrument function located between two pixels; panel B and C: maximum shifted relative to (A) for 0.1 and 0.25 pixel, respectively; panel C: maximum of the instrument function located at the centre of a pixel.



Figure 4.6: RMS residual as a function of wavelength shift between two identical high resolution spectra between 320 and 420 nm, convoluted using gauss functions of different line width as indicated in the legend.

In other words: the change of the instrument's wavelength alignment are equivalent to the convolution of a shifted spectrum with the instrument function. This transformation is not equal to the wavelength shift of a convoluted spectrum, which is done by the retrieval algorithm in order to compensate for the wavelength disalignment. This is illustrated in figure 4.4, where a Gaussian function is sampled on two different wavelength grids: wavelength grid b is shifted by 0.5 channels relative to grid a. Interpolation errors occur since the spline interpolations of both functions are not equal. Figure 4.5 illustrates that the shape of the instrument function, sampled with a resolution of only 2 channel (FWHM), strongly depends on the position of the emission line on the photo diode array. Thus wavelength disalignments of only tenths of a channel lead to a strong change in the observed line shape if the sampling ratio is too small.

The influence of these interpolation errors was investigated using a high resolution solar Fraunhofer spectrum in the wavelength range between 320 and 420nm. It was convoluted on a wavelength grid of 0.1 nm using a Gaussian slit function $T(\lambda)$ with varying line widths ΔT . The spectrum $[\mathbf{S}_{\Delta\lambda}[I] \circ T](\lambda)$, shifted in wavelength prior to the convolution, was compared to the spectrum $\mathbf{S}_{\Delta\lambda}[I \circ T](\lambda)$, shifted after the convolution procedure. The RMS of the residual structure χ , defined as

$$\chi_{\Delta\lambda,T}(\lambda) = -ln\left(\frac{\mathbf{S}_{\Delta\lambda}[I \circ T](\lambda)}{[\mathbf{S}_{\Delta\lambda}[I] \circ T](\lambda)}\right)$$
(4.23)

was calculated. The results shown in figure 4.6 can be summarised as follows:

- the interpolation error strongly decreases with increasing slit function width ΔT .
- the largest interpolation errors occur if the wavelength shift is 1/2, 3/2, ... channels. As expected, no interpolation error occurs if the wavelength shift is a multiple of the grid size.
- For the instrument used in this work, we find a maximum RMS residual due to interpolation errors of $2.2 \cdot 10^{-5}$ for the UV spectrograph (FWHM ≈ 5 channels) and $4.3 \cdot 10^{-5}$ for the Vis spectrograph (FWHM ≈ 6 channels), a factor of 5-10 below typical residual structures obtained in the fitting procedures. Thus, effects due to insufficient oversampling can be neglected.

4.5 The solar I_0 effect

The resolution of DOAS instruments usually ranges between tenths of a nanometre to several nanometres. The highly structured Fraunhofer spectrum is not fully resolved by the instrument. This leads to variations of in the observed absorption structures when measuring scattered (or direct) sunlight compared to observations using an unstructured light source. This effect is referred to as the *solar* I_0 *effect*, which is discussed in the following.

The DOAS retrieval is based on the estimation of the optical density, defined as the ratio of two intensities (see equation 4.3):

$$\tau(\lambda) = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = -\ln\left(\frac{I_0(\lambda) e^{-c\sigma(\lambda)}}{I_0(\lambda)}\right) = -c\sigma(\lambda)$$
(4.24)

The intensity I^m measured with the instrument is the convolution of the 'true' intensity I with the instrument function T:

$$I^{m}(\lambda) = (I \circ T)(\lambda) \equiv \int I(\lambda')T(\lambda - \lambda') \ d\lambda'$$
(4.25)

Thus the observed optical density τ^m of an absorber is the logarithmic ratio of the observed intensities I_0^m and I^m :

$$\tau^{m}(\lambda) = -\ln\left(\frac{I^{m}(\lambda)}{I_{0}^{m}(\lambda)}\right) = -\ln\left(\frac{(I \circ T)(\lambda)}{(I_{0} \circ T)(\lambda)}\right) = -\ln\left(\frac{((I_{0} e^{-c\sigma}) \circ T)(\lambda)}{(I_{0} \circ T)(\lambda)}\right)$$
(4.26)

Cross sections calculated using the traditional method $\sigma^{trad}(\lambda) = (\sigma \circ T)(\lambda)$ (see figure 4.7) cannot account for the observed optical density:

$$\tau^{m}(\lambda) \neq -c\,\sigma^{trad}(\lambda) = -c\,(\sigma \circ T)(\lambda) \tag{4.27}$$

Left and right side of equation (4.27) are only equal if $I(\lambda) \equiv const$, $T(\lambda) = \delta(\lambda)$ or $\sigma(\lambda) \equiv const$. Thus the traditional method of converting cross sections to the instrument resolution by simply applying a convolution with the instrument function cannot account properly for the observed absorption structures, in particular if both the cross section and the Fraunhofer spectrum are highly structured.

However, for small optical densities, $c \cdot \sigma \ll 1$, the exponent in equation (4.26) can be approximated by a Taylor expansion of first order:

$$e^{-c\sigma} \approx 1 - c\sigma \tag{4.28}$$

and equation (4.26) yields

$$\tau^{m}(\lambda) \approx -\ln\left(\frac{\left(\left(I_{0}\left(1-c\,\sigma\right)\right)\circ T\right)\left(\lambda\right)}{\left(I_{0}\circ T\right)\left(\lambda\right)}\right) = -\ln\left(1-c\cdot\frac{\left(\left(I_{0}\,\sigma\right)\circ T\right)\left(\lambda\right)}{\left(I_{0}\circ T\right)\left(\lambda\right)}\right)$$

$$\approx c\cdot\frac{\left(\left(I_{0}\,\sigma\right)\circ T\right)\left(\lambda\right)}{\left(I_{0}\circ T\right)\left(\lambda\right)}$$
(4.29)

The approximation of the logarithm in the last step can be performed since $\ln(1-x) \approx -x$ for $x \ll 1$. Thus optical density τ^m measured with an instrument with finite resolution is proportional to the column density c in a first order approximation, which is an important prerequisite for the meaningful interpretation of DOAS measurements.

Figure 4.8 shows how to prepare I_0 corrected cross sections by creating synthetic spectra according to equation (4.26) [Johnston, 1996]:

- 1. The high resolution Fraunhofer spectrum I_0 is convoluted to the instrument resolution by the instrument function $T: I_0^m = I_0 \circ T$
- 2. A synthetic absorption spectrum is calculated using the high resolution cross section σ and a column density c, which is in the order of magnitude typically found in the atmosphere. The synthetic absorption spectrum is convoluted to the instrument resolution: $I^m = (I_0 e^{-\sigma c}) \circ T$
- 3. The I_0 corrected cross section is calculated according to $\sigma^{I0} = -\frac{1}{c} \ln(I^m/I_0^m)$

Figure 4.9 shows the impact of the I₀ effect on the spectral retrieval of iodine oxide in the wavelength range between 410 and 465nm (left Panel) and bromine oxide between 340 and 365 nm (right Panel). The dotted line shows the simulated structure that would remain for an NO₂ column density of 10^{17} molec/cm², a value typically found at twilight during summer, if the NO₂ cross section is not I₀ corrected. The optical density of the I₀ structure is comparable to the residual of the spectral retrieval (around $(0.1 - 0.5) \cdot 10^{-3}$). This structure is small compared to the NO₂ absorption, but may have a significant impact on the retrieval of much weaker absorbers such as iodine oxide with optical densities smaller than 10^{-3} (solid line in left Panel of figure 4.9). It is noteworthy that the I₀ effect increases for smaller wavelengths.

Figure 4.10 shows the influence of the NO₂ I₀ correction on the spectral retrieval of iodine oxide. While the residual structure is slightly larger ($\approx 10\%$) when using I₀ corrected NO₂, the retrieved IO column density is about 6% smaller.

The impact of the I_0 effect on the spectral retrieval can be summarised as follows:

- The I_0 effect is caused by the observation of highly structured spectra and absorption structures using a low resolution spectrograph.
- It can only be properly accounted for the I_0 effect if high resolution cross sections and solar Fraunhofer spectra with a precise wavelength calibration are available, for example measured by Fourier transform spectrographs.



Figure 4.7: Schematic diagram for the traditional method to calculate cross sections by convoluting a high resolution cross section σ with the instrument function T.

- The I_0 effect of NO₂ is small compared to the absorption structure of NO₂ and therefore does not affect the retrieval of the NO₂ SCD. However, the I_O effect of NO₂ can have a significant impact on the retrieval of very weak absorbers, such as iodine oxide and bromine oxide.
- The I_0 effect could, in principle, be completely removed using the following iterative method:
 - 1. An I₀ corrected cross section σ_0 is created using an initial column density c_0 .
 - 2. The actual column density c is determined by performing a spectral retrieval using σ_0 .
 - 3. A new I₀ corrected cross section σ is calculated using the actual column density c.
 - 4. The spectral retrieval is performed again using the cross section σ , which accounts properly for the I₀ effect.

This method is, however, very time and memory consuming, even if fast Fourier transform techniques are used for the calculation of I_0 corrected cross sections.

In this work, the I_0 correction is applied to all cross sections available in high resolution and, to ensure a correct wavelength alignment, recorded with a Fourier transform spectrograph. The high resolution solar Fraunhofer spectrum was adapted from Kurucz [1984].



Figure 4.8: Schematic diagram for the calculation of I_0 corrected cross sections using the high resolution Fraunhofer spectrum from Kurucz and a high resolution NO_2 cross section. The mercury emission line at 436nm recorded with the vis spectrograph is used as the instrument function. A column density of $c = 10^{17} \text{molec/cm}^2$ was assumed.



Figure 4.9: Simulated absorption structure of $5 \cdot 10^{13}$ molec/cm² iodine oxide (left Panel, solid line) and $1 \cdot 10^{14}$ molec/cm² bromine oxide (right Panel, solid line). The dotted lines denote the I_0 effect for 10^{17} molec/cm² NO₂, i.e. the structure that remains if a standard convoluted NO₂ cross section is used in the spectral retrieval.



Figure 4.10: Example for the spectral retrieval of iodine oxide using I_0 corrected (red lines) and uncorrected (black lines) NO₂ cross sections. Panel A: Fitted IO cross sections (thick lines) and the retrieved spectral signatures (thin lines). Panel B: residual structure. Both atmospheric spectrum and Fraunhofer reference are recorded at October 30, 1999 at 92° and 80° SZA, respectively.

4.6 Radiative transport

The concept of air mass factors for the interpretation of DOAS measurements using scattered radiation is described in this section. Section 4.6.1 gives a brief summary of the radiative transport theory, the different approaches to model air mass factors and some intrinsic problems concerning the interpretation of results from radiative transport models. The Langley plot method to derive absolute slant column densities from differential slant column densities is described in section 4.6.2. Section 4.6.3 discusses the relevant input parameters for the calculation of air mass factors. The results of the radiative transport calculations are presented in sections 4.6.4 and 4.6.5

4.6.1 Theory of radiative transport in the atmosphere

As discussed in section 4.1, the primary product of a DOAS analysis is the *slant column density* (SCD) S. Since the SCD depends on the observation geometry and the current meteorological conditions, it is more convenient to express the results of a DOAS measurement in terms of the *vertical column density* (VCD) V, which is defined as the integrated trace gas concentration $\rho(z)$ as a function of altitude z:

$$V = \int \rho(z) \, dz \tag{4.30}$$

The VCD V is a quantity that only depends on the trace gas profile. It is independent of the viewing geometry and the trajectories on which the light traversed the atmosphere before reaching the instrument. The *air mass factor* (AMF) A is defined as the ratio of SCD S and VCD V:

$$A(\lambda,\Theta) = \frac{S(\lambda,\Theta)}{V}$$
(4.31)

where Θ is a set of parameters describing the observation geometry (i.e., solar zenith angle and viewing angle of the instrument). The AMF depends on the state of the atmosphere (i.e. pressure, temperature and ozone profile, aerosol loading, etc.).

This section discusses

- 1. how vertical column densities can be calculated from slant column densities using air mass factors derived by radiative transport models
- 2. to which extend the radiative transport can have an influence on the observed optical density and how those effects can be corrected for in the spectral analysis.

To determine the relationship between SCD S and VCD V, consider the definition of the optical density τ of radiation passing through a concentration field $\rho(\vec{x})$ under the assumption that the temperature and pressure dependency of the cross section σ is small:

$$\tau(\lambda) = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \sigma(\lambda) \cdot \int_0^L \rho(\vec{\gamma}(s)) \, ds = \sigma(\lambda) \cdot S(\lambda) \tag{4.32}$$

Here, $I_0(\lambda)$ is the intensity observed in absence of the absorber in the atmosphere. Combining equations (4.31) and (4.32), the air mass factor can also be written as



Figure 4.11: Observation geometry for direct sunlight observations in a plane parallel atmosphere without refraction.

$$A(\lambda) = \frac{\tau(\lambda)}{\sigma(\lambda) \cdot V} \tag{4.33}$$

Equation (4.32) is only valid if a well defined light path $\vec{\gamma}(s)$ between the position of the light source $\vec{\gamma}(0)$ and the measurement location $\vec{\gamma}(L)$ exists.

A simple scenario, the observation of direct sun- or moonlight in a plane parallel atmosphere with a trace gas distributed uniformly in horizontal direction, is sketched in figure 4.11. In this case (and if refraction is not taken into account), the path integral in equation (4.32) is calculated along a straight line between the spectrograph and the sun. Then the line element for a given solar zenith angle Θ is $ds = dz/\cos(\Theta)$ with dz being the vertical line element. Therefore, the slant column density S can be calculated as follows:

$$S(\Theta) = \int \rho(s)ds = \int \rho(z) \ \frac{dz}{\cos(\Theta)} = \frac{V}{\cos(\Theta)}$$
(4.34)

Hence, when neglecting refraction, the air mass factor for direct light observations on a plane earth,

$$A(\Theta) = \frac{S(\Theta)}{V} = \frac{1}{\cos(\Theta)}$$
(4.35)

is simply a function of the solar zenith angle, independent from the temperature, pressure and trace gas profile. For small solar zenith angles ($\Theta \leq 70^{\circ}$), equation (4.35) is also a good approximation for the air mass factor of zenith scattered sunlight [Frank, 1991]. In case of measurements of scattered radiation, the observed intensity is a sum of photons traversing the atmosphere on many different light pathes. This can be described as follows: assume that the set of possible light pathes can be described by a parameter α and let $p(\alpha, \lambda)$ be the probability that a photon with wavelength λ traverses the atmosphere on a given light path $\vec{\gamma}_{\alpha}(s)$ from the light source (sun) to the observation location¹. Then the observed intensity is the integrated intensity over all possible light pathes reaching the instrument, weighted with the according probability p [Marquard et al., 2000] and the observed optical density is:

$$\tau(\lambda) = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \ln\left(\int p(\alpha,\lambda) e^{-\sigma(\lambda)V \int \hat{\rho}(\vec{\gamma}_{\alpha}(s)) \ ds} \ d\alpha\right)$$
(4.36)

Again, σ is assumed to be independent from temperature and pressure and can therefore be written outside the inner path integral. The trace gas profile $\rho(\vec{s})$ is written as the product of the vertical column density and the 'relative' profile shape $\hat{\rho}(\vec{s}) = \rho(\vec{s})/V$ which is independent of the trace gas amount. Combining equation (4.33) and (4.36), the air mass factor A for the observation of scattered light is

$$A(\lambda) = -\frac{1}{\sigma(\lambda) \cdot V} \ln\left(\int p(\alpha, \lambda) e^{-\sigma(\lambda)V \int \hat{\rho}(\vec{\gamma}_{\alpha}(s)) \, ds} \, d\alpha\right) \tag{4.37}$$

Equations (4.36) and (4.37) have several important implications for the interpretation of measurements of scattered radiation:

- Equation (4.36) implies that the observed optical density is not a linear superposition of the optical densities along the individual light pathes $\vec{\gamma}_{\alpha}$. Therefore the Lambert Beer law is not strictly fulfilled.
- The Lambert Beer law is strictly fulfilled if and only if there exists a single well defined light path $\vec{\gamma}_0(s)$, i.e. when observing direct light. Then the probability density is delta distributed, $p(\lambda, \alpha) = \delta(\alpha)$. In this case, equations (4.36) and (4.32) are equivalent.
- The vertical column density cannot be divided out in equation (4.37). Hence, the air mass factor for scattered radiation is not only a function of the relative profile shape $\hat{\rho}$ but also depends on the vertical column density: $A(\lambda) = A(\lambda, V)$. Therefore, the determination of the vertical column density is equivalent to the solution of the implicit relationship (see equation (4.31))

$$V = \frac{S(\lambda)}{A(\lambda, V)} \tag{4.38}$$

This equation can in principle be solved using an iterative approach [Marquard et al., 2000]. Since the air mass factor needs to be calculated for each iteration step, this method is very time consuming and therefore not applied within this work.

• The air mass factor depends not only on wavelength λ , but also on the product of the absorption cross section $\sigma(\lambda)$ with the slant column density $S: A(\lambda) = A(\lambda, \sigma(\lambda) \cdot S)$.

 $^{{}^{1}}p(\lambda)$ is actually the probability density function of a continuous manyfold of possible light pathes. It is not evident that this function can be parameterised using one ore more parameter α . Therefore the path integrals in the following equations are not necessarily analytically solvable and should be regarded as a symbolic formalism.

4.6. RADIATIVE TRANSPORT

The air mass factor, and therefore also the slant column density, are modulated with the wavelength dependency of the trace gas cross section. This implies that the optical density is not a linear function of the cross section:

$$\tau(\lambda) = \sigma(\lambda) \cdot S(\lambda) = \sigma(\lambda) \cdot V \cdot A(\lambda, \sigma(\lambda) \cdot S)$$
(4.39)

This has important implications for the spectral retrieval since it is performed over a finite wavelength interval. For strong absorbers, such as ozone in the Huggins bands, the wavelength dependence of the air mass factors leads to a modulation of the absorption structure which can be compensated for by using $\sigma(\lambda) \cdot A(\lambda)$ instead of $\sigma(\lambda)$ as the trace gas reference spectrum ('modified DOAS') [Diebel et al., 1995; Richter, 1997].

• If a single absorber is present in the atmosphere, the probability density function $p(\lambda, \alpha)$ depends only on Rayleigh and Mie scattering. In this case, $p(\lambda, \alpha)$ is expected to be a broad banded function of λ . If more than one species absorbs in the considered wavelength interval, equation (4.32) implies that the probability density $p(\lambda, \alpha)$ is also a function of the cross sections $\sigma_n(\lambda)$ and concentration fields $\rho_n(\vec{s})$ of all other absorbers:

$$p(\lambda, \sigma_n(\lambda), \alpha) = p_0(\lambda, \alpha) \cdot e^{-\sum_n \sigma_n(\lambda)V_n \int \hat{\rho_n}(\vec{\gamma}_\alpha(s)) \, ds}$$
(4.40)

with $p_0(\lambda, \alpha)$ being the probability density function in absence of all absorbers. Therefore, the air mass factor for a trace gas depends also on the abundance of all other species absorbing in the given wavelength range. For example, the air mass factor for BrO can change significantly under ozone hole conditions due to the influence of the strong ozone absorption in the Huggins bands on the radiative transport.

- Precise air mass factors can be determined by modeling the intensities $I^M(\lambda)$ and $I_0^M(\lambda)$ in presence and absence of the absorber using a radiative transport model and by applying a spectral retrieval to these modeled spectra. Then the air mass factor is the ratio of the slant column density S^M (derived by the spectral retrieval) and the vertical column density V^M (which is a known input parameter for the radiative transport calculation): $A = S^M/V^M$. This approach is also very time consuming if variable atmospheric conditions need to be taken into account during long term measurements. Therefore this method is not applied within this work.
- Due to photochemistry, the profile of a trace gas possibly changes with solar zenith angle (chemical enhancement). This fact can be taken into account in the radiative transport model by using a two dimensional concentration field $\rho(z, \theta)$ which depends not only on the altitude z but also on the local solar zenith angle θ . The concentration field can be determined by photochemical model calculations. Unfortunately, the AMFTRAN program does not support the modeling of chemical enhancement.

A possible approach to calculate the radiative transport according to equation (4.37) is the single scattering approximation [Frank, 1991]. In this case, air mass factors are calculated under the assumption that each photon is scattered only once in the atmosphere. It follows that the light is scattered along the line of sight of the instrument (see figure 4.12). The individual light pathes can be expressed as a well defined function of the scattering position z along the line of sight, i.e. $\alpha \equiv z$, $\vec{\gamma}_{\alpha}(s) = \vec{\gamma}_z(s)$ and $p(z, \lambda)$ is now the probability that a photon is scattered into the viewing direction of the instrument in a distance z relative to the instrument. It follows that



Figure 4.12: Observation geometry for the measurement of zenith scattered sunlight with spherical geometry and refraction in single scattering approximation.

$$A(\lambda) = -\frac{1}{\sigma(\lambda) V} \int p(z,\lambda) \cdot e^{-\sigma(\lambda) V \cdot \int \hat{\rho}(\vec{\gamma}_z(s)) \, ds} \, dz \tag{4.41}$$

Single scattering radiative transport models have the advantage to be fast and relatively easy to implement. Reliable air mass factors can be modeled if the probability of multiple scattering is small, i.e. for stratospheric absorbers, small atmospheric aerosol loading and small solar zenith angles.

Multiple scattering in the atmosphere can be taken into account by using Monte Carlo radiative transport models. In this case, the pathes of individual photons are treated as a random process with given probabilities for scattering and absorption events. Equation (4.37) is solved by averaging over many light pathes. If the physical processes are modeled correctly within the Monte Carlo model, the precision of the air mass factor only depends on the number of modeled light pathes and the accuracy of the atmospheric input parameters.

The AMFTRAN Monte Carlo radiative transport model [Marquard, 1998] was used here to calculate air mass factors for ozone and NO_2 . It includes multiple Rayleigh and Mie scattering, refraction and full spherical geometry.

4.6.2 The Langley plot

The primary result of a DOAS retrieval according to equation (4.12) is the differential slant column density (dSCD) ΔS . The dSCD ΔS is the difference between the slant column density in the spectrum I, measured at solar zenith angle Θ , and in the reference spectrum I_0 , measured at a fixed solar zenith angle (usually at noon):

$$\Delta S(\Theta) = S(\Theta) - S_{ref} \tag{4.42}$$

The dependency of the air mass factor on the solar zenith angle Θ can be used to convert the differential slant column densities $\Delta S(\Theta)$ into absolute slant column densities $S(\Theta)$. Combining equations (4.42) and (4.31) leads to

$$\Delta S(\Theta) = A(\Theta) \cdot V - S_{ref} \tag{4.43}$$

The differential slant column density is a linear function of the air mass factor, if the vertical column density does not depend on the solar zenith angle. Equation (4.43) implies that the slant column density of the Fraunhofer reference spectrum, S_{ref} , is given by the intercept of the straight line when plotting $\Delta S(\Theta)$ versus $A(\Theta)$ and the slope is the vertical column density. Examples for Langley plots are shown in sections 4.6.4 and 4.6.5.

4.6.3 Atmospheric input parameters for the radiative transport

The modeling of the radiative transport according to equation (4.37) requires the knowledge of the probability density function $p(\lambda)$, which depends on the current atmospheric conditions. The input parameters for the AMFTRAN radiative transport model are as follows.

- Temperature and pressure profiles T(z) and p(z) are necessary to calculate the pressure dependent Rayleigh cross section as a function of altitude z and to take into account the temperature dependence of the absorption cross sections $\sigma(\lambda, T(z))$. The temperature and pressure profiles were taken from the regular ozone soundings at Neumayer (G. König-Langlo, AWI Bremerhaven, pers. communication). Ozone soundings are performed about once per week. The sounding program is intensified during the ozone hole period (September and October), when balloons are launched several times per week. An overview of the meteorological conditions derived from the ozone soundings is given in section 5.1.
- Ozone profiles are a necessary input parameter for the air mass factor calculation since the strong absorption in the Chappuis and Huggins band caused by this trace gas has a strong impact on the radiative transport. An overview of the ozone profiles from the sounding data is also given in section 5.1.
- Aerosol extinction profiles for the stratosphere are adapted from Stratospheric Aerosol and Gas Experiment II (SAGEII) satellite measurements. This instrument aboard the Earth Radiation Budget Satellite determines profiles of the aerosol extinction, NO₂, ozone and other trace gases in solar occultation [Mauldin et al., 1985; Russell and McCormick, 1989]. The aerosol extinction data is available for 385, 453, 505 and 1020nm. As shown in figure 4.13, SAGEII measurements in polar regions are sparse. Therefore all profiles south of -50° latitude were averaged (see figure 4.14). The radiative transport modeling requires to retrieve aerosol profiles for a particular wavelength. This was done by assuming that the extinction as a function of wavelength and altitude is given as $k(\lambda, z) = k(\lambda_0, z) \cdot \lambda^{\alpha(z)}$. With this relationship, the Junge exponent $\alpha(z)$ as a function of altitude was determined by interpolating between the annual mean of SAGEII extinction profiles at different wavelength.

Since the lowermost altitude of SAGEII aerosol profiles is approximately 7km, no extinction data for the troposphere is available. Besides, the tropospheric aerosol loading



function of season. The solid line indicates the profiles at latitudes south of -50° . The erlatitude of the Neumayer station $(70^{\circ}39'S)$. ror bars indicate the standard deviation of the The aerosol profiles shown in figure 4.14 are derived by averaging the data below the dashed line $(50^{\circ}S)$.

Figure 4.13: SAGEII overpass latitude as a Figure 4.14: Annual mean SAGEII aerosol data.

is highly variable, which has a large impact on the ozone air mass factors (see section 4.6.4). A constant extinction coefficient of 0.001km^{-1} was assumed for altitudes below 9km.

- NO₂ profiles were also adapted from SAGEII satellite measurements. The seasonal variation of the NO_2 profiles were derived as follows:
 - 1. monthly average NO₂ profiles south of -50° latitude were calculated (shown as solid lines in the left panel of figure 4.15).
 - 2. Since NO_2 profile data is not available below an altitude of 20km, a Gaussian function was fitted to the monthly average profile data. Figure 4.15 shows that this is a good approximation for the actual NO₂ profiles (left panel, dashed lines). The centre of the NO_2 profiles are located around 25km, with a decreasing altitude during winter due to the diabatic descent in the polar vortex. Since the fitted Gaussian profiles reach down into the troposphere, the NO_2 concentration below 10km was set to zero.
 - 3. The centre and width of the Gaussian profiles was then interpolated as a function of season in order to derive the altitude and time dependent NO_2 concentration $\rho_{NO_2}(z,t)$ as shown in the right panel of figure 4.15.



Figure 4.15: Left panel: monthly average SAGEII NO₂ profiles during 1999 south of -50° latitude (solid lines) and fitted Gaussian profiles (dashed lines). Right panel: seasonal variation of the NO₂ profile, calculated using the fitted Gaussian profiles.



Figure 4.16: Air mass factor for ozone at 520nm as a function of solar zenith angle and season (left) and deviation of the air mass factor from the average (right).

4.6.4 Air mass factors for ozone

Caused by the strong seasonal variation of the ozone profile due to the ozone hole, the air mass factor for stratospheric ozone varies strongly with time. Additional causes for the variation of the ozone air mass factor are seasonal changes of the tropopause height and stratospheric temperature. Therefore, a conversion of ozone slant column densities in vertical column densities requires the modeling of air mass factors using the current atmospheric conditions.

The air mass factor $A(\Theta, t)$ as a function of solar zenith angle Θ and time t (i.e., Julian day) has been calculated using monthly ozone, temperature and pressure profiles from representative ozone soundings. For September and October, where the largest variations in the ozone profile occur, weekly ozone soundings were used to calculate ozone air mass factors. From these model calculations, an air mass factor matrix $A_{i,j} = A(\Theta_i, t_j)$ was calculated by interpolating the air mass factors on equidistant grid points (Θ_i, t_j) .

As shown in figure 4.16, the air mass factor for ozone at 520nm changes strongly with season. The largest increase in the air mass factor of more than 10% at twilight occurs during late July, when the ozone depletion is not yet in progress and the diabatic descent of air masses in the polar vortex leads to a downward movement of the ozone profile. The twilight air mass



Figure 4.17: Variation of the ozone air mass factors at 520nm with the aerosol extinction profile for the standard profile derived from SAGEII data, for a pure Rayleigh atmosphere, for twice and half the standard extinction profile and for a 10 times enhanced extinction in the troposphere. Upper Panel: absolute AMF values. Lower panel: deviation of the AMFs relative to the standard aerosol scenario. The air mass factors were calculated using the ozone sounding from September 27, 1999.

factor decreases by up to 20% at the beginning of October, when almost all ozone is destroyed in the lower stratosphere. The vertical column density of ozone is determined by calculating the average VCD between $84^{\circ} \leq \Theta \leq 90^{\circ}$. The seasonal variation of the ozone air mass factor in this solar zenith angle interval ranges between +4% and -10%.

While the temperature, pressure and ozone profiles are well known from ozone soundings, there is a large uncertainty in the aerosol profile as adapted from SAGEII data. The aerosol extinction profile is derived by averaging the measurements south of -50° latitude. No seasonal changes are taken into account. Figure 4.17 shows the influence of possible changes in the aerosol profile. When varying the stratospheric aerosol extinction, the largest relative changes occur for small solar zenith angles (about 10% compared to the standard scenario if an aerosol free atmosphere is assumed). There are very large uncertainties concerning the tropospheric aerosol loading, which has a high variability due to tropospheric clouds and snow drift. Increasing the tropospheric extinction coefficient by a factor of 10 compared to the standard scenario (0.001km⁻¹) leads to a constant increase of the air mass factor of 5% for $\Theta < 85^{\circ}$, mainly due to the tropospheric light path enhancement which increases the tropospheric part of the observed ozone slant column density.

As discussed in section 4.6.1, the air mass factor is a function of wavelength and ozone cross section. The variation of the air mass factor for ozone within the wavelength range of the spectral retrieval in the Chappuis band is relatively small (< 2.5% for $\Theta < 93^{\circ}$) (see figure 4.18), and therefore should have only a minor impact on the error of the ozone vertical column density compared to the other error sources discussed in this section.

Both the slant column density of the Fraunhofer reference spectrum, S_{ref} , and the vertical column density can be determined simultaneously using Langley plots (see section 4.6.2). Therefore this method provides a test of the accuracy of the air mass factors: when using a


Figure 4.18: Variation of the ozone air mass factors with wavelength for 505, 520 and 530nm. The inlay shows the ozone cross section in the wavelength range of the spectral analysis (490 - 550nm). As indicated with arrows, the air mass factors are calculated inside and between the absorption bands. Upper Panel: absolute AMF values. Lower panel: deviation of the AMFs relative to the standard wavelength of 520nm. The air mass factors were calculated using the ozone sounding from September 27, 1999.



Figure 4.19: Langley plots for ozone for some clear days during 1999. The linear regression was performed for airmass factors of A < 20 ($\Theta \leq 90.5^{\circ}$) using a single Fraunhofer reference spectrum recorded at noon on September 27, 1999. The slope and intercept of the linear regression indicated in the legend is given in units of 10^{19} molec/cm².



Figure 4.20: Air mass factor for NO_2 at 435nm as a function of solar zenith angle and season (left) and deviation of the air mass factor from the average (right).

single Fraunhofer reference spectrum, the intercept of the Langley plot should be constant with time. Langley plots for selected days under clear sky conditions during 1999 are shown in figure 4.19. The linear relationship between the dSCD ΔS and the air mass factor Ais achieved very well up to $A \approx 25$, but the inferred S_{ref} varies strongly with time. This indicates either that the air mass factors are inaccurate (although their seasonal dependence is taken into account using the above mentioned air mass factor matrix) or that there is a time dependent offset on the inferred dSCDs. Since a very good linearity of the Langley plots is achieved during all seasons, a possible explanation for the variation of S_{ref} is the seasonal variation of the tropospheric aerosol loading. As discussed above (see figure 4.17), this would lead to a constant offset in the air mass factor independent from solar zenith angle, which is in agreement with the observations. It can be concluded that there is a large uncertainty of more than 50% in S_{ref} , which leads to an additional systematic vertical column density error of approximately 20DU.

4.6.5 Air mass factors for NO₂

As for ozone, NO_2 air mass factors are expected to show a seasonal variation due to changes in the ozone profile as well as in the NO_2 profile. Since NO_2 is a weak absorber, it has no significant influence on the radiative transport. Changes in the NO_2 vertical column density therefore only have a small impact on the air mass factor, in contrast to variations of the NO_2 profile shape.

As for ozone, the seasonality of the NO₂ air mass factors was taken into account by using atmospheric data from representative ozone soundings (as described in section 4.6.4) and the Gaussian shaped NO₂ profiles derived from SAGEII data as described in section 4.6.3. The dependence of the NO₂ air mass factor on solar zenith angle and season is shown in figure 4.20. Significant seasonal changes (> 5%) of the NO₂ air mass factor only occur for very high SZA (Θ > 91.5°). The deviation from the average NO₂ AMF at 90° SZA (±3.5%) is small compared to the variations of the ozone AMF (-10% to +5%).

Figure 4.21 shows Langley plots for some clear days during 1999, derived using the seasonal dependent NO₂ air mass factors. Although NO₂ has a strong diurnal variation due to photochemistry (which leads to the two branches in the Langley plots for am and pm), the linearity of the Langley plots is surprisingly good up to airmass factors of A = 45 (*Theta* = 95°). The



Figure 4.21: Langley plots for NO₂ for some clear days during 1999. The linear regression was performed for airmass factors of A < 25 ($\Theta \leq 91.5^{\circ}$) using a single Fraunhofer reference spectrum recorded at noon on October 06, 1999. The slope and intercept of the linear regression indicated in the legend is given in units of 10^{16} molec/cm².

inferred intercept remains constant with time (within 20%), except for the March 19 observation, where the am/pm difference in the NO₂ SCD is large. these findings give confidence that the radiative transport for NO₂ is well modeled.

A possible reason for the good accuracy of the NO_2 AMFs compared to ozone is the fact that only a very small fraction of the NO_2 total column is located in the Antarctic troposphere. In contrast, multiple scattering in the troposphere can lead to an increase in the observed ozone column density which cannot be captured by the radiative transport model since the tropospheric extinction profile is unknown.

4.7 The Ring effect

When observing scattered sun light, the depth of the Fraunhofer lines are reduced compared to direct sun light obserations [Grainger and Ring, 1962]. This so called Ring effect is most likely caused by rotational Raman scattering on air molecules [Brinkmann, 1968]. As a result of the interaction between an oscillating electric field and a rotation molecule, such inelastic scattering processes lead to a change of the photon's wavelength (see figure 4.22). Because the magnitude of the Ring effect changes with solar zenith angle, the filling in of the Fraunhofer line must be taken into account in the spectral analysis. The observed intensity is the sum of sun light scattered by elastic and inelastic processes:

$$I_{scat} = I_{elastic} + I_{inelastic} \tag{4.44}$$

Since the DOAS method is based on the determination of optical densities, the logarithm of intensities is compared in the spectral analysis. The inelastic part of the scattered light is



Figure 4.22: The raman scattering cross sections of O_2 and N_2 , adapted from Fish and Jones [1995].

small compared to the elastically scattered intensity. Therefore, a Taylor expansion can be applied to the logarithm of equation (4.44):

$$ln(I_{scat}) \approx ln(I_{elastic}) - \frac{I_{inelastic}}{I_{elastic}} = ln(I_{elastic}) + \tau_{Ring}$$
(4.45)

The Ring spectrum, $\tau_{Ring} = -I_{inelastic}/I_{elastic}$, can be determined according to the following methods:

- 1. *Measured Ring spectrum*: The polarisation of Raman scattered light is very small compared to Rayleigh scattered light. This fact can be used to determine the Ring spectrum by measuring spectra at different polarisation orientations [Solomon et al., 1987b]. This method has several shortcomings. First, it requires that only Rayleigh and Raman scattering occurs in the atmosphere. Since the scattering on aerosols also has a weak wavelength dependence, the measured Ring spectrum contains structures caused by Mie scattering. Second, the light path through the atmosphere depends on the polarisation direction, which possibly leads to trace gas absorption structures in the measured Ring spectrum [Wagner, 1999].
- 2. Modeled Ring spectrum: Using the known rotational states of oxygen and nitrogen, the spectrum of inelastically scattered light can be calculated [Bussemer, 1993; Fish and Jones, 1995]. This method avoids the above mentioned disadvantages of polarisation measurements. Comparisons between calculated Ring spectra and atmospheric observations in high spectral resolution have shown very good agreement [Aben et al., 2001]. Therefore, modeled Ring spectra [Chance and Spurr, 1997] were used for the spectral analysis in this work.

4.8. TRACE GAS CROSS SECTIONS

Species	Source	Resolution	Temperatures [K]	Reference
Ozone	FT^{a}	$5 \mathrm{cm}^{-1}$	203, 223, 246	[Voigt et al., 1999]
Ozone	Gr^b	0.2 - 0.4nm	202, 221, 241, 273	[Burrows et al., 1999]
NO_2	\mathbf{FT}	$0.5 - 1 \text{cm}^{-1}$	223, 260, 280, 293	[Voigt et al., 1999]
BrO	\mathbf{FT}	$10 \mathrm{cm}^{-1}$	228, 298	[Wilmouth et al., 1999]
OClO	\mathbf{FT}	$1 \mathrm{cm}^{-1}$	213, 233, 253,	[Kromminga et al., 1999]
			273, 293	
OClO	Gr		204	[Wahner et al., 1987]
IO	Gr^c	0.09nm	$295 \mathrm{K}$	[Hönninger, 1999]
O_4	\mathbf{FT}	$1 \mathrm{cm}^{-1}$	298	C. Hermans, pers.comm.
H_2O	HITRAN	$0.001 \mathrm{nm}$	273	[Rothman et al., 1998]

^{*a*}Fourier transform spectrometer

^bGrating spectrograph

 $^c\mathrm{Scaled}$ to the cross section of [Cox et al., 1999]

<i>Table 4.1:</i>	Trace qas	cross sections us	sed within this work
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4.8 Trace gas cross sections

In this section, a brief overview over the cross sections used for the spectral retrieval is presented and the influence of the temperature dependence on the spectral retrieval is discussed.

All cross sections were taken from the literature. As far as available, cross sections measured using Fourier transform (FT) spectrometer were used for the spectral retrieval, since they have a precise wavelength alignment and a high spectral resolution. This is particularly important when correcting for the I_0 effect. The cross sections used within this work are listed in table 4.1. The major absorbers in the wavelength regions of both spectrographs, together with Fraunhofer spectra, are shown in figure 4.23.

The temperature dependence of absorption structures can be taken into account by using cross sections recorded at different temperatures in the spectral analysis. If cross sections $\sigma(\lambda, T_0)$ and $\sigma(\lambda, T_1)$ recorded at temperatures T_0 and T_1 are fitted simultaneously in the spectral analysis, equation (4.12) implies that the temperature dependence of the cross section must fulfill the following linear relationship:

$$\sigma(\lambda, T) = a_0(T) \cdot \sigma(\lambda, T_0) + a_1(T) \cdot \sigma(\lambda, T_1) + \sum_n c_n \lambda^n$$
(4.46)

with the linear coefficients $a_i(T_j) = \delta_{ij}$ and an additive polynomial $\sum_n c_n \lambda^n$. To ensure that the sum of the retrieved fit coefficients for $\sigma(T_0)$ and $\sigma(T_1)$ results in the slant column density, an additional demand is

$$a_0(T) = 1 - a_1(T) \tag{4.47}$$

and that $a_0(T)$ is a monotonous increasing function of temperature.

Equations (4.46) and (4.47) can be used to investigate if the temperature dependence of the absorption structure can be removed by fitting the linear superposition of cross sections recorded at different temperatures. For these purposes, two cross sections $\sigma(\lambda, T_0)$ and $\sigma(\lambda, T_1)$ and a polynomial of third degree were simultaneously fitted to a third cross section $\sigma(\lambda, T)$ with $T_0 < T < T_1$.



Figure 4.23: Fraunhofer spectra and trace gas cross sections for the UV (upper figure) and Vis (lower figure) spectral region, convoluted to the instrument's resolution.

	T	T_0	T_1	a_0	a_1	$a_0 + a_1$
Α	223K	203K	246K	1.3020	-0.1898	1.1122
В	223K	203K	280K	1.2460	-0.1470	1.0990
С	246K	203K	280K	0.8671	0.1794	1.0465
D	246K	223K	280K	0.6871	0.2911	0.9782

Table 4.2: Fit coefficients retrieved by fitting the ozone cross sections $\sigma(\lambda, T_0)$ and $\sigma(\lambda, T_1)$ against $\sigma(\lambda, T)$ in the UV region (323 - 360nm).

	T	T_0	T_1	a_0	a_1	$a_0 + a_1$
Α	223K	203K	246K	0.1240	0.8591	0.9831
В	223K	203K	$280 \mathrm{K}$	0.7169	0.2475	0.9644
С	246K	203K	$280 \mathrm{K}$	0.4282	0.5601	0.9883
D	246K	223K	$280 \mathrm{K}$	0.4223	0.5858	1.0081

Table 4.3: Fit coefficients retrieved by fitting the ozone cross sections $\sigma(\lambda, T_0)$ and $\sigma(\lambda, T_1)$ against $\sigma(\lambda, T)$ in the visible region (485 - 650nm).

The results of this test for the ozone cross section in the Huggins and Chappuis band are summarised in tables 4.2 and 4.3, respectively. Particularly in the UV region, the sum of the coefficients a_0 and a_1 strongly differs from one. Also negative fit coefficients were retrieved, indicating a strongly nonlinear temperature dependence of the ozone cross section in the Huggins band. The residuals of the analysis, $\Delta\sigma(\lambda, T) = \sigma(\lambda, T) - (a_0(T) \cdot \sigma(\lambda, T_0) + a_1(T) \cdot \sigma(\lambda, T_1))$, are shown in figure 4.24. Due to the nonlinear temperature dependence, accounting for the ozone temperature dependence using two cross sections would lead to a residual of up to 2% in the UV for an ozone slant column density of 10^{20} molec/cm². The temperature dependence of the ozone cross section in the visible wavelength region is by far smaller, but residuals in the order of 10^{-3} can still remain if two ozone cross sections at different temperatures are fitted simultaneously.

Similar tests were performed to investigate the temperature dependence of the NO₂ cross section. Unfortunately, the NO₂ cross section at 260K [Voigt et al., 1999] was found to be of bad quality since its structure is distinctly different to the cross sections at other temperatures. Therefore, only one combination of cross sections (T = 280K, $T_0 = 223K$, $T_1 = 293K$) is available for testing the temperature dependence of the NO₂ cross section. The sum of the fit coefficients a_0 and a_1 as listed in table 4.4 are close to one, but distinctly different fit coefficients are obtained for the UV (322 - 421nm) and visible (403 - 652nm) wavelength regions. The residuals of the test analysis shown in figure 4.25 indicate a residual in the order of $(0.4 - 1.0) \cdot 10^{-3}$ (with maximum values in the wavelength region between 400 and 550 nm) if two cross sections at different temperatures are used in the spectral analysis. As for ozone, this finding is due to the nonlinear temperature dependence of the NO₂ absorption.

The above described analysis of temperature dependence of the cross sections can be

	Т	T_0	T_1	a_0	a_1	$a_0 + a_1$
UV	280K	223K	293K	0.1039	0.8909	0.9948
Vis	280K	223K	293K	0.5619	0.4474	1.0093

Table 4.4: Fit coefficients retrieved by fitting the NO₂ cross sections $\sigma(\lambda, T_0)$ and $\sigma(\lambda, T_1)$ against $\sigma(\lambda, T)$.



Figure 4.24: Residuals of the ozone cross section temperature dependence analysis, $\Delta\sigma(\lambda,T) = \sigma(\lambda,T) - (a_0(T) \cdot \sigma(\lambda,T_0) + a_1(T) \cdot \sigma(\lambda,T_1)))$ for the UV (left) and visible (right) wavelength region. The labels denoted in the legend correspond temperatures listed in Tables 4.2 and 4.3.



Figure 4.25: Residuals of the NO₂ cross section temperature dependence analysis, $\Delta\sigma(\lambda,T) = \sigma(\lambda,T) - (a_0(T) \cdot \sigma(\lambda,T_0) + a_1(T) \cdot \sigma(\lambda,T_1)))$ for the UV (left) and visible (right) wavelength region.

summarised as follows:

- Since the observed radiation passes through atmospheric layers with different temperatures, the temperature dependence of ozone and NO₂ must be considered in the spectral retrieval. This can be done by simultaneously fitting two or more cross sections recorded at different temperatures. The cross section temperatures should cover the expected temperature range of the absorber in the atmosphere.
- Due to the strong nonlinear temperature dependence of the ozone cross section in the Huggins bands (below 340nm), a spectral retrieval in this wavelength region would lead to residuals in the order of several percent with the available set of cross sections.
- When using two ozone cross sections at different temperatures in the Chappuis bands, residuals in the order of $2 \cdot 10^{-3}$ can still remain due to the nonlinear temperature dependence of the ozone absorption structure.
- The temperature dependence of the NO₂ absorption is nonlinear over the whole wavelength region. For a NO₂ SCD of 10^{17} molec/cm² (which is a typical value during summer), residual structures in the order of $1 \cdot 10^{-3}$ can still remain if two NO₂ cross sections at different temperatures are used for the spectral retrieval.

4.9 Spectral retrieval of ozone

Ozone has strong absorption structures both in the UV below 350nm (Huggins bands) and in the visible wavelength region above 470nm (Chappuis bands) (see also figure 4.23). Caused by the strong temperature dependence of the cross section (see section 4.8) and the wavelength dependence of the air mass factor (see section 4.6.1), the spectral retrieval of ozone in the UV is problematic. Therefore, the spectral retrieval of ozone was performed in the visible wavelength region, between 490 and 555nm, where two ozone absorption bands are located. A single Fraunhofer reference spectrum recorded at noon of September 27, 1999 (69° SZA) was used for the spectral analysis of both years (February 1999 to December 2000), except for the period between February 8 and April 9, 2000, where the spectral resolution changed strongly because the temperature controller of the water cooling device failed. For the latter period, a separate reference spectrum recorded at noon of March 7, 2000 was used.

The absorption of Ozone, NO₂, O₄, H₂O, and the Ring effect was accounted for using the cross sections listed in table 4.5. All cross sections were convoluted to the resolution of the instrument using the mercury emission line at 546nm. Three ozone cross sections recorded at 203K, 223K and 280K were fitted simultaneously to account for the temperature dependence of the ozone absorption. The ozone cross sections at 203K and 280K were orthogonalised to the 246K cross section so that the slant column density is given by fit coefficient of the latter one. A polynomial of fourth degree removes the broad-banded structures caused by Rayleigh and Mie scattering and possible nonlinearities are compensated by fitting a nonlinear intensity offset of second degree according to equation (4.16). The cross sections and the Fraunhofer reference spectrum are fixed in wavelength. The measured spectrum is allowed to shift and squeeze in first order to compensate for possible changes in the instrument's wavelength calibration.

Figure 4.26 shows an example for the spectral retrieval of ozone for a spectrum recorded during twilight of March 31, 1999. The residual RMS ranges between 0.2 and $0.7 \cdot 10^{-3}$ (see figure 4.27), and the average of the relative fit error is 3-5%, with increasing values during 2000



Figure 4.26: Example for the spectral retrieval of ozone on March 31, 1999 at 90° SZA. The Fraunhofer reference spectrum was recorded at noon of September 27, 1999 (69° SZA).

Spectral range				
490 - 555nm				
	Cross sections			
Species	Temperatures ^a	Reference		
Ozone	203K, <u>246K</u> , 280K	[Voigt et al., 1999]		
NO_2	<u>223K</u> , 280K	[Voigt et al., 1999]		
O_4	298K	C. Hermans, pers.comm.		
H_2O	273K	[Rothman et al., 1998]		
Ring		[Chance and Spurr, 1997]		
	Fit parameters	3		
Polynomial degree		4		
Nonlinear offset order		2		
Triangular smoothing		1		
Fraunhofer reference spectra				
Period	Recorded on	SZA		
99/01/29 - 00/07/02,				
00/04/10 - 00/12/31	99/09/27	69.0°		
00/08/02 - 00/04/09	00/03/07	65.6°		

^aUnderlined temperatures indicate the cross sections to which all others are orthogonalised.

Table 4.5: Cross sections, fit parameters and Fraunhofer reference spectra for the spectral retrieval of ozone.



Figure 4.27: Histograms of the RMS residual (left) and relative fit error (right) of the ozone retrieval for $80^{\circ} \le \Theta \le 90^{\circ}$ during 1999 and 2000.

compared to 1999 because of the increased time distance between the Fraunhofer reference spectrum and the measured spectrum. The smaller variability of the residual during 2000 reflects the improved thermal stabilisation of the spectrograph in this period (see section 3.12.3).

The wavelength window for the ozone retrieval is relatively small (258 channels), but the modulation of the radiative transport in the troposphere due to changes in the ratio of Rayleigh and Mie scattering if aerosols or clouds are abundant leads to a variation of the air mass factor. Therefore the observed O_4 slant column changes strongly with wavelength, depending on the meteorological conditions [Wagner et al., 2001]. The retrieval algorithm cannot account for this fact when including more than one O_4 absorption band in the fit window. This is

illustrated in figure 4.28, where the spectral retrieval of O_4 is shown for different fit windows in the visible wavelength region. The O_4 absorption structure is captured well by the fitted cross section if only a single O_4 absorption line is included in the fit window. In this case, the O_4 fit coefficients for the different absorption lines differ strongly, ranging between 4.6 at 477nm and 9.4 for the 578nm absorption band. Extending the wavelength range of the ozone retrieval by including the three O_4 absorption bands at 477, 532 and 578nm therefore leads to a strong increase in the residual structure by a factor of 10.

Daily ozone vertical column densities were determined by calculating the average VCD between 84° and 90° SZA. This SZA range is a compromise between the relative error of the retrieved ozone differential slant column densities, which has a minimum between 92° and 94° SZA (see figure 4.29), and the accuracy of the ozone air mass factor. The Langley plots shown in figure 4.19 deviate from the expected linear relationship for A > 20, corresponding to $\Theta > 91^{\circ}$. This indicates an inaccurate radiative transport modeling during twilight. During winter, when the solar zenith angle is always above 90°, the VCD was calculated by averaging between 88° and 94° SZA.

The error sources of the ozone vertical column density can be summarised as follows:

1. Statistical errors: As discussed above (see figure 4.27), typical values of the relative fit error for the spectral retrieval of ozone, σ_{fit} , range between 3% and 5%.

2. Systematic errors:

- (a) Air mass factor: Although the stratospheric AMF for ozone is well known since the current meteorological conditions derived from the ozone soundings are used for the radiative transport modeling, multiple scattering in the troposphere can have a large impact on the tropospheric AMF. This leads to uncertainties in the slant column density of ozone located in the troposphere (see section 4.6.4). Therefore, an error of the AMF of $\sigma_A = 10\%$ is assumed.
- (b) Reference slant column density: As discussed in section 4.6.4, the uncertainty of the amount of ozone in the Fraunhofer reference spectrum, S_{ref} , is relatively large. The error of S_{ref} , as determined by comparing Langley plots on different days under clear sky conditions, is $\sigma_{S_{ref}} \approx 5 \cdot 10^{18}$ molec/cm² (see figure 4.19).
- (c) Errors due to an improper spectral calibration: The spectral calibration of the cross sections is expected to be very precise, since they are recorded using FT spectrometers (except for water vapour, where a modeled spectrum is used). An uncertainty is given by the spectral calibration of the instrument itself. The numerical error of the wavelength shift determined by the WINDOAS wavelength calibration algorithm is about 0.015nm, corresponding to 0.06 channel. Shifting the Fraunhofer reference spectrum for ± 0.1 channel leads to variations of the ozone SCD of only $\pm 0.5\%$. This error is negligible compared to the other error sources.
- (d) Ozone cross section: The error of the ozone cross section, σ_{xs} , is assumed to be in the order of 5%.

The relative error of the slant column density is the square sum of the fit error and cross section error:

$$\frac{\sigma_S}{S} = \sqrt{\left(\frac{\sigma_{fit}}{S}\right)^2 + \left(\frac{\sigma_{xs}}{\sigma}\right)^2} \tag{4.48}$$







Figure 4.29: Relative fit error $\frac{\sigma_{\Delta S}}{\Delta S}$ of the ozone spectral retrieval as a function of SZA for October 7,1999.

Spectral range				
346 - 358.5nm				
	Cross sections			
Species	Temperatures	Reference		
Ozone	203K, 246K, 280K	[Voigt et al., 1999]		
NO_2	223K, 280K	[Voigt et al., 1999]		
O_4	298K	C. Hermans, pers.comm.		
BrO	228K	[Wilmouth et al., 1999]		
OClO	233K	[Kromminga et al., 1999]		
Ring		[Chance and Spurr, 1997]		
	Fit parameters			
Polynomial degree		3		
Nonlinear offset order		2		
Triangular smoothing		1		
Fraunhofer reference spectra				
Period	Recorded on	SZA		
99/01/29 - 00/02/07,	99/10/06	65.6°		
00/04/09 - $00/12/13$	00/10/16	66.5°		

Table 4.6: Cross sections, fit parameters and Fraunhofer reference spectra for the spectral retrieval of BrO.

The total error of the vertical column density, $V = \frac{\Delta S + S_{ref}}{A}$, is

$$\sigma_V = \sqrt{\left(\frac{\sigma_{\Delta S}}{A}\right)^2 + \left(\frac{\sigma_{S_{ref}}}{A}\right)^2 + \left(\frac{\Delta S + S_{ref}}{A^2} \cdot \sigma_A\right)^2} \tag{4.49}$$

The error of the VCD, typically in the order of 12% - 15%, is by far dominated by the uncertainties of the air mass factor.

4.10 Spectral retrieval of BrO

The BrO retrieval was performed in the wavelength region between 346 and 358.5nm (124 channel), according to the recommendations of Van Roozendael et al. [1999]. This wavelength region encompasses two absorption bands of BrO. The absorption of BrO, Ozone, NO_2 , O_4 , OCIO, and the Ring effect was accounted for using the cross sections listed in table 4.6. The cross sections were convoluted to the instrument resolution using the mercury emission line at 334nm. The strong temperature dependence of the ozone absorption in this wavelength region (see section 4.8) was accounted for by using three ozone cross sections recorded at 203, 246 and 280K. Two Fraunhofer reference spectra were used for the retrieval of 1999 and 2000, both recorded on mid October of the respective year. Due to the failure of the water cooling controller and the resulting spectral disalignment during February and March 2000, no BrO data is available for this period.

An example for the spectral retrieval of BrO for a spectrum recorded at 90° SZA on Mai 11, 1999 is shown in figure 4.30. The RMS residual of the spectral retrieval ranges between $5 \cdot 10^{-4}$ during 2000 and $7 \cdot 10^{-4}$ during 1999 (see the histograms in figure 4.31), with an average fit error of $(3.1 - 4.2) \cdot 10^{13}$ molec/cm². Both the average and the standard deviation of the BrO fit error is reduced for the measurements during 2000. The fit error does not exceed $7 \cdot 10^{13}$ molec/cm² during this period, again indicating that the improved thermal stability of the instrument causes more stable results. According to the definition of Stutz and Platt [1996], the detection limit S_{limit} of the BrO SCD is given by

$$S_{limit} = 2 \frac{\chi}{\sqrt{\sum_{k} (\sigma(\lambda_k) - \overline{\sigma})^2}}$$
(4.50)

where the sum covers the fit region and $\overline{\sigma}$ is the average of the cross section. For an RMS residual of $\chi = 5 \cdot 10^{-4}$, equation (4.50) yields a detection limit of $S_{limit} \approx 3.7 \cdot 10^{13} \text{ molec/cm}^2$, while typical values for BrO SCDs during winter are $(2 - 4) \cdot 10^{14} \text{ molec/cm}^2$. As shown in figure 4.32, BrO can be clearly detected for solar zenith angles of up to 95°.

Figure 4.33 illustrates that it is possible to include further BrO absorption bands by extending the wavelength interval of the spectral analysis. The residual RMS increases strongly and the BrO slant column decreases by about 7% if the absorption band at 344nm is included in the fit, indicating that the increasing ozone absorption structure at shorter wavelengths cannot be removed properly. Since the BrO absorption band at 360.5nm is relatively weak, extending the fit region to longer wavelengths does not improve the retrieval significantly. In addition, using the wavelength interval commonly used for the BrO retrieval [Van Roozendael et al., 1999] ensures that the results are consistent with other BrO measurements.

To create a consistent BrO data set for the whole measurement period and to gain information on the year to year variability of BrO, it is necessary to scale all dSCDs relative to a single Fraunhofer reference spectrum. The difference between the BrO dSCDs derived by the two Fraunhofer reference spectra for the 1999 and 2000 period as a function of SZA is shown in figure 4.34. The difference remains constant for $\Theta \leq 88^{\circ}$, but shows a relatively large scatter of $\pm 3 \cdot 10^{13}$ molec/cm². No good agreement between both data sets is achieved during twilight. This is most likely due to changes in the spectral calibration caused by the failure of the water cooling device, which causes a large error in the BrO dSCDs after April 2000 using the 1999 Fraunhofer reference. The difference of both BrO data sets below 80° SZA, $1.78 \cdot 10^{14}$ molec/cm², was added to the dSCDs retrieved using the Fraunhofer reference spectrum recorded on October 2000.



Figure 4.30: Example for the spectral retrieval of BrO on Mai 11, 1999 at 90° SZA. The Fraunhofer reference spectrum was recorded at noon of October 6, 1999 (66° SZA).



Figure 4.31: Histograms of the RMS residual (left) and relative fit error (right) of the BrO retrieval for $89.5^{\circ} \leq \Theta \leq 90.5^{\circ}$ during 1999 and 2000.



Figure 4.32: Examples for the variation of the BrO differential slant column density and residual RMS during spring 2000.



Figure 4.33: Spectral retrieval of BrO for different fit regions. Left: 346 - 358.5nm (standard retrieval); middle: 341.5 - 358.5nm; right: 341.5 - 364nm. The spectrum was recorded on September 20, 2000 at 90° SZA.



Figure 4.34: Difference of the BrO dSCDs determined using the 1999 and 2000 Fraunhofer reference spectrum as a function of SZA. The data is from the period between April 9 and April 31, 2000.

Within this work, BrO dSCDs relative to the Fraunhofer reference spectrum recorded on October 6, 1999 are reported. Daily am/pm values at 90° SZA are calculated by linearly interpolating the BrO dSCDs between 89° and 91° SZA. The following error sources for the BrO dSCDs must be considered:

- 1. Statistical errors: as denoted above, the BrO retrieval error during twilight is in the order of $(3-5)\cdot 10^{13}$ molec/cm², corresponding to a relative error of typically 10% during late autumn and early spring, when the highest BrO amounts are observed.
- 2. Systematic errors:
 - (a) Errors due to an improper spectral calibration: A precise wavelength alignment of the cross sections is guaranteed since they are recorded using FT spectrometers. The numerical error of the spectral alignment using the WINDOAS calibration algorithm is only 0.0015nm (0.015 channel). The BrO slant column density variation is only $\pm 2.5\%$ when shifting the Fraunhofer reference spectrum for ± 0.005 nm.
 - (b) *BrO cross section*: Wilmouth et al. [1999] report an error of 7.6% on the BrO cross section at 228K.
 - (c) Error due to the adjustment of the Fraunhofer reference spectra: Since the data analysed using the year 2000 reference spectrum is adjusted to the year 1999 data (see figure 4.34), the BrO dSCDs for the year 2000 have an additional systematic error of $\pm 3 \cdot 10^{13}$ molec/cm².

4.11 Spectral retrieval of NO₂

The spectral retrieval of NO_2 was performed in the wavelength region between 415 and 461.5nm (174 channel). The NO_2 slant column density could also be derived from the ozone retrieval procedure (see section 4.9), but a separate NO_2 analysis in the above wavelength region has some advantages:

- 1. The ozone absorption in the NO_2 fit window is relatively small. Therefore spectral interferences between ozone and NO_2 are less probable.
- 2. Ozone has only a minor impact on the radiative transport in this wavelength region. Therefore a better accuracy and smaller seasonal variation of the NO_2 air mass factor is achieved.
- 3. The differential cross section of NO_2 is larger in this wavelength region.

The cross sections used for the spectral retrieval of NO₂ are listed in table 4.7. In addition to NO₂ and ozone, the cross sections of the weaker absorbers O₄, OClO, H₂O and IO are included in the spectral retrieval. Since the optical density of these species is typically below 10^{-3} , they only have a small impact on the inferred NO₂ SCDs. The spectral retrieval of IO, which is performed in the same wavelength interval, and the impact of the O₄, H₂O and OClO absorption is discussed in detail in section 4.12.

Unfortunately, no high quality ozone cross section is available in the wavelength region between 415 and 461.5nm. This is illustrated in figure 4.35: the high resolution FT cross

Spectral range				
415 - 461.5nm				
	Cross section	ns		
Species	$Temperatures^2$	Reference		
Ozone	221K, 271K	[Burrows et al., 1999]		
NO_2	<u>223K</u> , 280K	[Voigt et al., 1999]		
O_4	298K	C. Hermans, pers.comm.		
OClO	233K	[Kromminga et al., 1999]		
H_2O	273K	[Rothman et al., 1998]		
IO	???	[Hönninger, 1999]		
Ring		[Chance and Spurr, 1997]		
	Fit parameters			
Polynomial degree		4		
Nonlinear offset order		2		
Triangular smoothing		1		
Fraunhofer reference spectra				
Period	Recorded on	SZA		
99/01/29 - 00/06/30	99/10/06	65.6°		
00/07/01 - 00/12/13	00/10/16	66.5°		

Table 4.7: Cross sections, fit parameters and Fraunhofer reference spectra for the spectral retrieval of NO_2 .



Figure 4.35: Comparison of the ozone cross sections available in the wavelength region between 415 and 461.5nm. Upper panel: differential ozone cross sections convoluted to the instrument's resolution (a) from GOME in the original wavelength calibration (solid line); (b) as (a), but shifted and squeezed to achieve the best fit (dashed line); (c) FT cross section (dotted line). Lower panel: absolute FT ozone cross section in high resolution.

section shown in the lower panel [Voigt et al., 1999] is very noisy in this wavelength region and therefore not suitable for the spectral retrieval. A highly structured residual was found when fitting the GOME ozone cross section [Burrows et al., 1999] using its original wavelength calibration. To obtain an agreement between the GOME ozone cross section and the ozone absorption structure, it was necessary to allow the cross section to shift and squeeze in wavelength (compare the solid and dashed lines in figure 4.35). The spectral alignment of the ozone cross section was derived by performing a nonlinear fit on a spectrum with large ozone absorption ($\Theta = 92^{\circ}$). The ozone shift and squeeze parameters derived by this procedure were then kept constant for the spectral retrieval of NO₂ (and IO). However, a relatively large uncertainty of about ±0.05nm (0.2 channel) remains for the wavelength alignment of the ozone cross section.

An example for the spectral retrieval of NO₂ is shown in figure 4.36. The average fit error at 90° SZA ranges between $(0.8 - 1.5) \cdot 10^{15}$ molec/cm² (compared to slant column densities of more than 10^{17} molec/cm² during summer), and the RMS residual are smaller than $1 \cdot 10^{-3}$ and $0.4 \cdot 10^{-3}$ during 1999 and 2000, respectively (see figure 4.37).

NO₂ vertical column densities were derived using two Fraunhofer reference spectra for 1999 and 2000, as denoted in table 4.7. The VCDs during twilight were linearly interpolated for $89^{\circ} \leq \Theta leq 91^{\circ}$ to obtain the VCD at 90° SZA. The following error sources must be considered for the NO₂ vertical column density:

1. Statistical errors: As discussed above (see figure 4.37), typical values of the fit error of the NO₂ VCD, σ_{fit} , range between $(0.8 - 1.5) \cdot 10^{15}$ molec/cm² at 90° SZA.

2. Systematic errors:

- (a) Air mass factor: As discussed in section 4.6.5, the consistent results derived by Langley plots for different days give confidence that the NO₂ air mass factors are reliable. An error of 10% is assumed for the NO₂ AMFs.
- (b) Reference slant column density: As discussed in section 4.6.5, the uncertainty of the amount of NO₂ in the Fraunhofer reference spectrum, S_{ref} , is relatively small. The error of S_{ref} , as determined by comparing Langley plots on different days under clear sky conditions, is $\sigma_{S_{ref}} \approx 1 \cdot 10^{15}$ molec/cm² (see figure 4.21).
- (c) Errors due to an improper spectral calibration: As mentioned above, the spectral alignment of the ozone cross section is a factor of uncertainty. When allowing the ozone cross section to shift in wavelength, the nonlinear fit algorithm suggests an error of approximately 0.05nm (0.2 channel). A wavelength shift of the ozone cross section of ± 0.1 nm leads to a variation of the NO₂ dSCD of less than 0.1%. The uncertainty of the spectral alignment of the Fraunhofer reference spectrum, as derived by the WINDOAS calibration algorithm, is in the order of 0.015nm (0.06 channel). Shifting the Fraunhofer reference spectrum for this amount leads to a variation of the NO₂ dSCD of less than 0.1%. Thus the error of the NO₂ dSCD due to improper wavelength alignment is negligible.
- (d) NO_2 cross section: The error of the NO₂ section, σ_{xs} , is assumed to be in the order of 5%.

According to equation (4.49), the relative error of the NO₂ vertical column density for typical values during summer $(5 \cdot 10^{15} \text{ molec/cm}^2)$ is 10%.



Figure 4.36: Example for the spectral retrieval of NO_2 on November 13, 2000 at 90° SZA. The Fraunhofer reference spectrum was recorded at noon of October 16, 2000 (67° SZA). The weaker absorbers OClO, H_2O and O_4 are not shown.



Figure 4.37: Histograms of the RMS residual (left) and relative fit error (right) of the NO₂ retrieval for $89.5^{\circ} \leq \Theta \leq 90.5^{\circ}$ during 1999 and 2000.

4.12 Spectral retrieval of IO

The spectral retrieval of iodine oxide was performed using the same settings as for NO₂ (see section 4.11). Since the optical density of IO is very small (typically below 10^{-3}), it is necessary to keep the signal to noise ratio of the spectral analysis as small as possible. Changes in the spectral resolution with time can strongly affect the spectral retrieval, since in this case the Fraunhofer structure cannot be removed properly by calculating the ratio of two spectra. Therefore, daily Fraunhofer reference spectra recorded at 80° SZA were used to analyse the twilight measurements of the respective dusk/dawn. This procedure has two shortcomings:

- 1. Since the differential slant columns relative to a daily Fraunhofer reference spectrum have an unknown offset, which can vary from day to day, these measurements gain no direct information on the seasonal variation of iodine oxide but only on changes of the slant columns during twilight.
- 2. The period of available data is restricted to those days were the solar zenith angle reaches less than 80°. This leads to a gap in the time series between mid April and late August.

Figure 4.38 shows an example for the spectral retrieval of iodine oxide. The five vibrational bands of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ transition of IO in the wavelength region between 415 and 461.5nm have an optical density of up to $1 \cdot 10^{-3}$, while the residual RMS is only $1.4 \cdot 10^{-4}$. A negative IO dSCD is determined, which means that there is less IO abundant along the light path at 92° compared to 80° SZA. This is also illustrated in figure 4.39: a strongly increasing negative spectral signature with increasing SZA is observed and IO can be clearly detected for solar zenith angles of up to 95°.

Since the optical density of IO is very small, it must be guaranteed that the observed absorption structure is not an artefact. An element of uncertainty is the improper wavelength alignment of the reference spectra. Possible candidates for a spectral disalignment are the Fraunhofer reference spectrum, the cross sections for ozone [Burrows et al., 1999], for OCIO [Wahner et al., 1987], and (to a small extend) for iodine oxide [Hönninger, 1999]. The influence of the uncertainty of the wavelength alignment was investigated according to the procedure recommended by Stutz and Platt [1996]: the cross sections and the Fraunhofer reference spectrum were shifted in wavelength by the uncertainty of their wavelength calibration. The change of the retrieved IO dSCD due to these wavelength shifts is a measure for the error caused by improper spectral alignment of the reference spectra.



Figure 4.38: Example for the spectral retrieval of IO on October 30, 1999 at 92° SZA. The Fraunhofer reference spectrum was recorded at 80° SZA of the same day.



Figure 4.39: Detected IO absorption structure during twilight as a function of SZA, observed on October 30, 1999. The Fraunhofer reference spectrum is recorded on the same day at $\Theta = 80^{\circ}$. An offset is added to the individual absorption structures and the corresponding SZA is denoted at the right.

These tests were performed in two separate ways: (1) by using a measured spectrum and Fraunhofer reference and (2) by using synthetic spectra. A synthetic Fraunhofer reference spectrum I_0 was created by convoluting a high resolution Fraunhofer spectrum [Kurucz et al., 1984] to the resolution of the instrument. A second spectrum I was calculated by adding the absorption structure of the trace gases to the high resolution Fraunhofer spectrum prior to the convolution: $I = I_0 \cdot \exp(-\sum_k c_k^0 \sigma_k)$. To simulate the noise of the instrument, random noise was added to the synthetic spectra in order to obtain the same RMS residual as when analysing atmospheric spectra. The spectral analysis using the synthetic spectra I and I_0 was performed with the same settings as for measured spectra. Compared to the analysis of measured spectra, using synthetic spectra has the advantage that the 'true' fit coefficients c_k^0 are known and can be compared to the fit coefficients c_k determined by the spectral analysis. On the other hand, no systematic errors, caused for example by improperly prepared cross sections or other instrumental shortcomings, can be simulated using synthetic spectra.

Figure 4.40 shows how the IO fit coefficient changes when shifting the reference spectra in wavelength. For measured spectra (solid lines), the change of the fit coefficient is determined relative to the fit coefficient when all reference spectra remain unshifted. The change of the fit coefficient for synthetic spectra (dashed lines) is relative to the initial fit coefficient used to create the synthetic spectrum, that is $(c_k - c_k^0)/c_k^0$. The y-intercept for the synthetic spectra of about -2.5% indicates that the random noise added to the spectra and/or the smoothing procedure leads to an underestimation of the IO dSCD. The spectral retrieval of IO shows a remarkable stability when shifting the reference spectra in wavelength. The largest uncertainty is given by the spectral calibration of the ozone cross section. However, the relative change of the IO dSCD is negative when shifting ozone both to positive and negative wavelengths, which means that the absolute value of the (negative) IO dSCD even increases.

Table 4.8 summarises the estimated errors of the IO dSCD due to improper wavelength calibration of the reference spectra. A total error of only about 3% is inferred, leading to the



Figure 4.40: Relative change of the IO fit coefficient when shifting the ozone, OClO and IO cross section and the Fraunhofer reference in wavelength. Solid lines: Results for a measured twilight spectra on October 15, 1999 (92° SZA); dashed lines: Results for synthetic spectra, calculated as described in the text.

Reference	Wavelength uncertainty	Change of
spectrum	uncertainty [nm]	IO dSCD
Fraunhofer	0.02	2.0%
O_3	0.10	2.3%
OClO	0.20	0.5%
IO	0.01	0.1%
Total error	3.1 %	

Table 4.8: Error of the IO dSCD due to uncertainties in the wavelength calibration.



Figure 4.41: Histograms of the RMS residual (left) and relative fit error (right) of the IO retrieval for $91.5^{\circ} \leq \Theta \leq 92.5^{\circ}$ during 1999 and 2000.

conclusion that errors in the wavelength calibration cannot cause artificial structures which would explain the observed IO absorption.

A further test of the reliability of the IO retrieval was performed by comparing the initial and retrieved IO dSCD using synthetic spectra. This was done in the following way:

- 1. A synthetic Fraunhofer reference spectrum I_0 was created by convoluting the high resolution Fraunhofer spectrum to the instrument's resolution.
- 2. A synthetic spectrum I with the absorption structures according to typical slant column densities of all absorbers was created: $I = I_0 \cdot \exp(-\sum_k c_k^0 \sigma_k)$. The initial IO slant column density in the synthetic spectrum was set to $c_0 = -8 \cdot 10^{13} \text{ molec/cm}^2$.
- 3. Two sets of 500 spectra each were calculated using the synthetic spectrum I:
 - (a) by adding random noise S: $I_1 = I + S$
 - (b) by adding random noise plus the average residual structure of the spectral retrieval R at 92° SZA during October 1999: $I_2 = I + S + R$.

In both cases, the variance of the noise was adjusted so that an average RMS residual of $2.5 \cdot 10^{-4}$ was obtained in the spectral retrieval.

4. The IO dSCDs were determined by the spectral analysis procedure, performed using the Fraunhofer reference spectrum I_0 and both the sets of spectra I_1 and I_2 .

Figure 4.42 shows the histogram of the retrieved IO dSCDs using the above described synthetic spectra. As expected, the average IO dSCD from spectra with pure random noise is close to the initial value of $-8 \cdot 10^{13}$ molec/cm², but the standard deviation of about $2.5 \cdot 10^{13}$ molec/cm² is about twice as high as the fit error from measured spectra shown in figure 4.41. This is likely caused by the triangular smoothing applied to the spectra, which leads to an underestimation of the fit error since the smoothing causes a correlation of neighbouring pixels [Stutz and Platt, 1996]. When adding both random noise and the average residual to the synthetic spectra, the impact of systematic structure on the IO retrieval is simulated. In this case, the absolute value of the IO dSCD is underestimated by about 3.5%, while the standard deviation $(1.5 \cdot 10^{13})$ is smaller compared to the case with pure noise, but still larger than the IO fit error of measured spectra.



Figure 4.42: Histogram of the retrieved IO dSCDs using synthetic spectra with (a) random noise and (b) random noise plus the average residual of the IO retrieval at 92° SZA during October 1999. The synthetic spectra were created with and initial IO dSCD of $-8 \cdot 10^{13}$ molec/cm².



Figure 4.43: Influence of the smoothing on the spectral retrieval of IO using synthetic spectra with a modeled IO dSCD of $-8 \cdot 10^{13}$ molec/cm². The error bars indicate the standard deviation of the data using 500 spectra with random noise.



Figure 4.44: Influence of the intensity offset on the spectral retrieval of IO using synthetic spectra with a modeled IO dSCD of $-5 \cdot 10^{13}$ molec/cm². The x axis denotes the intensity offset which was added to the synthetic spectra prior to the fit. Upper panel: Retrieved dSCD IO with (squares) and without (circles) fitting the intensity offset; middle panel: retrieved intensity offset; lower panel: RMS residual with (squares) and without (circles) fitting the intensity offset.

The influence of smoothing the spectra prior to the analysis was also tested using synthetic spectra with a modeled IO dSCD of $-8 \cdot 10^{13}$ molec/cm². As shown in figure 4.43, applying a single triangular smoothing has only a small impact of less than 1% on the retrieved IO dSCD.

A further uncertainty of the IO retrieval is given by possible nonlinearities of the instrument, which can be caused by an improper dark current correction or instrumental stray light. Those effects could cause artificial structures and are compensated for by fitting a nonlinear intensity offset of second order according to equation (4.16). To investigate this, synthetic spectra I_0 and $I = (I_0 + q) \cdot \exp(-c_0\sigma)$ with a varying offset q and a constant IO dSCD of $c_0 = -5 \cdot 10^{13}$ molec/cm² were calculated. The result of the spectral retrieval using these spectra is shown in figure 4.44. It is obvious that a small intensity offset of only a few percent leads to completely wrong results, while the nonlinear offset fit if no nonlinear offset is fitted. The nonlinear offset fit can compensate well for these nonlinearities.

The following can be concluded the above sensitivity tests:

- 1. The RMS residual of the IO retrieval is typically in the order of $2 \cdot 10^{-4}$, while optical densities of more than $1 \cdot 10^{-3}$ are observed. This leads to typical IO retrieval errors of $8 \cdot 10^{12}$ molec/cm², compared to maximum IO dSCDs of more than $1 \cdot 10^{14}$ molec/cm². However, the tests using synthetic spectra indicate that the error of the IO dSCD may be underestimated by the retrieval algorithm by a factor of two.
- 2. The detection limit of IO is $1 \cdot 10^{13}$ molec/cm² (according to equation (4.50)).
- 3. Systematic residual structures have only a small impact on the retrieved IO dSCDs.



Figure 4.45: Comparison of the IO dSCDs **Figure 4.46:** (92° SZA relative to 80° SZA) during spring dSCDs at 92° 2000, derived using a daily (x- axis) and a rived using the fixed (y- axis) Fraunhofer reference spectrum. rithm (x- axis) of

Figure 4.46: Comparison of the OClO dSCDs at 92° SZA during spring 2000, derived using the standard OClO retrieval algorithm (x- axis) and the IO analysis with a fixed Fraunhofer reference spectrum (y- axis).

- 4. Changes of the instrument properties have only a small impact on the IO retrieval when using daily Fraunhofer reference spectra.
- 5. The IO retrieval is insensitive to possible wavelength disalignments of the reference spectra.
- 6. Possible nonlinearities of the instrument can be compensated well by applying a nonlinear offset fit.

The IO retrieval is found to be very robust against changes of the analysis settings. The above findings give confidence that the observed absorption structure is really related to the abundance of iodine oxide along the light path.

Since the stability of the instrument and therefore the quality of the NO_2 retrieval was strongly improved during spring 2000 (compare the histograms shown figures 4.37 and 4.41), it was possible to detect iodine oxide using the standard NO_2 retrieval procedure with a fixed Fraunhofer reference spectrum recorded on October 16, 2000.

Figure 4.45 compares the IO dSCDs at 92° SZA relative to the $\Theta = 80^{\circ}$ measurements during spring 2000 for the retrieval using a daily reference spectrum and a fixed Fraunhofer reference spectrum. Note that the dSCD at 80° SZA, calculated using a fixed Fraunhofer reference, is the linearly interpolated value between 79° and 81° SZA, so that an additional (small) interpolation error arises compared to the measurements with a daily Fraunhofer reference. The measurements agree very well within the error bars, indicating that the quality of the IO analysis is not reduced using a single Fraunhofer reference spectrum during this period. In addition, this finding gives further evidence that the detected IO absorption is not an artefact.



Figure 4.47: Spectral retrieval of IO at 92° SZA on October 25, 2000 using a daily (left) and a fixed (right) Fraunhofer reference spectrum 2000. The spectral signature of IO is shown both for the retrieval including and omitting the OClO cross section in the fit.

One problem, however, arises when using a fixed Fraunhofer reference spectrum for the IO analysis. For measurements outside the polar vortex, where OCIO is not expected to be abundant, negative OCIO absorption structures are detected. This finding is illustrated in figure 4.46, where the OCIO dSCDs from the OCIO standard analysis is compared to the OCIO dSCDs derived by the IO retrieval. Both observations fit well for OCIO dSCDs $> 2 \cdot 10^{14}$ molec/cm², but negative OCIO dSCDs are determined by the IO analysis when the OCIO analysis indicates a dSCD of zero.

As shown in figure 4.47, the retrieval of IO using a fixed Fraunhofer reference spectrum changes only slightly for measurements outside the polar vortex (where no OClO is expected to be found) when omitting the OClO cross section in the analysis. Thus this effect has only a minor impact on the IO retrieval.

4.13 Spectral retrieval of OClO

The spectral retrieval of OClO was performed in the wavelength region between 361 and 391nm (218 channel), where three OClO absorption bands are located. In addition to OClO, only NO₂ and O₄ have a significant absorption structure in this wavelength region, which is accounted for by using the cross sections listed in table 4.9. The ozone cross section has only a broad structure in this fit window, but is also included in the analysis. A single Fraunhofer reference spectrum recorded at noon outside the polar vortex was used for the analysis of each season. Due to its short photolytic lifetime, OClO is not abundant in the sunlit atmosphere. Therefore the Fraunhofer reference spectra can be expected to contain no OClO. Thus the slant column densities relative to the Fraunhofer reference spectra are absolute SCDs.



Figure 4.48: Example for the spectral retrieval of OClO at 90° SZA on August 15, 1999, using a Fraunhofer reference spectrum recorded on October 06, 1999. The broad banded absorption structure of ozone is not shown.

Spectral range				
361 - 391nm				
	Cross section	ns		
Species	Temperatures	Reference		
Ozone	223K,	[Voigt et al., 1999]		
NO_2	223K, 280K	[Voigt et al., 1999]		
O_4	298K	C. Hermans, pers.comm.		
OClO	233K	[Kromminga et al., 1999]		
Ring		[Chance and Spurr, 1997]		
	Fit paramete	ers		
Polynomial degree		4		
Nonlinear offset order		2		
Triangular smoothing		1		
Fraur	nhofer referenc	e spectra		
Period	Recorded on	SZA		
99/01/29 - 99/06/30,	99/02/05	57.4°		
99/07/01 - 99/12/31	99/10/06	65.6°		
00/04/08 - 00/06/30,	00/04/18	81.7°		
00/07/01 - 00/12/31	00/10/16	61.5°		

Table 4.9: Cross sections, fit parameters and Fraunhofer reference spectra for the spectral retrieval of OClO.



Figure 4.49: Histograms of the RMS residual (left) and relative fit error (right) of the OClO retrieval for $89.5^{\circ} \leq \Theta \leq 90.5^{\circ}$ during spring 1999 and 2000.



Figure 4.50: Dependence of the RMS residual of the OClO retrieval at $\Theta = 90^{\circ}$ on the width of the instrument function between 370 and 378nm.

Figure 4.48 shows an example for the spectral retrieval of OCIO in the chlorine activated polar vortex, where OClO SCDs of typically $4 \cdot 10^{14}$ molec/cm² are observed. This corresponds to maximum optical densities of about $4 \cdot 10^{-3}$ compared to a residual RMS of $4.7 \cdot 10^{-4}$ for the example in figure 4.48. Such a good signal to noise ratio is, however, not always observed for the measurements during 1999. Figure 4.49 shows that residuals of more than $4 \cdot 10^{-3}$ are found during this period, leading to very large OClO retrieval errors of up to $9 \cdot 10^{13}$ molec/cm². The situation is by far better for the year 2000 observations, where the residual RMS is mostly below $0.75 \cdot 10^{-4}$.

Figure 4.50 shows the relationship between the residual RMS of the OCIO analysis and the width of the instrument function, which was determined using the WINDOAS calibration algorithm (see figure 3.28). The strong correlation between the instrument function and the amount of residual structure suggests that the OCIO retrieval is very sensitive to changes in the spectral resolution.

Figure 4.51 illustrates that it is possible to extend the OClO analysis to a very large fit window with up to seven absorption bands. However, this requires that the instrument operates under stable conditions, as they were achieved during spring 2000. The subsequent inclusion of OClO absorption bands at shorter wavelength leads to only a moderate increase in the residual RMS. The OClO SCDs determined using the different wavelength windows agree within the error bars. However, it was necessary to increase the degree of the fitted



Figure 4.51: Spectral retrieval of OClO for different wavelength windows between 333 and 391 nm. Left: Retrieved spectral signature and fitted cross section of OClO; right: residual structure. The spectrum was recorded at 90° SZA on September 05, 2000, using a Fraunhofer reference spectrum recorded on October 16, 2000.

polynomial and to include three ozone cross sections at different temperatures for wavelengths below 555nm. Furthermore, a scaling fit according to equation (4.17) was applied to the ozone cross sections to obtain such a good signal to noise ratio when extending the wavelength region of the OClO analysis below 350nm. The analysis window between 361 and 391nm was found to produce the most reliable results due to the following reasons:

- Extending the wavelength region to longer wavelengths is not possible because of the strong Fraunhofer lines at 393 and 397nm.
- The strong O₄ absorption line at 360nm could possibly interfere with the OClO absorption and should therefore not be included in the analysis.
- The increasing ozone absorption towards shorter wavelengths leads to an increasing residual structure below 350nm.
- As discussed above, the sensitivity of the OClO analysis on changes of the instrument function would be further increased when using a larger fit window.

According to equation (4.50), the detection limit of the OClO SCD is $2.3 \cdot 10^{13}$ molec/cm² for an RMS residual of $6 \cdot 10^{-4}$. However, the strongly increased residual during the 1999 observations leads to an accordingly increased OClO detection limit.

The following error sources must be considered for the retrieval of OClO SCDs:

1. Statistical errors: As illustrated in figure 4.49, the OClO retrieval error during twilight is in the order of $2 \cdot 10^{13}$ molec/cm² if the instrument is operated under stable conditions, but may reach values of more than $8 \cdot 10^{13}$ molec/cm² during 1999. The corresponding relative errors of the slant column density S during periods of chlorine activation ($S \approx 4 \cdot 10^{14}$ molec/cm²) ranges between 5 and 20% during 1999, and is always below 12% during 2000.

2. Systematic errors:

- (a) Errors due to an improper spectral calibration: A precise wavelength alignment of the cross sections is guaranteed since they are recorded using FT spectrometers. The numerical error of the spectral alignment using the WINDOAS calibration algorithm is only 0.0011nm (0.011 channel). The OClO slant column density variation is less than 0.5% when shifting the Fraunhofer reference spectrum for ± 0.005 nm.
- (b) OClO cross section: An error of 10% in the OClO cross section is assumed.
- (c) *Reference slant column density*: OClO is most likely not abundant in the sunlit atmosphere outside the polar vortex, where the Fraunhofer reference spectra are recorded. Therefore, the measurements relative to the Fraunhofer reference spectra are in very good approximation absolute SCDs.
Chapter 5

Results

In this chapter the results of the DOAS observations performed at Neumayer station during 1999 and 2000 are presented. Section 5.1 gives and overview over the meteorological conditions in the stratosphere during this period. The seasonal cycle of ozone together with a comparison of the DOAS measurements with ozone soundings and satellite borne observations is discussed in section 5.2. The observations of the mainly stratospheric trace gases NO_2 and OClO are subject of sections 5.3 and 5.4. The discussion of the BrO measurements presented in section 5.5 is splitted in two parts: the seasonal cycle with the main focus on stratospheric BrO is discussed in section 5.5.1 and the numerous tropospheric BrO events during spring are analysed in section 5.5.2. The first observations of tropospheric iodine oxide in the Antarctic marine boundary layer are subject of section 5.6.

5.1 Meteorological conditions

This section provides an overview on the meteorology in the stratosphere over the Neumayer station during the years 1999 and 2000 and presents a comparison between both years.

Figure 5.1 shows the potential vorticity over the Neumayer station at a potential temperature level of 475K, corresponding to an altitude of approximately 17km. The data is adapted from the European Centre of Medium range Weather Forecasts (ECMWF). The potential vorticity is given in PV units (PVU), defined as $1PVU = 10^{-6} \frac{K \cdot m^2}{kg \cdot s}$. The vortex edge is commonly defined as |PV| = 35PVU (shown as dotted line in figure 5.1), higher (absolute) PV values indicate inner vortex air masses. Other definitions include the analysis of the latitudinal gradient of PV and the wind speed along PV isolines [Nash et al., 1996]. However, figure 5.1 shows that the largest PV gradients occur for $|PV| \approx 35PVU$, indicating that the vortex edge is well described by this threshold value.

Both years are characterised by a stable polar vortex during winter, which formed about two weeks earlier during 1999 (mid April) than during 2000 (early Mai). Some sudden decreases in potential vorticity occurred during winter, e.g. on June 19 and August 1, 1999. The PV maps shown in figure 5.3 illustrate that the polar vortex sometimes shows a considerable asymmetry. Such events, driven mainly by planetary wave activity, can cause the Neumayer station to be located outside the vortex for short periods during mid- winter, as around June 19, 1999.

While on December 1, 2000, the polar vortex broke suddenly down, it lasted unusually long during 1999. After a drop around December 15, the PV increased again up to 40PVU,



Figure 5.1: ECMWF potential vorticity at the 475K isentropic level (\approx 17km altitude) above Neumayer station during 1999 (upper panel) and 2000 (lower panel). The threshold value for inner/outer vortex conditions (-35 PVU) is shown as dotted line.



Figure 5.2: ECMWF temperature at pressure levels of p = 30hPa and p = 50hPa (≈ 25 and 20km altitude, respectively) above Neumayer station during 1999 (upper panel) and 2000 (lower panel). The threshold temperatures for the formation of type 1 (195K) and type 2 (188K) PSCs are shown as dashed and solid lines, respectively.



Figure 5.3: ECMWF potential vorticity at the 475K potential temperature level over the southern hemisphere during spring 1999. The Neumayer station is located at the centre of the maps (marked with a black circle in the upper left figure).



Figure 5.3 (continued)



Figure 5.3 (continued)



Figure 5.4: Potential vorticity at the 475K theta level over the southern hemisphere during early summer 2000.

indicating that the Neumayer station was located inside the vortex until December 27, 1999. The PV maps in figures 5.3 and 5.4 illustrate that the vortex breakdown during 1999 occurred about one month later than during 2000, where the vortex has completely vanished at the beginning of December. Chlorine activation can of course not be expected during November and December since the stratospheric temperatures are by far too warm. However, air masses depleted in ozone during spring are potentially confined inside this long lasting vortex. This will be discussed in section 5.2.

In contrast to the vortex strength discussed above, the stratospheric temperatures are quite similar for both years (see figure 5.2). During both years, the temperatures fell below the threshold value for the formation of type 1 PSCs at the beginning of June. The stratospheric temperatures were already cold enough for possible PSC formation during a short period around Mai 6, 2000. However, it strongly depends on the temperature history of the air masses if chlorine activation can take place in such cases of early cooling (see the discussion of the OCIO observations in section 5.4). In both years, the temperature remained below the PSC threshold during the whole winter except for some short periods of warming around September 19, 1999 and September 4, 2000. Both warmings did not coincide with a decrease in the potential vorticity, indicating that the warm air did not originate from outside the vortex. From mid June to late August, the temperature dropped below the formation temperature for type 2 PSCs, about one week later, however, during 1999 than 2000. The temperatures were rising above 195K at the beginning of October. During 1999, however, the 50hPa temperature remained cold enough to form PSCs until end of October.

An overall picture of the stratospheric temperatures is provided by the temperature contour plots¹ shown in figure 5.5. During late autumn, the decrease in temperature starts in the upper stratosphere due to radiative cooling. This cooling process propagates slowly into the lower stratosphere, partly due to the diabatic heating caused by the descent of air masses. The coldest temperatures are found during June in an altitude range between 18-20km. During both winters, the temperatures were cold enough to form type 2 PSCs (see the area confined

¹The contour plots were derived from the ozone sounding raw data as follows: (1) each temperature data set T(h,t) (t: day of launch, h: altitude) from an individual sounding was spline- interpolated on an altitude grid $T(h_i,t)$ with $h_i = i \cdot 100m$; (2) the temperature data on a given altitude level h_i was spline- interpolated on a time grid $t_j = j \cdot 1day$, resulting in a matrix $T_{ij} = T(h_i, t_j)$



Figure 5.5: Temperature as a function of altitude and time during 1999 (left) and 2000 (right), derived using the Neumayer ozone sounding data. The black and red contour lines confine regions colder than the formation temperatures for type 1 and 2 PSCs, respectively.



Figure 5.6: ECMWF temperature maps at a pressure level of 50mPa during the coldest periods of 1999 (left) and 2000 (right).

by the red contour line in figure 5.5). The warming during spring occurs first at high altitudes, while the lower stratosphere still remains cold. This is due to the fact that the vortex breakdown occurs first at high altitudes, so that warm (and ozone-rich) air from higher latitudes enters the polar region from above.

Figure 5.6 shows maps of the stratospheric temperature at 50mPa during the coldest periods of both years. Almost the whole inner vortex temperature is below the formation threshold for type 2 PSCs. This illustrates that, in contrast to the northern hemispheric winter, chlorine activation can be expected to occur over the whole Antarctic continent.

5.2 Results of the ozone measurements

In this section, the seasonal variation of the ozone vertical column densities during 1999 and 2000 is discussed and the DOAS ozone measurements are compared with the integrated profiles from the ozone soundings and the vertical column density from the TOMS satellite instrument.

5.2.1 Ozone vertical column densities from ozone soundings

The ozone sondes² use a wet-chemical method to measure the ozone partial pressure. In addition, vertical profiles of temperature, wind direction and speed, pressure and relative humidity are measured by the ozone soundings. The balloons usually reach a float altitude of more than 30km. Ozone soundings at Neumayer are launched about once per week. More frequent measurements with two or three launches per week are performed during the ozone hole period (September and October).

Only ozone soundings with float altitudes of more than 30km were used to derive vertical column densities as follows:

- 1. The ozone concentration profile $\rho(z) = p(z)/(k \cdot T(z))$ was integrated from the ground to the float altitude: $V_0 = \int_0^H \rho(z) dz$. Here, *H* is the float altitude and p(z) and T(z)are the ozone partial pressure and temperature profiles, respectively.
- 2. Under the assumption that the ozone mixing ratio above the float altitude is constantly decreasing from the value at float altitude to zero at 70km, the ozone concentration profile $\rho_{res}(z)$ was calculated using pressure and temperature data adapted from the U.S. standard atmosphere. The ozone profile above the float altitude was integrated up to an altitude of 70km to derive the residual ozone column: $V_{res} = \int_{H}^{70km} \rho_{res}(z) dz$.
- 3. The total ozone column density is the sum of the column densities below the flow altitude and the residual column: $V = V_0 + V_{res}$.

The modeling of the upper stratosphere and mesosphere using the U.S. standard atmosphere might not be realistic since it is representative for mid- latitudinal conditions and no seasonal variations of pressure and temperature are taken into account. Also, the assumption that the ozone mixing ratio is constantly decreasing above the float altitude is not necessarily a realistic scenario. However, the bulk of the ozone column is located below the float altitude and the residual column above ranges between 10 and 15DU. The error in the VCDs due to the uncertainty of the residual column is therefore at most a few percent.

5.2.2 Ozone vertical column densities from TOMS

The Total Ozone Mapping Spectrometer (TOMS) aboard the Earth Probe satellite was launched during 1996 [McPeters et al., 1998]. The TOMS instrument provides measurements of total column ozone by measuring the backscattered earth radiance in six bands of 1nm width in the UV spectral region. The data is available on a grid of 1° in latitude by 1.25° in longitude over the entire globe. The daily global coverage of the instrument is about 90%, so that daily overpass data for a particular measurement site is available.

The TOMS instrument aboard the Earth Probe is the successor of three TOMS instruments which were almost continuously measuring the global distribution of ozone since 1978. It is therefore one of the best calibrated instruments for the measurement of total ozone. For TOMS total ozone, the absolute error reported in the literature is $\pm 3\%$, the random error is $\pm 2\%$ (though somewhat higher at high latitudes) and the drift after 1.5 years of operation is less than $\pm 0.6\%$ [McPeters et al., 1998]. This has been validated by comparing TOMS and ground based measurements of total ozone. The EP/TOMS ozone is approximately 1.0%

²The ozone sounding data was kindly provided by G. König Langlo, AWI Bremerhaven



Figure 5.7: Seasonal variation of the ozone vertical column density over Neumayer during 1999 (upper panel) and 2000 (lower panel): ground- based DOAS measurements averaged between 84° and 90° SZA (black squares) and between 88° and 94° SZA (open squares), VCDs from the ozone soundings (blue circles) and from TOMS (red squares).

higher than a 30 station network of ground measurements located on the northern hemisphere [McPeters et al., 1998]. However, recent studies suggest that TOMS instrument systematically overestimates the ozone VCD for about 20% at southern high latitudes [Bodeker et al., 2001].

5.2.3 Seasonal variation of the ozone vertical column density

Figure 5.7 shows the seasonal variation of the ozone vertical column density during 1999 and 2000. The data from the ground based DOAS instrument, from TOMS and from the ozone soundings are shown. In order to close the gap during winter when the sun is below the horizon all day long, averaged VCDs from DOAS are not only shown for $84^{\circ} \leq \Theta \leq 90^{\circ}$, but also for $88^{\circ} \leq \Theta \leq 94^{\circ}$.

The uncertainty of the ozone VCD increases with SZA, caused both by the systematic error of the airmass factor (see the Langley plot in figure 4.19) and by the increased retrieval error for large SZAs. The correlation between ozone VCDs derived by averaging over different SZA intervals is shown in figure 5.8. The ozone VCD is systematically underestimated by about 10DU when averaging between 88° and 90° SZA compared to the 'standard' SZA interval between 84° and 90° SZA. The error is even larger during mid-winter, when the solar zenith angle is always larger than 93° (red circles in figure 5.8). However, even if the ozone VCD has a large systematic error when averaging between 88° and 94° SZA, it is useful to include



Figure 5.8: Comparison of the VCDs derived using different SZA averaging intervals during spring 2000. X-axis: Average VCD between 84° and 90° SZA. The average VCD between 88° and 94° SZA is shown as black squares with the respective linear interpolation (black dashed line); the average VCD between 93° and 94° SZA is shown as red circles with the respective linear interpolation (red line). The black solid line is the function y = x

these data in figure 5.7 since they provide information on the variability of stratospheric ozone during mid-winter.

The ozone VCDs from TOMS are systematically higher for about 20DU than both from DOAS measurements and ozone soundings. This is also shown in figure 5.9, where the TOMS and ozone sounding VCDs are plotted versus the ozone VCDs from DOAS. Caused by the large systematic uncertainty in the airmass factor, the error of the O_3 VCD is estimated to 12% -15% (see section 4.9). However, DOAS measurements and ozone sounding data agree very well within ± 10 DU, although not necessarily the same air mass is probed by both instruments. In contrast, the TOMS ozone VCDs are about 20DU higher. This systematic difference between DOAS and TOMS occurs both for low and high ozone conditions, indicating that a systematic error is responsible for this disagreement. Possible causes for this discrepancy could be errors in the ozone airmass factor, the uncertainty in the determination of the Fraunhofer reference slant column amount (see section 4.6.4) or the uncertainty of the ozone cross section (see section 4.9). However, a recent comparison between the TOMS measurements and data from the global Dobson network for the period from 1978 to 1988 shows that the TOMS measurements systematically overestimate the ozone VCD for 20DU at southern high latitudes [Bodeker et al., 2001, in agreement with the discrepancies observed here. The difference between Dobson and TOMS at 70°S ranges from 10% during winter to 26% during summer, as shown in figure 5.10.

The strength and duration of the ozone hole during spring 1999 and 2000 is consistent with the expectations from the meteorological data discussed in section 5.1. During both years, the ozone VCD starts to decrease during early August and the minimum values are observed



Figure 5.9: Correlation between the Ozone vertical column density from DOAS (x-axis), TOMS (black squares, dashed black line) and ozone soundings (red circles, solid red line). The solid black line is the function y = x.



Figure 5.10: Difference between the ozone vertical column from the global Dobson network and the TOMS instruments aboard Nimbus 7 and Earth Probe as a function of time and latitude. Adapted from Bodeker et al. [2001].



Figure 5.11: Ozone profiles on June 28, July 19 and August 27, 2000.

at the end of September. The ozone values remain constantly low during 1999 - with VCDs around 125DU - for more than six weeks, reflecting that the Neumayer station was located below the polar vortex during this time (see figure 5.1).

The recovery of the 1999 ozone hole occurs very slowly and lasts until the end of the year. This unusually long ozone hole period is only interrupted by two short periods of increased ozone VCDs around November 20 and December 14. While the latter period of increased ozone VCDs is clearly due to outer vortex air over Neumayer (indicated both by a decrease in PV and increase in temperature, see figures 5.2 and 5.1), the increase on November 20 is accompanied by only a small decrease in the potential vorticity. However, a sudden increase in stratospheric temperatures from 193K to 215K occurs during this time (see figure 5.2), indicating that - despite of the high potential vorticity - outer vortex air was above the Neumayer Station during this period.

While the ozone hole of 1999 lasted until summer, a stronger depletion with a minimum ozone VCD of 102.2DU was observed during 2000 (compared to a minimum ozone VCD of 117.6DU during 1999). This finding is most likely related to the lower stratospheric temperatures during spring 2000 compared to 1999 (see figure 5.5). However, the ozone column density started to increase again right after reaching the minimum at the beginning of October 2000 and VCDs of more than 250DU were already present during late November.

An interesting feature of the ozone data is the strong and sudden decrease in the ozone VCD during mid-winter 2000. On July 17, the ozone VCD suddenly drops from 220DU to less than 150DU. This unusual event lasts approximately three days. The ozone profile observed at the very end of this period, on July 19, is shown in figure 5.11, together with two other mid-winter profiles from June 28 and August 27. On July 19, the ozone partial pressure had significantly decreased in an altitude range between 14 and 15km, indicating that ozone depletion may have occurred in these air masses. Figure 5.12 shows five day backward trajectories ending on July 12, 17 and 22 on isentropic levels of 375, 425 and 500K (approx. 12, 15 and 18km) over Neumayer, together with the solar zenith angle and temperature along the trajectories. The temperatures were most of the time low enough to form PSCs, except for the 425K trajectory on July 17. The solar zenith angle of air masses arriving on July 12 was always above 93.5°, making a photochemical ozone depletion unlikely. In contrast, the



Figure 5.12: Isentropic backward trajectories ending on July 12 (red lines), 17 (black lines) and 22 (green lines), 2000, 00:00 at isentropic levels of 375 (solid lines), 425 (dashed lines) and 500K (dotted lines) over Neumayer. Each symbol represents one day of model run. The lower panel shows the solar zenith angle and temperature along the trajectories as a function of time.



Figure 5.13: Ozone partial pressure as a function of altitude and time during 1999 (left) and 2000 (right), derived using the Neumayer ozone sounding data.

trajectory analysis indicates that the stratospheric air masses observed on July 17 originated from latitudes north of 60°S and were thereby exposed to sunlight 40, 60 and 100 hours prior to their arrival over Neumayer. Therefore it is likely that chemical ozone depletion took place during this period. However, the air masses arriving after the ozone depletion event (July 22), when an ozone column density of 210DU was observed, were also exposed to sunlight, although only for shorts periods 65 and 85 hours prior to their arrival at Neumayer.

An overall picture of the variation of stratospheric ozone with altitude and season is provided by the contour plots in figure 5.13. The ozone observations can be summarised as follows:

- The polar vortex of 1999 was unusually stable and lasted until the end of the year. Simultaneously, ozone depleted air masses were observed until end of December 1999. Due to the high temperatures inside the vortex, a chemical ozone depletion cannot occur during early summer. Instead, the inner vortex air remained low in ozone for almost two months since it was effectively isolated from mid-latitudinal air.
- During 2000, the vortex breakdown occurred much earlier. However, the depletion was stronger with minimum ozone VCDs of only 102DU, mainly due to the lower stratospheric temperatures compared to 1999.
- A short period of mid-winter ozone depletion was observed during July 2000. This finding is supported by trajectory calculations, which indicate that the observed air masses were previously exposed to sunlight so that a photochemical ozone depletion was possible.

5.3 Results of the NO₂ measurements

Figure 5.14 shows the seasonal variation of the NO₂ vertical column density at 90° SZA during 1999 and 2000, together with the temperature at 50hPa. NO₂ is almost completely removed from the stratosphere during winter, indicating that an effective denoxification by conversion of NO₂ to N₂O₅ and a subsequent heterogeneous conversion to HNO₃ on PSC particles takes place during winter (see reactions (2.22), (2.45) and (2.46)). This result is supported by



Figure 5.14: Seasonal variation of the NO_2 vertical column density at 90° SZA over Neumayer during 1999 (upper panel) and 2000 (lower panel). Morning and evening values are shown as black squares and red circles, respectively. Also shown is the ECMWF temperature at the 50hPa pressure level (blue line, right axis).

model calculations, showing that N_2O_5 is completely removed from the stratosphere during early spring [Danilin and McConnell, 1994].

The recovery of NO_2 occurs slower during spring 1999 than during 2000. This slower renoxification process is most likely caused by the much longer lasting polar vortex during 1999, which prevents NO_2 -rich air from mid-latitudes from mixing with the denoxified air inside the vortex.

A remarkable feature of the NO₂ observations is the difference in the diurnal variation during autumn and spring. While the NO₂ VCDs are significantly smaller at morning than at evening during autumn, this is not the case at springtime where only a small difference between am/pm values is observed. Examples for the diurnal variation of the NO₂ VCD during autumn and spring 1999 are shown in figure 5.15. During both seasons, the VCD decreases rapidly in the morning until a photochemical steady state between NO₂ and NO is established (see reactions (2.19) and (2.20)). The autumn measurements show a steady increase of the NO₂ VCD during day, which is caused by the slow photolysis of N₂O₅ under solar illumination. This indicates that the am/pm ratio of the NO₂ VCD is mainly controlled by gas phase chemistry: the duration of solar illumination determines the amount of NO₂ released from N₂O₅ during day and the time available to form N₂O₅ during night by reaction of NO₂ with NO₃. In contrast, the NO₂ VCD increases by far slower during spring, indicating that N₂O₅ is much less abundant in the stratosphere due to heterogeneous conversion to HNO₃



Figure 5.15: Diurnal variation of the NO_2 vertical column density as a function of SZA on April 1 and October 13, 1999.



Figure 5.16: Temperature dependence of the photostationary steady state NO/NO₂ ratio for an ozone concentration of $4 \cdot 10^{12}$ molec/cm² (≈ 17 km altitude) and 70° SZA, calculated using equation 2.11.

on PSCs.

Both the decrease in the NO₂ VCD at morning and the increase at evening occur slower during spring compared to autumn. As shown in figure 5.15, the minimum VCD at noon is observed around 90° SZA on Apr. 1, while the decrease of the NO₂ VCD during twilight lasts munch longer, until $\Theta = 87^{\circ}$, on Oct. 13. It is likely that this finding is caused by the slower release of NO and NO₂ from HNO₃, which is the major nitrogen reservoir species during spring. HNO₃ has a much longer photolytic lifetime compared to N₂O₅, which is the dominant nighttime species in the absence of heterogeneous reactions.

The NO₂ VCD is remarkably well correlated with the stratospheric temperature. This pronounced relationship between temperature and NO₂ abundance has two causes: (1) the rate constant for thermal dissociation of N_2O_5 is strongly temperature dependent. N_2O_5 is

more stable and therefore more abundant at cold temperatures and (2) the strong temperature dependence of the reaction $NO + O_3 \longrightarrow NO_2$ has an influence on the NO_x partitioning. The rate constant for this reaction is twice as large at 205K as at 185K. As shown in figure 5.16, this leads to a reduction in the NO/NO₂ ratio at higher temperatures and thus to smaller stratospheric NO₂ concentrations.

The NO_2 observations during 1999 and 2000 can be summarised as follows:

- The overall seasonal cycle is characterised by a strong decrease in the NO₂ VCD to values below $5 \cdot 10^{14}$ molec/cm² during winter, reflecting the strong denoxification in the cold polar vortex.
- The durability of the polar vortex and the slower increase in the stratospheric temperatures during spring 1999 lead to a slower renoxification process compared to spring 2000.
- Due to the strong temperature dependence of the N₂O₅ formation and the reaction of NO with ozone, the NO₂ VCDs have a strong correlation to the stratospheric temperatures.
- The NO₂ abundance is controlled mainly by gas phase chemistry during autumn, which leads to smaller NO₂ VCDs at morning and at evening.
- The strong influence of heterogeneous chemistry during spring is reflected by a less pronounced diurnal variability of NO₂ due to N₂O₅ hydrolysis on PSC particles.

5.4 Results of the OClO measurements

The seasonal variation of the OClO slant column density at 90° SZA is shown in figure 5.17, together with the ECMWF potential vorticity at the 475K isentropic level. The high OClO SCDs during spring of both years indicate that, as expected, a pronounced chlorine activation has occurred inside the polar vortex.

The development of the chlorine activation can be seen more clearly in figure 5.18, where the OCIO SCDs are shown for 94° SZA. For this solar zenith angle, only a small gap of 10 days without observations remains during mid-winter. Also, the OCIO SCDs are larger compared to the 90° SZA observations, both because OCIO forms during twilight and because the airmass factor is larger at higher SZAs.

The observed OCIO SCDs are very well correlated to the potential vorticity during winter and early spring. This relationship between OCIO and vortex strength indicates an increase in the abundance of reactive chlorine or photolable chorine compounds, such as BrCl and HOCl, from the vortex edge towards the centre of the vortex. OCIO dSCDs of up to $4.5 \cdot 10^{14}$ molec/cm² are observed at 90° SZA between mid-July and mid-September. OCIO starts to decrease during mid-September and drops below the detection limit at the beginning of October, although somewhat later during 1999 compared to 2000 due to the longer lasting cold stratospheric temperature and vortex strength. The drop of the OCIO SCDs below the detection limit is coincident with stratospheric temperatures raising above the type 1 PSC threshold (see figure 5.2), indicating that the reactive chlorine is rapidly converted to HCl in absence of PSCs.

During both years, a significant chlorine activation already occurs during autumn. A sudden increase of the OClO SCD from zero to almost $4 \cdot 10^{14}$ molec/cm² at 94° SZA is



Figure 5.17: Seasonal variation of the OClO slant column density at 90° SZA over Neumayer during 1999 (upper panel) and 2000 (lower panel). Morning and evening values are shown as black squares and red circles, respectively. The average detection limit is shown as dashed line. Also shown is the ECMWF potential vorticity at the 475K isentropic level (blue line, right axis).

observed between Mai 1 and Mai 7, 2000, accompanied by an increase in the potential vorticity (figure 5.4) and a decrease in NO₂ (figure 5.14). A chlorine activation on PSCs is unlikely to occur during this period, since the stratospheric temperatures above Neumayer are still too high to form polar stratospheric clouds, as the temperature profiles from ozone soundings (figure 5.19) and the ECMWF temperature map (figure 5.20) show. However, the trajectory calculations shown in figures 5.21 and 5.22 indicate that the air masses arriving at Neumayer on Mai 6, 2000 at isentropic levels of 475 and 500K originated from the vortex core and were exposed to temperatures cold enough for the formation of type 1 PSCs (below 195K). these cold temperatures lasted for more than 25 hours on the 500K level, allowing for a chlorine activation on PSCs.

It is also possible that the early chlorine activation during autumn is caused by the heterogeneous conversion of HCl to BrCl by bromine nitrate and HOBr on cold stratospheric sulfate aerosols via reactions (2.51) and (2.52). Similar observations of chlorine activation outside the polar vortex were found by airborne measurements in the northern hemisphere [Erle et al., 1998a]. Model calculations show that the heterogeneous processing on cold sulphate aerosols in the stratosphere can lead to a significant release of reactive chlorine at temperatures below ≈ 205 K [Danilin and McConnell, 1995; Tie and Brasseur, 1996; Erle et al., 1998a; Fitzenberger, 2000].



Figure 5.18: Same as figure 5.17, but for $\Theta = 94^{\circ}$





Figure 5.19: Stratospheric temperature profiles from ozone soundings on Mai 5 and 10, 2000.

Figure 5.20: ECMWF temperature at the 50hPa pressure level over the southern hemisphere on Mai 7, 2000.



Figure 5.21: Solar zenith angle (upper panel) and temperature (lower panel) along trajectories arriving at Neumayer on Mai 6, 2000, 12:00 UT at isentropic levels of 475 and 500K. The dotted line in the lower panel indicates the threshold temperature for type 1 PSC formation.

5.5 Results of the BrO measurements

5.5.1 Seasonal variation of the BrO DSCD

Figure 5.23 shows the seasonal variation of the BrO differential slant column density at 90° SZA during 1999 and 2000. Except for the observations during spring, when various strong and sudden enhancements of the BrO dSCD were observed, the overall picture of the BrO dSCDs is consistent with our current understanding of stratospheric bromine chemistry: The BrO dSCD increases in autumn, has a maximum during winter and decreases in spring. BrONO₂ contributes significantly to the total inorganic bromine during day and leads to the observed small BrO concentration during summer. In addition, the temperature independent bromine nitrate hydrolysis on sulphate aerosols during night (reactions (2.50) and (2.51)) leads to the conversion of BrONO₂ to HOBr which is the most abundant bromine reservoir species is distinctly different in chlorine activated, denoxified air masses: BrONO₂ cannot be produced since there is no NO₂ available. Instead, BrO and ClO react to BrCl (see reaction (2.42c)), which is the major reservoir species during night during polar spring. Since the formation of BrONO₂ is strongly reduced and the major nighttime reservoir species BrCl is rapidly photolysed after sunrise, increased BrO concentrations are observed during winter.

The BrO dSCD as a function of the NO_2 VCD for the observations during autumn 1999 is shown in figure 5.24. A nearly linear anti-correlation between BrO and NO_2 is observed for



Figure 5.22: Five day back trajectories arriving at Neumayer on Mai 6, 2000, 12:00 UT at isentropic levels of 475K (solid red line) and 500K (dashed red line). Each symbol represents 1 day of model run.

 NO_2 VCDs below $3.5 \cdot 10^{14}$ molec/cm², indicating that the formation of BrONO₂ decreases the stratospheric BrO concentration.

The difference in bromine partitioning under outer-vortex and chlorine activated conditions is illustrated in figure 5.25, where results from model calculations of the diurnal variation of several bromine species are shown. They are calculated from the global 3D chemical transport model SLIMCAT [Chipperfield, 1999] for mid and high latitudes under chlorine activation [Sinnhuber et al., 2001]. In the latter scenario, almost 100% of bromine is converted to BrCl during night.

The am/pm ratio of the BrO dSCD is expected to vary with the availability of NO_x: under high NO_x conditions, daytime BrO concentrations are limited by the rate at which bromine nitrate photolyses during day. Model calculations indicate that this causes BrO concentrations to be more higher in the evening than in the morning (e.g., [Fish et al., 1995]). Under high chlorine loading conditions, a reversed am/pm ratio can be expected since BrO is rapidly formed at sunrise due to the fast photolysis of the major nighttime reservoir species BrCl. Since the BrO measurements during spring are dominated by tropospheric events, it is not possible to determine the BrO am/pm ratio under chlorine activated conditions. However, at least the influence of the availability of NO_x on the diurnal variation of BrO can be investigated using the autumn measurements. Figure 5.26 shows the am/pm ratio of the BrO dSCDs during autumn 1999 and 2000. No significant deviation of this ratio from one is observed, as also shown by the histogram in figure 5.27.

The most noticeable feature of the BrO measurements, namely the strong and sudden BrO enhancements observed during spring, are subject of the following sections. These events with BrO dSCDs rising to values of more than $1.6 \cdot 10^{15}$ molec/cm² are unequivocally caused by



Figure 5.23: Seasonal variation of the BrO differential slant column density at 90° SZA over Neumayer during 1999 (upper panel) and 2000 (lower panel). All data is relative to the Fraunhofer reference spectrum recorded on August 6, 1999 (see section 4.10 for details). Morning and evening values are shown as black squares and red circles, respectively.



Figure 5.24: Correlation of the NO₂ VCD and the BrO dSCD during autumn 1999.



Figure 5.25: Diurnal cycle of the relative contribution of the most abundant bromine species BrO, BrONO₂, HBr and BrCl in the lower stratosphere (480K isentropic level, 58 hPa), calculated by the Slimcat CTM, for Bremen (54°N) on March 1, 1999 (left) and Harestua (60°N) on January 26, 1999. Adapted from Sinnhuber et al. [2001].



the NO_2 VCD.

Figure 5.26: Am/pm ratio of the BrO dSCD Figure 5.27: Histogram of the am/pm raduring autumn 1999 and 2000 as a function of tio of the BrO dSCD during autumn 1999 and 2000.



Figure 5.28: BrO differential slant column density (upper panel) and surface ozone mixing ratio at (lower panel) between August 27 and September 18, 1999.



Figure 5.29: Diurnal variation of the BrO dSCD observed on Aug. 24, 1999.

the appearance of tropospheric BrO.

5.5.2 BrO in the lower troposphere

Figure 5.28 shows a subset of the BrO dSCD observations during early spring, together with the ozone mixing ratio observed using a commercial ozone monitor installed at the Neumayer trace gas observatory. The sampling time of the ozone monitor is one minute. The values reported within this section are averaged over one hour to reduce the amount of data.

A clear relationship between the appearance of elevated BrO dSCDs and a strong decrease in the ozone mixing ratio is found. Typical background ozone mixing ratios of about 30ppb are observed at the beginning and end of the period shown in figure 5.28 (August 27/28 and September 16-19), while the diurnal variation of BrO shows the typical shape of a purely stratospheric profile, which is indicated by (1) the increase of the BrO dSCD during twilight due to the increased light path, with values typical for BrO located in the stratosphere (\approx $3.5 \cdot 10^{14}$ molec/cm² at 90° SZA), (2) the symmetric shape of the diurnal variation and (3) the 'smoothness' of the data. A long lasting period of enhanced BrO is observed after August 29. These events are characterised by very high BrO dSCDs of more than $12 \cdot 10^{14}$ molec/cm². BrO slant columns of that amount are very unlikely to occur in the stratosphere since that would require BrO mixing ratios of far more than the current estimate of 20-22 ppt [Fitzenberger, 2000]. Consider, for example, the BrO observations on Aug. 24 shown in figure 5.29: BrO dSCDs of more than $20 \cdot 10^{14}$ molec/cm² are observed at noon ($\Theta \approx 82^{\circ}$). When neglecting the BrO amount in the Fraunhofer reference spectrum, a stratospheric airmass factor of ≈ 6.5 (see figure 5.31) would yield a BrO mixing ratio of more than 40ppt (assumed a constant mixing ratio above 11km altitude). In addition, the BrO enhancements are characterised by a strong variability of the BrO dSCD. Such strong temporal and/or spatial inhomogeneities in the BrO abundance are very unlikely to occur in the well mixed stratosphere.

The overall picture given by the comparison of BrO and ozone observations in figure 5.28 suggests that the strong ozone depletion in the boundary layer is caused by air masses containing reactive bromine. Reactive bromine is believed be released by heterogeneous processes on sea salt surfaces as described in section 2.4.2. However, a closer look at the time series of BrO and ozone raises several questions:

- Why is there no clear anti-correlation between elevated levels of BrO and surface ozone destruction? A strong increase in the BrO dSCD is, for example, observed at the morning of August 30, while there is only a slight decrease in the ozone mixing ratio of about 5ppb. Elevated BrO levels of the same amount are also found on September 11/12, but ozone is almost completely depleted in this case, with mixing ratios between 0 and 8ppb.
- Which are the mechanisms that control the temporal variability of the BrO dSCDs? A strong temporal variability of the BrO dSCD occurs, for example, on September 1, while some days show elevated BrO levels without such a variability, such as on September 3, suggesting that the tropospheric BrO leads to an additional constant offset to the stratospheric part of the column density.
- Why are there sometimes no indications for surface ozone depletion if highly elevated BrO amounts are observed? A striking example is the strong increase of the BrO dSCD up to values of $10 \cdot 10^{14}$ molec/cm² in the afternoon of September 10, while the ozone mixing ratio shows typical background levels of about 30ppb.

To explain these discrepancies between the BrO and ozone observations, the impact of the following parameters on the observations must be considered:

- *Radiative transfer*: The path of the observed light through the troposphere can be influenced by clouds, aerosols and snow drift, which can cause strong enhancements of the observed BrO dSCDs due to multiple scattering.
- Vertical distribution of tropospheric BrO: Since the slant column density is the integrated concentration along the light path, it is a priory not clear if the observed enhancements are related to a BrO layer touching the surface of if the BrO profile is located at higher altitudes.



Figure 5.30: Sketch draw illustrating the radiative transfer in the troposphere under clear (left) and cloudy (right) sky conditions.

• *Dynamical influences:* The episodes of enhanced BrO and boundary layer ozone depletion are expected to be correlated with air masses originated from the ice covered ocean, since this is believed to be the source region of reactive bromine.

5.5.2.1 Characterisation of the tropospheric light path using O_4 absorption

Figure 5.30 illustrates how clouds or snow drift can enhance the light path of absorbers located in the lower troposphere due to multiple scattering. It is important to note that the probability density function for the scattering altitude has its maximum in altitudes above 8km for light in the near UV, where BrO is detected [Frank, 1991]. The majority of light reaching the instrument is scattered in the stratosphere under clear sky conditions. The airmass factors for a purely stratospheric profile and for BrO being uniformly distributed over the lowermost 8 km is shown in figure 5.31. The variation of the airmass factor with solar zenith angle is by far smaller for BrO located in the lowermost 2km of the troposphere compared to stratospheric BrO if no clouds or snow drift is present.

However, modeling the radiative transfer in presence of clouds or snow drift is not possible, since

- 1. the properties of the scattering particles, such as Mie extinction profile, size distribution and phase function, are unknown.
- 2. the scattering processes in the presence of snow and ice particles or droplets are characterised by high spatial and temporal variability.
- 3. the existing models are not able to reproduce the radiative transport realistically if multiple scattering on macroscopic particles dominates.

The influence of the radiative transfer on observations of trace gases mainly located in the lower troposphere are investigated using the absorption features of the oxygen dimer (O_4) . O_4 is believed to be a short-lived collision complex of the oxygen molecule [Osterkamp, 1997]. Since the concentration of O_4 is proportional to the square of the oxygen concentration, its profile is mainly located in the lower troposphere, with a scale height of approximately 4km.



Figure 5.31: Airmass factor at $\lambda = 349$ nm for a stratospheric absorber with a constant mixing ratio above the tropopause (upper panel) and for a tropospheric absorber with a constant mixing ratio in the lowermost 2km (lower panel, solid line). Dashed line: O_4 airmass factor at 361nm.

The O₄ airmass factor at 361nm under clear sky conditions shown as dashed line in figure 5.31. Although the O₄ AMF is about 20% higher than the AMF of an absorber uniformly distributed in the lowermost 2km of the troposphere for $70^{\circ} \leq \Theta \leq 90^{\circ}$, their diurnal variation are comparable. The optical density of O₄ absorption bands is therefore a suitable indicator for possible light path enhancements due to multiple scattering in the lower troposphere [Wagner et al., 2001]. The O₄ absorption strength was determined using the absorption band at 361nm, which is close to the BrO retrieval window between 346 and 358.5nm. The optical density of this absorption band is therefore suitable for the characterisation of the radiative transfer concerning the observed BrO dSCDs.

Figure 5.32 shows the average O_4 absorption observed on clear days as a function of solar zenith angle. The amount of O_4 in the Fraunhofer reference spectrum was derived from a Langley plot with airmass factors derived using the atmospheric scenario described in section 4.6.3. Clear days were identified (1) by a 'smooth' diurnal variation of O_4 without short term variations (2) by the smaller O_4 absorption coefficients compared to periods with clouds or snow drift; (3) by a 'smooth' temporal variation and much smaller light intensity on clear days compared to periods where multiple scattering dominates and (4) by the meteorological observations regularly performed at Neumayer. Using these criteria, only 26 clear days were identified during 1999. Figures 5.33 and 5.34 show examples for the different variation of the O_4 absorption and intensity with SZA, illustrating that clear sky conditions and conditions with clouds or snow drift can be clearly distinguished by eye.

As a measure for the light path enhancement in the lower troposphere due to multiple scattering, the *light path enhancement factor* L can be defined as the ratio between the O₄ absorption coefficient $C_{O_4}(\Theta)$ at a given SZA Θ and the above described average O₄ absorption coefficient under clear sky conditions $\overline{C_{O_4}^{cl}}(\Theta)$:



Figure 5.32: Average O_4 absorption at 360nm on clear days of 1999 as a function of solar zenith angle. The error bars represent the standard deviation of the data.



(Oct. 11, 1999). Also shown is the average and a cloudy day (Oct. 11, 1999). O_4 absorption (dashed line).

Figure 5.33: Example for the variation of Figure 5.34: Example for the variation of the O_4 absorption with solar zenith angle on the intensity in the UV spectral region with soa clear day (Oct. 7, 1999) and a cloudy day lar zenith angle on a clear day (Oct. 7, 1999)



Figure 5.35: Examples for the relationship between the BrO dSCD and the light path enhancement, observed on September 6, 13 and 27, 1999.

$$L(\Theta) = \frac{C_{O_4}(\Theta)}{\overline{C_{O_4}^{cl}}(\Theta)}$$
(5.1)

 $L(\Theta)$ determines the increase in light path in the presence of multiple scattering compared to clear sky conditions. Thus the O₄ airmass factor A_{O_4} under cloudy or snow drift conditions is scaled with $L(\Theta)$:

$$A_{O_4}(\Theta) = L(\Theta) \cdot A_{O_4}^{cl}(\Theta) \tag{5.2}$$

with $A_{O_4}^{cl}$ being the O₄ airmass factor under clear sky conditions. The situation is complicated since the aerosol loading of the troposphere can have a large temporal variability even under clear sky conditions so that the O₄ airmass factor varies with time. No information about the tropospheric aerosol loading is available and it was not possible to 'guess' an aerosol profile that leads to airmass factors compatible with all clear sky O₄ observations. Therefore equation (5.1) is not strictly fulfilled. One must take care when using the light path enhancement factor for the interpretation of measurements of an absorber located in the lower troposphere with a profile shape that is not identical with the O₄ profile. The airmass factor of an absorber is expected to be only slightly affected by multiple scattering and thus by the light path enhancement factor if its profile is located above or below the cloud layer. However, $L(\Theta)$ can be expected to be at least a qualitative indicator for the influence of multiple scattering on the observed slant column density of an absorber located in the lower troposphere.



Figure 5.36: Surface ozone (upper panel) and wind direction and speed (lower panel) at Neumayer station from August 27 to September 29, 1999.

The benefit of the light path enhancement factor for the interpretation of observations of tropospheric absorbers is illustrated in figure 5.35, where examples for the relationship between light path enhancement and BrO dSCDs are shown. The light path enhancement factor has values of up to 4 at noon of Sept. 13. The simultaneous increase of the BrO dSCDs compared to the evening values indicates that the observed enhancement is of tropospheric origin and that at least a part of the tropospheric BrO profile is located at altitudes where multiple scattering occurs. In contrast, no relationship between the light path enhancement factors as on Sept. 13 are observed. This strongly suggests that the majority of the detected BrO is located in the stratosphere. The correlation of the light path enhancement factor and the BrO dSCD during tropospheric BrO events can be seen more clearly for the measurements on Sept. 6, where highly variable light path enhancement factors correlate very well with the observed BrO dSCDs. Reflecting the 'amplification' of the observed tropospheric BrO column, the light path enhancement leads to BrO dSCDs of more than $10 \cdot 10^{14} \text{ molec/cm}^2$ on Sept. 6.

As shown in figure 5.35, the error bars of the BrO dSCDs do not increase during BrO enhancements, indicating that they are not caused by any errors of the spectral analysis.

5.5.2.2 Determination of the source region of air masses during enhanced BrO events

Since sea salt surfaces are believed to be the origin of reactive bromine released by heterogeneous processes (see section 2.4.2), it can be expected that air masses depleted in ozone originate from the sea ice surface. Figure 5.36 shows the relationship between surface ozone depletion events and wind direction and speed. Air masses low in ozone are obviously not well correlated with northerly wind directions, which would indicate that the air masses come from the sea ice. Short periods or northerly winds often occur at the beginning of ozone depletion events, but ozone remains low although the wind direction changes. Therefore the local wind direction is obviously not suitable for the characterisation of the medium and long range transport of air masses. Easterly and sometimes southerly winds dominate over the whole period. This is in agreement with the meteorological conditions typically found at Neumayer, which are strongly dominated by easterly winds [König-Langlo et al., 1998]. Katabatic winds coming from the Antarctic plateau are rarely observed at Neumayer.

Although easterly winds dominate at Neumayer station, the origin of the air masses reaching the station is strongly affected by the large-scale meteorological situation. Air masses originating from the sea ice are mostly related to cyclonic activity over the south polar sea [Kottmeier and Fay, 1998]. A typical situation is shown in the meteorological plots of figure 5.37, where the pressure and wind vector fields around Neumayer on Aug. 6 and 9, 2000 are shown: the local wind direction at Neumayer remains easterly as a cyclone travels eastward along the coast at about 60°S. The air reaching the station is of continental origin before the cyclone passes the station (on Aug. 6) and is originated from the sea ice afterwards (on Aug. 9), although the local wind direction has not changed. This example illustrates the importance of taking the large-scale meteorological situation into account to determine the origin of air masses reaching the Neumayer station.

Back trajectory calculations are a commonly used technique to gain information on the sources of air masses arriving at a specific location. However, back trajectory calculations in connection with BrO events only have been performed for some selected cases (e.g., [Wessel, 1996]) and in most cases for trajectories ending at the surface. In the following, it is demonstrated that trajectory calculations of high temporal and altitude resolution in connection with sea ice maps can be a powerful technique for the interpretation of tropospheric BrO events.

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler and Hess, 1997; Draxler, 1999] is a freely available, PC compatible trajectory and dispersion model code³ which can process various meteorological data sets. Trajectories can be calculated on isentropic, isobaric and constant air density surfaces, or by using the modeled vertical motion given by the meteorological input data. The latter option is recommended by the authors and therefore used within this thesis.

The freely available FNL meteorological data-set [Stunder, 1997] was used as input data for the HYSPLIT trajectory model ⁴. The 6-hourly FNL archive data on a 1° latitude- longitude grid is an operational product of the Global Data Assimilation System (GDAS) [Kanamitsu, 1989], provided by the National Center of Environmental Prediction (NCEP). Details of the GDAS are described by Kanamitsu [1989], Derber et al. [1991], and Parrish and Derber [1992].

To determine the source regions of the bromine containing and ozone depleted air masses, the HYSPLIT model in combination with the FNL data-set was used for calculating trajectories in high temporal and vertical resolution. For August and September of 1999 and 2000, five day back trajectories were calculated in time steps of one hour and altitude steps of 100 metre from the ground up to an altitude of 5000 metres. The sea ice coverage of the

³The HYSPLIT trajectory model code is available at http://gus.arlhq.noaa.gov/ready/hysplit4.html. This link also provides the possibility to calculate trajectories online.

⁴The FNL data-set is available at ftp://www.arl.noaa.gov/pub/archives/fnl/.





south polar ocean was determined using sea ice maps provided by NCEP⁵. They are measured using a passive microwave instrument aboard the Defense Meteorological Satellite Program [Goodberlet and Swift, 1992].

The high resolution trajectory calculations result in a set of positions of air parcels. They can be described as $\vec{x} = (\Theta, \Phi, z)$ (Θ : latitude, Φ : longitude, z: altitude), which depend on the time t < 0 (in hours) before the air parcel reaches the Neumayer station at arrival time T and altitude h.

$$\vec{x} = \vec{x}(T, h, t)$$
 with $\vec{x}(T, h, 0) = (\Theta_0, \Phi_0, h)$ (5.3)

with Θ_0 and Φ_0 being the latitudinal and longitudinal coordinates of the Neumayer Station, respectively.

The *duration of sea ice contact* of an air parcel arriving at the Neumayer station is defined as

$$\tau(T,h) = \int_{-120hr}^{0} I_z(\vec{x}(T,h,t)) \cdot I_{ice}(\vec{x}(T,h,t)) dt$$
(5.4)

with the indicators I_z and I_{ice} being defined as

$$I_z(\vec{x}) \equiv I_z(\Theta, \Phi, z) = \begin{cases} 1 & \text{if } z \le z_0 \\ 0 & \text{if } z > z_0 \end{cases}$$
(5.5)

$$I_{ice}(\vec{x}) \equiv I_{ice}(\Theta, \Phi, z) = \begin{cases} 1 & \text{if } \rho_{ice}(\Theta, \Phi) > 0\\ 0 & \text{if } \rho_{ice}(\Theta, \Phi) = 0 \end{cases}$$
(5.6)

Here it is assumed that an uptake of BrO from the sea ice surface can take place if the altitude of a given air parcel is below the threshold altitude z_0 . ρ_{ice} is the sea ice concentration at the location (Θ, Φ) as given by the NCEP sea ice maps. ρ_{ice} is set to zero above land and open sea and has values > 0 above the sea ice covered ocean. Since the NCEP sea ice maps do not distinguish between shelf ice and sea ice, the regions with sea ice coverage at the end of February were set to $\rho_{ice} = 0$. In addition, this excludes more than one year old sea ice, which has a too low salinity for the release of reactive bromine [Lehrer, 1999], from the calculation of τ .

The duration of sea ice contact $\tau(T, h)$ defined in equation (5.4) is the time an air parcel has has stayed over the sea ice in an altitude below the threshold value z_0 before it reaches the Neumayer station at the time T in an altitude h during the last five days. The threshold altitude was set to $z_0 = 100$ m since it can be assumed that the air is well mixed in this layer close to the surface so that an uptake of reactive bromine or sea salt aerosols from sea ice is possible. The inferred durations of sea ice contact were found to vary only slightly if z_0 were set to higher altitudes.

An example for the determination of the duration of sea ice contact is shown in figure 5.38. The trajectories are ending on T = Sept. 2, 1999, 18:00 at altitudes of h = 0, 500 and 1000m over the Neumayer station. The lowermost trajectory comes from the Antarctic continent and thus had no contact to the sea ice: $\tau(T, h = 0) = 0hr$. The 500m trajectory

⁵NCEP gridded sea ice data is available at ftp://polar.wwb.noaa.gov/pub/ice/.



Figure 5.38: Example for the determination of the duration of sea ice contact. The 120hr back trajectories ending at altitudes of 0, 500 and 1000m at the Neumayer station on Sept. 2, 1999, 18:00, are shown in black, red and blue, respectively. The sea ice coverage from NCEP is shown as coloured areas, the open sea is shown in pink.

has passed the sea ice in an altitude below 100m for 53 hours, started to ascend 30 hours prior to the arrival at Neumayer and traveled along the coast line before reaching the station: $\tau(T, h = 500m) = 53hr$. The trajectory ending at 1000m came from the open sea and reached the sea ice edge at t = -96hr. The air parcel stayed over the sea ice in an altitude $z < z_0$ and started to ascend 2 days prior to the arrival at Neumayer: $\tau(T, h = 1000m) = 44hr$.

Figure 5.39 shows an example for the inferred duration of sea ice contact, together with the BrO dSCDs and the surface ozone mixing ratio during two days of September 1999. The contour plot shows the number of hours the air parcel had contact to the sea ice surface (as defined in equation (5.4)) according to the colour scale as a function of arrival time (x-axis) and arrival altitude (y-axis). A very consistent picture arises when comparing the trajectory calculations with both the BrO observations and the surface ozone mixing ratio: The BrO measurements on Sept. 10 show no enhancement until about 09:00 UT. Afterwards, a strong increase in the BrO dSCDs up to values of almost $10 \cdot 10^{14}$ molec/cm² is accompanied by air masses located in a layer of about 2km altitude which have previously passed the sea ice surface for about 60 hours. Simultaneously, no decrease in the surface ozone mixing ratio is observed. This leads to the conclusion that the observed BrO enhancement on Sept. 10 is not related to an increase of BrO on the ground. Instead, advection processes lead the ascent of BrO containing air masses from the sea ice surface to an altitude of about 2km. Therefore no ozone depletion is observed on the surface. About 5 hours after the trajectory



Figure 5.39: Example for the relationship between the observed BrO dSCDs (upper panel), the duration of sea ice contact as a function of time and altitude (middle panel) and the surfae ozone mixing ratio (lower panel) on Sept. 10 and 11, 1999. White areas indicate that the air parcel had no contact with sea ice prior to the arrival at Neumayer.

calculations indicate that air masses arriving at the ground came from the sea ice surface, a strong depletion of surface ozone is observed at 05:00UT on Sept. 11, with mixing ratios below 10ppb. The BrO observations and trajectory calculations on Sept. 11 indicate that the air masses within the boundary layer came from the sea ice surface, that they were therefore enriched in BrO and that ozone depletion has occurred.

An intercomparison of three trajectory models applied to Arctic haze has shown that both the parameterisations of the vertical motion and the meteorological data-set on which the trajectory modeling is based contribute substantially to the overall uncertainty of the inferred trajectories [Kahl et al., 1989]. A detailed analysis of trajectories in the Antarctic lower troposphere [Kottmeier and Fay, 1998] shows that the errors due to atmospheric wind shear and interpolation errors of the vertical wind component may lead to position uncertainties in the trajectories of up to thousand kilometres after 5 days integration time. Concerning the trajectory calculations performed here, the uncertainties in the horizontal position are not the limiting factor in the accuracy of the inferred duration of sea ice contact since it is based only on distinguishing between air masses originated from the continent, the sea ice and the open sea. Uncertainties mainly arise if air parcels travel along the coast line of Antarctica. Of more importance is the uncertainty of the z-coordinate of the air parcels, which depends on how realistic advection processes are represented in the trajectory model and the meteorological data-set. In addition, no mixing processes are taken into account in the trajectory model. Thus air parcels traveling along the coast line or in altitudes above the threshold altitude of $z_0 = 100 \text{m}$ may be depleted in ozone or contain reactive bromine due to horizontal or vertical



Figure 5.40: Comparison between wind direction and speed measured by the ozone soundings and determined by modeled trajectories during September 1999.

mixing processes, although the calculated duration of sea ice contact is zero.

Figure 5.40 compares vertical profiles of wind direction and speed measured by ozone soundings and inferred from the trajectory calculations. A good overall agreement between modeled and observed wind profiles is achieved. This result gives confidence that the HYS-PLIT trajectory model and the FNL meteorological data-set produce fairly reliable results.

5.5.2.3 Tropospheric BrO events during spring 1999

Figure 5.41 summarises the observations during August and September 1999. The time series of the BrO dSCD is shown together with the duration of sea ice contact as determined using the trajectory calculations, the tropospheric light path enhancement from O_4 measurements and the hourly averaged surface ozone mixing ratio. Numerous BrO enhancements are observed during this period, which do not always coincide with ozone depletion at the ground. The observations are described in chronological order below:

• August 1 - 5: Enhanced BrO dSCDs are observed during this period. The trajectory calculations indicate that the air masses in a layer from the surface up to altitudes of 1000m were previously exposed to sea ice. The large values of the light path enhancement factor indicate that the BrO dSCDs are influenced by multiple scattering










Figure 5.42: Trajectories arriving at Neumayer on Aug. 07, 1999 at 12:00 UT.

in the lowermost troposphere. However, no significant decrease in the ozone mixing ratio is observed during this period. The light intensity is possibly too small to initiate photochemical ozone depletion by reactive bromine during early August. However, the trajectory calculations indicate that the air masses were exposed to sunlight for up to 30 hours after the first contact with the sea ice so this might not be a likely explanation for the fact that no ozone depletion has occurred.

- August 5 and 6: Enhanced BrO dSCDs are observed, together with a high variability which is related to the tropospheric light path enhancement. However, the trajectory calculations indicate that the probed air masses do not come from the sea ice surface. The trajectories resented in figure 5.42 indicate that the air masses arriving at the surface originated from the Antarctic continent. The 500m trajectory previously descended over the continent and passed the sea ice for about 60 hours, but in altitudes above 700m. It is therefore unlikely that an uptake of BrO from the sea ice took place for the 500m trajectory. An uptake of BrO possibly occurred for the 1000m trajectory: the air parcel was previously over the sea ice in altitudes below 500m, and it is possible that reactive bromine was mixed into this layer. This example shows the limitations of the trajectory analysis, since no mixing processes are taken into account and the trajectory model has only a limited accuracy.
- August 8 10: The diurnal variation of the BrO dSCD is consistent with BrO being located only in the stratosphere. Also, the trajectory calculations indicate that no contact of the probed air masses with sea ice took place, except for the afternoon of August 10, where a layer of air with less than 20 hours of sea ice contact is located at about 1200m altitude and the BrO dSCD slightly increases.
- August 11 19: During this period, the first decrease in the ozone mixing ratio at the surface occurs, with minimum values of 15 ppb. This depletion event is accompanied



Figure 5.43: BrO dSCD and light path enhancement on Aug. 8, 16 and 27.

by air masses which have previously touched the sea ice before they arrive at Neumayer station at ground level. Simultaneously, increased BrO dSCDs are observed, indicating that reactive bromine is abundant in the boundary layer.

The influence of tropospheric BrO on the observed diurnal variation for conditions when the radiative transport is not dominated by multiple scattering can be investigated using the observations on Aug. 16, since no light path enhancement was detected on this day. The observations on Aug. 16 also allow for a rough estimation of the tropospheric BrO mixing ratio. The diurnal variation of the BrO dSCD has a 'smooth' shape, but is increased by a constant factor compared to the observations of mainly stratospheric BrO. The lack of short- term variability indicates that BrO is homogeneously distributed within the boundary layer. Figure 5.43 compares the BrO diurnal variation on Aug. 16 with the observations on Aug. 8 and 27. On the latter two days, it is likely that no tropospheric BrO was abundant since the duration of sea ice contact was zero. The BrO dSCD is significantly increased on Aug. 16 compared to Aug. 8 and 27, when mainly stratospheric BrO was observed. The BrO dSCD at $\Theta = 87^{\circ}$ (corresponding to a tropospheric airmass factor of 3.14, see figure 5.31) on Aug. 8 and 27 is $2.3 \cdot 10^{14}$ and $2.75 \cdot 10^{14}$ molec/cm², respectively, compared to $4.3 \cdot 10^{14}$ molec/cm² on Aug. 16. Assuming that the stratospheric part of the BrO dSCD on Aug. 16 is the average of the dSCDs observed on Aug. 8 and 27 yields a tropospheric BrO SCD of $1.8 \cdot 10^{14}$ molec/cm². The boundary layer height on Aug. 16 was 1500m. Assuming that BrO was uniformly distributed within the boundary layer, a tropospheric mixing ratio of approximately 13ppt is inferred.

The period of ozone depletion is interrupted on August 14. No air masses come from the

sea ice on this day and the diurnal variation of BrO indicates that no significant BrO amounts are located in the troposphere, although the tropospheric light path is strongly enhanced.

- August 20 22: Although the BrO dSCDs are enhanced and the trajectory calculations indicate that the air parcels located at the surface were exposed to sea ice within 5 days prior to the arrival at Neumayer, no ozone depletion is observed during this period. It remains unclear why no chemical ozone loss occurred although the air masses most likely contain reactive bromine and were exposed to sunlight.
- August 23: The trajectory calculations indicate that a layer of only 100-200m thickness at about 1000m altitude was in contact with sea ice. A strongly increased BrO dSCD together with a very large light path enhancement factor suggests that BrO is abundant in this layer. The coincidence between BrO enhancement and an increase of the light path enhancement factor suggests that multiple scattering occurs within this layer, which is possibly caused by sea salt aerosols transported from the sea ice surface to altitudes of 1000m above the Neumayer station.
- August 24: The strongest enhancements of the BrO dSCDs during spring 1999 are observed on this day, accompanied by a light path enhancement factor of up to 10. The trajectory calculations indicate that air masses from the surface up to altitudes of more than 3000 metres were previously exposed to sea ice. However, the ozone mixing ratio has only slightly decreased, which is most likely related to the short duration of sea ice contact of less than 60 hours. This example shows that air masses from the sea ice surface can be transported into the free troposphere due to advection processes. In connection with the analysis of the ozone soundings, this aspect will be discussed in more detail later in this section.
- August 25 28: As the trajectory calculations indicate, the air masses over Neumayer do not come from the sea ice surface. However, enlarged BrO dSCDs are still observed on Aug. 25 and 26, which may be caused by mixing processes. It is also possible that the uncertainties of the trajectory calculations are responsible for this discrepancy. Diurnal variations indicating mainly stratospheric BrO are observed on August 27 and 28.
- August 29 30: A cloud of air originated from the sea ice is present at altitudes around 1000m. This does not lead to a significant increase in the BrO dSCD as no tropospheric light path enhancement is observed on August 29. The strong light path enhancement of up to 15 on August 30 leads to a corresponding increase in the BrO dSCD, indicating that the air masses coming from the sea ice contain reactive bromine. A slight decrease of the surface ozone mixing ratio with a rate of 3 ppb/day occurs while the 'cloud' of air masses with sea ice contact moves downward during this period.
- August 31 September 2: The trajectory calculations indicate that air masses on the ground are originated from the sea ice. Also, elevated levels of BrO are observed, but only a very slight (< 2.5ppb) decrease in the surface ozone mixing ratio occurs. The meteorological map in figure 5.44 and the corresponding trajectory plot in figure 5.45 indicate that the particular meteorological conditions during this period may be responsible for that: The Neumayer station is located in the centre of a cyclone, causing the air masses to circulate within a small region over the sea ice north of Neumayer. However, it remains unclear why no ozone depletion occurs under such circumstances although tropospheric BrO is detected. The same wind pattern is determined by the trajectory



Figure 5.44: Sea level pressure and wind field on Sept. 02, 1999, 12:00 UT.



Figure 5.45: Trajectories ending at Neumayer on Sept. 02 and 03, 1999, 12:00 UT at 0, 500 and 1000m altitude.

model for the following day, when the ozone mixing ratio drops below 10ppb. The accuracy of the meteorological data-set is possibly reduced when such strong pressure gradients are present, leading to large uncertainties in the trajectory model.

- September 3 13: The most severe ozone depletion occurs during this period, with ozone mixing ratios dropping to zero on Sept. 12. The simultaneously detected BrO enhancements and the duration of sea ice contact of the air masses agree very well with the ozone measurements. Air masses coming from the sea ice always coincide with an increase of the BrO dSCD. Surface ozone only decreases when this is the case for the air masses at the ground. The O_4 measurements indicate that the tropospheric light path is strongly enhanced most of the time. Since the BrO dSCDs correlate very well with the light path enhancement, this may indicate that multiple scattering occurs on sea salt aerosols which are transported from the sea ice surface to the Neumayer station. If this is the case, heterogeneous release of reactive bromine on sea salt surfaces could still take place in the probed air masses. Some periods with background ozone levels of about 30ppb (on Sept. 4, 8 and 10) agree very well both with the trajectory calculations, which indicate that the air masses at the surface do not come from the sea ice, and with the BrO measurements, which are not or only slightly elevated during these periods. A very strong BrO enhancement is observed in the afternoon of Sept. 10, when the trajectory calculations indicate that tropospheric BrO is located at altitudes of up to 4000m.
- September 14 29: The air masses in the lowermost 5000m mainly came from the Antarctic continent. Therefore, typical background ozone levels of about 30ppb and no BrO enhancements are observed during this period, except for two cases. For only some hours, air at the surface comes from the sea ice on the afternoon of Sept. 15. Simultaneously, an increase in the BrO dSCD is observed and the surface ozone mixing ratio drops to 20ppb. It is remarkable how well the trajectory model reproduces the short term variation of the origin of the air masses in this case. The last event of enhanced BrO occurring on Sept. 23 and 24 is also supported by the results of the trajectory calculations, but only a slight decrease in the ozone mixing ratio is observed during this period.

The ozone monitor data together with the duration of sea ice contact of the trajectories arriving at the ground are shown in figure 5.46. Ozone depletion at ground is only observed when the trajectory calculations indicate that the probed air masses originated from the sea ice. However, ozone depletion is sometimes not observed although the air comes from the sea ice and enhanced BrO dSCDs are measured. It still remains unclear why boundary layer ozone is sometimes unaffected by the presence of reactive bromine. For example, the trajectory calculations show that the air masses in the boundary layer come from the same source region both on Sept. 2 and 3 and had contact with the sea ice during the last 5 days. It should be expected that photochemical ozone destruction takes place in both cases. However, typical background ozone mixing ratios of 28ppb are observed on Sept. 2, while a drop below 10ppb occurs on Sept. 3 would lead to a stronger vertical mixing of boundary layer and the free tropospheric air. Unfortunately, no temperature profiles from ozone soundings are available for these days.

Using the ozone sounding data and vertical profiles of the duration of sea ice contact, some examples for the vertical structure of tropospheric ozone depletion during spring 1999 are presented in figure 5.47:



Figure 5.46: Surface ozone mixing ratio (upper panel) and duration of sea ice contact of the lowermost trajectory (lower panel) during August and September 1999.

- August 11: This ozone sounding was performed at the beginning of an ozone depletion event. While the trajectory calculations indicate that the air masses in the lowermost 500m were exposed to the sea ice surface for 50 hours prior to their arrival at Neumayer, only a slight decrease of the ozone partial pressure of less than 0.5mPa (5ppb) is observed. As the vertical profile of the potential temperature indicates, only a weak inversion separates the boundary layer from the free troposphere, so that vertical mixing with ozone rich air from above is likely to occur.
- August 30: The air in a layer within two inversions, located at 500 and 1600m altitude, is significantly depleted in ozone, with minimum mixing ratios of about 20ppb in 1000m altitude. The lowermost part of this layer, between 700 and 900m, originated from the sea ice surface, indicating that heterogeneously released reactive bromine abundant in these altitudes is responsible for the observed destruction of ozone.
- September 1: The air masses within the boundary layer, which has a vertical extension of 850m, originated from the sea ice. As already discussed above, only a slight (< 1.5ppb) decrease in the surface ozone mixing ratio is observed. The ozone profile within the boundary layer is in agreement with this observation: the ozone mixing ratio of the lowermost data point in 53m altitude is 21ppb, in agreement with the value from the ozone monitor (26ppb). A sharp drop of the ozone mixing ratio to 17ppb occurs in 62m altitude, followed by a linear increase to 24ppb in 100m altitude. It remains unclear why the lowermost part of the boundary layer remains unaffected from the ozone depleted air masses above and why such a strong negative gradient in the ozone profile is observed.



Figure 5.47: Comparison between ozone sounding data and the results of the trajectory calculations in the lower troposphere during August and September 1999. From left to right: Ozone partial pressure, duration of sea ice contact, potential temperature and relative humidity as a function of altitude in the lowermost 5000m.

in the lowermost 100m.

- September 8: A decreased ozone mixing ratio (≈ 18 ppb) is observed within the boundary layer, which has a vertical extent of 400m. At the same time, the trajectory calculations indicate that the ozone depleted air masses were previously in contact with the sea ice surface for only about 5 hours, which was sufficient to cause a heterogeneous bromine release and a subsequent ozone depletion.
- September 9: A severe ozone depletion is observed in the lowermost 1200m, with mixing ratios ranging from 5ppb at the ground (in agreement with the measurements of the ozone monitor) to 20ppb in 1200m altitude, where a strong inversion layer prevents the ozone poor air from mixing with air from the free troposphere. As a prerequisite for the heterogeneous release of reactive bromine, the air arriving at Neumayer at this time was almost permanently in contact with the sea ice surface during the last five days.

As recently pointed out by von Glasow and Sander [2001], the acidity of sea salt aerosols and therefore the amount of heterogeneous bromine release on their surface [Sander and Crutzen, 1996; Vogt et al., 1996] depends on the relative humidity. In brief, HCl is present in the MBL as a consequence of acidification of sea salt aerosols, e.g. by HNO₃ or H₂SO₄. The HCl concentration in the gas phase is almost independent from the liquid water content of the atmosphere. Therefore the product $[H^+] \cdot [Cl^-]$ in the aerosol remains constant according to Henry's law: $[H^+] \cdot [Cl^-] = k_H \cdot p(HCl)$. Dilution in the liquid phase causes $[Cl^-]$ to decrease if the liquid water contents increases, while p(HCl) remains constant. Thus $[H^+]$ must increase to keep the product in Henry's law constant, leading to a decrease of aerosol pH.

No clear relationship between the vertical profiles of relative humidity shown in figure 5.47 and ozone depletion is observed. However, the relative humidity in the boundary layer is always above 70%. It is therefore not possible to determine a relationship between relative humidity and ozone destruction with the available data.

The maps of the BrO vertical column density over Antarctica from the GOME satellite instrument shown in figure 5.48 are in good agreement with the ground based BrO measurements at Neumayer. Huge clouds of enhanced BrO, covering areas of more than $5 \cdot 10^6$ km² [Wagner, 1999], are detected over the sea ice around the Antarctic continent. The bulk of the tropospheric BrO is typically located over the Weddell and Ross sea. Particularly the GOME observations of enhanced BrO close to the Antarctic coastline near Neumayer station on Aug. 24, Sept. 3 and Sept. 12 agree well with periods of ozone depletion and BrO enhancement at Neumayer. As discussed above, it strongly depends on the meteorological situation if these BrO containing air masses located over the sea ice are transported to the Neumayer station or not.

5.5.2.4 Tropospheric BrO events during spring 2000

As shown in figure 5.49, less frequent BrO enhancements were observed during spring 2000:

• August 8: A 'cloud' of air masses coming from the sea ice appears at noon at altitudes of approximately 1000m and descents to the surface until midnight. This is in agreement with the detected enhanced BrO dSCDs. Simultaneously, a drop in the surface ozone mixing ratio from background values of 32ppb to 22ppb occurs at noon. It is unlikely that vertical mixing processes could lead to surface ozone destruction if BrO is located



Figure 5.48: GOME maps of the BrO vertical column density over Antarctica during August and September 1999. Kindly provided by M. Wenig and J. Hollwedel.

factor and surface ozone mixing ratio.

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Figure 5.50: Trajectories ending at Neumayer on Aug. 08, 2000, 12:00 UT at 0, 500 and 1000m altitude.

at 1000m altitude. A possible cause for this discrepancy could by the uncertainty in the trajectory model. However, the trajectory calculations indicate that the air masses arriving at noon of Aug. 8 came from the Antarctic continent and descended from more than 3000m to the surface during the last 5 days. It is therefore unlikely that the air masses were in contact with sea ice prior to their arrival at Neumayer.

- August 9 13: The trajectory calculations and the enhanced BrO dSCDs indicate that air masses coming from the sea ice contain reactive bromine. Simultaneously, the surface ozone mixing ratio decreases almost constantly from background values of about 30ppb on Aug. 9 to 10ppb on Aug. 12. Short term variations of modeled duration of sea ice contact are in very good agreement with changes in the ozone mixing ratio. For example, ozone is slowly increasing at the morning of Aug. 10, while the air masses had no sea ice contact. Together with a decrease of the BrO dSCD to typical stratospheric background values, the recovery of the surface ozone occurs during Aug. 12, accompanied by a decrease in the duration of sea ice contact. On Aug. 9 and 11, the diurnal variation of the BrO dSCD is characterised by a high variability although the O₄ measurements do not indicate a light path enhancement. Since the vertically integrated duration of sea ice contact also varies strongly during these periods, it is likely that the variation of the BrO dSCD is related to variations in the abundance of BrO and not to changes in the radiative transport due to multiple scattering in the troposphere.
- August 18 and 19: A small layer of air with a duration of sea ice contact of less than 60 hours is located in the lowermost 500m. This coincides with a slight reduction in ozone mixing ratio from 30ppb to 22ppb and an increase in the BrO dSCD.
- August 24 28: The trajectory calculations indicate a thin layer of air originated from the sea ice at an altitude of 1000m. This is accompanied by an increase in the BrO dSCD, which is also correlated with some light path enhancement. The decrease of the surface ozone mixing ratio to values below 15ppb (on Aug. 26) is possibly due to vertical mixing within the boundary layer.

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- September 12 14: Extremely high BrO dSCDs are observed during this period, rising up to values of $18 \cdot 10^{14}$ molec/cm². The trajectory calculations and the light path enhancement indicate that the enhancement and high temporal variability of the BrO dSCDs are most likely caused by BrO being located in the lowermost 500m together with multiple scattering near the surface. Surface ozone decreases suddenly from background values to 9.3ppb at morning of Sept. 12 and increases constantly with a rate of about 7.5ppb/day during the next three days.
- September 16 18: The trajectory calculations indicate two thin layers which potentially contain reactive bromine due to previous sea ice contact for up to 50 hours: at the surface (with a vertical extension of approximately 200m) and in altitudes between 2000 and 4000m. The BrO dSCD increases to values of up to $9 \cdot 10^{14}$ molec/cm², while only a slight decrease of the surface ozone of 5.5ppb is observed.
- September 20 25: The air masses at the surface originated from the sea ice surface for almost the whole period, in agreement with the observation of enhanced BrO dSCDs. However, ozone only slightly decreases with rates of approximately 1.5ppb/day during the first two days, while the trajectory calculations indicate a duration of sea ice contact of less than 50 hours for the air masses within the boundary layer. A strong decrease of surface ozone occurs when the duration of sea ice contact exceeds 100 hours on Sept. 22, and the lowest ozone mixing ratios during spring 2000 (2.7ppb) are observed on Sept. 23. A slow recovery in surface ozone during the next two days is accompanied by a decrease in the BrO dSCDs. A sudden change of the duration of sea ice contact from more than 100 hours to 0 hours at the evening of Sept. 25 is coincident with a rapid increase of the ozone mixing ratio from 16ppb to 30ppb within 9 hours.

Unfortunately, only the two ozone soundings shown in figure 5.51 were launched during spring 2000 while enhanced BrO was detected:

- August 9: The trajectory calculations indicate two layers of air masses with previous sea ice contact: in the boundary layer (from the surface to 200m altitude) and between 900 and 1500m altitude. As described above, a decrease in surface ozone is detected by the ozone monitor, but not captured by the ozone sounding with the lowermost data-point located at 92m above ground. The upper layer of air coming from the sea ice, located above an inversion layer, is significantly depleted in ozone with mixing ratios of 20ppb in 1500m altitude.
- September 23: This sonde was launched some hours prior to the strongest surface ozone depletion event during spring 2000. The lowermost 1500m of the troposphere show a severe ozone depletion with minimum mixing ratios of 5ppb in 1000m altitude. The trajectory model indicates that only the lowermost 200m of the boundary layer were previously exposed to sea ice. However, the strong negative gradient of the potential temperature (-4.8K/km) allows for a vertical mixing of air. It is therefore likely that reactive bromine is well mixed within the boundary layer.

The GOME BrO maps in figure 5.52 show that the area of enhanced BrO around the Antarctic continent during spring 2000 is similar to the observations of 1999. However, less frequent BrO enhancements were observed at Neumayer during 2000. This shows that the occurrence of BrO enhancements and surface ozone depletion at Neumayer during spring is mainly controlled by the current meteorological conditions which determine the origin of the probed air masses.



Figure 5.51: Comparison between the ozone sounding data and the results of the trajectory calculations in the lower troposphere during August and September 2000. From left to right: Ozone partial pressure, duration of sea ice contact, potential temperature and relative humidity as a function of altitude in the lowermost 5000m.

5.5.2.5 Gaseous mercury and its relation to bromine chemistry

Observations of episodic depletions of gaseous elemental mercury in the Arctic MBL [Schroeder et al., 1998; MacDonald et al., 2000], correlated with ozone depletion events, indicate that the chemistry of gaseous mercury is linked to the chemistry of reactive bromine: gaseous elemental mercury (Hg^0) is rapidly oxidised to Hg^{2+} by reaction with BrO. This conversion of elemental mercury vapour to oxidised Hg species results in a strongly enhanced atmospheric mercury deposition to frozen surfaces. Since January 2000, two commercial gas phase mercury analysers were installed at the trace gas observatory of the Neumayer station by the Institute of Inorganic and Analytical Chemistry, University of Jena. They were operated continuously until February 2001 and provided the first observations of gaseous mercury in the Antarctic troposphere. A subset of the gaseous mercury measurements at Neumayer during a surface ozone depletion event in early August 2000 is shown in figure 5.53. Gaseous mercury with typical background concentrations of 1.2 ng/m^3 is found to be very well correlated with the surface ozone mixing ratio, indicating that reactive bromine is responsible for the depletion of both compounds.

5.5.2.6 Summary of the observations of tropospheric BrO events and surface ozone depletion

The numerous BrO enhancements and surface ozone depletion events during spring of 1999 and 2000 offered the possibility to study the dynamical and chemical aspects of this phenomenon



Figure 5.52: GOME maps of the BrO vertical column density over Antarctica during August and September 2000.



Figure 5.53: Total gaseous mercury (red and blue lines), observed using two gas phase mercury analysers, and surface ozone mixing ratio (brown dots) during August 2000. Data kindly provided by C. Temme, University of Jena.

in detail:

- Enhanced BrO events occur if and only if the probed air masses originated from the sea ice, except for some rare cases which most likely caused by mixing processes and/or uncertainties in the trajectory model. This surprisingly good agreement between the BrO measurements and the results from trajectory calculations in combination with sea ice maps supports the theory that reactive bromine is released from sea salt surfaces, which are provided either by sea ice surfaces or by uptake of sea salt aerosols.
- Air masses at ground coming from the sea ice surface, accompanied by BrO enhancements, are found to be a necessary prerequisite for surface ozone destruction. However, no reduction in the surface ozone mixing ratio is observed in many cases although the BrO dSCD is strongly enhanced and the trajectory calculations suggest that the probed air masses were in contact with the sea ice for several days. Either a liquid layer with high salinity on the sea ice surface or the formation of sea salt aerosols, for example by frost flowers, are necessary for a heterogeneous bromine release. Therefore the local sea ice conditions could be a possible cause for these discrepancies. However, the trajectory calculations indicate that, for example, the surface ozone mixing ratio shows typical background values on Sept. 2 while ozone is strongly depleted on Sept. 3 although the air masses came from the same source region both days. It remains unclear which processes control whether or not an ozone destruction occurs in such cases.
- The trajectory calculations suggest that air masses from the sea ice are transported to



altitudes of more than 4000m due to advection processes. A frequently observed pattern of the duration of sea ice contact at the beginning of a surface ozone destruction event is shown in figure 5.54: Starting above the boundary layer, the air masses coming from the sea descent to the ground within 12-24 hours and the surface ozone depletion starts when these air masses touch the surface. As sketched in figure 5.54, these findings suggest the following meteorological scenario:

- I. Driven by eastward moving cyclones passing north of the Neumayer station, a warm front located over the sea ice moves southward.
- II. The boundary layer over the shelf ice is very stable due to a strong inversion layer in the lowermost troposphere. This causes the warm air from the sea ice to be pushed above the boundary layer. Now two inversion layers are located above the observation site. Air from the sea ice (which potentially contains reactive bromine) moves southward in the altitude range between both inversion layers.
- III. The original boundary layer retreats southward and air from the sea ice is transported to the Neumayer station at the ground. Due to the reactive bromine heterogeneously released either on the sea ice surface or on the aerosols transported with the air masses, surface ozone depletion is observed.

A possible consequence of these advection processes could be an input of reactive bromine into the free troposphere, as it was already observed in the Arctic by airborne spectroscopic measurements [McElroy et al., 1999]. McElroy et al. speculated that BrO from the surface would be transported into the free troposphere by convection processes. The analysis of trajectory calculations performed here strongly suggests that not convection, but the above described advection processes are responsible for the transport of reactive bromine from the surface into the free troposphere. Br and BrO are rapidly converted to HBr in the absence of bromine enriched sea salt surfaces with high acidity. In contrast to the direct release of Br_x from bromocarbons, these advection processes are therefore expected to be a source of reactive bromine for the free troposphere only on a short time scale.

- In most cases, the observation of air masses originated from the sea ice is accompanied by a strong tropospheric light path enhancement, which amplifies the observed BrO dSCD due to multiple scattering. It is very likely that the light path enhancements are at least partially caused by sea salt aerosols which are transported from the sea ice surface to the observation site. Therefore it is possible that heterogeneous bromine release on the aerosol surfaces is still in progress at the observation site. Due to the strong light path enhancements during BrO events, it is very difficult to quantify the tropospheric abundance of BrO.
- Using DOAS observations of zenith scattered skylight, it is not possible to quantify the tropospheric BrO abundance in terms of mixing ratio due to several reasons:
 - The tropospheric and stratospheric part of the BrO column must be separated. This is difficult even under clear sky conditions (which are rarely observed during BrO enhancement events) since tropospheric BrO adds an almost constant amount to the total column in this case.
 - BrO enhancements are mostly accompanied by strong increases in the light path enhancement due to near surface multiple scattering. Since there is only limited knowledge about the scattering parameters in the troposphere, it is not yet possible to model the radiative transport under such conditions.
 - The tropospheric BrO profile is unknown, although some very limited information on the vertical distribution is supported by the trajectory calculations.
- The concentration of total gaseous mercury measured during spring 2000 is very well correlated with the surface ozone mixing ratio. In agreement with recent observations in the Arctic [Schroeder et al., 1998; Schroeder and Barrie, 1998; Barrie and Platt, 1997], the observed reduction of gaseous mercury during ozone depletion events is believed to be caused by the oxidation of Hg⁰ to Hg²⁺ by reaction with BrO. The concentration of gaseous mercury in the atmosphere can therefore act as an indicator for the abundance of reactive bromine. Of more importance is, however, the indirect impact of BrO enhancements on the Arctic environment: by deposition of the oxidised mercury on the ice surface, this toxic compound enters the food chain. Together with the increasing anthropogenic mercury release in the atmosphere [Fitzgerald et al., 1998; Martinez-Cortizas et al., 1999], these processes can have a growing hazardous impact on the Antarctic biosphere.



Figure 5.55: Diurnal variation of the IO dSCD on September 5 (panel A) and October 27 (panel B), 1999. The position of the Fraunhofer reference spectrum is marked with an arrow. Left-hand axis: inferred IO dSCD; Right-hand axis: absolute IO SCD under the assumption that IO is totally removed from the atmosphere at $\Theta = 95^{\circ}$. The error bars denote the 1σ retrieval error. Panel C: RMS residual of the spectral retrieval on October 27.

5.6 Results of the IO measurements

As already described in section 4.12, it was possible to detect iodine oxide throughout the whole measurement period using daily Fraunhofer reference spectra recorded at 80° SZA. Examples of the diurnal variation of the inferred IO differential slant column density ΔS , i.e. the difference $\Delta S = S(\Theta) - S(80^{\circ})$ between the SCDs $S(\Theta)$ and $S(80^{\circ})$, are shown in figure 5.55. Throughout daytime, the IO DSCDs remain almost constant, while they rapidly decrease for $\Theta > 86^{\circ}$. The largest negative IO DSCDs are observed at 95° SZA when the IO DSCDs drop below $-9.5 \cdot 10^{13}$ molec/cm². The diurnal variation of the IO-DSCD under clear sky conditions is characterised by almost no change during daytime and a sudden drop during twilight. The data show a larger scatter for cloudy days and snow drift conditions than for clear sky days, indicating that near surface multiple Mie scattering modifies the radiative transfer by changing the light pathes and accordingly the observed IO SCD, which will be discussed in detail later in this section.

The amount of IO in the Fraunhofer reference spectrum can be estimated by assuming that IO is completely converted into its nighttime reservoir species at high solar zenith angles $(\Theta \ge 95^{\circ})$, an assumption that is justified by photochemical model studies of reactive iodine in the stratosphere [Pundt et al., 1998] and the troposphere [Vogt et al., 1999; Stutz et al., 1999; McFiggans et al., 2000] (see also figure 2.18). Accordingly, defining the $\Theta = 95^{\circ}$ observation as the zero of the ordinate indicates an absolute IO SCD of about $9.5 \cdot 10^{13}$ molec/cm² for



Figure 5.56: Airmass factors calculated for $\lambda = 435$ nm using the AMFTRAN Monte Carlo radiative transfer model. Panel A: Stratospheric airmass factors for the scenario described in the text. Panel B: Tropospheric airmass factors for a constant IO mixing ratio from ground up to different layer heights (1, 2, 5, 8 and 10 km) as indicated in the legend.

 $\Theta < 80^{\circ}$ for the observation on October 27. These values are given in the right-hand scale of figure 5.55. Since some IO could remain in the atmosphere even at 95° SZA, they should be regarded only as a lower limit.

Information about the location of the observed IO in the atmosphere is gained using radiative transport calculations. Two sets of airmass factors are calculated for $\lambda = 435$ nm, assuming that IO is either completely located in the stratosphere or in the troposphere. For the calculation of stratospheric airmass factors, a linearly increasing IO mixing ratio from the tropopause to an altitude of 14 km and a constant mixing ratio above was assumed. Tropospheric AMFs are calculated by assuming a constant mixing ratio profile from the ground level up to varying altitudes (1 to 10 km). The actual meteorological conditions (temperature, pressure and ozone profile) are taken from a balloon sounding on Sept. 27, 1999. An albedo of 0.85 was assumed and SAGE II data was used to determine the stratospheric aerosol extinction profile as described in section 4.6.3. The tropospheric aerosol was modeled using a linearly increasing extinction coefficient from 12 km altitude to a value of $5 \cdot 10^{-3}$ km⁻¹ on the ground. Any influences of changes in the shape of the trace gas profile due to the photochemistry (chemical enhancement) are not included in the radiative transfer model, although photochemistry may significantly change the stratospheric AMFs during twilight (i.e. for $\Theta > 85^{\circ}$) [Wittrock et al., 2000]. Since a photochemical steady state and thus small changes of the IO concentrations at daytime compared to the rapid variations during twilight can be expected, the discussion of stratospheric AMFs and the resulting vertical column densities is restricted to $\Theta < 82^{\circ}$.

The inferred airmass factors are shown in figure 5.56. While the stratospheric AMFs increase strongly with increasing SZA, the AMFs for the tropospheric profiles are smaller and show a much weaker dependence on SZA with a maximum around $\Theta = 85^{\circ}$.

In a next step, IO VCDs are calculated. Again, the amount of IO in the reference spec-



Figure 5.57: Diurnal variation of the IO VCD on October 27, 1999, under the assumption that all IO is removed from the atmosphere at 95° SZA, using the stratospheric (panel A) and tropospheric (Panel B) airmass factors shown in figure 5.56. A layer height of 2 km was assumed to calculate the tropospheric VCD.

trum is estimated under the assumption that, due to the conversion into reservoir species, no IO is present in the atmosphere at $\Theta = 95^{\circ}$. As shown in the upper panel of figure 5.57, assuming that IO is located in the stratosphere results in a strong increase of the IO VCD towards noon, which contradicts the expected photochemical steady state of the reactive iodine species (I, IO). In contrast, for tropospheric IO (lower panel of figure 5.57) the expected and observed diurnal variation of the IO VCD are in much better agreement: the IO VCD remains almost constant for $\Theta < 82^{\circ}$, which reflects the photochemical steady state during daytime, and decreases rapidly during twilight, in agreement with the model studies. Therefore, the observations strongly suggest that the bulk of the detected IO is located in the troposphere. Further assuming that IO is completely located in the in the lowermost 1300m (which is the altitude of the inversion layer as inferred from the ozone sounding on October 27, 1999), the observed IO VCDs would correspond to mixing ratios of ~6.5 ppt. IO mixing ratios of that amount are also reported from the marine boundary layer at Mace Head, Ireland (3.5 - 6.5 ppt) [Alicke et al., 1999] and several other locations in the mid-latitudes [Allan et al., 2000].

The seasonal variation of the IO dSCD with respect to a daily Fraunhofer reference spectrum at $\Theta = 80^{\circ}$, where the best signal to noise ratio is obtained, is shown in figure 5.58. The smaller day to day variability achieved during spring 2000 is caused by a better signal to noise ratio of the IO retrieval due to the improved thermal stability of the instrument. In addition, more frequent snow drift events during 1999 compared to 2000 cause a stronger short term variability of the IO dSCD due to multiple scattering. This will be discussed in more detail below.

A pronounced seasonal variation of the IO dSCD is observed both during 1999 and 2000, with larger values during summer than during winter. Since the retrieval is performed using daily Fraunhofer reference spectra, the data only contain information on the variation of the IO dSCD for each particular day. Therefore, the observed seasonality of the IO dSCD could either indicate a slower conversion of IO into its nighttime reservoir species during twilight



Figure 5.58: Seasonal variation of the IO dSCD during 1999 (upper panel) and 2000 (lower panel) at $\Theta = 92^{\circ}$, with respect to daily Fraunhofer reference spectra recorded at $\Theta = 80^{\circ}$.

or a smaller abundance of IO at 80° SZA during winter than during summer. It was recently speculated that the observed seasonal variation of the IO dSCD is caused by a higher IO concentration during summer [Frieß et al., 2001] due to the following processes:

- 1. The stronger solar illumination during summer allows a more efficient photo-dissociation of the organic iodine precursor molecules and thus a larger formation rate of inorganic iodine compounds.
- 2. Due to the retreating sea ice, the distance from the observation site to the open sea from which the precursors are likely to be emitted is smaller in summer than in winter.
- 3. More biological activity is expected to occur during summer.
- 4. The abundance of the reactants needed for the formation of the night time reservoirs may have an influence on the speed of the IO reduction at twilight.
- 5. The time elapsed between 80 and 92° SZA changes with season, and might influence the difference in IO concentrations if it is not in photo-stationary steady state at low sun.

As already discussed in section 4.12, it was possible to perform the spectral retrieval of IO using a single Fraunhofer reference spectrum recorded at noon of October 16, 2000 for the spring 2000 measurements. Compared to the above discussed IO dSCDs obtained using daily Fraunhofer reference spectra, this new data-set provides additional information on the



Figure 5.59: Seasonal variation of the IO dSCD during spring 2000 at $\Theta = 80^{\circ}$ (black squares), 90° (red circles) and 92° (green triangles), with respect to a single Fraunhofer reference spectra recorded on October 16, 2000. Closed and open symbols denote am and pm values, respectively.

seasonal variability of IO. The seasonal variation of the IO dSCD at 80° , 90° and 92° SZA using a single Fraunhofer reference spectrum shown in figure 5.59 is contradicting the conclusions of Friess et al. [2001], since it implies the following conclusions:

1. The IO dSCD at 80° SZA remains fairly constant throughout spring 2000. It thus can be concluded that the tropospheric IO abundance during daytime does not change with season. This is a surprising finding, since the source strength for iodocarbons and their subsequent decomposition by photolysis or reaction with OH should vary with distance to the open sea and solar illumination, as already discussed above. However, there is only limited knowledge about the primary production of biomass related to algaes and phytoplankton in the sea ice covered ocean and about the related release of iodinated compounds into the atmosphere, as already discussed in section 2.4.1. During winter, the total primary biological production taking place below, in, or on the surface of the sea ice is roughly estimated to be 33% of the annual mean production in the Southern Ocean. Since the biological activity related to sea ice occurs near the surface, it is possible that the release of iodocarbons is not strongly reduced during winter. Measurements of atmospheric iodocarbons during austral summer indicate that methyl iodide, with a lifetime of several days, is uniformly distributed over the Antarctic continent: $(2.4 \pm$ 1.5)ppt CH₃I were observed at the Antarctic Peninsula [Reifenhäuser and Heumann, 1992] and at Tasmania [Rasmussen et al., 1982], while (1.8 ± 0.4) ppt were found at



Figure 5.60: Monthly averaged diurnal variation of the IO dSCD during spring 2000 using a fixed Fraunhofer reference spectrum.

the South Pole [Rasmussen et al., 1982], in a distance of more than 1500km to the ocean. These observations suggest a small variation of in atmospheric methyl iodide concentrations with distance to the open sea and thus with season. Iodine oxide could be already partly released from methyl iodide or other organic iodine precursors with shorter photolytic lifetime, such as CH_2I_2 , during the transport of the air masses from the source regions, i.e. the open sea and possibly the sea ice, to the Neumayer station. However, recent measurements of methyl iodide in firn air drillings at Dronning Maud Land (77°S, 10°W), suggest a pronounced seasonal cycle of methyl iodide [Sturges et al., 2001]. The measurements were performed on the Antarctic continent in a distance of approximately 800km to the open sea. An average methyl iodide mixing ratio of about 0.6ppt in depths of up to 75m was observed. Maximum CH_3I mixing ratios of $\approx 1.1ppt$ in June and a minimum of $\approx 0.2ppt$ in January were inferred by model calculations.

2. A smaller decrease of the IO dSCD during twilight is observed during winter than during summer, suggesting a slower conversion of reactive iodine into its reservoir species. This is also illustrated in figure 5.60, where the monthly averaged diurnal variation of the IO dSCD as a function of SZA is shown. While the IO levels remain constant for $\Theta < 80^{\circ}$ throughout the whole period (as discussed below, the variability of the September observations is due to the variation of the light path by weather conditions), the twilight variation changes strongly with season: During July and August, the decrease of the IO dSCD occurs at 90° SZA, while the conversion to and the release from nighttime reservoir species starts at 80° SZA during November. It remains unclear which processes control the observed seasonality of the IO twilight variation. Higher concentrations of organic peroxy radicals (RO₂, R = organic group) due to the shorter distance to the open sea

and the increased biological activity during summer could possibly have an influence on the formation of HOI during twilight by the reaction $IO + RO_2 \longrightarrow HOI + RO$.

- 3. The IO diurnal variation shown in figure 5.60 suggests that the decrease of IO in the evening occurs slower than the release in the morning. Caused by the heterogeneous conversion of HOI to I_2 , IBr and ICl during night and the rapid photolysis of these compounds at sunrise, this asymmetry of the IO diurnal variation is in agreement with model calculations [Vogt et al., 1999].
- 4. The IO dSCDs show a strong variability during August and September. As discussed below, this can be clearly related to the weather conditions.

A further question is if a relationship between the tropospheric BrO enhancements during early spring and the abundance of IO exists. As already described in section 2.4.2, the reaction of HOI on aerosol surfaces can stimulate an additional release of reactive bromine to the atmosphere in form of IBr, which is rapidly photolysed [Vogt et al., 1999]. The IO and BrO dSCDs during August and September 2000 are shown in figure 5.61. To emphasise the daytime variation, the IO dSCDs are shown for $\Theta < 90^{\circ}$ only. Also plotted are the light path enhancement factors as derived using the O₄ absorption bands located at wavelengths close to the retrieval windows of BrO (361nm) and IO (477nm) and the periods where snow drift is reported from the meteorological observations at Neumayer⁶ (hashed areas in figure 5.61).

It is important to note that the radiative transport in the troposphere strongly depends on wavelength: under clear sky conditions, the majority of UV light is scattered in the stratosphere, while a significant part of visible light is scattered in the troposphere before it is detected by the spectrograph. The tropospheric airmass factor under clear sky conditions is therefore larger for IO than for BrO, while multiple scattering on macroscopic particles under cloudy or snow drift conditions is almost independent from wavelength. Thus the light path enhancement factor is generally smaller for the 477nm than for the 361nm O_4 absorption band. Assuming that both trace gases are located in altitudes where multiple scattering occurs, this leads to a stronger 'amplification' of the BrO dSCD compared to the IO dSCD due to multiple scattering in the lower troposphere.

The IO dSCDs shown in figure 5.61 are found to be strongly sensitive to changes in the radiative transport. While the IO dSCDs remain constant for clear sky conditions (indicated by a light path enhancement factor of one), already small increases in the light path enhancement factor lead to strong enhancements in the IO dSCD with values of up to $5 \cdot 10^{13}$ $molec/cm^2$. Most of the observed IO enhancements are coincident with observations of snow drift. Since the vertical extend of snow drift is limited to the lowermost few hundred metres above ground, this strongly suggests that the majority of IO is located near the surface, where multiple scattering occurs. On the other hand, multiple scattering in a thin layer near the surface does not necessarily increase the O_4 absorption. If the snow drift has, for example, a vertical extension of 25 metres, then only a fraction of 0.6% of the O₄ profile is affected by multiple scattering. An increase in the light path in the lowermost 25 metres of a factor of 5 would then lead to a light path enhancement factor of 1.025, which is hardly detectable. However, an increase in the IO SCD of 20% would be observed in this case if IO would be located in the lowermost 500 metres of the troposphere. This explains why increases in the IO dSCD are not well correlated with the light path enhancement factor, but with observations of snow drift.

⁶The archived meteorological data from Neumayer station is freely accessible via http://www.awi-bremerhaven.de/MET/Neumayer/obse.html.





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Figure 5.62: Five day back trajectories ending at Neumayer on Aug. 24, 2000, 18:00 UT at 0, 500 and 1000m altitude.

An interesting observation was made on August 24, 2000: the IO dSCD decreases, while the light path enhancement factor strongly increases. Simultaneously, heavy blowing snow with a visibility of less than 50m was observed. As the trajectory calculations shown in figure 5.62 indicate, catabatic fall winds occur at Neumayer station on this particular day. The air masses arriving at the surface come from the dark Antarctic continent and descend from more than 1000m above ground to the surface during the last five days. In contrast, the air masses arriving at 500m altitude come from the sea ice and the 1000m trajectory has passed the open sea for two days. Due to the rarely observed catabatic fall winds on this particular day, it is likely that the maximum of the IO profile is located above the surface. Under such circumstances, the airmass factor can be even smaller than under clear sky conditions if the maximum of the IO profile is located at altitudes where the IO absorption is not affected by near surface multiple scattering [Wagner et al., 2001].

Due to the strong sensitivity of the IO dSCD to near surface multiple scattering, a relationship between BrO and IO due to their coupling by chemistry is difficult to estimate using observations of zenith scattered skylight. Furthermore, enhanced BrO dSCDs are mostly accompanied by tropospheric light path enhancement. It is therefore not possible to separate effects caused by changes in the radiative transport from possible changes in the partitioning of the observed halogen species caused by chemical interactions between iodine and bromine compounds. IO enhancements are primarily caused by multiple scattering in the lowermost troposphere and also occur during summer, when BrO is unlikely to be abundant in the troposphere. This is shown in figure 5.63, where the IO dSCD and the light path enhancement factor are plotted for a period of four days during mid December of 2000. No pronounced diurnal variation of IO due to photochemistry is expected during this period since the solar zenith angle is always below 86° . The light path enhancement factor has a constant value of one during the last two days (Dec. 14 and 15), indicating that no multiple scattering due to clouds or snow drift occurs. Simultaneously, the IO dSCD remains constant within the uncertainty of the measurement. In contrast, a very strong variability of the light path enhancement factor is observed on Dec. 12 and 13 (with values between 0.7 and 2.2), while the IO dSCD is strongly increased with values of up to $4 \cdot 10^{13}$ molec/cm², but is not correlated



Figure 5.63: IO dSCD using a fixed Fraunhofer reference spectrum (upper panel) and light path enhancement factor at 477nm (lower panel) between Dec. 12 and 16, 2000. The error bars represent the 1σ fit error.

with the variability of the light path enhancement factor. No increase in the error of the IO dSCD occurs during these enhancements, indicating that they are not caused by a spectral interference of the IO absorption structure with the (very weak) O_4 absorption band at 447nm. Snow drift and partially cloudy sky is reported from Neumayer station during Dec. 12 and 13, while the sky was cloud free and no snow drift was observed on Dec. 14 and 15. These observations are compatible with the following hypothetic scenario:

- 1. The bulk of O_4 is located above the layer where multiple scattering occurs. This is likely the case since the O_4 profile has a scale height of approximately 4km and snow drift is restricted to at most a few hundred metres above ground. This explains why the light path enhancement factor is not only increased, but sometimes also decreased (values smaller than one) compared to clear sky conditions.
- 2. The majority of IO is located within the layer where multiple scattering occurs, i.e. close to the surface, leading to the observed strong increase of the IO dSCD.
- 3. The variability of the light path enhancement factor is likely caused by temporal and spatial inhomogeneities in the vertical extension of the snow drift layer, and possibly by altocumulus clouds which were observed on Dec. 12 and 13.
- 4. A homogeneous distribution of the snow and ice particles near the surface, which leads to a constant enhancement of the IO absorption, explains the small variability of the enhanced IO dSCDs.

It is also important to note that IO dSCDs at midnight ($\Theta \approx 86^{\circ}$) are equal both for snow drift and clear sky conditions ($\Delta S \approx -2 \cdot 10^{13} \text{ molec/cm}^2$). The finding that multiple scattering does not affect the IO column density at large SZA indicates that only small IO concentrations are abundant due to the conversion of reactive iodine into its reservoir species.

The observations of iodine oxide at Neumayer station during 1999 and 2000 can be summarised as follows:

- The spectral signature of iodine oxide was clearly detected in the zenith sky spectra recorded at Neumayer station during 1999 and 2000.
- Although DOAS observations of zenith scattered sunlight provide no direct information on the altitude distribution of the observed trace gases, arguments based on radiative transfer model calculations and photochemistry indicate that the observed diurnal variation of the IO DSCD is caused by tropospheric rather than stratospheric IO.
- Assuming the observed IO to be located completely in the boundary layer leads to mixing ratios of roughly 5-10 ppt during summer, similar concentrations as typically found in the mid-latitude MBL.
- In contrast to the findings of Wittrock et al. [2000], no evidence for stratospheric IO was found, mainly because the expected small stratospheric signature of IO may be masked by the strong tropospheric signal observed at Neumayer.
- The data analysis of the spring 2000 measurements using a fixed Fraunhofer reference spectrum adds new information to the findings of Frieß et al. [2001]. The observations suggest a constant IO abundance during early spring and summer, which is a very surprising result since the rate of iodocarbon emission should vary with sea ice coverage. However, this finding is in agreement with measurements of iodocarbons: similar methyl iodide concentrations were observe both at the Antarctic Peninsula and at the South Pole station, suggesting that this source species is uniformly distributed over the whole Antarctic continent.
- The pronounced sensitivity of the IO dSCD to near surface multiple scattering due to snow drift supports the conclusion that the bulk of IO is located close to the ground.
- An important information for the interpretation of the observed IO seasonality, namely the seasonal variation of the iodocarbon source strength, remains unknown. Only limited information on the biological activity on/in the sea ice is available. To our knowledge, no measurements concerning the emission of organic iodine precursors from the sea ice covered Southern Ocean exist. It is also an open question to which extend long range transport over more than thousand kilometres of organic or inorganic iodine compounds from the open sea to the coastal regions of Antarctica can take place during winter.
- The diurnal variation of IO shows a pronounced seasonal cycle: IO starts to decrease at lower SZA during summer than during winter, indicating that the conversion of IO into and its release from reservoir species occurs at lower SZA during summer. The processes controlling this behaviour remain unclear. Peroxy radicals emitted due to biological activity in the ocean could have an impact on IO chemistry due to additional formation of HOI. They could therefore modify the diurnal cycle of IO. A test of this hypothesis using photochemical model calculations is still an outstanding issue.

Chapter 6

Summary and Outlook

Within the scope of thesis, a two years record of DOAS measurements of ozone, OClO, BrO and IO at Neumayer station, Antarctica, was presented. The newly developed UV/Vis spectrograph system is characterised by high mechanical and thermal stability. Together with an excellent light yield due to the renunciation of any additional optical components, it was possible to detect atmospheric trace gases with a very good signal to noise ratio for solar zenith angles of up to 97° over almost the entire period. The time series are only interrupted for a period of two months during autumn 2000 due to a failure of the cooling device controller.

The diurnal and seasonal variation of the observed stratospheric trace gases NO_2 , OClO, BrO and ozone is in good agreement with the present knowledge of halogen chemistry:

- 1. Denoxification and denitrification: Due to the conversion to N_2O_5 during the long and cold stratospheric nights, the NO₂ vertical column densities decreased by more than an order of magnitude during both winters, with minimum VCDs of only $5 \cdot 10^{14}$ molec/cm² compared to about $7 \cdot 10^{15}$ molec/cm² during summer. The abundances of NO₂ were found to be well correlated with stratospheric temperatures, caused by (1) N₂O₅ being more stable at low temperatures and (2) an increase in the [NO]/[NO₂] ratio with decreasing temperature. The diurnal variation of NO₂ is characterised by a large asymmetry: an increase of daytime the NO₂ VCD is observed during autumn, while the diurnal variation is less pronounced during spring. This finding reflects the strong influence of heterogeneous processes on the partitioning of stratospheric compounds: the species responsible for the increase in NO₂ in presence of solar illumination, N₂O₅, is heterogeneously converted to HNO₃ on surfaces of polar stratospheric clouds in the cold polar vortex. HNO₃ can therefore be expected to be the major nitrogen reservoir species during late winter and spring. Since HNO₃ has a longer photolytic lifetime than N₂O₅, the diurnal variation of NO₂ becomes small in late winter and spring.
- 2. Chlorine activation: Symmetric chlorine dioxide is formed by the reaction of BrO with ClO. Thus measurements of OClO provide an indicator for chlorine activation. Since it was possible to detect OClO at solar zenith angles > 94°, OClO time series are available for the whole winter period, except for a small gap of two weeks, when the solar zenith angle is always above 94°, during mid-winter. OClO slant column densities above the detection limit were observed whenever the lower stratosphere above Neumayer was cold enough to form polar stratospheric clouds, indicating that heterogeneous conversion of HCl and ClONO₂ to reactive chlorine compounds (including ClO) occurred in the presence of PSCs. A significant chlorine activation was already observed during late

autumn, with OClO SCDs of up to $7.5 \cdot 10^{13}$ molec/cm² at 90° SZA during early Mai of 2000. Maximum OClO SCDs of $\approx 4 \cdot 10^{14}$ molec/cm² at 90° SZA were observed from late June to mid September. A rapid decrease in OClO SCDs occurs when stratospheric temperatures raise above the PSC threshold in late September. During both years, OClO drops below the detection limit at the beginning of October. The OClO SCDs are remarkably well correlated with the potential vorticity, confirming the strong gradient of reactive chlorine abundances from the edge towards the centre of the polar vortex.

- 3. Change in bromine partitioning: The daytime abundance of reactive bromine is controlled by the steady state of BrONO₂ formation via reaction of BrO with NO₂ and its photolysis. Therefore BrO concentrations increase if NO₂ concentrations decrease. This leads to a pronounced seasonal variation of the BrO dSCD with a maximum during winter, when $(5-6) \cdot 10^{14}$ molec/cm² are observed. The increased BrO concentrations are expected to lead to a more pronounced ozone depletion, particularly under chlorine activated conditions due to the coupling of bromine and chlorine chemistry via the BrO/ClO cycle. The observations in spring (September/October) are dominated by BrO located in the troposphere (see below). Therefore the abundance of stratospheric BrO is difficult to estimate during this period.
- 4. Ozone destruction: The above prerequisites (denoxification, chlorine activation and high concentrations of reactive bromine) lead to a severe ozone destruction during spring of 1999 and 2000. The ozone hole lasted unusually long during 1999: due to the persistent polar vortex, ozone VCDs below 200DU are observed until late December. In contrast, the recovery of the ozone hole in 2000 occurred already in late November due to the earlier vortex breakdown. Caused by colder vortex temperatures, smaller minimum ozone VCDs were observed in 2000 (102.2DU) compared to 1999 (117.6DU). A short period of mid-winter ozone depletion was observed in mid-July of 2000, when the ozone VCD dropped from 240DU below 150DU within two days. Trajectory calculations indicate that the observed chlorine activated air masses were previously located at low latitudes (> -60° S) and thereby exposed to sunlight, making a photochemical ozone depletion very likely.

The most remarkable features of the BrO time series are the strong and sudden enhancements during September and October of both years. These events can be unambiguously related to BrO being located in the lower troposphere. The detailed analysis of the BrO time series during spring performed within this theses includes the comparison with surface ozone measurements, ozone soundings, O_4 observations as well as an extended approach for the trajectory analysis in combination with sea ice maps. The BrO observations were found to be influenced by atmospheric chemistry, dynamics and radiative transport. The most important findings can be summarised as follows:

- A necessary prerequisite for ozone depletion at ground is the probing of air masses which were previously exposed to the sea ice surface. Furthermore, ozone depletions at ground are always accompanied by BrO enhancements, indicating that autocatalytic release on sea salt surfaces and a subsequent ozone destruction took place.
- BrO enhancements where detected whenever air masses above the measurement site came from sea ice surfaces. The trajectory calculations strongly suggest that BrO is not only located near the surface: advection processes frequently lead to the transport of BrO to altitudes of more than 4000 metres. This is supported by ozone profiles in the lower troposphere, which indicate ozone depletion at high altitudes.

- The comparison of O_4 and BrO measurements shows that the observed BrO dSCDs are frequently amplified by multiple scattering in the lowermost troposphere.
- Air masses coming from the sea ice surface are mostly coincident with an increase in the tropospheric light path, suggesting that these air masses contain sea salt aerosols. If this is the case, heterogeneous bromine release, or at least 'recycling', can still take place above Neumayer.
- The comparison between BrO observations and measurements of gaseous mercury during spring 2000 show that the autocatalytic release of reactive bromine can affect the fragile Antarctic ecosystem: the oxidation of Hg to Hg²⁺ by reaction with BrO leads the deposition of this toxic compound on the ice surface. These processes illustrate how a complex interaction between natural phenomena (the bromine explosion) and anthropogenic activities (the growing emission of gaseous mercury) can have an hazardous impact on the biosphere, even in very remote regions.

However, some questions concerning the observed tropospheric BrO events remain unanswered:

- Why is sometimes no surface ozone depletion observed, although BrO is enhanced and the trajectory calculations indicate that air masses at the surface come from the sea ice?
- Are the observed advection processes at least on a local scale a source for the recently suggested BrO background in the free troposphere?
- Are the observed light path enhancements during BrO events caused by multiple scattering on sea salt aerosols?
- What is the impact of deposition of oxidised mercury due to high tropospheric BrO concentrations on the fragile Antarctic ecosystem?

Iodine oxide was observed for the first time in the Antarctic marine boundary layer within the scope of this work. A precise quantification of IO concentrations is difficult using DOAS measurements of zenith scattered sunlight, particularly because the IO vertical profile is unknown. Assuming that IO is completely located in the boundary layer leads to mixing ratios of roughly 5-10ppt. Being present in such high concentrations, IO is probably the dominating sink for boundary layer ozone in the Antarctic coastal region. Caused by the fast formation of iodine reservoir species in the absence of sunlight, the diurnal variation of the IO dSCD is characterised by a rapid decrease during twilight. It remains an open question why the conversion into reservoir species occurs at lower solar zenith angle ($\approx 80^{\circ}$ SZA) during summer than during early spring ($\approx 90^{\circ}$ SZA). The availability of peroxy radicals during summer possibly leads to an increased formation of HOI and therefore to a reduction of IO during twilight. IO was found to be abundant on a constant level throughout the year. This is a very surprising result since the IO concentration is expected to vary with the distance to the open sea, which is the source of organic precursors for reactive iodine. It remains an open question if the high IO abundances during early spring are caused by long-range transport from the open sea and to which extend the sea-ice covered ocean can act as a source of iodocarbons.

A number of outstanding issues remain, particularly concerning the interpretation and quantification of halogen compounds observed in the troposphere:

- The quantification of source regions for reactive bromine can be improved by taking vertical mixing processes into account when modeling the duration of sea ice contact.
- Measurements of filterable bromine in high temporal resolution (low-volume filter) would be an important information in order to quantify the bromine content of sea salt aerosols and its relation to tropospheric BrO. As it was already done in the past [Lehrer, 1999], it is planned to perform those measurements during the next spring season (D. Wagenbach, pers. communication).
- The modeling of boundary layer iodine chemistry could improve the understanding of the observed diurnal and seasonal variation of IO and would be important to determine the impact of reactive iodine on the ozone budget in the Antarctic marine boundary layer. The available trajectory calculations provide a suitable set of input parameters for a Lagrangian box model.
- A variation of the instrument's viewing angle from the zenith to directions close to the horizon (off-axis or multi-axis DOAS) strongly improves the sensitivity for tropospheric absorbers due to the longer light path through the lowermost layers of the atmosphere. Furthermore, multi-axis DOAS provides information on the vertical profile of tropospheric absorbers. For these purposes, is planned to equip the telescope with a variable mirror system in the near future.

Appendix A

Construction Plans

A.1 Spectrograph unit






























A.2 Spectrograph housing



A.3 Quartz fiber bundles





A.4 Telescope













A.5 Insulation box



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